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Theoretical Considerations in the application of Non-equilibrium Green's Functions (NEGF) and Quantum Kinetic Equations (QKE) to Thermal Transport

Leek Meng Lee HT071399B
Supervisor: Prof Feng Yuan Ping
Co-Supervisor: Prof Wang Jian-Sheng

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Abstract

In this thesis we showed that Non-equilibrium Green's Function Perturbation Theory (NEGF) is really the overarching perturbative transport theory. This is shown in great detail by using NEGF as a starting point and developing in 3 directions to obtain the usual transport-related expressions. The 3 directions are: Landauer-like theory, kinetic theory and Green-Kubo linear response theory. This thesis is concerned with using NEGF to generalize the 2 directions of Landauer-like theory and the kinetic theory.

Firstly, NEGF is used to derive phonon-phonon Hedin-like functional derivative equations which generates conserving self energy approximations for phonon-phonon interaction.

Secondly, for the Landauer-like theory, using the perturbation expansion, we easily obtain anharmonic (or phonon-phonon interaction) corrections to the ballistic energy current and to the noise associated to the energy current. The lowest 3-phonon interaction, the lowest and the second lowest 4-phonon interaction corrections to the ballistic energy current are obtained. The lowest 3-phonon interaction correction to the noise is obtained. Along a seperate line, we found that we can incooperate high mass disorder into the ballistic energy current formula. The coherent potential approximation (CPA) for treating high mass disorder is found to be compatible with the ballistic energy current expression.

Lastly, for the kinetic theory, Wigner coordinates + gradient expansion easily allow the reproduction of the usual phonon Boltzmann kinetic equation. It is also straightforward to derive phonon-phonon correlation corrections to kinetic equations. Kinetic equations lead to hydrodynamic (balance) equations and we derived phonon-phonon correlation corrections to the entropy, energy and momentum balance equations.

Chapter 1

Preface

[**Organisation of the thesis**] The thesis is structured to compare 3 types of transport theories emanating from Nonequilibrium Green's Functions (NEGF): Landauer-like theory, kinetic theory and Linear Response Green-Kubo theory. That is why for each type of interaction, all 3 versions are presented as far as possible. Then for each interaction, the Hedin-like functional derivative equations describing the self consistent treatment of that interaction are presented. Such Hedin-like equations generate conserving approximations for that interaction.

1.1 Main Objectives of the Research

1. Seek a rigorous framework of NEGF for phonons. This is done along 2 lines of development: the Landauer development, and the kinetic theory development Here, rigorous means the derivations are done with minimal "mysterious steps" like dropping terms without notice. The anharmonic corrections to Landauer energy current is done rigorously by expanding the S-matrix properly and checking all usages of Wick's factorization theorem properly.

2. Phonon-phonon and electron-phonon interactions are recasted into self consistent functional derivative Hedin-like equations. These equations generate self consistent skeleton diagrams of the interaction. The self consistent skeleton diagrams are conserving approximations [1] . In other words, we want to derive equations that generate conserving approximations for as many types of interactions as possible.

3. We want to survey bulk theories that handle high concentrations of disorder in lattices to see which one works best for finite nanosystems (at least numerically).

1.2 Guide to Reading the Thesis

For the thesis examiners, I include here a guide to point out the main flow and to list the results in the thesis to facilitate an easy access to the thesis. There are several features in the thesis that the examiner can use as guides.

[1] The meaning of conserving approximations is in the sense in [Baym1962] by Gordon Baym. Essentially, the idea is simple: The Green's functions are approximated by retaining some subset of self energy terms/diagrams. These approximated Green's functions are used to calculate the physical quantities. Conserving approximations are self energy approximations that give approximated Green's functions that give approximated physical quantities which satisfy continuity equations between these physical quantities. I have to admit that Baym derived the criteria in a particular context (2-particle interaction) and this criteria may be modified in this particular context of particle number non-conserving 3,4-particle interaction. This needs to be checked in future.

[Features:]

1. The contents page gives the overall structure of the thesis. The logical flow of concepts and developments can be seen in the contents page. Please always refer back to the contents page for the logic of a particular development.

2. The asterisked sections in the contents page indicate sections with my contributions. Comments at the end of those sections explain the contributions. All un-asterisked sections are reproductions from the literature.

3. Some long subsections has a bold paragraph heading in square brackets. That heading summarizes the objective of that subsection. For readers who are lost in the reading or lost in the derivation can refer back to the bold heading and stay on track.

4. Final and important equations are boxed. A receipe is given in some sections where the derivation is very long.

For the examiners of this thesis, I shall now list the parts of the thesis which contain my contribution and what they are.

1. The chapters which have my contribution are: chapter 3 on NEGF (mostly phonons), chapter 5 on anharmonicity and chapter 7 on disordered systems.

2. The results in the chapter on NEGF (mostly phonons) are:

   (a) Langreth's theorem for terms in vertex multiplication.

   (b) Noise associated with Energy Current (for a noninteracting central) where we obtained the Satio & Dhar's formula via a different way. They did it using generating functionals based on a 2-time measurement process. We did it by pure NEGF only.

   (c) H-Theorem for correlated phonons is explicitly derived. The corrections due to correlations enter the entropy density and the entropy flux density.

   (d) Generalized Kadanoff-Baym Ansatz (Phonons) was constructed but it turned out to be unsuccessful. We hope the derivation given there allows the problem in construction to be uncovered.

3. The results in the chapter on anharmonicity are:

   (a) Anharmonic corrections to the Landauer ballistic current are systematically derived.

   (b) Anharmonic corrections to the ballistic noise are systematically derived.

   (c) Phonon-phonon Hedin-like equations are derived and a library of self consistent phonon self energies which gives conserving approximations is collected.

   (d) In the section on applications of QKE on top of BE, correlation corrections to phonon energy and momentum balance equations are derived.

4. The result in the chapter on disordered systems is:

   (a) In section 7.4.1.1.3, the 2-particle configuration average within CPA is incooperated into the Landauer formula. Hence it becomes possible to modify Landauer formula for high mass disordered systems. This leads to the publication [NiMLL2011].

5. We state here briefly the aims of including the other chapters:

(a) Chapter 4 on Reduced density matrix is included to provide another dimension besides NEGF. A promising numerical method - stochastic unravelling - is also illustrated.

(b) Chapter 6 on Electron-phonon interaction is included to show that electron-phonon interaction has also been rewritten into Hedin-like equations.

(c) Appendix D on NEGF for electrons is included to show the corresponding development for electrons. This provides a comparison with the main text which is concentrated on phonons.

1.3 Incomplete Derivations in the Thesis

1. The derivation of the exponent in the influence functional.
2. The checking of the Landauer energy conservation sum rule in the appendix. It is not exactly an incomplete derivation, the derivation gives contradictory results.
3. In the section on electron-phonon Hedin-like equations, the derivations on "normal modes in body-fixed frame" and "phonon-induced effective electron-electron interaction" are not included.

1.4 Notation used in this Thesis

Notation used in this thesis

G	–	Electron Green's function
$\vec{k}$	–	Electron momentum
n	–	Electron band index
D	–	Phonon Green's function
u	–	displacement vector
Q	–	normal coordinate
$a^{\dagger}, a$	–	mode amplitudes
$\vec{R}_l^{eq}, \vec{R}_l^0 \equiv l$	–	position vector of site l or cell l.
k	–	kth atom in the cell.
α	–	cartesian component of the displacement vector
$\vec{q}$	–	Phonon Momentum
j	–	Phonon branch index
$G^<,\ D^<$	–	Lesser Green's functions
$G^>,\ D^>$	–	Greater Green's functions
$G^R,\ D^R$	–	Retarded Green's functions
$G^A,\ D^A$	–	Advanced Green's functions
$G^K,\ D^K$	–	Keldysh Green's functions
$\Gamma^{(L)}$	–	Left lead related function
$\Gamma^{(R)}$	–	Right lead related function
f^{eq}	–	Equilibrium electronic distribution (Fermi-Dirac distribution)
f	–	Non-equilibrium electronic distribution
N^{eq}	–	Equilibrium phononic distribution (Bose-Einstein distribution)
N	–	Non-equilibrium phononic distribution

Fourier Transforms:

$$A(\vec{r}) = \int \frac{d\vec{q}}{(2\pi)^3} e^{i\vec{q}\cdot\vec{r}} A(\vec{q}) \quad , \quad A(\vec{q}) = \int d\vec{r} e^{-i\vec{q}\cdot\vec{r}} A(\vec{r}) \tag{1.1}$$

$$A(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t} A(\omega) \quad , \quad A(\omega) = \int dt e^{i\omega t} A(t) \tag{1.2}$$

Delta function representation:

$$\delta(\vec{r}) = \frac{1}{(2\pi)^3} \int d\vec{q} e^{i\vec{q}\cdot\vec{r}} \quad , \quad \delta(\vec{q}) = \frac{1}{(2\pi)^3} \int d\vec{r} e^{-i\vec{q}\cdot\vec{r}} \tag{1.3}$$

$$\delta(t) = \frac{1}{2\pi} \int d\omega e^{-i\omega t} \quad , \quad \delta(\omega) = \frac{1}{2\pi} \int dt e^{i\omega t} \tag{1.4}$$

[Recommended Phonon and or Transport related books] These are references that serve me well to cover the background of the topic. Obviously the list is strictly a personal one and is neither complete nor all inclusive.

- Description of phonons and anharmonicity at the level of solid state or condensed matter textbooks: [Madelung1978] and [Callaway1991].
- Specialized books on phonons: [Maradudin1974] especially chapter 1, [Srivastava1990], [Gruevich1986], [Ziman2001] and [Reissland1973].
- Specialized articles on phonons: [Kwok1968] and [Klemens1958].
- Good books on transport: [Smith1989], [DiVentra2008], [Bonitz1998] and [Vasko2005]. These books on transport are more in the engineering style: [Chen2005] and [Kaivany2008].

1.5 Acknowledgements

I would like to thank my supervisors; Prof Feng for his support and Prof Wang for always asking penetrating questions that provoke deeper thinking. I would like to thank my family and my friends for their support.

Chapter 2

Introduction

2.1 Discussion on Theoretical Issues in Thermal Transport

In this section, we discuss only theoretical issues in thermal transport with a mind for nanosystems. These are essentially the big questions that the thesis will try to address.

1. [**Transport Theories:**]

   (a) [**Boltzmann Kinetic Theory**] Historically, this transport theory came first and it came as the classical version. Some quantum effects are taken into account by using Golden Rule transition rates for the rate of change in distribution due to collisions.

   (b) [**Kubo Linear Response**] This came from a complete quantum treatment although it is truncated at first order (hence the name linear response). It is written into a response function form which makes it very attractive because transport coefficients are response functions!

   (c) [**NEGF**] This is still a perturbative theory but the step forward is that, a time dependent Hamiltonian can also written into a perturbative form that allows a Feynman diagrammatic treatment thus immediately there are various ways to go beyond first order perturbation. There are other developments from NEGF: (voltage/thermal) leads can be dynamically treated (called the Landauer-like treatment); kinetic theory can be derived from a complete quantum treatment and quantum corrections to kinetic theory can be done systematically (called quantum kinetic theory (QKE)).

   Thus as far as quantum effects are concerned, NEGF gives the most complete treatment although it is still perturbative.

2. [**Non-equilibrium Situation**] Due to the small sizes of the system and due to the small sizes of the contacts the transport in the system is likely to be in a highly non-equilibrium state. The question is, can such a non-equilibrium state be reached by perturbation theory? Most likely no. We hope that by employing self consistent methods (such as Hedin's equations) the non-perturbative regime can be reached (computationally).

3. [**Finite Size Effects**] The finite size of nanosystems means that surface and interface effects are going to be significant and perhaps dominate the transport properties. What is the most realistic way of taking these effects into account? The typical Physics/Engineering treatment is to treat surface and interface effects as some kind of "rough reflective surface" where particles' momentum get degraded and changes direction. A parameter is introduced to denote the amount of degradation. Chemists' treatment is a bottom-up approach where bigger and bigger molecules are considered and all internal and external degrees of freedom are taken into account. The Coriolis

and Mass Polarization terms calculated in the chapter on electron-phonon interaction are terms which decrease in effect as the system gets larger and larger. Thus these are finite size effects which the Physics/Engineering treatment miss.

4. [N **and** U**-processes**] [1] In the well-established treatment of phonon transport by the phonon Boltzmann equation the argument of N-processes redistributing phonons and of U-processes "killing" crystal momentum is convincing and physically sound but Brillouin zones and momenta are all bulk concepts. Thus for finite systems, the ideas of elastic scattering (N-processes) and inelastic processes (U-processes) are not very obvious. It is important because we need to know what processes "kills" the momenta of the carriers.

5. [**Controlled Approximations**] Many-body problems are not solvable. Approximations are unavoidable. The issues we need to keep in mind are that approximations must be tracked so that we know exactly the approximations within the theory then it can be systematically checked which set of approximations work in a particular situation. Example: do approximations that work in describing bulk systems work for nanosystems?

6. [**Experiments**] Thermal transport experiments are extremely difficult to carry out because there is no direct way to meansure a heat current so there are not many experimental results. Thus our real picture of thermal transport in nanosystems is still sketchy but there are a few hints which I will state now. [2]

   (a) [**Depressed Melting Points**] There are plentiful and definitive experimental results showing that nanomaterials have much depressed melting points compared to their bulk counterparts. No references are given here as such data can be found in many articles, tables and handbooks. There are also various (surface to volume ratio related) models to explain for the depression but in the context of anharmonicity, we simply need to know that melting requires the particles to move apart from their average equilibrium positions and thus anharmonic excitations are needed. The lowered melting point implies the ease of creating anharmonic excitations in nanosystems over their bulk counterparts. This means 2 things: we should have theoretical developments including higher phonon-phonon interactions and simple renormalization may not be sufficient as anharmonicity is not really "small". [3]

   (b) [**Ballistic or diffusive transport? Fourier's Law?**] The usual understanding of bulk thermal transport is that there is diffusive transport since the system size is far larger than the phonon mean free path and Fourier's Law is obeyed. For nanosystems, experiments tell a different story. The measurement in [Schwab2000] showed conclusive phonon ballistic transport at very low temperatures. This brings in the need to consider coherent (or semi-coherent) phonon transport. This motivates the theoretical development of transport theories with correlations on top of the usual collision scenario. The measurement in [Chang2008]

[1] Here is a quick recap of the definition of the N and U-processes. N-process stand for *Normal* process and represents the conservation of "crystal momentum", i.e. $\left(\sum_i \vec{q}_i\right)_{\text{initial}} = \left(\sum_f \vec{q}_f\right)_{\text{final}}$ is obeyed in an interaction. U-process stand for *Umklapp* process and represents the conservation of "crystal momentum" modulo reciprocal lattice vectors $\vec{g}$, i.e. $\left(\sum_i \vec{q}_i\right)_{\text{initial}} = n\vec{g} + \left(\sum_f \vec{q}_f\right)_{\text{final}}$ is obeyed in an interaction (with $n = 1, \ldots$). U-process maps the final vectors back into the first Brillouin zone and these mapped-back-vectors typically have a smaller magnitude and have their directions "flipped backwards".

[2] Obviously, this is an incomplete coverage of experimental results but I hope that this coverage is representative. There is a huge amount of numerical results but I choose to be skeptical and exclude numerical simulation results from this introduction.

[3] It is also important to note that the reduced dimensionality of nanosystems results in different phonon dispersion relations and also severely limit 3-phonon anharmonic excitations upon the application of selection rules. Thus higher phonon-phonon interactions will also need to be considered as well.

and in other measurements [Eletskii2009] showed that violations of Fourier's Law occur even when the system size is much larger than the phonon mean free path. It appears to be common that low dimensional systems do not obey Fourier's Law and there is real urgency to theoretically understand what sort of "diffusive" transport this is. This review article [Dubi2011] and the references therein are useful for following more experimental work.

2.2 The Hamiltonian of a Solid

To describe interactions in a solid, it is very important to know the most basic Hamiltonian which is the Hamiltonian of a solid. We follow [Madelung1978].

We make the following simplifications [4]

$$\text{Divide electrons into 2 types} \longrightarrow \text{core electrons} + \text{valence electrons}$$
$$\text{Define an ion as} \longrightarrow \text{nucleus} + \text{core electrons}$$

So hereafter, "electrons" means "valence electrons". The Hamiltonian of the solid (in position representation) is

$$H^{\text{solid}} = T^{\text{I-I}} + W^{\text{I-I}} + T^{\text{el}} + W^{\text{el-el}} + W^{\text{el-I}} \tag{2.1}$$

where

$$\text{Kinetic energy of the ions} \quad T^{\text{I-I}} = \sum_{l=1,k}^{N_n} \left(-\frac{\hbar^2}{2m_k}\right) \nabla^2_{\vec{R}_l} \tag{2.2}$$

$$\text{Kinetic energy of the electrons} \quad T^{\text{el}} = \sum_{i=1}^{N_e} \left(-\frac{\hbar^2}{2m_e}\right) \nabla^2_{\vec{r}^e_i} \tag{2.3}$$

$$\text{Inter-ionic potential energy} \quad W^{\text{I-I}} = \frac{1}{2} \sum_{l_1 \neq l_2}^{N_n} \Phi\left(\vec{R}_{l_1} - \vec{R}_{l_2}\right) \tag{2.4}$$

$$\text{Inter-electronic potential energy} \quad W^{\text{el-el}} = \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{\left|\vec{r}^e_i - \vec{r}^e_j\right|} \tag{2.5}$$

$$\text{Ion-electron interaction potential energy} \quad W^{\text{el-I}} = -\sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l}{\left|\vec{r}^e_i - \vec{R}_l\right|} \equiv \sum_{il} V(\vec{r}_i - \vec{R}_l) \tag{2.6}$$

where Gaussian units are used and charges are in units of electronic charge. Thus the electron has charge -1 and the ion at site l has integer charge Z_l. Note that there is no need to assume these explicit expressions for $W^{\text{I-I}}$ and $W^{\text{el-I}}$.

2.2.1 Adiabatic Decoupling (Born-Oppenheimer Version)

Here we follow [Maradudin1974] including his notation. After the Hamiltonian of the solid is specified the next step is to seperate the quantum problem of the solid into the quantum problem of the electrons and the quantum problem of the ions. Note that it should be obvious that the seperation cannot be

[4] This is the rigid ion model where the core electrons and the nucleus is one object. A well known example where the core electrons and the nucleus are considered seperately is the shell model.

complete. The physical basis here is that the ions are slow and have small kinetic energy so $T^{\text{I-I}}$ is treated as the perturbation in the Hamiltonian of the solid,

$$H^{\text{solid}} = T^{\text{I-I}} + W^{\text{I-I}} + T^{\text{el}} + W^{\text{el-el}} + W^{\text{el-I}} \tag{2.7}$$

The "unperturbed" Hamiltonian is [5]

$$H_0(\vec{r},\vec{R}) \equiv W^{\text{I-I}} + T^{\text{el}} + W^{\text{el-el}} + W^{\text{el-I}} \tag{2.11}$$

The expansion parameter of the theory is some power of the ratio $\frac{m}{M_0}$ where m is the mass of the electron and M_0 is of the order of the mass of a nucleus. Let,

$$\kappa \equiv \left(\frac{m}{M_0}\right)^{\alpha} \tag{2.12}$$

Assume that we know the solution of this Schrodinger equation for fixed nuclei positions $\vec{R}$ (so $\vec{R}$ is a parameter)

$$H_0(\vec{r},\vec{R})\Phi_n(\vec{r},\vec{R}) = E_n(\vec{R})\Phi_n(\vec{r},\vec{R}) \tag{2.13}$$

where n is an electronic quantum number. We want to solve (actually, to seperate) the exact Schrodinger equation

$$H^{\text{solid}}(\vec{r},\vec{R})\Psi(\vec{r},\vec{R}) = \mathcal{E}\Psi(\vec{r},\vec{R}) \tag{2.14}$$

We define some equilibrium position $\vec{R}^0$

$$\vec{R} - \vec{R}^0 = \kappa\vec{u} \tag{2.15}$$

We will find that the equilibrium position will be defined in the course of the calculation. Expand $H_0(\vec{r},\vec{R})$ in powers of the ion displacements

$$H_0(\vec{r},\vec{R}) = H_0(\vec{r},\vec{R}^0+\kappa\vec{u}) = H_0^{(0)} + \kappa H_0^{(1)} + \kappa^2 H_0^{(2)} + \cdots \tag{2.16}$$

Expand also $E_n(\vec{R})$ and $\Phi_n(\vec{r},\vec{R})$

$$E_n(\vec{R}) = E_n(\vec{R}^0+\kappa\vec{u}) = E_n^{(0)} + \kappa E_n^{(1)} + \kappa^2 E_n^{(2)} + \cdots \tag{2.17}$$

$$\Phi_n(\vec{r},\vec{R}) = \Phi_n(\vec{r},\vec{R}^0+\kappa\vec{u}) = \Phi_n^{(0)} + \kappa \Phi_n^{(1)} + \kappa^2 \Phi_n^{(2)} + \cdots \tag{2.18}$$

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[5] Actually, in the thesis and in most literature, we expand $W^{\text{el-I}}$ about equilibrium position $\vec{R}^0$,

$$H^{\text{solid}} = T^{\text{I-I}} + W^{\text{I-I}} + T^{\text{el}} + W^{\text{el-el}} + W^{\text{el-I}}(\vec{r},\vec{R}) \tag{2.8}$$

$$= T^{\text{I-I}} + W^{\text{I-I}} + T^{\text{el}} + W^{\text{el-el}} + W^{\text{el-I}(0)}(\vec{r},\vec{R}^0) + \text{“electron-phonon terms”} \tag{2.9}$$

We ignore the "electron-phonon terms" for the time being and define the "unperturbed" Hamiltonian as,

$$H_0(\vec{r},\vec{R}) \equiv W^{\text{I-I}} + T^{\text{el}} + W^{\text{el-el}(0)} + W^{\text{el-I}}(\vec{r},\vec{R}^0) \tag{2.10}$$

The "electron-phonon terms" will be brought back via perturbation theory. See Chapter on el-ph. The difference is that the "electron-phonon terms" are not included in the calculation of the effective ion-ion potential. It will be seen at the end of the section, from the derivation of the harmonic approximation, that the effective ion-ion potential is the eigenenergy of H_0, i.e. $E_n(\vec{R})$.

$T^{\text{I-I}}$ takes the form [6]

$$T^{\text{I-I}}(\vec{R}) = -\kappa^{\frac{1}{\alpha}-2}\sum_l \left(\frac{M_0}{M_l}\right)\frac{\hbar^2}{2m}\nabla^2_{\vec{u}_l} \equiv \kappa^{\frac{1}{\alpha}-2}H_1^{(\frac{1}{\alpha}-2)} \tag{2.23}$$

It is actually possible to show that the harmonic approximation can be accommodated into the theory. This is done simply by requiring that $T^{\text{I-I}}$ have the same order in κ as $H_0^{(2)}$ which is quadratic in ion displacement. Thus,

$$\begin{aligned}
\frac{1}{\alpha}-2 &= 2 \Rightarrow \alpha = \frac{1}{4} \Rightarrow \kappa = \left(\frac{m}{M_0}\right)^{1/4} && (2.24)\\
T^{\text{I-I}} &= \kappa^2 H_1^{(2)} && (2.25)
\end{aligned}$$

The total expanded Hamiltonian is now in the form,

$$H = H_0^{(0)} + \kappa H_0^{(1)} + \kappa^2\left(H_0^{(2)} + H_1^{(2)}\right) + \kappa^3 H_0^{(3)} + \cdots \tag{2.26}$$

We seek a solution of the form

$$\Psi(\vec{r},\vec{u}) = \sum_n \chi_n(\vec{u})\Phi_n(\vec{r},\vec{u}) \tag{2.27}$$

We want to know the conditions for seperable solutions.

$$\begin{aligned}
H^{\text{solid}}(\vec{r},\vec{R})\Psi(\vec{r},\vec{R}) &= \mathcal{E}\Psi(\vec{r},\vec{R}) && (2.28)\\
H^{\text{solid}}(\vec{r},\vec{u})\Psi(\vec{r},\vec{u}) &= \mathcal{E}\Psi(\vec{r},\vec{u}) && (2.29)\\
\left(H_0^{(0)} + \kappa H_0^{(1)} + \kappa^2\left(H_0^{(2)} + H_1^{(2)}\right) + \kappa^3 H_0^{(3)} + \cdots\right)\sum_n \chi_n\Phi(\vec{r},\vec{u}) &= \mathcal{E}\sum_n \chi_n\Phi_n(\vec{r},\vec{u}) && (2.30)\\
\text{use } H_0\Phi_n(\vec{r},\vec{u}) = E_n\Phi_n(\vec{r},\vec{u}) &\quad | &&\\
\sum_n\left(E_n^{(0)} + \kappa E_n^{(1)} + \kappa^2\left(H_1^{(2)} + E_n^{(2)}\right) + \kappa^3 E_n^{(3)} + \cdots\right)\chi_n\Phi_n(\vec{r},\vec{u}) &= \mathcal{E}\sum_n \chi_n(\vec{u})\Phi_n(\vec{r},\vec{u}) && (2.31)
\end{aligned}$$

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[6] We check backwards

$$\begin{aligned}
T^{\text{I-I}}(\vec{R}) &= -\kappa^{\frac{1}{\alpha}-2}\sum_l\left(\frac{M_0}{M_l}\right)\frac{\hbar^2}{2m}\nabla^2_{\vec{u}_l} && (2.19)\\
&\quad | \quad \text{note that } \nabla^2_{\vec{R}_l} = \kappa^{-2}\nabla^2_{\vec{u}_l} &&\\
&= -\kappa^{\frac{1}{\alpha}-2}\kappa^2\sum_l\left(\frac{M_0}{M_l}\right)\frac{\hbar^2}{2m}\nabla^2_{\vec{R}_l} && (2.20)\\
&= -\kappa^{\frac{1}{\alpha}}\sum_l\left(\frac{M_0}{M_l}\right)\frac{\hbar^2}{2m}\nabla^2_{\vec{R}_l} && (2.21)\\
&\quad | \quad \text{recall that } \kappa = m^\alpha/M_0^\alpha &&\\
&= -\sum_l\frac{\hbar^2}{2M_l}\nabla^2_{\vec{R}_l} && (2.22)
\end{aligned}$$

Multiply (project) from the left by $\Phi_m^*(\vec{r},\vec{u})$ and integrate over $\vec{r}$. We can assume that eigenvectors Φ are orthonormal for all values of $\vec{u}$. We get,

$$\begin{aligned}
\kappa^2 \sum_n \int d\vec{r}\Phi_m^*(\vec{r},\vec{u}) H_1^{(2)}(\vec{u})\Phi_n(\vec{r},\vec{u})\chi_n(\vec{u}) + \sum_n \left(E_n^{(0)} + \kappa E_n^{(1)} + \cdots\right)\chi_n\delta_{nm} &= \mathcal{E}\sum_n \chi_n(\vec{u})\delta_{nm} \\
\kappa^2 \sum_n \int d\vec{r}\Phi_m^*(\vec{r},\vec{u}) H_1^{(2)}(\vec{u})\Phi_n(\vec{r},\vec{u})\chi(\vec{u}) + \left(E_m^{(0)} + \kappa E_m^{(1)} + \kappa^2 E_m^{(2)} + \cdots\right)\chi_m(\vec{u}) &= \mathcal{E}\chi_m(\vec{u}) \qquad (2.32)
\end{aligned}$$

We focus on the first term on the LHS,

$$\begin{aligned}
H_1^{(2)}(\vec{u})\Phi_n(\vec{r},\vec{u})\chi_n(\vec{u}) &= -\frac{M_0}{m}\sum_l \frac{\hbar^2}{2M_l}\nabla^2_{\vec{u}_l}\left(\Phi_n(\vec{r},\vec{u})\chi_n(\vec{u})\right) \qquad (2.33) \\
&= -\frac{M_0}{m}\sum_l \frac{\hbar^2}{2M_l}\left(\nabla^2_{\vec{u}_l}\Phi_n(\vec{r},\vec{u})\right)\chi_n(\vec{u}) \\
&\quad -\frac{M_0}{m}\sum_l \frac{\hbar^2}{M_l}\left(\nabla_{\vec{u}_l}\Phi_n(\vec{r},\vec{u})\right)\cdot\left(\nabla_{\vec{u}_l}\chi_n(\vec{u})\right) + \Phi_n(\vec{r},\vec{u})H_1^{(2)}(\vec{u})\chi_n(\vec{u}) \qquad (2.34)
\end{aligned}$$

$$\begin{aligned}
& \kappa^2 \sum_n \int d\vec{r}\Phi_m^*(\vec{r},\vec{u}) H_1^{(2)}(\vec{u})\Phi_n(\vec{r},\vec{u})\chi_n(\vec{u}) \\
= \; & \kappa^2 \sum_n \int d\vec{r}\Phi_m^*(\vec{r},\vec{u})\Phi_n(\vec{r},\vec{u}) H_1^{(2)}(\vec{u})\chi_n(\vec{u}) \\
& -\kappa^2 \sum_n\sum_l \left(\frac{M_0}{M_l}\right)\frac{\hbar^2}{m}\int d\vec{r}\Phi_m^*(\vec{r},\vec{u})\left(\nabla_{\vec{u}_l}\Phi_n(\vec{r},\vec{u})\right)\cdot\left(\nabla_{\vec{u}_l}\chi_n(\vec{u})\right) \\
& -\kappa^2 \sum_n\sum_l \left(\frac{M_0}{M_l}\right)\frac{\hbar^2}{2m}\int d\vec{r}\Phi_m^*(\vec{r},\vec{u})\left(\nabla^2_{\vec{u}_l}\Phi_n(\vec{r},\vec{u})\right)\chi_n(\vec{u}) \qquad (2.35) \\
| \; & \text{use } \int d\vec{r}\Phi_m^*(\vec{r},\vec{u})\Phi_n(\vec{r},\vec{u}) = \delta_{nm} \text{ in the first line} \\
| \; & \text{seperate } m=n \text{ terms and } m\neq n \text{ terms for the other 2 lines} \\
= \; & \kappa^2 H_1^{(2)}(\vec{u})\chi_m(\vec{u}) \\
& -\kappa^2 \sum_l \left(\frac{M_0}{M_l}\right)\frac{\hbar^2}{m}\int d\vec{r}\Phi_m^*(\vec{r},\vec{u})\left(\nabla_{\vec{u}_l}\Phi_m(\vec{r},\vec{u})\right)\cdot\left(\nabla_{\vec{u}_l}\chi_m(\vec{u})\right) \\
& -\kappa^2 \sum_{n(\neq m)}\sum_l \left(\frac{M_0}{M_l}\right)\frac{\hbar^2}{m}\int d\vec{r}\Phi_m^*(\vec{r},\vec{u})\left(\nabla_{\vec{u}_l}\Phi_n(\vec{r},\vec{u})\right)\cdot\left(\nabla_{\vec{u}_l}\chi_n(\vec{u})\right) \\
& -\kappa^2 \sum_l \left(\frac{M_0}{M_l}\right)\frac{\hbar^2}{2m}\int d\vec{r}\Phi_m^*(\vec{r},\vec{u})\left(\nabla^2_{\vec{u}_l}\Phi_m(\vec{r},\vec{u})\right)\chi_m(\vec{u}) \\
& -\kappa^2 \sum_{n(\neq m)}\sum_l \left(\frac{M_0}{M_l}\right)\frac{\hbar^2}{2m}\int d\vec{r}\Phi_m^*(\vec{r},\vec{u})\left(\nabla^2_{\vec{u}_l}\Phi_n(\vec{r},\vec{u})\right)\chi_n(\vec{u}) \qquad (2.36) \\
| \; & \text{in the absence of magnetic field, } \Phi \text{ can always be chosen to be real} \\
| \; & \text{then in the second line, we write } \Phi_m(\vec{r},\vec{u})\left(\nabla_{\vec{u}_l}\Phi_m(\vec{r},\vec{u})\right) = \frac{1}{2}\nabla_{\vec{u}_l}\Phi_m^2(\vec{r},\vec{u}) \\
| \; & \text{then } \nabla_{\vec{u}_l}\int d\vec{r}\Phi_m^2(\vec{r},\vec{u}) = 0 \text{ due to normalization}
\end{aligned}$$

$$
\begin{aligned}
| \quad & \text{define } C_m(\vec{u}) = -\kappa^2 \sum_l \left(\frac{M_0}{M_l}\right) \frac{\hbar^2}{2m} \int d\vec{r}\Phi_m(\vec{r},\vec{u}) \left(\nabla^2_{\vec{u}_l}\Phi_m(\vec{r},\vec{u})\right) \\
| \quad & \text{define } C_{mn} = -\kappa^2 \sum_l \left(\frac{M_0}{M_l}\right) \frac{\hbar^2}{m} \int d\vec{r}\Phi_m(\vec{r},\vec{u}) \left[\left(\nabla_{\vec{u}_l}\Phi_n(\vec{r},\vec{u})\right)\cdot\nabla_{\vec{u}_l} + \left(\nabla^2_{\vec{u}_l}\Phi_n(\vec{r},\vec{u})\right)\right] \\
= \quad & \kappa^2 H_1^{(2)}(\vec{u})\chi_m(\vec{u}) + C_m(\vec{u}) + C_{mn} \qquad (2.37)
\end{aligned}
$$

The complete Schrodinger equation becomes

$$\left(\kappa^2 H_1^{(2)} + E_m(\vec{u}) + C_m(\vec{u})\right)\chi_m + \sum_{n(\neq m)} C_{mn}\chi_n = \mathcal{E}\chi_m \qquad (2.38)$$

The lowest order for C_m is $\sim \kappa^4$ and the lowest order for C_{mn} is $\sim \kappa^3$. [7] The adiabatic approximation is where C_{mn} is ignored. The (nuclear) eigenvalue equation in this approximation is,

$$\left(\kappa^2 H_1^{(2)} + E_m(\vec{u}) + C_m(\vec{u})\right)\chi_{mv} = \epsilon_{mv}\chi_{mv} \qquad (2.41)$$

where v can be regarded as a vibrational quantum number. Since C_{mn} is at least of the order κ^3, the adiabatic approximation fails beyond κ^2. We expand the eigenvalue equation up to κ^2 (so C_m does not contribute) and compare order by order.

$$
\begin{aligned}
\left(\kappa^2 H_1^{(2)} + E_m(\vec{u}) + C_m(\vec{u})\right)\chi_{mv} &= \epsilon_{mv}\chi_{mv} \qquad (2.42) \\
\left(\kappa^2 H_1^{(2)} + E_m^{(0)} + \kappa E_m^{(1)} + \kappa^2 E_m^{(2)}\right)\left(\chi_{mv}^{(0)} + \kappa\chi_{mv}^{(1)} + \kappa^2\chi_{mv}^{(2)}\right) &= \left(\epsilon_{mv}^{(0)} + \kappa\epsilon_{mv}^{(1)} + \kappa^2\epsilon_{mv}^{(2)}\right) \\
&\quad \times \left(\chi_{mv}^{(0)} + \kappa\chi_{mv}^{(1)} + \kappa^2\chi_{mv}^{(2)}\right) \qquad (2.43)
\end{aligned}
$$

Zeroth order in κ gives,

$$E_m^{(0)}\chi_{mv}^{(0)} = \epsilon_{mv}^{(0)}\chi_{mv}^{(0)} \qquad (2.44)$$

First order in κ gives,

$$E_m^{(1)}\chi_{mv}^{(0)} + E_m^{(0)}\chi_{mv}^{(1)} = \epsilon_{mv}^{(1)}\chi_{mv}^{(0)} + \epsilon_{mv}^{(0)}\chi_{mv}^{(1)} \qquad (2.45)$$

Second order in κ gives,

$$\left(H_1^{(2)} + E_m^{(2)}\right)\chi_{mv}^{(0)} + E_m^{(1)}\chi_{mv}^{(1)} + E_m^{(0)}\chi_{mv}^{(2)} = \epsilon_{mv}^{(2)}\chi_{mv}^{(0)} + \epsilon_{mv}^{(1)}\chi_{mv}^{(1)} + \epsilon_{mv}^{(0)}\chi_{mv}^{(2)} \qquad (2.46)$$

From the zeroth order equation, we immediately get $\epsilon_{mv}^{(0)} = E_m^{(0)} = E_m^{(0)}(\vec{R}^0)$ and we use it in the first order equation to get,

$$E_m^{(1)}\chi_{mv}^{(0)} = \epsilon_{mv}^{(1)}\chi_{mv}^{(0)} \Rightarrow E_m^{(1)} = \epsilon_{mv}^{(1)} \qquad (2.47)$$

[7] We estimate as follows,

$$
\begin{aligned}
\text{lowest } C_m &\sim \kappa^2\Phi^{(2)}\nabla^2_{\vec{u}}\Phi^{(2)} = \kappa^2\Phi^{(2)} = \kappa^4 \qquad (2.39) \\
\text{lowest } C_{mn} &\sim \kappa^2\Phi^{(1)}\nabla_{\vec{u}}\Phi^{(1)} = \kappa^2\Phi^{(1)} = \kappa^3 \qquad (2.40)
\end{aligned}
$$

However $E_m^{(1)}$ is first order in $\vec{u}$ and $\epsilon_{mv}^{(1)}$ is a constant, thus to satisfy the equality, we need $E_m^{(1)} = 0$,(and so $\epsilon_{mv}^{(1)} = 0$) i.e.

$$E_m^{(1)} = \sum_l \left(\nabla_{\vec{R}_l} E_m(\vec{R})\right) \cdot \vec{u}_l \Bigg|_{\vec{R}=\vec{R}^0} = 0 \tag{2.48}$$

Thus the equilibrium configuration $\vec{R}^0$, corresponding to the mth electronic state is defined. We use $\epsilon_{mv}^{(0)} = E_m^{(0)}$ and $E_m^{(1)} = 0 = \epsilon_{mv}^{(1)}$ in the second order equation to get

$$\begin{aligned}
\left(H_1^{(2)} + E_m^{(2)}\right) \chi_{mv}^{(0)} + \epsilon_{mv}^{(0)} \chi_{mv}^{(2)} &= \epsilon_{mv}^{(2)} \chi_{mv}^{(0)} + \epsilon_{mv}^{(0)} \chi_{mv}^{(2)} && (2.49)\\
\left(H_1^{(2)} + E_m^{(2)}\right) \chi_{mv}^{(0)} &= \epsilon_{mv}^{(2)} \chi_{mv}^{(0)} && (2.50)\\
&| \quad \text{multiply } \kappa^2 \text{ on both sides} \\
\left(\kappa^2 H_1^{(2)} + \kappa^2 E_m^{(2)}\right) \chi_{mv}^{(0)} &= \left(\kappa^2 \epsilon_{mv}^{(2)}\right) \chi_{mv}^{(0)} && (2.51)\\
\text{Recall, Ion kinetic energy term : } \kappa^2 H_1^{(2)} &= T^{\text{I-I}}(\vec{R}) && (2.52)\\
\text{Effective ion-ion harmonic potential term : } \kappa^2 E_m^{(2)} &= \kappa^2 \frac{1}{2} \sum_{l_1 l_2} \sum_{\alpha_1 \alpha_2} \frac{\partial^2 E_m}{\partial R_{l_1\alpha_1} \partial R_{l_2\alpha_2}} u_{l_1\alpha_1} u_{l_2\alpha_2} \Bigg|_{\vec{R}=\vec{R}^0} && (2.53)\\
&= \frac{1}{2} \sum_{l_1 l_2} \sum_{\alpha_1 \alpha_2} \frac{\partial^2 E_m}{\partial u_{l_1\alpha_1} \partial_{l_2\alpha_2}} \Bigg|_{\vec{u}=0} u_{l_1\alpha_1} u_{l_2\alpha_2} && (2.54)
\end{aligned}$$

And so we get the usual ion-ion Schrodinger equation in the harmonic approximation, where $\kappa^2 \epsilon_{mv}^{(2)}$ is the harmonic phonon energy. Thus the harmonic approximation is really part of the adiabatic approximation. The effective ion-ion potential is given by E_m which implies that there is electronic contribution to the ion-ion interaction as it should because the electron-ion problem cannot be completely seperated. This results in some form of uncontrolled double counting of the electronic contribution when electron-phonon interaction is treated. Electrons enter the phonon frequency via E_m and also enter the electron-phonon interaction.

For the rest of the thesis, the effective ion-ion potential will be denoted by Φ instead of E_m and for solids with multi-atoms in a unit cell, we need to generalize the index notation of the displacement vector to $u_{lk\alpha}$ where l denotes the unit cell at position $\vec{R}_l^{eq}$, k denotes the kth atom in the unit cell and α denotes the Cartesian component of displacement of that kth atom. Effectively, we can write such an expansion for $W^{\text{I-I}}$.

$$\begin{aligned}
W^{\text{I-I}} &= \Phi \Bigg|_{\vec{u}=0} + \sum_{lk\alpha} \frac{\partial \Phi}{\partial u_{lk\alpha}} \Bigg|_{\vec{u}=0} u_{lk\alpha} + \frac{1}{2!} \sum_{l_1k_1\alpha_1 l_2k_2\alpha_2} \frac{\partial^2 \Phi}{\partial u_{l_1k_1\alpha_1} \partial u_{l_2k_2\alpha_2}} \Bigg|_{\vec{u}=0} u_{l_1k_1\alpha_1} u_{l_2k_2\alpha_2} + \cdots \\
&| \quad \text{the first term is a constant shift in the Hamiltonian which can be absorbed} \\
&| \quad \text{the second term is zero as the minimum of } \Phi \text{ is at } \vec{R}_{lk}^{eq} \text{ (BO energy surface)} \\
&| \quad \text{the third term together with } T^{\text{I-I}} \text{ is known as the harmonic approximation} \\
&| \quad \text{higher order terms are called anharmonic corrections} \\
&= \frac{1}{2!} \sum_{l_1k_1\alpha_1 l_2k_2\alpha_2} \frac{\partial^2 \Phi}{\partial u_{l_1k_1\alpha_1} \partial u_{l_2k_2\alpha_2}} \Bigg|_{\vec{u}=0} u_{l_1k_1\alpha_1} u_{l_2k_2\alpha_2} + \cdots && (2.55)
\end{aligned}$$

Taylor expansion of $W^{\text{el-I}}$ around equilibrium positions is treated in the chapter on electron-phonon interaction.

Part I

Theories and Methods

Chapter 3

Non-Equilibrium Green's Functions (NEGF)(Mostly Phonons)

[**Chapter Introduction and Roadmap:**] We enumerate the introduction and the scope of the chapter to make it easy to read. (All acronyms can be deciphered from the Contents Page.)

1. In transport, we have to deal with non-equilibrium systems (from time dependent Hamiltonians) and many-body interactions (from many-body interaction Hamiltonians).

2. This chapter aims to show in great detail that, at the pertubative level, NEGF is the "Mother Theory" of transport theories. We develop from NEGF into three forms for transport; the Landauer-like form, the (quantum) kinetic equation form and the linear response form.

3. This chapter also presents NEGF rigorously and systematically, thus exhibiting its full generality. This allows NEGF to guide us through generalizations beyond the three forms of transport mentioned. (This thesis is only concerned with the first two forms.)

4. We show that despite starting from a time dependent and a many-body interacting Hamiltonian, a perturbative expression can still be obtained. This expression originated from Kadanoff, Baym in [Kadanoff1962] and Keldysh in [Keldysh1965]. It looks symbolically similar to the usual finite temperature equilibrium Matsubara Field Theory. Thus all the nice features of Feynman diagrams expansions and resummations are automatically available in this theory!

5. A contour time parameterization of Heisenberg operators is needed to arrive at the pertubation expansion. Once the perturbation is done, we need to go back to the physical problem in real time. This is done by applying Langreth's theorem to the (contour time) terms we kept in the perturbation expansion.

6. We summarize the perturbation procedure using NEGF with the section "Receipe of NEGF".

7. We then use NEGF in Landauer-like theory to derive the energy current for an (arbitrary) interacting central system. It was specialized to two cases: (1) the left-central coupling and the right-central coupling are proportional to each other (2) the central is harmonic with no many-body interactions. We also showed that calculation of noise (associated to energy current) is possible with the help of NEGF.

8. NEGF is then used to develop kinetic theory. First the Green's functions give us an equation that looks like a kinetic equation - I call it "pre-QKE". Then we turn pre-QKE to QKE (i.e. turn Green's functions to distributions) via two different ways: (1) KB ansatz and (2) GKB ansatz.

9. Finally NEGF is shown to develop into linear response theory but this is not the main theme of this thesis so linear response theory is briefly mentioned throughout the thesis only for completeness.

As our focus is on phonon transport, we will present the theory in phonon variables. The parallel presentation for electrons is shown in the appendix.

3.1 Foundations

3.1.1 Expression for Perturbation

The references we follow in this section are [Haug2007], [Rammer2007] and [Leeuwen2005]. For a concise review which is intended for phonon transport, see [Wang2008]

[The Statistical Average] We write the time dependent Hamiltonian in this form,

$$H(t) = H_0 + H_{\text{int}} + V(t)\theta(t - t_0) \tag{3.1}$$

where H_0 is quadratic in the variables and the (parametric) time dependent $V(t)$ is switched on at $t = t_0^+$. The step function is there only to symbolise the (sudden) switch on. [1]

The purpose of the switch on allows us to write statistical averages using Heisenberg picture and a simpler form results because we choose t_0 to be the time when the pictures coincide.

The non-equilibrium average is thus defined as,

$$\boxed{\langle A(t)\rangle = \text{Tr}\left(\rho_{t_0} A_H(t)\right) = \frac{\text{Tr}\left(e^{-\beta(H_0+H_{\text{int}})} A_H(t)\right)}{\text{Tr}\left(e^{-\beta(H_0+H_{\text{int}})}\right)}} \tag{3.3}$$

where $\beta = \frac{1}{k_B T}$ and T is the equilibrium temperature before the switch-on.[2]

[Establishing the Contour ordering identity] The idea is simply that Heisenberg operators can be written as a contour parameterized Interaction operator. The parameter on the contour is denoted by "τ", the so-called contour time variable.[3]

First we artifically partition the Hamiltonian as

$$H(t) = H_0 + (H_{\text{int}} + V(t)) \tag{3.4}$$

[1] This is not to be confused with the adiabatic switch on as seen in [Gross1991] chapter 18 and [Fetter2003] pg 59. It means we can use a mathematical device

$$H(t) \equiv H_0 + e^{-\epsilon|t|} H_{\text{int}} \tag{3.2}$$

and prove that (within perturbation theory) if we start with an eigenstate of H_0, we will land up in some eigenstate of $H_0 + H_{\text{int}}$. This is protected by Gell-Mann and Low theorem. We are thus assured that within perturbation theory, an adiabatic switch on of H_{int} will give us something sensible. I am unaware if there is such a corresponding "protection" for the time dependent Hamiltonian $H(t) = H_0 + H_{\text{int}} + V(t)$, i.e. using the mathematical device, we write $H(t) = H_0 + H_{\text{int}} + e^{-\epsilon|t|}V(t)$ and do we have the guarantee that if we start from some $H_0 + H_{\text{int}}$ eigenstate, we will land up in some eigenstate of $H(t) = H_0 + H_{\text{int}} + V(t)$? Because of this, I will avoid using the phrase "adiabatic switch on of $V(t)$" in the main text.

[2] Before the switching on of $V(t)$, the system is in equilibrium which is a canonical distribution $\rho_{t_0} = \frac{e^{-\beta(H_0+H_{\text{int}})}}{\text{Tr}\left(e^{-\beta(H_0+H_{\text{int}})}\right)}$.

[3] Note that in quantum dynamics, a "picture" consists of 2 components, the operator and the state, eg the Heisenberg picture consists of the Heisenberg operator and the Heisenberg state. Here we are rewriting the Heisenberg operator to the Interaction operator, so there is no change in "picture". It is just an operator transformation. Strictly speaking, in terms of dynamics, we are in Heisenberg picture throughout.

and use Dyson's identity (see Appendix A) and write the Heisenberg evolution from the coincident time t_0 as

$$
\begin{aligned}
A_H(t) &= U_H(t,t_0)^\dagger A(t_0) U_H(t,t_0) &(3.5)\\
&= \left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt'(H_{\text{int}}+V(t'))_{H_0}}\right)^\dagger e^{\frac{i}{\hbar}H_0(t-t_0)} A(t_0) e^{-\frac{i}{\hbar}H_0(t-t_0)} \left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt'(H_{\text{int}}+V(t'))_{H_0}}\right) &(3.6)\\
&= \left(\bar{T}e^{\frac{i}{\hbar}\int_{t_0}^{t} dt'(H_{\text{int}}+V(t'))_{H_0}}\right) A_{H_0}(t) \left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt'(H_{\text{int}}+V(t'))_{H_0}}\right) &(3.7)
\end{aligned}
$$

where T is the time ordering operator and $\bar{T}$ is the anti-time ordering operator [4]. Also such notation has the meaning

$$
(H_{\text{int}}+V(t'))_{H_0} = e^{\frac{i}{\hbar}H_0(t'-t_0)}(H_{\text{int}}+V(t'))e^{-\frac{i}{\hbar}H_0(t'-t_0)} \tag{3.8}
$$

The identity we want to prove is the following,

$$
\begin{aligned}
A_H(t) &= \left(\bar{T}e^{\frac{i}{\hbar}\int_{t_0}^{t} dt'(H_{\text{int}}+V(t'))_{H_0}}\right) A_{H_0}(t) \left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt'(H_{\text{int}}+V(t'))_{H_0}}\right) &(3.9)\\
&= \left(T_{\overleftarrow{c}_t}e^{-\frac{i}{\hbar}\int_{\overleftarrow{c}_t} dt'(H_{\text{int}}+V(t'))_{H_0}}\right) A_{H_0}(t) \left(T_{\overrightarrow{c}_t}e^{-\frac{i}{\hbar}\int_{\overrightarrow{c}_t} dt'(H_{\text{int}}+V(t'))_{H_0}}\right) &(3.10)\\
&\quad | \ \text{where } T_{\overrightarrow{c}_t} \text{ denotes time ordering parameterized by the "upper" contour}\\
&\quad | \ \text{and } T_{\overleftarrow{c}_t} \text{ denotes anti-time ordering parameterized by the "lower" contour}\\
&= T_{c_t}\left(e^{-\frac{i}{\hbar}\int_{c_t} d\tau(H_{\text{int}}+V(\tau))_{H_0}} A_{H_0}(t)\right) &(3.11)
\end{aligned}
$$

$$
\boxed{A_H(t) = T_{c_t}\left(e^{-\frac{i}{\hbar}\int_{c_t} d\tau(H_{\text{int}}+V(\tau))_{H_0}} A_{H_0}(t)\right)} \tag{3.12}
$$

where contour c_t is the oriented path parametrized by contour variable τ as shown below.

Figure 3.1: *The contour c_t parameterised by τ. The diagram on the left is the actual path. The diagram on the right is artifically "blown up" for clarity. On the right, the "upper" contour parameterizes evolution from t_0 to t and the "lower" contour parameterizes evolution from t to t_0. This is the sequence of evolution when we read the Interaction operator from right to left.*

[4] The Hermitian conjugate changes the sign of the exponent and it also reverses the order of the operators giving rise to $\bar{T}$.

The proof is as follows, starting from the RHS (we write $(H_{\text{int}} + V(\tau))_{H_0}$ as $(\tau)_{H_0}$ and c_t as c to save some writing)

$$\begin{aligned}
\text{RHS} &= T_c\left(e^{-\frac{i}{\hbar}\int_c d\tau(\tau)_{H_0}} A_{H_0}(t)\right) && (3.13)\\
&= \sum_{n=0}^{\infty}\left(-\frac{i}{\hbar}\right)^n \frac{1}{n!}\int_c d\tau_1 \ldots \int_c d\tau_n T_c\left((\tau_1)_{H_0}\ldots(\tau_n)_{H_0} A_{H_0}(t)\right) && (3.14)
\end{aligned}$$

Divide each contour integral into 2 branches,

$$\int_c = \int_{\overrightarrow{c}} + \int_{\overleftarrow{c}} \qquad \text{where } \int_{\overrightarrow{c}} = \int_{t_0}^{t} \text{ and } \int_{\overleftarrow{c}} = \int_{t}^{t_0} \tag{3.15}$$

The nth order term has 2^n real time integrals. Take the example of $\binom{n}{2}$ term,

$$\begin{aligned}
&\int_{\overrightarrow{c}} d\tau_1 \int_{\overrightarrow{c}} d\tau_2 \int_{\overleftarrow{c}} d\tau_3 \ldots \int_{\overleftarrow{c}} d\tau_n\ T_c\left((\tau_1)_{H_0}\ldots(\tau_n)_{H_0} A_{H_0}(t)\right)\\
= &\int_{\overleftarrow{c}} d\tau_3 \ldots \int_{\overleftarrow{c}} d\tau_n\ T_{\overleftarrow{c}}\left((\tau_3)_{H_0}\ldots(\tau_n)_{H_0}\right) A_{H_0}(t) \int_{\overrightarrow{c}} d\tau_1 \int_{\overrightarrow{c}} d\tau_2\ T_{\overrightarrow{c}}\left((\tau_1)_{H_0}(\tau_2)_{H_0}\right) && (3.16)
\end{aligned}$$

where the factors to the left of $A_{H_0}(t)$ are later than time t ("lower" contour) and the factors to the right of $A_{H_0}(t)$ are earlier than time t ("upper" contour). This term has mulitiplicity $\binom{n}{2}$. For a general term in the nth order, it has multiplicity $\binom{n}{m}$. So we can write the nth order term as

$$\begin{aligned}
&\int_c d\tau_1 \ldots \int_c d\tau_n T_c((\tau_1)_{H_0}\ldots(\tau_n)_{H_0} A_{H_0}(t))\\
= &\sum_{m=0}^{n}\binom{n}{m}\int_{\overleftarrow{c}} d\tau_{m+1}\ldots d\tau_n T_{\overleftarrow{c}}((\tau_{m+1})_{H_0}\ldots(\tau_n)_{H_0}) A_{H_0}(t)\int_{\overrightarrow{c}} d\tau_1 \ldots d\tau_m T_{\overrightarrow{c}}((\tau_1)_{H_0}\ldots(\tau_m)_{H_0})\\
| \quad &\text{note } \binom{n}{m} = \frac{n!}{m!(n-m)!} \text{ and we can rewrite into}\\
= &\sum_{m=0}^{\infty}\sum_{k=0}^{\infty}\frac{n!}{m!k!}\delta_{n,k+m}\int_{\overleftarrow{c}} d\tau_1 \ldots d\tau_k T_{\overleftarrow{c}}((\tau_1)_{H_0}\ldots(\tau_k)_{H_0}) A_{H_0}(t)\int_{\overrightarrow{c}} d\tau_1 \ldots d\tau_m T_{\overrightarrow{c}}((\tau_1)_{H_0}\ldots(\tau_m)_{H_0})
\end{aligned}$$

And for the full series,

$$\begin{aligned}
T_c\left(e^{-\frac{i}{\hbar}\int_c d\tau(\tau)_{H_0} A_{H_0}(t)}\right) &= \sum_{m=0}^{\infty}\sum_{k=0}^{\infty}\frac{n!}{m!k!}\frac{1}{n!}\left(-\frac{i}{\hbar}\right)^{k+m}\int_{\overleftarrow{c}} d\tau_1 \ldots d\tau_k T_{\overleftarrow{c}}((\tau_1)_{H_0}\ldots(\tau_k)_{H_0}) A_{H_0}(t)\\
&\quad \times \int_{\overrightarrow{c}} d\tau_1 \ldots d\tau_m T_{\overrightarrow{c}}((\tau_1)_{H_0}\ldots(\tau_m)_{H_0})\\
&= \sum_{k=0}^{\infty}\frac{1}{k!}\left(-\frac{i}{\hbar}\right)^{k}\int_{\overleftarrow{c}} d\tau_1 \ldots d\tau_k T_{\overleftarrow{c}}((\tau_1)_{H_0}\ldots(\tau_k)_{H_0}) A_{H_0}(t)\\
&\quad \times \sum_{m=0}^{\infty}\frac{1}{m!}\left(-\frac{i}{\hbar}\right)^{m}\int_{\overrightarrow{c}} d\tau_1 \ldots d\tau_m T_{\overrightarrow{c}}((\tau_1)_{H_0}\ldots(\tau_m)_{H_0})\\
&\quad | \quad \text{write } T_{\overleftarrow{c}} \text{ as } \bar{T} \text{ and } T_{\overrightarrow{c}} \text{ as } T\\
&\quad | \quad \text{write in } \int_{\overrightarrow{c}} = \int_{t_0}^{t} \text{ and } \int_{\overleftarrow{c}} = \int_{t}^{t_0}
\end{aligned}$$

$$
\begin{aligned}
&= \left(\bar{T}e^{-\frac{i}{\hbar}\int_t^{t_0} dt'(H_{\rm int}+V(t'))_{H_0}}\right) A_{H_0}(t) \left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt'(H_{\rm int}+V(t'))_{H_0}}\right) \\
&| \quad \text{invert the integral limits in the operator on the left to get a sign change} \\
&= \left(\bar{T}e^{\frac{i}{\hbar}\int_{t_0}^{t} dt'(H_{\rm int}+V(t'))_{H_0}}\right) A_{H_0}(t) \left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt'(H_{\rm int}+V(t'))_{H_0}}\right) \\
&= \text{LHS}
\end{aligned}
$$

Hence the proof is completed.

[Derivation of the perturbation expression] We will now make use of the contour ordering identity and apply it to the time-ordered Green's function (just take it to be a strangely defined two operator averaged function for now, the proper definitions are given later) so that we get an expression amendable for perturbation. Recall the definition of the phonon displacement operator [5] $u_{lk\alpha}$ from the appendix and so using the phonon Green's function as example,

$$
\begin{aligned}
& D(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) \\
\equiv\ & -\frac{i}{\hbar}\frac{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\rm int})}T(u_H(l_1k_1\alpha_1t_1)u_H(l_2k_2\alpha_2t_2))\right)}{\mathrm{Tr}(e^{-\beta(H_0+H_{\rm int})})} && (3.17)\\
=\ & -\frac{i}{\hbar}\langle T(u_H(l_1k_1\alpha_1t_1)u_H(l_2k_2\alpha_2t_2))\rangle && (3.18)\\
|\ & \text{ where } T \text{ is a time ordering symbol} \\
|\ & \text{ the } T \text{ symbol only serves to remind that } t_1 \text{ and } t_2 \text{ are arbitrary and unrelated} \\
|\ & \text{ a proper meaning of } T \text{ will emerge in the derivation} \\
|\ & \ u_H \text{ is the phonon displacement operator in the Heisenberg picture.} \\
|\ & \text{ Use the contour identity for each Heisenberg operator} \\
=\ & -\frac{i}{\hbar}\left\langle T_{c_{t_1}}\left(e^{-\frac{i}{\hbar}\int_{c_{t_1}} d\tau(H_{\rm int}+V(\tau))_{H_0}}u_{H_0}(l_1k_1\alpha_1t_1)\right) T_{c_{t_2}}\left(e^{-\frac{i}{\hbar}\int_{c_{t_2}} d\tau(H_{\rm int}+V(\tau))_{H_0}}u_{H_0}(l_2k_2\alpha_2t_2)\right)\right\rangle \\
|\ & \text{ combine the 2 contours, see the diagram} \\
=\ & -\frac{i}{\hbar}\left\langle T_{c_{t_1}+c_{t_2}}\left(e^{-\frac{i}{\hbar}\int_{c_{t_1}+c_{t_2}} d\tau(H_{\rm int}+V(\tau))_{H_0}}u_{H_0}(l_1k_1\alpha_1t_1)u_{H_0}(l_2k_2\alpha_2t_2)\right)\right\rangle
\end{aligned}
$$

where we avoided commas in the arguments whenever possible to reduce cluttering. Thus we can

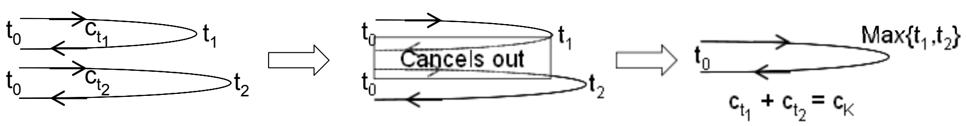


Figure 3.2: *Combining 2 contours to form the Keldysh contour for the one-particle Green's function. The first 2 diagrams take $t_2 > t_1$ and the last diagram is general. Again, be reminded that these are artifically blown up diagrams.*

generalize and state that the final contour is from t_0 to $\max\{t_1, t_2\}$ which we shall call it the Keldysh

[5]Without reading the appendix, the indices l, k and α refer to unit cell l, kth atom in the unit cell and the αth Cartesian component of the displacement vector.

contour c_K. So

$$\begin{aligned} D(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) &= -\frac{i}{\hbar}\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau(H_{\text{int}}+V(\tau))_{H_0}}u_{H_0}(l_1k_1\alpha_1t_1)u_{H_0}(l_2k_2\alpha_2t_2)\right)\right\rangle \quad (3.19)\\ &= -\frac{i}{\hbar}\frac{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\text{int}})}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau(H_{\text{int}}+V(\tau))_{H_0}}u_{H_0}(l_1k_1\alpha_1t_1)u_{H_0}(l_2k_2\alpha_2t_2)\right)\right)}{\mathrm{Tr}(e^{-\beta(H_0+H_{\text{int}})})} \quad (3.20)\end{aligned}$$

The final step to do is to change the statistical weight to $e^{-\beta H_0}$ where H_0 is quadratic in the variables so that Wick's factorization theorem can be applied. So we apply Dyson's identity again simply by letting $\beta = \frac{i}{\hbar}(t-t_0)$,

$$e^{-\beta(H_0+H_{\text{int}})} = e^{-\beta H_0}\left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t_0-i\beta\hbar}dt'(H_{\text{int}})_{H_0}(t')}\right) \quad (3.21)$$

where $(H_{\text{int}})_{H_0}(t) = e^{\frac{i}{\hbar}H_0(t-t_0)}H_{\text{int}}(t_0)e^{-\frac{i}{\hbar}H_0(t-t_0)}$ and T orders from t_0 to $t_0 - i\hbar\beta$. The term in round brackets can also be treated as a contour ordered expression. In this case, we call this the Matsubara contour, c_M that parameterizes $t_0 - i\hbar 0$ to $t_0 - i\hbar\beta$. The Green's function is now given by

$$\begin{aligned} &D(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2)\\ = &-\frac{i}{\hbar}\frac{\mathrm{Tr}\left(e^{-\beta H_0}\left(T_{c_M}e^{-\frac{i}{\hbar}\int_{c_M}d\tau(H_{\text{int}})_{H_0}(\tau)}\right)T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau((H_{\text{int}}+V(\tau))_{H_0}}u_{H_0}(l_1k_1\alpha_1t_1)u_{H_0}(l_2k_2\alpha_2t_2)\right)\right)}{\mathrm{Tr}\left(e^{-\beta H_0}T_{c_M}e^{-\frac{i}{\hbar}\int_{c_M}d\tau(H_{\text{int}})_{H_0}(\tau)}\right)}\end{aligned}$$

| Insert a unity term $T_{c_K}e^{-\frac{i}{\hbar}\int_{c_K}d\tau\left((H_{\text{int}}+V(\tau))_{H_0}\right)}$ into the denominator.
| to see why it is unity, write it back into Heisenberg operators using the contour ordering identity
| and combine the contours c_K and c_M into one contour path, $c_K + c_M$.
| we denote $t_1 \to \tau_1$ and $t_2 \to \tau_2$
| this is to emphasize that t_1 and t_2 have no specific relationship until the perturbation is done

$$\boxed{\begin{aligned} &D(l_1k_1\alpha_1\tau_1l_2k_2\alpha_2\tau_2)\\ &= -\frac{i}{\hbar}\frac{\mathrm{Tr}\left(e^{-\beta H_0}T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K+c_M}d\tau(H_{\text{int}})_{H_0}(\tau)}e^{-\frac{i}{\hbar}\int_{c_K}d\tau V_{H_0}(\tau)}u_{H_0}(l_1k_1\alpha_1\tau_1)u_{H_0}(l_2k_2\alpha_2\tau_2)\right)\right)}{\mathrm{Tr}\left(e^{-\beta H_0}T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K+c_M}d\tau(H_{\text{int}})_{H_0}(\tau)}e^{-\frac{i}{\hbar}\int_{c_K}d\tau V_{H_0}(\tau)}\right)\right)}\end{aligned}} \quad (3.22)$$

This is the final form where Wick's theorem applies and the denominator cancels disconnected diagrams. [6] The relationship between t_1 and t_2 only affects the choice of c_K but that is after the perturbation. Also, it is clear that any number of Heisenberg operators give only one c_K after combining the contours. Now, at least in perturbation theory, we have an expression that can potentially probe non-equilibrium

[6] Following the literature, we can write eqn (3.22) as $D(l_1k_1\alpha_1\tau_1l_2k_2\alpha_2\tau_2) \equiv -\frac{i}{\hbar}\langle T_{c_K+c_M}(u_H(l_1k_1\alpha_1\tau_1)u_H(l_2k_2\alpha_2\tau_2))\rangle$ which is the so called contour ordered Green's function. Thus the contour ordered Green's function is really a nice symbolic form that represents eqn (3.22) where really the calculation happens.

regimes. [7] Thus now the machinary of Feynman diagrams is also available in NEGF. [8]

[7]We could take on a different way of "partitioning" the Hamiltonian and we can derive a different expression for the Green's function.

$$\begin{aligned}
& D(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) \\
= \quad & -\frac{i}{\hbar}\frac{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\mathrm{int}})}T(u_H(l_1k_1\alpha_1t_1)u_H(l_2k_2\alpha_2t_2))\right)}{\mathrm{Tr}(e^{-\beta(H_0+H_{\mathrm{int}})})} \\
| \quad & \text{Change each Heisenberg operator with the differently partitioned contour-ordering identity} \\
| \quad & \text{i.e. use } A_H(t) = T_c\left(e^{-\frac{i}{\hbar}\int_c d\tau V_{H_0+H_{\mathrm{int}}}(\tau)}A_{H_0+H_{\mathrm{int}}}(t)\right) \\
| \quad & \text{proceed to combine the contours and then "split" the statistical operator just like in the main text, we get,} \\
= \quad & -\frac{i}{\hbar}\frac{\mathrm{Tr}\left(e^{-\beta H_0}\left(T_{c_M}e^{-\frac{i}{\hbar}\int_{c_M}d\tau(H_{\mathrm{int}})_{H_0}(\tau)}\right)T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau V_{H_0+H_{\mathrm{int}}}}u_{H_0+H_{\mathrm{int}}}(l_1k_1\alpha_1t_1)u_{H_0+H_{\mathrm{int}}}(l_2k_2\alpha_2t_2)\right)\right)}{\mathrm{Tr}\left(e^{-\beta H_0}T_{c_M}e^{-\frac{i}{\hbar}\int_{c_M}d\tau(H_{\mathrm{int}})_{H_0}(\tau)}\right)}
\end{aligned}$$

However, we are stuck as the operators are in different unitary-transformed form so we can't combine the expression into one single S-matrix form.

We could even start from H_0 and switch on $H_{\mathrm{int}} + V(t)$ so that the statistical average to use is

$$\langle\ldots\rangle = \frac{\mathrm{Tr}e^{-\beta H_0}\ldots}{\mathrm{Tr}e^{-\beta H_0}} \tag{3.23}$$

The final perturbation expression is actually simpler with only Keldysh contour and the availability of Wick's theorem is immediate.

$$D(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) = -\frac{i}{\hbar}\frac{\mathrm{Tr}\left(e^{-\beta H_0}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau(H_{\mathrm{int}})_{H_0}(\tau)}e^{-\frac{i}{\hbar}\int_{c_K}d\tau V_{H_0}(\tau)}u_{H_0}(l_1k_1\alpha_1t_1)u_{H_0}(l_2k_2\alpha_2t_2)\right)\right)}{\mathrm{Tr}\left(e^{-\beta H_0}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau(H_{\mathrm{int}})_{H_0}(\tau)}e^{-\frac{i}{\hbar}\int_{c_K}d\tau V_{H_0}(\tau)}\right)\right)} \tag{3.24}$$

However we are not in favor of this expression because it seems artifical in switching on H_{int} which may represent Coulomb interaction, phonon-phonon interaction or electron-phonon interaction which cannot really be switched on or off.

[8]Here is quick summary of the various levels of approximations in diagrammatic perturbation theory. This is stated in increasing order of sophistication.

1. We need to pick out irreducible (proper) self energy diagrams. Irreducible (proper) self energy diagrams are diagrams that cannot be split into 2 by "cutting" only 1 Green's function line.
2. Inserting an irreducible self energy diagram into the Dyson's equation amounts to an infinite sum of that diagram.
3. To set up a self consistent self energy diagram, we need to pick skeleton diagrams from the irreducible self energy diagrams. Then replace free Green's functions with full Green's functions in the diagrams. Skeleton diagrams are irreducible diagrams with no self energy insertions. We can make skeleton diagrams by removing self energy insertions from irreducible diagrams.
4. The self consistent diagram is then inserted into the Dyson's equation and the full Green's function is solved self consistently. It appears that Hedin-like equations generate the self consistent diagrams within the theory itself.

Now the final contour, $c_K + c_M$ is of this form

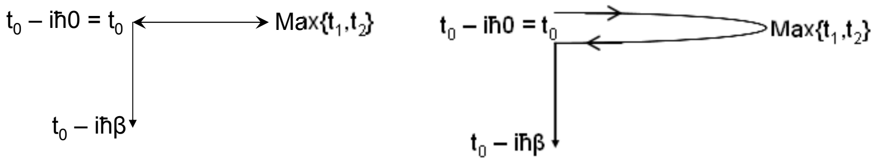


Figure 3.3: *The combined Keldysh contour c_K with the Matsubara contour c_M. The diagram on the left is the actual path. The diagram on the right is the "blown up" path shown for clarity. It appears that c_M is later than c_K but actually it is the other way round, c_K is later than c_M. Recall that c_K appears when $V(t)$ is switched on.*

We mention some special limits to indicate the generality of NEGF.

1. Matsubara $T \neq 0$ field theory: set $V(t) = 0$ and restrict $t_0 < \tau < t_0 - i\beta\hbar$. See appendix for the derivation.

2. Linear Response Theory: simply just take first order perturbation in $V(t)$ (this is true for mechanical perturbations). See the last section of this chapter.

3.1.2 Wick's Theorem (Phonons)

We now quickly digress to fill in the proof for Wick's theorem following [Rammer2007]. We consider the case of bosonic operators which is the main interest in this thesis. The crux is that the statistical weight is a quadratic Hamiltonian.[9]

First we establish 2 identities:

Identity 1:

$$\begin{aligned} \left[a_q^\dagger, \rho(H_0)\right]_- &= \rho(H_0) a_q^\dagger \left(e^{\hbar\omega_q/k_BT} - 1\right) && (3.25) \\ \left[a_q, \rho(H_0)\right]_- &= \rho(H_0) a_q \left(e^{-\hbar\omega_q/k_BT} - 1\right) && (3.26) \end{aligned}$$

where $a_q^\dagger \equiv a_{\vec{q}H_0}^\dagger$, $a_q \equiv a_{\vec{q}H_0}$ are bosonic operators in the for mode q and ω_q is the angular frequency of mode q. We omitted the vector notation and the H_0 unitary transformation here just to simplify writing.

Proof of identity 1:

Write $\rho(H_0)$ explicitly into modes:

$$\begin{aligned} a_q^\dagger \rho(H_0) &= a_q^\dagger \prod_{q'} \frac{e^{-\beta\hbar\omega_{q'} a_{q'}^\dagger a_{q'}}}{\mathrm{Tr}\left(e^{-\beta\hbar\omega_{q'} a_{q'}^\dagger a_{q'}}\right)} && (3.27) \\ &= \left(\prod_{q'(\neq q)} \frac{e^{-\beta\hbar\omega_{q'} a_{q'}^\dagger a_{q'}}}{\mathrm{Tr}\left(e^{-\beta\hbar\omega_{q'} a_{q'}^\dagger a_{q'}}\right)}\right) a_q^\dagger \frac{e^{-\beta\hbar\omega_q a_q^\dagger a_q}}{\mathrm{Tr}\left(e^{-\beta\hbar\omega_q a_q^\dagger a_q}\right)} && (3.28) \end{aligned}$$

[9] A slightly more general Wick's theorem is proved in section 5.3.1. That case is when the statistical weight is quadratic + linear.

$$
\begin{aligned}
& \mid \text{ use } [a_q, a_q^\dagger] = 1 \Rightarrow a_q^\dagger a_q = a_q a_q^\dagger - 1 \text{ in the exponent.} \\
= & \left(\prod_{q'(\neq q)} \frac{e^{-\beta\hbar\omega_{q'} a_{q'}^\dagger a_{q'}}}{\mathrm{Tr}\left(e^{-\beta\hbar\omega_{q'} a_{q'}^\dagger a_{q'}}\right)} \right) \frac{1}{\mathrm{Tr}\left(e^{-\beta\hbar\omega_q a_q^\dagger a_q}\right)} e^{\beta\hbar\omega_q} a_q^\dagger e^{-\beta\hbar\omega_q a_q a_q^\dagger} \qquad (3.29) \\
& \mid \text{ Expand the exponential term, insert } a_q^\dagger \text{ from left and remove } a_q^\dagger \text{ from right.} \\
= & \left(\prod_{q'(\neq q)} \frac{e^{-\beta\hbar\omega_{q'} a_{q'}^\dagger a_{q'}}}{\mathrm{Tr}\left(e^{-\beta\hbar\omega_{q'} a_{q'}^\dagger a_{q'}}\right)} \right) \frac{e^{\beta\hbar\omega_q}}{\mathrm{Tr}\left(e^{-\beta\hbar\omega_q a_q^\dagger a_q}\right)} e^{-\beta\hbar\omega_q a_q^\dagger a_q} a_q^\dagger \qquad (3.30) \\
= & \rho(H_0) a_q^\dagger e^{\beta\hbar\omega_q} \qquad (3.31)
\end{aligned}
$$

then,

$$
\begin{aligned}
a_q^\dagger \rho(H_0) &= \rho(H_0) a_q^\dagger e^{\beta\hbar\omega_q} && (3.32) \\
a_q^\dagger \rho(H_0) - \rho(H_0) a_q^\dagger &= \rho(H_0) a_q^\dagger e^{\beta\hbar\omega_q} - \rho(H_0) a_q^\dagger && (3.33) \\
\left[a_q^\dagger, \rho(H_0)\right]_- &= \rho(H_0) a_q^\dagger \left(e^{\beta\hbar\omega_q} - 1\right) && (3.34)
\end{aligned}
$$

The proof for $[a_q, \rho(H_0)]_- = \rho(H_0) a_q \left(e^{-\beta\hbar\omega_q} - 1\right)$ follows in an analgous way.

<u>Identity 2:</u>

$$
\begin{aligned}
\left\langle \left[a_q^\dagger, A\right]_- \right\rangle &= \left(1 - e^{\hbar\omega_q / k_B T}\right) \langle a_q^\dagger A \rangle && (3.35) \\
\left\langle [a_q, A]_- \right\rangle &= \left(1 - e^{-\hbar\omega_q / k_B T}\right) \langle a_q A \rangle && (3.36)
\end{aligned}
$$

where A is an arbitrary operator.

Proof of identity 2:

$$
\begin{aligned}
\left\langle \left[a_q^\dagger, A\right]_- \right\rangle &= \mathrm{Tr}\left(\rho(H_0)\left(a_q^\dagger A - A a_q^\dagger\right)\right) && (3.37) \\
&= \mathrm{Tr}\left(\rho a_q^\dagger A\right) - \mathrm{Tr}\left(\rho A a_q^\dagger\right) && (3.38) \\
& \mid \text{ Use trace cyclicity in the second term.} \\
&= \mathrm{Tr}\left(\rho a_q^\dagger A\right) - \mathrm{Tr}\left(a_q^\dagger \rho A\right) && (3.39) \\
&= -\mathrm{Tr}\left(\left[a_q^\dagger, \rho(H_0)\right]_- A\right) && (3.40) \\
& \mid \text{ Now, use identity 1.} \\
&= -\mathrm{Tr}\left(\rho(H_0) a_q^\dagger \left(e^{\hbar\omega_q / k_B T} - 1\right) A\right) && (3.41) \\
&= \left(1 - e^{\hbar\omega_q / k_B T}\right) \left\langle a_q^\dagger A \right\rangle && (3.42)
\end{aligned}
$$

The proof for $\left\langle [a_q, A]_- \right\rangle = \left(1 - e^{-\hbar\omega_q / k_B T}\right) \langle a_q A \rangle$ follows in a similar way.

Now we proceed to prove Wick's theorem using identity 2. Consider a typical expression upon expanding equation (3.22) which is a N-string of 2N operators

$$
S_N = \langle T_c \left(c(\tau_{2N}) c(\tau_{2N-1}) \ldots c(\tau_2) c(\tau_1)\right) \rangle \qquad (3.43)
$$

where $c(\tau)$ is either $a_q^\dagger$ or a_q and we display only the contour time arguments. Since these are Bose operators, we can forget writing the contour ordering operator T_c for a while (of course it is still there!) and reorder them freely.[10]

$$S_N = \left\langle \prod_{n=1}^{2N} c(\tau_n) \right\rangle \tag{3.44}$$

$$= \left\langle c(\tau_{2N}) \prod_{n=1}^{2N-1} c(\tau_n) \right\rangle \tag{3.45}$$

| Use identity 2 to write,

$$= \left(1 - e^{\pm\hbar\omega_q/k_BT}\right)^{-1} \left\langle \left[c(\tau_{2N}), \prod_{n=1}^{2N-1} c(\tau_n) \right]_- \right\rangle \tag{3.46}$$

| where $+$ is for $a_q^\dagger$, $-$ is for a_q.

$$= \left(1 - e^{\pm\hbar\omega_q/k_BT}\right)^{-1} \left\langle \left[c(\tau_{2N}), c(\tau_{2N-1}) \prod_{n=1}^{2N-2} c(\tau_n) \right]_- \right\rangle \tag{3.47}$$

| Use the product rule of commutators.

$$= \left(1 - e^{\pm\hbar\omega_q/k_BT}\right)^{-1} \left\langle c(\tau_{2N-1}) \left[c(\tau_{2N}), \prod_{n=1}^{2N-2} c(\tau_n) \right]_- + [c(\tau_{2N}), c(\tau_{2N-1})]_- \prod_{n=1}^{2N-2} c(\tau_n) \right\rangle \tag{3.48}$$

$$\begin{aligned} = & \left(1 - e^{\pm\hbar\omega_q/k_BT}\right)^{-1} \\ & \times \left\langle c(\tau_{2N-1}) c(\tau_{2N}) \prod_{n=1}^{2N-2} c(\tau_n) - c(\tau_{2N-1}) \left(\prod_{n=1}^{2N-2} c(\tau_n) \right) c(\tau_{2N}) + [c(\tau_{2N}), c(\tau_{2N-1})]_- \prod_{n=1}^{2N-2} c(\tau_n) \right\rangle \end{aligned}$$

| We keep commuting $c(\tau_{2N})$ to the right in the first term.

$$\begin{aligned} = & \left(1 - e^{\pm\hbar\omega_q/k_BT}\right)^{-1} \\ & \times \left\langle c(\tau_{2N-1}) c(\tau_{2N-2}) \ldots c(\tau_1) c(\tau_{2N}) - c(\tau_{2N-1}) \left(\prod_{n=1}^{2N-2} c(\tau_n) \right) c(\tau_{2N}) \right. \\ & \left. + \sum_{n=1}^{2N-1} [c(\tau_{2N}), c(\tau_n)]_- \prod_{m(\neq n)=1}^{2N-1} c(\tau_m) \right\rangle \end{aligned} \tag{3.49}$$

$$= \left(1 - e^{\pm\hbar\omega_q/k_BT}\right)^{-1} \left\langle \sum_{n=1}^{2N-1} [c(\tau_{2N}), c(\tau_n)]_- \prod_{m(\neq n)=1}^{2N-1} c(\tau_m) \right\rangle \tag{3.50}$$

| The average is independent as the commutator is a c-number.

| $\left[c_q(\tau_{2N}), c_{q'}(\tau_n)\right]_- \overset{\text{trivial}}{=} \left\langle \left[c_q(\tau_{2N}), c_{q'}(\tau_n)\right]_- \right\rangle$

$$= \left(1 - e^{\pm\hbar\omega_q/k_BT}\right)^{-1} \left\langle \sum_{n=1}^{2N-1} [c(\tau_{2N}), c(\tau_n)]_- \right\rangle \left\langle \prod_{m(\neq n)=1}^{2N-1} c(\tau_m) \right\rangle \tag{3.51}$$

| Now use identity 2: $\left\langle \left[c_q(\tau_{2N}), c_{q'}(\tau_n)\right]_- \right\rangle = \delta_{qq'} \left(1 - e^{\pm\hbar\omega_q/k_BT}\right) \left\langle c_q(\tau_{2N}) c_{q'}(\tau_n) \right\rangle$.

[10]For fermions, there are sign changes to keep track of. See footnote 28 on page 100 of [Rammer2007].

$$= \sum_{n=1}^{2N-1} \langle c(\tau_{2N})c(\tau_n)\rangle \left\langle \prod_{m(\neq n)=1}^{2N-1} c(\tau_m) \right\rangle \quad (3.52)$$

| We remember to write T_c again

$$= \sum_{n=1}^{2N-1} \langle T_c c(\tau_{2N})c(\tau_n)\rangle \left\langle T_c \prod_{m(\neq n)=1}^{2N-1} c(\tau_m) \right\rangle \quad (3.53)$$

The 2nd factor is a string of $2N-2$ operators and the same procedure is repeated until 2 operators are left. By writing out explicitly some simple examples, we can see that the total sum is over all possible pairs (APP). This concludes the proof.

We can thus write expicitly, say for a bosonic phonon displacement field, (where this statistical average is done with $\rho(H_0)$) [11]

$$\begin{aligned} &\langle T_c\,(u_{H_0}(l_{2n}k_{2n}\alpha_{2n},\tau_{2n})u_{H_0}(l_{2n-1}k_{2n-1}\alpha_{2n-1},\tau_{2n-1})\ldots u_{H_0}(l_1k_1\alpha_1,\tau_1))\rangle \\ =\ &\sum_{\text{APP}}\prod_{i\neq j}\langle T_c\,(u_{H_0}(l_ik_i\alpha_i,\tau_i)u_{H_0}(l_jk_j\alpha_j,\tau_j))\rangle \end{aligned} \quad (3.54)$$

3.1.3 Definitions of Green's functions

Now we will properly define the single particle Green's functions. Based on the 3-branched contour $(c_K + c_M)$ used for perturbation, we can write down 7 (real time) Green's functions [12] (supressing the lattice indices l, k, α and recalling that $\overrightarrow{c_K}$ and $\overleftarrow{c_K}$ refer to the "upper" contour and the "lower" contour respectively)

$$D(\tau_1,\tau_2) = \begin{cases} D^t(t_1,t_2) & t_1,t_2 \in \overrightarrow{c_K} \\ D^>(t_1,t_2) & t_1 \in \overleftarrow{c_K}, t_2 \in \overrightarrow{c_K}, \Rightarrow t_1 > t_2 \\ D^<(t_1,t_2) & t_1 \in \overrightarrow{c_K}, t_2 \in \overleftarrow{c_K}, \Rightarrow t_1 < t_2 \\ D^{\bar t}(t_1,t_2) & t_1,t_2 \in \overleftarrow{c_K} \\ D^{\urcorner}(t_1,\tau_2^M) & t_1 \in c_K, \tau_2^M \in c_M \\ D^{\ulcorner}(\tau_1^M,t_2) & \tau_1^M \in c_M, t_2 \in c_K \\ D^M(\tau_1^M,\tau_2^M) & \tau_1^M,\tau_2^M \in c_M \end{cases} \quad (3.55)$$

The last Green's function D^M is the Matsubara Green's function (see appendix on Matsubara theory). The Green's functions $D^{\urcorner}$ and $D^{\ulcorner}$ are symbolized as such to graphically denote the contour branch where the time argument is taken from. The explicit expressions for the first 4 (real time) Green's functions are,

Time-ordered Green's function

$$\begin{aligned} &D^t(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) \\ \equiv\ &-\frac{i}{\hbar}\langle T(u_H(l_1k_1\alpha_1t_1)u_H(l_2k_2\alpha_2t_2))\rangle \quad (3.56)\\ \equiv\ &-\frac{i}{\hbar}\theta(t_1-t_2)\langle u_H(l_1k_1\alpha_1t_1)u_H(l_2k_2\alpha_2t_2)\rangle - \frac{i}{\hbar}\theta(t_2-t_1)\langle u_H(l_2k_2\alpha_2t_2)u_H(l_1k_1\alpha_1t_1)\rangle \quad (3.57)\end{aligned}$$

[11] For phonons, there are three types of operators that can be used. The proof for Wick's theorem was done with the "a, $a^\dagger$" operators. The other two operators are linear combinations of them, i.e. u, $Q \propto (a^\dagger + a)$ and so Wick's theorem applies to these two operators. A crucial ingredient is that, (in schematic form) harmonic averages $\langle aa\rangle$ and $\langle a^\dagger a^\dagger\rangle$ vanish. This ingredient ensures that for an expression expressed in whichever of the three variables, they will give the same number of pairs after applying Wick's theorem.

[12] All permutations would seem to indicate 9 possible definitions of Green's functions. However for $D^{\urcorner}$ and $D^{\ulcorner}$ there is only one distinct choice each because $t \in c_K > t_0 - i\hbar\tau^M \in c_M$.

Greater Green's function

$$D^{>}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) \equiv -\frac{i}{\hbar}\langle u_H(l_1k_1\alpha_1t_1)u_H(l_2k_2\alpha_2t_2)\rangle \tag{3.58}$$

Lesser Green's function

$$D^{<}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) \equiv -\frac{i}{\hbar}\langle u_H(l_2k_2\alpha_2t_2)u_H(l_1k_1\alpha_1t_1)\rangle \tag{3.59}$$

Anti-time ordered Green's function ($\tilde{T}$ is the anti-time ordering operator)

$$\begin{aligned} & D^{\bar{t}}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) \\ \equiv\ & -\frac{i}{\hbar}\langle\tilde{T}(u_H(l_1k_1\alpha_1t_1)u_H(l_2k_2\alpha_2t_2))\rangle & (3.60) \\ \equiv\ & -\frac{i}{\hbar}\theta(t_2-t_1)\langle u_H(l_1k_1\alpha_1t_1)u_H(l_2k_2\alpha_2t_2)\rangle - \frac{i}{\hbar}\theta(t_1-t_2)\langle u_H(l_2k_2\alpha_2t_2)u_H(l_1k_1\alpha_1t_1)\rangle & (3.61) \end{aligned}$$

Immediately we see a relation

$$D^{t} + D^{\bar{t}} = D^{<} + D^{>} \tag{3.62}$$

Thus are only 3 linearly independent Green's functions in non-equilibrium (i.e. non-homogenous & non-time translational invariant) systems. We define 3 more Green's function for later considerations.

Advanced Green's function

$$\begin{aligned} D^{A}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) &\equiv -\theta(t_2-t_1)(D^{>}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) - D^{<}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2)) & (3.63) \\ &= \frac{i}{\hbar}\theta(t_2-t_1)\,\langle[u_H(l_1k_1\alpha_1t_1), u_H(l_2k_2\alpha_2t_2)]_-\rangle & (3.64) \end{aligned}$$

Retarded Green's function [13]

$$\begin{aligned} D^{R}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) &\equiv \theta(t_1-t_2)(D^{>}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) - D^{<}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2)) & (3.67) \\ &= -\frac{i}{\hbar}\theta(t_1-t_2)\langle[u_H(l_1k_1\alpha_1t_1), u_H(l_2k_2\alpha_2t_2)]_-\rangle & (3.68) \end{aligned}$$

Keldysh Green's function

$$D^{K}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) \equiv D^{>}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) + D^{<}(l_1k_1\alpha_1t_1l_2k_2\alpha_2t_2) \tag{3.69}$$

where $[\ ,\ ]_-$ represents the commutator.

3.1.4 Langreth's Theorem

Now suppose the perturbation has been done by expanding the S-matrix in the pertubation expression (i.e. eqn(3.22)) in contour time and we get a collection of terms that could be convolved or multiplied

[13] Actually if there is a time singular part (denoted by superscript δ), the definitions of the retarded and advanced functions should be

$$\begin{aligned} D^{R}(t_1t_2) &\equiv D^{\delta}(t_1)\delta(t_1-t_2) + \theta(t_1-t_2)\left(D^{>}(t_1t_2) - D^{<}(t_1t_2)\right) & (3.65) \\ D^{A}(t_1t_2) &\equiv D^{\delta}(t_1)\delta(t_1-t_2) - \theta(t_2-t_1)\left(D^{>}(t_1t_2) - D^{<}(t_1t_2)\right) & (3.66) \end{aligned}$$

with each other. We need a method to change these expressions from contour time expressions to real time and/or to Matsubara time expressions so that explicit evaluation of observables in real time can be done. [14] This is called Langreth's theorem. There are actually three types of "multiplication" that we have to deal with. The references are [Rammer2007] and [Leeuwen2005].

3.1.4.1 Series Multiplication

Consider the first type which is a convolution in contour time (encountered in Dyson-type of equations) and we evaluate a lesser function as example.

$$C^<(\tau_1,\tau_{1'}) = \int_{c_K+c_M} d\tau A(\tau_1,\tau)B(\tau,\tau_{1'}) \tag{3.70}$$

$$= \int_{c_K} d\tau A(\tau_1,\tau)B(\tau,\tau_{1'}) + \int_{c_M} d\tau A(\tau_1,\tau)B(\tau,\tau_{1'}) \tag{3.71}$$

We take τ_1,$\tau_{1'}$ to be real times and we do the 2 terms seperately

$$\text{1st term of } C^< \text{ (on Keldysh contour)} = \int_{c_K} d\tau A(\tau_1,\tau)B(\tau,\tau_{1'}) \tag{3.72}$$

using the group property of contour evolution operators, consider the "deformed" contour and the lesser function, (take $\tau_1 < \tau_{1'}$)

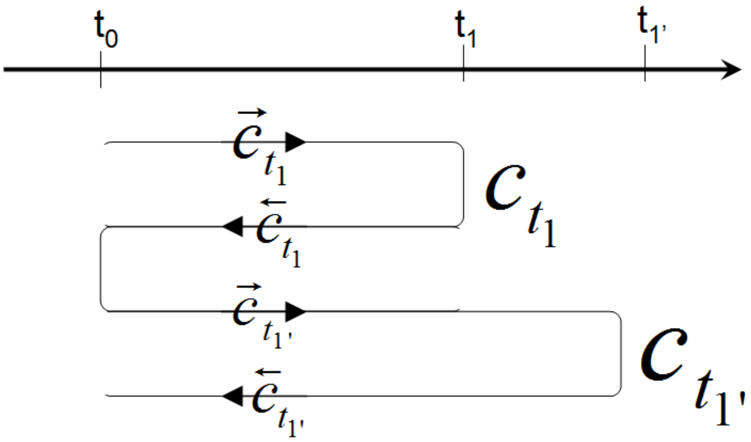


Figure 3.4: *The deformed contour for proving Langreth's theorem. This is for the case of* $t_{1'} > t_1$.

$$\text{1st term of } C^<(\tau_1,\tau_{1'})$$

$$= \int_{c_1} d\tau A(\tau_1,\tau) \underbrace{B(\tau,\tau_{1'})}_{\text{along } c_1,\, \tau<\tau_{1'}} + \int_{c_{1'}} d\tau \underbrace{A(\tau_1,\tau)}_{\text{along } c_{1'},\, \tau_1<\tau} B(\tau,\tau_{1'}) \tag{3.73}$$

$$= \int_{c_1} d\tau A(\tau_1,\tau)B^<(\tau,\tau_{1'}) + \int_{c_{1'}} d\tau A^<(\tau_1,\tau)B(\tau,\tau_{1'}) \tag{3.74}$$

| split c_1 into $\overrightarrow{c_1}$ and $\overleftarrow{c_1}$, split $c_{1'}$ into $\overrightarrow{c_{1'}}$ and $\overleftarrow{c_{1'}}$.

[14] Recall that the contour time is just a trick for us to carry out the perturbation and now the trick is over.

$$\begin{aligned}
&= \int_{\overrightarrow{c_1}} d\tau \underbrace{A(\tau_1,\tau)}_{\text{along } \overrightarrow{c_{1'}}, \tau_1 > \tau} B^<(\tau,\tau_{1'}) + \int_{\overleftarrow{c_1}} d\tau \underbrace{A(\tau_1,\tau)}_{\text{along } \overrightarrow{c_{1'}}, \tau_1 < \tau} B^<(\tau,\tau_{1'}) \\
&\quad + \int_{\overrightarrow{c_{1'}}} d\tau A^<(\tau_1,\tau) \underbrace{B(\tau,\tau_{1'})}_{\text{along } \overrightarrow{c_{1'}}, \tau < \tau_{1'}} + \int_{\overleftarrow{c_{1'}}} d\tau A^<(\tau_1,\tau) \underbrace{B(\tau,\tau_{1'})}_{\text{along } \overrightarrow{c_{1'}}, \tau > \tau_{1'}} \qquad (3.75) \\
&= \int_{\overrightarrow{c_1}} d\tau A^>(\tau_1,\tau)B^<(\tau,\tau_{1'}) + \int_{\overleftarrow{c_1}} d\tau A^<(\tau_1,\tau)B^<(\tau,\tau_{1'}) \\
&\quad + \int_{\overrightarrow{c_{1'}}} d\tau A^<(\tau_1,\tau)B^<(\tau,\tau_{1'}) + \int_{\overleftarrow{c_{1'}}} d\tau A^<(\tau_1,\tau)B^>(\tau,\tau_{1'}) \qquad (3.76) \\
&\mid \quad \text{Now we can write in real time.} \\
&= \int_{t_0}^{t_1} dt \left(A^>(t_1,t) - A^<(t_1,t)\right) B^<(t,t_{1'}) + \int_{t_0}^{t_{1'}} dt A^<(t_1,t) \left(B^<(t,t_{1'}) - B^>(t,t_{1'})\right) \qquad (3.77) \\
&= \int_{t_0}^{\infty} dt \theta(t_1 - t) \left(A^>(t_1,t) - A^<(t_1,t)\right) B^<(t,t_{1'}) + \theta(t_{1'} - t) A^<(t_1,t) \left(B^<(t,t_{1'} - B^>(t,t_{1'})\right) \\
&\mid \quad \text{recall the definition of the retarded function, } A^R = \theta(t_a - t_b)(A^>(t_a,t_b) - A^<(t_a,t_b)). \\
&\mid \quad \text{and the definition of the advanced function } A^A = \theta(t_b - t_a)(A^<(t_a,t_b) - A^>(t_a,t_b)). \\
&= \int_{t_0}^{\infty} dt A^R(t_1,t)B^<(t,t_{1'}) + A^<(t_1,t)B^A(t,t_{1'}) \qquad (3.78)
\end{aligned}$$

$$\begin{aligned}
\text{2nd term of } C^<(\tau_1,\tau_{1'}) &= \int_{c_M} d\tau A(\tau_1,\tau)B(\tau,\tau_{1'}) = \int_{c_M} d\tau^M A^{\urcorner}(t_1,\tau^M)B^{\ulcorner}(\tau^M,t_{1'}) \qquad (3.79) \\
&= \int_{t_0}^{t_0 - i\beta\hbar} d\tau^M A^{\urcorner}(t_1,\tau^M)B^{\ulcorner}(\tau^M,t_{1'}) \qquad (3.80)
\end{aligned}$$

In total, we have,

$$C^<(t_1,t_{1'}) = \int_{t_0}^{\infty} dt A^R(t_1,t)B^<(t,t_{1'}) + A^<(t_1,t)B^A(t,t_{1'}) + \int_{t_0}^{t_0 - i\beta\hbar} d\tau^M A^{\urcorner}(t_1,\tau^M)B^{\ulcorner}(\tau^M,t_{1'}) \qquad (3.81)$$

Similarly for $C^>$,

$$C^>(t_1,t_{1'}) = \int_{t_0}^{\infty} dt A^R(t_1,t)B^>(t,t_{1'}) + A^>(t_1,t)B^A(t,t_{1'}) + \int_{t_0}^{t_0 - i\beta\hbar} d\tau^M A^{\urcorner}(t_1,\tau^M)B^{\ulcorner}(\tau^M,t_{1'}) \qquad (3.82)$$

Using the above equations for $C^<$ and $C^>$, we can further calculate

$$\begin{aligned}
C^R(t_1,t_{1'}) &= \theta(t_1 - t_{1'})(C^>(t_1,t_{1'}) - C^<(t_1,t_{1'})) \qquad (3.83) \\
&\mid \quad \text{note that the Matsubara time functions cancel out,} \\
&\mid \quad \text{i.e. the initial correlations do not affect the retarded quantity} \\
&= \int_{t_0}^{\infty} dt A^R(t_1,t)B^R(t,t_{1'}) \qquad (3.84)
\end{aligned}$$

Similarly for C^A,

$$C^A(t_1, t_{1'}) = \int_{t_0}^{\infty} dt A^A(t_1, t) B^A(t, t_{1'}) \tag{3.85}$$

Then,

$$C^{\urcorner}(t_1, \tau_1^M) = \int_{t_0}^{\infty} dt A^R(t_1, t) B^{\urcorner}(t, \tau_{1'}^M) + \int_{t_0}^{t_0 - i\beta\hbar} d\tau^M A^{\urcorner}(t_1, \tau^M) B^M(\tau^M, \tau_{1'}^M) \tag{3.86}$$

$$C^{\ulcorner}(\tau_1^M, t_{1'}) = \int_{t_0}^{\infty} dt A^{\ulcorner}(\tau_1^M, t) B^A(t, t_{1'}) + \int_{t_0}^{t_0 - i\beta\hbar} d\tau^M A^M(\tau_1^M, \tau^M) B^{\ulcorner}(\tau^M, t_{1'}) \tag{3.87}$$

$$C^M(\tau_1^M, \tau_{1'}^M) = \int_{t_0}^{t_0 - i\beta\hbar} d\tau^M A^M(\tau_1^M, \tau^M) B^M(\tau^M, \tau_{1'}^M) \tag{3.88}$$

Now we give 2 examples on calculating 3-term convolutions and the generalization to convolutions of more than 3 terms will be obvious. Consider,

$$D^<(t_1, t_{1'})$$

$$= \int_{c_K + c_M} d\tau_2 \int_{c_K + c_M} d\tau_{2'} A(t_1, \tau_2) B(\tau_2, \tau_{2'}) C(\tau_{2'}, t_{1'}) \tag{3.89}$$

$$= \int_{c_K + c_M} d\tau_2 A(t_1 \tau_2) \left(\int_{c_K + c_M} d\tau_{2'} B(\tau_2, \tau_{2'}) C(\tau_{2'}, t_{1'}) \right) \tag{3.90}$$

$$\equiv \int_{c_K + c_M} d\tau_2 A(t_1, \tau_2) E(\tau_2, t_{1'}) \tag{3.91}$$

| we simply apply the 2-term convolution formula.

$$= \int_t (A^R E^< + A^< E^A) + \int_{\tau^M} A^{\urcorner} E^{\ulcorner} \tag{3.92}$$

| since E is also a 2-term convolution, we simply use the 2-term convolution formula again.

$$= \int_t \left(A^R \left(\int_t B^R C^< + B^< C^A + \int_{\tau^M} B^{\urcorner} C^{\ulcorner} \right) + A^< \left(\int_t B^A C^A \right) \right) + \int_{\tau^M} A^{\urcorner} \left(\int_t B^{\ulcorner} C^A + \int_{\tau^M} B^M C^{\ulcorner} \right)$$

$$= \int_t \int_t (A^R B^R C^< + A^R B^< C^A + A^< B^A C^A) + \int_t \int_{\tau^M} A^R B^{\urcorner} C^{\ulcorner} + \int_{\tau^M} \int_t A^{\urcorner} B^{\ulcorner} C^A + \int_{\tau^M} \int_{\tau^M} A^{\urcorner} B^M C^{\ulcorner} \tag{3.93}$$

The second example is

$$D^>(t_1, t_{1'}) = \int_{c + c_A} d\tau_2 A(t_1, \tau_2) \left(\int_{c + c_A} d\tau_{2'} B(\tau_2, \tau_{2'}) C(\tau_{2'}, t_{1'}) \right) \tag{3.94}$$

$$\equiv \int_{c + c_A} d\tau_2 A(t_1, \tau_2) E(\tau_2, t_{1'}) \tag{3.95}$$

$$= \int_t (A^R E^> + A^> E^A) + \int_{\tau^M} A^{\urcorner} E^{\ulcorner} \tag{3.96}$$

$$= \int_t \int_t (A^R B^R C^> + A^R B^> C^A + A^> B^A C^A) + \int_t \int_{\tau^M} A^R B^{\urcorner} C^{\ulcorner} + \int_{\tau^M} \int_t A^{\urcorner} B^{\ulcorner} C^A + \int_{\tau^M} \int_{\tau^M} A^{\urcorner} B^M C^{\ulcorner} \tag{3.97}$$

3.1.4.1.1 Keldysh RAK Matrix for Series Multiplication In the literature, it was mentioned that the non-equilibrium field theory is simply done by treating the contour ordered Green's function as a 2×2 matrix in "Keldysh" space with real time Green's functions as matrix elements. We do not adopt this view here as we feel that this perspective is not only unnecessary and it obscures the physics and generality of NEGF. Here we only want to mention that if the 2 time functions are expressed in the R (Retarded), A (Advanced), K (Keldysh) matrix form then there is a neat way to handle Langreth's theorem "series multiplication" type of terms.

We illustrate this with the so-called Dyson equation (just treat it as a 3 term convolved object).[15]

$$G(1,1') = G^{(0)}(1,1') + \int_{c_K+c_M} d2 \int_{c_K+c_M} d3 G^{(0)}(1,2)\Sigma(2,3)G(3,1') \tag{3.98}$$

Now we apply Langreth's theorem to get the terms to be expressed in RAK form.

$$G^R(1,1') = G^{(0)R}(1,1') + \int_t d2 \int_t d3 G^{(0)R}(1,2)\Sigma^R(2,3)G^R(3,1') \tag{3.99}$$

Also,

$$G^A(1,1') = G^{(0)A}(1,1') + \int_t d2 \int_t d3 G^{(0)A}(1,2)\Sigma^A(2,3)G^A(3,1') \tag{3.100}$$

And the Keldysh Green's function

$$\begin{aligned} G^K(1,1') &= G^>(1,1') + G^<(1,1') &(3.101)\\ &= G^{(0)K}(1,1') + \int_t d2 \int_t d3 \Big(G^{(0)R}(1,2)\Sigma^R(2,3)G^K(3,1') \\ &\quad + G^{(0)R}(1,2)\Sigma^K(2,3)G^A(3,1') + G^{(0)K}(1,2)\Sigma^A(2,3)G^A(3,1') \Big) \\ &\quad + 2\int_{\tau^M}\int_t G^{(0)\urcorner}\Sigma^R G^{\urcorner} + 2\int_{\tau^M}\int_{\tau^M} G^{(0)\urcorner}\Sigma^{\urcorner} G^M &(3.102) \end{aligned}$$

Now we will follow [Wagner1991] and introduce the (rotated) Keldysh matrix which allows us to get the RAK (and $\ulcorner$, $\urcorner$, M) components conveniently simply by matrix mulitiplication. When we have an n- term convolution, we simply perform n matrix multiplications.

$$\begin{aligned} &\begin{pmatrix} G^R & G^K & \sqrt{2}G^{\urcorner} \\ 0 & G^A & 0 \\ 0 & \sqrt{2}G^{\ulcorner} & G^M \end{pmatrix}(1,1') \\ = &\begin{pmatrix} G^{(0)R} & G^{(0)K} & \sqrt{2}G^{(0)\urcorner} \\ 0 & G^{(0)A} & 0 \\ 0 & \sqrt{2}G^{(0)\ulcorner} & G^{(0)M} \end{pmatrix}(1,1') \\ &+ \int d2 \int d3 \begin{pmatrix} G^{(0)R} & G^{(0)K} & \sqrt{2}G^{(0)\urcorner} \\ 0 & G^{(0)A} & 0 \\ 0 & \sqrt{2}G^{(0)\ulcorner} & G^{(0)M} \end{pmatrix} \begin{pmatrix} \Sigma^R & \Sigma^K & \sqrt{2}\Sigma^{\urcorner} \\ 0 & \Sigma^A & 0 \\ 0 & \sqrt{2}\Sigma^{\ulcorner} & \Sigma^M \end{pmatrix} \begin{pmatrix} G^R & G^K & \sqrt{2}G^{\urcorner} \\ 0 & G^A & 0 \\ 0 & \sqrt{2}G^{\ulcorner} & G^M \end{pmatrix} \end{aligned} \tag{3.103}$$

So we see that by simply carrying out the matrix mulitplication, we reproduce the Dyson equations

[15]The notation here is generic, it works for both Bosons and Fermions.

for the RAK components (as well as the other 3 components).

3.1.4.2 Parallel Multiplication

Now we proceed to calculate the second type of multiplication (it occurs when evaluating self energy diagrams). This is of the form,

$$C(\tau_1, \tau_{1'}) = A(\tau_1, \tau_{1'})B(\tau_1, \tau_{1'}) \tag{3.104}$$

The conversion to real time and/or Matsubara time is straightforward,

$$\begin{aligned}
C^<(t_1, t_{1'}) &= A^<(t_1, t_{1'})B^<(t_1, t_{1'}) && (3.105)\\
C^>(t_1, t_{1'}) &= A^>(t_1, t_{1'})B^>(t_1, t_{1'}) && (3.106)\\
C^R(t_1, t_{1'}) &= \theta(t_1 - t_{1'})\left(C^>(t_1, t_{1'}) - C^<(t_1, t_{1'})\right) &&\\
&= \theta(t_1 - t_{1'})\left(A^>(t_1, t_{1'})B^>(t_1, t_{1'}) - A^<(t_1, t_{1'})B^<(t_1, t_{1'})\right) \neq A^R B^R && (3.107)\\
C^A(t_1, t_{1'}) &= -\theta(t_{1'} - t_1)\left(C^>(t_1, t_{1'}) - C^<(t_1, t_{1'})\right) &&\\
&= -\theta(t_{1'} - t_1)\left(A^>(t_1, t_{1'})B^>(t_1, t_{1'}) - A^<(t_1, t_{1'})B^<(t_1, t_{1'})\right) \neq A^A B^A && (3.108)\\
C^\rceil(t_1, \tau_{1'}^M) &= A^\rceil(t_1, \tau_{1'}^M)B^\rceil(t_1, \tau_{1'}^M) && (3.109)\\
C^\lceil(\tau_1^M, t_{1'}) &= A^\lceil(\tau_1^M, t_{1'})B^\lceil(\tau_1^M, t_{1'}) && (3.110)\\
C^M(\tau_1^M, \tau_{1'}^M) &= A^M(\tau_1^M, \tau_{1'}^M)B^M(\tau_1^M, \tau_{1'}^M)^{16} && (3.111)
\end{aligned}$$

Now we provide a table to summarize the results:

Series Multiplication
Contour time: $C(\tau, \tau') = \int_{c_K + c_M} d\tau_1 A(\tau, \tau_1)B(\tau_1, \tau')$
Real/Matsubara time: $C^<(t, t') = \int_{t_0}^{\infty} dt_1 \left(A^R(t, t_1)B^<(t_1, t')) + A^<(t, t_1)B^A(t_1, t')\right) + \int_0^\beta d\tau^M A^\rceil(t, t_0 - i\hbar\tau^M)B^\lceil(t_0 - i\hbar\tau^M, t')$ $C^>(t, t') = \int_{t_0}^{\infty} dt_1 \left(A^R(t, t_1)B^>(t_1, t) + A^>(t, t_1)B^A(t_1, t')\right) + \int_0^\beta d\tau^M A^\rceil(t, t_0 - i\hbar\tau^M)B^\lceil(t_0 - i\hbar\tau^M, t')$ $C^R(t, t') = \int_{t_0}^{\infty} dt_1 A^R(t, t_1)B^R(t_1, t')$ $C^A(t, t') = \int_{t_0}^{\infty} A^A(t, t_1)B^A(t_1, t')$ $C^\rceil(t, t_0 - i\hbar\tau^M) = \int_{t_0}^{\infty} dt_1 A^R(t, t_1)B^\rceil(t_1, t_0 - i\hbar\tau^M) + \int_0^\beta d\tau_1^M A^\rceil(t, t_0 - i\hbar\tau_1^M)B^M(t_0 - i\hbar\tau_1^M, t_0 - i\hbar\tau^M)$ $C^\lceil(t_0 - i\hbar\tau^M, t') = \int_{t_0}^{\infty} dt_1 A^\lceil(t_0 - i\hbar\tau^M, t_1)B^A(t_1, t')$ $+ \int_0^\beta d\tau_1^M A^M(t_0 - i\hbar\tau^M, t_0 - i\hbar\tau_1^M)B^\lceil(t_0 - i\hbar\tau_1^M, t_0 - i\hbar\tau^M)$ $C^M(t_0 - i\hbar\tau^M, t_0 - i\hbar\tau^{M'}) = \int_0^\beta d\tau_1^M A^M(t_0 - i\hbar\tau^M, t_0 - i\hbar\tau_1^M)B^M(t_0 - i\hbar\tau_1^M, t_0 - i\hbar\tau^{M'})$
Parallel Multiplication
Contour time: $C(\tau, \tau') = A(\tau, \tau')B(\tau, \tau')$
Real/Matsubara time: $C^<(t, t') = A^<(t, t')B^<(t, t')$ $C^>(t, t') = A^>(t, t')B^>(t, t')$ $C^\rceil(t, t_0 - i\hbar\tau^M) = A^\rceil(t, t_0 - i\hbar\tau^M)B^\rceil(t, t_0 - i\hbar\tau^M)$ $C^\lceil(t_0 - i\hbar\tau^M, t') = A^\lceil(t_0 - i\hbar\tau^M, t')B^\lceil(t_0 - i\hbar\tau^M, t')$ $C^M(t_0 - i\hbar\tau^M, t_0 - i\hbar\tau^{M'}) = A^M(t_0 - i\hbar\tau^M, t_0 - i\hbar\tau^{M'})B^M(t_0 - i\hbar\tau^M, t_0 - i\hbar\tau^{M'})$

[16] The derivation requires noting that $\theta(\tau_1^M - \tau_{1'}^M) \times \theta(\tau_{1'}^M - \tau_1^M) = 0$.

3.1.4.3 Vertex Multiplication*

The third type of mulitiplication occurs when we evaluate self energy diagrams with vertex corrections. We simply illustrate with an example here. The example is for a self energy term with a one-ladder vertex correction (just treat it as a term with a complicated type of multiplication). [17]

The term in contour time is (nevermind about the notation, just look at how the contour times convolve),

$$\Sigma^{(3ph)}(\tau_1\tau_2) = \int_{c_K+c_M} d\tau_3 d\tau_4 D(\tau_1\tau_3)D(\tau_3\tau_4)D(\tau_1\tau_4)D(\tau_3\tau_2)D(\tau_4\tau_2) \tag{3.112}$$

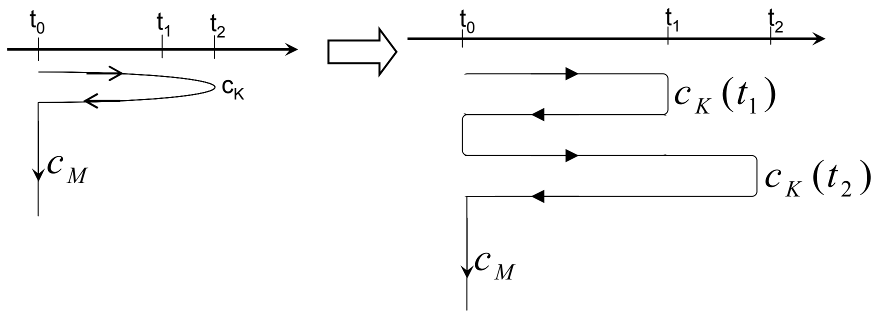


Figure 3.5: *Contour to be use for calculating the lesser (real time) expression of* $\Sigma^{(3ph)}(\tau_1\tau_2)$.

$$\begin{aligned}\Sigma^{(3ph)<}(t_1t_2) &= \left(\int_{c_K(t_1)} d\tau_3 + \int_{c_K(t_2)} d\tau_3 + \int_{c_M} d\tau_3^M\right)\left(\int_{c_K(t_1)} d\tau_4 + \int_{c_K(t_2)} d\tau_4 + \int_{c_M} d\tau_4^M\right) \\ &\quad \times D(t_1\tau_3)D(\tau_3\tau_4)D(t_1\tau_4)D(\tau_3t_2)D(\tau_4t_2) \end{aligned} \tag{3.113}$$

Thus we got 9 terms that we shall work out explicitly.

$$\begin{aligned}
& \text{1st Term} \\
= & \int_{c_K(t_1)} d\tau_3 \int_{c_K(t_1)} d\tau_4 D(t_1\tau_3 D(\tau_3\tau_4)D(t_1\tau_4)D(\tau_3t_2)D(\tau_4t_2) \\
| & \text{ thus } t_2 \text{ is later than } \tau_3 \text{ and } \tau_4 \\
= & \int_{c_K(t_1)} d\tau_3 \int_{c_K(t_1)} d\tau_4 D(t_1\tau_3 D(\tau_3\tau_4)D(t_1\tau_4)D^<(\tau_3t_2)D^<(\tau_4t_2) \\
| & \text{ break up } c_K(t_1) = \overrightarrow{c_K(t_1)} + \overleftarrow{c_K(t_1)} \\
= & \left(\int_{\overrightarrow{c_K(t_1)}} d\tau_3 + \int_{\overleftarrow{c_K(t_1)}} d\tau_3\right)\left(\int_{\overrightarrow{c_K(t_1)}} d\tau_4 + \int_{\overleftarrow{c_K(t_1)}} d\tau_4\right) D(t_1\tau_3 D(\tau_3\tau_4)D(t_1\tau_4)D^<(\tau_3t_2)D^<(\tau_4t_2) \\
= & \int_{\overrightarrow{c_K(t_1)}} d\tau_3 \int_{\overrightarrow{c_K(t_1)}} d\tau_4 D^>(t_1\tau_3)D^t(\tau_3\tau_4)D^>(t_1\tau_4)D^<(\tau_3t_2)D^<(\tau_4t_2) \\
& + \int_{\overrightarrow{c_K(t_1)}} d\tau_3 \int_{\overleftarrow{c_K(t_1)}} d\tau_4 D^>(t_1\tau_3)D^<(\tau_3\tau_4)D^<(t_1\tau_4)D^<(\tau_3t_2)D^<(\tau_4t_2)
\end{aligned}$$

[17]Note that the calculational method used here can also be used for Series Multiplication. In fact the method here is a slight generalization of that used in Series Multiplication.

$$
\begin{aligned}
&+\int_{\overleftarrow{c_K(t_1)}} d\tau_3 \int_{\overrightarrow{c_K(t_1)}} d\tau_4 D^<(t_1\tau_3)D^>(\tau_3\tau_4)D^>(t_1\tau_4)D^<(\tau_3 t_2)D^<(\tau_4 t_2)\\
&+\int_{\overleftarrow{c_K(t_1)}} d\tau_3 \int_{\overleftarrow{c_K(t_1)}} d\tau_4 D^<(t_1\tau_3)D^{\bar{t}}(\tau_3\tau_4)D^<(t_1\tau_4)D^<(\tau_3 t_2)D^<(\tau_4 t_2)\\
|\quad &\text{write integration limits explicitly and write in real time}\\
= \quad &\int_{t_0}^{t_1} dt_3 \int_{t_0}^{t_1} dt_4 D^>(t_1t_3)D^t(t_3t_4)D^>(t_1t_4)D^<(t_3t_2)D^<(t_4t_2)\\
&+\int_{t_0}^{t_1} dt_3 \int_{t_1}^{t_0} dt_4 D^>(t_1t_3)D^<(t_3t_4)D^<(t_1t_4)D^<(t_3t_2)D^<(t_4t_2)\\
&+\int_{t_1}^{t_0} dt_3 \int_{t_0}^{t_1} dt_4 D^<(t_1t_3)D^>(t_3t_4)D^>(t_1t_4)D^<(t_3t_2)D^<(t_4t_2)\\
&+\int_{t_1}^{t_0} dt_3 \int_{t_1}^{t_0} dt_4 D^<(t_1t_3)D^{\bar{t}}(t_3t_4)D^<(t_1t_4)D^<(t_3t_2)D^<(t_4t_2)
\end{aligned}
$$

It should be now clear that the evaluation of the remaining 8 terms simply follows the same procedure. Hence we shall shorten some steps in the subsequent working.

$$
\begin{aligned}
\text{2nd Term} \quad = \quad & \int_{c_K(t_1)} d\tau_3 \int_{c_K(t_2)} d\tau_4 D(t_1\tau_3)D(\tau_3\tau_4)D(t_1\tau_4)D(\tau_3 t_2)D(\tau_4 t_2)\\
| \quad & \text{so } \tau_4 \text{ and } t_2 \text{ are definitely later than } \tau_3\\
= \quad & \int_{c_K(t_1)} d\tau_3 \int_{c_K(t_2)} d\tau_4 D(t_1\tau_3)D^<(\tau_3\tau_4)D^<(t_1\tau_4)D^<(\tau_3 t_2)D(\tau_4 t_2)\\
| \quad & \text{break up } c_K(t_1) = \overrightarrow{c_K(t_1)} + \overleftarrow{c_K(t_1)} \text{ and } c_K(t_2) = \overrightarrow{c_K(t_2)} + \overleftarrow{c_K(t_2)}\\
| \quad & \text{then write integration limits explicitly and write in real time}\\
= \quad & \int_{t_0}^{t_1} dt_3 \int_{t_0}^{t_2} dt_4 D^>(t_1t_3)D^<(t_3t_4)D^<(t_1t_4)D^<(t_3t_2)D^<(t_4t_2)\\
& +\int_{t_0}^{t_1} dt_3 \int_{t_2}^{t_0} dt_4 D^>(t_1t_3)D^<(t_3t_4)D^<(t_1t_4)D^<(t_3t_2)D^>(t_4t_2)\\
& +\int_{t_1}^{t_0} dt_3 \int_{t_0}^{t_2} dt_4 D^<(t_1t_3)D^<(t_3t_4)D^<(t_1t_4)D^<(t_3t_2)D^<(t_4t_2)\\
& +\int_{t_1}^{t_0} dt_3 \int_{t_2}^{t_0} dt_4 D^<(t_1t_3)D^<(t_3t_4)D^<(t_1t_4)D^<(t_3t_2)D^>(t_4t_2)
\end{aligned}
$$

$$
\begin{aligned}
\text{3rd Term} \quad = \quad & \int_{c_K(t_1)} d\tau_3 \int_{c_M} d\tau_4^M D(t_1\tau_3)D^{\urcorner}(\tau_3\tau_4^M)D^{\urcorner}(t_1\tau_4^M)D^<(\tau_3 t_2)D^{\ulcorner}(\tau_4^M t_2)\\
| \quad & \text{break up } c_K(t_1) = \overrightarrow{c_K(t_1)} + \overleftarrow{c_K(t_1)}\\
= \quad & \int_{\overrightarrow{c_K(t_1)}} d\tau_3 \int_{c_M} d\tau_4^M D^>(t_1\tau_3)D^{\urcorner}(\tau_3\tau_4^M)D^{\urcorner}(t_1\tau_4^M)D^<(\tau_3 t_2)D^{\ulcorner}(\tau_4^M t_2)\\
& +\int_{\overleftarrow{c_K(t_1)}} d\tau_3 \int_{c_M} d\tau_4^M D^<(t_1\tau_3)D^{\urcorner}(\tau_3\tau_4^M)D^{\urcorner}(t_1\tau_4^M)D^<(\tau_3 t_2)D^{\ulcorner}(\tau_4^M t_2)\\
| \quad & \text{then write integration limits explicitly and write in real time}\\
= \quad & \int_{t_0}^{t_1} dt_3 \int_{t_0}^{t_0 - i\hbar\beta} d\tau_4^M D^>(t_1t_3)D^{\urcorner}(t_3\tau_4^M)D^{\urcorner}(t_1\tau_4^M)D^<(t_3t_2)D^{\ulcorner}(\tau_4^M t_2)
\end{aligned}
$$

$$+\int_{t_1}^{t_0} dt_3 \int_{t_0}^{t_0-i\hbar\beta} d\tau_4^M D^<(t_1t_3)D^\rceil(t_3\tau_4^M)D^\rceil(t_1\tau_4^M)D^<(t_3t_2)D^\lceil(\tau_4^M t_2)$$

$$\text{4th Term} \;=\; \int_{c_K(t_2)} d\tau_3 \int_{c_K(t_1)} d\tau_4 D(t_1\tau_3)D(\tau_3\tau_4)D(t_1\tau_4)D(\tau_3t_2)D(\tau_4t_2)$$

which is the same as 2nd Term after renaming $\tau_3 \leftrightarrow \tau_4$. Note that it does not happen in general. In this case $\Sigma^{(3ph)}$ has that symmetry in τ_3 and τ_4.

$$\begin{aligned}
\text{5th Term} \;&=\; \int_{c_K(t_2)} d\tau_3 \int_{c_K(t_2)} d\tau_4 D(t_1\tau_3)D(\tau_3\tau_4)D(t_1\tau_4)D(\tau_3t_2)D(\tau_4t_2) \\
&|\;\; \text{thus } t_1 \text{ is earlier than } \tau_3 \text{ and } \tau_4 \\
&=\; \int_{c_K(t_2)} d\tau_3 \int_{c_K(t_2)} d\tau_4 D^<(t_1\tau_3)D(\tau_3\tau_4)D^<(t_1\tau_4)D(\tau_3t_2)D(\tau_4t_2) \\
&|\;\; \text{break up } c_K(t_2) = \overrightarrow{c_K(t_2)} + \overleftarrow{c_K(t_2)} \\
&|\;\; \text{then write integration limits explicitly and write in real time} \\
&=\; \int_{t_0}^{t_2} dt_3 \int_{t_0}^{t_2} dt_4 D^<(t_1t_3)D^t(t_3t_4)D^<(t_1t_4)D^<(t_3t_2)D^<(t_4t_2) \\
&\quad + \int_{t_0}^{t_2} dt_3 \int_{t_2}^{t_0} dt_4 D^<(t_1t_3)D^<(t_3t_4)D^<(t_1t_4)D^<(t_3t_2)D^>(t_4t_2) \\
&\quad + \int_{t_2}^{t_0} dt_3 \int_{t_0}^{t_2} dt_4 D^<(t_1t_3)D^>(t_3t_4)D^<(t_1t_4)D^>(t_3t_2)D^<(t_4t_2) \\
&\quad + \int_{t_2}^{t_0} dt_3 \int_{t_2}^{t_0} dt_4 D^<(t_1t_3)D^{\bar{t}}(t_3t_4)D^<(t_1t_4)D^>(t_3t_2)D^>(t_4t_2)
\end{aligned}$$

$$\begin{aligned}
\text{6th Term} \;&=\; \int_{c_K(t_2)} d\tau_3 \int_{c_M} d\tau_4^M D^<(t_1\tau_3)D^\rceil(\tau_3\tau_4^M)D^\rceil(t_1\tau_4^M)D(\tau_3t_2)D^\lceil(\tau_4^M t_2) \\
&|\;\; \text{break up } c_K(t_2) = \overrightarrow{c_K(t_2)} + \overleftarrow{c_K(t_2)} \\
&|\;\; \text{then write integration limits explicitly and write in real time} \\
&=\; \int_{t_0}^{t_2} dt_3 \int_{t_0}^{t_0-i\hbar\beta} d\tau_4^M D^<(t_1t_3)D^\rceil(t_3\tau_4^M)\left(D^<(t_3t_2) - D^>(t_3t_2)\right)D^\lceil(\tau_4^M t_2)
\end{aligned}$$

$$\begin{aligned}
\text{7th Term} \;&=\; \int_{c_M} d\tau_3^M \int_{c_K(t_1)} d\tau_4 D^\rceil(t_1\tau_3^M)D^\lceil(\tau_3^M\tau_4)D(t_1\tau_4)D^\lceil(\tau_3^M t_2)D^<(\tau_4t_2) \\
&|\;\; \text{break up } c_K(t_1) = \overrightarrow{c_K(t_1)} + \overleftarrow{c_K(t_1)} \\
&|\;\; \text{then write integration limits explicitly and write in real time} \\
&=\; \int_{t_0}^{t_0-i\hbar\beta} d\tau_3^M \int_{t_0}^{t_1} dt_4 D^\rceil(t_1\tau_3^M)D^\lceil(\tau_3^M\tau_4)D^>(t_1t_4)D^\lceil(\tau_3^M t_2)D^<(t_4t_2) \\
&\quad + \int_{t_0}^{t_0-i\hbar\beta} d\tau_3^M \int_{t_1}^{t_0} dt_4 D^\rceil(t_1\tau_3^M)D^\lceil(\tau_3^M\tau_4)D^<(t_1t_4)D^\lceil(\tau_3^M t_2)D^>(t_4t_2)
\end{aligned}$$

$$
\begin{aligned}
\text{8th Term} &= \int_{c_M} d\tau_3^M \int_{c_K(t_2)} d\tau_4 D^{\rceil}(t_1\tau_3^M) D^{\ulcorner}(\tau_3^M\tau_4) D^{<}(t_1\tau_4) D^{\ulcorner}(\tau_3^M t_2) D(\tau_4 t_2) \\
&\quad | \quad \text{the derivation is very similar to the 7th Term} \\
&= \int_{t_0}^{t_0-i\hbar\beta} d\tau_3^M \int_{t_0}^{t_1} dt_4 D^{\rceil}(t_1\tau_3^M) D^{\ulcorner}(\tau_3^M t_4) D^{<}(t_1 t_4) D^{\ulcorner}(\tau_3^M t_2) \left(D^{<}(t_4 t_2) - D^{>}(t_4 t_2)\right)
\end{aligned}
$$

$$
\begin{aligned}
\text{9th Term} &= \int_{c_M} d\tau_3^M \int_{c_M} d\tau_4^M D^{\rceil}(t_1\tau_3^M) D^{M}(\tau_3^M\tau_4^M) D^{\rceil}(t_1\tau_4^M) D^{\ulcorner}(\tau_3^M t_2) D^{\ulcorner}(\tau_4^M t_2) \\
&\quad | \quad \text{write integration limits explicitly} \\
&= \int_{t_0}^{t_0-i\hbar\beta} d\tau_3^M \int_{t_0}^{t_0-i\hbar\beta} d\tau_4^M D^{\rceil}(t_1\tau_3^M) D^{M}(\tau_3^M\tau_4^M) D^{\rceil}(t_1\tau_4^M) D^{\ulcorner}(\tau_3^M t_2) D^{\ulcorner}(\tau_4^M t_2)
\end{aligned}
$$

[**Contribution:**] Here I will briefly state what this contribution is about. Vertex corrections was never really mentioned in any NEGF literature but they are needed in linear response theory and from the experience in equilibrium many-body field theory, we know that vertex corrections are important in bringing out hidden physics. Thus I have given here a systematic way to calculate vertex corrections explicitly though they are very complicated (as expected). With vertex corrections, we can perform even more sophisticated renormalizations and probe regimes where the perturbation is not really considered as "weak".

3.1.5 BBGKY Hierarchy Equations of Motion: The Many-Body Problem

This section is essentially trying to explain what the many-body problem is. It can be stated simply: in a N-body system, if there exists an interaction involving pairs (or more) particles, full knowledge of the system requires N-particle quantities. We are mostly working with the 1-particle Green's functions, trying to get as much knowledge of the N-body system out of it.

When we derive the equation of motion of the 1-particle Green's function (of a many-body problem), we do not get a closed equation and we led to a higher particle quantity. Seeking the equation of motion of the higher particle quantity will lead to even higher particle quantities. This hierarchy of equations, which ends at the full N-particle quantity is called the BBGKY (Bogoliubov-BornGreenKirkwoodYvon) hierarchy. [18]

The purpose of the Green's function hierarchy of equations is to present us with a hierarchy of correlations. Then assuming that many-particle correlations are weaker, the hierarchy can now be truncated. Thus applying the BBGKY hierarchy to Green's function allows us to make approximations based on correlations.

Finally for completeness, we now list down the many-body problems and non-many-body problems that are dealt with in this thesis. [19]

[18] Pause for a moment to ponder, and you will realise that this has nothing to do with physics. This is simply mathematics. This is why the BBGKY hierarchy appears in so many different branches of (classical or quantum) physics.

[19] Here we note some subtleties regarding many-body problems and equations of motion by looking at some terminology:

- Space Translational Invariance. In the equilibrium many-body problem, the interacting system is space translational invariant since it is in equilibrium. All quantities only depend on differences in position. An appropriate description will be to use reciprocal vectors $\vec{k}$ or $\vec{q}$. Homogenous system is a special case where quantities are the same for any differences in position or in reciprocal space, it means $\vec{k}$, $\vec{q} = 0$. For systems without this invariance, every position variable is a seperate dynamical variable!
- Time Translational Invariance. In the equilibrium or steady state problem, the system has time translational invariance. All quantities only depend on time differences. Fourier transforming to frequency variables provides a slightly more compact description. For systems neither in equilibrium nor steady state, then each time variable is a seperate variable. For the non-equilibrium 1-particle Green's function (which has 2 time variables), we therefore

1. 0-particle problem. A general name for this class of problems is the "mean field theory". An example given in this thesis is the CPA mean field theory which deals with mass-disordered systems. There is no many-body problem here.

2. 1-particle problem. 3 examples are given in this thesis: the linear coupling between system and lead, electrons interacting with electric fields and magnetic fields (in appendix). The 1-particle description is sufficient for the 1-particle problem, there is no many-body problem here.

3. 2-particle problem. The most famous example is the Coulomb interaction and it is treated in this thesis in the appendix. The equations are (D.52) and (D.53). This is the starting example of a many-body problem.

4. 3-particle problem. In this thesis, the case treated is the 3-phonon interaction. The equation is (5.147).

5. 4-particle problem. In this thesis, the case treated is the 4-phonon interaction. The equation is (5.147).

3.1.6 (Left and Right) Non-equilibrium Dyson's Equation

Since the structure of the Green's function for the non-equilibrium theory is similar in structure to the Green's function in equilibrium theory, we expect a non-equilibrium Dyson equation of the same structure but the quantities are in contour times. Also, we need to have the "left" Dyson's equation and the "right" Dyson's equation in order to describe the non-equilibrium problem (which does not have time translational invariance). Here, we merely state the Dyson's equations because the rigorous derivation is one of the main theme of the thesis. The Coulomb case, the electron-phonon case and phonon-phonon case are derived in the form of Hedin-like equations in their respective chapters.

In integral and contour time form,[20]

"Left" Dyson's Equation:

$$G(1,1') = G^{(0)}(1,1') + \int_{c_K+c_M} d2 \int_{c_K+c_M} d3 G^{(0)}(1,2)\Sigma(2,3)G(3,1') \tag{3.114}$$

"Right" Dyson's Equation:

$$G(1,1') = G^{(0)}(1,1') + \int_{c_K+c_M} d2 \int_{c_K+c_M} d3 G(1,2)\Sigma(2,3)G^{(0)}(3,1') \tag{3.115}$$

Here we explicitly show the (differential) Dyson's equations for the contour ordered phonon's Green's function defined as (cross reference with equation (5.147))

$$D(l\tau l\tau') \equiv -\frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(u_H(l\tau)u_H(l\tau')\right)\right\rangle \tag{3.116}$$

Left equation:

$$\sum_{l_1}\left(\delta_{l_1 l}\frac{\partial^2}{\partial\tau^2} + \Phi_{ll_1}\right)D(l_1\tau l'\tau') = -\delta_{ll'}\delta(\tau,\tau') + \sum_{l_1}\int_{c_K+c_M} d\tau_1 \Sigma(l\tau l_1\tau_1)D(l_1\tau_1 l'\tau') \tag{3.117}$$

---

need 2 equations; the "left" and the "right" equations for the time variable on the left and for the time variable on the right.

[20] Again this is in generic notation, it applies to both Bosons and Fermions.

Right equation:

$$\sum_{l_1}\left(\delta_{l_1 l'}\frac{\partial^2}{\partial \tau'^2}+\Phi_{l_1 l'}\right)D(l\tau l_1\tau') = -\delta_{ll'}\delta(\tau,\tau')+\sum_{l_1}\int_{c_K+c_M} d\tau_1 D(l\tau l_1\tau_1)\Sigma(l_1\tau_1 l'\tau') \tag{3.118}$$

where the Hamiltonian $H = H_0 + H_{\text{int}} + V(t)$ which I only need to specify that H_0 is the harmonic (quadratic) term. The self energy Σ need not be specified now. The contour delta function shall be defined from the contour step function.

$$\theta(\tau-\tau') = \begin{cases} \theta(t-t') & t,t'\in \overrightarrow{c_K} \\ \theta(t'-t) & t,t'\in \overleftarrow{c_K} \\ 0 & t\in \overrightarrow{c_K}, t'\in \overleftarrow{c_K} \\ 1 & t\in \overleftarrow{c_K}, t'\in \overrightarrow{c_K} \\ 1 & t\in c_K, \tau^{M'}\in c_M \\ 0 & \tau^M\in c_M, t'\in c_K \\ \theta(\tau^M-\tau^{M'}) & \tau^M\in c_M, \tau^{M'}\in c_M \end{cases} \tag{3.119}$$

$$\delta(\tau,\tau') = \delta(\tau-\tau') = \frac{d\theta(\tau-\tau')}{d\tau} = \begin{cases} \delta(t-t') & t,t'\in \overrightarrow{c_K} \\ -\delta(t'-t) & t,t'\in \overleftarrow{c_K} \\ 0 & t\in \overrightarrow{c_K}, t'\in \overleftarrow{c_K} \\ 0 & t\in \overleftarrow{c_K}, t'\in \overrightarrow{c_K} \\ 0 & t\in c_K, \tau^{M'}\in c_M \\ 0 & \tau^M\in c_M, t'\in c_K \\ \delta(\tau^M-\tau^{M'}) & \tau^M\in c_M, \tau^{M'}\in c_M \end{cases} \tag{3.120}$$

3.1.6.1 Kadanoff-Baym Equations

These are simply the differential form of Dyson's equations written *in real time* upon the application of Langreth's theorem (involving series multiplication). Here we will present the Kadanoff-Baym equations for the phonon Green's function (3.116). Looking at the table collecting Langreth's theorem, the 4 Kandanoff-Baym equations from the left Dyson equation are

$$\begin{aligned} (a)\quad & \sum_{l_1}\left(\delta_{l_1 l}\frac{\partial^2}{\partial t^2}+\Phi_{ll_1}\right)D^<(l_1 t l' t) \\ &= \sum_{l_1}\int_{t_0}^{\infty} dt_1 \Sigma^R(ltl_1t_1)D^<(l_1t_1l't') + \sum_{l_1}\int_{t_0}^{\infty} dt_1 \Sigma^<(ltl_1t_1)D^A(l_1t_1l't') \\ &\quad + \sum_{l_1}\int_0^{\beta} d\tau_1^M \Sigma^{\urcorner}(ltl_1, t_0 - i\hbar\tau_1^M)D^{\ulcorner}(l_1, t_0-i\hbar\tau_1^M, l't') \end{aligned} \tag{3.121}$$

$$\begin{aligned} (b)\quad & \sum_{l_1}\left(\delta_{l_1 l}\frac{\partial^2}{\partial t^2}+\Phi_{ll_1}\right)D^>(l_1 t l' t') \\ &= \sum_{l_1}\int_{t_0}^{\infty} dt_1 \Sigma^R(ltl_1t_1)D^>(l_1t_1l't') + \sum_{l_1}\int_{t_0}^{\infty} dt_1 \Sigma^>(ltl_1t_1)D^A(l_1t_1l't') \\ &\quad + \sum_{l_1}\int_0^{\beta} d\tau_1^M \Sigma^{\urcorner}(ltl_1, t_0 - i\hbar\tau_1^M)D^{\ulcorner}(l_1, t_0-i\hbar\tau_1^M, l't') \end{aligned} \tag{3.122}$$

$$
\begin{aligned}
(c) \quad & \sum_{l_1}\left(\delta_{l_1 l}\frac{\partial^2}{\partial t^2}+\Phi_{ll_1}\right)D^{\urcorner}(l_1 t l', t_0 - i\hbar\tau^{M'}) \\
&= \sum_{l_1}\int_{t_0}^{\infty} dt_1 \Sigma^R(ltl_1t_1)D^{\urcorner}(l_1t_1l', t_0 - i\hbar\tau^{M'}) \\
&\quad + \sum_{l_1}\int_0^{\beta} d\tau_1^M \Sigma^{\urcorner}(ltl_1, t_0 - i\hbar\tau_1^M)D^M(l_1, t_0 - i\hbar\tau_1^M, l', t_0 - i\hbar\tau^{M'}) \qquad (3.123)\\
(d) \quad & \sum_{l_1}\left(\delta_{l_1 l}\frac{\partial^2}{\partial (t_0 - i\hbar\tau^M)^2}+\Phi_{ll_1}\right)D^M(l_1, t_0 - \hbar\tau^M, l', t_0 - i\hbar^{M'}) \\
&= -\delta((t_0 - i\hbar\tau^M) - (t_0 - i\hbar\tau^{M'}))\delta_{ll'} \\
&\quad \sum_{l_1}\int_0^{\beta} d\tau_1^M \Sigma^M(l, t_0 - i\hbar\tau^M, l', t_0 - i\hbar\tau_1^M)D^M(l, t_0 - i\hbar\tau_1^M, l', t_0 - i\hbar\tau^{M'}) \qquad (3.124)
\end{aligned}
$$

We note that the left equation for $D^{\ulcorner}$ is not needed as $D^{\ulcorner}$ is related to $D^{\urcorner}$ according to equations (30) and (31) in [Stan2009].

Then the 4 Kandanoff-Baym equations from the right Dyson equation are

$$
\begin{aligned}
(a) \quad & \sum_{l_1}\left(\delta_{l_1 l'}\frac{\partial^2}{\partial t'^2}+\Phi_{l_1 l'}\right)D^<(ltl_1t') \\
&= \sum_{l_1}\int_{t_0}^{\infty} dt_1 D^R(ltl_1t_1)\Sigma^<(l_1t_1l't') + \sum_{l_1}\int_{t_0}^{\infty} dt_1 D^<(ltl_1t_1)\Sigma^A(l_1t_1l't') \\
&\quad + \sum_{l_1}\int_0^{\beta} d\tau_1^M D^{\urcorner}(ltl_1, t_0 - i\hbar\tau_1^M)\Sigma^{\ulcorner}(l_1, t_0 - i\hbar\tau_1^M, l't') \qquad (3.125)\\
(b) \quad & \sum_{l_1}\left(\delta_{l_1 l'}\frac{\partial^2}{\partial t'^2}+\Phi_{l_1 l'}\right)D^>(ltl_1t') \\
&= \sum_{l_1}\int_{t_0}^{\infty} dt_1 D^R(ltl_1t_1)\Sigma^>(l_1t_1l't') + \sum_{l_1}\int_{t_0}^{\infty} dt_1 D^>(ltl_1t_1)\Sigma^A(l_1t_1l't') \\
&\quad + \sum_{l_1}\int_0^{\beta} d\tau_1^M D^{\urcorner}(ltl_1, t_0 - i\hbar\tau_1^M)\Sigma^{\ulcorner}(l_1, t_0 - i\hbar\tau_1^M, l't') \qquad (3.126)\\
(c) \quad & \sum_{l_1}\left(\delta_{l_1 l'}\frac{\partial^2}{\partial t'^2}+\Phi_{l_1 l'}\right)D^{\urcorner}(lt_0 - i\hbar\tau^M, l_1, t') \\
&= \sum_{l_1}\int_{t_0}^{\infty} dt_1 D^{\ulcorner}(l, t_0 - i\hbar\tau^M, l_1t_1)\Sigma^A(l_1t_1l't') \\
&\quad + \sum_{l_1}\int_0^{\beta} d\tau_1^M D^M(l, t_0 - i\hbar\tau^M, l_1, t_0 - i\hbar\tau_1^M)\Sigma^{\urcorner}(l_1, t_0 - i\hbar\tau_1^M, l't') \qquad (3.127)\\
(d) \quad & \sum_{l_1}\left(\delta_{l_1 l'}\frac{\partial^2}{\partial (t_0 - i\hbar\tau^{M'})^2}+\Phi_{l_1 l'}\right)D^M(l, t_0 - \hbar\tau^M, l_1, t_0 - i\hbar\tau^{M'}) \\
&= -\delta((t_0 - i\hbar\tau^M) - (t_0 - i\hbar\tau^{M'}))\delta_{ll'} \\
&\quad \sum_{l_1}\int_0^{\beta} d\tau_1^M \Sigma^M(l, t_0 - i\hbar\tau^M, l_1, t_0 - i\hbar\tau_1^M)D^M(l_1, t_0 - i\hbar\tau_1^M, l', t_0 - i\hbar\tau^{M'}) \qquad (3.128)
\end{aligned}
$$

Again, note that the right equation for $D^{\urcorner}$ is not needed as $D^{\urcorner}$ is related to $D^{\ulcorner}$ according to equations (30) and (31) in [Stan2009].

[Relations and Initial Conditions] Now we shall list the relations between the Green's functions and list the initial conditions for solving the 8 Kandanoff-Baym equations.

According to [Stan2009], there are 2 relations, first consider,

$$\begin{aligned}
\left(D^{<}(ltl't')\right)^{*} &= \left(-\frac{i}{\hbar}\langle T_{c_K+c_M}(u_H(l't')u_H(lt))\rangle\right)^{*} && (3.129)\\
&\quad \mid \text{ note that they are Hermitian} \\
&= \frac{i}{\hbar}\langle T_{c_K+c_M}(u_H(lt)u_H(l't'))\rangle && (3.130)\\
&= -D^{<}(l't'lt) && (3.131)
\end{aligned}$$

Similarly, $(D^{>}(ltl't'))^{*} = -D^{>}(l't'lt)$. Next we consider the equal time situation where we know the equal time commutation relations,

$$\begin{aligned}
\left[u_H(lt), u_H(l't')\right]_{-}\Big|_{t'=t} &= 0 && (3.132)\\
&\quad \mid \text{ expand the commutator and take statistical average} \\
D^{>}(ltl't')|_{t'=t} - D^{<}(ltl't')|_{t'=t} &= 0 && (3.133)
\end{aligned}$$

This means that in the time propagation, we only need to solve $D^{>}(ltl't')$ for $t > t'$ and $D^{<}(ltl't')$ for $t \leq t'$.

The initial conditions for the time propagation of Kandanoff-Baym equations are,

$$\begin{aligned}
D^{\urcorner}(lt_0l', t_0 - i\hbar\tau^M) &= D^M(l, t_0 - i\hbar 0, l', t_0 - i\hbar\tau^M) && (3.134)\\
D^{\ulcorner}(l, t_0 - i\hbar\tau^M, l't_0) &= D^M(l, t_0 - i\hbar\tau^M, l', t_0 - i\hbar 0) && (3.135)\\
D^{<}(lt_0l', t_0) &= D^M(l, t_0 - i\hbar 0, l', t_0 - i\hbar 0^{+}) && (3.136)\\
D^{>}(lt_0l', t_0) &= D^M(l, t_0 - i\hbar 0^{+}, l', t_0 - i\hbar 0) && (3.137)
\end{aligned}$$

[Numerical Implementation] We follow [Stan2009] section IV and for the first numerical results see [Bonitz1998] pg 285. Fortran codes are in [Kohler1999]. For an (electronic) application see [Myohanen2008].

Recall that we only need to propagate $D^{>}_{ll'}(tt')$ for $t > t'$ and $D^{<}_{ll'}(tt')$ for $t \leq t'$ and the equal time synchronization condition is $D^{>}_{ll'}(tt')\big|_{t'=t} = D^{<}_{ll'}(tt')\big|_{t'=t}$. So we only time step $D^{>}$ in the first time argument and time step $D^{<}$ in the second time argument. $D^{\ulcorner}(t_0 - i\hbar\tau^M, t)$ and $D^{\urcorner}(t, t_0 - i\hbar\tau^M)$ are time stepped in t for fixed τ^M.

The general outline for time stepping is,

1. Time step $T \to T + \Delta$ once for the Green's functions.

2. Use that to recalculate the RHS of the Kadanoff-Baym equations.

3. Time step $T \to T + \Delta$ again using the average of the old and new RHS.

In [Stan2009], a method was given to absorb the time singular part of the self energy Σ^{δ} into the time stepping process for the sake of numerical stability. It appears that the method requires the first order time derivative in KB equations to work and in this case, we have second order time derivatives so the method seems to fail here. So we need to be careful if we use time singular (phonon-phonon) self energy for calculations.

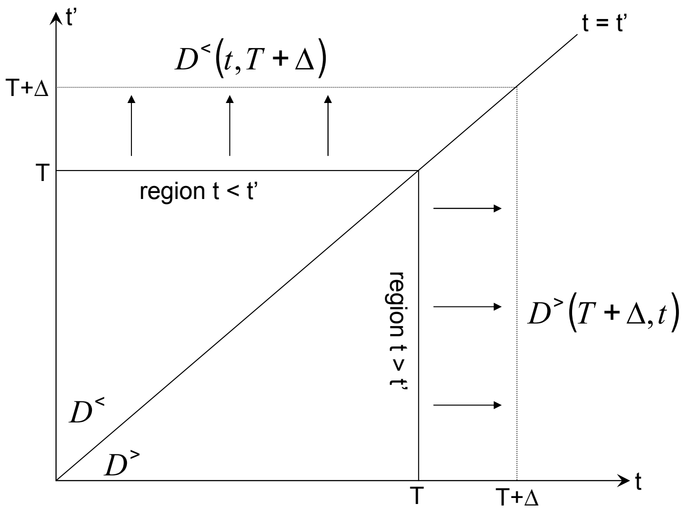


Figure 3.6: *Time stepping scheme.*

3.1.6.2 Keldysh Equations

These are simply the integral form of Dyson's equations written *in real time* upon the application of Langreth's theorem (involving series multiplication). We start with the integral form of the left Dyson's equation (in contour time).[21]

$$G = G^{(0)} + \int_{c_K+c_M} G^{(0)}\Sigma G \tag{3.138}$$

Apply Langreth's theorem to get the lesser component (in real time),

$$\begin{aligned}
G^< &= G^{(0)<} + \int_t G^{(0)R}\left(\int_{c_K+c_M}\Sigma G\right)^< + \int_t G^{(0)<}\left(\int_{c_K+c_M}\Sigma G\right)^A + \int_{\tau^M} G^{(0)\urcorner}\left(\int_{c_K+c_M}\Sigma G\right)^{\ulcorner} \\
&= G^{(0)<} + \int_t G^{(0)R}\left(\int_t \Sigma^R G^< + \int_t \Sigma^< G^A + \int_{\tau^M}\Sigma^{\urcorner} G^{\ulcorner}\right) + \int_t G^{(0)<}\int_t \Sigma^A G^A \\
&\quad + \int_{\tau^M} G^{(0)\urcorner}\left(\int_t \Sigma^{\ulcorner} G^A + \int_{\tau^M}\Sigma^M G^{\ulcorner}\right) \qquad (3.139) \\
&= G^{(0)<} + \int_t G^{(0)R}\Sigma^R G^< + \int_t G^{(0)R}\Sigma^< G^A + \int_t G^{(0)<}\Sigma^A G^A \\
&\quad + \int_t G^{(0)R}\int_{\tau^M}\Sigma^{\urcorner} G^{\ulcorner} + \int_{\tau^M} G^{(0)\urcorner}\int_t \Sigma^{\ulcorner} G^A + \int_{\tau^M} G^{(0)\urcorner}\int_{\tau^M}\Sigma^M G^{\ulcorner} \qquad (3.140)
\end{aligned}$$

We further rewrite the first line

$$\begin{aligned}
&\text{“First line”} \\
=\ & G^{(0)<} + \int_t G^{(0)R}\Sigma^R G^< + \int_t G^{(0)R}\Sigma^< G^A + \int_t G^{(0)<}\Sigma^A G^A \qquad (3.141) \\
|\ & \text{iterate once}
\end{aligned}$$

[21]The arguments are left out and the convolution is written in symbolic form. Again here we use the generic notation of Green's functions. The calculations here apply to Bosons and Fermions.

$$
\begin{aligned}
&= G^{(0)<} + \int_t G^{(0)R}\Sigma^{<}G^{A} + \int_t G^{(0)<}\Sigma^{A}G^{A} \\
&\quad + \int_t G^{(0)R}\Sigma^{R}\left(G^{(0)<} + G^{(0)R}\Sigma^{<}G^{A} + G^{(0)<}\Sigma^{A}G^{A} + G^{(0)R}\Sigma^{R}G^{<}\right) \qquad (3.142)\\
&= G^{(0)<} + \int_t G^{(0)R}\Sigma^{<}G^{A} + \int_t G^{(0)<}\Sigma^{A}G^{A} + \int_t G^{(0)R}\Sigma^{R}G^{(0)<} + \int_t G^{(0)R}\Sigma^{R}G^{(0)R}\Sigma^{<}G^{A} \\
&\quad + \int_t G^{(0)R}\Sigma^{R}G^{(0)<}\Sigma^{A}G^{A} + \int_t G^{(0)R}\Sigma^{R}G^{(0)R}\Sigma^{R}G^{<} \qquad (3.143)\\
&= \int_t G^{(0)<}\left(1+\Sigma^{A}G^{A}\right) + \int_t G^{(0)R}\Sigma^{R}G^{(0)<} + \int_t \left(G^{(0)R} + G^{(0)R}\Sigma^{R}G^{(0)R}\right)\Sigma^{<}G^{A} \\
&\quad + \int_t G^{(0)R}\Sigma^{R}G^{(0)<}\Sigma^{A}G^{A} + \int_t G^{(0)R}\Sigma^{R}G^{(0)R}\Sigma^{R}G^{<} \qquad (3.144)\\
&= \int_t \left(1 + G^{(0)R}\Sigma^{R}\right)G^{(0)<}\left(1+\Sigma^{A}G^{A}\right) + \int_t \left(G^{(0)R} + G^{(0)R}\Sigma^{R}G^{(0)R}\right)\Sigma^{<}G^{A} \\
&\quad + \int_G^{(0)R} \Sigma^{R}G^{(0)R}\Sigma^{R}G^{<} \qquad (3.145)\\
&| \quad \text{iterate more} \\
&= \int_t \left(1 + G^{(0)R}\Sigma^{R} + G^{(0)R}\Sigma^{R}G^{(0)R} + \cdots\right)G^{(0)<}\left(1+\Sigma^{A}G^{A}\right) \\
&\quad + \int_t \left(G^{(0)R} + G^{(0)R}\Sigma^{R}G^{(0)R} + G^{(0)R}\Sigma^{R}G^{(0)R}\Sigma^{R}G^{(0)R} + \cdots\right)\Sigma^{<}G^{A} \qquad (3.146)\\
&= \int_t \left(1+G^{R}\Sigma^{R}\right)G^{(0)<}\left(1+\Sigma^{A}G^{A}\right) + \int_t G^{R}\Sigma^{<}G^{A} \qquad (3.147)
\end{aligned}
$$

The full (left) Keldysh equation (with initial correlations) is

$$
\boxed{
\begin{aligned}
G^{<} &= \int_t \left(1+G^{R}\Sigma^{R}\right)G^{(0)<}\left(1+\Sigma^{A}G^{A}\right) + \int_t G^{R}\Sigma^{<}G^{A} \\
&\quad + \int_t G^{(0)R}\int_{\tau^M}\Sigma^{\urcorner}G^{\ulcorner} + \int_{\tau^M} G^{(0)\urcorner}\int_t \Sigma^{\ulcorner}G^{A} + \int_{\tau^M} G^{(0)\urcorner}\int_{\tau^M}\Sigma^{M}G^{\ulcorner}
\end{aligned}
}
\qquad (3.148)
$$

When $G^{(0)}$ describes non-interacting particles then $G^{(0)<}$ is of the form,[22]

$$
G^{(0)<} \propto \left\{ \begin{array}{ll} \delta(\epsilon - \epsilon(\vec{k})) & \text{for electrons} \\ \delta(\omega^2 - \omega^2(j\vec{q})) & \text{for phonons} \end{array} \right. \qquad (3.149)
$$

then the first term of $G^{<}$ becomes (e.g for phonons),

$$
\int_t \left(1+G^{R}\Sigma^{R}\right)G^{(0)<}\left(1+\Sigma^{A}G^{A}\right) \propto \left(1 + \frac{\Sigma^{R}}{\omega^2 - \omega^2(j\vec{q}) - \Sigma^{R}}\right)\delta(\omega^2 - \omega^2(j\vec{q}))\left(1+\Sigma^{A}G^{A}\right) = 0
$$

then the Keldysh equation (when the free Green's function is the non-interacting Green's function)

[22] To see why $G^{(0)}$ represents non-interacting particles, just take the lowest order term in the perturbation expansion. It is the term $G^{(0)}$. Remember that this choice is made so that Wick's theorem works. However the original physics is that we perturb from an interacting equilibrium state (due to $H_0 + H_{\text{int}}$). This piece of physics is unchanged.

becomes

$$\boxed{G^< = \int_t G^R\Sigma^<G^A + \int_t G^{(0)R}\int_{\tau^M}\Sigma^\rceil G^\ulcorner + \int_{\tau^M} G^{(0)\rceil}\int_t \Sigma^\ulcorner G^A + \int_{\tau^M} G^{(0)\rceil}\int_{\tau^M}\Sigma^M G^\ulcorner} \tag{3.150}$$

If we assume that initial conditions do not affect long time evolution (which we can check numerically or theoretically by solving the Kadanoff-Baym equations) which is usually stated as "dropping the Matsubara contour c_M" and/or "taking $t_0 \to -\infty$" then only the first term survives. The (left) Keldysh equation (when the free Green's function is the non-interacting Green's function and initial correlations are ignored) simplifies to

$$\boxed{G^< = \int_t G^R\Sigma^<G^A} \tag{3.151}$$

3.1.7 Receipe of NEGF

It looks like as if NEGF is abstract and complicated. In reality, it is really just a bag of clever tricks which is quite straightforward to apply. Here we give a step by step receipe.

1. Look at the Hamiltonian of your problem and decide which part goes into H_0, H_{int} and $V(t)$. Remember that H_0 should be the quadratic part, H_{int} must not be time dependent and $V(t)$ can be time dependent or time independent. Once the partitioning is done, the contour is chosen, i.e.,

$$\text{contour} \quad = \quad \begin{cases} c_K + c_M & \text{when } H_{\text{int}} \neq 0 \text{ and } V(t) \neq 0 \\ c_K & \text{when } H_{\text{int}} = 0 \text{ and } V(t) \neq 0 \end{cases} \tag{3.152}$$

2. For the quantity to calculate, write it into some Green's function "component". Eg. in the Landauer-like case, the current is purposely written as the (time derivative of the) lesser component of a mixed Green's function.

3. Then define the contour ordered version of this Green's function because a perturbative treatment only exists for this object. Choose a suitable (contour time) self energy.

4. The contour time trick is over and we apply Langreth's theorem to give us the (real time) component that we want in step (2). One can also just pick the relevant component KB or Keldysh equations to solve for the particular Green's function component of interest. Note that the real time self energies in KB or Keldysh equations are obtained from the contour time ones by using Langreth's theorem (involving parallel multiplication).

5. Once we have the (real time) Green's function component, we carry on with the calculation of the physical quantity (eg current or noise).

3.2 From NEGF to Landauer-like equations

3.2.1 General expression for the Current

This is the first of three developments of NEGF. [23] We follow [Haug2007] chapter 12, [DiVentra2008] chapter 4 and [Meir1992]. This development deals with systems with leads attached. The (rather artificial) time dependent problem is that, at t_0, the leads are attached to the system. After the leads are attached, the Hamiltonian is time independent actually, thus the physical quantities (in this case, the current) is a constant. This constant is the steady state value.

[23] The three developments are: Landauer-like theory, Quantum Kinetic equations and Linear Response theory.

We work out the simplest case[24] of two thermal leads and a central interacting system. The (sudden) switch on in NEGF is now used as the system-lead attachment.We assume that the left lead and the right lead are independent, infinite and non-interacting.

$$H = H_0^L + H_0^C + H_{\text{int}}^C + H^{LC}\theta(t-t_0) \tag{3.153}$$

where H_0^L and H_0^C are the harmonic non-interacting Hamiltonians of the left lead and the central system respectively. H_{int}^C is the interacting Hamiltonian of the central system where the interaction may be mass disorder, anharmonicity, electron-phonon interaction and so on. H^{LC} is the Hamiltonian that describes the connection of the left lead and the central system.

We choose to partition it as follows (let $H^C = H_0^C + H_{\text{int}}^C$),

$$\begin{aligned}
H_0 &= H_0^L + H_0^C + H_{\text{int}}^C = H_0^L + H^C \ \ \text{(see footnote)}^{25} && (3.154)\\
H_{\text{int}} &= 0 && (3.155)\\
V(t)\theta(t-t_0) &= H^{LC}\theta(t-t_0) && (3.156)
\end{aligned}$$

We define the energy current from the left lead to the central device as the change in expectation value of the left lead Hamiltonian (again we supress the indices k and α)

$$\begin{aligned}
J_{\text{thermal}}^{L\to C}(t) &= \left\langle -\dot{H}_{0H}^L(t)\right\rangle && (3.157)\\
&\quad \Big|\ \text{where } \langle\ldots\rangle = \frac{\operatorname{Tr}\left(e^{-\beta^L H_0^L - \beta^C H^C}\ldots\right)}{\operatorname{Tr}\left(e^{-\beta^L H_0^L - \beta^C H^C}\right)} \\
&\quad \Big|\ \text{and } H_{0H}^L \text{ is the Heisenberg picture operator of } H_0^L \\
&= -\left\langle \frac{d}{dt} H_{0H}^L(t)\right\rangle && (3.158)\\
&\quad \Big|\ \text{use the Heisenberg equation of motion } \frac{d}{dt}H_{0H}^L(t) = \frac{i}{\hbar}\left[H_H(t), H_{0H}^L(t)\right]_- \\
&= \frac{i}{\hbar}\left\langle \left[H_{0H}^L(t), H_H(t)\right]_-\right\rangle && (3.159)\\
&= \frac{i}{\hbar}\left\langle \left[H_{0H}^L(t), H_H^{LC}(t)\right]_-\right\rangle && (3.160)\\
&= \frac{i}{\hbar}\left\langle \left[\frac{1}{2M^L}\sum_l p_H^L(lt)^2, \sum_{l_1 l_2}^{\text{interface}} V_{l_1 l_2}^{LC} u_H^L(l_1 t) u_H^C(l_2 t)\right]_-\right\rangle && (3.161)\\
&\quad \Big|\ \text{use the fundamental commutator } \left[u^L(l_1 t), p^L(l_2 t)\right]_- = i\hbar\delta_{l_1 l_2} \\
&\quad \Big|\ \text{recall that } p^L = M^L \dot{u}^L \\
&= \sum_{l_1 l_2}^{\text{interface}} V_{l_1 l_2}^{LC}\left\langle \left(\frac{d}{dt}u_H^L(lt)\right) u_H^C(l't)\right\rangle && (3.162)
\end{aligned}$$

Now we want to use NEGF methods to deal with the $\langle \dot{u}_H^L u_H^C\rangle$ correlation. To maintain u_H^L on the

[24] A one lead + one system problem is also an open system problem but it is not, strictly speaking, a transport problem.

[25] This is an unusual way of partitioning the Hamiltonian where H_0 is actually nonquadratic. We will pay the price for it in the final result of the current. The current expression, equation (3.182) looks nice but the expressions $D^{(C)R}$ and $D^{(C)<}$ are not known and are most likely not closed expressions.

left and that $\frac{d}{dt}$ only acts on u_H^L, we write $u_H^L(lt) \to u_H^L(lt')$ with $t' > t$, hence defining a (hybrid) lesser Green's function $D^<$ [26]

$$D^{(CL)<}(ltl't') = -\frac{i}{\hbar}\left\langle u_H^L(l't')u_H^C(lt)\right\rangle \tag{3.163}$$

$$J_{\text{thermal}}^{L\to C}(t) = \lim_{t'\to t}\sum_{ll'}^{\text{interface}} V_{ll'}^{LC}\frac{d}{dt'}\left\langle u_H^L(l't')u_H^C(lt)\right\rangle = i\hbar\lim_{t'\to t}\sum_{ll'}^{\text{interface}} V_{ll'}^{LC}\frac{d}{dt'}D^{(CL)<}(ltl't') \tag{3.164}$$

Now we define and work with the contour-ordered version of D in order to employ NEGF perturbation techniques,

$$D^{(CL)}(l\tau l'\tau') = -\frac{i}{\hbar}\left\langle T_{c_K}\left(u_H^L(l'\tau')u_H^C(l\tau)\right)\right\rangle \tag{3.165}$$

The contour ordering is only over c_K because we choose to partition such that $H_{\text{int}} = 0$. We can copy over the perturbation expression from the first section,

$$D^{(CL)}(l\tau l'\tau') = -\frac{i}{\hbar}\frac{\operatorname{Tr}\left(e^{-\beta^L H_0^L-\beta^C H^C}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_1 H_{H_0}^{LC}(\tau_1)}u_{H_0}^L(l'\tau')u_{H_0}^C(l\tau)\right)\right)}{\operatorname{Tr}\left(e^{-\beta^L H_0^L-\beta^C H^C}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_1 H_{H_0}^{LC}(\tau_1)}\right)\right)} \tag{3.166}$$

We can make some slight simplifications in the expressions,

$$\begin{aligned}
u_{H_0}^C(l\tau) &= e^{\frac{i}{\hbar}(H_0^L+H^C)(\tau-t_0)}u^C(lt_0)e^{-\frac{i}{\hbar}(H_0^L+H^C)(\tau-t_0)} && (3.167)\\
&\mid\ \text{note that } H_0^L \text{ commutes with } H^C \text{ and } u^C\\
&= e^{\frac{i}{\hbar}H^C(\tau-t_0)}u^C(lt_0)e^{-\frac{i}{\hbar}H^C(\tau-t_0)} && (3.168)\\
&= u_{H^C}^C(l\tau) && (3.169)\\
\text{Similarly,}\ & && (3.170)\\
u_{H_0}^L(l'\tau') &= u_{H_{H_0}^L}^L(l'\tau') && (3.171)\\
H_{H_0}^{LC}(\tau) &= \sum_{ll'}^{\text{interface}} V_{ll'}^{LC}u_{H_0^L}^L(l\tau)u_{H^C}^C(l'\tau') \equiv \tilde{H}^{LC}(\tau) && (3.172)
\end{aligned}$$

We will carry out the S-matrix expansion and we assume that $H^C = H_0^C + H_{\text{int}}^C$ is not quadratic, hence Wick's theorem cannot be applied to u^C correlation terms at this stage.

$$\begin{aligned}
&D^{(CL)}(l\tau l'\tau')\\
&= -\frac{i}{\hbar}\frac{\operatorname{Tr}\left(e^{-\beta^L H_0^L-\beta^C H^C}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_1\tilde{H}^{LC}(\tau_1)}u_{H_0^L}^L(l'\tau')u_{H^C}^C(l\tau)\right)\right)}{\operatorname{Tr}\left(e^{-\beta^L H_0^L-\beta^C H^C}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_1\tilde{H}^{LC}(\tau_1)}\right)\right)} && (3.173)\\
&= -\frac{i}{\hbar}\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_1\tilde{H}^{LC}(\tau_1)}u_{H_0^L}^L(l'\tau')u_{H^C}^C(l\tau)\right)\right\rangle && (3.174)\\
&\mid\ \text{expand out the } S\text{-matrix following [Haug2007] pg188}\\
&= -\frac{i}{\hbar}\sum_{k=0}^{\infty}\frac{1}{k!}\left(-\frac{i}{\hbar}\right)^k\int_{c_K}d\tau_1\dots d\tau_k\left\langle T_{c_K}\left(\tilde{H}^{LC}(\tau_1)\dots\tilde{H}^{LC}(\tau_k)u_{H_0^L}^L(l'\tau')u_{H^C}^C(l\tau)\right)\right\rangle && (3.175)
\end{aligned}$$

[26] Define a $D^{(CL)>}$ if the reader prefers. Note that the fermionic version has a different sign.

$$
\begin{aligned}
&= -\frac{i}{\hbar}\sum_{k=0}^{\infty}\frac{1}{k!}\left(-\frac{i}{\hbar}\right)^k\int_{c_K} d\tau_1\ldots d\tau_k \\
&\quad\times\sum_{l_1l_2}\left\langle T_{c_K}\left(u^L_{H_0^L}(l'\tau')u^L_{H_0^L}(l_1\tau_1)\right)\right\rangle V^{LC}_{l_1l_2}\left\langle T_{c_K}\left(u^C_{H^C}(l\tau)u^C_{H^C}(l_2\tau_1)\tilde{H}^{LC}(\tau_2)\ldots\tilde{H}^{LC}(\tau_k)\right)\right\rangle && (3.176)\\
&\quad|\ \text{there are } k-1 \text{ terms more due to } u^L_{H_0^L}(l'\tau') \text{ pairing with } u^L_{H_0^L}(l_1\tau_2),\ldots,u^L_{H_0^L}(l_1\tau_k)\\
&\quad|\ \text{note that the } u^C \text{ terms on the right cannot be factorised}\\
&\quad|\ \text{all } k \text{ terms are the same after relabeling indices, giving a factor } k\\
&\quad|\ \text{note that } -\frac{i}{\hbar}\left\langle T_{c_K}\left(u^L_{H_0^L}(l'\tau')u^L_{H_0^L}(l_1\tau_1)\right)\right\rangle = D^{(0)(L)}(l'\tau'l_1\tau_1)\\
&= -\frac{i}{\hbar}\sum_{k=0}^{\infty}\frac{1}{(k-1)!}\left(-\frac{i}{\hbar}\right)^{k-1}\int_{c_K} d\tau_1\int_{c_K} d\tau_2\ldots d\tau_k\\
&\quad\times\sum_{l_1l_2} D^{(0)(L)}(l_1\tau_1l'\tau')V^{LC}_{l_1l_2}\left(\frac{i}{\hbar}\right)\left\langle T_{c_K}\left(u^C_{H^C}(l\tau)u^C_{H^C}(l_2\tau_1)\tilde{H}^{LC}(\tau_2)\ldots\tilde{H}^{LC}(\tau_k)\right)\right\rangle && (3.177)\\
&\quad|\ \text{since the sum is infinite, we can reconstruct the } S\text{-matrix}\\
&= \int_{c_K} d\tau_1\sum_{l_1l_2} D^{(0)(L)}(l_1\tau_1l'\tau')V^{LC}_{l_1l_2}\left(-\frac{i}{\hbar}\right)\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C}(l\tau)u^C_{H^C}(l_2\tau_1)\right)\right\rangle && (3.178)\\
&\quad|\ \text{we now define the interacting central Green's function } D^{(C)}\\
&= \int_{c_K} d\tau_1\sum_{l_1l_2} D^{(0)(L)}(l_1\tau_1l'\tau')V^{LC}_{l_1l_2}D^{(C)}(l\tau l_2\tau_1) && (3.179)\\
&= \int_{c_K} d\tau_1\sum_{l_1l_2} D^{(C)}(l\tau l_2\tau_1)V^{LC}_{l_2l_1}D^{(0)(L)}(l_1\tau_1l'\tau') && (3.180)
\end{aligned}
$$

Since we only want the $D^{(CL)<}(ltl't')$ component, we will now apply Langreth's theorem on the above equation.

$$
D^{(CL)<}(ltl't') = \int_{t_0}^{\infty} dt_1\sum_{l_1l_2}V^{LC}_{l_2l_1}\left(D^{(C)R}(ltl_2t_1)D^{(0)(L)<}(l_1t_1l't') + D^{(C)<}(ltl_2t_1)D^{(0)(L)A}(l_1t_1l't')\right) \tag{3.181}
$$

Now the thermal current expression takes the final form,

$$
\begin{aligned}
J^{L\to C}_{\text{thermal}}(t) &= i\hbar\lim_{t'\to t}\sum_{ll'}^{\text{interface}} V^{LC}_{ll'}\frac{d}{dt'}D^{(CL)<}(ltl't')\\
&\quad|\ \text{define the lead self energies as follows}\\
&\quad|\ \Sigma^{(L)<}(lt_1l_2t') \equiv \sum_{l_1l'}^{\text{interface}} V^{LC}_{ll'}D^{(0)(L)<}(l_1t_1l't')V^{LC}_{l_1l_2}\\
&\quad|\ \Sigma^{(L)A}(lt_1l_2t') \equiv \sum_{l_1l'}^{\text{interface}} V^{LC}_{ll'}D^{(0)(L)A}(l_1t_1l't')V^{LC}_{l_1l_2}\\
&= i\hbar\lim_{t'\to t}\sum_{ll_2}\frac{d}{dt'}\int_{t_0}^{\infty}dt_1\left(D^{(C)R}(ltl_2t_1)\Sigma^{(L)<}(lt_1l_2t') + D^{(C)<}(ltl_2t_1)\Sigma^{(L)A}(l_1t_1l't')\right)
\end{aligned}
$$

This is the time dependent expression that has information on transients due to the lead-system coupling switch on.

$$\boxed{J^{L\to C}_{\text{thermal}}(t) = i\hbar \lim_{t'\to t}\sum_{ll_2}\frac{d}{dt'}\int_{t_0}^{\infty} dt_1 \left(D^{(C)R}(ltl_2t_1)\Sigma^{(L)<}(lt_1l_2t') + D^{(C)<}(ltl_2t_1)\Sigma^{(L)A}(l_1t_1l't')\right)} \tag{3.182}$$

We now just want to make a formal remark on how the transient problem is handled. The Green's functions $D^{(C)R}$ and $D^{(C)<}$ are solved from the Kadanoff-Baym (KB) equations using the self energies of the lead-system coupling and the interacting central. Then the Green's functions and the lead-system coupling self energy is used to solve the (time dependent) current expression above. Transient information is contained before the steady state value is reached.

Subsequently, we are going to assume steady state and derive steady state (or DC) currents for 3 cases.

3.2.1.1 Current for an Interacting Central

First we note that the leads are in a stationary state so we can write $\Sigma^{(L)<}(lt_1l_2t_1) = \Sigma^{(L)<}(ll_2, t_1 - t')$ and $\Sigma^{(L)A}(l_1t_1l't') = \Sigma^{(L)A}(l_1l', t_1 - t')$. Now if we assume that a steady state current has occurred in the central then the 2-time dependence in the central Green's function becomes a time difference dependence due to time translational invariance. Thus it is advantageous to take the Fourier transform and work in frequency space.

$$\begin{aligned}
J^{L\to C}_{\text{thermal}} &= i\hbar \lim_{t'\to t}\sum_{ll_1}\frac{d}{dt'}\int_{t_0}^{\infty} dt_1 \left(D^{(C)R}_{ll_1}(t-t_1)\Sigma^{(L)<}_{ll_1}(t_1-t') + D^{(C)<}_{ll_1}(t-t_1)\Sigma^{(L)A}_{l_1l}(t_1-t')\right)\\
&\quad |\quad \text{temporal Fourier transform can be done when } t_0\to-\infty \text{ which is taken now}\\
&\quad |\quad \text{thus we see a time-convolved expression which we can write as a Fourier transform}\\
&= i\hbar \lim_{t'\to t}\sum_{ll_1}\frac{d}{dt'}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega(t-t')}\left[D^{(C)R}_{ll_1}(\omega)\Sigma^{(L)<}_{ll_1}(\omega) + D^{(C)<}_{ll_1}(\omega)\Sigma^{(L)A}(\omega)\right] &(3.183)\\
&\quad |\quad \text{now we can differentiate with respect to } t' \text{ and take the limit } t'\to t\\
&= \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\sum_{ll_1}\left[D^{(C)R}_{ll_1}(\omega)\Sigma^{(L)<}_{ll_1}(\omega) + D^{(C)<}_{ll_1}(\omega)\Sigma^{(L)A}_{l_1l}(\omega)\right] &(3.184)\\
&\quad |\quad \text{write as trace (over } lk\alpha \text{ indices)}\\
&= \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\,\mathrm{Tr}\left[D^{(C)R}(\omega)\Sigma^{(L)<}(\omega) + D^{(C)<}(\omega)\Sigma^{(L)A}(\omega)\right] &(3.185)\\
&\quad |\quad \text{use identities } D^{(C)A\dagger}(\omega) = D^{(C)R}(\omega) \text{ and } \Sigma^{(L)<\dagger}(\omega) = -\Sigma^{(L)<}(\omega)\\
&= \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\,\mathrm{Tr}\left[-D^{(C)A\dagger}(\omega)\Sigma^{(L)<\dagger}(\omega) + (-1)D^{(C)<\dagger}(\omega)\Sigma^{(L)R\dagger}(\omega)\right] &(3.186)\\
&= -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\,\mathrm{Tr}\left[\left(\Sigma^{(L)<}(\omega)D^{(C)A}(\omega) + \Sigma^{(L)R}(\omega)D^{(C)<}(\omega)\right)^{\dagger}\right] &(3.187)
\end{aligned}$$

With the previous expression, it is now easy to write down the Hermitian conjugate of the current, $J^{L\to C\dagger}_{\text{thermal}}$.

$$J^{L\to C\dagger}_{\text{thermal}} = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\,\mathrm{Tr}\left[\Sigma^{(L)<}(\omega)D^{(C)A}(\omega) + \Sigma^{(L)R}(\omega)D^{(C)<}(\omega)\right] \tag{3.188}$$

Since current is an observable, the current expression must be Hermitian, thus we symmetrise and make it Hermitian.

$$
\begin{aligned}
J_{\text{thermal}}^{L\to C\dagger} &= \frac{1}{2}\left(J_{\text{thermal}}^{L\to C} + J_{\text{thermal}}^{L\to C\dagger}\right) && (3.189)\\
&\mid \ \text{use trace cyclicity}\\
&= \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left[(D^{(C)R}-D^{(C)A})\Sigma^{(L)<} - D^{(C)<}(\Sigma^{(L)R}-\Sigma^{(L)A})\right] && (3.190)\\
&\mid \ \text{use the identities } D^{(C)>}-D^{(C)<}=D^{(C)R}-D^{(C)A} \text{ and } \Sigma^{(L)>}-\Sigma^{(L)<}=\Sigma^{(L)R}-\Sigma^{(L)A}\\
&= \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left[(D^{(C)>}-D^{(C)<})\Sigma^{(L)<} - D^{(C)<}(\Sigma^{(L)>}-\Sigma^{(L)<})\right] && (3.191)\\
&= \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left[D^{(C)>}\Sigma^{(L)<} - D^{(C)<}\Sigma^{(L)>}\right] && (3.192)
\end{aligned}
$$

A similar treatment for $J_{\text{thermal}}^{R\to C}$ gives

$$
J_{\text{thermal}}^{R\to C} = \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left[D^{(C)>}\Sigma^{(R)<} - D^{(C)<}\Sigma^{(R)>}\right] \qquad (3.193)
$$

At steady state, $J_{\text{thermal}} = J_{\text{thermal}}^{L\to C} = -J_{\text{thermal}}^{R\to C}$, thus we now (left-right) symmetrise the current expression as

$$
\begin{aligned}
J_{\text{thermal}} &= \frac{1}{2}\left(J_{\text{thermal}}^{L\to C} + J_{\text{thermal}}^{L\to C}\right) && (3.194)\\
&= \frac{1}{2}\left(J_{\text{thermal}}^{L\to C} - J_{\text{thermal}}^{R\to C}\right) && (3.195)\\
&= \frac{1}{4}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left[D^{(C)>}(\Sigma^{(L)<}-\Sigma^{(R)<}) - D^{(C)<}(\Sigma^{(L)>}-\Sigma^{(R)>})\right] && (3.196)
\end{aligned}
$$

Now we make a small digression to introduce some identities and after that we can write the current into the more usual form found in the literature.

Define the level width function (level means state, width means the inverse lifetime which is essentially the imaginary part of the self energy)

$$
\begin{aligned}
\Gamma^{(L)}(\omega) &= i\left(\Sigma^{(L)R}-\Sigma^{(L)A}\right) = i\left(\Sigma^{(L)>}-\Sigma^{(L)<}\right) && (3.197)\\
\Gamma^{(R)}(\omega) &= i\left(\Sigma^{(R)R}-\Sigma^{(R)A}\right) = i\left(\Sigma^{(R)>}-\Sigma^{(R)<}\right) && (3.198)
\end{aligned}
$$

Since the leads are in equilibrium, we can use the equilibrium relations, for phonons (bosons) we have the general equilibrium relation,

$$
D^{<}(\omega) = N^{eq}(\omega)\left(D^{R}(\omega)-D^{A}(\omega)\right) = N^{eq}(\omega)\left(D^{>}(\omega)-D^{<}(\omega)\right) \qquad (3.199)
$$

where $N^{eq}(\omega) = \frac{1}{e^{\beta\hbar\omega}-1}$, thus we get [27]

$$D^<(\omega) = \frac{N^{eq}(\omega)}{1+N^{eq}(\omega)} D^>(\omega) \tag{3.202}$$

and for the width function,

$$\begin{aligned}
\Gamma^{(L)}(\omega) &= i\left(\Sigma^{(L)>} - \frac{N^{eq(L)}}{1+N^{eq(L)}}\Sigma^{(L)>}\right) = i\frac{1}{1+N^{eq(L)}}\Sigma^{(L)>} && (3.203)\\
\therefore \Sigma^{(L)>} &= -i\left(1+N^{eq(L)}\right)\Gamma^{(L)}(\omega) && (3.204)\\
\text{and, } \Sigma^{(L)<} &= \frac{N^{eq(L)}}{1+N^{eq(L)}}\Sigma^{(L)>} = -iN^{eq(L)}\Gamma^{(L)} && (3.205)\\
\text{similarly, } \Sigma^{(R)>} &= -i\left(1+N^{eq(R)}\right)\Gamma^{(R)} && (3.206)\\
\Sigma^{(R)<} &= -iN^{eq(R)}\Gamma^{(R)} && (3.207)
\end{aligned}$$

Now the current expression can be written as

$$\begin{aligned}
J_{\text{thermal}} &= \frac{1}{4}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega \mathrm{Tr}\left[\left(D^{(C)R} - D^{(C)A} + D^{(C)<}\right)\left(-iN^{eq(L)}\Gamma^{(L)} + iN^{eq(R)}\Gamma^{(R)}\right)\right.\\
&\quad \left. -D^{(C)<}\left(-i(1+N^{eq(L)})\Gamma^{(L)} + i(1+N^{eq(R)})\Gamma^{(R)}\right)\right]\\
&\quad | \ \text{where we have substituted } D^{(C)>} = D^{(C)R} - D^{(C)A} + D^{(C)<}\\
&= \frac{1}{4}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega \mathrm{Tr}\left[-i\left(D^{(C)R} - D^{(C)A}\right)\left(N^{eq(L)}\Gamma^{(L)} - N^{eq(R)}\Gamma^{(R)}\right)\right.\\
&\quad -iD^{(C)<}\left(N^{eq(L)}\Gamma^{(L)} - N^{eq(R)}\Gamma^{(R)}\right) - iD^{(C)<}(\Gamma^{(R)} - \Gamma^{(L)})\\
&\quad \left. +iD^{(C)<}\left(N^{eq(L)}\Gamma^{(L)} - N^{eq(R)}\Gamma^{(R)}\right)\right]\\
&= \frac{1}{4}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega \mathrm{Tr}\left[iD^{(C)<}(\Gamma^{(L)} - \Gamma^{(R)}) - i(D^{(C)R} - D^{(C)A})(N^{eq(L)}\Gamma^{(L)} - N^{eq(R)}\Gamma^{(R)})\right]\\
&= \frac{i}{4}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega \mathrm{Tr}\left[D^{(C)<}(\Gamma^{(L)} - \Gamma^{(R)}) - (D^{(C)R} - D^{(C)A})(N^{eq(L)}\Gamma^{(L)} - N^{eq(R)}\Gamma^{(R)})\right]
\end{aligned}$$

$$\boxed{J_{\text{thermal}} = \frac{i}{4}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega \mathrm{Tr}\left[D^{(C)<}(\Gamma^{(L)} - \Gamma^{(R)}) - (D^{(C)R} - D^{(C)A})(N^{eq(L)}\Gamma^{(L)} - N^{eq(R)}\Gamma^{(R)})\right]} \tag{3.208}$$

The last expression is the final expression of the steady state current with an interacting central region. Note that there is a sign difference when we compare this expression with the electron version. This is due to the difference in expression in the equilibrium relations.

[27] For electrons,

$$\begin{aligned}
f^{eq}(\omega) &= \frac{1}{e^{\beta(\hbar\omega-\mu)}+1} \quad \text{where } \mu \text{ is the chemical potential} && (3.200)\\
G^<(\omega) &= -\frac{f^{eq}}{1-f^{eq}}G^>(\omega) && (3.201)
\end{aligned}$$

3.2.1.1.1 Current Conservation Sum Rule

Recall the equation

$$J^L_{\text{thermal}} = -\frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\text{Tr}\left(D^{(C)>}\Sigma^{(L)<} - D^{(C)<}\Sigma^{(L)>}\right) \tag{3.209}$$

where we can interprete the first term in the trace as tunnelling out from the left and the second term as tunnelling into the left.

Define the total self energy (in the non-crossing approximation [28]),

$$\Sigma^{(\text{total})} \equiv \Sigma^{(C)} + \Sigma^{(L)} + \Sigma^{(R)} \tag{3.210}$$

The current conservation statement is

$$J^L_{\text{thermal}} + J^R_{\text{thermal}} = 0 \tag{3.211}$$

which we will turn it into a sum rule involving the self energy of the central region, Σ^C.

First, rewrite the earlier identity,

$$\begin{aligned} D^{(C)R-1} - D^{(C)A-1} &= \Sigma^{(\text{total})A} - \Sigma^{(\text{total})R} && (3.212)\\ &\mid \text{ use } \Sigma^R - \Sigma^A = \Sigma^> - \Sigma^< \\ &= \Sigma^{(\text{total})<} - \Sigma^{(\text{total})>} && (3.213)\end{aligned}$$

We derive another identity by considering this expression.

$$\begin{aligned} & \text{Tr}\left(\Sigma^{(\text{total})<}D^{(C)>} - \Sigma^{(\text{total})>}D^{(C)<}\right)\\ \mid\ & \text{use Keldysh equations, } D^{(C)>} = D^{(C)R}\Sigma^{(\text{total})>}D^{(C)A} \text{ and } D^{(C)<} = D^{(C)R}\Sigma^{(\text{total})<}D^{(C)A}\\ =\ & \text{Tr}\left(\Sigma^{(\text{total})<}D^{(C)R}\Sigma^{(\text{total})>}D^{(C)A} - \Sigma^{(\text{total})>}D^{(C)R}\Sigma^{(\text{total})<}D^{(C)A}\right) && (3.214)\\ \mid\ & \text{use the above identity, } \Sigma^{(\text{total})>} = \Sigma^{(\text{total})<} - D^{(C)R-1} + D^{(C)A-1}\\ =\ & \text{Tr}\left(\Sigma^{(\text{total})<}D^{(C)R}\left(\Sigma^{(\text{total})<} - D^{(C)R-1} + D^{(C)A-1}\right)D^{(C)A}\right.\\ & \left. - \left(\Sigma^{(\text{total})<} - D^{(C)R-1} + D^{(C)A-1}\right)D^{(C)R}\Sigma^{(\text{total})<}D^{(C)A}\right) && (3.215)\\ =\ & \text{Tr}\left(\Sigma^{(\text{total})<}D^{(C)R}\Sigma^{(\text{total})<}D^{(C)A} - \Sigma^{(\text{total})<}D^{(C)A} + \Sigma^{(\text{total})<}D^{(C)R}\right.\\ & \left. -\Sigma^{(\text{total})<}D^{(C)R}\Sigma^{(\text{total})<}D^{(C)A} + \Sigma^{(\text{total})<}D^{(C)A} - D^{(C)A-1}D^{(C)R}\Sigma^{(\text{total})<}D^{(C)A}\right) && (3.216)\\ \mid\ & \text{1st cancels 4th, 2nd cancels 5th, 3rd cancels (cyclic traced) 6th}\\ =\ & 0 && (3.217)\end{aligned}$$

And now we are ready to use the current conservation for getting a sum rule.

$$0 = J^L_{\text{thermal}} + J^R_{\text{thermal}} \tag{3.218}$$

[28] Suppose the interacting part of the Hamiltonian is made up of 2 terms, there will be 2 S-matrices to expand in the Green's function. Expanded terms will be factorized according to Wick's theorem. The total self energy can then be identified and generally, the total self energy is not just a sum of the self energies of each interaction. The non-crossing approximation simply means that we assume that the total self energy is a sum of the self energies of each interaction. Physically, such an approximation implies that when a particle undergoes scattering due to one interaction from start to end. All intermediate scatterings are due to the same interaction with no scatterings due to the other interaction. A counter example to this is actually given in this thesis in sections 5.4.2.4, 5.4.2.5 and 5.4.2.6 where intermediate scatterings are due to both 3-phonon and 4-phonon interactions.

$$= -\frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(D^{(C)>}\left(\Sigma^{(L)<}+\Sigma^{(R)<}\right)-D^{(C)<}\left(\Sigma^{(L)>}+\Sigma^{(R)>}\right)\right) \tag{3.219}$$

| use the definition of total self energy, $\Sigma^{(L)\gtrless}+\Sigma^{(R)\gtrless}=\Sigma^{(\mathrm{total})\gtrless}-\Sigma^{(C)\gtrless}$

$$= -\frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(D^{(C)>}\Sigma^{(\mathrm{total})<}-D^{(C)>}\Sigma^{(C)<}-D^{(C)<}\Sigma^{(\mathrm{total})>}+D^{(C)<}\Sigma^{(C)>}\right) \tag{3.220}$$

| use the identity, $\mathrm{Tr}\left(\Sigma^{(\mathrm{total})<}D^{(C)>}-\Sigma^{(\mathrm{total})>}D^{(C)<}\right)=0$

$$= -\frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(D^{(C)<}\Sigma^{(C)>}-D^{(C)>}\Sigma^{(C)<}\right) \tag{3.221}$$

$$= \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(\Sigma^{(C)<}D^{(C)>}-\Sigma^{(C)>}D^{(C)<}\right) \tag{3.222}$$

which is the sum rule that the self energy of the interacting central is required to satisfy in order to fulfill the conservation of current (in this case, it is energy current) at steady state.

3.2.1.2 Current for an Interacting Central with Proportional Coupling

Suppose that the leads are proportional matrices,

$$\Gamma^L = \lambda\Gamma^R \tag{3.223}$$

where λ is a proportionality constant. At steady state, $J^{L\to C}_{\mathrm{thermal}}=-J^{R\to C}_{\mathrm{thermal}}$, so we can symmetrise the total current with different weights.

$$J_{\mathrm{thermal}} = xJ^{L\to C}_{\mathrm{thermal}}-(1-x)J^{R\to C}_{\mathrm{thermal}} \tag{3.224}$$

First we rewrite $J^{L\to C}_{\mathrm{thermal}}$ and $J^{R\to C}_{\mathrm{thermal}}$ into a more suggestive form (following [DiVentra2008]),

$$J^{L\to C}_{\mathrm{thermal}} = \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(D^{(C)>}\Sigma^{(L)<}-D^{(C)<}\Sigma^{(L)>}\right) \tag{3.225}$$

| substitute the identities $\Sigma^{(L)<}=-iN^{eq(L)}\Gamma^{(L)}$ and $\Sigma^{(L)>}=-i(1+N^{eq(L)})\Gamma^{(L)}$

$$= \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(D^{(C)>}\left(-iN^{eq(L)}\Gamma^{(L)}\right)-D^{(C)<}\left(-i(1+N^{eq(L)})\Gamma^{(L)}\right)\right) \tag{3.226}$$

| substitute $D^{(C)>}=D^{(C)R}-D^{(C)A}+D^{(C)<}$

$$= \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(-iN^{eq(L)}\Gamma^{(L)}(D^{(C)R}-D^{(C)A})+iD^{(C)<}\Gamma^{(L)}\right) \tag{3.227}$$

$$= \frac{i}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(\Gamma^{(L)}\left(D^{(C)<}-N^{eq(L)}\left(D^{(C)R}-D^{(C)A}\right)\right)\right) \tag{3.228}$$

Similarly,

$$J^{R\to C}_{\mathrm{thermal}} = \frac{i}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(\Gamma^{(R)}\left(D^{(C)<}-N^{eq(R)}\left(D^{(C)R}-D^{(C)A}\right)\right)\right) \tag{3.229}$$

Now symmetrizing the current using the new weights.

$$\begin{aligned} & J_{\mathrm{thermal}} \\ = \; & xJ^{L\to C}_{\mathrm{thermal}}-(1-x)J^{R\to C}_{\mathrm{thermal}} \qquad (3.230) \\ = \; & \frac{i}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(x\Gamma^{(L)}\left(D^{(C)<}+N^{eq(L)}\left(D^{(C)R}-D^{(C)A}\right)\right)\right.\end{aligned}$$

$$-(1-x)\Gamma^{(R)}\left(D^{(C)<} - N^{eq(R)}\left(D^{(C)R} - D^{(C)A}\right)\right)\right) \quad (3.231)$$

$$= \frac{i}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(\left(x\lambda-(1-x)\right)\Gamma^{(R)}D^{(C)<} + \left(x\Gamma^{(L)}N^{eq(L)} - (1-x)\Gamma^{(R)}N^{eq(R)}\right)\left(D^{(C)A} - D^{(C)R}\right)\right)$$

$|$ choose x such that the first term vanishes, $x\lambda - 1 + x = 0$ so $x = \dfrac{1}{1+\lambda}$

$$= \frac{i}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(\left(\frac{1}{1+\lambda}\Gamma^{(L)}N^{eq(L)} - \left(1-\frac{1}{1+\lambda}\right)\Gamma^{(R)}N^{eq(R)}\right)\left(D^{(C)A} - D^{(C)R}\right)\right) \quad (3.232)$$

$$= \frac{i}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(\left(\frac{1}{1+\lambda}\Gamma^{(L)}N^{eq(L)} - \frac{\lambda}{1+\lambda}\Gamma^{(R)}N^{eq(R)}\right)\left(D^{(C)A} - D^{(C)R}\right)\right) \quad (3.233)$$

$$= \frac{i}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(\frac{\Gamma^{(L)}}{1+\lambda}(N^{eq(L)} - N^{eq(R)})(D^{(C)A} - D^{(C)R})\right) \quad (3.234)$$

$|$ note the identity, $\dfrac{\Gamma^{(L)}\Gamma^{(R)}}{\Gamma^{(L)}+\Gamma^{(R)}} = \dfrac{\Gamma^{(L)}\Gamma^{(R)}}{(\lambda+1)\Gamma^{(R)}} = \dfrac{\Gamma^{(L)}}{\lambda+1}$

$$= \frac{i}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(\frac{\Gamma^{(L)}\Gamma^{(R)}}{\Gamma^{(L)}+\Gamma^{(R)}}(N^{eq(L)} - N^{eq(R)})(D^{(C)A} - D^{(C)R})\right) \quad (3.235)$$

The final expression of steady state current for an interacting central with proportional lead-system coupling is

$$\boxed{J_{\text{thermal}} = \frac{i}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\left(\frac{\Gamma^{(L)}\Gamma^{(R)}}{\Gamma^{(L)}+\Gamma^{(R)}}(N^{eq(L)} - N^{eq(R)})(D^{(C)A} - D^{(C)R})\right)} \quad (3.236)$$

3.2.1.3 Current for a Non-interacting Central (Ballistic Current)

We get the non-interacting case by expanding the full interacting Green's function to zeroth order in interaction

$$D^{(C)}(l\tau l'\tau') = -\frac{i}{\hbar}\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C}(l\tau)u^C_{H^C}(l'\tau')\right)\right\rangle \quad (3.237)$$

$|$ recall $H^C = H^C_0 + H^C_{\text{int}}$ and H^C_{int} exists before the switch on

$|$ go back to Heisenberg operators and rewrite into another set of interaction operators

$|$ so we arrive at the full perturbation expansion in chapter 1

$|$ the whole idea is, this set of interaction operators allow Wick's theorem

$$= -\frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}e^{-\frac{i}{\hbar}\int_{c_K+c_M}d\tau_3 H^C_{\text{int}H^C_0}(\tau_3)}u^C_{H^C_0}(l\tau)u^C_{H^C_0}(l'\tau')\right)\right\rangle \quad (3.238)$$

$|$ where the statistical operator is now quadratic and Wick's theorem is applicable

$|$ expand the 2nd S-matrix to first order

$$\approx -\frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}\left(1-\frac{i}{\hbar}\int_{c_K+c_M}d\tau_3 H^C_{\text{int}H^C_0}(\tau_3)\right)u^C_{H^C_0}(l\tau)u^C_{H^C_0}(l'\tau')\right)\right\rangle$$

$|$ the first term thus represents no interactions (and no c_M)

$$= -\frac{i}{\hbar}\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C_0}(l\tau)u^C_{H^C_0}(l'\tau')\right)\right\rangle$$
$$+\left(\frac{i}{\hbar}\right)^2\int_{c_K+c_M}d\tau_3\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}H^C_{\text{int}H^C_0}(\tau_3)u^C_{H^C_0}(l\tau)u^C_{H^C_0}(l'\tau')\right)\right\rangle \quad (3.239)$$

$$
\begin{aligned}
&\quad | \quad \text{for the non-interacting (or mean field) central, we retain only the first term} \\
&\approx \quad -\frac{i}{\hbar}\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)} u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right)\right\rangle
\end{aligned} \tag{3.240}
$$

The second term is thus the first correction to the ballistic current. This correction term will be calculated in the chapter on anharmonicity.

The Dyson equation is now exact as we only have a 1-point interaction.

$$
D^{(C)}(l\tau l'\tau') = D^{(0)(C)}(l\tau l'\tau') + \int_{c_K} d\tau_1 \int_{c_K} d\tau_2 \sum_{l_1 l_2} D^{(0)(C)}(l\tau l_1\tau_1)\Sigma^{(L)}(l_1\tau_1 l_2\tau_2) D^{(C)}(l_2\tau_2 l'\tau') \tag{3.241}
$$

We expand out the second order term just to illustrate.

$$
\begin{aligned}
& D^{(2)(C)}(l\tau l'\tau') \\
= \;& \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 \int_{c_K} d\tau_1 d\tau_2 \left\langle T_{c_K}\left(\tilde{H}^{LC}(\tau_1)\tilde{H}^{LC}(\tau_2) u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right)\right\rangle && (3.242) \\
| \;& \text{recall that } \tilde{H}^{LC}(\tau_1) = \sum_{l_1 l_2} V^{LC}_{l_1 l_2} u^L_{H_0^L}(l_1\tau_1) u^C_{H_0^C}(l_2\tau_1) \\
= \;& \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 \int_{c_K} d\tau_1 d\tau_2 \\
& \times \left\langle T_{c_K} \sum_{l_1 l_2}\sum_{l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} u^L_{H_0^L}(l_1\tau_1) u^C_{H_0^C}(l_2\tau_1) u^L_{H_0^L}(l_3\tau_2) u^C_{H_0^C}(l_4\tau_2) u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right\rangle && (3.243) \\
= \;& \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 \int_{c_K} d\tau_1 d\tau_2 \sum_{l_1 l_2}\sum_{l_3 l_4} \\
& \times V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \left\langle T_{c_K}\left(u^L_{H_0^L}(l_1\tau_1) u^L_{H_0^L}(l_3\tau_2)\right)\right\rangle \left\langle T_{c_K}\left(u^C_{H_0^C}(l_2\tau_1) u^C_{H_0^C}(l_4\tau_2) u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right)\right\rangle \\
| \;& \text{the connected pairings for the } u^C \text{ terms are } \langle\tau\tau_1\rangle\langle\tau_2\tau'\rangle \text{ and } \langle\tau\tau_2\rangle\langle\tau_1\tau'\rangle \\
| \;& \text{the first pair gives (symbolically), } V^{LC}V^{LC}\langle T_{c_K}(u^L u^L)\rangle = V^{LC}V^{LC}(i\hbar D^{(0)(L)}) = i\hbar\Sigma^L \\
| \;& \text{the second pair gives, } 2\times(i\hbar)^2 D^{(0)(C)}(l\tau l_1\tau_1) D^{(0)(C)}(l_2\tau_2 l'\tau') \\
= \;& i\hbar \int_{c_K} d\tau_1 d\tau_2 \sum_{l_1 l_2} D^{(0)(C)}(l\tau l_1\tau_1)\Sigma^{(L)}(l_1\tau_1 l_2\tau_2) D^{(0)(C)}(l_2\tau_2 l'\tau') && (3.244)
\end{aligned}
$$

Thus the pattern is clear and summing all orders we get the Dyson's equation exactly. Now we include an independent right lead. With 2 independent leads, the Dyson's equation is,

$$
\begin{aligned}
D^{(C)}(l\tau l'\tau') \;=\;& D^{(0)(C)}(l\tau l'\tau') \\
& + \int_{c_K} d\tau_1 \int_{c_K} d\tau_2 \sum_{l_1 l_2} D^{(0)(C)}(l\tau l_1\tau_1)\left(\Sigma^{(L)}(l_1\tau_1 l_2\tau_2) + \Sigma^{(R)}(l_1\tau_1 l_2\tau_2)\right) D^{(C)}(l_2\tau_2 l'\tau')
\end{aligned} \tag{3.245}
$$

Now the aim is to insert the expression into the full interacting formula for current and we will be able to obtain the often-seen expression for current. We will need some identities. (from Datta in [Datta1997]) First is a rewriting of Keldysh equation (in frequency domain). Note that $D^{(0)}$ describes the non-interacting system so we have,

$$
D^{(C)<}(\omega) \;=\; D^{(C)R}\Sigma^< D^{(C)A} \tag{3.246}
$$

$$= D^{(C)R}\left(\Sigma^{(L)<} + \Sigma^{(R)<}\right) D^{(C)A} \tag{3.247}$$

$|$ use the identities, $\Sigma^{(L)<} = -iN^{eq(L)}\Gamma^{(L)}$ and $\Sigma^{(R)<} = -iN^{eq(R)}\Gamma^{(R)}$

$$= -iN^{eq(L)}D^{(C)R}(\omega)\Gamma^{(L)}(\omega)D^{(C)A}(\omega) - iN^{eq(R)}(\omega)D^{(C)R}(\omega)\Gamma^{(R)}(\omega)D^{(C)A}(\omega) \tag{3.248}$$

We still require 2 more identities ([Datta1997] eqn (3.6.4)).

Identity (a)

$$D^{(C)A} - D^{(C)R} = iD^{(C)R}\left(\Gamma^{(L)} + \Gamma^{(R)}\right) D^{(C)A} \tag{3.249}$$

Identity (b)

$$D^{(C)A} - D^{(C)R} = iD^{(C)A}\left(\Gamma^{(L)} + \Gamma^{(R)}\right) D^{(C)R} \tag{3.250}$$

[Proof of Identities (a) and (b)]

From Dyson's equation $$D^{(C)R} = D^{(0)R} + D^{(0)R}\Sigma^R D^R \tag{3.251}$$

$|$ then $\times D^{(C)R-1}$ and $\times D^{(0)R-1}$

$$D^{(0)-1} = D^{(C)A-1} + \Sigma^R \tag{3.252}$$

Similarly, $$D^{(0)A-1} = D^{(C)A-1} + \Sigma^A \tag{3.253}$$

Subtract them

$$D^{(C)R-1} - D^{(C)A-1} = \Sigma^A - \Sigma^R + D^{(0)R-1} - D^{(0)A-1} \tag{3.254}$$

$|$ last 2 terms on RHS cancel out because they are actually the same

$|$ recall $\Sigma^R = \Sigma^{(L)R} + \Sigma^{(R)R}$

$$= \Sigma^{(L)A} - \Sigma^{(R)A} - \Sigma^{(L)R} + \Sigma^{(R)R} \tag{3.255}$$

$$= i\Gamma^{(L)} + i\Gamma^{(R)} \tag{3.256}$$

$|$ $\times D^{(C)R}$ and $\times D^{(C)A}$, we get identity (a)

$$D^{(C)A} - D^{(C)R} = iD^{(C)R}\left(\Gamma^{(L)} + \Gamma^{(R)}\right) D^{(C)A} \tag{3.257}$$

$|$ $\times D^{(C)A}$ and $\times D^{(C)R}$, we get identity (b)

$$D^{(C)A} - D^{(C)R} = iD^{(C)A}\left(\Gamma^{(L)} + \Gamma^{(R)}\right) D^{(C)R} \tag{3.258}$$

Now we can substitute these 3 identities into the full interacting current equation (3.208).

$$J_{\text{thermal}} = \frac{i}{4}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\text{Tr}\left(D^{(C)<}\left(\Gamma^{(L)} - \Gamma^{(R)}\right) - \left(D^{(C)R} - D^{(C)A}\right)\left(N^{eq(L)}\Gamma^{(L)} - N^{eq(R)}\Gamma^{(R)}\right)\right)$$

$|$ use $D^{(C)<}(\omega)$ from Keldysh equation rewritten earlier

$$= \frac{i}{4}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\text{Tr}\left(i\left(N^{eq(L)}D^{(C)R}\Gamma^{(L)}D^{(C)A} + N^{eq(R)}D^{(C)R}\Gamma^{(R)}D^{(C)A}\right)\left(\Gamma^{(R)} - \Gamma^{(L)}\right)\right.$$
$$\left. - \left(D^{(C)R} - D^{(C)A}\right)\left(N^{eq(L)}\Gamma^{(L)} - N^{eq(R)}\Gamma^{(R)}\right)\right) \tag{3.259}$$

$|$ use identity (a) $D^{(C)R} - D^{(C)A} = -iD^{(C)R}\left(\Gamma^{(L)} + \Gamma^{(R)}\right) D^{(C)A}$

$$\begin{aligned}
&= -\frac{1}{4}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\mathrm{Tr}\Big(N^{eq(L)}D^{(C)R}\Gamma^{(L)}D^{(C)A}\Gamma^{(L)} - N^{eq(L)}D^{(C)R}\Gamma^{(L)}D^{(C)A}\Gamma^{(R)} \\
&\quad +N^{eq(R)}D^{(C)R}\Gamma^{(R)}D^{(C)A}\Gamma^{(L)} - N^{eq(R)}D^{(C)R}\Gamma^{(R)}D^{(C)A}\Gamma^{(R)} - D^{(C)R}\Gamma^{(L)}D^{(C)A}N^{eq(L)}\Gamma^{(L)} \\
&\quad +D^{(C)R}\Gamma^{(L)}D^{(C)A}N^{eq(R)}\Gamma^{(R)} - D^{(C)R}\Gamma^{(R)}D^{(C)A}N^{eq(L)}\Gamma^{(L)} + D^{(C)R}\Gamma^{(R)}D^{(C)A}N^{eq(R)}\Gamma^{(R)}\Big) \\
&\mid \text{ inside the brackets, 1st cancels 5th, 4th cancels 8th} \\
&= \frac{1}{4}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\left(N^{eq(L)} - N^{eq(R)}\right)\mathrm{Tr}\left(D^{(C)R}\Gamma^{(L)}D^{(C)A}\Gamma^{(R)} + D^{(C)R}\Gamma^{(R)}D^{(C)A}\Gamma^{(L)}\right) \qquad (3.260) \\
&\mid \text{ from identities (a) and (b), we get, } D^{(C)R}(\Gamma^{(L)}+\Gamma^{(R)})D^{(C)A} = D^{(C)A}(\Gamma^{(L)}+\Gamma^{(R)})D^{(C)R} \\
&\mid \text{ then } \times\Gamma^{(R)} \text{ and trace over both sides to get,} \\
&\mid \ \mathrm{Tr}(D^{(C)R}\Gamma^{(L)}D^{(C)A}\Gamma^{(R)}) + \mathrm{Tr}(D^{(C)R}\Gamma^{(R)}D^{(C)A}\Gamma^{(R)}) \\
&\mid \ = \mathrm{Tr}(D^{(C)A}\Gamma^{(L)}D^{(C)R}\Gamma^{(R)}) + \mathrm{Tr}(D^{(C)A}\Gamma^{(R)}D^{(C)R}\Gamma^{(R)}) \\
&\mid \text{ 2 terms to cancel to give, } \mathrm{Tr}(D^{(C)R}\Gamma^{L}D^{(C)A}\Gamma^{(R)}) = \mathrm{Tr}(D^{(C)A}\Gamma^{(L)}D^{(C)R}\Gamma^{(R)}) \\
&= \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\left(N^{eq(L)} - N^{eq(R)}\right)\mathrm{Tr}\left(D^{(C)R}\Gamma^{(L)}D^{(C)A}\Gamma^{(R)}\right) \qquad (3.261)
\end{aligned}$$

$$\boxed{J_{\text{thermal}} = \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hbar\omega\left(N^{eq(L)} - N^{eq(R)}\right)\mathrm{Tr}\left(D^{(C)R}\Gamma^{(L)}D^{(C)A}\Gamma^{(R)}\right)} \qquad (3.262)$$

which is the commonly seen Landauer formula for ballistic (non-interacting central) transport.

3.2.2 Noise associated with Energy Current (for a noninteracting central)*

We follow [Haug2007] section 13.8. We attempt to calculate by brute force [29] the DC ($\omega = 0$) noise of thermal current in a noninteracting central device connected to 2 thermal leads. By going through the calculation, we can see how interaction (eg anharmonicity) could enter the noise calculation and how we could possibly generalize the calculation to AC noise. We use the same Hamiltonian as that in the Landauer theory in the previous section. We will treat left (L) and central (C) first and add in the right (R) towards the end. This can be done due to the assumption that that leads are independent. So we have exactly the same expression as in the previous section,

$$\begin{aligned}
H &= H_0^L + H^C + H^{LC}\theta(t-t_0) \qquad (3.263) \\
H^C &= H_0^C + H_{\text{int}}^C \qquad (3.264)
\end{aligned}$$

where the step function is written to indicate the term being "switched on". We partition the Hamiltonian in exactly the same way as in the previous section.

$$\begin{aligned}
H_0 &= H_0^L + H^C \quad \text{(not quadratic in central variables)} \qquad (3.265) \\
H_{\text{int}} &= 0 \quad (\text{no } c_M \text{ contour}) \qquad (3.266) \\
V(t)\theta(t-t_0) &= H^{LC}\theta(t-t_0) \qquad (3.267)
\end{aligned}$$

Essentially, just as in the Landauer calculation, we give up Wick's theorem in the central variables, in favour of dropping the c_M contour. We simply define the thermal current operator based on the current

[29] i.e. We do not calculate via a generating functional.

expression.

$$\text{(current expression)} \quad J^{L\to C}_{\text{thermal}}(t) \equiv J^{LC}(t) = \sum_{l_1 l_2}^{\text{interface}} V^{LC}_{l_1 l_2} \left\langle \frac{du^L_{Hl_1}(t)}{dt} u^C_{Hl_2}(t) \right\rangle \tag{3.268}$$

$$\text{(current operator)} \quad \hat{J}^{LC}(t) = \sum_{l_1 l_2}^{\text{interface}} V^{LC}_{l_1 l_2} \frac{du^L_{Hl_1}(t)}{dt} u^C_{Hl_2}(t) \tag{3.269}$$

Define the current fluctuation operator

$$\delta\hat{J}^{LC} \equiv \hat{J}^{LC} - J^{LC} \tag{3.270}$$

Define the noise spectrum correlation function (which is the quantity to evaluate),

$$\begin{aligned}
S(t,t') &\equiv \frac{1}{2}\left\langle \left[\delta\hat{J}^{LC}(t), \delta\hat{J}^{LC}(t')\right]_+ \right\rangle && (3.271)\\
&\quad | \quad \text{the symmetrization ensures that we get a Hermitian operator to represent an observable}\\
&= \frac{1}{2}\left\langle \hat{J}^{LC}(t)\hat{J}^{LC}(t')\right\rangle + \frac{1}{2}\left\langle \hat{J}^{LC}(t')\hat{J}^{LC}(t)\right\rangle - (J^{LC})^2 && (3.272)\\
&\quad | \quad \text{the first expression needs } t \text{ on the left of } t'\\
&\quad | \quad \text{the second expression needs } t' \text{ on the left of } t\\
&= \frac{1}{2}\sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4}\left[\left\langle \frac{du^L_{Hl_1}(t)}{dt} u^C_{Hl_2}(t) \frac{du^L_{Hl_3}(t')}{dt'} u^C_{Hl_4}(t')\right\rangle + (t' \leftrightarrow t)\right] - (J^{LC})^2 && (3.273)\\
&= \frac{1}{2}\sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \lim_{t_1\to t}\lim_{t_1'\to t'}\\
&\quad \times \frac{d}{dt_1}\frac{d}{dt_1'}\left[\left\langle u^L_{Hl_1}(t_1)u^C_{Hl_2}(t)u^L_{Hl_3}(t_1')u^C_{Hl_4}(t')\right\rangle + \left\langle u^L_{Hl_1}(t_1')u^C_{Hl_2}(t')u^L_{Hl_3}(t_1)u^C_{Hl_4}(t)\right\rangle\right] - (J^{LC})^2\\
&\quad | \quad \text{define 2-particle Green's functions (with no names for them)}\\
&\quad | \quad \frac{(-i)^2}{\hbar}\left\langle u^L_{Hl_1}(t_1)u^C_{Hl_2}(t)u^L_{Hl_3}(t_1')u^C_{Hl_4}(t')\right\rangle \equiv D_{l_1 l_2 l_3 l_4}(t_1 t t_1' t'; t_1 > t > t_1' > t')\\
&\quad | \quad \frac{(-i)^2}{\hbar}\left\langle u^L_{Hl_1}(t_1')u^C_{Hl_2}(t')u^L_{Hl_3}(t_1)u^C_{Hl_4}(t)\right\rangle \equiv D_{l_1 l_2 l_3 l_4}(t_1 t t_1' t'; t_1' > t' > t_1 > t)\\
&= \frac{-\hbar}{2}\sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \lim_{t_1\to t}\lim_{t_1'\to t'}\\
&\quad \times \frac{d}{dt_1}\frac{d}{dt_1'}\left[D_{l_1 l_2 l_3 l_4}(t_1 t t_1' t'; t_1 > t > t_1' > t') + D_{l_1 l_2 l_3 l_4}(t_1 t t_1' t'; t_1' > t' > t_1 > t)\right] - (J^{LC})^2\\
&&& (3.274)
\end{aligned}$$

Thus the evaluation of noise, is reduced to the evaluation of two 2-particle Green's functions. To carry out perturbation expansion, we need to work with the contour ordered 2-particle Green's function. We define it as

$$D_{l_1 l_2 l_3 l_4}(\tau_1 \tau \tau_1' \tau') \equiv \frac{(-i)^2}{\hbar}\left\langle T_{c_K}\left(u^L_{Hl_1}(\tau_1)u^C_{Hl_2}(\tau)u^L_{Hl_3}(\tau_1')u^C_{Hl_4}(\tau')\right)\right\rangle \tag{3.275}$$

We use the S-matrix expansion to seperate the hybrid Green's function. [30]

$$
\begin{aligned}
& D_{l_1l_2l_3l_4}(\tau_1\tau\tau_1'\tau') \\
= \quad & \frac{(-i)^2}{\hbar}\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^L_{H_0^Ll_1}(\tau_1)u^C_{H^Cl_2}(\tau)u^L_{H_0^Ll_3}(\tau_1')u^C_{H^Cl_4}(\tau')\right)\right\rangle \qquad (3.276)\\
| \quad & \text{recall that } \tilde{H}^{LC}(\tau)=\sum_{l_1l_2}V^{LC}_{l_1l_2}u^L_{H_0^Ll_1}(\tau)u^C_{H^Cl_2}(\tau)\\
| \quad & \text{expand the exponential term to second order}\\
= \quad & \frac{(-i)^2}{\hbar}\left\langle T_{c_K}\left(\left(1-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)+\frac{1}{2}\left(-\frac{i}{\hbar}\right)^2\int_{c_K}d\tau_2d\tau_3\tilde{H}^{LC}(\tau_2)\tilde{H}^{LC}(\tau_3)+\cdots\right)\right.\right.\\
& \left.\left.\times u^L_{H_0^Ll_1}(\tau_1)u^C_{H^Cl_2}(\tau)u^L_{H_0^Ll_3}(\tau_1')u^C_{H^Cl_4}(\tau')\right)\right\rangle \qquad (3.277)\\
| \quad & \text{the first order has an odd number of } u^C \text{ and } u^L \text{ which averages to zero (in “interaction” picture)}\\
= \quad & \frac{(-i)^2}{\hbar}\left\langle T_{c_K}\left(u^L_{H_0^Ll_1}(\tau_1)u^C_{H^Cl_2}(\tau)u^L_{H_0^Ll_3}(\tau_1')u^C_{H^Cl_4}(\tau')\right)\right\rangle\\
& +\frac{(-i)^2}{\hbar}\left(-\frac{i}{\hbar}\right)^2\frac{1}{2}\int_{c_K}d\tau_2d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}\\
& \times\left\langle T_{c_K}\left(u^L_{H_0^Ll_5}(\tau_2)u^C_{H^Cl_6}(\tau_2)u^L_{H_0^Ll_7}(\tau_3)u^C_{H^Cl_8}(\tau_3)u^L_{H_0^Ll_1}(\tau_1)u^C_{H^Cl_2}(\tau)u^L_{H_0^Ll_3}(\tau_1')u^C_{H^Cl_4}(\tau')\right)\right\rangle\\
& +\cdots \qquad (3.278)\\
| \quad & \text{use Wick's theorem only on } u^L_{H_0^L}\\
= \quad & \frac{(-i)^2}{\hbar}\left\langle T_{c_K}\left(u^L_{H_0^Ll_1}(\tau_1)u^L_{H_0^Ll_3}(\tau_1')\right)\right\rangle\left\langle T_{c_K}\left(u^C_{H^Cl_2}(\tau)u^C_{H^Cl_4}(\tau')\right)\right\rangle\\
& +\frac{(-i)^2}{\hbar}\left(-\frac{i}{\hbar}\right)^2\frac{1}{2}\int_{c_K}d\tau_2d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}\\
& \times\left\langle T_{c_K}\left(u^L_{H_0^Ll_5}(\tau_2)u^L_{H_0^Ll_7}(\tau_3)u^L_{H_0^Ll_1}(\tau_1)u^L_{H_0^Ll_3}(\tau_1')\right)\right\rangle\left\langle T_{c_K}\left(u^C_{H^Cl_6}(\tau_2)u^C_{H^Cl_8}(\tau_3)u^C_{H^Cl_2}(\tau)u^C_{H^Cl_4}(\tau')\right)\right\rangle\\
& +\cdots \qquad (3.279)\\
| \quad & \text{use Wick's theorem on } \langle T_{c_K}(u^Lu^Lu^Lu^L)\rangle \text{ to get 3 terms}\\
| \quad & \text{one of the terms pairs up with the lst line}\\
= \quad & \frac{(-i)^2}{\hbar}\left\langle T_{c_K}\left(u^L_{H_0^Ll_1}(\tau_1)u^L_{H_0^Ll_3}(\tau_1')\right)\right\rangle\left(\left\langle T_{c_K}\left(u^C_{H^Cl_2}(\tau)u^C_{H^Cl_4}(\tau')\right)\right\rangle+\frac{1}{2}\left(-\frac{i}{\hbar}\right)^2\int_{c_K}d\tau_2d\tau_3\right.\\
& \times\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}\left\langle T_{c_K}\left(u^L_{H_0^Ll_5}(\tau_2)u^L_{H_0^Ll_7}(\tau_3)\right)\right\rangle\left\langle T_{c_K}\left(u^C_{H^Cl_6}(\tau_2)u^C_{H^Cl_8}(\tau_3)u^C_{H^Cl_2}(\tau)u^C_{H^Cl_4}(\tau')\right)\right\rangle\\
& \left.+\cdots\right)\\
& +\frac{(-i)^2}{\hbar}\frac{1}{2}\left(-\frac{i}{\hbar}\right)^2\int_{c_K}d\tau_2d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}\left\langle T_{c_K}\left(u^C_{H^Cl_6}(\tau_2)u^C_{H^Cl_8}(\tau_3)u^C_{H^Cl_2}(\tau)u^C_{H^Cl_4}(\tau')\right)\right\rangle\\
& \times\left(\quad\left\langle T_{c_K}\left(u^L_{H_0^Ll_5}(\tau_2)u^L_{H_0^Ll_1}(\tau_1)\right)\right\rangle\left\langle T_{c_K}\left(u^L_{H_0^Ll_7}(\tau_3)u^L_{H_0^Ll_3}(\tau_1')\right)\right\rangle\right.
\end{aligned}
$$

[30] The equation of motion seems to work here as well since Wick's theorem applies to the left variables (due to the very important assumption that the leads are noninteracting).

$$+\left\langle T_{c_K}\left(u^L_{H^L_0 l_5}(\tau_2)u^L_{H^L_0 l_3}(\tau_1')\right)\right\rangle\left\langle T_{c_K}\left(u^L_{H^L_0 l_7}(\tau_3)u^L_{H^L_0 l_1}(\tau_1)\right)\right\rangle\quad\Bigg)+\cdots \tag{3.280}$$

| the first term reconstructs to the S-matrix, recall that odd powers of $\tilde{H}^{LC}$ are zero

| the second term also reconstructs to the S-matrix where above is the zeroth order term

| (the $\frac{1}{2}$ vanishes since the 2 terms add up after renaming indices

$$\begin{aligned}
=\;& \frac{(-i)^2}{\hbar}\left\langle T_{c_K}\left(u^L_{H^L_0 l_1}(\tau_1)u^L_{H^L_0 l_3}(\tau_1')\right)\right\rangle\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C l_2}(\tau)u^C_{H^C l_4}(\tau')\right)\right\rangle \\
&+\frac{(-i)^2}{\hbar}\left(-\frac{i}{\hbar}\right)^2\int_{c_K}d\tau_2 d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}\left\langle T_{c_K}\left(u^L_{H^L_0 l_5}(\tau_2)u^L_{H^L_0 l_1}(\tau_1)\right)\right\rangle \\
&\times\left\langle T_{c_K}\left(u^L_{H^L_0 l_7}(\tau_3)u^L_{H^L_0 l_3}(\tau_1')\right)\right\rangle\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C l_6}(\tau_2)u^C_{H^C l_8}(\tau_3)u^C_{H^C l_2}(\tau)u^C_{H^C l_4}(\tau')\right)\right\rangle
\end{aligned}\tag{3.281}$$

Therefore the hybrid 2-particle Green's function is made of 2 terms exactly.

However we cannot proceed further without approximations. For the first term, we take the same level of approximation as in the calculation of ballistic current, i.e.

$$\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C l_2}(\tau)u^C_{H^C l_4}(\tau')\right)\right\rangle\approx\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C_0 l_2}(\tau)u^C_{H^C_0 l_4}(\tau')\right)\right\rangle \tag{3.282}$$

Now we will approximate the 2-particle (central) Green's function in the second term by expanding and truncating at the level without vertex corrections and without interactions. Eventually, we will get the ballistic/mean field noise formula, and in the chapter on anharmonicity we will retain the first vertex correction terms to calculate the correction to (ballistic) noise due to phonon-phonon interaction.

$$\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C l_6}(\tau_2)u^C_{H^C l_8}(\tau_3)u^C_{H^C l_2}(\tau)u^C_{H^C l_4}(\tau')\right)\right\rangle$$

| recall $H^C=H^C_0+H^C_{\text{int}}$ and H^C_{int} exists before the switch on

| go back to Heisenberg operators and rewrite into another set of interaction operators

| so we arrive at the full perturbation expansion eqn (3.22)

| the whole idea is, this set of interaction operators allow Wick's theorem

$$=\;\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}e^{-\frac{i}{\hbar}\int_{c_K+c_M}d\tau'''H^C_{\text{int}H^C_0}(\tau''')}u^C_{H^C_0 l_6}(\tau_2)u^C_{H^C_0 l_8}(\tau_3)u^C_{H^C_0 l_2}(\tau)u^C_{H^C_0 l_4}(\tau')\right)\right\rangle$$

| expand the 2nd S-matrix to first order

$$\begin{aligned}
\approx\;&\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}\left(1-\frac{i}{\hbar}\int_{c_K+c_M}d\tau'''H^C_{\text{int}H^C_0}(\tau''')\right)\right.\right. \\
&\left.\left.\times\; u^C_{H^C_0 l_6}(\tau_2)u^C_{H^C_0 l_8}(\tau_3)u^C_{H^C_0 l_2}(\tau)u^C_{H^C_0 l_4}(\tau')\quad\right)\right\rangle
\end{aligned}\tag{3.283}$$

| the first term thus represents no interactions (and no c_M)

$$\begin{aligned}
=\;&\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C_0 l_6}(\tau_2)u^C_{H^C_0 l_8}(\tau_3)u^C_{H^C_0 l_2}(\tau)u^C_{H^C_0 l_4}(\tau')\right)\right\rangle \\
&-\frac{i}{\hbar}\int_{c_K+c_M}d\tau'''\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^C_{\text{int}H^C_0}(\tau''')u^C_{H^C_0 l_6}(\tau_2)u^C_{H^C_0 l_8}(\tau_3)u^C_{H^C_0 l_2}(\tau)u^C_{H^C_0 l_4}(\tau')\right)\right\rangle
\end{aligned}$$

| the second term is the first correction term due to interactions

| and will be calculated in the chapter on anharmonicity, here we retain only the first term here

$$\approx\;\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C_0 l_6}(\tau_2)u^C_{H^C_0 l_8}(\tau_3)u^C_{H^C_0 l_2}(\tau)u^C_{H^C_0 l_4}(\tau')\right)\right\rangle \tag{3.284}$$

$$
\begin{aligned}
& | \quad \text{since the } S\text{-matrix is a 1-point interaction Wick's theorem applies}^{31} \\
= & \left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau'' \tilde{H}^{LC}(\tau'')} u^C_{H_0^C l_6}(\tau_2) u^C_{H_0^C l_8}(\tau_3)\right)\right\rangle \left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau'' \tilde{H}^{LC}(\tau'')} u^C_{H_0^C l_2}(\tau) u^C_{H_0^C l_4}(\tau')\right)\right\rangle \\
& + \left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau'' \tilde{H}^{LC}(\tau'')} u^C_{H_0^C l_6}(\tau_2) u^C_{H_0^C l_2}(\tau)\right)\right\rangle \left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau'' \tilde{H}^{LC}(\tau'')} u^C_{H_0^C l_8}(\tau_3) u^C_{H_0^C l_4}(\tau')\right)\right\rangle \\
& + \left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau'' \tilde{H}^{LC}(\tau'')} u^C_{H_0^C l_6}(\tau_2) u^C_{H_0^C l_4}(\tau')\right)\right\rangle \left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau'' \tilde{H}^{LC}(\tau'')} u^C_{H_0^C l_8}(\tau_3) u^C_{H_0^C l_2}(\tau)\right)\right\rangle
\end{aligned} \tag{3.285}
$$

Define the (contour-ordered) Green's functions

$$
D^{(0)(L)}_{l_1 l_3}(\tau_1 \tau_1') \equiv -\frac{i}{\hbar}\left\langle T_{c_K}\left(u^L_{H_0^L l_1}(\tau_1) u^L_{H_0^L l_3}(\tau_1')\right)\right\rangle \tag{3.286}
$$

$$
D^{(C)}_{l_6 l_8}(\tau \tau_8) \equiv -\frac{i}{\hbar}\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau'' \tilde{H}^{LC}(\tau'')} u^C_{H_0^C l_6}(\tau) u^C_{H_0^C l_8}(\tau_3)\right)\right\rangle \tag{3.287}
$$

In this approximation, the hybrid 2-particle Green's function is

$$
\begin{aligned}
\frac{1}{\hbar} D_{l_1 l_2 l_3 l_4}(\tau_1 \tau \tau_1' \tau') = & D^{(0)(L)}_{l_1 l_3}(\tau_1 \tau_1') D^{(C)}_{l_2 l_4}(\tau \tau') \\
& + \int_{c_K} d\tau_2 d\tau_3 \sum_{l_5 l_6 l_7 l_8} V^{LC}_{l_5 l_6} V^{LC}_{l_7 l_8} D^{(0)(L)}_{l_5 l_1}(\tau_2 \tau_1) D^{(0)(L)}_{l_7 l_3}(\tau_3 \tau_1') \\
& \times \left(D^{(C)}_{l_6 l_8}(\tau_2 \tau_3) D^{(C)}_{l_2 l_4}(\tau \tau') + D^{(C)}_{l_6 l_2}(\tau_2 \tau) D^{(C)}_{l_8 l_4}(\tau_3 \tau') + D^{(C)}_{l_6 l_4}(\tau_2 \tau') D^{(C)}_{l_8 l_2}(\tau_3 \tau)\right)
\end{aligned} \tag{3.288}
$$

The next step is to apply Langreth's theorem to get those 2-particle (real time) Green's functions in the expression for noise. The first Green's function we need is

$$
\begin{aligned}
& \frac{1}{\hbar} D_{l_1 l_2 l_3 l_4}(t_1 t t_1' t'; t_1 > t > t_1' > t') \\
= & D^{(0)(L)>}_{l_1 l_3}(t_1 t_1') D^{(C)>}_{l_2 l_4}(t t') \\
& + \left(\int_{c_K} d\tau_2 d\tau_3 \sum_{l_5 l_6 l_7 l_8} V^{LC}_{l_5 l_6} V^{LC}_{l_7 l_8} D^{(0)(L)}_{l_5 l_1}(\tau_2 \tau_1) D^{(0)(L)}_{l_7 l_3}(\tau_3 \tau_1') D^{(C)}_{l_6 l_8}(\tau_2 \tau_3) D^{(C)}_{l_2 l_4}(\tau \tau')\right)_{t_1 > t > t_1' > t'} \\
& + \left(\int_{c_K} \sum_{l_5 l_6} V^{LC}_{l_5 l_6} D^{(C)}_{l_2 l_6}(\tau \tau_2) D^{(0)(L)}_{l_5 l_1}(\tau_2 \tau_1)\right)_{t < t_1} \left(\int_{c_K} \tau_3 \sum_{l_7 l_8} V^{LC}_{l_7 l_8} D^{(C)}_{l_4 l_8}(\tau' \tau_3) D^{(0)(L)}_{l_7 l_3}(\tau_3 \tau_1')\right)_{t' < t_1'} \\
& + \left(\int_{c_K} \sum_{l_5 l_6} V^{LC}_{l_5 l_6} D^{(C)}_{l_4 l_6}(\tau' \tau_2) D^{(0)(L)}_{l_5 l_1}(\tau_2 \tau_1)\right)_{t' < t_1} \left(\int_{c_K} \tau_3 \sum_{l_7 l_8} V^{LC}_{l_7 l_8} D^{(C)}_{l_2 l_8}(\tau \tau_3) D^{(0)(L)}_{l_7 l_3}(\tau_3 \tau_1')\right)_{t > t_1'}
\end{aligned} \tag{3.289}
$$

$$
\begin{aligned}
& | \quad \text{recognise the last 2 lines is the hybrid Green's function } D^{(CL)<} \text{ and } D^{(CL)>} \\
= & D^{(0)(L)>}_{l_1 l_3}(t_1 t_1') D^{(C)>}_{l_2 l_4}(t t') \\
& + \left(\int_{c_K} d\tau_2 d\tau_3 \sum_{l_5 l_6 l_7 l_8} V^{LC}_{l_5 l_6} V^{LC}_{l_7 l_8} D^{(0)(L)}_{l_1 l_5}(\tau_1 \tau_2) D^{(C)}_{l_6 l_8}(\tau_2 \tau_3) D^{(0)(L)}_{l_7 l_3}(\tau_3 \tau_1')\right)_{t_1 > t_1'} D^{(C)>}_{l_2 l_4}(t t')
\end{aligned}
$$

[31] Here, I have no space to prove that Wick's theorem applies for this case. The proof is done in the chapter on anharmonicity where the corrections to Landauer's theory are calculated.

$$+D^{(CL)<}_{l_2l_1}(tt_1)D^{(CL)<}_{l_4l_3}(t't'_1)+D^{(CL)<}_{l_4l_1}(t't_1)D^{(CL)>}_{l_2l_3}(tt'_1) \quad (3.290)$$

The second term is a 3-term "series multiplication" for a "greater" quantity which the Langreth's theorem for it will be carried out later. The other Green's function to solve for is

$$\begin{aligned}
& \frac{1}{\hbar}D_{l_1l_2l_3l_4}(t_1tt'_1;t'_1>t'>t_1>t) \\
= \; & D^{(0)(L)<}_{l_1l_3}(t_1t'_1)D^{(C)<}_{l_2l_4}(tt') \\
& +\left(\int_{c_K}d\tau_2d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}D^{(0)(L)}_{l_5l_1}(\tau_2\tau_1)D^{(0)(L)}_{l_7l_3}(\tau_3\tau'_1)D^{(C)}_{l_6l_8}(\tau_2\tau_3)D^{(C)}_{l_2l_4}(\tau\tau')\right)_{t'_1>t'>t_1>t} \\
& +\left(\int_{c_K}\sum_{l_5l_6}V^{LC}_{l_5l_6}D^{(C)}_{l_2l_6}(\tau\tau_2)D^{(0)(L)}_{l_5l_1}(\tau_2\tau_1)\right)_{t<t_1}\left(\int_{c_K}\tau_3\sum_{l_7l_8}V^{LC}_{l_7l_8}D^{(C)}_{l_4l_8}(\tau'\tau_3)D^{(0)(L)}_{l_7l_3}(\tau_3\tau'_1)\right)_{t'<t'_1} \\
& +\left(\int_{c_K}\sum_{l_5l_6}V^{LC}_{l_5l_6}D^{(C)}_{l_4l_6}(\tau'\tau_2)D^{(0)(L)}_{l_5l_1}(\tau_2\tau_1)\right)_{t_1<t'}\left(\int_{c_K}\tau_3\sum_{l_7l_8}V^{LC}_{l_7l_8}D^{(C)}_{l_2l_8}(\tau\tau_3)D^{(0)(L)}_{l_7l_3}(\tau_3\tau'_1)\right)_{t<t'_1} \quad (3.291)
\end{aligned}$$

| recognise the last 2 lines is the hybrid Green's function $D^{(CL)<}$ and $D^{(CL)>}$

$$\begin{aligned}
= \; & D^{(0)(L)<}_{l_1l_3}(t_1t'_1)D^{(C)<}_{l_2l_4}(tt') \\
& +\left(\int_{c_K}d\tau_2d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}D^{(0)(L)}_{l_1l_5}(\tau_1\tau_2)D^{(C)}_{l_6l_8}(\tau_2\tau_3)D^{(0)(L)}_{l_7l_3}(\tau_3\tau'_1)\right)_{t'_1>t_1}D^{(C)<}_{l_2l_4}(tt') \\
& +D^{(CL)<}_{l_2l_1}(tt_1)D^{(CL)<}_{l_4l_3}(t't'_1)+D^{(CL)>}_{l_4l_1}(t't_1)D^{(CL)<}_{l_2l_3}(tt'_1) \quad (3.292)
\end{aligned}$$

The second term is a 3-term "series multiplication" for a "lesser" quantity which the Langreth's theorem for it will be carried out later. Putting all 8 terms back into the expression $S(tt')$

$$\begin{aligned}
S(tt') = \; & \frac{-\hbar}{2}\sum_{l_1l_2l_3l_4}V^{LC}_{l_1l_2}V^{LC}_{l_3l_4}\lim_{t_1\to t}\lim_{t'_1\to t'} \\
& \times\frac{d}{dt_1}\frac{d}{dt'_1}\left[D_{l_1l_2l_3l_4}(t_1tt'_1t';t_1>t>t'_1>t')+D_{l_1l_2l_3l_4}(t_1tt'_1;t'_1>t'>t_1>t)\right]-(J^{LC})^2
\end{aligned}$$

| note that the third term of each $D_{l_1l_2l_3l_4}$ gives a cancellation

$$\begin{aligned}
= \; & \frac{-\hbar}{2}\sum_{l_1l_2l_3l_4}V^{LC}_{l_1l_2}V^{LC}_{l_3l_4}\lim_{t_1\to t}\lim_{t'_1\to t'} \\
& \times\frac{d}{dt_1}\frac{d}{dt'_1}\left[2\hbar D^{(CL)<}_{l_2l_1}(tt_1)D^{(CL)<}_{l_4l_3}(t't'_1)+6\text{ other terms}\right]-(J^{LC})^2 \quad (3.293) \\
= \; & \left(i\hbar\sum_{l_1l_2}V^{LC}_{l_1l_2}\lim_{t_1\to t}\frac{d}{dt_1}D^{(CL)<}_{l_2l_1}(tt_1)\right)\left(i\hbar\sum_{l_3l_4}\lim_{t'_1\to t'}\frac{d}{dt'_1}D^{(CL)<}_{l_4l_3}(t't'_1)\right) \\
& +\frac{-\hbar}{2}\sum_{l_1l_2l_3l_4}V^{LC}_{l_1l_2}V^{LC}_{l_3l_4}\lim_{t_1\to t}\lim_{t'_1\to t'}\frac{d}{dt_1}\frac{d}{dt'_1}[6\text{ other terms}]-(J^{LC})^2 \quad (3.294)
\end{aligned}$$

| in the first line, each round bracket is the expression for J^{LC} (3.164)

| the first line cancels the term $(J^{LC})^2$

$$= \frac{-\hbar}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \lim_{t_1 \to t} \lim_{t'_1 \to t'} \frac{d}{dt_1} \frac{d}{dt'_1} \text{[6 other terms]} \tag{3.295}$$

$$\begin{aligned} &= \frac{-\hbar^2}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \lim_{t_1 \to t} \lim_{t'_1 \to t'} \frac{d}{dt_1} \frac{d}{dt'_1} \\ &\times \Bigg[D^{(0)(L)>}_{l_1 l_3}(t_1 t'_1) D^{(C)>}_{l_2 l_4}(tt') + D^{(0)(L)<}_{l_1 l_3}(t_1 t'_1) D^{(C)<}_{l_2 l_4}(tt') \\ &+ \left(\int_{c_K} d\tau_2 d\tau_3 \sum_{l_5 l_6 l_7 l_8} V^{LC}_{l_5 l_6} V^{LC}_{l_7 l_8} D^{(0)(L)}_{l_1 l_5}(\tau_1 \tau_2) D^{(C)}_{l_6 l_8}(\tau_2 \tau_3) D^{(0)(L)}_{l_7 l_3}(\tau_3 \tau'_1) \right)_{t_1 > t'_1} D^{(C)>}_{l_2 l_4}(tt') \\ &+ \left(\int_{c_K} d\tau_2 d\tau_3 \sum_{l_5 l_6 l_7 l_8} V^{LC}_{l_5 l_6} V^{LC}_{l_7 l_8} D^{(0)(L)}_{l_1 l_5}(\tau_1 \tau_2) D^{(C)}_{l_6 l_8}(\tau_2 \tau_3) D^{(0)(L)}_{l_7 l_3}(\tau_3 \tau'_1) \right)_{t'_1 > t_1} D^{(C)<}_{l_2 l_4}(tt') \\ &+ D^{(CL)<}_{l_4 l_1}(t' t_1) D^{(CL)>}_{l_2 l_3}(tt'_1) + D^{(CL)>}_{l_4 l_1}(t' t_1) D^{(CL)<}_{l_2 l_3}(tt'_1) \Bigg] \end{aligned} \tag{3.296}$$

Thus we see 3 types of terms to handle in $S(tt')$. We assume steady state, i.e. $S(tt') = S(t-t')$ and seek to calculate the DC noise i.e. $S(\omega = 0) = \int d(t-t') e^{i(\omega=0)(t-t')} S(t-t') = \int d(t-t') S(t-t')$.

$$\begin{aligned} &\text{Type 1 term for } S(\omega=0) \\ &= \int d(t-t') \frac{-\hbar^2}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{l_3 l_4} \\ &\times \lim_{t_1 \to t} \lim_{t'_1 \to t'} \frac{d}{dt_1} \frac{d}{dt'_1} \left[D^{(0)(L)}_{l_1 l_3}(t_1 t'_1) D^{(C)>}_{l_1 l_4}(tt') + D^{(0)(L)<}_{l_1 l_3}(t_1 t'_1) D^{(C)<}_{l_2 l_4}(tt') \right] \end{aligned} \tag{3.297}$$

$$\begin{aligned} &| \quad \text{introduce the Fourier transforms} \\ &= \int d(t-t') \frac{-\hbar^2}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{l_3 l_4} \lim_{t_1 \to t} \lim_{t'_1 \to t'} \frac{d}{dt_1} \frac{d}{dt'_1} \\ &\times \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} e^{-i\omega_1(t_1 - t'_1)} e^{-i\omega_2(t-t')} \left[D^{(0)(L)>}_{l_1 l_3}(\omega_1) D^{(C)>}_{l_2 l_4}(\omega_2) + D^{(0)(L)<}_{l_1 l_3}(\omega_1) D^{(C)<}_{l_2 l_4}(\omega_2) \right] \end{aligned} \tag{3.298}$$

$$\begin{aligned} &= \int d(t-t') \frac{-\hbar^2}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \\ &\times \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} \omega_1^2 e^{-i(\omega_1+\omega_2)(t-t')} \left[D^{(0)(L)>}_{l_1 l_3}(\omega_1) D^{(C)>}_{l_2 l_4}(\omega_2) + D^{(0)(L)<}_{l_1 l_3}(\omega_1) D^{(C)<}_{l_2 l_4}(\omega_2) \right] \end{aligned} \tag{3.299}$$

$$| \quad \text{evaluate } \int d(t-t') e^{-i(\omega_1+\omega_2)(t-t')} = \delta(\omega_1 + \omega_2)$$

$$| \quad \text{then evaluate } \int \frac{d\omega_2}{2\pi} \text{ and use } D^{(C)\lessgtr}(-\omega) = D^{(C)\gtrless}(\omega)$$

$$= \frac{-\hbar^2}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \int \frac{d\omega_1}{2\pi} \omega_1^2 \left[D^{(0)(L)>}_{l_1 l_3}(\omega_1) D^{(C)>}_{l_2 l_4}(\omega_1) + D^{(0)(L)<}_{l_1 l_3}(\omega_1) D^{(C)<}_{l_2 l_4}(\omega_1) \right] \tag{3.300}$$

$$| \quad \text{use the definition of lead self energies and rename } \omega_1 \text{ to } \omega$$

$$= \frac{-\hbar^2}{2} \sum_{l_2 l_4} \int \frac{d\omega}{2\pi} \omega^2 \left[\Sigma^{(L)>}_{l_2 l_4}(\omega) D^{(C)<}_{l_2 l_4}(\omega) + \Sigma^{(L)<}_{l_2 l_4}(\omega) D^{(C)>}_{l_2 l_4}(\omega) \right] \tag{3.301}$$

$$| \quad \text{recall relations } \Sigma^{(L)>}_{l_2 l_4}(\omega) = -i \left(1 + N^{eq(L)}(\omega) \right) \Gamma^{(L)}_{l_2 l_4}(\omega) \text{ and } \Sigma^{(L)<}_{l_2 l_4}(\omega) = -i N^{eq(L)}(\omega) \Gamma^{(L)}_{l_2 l_4}(\omega)$$

$$
\begin{aligned}
& \quad | \quad \text{use the relation } D^{(C)>} = D^{(C)<} + D^{(C)R} - D^{(C)A} \\
= & \ \frac{i\hbar^2}{2} \sum_{l_2 l_4} \int \frac{d\omega}{2\pi} \omega^2 \\
& \times \left[\left(1 + 2N^{eq(L)}(\omega)\right) \Gamma^{(L)}_{l_2 l_4}(\omega) D^{(C)<}_{l_2 l_4}(\omega) + N^{eq(L)}(\omega) \Gamma^{(L)}_{l_2 l_4}(\omega) \left(D^{(C)R}_{l_2 l_4}(\omega) - D^{(C)A}_{l_2 l_4}(\omega) \right) \right] \quad (3.302)
\end{aligned}
$$

$$
\begin{aligned}
& \text{Type 2 term for } S(\omega = 0) \\
= & \int d(t-t') \frac{-\hbar^2}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \lim_{t_1 \to t} \lim_{t_1' \to t'} \frac{d}{dt_1} \frac{d}{dt_1'} \\
& \times \left[D^{(CL)<}_{l_4 l_1}(t' t_1) D^{(CL)>}_{l_2 l_3}(t t_1') + D^{(CL)>}_{l_4 l_1}(t' t_1) D^{(CL)<}(t t_1') \right] \quad (3.303) \\
& | \quad \text{assume steady state and Fourier transform to frequency domain} \\
= & \int d(t-t') \frac{-\hbar^2}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \lim_{t_1 \to t} \lim_{t_1' \to t'} \frac{d}{dt_1} \frac{d}{dt_1'} \\
& \times \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} e^{-i\omega_1 (t'-t_1)} e^{-i\omega_2 (t-t_1')} \left[D^{(CL)<}_{l_4 l_1}(\omega_1) D^{(CL)>}(\omega_2) + D^{(CL)>}_{l_4 l_1}(\omega_1) D^{(CL)<}_{l_2 l_3}(\omega_2) \right] \quad (3.304) \\
= & \int d(t-t') \frac{-\hbar^2}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \\
& \times \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} \omega_1 \omega_2 e^{-i(\omega_2 - \omega_1)(t-t')} \left[D^{(CL)<}_{l_4 l_1}(\omega_1) D^{(CL)>}(\omega_2) + D^{(CL)>}_{l_4 l_1}(\omega_1) D^{(CL)<}_{l_2 l_3}(\omega_2) \right] \quad (3.305) \\
& | \quad \text{use } \int d(t-t') e^{-i(\omega_2 - \omega_1)(t-t')} = \delta(\omega_2 - \omega_1) \text{ then evaluate } \int \frac{d\omega_2}{2\pi} \text{ and rename } \omega_1 \to \omega \\
= & \ \frac{\hbar^2}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \int \frac{d\omega}{2\pi} \omega^2 \left[D^{(CL)<}_{l_4 l_1}(\omega) D^{(CL)>}(\omega) + D^{(CL)>}_{l_4 l_1}(\omega) D^{(CL)<}_{l_2 l_3}(\omega) \right] \quad (3.306)
\end{aligned}
$$

We thus need the Fourier component $D^{(CL)>}$ and $D^{(CL)<}$. Recall from the earlier section on Landauer current,

$$
\begin{aligned}
D^{(CL)\lessgtr}_{ll'}(tt') &= \int_{t_0}^{\infty} dt_1 \sum_{l_1 l_2} V^{LC}_{l_2 l_1} \left(D^{(C)R}_{l l_2}(t t_1) D^{(0)(L)\lessgtr}_{l_1 l'}(t_1 t') + D^{(C)\lessgtr}_{l l_2}(t t_1) D^{(0)(L)A}_{l_1 l'}(t_1 t') \right) \\
& \quad | \quad \text{take } t_0 \to -\infty \text{ and assume steady state and the Fourier form is} \\
&= \sum_{l_1 l_2} V^{LC}_{l_2 l_1} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t')} \left(D^{(C)R}_{l l_2}(\omega) D^{(0)(L)\lessgtr}_{l_1 l'}(\omega) + D^{(C)\lessgtr}_{l l_2}(\omega) D^{(0)(L)A}_{l_1 l'}(\omega) \right)
\end{aligned}
$$

The required Fourier component is

$$
D^{(CL)\lessgtr}_{ll'}(\omega) = \sum_{l_1 l_2} V^{LC}_{l_1 l_2} \left(D^{(C)R}_{l l_2}(\omega) D^{(0)(L)\lessgtr}_{l_1 l'}(\omega) + D^{(C)\lessgtr}_{l l_2}(\omega) D^{(0)(L)A}_{l_1 l'}(\omega) \right) \quad (3.307)
$$

$$
\begin{aligned}
& \text{Type 2 term for } S(\omega = 0) \\
= & \ \frac{\hbar^2}{2} \sum_{l_1 l_2 l_3 l_4} V^{LC}_{l_1 l_2} V^{LC}_{l_3 l_4} \int \frac{d\omega}{2\pi} \omega^2
\end{aligned}
$$

$$\times\left[\sum_{l_5l_6}V^{LC}_{l_5l_6}\left(D^{(C)R}_{l_4l_5}D^{(0)(L)<}_{l_6l_1}+D^{(C)<}_{l_4l_5}D^{(0)(L)A}_{l_6l_1}\right)\sum_{l_7l_8}V^{LC}_{l_7l_8}\left(D^{(C)R}_{l_2l_7}D^{(0)(L)>}_{l_8l_3}+D^{(C)>}_{l_2l_7}D^{(0)(L)A}_{l_8l_3}\right)\right.$$

$$\left.+\sum_{l_5l_6}V^{LC}_{l_5l_6}\left(D^{(C)R}_{l_4l_5}D^{(0)(L)>}_{l_6l_1}+D^{(C)>}_{l_4l_5}D^{(0)(L)A}_{l_6l_1}\right)\sum_{l_7l_8}V^{LC}_{l_7l_8}\left(D^{(C)R}_{l_2l_7}D^{(0)(L)<}_{l_8l_3}+D^{(C)<}_{l_2l_7}D^{(0)(L)A}_{l_8l_3}\right)\right] \quad (3.308)$$

| recall the definitions of the leads self energies and write the expression into a trace
| use trace cyclicity and find that the 2 terms add up

$$= \int\frac{d\omega}{2\pi}(\hbar\omega)^2\mathrm{Tr}\left[D^{(C)R}\Sigma^{(L)<}D^{(C)R}\Sigma^{(L)>}+D^{(C)R}\Sigma^{(L)<}D^{(C)>}\Sigma^{(L)A}\right.$$
$$\left.+D^{(C)<}\Sigma^{(L)A}D^{(C)R}\Sigma^{(L)>}+D^{(C)<}\Sigma^{(L)A}D^{(C)>}\Sigma^{(L)A}\right] \quad (3.309)$$

| we simplify notation for the time being by writing $D^{(C)}\to D$ and $\Sigma^{(L)}\to\Sigma$
| note the identities $D^R-D^A=D^>-D^<$ and $\Sigma^R-\Sigma^A=\Sigma^>-\Sigma^<$
| for 1st term, write $D^R\Sigma^<D^R\Sigma^>=\frac{1}{2}D^R\Sigma^<D^R\Sigma^>+\frac{1}{2}(D^A+D^>-D^<)\Sigma^<(D^A+D^>-D^<)\Sigma^>$
| for 2nd term, write $D^R\Sigma^<D^>\Sigma^A=\frac{1}{2}D^R\Sigma^<D^>\Sigma^A+\frac{1}{2}(D^A+D^>-D^<)\Sigma^<D^>(\Sigma^R-\Sigma^>+\Sigma^<)$
| for 3rd term, write $D^<\Sigma^AD^R\Sigma^>=\frac{1}{2}D^<\Sigma^AD^R\Sigma^>+\frac{1}{2}D^<(\Sigma^R-(\Sigma^>-\Sigma^<))(D^A+D^>-D^<)\Sigma^>$
| for 4th term, write $D^<\Sigma^AD^>\Sigma^A=\frac{1}{2}D^<\Sigma^AD^>\Sigma^A+\frac{1}{2}D^<(\Sigma^R-(\Sigma^>-\Sigma^<))D^>(\Sigma^R-(\Sigma^>-\Sigma^<))$
| expand to get 24 terms but 4 pairs of terms cancel leaving 16 terms

$$= \int\frac{d\omega}{2\pi}(\hbar\omega)^2\frac{1}{2}\mathrm{Tr}\left(D^R\Sigma^<D^R\Sigma^>+D^A\Sigma^<D^A\Sigma^>-D^A\Sigma^<D^<\Sigma^>+D^>\Sigma^<D^R\Sigma^>\right.$$
$$+D^R\Sigma^<D^>\Sigma^A+D^A\Sigma^<D^>\Sigma^R+D^A\Sigma^<D^>\Sigma^<+D^>\Sigma^<D^>\Sigma^A$$
$$+D^<\Sigma^AD^R\Sigma^>+D^<\Sigma^RD^A\Sigma^>-D^<\Sigma^RD^<\Sigma^>-D^<\Sigma^>D^R\Sigma^>$$
$$\left.+D^<\Sigma^AD^>\Sigma^A+D^<\Sigma^RD^>\Sigma^R+D^<\Sigma^RD^>\Sigma^<-D^<\Sigma^>D^>\Sigma^A\right) \quad (3.310)$$

Type 3 term for $S(\omega=0)$

$$= \int d(t-t')\frac{-\hbar^2}{2}\sum_{l_1l_2l_3l_4}V^{LC}_{l_1l_2}V^{LC}_{l_3l_4}\lim_{t_1\to t}\lim_{t_1'\to t'}\frac{d}{dt_1}\frac{d}{dt_1'}$$
$$\times\left[\left(\int_{c_K}d\tau_2d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}D^{(0)(L)}_{l_1l_5}(\tau_1\tau_2)D^{(C)}_{l_6l_8}(\tau_2\tau_3)D^{(0)(L)}_{l_7l_3}(\tau_3\tau_1')\right)_{t_1>t_1'}D^{(C)>}_{l_2l_4}(tt')\right.$$
$$\left.+\left(\int_{c_K}d\tau_2d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}D^{(0)(L)}_{l_1l_5}(\tau_1\tau_2)D^{(C)}_{l_6l_8}(\tau_2\tau_3)D^{(0)(L)}_{l_7l_3}(\tau_3\tau_1')\right)_{t_1<t_1'}D^{(C)<}_{l_2l_4}(tt')\right] \quad (3.311)$$

| the first round bracket is a 3-term "series multiplication" for a "greater" quantity
| the second round bracket is a 3-term "series multiplication" for a "lesser" quantity

$$= \int d(t-t')\frac{-\hbar^2}{2}\sum_{l_1l_2l_3l_4}V^{LC}_{l_1l_2}V^{LC}_{l_3l_4}\lim_{t_1\to t}\lim_{t_1'\to t'}\frac{d}{dt_1}\frac{d}{dt_1'}\left[\int dt_2dt_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}\right.$$
$$\times\left[\left(D^{(0)(L)R}_{l_1l_5}D^{(C)R}_{l_6l_8}D^{(0)(L)>}_{l_7l_3}+D^{(0)(L)R}_{l_1l_5}D^{(C)>}_{l_6l_8}D^{(0)(L)A}_{l_7l_3}+D^{(0)(L)>}_{l_1l_5}D^{(C)A}_{l_6l_8}D^{(0)(L)A}_{l_7l_3}\right)D^{(C)>}_{l_2l_4}(tt')\right.$$

$$+\left(D^{(0)(L)R}_{l_1l_5}D^{(C)R}_{l_6l_8}D^{(0)(L)<}_{l_7l_3}+D^{(0)(L)R}_{l_1l_5}D^{(C)<}_{l_6l_8}D^{(0)(L)A}_{l_7l_3}+D^{(0)(L)<}_{l_1l_5}D^{(C)A}_{l_6l_8}D^{(0)(L)A}_{l_7l_3}\right)D^{(C)<}_{l_2l_4}(tt')\Big]\Big\} \quad (3.312)$$

| where the time arguments are in the sequence $(t_1t_2)(t_2t_3)(t_3t_1')$
| use the definition of the lead self energies and we also write these into a trace
| assume steady state and introduce their Fourier forms

$$= \int d(t-t')\frac{-\hbar^2}{2}\sum_{l_2l_4l_6l_8}\lim_{t_1\to t}\lim_{t_1'\to t'}\frac{d}{dt_1}\frac{d}{dt_1'}\int dt_2dt_3\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}e^{-i\omega_1(t_1-t_2)}e^{-i\omega_2(t_2-t_3)}e^{-i\omega_3(t_3-t_1')}$$
$$\times\Big[D^{(C)<}_{l_4l_2}(t't)\left(\Sigma^{(L)R}_{l_2l_6}D^{(C)R}_{l_6l_8}\Sigma^{(L)>}_{l_8l_4}+\Sigma^{(L)R}_{l_2l_6}D^{(C)>}_{l_6l_8}\Sigma^{(L)A}_{l_8l_4}+\Sigma^{(L)>}_{l_2l_6}D^{(C)A}_{l_6l_8}\Sigma^{(L)A}_{l_8l_4}\right)(\omega_1)(\omega_2)(\omega_3)$$
$$+D^{(C)>}_{l_4l_2}(t't)\left(\Sigma^{(L)R}_{l_2l_6}D^{(C)R}_{l_6l_8}\Sigma^{(L)<}_{l_8l_4}+\Sigma^{(L)R}_{l_2l_6}D^{(C)<}_{l_6l_8}\Sigma^{(L)A}_{l_8l_4}+\Sigma^{(L)<}_{l_2l_6}D^{(C)A}_{l_6l_8}\Sigma^{(L)A}_{l_8l_4}\right)(\omega_1)(\omega_2)(\omega_3)\Big] \quad (3.313)$$

| write $e^{-i\omega_1(t_1-t_2)}e^{-i\omega_2(t_2-t_3)}e^{-i\omega_3(t_3-t_1')}=e^{-i\omega_1t_1}e^{-i(\omega_2-\omega_1)t_2}e^{-i(\omega_3-\omega_2)t_3}e^{i\omega_3t_1'}$
| use $\int dt_2e^{-i(\omega_2-\omega_1)t_2}=\delta(\omega_2-\omega_1)$ and $\int dt_3e^{-i(\omega_3-\omega_1)t_3}=\delta(\omega_3-\omega_1)$
| then evaluate $\int\frac{d\omega_2}{2\pi}$ and $\int\frac{d\omega_3}{2\pi}$
| then carry out $\frac{d}{dt_1}\frac{d}{dt_1'}$ and take the limits
| finally carry out $\int d(t-t')$ and rename $\omega_1\to\omega$

$$= \frac{-\hbar^2}{2}\int\frac{d\omega}{2\pi}\omega^2\mathrm{Tr}\Big[D^{(C)<}\left(\Sigma^{(L)R}D^{(C)R}\Sigma^{(L)>}+\Sigma^{(L)R}D^{(C)>}\Sigma^{(L)A}+\Sigma^{(L)>}D^{(C)A}\Sigma^{(L)A}\right)$$
$$+D^{(C)>}\left(\Sigma^{(L)R}D^{(C)R}\Sigma^{(L)<}+\Sigma^{(L)R}D^{(C)<}\Sigma^{(L)A}+\Sigma^{(L)<}D^{(C)A}\Sigma^{(L)A}\right)\Big] \quad (3.314)$$

| where all the arguments are (ω)
| recall $D^{(C)A\dagger}(\omega)=D^{(C)R}(\omega)$ and $\Sigma^{(L)<\dagger}(\omega)=-\Sigma^{(L)<}(\omega)$
| so the complex conjugate pairs of terms are: 1st & 3rd, 4th & 6th and 2nd & 5th

$$= -\int\frac{d\omega}{2\pi}(\hbar\omega)^2\Re\mathrm{Tr}\left(D^{(C)<}\Sigma^{(L)R}D^{(C)R}\Sigma^{(L)>}+D^{(C)<}\Sigma^{(L)R}D^{(C)>}\Sigma^{(L)A}+D^{(C)>}\Sigma^{(L)R}D^{(C)R}\Sigma^{(L)<}\right) \quad (3.315)$$

We work out each term seperately. First we note that in this problem, retarded and advanced "objects" are complex numbers, in fact, they are complex conjugates of each other. Greater and lesser "objects" are pure imaginary. We take Type 3 1st term as example, let

$$D^{(C)<}\equiv ia\ ,\Sigma^{(L)R}\equiv b+ic\ ,D^{(C)R}\equiv d+ie\ ,\Sigma^{(L)>}\equiv if \quad (3.316)$$

Then, (we omit the trace but we maintain the order of the terms)

$$\begin{aligned}\Re\left(D^{(C)<}\Sigma^{(L)R}D^{(C)R}\Sigma^{(L)>}\right) &= \Re\left(ia(b+ic)(d+ie)if\right)=\Re\left(ia(bd+ibe+icd-ce)if\right)\\ &= ia(bd-ce)if=(ia)bd(if)-(ia)ce(if)\\ &= D^{(C)<}\left(\Re\Sigma^{(L)R}\right)\left(\Re D^{(C)R}\right)\Sigma^{(L)>}-D^{(C)<}\left(\Im\Sigma^{(L)R}\right)\left(\Im D^{(C)R}\right)\Sigma^{(L)>}\end{aligned}$$

We apply the identity in calculating all 3 terms in Type 3.

Type 3 1st term

$$
\begin{aligned}
&= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \Re\mathrm{Tr}\left(D^{(C)>}\Sigma^{(L)R}D^{(C)R}\Sigma^{(L)>}\right) \\
&\mid \text{ use the above identity} \\
&= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\mathrm{Tr}\left(D^{(C)<}\left(\Re\Sigma^{(L)R}\right)\left(\Re D^{(C)R}\right)\Sigma^{(L)>}\right) - \mathrm{Tr}\left(D^{(C)<}\left(\Im\Sigma^{(L)R}\right)\left(\Im D^{(C)R}\right)\Sigma^{(L)>}\right)\right] \\
&\mid \text{ note } \Re A^{R\mathrm{or}A} = \frac{1}{2}(A^R + A^A),\ \Im A^R = \frac{1}{2i}(A^R - A^A) \text{ and } \Im A^A = -\frac{1}{2i}(A^R - A^A) \\
&\mid \text{ drop the device-lead indices to simplify writing} \\
&= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{4}\mathrm{Tr}\left(D^<(\Sigma^R + \Sigma^A)(D^R + D^A)\Sigma^>\right) + \frac{1}{4}\mathrm{Tr}\left(D^<(\Sigma^R - \Sigma^A)(D^R - D^A)\Sigma^>\right)\right] \\
&\mid \text{ use the definition } i(\Sigma^{(L)R} - \Sigma^{(L)A}) = \Gamma^{(L)} \Rightarrow i(\Sigma^R - \Sigma^A) = \Gamma \\
&= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{4}\mathrm{Tr}\left(D^<\left(\frac{\Gamma}{i} + 2\Sigma^A\right)(D^R - D^A + 2D^A)\Sigma^>\right) + \frac{1}{4}\mathrm{Tr}\left(D^<\frac{\Gamma}{i}(D^R - D^A)\Sigma^>\right)\right] \\
&= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{4}\mathrm{Tr}\left(D^<\frac{\Gamma}{i}(D^R - D^A + 2D^A)\Sigma^>\right) + \frac{1}{2}\mathrm{Tr}\left(D^<\Sigma^A(D^R - D^A + 2D^A)\Sigma^>\right)\right. \\
&\quad \left.+\frac{1}{4}\mathrm{Tr}\left(D^<\frac{\Gamma}{i}(D^R - D^A)\Sigma^>\right)\right] \\
&= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{2}\mathrm{Tr}\left(D^<\frac{\Gamma}{i}(D^R - D^A)\Sigma^>\right) + \frac{1}{2}\mathrm{Tr}\left(D^<\frac{\Gamma}{i}D^A\Sigma^>\right) + \frac{1}{2}\mathrm{Tr}\left(D^<\Sigma^A(D^R + D^A)\Sigma^>\right)\right] \\
&\mid \text{ use } \Sigma^{(L)>} = -i\left(1 + N^{eq(L)}\right)\Gamma^{(L)} \text{ in the first term} \\
&= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[-\frac{1}{2}\mathrm{Tr}\left(D^<\Gamma(D^R - D^A)(1 + N^{eq})\Gamma\right) + \frac{1}{2}\mathrm{Tr}\left(D^<\Sigma^R D^A\Sigma^>\right) + \frac{1}{2}\mathrm{Tr}\left(D^<\Sigma^A D^R\Sigma^>\right)\right]
\end{aligned}
$$

and the last 2 terms cancel with 2 terms in Type 2.

Type 3 2nd term

$$= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \Re\mathrm{Tr}\left(D^<\Sigma^R D^>\Sigma^A\right) \tag{3.317}$$

$\mid$ use the above identity

$$= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\mathrm{Tr}\left(D^<(\Re\Sigma^R)D^>(\Re\Sigma^A)\right) - \mathrm{Tr}\left(D^<(\Im\Sigma^R)D^>(\Im\Sigma^A)\right)\right] \tag{3.318}$$

$\mid$ note $\Re A^{R\mathrm{or}A} = \frac{1}{2}(A^R + A^A)$, $\Im A^R = \frac{1}{2i}(A^R - A^A)$ and $\Im A^A = -\frac{1}{2i}(A^R - A^A)$

$\mid$ we also need $i\left(\Sigma^R - \Sigma^A\right) = \Gamma$

$$= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{4}\mathrm{Tr}\left(D^<\left(2\Sigma^R - \frac{\Gamma}{i}\right)D^>\left(\frac{\Gamma}{i} + 2\Sigma^A\right)\right) + \frac{1}{4}\mathrm{Tr}\left(D^<\Gamma D^>\Gamma\right)\right] \tag{3.319}$$

$$= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{2}\mathrm{Tr}\left(D^<\Sigma^R D^>\left(\frac{\Gamma}{i} + 2\Sigma^A\right)\right) - \frac{1}{4}\mathrm{Tr}\left(D^<\frac{\Gamma}{i}D^>\left(\frac{\Gamma}{i} + 2\Sigma^A\right)\right) + \frac{1}{4}\mathrm{Tr}\left(D^<\Gamma D^>\Gamma\right)\right]$$

$$= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{2}\mathrm{Tr}\left(D^<\Sigma^R D^>(\Sigma^R + \Sigma^A)\right) - \frac{1}{2}\mathrm{Tr}\left(D^<\frac{\Gamma}{i}D^>\Sigma^A\right) + \frac{1}{2}\mathrm{Tr}\left(D^<\Gamma D^>\Gamma\right)\right] \tag{3.320}$$

$\mid$ use $D^> = D^R - D^A + D^<$ in the third term

$$= -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{2}\mathrm{Tr}\left(D^<\Gamma(D^R - D^A + D^<)\Gamma\right) + \frac{1}{2}\mathrm{Tr}\left(D^<\Sigma^R D^>\Sigma^R\right) + \frac{1}{2}\mathrm{Tr}\left(D^<\Sigma^A D^>\Sigma^A\right)\right] \tag{3.321}$$

and the last 2 terms cancel with 2 terms in Type 2.

$$
\begin{aligned}
& \text{Type 3 3rd term} \\
= & -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \Re\mathrm{Tr}\left(D^{>}\Sigma^R D^R \Sigma^{<}\right) && (3.322)\\
| & \text{ use the above identity} \\
= & -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\mathrm{Tr}\left(D^{>}(\Re\Sigma^R)(\Re D^R)\Sigma^{<}\right) - \mathrm{Tr}\left(D^{>}(\Im\Sigma^R)(\Im D^R)\Sigma^R\right)\right] && (3.323)\\
| & \text{ note } \Re A^{R \text{ or } A} = \frac{1}{2}(A^R + A^A),\ \Im A^R = \frac{1}{2i}(A^R - A^A) \text{ and } \Im A^A = -\frac{1}{2i}(A^R - A^A) \\
= & -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{4}\mathrm{Tr}\left(D^{>}(\Sigma^R + \Sigma^A)(D^R + D^A)\Sigma^{<}\right) + \frac{1}{4}\mathrm{Tr}\left(D^{>}\frac{\Gamma}{i}(D^R - D^A)\Sigma^{<}\right)\right] && (3.324)\\
| & \text{ we also need } i\left(\Sigma^R - \Sigma^A\right) = \Gamma \\
= & -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{4}\mathrm{Tr}\left(D^{>}\left(\frac{\Gamma}{i} + 2\Sigma^A\right)(D^R - D^A + 2D^A)\Sigma^{<}\right) + \frac{1}{4}\mathrm{Tr}\left(D^{>}\frac{\Gamma}{i}(D^R - D^A)\Sigma^{<}\right)\right] \\
= & -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{4}\mathrm{Tr}\left(D^{>}\frac{\Gamma}{i}(D^R - D^A + 2D^A)\Sigma^{<}\right) + \frac{1}{2}\mathrm{Tr}\left(D^{>}\Sigma^A(D^R + D^A)\Sigma^{<}\right)\right. \\
& \left. + \frac{1}{4}\mathrm{Tr}\left(D^{>}\frac{\Gamma}{i}(D^R - D^A)\Sigma^{<}\right)\right] && (3.325)\\
= & -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[\frac{1}{2}\mathrm{Tr}\left(D^{>}\frac{\Gamma}{i}(D^R - D^A)\Sigma^{<}\right) + \frac{1}{2}\mathrm{Tr}\left(D^{>}\frac{\Gamma}{i}D^A\Sigma^{<}\right) + \frac{1}{2}\mathrm{Tr}\left(D^{>}\Sigma^A(D^R + D^A)\Sigma^{<}\right)\right] \\
| & \text{ use } \Sigma^{<} = -iN^{eq}\Gamma \text{ and } D^{>} = D^{<} + D^R - D^A \text{ in the first term} \\
= & -\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \left[-\frac{1}{2}\mathrm{Tr}\left(D^{<}\Gamma(D^R - D^A)N^{eq}\Gamma\right) - \frac{1}{2}\mathrm{Tr}\left((D^R - D^A)\Gamma(D^R - D^A)N^{eq}\Gamma\right)\right. \\
& \left. + \frac{1}{2}\mathrm{Tr}\left(D^{>}\Sigma^R D^A \Sigma^{<}\right) + \frac{1}{2}\mathrm{Tr}\left(D^{>}\Sigma^A D^R \Sigma^{<}\right)\right] && (3.326)
\end{aligned}
$$

and the last 2 terms cancel with 2 terms in Type 2. Thus there are now 10 terms in Type 2 and 4 terms in Type 3.

The expression for the DC noise $S(\omega = 0)$ is, (restoring all device-lead indices)

$$
\begin{aligned}
S(\omega = 0) = & \ \text{Type 1} + \text{Type 2} + \text{Type 3} && (3.327)\\
| & \text{ use } \Sigma^{<} = -iN^{eq}\Gamma \text{ and } \Sigma^{>} = -i(1 + N^{eq})\Gamma \text{ on } \frac{1}{2}D^R\Sigma^{<}D^R\Sigma^{>} + \frac{1}{2}D^A\Sigma^{<}D^A\Sigma^{>} \\
= & \ \frac{1}{2}\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \mathrm{Tr}\left[i\left(1 + 2N^{eq(L)}\right)\Gamma^{(L)}D^{(C)<} + iN^{eq(L)}\Gamma^{L}\left(D^{(C)R} - D^{(C)A}\right)\right. \\
& + \left(D^{(C)R} - D^{(C)A}\right)N^{eq(L)}\Gamma^{(L)}\left(D^{(C)R} - D^{(C)A}\right)\Gamma^{(L)} \\
& + \left(D^{(C)R} - D^{(C)A}\right)\left(1 + 2N^{eq(L)}\right)\Gamma^{(L)}D^{(C)<}\Gamma^{(L)} \\
& - N^{eq(L)}\left(1 + N^{eq(L)}\right)\left(D^{(C)A}\Gamma^{(L)}D^{(C)A}\Gamma^{(L)} + D^{(C)R}\Gamma^{(L)}D^{(C)R}\Gamma^{(L)}\right) \\
& - D^{(C)<}\Gamma^{(L)}\left(D^{(C)R} - D^{(C)A}\right)\Gamma^{(L)} - D^{(C)<}\Gamma^{(L)}D^{(C)<}\Gamma^{(L)} \\
& \left. + 8 \text{ other terms from Type 2}\right] && (3.328)\\
| & \text{ these 8 other terms are shown to cancel in the footnote}^{32}
\end{aligned}
$$

Now to incoporate the right lead, we will use 4 identities which some of them were used in the derivation of the Landauer formula earlier.

1. Keldysh equation

$$D^{(C)<} = D^{(C)R}\left(\Sigma^{(L)<} + \Sigma^{(R)<}\right)D^{(C)A} = -iD^{(C)R}\left(N^{eq(L)}\Gamma^{(L)} + N^{(eq(R)}\Gamma^{(R)}\right)D^{(C)A} \tag{3.330}$$

2. Identity from Datta's book [Datta1997] eqn (3.6.4)

$$D^{(C)R} - D^{(C)A} = -iD^{(C)R}\left(\Gamma^{(L)} + \Gamma^{(R)}\right)D^{(C)A} \tag{3.331}$$

3. No name for this identity and it can be checked by simply expanding the brackets and use trace cyclicity.

$$\begin{aligned} & D^{(C)A}\Gamma^{(L)}D^{(C)R}\Gamma^{(L)} + D^{(C)R}\Gamma^{(L)}D^{(C)R}\Gamma^{(L)} \\ = & \left(D^{(C)A} - D^{(C)R}\right)\Gamma^{(L)}\left(D^{(C)A} - D^{(C)R}\right)\Gamma^{(L)} + 2D^{(C)R}\Gamma^{(L)}D^{(C)A}\Gamma^{(L)} \end{aligned} \tag{3.332}$$

4. Definition of Transmission (operator)

$$\mathcal{T} = \Gamma^{(L)}D^{(C)A}\Gamma^{(R)}D^{(C)R} = \Gamma^{(L)}D^{(C)R}\Gamma^{(R)}D^{(C)A} \tag{3.333}$$

---

[32]These 8 terms from Type 2 are

$$\begin{aligned} \text{8 terms} = & \frac{1}{4}\int\frac{d\omega}{2\pi}\omega^2\mathrm{Tr}\Big[D^>\Sigma^<D^R\Sigma^> - D^A\Sigma^<D^<\Sigma^> + D^A\Sigma^<D^>\Sigma^< + D^>\Sigma^<D^>\Sigma^A \\ & -D^<\Sigma^RD^<\Sigma^> - D^<\Sigma^>D^R\Sigma^> + D^<\Sigma^RD^>\Sigma^< - D^<\Sigma^>D^>\Sigma^A\Big] \end{aligned} \tag{3.329}$$

which vanishes upon using 2 identities (i) Keldysh equation: $D^{\lessgtr} = D^R\Sigma^{\lessgtr}D^A$ and (ii) $\Sigma^< = -iN^{eq}\Gamma$ and $\Sigma^> = -i(1+N^{eq})\Gamma$. We write out the 8 terms in symbolic form.

$$\text{Term 1} = \mathrm{Tr}\left(D^>\Sigma^<D^R\Sigma^>\right) \overset{\text{use (i)}}{=} \mathrm{Tr}\left(D^R\Sigma^>D^A\Sigma^<D^R\Sigma^>\right) \overset{\text{use (ii)}}{=} (-i)^3(1+N^{eq})^2N^{eq}\mathrm{Tr}\left(D^R\Gamma D^A\Gamma D^R\Gamma\right)$$

Simply repeat the same steps 7 more times.

$$\begin{aligned} \text{Term 2} &= \mathrm{Tr}\left(D^A\Sigma^<D^<\Sigma^>\right) = (-i)^3(1+N^{eq})N^{eq^2}\mathrm{Tr}\left(D^A\Gamma D^R\Gamma D^A\Gamma\right) \\ \text{Term 3} &= \mathrm{Tr}\left(D^A\Sigma^<D^>\Sigma^<\right) = (-i)^3(1+N^{eq})N^{eq^2}\mathrm{Tr}\left(D^A\Gamma D^R\Gamma D^A\Gamma\right) \\ \text{Term 4} &= \mathrm{Tr}\left(D^>\Sigma^<D^>\Sigma^A\right) = (-i)^3(1+N^{eq})^2N^{eq}\mathrm{Tr}\left(D^R\Gamma D^A\Gamma D^R\Gamma D^A\Sigma^A\right) \\ \text{Term 5} &= \mathrm{Tr}\left(D^<\Sigma^RD^<\Sigma^>\right) = (-i)^3(1+N^{eq})N^{eq^2}\mathrm{Tr}\left(D^R\Gamma D^A\Sigma^RD^R\Gamma D^A\Gamma\right) \\ \text{Term 6} &= \mathrm{Tr}\left(D^<\Sigma^>D^R\Sigma^>\right) = (-i)^3(1+N^{eq})^2N^{eq}\mathrm{Tr}\left(D^R\Gamma D^A\Gamma D^R\Gamma\right) \\ \text{Term 7} &= \mathrm{Tr}\left(D^<\Sigma^RD^>\Sigma^<\right) = (-i)^3(1+N^{eq})N^{eq^2}\mathrm{Tr}\left(D^R\Gamma D^A\Sigma^RD^R\Gamma D^A\Gamma\right) \\ \text{Term 8} &= \mathrm{Tr}\left(D^<\Sigma^>D^>\Sigma^A\right) = (-i)^3(1+N^{eq})^2N^{eq}\mathrm{Tr}\left(D^R\Gamma D^A\Gamma D^R\Gamma D^A\Sigma^A\right) \end{aligned}$$

And the pairwise cancellation is as follows: term 4 cancels term 8, term 5 cancels term 7, term 6 cancels term 1 and term 2 cancels term 3.

Insert these identities into $S(\omega = 0)$ to get,

$$
\begin{aligned}
& S(\omega=0) \\
= \quad & \frac{1}{2}\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \\
& \times \mathrm{Tr}\left[N^{eq(L)}\Gamma^{(L)}D^{(C)R}\left(\Gamma^{(L)}+\Gamma^{(R)}\right)D^{(C)A}\right. \\
& +\left(1+2N^{eq(L)}\right)\Gamma^{(L)}D^{(C)R}\left(N^{eq(L)}\Gamma^{(L)}+N^{eq(R)}\Gamma^{(R)}\right)D^{(C)A} \\
& -D^{(C)R}\left(\Gamma^{(L)}+\Gamma^{(R)}\right)D^{(C)A}N^{eq(L)}\Gamma^{(L)}D^{(C)R}\left(\Gamma^{(L)}+\Gamma^{(R)}\right)D^{(C)A}\Gamma^{(L)} \\
& -D^{(C)R}\left(\Gamma^{(L)}+\Gamma^{(R)}\right)D^{(C)A}\left(1+2N^{eq(L)}\right)\Gamma^{(L)}D^{(C)R}\left(N^{eq(L)}\Gamma^{(L)}+N^{eq(R)}\Gamma^{(R)}\right)D^{(C)A}\Gamma^{(L)} \\
& -N^{eq(L)}\left(1+N^{eq(L)}\right)\left(-D^{(C)R}\left(\Gamma^{(L)}+\Gamma^{(R)}\right)D^{(C)A}\Gamma^{(L)}D^{(C)R}\left(\Gamma^{(L)}+\Gamma^{(R)}\right)D^{(C)A}\Gamma^{(L)}\right. \\
& \left.+2D^{(C)R}\Gamma^{(L)}D^{(C)A}\Gamma^{(L)}\right) \\
& +D^{(C)R}\left(N^{eq(L)}\Gamma^{(L)}+N^{eq(R)}\Gamma^{(R)}\right)D^{(C)A}\Gamma^{(L)}D^{(C)R}\left(\Gamma^{(L)}+\Gamma^{(R)}\right)D^{(C)A}\Gamma^{(L)} \\
& \left.+D^{(C)R}\left(N^{eq(L)}\Gamma^{(L)}+N^{eq(R)}\Gamma^{(R)}\right)D^{(C)A}\Gamma^{(L)}D^{(C)R}\left(N^{eq(L)}\Gamma^{(L)}+N^{eq(R)}\Gamma^{(R)}\right)D^{(C)A}\Gamma^{(L)}\right]
\end{aligned}
\tag{3.334}
$$

Since the final result should be symmetric in the left and right leads, the coefficients of terms which are not symmetrical in left and right should be zero. We pick out these coefficients and check them explicitly.

$$
\begin{aligned}
& \text{coefficient of term } \Gamma^{(L)^4}\Gamma^{(R)^0} \\
= \quad & -N^{eq(L)}-\left(1+2N^{eq(L)}\right)N^{eq(L)}+N^{eq(L)}\left(1+N^{eq(L)}\right)+N^{eq(L)}+N^{eq(L)}N^{eq(L)} \\
| \quad & \text{expand all terms and they cancel} \\
= \quad & 0
\end{aligned}
$$

$$
\begin{aligned}
& \text{coefficient of term } \Gamma^{(L)^3}\Gamma^{(R)} \\
= \quad & -2N^{eq(L)}-\left(1+2N^{eq(L)}\right)N^{eq(L)}-\left(1+2N^{eq(L)}\right)N^{eq(R)} \\
& +2N^{eq(L)}\left(1+N^{eq(L)}\right)+N^{eq(L)}+N^{eq(R)}+2N^{eq(L)}N^{eq(R)} \\
| \quad & \text{expand all terms and they cancel} \\
= \quad & 0
\end{aligned}
$$

$$
\begin{aligned}
& \text{coefficient of term } \Gamma^{(L)^2}\Gamma^{(R)^0} \\
= \quad & N^{eq(L)}+\left(1+2N^{eq(L)}\right)N^{eq(L)}-2N^{eq(L)}\left(1+N^{eq(L)}\right) \\
| \quad & \text{expand all terms and they cancel} \\
= \quad & 0
\end{aligned}
$$

Now we gather the remaining terms and use the definition of the transmission operator to simplify the expression $S(\omega = 0)$.

$$\begin{aligned}
S(0) &= \frac{1}{2}\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \mathrm{Tr}\left[N^{eq(L)}\Gamma^{(L)}D^{(C)R}\Gamma^{(R)}D^{(C)A} + \left(1+2N^{eq(L)}\right)\Gamma^{(L)}D^{(C)R}N^{eq(R)}\Gamma^{(R)}D^{(C)A}\right. \\
& -D^{(C)R}\Gamma^{(R)}D^{(C)A}N^{eq(L)}\Gamma^{(L)}D^{(C)R}\Gamma^{(R)}D^{(C)A}\Gamma^{(L)} \\
& -D^{(C)R}\Gamma^{(R)}D^{(C)A}\left(1+2N^{eq(L)}\right)\Gamma^{(L)}D^{(C)R}N^{eq(R)}\Gamma^{(R)}D^{(C)A}\Gamma^{(L)} \\
& +N^{eq(L)}\left(1+N^{eq(L)}\right)D^{(C)R}\Gamma^{(R)}D^{(C)A}\Gamma^{(L)}D^{(C)R}\Gamma^{(R)}D^{(C)A}\Gamma^{(L)} \\
& +D^{(C)R}N^{eq(R)}\Gamma^{(R)}D^{(C)A}\Gamma^{(L)}D^{(C)R}\Gamma^{(R)}D^{(C)A}\Gamma^{(L)} \\
& \left.+D^{(C)R}N^{eq(R)}\Gamma^{(R)}D^{(C)A}\Gamma^{(L)}D^{(C)R}N^{eq(R)}\Gamma^{(R)}D^{(C)A}\Gamma^{(L)}\right] \qquad (3.335)
\end{aligned}$$

| use the definition of transmission operator

$$\begin{aligned}
&= \frac{1}{2}\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \mathrm{Tr}\left[N^{eq(L)}\mathcal{T} + \left(1+2N^{eq(L)}\right)N^{eq(R)}\mathcal{T} - N^{eq(L)}\mathcal{T}^2 - \left(1+2N^{eq(L)}\right)N^{eq(R)}\mathcal{T}^2\right. \\
& \left.+N^{eq(L)}\left(1+N^{eq(L)}\right)\mathcal{T}^2 + N^{eq(R)}\mathcal{T}^2 + N^{eq(R)^2}\mathcal{T}^2\right] \qquad (3.336)
\end{aligned}$$

| write terms involving $\mathcal{T}$ into a symmetric form

$$= \frac{1}{2}\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \mathrm{Tr}\left[\mathcal{T}\left(N^{eq(L)}\left(1+N^{eq(R)}\right) + N^{eq(R)}\left(1+N^{eq(L)}\right)\right) + \mathcal{T}^2\left(N^{eq(L)} - N^{eq(R)}\right)^2\right]$$

$$\boxed{\begin{aligned}&S(\omega = 0)\\ &= \frac{1}{2}\int \frac{d\omega}{2\pi}(\hbar\omega)^2 \mathrm{Tr}\left[\mathcal{T}\left(N^{eq(L)}\left(1+N^{eq(R)}\right) + N^{eq(R)}\left(1+N^{eq(L)}\right)\right) + \mathcal{T}^2\left(N^{eq(L)} - N^{eq(R)}\right)^2\right]\end{aligned}} \qquad (3.337)$$

which is indeed the expression for the DC thermal noise in ballistic phonon transport. To make contact with Satio & Dhar's expression in [Saito2007] eqn (9), recall $N^{eq}(-\omega) = -(1 + N^{eq}(\omega))$.

We give an immediate physical interpretation to the noise expression:

- The term $\mathcal{T}\left(N^{eq(L)}\left(1+N^{eq(R)}\right) + N^{eq(R)}\left(1+N^{eq(L)}\right)\right)$ is called the equilibrium thermal noise. At $T \to 0$, $N^{eq(L)}, N^{eq(R)} \to 0$ so this noise term vanishes at zero temperature [33]. Thermal fluctuations of occupation numbers in the leads seem to be the source of this noise term [34].

- The term $\mathcal{T}^2\left(N^{eq(L)} - N^{eq(R)}\right)^2$ is the nonequilibrium noise. Assuming the left and right leads have the same harmonic spectrum, when the leads have the same temperature, we have $N^{eq(L)} = N^{eq(R)}$ and this noise term vanishes. Obviously it also vanishes at zero temperature. Hence this noise contribution is essentially due to the magnitude of the temperature difference between the 2 leads.

[Contribution:] Here I will briefly state what this contribution is about. Note that noise is an important quantity to measure as it may provide more information on the current on top of information obtained by conductance measurements. The result here is not new but this method of derivation shows a way of calculating the AC ($\omega \neq 0$) noise and/or including interactions which is done in Chapter 5. AC

[33] These are phonons and so there is no Bose Einstein Condensation (BEC)!

[34] In statistical mechanics, we calculate the dispersion of occupation numbers via $\overline{N^2} - \overline{N}^2 = -k_B T \frac{\partial \overline{N}}{\partial E}$ with $\overline{N} = N^{eq}$ in this case. The result is simply $\overline{N^2} - \overline{N}^2 = N^{eq}(1 + N^{eq})$. Thus the noise term is made up of dispersions of left and right leads occupation numbers.

noise may not be that physically relevant but as mentioned in the Introduction (Chapter 2), interactions cannot really be ignored at the working temperature of these devices. It is not clear how to include interactions in the calculation of noise using Saito and Dhar's method.

3.3 From NEGF to Quantum Kinetic Equations (QKE)

3.3.1 Pre-Kinetic (pre-QKE) Equations

This is the second development from NEGF. Essentially, NEGF allows a rigorous derivation of kinetic equations and that means the quantum corrections to kinetic equations can be calculated rigorously. The main advantages of kinetic equations (to my knowledge) are that physical quantities are easy to construct and thus physical interpretations are not obscure.

We start by rewriting Kadanoff-Baym (KB) equations into the Pre-Quantum Kinetic Equations (or pre-QKE equations).[35]

The credits for the fundamental and deep physical insight that NEGF actually allows this rigorous derivation are undoubtedly due to Kadanoff, Baym and Keldysh in [Kadanoff1962] and in [Keldysh1965] respectively. Here we follow chapter 5 of [Haug2007]. We use the Kadanoff-Baym equations in (particle statistics independent) symbolic form to save writing and we are concerned with the evolution after $V(t)$ has been switched on. We will only use the Kadanoff-Baym equations for $G^<$ and $G^>$ since the quantities are related to the particle numbers.[36]

The left KB equations are

$$G^{(0)-1}G^< = \int_t \Sigma^R G^< + \int_t \Sigma^< G^A + \int_{\tau^M} \Sigma^{\urcorner} G^{\ulcorner} \quad (1) \tag{3.338}$$

$$G^{(0)-1}G^> = \int_t \Sigma^R G^> + \int_t \Sigma^> G^A + \int_{\tau^M} \Sigma^{\urcorner} G^{\ulcorner} \quad (2) \tag{3.339}$$

The other KB equations determine $G^{\ulcorner}$ which brings in the effects from the initially correlated state. The right KB equations are (here we write $G^{(0)-1}$ on the right side of $G^<$ and $G^>$ simply to serve as a reminder that this is the right KB equation)

$$G^< G^{(0)-1} = \int_t G^R \Sigma^< + \int_t G^< \Sigma^A + \int_{\tau^M} G^{\urcorner} \Sigma^{\ulcorner} \quad (3) \tag{3.340}$$

$$G^> G^{(0)-1} = \int_t G^R \Sigma^> + \int_t G^> \Sigma^A + \int_{\tau^M} G^{\urcorner} \Sigma^{\ulcorner} \quad (4) \tag{3.341}$$

Take (1) - (3) to get

$$\left[G^{(0)-1}, G^<\right]_- = \int_t \Sigma^R G^< - \int_t G^< \Sigma^A + \int_t \Sigma^< G^A - \int_t G^R \Sigma^< + \int_{\tau^M} \Sigma^{\urcorner} G^{\ulcorner} - \int_{\tau^M} G^{\urcorner} \Sigma^{\ulcorner} \tag{3.342}$$

$$| \quad \text{label the last 2 terms as "initial"}$$

$$= \int_t \Sigma^R G^< - \int_t G^< \Sigma^A + \int_t \Sigma^< G^A - \int_t G^R \Sigma^< + \text{"initial"} \tag{3.343}$$

[35] We take Kinetic equations to be equations that concern the evolution of a single time distribution function. Pre-QKE equations still deal with a 2-time quantity.

[36] Recall that $G^<$ is of the form $\langle a^\dagger a\rangle$ or $\langle \psi^\dagger \psi\rangle$ and $G^>$ is of the form $\langle a a^\dagger\rangle$ and $\langle \psi\psi^\dagger\rangle$ which are related to particle number operators.

Take (2) - (4) to get

$$\begin{aligned}
\left[G^{(0)-1}, G^{>}\right]_{-} &= \int_t \Sigma^R G^> - \int_t G^> \Sigma^A + \int_t \Sigma^> G^A - \int_t G^R \Sigma^> + \int_{\tau^M} \Sigma^{\rceil} G^{\lceil} - \int_{\tau^M} G^{\rceil} \Sigma^{\lceil} && (3.344)\\
&\mid \ \text{label the last 2 terms as "initial"}\\
&= \int_t \Sigma^R G^> - \int_t G^> \Sigma^A + \int_t \Sigma^> G^A - \int_t G^R \Sigma^> + \text{"initial"} && (3.345)
\end{aligned}$$

We define these identities to symmetrize the retarded and advanced expressions (C is arbitrary)

$$\begin{aligned}
C^R &\equiv \frac{1}{2}\left(C^R + C^A\right) + \frac{1}{2}\left(C^R - C^A\right) && (3.346)\\
C^A &\equiv \frac{1}{2}\left(C^R + C^A\right) + \frac{1}{2}\left(C^A - C^R\right) && (3.347)
\end{aligned}$$

and symmetrize the RHS 4 terms of the $G^<$ equation.

$$\begin{aligned}
&\left[G^{(0)-1}, G^{<}\right]_{-} - \text{"initial"}\\
&= \int_t \left(\Sigma^R G^< - G^< \Sigma^A + \Sigma^< G^A - G^R \Sigma^<\right) && (3.348)\\
&= \int_t \Bigg(\frac{1}{2}\left(\Sigma^R + \Sigma^A\right) G^< + \frac{1}{2}\left(\Sigma^R - \Sigma^A\right) G^< - G^< \frac{1}{2}\left(\Sigma^R + \Sigma^A\right) - G^< \frac{1}{2}\left(\Sigma^A - \Sigma^R\right)\\
&\quad + \Sigma^< \frac{1}{2}\left(G^A + G^R\right) + \Sigma^< \frac{1}{2}\left(G^A - G^R\right) - \frac{1}{2}\left(G^R + G^A\right)\Sigma^< - \frac{1}{2}\left(G^R - G^A\right)\Sigma^<\Bigg)\\
&\mid \ \text{use } G^R - G^A = G^> - G^<\\
&= \int_t \left(\frac{1}{2}\left[\Sigma^R + \Sigma^A, G^<\right]_- + \frac{1}{2}\left[\Sigma^R - \Sigma^A, G^<\right]_+ + \frac{1}{2}\left[\Sigma^<, G^R + G^A\right]_- + \frac{1}{2}\left[\Sigma^<, G^< - G^>\right]_+\right)\\
&\mid \ \text{use } \Sigma^R - \Sigma^A = \Sigma^> - \Sigma^<\\
&= \int_t \left(\frac{1}{2}\left[\Sigma^R + \Sigma^A, G^<\right]_- + \frac{1}{2}\left[\Sigma^<, G^R + G^A\right]_- + \frac{1}{2}\left[\Sigma^> - \Sigma^<, G^<\right]_+ + \frac{1}{2}\left[\Sigma^<, G^< - G^>\right]_+\right)\\
&= \int_t \left(\frac{1}{2}\left[\Sigma^R + \Sigma^A, G^<\right]_- + \frac{1}{2}\left[\Sigma^<, G^R + G^A\right]_- + \frac{1}{2}\left[\Sigma^>, G^<\right]_+ - \frac{1}{2}\left[\Sigma^<, G^>\right]_+\right) && (3.349)\\
&\mid \ \text{we rewrite a bit more following [Haug2007]}\\
&\mid \ \text{since the self energies and Green's functions are complex,}\\
&\mid \ \text{we write } \Sigma^R + \Sigma^A = 2\Re\Sigma^{\text{R or A}} \text{ and } G^R + G^A = 2\Re G^{\text{R or A}}\\
&= \int_t \left(\frac{1}{2}\left[\Re\Sigma^{\text{R or A}}, G^<\right]_- + \frac{1}{2}\left[\Sigma^<, \Re G^{\text{R or A}}\right]_- + \frac{1}{2}\left[\Sigma^>, G^<\right]_+ - \frac{1}{2}\left[\Sigma^<, G^>\right]_+\right) && (3.350)
\end{aligned}$$

Similarly for $G^>$, we get

$$\begin{aligned}
&\left[G^{(0)-1}, G^{>}\right]_{-} - \text{"initial"}\\
&= \int_t \left(\frac{1}{2}\left[\Sigma^R + \Sigma^A, G^>\right]_- + \frac{1}{2}\left[\Sigma^>, G^R + G^A\right]_- + \frac{1}{2}\left[\Sigma^>, G^<\right]_+ - \frac{1}{2}\left[\Sigma^<, G^>\right]_+\right) && (3.351)
\end{aligned}$$

Note that for the case of electrons subjected to a switched on external field V, we just need to modify the LHS as follows,

$$\left[G^{(0)-1}, G^{\gtrless}\right]_- \longrightarrow \left[G^{(0)-1} - V, G^{\gtrless}\right]_- \tag{3.352}$$

In anticipation of the gradient expansion approximation later, we define the spectral function and the level width function.

$$\text{Spectral function} \quad : \quad A \equiv i(G^R - G^A) = i(G^> - G^<) \tag{3.353}$$

$$\text{Level width function} \quad : \quad \Gamma \equiv i(\Sigma^R - \Sigma^A) = i(\Sigma^> - \Sigma^<) \tag{3.354}$$

then the pre-QKE equations become (use the second last line for easier rewriting),

$$\begin{aligned} & \left[G^{(0)-1}, G^<\right]_- - \text{“initial”} \\ = & \int_t \left(\frac{1}{2}\left[\Sigma^R + \Sigma^A, G^<\right]_- + \frac{1}{2}\left[\Sigma^<, G^R + G^A\right]_- + \frac{1}{2i}\left[\Gamma, G^<\right]_+ - \frac{1}{2i}\left[A, \Sigma^<\right]_+ \right) \end{aligned} \tag{3.355}$$

$$\begin{aligned} & \left[G^{(0)-1}, G^>\right]_- - \text{“initial”} \\ = & \int_t \left(\frac{1}{2}\left[\Sigma^R + \Sigma^A, G^>\right]_- + \frac{1}{2}\left[\Sigma^>, G^R + G^A\right]_- + \frac{1}{2i}\left[\Gamma, G^<\right]_+ - \frac{1}{2i}\left[A, \Sigma^<\right]_+ \right) \end{aligned} \tag{3.356}$$

Note that the subtraction has caused the loss of boundary conditions, so (according to Gerald D. Mahan in [Mahan2000] pg 554) we should actually solve the retarded Green's function from the (retarded) Dyson's equation and use that G^R to solve the pre-QKE (or QKE) equations. Note that in general, as can be seen from the Kadanoff-Baym equations, the lesser or greater KB equations are coupled to the retarded or advanced Green's functions. Thus, typically, the lesser or greater KB equations and the retarded or advanced Dyson's equations are to be solved simultaneously.

3.3.2 QKE based on Kadanoff-Baym (KB) Ansatz

[Transformation to Wigner coordinates and gradient expansion] The main idea in employing Wigner coordinates, i.e. going to center and relative coordinates is that the center coordinates describe the "center of mass (CM)" of the phase space distribution and thus provide a way to handle the dynamics of the distribution as a whole. When we assume that the system is near equilibrium, we can say that the center coordinates are slowly varying. Then, we can further assume that the Green's functions are sharply peaked near where the relative coordinates ≈ 0 (think of the equilibrium Green's functions for motivation). A gradient expansion, which is a Taylor expansion in the small relative coordinates, allows the "sharply peaked" correlation to be retained in the theory while simplifying the equations.

The Green's function that we choose to calculate is [37]

$$D^<_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 t_2) = D^<_{j_1 j_2}(\vec{q}_1 t_1 \vec{q}_2 t_2) = -\frac{i}{\hbar}\left\langle Q_{Hj_2}(\vec{q}_2 t_2) Q_{Hj_1}(\vec{q}_1 t_1)\right\rangle \tag{3.357}$$

[37] For electrons, in the kinetic description, the (distribution of) electrons are driven by an external field and there are collisions/interactions within the distribution. See the appendix for the derivation. For phonons, in the kinetic description, the (distribution of) phonons are "driven" by temperature gradients which is not a mechanical perturbation and so there is not perturbation Hamiltonian for it. We follow Peierls in [Peierls2001] and take that into account by treating the phonon distribution as a function of position. The Hamiltonian H is the sum of the harmonic and the anharmonic terms but we will not state it as it might cause the misunderstanding that time-independent Hamiltonians has no kinetic description in the first place!

The contour time (left and right) Dyson's equations are,

$$\text{left:} \quad \left(\frac{\partial^2}{\partial \tau_1^2} + \omega^2_{j_1\vec{q}_1}\right) D_{j_1j_2}(\vec{q}_1\tau_1\vec{q}_2\tau_2) = \delta_{j_1j_2}\delta_{\vec{q}_1\vec{q}_2}\delta(\tau_1,\tau_2) + \int_{c_K} \Sigma D \tag{3.358}$$

$$\text{right:} \quad \left(\frac{\partial^2}{\partial \tau_2^2} + \omega^2_{j_2\vec{q}_2}\right) D_{j_1j_2}(\vec{q}_1\tau_1\vec{q}_2\tau_2) = \delta_{j_1j_2}\delta_{\vec{q}_1\vec{q}_2}\delta(\tau_1,\tau_2) + \int_{c_K} D\Sigma \tag{3.359}$$

With Langreth's theorem for the lesser component, we get the pre-QKE by subtracting the left and right equations to get (we wrote $t_0 \to -\infty$ to indicate that the "initial" terms are dropped),

$$\left(\frac{\partial^2}{\partial t_1^2} - \frac{\partial^2}{\partial t_2^2} + \omega^2_{j_1\vec{q}_1} - \omega^2_{j_2\vec{q}_2}\right) D^<_{j_1j_2}(\vec{q}_1t_1\vec{q}_2t_2) = \int_{t_0\to\infty} \Sigma^R D^< + \Sigma^< D^A - D^R\Sigma^< - D^<\Sigma^A \tag{3.360}$$

We will work with the LHS of pre-QKE and RHS of pre-QKE seperately. We introduce Wigner coordinates and apply it to LHS first.[38]

$$\begin{array}{rll} \text{Wigner Coordinates:} & \vec{q}_1^{\,+} = \frac{1}{2}(\vec{q}_1 + \vec{q}_2) & t_1^+ = \frac{1}{2}(t_1+t_2) \\ & \vec{q}_1^{\,-} = \vec{q}_1 - \vec{q}_2 & t_1^- = t_1 + t_2 \\ \text{Inverse:} & \vec{q}_1 = \vec{q}_1^{\,+} + \frac{1}{2}\vec{q}_1^{\,-} & t_1 = t_1^+ + \frac{1}{2}t_1^- \\ & \vec{q}_2 = \vec{q}_1^{\,+} - \frac{1}{2}\vec{q}_1^{\,-} & t_2 = t_1^+ - \frac{1}{2}t_1^- \end{array} \tag{3.361}$$

So we rewrite the LHS as

$$\begin{aligned}
\text{LHS first term} &= \frac{\partial^2}{\partial t_1^2} - \frac{\partial^2}{\partial t_2^2} && (3.362)\\
&= \left(\frac{\partial t_1^+}{\partial t_1}\frac{\partial}{t_1^+} + \frac{\partial t_1^-}{\partial t_1}\frac{\partial}{\partial t_1^-}\right)^2 - \left(\frac{\partial t_1^+}{\partial t_2}\frac{\partial}{t_1^+} + \frac{\partial t_1^-}{\partial t_2}\frac{\partial}{\partial t_1^-}\right)^2 && (3.363)\\
&= \left(\frac{1}{2}\frac{\partial}{\partial t_1^+} + \frac{\partial}{\partial t_1^-}\right)^2 - \left(\frac{1}{2}\frac{\partial}{\partial t_1^+} - \frac{\partial}{\partial t_1^-}\right)^2 && (3.364)\\
&= 2\frac{\partial}{\partial t_1^+}\frac{\partial}{\partial t_1^-} && (3.365)
\end{aligned}$$

$$\begin{aligned}
\text{LHS second term} &= \omega^2_{j_1\vec{q}_1} - \omega^2_{j_2\vec{q}_2} && (3.366)\\
&= \omega^2_{j_1}(\vec{q}_1) - \omega^2_{j_2}(\vec{q}_2) && (3.367)\\
&= \omega^2_{j_1}(\vec{q}_1^{\,+} + \frac{1}{2}\vec{q}_1^{\,-}) - \omega^2_{j_2}(\vec{q}_1^{\,+} - \frac{1}{2}\vec{q}_1^{\,-}) && (3.368)\\
&\mid \quad \text{Taylor expand (gradient expansion) to first order} \\
&\approx \left(1 + \frac{1}{2}\vec{q}_1 \cdot \nabla_{\vec{q}_1^{\,+}}\right)\omega^2_{j_1}(\vec{q}_1^{\,+}) - \left(1 - \frac{1}{2}\vec{q}_1^{\,-} \cdot \nabla_{\vec{q}_1^{\,+}}\right)\omega^2_{j_2}(\vec{q}_1^{\,+}) && (3.369)\\
&\mid \quad \text{take } j_1 = j_2 \text{ now} \\
&= \vec{q}_1^{\,-} \cdot \nabla_{\vec{q}_1^{\,+}}\omega^2_{j_1\vec{q}_1^{\,+}} && (3.370)
\end{aligned}$$

[38]Note that the coordinate transformation has Jacobian = 1 where the Jacobian is the absolute value of the determinant of the Jacobian matrix.

The LHS of pre-QKE is now [39]

$$\text{LHS} = \left(2\frac{\partial}{\partial t_1^+}\frac{\partial}{\partial t_1^-} + \left(\vec{q}_1^{\,-}\cdot\nabla_{\vec{q}_1^{\,+}}\omega^2_{j_1\vec{q}_1^{\,+}}\right)\right) D^<_{j_1j_2}(\vec{q}_1^{\,-}t_1^-\vec{q}_1^{\,+}t_1^+)\Big|_{j_1=j_2} \tag{3.371}$$

Now define the Fourier transform so that we can move over to QKE. We will Fourier transform the variables $\vec{q}_1^{\,-}\to\vec{r}_1$ and $t_1^-\to\omega_1$.[40]

$$D(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) = \int\frac{d\vec{q}_1^{\,-}}{(2\pi)^3}\int dt_1^- e^{i\vec{q}^{\,-}\cdot\vec{r}_1+i\omega_1t_1^-}D(\vec{q}_1^{\,-}t_1^-\vec{q}_1^{\,+}t_1^+) \tag{3.372}$$

We apply it to LHS of QKE

$$\begin{aligned}
\text{LHS first term} &= 2\frac{\partial}{\partial t_1^+}\frac{\partial}{\partial t_1^-}D^<_{j_1j_2}(\vec{q}_1^{\,-}t_1^-\vec{q}_1^{\,+}t_1^+) && (3.373)\\
&= 2\frac{\partial}{\partial t_1^+}\frac{\partial}{\partial t_1^-}\int d\vec{r}_1\frac{d\omega_1}{2\pi}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_1-i\omega_1t_1^-}D^<_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) && (3.374)\\
&= \frac{\partial}{\partial t_1^+}\int d\vec{r}_1\frac{d\omega_1}{2\pi}\frac{2\omega_1}{i}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_1-i\omega_1t_1^-}D^<_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) && (3.375)
\end{aligned}$$

$$\begin{aligned}
\text{LHS second term} &= \vec{q}_1^{\,-}\cdot\nabla_{\vec{q}_1^{\,+}}\omega^2_{j_1\vec{q}_1^{\,+}}\int d\vec{r}_1\frac{d\omega_1}{2\pi}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_1-i\omega_1t_1^-}D^<_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) && (3.376)\\
&= \int d\vec{r}_1\frac{d\omega_1}{2\pi}\left(i\nabla_{\vec{r}_1}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_1}\right)\cdot\left(\nabla_{\vec{q}_1^{\,+}}\omega^2_{j_1\vec{q}_1^{\,+}}\right)D^<_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) && (3.377)\\
&\mid\ \text{integrate by parts for } \nabla_{\vec{r}_1}\text{ and drop surface term}\\
&= \int d\vec{r}_1\frac{d\omega_1}{2\pi}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_1-i\omega_1t_1^-}\left(-i\nabla_{\vec{q}_1^{\,+}}\omega^2_{j_1\vec{q}_1^{\,+}}\right)\cdot\left(\nabla_{\vec{r}_1}D^<_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right) && (3.378)
\end{aligned}$$

So,

$$\begin{aligned}
&\text{LHS of pre-QKE}\\
&= \int d\vec{r}_1\frac{d\omega_1}{2\pi}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_1-i\omega_1t_1^-}\left((-2i\omega_1)\frac{\partial}{\partial t_1^+}+(-2i\omega_{j_1\vec{q}_1^{\,+}})\left(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}}\right)\cdot\nabla_{\vec{r}_1}\right)D^<_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)
\end{aligned} \tag{3.379}$$

We only require the Fourier component (which is a single normal mode component here) which is simply,

$$\begin{aligned}
&\text{LHS of pre-QKE (Fourier component)}\\
&= \left((-2i\omega_1)\frac{\partial}{\partial t_1^+}+(-2i\omega_{j_1\vec{q}_1^{\,+}})\left(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}}\right)\cdot\nabla_{\vec{r}_1}\right)D^<_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)
\end{aligned} \tag{3.380}$$

Now we go over to the RHS and transform to Wigner coordinates, gradient expand [41] to first order

[39] The LHS represents the driving term for the phonon distribution, so one can interprete the imposition of $j_1 = j_2$ as that the temperature gradient drives each phonon branch seperately.

[40] Note that we are restricting our description to one phonon branch and the normal mode transform of one branch is just like a Fourier transform. The "mixing" of the branches will enter the RHS (collision term) due to anharmonic interactions. The physical meaning of $\vec{r}$ was already mentioned. It is to denote the fact that driving by a temperature gradient results in a position dependent distribution.

[41] Gradient expansion is simply Taylor expansion in Wigner coordinates about the center of mass variables.

and extract the Fourier component.

$$
\begin{aligned}
& \text{RHS of pre-QKE} \\
= & \int_{t_0\to-\infty}^{\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \Big(\Sigma^R_{j_1j_3}(\vec{q}_1 t_1 \vec{q}_3 t_3) D^<_{j_3j_2}(\vec{q}_3 t_3 \vec{q}_2 t_2) + \Sigma^<_{j_1j_3}(\vec{q}_1 t_1 \vec{q}_3 t_3) D^R_{j_3j_2}(\vec{q}_3 t_3 \vec{q}_2 t_2) \\
& - D^R_{j_1j_3}(\vec{q}_1 t_1 \vec{q}_3 t_3) \Sigma^<_{j_3j_2}(\vec{q}_3 t_3 \vec{q}_2 t_2) - D^<_{j_1j_3}(\vec{q}_1 t_1 \vec{q}_3 t_3) \Sigma^A_{j_3j_2}(\vec{q}_3 t_3 \vec{q}_2 t_2) \Big) \qquad (3.381) \\
| \quad & \text{write the retarded and advanced functions into the lesser and greater functions} \\
= & \int_{t_0\to-\infty}^{t_1} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(\Sigma^> - \Sigma^<\right)_{j_1j_3} (\vec{q}_1 t_1 \vec{q}_3 t_3) D^<_{j_3j_2}(\vec{q}_3 t_3 \vec{q}_2 t_2) \\
& + \int_{t_0\to-\infty}^{t_2} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \Sigma^<_{j_1j_3}(\vec{q}_1 t_1 \vec{q}_3 t_3) \left(D^< - D^>\right)_{j_3j_2} (\vec{q}_3 t_3 \vec{q}_2 t_2) \\
& - \int_{t_0\to-\infty}^{t_1} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(D^> - D^<\right)_{j_1j_3} (\vec{q}_1 t_1 \vec{q}_3 t_3) \Sigma^<_{j_3j_2}(\vec{q}_3 t_3 \vec{q}_2 t_2) \\
& - \int_{t_0\to-\infty}^{t_2} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} D^<_{j_1j_3}(\vec{q}_1 t_1 \vec{q}_3 t_3) \left(\Sigma^< - \Sigma^>\right)_{j_3j_2} (\vec{q}_3 t_3 \vec{q}_2 t_2) \qquad (3.382)
\end{aligned}
$$

We go over to Wigner coordinates and gradient expand to first order term by term.

$$
\begin{aligned}
& \text{RHS of pre-QKE first line} \\
= & \int_{t_0\to-\infty}^{t_1} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(\Sigma^> - \Sigma^<\right)_{j_1j_3} (\vec{q}_1 t_1 \vec{q}_3 t_3) D^<_{j_3j_2}(\vec{q}_3 t_3 \vec{q}_2 t_2) \qquad (3.383) \\
= & \int_{t_0\to-\infty}^{t_1} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \\
& \times \left(\Sigma^> - \Sigma^<\right)_{j_1j_3} (\vec{q}_1 - \vec{q}_3, t_1 - t_3, \tfrac{\vec{q}_1+\vec{q}_3}{2}, \tfrac{t_1+t_3}{2}) D^<_{j_3j_2}(\vec{q}_3 - \vec{q}_2, t_3 - t_2, \tfrac{\vec{q}_3+\vec{q}_2}{2}, \tfrac{t_3+t_2}{2}) \qquad (3.384) \\
| \quad & \text{change } \vec{q}_3 \to \vec{q}_4 \text{ by } \vec{q}_3 = \vec{q}_2 + \vec{q}_4 \text{ and } t_3 \to t_4 \text{ by } t_3 = t_2 + t_4 \\
| \quad & \text{recall the definition of the Wigner coordinates } t_1^+,\ t_1^-,\ \vec{q}_1^{\,+} \text{ and } \vec{q}_1^{\,-} \\
= & \int_{-\infty}^{t_1-t_2} dt_4 \int \frac{d\vec{q}_4}{(2\pi)^3} \sum_{j_3} \left(\Sigma^> - \Sigma^<\right)_{j_1j_3} (\vec{q}_1^{\,-} - \vec{q}_4, t_1^- - t_4, \vec{q}_1^{\,+} + \tfrac{1}{2}\vec{q}_4, t_1^+ + \tfrac{1}{2}t_4) \\
& \times D^<_{j_3j_2}(\vec{q}_4, t_4, \vec{q}_1^{\,+} - \frac{1}{2}\vec{q}_1^{\,-} + \frac{1}{2}\vec{q}_4, t_1^+ - \frac{1}{2}t_1^- + \frac{1}{2}t_4) \qquad (3.385) \\
= & \int_{-\infty}^{t_1^-} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(\Sigma^> - \Sigma^<\right)_{j_1j_3} (\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+} + \tfrac{1}{2}\vec{q}_3, t_1^+ + \tfrac{1}{2}t_3) \\
& \times D^<_{j_3j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+} - \frac{1}{2}\vec{q}_1^{\,-} + \frac{1}{2}\vec{q}_3, t_1^+ - \frac{1}{2}t_1^- + \frac{1}{2}t_3) \qquad (3.386) \\
| \quad & \text{gradient expand to first order} \\
\approx & \int_{-\infty}^{t_1^-} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(1 + \frac{1}{2}\vec{q}_3 \cdot \nabla_{\vec{q}_1^{\,+}} + \frac{1}{2} t_3 \frac{\partial}{\partial t_1^+}\right) \left(\Sigma^> - \Sigma^<\right)_{j_1j_3} (\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+}, t_1^+) \\
& \times \left(1 + \left(-\frac{1}{2}\vec{q}_1^{\,-} + \frac{1}{2}\vec{q}_3\right) \nabla_{\vec{q}_1^{\,+}} + \left(-\frac{1}{2}t_1^- + \frac{1}{2}t_3\right) \frac{\partial}{\partial t_1^+}\right) D^<_{j_3j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+}, t_1^+) \qquad (3.387) \\
| \quad & \text{seperate the zeroth order and first order terms}
\end{aligned}
$$

$$
\begin{aligned}
= \quad & \int_{-\infty}^{t_1^-} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(\Sigma^> - \Sigma^<\right)_{j_1 j_3} (\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+} t_1^+) D^<_{j_3 j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+}, t_1^+) \\
& + \int_{-\infty}^{t_1^-} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(\vec{q}_3 \cdot \nabla_{\vec{q}_1^{\,+}} + t_3 \frac{\partial}{\partial t_1^+} - (\vec{q}_1^{\,-} - \vec{q}_3) \nabla_{\vec{q}_1^{\,+'}} - (t_1^- - t_3) \frac{\partial}{\partial t_1^{+'}} \right) \\
& \times \sigma_{j_1 j_3}(\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+}, t_1^+) D^<_{j_3 j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+'}, t_1^{+'}) \Bigg|_{\vec{q}_1^{\,+'} = \vec{q}^{\,+}, t_1^{+'} = t_1^+}
\end{aligned} \tag{3.388}
$$

where $\sigma_{j_1 j_3}(\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+}, t_1^+) \equiv \frac{1}{2} \left(\Sigma^> - \Sigma^<\right)_{j_1 j_3} (\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+}, t_1^+)$.

RHS of pre-QKE fourth line

$$
= \quad - \int_{t_0 \to -\infty}^{t_2} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} D^<_{j_1 j_3}(\vec{q}_1 t_1 \vec{q}_3 t_3) \left(\Sigma^< - \Sigma^>\right)_{j_3 j_2} (\vec{q}_3 t_3 \vec{q}_2 t_2) \tag{3.389}
$$

| change to centre and relative coordinates
| change $\vec{q}_3 \to \vec{q}_4$ by $\vec{q}_4 = \vec{q}_1 - \vec{q}_3$ and $t_3 \to t_4$ by $t_4 = t_1 - t_3$
| going through the same steps as above, we get to first order

$$
\begin{aligned}
\approx \quad & \int_{t_1^-}^{+\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(\Sigma^> - \Sigma^<\right)_{j_1 j_3} (\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+} t_1^+) D^<_{j_3 j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+}, t_1^+) \\
& + \int_{t_1^-}^{+\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} (-1) \left(\vec{q}_3 \cdot \nabla_{\vec{q}_1^{\,+}} + t_3 \frac{\partial}{\partial t_1^+} - (\vec{q}_1^{\,-} - \vec{q}_3) \nabla_{\vec{q}_1^{\,+'}} - (t_1^- - t_3) \frac{\partial}{\partial t_1^{+'}} \right) \\
& \times \sigma_{j_1 j_3}(\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+}, t_1^+) D^<_{j_3 j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+'}, t_1^{+'}) \Bigg|_{\vec{q}_1^{\,+'} = \vec{q}^{\,+}, t_1^{+'} = t_1^+}
\end{aligned} \tag{3.390}
$$

If we define a more general term, we can formally sum the 2 terms. Define

$$
\tilde{\sigma}_{j_1 j_2}(\vec{q}^{\,-} t^- \vec{q}^{\,+} t^+) \quad \equiv \quad \frac{t^-}{|t^-|} \sigma_{j_1 j_2}(\vec{q}^{\,-} t^- \vec{q}^{\,+} t^+) = \frac{t^-}{|t^-|} \frac{1}{2} \left(\Sigma^> - \Sigma^<\right) (\vec{q}^{\,-} t^- \vec{q}^{\,+} t^+) \tag{3.391}
$$

This definition is motivated by the fact that, in RHS first line, t^- is the upper limit and the term is positive, whereas in RHS fourth line, t^- is the lower limit and that term is negative. So now we can combine the integrals to get,

RHS first line + RHS fourth line

$$
\begin{aligned}
= \quad & \int_{-\infty}^{+\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(\Sigma^> - \Sigma^<\right)_{j_1 j_3} (\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+} t_1^+) D^<_{j_3 j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+}, t_1^+) \\
& + \int_{-\infty}^{+\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(\vec{q}_3 \cdot \nabla_{\vec{q}_1^{\,+}} + t_3 \frac{\partial}{\partial t_1^+} - (\vec{q}_1^{\,-} - \vec{q}_3) \nabla_{\vec{q}_1^{\,+'}} - (t_1^- - t_3) \frac{\partial}{\partial t_1^{+'}} \right) \\
& \times \tilde{\sigma}_{j_1 j_3}(\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+}, t_1^+) D^<_{j_3 j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+'}, t_1^{+'}) \Bigg|_{\vec{q}_1^{\,+'} = \vec{q}^{\,+}, t_1^{+'} = t_1^+}
\end{aligned} \tag{3.392}
$$

We can immediately see that a very similar situation occurs for RHS second line and RHS third line and so we can write down the terms in Wigner coordinates, gradient expanded to first order.

RHS second term + RHS third term

$$
\begin{aligned}
= & -\int_{-\infty}^{+\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(D^> - D^<\right)_{j_1 j_3} (\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+} t_1^+) \Sigma^<_{j_3 j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+}, t_1^+) \\
& -\int_{-\infty}^{+\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(\vec{q}_3 \cdot \nabla_{\vec{q}_1^{\,+}} + t_3 \frac{\partial}{\partial t_1^+} - (\vec{q}_1^{\,-} - \vec{q}_3) \nabla_{\vec{q}_1^{\,+\prime}} - (t_1^- - t_3) \frac{\partial}{\partial t_1^{+\prime}} \right) \\
& \times \tilde{b}_{j_1 j_3}(\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+}, t_1^+) \Sigma^<_{j_3 j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+\prime}, t_1^{+\prime}) \Bigg|_{\vec{q}_1^{\,+\prime} = \vec{q}^{\,+}, t_1^{+\prime} = t_1^+}
\end{aligned} \tag{3.393}
$$

where

$$
\tilde{b}_{j_1 j_2}(\vec{q}^{\,-} t^- \vec{q}^{\,+} t^+) \equiv \frac{t^-}{|t^-|} \frac{1}{2} \left(D^> - D^<\right)_{j_1 j_2} (\vec{q}^{\,-} t^- \vec{q}^{\,+} t^+) \tag{3.394}
$$

Now we proceed to extract the Fourier component. We denote the Fourier components of $\tilde{\sigma}$ and $\tilde{b}$ as,

$$
\tilde{\sigma}_{j_1 j_2}(\vec{q}^{\,-} t^- \vec{q}^{\,+} t^+) \longrightarrow \tilde{\sigma}_{j_1 j_2}(\vec{r} \omega \vec{q}^{\,+} t^+) \tag{3.395}
$$

$$
\tilde{b}_{j_1 j_2}(\vec{q}^{\,-} t^- \vec{q}^{\,+} t^+) \longrightarrow \tilde{b}_{j_1 j_2}(\vec{r} \omega \vec{q}^{\,+} t^+) \tag{3.396}
$$

We calculate for RHS second line + RHS third line and then write down the Fourier components for the other 2 lines by inspection.

RHS second line + RHS third line (zeroth order terms)

$$
= -\int_{-\infty}^{+\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \left(D^> - D^<\right)_{j_1 j_3} (\vec{q}_1^{\,-} - \vec{q}_3, t_1^- - t_3, \vec{q}_1^{\,+} t_1^+) \Sigma^<_{j_3 j_2}(\vec{q}_3, t_3, \vec{q}_1^{\,+}, t_1^+) \tag{3.397}
$$

$$
\begin{aligned}
= & -\int_{-\infty}^{+\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \int d\vec{r}_1 d\omega_1 e^{-i\vec{r}_1 \cdot (\vec{q}_1^{\,-} - \vec{q}_3) - i\omega_1 (t_1^- - t_3)} \left(D^> - D^<\right)_{j_1 j_3} (\vec{r}_1 \omega_1 \vec{q}_1^{\,+} t_1^+) \\
& \times \int d\vec{r}_2 \frac{d\omega_2}{2\pi} e^{-i\vec{q}_3 \cdot \vec{r}_2 - i\omega_2 t_3} \Sigma^<_{j_3 j_2}(\vec{r}_2 \omega_2 \vec{q}_1^{\,+} t_1^+)
\end{aligned} \tag{3.398}
$$

$$
\begin{aligned}
= & -\int_{-\infty}^{\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \int d\vec{r}_1 d\omega_1 d\vec{r}_2 d\omega_2 e^{-i\vec{q}_3 \cdot (\vec{r}_2 - \vec{r}_1)} e^{-i(\omega_2 - \omega_1) t_3} e^{-i\vec{q}_1^{\,-} \cdot \vec{r}_1 - i\omega_1 t_1^-} \\
& \times \left(D^> - D^<\right)_{j_1 j_3} (\vec{r}_1 \omega_1 \vec{q}_1^{\,+} t_1^+) \Sigma^<_{j_3 j_2}(\vec{r}_2 \omega_2 \vec{q}_1^{\,+} t_1^+)
\end{aligned} \tag{3.399}
$$

| integrate out t_3 and $\vec{q}_3$ to get $\delta(\vec{r}_2 - \vec{r}_1)$ and $\delta(\omega_2 - \omega_1)$ respectively

| evaluate the delta functions on variables $\vec{r}_2$ and ω_2

$$
= -\int d\vec{r}_1 \frac{d\omega_1}{2\pi} \sum_{j_3} e^{-i\vec{q}_1^{\,-} \cdot \vec{r}_1 - i\omega_1 t_1^-} \left(D^> - D^<\right)_{j_1 j_3} (\vec{r}_1 \omega_1 \vec{q}_1^{\,+} t_1^+) \Sigma^<_{j_3 j_2}(\vec{r}_1 \omega_1 \vec{q}_1^{\,+} t_1^+) \tag{3.400}
$$

Fourier component of RHS line 3 + RHS line 2 (zeroth order gradient terms)

$$
= -\sum_{j_3} \left(D^> - D^<\right)_{j_1 j_3} (\vec{r}_1 \omega_1 \vec{q}_1^{\,+} t_1^+) \Sigma^<_{j_3 j_2}(\vec{r}_1 \omega_1 \vec{q}_1^{\,+} t_1^+) \tag{3.401}
$$

RHS line 3 + RHS line 2 (first order gradient terms)

$$
= -\int_{-\infty}^{+\infty} dt_3 \int \frac{d\vec{q}_3}{(2\pi)^3} \sum_{j_3} \int d\vec{r}_1 \frac{d\omega_1}{2\pi} d\vec{r}_2 \frac{d\omega_2}{2\pi}
$$

$$
\begin{aligned}
& \times\left(\vec{q}_3\cdot\nabla_{\vec{q}_1^{\,+}}+t_3\frac{\partial}{\partial t_1^+}-(\vec{q}_1^{\,-}-\vec{q}_3)\nabla_{\vec{q}_1^{\,+\prime}}-(t_1^--t_3)\frac{\partial}{\partial t_1^{+\prime}}\right)\\
& \times e^{-i(\vec{q}_1^{\,-}-\vec{q}_3)\cdot\vec{r}_1-i\omega_1(t_1^--t_3)}e^{-i\vec{q}_3\cdot\vec{r}_2-i\omega_2 t_3}\tilde{b}_{j_1j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\Sigma^<_{j_3j_2}(\vec{r}_2\omega_2\vec{q}_1^{\,+\prime}t_1^{+\prime})\Bigg|_{\vec{q}_1^{\,+\prime}=\vec{q}^{\,+},t_1^{+\prime}=t_1^+} \qquad (3.402)\\
| \quad & \text{integrate by parts and drop surface term, as example, we show for the first term,}\\
| \quad & e^{-i\vec{q}_3\cdot\vec{r}_2}q_3\cdot\nabla_{\vec{q}_1^{\,+}}\tilde{b}\Sigma^<=\left(\frac{1}{-i}\nabla_{\vec{r}_1}e^{-i\vec{q}_3\cdot\vec{r}_2}\right)\cdot\left(\nabla_{\vec{q}_1^{\,+}}\tilde{b}\Sigma^<\right)\\
| \quad & =\frac{1}{-i}\nabla_{\vec{r}_2}\left(e^{-i\vec{q}_3\cdot\vec{r}_2}\nabla_{\vec{q}_1^{\,+}}\tilde{b}\Sigma^<\right)-\frac{1}{-i}e^{-i\vec{q}_3\cdot\vec{r}_2}\nabla_{\vec{r}_2}\cdot\nabla_{\vec{q}_1^{\,+}}\tilde{b}\Sigma^< \text{ then drop first term}\\
= \quad & -\frac{1}{i}\int_{-\infty}^{+\infty}dt_3\int\frac{d\vec{q}_3}{(2\pi)^3}\sum_{j_3}\int d\vec{r}_1\frac{d\omega_1}{2\pi}d\vec{r}_2\frac{d\omega_2}{2\pi}e^{-i\vec{q}_3\cdot(\vec{r}_2-\vec{r}_1)}e^{-i(\omega_2-\omega_1)t_3}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_1-i\omega_1t_1^-}\\
& \left(\nabla_{\vec{r}_2}\cdot\nabla_{\vec{q}_1^{\,+}}+\frac{\partial}{\partial\omega_2}\frac{\partial}{\partial t_1^+}-\nabla_{\vec{r}_1}\cdot\nabla_{\vec{q}_1^{\,+\prime}}-\frac{\partial}{\partial\omega_1}\frac{\partial}{\partial t_1^{+\prime}}\right)\\
& \times\tilde{b}_{j_1j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\Sigma^<_{j_3j_2}(\vec{r}_2\omega_2\vec{q}_1^{\,+\prime}t_1^{+\prime})\Bigg|_{\vec{q}_1^{\,+\prime}=\vec{q}^{\,+},t_1^{+\prime}=t_1^+} \qquad (3.403)\\
| \quad & \text{integrate out } \vec{q}_3 \text{ and } t_3 \text{ to get } \delta(\vec{r}_2-\vec{r}_1) \text{ and } \delta(\omega_2-\omega_1) \text{ respectively}\\
| \quad & \text{then integrate out } \omega_2 \text{ and } \vec{r}_2 \text{ using the delta functions}\\
= \quad & -\frac{1}{i}\int d\vec{r}_1\frac{d\omega_1}{2\pi}\sum_{j_3}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_1-i\omega_1t_1^-}\left(\nabla_{\vec{r}_2}\cdot\nabla_{\vec{q}_1^{\,+}}+\frac{\partial}{\partial\omega_2}\frac{\partial}{\partial t_1^+}-\nabla_{\vec{r}_1}\cdot\nabla_{\vec{q}_1^{\,+\prime}}-\frac{\partial}{\partial\omega_1}\frac{\partial}{\partial t_1^{+\prime}}\right)\\
& \times\tilde{b}_{j_1j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\Sigma^<_{j_3j_2}(\vec{r}_2\omega_2\vec{q}_1^{\,+\prime}t_1^{+\prime})\Bigg|_{\vec{q}_1^{\,+\prime}=\vec{q}^{\,+},t_1^{+\prime}=t_1^+,\vec{r}_2=\vec{r}_1,\omega_2=\omega_1} \qquad (3.404)
\end{aligned}
$$

We define a generalized Poisson bracket so that we have a more compact notation.

$$
\begin{aligned}
& [X,Y]_{GPB}(\vec{r}\omega\vec{q}^{\,+}t^+)\\
\equiv \quad & \frac{\partial X(\vec{r}\omega\vec{q}^{\,+}t^+)}{\partial\omega}\frac{\partial Y(\vec{r}\omega\vec{q}^{\,+}t^+)}{\partial t^+}-\frac{\partial X(\vec{r}\omega\vec{q}^{\,+}t^+)}{\partial t^+}\frac{\partial Y(\vec{r}\omega\vec{q}^{\,+}t^+)}{\partial\omega}\\
& -\left(\nabla_{\vec{r}}X(\vec{r}\omega\vec{q}^{\,+}t^+)\right)\cdot\left(\nabla_{\vec{q}^{\,+}}Y(\vec{r}\omega\vec{q}^{\,+}t^+)\right)+\left(\nabla_{\vec{q}^{\,+}}X(\vec{r}\omega\vec{q}^{\,+}t^+)\right)\cdot\left(\nabla_{\vec{r}}Y(\vec{r}\omega\vec{q}^{\,+}t^+)\right) \qquad (3.405)
\end{aligned}
$$

So the compact expression is

$$
\begin{aligned}
& \text{RHS line 3 + RHS line 2 (first order gradient terms)}\\
= \quad & -\frac{1}{i}\int d\vec{r}_1\frac{d\omega_1}{2\pi}\sum_{j_3}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_1-i\omega_1t_1^-}\left[\tilde{b}_{j_1j_3},\Sigma^<_{j_3j_2}\right]_{GPB}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) \qquad (3.406)
\end{aligned}
$$

$$
\begin{aligned}
& \text{Fourier component of RHS line 3 + RHS line 2 (first order gradient terms)}\\
= \quad & -\frac{1}{i}\sum_{j_3}\left[\tilde{b}_{j_1j_3},\Sigma^<_{j_3j_2}\right]_{GPB}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) \qquad (3.407)
\end{aligned}
$$

$$
\begin{aligned}
& \text{Fourier component of RHS line 3 + RHS line 2 (zero + first order gradient terms)}\\
= \quad & -\sum_{j_3}\left(D^>-D^<\right)_{j_1j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\Sigma^<_{j_3j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)-\frac{1}{i}\sum_{j_3}\left[\tilde{b}_{j_1j_3},\Sigma^<_{j_3j_2}\right]_{GPB}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) \qquad (3.408)
\end{aligned}
$$

By inspection, we can now write down the Fourier components of the other 2 lines.

$$\begin{aligned}
&\text{Fourier component of RHS line 1 + RHS line 4 (zero + first order gradient terms)}\\
=\ &\sum_{j_3}\left(\Sigma^> - \Sigma^<\right)_{j_1 j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)D^<_{j_3 j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) + \frac{1}{i}\sum_{j_3}\left[\tilde{\sigma}_{j_1 j_3}, D^<_{j_3 j_2}\right]_{GPB}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) \qquad (3.409)
\end{aligned}$$

Summing then up gives the full RHS. (2 terms cancel due to $j_1 = j_2$ which we have to impose eventually)

$$\begin{aligned}
&\text{Fourier component of RHS (zero + first order gradient terms)}\\
=\ &\sum_{j_3}\Sigma^>_{j_1 j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)D^<_{j_3 j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) - \sum_{j_3}D^>_{j_1 j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\Sigma^<_{j_3 j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\\
&+\frac{1}{i}\sum_{j_3}\left[\tilde{\sigma}_{j_1 j_3}, D^<_{j_3 j_2}\right]_{GPB}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) - \frac{1}{i}\sum_{j_3}\left[\tilde{b}_{j_1 j_3}, \Sigma^<_{j_3 j_2}\right]_{GPB}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) \qquad (3.410)
\end{aligned}$$

Finally, we need to work out the explicit expressions of the Fourier components of $\tilde{\sigma}$ and $\tilde{b}$.

$$\begin{aligned}
\tilde{b}_{j_1 j_2}(\vec{r}\omega\vec{q}^{\,+}t^+) &= \int \frac{d\vec{q}^{\,-}}{(2\pi)^3}dt^- e^{i\vec{q}^{\,-}\cdot\vec{r}+i\omega t^-}\frac{t^-}{|t^-|}\frac{1}{2}\left(D^> - D^<\right)_{j_1 j_2}(\vec{q}^{\,-}t^-\vec{q}^{\,+}t^+) && (3.411)\\
&= \frac{1}{2}\int dt^-\frac{t^-}{|t^-|}e^{i\omega t^-}\int\frac{d\vec{q}^{\,-}}{(2\pi)^3}e^{i\vec{q}^{\,-}\cdot\vec{r}}\left(D^> - D^<\right)_{j_1 j_2}(\vec{q}^{\,-}t^-\vec{q}^{\,+}t^+) && (3.412)\\
&\ \ |\ \ \text{recall that} \int\frac{d\vec{q}^{\,-}}{(2\pi)^3}dt^- e^{i\vec{q}^{\,-}\cdot\vec{r}+i\omega t^-} i\left(D^> - D^<\right)_{j_1 j_2}(\vec{q}^{\,-}t^-\vec{q}^{\,+}t^+) = A_{j_1 j_2}(\vec{r}\omega\vec{q}^{\,+}t^+)\\
&\ \ |\ \ \text{so} \int\frac{d\vec{q}^{\,-}}{(2\pi)^3}e^{i\vec{q}^{\,-}\cdot\vec{r}}\left(D^> - D^<\right)_{j_1 j_2}(\vec{q}^{\,-}t^-\vec{q}^{\,+}t^+) = \frac{1}{i}\int d\omega' e^{-i\omega' t^-}A_{j_1 j_2}(\vec{r}\omega'\vec{q}^{\,+}t^+)\\
&= \frac{1}{2i}\int dt^-\frac{t^-}{|t^-|}\int\frac{d\omega'}{2\pi}e^{-i\omega' t^-}e^{i\omega t^-}A_{j_1 j_2}(\vec{r}\omega'\vec{q}^{\,+}t^+) && (3.413)\\
&= \frac{1}{2i}\int\frac{d\omega'}{2\pi}A_{j_1 j_2}(\vec{r}\omega'\vec{q}^{\,+}t^+)\left(\int_0^\infty dt^- e^{i(\omega-\omega')t^-} - \int_{-\infty}^0 dt^- e^{i(\omega-\omega')t^-}\right) && (3.414)\\
&\ \ |\ \ \text{use identity} \int_0^\infty dx e^{i\alpha x} = \pi\delta(\alpha) + \frac{i}{\alpha}\\
&= \frac{1}{2i}\int\frac{d\omega'}{2\pi}A_{j_1 j_2}(\vec{r}\omega'\vec{q}^{\,+}t^+)\left(\frac{2i}{\omega-\omega'}\right) && (3.415)\\
&\ \ |\ \ \text{write it as a principal value integral to make sense of the singularity when } \omega = \omega'\\
&= \mathcal{P}\int\frac{d\omega'}{2\pi}\frac{A_{j_1 j_2}(\vec{r}\omega'\vec{q}^{\,+}t^+)}{\omega-\omega'} && (3.416)\\
&\ \ |\ \ \text{if we assume an analogy with Kramers-Kronig relation, then we can write}\\
&= \Re G^{\mathrm{R\ or\ A}}(\vec{r}\omega\vec{q}^{\,+}t^+) && (3.417)
\end{aligned}$$

Everything is the same for $\tilde{\sigma}_{j_1 j_2}(\vec{r}\omega\vec{q}^{\,+}t^+)$ with the replacement of Green's functions, $D^> - D^<$ with self energies, $\Sigma^> - \Sigma^<$ and so the spectral function, A is replaced with the level width function, Γ.

$$\begin{aligned}
\tilde{\sigma}_{j_1 j_2}(\vec{r}\omega\vec{q}^{\,+}t^+) &= \mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma_{j_1 j_2}(\vec{r}\omega'\vec{q}^{\,+}t^+)}{\omega-\omega'} && (3.418)\\
&\ \ |\ \ \text{if we assume an analogy with Kramers-Kronig relation, then we can write}\\
&= \Re\Sigma^{\mathrm{R\ or\ A}}(\vec{r}\omega\vec{q}^{\,+}t^+) && (3.419)
\end{aligned}$$

We collect the final expression of pre-QKE.

$$\begin{aligned}
&\left((-2i\omega_1)\frac{\partial}{\partial t_1^+} + (-2i\omega_{j_1\vec{q}_1^+})\left(\nabla_{\vec{q}_1^+}\omega_{j_1\vec{q}_1^+}\right)\cdot\nabla_{\vec{r}_1}\right) D^<_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\Big|_{j_1=j_2} \\
= &\sum_{j_3}\Sigma^>_{j_1j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)D^<_{j_3j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) - \sum_{j_3}D^>_{j_1j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\Sigma^<_{j_3j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) \\
&+\frac{1}{i}\sum_{j_3}\left[\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'}, D^<_{j_3j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB} \\
&-\frac{1}{i}\sum_{j_3}\left[\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{A_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'}, \Sigma^<_{j_3j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\Bigg|_{j_1=j_2} \qquad (3.420)
\end{aligned}$$

We can't proceed further with the pre-QKE and we need to impose an ansatz to turn pre-QKE into QKE which describes a distribution.

3.3.2.1 Kadanoff-Baym Ansatz

The Kadanoff-Baym ansatz is defined as

$$D^<_{j_1j_2}(\vec{r}\omega\vec{q}^{\,+}t^+) \equiv -i\delta_{j_1j_2}A_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+) \qquad (3.421)$$

$$D^>_{j_1j_2}(\vec{r}\omega\vec{q}^{\,+}t^+) \equiv -i\delta_{j_1j_2}A_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)\left(1+N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)\right) \qquad (3.422)$$

so that A is like some kind of non-equilibrium spectral function satisfying the relation $A = i(D^> - D^<)$. N_j is defined to be a (real) distribution function for phonons. [42]

We pick the free ("QQ") spectral function to use in KB ansatz.

$$\begin{aligned}
A_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) &= A^{(0)}_{j_1}(\omega_1\vec{q}_1^{\,+}) \qquad (3.425)\\
&= \frac{2\pi}{2\omega_{j_1\vec{q}_1^+}}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+}) - \delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right) \qquad (3.426)
\end{aligned}$$

This expression is odd in ω_1 and even in $\vec{q}_1^{\,+}$. Notice that $A^{(0)}$ is real and so the lesser and greater functions are now pure imaginary. KB ansatz with free spectral function is,

$$D^<_{j_1j_2}(\vec{r}\omega\vec{q}^{\,+}t^+) = \delta_{j_1j_2}\frac{-i2\pi}{2\omega_{j_1\vec{q}_1^+}}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+}) - \delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+) \qquad (3.427)$$

$$D^>_{j_1j_2}(\vec{r}\omega\vec{q}^{\,+}t^+) = \delta_{j_1j_2}\frac{-i2\pi}{2\omega_{j_1\vec{q}_1^+}}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+}) - \delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)\left(1+N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)\right) \qquad (3.428)$$

[42] For the case of retaining RHS to zeroth order only, we can also write down the equation that A satisfies by subtracting the $D^<$ and $D^>$ equations. These 2 equations have the same zeroth order RHS, thus we get,

$$\left(\omega_1\frac{\partial}{\partial t_1^+} + \omega_{j_1\vec{q}_1^+}\left(\nabla_{\vec{q}_1^+}\omega_{j_1\vec{q}_1^+}\right)\cdot\nabla_{\vec{r}_1}\right) i(D^> - D^<) = 0 \qquad (3.423)$$

$$\Rightarrow \left(\omega_1\frac{\partial}{\partial t_1^+} + \omega_{j_1\vec{q}_1^+}\left(\nabla_{\vec{q}_1^+}\omega_{j_1\vec{q}_1^+}\right)\cdot\nabla_{\vec{r}_1}\right) A_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) = 0 \qquad (3.424)$$

The importance is that, any choice of spectral function that satisfies the above equation "commutes" with the driving term. The simplest solution is the free spectral function.

Based on the sum rule for the spectral function, it is an odd function of ω, together with KB ansatz, we can prove an identity for the nonequilibrium distribution function. We start with the KB ansatz.

$$\begin{aligned}
D^{<}_{j_1j_2}(\vec{r}\omega\vec{q}^{\,+}t^+) &= \delta_{j_1j_2}A_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+) && (3.429)\\
&\Big| \text{ write } \omega \longrightarrow -\omega \\
D^{<}_{j_1j_2}(\vec{r},-\omega,\vec{q}^{\,+},t^+) &= \delta_{j_1j_2}A_{j_1}(\vec{r},-\omega,\vec{q}^{\,+},t^+)N_{j_1}(\vec{r},-\omega,\vec{q}^{\,+},t^+) && (3.430)\\
\Rightarrow D^{>}_{j_2j_1}(\vec{r}\omega\vec{q}^{\,+}t^+) &= \delta_{j_1j_2}\left(-A_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)\right)N_{j_1}(\vec{r},-\omega,\vec{q}^{\,+},t^+) && (3.431)\\
& && (3.432)
\end{aligned}$$

Compare with $D^{>}_{j_1j_2}(\vec{r}\omega\vec{q}^{\,+}t^+) = \delta_{j_1j_2}A_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)\left(1+N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)\right)$ and that $j_1 = j_2$, we get,

$$\boxed{-N_{j_1}(\vec{r},-\omega,\vec{q}^{\,+},t^+) = 1 + N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)} \tag{3.433}$$

We substitute this form of KB ansatz into the $D^<$ pre-QKE (we take $j_1 = j_2$ on the RHS and abbreviate the first order terms and delay writing out the explicit form.)

$$\begin{aligned}
&\left((-2i\omega_1)\frac{\partial}{\partial t_1^+} + (-2i\omega_{j_1\vec{q}_1^{\,+}})\left(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}}\right)\cdot\nabla_{\vec{r}_1}\right)\frac{-i2\pi N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\right)\\
=\;& \sum_{j_3}\Sigma^{>}_{j_1j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\delta_{j_3j_1}\frac{-i2\pi}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\right)N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)\\
&-\sum_{j_3}\Sigma^{<}_{j_1j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\delta_{j_3j_1}\frac{-i2\pi}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\right)\left(1+N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)\right)\\
&+\text{"First Order Gradient Terms"}
\end{aligned} \tag{3.434}$$

By construction, we carry out $\int_0^\infty d\omega_1$ and thus only pick up the first delta function.

$$\begin{aligned}
&\left((-2i\omega_{j_1\vec{q}_1^{\,+}})\frac{\partial}{\partial t_1^+} + (-2i\omega_{j_1\vec{q}_1^{\,+}})\left(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}}\right)\cdot\nabla_{\vec{r}_1}\right)N_{j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)\\
=\;& \Sigma^{>}_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)N_{j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+) - \Sigma^{<}_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)\left(1+N_{j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)\right)\\
&+\frac{1}{2\pi}\int_0^\infty d\omega_1\frac{2\omega_{j_1\vec{q}_1^{\,+}}}{-i}\text{"First Order Gradient Terms"}\Bigg|_{j_2=j_1,\text{Free spectral KB ansatz}}
\end{aligned} \tag{3.435}$$

$$\begin{aligned}
\Rightarrow\;& \left(\frac{\partial}{\partial t_1^+} + \left(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}}\right)\cdot\nabla_{\vec{r}_1}\right)N_{j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)\\
=\;& \frac{i}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\Sigma^{>}_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)N_{j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+) - \Sigma^{<}_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)\left(1+N_{j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)\right)\right)\\
&+\frac{1}{2\pi}\frac{i}{2\omega_{j_1\vec{q}_1^{\,+}}}\int_0^\infty d\omega_1\frac{2\omega_{j_1\vec{q}_1^{\,+}}}{-i}\text{"First Order Gradient Terms"}\Bigg|_{j_2=j_1,\text{Free spectral KB ansatz}}
\end{aligned} \tag{3.436}$$

Now the LHS has indeed the same form as the LHS of phonon Boltzmann equation and we can call the RHS the "collision integral". We will reassign the notation $N_{j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+) \to N_{j_i\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)$ since now N_{j_1} takes on the meaning of the non-equilibrium phonon distribution function and that the frequency $\omega_{j_1\vec{q}_1^{\,+}}$ and wavevector $\vec{q}^{\,+}$ are no longer independent. They are related by the dispersion relations. The final equation is,

$$\begin{aligned}
&\left(\frac{\partial}{\partial t_1^+} + \left(\nabla_{\vec{q}_1^+}\omega_{j_1\vec{q}_1^+}\right)\cdot\nabla_{\vec{r}_1}\right) N_{j_i\vec{q}_1^+}(\vec{r}_1 t_1^+) \\
=& \frac{i}{2\omega_{j_1\vec{q}_1^+}}\left(\Sigma^>_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)N_{j_i\vec{q}_1^+}(\vec{r}_1t_1^+) - \Sigma^<_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)\left(1+N_{j_i\vec{q}_1^+}(\vec{r}_1t_1^+)\right)\right) \\
&+\frac{1}{2\pi}\frac{i}{2\omega_{j_1\vec{q}_1^+}}\int_0^\infty d\omega_1\frac{2\omega_{j_1\vec{q}_1^+}}{-i}\text{“First Order Gradient Terms”}\Bigg|_{j_2=j_1,\text{Free spectral KB ansatz}}
\end{aligned} \tag{3.437}$$

[Energy Conservation Sum Rule] The energy conservation sum rule (for each order) is simply derived by writing $\sum_{j_1\vec{q}_1^+}\hbar\omega_{j_1\vec{q}_1^+}\times$ “collision integral” $\stackrel{!}{=}0$. For the zeroth order,

$$0\stackrel{!}{=}\sum_{j_1\vec{q}_1^+}\left(\Sigma^>_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)N_{j_i\vec{q}_1^+}(\vec{r}_1t_1^+) - \Sigma^<_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)\left(1+N_{j_i\vec{q}_1^+}(\vec{r}_1t_1^+)\right)\right) \tag{3.438}$$

Now we write out the first order collision integral explicitly,

$$\begin{aligned}
&\text{Collision Integral in first order gradient expansion} \\
=& \frac{1}{2\pi}\frac{i}{2\omega_{j_1\vec{q}_1^+}}\int_0^\infty d\omega_1\frac{2\omega_{j_1\vec{q}_1^+}}{-i}\text{“First Order”}\Bigg|_{j_2=j_1,\text{Free spectral KB ansatz}}
\end{aligned} \tag{3.439}$$

$$\begin{aligned}
=& \frac{1}{2\pi}\frac{1}{i}\int_0^\infty d\omega_1\sum_{j_3}\left(\left[\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{A_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'},\Sigma^<_{j_3j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\right. \\
&\left.-\left[\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'},D^<_{j_3j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\right)_{\text{Free spectral KB ansatz}}
\end{aligned} \tag{3.440}$$

The first order energy conservation sum rule is thus,

$$\begin{aligned}
0 =& \sum_{j_1\vec{q}_1^+}\hbar\omega_{j_1\vec{q}_1^+}\int_0^\infty d\omega_1\sum_{j_3}\left(\left[\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{A_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'},\Sigma^<_{j_3j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\right. \\
&\left.-\left[\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'},D^<_{j_3j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\right)_{\text{Free spectral KB ansatz}}
\end{aligned} \tag{3.441}$$

3.3.2.2 Relaxation Time Approximation

The usual relaxation time approximation is to assume that the nonequilibrium distribution relaxes to the equilibrium one with characteristic time $\tau_{j_1\vec{q}_1}$.

$$N_{j_1\vec{q}_1} = N^{eq}_{j_1\vec{q}_1}\left(1-e^{-t/\tau_{j_1\vec{q}_1}}\right) \tag{3.442}$$

so the relaxation time collision integral is,

$$\left.\frac{\partial N_{j_1\vec{q}_1}}{\partial t}\right|_{\text{coll}} = \frac{\partial}{\partial t}N^{eq}_{j_1\vec{q}_1}\left(1-e^{-t/\tau_{j_1\vec{q}_1}}\right) = -\frac{N_{j_1\vec{q}_1}-N^{eq}_{j_1\vec{q}_1}}{\tau_{j_1\vec{q}_1}} \tag{3.443}$$

The usual way to linearize the (bosonic) distribution is

$$N_{j_1\vec{q}_1} \approx N^{eq}_{j_1\vec{q}_1} + N^{eq}_{j_1\vec{q}_1}\left(1 + N^{eq}_{j_1\vec{q}_1}\right) y_{j_1\vec{q}_1} \tag{3.444}$$

where $y_{j_1\vec{q}_1}$ is the (small) nonequilibrium part of the distribution. We substitute it into the relaxation time collision integral.

$$\left.\frac{\partial N_{j_1\vec{q}_1}}{\partial t}\right|_{\text{coll}} \approx -\frac{N^{eq}_{j_1\vec{q}_1} + N^{eq}_{j_1\vec{q}_1}(1 + N^{eq}_{j_1\vec{q}_1})y_{j_1\vec{q}_1} - N^{eq}_{j_1\vec{q}_1}}{\tau_{j_1\vec{q}_1}} = -\frac{N^{eq}_{j_1\vec{q}_1}(1 + N^{eq}_{j_1\vec{q}_1})y_{j_1\vec{q}_1}}{\tau_{j_1\vec{q}_1}} \tag{3.445}$$

From QKE (in KB ansatz), we can now work out the relationship between the self energy and the relaxation time. [43] We follow [DiVentra2008] pg 255.

$$\begin{aligned}
& \text{Zeroth order collision integral} \\
= \; & \frac{i}{2\omega_{j_1\vec{q}_1^+}}\left[\Sigma^>_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)N_{j_i\vec{q}_1^+}(\vec{r}_1t_1^+) - \Sigma^<_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)\left(1 + N_{j_i\vec{q}_1^+}(\vec{r}_1t_1^+)\right)\right] && (3.446)\\
| \; & \text{substitute the linearized distribution} \\
\approx \; & \frac{i}{2\omega_{j_1\vec{q}_1^+}}\left[\Sigma^>_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)\left(N^{eq}_{j_i\vec{q}_1^+} + N^{eq}_{j_i\vec{q}_1^+}(1 + N^{eq}_{j_i\vec{q}_1^+})y_{j_1\vec{q}_1^+}\right)\right. \\
& \left. -\Sigma^<_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)\left(1 + N^{eq}_{j_i\vec{q}_1^+} + N^{eq}_{j_i\vec{q}_1^+}(1 + N^{eq}_{j_i\vec{q}_1^+})y_{j_1\vec{q}_1^+}\right)\right] && (3.447)\\
= \; & \frac{i}{2\omega_{j_1\vec{q}_1^+}}\left[\Sigma^>_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)N^{eq}_{j_i\vec{q}_1^+} - \Sigma^<_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)\left(1 + N^{eq}_{j_i\vec{q}_1^+}\right)\right. \\
& \left.(\Sigma^> - \Sigma^<)_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)N^{eq}_{j_i\vec{q}_1^+}\left(1 + N^{eq}_{j_i\vec{q}_1^+}\right)y_{j_1\vec{q}_1^+}\right] && (3.448)\\
| \; & \text{we claim that the first 2 terms cancel within linearization} \\
| \; & \text{explicit examples are shown in the chapter on anharmonicity} \\
| \; & \text{then use } i(\Sigma^> - \Sigma^<) = \Gamma = -2\Im\Sigma^R \\
= \; & -\frac{\Im\Sigma^R_{j_1j_1}}{\omega_{j_1\vec{q}_1^+}}N^{eq}_{j_i\vec{q}_1^+}\left(1 + N^{eq}_{j_i\vec{q}_1^+}\right)y_{j_i\vec{q}_1^+} && (3.449)
\end{aligned}$$

and we compare with the (linearized) relaxation time collision integral, we get

$$\frac{1}{\tau_{j_1\vec{q}_1^+}} = \frac{\Im\Sigma^R_{j_1j_1}}{\omega_{j_1\vec{q}_1^+}} \tag{3.450}$$

which is the quite well known relation that the relaxation time of the interaction is related to the imaginary part of the (retarded or advanced) self energy.

[43] This illustrates how easy the kinetic formulation allows abstract quantities to be physically interpreted.

3.3.2.3 H-Theorem*

[H-Theorem for (zeroth order) Phonon Boltzmann Equation] Here we follow [Gruevich1986] section 1.14. [44] From the nonequilibrium distribution, we define the quantity, [45]

$$\sigma_{j\vec{q}}(N) \equiv (N_{j\vec{q}}+1)\ln(N_{j\vec{q}}+1) - N_{j\vec{q}}\ln N_{j\vec{q}} \tag{3.451}$$

then define the entropy density

$$s(\vec{r}) \equiv \int \frac{d\vec{q}}{(2\pi)^3}\sigma_{j\vec{q}}(N) \tag{3.452}$$

Entropy of the phonon system is thus given as

$$S = \int d\vec{r} s(\vec{r}) \tag{3.453}$$

Consider the rate of change of entropy density,

$$\begin{aligned}
\frac{\partial s(\vec{r})}{\partial t} &= \int \frac{d\vec{q}}{(2\pi)^3}\frac{\partial \sigma_{j\vec{q}}}{\partial t} && (3.454)\\
&= \int \frac{d\vec{q}}{(2\pi)^3}\frac{\partial \sigma_{j\vec{q}}}{\partial N_{j\vec{q}}}\frac{\partial N_{j\vec{q}}}{\partial t} && (3.455)\\
&\quad | \text{ use the phonon Boltzmann equation } \frac{\partial N_{j\vec{q}}}{\partial t} + (\nabla_{\vec{q}}\,\omega_{j\vec{q}})\cdot\nabla_{\vec{r}}N_{j\vec{q}} = \left(\frac{\partial N_{j\vec{q}}}{\partial t}\right)_{\text{coll}}\\
&= \int \frac{d\vec{q}}{(2\pi)^3}\frac{\partial \sigma_{j\vec{q}}}{\partial N_{j\vec{q}}}\left(-(\nabla_{\vec{q}}\,\omega_{j\vec{q}})\cdot\nabla_{\vec{r}}N_{j\vec{q}} + \left(\frac{\partial N_{j\vec{q}}}{\partial t}\right)_{\text{coll}}\right) && (3.456)\\
&= \int \frac{d\vec{q}}{(2\pi)^3}\left(-(\nabla_{\vec{q}}\,\omega_{j\vec{q}})\cdot(\nabla_{\vec{r}}\sigma_{j\vec{q}}) + \frac{\partial \sigma_{j\vec{q}}}{\partial N_{j\vec{q}}}\left(\frac{\partial N_{j\vec{q}}}{\partial t}\right)_{\text{coll}}\right) && (3.457)\\
&\quad | \text{ write } \nabla_{\vec{q}}\,\omega_{j\vec{q}} = \vec{v}_{j\vec{q}}\\
&= \int \frac{d\vec{q}}{(2\pi)^3}\left(-\nabla_{\vec{r}}\cdot(\sigma_{j\vec{q}}\vec{v}_{j\vec{q}}) + \frac{\partial \sigma_{j\vec{q}}}{\partial N_{j\vec{q}}}\left(\frac{\partial N_{j\vec{q}}}{\partial t}\right)_{\text{coll}}\right) && (3.458)\\
&\quad | \text{ we can define the entropy flux density as } \vec{j}_s(\vec{r}) \equiv \int \frac{d\vec{q}}{(2\pi)^3}\sigma_{j\vec{q}}\vec{v}_{j\vec{q}}\\
&\quad | \text{ we have the form of a continuity equation}\\
\frac{\partial s(\vec{r})}{\partial t} + \nabla_{\vec{r}}\cdot\vec{j}_s &= \int \frac{d\vec{q}}{(2\pi)^3}\frac{\partial \sigma_{j\vec{q}}}{\partial N_{j\vec{q}}}\left(\frac{\partial N_{j\vec{q}}}{\partial t}\right)_{\text{coll}} && (3.459)
\end{aligned}$$

Integrate over the whole space

$$\begin{aligned}
\int d\vec{r}\frac{\partial s(\vec{r})}{\partial t} + \int d\vec{r}\,\nabla_{\vec{r}}\cdot\vec{j}_s &= \int d\vec{r}\int \frac{d\vec{q}}{(2\pi)^3}\frac{\partial \sigma_{j\vec{q}}}{\partial N_{j\vec{q}}}\left(\frac{\partial N_{j\vec{q}}}{\partial t}\right)_{\text{coll}} && (3.460)\\
&\quad | \text{ we assume that the flux is zero through the boundary}\\
\frac{\partial S}{\partial t} &= \int d\vec{r}\int \frac{d\vec{q}}{(2\pi)^3}\frac{\partial \sigma_{j\vec{q}}}{\partial N_{j\vec{q}}}\left(\frac{\partial N_{j\vec{q}}}{\partial t}\right)_{\text{coll}} && (3.461)
\end{aligned}$$

[44] Note that he used an even more general dispersion, which is space dependent $\omega_{j\vec{q}}(\vec{r})$.

[45] For the derivation of $\sigma_{j\vec{q}}(N)$, see section 55 of *Statistical Physics Part 1 3rd Edition* by L. D. Landau and E. M. Lifshitz (1980). The expression for electrons are in that section as well.

$$
\begin{aligned}
&\quad | \quad \text{insert } \frac{\partial \sigma_{j\vec{q}}}{\partial N_{j\vec{q}}} = \ln\left(\frac{N_{j\vec{q}}+1}{N_{j\vec{q}}}\right) \\
&= \int d\vec{r} \int \frac{d\vec{q}}{(2\pi)^3} \ln\left(\frac{N_{j\vec{q}}+1}{N_{j\vec{q}}}\right)\left(\frac{\partial N_{j\vec{q}}}{\partial t}\right)_{\text{coll}}
\end{aligned} \tag{3.462}
$$

The H-theorem for kinetic theory can now be stated as

$$
\frac{\partial S}{\partial t} \geq 0 \Longrightarrow \int d\vec{r} \int \frac{d\vec{q}}{(2\pi)^3} \ln\left(\frac{N_{j\vec{q}}+1}{N_{j\vec{q}}}\right)\left(\frac{\partial N_{j\vec{q}}}{\partial t}\right)_{\text{coll}} \geq 0 \tag{3.463}
$$

which should be checked for explicit collision integrals. [Gruevich1986] section 1.14 checks the 3-phonon collision integral, mass defect collision integral and the equilibrium Bose-Einstein distribution (which gives 0). The meaning is simply that collisions increase entropy in the system until equilibrium is reached. This also means that entropy is maximum at equilibrium.

[H-Theorem for QKE (Kita's paper)] The question here is, with the additional first order gradient terms in the kinetic equation, how will the definitions of the entropy related quantities change?

We follow Kita in [Kita2010]. The QKE in KB ansatz (which is Boltzmann equation + first order gradient terms) is,

$$
\begin{aligned}
&\frac{\partial N_{j_1\vec{q}_1^+}(\vec{r}_1 t_1^+)}{\partial t_1^+} + \left(\nabla_{\vec{q}_1^+}\omega_{j_1\vec{q}_1^+}\right)\cdot \nabla_{\vec{r}_1} N_{j_1\vec{q}_1^+}(\vec{r}_1 t_1^+) \\
= &\left(\frac{\partial N_{j_1\vec{q}_1^+}(\vec{r}_1 t_1^+)}{\partial t_1^+}\right)_{\text{coll}} + i\sum_{j_3}\int_0^\infty \frac{d\omega_1}{2\pi}\left\{\left[\Re\Sigma^R_{j_1 j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+), D^<_{j_3 j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{\text{GPB}}\right. \\
&\left.\left. - \left[\Re D^R_{j_1 j_3}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+), \Sigma^<_{j_3 j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{\text{GPB}}\right\}\right|_{j_1=j_2,\text{free spectral KB ansatz}}
\end{aligned} \tag{3.464}
$$

Here we need some physical intuition in order to proceed. The zeroth order terms (on RHS) represent entropy increase due to collisions until equilibrium is reached. The first order gradient terms represent correlations between the particles so they should not have anything to do with the entropy change due to collisions. These first order terms should be either in the entropy density term or in the entropy flux density term. This applies to higher order gradient terms as well. We make the judgement by looking at the explicit form of GPB,

$$
[X,Y]_{\text{GPB}}(\vec{r}\omega\vec{q}^{\,+}t^+) = \frac{\partial X}{\partial \omega}\frac{\partial Y}{\partial t^+} - \frac{\partial X}{\partial t^+}\frac{\partial Y}{\partial \omega} - (\nabla_{\vec{r}}X)\cdot(\nabla_{\vec{q}^+}Y) + (\nabla_{\vec{q}^+}X)\cdot(\nabla_{\vec{r}}Y) \tag{3.465}
$$

And so we collect together the terms with time and frequency derivatives with $\frac{\partial N}{\partial t^+}$ on the LHS and collect the terms with space and momentum derivatives with $(\nabla_{\vec{q}^+}\omega)\cdot\nabla_{\vec{r}}N$ on the LHS. Then we will need to multiply $\frac{\partial \sigma}{\partial N}$ and integrate $\int \frac{d\vec{q}^+}{(2\pi))^3}$ to turn the kinetic equation into an entropy continuity equation just like in the previous section. The calculation of the entropy continuity equation looks like,

$$
\begin{aligned}
\text{LHS} = &\int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\frac{\partial \sigma_{j_1\vec{q}_1^+}}{\partial N_{j_1\vec{q}_1^+}} \times \left\{\frac{\partial N_{j_1\vec{q}_1^+(\vec{r}_1 t_1^+)}}{\partial t_1^+} - i\sum_{j_3}\int_0^\infty \frac{d\omega_1}{2\pi}\left(\frac{\partial \Re\Sigma^R_{j_1 j_3}}{\partial \omega_1}\frac{\partial D^<_{j_3 j_2}}{\partial t_1^+} - \frac{\partial \Re\Sigma^R_{j_1 j_3}}{\partial t_1^+}\frac{\partial D^<_{j_3 j_2}}{\partial \omega_1}\right.\right. \\
&\left.\left.\left. - \frac{\partial \Re D^R_{j_1 j_3}}{\partial \omega_1}\frac{\partial \Sigma^<_{j_3 j_2}}{\partial t_1^+} + \frac{\partial \Re D^R_{j_1 j_3}}{\partial t_1^+}\frac{\partial \Sigma^<_{j_3 j_2}}{\partial \omega_1}\right)\right|_{j_1=j_2,\text{free spectral KB}}\right\}
\end{aligned}
$$

$$
\begin{aligned}
&+\int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\times\Bigg\{\quad\left(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}}\right)\cdot\left(\nabla_{\vec{r}_1}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\right)\\
&-i\sum_{j_3}\int_0^\infty\frac{d\omega_1}{2\pi}\left(\left(\nabla_{\vec{q}_1^{\,+}}\Re\Sigma^R_{j_1j_3}\right)\cdot\left(\nabla_{\vec{r}_1}D^<_{j_3j_2}\right)-\left(\nabla_{\vec{r}_1}\Re\Sigma^R_{j_1j_3}\right)\cdot\left(\nabla_{\vec{q}_1^{\,+}}D^<_{j_3j_2}\right)\right.\\
&\left.\left.-\left(\nabla_{\vec{q}_1^{\,+}}\Re D^R_{j_1j_3}\right)\cdot\left(\nabla_{\vec{r}_1}\Sigma^<_{j_3j_2}\right)+\left(\nabla_{\vec{r}_1}\Re D^R_{j_1j_3}\right)\cdot\left(\nabla_{\vec{q}_1^{\,+}}\Sigma^<_{j_3j_2}\right)\right)\right|_{j_1=j_2,\text{free spectral KB}}\Bigg\} \qquad (3.466)\\
\text{RHS} \;=\; &\int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\times\left(\frac{\partial N_{j_1\vec{q}_1^{\,+}}}{\partial t_1^+}\right)_{\text{coll}} \qquad (3.467)
\end{aligned}
$$

So the RHS is the same as before. We carry out the calculation term by term.

Terms with time and frequency derivatives (LHS)

$$
\begin{aligned}
=\;&\int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\times\Bigg\{\frac{\partial N_{j_1\vec{q}_1^{\,+}(\vec{r}_1t_1^+)}}{\partial t_1^+}-i\sum_{j_3}\int_0^\infty\frac{d\omega_1}{2\pi}\left(\frac{\partial\Re\Sigma^R_{j_1j_3}}{\partial\omega_1}\frac{\partial D^<_{j_3j_2}}{\partial t_1^+}-\frac{\partial\Re\Sigma^R_{j_1j_3}}{\partial t_1^+}\frac{\partial D^<_{j_3j_2}}{\partial\omega_1}\right.\\
&\left.\left.-\frac{\partial\Re D^R_{j_1j_3}}{\partial\omega_1}\frac{\partial\Sigma^<_{j_3j_2}}{\partial t_1^+}+\frac{\partial\Re D^R_{j_1j_3}}{\partial t_1^+}\frac{\partial\Sigma^<_{j_3j_2}}{\partial\omega_1}\right)\right|_{j_1=j_2,\text{free spectral KB}}\Bigg\} \qquad (3.468)
\end{aligned}
$$

| use the product rule of differentiation

| to save writing, I will use | to denote $|_{j_1=j_2,\text{free spectral KB}}$

$$
\begin{aligned}
=\;&\int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\times\Bigg\{\frac{\partial N_{j_1\vec{q}_1^{\,+}(\vec{r}_1t_1^+)}}{\partial t_1^+}\\
&-i\sum_{j_3}\int_0^\infty\frac{d\omega_1}{2\pi}\left(\frac{\partial}{\partial\omega_1}\left(D^<_{j_3j_2}\frac{\partial\Re\Sigma^R_{j_1j_3}}{\partial t_1^+}\right)-D^<_{j_3j_2}\frac{\partial^2\Re\Sigma^R_{j_1j_3}}{\partial\omega_1\partial t_1^+}-\frac{\partial}{\partial t_1^+}\left(D^<_{j_3j_2}\frac{\partial\Re\Sigma^R_{j_1j_3}}{\partial\omega_1}\right)+D^<_{j_3j_2}\frac{\partial^2\Sigma^R_{j_1j_3}}{\partial t_1^+\partial\omega_1}\right.\\
&\left.\left.-\frac{\partial}{\partial\omega_1}\left(\Sigma^<_{j_3j_2}\frac{\partial\Re D^R_{j_1j_3}}{\partial t_1^+}\right)+\Sigma^<_{j_3j_2}\frac{\partial^2\Re D^R_{j_1j_3}}{\partial\omega_1\partial t_1^+}+\frac{\partial}{\partial t_1^+}\left(\Sigma^<_{j_3j_2}\frac{\partial\Re D^R_{j_1j_3}}{\partial\omega_1}\right)-\Sigma^<_{j_3j_2}\frac{\partial^2\Sigma^R_{j_1j_3}}{\partial t_1^+\partial\omega_1}\right)\right|\Bigg\} \qquad (3.469)
\end{aligned}
$$

| assume cross derivatives "commute" and so 2 pairs of terms cancel

$$
\begin{aligned}
=\;&\int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\times\Bigg\{\frac{\partial N_{j_1\vec{q}_1^{\,+}(\vec{r}_1t_1^+)}}{\partial t_1^+}\\
&-\frac{i}{2\pi}\sum_{j_3}\left[D^<_{j_3j_2}\frac{\partial\Re\Sigma^R_{j_1j_3}}{\partial t_1^+}\right]_0^\infty\Bigg|+\frac{i}{2\pi}\sum_{j_3}\int_0^\infty d\omega_1\frac{\partial}{\partial t_1^+}\left(D^<_{j_3j_2}\frac{\partial\Re\Sigma^R_{j_1j_3}}{\partial\omega_1}\right)\Bigg|\\
&+\frac{i}{2\pi}\sum_{j_3}\left[\Sigma^<_{j_3j_2}\frac{\partial\Re D^R_{j_1j_3}}{\partial t_1^+}\right]_0^\infty\Bigg|-\frac{i}{2\pi}\sum_{j_3}\int_0^\infty d\omega_1\frac{\partial}{\partial t_1^+}\left(\Sigma^<_{j_3j_2}\frac{\partial\Re D^R_{j_1j_3}}{\partial\omega_1}\right)\Bigg|\Bigg\} \qquad (3.470)
\end{aligned}
$$

| assume that there is at least one $D^<$ inside $\Sigma^<$ i.e. we write $\Sigma^<_{j_3j_2}=D^<_{j_3j_2}\tilde{\Sigma}^<_{j_3j_2}$

| where $\tilde{\Sigma}^<_{j_3j_2}$ is the remaining part[46]

| apply the KB ansatz, i.e. $D^<=$ free spectral function $\times\, N$

| thus the 2 terms are zero for the limits $\omega_1=0,\infty$ as both delta functions are missed

$$
=\int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\times\Bigg\{\frac{\partial N_{j_1\vec{q}_1^{\,+}(\vec{r}_1t_1^+)}}{\partial t_1^+}+\frac{i}{2\pi}\sum_{j_3}\int_0^\infty d\omega_1\frac{\partial}{\partial t_1^+}\left(D^<_{j_3j_2}\frac{\partial\Re\Sigma^R_{j_1j_3}}{\partial\omega_1}\right)\Bigg|
$$

$$-\frac{i}{2\pi}\sum_{j_3}\int_0^\infty d\omega_1 \frac{\partial}{\partial t_1^+}\left(D^<_{j_3j_2}\tilde{\Sigma}^<_{j_3j_2}\frac{\partial\Re D^R_{j_1j_3}}{\partial\omega_1}\right)\Bigg|\Bigg\} \tag{3.471}$$

| apply the KB ansatz to the other 2 terms

| 2π cancels and $\int_0^\infty d\omega_1$ only picks up the first delta function

$$= \int\frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\times\Bigg\{\frac{\partial N_{j_1\vec{q}_1^{\,+}(\vec{r}_1t_1^+)}}{\partial t_1^+}$$

$$+\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\frac{\partial}{\partial t_1^+}\left(N_{j_1\vec{q}_1^{\,+}}\left(\frac{\partial\Re\Sigma^R_{j_1j_1}(\omega_{j_1\vec{q}_1^{\,+}})}{\partial\omega_{j_1\vec{q}_1^{\,+}}}-\tilde{\Sigma}^<_{j_1j_1}(\omega_{j_1\vec{q}_1^{\,+}})\frac{\partial\Re D^R_{j_1j_1}(\omega_{j_1\vec{q}_1^{\,+}})}{\partial\omega_{j_1\vec{q}_1^{\,+}}}\right)\right)\Bigg\} \tag{3.472}$$

$$= \int\frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\Bigg\{\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\frac{\partial N_{j_1\vec{q}_1^{\,+}(\vec{r}_1t_1^+)}}{\partial t_1^+}+\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\Bigg[\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\frac{\partial N_{j_1\vec{q}_1^{\,+}}}{\partial t_1^+}\left(\frac{\partial\Re\Sigma^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}-\tilde{\Sigma}^<_{j_1j_1}\frac{\partial\Re D^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}\right)$$

$$+\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}N_{j_1\vec{q}_1^{\,+}}\frac{\partial}{\partial t_1^+}\left(\frac{\partial\Re\Sigma^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}-\tilde{\Sigma}^<_{j_1j_1}\frac{\partial\Re D^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}\right)\Bigg]\Bigg\} \tag{3.473}$$

| use the definition of σ to get $\frac{\partial\sigma}{\partial N}N = \sigma - \ln(N+1)$

| note that $\sigma \backsim \mathcal{O}(N)$ and $\ln(N+1) \backsim \mathcal{O}(\ln N)$ so approximate $\frac{\partial\sigma}{\partial N}N \approx \sigma$

| also we write $\frac{\partial\sigma}{\partial N}\frac{\partial N}{\partial t^+} = \frac{\partial\sigma}{\partial t^+}$

$$\approx \int\frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\Bigg\{\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial t_1^+}+\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\Bigg[\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial t_1^+}\left(\frac{\partial\Re\Sigma^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}-\tilde{\Sigma}^<_{j_1j_1}\frac{\partial\Re D^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}\right)$$

$$+\sigma_{j_1\vec{q}_1^{\,+}}\frac{\partial}{\partial t_1^+}\left(\frac{\partial\Re\Sigma^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}-\tilde{\Sigma}^<_{j_1j_1}\frac{\partial\Re D^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}\right)\Bigg]\Bigg\} \tag{3.474}$$

$$= \int\frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\Bigg\{\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial t_1^+}+\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\frac{\partial}{\partial t_1^+}\left(\sigma_{j_1\vec{q}_1^{\,+}}\left(\frac{\partial\Re\Sigma^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}-\tilde{\Sigma}^<_{j_1j_1}\frac{\partial\Re D^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}\right)\right)\Bigg\} \tag{3.475}$$

$$= \frac{\partial}{\partial t_1^+}\int\frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\sigma_{j_1\vec{q}_1^{\,+}}\left(1+\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\frac{\partial\Re\Sigma^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}-\tilde{\Sigma}^<_{j_1j_1}\frac{\partial\Re D^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}\right)\right) \tag{3.476}$$

And so we can define the entropy density as

$$\boxed{s(\vec{r}_1) \equiv \int\frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\sigma_{j_1\vec{q}_1^{\,+}}\left(1+\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\frac{\partial\Re\Sigma^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}-\tilde{\Sigma}^<_{j_1j_1}\frac{\partial\Re D^R_{j_1j_1}}{\partial\omega_{j_1\vec{q}_1^{\,+}}}\right)\right)} \tag{3.477}$$

It is obvious that without the first order gradient terms, the expression for entropy density is exactly the same as in Boltzmann equation.

Now we gather the remaining bunch of terms on LHS which are terms with spatial and momentum derivatives. Of course the derivation is very similar, so we shall shorten the working.

Terms with spatial and momentum derivatives (LHS)

[46]For the simplest type of 3-phonon interaction, the lesser self energy is of the form $\Sigma^< = D^<D^<$ and for the simplest type of 4-phonon interaction, the lesser self energy is of the form $\Sigma^< = D^<D^<D^<$. See the chapter on anharmonicity for the explicit expressions. Thus the assumption made seems perfectly reasonable.

$$
\begin{aligned}
= \quad & \int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3} \frac{\partial \sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}} \times \Big\{ \quad \left(\nabla_{\vec{q}_1^{\,+}} \omega_{j_1\vec{q}_1^{\,+}}\right) \cdot \left(\nabla_{\vec{r}_1} N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+)\right) \\
& -i \sum_{j_3} \int_0^\infty \frac{d\omega_1}{2\pi} \left(\left(\nabla_{\vec{q}_1^{\,+}} \Re\Sigma^R_{j_1j_3}\right) \cdot \left(\nabla_{\vec{r}_1} D^<_{j_3j_2}\right) - \left(\nabla_{\vec{r}_1} \Re\Sigma^R_{j_1j_3}\right) \cdot \left(\nabla_{\vec{q}_1^{\,+}} D^<_{j_3j_2}\right) \right. \\
& \left. - \left(\nabla_{\vec{q}_1^{\,+}} \Re D^R_{j_1j_3}\right) \cdot \left(\nabla_{\vec{r}_1} \Sigma^<_{j_3j_2}\right) + \left(\nabla_{\vec{r}_1} \Re D^R_{j_1j_3}\right) \cdot \left(\nabla_{\vec{q}_1^{\,+}} \Sigma^<_{j_3j_2}\right) \right) \Big|_{j_1=j_2,\text{free spectral KB}} \Big\}
\end{aligned} \tag{3.478}
$$

| write $\Sigma^< = D^< \tilde{\Sigma}^<$

| implement KB ansatz and only pick up one delta function from the spectral function & 2π cancels

$$
\begin{aligned}
= \quad & \int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3} \frac{\partial \sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}} \times \Big\{ \quad \left(\nabla_{\vec{q}_1^{\,+}} \omega_{j_1\vec{q}_1^{\,+}}\right) \cdot \left(\nabla_{\vec{r}_1} N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+)\right) \\
& -\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}} \left(\left(\nabla_{\vec{q}_1^{\,+}} \Re\Sigma^R_{j_1j_1}\right) \cdot \left(\nabla_{\vec{r}_1} N_{j_1\vec{q}_1^{\,+}}\right) - \left(\nabla_{\vec{r}_1} \Re\Sigma^R_{j_1j_1}\right) \cdot \left(\nabla_{\vec{q}_1^{\,+}} N_{j_1\vec{q}_1^{\,+}}\right) \right. \\
& \left. - \left(\nabla_{\vec{q}_1^{\,+}} \Re D^R_{j_1j_1}\right) \cdot \left(\nabla_{\vec{r}_1} N_{j_1\vec{q}_1^{\,+}} \tilde{\Sigma}^<_{j_1j_1}\right) + \left(\nabla_{\vec{r}_1} \Re D^R_{j_1j_1}\right) \cdot \left(\nabla_{\vec{q}_1^{\,+}} N_{j_1\vec{q}_1^{\,+}} \tilde{\Sigma}^<_{j_1j_1}\right) \right)
\end{aligned} \tag{3.479}
$$

| write $\dfrac{\partial \sigma}{\partial N} \nabla_{\vec{r}} N = \nabla_{\vec{r}} N$ and $\dfrac{\partial \sigma}{\partial N} \nabla_{\vec{q}} N = \nabla_{\vec{q}} N$

| just as in the previous term, approximate $\dfrac{\partial \sigma}{\partial N} N \approx \sigma$

$$
\begin{aligned}
\approx \quad & \int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3} \Big\{ \left(\nabla_{\vec{q}_1^{\,+}} \omega_{j_1\vec{q}_1^{\,+}}\right) \cdot \left(\nabla_{\vec{r}_1} \sigma_{j_1\vec{q}_1^{\,+}}\right) \\
& -\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}} \left(\left(\nabla_{\vec{q}_1^{\,+}} \Re\Sigma^R_{j_1j_1}\right) \cdot \left(\nabla_{\vec{r}_1} \sigma_{j_1\vec{q}_1^{\,+}}\right) - \left(\nabla_{\vec{r}_1} \Re\Sigma^R_{j_1j_1}\right) \cdot \left(\nabla_{\vec{q}_1^{\,+}} \sigma_{j_1\vec{q}_1^{\,+}}\right) \right. \\
& \left. - \left(\nabla_{\vec{q}_1^{\,+}} \Re D^R_{j_1j_3}\right) \cdot \left(\nabla_{\vec{r}_1} (\sigma_{j_1\vec{q}_1^{\,+}} \tilde{\Sigma}^<_{j_1j_1})\right) + \left(\nabla_{\vec{r}_1} \Re D^R_{j_1j_1}\right) \cdot \left(\nabla_{\vec{q}_1^{\,+}} (\sigma_{j_1\vec{q}_1^{\,+}} \tilde{\Sigma}^<_{j_1j_1})\right) \right)
\end{aligned} \tag{3.480}
$$

| use the product rule of differentiation, note that $\nabla_{\vec{r}_1} \cdot \nabla_{\vec{q}_1^{\,+}} \omega_{j_1\vec{q}_1^{\,+}} = 0$

$$
\begin{aligned}
= \quad & \int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3} \Big\{ \nabla_{\vec{r}_1} \cdot \left(\sigma_{j_1\vec{q}_1^{\,+}} \nabla_{\vec{q}_1^{\,+}} \omega_{j_1\vec{q}_1^{\,+}}\right) \\
& -\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}} \Big[\nabla_{\vec{r}_1} \cdot \left(\sigma_{j_1\vec{q}_1^{\,+}} \nabla_{\vec{q}_1^{\,+}} \Re\Sigma^R_{j_1j_1}\right) - \sigma_{j_1\vec{q}_1^{\,+}} \nabla_{\vec{r}_1} \cdot \nabla_{\vec{q}_1^{\,+}} \Re\Sigma^R_{j_1j_1} \\
& -\nabla_{\vec{q}_1^{\,+}} \cdot \left(\sigma_{j_1\vec{q}_1^{\,+}} \nabla_{\vec{r}_1} \Re\Sigma^R_{j_1j_1}\right) + \sigma_{j_1\vec{q}_1^{\,+}} \nabla_{\vec{q}_1^{\,+}} \cdot \nabla_{\vec{r}_1} \Re\Sigma^R_{j_1j_1} \\
& -\nabla_{\vec{r}_1} \cdot \left(\sigma_{j_1\vec{q}_1^{\,+}} \tilde{\Sigma}^<_{j_1j_1} \nabla_{\vec{q}_1^{\,+}} \Re D^R_{j_1j_1}\right) + \sigma_{j_1\vec{q}_1^{\,+}} \tilde{\Sigma}^<_{j_1j_1} \nabla_{\vec{r}_1} \cdot \nabla_{\vec{q}_1^{\,+}} \Re D^R_{j_1j_1} \\
& +\nabla_{\vec{q}_1^{\,+}} \cdot \left(\sigma_{j_1\vec{q}_1^{\,+}} \tilde{\Sigma}^<_{j_1j_1} \nabla_{\vec{r}_1} \Re D^R_{j_1j_1}\right) - \sigma_{j_1\vec{q}_1^{\,+}} \tilde{\Sigma}^<_{j_1j_1} \nabla_{\vec{q}_1^{\,+}} \cdot \nabla_{\vec{r}} \Re D^R_{j_1j_1} \Big] \Big\}
\end{aligned} \tag{3.481}
$$

| assume that cross derivatives "commute" and so 2 pairs of terms cancel

| assume surface integrals of $\vec{q}_1^{\,+}$ vanish[47]

$$
= \quad \nabla_{\vec{r}_1} \cdot \int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3} \sigma_{j_1\vec{q}_1^{\,+}} \left(\nabla_{\vec{q}_1^{\,+}} \omega_{j_1\vec{q}_1^{\,+}} - \frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}} \left(\nabla_{\vec{q}_1^{\,+}} \Re\Sigma^R_{j_1j_1}\right) - \frac{\tilde{\Sigma}^<_{j_1j_1}}{2\omega_{j_1\vec{q}_1^{\,+}}} \left(\nabla_{\vec{q}_1^{\,+}} \Re D^R_{j_1j_1}\right) \right) \tag{3.482}
$$

And so we can define the entropy flux density as

$$\boxed{\vec{j}_s \equiv \int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\sigma_{j_1\vec{q}_1^{\,+}}\left(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}} - \frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\nabla_{\vec{q}_1^{\,+}}\Re\Sigma^R_{j_1j_1}\right) - \frac{\tilde{\Sigma}^<_{j_1j_1}}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\nabla_{\vec{q}_1^{\,+}}\Re D^R_{j_1j_1}\right)\right)} \tag{3.483}$$

It is obvious that without the first order gradient terms, the expression for entropy flux density is exactly the same as in Boltzmann equation.

The (entropy) continuity equation has exactly the same form (as it should be)

$$\frac{\partial s(\vec{r}_1)}{\partial t_1^+} + \nabla_{\vec{r}_1}\cdot\vec{j}_s = \int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\left(\frac{\partial N_{j_1\vec{q}_1^{\,+}}}{\partial t_1^+}\right)_{\text{coll}} \tag{3.484}$$

The H-theorem is the same as before,

$$\frac{\partial S}{\partial t_1^+} \geq 0 \Longrightarrow \int d\vec{r}_1 \int \frac{d\vec{q}_1^{\,+}}{(2\pi)^3}\frac{\partial\sigma_{j_1\vec{q}_1^{\,+}}}{\partial N_{j_1\vec{q}_1^{\,+}}}\left(\frac{\partial N_{j_1\vec{q}_1^{\,+}}}{\partial t_1^+}\right)_{\text{coll}} \geq 0 \tag{3.485}$$

Finally we shall explain the meaning of the extra terms in $s(\vec{r}_1)$ and $\vec{j}_s$. The first order gradient terms (and the higher order gradient terms) imply correlation between the particles. The function $\sigma_{j_1\vec{q}_1^{\,+}}$ is about the rearrangement of large numbers of uncorrelated (bosonic) particles. Thus we can view the extra terms as corrections to the rearrangement of large numbers of correlated (bosonic) particles.

3.3.3 QKE based on Generalized Kadanoff-Baym (GKB) Ansatz

See the discussion on pg 95 in [Haug2007]. In the electron case, we have the exact (but first order) Kubo formula to compare with QKE (KB ansatz) and it turns out that they give different results. Kubo formula results are more trustworthy because it is derived exactly without any ansatz, so the suspicion is on KB ansatz. An ansatz that is to be applied to pre-QKE is supposed to give us an evolution equation of a one-time distribution function, KB ansatz employs the "center of mass" time as that one-time. We now seek a different route and derive an expansion around the time-diagonal. This gives the Generalized Kadanoff-Baym (GKB) Ansatz. We hope to reduce pre-QKE to QKE using GKB ansatz.

[Disclaimer:] In the phonon case, the Kubo formulation is hardly trustable as its derivation was founded mostly on analogy. We do not really have an exact theory (even if it is low order) to compare the results against. Probably the most reliable theory for phonons is the phonon Boltzmann equation, thus it is not clear if we derive a GKB ansatz for phonons and use it to reduce pre-QKE to QKE is of any use at all. Nonetheless we proceed with it.

3.3.3.1 Generalized Kadanoff-Baym Ansatz (Phonons)*

If we follow the derivation as in the electronic case (see the appendix on electrons), we realize that the first order time derivative in the equation of motion of the electronic Green's function is vital for the derivation. Phonon Green's function $\langle QQ\rangle$ or $\langle uu\rangle$ (which takes into account phonon number nonconservation) obeys a second order time derivative equation of motion. Thus the derivation of GKB ansatz does not go through. We propose to treat $\langle QQ\rangle$ as a sum of 4 bosonic Green's functions. Since each bosonic Green's function obeys a first order time derivative equation, we can work out the GKB

[47] I am not sure how this can be proved or justified.

ansatz for each of them. Then we sum them up and get the GKB ansatz for $\langle QQ \rangle$.

$$
\begin{aligned}
D^<_{j\vec{q}j'\vec{q}\,'}(tt') &= -\frac{i}{\hbar}\left\langle Q_{j'\vec{q}\,'}(t')Q_{j\vec{q}}(t)\right\rangle && (3.486)\\
&= -\frac{i}{\hbar}\sqrt{\frac{\hbar}{2\omega_{j'\vec{q}\,'}}}\sqrt{\frac{\hbar}{2\omega_{j\vec{q}}}}\left\langle\left(a^\dagger_{j'-\vec{q}\,'}(t') + a_{j'\vec{q}\,'}(t')\right)\left(a^\dagger_{j,-\vec{q}}(t) + a_{j\vec{q}}(t)\right)\right\rangle && (3.487)\\
&= -\frac{i}{\hbar}\sqrt{\frac{\hbar}{2\omega_{j'\vec{q}\,'}}}\sqrt{\frac{\hbar}{2\omega_{j\vec{q}}}}\left\{\left\langle a^\dagger_{j',-\vec{q}\,'}(t')a^\dagger_{j,-\vec{q}}(t)\right\rangle + \left\langle a^\dagger_{j',-\vec{q}\,'}(t')a_{j\vec{q}}(t)\right\rangle\right.\\
&\quad \left.\left\langle a_{j'\vec{q}\,'}(t')a^\dagger_{j,-\vec{q}}(t)\right\rangle + \left\langle a_{j'\vec{q}\,'}(t')a_{j\vec{q}}(t)\right\rangle\right\} && (3.488)\\
&\equiv \sqrt{\frac{\hbar}{2\omega_{j'\vec{q}\,'}}}\sqrt{\frac{\hbar}{2\omega_{j\vec{q}}}}\left\{D^<_{a^\dagger a^\dagger}(tt') + D^<_{aa^\dagger}(tt') + D^<_{a^\dagger a}(tt') + D^<_{aa}(tt')\right\} && (3.489)
\end{aligned}
$$

Now we have 4 "lesser" Green's functions to handle. We write down 2 useful equations of motion.

$$
\begin{aligned}
\left(\frac{d}{dt} - i\omega_{j\vec{q}}\right)a^\dagger_{j,-\vec{q}}(t) &= \left[H_{\text{int}}, a^\dagger_{j,-\vec{q}}(t)\right]_- && (3.490)\\
\left(\frac{d}{dt} + i\omega_{j\vec{q}}\right)a_{j\vec{q}}(t) &= \left[H_{\text{int}}, a_{j\vec{q}}(t)\right]_- && (3.491)
\end{aligned}
$$

To explore the causal structure, we need the respective reatrded Green's function and advanced Green's function. Note that because we are dealing with a nonequilibrium situation, both the left and the right equations of motion are needed.

We start with $D^<_{a^\dagger a^\dagger}(tt')$ and define its retarded version.

$$
D^R_{a^\dagger a^\dagger}(tt') \equiv -\frac{i}{\hbar}\theta(t-t')\left\langle\left[a^\dagger_{j,-\vec{q}}(t), a^\dagger_{j',-\vec{q}\,'}(t')\right]_-\right\rangle \tag{3.492}
$$

We seek its left equation of motion.

$$
\begin{aligned}
\frac{d}{dt}D^R_{a^\dagger a^\dagger}(tt') &= -\frac{i}{\hbar}\delta(t-t')\left\langle\left[a^\dagger_{j,-\vec{q}}(t), a^\dagger_{j',-\vec{q}\,'}(t')\right]_-\right\rangle - \frac{i}{\hbar}\theta(t-t')\left\langle\left[\frac{d}{dt}a^\dagger_{j,-\vec{q}}(t), a^\dagger_{j',-\vec{q}\,'}(t')\right]_-\right\rangle\\
&\quad | \quad \text{use the equal time commutation in the first term and we get zero}\\
&= -\frac{i}{\hbar}\theta(t-t')\left\langle\left[\frac{d}{dt}a^\dagger_{j,-\vec{q}}(t), a^\dagger_{j',-\vec{q}\,'}(t')\right]_-\right\rangle && (3.493)
\end{aligned}
$$

We need to pause here and realize that this Green's function is missing the time diagonal term! Thus in the time diagonal expansion, it does not contribute a time diagonal term which is what we are seeking. Considering the equal time commutation relations, we can ignore $D^<_{aa}(tt')$ in the subsequent discussion as well.

Thus there are only 2 "lesser" Green's functions to work with. We now work with $D^<_{aa^\dagger}(tt') = -\frac{i}{\hbar}\left\langle a^\dagger_{j',-\vec{q}\,'}(t')a_{j\vec{q}}(t)\right\rangle$. Define the retarded version,

$$
D^R_{aa^\dagger}(tt') \equiv -\frac{i}{\hbar}\theta(t-t')\left\langle\left[a_{j\vec{q}}(t), a^\dagger_{j',-\vec{q}\,'}(t')\right]_-\right\rangle \tag{3.494}
$$

Derive the left equation of motion.

$$\begin{aligned}
\frac{d}{dt} D^R_{aa^\dagger}(tt') &= -\frac{i}{\hbar}\left\langle \left[a_{j\vec{q}}(t), a^\dagger_{j',-\vec{q}\,'}(t')\right]_-\right\rangle - \frac{i}{\hbar}\theta(t-t')\left\langle \left[\frac{d}{dt}a_{j\vec{q}}(t), a^\dagger_{j',-\vec{q}\,'}(t')\right]_-\right\rangle \\
&\quad | \quad \text{use equal time commutation relations in the first term} \\
&\quad | \quad \text{use the equation of motion of } a_{j\vec{q}}(t) \text{ in the second term} \\
&= -\frac{i}{\hbar}\delta(t-t')\delta_{jj'}\delta_{\vec{q},-\vec{q}\,'} - \frac{i}{\hbar}\theta(t-t')(-i\omega_{j\vec{q}}\left\langle \left[a_{j\vec{q}}(t), a^\dagger_{j',-\vec{q}\,'}(t')\right]_-\right\rangle \\
&\quad -\frac{i}{\hbar}\theta(t-t')\left\langle \left[\left[H_{\text{int}}, a_{j\vec{q}}(t)\right]_-, a^\dagger_{j',-\vec{q}\,'}(t')\right]_-\right\rangle \qquad (3.495)\\
\left(i\hbar\frac{d}{dt} - \hbar\omega_{j\vec{q}}\right) D^R_{aa^\dagger}(tt') &= \delta(t-t')\delta_{jj'}\delta_{\vec{q},-\vec{q}\,'} + \theta(t-t')\left\langle \left[\left[H_{\text{int}}, a_{j\vec{q}}(t)\right]_-, a^\dagger_{j',-\vec{q}\,'}(t')\right]_-\right\rangle \qquad (3.496)
\end{aligned}$$

We shall denote it with the form of a left Dyson equation

$$\left(i\hbar\frac{d}{dt} - \hbar\omega_{j\vec{q}}\right) D^R_{aa^\dagger}(tt') = \delta(t-t')\delta_{jj'}\delta_{\vec{q},-\vec{q}\,'} + \int d1 \Sigma^R_{aa^\dagger}(t1) D^R_{aa^\dagger}(1t') \qquad (3.497)$$

where we assume that there is an associated self energy $\Sigma^R_{aa^\dagger}$ and index "1" represents all variables including time. We write into the inverse form.

$$\text{left:} \quad D^{R-1}_{aa^\dagger}(tt') = \left(i\hbar\frac{d}{dt}\delta(t-t') - \hbar\omega_{j\vec{q}}\delta_{jj'}\delta_{\vec{q},-\vec{q}\,'}\right) - \Sigma^R_{aa^\dagger}(tt') \qquad (3.498)$$

It is obvious that the same working will be repeated for the subsequent derivation, so we will only give the results here.

The right equation of motion in the form of a right Dyson equation is

$$\left(-i\hbar\frac{d}{dt'} - \hbar\omega_{j'\vec{q}\,'}\right) D^R_{aa^\dagger}(tt') = \delta(t-t')\delta_{jj'}\delta_{\vec{q},-\vec{q}\,'} + \int d1 D^R_{aa^\dagger}(t1)\Sigma^R_{aa^\dagger}(1t') \qquad (3.499)$$

The inverse form is

$$\text{right:} \quad D^{R-1}_{aa^\dagger}(tt') = \left(-i\hbar\frac{d}{dt'}\delta(t-t') - \hbar\omega_{j'\vec{q}\,'}\delta_{jj'}\delta_{\vec{q},-\vec{q}\,'}\right) - \Sigma^R_{aa^\dagger}(tt') \qquad (3.500)$$

Define the advanced version,

$$D^A_{aa^\dagger}(tt') \equiv \frac{i}{\hbar}\theta(t'-t)\left\langle \left[a_{j\vec{q}}(t), a^\dagger_{j',-\vec{q}\,'}\right]_-\right\rangle \qquad (3.501)$$

The inverse forms are

$$\begin{aligned}
\text{left:} \quad D^{A-1}_{aa^\dagger}(tt') &= \left(i\hbar\frac{d}{dt}\delta(t'-t) - \hbar\omega_{j\vec{q}}\delta_{jj'}\delta_{\vec{q},-\vec{q}\,'}\right) - \Sigma^A_{aa^\dagger}(tt') \qquad (3.502)\\
\text{right:} \quad D^{A-1}_{aa^\dagger}(tt') &= \left(-i\hbar\frac{d}{dt'}\delta(t'-t) - \hbar\omega_{j\vec{q}}\delta_{jj'}\delta_{\vec{q},-\vec{q}\,'}\right) - \Sigma^A_{aa^\dagger}(tt') \qquad (3.503)
\end{aligned}$$

Now we can carry out the expansion about the time diagonal, i.e. the GKB ansatz derivation. We define the auxiliary functions,

$$D^{R<}_{aa^\dagger}(tt') \equiv \theta(t-t')D^<_{aa^\dagger}(tt') \qquad (3.504)$$

$$D^{A<}_{aa^\dagger}(tt') \equiv \theta(t'-t)D^{<}_{aa^\dagger}(tt') \tag{3.505}$$

where obviously,

$$D^{<}_{aa^\dagger}(tt') = D^{R<}_{aa^\dagger}(tt') + D^{A<}_{aa^\dagger}(tt') \tag{3.506}$$

Convolve D^{R-1} on the left of $D^{R<}$ in time using the left equation,

$$\begin{aligned}
& \int dt_1 D^{R-1}_{aa^\dagger}(tt_1)D^{R<}_{aa^\dagger}(t_1t') \\
= & \int dt_1 \left[\left(i\hbar\frac{d}{dt}\delta(t-t_1) - \hbar\omega_{j\vec{q}}\delta_{jj'}\delta_{\vec{q},-\vec{q}\,'}\right) - \Sigma^R_{aa^\dagger}(tt')\right] D^{R<}_{aa^\dagger}(t_1t') && (3.507) \\
| & \quad \text{we retain only the first 2 terms for illustration} \\
| & \quad \text{see the appendix on electrons on how to handle the self energy term} \\
= & \int dt_1 i\hbar\frac{d}{dt}\delta(t-t_1)\theta(t_1-t')D^{<}_{aa^\dagger}(t_1t') + \cdots && (3.508) \\
= & \; i\hbar\frac{d}{dt}\theta(t-t')D^{<}_{aa^\dagger}(tt') + \cdots && (3.509) \\
= & \; i\hbar\delta(t-t')D^{<}_{aa^\dagger}(tt') + i\hbar\theta(t-t')\frac{d}{dt}D^{<}_{aa^\dagger}(tt') + \cdots && (3.510) \\
| & \quad \text{convolve } D^R \text{ in time from the left} \\
D^{R<}_{aa^\dagger}(tt') = & \; i\hbar D^{R}_{aa^\dagger}(tt')D^{<}_{aa^\dagger}(t't') + \cdots && (3.511)
\end{aligned}$$

We repeat the same derivation for $D^{A<}_{aa^\dagger}(tt')$. Convolve D^{A-1} on the right of $D^{A<}$ in time using the right equation,

$$\begin{aligned}
& \int dt_1 D^{A<}_{aa^\dagger}(tt_1)D^{A-1}_{aa^\dagger}(t_1t') \\
= & \int dt_1 \left[\left(-i\hbar\frac{d}{dt'}\delta(t_1-t') - \hbar\omega_{j'\vec{q}\,'}\delta_{jj'}\delta_{\vec{q},-\vec{q}\,'}\right) D^{A<}_{aa^\dagger}(tt_1) - D^{A<}_{aa^\dagger}(tt_1)\Sigma^A_{aa^\dagger}(t_1t')\right] && (3.512) \\
= & -i\hbar\int dt_1 \frac{d}{dt'}\delta(t_1-t')\theta(t_1-t)D^{<}_{aa^\dagger}(tt_1) + \cdots && (3.513) \\
= & -i\hbar\delta(t'-t)D^{<}_{aa^\dagger}(tt') - i\hbar\theta(t'-t)\frac{d}{dt'}D^{<}_{aa^\dagger}(tt') + \cdots && (3.514) \\
| & \quad \text{convolve } D^A \text{ in time from the right} \\
D^{A<}_{aa^\dagger}(tt') = & -i\hbar D^{<}_{aa^\dagger}(tt)D^{A}_{aa^\dagger}(tt') + \cdots && (3.515)
\end{aligned}$$

So,

$$D^{<}_{aa^\dagger}(tt') = i\hbar D^{R}_{aa^\dagger}(tt')D^{<}_{aa^\dagger}(t't') - i\hbar D^{<}_{aa^\dagger}(tt)D^{A}_{aa^\dagger}(tt') + \cdots \tag{3.516}$$

The equal time lesser Green's functions are the one-time distribution functions that we are seeking.

We now proceed to deal with the last Green's function $D^{<}_{a^\dagger a} = -\frac{i}{\hbar}\left\langle a_{j'\vec{q}\,'}(t')a^\dagger_{j,-\vec{q}}(t)\right\rangle$. The derivation is exactly the same as above so we list down only the important expressions.

Define the retarded version,

$$D^{R}_{a^\dagger a}(tt') \equiv -\frac{i}{\hbar}\theta(t-t')\left\langle\left[a^\dagger_{j,-\vec{q}}(t), a_{j'\vec{q}\,'}(t')\right]_-\right\rangle \tag{3.517}$$

The left and the right inverse form of Dyson equations are

$$\begin{aligned}
\text{left:} \quad D^{R-1}_{a^\dagger a}(tt') &= \left(-i\hbar\frac{d}{dt}\delta(t-t') - \hbar\omega_{j\vec{q}}\delta_{jj'}\delta_{-\vec{q},\vec{q}\,'}\right) - \Sigma^R_{a^\dagger a}(tt') \quad (3.518)\\
\text{right:} \quad D^{R-1}_{a^\dagger a}(tt') &= \left(i\hbar\frac{d}{dt'}\delta(t-t') - \hbar\omega_{j'\vec{q}\,'}\delta_{jj'}\delta_{-\vec{q},\vec{q}\,'}\right) - \Sigma^R_{a^\dagger a}(tt') \quad (3.519)
\end{aligned}$$

Define the advanced version,

$$D^A_{a^\dagger a}(tt') \equiv \frac{i}{\hbar}\theta(t'-t)\left\langle \left[a^\dagger_{j,-\vec{q}}(t), a_{j'\vec{q}\,'}(t')\right]_-\right\rangle \quad (3.520)$$

The left and the right inverse form of Dyson equations are

$$\begin{aligned}
\text{left:} \quad D^{A-1}_{a^\dagger a}(tt') &= \left(-i\hbar\frac{d}{dt}\delta(t-t') - \hbar\omega_{j\vec{q}}\delta_{jj'}\delta_{-\vec{q},\vec{q}\,'}\right) - \Sigma^A_{a^\dagger a}(tt') \quad (3.521)\\
\text{right:} \quad D^{A-1}_{a^\dagger a}(tt') &= \left(i\hbar\frac{d}{dt'}\delta(t-t') - \hbar\omega_{j'\vec{q}\,'}\delta_{jj'}\delta_{-\vec{q},\vec{q}\,'}\right) - \Sigma^A_{a^\dagger a}(tt') \quad (3.522)
\end{aligned}$$

Now we can carry out the expansion about the time diagonal, i.e. the GKB ansatz derivation. We define the auxiliary functions

$$\begin{aligned}
D^{R<}_{a^\dagger a}(tt') &\equiv \theta(t-t')D^<_{a^\dagger a}(tt') \quad (3.523)\\
D^{A<}_{a^\dagger a}(tt') &\equiv \theta(t'-t)D^<_{a^\dagger a}(tt') \quad (3.524)
\end{aligned}$$

where obviously, $D^<_{a^\dagger a}(tt') = D^{R<}_{a^\dagger a}(tt') + D^{A<}_{a^\dagger a}(tt')$. Again we convolve D^{R-1} to the left of $D^{R<}$ in time and retain only the time diagonal term after which D^R is convolved to the left. Then convolve D^{A-1} to the right of $D^{A<}$ and retain only the time diagonal term after which D^A is convolved to the right. Sum them to get

$$\begin{aligned}
D^<_{a^\dagger a}(tt') &= D^{R<}_{a^\dagger a}(tt') + D^{A<}_{a^\dagger a}(tt') \quad (3.525)\\
&= -i\hbar D^R_{a^\dagger a}(tt')D^<_{a^\dagger a}(t't') + i\hbar D^<_{a^\dagger a}(tt)D^A_{a^\dagger a}(tt') + \cdots \quad (3.526)
\end{aligned}$$

The final result for the $\langle QQ\rangle$ lesser Green's function is

$$\begin{aligned}
D^<_{j\vec{q}j'\vec{q}\,'}(tt') \approx \; & \sqrt{\frac{\hbar}{2\omega_{j'\vec{q}\,'}}}\sqrt{\frac{\hbar}{2\omega_{j\vec{q}}}}\left\{i\hbar D^R_{aa^\dagger}(tt')D^<_{aa^\dagger}(t't') - i\hbar D^<_{aa^\dagger}(tt)D^A_{aa^\dagger}(tt')\right.\\
& \left. -i\hbar D^R_{a^\dagger a}(tt')D^<_{a^\dagger a}(t't') + i\hbar D^<_{a^\dagger a}(tt)D^A_{a^\dagger a}(tt')\right\} \quad (3.527)
\end{aligned}$$

We want to quickly digress and discuss what happens if we directly guess the expression of GKB ansatz from the electronic GKB ansatz without going through the causal expansion.

The guess is, [48]

$$D^<_{j\vec{q}j'\vec{q}\,'}(tt') \approx i\hbar\sqrt{\frac{2\omega_{j\vec{q}}}{\hbar}}\sqrt{\frac{2\omega_{j'\vec{q}\,'}}{\hbar}}D^R_{j\vec{q}j'\vec{q}\,'}(tt')D^<_{j\vec{q}j'\vec{q}\,'}(t't') - i\hbar\sqrt{\frac{2\omega_{j\vec{q}}}{\hbar}}\sqrt{\frac{2\omega_{j'\vec{q}\,'}}{\hbar}}D^<_{j\vec{q}j'\vec{q}\,'}(tt)D^A_{j\vec{q}j'\vec{q}\,'}(tt')$$

[48] The factors are due to dimensional reasons. This can be seen schematically as

$$-\frac{i}{\hbar}\langle QQ\rangle = -\frac{i}{\hbar}\sqrt{\frac{\hbar}{2\omega}}\sqrt{\frac{\hbar}{2\omega}}\langle aa\rangle$$

$$
\begin{aligned}
= \quad & i\hbar\sqrt{\frac{2\omega_{j\vec{q}}}{\hbar}}\sqrt{\frac{2\omega_{j'\vec{q}\,'}}{\hbar}}\left(-\frac{i}{\hbar}\right)\theta(t-t')\left\langle\left[Q_{j\vec{q}}(t),Q_{j'\vec{q}\,'}(t')\right]_-\right\rangle\left(-\frac{i}{\hbar}\right)\left\langle Q_{j'\vec{q}\,'}(t')Q_{j\vec{q}}(t')\right\rangle \\
& -i\hbar\sqrt{\frac{2\omega_{j\vec{q}}}{\hbar}}\sqrt{\frac{2\omega_{j'\vec{q}\,'}}{\hbar}}\left(-\frac{i}{\hbar}\right)\left\langle Q_{j'\vec{q}\,'}(t)Q_{j\vec{q}}(t)\right\rangle\left(\frac{i}{\hbar}\right)\theta(t'-t)\left\langle\left[Q_{j\vec{q}}(t),Q_{j'\vec{q}\,'}(t')\right]_-\right\rangle
\end{aligned}
\tag{3.528}
$$

If we write $Q_{j\vec{q}}(t)=\sqrt{\frac{\hbar}{2\omega_{j\vec{q}}}}\left(a^\dagger_{j,-\vec{q}}(t)+a_{j\vec{q}}(t)\right)$ and expand out the above expression, we get 32 terms! [49] We do see that 4 out of 32 terms correspond to our derived result (3.527) but there are 28 spurious terms at the same order! So now we need to collect our thoughts:

- Derivation by casual expansion (3.527): The expression was obtained by proper casual expansion so it should be correct. However, during the derivation, particle non-conserving (retarded) Green's functions $\langle[a,a]_-\rangle$ and $\langle a^\dagger,a^\dagger]_-\rangle$ had no contribution. So it seems to have lost the particle number non-conserving part of the theory. I also have no idea on how to implement this expression into pre-QKE.

- Guessed from the electronic case (3.528): The expression is inspired by the electronic version and implementing it into pre-QKE is well known from the electronic case. However the spurious terms makes the physical correctness of this expression dubious.

Thus at this point, I have to admit that I can't proceed further because it seems that both expressions are not really making sense.

[Contribution:] Here I will briefly state what this contribution is about. Note that if Kadanoff-Baym (KB) equations can be solved then we do not have any need for the kinetic theory! Thus we hope that the kinetic theory has as many features of the original exact KB equations as possible. Kinetic theory starts off having only the collisional treatment of interactions then gradient expansion restores some of the correlational aspect of interactions. This GKBA allows some restoration of the casual structure of the equations and thus we can have as much physics in the kinetic theory as that in the exact KB equations (hopefully). For the electronic case, it was even found that the kinetic theory only agreed with linear response theory when GKBA is used and the kinetic theory with GKBA allows going beyond linear response theory.

3.4 From NEGF to Linear Response Theory

We follow [DiVentra2008] section 2.3. The classics, without a doubt, are Kubo's original papers [Kubo1957].

This is the third development from NEGF. Strictly speaking, this does not use any tricks from NEGF, this is simply a theory developed by truncating at the first order from an expansion in the unitary evolution operator. Thus it is at the same level as Fermi's Golden Rule. The beauty is that, it can be written into a response form which so many phenomenological laws resemble. [50] It is completely quantum though only to first order.

We recall the time-dependent Hamiltonian used in NEGF

$$H(t)=H_0+H_{\text{int}}+V(t)\theta(t-t_0) \tag{3.529}$$

[49] Note that terms $\langle[a(t),a(t')]_-\rangle$ and $\langle[a^\dagger(t),a^\dagger(t')]_-\rangle$ are not necessarily zero. Recall that these operators are in Heisenberg picture and the Hamiltonian involves particle number non-conserving terms.

[50] This form is schematically, "Effect = response coefficient × driver". Examples of laws that have this form are; Ohm's law: $\vec{J}=\sigma\vec{E}$, Fourier's law: $\vec{J}=-\kappa\nabla T$ and Magnetization: $\vec{M}=\chi\vec{H}$.

We start with the NEGF time-dependent expectation value and proceed in the Heisenberg picture (most derivations in the literature use Schrodinger picture but obviously it does not matter). There is no need to introduce contour-time quantities since we are only working up to first order.

$$\begin{aligned}
\langle A(t)\rangle &= \frac{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\mathrm{int}})}A_H(t)\right)}{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\mathrm{int}})}\right)} && (3.530)\\
&\quad |\quad \text{where } A \text{ is an arbitrary operator}\\
&\quad |\quad \text{define } \rho_{t_0} = \frac{\mathrm{Tr} e^{-\beta(H_0+H_{\mathrm{int}})}}{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\mathrm{int}})}\right)}\\
&\quad |\quad \text{where the subscript } t_0 \text{ is really redundant}\\
&= \mathrm{Tr}\left(\rho_{t_0}\left(Te^{\frac{i}{\hbar}\int_{t_0}^t dt_1 H(t_1)}\right)A_{t_0}\left(Te^{-\frac{i}{\hbar}\int_{t_0}^t dt_2 H(t_2)}\right)\right) && (3.531)\\
&\quad |\quad \text{use Dyson's identity and expand to first order}\\
&\quad |\quad Te^{-\frac{i}{\hbar}\int_{t_0}^t dt_1 H(t_1)} = e^{-\frac{i}{\hbar}(H_0+H_{\mathrm{int}})(t-t_0)}Te^{-\frac{i}{\hbar}\int_{t_0}^t dt_1 V_{H_0+H_{\mathrm{int}}}(t_1)}\\
&\quad |\quad \approx e^{-\frac{i}{\hbar}(H_0+H_{\mathrm{int}})(t-t_0)}\left(1-\frac{i}{\hbar}\int_{t_0}^t dt_1 V_{H_0+H_{\mathrm{int}}}(t_1)\right)\\
&\quad |\quad \text{where we defined interaction operators,}\\
&\quad |\quad A_{H_0+H_{\mathrm{int}}}(t_1) = e^{\frac{i}{\hbar}(H_0+H_{\mathrm{int}})(t_1-t_0)}A_{t_0}e^{-\frac{i}{\hbar}(H_0+H_{\mathrm{int}})(t_1-t_0)}\\
&= \mathrm{Tr}\left(\rho_{t_0}\left(1+\frac{i}{\hbar}\int_{t_0}^t dt_1 V_{H_0+H_{\mathrm{int}}}(t_1)\right)V_{H_0+H_{\mathrm{int}}}(t)\left(1-\frac{i}{\hbar}\int_{t_0}^t dt_2 V_{H_0+H_{\mathrm{int}}}(t_2)\right)\right) && (3.532)\\
&\quad |\quad \text{keeping only to first order in } V\\
&= \mathrm{Tr}\left(\rho_{t_0}A_{H_0+H_{\mathrm{int}}}(t)\right) - \frac{i}{\hbar}\int_{t_0}^t dt_1 \mathrm{Tr}\left(\rho_{t_0}\left[A_{H_0+H_{\mathrm{int}}}(t), V_{H_0+H_{\mathrm{int}}}(t_1)\right]_-\right) && (3.533)
\end{aligned}$$

Assume that the time-dependent Hamiltonian takes the following form

$$V(t) = \hat{V}_{t_0}f(t) \tag{3.534}$$

where $\hat{V}_{t_0}$ is the operator part and $f(t)$ is the function part with parametric time dependence. We define the change in expectation value (i.e. response) as $\delta\langle A(t)\rangle = \langle A(t)\rangle - \mathrm{Tr}\left(\rho_{t_0}A_{H_0+H_{\mathrm{int}}}(t)\right)$ and get,

$$\delta\langle A(t)\rangle = -\frac{i}{\hbar}\int_{t_0}^t dt_1 \mathrm{Tr}\left(\rho_{t_0}\left[A_{H_0+H_{\mathrm{int}}}(t), \hat{V}_{H_0+H_{\mathrm{int}}}(t_1)\right]_-\right)f(t_1) \tag{3.535}$$

Now it has the form of a linear response formula and we can define the retarded response function χ^R

$$\begin{aligned}
\chi^R_{A\hat{V}}(t,t_1) &= -\frac{i}{\hbar}\theta(t-t_1)\mathrm{Tr}\left(\rho_{t_0}\left[A_{H_0+H_{\mathrm{int}}}(t), \hat{V}_{H_0+H_{\mathrm{int}}}(t_1)\right]_-\right) && (3.536)\\
&\quad |\quad \text{use trace cyclicity and that } H_0+H_{\mathrm{int}} \text{ commutes with } \rho_{t_0} \text{ in the second term}\\
&\quad |\quad \text{to show that it is only a function of the time difference.}\\
&= -\frac{i}{\hbar}\theta(t-t_1)\mathrm{Tr}\left(\rho_{t_0}\left[A_{H_0+H_{\mathrm{int}}}(t-t_1), \hat{V}_{t_0}\right]_-\right) && (3.537)\\
&= \chi^R_{A\hat{V}}(t-t_1) && (3.538)
\end{aligned}$$

We can now write the linear response formula into a compact form and we can write $t\to\infty$ due to the step function

$$\delta\langle A(t)\rangle = \int_{t_0}^{\infty} dt_1 \chi^R_{A\hat{V}}(t-t_1) f(t_1) \tag{3.539}$$

Define the Fourier transform to frequency domain as

$$\delta\langle A(\omega)\rangle = \int_{-\infty}^{\infty} dt e^{i\omega t}\delta\langle A(t)\rangle \tag{3.540}$$

we can now write the linear response formula (which is convolved in time domain) in the frequency domain as

$$\delta\langle A(\omega)\rangle = \chi^R_{A\hat{V}}(\omega) f(\omega) \tag{3.541}$$

The retarded response function is thus written as (with the adiabatic damping term for reasons of convergence)

$$\begin{aligned}
\chi^R_{A\hat{V}}(\omega) &= \lim_{\epsilon\to 0^+}\int_{-\infty}^{\infty} d(t-t_1) e^{(i\omega-\epsilon)(t-t_1)}\chi^R_{A\hat{V}}(t-t_1) && (3.542)\\
&= -\frac{i}{\hbar}\int_{-\infty}^{\infty} d(t-t_1)\theta(t-t_1) e^{(i\omega-\epsilon)(t-t_1)}\left\langle \left[A_{H_0+H_{\text{int}}}(t-t_1), \hat{V}_{t_0}\right]_-\right\rangle && (3.543)\\
&\quad | \quad \text{use the step function}\\
&= -\frac{i}{\hbar}\lim_{\epsilon\to 0^+}\int_{0}^{\infty} dt e^{(i\omega-\epsilon)t}\left\langle \left[A_{H_0+H_{\text{int}}}(t), \hat{V}_{t_0}\right]_-\right\rangle && (3.544)
\end{aligned}$$

$$\boxed{\chi^R_{A\hat{V}}(\omega) = -\frac{i}{\hbar}\lim_{\epsilon\to 0^+}\int_{0}^{\infty} dt e^{(i\omega-\epsilon)t}\left\langle \left[A_{H_0+H_{\text{int}}}(t), \hat{V}_{t_0}\right]_-\right\rangle} \tag{3.545}$$

We call it the commutator form of the response function. Rewriting into a slightly different form,

$$\begin{aligned}
\chi^R_{A\hat{V}}(t,t_1) &= -\frac{i}{\hbar}\theta(t-t_1)\left\langle \left[A_{H_0+H_{\text{int}}}(t), \hat{V}_{H_0+H_{\text{int}}}(t_1)\right]_-\right\rangle && (3.546)\\
&\quad | \quad \text{assuming that } \hat{V} \text{ and } A \text{ are Hermitian (of course } \rho_{t_0} \text{ is Hermitian), we can write}\\
&= -\frac{i}{\hbar}\theta(t-t_1)\left(\left\langle A_{H_0+H_{\text{int}}}(t), \hat{V}_{H_0+H_{\text{int}}}(t_1)\right\rangle - \left\langle A_{H_0+H_{\text{int}}}(t), \hat{V}_{H_0+H_{\text{int}}}(t_1)\right\rangle^*\right) && (3.547)\\
&\quad | \quad \text{let the complex number } \langle A\hat{V}\rangle = x+iy\\
&= -\frac{i}{\hbar}\theta(t-t_1)2iy && (3.548)\\
&= \frac{1}{\hbar}\theta(t-t_1)2y && (3.549)\\
&= \frac{2}{\hbar}\theta(t-t_1)\Im\left\langle A_{H_0+H_{\text{int}}}(t), \hat{V}_{H_0+H_{\text{int}}}(t_1)\right\rangle && (3.550)\\
&\quad | \quad \text{again using trace cyclicity and that } H_0+H_{\text{int}} \text{ commutes with } \rho_{t_0}\\
&= \frac{2}{\hbar}\theta(t-t_1)\Im\left\langle A_{H_0+H_{\text{int}}}(t-t_1), \hat{V}_{t_0}\right\rangle && (3.551)
\end{aligned}$$

Writing this second commutator form in the frequency domain, we get

$$\chi^R_{A\hat{V}}(\omega) = \lim_{\epsilon\to 0^+}\int_{-\infty}^{\infty} d(t-t_1) e^{(i\omega-\epsilon)(t-t_1)}\chi^R_{A\hat{V}}(t-t_1) \tag{3.552}$$

$$
\begin{aligned}
&= \frac{2}{\hbar}\lim_{\epsilon\to 0^+}\int_{-\infty}^{\infty} d(t-t_1)\theta(t-t_1)e^{(i\omega-\epsilon)(t-t_1)}\Im\left\langle A_{H_0+H_{\text{int}}}(t-t_1),\hat{V}_{t_0}\right\rangle && (3.553)\\
&\mid \quad \text{use the step function}\\
&= \frac{2}{\hbar}\lim_{\epsilon\to 0^+}\int_{0}^{\infty} dt e^{(i\omega-\epsilon)t}\Im\left\langle A_{H_0+H_{\text{int}}}(t),\hat{V}_{t_0}\right\rangle && (3.554)
\end{aligned}
$$

$$
\boxed{\chi^R_{A\hat{V}}(\omega) = \frac{2}{\hbar}\lim_{\epsilon\to 0^+}\int_{0}^{\infty} dt e^{(i\omega-\epsilon)t}\Im\left\langle A_{H_0+H_{\text{int}}}(t),\hat{V}_{t_0}\right\rangle} \quad (3.555)
$$

This is the final form of the second commutator form. Now we will write it into the Kubo correlator form. First we need the Kubo correlator identity (from Mahan of [Mahan2000] eqn(3.427))

Kubo Correlator Identity:

$$
\begin{aligned}
\left[\hat{V}_{H_0+H_{\text{int}}}(t),\rho_{t_0}\right]_- &= -i\hbar\rho_{t_0}\int_0^{\beta} d\tau^M \frac{d\hat{V}_{H_0+H_{\text{int}}(t-i\hbar\tau^M)}}{dt} && (3.556)\\
&= \rho_{t_0}\int_0^{\beta} d\tau^M e^{\tau^M(H_0+H_{\text{int}})}\left[H_0+H_{\text{int}},\hat{V}_{H_0+H_{\text{int}}}(t)\right]_- e^{\tau^M(H_0+H_{\text{int}})} && (3.557)
\end{aligned}
$$

Proof starting from first line on RHS

$$
\begin{aligned}
&= -i\hbar\int_0^{\beta} d\tau^M \frac{d}{dt}V_{H_0+H_{\text{int}}}(t-i\hbar\tau^M) && (3.558)\\
&\mid \quad \text{use the relation between real time and Matsubara time}\\
&\mid \quad t = t_0 - i\hbar\tau^M \Rightarrow \frac{d}{dt} = \frac{\partial\tau^M}{\partial t}\frac{d}{d\tau^M} = -\frac{1}{i\hbar}\frac{d}{d\tau^M}\\
&= \rho_{t_0}\int_0^{\beta} d\tau^M \frac{d}{d\tau^M}V_{H_0+H_{\text{int}}}(t-i\hbar\tau^M) && (3.559)\\
&= \rho_{t_0}\left[V_{H_0+H_{\text{int}}}(t-i\hbar\tau^M)\right]_0^{\beta} && (3.560)\\
&= \rho_{t_0}\left(V_{H_0+H_{\text{int}}}(t-i\hbar\beta)-V_{H_0+H_{\text{int}}}(t)\right) && (3.561)\\
&= \frac{e^{-\beta(H_0+H_{\text{int}})}}{\text{Tr}\left(e^{-\beta(H_0+H_{\text{int}})}\right)}\text{Tr}\left(e^{\frac{i}{\hbar}(H_0+H_{\text{int}})(-i\hbar\beta)}V_{H_0+H_{\text{int}}}(t)e^{-\frac{i}{\hbar}(H_0+H_{\text{int}})(-i\hbar\beta)}V_{H_0+H_{\text{int}}}(t)\right) && (3.562)\\
&= \frac{e^{-\beta(H_0+H_{\text{int}})}}{\text{Tr}\left(e^{-\beta(H_0+H_{\text{int}})}\right)}\left(e^{\beta(H_0+H_{\text{int}})}V_{H_0+H_{\text{int}}}(t)e^{-\beta(H_0+H_{\text{int}})}-V_{H_0+H_{\text{int}}}(t)\right) && (3.563)\\
&= V_{H_0+H_{\text{int}}}(t)\rho_{t_0}-\rho_{t_0}V_{H_0+H_{\text{int}}}(t) && (3.564)\\
&= \left[V_{H_0+H_{\text{int}}}(t),\rho_{t_0}\right]_- && (3.565)\\
&= \text{LHS (shown)} && (3.566)
\end{aligned}
$$

Now use Heisenberg equation of motion to show the second term on RHS.

Proof starting from first line on RHS

$$
\begin{aligned}
&= -i\hbar\int_0^{\beta} d\tau^M e^{\tau^M(H_0+H_{\text{int}})}\left(\frac{d}{dt}V_{H_0+H_{\text{int}}}(t)\right)e^{-\tau^M(H_0+H_{\text{int}})} && (3.567)\\
&\mid \quad \text{use Heisenberg equation of motion } i\hbar\frac{dV}{dt} = [V,H]_-
\end{aligned}
$$

$$
\begin{aligned}
&= \rho_{t_0} \int_0^\beta d\tau^M e^{\tau^M (H_0+H_{\rm int})} \left[H_0 + H_{\rm int}, V_{H_0+H_{\rm int}}(t)\right]_- e^{-\tau^M (H_0+H_{\rm int})} && (3.568)\\
&= \text{second line on RHS (shown)} && (3.569)
\end{aligned}
$$

We can write the response function χ^R into the Kubo correlator form. This is said to be a simplification as the final expression is not in a commutator form.

$$
\begin{aligned}
\chi^R_{A\hat{V}}(t,t_1) &= \chi^R_{A\hat{V}}(t-t_1) && (3.570)\\
&= -\frac{i}{\hbar}\theta(t-t_1)\mathrm{Tr}\left(\rho_{t_0}\left[A_{H_0+H_{\rm int}}(t), \hat{V}_{H_0+H_{\rm int}}(t_1)\right]_-\right) && (3.571)\\
&= -\frac{i}{\hbar}\theta(t-t_1)\mathrm{Tr}\left(\rho_{t_0}A_{H_0+H_{\rm int}}(t)\hat{V}_{H_0+H_{\rm int}}(t_1) - \rho_{t_0}\hat{V}_{H_0+H_{\rm int}}(t_1)A_{H_0+H_{\rm int}}(t)\right) && (3.572)\\
&| \quad \text{use trace cyclicity}\\
&= -\frac{i}{\hbar}\theta(t-t_1)\mathrm{Tr}\left(A_{H_0+H_{\rm int}}(t)\hat{V}_{H_0+H_{\rm int}}(t_1)\rho_{t_0} - A_{H_0+H_{\rm int}}(t)\rho_{t_0}\hat{V}_{H_0+H_{\rm int}}(t_1)\right) && (3.573)\\
&= -\frac{i}{\hbar}\theta(t-t_1)\mathrm{Tr}\left(A_{H_0+H_{\rm int}}(t)\left[\hat{V}_{H_0+H_{\rm int}}(t_1), \rho_{t_0}\right]_-\right) && (3.574)\\
&| \quad \text{use the Kubo correlator identity}\\
&= -\frac{i}{\hbar}\theta(t-t_1)(-i\hbar)\int_0^\beta d\tau^M \mathrm{Tr}\left(A_{H_0+H_{\rm int}}(t)\rho_{t_0}\frac{d}{dt_1}\hat{V}_{H_0+H_{\rm int}}(t_1 - i\hbar\tau^M)\right) && (3.575)\\
&| \quad \text{use trace cyclicity}\\
&= -\theta(t-t_1)\int_0^\beta d\tau^M \left\langle \frac{d\hat{V}_{H_0+H_{\rm int}}(t_1 - i\hbar\tau^M)}{dt_1} A_{H_0+H_{\rm int}}(t)\right\rangle && (3.576)\\
&| \quad \text{or,}\\
&= -\theta(t-t_1)\int_0^\beta d\tau^M \left\langle e^{\tau^M(H_0+H_{\rm int})}\frac{d\hat{V}_{H_0+H_{\rm int}}(t_1)}{dt_1}e^{-\tau^M(H_0+H_{\rm int})} A_{H_0+H_{\rm int}}(t)\right\rangle && (3.577)\\
&\equiv \chi^R_{A\dot{\hat{V}}}(t-t_1) && (3.578)
\end{aligned}
$$

This newly introduced notation $\chi^R_{A\dot{\hat{V}}}(t-t_1)$ is to remind ourselves that we need to take the (dynamical) time derivative of the perturbation Hamiltonian. It should be noted that it can only be written as an operator with argument $(t-t_1)$ explicitly after the time derivative has been taken.

In frequency domain, the expression is,

$$
\begin{aligned}
\chi^R_{A\dot{\hat{V}}}(\omega) &= \lim_{\epsilon\to 0^+}\int_{-\infty}^{\infty} d(t-t_1)e^{(i\omega-\epsilon)(t-t_1)}\chi^R_{A\dot{\hat{V}}}(t-t_1) && (3.579)\\
&| \quad \text{use the step function}\\
&= -\lim_{\epsilon\to 0^+}\int_0^\infty d(t-t_1)e^{(i\omega-\epsilon)(t-t_1)}\int_0^\beta d\tau^M \left\langle \frac{d\hat{V}_{H_0+H_{\rm int}(t-i\hbar\tau^M)}}{dt_1} A_{H_0+H_{\rm int}}(t)\right\rangle && (3.580)
\end{aligned}
$$

We collect the final formula in Kubo correlator form.

$$
\boxed{\chi^R_{A\dot{\hat{V}}}(\omega) = -\lim_{\epsilon\to 0^+}\int_0^\infty d(t-t_1)e^{(i\omega-\epsilon)(t-t_1)}\int_0^\beta d\tau^M \left\langle \frac{d\hat{V}_{H_0+H_{\rm int}(t-i\hbar\tau^M)}}{dt_1} A_{H_0+H_{\rm int}}(t)\right\rangle} \qquad (3.581)
$$

For applications, one starts by picking his favorite law and insert the relevant expressions for A and

$\hat{V}$ and χ represents the coefficient in that law. In this thesis, we cover $\chi = \kappa$ which is the thermal conductivity in the next section and $\chi = \sigma$ which is the electrical conductivity in the appendix.

3.4.1 Application to Thermal Conductivity

[Disclaimer] Linear response theory is rigorous for mechanical pertubrations but for the case of heat current which is driven by temperature gradients is not a mechanical perturbation. It is because temperature is a statistical quantity. Thus the application to thermal conductivity is not rigorous and one should be skeptical about the following "derivation".

First, we "derive" the effective Hamiltonian that represents the perturbation and then we derive the Kubo correlator form of thermal conductivity. Since linear response theory assumes a weak perturbation, we follow suit and assume that there is almost thermal equilibrium in the solid and so the thermal gradients are small.

We take the local equilibrium density matrix to be

$$\rho = \frac{1}{Z}e^{-\int d\vec{r}\frac{\epsilon(\vec{r})}{k_B T(\vec{r})}} \approx \frac{1}{Z}e^{-\int d\vec{r}\frac{\epsilon(\vec{r})}{k_B(T+\delta T(\vec{r}))}} \approx \frac{1}{Z}e^{-\int d\vec{r}\frac{\epsilon(\vec{r})}{k_B T}\left(1-\frac{\delta T(\vec{r})}{T}\right)} \tag{3.582}$$

where $\epsilon(\vec{r})$ is the local energy operator and we take the second term which is a deviation from equilibrium to be the effective perturbation Hamiltonian that causes a current, i.e.

$$V(t) \equiv -\frac{1}{T}\int d\vec{r}\delta T(\vec{r})\epsilon(\vec{r}) \tag{3.583}$$

with δT taken to the function part and $\epsilon(\vec{r})$ taken to be the operator part. Now we can derive the Kubo correlator form of the linear response formula. Choose A to be $\vec{J}$. Following the procedure, first we need the time derivative.

$$\begin{aligned}
\frac{dV(t)}{dt} &= -\frac{1}{T}\int d\vec{r}\delta T(\vec{r},t)\frac{\partial\epsilon(\vec{r},t)}{\partial t} && (3.584)\\
&\mid \text{ use continuity equation } \frac{\partial \epsilon}{\partial t} + \nabla_{\vec{r}}\cdot\vec{J} = 0\\
&\mid \text{ it should be valid in this near equilibrium situation}\\
&= \frac{1}{T}\int d\vec{r}\delta T(\vec{r},t)\left(\nabla_{\vec{r}}\cdot\vec{J}\right) && (3.585)\\
&\mid \text{ integrate by parts and drop surface term}\\
&= \int d\vec{r}\left(-\frac{1}{T}\nabla_{\vec{r}}\delta T(\vec{r},t)\right)\cdot\vec{J} && (3.586)
\end{aligned}$$

which we can now identify f to be $\left(-\frac{1}{T}\nabla_{\vec{r}}\delta T(\vec{r},t)\right)$ and $\dot{\hat{V}}$ to be $\vec{J}$. With that, the linear response formula becomes

$$\langle\vec{J}(\vec{r},t)\rangle = \int_{-\infty}^{\infty}dt_1\int d\vec{r}_1\overleftrightarrow{\chi}^R_{A=\vec{J},\dot{\hat{V}}=\vec{J}}(\vec{r}-\vec{r}_1,t-t_1)\left(-\frac{1}{T}\nabla_{\vec{r}}\delta T(\vec{r},t)\right) \tag{3.587}$$

Taking spatial and temporal Fourier transforms

$$\langle\vec{J}(\vec{q},\omega)\rangle = -\frac{1}{T}\overleftrightarrow{\chi}^R_{A=\vec{J},\dot{\hat{V}}=\vec{J}}(\vec{q},\omega)\nabla_{\vec{r}}\delta T(\vec{q},\omega) \tag{3.588}$$

Comparing with Fourier's law $\vec{J} = -\overleftrightarrow{\kappa}\nabla_{\vec{r}}T$, we get

$$\begin{aligned}
\kappa_{\alpha\beta}(\vec{q},\omega) &= \frac{1}{T}\chi^R_{\vec{J}\vec{J},\alpha\beta}(\vec{q},\omega) \qquad (3.589)\\
&\quad \mid \ \text{using the trick of inserting } \frac{1}{V}\int d\vec{r} = 1 \text{ and renaming } (\vec{r},\vec{r}-\vec{r}_1)\rightarrow(\vec{r},\vec{r}_1)\\
&= -\frac{1}{VT}\lim_{\epsilon\to 0^+}\int_0^\infty dt e^{(i\omega-\epsilon)t}\int_0^\beta d\tau^M \left\langle J_{\beta,H_0+H_{\text{int}}}(-\vec{q},-i\hbar\tau^M)J_{\alpha,H_0+H_{\text{int}}}(\vec{q},t)\right\rangle \qquad (3.590)
\end{aligned}$$

$$\boxed{\kappa_{\alpha\beta}(\vec{q},\omega) = -\frac{1}{VT}\lim_{\epsilon\to 0^+}\int_0^\infty dt e^{(i\omega-\epsilon)t}\int_0^\beta d\tau^M \left\langle J_{\beta,H_0+H_{\text{int}}}(-\vec{q},-i\hbar\tau^M)J_{\alpha,H_0+H_{\text{int}}}(\vec{q},t)\right\rangle} \qquad (3.591)$$

This is the final form of thermal conductivity in Kubo correlator form.

3.4.1.1 Hardy's Energy Flux Operators: General Expression

Here we follow Hardy's derivation in [Hardy1963] where he provided a method of deriving explicit operator expressions for energy current to be used in the thermal conductivity Kubo formula "derived" earlier.

We start by defining the quantities

$$\begin{aligned}
\text{local energy flux (vector) operator:} &\quad \vec{j}(\vec{r}) \qquad (3.592)\\
\text{local energy density (scalar) operator:} &\quad \epsilon(\vec{r}) \qquad (3.593)
\end{aligned}$$

Assume that they obey the (operator) continuity equation.

$$\frac{\partial\epsilon}{\partial t} + \nabla_{\vec{r}}\cdot\vec{j} = 0 \qquad (3.594)$$

We also have the Heisenberg equation of motion

$$\frac{\partial\epsilon}{\partial t} = \frac{1}{i\hbar}\left[\epsilon(\vec{r}),H\right]_- \Rightarrow \nabla_{\vec{r}}\cdot\vec{j} = \frac{i}{\hbar}\left[\epsilon(\vec{r}),H\right]_- \qquad (3.595)$$

where H is the Hamiltonian of the system and assume that it can be written into a one particle form,

$$H = \sum_i\left(\frac{\vec{p}_i^2}{2M_i} + V(\vec{r}_i)\right) \qquad (3.596)$$

To proceed further in getting an expression for $\vec{j}$, we need to have a physically reasonable definition of $\epsilon(\vec{r})$. This is done by defining the local energy density to be a smeared Hamiltonian over a small region.

$$\epsilon(\vec{r}) \equiv \frac{1}{2}\sum_i\left[\Delta(\vec{r}-\vec{r}_i)\left(\frac{\vec{p}_i^2}{2M_i} + V(\vec{r}_i)\right) + \text{h.c.}\right] \qquad (3.597)$$

where h.c. means hermitian conjugate and $\epsilon = A + A^\dagger$ ensures that ϵ is hermitian as it is an observable. We need to specify certain features of the smearing function $\Delta(\vec{r}-\vec{r}_i)$. These features are needed to make the definition of ϵ physically reasonable.

We require the total energy (summed over all space) to be equal to the total energy H.

$$\int d\vec{r}\epsilon(\vec{r}) = H \tag{3.598}$$

$$\int d\vec{r}\frac{1}{2}\sum_i \left[\Delta(\vec{r}-\vec{r}_i)\left(\frac{\vec{p}_i^{\,2}}{2M_i}+V(\vec{r}_i)\right)+\left(\frac{\vec{p}_i^{\,2}}{2M_i}+V(\vec{r}_i)\right)^\dagger \Delta^\dagger(\vec{r}-\vec{r}_i)\right] = H \tag{3.599}$$

$$\text{note that } \left(\frac{\vec{p}_i^{\,2}}{2M_i}+V(\vec{r}_i)\right) \text{ is hermitian} \quad |$$

$$\text{assume that } \Delta(\vec{r}-\vec{r}_i) \text{ is hermitian} \quad |$$

$$\sum_i \left(\int d\vec{r}\Delta(\vec{r}-\vec{r}_i)\right)\left(\frac{\vec{p}_i^{\,2}}{2M_i}+V(\vec{r}_i)\right) = H \tag{3.600}$$

so we need

$$\int d\vec{r}\Delta(\vec{r}-\vec{r}_i) = 1 \tag{3.601}$$

A possible hermitian form for $\Delta(\vec{r}-\vec{r}_i)$ is

$$\Delta(\vec{r}-\vec{r}_i) = \frac{1}{l^3\pi^{3/2}}e^{-\frac{|\vec{r}-\vec{r}_i|^2}{l^2}} \tag{3.602}$$

where l characterize the length scale where the energy density is localized. Now we can use this setup to calculate the commutator.

$$\begin{aligned}
\nabla_{\vec{r}}\cdot\vec{j}(\vec{r}) &= \frac{i}{\hbar}\left[\epsilon(\vec{r}),H\right]_- &(3.603)\\
&= \frac{i}{\hbar}\left[\frac{1}{2}\sum_{i_1}\left(\Delta(\vec{r}-\vec{r}_{i_1})\left(\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}}+V(\vec{r}_{i_1})\right)+\text{h.c.}\right),\sum_{i_2}\left(\frac{\vec{p}_{i_2}^{\,2}}{2M_{i_2}}+V(\vec{r}_{i_2})\right)\right]_- &(3.604)\\
&\quad | \quad \text{we denote the commutator with the “h.c.” term as “h.c.”}\\
&= \frac{i}{\hbar}\frac{1}{2}\sum_{i_1i_2}\left[\Delta(\vec{r}-\vec{r}_{i_1}),\frac{\vec{p}_{i_2}^{\,2}}{2M_{i_2}}+V(\vec{r}_{i_2})\right]_-\left(\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}}+V(\vec{r}_{i_1})\right)\\
&\quad +\frac{i}{\hbar}\frac{1}{2}\sum_{i_1i_2}\Delta(\vec{r}-\vec{r}_{i_1})\left[\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}}+V(\vec{r}_{i_1}),\frac{\vec{p}_{i_2}^{\,2}}{2M_{i_2}}+V(\vec{r}_{i_2})\right]_- +\text{h.c.} &(3.605)\\
&\quad | \quad \text{use the fundamental relations } [r_{i_1\alpha_1},p_{i_2\alpha_2}]_- = i\hbar\delta_{i_1i_2}\delta_{\alpha_1\alpha_2}\\
&= \frac{i}{\hbar}\frac{1}{2}\sum_{i_1i_2}\left[\Delta(\vec{r}-\vec{r}_{i_1}),\frac{\vec{p}_{i_2}^{\,2}}{2M_{i_2}}\right]_-\left(\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}}+V(\vec{r}_{i_1})\right)\\
&\quad +\frac{i}{\hbar}\frac{1}{2}\Delta(\vec{r}-\vec{r}_{i_1})\left(\left[\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}},V(\vec{r}_{i_2})\right]_- +\left[V(\vec{r}_{i_1}),\frac{\vec{p}_{i_2}^{\,2}}{2M_{i_2}}\right]_-\right)+\text{h.c.} &(3.606)\\
&\quad | \quad \text{for first term use “product rule”, for second term rename } i_1\leftrightarrow i_2\\
&= \frac{i}{\hbar}\frac{1}{2}\sum_{i_1i_2}\left(\frac{\vec{p}_{i_2}^{\,2}}{2M_{i_2}}\left[\Delta(\vec{r}-\vec{r}_{i_1}),\vec{p}_{i_2}\right]_- +\left[\Delta(\vec{r}-\vec{r}_{i_1}),\vec{p}_{i_2}\right]_-\frac{\vec{p}_{i_2}}{2M_{i_2}}\right)\left(\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}}+V(\vec{r}_{i_1})\right)\\
&\quad +\frac{i}{\hbar}\frac{1}{2}\sum_{i_1i_2}\left(\Delta(\vec{r}-\vec{r}_{i_1})-\Delta(\vec{r}-\vec{r}_{i_2})\right)\left[\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}},V(\vec{r}_{i_1})\right]_- +\text{h.c.} &(3.607)
\end{aligned}$$

$$
\begin{aligned}
& | \quad \text{to get } \vec{j}\text{, we need to write each term as a divergence } \nabla_{\vec{r}} \cdot \ldots \\
& | \quad \text{for first line } \vec{p}_{i_2}\left[\Delta(\vec{r}-\vec{r}_{i_1}), \vec{p}_{i_2}\right]_- = \vec{p}_{i_2} i\hbar\delta_{i_1 i_2}\nabla_{\vec{r}_{i_1}}\Delta(\vec{r}-\vec{r}_{i_1}) = -\vec{p}_{i_2} i\hbar\delta_{i_1 i_2}\nabla_{\vec{r}}\Delta(\vec{r}-\vec{r}_{i_1}) \\
& | \quad \text{and since } \nabla_{\vec{r}} \text{ only acts on } \Delta(\vec{r}-\vec{r}_{i_1}) \text{ we can write } -\nabla_{\vec{r}}\cdot(\vec{p}_{i_2} i\hbar\delta_{i_1 i_2}\Delta(\vec{r}-\vec{r}_{i_1})) \\
& | \quad \text{for second term, we use Taylor expansion} \\
& | \quad \Delta(\vec{r}-\vec{r}_{i_1}) - \Delta(\vec{r}-\vec{r}_{i_2}) = \Delta(\vec{r}-\vec{r}_{i_1}) - \Delta(\vec{r}-\vec{r}_{i_1}+\vec{r}_{i_1}-\vec{r}_{i_2}) \\
& | \quad = \Delta(\vec{r}-\vec{r}_{i_1}) - \left(1 + (\vec{r}_{i_1}-\vec{r}_{i_2})\cdot\nabla_{\vec{r}-\vec{r}_{i_1}} + \frac{1}{2!}((\vec{r}_{i_1}-\vec{r}_{i_2})\cdot\nabla_{\vec{r}-\vec{r}_{i_1}})^2 + \cdots\right)\Delta(\vec{r}-\vec{r}_{i_1}) \\
& | \quad = -\left((\vec{r}_{i_1}-\vec{r}_{i_2})\cdot\nabla_{\vec{r}} + \frac{1}{2!}((\vec{r}_{i_1}-\vec{r}_{i_2})\cdot\nabla_{\vec{r}})^2 + \cdots\right)\Delta(\vec{r}-\vec{r}_{i_1}) \\
& | \quad = -\nabla_{\vec{r}}\cdot(\vec{r}_{i_1}-\vec{r}_{i_2})\left(1 + \frac{1}{2!}(\vec{r}_{i_1}-\vec{r}_{i_2})\cdot\nabla_{\vec{r}} + \cdots\right)\Delta(\vec{r}-\vec{r}_{i_1}) \\
= \; & \frac{1}{2}\nabla_{\vec{r}}\cdot\left\{\sum_{i_1}\left(\frac{\vec{p}_{i_1}}{2M_{i_1}}\Delta(\vec{r}-\vec{r}_{i_1}) + \Delta(\vec{r}-\vec{r}_{i_1})\frac{\vec{p}_{i_1}}{2M_{i_1}}\right)\left(\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}} + V(\vec{r}_{i_1})\right)\right. \\
& \left. + \sum_{i_1 i_2}(\vec{r}_{i_1}-\vec{r}_{i_2})\left(1 + \frac{1}{2!}(\vec{r}_{i_1}-\vec{r}_{i_2})\cdot\nabla_{\vec{r}} + \cdots\right)\Delta(\vec{r}-\vec{r}_{i_1})\frac{1}{i\hbar}\left[\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}}, V(\vec{r}_{i_2})\right]_-\right\} + \text{h.c.}
\end{aligned}
\tag{3.608}
$$

So now we can simply identify the expression for $\vec{j}(\vec{r})$,

$$
\begin{aligned}
\vec{j}(\vec{r}) = \; & \frac{1}{2}\left\{\sum_{i_1}\left(\frac{\vec{p}_{i_1}}{2M_{i_1}}\Delta(\vec{r}-\vec{r}_{i_1}) + \Delta(\vec{r}-\vec{r}_{i_1})\frac{\vec{p}_{i_1}}{2M_{i_1}}\right)\left(\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}} + V(\vec{r}_{i_1})\right)\right. \\
& \left. + \sum_{i_1 i_2}(\vec{r}_{i_1}-\vec{r}_{i_2})\left(1 + \frac{1}{2!}(\vec{r}_{i_1}-\vec{r}_{i_2})\cdot\nabla_{\vec{r}} + \cdots\right)\Delta(\vec{r}-\vec{r}_{i_1})\frac{1}{i\hbar}\left[\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}}, V(\vec{r}_{i_2})\right]_-\right\} + \text{h.c.}
\end{aligned}
\tag{3.609}
$$

In Kubo formula for thermal conductivity, we need the average energy flux defined by

$$
\vec{J} \equiv \frac{1}{V}\int d\vec{r}\,\vec{j}(\vec{r}) \tag{3.610}
$$

so we integrate $\int d\vec{r}$ on both sides and use $\int d\vec{r}\Delta(\vec{r}-\vec{r}_{i_1}) = 1$ and $\int d\vec{r}\nabla^n_{\vec{r}}\Delta(\vec{r}-\vec{r}_{i_1}) \approx 0$. This is because the function falls off quickly so the function and its derivatives gives roughly zero when evaluated at the limits.

$$
\boxed{\vec{J} = \frac{1}{2V}\left\{\sum_{i_1}\frac{\vec{p}_{i_1}}{M_{i_1}}\left(\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}} + V(\vec{r}_{i_1})\right) + \sum_{i_1 i_2}(\vec{r}_{i_1}-\vec{r}_{i_2})\frac{1}{i\hbar}\left[\frac{\vec{p}_{i_1}^{\,2}}{2M_{i_1}}, V(\vec{r}_{i_2})\right]_-\right\} + \text{h.c.}} \tag{3.611}
$$

which is the final equation for the energy current operator. This is Hardy's eqn (2.14) in [Hardy1963].

We do not proceed further with the linear response method as it is not the main approach in the thesis. A receipe for the subsequent calculations are stated for completeness.

1. Use the above equation to obtain explicit operator expressions of $\vec{J}$ for the system of interest. Make sure to use $\vec{J}$ in the unitary transformed form $\vec{J}_{H_0+H_{\text{int}}}(t)$.

2. Substitute $\vec{J}_{H_0+H_{\text{int}}}(t)$ back into the Kubo formula for thermal conductivity. Note that we have a 2-particle "Green's function".

3. Write as Interaction operators $\vec{J}_{H_0}(t)$ and we get a S-matrix.
4. Expand the S-matrix and work out some vertex diagrams.
5. Decide on the form of the Bethe-Salpeter equation to solve based on the diagrams. The solution of the Bethe-Salpeter equation gives the thermal conductivity.

3.4.1.1.1 [Hardy's Energy Current Operators: Harmonic Case] The harmonic Hamiltonian is

$$H_0 = \sum_{l\alpha} \frac{p_{l\alpha}^2}{2M} + \frac{1}{2} \sum_{l\alpha l_1\alpha_1} \Phi_{l\alpha l_1\alpha_1} u_{l\alpha} u_{l_1\alpha_1} \tag{3.612}$$

and so we substitute

$$V(\vec{r}_{i_1}) \longrightarrow V_l^{\text{har}} \equiv \frac{1}{2} \sum_{\alpha l_1\alpha_1} \Phi_{l\alpha l_1\alpha_1} u_{l\alpha} u_{l_1\alpha_1} \tag{3.613}$$

and $\vec{r}$ is treated as the equilibrium position $\vec{r} \to \vec{R}_{l_1}^{eq}$ and $\vec{r}_{l_1}$ is the actual position of the ions, so the displacement vector which is $\vec{u}_{l_1} = \vec{r}_{l_1} - \vec{R}_{l_1}^{eq}$ and so $\vec{r}_{l_1} - \vec{r}_{l_2} = \vec{u}_{l_1} - \vec{u}_{l_2} + \vec{R}_{l_1}^{eq} - \vec{R}_{l_2}^{eq}$.

Substitute into Hardy's formula,

$$\begin{aligned}
\vec{J}^{\text{ har}} &= \frac{1}{2V}\left\{\sum_l \frac{\vec{p}_l}{M}\left(\frac{\vec{p}_l^{\,2}}{2M} + V_l^{\text{har}}\right) + \sum_{l_1 l_2}(\vec{u}_{l_1} - \vec{u}_{l_2} + \vec{R}_{l_1}^{eq} - \vec{R}_{l_2}^{eq})\frac{1}{i\hbar}\left[\frac{\vec{p}_{l_1}^{\,2}}{2M}, V_{l_2}^{\text{har}}\right]_-\right\} + \text{h.c.} \\
&\quad | \text{ following Hardy, we expand and seperate terms as follows} \\
&= \frac{1}{2V}\frac{1}{2M}\sum_{l_1 l_2}(\vec{R}_{l_1}^{eq} - \vec{R}_{l_2}^{eq})\left(\vec{p}_{l_1} \cdot \frac{1}{i\hbar}\left[\vec{p}_{l_1}, V_{l_2}^{\text{har}}\right]_- + \frac{1}{i\hbar}\left[\vec{p}_{l_1}, V_{l_2}^{\text{har}}\right]_- \cdot \vec{p}_{l_1}\right) + \text{h.c.} \\
&\quad + \frac{1}{2V}\left\{\sum_l \frac{\vec{p}_l}{M}\left(\frac{\vec{p}_l^{\,2}}{2M} + V_l^{\text{har}}\right)\right. \\
&\quad \left. + \frac{1}{2M}\sum_{l_1 l_2}(\vec{u}_{l_1} - \vec{u}_{l_2})\left(\vec{p}_{l_1} \cdot \frac{1}{i\hbar}\left[\vec{p}_{l_1}, V_{l_2}^{\text{har}}\right]_- + \frac{1}{i\hbar}\left[\vec{p}_{l_1}, V_{l_2}^{\text{har}}\right]_- \cdot \vec{p}_{l_1}\right)\right\} + \text{h.c.} \qquad (3.614) \\
&\quad | \text{ the first line and second line are denoted respectively as} \\
&\equiv \vec{J}^{\text{ har}}(\vec{S}_2^0) + \vec{J}^{\text{ har}}(\vec{S}_3^0) \qquad (3.615)
\end{aligned}$$

This definition follows Hardy (as much as possible so as to allow comparison) and we analyse each term seperately. Following Hardy, $\vec{J}^{\text{ har}}(\vec{S}_2^0)$ is called the quadratic part and $\vec{J}^{\text{ har}}(\vec{S}_3^0)$ is called the cubic part. Do not confuse that with cubic anharmonicity.

$$\begin{aligned}
\vec{J}^{\text{ har}}(\vec{S}_2^0) &= \frac{1}{2V}\frac{1}{2M}\sum_{l_1 l_2}(\vec{R}_{l_1}^{eq} - \vec{R}_{l_2}^{eq})\left(\vec{p}_{l_1} \cdot \frac{1}{i\hbar}\left[\vec{p}_{l_1}, V_{l_2}^{\text{har}}\right]_- + \frac{1}{i\hbar}\left[\vec{p}_{l_1}, V_{l_2}^{\text{har}}\right]_- \cdot \vec{p}_{l_1}\right) + \text{h.c.} \qquad (3.616) \\
&\quad | \text{ the hermitian conjugate term is the exactly the same, so we have a factor of 2} \\
&\quad | \text{ use fundamental commutator } [u_{l_1\alpha_1}, p_{l_2\alpha_2}]_- = i\hbar\delta_{l_1 l_2}\delta_{\alpha_1\alpha_2} \\
&\quad | \text{ so } \left[\vec{p}_{l_1}, V_{l_2}^{\text{har}}\right]_- = -i\hbar\frac{1}{2}\left(\delta_{l_1 l_2}\sum_{l_3}\Phi_{l_2 l_3}\vec{u}_{l_3} + \vec{u}_{l_2}\Phi_{l_2 l_1}\right)
\end{aligned}$$

$$
\begin{aligned}
& | \quad \text{but the first term} = 0 \text{ due to } \delta_{l_1 l_2} \text{ causing } \vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2} = 0 \\
= \; & -\frac{1}{V}\frac{1}{2M}\frac{1}{2}\sum_{l_1 l_2}(\vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2})\sum_{\alpha_1\alpha_2}\left(p_{l_1\alpha_2}u_{l_2\alpha_1}\Phi_{l_2\alpha_1 l_1\alpha_2} + u_{l_2\alpha_1}\Phi_{l_2\alpha_1 l_1\alpha_2}p_{l_1\alpha_2}\right) \qquad (3.617) \\
& | \quad \text{use again } [u_{l_1\alpha_1}, p_{l_2\alpha_2}]_- = i\hbar\delta_{l_1 l_2}\delta_{\alpha_1\alpha_2} \text{ get } u_{l_2\alpha_2}p_{l_1\alpha_1} = i\hbar\delta_{l_1 l_2}\delta_{\alpha_1\alpha_2} + p_{l_1\alpha_1}u_{l_2\alpha_2} \\
& | \quad \text{and } \delta_{l_1 l_2} \text{ causes } \vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2} = 0 \text{ and one term vanishes} \\
= \; & -\frac{1}{V}\frac{1}{2M}\sum_{l_1 l_2}(\vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2})\sum_{\alpha_1\alpha_2}\Phi_{l_2\alpha_2 l_1\alpha_1}p_{l_1\alpha_1}u_{l_2\alpha_2} \qquad (3.618) \\
& | \quad \text{now write into variables } P \text{ and } Q \text{ defined as} \\
& | \quad u_{l_2\alpha_2} = \frac{1}{\sqrt{NM}}\sum_{j\vec{q}}\epsilon_{\alpha_2}(j\vec{q})Q_{j\vec{q}}e^{i\vec{q}\cdot\vec{R}^{eq}_{l_2}} \\
& | \quad p_{l_1\alpha_1} = M\dot{u}_{l_1\alpha_1} = \sqrt{\frac{M}{N}}\sum_{j\vec{q}}\epsilon_{\alpha_1}(j\vec{q})\dot{Q}_{j\vec{q}}e^{i\vec{q}\cdot\vec{R}^{eq}_{l_1}} = \sqrt{\frac{M}{N}}\sum_{j\vec{q}}\epsilon_{\alpha_1}(j\vec{q})P_{j\vec{q}}e^{i\vec{q}\cdot\vec{R}^{eq}_{l_1}} \\
= \; & \frac{1}{V}\frac{1}{2M}\frac{1}{N}\sum_{j_1\vec{q}_1 j_2\vec{q}_2}P_{j_1\vec{q}_1}Q_{j_2\vec{q}_2}\sum_{\alpha_1\alpha_2}\epsilon_{\alpha_1}(j_1\vec{q}_1)\left(\sum_{l_1 l_2}(\vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2})\Phi_{l_2\alpha_2 l_1\alpha_1}e^{i\vec{q}\cdot\vec{R}^{eq}_{l_1}}e^{i\vec{q}\cdot\vec{R}^{eq}_{l_2}}\right)\epsilon_{\alpha_2}(j_2\vec{q}_2) \\
& | \quad \text{due to translational invariance of the current, it only depends on } \vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2} \text{ so } \vec{q}_2 = -\vec{q}_1 \\
= \; & \frac{1}{V}\frac{1}{2M}\sum_{j_1\vec{q}_1 j_2}P_{j_1\vec{q}_1}Q_{j_2,-\vec{q}_1}\sum_{\alpha_1\alpha_2}\epsilon_{\alpha_1}(j_1\vec{q}_1)\left(\sum_{l_1 l_2}(\vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2})\Phi_{l_2\alpha_2 l_1\alpha_1}e^{i\vec{q}_1\cdot(\vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2})}\right)\epsilon_{\alpha_2}(j_2,-\vec{q}_1) \\
& | \quad \text{write } \epsilon_{\alpha_2}(j_2,-\vec{q}_1) = \epsilon^*_{\alpha_2}(j_2\vec{q}_1) \\
& | \quad \text{define a “multibranch” group velocity expression} \\
& | \quad \vec{v}_{j_1 j_2\vec{q}_1} \equiv \frac{i}{2M\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_1}}}\sum_{\alpha_1\alpha_2}\epsilon_{\alpha_1}(j_1\vec{q}_1)\left(\sum_{l_1 l_2}(\vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2})\Phi_{l_2\alpha_2 l_1\alpha_1}e^{i\vec{q}_1\cdot(\vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2})}\right)\epsilon^*_{\alpha_2}(j_2\vec{q}_1) \\
& | \quad \text{the “branch diagonal” } j_1 = j_2 \text{ expression is} \\
& | \quad \vec{v}_{j_1 j_1\vec{q}_1} = \frac{i}{2M\omega_{j_1\vec{q}_1}}\sum_{\alpha_1\alpha_2}\epsilon_{\alpha_1}(j_1\vec{q}_1)\left(\sum_{l_1 l_2}(\vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2})\Phi_{l_2\alpha_2 l_1\alpha_1}e^{i\vec{q}_1\cdot(\vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2})}\right)\epsilon^*_{\alpha_2}(j_1\vec{q}_1) \\
= \; & \frac{1}{V}\frac{1}{2M}\sum_{j_1\vec{q}_1}P_{j_1\vec{q}_1}Q_{j_1,-\vec{q}_1}\frac{2M\omega_{j_1\vec{q}_1}}{i}\vec{v}_{j_1 j_1\vec{q}_1} + \frac{1}{V}\frac{1}{2M}\sum_{j_1\vec{q}_1 j_2(j_1\neq j_2)}P_{j_1\vec{q}_1}Q_{j_2,-\vec{q}_1}\frac{2M\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_1}}}{i} \\
& | \quad \text{introduce the creation and annihilation operators into the first term only} \\
& | \quad P_{j_1\vec{q}_1} = \frac{1}{i}\sqrt{\frac{\hbar\omega_{j_1\vec{q}_1}}{2}}\left(a_{j_1\vec{q}_1} - a^\dagger_{j_1,-\vec{q}_1}\right) \quad \text{and} \quad Q_{j_2,-\vec{q}_1} = \sqrt{\frac{\hbar}{2\omega_{j_2\vec{q}_1}}}\left(a^\dagger_{j_2\vec{q}_1} + a_{j_2,-\vec{q}_1}\right) \\
= \; & \frac{1}{V}\sum_{j_1\vec{q}_1}\frac{\omega_{j_1\vec{q}_1}}{i}\frac{1}{i}\sqrt{\frac{\hbar\omega_{j_1\vec{q}_1}}{2}}\sqrt{\frac{\hbar}{2\omega_{j_1\vec{q}_1}}}\left(a_{j_1\vec{q}_1} - a^\dagger_{j_1,-\vec{q}_1}\right)\left(a^\dagger_{j_1\vec{q}_1} + a_{j_1,-\vec{q}_1}\right)\vec{v}_{j_1 j_1\vec{q}_1} \\
& + \frac{1}{V}\sum_{j_1\vec{q}_1 j_2(j_1\neq j_2)}\frac{\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_1}}}{i}P_{j_1\vec{q}_1}Q_{j_2,-\vec{q}_1}\vec{v}_{j_1 j_2\vec{q}_1} \qquad (3.619) \\
= \; & \frac{1}{V}\sum_{j_1\vec{q}_1}\frac{\hbar\omega_{j_1\vec{q}_1}}{-2}\left(a_{j_1\vec{q}_1}a^\dagger_{j_1\vec{q}_1} - a^\dagger_{j_1,-\vec{q}_1}a_{j_1,-\vec{q}_1} + a_{j_1\vec{q}_1}a_{j_1,-\vec{q}_1} - a^\dagger_{j_1,-\vec{q}_1}a^\dagger_{j_1\vec{q}_1}\right)\vec{v}_{j_1 j_1\vec{q}_1}
\end{aligned}
$$

$$
\begin{aligned}
& +\frac{1}{V}\sum_{j_1\vec{q}_1 j_2(j_1\neq j_2)}\frac{\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_1}}}{i}P_{j_1\vec{q}_1}Q_{j_2,-\vec{q}_1}\vec{v}_{j_1j_2\vec{q}_1} && (3.620)\\
& \mid \quad \text{for second term rename } \vec{q}_1\leftrightarrow-\vec{q}_1\text{, so } \omega_{j_1\vec{q}_1}a^\dagger_{j_1,-\vec{q}_1}a_{j_1,-\vec{q}_1}\vec{v}_{j_1j_1\vec{q}_1}=\omega_{j_1\vec{q}_1}a^\dagger_{j_1\vec{q}_1}a_{j_1\vec{q}_1}(-\vec{v}_{j_1j_1\vec{q}_1})\\
& \mid \quad \text{we will show } \vec{v}_{j_1j_1,-\vec{q}_1}=-\vec{v}_{j_1j_1\vec{q}_1}\text{ later}\\
= & \frac{1}{V}\sum_{j_1\vec{q}_1}\sum_{j_1\vec{q}_1}\frac{\hbar\omega_{j_1\vec{q}_1}}{-2}\left(a_{j_1\vec{q}_1}a^\dagger_{j_1\vec{q}_1}+a^\dagger_{j_1\vec{q}_1}a_{j_1\vec{q}_1}+a_{j_1\vec{q}_1}a^\dagger_{j_1,-\vec{q}_1}-a^\dagger_{j_1,-\vec{q}_1}a^\dagger_{j_1\vec{q}_1}\right)\vec{v}_{j_1j_1\vec{q}_1}\\
& +\frac{1}{V}\sum_{j_1\vec{q}_1 j_2(j_1\neq j_2)}\frac{\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_1}}}{i}P_{j_1\vec{q}_1}Q_{j_2,-\vec{q}_1}\vec{v}_{j_1j_2\vec{q}_1} && (3.621)\\
& \mid \quad \text{use } \left[a_{j_1\vec{q}_1},a^\dagger_{j_1\vec{q}_1}\right]_-=1\text{, so } a_{j_1\vec{q}_1}a^\dagger_{j_1\vec{q}_1}=1+a^\dagger_{j_1\vec{q}_1}a_{j_1\vec{q}_1}\\
= & -\frac{1}{V}\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}a^\dagger_{j_1\vec{q}_1}a_{j_1\vec{q}_1}\vec{v}_{j_1j_1\vec{q}_1}+\frac{1}{V}\sum_{j_1\vec{q}_1}\frac{\hbar\omega_{j_1\vec{q}_1}}{-2}\left(1+a_{j_1\vec{q}_1}a_{j_1,-\vec{q}_1}-a^\dagger_{j_1,-\vec{q}_1}a^\dagger_{j_1\vec{q}_1}\right)\vec{v}_{j_1j_1\vec{q}_1}\\
& +\frac{1}{V}\sum_{j_1\vec{q}_1 j_2(j_1\neq j_2)}\frac{\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_1}}}{i}P_{j_1\vec{q}_1}Q_{j_2,-\vec{q}_1}\vec{v}_{j_1j_2\vec{q}_1} && (3.622)\\
& \mid \quad \text{the negative sign is due to the definition of } P \text{ and } Q\\
& \mid \quad \text{the second term has a constant 1 that we can offset}\\
& \mid \quad \text{recall these operators are to be used as } \vec{J}_{H_0+H_{\text{int}}}=\vec{J}_{H_0}\text{ in Kubo formula}\\
& \mid \quad H_0\text{ is the harmonic Hamiltonian}\\
& \mid \quad \text{thus terms } aa-a^\dagger a^\dagger\text{ are zero in the Kubo formula that can drop now}\\
= & -\frac{1}{V}\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}a^\dagger_{j_1\vec{q}_1}a_{j_1\vec{q}_1}\vec{v}_{j_1j_1\vec{q}_1}+\frac{1}{V}\sum_{j_1\vec{q}_1 j_2(j_1\neq j_2)}\frac{\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_1}}}{i}P_{j_1\vec{q}_1}Q_{j_2,-\vec{q}_1}\vec{v}_{j_1j_2\vec{q}_1} && (3.623)
\end{aligned}
$$

The first term is the usually assumed current expression. This derivation shows that even in the harmonic case, the energy current operator (to be used in the Kubo formula) has 2 more correction terms as compared to the usual assumed expression! We shall not proceed further as this is not the main approach of the thesis.

Finally we want to clean up 2 loose ends in the earlier derivation. First, we need to show $\vec{v}_{j_1j_1,-\vec{q}_1}=-\vec{v}_{j_1j_1\vec{q}_1}$.

$$
\begin{aligned}
\vec{v}_{j_1j_1,-\vec{q}_1} = & \frac{i}{2M\omega_{j_1,-\vec{q}_1}}\sum_{\alpha_1\alpha_2}\epsilon_{\alpha_1}(j_1,-\vec{q}_1)\sum_{l_1l_2}\left((\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l_2})\Phi_{l_2\alpha_2l_1\alpha_1}e^{-i\vec{q}_1\cdot(R^{eq}_{l_1}-\vec{R}^{eq}_{l_2})}\right)\epsilon^*_{\alpha_2}(j_1,-\vec{q}_1)\\
& \mid \quad \text{use } \omega_{j_1,-\vec{q}_1}=\omega_{j_1\vec{q}_1}\text{ and } \epsilon_{\alpha_1}(j_1,-\vec{q}_1)=\epsilon^*_{\alpha_1}(j_1\vec{q}_1)\\
= & \frac{i}{2M\omega_{j_1\vec{q}_1}}\sum_{\alpha_1\alpha_2}\epsilon^*_{\alpha_1}(j_1\vec{q}_1)\sum_{l_1l_2}\left((\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l_2})\Phi_{l_2\alpha_2l_1\alpha_1}e^{i\vec{q}_1\cdot(R^{eq}_{l_2}-\vec{R}^{eq}_{l_1})}\right)\epsilon_{\alpha_2}(j_1\vec{q}_1) && (3.624)\\
& \mid \quad \text{rename } \alpha_1\leftrightarrow\alpha_2,\ l_1\leftrightarrow l_2\\
= & \frac{i}{2M\omega_{j_1\vec{q}_1}}\sum_{\alpha_1\alpha_2}\epsilon^*_{\alpha_2}(j_1\vec{q}_1)\sum_{l_1l_2}\left((\vec{R}^{eq}_{l_2}-\vec{R}^{eq}_{l_1})\Phi_{l_1\alpha_1l_2\alpha_2}e^{i\vec{q}_1\cdot(R^{eq}_{l_1}-\vec{R}^{eq}_{l_2})}\right)\epsilon_{\alpha_1}(j_1\vec{q}_1) && (3.625)\\
& \mid \quad \text{use } \vec{R}^{eq}_{l_2}-\vec{R}^{eq}_{l_1}=-(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l_2})\text{ and } \Phi_{l_1\alpha_1l_2\alpha_2}=\Phi_{l_2\alpha_2l_1\alpha_1}\\
= & -\vec{v}_{j_1j_1\vec{q}_1} && (3.626)
\end{aligned}
$$

Second, we want to check that $\vec{v}_{jj\vec{q}} = \nabla_{\vec{q}}\, \omega_{j\vec{q}}$. We start with the dynamical matrix equation.

$$\begin{aligned}
\omega_{j\vec{q}}^2\, \epsilon_\alpha(j\vec{q}) &= \sum_{\alpha_1} D_{\alpha\alpha_1}(\vec{q})\epsilon_{\alpha_1}(j\vec{q}) && (3.627)\\
&\mid\ \text{substitute } D_{\alpha\alpha_1}(\vec{q}) = \frac{1}{M}\sum_{ll_1}\Phi_{l\alpha l_1\alpha_1}e^{i\vec{q}\cdot(l_1-l)}\\
&= \frac{1}{M}\sum_{ll_1\alpha_1}\Phi_{l\alpha l_1\alpha_1}e^{i\vec{q}\cdot(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l})}\epsilon_{\alpha_1}(j\vec{q}) && (3.628)\\
&\mid\ \text{multiply } \epsilon^*_\alpha(j_1\vec{q}) \text{ on both sides and sum over } \alpha\\
\omega_{j\vec{q}}^2\, \delta_{jj_1} &= \frac{1}{M}\sum_{l\alpha l_1\alpha_1}\epsilon^*_\alpha(j_1\vec{q})\Phi_{l\alpha l_1\alpha_1}e^{i\vec{q}\cdot(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l})}\epsilon_{\alpha_1}(j\vec{q}) && (3.629)\\
&\mid\ \text{take } \nabla_{\vec{q}} \text{ on both sides, there will be 3 terms on RHS}\\
2\omega_{j\vec{q}}\left(\nabla_{\vec{q}}\,\omega_{j\vec{q}}\right)\delta_{jj_1} &= \frac{1}{M}\sum_{l\alpha l_1\alpha_1}\Big[\left(\nabla_{\vec{q}}\epsilon^*_\alpha(j_1\vec{q})\right)\Phi_{l\alpha l_1\alpha_1}e^{i\vec{q}\cdot(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l})}\epsilon_{\alpha_1}(j\vec{q})\\
&\quad+\epsilon^*_\alpha(j_1\vec{q})\Phi_{l\alpha l_1\alpha_1}i(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l})e^{i\vec{q}\cdot(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l})}\epsilon_{\alpha_1}(j\vec{q})\\
&\quad+\epsilon^*_\alpha(j_1\vec{q})\Phi_{l\alpha l_1\alpha_1}e^{i\vec{q}\cdot(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l})}\left(\nabla_{\vec{q}}\epsilon_{\alpha_1}(j\vec{q})\right)\Big] && (3.630)\\
&\mid\ \text{use the dynamical matrix equation for RHS 1st and 3rd terms}\\
&= \frac{i}{M}\sum_{l\alpha l_1\alpha_1}\epsilon^*_\alpha(j_1\vec{q})\Phi_{l\alpha l_1\alpha_1}(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l})e^{i\vec{q}\cdot(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l})}\epsilon_{\alpha_1}(j\vec{q})\\
&\quad+\sum_{\alpha}\left(\nabla_{\vec{q}}\epsilon^*_\alpha(j_1\vec{q})\right)\omega^2_{j\vec{q}}\epsilon_\alpha(j\vec{q})+\sum_{\alpha_1}\omega^2_{j\vec{q}}\epsilon^*_{\alpha_1}(j_1\vec{q})\left(\nabla_{\vec{q}}\epsilon_{\alpha_1}(j\vec{q})\right) && (3.631)\\
&\mid\ \text{now set } j=j_1 \text{ on both sides}\\
2\omega_{j\vec{q}}\left(\nabla_{\vec{q}}\,\omega_{j\vec{q}}\right) &= \frac{i}{M}\sum_{l\alpha l_1\alpha_1}\epsilon^*_\alpha(j\vec{q})\Phi_{l\alpha l_1\alpha_1}(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l})e^{i\vec{q}\cdot(\vec{R}^{eq}_{l_1}-\vec{R}^{eq}_{l})}\epsilon_{\alpha_1}(j\vec{q})+\sum_\alpha\omega^2_{j\vec{q}}\nabla_{\vec{q}}\left(\epsilon_\alpha(j\vec{q})\epsilon_\alpha(j\vec{q})\right)\\
&\mid\ \text{but } \nabla_{\vec{q}}\sum_\alpha\epsilon^*_\alpha(j\vec{q})\epsilon_\alpha(j\vec{q}) = \nabla_{\vec{q}}1 = 0 \text{ and use the expression for } \vec{v}_{jj\vec{q}}\\
&= 2\omega_{j\vec{q}}\,\vec{v}_{jj\vec{q}} && (3.632)\\
\nabla_{\vec{q}}\,\omega_{j\vec{q}} &= \vec{v}_{jj\vec{q}} && (3.633)
\end{aligned}$$

indeed as required.

Chapter 4

Reduced Density Matrix Related Methods

[Chapter Introduction and Roadmap:] We enumerate this introduction for easy reading.

1. This chapter is included to provide another dimension to NEGF. Reduced density matrix method is the most common method to tackle open quantum systems. The 2 methods can serve as cross-checks for each other.
2. The aim is to present a promising numerical method in this area: stochastic unravelling.
3. The standard partial tracing over the environmental degrees of freedom is done (by path integrals) to derive the influence functional. This functional contains all the effects of the environment on the system.
4. The influence functional is conceptually clean but mathematically intractable. Stochastic unravelling is a method that allows a rewriting of the influence functional into a stochastic problem which is numerically tractable.

4.1 Derivation: Projection Operator Derivation

We follow [Altland2010] pg 696. We shall use a one lead/bath problem. Since leads/baths are always assumed to be independent, additional lead/baths are added by simple addition.

The Hamiltonian is

$$H = H^L + H^C + \alpha H^{LC} \tag{4.1}$$

where L is the left lead/bath, C is the central system/device, LC refers to the coupling between the left lead/bath and the central system/device and α is the coupling constant shown explicitly for convenience.

The initial condition is chosen as

$$\rho^{\mathrm{tot}}(t=0) \equiv \rho^C(0) \otimes \rho^{\mathrm{eq},L} \tag{4.2}$$

The dynamics of the total density matrix is governed by the Liouville equation

$$\left(\frac{\partial}{\partial t} - \mathcal{L}\right)\rho^{\mathrm{tot}} = 0 \tag{4.3}$$

where the Liouville operator is defined as

$$\begin{aligned} \mathcal{L} &= \mathcal{L}^L + \mathcal{L}^C + \alpha\mathcal{L}^{LC} && (4.4)\\ \text{where}\quad \mathcal{L}^{L,C,LC} &= -i\left[H^{L,C,LC}, \quad\right]_- && (4.5) \end{aligned}$$

We simply define the projector to project out the quantity of interest. In this case, we are interested in the reduced density matrix of the central system, thus the projector is correspondingly defined as

$$P \equiv \rho^{L,\mathrm{eq}}\mathrm{Tr}_L(\quad) \tag{4.6}$$

where Tr_L means a partial trace over the lead/bath degrees of freedom.

We assume that $\mathrm{Tr}_L\left(\rho^{L,\mathrm{eq}}H^{LC}\right) = 0$ and we establish these identities for further calculations

$$\begin{aligned} &(a)\quad P\mathcal{L}^L = \mathcal{L}^L P = 0 && (4.7)\\ &(b)\quad \left[\mathcal{L}^C, P\right]_- = 0 && (4.8)\\ &(c)\quad P\mathcal{L}^{LC}P = 0 && (4.9) \end{aligned}$$

$$\begin{aligned} \text{Proof of (a):}\quad P\mathcal{L}^L\rho^{\mathrm{tot}} &= \rho^{L,\mathrm{eq}}\mathrm{Tr}_L\left(\mathcal{L}\rho^{\mathrm{tot}}\right) && (4.10)\\ &= -i\rho^{L,\mathrm{eq}}\mathrm{Tr}_L\left(\left[H^L, \rho^{\mathrm{tot}}\right]_-\right) && (4.11)\\ &\mid\ \text{use trace cyclicity}\\ &= 0 && (4.12) \end{aligned}$$

$$\begin{aligned} \text{Proof of (b):}^1\quad \left[\mathcal{L}^C, P\right]_-\rho &= \mathcal{L}^C P\rho - P\mathcal{L}^C\rho && (4.13)\\ &= \mathcal{L}^C\rho^{L,\mathrm{eq}}\mathrm{Tr}_L\rho - \rho^{L,\mathrm{eq}}\mathrm{Tr}_L(\mathcal{L}^C\rho) && (4.14)\\ &\mid\ \text{use } \mathrm{Tr}_L\rho = \rho^C \text{ and } \mathrm{Tr}_L\mathcal{L}^C = \mathcal{L}^C\mathrm{Tr}_L\\ &= \rho^{L,\mathrm{eq}}\mathcal{L}^C\rho^C - \rho^{L,\mathrm{eq}}\mathcal{L}^C\mathrm{Tr}_L\rho && (4.15)\\ &= 0 && (4.16) \end{aligned}$$

$$\begin{aligned} \text{Proof of (c):}\quad P\mathcal{L}^{LC}P\rho &= P\mathcal{L}^{LC}\left(\mathrm{Tr}_L\rho\right)\rho^{L,\mathrm{eq}} && (4.17)\\ &= \rho^{L,\mathrm{eq}}\mathrm{Tr}_L\left(\rho^{L,\mathrm{eq}}\mathcal{L}^{LC}\rho^C\right) && (4.18)\\ &= -i\rho^{L\mathrm{eq}}\mathrm{Tr}_L\left(\rho^{L,\mathrm{eq}}\left[H^{LC}, \rho^C\right]_-\right) && (4.19)\\ &= -i\rho^{L,\mathrm{eq}}\mathrm{Tr}_L\left(\rho^{L,\mathrm{eq}}H^{LC}\rho^C - \rho^{L,\mathrm{eq}}\rho^C H^{LC}\right) && (4.20)\\ &\mid\ \text{use trace cyclicity to rewrite the last term to } H^{LC}\rho^{L,\mathrm{eq}}\rho^C\\ &= -i\rho^{L,\mathrm{eq}}\mathrm{Tr}_L\left(\rho^{L,\mathrm{eq}}H^{LC} - H^{LC}\rho^{L,\mathrm{eq}}\right)\rho^C && (4.21)\\ &\mid\ \text{each term is zero due to the assumption } \mathrm{Tr}_L\left(\rho^{L,\mathrm{eq}}H^{LC}\right) = 0\\ &= 0 && (4.22) \end{aligned}$$

Define the complementary projector, $Q \equiv \mathbb{I} - P$ and introduce the standard shorthand of "relevant variables" and "irrelevant variables".

$$\begin{aligned} \text{relevant variables:}\quad & P\rho \equiv \rho^r && (4.23)\\ \text{irrelevant variables:}\quad & Q\rho \equiv \rho^{irr} && (4.24) \end{aligned}$$

We are only interested in the evolution of the relevant variables thus we will derive the equation of motion of only the relevant part. Start by writing the relevant part,

$$\begin{aligned}
\frac{\partial}{\partial t}\rho &= \left(\mathcal{L}^C + \mathcal{L}^L + \alpha\mathcal{L}^{LC}\right)\rho && (4.25)\\
&\mid \ \text{operate } P \text{ on both sides} \\
\frac{\partial}{\partial t}\rho^r &= P\mathcal{L}^C\rho + P\mathcal{L}^L\rho + \alpha P\mathcal{L}^{LC}\rho && (4.26)\\
&\mid \ \text{use (b) for RHS first term, use (a) for RHS second term} \\
&\mid \ \text{for RHS third term, write } \mathcal{L}^{LC}\rho = \mathcal{L}^{LC}(P+Q)\rho \text{ then use (c)} \\
&= \mathcal{L}^C\rho^r + \alpha P\mathcal{L}^{LC}\rho^r + \alpha P\mathcal{L}^{LC}\rho^{irr} && (4.27)\\
&\mid \ \text{RHS second term} = 0 \text{ due to (c)} \\
&= \mathcal{L}^C\rho^r + \alpha P\mathcal{L}^{LC}\rho^{irr} && (4.28)
\end{aligned}$$

Now we write the irrelevant part,

$$\begin{aligned}
\frac{\partial}{\partial t}\rho &= \left(\mathcal{L}^C + \mathcal{L}^L + \alpha\mathcal{L}^{LC}\right)\rho && (4.29)\\
&\mid \ \text{operate } Q \text{ on both sides} \\
\frac{\partial}{\partial t}\rho^{irr} &= Q\mathcal{L}\rho && (4.30)\\
&\mid \ \text{write } \mathcal{L}\rho = \mathcal{L}(P+Q^2)\rho \text{ where } Q^2 = Q \\
&= Q\mathcal{L}Q\rho^{irr} + Q\mathcal{L}\rho^r && (4.31)\\
&= Q\mathcal{L}Q\rho^{irr} + Q\mathcal{L}^C\rho^r + Q\mathcal{L}^L\rho^r + \alpha Q\mathcal{L}^{LC}\rho^r && (4.32)\\
&\mid \ \text{for RHS second term, use (b) to get } QP\mathcal{L}^C\rho = 0 \\
&\mid \ \text{for RHS third term, } \rho^r \text{ is a number in } L \text{ space, thus term} = 0 \\
&= Q\mathcal{L}Q\rho^{irr} + \alpha Q\mathcal{L}^{LC}\rho^r && (4.33)
\end{aligned}$$

We treat the irrelevant equation as a linear inhomogenous (operator) equation and solve ρ^{irr} by using the method of integrating factor. [2]

The solution is

$$\begin{aligned}
\rho^{irr}(t) &= (\text{const})e^{Q\mathcal{L}Qt} + e^{Q\mathcal{L}Qt}\int_0^t dt_1 e^{-Q\mathcal{L}Qt_1}\alpha Q\mathcal{L}^{LC}\rho^r(t_1) && (4.36)\\
&\mid \ \text{drop the first term by the “molecular chaos” assumption} \\
&\approx \alpha\int_0^t dt_1 e^{Q\mathcal{L}Q(t-t_1)}Q\mathcal{L}^{LC}\rho^r(t_1) && (4.37)\\
&\mid \ \text{rename the time } t_1 \to t - t_1 \text{ to write}
\end{aligned}$$

[2] The general form of the linear inhomogenous first order differential equation is

$$\frac{dy}{dx} + R(x)y = S(x) \tag{4.34}$$

the integrating factor is then $\mu(x) = e^{\int dx R(x)}$ and the solution is

$$y = \frac{\text{const}}{\mu(x)} + \frac{1}{\mu(x)}\int dx S(x)\mu(x) \tag{4.35}$$

In this case, we identify “$R(x)$” $= -Q\mathcal{L}Q$ and “$S(x)$” $= \alpha Q\mathcal{L}^{LC}\rho^r$ and the integrating factor “$\mu(x)$” $= e^{-Q\mathcal{L}Qt}$

$$= \alpha \int_0^t dt_1 e^{Q\mathcal{L}Qt_1} Q\mathcal{L}^{LC} \rho^r(t-t_1) \tag{4.38}$$

We substitute this result into the relevant equation to get

$$\begin{aligned}
\frac{\partial}{\partial t}\rho^r &= \mathcal{L}^C \rho^r + \alpha^2 \int_0^t dt_1 P\mathcal{L}^{LC} e^{Q\mathcal{L}Qt_1} Q\mathcal{L}^{LC} \rho^r(t-t_1) && (4.39)\\
&| \quad \text{recall that } \rho^r = P\rho = \rho^{L,\text{eq}} \text{Tr}_L \rho = \rho^{L,\text{eq}} \rho^C \\
\frac{\partial}{\partial t}\rho^C &= \mathcal{L}^C \rho^C + \alpha^2 \int_0^t dt_1 \rho^{L,\text{eq}} \text{Tr}_L \left(\mathcal{L}^{LC} e^{Q\mathcal{L}Qt_1} Q\mathcal{L}^{LC}\right) \rho^C(t-t_1) && (4.40)
\end{aligned}$$

This is the generalized (Non-Markovian) Quantum Master equation.

We now go over to the weak coupling approximation. Drop $\alpha\mathcal{L}^{LC}$ in the exponent since we are only going to expand up to α^2. Writing only the integration kernel,

$$\begin{aligned}
& P\mathcal{L}^{LC} e^{Q\mathcal{L}Qt_1} Q\mathcal{L}^{LC} \rho^r(t-t_1) && (4.41)\\
\approx\ & P\mathcal{L}^{LC} e^{Q(\mathcal{L}^L+\mathcal{L}^C)Qt_1} Q\mathcal{L}^{LC} \rho^r(t-t_1) && (4.42)\\
=\ & P\mathcal{L}^{LC} e^{(\mathbb{I}-P)(\mathcal{L}^L+\mathcal{L}^C)(\mathbb{I}-P)t_1} Q\mathcal{L}^{LC} \rho^r(t-t_1) && (4.43)\\
|\ & \text{recall } (a): P\mathcal{L}^L = \mathcal{L}^L P = 0 \text{ and } (b): \mathcal{L}^C P = P\mathcal{L}^C \text{ also use } P^2 = P \\
=\ & P\mathcal{L}^{LC} e^{(\mathcal{L}^L+\mathcal{L}^C-P\mathcal{L}^C-\mathcal{L}^C P+P\mathcal{L}^C P)} Q\mathcal{L}^{LC} \rho^r(t-t_1) && (4.44)\\
|\ & \text{use } (b): [\mathcal{L}^C, P]_- = 0 \\
=\ & P\mathcal{L}^{LC} e^{(\mathcal{L}^L+\mathcal{L}^C-\mathcal{L}^C P)} Q\mathcal{L}^{LC} \rho^r(t-t_1) && (4.45)\\
|\ & \text{expansion of third exponent gives terms of the form } \mathcal{L}^C PQ\mathcal{L}^{LC}\rho^r = 0 \text{ since } PQ = 0 \\
=\ & P\mathcal{L}^{LC} e^{(\mathcal{L}^L+\mathcal{L}^C)t_1} \mathcal{L}^{LC} \rho^r(t-t_1) && (4.46)\\
|\ & \text{define the evolution “picture” as } e^{(\mathcal{L}^L+\mathcal{L}^C)t_1} A = A(-t_1) \text{ and neglect the evolution on } \rho^r \\
\approx\ & P\mathcal{L}^{LC} \mathcal{L}^{LC}(-t_1) \rho^r(t-t_1) && (4.47)\\
|\ & \text{write trivally } \mathcal{L}^{LC} = \mathcal{L}^{LC}(0) \\
=\ & P\mathcal{L}^{LC}(0) \mathcal{L}^{LC}(-t_1) \rho^r(t-t_1) && (4.48)
\end{aligned}$$

Finally we will include the Markovian approximation by assuming that $\rho^C(t)$ is essentially constant over the relaxation times t_1 so that we can take it out of the integral and take $t \to \infty$. The final (weak-coupling, Markovian) quantum master equation is

$$\frac{\partial}{\partial t}\rho^C(t) = \left(\mathcal{L}^C + \alpha^2 \int_0^\infty dt_1 \rho^{L,\text{eq}} \text{Tr}_L \left(\mathcal{L}^{LC}(0)\mathcal{L}^{LC}(-t_1)\right)\right) \rho^C(t) \tag{4.49}$$

4.2 Numerical Implementation: Conversion to Stochastics

The object to calculate here is the reduced density matrix of the central system. Here, first, we will derive the formal exact expression of the reduced density matrix via path integration. It is exact but the non-Markovian memory integral is not tractable. Then stochastic unravelling is used to provide a numerical method to calculate the reduced density matrix by going around the memory integrals.

4.2.1 Influence Functional

We follow [Weiss2008] section 5.1 to derive the Feynaman-Vernon Influence Functional in real time. The influence functional is a functional expression of the effects of the environment on the system after tracing over the environment degrees of freedom.

The notation here follows the notation standard in the literature which differs somewhat from the rest of the thesis.

We write down the system + bath Hamiltonian. [3]

$$\begin{aligned} H &= H_S + H_B + H_{SB} && (4.50)\\ &= \frac{P^2}{2M} + V(q) + \sum_{\alpha=1}^{N} \frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}\sum_{\alpha=1}^{N} m_\alpha\omega_\alpha^2\left(x_\alpha - \frac{c_\alpha}{m_\alpha\omega_\alpha^2}q\right)^2 && (4.51)\end{aligned}$$

$$\begin{aligned} \text{with,} \quad H_B &= \sum_{\alpha=1}^{N}\left(\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}m_\alpha\omega_\alpha^2 x_\alpha^2\right) && (4.52)\\ H_{SB} &= -q\sum_{\alpha=1}^{N} c_\alpha x_\alpha + q^2\sum_{\alpha=1}^{N}\frac{c_\alpha^2}{2m_\alpha\omega_\alpha^2} && (4.53)\end{aligned}$$

The notation (standard in literature) used in this chapter are

- P: momentum of the system particle
- M: mass of the system particle
- V: potential experienced by the system particle
- q: configuration variable of the system particle
- p_α: momentum of the αth particle (or degree of freedom) in the bath
- m_α: mass of the αth particle in the bath
- ω_α: frequency of the αth particle in the bath
- x_α: position of the αth particle in the bath
- c_α: coupling constant between x_α and q

We write down the definition of the reduced density matrix.

$$\begin{aligned} \rho^{\text{reduced}}(q_f, q_f', t) &= \int d\vec{x}_0 \left\langle q_f\vec{x}_0 \left|\rho^{\text{total}}(t)\right| q_f'\vec{x}_0\right\rangle && (4.54)\\ &\quad | \ \text{the vector notation } \vec{x}_0 \text{ represents the complete set of bath variables}\\ &\quad | \ \text{use Schrodinger picture and note that the Hamiltonian is time independent}\\ &= \int d\vec{x}_0 \left\langle q_f\vec{x}_0 \left|e^{-\frac{i}{\hbar}Ht}\rho^{\text{total}}(0)e^{\frac{i}{\hbar}Ht}\right| q_f'\vec{x}_0\right\rangle && (4.55)\\ &\quad | \ \text{insert 2 complete sets}\\ &= \int \vec{x}_0 \int dq_i dq_i' d\vec{x}_1 d\vec{x}_1' \left\langle q_f\vec{x}_0 \left|e^{-\frac{i}{\hbar}Ht}\right| q_i\vec{x}_1\right\rangle \left\langle q_i\vec{x}_1 \left|\rho^{\text{total}}(0)\right| q_i'\vec{x}_1'\right\rangle \left\langle q_i'\vec{x}_1' \left|e^{\frac{i}{\hbar}Ht}\right| q_f'\vec{x}_0\right\rangle && (4.56)\end{aligned}$$

[3] As usual, the baths are taken to be independent and so it is straightforward to include more baths.

We write the evolution matrix elements as path integrals.

$$\left\langle q_f\vec{x}_0 \left| e^{-\frac{i}{\hbar}Ht} \right| q_i\vec{x}_1 \right\rangle \equiv F[q_f q_i \vec{x}_0 \vec{x}_1] = \int_{q(0)=q_i}^{q(t)=q_f} Dq \int_{\vec{x}(0)=\vec{x}_1}^{\vec{x}(t)=\vec{x}_0} D\vec{x} e^{\frac{i}{\hbar}S[q,\vec{x}]} \tag{4.57}$$

$$\left\langle q_i'\vec{x}_1 \left| e^{\frac{i}{\hbar}Ht} \right| q_f'\vec{x}_0 \right\rangle \equiv F^*[q_i' q_f' \vec{x}_1' \vec{x}_0] = \int_{q'(0)=q_i'}^{q'(t)=q_f'} Dq' \int_{\vec{x}'(0)=\vec{x}_1'}^{\vec{x}'(t)=\vec{x}_0} D\vec{x}' e^{-\frac{i}{\hbar}S[q',\vec{x}']} \tag{4.58}$$

[4] where $S[q,\vec{x}]$ is the total action derived from the total Hamiltonian.

We take the initial density matrix (at $t=0$) to be factorizable.

$$\rho^{\text{total}}(t=0) = \rho^S(0) \otimes \rho^B(0) \tag{4.59}$$

and this allows the rewriting,

$$\left\langle q_i\vec{x}_1 \left| \rho^{\text{total}}(0) \right| q_i'\vec{x}_1' \right\rangle = \left\langle q_i\vec{x}_1 \left| \rho^S(0)\rho^B(0) \right| q_i'\vec{x}_1' \right\rangle \tag{4.60}$$

$$= \left\langle q_i \left| \rho^S(0) \right| q_i' \right\rangle \left\langle \vec{x}_1 \left| \rho^B(0) \right| \vec{x}_1' \right\rangle \tag{4.61}$$

And now we are ready to write the expression of the reduced density matrix in terms of the influence functional.

$$\begin{aligned}
& \rho^{\text{reduced}}(q_f, q_f', t) \\
= & \int d\vec{x}_0 \int dq_i dq_i' d\vec{x}_1 d\vec{x}_1' \int Dq D\vec{x} e^{\frac{i}{\hbar}S[q,\vec{x}]} \int Dq' D\vec{x}' e^{-\frac{i}{\hbar}S[q',\vec{x}']} \left\langle q_i \left| \rho^S(0) \right| q_i' \right\rangle \left\langle \vec{x}_1 \left| \rho^B(0) \right| \vec{x}_1' \right\rangle \quad (4.62) \\
| & \text{ write } S[q,\vec{x}] = S_S[q] + S_B[\vec{x}] + S_{SB}[q,\vec{x}] \\
\equiv & \int dq_i dq_i' \left\langle q_i \left| \rho^S(0) \right| q_i' \right\rangle \int Dq Dq' e^{\frac{i}{\hbar}(S_S[q]-S_S[q'])} F_{IF}[q,q'] \quad (4.63)
\end{aligned}$$

where the influence functional $F_{IF}[q,q']$ is

$$F_{IF}[q,q'] \equiv \int d\vec{x}_0 d\vec{x}_1 d\vec{x}_1' \int D\vec{x} D\vec{x}' \left\langle \vec{x}_1 \left| \rho^B(0) \right| \vec{x}_1' \right\rangle e^{\frac{i}{\hbar}(S_{SB}[q,\vec{x}] - S_{SB}[q',\vec{x}'] + S_B[\vec{x}] - S_B[\vec{x}'])} \tag{4.64}$$

$$= \int d\vec{x}_0 d\vec{x}_1 d\vec{x}_1' \left\langle \vec{x}_1 \left| \rho^B(0) \right| \vec{x}_1' \right\rangle \left(\int D\vec{x} e^{\frac{i}{\hbar}(S_{SB}[q,\vec{x}]+S_B[\vec{x}])} \right) \left(\int D\vec{x}' e^{-\frac{i}{\hbar}(S_{SB}[q',\vec{x}']+S_B[\vec{x}'])} \right) \tag{4.65}$$

The remainder of this section is to evaluate $F_{IF}[q,q']$ explicitly. It is easiest to evaluate $\left\langle \vec{x}_1 \left| \rho^B(0) \right| \vec{x}_1' \right\rangle$ first.

$$\begin{aligned}
& \left\langle \vec{x}_1 \left| \rho^B(0) \right| \vec{x}_1' \right\rangle \\
= & \frac{1}{Z} \left\langle \vec{x}_1 \left| e^{-\beta H_B} \right| \vec{x}_1' \right\rangle \quad (4.66) \\
| & \text{ where } Z \equiv \mathrm{Tr} e^{-\beta H_B} \text{ and we use } H_B \text{ in terms of number operators } n_\alpha \\
| & \text{ so } Z = \prod_{\alpha=1}^{N} \sum_{n_\alpha=0}^{\infty} e^{-\beta\hbar\omega_\alpha(n_\alpha+1/2)} = \prod_{\alpha=1}^{N} \frac{e^{-\beta\hbar\omega_\alpha/2}}{1-e^{-\beta\hbar\omega_\alpha/2}} = \prod_{\alpha=1}^{N} \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega_\alpha\right)}
\end{aligned}$$

[4] The expression FF^* is known as the forward-backward path integrals.

$$= \left(\prod_{\alpha=1}^{N} 2\sinh\left(\frac{1}{2}\beta\hbar\omega_\alpha\right)\right)\left(\prod_{\beta=1}^{N}\left\langle x_{1\beta}\left|e^{-\beta\hbar\omega_\beta\left(n_\beta+1/2\right)}\right|x'_{1\beta}\right\rangle\right) \quad (4.67)$$

$|$ the second factor is the single harmonic oscillator propagator in imaginary time $\frac{it}{\hbar}=\beta$

$$= \prod_{\alpha=1}^{N} 2\sinh\left(\frac{1}{2}\beta\hbar\omega_\alpha\right)\left(\frac{m_\alpha\omega_\alpha}{2\pi\hbar\sinh(\beta\hbar\omega_\alpha)}\right)^{1/2} e^{-\frac{m_\alpha\omega_\alpha}{2\hbar\sinh(\beta\hbar\omega_\alpha)}\left[(x_{1\alpha}^2+x_{1\alpha}'^2)\cosh(\beta\hbar\omega_\alpha)-2x_{1\alpha}x'_{1\alpha}\right]} \quad (4.68)$$

Next we evaluate the expression

$$\int D\vec{x} e^{\frac{i}{\hbar}(S_{SB}[q,\vec{x}]+S_B[\vec{x}])}$$

$|$ recall the definition of action $S=\int_0^t dt'\mathcal{L}(t')$

$|$ the Lagrangians are $\mathcal{L}_B(t)=\frac{1}{2}\sum_{\alpha=1}^{N} m_\alpha\left(\dot{x}_\alpha^2(t)-\omega_\alpha^2 x_\alpha^2(t)\right)$

$|$ and $\mathcal{L}_{SB}(t)=\sum_{\alpha=1}^{N}\left(c_\alpha x_\alpha(t)q(t)-\frac{c_\alpha^2}{2m_\alpha\omega_\alpha^2}q^2(t)\right)$

$$= \prod_{\alpha=1}^{N}\int_{x_\alpha(0)=x_{1\alpha}}^{x_\alpha(t)=x_{0\alpha}} Dx_\alpha e^{\frac{i}{\hbar}\int_0^t dt'\left[\frac{1}{2}m_\alpha\dot{x}_\alpha^2(t')-\frac{1}{2}m_\alpha\omega_\alpha^2x_\alpha^2(t')+c_\alpha x_\alpha(t')q(t')-\frac{c_\alpha^2}{2m_\alpha\omega_\alpha^2}q^2(t')\right]} \quad (4.69)$$

The last exponential term does not contain $\vec{x}$ and it goes out of the path integral. We treat $q(t')$ as an "external force" term and we continue evaluating the path integral by expanding about the classical path x_α^{cl}.

$$S[x_\alpha] = \int_0^t dt'\left[\frac{1}{2}m_\alpha\dot{x}_\alpha^2(t')-\frac{1}{2}m_\alpha\omega_\alpha^2x_\alpha^2(t')+c_\alpha x_\alpha(t')q(t')\right] \quad (4.70)$$

$$= S[x_\alpha^{cl}+\eta_\alpha] \quad (4.71)$$

$|$ where η_α are fluctuations about the classical path x_α^{cl}

$|$ expand about the classical path x_α^{cl}

$$= S[x_\alpha^{cl}]+\int dt_1\eta_\alpha(t_1)\left.\frac{\delta S}{\delta x_\alpha(t_1)}\right|_{x_\alpha=x_\alpha^{cl}}+\frac{1}{2!}\int dt_1dt_2\eta_\alpha(t_1)\eta_\alpha(t_2)\left.\frac{\delta^2 S}{\delta x_\alpha(t_1)\delta x_\alpha(t_2)}\right|_{x_\alpha=x_\alpha^{cl}} \quad (4.72)$$

$|$ the expansion truncates at second order since the action is quadratic in x

$|$ due to the classical equations of motion, we have $\left.\frac{\delta S}{\delta x_\alpha}\right|_{x_\alpha=x_\alpha^{cl}}=0$

$$= S[x_\alpha^{cl}] + \frac{1}{2}\int dt_1dt_2\eta_\alpha(t_1)\eta_\alpha(t_2)\frac{\delta^2}{\delta x_\alpha(t_1)\delta x_\alpha(t_2)}\left(\int_0^t dt'\left(\frac{1}{2}\dot{x}_\alpha^2-\frac{1}{2}m_\alpha\omega_\alpha^2x_\alpha^2+c_\alpha x_\alpha q\right)\right)\Bigg|_{x_\alpha=x_\alpha^{cl}} \quad (4.73)$$

$$= S[x_\alpha^{cl}]+\frac{1}{2}\int dt_1dt_2\int_0^t dt'\eta_\alpha(t_1)\eta_\alpha(t_2)\frac{\delta}{\delta x_\alpha(t_1)}\left(m_\alpha\dot{x}_\alpha\frac{\delta\dot{x}_\alpha}{\delta x_\alpha(t_2)}\right)\Bigg|_{x_\alpha=x_\alpha^{cl}} -\frac{1}{2}\int dt_1dt_2\int_0^t dt'm_\alpha\omega_\alpha^2\delta(t'-t_2)\delta(t'-t_1)\eta_\alpha(t_1)\eta_\alpha(t_2) \quad (4.74)$$

$|$ for second term, integrate by parts once and use $\eta_\alpha(0)=0=\eta_\alpha(t)$ to eliminate surface terms

$$
\begin{aligned}
&= S[x_\alpha^{cl}] - \frac{1}{2}m_\alpha \int dt_1 \int_0^t dt' \eta_\alpha(t_1)\eta_\alpha(t') \frac{\delta}{\delta x_\alpha(t_1)} \left(-\ddot{x}_\alpha \delta(t'-t_2)\right)\Big|_{x_\alpha = x_\alpha^{cl}} - \frac{1}{2}\int_0^t dt' m_\alpha \omega_\alpha^2 \eta_\alpha^2(t') \\
&= S[x_\alpha^{cl}] - \frac{1}{2}m_\alpha \int dt_1 \int_0^t dt' \eta_\alpha(t_1)\eta_\alpha(t') \frac{\delta \ddot{x}_\alpha(t')}{\delta x_\alpha(t_1)}\Big|_{x_\alpha = x_\alpha^{cl}} - \frac{1}{2}\int_0^t dt' m_\alpha \omega_\alpha^2 \eta_\alpha^2(t') \qquad (4.75)
\end{aligned}
$$

| for second term, integrate by parts twice and use $\eta_\alpha(0) = 0 = \eta_\alpha(t)$

$$
= S[x_\alpha^{cl}] - \frac{1}{2}m_\alpha \int dt_1 \int_0^t dt' \eta_\alpha(t_1)\ddot{\eta}_\alpha(t')\delta(t'-t_1) - \frac{1}{2}\int_0^t dt' m_\alpha \omega_\alpha^2 \eta_\alpha^2(t') \qquad (4.76)
$$

| for second term, integrate by parts once and use $\eta_\alpha(0) = 0 = \eta_\alpha(t)$

$$
= S[x_\alpha^{cl}] + \int_0^t dt' \left(\frac{1}{2}m_\alpha \dot{\eta}_\alpha^2(t') - \frac{1}{2}m_\alpha \omega_\alpha^2(t')\right) \qquad (4.77)
$$

So now the path integral is over all fluctuations η.

$$
\begin{aligned}
&\int d\vec{x} e^{\frac{i}{\hbar}(S_{SB}[q,\vec{x}] + S_B[\vec{x}])} \\
&= \prod_{\alpha=1}^N e^{\frac{i}{\hbar}\int_0^t dt' \left(-\frac{c_\alpha^2}{2m_\alpha \omega_\alpha^2} q^2(t')\right)} e^{\frac{i}{\hbar}S[x_\alpha^{cl}]} \int D\eta_\alpha e^{\frac{i}{2\hbar}\int_0^t dt' \left(\frac{1}{2}m_\alpha \dot{\eta}_\alpha^2(t') - \frac{1}{2}m_\alpha \omega_\alpha^2(t')\right)} \qquad (4.78)
\end{aligned}
$$

| the path integral of fluctuations is shown in the appendix to this chapter to be,

$$
| \quad \int D\eta_\alpha e^{\frac{i}{2\hbar}\int_0^t dt' \left(\frac{1}{2}m_\alpha \dot{\eta}_\alpha^2(t') - \frac{1}{2}m_\alpha \omega_\alpha^2(t')\right)} = \left(\frac{m_\alpha \omega_\alpha}{2\pi i \hbar \sin(\omega_\alpha t)}\right)^{1/2}
$$

$$
= \prod_{\alpha=1}^N \left(\frac{m_\alpha \omega_\alpha}{2\pi i \hbar \sin(\omega_\alpha t)}\right)^{1/2} e^{\frac{i}{\hbar}\int_0^t dt' \left(-\frac{c_\alpha^2}{2m_\alpha \omega_\alpha^2} q^2(t')\right)} e^{\frac{i}{\hbar}S[x_\alpha^{cl}]} \qquad (4.79)
$$

We show in the appendix that the classical action expressed in terms of the end points,

$$
\begin{aligned}
\vec{x}^{cl}(0) &= \vec{x}_1 \Rightarrow x_\alpha^{cl}(0) = x_{1\alpha} \qquad (4.80) \\
\vec{x}^{cl}(t) &= \vec{x}_0 \Rightarrow x_\alpha^{cl}(t) = x_{0\alpha} \qquad (4.81)
\end{aligned}
$$

$$
\begin{aligned}
S[x_\alpha^{cl}] &= S[x_\alpha^{cl}]_{x_{1\alpha}}^{x_{0\alpha}} \qquad (4.82) \\
&= \frac{m_\alpha \omega_\alpha}{2\sin(\omega_\alpha t)} \left[(x_{1\alpha}^2 + x_{0\alpha}^2)\cos(\omega_\alpha t) - 2x_{1\alpha}x_{0\alpha}\right] \\
&\quad + \frac{x_{1\alpha}c_\alpha}{\sin(\omega_\alpha t)} \int_0^t dt' q(t') \sin(\omega_\alpha(t-t')) + \frac{x_{0\alpha}c_\alpha}{\sin(\omega_\alpha t)} \int_0^t dt' q(t') \sin(\omega_\alpha t') \\
&\quad - \frac{c_\alpha^2}{m_\alpha \omega_\alpha \sin(\omega_\alpha t)} \int_0^t dt' \int_0^{t'} dt'' q(t') \sin(\omega_\alpha(t-t')) \sin(\omega_\alpha t'') q(t'') \qquad (4.83)
\end{aligned}
$$

We can now explicitly work out the influence functional.

$$
\begin{aligned}
F_{IF}[q,q'] &= \int d\vec{x}_0 d\vec{x}_1 d\vec{x}_1' \left\langle \vec{x}_1 \left| \rho^B(0) \right| \vec{x}_1' \right\rangle \left(\int D\vec{x}_1 e^{\frac{i}{\hbar}(S_{SB}[q,\vec{x}] + S_B[\vec{x}])}\right) \left(\int D\vec{x}_1' e^{-\frac{i}{\hbar}(S_{SB}[q',\vec{x}'] + S_B[\vec{x}'])}\right) \\
&= \prod_{\alpha=1}^N \int dx_{0\alpha} dx_{1\alpha} dx_{1\alpha}' \\
&\quad \times \left(2\sinh\left(\frac{1}{2}\beta\hbar\omega_\alpha\right)\right) \left(\frac{m_\alpha \omega_\alpha}{2\pi\hbar \sinh(\beta\hbar\omega_\alpha)}\right)^{1/2} e^{\frac{m_\alpha \omega_\alpha}{2\hbar \sinh(\beta\hbar\omega_\alpha)}\left[(x_{1\alpha}^2 + x_{1\alpha}'^2)\cosh(\beta\hbar\omega_\alpha) - 2x_{1\alpha}x_{1\alpha}'\right]}
\end{aligned}
$$

$$
\begin{aligned}
&\times e^{\frac{i}{\hbar}S[x_\alpha^{cl}]_{x_{1\alpha}}^{x_{0\alpha}}} \left(\frac{m_\alpha\omega_\alpha}{2\pi i\hbar\sin(\omega_\alpha t)}\right)^{1/2} e^{\frac{i}{\hbar}\int_0^t dt'\left(-\frac{c_\alpha^2}{2m_\alpha\omega_\alpha^2}q^2(t')\right)} \\
&\times e^{-\frac{i}{\hbar}S[x_\alpha^{'cl}]_{x'_{1\alpha}}^{x_{0\alpha}}} \left(\frac{m_\alpha\omega_\alpha}{2\pi(-i)\hbar\sin(\omega_\alpha t)}\right)^{1/2} e^{-\frac{i}{\hbar}\int_0^t dt'\left(-\frac{c_\alpha^2}{2m_\alpha\omega_\alpha^2}q'^2(t')\right)} \qquad (4.84)\\
= & \prod_{\alpha=1}^{N}\left(2\sinh\left(\frac{1}{2}\beta\hbar\omega_\alpha\right)\right)\left(\frac{m_\alpha\omega_\alpha}{2\pi\hbar\sinh(\beta\hbar\omega_\alpha)}\right)^{1/2}\left(\frac{m_\alpha\omega_\alpha}{2\pi\hbar\sin(\omega_\alpha t)}\right) \\
&\times e^{\frac{i}{\hbar}\int_0^t dt'\frac{c_\alpha^2}{2m_\alpha\omega_\alpha^2}\left(q'^2(t')-q^2(t')\right)} \\
&\times \int dx_{0\alpha}dx_{1\alpha}dx'_{1\alpha}e^{-\frac{m_\alpha\omega_\alpha}{2\hbar\sinh(\beta\hbar\omega_\alpha)}\left[(x_{1\alpha}^2+x_{1\alpha}'^2)\cosh(\beta\hbar\omega_\alpha)-2x_{1\alpha}x'_{1\alpha}\right]} e^{\frac{i}{\hbar}\left(S[x_\alpha^{cl}]_{x_{1\alpha}}^{x_{0\alpha}}-S[x_\alpha^{'cl}]_{x'_{1\alpha}}^{x_{0\alpha}}\right)} \qquad (4.85)
\end{aligned}
$$

It remains to work out the 3 Gaussian integrals $x_{0\alpha}$, $x_{1\alpha}$ and $x'_{1\alpha}$. The Gaussian integral identity to use is

$$\int_{-\infty}^{+\infty} dx e^{-ax^2+bx} = \sqrt{\frac{\pi}{a}}e^{\frac{b^2}{4a}} \qquad (4.86)$$

$$
\begin{aligned}
&\text{All exponential terms}\\
= & \frac{i}{2\hbar}\int_0^t dt'\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\left(q'^2(t')-q^2(t')\right)\\
&-\frac{m_\alpha\omega_\alpha}{2\hbar\sinh(\beta\hbar\omega_\alpha)}\left[(x_{1\alpha}^2+x_{1\alpha}'^2)\cosh(\beta\hbar\omega_\alpha)-2x_{1\alpha}x'_{1\alpha}\right]+\frac{i}{\hbar}\left(S[x_\alpha^{cl}]_{x_{1\alpha}}^{x_{0\alpha}}-S[x_\alpha^{'cl}]_{x'_{1\alpha}}^{x_{0\alpha}}\right) \qquad (4.87)\\
| \ & \text{the first term above does not contain } x_0,\ x_1 \text{ and } x'_1\\
| \ & \text{the last term of } S[x_\alpha^{cl}]_{x_{1\alpha}}^{x_{0\alpha}} \text{ and } S[x_\alpha^{'cl}]_{x'_{1\alpha}}^{x_{0\alpha}} \text{ do not contain } x_0,\ x_1 \text{ and } x'_1 \text{ and they cancel}\\
| \ & \text{drop } \alpha \text{ to simplify writing}\\
= & -\frac{m\omega}{2\hbar\sinh(\beta\hbar\omega)}\left[(x_1^2+x_1'^2)\cosh(\beta\hbar\omega)-2x_1x'_1\right]+\frac{i}{\hbar}\frac{m\omega}{2\sin\omega t}\left[(x_1^2-x_1'^2)\cos(\omega t)-2x_0(x_1-x'_1)\right]\\
&+\frac{i}{\hbar}\frac{c}{\sin\omega t}\int_0^t dt'\left(x_1q(t')-x'_1q'(t')\right)\sin(\omega(t-t'))+\frac{i}{\hbar}\frac{c}{\sin\omega t}x_0\int_0^t dt'\left(q(t')-q'(t')\right)\sin(\omega t)\\
&+1 \text{ term without } x_0,\ x_1 \text{ and } x'_1 \qquad (4.88)\\
| \ & \text{define notation to simplify writing}\\
| \ & a_1 \equiv \frac{m\omega}{2\hbar}\coth(\beta\hbar\omega)\\
| \ & a_2 \equiv \frac{m\omega}{2\hbar}i\cot(\omega t)\\
| \ & b_1 \equiv \frac{m\omega}{\hbar\sinh(\beta\hbar\omega)} = \frac{m\omega}{\hbar}\mathrm{csch}(\beta\hbar\omega)\\
| \ & b_2 \equiv \frac{m\omega i}{\hbar\sin(\omega t)} = \frac{m\omega}{\hbar}i\mathrm{cosec}\omega t\\
| \ & b_3 \equiv \frac{i}{\hbar}\frac{c}{\sin(\omega t)}\int_0^t dt' q(t')\sin(\omega(t-t'))\\
| \ & b'_3 \equiv \frac{i}{\hbar}\frac{c}{\sin(\omega t)}\int_0^t dt' q'(t')\sin(\omega(t-t'))\\
| \ & b_4 \equiv \frac{i}{\hbar}\frac{c}{\sin(\omega t)}\int_0^t dt'\left(q(t')-q'(t')\right)\sin(\omega t')
\end{aligned}
$$

$$\begin{aligned} &= -a_1(x_1^2+x_1'^2)+b_1x_1x_1'+a_2(x_1^2-x_1'^2)-b_2x_0(x_1-x_1')+b_3x_1-b_3'x_1'+b_4x_0 \\ &\quad +1 \text{ term without } x_0,\ x_1 \text{ and } x_1' \end{aligned} \tag{4.89}$$

First, we will gather the terms containing x_1 and then carry out the x_1 Gaussian integral.[5]

$$\begin{aligned} &\text{All exponential terms} \\ =\ &-(a_1-a_2)x_1^2+(b_1x_1'-b_2x_0+b_3)x_1 \\ &-(a_1+a_2)x_1'^2+b_2x_0x_1'-b_3'x_1'+b_4x_0+1 \text{ term without } x_0,\ x_1 \text{ and } x_1' \end{aligned} \tag{4.90}$$

The Gaussian integral for x_1 yields,

$$\text{Prefactor} = \sqrt{\frac{\pi}{a_1-a_2}} \tag{4.91}$$

$$\begin{aligned} &\text{All exponential terms} \\ =\ &\frac{(b_1x_1'-b_2x_0+b_3)^2}{4(a_1-a_2)}-(a_1+a_2)x_1'^2+b_2x_0x_1'-b_3'x_1'+b_4x_0 \\ &+1 \text{ term without } x_0,\ x_1 \text{ and } x_1' \qquad (4.92) \\ |\ &\text{gather the terms containing } x_1' \text{ and then carry out the } x_1' \text{ Gaussian integral} \\ =\ &\frac{b_1^2x_1'^2+(b_3-b_2x_0)^2+2b_1(b_3-b_2x_0)x_1'}{4(a_1-a_2)}-(a_1+a_2)x_1'^2+b_2x_0x_1'-b_3'x_1'+b_4x_0 \\ &+1 \text{ term without } x_0,\ x_1 \text{ and } x_1' \qquad (4.93) \\ =\ &-\left(a_1+a_2-\frac{b_1^2}{4(a_1-a_2)}\right)x_1'^2+x_1'\left(\frac{2b_1(b_3-b_2x_0)}{4(a_1-a_2)}+b_2x_0-b_3'\right) \\ &+\frac{(b_3-b_2x_0)^2}{4(a_1-a_2)}+b_4x_0+1 \text{ term without } x_0,\ x_1 \text{ and } x_1' \qquad (4.94) \end{aligned}$$

The Gaussian integral for x_1' yields

$$\text{Prefactor} = \sqrt{\frac{\pi}{a_1+a_2-\frac{b_1^2}{4(a_1-a_2)}}} \tag{4.95}$$

$$\begin{aligned} &\text{All exponential terms} \\ =\ &\left(4(a_1+a_2)-\frac{b_1^2}{a_1-a_2}\right)^{-1}\left(\frac{2b_1(b_3-b_2x_0)}{4(a_1-a_2)}+b_2x_0-b_3'\right)^2+\frac{(b_3-b_2x_0)^2}{4(a_1-a_2)}+b_4x_0 \\ &+1 \text{ term without } x_0,\ x_1 \text{ and } x_1' \qquad (4.96) \\ |\ &\text{gather the terms containing } x_0 \text{ and then carry out the } x_0 \text{ Gaussian integral} \\ =\ &\left(4(a_1+a_2)-\frac{b_1^2}{a_1-a_2}\right)^{-1} \\ &\times\left[\left(\frac{b_1b_3}{2(a_1-a_2)}-b_3'\right)^2+\left(b_2-\frac{b_1b_2}{2(a_1-a_2)}\right)^2x_0^2+2\left(\frac{b_1b_3}{2(a_1-a_2)}-b_3'\right)\left(b_2-\frac{b_1b_2}{2(a_1-a_2)}\right)x_0\right] \\ &+\frac{b_3^2}{4(a_1-a_2)}+\frac{b_2^2}{4(a_1-a_2)}x_0^2-\frac{b_2b_3}{2(a_1-a_2)}x_0+b_4x_0+1 \text{ term without } x_0,\ x_1 \text{ and } x_1' \qquad (4.97) \end{aligned}$$

[5] I don't understand how come if I try to perform the x_0 Gaussian integral first, I will run into problems.

$$= -\left[-\frac{b_2^2}{4(a_1-a_2)} - \left(4(a_1-a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1}\left(b_2 - \frac{b_1b_2}{2(a_1-a_2)}\right)^2\right]x_0^2$$
$$+\left[\left(4(a_1+a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1} 2\left(\frac{b_1b_3}{2(a_1-a_2)} - b_3'\right)\left(b_2 - \frac{b_1b_2}{2(a_1-a_2)}\right) - \frac{b_2b_3}{2(a_1-a_2)} + b_4\right]x_0$$
$$+\left(4(a_1+a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1}\left(\frac{b_1b_3}{2(a_1-a_2)} - b_3'\right)^2 + \frac{b_3^2}{4(a_1-a_2)} + 1 \text{ term without } x_0,\, x_1 \text{ and } x_1'$$

The Gaussian integral for x_0 yields

$$\text{Prefactor} = \sqrt{\frac{\pi}{-\frac{b_2^2}{4(a_1-a_2)} - \left(4(a_1-a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1}\left(b_2 - \frac{b_1b_2}{2(a_1-a_2)}\right)^2}} \tag{4.98}$$
$$= \pi^{1/2}\left[-\frac{b_2^2}{4(a_1-a_2)} - \left(4(a_1-a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1}\left(b_2 - \frac{b_1b_2}{2(a_1-a_2)}\right)^2\right]^{-1/2} \tag{4.99}$$

All exponential terms

$$= \left[-\frac{b_2^2}{4(a_1-a_2)} - \left(4(a_1-a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1}\left(b_2 - \frac{b_1b_2}{2(a_1-a_2)}\right)^2\right]^{-1}$$
$$\times\left[\left(4(a_1+a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1} 2\left(\frac{b_1b_3}{2(a_1-a_2)} - b_3'\right)\left(b_2 - \frac{b_1b_2}{2(a_1-a_2)}\right) - \frac{b_2b_3}{2(a_1-a_2)} + b_4\right]^2$$
$$+\left(4(a_1+a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1}\left(\frac{b_1b_3}{2(a_1-a_2)} - b_3'\right)^2 + \frac{b_3^2}{4(a_1-a_2)} + 1 \text{ term without } x_0,\, x_1 \text{ and } x_1'$$

We need to simplify the expressions. We will simplify all the prefactors of the influence functional first. We note a useful identity,

$$(a_1-a_2)\left(a_1+a_2-\frac{b_1^2}{4(a_1-a_2)}\right) = a_1^2 - a_2^2 - \frac{b_1^2}{4} \tag{4.100}$$
$$= \left(\frac{m\omega}{2\hbar}\right)^2\left[\coth^2(\beta\hbar\omega) - (i\cot(\omega t))^2 - \operatorname{csch}^2(\beta\hbar\omega)\right] \tag{4.101}$$
$$\mid \text{ note that } \coth^2 x - \operatorname{csch}^2 x = 1$$
$$= \left(\frac{m\omega}{2\hbar}\right)^2\left[1 + \cot^2(\omega t)\right] \tag{4.102}$$
$$\mid \text{ note that } 1 + \cot^2 x = \operatorname{cosec}^2 x$$
$$= \left(\frac{m\omega}{2\hbar}\right)^2 \operatorname{cosec}^2(\omega t) \tag{4.103}$$
$$= -\frac{b_2^2}{4} \tag{4.104}$$

All Prefactors of the influence functional

$$= \left(2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right)\left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}\left(\frac{m\omega}{2\pi\sin(\omega t)}\right)\sqrt{\frac{\pi}{a_1-a_2}}\sqrt{\frac{\pi}{a_1+a_2-\frac{b_1^2}{4(a_1-a_2)}}}$$

$$\times\pi^{1/2}\left[-\frac{b_2^2}{4(a_1-a_2)}-\left(4(a_1-a_2)-\frac{b_1^2}{a_1-a_2}\right)^{-1}\left(b_2-\frac{b_1b_2}{2(a_1-a_2)}\right)^2\right]^{-1/2} \tag{4.105}$$

$$| \quad \text{cancel } \pi \text{ and use the above identity , } (a_1-a_2)\left(a_1+a_2-\frac{b_1^2}{4(a_1-a_2)}\right)=-\frac{b_2^2}{4}$$

$$= \left(2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right)\left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}\left(\frac{m\omega}{2\pi\sin(\omega t)}\right)\sqrt{-\frac{4}{b_2^2}}$$

$$\times\left[-\frac{b_2^2}{4(a_1-a_2)}-\left(4(a_1-a_2)-\frac{b_1^2}{a_1-a_2}\right)^{-1}\left(b_2-\frac{b_1b_2}{2(a_1-a_2)}\right)^2\right]^{-1/2} \tag{4.106}$$

$$| \quad \text{note } \sqrt{-\frac{4}{b_2^2}}=\frac{2\hbar\sin(\omega t)}{m\omega} \text{ and cancels third factor}$$

$$= \left(2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right)\left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}$$

$$\times\left[-\frac{b_2^2}{4(a_1-a_2)}-\left(4(a_1-a_2)-\frac{b_1^2}{a_1-a_2}\right)^{-1}\left(b_2-\frac{b_1b_2}{2(a_1-a_2)}\right)^2\right]^{-1/2} \tag{4.107}$$

$$| \quad \text{expand } \left(b_2-\frac{b_1b_2}{2(a_1-a_2)}\right)^2=b_2^2+\frac{b_1^2b_2^2}{4(a_1-a_2)^2}-\frac{b_1b_2^2}{a_1-a_2}$$

$$| \quad \text{then multiply } \left(4(a_1-a_2)-\frac{b_1^2}{a_1-a_2}\right)^{-1}$$

$$| \quad \text{and use the identity } (a_1-a_2)\left(4(a_1-a_2)-\frac{b_1^2}{a_1-a_2}\right)=-b_2^2$$

$$= \left(2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right)\left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}$$

$$\times\left[a_1+a_2-\frac{b_1^2}{4(a_1-a_2)}-\frac{b_2^2}{\left(4(a_1-a_2)-\frac{b_1^2}{a_1-a_2}\right)}+\frac{b_1^2}{4(a_1-a_2)}-b_1\right]^{-1/2} \tag{4.108}$$

$$| \quad \text{use the identity to write } -\frac{b_2^2}{\left(4(a_1-a_2)-\frac{b_1^2}{a_1-a_2}\right)}=a_1-a_2$$

$$= \left(2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right)\left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}[a_1a_2+a_1-a_2-b_1]^{-1/2} \tag{4.109}$$

$$= \left(2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right)\left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}[2a_1-b_1]^{-1/2} \tag{4.110}$$

$$| \quad \text{write } a_1 \text{ and } b_1 \text{ in original form and write } \sinh\left(\frac{1}{2}x\right)=\sqrt{\frac{1}{2}(\cosh x-1)}$$

$$= \sqrt{\frac{1}{2}(\cosh(\beta\hbar\omega)-1)}\left(\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right)^{1/2}\left[\frac{m\omega}{\hbar}\coth(\beta\hbar\omega)-\frac{m\omega}{\hbar}\mathrm{csch}(\beta\hbar\omega)\right]^{-1/2} \tag{4.111}$$

$$= \left[\frac{m\omega}{\hbar}\left(\coth(\beta\hbar\omega)-\frac{1}{\sinh(\beta\hbar\omega)}\right)\right]^{1/2}\left[\frac{m\omega}{\hbar}\coth(\beta\hbar\omega)-\frac{m\omega}{\hbar}\mathrm{csch}(\beta\hbar\omega)\right]^{-1/2} \tag{4.112}$$

$$= 1 \tag{4.113}$$

Indeed as mentioned in [Weiss2008] on pg 110 in the text between equations (5.20) and (5.21) we get a factor of unity.

Now we go over to the exponential factor of the influence functional.

$$
\begin{aligned}
& \text{All exponential terms} \\
= & \left[-\frac{b_2^2}{a_1-a_2} - 4\left(4(a_1+a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1}\left(b_2 - \frac{b_1 b_2}{2(a_1-a_2)}\right)^2\right]^{-1} \\
& \times \left[\left(4(a_1+a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1} 2\left(\frac{b_1 b_3}{2(a_1-a_2} - b_3'\right)\left(b_2 - \frac{b_1 b_2}{2(a_1-a_2)}\right) - \frac{b_2 b_3}{2(a_1-a_2)} + b_4\right]^2 \\
& + \left(4(a_1+a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1}\left(\frac{b_1 b_3}{2(a_1-a_2)} - b_3'\right)^2 + \frac{b_3^2}{4(a_1-a_2)} + 1 \text{ term without } x_0,\, x_1 \text{ and } x_1' \\
| & \text{ also note that } \left[-\frac{b_2^2}{a_1-a_2} - 4\left(4(a_1+a_2) - \frac{b_1^2}{a_1-a_2}\right)^{-1}\left(b_2 - \frac{b_1 b_2}{2(a_1-a_2)}\right)^2\right] \\
| & \qquad = \frac{m\omega}{\hbar}\left(\coth(\beta\hbar\omega) - \operatorname{csch}(\beta\hbar\omega)\right) = \frac{m\omega}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right) \\
| & \text{ identities (4.267) and (4.268) in the appendix seems to be needed as well} \\
\vdots & \text{ I am supposed to get} \\
= & \frac{1}{\hbar}\Phi[q,q']
\end{aligned} \tag{4.114}
$$

Somehow I am unable to manipulate to the answer. I apologize for that. The influence functional is equation (5.22) in [Weiss2008]. It will also be shown explicitly shown in the next section.

4.2.2 Stochastic Unravelling

Here we follow [Koch2008] including notation. Related references are [Stockburger2002] and [Stockburger2004]. The following stochastic unravelling technique works around the problem by replacing the memory integrals with some form of noise average of the stochastic variables. The stochastic variables evolve according to "nice" differential equations. This makes the whole formalism possibly tractable at least numerically.

The influence functional is,

$$
F_{IF}[q,q'] \equiv e^{\frac{1}{\hbar}\Phi[q,q']} \tag{4.115}
$$

$$
\begin{aligned}
\Phi[q,q'] &= \frac{1}{\hbar}\int_0^t dt' \int_0^{t'} dt'' \left(q(t') - q'(t')\right)\left(L(t'-t'')q(t'') - L^*(t'-t'')q'(t'')\right) \\
&\quad + i\frac{\mu}{2}\int_0^t dt' \left(q^2(t') - q'^2(t')\right)
\end{aligned} \tag{4.116}
$$

with

$$
L(t) = \frac{\hbar}{\pi}\int_0^\infty d\omega J(\omega)\left(\coth\left(\frac{1}{2}\beta\hbar\omega\right)\cos(\omega t) - i\sin(\omega t)\right) \tag{4.117}
$$

$$
\equiv L'(t) + iL''(t) \tag{4.118}
$$

$$
L'(t) = \frac{\hbar}{\pi}\int_0^\infty d\omega J(\omega)\coth\left(\frac{1}{2}\beta\hbar\omega\right)\cos(\omega t) \tag{4.119}
$$

$$\begin{aligned}
L''(t) &= \frac{\hbar}{\pi}\int_0^\infty d\omega J(\omega)\left(-\sin(\omega t)\right) && (4.120)\\
\mu &= -\frac{1}{2\hbar}\int_0^\infty dt L''(t) && (4.121)\\
J(\omega) &= \pi\sum_{\alpha=1}^{N}\frac{c_\alpha^2}{2m_\alpha\omega_\alpha}\delta(\omega-\omega_\alpha) && (4.122)
\end{aligned}$$

We introduce the so-called symmetric and antisymmetric coordinates. These are called Wigner coordinates elsewhere in the thesis. We follow the notation in the paper instead of the notation for the Wigner coordinates. Define

$$\begin{array}{lll} r=\frac{1}{2}(q+q') & \text{inverse:} & q=r+\frac{1}{2}y \\ y=q-q' & & q'=r-\frac{1}{2}y \end{array} \qquad (4.123)$$

$$\begin{aligned}
&\Phi[q,q'] \\
=\ &\Phi[r,y] && (4.124)\\
=\ &\frac{1}{\hbar}\int_0^t dt'\int_0^{t'} dt'' \\
&\times\left[\frac{1}{2}y(t')+r(t')-r(t')+\frac{1}{2}y(t')\right]\left[L(t't-t'')\left(\frac{1}{2}y(t'')+r(t'')\right)-L^*(t'-t'')\left(r(t'')-\frac{1}{2}y(t'')\right)\right] \\
&+i\frac{\mu}{2}\int_0^t dt' 2r(t')y(t') && (4.125)\\
=\ &\frac{1}{\hbar}\int_0^t dt'\int_0^{t'} dt'' \\
&\times y(t')\Big\{\left(L'(t'-t'')+iL''(t'-t'')\right)\left(\frac{1}{2}y(t'')+r(t'')\right) \\
&-\left(L'(t'-t'')-iL''(t'-t'')\right)\left(r(t'')-\frac{1}{2}y(t'')\right)\Big\}+i\mu\int_0^t dt' y(t')r(t') && (4.126)\\
|\ \ &\text{expand and cancel 4 terms} \\
=\ &\frac{1}{\hbar}\int_0^t dt'\int_0^{t'} dt'' y(t')\left[L'(t'-t'')y(t'')+2iL''(t'-t'')r(t'')\right]+i\mu\int_0^t dt' y(t')r(t') && (4.127)
\end{aligned}$$

which is equation (3) in [Koch2008]. Now we will perform stochastic unravelling to the path integral expression of the reduced density matrix.

$$\rho^{\text{reduced}}(q_f,q_f',t)=\int dq_i dq_i'\left\langle q_i\left|\rho^S(0)\right|q_i'\right\rangle\underbrace{\int DqDq' e^{\frac{i}{\hbar}(S_S[q]-S_S[q'])}F_{IF}[q,q']}_{\text{to unravel}} \qquad (4.128)$$

Define the stochastic noise actions,

$$\begin{aligned}
S_{z_1}[q] &\equiv S_S[q]+\frac{\mu}{2}\int_0^t dt' q^2(t')+\int_0^t dt' q(t')z_1(t') && (4.129)\\
S_{z_2}[q'] &\equiv S_S[q']+\frac{\mu}{2}\int_0^t dt' q'^2(t')+\int_0^t dt' q'(t')z_2(t') && (4.130)
\end{aligned}$$

Define the stochastic propagators using the stochastic noise actions.

$$K_{z_1}(q_f,t;q_i,0) \equiv \int_{q(0)=q_i}^{q(t)=q_f} Dq e^{\frac{i}{\hbar}S_S[q]} e^{\frac{i}{\hbar}\frac{\mu}{2}\int_0^t dt' q^2(t')} e^{\frac{i}{\hbar}\int_0^t dt' q(t') z_1(t')} \tag{4.131}$$

$$K_{z_2}(q'_f,t;q'_i,0) \equiv \int_{q'(0)=q'_i}^{q'(t)=q'_f} Dq' e^{\frac{i}{\hbar}S_S[q']} e^{\frac{i}{\hbar}\frac{\mu}{2}\int_0^t dt' q'^2(t')} e^{\frac{i}{\hbar}\int_0^t dt' q'(t') z_2(t')} \tag{4.132}$$

Consider the expression,

$$\begin{aligned} & K_{z_1}(q_f,t;q_i,0)K^*_{z_2}(q'_f,t;q'_i,0) \\ = & \int DqDq' e^{\frac{i}{\hbar}(S_S[q]-S_S[q'])} e^{\frac{i}{\hbar}\frac{\mu}{2}\int_0^t dt'\left(q^2(t')-q'^2(t')\right)} e^{\frac{i}{\hbar}\int_0^t dt'\left(q(t')z_1(t')-q'(t')z_2^*(t')\right)} \end{aligned} \tag{4.133}$$

Define Wigner coordinates for the stochastic variables.

$$\begin{array}{ll} \xi(t) = \frac{1}{2}\left(z_1(t)+z_2^*(t)\right) \quad \text{inverse:} & z_1(t) = \xi(t) + \frac{\hbar}{2}\nu(t) \\ \nu(t) = \frac{1}{\hbar}\left(z_1(t)-z_2^*(t)\right) & z_2^*(t) = \xi(t) - \frac{\hbar}{2}\nu(t) \end{array} \tag{4.134}$$

Take noise average of the expression. The definition of the noise average is such that $\langle K_{z_1}K^*_{z_2}\rangle_{\text{noise}}$ equals the expression we want to unravel.[6]

$$\begin{aligned} & \left\langle K_{z_1}(q_f,t;q_i,0)K^*_{z_2}(q'_f,t;q'_i,0)\right\rangle_{\text{noise}} \\ = & \int DqDq' e^{\frac{i}{\hbar}(S_S[q]-S_S[q'])} e^{\frac{i}{\hbar}\frac{\mu}{2}\int_0^t dt'\left(q^2(t')-q'^2(t')\right)} \left\langle e^{\frac{i}{\hbar}\int_0^t dt'\left(q(t')\left(\xi(t')+\frac{\hbar}{2}\nu(t')\right)-q'(t')\left(\xi(t')-\frac{\hbar}{2}\nu(t')\right)\right)}\right\rangle_{\text{noise}} \end{aligned} \tag{4.135}$$

$|$ use symmetric and antisymmetric coordinates $y = q - q'$ and $r = \frac{1}{2}(q+q')$

$$= \int DqDq' e^{\frac{i}{\hbar}(S_S[q]-S_S[q'])} e^{\frac{i}{\hbar}\frac{\mu}{2}\int_0^t dt'\left(q^2(t')-q'^2(t')\right)} \left\langle e^{\frac{i}{\hbar}\int_0^t dt'(y(t')\xi(t')+r(t')\hbar\nu(t'))}\right\rangle_{\text{noise}} \tag{4.136}$$

$|$ introduce vector notation,

$|$ $\vec{y}(t') = \left(y_1(t')=y(t'), y_2(t')=r(t')\right)$ and $\vec{\xi}(t') = \left(\xi_1(t')=\xi(t'), \xi_2(t')=\hbar\nu(t')\right)$

$$= \int DqDq' e^{\frac{i}{\hbar}(S_S[q]-S_S[q'])} e^{\frac{i}{\hbar}\frac{\mu}{2}\int_0^t dt'\left(q^2(t')-q'^2(t')\right)} \left\langle e^{\frac{i}{\hbar}\int_0^t dt'\vec{y}(t')\cdot\vec{\xi}(t')}\right\rangle_{\text{noise}} \tag{4.137}$$

$|$ without loss of generality, assume that $\xi(t')$ and $\hbar\nu(t')$ are complex-valued Gaussian noises

$|$ use the standard result of cumulant expansion of Gaussian noises,[7]

$|$ $\left\langle e^{\frac{i}{\hbar}\int_0^t dt' y(t')\xi(t')}\right\rangle_{\text{noise}} = e^{-\frac{1}{\hbar^2}\int_0^t dt'\int_0^{t'} dt'' y(t')\langle\xi(t')\xi(t'')\rangle_{\text{noise}} y(t'')}$

$$= \int DqDq' e^{\frac{i}{\hbar}(S_S[q]-S_S[q'])} e^{\frac{i}{\hbar}\frac{\mu}{2}\int_0^t dt'\left(q^2(t')-q'^2(t')\right)} e^{-\frac{1}{\hbar^2}\int_0^t dt'\int_0^{t'} dt''\sum_{i_1,i_2=1}^N y_{i_1}(t')\langle\xi_{i_1}(t')\xi_{i_2}(t'')\rangle_{\text{noise}} y_{i_2}(t'')}$$

$$\begin{aligned} = & \int DqDq' e^{\frac{i}{\hbar}(S_S[q]-S_S[q'])} e^{\frac{i}{\hbar}\frac{\mu}{2}\int_0^t dt'\left(q^2(t')-q'^2(t')\right)} \\ & \times e^{-\frac{1}{\hbar^2}\int_0^t dt'\int_0^{t'} dt''[y(t')\langle\xi(t')\xi(t'')\rangle_{\text{noise}} y(t'') + y(t')\langle\xi(t')\hbar\nu(t'')\rangle_{\text{noise}} r(t'')]} \\ & \times e^{-\frac{1}{\hbar^2}\int_0^t dt'\int_0^{t'} dt''[r(t')\langle\hbar\nu(t')\xi(t'')\rangle_{\text{noise}} y(t'') + r(t')\langle\hbar\nu(t')\hbar\nu(t'')\rangle_{\text{noise}} r(t'')]} \end{aligned} \tag{4.138}$$

[6] The notation for noise average in the paper [Koch2008] is $M\{\ldots\}$.

Now we impose that

$$\langle K_{z_1}(q_f,t;q_i,0)K^*_{z_2}(q'_f,t;q'_i,0)\rangle_{\text{noise}} \stackrel{!}{=} \int DqDq' e^{\frac{i}{\hbar}(S_S[q]-S_S[q'])}F_{IF}[q,q'] \tag{4.139}$$

where we quickly recall that

$$F_{IF}[q,q'] = e^{\frac{1}{\hbar}\int_0^t dt'\int_0^{t'} dt'' y(t')[L'(t'-t'')y(t'')+2iL''(t'-t'')r(t'')]+i\mu\int_0^t dt' y(t')r(t')} \tag{4.140}$$

Comparing the exponents in $\langle K_{z_1}K^*_{z_2}\rangle_{\text{noise}}$ and in $\int DqDq' e^{\frac{i}{\hbar}(S_S[q]-S_S[q'])}F_{IF}[q,q']$, we make the following identifications. [8]

$$\begin{aligned}
\langle\xi(t')\xi(t'')\rangle_{\text{noise}} &= L'(t'-t'') && (4.141)\\
\langle\xi(t')\nu(t'')\rangle_{\text{noise}} &= \frac{2i}{\hbar}\theta(t'-t'')L''(t'-t'') && (4.142)\\
\langle\nu(t')\xi(t'')\rangle_{\text{noise}} &= \langle\xi(t'')\nu(t')\rangle_{\text{noise}} = \frac{2i}{\hbar}\theta(t''-t')L''(t''-t') && (4.143)\\
\langle\nu(t')\nu(t'')\rangle_{\text{noise}} &= 0 && (4.144)
\end{aligned}$$

Now the meaning of stochastic unravelling is clear. By including 2 noise terms ξ and ν (or z_1 and z_2) we can avoid performing the memory integral in F_{IF}. We will actually deal with the simpler problem of stochastic variables and then impose the above noise relations to go back to the original problem of evaluating the reduced density matrix. We shall call the (reduced) density matrix which is written in terms of the stochastic variables, the stochastic density matrix $\rho^{\text{stochastic}}$. In short, to go back to the reduced density matrix problem, we perform,

$$\left\langle\rho^{\text{stochastic}}\right\rangle_{\text{noise}} = \rho^{\text{reduced}} \tag{4.145}$$

We further simplify $\rho^{\text{stochastic}}$ for numerical implementation.

$$\begin{aligned}
\rho^{\text{stochastic}}(q_f,q'_f,t) &= \int dq_i dq'_i \rho^S(q_i,q'_i,0)K_{z_1}(q_f,t;q_i,0)K^*_{z_2}(q'_f,t;q'_i,0) && (4.146)\\
&\quad | \quad \text{where we denote } \langle q_i|\rho^S(0)|q'_i\rangle = \rho^S(q_i,q'_i,0)\\
&\quad | \quad \text{assume that the initial system density matrix } \rho^S(0) \text{ is of the form,}\\
&\quad | \quad \rho^S(0) = |\psi_1(0)\rangle\langle\psi_2(0)|\\
&= \int dq_i dq'_i \langle q_i|\psi_1(0)\rangle\langle\psi_2(0)|q'_i\rangle\\
&\quad \times\int Dq e^{\frac{i}{\hbar}\left(S_S[q]+\frac{\mu}{2}\int_0^t dt' q^2(t')+\int_0^t dt' q(t')z_1(t')\right)}\\
&\quad \times\int Dq' e^{-\frac{i}{\hbar}\left(S_S[q']+\frac{\mu}{2}\int_0^t dt' q'^2(t')+\int_0^t dt' q'(t')z_2^*(t')\right)} && (4.147)\\
&\quad | \quad \text{treat } \mu q^2 + qz \text{ terms as potential terms in the Lagrangian}\\
&\quad | \quad \text{write the path integrals back to matrix elements of “evolution operators”}\\
&= \int d_i dq'_i \langle q_i|\psi_1(0)\rangle\langle\psi_2(0)|q'_i\rangle
\end{aligned}$$

[7] The result can be seen by expanding the exponential, all odd averages are zero and even averages factorise by “Wick's theorem” and resum the series of even noise averages.

[8] The step function $\theta(t'-t'')$ ensures that only $t' > t''$ contributes to the integral.

$$\times \left\langle q_f \left| e^{-\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}q^2 - qz_1\right)t} \right| q_i \right\rangle \left\langle q'_f \left| e^{\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}{q'}^2 - q'z_2^*\right)t} \right| q'_i \right\rangle^* \tag{4.148}$$

| remove 2 complete set of states

$$= \left\langle q_f \left| e^{-\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}q^2 - qz_1\right)t} \right| \psi_1(0) \right\rangle \left\langle \psi_2(0) \left| e^{\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}{q'}^2 - q'z_2^*\right)t} \right| q'_f \right\rangle \tag{4.149}$$

The left hand side can be written as

$$\rho^{\text{stochastic}}(q_f, q'_f, t) = \langle q_f|\psi_1(t)\rangle\langle\psi_2(t)|q'_f\rangle \tag{4.150}$$

We compare both sides to get 2 (stochastic) Schrodinger equations. For $|\psi_1(t)\rangle$,

$$\begin{aligned}
|\psi_1(t)\rangle &= e^{-\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}q^2 - qz_1\right)t}|\psi_1(0)\rangle && (4.151)\\
i\hbar|\dot{\psi}_1(t)\rangle &= \left(H_S - \frac{\mu}{2}q^2 - qz_1\right)|\psi_1(t)\rangle && (4.152)\\
&\quad | \text{ write } z_1 = \xi + \frac{\hbar}{2}\nu \\
&= \left(H_S - \frac{\mu}{2}q^2 - \xi q - \frac{\hbar}{2}\nu q\right)|\psi_1(t)\rangle && (4.153)
\end{aligned}$$

For $|\psi_2(t)\rangle$,

$$\begin{aligned}
\langle\psi_2(t)| &= \langle\psi_1(0)|e^{\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}{q'}^2 - q'z_2^*\right)t} && (4.154)\\
i\hbar|\dot{\psi}_2(t)\rangle &= \left(H_S - \frac{\mu}{2}{q'}^2 - q'z_2\right)|\psi_2(t)\rangle && (4.155)\\
&\quad | \text{ write } z_2 = \left(\xi - \frac{\hbar}{2}\nu\right)^* = \xi^* - \frac{\hbar}{2}\nu^* \\
&= \left(H_S - \frac{\mu}{2}{q'}^2 - \xi^* q' + \frac{\hbar}{2}\nu^* q'\right)|\psi_2(t)\rangle && (4.156)
\end{aligned}$$

The full procedure is now to [9]

1. Propagate (numerically) the 2 stochastic Schrodinger equations.
2. Form $\rho^{\text{stochastic}}(t) = |\psi_1(t)\rangle\langle\psi_2(t)|$
3. Take noise average to get the reduced density matrix, i.e. $\langle\rho^{\text{stochastic}}(t)\rangle_{\text{noise}} = \rho^{\text{redcued}}(t)$. The rules for the noise averages of the stochastic variables are given earlier.

Finally for completeness, we will derive the Liouville form of $\rho^{\text{stochastic}}$.

$$\begin{aligned}
\langle q_f|\psi_1(t)\rangle\langle\psi_2(t)|q'_f\rangle &= \left\langle q_f \left| e^{-\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}q^2 - \xi q - \frac{\hbar}{2}\nu q\right)t} \right| \psi_1(0) \right\rangle \left\langle \psi_2(0) \left| e^{\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}q^2 - \xi q + \frac{\hbar}{2}\nu q\right)t} \right| q'_f \right\rangle && (4.157)\\
&\quad | \text{ note that } |q\rangle \text{ is a complete set and } \rho^{\text{stochastic}}(t) = |\psi_1(t)\rangle\langle\psi_2(t)| \text{ we write} \\
\rho^{\text{stochastic}}(t) &= e^{-\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}q^2 - \xi q - \frac{\hbar}{2}\nu q\right)t}\rho^{\text{stochastic}}(0)e^{\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}q^2 - \xi q + \frac{\hbar}{2}\nu q\right)t} && (4.158)\\
\frac{d\rho^{\text{stochastic}}(t)}{dt} &= -\frac{i}{\hbar}\left(H_S - \frac{\mu}{2}q^2 - \xi q - \frac{\hbar}{2}\nu q\right)\rho^{\text{stochastic}}(t) \\
&\quad + \frac{i}{\hbar}\rho^{\text{stochastic}}(t)\left(H_S - \frac{\mu}{2}q^2 - \xi q + \frac{\hbar}{2}\nu q\right) && (4.159)
\end{aligned}$$

[9]The notation q and q' is not important here since we have already seperated the 2 processes.

$$\begin{aligned} i\hbar\frac{d\rho^{\text{stochastic}}(t)}{dt} &= \left[H_S, \rho^{\text{stochastic}}(t)\right]_- + \frac{\mu}{2}\left[\rho^{\text{stochastic}}(t), q^2\right]_- + \xi\left[\rho^{\text{stochastic}}(t), q\right]_- \\ &\quad -\frac{\hbar}{2}\nu\left[q, \rho^{\text{stochastic}}(t)\right]_+ \end{aligned} \tag{4.160}$$

We proceed to find $\text{Tr}\rho^{\text{stochastic}}(t)$. Note that the trace of a commutator is zero.

$$i\hbar\frac{d}{dt}\text{Tr}\rho^{\text{stochastic}}(t) = -\frac{\hbar}{2}\nu\text{Tr}\left(\left[q, \rho^{\text{stochastic}}(t)\right]_+\right) \tag{4.161}$$

$$\frac{d}{dt}\text{Tr}\rho^{\text{stochastic}}(t) = i\nu\text{Tr}\left(q\rho^{\text{stochastic}}(t)\right) \tag{4.162}$$

Define the normalized $\rho^{\text{stochastic}}(t)$ as

$$\bar{\rho}^{\text{stochastic}}(t) \equiv \frac{\rho^{\text{stochastic}}(t)}{\text{Tr}\rho^{\text{stochastic}}(t)} \tag{4.163}$$

Obviously $\text{Tr}\bar{\rho}^{\text{stochastic}}(t) = 1$. We solve $\text{Tr}\rho^{\text{stochastic}}(t)$ explicitly. Divide by $\text{Tr}\rho^{\text{stochastic}}(t)$ on both sides.

$$\frac{1}{\text{Tr}\rho^{\text{stochastic}}(t)}\frac{d}{dt}\text{Tr}\rho^{\text{stochastic}}(t) = i\nu\text{Tr}\left(q\bar{\rho}^{\text{stochastic}}(t)\right) \tag{4.164}$$

$$| \quad \text{define } \bar{r}_t \equiv \text{Tr}\left(q\bar{\rho}^{\text{stochastic}}(t)\right)$$

$$\frac{d}{dt}\ln\left(\text{Tr}\rho^{\text{stochastic}}(t)\right) = i\nu\bar{r}_t \tag{4.165}$$

$$\text{Tr}\rho^{\text{stochastic}}(t) = e^{i\int_0^t dt'\nu(t')\bar{r}_{t'}} \tag{4.166}$$

And finally we can also write the Liouville form for $\bar{\rho}^{\text{stochastic}}(t)$. This is known as the "trace-conserving form" stochastic equation of motion. We divide by $\text{Tr}\rho^{\text{stochastic}}(t)$ in the above Liouville equation.

$$\begin{aligned} i\hbar\frac{1}{\text{Tr}\rho^{\text{stochastic}}}\frac{d}{dt}\rho^{\text{stochastic}} &= \left[H_S, \bar{\rho}^{\text{stochastic}}(t)\right]_- + \frac{\mu}{2}\left[\bar{\rho}^{\text{stochastic}}(t), q^2\right]_- \\ &\quad +\xi\left[\bar{\rho}^{\text{stochastic}}(t), q\right]_- - \frac{\hbar}{2}\nu\left[q, \bar{\rho}^{\text{stochastic}}(t)\right]_+ \end{aligned} \tag{4.167}$$

$$| \quad \text{note that } \frac{1}{\text{Tr}\rho^{\text{stochastic}}}\frac{d}{dt}\rho^{\text{stochastic}}$$

$$| \quad = \frac{d}{dt}\left(\frac{\rho^{\text{stochastic}}}{\text{Tr}\rho^{\text{stochastic}}}\right) - \rho^{\text{stochastic}}\frac{d}{dt}\frac{1}{\text{Tr}\rho^{\text{stochastic}}}$$

$$| \quad = \frac{d\bar{\rho}^{\text{stochastic}}}{dt} + \frac{\rho^{\text{stochastic}}}{\text{Tr}\rho^{\text{stochastic}}}i\nu(t)\bar{r}_t\left(\text{Tr}\rho^{\text{stochastic}}\right)$$

$$\begin{aligned} i\hbar\left(\frac{d}{dt}\bar{\rho}^{\text{stochastic}} + \bar{\rho}^{\text{stochastic}}i\nu(t)\bar{r}_t\right) &= \left[H_S, \bar{\rho}^{\text{stochastic}}\right]_- + \frac{\mu}{2}\left[\bar{\rho}^{\text{stochastic}}, q^2\right]_- \\ &\quad +\xi\left[\bar{\rho}^{\text{stochastic}}, q\right]_- - \frac{\hbar}{2}\nu\left[q, \bar{\rho}^{\text{stochastic}}\right]_+ \end{aligned} \tag{4.168}$$

$$\begin{aligned} i\hbar\frac{d}{dt}\bar{\rho}^{\text{stochastic}} &= \left[H_S, \bar{\rho}^{\text{stochastic}}\right]_- + \frac{\mu}{2}\left[\bar{\rho}^{\text{stochastic}}, q^2\right]_- \\ &\quad +\xi\left[\bar{\rho}^{\text{stochastic}}, q\right]_- - \frac{\hbar}{2}\nu\left(\left[q, \bar{\rho}^{\text{stochastic}}\right]_+ - 2\bar{\rho}^{\text{stochastic}}\bar{r}_t\right) \end{aligned}$$

$$| \quad \text{write } \bar{r}_t \text{ into anticommutator though its a function}$$

$$\begin{aligned} &= \left[H_S, \bar{\rho}^{\text{stochastic}}\right]_- + \frac{\mu}{2}\left[\bar{\rho}^{\text{stochastic}}, q^2\right]_- \\ &\quad +\xi\left[\bar{\rho}^{\text{stochastic}}, q\right]_- - \frac{\hbar}{2}\nu\left[q - \bar{r}_t, \bar{\rho}^{\text{stochastic}}\right]_+ \end{aligned} \tag{4.169}$$

Recall that we have to take noise average of $\rho^{\text{stochastic}}$ to get the reduced density matrix,

$$\rho^{\text{reduced}} = \langle \rho^{\text{stochastic}} \rangle_{\text{noise}} = \left\langle \bar{\rho}^{\text{stochastic}} \left(\text{Tr}\rho^{\text{stochastic}}\right)\right\rangle_{\text{noise}} \tag{4.170}$$

Thus we need to absorb $\text{Tr}\rho^{\text{stochastic}}$ into the Gaussian integration measure in the noise averaging. The change in the volume element is calculated from the Jacobian determinant.

Denote the new Gaussian measure as $W'[\xi_t, \xi_t^*, \nu_t, \nu_t^*]$ and the old Gaussian measure as $W[\xi, \xi^*, \nu, \nu^*]$, so the noise averaging notation can be written as

$$\begin{aligned} \langle \rho^{\text{stochastic}} \rangle_{\text{noise}} &= \langle \rho^{\text{stochastic}} \rangle_W &(4.171)\\ \left\langle \bar{\rho}^{\text{stochastic}} \left(\text{Tr}\rho^{\text{stochastic}}\right)\right\rangle_{\text{noise}} &= \left\langle \bar{\rho}^{\text{stochastic}} \left(\text{Tr}\rho^{\text{stochastic}}\right)\right\rangle_W \equiv \langle \bar{\rho}^{\text{stochastic}} \rangle_{W'} &(4.172) \end{aligned}$$

Thus W and W' are simply related by

$$W'[\xi_t, \xi_t^*, \nu_t, \nu_t^*] = W[\xi, \xi^*, \nu, \nu^*] e^{i\int_0^t dt' \nu(t')\bar{r}_{t'}} \tag{4.173}$$

The variables are related by a shift

$$\begin{aligned} \xi_t(t') &= \xi(t') - i\int_0^t dt_1 \langle \xi(t')\nu(t_1)\rangle_W \bar{r}_{t_1} &(4.174)\\ \xi_t^*(t') &= \xi^*(t') - i\int_0^t dt_1 \langle \xi^*(t')\nu(t_1)\rangle_W \bar{r}_{t_1} &(4.175)\\ \nu_t(t') &= \nu(t') &(4.176)\\ \nu_t^*(t') &= \nu^*(t') - i\int_0^t dt_1 \langle \nu^*(t')\nu(t_1)\rangle_W \bar{r}_{t_1} &(4.177) \end{aligned}$$

Finally we shall check that $W'[\xi_t, \xi_t^*, \nu_t, \nu_t^*]$ is indeed a Gaussian measure under the above variable relations [10] by checking that the Jacobian of the above transformation is 1.

As mentioned in [Stockburger2002] (just below eqn 14) and in [Stockburger2004] (just above eqn 13), ξ can be chosen real and we only have 3 independent variables. The Jacobian is

$$\begin{aligned} \begin{vmatrix} \frac{\delta\xi_t}{\delta\xi} & \frac{\delta\xi_t}{\delta\nu} & \frac{\delta\xi_t}{\delta\nu^*} \\ \frac{\delta\nu_t}{\delta\xi} & \frac{\delta\nu_t}{\delta\nu} & \frac{\delta nu_t}{\delta\nu^*} \\ \frac{\delta\nu_t^*}{\delta\xi} & \frac{\delta\nu_t^*}{\delta\nu} & \frac{\delta\nu_t^*}{\delta\nu^*} \end{vmatrix} &= \begin{vmatrix} \frac{\delta\xi_t}{\delta\xi} & \frac{\delta\xi_t}{\delta\nu} & 0 \\ 0 & 1 & 0 \\ \frac{\delta\nu_t^*}{\delta\xi} & \frac{\delta\nu_t^*}{\delta\nu} & 1 \end{vmatrix} &(4.178)\\ &\quad | \quad \text{carry out minor expansion} \\ &= \left|\frac{\delta\xi_t}{\delta\xi}\right| &(4.179)\\ &= \left|\frac{\delta}{\delta\xi(t')}\left(\xi(t') - i\int_0^t dt'' \langle \xi(t')\nu(t'')\rangle_W \bar{r}_{t''}\right)\right| &(4.180)\\ &\quad | \quad \text{in a matrix of time, the first term gives 1 on the diagonal} \\ &\quad | \quad \text{recall the identifications, second term is casual i.e. with } \theta(t'-t'') \end{aligned}$$

[10] This is essentially "completing the square".

$$
\begin{aligned}
&| \quad \text{we get a triangular matrix with 1 on diagonal} \\
&| \quad \text{determinant of triangular matrix is the product of its diagonal} \\
&= \quad 1 \qquad (4.181)
\end{aligned}
$$

The whole scheme looks exact and feasible, however there are many subtle problems which are mostly numerical. The paper [Koch2008] was in fact written to provide a method to overcome the numerical problems. I shall provide some of the highlights from [Koch2008]:

- A direct Monte Carlo sampling of the 2 stochastic equations is impractical as the samples do not stay normalized which slows down convergence.
- Modification to enforce trace-conservation (or norm-conservation) results in numerical instability unless the system is linear or classical.
- Thus [Koch2008] proposed to propagate individual samples with the (Herman and Kluk) HK semiclassical propagator which is known to be stable even when trace-conservation is imposed. Of course, the HK propagator is derived to be consistent with stochastic unravelling.

This concludes the stochastic unravelling method in handling non-Markovian problems, in this particular case, the non-Markovian problem of the reduced density matrix.

4.2.3 Appendix: Explanation of the Potential Renormalization term

Here we follow [Ingold2002]. The physical argument is as follows, first consider the minimum of the Hamiltonian with respect to the environment.

$$0 \overset{!}{=} \frac{\partial H}{\partial x_\alpha} = m_\alpha \omega_\alpha^2 x_\alpha - c_\alpha q \qquad (4.182)$$

$$\Rightarrow x_\alpha = \frac{c_\alpha}{m_\alpha \omega_\alpha^2} q \qquad (4.183)$$

Now consider the minimum of the Hamiltonian with respect to the system,

$$
\begin{aligned}
\frac{\partial H}{\partial q} &= \frac{\partial V}{\partial q} - \sum_{\alpha=1}^{N} c_\alpha x_\alpha + q \sum_{\alpha=1}^{N} \frac{c_\alpha^2}{m_\alpha \omega_\alpha^2} \qquad (4.184) \\
&| \quad \text{use the above result } x_\alpha = \frac{c_\alpha}{m_\alpha \omega_\alpha^2} q \\
&= \frac{\partial V}{\partial q} \qquad (4.185)
\end{aligned}
$$

Thus the potential renormalization term $q^2 \sum_{\alpha=1}^{N} \frac{c_\alpha^2}{2 m_\alpha \omega_\alpha^2}$ ensures that the minimum with respect to the system is only determined by the bare potential $V(q)$.

4.2.4 Appendix: From Evolution Operator to Configuration Path Integral

In this appendix, we will show how to write the matrix element of the temporal unitary evolution operator into a configuration path integral, i.e.

$$\left\langle q_f \vec{x}_0 \left| e^{-\frac{i}{\hbar} H t} \right| q_i \vec{x}_1 \right\rangle = \int_{q(0)=q_i}^{q(t)=q_f} Dq \int_{\vec{x}(0)=\vec{x}_1}^{\vec{x}(t)=\vec{x}_0} D\vec{x} e^{\frac{i}{\hbar} S[q,\vec{x}]} \qquad (4.186)$$

where the explicit form of the Hamiltonian is

$$H = \frac{P^2}{2M} + V(q) + \sum_{\alpha=1}^{N} \frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}\sum_{\alpha=1}^{N} m_\alpha \omega_\alpha^2 \left(x_\alpha - \frac{c_\alpha}{m_\alpha \omega_\alpha^2} q \right)^2 \tag{4.187}$$

We slice the time interval $(0, t)$ into $\tilde{N}$ equal intervals.

$$\begin{aligned} \frac{t-0}{\tilde{N}} &= \epsilon \quad \text{where } \epsilon \text{ is an infinitesimal interval} && (4.188) \\ t_n &= n\epsilon \quad n = 1, 2, \ldots, \tilde{N}-1 && (4.189) \end{aligned}$$

We label the quantum numbers with n.

$$\begin{aligned} q_f \equiv (q)_{\tilde{N}} \quad &, \quad q_i \equiv (q)_0 && (4.190) \\ \vec{x}_0 \equiv (\vec{x})_{\tilde{N}} \quad &, \quad \vec{x}_1 \equiv (\vec{x})_0 && (4.191) \end{aligned}$$

We start from the LHS,

$$\begin{aligned} & \left\langle q_f \vec{x}_0 \left| e^{-\frac{i}{\hbar}Ht} \right| q_i \vec{x}_1 \right\rangle \\ = & \left\langle (q)_{\tilde{N}} (\vec{x})_{\tilde{N}} \left| e^{-\frac{i}{\hbar}Ht} \right| (q)_0 (\vec{x})_0 \right\rangle && (4.192) \\ = & \langle (q)_{\tilde{N}} (\vec{x})_{\tilde{N}} t \mid (q)_0 (\vec{x})_0 0 \rangle && (4.193) \\ | \ & \text{at each interval, insert a complete set of states (total of } \tilde{N}-1 \text{ sets)} \\ = & \langle (q)_{\tilde{N}} (\vec{x})_{\tilde{N}} t | \int d(q)_{\tilde{N}-1} d(\vec{x})_{\tilde{N}-1} \ |(q)_{\tilde{N}-1} (\vec{x})_{\tilde{N}-1} t_{\tilde{N}-1}\rangle \langle (q)_{\tilde{N}-1} (\vec{x})_{\tilde{N}-1} t_{\tilde{N}-1} | \\ & \times \ldots \times \int d(q)_1 d(\vec{x})_1 \ |(q)_1 (\vec{x})_1 t_1\rangle \langle (q)_1 (\vec{x})_1 t_1 | (q)_0 (\vec{x})_0 0 \rangle && (4.194) \\ = & \int d(q)_{\tilde{N}-1} d(\vec{x})_{\tilde{N}-1} \cdots \int d(q)_1 d(\vec{x})_1 \\ & \langle (q)_{\tilde{N}} (\vec{x})_{\tilde{N}} t | (q)_{\tilde{N}-1} (\vec{x})_{\tilde{N}-1} t_{\tilde{N}-1} \rangle \times \cdots \times \langle (q)_1 (\vec{x})_1 t_1 | (q)_0 (\vec{x})_0 0 \rangle && (4.195) \end{aligned}$$

The advantage is that each matrix element is more easily evaluated. When ϵ is sufficiently small, the time evolution operator can be approximated by its linear term. It is exact when $\epsilon \to 0$.

Now we evaluate a general infinitesimal matrix elements (out of $\tilde{N}$ elements).

$$\begin{aligned} & \langle (q)_{n+1} (\vec{x})_{n+1} t_{n+1} | (q)_n (\vec{x})_n t_n \rangle \\ = & \langle (q)_{n+1} (\vec{x})_{n+1} | e^{-\frac{i}{\hbar}Ht_{n+1}} e^{\frac{i}{\hbar}Ht_n} | (q)_n (\vec{x})_n \rangle && (4.196) \\ = & \langle (q)_{n+1} (\vec{x})_{n+1} | e^{-\frac{i}{\hbar}H(t_{n+1}-t_n)} | (q)_n (\vec{x})_n \rangle && (4.197) \\ = & \langle (q)_{n+1} (\vec{x})_{n+1} | e^{-\frac{i}{\hbar}H\epsilon} | (q)_n (\vec{x})_n \rangle && (4.198) \\ = & \langle (q)_{n+1} (\vec{x})_{n+1} | \left(1 - \frac{i}{\hbar}\epsilon H \right) | (q)_n (\vec{x})_n \rangle + \mathcal{O}(\epsilon^2) && (4.199) \\ | \ & \text{insert a complete set of momentum states} \\ = & \langle (q)_{n+1} (\vec{x})_{n+1} | \int d(P)_n d(\vec{p})_n | (P)_n (\vec{p})_n \rangle \langle (P)_n (\vec{p})_n | \left(1 - \frac{i}{\hbar}\epsilon H \right) | (q)_n (\vec{x})_n \rangle + \mathcal{O}(\epsilon^2) && (4.200) \\ | \ & \text{use } \langle (q)_{n+1} | (P)_n \rangle = \frac{1}{(2\pi\hbar)^{1/2}} e^{\frac{i}{\hbar}(P)_n (q)_{n+1}} \ , \ \langle (\vec{x})_{n+1} | (\vec{p})_n \rangle = \frac{1}{(2\pi\hbar)^{N/2}} e^{\frac{i}{\hbar}(\vec{p})_n \cdot (\vec{x})_{n+1}} \end{aligned}$$

$$= \int \frac{d(P)_n}{(2\pi\hbar)^{1/2}} \int \frac{d(\vec{p}_n}{(2\pi\hbar)^{N/2}} e^{\frac{i}{\hbar}(P)_n(q)_{n+1}} e^{\frac{i}{\hbar}(\vec{p})_n\cdot(\vec{x})_{n+1}}$$
$$\times \left(\frac{e^{-\frac{i}{\hbar}(P)_n(q)_n}}{(2\pi\hbar)^{1/2}} \frac{e^{-\frac{i}{\hbar}(\vec{p})_n\cdot(\vec{x})_n}}{(2\pi\hbar)^{N/2}} - \frac{i}{\hbar}\epsilon\langle (P)_n(\vec{p})_n|H|(q)_n(\vec{x})_n\rangle \right) + \mathcal{O}(\epsilon^2) \tag{4.201}$$

| from the explicit form of H, H simply "passes through" the ket and the bra to become a number

$$= \int \frac{d(P)_n}{2\pi\hbar} \int \frac{d(\vec{p})_n}{2\pi\hbar} e^{\frac{i}{\hbar}(P)_n((q)_{n+1}-(q)_n)} e^{\frac{i}{\hbar}(\vec{p})_n\cdot((\vec{x})_{n+1}-(\vec{x})_n)} \left(1 - \frac{i}{\hbar}\epsilon H[(P)_n,(q)_n,(\vec{p})_n,(\vec{x})_n]\right)$$
$$+\mathcal{O}(\epsilon^2) \tag{4.202}$$

We put the expression back,

$$\left\langle q_f\vec{x}_0 \left| e^{-\frac{i}{\hbar}Ht} \right| q_i\vec{x}_1 \right\rangle$$
$$= \lim_{\epsilon\to 0}\lim_{\tilde{N}\to\infty} \int d(q)_{\tilde{N}-1}\cdots d(q)_1 \int d(\vec{x})_{\tilde{N}-1}\cdots d(\vec{x})_1 \int \frac{d(P)_{\tilde{N}-1}}{2\pi\hbar}\cdots\frac{d(P)_0}{2\pi\hbar} \int \frac{d(\vec{p})_{\tilde{N}-1}}{(2\pi\hbar)^N}\cdots\frac{d(\vec{p})_0}{(2\pi\hbar)^N}$$
$$\times e^{\frac{i}{\hbar}\epsilon\sum_{n=0}^{\tilde{N}-1}(P)_n\frac{(q)_{n+1}-(q)_n}{\epsilon}} e^{\frac{i}{\hbar}\epsilon\sum_{n=0}^{\tilde{N}-1}(\vec{p})_n\cdot\frac{(\vec{x})_{n+1}-(\vec{x})_n}{\epsilon}} \prod_{n=0}^{\tilde{N}-1}\left(1 - \frac{i}{\hbar}\epsilon H[(P)_n,(q)_n,(\vec{p})_n,(\vec{x})_n]\right) \tag{4.203}$$

| use a general mathematical identity $\lim_{\tilde{N}\to\infty}\prod_{n=0}^{\tilde{N}-1}\left(1+\frac{y_n}{\tilde{N}}\right) = \lim_{\tilde{N}\to\infty} e^{\frac{1}{\tilde{N}}\sum_{n=0}^{\tilde{N}-1}y_n}$

| with $y_n = -\frac{i}{\hbar}tH$ and recall $t = \tilde{N}\epsilon$

$$= \lim_{\epsilon\to 0}\lim_{\tilde{N}\to\infty} \int d(q)_{\tilde{N}-1}\cdots d(q)_1 \int d(\vec{x})_{\tilde{N}-1}\cdots d(\vec{x})_1 \int \frac{d(P)_{\tilde{N}-1}}{2\pi\hbar}\cdots\frac{d(P)_0}{2\pi\hbar} \int \frac{d(\vec{p})_{\tilde{N}-1}}{(2\pi\hbar)^N}\cdots\frac{d(\vec{p})_0}{(2\pi\hbar)^N}$$
$$\times e^{\frac{i}{\hbar}\epsilon\sum_{n=0}^{\tilde{N}-1}\left((P)_n\frac{(q)_{n+1}-(q)_n}{\epsilon}+(\vec{p})_n\cdot\frac{(\vec{x})_{n+1}-(\vec{x})_n}{\epsilon}-H[(P)_n,(q)_n,(\vec{p})_n,(\vec{x})_n]\right)} \tag{4.204}$$

| this Hamiltonian is quadratic in momentum variables so the Gaussian integrals can be done

$$= \lim_{\epsilon\to 0}\lim_{\tilde{N}\to\infty} \int d(q)_{\tilde{N}-1}\cdots d(q)_1 \int d(\vec{x})_{\tilde{N}-1}\cdots d(\vec{x})_1 \int \frac{d(P)_{\tilde{N}-1}}{2\pi\hbar}\cdots\frac{d(P)_0}{2\pi\hbar} \int \frac{d(\vec{p})_{\tilde{N}-1}}{(2\pi\hbar)^N}\cdots\frac{d(\vec{p})_0}{(2\pi\hbar)^N}$$
$$\times e^{\frac{i}{\hbar}\epsilon\sum_{n=0}^{\tilde{N}-1}\left((P)_n\frac{(q)_{n+1}-(q)_n}{\epsilon}+(\vec{p})_n\cdot\frac{(\vec{x})_{n+1}-(\vec{x})_n}{\epsilon}+\frac{(P)_n^2}{2M}+\sum_{\alpha=1}^N\frac{(p_\alpha)_n^2}{2m_\alpha}-V[(q)_n,(\vec{x})_n]\right)} \tag{4.205}$$

$$= \lim_{\epsilon\to 0}\lim_{\tilde{N}\to\infty} \int d(q)_{\tilde{N}-1}\cdots d(q)_1 \int d(\vec{x})_{\tilde{N}-1}\cdots d(\vec{x})_1 \int \frac{d(P)_{\tilde{N}-1}}{2\pi\hbar}\cdots\frac{d(P)_0}{2\pi\hbar} \int \frac{d(\vec{p})_{\tilde{N}-1}}{(2\pi\hbar)^N}\cdots\frac{d(\vec{p})_0}{(2\pi\hbar)^N}$$
$$\times e^{\epsilon\sum_{n=0}^{\tilde{N}-1}\left[-\frac{1}{2M}\frac{i}{\hbar}\left((P)_n^2-\frac{2M(P)_n((q)_{n+1}-(q)_n)}{\epsilon}\right)-\sum_{\alpha=1}^N\frac{1}{2m_\alpha}\frac{i}{\hbar}\left((p_\alpha)_n^2-\frac{2m_\alpha(p_\alpha)_n((x_\alpha)_{n+1}-(x_\alpha)_n)}{\epsilon}\right)-\frac{i}{\hbar}V[(q)_n,(\vec{x})_n]\right]}$$

| "complete the squares" for $(P)_n$ and $(p_\alpha)_n$

$$= \lim_{\epsilon\to 0}\lim_{\tilde{N}\to\infty} \int d(q)_{\tilde{N}-1}\cdots d(q)_1 \int d(\vec{x})_{\tilde{N}-1}\cdots d(\vec{x})_1 \int \frac{d(P)_{\tilde{N}-1}}{2\pi\hbar}\cdots\frac{d(P)_0}{2\pi\hbar} \int \frac{d(\vec{p})_{\tilde{N}-1}}{(2\pi\hbar)^N}\cdots\frac{d(\vec{p})_0}{(2\pi\hbar)^N}$$
$$\times e^{\epsilon\sum_{n=0}^{\tilde{N}-1}\left[-\frac{1}{2M}\frac{i}{\hbar}\left(\left((P)_n-\frac{M((q)_{n+1}-(q)_n)}{\epsilon}\right)^2-\left(\frac{M((q)_{n+1}-(q)_n)}{\epsilon}\right)^2\right)\right]}$$
$$\times e^{\epsilon\sum_{n=0}^{\tilde{N}-1}\left[-\sum_{\alpha=1}^N\frac{1}{2m_\alpha}\frac{i}{\hbar}\left(\left((p_\alpha)_n-\frac{m_\alpha((x_\alpha)_{n+1}-(x_\alpha)_n)}{\epsilon}\right)^2-\left(\frac{m_\alpha((x_\alpha)_{n+1}-(x_\alpha)_n)}{\epsilon}\right)^2\right)-\frac{i}{\hbar}V[(q)_n,(\vec{x})_n]\right]} \tag{4.206}$$

| the Gaussian integral is $\int dp e^{-\alpha p^2} = \sqrt{\frac{\pi}{\alpha}}$

$$= \lim_{\epsilon\to 0}\lim_{\tilde{N}\to\infty} \int d(q)_{\tilde{N}-1}\cdots d(q)_1 \int d(\vec{x})_{\tilde{N}-1}\cdots d(\vec{x})_1 \frac{1}{(2\pi\hbar)^{\tilde{N}}}\frac{1}{(2\pi\hbar)^{N\times\tilde{N}}}\left(\frac{2\pi M\hbar}{i\epsilon}\right)^{\frac{\tilde{N}}{2}}\left(\frac{2\pi m_\alpha\hbar}{i\epsilon}\right)^{\frac{\tilde{N}\times N}{2}}$$

$$\times e^{\epsilon\sum_{n=0}^{\tilde{N}-1}\left[\frac{i}{\hbar}\frac{M}{2}\left(\frac{(q)_{n+1}-(q)_n}{\epsilon}\right)^2+\sum_{\alpha=1}^{N}\frac{i}{\hbar}\frac{m_\alpha}{2}\left(\frac{(x_\alpha)_{n+1}-(x_\alpha)_n}{\epsilon}\right)^2-\frac{i}{\hbar}V[(q)_n,(\vec{x})_n]\right]} \tag{4.207}$$

| take the continuum limit, $\frac{(q)_{n+1}-(q)_n}{\epsilon}\to\dot{q}$, $\frac{(x_\alpha)_{n+1}-(x_\alpha)_n}{\epsilon}\to\dot{x}_\alpha$ and $\sum_{n=1}^{\tilde{N}-1}\epsilon\to\int_0^t dt$

$$= \lim_{\epsilon\to0}\lim_{\tilde{N}\to\infty}\int d(q)_{\tilde{N}-1}\cdots d(q)_1\prod_{\alpha=1}^{N}\int d(x_\alpha)_{\tilde{N}-1}\cdots d(x_\alpha)_1\left(\frac{M}{2\pi\hbar i\epsilon}\right)^{\frac{\tilde{N}}{2}}\left(\frac{m_\alpha}{2\pi\hbar i\epsilon}\right)^{\frac{\tilde{N}}{2}}$$
$$\times e^{\frac{i}{\hbar}\int_0^t dt\left(\frac{1}{2}M\dot{q}^2+\sum_{\alpha=1}^{N}\frac{1}{2}m_\alpha\dot{x}_\alpha^2-V[q,\vec{x}]\right)} \tag{4.208}$$

| the exponent is the temporal integral of the Lagrangian $\mathcal{L}(t)$ and so is the action $S[q,\vec{x}]$

$$= \lim_{\epsilon\to0}\lim_{\tilde{N}\to\infty}\left(\frac{M}{2\pi\hbar i\epsilon}\right)^{\frac{\tilde{N}}{2}}\int d(q)_{\tilde{N}-1}\cdots d(q)_1\prod_{\alpha=1}^{N}\left(\frac{m_\alpha}{2\pi\hbar i\epsilon}\right)^{\frac{\tilde{N}}{2}}\int d(x_\alpha)_{\tilde{N}-1}\cdots d(x_\alpha)_1 e^{\frac{i}{\hbar}S[q,\vec{x}]} \tag{4.209}$$

| define the shorthand symbols:

| $\lim_{\epsilon\to0}\lim_{\tilde{N}\to\infty}\left(\frac{M}{2\pi\hbar i\epsilon}\right)^{\frac{\tilde{N}}{2}}\int d(q)_{\tilde{N}-1}\cdots d(q)_1\equiv\int_{q(0)=q_i}^{q(t)=q_f}Dq$

| $\lim_{\epsilon\to0}\lim_{\tilde{N}\to\infty}\left(\frac{m_\alpha}{2\pi\hbar i\epsilon}\right)^{\frac{\tilde{N}}{2}}\int d(x_\alpha)_{\tilde{N}-1}\cdots d(x_\alpha)_1\equiv\int Dx_\alpha$ and $\int_{\vec{x}(0)=\vec{x}_1}^{\vec{x}(t)=\vec{x}_0}D\vec{x}\equiv\prod_{\alpha=1}^{N}\int Dx_\alpha$

$$= \int_{q(0)=q_i}^{q(t)=q_f}Dq\int_{\vec{x}(0)=\vec{x}_1}^{\vec{x}(t)=\vec{x}_0}D\vec{x}e^{\frac{i}{\hbar}S[q,\vec{x}]} \tag{4.210}$$

As required.

4.2.5 Appendix: Evaluating the Path Integral of Fluctuations

We follow [Das2006] section 3.3. The path integral is to be evaluated with the boundary conditions $\eta_\alpha(0)=0=\eta_\alpha(t)$.

$$\int D\eta_\alpha e^{\frac{i}{2\hbar}\int_0^t dt'\left(m_\alpha\dot{\eta}_\alpha^2(t')-m_\alpha\omega_\alpha^2\eta_\alpha^2(t')\right)}$$

| discretize the time interval 0 to t into N intervals and denote $\eta_\alpha(t_n)\equiv\eta_{\alpha n}$

| the boundary conditions in this discretized notation are $\eta_{\alpha0}=0=\eta_{\alpha N}$

| this N-interval time slicing has nothing to do with the N-degrees of freedom of the bath

$$= \lim_{\epsilon\to0}\lim_{N\to\infty}\left(\frac{m_\alpha}{2\pi i\hbar\epsilon}\right)^{N/2}\int d\eta_{\alpha1}\cdots d\eta_{\alpha(N-1)}e^{\frac{i\epsilon}{2\hbar}\sum_{n=1}^{N}\left[m_\alpha\left(\frac{\eta_{\alpha n}-\eta_{\alpha(n-1)}}{\epsilon}\right)^2-m_\alpha\omega_\alpha^2\left(\frac{\eta_{\alpha n}+\eta_{\alpha(n-1)}}{2}\right)^2\right]} \tag{4.211}$$

| rescale $\eta'_{\alpha n}\equiv\left(\frac{m_\alpha}{2\hbar\epsilon}\right)^{1/2}\eta_{\alpha n}$

$$= \lim_{\epsilon\to0}\lim_{N\to\infty}\left(\frac{m_\alpha}{2\pi i\hbar\epsilon}\right)^{N/2}\left(\frac{2\hbar\epsilon}{m_\alpha}\right)^{\frac{N-1}{2}}$$
$$\times\int d\eta'_{\alpha1}\cdots d\eta'_{\alpha(N-1)}e^{i\sum_{n=1}^{N}\left[m_\alpha\left(\eta'_{\alpha n}-\eta'_{\alpha(n-1)}\right)^2-\epsilon\omega_\alpha^2\left(\frac{\eta'_{\alpha n}+\eta'_{\alpha(n-1)}}{2}\right)^2\right]} \tag{4.212}$$

| denote a vector notation, $\vec{\eta}_\alpha=\left(\eta_{\alpha1}\cdots\eta_{\alpha(N-1)}\right)^T$ then we can write a matrix form

| note that this vector form has nothing to do with the vector notation for degrees of freedom

$$= \lim_{\epsilon\to 0}\lim_{N\to\infty}\left(\frac{m_\alpha}{2\pi i\hbar\epsilon}\right)^{N/2}\left(\frac{2\hbar\epsilon}{m_\alpha}\right)^{\frac{N-1}{2}}\int d\vec{\eta}^{\,\prime}_\alpha e^{i\vec{\eta}^{\,\prime T}_\alpha B\vec{\eta}^{\,\prime}_\alpha} \tag{4.213}$$

The $(N-1)\times(N-1)$ matrix B is

$$B = \begin{pmatrix} 2 & -1 & 0 & 0 & \cdots \\ -1 & 2 & -1 & 0 & \cdots \\ 0 & -1 & 2 & -1 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} - \frac{\epsilon^2\omega_\alpha^2}{4}\begin{pmatrix} 2 & 1 & 0 & 0 & \cdots \\ 1 & 2 & 1 & 0 & \cdots \\ 0 & 1 & 2 & 1 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{4.214}$$

$$= \begin{pmatrix} x & y & 0 & 0 & \cdots \\ y & x & y & 0 & \cdots \\ 0 & y & x & y & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{4.215}$$

$$\text{where} \quad x = 2\left(1 - \frac{\epsilon^2\omega_\alpha^2}{4}\right) \tag{4.216}$$

$$y = -\left(1 + \frac{\epsilon^2\omega_\alpha^2}{4}\right) \tag{4.217}$$

We use the standard Gaussian integral (for $N-1$ dimensional integrals) result.

$$\int d\vec{\eta}^{\,\prime}_\alpha e^{i\vec{\eta}^{\,\prime T}_\alpha B\vec{\eta}^{\,\prime}_\alpha} = (i\pi)^{\frac{N-1}{2}}(\det B)^{-1/2} \tag{4.218}$$

The path integral is now

$$\int D\eta_\alpha e^{\frac{i}{2\hbar}\int_0^t dt'\left(m_\alpha\dot{\eta}_\alpha^2(t') - m_\alpha\omega_\alpha^2\eta_\alpha^2(t')\right)} = \lim_{\epsilon\to 0}\lim_{N\to\infty}\left(\frac{m_\alpha}{2\pi i\hbar\epsilon}\right)^{N/2}\left(\frac{2\hbar\epsilon}{m_\alpha}\right)^{\frac{N-1}{2}}(i\pi)^{\frac{N-1}{2}}(\det B)^{-1/2}$$

$$= \lim_{\epsilon\to 0}\lim_{N\to\infty}\left(\frac{m_\alpha}{2\pi i\hbar\epsilon(\det B)}\right)^{1/2} \tag{4.219}$$

So, we need to work out $\det B$ and then take the limits for ϵ and N.

Denote the determinant of the $n\times n$ submatrix of B as I_n. We see that a recursion relation holds

$$I_{n+1} = xI_n - y^2 I_{n-1} \quad \text{with} \quad I_{-1} = 0, \quad I_0 = 1 \tag{4.220}$$

We write it as

$$\begin{pmatrix} I_{n+1} \\ I_n \end{pmatrix} = \begin{pmatrix} x & -y^2 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} I_n \\ I_{n-1} \end{pmatrix} \tag{4.221}$$

$$\begin{pmatrix} I_{N-1} \\ I_{N-2} \end{pmatrix} = \begin{pmatrix} x & -y^2 \\ 1 & 0 \end{pmatrix}\cdots\begin{pmatrix} x & -y^2 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} I_0 \\ I_{-1} \end{pmatrix} \tag{4.222}$$

$|$ where there are $N-1$ factors of the square matrix

$$= \begin{pmatrix} x & -y^2 \\ 1 & 0 \end{pmatrix}^{N-2}\begin{pmatrix} xI_0 - y^2 I_{-1} \\ I_0 \end{pmatrix} \tag{4.223}$$

$$= \begin{pmatrix} x & -y^2 \\ 1 & 0 \end{pmatrix}^{N-2}\begin{pmatrix} x \\ 1 \end{pmatrix} \tag{4.224}$$

We diagonalise each of them

$$\det \begin{vmatrix} x-\lambda & -y^2 \\ 1 & -\lambda \end{vmatrix} = 0 \tag{4.225}$$

$$\lambda_\pm = \frac{1}{2}\left(x \pm \sqrt{x^2-4y^2}\right) \tag{4.226}$$

The diagonalising transformation matrices are

$$S = \begin{pmatrix} c\lambda_+ & d\lambda_- \\ c & d \end{pmatrix} \tag{4.227}$$

$$S^{-1} = \frac{1}{\lambda_+-\lambda_-}\begin{pmatrix} \frac{1}{c} & -\frac{\lambda_-}{c} \\ -\frac{1}{d} & \frac{\lambda_+}{d} \end{pmatrix} \tag{4.228}$$

where c and d are arbitrary constants.

$$\begin{aligned}
\begin{pmatrix} I_{N-1} \\ I_{N-2} \end{pmatrix} &= S\begin{pmatrix} \lambda_+^{N-2} & 0 \\ 0 & \lambda_-^{N-2} \end{pmatrix} S^{-1}\begin{pmatrix} x \\ 1 \end{pmatrix} && (4.229)\\
&\mid \text{ note that } x = \lambda_+ + \lambda_- && (4.230)\\
&= \frac{1}{\lambda_+-\lambda_-}\begin{pmatrix} c\lambda_+ & d\lambda_- \\ c & d \end{pmatrix}\begin{pmatrix} \lambda_+^{N-2} & 0 \\ 0 & \lambda_-^{N-2} \end{pmatrix}\frac{1}{\lambda_+-\lambda_-}\begin{pmatrix} \frac{1}{c} & -\frac{\lambda_-}{c} \\ -\frac{1}{d} & \frac{\lambda_+}{d} \end{pmatrix}\begin{pmatrix} \lambda_++\lambda_- \\ 1 \end{pmatrix} \\
&\mid \text{ multiply all the matrices together} \\
&= \frac{1}{\lambda_+-\lambda_-}\begin{pmatrix} \lambda_+^N - \lambda_-^N \\ \lambda_+^{N-1} - \lambda_-^{N-1} \end{pmatrix} && (4.231)
\end{aligned}$$

Therefore the required solution $\det B = I_{N-1}$ is

$$\begin{aligned}
I_{N-1} &= \frac{1}{\lambda_+-\lambda_-}\left(\lambda_+^N - \lambda_-^N\right) && (4.232)\\
&= \frac{1}{\sqrt{x^2-4y^2}}\left[\left(\frac{2\left(1-\frac{\epsilon^2\omega_\alpha^2}{4}\right)+\sqrt{x^2-4y^2}}{2}\right)^N - \left(\frac{2\left(1-\frac{\epsilon^2\omega_\alpha^2}{4}\right)-\sqrt{x^2-4y^2}}{2}\right)^N\right] \\
&= \frac{1}{2i\epsilon\omega_\alpha}\left[\left(\frac{2\left(1-\frac{\epsilon^2\omega_\alpha^2}{4}\right)+2i\epsilon\omega_\alpha}{2}\right)^N - \left(\frac{2\left(1-\frac{\epsilon^2\omega_\alpha^2}{4}\right)-2i\epsilon\omega_\alpha}{2}\right)^N\right] && (4.233)\\
&\mid \text{ to first order in } \epsilon \\
&\approx \frac{1}{2i\epsilon\omega_\alpha}\left[\left(1+i\epsilon\omega_\alpha+\mathcal{O}(\epsilon^2)\right)^N - \left(1-i\epsilon\omega_\alpha+\mathcal{O}(\epsilon^2)\right)^N\right] && (4.234)
\end{aligned}$$

Finally,

$$\begin{aligned}
\lim_{\epsilon\to 0}\lim_{N\to\infty} \epsilon \det B &= \lim_{\epsilon\to 0}\lim_{N\to\infty} \epsilon I_{N-1} && (4.235)\\
&= \lim_{\epsilon\to 0}\lim_{N\to\infty} \frac{1}{2i\omega_\alpha}\left[(1+i\epsilon\omega_\alpha)^N - (1-i\epsilon\omega_\alpha)^N\right] && (4.236)\\
&\mid \text{ recall the size of one slice } \epsilon = \frac{t-0}{N}
\end{aligned}$$

$$
\begin{aligned}
&= \lim_{\epsilon\to 0}\lim_{N\to\infty}\frac{1}{2i\omega_\alpha}\left[\left(1+\frac{i\omega_\alpha t}{N}\right)^N-\left(1-\frac{i\omega_\alpha t}{N}\right)^N\right] && (4.237)\\
&\quad | \quad \text{the limit for } \epsilon \text{ is trivial}\\
&\quad | \quad \text{take the limit for N}\\
&= \frac{1}{2i\omega_\alpha}\left(e^{i\omega_\alpha t}-e^{-i\omega_\alpha t}\right) && (4.238)\\
&= \frac{\sin(\omega_\alpha t)}{\omega_\alpha} && (4.239)
\end{aligned}
$$

So, the fluctuating path integral amounts to,

$$
\int D\eta_\alpha e^{\frac{i}{2\hbar}\int_0^t dt'\left(m_\alpha\dot{\eta}_\alpha^2(t')-m_\alpha\omega_\alpha^2\eta_\alpha^2(t')\right)} = \left(\frac{m_\alpha\omega_\alpha}{2\pi i\hbar\sin(\omega_\alpha t)}\right)^{1/2} \tag{4.240}
$$

Lastly we remark that, the calculation of the undriven harmonic oscillator involves the same fluctuating path integral expression and the action term $e^{\frac{i}{\hbar}S[x^{cl}]}$ can be simply obtained by setting $q(t)$ to zero.

4.2.6 Appendix: Evaluating the Classical Action

Here we evaluate $S[x_\alpha^{cl}]_{x_{1\alpha}}^{x_{0\alpha}}$ and we drop the index α to simplfy writing.

The classical equation of motion is

$$
\begin{aligned}
\frac{\delta S}{\delta x_\alpha(t)} &= 0 && (4.241)\\
\Rightarrow m\ddot{x}^{cl}+m\omega^2x^{cl}-cq &= 0 && (4.242)
\end{aligned}
$$

We treat $cq(t)$ as a "time dependent force" and this is simply the driven harmonic oscillator problem. The (homogenous + inhomogenous) solution is (the initial time is 0 and the final time is t),[11]

$$
\begin{aligned}
x^{cl}(t'') &= A\cos(\omega t'')+B\sin(\omega t'')\\
&\quad +\frac{c}{m\omega}\left[\int_0^{t''}dt'\sin(\omega(t''-t'))q(t')-\frac{\sin(\omega t'')}{\sin(\omega t)}\int_0^t dt'\sin(\omega(t-t'))q(t')\right] && (4.243)
\end{aligned}
$$

We need to express the constants A and B in terms of the initial and final positions. At the initial time 0, the initial position $x^{cl}(0)=x_1$ and at the final time t, the final position $x^{cl}(t)=x_0$. Set $t''=0$,

$$
x^{cl}(0) = x_1 = A \tag{4.244}
$$

Set $t''=t$,

$$
\begin{aligned}
x^{cl}(t) &= x_0 = A\cos(\omega t)+B\sin(\omega t)+0 && (4.245)\\
&\quad | \quad \text{since } A=x_1\\
x_0 &= x_1\cos(\omega t)+B\sin(\omega t) && (4.246)\\
B &= \frac{x_0-x_1\cos(\omega t)}{\sin(\omega t)} && (4.247)
\end{aligned}
$$

[11] One can substitute the solution back into the classical equation of motion to verify it.

Thus the solution in terms of end points is

$$
\begin{aligned}
x^{cl}(t'') &= x_1\cos(\omega t'') + \frac{(x_0 - x_1\cos(\omega t))\sin(\omega t'')}{\sin(\omega t)} \\
&\quad + \frac{c}{m\omega}\left[\int_0^{t''} dt' \sin(\omega(t''-t'))q(t') - \frac{\sin(\omega t'')}{\sin(\omega t)}\int_0^t dt' \sin(\omega(t-t'))q(t')\right] \qquad (4.248)\\
&= x_0\frac{\sin(\omega t'')}{\sin(\omega t)} + x_1\frac{\sin(\omega(t-t''))}{\sin(\omega t)} \\
&\quad + \frac{c}{m\omega}\left[\int_0^{t''} dt' \sin(\omega(t''-t'))q(t') - \frac{\sin(\omega t'')}{\sin(\omega t)}\int_0^t dt' \sin(\omega(t-t'))q(t')\right] \qquad (4.249)
\end{aligned}
$$

We list some expressions for use in the evaluation of the action later.

$$
\begin{aligned}
x^{cl}(0) &= x_1 \qquad (4.250)\\
x^{cl}(t) &= x_0 \qquad (4.251)\\
\dot{x}^{cl}(0) &= \left.\frac{d}{dt''}x^{cl}(t'')\right|_{t''=0} \qquad (4.252)\\
&= \frac{\omega(x_0 - x_1\cos(\omega t))}{\sin(\omega t)} - \frac{c}{m\sin(\omega t)}\int_0^t dt' \sin(\omega(t-t'))q(t') \qquad (4.253)\\
\dot{x}^{cl}(t) &= \left.\frac{d}{dt''}x^{cl}(t'')\right|_{t''=t} \qquad (4.254)\\
&= \frac{\omega(x_0\cos(\omega t) - x_1)}{\sin(\omega t)} + \frac{c}{m}\left[\int_0^{t''} dt' \cos(\omega(t-t'))q(t') - \frac{\cos(\omega t)}{\sin(\omega t)}\int_0^t dt' \sin(\omega(t-t'))q(t')\right]\\
&= \frac{\omega(x_0\cos(\omega t) - x_1)}{\sin(\omega t)} + \frac{c}{m\sin(\omega t)}\int_0^t dt' \sin(\omega t')q(t') \qquad (4.255)
\end{aligned}
$$

Now we can evaluate the expression of the classical action of the driven oscillator.

$$
\begin{aligned}
S[x^{cl}]_{x_1}^{x_0} &= \int_0^t dt'' \left[\frac{1}{2}m\dot{x}^{cl^2}(t'') - \frac{1}{2}m\omega^2 x^{cl^2}(t'') + cx^{cl}(t'')q(t'')\right] \qquad (4.256)\\
&\mid \ \text{integrate by parts once for the first term}\\
&= \int_0^t dt'' \left[\frac{1}{2}m\frac{d}{dt''}(x^{cl}\dot{x}^{cl}) - \frac{1}{2}mx^{cl}\ddot{x}^{cl} - \frac{1}{2}m\omega^2 x^{cl^2} + cx^{cl}q\right] \qquad (4.257)\\
&= \left[\frac{1}{2}mx^{cl}\dot{x}^{cl}\right]_0^t - \int_0^t dt'' \left[\frac{1}{2}mx^{cl}\ddot{x}^{cl} + \frac{1}{2}m\omega^2 x^{cl^2} - cx^{cl}q\right] \qquad (4.258)\\
&\mid \ \text{use the classical equation of motion } m\ddot{x}^{cl} + m\omega^2 x^{cl} - cq = 0\\
&= \frac{1}{2}mx^{cl}(t)\dot{x}^{cl}(t) - \frac{1}{2}mx^{cl}(0)\dot{x}^{cl}(0) - \int_0^t dt'' \left[\frac{1}{2}cx^{cl}(t'')q(t'') - cx^{cl}(t'')q(t'')\right] \qquad (4.259)\\
&= \frac{1}{2}mx^{cl}(t)\dot{x}^{cl}(t) - \frac{1}{2}mx^{cl}(0)\dot{x}^{cl}(0) + \int_0^t dt''\frac{1}{2}cx^{cl}(t'')q(t'') \qquad (4.260)\\
&\mid \ \text{substitute in the 5 expressions } x^{cl}(0),\ \dot{x}^{cl}(0),\ x^{cl}(t)\ ,\ \dot{x}^{cl}(t) \text{ and } x^{cl}(t'')\\
&= \frac{m}{2}\frac{x_0\omega(x_0\cos(\omega t) - x_1)}{\sin(\omega t)} + \frac{cx_0}{2\sin(\omega t)}\int_0^t dt' \sin(\omega t')q(t')
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{m}{2}\frac{x_1\omega(x_0 - x_1\cos(\omega t))}{\sin(\omega t)} + \frac{cx_1}{2\sin(\omega t)}\int_0^t dt'\sin(\omega(t-t'))q(t') \\
&+\frac{cx_0}{2\sin(\omega t)}\int_0^t dt''\sin(\omega t'')q(t'') + \frac{cx_1}{2\sin(\omega t)}\int_0^t dt''\sin(\omega(t-t''))q(t'') \\
&+\frac{c^2}{2m\omega}\int_0^t dt''\int_0^{t''} dt' q(t'')\sin(\omega(t''-t'))q(t') \\
&-\frac{c^2}{2m\omega\sin(\omega t)}\int_0^t dt''\sin(\omega t'')q(t'')\int_0^t dt'\sin(\omega(t-t'))q(t') \qquad (4.261)
\end{aligned}
$$

| 2 pairs add up and the last pair requires some rewriting

$$
\begin{aligned}
= &\frac{m\omega}{2\sin(\omega t)}\left[x_0^2\cos(\omega t) - x_0x_1 - x_1x_0 + x_1^2\cos(\omega t)\right] \\
&+\frac{cx_1}{\sin(\omega t)}\int_0^t dt'\sin(\omega(t-t'))q(t') + \frac{cx_0}{\sin(\omega t)}\int_0^t dt'\sin(\omega t')q(t') + \text{last pair} \qquad (4.262)
\end{aligned}
$$

The last pair of terms requires some work. We establish an identity first and use it to simplify the last pair of terms. Consider the expression,

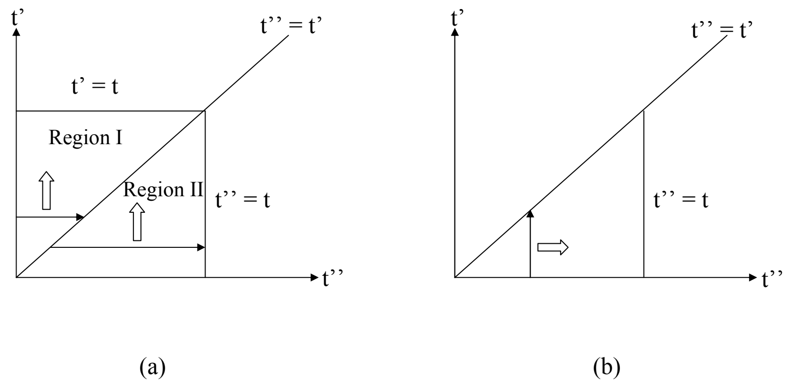


Figure 4.1: *Diagram showing integration regions for the derivation of an identity.*

$$
\begin{aligned}
&\int_0^t dt''\sin(\omega t'')q(t'')\int_0^t dt'\cos(\omega t')q(t') \\
= &\int_0^t dt'\int_0^t dt''\sin(\omega t'')q(t'')\cos(\omega t')q(t') \qquad (4.263) \\
= &\int_0^t dt'\int_0^{t'} dt''\sin(\omega t'')q(t'')\cos(\omega t')q(t') + \int_0^t dt'\int_{t'}^t dt''\sin(\omega t'')q(t'')\cos(\omega t')q(t') \qquad (4.264)
\end{aligned}
$$

| the first term operates in region I and the second term operates in region II (see Fig 4.1(a))

| for second term, (see Fig 4.1(b)) interchange order of integration,

| i.e. integrate with respect to t' first then t''

$$
= \int_0^t dt'\int_0^{t'} dt''\sin(\omega t'')q(t'')\cos(\omega t')q(t') + \int_0^t dt''\int_0^{t''} dt'\sin(\omega t'')q(t'')\cos(\omega t')q(t') \qquad (4.265)
$$

| for second term, relabel $t' \leftrightarrow t''$

$$= \int_0^t dt' \int_0^{t'} dt'' \sin(\omega t'') q(t'') \cos(\omega t') q(t') + \int_0^t dt' \int_0^{t'} dt'' \sin(\omega t') q(t') \cos(\omega t'') q(t'') \tag{4.266}$$

We call Identity (a) as:

$$\begin{aligned} & \int_0^t dt'' \sin(\omega t'') q(t'') \int_0^t dt' \cos(\omega t') q(t') \\ = & \int_0^t dt' \int_0^{t'} dt'' \sin(\omega t'') q(t'') \cos(\omega t') q(t') + \int_0^t dt' \int_0^{t'} dt'' \sin(\omega t') q(t') \cos(\omega t'') q(t'') \end{aligned} \tag{4.267}$$

For the special case where the functions are the same, we have a simplified version which we call Identity (b):

$$\int_0^t dt'' \sin(\omega t'') q(t'') \int_0^t dt' \sin(\omega t') q(t') = 2 \int_0^t dt' \int_0^{t'} dt'' \sin(\omega t'') q(t'') \sin(\omega t') q(t') \tag{4.268}$$

Now we are ready to rewrite the last pair of terms,

$$\begin{aligned} & \text{last pair of terms} \\ = & \frac{c^2}{2m\omega} \int_0^t dt'' \int_0^{t''} dt' q(t'') \sin(\omega(t'' - t')) q(t') \\ & - \frac{c^2}{2m\omega \sin(\omega t)} \int_0^t dt'' \sin(\omega t'') q(t'') \int_0^t dt' \sin(\omega(t - t')) q(t') \end{aligned} \tag{4.269}$$

$$\begin{aligned} | \quad & \text{expand the trignometric addition expressions} \\ = & \frac{c^2}{2m\omega} \int_0^t dt'' \int_0^{t''} dt' q(t'') \sin(\omega t'') \cos(\omega t') q(t') - \frac{c^2}{2m\omega} \int_0^t dt'' \int_0^{t''} dt' q(t'') \cos(\omega t'') \sin(\omega t') q(t') \\ & - \frac{c^2}{2m\omega} \int_0^t dt'' \sin(\omega t'') q(t'') \int_0^t dt' \cos(\omega t') q(t') \\ & + \frac{c^2}{2m\omega} \frac{\cos(\omega t)}{\sin(\omega t)} \int_0^t dt'' \sin(\omega t'') q(t'') \int_0^t dt' \sin(\omega t') q(t') \end{aligned} \tag{4.270}$$

$$\begin{aligned} | \quad & \text{use identity (a) on the 3rd term} \\ | \quad & \text{use identity (b) on the 4th term} \\ | \quad & \text{relabel } t' \leftrightarrow t'' \text{ in the first 2 terms} \\ = & \frac{c^2}{2m\omega} \int_0^t dt' \int_0^{t'} dt'' q(t') \sin(\omega t') \cos(\omega t'') q(t'') - \frac{c^2}{2m\omega} \int_0^t dt' \int_0^{t'} dt'' q(t') \cos(\omega t') \sin(\omega t'') q(t'') \\ & - \frac{c^2}{2m\omega} \int_0^t dt' \int_0^{t'} dt'' q(t'') \sin(\omega t'') \cos(\omega t') q(t') - \frac{c^2}{2m\omega} \int_0^t dt' \int_0^{t'} dt'' q(t'') \cos(\omega t'') \sin(\omega t') q(t') \\ & + \frac{c^2}{m\omega} \frac{\cos(\omega t)}{\sin(\omega t)} \int_0^t dt' \int_0^{t'} dt'' q(t'') \sin(\omega t'') \sin(\omega t') q(t') \end{aligned} \tag{4.271}$$

$$\begin{aligned} | \quad & \text{1st and 4th terms cancel, 2nd and 3rd terms add} \\ = & -\frac{c^2}{m\omega} \int_0^t dt' \int_0^{t'} dt'' q(t'') \sin(\omega t'') \cos(\omega t') q(t') \\ & + \frac{c^2}{m\omega \sin(\omega t)} \int_0^t dt' \int_0^{t'} dt'' q(t'') \cos(\omega t) \sin(\omega t'') \sin(\omega t') q(t') \end{aligned} \tag{4.272}$$

$$| \quad \text{multiply } \frac{\sin(\omega t)}{\sin(\omega t)} = 1 \text{ to the first term}$$

$$= -\frac{c^2}{m\omega\sin(\omega t)}\int_0^t dt'\int_0^{t'} dt''q(t')\left(\sin(\omega t)\cos(\omega t') - \cos(\omega t)\sin(\omega t')\right)\sin(\omega t'')q(t'') \quad (4.273)$$

$$= -\frac{c^2}{m\omega\sin(\omega t)}\int_0^t dt'\int_0^{t'} dt''q(t')\sin(\omega(t-t'))\sin(\omega t'')q(t'') \quad (4.274)$$

and finally we have the expression of the action (in terms of the end points) for the driven oscillator.

$$\begin{aligned} S[x^{cl}]_{x_1}^{x_0} &= \frac{m\omega}{2\sin(\omega t)}\left[\left(x_0^2+x_1^2\right)\cos(\omega t) - 2x_0x_1\right] \\ &+\frac{cx_1}{\sin(\omega t)}\int_0^t dt'\sin(\omega(t-t'))q(t') + \frac{cx_0}{\sin(\omega t)}\int_0^t dt'\sin(\omega t')q(t') \\ &-\frac{c^2}{m\omega\sin(\omega t)}\int_0^t dt'\int_0^{t'} dt''q(t')\sin(\omega(t-t'))\sin(\omega t'')q(t'') \end{aligned} \quad (4.275)$$

4.2.7 Appendix: Relationship between Dissipation Term γ and Spectral Density J

We follow [Ingold2002]. We derive Heisenberg equations of motion and thereby identify the dissipation term γ. Then we relate γ and J through their definitions. At the end, we mention some models for J inspired from the relationship between J and γ For the environment variables, we calculate,

$$\frac{dp_\alpha}{dt} = \frac{i}{\hbar}[H,p_\alpha]_- \quad (4.276)$$

$$| \quad \text{using } [x_\alpha,p_\alpha]_- = i\hbar$$

$$= -m_\alpha\omega_\alpha^2 x_\alpha + c_\alpha q \quad (4.277)$$

$$\frac{dx_\alpha}{dt} = \frac{i}{\hbar}[H,x_\alpha]_- = \frac{p_\alpha}{m_\alpha} \quad (4.278)$$

For the system variables, we calculate,

$$\frac{dP}{dt} = \frac{i}{\hbar}[H,P]_- \quad (4.279)$$

$$| \quad \text{recall that a commutator with } P \text{ is just like an operator differentiation of } q$$

$$= -\frac{\partial V}{\partial q} + \sum_{\alpha=1}^N c_\alpha x_\alpha - q\sum_{\alpha=1}^N \frac{c_\alpha}{m_\alpha\omega_\alpha^2} \quad (4.280)$$

$$\frac{dq}{dt} = \frac{i}{\hbar}[H,q]_- = \frac{P}{M} \quad (4.281)$$

From the environment equations, we write,

$$\frac{d^2x_\alpha}{dt^2} = \frac{1}{m_\alpha}\frac{dp_\alpha}{dt} \quad (4.282)$$

$$m\ddot{x}_\alpha = -m_\alpha\omega_\alpha^2 x_\alpha + c_\alpha q \quad (4.283)$$

The (homogenous + inhomogenous) solution is,

$$x_\alpha(t) = x_\alpha(0)\cos(\omega_\alpha t) + \frac{p_\alpha(0)}{m_\alpha\omega_\alpha}\sin(\omega_\alpha t) + \frac{c_\alpha}{m_\alpha\omega_\alpha}\int_0^t dt'\sin(\omega_\alpha(t-t'))q(t') \quad (4.284)$$

From the system equations, we get,

$$\frac{d^2q}{dt^2} = \frac{1}{M}\frac{dp}{dt} \tag{4.285}$$

$$M\ddot{q} = -\frac{\partial V}{\partial q} + \sum_{\alpha=1}^{N} c_\alpha x_\alpha - q\sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m_\alpha \omega_\alpha^2} \tag{4.286}$$

$|$ substitute in the above solution for $x_\alpha(t)$

$$\begin{aligned} &= -\frac{\partial V}{\partial q} + \sum_{\alpha=1}^{N} c_\alpha \left[x_\alpha(0)\cos(\omega_\alpha t) + \frac{p_\alpha(0)}{m_\alpha\omega_\alpha}\sin(\omega_\alpha t)\right] \\ &\quad + \sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m_\alpha\omega_\alpha}\int_0^t dt' \sin(\omega(t-t'))q(t') - q\sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2} \end{aligned} \tag{4.287}$$

$|$ integrate by parts for the third term by treating $\sin(\omega_\alpha(t-t')) = \frac{1}{\omega_\alpha}\frac{d}{dt'}\cos(\omega_\alpha(t-t'))$

$$\begin{aligned} &= -\frac{\partial V}{\partial q} + \sum_{\alpha=1}^{N} c_\alpha \left[x_\alpha(0)\cos(\omega_\alpha t) + \frac{p_\alpha(0)}{m_\alpha\omega_\alpha}\sin(\omega_\alpha t)\right] \\ &\quad + \sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\left[\cos(\omega_\alpha(t-t'))q(t')\right]_0^t - \sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m\alpha\omega_\alpha^2}\int_0^t dt' \cos(\omega_\alpha(t-t'))\dot{q}(t') - q\sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2} \end{aligned}$$

$|$ define an operator fluctuating force[12]

$|$ $\xi(t) \equiv \sum_{\alpha=1}^{N} c_\alpha\left[x_\alpha(0)\cos(\omega_\alpha t) - \frac{c_\alpha}{m_\alpha\omega_\alpha^2}\cos(\omega_\alpha t)q(0) + \frac{p_\alpha(0)}{m_\alpha\omega_\alpha}\sin(\omega_\alpha t)\right]$

$$= -\frac{\partial V}{\partial q} + \xi(t) - \sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\int_0^t dt' \cos(\omega_\alpha(t-t'))\dot{q}(t') \tag{4.288}$$

Comparing with the classical equation of the damped oscillator, we define the dissipation term γ to be

$$\gamma(t-t') \equiv \frac{1}{M}\sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\cos(\omega_\alpha(t-t')) \tag{4.293}$$

[12] It is very interesting to note that (See [Ingold2002] page 30) if we define,

$$\zeta(t) \equiv \xi(t) + \sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}q(0)\cos(\omega_\alpha t) = \xi(t) + M\gamma(t)q(0) \tag{4.289}$$

where $q(0)$ represents the initial position of the system particle (transient). Then consider the thermal average,

$$\begin{aligned} \frac{\mathrm{Tr}\left(e^{-\beta H_B}\zeta(t)\zeta(0)\right)}{\mathrm{Tr}e^{-\beta H_B}} &= \sum_{\alpha_1,\alpha_2} c_{\alpha_1}c_{\alpha_2}\left\langle\left(x_{\alpha_1}(0)\cos(\omega_{\alpha_1}t) + \frac{p_{\alpha_1}(0)}{m_{\alpha_1}\omega_{\alpha_1}\sin(\omega_{\alpha_1}t)}\right)x_{\alpha_2}(0)\right\rangle_B & (4.290) \\ &= \sum_{\alpha=1}^{N}\frac{\hbar c_\alpha^2}{2m_\alpha\omega_\alpha}\left(\coth\left(\frac{1}{2}\beta\hbar\omega_\alpha\right)\cos(\omega_\alpha t) - i\sin(\omega_\alpha t)\right) & (4.291) \\ &= L(t) & (4.292) \end{aligned}$$

which is the exponent term in the influence functional!

So that the quantum damped equation and the classical damped equation have the same form.

$$M\ddot{q} = -\frac{\partial V}{\partial q} + \xi(t) - M\int_0^t dt'\gamma(t-t')\dot{q}(t') \tag{4.294}$$

Recall the definition of the spectral density J,

$$J(\omega) = \pi\sum_{n=1}^{N}\frac{c_\alpha^2}{2m_\alpha\omega_\alpha}\delta(\omega-\omega_\alpha) \tag{4.295}$$

The relationship between the 2 quantities is (it can be checked by substituiting the expression of J)

$$\gamma(t) = \frac{2}{M}\int_0^\infty \frac{d\omega}{\pi}\frac{J(\omega)}{\pi}\cos(\omega t) \tag{4.296}$$

According to [Ingold2002], it is unnecessary to specify the parameters m_α, ω_α and c_α in practical calculations. It is instead sufficient to introduce models for $J(\omega)$.

We mention the most common model for $J(\omega)$, the Ohmic bath.

Ohmic Bath/Damping:

$$J(\omega) = M\gamma\omega \times \text{“cutoff function”} \tag{4.297}$$

where the cutoff function could be: identity or a step function $\theta(\omega_c-\omega)$ or a Drude/Lorentzian cutoff function $\frac{\omega_c^2}{\omega^2+\omega_c^2}$ with ω_c the cutoff frequency.

For the spectral density with identity cutoff function,

$$\begin{aligned} J(\omega) &= M\gamma\omega && (4.298)\\ \Rightarrow \gamma(t) &= 2\gamma\delta(t) && (4.299)\end{aligned}$$

For the spectral density with Drude/Lorentzian cutoff,

$$\begin{aligned} J(\omega) &= M\gamma\omega\frac{\omega_c^2}{\omega^2+\omega_c^2} && (4.300)\\ \Rightarrow \gamma(t) &= \gamma\omega_c e^{-\omega_c|t|} && (4.301)\end{aligned}$$

There are other models for $J(\omega)$ but we stop here as it will bring us too far from the main theme of the thesis.

Part II

Interactions

Chapter 5

Anharmonicity

[**Chapter Introduction and Roadmap:**] We enumerate this introduction for easy reading.

1. This chapter continues the development from the chapter on NEGF (mostly phonons) specializing to phonon-phonon interaction or anharmonicity. Recall the 3 developments of transport from NEGF.

2. Linear Response theory of anharmonicity is briefly mentioned.

3. Applying Landauer-like equations to anharmonicity easily give corrections to the energy current to a central system with 3 or 4-phonon interactions. Noise in the 3-phonon interacting central system is also derived.

4. Then using NEGF as "a trick", phonon-phonon equations of motion is rewritten into a set of functional derivative Hedin-like equations. A library of these self energies are collected. An appendix is devoted to check if these self energies are conserving or not. Such equations generate conserving self energy approximations, thus it is useful to write any many-body interaction into such a set of Hedin-like equations.

5. The other development is kinetic theory. The standard phonon Boltzmann equation with 3 or 4-phonon collision integrals is presented. Then these phonon Boltzmann equations are used to discuss second sound. Second sound excitation is of particular interest because the onset of U-processes is right at the heart of phonon transport.

6. Kinetic theory is revisited by QKE. QKE gives us correlation corrections which are quantum corrections to Boltzmann equation. Finally second sound is revisited by QKE to see how these corrections enter the usual Boltzmann description, i.e. to see how quantum corrections really affect the semi-classical description.

5.1 The Hamiltonian

The perturbation Hamiltonian involves the expansion of the interatomic potential up to the cubic and quartic order.[1] The cubic order gives

$$H^{(3ph)} = \frac{1}{3!}\sum_{l_1k_1\alpha_1}\sum_{l_2k_2\alpha_2}\sum_{l_3k_3\alpha_3}\Phi^{(3)}_{l_1k_1\alpha_1l_2k_2\alpha_2l_3k_3\alpha_3}u_{l_1k_1\alpha_1}u_{l_2k_2\alpha_2}u_{l_3k_3\alpha_3} \tag{5.1}$$

The force constants (where n is an integer and $n > 1$) are defined as

$$\Phi^{(n)}_{l_1k_1\alpha_1\cdots l_nk_n\alpha_n} = \left.\frac{\partial^n\Phi}{\partial u_{l_1k_1\alpha_1}\cdots\partial u_{l_nk_n\alpha_n}}\right|_{u_{l_1k_1\alpha_1}=0,\cdots,u_{l_nk_n\alpha_n}=0} \tag{5.2}$$

The Normal mode transformation is given as

$$\begin{aligned} u_{lk\alpha} &= \sqrt{\frac{\hbar}{2Nm_k}}\sum_{j\vec{q}}\frac{\epsilon_{k\alpha}(j\vec{q})}{\sqrt{\omega_{j\vec{q}}}}e^{i\vec{q}\cdot l}\left(a^\dagger_{j,-\vec{q}}+a_{j\vec{q}}\right) \equiv \sum_{j\vec{q}}\tilde{R}^{j\vec{q}}_{lk\alpha}\left(a^\dagger_{j,-\vec{q}}+a_{j\vec{q}}\right) && (5.3)\\ &= \frac{1}{\sqrt{Nm_k}}\sum_{j\vec{q}}\epsilon_{k\alpha}(j\vec{q})e^{i\vec{q}\cdot l}Q_{j\vec{q}} \equiv \sum_{j\vec{q}}R^{j\vec{q}}_{lk\alpha}Q_{j\vec{q}} && (5.4)\end{aligned}$$

where R and $\tilde{R}$ are shorthand symbols defined to simplify writing.

We substitute the transformation into the Hamiltonian.

$$\begin{aligned} H^{(3ph)} &= \frac{1}{3!}\sum_{j_1\vec{q}_1}\sum_{j_2\vec{q}_2}\sum_{j_3\vec{q}_3}\sum_{l_1k_1\alpha_1}\sum_{l_2k_2\alpha_2}\sum_{l_3k_3\alpha_3}\Phi^{(3)}_{l_1k_1\alpha_1l_2k_2\alpha_2l_3k_3\alpha_3}\tilde{R}^{j_1\vec{q}_1}_{l_1k_1\alpha_1}\tilde{R}^{j_2\vec{q}_2}_{l_2k_2\alpha_2}\tilde{R}^{j_3\vec{q}_3}_{l_3k_3\alpha_3}\\ &\quad\times\left(a^\dagger_{j_1,-\vec{q}_1}+a_{j_1\vec{q}_1}\right)\left(a^\dagger_{j_2,-\vec{q}_2}+a_{j_2\vec{q}_2}\right)\left(a^\dagger_{j_3,-\vec{q}_3}+a_{j_3\vec{q}_3}\right) && (5.5)\\ &\equiv \frac{1}{3!}\sum_{j_1\vec{q}_1}\sum_{j_2\vec{q}_2}\sum_{j_3\vec{q}_3}V^{(3ph)}_{j_1\vec{q}_1j_2\vec{q}_2j_3\vec{q}_3}\left(a^\dagger_{j_1,-\vec{q}_1}+a_{j_1\vec{q}_1}\right)\left(a^\dagger_{j_2,-\vec{q}_2}+a_{j_2\vec{q}_2}\right)\left(a^\dagger_{j_3,-\vec{q}_3}+a_{j_3\vec{q}_3}\right) && (5.6)\end{aligned}$$

where

$$\begin{aligned} V^{(3ph)}_{j_1\vec{q}_1j_2\vec{q}_2j_3\vec{q}_3} &= \sum_{l_1k_1\alpha_1}\sum_{l_2k_2\alpha_2}\sum_{l_3k_3\alpha_3}\Phi^{(3)}_{l_1k_1\alpha_1l_2k_2\alpha_2l_3k_3\alpha_3}\tilde{R}^{j_1\vec{q}_1}_{l_1k_1\alpha_1}\tilde{R}^{j_2\vec{q}_2}_{l_2k_2\alpha_2}\tilde{R}^{j_3\vec{q}_3}_{l_3k_3\alpha_3} && (5.7)\\ &= \sum_{l_1k_1\alpha_1}\sum_{l_2k_2\alpha_2}\sum_{l_3k_3\alpha_3}\sqrt{\frac{\hbar}{2Nm_{k_1}}}\sqrt{\frac{\hbar}{2Nm_{k_2}}}\sqrt{\frac{\hbar}{2Nm_{k_3}}}\frac{\epsilon_{k_1\alpha_1}(j_1\vec{q}_1)\epsilon_{k_2\alpha_2}(j_2\vec{q}_2)\epsilon_{k_3\alpha_3}(j_3\vec{q}_3)}{(\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}\omega_{j_3\vec{q}_3})^{1/2}}\\ &\quad\times e^{i\vec{q}_1\cdot l_1}e^{i\vec{q}_2\cdot l_2}e^{i\vec{q}_3\cdot l_3}\Phi^{(3)}_{l_1k_1\alpha_1l_2k_2\alpha_2l_3k_3\alpha_3} && (5.8)\\ &\mid\ \text{use lattice translation symmetry to write, }\sum_{l_1l_2l_3}e^{i\vec{q}_1\cdot l_1}e^{i\vec{q}_2\cdot l_2}e^{i\vec{q}_3\cdot l_3}\Phi^{(3)}_{l_1k_1\alpha_1l_2k_2\alpha_2l_3k_3\alpha_3}\\ &\mid\ = \sum_{l_1}e^{i(\vec{q}_1+\vec{q}_2+\vec{q}_3)\cdot l_1}\sum_{l_2l_3}e^{i\vec{q}_2\cdot(l_2-l_1)}e^{i\vec{q}_3\cdot(l_3-l_1)}\Phi^{(3)}_{0k_1\alpha_1,l_2-l_1,k_2\alpha_2,l_3-l_1,k_3\alpha_3}\end{aligned}$$

[1] Note that the "seperation" of the quantum problem of electrons and ions in the solid is an incomplete seperation. The effects of the electrons are in the interatomic potential Φ. See the section on Born-Oppenheimer adiabatic decoupling. E_m there is Φ here.

I am not giving references in this section because this is standard material in any respectable solid state physics or condensed matter physics textbook.

$$
\begin{aligned}
& \quad | \quad \text{rename } l_2 - l_1 \to l_2 \text{ and } l_3 - l_1 \to l_3 \text{ and so } \sum_{l_1} e^{i(\vec{q}_1+\vec{q}_2+\vec{q}_3)\cdot l_1} = N\Delta_{\vec{q}_1\vec{q}_2\vec{q}_3} \\
&= \frac{\hbar^{3/2}}{2^{3/2}N^{1/2}} \frac{\Delta_{\vec{q}_1\vec{q}_2\vec{q}_3}}{\left(\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}\omega_{j_3\vec{q}_3}\right)^{1/2}} \\
&\quad \times \sum_{k_1\alpha_1k_2\alpha_2k_3\alpha_3} \sum_{l_2l_3} \frac{\epsilon_{k_1\alpha_1}(j_1\vec{q}_1)\epsilon_{k_2\alpha_2}(j_2\vec{q}_2)\epsilon_{k_3\alpha_3}(j_3\vec{q}_3)}{\left(m_{k_1}m_{k_2}m_{k_3}\right)^{1/2}} e^{i\vec{q}_2\cdot l_2} e^{i\vec{q}_3\cdot l_3} \Phi^{(3)}_{0k_1\alpha_1l_2k_2\alpha_2l_3k_3\alpha_3} \qquad (5.9)
\end{aligned}
$$

Obviously, the 4-phonon interaction Hamiltonian takes on a very similar form.

$$
\begin{aligned}
H^{(4ph)} &= \frac{1}{4!}\sum_{l_1k_1\alpha_1}\sum_{l_2k_2\alpha_2}\sum_{l_3k_3\alpha_3}\sum_{l_4k_4\alpha_4} \Phi^{(4)}_{l_1k_1\alpha_1l_2k_2\alpha_2l_3k_3\alpha_3l_4k_4\alpha_4} u_{l_1k_1\alpha_1}u_{l_2k_2\alpha_2}u_{l_3k_3\alpha_3}u_{l_4k_4\alpha_4} \qquad (5.10) \\
&= \frac{1}{4!}\sum_{j_1\vec{q}_1}\sum_{j_2\vec{q}_2}\sum_{j_3\vec{q}_3}\sum_{j_4\vec{q}_4} V^{(4ph)}_{j_1\vec{q}_1j_2\vec{q}_2j_3\vec{q}_3j_4\vec{q}_4} \\
&\quad \times \left(a^\dagger_{j_1,-\vec{q}_1} + a_{j_1\vec{q}_1}\right)\left(a^\dagger_{j_2,-\vec{q}_2} + a_{j_2\vec{q}_2}\right)\left(a^\dagger_{j_3,-\vec{q}_3} + a_{j_3\vec{q}_3}\right)\left(a^\dagger_{j_4,-\vec{q}_4} + a_{j_4\vec{q}_4}\right) \qquad (5.11)
\end{aligned}
$$

$$
\begin{aligned}
& V^{(4ph)}_{j_1\vec{q}_1j_2\vec{q}_2j_3\vec{q}_3j_4\vec{q}_4} \\
&= \frac{\hbar^{4/2}}{2^{4/2}N} \frac{\Delta_{\vec{q}_1\vec{q}_2\vec{q}_3\vec{q}_4}}{\left(\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}\omega_{j_3\vec{q}_3}\omega_{j_4\vec{q}_4}\right)^{1/2}} \sum_{k_1\alpha_1l_2k_2\alpha_2l_3k_3\alpha_3l_4k_4\alpha_4} \frac{\epsilon_{k_1\alpha_1}(j_1\vec{q}_1)\epsilon_{k_2\alpha_2}(j_2\vec{q}_2)\epsilon_{k_3\alpha_3}(j_3\vec{q}_3)\epsilon_{k_4\alpha_4}(j_4\vec{q}_4)}{\left(m_{k_1}m_{k_2}m_{k_3}m_{k_4}\right)^{1/2}} \\
&\quad \times e^{i\vec{q}_2\cdot l_2} e^{i\vec{q}_3\cdot l_3} e^{i\vec{q}_4\cdot l_4} \Phi^{(4)}_{0k_1\alpha_1l_2k_2\alpha_2l_3k_3\alpha_3l_4k_4\alpha_4} \qquad (5.12)
\end{aligned}
$$

with $\Delta_{\vec{q}_1\vec{q}_2\vec{q}_3}$ and $\Delta_{\vec{q}_1\vec{q}_2\vec{q}_3\vec{q}_4}$ meaning $\vec{q}_1 + \vec{q}_2 + \vec{q}_3 = n\vec{g}$ and $\vec{q}_1 + \vec{q}_2 + \vec{q}_3 + \vec{q}_4 = n\vec{g}$ respectively with $n = 0, 1, \cdots$ and $\vec{g}$ is a reciprocal lattice vector.

[**Approximations and Directions:**] The main approach in this chapter is kinetic theory (semiclassical Boltzmann version and NEGF-derived Quantum Kinetic version) and we would like to collect the various approximations that the kinetic theory can take

1. In terms of distributions, the usual approximation is to assume that the non-equilibrium distribution is near to equilibrium and its difference from equilibrium is a linear term. This is called the linearized non-equilibrium distribution. From the linearized distribution, it is possible to iterate via a Chapman-Enskog-like expansion to solve for higher orders of the non-equilibrium distribution.

2. In terms of interaction collision integrals, the derivation within Boltzmann theory is done via the Golden Rule. There is no easy way of calculating collision integrals in higher powers of the coupling constant. Here, in the Green's function functional derivative development, we show that the Hedin-like equations which can generate self consistent self energies allow a direct calculation of collision integrals of any order in interaction. The usual collision integrals in Boltzmann theory will be derived from the leading terms of the (iterated) Hedin-like equations.

3. In terms of particle correlations (memory), the usual Boltzmann theory has none of it. The gradient expansion in QKE (using Wigner coordinates) is an expansion in terms of correlations. Thus particle correlations can either be accounted for. A caveat is that, KB ansatz based QKE messes up the causality of the theory while GKB ansatz based QKE respects causality.

5.2 Linear Response Treatment

5.2.1 Hardy's Anharmonic Current Operators

For the sake of completeness, we shall present the linear response theory of anharmonicity very briefly in this section. Here we follow Hardy in [Hardy1963] pg 173 and we will only consider the 3-phonon interaction. The reader may refer to the section on linear response theory for the derivation of Hardy's energy current formula. The Hamiltonian with 3-phonon anharmonic interaction is

$$H = \sum_{l\alpha} \frac{p_{l\alpha}^2}{2M} + \frac{1}{2} \sum_{l\alpha l_1 \alpha_1} \Phi^{(2)}_{l\alpha l_1 \alpha_1} u_{l\alpha} u_{l_1 \alpha_1} + \frac{1}{3!} \sum_{l\alpha l_1 \alpha_1 l_2 \alpha_2} \Phi^{(3)}_{l\alpha l_1 \alpha_1 l_2 \alpha_2} u_{l\alpha} u_{l_1 \alpha_1} u_{l_2 \alpha_2} \quad (5.13)$$

The following is thus the potential term to substitute into Hardy's formula.

$$V(\vec{r}_{i_1}) \to V_l^{\text{har}} + V_l^{(3ph)} \equiv \frac{1}{2} \sum_{\alpha l_1 \alpha_1} \Phi^{(2)}_{l\alpha l_1 \alpha_1} u_{l\alpha} u_{l_1 \alpha_1} + \frac{1}{3!} \sum_{l\alpha l_1 \alpha_1 l_2 \alpha_2} \Phi^{(3)}_{\alpha l_1 \alpha_1 l_2 \alpha_2} u_{l\alpha} u_{l_1 \alpha_1} u_{l_2 \alpha_2} \quad (5.14)$$

and as in the harmonic Hamiltonian treatment, $\vec{r} \to \vec{R}^{eq}_{l_1}$ and $\vec{r}_{l_1}$ is the actual position of the ion and with the displacement vector being $\vec{u}_{l_1} = \vec{r}_{l_1} - \vec{R}^{eq}_{l_1}$ so $\vec{r}_{l_1} - \vec{r}_{l_2} = \vec{u}_{l_1} - \vec{u}_{l_2} + \vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2}$. Hardy's energy current formula now looks like,

$$\vec{J} = \frac{1}{2V} \left\{ \sum_l \frac{\vec{p}_l}{M} \left(\frac{\vec{p}_l^{\,2}}{2M} + V_l^{\text{har}} + V_l^{(3ph)} \right) + \sum_{l_1 l_2} (\vec{u}_{l_1} - \vec{u}_{l_2} + \vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2}) \frac{1}{i\hbar} \left[\frac{\vec{p}_{l_1}^{\,2}}{2M}, V_{l_2}^{\text{har}} + V_{l_2}^{(3ph)} \right]_- \right\} + \text{h.c.} \quad (5.15)$$

The anharmonic contribution to the total current is

$$\vec{J}^{(3ph)} = \frac{1}{2V} \left\{ \sum_l \frac{\vec{p}_l}{M} V_l^{(3ph)} + \sum_{l_1 l_2} (\vec{u}_{l_1} - \vec{u}_{l_2} + \vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2}) \frac{1}{i\hbar} \left[\frac{\vec{p}_{l_1}^{\,2}}{2M}, V_{l_2}^{(3ph)} \right]_- \right\} + \text{h.c.} \quad (5.16)$$

which is eqn (4.16) in [Hardy1963]. The other contribution to the total current is $\vec{J}^{\,\text{har}}$.

Following Hardy, we seperate $\vec{J}^{(3ph)}$ into terms that are cubic in phonon operators and quartic in phonon operators. In the spirit of Hardy's notation, we denote

$$\vec{J}^{(3ph)} \equiv \vec{J}^{(3ph)}(\vec{S}_3') + \vec{J}^{(3ph)}(\vec{S}_4') \quad (5.17)$$

Explicitly, they are

$$\vec{J}^{(3ph)}(\vec{S}_3') = \frac{1}{2V} \frac{1}{2M} \sum_{l_1 l_2} (\vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2}) \frac{1}{i\hbar} \left[\vec{p}_{l_1}^{\,2}, V_{l_2}^{(3ph)} \right]_- + \text{h.c.} \quad (5.18)$$

$$\vec{J}^{(3ph)}(\vec{S}_4') = \frac{1}{2V} \left\{ \sum_l \frac{\vec{p}_l}{M} V_l^{(3ph)} + \frac{1}{2M} \sum_{l_1 l_2} (\vec{u}_{l_1} - \vec{u}_{l_2}) \frac{1}{i\hbar} \left[\vec{p}_{l_1}^{\,2}, V_{l_2}^{(3ph)} \right]_- \right\} + \text{h.c.} \quad (5.19)$$

We do not proceed further here as this is not the main approach of the thesis. For a receipe on how to calculate thermal conductivity using these energy current operators, we refer the reader to the section on linear response theory.

5.3 Anharmonic Corrections to Landauer Ballistic Theory

5.3.1 Corrections to Landauer Ballistic Current

In the section on Landauer-like equations a full interacting current formula is derived but it not of much use as it is essentially unsolvable. Here, in the context of anharmonic interaction, we shall systematically expand the S-matrix and calculate lowest order corrections to the Landauer (ballistic) current.

Recall the expression for the (left to central) time dependent current. [2]

$$J^{L\to C}_{\mathrm{thermal}}(t) \;=\; i\hbar \lim_{t'\to t}\sum_{1l_1}\frac{d}{dt'}\int_{t_0}^{\infty} dt_1\left(D^{(C)R}_{ll_1}(tt_1)\Sigma^{(L)<}_{ll_1}(t_1t') + D^{(C)<}_{ll_1}(tt_1)\Sigma^{(L)A}_{l_1l'}(t_1t')\right) \tag{5.20}$$

and the zeroth order expansion (in H_{int}) of $D^{(C)}_{ll'}(\tau\tau')$

$$D^{(C)}_{ll'}(\tau\tau') \approx -\frac{i}{\hbar}\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)} u^C_{H_0^C}(l\tau)u^C_{H_0^C}(l'\tau')\right)\right\rangle \tag{5.21}$$

where the retarded and the lesser components will be taken. Together with imposing the condition of steady state and symmetrizing with the $J^{R\to C}_{\mathrm{thermal}}(t)$ expression, we obtain the steady state (ballistic) Landauer current expression.

The plan to include interactions in the central is now straightforward (but tedious). We will retain the first non-zero terms due to H_{int} in $D^{(C)}_{ll'}(\tau\tau')$ and get the retarded and the lesser components. Substituting them into $J^{L\to C}_{\mathrm{thermal}}(t)$, we get

$$J^{L\to C}_{\mathrm{thermal}}(t) \;=\; J^{L\to C}_{\mathrm{thermal}}(t)(\mathrm{Landauer}) + J^{L\to C}_{\mathrm{thermal}}(t)(\mathrm{Anharmonic\ correction}) \tag{5.22}$$

Symmetrizing $J^{L\to C}_{\mathrm{thermal}}(t)$(Anharmonic correction) with $J^{R\to C}_{\mathrm{thermal}}(t)$(Anharmonic correction) will give the full correction to the Landauer current. Here, I will only provide explicit expressions but will not calculate to the end.

For the sake of clarity, we introduce the notation

$$D^{(C)}_{(Lan)ll'}(\tau\tau') \;\equiv\; -\frac{i}{\hbar}\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)} u^C_{H_0^C}(l\tau)u^C_{H_0^C}(l'\tau')\right)\right\rangle \tag{5.23}$$

We expand $D^{(C)}_{ll'}(\tau\tau')$ up to the first 2 non-zero terms in H_{int},

$$\begin{aligned} &D^{(C)}_{ll'}(\tau\tau') \\ \approx\;& D^{(C)}_{(Lan)ll'}(\tau\tau') - \frac{i}{\hbar}\left(-\frac{i}{\hbar}\right)\int_{c_K+c_M} d\tau_3\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)} H^C_{\mathrm{int}H_0^C}(\tau_3)u^C_{H_0^C}(l\tau)u^C_{H_0^C}(l'\tau')\right)\right\rangle \\ &-\frac{i}{\hbar}\left(-\frac{i}{\hbar}\right)^2\frac{1}{2!}\int_{c_K+c_M} d\tau_3 d\tau_4\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)} H^C_{\mathrm{int}H_0^C}(\tau_3)H^C_{\mathrm{int}H_0^C}(\tau_4)u^C_{H_0^C}(l\tau)u^C_{H_0^C}(l'\tau')\right)\right\rangle \end{aligned} \tag{5.24}$$

Before we proceed with explicit examples of interactions, we need to emphasize that this approach of including interactions is not the best approach one can use. The better way is to pick self consistent self energy diagrams and calculate $D^{(C)}_{ll'}(\tau\tau')$. These diagrams are derived in the next section and collected as a library and are shown to obey conservation laws (in the appendix) and they consist of infinite sums

[2] I wrote down the time dependent current expression instead of the steady state expression because we want to probe the transient behavior as well. The time dependent expression can capture the transients when the leads are attached to the interacting device at t_0.

of particular sets of diagrams. However it demands a large scale numerical computational effort.

For the treatment of lowest orders of phonon-phonon interaction, we follow the important and pioneering work of [Maradudin1962].

5.3.1.1 Lowest Corrections from 3-Phonon Interaction ($V^{(3ph)^2}$)*

[$V^{(3ph)^2}$ **Correction:**] For the 3-phonon interaction, the interaction Hamiltonian is

$$H^C_{\text{int}} = H^{(3ph)} = \frac{1}{3!}\sum_{l_1l_2l_3}\Phi^{(3)}_{l_1l_2l_3}u^C_{l_1}u^C_{l_2}u^C_{l_3} \tag{5.25}$$

where again be reminded that index l is the abbreviation for indices $lk\alpha$. In the expansion of $D^{(C)}_{ll'}(\tau\tau')$, the term linear in $H^C_{\text{int}} = H^{(3ph)}$ is zero due to an odd number of u^Cs in the statistical average. So the first non-zero term in $D^{(C)}_{ll'}(\tau\tau')$ due to $H^{(3ph)}$ is the term associated with $H^{(3ph)^2}$.

The plan is to expand it out and Wick factorise it completely then take the retarded and the lesser component.

$$\begin{aligned}
& D^{(C)}_{ll'}(\tau\tau') \\
\approx\ & D^{(C)}_{(Lan)ll'}(\tau\tau') \\
& -\frac{i}{\hbar}\left(-\frac{i}{\hbar}\right)^2\frac{1}{2!}\int_{c_K+c_M}d\tau_3 d\tau_4\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}H^C_{\text{int}H^C_0}(\tau_3)H^C_{\text{int}H^C_0}(\tau_4)u^C_{H^C_0}(l\tau)u^C_{H^C_0}(l'\tau')\right)\right\rangle \\
|\ \ & \text{be reminded that } \tau_3 \text{ and } \tau_4 \text{ runs over } c_K+c_M \text{ and } \tau_2 \text{ only over } c_K \\
=\ & D^{(C)}_{(Lan)ll'}(\tau\tau') - \frac{i}{\hbar}\left(-\frac{i}{\hbar}\right)\frac{1}{2!}\left(\frac{1}{3!}\right)^2\sum_{l_1l_2l_3l_4l_5l_6}\Phi^{(3)}_{l_1l_2l_3}\Phi^{(3)}_{l_4l_5l_6}\int_{c_K+c_M}d\tau_3\int_{c_K+c_M}d\tau_4 \\
& \times\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C_0}(l_1\tau_3)u^C_{H^C_0}(l_2\tau_3)u^C_{H^C_0}(l_3\tau_3)u^C_{H^C_0}(l_4\tau_4)\right.\right. \\
& \left.\left. u^C_{H^C_0}(l_5\tau_4)u^C_{H^C_0}(l_6\tau_4)u^C_{H^C_0}(l\tau)u^C_{H^C_0}(l'\tau')\right)\right\rangle
\end{aligned} \tag{5.26}$$

We now need to make a very important digression to answer a question: can we directly Wick factorize the above expression $\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C_0}(l_1\tau_3)\cdots\right)\right\rangle$? [3] i.e.

$$\begin{aligned}
& \left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C_0}(l_1\tau_3)u^C_{H^C_0}(l_2\tau_3)u^C_{H^C_0}(l_3\tau_3)u^C_{H^C_0}(l_4\tau_4)\right.\right. \\
& \left.\left. u^C_{H^C_0}(l_5\tau_4)u^C_{H^C_0}(l_6\tau_4)u^C_{H^C_0}(l\tau)u^C_{H^C_0}(l'\tau')\right)\right\rangle \\
\stackrel{?}{=}\ & \left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C_0}(l_1\tau_3)u^C_{H^C_0}(l_2\tau_3)\right)\right\rangle\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C_0}(l_3\tau_3)u^C_{H^C_0}(l_4\tau_4)\right)\right\rangle \\
& \left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C_0}(l_5\tau_4)u^C_{H^C_0}(l\tau)\right)\right\rangle\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C_0}(l_6\tau_4)u^C_{H^C_0}(l'\tau')\right)\right\rangle \\
& +\text{APP}
\end{aligned} \tag{5.27}$$

where "APP" means all possible pairs. We will take a diagrammatic approach to prove it. First expand

[3] I have already used the factorization when I calculated the (DC) ballisitic noise, so I apologize for locating the proof here. The restriction to connected diagrams simply means that cannot pair $u^C_{H^C_0}(l\tau)$ and $u^C_{H^C_0}(l'\tau')$ together.

the S-matrix $e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)}$ to the first non-zero order (i.e. the second order).

$$
\begin{aligned}
&\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)} u^C_{H_0^C}(l_1\tau_3) u^C_{H_0^C}(l_2\tau_3) u^C_{H_0^C}(l_3\tau_3) u^C_{H_0^C}(l_4\tau_4)\right.\right.\\
&\left.\left. u^C_{H_0^C}(l_5\tau_4) u^C_{H_0^C}(l_6\tau_4) u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right)\right\rangle\\
\approx\;& \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 \sum_{l_7 l_8 l_9 l_{10}} \int_{c_K} d\tau_2 \tau_{2'} V^{LC}_{l_7 l_8} V^{LC}_{l_9 l_{10}} \left\langle T_{c_K+c_M}\left(u^L_{H_0^L}(l_7\tau_2) u^C_{H_0^C}(l_8\tau_2) u^L_{H_0^L}(l_9\tau_2') u^C_{H_0^C}(l_{10}\tau_2')\right.\right.\\
&\left.\left.\times u^C_{H_0^C}(l_1\tau_3) u^C_{H_0^C}(l_2\tau_3) u^C_{H_0^C}(l_3\tau_3) u^C_{H_0^C}(l_4\tau_4) u^C_{H_0^C}(l_5\tau_4) u^C_{H_0^C}(l_6\tau_4) u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right)\right\rangle \qquad (5.28)\\
|\;\;& \text{factorize } u^L\text{s and use the definition of (left) lead self energy}\\
=\;& \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 \sum_{l_8 l_{10}} \int_{c_K} d\tau_2 \tau_{2'} \Sigma^{(L)}_{l_8 l_{10}}(\tau_2\tau_2') \left\langle T_{c_K+c_M}\left(u^C_{H_0^C}(l_8\tau_2) u^C_{H_0^C}(l_{10}\tau_2')\right.\right.\\
&\left.\left.\times u^C_{H_0^C}(l_1\tau_3) u^C_{H_0^C}(l_2\tau_3) u^C_{H_0^C}(l_3\tau_3) u^C_{H_0^C}(l_4\tau_4) u^C_{H_0^C}(l_5\tau_4) u^C_{H_0^C}(l_6\tau_4) u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right)\right\rangle \qquad (5.29)
\end{aligned}
$$

The expression $\left\langle T_{c_K+c_M}\left(u^C_{H_0^C}(l_8\tau_2)\cdots\right)\right\rangle$ is the one where Wick's theorem is known to apply. [4]

We define diagram rules to represent the expressions obtained when we Wick factorize the 10 displacement operators.

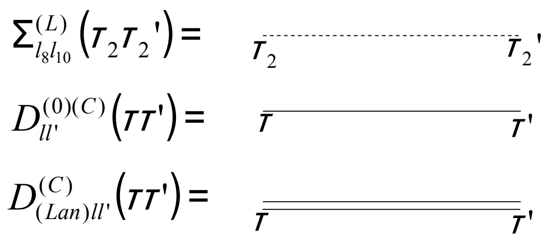


Figure 5.1: *Diagram rules.* Recall the definitions: $D^{(0)(C)}_{ll'}(\tau\tau') = -\frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right)\right\rangle$ and $D^{(C)}_{(Lan)ll'}(\tau\tau') = -\frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)} u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right)\right\rangle$. *Only time is labelled for simplicity.*

Note the diagrammatic form of the familiar Dyson equation of the central-lead coupling.

[4] It is a reminder that the Wick's theorem for displacement operators $u^C_{H_0^C}$ works because of the underlying Wick's theorem for the bosonic phonon operators a,$a^\dagger$.

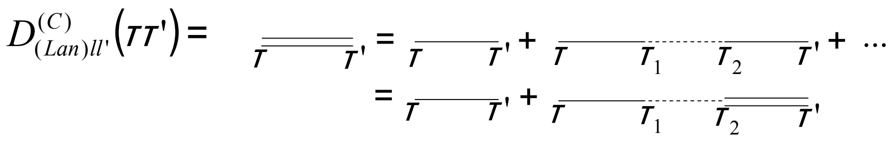


Figure 5.2: $D^{(C)}_{(Lan)ll'}(\tau\tau') = D^{(0)(C)}_{ll'}(\tau\tau') + \sum_{l_1 l_2} \int_{cK} d\tau_1 \int_{cK} d\tau_2 D^{(0)(C)}_{ll_1}(\tau\tau_1)\Sigma^{(L)}_{l_1 l_2}(\tau_1\tau_2) D^{(C)}_{(Lan)l_2 l'}(\tau_2\tau')$

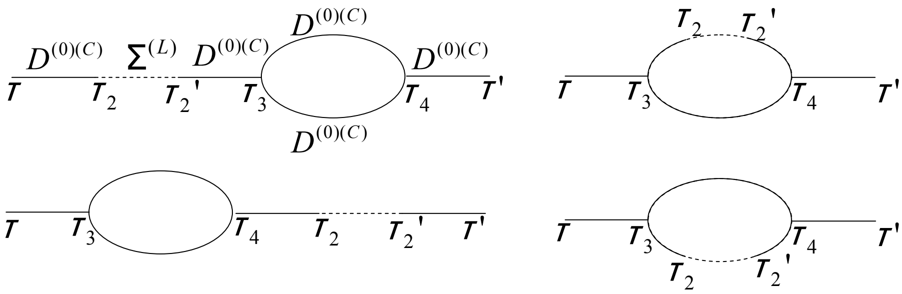


Figure 5.3: The "1-bubble" diagrams.

Wick factorizing the 10 $u^C_{H_0^C}$s gives the "1-bubble" diagrams and the cubic anharmonic "instantaneous phonon" (or lollipop) diagrams.

[Proof that "lollipop" diagrams vanish:] According to Maradudin in [Maradudin1962] pg 2598 text just above their Fig 4, the 4 "instantaneous phonon" diagrams vanish for lattices which are monoatomic or where each atom in the cell is a center of inversion symmetry. I am not sure how his proof goes and so I shall provide my version for a monoatomic cell. We examine the τ_4 vertex and it typically looks like,

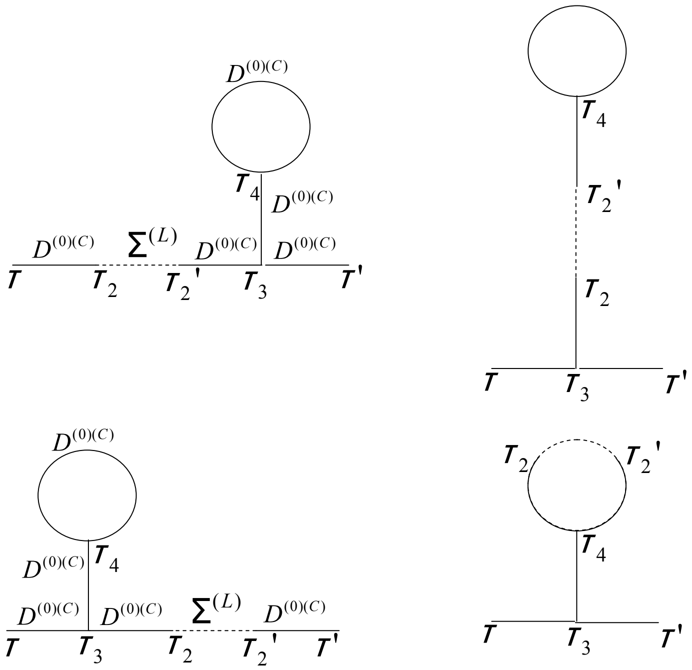


Figure 5.4: The cubic anharmonic "instantaneous phonon" (or lollipop) diagrams.

$$
\begin{aligned}
&\text{Typical Term: } \sum_{l_4 l_5 l_6} \Phi^{(3)}_{l_4 l_5 l_6} \int_{c_K + c_M} d\tau_4 D^{(0)(C)}_{l_2 l_4}(\tau_3 \tau_4) D^{(0)(C)}_{l_5 l_6}(\tau_4 \tau_4) \\
| \quad & \text{use } D^{(0)(C)}_{l_2 l_4}(\tau_3 \tau_4) = -\frac{i}{\hbar} \sum_{j_1 \vec{q}_1 j_2 \vec{q}_2} \tilde{R}^{j_1 \vec{q}_1}_{l_2} \tilde{R}^{j_2 \vec{q}_2}_{l_4} \left\langle T_{c_K + c_M} \left(a^\dagger_{j_1, -\vec{q}_1}(\tau_3) + a_{j_1 \vec{q}_1}(\tau_3) \right) \left(a^\dagger_{j_2, -\vec{q}_2}(\tau_4) + a_{j_2 \vec{q}_2}(\tau_4) \right) \right\rangle \\
| \quad & = -\frac{i}{\hbar} \sum_{j_1 \vec{q}_1 j_2 \vec{q}_2} \tilde{R}^{j_1 \vec{q}_1}_{l_2} \tilde{R}^{j_2 \vec{q}_2}_{l_4} \left(\left\langle T_{c_K + c_M} \left(a^\dagger_{j_1, -\vec{q}_1}(\tau_3) a_{j_2 \vec{q}_2}(\tau_4) \right) \right\rangle + \left\langle T_{c_K + c_M} \left(a_{j_1 \vec{q}_1}(\tau_3) a^\dagger_{j_2, -\vec{q}_2}(\tau_4) \right) \right\rangle \right) \\
| \quad & \propto \sum_{j_1 \vec{q}_1 j_2 \vec{q}_2} \tilde{R}^{j_1 \vec{q}_1}_{l_2} \tilde{R}^{j_2 \vec{q}_2}_{l_4} \left(\delta_{j_1 j_2} \delta_{-\vec{q}_1, \vec{q}_2} + \delta_{j_1 j_2} \delta_{-\vec{q}_2, \vec{q}_1} \right) \\
| \quad & D^{(0)(C)}_{l_5 l_6}(\tau_4 \tau_4) \propto \sum_{j_3 \vec{q}_3 j_4 \vec{q}_4} \tilde{R}^{j_3 \vec{q}_3}_{l_5} \tilde{R}^{j_4 \vec{q}_4}_{l_6} \left(\delta_{j_3 j_4} \delta_{-\vec{q}_3, \vec{q}_4} + \delta_{j_3 j_4} \delta_{-\vec{q}_4, \vec{q}_3} \right)
\end{aligned}
$$

$$
\propto \sum_{j_1 \vec{q}_1 j_2 \vec{q}_2 j_3 \vec{q}_3 j_4 \vec{q}_4} \tilde{R}^{j_1 \vec{q}_1}_{l_2} \tilde{R}^{j_2 \vec{q}_2}_{l_4} \tilde{R}^{j_3 \vec{q}_3}_{l_5} \tilde{R}^{j_4 \vec{q}_4}_{l_6} \Phi^{(3)}_{l_4 l_5 l_6} \delta_{j_1 j_2} \delta_{-\vec{q}_1, \vec{q}_2} \delta_{j_3 j_4} \delta_{-\vec{q}_4, \vec{q}_3} \tag{5.30}
$$

| recall the definition of $V^{(3ph)}$

$$
= \sum_{j_1 \vec{q}_1 j_2 \vec{q}_2 j_3 \vec{q}_3 j_4 \vec{q}_4} \tilde{R}^{j_1 \vec{q}_1}_{l_2} V^{(3ph)}_{j_2 \vec{q}_2 j_3 \vec{q}_3 j_4 \vec{q}_4} \delta_{j_1 j_2} \delta_{-\vec{q}_1, \vec{q}_2} \delta_{j_3 j_4} \delta_{-\vec{q}_4, \vec{q}_3} \tag{5.31}
$$

$$
= \sum_{j_1 \vec{q}_1 j_3 \vec{q}_3} \tilde{R}^{j_1 \vec{q}_1}_{l_2} V^{(3ph)}_{j_1, -\vec{q}_1 j_3 \vec{q}_3 j_3, -\vec{q}_3} \tag{5.32}
$$

| use the explicit expression for $V^{(3ph)}$ but drop index k for monoatomic lattices

$$
\begin{aligned}
&= \sum_{j_1\vec{q}_1 j_3\vec{q}_3} \tilde{R}_{l_2}^{j_1\vec{q}_1} \frac{\hbar^{3/2}}{2^{3/2}N^{1/2}} \frac{\Delta_{-\vec{q}_1,\vec{q}_3,-\vec{q}_3}}{(\omega_{j_1\vec{q}_1}\omega_{j_3\vec{q}_3}\omega_{j_3\vec{q}_3})^{1/2}} \sum_{\alpha_1\alpha_2\alpha_3} \frac{\epsilon_{\alpha_1}(j_1\vec{q}_1)\epsilon_{\alpha_2}(j_3\vec{q}_3)\epsilon_{\alpha_3}(j_3,-\vec{q}_3)}{m^{3/2}} \\
&\quad \times \sum_{l_2 l_3} e^{i\vec{q}_3\cdot l_2} e^{-i\vec{q}_3\cdot l_3} \Phi^{(3)}_{0\alpha_1 l_2\alpha_2 l_3\alpha_3} \qquad (5.33)\\
&\mid \quad \text{note that } \epsilon_{\alpha_3}(j_3,-\vec{q}_3\ ) = \epsilon^*_{\alpha_3}(j_3\vec{q}_3) \text{ and } \Delta_{-\vec{q}_1,\vec{q}_3,-\vec{q}_3} \text{ means } \vec{q}_1 = 0\\
&\mid \quad \text{thus it is a hint that it is about translating the whole lattice, we further rewrite to see it}\\
&= \sum_{j_1\vec{q}_1 j_3\vec{q}_3} \tilde{R}_{l_2}^{j_1\vec{q}_1} \frac{\hbar^{3/2}}{2^{3/2}N^{1/2}} \frac{\Delta_{-\vec{q}_1,\vec{q}_3,-\vec{q}_3}}{(\omega_{j_1\vec{q}_1}\omega_{j_3\vec{q}_3}\omega_{j_3\vec{q}_3})^{1/2}} \sum_{\alpha_1\alpha_2\alpha_3} \frac{\epsilon_{\alpha_1}(j_1\vec{q}_1)\epsilon_{\alpha_2}(j_3\vec{q}_3)\epsilon_{\alpha_3}(j_3,-\vec{q}_3)}{m^{3/2}} \\
&\quad \times \sum_{l_2 l_3} e^{i\vec{q}_3\cdot (l_2-l_3)} \Phi^{(3)}_{0\alpha_1 l_2\alpha_2 l_3\alpha_3} \qquad (5.34)\\
&\mid \quad \text{use lattice translation to write } \Phi^{(3)}_{0\alpha_1 l_2\alpha_2 l_3\alpha_3} = \Phi^{(3)}_{-l_3\alpha_1, l_2-l_3,\alpha_2,0\alpha_3}\\
&\mid \quad \text{then rename } l_2 - l_3 \to l_2 \text{ to get } \sum_{l_2} e^{i\vec{q}_3\cdot l_2} \sum_{l_3} \Phi^{(3)}_{-l_3\alpha_1 l_2\alpha_2 0\alpha_3}\\
&\mid \quad \text{where } \sum_{l_3} \Phi^{(3)}_{-l_3\alpha_1 l_2\alpha_2 0\alpha_3} = 0 \text{ is the force constant sum rule, see [Maradudin1974] eqn (2.8c)}\\
&= 0
\end{aligned}
$$

Thus the vanishing of the coefficient (and thus the vanishing of the cubic anharmonic "instantaneous phonon" or lollipop diagrams) is simply due to the fact that translations of the whole crystal changes no physics.

For the surviving "1-bubble" diagrams, we can infer the diagrams that appear when we expand the S-matrix $e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)}$ to all orders and (as expected), the diagrams can be summed exactly to all orders.

This completes the proof.

We can thus directly Wick factorize such expressions $\langle T_{c_K+c_M}(e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)} u^C \cdots u^C)\rangle$. Lastly we need to sort out the combinatorial factor. There are 3 ways of choosing one τ_3 to pair with τ and another 3 ways to choose one τ_4 to pair with τ'. The 2 remaining τ_3 and τ_4 have 2 ways to pair up. Swapping τ_3 and τ_4 gives a factor of 2. $3 \times 3 \times 2 \times 2 = 36$. Finally,

$$
\begin{aligned}
D^{(C)}_{ll'}(\tau\tau') &= D^{(C)}_{(Lan)ll'}(\tau\tau') + i\hbar \frac{1}{2!}\left(\frac{1}{3!}\right)^2 \times 36 \sum_{l_1l_2l_3l_4l_5l_6} \Phi^{(3)}_{l_1l_2l_3}\Phi^{(3)}_{l_4l_5l_6}\\
&\quad \times \int_{c_K+c_M} d\tau_3 \int_{c_K+c_M} d\tau_4 D^{(C)}_{(Lan)ll_1}(\tau\tau_3)\left[D^{(C)}_{(Lan)l_2l_4}(\tau_3\tau_4)D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)\right] D^{(C)}_{(Lan)l_6l'}(\tau_4\tau')\\
&\mid \quad \text{where terms in square brackets is the self energy (in parallel multiplication)}\\
&= D^{(C)}_{(Lan)ll'}(\tau\tau') + \frac{i\hbar}{2} \sum_{l_1l_2l_3l_4l_5l_6} \Phi^{(3)}_{l_1l_2l_3}\Phi^{(3)}_{l_4l_5l_6}\\
&\quad \times \int_{c_K+c_M} d\tau_3 \int_{c_K+c_M} d\tau_4 D^{(C)}_{(Lan)ll_1}(\tau\tau_3)\left[D^{(C)}_{(Lan)l_2l_4}(\tau_3\tau_4)D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)\right] D^{(C)}_{(Lan)l_6l'}(\tau_4\tau')
\end{aligned}
\tag{5.35}
$$

The next step is to apply Langreth's theorem to get the retarded and the lesser components. Note

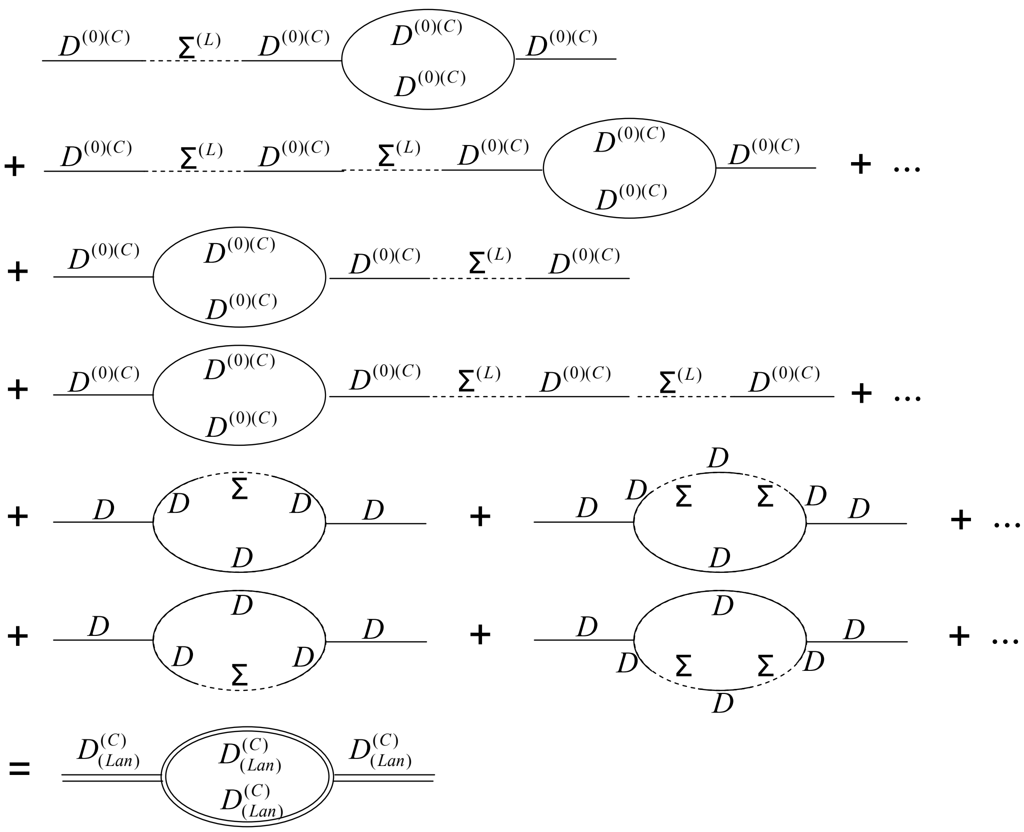


Figure 5.5: Diagrams that appear when we expand S-matrix $e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)}$ to all orders. The last diagram is the result of the infinite sum. (Labelling is further simplified in the last 2 rows of diagrams.)

that $\int\int D^{(C)}_{(Lan)}[\cdots]D^{(C)}_{(Lan)}$ is a 3 term series multiplication. The retarded component is,

$$\begin{aligned} D^{(C)R}_{ll'}(tt') &= D^{(C)R}_{(Lan)ll'}(tt') + \frac{i\hbar}{2}\sum_{l_1l_2l_3l_4l_5l_6}\Phi^{(3)}_{l_1l_2l_3}\Phi^{(3)}_{l_4l_5l_6} \\ &\times\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}d\tau_4 D^{(C)R}_{(Lan)ll_1}(tt_3)\left[D^{(C)}_{(Lan)l_2l_4}(\tau_3\tau_4)D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)\right]^R D^{(C)R}_{(Lan)l_6l'}(t_4t') \end{aligned} \tag{5.36}$$

The lesser component is,

$$\begin{aligned} & D^{(C)<}_{ll_1}(tt_1) \\ = \; & D^{(C)<}_{(Lan)ll_1}(tt_1) + \frac{i\hbar}{2}\sum_{l_2l_3l_4l_5l_6l_7}\Phi^{(3)}_{l_2l_3l_4}\Phi^{(3)}_{l_5l_6l_7} \\ & \times\left\{\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^R D^{(C)<}_{(Lan)l_7l_1}(t_4t_1)\right. \\ & +\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^< D^{(C)A}_{(Lan)l_7l_1}(t_4t_1) \\ & +\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)<}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^A D^{(C)A}_{(Lan)l_7l_1}(t_4t_1) \\ & +\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_3^M\int_{t_0}^{\infty}dt_4 D^{(C)\urcorner}_{(Lan)ll_2}(t\tau_3^M)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^{\ulcorner} D^{(C)A}_{(Lan)l_7l_1}(t_4t_1) \\ & +\int_{t_0}^{\infty}dt_3\int_{t_0}^{t_0-i\hbar\beta}d\tau_4^M D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^{\urcorner} D^{(C)\ulcorner}_{(Lan)l_7l_1}(\tau_4^M t_1) \\ & \left.+\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_3^M\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_4^M D^{(C)\urcorner}_{(Lan)ll_2}(t\tau_3^M)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^M D^{(C)\ulcorner}_{(Lan)l_7l_1}(\tau_4^M t_1)\right\} \end{aligned} \tag{5.37}$$

The expression for current with the correction terms are,

$$\begin{aligned} & J^{L\to C}_{\text{thermal}}(t) \\ = \; & i\hbar\lim_{t'\to t}\sum_{ll_1}\frac{d}{dt'}\int_{t_0}^{\infty}dt_1\left(D^{(C)R}_{(Lan)ll_1}(tt_1)\Sigma^{(L)<}_{ll_1}(t_1t') + D^{(C)<}_{(Lan)ll_1}(tt_1)\Sigma^{(L)A}_{l_1l'}(t_1t')\right) \\ & +i\hbar\lim_{t'\to t}\sum_{ll_1}\frac{d}{dt'}\int_{t_0}^{\infty}dt_1\left[\frac{i\hbar}{2}\sum_{l_2l_3l_4l_5l_6l_7}\Phi^{(3)}_{l_2l_3l_4}\Phi^{(3)}_{l_5l_6l_7}\right. \\ & \left.\times\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^R D^{(C)R}_{(Lan)l_6l_1}(t_4t_1)\right]\Sigma^{(L)<}_{ll_1}(t_1t') \\ & +i\hbar\lim_{t'\to t}\sum_{ll_1}\frac{d}{dt'}\int_{t_0}^{\infty}dt_1\left[\sum_{l_2l_3l_4l_5l_6l_7}\Phi^{(3)}_{l_2l_3l_4}\Phi^{(3)}_{l_5l_6l_7}\right. \\ & \times\left\{\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^R D^{(C)<}_{(Lan)l_7l_1}(t_4t_1)\right. \\ & +\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^< D^{(C)A}_{(Lan)l_7l_1}(t_4t_1) \end{aligned}$$

$$
\begin{aligned}
&+\int_{t_0}^{\infty} dt_3 \int_{t_0}^{\infty} dt_4 D^{(C)<}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^A D^{(C)A}_{(Lan)l_7l_1}(t_4t_1)\\
&+\int_{t_0}^{t_0-i\hbar\beta^C} d\tau_3^M \int_{t_0}^{\infty} dt_4 D^{(C)\urcorner}_{(Lan)ll_2}(t\tau_3^M)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^{\ulcorner} D^{(C)A}_{(Lan)l_7l_1}(t_4t_1)\\
&+\int_{t_0}^{\infty} dt_3 \int_{t_0}^{t_0-i\hbar\beta} d\tau_4^M D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^{\urcorner} D^{(C)\ulcorner}_{(Lan)l_7l_1}(\tau_4^M t_1)\\
&\left.\left.+\int_{t_0}^{t_0-i\hbar\beta^C} d\tau_3^M \int_{t_0}^{t_0-i\hbar\beta^C} d\tau_4^M D^{(C)\urcorner}_{(Lan)ll_2}(t\tau_3^M)\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^M D^{(C)\ulcorner}_{(Lan)l_7l_1}(\tau_4^M t_1)\right\}\right]\\
&\times\Sigma^{(L)A}_{l_1l'}(t_1t')
\end{aligned}
\tag{5.38}
$$

The first line is the Landauer term and the rest are the lowest order correction terms due to $V^{(3ph)^2}$.

Note that we assumed that the 2-time quantities $D^{(C)<,R,A}_{(Lan)ll'}(tt')$, $D^{(C)\urcorner}_{(Lan)ll'}(t\tau^{M'})$ and $D^{(C)\urcorner}_{(Lan)ll'}(\tau^M t')$ have been solved properly using the Kadanoff-Baym equations. [5]

We end this subsection by providing more explicit expressions of the self energies which are in parallel multiplication.

$$
\begin{aligned}
&\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^R\\
=\;&\theta(t_3-t_4)\left(D^{(C)>}_{(Lan)l_3l_5}(t_3t_4)D^{(C)>}_{(Lan)l_4l_6}(t_3t_4)-D^{(C)<}_{(Lan)l_3l_5}(t_3t_4)D^{(C)<}_{(Lan)l_4l_6}(t_3t_4)\right)
\end{aligned}
\tag{5.41}
$$

$$
\begin{aligned}
&\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^A\\
=\;&-\theta(t_4-t_3)\left(D^{(C)>}_{(Lan)l_3l_5}(t_3t_4)D^{(C)>}_{(Lan)l_4l_6}(t_3t_4)-D^{(C)<}_{(Lan)l_3l_5}(t_3t_4)D^{(C)<}_{(Lan)l_4l_6}(t_3t_4)\right)
\end{aligned}
\tag{5.42}
$$

$$
\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^< = D^{(C)<}_{(Lan)l_3l_5}(t_3t_4)D^{(C)<}_{(Lan)l_4l_6}(t_3t_4) \tag{5.43}
$$

$$
\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^{\ulcorner} = D^{(C)\ulcorner}_{(Lan)l_3l_5}(\tau_3^M t_4)D^{(C)\ulcorner}_{(Lan)l_4l_6}(\tau_3^M t_4) \tag{5.44}
$$

$$
\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^{\urcorner} = D^{(C)\urcorner}_{(Lan)l_3l_5}(t_3\tau_4^M)D^{(C)\urcorner}_{(Lan)l_4l_6}(t_3\tau_4^M) \tag{5.45}
$$

$$
\begin{aligned}
&\left[D^{(C)}_{(Lan)l_3l_5}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_6}(\tau_3\tau_4)\right]^M\\
=\;&D^{(C)M}_{(Lan)l_3l_5}(\tau_3^M\tau_4^M)D^{(C)M}_{(Lan)l_4l_6}(\tau_3^M\tau_4^M) = D^{(0)(C)M}_{l_3l_5}(\tau_3^M\tau_4^M)D^{(0)(C)M}_{l_4l_6}(\tau_3^M\tau_4^M)
\end{aligned}
\tag{5.46}
$$

We summarize 2 important points that can be utilized in later calculations.

1. The "modified" Wick's theorem works and will be employed directly in other parts of the thesis.
2. "Instantaneous phonons" of cubic anharmonicity are zero. The reason being that the translation of the whole crystal has no physical effects. Thus such 3-phonon "lollipop" diagrams will be

[5] The more general 2-time quantities are needed and NOT the steady state versions which are $D^{(C)<,R,A}_{(Lan)ll'}(t-t')$, $D^{(C)\urcorner}_{(Lan)ll'}(t\tau^{M'})=0$ and $D^{(C)\urcorner}_{(Lan)ll'}(\tau^M t')=0$. $D^{(C)M}_{(Lan)ll'}(\tau^M\tau^{M'})$ is obtained immediately by applying Langreth's theorem to the Dyson equation,

$$
D^{(C)}_{(Lan)ll'}(\tau\tau') = D^{(0)(C)}_{ll'}(\tau\tau')+\sum_{l_1l_2}\int_{c_K}d\tau_1\int_{c_K}d\tau_2 D^{(0)(C)}_{ll_1}(\tau\tau_1)\Sigma^{(L)}_{l_1l_2}(\tau_1\tau_2)D^{(C)}_{(Lan)l_2l'}(\tau_2\tau') \tag{5.39}
$$

$$
\Longrightarrow D^{(C)M}_{(Lan)ll'}(\tau^M\tau^{M'}) = D^{(0)(C)M}_{ll'}(\tau^M\tau^{M'}) \tag{5.40}
$$

since the contour variables τ_1 and τ_2 do not "pass through" c_M.

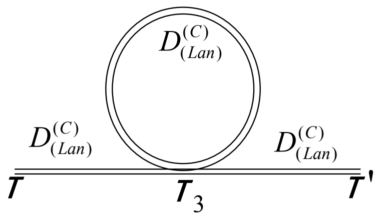


Figure 5.6: *"Instantaneous phonon" of quartic anharmonicity.*

dropped directly. "Instantaneous phonons" of quartic anharmonicity are not zero. One can go through the same calculation and not get zero for the coefficient.

5.3.1.2 Lowest Corrections from 4-Phonon Interaction ($V^{(4ph)}$)*

The interaction Hamiltonian is

$$H^C_{\text{int}} = H^{(4ph)} = \frac{1}{4!}\sum_{l_1l_2l_3l_4}\Phi^{(4)}_{l_1l_2l_3l_4}u^C_{l_1}u^C_{l_2}u^C_{l_3}u^C_{l_4} \tag{5.47}$$

The first non-zero term in this case is linear in $H^{(4ph)}$.

$$\begin{aligned} D^{(C)}_{ll'}(\tau\tau') &\approx D^{(C)}_{(Lan)ll'}(\tau\tau') \\ &\quad -\frac{i}{\hbar}\left(-\frac{i}{\hbar}\right)\int_{c_K+c_M}d\tau_3\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}H^{(4ph)}_{H^C_0}(\tau_3)u^C_{H^C_0}(l\tau)u^C_{H^C_0}(l'\tau')\right)\right\rangle \qquad (5.48) \\ &= D^{(C)}_{(Lan)ll'}(\tau\tau') - \frac{i}{\hbar}\left(-\frac{i}{\hbar}\right)\frac{1}{4!}\sum_{l_1l_2l_3l_4}\Phi^{(4)}_{l_1l_2l_3l_4}\int_{c_K+c_M}d\tau_3 \\ &\quad\times\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\tilde{H}^{LC}(\tau_2)}u^C_{H^C_0}(l_1\tau_3)u^C_{H^C_0}(l_2\tau_3)u^C_{H^C_0}(l_3\tau_3)u^C_{H^C_0}(l_4\tau_3)u^C_{H^C_0}(l\tau)u^C_{H^C_0}(l'\tau')\right)\right\rangle \end{aligned}$$
(5.49)

Using the "modified" Wick's theorem and keeping only connected diagrams, i.e. we cannot pair τ and τ' together, we get only 1 diagram.

And now we need to figure out the combinatorical factor. There are 4 ways to choose a τ_3 to pair with τ. 3 ways remain to choose a τ_3 to pair with τ' and the 2 remaining τ_3s can pair only in 1 way. $4\times3\times1=12$. So the term is now,

$$\begin{aligned} D^{(C)}_{ll'}(\tau\tau') &= D^{(C)}_{(Lan)ll'}(\tau\tau') + \frac{i\hbar}{2}\sum_{l_1l_2l_3l_4}\Phi^{(4)}_{l_1l_2l_3l_4}\int_{c_K+c_M}d\tau_3 D^{(C)}_{(Lan)ll_1}(\tau\tau_3)D^{(C)}_{(Lan)l_2l_3}(\tau_3\tau_3)D^{(C)}_{(Lan)l_4l'}(\tau_3\tau') \\ &\quad|\ \text{we need to offset the time to carry out Langreth's theorem} \\ &= D^{(C)}_{(Lan)ll'}(\tau\tau') \\ &\quad+\frac{i\hbar}{2}\sum_{l_1l_2l_3l_4}\Phi^{(4)}_{l_1l_2l_3l_4}\lim_{\tau_3'=\tau_3}\int_{c_K+c_M}d\tau_3\int_{c_K+c_M}d\tau_3' D^{(C)}_{(Lan)ll_1}(\tau\tau_3)D^{(C)}_{(Lan)l_2l_3}(\tau_3\tau_3')D^{(C)}_{(Lan)l_4l'}(\tau_3'\tau') \end{aligned}$$
(5.50)

We take the retarded component (and relabel the indices),

$$
\begin{aligned}
D^{(C)R}_{ll_1}(tt_1) &= D^{(C)R}_{(Lan)ll_1}(tt_1) \\
&\quad + \frac{i\hbar}{2}\sum_{l_2l_3l_4l_5}\Phi^{(4)}_{l_2l_3l_4l_5}\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt'_3 D^{(C)R}_{(Lan)ll_2}(tt_3)D^{(C)R}_{(Lan)l_3l_4}(t_3t'_3)D^{(C)R}_{(Lan)l_5l_1}(t'_3t_1)\delta(t'_3-t_3) \\
&= D^{(C)R}_{(Lan)ll_1}(tt_1) + \frac{i\hbar}{2}\sum_{l_2l_3l_4l_5}\Phi^{(4)}_{l_2l_3l_4l_5}\int_{t_0}^{\infty}dt_3 D^{(C)R}_{(Lan)ll_2}(tt_3)D^{(C)R}_{(Lan)l_3l_4}(t_3t_3)D^{(C)R}_{(Lan)l_5l_1}(t_3t_1)
\end{aligned}
\tag{5.51}
$$

It might be useful to note that $D^{(0)R}(tt) \propto D^{(0)>}(tt) - D^{(0)<}(tt) = 0$ due to the equal time commutation relations of u^C. Similarly, $D^{(0)A}(tt) = 0$.

The lesser component is,

$$
\begin{aligned}
& D^{(C)<}_{ll_1}(tt_1) \\
= \; & D^{(C)<}_{(Lan)ll_1}(tt_1) + \frac{i\hbar}{2}\sum_{l_2l_3l_4l_5}\Phi^{(4)}_{l_2l_3l_4l_5} \\
& \times\Bigg\{\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt'_3 D^{(C)R}_{(Lan)ll_2}(tt_3)D^{(C)R}_{(Lan)l_3l_4}(t_3t'_3)D^{(C)<}_{(Lan)l_5l_1}(t'_3t_1)\delta(t'_3-t_3) \\
& + \int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt'_3 D^{(C)R}_{(Lan)ll_2}(tt_3)D^{(C)<}_{(Lan)l_3l_4}(t_3t'_3)D^{(C)A}_{(Lan)l_5l_1}(t'_3t_1)\delta(t'_3-t_3) \\
& + \int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt'_3 D^{(C)<}_{(Lan)ll_2}(tt_3)D^{(C)A}_{(Lan)l_3l_4}(t_3t'_3)D^{(C)A}_{(Lan)l_5l_1}(t'_3t_1)\delta(t'_3-t_3) \\
& + \int_{t_0}^{t_0-i\hbar\beta^C}d\tau^M_3\int_{t_0}^{\infty}dt'_3 D^{(C)\urcorner}_{(Lan)ll_2}(t\tau^M_3)D^{(C)\ulcorner}_{(Lan)l_3l_4}(\tau^M_3t'_3)D^{(C)A}_{(Lan)l_5l_1}(t'_3t_1)\delta(t'_3-\tau^M_3) \\
& + \int_{t_0}^{\infty}dt_3\int_{t_0}^{t_0-i\hbar\beta^C}d\tau^{M'}_3 D^{(C)R}_{(Lan)ll_2}(tt_3)D^{(C)\urcorner}_{(Lan)l_3l_4}(t_3\tau^{M'}_3)D^{(C)\ulcorner}_{(Lan)l_5l_1}(\tau^{M'}_3t_1)\delta(\tau^{M'}_3-t_3) \\
& + \int_{t_0}^{t_0-i\hbar\beta^C}d\tau^M_3\int_{t_0}^{t_0-i\hbar\beta^C}d\tau^{M'}_3 D^{(C)\urcorner}_{(Lan)ll_2}(t\tau^M_3)D^{(C)M}_{(Lan)l_3l_4}(\tau^M_3\tau^{M'}_3)D^{(C)\ulcorner}_{(Lan)l_5l_1}(\tau^{M'}_3t_1)\delta(\tau^{M'}_3-\tau^M_3)\Bigg\} \\
| \; & \text{the condition } D^{(C)\ulcorner}_{(Lan)l_3l_4}(\tau^M_3t'_3)\delta(t'_3-\tau^M_3) \text{ is only fulfilled at } t_0. \\
= \; & D^{(C)<}_{(Lan)ll_1}(tt_1) + \frac{i\hbar}{2}\sum_{l_2l_3l_4l_5}\Phi^{(4)}_{l_2l_3l_4l_5}\Bigg\{\int_{t_0}^{\infty}dt_3 D^{(C)R}_{(Lan)ll_2}(tt_3)D^{(C)R}_{(Lan)l_3l_4}(t_3t_3)D^{(C)<}_{(Lan)l_5l_1}(t_3t_1) \\
& + \int_{t_0}^{\infty}dt_3 D^{(C)R}_{(Lan)ll_2}(tt_3)D^{(C)<}_{(Lan)l_3l_4}(t_3t_3)D^{(C)A}_{(Lan)l_5l_1}(t_3t_1) \\
& + \int_{t_0}^{\infty}dt_3 D^{(C)<}_{(Lan)ll_2}(tt_3)D^{(C)A}_{(Lan)l_3l_4}(t_3t_3)D^{(C)A}_{(Lan)l_5l_1}(t_3t_1) \\
& + D^{(C)\urcorner}_{(Lan)ll_2}(tt_0)D^{(C)\ulcorner}_{(Lan)l_3l_4}(t_0t_0)D^{(C)A}_{(Lan)l_5l_1}(t_0t_1) + D^{(C)R}_{(Lan)ll_2}(tt_0)D^{(C)\urcorner}_{(Lan)l_3l_4}(t_0t_0)D^{(C)\ulcorner}_{(Lan)l_5l_1}(t_0t_1) \\
& + \int_{t_0}^{t_0-i\hbar\beta^C}d\tau^M_3 D^{(C)\urcorner}_{(Lan)ll_2}(t\tau^M_3)D^{(C)M}_{(Lan)l_3l_4}(\tau^M_3\tau^M_3)D^{(C)\ulcorner}_{(Lan)l_5l_1}(\tau^M_3t_1)\Bigg\}
\end{aligned}
\tag{5.52}
$$

It might be of further use to note these expressions from the Appendix,

$$D^{(0)(C)<}_{l_3l_4}(t_3t_3) = -\frac{i}{\hbar}\sum_{j_1\vec{q}_1j_2\vec{q}_2}\left(2N^{eq(C)}_{j_1\vec{q}_1}+1\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2}R^{j_1\vec{q}_1}_{l_3}R^{j_2\vec{q}_2}_{l_4}\frac{\hbar}{2\omega_{j_1\vec{q}_1}} \tag{5.53}$$

$$= -\frac{i}{\hbar}\sum_{j_1\vec{q}_1}\left(2N^{eq(C)}_{j_1\vec{q}_1}+1\right)R^{j_1\vec{q}_1}_{l_3}R^{j_1,-\vec{q}_1}_{l_4}\frac{\hbar}{2\omega_{j_1\vec{q}_1}} \tag{5.54}$$

$$D^{(0)(C)M}_{l_3l_4}(\tau_3^M\tau_3^M) = D^{(0)(C)M}_{l_3l_4}(\tau_3^M\tau_3^M) = -\frac{i}{\hbar}\sum_{j_1\vec{q}_1j_2\vec{q}_2}\left(2N^{eq(C)}_{j_1\vec{q}_1}+1\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2}R^{j_1\vec{q}_1}_{l_3}R^{j_2\vec{q}_2}_{l_4}\frac{-\hbar}{2\omega_{j_1\vec{q}_1}}$$

$$= \frac{i}{\hbar}\sum_{j_1\vec{q}_1}\left(2N^{eq(C)}_{j_1\vec{q}_1}+1\right)R^{j_1\vec{q}_1}_{l_3}R^{j_1,-\vec{q}_1}_{l_4}\frac{\hbar}{2\omega_{j_1\vec{q}_1}} \tag{5.55}$$

Thus as expected, these expressions tell us that in the usual equilibrium theory (i.e. without leads), the "instantaneous phonons" of quartic anharmonicity only contribute a Hartree shift (a real function of ω), in this case $2N^{eq(C)}+1 = \coth\left(\frac{\beta^C\hbar\omega^C}{2}\right)$.

The expression for current with the correction terms are,

$$\begin{aligned}
& J^{L\to C}_{\text{thermal}}(t) \\
= \; & i\hbar\lim_{t'\to t}\sum_{ll_1}\frac{d}{dt'}\int_{t_0}^{\infty}dt_1\left(D^{(C)R}_{(Lan)ll_1}(tt_1)\Sigma^{(L)<}_{ll_1}(t_1t')+D^{(C)<}_{(Lan)ll_1}(tt_1)\Sigma^{(L)A}_{l_1l'}(t_1t')\right) \\
& +i\hbar\lim_{t'\to t}\sum_{ll_1}\frac{d}{dt'}\int_{t_0}^{\infty}dt_1 \\
& \times\left[\frac{i\hbar}{2}\sum_{l_2l_3l_4l_5}\Phi^{(4)}_{l_2l_3l_4l_5}\int_{t_0}^{\infty}dt_3D^{(C)R}_{(Lan)ll_2}(tt_3)D^{(C)R}_{(Lan)l_3l_4}(t_3t_3)D^{(C)R}_{(Lan)l_5l_1}(t_3t_1)\right]\Sigma^{(L)<}_{ll_1}(t_1t') \\
& +i\hbar\lim_{t'\to t}\sum_{ll_1}\frac{d}{dt'}\int_{t_0}^{\infty}dt_1\left[\frac{i\hbar}{2}\sum_{l_2l_3l_4l_5}\Phi^{(4)}_{l_2l_3l_4l_5}\left\{\int_{t_0}^{\infty}dt_3D^{(C)R}_{(Lan)ll_2}(tt_3)D^{(C)R}_{(Lan)l_3l_4}(t_3t_3)D^{(C)<}_{(Lan)l_5l_1}(t_3t_1)\right.\right. \\
& +\int_{t_0}^{\infty}dt_3D^{(C)R}_{(Lan)ll_2}(tt_3)D^{(C)<}_{(Lan)l_3l_4}(t_3t_3)D^{(C)A}_{(Lan)l_5l_1}(t_3t_1) \\
& +\int_{t_0}^{\infty}dt_3D^{(C)<}_{(Lan)ll_2}(tt_3)D^{(C)A}_{(Lan)l_3l_4}(t_3t_3)D^{(C)A}_{(Lan)l_5l_1}(t_3t_1) \\
& +D^{(C)\urcorner}_{(Lan)ll_2}(tt_0)D^{(C)\ulcorner}_{(Lan)l_3l_4}(t_0t_0)D^{(C)A}_{(Lan)l_5l_1}(t_0t_1)+D^{(C)R}_{(Lan)ll_2}(tt_0)D^{(C)\urcorner}_{(Lan)l_3l_4}(t_0t_0)D^{(C)\ulcorner}_{(Lan)l_5l_1}(t_0t_1) \\
& \left.\left.+\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_3^MD^{(C)\urcorner}_{(Lan)ll_2}(t\tau_3^M)D^{(C)M}_{(Lan)l_3l_4}(\tau_3^M\tau_3^M)D^{(C)\ulcorner}_{(Lan)l_5l_1}(\tau_3^Mt_1)\right\}\right]\Sigma^{(L)A}_{l_1l'}(t_1t')
\end{aligned} \tag{5.56}$$

The first line is the Landauer term and the rest are the lowest order correction terms due to $V^{(4ph)}$.

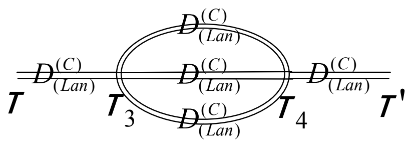


Figure 5.7: *Diagram for the $V^{(4ph)^2}$ correction.*

5.3.1.3 Second Lowest Correction from 4-Phonon Interaction ($V^{(4ph)^2}$)*

The $V^{(4ph)^2}$ correction term is the second term in the expansion of $H_{\text{int}} = H^{(4ph)}$ in $D^{(C)}_{ll'}(\tau\tau')$. We denote it as $D^{(C)(2)}_{ll'}(\tau\tau')$.

$$\begin{aligned}
D^{(C)(2)}_{ll'}(\tau\tau') &= -\frac{i}{\hbar}\left(-\frac{i}{\hbar}\right)^2 \frac{1}{2!}\int_{c_K+c_M} d\tau_3 \int_{c_K+c_M} d\tau_4 \\
&\quad \times \left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)} H^{(4ph)}_{H_0^C}(\tau_3) H^{(4ph)}_{H_0^C}(\tau_4) u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right)\right\rangle \quad (5.57)\\
&= -\frac{i}{\hbar}\left(-\frac{i}{\hbar}\right)^2 \frac{1}{2!}\left(\frac{1}{4!}\right)^2 \sum_{l_2l_3l_4l_5l_6l_7l_8l_9} \Phi^{(4)}_{l_2l_3l_4l_5}\Phi^{(4)}_{l_6l_7l_8l_9}\int_{c_K+c_M} d\tau_3 \int_{c_K+c_M} d\tau_4 \\
&\quad \times \left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau_2 \tilde{H}^{LC}(\tau_2)} u^C_{H_0^C}(l_2\tau_3) u^C_{H_0^C}(l_3\tau_3) u^C_{H_0^C}(l_4\tau_3) u^C_{H_0^C}(l_5\tau_3)\right.\right. \\
&\quad \times \left.\left. u^C_{H_0^C}(l_6\tau_4) u^C_{H_0^C}(l_7\tau_4) u^C_{H_0^C}(l_8\tau_4) u^C_{H_0^C}(l_9\tau_4) u^C_{H_0^C}(l\tau) u^C_{H_0^C}(l'\tau')\right)\right\rangle \quad (5.58)
\end{aligned}$$

Using the "modified" Wick's theorem and keeping only connected diagrams, i.e. we cannot pair τ and τ' together, we get one diagram.

And now we need to figure out the combinatorical factor. There are 4 ways to choose a τ_3 to pair with τ. There are 4 ways to choose a τ_4 to pair with τ'. There are 6 ways to pair the 3 remaining τ_3 terms with each of the 3 remaining τ_4 terms. Swapping τ_3 and τ_4 gives a factor of 2. $4\times4\times6\times2 = 192$. So,

$$\begin{aligned}
D^{(C)(2)}_{ll'}(\tau\tau') &= \frac{(i\hbar)^2}{6}\sum_{l_2l_3l_4l_5l_6l_7l_8l_9} \Phi^{(4)}_{l_2l_3l_4l_5}\Phi^{(4)}_{l_6l_7l_8l_9}\int_{c_K+c_M} d\tau_3 \int_{c_K+c_M} d\tau_4 \\
&\quad \times D^{(C)}_{(Lan)ll_2}(\tau\tau_3)\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4) D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4) D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right] D^{(C)}_{(Lan)l_9l'}(\tau_4\tau')
\end{aligned} \quad (5.59)$$

where the square brackets enclose the self energy terms in parallel multiplication. We take the retarded component (and relabel the indices),

$$\begin{aligned}
D^{(C)(2)R}_{ll_1}(tt_1) &= \frac{(i\hbar)^2}{6}\sum_{l_2l_3l_4l_5l_6l_7l_8l_9} \Phi^{(4)}_{l_2l_3l_4l_5}\Phi^{(4)}_{l_6l_7l_8l_9}\int_{t_0}^{\infty} dt_3 \int_{t_0}^{\infty} dt_4 \\
&\quad \times D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4) D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4) D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^R D^{(C)R}_{(Lan)l_9l_1}(t_4t_1)
\end{aligned} \quad (5.60)$$

The lesser component is,

$$D^{(C)(2)<}_{ll_1}(tt_1)$$

$$\begin{aligned}
= \quad & \frac{(i\hbar)^2}{6}\sum_{l_2l_3l_4l_5l_6l_7l_8l_9}\Phi^{(4)}_{l_2l_3l_4l_5}\Phi^{(4)}_{l_6l_7l_8l_9}\\
&\times\left\{\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^R D^{(C)<}_{(Lan)l_9l_1}(t_4t_1)\right.\\
&+\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^< D^{(C)A}_{(Lan)l_9l_1}(t_4t_1)\\
&+\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)<}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^A D^{(C)A}_{(Lan)l_9l_1}(t_4t_1)\\
&+\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_3^M\int_{t_0}^{\infty}dt_4 D^{(C)\urcorner}_{(Lan)ll_2}(t\tau_3^M)\left[\cdots\right]^{\ulcorner} D^{(C)A}_{(Lan)l_9l_1}(t_4t_1)\\
&+\int_{t_0}^{\infty}dt_3\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_4^M D^{(C)R}_{(Lan)ll_2}(tt_3)\left[\cdots\right]^{\urcorner} D^{(C)\ulcorner}_{(Lan)l_9l_1}(\tau_4^Mt_1)\\
&\left.+\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_3^M\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_4^M D^{(C)\urcorner}_{(Lan)ll_2}(t\tau_3^M)\left[\cdots\right]^M D^{(C)\ulcorner}_{(Lan)l_9l_1}(\tau_4^Mt_1)\right\} \qquad (5.61)
\end{aligned}$$

where the notation $[\cdots]$ is simply introduced so that the equation can fit on the page. The correction term to the current expression is

$$\begin{aligned}
& J^{L\to C(2)}_{\text{thermal}}(t)\\
= \quad & i\hbar\lim_{t'\to t}\sum_{ll_1}\frac{d}{dt'}\int_{t_0}^{\infty}dt_1\left[\frac{(i\hbar)^2}{6}\sum_{l_2l_3l_4l_5l_6l_7l_8l_9}\Phi^{(4)}_{l_2l_3l_4l_5}\Phi^{(4)}_{l_6l_7l_8l_9}\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4\right.\\
&\left.\times D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^R D^{(C)R}_{(Lan)l_9l_1}(t_4t_1)\right]\Sigma^{(L)<}_{ll_1}(t_1t')\\
&+i\hbar\lim_{t'\to t}\sum_{ll_1}\frac{d}{dt'}\int_{t_0}^{\infty}dt_1\left[\frac{(i\hbar)^2}{6}\sum_{l_2l_3l_4l_5l_6l_7l_8l_9}\Phi^{(4)}_{l_2l_3l_4l_5}\Phi^{(4)}_{l_6l_7l_8l_9}\right.\\
&\times\left\{\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^R D^{(C)<}_{(Lan)l_9l_1}(t_4t_1)\right.\\
&+\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)R}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^< D^{(C)A}_{(Lan)l_9l_1}(t_4t_1)\\
&+\int_{t_0}^{\infty}dt_3\int_{t_0}^{\infty}dt_4 D^{(C)<}_{(Lan)ll_2}(tt_3)\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^A D^{(C)A}_{(Lan)l_9l_1}(t_4t_1)\\
&+\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_3^M\int_{t_0}^{\infty}dt_4 D^{(C)\urcorner}_{(Lan)ll_2}(t\tau_3^M)\left[\cdots\right]^{\ulcorner} D^{(C)A}_{(Lan)l_9l_1}(t_4t_1)\\
&+\int_{t_0}^{\infty}dt_3\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_4^M D^{(C)R}_{(Lan)ll_2}(tt_3)\left[\cdots\right]^{\urcorner} D^{(C)\ulcorner}_{(Lan)l_9l_1}(\tau_4^Mt_1)\\
&\left.\left.+\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_3^M\int_{t_0}^{t_0-i\hbar\beta^C}d\tau_4^M D^{(C)\urcorner}_{(Lan)ll_2}(t\tau_3^M)\left[\cdots\right]^M D^{(C)\ulcorner}_{(Lan)l_9l_1}(\tau_4^Mt_1)\right\}\right]\Sigma^{(L)A}_{l_1l'}(t_1t') \qquad (5.62)
\end{aligned}$$

$J^{L\to C(2)}_{\text{thermal}}(t)$ is the correction term to the Landauer current due to $V^{(4ph)^2}$. We end by providing more explicit expressions of the self energies which are in parallel multiplication.

$$\begin{aligned}
&\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^R \\
=\;& \theta(t_3-t_4)\Big(D^{(C)>}_{(Lan)l_3l_6}(t_3t_4)D^{(C)>}_{(Lan)l_4l_7}(t_3t_4)D^{(C)>}_{(Lan)l_5l_8}(t_3t_4) \\
& -D^{(C)<}_{(Lan)l_3l_6}(t_3t_4)D^{(C)<}_{(Lan)l_4l_7}(t_3t_4)D^{(C)<}_{(Lan)l_5l_8}(t_3t_4)\Big) \qquad (5.63)\\
&\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^A \\
=\;& -\theta(t_4-t_3)\Big(D^{(C)>}_{(Lan)l_3l_6}(t_3t_4)D^{(C)>}_{(Lan)l_4l_7}(t_3t_4)D^{(C)>}_{(Lan)l_5l_8}(t_3t_4) \\
& -D^{(C)<}_{(Lan)l_3l_6}(t_3t_4)D^{(C)<}_{(Lan)l_4l_7}(t_3t_4)D^{(C)<}_{(Lan)l_5l_8}(t_3t_4)\Big) \qquad (5.64)\\
&\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^< \\
=\;& D^{(C)<}_{(Lan)l_3l_6}(t_3t_4)D^{(C)<}_{(Lan)l_4l_7}(t_3t_4)D^{(C)<}_{(Lan)l_5l_8}(t_3t_4) \qquad (5.65)\\
&\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^\ulcorner \\
=\;& D^{(C)\ulcorner}_{(Lan)l_3l_6}(\tau_3^Mt_4)D^{(C)\ulcorner}_{(Lan)l_4l_7}(\tau_3^Mt_4)D^{(C)\ulcorner}_{(Lan)l_5l_8}(\tau_3^Mt_4) \qquad (5.66)\\
&\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^\urcorner \\
=\;& D^{(C)\urcorner}_{(Lan)l_3l_6}(t_3\tau_4^M)D^{(C)\urcorner}_{(Lan)l_4l_7}(t_3\tau_4^M)D^{(C)\urcorner}_{(Lan)l_5l_8}(t_3\tau_4^M) \qquad (5.67)\\
&\left[D^{(C)}_{(Lan)l_3l_6}(\tau_3\tau_4)D^{(C)}_{(Lan)l_4l_7}(\tau_3\tau_4)D^{(C)}_{(Lan)l_5l_8}(\tau_3\tau_4)\right]^M \\
=\;& D^{(C)M}_{(Lan)l_3l_6}(\tau_3^M\tau_4^M)D^{(C)M}_{(Lan)l_4l_7}(\tau_3^M\tau_4^M)D^{(C)M}_{(Lan)l_5l_8}(\tau_3^M\tau_4^M) \qquad (5.68)\\
=\;& D^{(0)(C)M}_{(Lan)l_3l_6}(\tau_3^M\tau_4^M)D^{(0)(C)M}_{(Lan)l_4l_7}(\tau_3^M\tau_4^M)D^{(0)(C)M}_{(Lan)l_5l_8}(\tau_3^M\tau_4^M) \qquad (5.69)
\end{aligned}$$

[Contribution:] Here I will briefly state what this contribution of lowest anharmonic corrections to ballistic current is about. As mentioned many times, anharmonic interactions cannot really be ignored at the device operating temperature but there is overwhelming literature that treats only ballistic current. In the literature, interactions seem to be incorporated unsystematically and transient terms are often not calculated by simply assuming that steady state current wipes out transient current. Thus I did a systematic calculation here showing the current including transient terms for various anharmonic interactions. The transient terms can be checked for survivability by numerically integrating the given current expression. The anharmonic corrections to the current and the ballistic current are seperate terms so the physical effects of anharmonicity can be clearly interpreted once the integrals are solved.

5.3.2 Corrections to Ballistic Noise

We need to warn the reader that the calculations here are much more complicated because noise is a "2-particle" quantity. The current which is a "1-particle" quantity only has self energy corrections and noise has both self energy corrections and vertex corrections.

We recall the (time dependent) noise expression, [6]

$$
\begin{aligned}
S(tt') &= \frac{-\hbar}{2}\sum_{l_1l_2l_3l_4} V^{LC}_{l_1l_2}V^{LC}_{l_3l_4}\lim_{t_1\to t}\lim_{t'_1\to t'} \\
&\quad \times\frac{d}{dt_1}\frac{d}{dt'_1}\left[D_{l_1l_2l_3l_4}(t_1tt'_1t';t_1>t>t'_1>t')+D_{l_1l_2l_3l_4}(t_1tt'_1t';t'_1>t't_1>t)\right]-(J^{LC})^2
\end{aligned} \tag{5.70}
$$

and also recall the expression where the hybrid 2-particle Green's function (in contour time) has been seperated,

$$
\begin{aligned}
& D_{l_1l_2l_3l_4}(\tau_1\tau\tau'_1\tau') \\
= \; & \frac{(-i)^2}{\hbar}\left\langle T_{c_K}\left(u^L_{H^L_0}(l_1\tau_1)u^L_{H^L_0}(l_3\tau'_1)\right)\right\rangle\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C}(l_2\tau)u^C_{H^C}(l_4\tau')\right)\right\rangle \\
& +\frac{(-i)^2}{\hbar}\left(-\frac{i}{\hbar}\right)^2\int_{c_K}d\tau_2d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}\left\langle T_{c_K}\left(u^L_{H^L_0}(l_5\tau_2)u^L_{H^L_0}(l_1\tau_1)\right)\right\rangle \\
& \times\left\langle T_{c_K}\left(u^L_{H^L_0}(l_7\tau_3)u^L_{H^L_0}(l_3\tau'_1)\right)\right\rangle\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C}(l_6\tau_2)u^C_{H^C}(l_8\tau_3)u^C_{H^C}(l_2\tau)u^C_{H^C}(l_4\tau')\right)\right\rangle
\end{aligned} \tag{5.71}
$$

We also recall the expansions (in $H^C_{\rm int}$) where we went from the interaction operator $u^C_{H^C}$ back to the Heisenberg operator u^C_H and to another interaction operator $u^C_{H^C_0}$.

$$
\begin{aligned}
& \left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C}(l_2\tau)u^C_{H^C}(l_4\tau')\right)\right\rangle \\
\approx\; & \left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C_0}(l_2\tau)u^C_{H^C_0}(l_4\tau')\right)\right\rangle \\
& +\left(-\frac{i}{\hbar}\right)\int_{c_K+c_M}d\tau_3\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^C_{{\rm int}H^C_0}(\tau_3)u^C_{H^C_0}(l_2\tau)u^C_{H^C_0}(l_4\tau')\right)\right\rangle \\
& +\left(-\frac{i}{\hbar}\right)^2\frac{1}{2!}\int_{c_K+c_M}d\tau_3d\tau_4\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^C_{{\rm int}H^C_0}(\tau_3)H^C_{{\rm int}H^C_0}(\tau_4)u^C_{H^C_0}(l_2\tau)u^C_{H^C_0}(l_4\tau')\right)\right\rangle
\end{aligned} \tag{5.72}
$$

$$
\begin{aligned}
& \left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C}(l_6\tau_2)u^C_{H^C}(l_5\tau_3)u^C_{H^C}(l_2\tau)u^C_{H^C}(l_4\tau')\right)\right\rangle \\
\approx\; & \left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H^C_0}(l_6\tau_2)u^C_{H^C_0}(l_5\tau_3)u^C_{H^C_0}(l_2\tau)u^C_{H^C_0}(l_4\tau')\right)\right\rangle \\
& +\left(-\frac{i}{\hbar}\right)\int_{c_K+c_M}d\tau_5\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^C_{{\rm int}H^C_0}(\tau_5)u^C_{H^C_0}(l_6\tau_2)u^C_{H^C_0}(l_5\tau_3)u^C_{H^C_0}(l_2\tau)u^C_{H^C_0}(l_4\tau')\right)\right\rangle \\
& +\left(-\frac{i}{\hbar}\right)^2\frac{1}{2!}\int_{c_K+c_M}d\tau_5d\tau_6\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^C_{{\rm int}H^C_0}(\tau_5)H^C_{{\rm int}H^C_0}(\tau_6)\right.\right. \\
& \left.\left.\times\; u^C_{H^C_0}(l_6\tau_2)u^C_{H^C_0}(l_5\tau_3)u^C_{H^C_0}(l_2\tau)u^C_{H^C_0}(l_4\tau')\right)\right\rangle
\end{aligned} \tag{5.73}
$$

[6] Again we use the full time dependent expression $S(tt')$ instead of the DC expression because we want to probe the transient behavior as well. The full $S(tt')$ can capture the transients when the leads are attached to the interacting central device at t_0.

We have already seen that in the ballistic noise calculation, only the first term in each expansion is required. Then the component $t_1 > t > t_1' > t'$ and the component $t_1' > t' > t_1 > t$ are taken and the DC limit is taken to give the ballistic noise formula. We denote the terms that gives the ballistic noise formula as $D^{(Lan)}_{l_1l_2l_3l_4}(\tau_1\tau\tau_1'\tau')$.

$$\begin{aligned}
&D^{(Lan)}_{l_1l_2l_3l_4}(\tau_1\tau\tau_1'\tau')\\
\equiv\;& \frac{(-i)^2}{\hbar}\left\langle T_{c_K}\left(u^L_{H_0^L}(l_1\tau_1)u^L_{H_0^L}(l_3\tau_1')\right)\right\rangle\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H_0^C}(l_2\tau)u^C_{H_0^C}(l_4\tau')\right)\right\rangle\\
&+\frac{(-i)^2}{\hbar}\left(-\frac{i}{\hbar}\right)^2\int_{c_K}d\tau_2d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}\left\langle T_{c_K}\left(u^L_{H_0^L}(l_5\tau_2)u^L_{H_0^L}(l_1\tau_1)\right)\right\rangle\\
&\times\left\langle T_{c_K}\left(u^L_{H_0^L}(l_7\tau_3)u^L_{H_0^L}(l_3\tau_1')\right)\right\rangle\left\langle T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}u^C_{H_0^C}(l_6\tau_2)u^C_{H_0^C}(l_8\tau_3)u^C_{H_0^C}(l_2\tau)u^C_{H_0^C}(l_4\tau')\right)\right\rangle
\end{aligned}\tag{5.74}$$

Thus it is noted that there are 2 types of correction terms for noise as mentioned earlier. The first expansion involves the so-called self energy corrections which have already been calculated for the corrections to current. The second expansion involves the so-called vertex corrections. The vertex corrections are very complicated and so we will only calculate the corrections due to $V^{(3ph)^2}$. It will be seen that the calculations are straightforward but very tedious.

The 2-particle Green's function, ready for perturbative calculations in $H^C_{\rm int}$ is,

$$\begin{aligned}
&D_{l_1l_2l_3l_4}(\tau_1\tau\tau_1'\tau')\\
=\;& D^{(Lan)}_{l_1l_2l_3l_4}(\tau_1\tau\tau_1'\tau')+\frac{(-i)^2}{\hbar}\left\langle T_{c_K}\left(u^L_{H_0^L}(l_1\tau_1)u^L_{H_0^L}(l_3\tau_1')\right)\right\rangle\\
&\times\left\{\left(-\frac{i}{\hbar}\right)\int_{c_K+c_M}d\tau_3\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^C_{{\rm int}H_0^C}(\tau_3)u^C_{H_0^C}(l_2\tau)u^C_{H_0^C}(l_4\tau')\right)\right\rangle\right.\\
&\left.+\left(-\frac{i}{\hbar}\right)^2\frac{1}{2!}\int_{c_K+c_M}d\tau_3d\tau_4\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^C_{{\rm int}H_0^C}(\tau_3)H^C_{{\rm int}H_0^C}(\tau_4)u^C_{H_0^C}(l_2\tau)u^C_{H_0^C}(l_4\tau')\right)\right\rangle\right\}\\
&+\frac{(-i)^2}{\hbar}\left(-\frac{i}{\hbar}\right)^2\int_{c_K}d\tau_2d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}\left\langle T_{c_K}\left(u^L_{H_0^L}(l_5\tau_2)u^L_{H_0^L}(l_1\tau_1)\right)\right\rangle\left\langle T_{c_K}\left(u^L_{H_0^L}(l_7\tau_3)u^L_{H_0^L}(l_3\tau_1')\right)\right\rangle\\
&\times\left\{\left(-\frac{i}{\hbar}\right)\int_{c_K+c_M}d\tau_5\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^C_{{\rm int}H_0^C}(\tau_5)u^C_{H_0^C}(l_6\tau_2)u^C_{H_0^C}(l_5\tau_3)u^C_{H_0^C}(l_2\tau)u^C_{H_0^C}(l_4\tau')\right)\right\rangle\right.\\
&+\left(-\frac{i}{\hbar}\right)^2\frac{1}{2!}\int_{c_K+c_M}d\tau_5d\tau_6\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^C_{{\rm int}H_0^C}(\tau_5)H^C_{{\rm int}H_0^C}(\tau_6)\right.\right.\\
&\left.\left.\left.\times\; u^C_{H_0^C}(l_6\tau_2)u^C_{H_0^C}(l_5\tau_3)u^C_{H_0^C}(l_2\tau)u^C_{H_0^C}(l_4\tau')\right)\right\rangle\right\}
\end{aligned}\tag{5.75}$$

5.3.2.1 Lowest Corrections from 3-Phonon Interaction $(V^{(3ph)^2})$*

Since there are $3u^C$s in $H^C_{\rm int} = H^{(3ph)}$, only the quadratic term in $H^C_{\rm int}$ survives as the first non-zero correction. We use the definition, as usual,

$$D^{(0)(L)}_{l_1l_3} \equiv -\frac{i}{\hbar}\left\langle T_{c_K}\left(u^L_{H_0^L}(l_1\tau_1)u^L_{H_0^L}(l_3\tau_1')\right)\right\rangle \tag{5.76}$$

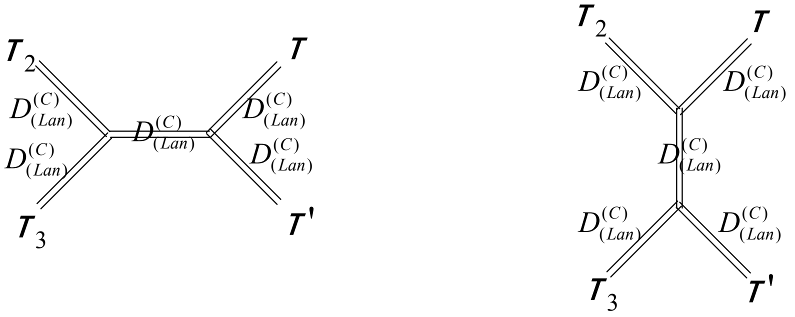


Figure 5.8: *Diagrams for the $V^{(3ph)^2}$ vertex correction.*

$$
\begin{aligned}
& D_{l_1l_2l_3l_4}(\tau_1\tau\tau_1'\tau') \\
= \; & D^{(Lan)}_{l_1l_2l_3l_4}(\tau_1\tau\tau_1'\tau') + (-i)D^{(0)(L)}_{l_1l_3}(\tau_1\tau_1')\left(-\frac{i}{\hbar}\right)^2\frac{1}{2!}\int_{c_K+c_M} d\tau_3 d\tau_4 \\
& \times\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^{(3ph)}_{H_0^C}(\tau_3)H^{(3ph)}_{H_0^C}(\tau_4)u^C_{H_0^C}(l_2\tau)u^C_{H_0^C}(l_4\tau')\right)\right\rangle \\
& +\frac{(-i)^2}{\hbar}\left(-\frac{i}{\hbar}\right)^2\int_{c_K}d\tau_2 d\tau_3\sum_{l_5l_6l_7l_8}V^{LC}_{l_5l_6}V^{LC}_{l_7l_8}D^{(0)(L)}_{l_5l_1}(\tau_2\tau_1)D^{(0)(L)}_{l_7l_3}(\tau_3\tau_1')\left(-\frac{i}{\hbar}\right)^2\frac{1}{2!}\int_{c_K+c_M}d\tau_5 d\tau_6 \\
& \times\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}H^{(3ph)}_{H_0^C}(\tau_5)H^{(3ph)}_{H_0^C}(\tau_6)u^C_{H_0^C}(l_6\tau_2)u^C_{H_0^C}(l_5\tau_3)u^C_{H_0^C}(l_2\tau)u^C_{H_0^C}(l_4\tau')\right)\right\rangle
\end{aligned} \tag{5.77}
$$

The 2nd term is the self energy correction and the 3rd term is the vertex correction. The self energy correction has been calculated in the section on current correction and we will just carry over the result.

$$
\begin{aligned}
& \text{Self Energy Correction} \\
= \; & \frac{(-i)^3}{\hbar^2 2!}D^{(0)(L)}_{l_1l_3}(\tau_1\tau_1')\left(\frac{1}{3!}\right)^2\sum_{l_5l_6l_7l_8l_9l_{10}}\Phi^{(3)}_{l_5l_6l_7}\Phi^{(3)}_{l_8l_9l_{10}}\int_{c_K+c_M}d\tau_3 d\tau_4\left\langle T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau''\tilde{H}^{LC}(\tau'')}\right.\right. \\
& \times\left.\left. u^C_{H_0^C}(l_5\tau_3)u^C_{H_0^C}(l_6\tau_3)u^C_{H_0^C}(l_7\tau_3)u^C_{H_0^C}(l_8\tau_4)u^C_{H_0^C}(l_9\tau_4)u^C_{H_0^C}(l_{10}\tau_4)u^C_{H_0^C}(l_2\tau)u^C_{H_0^C}(l_4\tau')\right)\right\rangle
\end{aligned} \tag{5.78}
$$

$$
\begin{aligned}
| \; & \text{we carry over the result from } V^{(3ph)^2} \text{ current correction} \\
= \; & \frac{i\hbar^2}{2}D^{(0)(L)}_{l_1l_3}(\tau_1\tau_1')\sum_{l_5l_6l_7l_8l_9l_{10}}\Phi^{(3)}_{l_5l_6l_7}\Phi^{(3)}_{l_8l_9l_{10}}\int_{c_K+c_M}d\tau_3\int_{c_K+c_M}d\tau_4 \\
& \times D^{(C)}_{(Lan)l_2l_5}(\tau\tau_3)\left[D^{(C)}_{(Lan)l_6l_8}(\tau_3\tau_4)D^{(C)}_{(Lan)l_7l_9}(\tau_3\tau_4)\right]D^{(C)}_{(Lan)l_{10}l_4}(\tau_4\tau')
\end{aligned} \tag{5.79}
$$

For the vertex correction, we only consider diagrams with no "lollipops" since they are shown to vanish in the earlier section on current corrections. Two distinct types of diagrams are obtained.

Now the combinatorical factor. There are 3 ways to choose a τ_5 to pair with τ_2 and 2 ways to choose one of 2 remaining τ_5s to pair with τ_3. The same 6 combinations occur for τ_6. Swapping τ_5 and τ_6 gives a factor of 2. $6\times 6\times 2 = 72$. The second diagram has the same combinatorical factor of 72.

Vertex Correction

$$= \frac{(-i)^2}{\hbar}\left(-\frac{i}{\hbar}\right)^2 \frac{1}{2!} \sum_{l_5 l_6 l_7 l_8} V^{LC}_{l_5 l_6} V^{LC}_{l_7 l_8} \int_{c_K} d\tau_2 d\tau_3 D^{(0)(L)}_{l_5 l_1}(\tau_2 \tau_1) D^{(0)(L)}_{l_7 l_3}(\tau_3 \tau_1')$$
$$\times \int_{c_K + c_M} d\tau_5 d\tau_6 \left(\frac{1}{3!}\right)^2 \sum_{l_9 l_{10} l_{11} l_{12} l_{13} l_{14}} \Phi^{(3)}_{l_9 l_{10} l_{11}} \Phi^{(3)}_{l_{12} l_{13} l_{14}}$$
$$\times \Big\langle T_{c_K + c_M} \Big(e^{-\frac{i}{\hbar}\int_{c_K} d\tau'' \tilde{H}^{LC}(\tau'')} u^C_{H_0^C}(l_9 \tau_5) u^C_{H_0^C}(l_{10}\tau_5) u^C_{H_0^C}(l_{11}\tau_5)$$
$$\times u^C_{H_0^C}(l_{12}\tau_6) u^C_{H_0^C}(l_{13}\tau_6) u^C_{H_0^C}(l_{14}\tau_6) u^C_{H_0^C}(l_6\tau_2) u^C_{H_0^C}(l_8\tau_3) u^C_{H_0^C}(l_2\tau) u^C_{H_0^C}(l_4\tau') \Big) \Big\rangle \tag{5.80}$$
$$= i\hbar^2 \sum_{l_5 l_6 l_7 l_8 l_9 l_{10} l_{11} l_{12} l_{13} l_{14}} V^{LC}_{l_5 l_6} V^{LC}_{l_7 l_8} \Phi^{(3)}_{l_9 l_{10} l_{11}} \Phi^{(3)}_{l_{12} l_{13} l_{14}} \int_{c_K} d\tau_2 d\tau_3 \int_{c_K + c_M} d\tau_5 d\tau_6 D^{(0)(L)}_{l_5 l_1}(\tau_2 \tau_1) D^{(0)(L)}_{l_7 l_3}(\tau_3 \tau_1')$$
$$\times \Big\{ D^{(C)}_{(Lan) l_6 l_9}(\tau_2 \tau_5) D^{(C)}_{(Lan) l_8 l_{10}}(\tau_3 \tau_5) D^{(C)}_{(Lan) l_{11} l_{12}}(\tau_5 \tau_6) D^{(C)}_{(Lan) l_{13} l_2}(\tau_6 \tau) D^{(C)}_{(Lan) l_{14} l_4}(\tau_6 \tau')$$
$$+ D^{(C)}_{(Lan) l_6 l_9}(\tau_2 \tau_5) D^{(C)}_{(Lan) l_{10} l_2}(\tau_5 \tau) D^{(C)}_{(Lan) l_{11} l_{12}}(\tau_5 \tau_6) D^{(C)}_{(Lan) l_{13} l_8}(\tau_6 \tau_3) D^{(C)}_{(Lan) l_{14} l_4}(\tau_6 \tau') \Big\} \tag{5.81}$$

The perturbation is done and we need to go back to real time where 2 components are required. They are the $t_1 > t > t_1' > t'$ component and the $t_1' > t' > t_1 > t$ component. We carry out Langreth's theorem on the self energy correction term and the vertex correction term seperately. We will soon see that the vertex corrections will get so complicated that we decided not to proceed further as it deserves to be a Master's project of its own.

Self energy correction ($t_1 > t > t_1' > t'$) component

$$= \frac{i\hbar^2}{2} D^{(0)(L)>}_{l_1 l_3}(t_1 t_1') \sum_{l_5 l_6 l_7 l_8 l_9 l_{10}} \Phi^{(3)}_{l_5 l_6 l_7} \Phi^{(3)}_{l_8 l_9 l_{10}}$$
$$\times \left(\int_{c_K + c_M} d\tau_3 \int_{c_K + c_M} d\tau_4 D^{(C)}_{(Lan) l_2 l_5}(\tau \tau_3) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3 \tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3 \tau_4) \right] D^{(C)}_{(Lan) l_{10} l_4}(\tau_4 \tau') \right)_{t > t'} \tag{5.82}$$
$$= \frac{i\hbar^2}{2} D^{(0)(L)>}_{l_1 l_3}(t_1 t_1') \sum_{l_5 l_6 l_7 l_8 l_9 l_{10}} \Phi^{(3)}_{l_5 l_6 l_7} \Phi^{(3)}_{l_8 l_9 l_{10}}$$
$$\times \Big\{ \int_{t_0}^{\infty} dt_3 \int_{t_0}^{\infty} dt_4 D^{(C)R}_{(Lan) l_2 l_5}(t t_3) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3 \tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3 \tau_4) \right]^R D^{(C)>}_{(Lan) l_1 0 l_4}(t_4 t')$$
$$+ \int_{t_0}^{\infty} dt_3 \int_{t_0}^{\infty} dt_4 D^{(C)R}_{(Lan) l_2 l_5}(t t_3) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3 \tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3 \tau_4) \right]^> D^{(C)A}_{(Lan) l_1 0 l_4}(t_4 t')$$
$$+ \int_{t_0}^{\infty} dt_3 \int_{t_0}^{\infty} dt_4 D^{(C)>}_{(Lan) l_2 l_5}(t t_3) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3 \tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3 \tau_4) \right]^A D^{(C)A}_{(Lan) l_1 0 l_4}(t_4 t')$$
$$+ \int_{t_0}^{t_0 - i\hbar\beta^C} d\tau_3^M \int_{t_0}^{\infty} dt_4 D^{(C)\urcorner}_{(Lan) l_2 l_5}(t \tau_3^M) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3 \tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3 \tau_4) \right]^{\ulcorner} D^{(C)A}_{(Lan) l_1 0 l_4}(t_4 t')$$
$$+ \int_{t_0}^{\infty} dt_3 \int_{t_0}^{t_0 - i\hbar\beta^C} d\tau_4^M D^{(C)R}_{(Lan) l_2 l_5}(t t_3) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3 \tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3 \tau_4) \right]^{\urcorner} D^{(C)\ulcorner}_{(Lan) l_1 0 l_4}(\tau_4^M t')$$
$$+ \int_{t_0}^{t_0 - i\hbar\beta^C} d\tau_3^M \int_{t_0}^{t_0 - i\hbar\beta^C} d\tau_4^M D^{(C)\urcorner}_{(Lan) l_2 l_5}(t \tau_3^M) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3 \tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3 \tau_4) \right]^M D^{(C)\ulcorner}_{(Lan) l_1 0 l_4}(\tau_4^M t') \Big\} \tag{5.83}$$

Self energy correction ($t_1' > t' > t_1 > t$) component

$$
\begin{aligned}
= \; & \frac{i\hbar^2}{2} D^{(0)(L)<}_{l_1 l_3}(t_1 t_1') \sum_{l_5 l_6 l_7 l_8 l_9 l_{10}} \Phi^{(3)}_{l_5 l_6 l_7} \Phi^{(3)}_{l_8 l_9 l_{10}} \\
& \times \left(\int_{c_K + c_M} d\tau_3 \int_{c_K + c_M} d\tau_4 D^{(C)}_{(Lan) l_2 l_5}(\tau\tau_3) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3\tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3\tau_4) \right] D^{(C)}_{(Lan) l_{10} l_4}(\tau_4 \tau') \right)_{t'>t} \qquad (5.84) \\
= \; & \frac{i\hbar^2}{2} D^{(0)(L)<}_{l_1 l_3}(t_1 t_1') \sum_{l_5 l_6 l_7 l_8 l_9 l_{10}} \Phi^{(3)}_{l_5 l_6 l_7} \Phi^{(3)}_{l_8 l_9 l_{10}} \\
& \times \left\{ \int_{t_0}^{\infty} dt_3 \int_{t_0}^{\infty} dt_4 D^{(C)R}_{(Lan) l_2 l_5}(t t_3) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3\tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3\tau_4) \right]^R D^{(C)<}_{(Lan) l_1 0 l_4}(t_4 t') \right. \\
& + \int_{t_0}^{\infty} dt_3 \int_{t_0}^{\infty} dt_4 D^{(C)R}_{(Lan) l_2 l_5}(t t_3) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3\tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3\tau_4) \right]^< D^{(C)A}_{(Lan) l_1 0 l_4}(t_4 t') \\
& + \int_{t_0}^{\infty} dt_3 \int_{t_0}^{\infty} dt_4 D^{(C)<}_{(Lan) l_2 l_5}(t t_3) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3\tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3\tau_4) \right]^A D^{(C)A}_{(Lan) l_1 0 l_4}(t_4 t') \\
& + \int_{t_0}^{t_0 - i\hbar\beta^C} d\tau_3^M \int_{t_0}^{\infty} dt_4 D^{(C)\urcorner}_{(Lan) l_2 l_5}(t \tau_3^M) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3\tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3\tau_4) \right]^{\ulcorner} D^{(C)A}_{(Lan) l_1 0 l_4}(t_4 t') \\
& + \int_{t_0}^{\infty} dt_3 \int_{t_0}^{t_0 - i\hbar\beta^C} d\tau_4^M D^{(C)R}_{(Lan) l_2 l_5}(t t_3) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3\tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3\tau_4) \right]^{\urcorner} D^{(C)\ulcorner}_{(Lan) l_1 0 l_4}(\tau_4^M t') \\
& \left. + \int_{t_0}^{t_0 - i\hbar\beta^C} d\tau_3^M \int_{t_0}^{t_0 - i\hbar\beta^C} d\tau_4^M D^{(C)\urcorner}_{(Lan) l_2 l_5}(t \tau_3^M) \left[D^{(C)}_{(Lan) l_6 l_8}(\tau_3\tau_4) D^{(C)}_{(Lan) l_7 l_9}(\tau_3\tau_4) \right]^M D^{(C)\ulcorner}_{(Lan) l_1 0 l_4}(\tau_4^M t') \right\}
\end{aligned}
$$

(5.85)

The taking of components of the vertex correction terms is very complicated, i.e. the real time expressions of the vertex correction terms are very complicated. Hence we will only show part of the calculation for the first term and we will use a simplified notation. The contour shown in the figure is needed the purpose. Be reminded that τ_2 and τ_3 runs over c_K only and τ_5 and τ_6 runs over $c_K + c_M$.

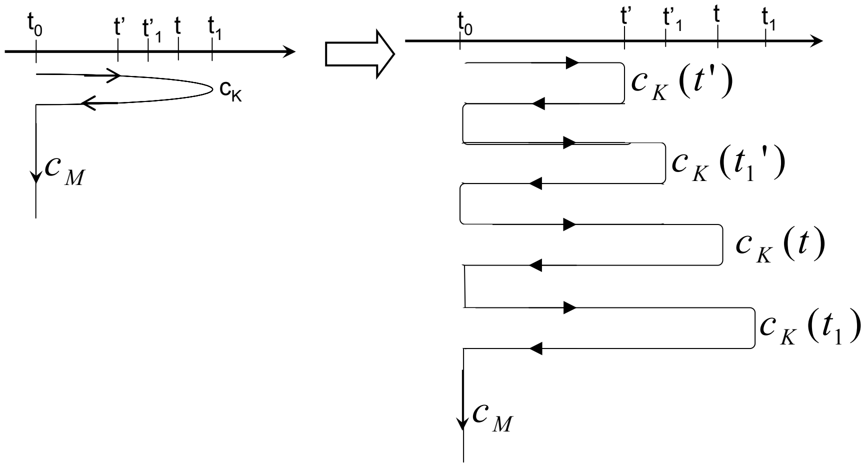


Figure 5.9: *Contour used to calculate the $t_1 > t > t_1' > t'$ vertex correction component.*

Vertex Correction ($t_1 > t > t_1' > t'$) component 1st term

$$
\begin{aligned}
&= i\hbar^2 \sum_{l_5 l_6 l_7 l_8 l_9 l_{10} l_{11} l_{12} l_{13} l_{14}} V^{LC}_{l_5 l_6} V^{LC}_{l_7 l_8} \Phi^{(3)}_{l_9 l_{10} l_{11}} \Phi^{(3)}_{l_{12} l_{13} l_{14}} \int_{c_K} d\tau_2 d\tau_3 \int_{c_K + c_M} d\tau_5 d\tau_6 D^{(0)(L)}_{l_5 l_1}(\tau_2 \tau_1) D^{(0)(L)}_{l_7 l_3}(\tau_3 \tau_1') \\
&\quad \times D^{(C)}_{(Lan) l_6 l_9}(\tau_2 \tau_5) D^{(C)}_{(Lan) l_8 l_{10}}(\tau_3 \tau_5) D^{(C)}_{(Lan) l_{11} l_{12}}(\tau_5 \tau_6) D^{(C)}_{(Lan) l_{13} l_2}(\tau_6 \tau) D^{(C)}_{(Lan) l_{14} l_4}(\tau_6 \tau') \qquad (5.86)
\end{aligned}
$$

| we introduce a simplified notation

$$
\Rightarrow \int_{c_K} d\tau_2 d\tau_3 \int_{c_K + c_M} d\tau_5 d\tau_6 D^L(\tau_2 t_1) D^L(\tau_3 t_1') D^C(\tau_2 \tau_5) D^C(\tau_3 \tau_5) D^C(\tau_5 \tau_6) D^C(\tau_6 t) D^C(\tau_6 t') \qquad (5.87)
$$

$$
\begin{aligned}
&= \left(\int_{c_K(t')} d\tau_2 + \int_{c_K(t_1')} d\tau_2 + \int_{c_K(t)} d\tau_2 + \int_{c_K(t_1)} d\tau_2 \right) \\
&\quad \times \left(\int_{c_K(t')} d\tau_3 + \int_{c_K(t_1')} d\tau_3 + \int_{c_K(t)} d\tau_3 + \int_{c_K(t_1)} d\tau_3 \right) \\
&\quad \times \left(\int_{c_K(t')} d\tau_5 + \int_{c_K(t_1')} d\tau_5 + \int_{c_K(t)} d\tau_5 + \int_{c_K(t_1)} d\tau_5 + \int_{c_M} d\tau_5^M \right) \\
&\quad \times \left(\int_{c_K(t')} d\tau_6 + \int_{c_K(t_1')} d\tau_6 + \int_{c_K(t)} d\tau_6 + \int_{c_K(t_1)} d\tau_6 + \int_{c_M} d\tau_6^M \right) \\
&\quad \times D^L(\tau_2 t_1) D^L(\tau_3 t_1') D^C(\tau_2 \tau_5) D^C(\tau_3 \tau_5) D^C(\tau_5 \tau_6) D^C(\tau_6 t) D^C(\tau_6 t') \qquad (5.88)
\end{aligned}
$$

It is obvious that there is a large number of terms here. Note that τ_2 and τ_3 do not convolve and actually many of the terms are zero due to the lack of a term like $D(\tau_2 \tau_3)$ that directly convolves them. We give an example of such a vanishing term.

A Vanishing Term

$$
\begin{aligned}
&= \int_{c_K(t')} d\tau_2 \int_{c_K(t_1')} d\tau_3 \int_{c_K(t_1')} d\tau_5 \int_{c_M} d\tau_6^M \\
&\quad \times D^{L<}(\tau_2 t_1) D^L(\tau_3 t_1') D^{C<}(\tau_2 \tau_5) D^C(\tau_3 \tau_5) D^{C\urcorner}(\tau_5 \tau_6^M) D^{C\ulcorner}(\tau_6^M t) D^{C\ulcorner}(\tau_6^M t') \qquad (5.89) \\
&= \int_{c_K(t')} d\tau_2 \left(\int_{\overrightarrow{c_K(t_1')}} d\tau_3 + \int_{\overleftarrow{c_K(t_1')}} d\tau_3 \right) \left(\int_{\overrightarrow{c_K(t_1')}} d\tau_5 + \int_{\overleftarrow{c_K(t_1')}} d\tau_5 \right) \int_{c_M} d\tau_6^M \\
&\quad \times D^{L<}(\tau_2 t_1) D^L(\tau_3 t_1') D^{C<}(\tau_2 \tau_5) D^C(\tau_3 \tau_5) D^{C\urcorner}(\tau_5 \tau_6^M) D^{C\ulcorner}(\tau_6^M t) D^{C\ulcorner}(\tau_6^M t') \qquad (5.90) \\
&= \int_{c_K(t')} d\tau_2 \int_{\overrightarrow{c_K(t_1')}} d\tau_3 \int_{\overrightarrow{c_K(t_1')}} d\tau_5 \int_{c_M} d\tau_6^M \\
&\quad \times D^{L<}(\tau_2 t_1) D^{L<}(\tau_3 t_1') D^{C<}(\tau_2 \tau_5) D^{Ct}(\tau_3 \tau_5) D^{C\urcorner}(\tau_5 \tau_6^M) D^{C\ulcorner}(\tau_6^M t) D^{C\ulcorner}(\tau_6^M t') \\
&\quad + \int_{c_K(t')} d\tau_2 \int_{\overrightarrow{c_K(t_1')}} d\tau_3 \int_{\overleftarrow{c_K(t_1')}} d\tau_5 \int_{c_M} d\tau_6^M \\
&\quad \times D^{L<}(\tau_2 t_1) D^{L<}(\tau_3 t_1') D^{C<}(\tau_2 \tau_5) D^{C<}(\tau_3 \tau_5) D^{C\urcorner}(\tau_5 \tau_6^M) D^{C\ulcorner}(\tau_6^M t) D^{C\ulcorner}(\tau_6^M t') \\
&\quad + \int_{c_K(t')} d\tau_2 \int_{\overleftarrow{c_K(t_1')}} d\tau_3 \int_{\overrightarrow{c_K(t_1')}} d\tau_5 \int_{c_M} d\tau_6^M \\
&\quad \times D^{L<}(\tau_2 t_1) D^{L<}(\tau_3 t_1') D^{C<}(\tau_2 \tau_5) D^{C>}(\tau_3 \tau_5) D^{C\urcorner}(\tau_5 \tau_6^M) D^{C\ulcorner}(\tau_6^M t) D^{C\ulcorner}(\tau_6^M t') \\
&\quad + \int_{c_K(t')} d\tau_2 \int_{\overleftarrow{c_K(t_1')}} d\tau_3 \int_{\overleftarrow{c_K(t_1')}} d\tau_5 \int_{c_M} d\tau_6^M \\
&\quad \times D^{L<}(\tau_2 t_1) D^{L<}(\tau_3 t_1') D^{C<}(\tau_2 \tau_5) D^{C\bar{t}}(\tau_3 \tau_5) D^{C\urcorner}(\tau_5 \tau_6^M) D^{C\ulcorner}(\tau_6^M t) D^{C\ulcorner}(\tau_6^M t') \qquad (5.91)
\end{aligned}
$$

which means all the functions are completely determined in each term even before the integral $\int_{c_K(t')} d\tau_2$

is broken up. Thus the same expression will go under the integral $\int_{c_K(t')} d\tau_2 = \int_{\overrightarrow{c_K(t')}} d\tau_2 + \int_{\overleftarrow{c_K(t')}} d\tau_2$ $= \int_{t_0}^{t'} dt_2 + \int_{t'}^{t_0} dt_2$ which gives zero.

We illustrate another term which is non-vanishing.

$$\begin{aligned}
& \text{A Non-vanishing Term} \\
= & \int_{c_K(t')} d\tau_2 \int_{c_K(t')} d\tau_3 \int_{c_K(t')} d\tau_5 \int_{c_K(t')} d\tau_6 \\
& \times D^{L<}(\tau_2 t_1) D^{L<}(\tau_3 t_1') D^{C}(\tau_2 \tau_5) D^{C}(\tau_3 \tau_5) D^{C}(\tau_5 \tau_6) D^{C<}(\tau_6 t) D^{C}(\tau_6 t') \qquad (5.92) \\
| \; & \text{break up } c_K(t') = \overrightarrow{c_K(t')} + \overleftarrow{c_K(t')} \\
= & \left(\int_{\overrightarrow{c_K(t')}} d\tau_2 + \int_{\overleftarrow{c_K(t')}} d\tau_2 \right) \left(\int_{\overrightarrow{c_K(t')}} d\tau_3 + \int_{\overleftarrow{c_K(t')}} d\tau_3 \right) \left(\int_{\overrightarrow{c_K(t')}} d\tau_5 + \int_{\overleftarrow{c_K(t')}} d\tau_5 \right) \\
& \times \left(\int_{\overrightarrow{c_K(t')}} d\tau_6 + \int_{\overleftarrow{c_K(t')}} d\tau_6 \right) D^{L<}(\tau_2 t_1) D^{L<}(\tau_3 t_1') D^{C}(\tau_2 \tau_5) D^{C}(\tau_3 \tau_5) D^{C}(\tau_5 \tau_6) D^{C<}(\tau_6 t) D^{C}(\tau_6 t') \\
& \qquad (5.93)
\end{aligned}$$

Thus there are 16 terms actually and we work out 2 terms just for interest.

$$\begin{aligned}
& \text{A Non-vanishing Term (1st and 2nd)} \\
= & \int_{\overrightarrow{c_K(t')}} d\tau_2 \int_{\overrightarrow{c_K(t')}} d\tau_3 \int_{\overrightarrow{c_K(t')}} d\tau_5 \left(\int_{\overrightarrow{c_K(t')}} d\tau_6 + \int_{\overleftarrow{c_K(t')}} d\tau_6 \right) \\
& \times D^{L<}(\tau_2 t_1) D^{L<}(\tau_3 t_1') D^{Ct}(\tau_2 \tau_5) D^{Ct}(\tau_3 \tau_5) D^{Ct}(\tau_5 \tau_6) D^{C<}(\tau_6 t) D^{C}(\tau_6 t') \qquad (5.94) \\
| \; & \text{write integration limits explicitly and write in real time} \\
= & \int_{t_0}^{t'} dt_2 \int_{t_0}^{t'} dt_3 \int_{t_0}^{t'} dt_5 \int_{t_0}^{t'} dt_6 \\
& \times D^{L<}(t_2 t_1) D^{L<}(t_3 t_1') D^{Ct}(t_2 t_5) D^{Ct}(t_3 t_5) D^{Ct}(t_5 t_6) D^{C<}(t_6 t) \left(D^{C<}(t_6 t') - D^{C>}(t_6 t') \right) \qquad (5.95)
\end{aligned}$$

By now it is clear that further evaluation is straightforward but tedious, so we shall not proceed further. Hopefully an interested Master student can pick up from here. We will just describe the remaining steps. The remaining 14 terms need to be evaluated and the second term of the $(t_1 > t > t_1' > t')$ component is to be calculated, then we require the $(t_1' > t' > t_1 > t)$ component of the vertex correction. The self energy corrections and the vertex corrections are substituted into $D_{l_1 l_2 l_3 l_4}(t_1 t t_1' t'; t_1 > t > t_1' > t')$ and $D_{l_1 l_2 l_3 l_4}(t_1 t t_1' t'; t_1' > t' > t_1 > t)$ which are then substituted into $S(tt')$. Beyond the terms involving $D^{(Lan)}_{l_1 l_2 l_3 l_4}$ are the correction terms to ballistic noise.

[Contribution:] Here I will briefly state what this contribution of lowest anharmonic corrections to ballistic noise is about. As mentioned earlier in section 3.2.2, information on noise may give extra information on the current. In this aspect, information on anharmonic corrected noise may give extra information on the anharmonic corrected current. Again, no systematic inclusion of interaction into (DC) noise is found in the literature and I provided one here but it is extremely complicated so its physical complications are unclear.

5.4 NEGF Treatment: Functional Derivative formulation of Anharmonicity

5.4.1 (Functional Derivative) Hedin-like equations for Anharmonicity

We follow [Kwok1968] in this section. (See [Leeuwen2005]) For Coulomb interaction, a set of Hedin equations was derived and self consistent self energies were derived naturally. These self energies are shown to obey the conservation laws. Thus the natural question to ask is "Can we derive Hedin-like equations for most known interactions?" The answer is affirmative. Hedin-like equations for electron-phonon interaction is described in the chapter on electron-phonon interaction. It has the added bonus that it can circumvent the Born-Oppenheimer approximation! Hedin-like equations for phonon-phonon interaction is derived in this section and it will be applied to kinetic theory. Boltzmann kinetic equation for phonon-phonon interaction is derived and it is very clear on how to go beyond that.

[Objective:] Use the techniques of NEGF to turn the many-body $H_0 + H_{\text{int}}$ problem into a set of exact functional derivative equations. In the case where H_{int} is the Coulomb interaction, these functional derivative equations are called Hedin's equations. More precisely, we have the Hamiltonian terms $H_0 + H_{\text{int}} + V(t)\theta(t - t_0)$ in NEGF and we are going to use $V(t)$ like a variational parameter to generate the function derivative equations, then set $V(t) = 0$ at the end. This method is also called the Schwinger source field method.

Explicitly the Hamiltonian is,

$$H(t) = H_0 + H^{(3ph)} + H^{(4ph)} + \sum_{j\vec{q}} J_{j\vec{q}}(t) Q_{j\vec{q}}\, \theta(t - t_0) \tag{5.96}$$

where H_0 is the usual harmonic part and the other definitions are

$$\begin{aligned} H[J] &\equiv H(t) && (5.97)\\ H_{\text{int}} &\equiv H^{(3ph)} + H^{(4ph)} && (5.98)\\ V(t) &\equiv \sum_{j\vec{q}} J_{j\vec{q}}(t) Q_{j\vec{q}} && (5.99)\\ H[J=0] &\equiv H_0 + H_{\text{int}} = H_0 + H^{(3ph)} + H^{(4ph)} && (5.100) \end{aligned}$$

The explanations for the various terms are[7]

$$\begin{aligned} J_{j\vec{q}} &= \text{time-dependent source term} && (5.103)\\ H^{(3ph)} &= \frac{1}{3!} \sum_{j_1\vec{q}_1} \sum_{j_2\vec{q}_2} \sum_{j_3\vec{q}_3} \tilde{V}^{(3ph)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} Q_{j_1\vec{q}_1} Q_{j_2\vec{q}_2} Q_{j_3\vec{q}_3} && (5.104)\\ H^{(4ph)} &= \frac{1}{4!} \sum_{j_1\vec{q}_1} \sum_{j_2\vec{q}_2} \sum_{j_3\vec{q}_3} \sum_{j_4\vec{q}_4} \tilde{V}^{(4ph)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} Q_{j_1\vec{q}_1} Q_{j_2\vec{q}_2} Q_{j_3\vec{q}_3} Q_{j_4\vec{q}_4} && (5.105) \end{aligned}$$

[7] Througout the thesis, $V^{(3ph)}$ and $V^{(4ph)}$ are defined when the Hamiltonian is written in terms of $a, a^\dagger$ variables. So now we are using $\tilde{V}^{(3ph)}$ and $\tilde{V}^{(4ph)}$ with the relationship,

$$\begin{aligned} \tilde{V}^{(3ph)}_{1,2,3} &= V^{(3ph)} \sqrt{\frac{2^3 \omega_1 \omega_2 \omega_3}{\hbar^3}} && (5.101)\\ \tilde{V}^{(4ph)}_{1,2,3,4} &= V^{(4ph)} \sqrt{\frac{2^4 \omega_1 \omega_2 \omega_3 \omega_4}{\hbar^4}} && (5.102) \end{aligned}$$

The statistical average is defined as (the usual)

$$\langle \cdots \rangle = \frac{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\rm int})}\ldots\right)}{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\rm int})}\right)} \tag{5.106}$$

We will establish some functional derivative identities for later calculations.

Consider the expectation value (note that we write the times in contour times τ to indicate that these times are unspecified for the time being),

$$\begin{aligned}
\left\langle Q_{j_1\vec{q}_1 H[J]}(\tau_1)\right\rangle &= \left\langle Q_{H[J]}(1)\right\rangle && (5.107)\\
&\mid \text{ where we denote } j_1\vec{q}_1\tau_1 \equiv 1\\
&\mid \text{ we choose to split the Hamiltonian as } H_0+H_{\rm int} \text{ and } \sum_{j\vec{q}} J_{j\vec{q}}(t)Q_{j\vec{q}}\\
&\mid \text{ use the contour identity,}\\
&\mid \ Q_{H[J]}(1) = T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d\tau_2\sum_{j_2\vec{q}_2}(J_{j_2\vec{q}_2}(\tau_2)Q_{H[J=0]}(2))}Q_{H[J=0]}(1)\right)\\
&\mid \ = T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K}d2J(2)Q_{H[J=0]}(2)}Q_{H[J=0]}(1)\right) \equiv T_{c_K}\left(S_{c_K}Q_{H[J=0]}(1)\right)\\
&\mid \text{ insert unity term } T_{c_K}S_{c_K} = \mathbb{I} \text{ into denominator}\\
&= \frac{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\rm int})}T_{c_K}\left(S_{c_K}Q_{H[J=0]}(1)\right)\right)}{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\rm int})}T_{c_K}S_{c_K}\right)} && (5.108)\\
&= \frac{\mathrm{Tr}\left(e^{-\beta H[J=0]}T_{c_K}\left(S_{c_K}Q_{H[J=0]}(1)\right)\right)}{\mathrm{Tr}\left(e^{-\beta H[J=0]}T_{c_K}S_{c_K}\right)} && (5.109)\\
&\mid \text{ denote } Z[J] = \mathrm{Tr}\left(e^{-\beta H[J=0]}T_{c_K}S_{c_K}\right)\\
&\mid \text{ so, } Z[J=0] = \mathrm{Tr}\left(e^{-\beta H[J=0]}\right)\\
&= \frac{1}{Z[J]}\mathrm{Tr}\left(e^{-\beta H[J=0]}T_{c_K}\left(S_{c_K}Q_{H[J=0]}(1)\right)\right) && (5.110)
\end{aligned}$$

Note that this way of splitting the Hamiltonian does not allow Wick's theorem to be used as $H_0+H_{\rm int}$ is not quadratic in general. It does not matter as we will not use Wick's theorem here.

When $J=0$,

$$\begin{aligned}
\lim_{J\to 0}\left\langle Q_{H[J]}(1)\right\rangle &\mid \text{ we simply go back to the equilibrium expectation value}\\
&= \frac{1}{Z[J=0]}\mathrm{Tr}\left(e^{-\beta H[J=0]}Q_{H[J=0]}(1)\right) && (5.111)\\
&= \left\langle Q_{H[J=0]}(1)\right\rangle && (5.112)\\
&\stackrel{!}{=} 0 && (5.113)
\end{aligned}$$

The value of $\left\langle Q_{H[J=0]}(1)\right\rangle$ in equilibrium theory represents thermal expansion (as it is related to the expectation value of displacement) and is typically non-zero but we set it to be zero for the sake of only concentrating on phonon-phonon scattering effects. [8]

[8] Following [Kwok1968] footnote 39, when we set $\left\langle Q_{H[J=0]}(1)\right\rangle_{H[J=0]}$ to be zero, we lost the physics of thermal expansion. Thus we also lost the physics of describing displacive phase transitions. Ferroelectric solids are such solids that undergo displacive phase transition. Of course one can retain it and work in a more general framework where one has to deal with a self consistent problem of: phonon-phonon scattering $\leftrightarrow$ thermal expansion.

Now we will define the functional derivative, we start by introducing variations. Consider

$$J(1) \to J(1) + \delta J(1) \tag{5.114}$$

Expand $\langle Q_{H[J+\delta J]}(1)\rangle$ in powers of δJ and keep only terms linear in δJ

$$\langle Q_{H[J+\delta J]}(1)\rangle = \frac{1}{Z[J+\delta J]}\mathrm{Tr}\left(e^{-\beta H[J=0]}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d2(J(2)+\delta J(2))Q_{H[J=0]}(2)}Q_{H[J=0]}(1)\right)\right)$$

We work out the numerator and denominator seperately.

$$\begin{aligned}
\text{Prefactor} &= \frac{1}{Z[J+\delta J]} && (5.115)\\
&= \left(\mathrm{Tr}\left(e^{-\beta H[J=0]}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d1(J(1)+\delta J(1))Q_{H[J=0]}(1)}\right)\right)\right)^{-1} && (5.116)\\
&\approx \left(\mathrm{Tr}\left(e^{-\beta H[J=0]}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d1J(1)Q_{H[J=0]}(1)}\left(1-\frac{i}{\hbar}\int_{c_K} d2\delta J(2)Q_{H[J=0]}(2)\right)\right)\right)\right)^{-1}\\
&= \left(Z[J]-Z[J]\frac{i}{\hbar}\int_{c_K} d2\delta J(2)\langle Q_{H[J]}(2)\rangle\right)^{-1} && (5.117)\\
&\quad | \quad \text{use the (operator) binomial expansion } (1+x)^{-1}\approx 1-x\\
&= \frac{1}{Z[J]}\left(1+\frac{i}{\hbar}\int_{c_K} d2\langle Q_{H[J]}(2)\rangle\delta J(2)\right) && (5.118)
\end{aligned}$$

$$\begin{aligned}
&\text{Numerator term}\\
&= \mathrm{Tr}\left(e^{-\beta H[J=0]}T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d3J(3)Q_{H[J=0]}(3)}\left(1-\frac{i}{\hbar}\int_{c_K} d2\delta J(2)Q_{H[J=0]}(2)\right)Q_{H[J=0]}(1)\right)\right)\\
&= \left(\langle Q_{H[J]}(1)\rangle-\frac{i}{\hbar}\int_{c_K} d2\delta J(2)\langle T_{c_K}(Q_{H[J]}(1)Q_{H[J]}(2))\rangle\right)\times Z[J] && (5.119)
\end{aligned}$$

Reconstruct the term and only retain up to first order terms

$$\langle Q_{H[J+\delta J]}(1)\rangle = \langle Q_{H[J]}(1)\rangle-\frac{i}{\hbar}\int_{c_K} d2\delta J(2)\left(\langle T_{c_K}(Q_{H[J]}(1)Q_{H[J]}(2))\rangle-\langle Q_{H[J]}(1)\rangle\langle Q_{H[J]}(2)\rangle\right)$$

Define,

$$\begin{aligned}
D^J(1,2) &\equiv -\frac{i}{\hbar}\left(\langle T_{c_K}(Q_{H[J]}(1)Q_{H[J]}(2))\rangle-\langle Q_{H[J]}(1)\rangle\langle Q_{H[J]}(2)\rangle\right) && (5.120)\\
\text{where explicitly,}&\\
\langle T_{c_K}(Q_{H[J]}(1)Q_{H[J]}(2))\rangle &= \frac{\mathrm{Tr}\left(e^{-\beta H[J=0]}T_{c_K}\left(S_{c_K}Q_{H[J=0]}(1)Q_{H[J=0]}(2)\right)\right)}{\mathrm{Tr}\left(e^{-\beta H[J=0]}S_{c_K}\right)} && (5.121)\\
\text{then,}&\\
\langle Q_{H[J+\delta J]}(1)\rangle &\approx \langle Q_{H[J]}(1)\rangle+\int_{c_K} d2D^J(1,2)\delta J(2) && (5.122)
\end{aligned}$$

If we consider a Taylor series, then we can write D^J as the functional derivative with respect to

$\langle Q \rangle_J$

$$D^J(1,2) = \frac{\delta \left\langle Q_{H[J]}(1) \right\rangle}{\delta J(2)} \tag{5.123}$$

Since normal coordinates commute, we can also write

$$D^J(1,2) = \frac{\delta \left\langle Q_{H[J]}(2) \right\rangle}{\delta J(1)} \tag{5.124}$$

We now consider D^J as a functional of J and calculate the functional derivative of D^J. Following earlier lines, we define the required functional derivative, $\frac{\delta D^J(1,2)}{\delta J(3)}$ as the coefficient of the linear term in the Taylor expansion of $D^{J+\delta J}$.

$$D^{J+\delta J}(1,2) \quad = \quad -\frac{i}{\hbar}\left(\left\langle T_{c_K}\left(Q_{H[J+\delta J]}(1)Q_{H[J+\delta J]}(2)\right)\right\rangle - \left\langle Q_{H[J+\delta J]}(1)\right\rangle \left\langle Q_{H[J+\delta J]}(2)\right\rangle\right) \tag{5.125}$$

Writing each term to first order in δJ,

$$\begin{aligned}
& \text{First term} \\
= \; & \left\langle T_{c_K}\left(Q_{H[J+\delta J]}(1)Q_{H[J+\delta J]}(2)\right)\right\rangle & (5.126) \\
| \; & \text{based on the calculation for } \langle Q_{H[J+\delta J]}(1)\rangle\text{, we deduce (to first order in } \delta J) \\
\approx \; & \left\langle T_{c_K}\left(Q_{H[J]}(1)Q_{H[J]}(2)\right)\right\rangle \\
& -\frac{i}{\hbar}\int_{c_K} d3\delta J(3)\left(-\frac{i}{\hbar}\right)\left[\left\langle T_{c_K}\left(Q_{H[J]}(1)Q_{H[J]}(2)Q_{H[J]}(3)\right)\right\rangle - \left\langle T_{c_K}\left(Q_{H[J]}(1)Q_{H[J]}(2)\right)\right\rangle \left\langle Q_{H[J]}(3)\right\rangle\right] & (5.127)
\end{aligned}$$

$$\begin{aligned}
& \text{Second term} \\
= \; & \left\langle Q_{H[J+\delta J]}(1)\right\rangle \left\langle Q_{H[J+\delta J]}(2)\right\rangle & (5.128) \\
\approx \; & \left(\left\langle Q_{H[J]}(1)\right\rangle + \int_{c_K} d3D^J(1,3)\delta J(3)\right)\left(\left\langle Q_{H[J]}(2)\right\rangle + \int_{c_K} d3D^J(2,3)\delta J(3)\right) & (5.129) \\
| \; & \text{expand up to first order in } \delta J \\
\approx \; & \left\langle Q_{H[J]}(1)\right\rangle \left\langle Q_{H[J]}(2)\right\rangle \\
& + \left\langle Q_{H[J]}(1)\right\rangle \int_{c_K} d3D^J(2,3)\delta J(3) + \left\langle Q_{H[J]}(2)\right\rangle \int_{c_K} d3D^J(1,3)\delta J(3) & (5.130)
\end{aligned}$$

So we can conclude that the required derivative is

$$\begin{aligned}
\frac{\delta D^J(1,2)}{\delta J(3)} \quad = \quad & -\frac{i}{\hbar}\left\{-\frac{i}{\hbar}\left\langle T_{c_K}\left(Q_{H[J]}(1)Q_{H[J]}(2)Q_{H[J]}(3)\right)\right\rangle\right. \\
& +\frac{i}{\hbar}\left\langle T_{c_K}\left(Q_{H[J]}(1)Q_{H[J]}(2)\right)\right\rangle \left\langle Q_{H[J]}(3)\right\rangle \\
& \left. -D^J(1,3)\left\langle Q_{H[J]}(2)\right\rangle - D^J(2,3)\left\langle Q_{H[J]}(1)\right\rangle\right\} & (5.131) \\
| \quad & \text{from the defintion of } D^J\text{, we write} \\
| \quad & -\frac{\hbar}{i}D^J(1,2) + \left\langle Q_{H[J]}(1)\right\rangle \left\langle Q_{H[J]}(2)\right\rangle = \left\langle T_{c_K}\left(Q_{H[J]}(1)Q_{H[J]}(2)\right)\right\rangle
\end{aligned}$$

$$
\begin{aligned}
&= -\frac{i}{\hbar}\left\{-\frac{i}{\hbar}\left\langle T_{c_K}\left(Q_{H[J]}(1)Q_{H[J]}(2)Q_{H[J]}(3)\right)\right\rangle\right. && (5.132)\\
&\quad -D^J(1,2)\left\langle Q_{H[J]}(3)\right\rangle - D^J(1,3)\left\langle Q_{H[J]}(2)\right\rangle - D^J(2,3)\left\langle Q_{H[J]}(1)\right\rangle \\
&\quad \left.+\frac{i}{\hbar}\left\langle Q_{H[J]}(1)\right\rangle\left\langle Q_{H[J]}(2)\right\rangle\left\langle Q_{H[J]}(3)\right\rangle\right\} && (5.133)
\end{aligned}
$$

Now we need the equation of motion of $\left\langle Q_{H[J]}(1)\right\rangle$ to later help us obtain the equation of motion of $D^J(1,2)$.

We rewrite $\left\langle Q_{H[J]}(1)\right\rangle$ slightly,

$$
\begin{aligned}
\left\langle Q_{H[J]}(1)\right\rangle &= \frac{1}{Z[J]}\mathrm{Tr}\left(e^{-\beta H[J=0]}T_{c_K}\left(S_{c_K}Q_{H[J=0]}(1)\right)\right) && (5.134)\\
&\quad | \quad \text{write the contour identity back into interaction operators}\\
&= \frac{1}{Z[J]}\mathrm{Tr}\left(e^{-\beta H[J=0]}\left(Te^{\frac{i}{\hbar}\int_{t_0}^{\tau_1} d2J(2)Q_{H[J=0]}(2)}\right)Q_{H[J=0]}(1)\left(Te^{-\frac{i}{\hbar}\int_{t_0}^{\tau_1} d2J(2)Q_{H[J=0]}(2)}\right)\right)\\
&= \frac{1}{Z[J]}\mathrm{Tr}\left(e^{-\beta H[J=0]}S(t_0\tau_1)Q_{H[J=0]}(1)S(\tau_1 t_0)\right) && (5.135)
\end{aligned}
$$

Again we emphasize that we wrote t_1 as τ_1 to indicate that t_1 is arbitrary. Take the time derivative with respect to τ_1,

$$
\begin{aligned}
\frac{\partial\left\langle Q_{H[J]}(1)\right\rangle}{\partial\tau_1} &= \left\{\mathrm{Tr}\left(e^{-\beta H[J=0]}S(t_0\tau_1)\dot{Q}_{H[J=0]}(1)S(\tau_1 t_0)\right)\right.\\
&\quad +\mathrm{Tr}\left(e^{-\beta H[J=0]}\dot{S}(t_0\tau_1)Q_{H[J=0]}(1)S(\tau_1 t_0)\right)\\
&\quad \left.+\mathrm{Tr}\left(e^{-\beta H[J=0]}S(t_0\tau_1)Q_{H[J=0]}(1)\dot{S}(\tau_1 t_0)\right)\right\} && (5.136)
\end{aligned}
$$

where

$$
\begin{aligned}
\dot{S}(t_0\tau_1) &= \frac{\partial}{\partial\tau_1}Te^{-\frac{i}{\hbar}\int_{\tau_1}^{t_0} d2J(2)Q_{H[J=0]}(2)} && (5.137)\\
&= S(t_0\tau_1)\left(\frac{i}{\hbar}\right)\sum_{j_2\vec{q}_2}J_{j_2\vec{q}_2}(\tau_1)Q_{j_2\vec{q}_2H[J=0]}(\tau_1) && (5.138)\\
&\quad | \quad \text{abbreviate as}^9\\
&= S(t_0\tau_1)\left(\frac{i}{\hbar}\right)\sum_{2}J_2(\tau_1)Q_{2H[J=0]}(\tau_1) && (5.139)
\end{aligned}
$$

$$
\dot{S}(\tau_1 t_0) = \frac{\partial}{\partial\tau_1}Te^{-\frac{i}{\hbar}\int_{t_0}^{\tau_1} d2J(2)Q_{H[J=0]}(2)} = S(\tau_1 t_0)\left(-\frac{i}{\hbar}\right)\sum_{2}J_2(\tau_1)Q_{2H[J=0]}(\tau_1) \qquad (5.140)
$$

where the evaluation is done by differentiating the lower and upper limits respectively. So

$$
\frac{\partial\left\langle Q_{H[J]}(1)\right\rangle}{\partial\tau_1} = \frac{1}{Z[J]}\left\{\mathrm{Tr}\left(e^{-\beta H[J=0]}S(t_0\tau_1)\dot{Q}_{H[J=0]}(1)S(\tau_1 t_0)\right)\right.
$$

[9] As an abbreviation in the subscript, we denote $j_1\vec{q}_1 \to 1$ and $j_1, -\vec{q}_1 \to \bar{1}$. As an abbreviation in the argument, we denote $j_1\vec{q}_1\tau_1 \to 1$.

$$
\begin{aligned}
& +\frac{i}{\hbar}\sum_{2} J_2(\tau_1)\mathrm{Tr}\left(e^{-\beta H[J=0]}S(t_0\tau_1)\left[Q_{2H[J=0]}(\tau_1),Q_{H[J=0]}(1)\right]_{-}S(\tau_1 t_0)\right)\Bigg\} \\
| \quad & \text{the commutator is zero due to the } QQ \text{ equal time commutation relations} \\
= \quad & \frac{1}{Z[J]}\mathrm{Tr}\left(e^{-\beta H[J=0]}S(t_0\tau_1)\dot{Q}_{H[J=0]}(1)S(\tau_1 t_0)\right) \qquad (5.141) \\
\equiv \quad & \left\langle \dot{Q}_{H[J]}(1)\right\rangle \qquad (5.142)
\end{aligned}
$$

Now take the second time derivative. Everything is the same but the commutator is now of this form $[Q,\dot{Q}]_{-}$.

$$
\begin{aligned}
\frac{\partial^2\left\langle Q_{H[J]}(1)\right\rangle}{\partial\tau_1^2} &= \frac{\partial}{\partial\tau_1}\left\langle \dot{Q}_{H[J]}(1)\right\rangle \qquad (5.143) \\
&= \frac{1}{Z[J]}\Bigg\{\mathrm{Tr}\left(e^{-\beta H[J=0]}S(t_0\tau_1)\ddot{Q}_{H[J=0]}(1)S(\tau_1 t_0)\right) \\
&\quad +\frac{i}{\hbar}\sum_{2} J_2(\tau_1)\mathrm{Tr}\left(e^{-\beta H[J=0]}S(t_0\tau_1)\left[Q_{2H[J=0]}(\tau_1),\dot{Q}_{H[J=0]}(1)\right]_{-}S(\tau_1 t_0)\right)\Bigg\} \\
&| \quad \text{the commutator evaluates to } \left(-\frac{\hbar}{i}\right)\delta_{\bar{1}2} \\
&= \frac{1}{Z[J]}\mathrm{Tr}\left(e^{-\beta H[J=0]}S(t_0\tau_1)\ddot{Q}_{H[J=0]}(1)S(\tau_1 t_0)\right) - J_{\bar{1}}(\tau_1) \qquad (5.144) \\
&= \left\langle \ddot{Q}_{H[J]}(1)\right\rangle - J_{\bar{1}}(\tau_1) \qquad (5.145)
\end{aligned}
$$

Use the Heisenberg equation of motion for $\ddot{Q}_{H[J]}(1)$

$$
\begin{aligned}
& \ddot{Q}_{H[J]}(1) \\
= \quad & -\omega_1^2 Q_{H[J]}(1) - \frac{1}{2!}\sum_{23}\tilde{V}^{(3ph)}_{\bar{1}23}Q_{2H[J]}(\tau_1)Q_{3H[J]}(\tau_1) - \frac{1}{3!}\sum_{234}\tilde{V}^{(4ph)}_{\bar{1}234}Q_{2H[J]}(\tau_1)Q_{3H[J]}(\tau_1)Q_{4H[J]}(\tau_1)
\end{aligned}
$$

The final equation of motion is

$$
\begin{aligned}
& \left(\frac{\partial^2}{\partial\tau_1^2}+\omega_1^2\right)\left\langle Q_{H[J]}(1)\right\rangle + J_{\bar{1}}(\tau_1) \\
= \quad & -\frac{1}{2!}\sum_{23}\tilde{V}^{(3ph)}_{\bar{1}23}\left\langle Q_{2H[J]}(\tau_1)Q_{3H[J]}(\tau_1)\right\rangle - \frac{1}{3!}\sum_{234}\tilde{V}^{(4ph)}_{\bar{1}234}\left\langle Q_{2H[J]}(\tau_1)Q_{3H[J]}(\tau_1)Q_{4H[J]}(\tau_1)\right\rangle
\end{aligned}
\qquad (5.146)
$$

Use the relation $D^J(1,2)=\frac{\delta}{\delta J(2)}\left\langle Q_{H[J]}(1)\right\rangle$ to get the equation of motion for D^J.

$$
\begin{aligned}
& \left(\frac{\partial^2}{\partial\tau_1^2}+\omega_1^2\right)D^J(1,2) + \frac{1}{2!}\sum_{23}\tilde{V}^{(3ph)}_{\bar{1}23}\frac{\delta}{\delta J(2)}\left\langle Q_{2H[J]}(\tau_1)Q_{3H[J]}(\tau_1)\right\rangle \\
& +\frac{1}{3!}\sum_{234}\tilde{V}^{(4ph)}_{\bar{1}234}\frac{\delta}{\delta J(2)}\left\langle Q_{2H[J]}(\tau_1)Q_{3H[J]}(\tau_1)Q_{4H[J]}(\tau_1)\right\rangle \\
= \quad & -\delta_{\bar{1}2}\delta(\tau_1-\tau_2) \qquad (5.147)
\end{aligned}
$$

This equation is the left BBGKY equation for the 3-phonon and 4-phonon many body interactions. We do not need the right BBGKY equation because we will eventually set $J \to 0$ (actually $\langle Q\rangle \to 0$) at the end and return to the equilibrium theory where it a function of time differences instead of a function of 2 seperate times.

Now we want to write it into a form that looks like Dyson's equation and yet it is a self consistent equation that retains the exactness of the left BBGKY equation. Start by using the equal time version of the identity.

$$-\frac{\hbar}{i}D^J_{12}(\tau_1\tau_1) + \left\langle Q_{1H[J]}(\tau_1)\right\rangle_J \left\langle Q_{2H[J]}(\tau_1)\right\rangle = \left\langle Q_{1H[J]}(\tau_1)Q_{2H[J]}(\tau_1)\right\rangle \tag{5.148}$$

The equation of motion becomes

$$\begin{aligned}
&\left(\frac{\partial^2}{\partial\tau_1^2} + \omega_1^2\right) D^J(1,2) + \frac{1}{2!}\sum_{34} \tilde{V}^{(3ph)}_{\bar{1}34} \frac{\delta}{\delta J(2)} \left(-\frac{\hbar}{i}D^J_{34}(\tau_1\tau_1) + \left\langle Q_{3H[J]}(\tau_1)\right\rangle_J \left\langle Q_{4H[J]}(\tau_1)\right\rangle\right) \\
&+\frac{1}{3!}\sum_{345} \tilde{V}^{(4ph)}_{\bar{1}345} \frac{\delta}{\delta J(2)} \left(-\frac{\hbar}{i}\right) \left(-\frac{\hbar}{i}\frac{\delta D^J_{34}(\tau_1\tau_1)}{\delta J_5(\tau_1)} + 3D^J_{34}(\tau_1\tau_1)\left\langle Q_{5H[J]}(\tau_1)\right\rangle\right. \\
&\left.-\frac{i}{\hbar}\left\langle Q_{3H[J]}(\tau_1)\right\rangle \left\langle Q_{4H[J]}(\tau_1)\right\rangle \left\langle Q_{5H[J]}(\tau_1)\right\rangle\right) \\
=\ & -\delta_{\bar{1}2}\delta(\tau_1-\tau_2)
\end{aligned} \tag{5.149}$$

Now take the functional derivatives explicitly and seperately

$$\begin{aligned}
&\text{“3-phonon term”} \\
=\ & \frac{\delta}{\delta J(2)}\left(-\frac{\hbar}{i}D^J_{34}(\tau_1\tau_1) + \left\langle Q_{3H[J]}(\tau_1)\right\rangle \left\langle Q_{4H[J]}(\tau_1)\right\rangle\right) && (5.150) \\
|\ & \text{use product rule and last 2 terms are the same after relabelling indices} \\
=\ & -\frac{\hbar}{i}\frac{\delta D^J_{34}(\tau_1\tau_1)}{\delta J(2)} + 2D^J_{32}(\tau_1\tau_2)\left\langle Q_{4H[J]}(\tau_1)\right\rangle && (5.151)
\end{aligned}$$

$$\begin{aligned}
&\text{“4-phonon term”} \\
=\ & \frac{\delta}{\delta J(2)}\left(-\frac{\hbar}{i}\frac{\delta D^J_{34}(\tau_1\tau_1)}{\delta J_5(\tau_1)} + 3D^J_{34}(\tau_1\tau_1)\left\langle Q_{5H[J]}(\tau_1)\right\rangle - \frac{i}{\hbar}\left\langle Q_{3H[J]}(\tau_1)\right\rangle \left\langle Q_{4H[J]}(\tau_1)\right\rangle \left\langle Q_{5H[J]}(\tau_1)\right\rangle\right) \\
=\ & -\frac{\hbar}{i}\frac{\delta^2 D^J_{34}(\tau_1\tau_1)}{\delta J(2)\delta J_5(\tau_1)} + 3\frac{\delta D^J_{34}(\tau_1\tau_1)}{\delta J(2)}\left\langle Q_{5H[J]}(\tau_1)\right\rangle + 3D^J_{34}(\tau_1\tau_1)\frac{\delta\left\langle Q_{5H[J]}(\tau_1)\right\rangle}{\delta J(2)} \\
&-3\frac{i}{\hbar}\frac{\delta\left\langle Q_{3H[J]}(\tau_1)\right\rangle}{\delta J(2)}\left\langle Q_{4H[J]}(\tau_1)\right\rangle_J \left\langle Q_{5H[J]}(\tau_1)\right\rangle && (5.152) \\
|\ & \text{where the factor of 3 in the last term is due to relabelling of indices} \\
=\ & -\frac{\hbar}{i}\frac{\delta^2 D^J_{34}(\tau_1\tau_1)}{\delta J(2)\delta J_5(\tau_1)} + 3\frac{\delta D^J_{34}(\tau_1\tau_1)}{\delta J(2)}\left\langle Q_{5H[J]}(\tau_1)\right\rangle + 3D^J_{34}(\tau_1\tau_1)D^J_{52}(\tau_1\tau_2) \\
&-3\frac{i}{\hbar}D^J_{32}(\tau_1\tau_2)\left\langle Q_{4H[J]}(\tau_1)\right\rangle \left\langle Q_{5H[J]}(\tau_1)\right\rangle && (5.153)
\end{aligned}$$

The left BBGKY equation becomes,

$$\left(\frac{\partial^2}{\partial\tau_1^2} + \omega_1^2\right) D^J(1,2) - \frac{1}{2!}\frac{\hbar}{i}\sum_{34} \tilde{V}^{(3ph)}_{\bar{1}34}\frac{\delta D^J_{34}(\tau_1\tau_1)}{\delta J(2)}$$

$$
\begin{aligned}
& +\sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}D^J_{32}(\tau_1\tau_2)\left\langle Q_{4H[J]}(\tau_1)\right\rangle+\frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\frac{\delta^2 D^J_{34}(\tau_1\tau_1)}{\delta J(2)\delta J_5(\tau_1)} \\
& -\frac{1}{2!}\frac{\hbar}{i}\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\frac{\delta D^J_{34}(\tau_1\tau_1)}{\delta J(2)}\left\langle Q_{5H[J]}(\tau_1)\right\rangle-\frac{1}{2!}\frac{\hbar}{i}\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}D^J_{34}(\tau_1\tau_1)D^J_{52}(\tau_1\tau_2) \\
& +\frac{1}{2!}\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}D^J_{32}(\tau_1\tau_2)\left\langle Q_{4H[J]}(\tau_1)\right\rangle\left\langle Q_{5H[J]}(\tau_1)\right\rangle \\
= \; & -\delta_{\bar{1}2}\delta(\tau_1-\tau_2) \qquad (5.154)
\end{aligned}
$$

To treat the functional dependence of J as the functional dependence of $\left\langle Q_{H[J]}\right\rangle_J$ we need to remove all remaining dependence of J by using the chain rule

$$
\frac{\delta}{\delta J(2)} = \int_{c_K} d3\left(\frac{\delta\left\langle Q_{H[J]}(3)\right\rangle_J}{\delta J(2)}\right)\frac{\delta}{\delta\left\langle Q_{H[J]}(3)\right\rangle_J} = \int_{c_K} d3D^J(3,2)\frac{\delta}{\delta\left\langle Q_{H[J]}(3)\right\rangle_J} \qquad (5.155)
$$

We also define the inverse Green's function which will be used later

$$
\int_{c_K} d2D^J(1,2)D^{-1J}(2,3) = \int_{c_K} d2D^{-1J}(1,2)D^J(2,3) = \delta_{13}\delta(\tau_1-\tau_3) \qquad (5.156)
$$

Now we can rewrite the dependences as $D^J \to D^Q$ and $\lim_{J\to 0} D^J \to \lim_{\left\langle Q_{H[J]}\right\rangle_J\to 0} D^Q$.

"Rewriting second term (and fifth term) in left BBGKY equation"

$$
\begin{aligned}
&= \frac{\delta D^J_{34}(\tau_1\tau_1)}{\delta J(2)} && (5.157)\\
&= \int_{c_K} d6D^Q(6,2)\frac{\delta D^Q_{34}(\tau_1\tau_1)}{\delta\left\langle Q_{H[J]}(6)\right\rangle_J} && (5.158)
\end{aligned}
$$

"Rewriting fourth term in left BBGKY equation"

$$
\begin{aligned}
&= \frac{\delta^2 D^J_{34}(\tau_1\tau_1)}{\delta J(2)\delta J_5(\tau_1)} && (5.159)\\
&= \int_{c_K} d7D^Q(7,2)\frac{\delta}{\delta\left\langle Q_{H[J]}(7)\right\rangle}\int_{c_K} d6D^Q_{65}(\tau_6\tau_1)\frac{\delta}{\delta\left\langle Q_{H[J]}(6)\right\rangle}D^Q_{34}(\tau_1\tau_1) && (5.160)\\
&= \int_{c_K} d7d6D^Q(7,2)\frac{\delta}{\delta\left\langle Q_{H[J]}(7)\right\rangle}\left(D^Q_{65}(\tau_6\tau_1)\frac{\delta}{\delta\left\langle Q_{H[J]}(6)\right\rangle}D^Q_{34}(\tau_1\tau_1)\right) && (5.161)
\end{aligned}
$$

The final expression for the left BBGKY equation is

$$
\begin{aligned}
& \left(\frac{\partial^2}{\partial\tau_1^2}+\omega_1^2\right)D^Q(1,2)+\sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}D^Q_{32}\left\langle Q_{4H[J]}(\tau_1)\right\rangle \\
& -\frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}\int_{c_K} d6D^Q(6,2)\frac{\delta D^Q_{34}(\tau_1\tau_1)}{\delta\left\langle Q_{H[J]}(6)\right\rangle} \\
& +\frac{1}{2!}\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}D^Q_{32}(\tau_1\tau_2)\left\langle Q_{4H[J]}(\tau_1)\right\rangle\left\langle Q_{5H[J]}(\tau_1)\right\rangle
\end{aligned}
$$

$$
\begin{aligned}
& -\frac{1}{2!}\frac{\hbar}{i}\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}D^Q_{34}(\tau_1\tau_1)D^Q_{52}(\tau_1\tau_2) \\
& -\frac{1}{2!}\frac{\hbar}{i}\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\int_{c_K} d6D^Q(6,2)\frac{\delta D^Q_{34}(\tau_1\tau_1)}{\delta\left\langle Q_{H[J]}(6)\right\rangle}\left\langle Q_{5H[J]}(\tau_1)\right\rangle \\
& +\frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\int_{c_K} d7d6D^Q(7,2)\frac{\delta}{\delta\left\langle Q_{H[J]}(7)\right\rangle}\left(D^Q_{65}(\tau_6\tau_1)\frac{\delta}{\delta\left\langle Q_{H[J]}(6)\right\rangle}D^Q_{34}(\tau_1\tau_1)\right) \\
= \quad & -\delta_{\bar{1}2}\delta(\tau_1-\tau_2)
\end{aligned}
\tag{5.162}
$$

Having the exact equation, we will now calculate the Dyson equation in the form of $D^{-1} = D^{(0)-1} - \Sigma$ so as to obtain the self energy, Σ in the exact form. We start by multiplying D^{-1Q} and sum over and integrate over the variables. We calculate each term seperately.

$$\text{“LHS first term”} = \left(\frac{\partial^2}{\partial\tau_1^2}+\omega_1^2\right)\int_{c_K} d2D^Q(1,2)D^{-1Q}(2,8) \tag{5.163}$$

$$= \left(\frac{\partial^2}{\partial\tau_1^2}+\omega_1^2\right)\delta_{18}\delta(\tau_1-\tau_8) \tag{5.164}$$

$$\equiv -D^{(0)-1}(1,8) \tag{5.165}$$

The negative sign in front of $D^{(0)-1}$ is due to the convention $D^{(0)-1}D^{(0)} = $ delta. One can also check directly by taking time derivatives of the harmonic $D^{(0)}$.

$$\text{“LHS second term”} = \sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}\int_{c_K} d2D^Q_{32}(t_1t_2)D^{-1Q}(2,8)\left\langle Q_{4H[J]}(\tau_1)\right\rangle \tag{5.166}$$

$$= \sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}\delta_{38}\delta(\tau_1-\tau_8)\left\langle Q_{4H[J]}(\tau_1)\right\rangle \tag{5.167}$$

$$= \sum_{4}\tilde{V}^{(3ph)}_{\bar{1}84}\left\langle Q_{4H[J]}(\tau_1)\right\rangle\delta(\tau_1-\tau_8) \tag{5.168}$$

$$\text{“LHS third term”} = -\frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}\int_{c_K} d6d2D^Q(6,2)D^{-1Q}(2,8)\frac{\delta D^Q_{34}(\tau_1\tau_1)}{\delta\left\langle Q_{H[J]}(6)\right\rangle} \tag{5.169}$$

$$= -\frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}\int_{c_K} d6\delta_{68}\delta(\tau_6-\tau_8)\frac{\delta D^Q_{34}(\tau_1\tau_1)}{\delta\left\langle Q_{H[J]}(6)\right\rangle} \tag{5.170}$$

$$= -\frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}\frac{\delta D^Q_{34}(\tau_1\tau_1)}{\delta\left\langle Q_{H[J]}(8)\right\rangle} \tag{5.171}$$

$$\text{“LHS fourth term”} = \frac{1}{2!}\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\int_{c_K} d2D^Q_{32}(\tau_1\tau_2)D^{-1Q}(2,8)\left\langle Q_{4H[J]}(\tau_1)\right\rangle\left\langle Q_{5H[J]}(\tau_1)\right\rangle \tag{5.172}$$

$$= \frac{1}{2!}\sum_{45}\tilde{V}^{(4ph)}_{\bar{1}845}\left\langle Q_{4H[J]}(\tau_1)\right\rangle\left\langle Q_{5H[J]}(\tau_1)\right\rangle\delta(\tau_1-\tau_8) \tag{5.173}$$

$$\text{“LHS fifth term”} = -\frac{1}{2!}\frac{\hbar}{i}\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\int_{c_K} d2D^Q_{34}(\tau_1\tau_1)D^Q_{52}(\tau_1\tau_2)D^{-1Q}(2,8) \tag{5.174}$$

$$= -\frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(4ph)}_{\bar{1}348}D^{Q}_{34}(\tau_1\tau_1)\delta(\tau_1-\tau_8) \tag{5.175}$$

$$\begin{aligned}\text{“LHS sixth term”} &= -\frac{1}{2!}\frac{\hbar}{i}\sum_{345}V^{(4ph)}_{\bar{1}345}\int_{c_K} d6d2D^{Q}(6,2)D^{-1Q}(2,8)\frac{\delta D^{Q}_{34}(\tau_1\tau_1)}{\delta\left\langle Q_{H[J]}(6)\right\rangle}\left\langle Q_{5H[J]}(\tau_1)\right\rangle \\ &= -\frac{1}{2!}\frac{\hbar}{i}\sum_{345}V^{(4ph)}_{\bar{1}345}\frac{\delta D^{Q}_{34}(\tau_1\tau_1)}{\delta\left\langle Q_{H[J]}(8)\right\rangle}\left\langle Q_{5H[J]}(\tau_1)\right\rangle \end{aligned} \tag{5.176}$$

$$\begin{aligned}&\text{“LHS seventh term”}\\ =\;& \frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345} \\ &\times\int_{c_K} d7d6d2D^{Q}(7,2)D^{-1Q}(2,8)\frac{\delta}{\delta\left\langle Q_{H[J]}(7)\right\rangle}\left(D^{Q}_{65}(\tau_6\tau_1)\frac{\delta}{\delta\left\langle Q_{H[J]}(6)\right\rangle}D^{Q}_{34}(\tau_1\tau_1)\right) && (5.177)\\ =\;& \frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\int_{c_K} d6\frac{\delta}{\delta\left\langle Q_{H[J]}(8)\right\rangle}\left(D^{Q}_{65}(\tau_6\tau_1)\frac{\delta}{\delta\left\langle Q_{H[J]}(6)\right\rangle}D^{Q}_{34}(\tau_1\tau_1)\right) && (5.178)\end{aligned}$$

$$\text{“RHS”} = -\int_{c_K} d2D^{-1Q}(2,8)\delta_{\bar{1}2}\delta(\tau_1-\tau_2) = -D^{-1Q}_{\bar{1}8}(\tau_1\tau_8) \tag{5.179}$$

We will now change $\frac{\delta D^Q}{\delta\langle Q\rangle} \to \frac{D^{-1Q}}{\delta\langle Q\rangle}$ by using the definition of the inverse Green's function. Then that allows us to define the vertex function and the self energy and that completes the derivation of Dyson equation in exact form. After that we will iterate these equations and generate diagrams for the self energy.

Start with the relation for the inverse Green's function

$$\begin{aligned}\delta_{13}\delta(\tau_1-\tau_3) &= \int_{c_K} d2D^{Q}(1,2)D^{-1Q}(2,3) && (5.180)\\ &\quad \Big|\ \text{take } \frac{\delta}{\delta\left\langle Q_{H[J]}(4)\right\rangle} \text{ on both sides} \\ 0 &= \int_{c_K} d2\left(\frac{\delta D^{Q}(1,2)}{\delta\left\langle Q_{H[J]}(4)\right\rangle}D^{-1Q}(2,3)+D^{Q}(1,2)\frac{\delta D^{-1Q}(2,3)}{\delta\left\langle Q_{H[J]}(4)\right\rangle}\right) && (5.181)\\ &\quad \Big|\ \text{apply } \int_{c_K} d3D^{Q}(3,5) \text{ on both sides} \\ 0 &= \int_{c_K} d2d3\left(\frac{\delta D^{Q}(1,2)}{\delta\left\langle Q_{H[J]}(4)\right\rangle}D^{-1Q}(2,3)D^{Q}(3,5)+D^{Q}(1,2)\frac{\delta D^{-1Q}(2,3)}{\delta\left\langle Q_{H[J]}(4)\right\rangle}D^{Q}(3,5)\right) \\ \frac{\delta D^{Q}(1,5)}{\delta\left\langle Q_{H[J]}(4)\right\rangle} &= -\int_{c_K} d2d3D^{Q}(1,2)\frac{\delta D^{-1Q}(2,3)}{\delta\left\langle Q_{H[J]}(4)\right\rangle}D^{Q}(3,5) && (5.182)\\ &\quad \Big|\ \text{define the vertex function } \Gamma(2,4,3)\equiv-\frac{\delta D^{-1Q}(2,3)}{\delta\left\langle Q_{H[J]}(4)\right\rangle} \\ \frac{\delta D^{Q}(1,2)}{\delta\left\langle Q_{H[J]}(3)\right\rangle} &= \int_{c_K} d4d5D^{Q}(1,4)\Gamma(4,3,5)D^{Q}(5,2) && (5.183)\end{aligned}$$

The left BBGKY equation is now in the Dyson equation form

$$D^{-1Q} = D^{(0)-1} + [\cdots] \tag{5.184}$$

where we define the terms in $[\cdots]$ as the self energy Σ which we will write it out explicitly very soon.

$$\boxed{D^{-1Q}(1,2) = D^{(0)-1}(1,2) - \Sigma(1,2)} \tag{5.185}$$

To see the relationship between the vertex function and the self energy, we act $\frac{\delta}{\delta\left\langle Q_{H[J]}(3)\right\rangle_J}$ on the Dyson's equation to get

$$\frac{\delta D^{-1Q}(1,2)}{\delta\left\langle Q_{H[J]}(3)\right\rangle_J} = 0 + \frac{\delta\Sigma(1,2)}{\delta\left\langle Q_{H[J]}(3)\right\rangle_J} \tag{5.186}$$

From the definition of the vertex function, we immediately see

$$\boxed{\Gamma(1,3,2) = -\frac{\delta\Sigma(1,2)}{\delta\left\langle Q_{H[J]}(3)\right\rangle_J}} \tag{5.187}$$

Now we will write down the (exact) explicit form of the self energy,

$$\boxed{\begin{aligned}
&\Sigma(1,2) \\
&= \sum_3 \tilde{V}^{(3ph)}_{\bar{1}23}\left\langle Q_{3H[J]}(\tau_1)\right\rangle\delta(\tau_1-\tau_2) - \frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}\int_{c_K} d5d6D^Q_{35}(\tau_1\tau_5)\Gamma(5,2,6)D^Q_{64}(\tau_6\tau_1) \\
&\quad + \frac{1}{2!}\sum_{34}\tilde{V}^{(4ph)}_{\bar{1}234}\left\langle Q_{3H[J]}(\tau_1)\right\rangle\left\langle Q_{4H[J]}(\tau_1)\right\rangle\delta(\tau_1-\tau_2) \\
&\quad - \frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(4ph)}_{\bar{1}342}D^Q_{34}(\tau_1\tau_1)\delta(\tau_1-\tau_2) \\
&\quad - \frac{1}{2!}\frac{\hbar}{i}\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\left\langle Q_{5H[J]}(\tau_1)\right\rangle\int_{c_K} d6d7D^Q_{36}(\tau_1\tau_6)\Gamma(6,2,7)D^Q_{74}(\tau_7\tau_1) \\
&\quad + \frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\int_{c_K} d6\frac{\delta}{\delta\left\langle Q_{H[J]}(2)\right\rangle}\left(D^Q_{65}(\tau_6\tau_1)\int_{c_K} d7d8D^Q_{37}(\tau_1\tau_7)\Gamma(7,6,8)D^Q_{84}(\tau_8\tau_1)\right)
\end{aligned}}$$

In the last term, we can only take the functional derivative $\frac{\delta}{\delta\langle Q(2)\rangle}$ only when the explicit form of Γ is known.

The rule for calculation is that the self energy is explicitly iterated by calculating the vertex function $\Gamma = -\frac{\delta\Sigma}{\delta\langle Q\rangle}$ then Γ is inserted into Σ to get an iterated self energy term, after that we will set $\langle Q_{H[J]}\rangle = 0$ and write $D^Q \to D$ in the iterated self energy term. We will iterate and explicitly show the 5 terms of the lowest order with coupling constants of the form, $\tilde{V}^{(3ph)^2}$, $\tilde{V}^{(4ph)}$, $\tilde{V}^{(4ph)^2}$, $\tilde{V}^{(3ph)^2}\tilde{V}^{(4ph)}$ and $\tilde{V}^{(3ph)^4}$.

5.4.2 Library of Phonon-Phonon Self-Consistent Self Energies

5.4.2.1 $V^{(4ph)}$ Term

This term is simply the third term in Σ.

$$\text{“}\tilde{V}^{(4ph)}\text{ self consistent self energy”} = -\frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(4ph)}_{\bar{1}342}D^{Q}_{34}(\tau_1\tau_1)\delta(\tau_1-\tau_2) \quad (5.188)$$

$$\Big| \text{ now set } \langle Q\rangle_J = 0 \text{ and } D^Q \to D$$

$$= -\frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(4ph)}_{\bar{1}342}D_{34}(\tau_1\tau_1)\delta(\tau_1-\tau_2) \quad (5.189)$$

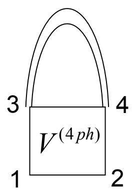


Figure 5.10: *The self consistent $V^{(4ph)}$ self energy.*

Now we need to assign signs to the wave vectors $\vec{q}$. Note that the sign for $\vec{q}_1$ has already been fixed. The reason (I believe) is to allow the final calculation to end up with some combination of coupling constants (which is complex) which is real. Assign “arrows” to (full) Green's functions to point to the right and “in” is denoted by $j_1, -\vec{q}_1 \equiv \bar{1}$ and “out” is denoted by $j_2\vec{q}_2 \equiv 2$.

$$\Sigma_{12}(\tau_1\tau_2) = -\frac{1}{2}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(4ph)}_{\bar{1}3\bar{4}2}D_{34}(\tau_1\tau_2)\delta(\tau_1-\tau_2) \quad (5.190)$$

In QKE, we will need the lesser and the greater components, so using Langreth's theorem, we have

$$\Sigma^{>}_{12}(t_1t_2) = -\frac{1}{2}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(4ph)}_{\bar{1}3\bar{4}2}D^{>}_{34}(t_1t_2)\delta(t_1-t_2) \quad (5.191)$$

$$\Sigma^{<}_{12}(t_1t_2) = -\frac{1}{2}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(4ph)}_{\bar{1}3\bar{4}2}D^{<}_{34}(t_1t_2)\delta(t_1-t_2) \quad (5.192)$$

This term is a Hartree term because it only contributes the equal time part of the self energy (or $\omega = 0$ part) i.e. the DC part of the self energy which is real only.

5.4.2.2 $V^{(3ph)^2}$ Term

This term is obtained by taking the first self energy term in Σ to generate the vertex functions. This vertex function, Γ is substituted into the second term in Σ to give the required self energy term.

$$\Gamma(5,2,6) = -\frac{\delta}{\delta\langle Q_{H[J]}(2)\rangle}\sum_{7}\tilde{V}^{(3ph)}_{567}\left\langle Q_{7H[J]}(t_5)\right\rangle\delta(\tau_5-\tau_6) \quad (5.193)$$

$$= -\sum_{7}\tilde{V}^{(3ph)}_{567}\delta_{27}\delta(\tau_5-\tau_2)\delta(\tau_5-\tau_6) \quad (5.194)$$

$$= -\tilde{V}^{(3ph)}_{562}\delta(\tau_5-\tau_2)\delta(\tau_5-\tau_6) \tag{5.195}$$

Use this Γ in the second term of Σ to generate the self energy term,

$$\begin{aligned}
&\text{“}\tilde{V}^{(3ph)^2}\text{ self consistent self energy”}\\
=\ & -\frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}\int_{c_K} d5d6D^Q_{35}(\tau_1\tau_5)\left(-V^{(3ph)}_{562}\delta(\tau_5-\tau_2)\delta(\tau_5-\tau_6)\right)D^Q_{64}(\tau_6\tau_1) && (5.196)\\
|\ & \text{ now take } \langle Q\rangle_J = 0 \text{ and write } D^Q\to D\\
=\ & \frac{1}{2!}\frac{\hbar}{i}\sum_{3456}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{562}D_{35}(\tau_1\tau_2)D_{64}(\tau_2\tau_1) && (5.197)
\end{aligned}$$

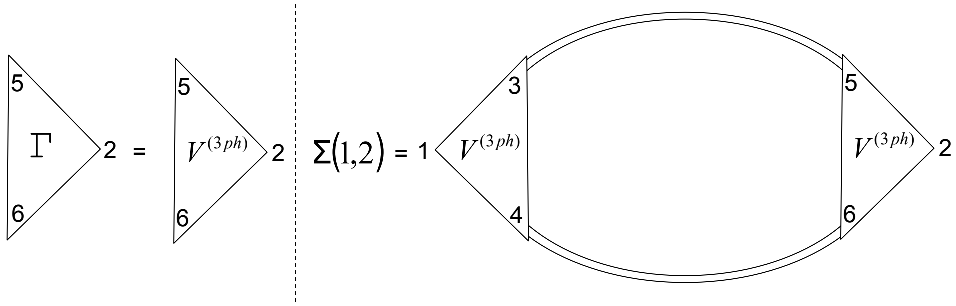


Figure 5.11: *The left diagram is the vertex function which is the coupling constant in this case. The right diagram is the self consistent $V^{(3ph)^2}$ self energy.*

We assign the signs to $\vec{q}$ according to the convention stated earlier. We get,

$$\Sigma_{12}(\tau_1\tau_2) = \frac{1}{2!}\frac{\hbar}{i}\sum_{3456}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D_{35}(\tau_1\tau_2)D_{64}(\tau_2\tau_1) \tag{5.198}$$

Using Langreth's theorem, we get the lesser and the greater components of $\Sigma_{12}(\tau_1\tau_2)$ which is in parallel multiplication.

$$\Sigma^>_{12}(t_1t_2) = \frac{1}{2}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D^>_{35}(t_1t_2)D^<_{64}(t_2t_1) \tag{5.199}$$

$$\Sigma^<_{12}(t_1t_2) = \frac{1}{2}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D^<_{35}(t_1t_2)D^>_{64}(t_2t_1) \tag{5.200}$$

5.4.2.3 $V^{(4ph)^2}$ Term

This self consistent self energy term is obtained by using the third term in Σ to construct Γ and substituting into the sixth term of Σ for iteration.

$$\begin{aligned}
\Gamma(7,6,8) =\ & -\frac{\delta}{\delta\left\langle Q_{H[J]}(6)\right\rangle}\frac{1}{2!}\sum_{9,10}\tilde{V}^{(4ph)}_{789,10}\left\langle Q_{9H[J]}(\tau_7)\right\rangle\left\langle Q_{10H[J]}(\tau_7)\right\rangle\delta(\tau_7-\tau_8) && (5.201)\\
=\ & -\frac{1}{2!}\sum_{9,10}\tilde{V}^{(4ph)}_{789,10}\delta(\tau_7-\tau_8)\left(\delta_{69}\delta(\tau_7-\tau_6)\left\langle Q_{10H[J]}(t_7)\right\rangle+\left\langle Q_{9H[J]}(\tau_7)\right\rangle\delta_{6,10}\delta(\tau_7-\tau_6)\right)\\
|\ & \text{ indices } 9,10 \text{ are symmetric after relabelling}
\end{aligned}$$

$$= -\sum_{9,10} \tilde{V}^{(4ph)}_{789,10}\delta(\tau_7-\tau_8)\delta(\tau_7-\tau_6)\delta_{6,10}\left\langle Q_{9H[J]}(\tau_7)\right\rangle \tag{5.202}$$

$$= -\sum_{9} \tilde{V}^{(4ph)}_{7896}\delta(\tau_7-\tau_8)\delta(\tau_7-\tau_6)\left\langle Q_{9H[J]}(\tau_7)\right\rangle \tag{5.203}$$

We substitute this Γ into the sixth term of $\Sigma(1,2)$ and retaining only the term where $\frac{\delta\Gamma(7,6,8)}{\delta\langle Q_{H[J]}(2)\rangle}$ because the rest vanish when we ignore thermal expansion.

$$\begin{aligned}
&\text{“}\tilde{V}^{(4ph)^2}\text{ self consistent self energy”}\\
=\;& \frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\\
&\times\int_{c_K} d6d7d8 D^{Q}_{65}(\tau_6\tau_1)D^{Q}_{37}(\tau_1\tau_7)\,(-1)\sum_{9}\tilde{V}^{(4ph)}_{7896}\delta(\tau_7-\tau_8)\delta(\tau_7-\tau_6)\frac{\delta\left\langle Q_{9H[J]}(\tau_7)\right\rangle}{\delta\left\langle Q_{H[J]}(2)\right\rangle}D^{Q}_{84}(\tau_8\tau_1)\\
=\;& -\frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{34568}\tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(4ph)}_{7826}\int_{c_K} d7 D^{Q}_{65}(\tau_7\tau_1)D^{Q}_{37}(\tau_1\tau_7)\delta(\tau_7-\tau_2)D^{Q}_{84}(\tau_7\tau_1) &(5.204)\\
|\;& \text{ we can set } D^Q\to D\\
=\;& -\frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{345678}\tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(4ph)}_{7826}D_{65}(\tau_2\tau_1)D_{37}(\tau_1\tau_2)D_{84}(\tau_2\tau_1) &(5.205)
\end{aligned}$$

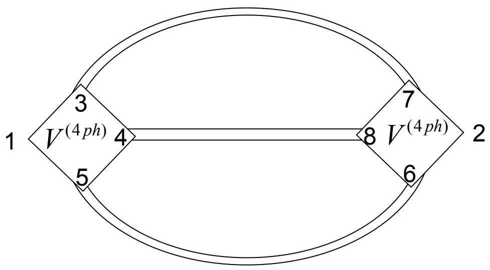


Figure 5.12: *The self consistent $V^{(4ph)^2}$ self energy.*

We assign the signs to $\vec{q}$ according to the convention assigned earlier. We get

$$\Sigma_{12}(\tau_1\tau_2) = -\frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{345678}\tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(4ph)}_{\bar{7}\bar{8}2\bar{6}}D_{65}(\tau_2\tau_1)D_{37}(\tau_1\tau_2)D_{84}(\tau_2\tau_1) \tag{5.206}$$

Using Langreth's theorem, we get the lesser and the greater components of $\Sigma_{12}(\tau_1\tau_2)$ which is in parallel multiplication.

$$\Sigma^{>}_{12}(t_1t_2) = -\frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{345678}\tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(4ph)}_{\bar{7}\bar{8}2\bar{6}}D^{<}_{65}(t_2t_1)D^{>}_{37}(t_1t_2)D^{<}_{84}(\tau_2\tau_1) \tag{5.207}$$

$$\Sigma^{<}_{12}(t_1t_2) = -\frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{345678}\tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(4ph)}_{\bar{7}\bar{8}2\bar{6}}D^{>}_{65}(t_2t_1)D^{<}_{37}(t_1t_2)D^{>}_{84}(\tau_2\tau_1) \tag{5.208}$$

5.4.2.4 $V^{(3ph)^2}V^{(4ph)}$ Type-1 Term

There are 3 types of diagrams of this order. We will calculate type 1 first, which is made up of a sum of 2 equal terms. We start with the first term of type 1 by constructing the vertex function from the first term of Σ.

$$\Gamma(6,2,7) = -\frac{\delta}{\delta\left\langle Q_{H[J]}(2)\right\rangle}\sum_{8}\tilde{V}^{(3ph)}_{678}\left\langle Q_{8H[J]}(\tau_6)\right\rangle\delta(\tau_6-\tau_7) \quad (5.209)$$

$$= -\sum_{8}\tilde{V}^{(3ph)}_{678}\delta_{82}\delta(\tau_6-\tau_2)\delta(\tau_6-\tau_7) \quad (5.210)$$

$$= -\tilde{V}^{(3ph)}_{672}\delta(\tau_6-\tau_2)\delta(\tau_6-\tau_7) \quad (5.211)$$

Put $\Gamma(6,2,7)$ into term 5 of $\Sigma(1,2)$ to generate the self energy term.

$$\Sigma(1,2) = -\frac{1}{2!}\frac{\hbar}{i}\sum_{345}\tilde{V}^{(4ph)}_{\bar{1}345}\left\langle Q_{5H[J]}(\tau_1)\right\rangle\int_{c_K}d6d7D^Q_{36}(\tau_1\tau_6)\Gamma(6,2,7)D^Q_{74}(\tau_7\tau_1) \quad (5.212)$$

$$= \frac{1}{2!}\frac{\hbar}{i}\sum_{345}\int_{c_K}d6d7\tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{672}\left\langle Q_{5H[J]}(\tau_1)\right\rangle D^Q_{36}(\tau_1\tau_6)\delta(\tau_6-\tau_2)\delta(\tau_6-\tau_7)D^Q_{74}(\tau_7\tau_1)$$

$$= \frac{1}{2!}\frac{\hbar}{i}\sum_{34567}\tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{672}\left\langle Q_{5H[J]}(\tau_1)\right\rangle D^Q_{36}(\tau_1\tau_2)D^Q_{74}(\tau_2\tau_1) \quad (5.213)$$

We take this self energy term to generate the vertex function $\Gamma(5,2,6)$.

$$\Gamma(5,2,6) = -\frac{\delta}{\delta\left\langle Q_{H[J]}(2)\right\rangle}\left(\frac{1}{2!}\frac{\hbar}{i}\sum_{789,10,11}\tilde{V}^{(4ph)}_{5789}\tilde{V}^{(3ph)}_{10,11,6}\left\langle Q_{9H[J]}(\tau_5)\right\rangle D^Q_{7,10}(\tau_5\tau_6)D^Q_{11,8}(\tau_6\tau_5)\right)$$

$$= -\frac{1}{2!}\frac{\hbar}{i}\sum_{789,10,11}\tilde{V}^{(4ph)}_{5789}\tilde{V}^{(3ph)}_{10,11,6}\delta_{29}\delta(\tau_2-\tau_5)D^Q_{7,10}(\tau_5\tau_6)D^Q_{11,8}(\tau_6\tau_5) \quad (5.214)$$

$$= -\frac{1}{2!}\frac{\hbar}{i}\sum_{78,10,11}\tilde{V}^{(4ph)}_{5782}\tilde{V}^{(3ph)}_{10,11,6}\delta(\tau_2-\tau_5)D^Q_{7,10}(\tau_5\tau_6)D^Q_{11,8}(\tau_6\tau_5) \quad (5.215)$$

and finally we substitute this vertex function into the second term of Σ to get the final self energy term.

"Term 1 of $\tilde{V}^{(3ph)^2}\tilde{V}^{(4ph)}$ type 1 self consistent self energy

$$= -\frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(3ph)}_{134}\int_{c_K}d5d6$$

$$\times D^Q_{35}(\tau_1\tau_5)\left(-\frac{1}{2!}\frac{\hbar}{i}\sum_{78,10,11}\tilde{V}^{(4ph)}_{5782}\tilde{V}^{(3ph)}_{10,11,6}\delta(\tau_2-\tau_5)D^Q_{7,10}(\tau_5\tau_6)D^Q_{11,8}(\tau_6\tau_5)\right)D^Q_{64}(\tau_6\tau_1) \quad (5.216)$$

| we can now write $D^Q \to D$

$$= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2\sum_{34578,10,11}\int_{c_K}d6\tilde{V}^{(3ph)}_{134}\tilde{V}^{(4ph)}_{5782}\tilde{V}^{(3ph)}_{10,11,6}D_{35}(\tau_1\tau_2)D_{7,10}(\tau_2\tau_6)D_{11,8}(\tau_6\tau_2)D_{64}(\tau_6\tau_1) \quad (5.217)$$

We calculate the second term of type 1 by generating the vertex function from the third term of Σ.

$$\Gamma(5,2,6) = -\frac{\delta}{\delta\left\langle Q_{H[J]}(2)\right\rangle}\frac{1}{2!}\sum_{78}\tilde{V}^{(4ph)}_{5678}\left\langle Q_{7H[J]}(\tau_5)\right\rangle\left\langle Q_{8H[J]}(\tau_5)\right\rangle\delta(\tau_5-\tau_6) \quad (5.218)$$

$$\begin{aligned}
& \quad | \quad \text{the 2 differentiated terms are the same after relabelling of indices} \\
&= -\sum_{78} \tilde{V}^{(4ph)}_{5678} \delta_{72} \delta(\tau_5 - \tau_2) \left\langle Q_{8H[J]}(\tau_5) \right\rangle \delta(\tau_5 - \tau_6) \qquad (5.219) \\
&= -\sum_{8} \tilde{V}^{(4ph)}_{5628} \left\langle Q_{8H[J]}(\tau_5) \right\rangle \delta(\tau_5 - \tau_2) \delta(\tau_5 - \tau_6) \qquad (5.220)
\end{aligned}$$

Now insert this vertex function into the second term of Σ to get an iterated self energy term.

$$\begin{aligned}
\Sigma(1,2) &= \frac{1}{2!}\frac{\hbar}{i} \sum_{3486} \int_{c_K} d5 \tilde{V}^{(3ph)}_{134} D^Q_{35}(\tau_1\tau_5) \tilde{V}^{(4ph)}_{5628} \delta(\tau_5 - \tau_2) \left\langle Q_{8H[J]}(\tau_5) \right\rangle D^Q_{64}(\tau_5\tau_1) \qquad (5.221) \\
&= \frac{1}{2!}\frac{\hbar}{i} \sum_{34568} \tilde{V}^{(3ph)}_{134} \tilde{V}^{(4ph)}_{5628} D^Q_{35}(\tau_1\tau_2) \left\langle Q_{8H[J]}(\tau_2) \right\rangle D^Q_{64}(\tau_2\tau_1) \qquad (5.222)
\end{aligned}$$

Use this self energy term to calculate the vertex function $\Gamma(5,2,6)$ and we only retain the term involving $\frac{\delta\left\langle Q_{8H[J]}(t_2)\right\rangle_J}{\delta\left\langle Q_{H[J]}(2)\right\rangle_J}$ because the other terms vanish when we ignore thermal expansion.

$$\begin{aligned}
\Gamma(5,2,6) &= -\frac{\delta}{\delta\left\langle Q_{H[J]}(2)\right\rangle} \left(\frac{1}{2!}\frac{\hbar}{i} \sum_{789,10,11} \tilde{V}^{(3ph)}_{578} \tilde{V}^{(4ph)}_{9,10,6,11} D^Q_{79}(\tau_5\tau_6) \left\langle Q_{11H[J]}(\tau_6) \right\rangle D^Q_{10,8}(\tau_6\tau_5) \right) \\
&= -\frac{1}{2!}\frac{\hbar}{i} \sum_{789,10} \tilde{V}^{(3ph)}_{578} \tilde{V}^{(4ph)}_{9,10,6,2} D^Q_{79}(\tau_5\tau_6) D^Q_{10,8}(\tau_6\tau_5) \delta(\tau_6 - \tau_2) \qquad (5.223)
\end{aligned}$$

Substitute this vertex function $\Gamma(5,2,6)$ into the second term of Σ to get the final self energy term.

$$\begin{aligned}
& \text{“Term 2 of } \tilde{V}^{(3ph)^2} \tilde{V}^{(4ph)} \text{ type 1 self consistent self energy”} \\
&= -\frac{1}{2!}\frac{\hbar}{i} \sum_{34} \tilde{V}^{(3ph)}_{134} \\
& \quad \times \int_{c_K} d5 d6 D^Q_{35}(\tau_1\tau_5) \left(-\frac{1}{2!}\frac{\hbar}{i} \sum_{789,10} \tilde{V}^{(3ph)}_{578} \tilde{V}^{(4ph)}_{9,10,6,2} D^Q_{79}(\tau_5\tau_6) D^Q_{10,8}(\tau_6\tau_5) \delta(\tau_6 - \tau_2) \right) D^Q_{64}(\tau_6\tau_1) \\
& \quad | \quad \text{we can write } D^Q \to D \\
&= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{346789,10} \int_{c_K} d5 \tilde{V}^{(3ph)}_{134} \tilde{V}^{(3ph)}_{578} \tilde{V}^{(4ph)}_{9,10,6,2} D_{35}(\tau_1\tau_5) D_{79}(\tau_5\tau_2) D_{10,8}(\tau_2\tau_5) D_{64}(\tau_2\tau_1) \qquad (5.224)
\end{aligned}$$

This is the same as the previous term, thus the 2 terms add up.

We assign the signs to $\vec{q}$ according to the convention assigned earlier. We get,

$$\Sigma_{12}(\tau_1\tau_2) = \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \int_{c_K} d\tau_5 \tilde{V}^{(3ph)}_{\bar{1}34} \tilde{V}^{(3ph)}_{\bar{5}78} \tilde{V}^{(4ph)}_{\bar{9},\bar{10},\bar{6},2} D_{35}(\tau_1\tau_5) D_{79}(\tau_5\tau_2) D_{10,8}(\tau_2\tau_5) D_{64}(\tau_2\tau_1) \qquad (5.225)$$

Using Langreth's theorem, we get the lesser and the greater components of $\Sigma_{12}(\tau_1\tau_2)$ which is in vertex multiplication. The contours to use are shown in the diagram.

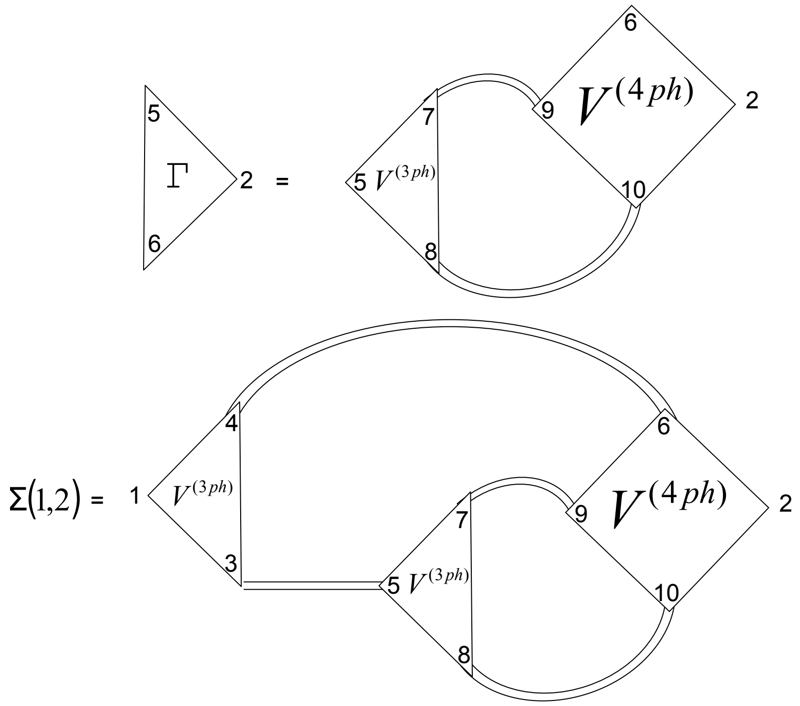


Figure 5.13: *The upper diagram is the vertex function. The lower diagram is the self consistent* $V^{(3ph)^2}V^{(3ph)}$ *Type-1 self energy.*

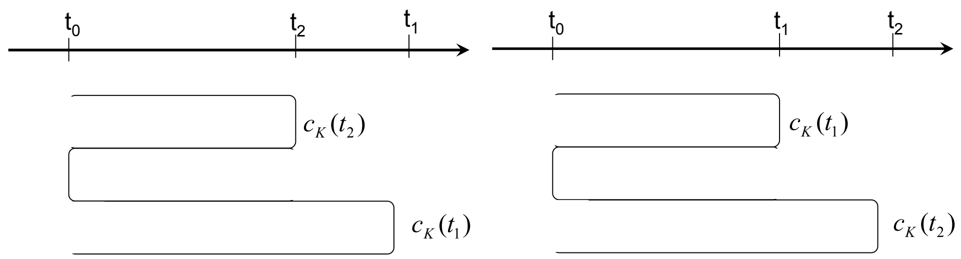


Figure 5.14: *The left diagram is for calculating* $\Sigma^{>}_{12}(t_1t_2)$ *and the right diagram is for calculating* $\Sigma^{<}_{12}(t_1t_2)$*. These contour diagrams are used for all calculations for all the remaining self consistent self energies in this section.*

$$
\begin{aligned}
\Sigma^{>}_{12}(t_1t_2) &= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \int_{c_K} d\tau_5 \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}78}\tilde{V}^{(4ph)}_{\bar{9},\bar{1}\bar{0},\bar{6},2} D_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D^{<}_{64}(t_2t_1) \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}78}\tilde{V}^{(4ph)}_{\bar{9},\bar{1}\bar{0},\bar{6},2} \\
&\quad \times \left(\int_{c_K(t_2)} d\tau_5 + \int_{c_K(t_1)} d\tau_5\right) D_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D^{<}_{64}(t_2t_1) \qquad (5.226)
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}78}\tilde{V}^{(4ph)}_{\bar{9},\bar{1}\bar{0},\bar{6},2} \\
&\quad\times\left\{\int_{c_K(t_2)} d\tau_5 D^{>}_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D^{<}_{64}(t_2t_1)\right. \\
&\quad\left.+\int_{c_K(t_1)} d\tau_5 D_{35}(t_1\tau_5)D^{>}_{79}(\tau_5t_2)D^{<}_{10,8}(t_2\tau_5)D^{<}_{64}(t_2t_1)\right\} \qquad (5.227)\\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}78}\tilde{V}^{(4ph)}_{\bar{9},\bar{1}\bar{0},\bar{6},2} \\
&\quad\times\left\{\int_{t_0}^{t_2} dt_5 D^{>}_{35}(t_1t_5)\left(D^{<}_{79}(t_5t_2)D^{>}_{10,8}(t_2t_5)-D^{>}_{79}(t_5t_2)D^{<}_{10,8}(t_2t_5)\right)D^{<}_{64}(t_2t_1)\right. \\
&\quad\left.+\int_{t_0}^{t_1} dt_5 \left(D^{>}_{35}(t_1t_5)-D^{<}_{35}(t_1t_5)\right)D^{>}_{79}(t_5t_2)D^{<}_{10,8}(t_2t_5)D^{<}_{64}(t_2t_1)\right\} \qquad (5.228)
\end{aligned}
$$

$$
\begin{aligned}
\Sigma^{<}_{12}(t_1t_2) &= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \int_{c_K} d\tau_5 \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}78}\tilde{V}^{(4ph)}_{\bar{9},\bar{1}\bar{0},\bar{6},2} D_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D^{>}_{64}(t_2t_1) \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}78}\tilde{V}^{(4ph)}_{\bar{9},\bar{1}\bar{0},\bar{6},2} \\
&\quad\times\left(\int_{c_K(t_1)} d\tau_5 + \int_{c_K(t_2)} d\tau_5\right) D_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D^{>}_{64}(t_2t_1) \qquad (5.229)\\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}78}\tilde{V}^{(4ph)}_{\bar{9},\bar{1}\bar{0},\bar{6},2} \\
&\quad\times\left\{\int_{c_K(t_1)} d\tau_5 D_{35}(t_1\tau_5)D^{<}_{79}(\tau_5t_2)D^{>}_{10,8}(t_2\tau_5)D^{>}_{64}(t_2t_1)\right. \\
&\quad\left.+\int_{c_K(t_2)} d\tau_5 D^{<}_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D^{>}_{64}(t_2t_1)\right\} \qquad (5.230)\\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}78}\tilde{V}^{(4ph)}_{\bar{9},\bar{1}\bar{0},\bar{6},2} \\
&\quad\times\left\{\int_{t_0}^{t_1} dt_5 \left(D^{>}_{35}(t_1t_5)-D^{<}_{35}(t_1t_5)\right)D^{<}_{79}(t_5t_2)D^{>}_{10,8}(t_2t_5)D^{>}_{64}(t_2t_1)\right. \\
&\quad\left.+\int_{t_0}^{t_2} dt_5 D^{<}_{35}(t_1t_5)\left(D^{<}_{79}(t_5t_2)D^{>}_{10,8}(t_2t_5)-D^{>}_{79}(t_5t_2)D^{<}_{10,8}(t_2t_5)\right)D^{>}_{64}(t_2t_1)\right\} \qquad (5.231)
\end{aligned}
$$

5.4.2.5 $V^{(3ph)^2}V^{(4ph)}$ Type-2 Term

For the type 2 term, we can get it when we use an earlier used vertex function to close the last term of Σ. The vertex function is

$$
\Gamma(7,6,8) = -\frac{\delta}{\delta\left\langle Q_{H[J]}(6)\right\rangle}\sum_{9}\tilde{V}^{(3ph)}_{789}\left\langle Q_{9H[J]}(\tau_7)\right\rangle\delta(\tau_7-\tau_8) \qquad (5.232)
$$

$$= -\sum_9 \tilde{V}^{(3ph)}_{789}\delta_{69}\delta(\tau_7-\tau_6)\delta(\tau_7-\tau_8) \quad (5.233)$$

$$= -\tilde{V}^{(3ph)}_{786}\delta(\tau_7-\tau_6)\delta(\tau_7-\tau_8) \quad (5.234)$$

As said, we now insert this vertex function into the last term of Σ.

$$\begin{aligned}
\Sigma(1,2) &= \frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2 \sum_{345}\tilde{V}^{(4ph)}_{1345}\int_{c_K} d6d7d8\frac{\delta}{\delta\left\langle Q_{H[J]}(2)\right\rangle} \\
&\quad \times \left(D^Q_{65}(\tau_6\tau_1)D^Q_{37}(\tau_1\tau_7)\left(-\tilde{V}^{(3ph)}_{786}\delta(\tau_7-\tau_6)\delta(\tau_7-\tau_8)\right)D^Q_{84}(\tau_8\tau_1)\right) &(5.235)\\
&= -\frac{1}{3!}\left(-\frac{\hbar}{i}\right)^2\sum_{34568}\tilde{V}^{(4ph)}_{1345}\tilde{V}^{(3ph)}_{786}\int_{c_K}d7\frac{\delta}{\delta\left\langle Q_{H[J]}(2)\right\rangle}\left(D^Q_{65}(\tau_7\tau_1)D^Q_{37}(\tau_1\tau_7)D^Q_{84}(\tau_8\tau_1)\right) &(5.236)\\
&\quad | \ \text{the 3 terms from differentiation are the same after relabelling indices}\\
&= -\frac{1}{2!}\left(-\frac{\hbar}{i}\right)^2\sum_{34568}\tilde{V}^{(4ph)}_{1345}\tilde{V}^{(3ph)}_{786}\int_{c_K}d7\frac{\delta D^Q_{65}(\tau_7\tau_1)}{\delta\left\langle Q_{H[J]}(2)\right\rangle}D^Q_{37}(\tau_1\tau_7)D^Q_{84}(\tau_7\tau_1) &(5.237)\\
&\quad | \ \text{use } \frac{\delta D^Q_{65}(\tau_7\tau_1)}{\delta\left\langle Q_{H[J]}(2)\right\rangle} = \int_{c_K}d9d(10)D^Q_{69}(\tau_7\tau_9)\Gamma(9,2,10)D^Q_{10,5}(\tau_10\tau_1)\\
&\quad | \ \text{and write } D^Q\to D\\
&= \frac{1}{2!}\left(-\frac{\hbar}{i}\right)^2\sum_{345689,10}\tilde{V}^{(4ph)}_{1345}\tilde{V}^{(3ph)}_{786}\tilde{V}^{(3ph)}_{9,2,10}\int_{c_K}d7D_{69}(\tau_7\tau_2)D_{10,5}(\tau_2\tau_1)D_{37}(\tau_1\tau_7)D_{84}(\tau_7\tau_1)
\end{aligned}$$

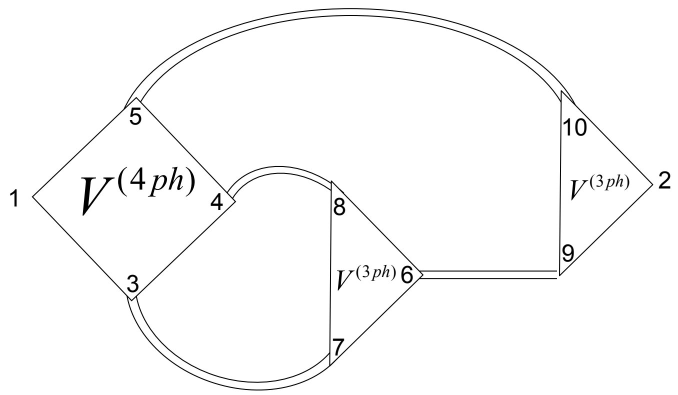


Figure 5.15: *The self consistent $V^{(3ph)^2}V^{(4ph)}$ Type-2 self energy.*

We assign the signs to $\vec{q}$ according to the convention assigned earlier. We get,

$$\Sigma_{12}(\tau_1\tau_2) = \frac{1}{2!}\left(\frac{\hbar}{i}\right)^2\sum_{3456789,10}\tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}6}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}}\int_{c_K}d\tau_7D_{69}(\tau_7\tau_2)D_{10,5}(\tau_2\tau_1)D_{37}(\tau_1\tau_7)D_{84}(\tau_7\tau_1)$$

Using Langreth's theorem, we get the lesser and the greater components of $\Sigma_{12}(\tau_1\tau_2)$ which is in vertex multiplication. The contours to use is given in the diagram given in the earlier self energy example.

$$\begin{aligned}
\Sigma^{>}_{12}(t_1t_2) &= \frac{1}{2!}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}6}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \int_{c_K} d\tau_7 D_{69}(\tau_7t_2)D^{<}_{10,5}(t_2t_1)D_{37}(t_1\tau_7)D_{84}(\tau_7t_1) \\
&= \frac{1}{2!}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}6}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad \times \left(\int_{c_K(t_2)} d\tau_7 + \int_{c_K(t_1)} d\tau_7\right) D_{69}(\tau_7t_2)D^{<}_{10,5}(t_2t_1)D_{37}(t_1\tau_7)D_{84}(\tau_7t_1) \qquad (5.238) \\
&= \frac{1}{2!}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}6}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad \times \left\{\int_{c_K(t_2)} d\tau_7 D_{69}(\tau_7t_2)D^{<}_{10,5}(t_2t_1)D^{>}_{37}(t_1\tau_7)D^{<}_{84}(\tau_7t_1)\right. \\
&\quad \left. + \int_{c_K(t_1)} d\tau_7 D^{>}_{69}(\tau_7t_2)D^{<}_{10,5}(t_2t_1)D_{37}(t_1\tau_7)D_{84}(\tau_7t_1)\right\} \qquad (5.239) \\
&= \frac{1}{2!}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}6}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad \times \left\{\int_{t_0}^{t_2} dt_7 \left(D^{<}_{69}(t_7t_2) - D^{>}_{69}(t_7t_2)\right) D^{<}_{10,5}(t_2t_1)D^{>}_{37}(t_1t_7)D^{<}_{84}(t_7t_1)\right. \\
&\quad \left. + \int_{t_0}^{t_1} dt_7 D^{>}_{69}(t_7t_2)D^{<}_{10,5}(t_2t_1)\left(D^{>}_{37}(t_1t_7)D^{<}_{84}(t_7t_1) - D^{<}_{37}(t_1t_7)D^{>}_{84}(t_7t_1)\right)\right\} \qquad (5.240)
\end{aligned}$$

$$\begin{aligned}
\Sigma^{<}_{12}(t_1t_2) &= \frac{1}{2!}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}6}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \int_{c_K} d\tau_7 D_{69}(\tau_7t_2)D^{>}_{10,5}(t_2t_1)D_{37}(t_1\tau_7)D_{84}(\tau_7t_1) \\
&= \frac{1}{2!}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}6}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad \times \left(\int_{c_K(t_1)} d\tau_7 + \int_{c_K(t_2)} d\tau_7\right) D_{69}(\tau_7t_2)D^{>}_{10,5}(t_2t_1)D_{37}(t_1\tau_7)D_{84}(\tau_7t_1) \qquad (5.241) \\
&= \frac{1}{2!}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}6}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad \times \left\{\int_{c_K(t_1)} d\tau_7 D^{<}_{69}(\tau_7t_2)D^{>}_{10,5}(t_2t_1)D_{37}(t_1\tau_7)D_{84}(\tau_7t_1)\right. \\
&\quad \left. + \int_{c_K(t_2)} d\tau_7 D_{69}(\tau_7t_2)D^{>}_{10,5}(t_2t_1)D^{<}_{37}(t_1\tau_7)D^{>}_{84}(\tau_7t_1)\right\} \qquad (5.242) \\
&= \frac{1}{2!}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(4ph)}_{\bar{1}345}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}6}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad \times \left\{\int_{t_0}^{t_1} dt_7 D^{<}_{69}(t_7t_2)D^{>}_{10,5}(t_2t_1)\left(D^{>}_{37}(t_1t_7)D^{<}_{84}(t_7t_1) - D^{<}_{37}(t_1t_7)D^{>}_{84}(t_7t_1)\right)\right.
\end{aligned}$$

$$+\int_{t_0}^{t_2} dt_7 \left(D^{<}_{69}(t_7t_2) - D^{>}_{69}(t_7t_2)\right) D^{>}_{10,5}(t_2t_1)D^{<}_{37}(t_1t_7)D^{>}_{84}(t_7t_1)\Big\} \tag{5.243}$$

5.4.2.6 $V^{(3ph)^2}V^{(4ph)}$ Type-3 Term

For the type 3 term, we use the fourth term of Σ to generate the vertex function and close the expression with the vertex function coming from first term of Σ.

$$\begin{aligned}
\Gamma(5,2,6) &= -\frac{\delta}{\delta\left\langle Q_{H[J]}(2)\right\rangle}\left(-\frac{1}{2!}\frac{\hbar}{i}\sum_{78}\tilde{V}^{(4ph)}_{5786}D^{Q}_{78}(\tau_5\tau_5)\delta(\tau_5-\tau_6)\right) && (5.244)\\
&= \frac{1}{2!}\frac{\hbar}{i}\sum_{78}\tilde{V}^{(4ph)}_{5786}\frac{\delta D^{Q}_{78}(\tau_5\tau_5)}{\delta\left\langle Q_{H[J]}(2)\right\rangle}\delta(\tau_5-\tau_6) && (5.245)\\
&\quad \Big|\ \text{use } \frac{\delta D^{Q}_{78}(t_5t_5)}{\delta\left\langle Q_{H[J]}(2)\right\rangle} = \int_{c_K} d9d(10)D^{Q}_{79}(\tau_5\tau_9)\Gamma(9,2,10)D^{Q}_{10,8}(t_10t_5)\\
&\quad \Big|\ \text{use the vertex function from first term of } \Sigma,\ \Gamma(9,2,10) = -\tilde{V}^{(3ph)}_{9,2,10}\delta(\tau_9-\tau_2)\delta(\tau_9-\tau_{10})\\
&= -\frac{1}{2!}\frac{\hbar}{i}\sum_{789,10}\tilde{V}^{(4ph)}_{5786}\tilde{V}^{(3ph)}_{9,2,10}D^{Q}_{7,9}(\tau_5\tau_2)D^{Q}_{10,8}(\tau_2\tau_5)\delta(\tau_5-\tau_6) && (5.246)
\end{aligned}$$

Insert this vertex function, $\Gamma(5,2,6)$ into second term of Σ to get an iterated self energy term.

$$\begin{aligned}
\Sigma(1,2) &= -\frac{1}{2!}\frac{\hbar}{i}\sum_{34}\tilde{V}^{(3ph)}_{134}\\
&\quad\times\int_{c_K} d5d6D^{Q}_{35}(\tau_1\tau_5)\left(-\frac{1}{2!}\frac{\hbar}{i}\sum_{789,10}\tilde{V}^{(4ph)}_{5786}\tilde{V}^{(3ph)}_{9,2,10}D^{Q}_{7,9}(\tau_5\tau_2)D^{Q}_{10,8}(\tau_2\tau_5)\delta(\tau_5-\tau_6)\right)D^{Q}_{64}(\tau_6\tau_1)\\
&\quad \Big|\ \text{write } D^{Q}\to D\\
&= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2\sum_{346789,10}\int_{c_K} d5\tilde{V}^{(3ph)}_{134}\tilde{V}^{(4ph)}_{5786}\tilde{V}^{(3ph)}_{9,2,10}D_{35}(\tau_1\tau_5)D_{79}(\tau_5\tau_2)D_{10,8}(\tau_2\tau_5)D_{64}(\tau_5\tau_1) && (5.247)
\end{aligned}$$

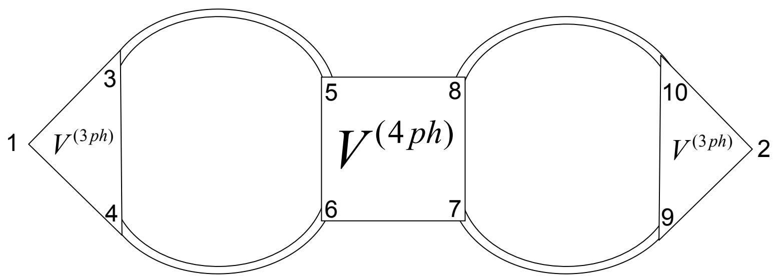


Figure 5.16: *The self consistent $V^{(3ph)^2}V^{(4ph)}$ Type-3 self energy.*

We assign the signs to $\vec{q}$ according to the convention assigned earlier. We get

$$\Sigma_{12}(\tau_1\tau_2) = \frac{1}{4}\left(\frac{\hbar}{i}\right)^2\sum_{3456789,10}\int_{c_K} d\tau_5\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(4ph)}_{\bar{5}78\bar{6}}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}}D_{35}(\tau_1\tau_5)D_{79}(\tau_5\tau_2)D_{10,8}(\tau_2\tau_5)D_{64}(\tau_5\tau_1)$$

Using Langreth's theorem, we get the lesser and the greater components of $\Sigma_{12}(\tau_1\tau_2)$ which is in vertex multiplication. The contours to use is given in the diagram given in the earlier self energy example.

$$\begin{aligned}
\Sigma^{>}_{12}(t_1t_2) &= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(4ph)}_{\bar{5}78\bar{6}}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \int_{c_K} d\tau_5 D_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D_{64}(\tau_5t_1) \\
&= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(4ph)}_{\bar{5}78\bar{6}}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad\times\left(\int_{c_K(t_2)} d\tau_5 + \int_{c_K(t_1)} d\tau_5\right) D_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D_{64}(\tau_5t_1) &(5.248)\\
&= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(4ph)}_{\bar{5}78\bar{6}}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad\times\left\{\int_{c_K(t_2)} d\tau_5 D^{>}_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D^{<}_{64}(\tau_5t_1)\right. \\
&\quad\left.+\int_{c_K(t_1)} d\tau_5 D_{35}(t_1\tau_5)D^{>}_{79}(\tau_5t_2)D^{<}_{10,8}(t_2\tau_5)D_{64}(\tau_5t_1)\right\} &(5.249)\\
&= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(4ph)}_{\bar{5}78\bar{6}}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad\times\left\{\int_{t_0}^{t_2} dt_5 D^{>}_{35}(t_1t_5)\left(D^{<}_{79}(t_5t_2)D^{>}_{10,8}(t_2t_5) - D^{>}_{79}(t_5t_2)D^{<}_{10,8}(t_2t_5)\right)D^{<}_{64}(t_5t_1)\right. \\
&\quad+\int_{t_0}^{t_1} dt_5\left(D^{>}_{35}(t_1t_5)D^{>}_{79}(t_5t_2)D^{<}_{10,8}(t_2t_5)D^{<}_{64}(t_5t_1)\right. \\
&\quad\left.\left.-D^{<}_{35}(t_1t_5)D^{>}_{79}(t_5t_2)D^{<}_{10,8}(t_2t_5)D^{>}_{64}(t_5t_1)\right)\right\} &(5.250)
\end{aligned}$$

$$\begin{aligned}
\Sigma^{<}_{12}(t_1t_2) &= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(4ph)}_{\bar{5}78\bar{6}}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \int_{c_K} d\tau_5 D_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D_{64}(\tau_5t_1) \\
&= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(4ph)}_{\bar{5}78\bar{6}}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad\times\left(\int_{c_K(t_1)} d\tau_5 + \int_{c_K(t_2)} d\tau_5\right) D_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D_{64}(\tau_5t_1) &(5.251)\\
&= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(4ph)}_{\bar{5}78\bar{6}}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}} \\
&\quad\times\left\{\int_{c_K(t_1)} d\tau_5 D_{35}(t_1\tau_5)D^{<}_{79}(\tau_5t_2)D^{>}_{10,8}(t_2\tau_5)D_{64}(\tau_5t_1)\right. \\
&\quad\left.+\int_{c_K(t_2)} d\tau_5 D^{<}_{35}(t_1\tau_5)D_{79}(\tau_5t_2)D_{10,8}(t_2\tau_5)D^{>}_{64}(\tau_5t_1)\right\} &(5.252)\\
&= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{3456789,10} \tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(4ph)}_{\bar{5}78\bar{6}}\tilde{V}^{(3ph)}_{\bar{9},2,\bar{10}}
\end{aligned}$$

$$\times \left\{ \int_{t_0}^{t_1} dt_5 \left(D^>_{35}(t_1t_5) D^<_{79}(t_5t_2) D^>_{10,8}(t_2t_5) D^<_{64}(t_5t_1) \right.\right.$$
$$\left. -D^<_{35}(t_1t_5) D^<_{79}(t_5t_2) D^>_{10,8}(t_2t_5) D^<_{64}(t_5t_1) \right)$$
$$\left. + \int_{t_0}^{t_2} dt_5 D^<_{35}(t_1t_5) \left(D^<_{79}(t_5t_2) D^>_{10,8}(t_2t_5) - D^>_{79}(t_5t_2) D^<_{10,8}(t_2t_5) \right) D^>_{64}(t_5t_1) \right\} \tag{5.253}$$

5.4.2.7 $V^{(3ph)^4}$ Term

We get this term by using the earlier $\tilde{V}^{(3ph)^2}$ self energy term to generate the vertex term. We will also use the vertex term from the $\tilde{V}^{(3ph)^2}$ calculation to close the expression. Then the vertex term is substituted into the second term of Σ to generate the self energy term.

$$\Gamma(5,2,6) = -\frac{\delta}{\delta \langle Q_{H[J]}(2) \rangle} \text{“}\tilde{V}^{(3ph)^2} \text{ term in } \Sigma(5,6)\text{”} \tag{5.254}$$
$$= -\frac{\delta}{\delta \langle Q_{H[J]}(2) \rangle} \left(\frac{1}{2!} \frac{\hbar}{i} \sum_{789,10} \tilde{V}^{(3ph)}_{578} \tilde{V}^{(3ph)}_{9,10,6} D^Q_{79}(\tau_5\tau_6) D^Q_{10,8}(\tau_6\tau_5) \right) \tag{5.255}$$
$$| \quad \text{use product rule and the 2 terms add after relabelling indices}$$
$$= \frac{\hbar}{i} \sum_{789,10} \tilde{V}^{(3ph)}_{578} \tilde{V}^{(3ph)}_{9,10,6} \left(-\frac{\delta D^Q_{79}(\tau_5\tau_6)}{\delta \langle Q_{H[J]}(2) \rangle} D^Q_{10,8}(\tau_6\tau_5) \right) \tag{5.256}$$
$$| \quad \text{recall the relation } -\frac{\delta D^Q_{79}(\tau_5\tau_6)}{\delta \langle Q_{H[J]}(2) \rangle} = \int_{c_K} d(11) d(12) D^Q_{7,11}(\tau_5\tau_{11}) \Gamma(11,2,12) D^Q_{12,9}(\tau_{12}\tau_6)$$
$$| \quad \text{use the } \tilde{V}^{(3ph)} \text{ vertex function, i.e. } \Gamma(11,2,12) = -\tilde{V}^{(3ph)}_{11,2,12} \delta(\tau_{11}-\tau_2)\delta(\tau_{11}-\tau_{12})$$
$$= -\frac{\hbar}{i} \sum_{789,10,11,12} \tilde{V}^{(3ph)}_{578} \tilde{V}^{(3ph)}_{9,10,6} \tilde{V}^{(3ph)}_{11,2,12} D^Q_{7,11}(\tau_5\tau_2) D^Q_{12,9}(\tau_2\tau_6) D^Q_{10,8}(\tau_6\tau_5) \tag{5.257}$$

Now substitute this vertex function into the second term of Σ to generate the self energy term.

$$\Sigma(1,2) = \frac{1}{2!} \frac{\hbar}{i} \sum_{34} \tilde{V}^{(3ph)}_{134} \int_{c_K} d5 d6 D^Q_{35}(\tau_1\tau_5) \frac{\hbar}{i}$$
$$\times \sum_{789,10,11,12} \tilde{V}^{(3ph)}_{578} \tilde{V}^{(3ph)}_{9,10,6} \tilde{V}^{(3ph)}_{11,2,12} D^Q_{7,11}(\tau_5\tau_2) D^Q_{12,9}(\tau_2\tau_6) D^Q_{10,8}(\tau_6\tau_5) D^Q_{64}(\tau_6\tau_1) \tag{5.258}$$
$$= \frac{1}{2!} \left(\frac{\hbar}{i} \right)^2 \sum_{34789,10,11,12} \int_{c_K} d5 d6 \tilde{V}^{(3ph)}_{134} \tilde{V}^{(3ph)}_{578} \tilde{V}^{(3ph)}_{9,10,6} \tilde{V}^{(3ph)}_{11,2,12}$$
$$\times D_{35}(\tau_1\tau_5) D_{7,11}(\tau_5\tau_2) D_{12,9}(\tau_2\tau_6) D_{10,8}(\tau_6\tau_5) D_{64}(\tau_6\tau_1) \tag{5.259}$$

We assign the signs to $\vec{q}$ according to the convention assigned earlier. We get

$$\Sigma_{12}(\tau_1\tau_2) = \frac{1}{2!} \left(\frac{\hbar}{i} \right)^2 \sum_{34789,10,11,12} \int_{c_K} d5 d6 \tilde{V}^{(3ph)}_{\bar{1}34} \tilde{V}^{(3ph)}_{\bar{5}78} \tilde{V}^{(3ph)}_{9,\bar{10},\bar{6}} \tilde{V}^{(3ph)}_{\bar{11},2,\bar{12}}$$
$$\times D_{35}(\tau_1\tau_5) D_{7,11}(\tau_5\tau_2) D_{12,9}(\tau_2\tau_6) D_{10,8}(\tau_6\tau_5) D_{64}(\tau_6\tau_1) \tag{5.260}$$

$\Sigma_{12}(\tau_1\tau_2)$ is in vertex multiplication and we see that the use of Langreth's theorem here is precisely the vertex multiplication example shown in the NEGF chapter. There are 16 terms for $\Sigma^<_{12}(t_1t_2)$ and

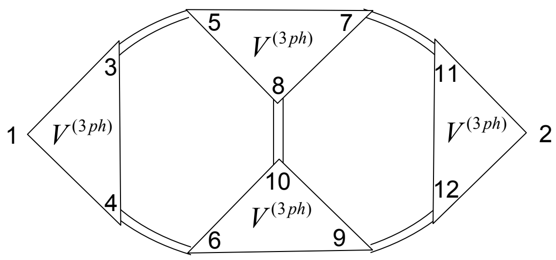


Figure 5.17: *The self consistent $V^{(3ph)^4}$ self energy.*

$\Sigma^{>}_{12}(t_1 t_2)$ each. We do not proceed further as it is worth a PhD project on its own.

5.5 Kinetic Theory: Boltzmann Equation (BE)

In this section, we go through the basics of Boltzmann kinetic theory for phonon-phonon scattering. This is to pave the way for the derivation of BE from QKE and to collect standard manipulations of BE that may help in handling QKE.

The notation $1 \equiv j_1 \vec{q}_1$ and $\bar{1} \equiv j_1, -\vec{q}_1$ is used in many instances to save writing.

5.5.1 LHS of BE: Driving Term

The driving term (due to a temperature gradient) is

$$\text{Full LHS:} \boxed{\left(\frac{\partial}{\partial t} + (\nabla_{\vec{q}_1}\omega_1) \cdot \nabla_{\vec{r}}\right) N_1} \tag{5.261}$$

Later, we will deal with the linearized theory, thus we will need the linearized driving term and so we now derive the form of the linearized driving term. We linearize the LHS of Boltzmann equation by $N_1 \to N_1^{eq}$.

$$\begin{aligned}
\text{LHS} &= \left(\frac{\partial}{\partial t} + (\nabla_{\vec{q}_1}\omega_1) \cdot \nabla_{\vec{r}}\right) N_1^{eq} && (5.262)\\
&= (\nabla_{\vec{q}_1}\omega_1) \cdot (\nabla_{\vec{r}} N_1^{eq}) && (5.263)\\
&= (\nabla_{\vec{q}_1}\omega_1) \cdot (\nabla_{\vec{r}} T) \frac{\partial N_1^{eq}}{\partial T} && (5.264)\\
| \quad & \text{with } \frac{\partial N_1^{eq}}{\partial T} = \frac{\partial}{\partial T}\left(e^{\hbar\omega_1/k_B T} - 1\right)^{-1} = N_1^{eq}(N_1^{eq}+1)\frac{\hbar\omega_1}{k_B T^2} \\
&= (\nabla_{\vec{q}_1}\omega_1) \cdot (\nabla_{\vec{r}} T) N_1^{eq}(N_1^{eq}+1)\frac{\hbar\omega_1}{k_B T^2} && (5.265)
\end{aligned}$$

$$\text{Linearized LHS:} \boxed{(\nabla_{\vec{q}_1}\omega_1) \cdot (\nabla_{\vec{r}} T) N_1^{eq}(N_1^{eq}+1)\frac{\hbar\omega_1}{k_B T^2}} \tag{5.266}$$

which is the linearized driving term (LHS) to use in a linearized distribution description.

5.5.2 RHS of BE: 3-Phonon Collision Operator

The so-called "semi-classical" feature (or "semi-quantum") in the phonon Boltzmann equation is incooperated in the collision operator where the transition rates between modes are calculated via Fermi's Golden Rule. The perturbation Hamiltonian is the cubic term in expansion of the interatomic potential.

$$
\begin{aligned}
H^{(3ph)} &= \frac{1}{3!}\sum_{1,2,3} V_{1,2,3}^{(3ph)} \left(a_{\bar{1}}^{\dagger} + a_1\right)\left(a_{\bar{2}}^{\dagger} + a_2\right)\left(a_{\bar{3}}^{\dagger} + a_3\right) && (5.267)\\
&= \frac{1}{3!}\sum_{1,2,3} V_{1,2,3}^{(3ph)} \left(a_{\bar{1}}^{\dagger}a_{\bar{2}}^{\dagger}a_{\bar{3}}^{\dagger} + a_{\bar{1}}^{\dagger}a_{\bar{2}}^{\dagger}a_3 + a_{\bar{1}}^{\dagger}a_2a_{\bar{3}}^{\dagger} + a_{\bar{1}}^{\dagger}a_2a_3 + a_1a_{\bar{2}}^{\dagger}a_{\bar{3}}^{\dagger} + a_1a_{\bar{2}}^{\dagger}a_3 + a_1a_2a_{\bar{3}}^{\dagger} + a_1a_2a_3\right) && (5.268)
\end{aligned}
$$

Fermi's Golden Rule by construction reinforces the conservation of energy, thus we ignore the first and last term as they do not conserve energy. Take distribution $N_{j_1\vec{q}_1} = N_1$ to be the reference mode. We will then calculate the transitions in or out of this reference mode. The Golden Rule formula for transition rate is

$$W_{i\leftrightarrow f} = \frac{2\pi}{\hbar}\left|\left\langle i\left|H^{(3ph)}\right|f\right\rangle\right|^2 \delta(E_f - E_i) \tag{5.269}$$

Thus it remains to calculate the transition rate of the 6 terms in the perturbation Hamiltonian. Actually we are treating it as if there are 6 perturbation Hamiltonians. State $1 = j_1\vec{q}_1$ is treated as the reference state.[10]

$$
\begin{aligned}
\text{“2nd term, } W_{\text{2nd}}\text{”} &= \frac{2\pi}{\hbar}\left|\left\langle i\left|a_{\bar{1}}^{\dagger}a_{\bar{2}}^{\dagger}a_3\right|f\right\rangle\right|^2 \delta(\hbar\omega_1 + \hbar\omega_2 - \hbar\omega_3)\left|V_{123}^{(3ph)}\right|^2 && (5.270)\\
&\mid \ \text{where } \hbar\omega_1 + \hbar\omega_2 \text{ is the final energy, } \hbar\omega_3 \text{ is the initial energy}\\
&\mid \ \text{where } \left|V_{123}^{(3ph)}\right|^2 = V_{123}^{(3ph)}V_{123}^{(3ph)*} = V_{123}^{(3ph)}V_{\bar{1}\bar{2}\bar{3}}^{(3ph)}\\
&\mid \ \text{use ladder operator relations, } a|N\rangle = \sqrt{N}|N-1\rangle \text{ and } a^{\dagger}|N\rangle = \sqrt{N+1}|N+1\rangle\\
&\mid \ \text{use also } \delta(bx) = \frac{1}{|b|}\delta(x)\\
&\mid \ \text{assign } \langle i|a_{\bar{1}}^{\dagger}|f\rangle|V_{123}^{(3ph)}|^2 = \langle i|a_{\bar{1}}^{\dagger}|f\rangle|V_{\bar{1}23}^{(3ph)}|^2\\
&= \frac{2\pi}{\hbar^2}(N_1+1)(N_2+1)N_3\left|V_{\bar{1}\bar{2}3}^{(3ph)}\right|^2\delta(\omega_1+\omega_2-\omega_3) && (5.271)\\
&= \text{(scatters into } N_1\text{)} && (5.272)
\end{aligned}
$$

We must mention here that the states $|i\rangle$ and $|f\rangle$ are the number states but the "number eigenvalues" are treated as the nonequilibrium, temperature dependent distribution function. With hindsight from QKE, labelling the RHS with nonequilibrium distribution functions seems to be very closely related to self consistency in QKE. We carry on with the other 5 terms in a very similar way.

$$
\begin{aligned}
\text{“3rd term, } W_{\text{3rd}}\text{”} &= \frac{2\pi}{\hbar}\left|\left\langle i\left|a_{\bar{1}}^{\dagger}a_2a_{\bar{3}}^{\dagger}\right|f\right\rangle\right|^2 \delta(\hbar\omega_1 + \hbar\omega_3 - \hbar\omega_2)\left|V_{123}^{(3ph)}\right|^2 && (5.273)\\
&= \frac{2\pi}{\hbar^2}(N_1+1)(N_3+1)N_2\left|V_{\bar{1}2\bar{3}}^{(3ph)}\right|^2\delta(\omega_1+\omega_3-\omega_2) && (5.274)\\
&= \text{(scatters into } N_1 \text{ and is the same as } W_{\text{2nd}} \text{ after } 2\leftrightarrow 3\text{)} && (5.275)
\end{aligned}
$$

$$\text{“4th term, } W_{\text{4th}}\text{”} = \frac{2\pi}{\hbar}\left|\left\langle i\left|a_{\bar{1}}^{\dagger}a_2a_3\right|f\right\rangle\right|^2 \delta(\hbar\omega_1 - \hbar\omega_2 - \hbar\omega_3)\left|V_{123}^{(3ph)}\right|^2 \tag{5.276}$$

[10] Since we picked out a unique state for reference, the factor $\frac{1}{3!}$ in the Hamiltonian can be ignored.

$$= \frac{2\pi}{\hbar^2}(N_1+1)N_2N_3\left|V^{(3ph)}_{\bar{1}23}\right|^2\delta(\omega_1-\omega_2-\omega_3) \tag{5.277}$$
$$= \text{(scatters into } N_1\text{)} \tag{5.278}$$

$$\text{“5th term, } W_{5\text{th}}\text{”} = \frac{2\pi}{\hbar}\left|\left\langle i\left|a_1a^\dagger_{\bar{2}}a^\dagger_{\bar{3}}\right|f\right\rangle\right|^2\delta(\hbar\omega_2+\hbar\omega_3-\hbar\omega_1)\left|V^{(3ph)}_{123}\right|^2 \tag{5.279}$$
$$= \frac{2\pi}{\hbar^2}N_1(N_2+1)(N_3+1)\left|V^{(3ph)}_{1\bar{2}\bar{3}}\right|^2\delta(\omega_2+\omega_3-\omega_1) \tag{5.280}$$
$$= \text{(scatters out of } N_1\text{)} \tag{5.281}$$

$$\text{“6th term, } W_{6\text{th}}\text{”} = \frac{2\pi}{\hbar}\left|\left\langle i\left|a_1a^\dagger_{\bar{2}}a_3\right|f\right\rangle\right|^2\delta(\hbar\omega_2-\hbar\omega_1-\hbar\omega_3)\left|V^{(3ph)}_{123}\right|^2 \tag{5.282}$$
$$= \frac{2\pi}{\hbar^2}N_1(N_2+1)N_3\left|V^{(3ph)}_{1\bar{2}3}\right|^2\delta(\omega_2-\omega_1-\omega_3) \tag{5.283}$$
$$= \text{(scatters out of } N_1\text{)} \tag{5.284}$$

$$\text{“7th term, } W_{7\text{th}}\text{”} = \frac{2\pi}{\hbar}\left|\left\langle i\left|a_1a_2a^\dagger_{\bar{3}}\right|f\right\rangle\right|^2\delta(\hbar\omega_3-\hbar\omega_2-\hbar\omega_1)\left|V^{(3ph)}_{123}\right|^2 \tag{5.285}$$
$$= \frac{2\pi}{\hbar^2}N_1N_2(N_3+1)\left|V^{(3ph)}_{12\bar{3}}\right|^2\delta(\omega_3-\omega_2-\omega_1) \tag{5.286}$$
$$= \text{(scatters out of } N_1 \text{ and is the same as } W_{6\text{th}} \text{ after } 2\leftrightarrow 3\text{)} \tag{5.287}$$

We allow an indiscriminant sum over 2 and 3 but we multiply $\frac{1}{2}$ to eliminate double counting. We assign “ + ” for in-scattering and “ − ” for out-scattering. The collision integral is then,

$$\left.\frac{\partial N_1}{\partial t}\right|_{\text{coll}} = \frac{1}{2}\sum_{2,3}(2W_{2\text{nd}}+W_{4\text{th}}-W_{5\text{th}}-2W_{6\text{th}}) \tag{5.288}$$
$$= \sum_{2,3}\frac{1}{2}(W_{4\text{th}}-W_{5\text{th}})+\sum_{2,3}(W_{2\text{nd}}-W_{6\text{th}}) \tag{5.289}$$

| relabel indices and use the fact that $V^{(3ph)}$ has completely symmetric indices

$$= \frac{1}{V}\sum_{2,3}\frac{1}{2}\delta(\omega_1-\omega_2-\omega_3)\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{\bar{1}23}\right|^2((N_1+1)N_2N_3-N_1(N_2+1)(N_3+1))$$
$$+\frac{1}{V}\sum_{2,3}\delta(\omega_1+\omega_2-\omega_3)\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{12\bar{3}}\right|^2((N_1+1)(N_2+1)N_3-N_1N_2(N_3+1))$$

$$\boxed{\begin{aligned} I^{(3ph)} =&\frac{1}{V}\sum_{2,3}\frac{1}{2}\delta(\omega_1-\omega_2-\omega_3)\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{\bar{1}23}\right|^2((N_1+1)N_2N_3-N_1(N_2+1)(N_3+1)) \\ &+\frac{1}{V}\sum_{2,3}\delta(\omega_1+\omega_2-\omega_3)\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{12\bar{3}}\right|^2((N_1+1)(N_2+1)N_3-N_1N_2(N_3+1))\end{aligned}} \tag{5.290}$$

which is our final result.

5.5.2.1 Conservation of energy

We will show that the term from RHS of the phonon Boltzmann is zero. We handle each term on RHS seperately.

$$
\begin{aligned}
& \text{“First term on RHS”} \\
= \; & \frac{1}{V}\sum_{1,2,3}\frac{1}{2}\frac{2\pi V}{\hbar^2}\delta(\omega_1-\omega_2-\omega_3)\left|V^{(3ph)}_{\bar{1},2,3}\right|^2\hbar\omega_1\left((N_1+1)N_2N_3-N_1(N_2+1)(N_3+1)\right) && (5.291)\\
| \; & \text{swop indices } 1\to 3,\ 3\to 2 \text{ and } 2\to 1 \\
= \; & \frac{1}{V}\frac{1}{2}\frac{2\pi V}{\hbar^2}\sum_{1,2,3}\left|V^{(3ph)}_{\bar{3},1,2}\right|^2\hbar\omega_3\delta(\omega_3-\omega_1-\omega_2)\left((N_3+1)N_1N_2-N_3(N_1+1)(N_2+1)\right) && (5.292)\\
| \; & \text{use identity } \delta(ax)=\frac{1}{|a|}\delta(x) \text{ so that } \delta(\omega_3-\omega_1-\omega_2)=\delta(\omega_3+\omega_1+\omega_2) \\
= \; & -\frac{1}{V}\frac{1}{2}\frac{2\pi V}{\hbar^2}\sum_{1,2,3}\left|V^{(3ph)}_{\bar{3},1,2}\right|^2\hbar\omega_3\delta(\omega_1+\omega_2-\omega_3)\left((N_1+1)(N_2+1)N_3-N_1N_2(N_3+1)\right) && (5.293)
\end{aligned}
$$

$$
\begin{aligned}
& \text{“Second term on RHS”} \\
= \; & \frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3}\delta(\omega_1+\omega_2-\omega_3)\left|V^{(3ph)}_{1,2,\bar{3}}\right|^2\hbar\omega_1\left((N_1+1)(N_2+1)N_3-N_1N_2(N_3+1)\right) && (5.294)\\
| \; & \text{write } \hbar\omega_1=\frac{1}{2}\hbar\omega_1+\frac{1}{2}\hbar\omega_1 \\
| \; & \text{due to } 1,2 \text{ symmetry, we swop } 1\to 2 \text{ in the second term, so } \hbar\omega_1=\frac{1}{2}\hbar\omega_1+\frac{1}{2}\hbar\omega_2 \\
= \; & \frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3}\left|V^{(3ph)}_{1,2,\bar{3}}\right|^2\delta(\omega_1+\omega_2-\omega_3)\frac{1}{2}\hbar(\omega_1+\omega_2)\left((N_1+1)(N_2+1)N_3-N_1N_2(N_3+1)\right) \\
| \; & \text{use the energy conservation delta function to get } \omega_1+\omega_2=\omega_3 \\
= \; & \frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3}\left|V^{(3ph)}_{1,2,\bar{3}}\right|^2\frac{1}{2}\hbar\omega_3\delta(\omega_1+\omega_2-\omega_3)\left((N_1+1)(N_2+1)N_3-N_1N_2(N_3+1)\right) && (5.295)
\end{aligned}
$$

Thus the 2 terms are the negatives of each other and so their sum is zero.

5.5.2.2 (Distribution) Linearization

We will now work with the linearized (with respect to the distribution) Boltzmann equation so as to achieve further progress analytically. Linearized quantities will be denoted with Δ. The linearized distribution is chosen to be in this form,

$$N_1 \approx N_1^{\mathrm{eq}}+\Delta N_1 \equiv N_1^{\mathrm{eq}}+N_1^{\mathrm{eq}}(N_1^{\mathrm{eq}}+1)y_1 \tag{5.296}$$

Now we linearize the 3-phonon collision operator and express it in terms of y_1. We do it term by term.

$$
\begin{aligned}
& \text{“first term of } I^{(3ph)}[N_1]\text{”} \\
= \; & (N_1+1)N_2N_3 && (5.297)\\
\approx \; & (N_1^{\mathrm{eq}}+N_1^{\mathrm{eq}}(N_1^{\mathrm{eq}}+1)y_1+1)(N_2^{\mathrm{eq}}+N_2^{\mathrm{eq}}(N_2^{\mathrm{eq}}+1)y_2)(N_3^{\mathrm{eq}}+N_3^{\mathrm{eq}}(N_3^{\mathrm{eq}}+1)y_3) && (5.298)\\
| \; & \text{expand and retain to first order in } y
\end{aligned}
$$

$$\approx \quad (N_1^{\text{eq}}+1)N_2^{\text{eq}}N_3^{\text{eq}}(1+N_1^{\text{eq}}y_1+(N_2^{\text{eq}}+1)y_2+(N_3^{\text{eq}}+1)y_3) \tag{5.299}$$

$|$ the zeroth order term, $(N_1^{\text{eq}}+1)N_2^{\text{eq}}N_3^{\text{eq}}$ (in total) makes $I^{(3ph)}=0$, but we drop it first

$$= \quad (N_1^{\text{eq}}+1)N_2^{\text{eq}}N_3^{\text{eq}}(N_1^{\text{eq}}y_1+(N_2^{\text{eq}}+1)y_2+(N_3^{\text{eq}}+1)y_3) \tag{5.300}$$

We can see that the special form of the linear distribution provides some mathematical convenience when doing calculations.

$$\text{“second term of } I^{(3ph)}[N_1]\text{”} = N_1(N_2+1)(N_3+1) \tag{5.301}$$

$$\approx N_1^{\text{eq}}(N_2^{\text{eq}}+1)(N_3^{\text{eq}}+1)((N_1^{\text{eq}}+1)y_1+N_2^{\text{eq}}y_2+N_3^{\text{eq}}y_3) \tag{5.302}$$

$|$ use identity, $N_1^{\text{eq}}(N_2^{\text{eq}}+1)(N_3^{\text{eq}}+1)=(N_1^{\text{eq}}+1)N_2^{\text{eq}}N_3^{\text{eq}}$

$|$ it can be directly checked using the Bose Einstein expressions

$$= (N_1^{\text{eq}}+1)N_2^{\text{eq}}N_3^{\text{eq}}((N_1^{\text{eq}}+1)y_1+N_2^{\text{eq}}y_2+N_3^{\text{eq}}y_3) \tag{5.303}$$

$$\text{“first term of } I^{(3ph)}[N_1]\text{”} - \text{“second term of } I^{(3ph)}[N_1]\text{”} = -(N_1^{\text{eq}}+1)N_2^{\text{eq}}N_3^{\text{eq}}(y_1-y_2-y_3)$$

Very similarly, for the other 2 terms in the collison integral,

$$\text{“third term of } I^{(3ph)}[N_1]\text{”} - \text{“fourth term of } I^{(3ph)}[N_1]\text{”} = -(N_3^{\text{eq}}+1)N_2^{\text{eq}}N_1^{\text{eq}}(y_1+y_2-y_3)$$

Thus the linearized 3-phonon collision integral is

$$\boxed{\begin{aligned}\Delta I^{(3ph)} = &-\frac{1}{V}\frac{1}{2}\frac{2\pi V}{\hbar^2}\sum_{2,3}\left|V_{\bar{1},2,3}^{(3ph)}\right|^2\delta(\omega_1-\omega_2-\omega_3)(N_1^{\text{eq}}+1)N_2^{\text{eq}}N_3^{\text{eq}}(y_1-y_2-y_3)\\ &-\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3}\left|V_{1,2,\bar{3}}^{(3ph)}\right|^2\delta(\omega_1+\omega_2-\omega_3)(N_3^{\text{eq}}+1)N_2^{\text{eq}}N_1^{\text{eq}}(y_1+y_2-y_3)\end{aligned}} \tag{5.304}$$

In subsequent sections, it is convenient to treat it as a sum of Normal and Umklapp parts, i.e. $\Delta I^{(3ph)} \equiv \Delta I_N^{(3ph)} + \Delta I_U^{(3ph)}$.

5.5.3 RHS of BE: 4-Phonon Collision Operator

The perturbation Hamiltonian is

$$H^{(4ph)} = \frac{1}{4!}\sum_{1,2,3,4} V_{1,2,3,4}^{(4ph)}\left(a_{\bar{1}}^\dagger+a_1\right)\left(a_{\bar{2}}^\dagger+a_2\right)\left(a_{\bar{3}}^\dagger+a_3\right)\left(a_{\bar{4}}^\dagger+a_4\right) \tag{5.305}$$

$$\begin{aligned}= \frac{1}{4!}\sum_{1,2,3,4} V_{1,2,3,4}^{(4ph)}\Big(&a_{\bar{1}}^\dagger a_{\bar{2}}^\dagger a_{\bar{3}}^\dagger a_{\bar{4}}^\dagger + a_{\bar{1}}^\dagger a_{\bar{2}}^\dagger a_3 a_{\bar{4}}^\dagger + a_{\bar{1}}^\dagger a_2 a_{\bar{3}}^\dagger a_{\bar{4}}^\dagger + a_{\bar{1}}^\dagger a_2 a_3 a_{\bar{4}}^\dagger + a_1 a_{\bar{2}}^\dagger a_{\bar{3}}^\dagger a_{\bar{4}}^\dagger + a_1 a_{\bar{2}}^\dagger a_3 a_{\bar{4}}^\dagger\\ &+a_1 a_2 a_{\bar{3}}^\dagger a_{\bar{4}}^\dagger + a_1 a_2 a_3 a_{\bar{4}}^\dagger + a_{\bar{1}}^\dagger a_{\bar{2}}^\dagger a_{\bar{3}}^\dagger + a_4 a_{\bar{1}}^\dagger a_{\bar{2}}^\dagger a_3 a_4 + a_{\bar{1}}^\dagger a_2 a_{\bar{3}}^\dagger a_4 + a_{\bar{1}}^\dagger a_2 a_3 a_4\\ &+a_1 a_{\bar{2}}^\dagger a_{\bar{3}}^\dagger a_4 + a_1 a_{\bar{2}}^\dagger a_3 a_4 + a_1 a_2 a_{\bar{3}}^\dagger a_4 + a_1 a_2 a_3 a_4\Big)\end{aligned} \tag{5.306}$$

We drop the first and the last term as they do not conserve energy. Take $N_{j_1\vec{q}_1} \equiv N_1$ to be the reference mode (and we can ignore the $\frac{1}{4!}$ factor), so indices $2, 3$ and 4 are free. From Golden Rule the transition rate is,

$$W = \frac{2\pi}{\hbar}\left|\left\langle i\left|H^{(4ph)}\right|f\right\rangle\right|^2\delta(E_f-E_i) \tag{5.307}$$

Now we calculate each of the $16-2=14$ terms.

$$\begin{aligned}
&\text{“ 2nd term } W_{\text{2nd}}\text{”} \\
=\ & \frac{2\pi}{\hbar}\left|\left\langle i\left|a_{\bar{1}}^{\dagger}a_{\bar{2}}^{\dagger}a_3a_{\bar{4}}^{\dagger}\right|f\right\rangle\right|^2\delta(\hbar\omega_1+\hbar\omega_2+\hbar\omega_4-\hbar\omega_3)\left|V_{1,2,3,4}^{(4ph)}\right|^2 && (5.308)\\
|\ & \text{use ladder operator relations, } a|N\rangle=\sqrt{N}|N-1\rangle \text{ and } a^{\dagger}|N\rangle=\sqrt{N+1}|N+1\rangle\\
|\ & \text{and use } \delta(\hbar x)=\frac{1}{|\hbar|}\delta(x)\\
|\ & \text{assign the sign } \langle i|a_{\bar{1}}^{\dagger}|f\rangle|V_{1234}^{(4ph)}|^2=\langle i|a_{\bar{1}}^{\dagger}|f\rangle|V_{\bar{1}234}^{(4ph)}|^2\\
=\ & \frac{2\pi}{\hbar^2}(N_1+1)(N_2+1)N_3(N_4+1)\left|V_{\bar{1},\bar{2},3,\bar{4}}^{(4ph)}\right|^2\delta(\omega_1+\omega_2+\omega_4-\omega_3) && (5.309)\\
=\ & \text{(scatters into } N_1\text{)} && (5.310)
\end{aligned}$$

The evaluation of the terms goes through the same process, so we only write the results for the other 13 terms.

$$\begin{aligned}
\text{“ 3rd term } W_{\text{3rd}}\text{”} &= \frac{2\pi}{\hbar^2}(N_1+1)N_2(N_3+1)(N_4+1)\left|V_{\bar{1},2,\bar{3},\bar{4}}^{(4ph)}\right|^2\delta(\omega_1+\omega_3+\omega_4-\omega_2) && (5.311)\\
&= \text{(scatters into } N_1\text{)} && (5.312)
\end{aligned}$$

$$\begin{aligned}
\text{“ 4th term } W_{\text{4th}}\text{”} &= \frac{2\pi}{\hbar^2}(N_1+1)N_2N_3(N_4+1)\left|V_{\bar{1},2,3,\bar{4}}^{(4ph)}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3) && (5.313)\\
&= \text{(scatters into } N_1\text{)} && (5.314)
\end{aligned}$$

$$\begin{aligned}
\text{“ 5th term } W_{\text{5th}}\text{”} &= \frac{2\pi}{\hbar^2}N_1(N_2+1)(N_3+1)(N_4+1)\left|V_{1,\bar{2},\bar{3},\bar{4}}^{(4ph)}\right|^2\delta(\omega_2+\omega_3+\omega_4-\omega_1) && (5.315)\\
&= \text{(scatters out of } N_1\text{)} && (5.316)
\end{aligned}$$

$$\begin{aligned}
\text{“ 6th term } W_{\text{6th}}\text{”} &= \frac{2\pi}{\hbar^2}N_1N_2(N_3+1)(N_4+1)\left|V_{1,\bar{2},3,\bar{4}}^{(4ph)}\right|^2\delta(\omega_2+\omega_4-\omega_3-\omega_1) && (5.317)\\
&= \text{(scatters out of } N_1\text{)} && (5.318)
\end{aligned}$$

$$\begin{aligned}
\text{“ 7th term } W_{\text{7th}}\text{”} &= \frac{2\pi}{\hbar^2}N_1N_2(N_3+1)(N_4+1)\left|V_{1,2,\bar{3},\bar{4}}^{(4ph)}\right|^2\delta(\omega_3+\omega_4-\omega_2-\omega_1) && (5.319)\\
&= \text{(scatters out of } N_1\text{)} && (5.320)
\end{aligned}$$

$$\begin{aligned}
\text{“ 8th term } W_{\text{8th}}\text{”} &= \frac{2\pi}{\hbar^2}N_1N_2N_3(N_4+1)\left|V_{1,2,3,\bar{4}}^{(4ph)}\right|^2\delta(\omega_4-\omega_1-\omega_2-\omega_3) && (5.321)\\
&= \text{(scatters out of } N_1\text{)} && (5.322)
\end{aligned}$$

$$\begin{aligned}
\text{“ 9th term } W_{\text{9th}}\text{”} &= \frac{2\pi}{\hbar^2}(N_1+1)(N_2+1)(N_3+1)N_4\left|V_{\bar{1},\bar{2},\bar{3},4}^{(4ph)}\right|^2\delta(\omega_1+\omega_2+\omega_3-\omega_4) && (5.323)\\
&= \text{(scatters into } N_1\text{)} && (5.324)
\end{aligned}$$

$$\text{“10th term } W_{\text{10th}}\text{”} = \frac{2\pi}{\hbar^2}(N_1+1)(N_2+1)N_3N_4\left|V_{\bar{1},\bar{2},3,4}^{(4ph)}\right|^2\delta(\omega_1+\omega_2-\omega_3-\omega_4) \quad (5.325)$$

$$= \text{(scatters into } N_1) \tag{5.326}$$

$$\text{“11th term } W_{11\text{th}}\text{”} = \frac{2\pi}{\hbar^2}(N_1+1)N_2(N_3+1)N_4 \left|V^{(4ph)}_{\bar{1},2,\bar{3},4}\right|^2 \delta(\omega_1+\omega_3-\omega_2-\omega_4) \tag{5.327}$$

$$= \text{(scatters into } N_1) \tag{5.328}$$

$$\text{“12th term } W_{12\text{th}}\text{”} = \frac{2\pi}{\hbar^2}(N_1+1)N_2N_3N_4 \left|V^{(4ph)}_{\bar{1},2,3,4}\right|^2 \delta(\omega_1-\omega_2-\omega_3-\omega_4) \tag{5.329}$$

$$= \text{(scatters into } N_1) \tag{5.330}$$

$$\text{“13th term } W_{13\text{th}}\text{”} = \frac{2\pi}{\hbar^2}N_1(N_2+1)(N_3+1)N_4 \left|V^{(4ph)}_{1,\bar{2},\bar{3},4}\right|^2 \delta(\omega_2+\omega_3-\omega_1-\omega_4) \tag{5.331}$$

$$= \text{(scatters out of } N_1) \tag{5.332}$$

$$\text{“14th term } W_{14\text{th}}\text{”} = \frac{2\pi}{\hbar^2}N_1(N_2+1)N_3N_4 \left|V^{(4ph)}_{1,\bar{2},3,4}\right|^2 \delta(\omega_2-\omega_1-\omega_3-\omega_4) \tag{5.333}$$

$$= \text{(scatters out of } N_1) \tag{5.334}$$

$$\text{“15th term } W_{15\text{th}}\text{”} = \frac{2\pi}{\hbar^2}N_1N_2(N_3+1)N_4 \left|V^{(4ph)}_{1,2,\bar{3},4}\right|^2 \delta(\omega_3-\omega_1-\omega_2-\omega_4) \tag{5.335}$$

$$= \text{(scatters out of } N_1) \tag{5.336}$$

We can now calculate the collision integral. A $\frac{1}{3!}$ is inserted to allow an indiscriminant sum over indices 2,3 and 4.

$$I^{(4ph)} = \left.\frac{\partial N_1}{\partial t}\right|_{\text{coll}}$$

$$= \frac{1}{3!}\sum_{2,3,4}\left(W_{2\text{nd}}+W_{3\text{rd}}+W_{4\text{th}}-W_{5\text{th}}-W_{6\text{th}}-W_{7\text{th}}-W_{8\text{th}}\right.$$
$$\left.+W_{9\text{th}}+W_{10\text{th}}+W_{11\text{th}}+W_{12\text{th}}-W_{13\text{th}}-W_{14\text{th}}-W_{15\text{th}}\right) \tag{5.337}$$

$|$ note, $W_{3\text{rd}} = W_{2\text{nd}} = W_{9\text{th}}$ and $W_{4\text{th}} = W_{10\text{th}} = W_{11\text{th}}$

$|$ note, $W_{7\text{th}} = W_{6\text{th}} = W_{13\text{th}}$ and $W_{8\text{th}} = W_{14\text{th}} = W_{15\text{th}}$

$$= \frac{1}{3!}\sum_{2,3,4}\left(3W_{2\text{nd}}+3W_{4\text{th}}+W_{12\text{th}}-3W_{6\text{th}}-3W_{8\text{th}}-W_{5\text{th}}\right) \tag{5.338}$$

$$= \frac{1}{2!}\sum_{2,3,4}\left(W_{2\text{nd}}-W_{8\text{th}}\right)+\frac{1}{2!}\sum_{2,3,4}\left(W_{4\text{th}}-W_{6\text{th}}\right)+\frac{1}{3!}\sum_{2,3,4}\left(W_{12\text{th}}-W_{5\text{th}}\right) \tag{5.339}$$

$$= \frac{1}{2!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},\bar{2},3,\bar{4}}\right|^2 \delta(\omega_1+\omega_2+\omega_4-\omega_3)\left((N_1+1)(N_2+1)N_3(N_4+1)-N_1N_2(N_3+1)N_4\right)$$
$$+\frac{1}{2!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,\bar{4}}\right|^2 \delta(\omega_1+\omega_4-\omega_2-\omega_3)\left((N_1+1)N_2N_3(N_4+1)-N_1(N_2+1)(N_3+1)N_4\right)$$
$$+\frac{1}{3!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,4}\right|^2 \delta(\omega_1-\omega_2-\omega_3-\omega_4)\left((N_1+1)N_2N_3N_4-N_1(N_2+1)(N_3+1)(N_4+1)\right)$$

$$\boxed{\begin{aligned}&I^{(4ph)}\\ =&\frac{1}{2!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},\bar{2},3,\bar{4}}\right|^2\delta(\omega_1+\omega_2+\omega_4-\omega_3)\left((N_1+1)(N_2+1)N_3(N_4+1)-N_1N_2(N_3+1)N_4\right)\\ &+\frac{1}{2!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,\bar{4}}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3)\left((N_1+1)N_2N_3(N_4+1)-N_1(N_2+1)(N_3+1)N_4\right)\\ &+\frac{1}{3!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,4}\right|^2\delta(\omega_1-\omega_2-\omega_3-\omega_4)\left((N_1+1)N_2N_3N_4-N_1(N_2+1)(N_3+1)(N_4+1)\right)\end{aligned}}$$

(5.340)

5.5.3.1 Conservation of energy

Here we check that the 4-phonon collision integral obeys energy conservation. This is done by checking

$$\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}I^{(4ph)}[N_{j_1\vec{q}_1}]\stackrel{?}{=}0 \tag{5.341}$$

$$\begin{aligned}
&\text{First 2 terms of expression }\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}I^{(4ph)}[N_{j_1\vec{q}_1}]\\
=\;&\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{1},\bar{2},3,\bar{4}}\right|^2\hbar\omega_1\delta(\omega_1+\omega_2+\omega_4-\omega_3)((N_1+1)(N_2+1)N_3(N_4+1)-N_1N_2(N_3+1)N_4)\\
|\;&\text{change }3\leftrightarrow 1\text{ then use }\delta(\omega_3+\omega_2+\omega_4-\omega_1)=\delta(\omega_1-\omega_3-\omega_2-\omega_4)\text{ due to }\delta(-x)=\frac{1}{|-1|}\delta(x)\\
=\;&\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{3},\bar{2},1,\bar{4}}\right|^2\hbar\omega_3\delta(\omega_1-\omega_3-\omega_2-\omega_4)((N_3+1)(N_2+1)N_1(N_4+1)-N_3N_2(N_1+1)N_4)\\
|\;&\text{write }\omega_3=\frac{1}{3}\omega_3+\frac{1}{3}\omega_3+\frac{1}{3}\omega_3\\
|\;&\text{due to 2,3,4 symmetry, swap }3\to 2\text{ in second term, }3\to 4\text{ in third term}\\
=\;&\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{3},\bar{2},1,\bar{4}}\right|^2\hbar\frac{1}{3}(\omega_3+\omega_2+\omega_4)\delta(\omega_1-\omega_3-\omega_2-\omega_4)\\
&\times((N_3+1)(N_2+1)N_1(N_4+1)-N_3N_2(N_1+1)N_4)\\
|\;&\text{use delta function to write }\omega_3+\omega_2+\omega_4=\omega_1\\
|\;&\text{also write }\left|V^{(4ph)}_{3,2,\bar{1},4}\right|^2=\left|V^{(4ph)}_{\bar{3},\bar{2},1,\bar{4}}\right|^2\\
=\;&\frac{1}{3!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{3},\bar{2},1,\bar{4}}\right|^2\hbar\omega_1\delta(\omega_1-\omega_3-\omega_2-\omega_4)((N_3+1)(N_2+1)N_1(N_4+1)-N_3N_2(N_1+1)N_4)
\end{aligned}$$

And so we see that the first 2 terms are the negatives of the last 2 terms and they thus cancel. Now we hope to rewrite the third term such that it cancels the fourth term.

$$\begin{aligned}
&\text{Third term of }\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}I^{(4ph)}[N_{j_1\vec{q}_1}]\\
=\;&\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\hbar\omega_1\left|V^{(4ph)}_{\bar{1},2,3,\bar{4}}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3)(N_1+1)N_2N_3(N_4+1)
\end{aligned}$$

$$
\begin{aligned}
&\quad | \quad \text{change } 1 \leftrightarrow 2 \text{ and } 3 \leftrightarrow 4 \\
&= \frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\hbar\left|V^{(4ph)}_{\bar{2},1,4,\bar{3}}\right|^2\omega_2\delta(\omega_2+\omega_3-\omega_1-\omega_4)(N_2+1)N_1N_4(N_3+1) \\
&\quad | \quad \text{use } \delta(\omega_2+\omega_3-\omega_1-\omega_4)=\delta(\omega_1+\omega_4-\omega_2-\omega_3) \\
&\quad | \quad \text{also note } \left|V^{(4ph)}_{\bar{2},1,4,\bar{3}}\right|^2=\left|V^{(4ph)}_{2,\bar{1},\bar{4},3}\right|^2 \\
&= \frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\hbar\left|V^{(4ph)}_{\bar{1},2,3,\bar{4}}\right|^2\omega_2\delta(\omega_2+\omega_3-\omega_1-\omega_4)(N_2+1)N_1N_4(N_3+1) \\
&\quad | \quad \text{write } \omega_2=\frac{1}{2}\omega_2+\frac{1}{2}\omega_2\text{, due to 2,3 symmetry, swap } 2\rightarrow 3 \text{ in second term} \\
&\quad | \quad \text{now } \frac{1}{2}\omega_2+\frac{1}{2}\omega_2=\frac{1}{2}(\omega_2+\omega_3) \\
&\quad | \quad \text{use delta function to write } \omega_2+\omega_3=\omega_1+\omega_4 \\
&\quad | \quad \text{due to 1,4 symmetry, swap } 4\rightarrow 1 \text{ in second term} \\
&\quad | \quad \text{we get, } \frac{1}{2}\omega_2+\frac{1}{2}\omega_2=\frac{1}{2}\omega_1+\frac{1}{2}\omega_4=\frac{1}{2}\omega_1+\frac{1}{2}\omega_1=\omega_1 \\
&= \frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\hbar\left|V^{(4ph)}_{\bar{1},2,3,\bar{4}}\right|^2\omega_1\delta(\omega_2+\omega_3-\omega_1-\omega_4)(N_2+1)N_1N_4(N_3+1)
\end{aligned}
$$

Indeed it is the negative of the fourth term and so $\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}I^{(4ph)}[N_{j_1\vec{q}_1}]=0$.

5.5.3.2 (Distribution) Linearization

The linearized distribution is chosen to be $N_1\approx N_1^{eq}+N_1^{eq}(N_1^{eq}+1)y_1$ as before. The steps are essentially the same as that in the linearization of the 3-phonon collision operator, thus now we proceed briefly.

$$
\begin{aligned}
&\quad \text{First term in 4-phonon collision integral} \\
&= (N_1+1)(N_2+1)N_3(N_4+1) && (5.342) \\
&\approx (N_1^{eq}+1)(N_2^{eq}+1)N_3^{eq}(N_4^{eq}+1)\left(N_1^{eq}y_1+N_2^{eq}y_2+(N_3^{eq}+1)y_3+N_4^{eq}y_4\right) && (5.343)
\end{aligned}
$$

$$
\begin{aligned}
&\quad \text{Second term in 4-phonon collision integral} \\
&= N_1N_2(N_3+1)N_4 && (5.344) \\
&= N_1^{eq}N_2^{eq}(N_3^{eq}+1)N_4^{eq}\left((N_1^{eq}+1)y_1+(N_2^{eq}+1)y_2+N_3^{eq}y_3+(N_4^{eq}+1)y_4\right) && (5.345) \\
&\quad | \quad \text{write } N_1^{eq}N_2^{eq}(N_3^{eq}+1)N_4^{eq}=(N_1^{eq}+1)(N_2^{eq}+1)N_3^{eq}(N_4^{eq}+1) \\
&\quad | \quad \text{it can be checked with the explicit Bose-Einstein expression} \\
&= (N_1^{eq}+1)(N_2^{eq}+1)N_3^{eq}(N_4^{eq}+1)\left((N_1^{eq}+1)y_1+(N_2^{eq}+1)y_2+N_3^{eq}y_3+(N_4^{eq}+1)y_4\right) && (5.346)
\end{aligned}
$$

$$
\begin{aligned}
&\quad \text{First term} - \text{Second term} \\
&= -\left((N_1^{eq}+1)y_1+(N_2^{eq}+1)y_2+N_3^{eq}y_3+(N_4^{eq}+1)y_4\right)(y_1+y_2-y_3+y_4) && (5.347)
\end{aligned}
$$

Similarly,

$$
\text{Third term} - \text{Fourth term} = -(N_1^{eq}+1)N_2^{eq}N_3^{eq}(N_4^{eq}+1)(y_1-y_2-y_3+y_4) \qquad (5.348)
$$

$$\text{Fifth term} - \text{Sixth term} = -(N_1^{eq}+1)N_2^{eq}N_3^{eq}N_4^{eq}(y_1 - y_2 - y_3 - y_4) \tag{5.349}$$

So the full expression of the linearized 4-phonon collision integral is

$$\boxed{\begin{aligned} &\Delta I^{(4ph)} \\ &= -\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},\bar{2},3,\bar{4}}\right|^2\delta(\omega_1+\omega_2+\omega_4-\omega_3)(N_1^{eq}+1)(N_2^{eq}+1)N_3^{eq}(N_4^{eq}+1)(y_1+y_2-y_3+y_4) \\ &\quad -\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3\bar{4}}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3)(N_1^{eq}+1)N_2^{eq}N_3^{eq}(N_4^{eq}+1)(y_1-y_2-y_3+y_4) \\ &\quad -\frac{1}{3!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,4}\right|^2\delta(\omega_1-\omega_2-\omega_3-\omega_4)(N_1^{eq}+1)N_2^{eq}N_3^{eq}N_4^{eq}(y_1-y_2-y_3-y_4) \end{aligned}}$$

(5.350)

5.5.4 Selection Rules (3-phonon interaction)

The references for this section are: [Ziman2001] sections 3.3 and 3.4 and [Srivastava1990] section 4.4 and pg 195-198. An extremely important work [Conyers1954] employs group theory to work out special features in dispersion relations of crystals of various symmetries, and then use that to find the low temperature behavior of relaxation times.

Here we shall only discuss 3-phonon interaction selection rules. When we examine the 3-phonon collision integral (full or linearized) we observe 2 types of energy delta functions: $\delta(\omega_1+\omega_2-\omega_3)$ corresponding to the merging of 2 phonons to make a third phonon; $\delta(\omega_1-\omega_2-\omega_3)$ corresponding to the break up of 1 phonon into 2 phonons. There is $\Delta_{\vec{q}_1\vec{q}_2\vec{q}_3}$ (in $V^{(3ph)}$) that enforces lattice translational symmetry. The final complication is that $\omega_{j\vec{q}}$ and $\vec{q}$ are related via the dispersion relation. This makes the sum over wavevectors in the collision integral restricted by the so-called selection rules.

Considering the process of 2 phonons merging to give a third phonon, the selection rules are,

- $\vec{q}_1+\vec{q}_2=\vec{q}_3+\vec{g}\begin{cases}\vec{g}=0 & \text{N-process}\\ \vec{g}\neq 0 & \text{U-process}\end{cases}$
- $\omega_{j_1\vec{q}_1}+\omega_{j_2\vec{q}_2}=\omega_{j_3\vec{q}_3}$

In terms of Cartesian components and fixing $j_1\vec{q}_1$ (and hence fixing $\omega_{j_1\vec{q}_1}$) the first rule has 6 unknown Cartesian components of $\vec{q}_2$ and $\vec{q}_3$. Together with the second rule, 4 conditions are fixed leaving 2 degrees of freedom (a surface) free. When $\vec{q}_2$ is chosen to lie on the surface, the selection rules are satisfied and there is a non-zero term in the collision integral. However solving for this surface is extremely difficult due to the complicated dispersion relations of realistic crystal lattices.

We shall look at an example (of N-process) of a monoatomic 3D solid (no optical branches) and the 3 wavevectors are collinear (one can also think of this as a monatomic 1D solid with 3D vibrations).

We can draw the following conclusions from the diagrams.

1. There is no process in which all three phonons belong to the same polarization branch. In the context of 1D solid with 1D vibrations where there is only 1 branch, this conclusion becomes: in 3-phonon interaction N-process is not possible.

2. The created phonon must lie in a higher branch then one of the destroyed phonons. The example

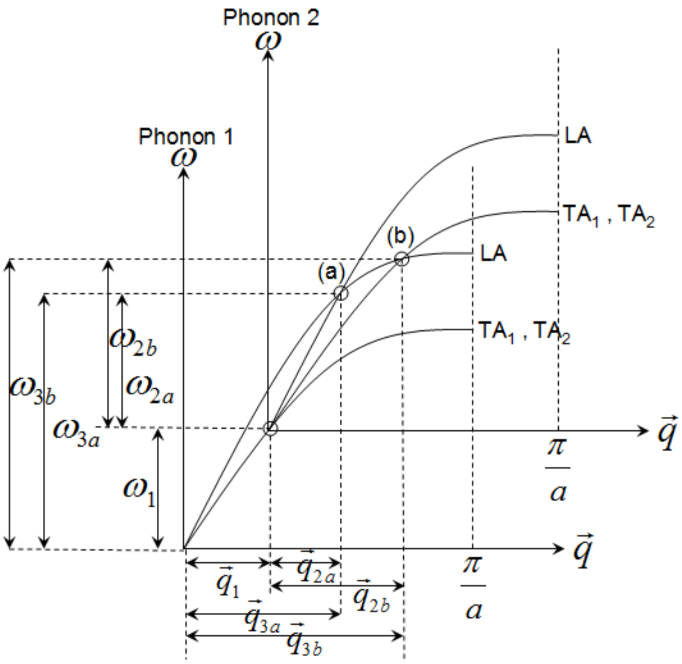


Figure 5.18: *Phonon 1 is a transverse phonon (TA_1 or TA_2) interacting with phonon 2 with 2 possibilities: case (a) where phonon 2 is a longitudinal phonon (LA) or case (b) where phonon 2 is a transverse phonon (TA_1 or TA_2).*

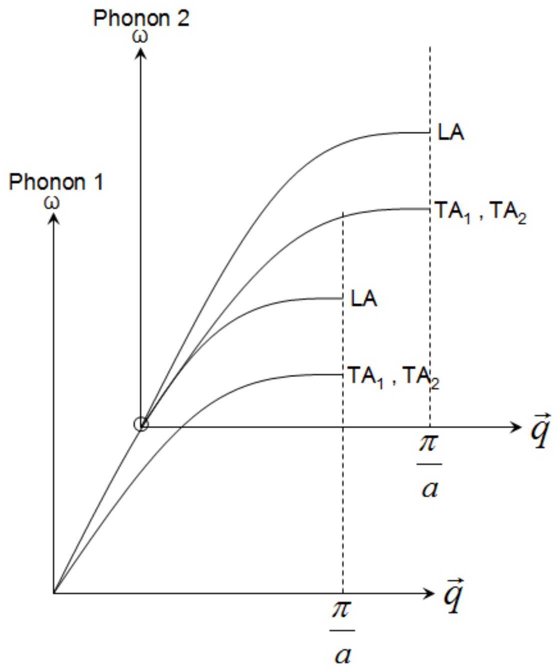


Figure 5.19: *Phonon 1 is a longitudinal phonon (LA) and it interacts with neither longitudinal nor transverse phonons.*

shows that, [11]

$$TA(\vec{q}_1) + TA(\vec{q}_2) \longrightarrow LA(\vec{q}_3) \tag{5.351}$$
$$TA(\vec{q}_1) + LA(\vec{q}_2) \longrightarrow LA(\vec{q}_3) \tag{5.352}$$

For U-processes, a detailed discussion would be extremely difficult hence we will only state some general rules following [Ziman2001] section 3.4.

1. The frequency of the phonon created in an Umklapp process is always comparable in magnitude to the highest frequencies of the lattice spectrum. More explicitly, $\vec{q}_3 \approx \frac{1}{2}\vec{g}$ in order to have a U-process and the Debye sphere $\gtrsim \frac{1}{2}\vec{g}$, so this means $\omega_{j_3\vec{q}_3} \approx \omega_{\text{Debye}}$.
2. Longwavelength (small $\vec{q}$) LA modes are not scattered by U-processes.
3. Again, there is no process in which all three phonons belong to the same polarization branch and the created phonon must lie in a higher branch than one of those destroyed. Thus in the context of 1D solid with 1D vibrations, 3-phonon N or U-processes are not possible at all.

The earlier discussion was only for acoustic modes and now we carry out brief discussions for the optical modes. Optical modes are typically excited by photons and it is relevant to thermal transport when optical modes decay into acoustic modes whose group velocities are much higher. (A - acoustic, O - optical) otherwise optical modes are really far more relevant for phonon-photon interaction problems.

1. A + O $\Longleftrightarrow$ A and O + O $\Longleftrightarrow$ A are ruled out as optical branches are usually higher than acoustic branches and so the energy conservation condition cannot be satisfied.
2. A + O_1 $\Longleftrightarrow$ O_2 is very restricted because O_2 branch must be higher than O_1 branch.
3. A + A $\Longleftrightarrow$ O satisfies the selection rules. However if the optical branch is too high then the energy conservation condition cannot be satisfied.

5.5.5 Relaxation Time Approximation

Assume that the effect of collisions causes an exponential "decay" of the nonequilibrium distribution to the equilibrium distribution in the long time limit, i.e. of the form (the reference mode is $j_1\vec{q}_1$)

$$N_{j_1\vec{q}_1} = N^{eq}_{j_1\vec{q}_1}\left(1 - e^{-t/\tau_{j_1\vec{q}_1}}\right) \tag{5.353}$$

Thus the nonequilibrium distribution "approaches" the equilibrium distribution from below with characteristic time (relaxation time) $\tau_{j_1\vec{q}_1}$.

The collision integral (or the rate of change of distribution) based on this assumption is

$$\left.\frac{\partial N_{j_1\vec{q}_1}}{\partial t}\right|_{\text{coll}} = \frac{\partial}{\partial t}N^{eq}_{j_1\vec{q}_1}\left(1 - e^{-t/\tau_{j_1\vec{q}_1}}\right) = \frac{N^{eq}_{j_1\vec{q}_1}e^{-t/\tau_{j_1\vec{q}_1}}}{\tau_{j_1\vec{q}_1}} = -\frac{N_{j_1\vec{q}_1} - N^{eq}_{j_1\vec{q}_1}}{\tau_{j_1\vec{q}_1}} \tag{5.354}$$

This is the relaxation time approximation for the collision integral.

[11] We see that transverse modes decay into longitudinal modes and longitudinal modes also decay into longitudinal modes. Although this conclusion is not general, it does indicate that N-processes (together with selection rules) redistributes phonons with a preference towards longitudinal phonons. This creates the "problem" of how to destroy longitudinal phonons especially at low temperatures.

We substitute the linearized nonequilibrium distribution and the approximation becomes

$$\left.\frac{\partial N_{j_1\vec{q}_1}}{\partial t}\right|_{\text{coll}} = -\frac{N^{eq}_{j_1\vec{q}_1} + N^{eq}_{j_1\vec{q}_1}(N^{eq}_{j_1\vec{q}_1}+1)y_{j_1\vec{q}_1} - N^{eq}_{j_1\vec{q}_1}}{\tau_{j_1\vec{q}_1}} \tag{5.355}$$

$$= -\frac{N^{eq}_{j_1\vec{q}_1}(N^{eq}_{j_1\vec{q}_1}+1)y_{j_1\vec{q}_1}}{\tau_{j_1\vec{q}_1}} \tag{5.356}$$

We include both (linearized) 3-phonon $\Delta I^{(3ph)}$ and 4-phonon $\Delta I^{(4ph)}$ collision integrals. Thus we can write,

$$-\frac{N^{eq}_{j_1\vec{q}_1}(N^{eq}_{j_1\vec{q}_1}+1)y_{j_1\vec{q}_1}}{\tau_{j_1\vec{q}_1}} = \Delta I^{(3ph)} + \Delta I^{(4ph)} \tag{5.357}$$

$$\frac{1}{\tau_{j_1\vec{q}_1}} = -\frac{\Delta I^{(3ph)}}{N^{eq}_{j_1\vec{q}_1}(N^{eq}_{j_1\vec{q}_1}+1)y_{j_1\vec{q}_1}} - \frac{\Delta I^{(4ph)}}{N^{eq}_{j_1\vec{q}_1}(N^{eq}_{j_1\vec{q}_1}+1)y_{j_1\vec{q}_1}} \tag{5.358}$$

which at this point, it is convenient to define a 3-phonon relaxation time $\tau^{(3ph)}_{j_1\vec{q}_1}$ and a 4-phonon relaxation time $\tau^{(4ph)}_{j_1\vec{q}_1}$. The effective relaxation time appears in the form of Matthiessen's rule.

$$\frac{1}{\tau_{j_1\vec{q}_1}} = \frac{1}{\tau^{(3ph)}_{j_1\vec{q}_1}} + \frac{1}{\tau^{(4ph)}_{j_1\vec{q}_1}} \tag{5.359}$$

The explicit expressions are

$$\frac{1}{\tau^{(3ph)}_{j_1\vec{q}_1}}$$

$$= -\frac{\Delta I^{(3ph)}}{N^{eq}_{j_1\vec{q}_1}(N^{eq}_{j_1\vec{q}_1}+1)y_{j_1\vec{q}_1}} \tag{5.360}$$

$$= \frac{1}{V}\sum_{j_2\vec{q}_2 j_3\vec{q}_3}\frac{1}{2}\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{j_1,-\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3}\right|^2\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2}-\omega_{j_3\vec{q}_3})\frac{N^{eq}_{j_2\vec{q}_2}N^{eq}_{j_3\vec{q}_3}}{N^{eq}_{j_1\vec{q}_1}}\frac{(y_{j_1\vec{q}_1}-y_{j_2\vec{q}_2}-y_{j_3\vec{q}_3})}{y_{j_1\vec{q}_1}}$$
$$+\frac{1}{V}\sum_{j_2\vec{q}_2 j_3\vec{q}_3}\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3,-\vec{q}_3}\right|^2\delta(\omega_{j_1\vec{q}_1}+\omega_{j_2\vec{q}_2}-\omega_{j_3\vec{q}_3})\frac{N^{eq}_{j_2\vec{q}_2}(N^{eq}_{j_3\vec{q}_3}+1)}{N^{eq}_{j_1\vec{q}_1}+1}\frac{(y_{j_1\vec{q}_1}+y_{j_2\vec{q}_2}-y_{j_3\vec{q}_3})}{y_{j_1\vec{q}_1}} \tag{5.361}$$

If we specialise it to the single mode relaxation time (SMRT) case by setting $y_{j_2\vec{q}_2}, y_{j_3\vec{q}_3} = 0$, we get a closed expression.

$$\boxed{\begin{aligned}\frac{1}{\tau^{(3ph)}_{j_1\vec{q}_1}} &= \frac{1}{V}\sum_{j_2\vec{q}_2 j_3\vec{q}_3}\frac{1}{2}\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{j_1,-\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3}\right|^2\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2}-\omega_{j_3\vec{q}_3})\frac{N^{eq}_{j_2\vec{q}_2}N^{eq}_{j_3\vec{q}_3}}{N^{eq}_{j_1\vec{q}_1}}\\ &+\frac{1}{V}\sum_{j_2\vec{q}_2 j_3\vec{q}_3}\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3,-\vec{q}_3}\right|^2\delta(\omega_{j_1\vec{q}_1}+\omega_{j_2\vec{q}_2}-\omega_{j_3\vec{q}_3})\frac{N^{eq}_{j_2\vec{q}_2}(N^{eq}_{j_3\vec{q}_3}+1)}{N^{eq}_{j_1\vec{q}_1}+1}\end{aligned}} \tag{5.362}$$

Now for the 4-phonon relaxation time, (here we use the shortened notation, $1 \equiv j_1, \vec{q}_1$ and $\bar{1} \equiv j_1, -\vec{q}_1$

to reduce clutter)

$$
\begin{aligned}
\frac{1}{\tau_1^{(4ph)}} &= \frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},\bar{2},3,\bar{4}}\right|^2\delta(\omega_1+\omega_2+\omega_4-\omega_3)\frac{(N_2^{eq}+1)N_3^{eq}(N_4^{eq}+1)}{N_1^{eq}}\frac{(y_1+y_2-y_3+y_4)}{y_1} \\
&+\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3\bar{4}}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3)\frac{N_2^{eq}N_3^{eq}(N_4^{eq}+1)}{N_1^{eq}}\frac{(y_1-y_2-y_3+y_4)}{y_1} \\
&+\frac{1}{3!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,4}\right|^2\delta(\omega_1-\omega_2-\omega_3-\omega_4)\frac{N_2^{eq}N_3^{eq}N_4^{eq}}{N_1^{eq}}\frac{(y_1-y_2-y_3-y_4)}{y_1} \qquad (5.363)
\end{aligned}
$$

If we specialise it to the single mode relaxation time (SMRT) case by setting $y_2, y_3, y_4 = 0$, we get a closed expression.[12]

$$
\boxed{
\begin{aligned}
\frac{1}{\tau_1^{(4ph)}} &= \frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},\bar{2},3,\bar{4}}\right|^2\delta(\omega_1+\omega_2+\omega_4-\omega_3)\frac{(N_2^{eq}+1)N_3^{eq}(N_4^{eq}+1)}{N_1^{eq}} \\
&+\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3\bar{4}}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3)\frac{N_2^{eq}N_3^{eq}(N_4^{eq}+1)}{N_1^{eq}} \\
&+\frac{1}{3!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,4}\right|^2\delta(\omega_1-\omega_2-\omega_3-\omega_4)\frac{N_2^{eq}N_3^{eq}N_4^{eq}}{N_1^{eq}}
\end{aligned}
} \qquad (5.364)
$$

5.5.6 Beyond Relaxation Time Approximation: Mingo's Iteration Method

Here we follow [Lindsay2005] [13]. This is an iteration method to solve the linearized 3-phonon Boltzmann equation together with a relaxation time approximation for boundary scattering. We set up the quasi-1D device along the z-axis and the temperature gradient is written as $\nabla_{\vec{r}}T = \frac{dT}{dz}$. We start by replacing the linearized distribution $y_{j_1\vec{q}_1}$ with another variable $F_{j_1\vec{q}_1}$.

$$
\begin{aligned}
N_{j_1\vec{q}_1} &= N^{eq}_{j_1\vec{q}_1} + N^{eq}_{j_1\vec{q}_1}\left(1+N^{eq}_{j_1\vec{q}_1}\right)y_{j_1\vec{q}_1} \qquad (5.365) \\
&\quad \Big| \text{ let } y_{j_1\vec{q}_1} = -\beta F_{j_1\vec{q}_1}\frac{dT}{dz} \text{ where } \beta = \frac{1}{k_BT} \\
&= N^{eq}_{j_1\vec{q}_1} - N^{eq}_{j_1\vec{q}_1}\left(1+N^{eq}_{j_1\vec{q}_1}\right)\beta F_{j_1\vec{q}_1}\frac{dT}{dz} \qquad (5.366)
\end{aligned}
$$

We apply the same substituition to the linearized 3-phonon collision operator.

$$
\begin{aligned}
&\Delta I^{(3ph)}[y_{j_1\vec{q}_1}] \\
=\ & -\frac{1}{V}\frac{1}{2}\frac{2\pi V}{\hbar^2}\sum_{j_2\vec{q}_2j_3\vec{q}_3}\left|V^{(3ph)}_{j_1,-\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3}\right|^2\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2}-\omega_{j_3\vec{q}_3}) \\
&\times(N^{\mathrm{eq}}_{j_1\vec{q}_1}+1)N^{\mathrm{eq}}_{j_2\vec{q}_2}N^{\mathrm{eq}}_{j_3\vec{q}_3}(y_{j_1\vec{q}_1}-y_{j_2\vec{q}_2}-y_{j_3\vec{q}_3}) \\
&-\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{j_2\vec{q}_2j_3\vec{q}_3}\left|V^{(3ph)}_{j_1,\vec{q}_1,j_2,\vec{q}_2,j_3,-\vec{q}_3}\right|^2\delta(\omega_{j_1\vec{q}_1}+\omega_{j_2\vec{q}_2}-\omega_{j_3\vec{q}_3}) \\
&\times(N^{\mathrm{eq}}_{j_3\vec{q}_3}+1)N^{\mathrm{eq}}_{j_2\vec{q}_2}N^{\mathrm{eq}}_{j_1\vec{q}_1}(y_{j_1\vec{q}_1}+y_{j_2\vec{q}_2}-y_{j_3\vec{q}_3}) \qquad (5.367)
\end{aligned}
$$

[12] By now it should be clear that this procedure of writing the SMRT works for any collision integral desired.
[13] Other relevant references are: [Mingo2005], [Omini1995] and [Lindsay2010]

$$
\begin{aligned}
& \quad | \quad \text{use the substitution } y_{j_1\vec{q}_1} = -\beta F_{j_1\vec{q}_1}\frac{dT}{dz} \\
& \quad | \quad \text{define } W^{(3ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} = \frac{1}{V}\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{j_1,-\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3}\right|^2 \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3})(N^{\text{eq}}_{j_1\vec{q}_1}+1)N^{\text{eq}}_{j_2\vec{q}_2}N^{\text{eq}}_{j_3\vec{q}_3} \\
& \quad | \quad \text{define } W^{(3ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} = \frac{1}{V}\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{j_1,\vec{q}_1,j_2,\vec{q}_2,j_3,-\vec{q}_3}\right|^2 \delta(\omega_{j_1\vec{q}_1} + \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3})(N^{\text{eq}}_{j_3\vec{q}_3}+1)N^{\text{eq}}_{j_2\vec{q}_2}N^{\text{eq}}_{j_1\vec{q}_1} \\
= {} & \beta\frac{dT}{dz}\left(\sum_{j_2\vec{q}_2 j_3\vec{q}_3}\left(W^{(3ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} + \frac{1}{2}W^{(3ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3}\right)F_{j_1\vec{q}_1}\right. \\
& \left. - \sum_{j_2\vec{q}_2 j_3\vec{q}_3}\left[W^{(3ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3}\left(F_{j_3\vec{q}_3} - F_{j_2\vec{q}_2}\right) + \frac{1}{2}W^{(3ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3}\left(F_{j_3\vec{q}_3} + F_{j_2\vec{q}_2}\right)\right]\right) \qquad (5.368)
\end{aligned}
$$

We use a relaxation time approximation for boundary scattering with the phenomenological form of the relaxation time $\tau^b_{j_1\vec{q}_1} = \frac{L}{2|\vec{v}_{j_1\vec{q}_1}|}$ where L is the length of the quasi-1D device.

$$
\left.\frac{\partial N_{j_1\vec{q}_1}}{\partial t}\right|_{\text{coll}} = -\frac{N_{j_1\vec{q}_1} - N^{eq}_{j_1\vec{q}_1}}{\tau^b_{j_1\vec{q}_1}} = \frac{N^{eq}_{j_1\vec{q}_1}(1+N^{eq}_{j_1\vec{q}_1})\beta\frac{dT}{dz}}{\tau^b_{j_1\vec{q}_1}}F_{j_1\vec{q}_1} \qquad (5.369)
$$

The LHS of the linearized phonon Boltzmann equation requires a slight rewriting,

$$
\begin{aligned}
\text{LHS} &= (\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1})\cdot(\nabla_{\vec{r}}T)N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1}+1\right)\frac{\hbar\omega_{j_1\vec{q}_1}}{k_BT^2} \qquad (5.370) \\
& \quad | \quad \text{write } \nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1} = \vec{v}_{j_1\vec{q}_1} \text{ and } \nabla_{\vec{r}}T = \frac{dT}{dz} \text{ and } \frac{1}{k_BT} = \beta \\
&= (\vec{v}_{j_1\vec{q}_1})_z\beta\frac{dT}{dz}N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1}+1\right)\frac{\hbar\omega_{j_1\vec{q}_1}}{T} \qquad (5.371)
\end{aligned}
$$

The linearized phonon Boltzmann equation has been written into,

$$
\begin{aligned}
\Longrightarrow {} & (\vec{v}_{j_1\vec{q}_1})_z\beta\frac{dT}{dz}N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1}+1\right)\frac{\hbar\omega_{j_1\vec{q}_1}}{T} \\
= {} & \beta\frac{dT}{dz}\left(\sum_{j_2\vec{q}_2 j_3\vec{q}_3}\left(W^{(3ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} + \frac{1}{2}W^{(3ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3}\right)F_{j_1\vec{q}_1}\right. \\
& \left. - \sum_{j_2\vec{q}_2 j_3\vec{q}_3}\left[W^{(3ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3}\left(F_{j_3\vec{q}_3} - F_{j_2\vec{q}_2}\right) + \frac{1}{2}W^{(3ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3}\left(F_{j_3\vec{q}_3} + F_{j_2\vec{q}_2}\right)\right]\right) \\
& + \frac{N^{eq}_{j_1\vec{q}_1}(1+N^{eq}_{j_1\vec{q}_1})\beta\frac{dT}{dz}}{\tau^b_{j_1\vec{q}_1}}F_{j_1\vec{q}_1} \qquad (5.372) \\
& \quad | \quad \text{cancel } \beta\frac{dT}{dz} \text{ on both sides} \\
& \quad | \quad \text{define } \mathcal{Q}_{j_1\vec{q}_1} = \mathcal{Q}^{(3ph)}_{j_1\vec{q}_1} + \mathcal{Q}^b_{j_1\vec{q}_1} \\
& \quad | \quad \mathcal{Q}^{(3ph)}_{j_1\vec{q}_1} = \sum_{j_2\vec{q}_2 j_3\vec{q}_3}\left(W^{(3ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} + \frac{1}{2}W^{(3ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3}\right), \mathcal{Q}^b_{j_1\vec{q}_1} = \frac{N^{eq}_{j_1\vec{q}_1}(1+N^{eq}_{j_1\vec{q}_1})}{\tau^b_{j_1\vec{q}_1}} \\
\Longrightarrow {} & \frac{(\vec{v}_{j_1\vec{q}_1})_z\hbar\omega_{j_1\vec{q}_1}N^{eq}_{j_1\vec{q}_1}\left(1+N^{eq}_{j_1\vec{q}_1}\right)}{T}
\end{aligned}
$$

$$= \quad \mathcal{Q}_{j_1\vec{q}_1} F_{j_1\vec{q}_1} - \sum_{j_2\vec{q}_2 j_3\vec{q}_3} \left[W^{(3ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} \left(F_{j_3\vec{q}_3} - F_{j_2\vec{q}_2}\right) + \frac{1}{2} W^{(3ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} \left(F_{j_3\vec{q}_3} + F_{j_2\vec{q}_2}\right) \right] \quad (5.373)$$

$$| \quad \text{divide by } \mathcal{Q}_{j_1\vec{q}_1} \text{ and rearrange the left and right sides} \quad (5.374)$$

$$\boxed{\begin{aligned} \Longrightarrow F_{j_1\vec{q}_1} &= \frac{(\vec{v}_{j_1\vec{q}_1})_z \hbar\omega_{j_1\vec{q}_1} N^{eq}_{j_1\vec{q}_1} \left(1 + N^{eq}_{j_1\vec{q}_1}\right)}{T \mathcal{Q}_{j_1\vec{q}_1}} \\ &\quad + \frac{1}{\mathcal{Q}_{j_1\vec{q}_1}} \sum_{j_2\vec{q}_2 j_3\vec{q}_3} \left[W^{(3ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} \left(F_{j_3\vec{q}_3} - F_{j_2\vec{q}_2}\right) + \frac{1}{2} W^{(3ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} \left(F_{j_3\vec{q}_3} + F_{j_2\vec{q}_2}\right) \right] \\ &\quad | \ \text{define the first term as } F^0_{j_1\vec{q}_1} \text{ and define the second term as } \Delta F_{j_1\vec{q}_1} \\ &= F^0_{j_1\vec{q}_1} + \Delta F_{j_1\vec{q}_1} \end{aligned}} \quad (5.375)$$

If we set $\Delta F_{j_1\vec{q}_1} = 0$ we get the SMRT approximation. The iteration procedure starts with $F_{j_1\vec{q}_1} = F^0_{j_1\vec{q}_1}$ which is substituted into $\Delta F_{j_1\vec{q}_1}$ to get a new $F_{j_1\vec{q}_1}$ which is substituted into $\Delta F_{j_1\vec{q}_1}$ to get a new $F_{j_1\vec{q}_1}$ and so on. It is trivial to include the linearized 4-phonon collision operator into the iteration scheme. We simply rewrite the linearized 4-phonon collision operator into the F variables.

$$\begin{aligned} & \Delta I^{(4ph)} \left[y_{j_1\vec{q}_1}\right] \\ | \quad & \text{let } y_{j_1\vec{q}_1} = -\beta F_{j_1\vec{q}_1} \frac{dT}{dz} \\ = \quad & \beta \frac{dT}{dz} \frac{1}{2} \frac{1}{V} \frac{2\pi V}{\hbar^2} \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left| V^{(4ph)}_{j_1,-\vec{q}_1,j_2,-\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4} \right|^2 \delta(\omega_{j_1\vec{q}_1} + \omega_{j_2\vec{q}_2} + \omega_{j_4\vec{q}_4} - \omega_{j_3\vec{q}_3}) \\ & \times (N^{eq}_{j_1\vec{q}_1} + 1)(N^{eq}_{j_2\vec{q}_2} + 1) N^{eq}_{j_3\vec{q}_3} (N^{eq}_{j_4\vec{q}_4} + 1)(F_{j_1\vec{q}_1} + F_{j_2\vec{q}_2} - F_{j_3\vec{q}_3} + F_{j_4\vec{q}_4}) \\ & + \beta \frac{dT}{dz} \frac{1}{2} \frac{1}{V} \frac{2\pi V}{\hbar^2} \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left| V^{(4ph)}_{j_1,-\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4} \right|^2 \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2} + \omega_{j_4\vec{q}_4} - \omega_{j_3\vec{q}_3}) \\ & \times (N^{eq}_{j_1\vec{q}_1} + 1) N^{eq}_{j_2\vec{q}_2} N^{eq}_{j_3\vec{q}_3} (N^{eq}_{j_4\vec{q}_4} + 1)(F_{j_1\vec{q}_1} - F_{j_2\vec{q}_2} - F_{j_3\vec{q}_3} + F_{j_4\vec{q}_4}) \\ & + \beta \frac{dT}{dz} \frac{1}{3!} \frac{1}{V} \frac{2\pi V}{\hbar^2} \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left| V^{(4ph)}_{j_1,-\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3,j_4,\vec{q}_4} \right|^2 \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2} - \omega_{j_4\vec{q}_4} - \omega_{j_3\vec{q}_3}) \\ & \times (N^{eq}_{j_1\vec{q}_1} + 1) N^{eq}_{j_2\vec{q}_2} N^{eq}_{j_3\vec{q}_3} N^{eq}_{j_4\vec{q}_4} (F_{j_1\vec{q}_1} - F_{j_2\vec{q}_2} - F_{j_3\vec{q}_3} - F_{j_4\vec{q}_4}) \qquad (5.376) \\ | \quad & \text{define } W^{(4ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} = \frac{1}{V} \frac{2\pi V}{\hbar^2} \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left| V^{(4ph)}_{j_1,-\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3,j_4,\vec{q}_4} \right|^2 \\ | \quad & \times \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2} - \omega_{j_4\vec{q}_4} - \omega_{j_3\vec{q}_3})(N^{eq}_{j_1\vec{q}_1} + 1) N^{eq}_{j_2\vec{q}_2} N^{eq}_{j_3\vec{q}_3} N^{eq}_{j_4\vec{q}_4} \\ | \quad & \text{define } \quad W^{(4ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} = \frac{1}{V} \frac{2\pi V}{\hbar^2} \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left| V^{(4ph)}_{j_1,-\vec{q}_1,j_2,-\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4} \right|^2 \\ | \quad & \times \delta(\omega_{j_1\vec{q}_1} + \omega_{j_2\vec{q}_2} + \omega_{j_4\vec{q}_4} - \omega_{j_3\vec{q}_3})(N^{eq}_{j_1\vec{q}_1} + 1)(N^{eq}_{j_2\vec{q}_2} + 1) N^{eq}_{j_3\vec{q}_3} (N^{eq}_{j_4\vec{q}_4} + 1) \\ | \quad & \text{define } \quad W^{(4ph)(++)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} = \frac{1}{V} \frac{2\pi V}{\hbar^2} \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left| V^{(4ph)}_{j_1,-\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4} \right|^2 \\ | \quad & \times \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2} + \omega_{j_4\vec{q}_4} - \omega_{j_3\vec{q}_3})(N^{eq}_{j_1\vec{q}_1} + 1) N^{eq}_{j_2\vec{q}_2} N^{eq}_{j_3\vec{q}_3} (N^{eq}_{j_4\vec{q}_4} + 1) \\ = \quad & \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left(\frac{1}{2} W^{(4ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} + \frac{1}{2} W^{(4ph)(++)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} + \frac{1}{3!} W^{(4ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \right) F_{j_1\vec{q}_1} \beta \frac{dT}{dz} \end{aligned}$$

$$
\begin{aligned}
&- \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left(\frac{1}{2} W^{(4ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left(F_{j_3\vec{q}_3} - F_{j_2\vec{q}_2} - F_{j_4\vec{q}_4}\right) \right. \\
&\left. + \frac{1}{2} W^{(4ph)(++)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left(F_{j_3\vec{q}_3} + F_{j_2\vec{q}_2} - F_{j_4\vec{q}_4}\right) + \frac{1}{3!} W^{(4ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left(F_{j_3\vec{q}_3} + F_{j_2\vec{q}_2} + F_{j_4\vec{q}_4}\right) \right) \beta \frac{dT}{dz} \\
| \quad & \text{define } Q^{(4ph)}_{j_1\vec{q}_1} = \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left(\frac{1}{2} W^{(4ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} + \frac{1}{2} W^{(4ph)(++)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} + \frac{1}{3!} W^{(4ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \right)
\end{aligned}
$$

Following above, the phonon Boltzmann equation becomes

$$
\begin{aligned}
\Longrightarrow \quad & \frac{(\vec{v}_{j_1\vec{q}_1})_z \hbar\omega_{j_1\vec{q}_1} N^{eq}_{j_1\vec{q}_1} \left(1 + N^{eq}_{j_1\vec{q}_1}\right)}{T} \\
= \quad & \left(\mathcal{Q}^{(3ph)}_{j_1\vec{q}_1} + \mathcal{Q}^{(4ph)}_{j_1\vec{q}_1} + \mathcal{Q}^{b}_{j_1\vec{q}_1} \right) F_{j_1\vec{q}_1} \\
& - \sum_{j_2\vec{q}_2 j_3\vec{q}_3} \left[W^{(3ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} \left(F_{j_3\vec{q}_3} - F_{j_2\vec{q}_2}\right) + \frac{1}{2} W^{(3ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} \left(F_{j_3\vec{q}_3} + F_{j_2\vec{q}_2}\right) \right] \\
& - \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left(\frac{1}{2} W^{(4ph)(+)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left(F_{j_3\vec{q}_3} - F_{j_2\vec{q}_2} - F_{j_4\vec{q}_4}\right) \right. \\
& \left. + \frac{1}{2} W^{(4ph)(++)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left(F_{j_3\vec{q}_3} + F_{j_2\vec{q}_2} - F_{j_4\vec{q}_4}\right) + \frac{1}{3!} W^{(4ph)(-)}_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left(F_{j_3\vec{q}_3} + F_{j_2\vec{q}_2} + F_{j_4\vec{q}_4}\right) \right) \\
| \quad & \text{divide by } \mathcal{Q}^{(3ph)}_{j_1\vec{q}_1} + \mathcal{Q}^{(4ph)}_{j_1\vec{q}_1} + \mathcal{Q}^{b}_{j_1\vec{q}_1} \text{ and rearrange left and right sides}
\end{aligned}
$$

$$
\boxed{
\begin{aligned}
F_{j_1\vec{q}_1} = \; & \frac{v_{j_1\vec{q}_1} \hbar\omega_{j_1\vec{q}_1} N^{eq}_{j_1\vec{q}_1} (1 + N^{eq}_{j_1\vec{q}_1})}{T \left(\mathcal{Q}^{(3ph)}_{j_1\vec{q}_1} + \mathcal{Q}^{(4ph)}_{j_1\vec{q}_1} + \mathcal{Q}^{b}_{j_1\vec{q}_1} \right)} \\
& + \frac{1}{\mathcal{Q}^{(3ph)}_{j_1\vec{q}_1} + \mathcal{Q}^{(4ph)}_{j_1\vec{q}_1} + \mathcal{Q}^{b}_{j_1\vec{q}_1}} \left(\sum_{j_2\vec{q}_2 j_3\vec{q}_3} [\cdots] + \sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} (\cdots) \right) \qquad (5.377) \\
& | \quad \text{we can define the first term as } F^0_{j_1\vec{q}_1} \text{ as before} \\
& | \quad \text{we can define the second term as } \Delta F_{j_1\vec{q}_1} \text{ as before} \\
& = F^0_{j_1\vec{q}_1} + \Delta F_{j_1\vec{q}_1} \qquad (5.378)
\end{aligned}
}
$$

5.5.7 Thermal Conductivity

In kinetic theory, the aim is to solve for the nonequilibrium distribution. Now we write explicit expressions of thermal conductivity once the nonequilibrium distribution is solved. We start with the linearized theory since the full theory is almost always unsolvable. The expression for energy current in Boltzmann's theory is

$$
\begin{aligned}
\vec{J} \; &= \; \frac{1}{V} \sum_{j_1\vec{q}_1} \left(\nabla_{\vec{q}_1} \omega_{j_1\vec{q}_1}\right) \hbar\omega_{j_1\vec{q}_1} N_{j_1\vec{q}_1} \qquad (5.379) \\
& | \quad \text{again we use the shorthand notation } 1 \equiv j_1\vec{q}_1,\ \bar{1} \equiv j_1, -\vec{q}_1 \\
& | \quad \text{substitute in the linearized distribution} \\
&= \; \frac{1}{V} \sum_{1} (\nabla_{\vec{q}_1} \omega_1) \hbar\omega_1 \left(N^{eq}_1 + N^{eq}_1 (N^{eq}_1 + 1) y_1\right) \qquad (5.380)
\end{aligned}
$$

$$\begin{aligned} &\mid \text{ first term is overall odd in } \vec{q} \text{ so the sum is zero} \\ =\ & \frac{1}{V}\sum_1 (\nabla_{\vec{q}_1}\omega_1)\hbar\omega_1 \left(N_1^{eq}(N_1^{eq}+1)y_1\right) \end{aligned} \tag{5.381}$$

To get the expression for thermal conductivity, we use Fourier's Law which defines the thermal conductivity.

$$J_{\alpha_1} = -\sum_{\alpha_2} \kappa_{\alpha_1\alpha_2}(\nabla_{\vec{r}}T)_{\alpha_2} \tag{5.382}$$

We invert it to write [14]

$$\kappa_{\alpha_1\alpha_2} = -\frac{J_{\alpha_1}(\nabla_{\vec{r}}T)_{\alpha_2}}{|\nabla_{\vec{r}}T|^2} \tag{5.386}$$

$$= -\frac{1}{V|\nabla_{\vec{r}}T|^2}\sum_1 (\nabla_{\vec{q}_1}\omega_1)_{\alpha_1}(\nabla_{\vec{r}}T)_{\alpha_2}\hbar\omega_1 N_1^{eq}(N_1^{eq}+1)y_1 \tag{5.387}$$

Take the cubic or isotropic geometry and the thermal conductivity tensor is diagonal, $\kappa = \kappa_{\alpha_1\alpha_2}\delta_{\alpha_1\alpha_2}$

$$\kappa = -\frac{1}{V|\nabla_{\vec{r}}T|^2}\sum_1 (\nabla_{\vec{q}_1}\omega_1)\cdot(\nabla_{\vec{r}}T)\hbar\omega_1 N_1^{eq}(N_1^{eq}+1)y_1 \tag{5.388}$$

We need an identity to write the thermal conductivity in terms of the relaxation time τ_1. We get it from the (linearized and relaxation time form of) Boltzmann equation

$$(\nabla_{\vec{q}_1}\omega_1)\cdot(\nabla_{\vec{r}}T)N_1^{eq}(N_1^{eq}+1)\frac{\hbar\omega_1}{k_BT^2} = -\frac{N_1^{eq}(N_1^{eq}+1)y_1}{\tau_1} \tag{5.389}$$

Thus we can write

$$-y_1 = \tau_1(\nabla_{\vec{q}_1}\omega_1)\cdot(\nabla_{\vec{r}}T)\frac{\hbar\omega_1}{k_BT^2} \tag{5.390}$$

The expression for thermal conductivity takes a familiar form.

$$\kappa = \frac{\hbar^2}{V|\nabla_{\vec{r}}T|^2 k_BT^2}\sum_1 \left((\nabla_{\vec{q}_1}\omega_1)\cdot(\nabla_{\vec{r}}T)\right)^2 \omega_1^2\tau_1 N_1^{eq}(N_1^{eq}+1) \tag{5.391}$$

$$\mid \text{ the isotropic case gives the average over } \vec{q} \text{ as } \left((\nabla_{\vec{q}_1}\omega_1)\cdot(\nabla_{\vec{r}}T)\right)^2 \to \frac{1}{3}|\nabla_{\vec{q}_1}\omega_1|^2|\nabla_{\vec{r}}T|^2$$

[14] To understand the inversion, we work backwards starting with the guess

$$\begin{pmatrix} & \kappa & \end{pmatrix} \stackrel{?}{=} -\begin{pmatrix} \vec{J} \end{pmatrix}\begin{pmatrix} \nabla T \end{pmatrix} \tag{5.383}$$

$$\begin{pmatrix} & \kappa & \end{pmatrix}\begin{pmatrix} \nabla T \end{pmatrix} \stackrel{?}{=} -\begin{pmatrix} \vec{J} \end{pmatrix}\begin{pmatrix} \nabla T \end{pmatrix}\begin{pmatrix} \nabla T \end{pmatrix} \tag{5.384}$$

$$\stackrel{?}{=} -\begin{pmatrix} \vec{J} \end{pmatrix}|\nabla T|^2 \tag{5.385}$$

Thus a normalization factor appears when we take the inverse.

$$= \frac{\hbar^2}{3Vk_BT^2}\sum_1 |\nabla_{\vec{q}_1}\omega_1|^2\omega_1^2\tau_1 N_1^{eq}(N_1^{eq}+1) \tag{5.392}$$

$| \quad$ define the single mode specific heat $C_1 \equiv \frac{1}{V}\frac{\hbar^2\omega_1^2}{k_BT^2}N_1^{eq}(N_1^{eq}+1)$

$$= \frac{1}{3}\sum_1 C_1|\nabla_{\vec{q}_1}\omega_1|^2\tau_1 \tag{5.393}$$

Therefore, we have now have 3 expressions of thermal conductivity at different levels of approximation: (a) thermal conductivity when the full nonequilibrium distribution is known, (b) thernal conductivity when the linearized distribution is known and, (c) thermal conductivity when the relaxation time is known.[15]

5.5.8 From BE to Phonon Hydrodynamics

The references for phonon hydrodynamics are stated here for convenience. The reference we follow most closely is [Vasko2005] section 25. Review articles are [Horton1975] chapter 4, [Beck1974] and [Enz1968]. The paper that marked the beginning is probably [Sussmann1963]. Articles that contributed to significant development are, [Kwok1966] which used NEGF and [Sham1967] which used equilibrium $T \neq 0$ field theory. The famous Guyer-Krumhansl collision integral eigenvectors method is detailed and applied to second sound in the following: [Guyer1966a], [Guyer1966b], [Horie1964], [Guyer1966c] and [Krumhansl1965]. Projection operator implementation is found in [Maradudin1974] chapter 9 and [Meier1973]. Further developments are done in these papers: [Niklasson1968], [Niklasson1970], [Sandstrom1972a] and [Sandstrom1972b].

5.5.8.1 Propagation Regimes

To understand why second sound is an interesting phenomena to explore, we need to understand the various lattice excitations possible in a solid: [16]

- Zero Sound: Propagation in the collision-less regime.
- First Sound: Ordinary (acoustic) sound wave in a solid, i.e. the elastic dilatation of a solid and is described by the continuum theory of elasticity in the form of a (continuum) displacement field.
- Second Sound: A Temperature wave or a well defined phonon energy density propagation.

And the various Thermal Conduction Regions are: [17]

[15] Typically, the SMRT is used for the calculation of thermal conductivity.

[16] I omitted first and second sound coupling in this thesis. The earliest theory for it, is called the two-fluid theory of dielectric solids since it was inspired by the two-fluid theory of superfluids. See the list of references for second sound.

[17] I omitted Poiseuille Flow in this whole thesis because it may not be applicable to nanosystems. For more information on it, I refer to the references mentioned in this section.

Regions	Condition	Momentum Loss Mechanism	κ estimate	Main Excitation / Remarks
Casimir /Ballistic	$\tau_N, \tau_U \gg \tau_B$	Boundary scattering	$\kappa \sim T^3 L$	Zero sound. Without taking into account boundary scattering then $\kappa \to \infty$. No equilibrium in background
Ziman	$\tau_N \ll \tau_U \ll \tau_B$	Umklapp scattering	$\kappa \sim T^8 e^{1/T}$	Second sound. Drift distribution background
Kinetic	$\tau_R \ll \tau_N \approx \tau_U \ll \tau_B$	Umklapp & other inelastic scatterings	$\kappa \sim 1/T$	Diffusive Transport Equilibrium background

The notations are: τ_N - N-processes relaxation time, τ_U - U-processes relaxation time, τ_B - boundary scattering relaxation time and τ_R - effective relaxation time of all the other inelastic processes. L is the characteristic length scale of the sample size, $L/v \approx \tau_B$ where v is the characteristic phonon group velocity. The Casimir region thermal conductivity is estimated by $\kappa \sim$ low T heat capacity ($\sim T^3$) $\times$ boundary scattering relaxation time ($\sim L/v$). The other estimates for κ are done at the end of the section. Note that at high temperatures, U-processes increase and become comparable to N-processes but it may not overwhelm it enough to achieve equilibrium, so to reach the kinetic region, other inelastic processes may have a strong participation in destroying the momentum and achieve equilibrium.

[Interest in Second Sound:] Now we state the reasons for being interested in second sound phenomena. This is in the regime where N-processes are actively redistributing the phonons and U-processes just started to kick in to "kill" the phonon momenta so loosely speaking, this is the regime where the macroscopic Fourier's law starts to be physically meaningful.[18]

5.5.8.2 Derivation of Balance Equations

The starting point for discussing second sound is to coarse grain the Boltzmann equation and the resulting equations are the so-called balance equations. Simply treat these balance equations as an "energy continuity equation" and a "momentum continuity equation". We define 4 variables for the hydrodynamic description.

1. Energy Density: $\epsilon(\vec{r}t) = \dfrac{1}{V}\sum_{1} \hbar\omega_1 N_1(\vec{r}t)$

2. Heat Current: $\vec{J}(\vec{r}t) = \dfrac{1}{V}\sum_{1} \hbar\omega_1 \left(\nabla_{\vec{q}_1}\omega_1\right) N_1(\vec{r}t)$

   We can define the thermal conductivity 2-tensor from $\vec{J}$ using Fourier's Law, $\vec{J}(\vec{r}t) \equiv -\overleftrightarrow{\kappa}(\nabla_{\vec{r}}T(\vec{r}))$.

3. Crystal Momentum Density: $\vec{P}(\vec{r}t) = \dfrac{1}{V}\sum_{1} \hbar\vec{q}_1 N_1(\vec{r}t)$

4. Crystal Momentum Flux Tensor: $G_{\alpha_1\alpha_2}(\vec{r}t) = \dfrac{1}{V}\sum_{1} \hbar(\vec{q}_1)_{\alpha_1}\left(\nabla_{\vec{q}_1}\omega_1\right)_{\alpha_2} N_1(\vec{r}t)$

The Boltzmann equation with 3-phonon and 4-phonon collision integrals is,

$$\frac{\partial}{\partial t}N_1(\vec{r}t) + \left(\nabla_{\vec{q}_1}\omega_1\right)\cdot\left(\nabla_{\vec{r}}N_1(\vec{r}t)\right) = I^{(3ph)}[N_1(\vec{r}t)] + I^{(4ph)}[N_1(\vec{r}t)] \tag{5.394}$$

[18] By "physically meaningful", I mean the thermal conductivity acquires a finite value.

where the 3-phonon and 4-phonon collision integrals are given earlier.

First we derive the energy balance equation by multiplying $\hbar\omega_1$ to both sides of the phonon Boltzmann equation and summing over index 1.

$$\begin{aligned}
& \text{“LHS of the phonon Boltzmann equation”} \\
= & \sum_1 \hbar\omega_1 \left(\frac{\partial}{\partial t} N_1(\vec{r}t) + \left(\nabla_{\vec{q}_1}\omega_1\right) \cdot \left(\nabla_{\vec{r}} N_1(\vec{r}t)\right) \right) \qquad (5.395) \\
| & \quad \text{they simply correspond to the definitions of energy density and heat current} \\
= & V \left(\frac{\partial \epsilon(\vec{r}t)}{\partial t} + \nabla_{\vec{r}} \cdot \vec{J}(\vec{r}t) \right) \qquad (5.396)
\end{aligned}$$

The RHS of the phonon Boltzmann equation was shown earlier to conserve energy. The energy balance equation is

$$\text{Energy Balance Equation:} \boxed{\frac{\partial \epsilon(\vec{r}t)}{\partial t} + \nabla_{\vec{r}} \cdot \vec{J}(\vec{r}t) = 0} \qquad (5.397)$$

To get the momentum balance equation, we multiply $\hbar\vec{q}_1$ to the phonon Boltzmann equation and sum over the index 1. For the LHS, the terms are simply the definitions of momentum density and momentum flux tensor.

$$\text{LHS} = V \left(\frac{\partial P_{\alpha_1}(\vec{r}t)}{\partial t} + \sum_{\alpha_2} \frac{\partial G_{\alpha_1\alpha_2}(\vec{r}t)}{\partial r_{\alpha_2}} \right) \qquad (5.398)$$

$$\begin{aligned}
\text{RHS} = & \sum_1 \hbar(\vec{q}_1)_{\alpha_1} I^{(3ph)} + \sum_1 \hbar(\vec{q}_1)_{\alpha_1} I^{(4ph)} \qquad (5.399) \\
| & \quad \text{write as, } I^{(3ph)} = I_U^{(3ph)} + I_N^{(3ph)},\ I^{(4ph)} = I_U^{(4ph)} + I_N^{(4ph)} \\
= & \sum_1 \hbar(\vec{q}_1)_{\alpha_1} I_U^{(3ph)} + \sum_1 \hbar(\vec{q}_1)_{\alpha_1} I_N^{(3ph)} + \sum_1 \hbar(\vec{q}_1)_{\alpha_1} I_U^{(4ph)} + \sum_1 \hbar(\vec{q}_1)_{\alpha_1} I_N^{(4ph)} \qquad (5.400) \\
| & \quad \text{we will show later that the Normal terms are zero} \\
= & \sum_1 \hbar(\vec{q}_1)_{\alpha_1} \left(I_U^{(3ph)} + I_U^{(4ph)} \right) \qquad (5.401)
\end{aligned}$$

$$\text{Momentum Balance Equation:} \boxed{\frac{\partial P_{\alpha_1}(\vec{r}t)}{\partial t} + \sum_{\alpha_2} \frac{\partial G_{\alpha_1\alpha_2}(\vec{r}t)}{\partial r_{\alpha_2}} = \frac{1}{V} \sum_1 \hbar(\vec{q}_1)_{\alpha_1} \left(I_U^{(3ph)} + I_U^{(4ph)} \right)} \qquad (5.402)$$

We fill in the working that shows that the Normal terms are zero.

$$\begin{aligned}
& \sum_1 \hbar(\vec{q}_1)_{\alpha_1} I_N^{(3ph)} \\
= & \frac{1}{V} \frac{1}{2} \frac{2\pi V}{\hbar^2} \sum_{1,2,3} \delta(\omega_1 - \omega_2 - \omega_3) \left| V^{(3ph)}_{\bar{1},2,3} \right|^2 \hbar(\vec{q}_1)_{\alpha_1} \left((N_1+1)N_2N_3 - N_1(N_2+1)(N_3+1) \right) \\
& + \frac{1}{V} \frac{2\pi V}{\hbar^2} \sum_{1,2,3} \delta(\omega_1 + \omega_2 - \omega_3) \left| V^{(3ph)}_{1,2,\bar{3}} \right|^2 \hbar(\vec{q}_1)_{\alpha_1} \left((N_1+1)(N_2+1)N_3 - N_1N_2(N_3+1) \right) \qquad (5.403) \\
| & \quad \text{in the first term of } I_N^{(3ph)}\text{, rename } 1 \leftrightarrow 3 \text{ and use } \delta(-x) = \frac{1}{|-1|}\delta(x)
\end{aligned}$$

$$= \frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3}\delta(\omega_1+\omega_2-\omega_3)\left|V^{(3ph)}_{1,2,\bar{3}}\right|^2\left(\hbar(\vec{q}_1)_{\alpha_1}-\frac{1}{2}\hbar(\vec{q}_3)_{\alpha_1}\right)$$
$$\times((N_1+1)(N_2+1)N_3-N_1N_2(N_3+1)) \quad (5.404)$$
| use Normal processes conservation law, $\vec{q}_3=\vec{q}_1+\vec{q}_2$ so $\left(\vec{q}_1-\frac{1}{2}\vec{q}_3\right)_{\alpha_1}=\frac{1}{2}(\vec{q}_1-\vec{q}_2)_{\alpha_1}$

| this is now odd in $1,2$ but the other terms are even in $1,2$, hence it is zero over the sum
$$= 0 \quad (5.405)$$

$$\sum_1\hbar(\vec{q}_1)_{\alpha_1}I^{(4ph)}_N = \frac{1}{2!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{1},\bar{2},3,\bar{4}}\right|^2\delta(\omega_1+\omega_2+\omega_4-\omega_3)\hbar(\vec{q}_1)_{\alpha_1}$$
$$\times((N_1+1)(N_2+1)N_3(N_4+1)-N_1N_2(N_3+1)N_4)$$
$$+\frac{1}{2!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,\bar{4}}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3)\hbar(\vec{q}_1)_{\alpha_1}$$
$$\times((N_1+1)N_2N_3(N_4+1)-N_1(N_2+1)(N_3+1)N_4)$$
$$+\frac{1}{3!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,4}\right|^2\delta(\omega_1-\omega_2-\omega_3-\omega_4)\hbar(\vec{q}_1)_{\alpha_1}$$
$$\times((N_1+1)N_2N_3N_4-N_1(N_2+1)(N_3+1)(N_4+1)) \quad (5.406)$$
| we identify 3 lines on the RHS

| for 3rd line, rename $1\leftrightarrow 3$ then use $\delta(-x)=\frac{1}{|-1|}\delta(x)$

| then note $\left|V^{(4ph)}_{\bar{3},2,1,4}\right|^2=\left|V^{(4ph)}_{3,\bar{2},\bar{1},\bar{4}}\right|^2$ and combine with 1st line
$$= \frac{1}{2!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{1},\bar{2},3,\bar{4}}\right|^2\delta(\omega_1+\omega_2+\omega_4-\omega_3)\hbar\left(\vec{q}_1-\frac{1}{3}\vec{q}_3\right)_{\alpha_1}$$
$$\times((N_1+1)(N_2+1)N_3(N_4+1)-N_1N_2(N_3+1)N_4)$$
$$+\frac{1}{2!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,\bar{4}}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3)\hbar(\vec{q}_1)_{\alpha_1}$$
$$\times((N_1+1)N_2N_3(N_4+1)-N_1(N_2+1)(N_3+1)N_4) \quad (5.407)$$
| use N-processes conservation law, $\vec{q}_3=\vec{q}_1+\vec{q}_2+\vec{q}_4$ to write

| $\vec{q}_1-\frac{1}{3}\vec{q}_3=\vec{q}_1-\frac{1}{3}(\vec{q}_1+\vec{q}_2+\vec{q}_4)=\frac{2}{3}\vec{q}_1-\frac{1}{3}(\vec{q}_2+\vec{q}_4)$

| due to $2,4$ symmetry, we can rename and sum the 2 terms, $\vec{q}_1-\frac{1}{3}\vec{q}_3=\frac{2}{3}(\vec{q}_1-\vec{q}_2)$

| $\frac{2}{3}(\vec{q}_1-\vec{q}_2)$ is odd in $1,2$ but the rest are even in $1,2$ hence vanishes
$$= \frac{1}{2!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,\bar{4}}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3)\hbar(\vec{q}_1)_{\alpha_1}$$
$$\times((N_1+1)N_2N_3(N_4+1)-N_1(N_2+1)(N_3+1)N_4) \quad (5.408)$$
| for 2nd term, rename, $1\leftrightarrow 2$, $3\leftrightarrow 4$

| then use $\delta(-x)=\frac{1}{|-1|}\delta(x)$ and $\left|V^{(4ph)}_{\bar{2},1,4,\bar{3}}\right|^2=\left|V^{(4ph)}_{2,\bar{1},\bar{4},3}\right|^2$

$$\begin{aligned}
&= \frac{1}{2!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{1,2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,\bar{4}}\right|^2 \delta(\omega_1+\omega_4-\omega_2-\omega_3)\hbar(\vec{q}_1-\vec{q}_2)_{\alpha_1}\left((N_1+1)N_2N_3(N_4+1)\right)\\
&\quad | \quad \text{for } \vec{q}_2\text{, write } \vec{q}_2 = \frac{1}{2}\vec{q}_2+\frac{1}{2}\vec{q}_2\\
&\quad | \quad \text{then use } 2,3 \text{ symmetry to write } \vec{q}_2 = \frac{1}{2}\vec{q}_2+\frac{1}{2}\vec{q}_3\\
&\quad | \quad \text{use N-processes conservation law } \vec{q}_2+\vec{q}_3=\vec{q}_1+\vec{q}_4 \text{ to write } \vec{q}_2=\frac{1}{2}(\vec{q}_1+\vec{q}_4)\\
&\quad | \quad \text{then use } 1,4 \text{ symmetry to rename and sum the terms, we get } \vec{q}_2=\frac{1}{2}(\vec{q}_1+\vec{q}_1)=\vec{q}_1\\
&= 0
\end{aligned} \tag{5.409}$$

The calculation thus shows that U-processes are the "sources and sinks" of crystal momentum which is precisely the piece of physics we want to probe.

[Drift Distribution] Now we note a very special distribution that allows us to probe the system when N-processes overwhelm all others. Mathematically, the previous statement means that the drift distribution, $N^{\text{drift}}_{j_1\vec{q}_1}$ is the "eigenvector of $I_N^{(3ph)}$ and of $I_N^{(4ph)}$ with zero eigenvalue", i.e. it is the "steady state" distribution due to (overwhelming) N-processes. The explicit expression is

$$\boxed{N^{\text{drift}}_{j_1\vec{q}_1} = \left(e^{(\hbar\omega_{j_1\vec{q}_1}-\hbar\vec{q}_1\cdot\vec{u})/T^{ph}}-1\right)^{-1}} \tag{5.410}$$

where T^{ph} and $\vec{u}$ are arbitrary parameters. The eigenvalue equations are

$$I_N^{(3ph)}\left[N^{\text{drift}}_{j_1\vec{q}_1}\right]=0\ ,\quad I_N^{(4ph)}\left[N^{\text{drift}}_{j_1\vec{q}_1}\right]=0 \tag{5.411}$$

and the proof (in abbreviated notation) is

$$\begin{aligned}
&\text{“First term of } I_N^{(3ph)}\left[N_1^{\text{drift}}\right]\\
&= \frac{1}{V}\frac{1}{2}\frac{2\pi V}{\hbar^2}\sum_{2,3}\delta(\omega_1-\omega_2-\omega_3)\left|V^{(3ph)}_{\bar{1},2,3}\right|^2\left(\left(N_1^{\text{drift}}+1\right)N_2^{\text{drift}}N_3^{\text{drift}}-N_1^{\text{drift}}\left(N_2^{\text{drift}}+1\right)\left(N_3^{\text{drift}}+1\right)\right)\\
&= \frac{1}{V}\frac{1}{2}\frac{2\pi V}{\hbar^2}\sum_{2,3}\delta(\omega_1-\omega_2-\omega_3)\left|V^{(3ph)}_{\bar{1},2,3}\right|^2\\
&\quad\times\left(N_1^{\text{drift}}N_2^{\text{drift}}N_3^{\text{drift}}e^{\hbar(\omega_1-\vec{q}_1\cdot\vec{u})/T^{ph}}-N_1^{\text{drift}}N_2^{\text{drift}}N_3^{\text{drift}}e^{\hbar(\omega_2-\vec{q}_2\cdot\vec{u})/T^{ph}}e^{\hbar(\omega_3-\vec{q}_3\cdot\vec{u})/T^{ph}}\right)
\end{aligned} \tag{5.412}$$

$$\begin{aligned}
&\quad | \quad \text{use the N process conservation law, } \vec{q}_1=\vec{q}_2+\vec{q}_3\\
&\quad | \quad \text{use the energy conservation law, } \omega_1=\omega_2+\omega_3\\
&= \frac{1}{V}\frac{1}{2}\frac{2\pi V}{\hbar^2}\sum_{2,3}\delta(\omega_1-\omega_2-\omega_3)\left|V^{(3ph)}_{\bar{1},2,3}\right|^2\\
&\quad\times e^{\hbar(\omega_1-\vec{q}_1\cdot\vec{u})/T^{ph}}\left(N_1^{\text{drift}}N_2^{\text{drift}}N_3^{\text{drift}}-N_1^{\text{drift}}N_2^{\text{drift}}N_3^{\text{drift}}\right)
\end{aligned} \tag{5.413}$$

$$= 0 \tag{5.414}$$

The second term of $I_N^{(3ph)}\left[N^{\text{drift}}_{j_1\vec{q}_1}\right]$ and all terms in $I_N^{(4ph)}\left[N^{\text{drift}}_{j_1\vec{q}_1}\right]$ are shown to be zero with exactly the same working.[19]

Again, the full theory is difficult to handle so we go over to the linearized theory. The justification is, we assume that the drift distribution is "near" (i.e. $\vec{u}$ is small and T^{ph} is near T, the equilibrium temperature) the equilibrium distribution. Now we Taylor expand N_1^{drift} to linear order around the equilibrium distribution.

$$
\begin{aligned}
N^{\text{drift}}_{j_1\vec{q}_1}(\vec{u},T^{ph}) &= \left(e^{\hbar(\omega_{j_1\vec{q}_1}-\vec{q}_1\cdot\vec{u})/T^{ph}}-1\right)^{-1} && (5.415)\\
&= N^{\text{drift}}_{j_1\vec{q}_1}(\vec{u},T^{ph})\Big|_{\vec{u}=0,T^{ph}=T} + \left(\nabla_{\vec{u}}N^{\text{drift}}_{j_1\vec{q}_1}\right)\Big|_{\vec{u}=0,T^{ph}=T}(\vec{u}-0)\\
&\quad + \left.\frac{\partial N^{\text{drift}}_{j_1\vec{q}_1}}{\partial T^{ph}}\right|_{\vec{u}=0,T^{ph}=T}(T^{ph}-T)+\cdots && (5.416)\\
&\mid\ \text{define the small quantity, } \Delta T\equiv T^{ph}-T\\
&\mid\ \text{use the identity } \frac{e^{\hbar\omega_{j_1\vec{q}_1}/T}}{\left(e^{\hbar\omega_{j_1\vec{q}_1}/T}-1\right)^2} = N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\\
&= N^{\text{eq}}_{j_1\vec{q}_1} + N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\left(\frac{\hbar}{T}\vec{q}_1\cdot\vec{u}+\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T\right) && (5.417)
\end{aligned}
$$

$$
\text{Linearized Drift Distribution: } \boxed{\Delta N^{\text{drift}}_{j_1\vec{q}_1}(\vec{u},T^{ph}) = N^{\text{eq}}_{j_1\vec{q}_1} + N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\left(\frac{\hbar}{T}\vec{q}_1\cdot\vec{u}+\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T\right)} \quad (5.418)
$$

Comparing with our chosen linear form, we have an explicit expression for $y_{j_1\vec{q}_1}$,

$$
y_{j_1\vec{q}_1} = \frac{\hbar}{T}\vec{q}_1\cdot\vec{u}+\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T \quad (5.419)
$$

In the full theory, $N^{\text{drift}}_{j_1\vec{q}_1}$ makes $I_N^{(3ph)}$ and $I_N^{(4ph)}$ zero, so as a consistency check, we now want to check if the linearized $N^{\text{drift}}_{j_1\vec{q}_1}$ makes the linearized versions of the collision integrals $\Delta I_N^{(3ph)}$ and $\Delta I_N^{(4ph)}$ zero.

$$
\begin{aligned}
&\text{"part of the first term of } \Delta I_N^{(3ph)}\text{"}\\
=\ & y_{j_1\vec{q}_1} - y_{j_2\vec{q}_2} - y_{j_3\vec{q}_3} && (5.420)\\
=\ & \frac{\hbar}{T}(\vec{q}_1-\vec{q}_2-\vec{q}_3)\cdot\vec{u} + \frac{\hbar\Delta T}{T^2}\left(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2}-\omega_{j_3\vec{q}_3}\right) && (5.421)\\
\mid\ & \text{use energy conservation law and N process momentum conservation law}\\
=\ & 0 && (5.422)
\end{aligned}
$$

$$
\begin{aligned}
&\text{"part of the second term of } \Delta I_N^{(3ph)}\text{"}\\
=\ & y_{j_1\vec{q}_1} + y_{j_2\vec{q}_2} - y_{j_3\vec{q}_3} && (5.423)\\
=\ & \frac{\hbar}{T}(\vec{q}_1+\vec{q}_2-\vec{q}_3)\cdot\vec{u} + \frac{\hbar\Delta T}{T^2}\left(\omega_{j_1\vec{q}_1}+\omega_{j_2\vec{q}_2}-\omega_{j_3\vec{q}_3}\right) && (5.424)\\
\mid\ & \text{use energy conservation law and N process momentum conservation law}
\end{aligned}
$$

[19] A deeper look at the proof will reveal that the drift distribution is the zero eigenvector of the normal part of collision integrals of any order in anharmonicity. It is truly a non-perturbative ansatz.

$$= \quad 0 \tag{5.425}$$

$$\begin{aligned}
& \text{“part of the first term of } \Delta I_N^{(4ph)}\text{”} \\
= \; & y_{j_1\vec{q}_1} + y_{j_2\vec{q}_2} - y_{j_3\vec{q}_3} + y_{j_4\vec{q}_4} && (5.426)\\
= \; & \frac{\hbar}{T}\left(\vec{q}_1 + \vec{q}_2 - \vec{q}_3 + \vec{q}_4\right)\cdot\vec{u} + \frac{\hbar\Delta T}{T^2}\left(\omega_{j_1\vec{q}_1} + \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3} + \omega_{j_4\vec{q}_4}\right) && (5.427)\\
| \; & \text{use energy conservation law } \delta(\omega_{j_1\vec{q}_1} + \omega_{j_2\vec{q}_2} + \omega_{j_4\vec{q}_4} - \omega_{j_3\vec{q}_3}) \\
| \; & \text{and use N processes momentum conservation law } \vec{q}_3 = \vec{q}_1 + \vec{q}_2 + \vec{q}_4 \\
= \; & 0 && (5.428)
\end{aligned}$$

$$\begin{aligned}
& \text{“part of the second term of } \Delta I_N^{(4ph)}\text{”} \\
= \; & y_{j_1\vec{q}_1} - y_{j_2\vec{q}_2} - y_{j_3\vec{q}_3} + y_{j_4\vec{q}_4} && (5.429)\\
= \; & \frac{\hbar}{T}\left(\vec{q}_1 - \vec{q}_2 - \vec{q}_3 + \vec{q}_4\right)\cdot\vec{u} + \frac{\hbar\Delta T}{T^2}\left(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3} + \omega_{j_4\vec{q}_4}\right) && (5.430)\\
| \; & \text{use energy conservation law } \delta(\omega_{j_1\vec{q}_1} + \omega_{j_4\vec{q}_4} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3}) \\
| \; & \text{and use N processes momentum conservation law } \vec{q}_2 + \vec{q}_3 = \vec{q}_1 + \vec{q}_4 \\
= \; & 0 && (5.431)
\end{aligned}$$

$$\begin{aligned}
& \text{“part of the third term of } \Delta I_N^{(4ph)}\text{”} \\
= \; & y_{j_1\vec{q}_1} - y_{j_2\vec{q}_2} - y_{j_3\vec{q}_3} - y_{j_4\vec{q}_4} && (5.432)\\
= \; & \frac{\hbar}{T}\left(\vec{q}_1 - \vec{q}_2 - \vec{q}_3 - \vec{q}_4\right)\cdot\vec{u} + \frac{\hbar\Delta T}{T^2}\left(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3} - \omega_{j_4\vec{q}_4}\right) && (5.433)\\
| \; & \text{use energy conservation law } \delta(\omega_{j_1\vec{q}_1} - \omega_{j_4\vec{q}_4} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3}) \\
| \; & \text{and use N processes momentum conservation law } \vec{q}_2 + \vec{q}_3 + \vec{q}_4 = \vec{q}_1 \\
= \; & 0 && (5.434)
\end{aligned}$$

Indeed the linearized theory is consistent in this aspect. In closing this section, we now show that $\vec{u}$ has the meaning of the average phonon group velocity. We start by simply calculating the average phonon group velocity.

$$\begin{aligned}
& \text{“Average group velocity (un-normalized)”} \\
= \; & \sum_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)\left(N^{\mathrm{eq}}_{j_1\vec{q}_1} + N^{\mathrm{eq}}_{j_1\vec{q}_1}(N^{\mathrm{eq}}_{j_1\vec{q}_1}+1)\left(\frac{\hbar}{T}\vec{q}_1\cdot\vec{u} + \frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T\right)\right) && (5.435)\\
| \; & \text{note that } \nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1} \text{ is odd in } \vec{q}_1 \text{ hence } \left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)\vec{q}_1\cdot\vec{u} \text{ is nonzero} \\
| \; & \text{note the identity, } N^{\mathrm{eq}}_{j_1\vec{q}_1}(N^{\mathrm{eq}}_{j_1\vec{q}_1}+1) = -\frac{T}{\hbar}\frac{\partial N^{\mathrm{eq}}_{j_1\vec{q}_1}}{\partial\omega_{j_1\vec{q}_1}} \\
| \; & \text{this can checked directly using the Bose Einstein expression} \\
= \; & -\sum_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)\frac{\partial N^{\mathrm{eq}}_{j_1\vec{q}_1}}{\partial\omega_{j_1\vec{q}_1}}\vec{q}_1\cdot\vec{u} && (5.436)\\
| \; & \text{reverse the chain rule} \\
= \; & -\sum_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}N^{\mathrm{eq}}_{j_1\vec{q}_1}\right)\vec{q}_1\cdot\vec{u} && (5.437)
\end{aligned}$$

$$\begin{aligned}
&\quad | \quad \text{integrate by parts with respect to } \vec{q}_1 \\
&= -\sum_{j_1\vec{q}_1} \nabla_{\vec{q}_1}\left(N^{\text{eq}}_{j_1\vec{q}_1}\vec{q}_1\cdot\vec{u}\right) + \sum_{j_1\vec{q}_1} N^{\text{eq}}_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}\vec{q}_1\cdot\vec{u}\right) && (5.438)\\
&\quad | \quad \text{we drop the surface term} \\
&= \sum_{j_1\vec{q}_1} N^{\text{eq}}_{j_1\vec{q}_1}\vec{u} && (5.439)
\end{aligned}$$

So,

$$\vec{u} = \frac{\sum_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)\left(N^{\text{eq}}_{j_1\vec{q}_1} + N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\left(\frac{\hbar}{T}\vec{q}_1\cdot\vec{u} + \frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T\right)\right)}{\sum_{j_1\vec{q}_1} N^{\text{eq}}_{j_1\vec{q}_1}} \tag{5.440}$$

which is the (normalized) average group velocity of the phonons.

5.5.8.3 Dissipative Phonon Hydrodynamics and Second Sound

The earlier section prepares us for this section where we will use the linearized theory with the balance equations together with an iteration similar to that of Chapman-Enskog to expand about the linearized drift distribution bringing in U-processes in the expansion. This allows us to see the dynamics of how U-processes brings about evolution to equilibrium, which is when $\vec{u} = 0$ and $\Delta T = 0$.

First we define and label the lowest order quantity,

$$y^{(1)}_{j_1\vec{q}_1} \equiv y_{j_1\vec{q}_1} = \frac{\hbar}{T}\vec{q}_1\cdot\vec{u} + \frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T \tag{5.441}$$

We will now use this linearized drift distribution to calculate the hydrodynamical variables to lowest order. The balance equations will then simply be turned into dynamical equations of $\vec{u}$ and ΔT.

$$\begin{aligned}
&\quad \text{First order Energy Density } \epsilon^{(1)}(\vec{r}t) \\
&= \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}\left(N^{\text{eq}}_{j_1\vec{q}_1} + N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\left(\frac{\hbar}{T}\vec{q}_1\cdot\vec{u} + \frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T\right)\right) && (5.442)\\
&\quad | \quad \text{drop the equilibrium energy density as it can be set as the “reference value”} \\
&\quad | \quad \text{note that } \omega_{j_1\vec{q}_1} \text{ is even in } \vec{q}_1 \text{ and } \vec{q}_1\cdot\vec{u} \text{ is odd in } \vec{q}_1 \text{ so } \sum_{j_1\vec{q}_1}\omega_{j_1\vec{q}_1}\vec{q}_1\cdot\vec{u} = 0 \\
&= \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T && (5.443)\\
&\quad | \quad \text{define specific heat, } C \equiv \frac{1}{V}\sum_{j_1\vec{q}_1}\frac{(\hbar\omega_1)^2}{T^2}N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1) \\
&= C\Delta T && (5.444)
\end{aligned}$$

$$\begin{aligned}
&\quad \text{First order Momentum Density } P^{(1)}_{\alpha_1}(\vec{r}t) \\
&= \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_{\alpha_1}\left(N^{\text{eq}}_{j_1\vec{q}_1} + N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\left(\frac{\hbar}{T}\vec{q}_1\cdot\vec{u} + \frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T\right)\right) && (5.445)\\
&\quad | \quad \text{note that } \hbar(\vec{q}_1)_{\alpha_1} \text{ is odd and } N^{\text{eq}}_{j_1\vec{q}_1} \text{ and } \omega_{j_1\vec{q}_1} \text{ are even in } \vec{q}_1
\end{aligned}$$

$$= \frac{\hbar^2}{VT}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_{\alpha_1}N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\vec{q}_1\cdot\vec{u} \quad (5.446)$$

$$| \quad \text{define the tensor, } \chi_{\alpha_1\alpha_2} \equiv \frac{\hbar^2}{VT}\sum_{j_1\vec{q}_1}(\vec{q}_1)_{\alpha_1}(\vec{q}_1)_{\alpha_2}N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1) \quad (5.447)$$

$$= \sum_{\alpha_2}\chi_{\alpha_1\alpha_2}u_{\alpha_2} \quad (5.448)$$

First order Energy Flow Density (Heat Current), $\vec{J}^{(1)}(\vec{r}t)$

$$= \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)\left(N^{\text{eq}}_{j_1\vec{q}_1}+N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\left(\frac{\hbar}{T}\vec{q}_1\cdot\vec{u}+\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T\right)\right) \quad (5.449)$$

| note that $\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}$ is odd in $\vec{q}_1$ but $N^{\text{eq}}_{j_1\vec{q}_1}$ and $\omega_{j_1\vec{q}_1}$ are even in $\vec{q}_1$

$$= \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\frac{\hbar}{T}\vec{q}_1\cdot\vec{u} \quad (5.450)$$

| note the identity, $N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1) = -\frac{T}{\hbar}\frac{\partial N^{\text{eq}}_{j_1\vec{q}_1}}{\partial\omega_{j_1\vec{q}_1}}$

| the identity can be checked directly using the Bose Einstein expression

| then use chain rule $\frac{\partial N^{\text{eq}}_{j_1\vec{q}_1}}{\partial\omega_{j_1\vec{q}_1}}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right) = \nabla_{\vec{q}_1}N^{\text{eq}}_{j_1\vec{q}_1}$

$$= -\frac{1}{V}\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}N^{\text{eq}}_{j_1\vec{q}_1}\right)\vec{q}_1\cdot\vec{u} \quad (5.451)$$

| note the identity, $\frac{\hbar\omega_{j_1\vec{q}_1}}{T} = \ln\left(\frac{N^{\text{eq}}_{j_1\vec{q}_1}+1}{N^{\text{eq}}_{j_1\vec{q}_1}}\right)$

| the identity can be checked directly using the Bose Einstein expression

$$| \quad \text{define entropy, } S \equiv \frac{1}{V}\sum_{j_1\vec{q}_1}S_{j_1\vec{q}_1} = \frac{1}{V}\sum_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\ln(N^{\text{eq}}_{j_1\vec{q}_1}+1) - N^{\text{eq}}_{j_1\vec{q}_1}\ln N^{\text{eq}}_{j_1\vec{q}_1} \quad (5.452)$$

| then note the expression, $\nabla_{\vec{q}_1}S_{j_1\vec{q}_1} = \left(\nabla_{\vec{q}_1}N^{\text{eq}}_{j_1\vec{q}_1}\right)\ln\left(\frac{N^{\text{eq}}_{j_1\vec{q}_1}+1}{N^{\text{eq}}_{j_1\vec{q}_1}}\right)$

$$= -T\frac{1}{V}\sum_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}S_{j_1\vec{q}_1}\right)\vec{q}_1\cdot\vec{u} \quad (5.453)$$

| then integrate by parts

$$= -\frac{1}{V}\sum_{j_1\vec{q}_1}\nabla_{\vec{q}_1}\left(TS_{j_1\vec{q}_1}\vec{q}_1\cdot\vec{u}\right)+\frac{1}{V}\sum_{j_1\vec{q}_1}TS_{j_1\vec{q}_1}\vec{u} \quad (5.454)$$

| take the surface term to be vanishing

$$= \frac{1}{V}\sum_{j_1\vec{q}_1}TS_{j_1\vec{q}_1}\vec{u} \quad (5.455)$$

$$= TS\vec{u} \quad (5.456)$$

First Order Crystal Momentum flux tensor $G^{(1)}_{\alpha_1\alpha_2}(\vec{r}t)$

$$= \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_{\alpha_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)_{\alpha_2}\left(N^{\rm eq}_{j_1\vec{q}_1}+N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)\left(\frac{\hbar}{T}\vec{q}_1\cdot\vec{u}+\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T\right)\right) \tag{5.457}$$

| $\hbar(\vec{q}_1)_{\alpha_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)_{\alpha_2}$ is odd × odd equals even in $\vec{q}_1$, thus retain $\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T$ term

$$= \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_{\alpha_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)_{\alpha_2}N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\Delta T \tag{5.458}$$

| recall the definition of entropy, S and the expression,

| $\nabla_{\vec{q}_1}S_{j_1\vec{q}_1} = \left(\nabla_{\vec{q}_1}N^{\rm eq}_{j_1\vec{q}_1}\right)\ln\left(\frac{N^{\rm eq}_{j_1\vec{q}_1}+1}{N^{\rm eq}_{j_1\vec{q}_1}}\right)$

| also the expression, $\nabla_{\vec{q}_1}N^{\rm eq}_{j_1\vec{q}_1} = \left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)\frac{\partial N^{\rm eq}_{j_1\vec{q}_1}}{\partial\omega_{j_1\vec{q}_1}} = \left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)\left(-\frac{\hbar}{T}N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)\right)$

| and that $\ln\left(\frac{N^{\rm eq}_{j_1\vec{q}_1}+1}{N^{\rm eq}_{j_1\vec{q}_1}}\right) = \hbar\omega_{j_1\vec{q}_1}$

| to get, $-T\left(\nabla_{\vec{q}_1}S_{j_1\vec{q}_1}\right)_{\alpha_2} = \hbar\omega_{j_1\vec{q}_1}N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)\frac{\hbar}{T}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)_{\alpha_2}$

$$= -\frac{1}{V}\sum_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}S_{j_1\vec{q}_1}\right)_{\alpha_2}(\vec{q}_1)_{\alpha_1}\Delta T \tag{5.459}$$

| integrate by parts and drop surface term

$$= \frac{1}{V}\sum_{j_1\vec{q}_1}\delta_{\alpha_1\alpha_2}S_{j_1\vec{q}_1}\Delta T \tag{5.460}$$

$$= \delta_{\alpha_1\alpha_2}S\Delta T \tag{5.461}$$

Now we substitute these lowest order quantities into the balance equations to get the hydrodynamical equations for $\vec{u}$ and ΔT.

Energy Balance equation:

$$\frac{\partial\epsilon^{(1)}(\vec{r}t)}{\partial t}+\nabla_{\vec{r}}\cdot\vec{J}(\vec{r}t) = 0 \tag{5.462}$$

$$\boxed{\Rightarrow C\frac{\partial\Delta T}{\partial t}+TS\left(\nabla_{\vec{r}}\cdot\vec{u}\right)=0} \tag{5.463}$$

Momentum Balance equation:

$$\frac{\partial P^{(1)}_{\alpha_1}(\vec{r}t)}{\partial t}+\sum_{\alpha_2}\frac{\partial G^{(1)}_{\alpha_1\alpha_2}(\vec{r}t)}{\partial r_{\alpha_2}} = \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_{\alpha_1}\left(\Delta I^{(3ph)}_U+\Delta I^{(4ph)}_U\right) \tag{5.464}$$

$$\Rightarrow\sum_{\alpha_2}\chi_{\alpha_1\alpha_2}\frac{\partial u_{\alpha_2}}{\partial t}+\sum_{\alpha_2}\delta_{\alpha_1\alpha_2}S\frac{\partial\Delta T}{\partial r_{\alpha_2}} = \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_{\alpha_1}\left(\Delta I^{(3ph)}_U+\Delta I^{(4ph)}_U\right) \tag{5.465}$$

$$\sum_{\alpha_2}\chi_{\alpha_1\alpha_2}\frac{\partial u_{\alpha_2}}{\partial t}+S\frac{\partial\Delta T}{\partial r_{\alpha_1}} = \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_{\alpha_1}\left(\Delta I^{(3ph)}_U+\Delta I^{(4ph)}_U\right) \tag{5.466}$$

The RHS is complicated, so we have to work it out term by term. First note that $\hbar(\vec{q}_1)_{\alpha_1}$ is odd in $\vec{q}_1$

so we only retain $\frac{\hbar}{T}\vec{q}_1 \cdot \vec{u}$ in $y^{(1)}_{j_1\vec{q}_1}$.

$$
\begin{aligned}
& \text{First term of } \frac{1}{V}\sum_{j_1\vec{q}_1} \hbar(\vec{q}_1)_{\alpha_1} \Delta I_U^{(3ph)} \\
= \; & -\frac{\hbar^2}{2V^2T}\frac{2\pi V}{\hbar^2} \sum_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} (\vec{q}_1)_{\alpha_1} \left| V^{(3ph)}_{j_1,-\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3} \right|^2 \\
& \times (N^{\mathrm{eq}}_{j_1\vec{q}_1}+1) N^{\mathrm{eq}}_{j_2\vec{q}_2} N^{\mathrm{eq}}_{j_3\vec{q}_3} \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3})(\vec{q}_1 - \vec{q}_2 - \vec{q}_3)\cdot\vec{u} \qquad (5.467) \\
| \; & \text{use Umklapp momentum conservation law } \vec{q}_1 = \vec{q}_2 + \vec{q}_3 + \vec{g} \text{ where } \vec{g} \text{ is a reciprocal lattice vector} \\
= \; & -\frac{\hbar^2}{2V^2T}\frac{2\pi V}{\hbar^2} \sum_{j_1} \sum_{j_2\vec{q}_2 j_3\vec{q}_3} (\vec{q}_2 + \vec{q}_3 + \vec{g})_{\alpha_1} \left| V^{(3ph)}_{j_1,-\vec{q}_2-\vec{q}_3-\vec{g},j_2,\vec{q}_2,j_3,\vec{q}_3} \right|^2 \qquad (5.468) \\
& \times (N^{\mathrm{eq}}_{j_1,\vec{q}_2+\vec{q}_3+\vec{g}}+1) N^{\mathrm{eq}}_{j_2\vec{q}_2} N^{\mathrm{eq}}_{j_3\vec{q}_3} \delta(\omega_{j_1,\vec{q}_2+\vec{q}_3+\vec{g}} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3})\vec{g}\cdot\vec{u} \qquad (5.469)
\end{aligned}
$$

$$
\begin{aligned}
& \text{Second term of } \frac{1}{V}\sum_{j_1\vec{q}_1} \hbar(\vec{q}_1)_{\alpha_1} \Delta I_U^{(3ph)} \\
= \; & -\frac{\hbar^2}{V^2T}\frac{2\pi V}{\hbar^2} \sum_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3} (\vec{q}_1)_{\alpha_1} N^{\mathrm{eq}}_{j_1\vec{q}_1} N^{\mathrm{eq}}_{j_2\vec{q}_2} (N^{\mathrm{eq}}_{j_3\vec{q}_3}+1) \left| V^{(3ph)}_{j_1,\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3} \right|^2 \\
& \times \delta(\omega_{j_1\vec{q}_1} + \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3})(\vec{q}_1 + \vec{q}_2 - \vec{q}_3)\cdot\vec{u} \qquad (5.470) \\
| \; & \text{use Umklapp momentum conservation law, } \vec{q}_1 + \vec{q}_2 + \vec{g} = \vec{q}_3 \\
= \; & \frac{\hbar^2}{V^2T}\frac{2\pi V}{\hbar^2} \sum_{j_3} \sum_{j_1\vec{q}_1 j_2\vec{q}_2} (\vec{q})_{\alpha_1} \left| V^{(3ph)}_{j_1,\vec{q}_1,j_2,\vec{q}_2,j_3,-\vec{q}_1-\vec{q}_2-\vec{g}} \right|^2 \qquad (5.471) \\
& \times N^{\mathrm{eq}}_{j_1\vec{q}_1} N^{\mathrm{eq}}_{j_2\vec{q}_2} (N^{\mathrm{eq}}_{j_3,\vec{q}_1+\vec{q}_2+\vec{g}}+1) \delta(\omega_{j_1\vec{q}_1} + \omega_{j_2\vec{q}_2} - \omega_{j_3,\vec{q}_1+\vec{q}_2+\vec{g}})\vec{g}\cdot\vec{u} \qquad (5.472) \\
| \; & \text{rename, } 1,2 \to 2,3 \text{ and } j_3 \to j_1 \\
| \; & \text{recall that the indices in } V^{(3ph)} \text{ are completely symmetric} \\
| \; & \text{use also } \delta(-x) = \frac{1}{|-1|}\delta(x) \\
= \; & \frac{\hbar^2}{V^2T}\frac{2\pi V}{\hbar^2} \sum_{j_1} \sum_{j_2\vec{q}_2 j_3\vec{q}_3} (\vec{q}_2)_{\alpha_1} \left| V^{(3ph)}_{j_1,-\vec{q}_2-\vec{q}_3-\vec{g},j_2,\vec{q}_2,j_3,\vec{q}_3} \right|^2 \\
& \times N^{\mathrm{eq}}_{j_2\vec{q}_2} N^{\mathrm{eq}}_{j_3\vec{q}_3} (N^{\mathrm{eq}}_{j_1,\vec{q}_2+\vec{q}_3+\vec{g}}+1) \delta(\omega_{j_1,\vec{q}_2+\vec{q}_3+\vec{g}} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3})\vec{g}\cdot\vec{u} \qquad (5.473)
\end{aligned}
$$

$$
\begin{aligned}
& \frac{1}{V}\sum_{j_1\vec{q}_1} \hbar(\vec{q}_1)_{\alpha_1} \Delta I_U^{(3ph)} = \text{First term} + \text{Second Term} \\
= \; & -\frac{\hbar^2}{2V^2T}\frac{2\pi V}{\hbar^2} \sum_{j_1} \sum_{j_2\vec{q}_2 j_3\vec{q}_3} (\vec{q}_2 + \vec{q}_3 + \vec{g} - 2\vec{q}_2)_{\alpha_1} \left| V^{(3ph)}_{j_1,-\vec{q}_2-\vec{q}_3-\vec{g},j_2,\vec{q}_2,j_3,\vec{q}_3} \right|^2 \\
& \times (N^{\mathrm{eq}}_{j_1,\vec{q}_2+\vec{q}_3+\vec{g}}+1) N^{\mathrm{eq}}_{j_2\vec{q}_2} N^{\mathrm{eq}}_{j_3\vec{q}_3} \delta(\omega_{j_1,\vec{q}_2+\vec{q}_3+\vec{g}} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3})\vec{g}\cdot\vec{u} \qquad (5.474) \\
| \; & \text{note that } \vec{q}_2 + \vec{q}_3 + \vec{g} - 2\vec{q}_2 = \vec{q}_3 - \vec{q}_2 + \vec{g} \\
| \; & \text{so the first 2 terms make an odd function in indices } 2,3 \text{ while the rest of RHS is even in } 2,3 \\
= \; & -\frac{\hbar^2}{2V^2T}\frac{2\pi V}{\hbar^2} \sum_{j_1} \sum_{j_2\vec{q}_2 j_3\vec{q}_3} \left| V^{(3ph)}_{j_1,-\vec{q}_2-\vec{q}_3-\vec{g},j_2,\vec{q}_2,j_3,\vec{q}_3} \right|^2 \\
& \times (N^{\mathrm{eq}}_{j_1,\vec{q}_2+\vec{q}_3+\vec{g}}+1) N^{\mathrm{eq}}_{j_2\vec{q}_2} N^{\mathrm{eq}}_{j_3\vec{q}_3} \delta(\omega_{j_1,\vec{q}_2+\vec{q}_3+\vec{g}} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3}) g_{\alpha_1}\vec{g}\cdot\vec{u} \qquad (5.475)
\end{aligned}
$$

$$
\begin{aligned}
&\quad\Big| \quad \text{define, } \lambda^{(3ph)}_{\alpha_1\alpha_2} = \frac{\hbar^2}{2V^2T}\cdots g_{\alpha_1}g_{\alpha_2} \\
&= -\sum_{\alpha_2}\lambda^{(3ph)}_{\alpha_1\alpha_2}u_{\alpha_2} && (5.476)\\
&= -TS^2\sum_{\alpha_2}\frac{1}{TS^2}\lambda^{(3ph)}_{\alpha_1\alpha_2}u_{\alpha_2} && (5.477)\\
&\quad\Big| \quad \text{define thermal conductivity, } \kappa^{(3ph)}_{\alpha_1\alpha_2} = TS^2\lambda^{(3ph)-1}_{\alpha_1\alpha_2} \text{ which we will justify immediately after} \\
&= -TS^2\sum_{\alpha_2}\kappa^{(3ph)-1}_{\alpha_1\alpha_2}u_{\alpha_2} && (5.478)
\end{aligned}
$$

First term of $\frac{1}{V}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_{\alpha_1}\Delta I^{(4ph)}_U$

$$
\begin{aligned}
&= -\frac{1}{2}\frac{\hbar^2}{V^2T}\frac{2\pi V}{\hbar^2}\sum_{j_1\vec{q}_1j_2\vec{q}_2j_3\vec{q}_3j_4\vec{q}_4}\left|V^{(4ph)}_{j_1,-\vec{q}_1,j_2,-\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4}\right|^2\delta(\omega_{j_1\vec{q}_1}+\omega_{j_2\vec{q}_2}+\omega_{j_4\vec{q}_4}-\omega_{j_3\vec{q}_3}) \\
&\quad\times\left(N^{eq}_{j_1\vec{q}_1}+1\right)\left(N^{eq}_{j_2\vec{q}_2}+1\right)N^{eq}_{j_3\vec{q}_3}\left(N^{eq}_{j_4\vec{q}_4}+1\right)(\vec{q}_1)_{\alpha_1}(\vec{q}_1+\vec{q}_2-\vec{q}_3+\vec{q}_4)\cdot\vec{u} && (5.479)\\
&\quad\Big| \quad \text{use U processes conservation law } \vec{q}_1+\vec{q}_2+\vec{q}_4=\vec{q}_3+\vec{g} \\
&= -\frac{1}{2}\frac{\hbar^2}{V^2T}\frac{2\pi V}{\hbar^2}\sum_{j_1}\sum_{j_2\vec{q}_2j_3\vec{q}_3j_4\vec{q}_4}\left|V^{(4ph)}_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g},j_2,-\vec{q}_2,j_3,-\vec{q}_3,j_4,-\vec{q}_4}\right|^2\delta(\omega_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g}}+\omega_{j_2\vec{q}_2}+\omega_{j_4\vec{q}_4}-\omega_{j_3\vec{q}_3}) \\
&\quad\times\left(N^{eq}_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g}}+1\right)(N^{eq}_{j_2\vec{q}_2}+1)N^{eq}_{j_3\vec{q}_3}(N^{eq}_{j_4\vec{q}_4}+1)(\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g})_{\alpha_1}\vec{g}\cdot\vec{u} && (5.480)
\end{aligned}
$$

Third term of $\frac{1}{V}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_{\alpha_1}\Delta I^{(4ph)}_U$

$$
\begin{aligned}
&= -\frac{1}{3!}\frac{\hbar^2}{V^2T}\frac{2\pi V}{\hbar^2}\sum_{j_1\vec{q}_1j_2\vec{q}_2j_3\vec{q}_3j_4\vec{q}_4}\left|V^{(4ph)}_{j_1,-\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3,j_4,\vec{q}_4}\right|^2\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2}-\omega_{j_3\vec{q}_3}-\omega_{j_4\vec{q}_4}) \\
&\quad\times(N^{eq}_{j_1\vec{q}_1}+1)N^{eq}_{j_2\vec{q}_2}N^{eq}_{j_3\vec{q}_3}N^{eq}_{j_4\vec{q}_4}(\vec{q}_1)_{\alpha_1}(\vec{q}_1-\vec{q}_2-\vec{q}_3-\vec{q}_4)\cdot\vec{u} && (5.481)\\
&\quad\Big| \quad \text{rename } 1\leftrightarrow 3\text{, then write } \delta(\omega_{j_3\vec{q}_3}-\omega_{j_2\vec{q}_2}-\omega_{j_1\vec{q}_1}-\omega_{j_4\vec{q}_4}) = \delta(-\omega_{j_3\vec{q}_3}+\omega_{j_2\vec{q}_2}+\omega_{j_1\vec{q}_1}+\omega_{j_4\vec{q}_4}) \\
&\quad\Big| \quad \text{then write } (N^{eq}_{j_3\vec{q}_3}+1)N^{eq}_{j_2\vec{q}_2}N^{eq}_{j_1\vec{q}_1}N^{eq}_{j_4\vec{q}_4} = N^{eq}_{j_3\vec{q}_3}(N^{eq}_{j_2\vec{q}_2}+1)(N^{eq}_{j_1\vec{q}_1}+1)(N^{eq}_{j_4\vec{q}_4}+1) \\
&\quad\Big| \quad \text{then write } \left|V^{(4ph)}_{j_3,-\vec{q}_3,j_2,\vec{q}_2,j_1,\vec{q}_1,j_4,\vec{q}_4}\right|^2 = \left|V^{(4ph)}_{j_3,\vec{q}_3,j_2,-\vec{q}_2,j_1,-\vec{q}_1,j_4,-\vec{q}_4}\right|^2 \\
&= -\frac{1}{3!}\frac{\hbar^2}{V^2T}\frac{2\pi V}{\hbar^2}\sum_{j_1\vec{q}_1j_2\vec{q}_2j_3\vec{q}_3j_4\vec{q}_4}\left|V^{(4ph)}_{j_3,\vec{q}_3,j_2,-\vec{q}_2,j_1,-\vec{q}_1,j_4,-\vec{q}_4}\right|^2\delta(\omega_{j_2\vec{q}_2}+\omega_{j_1\vec{q}_1}+\omega_{j_4\vec{q}_4}-\omega_{j_3\vec{q}_3}) \\
&\quad\times N^{eq}_{j_3\vec{q}_3}(N^{eq}_{j_2\vec{q}_2}+1)(N^{eq}_{j_1\vec{q}_1}+1)(N^{eq}_{j_4\vec{q}_4}+1)(\vec{q}_3)_{\alpha_1}(\vec{q}_3-\vec{q}_2-\vec{q}_1-\vec{q}_4)\cdot\vec{u} && (5.482)\\
&\quad\Big| \quad \text{use U processes conservation law } \vec{q}_1+\vec{q}_2+\vec{q}_4=\vec{q}_3+\vec{g}\text{ for } \vec{q}_1 \\
&= \frac{1}{3!}\frac{\hbar^2}{V^2T}\frac{2\pi V}{\hbar^2}\sum_{j_1}\sum_{j_1\vec{q}_1j_2\vec{q}_2j_3\vec{q}_3j_4\vec{q}_4}\left|V^{(4ph)}_{j_3,\vec{q}_3,j_2,-\vec{q}_2,j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g},j_4,-\vec{q}_4}\right|^2 \\
&\quad\times\delta(\omega_{j_2\vec{q}_2}+\omega_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g}}+\omega_{j_4\vec{q}_4}-\omega_{j_3\vec{q}_3})N^{eq}_{j_3\vec{q}_3}(N^{eq}_{j_2\vec{q}_2}+1)\left(N^{eq}_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g}}+1\right)(N^{eq}_{j_4\vec{q}_4}+1)(\vec{q}_3)_{\alpha_1}\vec{g}\cdot\vec{u}
\end{aligned}
$$

$$
\begin{aligned}
& \text{First term + Third term of } \frac{1}{V}\sum_{1} \hbar(\vec{q}_1)_{\alpha_1} \Delta I_U^{(4ph)} \\
= \quad & -\frac{1}{2}\frac{\hbar^2}{V^2 T}\frac{2\pi V}{\hbar^2}\sum_{j_1}\sum_{j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left|V^{(4ph)}_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g},j_2,-\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4}\right|^2 \delta(\omega_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g}} + \omega_{j_2\vec{q}_2} + \omega_{j_4\vec{q}_4} - \omega_{j_3\vec{q}_3}) \\
& \times \left(N^{eq}_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g}} + 1\right)(N^{eq}_{j_2\vec{q}_2}+1)N^{eq}_{j_3\vec{q}_3}(N^{eq}_{j_4\vec{q}_4}+1)\left(\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g}-\tfrac{1}{3}\vec{q}_3\right)_{\alpha_1}\vec{g}\cdot\vec{u} \qquad (5.483)
\end{aligned}
$$

$$
\begin{aligned}
& \text{Second term of } \frac{1}{V}\sum_{1} \hbar(\vec{q}_1)_{\alpha_1} \Delta I_U^{(4ph)} \\
= \quad & -\frac{1}{2}\frac{\hbar^2}{V^2 T}\frac{2\pi V}{\hbar^2}\sum_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left|V^{(4ph)}_{j_1,-\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4}\right|^2 \delta(\omega_{j_1\vec{q}_1} + \omega_{j_4\vec{q}_4} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3}) \\
& \times(N^{eq}_{j_1\vec{q}_1}+1)N^{eq}_{j_2\vec{q}_2}N^{eq}_{j_3\vec{q}_3}(N^{eq}_{j_4\vec{q}_4}+1)(\vec{q}_1)_{\alpha_1}(\vec{q}_1-\vec{q}_2-\vec{q}_3+\vec{q}_4)\cdot\vec{u} \qquad (5.484) \\
| \quad & \text{write } \left|V^{(4ph)}_{j_1,-\vec{q}_1,j_2,\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4}\right|^2 = \left|V^{(4ph)}_{j_1,\vec{q}_1,j_2,-\vec{q}_2,j_3,-\vec{q}_3,j_4,\vec{q}_4}\right|^2 \qquad (5.485) \\
| \quad & \text{use the U processes conservation law } \vec{q}_1+\vec{q}_4 = \vec{q}_2+\vec{q}_3+\vec{g} \text{ for } \vec{q}_1 \\
= \quad & -\frac{1}{2}\frac{\hbar^2}{V^2 T}\frac{2\pi V}{\hbar^2}\sum_{j_1}\sum_{j_1\vec{q}_1 j_2\vec{q}_2 j_3\vec{q}_3 j_4\vec{q}_4} \left|V^{(4ph)}_{j_1,\vec{q}_2+\vec{q}_3-\vec{q}_4+\vec{g},j_2,\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4}\right|^2 \delta(\omega_{j_1,\vec{q}_2+\vec{q}_3-\vec{q}_4+\vec{g}} + \omega_{j_4\vec{q}_4} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3}) \\
& \times\left(N^{eq}_{j_1,\vec{q}_2+\vec{q}_3-\vec{q}_4+\vec{g}}+1\right)N^{eq}_{j_2\vec{q}_2}N^{eq}_{j_3\vec{q}_3}(N^{eq}_{j_4\vec{q}_4}+1)(\vec{q}_2+\vec{q}_3-\vec{q}_4+\vec{g})_{\alpha_1}\vec{g}\cdot\vec{u} \qquad (5.486)
\end{aligned}
$$

$$
\begin{aligned}
& \frac{1}{V}\sum_{1} \hbar(\vec{q}_1)_{\alpha_1} \Delta I_U^{(4ph)} = \text{First term + Third term + Second term} \\
= \quad & -\frac{1}{2}\frac{\hbar^2}{V^2 T}\frac{2\pi V}{\hbar^2}\sum_{j_1}\sum_{j_2\vec{q}_2 j_3\vec{q}_3}\sum_{\alpha_2} \\
& \times\Bigg(\left|V^{(4ph)}_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g},j_2,-\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4}\right|^2 \delta(\omega_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g}} + \omega_{j_2\vec{q}_2} + \omega_{j_4\vec{q}_4} - \omega_{j_3\vec{q}_3}) \\
& \quad \times\left(N^{eq}_{j_1,\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g}}+1\right)(N^{eq}_{j_2\vec{q}_2}+1)N^{eq}_{j_3\vec{q}_3}(N^{eq}_{j_4\vec{q}_4}+1)\left(\vec{q}_2+\vec{q}_4-\vec{q}_3-\vec{g}-\tfrac{1}{3}\vec{q}_3\right)_{\alpha_1} g_{\alpha_2} \\
& \quad + \left|V^{(4ph)}_{j_1,\vec{q}_2+\vec{q}_3-\vec{q}_4+\vec{g},j_2,\vec{q}_2,j_3,\vec{q}_3,j_4,-\vec{q}_4}\right|^2 \delta(\omega_{j_1,\vec{q}_2+\vec{q}_3-\vec{q}_4+\vec{g}} + \omega_{j_4\vec{q}_4} - \omega_{j_2\vec{q}_2} - \omega_{j_3\vec{q}_3}) \\
& \quad \times\left(N^{eq}_{j_1,\vec{q}_2+\vec{q}_3-\vec{q}_4+\vec{g}}+1\right)N^{eq}_{j_2\vec{q}_2}N^{eq}_{j_3\vec{q}_3}(N^{eq}_{j_4\vec{q}_4}+1)(\vec{q}_2+\vec{q}_3-\vec{q}_4+\vec{g})_{\alpha_1} g_{\alpha_2}\Bigg) u_{\alpha_2} \qquad (5.487) \\
\equiv \quad & -\sum_{\alpha_2}\lambda^{(4ph)}_{\alpha_1\alpha_2}u_{\alpha_2} \qquad (5.488) \\
= \quad & -TS^2\sum_{\alpha_2}\frac{1}{TS^2}\lambda^{(4ph)}_{\alpha_1\alpha_2}u_{\alpha_2} \qquad (5.489) \\
| \quad & \text{define thermal conductivity, } \kappa^{(4ph)}_{\alpha_1\alpha_2} = TS^2\lambda^{(4ph)-1}_{\alpha_1\alpha_2} \text{ which we will justify immediately after} \\
= \quad & -TS^2\sum_{\alpha_2}\kappa^{(4ph)-1}_{\alpha_1\alpha_2}u_{\alpha_2} \qquad (5.490)
\end{aligned}
$$

Thus the momentum balance equation in first order (of distribution) takes this final form,

$$\boxed{\sum_{\alpha_2} \chi_{\alpha_1\alpha_2} \frac{\partial u_{\alpha_2}}{\partial t} + S\frac{\partial \Delta T}{\partial r_{\alpha_2}} = -TS^2 \sum_{\alpha_2} \left(\kappa^{(3ph)-1}_{\alpha_1\alpha_2} + \kappa^{(4ph)-1}_{\alpha_1\alpha_2}\right) u_{\alpha_2}} \tag{5.491}$$

Now we justify for the definition of thermal conductivity given earlier. Consider the special case of steady state where the drift velocity varies spatially but not temporally, i.e. $\frac{\partial \vec{u}}{\partial t} = 0$ then the momentum balance equation becomes

$$S\frac{\partial \Delta T}{\partial r_{\alpha_1}} = -\sum_{\alpha_2} \left(\lambda^{(3ph)}_{\alpha_1\alpha_2} + \lambda^{(4ph)}_{\alpha_1\alpha_2}\right) u_{\alpha_2} \tag{5.492}$$

and recall the expression of current from the energy balance equation,

$$\vec{J}^{(1)}(\vec{r}t) = TS\vec{u} \tag{5.493}$$

which we shall use to replace u_{α_2} in the momentum balance equation to get,

$$\begin{aligned}
S\frac{\partial \Delta T}{\partial r_{\alpha_1}} &= -\frac{1}{TS}\sum_{\alpha_2} \left(\lambda^{(3ph)}_{\alpha_1\alpha_2} + \lambda^{(4ph)}_{\alpha_1\alpha_2}\right) J^{(1)}_{\alpha_2} &(5.494)\\
J^{(1)}_{\alpha_1} &= -TS^2\sum_{\alpha_2} \left(\lambda^{(3ph)-1}_{\alpha_1\alpha_2} + \lambda^{(4ph)-1}_{\alpha_1\alpha_2}\right) \frac{\partial \Delta T}{\partial r_{\alpha_2}} &(5.495)\\
&\quad \Big| \quad \text{compare with Fourier's law, } J_{\alpha_1} = -\sum_{\alpha_2} \kappa_{\alpha_1\alpha_2}\frac{\partial \Delta T}{\partial r_{\alpha_2}}, \text{ we get} &\\
\kappa^{(3ph)}_{\alpha_1\alpha_2} + \kappa^{(4ph)}_{\alpha_1\alpha_2} &= TS^2\left(\lambda^{(3ph)-1}_{\alpha_1\alpha_2} + \lambda^{(4ph)-1}_{\alpha_1\alpha_2}\right) &(5.496)
\end{aligned}$$

which is the definition used earlier.

[Chapman-Enskog Iteration] Now we can carry out the first correction in distribution (due to U-processes) via a Chapman-Enskog-like iteration. This is done by finding the second order correction, $y^{(2)}_{j_1\vec{q}_1}$ using the phonon Boltzmann Equation.

$$\begin{aligned}
N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)\left(\frac{\partial}{\partial t} + (\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1})\cdot\nabla_{\vec{r}}\right) y^{(1)}_{j_1\vec{q}_1} &= \Delta I^{(3ph)}_N\left[y^{(2)}_{j_1\vec{q}_1}\right] + \Delta I^{(4ph)}_N\left[y^{(2)}_{j_1\vec{q}_1}\right] &(5.497)\\
\left(\frac{\partial}{\partial t} + (\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1})\cdot\nabla_{\vec{r}}\right) y^{(1)}_{j_1\vec{q}_1} &= \frac{1}{N^{\text{eq}}_{j_1\vec{q}_1}(N^{\text{eq}}_{j_1\vec{q}_1}+1)}\left(\Delta I^{(3ph)}_N\left[y^{(2)}_{j_1\vec{q}_1}\right] + \Delta I^{(4ph)}_N\left[y^{(2)}_{j_1\vec{q}_1}\right]\right) &(5.498)
\end{aligned}$$

We expand the LHS

$$\begin{aligned}
\text{LHS} &= \left(\frac{\partial}{\partial t} + (\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1})\cdot\nabla_{\vec{r}}\right)\left(\frac{\hbar\omega_{j_1\vec{q}_1}\Delta T}{T^2} + \frac{\hbar}{T}\vec{q}_1\cdot\vec{u}\right) &(5.499)\\
&= \frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\frac{\partial \Delta T}{\partial t} + \sum_\alpha \frac{\hbar}{T}(\vec{q}_1)_\alpha \frac{\partial u_\alpha}{\partial t} + \sum_\alpha (\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1})_\alpha \left(\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\frac{\partial \Delta T}{\partial r_\alpha} + \sum_{\alpha_1}\frac{\hbar}{T}(\vec{q}_1)_{\alpha_1}\frac{\partial u_{\alpha_1}}{\partial r_\alpha}\right) &(5.500)\\
&\quad \Big| \quad \text{change the temporal derivatives to spatial derivatives} &\\
&\quad \Big| \quad \text{by using the first order hydrodynamic equations without the Umklapp part} &
\end{aligned}$$

$$
\begin{aligned}
&= \frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\left(-\frac{TS}{C}\right)(\nabla_{\vec{r}}\cdot\vec{u}) + \sum_\alpha \frac{\hbar}{T}(\vec{q}_1)_\alpha\left(-S\sum_{\alpha_1}\chi^{-1}_{\alpha\alpha_1}\frac{\partial\Delta T}{\partial r_{\alpha_1}}\right) \\
&\quad + \sum_\alpha\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)\left(\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\frac{\partial\Delta T}{\partial r_\alpha} + \sum_{\alpha_1}\frac{\hbar}{T}(\vec{q}_1)_{\alpha_1}\frac{\partial u_{\alpha_1}}{\partial r_\alpha}\right) && (5.501) \\
&= \sum_{\alpha_1}\frac{\partial\Delta T}{\partial r_{\alpha_1}}\left(\frac{\hbar\omega_{j_1\vec{q}_1}}{T^2}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)_{\alpha_1} - \sum_\alpha\frac{\hbar S}{T}(\vec{q}_1)_\alpha\chi^{-1}_{\alpha\alpha_1}\right) \\
&\quad + \sum_{\alpha_1\alpha_2}\frac{\partial u_{\alpha_2}}{\partial r_{\alpha_1}}\left(\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)_{\alpha_1}\frac{\hbar}{T}(\vec{q}_1)_{\alpha_2} - \delta_{\alpha_1\alpha_2}\frac{\hbar\omega_{j_1\vec{q}_1}}{CT}S\right) && (5.502) \\
&\quad | \quad \text{note that the first round bracket is odd in } \vec{q}_1 \text{ and the second round bracket is even in } \vec{q}_1 \\
&\equiv \sum_{\alpha_1}\frac{\partial\Delta T}{\partial r_{\alpha_1}}A_{j_1\vec{q}_1\alpha} + \sum_{\alpha_1\alpha_2}\frac{\partial u_{\alpha_2}}{\partial r_{\alpha_1}}B_{j_1\vec{q}_1\alpha_1\alpha_2} && (5.503)
\end{aligned}
$$

We search for $y^{(2)}_{j_1\vec{q}_1}$ on the RHS in a similar even-odd (in $\vec{q}$) form.

$$
y^{(2)}_{j_1\vec{q}_1} = \sum_\alpha\frac{\partial\Delta T}{\partial r_{\alpha_1}}\tilde{A}_{j_1\vec{q}_1\alpha_1} + \sum_{\alpha_1\alpha_2}\frac{\partial u_{\alpha_2}}{\partial r_{\alpha_1}}\tilde{B}_{j_1\vec{q}_1\alpha_1\alpha_2} \tag{5.504}
$$

This form is substituted in the linearized collision integral. Then compare coefficients on both sides of the Phonon Boltzmann equation (recalling also the factor $\frac{1}{N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)}$ on RHS and abbreviated notation is used in order to fit the equations),[20]

$$
\begin{aligned}
A_{1\alpha} &= -\frac{1}{V}\sum_{23}\frac{1}{2}\frac{N^{\rm eq}_2N^{\rm eq}_3}{N^{\rm eq}_1}\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{\bar{1},2,3}\right|^2\delta(\omega_1-\omega_2-\omega_3)\left(\tilde{A}_{1\alpha}-\tilde{A}_{2\alpha}-\tilde{A}_{3\alpha}\right) \\
&\quad -\frac{1}{V}\sum_{23}\frac{(N^{\rm eq}_3+1)N^{\rm eq}_2}{N^{\rm eq}_1+1}\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{1,2,\bar{3}}\right|^2\delta(\omega_1+\omega_2-\omega_3)\left(\tilde{A}_{1\alpha}+\tilde{A}_{2\alpha}-\tilde{A}_{3\alpha}\right) \\
&\quad -\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},\bar{2},3,\bar{4}}\right|^2\delta(\omega_1+\omega_2+\omega_4-\omega_3) \\
&\quad \times\frac{(N^{eq}_2+1)N^{eq}_3(N^{eq}_4+1)}{N^{eq}_1}(\tilde{A}_{1\alpha}+\tilde{A}_{2\alpha}-\tilde{A}_{3\alpha}+\tilde{A}_{4\alpha}) \\
&\quad -\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3\bar{4}}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3)\frac{N^{eq}_2N^{eq}_3(N^{eq}_4+1)}{N^{eq}_1}(\tilde{A}_{1\alpha}-\tilde{A}_{2\alpha}-\tilde{A}_{3\alpha}+\tilde{A}_{4\alpha}) \\
&\quad -\frac{1}{3!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,4}\right|^2\delta(\omega_1-\omega_2-\omega_3-\omega_4)\frac{N^{eq}_2N^{eq}_3N^{eq}_4}{N^{eq}_1}(\tilde{A}_{1\alpha}-\tilde{A}_{2\alpha}-\tilde{A}_{3\alpha}-\tilde{A}_{4\alpha}) && (5.505) \\
B_{1\alpha\alpha'} &= -\frac{1}{V}\sum_{2,3}\frac{1}{2}\frac{N^{\rm eq}_2N^{\rm eq}_3}{N^{\rm eq}_1}\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{\bar{1},2,3}\right|^2\delta(\omega_1-\omega_2-\omega_3)\left(\tilde{B}_{1\alpha\alpha'}-\tilde{B}_{2\alpha\alpha'}-\tilde{B}_{3\alpha\alpha'}\right) \\
&\quad -\frac{1}{V}\sum_{2,3}\frac{(N^{\rm eq}_3+1)N^{\rm eq}_2}{N^{\rm eq}_1+1}\frac{2\pi V}{\hbar^2}\left|V^{(3ph)}_{1,2,\bar{3}}\right|^2\delta(\omega_1+\omega_2-\omega_3)\left(\tilde{B}_{1\alpha\alpha'}+\tilde{B}_{2\alpha\alpha'}-\tilde{B}_{3\alpha\alpha'}\right) \\
&\quad -\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},\bar{2},3,\bar{4}}\right|^2\delta(\omega_1+\omega_2+\omega_4-\omega_3)
\end{aligned}
$$

[20]Note that anharmonicity comes into the coefficients $\tilde{A}$ and $\tilde{B}$.

$$
\begin{aligned}
&\times \frac{(N_2^{eq}+1)N_3^{eq}(N_4^{eq}+1)}{N_1^{eq}}(\tilde{B}_{1\alpha\alpha'}+\tilde{B}_{2\alpha\alpha'}-\tilde{B}_{3\alpha\alpha'}+\tilde{B}_{4\alpha\alpha'}) \\
&-\frac{1}{2}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3\bar{4}}\right|^2\delta(\omega_1+\omega_4-\omega_2-\omega_3) \\
&\times \frac{N_2^{eq}N_3^{eq}(N_4^{eq}+1)}{N_1^{eq}}(\tilde{B}_{1\alpha\alpha'}-\tilde{B}_{2\alpha\alpha'}-\tilde{B}_{3\alpha\alpha'}+\tilde{B}_{4\alpha\alpha'}) \\
&-\frac{1}{3!}\frac{1}{V}\frac{2\pi V}{\hbar^2}\sum_{2,3,4}\left|V^{(4ph)}_{\bar{1},2,3,4}\right|^2\delta(\omega_1-\omega_2-\omega_3-\omega_4)\frac{N_2^{eq}N_3^{eq}N_4^{eq}}{N_1^{eq}}(\tilde{B}_{1\alpha\alpha'}-\tilde{B}_{2\alpha\alpha'}-\tilde{B}_{3\alpha\alpha'}-\tilde{B}_{4\alpha\alpha'})
\end{aligned}
\tag{5.506}
$$

The second order correction to the distribution can be written as $\Delta N^{(2)}_{j_1\vec{q}_1} = N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)y^{(2)}_{j_1\vec{q}_1}$ and to get the corrected hydrodynamic balance equations, we first calculate the corrected hydrodynamic quantities. Earlier, we have "transformed" temporal derivatives to spatial derivatives, thus all corrections enter as spatial derivatives. As local energy density $\epsilon(\vec{r}t)$ enters the balance equation as a temporal derivative, there are no further corrections to it.

$$
\begin{aligned}
&\text{Second Order Momentum Density } P^{(2)}_\alpha(\vec{r}t) \\
=\;& \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_\alpha N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)y^{(2)}_{j_1\vec{q}_1} && (5.507)\\
|\;& \text{since } (\vec{q}_1)_\alpha \text{ is odd, we retain the odd part of } y^{(2)}_{j_1\vec{q}_1}\text{, i.e. } \tilde{A}_{j_1\vec{q}_1\alpha} \\
=\;& \frac{\hbar}{V}\sum_{j_1\vec{q}_1}\sum_{\alpha_1}(\vec{q}_1)_\alpha\tilde{A}_{j_1\vec{q}_1\alpha_1}N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)\frac{\partial\Delta T}{\partial r_{\alpha_1}} && (5.508)\\
\equiv\;& \pi_{\alpha\alpha_1}\frac{\partial\Delta T}{\partial r_{\alpha_1}} && (5.509)
\end{aligned}
$$

$$
\begin{aligned}
&\text{Second Order Energy Flow Density (Heat Current) } J^{(2)}_\alpha(\vec{r}t) \\
=\;& \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)y^{(2)}_{j_1\vec{q}_1} && (5.510)\\
|\;& \text{since } \nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1} \text{ is odd in } \vec{q}_1\text{, we retain the odd part of } y^{(2)}_{j_1\vec{q}_1}\text{, i.e. } \tilde{A}_{j_1\vec{q}_1\alpha} \\
=\;& \frac{\hbar}{V}\sum_{j_1\vec{q}_1}\sum_{\alpha_1}\omega_{j_1\vec{q}_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)_\alpha\tilde{A}_{j_1\vec{q}_1\alpha_1}N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)\frac{\partial\Delta T}{\partial r_{\alpha_1}} && (5.511)\\
\equiv\;& -\sum_{\alpha_1}\mu_{\alpha\alpha_1}\frac{\partial\Delta T}{\partial r_{\alpha_1}} && (5.512)
\end{aligned}
$$

$$
\begin{aligned}
&\text{Second Order Crystal Momentum Flux Tensor } G^{(2)}_{\alpha_1\alpha_2}(\vec{r}t) \\
=\;& \frac{1}{V}\sum_{j_1\vec{q}_1}\hbar(\vec{q}_1)_{\alpha_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)_{\alpha_2}N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)y^{(2)}_{j_1\vec{q}_1} && (5.513)\\
|\;& \text{since } (\vec{q}_1)\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right) \text{ is even in } \vec{q}_1\text{, we retain the even part of } y^{(2)}_{j_1\vec{q}_1}\text{, i.e. } \tilde{B}_{j_1\vec{q}_1\alpha\alpha'} \\
=\;& \frac{\hbar}{V}\sum_{j_1\vec{q}_1}\sum_{\alpha_3\alpha_4}(\vec{q}_1)_{\alpha_1}\left(\nabla_{\vec{q}_1}\omega_{j_1\vec{q}_1}\right)_{\alpha_2}\tilde{B}_{j_1\vec{q}_1\alpha_3\alpha_4}N^{\rm eq}_{j_1\vec{q}_1}(N^{\rm eq}_{j_1\vec{q}_1}+1)\frac{\partial u_{\alpha_4}}{\partial r_{\alpha_3}} && (5.514)
\end{aligned}
$$

$$\equiv \sum_{\alpha_3\alpha_4} \gamma_{\alpha_1\alpha_2\alpha_3\alpha_4} \frac{\partial u_{\alpha_4}}{\partial r_{\alpha_3}} \tag{5.515}$$

Now calculate the second order corrected balance equations using these quantities,

$$\epsilon(\vec{r}t) = \epsilon^{(1)}(\vec{r}t) \tag{5.516}$$
$$P_{\alpha_1}(\vec{r}t) = P^{(1)}_{\alpha_1}(\vec{r}t) + P^{(2)}_{\alpha_1}(\vec{r}t) \tag{5.517}$$
$$J_{\alpha_1}(\vec{r}t) = J^{(1)}_{\alpha_1}(\vec{r}t) + J^{(2)}_{\alpha_1}(\vec{r}t) \tag{5.518}$$
$$G_{\alpha_1\alpha_2}(\vec{r}t) = G^{(1)}_{\alpha_1\alpha_2}(\vec{r}t) + G^{(2)}_{\alpha_1\alpha_2}(\vec{r}t) \tag{5.519}$$

For the energy balance equation, we get,

$$\boxed{C\frac{\partial \Delta T}{\partial t} + TS\sum_{\alpha_1}\frac{\partial u_{\alpha_1}}{\partial r_{\alpha_1}} - \sum_{\alpha_1\alpha_2}\mu_{\alpha_1\alpha_2}\frac{\partial^2 \Delta T}{\partial r_{\alpha_1}\partial r_{\alpha_2}} = 0} \tag{5.520}$$

For the momentum balance equation, we get,

$$\begin{aligned}
\frac{\partial P^{(1)}_{\alpha_1}(\vec{r}t)}{\partial t} + \frac{\partial P^{(2)}_{\alpha_1}(\vec{r}t)}{\partial t} + \sum_{\alpha_2}\frac{\partial G^{(1)}_{\alpha_1\alpha_2}(\vec{r}t)}{\partial r_{\alpha_2}} &+ \sum_{\alpha_2}\frac{\partial G^{(2)}_{\alpha_1\alpha_2}(\vec{r}t)}{\partial r_{\alpha_2}} \\
&= -TS^2\sum_{\alpha_2}\left(\kappa^{(3ph)-1}_{\alpha_1\alpha_2} + \kappa^{(4ph)-1}_{\alpha_1\alpha_2}\right)u_{\alpha_2} \\
\sum_{\alpha_2}\chi_{\alpha_1\alpha_2}\frac{\partial u_{\alpha_2}}{\partial t} + \sum_{\alpha_2}\pi_{\alpha_1\alpha_2}\frac{\partial^2 \Delta T}{\partial t\partial r_{\alpha_2}} + S\frac{\partial \Delta T}{\partial r_{\alpha_1}} &+ \sum_{\alpha_2\alpha_3\alpha_4}\gamma_{\alpha_1\alpha_2\alpha_3\alpha_4}\frac{\partial^2 u_{\alpha_4}}{\partial r_{\alpha_2}\partial r_{\alpha_3}} \\
&= -TS^2\sum_{\alpha_2}\left(\kappa^{(3ph)-1}_{\alpha_1\alpha_2} + \kappa^{(4ph)-1}_{\alpha_1\alpha_2}\right)u_{\alpha_2}
\end{aligned}$$

$\frac{\partial}{\partial r_{\alpha_2}}$ the first order energy balance equation to get |

$C\frac{\partial^2 \Delta T}{\partial r_{\alpha_2}\partial t} + TS\sum_{\alpha_1}\frac{\partial^2 u_{\alpha_1}}{\partial r_{\alpha_2}\partial r_{\alpha_1}} = 0$ and replace $\frac{\partial^2 \Delta T}{\partial t\partial r_{\alpha_2}}$ |

also define $\nu_{\alpha_1\alpha_2\alpha_3\alpha_4} = -\gamma_{\alpha_1\alpha_2\alpha_3\alpha_4} + \frac{TS}{C}\pi_{\alpha_1\alpha_2}\delta_{\alpha_3\alpha_4}$ |

$$\boxed{\sum_{\alpha_2}\chi_{\alpha_1\alpha_2}\frac{\partial u_{\alpha_2}}{\partial t} + S\frac{\partial \Delta T}{\partial r_{\alpha_1}} - \sum_{\alpha_2\alpha_3\alpha_4}\nu_{\alpha_1\alpha_2\alpha_3\alpha_4}\frac{\partial^2 u_{\alpha_4}}{\partial r_{\alpha_2}\partial r_{\alpha_3}} = -TS^2\sum_{\alpha_2}\left(\kappa^{(3ph)-1}_{\alpha_1\alpha_2} + \kappa^{(4ph)-1}_{\alpha_1\alpha_2}\right)u_{\alpha_2}} \tag{5.521}$$

The two corrected balance equations are called the dissipative hydrodynamic equations. We summarize the tensors involved in the equations.

1. $\kappa^{(3ph)}_{\alpha_1\alpha_2} + \kappa^{(4ph)}_{\alpha_1\alpha_2}$: Thermal conductivity tensors
2. $\nu_{\alpha_1\alpha_2\alpha_3\alpha_4}$: Phonon Hydrodynamical viscosity tensor [21]
3. $\mu_{\alpha_1\alpha_2}$: Correction to the thermal conductivity tensor or the thermal conductivity tensor in phonon hydrodynamics theory since its definition comes from a Fourier-like law. The interesting thing is that it is a dissipative term that comes from N-processes. [22]

[21] Note that $\nu_{\alpha_1\alpha_2\alpha_3\alpha_4}$ depends on the coefficients $\tilde{A}$ and $\tilde{B}$ and so it depends on the order of anharmonicity.
[22] Note that $\mu_{\alpha_1\alpha_2}$ depends on the coefficients $\tilde{A}$ and $\tilde{B}$ and so it depends on anharmonicity.

4. $\chi_{\alpha_1\alpha_2}$: Mass-like tensor that relates $\vec{P}$ to the drift velocity $\vec{u}$

Now we will estimate these tensors with respect to their dependence in temperature.

[Estimating λ (at low T):] See [Vasko2005] pg 200 and [Gruevich1986] pg 122. Observe that the definition of λ is related to the Umklapp part of the (linearized) collision integral. Thus we can define an Umklapp relaxation time,

$$\frac{1}{\tau_U} \equiv \lambda_{\alpha\alpha}\left[\frac{\hbar^2}{VT}\sum_{j\vec{q}}\vec{q}^{\,2}N_{j\vec{q}}^{eq}(N_{j\vec{q}}^{eq}+1)\right]^{-1} \tag{5.522}$$

where the factor $[\ldots]^{-1}$ is for dimensional reasons. We estimate this factor for its T dependence. The low T region is probed by using the Debye approximation which is approximately the spectrum at low T. We assume one branch for simplicity and we drop the index j.

$$\begin{aligned}
&\frac{\hbar^2}{VT}\sum_{\vec{q}}\vec{q}^{\,2}N_{\vec{q}}^{eq}(N_{\vec{q}}^{eq}+1) && (5.523)\\
&|\quad \text{use Debye approximation } \omega = v|\vec{q}| \text{ and } \sum_{\vec{q}} \to\sim \int d\omega\frac{\omega^2}{v^3}\\
&|\quad \text{where the group velocity } v \text{ is a constant}\\
\sim\ &\frac{\hbar^2}{T}\int d\omega\frac{\omega^4}{v^5}N_{\vec{q}}^{eq}(N_{\vec{q}}^{eq}+1) && (5.524)\\
&|\quad \text{let } x = \frac{\hbar\omega}{k_BT}\\
\sim\ &\frac{\hbar^2}{T}\frac{1}{v^5}\frac{k_B^4T^4}{\hbar^4}\frac{k_BT}{\hbar}\int dx\frac{x^4e^x}{(e^x-1)^2} && (5.525)\\
&|\quad \text{where the integral is some constant}\\
\sim\ &\frac{k_B^4T^4}{\hbar^3v^5} && (5.526)
\end{aligned}$$

So,

$$\boxed{\lambda \sim \frac{T^4}{\tau_U}} \tag{5.527}$$

[Estimating entropy density S (at low T):] See [Vasko2005] pg 200 and [Gruevich1986] pg 49. Recall the thermodynamic relation,

$$C_V = T\left(\frac{\partial S}{\partial T}\right) \tag{5.528}$$

and at low T, the specific heat C_V estimated in Debye approximation is $C_V \sim T^3$, thus

$$\boxed{S \sim T^3} \tag{5.529}$$

[Estimating κ (at low T):] See [Vasko2005] pg 200 and [Gruevich1986] pg 123. Recall the relation,

$$\begin{aligned} \kappa &= TS^2\lambda^{-1} && (5.530)\\ &\quad \Big| \text{ use } S \sim T^3 \text{ and } \lambda \sim \frac{T^4}{\tau_U} \\ &\sim TT^6\frac{\tau_U}{T^4} && (5.531) \end{aligned}$$

So,

$$\boxed{\kappa \sim \tau_U T^3} \tag{5.532}$$

At low T, τ_U diverges and so κ diverges but this is only true if τ_U diverges faster than T^{-3} for low T. Thus we need to estimate τ_U to confirm this.

[Estimating τ_U (at low T):] See [Vasko2005] pg 201 and [Gruevich1986] pg 123. We carry out this estimation by roughly solving λ for a 1D chain. Take the atomic spacing to be a, and there is only 1 phonon branch thus branch index j can be dropped. The first Brillouin zone (BZ) is $-\frac{\pi}{a} < q_2, q_3 < \frac{\pi}{a}$. Checking the selection rules gives only 2 possible Umklapp processes.

- q_2 , $q_3 > 0$, $g = -\frac{2\pi}{a}$ to map it back into first BZ
- q_2 , $q_3 < 0$, $g = \frac{2\pi}{a}$ to map it back into first BZ

$$\begin{aligned}
\lambda^{(3ph)}_{\alpha_1\alpha_2} &= \frac{\hbar^2}{2a^2T}\sum_{q_2,q_3}\left|V^{(3ph)}_{-q_2-q_3-g,q_2,q_3}\right|^2\left(N^{eq}_{q_2+q_3+g}+1\right)N^{eq}_{q_2}N^{eq}_{q_3}\delta(\omega_{q_2+q_3+g}-\omega_{q_2}-\omega_{q_3})g_{\alpha_1}g_{\alpha_2} && (5.533)\\
&\quad \Big| \text{ seperate the double sum into the 2 } U\text{-processes}\\
&= \frac{\hbar^2}{2a^2T}\Bigg\{\sum_{q_2,q_3>0}\left|V^{(3ph)}_{-q_2-q_3+\frac{2\pi}{a},q_2,q_3}\right|^2\left(N^{eq}_{q_2+q_3-\frac{2\pi}{a}}+1\right)N^{eq}_{q_2}N^{eq}_{q_3}\delta(\omega_{q_2+q_3-\frac{2\pi}{a}}-\omega_{q_2}-\omega_{q_3})\left(-\frac{2\pi}{a}\right)^2\\
&\quad +\sum_{q_2,q_3<0}\left|V^{(3ph)}_{|q_2|+|q_3|-\frac{2\pi}{a},-|q_2|,-|q_3|}\right|^2\left(N^{eq}_{-|q_2|-|q_3|-\frac{2\pi}{a}}+1\right)N^{eq}_{-|q_2|}N^{eq}_{-|q_3|}\\
&\quad \times\delta(\omega_{-|q_2|-|q_3|+\frac{2\pi}{a}}-\omega_{-|q_2|}-\omega_{-|q_3|})\left(\frac{2\pi}{a}\right)^2\Bigg\} && (5.534)\\
&\quad \Big| \text{ note that } \omega \text{ and } N^{eq} \text{ do not depend on the sign of } q\\
&\quad \Big| \ V^{(3ph)} \text{ appears as } |V^{(3ph)}|^2 \text{ and so the 2 coefficients are the same}\\
&\quad \Big| \text{ the 2 terms add up and cancels the factor } \frac{1}{2}\\
&= \frac{\hbar^2}{a^2T}\left(\frac{2\pi}{a}\right)^2\sum_{q_2,q_3>0}\left|V^{(3ph)}_{-q_2-q_3+\frac{2\pi}{a},q_2,q_3}\right|^2\left(N^{eq}_{q_2+q_3-\frac{2\pi}{a}}+1\right)N^{eq}_{q_2}N^{eq}_{q_3}\delta(\omega_{q_2+q_3-\frac{2\pi}{a}}-\omega_{q_2}-\omega_{q_3}) && (5.535)\\
&\quad \Big| \text{ write } \omega_{q_2} = vq_2 \text{ and for } q_2,q_3>0,\ q_2+q_3-\frac{2\pi}{a}<0, \text{ so } \omega_{q_2+q_3-\frac{2\pi}{a}} = (-v)(q_2+q_3-\frac{2\pi}{a})\\
&= \frac{\hbar^2}{a^2T}\left(\frac{2\pi}{a}\right)^2\sum_{q_2,q_3>0}\left|V^{(3ph)}_{-q_2-q_3+\frac{2\pi}{a},q_2,q_3}\right|^2\left(N^{eq}_{q_2+q_3-\frac{2\pi}{a}}+1\right)N^{eq}_{q_2}N^{eq}_{q_3}\frac{1}{2v}\delta(q_2+q_3-\frac{\pi}{a}) && (5.536)\\
&\quad \Big| \text{ for small } T,\ e^{\frac{\hbar\omega}{k_BT}} \text{ is large, so we estimate,}
\end{aligned}$$

$$
\begin{aligned}
&\quad | \quad (N^{eq}+1)N^{eq}N^{eq} \sim \frac{e^{\frac{\hbar\omega}{k_BT}}}{e^{\frac{\hbar\omega}{k_BT}}-1}\frac{1}{e^{\frac{\hbar\omega}{k_BT}}-1}\frac{1}{e^{\frac{\hbar\omega}{k_BT}}-1} \sim 1\times e^{-\frac{\hbar\omega_{q_2}}{k_BT}}\times e^{-\frac{\hbar\omega_{q_3}}{k_BT}} \sim e^{-\frac{\hbar}{k_BT}v\frac{\pi}{a}} \\
&\quad | \quad \text{since for } U\text{-processes, } q_2+q_3\sim\frac{\pi}{a}\text{, so } \omega\sim v\frac{\pi}{a} \\
&\sim \frac{\hbar^2}{a^2T}\left(\frac{2\pi}{a}\right)^2 e^{-\frac{\hbar}{k_BT}v\frac{\pi}{a}}\frac{1}{2v}\sum_{q_2,q_3>0}\left|V^{(3ph)}_{-q_2-q_3+\frac{2\pi}{a},q_2,q_3}\right|^2\delta(q_2+q_3-\frac{\pi}{a}) \qquad (5.537)
\end{aligned}
$$

So the temperature dependence is,

$$
\boxed{
\begin{aligned}
\lambda &\sim \frac{1}{T}e^{-\frac{1}{T}} && (5.538)\\
\frac{1}{\tau_U} &\sim \frac{\lambda}{T^4}\sim\frac{1}{T^5}e^{-\frac{1}{T}} && (5.539)\\
\kappa &\sim \tau_U T^3 \sim T^8 e^{\frac{1}{T}} && (5.540)
\end{aligned}}
$$

Indeed κ diverges at low T exponentially.

[Estimating κ (at high T):] See [Vasko2005] pg 201 and [Gruevich1986] pg 115. Recall the expression for thermal conductivity,

$$
\kappa = \frac{\hbar^2}{3Vk_BT^2}\sum_{j\vec{q}}|\nabla_{\vec{q}}\omega_{j\vec{q}}|^2\omega^2_{j\vec{q}}\tau_{j\vec{q}}N^{eq}_{j\vec{q}}(N^{eq}_{j\vec{q}}+1) \qquad (5.541)
$$

We will use the SMRT expressions for $\tau^{(3ph)}$ and $\tau^{(4ph)}$ to estimate the high T behavior of $\kappa^{(3ph)}$ and $\kappa^{(4ph)}$ respectively. For high T,

$$
\begin{aligned}
N^{eq} &= \left(e^{\frac{\hbar\omega}{k_BT}}-\right)^{-1} = \left(\left(1+\frac{\hbar\omega}{k_BT}+\cdots\right)-1\right)^{-1}\approx\frac{k_BT}{\hbar\omega} && (5.542)\\
\frac{1}{\tau^{(3ph)}} &\sim \frac{N^{eq}N^{eq}}{N^{eq}}\sim T \quad , \quad \frac{1}{\tau^{(4ph)}}\sim\frac{N^{eq}N^{eq}N^{eq}}{N^{eq}}\sim T^2 && (5.543)
\end{aligned}
$$

and using Einstein's approximation for high T, i.e. $\omega\sim$ constant and $|\nabla\omega|^2=\vec{v}^2$ is a (small) constant, we get,

$$
\begin{aligned}
\kappa^{(3ph)} &\sim \frac{1}{T^2}\tau^{(3ph)}N^{eq}(N^{eq}+1)\sim\frac{1}{T^2}\frac{1}{T}T^2\sim\frac{1}{T} && (5.544)\\
\kappa^{(4ph)} &\sim \frac{1}{T^2}\tau^{(4ph)}N^{eq}(N^{eq}+1)\sim\frac{1}{T^2}\frac{1}{T^2}T^2\sim\frac{1}{T^2} && (5.545)
\end{aligned}
$$

$$
\boxed{\kappa^{(3ph)}\sim\frac{1}{T} \quad , \quad \kappa^{(4ph)}\sim\frac{1}{T^2}} \qquad (5.546)
$$

[Estimating χ (at low T):] See [Vasko2005] pg 206 and [Gruevich1986] pg 135. [23] Recall its definition (taking the diagonal),

$$
\chi = \frac{\hbar^2}{VT}\sum_{j\vec{q}}\vec{q}^{\,2}N^{eq}_{j\vec{q}}(N^{eq}_{j\vec{q}}+1) \qquad (5.547)
$$

[23] Gurevich's script p is my χ.

which is exactly the factor we calculated in the low T estimate of λ, immediately we can write,

$$\boxed{\chi \sim T^4} \tag{5.548}$$

[Estimating μ (at low T):] See [Vasko2005] pg 206 and [Gruevich1986] pg 147. [24] Recall its definition,

$$\mu_{\alpha_1\alpha_2} = -\frac{\hbar}{V}\sum_{j\vec{q}} \omega_{j\vec{q}}(\nabla_{\vec{q}}\omega_{j\vec{q}})_{\alpha_1}\tilde{A}_{j\vec{q}\alpha_2}N^{eq}_{j\vec{q}}(N^{eq}_{j\vec{q}}+1) \tag{5.549}$$

and so we need an estimate of $\tilde{A}$ first. If we look at equation (5.505) and equation (5.506) and the SMRT expressions of $\tau^{(3ph)}$ and $\tau^{(4ph)}$, we can estimate these 2 equations as,

$$A \sim \left(\frac{1}{\tau^{(3ph)}}+\frac{1}{\tau^{(4ph)}}\right)_N \tilde{A} \Rightarrow \tau_N A \sim \tilde{A} \tag{5.550}$$

$$B \sim \left(\frac{1}{\tau^{(3ph)}}+\frac{1}{\tau^{(4ph)}}\right)_N \tilde{B} \Rightarrow \tau_N B \sim \tilde{B} \tag{5.551}$$

where we recall that the derivation at that point is within N-processes and τ_N is a generic symbol for the relaxation time of N-processes. Now we need to estimate A and B from their explicit expressions

$$A = \frac{\hbar\omega}{T^2}(\nabla_q\omega) - \frac{\hbar S}{T}q\chi^{-1} \quad , \quad B = (\nabla_q\omega)\frac{\hbar q}{T} - \frac{\hbar\omega}{CT}S \tag{5.552}$$

use Debye approximation, i.e. $\omega = vq$, $(\nabla_q\omega) = v$ and recall the earlier estimates: $\chi \sim T^4$, $C \sim T^3$ and $S \sim T^3$, we get,

$$A \sim \frac{qv^2}{T^2} \quad , \quad B \sim \frac{qv}{T} \tag{5.553}$$

$$\tilde{A} \sim \tau_N\frac{qv^2}{T^2} \quad , \quad \tilde{B} \sim \tau_N\frac{qv}{T} \tag{5.554}$$

Finally,

$$\mu \sim \sum_{\vec{q}} \omega v \tau_N \frac{qv^2}{T^2} N^{eq}_{\vec{q}}(N^{eq}_{\vec{q}}+1) \tag{5.555}$$

$$\Big| \quad \text{use the Debye approximation expressions } \omega = vq \text{ and } \sum_{\vec{q}} \rightarrow\sim \int d\omega\frac{\omega^2}{v^3}$$

$$\sim \int d\omega \frac{\omega^4}{v}\frac{\tau_N}{T^2}N^{eq}_{\vec{q}}(N^{eq}_{\vec{q}}+1) \tag{5.556}$$

$$\Big| \quad \text{let } x = \frac{\hbar\omega}{k_BT}$$

$$\sim \frac{\tau_N}{T^2}\frac{k_BT}{\hbar}\int dx \frac{k_B^4T^4}{\hbar^4}x^4\frac{e^x}{(e^x-1)^2} \tag{5.557}$$

So,

$$\boxed{\mu \sim \tau_N T^3} \tag{5.558}$$

[24] Gurevich's χ is my μ.

[Estimating ν (at low T):] See [Vasko2005] pg 206 and [Gruevich1986] pg 146. Recall its definition and related definitions,

$$\nu_{\alpha_1\alpha_2\alpha_3\alpha_4} = -\gamma_{\alpha_1\alpha_2\alpha_3\alpha_4} + \frac{TS}{C}\pi_{\alpha_1\alpha_2}\delta_{\alpha_3\alpha_4} \tag{5.559}$$

$$\gamma_{\alpha_1\alpha_2\alpha_3\alpha_4} = \frac{\hbar}{V}\sum_{j\vec{q}} \vec{q}_{\alpha_1}(\nabla_{\vec{q}}\omega)_{\alpha_2}\tilde{B}_{j\vec{q}\alpha_3\alpha_4}N^{eq}_{j\vec{q}}(N^{eq}_{j\vec{q}}+1) \tag{5.560}$$

$$\pi_{\alpha_1\alpha_2} = \frac{\hbar}{V}\sum_{j\vec{q}} \vec{q}_{\alpha_1}\tilde{A}_{j\vec{q}\alpha_2}N^{eq}_{j\vec{q}}(N^{eq}_{j\vec{q}}+1) \tag{5.561}$$

We shall estimate both terms in ν to be sure. We start by applying Debye approximation to γ and use the estimate for $\tilde{B}$.

$$\Gamma \sim \sum_{\vec{q}} \frac{\omega}{v} v\tau_N \frac{qv}{T} N^{eq}(N^{eq}+1) \tag{5.562}$$

$$\sim \frac{\tau_N}{T}\sum_{\vec{q}} \omega^2 N^{eq}(N^{eq}+1) \tag{5.563}$$

$$\Big|\ \text{use the Debye approximation, } \sum_{\vec{q}} \rightarrow\sim \int d\omega \frac{\omega^2}{v^3}$$

$$\sim \frac{\tau_N}{v^3T}\int d\omega\omega^4 N^{eq}(N^{eq}+1) \tag{5.564}$$

$$\Big|\ \text{let } x = \frac{\hbar\omega}{k_BT}$$

$$\sim \frac{\tau_N}{v^3T}\frac{k_BT}{\hbar}\int dx \frac{k_B^4T^4}{\hbar^4}\frac{x^4e^x}{(e^x-1)^2} \tag{5.565}$$

So,

$$\boxed{\gamma \sim \tau_N T^4} \tag{5.566}$$

Now estimate $\frac{TS}{C}\pi$,

$$\frac{TS}{C}\pi \sim \frac{TT^3}{T^3}\sum_{\vec{q}} q\tau_N\frac{qv^2}{T^2}N^{eq}(N^{eq}+1) \tag{5.567}$$

$$\sim \frac{\tau_N}{T}\sum_{\vec{q}} \omega^2 N^{eq}(N^{eq}+1) \tag{5.568}$$

which is the same as above. Indeed,

$$\boxed{\nu \sim \tau_N T^4} \tag{5.569}$$

Finally, we look at 2 examples of solving the hydrodynamical equations.

[Non Dissipative case (i.e. only N-processes):] We take the simplest case of an undamped wave equation. This is done by dropping the dissipative terms and the balance equations become,

$$C\frac{\partial^2\Delta T}{\partial t} + TS\nabla_{\vec{r}}\cdot\vec{u} = 0 \tag{5.570}$$

$$\sum_{\alpha_2} \chi_{\alpha_1\alpha_2} \frac{\partial u_{\alpha_2}}{\partial t} + S\frac{\partial \Delta T}{\partial r_{\alpha_1}} = 0 \quad (5.571)$$

We eliminate the drift velocity $\vec{u}$ by taking the temporal derivative of the first equation and taking the spatial derivative of the second equation.

$$C\frac{\partial^2 \Delta T}{\partial t^2} + TS\sum_{\alpha_1} \frac{\partial^2 u_{\alpha_1}}{\partial t \partial r_{\alpha_1}} = 0 \quad (5.572)$$

$$\sum_{\alpha_2} \chi_{\alpha_1\alpha_2} \frac{\partial^2 u_{\alpha_2}}{\partial r_{\alpha_2}\partial t} + S\frac{\partial^2 \Delta T}{\partial r_{\alpha_2}\partial r_{\alpha_1}} = 0 \quad (5.573)$$

eliminating the term $\frac{\partial^2 u}{\partial r \partial t}$, we get the single equation

$$\frac{\partial^2 \Delta T}{\partial t^2} - \frac{TS^2}{C}\sum_{\alpha_1\alpha_2} \chi^{-1}_{\alpha_1\alpha_2} \frac{\partial^2 \Delta T}{\partial r_{\alpha_1}\partial r_{\alpha_2}} = 0 \quad (5.574)$$

which is of the form of an undamped anisotropic (temperature) wave equation. To obtain the dispersion relation, we substitute the travelling wave ansatz.

$$\Delta T \propto e^{i(\vec{q}\cdot\vec{r}-\omega t)} \quad (5.575)$$

We get,

$$\omega^2 e^{i(\vec{q}\cdot\vec{r}-\omega t)} - \frac{TS^2}{C}\sum_{\alpha_1\alpha_2} \chi^{-1}_{\alpha_1\alpha_2} q_{\alpha_1} q_{\alpha_2} e^{i(\vec{q}\cdot\vec{r}-\omega t)} = 0 \quad (5.576)$$

$$\omega^2 = \frac{TS^2}{C}\sum_{\alpha_1\alpha_2} \chi^{-1}_{\alpha_1\alpha_2} q_{\alpha_1} q_{\alpha_2} \quad (5.577)$$

is the dispersion relation of the (anisotropic) undamped second sound (or temperture wave). We see that as long as only N processes occur, and the distribution is linearized, the above dispersion relation is the same for any order of anharmonicity.

[Dissipative (i.e. with U-processes) and Cubic Geometry] We take dissipative effects into account in this example, but we choose a simple (3D) cubic geometry so that all the tensors become scalars. We specialize by considering only the x-axis but there is no loss of generality in this context. Note that $\frac{\partial}{\partial r} \to \frac{\partial}{\partial x}$ and we will use the travelling wave ansatz,

$$\Delta T = \Delta T_0 e^{i(qx-\omega t)} \quad (5.578)$$

$$u_x = u_0 e^{i(qx-\omega t)} \quad (5.579)$$

and substitute them into the balance equations. The energy balance equation becomes,

$$C(-i\omega)\Delta T_0 + TS(iq)u_0 - \mu(iq)^2\Delta T_0 = 0 \quad (5.580)$$

The momentum balance equation becomes

$$\chi(-i\omega)u_0 + S(iq)\Delta T_0 - \nu(iq)^2 u_0 = -TS^2\left(\kappa^{(3ph)-1} + \kappa^{(4ph)-1}\right)u_0 \quad (5.581)$$

Together, we write

$$\begin{pmatrix} iqTS & \mu q^2 - i\omega C \\ \nu q^2 - i\omega\chi + \frac{TS^2}{\kappa^{(3ph)}+\kappa^{(4ph)}} & iqS \end{pmatrix} \begin{pmatrix} u_0 \\ \Delta T_0 \end{pmatrix} = 0 \tag{5.582}$$

Solutions exist when the determinant of the matrix of coefficients equals zero.

$$(iq)^2TS^2 - \left(\mu q^2 - i\omega C\right)\left(\nu q^2 - i\omega\chi + \frac{TS^2}{\kappa^{(3ph)} + \kappa^{(4ph)}}\right) = 0 \tag{5.583}$$

$$-q^2TS^2 - (-i\omega C)\left(1 + \frac{i\mu q^2}{C\omega}\right)(-i\omega\chi)\left(1 + \frac{i\nu q^2}{\chi\omega} + \frac{iTS^2}{(\kappa^{(3ph)} + \kappa^{(4ph)})\chi\omega}\right) = 0 \tag{5.584}$$

$$q^2TS^2 - \omega^2 C\chi\left(1 + \frac{i\mu q^2}{C\omega}\right)\left(1 + \frac{i\nu q^2}{\chi\omega} + \frac{iTS^2}{(\kappa^{(3ph)} + \kappa^{(4ph)})\chi\omega}\right) = 0 \tag{5.585}$$

$$\frac{q^2TS^2}{c\chi} = \omega^2\left(1 + \frac{i\mu q^2}{C\omega}\right)\left(1 + \frac{i\nu q^2}{\chi\omega} + \frac{iTS^2}{(\kappa^{(3ph)} + \kappa^{(4ph)})\chi\omega}\right) \tag{5.586}$$

Note that ω is real and q is complex. The imaginary part of q will cause damping to the second sound amplitude. Using the relation that intensity is the square of the amplitude, we define the absorption coefficient of second sound, Γ_{II} as follows,

$$\text{damping of intensity} = \left(e^{i(i\Im q)x}\right)^2 \tag{5.587}$$

$$= e^{-2(\Im q)x} \tag{5.588}$$

$$\equiv e^{-\Gamma_{\text{II}}x} \tag{5.589}$$

$$\text{where} \quad \Gamma_{\text{II}} = 2(\Im q) \tag{5.590}$$

Denote the velocity of second sound as $v_{\text{II}}^2 = \frac{TS^2}{C\chi}$ (which can be inspired from the previous example) and now we will calculate the lowest order terms of Γ_{II}. The relevant condition for light damping is $\Re q >> \Im q$.

In the first order where $q^{(1)} = \Re q$ (which means there is no damping and so all imaginary terms vanish), we get,

$$\frac{{q^{(1)}}^2TS^2}{C\chi} = \omega^2 \Longrightarrow v_{\text{II}}^2{q^{(1)}}^2 = \omega^2 \tag{5.591}$$

which is of course (see previous example) the dispersion relation of undamped second sound specialized to the cubic geometry. In the next order, we retain terms linear in Γ_{II}.

$$q = \Re q + i\Im q \tag{5.592}$$

$$= \frac{\omega}{v_{\text{II}}} + \frac{1}{2}i\Gamma_{\text{II}} \tag{5.593}$$

$$q^2 = \left(\frac{\omega}{v_{\text{II}}}\right)^2 - \frac{1}{4}\Gamma_{\text{II}}^2 + i\left(\frac{\omega}{v_{\text{II}}}\right)\Gamma_{\text{II}}^2 \tag{5.594}$$

$$\approx \left(\frac{\omega}{v_{\text{II}}}\right)^2 + i\left(\frac{\omega}{v_{\text{II}}}\right)\Gamma_{\text{II}} \tag{5.595}$$

and we substitute it into the "coefficients" equation (5.586).

$$(v_{\rm II}q)^2 = \omega^2\left(1+\frac{i\mu q^2}{\omega C}\right)\left(1+\frac{i\nu q^2}{\chi\omega}+\frac{iTS^2}{(\kappa^{(3ph)}+\kappa^{(4ph)})\chi\omega}\right) \tag{5.596}$$

$$(v_{\rm II}q)^2 = \omega^2\left(1+\frac{i\nu q^2}{\chi\omega}+\frac{i\mu q^2}{C\omega}+\frac{iTS^2}{(\kappa^{(3ph)}+\kappa^{(4ph)})\chi\omega}-\frac{\mu\nu q^4}{\omega^2 C\chi}-\frac{\mu q^2 TS^2}{\omega^2 C\kappa\chi}\right) \tag{5.597}$$

$$| \quad \text{drop the small } q^4 \text{ term}$$

$$\omega^2+i\omega v_{\rm II}\Gamma_{\rm II} = \omega^2\left(1-\frac{\mu TS^2}{\omega^2 C(\kappa^{(3ph)}+\kappa^{(4ph)})\chi}q^2\right)+i\omega^2\left(\frac{\nu}{\chi\omega}+\frac{\mu}{C\omega}\right)q^2+\frac{iTS^2\omega}{(\kappa^{(3ph)}+\kappa^{(4ph)})\chi} \tag{5.598}$$

$$i\omega v_{\rm II}\Gamma_{\rm II} = -\frac{\mu}{(\kappa^{(3ph)}+\kappa^{(4ph)})}v_{\rm II}^2 q^2+i\omega^2\left(\frac{\nu}{\chi\omega}+\frac{\mu}{C\omega}\right)\left(\frac{\omega^2}{v_{\rm II}^2}+i\left(\frac{\omega}{v_{\rm II}}\right)\Gamma_{\rm II}\right)+\frac{iTS^2}{(\kappa^{(3ph)}+\kappa^{(4ph)})\chi}$$

Take the imaginary part,

$$\omega v_{\rm II}\Gamma_{\rm II} = -\frac{\mu}{(\kappa^{(3ph)}+\kappa^{(4ph)})}v_{\rm II}^2\left(\frac{\omega}{v_{\rm II}}\right)\Gamma_{\rm II}+\omega^2\left(\frac{\nu}{\chi\omega}+\frac{\mu}{C\omega}\right)\frac{\omega^2}{v_{\rm II}^2}+\frac{TS^2\omega}{(\kappa^{(3ph)}+\kappa^{(4ph)})\chi} \tag{5.599}$$

$$\Gamma_{\rm II} = -\frac{\mu}{(\kappa^{(3ph)}+\kappa^{(4ph)})}\Gamma_{\rm II}+\omega^2\left(\frac{\nu}{\chi v_{\rm II}^3}+\frac{\mu}{Cv_{\rm II}^3}\right)+\frac{TS^2}{(\kappa^{(3ph)}+\kappa^{(4ph)})\chi v_{\rm II}} \tag{5.600}$$

$$| \quad \text{estimate } \frac{\mu}{(\kappa^{(3ph)}+\kappa^{(4ph)})}\sim\frac{\tau_N}{\tau_U} \text{ which is small in the hydrodynamic regime}$$

$$\Gamma_{\rm II} = \omega^2\left(\frac{\nu}{\chi v_{\rm II}^3}+\frac{\mu}{Cv_{\rm II}^3}\right)+\frac{TS^2}{(\kappa^{(3ph)}+\kappa^{(4ph)})\chi v_{\rm II}} \tag{5.601}$$

The first term depends on frequency squared and the second term is a constant term. Now if we recall the condition of existence of second sound,

$$\Re q >> \Im q \tag{5.602}$$

$$\text{and } \Re q \propto \omega \tag{5.603}$$

$$\text{with } \Im q \propto \Gamma_{\rm II}\propto\omega^2 \tag{5.604}$$

we see that the condition can be violated when ω is sufficiently small or sufficiently large.

5.6 Kinetic Theory: QKE Treatment (towards Quantum Phonon Hydrodynamics)

5.6.1 Recalling QKE

Recall that we have 2 types of QKE theories: one is based on KB ansatz and the other one is based on GKB ansatz. Let's state again, what they mean.

QKE based on KB ansatz is made up of NEGF + Wigner Coordinates + gradient expansion + (free spectral) KB ansatz. Gradient expansion is an expansion in correlations. The zeroth order term is a collision term with no particle correlations. The first order and higher terms are correlation terms. Causality is not obeyed.

QKE based on GKB ansatz is made up of NEGF + GKB ansatz and Wigner coordinates + gardient expansion are optional. The improvement here is that causality is obeyed.[25]

[25]However I did not manage to make it work for phonons in this thesis which I suspect has to do with the clash between causality and particle non-conservation. For the application to electrons, see the appendix. For the application

We recall the the QKE based on KB ansatz

$$\left(\frac{\partial}{\partial t_1^+} + \left(\nabla_{\vec{q}_1^+}\omega_{j_1\vec{q}_1^+}\right)\cdot\nabla_{\vec{r}_1}\right) N_{j_i\vec{q}_1^+}(\vec{r}_1 t_1^+) = I_{\text{zeroth}} + I_{\text{1st}} \tag{5.605}$$

where,

$$I_{\text{zeroth}} = \frac{i}{2\omega_{j_1\vec{q}_1^+}}\left(\Sigma^>_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)N_{j_i\vec{q}_1^+}(\vec{r}_1t_1^+) - \Sigma^<_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)\left(1+N_{j_i\vec{q}_1^+}(\vec{r}_1t_1^+)\right)\right) \tag{5.606}$$

Free Spectral KB ansatz:

$$\begin{aligned}
D^<_{j_1j_2}(\vec{r}\omega\vec{q}^{\,+}t^+) &= \delta_{j_1j_2}\frac{-i2\pi}{2\omega_{j_1\vec{q}_1^+}}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+}) - \delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+) & (5.607)\\
D^>_{j_1j_2}(\vec{r}\omega\vec{q}^{\,+}t^+) &= \delta_{j_1j_2}\frac{-i2\pi}{2\omega_{j_1\vec{q}_1^+}}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+}) - \delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)\left(1+N_{j_1}(\vec{r}\omega\vec{q}^{\,+}t^+)\right) & (5.608)
\end{aligned}$$

I_{1st} will be shown explicitly in the next section. Now we will proceed to solve I_{zeroth} for 3 self consistent self energies.

5.6.2 Zeroth Order Gradient expansion Collision Integrals

5.6.2.1 $V^{(4ph)}$ Term

We use the (sign assigned) self consistent self energies.

$$\begin{aligned}
\Sigma^>_{j_1j_2}(\vec{q}_1t_1\vec{q}_2t_2) &= -\frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4}\int d\vec{q}_3 d\vec{q}_4 \tilde{V}^{(4ph)}_{j_1j_3j_4j_2}(-\vec{q}_1,\vec{q}_3,-\vec{q}_4,\vec{q}_2)D^>_{j_3j_4}(\vec{q}_3t_1\vec{q}_4t_2)\delta(t_1-t_2) & (5.609)\\
\Sigma^<_{j_1j_2}(\vec{q}_1t_1\vec{q}_2t_2) &= -\frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4}\int d\vec{q}_3 d\vec{q}_4 \tilde{V}^{(4ph)}_{j_1j_3j_4j_2}(-\vec{q}_1,\vec{q}_3,-\vec{q}_4,\vec{q}_2)D^<_{j_3j_4}(\vec{q}_3t_1\vec{q}_4t_2)\delta(t_1-t_2) & (5.610)
\end{aligned}$$

Define ,

$$\begin{array}{llll}
\text{Wigner coordinates:} & \vec{q}_3^{\,+} = \frac{1}{2}(\vec{q}_3+\vec{q}_4) & \text{Inverse:} & \vec{q}_3 = \vec{q}_3^{\,+} + \frac{1}{2}\vec{q}_3^{\,-}\\
& \vec{q}_3^{\,-} = \vec{q}_3 - \vec{q}_4 & & \vec{q}_4 = \vec{q}_3^{\,+} - \frac{1}{2}\vec{q}_3^{\,-}
\end{array} \tag{5.611}$$

So now we move over to Wigner coordinates then make a gradient expansion then extract the Fourier components.

$$\begin{aligned}
&\Sigma^>_{j_1j_2}(\vec{q}_1^{\,-}t_1^-\vec{q}_1^{\,+}t_1^+)\\
=\ & -\frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4}\int d\vec{q}_3^{\,+}d\vec{q}_3^{\,-}\tilde{V}^{(4ph)}_{j_1j_3j_4j_2}(-\vec{q}_1^{\,+}-\tfrac{1}{2}\vec{q}_1^{\,-},\vec{q}_3^{\,+}+\tfrac{1}{2}\vec{q}_3^{\,-},-\vec{q}_3^{\,+}+\tfrac{1}{2}\vec{q}_3^{\,-},\vec{q}_1^{\,+}-\tfrac{1}{2}\vec{q}_1^{\,-})\\
&\times D^>_{j_3j_4}(\vec{q}_3^{\,-}t_1^-\vec{q}_3^{\,+}t_1^+)\delta(t_1^-) \qquad (5.612)\\
&|\quad \text{delta function in } \tilde{V}^{(4ph)} \text{ gives}\\
&|\quad -\vec{q}_1^{\,+}-\tfrac{1}{2}\vec{q}_1^{\,-}+\vec{q}_3^{\,+}+\tfrac{1}{2}\vec{q}_3^{\,-}-\vec{q}_3^{\,+}+\tfrac{1}{2}\vec{q}_3^{\,-}+\vec{q}_1^{\,+}-\tfrac{1}{2}\vec{q}_1^{\,-}=0 \Rightarrow -\vec{q}_1^{\,-}+\vec{q}_3^{\,-}=0\\
&|\quad \text{gradient expand } \tilde{V}^{(4ph)} \text{ and keep the lowest order terms}\\
&|\quad \text{write } D^> \text{ into the Fourier form}
\end{aligned}$$

to electron-phonon interaction, see the respective chapter.

$$\approx -\frac{1}{2}\frac{\hbar}{i}\sum_{j_3 j_4}\int d\vec{q}_3^{\,+} d\vec{q}_3^{\,-}\tilde{V}^{(4ph)}_{j_1 j_3 j_4 j_2}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})$$
$$\times\int d\vec{r}_3\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}e^{-i\vec{q}_3^{\,-}\cdot\vec{r}_3-i(\omega_2+\omega_3)t_1^-}D^>_{j_3 j_4}(\vec{r}_3\omega_2\vec{q}_3^{\,+}t_1^+)\delta(\omega_3) \quad (5.613)$$

| use $\vec{q}_3^{\,-}=\vec{q}_1^{\,-}$ to evaluate $\int d\vec{q}_3^{\,-}$

| add in the integral $2\pi\int\frac{d\omega_1}{2\pi}$

$$= -\frac{1}{2}\frac{\hbar}{i}\sum_{j_3 j_4}\int d\vec{q}_3^{\,+}\tilde{V}^{(4ph)}_{j_1 j_3 j_4 j_2}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})$$
$$\times 2\pi\int d\vec{r}_3\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_3-i\omega_1 t_1^-}\delta(\omega_1-\omega_2-\omega_3)\delta(\omega_3)D^>_{j_3 j_4}(\vec{r}_3\omega_2\vec{q}_3^{\,+}t_1^+) \quad (5.614)$$

| evaluate $\int d\omega_3$

$$= -\frac{1}{2}\frac{\hbar}{i}\sum_{j_3 j_4}\int d\vec{q}_3^{\,+}\tilde{V}^{(4ph)}_{j_1 j_3 j_4 j_2}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})$$
$$\times\int d\vec{r}_3\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_3-i\omega_1 t_1^-}\delta(\omega_1-\omega_2)D^>_{j_3 j_4}(\vec{r}_3\omega_2\vec{q}_3^{\,+}t_1^+) \quad (5.615)$$

The Fourier component is

$$\Sigma^>_{j_1 j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) = -\frac{1}{2}\frac{\hbar}{i}\sum_{j_3 j_4}\int d\vec{q}_3^{\,+}\tilde{V}^{(4ph)}_{j_1 j_3 j_4 j_2}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})\int\frac{d\omega_2}{2\pi}\delta(\omega_1-\omega_2)D^>_{j_3 j_4}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+) \quad (5.616)$$

The Fourier component of the lesser self energy is

$$\Sigma^<_{j_1 j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) = -\frac{1}{2}\frac{\hbar}{i}\sum_{j_3 j_4}\int d\vec{q}_3^{\,+}\tilde{V}^{(4ph)}_{j_1 j_3 j_4 j_2}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})\int\frac{d\omega_2}{2\pi}\delta(\omega_1-\omega_2)D^<_{j_3 j_4}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+) \quad (5.617)$$

Now we can calculate the I_{zeroth} collision integral based on this self energy.

First term of the Collision Integral I_{zeroth}

$$= \frac{i}{2\omega_{j_1\vec{q}_1^{\,+}}}\Sigma^>_{j_1 j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+)$$
$$= \frac{-i}{2\omega_{j_1\vec{q}_1^{\,+}}}\frac{1}{2}\frac{\hbar}{i}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+)\sum_{j_3 j_4}\int d\vec{q}_3^{\,+}\tilde{V}^{(4ph)}_{j_1 j_3 j_4 j_1}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_3^{\,+},\vec{q}_1^{\,+})$$
$$\times\int\frac{d\omega_2}{2\pi}\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_2)\delta_{j_3 j_4}\frac{-i2\pi}{2\omega_{j_3\vec{q}_3^{\,+}}}\left(\delta(\omega_2-\omega_{j_3\vec{q}_3^{\,+}})-\delta(\omega_2+\omega_{j_3\vec{q}_3^{\,+}})\right)\left(1+N_{j_3}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+)\right)$$

| evaluate $\int d\omega_2$ and drop the 2nd term that gives the unphysical $\delta(\omega_{j_1\vec{q}_1^{\,+}}+\omega_{j_3\vec{q}_3^{\,+}})$

$$= -\frac{1}{2}\frac{\hbar}{i}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+)\sum_{j_3\vec{q}_3^{\,+}}\tilde{V}^{(4ph)}_{j_1 j_3 j_3 j_1}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_3^{\,+},\vec{q}_1^{\,+})\frac{1}{2^2\omega_{j_1\vec{q}_1^{\,+}}\omega_{j_3\vec{q}_3^{\,+}}}$$
$$\times\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_3\vec{q}_3^{\,+}})\left(1+N_{j_3}(\vec{r}_1\omega_{j_3\vec{q}_3^{\,+}}\vec{q}_3^{\,+}t_1^+)\right)$$

$$
\begin{aligned}
& \mid \quad \text{recall } \tilde{V}^{(4ph)} = V^{(4ph)}\sqrt{\frac{2^4\omega\omega\omega\omega}{\hbar^4}} \\
& \mid \quad \text{use the notation } N_{j_3}(\vec{r}_1\omega_{j_3\vec{q}_3^+}\vec{q}_3^{\,+}t_1^+) = N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+) \\
= \;& -\frac{1}{2\hbar^2}\frac{\hbar}{i}N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\sum_{j_3\vec{q}_3^+}V^{(4ph)}_{j_1j_3j_3j_1}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})\delta(\omega_{j_1\vec{q}_1^+}-\omega_{j_3\vec{q}_3^+})\left(1+N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)\right)
\end{aligned}
$$

Second term of the Collision Integral I_{zeroth}

$$
\begin{aligned}
= \;& \frac{i}{2\omega_{j_1\vec{q}_1^+}}\Sigma^{<}_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)\left(1+N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\right) \\
= \;& -\frac{1}{2\hbar^2}\frac{\hbar}{i}\left(1+N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\right)\sum_{j_3\vec{q}_3^+}V^{(4ph)}_{j_1j_3j_3j_1}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})\delta(\omega_{j_1\vec{q}_1^+}-\omega_{j_3\vec{q}_3^+})N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)
\end{aligned}
$$

$$
\begin{aligned}
I_{\text{zeroth}} \;=\;& -\frac{1}{2\hbar^2}\frac{\hbar}{i}\sum_{j_3\vec{q}_3^+}V^{(4ph)}_{j_1j_3j_3j_1}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})\delta(\omega_{j_1\vec{q}_1^+}-\omega_{j_3\vec{q}_3^+}) \\
& \times\left(N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\left(1+N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)\right)-\left(1+N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\right)N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)\right) \qquad (5.618)
\end{aligned}
$$

Thus we see that the collision integral is pure imaginary (the reader will eventually notice that odd numbers of anharmonic coefficients in the self energies give imaginary collision integrals and even numbers of anharmonic coefficients in the self energies give real collision integrals) and physically it cannot be interpreted as the time rate of change of the distribution due to collisions. Nevertheless we check that it indeed satisfies the energy conservation sum rule.

$$
\begin{aligned}
& \sum_{j_1\vec{q}_1^+}\hbar\omega_{j_1\vec{q}_1^+}I^{\text{zeroth}} \\
= \;& -\frac{1}{2\hbar^2}\frac{\hbar^2}{i}\sum_{j_1\vec{q}_1^+j_3\vec{q}_3^+}V^{(4ph)}_{j_1j_3j_3j_1}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+}) \\
& \times\delta(\omega_{j_1\vec{q}_1^+}-\omega_{j_3\vec{q}_3^+})\omega_{j_1\vec{q}_1^+}\left(N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\left(1+N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)\right)-\left(1+N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\right)N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)\right) \\
& \mid \quad \text{rename } 1\leftrightarrow 3 \text{ in the second term} \\
= \;& -\frac{1}{2\hbar^2}\frac{\hbar^2}{i}\sum_{j_1\vec{q}_1^+j_3\vec{q}_3^+}V^{(4ph)}_{j_1j_3j_3j_1}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+}) \\
& \times\delta(\omega_{j_1\vec{q}_1^+}-\omega_{j_3\vec{q}_3^+})\left(N_{j_1\vec{q}_1^+}\left(1+N_{j_3\vec{q}_3^+}\right)\right)(\omega_{j_1\vec{q}_1^+}-\omega_{j_3\vec{q}_3^+}) \qquad (5.619) \\
& \mid \quad \text{use the delta function} \\
= \;& 0 \qquad (5.620)
\end{aligned}
$$

5.6.2.2 $V^{(3ph)^2}$ Term

We recall the (sign assigned) self consistent self energies.

$$
\Sigma^{\gtrless}_{j_1j_2}(\vec{q}_1t_1\vec{q}_2t_2) \;=\; \frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3d\vec{q}_4d\vec{q}_5d\vec{q}_6
$$

$$\times\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1,\vec{q}_3,\vec{q}_4)\tilde{V}^{(3ph)}_{j_5j_6j_2}(-\vec{q}_5,-\vec{q}_6,\vec{q}_2)D^{\gtrless}_{j_3j_5}(\vec{q}_3t_1\vec{q}_5t_2)D^{\lessgtr}_{j_6j_4}(\vec{q}_6t_1\vec{q}_4t_2) \quad (5.621)$$

$$| \quad \text{write } D^{\lessgtr}_{j_6j_4}(\vec{q}_6t_2\vec{q}_4t_1)=D^{\gtrless}_{j_4j_6}(\vec{q}_4t_1\vec{q}_6t_2)$$

$$= \frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3d\vec{q}_4d\vec{q}_5d\vec{q}_6$$

$$\times\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1,\vec{q}_3,\vec{q}_4)\tilde{V}^{(3ph)}_{j_5j_6j_2}(-\vec{q}_5,-\vec{q}_6,\vec{q}_2)D^{\gtrless}_{j_3j_5}(\vec{q}_3t_1\vec{q}_5t_2)D^{\gtrless}_{j_4j_6}(\vec{q}_4t_1\vec{q}_6t_2) \quad (5.622)$$

We go over to Wigner coordinates. We need to define 2 sets of it.

$$\begin{array}{llll} \text{Wigner coordinates:} & \vec{q}_3^{\,+}=\frac{1}{2}(\vec{q}_3+\vec{q}_5) & \text{Inverse:} & \vec{q}_3=\vec{q}_3^{\,+}+\frac{1}{2}\vec{q}_3^{\,-} \\ & \vec{q}_3^{\,-}=\vec{q}_3-\vec{q}_5 & & \vec{q}_5=\vec{q}_3^{\,+}-\frac{1}{2}\vec{q}_3^{\,-} \\ \text{Wigner coordinates:} & \vec{q}_4^{\,+}=\frac{1}{2}(\vec{q}_4+\vec{q}_6) & \text{Inverse:} & \vec{q}_4=\vec{q}_4^{\,+}+\frac{1}{2}\vec{q}_4^{\,-} \\ & \vec{q}_4^{\,-}=\vec{q}_4-\vec{q}_6 & & \vec{q}_6=\vec{q}_4^{\,+}-\frac{1}{2}\vec{q}_4^{\,-} \end{array} \quad (5.623)$$

$$\Sigma^{>}_{j_1j_2}(\vec{q}_1^{\,-}t_1^-\vec{q}_1^{\,+}t_1^+)$$

$$= \frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}d\vec{q}_3^{\,-}d\vec{q}_4^{\,-}$$

$$\times\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+}-\tfrac{1}{2}\vec{q}_1^{\,-},\vec{q}_3^{\,+}+\tfrac{1}{2}\vec{q}_3^{\,-},\vec{q}_4^{\,+}+\tfrac{1}{2}\vec{q}_4^{\,-})\tilde{V}^{(3ph)}_{j_5j_6j_2}(-\vec{q}_3^{\,+}+\tfrac{1}{2}\vec{q}_3^{\,-},-\vec{q}_4^{\,+}+\tfrac{1}{2}\vec{q}_4^{\,-},\vec{q}_1^{\,+}-\tfrac{1}{2}\vec{q}_1^{\,-})$$

$$\times D^{>}_{j_3j_5}(\vec{q}_3^{\,-}t_1^-\vec{q}_3^{\,+}t_1^+)D^{>}_{j_4j_6}(\vec{q}_4^{\,-}t_1^-\vec{q}_4^{\,+}t_1^+) \quad (5.624)$$

| we add the 2 delta functions from $\tilde{V}^{(3ph)}$ and get $\vec{q}_3^{\,-}+\vec{q}_4^{\,-}-\vec{q}_1^{\,-}=0$

| gradient expand $\tilde{V}^{(3ph)}$ to the zeroth order

| write the Green's functions into Fourier form

$$\approx \frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}d\vec{q}_3^{\,-}d\vec{q}_4^{\,-}\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\tilde{V}^{(3ph)}_{j_5j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})$$

$$\times\int d\vec{r}_3\frac{d\omega_2}{2\pi}d\vec{r}_4\frac{d\omega_3}{2\pi}e^{-i\vec{q}_3^{\,-}\cdot\vec{r}_3-i\vec{q}_4^{\,-}\cdot\vec{r}_4}e^{-i\omega_2t_1^--i\omega_3t_1^-}D^{>}_{j_3j_5}(\vec{r}_3\omega_2\vec{q}_3^{\,+}t_1^+)D^{>}_{j_4j_6}(\vec{r}_4\omega_3\vec{q}_4^{\,+}t_1^+) \quad (5.625)$$

| use the earlier relation $\vec{q}_4^{\,-}=\vec{q}_1^{\,-}-\vec{q}_3^{\,-}$ to evaluate $\int d\vec{q}_4^{\,-}$

$$= \frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}d\vec{q}_3^{\,-}\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\tilde{V}^{(3ph)}_{j_5j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})$$

$$\times\int d\vec{r}_3\frac{d\omega_2}{2\pi}d\vec{r}_4\frac{d\omega_3}{2\pi}e^{-i\vec{q}_3^{\,-}\cdot(\vec{r}_3-\vec{r}_4)-i\vec{q}_1^{\,-}\cdot\vec{r}_4}e^{-i(\omega_2+\omega_3)t_1^-}D^{>}_{j_3j_5}(\vec{r}_3\omega_2\vec{q}_3^{\,+}t_1^+)D^{>}_{j_4j_6}(\vec{r}_4\omega_3\vec{q}_4^{\,+}t_1^+) \quad (5.626)$$

| evaluate $\int d\vec{q}_3^{\,-}$ to get $\delta(\vec{r}_3-\vec{r}_4)$ then evaluate $\int d\vec{r}_4$

$$= \frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\tilde{V}^{(3ph)}_{j_5j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})$$

$$\times\int d\vec{r}_3\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_3}e^{-i(\omega_2+\omega_3)t_1^-}D^{>}_{j_3j_5}(\vec{r}_3\omega_2\vec{q}_3^{\,+}t_1^+)D^{>}_{j_4j_6}(\vec{r}_3\omega_3\vec{q}_4^{\,+}t_1^+) \quad (5.627)$$

| insert the integral $2\pi\int\frac{d\omega_1}{2\pi}$

$$= 2\pi\frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\tilde{V}^{(3ph)}_{j_5j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})$$

$$\times \int d\vec{r}_3 \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi} e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_3 - i\omega_1 t_1^-}\delta(\omega_1-\omega_2-\omega_3) D^{>}_{j_3j_5}(\vec{r}_3\omega_2\vec{q}_3^{\,+}t_1^+) D^{>}_{j_4j_6}(\vec{r}_3\omega_3\vec{q}_4^{\,+}t_1^+) \quad (5.628)$$

We extract the Fourier component and specialize the expression for the collision integral

$$\begin{aligned}\Sigma^{>}_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+) &= 2\pi\frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}\int\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+}\vec{q}_4^{\,+})\tilde{V}^{(3ph)}_{j_5j_6j_1}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+}) \\ &\times\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_2-\omega_3)D^{>}_{j_3j_5}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+)D^{>}_{j_4j_6}(\vec{r}_1\omega_3\vec{q}_4^{\,+}t_1^+) \quad (5.629)\end{aligned}$$

The other self energy term is

$$\begin{aligned}\Sigma^{<}_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+) &= 2\pi\frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}\int\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+}\vec{q}_4^{\,+})\tilde{V}^{(3ph)}_{j_5j_6j_1}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+}) \\ &\times\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_2-\omega_3)D^{<}_{j_3j_5}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+)D^{<}_{j_4j_6}(\vec{r}_1\omega_3\vec{q}_4^{\,+}t_1^+) \quad (5.630)\end{aligned}$$

We will now calculate the collision integral.

$$\begin{aligned}
& \text{First term of collision integral } I_{\text{zeroth}} \\
= \; & \frac{i}{2\omega_{j_1\vec{q}_1^{\,+}}}\Sigma^{>}_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+) \quad (5.631)\\
| \; & \text{insert the expression for } \Sigma^{>} \text{ and implement the Free spectral KB ansatz.} \\
= \; & 2\pi\frac{i}{2\omega_{j_1\vec{q}_1^{\,+}}}\frac{1}{2}\frac{\hbar}{i}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}\int\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+}\vec{q}_4^{\,+})\tilde{V}^{(3ph)}_{j_5j_6j_1}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+}) \\
& \times\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_2-\omega_3)\delta_{j_3j_5}\frac{-i2\pi}{2\omega_{j_3\vec{q}_3^{\,+}}}\left(\delta(\omega_2-\omega_{j_3\vec{q}_3^{\,+}})-\delta(\omega_2+\omega_{j_3\vec{q}_3^{\,+}})\right)\left(1+N_{j_3}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+)\right) \\
& \times\delta_{j_4j_6}\frac{-i2\pi}{2\omega_{j_4\vec{q}_4^{\,+}}}\left(\delta(\omega_3-\omega_{j_4\vec{q}_4^{\,+}})-\delta(\omega_3+\omega_{j_4\vec{q}_4^{\,+}})\right)\left(1+N_{j_4}(\vec{r}_1\omega_3\vec{q}_4^{\,+}t_1^+)\right) \quad (5.632)\\
| \; & \text{evaluate } \int d\omega_2 d\omega_3 \text{ with } \frac{1}{(2\pi)^2} \text{ leftover which cancels } (2\pi)^2 \text{ from KB ansatz} \\
| \; & \text{discard the non-physical delta function } \delta(\omega_{j_1\vec{q}_1^{\,+}}+\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}}) \\
| \; & \text{2 delta functions add up due to indices 3,4 symmetry} \\
= \; & -\frac{\hbar}{2^3\omega_{j_1\vec{q}_1^{\,+}}\omega_{j_3\vec{q}_3^{\,+}}\omega_{j_4\vec{q}_4^{\,+}}}2\pi\frac{1}{2}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\sum_{j_3j_4}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}\left|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\right|^2 \\
& \times\Big(\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}})\left(1+N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\right)\left(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\right) \\
& -2\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}})\left(1+N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\right)\left(1+N_{j_4}(\vec{r}_1,-\omega_{j_4\vec{q}_4^{\,+}}\vec{q}_4^{\,+}t_1^+)\right)\Big) \quad (5.633)\\
| \; & \text{use identity } N_{j_4}(\vec{r}_1,-\omega_{j_4\vec{q}_4^{\,+}}\vec{q}_4^{\,+}t_1^+) = -\left(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\right) \\
| \; & \text{recall } \tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+}) = V^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\sqrt{\frac{2^3\omega_{j_1\vec{q}_1^{\,+}}\omega_{j_3\vec{q}_3^{\,+}}\omega_{j_4\vec{q}_4^{\,+}}}{\hbar^3}} \\
= \; & -\frac{2\pi}{2\hbar^2}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}}\left|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\right|^2 \\
& \times\Big(\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}})\left(1+N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\right)\left(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\right)
\end{aligned}$$

$$+ 2\delta(\omega_{j_1\vec{q}_1^+} - \omega_{j_3\vec{q}_3^+} + \omega_{j_4\vec{q}_4^+}) \left(1 + N_{j_3\vec{q}_3^+}(\vec{r}_1 t_1^+)\right) N_{j_4\vec{q}_4^+}(\vec{r}_1 t_1^+)\Big) \tag{5.634}$$

Second term of collision integral I_{zeroth}

$$= \frac{i}{2\omega_{j_1\vec{q}_1^+}} \Sigma^<_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+) \left(1 + N_{j_1\vec{q}_1^+}(\vec{r}_1 t_1^+)\right) \tag{5.635}$$

| insert the expression for $\Sigma^<$ and implement the Free spectral KB ansatz.

$$\begin{aligned}
= \; & \frac{i}{2\omega_{j_1\vec{q}_1^+}} 2\pi \frac{1}{2}\frac{\hbar}{i} \left(1 + N_{j_1\vec{q}_1^+}(\vec{r}_1 t_1^+)\right) \sum_{j_3j_4j_5j_6} \int d\vec{q}_3^{\,+} d\vec{q}_4^{\,+} \int \frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi} \\
& \times \tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+}, \vec{q}_3^{\,+}\vec{q}_4^{\,+}) \tilde{V}^{(3ph)}_{j_5j_6j_1}(-\vec{q}_3^{\,+}, -\vec{q}_4^{\,+}, \vec{q}_1^{\,+}) \delta(\omega_{j_1\vec{q}_1^+} - \omega_2 - \omega_3) \\
& \times \delta_{j_3j_5} \frac{-i2\pi}{2\omega_{j_3\vec{q}_3^+}} \left(\delta(\omega_2 - \omega_{j_3\vec{q}_3^+}) - \delta(\omega_2 + \omega_{j_3\vec{q}_3^+})\right) N_{j_3}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+) \\
& \times \delta_{j_4j_6} \frac{-i2\pi}{2\omega_{j_4\vec{q}_4^+}} \left(\delta(\omega_3 - \omega_{j_4\vec{q}_4^+}) - \delta(\omega_3 + \omega_{j_4\vec{q}_4^+})\right) N_{j_4}(\vec{r}_1\omega_3\vec{q}_4^{\,+}t_1^+)
\end{aligned} \tag{5.636}$$

| evaluate $\int d\omega_2 d\omega_3$ and $\frac{1}{(2\pi)^2}$ cancels $(2\pi)^2$

| discard the non-physical delta function $\delta(\omega_{j_1\vec{q}_1^+} + \omega_{j_3\vec{q}_3^+} + \omega_{j_4\vec{q}_4^+})$

| 2 delta functions add up due to indices 3,4 symmetry

$$\begin{aligned}
= \; & -\frac{\hbar}{2^3\omega_{j_1\vec{q}_1^+}\omega_{j_3\vec{q}_3^+}\omega_{j_4\vec{q}_4^+}} 2\pi\frac{1}{2} \left(1 + N_{j_1\vec{q}_1^+}(\vec{r}_1 t_1^+)\right) \sum_{j_3j_4} \int d\vec{q}_3^{\,+} d\vec{q}_4^{\,+} \left|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+}, \vec{q}_3^{\,+}, \vec{q}_4^{\,+})\right|^2 \\
& \times \Big(\delta(\omega_{j_1\vec{q}_1^+} - \omega_{j_3\vec{q}_3^+} - \omega_{j_4\vec{q}_4^+}) N_{j_3\vec{q}_3^+}(\vec{r}_1 t_1^+) N_{j_4\vec{q}_4^+}(\vec{r}_1 t_1^+) \\
& -2\delta(\omega_{j_1\vec{q}_1^+} - \omega_{j_3\vec{q}_3^+} + \omega_{j_4\vec{q}_4^+}) N_{j_3\vec{q}_3^+}(\vec{r}_1 t_1^+) N_{j_4}(\vec{r}_1, -\omega_{j_4\vec{q}_4^+}\vec{q}_4^{\,+}t_1^+)\Big)
\end{aligned} \tag{5.637}$$

| use identity $N_{j_4}(\vec{r}_1, -\omega_{j_4\vec{q}_4^+}\vec{q}_4^{\,+}t_1^+) = -\left(1 + N_{j_4\vec{q}_4^+}(\vec{r}_1 t_1^+)\right)$

| recall $\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+}, \vec{q}_3^{\,+}, \vec{q}_4^{\,+}) = V^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+}, \vec{q}_3^{\,+}, \vec{q}_4^{\,+}) \sqrt{\frac{2^3\omega_{j_1\vec{q}_1^+}\omega_{j_3\vec{q}_3^+}\omega_{j_4\vec{q}_4^+}}{\hbar^3}}$

$$\begin{aligned}
= \; & -\frac{2\pi}{2\hbar^2} \left(1 + N_{j_1\vec{q}_1^+}(\vec{r}_1 t_1^+)\right) \sum_{j_3\vec{q}_3^+ j_4\vec{q}_4^+} \left|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+}, \vec{q}_3^{\,+}, \vec{q}_4^{\,+})\right|^2 \\
& \times \Big(\delta(\omega_{j_1\vec{q}_1^+} - \omega_{j_3\vec{q}_3^+} - \omega_{j_4\vec{q}_4^+}) N_{j_3\vec{q}_3^+}(\vec{r}_1 t_1^+) N_{j_4\vec{q}_4^+}(\vec{r}_1 t_1^+) \\
& + 2\delta(\omega_{j_1\vec{q}_1^+} - \omega_{j_3\vec{q}_3^+} + \omega_{j_4\vec{q}_4^+}) N_{j_3\vec{q}_3^+}(\vec{r}_1 t_1^+) \left(1 + N_{j_4\vec{q}_4^+}(\vec{r}_1 t_1^+)\right)\Big)
\end{aligned} \tag{5.638}$$

The total collision integral is I_{zeroth} = First term - Second term, and we see that we exactly reproduce the 3-phonon collision integral $I^{(3ph)}$. Although nothing new is derived, it is now clear that QKE (based on KB ansatz) gives us a perturbative and diagrammatic method to calculate higher 3-phonon collision integrals. The next 3-phonon collision integral comes from the $V^{(3ph)^4}$ term which we will briefly describe later.

5.6.2.3 $V^{(4ph)^2}$ Term

We recall the (sign assigned) self consistent self energies.

$$\Sigma^{\gtrless}_{j_1j_2}(\vec{q}_1 t_1 \vec{q}_2 t_2)$$

$$= \frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{j_3j_4j_5j_6j_7j_8} \int d\vec{q}_3 d\vec{q}_4 d\vec{q}_5 d\vec{q}_6 d\vec{q}_7 d\vec{q}_8$$

$$\times \tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1,\vec{q}_3,\vec{q}_4,\vec{q}_4)\tilde{V}^{(4ph)}_{j_7j_8j_6j_2}(-\vec{q}_7,-\vec{q}_8,-\vec{q}_6,\vec{q}_2)D^{\lessgtr}_{j_6j_5}(\vec{q}_6t_2\vec{q}_5t_1)D^{\gtrless}_{j_3j_7}(\vec{q}_3t_1\vec{q}_7t_2)D^{\lessgtr}_{j_8j_4}(\vec{q}_8t_2\vec{q}_4t_1)$$

| write $D^{\lessgtr}_{65} = D^{\gtrless}_{56}$ and $D^{\lessgtr}_{84} = D^{\gtrless}_{48}$

$$= \frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{j_3j_4j_5j_6j_7j_8} \int d\vec{q}_3 d\vec{q}_4 d\vec{q}_5 d\vec{q}_6 d\vec{q}_7 d\vec{q}_8$$

$$\times \tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1,\vec{q}_3,\vec{q}_4,\vec{q}_4)\tilde{V}^{(4ph)}_{j_7j_8j_6j_2}(-\vec{q}_7,-\vec{q}_8,-\vec{q}_6,\vec{q}_2)D^{\gtrless}_{j_5j_6}(\vec{q}_5t_1\vec{q}_6t_2)D^{\gtrless}_{j_3j_7}(\vec{q}_3t_1\vec{q}_7t_2)D^{\gtrless}_{j_4j_8}(\vec{q}_4t_1\vec{q}_8t_2)$$

We go over to Wigner coordinates. We need to define 3 sets of it.

$$\begin{array}{lll} \text{Wigner coordinates:} & \vec{q}_5^{\,+} = \frac{1}{2}(\vec{q}_5+\vec{q}_6) & \text{Inverse:} \quad \vec{q}_5 = \vec{q}_5^{\,+} + \frac{1}{2}\vec{q}_5^{\,-} \\ & \vec{q}_5^{\,-} = \vec{q}_5 - \vec{q}_6 & \qquad\qquad \vec{q}_6 = \vec{q}_5^{\,+} - \frac{1}{2}\vec{q}_5^{\,-} \\ \text{Wigner coordinates:} & \vec{q}_3^{\,+} = \frac{1}{2}(\vec{q}_3+\vec{q}_7) & \text{Inverse:} \quad \vec{q}_3 = \vec{q}_3^{\,+} + \frac{1}{2}\vec{q}_3^{\,-} \\ & \vec{q}_3^{\,-} = \vec{q}_3 - \vec{q}_7 & \qquad\qquad \vec{q}_7 = \vec{q}_3^{\,+} - \frac{1}{2}\vec{q}_3^{\,-} \\ \text{Wigner coordinates:} & \vec{q}_4^{\,+} = \frac{1}{2}(\vec{q}_4+\vec{q}_8) & \text{Inverse:} \quad \vec{q}_4 = \vec{q}_4^{\,+} + \frac{1}{2}\vec{q}_4^{\,-} \\ & \vec{q}_4^{\,-} = \vec{q}_4 - \vec{q}_8 & \qquad\qquad \vec{q}_8 = \vec{q}_4^{\,+} - \frac{1}{2}\vec{q}_4^{\,-} \end{array} \tag{5.639}$$

$$\Sigma^{>}_{j_1j_2}(\vec{q}_1^{\,-}t_1^-\vec{q}_1^{\,+}t_1^+)$$

$$= \frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{j_3j_4j_5j_6j_7j_8} \int d\vec{q}_3^{\,+} d\vec{q}_3^{\,-} d\vec{q}_5^{\,+} d\vec{q}_5^{\,-} d\vec{q}_4^{\,+} d\vec{q}_4^{\,-}$$

$$\times \tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+}-\tfrac{1}{2}\vec{q}_1^{\,-},\vec{q}_3^{\,+}+\tfrac{1}{2}\vec{q}_3^{\,-},\vec{q}_4^{\,+}+\tfrac{1}{2}\vec{q}_4^{\,-},\vec{q}_5^{\,+}+\tfrac{1}{2}\vec{q}_5^{\,-})$$

$$\times \tilde{V}^{(4ph)}_{j_7j_8j_6j_2}(-\vec{q}_3^{\,+}+\tfrac{1}{2}\vec{q}_3^{\,-},-\vec{q}_4^{\,+}+\tfrac{1}{2}\vec{q}_4^{\,-},-\vec{q}_5^{\,+}+\tfrac{1}{2}\vec{q}_5^{\,-},\vec{q}_1^{\,+}-\tfrac{1}{2}\vec{q}_1^{\,-})$$

$$\times D^{>}_{j_5j_6}(\vec{q}_5^{\,-}t_1^-\vec{q}_5^{\,+}t_1^+)D^{>}_{j_3j_7}(\vec{q}_3^{\,-}t_1^-\vec{q}_3^{\,+}t_1^+)D^{>}_{j_4j_8}(\vec{q}_4^{\,-}t_1^-\vec{q}_4^{\,+}t_1^+) \tag{5.640}$$

| add the 2 delta functions in $\tilde{V}^{(4ph)}$ to get $\vec{q}_3^{\,-}+\vec{q}_4^{\,-}+\vec{q}_5^{\,-}=\vec{q}_1^{\,-}$

| gradient expand $\tilde{V}^{(4ph)}$ to zeroth order

$$\approx \frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{j_3j_4j_5j_6j_7j_8} \int d\vec{q}_3^{\,+} d\vec{q}_3^{\,-} d\vec{q}_5^{\,+} d\vec{q}_5^{\,-} d\vec{q}_4^{\,+} d\vec{q}_4^{\,-}$$

$$\times \tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\tilde{V}^{(4ph)}_{j_7j_8j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},-\vec{q}_5^{\,+},\vec{q}_1^{\,+})$$

$$\times D^{>}_{j_5j_6}(\vec{q}_5^{\,-}t_1^-\vec{q}_5^{\,+}t_1^+)D^{>}_{j_3j_7}(\vec{q}_3^{\,-}t_1^-\vec{q}_3^{\,+}t_1^+)D^{>}_{j_4j_8}(\vec{q}_4^{\,-}t_1^-\vec{q}_4^{\,+}t_1^+) \tag{5.641}$$

| write the Green's functions into Fourier form

$$= \frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{j_3j_4j_5j_6j_7j_8} \int d\vec{q}_3^{\,+} d\vec{q}_3^{\,-} d\vec{q}_5^{\,+} d\vec{q}_5^{\,-} d\vec{q}_4^{\,+} d\vec{q}_4^{\,-}$$

$$\times \tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\tilde{V}^{(4ph)}_{j_7j_8j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},-\vec{q}_5^{\,+},\vec{q}_1^{\,+})$$

$$\times \int d\vec{r}_5 \frac{d\omega_2}{2\pi} e^{-i\vec{q}_5^{\,-}\cdot\vec{r}_5 - i\omega_2 t_1^-} D^{>}_{j_5j_6}(\vec{r}_5\omega_2\vec{q}_5^{\,+}t_1^+) \int d\vec{r}_3 \frac{d\omega_3}{2\pi} e^{-i\vec{q}_3^{\,-}\cdot\vec{r}_3 - i\omega_3 t_1^-} D^{>}_{j_3j_7}(\vec{r}_3\omega_3\vec{q}_3^{\,+}t_1^+)$$

$$\times \int d\vec{r}_4 \frac{d\omega_4}{2\pi} e^{-i\vec{q}_4^{\,-}\cdot\vec{r}_4 - i\omega_4 t_1^-} D^{>}_{j_4j_8}(\vec{r}_4\omega_4\vec{q}_4^{\,+}t_1^+) \tag{5.642}$$

| use the delta function $\vec{q}_3^{\,-}+\vec{q}_4^{\,-}+\vec{q}_5^{\,-}=\vec{q}_1^{\,-}$ to evaluate $\vec{q}_4^{\,-}$

| insert the integral $2\pi\int\frac{d\omega_1}{2\pi}$

$$\begin{aligned}
&= 2\pi\frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{j_3j_4j_5j_6j_7j_8}\int d\vec{q}_3^{\,+}d\vec{q}_3^{\,-}d\vec{q}_5^{\,+}d\vec{q}_5^{\,-}d\vec{q}_4^{\,+} \\
&\quad\times\tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\tilde{V}^{(4ph)}_{j_7j_8j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},-\vec{q}_5^{\,+},\vec{q}_1^{\,+}) \\
&\quad\times\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\frac{d\omega_4}{2\pi}\delta(\omega_1-\omega_2-\omega_3-\omega_4)e^{-i\omega_1t_1^-}\int d\vec{r}_3d\vec{r}_4d\vec{r}_5e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_4}e^{-i\vec{q}_5^{\,-}\cdot(\vec{r}_5-\vec{r}_4)}e^{-i\vec{q}_3^{\,-}\cdot(\vec{r}_3-\vec{r}_4)} \\
&\quad\times D^>_{j_5j_6}(\vec{r}_5\omega_2\vec{q}_5^{\,+}t_1^+)D^>_{j_3j_7}(\vec{r}_3\omega_3\vec{q}_3^{\,+}t_1^+)D^>_{j_4j_8}(\vec{r}_4\omega_4\vec{q}_4^{\,+}t_1^+) \qquad (5.643) \\
&\mid\ \text{evaluate }\int d\vec{q}_5^{\,-}\text{ to get }\delta(\vec{r}_5-\vec{r}_4)\text{ then evaluate }\int d\vec{r}_5 \\
&\mid\ \text{evaluate }\int d\vec{q}_3^{\,-}\text{ to get }\delta(\vec{r}_3-\vec{r}_4)\text{ then evaluate }\int d\vec{r}_3 \\
&= 2\pi\frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{j_3j_4j_5j_6j_7j_8}\int d\vec{q}_3^{\,+}d\vec{q}_5^{\,+}d\vec{q}_4^{\,+}\tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\tilde{V}^{(4ph)}_{j_7j_8j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},-\vec{q}_5^{\,+},\vec{q}_1^{\,+}) \\
&\quad\times\int\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\frac{d\omega_4}{2\pi}\delta(\omega_1-\omega_2-\omega_3-\omega_4)e^{-i\omega_1t_1^-}\int d\vec{r}_4e^{-i\vec{q}_1^{\,-}\cdot\vec{r}_4} \\
&\quad\times D^>_{j_5j_6}(\vec{r}_4\omega_2\vec{q}_5^{\,+}t_1^+)D^>_{j_3j_7}(\vec{r}_4\omega_3\vec{q}_3^{\,+}t_1^+)D^>_{j_4j_8}(\vec{r}_4\omega_4\vec{q}_4^{\,+}t_1^+) \qquad (5.644)
\end{aligned}$$

The Fourier component of the self energy, specialized for the collision integral, is

$$\begin{aligned}
&\Sigma^>_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+) \\
&= 2\pi\frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{j_3j_4j_5j_6j_7j_8}\int d\vec{q}_3^{\,+}d\vec{q}_5^{\,+}d\vec{q}_4^{\,+}\tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\tilde{V}^{(4ph)}_{j_7j_8j_6j_1}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},-\vec{q}_5^{\,+},\vec{q}_1^{\,+}) \\
&\quad\times\int\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\frac{d\omega_4}{2\pi}\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_2-\omega_3-\omega_4)D^>_{j_5j_6}(\vec{r}_1\omega_2\vec{q}_5^{\,+}t_1^+)D^>_{j_3j_7}(\vec{r}_1\omega_3\vec{q}_3^{\,+}t_1^+)D^>_{j_4j_8}(\vec{r}_1\omega_4\vec{q}_4^{\,+}t_1^+) \\
&\qquad (5.645)
\end{aligned}$$

The lesser self energy can be immediately deduced to be

$$\begin{aligned}
&\Sigma^<_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+) \\
&= 2\pi\frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{j_3j_4j_5j_6j_7j_8}\int d\vec{q}_3^{\,+}d\vec{q}_5^{\,+}d\vec{q}_4^{\,+}\tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\tilde{V}^{(4ph)}_{j_7j_8j_6j_1}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},-\vec{q}_5^{\,+},\vec{q}_1^{\,+}) \\
&\quad\times\int\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\frac{d\omega_4}{2\pi}\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_2-\omega_3-\omega_4)D^<_{j_5j_6}(\vec{r}_1\omega_2\vec{q}_5^{\,+}t_1^+)D^<_{j_3j_7}(\vec{r}_1\omega_3\vec{q}_3^{\,+}t_1^+)D^<_{j_4j_8}(\vec{r}_1\omega_4\vec{q}_4^{\,+}t_1^+) \\
&\qquad (5.646)
\end{aligned}$$

Now we can calculate the collision integral resulting from this self energy. We do it term by term.

$$\begin{aligned}
&\text{First term of collision integral } I_{\text{zeroth}} \\
&= \frac{i}{2\omega_{j_1\vec{q}_1^{\,+}}}\Sigma^>_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+) \qquad (5.647) \\
&\mid\ \text{substitute in the form of the self energy and the free spectral KB ansatz} \\
&= 2\pi\frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\frac{i}{2\omega_{j_1\vec{q}_1^{\,+}}}\sum_{j_3j_4j_5j_6j_7j_8}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}d\vec{q}_5^{\,+} \\
&\quad\times\tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\tilde{V}^{(4ph)}_{j_7j_8j_6j_1}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},-\vec{q}_5^{\,+},\vec{q}_1^{\,+})
\end{aligned}$$

$$
\begin{aligned}
&\times \int \frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\frac{d\omega_4}{2\pi}\delta(\omega_{j_1\vec{q}_1^{\,+}} - \omega_2 - \omega_3 - \omega_4) \\
&\times \delta_{j_5 j_6}\frac{-i2\pi}{2\omega_{j_5\vec{q}_5^{\,+}}}\left(\delta(\omega_2 - \omega_{j_5\vec{q}_5^{\,+}}) - \delta(\omega_2 + \omega_{j_5\vec{q}_5^{\,+}})\right)\left(1 + N_{j_5}(\vec{r}_1\omega_2\vec{q}_5^{\,+}t_1^+)\right) \\
&\times \delta_{j_3 j_7}\frac{-i2\pi}{2\omega_{j_3\vec{q}_3^{\,+}}}\left(\delta(\omega_3 - \omega_{j_3\vec{q}_3^{\,+}}) - \delta(\omega_3 + \omega_{j_3\vec{q}_3^{\,+}})\right)\left(1 + N_{j_3}(\vec{r}_1\omega_3\vec{q}_3^{\,+}t_1^+)\right) \\
&\times \delta_{j_4 j_8}\frac{-i2\pi}{2\omega_{j_4\vec{q}_4^{\,+}}}\left(\delta(\omega_4 - \omega_{j_4\vec{q}_4^{\,+}}) - \delta(\omega_4 + \omega_{j_4\vec{q}_4^{\,+}})\right)\left(1 + N_{j_4}(\vec{r}_1\omega_4\vec{q}_4^{\,+}t_1^+)\right) \qquad (5.648)
\end{aligned}
$$

| expansion gives 8 delta function terms and $\frac{1}{(2\pi)^3}$ cancels $(2\pi)^3$

| the last delta function term is dropped as it does not conserve energy

$$
\begin{aligned}
= \;& 2\pi\frac{-1}{3!}\left(\frac{\hbar}{i}\right)^2 N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+)\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}j_5\vec{q}_5^{\,+}}\frac{-1}{2^4\omega_{j_1\vec{q}_1^{\,+}}\omega_{j_3\vec{q}_3^{\,+}}\omega_{j_4\vec{q}_4^{\,+}}\omega_{j_5\vec{q}_5^{\,+}}} \\
&\times \int d\omega_2 d\omega_3 d\omega_4 \delta(\omega_{j_1\vec{q}_1^{\,+}} - \omega_2 - \omega_3 - \omega_4)\left|\tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2 (7 \text{ delta terms}) \\
&\times \left(1 + N_{j_3}(\vec{r}_1\omega_3\vec{q}_3^{\,+}t_1^+)\right)\left(1 + N_{j_4}(\vec{r}_1\omega_4\vec{q}_4^{\,+}t_1^+)\right)\left(1 + N_{j_5}(\vec{r}_1\omega_2\vec{q}_5^{\,+}t_1^+)\right) \qquad (5.649)
\end{aligned}
$$

| recall that $\tilde{V}^{(4ph)} = \sqrt{\frac{2^4\omega\omega\omega\omega}{\hbar^4}}V^{(4ph)}$

$$
\begin{aligned}
= \;& \frac{1}{3!}\frac{2\pi}{\hbar^2}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+)\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}j_5\vec{q}_5^{\,+}}\int d\omega_2 d\omega_3 d\omega_4 \delta(\omega_{j_1\vec{q}_1^{\,+}} - \omega_2 - \omega_3 - \omega_4) \\
&\times \left|V^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2 (7 \text{ delta terms}) \\
&\times \left(1 + N_{j_3}(\vec{r}_1\omega_3\vec{q}_3^{\,+}t_1^+)\right)\left(1 + N_{j_4}(\vec{r}_1\omega_4\vec{q}_4^{\,+}t_1^+)\right)\left(1 + N_{j_5}(\vec{r}_1\omega_2\vec{q}_5^{\,+}t_1^+)\right) \qquad (5.650)
\end{aligned}
$$

| use pairwise symmetry of the indices $3, 4, 5$

| then 2 sets of 3 delta functions add up giving 3 types of terms

$$
\begin{aligned}
= \;& \frac{1}{3!}\frac{2\pi}{\hbar^2}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+)\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}j_5\vec{q}_5^{\,+}}\left|V^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2 \\
&\times \Big[3\delta(\omega_{j_1\vec{q}_1^{\,+}} - \omega_{j_5\vec{q}_5^{\,+}} + \omega_{j_3\vec{q}_3^{\,+}} + \omega_{j_4\vec{q}_4^{\,+}})N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1 t_1^+)N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1 t_1^+)\left(1 + N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1 t_1^+)\right) \\
&+3\delta(\omega_{j_1\vec{q}_1^{\,+}} - \omega_{j_5\vec{q}_5^{\,+}} - \omega_{j_3\vec{q}_3^{\,+}} + \omega_{j_4\vec{q}_4^{\,+}})\left(1 + N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1 t_1^+)\right)N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1 t_1^+)\left(1 + N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1 t_1^+)\right) \\
&+ \delta(\omega_{j_1\vec{q}_1^{\,+}} - \omega_{j_5\vec{q}_5^{\,+}} - \omega_{j_3\vec{q}_3^{\,+}} - \omega_{j_4\vec{q}_4^{\,+}})\left(1 + N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1 t_1^+)\right)\left(1 + N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1 t_1^+)\right)\left(1 + N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1 t_1^+)\right)\Big]
\end{aligned}
$$

| this step could be non-rigorous $\Rightarrow$

| we adjust the signs in $V^{(4ph)}$ such that they follow the convention:

| if $\omega_{j_i\vec{q}_i^{\,+}}$ has a positive sign in the delta function, then $\vec{q}_i^{\,+}$ is negative in $V^{(4ph)}$

$$
\begin{aligned}
= \;& \frac{2\pi}{\hbar^2}\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}j_5\vec{q}_5^{\,+}}\Bigg[\frac{1}{2}\left|V^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2\delta(\omega_{j_1\vec{q}_1^{\,+}} - \omega_{j_5\vec{q}_5^{\,+}} + \omega_{j_3\vec{q}_3^{\,+}} + \omega_{j_4\vec{q}_4^{\,+}}) \\
&\times N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1 t_1^+)N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1 t_1^+)\left(1 + N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1 t_1^+)\right)N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+) \\
&+\frac{1}{2}\left|V^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2\delta(\omega_{j_1\vec{q}_1^{\,+}} - \omega_{j_5\vec{q}_5^{\,+}} - \omega_{j_3\vec{q}_3^{\,+}} + \omega_{j_4\vec{q}_4^{\,+}}) \\
&\times \left(1 + N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1 t_1^+)\right)N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1 t_1^+)\left(1 + N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1 t_1^+)\right)N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+)
\end{aligned}
$$

$$+\frac{1}{3!}\left|V^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}-\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}})$$
$$\times\Big(1+N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\Big)\Big(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\Big)\Big(1+N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1t_1^+)\Big)N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\quad\Bigg] \tag{5.651}$$

Second term of collision integral I_{zeroth}

$$= \frac{i}{2\omega_{j_1\vec{q}_1^{\,+}}}\Sigma^<_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)\Big(1+N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\Big) \tag{5.652}$$

| the working is very similar to the first term
| we also drop the non-energy conserving delta function

$$= \frac{1}{3!}\frac{2\pi}{\hbar^2}\Big(1+N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\Big)\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}j_5\vec{q}_5^{\,+}}\int d\omega_2d\omega_3d\omega_4\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_2-\omega_3-\omega_4)$$
$$\times\left|V^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2(\text{7 delta terms})N_{j_3}(\vec{r}_1\omega_3\vec{q}_3^{\,+}t_1^+)N_{j_4}(\vec{r}_1\omega_4\vec{q}_4^{\,+}t_1^+)N_{j_5}(\vec{r}_1\omega_2\vec{q}_5^{\,+}t_1^+)$$

| use pairwise symmetry of the indices $3,4,5$
| then 2 sets of 3 delta functions add up giving 3 types of terms
| also use $N_j(\vec{r},-\omega,\vec{q}^{\,+},t^+)=-(1+N_j(\vec{r}\omega\vec{q}^{\,+}t^+))$

$$= \frac{1}{3!}\frac{2\pi}{\hbar^2}\Big(1+N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\Big)\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}j_5\vec{q}_5^{\,+}}\left|V^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2$$
$$\times\Big[3\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}+\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}})\Big(1+N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\Big)\Big(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\Big)N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1t_1^+)$$
$$+3\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}-\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}})N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\Big(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\Big)N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1t_1^+)$$
$$+\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}-\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}})N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1t_1^+)\Big] \tag{5.653}$$

| this step could be non-rigorous $\Rightarrow$
| we adjust the signs in $V^{(4ph)}$ such that they follow the convention:
| if $\omega_{j_i\vec{q}_i^{\,+}}$ has a positive sign in the delta function, then $\vec{q}_i^{\,+}$ is negative in $V^{(4ph)}$

$$= \frac{2\pi}{\hbar^2}\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}j_5\vec{q}_5^{\,+}}\Bigg[\frac{1}{2}\left|V^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}+\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}})$$
$$\times\Big(1+N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\Big)\Big(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\Big)N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1t_1^+)\Big(1+N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\Big)$$
$$+\frac{1}{2}\left|V^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}-\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}})$$
$$\times N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\Big(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\Big)N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1t_1^+)\Big(1+N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\Big)$$
$$+\frac{1}{3!}\left|V^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2\delta(\omega_{j_1\vec{q}_1^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}-\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}})$$
$$\times N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)N_{j_5\vec{q}_5^{\,+}}(\vec{r}_1t_1^+)\Big(1+N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\Big)\quad\Bigg] \tag{5.654}$$

For completeness, we include the explicit expressions of the 8 delta function terms,

$$+\quad\delta(\omega_2-\omega_{j_5\vec{q}_5^{\,+}})\delta(\omega_3-\omega_{j_3\vec{q}_3^{\,+}})\delta(\omega_4-\omega_{j_4\vec{q}_4^{\,+}})\qquad\text{type 1} \tag{5.655}$$
$$-\quad\delta(\omega_2-\omega_{j_5\vec{q}_5^{\,+}})\delta(\omega_3-\omega_{j_3\vec{q}_3^{\,+}})\delta(\omega_4+\omega_{j_4\vec{q}_4^{\,+}})\qquad\text{type 2} \tag{5.656}$$

$$
\begin{array}{llr}
- \quad \delta(\omega_2 - \omega_{j_5\vec{q}_5^+})\delta(\omega_3 + \omega_{j_3\vec{q}_3^+})\delta(\omega_4 - \omega_{j_4\vec{q}_4^+}) & \text{type 2} & (5.657)\\
+ \quad \delta(\omega_2 - \omega_{j_5\vec{q}_5^+})\delta(\omega_3 + \omega_{j_3\vec{q}_3^+})\delta(\omega_4 + \omega_{j_4\vec{q}_4^+}) & \text{type 3} & (5.658)\\
- \quad \delta(\omega_2 + \omega_{j_5\vec{q}_5^+})\delta(\omega_3 - \omega_{j_3\vec{q}_3^+})\delta(\omega_4 - \omega_{j_4\vec{q}_4^+}) & \text{type 2} & (5.659)\\
+ \quad \delta(\omega_2 + \omega_{j_5\vec{q}_5^+})\delta(\omega_3 - \omega_{j_3\vec{q}_3^+})\delta(\omega_4 + \omega_{j_4\vec{q}_4^+}) & \text{type 3} & (5.660)\\
+ \quad \delta(\omega_2 + \omega_{j_5\vec{q}_5^+})\delta(\omega_3 + \omega_{j_3\vec{q}_3^+})\delta(\omega_4 - \omega_{j_4\vec{q}_4^+}) & \text{type 3} & (5.661)\\
- \quad \delta(\omega_2 + \omega_{j_5\vec{q}_5^+})\delta(\omega_3 + \omega_{j_3\vec{q}_3^+})\delta(\omega_4 + \omega_{j_4\vec{q}_4^+}) & \text{discarded} & (5.662)
\end{array}
$$

$$
\begin{aligned}
&\text{Total collision integral } I_{\text{zeroth}} \text{ in shorthand notation } 1 \equiv j_1, \vec{q}_1^{\,+} \text{ and } \bar{1} \equiv j_1, -\vec{q}_1^{\,+}\\
= \;& \text{First term} - \text{Second Term} \qquad (5.663)\\
= \;& \frac{2\pi}{\hbar^2} \sum_{3,4,5} \left[\frac{1}{2} \left| V^{(4ph)}_{\bar{1},\bar{3},4,5} \right|^2 \delta(\omega_1 - \omega_5 + \omega_3 + \omega_4) \left(N_1 N_3 N_4 (1+N_5) - (1+N_1)(1+N_3)(1+N_4) N_5 \right) \right.\\
& + \frac{1}{2} \left| V^{(4ph)}_{\bar{1},3,\bar{4},5} \right|^2 \delta(\omega_1 - \omega_5 - \omega_3 + \omega_4) \left(N_1 (1+N_3) N_4 (1+N_5) - (1+N_1) N_3 (1+N_4) N_5 \right)\\
& \left. + \frac{1}{3!} \left| V^{(4ph)}_{\bar{1},3,4,5} \right|^2 \delta(\omega_1 - \omega_5 - \omega_3 - \omega_4) \left(N_1 (1+N_3)(1+N_4)(1+N_5) - (1+N_1) N_3 N_4 N_5 \right) \right] \qquad (5.664)
\end{aligned}
$$

This expression is the same as $I^{(4ph)}$. Again, nothing new is derived here, it is the framework that encompasses the traditional kinetic theory that we want to emphasize here.

5.6.2.4 Discussion on other Self Energy Terms

As noted earlier, self consistent self energies with odd numbers of anharmonic coefficients are going to give imaginary collision integrals (within this framework) which are, strictly speaking, unphysical. Thus, $V^{(3ph)^2} V^{(4ph)}$ Type-1,2,3 self energies are unphysical and will not be discusssed further. They may be make physical sense in other theories.

Self consistent self energies with even numbers of anharmonic coefficients as going to give real collision integrals (within this framework), so $V^{(3ph)^4}$ self energy is the next physical self energy for QKE and it represents the next higher order of 3-phonon collisions. It is actually a vertex correction. This thesis provides enough tools to carry out the calculation of the collision integral but there may be a hundred terms or so, therefore, we shall only outline the steps: apply Langreth's theorem to get the lesser and the greater component of the $V^{(3ph)^4}$ self consistent self energy, define 5 sets of Wigner coordinates, gradient expand to zeroth order, extract the Fourier component, substitute into I_{zeroth} and dropping unphysical energy delta functions as necessary.

One more point that could be discussed in this framework is about the breakdown of Matthiessen's rule of adding inverse relaxation times, i.e. adding resistivities. In this case, we mean, at which order, is the collision integral of 3-phonon & 4-phonon interaction so mixed up that they cannot be written as a sum of 2 terms? I believe the answer is the $V^{(3ph)^2} V^{(4ph)^2}$ self consistent self energy shown in the diagram. One can deduce that the collision integral is made up of the 4 anharmonic coefficients multiplied together hence making the term inseperable. By the way, it is made up of an even number of anharmonic coefficients.

5.6.3 First Order Gradient expansion Collision Integrals

We recall the first order (in gradient expansion) collision integral $I_{1\text{st}}$.

First Order Collision Integral $I_{1\text{st}}$

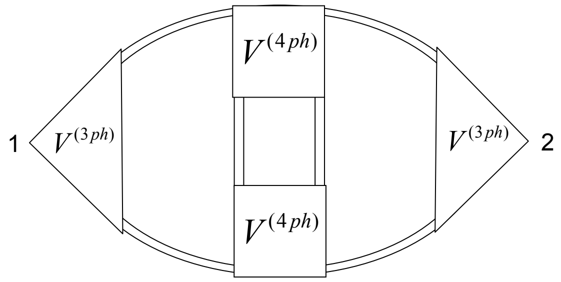


Figure 5.20: *Self consistent self energy that gives rise to a collision integral that violates Matthiessen's rule.*

$$
\begin{aligned}
&= \frac{1}{2\pi i}\int_0^\infty d\omega_1 \sum_{j_3}\left\{\left[\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{A_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'}, \Sigma^<_{j_3j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\right. \\
&\quad \left. -\left[\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'}, D^<_{j_3j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\right\}_{\text{Free spectral KB}} \qquad (5.665)
\end{aligned}
$$

We can simplfy $I_{1\text{st}}$ slightly by a partial implementation of the free spectral KB ansatz.[26]

$$
\begin{aligned}
\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{A_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'} &= \mathcal{P}\int\frac{d\omega'}{2\pi}\frac{A^{(0)}_{j_1}(\omega'\vec{q}_1^{\,+})\delta_{j_1j_3}}{\omega_1-\omega'} \qquad (5.666)\\
&\quad | \ \text{where the free spectral function is implemented}\\
&= \frac{2\pi\delta_{j_1j_3}}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\delta(\omega'-\omega_{j_1\vec{q}_1^{\,+}}}{\omega_1-\omega'} - \mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\delta(\omega'-\omega_{j_1\vec{q}_1^{\,+}}}{\omega_1-\omega'}\right) \qquad (5.667)\\
&\quad | \ \text{and the } 2\pi \text{ cancels}\\
&= \frac{\delta_{j_1j_3}}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\frac{1}{\omega_1-\omega_{j_1\vec{q}_1^{\,+}}} - \frac{1}{\omega_1+\omega_{j_1\vec{q}_1^{\,+}}}\right) \qquad (5.668)\\
&= \frac{\delta_{j_1j_3}}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}} \qquad (5.669)
\end{aligned}
$$

The first order collision integral becomes,

$$
\begin{aligned}
I_{1\text{st}} &= \frac{1}{2\pi i}\int_0^\infty d\omega_1\left[\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}}, \Sigma^<_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\Bigg|_{\text{Free spectral KB}}\\
&\quad -\frac{1}{2\pi i}\int_0^\infty d\omega_1\sum_{j_3}\left[\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'}\right.\\
&\quad \left., \delta_{j_1j_3}\frac{-i2\pi}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\Bigg|_{\text{Free spectral KB}} \qquad (5.670)
\end{aligned}
$$

[26]Do remember that ω_1 and $\vec{q}_1^{\,+}$ are independent until KB ansatz is applied. When KB ansatz is applied, ω_1 will be replaced by $\omega_{j_1\vec{q}_1^{\,+}}$ and $\omega_{j_1\vec{q}_1^{\,+}}$ is related to $\vec{q}_1^{\,+}$ via the dispersion relation.

$$
\begin{aligned}
= \quad & \frac{1}{i}\int_0^\infty \frac{d\omega_1}{2\pi}\left[\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}}, \Sigma^<_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\Bigg|_{\text{Free spectral KB}} \\
& + \frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\int_0^\infty d\omega_1\left[\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma_{j_1j_3}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'}\right. \\
& \left., \Big(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\Big)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\quad\right]_{GPB}\Bigg|_{\text{Free spectral KB}} \qquad (5.671)
\end{aligned}
$$

Now we are ready to work out explicitly 3 examples involving self energies of $V^{(4ph)}$, $V^{(3ph)^2}$ and $V^{(4ph)^2}$. This will give us QKEs with lowest order corrections in correlations. These QKEs are obviously unsolvable so we will just try to make physical sense out of them.

5.6.3.1 $V^{(4ph)}$ Term*

The self energy in Wigner coordinates is,

$$
\Sigma^{\gtrless}_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) \;=\; -\frac{1}{2}\frac{\hbar}{i}\sum_{j_4j_5}\int d\vec{q}_3^{\,+}\tilde{V}^{(4ph)}_{j_1j_4j_5j_2}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})D^{\gtrless}_{j_4j_5}(\vec{r}_1\omega_1\vec{q}_3^{\,+}t_1^+) \qquad (5.672)
$$

We work out the principal integral first.

$$
\begin{aligned}
& \mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma_{j_1j_1}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'} \\
| \quad & \text{recall that } \Gamma = i(\Sigma^> - \Sigma^<) \\
= \quad & -\frac{1}{2}\frac{\hbar}{i}\sum_{j_4j_5}\int d\vec{q}_3^{\,+}\tilde{V}^{(4ph)}_{j_1j_4j_5j_2}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{i(D^>_{j_4j_5}(\vec{r}_1\omega'\vec{q}_3^{\,+}t_1^+)-D^<_{j_4j_5}(\vec{r}_1\omega'\vec{q}_3^{\,+}t_1^+)}{\omega_1-\omega'} \\
| \quad & \text{within free spectral KB, we have } i(D^>-D^<)=A^{(0)} \text{ and the principal integral was done earlier} \\
| \quad & \text{rename } \vec{q}_3^{\,+}\to\vec{q}_4^{\,+} \\
= \quad & -\frac{1}{2}\frac{\hbar}{i}\sum_{j_4j_5}\int d\vec{q}_3^{\,+}\tilde{V}^{(4ph)}_{j_1j_4j_5j_2}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},-\vec{q}_3^{\,+},\vec{q}_1^{\,+})\frac{1}{\omega_1^2-\omega^2_{j_4\vec{q}_4^{\,+}}} \qquad (5.673)
\end{aligned}
$$

Now we calculate the first order collision integral.

$$
\begin{aligned}
& \text{First term of } I_{\text{1st}} \\
= \quad & \frac{1}{i}\int_0^\infty\frac{d\omega_1}{2\pi}\left[\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}},\Sigma^<_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\Bigg|_{\text{Free spectral KB}} \qquad (5.674) \\
= \quad & \frac{\hbar}{2}\int_0^\infty\frac{d\omega_1}{2\pi}\sum_{j_4j_5}\int d\vec{q}_4^{\,+}\left[\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}}\right. \\
& \left.,\tilde{V}^{(4ph)}_{j_1j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_4^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})\delta_{j_4j_5}\frac{-i2\pi}{2\omega_{j_4\vec{q}_4^{\,+}}}\Big(\delta(\omega_1-\omega_{j_4\vec{q}_4^{\,+}})-\delta(\omega_1+\omega_{j_4\vec{q}_4^{\,+}})\Big)N_{j_4}(\vec{r}_1\omega'\vec{q}_4^{\,+}t_1^+)\right]_{GPB} \qquad (5.675) \\
| \quad & \text{expand the Poisson brackets} \\
= \quad & -\frac{i\hbar}{2}\sum_{j_4\vec{q}_4^{\,+}}\frac{1}{2\omega_{j_4\vec{q}_4^{\,+}}}\int_0^\infty d\omega_1\tilde{V}^{(4ph)}_{j_1j_4j_4j_1}(-\vec{q}_1^{\,+},\vec{q}_4^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})
\end{aligned}
$$

$$\times\left\{\left(\frac{\partial}{\partial\omega_1}\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}}\right)\Big(\delta(\omega_1-\omega_{j_4\vec{q}_4^{\,+}})-\delta(\omega_1+\omega_{j_4\vec{q}_4^{\,+}})\Big)\frac{\partial N_{j_4}(\vec{r}_1\omega'\vec{q}_4^{\,+}t_1^+)}{\partial t_1^+}\right.$$
$$\left.+\left(\nabla_{\vec{q}_1^{\,+}}\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}}\right)\Big(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\Big)\cdot\big(\nabla_{\vec{r}}N_{j_4}(\vec{r}_1\omega'\vec{q}_4^{\,+}t_1^+)\big)\right\} \quad (5.676)$$

| only the first delta function is picked up, and use notation $N_{j_4}(\vec{r}_1\omega_{j_4\vec{q}_4^{\,+}}\vec{q}_4^{\,+}t_1^+)=N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)$

$$= -\frac{i\hbar}{2}\sum_{j_4\vec{q}_4^{\,+}}\frac{\tilde{V}^{(4ph)}_{j_1j_4j_4j_1}(-\vec{q}_1^{\,+},\vec{q}_4^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})}{2\omega_{j_4\vec{q}_4^{\,+}}}$$
$$\left\{\left(\frac{\partial}{\partial\omega_{j_4\vec{q}_4^{\,+}}}\frac{1}{\omega^2_{j_4\vec{q}_4^{\,+}}-\omega^2_{j_1\vec{q}_1^{\,+}}}\right)\frac{\partial N_{j_4\vec{q}_4^{\,+}}}{\partial t_1^+}+\left(\nabla_{\vec{q}_1^{\,+}}\frac{1}{\omega^2_{j_4\vec{q}_4^{\,+}}-\omega^2_{j_1\vec{q}_1^{\,+}}}\right)\cdot\Big(\nabla_{\vec{r}_1}N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\Big)\right\} \quad (5.677)$$

Second Term of $I_{1\mathrm{st}}$

$$= -\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\frac{1}{2}\frac{\hbar}{i}\sum_{j_4\vec{q}_4^{\,+}}\int_0^\infty d\omega_1$$
$$\times\left[\frac{\tilde{V}^{(4ph)}_{j_1j_4j_4j_1}(-\vec{q}_1^{\,+},\vec{q}_4^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})}{\omega_1^2-\omega^2_{j_4\vec{q}_4^{\,+}}},\Big(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\Big)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB} \quad (5.678)$$

| expand the Poisson brackets

$$= -\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\frac{1}{2}\frac{\hbar}{i}\sum_{j_4\vec{q}_4^{\,+}}\int_0^\infty d\omega_1$$
$$\times\left\{\tilde{V}^{(4ph)}_{j_1j_4j_4j_1}(-\vec{q}_1^{\,+},\vec{q}_4^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})\left(\frac{\partial}{\partial\omega_1}\frac{1}{\omega_1^2-\omega^2_{j_4\vec{q}_4^{\,+}}}\right)\Big(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\Big)\frac{\partial N_{j_1}}{\partial t_1^+}\right.$$
$$\left.+\Big(\nabla_{\vec{q}_1^{\,+}}\tilde{V}^{(4ph)}_{j_1j_4j_4j_1}(-\vec{q}_1^{\,+},\vec{q}_4^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})\Big)\frac{1}{\omega_1^2-\omega^2_{j_4\vec{q}_4^{\,+}}}\Big(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\Big)\cdot(\nabla_{\vec{r}_1}N_{j_1})\right\}$$

| only the first delta function is picked up

$$= -\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\frac{1}{2}\frac{\hbar}{i}\sum_{j_4\vec{q}_4^{\,+}}\left\{\tilde{V}^{(4ph)}_{j_1j_4j_4j_1}(-\vec{q}_1^{\,+},\vec{q}_4^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})\left(\frac{\partial}{\partial\omega_{j_1\vec{q}_1^{\,+}}}\frac{1}{\omega^2_{j_1\vec{q}_1^{\,+}}-\omega^2_{j_4\vec{q}_4^{\,+}}}\right)\frac{\partial N_{j_1\vec{q}_1^{\,+}}}{\partial t_1^+}\right.$$
$$\left.+\Big(\nabla_{\vec{q}_1}\tilde{V}^{(4ph)}_{j_1j_4j_4j_1}(-\vec{q}_1^{\,+},\vec{q}_4^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})\Big)\frac{1}{\omega^2_{j_1\vec{q}_1^{\,+}}-\omega^2_{j_4\vec{q}_4^{\,+}}}\cdot\Big(\nabla_{\vec{r}_1}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\Big)\right\} \quad (5.679)$$

The last term may be interpreted as renormalizing the group velocity.

Last term of $I_{1\mathrm{st}}$

$$= -\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\frac{1}{2}\frac{\hbar}{i}\sum_{j_4\vec{q}_4^{\,+}}\Big(\nabla_{\vec{q}_1}\tilde{V}^{(4ph)}_{j_1j_4j_4j_1}(-\vec{q}_1^{\,+},\vec{q}_4^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})\Big)\frac{1}{\omega^2_{j_1\vec{q}_1^{\,+}}-\omega^2_{j_4\vec{q}_4^{\,+}}}\cdot\Big(\nabla_{\vec{r}_1}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\Big) \quad (5.680)$$

| write $\nabla_{\vec{q}_1^{\,+}}=(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}})\dfrac{\partial}{\partial\omega_{j_1\vec{q}_1^{\,+}}}=\vec{v}_{j_1\vec{q}_1^{\,+}}\dfrac{\partial}{\partial\omega_{j_1\vec{q}_1^{\,+}}}$

$$= -\frac{1}{2\omega_{j_1\vec{q}_1^+}}\frac{1}{2}\frac{\hbar}{i}\sum_{j_4\vec{q}_4^+}\left(\frac{\partial}{\partial\omega_{j_1\vec{q}_1^+}}\tilde{V}^{(4ph)}_{j_1j_4j_4j_1}(-\vec{q}_1^{\,+},\vec{q}_4^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})\right)\frac{1}{\omega^2_{j_1\vec{q}_1^+}-\omega^2_{j_4\vec{q}_4^+}}\vec{v}_{j_1\vec{q}_1^+}\cdot\left(\nabla_{\vec{r}_1}N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\right) \quad (5.681)$$

Again, we have a pure imaginary collision integral for this case however it is not clear if they can be immediately deemed unphysical. These 4 terms are (spatial and temporal) correlation terms and are not collision terms as they do not have energy conserving delta functions. For example, in steady state, terms with $\frac{\partial}{\partial t_1^+}$ vanish and thus temporal correlation terms vanish. A deeper look seems to indicate that the meaning of correlations is due to interbranch and intrabranch mixing of phonons within the phonon distribution function. There is also one term (the last term) that renormalizes the harmonic group velocity. Calling it a collision integral seems to be unsuitable however we will still call it a collision integral for a lack of better terminology. This illustrates how complicated things can be when dealing with non-equilibrium problems. I would suspect that phonon mixing collision integrals should be real to acquire a sensible meaning, so this collision integral should be deemed unphysical.

5.6.3.2 $V^{(3ph)^2}$ Term*

The self energy in (Fourier transformed) Wigner coordinates is

$$\Sigma^{\lessgtr}_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) = 2\pi\frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}\int d\vec{q}_4^{\,+}\int\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\tilde{V}^{(3ph)}_{j_5j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})$$
$$\times\delta(\omega_1-\omega_2-\omega_3)D^{\lessgtr}_{j_3j_5}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+)D^{\lessgtr}_{j_4j_6}(\vec{r}_1\omega_3\vec{q}_4^{\,+}t_1^+) \quad (5.682)$$

We work out the principal integral first.

$$\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma_{j_1j_1}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'}$$
$$= 2\pi\frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}\int\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\tilde{V}^{(3ph)}_{j_5j_6j_1}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})$$
$$\times\left(\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\delta(\omega'-\omega_2-\omega_3)}{\omega_1-\omega'}\right)i\left(D^{>}_{j_3j_5}D^{>}_{j_4j_6}-D^{<}_{j_3j_5}D^{<}_{j_4j_6}\right)(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+)(\vec{r}_1\omega_3\vec{q}_4^{\,+}t_1^+) \quad (5.683)$$

| we have $\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\delta(\omega'-\omega_2-\omega_3)}{\omega_1-\omega'}=\frac{1}{2\pi}\frac{1}{\omega_1-\omega_2-\omega_3}$

| insert the free spectral KB ansatz for the 4 Green's functions

$$= \frac{1}{2}\frac{\hbar}{i}\sum_{j_3j_4j_5j_6}\int d\vec{q}_3^{\,+}d\vec{q}_4^{\,+}\int\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\tilde{V}^{(3ph)}_{j_5j_6j_1}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+})\frac{i}{\omega_1-\omega_2-\omega_3}$$
$$\times\delta_{j_3j_5}\frac{-i2\pi}{2\omega_{j_3\vec{q}_3^+}}\delta_{j_4j_6}\frac{-i2\pi}{2\omega_{j_4\vec{q}_4^+}}\left(\delta(\omega_2-\omega_{j_3\vec{q}_3^+})-\delta(\omega_2+\omega_{j_3\vec{q}_3^+})\right)\left(\delta(\omega_3-\omega_{j_4\vec{q}_4^+})-\delta(\omega_3+\omega_{j_4\vec{q}_4^+})\right)$$
$$\times\left(\left(1+N_{j_3}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+)\right)\left(1+N_{j_4}(\vec{r}_1\omega_3\vec{q}_4^{\,+}t_1^+)\right)-N_{j_3}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+)N_{j_4}(\vec{r}_1\omega_3\vec{q}_4^{\,+}t_1^+)\right) \quad (5.684)$$

| evaluate the 4 delta functions, and use $N(-\omega)=-(1+N(\omega))$

$$= -\frac{\hbar}{2}\sum_{j_3\vec{q}_3^+j_4\vec{q}_4^+}\frac{\left|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\right|^2}{2\omega_{j_3\vec{q}_3^+}2\omega_{j_4\vec{q}_4^+}}\left\{\frac{1+N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)+N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)}{\omega_1-\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}}\right.$$
$$\left.-\frac{N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)-N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)}{\omega_1-\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+}}+\frac{N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)-N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)}{\omega_1+\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}}-\frac{1+N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)+N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)}{\omega_1+\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+}}\right\}$$

$$
\begin{aligned}
&= -\frac{\hbar}{2} \sum_{j_3\vec{q}_3^{\,+} j_4\vec{q}_4^{\,+}} \frac{\left|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\right|^2}{2\omega_{j_3\vec{q}_3^{\,+}} 2\omega_{j_4\vec{q}_4^{\,+}}} \left\{ \frac{(1+N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+))(2\omega_{j_3\vec{q}_3^{\,+}}+2\omega_{j_4\vec{q}_4^{\,+}})}{\omega_1^2-(\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}})^2} \right. \\
&\quad \left. + \frac{(N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)-N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+))(2\omega_{j_3\vec{q}_3^{\,+}}-2\omega_{j_4\vec{q}_4^{\,+}})}{\omega_1^2-(\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}})^2} \right\} \qquad (5.685) \\
&\equiv E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) \qquad (5.686)
\end{aligned}
$$

The definition is to save some writing later.

$$
\begin{aligned}
&\text{First Term of } I_{1\text{st}} \\
&= \frac{1}{i}\int_0^\infty \frac{d\omega_1}{2\pi} \left[\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}}, \Sigma^<_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) \right]_{GPB} \Bigg|_{\text{Free spectral KB ansatz}} \qquad (5.687) \\
&= \frac{1}{i}\int_0^\infty \frac{d\omega_1}{2\pi} \left[\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}}, 2\pi\frac{1}{2}\frac{\hbar}{i} \sum_{j_3j_4j_5j_6\vec{q}_3^{\,+}\vec{q}_4^{\,+}} \int \frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi} \tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+}) \tilde{V}^{(3ph)}_{j_5j_6j_1}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},\vec{q}_1^{\,+}) \right. \\
&\quad \left. \times\delta(\omega_1-\omega_2-\omega_3) D^<_{j_3j_5}(\vec{r}_1\omega_2\vec{q}_3^{\,+}t_1^+) D^<_{j_4j_6}(\vec{r}_1\omega_3\vec{q}_3^{\,+}t_1^+) \right]_{GPB} \Bigg|_{\text{Free spectral KB}} \qquad (5.688)
\end{aligned}
$$

| insert free spectral KB ansatz for the Green's functions, all 2π cancels
| drop the 4th nonconserving delta function and use $N(-\omega) = -(1+N(\omega))$

$$
\begin{aligned}
&= -\frac{\hbar}{2}\int_0^\infty d\omega_1 \sum_{j_3\vec{q}_3^{\,+} j_4\vec{q}_4^{\,+}} \frac{-i}{2\omega_{j_3\vec{q}_3^{\,+}}} \frac{-i}{2\omega_{j_4\vec{q}_4^{\,+}}} \left[\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}}, \left|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\right|^2 \right. \\
&\quad \times \Big(\delta(\omega_1-\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}}) N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+) N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+) \\
&\quad + \delta(\omega_1-\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}}) N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+) \Big(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\Big) \\
&\quad \left. + \delta(\omega_1+\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}}) \Big(1+N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\Big) N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+) \Big) \right]_{GPB} \qquad (5.689)
\end{aligned}
$$

| expand the Poisson brackets

$$
\begin{aligned}
&= -\frac{\hbar}{2}\int_0^\infty d\omega_1 \sum_{j_3\vec{q}_3^{\,+} j_4\vec{q}_4^{\,+}} \frac{-i}{2\omega_{j_3\vec{q}_3^{\,+}}} \frac{-i}{2\omega_{j_4\vec{q}_4^{\,+}}} \\
&\quad \times \left\{ \left(\frac{\partial}{\partial\omega_1} \frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}} \right) \left|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\right|^2 \frac{\partial}{\partial t_1^+} (\cdots 3 \text{ terms} \cdots) \right. \\
&\quad \left. + \left(\nabla_{\vec{q}_1^{\,+}} \frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}} \right) \left|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})\right|^2 \cdot \nabla_{\vec{r}_1} (\cdots 3 \text{ terms} \cdots) \right\} \qquad (5.690)
\end{aligned}
$$

| write $\frac{\partial}{\partial\omega_1}\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}} = \frac{-2\omega_1}{(\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}}) ^2$ and evaluate $\int_0^\infty d\omega_1$
| rename $3 \leftrightarrow 4$ and terms $\frac{\partial}{\partial t_1^+} N_{j_3}(1+N_{j_4})$ and $\frac{\partial}{\partial t_1^+}(1+N_{j_3})N_{j_4}$ add up
| also, $\nabla_{\vec{r}_1} N_{j_3}(1+N_{j_4})$ and $\nabla_{\vec{r}_1}(1+N_{j_3})N_{j_4}$ add up

$$= \frac{\hbar}{2}\sum_{j_3\vec{q}_3^+ j_4\vec{q}_4^+}\frac{\left|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^+,\vec{q}_3^+,\vec{q}_4^+)\right|^2}{2\omega_{j_3\vec{q}_3^+}2\omega_{j_4\vec{q}_4^+}}$$

$$\times\Bigg\{-\frac{2(\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+})}{\left((\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+})^2-\omega^2_{j_1\vec{q}_1^+}\right)^2}\left(\frac{\partial}{\partial t_1^+}N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)\right)$$

$$-\frac{4|\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}|}{\left(|\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}|^2-\omega^2_{j_1\vec{q}_1^+}\right)^2}\left(\frac{\partial}{\partial t_1^+}N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)\left(1+N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)\right)\right)$$

$$+\left(\nabla_{\vec{q}_1^+}\frac{1}{(\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+})^2-\omega^2_{j_1\vec{q}_1^+}}\right)\cdot\left(\nabla_{\vec{r}_1}N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)\right)$$

$$+2\left(\nabla_{\vec{q}_1^+}\frac{1}{|\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+}|^2-\omega^2_{j_1\vec{q}_1^+}}\right)\cdot\left(\nabla_{\vec{r}_1}N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)\left(1+N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)\right)\right)\Bigg\} \tag{5.691}$$

Second Term of I_{1st}

$$= \frac{1}{2\omega_{j_1\vec{q}_1^+}}\int_0^\infty d\omega_1\left[E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+),\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right]_{GPB} \tag{5.692}$$

| expand the Poisson bracket

$$= \frac{1}{2\omega_{j_1\vec{q}_1^+}}\int_0^\infty d\omega_1\Bigg\{\frac{\partial E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)}{\partial\omega_1}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)\frac{\partial N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)}{\partial t_1^+}$$

$$-\frac{\partial E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)}{\partial t_1^+}\left(\frac{\partial}{\partial\omega_1}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)$$

$$+\left(\nabla_{\vec{q}_1^+}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)\cdot\left(\nabla_{\vec{r}_1}N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)$$

$$+\left(\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)\cdot\left(\nabla_{\vec{q}_1^+}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)\Bigg\} \tag{5.693}$$

| for 1st term, only the first delta is picked up

| for 2nd, 3rd and 4th term, use product rule of differentiation

$$= \frac{1}{2\omega_{j_1\vec{q}_1^+}}\Bigg\{\frac{\partial E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)}{\partial\omega_{j_1\vec{q}_1^+}}\frac{\partial N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)}{\partial t_1^+}$$

$$-\int_0^\infty d\omega_1\frac{\partial}{\partial\omega_1}\left(\frac{\partial E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)}{\partial t_1^+}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)$$

$$+\int_0^\infty d\omega_1\frac{\partial^2 E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)}{\partial\omega_1\partial t_1^+}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)$$

$$+\int_0^\infty d\omega_1\nabla_{\vec{r}_1}\cdot\left(\left(\nabla_{\vec{q}_1^+}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)$$

$$-\int_0^\infty d\omega_1\left(\nabla_{\vec{r}_1}\cdot\nabla_{\vec{q}_1^+}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)$$

$$-\int_0^\infty d\omega_1\nabla_{\vec{q}_1^+}\cdot\left(\left(\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)$$

$$+\int_0^\infty d\omega_1 \left(\nabla_{\vec{q}_1^+}\cdot\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\Big\}$$

| for 2nd term, integral limits vanishes

| assume cross derivatives "commute" then 5th and 7th term cancels

$$\begin{aligned}
&= \frac{1}{2\omega_{j_1\vec{q}_1^+}}\Bigg\{\frac{\partial E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)}{\partial\omega_{j_1\vec{q}_1^+}}\frac{\partial N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)}{\partial t_1^+}+\frac{\partial^2E_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)}{\partial\omega_{j_1\vec{q}_1^+}\partial t_1^+}N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\\
&\quad+\nabla_{\vec{r}_1}\cdot\left(\left(\nabla_{\vec{q}_1^+}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\Big|_{\omega_1=\omega_{j_1\vec{q}_1^+}}\\
&\quad-\int_0^\infty d\omega_1\nabla_{\vec{q}_1^+}\cdot\left((\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+))\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\Bigg\}\\
&= \frac{1}{2\omega_{j_1\vec{q}_1^+}}\Bigg\{\frac{\partial}{\partial t_1^+}\left(\frac{\partial E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)}{\partial\omega_{j_1\vec{q}_1^+}}N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\right)\\
&\quad+\nabla_{\vec{r}_1}\cdot\left(\left(\nabla_{\vec{q}_1^+}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\Big|_{\omega_1=\omega_{j_1\vec{q}_1^+}}\\
&\quad-\int_0^\infty d\omega_1\nabla_{\vec{q}_1^+}\cdot\left((\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+))\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\Bigg\}
\end{aligned}\tag{5.694}$$

We have a real collision integral here, so it should be physical just like its zeroth order collision integral. We can see that the third term $(\nabla_{\vec{q}_1^+}E)\cdot(\nabla_{\vec{r}_1}N_{j_1\vec{q}_1^+})$ is related to a renormalization of the harmonic group velocity. Again the other terms do not look like collision terms as they do not have the energy conservation delta functions. We can probably interprete them as interbranch and intrabranch phonon mode mixing terms due to spatial ($\nabla_{\vec{r}_1}$ terms) and temporal ($\frac{\partial}{\partial t_1^+}$ terms) correlations.

5.6.3.3 $V^{(4ph)^2}$ Term*

The self energy in (Fourier transformed) Wigner coordinates is

$$\begin{aligned}
&\Sigma^{\lessgtr}_{j_1j_2}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\\
&= 2\pi\frac{-1}{3}\left(\frac{\hbar}{i}\right)^2\sum_{j_1\vec{q}_3^+j_4\vec{q}_4^+j_5\vec{q}_5^+j_6j_7j_8}\tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\tilde{V}^{(4ph)}_{j_7j_8j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},-\vec{q}_5^{\,+},\vec{q}_1^{\,+})\\
&\quad\times\int\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\frac{d\omega_4}{2\pi}\delta(\omega_1-\omega_2-\omega_3-\omega_4)D^{\lessgtr}_{j_5j_6}(\vec{r}_1\omega_2\vec{q}_5^{\,+}t_1^+)D^{\lessgtr}_{j_3j_7}(\vec{r}_1\omega_3\vec{q}_3^{\,+}t_1^+)D^{\lessgtr}_{j_4j_8}(\vec{r}_1\omega_4\vec{q}_4^{\,+}t_1^+)
\end{aligned}$$

We work out the principal integral first but since the derivation is very similar to that for $V^{(3ph)^2}$, we try to omit steps here.

$$\begin{aligned}
&\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma_{j_1j_1}(\vec{r}_1\omega'\vec{q}_1^{\,+}t_1^+)}{\omega_1-\omega'}\\
&= 2\pi\frac{-1}{3}\left(\frac{\hbar}{i}\right)^2\sum_{j_1\vec{q}_3^+j_4\vec{q}_4^+j_5\vec{q}_5^+j_6j_7j_8}\tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\tilde{V}^{(4ph)}_{j_7j_8j_6j_2}(-\vec{q}_3^{\,+},-\vec{q}_4^{\,+},-\vec{q}_5^{\,+},\vec{q}_1^{\,+})\\
&\quad\times\int\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}\frac{d\omega_4}{2\pi}\left(\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\delta(\omega'-\omega_2-\omega_3-\omega_4)}{\omega_1-\omega'}\right)
\end{aligned}$$

$$\times i\left(D^{>}_{j_5j_6}D^{>}_{j_3j_7}D^{>}_{j_4j_8}-D^{<}_{j_5j_6}D^{<}_{j_3j_7}D^{<}_{j_4j_8}\right)(\vec{r}_1\omega_2\vec{q}_5^{\,+}t_1^+)(\vec{r}_1\omega_3\vec{q}_3^{\,+}t_1^+)(\vec{r}_1\omega_4\vec{q}_4^{\,+}t_1^+) \tag{5.695}$$

| note that $\mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\delta(\omega'-\omega_2-\omega_3-\omega_4)}{\omega_1-\omega'}=\frac{1}{2\pi}\frac{1}{\omega_1-\omega_2-\omega_3-\omega_4}$

| then insert the free spectral KB ansatz for $D^>$ and $D^<$, all 2π cancels

| there are 8 delta functions to evaluate & do not expand $(1+N)(1+N)(1+N)-NNN$

| also use identity $N(-\omega)=-(1+N(\omega))$

| and we drop the $(\vec{r}_1t_1^+)$ arguments in all distribution functions

$$\begin{aligned}
=\;& \frac{+1}{3}\left(\frac{\hbar}{i}\right)^2\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}j_5\vec{q}_5^{\,+}}\frac{\left|\tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+},\vec{q}_5^{\,+})\right|^2}{2\omega_{j_3\vec{q}_3^{\,+}}2\omega_{j_4\vec{q}_4^{\,+}}2\omega_{j_5\vec{q}_5^{\,+}}}\\
&\times\left\{\frac{\left(1+N_{j_3\vec{q}_3^{\,+}}\right)\left(1+N_{j_4\vec{q}_4^{\,+}}\right)\left(1+N_{j_5\vec{q}_5^{\,+}}\right)-N_{j_3\vec{q}_3^{\,+}}N_{j_4\vec{q}_4^{\,+}}N_{j_5\vec{q}_5^{\,+}}}{\omega_1-\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}}\right.\\
&+\frac{\left(1+N_{j_3\vec{q}_3^{\,+}}\right)N_{j_4\vec{q}_4^{\,+}}\left(1+N_{j_5\vec{q}_5^{\,+}}\right)-N_{j_3\vec{q}_3^{\,+}}\left(1+N_{j_4\vec{q}_4^{\,+}}\right)N_{j_5\vec{q}_5^{\,+}}}{\omega_1-\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}}\\
&+\frac{N_{j_3\vec{q}_3^{\,+}}\left(1+N_{j_4\vec{q}_4^{\,+}}\right)\left(1+N_{j_5\vec{q}_5^{\,+}}\right)-\left(1+N_{j_3\vec{q}_3^{\,+}}\right)N_{j_4\vec{q}_4^{\,+}}N_{j_5\vec{q}_5^{\,+}}}{\omega_1+\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}}\\
&+\frac{\left(1+N_{j_3\vec{q}_3^{\,+}}\right)\left(1+N_{j_4\vec{q}_4^{\,+}}\right)N_{j_5\vec{q}_5^{\,+}}-N_{j_3\vec{q}_3^{\,+}}N_{j_4\vec{q}_4^{\,+}}\left(1+N_{j_5\vec{q}_5^{\,+}}\right)}{\omega_1-\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}}+\omega_{j_5\vec{q}_5^{\,+}}}\\
&+\frac{N_{j_3\vec{q}_3^{\,+}}N_{j_4\vec{q}_4^{\,+}}\left(1+N_{j_5\vec{q}_5^{\,+}}\right)-\left(1+N_{j_3\vec{q}_3^{\,+}}\right)\left(1+N_{j_4\vec{q}_4^{\,+}}\right)N_{j_5\vec{q}_5^{\,+}}}{\omega_1+\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}}-\omega_{j_5\vec{q}_5^{\,+}}}\\
&+\frac{\left(1+N_{j_3\vec{q}_3^{\,+}}\right)N_{j_4\vec{q}_4^{\,+}}N_{j_5\vec{q}_5^{\,+}}-N_{j_3\vec{q}_3^{\,+}}\left(1+N_{j_4\vec{q}_4^{\,+}}\right)\left(1+N_{j_5\vec{q}_5^{\,+}}\right)}{\omega_1-\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}}+\omega_{j_5\vec{q}_5^{\,+}}}\\
&+\frac{N_{j_3\vec{q}_3^{\,+}}\left(1+N_{j_4\vec{q}_4^{\,+}}\right)N_{j_5\vec{q}_5^{\,+}}-\left(1+N_{j_3\vec{q}_3^{\,+}}\right)N_{j_4\vec{q}_4^{\,+}}\left(1+N_{j_5\vec{q}_5^{\,+}}\right)}{\omega_1+\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}}+\omega_{j_5\vec{q}_5^{\,+}}}\\
&\left.+\frac{N_{j_3\vec{q}_3^{\,+}}N_{j_4\vec{q}_4^{\,+}}N_{j_5\vec{q}_5^{\,+}}-\left(1+N_{j_3\vec{q}_3^{\,+}}\right)\left(1+N_{j_4\vec{q}_4^{\,+}}\right)\left(1+N_{j_5\vec{q}_5^{\,+}}\right)}{\omega_1+\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}}+\omega_{j_5\vec{q}_5^{\,+}}}\right\} \qquad (5.696)\\
\equiv\;& F_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+) \qquad (5.697)
\end{aligned}$$

where the definition of symbol $F_{j_1j_1}$ is simply to save writing later.

First Term of $I_{1\mathrm{st}}$

$$=\frac{1}{i}\int_0^\infty d\omega_1\left[\frac{1}{\omega_1^2-\omega^2_{j_1\vec{q}_1^{\,+}}},\Sigma^<_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right]_{GPB}\Bigg|_{\text{free spectral KB}} \tag{5.698}$$

| insert the self energy expression and then the free spectral KB ansatz

| 8 delta functions obtained and the 8th one dropped as it does not conserve energy

| then expand the Poisson brackets

$$
\begin{aligned}
= \;& 2\pi \frac{-1}{3}\left(\frac{\hbar}{i}\right)^2 \sum_{j_1\vec{q}_3{}^+ j_4\vec{q}_4{}^+ j_5\vec{q}_5{}^+} \int_0^\infty \frac{d\omega_1}{2\pi} \frac{1}{2\omega_{j_3\vec{q}_3{}^+} 2\omega_{j_4\vec{q}_4{}^+} 2\omega_{j_5\vec{q}_5{}^+}} \\
& \times \left\{ \left(\frac{\partial}{\partial\omega_1} \frac{1}{\omega_1^2 - \omega^2_{j_1\vec{q}_1{}^+}} \right) \left| \tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1{}^+, \vec{q}_3{}^+, \vec{q}_4{}^+, \vec{q}_5{}^+) \right|^2 \frac{\partial}{\partial t_1^+} (\cdots 7 \text{ terms} \cdots) \right. \\
& \left. + \left(\nabla_{\vec{q}_1{}^+} \frac{1}{\omega_1^2 - \omega^2_{j_1\vec{q}_1{}^+}} \right) \left| \tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1{}^+, \vec{q}_3{}^+, \vec{q}_4{}^+, \vec{q}_5{}^+) \right|^2 \cdot \nabla_{\vec{r}_1} (\cdots 7 \text{ terms} \cdots) \right\} \qquad (5.699) \\
| \;& \text{write } \frac{\partial}{\partial\omega_1} \frac{1}{\omega_1^2 - \omega^2_{j_1\vec{q}_1{}^+}} = \frac{-2\omega_1}{\left(\omega_1^2 - \omega^2_{j_1\vec{q}_1{}^+}\right)^2} \text{ and evaluate } \int_0^\infty d\omega_1 \\
| \;& \text{we drop the } (\vec{r}_1 t_1^+) \text{ in the distribution functions} \\
= \;& \frac{-1}{3}\left(\frac{\hbar}{i}\right)^2 \sum_{j_1\vec{q}_3{}^+ j_4\vec{q}_4{}^+ j_5\vec{q}_5{}^+} \int_0^\infty d\omega_1 \frac{\left| \tilde{V}^{(4ph)}_{j_1j_3j_4j_5}(-\vec{q}_1{}^+, \vec{q}_3{}^+, \vec{q}_4{}^+, \vec{q}_5{}^+) \right|^2}{2\omega_{j_3\vec{q}_3{}^+} 2\omega_{j_4\vec{q}_4{}^+} 2\omega_{j_5\vec{q}_5{}^+}} \\
& \times \left\{ -\frac{2(\omega_{j_3\vec{q}_3{}^+} + \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+})}{((\omega_{j_3\vec{q}_3{}^+} + \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+})^2 - \omega^2_{j_1\vec{q}_1{}^+})^2} \left(\frac{\partial}{\partial t_1^+} N_{j_3\vec{q}_3{}^+} N_{j_4\vec{q}_4{}^+} N_{j_5\vec{q}_5{}^+} \right) \right. \\
& - \frac{2|\omega_{j_3\vec{q}_3{}^+} + \omega_{j_4\vec{q}_4{}^+} - \omega_{j_5\vec{q}_5{}^+}|}{(|\omega_{j_3\vec{q}_3{}^+} + \omega_{j_4\vec{q}_4{}^+} - \omega_{j_5\vec{q}_5{}^+}|^2 - \omega^2_{j_1\vec{q}_1{}^+})^2} \left(\frac{\partial}{\partial t_1^+} N_{j_3\vec{q}_3{}^+} N_{j_4\vec{q}_4{}^+} \left(1 + N_{j_5\vec{q}_5{}^+}\right) \right) \\
& - \frac{2|\omega_{j_3\vec{q}_3{}^+} - \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+}|}{(|\omega_{j_3\vec{q}_3{}^+} - \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+}|^2 - \omega^2_{j_1\vec{q}_1{}^+})^2} \left(\frac{\partial}{\partial t_1^+} N_{j_3\vec{q}_3{}^+} \left(1 + N_{j_4\vec{q}_4{}^+}\right) N_{j_5\vec{q}_5{}^+} \right) \\
& - \frac{2|-\omega_{j_3\vec{q}_3{}^+} + \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+}|}{(|-\omega_{j_3\vec{q}_3{}^+} + \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+}|^2 - \omega^2_{j_1\vec{q}_1{}^+})^2} \left(\frac{\partial}{\partial t_1^+} \left(1 + N_{j_3\vec{q}_3{}^+}\right) N_{j_4\vec{q}_4{}^+} N_{j_5\vec{q}_5{}^+} \right) \\
& - \frac{2|-\omega_{j_3\vec{q}_3{}^+} - \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+}|}{(|-\omega_{j_3\vec{q}_3{}^+} - \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+}|^2 - \omega^2_{j_1\vec{q}_1{}^+})^2} \left(\frac{\partial}{\partial t_1^+} \left(1 + N_{j_3\vec{q}_3{}^+}\right) \left(1 + N_{j_4\vec{q}_4{}^+}\right) N_{j_5\vec{q}_5{}^+} \right) \\
& - \frac{2|\omega_{j_3\vec{q}_3{}^+} - \omega_{j_4\vec{q}_4{}^+} - \omega_{j_5\vec{q}_5{}^+}|}{(|\omega_{j_3\vec{q}_3{}^+} - \omega_{j_4\vec{q}_4{}^+} - \omega_{j_5\vec{q}_5{}^+}|^2 - \omega^2_{j_1\vec{q}_1{}^+})^2} \left(\frac{\partial}{\partial t_1^+} N_{j_3\vec{q}_3{}^+} \left(1 + N_{j_4\vec{q}_4{}^+}\right) \left(1 + N_{j_5\vec{q}_5{}^+}\right) \right) \\
& - \frac{2|-\omega_{j_3\vec{q}_3{}^+} + \omega_{j_4\vec{q}_4{}^+} - \omega_{j_5\vec{q}_5{}^+}|}{(|-\omega_{j_3\vec{q}_3{}^+} + \omega_{j_4\vec{q}_4{}^+} - \omega_{j_5\vec{q}_5{}^+}|^2 - \omega^2_{j_1\vec{q}_1{}^+})^2} \left(\frac{\partial}{\partial t_1^+} \left(1 + N_{j_3\vec{q}_3{}^+}\right) N_{j_4\vec{q}_4{}^+} \left(1 + N_{j_5\vec{q}_5{}^+}\right) \right) \\
& + \left(\nabla_{\vec{q}_1{}^+} \frac{1}{(\omega_{j_3\vec{q}_3{}^+} + \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+})^2 - \omega^2_{j_1\vec{q}_1{}^+}} \right) \cdot \left(\nabla_{\vec{r}_1} N_{j_3\vec{q}_3{}^+} N_{j_4\vec{q}_4{}^+} N_{j_5\vec{q}_5{}^+} \right) \\
& + \left(\nabla_{\vec{q}_1{}^+} \frac{1}{|-\omega_{j_3\vec{q}_3{}^+} + \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+}|^2 - \omega^2_{j_1\vec{q}_1{}^+}} \right) \cdot \left(\nabla_{\vec{r}_1} \left(1 + N_{j_3\vec{q}_3{}^+}\right) N_{j_4\vec{q}_4{}^+} N_{j_5\vec{q}_5{}^+} \right) \\
& + \left(\nabla_{\vec{q}_1{}^+} \frac{1}{|\omega_{j_3\vec{q}_3{}^+} - \omega_{j_4\vec{q}_4{}^+} + \omega_{j_5\vec{q}_5{}^+}|^2 - \omega^2_{j_1\vec{q}_1{}^+}} \right) \cdot \left(\nabla_{\vec{r}_1} N_{j_3\vec{q}_3{}^+} \left(1 + N_{j_4\vec{q}_4{}^+}\right) N_{j_5\vec{q}_5{}^+} \right)
\end{aligned}
$$

$$+\left(\nabla_{\vec{q}_1^+}\frac{1}{|\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+}-\omega_{j_5\vec{q}_5^+}|^2-\omega^2_{j_1\vec{q}_1^+}}\right)\cdot\left(\nabla_{\vec{r}_1}N_{j_3\vec{q}_3^+}N_{j_4\vec{q}_4^+}\left(1+N_{j_5\vec{q}_5^+}\right)\right)$$
$$+\left(\nabla_{\vec{q}_1^+}\frac{1}{|-\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}+\omega_{j_5\vec{q}_5^+}|^2-\omega^2_{j_1\vec{q}_1^+}}\right)\cdot\left(\nabla_{\vec{r}_1}\left(1+N_{j_3\vec{q}_3^+}\right)\left(1+N_{j_4\vec{q}_4^+}\right)N_{j_5\vec{q}_5^+}\right)$$
$$+\left(\nabla_{\vec{q}_1^+}\frac{1}{|\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}-\omega_{j_5\vec{q}_5^+}|^2-\omega^2_{j_1\vec{q}_1^+}}\right)\cdot\left(\nabla_{\vec{r}_1}N_{j_3\vec{q}_3^+}\left(1+N_{j_4\vec{q}_4^+}\right)\left(1+N_{j_5\vec{q}_5^+}\right)\right)$$
$$+\left(\nabla_{\vec{q}_1^+}\frac{1}{|-\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+}-\omega_{j_5\vec{q}_5^+}|^2-\omega^2_{j_1\vec{q}_1^+}}\right)\cdot\left(\nabla_{\vec{r}_1}\left(1+N_{j_3\vec{q}_3^+}\right)N_{j_4\vec{q}_4^+}\left(1+N_{j_5\vec{q}_5^+}\right)\right)\Bigg\} \tag{5.700}$$

For the second term of $I_{1\text{st}}$, we see that the self energy part is only in the principal integral, thus what we derived in $V^{(3ph)^2}$ is valid for this case and we simply need to replace E with F.

$$\begin{aligned}
&\text{Second Term of } I_{1\text{st}}\\
=\;&\frac{1}{2\omega_{j_1\vec{q}_1^+}}\left\{\frac{\partial}{\partial t_1^+}\left(\frac{\partial F_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)}{\partial\omega_{j_1\vec{q}_1^+}}N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\right)\right.\\
&+\nabla_{\vec{r}_1}\cdot\left(\left(\nabla_{\vec{q}_1^+}F_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)\Big|_{\omega_1=\omega_{j_1\vec{q}_1^+}}\\
&\left.-\int_0^\infty d\omega_1\nabla_{\vec{q}_1^+}\cdot\left(\left(\nabla_{\vec{r}_1}F_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^+t_1^+)\right)\right\}
\end{aligned} \tag{5.701}$$

We have a real collision integral here. Again the term $(\nabla_{\vec{q}_1^+}F)\cdot(\nabla_{\vec{r}_1}N_{j_1\vec{q}_1^+})$ appears to be related to a renormalization of the harmonic group velocity. The other terms seem to look like phonon modes mixing terms and the mixing due to $V^{(4ph)^2}$ appears to be even more complicated than that due to $V^{(3ph)^2}$.

[Contribution:] Here I will state briefly what this contribution of first order collision integrals is about. Recall that the exact Kadanoff-Baym equations have the following features: time reversibility (causality) and quantum interactions (collisions and correlations) but the kinetic equations in the Boltzmann form (or in the form containing only zeroth order collision integrals) have only the collisional part of interactions. The first order collision integrals restore a large portion of the correlational part of interactions to the kinetic equations. It is important to consider correlations as, mentioned in Introduction (Chapter 2), phonon transport is semi-coherent in such small systems and it was never clear how correlations affect transport. Here, explicit expressions are given for various phonon-phonon interactions and some interpretation has been given which is probably not the whole story. The full kinetic equation with the zeroth and first order terms needs to be solved and the distribution solution can be compared with that solved without the first order terms. The effects of correlation on the evolution of the distribution can then be seen. The effects of correlation on other physical quantities are calculated in section 5.6.4.

5.6.3.4 Discussion on other collision integrals

The trend is the same as that for the zeroth order terms: self consistent self energies with odd numbers of anharmonic coefficients give rise to imaginary first order collision integrals and self consistent self energies with even numbers of anharmonic coefficients give rise to real first order collision integrals. So, $V^{(3ph)^2}V^{(4ph)}$ Type-1,2,3 self energies give imaginary I_{1st} and $V^{(3ph)^4}$ self energy gives real I_{1st}.

It is obvious that the phonon mixing is going to get more complicated when higher orders of self consistent self energies are used. $V^{(3ph)^4}$ self consistent self energy is a vertex term, and the first order collision integral derived from it will contain phonon mixing due to vertex corrections which is exceedingly complicated and physically unclear to me.

5.6.4 Applications of QKE on top of BE (for second sound)*

In summary, what QKE (NEGF + Wigner coordinates + gradient expansion + free spectral KB ansatz) has to offer is a framework that allows the inclusion of higher orders of 3-phonon and 4-phonon collisions and the inclusion of 3-phonon and 4-phonon correlations. The higher order collision terms are given by the zeroth order gradient terms of higher self consistent self energies with even numbers of coupling constants. The correlations are given by first order (and higher orders) gradient terms. [27] can be included when $I^{(3ph)}_{\text{zeroth}}$ is already included. The other way round is obviously nonsense.

Our interest in this section is a specific discussion to see how QKE modifies the second sound description given by BE earlier. [28]

Recall that we defined 4 hydrodynamic variables and then rewrote BE into these variables to get the balance equations which are simply the "energy continuity equation" and the "momentum continuity equation". Now we turn the logic around. We will use that method of rewriting to turn QKE into balance equations and define the 4 hydrodynamic variables from them.

The $V^{(3ph)^2}$ QKE is used to illustrate the case, it is

$$\left(\frac{\partial}{\partial t_1^+} + \left(\nabla_{\vec{q}_1^+}\omega_{j_1\vec{q}_1^+}\right)\cdot\nabla_{\vec{r}_1}\right)N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+) = I^{(3ph)}_{\text{zeroth}} + I^{(3ph)}_{\text{1st}} \tag{5.702}$$

By now, there are many hints that $I^{(3ph)}_{\text{1st}}$ should be moved to LHS as it is unrelated to readjustments in particle distribution due to collisions. We will not need the explicit form of $I^{(3ph)}_{\text{zeroth}}$ but we need these 2 relations of $I^{(3ph)}_{\text{zeroth}}$.

$$\sum_{j_1\vec{q}_1^+}\hbar\omega_{j_1\vec{q}_1^+}I^{(3ph)}_{\text{zeroth}} = 0 \quad , \quad \sum_{j_1\vec{q}_1^+}\hbar\vec{q}_1 I^{(3ph)}_{\text{zeroth}} = \sum_{j_1\vec{q}_1^+}\hbar\vec{q}_1 I^{(3ph)}_{\text{zeroth,U}} \tag{5.703}$$

We write the QKE out, grouping similar terms,

$$\begin{aligned}
&\frac{\partial}{\partial t_1^+}\left\{N_{j_1\vec{q}_1^+} - \frac{1}{2\omega_{j_1\vec{q}_1^+}}\left(\frac{\partial E_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)}{\partial\omega_{j_1\vec{q}_1^+}}N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\right)\right.\\
&+\frac{\hbar}{2}\sum_{j_3\vec{q}_3^+j_4\vec{q}_4^+}\frac{|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})|^2}{2\omega_{j_3\vec{q}_3^+}2\omega_{j_4\vec{q}_4^+}}\left(\frac{2(\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+})}{((\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+})^2-\omega^2_{j_1\vec{q}_1^+})^2}N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)\right.\\
&\left.\left.+\frac{4|\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}|}{(|\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}|^2-\omega^2_{j_1\vec{q}_1^+})^2}N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)\left(1+N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)\right)\right)\right\}
\end{aligned}$$

[27] In writing down a QKE, a first order gradient term of a particular self energy can only be included if the corresponding zeroth order gradient term is already included. Example, $I^{(3ph)}_{\text{1st}}$

[28] It turns out that the discussion here will be similar to the discussion of QKE on H-theorem in the NEGF chapter.

$$
\begin{aligned}
& +\nabla_{\vec{r}_1}\cdot\left\{\left(\nabla_{\vec{q}_1^+}\omega_{j_1\vec{q}_1^+}\right)N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)-\frac{1}{2\omega_{j_1\vec{q}_1^+}}\left(\left(\nabla_{\vec{q}_1^+}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\Big|_{\omega_1=\omega_{j_1\vec{q}_1^+}}\right.\\
& -\frac{\hbar}{2}\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}}\frac{|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})|^2}{2\omega_{j_3\vec{q}_3^+}2\omega_{j_4\vec{q}_4^+}}\left(\left(\nabla_{\vec{q}_1^+}\frac{1}{(\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+})^2-\omega^2_{j_1\vec{q}_1^+}}\right)N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)\right.\\
& \left.\left.+2\left(\nabla_{\vec{q}_1^+}\frac{1}{|\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}|^2-\omega^2_{j_1\vec{q}_1^+}}\right)N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)\left(1+N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)\right)\right)\right\}\\
& +\frac{1}{2\omega_{j_1\vec{q}_1^+}}\int_0^\infty d\omega_1\nabla_{\vec{q}_1^+}\cdot\left(\left(\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\\
= \;& I^{(3ph)}_{\text{zeroth}} \qquad (5.704)
\end{aligned}
$$

For the energy balance equation, we multiply $\frac{1}{V}\hbar\omega_{j_1\vec{q}_1^+}$ and sum $\sum_{j_1\vec{q}_1^+}$ on both sides of the QKE. Use $\sum_{j_1\vec{q}_1^+}\hbar\omega_{j_1\vec{q}_1^+}I^{(3ph)}_{\text{zeroth}}=0$ and we get

$$
\begin{aligned}
& \frac{\partial\epsilon^{\text{corr}}(\vec{r}_1t_1^+)}{\partial t_1^+}+\nabla_{\vec{r}_1}\vec{J}^{\text{corr}}(\vec{r}_1t_1^+)\\
& +\frac{\hbar}{2V}\int_0^\infty d\omega_1\sum_{j_1\vec{q}_1^+}\nabla_{\vec{q}_1^+}\cdot\left(\left(\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^+})-\delta(\omega_1+\omega_{j_1\vec{q}_1^+})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\\
& =0 \qquad (5.705)
\end{aligned}
$$

The third term on LHS vanishes as it is a surface term in wave-vector space, giving

$$
\frac{\partial\epsilon^{\text{corr}}(\vec{r}_1t_1^+)}{\partial t_1^+}+\nabla_{\vec{r}_1}\vec{J}^{\text{corr}}(\vec{r}_1t_1^+)=0 \qquad (5.706)
$$

with the "correlated" energy density ϵ^{corr} defined as

$$
\begin{aligned}
& \epsilon^{\text{corr}}(\vec{r}_1t_1^+)\\
\equiv\;& \frac{1}{V}\sum_{j_1\vec{q}_1^+}\hbar\omega_{j_1\vec{q}_1^+}\left\{N_{j_1\vec{q}_1^+}-\frac{1}{2\omega_{j_1\vec{q}_1^+}}\left(\frac{\partial E_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^+}\vec{q}_1^{\,+}t_1^+)}{\partial\omega_{j_1\vec{q}_1^+}}N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\right)\right.\\
& +\frac{\hbar}{2}\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}}\frac{|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})|^2}{2\omega_{j_3\vec{q}_3^+}2\omega_{j_4\vec{q}_4^+}}\left(\frac{2(\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+})}{((\omega_{j_3\vec{q}_3^+}+\omega_{j_4\vec{q}_4^+})^2-\omega^2_{j_1\vec{q}_1^+})^2}N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)\right.\\
& \left.\left.+\frac{4|\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}|}{(|\omega_{j_3\vec{q}_3^+}-\omega_{j_4\vec{q}_4^+}|^2-\omega^2_{j_1\vec{q}_1^+})^2}N_{j_3\vec{q}_3^+}(\vec{r}_1t_1^+)\left(1+N_{j_4\vec{q}_4^+}(\vec{r}_1t_1^+)\right)\right)\right\} \qquad (5.707)
\end{aligned}
$$

and the "correlated" energy current $\vec{J}^{\text{corr}}$ defined as

$$
\begin{aligned}
& \vec{J}^{\text{corr}}(\vec{r}_1t_1^+)\\
\equiv\;& \frac{1}{V}\sum_{j_1\vec{q}_1^+}\hbar\omega_{j_1\vec{q}_1^+}\left\{\quad\left(\nabla_{\vec{q}_1^+}\omega_{j_1\vec{q}_1^+}\right)N_{j_1\vec{q}_1^+}(\vec{r}_1t_1^+)\right.
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\left(\nabla_{\vec{q}_1^{\,+}}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\Big|_{\omega_1=\omega_{j_1\vec{q}_1^{\,+}}}\\
&-\frac{\hbar}{2}\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}}\frac{|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})|^2}{2\omega_{j_3\vec{q}_3^{\,+}}2\omega_{j_4\vec{q}_4^{\,+}}}\left(\left(\nabla_{\vec{q}_1^{\,+}}\frac{1}{(\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}})^2-\omega^2_{j_1\vec{q}_1^{\,+}}}\right)N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\right.\\
&\left.\left.+2\left(\nabla_{\vec{q}_1^{\,+}}\frac{1}{|\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}}|^2-\omega^2_{j_1\vec{q}_1^{\,+}}}\right)N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\left(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\right)\right)\right\} \qquad (5.708)
\end{aligned}
$$

For the momentum balance equation, we multiply $\frac{1}{V}\hbar(\vec{q}_1^{\,+})_{\alpha_1}$ and sum $\sum_{j_1\vec{q}_1^{\,+}}$ on both sides of the QKE. Use

$$
\sum_{j_1\vec{q}_1^{\,+}}\hbar(\vec{q}_1^{\,+})_{\alpha_1}I^{(3ph)}_{\text{zeroth}}=\sum_{j_1\vec{q}_1^{\,+}}\hbar(\vec{q}_1^{\,+})_{\alpha_1}I^{(3ph)}_{\text{zeroth,U}} \qquad (5.709)
$$

We get,

$$
\begin{aligned}
&\frac{\partial P^{\text{corr}}_{\alpha_1}(\vec{r}_1t_1^+)}{\partial t_1^+}+\sum_{\alpha_2}\frac{\partial G^{\text{corr}}_{\alpha_1\alpha_2}}{\partial r_{\alpha_2}}\\
&+\frac{\hbar}{2V}\int_0^\infty d\omega_1\sum_{j_1\vec{q}_1^{\,+}}\sum_{\alpha_2}\frac{(\vec{q}_1^{\,+})_{\alpha_1}}{\omega_{j_1\vec{q}_1^{\,+}}}\frac{\partial}{\partial(\vec{q}_1^{\,+})_{\alpha_2}}\\
&\times\left(\left(\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\\
&=\frac{1}{V}\sum_{j_1\vec{q}_1^{\,+}}\hbar(\vec{q}_1^{\,+})_{\alpha_1}I^{(3ph)}_{\text{zeroth,U}} \qquad (5.710)
\end{aligned}
$$

with the "correlated" momentum density $P^{\text{corr}}_{\alpha_1}$ defined as

$$
\begin{aligned}
&P^{\text{corr}}_{\alpha_1}(\vec{r}_1t_1^+)\\
\equiv\;&\frac{1}{V}\sum_{j_1\vec{q}_1^{\,+}}\hbar(\vec{q}_1^{\,+})_{\alpha_1}\left\{N_{j_1\vec{q}_1^{\,+}}-\frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\frac{\partial E_{j_1j_1}(\vec{r}_1\omega_{j_1\vec{q}_1^{\,+}}\vec{q}_1^{\,+}t_1^+)}{\partial\omega_{j_1\vec{q}_1^{\,+}}}N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1t_1^+)\right)\right.\\
&+\frac{\hbar}{2}\sum_{j_3\vec{q}_3^{\,+}j_4\vec{q}_4^{\,+}}\frac{|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})|^2}{2\omega_{j_3\vec{q}_3^{\,+}}2\omega_{j_4\vec{q}_4^{\,+}}}\left(\frac{2(\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}})}{((\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}})^2-\omega^2_{j_1\vec{q}_1^{\,+}})^2}N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\right.\\
&\left.\left.+\frac{4|\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}}|}{(|\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}}|^2-\omega^2_{j_1\vec{q}_1^{\,+}})^2}N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\left(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\right)\right)\right\} \qquad (5.711)
\end{aligned}
$$

and the "correlated" momentum flux tensor $G^{\text{corr}}_{\alpha_1\alpha_2}$ defined as,

$$
\begin{aligned}
&G^{\text{corr}}_{\alpha_1\alpha_2}(\vec{r}_1t_1^+)\\
\equiv\;&\frac{1}{V}\sum_{j_1\vec{q}_1^{\,+}}\hbar(\vec{q}_1^{\,+})_{\alpha_1}
\end{aligned}
$$

$$
\times\Bigg\{\left(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}}\right)_{\alpha_2} N_{j_1\vec{q}_1^{\,+}}(\vec{r}_1 t_1^+) - \frac{1}{2\omega_{j_1\vec{q}_1^{\,+}}}\left(\left(\nabla_{\vec{q}_1^{\,+}} E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)_{\alpha_2} N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\Big|_{\omega_1=\omega_{j_1\vec{q}_1^{\,+}}}
$$

$$
-\frac{\hbar}{2}\sum_{j_3\vec{q}_3^{\,+} j_4\vec{q}_4^{\,+}} \frac{|\tilde{V}^{(3ph)}_{j_1j_3j_4}(-\vec{q}_1^{\,+},\vec{q}_3^{\,+},\vec{q}_4^{\,+})|^2}{2\omega_{j_3\vec{q}_3^{\,+}}2\omega_{j_4\vec{q}_4^{\,+}}}\left(\left(\nabla_{\vec{q}_1^{\,+}}\frac{1}{(\omega_{j_3\vec{q}_3^{\,+}}+\omega_{j_4\vec{q}_4^{\,+}})^2-\omega^2_{j_1\vec{q}_1^{\,+}}}\right)_{\alpha_2} N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\right.
$$

$$
\left.+2\left(\nabla_{\vec{q}_1^{\,+}}\frac{1}{|\omega_{j_3\vec{q}_3^{\,+}}-\omega_{j_4\vec{q}_4^{\,+}}|^2-\omega^2_{j_1\vec{q}_1^{\,+}}}\right)_{\alpha_2} N_{j_3\vec{q}_3^{\,+}}(\vec{r}_1t_1^+)\left(1+N_{j_4\vec{q}_4^{\,+}}(\vec{r}_1t_1^+)\right)\right)\Bigg\} \tag{5.712}
$$

But there is an extra term on LHS! I am unsure if this extra term could have the meaning of source/sink of momentum. All I can show is that at least in an isotropic solid (wave-vectors are orthogonal and equal in length) and in the regime of low temperature (where second sound can occur and isotropic Debye dispersion $\omega = v|\vec{q}^{\,+}|$ can be used as an approximation), the extra term vanishes.

$$
\begin{aligned}
&\quad \text{Extra term on LHS}\\
&= \frac{\hbar}{2V}\int_0^\infty d\omega_1 \sum_{j_1\vec{q}_1^{\,+}}\sum_{\alpha_2}\frac{(\vec{q}_1^{\,+})_{\alpha_1}}{\omega_{j_1\vec{q}_1^{\,+}}}\frac{\partial}{\partial(\vec{q}_1^{\,+})_{\alpha_2}}\\
&\quad \times\left(\left(\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)_{\alpha_2}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\\
&\quad |\ \text{use the product rule of differentiation}\\
&= \frac{\hbar}{2V}\int_0^\infty d\omega_1 \sum_{j_1\vec{q}_1^{\,+}}\sum_{\alpha_2}\frac{\partial}{\partial(\vec{q}_1^{\,+})_{\alpha_2}}\\
&\quad \times\left(\frac{(\vec{q}_1^{\,+})_{\alpha_1}}{\omega_{j_1\vec{q}_1^{\,+}}}\left(\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)_{\alpha_2}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)\\
&\quad -\frac{\hbar}{2V}\int_0^\infty d\omega_1 \sum_{j_1\vec{q}_1^{\,+}}\sum_{\alpha_2}\left(\frac{\partial}{\partial(\vec{q}_1^{\,+})_{\alpha_2}}\frac{(\vec{q}_1^{\,+})_{\alpha_1}}{\omega_{j_1\vec{q}_1^{\,+}}}\right)\\
&\quad \times\left(\left(\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)_{\alpha_2}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right) &(5.713)\\
&\quad |\ \text{first line vanishes as surface term in wave-vector space}\\
&= -\frac{\hbar}{2V}\int_0^\infty d\omega_1 \sum_{j_1\vec{q}_1^{\,+}}\sum_{\alpha_2}\left(\frac{\delta_{\alpha_1\alpha_2}}{\omega_{j_1\vec{q}_1^{\,+}}}-\frac{(\vec{q}_1^{\,+})_{\alpha_1}(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}})_{\alpha_2}}{\omega^2_{j_1\vec{q}_1^{\,+}}}\right)\\
&\quad \times\left(\left(\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)_{\alpha_2}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right) &(5.714)\\
&= -\frac{\hbar}{2V}\int_0^\infty d\omega_1 \sum_{j_1\vec{q}_1^{\,+}}\sum_{\alpha_2}\left(\frac{\delta_{\alpha_1\alpha_2}\omega_{j_1\vec{q}_1^{\,+}}-(\vec{q}_1^{\,+})_{\alpha_1}(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}})_{\alpha_2}}{\omega^2_{j_1\vec{q}_1^{\,+}}}\right)\\
&\quad \times\left(\left(\nabla_{\vec{r}_1}E_{j_1j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right)_{\alpha_2}\left(\delta(\omega_1-\omega_{j_1\vec{q}_1^{\,+}})-\delta(\omega_1+\omega_{j_1\vec{q}_1^{\,+}})\right)N_{j_1}(\vec{r}_1\omega_1\vec{q}_1^{\,+}t_1^+)\right) &(5.715)\\
&\quad |\ \text{use the isotropic Debye dispersion } \omega_{j_1\vec{q}_1^{\,+}} = v|\vec{q}_1^{\,+}| \text{ with } v=\left(\nabla_{\vec{q}_1^{\,+}}\omega_{j_1\vec{q}_1^{\,+}}\right)_\alpha\\
&= 0 &(5.716)
\end{aligned}
$$

Thus the correlations/mixing are (most reasonably) defined to be corrections to the 4 hydrodynamic variables, although we should note that the extra term in the momentum balance equation vanishes only under certain conditions.

We could push the calculation further by defining a "correlated" thermal conductivity $\overleftrightarrow{\kappa}^{\text{corr}}$ via the Fourier's law (in steady state)

$$\vec{J}^{\text{corr}}(\vec{r}_1) \equiv -\overleftrightarrow{\kappa}^{\text{corr}} \left(\nabla_{\vec{r}_1} T(\vec{r}_1)\right) \tag{5.717}$$

Finally we want to mention that in most of the second sound discussion earlier, the starting point was the use of the linearized drift distribution as an ansatz in the balance equations, so QKE does not seem to affect that discussion. Probably different effects will be seen when applying both QKE and BE in describing the evolution of an initial distribution to the drift distribution.

[**Contribution:**] Here I will state briefly what this contribution is about. These expressions given here are physical quantities with correlation included. They can only be evaluated with the distribution function solved from the kinetic equations with zeroth and first order collision integrals. Especially relevant for this thesis is the energy current. In fact, comparing the energy current $\vec{J}$ (solved with distribution containing only zeroth order collision integrals) and the correlated energy current $\vec{J}^{\text{corr}}$ (solved with distribution containing zeroth and first order collision integrals) will show clearly the effects of correlations on the energy current on top of collsional effects.

Chapter 6

Electron-Phonon Interaction

[Chapter Introduction and Roadmap:] We enumerate this introduction for easy reading.

1. The main aim of this chapter is to show that electron-phonon interaction has also been written into Hedin-like equations. This is done in the last section of the chapter. Recall that such a set of equations should generate conserving self energy approximations.

2. The first part of the chapter is standard treatment of deriving electron-phonon interaction Hamiltonian from the Hamiltonian of the solid. Then some phenomenological electron-phonon interaction Hamiltonians are discussed to indicate how the coupling constant can be chosen to fit a particular type of solid of interest. This is needed because electron-phonon interaction varies widely with the type of solid.

3. Then with regards to the 3 transport related developments, we discuss the kinetic theory first. The standard Boltzmann theory is given then QKE is given and the full quantum theory turns the kinetic equation into a non-Markovian one with intra-collisional field effect built in. Linear response theory is very briefly mentioned and Landauer-like theory is not mentioned at all.

6.1 General form of the electron-phonon interaction Hamiltonian

We are continuing the theoretical developments after Born-Oppenheimer adiabatic decoupling has "seperated" the electronic and ionic problems. Here, we will consider how the electrons interact with the ions but do not forget the uncontrolled double counting problem! There is already electronic contribution in the effective inter-ionic potential Φ (and hence in the phonon frequencies $\omega_{j\vec{q}}$), now we are considering their interaction via $W^{\text{el-I}}$ which makes the contribution of electrons coming in twice. Nevertheless, we will just carry on with this usual way of treating electron-ion interaction until we discuss van-Leeuwen's method of deriving electron-phonon Hedin-like equations where we will bypass the adiabatic decoupling.

In the section on Born-Oppenheimer adiabatic decoupling, we noted that if we make an expansion of $W^{\text{el-I}}$ about the equilibrium positions $\vec{R}_l^0$, we can perturbatively treat the electron-ion interaction.

$$\begin{aligned} W^{\text{el-I}} &= \sum_{il} V(\vec{r}_i - \vec{R}_l) && (6.1)\\ &= \sum_{il} V(\vec{r}_i - \vec{R}_l^0 - \vec{u}_l) && (6.2)\\ &= \sum_{il} V(\vec{r}_i - \vec{R}_l^0) - \sum_{il} \vec{u}_l \cdot \nabla_{\vec{R}_l} V(\vec{r}_i - \vec{R}_l)\Big|_{\vec{R}_l=\vec{R}_l^0} + \cdots && (6.3) \end{aligned}$$

We make some remarks at this point

1. Note that the first term $\sum_{il} V(\vec{r}_i - \vec{R}_l^0)$ is the term that is usually retained in calculating the effective ion-ion potential (from first principles).

2. The Hamiltonian terms $T^{\text{el}} + \sum_{il} V(\vec{r}_i - \vec{R}_l^0)$ can be further approximated to represent non-interacting electrons in a periodic potential. The solutions are Bloch functions.

3. The Hamiltonian terms

$$T^{\text{el}} + W^{\text{el-el}} + \sum_{il} V(\vec{r}_i - \vec{R}_l^0) \tag{6.4}$$

is usually further approximated by treating electrons as Coulomb-screened electrons in a periodic potential.

4. The second term $H^{(el-ph)} \equiv - \sum_{il} \vec{u}_l \cdot \nabla_{\vec{R}_l} V(\vec{r}_i - \vec{R}_l)\Big|_{\vec{R}_l = \vec{R}_l^0}$ is called the electron-phonon interaction Hamiltonian. We shall assume that electron-photon interaction causes electronic interband transitions and that electron-phonon interaction does not. Thus in writing the second quantized form for the electrons, we exclude electronic interband transitions.

We want to write $H^{(el-ph)}$ into second quantized form for field theoretic calculations. First, Fourier transform $V(\vec{r}_i - \vec{R}_l^0)$

$$\begin{aligned} V(\vec{r}_i - \vec{R}_l^0) &= \frac{1}{N} \sum_{\vec{k}} V_{\vec{k}} e^{i\vec{k}\cdot(\vec{r}_i - \vec{R}_l^0)} && (6.5) \\ \nabla_{\vec{R}_l} V(\vec{r}_i - \vec{R}_l^0)\Big|_{\vec{R}=\vec{R}^0} &= \frac{1}{N} \sum_{\vec{k}} (-i\vec{k}) V_{\vec{k}} e^{i\vec{k}\cdot(\vec{r}_i - \vec{R}_l^0)} && (6.6) \end{aligned}$$

The Hamiltonian is now

$$\begin{aligned} H^{(el-ph)} &= \frac{i}{N} \sum_l \sum_{\vec{k}} \left(\vec{u}_l \cdot \vec{k}\right) V_{\vec{k}} \left(\sum_i e^{i\vec{k}\cdot\vec{r}_i}\right) e^{-i\vec{k}\cdot\vec{R}_l^0} && (6.7) \\ &\quad | \text{ insert the second quantized form of displacement,}^1 \\ &\quad | \ \vec{u}_l = \sum_{j\vec{q}} \sqrt{\frac{\hbar}{2\rho V \omega_{j\vec{q}}}} \vec{\epsilon}(j\vec{q}) e^{i\vec{q}\cdot\vec{R}_l^0} \left(a_{j,-\vec{q}}^{\dagger} + a_{j\vec{q}}\right) \\ &= \frac{i}{N} \sum_l \sum_{\vec{k}} \sum_{j\vec{q}} \sqrt{\frac{\hbar}{2\rho V \omega_{j\vec{q}}}} \left(\vec{\epsilon}(j\vec{q}) \cdot \vec{k}\right) V_{\vec{k}} \left(\sum_i e^{i\vec{k}\cdot\vec{r}_i}\right) e^{i(\vec{q}-\vec{k})\cdot\vec{R}_l^0} \left(a^{j,-\vec{q}} + a_{j\vec{q}}\right) && (6.8) \end{aligned}$$

$H^{(el-ph)}$ can be seen as an electronic one-point function and we need to write it into the (fermionic) second quantized form. "Second quantizing" a one-point function in (real space) fermionic field operators

[1] The factor for displacement is usually $\sqrt{\frac{\hbar}{2MN\omega_{j\vec{q}}}}$. For theories in the long wavelength approximation, we will write $MN = \rho V$ and so the factor is $\sqrt{\frac{\hbar}{2\rho V \omega_{j\vec{q}}}}$. We consider a monoatomic solid here.

is simply done using the (real space) density $\psi^\dagger\psi$.

$$\begin{aligned}
& \sum_i e^{i\vec{k}\cdot\vec{r}_i} \\
= & \sum_{n\sigma} \int d\vec{r} e^{i\vec{k}\cdot\vec{r}} \psi^\dagger_{n\sigma}(\vec{r})\psi_{n\sigma}(\vec{r}) && (6.9) \\
| & \text{ write in momentum space form } \psi^\dagger_{n\sigma}(\vec{r}) = \frac{1}{\sqrt{V}}\sum_{\vec{k}_2} e^{-i\vec{k}_2\cdot\vec{r}}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})c^\dagger_{n\vec{k}_2\sigma} \text{ and hermitian conjugate} \\
= & \frac{1}{V}\sum_{n\sigma}\sum_{\vec{k}_1\vec{k}_2}\int d\vec{r} e^{i\left(\vec{k}+\vec{k}_1-\vec{k}_2\right)\cdot\vec{r}}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})c^\dagger_{n\vec{k}_2\sigma}c_{n\vec{k}_1\sigma} && (6.10) \\
| & \text{ take the long wavelength approximation,}^2 \\
| & \ \frac{1}{V}\int d\vec{r} e^{i\left(\vec{k}+\vec{k}_1-\vec{k}_2\right)\cdot\vec{r}}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r}) \approx \frac{1}{N}\sum_{\vec{R}^0} e^{i\left(\vec{k}+\vec{k}_1-\vec{k}_2\right)\cdot\vec{R}^0}\frac{1}{V_{\text{cell}}}\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r}) \\
| & \ = \sum_{\vec{g}}\delta_{\vec{k}_2,\vec{k}+\vec{k}_1+\vec{g}}\frac{N}{V}\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r}) \\
\approx & \sum_{n\sigma}\sum_{\vec{k}_1\vec{k}_2}\sum_{\vec{g}}\frac{N}{V}\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})\right)\delta_{\vec{k}_2,\vec{k}+\vec{k}_1+\vec{g}}c^\dagger_{n\vec{k}_2\sigma}c_{n\vec{k}_1\sigma} && (6.11) \\
| & \text{ evaluate the } \vec{k}_2 \text{ sum} \\
= & \sum_{n\sigma}\sum_{\vec{k}_1}\sum_{\vec{g}}\frac{N}{V}\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n,\vec{k}+\vec{k}_1+\vec{g}}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})\right)c^\dagger_{n,\vec{k}+\vec{k}_1+\vec{g},\sigma}c_{n\vec{k}_1\sigma} && (6.12)
\end{aligned}$$

The Hamiltonian written completely in second quantized (momentum variables) representation is,

$$\begin{aligned}
H^{(el-ph)} = & \frac{i}{V}\sum_l\sum_{\vec{k}}\sum_{j\vec{q}}\sum_{n\sigma}\sum_{\vec{k}_1}\sum_{\vec{g}}\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n,\vec{k}+\vec{k}_1+\vec{g}}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})\right)\sqrt{\frac{\hbar}{2\rho V\omega_{j\vec{q}}}}\left(\vec{\epsilon}(j\vec{q})\cdot\vec{k}\right) \\
& \times V_{\vec{k}}e^{i\left(\vec{q}-\vec{k}\right)\cdot\vec{R}^0_l}c^\dagger_{n,\vec{k}+\vec{k}_1+\vec{g},\sigma}c_{n\vec{k}_1\sigma}\left(a^\dagger_{j,-\vec{q}}+a_{j\vec{q}}\right) && (6.13) \\
| & \text{ write } \sum_l e^{i\left(\vec{q}-\vec{k}\right)\cdot\vec{R}^0_l} = \sum_{\vec{g}}\delta_{\vec{k},\vec{q}+\vec{g}} \text{ and combine the sum over } \vec{g} \\
| & \text{ evaluate the } \vec{k} \text{ sum and rename } \vec{k}_1 \text{ as } \vec{k} \\
= & \frac{i}{V}\sum_{\vec{k}}\sum_{j\vec{q}}\sum_{n\sigma}\sum_{\vec{g}}\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n,\vec{k}+\vec{k}_1+\vec{g}}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})\right)\sqrt{\frac{\hbar}{2\rho V\omega_{j\vec{q}}}}\left(\vec{\epsilon}(j\vec{q})\cdot(\vec{q}+\vec{g})\right) \\
& \times V_{\vec{q}+\vec{g}}c^\dagger_{n,\vec{q}+\vec{k}+\vec{g},\sigma}c_{n\vec{k}\sigma}\left(a^\dagger_{j,-\vec{q}}+a_{j\vec{q}}\right) && (6.14) \\
| & \text{ the general form of the interaction Hamiltonian can be written as} \\
= & \sum_{\vec{k}}\sum_{j\vec{q}}\sum_{n\sigma}\sum_{\vec{g}}M_{j\vec{q},\vec{k},\vec{g},n\sigma}c^\dagger_{n,\vec{q}+\vec{k}+\vec{g},\sigma}c_{n\vec{k}\sigma}\left(a^\dagger_{j,-\vec{q}}+a_{j\vec{q}}\right) && (6.15)
\end{aligned}$$

[2] The approximation is that if $\vec{k}$ is small, the wavelength $\gg$ size of the unit cell and so the phase over one cell is esentially constant i.e. $e^{i(\vec{k}+\vec{k}_1-\vec{k}_2)\cdot\vec{r}} \approx e^{i(\vec{k}+\vec{k}_1-\vec{k}_2)\cdot\vec{R}^0}$. The volume integral can then be approximated by a product of a one-cell integral and its constant phase factor and then sum over all cells.

The notation $\sum_{\vec{G}}\delta_{\vec{k}_2,\vec{k}+\vec{k}_1+\vec{G}}$, where $\vec{G}$ is a reciprocal space translation vector, is to remind us that the vectors are mapped back to the first Brillouin zone.

We note a few features; electron numbers are conserved since the electron number operator appears in the expression whereas phonon numbers are not conserved; momentum conservation is also explicit in the expression and the appearance of $\vec{\epsilon}\cdot\vec{q}$ indicates that only longitudinal modes contribute to electron-phonon interaction. The physical explanation is that, in longitudinal vibrations, compressions and rarefactions cause local ionic charge inhomogenity which couples to the electrons.

6.1.1 Some Phenomenological Electron-Phonon Interaction Hamiltonians

Electron-phonon interaction is very different in different types of solids, sometimes even new excitations such as polarons form, thus to model electron-phonon interaction for a particular material we need to model the coupling matrix M according to that material. Here we discuss some typical models. We follow [Mahan2000].

6.1.1.1 Frolich Hamiltonian

Electrons couple to strong $\vec{E}$ fields set up by LO vibrations and we work in the long wavelength limit where we can work with linear and homogenous material Maxwell's equations. The interaction Hamiltonian is defined as the coupling of the electron density with the scalar potential associated with the $\vec{E}$ field created by LO vibrations.

$$H^{\text{Frolich}(el-LO)} = -e\int d\vec{r}n(\vec{r})\phi^{LO}(\vec{r}) \tag{6.16}$$

where $n(\vec{r})$ is the electron density and ϕ^{LO} is that scalar potential. We will determine $\phi^{LO}(\vec{r})$ and then write the Hamiltonian in second quantized form. Since there are no free charges in the crystal, the material Maxwell equation is

$$\nabla\cdot\vec{D}=0\Rightarrow\nabla\cdot\left(\epsilon_0\vec{E}+\vec{P}\right)=0\Rightarrow\vec{E}=-\frac{1}{\epsilon_0}\vec{P} \tag{6.17}$$

Now we assume that the material polarization vector $\vec{P}$ is proportional to the amplitude of the LO vibrations.

$$\vec{P}\propto\vec{u}^{LO}\Rightarrow\vec{P}=F\vec{u}^{LO} \tag{6.18}$$

where F is a proportionality constant and $\vec{u}^{LO}$ means

$$\vec{u}^{LO}=\vec{u}\Bigg|_{\text{set }\omega_{j\vec{q}}=\omega^{LO}_{j\vec{q}}\text{ and }\epsilon_{k\alpha}(j\vec{q})=\frac{\vec{q}}{|\vec{q}|}\text{ (longitudinal)}} \tag{6.19}$$

We absorb all factors into F and write the second quantized version of $\vec{u}^{LO}$ as

$$\vec{P}=\sum_{\vec{q}}F(\omega^{LO}_{\vec{q}})\frac{\vec{q}}{|\vec{q}|}\left(a^{LO\dagger}_{\vec{q}}e^{-i\vec{q}\cdot\vec{r}}+a^{LO}_{\vec{q}}e^{i\vec{q}\cdot\vec{r}}\right) \tag{6.20}$$

Note that in this interaction, only one branch $j=LO$ is involved. The electric field is then

$$\vec{E}=-\frac{1}{\epsilon_0}\sum_{\vec{q}}F(\omega^{LO}_{\vec{q}})\frac{\vec{q}}{|\vec{q}|}\left(a^{LO\dagger}_{\vec{q}}e^{-i\vec{q}\cdot\vec{r}}+a^{LO}_{\vec{q}}e^{i\vec{q}\cdot\vec{r}}\right) \tag{6.21}$$

The scalar potential ϕ^{LO} is related by $\vec{E} = -\nabla\phi^{LO}(\vec{r})$ which can be solved by

$$
\begin{aligned}
\vec{E} &= -\nabla\phi^{LO}(\vec{r}) && (6.22)\\
\sum_{\vec{q}} \vec{E}_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} &= -\nabla_{\vec{r}} \sum_{\vec{q}} \phi^{LO}_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} = -i\sum_{\vec{q}} \vec{q}\phi^{LO}_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} && (6.23)\\
\therefore -i\vec{q}\phi^{LO}_{\vec{q}} &= \vec{E}_{\vec{q}} && (6.24)\\
\vec{q}^2\phi^{LO}_{\vec{q}} &= i\vec{q}\cdot\vec{E}_{\vec{q}} && (6.25)\\
\phi^{LO}_{\vec{q}} &= i\frac{\vec{q}\cdot\vec{E}_{\vec{q}}}{\vec{q}^2} && (6.26)
\end{aligned}
$$

We get for the scalar potential

$$
\phi^{LO}(\vec{r}) = -\frac{i}{\epsilon_0}\sum_{\vec{q}} F(\omega^{LO}_{\vec{q}})\frac{1}{|\vec{q}|}\left(-a^{LO\dagger}_{\vec{q}} e^{-i\vec{q}\cdot\vec{r}} + a^{LO}_{\vec{q}} e^{i\vec{q}\cdot\vec{r}}\right) \qquad (6.27)
$$

The interaction Hamiltonian is now,

$$
\begin{aligned}
H^{\text{Frolich}(el-LO)} &= -e\int d\vec{r} n(\vec{r})\phi^{LO}(\vec{r}) && (6.28)\\
&= \int d\vec{r} n(\vec{r})\frac{ei}{\epsilon_0}\sum_{\vec{q}} F(\omega^{LO}_{\vec{q}})\frac{1}{|\vec{q}|}\left(-a^{LO\dagger}_{\vec{q}} e^{-i\vec{q}\cdot\vec{r}} + a^{LO}_{\vec{q}} e^{i\vec{q}\cdot\vec{r}}\right) && (6.29)\\
&| \quad \text{write the electronic part into second quantized form}\\
&| \quad \text{there are no interband or spin flip transitions}\\
&| \quad n(\vec{r}) = \frac{1}{V}\sum_{n\sigma}\sum_{\vec{k}_1\vec{k}_2} e^{i(\vec{k}_1-\vec{k}_2)\cdot\vec{r}}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})c^\dagger_{n\vec{k}_2\sigma}c_{n\vec{k}_1\sigma}\\
&| \quad \text{use the long wavelength approximation,}\\
&| \quad \frac{1}{V}\int d\vec{r} e^{i(\vec{k}_1-\vec{k}_2\pm\vec{q})\cdot\vec{r}}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r}) \approx \sum_{\vec{g}}\delta_{\vec{k}_2,\vec{k}_1\pm\vec{q}+\vec{g}}\frac{N}{V}\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})\\
&= \frac{ei}{\epsilon_0}\frac{N}{V}\sum_{\vec{q}}\sum_{n\sigma}\sum_{\vec{k}_1\vec{k}_2}\sum_{\vec{g}} F(\omega^{LO}_{\vec{q}})\frac{1}{|\vec{q}|}\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})\right)\\
&\quad \times\left(a^{LO}_{\vec{q}}c^\dagger_{n\vec{k}_2\sigma}c_{n\vec{k}_1\sigma}\delta_{\vec{k}_2,\vec{k}_1+\vec{q}+\vec{g}} - a^{LO\dagger}_{\vec{q}}c^\dagger_{n\vec{k}_2\sigma}c_{n\vec{k}_1\sigma}\delta_{\vec{k}_2,\vec{k}_1-\vec{q}+\vec{g}}\right) && (6.30)\\
&| \quad \text{evaluate } \vec{k}_2 \text{ sum and then rename } \vec{k}_1 \text{ as } \vec{k}\\
&= \frac{ei}{\epsilon_0}\frac{N}{V}\sum_{\vec{q}}\sum_{n\sigma}\sum_{\vec{k}}\sum_{\vec{g}} F(\omega^{LO}_{\vec{q}})\frac{1}{|\vec{q}|}\left(\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n,\vec{k}+\vec{q}+\vec{g}}(\vec{r})\mathcal{U}_{n\vec{k}}(\vec{r})\right)a^{LO}_{\vec{q}}c^\dagger_{n,\vec{k}+\vec{q}+\vec{g},\sigma}c_{n\vec{k}\sigma}\right.\\
&\quad \left.-\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n,\vec{k}-\vec{q}+\vec{g}}(\vec{r})\mathcal{U}_{n\vec{k}}(\vec{r})\right)a^{LO\dagger}_{\vec{q}}c^\dagger_{n,\vec{k}-\vec{q}+\vec{g},\sigma}c_{n\vec{k}\sigma}\right) && (6.31)
\end{aligned}
$$

The constant F (not calculated here, see [Mahan2000] equation (1.278)) is

$$
F^2(\omega^{LO}_{\vec{q}}) = \frac{\hbar\omega^{LO}_{\vec{q}}\epsilon_0}{2V}\left(\frac{1}{\epsilon_r(\infty)} - \frac{1}{\epsilon_r(0)}\right) \qquad (6.32)
$$

where $\epsilon_r(\infty)$ is the screening due to electrons and $\epsilon_r(0)$ is the screening due to electrons and optical phonons. We can see that the general form of the interaction Hamiltonian is the same. The difference is essentially in the coupling constant.

6.1.1.2 Deformation Potential

This is the most generic type of electron-phonon interaction where a local change in ionic charge density interacts with the (charged) electrons. Here we consider a particular form of deformation of the lattice (that creates a change in local ionic charge density), namely a hydrostatic strain which retains crystal symmetry though the volume of the unit cell changes. Essentially, the deformation is diagonal in strain. Define the deformation (scalar) potential as $\Delta(\vec{r})$,

$$\begin{aligned}
\Delta(\vec{r}) &= \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} && (6.33)\\
&\quad | \text{ recall that strain is defined as } \epsilon_{\alpha_1\alpha_2} = \frac{1}{2}\left(\frac{\partial u_{\alpha_1}}{\partial x_{\alpha_2}} + \frac{\partial u_{\alpha_2}}{\partial x_{\alpha_1}}\right)\\
&= \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} && (6.34)\\
&= \nabla_{\vec{r}} \cdot \vec{u} && (6.35)
\end{aligned}$$

The deformation results in a variation of the local ion density and couples to the local electron density $n(\vec{r})$ via the deformation (scalar) potential. The divergence of displacement is related to longitudinal acoustic (LA) vibrations. The electron-phonon Hamiltonian can be defined as

$$H^{\text{deform}(el-LA)} = \int d\vec{r} n(\vec{r}) C \Delta(\vec{r}) \tag{6.36}$$

where C is called the deformation constant. It simply remains to write the Hamiltonian into the second quantized form. For the phonon part,

$$\begin{aligned}
\Delta(\vec{r}) &= \nabla_{\vec{r}} \cdot \vec{u}(\vec{r}) && (6.37)\\
&\quad | \text{ insert the second quantized form for } \vec{u}\\
&= \nabla_{\vec{r}} \cdot \sum_{j\vec{q}} \sqrt{\frac{\hbar}{2MN\omega_{j\vec{q}}}} \vec{\epsilon}(j\vec{q}) e^{i\vec{q}\cdot\vec{r}} \left(a^\dagger_{j,-\vec{q}} + a_{j\vec{q}}\right) && (6.38)\\
&= i\sum_{j\vec{q}} \sqrt{\frac{\hbar}{2MN\omega_{j\vec{q}}}} \left(\vec{\epsilon}(j\vec{q}) \cdot \vec{q}\right) e^{i\vec{q}\cdot\vec{r}} \left(a^\dagger_{j,\vec{q}} + a_{j\vec{q}}\right) && (6.39)\\
&\quad | \text{ the dot product } \vec{\epsilon}\cdot\vec{q} \text{ implies only pure longitudinal modes contribute}\\
&\quad | \text{ since we assume one atom per cell, the mode is LA}\\
&\quad | \text{ for longwavelength description, we write } MN = \text{total mass} = \text{density} \times \text{volume} = \rho V\\
&= i\sum_{j\vec{q}} \sqrt{\frac{\hbar}{2\rho V\omega^{LA}_{\vec{q}}}} \left(\vec{\epsilon}^{LA}_{\vec{q}} \cdot \vec{q}\right) e^{i\vec{q}\cdot\vec{r}} \left(a^{LA\dagger}_{-\vec{q}} + a^{LA}_{\vec{q}}\right) && (6.40)
\end{aligned}$$

The Hamiltonian is of the form,

$$\begin{aligned}
H^{\text{deform}(el-LA)} &= iC\int d\vec{r} n(\vec{r}) \sum_{j\vec{q}} \sqrt{\frac{\hbar}{2\rho V\omega^{LA}_{\vec{q}}}} \left(\vec{\epsilon}^{LA}_{\vec{q}} \cdot \vec{q}\right) e^{i\vec{q}\cdot\vec{r}} \left(a^{LA\dagger}_{-\vec{q}} + a^{LA}_{\vec{q}}\right) && (6.41)\\
&\quad | \text{ write the electronic part into second quantized form}\\
&\quad | \text{ there are no interband or spin flip transitions}
\end{aligned}$$

$$
\begin{aligned}
& \mid \quad n(\vec{r}) = \frac{1}{V}\sum_{n\sigma}\sum_{\vec{k}_1\vec{k}_2} e^{i(\vec{k}_1-\vec{k}_2)\cdot\vec{r}}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})c^\dagger_{n\vec{k}_2\sigma}c_{n\vec{k}_1\sigma} \\
& \mid \quad \text{use the long wavelength approximation} \\
& \mid \quad \frac{1}{V}\int d\vec{r}e^{i(\vec{k}_1-\vec{k}_2+\vec{q})\cdot\vec{r}}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r}) \approx \sum_{\vec{G}}\delta_{\vec{k}_2,\vec{k}_1+\vec{q}+\vec{G}}\frac{N}{V}\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r}) \\
= \; & \frac{iCN}{V}\sum_{j\vec{q}}\sum_{n\sigma}\sum_{\vec{k}_1\vec{k}_2}\sum_{\vec{G}}\sqrt{\frac{\hbar}{2\rho V\omega^{LA}_{\vec{q}}}}\left(\vec{\epsilon}^{\,LA}_{\vec{q}}\cdot\vec{q}\right)\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})\right) \\
& \times\delta_{\vec{k}_2,\vec{k}_1+\vec{q}+\vec{G}}c^\dagger_{n\vec{k}_2\sigma}c_{n\vec{k}_1\sigma}\left(a^{LA\dagger}_{-\vec{q}} + a^{LA}_{\vec{q}}\right) \qquad (6.42) \\
& \mid \quad \text{evaluate the } \vec{k}_2 \text{ sum and rename } \vec{k}_1 \text{ as } \vec{k} \\
= \; & \frac{iCN}{V}\sum_{j\vec{q}}\sum_{n\sigma}\sum_{\vec{k}}\sum_{\vec{G}}\sqrt{\frac{\hbar}{2\rho V\omega^{LA}_{\vec{q}}}}\left(\vec{\epsilon}^{\,LA}_{\vec{q}}\cdot\vec{q}\right)\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n,\vec{k}+\vec{q}+\vec{G}}(\vec{r})\mathcal{U}_{n\vec{k}}(\vec{r})\right) \\
& \times c^\dagger_{n,\vec{k}+\vec{q}+\vec{G},\sigma}c_{n\vec{k}\sigma}\left(a^{LA\dagger}_{-\vec{q}} + a^{LA}_{\vec{q}}\right) \qquad (6.43)
\end{aligned}
$$

Finally we make a quick order of magnitude estimate of constant C by using the free electron approximation. Recall the free electron Fermi energy,

$$
\epsilon_F = \frac{\hbar^2}{2m_e}\left(\frac{3\pi^2 N_e}{V}\right)^{2/3} \tag{6.44}
$$

The deformation gives the fractional change in volume, ie $\Delta(\vec{r}) = \nabla_{\vec{r}}\cdot\vec{u}(\vec{r}) = \frac{\delta V}{V}$, so variation of the free electron Fermi energy with respect to the variation of volume gives,

$$
\begin{aligned}
\delta\epsilon_F &= \frac{\hbar^2}{2m_e}(3\pi^2 N_e)^{2/3}\left(-\frac{2}{3}\right)V^{-5/3}\delta V & (6.45) \\
&= -\frac{2}{3}\epsilon_F\frac{\delta V}{V} & (6.46) \\
&= -\frac{2}{3}\epsilon_F\Delta(\vec{r}) & (6.47)
\end{aligned}
$$

So this gives $C \approx -\frac{2}{3}\epsilon_F$.

6.1.1.3 Piezoelectric Interaction

In some crystals, (external) strain causes electric polarization, the resulting internal electric field couples to the electron density. The Hamiltonian can thus be defined as,

$$
H^{\text{piezo}(el-ph)} = -e\int d\vec{r}n(\vec{r})\phi^{\text{piezo}}(\vec{r}) \tag{6.48}
$$

We assume that the dielectric constant ε is isotropic and so the internal electric field is given by

$$
E_{\alpha_1} = \frac{1}{\varepsilon}\sum_{\alpha_2\alpha_3} e_{\alpha_2\alpha_3\alpha_1}\epsilon_{\alpha_2\alpha_3} \tag{6.49}
$$

where $e_{\alpha_2\alpha_3\alpha_1}$ is the piezoelectric tensor and $\epsilon_{\alpha_2\alpha_3}$ is the strain tensor, $\epsilon_{\alpha_1\alpha_2} = \frac{1}{2}\left(\frac{\partial u_{\alpha_1}}{\partial x_{\alpha_2}} + \frac{\partial u_{\alpha_2}}{\partial x_{\alpha_1}}\right)$. We take the piezoelectric tensor to be symmetric $e_{\alpha_2\alpha_3\alpha_1} = e_{\alpha_3\alpha_2\alpha_1}$ so that the strain tensor simplifies.

$$
\begin{aligned}
E_{\alpha_1} &= \frac{1}{\varepsilon}\sum_{\alpha_2\alpha_3} e_{\alpha_2\alpha_3\alpha_1}\frac{\partial u_{\alpha_3}}{\partial x_{\alpha_2}} && (6.50)\\
&\quad | \quad \text{insert the second quantized form of } \vec{u}\\
&\quad | \quad u_\alpha = \sum_{j\vec{q}}\sqrt{\frac{\hbar}{2\rho V\omega_{j\vec{q}}}}\epsilon_\alpha(j\vec{q})\left(a_{j\vec{q}}e^{i\vec{q}\cdot\vec{r}} + a^\dagger_{j,-\vec{q}}e^{-i\vec{q}\cdot\vec{r}}\right)\\
&= \frac{1}{\varepsilon}\sum_{j\vec{q}}\sum_{\alpha_2\alpha_3} e_{\alpha_2\alpha_3\alpha_1}\epsilon_{\alpha_3}(j\vec{q})q_{\alpha_2}\sqrt{\frac{\hbar}{2\rho V\omega_{j\vec{q}}}}\,i\left(a_{j\vec{q}}e^{i\vec{q}\cdot\vec{r}} - a^\dagger_{j,-\vec{q}}e^{-i\vec{q}\cdot\vec{r}}\right) && (6.51)
\end{aligned}
$$

The scalar potential ϕ^{piezo} is related to the field by $\vec{E} = -\nabla\phi^{\text{piezo}}$ and so we solve it by the earlier formula $\phi^{\text{piezo}}_{\vec{q}} = i\frac{\vec{q}\cdot\vec{E}_{\vec{q}}}{\vec{q}^2}$.

$$
\phi^{\text{piezo}} = -\frac{1}{\varepsilon}\sum_{j\vec{q}}\sum_{\alpha_1\alpha_2\alpha_3} e_{\alpha_2\alpha_3\alpha_1}\frac{q_{\alpha_2}q_{\alpha_1}\epsilon_{\alpha_3}(j\vec{q})}{\vec{q}^2}\sqrt{\frac{\hbar}{2\rho V\omega_{j\vec{q}}}}\left(a_{j\vec{q}}e^{i\vec{q}\cdot\vec{r}} + a^\dagger_{j,-\vec{q}}e^{-i\vec{q}\cdot\vec{r}}\right) \qquad (6.52)
$$

The full electron-phonon interaction Hamiltonian is now,

$$
\begin{aligned}
H^{\text{piezo}(el-ph)} &= \frac{e}{\varepsilon}\int d\vec{r}n(\vec{r})\sum_{j\vec{q}}\sum_{\alpha_1\alpha_2\alpha_3} e_{\alpha_2\alpha_3\alpha_1}\frac{q_{\alpha_2}q_{\alpha_1}\epsilon_{\alpha_3}(j\vec{q})}{\vec{q}^2}\sqrt{\frac{\hbar}{2\rho V\omega_{j\vec{q}}}}\left(a_{j\vec{q}}e^{i\vec{q}\cdot\vec{r}} + a^\dagger_{j,-\vec{q}}e^{-i\vec{q}\cdot\vec{r}}\right) && (6.53)\\
&\quad | \quad \text{write the electronic part into second quantized form}\\
&\quad | \quad \text{there are no interband or spin flip transitions}\\
&\quad | \quad n(\vec{r}) = \frac{1}{V}\sum_{n\sigma}\sum_{\vec{k}_1\vec{k}_2} e^{i(\vec{k}_1-\vec{k}_2)\cdot\vec{r}}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})c^\dagger_{n\vec{k}_2\sigma}c_{n\vec{k}_1\sigma}\\
&\quad | \quad \text{use the long wavelength approximation}\\
&\quad | \quad \frac{1}{V}\int d\vec{r}e^{i(\vec{k}_1-\vec{k}_2+\vec{q})\cdot\vec{r}}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r}) \approx \sum_{\vec{G}}\delta_{\vec{k}_2,\vec{k}_1+\vec{q}+\vec{g}}\frac{N}{V}\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})\\
&= \frac{eN}{\varepsilon V}\sum_{j\vec{q}}\sum_{\alpha_1\alpha_2\alpha_3}\sum_{n\sigma}\sum_{\vec{k}_1\vec{k}_2}\sum_{\vec{g}} e_{\alpha_2}\frac{q_{\alpha_2}q_{\alpha_1}\epsilon_{\alpha_3}(j\vec{q})}{\vec{q}^2}\sqrt{\frac{\hbar}{2\rho V\omega_{j\vec{q}}}}\\
&\quad\times\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n\vec{k}_2}(\vec{r})\mathcal{U}_{n\vec{k}_1}(\vec{r})\right)\left(a_{j\vec{q}}c^\dagger_{n\vec{k}_2\sigma}c_{n\vec{k}_1\sigma}\delta_{\vec{k}_2,\vec{k}_1+\vec{q}+\vec{G}} + a^\dagger_{j,-\vec{q}}c^\dagger_{n\vec{k}_2\sigma}c_{n\vec{k}_1\sigma}\delta_{\vec{k}_2,\vec{k}_1-\vec{q}+\vec{G}}\right)\\
&\quad | \quad \text{evaluate } \vec{k}_2 \text{ sum and rename } \vec{k}_1 \text{ as } \vec{k}\\
&= \frac{eN}{\varepsilon V}\sum_{j\vec{q}}\sum_{n\sigma}\sum_{\vec{k}}\sum_{\vec{g}} e_{\alpha_2\alpha_3\alpha_1}\frac{q_{\alpha_2}q_{\alpha_1}\epsilon_{\alpha_3}(j\vec{q})}{\vec{q}^2}\sqrt{\frac{\hbar}{2\rho V\omega_{j\vec{q}}}}\\
&\quad\times\Bigg[\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n,\vec{k}+\vec{q}+\vec{g}}(\vec{r})\mathcal{U}_{n\vec{k}}(\vec{r})\right)a_{j\vec{q}}c^\dagger_{n,\vec{k}+\vec{q}+\vec{G},\sigma}c_{n\vec{k}\sigma}\\
&\quad+\left(\int_{V_{\text{cell}}} d\vec{r}\mathcal{U}^*_{n,\vec{k}-\vec{q}+\vec{G}}(\vec{r})\mathcal{U}_{n\vec{k}}(\vec{r})\right)a^\dagger_{j,-\vec{q}}c^\dagger_{n,\vec{k}-\vec{q}+\vec{g},\sigma}c_{n\vec{k}\sigma}\Bigg] && (6.54)
\end{aligned}
$$

Again it is the same form but with a different coupling matrix.

6.2 Kinetic Theory: Boltzmann Equation (BE)

6.2.1 Full Collision Integral

The electron-phonon interaction Hamiltonian is of the general form

$$H^{(el-ph)} = \sum_{\vec{k}\sigma j\vec{q}} M_{\vec{k}j\vec{q}} c^{\dagger}_{\vec{k}+\vec{q},\sigma} c_{\vec{k}\sigma} \left(a^{\dagger}_{j,-\vec{q}} + a_{j\vec{q}} \right) \tag{6.55}$$

The Golden Rule for transition rate is

$$W_{i\leftrightarrow f} = \frac{2\pi}{\hbar} \left| \left\langle \left| H^{(el-ph)} \right| f \right\rangle \right|^2 \delta(E_f - E_i) \tag{6.56}$$

The collision integral is with respect to the electronic distribution of momentum $\vec{k}$, i.e. $\left.\frac{\partial f_{\vec{k}}}{\partial t}\right|_{\text{coll}}$. Note that because in the interaction Hamiltonian, we labelled the electron annihilation operator with index $\vec{k}$, it seems as if the Hamiltonian only creates out-scattering from $\vec{k}$. This is of course not true and the in-scattering (into $f_{\vec{k}}$) terms appear when we relabel $c^{\dagger}_{\vec{k}+\vec{q}} \to c^{\dagger}_{\vec{k}}$. It is just a matter of labelling.

$$\begin{aligned}
& W_{1st} \ \text{(scatters out of } f_{\vec{k}}\text{)} \\
= \ & \frac{2\pi}{\hbar} \left| \left\langle i \left| M_{\vec{k}j\vec{q}} c^{\dagger}_{\vec{k}+\vec{q},\sigma} c_{\vec{k}\sigma} a^{\dagger}_{j,-\vec{q}} \right| f \right\rangle \right|^2 \delta(\epsilon_{\vec{k}+\vec{q}} + \hbar\omega_{j\vec{q}} - \epsilon_{\vec{k}}) & (6.57) \\
= \ & \frac{2\pi}{\hbar} \left| M_{\vec{k}j\vec{q}} \right|^2 \left| \left\langle i \left| c^{\dagger}_{\vec{k}+\vec{q},\sigma} c_{\vec{k}\sigma} a^{\dagger}_{j,-\vec{q}} \right| f \right\rangle \right|^2 \delta(\epsilon_{\vec{k}+\vec{q}} + \hbar\omega_{j\vec{q}} - \epsilon_{\vec{k}}) & (6.58) \\
| \ & \text{use bosonic ladder relation } a^{\dagger}_{j,-\vec{q}} |N_{j\vec{q}}\rangle = \sqrt{N_{j\vec{q}}+1} |N_{j\vec{q}}+1\rangle \\
| \ & \text{use fermionic ladder relations (see [Das2006] pg 78)} \\
| \ & c_{\vec{k}\sigma} \left| f_{\vec{k}} \right\rangle = \sqrt{f_{\vec{k}}} \left| 1 - f_{\vec{k}} \right\rangle \ , \ c^{\dagger}_{\vec{k}+\vec{q}} \left| f_{\vec{k}+\vec{q}} \right\rangle = \sqrt{1 - f_{\vec{k}+\vec{q}}} \left| 1 - f_{\vec{k}+\vec{q}} \right\rangle \\
= \ & \frac{2\pi}{\hbar} \left| M_{\vec{k}j\vec{q}} \right|^2 f_{\vec{k}} (1 - f_{\vec{k}+\vec{q}})(N_{j\vec{q}}+1) \delta(\epsilon_{\vec{k}+\vec{q}} + \hbar\omega_{j\vec{q}} - \epsilon_{\vec{k}}) & (6.59)
\end{aligned}$$

Now we relabel the indices so that it represents in-scattering into $f_{\vec{k}}$. The easiest way to understand the relabelling is to see that the out-scattering case can be represented by the diagram on the left and so the in-scattering case can be represented by the diagram on the right.

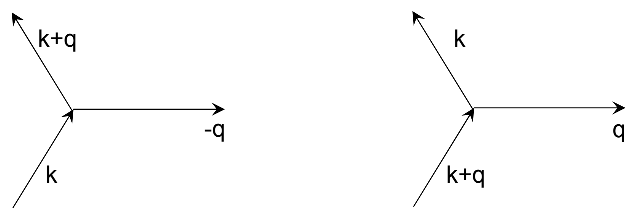


Figure 6.1: *Electron-phonon interaction diagrams (emission of phonon diagrams). Left: out-scattering from $f_{\vec{k}}$. Right: in-scattering into $f_{\vec{k}}$.*

$$W_{1st} \ \text{(scatters into } f_{\vec{k}}\text{)} = \frac{2\pi}{\hbar} \left| \left\langle i \left| M_{\vec{k}j\vec{q}} c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}+\vec{q},\sigma} a^{\dagger}_{j\vec{q}} \right| f \right\rangle \right|^2 \delta(\epsilon_{\vec{k}} + \hbar\omega_{j\vec{q}} - \epsilon_{\vec{k}+\vec{q}}) \tag{6.60}$$

$$
\begin{aligned}
&\quad | \quad \text{use the earlier mentioned ladder operator relations} \\
&= \frac{2\pi}{\hbar}\left|M_{\vec{k}j\vec{q}}\right|^2 f_{\vec{k}+\vec{q}}(1-f_{\vec{k}})(N_{j\vec{q}}+1)\delta(\epsilon_{\vec{k}}+\hbar\omega_{j\vec{q}}-\epsilon_{\vec{k}+\vec{q}}) \qquad (6.61)
\end{aligned}
$$

2 more rate terms with respect to phonon absorption are calculated:

$$
\begin{aligned}
W_{2nd}\ \ (\text{scatters out of } f_{\vec{k}}) &= \frac{2\pi}{\hbar}\left|\left\langle i\left|M_{\vec{k}j\vec{q}}c^{\dagger}_{\vec{k}+\vec{q},\sigma}c_{\vec{k}\sigma}a_{j\vec{q}}\right|f\right\rangle\right|^2\delta(\epsilon_{\vec{k}+\vec{q}}-\hbar\omega_{j\vec{q}}-\epsilon_{\vec{k}}) \qquad (6.62)\\
&\quad | \quad \text{use bosonic ladder relation } a_{j\vec{q}}|N_{j\vec{q}}\rangle = \sqrt{N_{j\vec{q}}}|N_{j\vec{q}}-1\rangle \\
&\quad | \quad \text{use also the earlier fermionic ladder relations} \\
&= \frac{2\pi}{\hbar}\left|M_{\vec{k}j\vec{q}}\right|^2 f_{\vec{k}}(1-f_{\vec{k}+\vec{q}})N_{j\vec{q}}\delta(\epsilon_{\vec{k}+\vec{q}}-\hbar\omega_{j\vec{q}}-\epsilon_{\vec{k}}) \qquad (6.63)
\end{aligned}
$$

Now we relabel the indices so that it represents in-scattering into $f_{\vec{k}}$. Again the diagrammatic way is the easiest way to understand. The out-scattering case can by represent by the diagram on the left and so the in-scattering case can be represented by the diagram on the right.

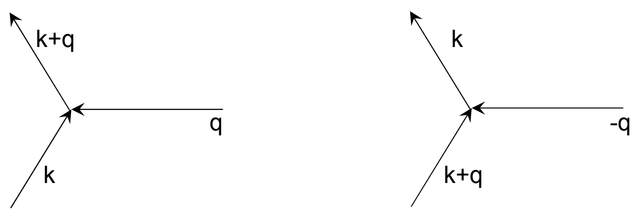


Figure 6.2: *Electron-phonon interaction diagrams (absorption of phonon diagrams). Left: out-scattering from* $f_{\vec{k}}$*. Right: in-scattering into* $f_{\vec{k}}$*.*

$$
\begin{aligned}
W_{2nd}\ \ (\text{scatters into } f_{\vec{k}}) &= \frac{2\pi}{\hbar}\left|\left\langle i\left|M_{\vec{k}j\vec{q}}c^{\dagger}_{\vec{k}\sigma}c_{\vec{k}+\vec{q},\sigma}a_{j,-\vec{q}}\right|f\right\rangle\right|^2\delta(\epsilon_{\vec{k}}-\hbar\omega_{j\vec{q}}-\epsilon_{\vec{k}}) \qquad (6.64)\\
&\quad | \quad \text{use the earlier mentioned ladder relations} \\
&= \frac{2\pi}{\hbar}\left|M_{\vec{k}j\vec{q}}\right|^2 f_{\vec{k}+\vec{q}}(1-f_{\vec{k}})N_{j\vec{q}}\delta(\epsilon_{\vec{k}}-\hbar\omega_{j\vec{q}}-\epsilon_{\vec{k}+\vec{q}}) \qquad (6.65)
\end{aligned}
$$

Recall the delta function relation, $\delta(a) = \delta(-a)$ and assign a negative sign to out-scattering terms and a positive sign to in-scattering terms. The collision integral is

$$
\begin{aligned}
I^{(el-ph)}[f_{\vec{k}}] &= \left.\frac{\partial f_{\vec{k}}}{\partial t}\right|_{\text{coll}} \qquad (6.66)\\
&= \frac{2\pi}{\hbar}\sum_{j\vec{q}\sigma}\left|M_{\vec{k}j\vec{q}}\right|^2\Big[\delta(\epsilon_{\vec{k}+\vec{q}}-\epsilon_{\vec{k}}+\hbar\omega_{j\vec{q}})\Big(f_{\vec{k}+\vec{q}}(1-f_{\vec{k}})N_{j\vec{q}}-f_{\vec{k}}(1-f_{\vec{k}+\vec{q}})(N_{j\vec{q}}+1)\Big)\\
&\quad +\delta(\epsilon_{\vec{k}+\vec{q}}-\epsilon_{\vec{k}}-\hbar\omega_{j\vec{q}})\Big(f_{\vec{k}+\vec{q}}(1-f_{\vec{k}})(N_{j\vec{q}}+1)-f_{\vec{k}}(1-f_{\vec{k}+\vec{q}})N_{j\vec{q}}\Big)\Big] \qquad (6.67)
\end{aligned}
$$

6.2.2 Linearized Collision Integral

We linearize the electron distribution and the phonon distribution according to [3]

$$\begin{aligned} N_{j\vec{q}} &\approx N^{eq}_{j\vec{q}} + N^{eq}_{j\vec{q}}(N^{eq}_{j\vec{q}}+1)y_{j\vec{q}} && (6.68)\\ f_{\vec{k}} &\approx f^{eq}_{\vec{k}} + f^{eq}_{\vec{k}}(1-f^{eq}_{\vec{k}})y_{\vec{k}} && (6.69)\end{aligned}$$

We linearize each term in the collision integral.

$$\begin{aligned}
& \text{Part of first term in collision integral (retain only to first order in } y)\\
= \;& f_{\vec{k}+\vec{q}}(1-f_{\vec{k}})N_{j\vec{q}} && (6.70)\\
\approx \;& \left(f^{eq}_{\vec{k}+\vec{q}} + f^{eq}_{\vec{k}+\vec{q}}(1-f^{eq}_{\vec{k}+\vec{q}})y_{\vec{k}+\vec{q}}\right)\left(1-f^{eq}_{\vec{k}} - f^{eq}_{\vec{k}}(1-f^{eq}_{\vec{k}})y_{\vec{k}}\right)\left(N^{eq}_{j\vec{q}} + N^{eq}_{j\vec{q}}(N^{eq}_{j\vec{q}}+1)y_{j\vec{q}}\right) && (6.71)\\
\approx \;& \left(f^{eq}_{\vec{k}+\vec{q}}(1-f^{eq}_{\vec{k}}) - f^{eq}_{\vec{k}+\vec{q}}f^{eq}_{\vec{k}}(1-f^{eq}_{\vec{k}})y_{\vec{k}} + (1-f^{eq}_{\vec{k}})f^{eq}_{\vec{k}+\vec{q}}(1-f^{eq}_{\vec{k}+\vec{q}})y_{\vec{k}+\vec{q}}\right)\left(N^{eq}_{j\vec{q}} + N^{eq}_{j\vec{q}}(N^{eq}_{j\vec{q}}+1)y_{j\vec{q}}\right)\\
\approx \;& f^{eq}_{\vec{k}+\vec{q}}(1-f^{eq}_{\vec{k}})N^{eq}_{j\vec{q}} + f^{eq}_{\vec{k}+\vec{q}}(1-f^{eq}_{\vec{k}})N^{eq}_{j\vec{q}}(N^{eq}_{j\vec{q}}+1)y_{j\vec{q}}\\
& - f^{eq}_{\vec{k}+\vec{q}}f^{eq}_{\vec{k}}(1-f^{eq}_{\vec{k}})N^{eq}_{j\vec{q}}y_{\vec{k}} + (1-f^{eq}_{\vec{k}})f^{eq}_{\vec{k}+\vec{q}}(1-f^{eq}_{\vec{k}+\vec{q}})N^{eq}_{j\vec{q}}y_{\vec{k}+\vec{q}} && (6.72)\\
| \;& \text{the equilibrium first term (with other 3 terms) makes the collision integral zero, we drop it first}\\
= \;& f^{eq}_{\vec{k}+\vec{q}}(1-f^{eq}_{\vec{k}})N^{eq}_{j\vec{q}}\left[(N^{eq}_{j\vec{q}}+1)y_{j\vec{q}} - f^{eq}_{\vec{k}}y_{\vec{k}} + (1-f^{eq}_{\vec{k}+\vec{q}})y_{\vec{k}+\vec{q}}\right] && (6.73)
\end{aligned}$$

From (part of) the first term of the collision integral, it is clear that the other 3 terms follow a pattern. We can simply write down the other 3 (partial) terms.

$$\begin{aligned}
& \text{Part of second term in collision integral (retain only to first order in } y)\\
= \;& f_{\vec{k}}(1-f_{\vec{k}+\vec{q}})(N_{j\vec{q}}+1) && (6.74)\\
\approx \;& f^{eq}_{\vec{k}}(1-f^{eq}_{\vec{k}+\vec{q}})(N^{eq}_{j\vec{q}}+1)\left[N^{eq}_{j\vec{q}}y_{j\vec{q}} - f^{eq}_{\vec{k}+\vec{q}}y_{\vec{k}+\vec{q}} + (1-f^{eq}_{\vec{k}})y_{\vec{k}}\right] && (6.75)\\
| \;& \text{use the explicit BE and FD distribution function and the energy delta function to get}\\
| \;& f^{eq}_{\vec{k}}(1-f^{eq}_{\vec{k}+\vec{q}})(N^{eq}_{j\vec{q}}+1) = (1-f^{eq}_{\vec{k}})f^{eq}_{\vec{k}+\vec{q}}N^{eq}_{j\vec{q}}\\
= \;& f^{eq}_{\vec{k}+\vec{q}}(1-f^{eq}_{\vec{k}})N^{eq}_{j\vec{q}}\left[N^{eq}_{j\vec{q}}y_{j\vec{q}} - f^{eq}_{\vec{k}+\vec{q}}y_{\vec{k}+\vec{q}} + (1-f^{eq}_{\vec{k}})y_{\vec{k}}\right] && (6.76)
\end{aligned}$$

$$\begin{aligned}
& \text{Part of third term in collision integral (retain only to first order in } y)\\
= \;& f_{\vec{k}+\vec{q}}(1-f_{\vec{k}})(N_{j\vec{q}}+1) && (6.77)\\
\approx \;& f^{eq}_{\vec{k}+\vec{q}}(1-f^{eq}_{\vec{k}})(N^{eq}_{j\vec{q}}+1)\left[N^{eq}_{j\vec{q}}y_{j\vec{q}} - f^{eq}_{\vec{k}}y_{\vec{k}} + (1-f^{eq}_{\vec{k}+\vec{q}})y_{\vec{k}+\vec{q}}\right] && (6.78)
\end{aligned}$$

$$\begin{aligned}
& \text{Part of fourth term in collision integral (retain only to first order in } y)\\
= \;& f_{\vec{k}}(1-f_{\vec{k}+\vec{q}})N_{j\vec{q}} && (6.79)\\
\approx \;& f^{eq}_{\vec{k}}(1-f^{eq}_{\vec{k}+\vec{q}})N^{eq}_{j\vec{q}}\left[(N^{eq}_{j\vec{q}}+1)y_{j\vec{q}} - f^{eq}_{\vec{k}+\vec{q}}y_{\vec{k}+\vec{q}} + (1-f^{eq}_{\vec{k}})y_{\vec{k}}\right] && (6.80)\\
| \;& \text{use the explicit BE and FD distribution function and the energy delta function to get}\\
| \;& f^{eq}_{\vec{k}}(1-f^{eq}_{\vec{k}+\vec{q}})N^{eq}_{j\vec{q}} = (1-f^{eq}_{\vec{k}})f^{eq}_{\vec{k}+\vec{q}}(N^{eq}_{j\vec{q}}+1)
\end{aligned}$$

[3] Here, we choose to label the electron distribution deviation function and the phonon distribution deviation function with the same symbol y. The indices in y should be clear enough which deviation function is being referred to.

$$= (1-f^{eq}_{\vec{k}})f^{eq}_{\vec{k}+\vec{q}}(N^{eq}_{j\vec{q}}+1)\left[(N^{eq}_{j\vec{q}}+1)y_{j\vec{q}} - f^{eq}_{\vec{k}+\vec{q}}y_{\vec{k}+\vec{q}} + (1-f^{eq}_{\vec{k}})y_{\vec{k}}\right] \tag{6.81}$$

The linearized collision integral is

$$\begin{aligned}\Delta I^{(el-ph)}[f_{\vec{k}}] &= \frac{2\pi}{\hbar}\sum_{j\vec{q}\sigma}\left|M_{\vec{k}j\vec{q}}\right|^2 f^{eq}_{\vec{k}+\vec{q}}(1-f^{eq}_{\vec{k}})\left[\delta(\epsilon_{\vec{k}+\vec{q}}-\epsilon_{\vec{k}}+\hbar\omega_{j\vec{q}})N^{eq}_{j\vec{q}}(y_{j\vec{q}}-y_{\vec{k}}+y_{\vec{k}+\vec{q}})\right.\\ &\left.+\delta(\epsilon_{\vec{k}+\vec{q}}-\epsilon_{\vec{k}}-\hbar\omega_{j\vec{q}})(N^{eq}_{j\vec{q}}+1)(-y_{j\vec{q}}-y_{\vec{k}}+y_{\vec{k}+\vec{q}})\right] \end{aligned}\tag{6.82}$$

6.2.3 Relaxation Time Approximation

Assume the (electron distribution) relaxation time approximation for the electron-phonon collision integral,

$$\left.\frac{\partial f_{\vec{k}}}{\partial t}\right|_{\text{coll}} = -\frac{f_{\vec{k}}-f^{eq}_{\vec{k}}}{\tau^{(el-ph)}_{\vec{k}}} \tag{6.83}$$

Substitute in the linearized distribution and the linearized collision integral expressions

$$\Delta I^{(el-ph)} = -\frac{f^{eq}_{\vec{k}}(1-f^{eq}_{\vec{k}})y_{\vec{k}}}{\tau^{(el-ph)}_{\vec{k}}} \tag{6.84}$$

The explicit expression for the electron-phonon relaxation time is

$$\frac{1}{\tau^{(el-ph)}_{\vec{k}}} = -\frac{\Delta I^{(el-ph)}}{f^{eq}_{\vec{k}}(1-f_{\vec{k}})y_{\vec{k}}} \tag{6.85}$$

$$\begin{aligned} &= -\frac{2\pi}{\hbar}\sum_{j\vec{q}\sigma}\left|M_{\vec{k}j\vec{q}}\right|^2\frac{f^{eq}_{\vec{k}+\vec{q}}}{f^{eq}_{\vec{k}}}\left[\delta(\epsilon_{\vec{k}+\vec{q}}-\epsilon_{\vec{k}}+\hbar\omega_{j\vec{q}})N^{eq}_{j\vec{q}}\frac{(y_{j\vec{q}}-y_{\vec{k}}+y_{\vec{k}+\vec{q}})}{y_{\vec{k}}}\right.\\ &\left.+\delta(\epsilon_{\vec{k}+\vec{q}}-\epsilon_{\vec{k}}-\hbar\omega_{j\vec{q}})(N^{eq}_{j\vec{q}}+1)\frac{(-y_{j\vec{q}}-y_{\vec{k}}+y_{\vec{k}+\vec{q}})}{y_{\vec{k}}}\right]\end{aligned} \tag{6.86}$$

We specialise to the single mode relaxation time (SMRT) case which means all the phonon modes are in equilibrium ($y_{j\vec{q}}=0$) and all other electron modes are in equilibrium ($y_{\vec{k}+\vec{q}}=0$). Thus the SMRT is

$$\frac{1}{\tau^{(el-ph)}_{\vec{k}}} = -\frac{2\pi}{\hbar}\sum_{j\vec{q}\sigma}\left|M_{\vec{k}j\vec{q}}\right|^2\frac{f^{eq}_{\vec{k}+\vec{q}}}{f^{eq}_{\vec{k}}}\left[\delta(\epsilon_{\vec{k}+\vec{q}}-\epsilon_{\vec{k}}+\hbar\omega_{j\vec{q}})N^{eq}_{j\vec{q}}+\delta(\epsilon_{\vec{k}+\vec{q}}-\epsilon_{\vec{k}}-\hbar\omega_{j\vec{q}})(N^{eq}_{j\vec{q}}+1)\right] \tag{6.87}$$

6.3 Kinetic Theory: Quantum Kinetic Equation (QKE)

Here we follow section 10.5 in [Haug2007]. We construct a constant $\vec{E}$, steady state and homogenous QKE for our discussion of the electron-phonon interaction. For LHS of QKE, we set $\vec{B}=0$, drop $\vec{r}^+$ and drop t^+.

$$\text{LHS} = -q\vec{E}\cdot\nabla_{\vec{p}}f^W(\vec{p}) \tag{6.88}$$

In constructing the RHS, we choose the full collision integral (for homogenous systems) and further impose the steady state condition by dropping t^+

$$
\begin{aligned}
I(\vec{p}t_1^+) &= \int_{-\infty}^{\infty} dt_3 X(\vec{p}+q\vec{E}\tfrac{t_3}{2}, -t_3, \tfrac{1}{2}t_1^+ + \tfrac{1}{2}t_3)Y(\vec{p}+q\vec{E}\tfrac{t_3}{2}, t_3, \tfrac{1}{2}t_1^+ + \tfrac{1}{2}t_3) && (6.89)\\
\Rightarrow I(\vec{p}) &= \int_{-\infty}^{\infty} dt_3 X(\vec{p}+q\vec{E}\tfrac{t_3}{2}, -t_3)Y(\vec{p}+q\vec{E}\tfrac{t_3}{2}, t_3) && (6.90)\\
\text{with } XY &= \Sigma^R G^< + \Sigma^< G^A - G^R\Sigma^< - G^<\Sigma^A && (6.91)\\
&= \Sigma^{(GI)R}G^{(GI)<} + \Sigma^{(GI)<}G^{(GI)A} - G^{(GI)R}\Sigma^{(GI)<} - G^{(GI)<}\Sigma^{(GI)A} && (6.92)
\end{aligned}
$$

We also need to construct the matching GKB ansatz for RHS. We simply set $\vec{B}=0$ and drop $\vec{r}^+$ to get the constant $\vec{E}$, homogenous and steady state GKB ansatz.

$$
\begin{aligned}
G^{(GI)<}(\vec{p}, t_1^-) &= iA(\vec{p}, t_1^-)f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_1^-|) && (6.93)\\
G^{(GI)>}(\vec{p}, t_1^-) &= -iA(\vec{p}, t_1^-)\left(1 - f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_1^-|)\right) && (6.94)
\end{aligned}
$$

Finally for the electron-phonon interaction, we choose the self-energy to be in the Born approximation.

$$
\Sigma(\vec{k}, \tau_1\tau_2) = i\sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 G(\vec{k}-\vec{q}, \tau_1, \tau_2)D^{(0)}(\vec{q}, \tau_1, \tau_2) \qquad (6.95)
$$

We need components $\Sigma^>(=\Sigma^{(GI)>})$ and $\Sigma^<(=\Sigma^{(GI)<})$ and so we apply Langreth's theorem for this parallel multiplication case.

$$
\begin{aligned}
\Sigma^{(GI)\lessgtr}(\vec{k}, t_1, t_2) &= i\sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 G^{(GI)\lessgtr}(\vec{k}-\vec{q}, t_1, t_2)D^{(0)\lessgtr}(\vec{q}, t_1, t_2) && (6.96)\\
&\mid\ \text{transform to Wigner time notation}\\
\Sigma^{(GI)\lessgtr}(\vec{k}, t_1^-) &= i\sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 G^{(GI)\lessgtr}(\vec{k}-\vec{q}, t_1^-)D^{(0)\lessgtr}(\vec{q}, t_1^-) && (6.97)
\end{aligned}
$$

The equilibrium phonon Green's functions are

$$
\begin{aligned}
D^{(0)<}(\vec{q}, t^-) &= -i\left[\left(N_{\vec{q}}^{eq}+1\right)e^{i\omega_{\vec{q}}t^-} + N_{\vec{q}}^{eq}e^{-i\omega_{\vec{q}}t^-}\right] && (6.98)\\
D^{(0)>}(\vec{q}, t^-) &= -i\left[\left(N_{\vec{q}}^{eq}+1\right)e^{-i\omega_{\vec{q}}t^-} + N_{\vec{q}}^{eq}e^{i\omega_{\vec{q}}t^-}\right] && (6.99)
\end{aligned}
$$

We will now insert all these expressions into RHS, [4]

$$
\begin{aligned}
& I(\vec{p})\\
= & \int_{-\infty}^{\infty} dt_3 \left(\Sigma^{(GI)R}G^{(GI)<} + \Sigma^{(GI)<}G^{(GI)A} - G^{(GI)R}\Sigma^{(GI)<} - G^{(GI)<}\Sigma^{(GI)A}\right)\\
& \times(\vec{p}+\tfrac{1}{2}q\vec{E}t_3, -t_3)(\vec{p}+\tfrac{1}{2}q\vec{E}t_3, t_3) \qquad (6.100)\\
\mid\ & \text{recall that a retarded quantity has the relation } C^R = \theta(t)(C^> - C^<)\\
\mid\ & \text{recall that an advanced quantity has the relation } C^A = \theta(-t)(C^< - C^>)\\
\mid\ & \text{note also } \int_{-\infty}^{\infty} dt_3\theta(t_3) = \int_0^{\infty} dt_3 \text{ and } \int_{-\infty}^{\infty} dt_3\theta(-t_3) = \int_{-\infty}^{0} dt_3
\end{aligned}
$$

[4] Note that the negative sign in [Haug2007] eqn (10.100) came from LHS. See [Haug2007] eqn (10.96)

$$
\begin{aligned}
= \quad & \left[\int_{-\infty}^{0} dt_3 \left(\Sigma^{(GI)>} - \Sigma^{(GI)<}\right) G^{(GI)<} + \int_{-\infty}^{0} dt_3 \Sigma^{(GI)<} \left(G^{(GI)<} - G^{(GI)>}\right)\right. \\
& \left. - \int_{-\infty}^{0} dt_3 \left(G^{(GI)>} - G^{(GI)<}\right) \Sigma^{(GI)<} - \int_{-\infty}^{0} dt_3 G^{(GI)<} \left(\Sigma^{(GI)<} - \Sigma^{(GI)>}\right)\right] \\
& \times(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, -t_3)(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, t_3) \qquad (6.101) \\
| \quad & \text{4 terms cancel pariwise} \\
= \quad & \int_{-\infty}^{0} dt_3 \left[\Sigma^{(GI)>}G^{(GI)<} - \Sigma^{(GI)<}G^{(GI)>} - G^{(GI)>}\Sigma^{(GI)<} + G^{(GI)<}\Sigma^{(GI)>}\right] \\
& \times(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, -t_3)(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, t_3) \qquad (6.102) \\
| \quad & \text{insert the expression for self-energy} \\
= \quad & \int_{-\infty}^{0} dt_3 i \sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 \\
& \times \left[G^{(GI)>}(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, -t_3) D^{(0)>}(\vec{q}, -t_3) G^{(GI)<}(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, t_3)\right. \\
& - G^{(GI)<}(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, -t_3) D^{(0)<}(\vec{q}, -t_3) G^{(GI)>}(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, t_3) \\
& - G^{(GI)>}(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, -t_3) G^{(GI)<}(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, t_3) D^{(0)<}(\vec{q}, t_3) \\
& \left. + G^{(GI)<}(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, -t_3) G^{(GI)>}(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, t_3) D^{(0)>}(\vec{q}, t_3)\right] \qquad (6.103) \\
| \quad & \text{insert GKB ansatz} \\
= \quad & \int_{-\infty}^{0} dt_3 i \sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 \\
& \times \left[A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, -t_3) \left(1 - f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3| - \vec{q})\right) D^{(0)>}(\vec{q}, -t_3) A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, t_3) f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3|)\right. \\
& - A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, -t_3) f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3| - \vec{q}) D^{(0)<}(\vec{q}, -t_3) A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, t_3) \left(1 - f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3|)\right) \\
& - A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, -t_3) \left(1 - f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3|)\right) A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, t_3) f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3| - \vec{q}) D^{(0)<}(\vec{q}, t_3) \\
& \left. + A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, -t_3) f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3|) A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, t_3) \left(1 - f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3| - \vec{q})\right) D^{(0)>}(\vec{q}, t_3)\right] \\
| \quad & \text{note } D^{(0)\gtrless}(\vec{q}, -t^-) = D^{(0)\lessgtr}(\vec{q}, t^-) \\
| \quad & \text{note also } A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, -t_3) = A^*(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, t_3) \\
| \quad & \text{recall that the distribution function } f^W \text{ is real (but not positive definite)} \\
= \quad & \int_{-\infty}^{0} dt_3 i \sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 \\
& \times \left[A^*(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, t_3) A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, t_3) D^{(0)<}(\vec{q}, t_3) \left(1 - f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3| - \vec{q})\right) f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3|)\right. \\
& - A^*(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, t_3) A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, t_3) D^{(0)>}(\vec{q}, t_3) \left(1 - f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3|)\right) f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3| - \vec{q}) \\
& - A^*(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, t_3) A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, t_3) D^{(0)<}(\vec{q}, t_3) \left(1 - f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3|)\right) f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3| - \vec{q}) \\
& \left. + A^*(\vec{p} + \tfrac{1}{2}q\vec{E}t_3, t_3) A(\vec{p} + \tfrac{1}{2}q\vec{E}t_3 - \vec{q}, t_3) D^{(0)>}(\vec{q}, t_3) \left(1 - f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3| - \vec{q})\right) f^W(\vec{p} + \tfrac{1}{2}q\vec{E}|t_3|)\right] \\
| \quad & \text{note that } \left(iD^{(0)\lessgtr}(\vec{q}, t_3)\right)^* = iD^{(0)\gtrless}(\vec{q}, t_3) \\
| \quad & \text{so, 1st line \& 4th line , 2nd line \& 3rd line are like } z + z^* = 2\Re(z)
\end{aligned}
$$

$$
\begin{aligned}
= & \int_{-\infty}^{0} dt_3 \sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 \\
& \times \Big[2\Re\left\{ A^*(\vec{p}+\tfrac{1}{2}q\vec{E}t_3-\vec{q},t_3)A(\vec{p}+\tfrac{1}{2}q\vec{E}t_3,t_3)iD^{(0)<}(\vec{q},t_3)\right\} \\
& \qquad \times \left(1-f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|-\vec{q})\right) f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|) \\
& -2\Re\left\{ A^*(\vec{p}+\tfrac{1}{2}q\vec{E}t_3,t_3)A(\vec{p}+\tfrac{1}{2}q\vec{E}t_3-\vec{q},t_3)iD^{(0)<}(\vec{q},t_3)\right\} \\
& \qquad \times \left(1-f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|)\right) f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|-\vec{q})\Big]
\end{aligned} \tag{6.104}
$$

The final QKE (after including LHS) is thus,

$$
\begin{aligned}
-q\vec{E}\cdot\nabla_{\vec{p}}f^W(\vec{p}) = & \int_{-\infty}^{0} dt_3 \sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 \\
& \times \Big[2\Re\left\{ A^*(\vec{p}+\tfrac{1}{2}q\vec{E}t_3-\vec{q},t_3)A(\vec{p}+\tfrac{1}{2}q\vec{E}t_3,t_3)iD^{(0)<}(\vec{q},t_3)\right\} \\
& \qquad \times \left(1-f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|-\vec{q})\right) f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|) \\
& -2\Re\left\{ A^*(\vec{p}+\tfrac{1}{2}q\vec{E}t_3,t_3)A(\vec{p}+\tfrac{1}{2}q\vec{E}t_3-\vec{q},t_3)iD^{(0)<}(\vec{q},t_3)\right\} \\
& \qquad \times \left(1-f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|)\right) f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|-\vec{q})\Big]
\end{aligned} \tag{6.105}
$$

which is eqn (10.101) in [Haug2007]. In this QKE, we see the usual quantum effects; intracollisional field effect and non-Markovian integrals.

We recover the Boltzmann equation (for homogenous systems in steady state condition) by setting $\vec{E}=0$ and substituting free spectral functions into the collision integral, then we get the usual energy conserving delta functions. (Equivalently, we can start with the zeroth order collision integral, use KB ansatz and substitute free spectral functions.) Here we will take a particular approximation where we take the spectral function of a single particle under the influence of a constant force, $\vec{F}=q\vec{E}$.

$$
A(\vec{p},t^-) = e^{-\frac{i}{\hbar}\left(\epsilon_{\vec{p}}t^- + \frac{|\vec{F}|^2(t^-)^3}{24m}\right)} = e^{-\frac{i}{\hbar}\left(\epsilon_{\vec{p}}t^- + \frac{q^2|\vec{E}|^2(t^-)^3}{24m}\right)} \tag{6.106}
$$

The QKE becomes

$$
\begin{aligned}
& -q\vec{E}\cdot\nabla_{\vec{p}}f^W(\vec{p}) \\
= & \int_{-\infty}^{0} dt_3 \sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 \\
& \times \left[2\Re\left\{ e^{\frac{i}{\hbar}\left(\epsilon_{\vec{p}+q\vec{E}t_3/2-\vec{q}}t_3+\frac{q^2|\vec{E}|^2}{24m}t_3^3\right)} e^{-\frac{i}{\hbar}\left(\epsilon_{\vec{p}+q\vec{E}t_3/2}t_3+\frac{q^2|\vec{E}|^2}{24m}t_3^3\right)} iD^{(0)<}(\vec{q},t_3)\right\} \right. \\
& \qquad \times \left(1-f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|-\vec{q})\right) f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|) \\
& -2\Re\left\{ e^{\frac{i}{\hbar}\left(\epsilon_{\vec{p}+q\vec{E}t_3/2}t_3+\frac{q^2|\vec{E}|^2}{24m}t_3^3\right)} e^{-\frac{i}{\hbar}\left(\epsilon_{\vec{p}+q\vec{E}t_3/2-\vec{q}}t_3+\frac{q^2|\vec{E}|^2}{24m}t_3^3\right)} iD^{(0)<}(\vec{q},t_3)\right\} \\
& \qquad \left. \times \left(1-f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|)\right) f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|-\vec{q}) \right]
\end{aligned} \tag{6.107}
$$

| recall that $iD^{(0)<}(\vec{q},t_3) = (N_{\vec{q}}^{eq}+1)e^{i\omega_{\vec{q}}t_3} + N_{\vec{q}}^{eq}e^{-i\omega_{\vec{q}}t_3}$

$$
\begin{aligned}
& | \quad \text{and actually the force terms in the spectral functions cancel} \\
& | \quad \text{the real parts are the cosine terms} \\
= \;& 2\int_{-\infty}^{0} dt_3 \sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 \\
& \times \Big\{ \Big(\cos\Big((\epsilon_{\vec{p}+q\vec{E}t_3/2-\vec{q}} - \epsilon_{\vec{p}+q\vec{E}t_3/2} + \omega_{\vec{q}})t_3\Big)\Big(N^{eq}_{\vec{q}}+1\Big) \\
& + \cos\Big((\epsilon_{\vec{p}+q\vec{E}t_3/2-\vec{q}} - \epsilon_{\vec{p}+q\vec{E}t_3/2} - \omega_{\vec{q}})t_3\Big) N^{eq}_{\vec{q}}\Big)\Big(1 - f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|-\vec{q})\Big) f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|) \\
& - \Big(\cos\Big((\epsilon_{\vec{p}+q\vec{E}t_3/2} - \epsilon_{\vec{p}+q\vec{E}t_3/2-\vec{q}} + \omega_{\vec{q}})t_3\Big)\Big(N^{eq}_{\vec{q}}+1\Big) \\
& + \cos\Big((\epsilon_{\vec{p}+q\vec{E}t_3/2} - \epsilon_{\vec{p}+q\vec{E}t_3/2-\vec{q}} - \omega_{\vec{q}})t_3\Big) N^{eq}_{\vec{q}}\Big)\Big(1 - f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|)\Big) f^W(\vec{p}+\tfrac{1}{2}q\vec{E}|t_3|-\vec{q})\Big\}
\end{aligned}
\tag{6.108}
$$

This is the equation (10.102) in [Haug2007] and is known as the Barker-Ferry equation.

6.4 Perturbative Approach: Linear Response Treatment (Holstein's Formula)

I am unaware of very extensive calculations of thermal conductivity renormalized by electron-phonon interaction, hence I shall briefly mention here for completeness, the results of electrical conductivity which have been renormalized to a very sophisticated form by phonon ladder vertices.

This renormalized electrical conductivity formula is called the Holstein's formula and is derived in the famous article in [Holstein1964]. A shorter derivation is seen in [Mahan2000]. The result is equation (8.235) in [Mahan2000].

6.5 Functional Derivative Approach: Electron-Phonon Hedin-like Equations

In this section, we describe Robert van Leeuwen's ([Leeuwen2004]) derivation of self consistent Hedin-like equations for electron-phonon interaction. His derivation is an improvement over a previous derivation in [Hedin1970]. The previous derivation started from Born-Oppenheimer adiabatic decoupling and the uncontrolled double counting problem is therefore an unsatisfactory feature of the theory.

Robert van Leeuwen managed to choose a body frame (and impose Eckart conditions) and derived the equations circumventing the Born-Oppenheimer approximation.[5]

[5] It is important to see that he has done such a general derivation that it should really be called the Hedin-like equations of the solid! Coulomb Hedin-like equations is a special case of his theory as shown in the appendix at the end of the thesis. I believe, that if an expansion about ionic equilibrium is done, the phonon Hedin-like equations should also be a special case of his theory!

6.5.1 Preliminaries

[The Hamiltonian] The electron-ion (solid) Hamiltonian is the sum of these terms. [6] [7]

$$T_n = \sum_{l=1}^{N_n} \left(-\frac{\hbar^2}{2M_l}\right) \nabla^2_{\vec{R}_l} \tag{6.109}$$

$$T_e = \sum_{i=1}^{N_e} \left(-\frac{\hbar^2}{2m_e}\right) \nabla^2_{\vec{r}^e_i} \tag{6.110}$$

$$W_{nn} = \frac{1}{2} \sum_{l_1 \neq l_2}^{N_e} \frac{Z_{l_1} Z_{l_2}}{\left|\vec{R}_{l_1} - \vec{R}_{l_2}\right|} \tag{6.111}$$

$$W_{ee} = \frac{1}{2} \sum_{i \neq i_1}^{N_e} \frac{1}{\left|\vec{r}^e_i - \vec{r}^e_{i_1}\right|} \tag{6.112}$$

$$W_{en} = -\sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l}{\left|\vec{r}^e_i - \vec{R}_l\right|} \tag{6.113}$$

[Body Fixed Frame + Eckart Condition] [8]

---

[6] The notation is slightly different from that in the introduction chapter. This is because we are following notation closer to that used by van Leeuwen.

[7] A notational reminder: $l, l_1, l_2 \ldots$ indices denote sites for monoatomic solids or denote cells for polyatomic solids ($k, k_1, k_2, \ldots$ indices label the atoms in each cell), cartesian components are denoted by $\alpha, \alpha_1, \alpha_2, \ldots$.

[8] Search Wikipedia under "Eckart Conditions" and it gives a good article!

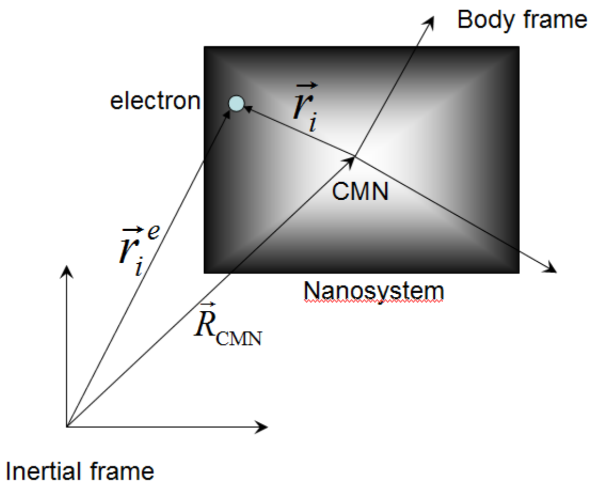


Figure 6.3: *The transformation to the (instantaneous) nuclear center of mass body frame.*

Define the (instaneous) center of mass of the nuclei.

$$\vec{R}_{\rm CMN} = \frac{1}{M_{\rm nuc}}\sum_{l}^{N_n} M_l\vec{R}_l = \frac{1}{\sum_l^{N_n} M_l}\sum_l^{N_n} M_l\vec{R}_l \tag{6.114}$$

We will proceed to transform the electronic coordinates and nuclear coordinates to the body fixed frame (with origin at $\vec{R}_{\rm CMN}$) as follows,

$$\vec{r}_i^{\,e} \longrightarrow \vec{r}_i = \mathcal{R}(\alpha\beta\gamma)(\vec{r}_i^{\,e} - \vec{R}_{\rm CMN}) \tag{6.115}$$

$$\vec{R}_l \longrightarrow \vec{R}_l' = \mathcal{R}(\alpha\beta\gamma)(\vec{R}_l - \vec{R}_{\rm CMN}) \tag{6.116}$$

where $\mathcal{R}(\alpha\beta\gamma)$ is the Euler Rotation matrix which will be given explicitly later.

We use 2 conditions (which we call "Eckart conditions") to fix the coordinates such that they will minimize the coupling of rotational and vibrational motion. They are,

1. $\sum_l^{N_n} M_l\vec{R}_l^{eq} = 0$ is the equilibrium center of mass condition where the equilibrium position parameter $\vec{R}_l^{eq}$ is fixed from Born-Oppenheimer adiabatic decoupling. This condition means that when all the ions are "frozen" in $\vec{R}_l^{eq}$, the body fixed frame is the principal axis frame or in other words, the nuclear inertia tensor is diagonal under $\vec{R}_l^{eq}$.

2. $0 = \sum_l^{N_n} M_l\vec{R}_l^{eq}\times\vec{R}_l' = \sum_l^{N_n} M_l\vec{R}_l^{eq}\times\mathcal{R}(\alpha\beta\gamma)(\vec{R}_l - \vec{R}_{\rm CMN})$ gives 3 conditions to fix the Euler angles. So the Euler angles are a function of the nuclear coordinates.

[**Reminder on Euler Angles and Some Identities**] We now recall some basic facts of body frame and Euler angles in Classical Dynamics. The rotation matrix and Euler angles in the so-called "y-convention (Classical Mechanics (3rd Edition), Herbert Goldstein, Charles Poole and John Safko

(Addison Wesley 2001) pg 601):

$$\begin{aligned}
\mathcal{R}(\alpha\beta\gamma) &= \mathcal{R}_z(\gamma)\mathcal{R}_y(\alpha)\mathcal{R}_z(\beta) \qquad (6.117)\\
&= \begin{pmatrix} -\sin\gamma\sin\beta+\cos\alpha\cos\beta\cos\gamma & \sin\gamma\cos\beta+\cos\alpha\sin\beta\cos\gamma & -\cos\gamma\sin\alpha \\ -\cos\gamma\sin\beta-\cos\alpha\cos\beta\sin\gamma & \cos\gamma\cos\beta-\cos\alpha\sin\beta\sin\gamma & \sin\gamma\sin\alpha \\ \sin\alpha\cos\gamma & \sin\alpha\sin\gamma & \cos\alpha \end{pmatrix}
\end{aligned}$$

Denote the column vectors of this rotation matrix by $\vec{e}_{\alpha_1}$, $\vec{e}_{\alpha_2}$ and $\vec{e}_{\alpha_3}$ and the matrix elements $\mathcal{R}_{\alpha_1\alpha_2}$ can be written as

$$\mathcal{R}_{\alpha_1\alpha_2} = (\vec{e}_{\alpha_2})_{\alpha_1} \qquad (6.118)$$

as we can see from here

$$\mathcal{R} = \begin{pmatrix} \vdots & \vdots & \vdots \\ \vec{e}_{\alpha_1} & \vec{e}_{\alpha_2} & \vec{e}_{\alpha_3} \\ \vdots & \vdots & \vdots \end{pmatrix} = \begin{pmatrix} \mathcal{R}_{11} & \mathcal{R}_{12} & \mathcal{R}_{13} \\ \mathcal{R}_{21} & \mathcal{R}_{22} & \mathcal{R}_{23} \\ \mathcal{R}_{31} & \mathcal{R}_{32} & \mathcal{R}_{33} \end{pmatrix} \qquad (6.119)$$

and for example $\mathcal{R}_{23} = (\vec{e}_{\alpha_3})_{\alpha_2}$. They are related to the angular velocity vectors by [9]

$$\begin{aligned}
\frac{\partial\vec{e}_{\alpha_1}}{\partial\alpha} &= \vec{e}_{\alpha_1}\times\omega_\alpha \qquad (6.120)\\
\frac{\partial\vec{e}_{\alpha_1}}{\partial\beta} &= \vec{e}_{\alpha_1}\times\omega_\beta \qquad (6.121)\\
\frac{\partial\vec{e}_{\alpha_1}}{\partial\gamma} &= \vec{e}_{\alpha_1}\times\omega_\gamma \qquad (6.122)
\end{aligned}$$

and the angular velocity vectors are defined as

$$\omega_\alpha = \begin{pmatrix} \sin\gamma \\ \cos\gamma \\ 0 \end{pmatrix} \quad , \quad \omega_\beta = \begin{pmatrix} -\sin\alpha\cos\gamma \\ \sin\alpha\sin\gamma \\ \cos\alpha \end{pmatrix} \quad , \quad \omega_\gamma = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad (6.123)$$

Recall that the Eckart choice of the body fixed frame says that all Euler angles depend on nuclear coordinates $\vec{R}_l$. Then consider the expression, where chain rule is used,

$$\begin{aligned}
\frac{\partial(\vec{e}_{\alpha_2})_{\alpha_1}}{\partial R_{l_1\alpha_3}} &= \frac{\partial(\vec{e}_{\alpha_2})_{\alpha_1}}{\partial\alpha}\frac{\partial\alpha}{\partial R_{l_1\alpha_3}} + \frac{\partial(\vec{e}_{\alpha_2})_{\alpha_1}}{\partial\beta}\frac{\partial\beta}{\partial R_{l_1\alpha_3}} + \frac{\partial(\vec{e}_{\alpha_2})_{\alpha_1}}{\partial\gamma}\frac{\partial\gamma}{\partial R_{l_1\alpha_3}} \qquad (6.124)\\
&\quad | \ \text{use the relations with angular velocity vectors}\\
&\quad | \ \text{then write } (\vec{e}_{\alpha_2}\times\omega_{\alpha,\beta,\gamma})_{\alpha_1} = \sum_{\alpha_4\alpha_5}\epsilon_{\alpha_1\alpha_4\alpha_5}(\vec{e}_{\alpha_2})_{\alpha_4}(\omega_{\alpha,\beta,\gamma})_{\alpha_5}\\
&\quad | \ \text{where } \epsilon \text{ is the antisymmetric tensor}\\
&\quad | \ \text{define } \Omega^{l_1}_{\alpha_5\alpha_3} = (\omega_\alpha)_{\alpha_5}\frac{\partial\alpha}{\partial R_{l_1\alpha_3}} + (\omega_\beta)_{\alpha_5}\frac{\partial\beta}{\partial R_{l_1\alpha_3}} + (\omega_\gamma)_{\alpha_5}\frac{\partial\gamma}{\partial R_{l_1\alpha_3}}\\
&= \sum_{\alpha_4\alpha_5}\epsilon_{\alpha_1\alpha_4\alpha_5}(\vec{e}_{\alpha_2})_{\alpha_4}\Omega^{l_1}_{\alpha_5\alpha_3} \qquad (6.125)
\end{aligned}$$

[9] The reader may take the explicit expressions of $\mathcal{R}$ and $\omega_{\alpha,\beta,\gamma}$ and check backwards.

It will be shown in the appendix to this chapter that since $\alpha\beta\gamma$ are invariant under translations of all $\vec{R}_{l_1}$, we get a sum rule,

$$\sum_{l_1=1}^{N_n} \Omega^{l_1}_{\alpha_5\alpha_3} = 0 \tag{6.126}$$

From above, recall that $\mathcal{R}_{\alpha_1\alpha_2} = (\vec{e}_{\alpha_2})_{\alpha_1}$, we can immediately derive

$$\frac{\partial \mathcal{R}_{\alpha_1\alpha_2}}{\partial R_{l_1\alpha_3}} = \sum_{\alpha_4\alpha_5} \epsilon_{\alpha_1\alpha_4\alpha_5} \mathcal{R}_{\alpha_4\alpha_2} \Omega^{l_1}_{\alpha_5\alpha_3} \tag{6.127}$$

Now we define rotated electronic and nuclear coordinates,

$$r''_{i_1\alpha_1} \equiv \sum_{\alpha_2} \mathcal{R}_{\alpha_1\alpha_2} r_{i_1\alpha_2} \tag{6.128}$$

$$R''_{l_1\alpha_1} \equiv \sum_{\alpha_2} \mathcal{R}_{\alpha_1\alpha_1} R_{l_1\alpha_2} \tag{6.129}$$

then we derive

$$\frac{\partial r''_{i_1\alpha_1}}{\partial R_{l_3\alpha_3}} = \sum_{\alpha_2} \frac{\partial \mathcal{R}_{\alpha_1\alpha_2}}{\partial R_{l_3\alpha_3}} r_{i_1\alpha_2} \tag{6.130}$$

$$= \sum_{\alpha_2} \sum_{\alpha_4\alpha_5} \epsilon_{\alpha_1\alpha_4\alpha_5} \mathcal{R}_{\alpha_4\alpha_2} \Omega^{l_3}_{\alpha_5\alpha_3} r_{i_1\alpha_2} \tag{6.131}$$

$$= \sum_{\alpha_4\alpha_5} \epsilon_{\alpha_1\alpha_4\alpha_5} r''_{i_1\alpha_4} \Omega^{l_3}_{\alpha_5\alpha_3} \tag{6.132}$$

and

$$\frac{\partial R''_{l_1\alpha_1}}{\partial R_{l_3\alpha_3}} = \sum_{\alpha_2} \left(\frac{\partial \mathcal{R}_{\alpha_1\alpha_2}}{\partial R_{l_3\alpha_3}} R_{l_1\alpha_2} + \mathcal{R}_{\alpha_1\alpha_2} \frac{\partial R_{l_1\alpha_2}}{\partial R_{l_3\alpha_3}} \right) \tag{6.133}$$

$$= \sum_{\alpha_2} \left(\mathcal{R}_{\alpha_1\alpha_2} \delta_{l_1 l_3} \delta_{\alpha_2\alpha_3} + \sum_{\alpha_4\alpha_5} \epsilon_{\alpha_1\alpha_4\alpha_5} \mathcal{R}_{\alpha_4\alpha_2} \Omega^{l_3}_{\alpha_5\alpha_3} R_{l_1\alpha_2} \right) \tag{6.134}$$

$$= \mathcal{R}_{\alpha_1\alpha_3} \delta_{l_1 l_3} + \sum_{\alpha_4\alpha_5} \epsilon_{\alpha_1\alpha_4\alpha_5} R''_{l_1\alpha_4} \Omega^{l_3}_{\alpha_5\alpha_3} \tag{6.135}$$

which will be used in the appendix to this chapter.

[**Transformed Hamiltonian**] The old and new wavefunctions in the Schrodinger equation are related by

$$\Phi_{\text{old}}(\vec{r}^{\,e}_1 \ldots \vec{r}^{\,e}_{N_e}, \vec{R}_1 \ldots \vec{R}_{N_n}) = \Phi_{\text{new}}(\vec{r}_1 \ldots \vec{r}_{N_e}, \vec{R}'_1 \ldots \vec{R}'_{N_n}) \equiv \Phi_{\text{new}}(\vec{r}_1 \ldots \vec{r}_{N_e}, \vec{R}_1 \ldots \vec{R}_{N_n}) \tag{6.136}$$

and recall that $\vec{r}_i$ is a function of $\vec{r}^{\,e}_i$ and $\vec{R}_l$ and $\vec{R}'_l$ is a function of $\vec{R}_l$ so we can write Φ_{new} as if the independent variables are $\vec{r}_i$ and $\vec{R}_l$. However, one must not forget that variables $\vec{R}_l$ are "inside" $\vec{r}_i$.

The term by term transformed Hamiltonian (which is taken to be acting on $\Phi_{\text{new}}(\vec{r}_1 \ldots \vec{r}_{N_e}, \vec{R}_1 \ldots \vec{R}_{N_n})$)

is,

$$T_n = -\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \nabla^2_{\vec{R}_l} \tag{6.137}$$

$$= -\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \left(\sum_{l_1} \frac{\partial \vec{R}'_{l_1}}{\partial \vec{R}_l} \nabla_{\vec{R}'_{l_1}} + \sum_i \frac{\partial \vec{r}_i}{\partial \vec{R}_l} \nabla_{\vec{r}_i} \right)^2 \tag{6.138}$$

$|$ take it to be acting on $\Phi_{\text{new}}(\vec{r}_1 \ldots \vec{r}_{N_e}, \vec{R}_1 \ldots \vec{R}_{N_n})$

$$= -\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \left(\nabla_{\vec{R}_{l_1}} + \sum_i \frac{\partial \vec{r}_i}{\partial \vec{R}_l} \nabla_{\vec{r}_i} \right)^2 \tag{6.139}$$

$|$ add and subtract $-\sum_l \frac{\hbar^2}{2M_l} \nabla^2_{\vec{R}_l}$

$$= -\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \left[\left(\nabla_{\vec{R}_{l_1}} + \sum_i \frac{\partial \vec{r}_i}{\partial \vec{R}_l} \nabla_{\vec{r}_i} \right)^2 + \nabla^2_{\vec{R}_l} - \nabla^2_{\vec{R}_l} \right] \tag{6.140}$$

$$T_e = -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \nabla^2_{\vec{r}^e_i} \tag{6.141}$$

$$= -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \left(\sum_l \frac{\partial \vec{R}'_l}{\partial \vec{r}^e_i} \nabla_{\vec{R}'_l} + \sum_{i_1} \frac{\partial \vec{r}_{i_1}}{\partial \vec{r}^e_i} \nabla_{\vec{r}_{i_1}} \right)^2 \tag{6.142}$$

$|$ we have $\frac{\partial \vec{R}'_l}{\partial \vec{r}^e_i} = 0$ and $\frac{\partial \vec{r}_{i_1}}{\partial \vec{r}^e_i} = \delta_{ii_1}$ since $\mathcal{R}(\alpha\beta\gamma)$ is a function of nuclear coordinates

$$= -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \nabla^2_{\vec{r}_i} \tag{6.143}$$

W_{nn} is obviously unchanged under the transformation by direct substituition.

$$W_{ee} = \frac{1}{2} \sum_{i \neq i_1}^{N_e} \frac{1}{|\vec{r}^e_i - \vec{r}^e_{i_1}|} \tag{6.144}$$

$$= \frac{1}{2} \sum_{i \neq i_1}^{N_e} \frac{1}{\left|\mathcal{R}^{-1}\vec{r}_i + \vec{R}_{\text{CMN}} - \mathcal{R}^{-1}\vec{r}_{i_1} - \vec{R}_{\text{CMN}}\right|} \tag{6.145}$$

$$= \frac{1}{2} \sum_{i \neq i_1}^{N_e} \frac{1}{|\mathcal{R}^{-1}(\vec{r}_i - \vec{r}_{i_1})|} \tag{6.146}$$

$|$ magnitude of vectors is unchanged by rotation

$$= \frac{1}{2} \sum_{i \neq i_1}^{N_e} \frac{1}{|\vec{r}_i - \vec{r}_{i_1}|} \tag{6.147}$$

and lastly for W_{en}

$$
\begin{aligned}
W_{en} &= -\sum_{i=1}^{N_e}\sum_{l=1}^{N_n} \frac{Z_l}{\left|\mathcal{R}^{-1}\vec{r}_i + \vec{R}_{\text{CMN}} - \vec{R}_l\right|} && (6.148)\\
&\quad | \quad \text{magnitude is unchanged by rotations, so we can multiply by } \mathcal{R}\\
&= -\sum_{i=1}^{N_e}\sum_{l=1}^{N_n} \frac{Z_l}{\left|\vec{r}_i + \mathcal{R}\left(\vec{R}_{\text{CMN}} - \vec{R}_l\right)\right|} && (6.149)\\
&= -\sum_{i=1}^{N_e}\sum_{l=1}^{N_n} \frac{Z_l}{\left|\mathcal{R}\left(\vec{R}_l - \vec{R}_{\text{CMN}}\right) - \vec{r}_i\right|} = -\sum_{i=1}^{N_e}\sum_{l=1}^{N_n} \frac{Z_l}{\left|\vec{R}'_l - \vec{r}_i\right|} && (6.150)
\end{aligned}
$$

so W_{en} is a N_n nuclei potential and a one-electron potential.

The Hamiltonian is now,

$$H = H_n + H_e + T_{MPC} + W_{en} \tag{6.151}$$

where

$$
\begin{aligned}
T_{MPC} &\equiv \sum_{l=1}^{N_n}\left(-\frac{\hbar^2}{2M_l}\right)\left[\left(\nabla_{\vec{R}_{l_1}} + \sum_i \frac{\partial \vec{r}_i}{\partial \vec{R}_l}\nabla_{\vec{r}_i}\right)^2 - \nabla^2_{\vec{R}_l}\right] && (6.152)\\
H_e &= \sum_{i=1}^{N_e}\left(-\frac{\hbar^2}{2m_e}\right)\nabla^2_{\vec{r}_i} + \frac{1}{2}\sum_{i\neq i_1}^{N_e}\frac{1}{|\vec{r}_i - \vec{r}_{i_1}|} && (6.153)\\
H_n &= \sum_{l=1}^{N_n}\left(-\frac{\hbar^2}{2M_l}\right)\nabla^2_{\vec{R}_l} + \frac{1}{2}\sum_{l,l_1}^{N_n}\frac{Z_l Z_{l_1}}{\left|\vec{R}_l - \vec{R}_{l_1}\right|} && (6.154)\\
W_{en} &= \sum_{i=1}^{N_e}\sum_{l=1}^{N_n}\frac{-Z_l}{\left|\mathcal{R}(\alpha\beta\gamma)\left(\vec{R}_l - \vec{R}_{\text{CMN}}\right) - \vec{r}_i\right|} && (6.155)
\end{aligned}
$$

In the appendix at the end of the chapter, T_{MPC} will be shown to be written as

$$T_{MPC} = T_{MP} + T_C \tag{6.156}$$

and T_{MP} (MP - Mass Polarization) is neglected since we are considering a solid and it is not negligible for small systems, T_C (C - Coriolis) is neglected due to Eckart conditions.[10] The approximated Hamiltonian is then

$$H = H_n + H_e + W_{en} \tag{6.157}$$

We have achieved what looks like the result of adiabatic decoupling but in a more rigorous and controlled manner.

[10]So for finite systems, the term T_{MP} is not negligible and it is worth investigating its role in nanosystems!

6.5.2 Derivation of Electron-Phonon Hedin-like Equations

To cater for a field theoretic description, we go over to the (real space) second quantized representation. Both electronic coordinates and nuclear coordinates have been written in second quantized form.

$$\begin{aligned} H &= H_n + H_e + W_{en} && (6.158)\\ &= T_n + T_e + W_{nn} + W_{ee} + W_{en} && (6.159)\\ T_e &= -\frac{1}{2}\sum_{\sigma}\int d\vec{r}\psi^\dagger_\sigma(\vec{r})\nabla^2\psi_\sigma(\vec{r}) && (6.160)\\ W_{ee} &= \frac{1}{2}\sum_{\sigma_1\sigma_2}\int d\vec{r}_1\int d\vec{r}_2\psi^\dagger_{\sigma_2}(\vec{r}_2)\psi^\dagger_{\sigma_1}(\vec{r}_1)\psi_{\sigma_1}(\vec{r}_1)\psi_{\sigma_2}(\vec{r}_2)w(\vec{r}_1,\vec{r}_2) && (6.161)\\ W_{en} &= \sum_{\sigma}\int d\vec{r}\int dV\psi^\dagger_\sigma(\vec{r})\psi_\sigma(\vec{r})\Gamma(\vec{R}_1\cdots\vec{R}_{N_m})\sum_l\frac{-Z_l}{\left|\mathcal{R}\left(\vec{R}_l-\vec{R}_{\mathrm{CMN}}\right)-\vec{r}\right|} && (6.162)\end{aligned}$$

Notice that $\mathcal{R}(\vec{R}_\alpha - \vec{R}_{\mathrm{CMN}})$ is made up of N_n nuclei terms so we need a N_n nuclear particle density operator, $\Gamma(\vec{R}_1\cdots\vec{R}_{N_n})$, to write its second quantized expression. It is explicitly,

$$\Gamma(\vec{R}_1\cdots\vec{R}_{N_n}) = \sum_{\sigma_1\cdots\sigma_{N_n}}\phi^\dagger_{\sigma_1}(\vec{R}_1)\cdots\phi^\dagger_{\sigma_{N_n}}(\vec{R}_{N_n})\phi_{\sigma_{N_n}}(\vec{R}_{N_n})\cdots\phi_{\sigma_1}(\vec{R}_1) \tag{6.163}$$

where index σ_1 represents all the nuclear quantum numbers and the volume element $dV = d\vec{R}_1\cdots d\vec{R}_{N_n}$. Note that we do not have to assume the statistics of these nuclear operators. We only require that ϕ and $\phi^\dagger$ commutes with any operator that depends only on electronic coordinates.

We define a potential operator

$$V_n(\vec{r}) \equiv \int dV \quad \Gamma(\vec{R}_1\cdots\vec{R}_{N_n})\sum_{l=1}^{N_n}\frac{Z_l}{\left|\mathcal{R}\left(\vec{R}_l-\vec{R}_{\mathrm{CMN}}\right)-\vec{r}\right|} \tag{6.164}$$

and define a nuclear density operator (refer to Electrostatics)

$$\begin{aligned} N(\vec{r}) &\equiv \frac{1}{4\pi}\nabla^2 V_n(\vec{r}) && (6.165)\\ &= \int dV \quad \Gamma(\vec{R}_1\cdots\vec{R}_{N_n})\sum_{l=1}^{N_n}Z_l\delta\left(\vec{r}-\mathcal{R}\left(\vec{R}_l-\vec{R}_{\mathrm{CMN}}\right)\right) && (6.166)\end{aligned}$$

The electronic density is the usual expression

$$n(\vec{r}) = \sum_\sigma \psi^\dagger_\sigma(\vec{r})\psi_\sigma(\vec{r}) \tag{6.167}$$

Define a total density,

$$\rho(\vec{r}) = n(\vec{r}) - N(\vec{r}) \tag{6.168}$$

and W_{en} can be written as

$$W_{en} = -\int d^3\vec{r}\int d\vec{R}\frac{n(\vec{r})N(\vec{R})}{\left|\vec{r}-\vec{R}\right|} \tag{6.169}$$

which we quickly check backwards

$$W_{en} = -\int d^3\vec{r}\int d\vec{R}\frac{n(\vec{r})N(\vec{R})}{\left|\vec{r}-\vec{R}\right|} \tag{6.170}$$

$$= -\int d^3\vec{r}d^3\vec{R}\sum_{\sigma}\psi^{\dagger}_{\sigma}(\vec{r})\psi_{\sigma}(\vec{r})\frac{N(\vec{R})}{\left|\vec{r}-\vec{R}\right|} \tag{6.171}$$

$$= -\int d^3\vec{r}d^3\vec{R}\sum_{\sigma}\psi^{\dagger}_{\sigma}(\vec{r})\psi_{\sigma}(\vec{r})\int dV\Gamma(\vec{R}_1\cdots\vec{R}_{N_n})\sum_{\alpha=1}^{N_n}\frac{Z_{\alpha}}{\left|\vec{r}-\vec{R}\right|}\delta\left(\vec{R}-\mathcal{R}(\vec{R}_{\alpha}-\vec{R}_{\mathrm{CMN}})\right) \tag{6.172}$$

$$= \int d^3\vec{r}d^3\vec{R}\sum_{\sigma}\psi^{\dagger}_{\sigma}(\vec{r})\psi_{\sigma}(\vec{r})\int dV\Gamma(\vec{R}_1\cdots\vec{R}_{N_n})\sum_{\alpha=1}^{N_n}\frac{-Z_{\alpha}}{\left|\vec{r}-\mathcal{R}\left(\vec{R}_{\alpha}-\vec{R}_{\mathrm{CMN}}\right)\right|} \tag{6.173}$$

Indeed.

The final expression of the Hamiltonian is then,

$$\begin{aligned} H(t) = {} & T_n + W_{nn} - \frac{1}{2}\int d\vec{r}\sum_{\sigma}\psi^{\dagger}_{\sigma}(\vec{r})\nabla^2\psi_{\sigma}(\vec{r}) + \frac{1}{2}\int d\vec{r}_1 d\vec{r}_2\sum_{\sigma_1\sigma_2}\psi^{\dagger}_{\sigma_1}(\vec{r}_1)\psi^{\dagger}_{\sigma_2}(\vec{r}_2)\psi_{\sigma_2}(\vec{r}_2)\psi_{\sigma_1}(\vec{r}_1)w(\vec{r}_1,\vec{r}_2) \\ & -\int d^3\vec{r}d^3\vec{R}\;\frac{n(\vec{r})N(\vec{R})}{\left|\vec{r}-\vec{R}\right|} + \int d^3r\rho(\vec{r})\varphi(\vec{r}t) \end{aligned} \tag{6.174}$$

where a time-dependent source term, $\varphi(\vec{r}t)$ is added for the functional derivative approach. [11]

Define the Heisenberg operator,

$$\psi_H(\vec{r}\sigma t) = V(t,t_0)^{\dagger}\psi(\vec{r}\sigma t_0)V(t,t_0) \tag{6.175}$$

$$\text{where}\quad V(t_2,t_1) = Te^{-\frac{i}{\hbar}\int_{t_1}^{t_2}dtH(t)} \tag{6.176}$$

where $H(t)$ is time-dependent since it contains the time-dependent source term $\varphi(\vec{r}t)$.

Now we want to write the equations of motion for the Green's function. This means we need the Heisenberg equations of motion for the field operators first.

$$i\hbar\frac{\partial}{\partial t}\psi_H(\vec{r}\sigma t) = [\psi_H(\vec{r}\sigma t), H_H(t)]_- \tag{6.177}$$

Note that we will use the assumption that $\psi_H(\vec{r}\sigma t)$ commutes with all nuclear operators. We carry out the commutator term by term.

$$\text{RHS} = [\psi_H(\vec{r}\sigma t), H_H(t)]_- \tag{6.178}$$

$$\text{RHS first term} = [\psi_H(\vec{r}\sigma t), (T_n + W_{nn})_H]_- \tag{6.179}$$

$$= \left([\psi(\vec{r}\sigma t), T_n + W_{nn}]_-\right)_H \tag{6.180}$$

$$= 0 \tag{6.181}$$

RHS second term

[11] The notation for the source term is J in other chapters. Here we follow van Leeuwen's notation.

$$= \left[\psi_H(\vec{r}\sigma t), \frac{1}{2}\int d\vec{r}_1 d\vec{r}_2 \sum_{\sigma_1\sigma_2} \psi_H^\dagger(\vec{r}_1\sigma_1 t)\psi_H^\dagger(\vec{r}_2\sigma_2 t)\psi_H(\vec{r}_2\sigma_2 t)\psi_H(\vec{r}_1\sigma_1 t)w(\vec{r}_1,\vec{r}_2)\right]_- \tag{6.182}$$

$$= \frac{1}{2}\int d\vec{r}_1 d\vec{r}_2 \sum_{\sigma_1\sigma_2} \left[\psi_H(\vec{r}\sigma t), \psi_H^\dagger(\vec{r}_1\sigma_1 t)\psi_H^\dagger(\vec{r}_2\sigma_2 t)\right]_- \psi_H(\vec{r}_2\sigma_2 t)\psi_H(\vec{r}_1\sigma_1 t)w(\vec{r}_1,\vec{r}_2) \tag{6.183}$$

| change commutators to anti-commutators using the identity $[A, CD]_- = -C\,[D,A]_+ + [C,A]_+\,D$

$$= \frac{1}{2}\int d\vec{r}_1 d\vec{r}_2 \sum_{\sigma_1\sigma_2} \left(-\psi_H^\dagger(\vec{r}_1\sigma_1 t)\left[\psi_H^\dagger(\vec{r}_2\sigma_2 t), \psi_H(\vec{r}\sigma t)\right]_+ + \left[\psi_H^\dagger(\vec{r}_1\sigma_1 t), \psi_H(\vec{r}\sigma t)\right]_+ \psi_H^\dagger(\vec{r}_2\sigma_2 t)\right)$$
$$\times\psi_H(\vec{r}_2\sigma_2 t)\psi_H(\vec{r}_1\sigma_1 t)w(\vec{r}_1,\vec{r}_2) \tag{6.184}$$

$$= \frac{1}{2}\int d\vec{r}_1 d\vec{r}_2 \sum_{\sigma_1\sigma_2} \left(-\psi_H^\dagger(\vec{r}_1\sigma_1 t)\delta(\vec{r}_2-\vec{r})\delta_{\sigma_2\sigma} + \delta(\vec{r}_1-\vec{r})\delta_{\sigma_1\sigma}\psi_H^\dagger(\vec{r}_2\sigma_2 t)\right)$$
$$\times\psi_H(\vec{r}_2\sigma_2 t)\psi_H(\vec{r}_1\sigma_1 t)w(\vec{r}_1,\vec{r}_2) \tag{6.185}$$

$$= \frac{1}{2}\int d\vec{r}_1 n_H(\vec{r}_1 t)\psi_H(\vec{r}\sigma t)w(\vec{r}_1,\vec{r}) + \frac{1}{2}\int d\vec{r}_2 n_H(\vec{r}_2 t)\psi_H(\vec{r}\sigma t)w(\vec{r},\vec{r}_2) \tag{6.186}$$

$$= \int d\vec{r}_1 n_H(\vec{r}_1 t)w(\vec{r}_1,\vec{r})\psi_H(\vec{r}\sigma t) \tag{6.187}$$

$$\text{RHS third term} = \left[\psi_H(\vec{r}\sigma t), -\int d^3\vec{r}_1 \int d\vec{R}\frac{n_H(\vec{r}_1 t)N_H(\vec{R}t)}{\left|\vec{r}_1-\vec{R}\right|}\right]_- \tag{6.188}$$

$$= -\int d^3\vec{r}_1 \int d^3\vec{R}\,[\psi_H(\vec{r}\sigma t), n_H(\vec{r}_1 t)]_- \frac{N_H(\vec{R}t)}{\left|\vec{r}_1-\vec{R}\right|} \tag{6.189}$$

$$= -\int d^3\vec{r}_1 \int d^3 d\vec{R}\left[\psi_H(\vec{r}\sigma t), \sum_{\sigma_1}\psi_H^\dagger(\vec{r}_1\sigma_1 t)\psi_H(\vec{r}_1\sigma_1 t)\right]_- \frac{N_H(\vec{R}t)}{\left|\vec{r}_1-\vec{R}\right|} \tag{6.190}$$

| use the identity to change commutators to anti-commutators

$$= -\int d^3\vec{r}_1 \int d^3\vec{R}\sum_{\sigma_1}\left[\psi_H^\dagger(\vec{r}_1\sigma_1 t), \psi_H(\vec{r}\sigma t)\right]_+ \psi_H(\vec{r}_1\sigma_1 t)\frac{N_H(\vec{R}t)}{\left|\vec{r}_1-\vec{R}\right|} \tag{6.191}$$

$$= -\int d^3\vec{r}_1 \int d^3\vec{R}\sum_{\sigma_1}\delta(\vec{r}_1-\vec{r})\delta_{\sigma\sigma_1}\psi_H(\vec{r}_1\sigma_1 t)\frac{N_H(\vec{R}t)}{\left|\vec{r}_1-\vec{R}\right|} \tag{6.192}$$

$$= -\int d^3\vec{R}\frac{N_H(\vec{R}t)}{\left|\vec{r}-\vec{R}\right|}\psi_H(\vec{r}\sigma t) \tag{6.193}$$

$$\text{RHS fourth term} = \left[\psi_H(\vec{r}\sigma t), \int d^3\vec{r}_1 \rho_H(\vec{r}_1 t)\varphi(\vec{r}_1 t)\right]_- \tag{6.194}$$

$$= \int d^3\vec{r}_1\,[\psi_H(\vec{r}\sigma t), n_H(\vec{r}_1 t)]_-\,\varphi(\vec{r}_1 t) \tag{6.195}$$

| this commutator is done in RHS third term, equals $\sum_{\sigma_1}\delta(\vec{r}_1-\vec{r})\delta_{\sigma\sigma_1}\psi_H(\vec{r}_1\sigma_1 t)$

$$= \varphi(\vec{r}t)\psi_H(\vec{r}\sigma t) \tag{6.196}$$

$$\therefore i\hbar\frac{\partial}{\partial t}\psi_H(\vec{r}\sigma t) = \left(-\frac{1}{2}\nabla^2+\varphi(\vec{r}t)+\int d^3\vec{r}_1\frac{\rho_H(\vec{r}_1 t)}{|\vec{r}-\vec{r}_1|}\right)\psi_H(\vec{r}\sigma t) \tag{6.197}$$

| take the Hermitian conjugate on both sides

| note that, $\frac{\partial}{\partial t}$ and ∇ is anti-Hermitian

| note that, φ is real and ρ is Hermitian, we get

$$\therefore i\hbar\frac{\partial}{\partial t}\psi_H^\dagger(\vec{r}\sigma t) = \left(-\frac{1}{2}\nabla^2+\varphi(\vec{r}t)+\int d^3\vec{r}_1\frac{\rho_H(\vec{r}_1 t)}{|\vec{r}-\vec{r}_1|}\right)\psi_H^\dagger(\vec{r}\sigma t) \tag{6.198}$$

The next step requires the equation of motion of the time-ordered function. This is defined as

$$T\left(\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right) = \theta(t-t_1)\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)-\theta(t_1-t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\psi_H(\vec{r}\sigma t) \tag{6.199}$$

Consider the action on the time-ordered function, ($\partial_t \equiv \frac{\partial}{\partial t}$)

$$\left(i\hbar\partial_t+\frac{1}{2}\nabla^2-\varphi(\vec{r}t)\right)T\left(\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right) \tag{6.200}$$

and we work out each term seperately

First term

$$= \left(i\hbar\partial_t+\frac{1}{2}\nabla^2-\varphi(\vec{r}t)\right)\left(\theta(t-t_1)\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right) \tag{6.201}$$

$$= i\hbar\delta(t-t_1)\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)+\theta(t-t_1)\left(\left(\left(i\hbar\partial_t+\frac{1}{2}\nabla^2-\varphi(\vec{r}t)\right)\psi_H(\vec{r}\sigma t)\right)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right.$$
$$\left.+\psi_H(\vec{r}\sigma t)\left(i\hbar\partial_t+\frac{1}{2}\nabla^2-\varphi(\vec{r}t)\right)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right) \tag{6.202}$$

$$= i\hbar\delta(t-t_1)\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)$$
$$+\theta(t-t_1)\left[\int d^3\vec{r}_2\frac{\rho_H(\vec{r}_2 t)}{|\vec{r}-\vec{r}_2|}\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)+\psi_H(\vec{r}\sigma t)\int d^3\vec{r}_2\frac{\rho_H(\vec{r}_2 t_1)}{|\vec{r}_1-\vec{r}_2|}\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right] \tag{6.203}$$

Second term

$$= -\left(i\hbar\partial_t+\frac{1}{2}\nabla^2-\varphi(\vec{r}t)\right)\left(\theta(t_1-t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\psi_H(\vec{r}\sigma t)\right) \tag{6.204}$$

$$= i\hbar\delta(t_1-t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\psi_H(\vec{r}\sigma t)$$
$$+\theta(t_1-t)\left[\int d^3\vec{r}_2\frac{\rho_H(\vec{r}_2 t_1)}{|\vec{r}_1-\vec{r}_2|}\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\psi_H(\vec{r}\sigma t)+\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\int d^3\vec{r}_2\frac{\rho_H(\vec{r}_2 t)}{|\vec{r}-\vec{r}_2|}\psi_H(\vec{r}\sigma t)\right] \tag{6.205}$$

$$\therefore \left(i\hbar\partial_t+\frac{1}{2}\nabla^2-\varphi(\vec{r}t)\right)T\left(\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right)$$

$$= i\hbar\delta(t_1-t)\left[\psi_H(\vec{r}\sigma t),\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right]_+ +\int d^3\vec{r}_1\frac{1}{|\vec{r}-\vec{r}_1|}T\left(\rho_H(\vec{r}_1 t)\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right) \tag{6.206}$$

$$= i\hbar\delta(t_1-t)\delta_{\sigma\sigma_1}\delta(\vec{r}-\vec{r}_1)+\int d^3\vec{r}_1\frac{1}{|\vec{r}-\vec{r}_1|}T\left(\rho_H(\vec{r}_1 t)\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right) \tag{6.207}$$

Now we will denote the Hamiltonian $H(t)$ into the form,

$$H(t) = H_0 + H_{\text{int}} + \int d^3\vec{r}\rho(\vec{r})\varphi(\vec{r}t) \tag{6.208}$$

and the Green's function is defined as

$$\begin{aligned} G(1,1') &= \left\langle T\left(\psi_H(1)\psi_H^\dagger(1')\right)\right\rangle && (6.209)\\ &= \frac{\text{Tr}\left(U(t_0 - i\hbar\beta, t_0)T\left(\psi_H(1)\psi_H^\dagger(1')\right)\right)}{\text{Tr}\left(U(t_0 - i\hbar\beta, t_0)\right)} && (6.210)\\ \text{where, } U(t_0 - i\hbar\beta, t_0) &= Te^{i\frac{i}{\hbar}\int_{t_0}^{t_0 - i\hbar\beta} dtH(t)} && (6.211)\end{aligned}$$

So note that I defined the interacting but equilibrium Green's function for this problem because the main interest here is to turn the interacting problem into a set a functional differential equations. Source field φ is used as a mathematical device and will be set to zero at the end. Of course, an immediate extension is to work with non-equilibrium Green's functions.

First we need to know the variation of the evolution operator.

$$V(t_2, t_1) = Te^{-\frac{i}{\hbar}\int_{t_1}^{t_2} dtH(t)} = Te^{-\frac{i}{\hbar}\int_{t_1}^{t_2} dtH_0 + H_{\text{int}} + \int d^3\vec{r}\rho(\vec{r})\varphi(\vec{r}t)} \tag{6.212}$$

which is

$$\frac{\delta V(t_2, t_1)}{\delta\varphi(\vec{r}_3 t_3)} = -\frac{i}{\hbar}\text{sgn}(t_2 - t_1)V(t_2, t_1)\rho(\vec{r}_3)V(t_3, t_1) \tag{6.213}$$

where t_3 is between t_1 and t_2. Otherwise $\frac{\delta V}{\delta\varphi} = 0$. Now we work out

$$\begin{aligned} \frac{\delta\psi_H(1)}{\delta\varphi(3)} &= \frac{\delta}{\delta\varphi(3)}V(t_0, t_1)\psi V(t_1, t_0) && (6.214)\\ &= \frac{\delta V(t_0, t_1)}{\delta\varphi(3)}\psi V(t_1, t_0) + V(t_0, t_1)\psi\frac{\delta V(t_1, t_0)}{\delta\varphi(3)} && (6.215)\\ &= -\frac{i}{\hbar}\text{sgn}(t_0 - t_1)V(t_0, t_3)\rho(\vec{r}_3)V(t_3, t_1)\psi V(t_1, t_0) \\ &\quad -\frac{i}{\hbar}\text{sgn}(t_1 - t_0)V(t_0, t_1)\psi V(t_1, t_3)\rho(\vec{r}_3)V(t_3, t_0) && (6.216)\\ &= \frac{i}{\hbar}\rho_H(3)\psi_H(1) - \frac{i}{\hbar}\psi_H(1)\rho_H(3) && (6.217)\\ &= \frac{i}{\hbar}\theta(t_3 - t_1)\rho_H(3)\psi_H(1) - \frac{i}{\hbar}\theta(t_1 - t_3)\psi_H(1)\rho_H(3) && (6.218)\end{aligned}$$

Now we can work out the numerator of the Green's function,

$$\begin{aligned} &\frac{\delta}{\delta\varphi(3)}U(t_0 - i\hbar\beta, t_0)T\left(\psi_H(1)\psi_H^\dagger(2)\right) \\ &= \frac{\delta U(t_0 - i\hbar\beta, t_0)}{\delta\varphi(3)}T\left(\psi_H(1)\psi_H^\dagger(2)\right) + U(t_0 - i\hbar\beta, t_0)\frac{\delta T\left(\psi_H(1)\psi_H^\dagger(2)\right)}{\delta\varphi(3)} && (6.219)\\ &= -\frac{i}{\hbar}\text{sgn}(t_0 - i\hbar\beta - t_0)U(t_0 - i\hbar\beta, t_3)\rho(\vec{r}_3)U(t_3, t_0)T\left(\psi_H(1)\psi_H^\dagger(2)\right)\end{aligned}$$

$$
\begin{aligned}
& +U(t_0 - i\hbar\beta, t_0)\frac{\delta}{\delta\varphi(3)}\left(\theta(t_1-t_2)\psi_H(1)\psi_H^\dagger(2) + \theta(t_2-t_1)\psi_H^\dagger(2)\psi_H(1)\right) && (6.220)\\
= \; & \frac{i}{\hbar}U(t_0 - i\hbar\beta, t_0)\rho_H(3)T\left(\psi_H(1)\psi_H^\dagger(2)\right) \\
& +U(t_0 - i\hbar\beta, t_0)\theta(t_1-t_2)\left(\frac{\psi_H(1)}{\delta\varphi(3)}\psi_H^\dagger(2) + \psi_H(1)\frac{\psi_H^\dagger(2)}{\delta\varphi(3)}\right) \\
& +U(t_0 - i\hbar\beta, t_0)\theta(t_2-t_1)\frac{\delta}{\delta\varphi(3)}\psi_H^\dagger(2)\psi_H(1) && (6.221)\\
| \; & \text{working the terms in the 2nd line round brackets:} \\
| \; & \frac{i}{\hbar}\Big(\theta(t_3-t_1)\rho_H(3)\psi_H(1)\psi_H^\dagger(2) - \theta(t_1-t_3)\psi_H(1)\rho_H(3)\psi_H^\dagger(2) \\
| \; & +\theta(t_3-t_2)\psi_H(1)\rho_H(3)\psi_H^\dagger(2) - \theta(t_2-t_3)\psi_H(1)\psi_H^\dagger(2)\rho_H(3)\Big) \\
| \; & \text{the first line takes into account } t_3 > t_1, t_2 \text{ so we have} \\
= \; & \frac{i}{\hbar}U(t_0 - i\hbar\beta, t_0)T\left(\rho_H(3)\psi_H(1)\psi_H^\dagger(2)\right) && (6.222)
\end{aligned}
$$

Now we work out the denominator of the Green's function which is simply the first term in the numerator.

$$\frac{\delta U(t_0 - i\hbar\beta, t_0)}{\delta\varphi(3)} = \frac{i}{\hbar}U(t_0 - i\hbar\beta, t_0)\rho_H(3) \tag{6.223}$$

So now we can take the functional derivative of the Green's function.

$$
\begin{aligned}
\frac{\delta G(1,2)}{\delta\varphi(3)} &= \frac{\delta}{\delta\varphi(3)}\frac{\mathrm{Tr}\left(U(t_0 - i\hbar\beta, t_0)T\left(\psi_H(1)\psi_H^\dagger(2)\right)\right)}{\mathrm{Tr}\left(U(t_0 - i\hbar\beta, t_0)\right)} && (6.224)\\
&= \frac{i}{\hbar}\frac{\mathrm{Tr}\left(U(t_0 - i\hbar\beta, t_0)T\left(\rho_H(3)\psi_H(1)\psi_H^\dagger(2)\right)\right)}{\mathrm{Tr}\left(U(t_0 - i\hbar\beta, t_0)\right)} \\
&\quad -\frac{i}{\hbar}\frac{\mathrm{Tr}\left(U(t_0 - i\hbar\beta, t_0)\rho_H(3)\right)}{\mathrm{Tr}\left(U(t_0 - i\hbar\beta, t_0)\right)}\frac{\mathrm{Tr}\left(U(t_0 - i\hbar\beta, t_0)T\left(\psi_H(1)\psi_H^\dagger(2)\right)\right)}{\mathrm{Tr}\left(U(t_0 - i\hbar\beta, t_0)\right)} && (6.225)\\
&= \frac{i}{\hbar}\left\langle T\left(\rho_H(3)\psi_H(1)\psi_H^\dagger(2)\right)\right\rangle - G(1,2)\left\langle\rho_H(3)\right\rangle && (6.226)
\end{aligned}
$$

We go back to the equation of motion and take the statistical average so as to link it to the Green's function.

$$
\begin{aligned}
\left(i\hbar\partial_t + \frac{1}{2}\nabla^2 - \varphi(\vec{r}t)\right)T\left(\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right) &= i\hbar\delta(t_1-t)\delta_{\sigma\sigma_1}\delta(\vec{r}-\vec{r}_1) \\
&\quad + \int d^3\vec{r}_1\frac{1}{|\vec{r}-\vec{r}_1|}T\left(\rho_H(\vec{r}_1 t)\psi_H(\vec{r}\sigma t)\psi_H^\dagger(\vec{r}_1\sigma_1 t_1)\right) \\
&\quad | \; \text{Multiply both sides by } -\frac{i}{\hbar}U(t_0 - i\hbar\beta, t_0) \\
&\quad | \; \text{then take trace on both sides} \\
&\quad | \; \text{divide both sides by } \mathrm{Tr}U(t_0 - i\hbar\beta) \\
&\quad | \; \text{replace the time-ordered 3 terms by } \frac{\delta G}{\delta\varphi}
\end{aligned}
$$

$$\left(i\hbar\partial_{t_1}+\frac{1}{2}\nabla^2_{\vec{r}_1}-\varphi(\vec{r}_1t_1)\right)\frac{-i}{\hbar}\left\langle T\left(\psi_H(1)\psi^\dagger_H(2)\right)\right\rangle = \delta_{\sigma_1\sigma_2}\delta(1-2) + \int d\vec{r}_3dt_3w(\vec{r}_1t_1^+,\vec{r}_3t_3)\frac{\delta G_{\sigma_1\sigma_2}(1,2)}{\delta\varphi(3)} + \int d\vec{r}_3dt_3w(\vec{r}_1t_1,\vec{r}_3t_3)\left\langle\rho_H(3)\right\rangle G_{\sigma_1\sigma_2}(1,2) \quad (6.227)$$

$$\left(i\hbar\partial_{t_1}+\frac{1}{2}\nabla^2_{\vec{r}_1}-V(1)\right)G_{\sigma_1\sigma_2}(1,2) = \delta_{\sigma_1\sigma_2}\delta(1-2)+\int d3w(\vec{r}_1t_1^+,3)\frac{\delta G_{\sigma_1\sigma_2}(1,2)}{\delta\varphi(3)} \quad (6.228)$$

where $V(1)\equiv\varphi(1)+\int d3w(1,3)\left\langle\rho_H(3)\right\rangle$. So $V(1)$ corresponds to the external potential and the Hartree (time-local) potential due to the electronic and nuclear charge distributions.

Now we relate the earlier equation to the self energy so that we can have a relation of self energy in terms of functional derivatives. We define the self energy, Σ based on the Dyson's equation.

$$\left(i\hbar\partial_t+\frac{1}{2}\nabla^2_{\vec{r}_1}-V(\vec{r}_1t_1)\right)G_{\sigma_1\sigma_2}(\vec{r}_1t_1\vec{r}_2t_2) = \delta_{\sigma_1\sigma_2}\delta(\vec{r}_1-\vec{r}_2)\delta(t_1-t_2) + \int d\vec{r}_3dt_3\sum_{\sigma_3}\Sigma_{\sigma_1\sigma_3}(\vec{r}_1t_1\vec{r}_3t_3)G_{\sigma_3\sigma_2}(\vec{r}_3t_3\vec{r}_2t_2) \quad (6.229)$$

Thus to relate the self energy to the functional derivatives, we need to define the inverse Green's function.

$$\sum_{\sigma_3}\int d3G_{\sigma_1\sigma_3}(1,3)G^{-1}_{\sigma_3\sigma_2}(3,2)=\delta_{\sigma_1\sigma_2}\delta(1-2) \quad (6.230)$$

and take the functional derivative with respect to $\varphi(3)$

$$\frac{\delta}{\delta\varphi(3)}\int d4\sum_{\sigma_4}G_{\sigma_1\sigma_4}(1,4)G^{-1}_{\sigma_4\sigma_2}(4,2) = \frac{\delta}{\delta\varphi(3)}\delta_{\sigma_1\sigma_2}\delta(1-2) \quad (6.231)$$

$$\int d4\sum_{\sigma_4}\frac{\delta G_{\sigma_1\sigma_4(1,4)}}{\delta\varphi(3)}G^{-1}_{\sigma_4\sigma_2}(4,2)+\int d4G_{\sigma_1\sigma_4}(1,4)\frac{\delta G^{-1}_{\sigma_4\sigma_2}(4,2)}{\delta\varphi(3)} = 0 \quad (6.232)$$

$\times\int d2G_{\sigma_2\sigma_5}(2,5)$ on both sides

$$\int d4d2\frac{\delta G_{\sigma_1\sigma_4(1,4)}}{\delta\varphi(3)}G^{-1}_{\sigma_4\sigma_2}(4,2)G_{\sigma_2\sigma_5}(2,5)=-\int d4d2G_{\sigma_1\sigma_4}(1,4)\frac{\delta G^{-1}_{\sigma_4\sigma_2}(4,2)}{\delta\varphi(3)}G_{\sigma_2\sigma_5}(2,5) \quad (6.233)$$

use the inverse Green's function relation,

$$\frac{\delta G_{\sigma_1\sigma_5}(1,5)}{\delta\varphi(3)} = -\int d4d2\sum_{\sigma_4\sigma_2}G_{\sigma_1\sigma_4}(1,4)\frac{\delta G^{-1}_{\sigma_4\sigma_2}(4,2)}{\delta\varphi(3)}G_{\sigma_2\sigma_5}(2,5) \quad (6.234)$$

$$\Big| \quad \text{rename } 2\leftrightarrow 5$$

$$\frac{\delta G_{\sigma_1\sigma_2}(1,2)}{\delta\varphi(3)} = -\int d4d5\sum_{\sigma_4\sigma_5}G_{\sigma_1\sigma_4}(1,4)\frac{\delta G^{-1}_{\sigma_4\sigma_5}(4,5)}{\delta\varphi(3)}G_{\sigma_5\sigma_2}(5,2) \quad (6.235)$$

Substituting this back to the RHS of the equation of motion, we get

$$\begin{aligned}
&\text{RHS of equation of motion} \\
= \;& i\int d3w(\vec{r}_1t_1^+\vec{r}_3t_3)\left(-\int d4d5\sum_{\sigma_4\sigma_5}G_{\sigma_1\sigma_4}(1,4)\frac{\delta G^{-1}_{\sigma_4\sigma_5}(4,5)}{\delta\varphi(3)}G_{\sigma_5\sigma_2}(5,2)\right) \qquad (6.236)
\end{aligned}$$

comparing with the RHS of Dyson's equation $= \int d3\sum_{\sigma_3}\Sigma_{\sigma_1\sigma_3}(1,3)G_{\sigma_3\sigma_2}(3,2)$ and we get an exact formal expression for self energy.

$$\Sigma_{\sigma_1\sigma_2}(1,2) = -i\int d3d4\sum_{\sigma_4}w(\vec{r}_1t_1^+\vec{r}_3t_3)G_{\sigma_1\sigma_4}(1,4)\frac{\delta G^{-1}_{\sigma_4\sigma_2}(4,2)}{\delta\varphi(3)} \qquad (6.237)$$

Now we define a dielectric function ϵ and a screened (renormalized) interaction W as follows,

$$\begin{aligned}
\epsilon^{-1}(1,2) &= \frac{\delta V(1)}{\delta\varphi(2)} && (6.238)\\
&= \delta(1-2)+\int d3w(\vec{r}_1t_1\vec{r}_3t_3)\frac{\langle\rho_H(3)\rangle}{\delta\varphi(2)} && (6.239)\\
\text{and,}\quad W(1,2) &\equiv \int d3w(\vec{r}_1t_1\vec{r}_3t_3)\epsilon^{-1}(2,3) && (6.240)
\end{aligned}$$

Note that it contains both changes in electronic and nuclear charge densities. We now try to seperate them. We define the electronic polarization as the electronic charge response due to the effective field V.

$$P_e(1,2) \equiv \frac{\delta\langle n(1)\rangle}{\delta V(2)} \qquad (6.241)$$

where the electronic charge density is the diagonal of the Green's function

$$\begin{aligned}
\langle n(3)\rangle &\equiv -i\sum_{\sigma_3}G_{\sigma_3\sigma_3}(\vec{r}_3t_3\vec{r}_3t_3^+) && (6.242)\\
\Rightarrow P_e(1,2) &= -i\sum_{\sigma_1}\frac{\delta G_{\sigma_1\sigma_1}(\vec{r}_1t_1\vec{r}_1t_1^+)}{\delta V(2)} && (6.243)\\
&\quad \mid \;\text{use the inverse Green's function relation} \\
&= -i\sum_{\sigma_1}\left(-\int d3d4\sum_{\sigma_3\sigma_4}G_{\sigma_1\sigma_3}(1,3)\frac{\delta G^{-1}_{\sigma_3\sigma_4}(3,4)}{\delta V(2)}G_{\sigma_4\sigma_1}(4,\vec{r}_1t_1^+)\right) && (6.244)\\
&= i\sum_{\sigma_1}\int d3d4\sum_{\sigma_3\sigma_4}G_{\sigma_1\sigma_3}(1,3)G_{\sigma_4\sigma_1}(4,\vec{r}_1t_1^+)\frac{\delta G^{-1}_{\sigma_3\sigma_4}(3,4)}{\delta V(2)} && (6.245)
\end{aligned}$$

Define the vertex function Γ by

$$\Gamma_{\sigma_3\sigma_4}(34,2) = -\frac{\delta G^{-1}_{\sigma_3\sigma_4}(3,4)}{\delta V(2)} \qquad (6.246)$$

and we get the first Hedin's equation,

$$P_e = -i\sum_{\sigma_1}\int d3d4G_{\sigma_1\sigma_3}(1,3)G_{\sigma_4\sigma_1}(4,\vec{r}_1t_1^+)\Gamma_{\sigma_3\sigma_4}(34,2) \qquad (6.247)$$

Recall the definition of self energy and use product rule to derive the second Hedin's equation,

$$
\begin{aligned}
\Sigma_{\sigma_1\sigma_2}(1,2) &= -i\int d3d4\sum_{\sigma_4} w(\vec{r}_1t_1^+\vec{r}_3t_3)G_{\sigma_1\sigma_4}(1,4)\frac{\delta G^{-1}_{\sigma_4\sigma_2}(4,2)}{\delta\varphi(3)} && (6.248)\\
&= -i\int d3d4d5\sum_{\sigma_4} w(\vec{r}_1t_1^+\vec{r}_3t_3)G_{\sigma_1\sigma_4}(1,4)\frac{\delta G^{-1}_{\sigma_4\sigma_2}(4,2)}{\delta V(5)}\frac{\delta V(5)}{\delta\varphi(3)} && (6.249)\\
&\mid \quad \text{use the definition of } \Gamma \text{ and } W\\
&= i\int d4d5\sum_{\sigma_4} G_{\sigma_1\sigma_4}(1,4)W(\vec{r}_1t_1^+,5)\Gamma_{\sigma_4\sigma_2}(42,5) && (6.250)
\end{aligned}
$$

The third Hedin's equation follows from the definition of the vertex function.

$$
\begin{aligned}
\Gamma_{\sigma_1\sigma_2}(12,3) &= -\frac{\delta G^{-1}_{\sigma_1\sigma_2}(1,2)}{\delta V(3)} && (6.251)\\
&\mid \quad \text{we relate self energy to } G^{-1} \text{ using the Dyson's equation}\\
&\mid \quad \left(i\hbar\partial_{t_1}+\frac{1}{2}\nabla^2_{\vec{r}_1}-V(1)\right)G_{\sigma_1\sigma_2}(1,2)=\delta_{\sigma_1\sigma_2}\delta(1-2)+\int d3\sum_{\sigma_3}\Sigma_{\sigma_1\sigma_3}(1,3)G_{\sigma_3\sigma_2}(3,2)\\
&\mid \quad \times G^{-1}_{\sigma_2\sigma_4}(2,4) \text{ from the right and } \int d2\sum_{\sigma_2} \text{ to get,}\\
&\mid \quad \left(i\hbar\partial_{t_1}+\frac{1}{2}\nabla^2_{\vec{r}_1}-V(1)\right)\delta_{\sigma_1\sigma_4}\delta(1-4)=G^{-1}_{\sigma_1\sigma_4}(1,4)+\Sigma_{\sigma_1\sigma_4}(1,4)\\
&\mid \quad \times\frac{\delta}{\delta V(5)} \text{ to get } -\delta_{\sigma_1\sigma_4}\delta(1-4)\delta(1-5)=\frac{\delta G^{-1}_{\sigma_1\sigma_4}(1,4)}{\delta V(5)}+\frac{\delta\Sigma_{\sigma_1\sigma_4}(1,4)}{\delta V(5)}\\
&= \delta_{\sigma_1\sigma_2}\delta(1-2)\delta(1-3)+\frac{\delta\Sigma_{\sigma_1\sigma_2}(1,2)}{\delta V(3)} && (6.252)\\
&\mid \quad \text{use chain rule of functional derivatives}\\
&= \delta_{\sigma_1\sigma_2}\delta(1-2)\delta(1-3)+\int d4d5\sum_{\sigma_4\sigma_5}\frac{\delta\Sigma_{\sigma_1\sigma_2}(1,2)}{\delta G_{\sigma_4\sigma_5}(4,5)}\frac{\delta G_{\sigma_4\sigma_5}(4,5)}{\delta V(3)} && (6.253)\\
&\mid \quad \text{use definition of } G^{-1} \text{ and definition of } \Gamma \text{ to write the third Hedin's equation}\\
&\mid \quad \frac{\delta G}{\delta V}=-\int\int G\frac{\delta G^{-1}}{\delta V}G=-\int\int GG\Gamma\\
&= \delta_{\sigma_1\sigma_2}\delta(1-2)\delta(1-3)\\
&\quad +\int d4d5d6d7\sum_{\sigma_4\sigma_5\sigma_6\sigma_7}\frac{\delta\Sigma_{\sigma_1\sigma_2}(1,2)}{\delta G_{\sigma_4\sigma_5}(4,5)}G_{\sigma_4\sigma_6}(4,6)G_{\sigma_7\sigma_5}(7,5)\Gamma_{\sigma_6\sigma_7}(67,3) && (6.254)
\end{aligned}
$$

Now we proceed to seperate the nuclear density which we can call it the "phonon part". We start with the definition of W.

$$
\begin{aligned}
W(1,2) &= \int d3w(\vec{r}_1t_1\vec{r}_3t_3)\epsilon^{-1}(2,3) && (6.255)\\
&= \int d3w(\vec{r}_1t_1\vec{r}_3t_3)\frac{\delta V(2)}{\delta\varphi(3)} && (6.256)\\
&\mid \quad \text{use } V(2)=\varphi(2)+\int d4w(2,4)\langle\rho_H(4)\rangle
\end{aligned}
$$

$$\begin{aligned}
&= w(1,2) + \int d3d4w(1,3)w(2,4)\frac{\delta\langle\rho_H(4)\rangle}{\delta\varphi(3)} &(6.257)\\
&\mid \quad \text{note that } w(2,4) = w(4,2)\\
&= w(1,2) + \int d3d4w(1,3)\frac{\delta\langle\rho_H(4)\rangle}{\delta\varphi(3)}w(4,2) &(6.258)\\
&\mid \quad \text{split } \langle\rho_H\rangle \text{ into the nuclear part and electronic part \& use chain rule}\\
&= w(1,2) + \int d3d4d5w(1,3)\frac{\delta\langle n_H(4)\rangle}{\delta V(5)}\frac{\delta V(5)}{\delta\varphi(3)}w(4,2) - \int d3d4w(1,3)\frac{\delta\langle N_H(4)\rangle}{\delta\varphi(3)}w(4,2)\\
&\mid \quad \text{use the definition of } P_e \text{ and } W\\
&= w(1,2) + \int d4d5W(1,5)P_e(4,5)w(4,2) - \int d3d4w(1,3)\frac{\delta\langle N_H(4)\rangle}{\delta\varphi(3)}w(4,2) &(6.259)
\end{aligned}$$

We look at the last term in more detail.

$$\begin{aligned}
-\frac{\delta\langle N_H(4)\rangle}{\delta\varphi(3)} &= -\frac{\delta}{\delta\varphi(3)}\frac{\mathrm{Tr}\,(U(t_0-i\hbar\beta)N_H(4))}{\mathrm{Tr}\,(U(t_0-i\hbar\beta)} &(6.260)\\
&\mid \quad \text{recall the earlier results}\\
&= -\langle T\,(\rho_H(3)N_H(4))\rangle + \langle N_H(4)\rangle\langle\rho_H(3)\rangle &(6.261)\\
&= -\theta(t_3-t_4)\,\langle(\rho_H(3)N_H(4))\rangle - \theta(t_4-t_3)\,\langle(N_H(4)\rho_H(3))\rangle + \langle N_H(4)\rangle\langle\rho_H(3)\rangle &(6.262)\\
&\mid \quad \text{add and subtract the same term}\\
&= -\theta(t_3-t_4)\,(\langle(\rho_H(3)N_H(4))\rangle - \langle\rho_H(3)\rangle\langle N_H(4)\rangle + \langle\rho_H(3)\rangle\langle N_H(4)\rangle - \langle\rho_H(3)\rangle\langle N_H(4)\rangle)\\
&\quad -\theta(t_4-t_3)\,(\langle(N_H(4)\rho_H(3))\rangle - \langle N_H(4)\rangle\langle\rho_H(3)\rangle + \langle N_H(4)\rangle\langle\rho_H(3)\rangle - \langle N_H(4)\rangle\langle\rho_H(3)\rangle)\\
&\mid \quad \text{define } \rho_H(3) - \langle\rho_H(3)\rangle \equiv \Delta\rho_H(3) \text{ and so on}\\
&= -\theta(t_3-t_4)\,\langle(\Delta\rho_H(3)\Delta N_H(4))\rangle - \theta(t_4-t_3)\,\langle(\Delta N_H(4)\Delta\rho_H(3))\rangle &(6.263)\\
&= -\langle T\,(\Delta N_H(4)\Delta\rho_H(3))\rangle &(6.264)\\
&\mid \quad \text{recall that } \rho = n - N\\
&= +\langle T\,(\Delta N_H(4)\Delta N_H(3))\rangle - \langle T\,(\Delta N_H(4)\Delta n_H(3))\rangle &(6.265)
\end{aligned}$$

Since the term $-\frac{i}{\hbar}\langle T\,(\Delta N_H(4)\Delta N_H(3))\rangle$ represents nuclear desnity fluctuations correlation, we shall define this as the phonon-like Green's function.

$$D(1,2) \equiv -\frac{i}{\hbar}\langle T\,(\Delta N_H(1)\Delta N_H(2))\rangle \tag{6.266}$$

We want this term to be in Hedin's equations, so according to Schwinger's variational principle, we add another source term into the Hamiltonian.

$$H_2 = -\int d\vec{R}N(\vec{R})J(\vec{R},t) \tag{6.267}$$

Recall the earlier relation, $-\frac{\delta\langle N_H(2)\rangle}{\delta\varphi(1)} = \frac{i}{\hbar}\langle T\,(\Delta N_H(2)\Delta\rho_H(1))\rangle$ and now we will calculate

$$\begin{aligned}
\frac{\delta\langle\rho_H(1)\rangle}{\delta J(2)\rangle} &\mid \quad \text{deduce from } \frac{\delta}{\delta\varphi}\text{, only that } N_H \text{ expressions are produced}\\
&= \langle T\,(N_H(2)\rho_H(1))\rangle - \langle N_H(2)\rangle\langle\rho_H(1)\rangle &(6.268)\\
&\mid \quad \text{we will add and subtract terms and we get the a similar expression}\\
&= \langle T\,(\Delta N_H(2)\Delta\rho_H(1))\rangle &(6.269)
\end{aligned}$$

Comparing gives

$$\frac{\delta\langle\rho_H(1)\rangle}{\delta J(2)} = -\frac{\delta\langle N_H(2)\rangle}{\delta\varphi(1)} \tag{6.270}$$

We further rewrite the LHS

$$\begin{aligned}
\frac{\delta\langle\rho_H(1)\rangle}{\delta J(2)\rangle} &= \frac{\delta\langle n_H(1)\rangle}{\delta J(2)\rangle} - \frac{\delta\langle N_H(1)\rangle}{\delta J(2)\rangle} && (6.271)\\
&\quad | \quad \text{for the second term, } \frac{\delta}{\delta J(2)} \text{ gives } N_H\text{, and so } \langle N_H N_H\rangle \sim D \\
&= D(1,2) + \frac{\delta\langle n_H(1)\rangle}{\delta J(2)\rangle} && (6.272)\\
&\quad | \quad \text{use chain rule} \\
&= D(1,2) + \int d3 \frac{\delta\langle n_H(1)\rangle}{\delta V(3)} \frac{\delta V(3)}{\delta J(2)\rangle} && (6.273)\\
&\quad | \quad \text{recall } \frac{\delta\langle n_H(1)\rangle}{\delta V(3)} = P_e(1,3) \\
&\quad | \quad \text{use chain rule again} \\
&= D(1,2) + \int d3d4 \sum_{\sigma_4} P_e(1,3) \frac{\delta V(3)}{\delta\langle\rho_H(4)\rangle} \frac{\langle\rho_H(4)\rangle}{\delta J(2)} && (6.274)\\
&\quad | \quad \text{use the explicit expression, } V(3) = \varphi(3) + \int d4 w(3,4)\langle\rho_H(4)\rangle \\
&= D(1,2) + \int d3d4 \sum_{\sigma_4} P_e(1,3) w(3,4) \frac{\delta\langle\rho_H(4)\rangle}{\delta J(2)} && (6.275)
\end{aligned}$$

So this integral equation can be iterated and solved. Symbolically, the solution is

$$\frac{\delta\langle\rho_H(1)\rangle}{\delta J(2)} = \left[(\mathbb{I} - P_e w)^{-1} D\right](1,2) = -\frac{\delta\langle N_H(2)\rangle}{\delta\varphi(1)} \tag{6.276}$$

which we insert into this earlier equation

$$W(1,2) = w(1,2) + \int d4d5 W(1,5)P_e(4,5)w(4,2) - \int d3d4 w(1,2)\frac{\delta\langle N_H(4)\rangle}{\delta\varphi(3)} w(4,2) \tag{6.277}$$

We get (symbolically),

$$\begin{aligned}
W &= w + WP_e w + w\left(\mathbb{I} - P_e w\right)^{-1} D w && (6.278)\\
&\quad | \quad \text{define the electronic part of the screened interaction } W_e \text{ as } W_e = w(\mathbb{I} - P_e w)^{-1} \\
W - WP_e w &= w + W_e D w && (6.279)\\
W &= w(\mathbb{I} - P_e w)^{-1} + W_e D w(\mathbb{I} - P_e w)^{-1} && (6.280)\\
&= W_e + W_e D W_e && (6.281)\\
W(1,2) &= W_e(1,2) + \int d3d4 W_e(1,3) D(3,4) W_e(4,2) && (6.282)
\end{aligned}$$

The derivation of Hedin's equations is complete. We summarize the set of Hedin's equations here.

$$\begin{aligned}
\Sigma_{\sigma_1\sigma_2}(1,2) &= \frac{i}{\hbar}\int d3d4\sum_{\sigma_3} G_{\sigma_1\sigma_3}(1,3)W(\vec{r}_1t_1^+,4)\Gamma_{\sigma_3\sigma_2}(32,4) &(6.283)\\
W(1,2) &= W_e(1,2)+\int d3d4W_e(1,3)D(3,4)W_e(4,2) &(6.284)\\
\text{where}\quad W_e &= w\left(\mathbb{I}-P_e w\right)^{-1} &(6.285)\\
P_e(1,2) &= -i\sum_{\sigma_1}\int d3d4\sum_{\sigma_3\sigma_4} G_{\sigma_1\sigma_3}(1,3)G_{\sigma_4\sigma_1}(4,1)\Gamma_{\sigma_3\sigma_4}(34,2) &(6.286)\\
\Gamma_{\sigma_1\sigma_2}(12,3) &= \delta_{\sigma_1\sigma_2}\delta(1-2)\delta(1-3)\\
&\quad+\int d4d5d6d7\sum_{\sigma_4\sigma_5\sigma_6\sigma_7}\frac{\delta\Sigma_{\sigma_1\sigma_2}(1,2)}{\delta G_{\sigma_4\sigma_5}(4,5)}G_{\sigma_4\sigma_6}(4,6)G_{\sigma_7\sigma_5}(7,5)\Gamma_{\sigma_6\sigma_7}(67,3) &(6.287)
\end{aligned}$$

A diagramatic representation is shown in

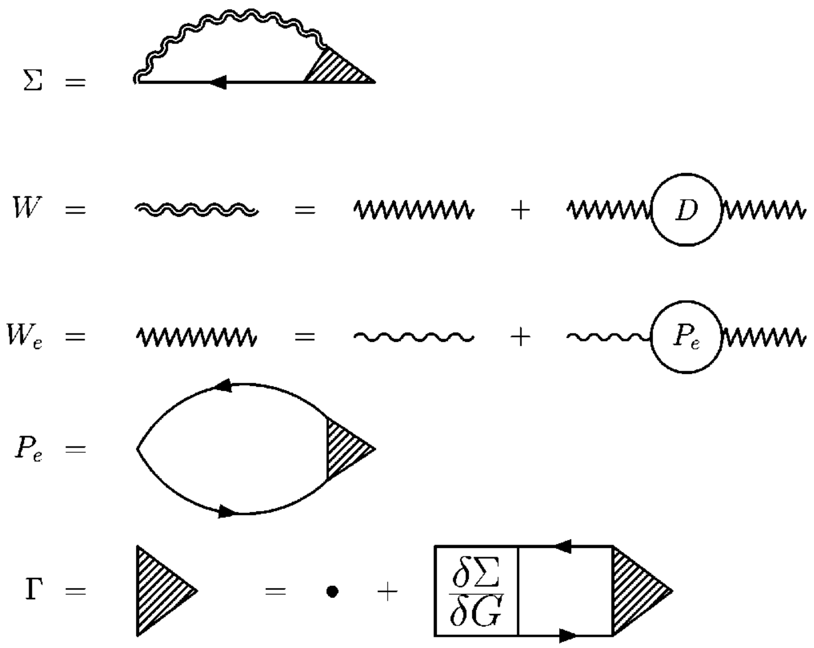


Figure 6.4: *The diagrammatic representation of the electron-phonon Hedin-like equations. From [Leeuwen2004].*

If we put $D = 0$ which means there are no nuclear fluctuations or "frozen nuclei" then we obtain the usual Hedin's equations for Coulomb interaction. This is shown in the appendix for electrons.

6.5.3 Appendix: General Form for the Coriolis & Mass Polarisation Terms

Recall the transformation made

$$\begin{aligned}
\vec{r}_{i_1} &= \mathcal{R}(\alpha\beta\gamma)\left(\vec{r}^{\,e}_{i_1}-\vec{R}_{CMN}\right) &(6.288)\\
\text{or}\quad r_{i_1\alpha_1} &= \sum_{\alpha_2}\mathcal{R}_{\alpha_1\alpha_2}\left(\vec{r}^{\,e}_{i_1}-\vec{R}_{CMN}\right)_{\alpha_2} &(6.289)
\end{aligned}$$

Recall that the old and the new wavefunctions are related by

$$\Phi_{\text{old}}(\vec{r}^e_1 \dots \vec{r}^e_{N_e}, \vec{R}_1 \dots \vec{R}_{N_n}) = \Phi_{\text{new}}(\vec{r}_1 \dots \vec{r}_{N_e}, \vec{R}'_1 \dots \vec{R}'_{N_n}) \equiv \Phi_{\text{new}}(\vec{r}_1 \dots \vec{r}_{N_e}, \vec{R}_1 \dots \vec{R}_{N_n}) \tag{6.290}$$

and the Hamiltonian is acting on the last wavefunction. Now we work out an identity,

$$\frac{\partial r_{i_1\alpha_1}}{\partial R_{l_3\alpha_3}} = \sum_{\alpha_2}\left(\frac{\partial \mathcal{R}_{\alpha_1\alpha_2}}{\partial R_{l_3\alpha_3}}\left(r^e_{i_1\alpha_2} - R_{CMN,\alpha_2}\right) - \mathcal{R}_{\alpha_1\alpha_2}\frac{\partial R_{CMN,\alpha_2}}{\partial R_{l_3\alpha_3}}\right) \tag{6.291}$$

$$= \sum_{\alpha_2}\left(\sum_{\alpha_4\alpha_5}\epsilon_{\alpha_1\alpha_4\alpha_5}\mathcal{R}_{\alpha_4\alpha_2}\Omega^{l_3}_{\alpha_5\alpha_3}\left(r^e_{i_1\alpha_2} - R_{CMN,\alpha_2}\right) - \mathcal{R}_{\alpha_1\alpha_2}\frac{\partial}{\partial R_{l_3\alpha_3}}\frac{\sum_{l_4}^{N_n} M_{l_4}R_{l_4\alpha_2}}{M_{\text{nuc}}}\right) \tag{6.292}$$

$$= \sum_{\alpha_4\alpha_5}\epsilon_{\alpha_1\alpha_4\alpha_5}\sum_{\alpha_2}\mathcal{R}_{\alpha_4\alpha_2}\left(r^e_{i_1\alpha_2} - R_{CMN,\alpha_2}\right)\Omega^{l_3}_{\alpha_5\alpha_3} - \mathcal{R}_{\alpha_1\alpha_3}\frac{M_{l_3}}{M_{\text{nuc}}} \tag{6.293}$$

$$= \sum_{\alpha_4\alpha_5}\epsilon_{\alpha_1\alpha_4\alpha_5}r_{i_1\alpha_4}\Omega^{l_3}_{\alpha_5\alpha_3} - \mathcal{R}_{\alpha_1\alpha_3}\frac{M_{l_3}}{M_{\text{nuc}}} \tag{6.294}$$

Then differentiating the wavefunction gives,

$$\frac{\partial \Phi_{\text{old}}}{\partial R_{l_3\alpha_3}} = \frac{\partial \Phi_{\text{new}}}{\partial R_{l_3\alpha_3}} \tag{6.295}$$

| recall that Φ_{new} is the rightmost wavefunction stated above

$$= \frac{\partial \Phi_{\text{new}}}{\partial R_{l_3\alpha_3}} + \sum_{\alpha_4=1}^{3}\sum_{i_4=1}^{N_e}\frac{\partial r_{i_4\alpha_4}}{\partial R_{l_3\alpha_3}}\frac{\partial \Phi_{\text{new}}}{\partial r_{i_4\alpha_4}} \tag{6.296}$$

$$= \left(\frac{\partial}{\partial R_{l_3\alpha_3}} + \sum_{\alpha_4=1}^{3}\sum_{i_4=1}^{N_e}\frac{\partial r_{i_4\alpha_4}}{\partial R_{l_3\alpha_3}}\frac{\partial}{\partial r_{i_4\alpha_4}}\right)\Phi_{\text{new}} \tag{6.297}$$

| use the earlier identity for $\frac{\partial r_{i_4\alpha_4}}{\partial R_{l_3\alpha_3}}$

$$= \left(\frac{\partial}{\partial R_{l_3\alpha_3}} + \sum_{\alpha_4}\sum_{k_4}\left(\sum_{\alpha_5\alpha_6}\epsilon_{\alpha_4\alpha_5\alpha_6}r_{k_4\alpha_5}\Omega^{k_3}_{\alpha_6\alpha_3} - \mathcal{R}_{\alpha_4\alpha_3}\frac{M_{k_3}}{M_{\text{nuc}}}\right)\frac{\partial}{\partial r_{k_4\alpha_4}}\right)\Phi_{\text{new}}$$

$$= \left(\frac{\partial}{\partial R_{l_3\alpha_3}} - i\sum_{\alpha_4\alpha_5\alpha_6}\sum_{k_4} i\epsilon_{\alpha_6\alpha_4\alpha_5}\Omega^{k_3}_{\alpha_6\alpha_3}r_{k_4\alpha_5}\frac{\partial}{\partial r_{k_4\alpha_4}} - i\sum_{\alpha_4k_4}\frac{-iM_{k_3}}{M_{\text{nuc}}}\mathcal{R}_{\alpha_4\alpha_3}\frac{\partial}{\partial r_{k_4\alpha_4}}\right)\Phi_{\text{new}}$$

| note that $\epsilon_{\alpha_6\alpha_4\alpha_5} = -\epsilon_{\alpha_6\alpha_5\alpha_4}$

$$= \left(\frac{\partial}{\partial R_{l_3\alpha_3}} - i\sum_{\alpha_6}\Omega^{k_3}_{\alpha_6\alpha_3}\left(-i\sum_{k_4}\vec{r}_{k_4}\times\frac{\partial}{\partial \vec{r}_{k_4}}\right)_{\alpha_6} - i\frac{M_{k_3}}{M_{\text{nuc}}}\sum_{\alpha_4}\mathcal{R}_{\alpha_4\alpha_3}\left(-i\sum_{k_4}\frac{\partial}{\partial r_{k_4\alpha_4}}\right)\right)\Phi_{\text{new}}$$

| define angular momentum $\vec{L}^e \equiv -i\sum_{k_4}\vec{r}_{k_4}\times\frac{\partial}{\partial \vec{r}_{k_4}}$

| define total electronic momentum $\vec{P}^e \equiv -i\sum_{k_4}\frac{\partial}{\partial \vec{r}_{k_4}}$

$$= \left(\frac{\partial}{\partial R_{l_3\alpha_3}} - i\sum_{\alpha_6}\Omega^{k_3}_{\alpha_6\alpha_3}L^e_{\alpha_6} - i\frac{M_{k_3}}{M_{\text{nuc}}}\sum_{\alpha_4}\mathcal{R}_{\alpha_4\alpha_3}P^e_{\alpha_4}\right)\Phi_{\text{new}} \tag{6.298}$$

We now recall the kinetic energy operator

$$T_{\text{MPC}} = \sum_{l_1=1}^{N_n}\left(-\frac{\hbar^2}{2M_{l_1}}\right)\left[\left(\nabla_{\vec{R}_{l_1}} + \sum_{i_2}\frac{\partial \vec{r}_{i_2}}{\partial R_{l_1}}\nabla_{\vec{r}_{i_2}}\right)^2 - \nabla^2_{\vec{R}_{l_1}}\right] \tag{6.299}$$

$$\mid \quad \text{recall that } T_n = -\sum_{l_1}\frac{\hbar^2}{2M_{l_1}}\nabla^2_{\vec{R}_{l_1}} \text{ and use the above expression}$$

$$T_{\text{MPC}} + T_n = -\sum_{l_1=1}^{N_n}\left(\frac{\hbar^2}{2M_{l_1}}\right)\sum_{\alpha_3}\left(\frac{\partial}{\partial R_{l_1\alpha_3}} - i\sum_{\alpha_6}\Omega^{l_1}_{\alpha_6\alpha_3}L^e_{\alpha_6} - i\frac{M_{l_1}}{M_{\text{nuc}}}\sum_{\alpha_4}\mathcal{R}_{\alpha_4\alpha_3}P^e_{\alpha_4}\right)^2 \tag{6.300}$$

Note that T_n term cancels with $\sim \left(\frac{\partial}{\partial R_{l_3\alpha_3}}\right)^2$ and T_{MPC} can be split as $T_{\text{MPC}} \equiv T_{\text{MP}} + T_{\text{C}}$. T_{MP} is the mass polarisation term (which involves $\vec{P}^e$) and T_{C} is the Coriolis term (which involves $\vec{L}^e$). There are 8 terms left in the expression, we expand them all symbolically

$$\begin{aligned}
&(T_{MPC} + T_n)\,\Phi_{\text{new}} \\
\sim\;& \left(\frac{\partial}{\partial R} - i\sum \Omega L^e - i\sum \mathcal{R}P^e\right)\left(\frac{\partial \Phi_{\text{new}}}{\partial R} - i\sum \Omega L^e\Phi_{\text{new}} - i\sum \mathcal{R}P^e\Phi_{\text{new}}\right) \\
=\;& \frac{\partial^2\Phi_{\text{new}}}{\partial R^2} - i\sum\frac{\partial(\Omega L^e\Phi_{\text{new}})}{\partial R} - i\sum\frac{\partial(\mathcal{R}P^e\Phi_{\text{new}})}{\partial R} - i\sum\Omega L^e\frac{\partial\Phi_{\text{new}}}{\partial R} - \sum\sum\Omega\Omega L^eL^e\Phi_{\text{new}} \\
&- \sum\sum\Omega\mathcal{R}L^eP^e\Phi_{\text{new}} - i\sum\mathcal{R}P^e\frac{\partial\Phi_{\text{new}}}{\partial R} - \sum\sum\mathcal{R}\Omega P^eL^e\Phi_{\text{new}} - \sum\sum\mathcal{R}\mathcal{R}P^eP^e\Phi_{\text{new}}
\end{aligned}$$

The first term cancels T_n as mentioned above. The second term is related to T_{C}. The third term is related to T_{MP}. The fourth term is related to T_{C}. The fifth term is related to T_{C}. The sixth term is zero since L^e and P^e are perpendicular [12]. The seventh term is related to T_{MP}. The eighth term is zero since L^e and P^e are perpendicular [13]. The ninth term is related to T_{MP}. Thus we can write

$$T_{\text{MPC}} = T_{\text{MP}} + T_{\text{C}} \tag{6.301}$$

$$\begin{aligned}
=\;& \sum_{\alpha_1}^{3}\left[\frac{\hbar^2}{2M_{\text{nuc}}}\sum_{l_1=1}^{N_n}\sum_{\alpha_2}^{3}\left(i\mathcal{R}_{\alpha_1\alpha_2}\frac{\partial}{\partial R_{l_1\alpha_2}}\right)^\dagger + \left(i\mathcal{R}_{\alpha_1\alpha_2}\frac{\partial}{\partial R_{l_1\alpha_2}}\right)\right]P^e_{\alpha_1} \\
&+ \sum_{\alpha_3\alpha_4}\frac{\hbar^2}{2M^2_{\text{nuc}}}\sum_{l_1=1}^{N_n}M_{l_1}\sum_{\alpha_5}^{3}\mathcal{R}_{\alpha_3\alpha_5}\mathcal{R}_{\alpha_4\alpha_5}P^e_{\alpha_3}P^e_{\alpha_4} \\
&+ \sum_{\alpha_1}^{3}\left[\sum_{l_1=1}^{N_n}\frac{\hbar^2}{2M_{l_1}}\sum_{\alpha_2}^{3}\left(i\Omega^{l_1}_{\alpha_1\alpha_2}\frac{\partial}{\partial R_{l_1\alpha_2}}\right)^\dagger + \left(i\Omega^{l_1}_{\alpha_1\alpha_2}\frac{\partial}{\partial R_{l_1\alpha_2}}\right)\right]L^e_{\alpha_1} \\
&+ \sum_{\alpha_3\alpha_4}\sum_{l_1=1}^{N_n}\frac{\hbar^2}{2M_{l_1}}\sum_{\alpha_5}^{3}\Omega^{l_1}_{\alpha_3\alpha_5}\Omega^{l_1}_{\alpha_4\alpha_5}L^e_{\alpha_3}L^e_{\alpha_4}
\end{aligned} \tag{6.302}$$

So if we define

$$T_{\text{MP}} = \sum_{\alpha_1}^{3}(\mu^\dagger_{\alpha_1} + \mu_{\alpha_1})P^e_{\alpha_1} + \sum_{\alpha_3\alpha_4}^{3}\beta_{\alpha_3\alpha_4}P^e_{\alpha_3}P^e_{\alpha_4} \tag{6.303}$$

---

[12] I am not very sure about it

[13] I am not very sure about it

$$T_{\mathrm{C}} = \sum_{\alpha_1}^{3}(\nu^{\dagger}_{\alpha_1}+\nu_{\alpha_1})L^e_{\alpha_1}+\sum_{\alpha_3\alpha_4}^{3}\alpha_{\alpha_3\alpha_4}L^e_{\alpha_3}L^e_{\alpha_4} \tag{6.304}$$

We can identify

$$\mu_{\alpha_1} = \frac{\hbar^2}{2M_{\mathrm{nuc}}}\sum_{l_1=1}^{N_n}\sum_{\alpha_2}^{3} i\mathcal{R}_{\alpha_1\alpha_2}\frac{\partial}{\partial R_{l_1\alpha_2}} \tag{6.305}$$

$$\equiv -\frac{\hbar^2}{2M_{\mathrm{nuc}}}P'^{n}_{\alpha_1} \quad \text{nuclear momentum in body fixed frame} \tag{6.306}$$

$$\beta_{\alpha_3\alpha_4} = \frac{\hbar^2}{2M^2_{\mathrm{nuc}}}\sum_{l_1=1}^{N_n}M_{l_1}\sum_{\alpha_5}^{3}\mathcal{R}_{\alpha_3\alpha_5}\mathcal{R}_{\alpha_4\alpha_5} \tag{6.307}$$

$$\Big| \quad \text{note that } \sum_{l_1=1}^{N_n}M_{l_1}=M_{\mathrm{nuc}} \text{ and use orthonormality in the second factor}$$

$$= \frac{\delta_{\alpha_3\alpha_4}}{2M_{\mathrm{nuc}}} \tag{6.308}$$

$$\nu_{\alpha_1} = \sum_{l_1=1}^{N_n}\frac{\hbar^2}{2M_{l_1}}\sum_{\alpha_2=1}^{3}\Omega^{l_1}_{\alpha_1\alpha_2}\frac{\partial}{\partial R_{l_1\alpha_2}} \tag{6.309}$$

$$\alpha_{\alpha_3\alpha_4} = \sum_{l_1=1}^{N_n}\frac{\hbar^2}{2M_{l_1}}\sum_{\alpha_5=1}^{3}\Omega^{l_1}_{\alpha_3\alpha_5}\Omega^{l_1}_{\alpha_5\alpha_4} \tag{6.310}$$

6.5.4 Appendix: Explicit Form of the Corolis Term in the Eckart Frame

Now we further evaluate ν_{α_1} and $\alpha_{\alpha_3\alpha_4}$ in the Eckart frame to show that the Coriolis terms are negligible in the Eckart frame. This justifies the choice that the Eckart frame is a suitable choice that seperates the "internal motions" and the "external motions" as much as possible.

Recall the Eckart conditions (condition 2):

$$0 = \sum_{l_1=1}^{N_n}M_{l_1}\vec{R}^{eq}_{l_1}\times\mathcal{R}(\alpha\beta\gamma)\left(\vec{R}_{l_1}-\vec{R}_{CMN}\right) \tag{6.311}$$

$$\Big| \quad \text{take condition 1, } 0=\sum_{l_1=1}^{N_n}M_{l_1}\vec{R}^{eq}_{l_1} \text{ cross with } \mathcal{R}\vec{R}_{\mathrm{CMN}} \text{ to get } 0=\sum_{l_1=1}^{N_n}M_{l_1}\vec{R}^{eq}_{l_1}\times\mathcal{R}(\alpha\beta\gamma)\vec{R}_{\mathrm{CMN}}$$

$$0 = \sum_{l_1=1}^{N_n}M_{l_1}\vec{R}^{eq}_{l_1}\times\mathcal{R}(\alpha\beta\gamma)\vec{R}_{l_1} \tag{6.312}$$

We now calculate the angular velocity vectors $\Omega^{l_1}_{\alpha_1\alpha_2}$. First we get a relation by differentiating the Eckart conditions with respect to $\vec{R}_{l_1}$. Denote $\vec{R}''_l=\mathcal{R}\vec{R}_l$.

$$0 = \frac{\partial}{\partial R_{l\alpha_0}}\left(\sum_{l_1}\sum_{\alpha_1\alpha_2}M_{l_1}\epsilon_{\alpha\alpha_1\alpha_2}R^{eq}_{l_1\alpha_1}R''_{l_1\alpha_2}\right) \tag{6.313}$$

$$\Big| \quad R^{eq}_{l_1\alpha_1} \text{ is constant in differentiation}$$

$$
\begin{aligned}
&= \sum_{l_1}\sum_{\alpha_1\alpha_2} M_{l_1}\epsilon_{\alpha\alpha_1\alpha_2}R^{eq}_{l_1\alpha_1}\frac{\partial R''_{l_1\alpha_2}}{\partial R_{l\alpha_0}} && (6.314)\\
&\mid \text{ use identity from preliminaries section for } \frac{\partial R''_{l_1\alpha_2}}{\partial R_{l\alpha_0}}\\
&= \sum_{l_1}\sum_{\alpha_1\alpha_2} M_{l_1}\epsilon_{\alpha\alpha_1\alpha_2}R^{eq}_{l_1\alpha_1}\left(\sum_{\alpha_3\alpha_4}\epsilon_{\alpha_2\alpha_3\alpha_4}R''_{l_1\alpha_3}\Omega^l_{\alpha_4\alpha_0}+\mathcal{R}_{\alpha_2\alpha_0}\delta_{ll_1}\right) && (6.315)\\
&\mid \text{ use } \sum_{\alpha_2}\epsilon_{\alpha\alpha_1\alpha_2}\epsilon_{\alpha_2\alpha_3\alpha_4}=\delta_{\alpha\alpha_3}\delta_{\alpha_1\alpha_4}-\delta_{\alpha\alpha_4}\delta_{\alpha_1\alpha_3}\\
&= \sum_{\alpha_2\alpha_2} M_l\epsilon_{\alpha\alpha_1\alpha_2}R^{eq}_{l\alpha_1}\mathcal{R}_{\alpha_2\alpha_0}+\sum_{l_1\alpha_1}M_{l_1}R^{eq}_{l_1\alpha_1}R''_{l_1\alpha}\Omega^l_{\alpha_1\alpha_0}-\sum_{l_1\alpha_1}M_{l_1}R^{eq}_{l_1\alpha_1}R''_{l_1\alpha_1}\Omega^l_{\alpha\alpha_0} && (6.316)\\
&\equiv a^l_{\alpha_0\alpha}-\sum_{\alpha_1}J_{\alpha\alpha_1}\Omega^l_{\alpha_1\alpha_0} && (6.317)
\end{aligned}
$$

where

$$
\begin{aligned}
a^l_{\alpha_0\alpha} &= \sum_{\alpha_1\alpha_2} M_l\epsilon_{\alpha\alpha_1\alpha_2}R^{eq}_{l\alpha_1}\mathcal{R}_{\alpha_2\alpha_0} && (6.318)\\
&\mid \text{ recall that } \mathcal{R}_{\alpha_2\alpha_0}=(\vec{e}_{\alpha_0})_{\alpha_2}\\
&= M_l\left(\vec{R}^{eq}_l\times\vec{e}_{\alpha_0}\right)_\alpha && (6.319)\\
J_{\alpha\alpha_1}(\vec{R}'') &= \sum_{l_1}M_{l_1}\left(\vec{R}^{eq}_{l_1}\cdot\vec{R}''_{l_1}\delta_{\alpha_1\alpha}-R^{eq}_{l_1\alpha_1}R''_{l_1\alpha}\right) && (6.320)
\end{aligned}
$$

For $J(\vec{R}^{eq})$, it is the inertia tensor and it is diagonal. Writing the above as a symbolic matrix equation, we manipulate

$$
\begin{aligned}
0 &= a-J\cdot\Omega\Rightarrow\Omega=J^{-1}\cdot a && (6.321)\\
\Omega^l_{\alpha_1\alpha_2} &= \sum_{\alpha_3}^{3}J^{-1}_{\alpha_1\alpha_3}a^l_{\alpha_3\alpha_2}=\sum_{\alpha_3}^{3}J^{-1}_{\alpha_1\alpha_3}a^l_{\alpha_2\alpha_3} && (6.322)
\end{aligned}
$$

With this expression, we can check a relation, by summing over all sites l,

$$
\begin{aligned}
\sum_l\Omega^l_{\alpha_1\alpha_2} &= \sum_{\alpha_3}^{3}J^{-1}_{\alpha_1\alpha_3}\sum_l a^l_{\alpha_2\alpha_3} && (6.323)\\
&= \sum_{\alpha_3}^{3}\sum_l M_l(\vec{R}^{eq}_l\times\vec{e}_{\alpha_2})_{\alpha_3} && (6.324)\\
&\mid \text{ note that } \sum_l M_l\vec{R}^{eq}_l=0 \text{ is condition 1}\\
&= 0 \text{ indeed} && (6.325)
\end{aligned}
$$

Now we carry out the main line of calculation in this appendix to evaluate the Coriolis terms, We start with $\alpha_{\alpha_1\alpha_2}$

$$
\alpha_{\alpha_1\alpha_2} = \sum_{l_1=1}^{N_n}\frac{\hbar^2}{2M_{l_1}}\sum_{\alpha_3=1}^{3}\Omega^{l_1}_{\alpha_1\alpha_3}\Omega^{l_1}_{\alpha_3\alpha_2} \qquad (6.326)
$$

$$
\begin{aligned}
& \mid \quad \text{then we use the above equation for } \Omega \text{ to get} \\
= \quad & \sum_{l_1}^{N_n} \frac{\hbar^2}{2M_{l_1}} \sum_{\alpha_3}^{3} \sum_{\alpha_4} J^{-1}_{\alpha_1\alpha_4} a^{l_1}_{\alpha_3\alpha_4} \sum_{\alpha_5} J^{-1}_{\alpha_2\alpha_5} a^{l_1}_{\alpha_3\alpha_5} && (6.327) \\
& \mid \quad \text{note that } \sum_{\alpha_3} a^{l_1}_{\alpha_3\alpha_4} a^{l_1}_{\alpha_3\alpha_5} = \sum_{\alpha_3} \sum_{\alpha_6\alpha_7} M_{l_1} \epsilon_{\alpha_4\alpha_6\alpha_7} R^{eq}_{l_1\alpha_6} \mathcal{R}_{\alpha_7\alpha_3} \sum_{\alpha_8\alpha_9} M_{l_1} \epsilon_{\alpha_5\alpha_8\alpha_9} R^{eq}_{l_1\alpha_8} \mathcal{R}_{\alpha_9\alpha_3} \\
& \mid \quad \text{now use } \sum_{\alpha_3} \mathcal{R}_{\alpha_7\alpha_3} \mathcal{R}_{\alpha_9\alpha_3} = \delta_{\alpha_7\alpha_9} \text{ and } \sum_{\alpha_7} \epsilon_{\alpha_4\alpha_6\alpha_7} \epsilon_{\alpha_5\alpha_8\alpha_7} = \delta_{\alpha_4\alpha_5}\delta_{\alpha_6\alpha_8} - \delta_{\alpha_4\alpha_8}\delta_{\alpha_6\alpha_5} \\
& \mid \quad \text{we get } \sum_{\alpha_3} a^{l_1}_{\alpha_3\alpha_4} a^{l_1}_{\alpha_3\alpha_5} = \sum_{\alpha_6} M^2_{l_1} R^{0^2}_{l_1\alpha_6} \delta_{\alpha_4\alpha_5} - M^2_{l_1} R^{eq}_{l_1\alpha_5} R^{eq}_{l_1\alpha_4} \\
= \quad & \sum_{l_1} \frac{\hbar^2}{2M_{l_1}} \sum_{\alpha_4\alpha_5} J^{-1}_{\alpha_1\alpha_4} J^{-1}_{\alpha_2\alpha_5} \left(\sum_{\alpha_6} M^2_{l_1} R^{eq}_{l_1\alpha_6} R^{eq}_{l_1\alpha_6} \delta_{\alpha_4\alpha_5} - M^2_{l_1} R^{eq}_{l_1\alpha_5} R^{eq}_{l_1\alpha_4} \right) && (6.328) \\
& \mid \quad \text{note } \sum_{l_1} \left(M_{l_1} \vec{R}^{eq}_{l_1} \cdot \vec{R}^{eq}_{l_1} \delta_{\alpha_4\alpha_5} - M_{l_1} R^{eq}_{l_1\alpha_4} R^{eq}_{l_1\alpha_5} \right) = J_{\alpha_4\alpha_5}(\vec{R}^{eq}) \equiv I_{\alpha_4\alpha_5}(\vec{R}^{eq}) \\
= \quad & \frac{\hbar^2}{2} \sum_{\alpha_4} J^{-1}_{\alpha_1\alpha_4} I_{\alpha_4\alpha_4}(\vec{R}^0) J^{-1}_{\alpha_2\alpha_4} && (6.329) \\
& \mid \quad \text{writing in matrix form} \\
= \quad & \frac{\hbar^2}{2} \left[J^{-1}(\vec{R}'') I(\vec{R}^0) J^{-1}(\vec{R}'') \right]_{\alpha_1\alpha_2} && (6.330)
\end{aligned}
$$

Since $J(\vec{R}) = J(\vec{R} + \vec{a})$ then we translate $\vec{a} = -\mathcal{R}\vec{R}_{CMN}$

$$
\begin{aligned}
J(\vec{R}'') &= J(\vec{R}'' - \mathcal{R}\vec{R}_{CMN}) && (6.331) \\
&= J(\mathcal{R}(\vec{R} - \vec{R}_{CMN})) && (6.332) \\
&= J(\vec{R}') && (6.333)
\end{aligned}
$$

so $\alpha_{\alpha_1\alpha_2} = \frac{\hbar^2}{2}\left[J^{-1}(\vec{R}')I(\vec{R}^0)J^{-1}(\vec{R}')\right]_{\alpha_1\alpha_2}$. Finally, we need an explicit form for the operator ν_{α_1} in the Coriolis term.

$$
\begin{aligned}
\nu_{\alpha_1} &= i \sum_{l_1=1}^{N_n} \frac{\hbar^2}{2M_{l_1}} \sum_{\alpha_2} \Omega^{l_1}_{\alpha_1\alpha_2} \frac{\partial}{\partial R_{l_1\alpha_2}} && (6.334) \\
&= i \sum_{l_1=1}^{N_n} \frac{\hbar^2}{2M_{l_1}} \sum_{\alpha_2\alpha_3} J^{-1}_{\alpha_1\alpha_3} a^{l_1}_{\alpha_2\alpha_3} \frac{\partial}{\partial R_{l_1\alpha_2}} && (6.335) \\
& \mid \quad \text{use the explicit form of } a^{l_1}_{\alpha_2\alpha_3} \\
&= i\frac{\hbar^2}{2} \sum_{l_1=1}^{N_n} \sum_{\alpha_2\alpha_3\alpha_4\alpha_5} J^{-1}_{\alpha_1\alpha_3} \epsilon_{\alpha_3\alpha_4\alpha_5} R^{eq}_{l_1\alpha_4} \mathcal{R}_{\alpha_5\alpha_2} \frac{\partial}{\partial R_{l_1\alpha_2}} && (6.336) \\
&= -\frac{\hbar^2}{2} \sum_{\alpha_3} J^{-1}_{\alpha_1\alpha_3} L^N_{\alpha_3} && (6.337)
\end{aligned}
$$

where $\vec{L}^N$ is defined as the vibrational angular momentum of the nuclei,

$$\vec{L}^N \equiv -i \sum_{l_1=1}^{N_n} \vec{R}_{l_1}^{eq} \times \mathcal{R} \frac{\partial}{\partial \vec{R}_{l_1}} \tag{6.338}$$

If $\vec{R}' = \vec{R}^{eq}$ then $\alpha_{\alpha_1\alpha_2}$ is diagonal and inversely proportional to the diagonal elements of the inertia tensor. ν_{α_1} is similarly inversely proportional to the diagonal elements of the inertia tensor. The diagonal elements of the inertia tensor is related to the total mass of the system, thus these 2 quantities are small when the system is large.

We close by mentioning that the subsequent developments are (a) the development of normal modes in the body-fixed frame and (b) the development of phonon-induced effective electron-electron interaction which are covered in [Leeuwen2004].

Development (a) of normal modes becomes very rigorous because internal and external degrees of freedom have been "seperated" in a rigorous way. Typically in solid state physics, external degrees of freedom (3 translations and 3 rotations) are simply ignored and normal modes (phonons) are developed.

Development (b) would also be a more rigorous look at the formation of Cooper pairs and therefore superconductivity. The usual Cooper instability theory was all developed under the umbrella of Born-Oppenheimer adiabatic decoupling approximation.

Chapter 7

Disordered Systems

[Chapter Introduction and Roadmap:] We enumerate this introduction for easy reading.

1. This chapter aims to treat transport in high concentrations of disorder in systems. The key phrase here is "high concentration" because it is easy to reach high concentrations of disorder due to the smaller number of particles in small systems.

2. Throughout the whole chapter, we will deal with binary disorder. The host atoms are labelled as A with concentration c_A and the defect atoms are labelled as B with concentration c_B. There are 4 types of disorder associated with a lattice of atoms.

   (a) Diagonal disorder. This disorder is due to a substitution of atoms of different masses in the lattice. All other parameters, such as force constants, are unchanged. This could happen if the substitution is by isotopes of the host. Since only single sites are involved, it is "diagonal" in the sense of lattice sites.

   (b) Off Diagonal disorder. This is essentially the first model but taking into account changes in force constants due to the fact that different types of atoms creates different interatomic potentials. As the force constants involve neighbouring sites, it is "off diagonal" in the sense of lattice sites.

   (c) Environmental disorder. There should be no excitations when the whole disordered solid is translated (i.e. this means translational invariance). This is taken into account by enforcing the force constant sum rule in the theory i.e. $\Phi_{ll} = -\sum_{l' \neq l} \Phi_{ll'}$ where l' are the neighbouring sites to l.[1]

   (d) Short Range Order (SRO). This is the effect that the defect sites could affect the occupancy of nearby sites.

3. The key difficulty in dealing with disorder theory is how to calculate the configurational average of physical quantities. There are simply too many configurations to average! These configurationally averaged quantities are the ones that can be compared to experiments. [2] The main physical quantities to calculate in this chapter are the configurational averaged 1-particle and 2-particle Green's functions. The different theories presented in this chapter are simply various ways of approximating the configurational average.

[1] You may call this the "Newton's first law" of lattice dynamics. Such a sum rule does not exist for disordered electronic systems.

[2] Here, I can give a simple high school math example. In a factory that makes light bulbs, to determine the lifetime of the bulbs, a good experimentalist will have to draw samples (which represents different configurations) and determine their lifetime and make a statistical claim of the lifetime. This statistical claim is the configurational averaged lifetime.

4. Firstly, we show simple examples of one-configuration-disorder theory to guide us through some physics of disordered systems. This gives us physical intuition to interprete the complicated theories that follow.

5. Secondly, with regards to the 3 transport related developments, the kinetic theory is presented for mass disorder is given. Linear response theory for mass and force constant disorder is then briefly mentioned.

6. Thirdly, for Landauer-like theory, we found that it works perfectly with the most powerful approximation for mass disordered systems, the CPA. The resulting publication is [NiMLL2011].

7. We also supply 3 derivations for CPA because the subsequent generalized theories are all inspired by 1 of the 3 derivations.

8. The subsequent generalized theories are meant to handle 2 types of disorder: mass and force constant disorder. Well, this is simply because only mass disorder in a system is somewhat artificial. We present 4 such theories. We hope to investigate which of these theories is suitable to describe (disordered) finite systems numerically. [3]

7.1 Simple but Exact Examples for Illustration:

7.1.1 1D Chain with 1 Mass Impurity

Theories that assume low concentrations of impurities are classified as "old theories of disorder". Although these theories may be somewhat outdated, they actually allow the physics of disordered systems to be clearly exhibited. Thus it is worthwhile spending the first section discussing the one impurity problem. We will only mention some very good review articles covering these old theories. They are [Maradudin1958], [Maradudin1965], [Bell1972], [Maradudin1966] and [Maradudin1967].

For the 1 mass impurity problem, we follow [Enns1969]. The problem is described by the following diagram. The impurity atom with mass M_0 is at $l = 0$. M is the mass of the host atom. All force

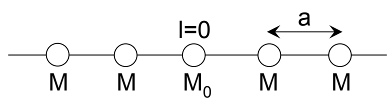


Figure 7.1: *Setup for the 1D chain, 1 mass impurity problem.*

constants are that of the host, denoted by Φ. Considering only nearest neighbour interactions, the equations of motion are,

$$\text{For } l \neq 0 \quad M\ddot{u}_l = -\Phi\left(2u_l - u_{l-1} - u_{l+1}\right) \tag{7.1}$$

$$\text{For } l = 0 \quad M_0\ddot{u}_0 = -\Phi\left(2u_0 - u_{-1} - u_1\right) \tag{7.2}$$

We can combine both equations into the form

$$M\ddot{u}_l + \Phi\left(2u_l - u_{l-1} - u_{l+1}\right) = \delta_{l0}(M - M_0)\ddot{u}_0 \tag{7.3}$$

[3] Unfortunately, my fellow group member graduated before she can carry out the numerical investigations.

Denote $\omega^2_{\text{max LA}} = \frac{4\Phi}{M}$ and Fourier transform to the frequency domain using $u_l(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t} u_l(\omega)$ and we get

$$-\omega^2 u_l + \frac{1}{4}\omega^2_{\text{max LA}}\left(2u_l - u_{l-1} - u_{l+1}\right) = -\delta_{l0}\frac{M - M_0}{M}\omega^2 u_0 \tag{7.4}$$

Note that we do not have space translational invariance but we are still going to perform normal mode transformation and use the host normal coordinates as the basis. The normal coordinates are

$$Q_q(\omega) = \frac{1}{\sqrt{N}}\sum_l u_l(\omega) e^{-iqla} \tag{7.5}$$

The normal component of the equation is

$$-\omega^2 Q_q(\omega) + \frac{1}{4}\omega^2_{\text{max LA}}\left(2 - e^{-iqa} - e^{iqa}\right) Q_q(\omega) = -\frac{M - M_0}{M}\omega^2 \frac{1}{\sqrt{N}}\sum_l \delta_{l0} u_0(\omega) e^{-iqla} \tag{7.6}$$

$$-\omega^2 Q_q(\omega) + \frac{1}{4}\omega^2_{\text{max LA}}\left(2 - 2\cos(qa)\right) Q_q(\omega) = -\frac{1}{\sqrt{N}}\frac{M - M_0}{M}\omega^2 u_0(\omega) \tag{7.7}$$

$$-\omega^2 Q_q(\omega) + \omega^2_{\text{max LA}}\sin^2\left(\frac{qa}{2}\right) Q_q(\omega) = -\frac{1}{\sqrt{N}}\frac{M - M_0}{M}\omega^2 u_0(\omega) \tag{7.8}$$

$$\text{denote } \omega^2_{\text{max LA}}\sin^2\left(\frac{qa}{2}\right) \equiv \omega_q^2 \quad |$$

$$Q_q(\omega) = \frac{-\frac{1}{\sqrt{N}}\frac{M-M_0}{M}\omega^2 u_0(\omega)}{\omega_q^2 - \omega^2} \tag{7.9}$$

Use the inverse normal mode transform,

$$u_l(\omega) = \frac{M - M_0}{M}\frac{1}{N}\sum_q \frac{\omega^2}{\omega^2 - \omega_q^2} u_0(\omega) e^{iqla} \tag{7.10}$$

A self consistent condition is that at $l = 0$, $u_0(\omega)$ on LHS and $u_0(\omega)$ on RHS must be the same. This implies the assumption that the impurity atom has a non-zero vibrational amplitude ($u_0 \neq 0$). We set $l = 0$ to get

$$u_0(\omega) = \frac{M - M_0}{M}\frac{1}{N}\sum_q \frac{\omega^2}{\omega^2 - \omega_q^2} e^{i0} \tag{7.11}$$

$$1 = \frac{M - M_0}{M}\frac{1}{N}\sum_q \frac{\omega^2}{\omega^2 - \omega_q^2} \tag{7.12}$$

$$\frac{1}{N}\sum_q \frac{\omega^2}{\omega^2 - \omega_q^2} = \frac{M}{M - M_0} \tag{7.13}$$

Let $f(\omega^2) \equiv \frac{1}{N}\sum_q \frac{\omega^2}{\omega^2 - \omega_q^2}$ which is of degree N and thus has N solutions. The intersections of $f(\omega^2)$ and the line $\frac{M}{M-M_0}$ gives the vibrational frequencies of the 1 impurity 1D chain.

- Case where $0 < M_0 < M$. The impurity is lighter than the host atoms. The frequencies are shifted slightly upwards. An additional frequency is higher than the band. This is the localized mode. We can infer that when there are more impurity atoms, a band of localized modes will form.

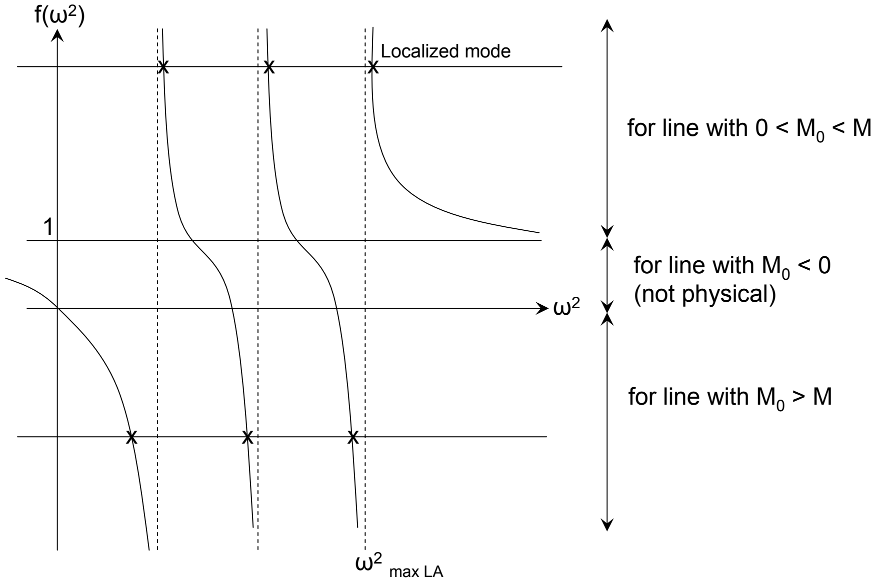


Figure 7.2: *Schematic plot of the self consistent condition in the 1D 1 mass impurity problem. The crosses mark the frequencies of the disordered system.*

- Case where $M_0 > M$. The impurity is heavier than the host. The frequencies are shifted downwards (unevenly). There are no localized modes. Due to the uneven shift, a resonance is created where the density of states (DOS) within the band is enhanced somewhere within the band.

Finally, note that the ordered chain has a $\omega = 0$ solution which does not appear here. This is due to the lack of space translational invariance in this system. For systems with more than one atom per unit cell, the localized mode may appear between the acoustic and optical branches or above the optical branch.

7.1.2 3D Solid with 1 Mass Impurity

Here we follow the same reference [Enns1969]. The impurity has mass M_0 and is at position vector $\vec{R}_{l=0}$. The host atoms have mass M each and all force constants are that of the host. Each unit cell is taken to be monoatomic for simplicity. The equations of motion are,

$$\text{For } l \neq 0 \quad M\ddot{u}_{l\alpha} = -\sum_{l_1\alpha_1} \Phi_{l\alpha l_1\alpha_1} u_{l_1\alpha_1} \tag{7.14}$$

$$\text{For } l = 0 \quad M_0\ddot{u}_{0\alpha} = -\sum_{l_1\alpha_1} \Phi_{0\alpha l_1\alpha_1} u_{l_1\alpha_1} \tag{7.15}$$

We combine both equations into,

$$M\ddot{u}_{l\alpha} + \sum_{l_1\alpha_1} \Phi_{l\alpha l_1\alpha_1} u_{l_1\alpha_1} = \delta_{0\alpha}(M - M_0)\ddot{u}_{0\alpha} \tag{7.16}$$

Fourier transform to frequency domain,

$$\sum_{l_1\alpha_1} \left[-\omega^2 M\delta_{ll_1}\delta_{\alpha\alpha_1} + \Phi_{l\alpha l_1\alpha_1}\right] u_{l_1\alpha_1} = -\delta_{l0}\omega^2(M - M_0)u_{0\alpha} \tag{7.17}$$

We will use the host normal coordinates for the discussion but we will carry out the derivation in a slightly different way. This derivation is more in the spirit of the Green's function approach.

Define the matrices,

$$L^{\text{host}}_{l\alpha l_1\alpha_1}(\omega^2) \equiv \omega^2 M\delta_{ll_1}\delta_{\alpha\alpha_1} - \Phi_{l\alpha l_1\alpha_1} \tag{7.18}$$

$$\delta L_{l\alpha l_1\alpha_1}(\omega^2) \equiv -\delta_{l0}\delta_{l_1 0}\delta_{\alpha\alpha_1}(M - M_0)\omega^2 \tag{7.19}$$

The equation of motion in matrix form is then

$$\left(L^{\text{host}} + \delta L\right) u = 0 \tag{7.20}$$

We seek the inverse of L^{host} which is defined through

$$\sum_{l_1\alpha_1} L^{\text{host}-1}_{l\alpha l_1\alpha_1}(\omega^2) L^{\text{host}}_{l_1\alpha_1 l_2\alpha_2}(\omega^2) = \delta_{ll_2}\delta_{\alpha\alpha_2} \tag{7.21}$$

This is carried out in normal coordinates. The spring constant matrix in normal coordinates is

$$\Phi_{l\alpha l_1\alpha_1} = \Phi_{\alpha\alpha_1}(l - l_1) = \frac{M}{N}\sum_{j\vec{q}} \epsilon^*_\alpha(j\vec{q})\epsilon_{\alpha_1}(j\vec{q})\omega^2_{j\vec{q}} e^{i\vec{q}\cdot(l-l_1)} \tag{7.22}$$

Thus the normal component of L^{host} is

$$L^{\text{host}}_{j\vec{q}} = M\omega^2 - M\omega^2_{j\vec{q}} \tag{7.23}$$

And so the normal component of the inverse is

$$L^{\text{host}-1}_{j\vec{q}} = \frac{1}{M}\frac{1}{\omega^2 - \omega^2_{j\vec{q}}} \tag{7.24}$$

Take the inverse normal mode transform,

$$L^{\mathrm{host}-1}_{l\alpha l_1\alpha_1} = \frac{1}{NM}\sum_{j\vec{q}}\frac{1}{\omega^2-\omega^2_{j\vec{q}}}\epsilon^*_\alpha(j\vec{q})\epsilon_{\alpha_1}(j\vec{q})e^{i\vec{q}\cdot(l-l_1)} \tag{7.25}$$

Solve the (matrix) equation of motion using $L^{\mathrm{host}-1}$,

$$\left(L^{\mathrm{host}}+\delta L\right)u = 0 \tag{7.26}$$

$$L^{\mathrm{host}-1}\times\left(L^{\mathrm{host}}+\delta L\right)u = 0 \tag{7.27}$$

$$\left(1+L^{\mathrm{host}-1}\delta L\right)u = 0 \tag{7.28}$$

$$\sum_{l_2\alpha_2}\left(\delta_{ll_2}\delta_{\alpha\alpha_2}+\sum_{l_1\alpha_1}L^{\mathrm{host}-1}_{l\alpha l_1\alpha_1}\delta L_{l_1\alpha_1 l_2\alpha_2}\right)u_{l_2\alpha_2} = 0 \tag{7.29}$$

$$u_{l\alpha}+\sum_{l_1\alpha_1}\sum_{l_2\alpha_2}L^{\mathrm{host}-1}_{l\alpha l_1\alpha_1}\left(-\delta_{l_10}\delta_{l_20}\delta_{\alpha_1\alpha_2}(M-M_0)\omega^2\right)u_{l_2\alpha_2} = 0 \tag{7.30}$$

$$u_{l\alpha}+\sum_{\alpha_1}L^{\mathrm{host}-1}_{l\alpha 0\alpha_1}(M_0-M)\omega^2 u_{0\alpha_1} = 0 \tag{7.31}$$

$$u_{l\alpha}+\sum_{\alpha_1}\frac{M_0-M}{M}\frac{1}{N}\sum_{j\vec{q}}\frac{\omega^2}{\omega^2-\omega^2_{j\vec{q}}}\epsilon^*_\alpha(j\vec{q})\epsilon_{\alpha_1}(j\vec{q})e^{i\vec{q}\cdot l}u_{0\alpha_1} = 0 \tag{7.32}$$

If we further assume that the defect site has cubic or tetrahedral symmetry, the cartesian directions are orthogonal and it is nonvanishing when $\alpha_1=\alpha$.

$$u_{l\alpha}+\frac{M_0-M}{M}\frac{1}{N}\sum_{j\vec{q}}\frac{\omega^2}{\omega^2-\omega^2_{j\vec{q}}}\left|\epsilon_\alpha(j\vec{q})\right|^2 e^{i\vec{q}\cdot l}u_{0\alpha} = 0 \tag{7.33}$$

Following the earlier section on the 1D chain, the self consistent condition is obtained by setting $l=0$ and assuming $u_{l\alpha}\neq 0$, we thus get a very similar result.

$$1 = \frac{M-M_0}{M}\frac{1}{N}\sum_{j\vec{q}}\frac{\omega^2}{\omega^2-\omega^2_{j\vec{q}}}\left|\epsilon_\alpha(j\vec{q})\right|^2 \tag{7.34}$$

Thus we can make similar conclusions to that for a 1D chain. For a light impurity ($M_0<M$), there is a localized mode above the band. For a heavy impurity ($M_0>M$), we do not have localized modes. However we may have resonance (enhanced DOS) within the band.

7.2 Mass Disorder: Boltzmann Treatment

7.2.1 Mass Difference Scattering: Full Collision Integral

Here we want to derive the full collision integral for mass difference scattering in the solid. We follow [Srivastava1990] section 6.2.1.

We start with the Hamiltonian of the solid with randomly distributed mass impurities in the harmonic approximation. The force constants are assumed to be that of the host.

$$
\begin{aligned}
H &= \sum_{l\alpha} \frac{1}{2} M_l \dot{u}_{l\alpha}^2 + \frac{1}{2} \sum_{l\alpha} \sum_{l_1\alpha_1} \Phi_{l\alpha l_1\alpha_1} u_{l\alpha} u_{l_1\alpha_1} && (7.35)\\
&\mid \text{ define average mass per unit cell } \bar{M} \equiv c_A M_A + c_B M_B = \frac{1}{N} \sum_l M_l \\
&\mid \text{ and we split the Hamiltonian as follows} \\
&= \sum_{l\alpha} \frac{1}{2} \bar{M} \dot{u}_{l\alpha}^2 - \sum_{l\alpha} \frac{1}{2} \bar{M} \dot{u}_{l\alpha}^2 + \sum_{l\alpha} \frac{1}{2} M_l \dot{u}_{l\alpha}^2 + \frac{1}{2} \sum_{l\alpha} \sum_{l_1\alpha_1} \Phi_{l\alpha l_1\alpha_1} u_{l\alpha} u_{l_1\alpha_1} && (7.36)\\
&= \left(\sum_{l\alpha} \frac{1}{2} \bar{M} \dot{u}_{l\alpha}^2 + \frac{1}{2} \sum_{l\alpha} \sum_{l_1\alpha_1} \Phi_{l\alpha l_1\alpha_1} u_{l\alpha} u_{l_1\alpha_1} \right) + \left(\sum_{l\alpha} \frac{1}{2} (M_l - \bar{M}) \dot{u}_{l\alpha}^2 \right) && (7.37)\\
&\mid \text{ define the unperturbed Hamiltonian } H_0 \equiv \sum_{l\alpha} \frac{1}{2} \bar{M} \dot{u}_{l\alpha}^2 + \frac{1}{2} \sum_{l\alpha} \sum_{l_1\alpha_1} \Phi_{l\alpha l_1\alpha_1} u_{l\alpha} u_{l_1\alpha_1} \\
&\mid \text{ define the mass difference perturbation Hamiltonian } H_{\text{int}}^{MD} \equiv \sum_{l\alpha} \frac{1}{2} (M_l - \bar{M}) \dot{u}_{l\alpha}^2 \\
&= H_0 + H_{\text{int}}^{MD} && (7.38)
\end{aligned}
$$

Write H_{int}^{MD} into second quantized form before we substitute it into the Golden Rule.

$$
\begin{aligned}
H_{\text{int}}^{MD} &= \sum_{l\alpha} \frac{1}{2} (M_l - \bar{M}) \dot{u}_{l\alpha}^2 && (7.39)\\
&\mid \text{ use the second quantized form of } u_{l\alpha} \text{ according to the above } H_0 \\
&\mid \ u_{l\alpha} = \sum_{j\vec{q}} \sqrt{\frac{\hbar}{2N\bar{M}\omega_{j\vec{q}}}} \epsilon_\alpha(\vec{q}) \left(a_{j,-\vec{q}}^\dagger + a_{j\vec{q}} \right) e^{i\vec{q}\cdot l} \\
&\mid \text{ recall the harmonic solutions } a_{H_0 j_1\vec{q}_1}(t) = e^{-i\omega_{j_1\vec{q}_1} t} a_{j_1\vec{q}_1} \text{ and } a_{H_0 j_1\vec{q}_1}^\dagger(t) = e^{i\omega_{j_1\vec{q}_1} t} a_{j_1\vec{q}_1}^\dagger \\
&= \frac{1}{2} \sum_l (M_l - \bar{M}) \sum_{j_1\vec{q}_1} \sum_{j_2\vec{q}_2} \frac{\hbar}{2N\bar{M}} \frac{-\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}{\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}} \left(\vec{\epsilon}(j_1\vec{q}_1) \cdot \vec{\epsilon}(j_2\vec{q}_2) \right) \\
&\quad \times \left(a_{j_1,-\vec{q}_1}^\dagger - a_{j_1\vec{q}_1} \right) \left(a_{j_2,-\vec{q}_2}^\dagger - a_{j_2\vec{q}_2} \right) e^{i(\vec{q}_1+\vec{q}_2)\cdot l} && (7.40)\\
&\mid \text{ rename } \vec{q}_2 \to -\vec{q}_2, \text{ so } \omega_{j_2,-\vec{q}_2} \to \omega_{j_2\vec{q}_2} \text{ and } \vec{\epsilon}(j_2,-\vec{q}_2) = \vec{\epsilon}^*(j_2\vec{q}_2) \\
&= \sum_{j_1\vec{q}_1} \sum_{j_2\vec{q}_2} \sum_l (M_l - \bar{M}) \frac{-\hbar\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}}{4N\bar{M}} \left(\vec{\epsilon}(j_1\vec{q}_1) \cdot \vec{\epsilon}^*(j_2\vec{q}_2) \right) \\
&\quad \times \left(a_{j_1,-\vec{q}_1}^\dagger - a_{j_1\vec{q}_1} \right) \left(a_{j_2\vec{q}_2}^\dagger - a_{j_2,-\vec{q}_2} \right) e^{i(\vec{q}_1-\vec{q}_2)\cdot l} && (7.41)\\
&\mid \text{ define the “coupling constant” } M_{\vec{q}_1\vec{q}_2} \equiv \sum_l (M_l - \bar{M}) e^{i(\vec{q}_1-\vec{q}_2)\cdot l} \\
&= \sum_{j_1\vec{q}_1} \sum_{j_2\vec{q}_2} M_{\vec{q}_1\vec{q}_2} \frac{-\hbar\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}}{4N\bar{M}} \left(\vec{\epsilon}(j_1\vec{q}_1) \cdot \vec{\epsilon}^*(j_2\vec{q}_2) \right) \\
&\quad \times \left(a_{j_1,-\vec{q}_1}^\dagger a_{j_2\vec{q}_2}^\dagger - a_{j_1,-\vec{q}_1}^\dagger a_{j_2,-\vec{q}_2} - a_{j_1\vec{q}_1} a_{j_2\vec{q}_2}^\dagger + a_{j_1\vec{q}_1} a_{j_2,-\vec{q}_2} \right) && (7.42)
\end{aligned}
$$

Although there are 4 terms in the interaction Hamiltonian, the first and the last term do not conserve energy. We drop these 2 terms. The remaining 2 terms represent in-scattering and out-scattering with respect to a reference state and we proceed to calculate their Golden Rule transition rates. The Golden Rule is

$$W_{i\leftrightarrow f} = \frac{2\pi}{\hbar}\left|\langle i\left|H_{\rm int}^{MD}\right|f\rangle\right|^2\delta(E_f-E_i) \tag{7.43}$$

The reference state is chosen to be $j_1\vec{q}_1$ so the collision integral is written as $I^{MD} = \left.\frac{\partial N_{j_1\vec{q}_1}}{\partial t}\right|_{\rm coll}$

$$\begin{aligned}
& W_{i\leftrightarrow f} \text{ 1st term}\\
= \;& \frac{2\pi}{\hbar}\sum_{j_2\vec{q}_2}\left|M_{\vec{q}_1\vec{q}_2}\right|^2\frac{\hbar^2\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}{16N^2\bar{M}^2}\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\left|\left\langle i\left|a^\dagger_{j_1,-\vec{q}_1}a_{j_2,-\vec{q}_2}\right|f\right\rangle\right|^2\delta(\hbar\omega_{j_1\vec{q}_1}-\hbar\omega_{j_2\vec{q}_2})\\
| \;& \text{use identity } \delta(ax)=\frac{1}{|a|}\delta(x) \text{ and the ladder relations}\\
| \;& a_{j_2,-\vec{q}_2}|f\rangle = \sqrt{N_{j_2\vec{q}_2}}|N_{j_2\vec{q}_2}-1\rangle \text{ and } a^\dagger_{j_1,-\vec{q}_1}|f\rangle = \sqrt{N_{j_1\vec{q}_1}+1}|N_{j_1\vec{q}_1}+1\rangle\\
= \;& \sum_{j_2\vec{q}_2}\left|M_{\vec{q}_1\vec{q}_2}\right|^2\frac{\pi\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}{8N^2\bar{M}^2}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\left(N_{j_1\vec{q}_1}+1\right)N_{j_2\vec{q}_2} \qquad (7.44)\\
= \;& \text{scatters into } j_1\vec{q}_1
\end{aligned}$$

$$\begin{aligned}
& W_{i\leftrightarrow f} \text{ 2nd term}\\
= \;& \frac{2\pi}{\hbar}\sum_{j_2\vec{q}_2}\left|M_{\vec{q}_1\vec{q}_2}\right|^2\frac{\hbar^2\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}{16N^2\bar{M}^2}\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\left|\left\langle i\left|a_{j_1\vec{q}_1}a^\dagger_{j_2\vec{q}_2}\right|f\right\rangle\right|^2\delta(\hbar\omega_{j_1\vec{q}_1}-\hbar\omega_{j_2\vec{q}_2}) \quad (7.45)\\
| \;& \text{use identity } \delta(ax)=\frac{1}{|a|}\delta(x) \text{ and the ladder relations}\\
| \;& a^\dagger_{j_2\vec{q}_2}|f\rangle = \sqrt{N_{j_2\vec{q}_2}+1}|N_{j_2\vec{q}_2}+1\rangle \text{ and } a_{j_1\vec{q}_1}|f\rangle = \sqrt{N_{j_1\vec{q}_1}}|N_{j_1\vec{q}_1}-1\rangle\\
= \;& \sum_{j_2\vec{q}_2}\left|M_{\vec{q}_1\vec{q}_2}\right|^2\frac{\pi\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}{8N^2\bar{M}^2}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2 N_{j_1\vec{q}_1}\left(N_{j_2\vec{q}_2}+1\right) \qquad (7.46)\\
= \;& \text{scatters out of } j_1\vec{q}_1
\end{aligned}$$

The collision integral is

$$\begin{aligned}
I^{MD} &= \left.\frac{\partial N_{j_1\vec{q}_1}}{\partial t}\right|_{\rm coll} && (7.47)\\
&= W_{i\leftrightarrow f}\text{ 1st term} - W_{i\leftrightarrow f}\text{ 2nd term} && (7.48)\\
&= \sum_{j_2\vec{q}_2}\left|M_{\vec{q}_1\vec{q}_2}\right|^2\frac{\pi\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}{8N^2\bar{M}^2}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2 && (7.49)\\
&\quad\times\left[\left(N_{j_1\vec{q}_1}+1\right)N_{j_2\vec{q}_2} - N_{j_1\vec{q}_1}\left(N_{j_2\vec{q}_2}+\right)\right] && (7.50)
\end{aligned}$$

We need to further rewrite $\left|M_{\vec{q}_1\vec{q}_2}\right|^2$ so that we can bring in the experimental parameters of host concentration c_A and impurity concentration c_B.

$$\begin{aligned}
\left|M_{\vec{q}_1\vec{q}_2}\right|^2 &= \left|\sum_{l_1}(M_{l_1}-\bar{M})e^{i(\vec{q}_1-\vec{q}_2)\cdot l_1}\right|^2 && (7.51)\\
&= \sum_{l_1l_2}(M_{l_1}-\bar{M})(M_{l_2}-\bar{M})e^{i(\vec{q}_1-\vec{q}_2)\cdot(l_1-l_2)} && (7.52)
\end{aligned}$$

$$
\begin{aligned}
&= \sum_{l_1}(M_{l_1}-\bar{M})^2 + \sum_{l_2(\neq l_1)}(M_{l_1}-\bar{M})(M_{l_2}-\bar{M})e^{i(\vec{q}_1-\vec{q}_2)\cdot(l_1-l_2)} && (7.53)\\
&\quad | \quad \text{assume that the impurities are distributed randomly}\\
&\quad | \quad \text{so the 2nd term averages to zero due to isotropy}\\
&= \sum_{l_1}(M_{l_1}-\bar{M})^2 && (7.54)\\
&\quad | \quad \text{recall the single site average } \sum_{l_1} M_{l_1} = N\bar{M} = N(c_A M_A + c_B M_B) = N\sum_m c_m M_m\\
&= N\sum_m c_m (M_m-\bar{M})^2 && (7.55)
\end{aligned}
$$

The collision integral becomes

$$
\begin{aligned}
I^{MD} &= \left.\frac{\partial N_{j_1\vec{q}_1}}{\partial t}\right|_{\text{coll}} && (7.56)\\
&= \sum_{j_2\vec{q}_2}\sum_m c_m\left(\frac{M_m}{\bar{M}}-1\right)^2 \frac{\pi\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}{8N}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\\
&\quad\times\left[\left(N_{j_1\vec{q}_1}+1\right)N_{j_2\vec{q}_2} - N_{j_1\vec{q}_1}\left(N_{j_2\vec{q}_2}+\right)\right] && (7.57)\\
&\quad | \quad \text{define } \Gamma^{MD} \equiv \sum_m c_m\left(\frac{M_m}{\bar{M}}-1\right)^2\\
&= \sum_{j_2\vec{q}_2}\frac{\pi\Gamma^{MD}}{8N}\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\left[\left(N_{j_1\vec{q}_1}+1\right)N_{j_2\vec{q}_2} - N_{j_1\vec{q}_1}\left(N_{j_2\vec{q}_2}+\right)\right]
\end{aligned}
$$

$$
\boxed{I^{MD} = \sum_{j_2\vec{q}_2}\frac{\pi\Gamma^{MD}}{8N}\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\left[\left(N_{j_1\vec{q}_1}+1\right)N_{j_2\vec{q}_2} - N_{j_1\vec{q}_1}\left(N_{j_2\vec{q}_2}+\right)\right]} \tag{7.58}
$$

Which is our final full mass-difference collision integral.

[Checking energy conservation] We quickly digress to show that this collision integral conserves energy as expected. This is done by checking

$$
\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}\left.\frac{\partial N_{j_1\vec{q}_1}}{\partial t}\right|_{\text{coll}} \stackrel{?}{=} 0 \tag{7.59}
$$

$$
\begin{aligned}
&\sum_{j_1\vec{q}_1}\hbar\omega_{j_1\vec{q}_1}\left.\frac{\partial N_{j_1\vec{q}_1}}{\partial t}\right|_{\text{coll}}\\
&= \hbar\sum_{j_1\vec{q}_1}\sum_{j_2\vec{q}_2}\frac{\pi\Gamma^{MD}}{8N}\omega^2_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\left[\left(N_{j_1\vec{q}_1}+1\right)N_{j_2\vec{q}_2} - N_{j_1\vec{q}_1}\left(N_{j_2\vec{q}_2}+\right)\right]\\
&\quad | \quad \text{in 2nd term, rename } j_1\vec{q}_1 \leftrightarrow j_2\vec{q}_2 \text{ and use } \delta(ax) = \frac{1}{|a|}\delta(x)
\end{aligned}
$$

$$
\begin{aligned}
&= \hbar \sum_{j_1\vec{q}_1} \sum_{j_2\vec{q}_2} \frac{\pi\Gamma^{MD}}{8N} \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2}) \left(N_{j_1\vec{q}_1} + 1\right) N_{j_2\vec{q}_2} \\
&\quad \times \left[\omega^2_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2} \left(\vec{\epsilon}(j_1\vec{q}_1) \cdot \vec{\epsilon}^*(j_2\vec{q}_2)\right)^2 - \omega_{j_2\vec{q}_2}\omega_{j_1\vec{q}_1} \left(\vec{\epsilon}(j_2\vec{q}_2) \cdot \vec{\epsilon}^*(j_1\vec{q}_1)\right)^2\right] \qquad (7.60) \\
&\mid \quad \text{in 2nd term, } \vec{q}_2 \to -\vec{q}_2 \text{ and } \vec{q}_1 \to -\vec{q}_1 \\
&\mid \quad \text{only polarization vectors are affected } \vec{\epsilon}(j_2\vec{q}_2) \to \vec{\epsilon}^*(j_2\vec{q}_2) \text{ and } \vec{\epsilon}^*(j_1\vec{q}_1) \to \vec{\epsilon}(j_1\vec{q}_1) \\
&= \hbar \sum_{j_1\vec{q}_1} \sum_{j_2\vec{q}_2} \frac{\pi\Gamma^{MD}}{8N} \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2}) \left(N_{j_1\vec{q}_1} + 1\right) N_{j_2\vec{q}_2} \left(\vec{\epsilon}(j_1\vec{q}_1) \cdot \vec{\epsilon}^*(j_2\vec{q}_2)\right)^2 \left[\omega^2_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2} - \omega^2_{j_2\vec{q}_2}\omega_{j_1\vec{q}_1}\right] \qquad (7.61) \\
&\mid \quad \text{use the delta function} \\
&= 0
\end{aligned}
$$

7.2.2 Mass Difference Scattering: Linearized Collision Integral

The standard expression for the linearized distribution is defined to be of the form

$$
N_{j_1\vec{q}_1} \approx N^{eq}_{j_1\vec{q}_1} + N^{eq}_{j_1\vec{q}_1} \left(N^{eq}_{j_1\vec{q}_1} + 1\right) y_{j_1\vec{q}_1} \qquad (7.62)
$$

and we substitute it into the collision integral to get the linearized collision integral.

$$
\begin{aligned}
&\Delta I^{MD} \\
&= \sum_{j_2\vec{q}_2} \frac{\pi\Gamma^{MD}}{8N} \omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2} \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2}) \left(\vec{\epsilon}(j_1\vec{q}_1) \cdot \vec{\epsilon}^*(j_2\vec{q}_2)\right)^2 \\
&\quad \times \left[\left(1 + N^{eq}_{j_1\vec{q}_1} + N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1} + 1\right) y_{j_1\vec{q}_1}\right)\left(N^{eq}_{j_2\vec{q}_2} + N^{eq}_{j_2\vec{q}_2}\left(N^{eq}_{j_2\vec{q}_2} + 1\right) y_{j_2\vec{q}_2}\right)\right. \\
&\quad \left. -\left(N^{eq}_{j_1\vec{q}_1} + N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1} + 1\right) y_{j_1\vec{q}_1}\right)\left(1 + N^{eq}_{j_2\vec{q}_2} + N^{eq}_{j_2\vec{q}_2}\left(N^{eq}_{j_2\vec{q}_2} + 1\right) y_{j_2\vec{q}_2}\right)\right] \qquad (7.63) \\
&\mid \quad \text{expand and keep only up to 1st order in } y \\
&\approx \sum_{j_2\vec{q}_2} \frac{\pi\Gamma^{MD}}{8N} \omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2} \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2}) \left(\vec{\epsilon}(j_1\vec{q}_1) \cdot \vec{\epsilon}^*(j_2\vec{q}_2)\right)^2 \\
&\quad \times \left[\left(1 + N^{eq}_{j_1\vec{q}_1}\right) N^{eq}_{j_2\vec{q}_2} + \left(1 + N^{eq}_{j_1\vec{q}_1}\right)\left(N^{eq}_{j_2\vec{q}_2}\left(N^{eq}_{j_2\vec{q}_2} + 1\right) y_{j_2\vec{q}_2}\right) + N^{eq}_{j_2\vec{q}_2} N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1} + 1\right) y_{j_1\vec{q}_1}\right. \\
&\quad \left. -N^{eq}_{j_1\vec{q}_1}\left(1 + N^{eq}_{j_2\vec{q}_2}\right) - N^{eq}_{j_1\vec{q}_1} N^{eq}_{j_2\vec{q}_2}\left(N^{eq}_{j_2\vec{q}_2} + 1\right) y_{j_2\vec{q}_2} - \left(1 + N^{eq}_{j_2\vec{q}_2}\right) N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1} + 1\right) y_{j_1\vec{q}_1}\right] \qquad (7.64) \\
&\mid \quad \text{the terms } \left(1 + N^{eq}_{j_1\vec{q}_1}\right) N^{eq}_{j_2\vec{q}_2} - N^{eq}_{j_1\vec{q}_1}\left(1 + N^{eq}_{j_2\vec{q}_2}\right) = 0 \text{ using BE distribution and delta function} \\
&\mid \quad \text{using BE distribution and delta function we rewrite } \left(1 + N^{eq}_{j_1\vec{q}_1}\right) N^{eq}_{j_2\vec{q}_2} = N^{eq}_{j_1\vec{q}_1}\left(1 + N^{eq}_{j_2\vec{q}_2}\right) \\
&= \sum_{j_2\vec{q}_2} \frac{\pi\Gamma^{MD}}{8N} \omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2} \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2}) \left(\vec{\epsilon}(j_1\vec{q}_1) \cdot \vec{\epsilon}^*(j_2\vec{q}_2)\right)^2 \\
&\quad \times \left[N^{eq}_{j_1\vec{q}_1}\left(1 + N^{eq}_{j_2\vec{q}_2}\right)\left(N^{eq}_{j_2\vec{q}_2} + 1\right) y_{j_2\vec{q}_2} + \left(1 + N^{eq}_{j_2\vec{q}_2}\right) N^{eq}_{j_1\vec{q}_1} N^{eq}_{j_1\vec{q}_1} y_{j_1\vec{q}_1}\right. \\
&\quad \left. -N^{eq}_{j_1\vec{q}_1} N^{eq}_{j_2\vec{q}_2}\left(N^{eq}_{j_2\vec{q}_2} + 1\right) y_{j_2\vec{q}_2} - \left(1 + N^{eq}_{j_2\vec{q}_2}\right) N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1} +\right) y_{j_1\vec{q}_1}\right] \qquad (7.65) \\
&= \sum_{j_2\vec{q}_2} \frac{\pi\Gamma^{MD}}{8N} \omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2} \delta(\omega_{j_1\vec{q}_1} - \omega_{j_2\vec{q}_2}) \left(\vec{\epsilon}(j_1\vec{q}_1) \cdot \vec{\epsilon}^*(j_2\vec{q}_2)\right)^2 N^{eq}_{j_1\vec{q}_1}\left(1 + N^{eq}_{j_2\vec{q}_2}\right)\left(y_{j_2\vec{q}_2} - y_{j_1\vec{q}_1}\right) \qquad (7.66)
\end{aligned}
$$

$$\boxed{\Delta I^{MD} = \sum_{j_2\vec{q}_2} \frac{\pi\Gamma^{MD}}{8N}\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2 N^{eq}_{j_1\vec{q}_1}\left(1+N^{eq}_{j_2\vec{q}_2}\right)\left(y_{j_2\vec{q}_2}-y_{j_1\vec{q}_1}\right)} \tag{7.67}$$

which is the final result of the linearized (in distribution) mass difference collision integral.

7.2.3 Mass Difference Scattering: Relaxation Time Approximation

A further simplification is to impose the relaxation time approximation. We equate the linearized collision integral to the relaxation time form. This definition defines the relaxation time itself.

$$\begin{aligned}
\Delta I^{MD} &\equiv -\frac{N_{j_1\vec{q}_1}-N^{eq}_{j_1\vec{q}_1}}{\tau^{MD}_{j_1\vec{q}_1}} && (7.68)\\
&\mid \quad \text{insert } N_{j_1\vec{q}_1} \approx N^{eq}_{j_1\vec{q}_1} + N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1}+1\right)y_{j_1\vec{q}_1}\\
&= -\frac{N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1}+1\right)y_{j_1\vec{q}_1}}{\tau^{MD}_{j_1\vec{q}_1}} && (7.69)\\
\frac{1}{\tau^{MD}_{j_1\vec{q}_1}} &= -\frac{\Delta I^{MD}}{N^{eq}_{j_1\vec{q}_1}\left(N^{eq}_{j_1\vec{q}_1}+1\right)y_{j_1\vec{q}_1}} && (7.70)\\
&= -\sum_{j_2\vec{q}_2}\frac{\pi\Gamma^{MD}}{8N}\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\frac{N^{eq}_{j_2\vec{q}_2}+1}{N^{eq}_{j_1\vec{q}_1}+1}\frac{y_{j_2\vec{q}_2}-y_{j_1\vec{q}_1}}{y_{j_1\vec{q}_1}} && (7.71)
\end{aligned}$$

This form is actually still too difficult to handle. Further specialise to the single mode relaxation time (SMRT) by setting $y_{j_2\vec{q}_2}=0$. This means that only the reference state is out of equilibrium, the other states are all in equilibrium.

$$\boxed{\frac{1}{\tau^{MD}_{j_1\vec{q}_1}} = \sum_{j_2\vec{q}_2}\frac{\pi\Gamma^{MD}}{8N}\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\frac{N^{eq}_{j_2\vec{q}_2}+1}{N^{eq}_{j_1\vec{q}_1}+1}} \tag{7.72}$$

We can make further approximations to get an order of magnitude estimate for $\tau^{MD}_{j_1\vec{q}_1}$.

$$\begin{aligned}
\frac{1}{\tau^{MD}_{j_1\vec{q}_1}} &= \sum_{j_2\vec{q}_2}\frac{\pi\Gamma^{MD}}{8N}\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\frac{N^{eq}_{j_2\vec{q}_2}+1}{N^{eq}_{j_1\vec{q}_1}+1} && (7.73)\\
&\mid \quad \sum_{\vec{q}_2}\rightarrow\int d\vec{q}_2\vec{q}_2^{\,2} \text{ using spherical coordinates in reciprocal space} && (7.74)\\
&\mid \quad \text{use Debye approximation } \omega_{j_2\vec{q}_2}=v_{j_2}\vec{q}_2 && (7.75)\\
&\approx \frac{\pi\Gamma^{MD}}{8N}\sum_{j_2}\int d\vec{q}_2\frac{\omega^3_{j_2\vec{q}_2}\omega_{j_1\vec{q}_1}}{v^2_{j_2}}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2})\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\frac{N^{eq}_{j_2\vec{q}_2}+1}{N^{eq}_{j_1\vec{q}_1}+1} && (7.76)\\
&\mid \quad \text{change } \int d\vec{q}_2 = \frac{1}{v_{j_2}}\int d\omega_{j_2\vec{q}_2} && (7.77)\\
&= \frac{\pi\Gamma^{MD}}{8N}\sum_{j_2}\int d\omega_{j_2\vec{q}_2}\frac{\omega^3_{j_2\vec{q}_2}\omega_{j_1\vec{q}_1}}{v^3_{j_2}}\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2\frac{N^{eq}_{j_2\vec{q}_2}+1}{N^{eq}_{j_1\vec{q}_1}+1}\delta(\omega_{j_1\vec{q}_1}-\omega_{j_2\vec{q}_2}) && (7.78)
\end{aligned}$$

$$
\begin{aligned}
& \mid \text{ evaluate the delta function and so } \frac{N^{eq}_{j_1\vec{q}_1}+1}{N^{eq}_{j_1\vec{q}_1}+1} = 1 && (7.79)\\
= & \frac{\pi\Gamma^{MD}}{8N}\sum_{j_2}\frac{\left(\vec{\epsilon}(j_1\vec{q}_1)\cdot\vec{\epsilon}^*(j_2\vec{q}_2)\right)^2}{v^3_{j_2}}\omega^4_{j_1\vec{q}_1} && (7.80)
\end{aligned}
$$

This is the famous Rayleigh-Klemens scattering where $\frac{1}{\tau^{MD}_{j_1\vec{q}_1}} \propto \omega^4$. This result tells us that at low temperatures, where only low energy (small ω) phonons exists, the relaxation time is large. This means point defect scattering is rare at small T.

7.3 Mass Disorder: Linear Response Treatment (Hardy Energy Current Operators)

We follow Hardy in [Hardy1963] section 4. Mass at each site is a (binomial) random variable. The force constant is that of the host. The disordered harmonic Hamiltonian is

$$
\begin{aligned}
H = & \sum_{l\alpha}\frac{1}{2}M_l\dot{u}^2_{l\alpha} + \frac{1}{2}\sum_{l\alpha l_1\alpha_1} u_{l\alpha}u_{l_1\alpha_1} && (7.81)\\
& \mid \text{ define the ion momentum } p_{l\alpha} \equiv M_l\dot{u}_{l\alpha} \\
= & \sum_{l\alpha}\frac{p^2_{l\alpha}}{2M_l} + \frac{1}{2}\sum_{l\alpha l_1\alpha_1}\Phi_{l\alpha l_1\alpha_1}u_{l\alpha}u_{l_1\alpha_1} && (7.82)\\
& \mid \text{ write } \frac{1}{2M_l} = \frac{1}{2M}\left(\frac{M}{M_l}\right) = \frac{1}{2M}\left(1-1+\frac{M}{M_l}\right) = \frac{1}{2M}\left(1-\frac{M_l-M}{M_l}\right)\\
& \mid \text{ where } M \text{ is some nonrandom mass parameter}\\
& \mid \text{ which could be } M = \bar{M} \equiv c_A M_A + c_B M_B \text{ or } M = M_A\\
& \mid \text{ but we need not specify } M \text{ for this derivation}\\
= & \sum_{l\alpha}\frac{p^2_{l\alpha}}{2M} + \frac{1}{2}\sum_{l\alpha l_1\alpha_1}\Phi_{l\alpha l_1\alpha_1}u_{l\alpha}u_{l_1\alpha_1} - \frac{1}{2M}\sum_{l\alpha}\frac{M_l-M}{M_l}p^2_{l\alpha} && (7.83)
\end{aligned}
$$

Looking at the Hamiltonian, we are going to carry out the following substitution into Hardy's energy current operator formula.

$$
\begin{aligned}
\frac{\vec{p}_{i_1}}{M_{i_1}} & \longrightarrow \frac{\vec{p}_l}{M_l} \text{ after which, use } \frac{1}{M_l} = \frac{1}{M}\left(1-\frac{M_l-M}{M_l}\right) = \frac{1}{M} - \frac{1}{M}\frac{M_l-M}{M_l} && (7.84)\\
V(\vec{r}_{i_1}) & \longrightarrow V^{\text{har}}_l \equiv \frac{1}{2}\sum_{\alpha l_1\alpha_1}\Phi_{l\alpha l_1\alpha_1}u_{l\alpha}u_{l_1\alpha_1} && (7.85)
\end{aligned}
$$

The splitting of $\frac{1}{M_l}$ allows the current to be split into the harmonic part and the mass disorder (MD) part. This is somewhat different from the usual usage of Hardy's formula because the "perturbation" enters through the kinetic term rather than the potential term!

Also, as in the harmonic current operator section, $\vec{r}$ is treated as the equilibrium position of the ion, i.e. $\vec{r} \longrightarrow \vec{R}^{eq}_{l_1}$ and $\vec{r}_{l_1}$ is the displaced position, so the displacement vector is $\vec{u}_{l_1} = \vec{r}_{l_1} - \vec{R}^{eq}_{l_1}$ and $\vec{r}_{l_1} - \vec{r}_{l_2} = \vec{u}_{l_1} - \vec{u}_{l_2} + \vec{R}^{eq}_{l_1} - \vec{R}^{eq}_{l_2}$.

Hardy's current operator for mass disorder now looks like,

$$
\begin{aligned}
\vec{J} &= \frac{1}{2V}\left\{\sum_l \frac{\vec{p}_l}{M_l}\left(\frac{\vec{p}_l^{\,2}}{2M_l}+V_l^{\text{har}}\right)+\sum_{l_1l_2}(\vec{u}_{l_1}-\vec{u}_{l_2}+\vec{R}_{l_1}^{eq}-\vec{R}_{l_2}^{eq})\frac{1}{i\hbar}\left[\frac{\vec{p}_{l_1}^{\,2}}{2M_{l_1}},V_{l_2}^{\text{har}}\right]_-\right\}+\text{h.c.} \qquad (7.86)\\
&= \frac{1}{2V}\left\{\sum_l \frac{1}{M_l}\frac{1}{2M_l}\vec{p}_l\vec{p}_l^{\,2}+\frac{1}{M_l}\vec{p}_lV_l^{\text{har}}+\sum_{l_1l_2}(\vec{u}_{l_1}-\vec{u}_{l_2}+\vec{R}_{l_1}^{eq}-\vec{R}_{l_2}^{eq})\frac{1}{i\hbar}\frac{1}{2M_{l_1}}\left[\vec{p}_{l_1}^{\,2},V_{l_2}^{\text{har}}\right]_-\right\}+\text{h.c.}\\
&\quad | \quad \text{use } \frac{1}{M_l}=\frac{1}{M}-\frac{1}{M}\frac{M_l-M}{M_l}\\
&\quad | \quad \text{use } \frac{1}{M_l}\frac{1}{2M_l}=\left(\frac{1}{M}-\frac{1}{M}\frac{M_l-M}{M_l}\right)\left(\frac{1}{2M}-\frac{1}{2M}\frac{M_l-M}{M_l}\right)=\frac{1}{M}\frac{1}{2M}-\frac{M_l-M}{M^2}\frac{\frac{1}{2}(M_l+M)}{M_l^2}\\
&= \frac{1}{2V}\left\{\sum_l \frac{1}{M}\frac{1}{2M}\vec{p}_l\vec{p}_l^{\,2}+\frac{1}{M}\vec{p}_lV_l^{\text{har}}+\sum_{l_1l_2}(\vec{u}_{l_1}-\vec{u}_{l_2}+\vec{R}_{l_1}^{eq}-\vec{R}_{l_2}^{eq})\frac{1}{i\hbar}\frac{1}{2M}\left[\vec{p}_{l_1}^{\,2},V_{l_2}^{\text{har}}\right]_-\right\}+\text{h.c.}\\
&\quad -\frac{1}{2V}\left\{\sum_l \frac{M_l-M}{M^2}\frac{\frac{1}{2}(M_l+M)}{M_l^2}\vec{p}_l\vec{p}_l^{\,2}+\frac{1}{M}\frac{M_l-M}{M_l}\vec{p}_lV_l^{\text{har}}\right.\\
&\quad \left.+\sum_{l_1l_2}(\vec{u}_{l_1}-\vec{u}_{l_2}+\vec{R}_{l_1}^{eq}-\vec{R}_{l_2}^{eq})\frac{1}{i\hbar}\frac{1}{2M}\frac{M_l-M}{M_l}\left[\vec{p}_{l_1}^{\,2},V_{l_2}^{\text{har}}\right]_-\right\}+\text{h.c.} \qquad (7.87)
\end{aligned}
$$

The first line is simply $\vec{J}^{\,\text{har}}$ which was treated in Chapter 1. The second line is Hardy's equation (4.17) in [Hardy1963] which is the mass disorder contribution to energy current.

$$
\boxed{
\begin{aligned}
\vec{J}^{\,\text{MD}} &= -\frac{1}{2V}\left\{\sum_l \frac{M_l-M}{M^2}\frac{\frac{1}{2}(M_l+M)}{M_l^2}\vec{p}_l\vec{p}_l^{\,2}+\frac{1}{M}\frac{M_l-M}{M_l}\vec{p}_lV_l^{\text{har}}\right. \qquad (7.88)\\
&\quad \left.+\frac{1}{2M}\sum_{l_1l_2}(\vec{u}_{l_1}-\vec{u}_{l_2}+\vec{R}_{l_1}^{eq}-\vec{R}_{l_2}^{eq})\frac{M_l-M}{M_l}\frac{1}{i\hbar}\left[\vec{p}_{l_1}^{\,2},V_{l_2}^{\text{har}}\right]_-\right\}+\text{h.c.} \qquad (7.89)
\end{aligned}
}
$$

We do not proceed further as this is not the main approach of the thesis. The main aim is only to write an (operator) expression of current in terms of phonon operators. The subsequent calculation of thermal conductivity using this current operator will follow the receipe mentioned in Chapter 1.

Finally, we just want to note that for force constant disorder, the "perturbation potential" is of the form,

$$
V_l^{\text{FC}} \equiv \frac{1}{2}\sum_{\alpha l_1\alpha_1}\Phi^{\text{FC}}_{l\alpha l_1\alpha_1}u_{l\alpha}u_{l_1\alpha_1} \qquad (7.90)
$$

which means its contribution to energy current is similar to V_l^{har} with a different "coupling constant". So its calculation follows that of V_l^{har} in Chapter 1.

7.4 Mass Disorder : Coherent Potential Mean Field Approximation (CPA)

[Literature] The first paper (on phonons) is [Taylor1967]. Three comprehensive review articles are [Yonezawa1973], [Elliott1974] and [Matsubara1982]. A very comprehensive numerical work is found in [Dean1972]. Our published work on the application of CPA vertex corrections to thermal transport is [NiMLL2011].

7.4.1 3 Ways to Derive CPA

The coherent potential approximation (CPA) is the best method in handling diagonal disorder. Electrons (in tight binding form), phonons, excitons and magnons have similar forms of disordered Hamiltonian, so CPA applies to all these systems. Here we use it on phonons, particularly on phonon transport. We show 3 derivations in great detail. The effective medium derivation gives the complete CPA theory for the calculation of (configurationally averaged) 1-particle Green's function and 2-particle Transmission coefficient. The diagrammatic derivation shows that in CPA, almost all possible diagrams are summed, justifying its position as the best diagonal disorder theory. The locator derivation is given to prepare for the generalization to theories with both mass and force constant disorder. The first 2 derivations also prepare the reader for the generalization in the subsequent sections.

7.4.1.1 Effective Medium Derivation

7.4.1.1.1 [Configurational Average of the 1-Particle Green's function] We essentially follow this [Velicky1969] in this whole section. As standard in this chapter, we work at the level of harmonic approximation and the mass disordered solid is a monoatomic lattice [4]. The Hamiltonian is,

$$H = \frac{1}{2}\sum_{l\alpha} M_l' \dot{u}_{l\alpha}^2 + \frac{1}{2}\sum_{ll'}\sum_{\alpha\alpha'} \Phi_{l\alpha l'\alpha'} u_{l\alpha} u_{l'\alpha'} \tag{7.91}$$

where M_l' is the mass random variable at site l.

We define the time-ordered displacement-displacement thermal Green's function with the harmonic (random) Hamiltonian as the 1-particle quantity to calculate.

$$D_{l\alpha l'\alpha'}(t) \quad = \quad -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}e^{-\beta H}}\mathrm{Tr}\left(e^{-\beta H} T\left(u_{l\alpha}(t) u_{l'\alpha'}(0)\right)\right) \tag{7.92}$$

where $\beta = \frac{1}{k_B T}$ and T is the (equilibrium) temperature of the disordered solid. The aim of this section is to calculate the configuration averaged Green's function in an approximate way using CPA. We start with the equation of motion

$$-M_l' \frac{d^2}{dt^2} D_{l\alpha l'\alpha'}(t) \quad = \quad 2\pi\delta(t)\delta_{\alpha\alpha'}\delta_{ll'} + \sum_{l_1\alpha_1} \Phi_{l\alpha l_1\alpha_1} D_{l_1\alpha_1 l'\alpha'}(t) \tag{7.93}$$

Fourier transform to frequency domain,

$$\sum_{l_1\alpha_1}\left(M_l'\omega^2\delta_{\alpha\alpha_1}\delta_{ll_1} - \Phi_{l\alpha l_1\alpha_1}\right) D_{l_1\alpha_1 l'\alpha'}(\omega) \quad = \quad \delta_{ll'}\delta_{\alpha\alpha'} \tag{7.94}$$

[4] We specialise to the monatomic case for the sake of a less complicated notation. There should be no loss in generality.

Writing in (Cartesian) matrix form and we perform symbolic manipulations.

$$\begin{aligned}
D_{ll'}(\omega) &= \left(M'_l\omega^2\mathbb{I} - \Phi_{ll'}\right)^{-1} && (7.95)\\
&\mid \quad \text{seperate out the host and the impurity part}\\
&= \left(\left(M_A\omega^2\mathbb{I} - \Phi_{ll'}\right) - M_l\omega^2\mathbb{I}\right)^{-1} && (7.96)\\
&\mid \quad \text{where the inner bracket is the inverse Green's function of the host, } D^{(A)-1}\\
&= \left(D^{(A)-1}_{ll'} - \tilde{V}_{ll'}\right)^{-1} && (7.97)
\end{aligned}$$

where the random variable M_l takes on the values

$$M_l = \begin{cases} 0 & l = \text{atom A} \\ M_A - M_B & l = \text{atom B} \end{cases} \tag{7.98}$$

Manipulate to get a Dyson equation.

$$D = D^{(A)} + D^{(A)}\tilde{V}D \tag{7.99}$$

We introduce an effective medium mean field $\Sigma^{\mathrm{CPA}}(\omega)$ and add and subtract it to the Green's function.

$$\begin{aligned}
D_{ll'}(\omega) &= \left(M^A\omega^2\mathbb{I} - \Phi_{ll'} - \Sigma^{\mathrm{CPA}}(\omega) - M_l\omega^2\mathbb{I} + \Sigma^{\mathrm{CPA}}(\omega)\right)^{-1} && (7.100)\\
&\mid \quad \text{define } D^{\mathrm{CPA}}_{ll'}(\omega) \equiv M^A\omega^2\mathbb{I} - \Phi_{ll'} - \Sigma^{\mathrm{CPA}}(\omega)\\
&\mid \quad \text{define } -V_l \equiv -M_l\omega^2\mathbb{I} + \Sigma^{\mathrm{CPA}}(\omega)\\
&= \left(D^{\mathrm{CPA}}_{ll'}(\omega) - V\right)^{-1} && (7.101)
\end{aligned}$$

Again we manipulate it into a Dyson equation and then into a scattering equation,

$$\begin{aligned}
D &= D^{\mathrm{CPA}} + D^{\mathrm{CPA}}VD && (7.102)\\
D_{ll'}(\omega) &= D^{\mathrm{CPA}}_{ll'}(\omega) + \sum_{l_1} D^{\mathrm{CPA}}_{ll_1}(\omega)V_{l_1}D_{l_1l'}(\omega) && (7.103)\\
&\mid \quad \text{iterate it into a scattering equation}\\
&= D^{\mathrm{CPA}} + D^{\mathrm{CPA}}VD^{\mathrm{CPA}} + D^{\mathrm{CPA}}VD^{\mathrm{CPA}}VD^{\mathrm{CPA}} + \cdots && (7.104)\\
&= D^{\mathrm{CPA}} + D^{\mathrm{CPA}}V\left(D^{\mathrm{CPA}} + D^{\mathrm{CPA}}VD^{\mathrm{CPA}} + \cdots\right) && (7.105)\\
&\mid \quad \text{sum the infinite geometric progression}\\
&= D^{\mathrm{CPA}} + D^{\mathrm{CPA}}V\frac{D^{\mathrm{CPA}}}{1 - VD^{\mathrm{CPA}}} && (7.106)\\
&\mid \quad \text{define the scattering } T\text{-matrix, } T \equiv \frac{V}{1 - VD^{\mathrm{CPA}}}\\
&= D^{\mathrm{CPA}} + D^{\mathrm{CPA}}TD^{\mathrm{CPA}} && (7.107)
\end{aligned}$$

Note that V is diagonal in l so we can take the inverse on either side of D^{CPA}. Now we take the configuration average represented by the notation $\langle\cdots\rangle_c$. All the random variables are only in T, and so we get,

$$\langle D\rangle_c = D^{\mathrm{CPA}} + D^{\mathrm{CPA}}\langle T\rangle_c D^{\mathrm{CPA}} \tag{7.108}$$

We shall choose a physical condition to fix Σ^{CPA}. It turns out that by doing this, we actually get a self consistent condition as well. The physical condition is that we assume the mean field results in an effective medium that has no scattering on average, i.e.

$$\langle T\rangle_c \stackrel{!}{=} 0 \tag{7.109}$$

This gives a simple approximation for the (exact) configuration averaged Green's function.

$$\langle D\rangle_c = D^{\mathrm{CPA}} \tag{7.110}$$

However, the condition $\langle T\rangle_c = 0$ is still not tractable. We need further approximations. We start by defining the single site t-matrix.

$$t_l \equiv \frac{V_l}{1 - V_l D^{\mathrm{CPA}}} \quad = \quad \frac{V_l}{1 - V_l D_{ll}^{\mathrm{CPA}}(\omega)} \tag{7.111}$$

since D^{CPA} multiplying the diagonal V_l would only involve the diagonal elements of D^{CPA}.

We write an identity

$$V_l \quad = \quad t_l - t_l D_{ll}^{\mathrm{CPA}}(\omega) V_l \tag{7.112}$$

which is substituted into the Dyson equation and iterated.

$$\begin{aligned} D_{ll'}(\omega) &= D_{ll'}^{\mathrm{CPA}}(\omega) + \sum_{l_2} D_{ll_2}^{\mathrm{CPA}}(\omega)\left(t_{l_2} - t_{l_2} D_{l_2 l_2}^{\mathrm{CPA}}(\omega) V_{l_2}\right) D_{l_2 l'}^{\mathrm{CPA}}(\omega) && (7.113)\\ &\mid \quad \text{iterate } D \text{ and } V_l \\ &= D_{ll'}^{\mathrm{CPA}} + \sum_{l_1} D_{ll_1}^{\mathrm{CPA}} t_{l_1} D_{l_1 l'}^{\mathrm{CPA}} + \sum_{l_1, l_2 (\neq l_1)} D_{ll_1}^{\mathrm{CPA}} t_{l_1} D_{l_1 l_2}^{\mathrm{CPA}} t_{l_2} D_{l_2 l'}^{\mathrm{CPA}} + \cdots && (7.114)\end{aligned}$$

When we compare with the scattering equation

$$D = D^{\mathrm{CPA}} + D^{\mathrm{CPA}} T D^{\mathrm{CPA}} \tag{7.115}$$

we get,

$$\begin{aligned} T &= \sum_{l_1} t_{l_1} + \sum_{l_1, l_2(\neq l_1)} t_{l_1} D_{l_1 l_2}^{\mathrm{CPA}} t_{l_2} + \cdots && (7.116)\\ &\mid \quad \text{take configuration average} \\ \langle T\rangle_c &= \sum_{l_1} \langle t_{l_1}\rangle_c + \sum_{l_1, l_2(\neq l_1)} \langle t_{l_1} D_{l_1 l_2}^{\mathrm{CPA}} t_{l_2}\rangle_c + \cdots && (7.117)\\ &\mid \quad \text{assume sites to be independent and decouple the averages} \\ &\mid \quad \text{this is known as the “Single Site Approximation” (SSA)} \\ &\approx \sum_{l_1} \langle t_{l_1}\rangle_c + \sum_{l_1, l_2(\neq l_1)} \langle t_{l_1}\rangle_c D_{l_1 l_2}^{\mathrm{CPA}} \langle t_{l_2}\rangle_c + \cdots && (7.118)\end{aligned}$$

From the CPA condition, $\langle T\rangle_c = 0$, we can now further approximate (reasonably) $\langle t_l\rangle_c = 0$. This single site average is simple to evaluate: $\langle t_l\rangle_c = c_A t_A + c_B t_B$.

$$\begin{aligned} \langle t_l\rangle_c = \left\langle \frac{V_l}{1 - V_l D_{ll}^{\mathrm{CPA}}(\omega)} \right\rangle &= 0 \\ \text{recall } -V_l = -M_l\omega^2\mathbb{I} + \Sigma^{\mathrm{CPA}}(\omega), \text{ so } V_A = 0 - \Sigma^{\mathrm{CPA}} \text{ and } V_B = (M_A - M_B)\omega^2\mathbb{I} - \Sigma^{\mathrm{CPA}} &\mid \end{aligned}$$

$$c_A \frac{-\Sigma^{\text{CPA}}}{1+\Sigma^{\text{CPA}} D^{\text{CPA}}} + c_B \frac{(M_A - M_B)\omega^2 - \Sigma^{\text{CPA}}}{1 - \left((M_A - M_B)\omega^2 - \Sigma^{\text{CPA}}\right) D^{\text{CPA}}} = 0$$

The set of self consistent CPA equations is,

$$\boxed{\begin{aligned} 0 &= c_A \frac{-\Sigma^{\text{CPA}}}{1+\Sigma^{\text{CPA}} D^{\text{CPA}}} + c_B \frac{(M_A - M_B)\omega^2 - \Sigma^{\text{CPA}}}{1 - \left((M_A - M_B)\omega^2 - \Sigma^{\text{CPA}}\right) D^{\text{CPA}}} \\ D^{\text{CPA}} &= \left(M_A\omega^2 - \Phi_{ll'} - \Sigma^{\text{CPA}}(\omega)\right)^{-1} \end{aligned}} \quad \begin{aligned} (7.119) \\ (7.120) \end{aligned}$$

Σ^{CPA} and D^{CPA} are solved self consistently and $\langle D \rangle_c = D^{\text{CPA}}$ under CPA gives the required configuration averaged 1-particle Green's function.

7.4.1.1.2 [CPA → Virtual Crystal Approximation (VCA) limit] Take the CPA equation and write as it a single fraction. (We drop the CPA superscript in the first line to fit it to the page.)

$$\frac{-c_A\Sigma(1-(M_A-M_B)\omega^2 D + \Sigma D) + (c_B(M_A-M_B)\omega^2 - c_B\Sigma)(1+\Sigma D)}{(1+\Sigma D)(1-(M_A-M_B)\omega^2 D + \Sigma D)} = 0 \quad (7.121)$$

$$\begin{aligned} -c_A\Sigma^{\text{CPA}} + c_A(M_A-M_B)\omega^2\Sigma^{\text{CPA}}D^{\text{CPA}} - c_A{\Sigma^{\text{CPA}}}^2 D^{\text{CPA}} & \\ +c_B(M_A-M_B)\omega^2 - c_B\Sigma^{\text{CPA}} + c_B(M_A-M_B)\omega^2\Sigma^{\text{CPA}}D^{\text{CPA}} - c_B{\Sigma^{\text{CPA}}}^2 D^{\text{CPA}} &= 0 \quad (7.122) \\ \text{recall that } c_A + c_B = 1 & \quad | \\ -\Sigma^{\text{CPA}} + (M_A-M_B)\omega^2\Sigma^{\text{CPA}}D^{\text{CPA}} - {\Sigma^{\text{CPA}}}^2 D^{\text{CPA}} + c_B(M_A-M_B)\omega^2 &= 0 \quad (7.123) \end{aligned}$$

Now we invoke the physics of VCA, which states that the isotopes are very similar to the host atoms thus implying $M_A - M_B \to$ small and the Green's function $D^{\text{CPA}} = (M_A\omega^2 - \Phi_{ll'} - \Sigma^{\text{CPA}})^{-1}$ is similar to the host's Green's function, i.e. $D^{\text{CPA}} \approx D^{(A)}$, so $\Sigma^{\text{CPA}} \to$ small. We then only retain the "largest" terms, which are the first and last terms at the LHS of the above equation.

$$\begin{aligned} -\Sigma^{\text{CPA}} + c_B(M_A-M_B)\omega^2 &\approx 0 & (7.124) \\ \Sigma^{\text{CPA}} &= c_B(M_A-M_B)\omega^2 & (7.125) \\ \text{so,} \quad D^{\text{CPA}} &\approx \left(M_A\omega^2 - \Phi_{ll'} - c_B(M_A-M_B)\omega^2\right)^{-1} & (7.126) \\ &| \quad \text{use } 1 - c_B = c_A & \\ &= \left((c_A M_A + c_B M_B)\omega^2 - \Phi_{ll'}\right)^{-1} & (7.127) \\ &| \quad \text{define average mass } \bar{M} \equiv c_A M_A + c_B M_B & \\ &= \left(\bar{M}\omega^2 - \Phi_{ll'}\right)^{-1} & (7.128) \\ &\equiv D^{\text{VCA}} & (7.129) \end{aligned}$$

VCA is mentioned in the diagrammatic derivation and the reader can check that the expressions are exactly the same.

7.4.1.1.3 [Configurational Average of a 2-Particle Quantity (Vertex Corrections)]* In general, the calculation of transport coefficients require 2-particle functions of the form $D\Gamma D\Gamma$ to be evaluated [5]. For disordered systems, we need the configuration average of such quantities i.e. $\langle D\Gamma D\Gamma \rangle_c$. Such averages are calculated in terms of the averaged Green's functions, $\langle D \rangle_c$, and we get corrections between the 2 Green's functions which are called (impurity) vertex corrections. We will use the Caroli

[5] An electronic version can be seen in [Ke2008].

formula as the example in calculating an approximate configuration averaged 2-particle quantity. The approximation is done in the same spirit as CPA. (Recall that the superscripts (R) and (L) refers to the right lead and the left lead respectively. The superscripts R and A denotes a retarded quantity and an advanced quantity respectively.)

$$\begin{aligned}
\langle \mathcal{T} \rangle_c &= \mathrm{Tr}\langle D^R \Gamma^{(R)} D^A \Gamma^{(L)} \rangle_c && (7.130)\\
&\mid \text{ recall } D = D^{\mathrm{CPA}} + D^{\mathrm{CPA}} T D^{\mathrm{CPA}} \text{ so under CPA, } \langle D \rangle_c = D^{\mathrm{CPA}}, \\
&\mid \text{ we can write } D = \langle D \rangle_c + \langle D \rangle_c T \langle D \rangle_c \text{ which we substitute into the Caroli formula} \\
&= \mathrm{Tr}\left\langle \left(\langle D^R \rangle_c + \langle D^R \rangle_c T^R \langle D^R \rangle_c\right) \Gamma^{(R)} \left(\langle D^A \rangle_c + \langle D^A \rangle_c T^A \langle D^A \rangle_c\right) \Gamma^{(L)} \right\rangle && (7.131)\\
&\mid \text{ expand and 2 terms vanish due to } \langle T^A \rangle_c = 0 = \langle T^R \rangle_c \\
&= \mathrm{Tr}\left(\langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c \Gamma^{(L)}\right) + \mathrm{Tr}\left(\langle D^R \rangle_c \left\langle T^R \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c T^A \right\rangle_c \langle D^A \rangle_c \Gamma^{(L)}\right) && (7.132)\\
&\mid \text{ define } \Omega \equiv \left\langle T^R \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c T^A \right\rangle_c \\
&= \mathrm{Tr}\left(\langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c \Gamma^{(L)}\right) + \mathrm{Tr}\left(\langle D^R \rangle_c \Omega \langle D^A \rangle_c \Gamma^{(L)}\right) && (7.133)
\end{aligned}$$

Although we have achieved some simplification with the CPA condition and it is now reduced to solving $\Omega \equiv \left\langle T^R \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c T^A \right\rangle_c$, it is still difficult to evaluate the average. Thus we will further expand Ω and insert the CPA condition to further simplify the problem.

We start by rewriting the full T-matrix.

$$\begin{aligned}
T &= \frac{V}{1 - V D^{\mathrm{CPA}}} && (7.134)\\
&\mid \text{ numerator is diagonal so we can write on left or right} \\
&= \left(1 - V D^{\mathrm{CPA}}\right)^{-1} V && (7.135)\\
&= V + V D^{\mathrm{CPA}} T && (7.136)\\
&= \sum_l V_l \left(1 + D^{\mathrm{CPA}} T\right) && (7.137)\\
&\mid \text{ write } D^{\mathrm{CPA}} = \langle D \rangle_c \\
&= \sum_i V_l \left(1 + \langle D \rangle_c T\right) && (7.138)\\
&\equiv \sum_l Q_l && (7.139)
\end{aligned}$$

So,

$$\begin{aligned}
Q_l &= V_l \left(1 + \langle D \rangle_c T\right) && (7.140)\\
&= V_l \left(1 + \langle D \rangle_c \sum_{l_1} Q_{l_1}\right) && (7.141)\\
&= V_l \left(1 + \langle D \rangle_c Q_l + \langle D \rangle_c \sum_{l_1 (\neq l)} Q_{l_1}\right) && (7.142)\\
(1 - V_l \langle D \rangle_c) Q_l &= V_l \left(1 + \langle D \rangle_c \sum_{l_1 (\neq l)} Q_{l_1}\right) && (7.143)
\end{aligned}$$

$$
\begin{aligned}
Q_l &= (1 - V_l \langle D \rangle_c)^{-1} V_l \left(1 + \langle D \rangle_c \sum_{l_1 (\neq l)} Q_{l_1} \right) && (7.144)\\
&\mid \quad \text{recall the definition of } t_l \\
&= t_l \left(1 + \langle D \rangle_c \sum_{l_1 (\neq l)} Q_{l_1} \right) && (7.145)
\end{aligned}
$$

Take transpose on both sides of the equation and since Q_l is diagonal, $Q^T = Q$ and the averaged Green's function has (site) translational symmetry, so $\langle D \rangle_c^T = \langle D \rangle_c$. We get

$$
Q_l = \left(1 + \sum_{l_1 (\neq l)} Q_{l_1} \langle D \rangle_c \right) t_l \qquad (7.146)
$$

And insert it into Ω.

$$
\begin{aligned}
\Omega &= \left\langle T^R \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c T^A \right\rangle && (7.147)\\
&= \sum_{l_1 l_2} \left\langle Q^R_{l_1} \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c Q^A_{l_2} \right\rangle && (7.148)\\
&= \sum_{l_1 l_2} \left\langle t^R_{l_1} \left(1 + \langle D^R \rangle_c \sum_{l_3 (\neq l_1)} Q^R_{l_3} \right) \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c \left(1 + \sum_{l_4 (\neq l_2)} Q^A_{l_4} \langle D^A \rangle_c \right) t^A_{l_2} \right\rangle && (7.149)
\end{aligned}
$$

We bring in the SSA

$$
\left\langle t^R_{l_1} \cdots t^A_{l_2} \right\rangle_c \overset{\text{SSA}}{\approx} \left\langle t^R_{l_1} \right\rangle_c \langle \cdots \rangle_c \left\langle t^A_{l_2} \right\rangle_c \overset{\text{CPA}}{=} 0 \qquad (7.150)
$$

And we expect $\left\langle t^R_{l_1} t^A_{l_1} \right\rangle_c$ to be non-zero and we keep only terms where $l_1 = l_2$ and denote the approximate Ω by Ω^{CPA}.

$$
\begin{aligned}
\Omega^{\text{CPA}} &= \sum_{l_1} \left\langle t^R_{l_1} \left\langle \left(1 + \langle D^R \rangle_c \sum_{l_2 (\neq l_1)} Q^R_{l_2} \right) \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c \left(1 + \sum_{l_3 (\neq l_1)} Q^A_{l_3} \langle D^A \rangle_c \right) \right\rangle_c t^A_{l_1} \right\rangle_c && (7.151)\\
&\mid \quad \text{note, } Q_l = t_l \left(1 + \langle D^R \rangle_c \sum_{l_1 (\neq l)} Q_l \right) \overset{\text{SSA}}{\Rightarrow} \langle Q_l \rangle_c = \langle t_l \rangle_c \left(1 + \langle D^R \rangle_c \sum_{l_1 (\neq l)} \langle Q_{l_1} \rangle_c \right) \overset{\text{CPA}}{=} 0 \\
&\mid \quad \text{then we expand the average in the middle} \\
&\mid \quad \langle \cdots \rangle_c = \left\langle \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c + \langle D^R \rangle_c \sum_{l_2 (\neq l_1)} Q^R_{l_2} \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c \right. \\
&\mid \quad \left. + \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c \sum_{l_3 (\neq l_1)} Q^A_{l_3} \langle D^A \rangle_c + \langle D^R \rangle_c \sum_{l_2 (\neq l_1)} Q^R_{l_2} \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c \sum_{l_3 (\neq l_1)} Q^A_{l_3} \langle D^A \rangle_c \right\rangle_c \\
&\mid \quad \text{middle 2 terms vanish because of } \langle Q_l \rangle_c \\
&= \sum_{l_1} \left\langle t^R_{l_1} \langle D^R \rangle_c \Gamma^{(R)} \langle D^A \rangle_c t^A_{l_1} \right\rangle_c
\end{aligned}
$$

$$+\left\langle t^R_{l_1}\langle D^R\rangle_c \sum_{l_2(\neq l_1)}\sum_{l_3(\neq l_1)} \left\langle Q^R_{l_2}\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c Q^A_{l_3}\right\rangle_c \langle D^A\rangle_c t^A_{l_1}\right\rangle_c \tag{7.152}$$

| recall $\Omega = \sum_{l_1 l_2}\left\langle Q^R_{l_1}\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c Q^A_{l_2}\right\rangle_c$ and Ω^{CPA} is the site diagonal version

| so, $\Omega^{\text{CPA}} = \sum_{l_1}\left\langle Q^R_{l_1}\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c Q^A_{l_1}\right\rangle_c \equiv \sum_{l_1}\Omega^{\text{CPA}}_{l_1}$

| we approximate by keeping the site diagonal part of the 2nd term

| $\sum_{l_2(\neq l_1)}\sum_{l_3(\neq l_1)}\langle Q^R_{l_2}\cdots Q^A_{l_3}\rangle_c \approx \sum_{l_2(\neq l_1)}\langle Q^R_{l_2}\cdots Q^A_{l_2}\rangle_c = \sum_{l_2(\neq l_1)}\Omega^{\text{CPA}}_{l_2}$

$$= \sum_{l_1}\left\langle t^R_{l_1}\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c t^A_{l_1}\right\rangle_c + \left\langle t^R_{l_1}\langle D^R\rangle_c \sum_{l_2(\neq l_1)}\Omega^{\text{CPA}}_{l_2}\langle D^A\rangle_c t^A_{l_1}\right\rangle_c \tag{7.153}$$

$$\Omega^{\text{CPA}}_{l_1} = \left\langle t^R_{l_1}\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c t^A_{l_1}\right\rangle_c + \left\langle t^R_{l_1}\langle D^R\rangle_c \sum_{l_2(\neq l_1)}\Omega^{\text{CPA}}_{l_2}\langle D^A\rangle_c t^A_{l_1}\right\rangle_c \tag{7.154}$$

Finally we need to solve for Ω^{CPA} explicitly to complete the calculation of the configuration averaged transmission coefficient. We will take a linear algebra approach.

Note that since t^R and t^A are (site) disgonal, the contribution of the matrix, $\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c$, is only from its diagonal, which we denote by

$$\xi_{ll} \equiv \left[\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c\right]_{ll} \tag{7.155}$$

So,

$$\Omega^{\text{CPA}}_{l_1} = \langle t^R_{l_1}\xi_{l_1l_1}t^A_{l_1}\rangle_c + \left\langle t^R_{l_1}\left(\langle D^R\rangle_c \sum_{l_2(\neq l_1)}\Omega^{\text{CPA}}_{l_2}\langle D^A\rangle_c\right)_{l_1l_1} t^A_{l_1}\right\rangle_c \tag{7.156}$$

| recall a single site average is explicitly $\langle V_l\rangle_c = c_A V_A + c_B V_B$

$$= \sum_m c_m t^R_{l_1}\xi_{l_1l_1}t^A_{l_1} + \sum_m c_m t^R_{l_1}\left(\langle D^R\rangle_c\sum_{l_2}\Omega^{\text{CPA}}_{l_2}(1-\delta_{l_2l_1})\langle D^A\rangle_c\right)_{l_1l_1} t^A_{l_1} \tag{7.157}$$

| define $w_{l_1} \equiv \sum_m c_m t^R_{l_1}t^A_{l_1}$

$$= w_{l_1}\xi_{l_1l_1} + \sum_{l_2} w_{l_1}\langle D^R\rangle_{c,l_1l_2}(1-\delta_{l_2l_1})\langle D^A\rangle_{c,l_2l_1}\Omega^{\text{CPA}}_{l_2} \tag{7.158}$$

| define $\chi_{l_1l_2} \equiv \langle D^R\rangle_{c,l_1l_2}(1-\delta_{l_2l_1})\langle D^A\rangle_{c,l_2l_1}$

$$= w_{l_1}\xi_{l_1l_1} + \sum_{l_2} w_{l_1}\chi_{l_1l_2}\Omega^{\text{CPA}}_{l_2} \tag{7.159}$$

We symbolically solve for Ω^{CPA}.

$$\Omega^{\text{CPA}} = \xi w + w\chi\Omega^{\text{CPA}} \tag{7.160}$$

$$(1-w\chi)\,\Omega^{\text{CPA}} = \xi w \tag{7.161}$$

$$\Omega^{\text{CPA}} = (1-w\chi)^{-1}\,\xi w \tag{7.162}$$

$$
\begin{aligned}
& \quad | \quad \xi w \text{ commute as they are (site) diagonal} \\
&= \left(w^{-1}-\chi\right)^{-1}\xi && (7.163)\\
\Omega^{\mathrm{CPA}}_{l_1} &= \sum_{l_2}\left[\left(w^{-1}-\chi\right)^{-1}\right]_{l_1 l_2}\xi_{l_2 l_2} && (7.164)\\
&= \sum_{l_2}\left[\left(w^{-1}-\chi\right)^{-1}\right]_{l_1 l_2}\left[\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c\right]_{l_2 l_2} && (7.165)
\end{aligned}
$$

So finally, the 2-particle quantity can be written explicitly with vertex corrections which is approximated in the spirit of CPA.

$$
\begin{aligned}
\langle\mathcal{T}\rangle_c &= \mathrm{Tr}\left(\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c\Gamma^{(L)}\right)+\mathrm{Tr}\left(\langle D^R\rangle_c\Omega\langle D^A\rangle_c\Gamma^{(L)}\right) && (7.166)\\
&\approx \mathrm{Tr}\left(\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c\Gamma^{(L)}\right)+\mathrm{Tr}\left(\langle D^R\rangle_c\Omega^{\mathrm{CPA}}\langle D^A\rangle_c\Gamma^{(L)}\right) && (7.167)\\
&= \mathrm{Tr}\left(\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c\Gamma^{(L)}\right)+\mathrm{Tr}\left(\langle D^R\rangle_c\left(w^{-1}-\chi\right)^{-1}\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c\langle D^A\rangle_c\Gamma^{(L)}\right) && (7.168)\\
& \quad | \quad \text{use trace cyclicity on the second term}\\
&= \mathrm{Tr}\left(\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c\Gamma^{(L)}\right)+\mathrm{Tr}\left[\langle D^A\rangle_c\Gamma^{(L)}\langle D^R\rangle_c\left(w^{-1}-\chi\right)^{-1}\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c\right] && (7.169)
\end{aligned}
$$

$$
\boxed{\langle\mathcal{T}\rangle_c = \mathrm{Tr}\left(\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c\Gamma^{(L)}\right)+\mathrm{Tr}\left[\langle D^A\rangle_c\Gamma^{(L)}\langle D^R\rangle_c\left(w^{-1}-\chi\right)^{-1}\langle D^R\rangle_c\Gamma^{(R)}\langle D^A\rangle_c\right]} \qquad (7.170)
$$

[Contribution:] Here I will briefly state what this contribution is about. Previously, CPA vertex corrections for linear response theory has been calculated and is well known. This contribution simply carries out a very similar derivation for the Caroli formula (or Landauer transmission formula). The physical implications in this case is different: high concentrations of mass disorder in a ballistic system is being investigated in contrast to the literature where (low) concentration is a perturbation parameter for disordered ballistic systems. In [NiMLL2011], it is shown that high mass disorder has a gradual effect on suppressing ballistic transport though it does not really result in diffusive transport. This contribution is also a step towards calculating vertex corrections for high concentrations of mass & force constant disorder which is more realistic.

7.4.1.1.4 [CPA is a Φ-Derivable Conserving Approximation] Recall Baym's conserving condition (written in site indices here)

$$
\frac{\delta\Sigma_{l_1 l_2}(\omega_1)}{\delta D_{l_3 l_4}(\omega_2)} = \frac{\delta\Sigma_{l_3 l_4}(\omega_1)}{\delta D_{l_1 l_2}(\omega_1)} \qquad (7.171)
$$

In CPA, we have a (site) diagonal theory so we have (almost) trivial equality.

$$
\frac{\delta\Sigma^{\mathrm{CPA}}_{l_1 l_1}(\omega_1)}{\delta D^{\mathrm{CPA}}_{l_3 l_3}(\omega_2)} = \frac{\delta\Sigma^{\mathrm{CPA}}_{l_3 l_3}(\omega_1)}{\delta D^{\mathrm{CPA}}_{l_1 l_1}(\omega_2)} \qquad (7.172)
$$

Now we will check this equality explicitly. First we rewrite the CPA equation for easier functional differentiation. We start with the expression,

$$
\begin{aligned}
-\Sigma^{\mathrm{CPA}}+(M_A-M_B)\omega^2\Sigma^{\mathrm{CPA}}D_{\mathrm{CPA}}-\Sigma^{\mathrm{CPA}^2}D^{\mathrm{CPA}}+c_B(M_A-M_B)\omega^2 &= 0 && (7.173)\\
-\Sigma^{\mathrm{CPA}}\left(1-(M_A-M_B)\omega^2D^{\mathrm{CPA}}+\Sigma^{\mathrm{CPA}}D^{\mathrm{CPA}}\right)+c_B(M_A-M_B)\omega^2 &= 0 && (7.174)\\
\Sigma^{\mathrm{CPA}}_{l_1 l_1}(\omega_1)\left(1-(M_A-M_B)\omega_1^2D^{\mathrm{CPA}}_{l_1 l_1}(\omega_1)+\Sigma^{\mathrm{CPA}}_{l_1 l_1}(\omega_1)D^{\mathrm{CPA}}_{l_1 l_1}(\omega_1)\right) &= c_B(M_A-M_B)\omega_1^2
\end{aligned}
$$

Note that there is no sum over sites because all matrices here are diagonal. Differentiate on both sides with $\delta/\delta D^{\rm CPA}_{l_3l_3}(\omega_2)$.

$$\begin{aligned}
0 &= \frac{\delta\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)}{\delta D^{\rm CPA}_{l_3l_3}(\omega_2)}\left(1-(M_A-M_B)\omega_1^2 D^{\rm CPA}_{l_1l_1}(\omega_1)+\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)D^{\rm CPA}_{l_1l_1}(\omega_1)\right)\\
&\quad +\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)\left(-(M_A-M_B)\omega_1^2\delta(\omega_1-\omega_2)\delta_{l_1l_3}+\frac{\delta\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)}{\delta D^{\rm CPA}_{l_3l_3}(\omega_2)}D^{\rm CPA}_{l_1l_1}(\omega_1)+\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)\delta(\omega_1-\omega_2)\delta_{l_1l_3}\right)\\
0 &= \frac{\delta\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)}{\delta D^{\rm CPA}_{l_3l_3}(\omega_2)}\left(1-(M_A-M_B)\omega_1^2 D^{\rm CPA}_{l_1l_1}(\omega_1)+2\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)D^{\rm CPA}_{l_1l_1}(\omega_1)\right)\\
&\quad -\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)\left((M_A-M_B)\omega_1^2-\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)\right)\delta(\omega_1-\omega_2)\delta_{l_1l_2} &(7.175)\\
&\Rightarrow \frac{\delta\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)}{\delta D^{\rm CPA}_{l_3l_3}(\omega_2)} = \frac{\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)\left((M_A-M_B)\omega_1^2-\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)\right)}{1-(M_A-M_B)\omega_1^2 D^{\rm CPA}_{l_1l_1}(\omega_1)+2\Sigma^{\rm CPA}_{l_1l_1}(\omega_1)D^{\rm CPA}_{l_1l_1}(\omega_1)}\delta(\omega_1-\omega_2)\delta_{l_1l_3} &(7.176)
\end{aligned}$$

It should be obvious that if we relabel the indices and redo the differentiation, we get

$$\frac{\delta\Sigma^{\rm CPA}_{l_3l_3}(\omega_2)}{\delta D^{\rm CPA}_{l_1l_1}(\omega_1)} = \frac{\Sigma^{\rm CPA}_{l_3l_3}(\omega_2)\left((M_A-M_B)\omega_2^2-\Sigma^{\rm CPA}_{l_3l_3}(\omega_2)\right)}{1-(M_A-M_B)\omega_2^2 D^{\rm CPA}_{l_3l_3}(\omega_2)+2\Sigma^{\rm CPA}_{l_3l_3}(\omega_2)D^{\rm CPA}_{l_3l_3}(\omega_2)}\delta(\omega_2-\omega_1)\delta_{l_3l_1} \quad (7.177)$$

Due to the delta functions, the equality is satisfied and CPA is thus a Φ-derivable conserving approximation.

Finally we shall deduce the Φ diagrams that gives us the conserving CPA self energy diagrams. The definition of self energy from Φ is

$$\Sigma^{\rm CPA}_{l_1l_1}(\omega_1) = \frac{\delta\Phi}{\delta D^{\rm CPA}_{l_1l_1}(\omega_1)} \quad (7.178)$$

which in diagrammatic language is (roughly speaking) "remove a $D^{\rm CPA}$ line (denoted by a double line here) from a Φ diagram and we get a $\Sigma^{\rm CPA}$ diagram". We reverse it and so closing a Σ^{CPA} diagram with a double line, we get a Φ diagram. The Φ diagrams (from [Leath1970] figure 5 which he calls them the "wagon-wheel diagrams") associated with CPA (with the correct weights) are,

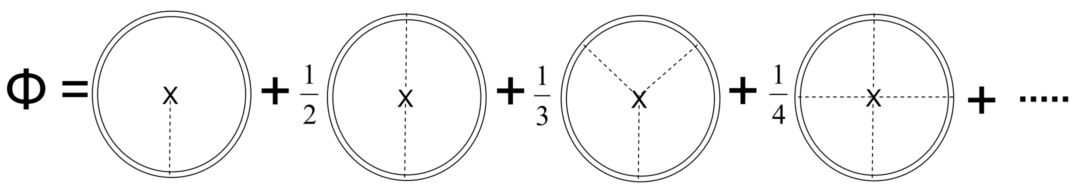


Figure 7.3: Φ diagrams that give the (conserving) CPA self energy diagrams.

7.4.1.2 Diagrammatic Derivation

Here we follow [Leath1970] and [Nolting2009] Chapter 4. As mentioned earlier, the objective of this derivation is to show why CPA is the best single site approximation. As we will see, CPA is made up of the sum of a huge number of diagrams which is as many as one could possibly sum.

Recall the the Dyson equation,

$$
\begin{aligned}
D_{ll'}(\omega) &= \left(M_A\omega^2\mathbb{I} - \Phi_{ll'} - M_l\omega^2\mathbb{I}\right)^{-1} && (7.179)\\
&\equiv \left(D_{ll'}^{(A)-1} - \tilde{V}_l\right)^{-1} && (7.180)\\
&| \quad \text{multiply out to get the form of Dyson equation}\\
&| \quad D_{ll'}^{(A)}(\omega) + \sum_{l_1} D_{ll_1}^{(A)}(\omega)\tilde{V}_{l_1}D_{l_1l'}(\omega)\\
&| \quad \text{iterate on the right side}\\
&= D_{ll'}^{(A)}(\omega) + \sum_{l_1} D_{ll_1}^{(A)}(\omega)\tilde{V}_{l_1}D_{l_1l'}^{(A)}(\omega) + \sum_{l_1l_2} D_{ll_1}^{(A)}(\omega)\tilde{V}_{l_1}D_{l_1l_2}^{(A)}(\omega)\tilde{V}_{l_2}D_{l_2l'}^{(A)}(\omega) + \cdots && (7.181)\\
&| \quad \text{configuration average both sides, only } \tilde{V}_l \text{ is random}\\
\langle D_{ll'}(\omega)\rangle_c &= D_{ll'}^{(A)}(\omega) + \sum_{l_1 D_{ll_1}^{(A)}(\omega)} \langle\tilde{V}_{l_1}\rangle_c D_{l_1l'}^{(A)}(\omega) + \sum_{l_1l_2} D_{ll_1}^{(A)}(\omega)D_{l_1l_2}^{(A)}(\omega)D_{l_2l'}^{(A)}(\omega)\langle\tilde{V}_{l_1}\tilde{V}_{l_2}\rangle_c + \cdots && (7.182)
\end{aligned}
$$

where we recall that $\tilde{V}_l = M_l\omega^2\mathbb{I}$ with $M_l = 0$ when $l = A$ and $M_l = M_A - M_B$ when $l = B$.

We take sites to be independent (SSA),

$$
\begin{aligned}
\langle\tilde{V}_{l_2}\tilde{V}_{l_3}\rangle_c &= \begin{cases} \langle\tilde{V}_{l_2}^2\rangle_c & \text{for } l_2 = l_3\\ \langle\tilde{V}_{l_2}\rangle_c^2 & \text{for } l_2 \neq l_3 \end{cases} && (7.183)\\
&= \delta_{l_2l_3}\langle\tilde{V}_{l_2}^2\rangle_c + (1-\delta_{l_2l_3})\langle\tilde{V}_{l_2}\rangle_c^2 && (7.184)
\end{aligned}
$$

We want to pick out (irreducible/proper) self energy terms for the Dyson equation.

$$
\langle D(\omega)\rangle_c = D^{(A)}(\omega) + D^{(A)}\Sigma\langle D(\omega)\rangle_c \qquad (7.185)
$$

Now we assign diagrammatic rules for the (impurity) diagrams.

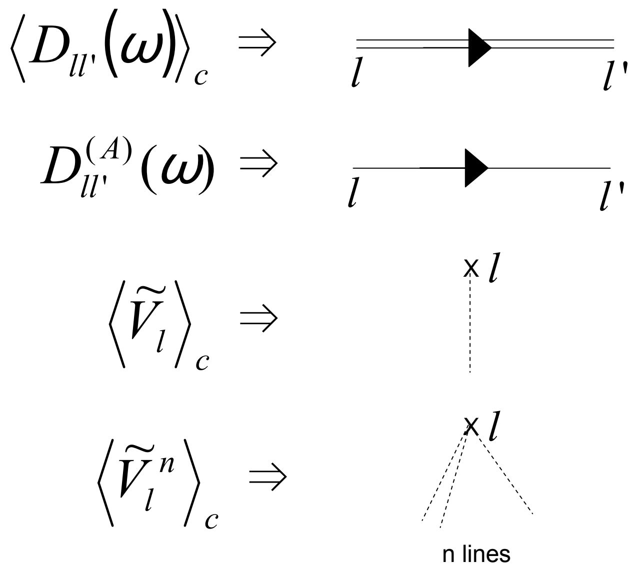


Figure 7.4: *Diagram rules for impurity scattering.*

Note that the last 2 rules are single site averages which are easy to calculate, i.e. $\langle \tilde{V}_l^n \rangle_c = c_A \tilde{V}_A^n + c_B \tilde{V}_B^n$.

Based on the iterated Dyson equation above, we recognise these (irreducible) self energy diagrams,

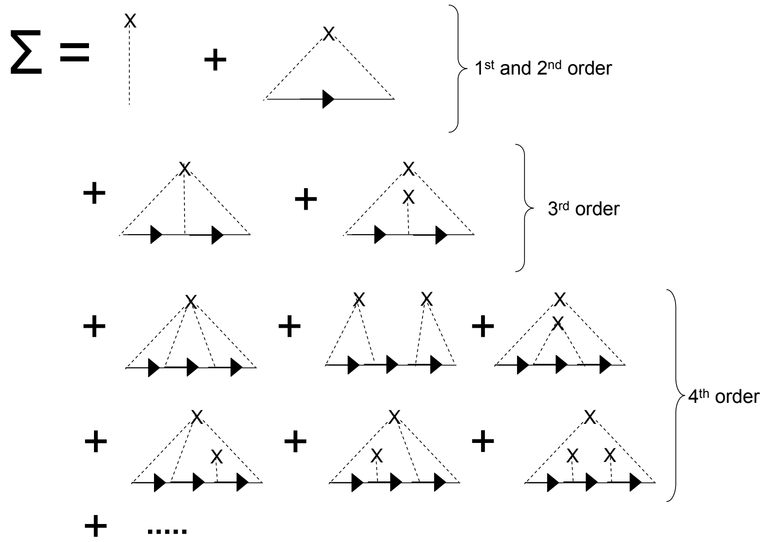


Figure 7.5: *Irreducible (impurity) self energy diagrams.*

Now we run through 5 known approximations where we will progressively sum more and more diagrams, ending with CPA. We will evaluate the configuration averaged Green's function for each case.

[(a) Virtual Crystal Approximation] Only the first (irreducible) self energy term is included.

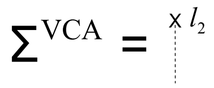


Figure 7.6: *Self energy in Virtual Crystal Approximation (VCA)*

$$\langle D_{ll'}(\omega)\rangle_c^{\rm VCA} = D_{ll'}^{(A)}(\omega) + \sum_{l_2} D_{ll_2}^{(A)}(\omega)\langle\tilde V_{l_2}\rangle_c \langle D_{l_2l'}(\omega)\rangle_c^{\rm VCA} \tag{7.186}$$

| recall $\langle\tilde V_{l_2}\rangle_c = c_A\tilde V_A + c_B\tilde V_B = c_A 0\omega^2 + c_B(M_A - M_B)\omega^2$

$$= D_{ll'}^{(A)}(\omega) + c_B(M_A - M_B)\omega^2 \sum_{l_2} D_{ll_2}^{(A)}\langle D_{l_2l'}\rangle_c^{\rm VCA} \tag{7.187}$$

| manipulate $\langle D\rangle_c^{\rm VCA}$ to be the subject symbolically to get

$$\langle D\rangle_c^{\rm VCA} = \left(1 - c_B(M_A - M_B)\omega^2 D^{(A)}\right)^{-1} D^{(A)} \tag{7.188}$$

$$= \left(D^{(A)-1} - c_B(M_A - M_B)\omega^2\right)^{-1} \tag{7.189}$$

$$= \left(M_A\omega^2 - \Phi_{ll'} - c_B(M_A - M_B)\omega^2\right)^{-1} \tag{7.190}$$

| recall $1 - c_B = c_A$ and the definition of average mass $\bar M = c_A M_A + c_B M_B$

$$= \left(\bar M\omega^2 - \Phi_{ll'}\right)^{-1} \tag{7.191}$$

This is a simple but very crude approximation. The disordered solid is simply treated as if it is a perfect lattice with a mass $\bar M$ at each site. This is valid when the mass of the defect atom is very close to that of the host. It does imply a low defect concentration approximation.

[(b) Single Site Approximation] We take into account this set of diagrams.

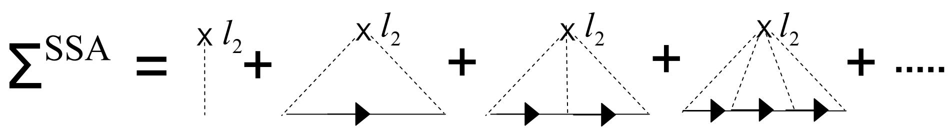


Figure 7.7: *Self energy in Single Site Approximation (SSA)*

$$\Sigma^{\rm SSA} = \langle\tilde V_{l_2}\rangle_c + D_{l_2l_2}^{(A)}(\omega)\langle\tilde V_{l_2}^2\rangle_c + D_{l_2l_2}^{(A)}(\omega)D_{l_2l_2}^{(A)}(\omega)\langle\tilde V_{l_2}^3\rangle_c + \cdots \tag{7.192}$$

| recall the standard single site average $\langle\tilde V_{l_2}^n\rangle_c = c_B(M_A - M_B)^n\omega^{2n}$

$$= c_B(M_A - M_B)\omega^2\left(1 + D^{(A)}(M_A - M_B)\omega^2 + (D^{(A)}(M_A - M_B)\omega^2)^2 + \cdots\right) \tag{7.193}$$

$$= \quad c_B(M_A - M_B)\omega^2 \left(\frac{1}{1 - D^{(A)}(M_A - M_B)\omega^2} \right) \tag{7.194}$$

The configuration averaged Green's function is simply obtained by substituting Σ^{SSA} into the Dyson equation.

$$\langle D \rangle_c^{\mathrm{SSA}} \quad = \quad \frac{1}{D^{(A)-1} - \Sigma^{\mathrm{SSA}}} \tag{7.195}$$

[(c) Modified Propagator Method (MPM)] This is simply the self consistent version of SSA. We simply replace the host Green's function $D^{(A)}$ with the "full" Green's function $\langle D \rangle_c$.

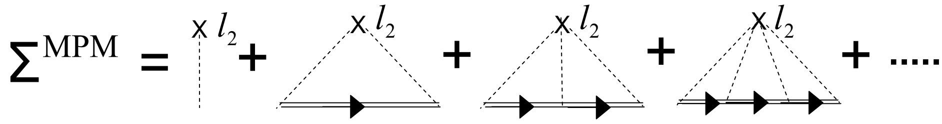


Figure 7.8: *Self energy in Modified Propagator Method (MPM)*

So the result for Σ^{MPM} is immediate.

$$\Sigma^{\mathrm{MPM}} \quad = \quad \frac{c_B(M_A - M_B)\omega^2}{1 - (M_A - M_B)\omega^2 \langle D_{ll}(\omega) \rangle_c^{\mathrm{MPM}}} \tag{7.196}$$

and

$$\langle D \rangle_c^{\mathrm{MPM}} \quad = \quad \frac{1}{D^{(A)-1} - \Sigma^{\mathrm{MPM}}} \tag{7.197}$$

Note that in this approximation, certain 4th order diagrams are not included, eg

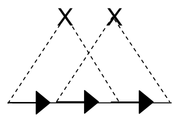


Figure 7.9: *Diagram not included in MPM.*

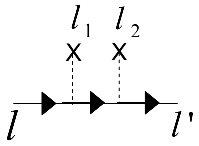
[(d) Average T-matrix Approximation] This approximation is simply SSA with multiple counting corrections. This is called "multiple occupancy corrections" in the literature.

To see why such corrections are needed, we give an example of counting error in SSA. Consider this diagram in SSA which appears when we iterate the first (irreducible) self energy diagram in the Dyson equation.

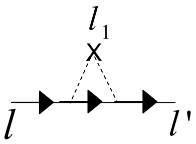
When $l_1 = l_2$, the expression becomes

$$\sum_{l_1} D_{ll_1}^{(A)}(\omega) \langle \tilde{V} \rangle_c^2 D_{l_1 l_1}^{(A)}(\omega) D_{l_1 l'}^{(A)}(\omega) \tag{7.198}$$

which is incorrect. The correct diagram and expression is

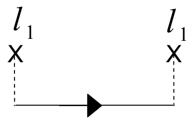


$$= \sum_{l_1 l_2} D^{(A)}_{ll_1}(\omega)\left\langle \widetilde{V}_{l_1}\right\rangle_c D^{(A)}_{l_1 l_2}(\omega)\left\langle \widetilde{V}_{l_2}\right\rangle_c D^{(A)}_{l_2 l'}(\omega)$$



$$= \sum_{l_1} D^{(A)}_{ll_1}(\omega) D^{(A)}_{l_1 l_1}(\omega) D^{(A)}_{l_1 l'}(\omega)\left\langle \widetilde{V}^2_{l_1}\right\rangle_c$$

The correct counting would then require subtracting the diagram from the self energy.



$$= D^{(A)}_{l_1 l_1}(\omega)\left\langle \widetilde{V}_{l_1}\right\rangle_c^2$$

We tabulate all these corrections,

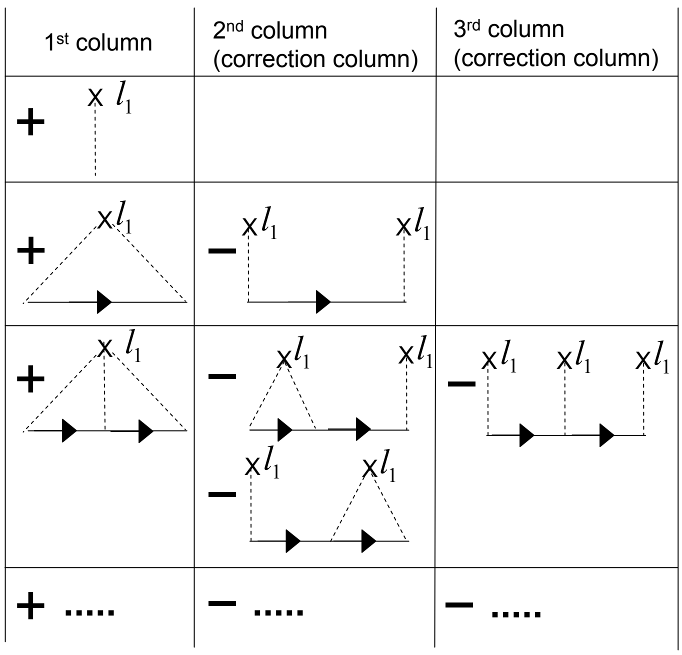


Figure 7.10: *Self energy diagrams and multiple occupancy corrections in ATA. See Fig 9 of [Elliott1974] for an extended tabulation.*

1st column sums to Σ^{SSA} as was done earlier

$$\text{1st column sum} = \Sigma^{\text{SSA}} = \frac{c_B(M_A - M_B)\omega^2}{1 - D^{(A)}(M_A - M_B)\omega^2} \tag{7.199}$$

2nd column contains diagrams that can be severed by cutting one $D^{(A)}$ line. There are 2 irreducible parts and we treat them as corrected irreducible parts so they sum to the result we want, Σ^{ATA}. The 2nd column sums to,

$$\text{2nd column sum} = \Sigma^{\text{ATA}} D^{(A)}_{l_1 l_1}(\omega) \Sigma^{\text{ATA}} \tag{7.200}$$

Similarly, the 3rd column sums to,

$$\begin{aligned} \text{3rd column sum} &= \Sigma^{\text{ATA}} D^{(A)}_{l_1 l_1} \Sigma^{\text{ATA}} D^{(A)}_{l_1 l_1} \Sigma^{\text{ATA}} & (7.201) \\ &= \Sigma^{\text{ATA}} \left(D^{(A)}_{l_1 l_1} \Sigma^{\text{ATA}} \right)^2 & (7.202) \end{aligned}$$

The nth column sum is,

$$\text{nth column sum} = \Sigma^{\text{ATA}} \left(D^{(A)}_{l_1 l_1} \Sigma^{\text{ATA}} \right)^{n-1} \tag{7.203}$$

We can write a self consistent equation for the self energy

$$\begin{aligned} \Sigma^{\text{ATA}} &= \text{1st column sum} - \text{2nd column sum} - \text{3rd column sum} - \cdots & (7.204) \\ &= \Sigma^{\text{SSA}} - \Sigma^{\text{ATA}} \sum_{n=1}^{\infty} \left(D^{(A)}_{l_1 l_1}(\omega) \Sigma^{\text{ATA}} \right)^n & (7.205) \\ &\quad | \quad \text{sum the infinite geometric progression} \\ &= \Sigma^{\text{SSA}} + \Sigma^{\text{ATA}} - \Sigma^{\text{ATA}} \sum_{n=0}^{\infty} \left(D^{(A)}_{l_1 l_1}(\omega) \Sigma^{\text{ATA}} \right)^n & (7.206) \\ 0 &= \Sigma^{\text{SSA}} - \Sigma^{\text{ATA}} \left(1 - D^{(A)}_{l_1 l_1}(\omega) \Sigma^{\text{ATA}} \right)^{-1} & (7.207) \\ \Sigma^{\text{ATA}} &= \frac{\Sigma^{\text{SSA}}}{1 + \Sigma^{\text{SSA}} D^{(A)}_{l_1 l_1}(\omega)} & (7.208) \end{aligned}$$

and the averaged Green's function is the usual expression,

$$\langle D \rangle_c^{\text{ATA}} = \frac{1}{D^{(A)-1} - \Sigma^{\text{ATA}}} \tag{7.209}$$

[(e) Coherent Potential Approximation (CPA)] This is the final and the only obvious improvement left. This approximation is essentially the self consistent version of ATA or the "multiple occupancy corrected" version of MPM.

An example of a diagram that is included in this approximation is this nested diagram.

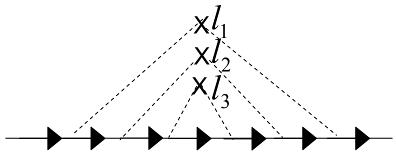


Figure 7.11: *Nested Diagram included in CPA.*

We tabulate the terms to sum up and their corresponding "mutiple occupancy corrections".

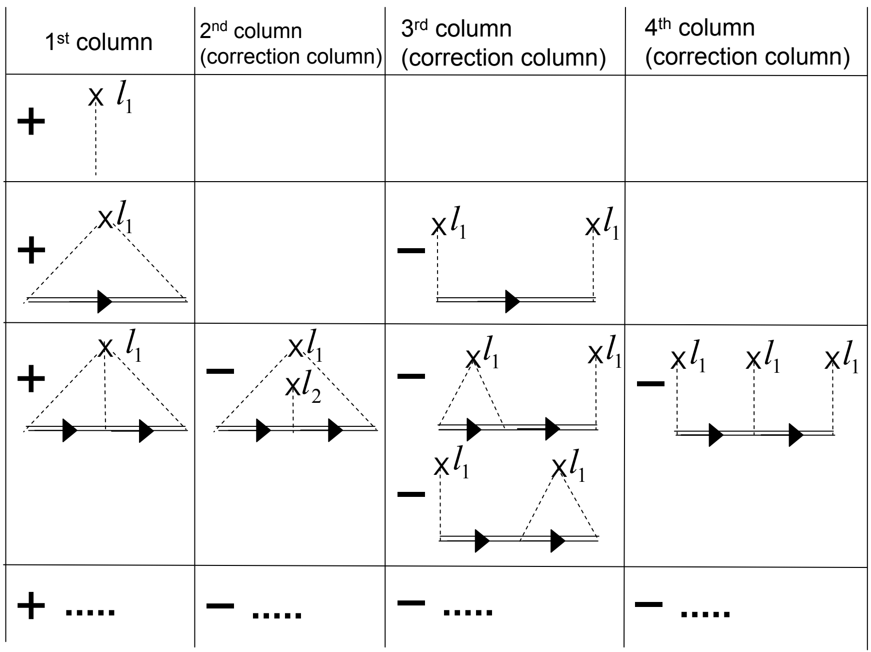


Figure 7.12: *Self energy diagrams and multiple occupancy corrections in CPA. See Fig 11 of [Elliott1974] for an extended tabulation. The same table will be used for calculating the renormalized locator σ in the next section.*

1st column sum is simply Σ^{MPM}

$$\Sigma^{\mathrm{MPM}} = \frac{c_B(M_A - M_B)\omega^2}{1 - (M_A - M_B)\omega^2\langle D_{ll}\rangle_c} \tag{7.210}$$

The 2nd column is made up of one irreducible part with all possible insertions "inside". To pick out all these terms, we use a trick. First, define and denote the usual self energy as a functional of its internal propagator.

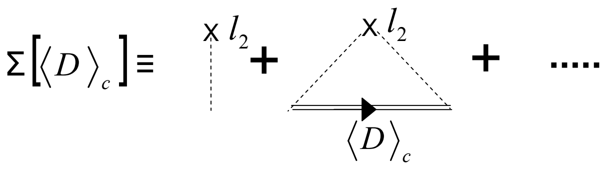


Figure 7.13: *Defining the self energy as a functional of its internal propagator.*

In simple terms, the functional argument of Σ represents what that "line" in the diagram is made up of. With that, we can now define self energy diagrams with self energy diagrams inserted into its "line". Define

$$\Sigma\left[\Gamma_0\right] = \langle D\rangle_c + \langle D\rangle_c\Sigma[\Gamma_0]\langle D\rangle_c + \langle D\rangle_c\Sigma[\Gamma_0]\langle D\rangle_c\Sigma[\Gamma_0]\langle D\rangle_c + \cdots \quad = \quad \Sigma\left[\frac{\langle D\rangle_c}{1-\Sigma[\Gamma_0]\langle D\rangle_c}\right] \tag{7.211}$$

So $\Sigma[\langle D\rangle_c]$ represents self energy diagrams with no insertions and $\Sigma[\Gamma_0]$ represents self energy diagrams with all possible insertions (including no insertions). The 2nd column sum is over all diagrams with all possible insertions, which is thus

$$\text{2nd column sum} = \Sigma[\Gamma_0] - \Sigma[\langle D\rangle_c] \tag{7.212}$$

From the 3rd column onwards, it is just like in ATA but the self energy to use is $\Sigma[\Gamma_0]$ which has all possible insertions (including no insertions),

$$\text{3rd column sum} = \Sigma[\Gamma_0]\langle D\rangle_c\Sigma[\Gamma_0] \tag{7.213}$$

The nth column sum is

$$\text{nth column sum} = \Sigma[\Gamma_0]\left(\langle D\rangle_c\Sigma[\Gamma_0]\right)^{n-2} \tag{7.214}$$

Again, we treat terms from 2nd column onwards as corrected terms, we can write a self consistent equation of the quantity we want to solve

$$\Sigma^{\text{CPA}} = \Sigma[\langle D\rangle_c] = \Sigma[\Gamma_0]|_{\text{no insertions}} \tag{7.215}$$

$$\begin{aligned}
\Sigma^{\text{CPA}} &= \Sigma[\langle D\rangle_c] && (7.216)\\
&= \text{1st column sum} - \text{2nd column sum} - \text{3rd column sum} - \cdots && (7.217)\\
&= \Sigma^{\text{MPM}} - \Sigma[\Gamma_0] + \Sigma[\langle D\rangle_c] - \Sigma[\Gamma_0]\sum_{n=1}^{\infty}\left(\langle D\rangle_c\Sigma[\Gamma_0]\right)^n && (7.218)\\
0 &= \Sigma^{\text{MPM}} - \Sigma[\Gamma_0] + \Sigma[\Gamma_0] - \Sigma[\Gamma_0]\sum_{n=0}^{\infty}\left(\langle D\rangle_c\Sigma[\Gamma_0]\right)^n && (7.219)\\
0 &= \Sigma^{\text{MPM}} - \frac{\Sigma[\Gamma_0]}{1-\langle D\rangle_c\Sigma[\Gamma_0]} && (7.220)\\
\Sigma[\Gamma_0] &= \frac{\Sigma^{\text{MPM}}}{1+\Sigma^{\text{MPM}}\langle D\rangle_c} && (7.221)\\
&| \quad \text{substitute in the explicit expression of } \Sigma^{\text{MPM}} \text{ and recall } c_A = 1 - c_B
\end{aligned}$$

$$
\begin{aligned}
&= \frac{c_B(M_A-M_B)\omega^2}{1-c_A(M_A-M_B)\omega^2\langle D\rangle_c} && (7.222)\\
\Sigma\left[\frac{\langle D\rangle_c}{1-\Sigma[\Gamma_0]\langle D\rangle_c}\right] &= \frac{c_B(M_A-M_B)\omega^2}{1-c_A(M_A-M_B)\omega^2\langle D\rangle_c} && (7.223)\\
&\mid \quad \text{to get } \Sigma[\langle D\rangle_c]=\Sigma^{\mathrm{CPA}}\text{, transform } \langle D\rangle_c \to \frac{\langle D\rangle_c}{1+\Sigma\langle D\rangle_c}\\
\Sigma[\langle D\rangle_c] &= \frac{c_B(M_A-M_B)\omega^2}{1-c_A(M_A-M_B)\omega^2\frac{\langle D\rangle_c}{1+\Sigma\langle D\rangle_c}} && (7.224)\\
&\mid \quad \text{now we can write the self energy as } \Sigma^{\mathrm{CPA}}\\
\Sigma^{\mathrm{CPA}} &= \frac{c_B(M_A-M_B)\omega^2}{1-c_A(M_A-M_B)\omega^2\frac{\langle D\rangle_c}{1+\Sigma^{\mathrm{CPA}}\langle D\rangle_c}} && (7.225)
\end{aligned}
$$

$$
\begin{aligned}
\Sigma^{\mathrm{CPA}}-c_A(M_A-M_B)\langle D\rangle_c\frac{\Sigma^{\mathrm{CPA}}\omega^2}{1+\Sigma^{\mathrm{CPA}}\langle D\rangle_c} &= c_B(M_A-M_B)\omega^2 && (7.226)\\
&\mid \quad \text{write } \Sigma^{\mathrm{CPA}}=c_A\Sigma^{\mathrm{CPA}}+c_B\Sigma^{\mathrm{CPA}}\\
c_A\Sigma^{\mathrm{CPA}}-c_A(M_A-M_B)\langle D\rangle_c\frac{\Sigma^{\mathrm{CPA}}\omega^2}{1+\Sigma^{\mathrm{CPA}}\langle D\rangle_c} &= c_B(M_A-M_B)\omega^2-c_B\Sigma^{\mathrm{CPA}} && (7.227)\\
\frac{c_A\Sigma^{\mathrm{CPA}}(1+\Sigma^{\mathrm{CPA}}\langle D\rangle_c)-c_A(M_A-M_B)\langle D\rangle_c\Sigma^{\mathrm{CPA}}\omega^2}{1+\Sigma^{\mathrm{CPA}}\langle D\rangle_c} &= c_B(M_A-M_B)\omega^2-c_B\Sigma^{\mathrm{CPA}} && (7.228)\\
\frac{c_A\Sigma^{\mathrm{CPA}}(1+\Sigma^{\mathrm{CPA}}\langle D\rangle_c-(M_A-M_B)\omega^2\langle D\rangle_c)}{1+\Sigma^{\mathrm{CPA}}\langle D\rangle_c} &= c_B(M_A-M_B)\omega^2-c_B\Sigma^{\mathrm{CPA}} && (7.229)\\
\frac{c_A\Sigma^{\mathrm{CPA}}}{1+\Sigma^{\mathrm{CPA}}\langle D\rangle_c} &= c_B\frac{(M_A-M_B)\omega^2-\Sigma^{\mathrm{CPA}}}{1-(M_A-M_B)\omega^2\langle D\rangle_c+\Sigma^{\mathrm{CPA}}\langle D\rangle_c} && (7.230)
\end{aligned}
$$

which is indeed the CPA equation and the averaged Green's function is solved by

$$\langle D\rangle_c=\frac{1}{D^{(A)-1}-\Sigma^{\mathrm{CPA}}} \tag{7.231}$$

which is indeed the same as that derived using effective medium method when we identify $\langle D\rangle_c=D^{\mathrm{CPA}}$.

7.4.1.3 Locator Derivation

Recall the equation of motion of the harmonic disordered lattice in frequency domain.

$$\sum_{l_1\alpha_1}\left(M_l\omega^2\delta_{\alpha\alpha_1}\delta_{ll_1}-\Phi_{l\alpha l_1\alpha_1}\right)D_{l_1\alpha_1 l'\alpha'}(\omega) \quad = \quad \delta_{\alpha\alpha'}\delta_{ll'} \tag{7.232}$$

From here we carry out a locator expansion. Define the site diagonal locator d_{ll}

$$d^{-1}_{l\alpha l\alpha'}\equiv M_l\omega^2\delta_{\alpha\alpha'}-\Phi_{l\alpha l\alpha'} \tag{7.233}$$

Now we write the equation of motion in terms of d_{ll} as matrices in Cartesian indices. Note that the random variable is only in d_{ll}.

$$\begin{aligned} d_{ll}^{-1} D_{ll'}(\omega) \quad &- \sum_{l_1(\neq l)} \Phi_{ll_1} D_{l_1 l'}(\omega) = \mathbb{I}\delta_{ll'} && (7.234) \\ &| \quad \times d_{ll} \text{ on both sides} \\ D_{ll'}(\omega) \quad &= \quad d_{ll}\delta_{ll'} + d_{ll} \sum_{l_1(\neq l)} \Phi_{ll_1} D_{l_1 l'}(\omega) && (7.235) \\ &| \quad \text{iterate and take configurational average} \\ \langle D_{ll'}(\omega)\rangle_c \quad &= \quad \langle d_{ll}\rangle_c \delta_{ll'} + \langle d_{ll}\Phi_{ll'} d_{l'l'}\rangle_c + \sum_{l_1(\neq l)} \langle d_{ll}\Phi_{ll_1} d_{l_1 l_1}\Phi_{l_1 l'} d_{l'l'}\rangle_c + \cdots && (7.236) \end{aligned}$$

We can again assume site independence and assign diagrammatic rules for the above expansion.

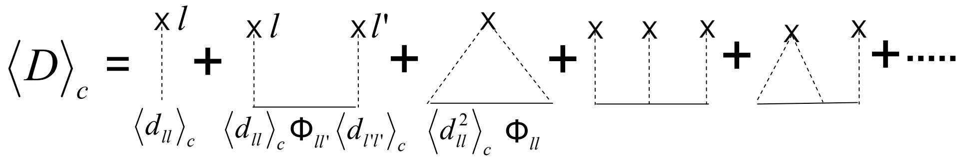


Figure 7.14: *Locator expansion in terms of diagrams.*

We will now renormalize the locator d, and the interactor Φ. In the end, we will show that this renormalized theory is the same as CPA. Denote

$$\begin{aligned} \sigma \quad &\equiv \quad \text{renormalized } d && (7.237) \\ U \quad &\equiv \quad \text{renormalized } \Phi && (7.238) \end{aligned}$$

The diagrams for the renormalized quantities are,

The expansion of the configuration averaged Green's function can now be rewritten in the renormalized form.

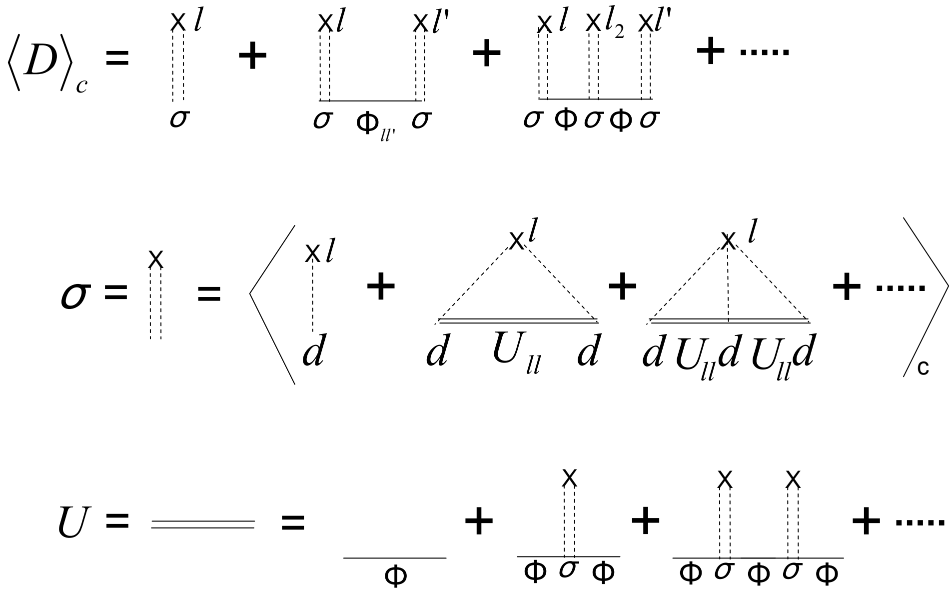


Figure 7.15: *Renormalized locator expansion in terms of diagrams.*

Now we will derive some equations relating these quantities. These are Dyson-like equations.

$$\langle D\rangle_c = \sigma + \sigma\Phi\sigma + \sigma\Phi\sigma\Phi\sigma + \cdots = \sigma + \sigma\Phi\left(\sigma + \sigma\Phi\sigma + \cdots\right) = \sigma + \sigma\Phi\langle D\rangle_c \tag{7.239}$$

$$U = \Phi + \Phi\sigma\Phi + \Phi\sigma\Phi\sigma\Phi + \cdots = \Phi + \Phi\left(\sigma + \sigma\Phi\sigma + \cdots\right)\Phi = \Phi + \Phi\langle D\rangle_c\Phi \tag{7.240}$$

$$\begin{aligned}
\sigma = \langle d + dU_{ll}d + dU_{ll}dU_{ll}d + \cdots\rangle_c \quad &= \quad \langle d + dU_{ll}\sigma\rangle_c && (7.241)\\
&| \quad \text{or,} \\
&= \quad \langle d\left(1 + U_{ll}d + U_{ll}dU_{ll}d + \cdots\right)\rangle_c && (7.242)\\
&= \quad \left\langle d\left(1 - U_{ll}d\right)^{-1}\right\rangle_c && (7.243)
\end{aligned}$$

where U_{ll} denotes the (site) diagonal part of U. Use the first 2 equations to get rid of Φ and we get,

$$\begin{aligned}
\langle D\rangle_c &= \sigma + \sigma\Phi\langle D\rangle_c && (7.244)\\
\Rightarrow \Phi &= \sigma^{-1}\left(\langle D\rangle_c - \sigma\right)\langle D\rangle_c^{-1} = \sigma^{-1} - \langle D\rangle_c^{-1} && (7.245)\\
U &= \Phi + \Phi\langle D\rangle_c\Phi && (7.246)\\
&= \sigma^{-1} - \langle D\rangle_c^{-1} + \left(\sigma^{-1} - \langle D\rangle_c^{-1}\right)\langle D\rangle_c\left(\sigma^{-1} - \langle D\rangle_c^{-1}\right) && (7.247)\\
&| \quad \text{expand and cancel terms} \\
&= \sigma^{-1}\langle D\rangle_c\sigma^{-1} - \sigma^{-1} && (7.248)
\end{aligned}$$

Now we carry out multiple occupancy corrections for σ. As usual, the first column are the diagrams that we sum for renormalization and subsequent columns are corrections to the renormalization. In fact, due to the way the diagrams are defined, the table of corrections are exactly the same as in CPA in

Fig 8.12 (but recall that the double line here represents the renormalized interactor U and for σ, there is an overall configuration average).

$$\begin{aligned}\text{1st column sum} &= \langle d_{ll} + d_{ll}U_{ll}d_{ll} + \cdots \rangle_c & (7.249)\\ &= \left\langle \frac{d_{ll}}{1 - U_{ll}d_{ll}} \right\rangle_c & (7.250)\end{aligned}$$

We sum the correction columns using the trick used in CPA. We simply translate the result over.

$$\begin{aligned}\Sigma[\langle D \rangle_c] &= \Sigma^{\text{MPM}} + \Sigma[\langle D \rangle_c] - \frac{\Sigma[\Gamma_0]}{1 - \langle D \rangle_c \Sigma[\Gamma_0]} & (7.251)\\ \Rightarrow \sigma[U_{ll}] &= \left\langle \frac{d_{ll}}{1 - U_{ll}d_{ll}} \right\rangle_c - \left(\frac{\sigma[\phi_0]}{1 - \sigma[\phi_0]U_{ll}} - \sigma[U_{ll}] \right) & (7.252)\end{aligned}$$

where $\phi_0 = \frac{U_{ll}}{1-\sigma[\phi_0]U_{ll}}$. We solve it in the same way.

$$\begin{aligned}\sigma[\phi_0] &= \frac{\left\langle \frac{d_{ll}}{1-U_{ll}d_{ll}} \right\rangle_c}{1 + \left\langle \frac{d_{ll}}{1-U_{ll}d_{ll}} \right\rangle_c U_{ll}} & (7.253)\\ &\quad | \quad \text{use the inverse transform } U_{ll} \to \frac{U_{ll}}{1 + \sigma U_{ll}} \equiv \phi_0' \\ \sigma[U_{ll}] &= \frac{\left\langle \frac{d_{ll}}{1-\phi_0' d_{ll}} \right\rangle_c}{1 + \phi_0' \left\langle \frac{d_{ll}}{1-\phi_0' d_{ll}} \right\rangle_c} & (7.254)\\ &\quad | \quad \text{note that only } d_{ll} \text{ is a random quantity, the rest are averaged quantities} \\ &\quad | \quad \text{denote } \sigma[U_{ll}] \text{ as } \sigma \\ \Sigma &= \frac{\left\langle \frac{d_{ll}}{1-\phi_0' d_{ll}} \right\rangle_c}{\left\langle \frac{1}{1-\phi_0' d_{ll}} \right\rangle_c} & (7.255)\\ \left\langle \frac{\sigma}{1 - \phi_0' d_{ll}} \right\rangle_c &= \left\langle \frac{d_{ll}}{1 - \phi_0' d_{ll}} \right\rangle_c & (7.256)\\ 0 &= \left\langle \frac{d_{ll} - \sigma}{1 - \phi_0' d_{ll}} \right\rangle_c & (7.257)\\ &\quad | \quad \text{use } \phi_0' = \frac{U_{ll}}{1 + \sigma U_{ll}} \\ 0 &= \left\langle \frac{(d_{ll} - \sigma)(1 + \sigma U_{ll})}{1 - (d_{ll} - \sigma)U_{ll}} \right\rangle_c & (7.258)\\ &\quad | \quad \text{drop the non-zero (and non-random) factor } (1 + \sigma U) \\ 0 &= \left\langle \frac{d_{ll}}{1 - (d_{ll} - \sigma)U_{ll}} \right\rangle_c - \sigma \left\langle \frac{1}{1 - (d_{ll} - \sigma)U_{ll}} \right\rangle_c & (7.259)\end{aligned}$$

which we now need to solve $\left\langle \frac{1}{1-(d_{ll}-\sigma)U_{ll}} \right\rangle_c$ seperately. We start from

$$\begin{aligned}0 &= \left\langle \frac{d_{ll} - \sigma}{1 - (d_{ll} - \sigma)U_{ll}} \right\rangle_c & (7.260)\\ &\quad | \quad \text{multiply by } -U_{ll}\end{aligned}$$

$$\begin{aligned}
0 &= \left\langle \frac{-(d_{ll}-\sigma)U_{ll}}{1-(d_{ll}-\sigma)U_{ll}} \right\rangle_c && (7.261)\\
&\quad | \quad \text{add and subtract 1 in the numerator}\\
0 &= \left\langle \frac{1-(d_{ll}-\sigma)U_{ll}-1}{1-(d_{ll}-\sigma)U_{ll}} \right\rangle_c && (7.262)\\
&\quad | \quad \text{then note } \langle 1\rangle_c = c_A + c_B = 1\\
0 &= 1-\left\langle \frac{1}{1-(d_{ll}-\sigma)U_{ll}} \right\rangle_c && (7.263)
\end{aligned}$$

So,

$$\begin{aligned}
\sigma &= \left\langle \frac{1}{1-(d_{ll}-\sigma)U_{ll}} \right\rangle_c && (7.264)\\
&\quad | \quad \text{now use the diagonal of } U = \sigma^{-1}\langle D\rangle_c\sigma^{-1} - \sigma^{-1} \Rightarrow U_{ll} = \sigma^{-2}\langle D_{ll}\rangle_c - \sigma^{-1}\\
\sigma &= \left\langle \frac{1}{1-(d_{ll}-\sigma)\left(\sigma^{-2}\langle D_{ll}\rangle_c - \sigma^{-1}\right)} \right\rangle_c && (7.265)\\
\sigma &= \left\langle \frac{1}{1-d_{ll}\sigma^{-2}\langle D_{ll}\rangle_c + d_{ll}\sigma^{-1} + \sigma^{-1}\langle D_{ll}\rangle_c - 1} \right\rangle_c && (7.266)\\
&\quad | \quad \text{divide } \sigma \text{ on both sides and divide } d_{ll} \text{ in numerator and denominator}\\
1 &= \left\langle \frac{1}{1-\left(\sigma^{-1}-d_{ll}^{-1}\right)\langle D_{ll}\rangle_c} \right\rangle_c && (7.267)
\end{aligned}$$

Finally, we shall relate σ^{-1} and d_{ll}^{-1} to V_l and Σ^{CPA} to complete the derivation of CPA equations from the locator expansion. We achieve that by comparing their definitions.

$$\begin{aligned}
\text{recall, } \langle D\rangle_c &= \left(M_A\omega^2 - \Phi_{ll'} - \Sigma^{\text{CPA}}\right)^{-1} && (7.268)\\
&= \left(M_A\omega^2 - \Phi_{ll} - \Phi_{ll'(l\neq l')} - \Sigma^{\text{CPA}}\right)^{-1} = D^{\text{CPA}} && (7.269)\\
\text{recall, } \langle D\rangle_c &= \left(\sigma^{-1} - \Phi_{ll'(l\neq l')}\right)^{-1} && (7.270)\\
\text{so, } \sigma^{-1} &= M_A\omega^2 - \Phi_{ll} - \Sigma^{\text{CPA}} && (7.271)
\end{aligned}$$

$$\begin{aligned}
\text{recall, } d_{ll}^{-1} &= M_l'\omega^2 - \Phi_{ll} \quad (\text{where } M_l' = M_A \text{ if } l = A \text{ and } M_l' = M_B \text{ if } l = B) && (7.272)\\
\text{recall, } V_l &= M_l\omega^2 - \Sigma^{\text{CPA}} \quad (\text{where } M_l = 0 \text{ if } l = A \text{ and } M_l = M_A - M_B \text{ if } l = B) && (7.273)\\
\text{so, } d_{ll}^{-1} &= M_A\omega^2 - M_l\omega^2 - \Phi_{ll} && (7.274)\\
&= M_A\omega^2 - V_l - \Sigma^{\text{CPA}} - \Phi_{ll} && (7.275)\\
\text{so, } \sigma^{-1} - d_{ll}^{-1} &= V_l && (7.276)
\end{aligned}$$

where

$$V_l = \begin{cases} -\Sigma^{\text{CPA}} & l = A \\ (M_A - M_B)\omega^2 - \Sigma^{\text{CPA}} & l = B \end{cases} \qquad (7.277)$$

Finally we will subsitute $\sigma^{-1} - d_{ll}^{-1} = V_l$ and show that it becomes the CPA equation.

$$1 = \left\langle \frac{1}{1 - V_l\langle D_{ll}\rangle_c} \right\rangle \qquad (7.278)$$

$$\left\langle \frac{1 - V_l \langle D_{ll} \rangle_c}{1 - V_l \langle D_{ll} \rangle_c} \right\rangle = \left\langle \frac{1}{1 - V_l \langle D_{ll} \rangle_c} \right\rangle \quad (7.279)$$

$$0 = \left\langle \frac{1 - 1 + V_l \langle D_{ll} \rangle_c}{1 - V_l \langle D_{ll} \rangle_c} \right\rangle \quad (7.280)$$

$$0 = \left\langle \frac{V_l \langle D_{ll} \rangle_c}{1 - V_l \langle D_{ll} \rangle_c} \right\rangle \quad (7.281)$$

$$| \quad \text{drop the non-zero (and non-random) factor } \langle D_{ll} \rangle_c$$

$$0 = \left\langle \frac{V_l}{1 - V_l \langle D_{ll} \rangle_c} \right\rangle \quad (7.282)$$

$$0 = c_A \frac{-\Sigma^{\mathrm{CPA}}}{1 + \Sigma^{\mathrm{CPA}} \langle D_{ll} \rangle_c} + c_B \frac{(M_A - M_B)\omega^2 - \Sigma^{\mathrm{CPA}}}{1 - ((M_A - M_B)\omega^2 - \Sigma^{\mathrm{CPA}}) \langle D_{ll} \rangle_c} \quad (7.283)$$

which is precisely the CPA equation.

7.4.2 Discussion on Localization

No discussion of disorder is complete without a discussion of localization. This is because disorder scattering typically is not phase breaking and so constructive or destructive superposition of waves plays a part. However the scope of this topic is large and I do not know much about this topic and the results for phonon localization are somewhat more confusing than that for electrons. Thus here we will only state some basic facts and go through some literature. First we mention 4 references that introduce this topic. [Kramer1993] is a readable review article though it is for electron localization. Introductory literature for phonon localization can be found at [Vollhardt1987], [Singh1990] and [Sheng2006].

[Phonon Weak Localization] Weak localization is where coherent backscattering is taken into account. Coherent backscattering is a constructive superposition between the forward scattering path and its time reversed path. This means that the backscattering amplitude is enhanced. In terms of transport, the weak localization correction to conductivity is negative but have different forms in different dimensions. Rayleigh-Klemens scattering relation (see section on Boltzmann treatment) $\frac{1}{\tau^{MD}_{j\vec{q}}} \propto \omega^4$ shows that at low temperature (ω is small), the mass defect scattering time τ^{MD} is large and the probability of mass defect scattering is low, thus the probability of backscattering is negligible, so we may conclude that the weak localization correction to phonon transport is negligible. Note that for electrons in metal, transport involves a small energy window around the Fermi level, so localization effects on electron transport are more dramatic and more important.

The backscattering correction to transport (2-particle quantity) is calculated by summing the maximally crossed (Cooperon) diagrams. These diagrams represent backscattering because they include interactions (crossed lines) of $\vec{q}$ (forward) and $-\vec{q}$ (backward) scattering.

There is far less literature on theoretical calculations of phonon weak localization. I mention some references that I found. [Jackle1981] discusses the experimental possibility of observing phonon localization. [John1983] followed the electronic case and used a nonlinear σ model (continuum field theory) to calculate quantities related to localization such as the mobility edge. [Polishchuk1997] and [Chu1988] applied the self consistent method to calculate phonon weak localization corrections. [Akkermans1985] considers phonon weak localization with anharmonicity to see how the anharmonic-modified spectrum affects the mobility edge.

[Phonon Strong Localization] Strong localization is where there is such a large amount of disorder that the superposition of waves is almost random and could result in complete localization resulting in the formation of an insulator. We can visualize this by imagining that the mobility edge goes down towards $\omega = 0$ as disorder increases. When the mobility edge is at $\omega = 0$ i.e. all states are localized, we get an insulator. This is called Anderson transition. Analytical work on the Anderson transition for phonons is not conclusive, so the favorite method of dealing phonon strong localization is by using numerical methods.

[Numerical Work on Phonon Localization] Numerical work can only be done on finite systems and so bulk properties are deduced by working out the asymptotic limit of the numerical results. Typically the numerical work is done on 1D systems and there is huge controversy (in 1D) on the exponent in the expression $J \sim \frac{1}{N^{\text{exponent}}}$ where J is the current through the disordered chain and N is the number of particles in the chain. Due to the large amount of literature making various claims, we will not make any stand, we will only state some of the more prominent literature.[6]

The original literature that started the argument are the following: [O'Connor1974], [Casher1971], [Rubin1971], [Matsuda1970], [Ishii1973] and [Visscher1971].

Some recent follow-up literature are: [Chaudhuri2010], [Dhar2001], [Likhachev2006], [Livi2003], [Lepri1998] and [Lepri2003].

7.5 Mass & Force Constant Disorder : Blackman, Esterling and Beck (BEB) Theory

[Literature] The main references are [Esterling1975] and [Blackman1971]. Reference [Katayama1978] accounts for the force constant sum rule. References [Gonis1977] and [Koepernik1998] follow up on its mathematical properties and its applications.

Now the force constant matrix is random and is associated with neighboring sites so the randomness is now (site) off-diagonal.

We will use projection operators so that we can "consolidate" the randomness in them. They are defined as

$$x_l = 1 - y_l = \begin{cases} 1 & \text{if } l = A \\ 0 & \text{if } l = B \end{cases} \tag{7.284}$$

with the (defining) properties,

$$x_l^2 = x_l, \quad y_l^2 = y_l, \quad x_l y_l = 0, \quad \langle x_l \rangle_c = c_A, \quad \langle y_l \rangle_c = c_B \tag{7.285}$$

For the disordered harmonic Green's function, we denote its various projections

$$D^{AA}_{l\alpha l'\alpha'} \equiv x_l D_{l\alpha l'\alpha'} x_{l'} \tag{7.286}$$

$$D^{AB}_{l\alpha l'\alpha'} \equiv x_l D_{l\alpha l'\alpha'} y_{l'} \tag{7.287}$$

$$D^{BA}_{l\alpha l'\alpha'} \equiv y_l D_{l\alpha l'\alpha'} x_{l'} \tag{7.288}$$

$$D^{BB}_{l\alpha l'\alpha'} \equiv y_l D_{l\alpha l'\alpha'} y_{l'} \tag{7.289}$$

[6] Personally, I think the expression $J \sim \frac{1}{N^{\text{exponent}}}$ is physically justified. However, there is a huge amount of literature that defines a thermal conductivity κ out of that expression. I feel that it is highly objectional to do that. I believe that the physics of disorder is not enough to provide the physics that κ contains. A lot of literature even tried to check Fourier's law using disorder physics. I choose to ignore such literature. In fact, the original literature [Casher1971] knew of such problems and explicitly avoided defining κ!

So the Green's function in terms of its projected components is

$$\begin{aligned}
D_{l\alpha l'\alpha'} &= x_l D_{l\alpha l'\alpha'} x_{l'} + x_l D_{l\alpha l'\alpha'} y_{l'} + y_l D_{l\alpha l'\alpha'} x_{l'} + y_l D_{l\alpha l'\alpha'} y_{l'} && (7.290)\\
&= D^{AA}_{l\alpha l'\alpha'} + D^{AB}_{l\alpha l'\alpha'} + D^{BA}_{l\alpha l'\alpha'} + D^{BB}_{l\alpha l'\alpha'} && (7.291)\\
&\mid \text{ taking configuration average}\\
\langle D_{l\alpha l'\alpha'}\rangle_c &= \langle D^{AA}_{l\alpha l'\alpha'}\rangle_c + \langle D^{AB}_{l\alpha l'\alpha'}\rangle_c + \langle D^{BA}_{l\alpha l'\alpha'}\rangle_c + \langle D^{BB}_{l\alpha l'\alpha'}\rangle_c && (7.292)
\end{aligned}$$

So we need 4 "components" to construct the desired configuration averaged Green's function. Note an important implied consistency relationship. When $l = l'$,

$$D^{AB}_{l\alpha l'\alpha'} = x_l D_{l\alpha l\alpha'} y_l = 0 \quad \text{and} \quad D^{BA}_{l\alpha l'\alpha'} = 0 \qquad (7.293)$$

The physical meaning is that A and B cannot be at the same site.

We define similar notations for the various projections of the force constant matrix.

$$\begin{aligned}
\Phi^{AA}_{l\alpha l'\alpha'} &\equiv x_l \Phi_{l\alpha l'\alpha'} x_{l'} && (7.294)\\
\Phi^{AB}_{l\alpha l'\alpha'} &\equiv x_l \Phi_{l\alpha l'\alpha'} y_{l'} && (7.295)\\
\Phi^{BA}_{l\alpha l'\alpha'} &\equiv y_l \Phi_{l\alpha l'\alpha'} x_{l'} && (7.296)\\
\Phi^{BB}_{l\alpha l'\alpha'} &\equiv y_l \Phi_{l\alpha l'\alpha'} y_{l'} && (7.297)
\end{aligned}$$

Define the locator,[7]

$$\begin{aligned}
d^{-1}_{l\alpha l\alpha'} &\equiv M_l \omega^2 \delta_{\alpha\alpha'} && (7.298)\\
d^{-1}_{ll} &= M_l \omega^2 && (7.299)\\
d_{ll} &= \frac{1}{M_l \omega^2} && (7.300)
\end{aligned}$$

since it is site diagonal, there are only 2 projections,

$$\begin{aligned}
d_{ll} &= x_l d_{ll} + y_l d_{ll} && (7.301)\\
&= x_l \frac{1}{M_A \omega^2} + y_l \frac{1}{M_B \omega^2} && (7.302)\\
&\equiv x_l d^A_{ll} + y_l d^B_{ll} && (7.303)\\
\langle d_{ll}\rangle_c &= \langle x_l d^A_{ll}\rangle_c + \langle y_l d^B_{ll}\rangle_c && (7.304)\\
&= \frac{c_A}{M_A \omega^2} + \frac{c_B}{M_B \omega^2} && (7.305)
\end{aligned}$$

Recall the locator expansion, (in Cartesian matrices)

$$\begin{aligned}
D_{ll'} &= d_{ll}\delta_{ll'} + d_{ll} \sum_{l_1(\neq l)} \Phi_{ll_1} D_{l_1 l'} && (7.306)\\
&\mid \text{ write } \Phi_{ll_1} \text{ in projected form}\\
&= d_{ll}\delta_{ll'} + d_{ll} \sum_{l_1(\neq l)} \left(x_l \Phi_{ll_1} x_{l_1} + x_l \Phi_{ll_1} y_{l_1} + y_l \Phi_{ll_1} x_{l_1} + y_l \Phi_{ll_1} y_{l_1}\right) D_{l_1 l'} && (7.307)\\
&\mid \text{ use } x_l^2 = x_l \text{ and } y_l^2 = y_l
\end{aligned}$$

[7]Note that following Esterling in [Esterling1975], we have set $\Phi_{l\alpha l\alpha'} = 0$ in the definition of the locator. This breaks the force constant sum rule. However, the algebra is easier to handle later.

$$= d_{ll}\delta_{ll'} + d_{ll}\sum_{l_1(\neq l)}\left(x_l\Phi^{AA}_{ll_1}x_{l_1} + x_l\Phi^{AB}_{ll_1}y_{l_1} + y_l\Phi^{BA}_{ll_1}x_{l_1} + y_l\Phi^{BB}_{ll_1}y_{l_1}\right)D_{l_1l'} \tag{7.308}$$

Project out the 4 components of the expansion by multiplying projection operators on the left and on the right. Firstly,

$$x_lD_{ll'}x_{l'} = x_ld_{ll}\delta_{ll'}x_{l'} + x_ld_{ll}\sum_{l_1(\neq l)}\left(x_l\Phi^{AA}_{ll_1}x_{l_1} + x_l\Phi^{AB}_{ll_1}y_{l_1}\right)D_{l_1l'}x_{l'} \tag{7.309}$$

$$D^{AA}_{ll'} = x_ld^A_{ll}\delta_{ll'} + x_ld^A_{ll}\sum_{l_1(\neq l)}\left(\Phi^{ll_1}D^{AA}_{l_1l'} + \Phi^{AB}_{ll_1}D^{BA}_{l_1l'}\right) \tag{7.310}$$

Secondly, multiply x_l on the left and $y_{l'}$ on the right,

$$x_lD_{ll'}y_{l'} = x_ld_{ll}\delta_{ll'}y_{l'} + x_ld_{ll}\sum_{l_1(\neq l)}\left(x_l\Phi^{AA}_{ll_1}x_{l_1} + x_l\Phi^{AB}_{ll_1}y_{l_1}\right)D_{l_1l'}y_{l'} \tag{7.311}$$

$$D^{AB}_{ll'} = x_ld^A_{ll}\sum_{l_1(\neq l)}\left(\Phi^{AA}_{ll_1}D^{AB}_{l_1l'} + \Phi^{AB}_{ll_1}D^{BB}_{l_1l'}\right) \tag{7.312}$$

In a similar way, the other 2 equations are

$$D^{BA}_{ll'} = y_ld^B_{ll}\sum_{l_1(\neq l)}\left(\Phi^{BA}_{ll_1}D^{AA}_{l_1l'} + \Phi^{BB}_{ll_1}D^{BA}_{l_1l'}\right) \tag{7.313}$$

$$D^{BB}_{ll'} = y_ld^B_{ll}\delta_{ll'} + y_ld^B_{ll}\sum_{l_1(\neq l)}\left(\Phi^{BA}_{ll_1}D^{AB}_{l_1l'} + \Phi^{BB}_{ll_1}D^{BB}_{l_1l'}\right) \tag{7.314}$$

These 4 "components" can be written into a "defect matrix" form.

$$\begin{pmatrix} D^{AA} & D^{AB} \\ D^{BA} & D^{BB} \end{pmatrix}_{l\alpha l'\alpha'} \tag{7.315}$$

$$= \begin{pmatrix} xd^A & 0 \\ 0 & yd^B \end{pmatrix}_{l\alpha l\alpha'}\delta_{ll'}\delta_{\alpha\alpha'} \tag{7.316}$$

$$+\sum_{l_1(\neq l)}\sum_{\alpha_1}\begin{pmatrix} xd^A & 0 \\ 0 & yd^B \end{pmatrix}_{l\alpha l\alpha_1}\begin{pmatrix} \Phi^{AA} & \Phi^{AB} \\ \Phi^{BA} & \Phi^{BB} \end{pmatrix}_{l\alpha l_1\alpha_1}\begin{pmatrix} D^{AA} & D^{AB} \\ D^{BA} & D^{BB} \end{pmatrix}_{l_1\alpha_1 l'\alpha'} \tag{7.317}$$

So we can define a "defect matrix" locator expansion where "defect matrices" are denoted by quantities with a $\hat{}$ over them.

$$\hat{D}_{l\alpha l'\alpha'} = \hat{d}_{l\alpha l\alpha'}\delta_{ll'}\delta_{\alpha\alpha'} + \sum_{\alpha_1}\hat{d}_{l\alpha l\alpha_1}\sum_{l_1(\neq l)}\hat{\Phi}_{l\alpha l_1\alpha_1}\hat{D}_{l_1\alpha_1 l'\alpha'} \tag{7.318}$$

We can rewrite as

$$\hat{D}^{-1}_{l\alpha l'\alpha'} = \hat{d}^{-1}_{l\alpha l\alpha'}\delta_{ll'}\delta_{\alpha\alpha'} - \hat{\Phi}_{l\alpha l'\alpha'} \tag{7.319}$$

where the inverse here is really the 2×2 block matrix inverse.

Although we started off with the locator expansion, the BEB method is really about defining effective medium quantities and fixing the effective medium by the condition that the averaged single site t-matrix is zero.

We define the effective medium Green's function. Here we label it D^{BEB} instead of D^{CPA} to use notation in line with the respective theory.

$$\hat{D}^{\text{BEB}-1}_{l\alpha l'\alpha'} \equiv M_A\omega^2\delta_{ll'}\delta_{\alpha\alpha'}\hat{\mathbb{I}} - \hat{\Sigma}^{\text{BEB}}_{\alpha\alpha'} - \hat{\Phi}_{l\alpha l'\alpha'} \tag{7.320}$$

$$= \begin{pmatrix} M_A\omega^2 & 0 \\ 0 & M_A\omega^2 \end{pmatrix}\delta_{ll'}\delta_{\alpha\alpha'} - \begin{pmatrix} \Sigma^{\text{BEB}(AA)}_{\alpha\alpha'} & \Sigma^{\text{BEB}(AB)}_{\alpha\alpha'} \\ \Sigma^{\text{BEB}(BA)}_{\alpha\alpha'} & \Sigma^{\text{BEB}(BB)}_{\alpha\alpha'} \end{pmatrix} - \begin{pmatrix} \Phi^{AA} & \Phi^{AB} \\ \Phi^{BA} & \Phi^{BB} \end{pmatrix}_{l\alpha l'\alpha'} \tag{7.321}$$

So,

$$\hat{D}^{-1}_{l\alpha l'\alpha'} = \hat{d}^{-1}_{l\alpha l\alpha'}\delta_{ll'}\delta_{\alpha\alpha'} + \hat{D}^{\text{BEB}-1}_{l\alpha l'\alpha'} - M_A\omega^2\delta_{ll'}\delta_{\alpha\alpha'}\hat{\mathbb{I}} + \hat{\Sigma}^{\text{BEB}}_{\alpha\alpha'} \tag{7.322}$$

$$= \hat{D}^{\text{BEB}-1}_{l\alpha l'\alpha'} - \left(M_A\omega^2\delta_{ll'}\delta_{\alpha\alpha'}\hat{\mathbb{I}} - \hat{d}^{-1}_{l\alpha l\alpha'} - \hat{\Sigma}^{\text{BEB}}_{\alpha\alpha'}\right) \tag{7.323}$$

$$= \hat{D}^{\text{BEB}-1}_{l\alpha l'\alpha'} - \hat{V}_{l\alpha l\alpha'}\delta_{ll'} \tag{7.324}$$

Just as in effective medium theory of CPA, we will write the equation into a T-matrix form, then take configuration average and set the condition $\langle T\rangle_c = 0$. Then define the single site t-matrix and set its average to zero. This gives us the self consistent equations of the theory. We carry it out symbolically.[8]

$$\hat{D} = \hat{D}^{\text{BEB}} + \hat{D}^{\text{BEB}}\hat{T}\hat{D}^{\text{BEB}} \tag{7.325}$$

$$\langle D\rangle_c = \hat{D}^{\text{BEB}} + \hat{D}^{\text{BEB}}\langle T\rangle_c\hat{D}^{\text{BEB}} \tag{7.326}$$

If we set $\langle\hat{T}\rangle_c = 0$, we get

$$\langle\hat{D}\rangle_c \overset{\text{BEB}}{=} \hat{D}^{\text{BEB}} \tag{7.327}$$

but as before, $\langle\hat{T}\rangle_c = 0$ is not a tractable expression so we define the (defect matrix) single site t-matrix.

$$\hat{t}_l \equiv \left(\hat{\mathbb{I}} - \hat{V}_{ll}\hat{D}^{\text{BEB}}_{ll}\right)^{-1}\hat{V}_{ll} = \left(\hat{V}^{-1}_{ll} - \hat{D}^{\text{BEB}}_{ll}\right)^{-1} \tag{7.328}$$

where the inverse is a 2×2 block matrix inverse and $\hat{D}^{\text{BEB}}_{ll}$ is the (site) diagonal part of $\hat{D}^{\text{BEB}}_{ll'}$ which is the same as that in CPA theory. For the sake of a simpler notation, we define

$$\hat{D}^{\text{BEB}}_{ll} \equiv \begin{pmatrix} \gamma_A & 0 \\ 0 & \gamma_B \end{pmatrix} = \begin{pmatrix} \left(M_A\omega^2 - \Sigma^{\text{BEB}(AA)}\right)^{-1} & 0 \\ 0 & \left(M_A\omega^2 - \Sigma^{\text{BEB}(BB)}\right)^{-1} \end{pmatrix} \tag{7.329}$$

Note that we used the physical condition that $D^{\text{BEB}(AB)}_{ll} = 0 = D^{\text{BEB}(BA)}$ and the earlier rule that $\Phi^{AA}_{ll} = 0 = \Phi^{BB}_{ll}$. (Again, one may worry about the violation of the force constant sum rule.)

We will work out $\hat{t}$ before averaging it. First we need an expression for $\hat{V}^{-1}_{ll}$.

$$\hat{V}_{ll} = M_A\omega^2\hat{\mathbb{I}} - \hat{d}^{-1}_{ll} - \hat{\Sigma}^{\text{BEB}} \tag{7.330}$$

$$= \begin{pmatrix} M_A\omega^2 & 0 \\ 0 & M_A\omega^2 \end{pmatrix} - \hat{d}^{-1} - \begin{pmatrix} \Sigma^{\text{BEB}(AA)} & \Sigma^{\text{BEB}(AB)} \\ \Sigma^{\text{BEB}(BA)} & \Sigma^{\text{BEB}(BB)} \end{pmatrix} \tag{7.331}$$

$|$ multiply $\hat{d}$ from the left

$$\hat{d}\hat{V}_{ll} = \hat{d}\begin{pmatrix} M_A\omega^2 & 0 \\ 0 & M_A\omega^2 \end{pmatrix} - \hat{\mathbb{I}} - \hat{d}\begin{pmatrix} \Sigma^{\text{BEB}(AA)} & \Sigma^{\text{BEB}(AB)} \\ \Sigma^{\text{BEB}(BA)} & \Sigma^{\text{BEB}(BB)} \end{pmatrix} \tag{7.332}$$

$|$ take inverse on both sides

[8] Configuration averaging a "defect matrix" means configuration averaging each matrix element. This can be seen by the fact that each matrix element is a component of a quantity. The quantity is the sum of the 4 components.

$$\hat{V}_{ll}^{-1}\hat{d}^{-1} = \left[\hat{d}\begin{pmatrix} M_A\omega^2 & 0 \\ 0 & M_A\omega^2 \end{pmatrix} - \hat{\mathbb{I}} - \hat{d}\begin{pmatrix} \Sigma^{\text{BEB}(AA)} & \Sigma^{\text{BEB}(AB)} \\ \Sigma^{\text{BEB}(BA)} & \Sigma^{\text{BEB}(BB)} \end{pmatrix}\right]^{-1} \tag{7.333}$$

| multiply $\hat{d}$ from the right

$$\hat{V}_{ll}^{-1} = \left[\hat{d}\begin{pmatrix} M_A\omega^2 & 0 \\ 0 & M_A\omega^2 \end{pmatrix} - \hat{\mathbb{I}} - \hat{d}\begin{pmatrix} \Sigma^{\text{BEB}(AA)} & \Sigma^{\text{BEB}(AB)} \\ \Sigma^{\text{BEB}(BA)} & \Sigma^{\text{BEB}(BB)} \end{pmatrix}\right]^{-1}\hat{d} \tag{7.334}$$

$$= \left[\begin{pmatrix} xd^A & 0 \\ 0 & yd^B \end{pmatrix}\left(\begin{pmatrix} M_A\omega^2 & 0 \\ 0 & M_A\omega^2 \end{pmatrix} - \begin{pmatrix} \Sigma^{\text{BEB}(AA)} & \Sigma^{\text{BEB}(AB)} \\ \Sigma^{\text{BEB}(BA)} & \Sigma^{\text{BEB}(BB)} \end{pmatrix}\right) - \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right]^{-1} \times \begin{pmatrix} xd^A & 0 \\ 0 & yd^B \end{pmatrix} \tag{7.335}$$

$$= -\begin{bmatrix} 1 - xd^A(M_A\omega^2 - \Sigma^{\text{BEB}(AA)} & xd^A\Sigma^{\text{BEB}(AB)} \\ yd^B\Sigma^{\text{BEB}(BA)} & 1 - yd^B(M_A\omega^2 - \Sigma^{\text{BEB}(BB)} \end{bmatrix}^{-1}\begin{pmatrix} xd^A & 0 \\ 0 & yd^B \end{pmatrix} \tag{7.336}$$

Use the 2×2 block matrix inverse,

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix}^{-1} = \begin{bmatrix} (A - BD^{-1}C)^{-1} & -(DB^{-1}A - C)^{-1} \\ -(AC^{-1}D - B)^{-1} & (D - CA^{-1}B)^{-1} \end{bmatrix} \tag{7.337}$$

We evaluate each block of the square matrix seperately.

Upper left block of square matrix

$$= \left[(1 - xd^A(M_A\omega^2 - \Sigma^{\text{BEB}(AA)})) - xd^A\Sigma^{\text{BEB}(AB)}(1 - yd^B(M_A\omega^2 - \Sigma^{\text{BEB}(BB)}))^{-1}yd^B\Sigma^{\text{BEB}(BA)}\right]^{-1}$$

| 2nd term is zero due to $xy = 0$

$$= \frac{1}{1 - xd^A(M_A\omega^2 - \Sigma^{\text{BEB(AA)}})} \tag{7.338}$$

Upper right block of square matrix

$$= -\left[(1 - yd^B(M_A\omega^2 - \Sigma^{\text{BEB}(BB)}))(xd^A\Sigma^{\text{BEB}(AB)})^{-1}(1 - xd^A(M_A\omega^2 - \Sigma^{\text{BEB}(AA)})) - yd^B\Sigma^{\text{BEB}(BA)}\right]^{-1}$$

| use $xy = 0$ in numerator

$$= -\left(\frac{1 - yd^B(M_A\omega^2 - \Sigma^{\text{BEB}(BB)}) - xd^A(M_A\omega^2 - \Sigma^{\text{BEB}(AA)})}{xd^A\Sigma^{\text{BEB}(AB)}} - yd^B\Sigma^{\text{BEB}(BA)}\right)^{-1}$$

| second term is zero when we combine fraction and get $xy = 0$

$$= -\frac{xd^A\Sigma^{\text{BEB}(AB)}}{1 - yd^B(M_A\omega^2 - \Sigma^{\text{BEB}(BB)}) - xd^A(M_A\omega^2 - \Sigma^{\text{BEB}(AA)})} \tag{7.339}$$

Very similarly,

Lower left block of square matrix

$$= -\frac{yd^B\Sigma^{\text{BEB}(BA)}}{1 - yd^B(M_A\omega^2 - \Sigma^{\text{BEB}(BB)}) - xd^A(M_A\omega^2 - \Sigma^{\text{BEB}(AA)})} \tag{7.340}$$

$$\text{Lower right block of square matrix} = \frac{1}{1 - yd^B(M_A\omega^2 - \Sigma^{\text{BEB}(BB)})} \tag{7.341}$$

$$\hat{V}_{ll}^{-1} = -\begin{pmatrix} \frac{xd^A}{1-xd^A(M_A\omega^2-\Sigma^{\mathrm{BEB}(AA)})} & 0 \\ 0 & \frac{yd^B}{1-yd^B(M_A\omega^2-\Sigma^{\mathrm{BEB}(BB)})} \end{pmatrix} \tag{7.342}$$

The $\hat{t}$-matrix is thus

$$\hat{t}_l = \left(\hat{V}_{ll}^{-1} - \hat{D}_{ll}^{\mathrm{BEB}}\right)^{-1} \tag{7.343}$$

$$= \left[-\begin{pmatrix} \frac{xd^A}{1-xd^A(M_A\omega^2-\Sigma^{\mathrm{BEB}(AA)})} & 0 \\ 0 & \frac{yd^B}{1-yd^B(M_A\omega^2-\Sigma^{\mathrm{BEB}(BB)})} \end{pmatrix} - \begin{pmatrix} \gamma_A & 0 \\ 0 & \gamma_B \end{pmatrix}\right]^{-1} \tag{7.344}$$

| take 2×2 block inverse which is trivial here

$$= \begin{pmatrix} \frac{xd^A(M_A\omega^2-\Sigma^{\mathrm{BEB}(AA)})-1}{xd^A-\gamma_A-\gamma_A xd^A(M_A\omega^2-\Sigma^{\mathrm{BEB}(AA)})} & 0 \\ 0 & \frac{yd^B(M_A\omega^2-\Sigma^{\mathrm{BEB}(BB)})-1}{yd^B-\gamma_B-\gamma_B yd^B(M_A\omega^2-\Sigma^{\mathrm{BEB}(BB)})} \end{pmatrix} \tag{7.345}$$

| recall $\gamma_A = (M_A\omega^2 - \Sigma^{\mathrm{BEB}(AA)})^{-1}$ and $\gamma_B = (M_A\omega^2 - \Sigma^{\mathrm{BEB}(BB)})^{-1}$

$$= \begin{pmatrix} \frac{1-xd^A(M_A\omega^2-\Sigma^{\mathrm{BEB}(AA)})}{\gamma_A} & 0 \\ 0 & \frac{1-yd^B(M_A\omega^2-\Sigma^{\mathrm{BEB}(BB)})}{\gamma_B} \end{pmatrix} \tag{7.346}$$

Now employ the effective medium condition $\langle t_l \rangle_c \stackrel{!}{=} 0$.

$$\langle t_l \rangle_c = \left\langle x\left(\frac{1}{\gamma_A} - \frac{1}{\gamma_A}xd^A(M_A\omega^2 - \Sigma^{\mathrm{BEB}(AA)})\right)\right\rangle_c + \left\langle y\left(\frac{1}{\gamma_B} - \frac{1}{\gamma_B}yd^B(M_A\omega^2 - \Sigma^{\mathrm{BEB}(BB)})\right)\right\rangle_c$$

| recall $d_A = \dfrac{1}{M_A\omega^2}$ and $d^B = \dfrac{1}{M_B\omega^2}$

$$= \frac{c_A}{\gamma_A}\left(1 - \frac{M_A\omega^2 - \Sigma^{\mathrm{BEB}(AA)}}{M_A\omega^2}\right) + \frac{c_B}{\gamma_B}\left(1 - \frac{M_A\omega^2 - \Sigma^{\mathrm{BEB}(BB)}}{M_B\omega^2}\right)$$

$$= \frac{c_A}{\gamma_A}\frac{\Sigma^{\mathrm{BEB}(AA)}}{M_A\omega^2} + \frac{c_B}{\gamma_B}\left(\frac{\Sigma^{\mathrm{BEB}(BB)} - (M_A\omega^2 - M_B\omega^2)}{M_B\omega^2}\right) \tag{7.347}$$

We like to suggest this scenerio to satisfy the condition $\langle t_l \rangle_c = 0$,

$$0 = \frac{c_A}{\gamma_A}\frac{c_B}{\gamma_B} - \frac{c_B}{\gamma_B}\frac{c_A}{\gamma_A} \tag{7.348}$$

So,[9]

$$\boxed{\frac{\Sigma^{\mathrm{BEB}(AA)}}{M_A\omega^2} = \frac{c_B}{\gamma_B} \Longrightarrow \Sigma^{\mathrm{BEB}(AA)} = M_A\omega^2\frac{c_B}{\gamma_B}} \tag{7.349}$$

$$\boxed{\frac{\Sigma^{\mathrm{BEB}(BB)} - (M_A\omega^2 - M_B\omega^2)}{M_B\omega^2} = -\frac{c_A}{\gamma_A} \Longrightarrow \Sigma^{\mathrm{BEB}(BB)} = -M_B\omega^2\frac{c_A}{\gamma_A} + (M_A - M_B)\omega^2} \tag{7.350}$$

And to solve for $\Sigma^{\mathrm{BEB}(AB)}$ and $\Sigma^{\mathrm{BEB}(BA)}$, we use the conditions

$$\boxed{D_{ll}^{\mathrm{BEB}(AB)} = 0 = D_{ll}^{\mathrm{BEB}(BA)}} \tag{7.351}$$

[9] Somehow the final self consistent equations here is different from [Esterling1975] eqn (43a) and eqn (43b) though the form of equations is similar.

The configuration averaged Green's function in this theory is calculated with

$$\boxed{\langle D_{ll'}\rangle_c = D_{ll'}^{\mathrm{BEB}(AA)} + D_{ll'}^{\mathrm{BEB}(AB)} + D_{ll'}^{\mathrm{BEB}(BA)} + D_{ll'}^{\mathrm{BEB}(BB)}} \tag{7.352}$$

7.6 Mass & Force constant Disorder : Kaplan & Mostoller (K&M) Theory

The main reference is [Kaplan1974]. We shall state the essential ideas of the theory before we carry out the derivation. K&M follows the analogy that CPA is a site diagonal theory, it is a "cluster diagonal" theory. Here we will assume the cluster to be the nearest neighbors of a particular site $\hat{l}$. Following K&M, site indices s denotes nearest neighbor sites around the particular site $\hat{l}$.

The model is the (standard) harmonic and disordered (in mass and in force constant disorder) Hamiltonian. The aim is to calculate the (one-particle) configuration averaged displacement-displacement Green's function. We start with the equation of motion in frequency domain for the Green's function is

$$\begin{aligned}
\delta_{\alpha\alpha'}\delta_{ll'} &= \sum_{l_1\alpha_1}\left(M_l\omega^2\delta_{\alpha\alpha_1}\delta_{ll_1} - \Phi_{l\alpha l_1\alpha_1}\right)D_{l_1\alpha_1 l'\alpha'} && (7.353)\\
&\quad \mid \ \text{where } M_l \text{ and } \Phi_{l\alpha l_1\alpha_1} \text{ are both random, single out the host quantities}\\
&= \sum_{l_1\alpha_1}\left(M_A\omega^2\delta_{\alpha\alpha_1}\delta_{ll_1} - (M_A - M_l)\,\omega^2\delta_{\alpha\alpha_1}\delta_{ll_1} - \Phi^{AA}_{l\alpha l_1\alpha_1} - \left(\Phi_{l\alpha l_1\alpha_1} - \Phi^{AA}_{l\alpha l_1\alpha_1}\right)\right)D_{l_1\alpha_1 l'\alpha'}\\
&\quad \mid \ \text{define the host Green's function } D^{A-1}_{l\alpha l_1\alpha_1} = M_A\omega^2\delta_{\alpha\alpha_1}\delta_{ll_1} - \Phi^{AA}_{l\alpha l_1\alpha_1}\\
&= \sum_{l_1\alpha_1}\left(D^{A-1}_{l\alpha l_1\alpha_1} - (M_A - M_l)\,\omega^2\delta_{\alpha\alpha_1}\delta_{ll_1} - \left(\Phi_{l\alpha l_1\alpha_1} - \Phi^{AA}_{l\alpha l_1\alpha_1}\right)\right)D_{l_1\alpha_1 l'\alpha'} && (7.354)
\end{aligned}$$

To proceed further, we need to restrict $\Phi_{l\alpha l_1\alpha_1} - \Phi^{AA}_{l\alpha l_1\alpha_1}$ to a particular model so that it is more tractable. In this theory, the additive model is used.

$$\begin{aligned}
\Phi_{l\alpha l_1\alpha_1} - \Phi^{AA}_{l\alpha l_1\alpha_1} &= \Phi_{ll_1} - \Phi^{AA}_{ll_1} && (7.355)\\
&\quad \mid \ \text{where we wrote it as Cartesian matrices}\\
&= \begin{cases} 0 & l = A, l_1 = A\\ \Phi^{AB}_{ll_1} - \Phi^{AA}_{ll_1} & l = A, l_1 = B\\ \Phi^{BA}_{ll_1} - \Phi^{AA}_{ll_1} & l = B, l_1 = A\\ \Phi^{BB}_{ll_1} - \Phi^{AA}_{ll_1} & l = B, l_1 = B\end{cases} && (7.356)\\
&\quad \mid \ \text{assume an additive relationship } \Phi^{AB}_{ll_1} = \Phi^{BA}_{ll_1} = \frac{1}{2}\left(\Phi^{AA}_{ll_1} + \Phi^{BB}_{ll_1}\right)\\
&= \begin{cases} 0 & l = A, l_1 = A\\ \frac{1}{2}\left(\Phi^{BB}_{ll_1} - \Phi^{AA}_{ll_1}\right) \equiv -\Delta & l = A, l_1 = B\\ \frac{1}{2}\left(\Phi^{BB}_{ll_1} - \Phi^{AA}_{ll_1}\right) \equiv -\Delta & l = B, l_1 = A\\ \Phi^{BB}_{ll_1} - \Phi^{AA}_{ll_1} \equiv -2\Delta & l = B, l_1 = B\end{cases} && (7.357)
\end{aligned}$$

We want to use these conditions together with a cluster description. Let $\hat{l}$ be the site at the "center of the cluster". We now assume these conditions,

$$\Phi^{\hat{l}}_{ll_1} \equiv \begin{cases} 0 & \hat{l}=A \quad l,l_1 = \text{any atom} \\ \frac{1}{2}\left(\Phi^{BB}_{ll_1}-\Phi^{AA}_{ll_1}\right)\equiv -\Delta & \hat{l}=B \quad l=A,l_1=B \\ \frac{1}{2}\left(\Phi^{BB}_{ll_1}-\Phi^{AA}_{ll_1}\right)\equiv -\Delta & \hat{l}=B \quad l=B,l_1=A \\ \Phi^{BB}_{ll_1}-\Phi^{AA}_{ll_1}\equiv -2\Delta & \hat{l}=B \quad l=B,l_1=B \end{cases} \tag{7.358}$$

So if the center of the cluster is the host atom, we assume no force constant changes. Force constant changes only when the center of the cluster is a defect atom. These rules are only for $l \neq l_1$. For $l = l_1$, we will use the force constant sum rule $\Phi_{ll} = -\sum_{l_1(\neq l)\Phi_{ll_1}}$.

The remaining derivation is in line with CPA only that we are dealing with cluster quantities instead of site diagonal scalar quantities. So we put this force constant model back into the equation of motion.

$$\begin{aligned} \delta_{ll'} &= \sum_{l_1}\left(D^{A-1}_{ll_1}-(M_A-M_l)\,\omega^2\delta_{ll_1}-\sum_{\hat{l}}^{\text{all clusters}}\Phi^{\hat{l}}_{ll_1}\right)D_{l_1l'} && (7.359)\\ &= \sum_{l_1}\left(D^{A-1}_{ll_1}-\sum_{\hat{l}}\left(\left(M_A-M_{\hat{l}}\right)\omega^2\delta_{ll_1}\delta_{l\hat{l}}+\Phi^{\hat{l}}_{ll_1}\right)\right)D_{l_1l'} && (7.360)\\ &\quad|\quad \text{define } \tilde{V}^{\hat{l}}_{ll_1}=\left(M_A-M_{\hat{l}}\right)\omega^2\delta_{ll_1}\delta_{l\hat{l}}+\Phi^{\hat{l}}_{ll_1} \\ &= \sum_{l_1}\left(D^{A-1}_{ll_1}-\sum_{\hat{l}}\tilde{V}^{\hat{l}}_{ll_1}\right)D_{l_1l'} && (7.361)\end{aligned}$$

We can rearrange it to the form of a Dyson equation.

$$\begin{aligned} D_{ll'} &= D^A_{ll'}+\sum_{l_1l_2}D^A_{ll_1}\sum_{\hat{l}}\tilde{V}^{\hat{l}}_{l_1l_2}D_{l_2l'} && (7.362)\\ \text{or,}\quad D_{ll'} &= \left(D^{A-1}-\sum_{\hat{l}}\tilde{V}^{\hat{l}}\right)^{-1}_{ll'} && (7.363)\end{aligned}$$

Just like in the effective medium derivation of CPA, we define the effective medium Green's function and self energy. We label them with a superscript "K&M".

$$D^{\text{K\&M}}_{ll'} \equiv \left(D^{A-1}-\Sigma^{\text{K\&M}}\right)^{-1}_{ll'} \tag{7.364}$$

As usual, we eliminate D^{A-1}. We carry it out symbolically using a rewritten expression from above

$$\begin{aligned} D^{A-1} &= D^{\text{K\&M}-1}+\Sigma^{\text{K\&M}} && (7.365)\\ D &= \left(D^{\text{K\&M}}-\left(\sum_{\hat{l}}\tilde{V}^{\hat{l}}-\Sigma^{\text{K\&M}}\right)\right)^{-1} && (7.366)\end{aligned}$$

For the sake of reinforcing the cluster description and to follow K&M, we will now denote nearest neighbor sites with indices s. Define

$$\Sigma^{\text{K\&M}}_{ll'} = \sum_{\hat{l}}\sum_{s_1s_2}\Sigma^{\hat{l}}_{s_1s_2}\delta_{l,s_1+\hat{l}}\delta_{l',s_2+\hat{l}} \tag{7.367}$$

$$\text{so,} \quad D = \left(D^{\text{K\&M}} - \sum_{\hat{l}} \left(\tilde{V}^{\hat{l}} - \Sigma^{\hat{l}} \right) \right)^{-1} \tag{7.368}$$

We write it into the T-matrix form using the single cluster t-matrix expression.

$$\begin{aligned}
t^{\hat{l}}_{s_1 s_2} &\equiv \sum_{s_3} \left(\tilde{V}^{\hat{l}} - \Sigma^{\hat{l}} \right)_{s_1 s_3} \left(\mathbb{I}\delta_{s_3 s_2} - \sum_{s_4} D^{\text{K\&M}}_{s_3 s_4} \left(\tilde{V}^{\hat{l}} - \Sigma^{\hat{l}} \right)_{s_4 s_2} \right)^{-1} && (7.369) \\
\Rightarrow D_{ll'} &= D^{\text{K\&M}}_{ll'} + \sum_{\hat{l}} \sum_{s_1 s_2} D^{\text{K\&M}}_{l, s_1 + \hat{l}} t^{\hat{l}}_{s_1 s_2} D^{\text{K\&M}}_{s_2 + \hat{l}, l'} && (7.370) \\
&| \quad \text{take configuration average} \\
\langle D_{ll'} \rangle_c &= D^{\text{K\&M}}_{ll'} + \left\langle \sum_{\hat{l}} \sum_{s_1 s_2} D^{\text{K\&M}}_{l, s_1 + \hat{l}} t^{\hat{l}}_{s_1 s_2} D^{\text{K\&M}}_{s_2 + \hat{l}, l'} \right\rangle_c && (7.371)
\end{aligned}$$

Then, again, the self consistency condition is where we impose the full configuration averaged T-matrix to be zero so that $\langle D_{ll'} \rangle_c = D^{\text{K\&M}}_{ll'}$ and, again, it is not tractable, so we assume that the clusters are independent which we may call this the "Single Cluster Approximation" in analogy to SSA in CPA. Then we set the single cluster configuration averaged t-matrix to zero instead.

$$\begin{aligned}
0 &= \left\langle t^{\hat{l}}_{s_1 s_2} \right\rangle_c && (7.372) \\
0 &= c_A t^{\hat{l}=A}_{s_1 s_2} + c_B t^{\hat{l}=B}_{s_1 s_2} && (7.373) \\
&| \quad \text{write as matrices in cluster (or nearest neighbors) space} \\
0 &= c_A t^{\hat{l}=A} + c_B t^{\hat{l}=B} && (7.374) \\
&| \quad \text{recall } \tilde{V}^{\hat{l}=A} = 0, \Sigma^{\hat{l}=A} = \Sigma^{\hat{l}=B} \equiv \Sigma \text{ since it is an effective medium quantity.} \\
0 &= c_A(-\Sigma) \left(\mathbb{I} - D^{\text{K\&M}}(-\Sigma) \right)^{-1} + c_B \left(\tilde{V}^{\hat{l}=B} - \Sigma \right) \left(\mathbb{I} - D^{\text{K\&M}} \left(\tilde{V}^{\hat{l}=B} - \Sigma \right) \right)^{-1} && (7.375) \\
0 &= -c_A \Sigma \left(\mathbb{I} + D^{\text{K\&M}} \Sigma \right)^{-1} - c_B \left(\Sigma - \tilde{V}^{\hat{l}=B} \right) \left(\mathbb{I} + D^{\text{K\&M}} \left(\Sigma - \tilde{V}^{\hat{l}=B} \right) \right)^{-1} && (7.376)
\end{aligned}$$

$$\boxed{-c_A \Sigma \left(\mathbb{I} + D^{\text{K\&M}} \Sigma \right)^{-1} - c_B \left(\Sigma - \tilde{V}^{\hat{l}=B} \right) \left(\mathbb{I} + D^{\text{K\&M}} \left(\Sigma - \tilde{V}^{\hat{l}=B} \right) \right)^{-1} = 0} \tag{7.377}$$

Just as in CPA, together with the Dyson equation $D^{\text{K\&M}} = \left(D_{A-1} - \Sigma^{\text{K\&M}} \right)^{-1}_{ll'}$ forms the set of self consistent equations to calculate $D^{\text{K\&M}}$.

[1D Disordered Chain Example] We want to illustrate the cluster matrices explicitly for a 1D disordered chain with 2 nearest neighbors. The cluster matrices are 3×3 in size.

$$\tilde{V}^{\hat{l}=B} = \begin{array}{c} \\ \hat{l}-1 \\ \hat{l} \\ \hat{l}+1 \end{array} \!\!\begin{array}{c} \begin{array}{ccc} \hat{l}-1 & \hat{l} & \hat{l}+1 \end{array} \\ \begin{pmatrix} 0 & 0 & 0 \\ 0 & (M_A - M_B)\omega^2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{array} + \begin{array}{c} \\ \hat{l}-1 \\ \hat{l} \\ \hat{l}+1 \end{array} \!\!\begin{array}{c} \begin{array}{ccc} \hat{l}-1 & \hat{l} & \hat{l}+1 \end{array} \\ \begin{pmatrix} \Delta & -\Delta & 0 \\ -\Delta & 2\Delta & -\Delta \\ 0 & -\Delta & \Delta \end{pmatrix} \end{array} \tag{7.378}$$

The elements in the form (row,column),

$$(\hat{l}-1, \hat{l}), (\hat{l}, \hat{l}-1), (\hat{l}, \hat{l}+1), (\hat{l}+1, \hat{l}) = -\Delta \tag{7.379}$$

are due to the rules of the force constant model. The elements,

$$(\hat{l}-1,\hat{l}-1),(\hat{l}+1,\hat{l}+1)=\Delta \quad \text{and} \quad (\hat{l},\hat{l})=2\Delta \tag{7.380}$$

are due to the force constant sum rule.

The cluster effective medium self energy is of the form,

$$\Sigma = \begin{array}{c} \\ \hat{l}-1 \\ \hat{l} \\ \hat{l}+1 \end{array} \begin{array}{c} \begin{array}{ccc} \hat{l}-1 & \hat{l} & \hat{l}+1 \end{array} \\ \left(\begin{array}{ccc} \alpha & \beta & \gamma \\ \beta & \delta & \beta \\ \gamma & \beta & \alpha \end{array}\right) \end{array} \tag{7.381}$$

based on general symmetry considerations. Thus the 4 unknowns, α, β, γ and δ have to be solved self consistently.

7.7 Mass & Force constant Disorder: Gruewald Theory

The main reference is [Gruewald1976]. The mass disorder is defined as usual with $M(l)$ being the mass random variable at site l. We define the force constant disorder model with λ being a fitting parameter of the theory.

$$\Phi_{\alpha\beta}(l,l') = \lambda_l \Phi^{AA}_{\alpha\beta}(l-l')\lambda_{l'} \tag{7.382}$$

Random variable λ_l takes on these values,

$$\lambda_l = \begin{cases} 1 & \text{if A is at } l \\ \lambda & \text{if B is at } l \end{cases} \tag{7.383}$$

We immediately get some relations which shows that we are modelling the disordered force constant as the geometric mean of the 2 ordered spring constants.

$$\Phi^{BB}_{\alpha\beta}(l,l') = \lambda^2 \Phi^{AA}_{\alpha\beta}(l,l') \tag{7.384}$$

$$\Phi^{AB}_{\alpha\beta}(l,l') = \lambda \Phi^{AA}_{\alpha\beta}(l-l') \tag{7.385}$$

$$\Rightarrow \Phi^{AB} = \sqrt{\Phi^{AA}\Phi^{BB}} \tag{7.386}$$

Again, the concern here is to calculate the configuration averaged (harmonic and disordered) Green's function. This theory requires identities coming from other Green's functions, so we define 4 Green's functions for this theory.

$$\text{displacement-displacement:} D_{\alpha\alpha'}(l,l',t) = -\frac{i}{\hbar}\langle T u_\alpha(l,t) u_{\alpha'}(l',0)\rangle \tag{7.387}$$

$$\text{displacement-momentum:} H_{\alpha\alpha'}(l,l',t) = -\frac{i}{\hbar}\langle T u_\alpha(l,t) p_{\alpha'}(l',0)\rangle \tag{7.388}$$

$$\text{momentum-displacement:} \bar{H}_{\alpha\alpha'}(l,l',t) = -\frac{i}{\hbar}\langle T p_\alpha(l,t) u_{\alpha'}(l',0)\rangle \tag{7.389}$$

$$\text{momentum-momentum:} F_{\alpha\alpha'}(l,l',t) = -\frac{i}{\hbar}\langle T p_\alpha(l,t) p_{\alpha'}(l',0)\rangle \tag{7.390}$$

where T is the usual time ordering operator (not temperature).

The equations of motion for all 4 Green's functions (after Fourier transforming to the frequency domain) are,

$$\begin{aligned}
M(l)\omega^2 D_{\alpha\alpha'}(l,l',\omega) &= \delta_{\alpha\alpha'}\delta_{ll'} + \sum_{l_2\alpha_1} \Phi_{\alpha\alpha_1}(l,l_2) D_{\alpha_1\alpha'}(l_2,l',\omega) &(7.391)\\
M(l)\omega^2 H_{\alpha\alpha'}(l,l',\omega) &= i\omega M(l)\delta_{\alpha\alpha'}\delta_{ll'} + \sum_{l_2\alpha_1} \Phi_{\alpha\alpha_1}(l,l_2) H_{\alpha_1\alpha'}(l_2,l',\omega) &(7.392)\\
\omega^2 \bar{H}_{\alpha\alpha'}(l,l',\omega) &= -i\omega\delta_{\alpha\alpha'}\delta_{ll'} + \sum_{l_2\alpha_1} \Phi_{\alpha\alpha_1}(l,l_2)\frac{1}{M(l_2)} \bar{H}_{\alpha_1\alpha'}(l_2,l',\omega) &(7.393)\\
\omega^2 F_{\alpha\alpha'}(l,l',\omega) &= \Phi_{\alpha\alpha'}(l,l') + \sum_{l_2\alpha_1} \Phi_{\alpha\alpha_1}(l,l_2)\frac{1}{M(l_2)} F_{\alpha_1\alpha'}(l_2,l',\omega) &(7.394)
\end{aligned}$$

We redefine the last equation to put it into a more comparable form with respect to the other 3 Green's functions.

$$F'_{\alpha\alpha'}(l,l') \equiv F_{\alpha\alpha'}(l,l') + M(l)\delta_{\alpha\alpha'}\delta_{ll'} \tag{7.395}$$

and its equation of motion is

$$\omega^2 F'_{\alpha\alpha'}(l,l',\omega) = M(l)\omega^2\delta_{\alpha\alpha'}\delta_{ll'} + \sum_{l_2\alpha_1} \Phi_{\alpha\alpha_1}(l,l_1)\frac{1}{M(l_1)} F'_{\alpha_1\alpha'}(l_1,l',\omega) \tag{7.396}$$

We emphasize that the quantity of interest is the configuration averaged displacement-displacement Green's function. The other Green's functions are only used to supply some self-consistent relations to close the theory. The locator method is used to carry out perturbation expansion, renomalization and multiple occupancy corrections.

Start by inserting the force constant disorder model into the equation of motion.

$$\begin{aligned}
M(l)\omega^2 D_{\alpha\alpha'}(l,l',\omega) &= \delta_{\alpha\alpha'}\delta_{ll'} + \Phi_{\alpha\alpha_1}(l,l) D_{\alpha_1\alpha'}(l,l',\omega) + \sum_{l_2(\neq l)\alpha_1} \Phi_{\alpha\alpha_1}(l,l_2) D_{\alpha_1\alpha'}(l_2,l',\omega)\\
&\quad | \quad \text{insert } \Phi_{\alpha\alpha_1}(l,l_2) = \lambda_l \Phi^{AA}_{\alpha\alpha_1}\lambda_{l_2}\\
&\quad | \quad \text{writing as matrices of Cartesian indices}\\
\left(M(l)\omega^2\mathbb{I} - \Phi(l,l)\right) D(l,l',\omega) &= \mathbb{I}\delta_{ll'} + \lambda_l \sum_{l_2(\neq l)} \Phi^{AA}(l-l_2)\lambda_{l_2} D(l_2,l',\omega) &(7.397)\\
&\quad | \quad \text{divide by } M(l)\\
\left(\omega^2\mathbb{I} - \frac{\Phi(l,l)}{M(l)}\right) D(l,l',\omega) &= \frac{\mathbb{I}}{M(l)}\delta_{ll'} + \frac{\lambda_l}{M(l)} \sum_{l_2(\neq l)} \Phi^{AA}(l-l_2)\lambda_{l_2} D(l_2,l',\omega) &(7.398)\\
&\quad | \quad \text{Divide by } \left(\omega^2\mathbb{I} - \frac{\Phi(l,l)}{M(l)}\right)\\
D(l,l',\omega) &= \frac{\delta_{ll'}}{(M(l)\omega^2\mathbb{I} - \Phi(l,l))}\\
&\quad + \frac{\lambda_l}{(M(l)\omega^2\mathbb{I} - \Phi(l,l))} \sum_{l_2(\neq l)} \Phi^{AA}(l-l_2)\lambda_{l_2} D(l_2,l',\omega) &(7.399)
\end{aligned}$$

Define the locator $d(l)^{-1} \equiv M(l)\omega^2\mathbb{I} - \Phi(l,l)$ and iterate D.

$$D(l,l',\omega) = d(l)\delta_{ll'} + \lambda_l d(l) \sum_{l_2(\neq l)} \Phi^{AA}(l-l_2)\lambda_{l_2} d(l_2)\delta_{l_2 l'} + \ldots \quad (7.400)$$

$$= d(l)\delta_{ll'} + d(l)\lambda_l \sum_{l_2} \Phi^{AA}(l-l_2)(1-\delta_{l_2 l})d(l_2)\lambda_{l_2}\delta_{l_2 l'} + \ldots \quad (7.401)$$

$$= d(l)\delta_{ll'} + d(l)\lambda_l \Phi^{AA}(l-l')(1-\delta_{ll'})d(l')\lambda_{l'} + \sum_{l_2} d(l)\lambda_l \Phi^{AA}(l-l_2)(1-\delta_{ll_2})d(l_2)\lambda_{l_2}^2 \Phi^{AA}(l_2-l')(1-\delta_{l_2 l'})d(l')\lambda_{l'} + \ldots \quad (7.402)$$

| define on the left, $d_L(l) \equiv d(l)\lambda_l$
| define on the right, $d_R(l) \equiv d(l)\lambda_l$
| define in the middle, $\tilde{d}(l) \equiv d(l)\lambda_l^2$
| and define $\Phi'(l-l') \equiv \Phi^{AA}(l-l')(1-\delta_{ll'})$

$$= d(l)\delta_{ll'} + d_L(l)\Phi'(l-l')d_R(l') + \sum_{l_2} d_L(l)\Phi'(l-l_2)\tilde{d}(l_2)\Phi'(l_2-l')d_R(l') + \ldots \quad (7.403)$$

There are 4 locators d_L, d_R, d and $\tilde{d}$ and the random variables are all contained in the locators. One can think of it as a "transfer" of randomness from the force constant to the locator via λ_l. In the spirit of the locator CPA method, we shall use the following Dyson equations to define the approximate expression for the configuration averaged Green's function. ($\langle \ldots \rangle_c$ stands for configuration averaging.)

$$\langle D(l,l',\omega)\rangle_c = \sigma\delta_{ll'} + \sigma_L U(l,l')\sigma_R \quad (7.404)$$

$$U(l,l') = \Phi'(l-l') + \sum_{l_1 l_2} \Phi'(l-l_1)\tilde{D}(l_1,l_2)\Phi'(l_2-l') \quad (7.405)$$

$$\tilde{D}(l,l') = \tilde{\sigma}\delta_{ll'} + \sum_{l_2} \tilde{\sigma}\Phi'(l-l_2)\tilde{D}(l_2,l') \quad (7.406)$$

where $U(l,l')$ is the renormalised interactor and σ, σ_L, σ_R and $\tilde{\sigma}$ are the renormalized locators of d, d_L, d_R and $\tilde{d}$ respectively.

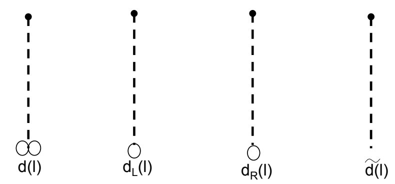


Figure 7.16: Assignment of diagrams for the (unrenormalized) locators d, d_L, d_R and $\tilde{d}$.

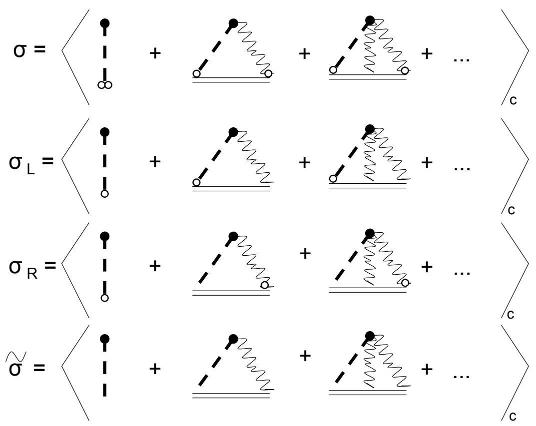


Figure 7.17: Assignment of diagrams for the (renormalized) locators σ, σ_L, σ_R and $\tilde{\sigma}$.

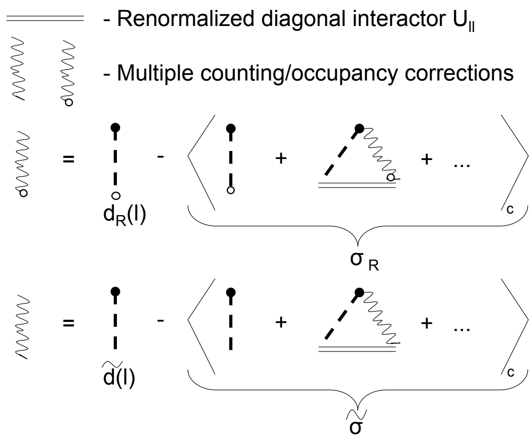


Figure 7.18: Multiple occupancy corrections. We define $\mu_R(l) \equiv d_R(l) - \sigma_R$ and $\tilde{\mu}(l) \equiv \tilde{d}(l) - \tilde{\sigma}$.

The explicit expressions for the re-summation are,

$$\begin{aligned} \sigma &= \langle d(l) + d_L U_{ll} \mu_R + d_L U_{ll} \tilde{\mu} U_{ll} \mu_R + \ldots \rangle && (7.407) \\ &= \langle d(l) + d_L (\mathbb{I} + U_{ll} \tilde{\mu} + \ldots) U_{ll} \mu_R \rangle && (7.408) \\ &= \langle d(l) + d_L(l) (\mathbb{I} - U_{ll} \tilde{\mu})^{-1} U_{ll} \mu_R \rangle && (7.409) \end{aligned}$$

$$\begin{aligned} \sigma_L &= \langle d_L(l) + d_L(l) U_{ll} \tilde{\mu}(l) + d_L(l) U_{ll} \tilde{\mu}(l) U_{ll} \tilde{\mu}(l) + \ldots \rangle && (7.410) \\ &= \langle d_L(l) (\mathbb{I} + U_{ll} \tilde{\mu}(l) + U_{ll} \tilde{\mu}(l) U_{ll} \tilde{\mu}(l) + \ldots) \rangle && (7.411) \\ &= \langle d_L(l) (\mathbb{I} - U_{ll} \tilde{\mu}(l))^{-1} \rangle && (7.412) \end{aligned}$$

Similarly for σ_R and $\tilde{\sigma}$, we get the results,

$$\begin{aligned} \sigma_R &= \langle d_R(l) + \tilde{d}(l) (\mathbb{I} - U_{ll} \tilde{\mu}(l))^{-1} U_{ll} \mu_R(l) \rangle && (7.413) \\ \tilde{\sigma} &= \langle \tilde{d}(l) (\mathbb{I} - U_{ll} \tilde{\mu}(l))^{-1} \rangle && (7.414) \end{aligned}$$

where U_{ll} is the diagonal part of $U(l, l')$. We eliminate U in favour of $\tilde{D}$ (writing in matrices of ll' and

$\alpha\alpha'$),

$$\begin{aligned}
U &= \Phi' + \Phi'\tilde{D}\Phi' && (7.415)\\
\tilde{D} &= \tilde{\sigma} + \tilde{\sigma}\Phi'\tilde{D} && (7.416)\\
&| \;\; \text{make } \Phi' \text{ the subject}\\
\Phi' &= \tilde{\sigma}^{-1}(\tilde{D} - \tilde{\sigma})\tilde{D}^{-1} && (7.417)\\
&= \tilde{\sigma}^{-1} - \tilde{D}^{-1} && (7.418)\\
&| \;\; \text{substitute into the first equation,}\\
U &= (\tilde{\sigma}^{-1} - \tilde{D}^{-1}) + (\tilde{\sigma}^{-1} - \tilde{D}^{-1})\tilde{D}(\tilde{\sigma}^{-1} - \tilde{D}^{-1}) && (7.419)\\
&= \tilde{\sigma}^{-1}\tilde{D}\tilde{\sigma}^{-1} - \tilde{\sigma}^{-1} && (7.420)\\
U(l, l') &= \tilde{\sigma}^{-1}(l)\tilde{D}(l, l')\tilde{\sigma}^{-1}(l) - \tilde{\sigma}^{-1}(l)\delta_{ll'} && (7.421)\\
\Rightarrow U_{ll} &= \tilde{\sigma}^{-1}\tilde{D}_{ll}\tilde{\sigma}^{-1} - \tilde{\sigma}^{-1} && (7.422)
\end{aligned}$$

where $\tilde{D}_{ll}$ is the diagonal of $\tilde{D}(l, l')$. Insert the expression of U_{ll} into $\tilde{\sigma}$

$$\begin{aligned}
\tilde{\sigma} &= \langle \tilde{d}(l)(\mathbb{I} - \tilde{\sigma}^{-1}\tilde{D}_{ll}\tilde{\sigma}\tilde{\mu} + \tilde{\sigma}^{-1}\tilde{\mu})^{-1}\rangle_c && (7.423)\\
&| \;\; \text{use } \tilde{\sigma}^{-1}\tilde{\mu} = \tilde{\sigma}^{-1}(\tilde{d} - \tilde{\sigma}) = \tilde{\sigma}^{-1}\tilde{d} - \mathbb{I}\\
&= \langle(-\tilde{\sigma}^{-1}\tilde{D}_{ll}\tilde{\sigma}^{-1} + \tilde{\sigma}^{-1}\tilde{D}_{ll}\tilde{d}^{-1} + \tilde{\sigma}^{-1})^{-1}\rangle_c && (7.424)\\
&= \langle\tilde{\sigma}(\mathbb{I} + \tilde{D}_{ll}(\tilde{d}^{-1} - \tilde{\sigma}^{-1}))^{-1}\rangle_c && (7.425)\\
&| \;\; \text{we can take } \tilde{\sigma} \text{ out since it is an averaged quantity.}\\
&= \tilde{\sigma}\langle(\mathbb{I} + \tilde{D}_{ll}(\tilde{d}^{-1} - \tilde{\sigma}^{-1}))^{-1}\rangle_c && (7.426)\\
\Rightarrow \mathbb{I} &= \langle(\mathbb{I} + \tilde{D}_{ll}(\tilde{d}^{-1} - \tilde{\sigma}^{-1}))^{-1}\rangle_c && (7.427)\\
&| \;\; \text{let } \eta(l) = (\mathbb{I} + \tilde{D}_{ll}(\tilde{d}^{-1} - \tilde{\sigma}^{-1}))^{-1}\\
&= \langle\eta(l)\rangle_c && (7.428)\\
&= c_A\eta_A + c_B\eta_B && (7.429)
\end{aligned}$$

Similarly for the other 3 renormalized locators, we get,

$$\begin{aligned}
\sigma &= \langle d_L(l)\tilde{d}^{-1}(l)\eta(l)\tilde{D}_{ll}\tilde{d}^{-1}(l)d_R(l)\rangle - \langle d_L(l)\tilde{d}^{-1}(l)\eta(l)\rangle(\tilde{D}_{ll} - \tilde{\sigma})\langle\eta^\dagger(l)\tilde{d}^{-1}(l)d_R(l)\rangle_c && (7.430)\\
\sigma_L &= \langle d_L(l)\tilde{d}^{-1}(l)\eta(l)\rangle_c\tilde{\sigma} && (7.431)\\
\sigma_R &= \tilde{\sigma}\langle\eta^\dagger(l)\tilde{d}^{-1}(l)d_R(l)\rangle_c && (7.432)
\end{aligned}$$

Now we can substitute all 4 expressions back to calculate $\langle D(l, l', \omega)\rangle_c$,

$$\begin{aligned}
\langle D(l, l', \omega)\rangle_c &= \sigma(l)\delta_{ll'} + \sigma_L(l)U(l, l')\sigma_R(l') && (7.433)\\
&= \sigma(l)\delta_{ll'} + \sigma_L(l)\tilde{\sigma}^{-1}(l)\tilde{D}(l, l')\tilde{\sigma}^{-1}(l')\sigma_R(l') - \sigma_L(l)\tilde{\sigma}^{-1}(l)\delta_{ll'}\sigma_R(l') && (7.434)\\
&| \;\; \text{let } d_L(l)\tilde{d}^{-1}(l) \equiv a_L(l) = \frac{1}{\lambda_l}\\
&| \;\; \text{let } \tilde{d}^{-1}(l)d_R(l) \equiv a_R(l) = \frac{1}{\lambda_l}\\
&= \langle a_L(l)\eta(l)\tilde{D}_{ll}a_R(l)\rangle_c\delta_{ll'} - \langle a_L(l)\eta(l)\rangle_c(\tilde{D}_{ll} - \tilde{\sigma})\langle\eta^\dagger(l')a_R(l')\rangle_c\delta_{ll'}\\
&\quad + \langle a_L(l)\eta(l)\rangle_c\tilde{D}(l, l')\langle\eta^\dagger(l')a_R(l')\rangle_c - \langle a_L(l)\eta(l)\rangle_c\tilde{\sigma}\langle\eta^\dagger(l')a_R(l')\rangle_c\delta_{ll'} && (7.435)\\
&| \;\; \text{the 2 } \tilde{\sigma} \text{ terms cancel.}\\
&= \langle a_L(l)\eta(l)\tilde{D}_{ll}a_R(l)\rangle_c\delta_{ll'} + \langle a_L(l)\eta(l)\rangle_c\tilde{D}(l, l')(1 - 1\delta_{ll'})\langle\eta^\dagger(l')a_R(l')\rangle_c && (7.436)
\end{aligned}$$

Since now they are single site averages, we can calculate them explicitly. Right now, we still need to solve for 2 quantities, $\tilde{D}$ and η before we can evaluate $\langle D\rangle_c$.

First we tackle $\tilde{D}(l,l')$. We recall the earlier equation

$$\tilde{D}(l,l') = \tilde{\sigma}\delta_{ll'} + \sum_{l_2} \tilde{\sigma}(l)\Phi'(l-l_2)\tilde{D}(l_2,l') \tag{7.437}$$

We want to write it into another form that relates it to the host lattice Green's function. In matrix form,

$$\begin{aligned}
\tilde{D} &= \tilde{\sigma} + \tilde{\sigma} + \tilde{\sigma}\Phi'\tilde{D} & (7.438)\\
(\tilde{\sigma}^{-1} - \Phi')\tilde{D} &= \mathbb{I} & (7.439)\\
\tilde{D} &= (\tilde{\sigma}^{-1} - \Phi')^{-1} & (7.440)
\end{aligned}$$

Add and subtract $M_A\omega^2$ and write out $\Phi' = \Phi^{AA}(1-\delta_{ll'})$

$$\begin{aligned}
\tilde{D} &= (M_A\omega^2 - M_A\omega^2 + \tilde{\omega}^{-1} - \Phi^{AA}(l-l')(1-\delta_{ll'}))^{-1} & (7.441)\\
&\mid \quad \text{define } D^A(l,l')^{-1} \equiv M_A\omega^2 - \Phi^{AA}(l-l') \\
&\mid \quad \text{define } \tilde{\Sigma} \equiv M_A\omega^2 - \Phi^{AA}_{ll} - \tilde{\sigma}^{-1} \\
&= \left(D^A(l,l')^{-1} - \tilde{\Sigma}\right)^{-1} & (7.442)\\
&\mid \quad \text{normal decompose with respect to the host lattice } A \\
&= \frac{1}{N}\sum_{j\vec{q}} \epsilon_\alpha(j\vec{q})\epsilon_{\alpha'}(j\vec{q})e^{i\vec{q}\cdot(l-l')}\frac{1}{M_A\omega^2 - M_A\omega_A^2(j\vec{q}) - \tilde{\Sigma}} & (7.443)\\
&\equiv \frac{1}{N}\sum_{j\vec{q}} \epsilon_\alpha(j\vec{q})\epsilon_{\alpha'}(j\vec{q})e^{i\vec{q}\cdot(l-l')}\tilde{D}(j\vec{q},\omega) & (7.444)
\end{aligned}$$

The Green's function of the host lattice, D^A is assumed to be known. We can derive a self-consistent equation for $\tilde{\Sigma}$ based on the knowledge of the host lattice. First we simplify by assuming a cubic symmetry with which $\Phi^{AA}(l,l)$ is proportional to the unit matrix. We also need the diagonal quantity,

$$\begin{aligned}
\tilde{D}_{l\alpha l\alpha} &= \frac{1}{N}\sum_{j\vec{q}} \epsilon_\alpha(j\vec{q})\epsilon_\alpha(j\vec{q})\tilde{D}(j\vec{q},\omega) & (7.445)\\
&= \frac{1}{N}\sum_{j\vec{q}} \tilde{D}(j\vec{q},\omega) & (7.446)\\
&\equiv \frac{f(\omega)}{M_A} & (7.447)
\end{aligned}$$

Explicitly,

$$\begin{aligned}
f(\omega) &= \frac{M_A}{N}\sum_{j\vec{q}} \frac{1}{\omega^2 - \omega_A^2(j\vec{q}) - \tilde{\Sigma}/M_A} & (7.448)\\
&\mid \quad \text{define } \tilde{\epsilon} = \frac{\tilde{\Sigma}}{M_A\omega^2} \\
&= \frac{M_A}{N}\sum_{j\vec{q}} \frac{1}{\omega^2(1-\tilde{\epsilon}) - \omega_A^2(j\vec{q})} & (7.449)
\end{aligned}$$

The normal mode component of the configuration averaged Green's function is,

$$
\begin{aligned}
& \langle D(j\vec{q},\omega)\rangle_c && (7.450)\\
= \;& \langle a_L(l)\eta(l)a_R(l)\rangle_c \tilde{D}_{ll} + \langle a_L(l)\eta(l)\rangle_c (\tilde{D}(j\vec{q},\omega) - \tilde{D}_{ll})\langle \eta^\dagger(l')a_R(l')\rangle_c && (7.451)\\
| \;& \text{substitute } \tilde{D}_{ll} = f(\omega)/M_A \text{ and } a_L(l) = \frac{1}{\lambda_l} = a_R(l) \\
= \;& \left\langle \eta(l)\frac{1}{\lambda_l^2}\right\rangle_c \frac{f(\omega)}{M_A} + \left\langle \frac{1}{\lambda_l}\eta(l)\right\rangle_c (\tilde{D}(j\vec{q},\omega) - f(\omega)/M_A)\left\langle \frac{1}{\lambda_{l'}}\eta(l')\right\rangle_c && (7.452)\\
| \;& \text{take the single site averages}\\
| \;& \text{use the relation to eliminate } \eta_A,\ \langle \eta\rangle_c = 1 \Rightarrow c_A\eta_A + c_B\eta_B = 1 \Rightarrow c_A\eta_A = 1 - c_B\eta_B\\
= \;& \left(1 - c_B\eta_B + \frac{c_B\eta_B}{\lambda^2}\right)\frac{f(\omega)}{M_A} + \left(1 + c_B\eta_B\left(\frac{1}{\lambda}-1\right)\right)^2\left(\tilde{D}(j\vec{q},\omega) - \frac{f(\omega)}{M_A}\right) && (7.453)\\
= \;& \frac{f(\omega)}{M_A}\left(1 - c_B\eta_B + \frac{c_B\eta_B}{\lambda^2} - \left(1 + c_B\eta_B\left(\frac{1}{\lambda}-1\right)\right)^2\right) + \tilde{D}(j\vec{q},\omega)\left(1 + c_B\eta_B\left(\frac{1}{\lambda}-1\right)\right)^2 \\
= \;& \frac{f(\omega)}{M_A}\left(c_B\eta_B\left(\frac{1}{\lambda}-1\right)^2 - (c_B\eta_B)^2\left(\frac{1}{\lambda}-1\right)^2\right) + \tilde{D}(j\vec{q},\omega)\left(1 + c_B\eta_B\left(\frac{1}{\lambda}-1\right)\right)^2 && (7.454)\\
= \;& \frac{f(\omega)}{M_A}(1 - c_B\eta_B)c_B\eta_B\left(\frac{1}{\lambda}-1\right)^2 + \tilde{D}(j\vec{q},\omega)\left(1 + c_B\eta_B\left(\frac{1}{\lambda}-1\right)\right)^2 && (7.455)\\
| \;& \text{let } \mathcal{D} \equiv c_B\eta_B\\
= \;& \frac{1}{M_A}\left[f(\omega)(1-\mathcal{D})\mathcal{D}\left(\frac{1}{\lambda}-1\right)^2 + \left(1 + \mathcal{D}\left(\frac{1}{\lambda}-1\right)\right)^2 \frac{1}{\omega^2(1-\tilde{\epsilon}) - \omega_A^2(j\vec{q})}\right] && (7.456)
\end{aligned}
$$

So this final equation has 2 unknowns, $\tilde{\epsilon}$ and $\mathcal{D}$. We will determine these 2 unknowns by using identities from 2 other Green's functions, namely $\bar{H}$ and F'.

[Derivation of equations to solve $\tilde{\epsilon}$ and $\mathcal{D}$] We start by deriving an exact relation from the equation of motion of $\bar{H}$ and from the force constant sum-rule. Recall the equation of motion of $\bar{H}$,

$$
\begin{aligned}
\omega^2 \bar{H}_{\alpha\alpha'}(l,l',\omega) &= -i\omega\delta_{\alpha\alpha'}\delta_{ll'} + \sum_{l_2\alpha_1}\Phi_{\alpha\alpha_1}(l,l_2)\frac{1}{M(l_2)}\bar{H}_{\alpha_1\alpha'}(l_2,l',\omega) && (7.457)\\
&| \;\; \text{sum over } l \text{ and use the sum-rule } \sum_l \Phi_{\alpha\alpha'}(l,l') = 0\\
\omega^2\sum_l \bar{H}_{\alpha\alpha'}(l,l',\omega) &= -i\omega\delta_{\alpha\alpha'} && (7.458)\\
&| \;\; \text{take configuration average}\\
\left\langle \sum_l \bar{H}_{\alpha\alpha'}(l,l',\omega)\right\rangle_c &= -\frac{i}{\omega}\delta_{\alpha\alpha'} && (7.459)\\
&| \;\; \text{realise that this is } \vec{q}=0 \text{ Fourier component.}\\
\left\langle \bar{H}_{\alpha\alpha'}(\vec{q}=0,\omega)\right\rangle_c &= -\frac{i}{\omega}\delta_{\alpha\alpha'} && (7.460)
\end{aligned}
$$

Now we repeat the calculation that was done for the displacement-displacement Green's function in order to obtain an explicit expression for the left hand side of the above equation. We start by writing the equation of motion into the locator form.

$$\begin{aligned}&\omega^2\bar{H}_{\alpha\alpha'}(l,l',\omega)\\=\;&-i\omega\delta_{\alpha\alpha'}\delta_{ll'}+\Phi_{\alpha\alpha'}(l,l)\frac{1}{M(l)}\bar{H}_{\alpha_1\alpha'}(l,l',\omega)+\sum_{l_2(\neq l)\alpha_1}\lambda_l\Phi^{AA}_{\alpha\alpha_1}(l-l_2)\frac{1}{M(l_2)}\lambda_{l_2}\bar{H}_{\alpha_1\alpha'}(l_2,l',\omega)\end{aligned}\tag{7.461}$$

writing as matrices of Cartesian indices,

$$\left(\omega^2\mathbb{I}-\frac{\Phi(l,l)}{M(l)}\right)\bar{H}(l,l',\omega)=-i\omega\mathbb{I}\delta_{ll'}+\lambda_l\sum_{l_2(\neq l)}\Phi^{AA}(l-l_2)\frac{\lambda_{l_2}}{M(l_2)}\bar{H}(l_2,l',\omega)\tag{7.462}$$

again, multiply by $M(l)$ and divide by $M(l)\omega^2\mathbb{I}-\Phi_{ll}$,

$$\bar{H}(l,l',\omega)=\frac{-i\omega M(l)}{M(l)\omega^2\mathbb{I}-\Phi_{ll}}\delta_{ll'}+\frac{M(l)\lambda_l}{M(l)\omega^2\mathbb{I}-\Phi(l,l)}\sum_{l_2(\neq l)}\Phi^{AA}(l-l_2)\frac{\lambda_{l_2}}{M(l_2)}\bar{H}(l_2,l',\omega)\tag{7.463}$$

From this expression, it is now clear that the details of the subsequent derivation is the same, the only difference lies in the definition of the locators d, d_L, d_R and $\tilde{d}$ which we can now define for $\bar{H}$ from the above equation,

$$d(l) \equiv -i\omega M(l)(M(l)\omega^2\mathbb{I}-\Phi_{ll})^{-1}\tag{7.464}$$
$$d_L(l) \equiv M(l)\lambda_l(M(l)\omega^2\mathbb{I}-\Phi_{ll})^{-1}\tag{7.465}$$
$$d_R(l) \equiv -i\omega\lambda_l(M(l)\omega^2\mathbb{I}-\Phi_{ll})^{-1}\tag{7.466}$$
$$\tilde{d}(l) \equiv \lambda_l^2(M(l)\omega^2\mathbb{I}-\Phi_{ll})^{-1}\tag{7.467}$$

and subsequently,

$$a_L(l) \equiv d_L(l)\tilde{d}^{-1}(l)=\frac{M(l)}{\lambda_l}\tag{7.468}$$
$$a_R(l) \equiv \tilde{d}^{-1}(l)d_R(l)=-\frac{i\omega}{\lambda_l}\tag{7.469}$$

Thus we can directly calculate the normal mode component of $\langle\bar{H}\rangle_c$,

$$\begin{aligned}&\langle\bar{H}(j\vec{q},\omega)\rangle_c\\=\;&\langle a_L(l)\eta(l)a_R(l)\rangle_c\frac{f(\omega)}{M_A}+\langle a_L(l)\eta(l)\rangle_c\left(\tilde{D}(j\vec{q},\omega)-\frac{f(\omega)}{M_A}\right)\langle\eta^\dagger(l')a_R(l')\rangle_c\end{aligned}\tag{7.470}$$

$$\begin{aligned}&\langle\bar{H}(j\vec{q},\omega)\rangle_c\frac{i}{\omega}\\=\;&\left\langle\eta(l)\frac{M(l)}{\lambda_l^2}\right\rangle_c\frac{f(\omega)}{M_A}+\left\langle\frac{M(l)}{\lambda_l}\eta(l)\right\rangle_c\left(\tilde{D}(j\vec{q},\omega)-\frac{f(\omega)}{M_A}\right)\left\langle\frac{1}{\lambda_{l'}}\eta(l')\right\rangle_c\end{aligned}\tag{7.471}$$

$$\begin{aligned}|\;&\text{take the single site averages and use } c_A\eta_A=1-c_B\eta_B \text{ to eliminate } \eta_A\\=\;&\left(1-c_B\eta_B+c_B\eta_B\frac{M_B}{M_A}\frac{1}{\lambda^2}\right)f(\omega)\\&+\left((1-c_B\eta_B)M_A+c_B\eta_B\frac{M_B}{\lambda}\right)\left(\tilde{D}(j\vec{q},\omega)-\frac{f(\omega)}{M_A}\right)\left(1-c_B\eta_B+\frac{1}{\lambda}c_B\lambda_B\right)\end{aligned}\tag{7.472}$$

$$
\begin{aligned}
&= f(\omega)\left(1 - c_B\eta_B + c_B\eta_B\frac{M_B}{M_A}\frac{1}{\lambda^2} - 1 - \left(\frac{1}{\lambda}-1\right)c_B\eta_B - \left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)c_B\eta_B\right. \\
&\quad \left. - \left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)\left(\frac{1}{\lambda}-1\right)(c_B\eta_B)^2\right) \\
&\quad + \tilde{D}(j\vec{q},\omega)M_A\left(1+\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)c_B\eta_B\right)\left(1+\left(\frac{1}{\lambda}-1\right)c_B\eta_B\right) \qquad (7.473) \\
&= f(\omega)\left(\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)\frac{1}{\lambda}c_B\eta_B - \left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)c_B\eta_B - \left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)\left(\frac{1}{\lambda}-1\right)(c_B\eta_B)^2\right) \\
&\quad + \tilde{D}(j\vec{q},\omega)M_A\left(1+\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)c_B\eta_B\right)\left(1+\left(\frac{1}{\lambda}-1\right)c_B\eta_B\right) \qquad (7.474) \\
&= f(\omega)\left(\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)\left(\frac{1}{\lambda}-1\right)c_B\eta_B(1-c_B\eta_B)\right) \\
&\quad + \tilde{D}(j\vec{q},\omega)M_A\left(1+\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)c_B\eta_B\right)\left(1+\left(\frac{1}{\lambda}-1\right)c_B\eta_B\right) \qquad (7.475) \\
&| \quad \text{recall the expression for } \tilde{D}(j\vec{q},\omega) \\
&= f(\omega)\left(\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)\left(\frac{1}{\lambda}-1\right)c_B\eta_B(1-c_B\eta_B)\right) \\
&\quad + \left(1+\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)c_B\eta_B\right)\left(1+\left(\frac{1}{\lambda}-1\right)c_B\eta_B\right)\frac{1}{\omega^2(1-\tilde{\epsilon})-\omega_A^2(j\vec{q})} \qquad (7.476)
\end{aligned}
$$

We can now relate this expression to our exact relation for $\bar{H}$ obtained earlier. Take $\vec{q}=0$ and since we only have acoustic modes (in our cubic example), we have $\omega_A^2(j\vec{q}=0)=0$.

$$
\begin{aligned}
&\langle \bar{H}(j\vec{q}=0,\omega)\rangle\frac{i}{\omega} \\
&= f(\omega)\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)\left(\frac{1}{\lambda}-1\right)c_B\eta_B(1-c_B\eta_B) \\
&\quad + \left(1+\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)c_B\eta_B\right)\left(1+\left(\frac{1}{\lambda}-1\right)c_B\eta_B\right)\frac{1}{\omega^2(1-\tilde{\epsilon})} \qquad (7.477)
\end{aligned}
$$

Use the exact relation $\langle \bar{H}(j\vec{q}=0,\omega)\rangle = -\frac{i}{\omega}$ and define these notation, $\mathcal{D}\equiv c_B\eta_B$, $\epsilon = 1-\frac{M_B}{M_A}$, $\beta \equiv \frac{M_B}{M_A}\frac{1}{\lambda}-1 = \frac{1-\epsilon}{\lambda}-1$ and $\delta = \frac{1}{\lambda}-1$. We get,

$$
1 = \beta\delta\omega^2 f(\omega)\mathcal{D}(1-\mathcal{D}) + (1+\beta\mathcal{D})(1+\delta\mathcal{D})\frac{1}{1-\tilde{\epsilon}} \qquad (7.478)
$$

Now we repeat the whole procedure for F'. First, based on the derivation of an exact relation for $\bar{H}$, we write down an exact relation for F',

$$
\langle F'_{\alpha\alpha'}(\vec{q}=0,\omega)\rangle = \langle M(l)\rangle\delta_{\alpha\alpha'} = (c_AM_A + c_BM_B)\delta_{\alpha\alpha'} \qquad (7.479)
$$

Then we write the equation of motion of F' into the locator form in order to derive an equation for the left hand side.

$$
\begin{aligned}
&\omega^2 F'_{\alpha\alpha'}(l,l',\omega) \\
&= M(l)\omega^2\delta_{\alpha\alpha'}\delta_{ll'} + \sum_{l_2\alpha_1}\Phi_{\alpha\alpha_1}(l,l_2)\frac{1}{M(l_2)}F'_{\alpha_1\alpha'}(l_2,l',\omega) \qquad (7.480)
\end{aligned}
$$

$$= \quad M(l)\omega^2\delta_{\alpha\alpha'}\delta_{ll'} + \Phi_{\alpha\alpha_1}(l,l)\frac{1}{M(l)}F'_{\alpha_1\alpha'}(l,l',\omega) + \sum_{l_2(\neq l)\alpha_1}\lambda_l\Phi^{AA}_{\alpha\alpha_1}(l-l_2)\frac{1}{M(l_2)}\lambda_{l_2}F'_{\alpha_1\alpha'}(l_2,l',\omega) \tag{7.481}$$

Writing as matrices of Cartesian indices,

$$\left(\omega\mathbb{I} - \frac{\Phi_{ll}}{M(l)}\right)F'(l,l',\omega) = M(l)\omega^2\delta_{ll'}\mathbb{I} + \lambda_l\sum_{l_2(\neq l)}\Phi^{AA}(l-l_2)\frac{\lambda_{l_2}}{M(l_2)}F'(l_2,l',\omega) \tag{7.482}$$

multiply by $M(l)$ and divide by $M(l)\omega^2\mathbb{I} - \Phi_{ll}$,

$$F'(l,l',\omega) = \frac{M(l)^2\omega^2}{M(l)\omega^2\mathbb{I} - \Phi_{ll}}\delta_{ll'} + \frac{M(l)\lambda_l}{M(l)\omega^2\mathbb{I} - \Phi(l,l)}\sum_{l_2(\neq l)}\Phi^{AA}(l-l_2)\frac{\lambda_{l_2}}{M(l_2)}F'(l_2,l',\omega) \tag{7.483}$$

We again define the locators,

$$d(l) \equiv M(l)^2\omega^2(M(l)\omega^2\mathbb{I} - \Phi_{ll})^{-1} \tag{7.484}$$
$$d_L(l) \equiv \omega^2\lambda_l M(l)(M(l)\omega^2\mathbb{I} - \Phi_{ll})^{-1} \tag{7.485}$$
$$d_R(l) \equiv \lambda_l M(l)(M(l)\omega^2\mathbb{I} - \Phi_{ll})^{-1} \tag{7.486}$$
$$\tilde{d}(l) \equiv \lambda_l^2(M(l)\omega^2\mathbb{I} - \Phi_{ll})^{-1} \tag{7.487}$$

and also define

$$a_L(l) \equiv d_L(l)\tilde{d}^{-1}(l) = \frac{\omega^2 M(l)}{\lambda_l} \tag{7.488}$$
$$a_R(l) \equiv \tilde{d}^{-1}(l)d_R(l) = \frac{M(l)}{\lambda_l} \tag{7.489}$$

Now we can calculate the normal mode component of the configuration averaged Green's function directly.

$$\langle F'(j\vec{q},\omega)\rangle_c$$
$$= \langle a_L(l)\eta(l)a_R(l)\rangle_c\frac{f(\omega)}{M_A} + \langle a_L(l)\eta(l)\rangle_c\left(\tilde{D}(j\vec{q}) - \frac{f(\omega)}{M_A}\right)\langle\eta^\dagger(l')a_R(l')\rangle_c \tag{7.490}$$
$$= \left\langle\frac{\omega^2 M(l)^2}{\lambda_l^2}\eta(l)\right\rangle_c\frac{f(\omega)}{M_A} + \left\langle\frac{\omega^2 M(l)}{\lambda_l}\eta(l)\right\rangle_c\left(\tilde{D}(j\vec{q},\omega) - \frac{f(\omega)}{M_A}\right)\left\langle\eta(l')\frac{M(l')}{\lambda_{l'}}\right\rangle_c \tag{7.491}$$

| again, use $c_A\eta_A = 1 - c_B\eta_B$ to eliminate η_A

$$\langle F'(j\vec{q},\omega)\rangle_c\frac{1}{\omega^2}$$
$$= \left(M_A^2(1-c_B\eta_B) + c_B\eta_B\frac{M_B^2}{\lambda^2}\right)\frac{f(\omega)}{M_A} + \left(M_A(1-c_B\eta_B) + c_B\eta_B\frac{M_B}{\lambda}\right)^2\left(\tilde{D}(j\vec{q},\omega) - \frac{f(\omega)}{M_A}\right)$$
$$= f(\omega)M_A\left(1 - c_B\eta_B + c_B\eta_B\frac{M_B^2}{M_A^2}\frac{1}{\lambda^2} - \left(1 + \left(\frac{M_B}{M_A}\frac{1}{\lambda} - 1\right)c_B\eta_B\right)^2\right)$$
$$+M_A^2\left(1 + \left(\frac{M_B}{M_A}\frac{1}{\lambda} - 1\right)c_B\eta_B\right)^2\tilde{D}(j\vec{q},\omega) \tag{7.492}$$

$$\begin{aligned}
&= f(\omega)M_A\left(c_B\eta_B\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)\left(\frac{M_B}{M_A}\frac{1}{\lambda}+1-2\right)-\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)^2(c_B\eta_B)\right)\\
&\quad +M_A^2\left(1+\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)c_B\eta_B\right)^2\tilde{D}(j\vec{q},\omega) \qquad (7.493)\\
&\mid \ \text{use the explicit expression for } \tilde{D}(j\vec{q},\omega)\\
&= M_A\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)^2 c_B\eta_B(1-c_B\eta_B)f(\omega)\\
&\quad +M_A\left(1+\left(\frac{M_B}{M_A}\frac{1}{\lambda}-1\right)c_B\eta_B\right)^2\frac{1}{\omega^2(1-\tilde{\epsilon})-\omega_A^2(j\vec{q})} \qquad (7.494)
\end{aligned}$$

We use the earlier relation $\langle F'(j\vec{q}=0,\omega)\rangle_c = c_AM_A + c_BM_B$ and again for acoustic modes $\omega_A^2(j\vec{q}=0)=0$. We also use the earlier defined notations, $c_B\eta_B \equiv \mathcal{D}$, $\epsilon \equiv 1-\frac{M_B}{M_A}$ and $\beta \equiv \frac{M_B}{M_A}\frac{1}{\lambda}-1 = \frac{1-\epsilon}{\lambda}-1$.

$$\begin{aligned}
\frac{c_AM_A+c_BM_B}{M_A\omega^2} &= \beta^2 f(\omega)\mathcal{D}(1-\mathcal{D})+(1+\beta\mathcal{D})^2\frac{1}{\omega^2(1-\tilde{\epsilon})} &(7.495)\\
&\mid \ \text{use } c_A+c_B=1\\
1-c_B\epsilon &= \beta^2\omega^2 f(\omega)\mathcal{D}(1-\mathcal{D})+(1+\beta\mathcal{D})^2\frac{1}{1-\tilde{\epsilon}} &(7.496)
\end{aligned}$$

With these 2 equations from $\bar{H}$ and F' we can now evaluate $\mathcal{D}$ and $\tilde{\epsilon}$. We rewrite the equation from F' as $\frac{1}{\beta}\left(1-c_B\epsilon-(1+\beta\mathcal{D})^2\frac{1}{1-\tilde{\epsilon}}\right)=\beta\omega^2 f(\omega)\mathcal{D}(1-\mathcal{D})$ and substitute into the equation from $\bar{H}$, then make $\mathcal{D}$ the subject.

$$\begin{aligned}
1 &= \frac{\delta}{\beta}\left(1-c_B\epsilon-(1+\beta\mathcal{D})^2\frac{1}{1-\tilde{\epsilon}}\right)+(1+\beta\mathcal{D})(1+\delta\mathcal{D})\frac{1}{1-\tilde{\epsilon}} &(7.497)\\
\frac{\beta}{\delta} &= 1-c_B\epsilon+(1+\beta\mathcal{D})\frac{1}{1-\tilde{\epsilon}}\left(\frac{\beta}{\delta}(1+\delta\mathcal{D})-(1+\beta\mathcal{D})\right) &(7.498)\\
&= 1-c_B\epsilon+(1+\beta\mathcal{D})\frac{1}{1-\tilde{\epsilon}}\left(\frac{\beta}{\delta}-1\right) &(7.499)\\
\beta\mathcal{D} &= \left(\frac{\beta}{\delta}-1+c_B\epsilon\right)\frac{1-\tilde{\epsilon}}{\frac{\beta}{\delta}-1}-1 &(7.500)\\
&= \frac{c_B\epsilon}{\frac{\beta}{\delta}-1}-\tilde{\epsilon}\left(1+\frac{c_B\epsilon}{\frac{\beta}{\delta}-1}\right) &(7.501)\\
&\mid \ \text{note that } \frac{\epsilon}{\frac{\beta}{\delta}-1}=\frac{\epsilon}{\left(\frac{1-\epsilon}{\lambda}-1\right)\div\left(\frac{1}{\lambda}-1\right)-1}=-(1-\lambda)\equiv-\Delta\\
\beta\mathcal{D} &= -\Delta c_B-\tilde{\epsilon}(1-\Delta c_B) &(7.502)
\end{aligned}$$

We substitute this equation into the equation from F' and get an equation only for $\tilde{\epsilon}$.

$$\begin{aligned}
1-c_B\epsilon &= \beta^2\omega^2 f(\omega)\left(-\frac{\Delta}{\beta}c_B-\frac{\tilde{\epsilon}}{\beta}(1-c_B\Delta)\right)\left(1+\frac{\Delta}{\beta}c_B+\frac{\tilde{\epsilon}}{\beta}(1-c_B\Delta)\right)\\
&\quad +(1-c_B\Delta-\tilde{\epsilon}(1-c_B\Delta))^2\frac{1}{1-\tilde{\epsilon}} &(7.503)\\
&\mid \ \text{multiply on both sides, } \frac{\beta^2}{(1-c_B\Delta)^2}
\end{aligned}$$

$$\begin{aligned}
\frac{\beta^2(1-c_B\epsilon)}{(1-\Delta c_B)^2} &= \beta^2\omega^2 f(\omega)\left(\frac{-\frac{\Delta}{\beta}c_B\beta}{1-\Delta c_B}-\tilde{\epsilon}\right)\left(\frac{\left(1+\frac{\Delta}{\beta}c_B\right)\beta}{1-\Delta c_B}+\tilde{\epsilon}\right) \\
&\quad +\frac{\beta^2(1-\Delta c_B-\tilde{\epsilon}(1-\Delta c_B))^2}{(1-\Delta c_B)^2(1-\tilde{\epsilon})} && (7.504)\\
\frac{1-c_B\epsilon}{(1-\Delta c_B)^2} &= -\omega^2 f(\omega)\left(\tilde{\epsilon}+\frac{\Delta c_B}{1-\Delta c_B}\right)\left(\tilde{\epsilon}+\frac{\beta+\Delta c_B}{1-\Delta c_B}\right)+\frac{(1-\tilde{\epsilon})^2}{1-\tilde{\epsilon}} && (7.505)\\
\tilde{\epsilon} &= 1-\frac{1-c_B\epsilon}{(1-\Delta c_B)^2}-\left(\tilde{\epsilon}+\frac{\Delta c_B}{1-\Delta c_B}\right)\left(\tilde{\epsilon}+\frac{\beta+\Delta c_B}{1-\Delta c_B}\right)\omega^2 f(\omega) && (7.506)\\
&\mid \quad \text{note that } 1-\frac{1-c_B\epsilon}{(1-\Delta c_B)^2}=\frac{1-2\Delta c_B+\Delta^2 c_B^2-1+c_B\epsilon}{(1-\Delta c_B)^2}\\
&\mid \quad =\frac{c_B(\epsilon-\Delta)}{(1-\Delta c_B)^2}-\frac{\Delta c_B}{1-\Delta c_B}\\
\tilde{\epsilon} &= \frac{c_B(\epsilon-\Delta)}{(1-\Delta c_B)^2}-\frac{c_B\Delta}{1-\Delta c_B}-\left(\tilde{\epsilon}+\frac{c_B\Delta}{1-c_B\Delta}\right)\left(\tilde{\epsilon}+\frac{\beta+c_B\Delta}{1-c_B\Delta}\right)\omega^2 f(\omega) && (7.507)
\end{aligned}$$

Caveat observed by Moller and Kaplan It was noticed by Kaplan & Mostoller in [Mostoller1979] that a particular solution in Gruewald's theory is similar to VCA which implies that the theory is probably lacking in important mass and force constant defect physics for that solution.

Recall the equation for $\tilde{\epsilon}$,

$$\tilde{\epsilon} = \frac{c_B(\epsilon-\Delta)}{(1-c_B\Delta)^2}-\frac{c_B\Delta}{1-\Delta c_B}-\left(\tilde{\epsilon}+\frac{c_B\Delta}{1-c_B\Delta}\right)\left(\tilde{\epsilon}+\frac{\beta+c_B\Delta}{1-c_B\Delta}\right)\omega^2 f(\omega) \qquad (7.508)$$

and consider this particular solution $\epsilon=\Delta$, $\frac{M_B}{M_A}=\lambda$ which implies $\beta=\frac{M_B}{M_A}\frac{1}{\lambda}-1=0$. Then the equation for $\tilde{\epsilon}$ becomes

$$\begin{aligned}
\tilde{\epsilon} &= -\frac{c_B\Delta}{1-\Delta c_B}-\left(\tilde{\epsilon}+\frac{c_B\Delta}{1-c_B\Delta}\right)^2\omega^2 f(\omega) && (7.509)\\
0 &= \left(\tilde{\epsilon}+\frac{c_B\Delta}{1-\Delta c_B}\right)\left(1+\left(\tilde{\epsilon}+\frac{c_B\Delta}{1-c_B\Delta}\right)\omega^2 f(\omega)\right) && (7.510)
\end{aligned}$$

which is a quadratic equation whose 2 roots are

$$\tilde{\epsilon}=-\frac{c_B\Delta}{1-c_B\Delta}\ , \qquad \tilde{\epsilon}=-\frac{1}{\omega^2 f(\omega)}-\frac{c_B\Delta}{1-c_B\Delta} \qquad (7.511)$$

To choose the proper root, we recall the equation for $\mathcal{D}$

$$\beta\mathcal{D} = -\Delta c_B-\tilde{\epsilon}(1-c_B\Delta) \qquad (7.512)$$

and its LHS $=0$ due to $\beta=0$. Only the first root, $\tilde{\epsilon}=-\frac{c_B\Delta}{1-c_B\Delta}$ gives RHS $=0$. Thus $\tilde{\epsilon}=-\frac{c_B\Delta}{1-c_B\Delta}$ is the proper root however it is independent of ω! If we substitute this root into the frequency spectrum formula,

$$f(\omega) = \frac{M_A}{N}\sum_{j\vec{q}}\frac{1}{\omega^2(1-\tilde{\epsilon})-\omega_A^2(j\vec{q})} \qquad (7.513)$$

Thus this (independent of ω) $\tilde{\epsilon}$ results in $f(\omega)$ having the same form as the harmonic one. So $\tilde{\epsilon}$ is essentially causing a “mean-field” kind of shift in frequency. In this context, this solution is similar to VCA (in other contexts, it is similar to the ”Hartree” approximation).

[Receipe for calculation] As we can see, this theory is quite complicated so instead of boxing up final equations, we provide a receipe here.

1. Recall that the model is a cubic model. Specify c_A, c_B, M_A, M_B and λ, then we get $\epsilon = 1 - \frac{M_B}{M_A}$, $\Delta = 1 - \lambda$ and $\beta = \frac{M_A}{M_B}\frac{1}{\lambda} - 1$. Solve for $\tilde{\epsilon}$ from the 2 self consistent equations:

$$\begin{aligned} 0 &= \tilde{\epsilon} + \frac{c_B\Delta}{1-c_B\Delta} + \frac{c_B(\Delta-\epsilon)}{(1-c_B\Delta)^2} + \left(\tilde{\epsilon} + \frac{c_B\Delta}{1-c_B\Delta}\right)\left(\tilde{\epsilon} + \frac{\beta + c_B\Delta}{1-c_B\Delta}\right)\omega^2 f(\omega) \\ f(\omega) &= \frac{M_A}{N}\sum_{j\vec{q}} \frac{1}{\omega^2(1-\tilde{\epsilon}) - \omega_A^2(j\vec{q})} \end{aligned}$$

2. Use $\tilde{\epsilon}$ and solve $\mathcal{D}$ by using,

$$\beta\mathcal{D} = -\Delta c_B - \tilde{\epsilon}(1 - c_B\Delta)$$

3. Solve for $f(\omega)$ first then use $\tilde{\epsilon}$ and $\mathcal{D}$ to solve for $\langle D(j\vec{q},\omega)\rangle$ by using,

$$\langle D(j\vec{q},\omega)\rangle_c = \frac{1}{M_A}\left[f(\omega)(1-\mathcal{D})\mathcal{D}\left(\frac{1}{\lambda}-1\right)^2 + \left(1+\mathcal{D}\left(\frac{1}{\lambda}-1\right)\right)^2 \frac{1}{\omega^2(1-\tilde{\epsilon}) - \omega_A^2(j\vec{q})}\right]$$

4. Reconstruct the (real-space) configuration averaged $\langle D\rangle_c$ from

$$\langle D_{\alpha\alpha'}(l,l',\omega)\rangle_c = \frac{1}{N}\sum_{j\vec{q}} \epsilon_\alpha(j\vec{q})\epsilon_{\alpha'}(j\vec{q})\langle D(j\vec{q},\omega)\rangle e^{i\vec{q}\cdot(l-l')}$$

7.7.1 Appendix: Generic 2-Particle theory: Vertex corrections and the configuration averaged transmission function

Note that for transport, we really need the configuration average of 2-particle quantities. All these generalized theories are only 1-particle configuration averaged quantities. It is an open problem to construct consistent 2-particle theories just like in CPA. This development will be future work. Here we only describe a generic (and standard) way of handling the 2-particle configuration average. We will use the configuration average of the transmission function as our example of a 2-particle quantity. A simple ladder resummation is employed in the context of Gruewald theory. (Again, superscript (R) and (L) denote right and left respectively and superscript R and A denote retarded and advanced respectively.)

$$\begin{aligned} \langle\mathcal{T}\rangle_c &= \mathrm{Tr}\langle D^R\Gamma^{(R)}D^A\Gamma^{(L)}\rangle && (7.514) \\ &= \mathrm{Tr}\left[\left\langle D^R\right\rangle\Gamma^{(R)}\left\langle D^A\right\rangle\Gamma^{(L)}\right] \\ &\quad + \sum_{\text{all indices}}\left[\left\langle D^A\right\rangle_{l_7l_8}(\Gamma^{(L)})_{l_8l_1}\left\langle D^R\right\rangle_{l_1l_2}\right]\Lambda_{l_2l_7l_3l_6}\left[\left\langle D^R\right\rangle_{l_3l_4}(\Gamma^{(R)})_{l_4l_5}\left\langle D^A\right\rangle_{l_5l_6}\right] && (7.515) \\ &= \mathrm{Tr}\left[\left\langle D^R\right\rangle\Gamma^{(R)}\left\langle D^A\right\rangle\Gamma^{(L)}\right] \\ &\quad + \sum_{\text{all indices}}\left[\left\langle D^A\right\rangle\cdot\Gamma^{(L)}\cdot\left\langle D^R\right\rangle\right]_{l_7l_2}\Lambda_{l_2l_7l_3l_6}\left[\left\langle D^R\right\rangle\cdot\Gamma^{(R)}\cdot\left\langle D^A\right\rangle\right]_{l_3l_6} && (7.516) \end{aligned}$$

The vertex function Λ will be made up of the ladder summation. The remaining of the section is thus to get an explicit expression for Λ. The equation can be denoted by diagrams as,

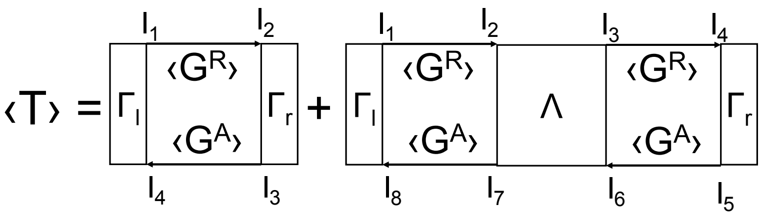


Figure 7.19: Diagrammatics of vertex corrections.

$$\begin{aligned}
\Lambda_{l_2l_7l_3l_6} &= L_{l_2l_7}\delta_{l_2l_3}\delta_{l_7l_6} + L_{l_2l_7}\sum_{l_8l_9}\left\langle D^R\right\rangle_{l_2l_8}\left\langle D^A\right\rangle_{l_9l_7}\Lambda_{l_8l_9l_3l_6} && (7.517)\\
&= L_{l_2l_7}\delta_{l_2l_3}\delta_{l_7l_6} + L_{l_2l_7}\sum_{l_8l_9}\left(\left\langle D^R\right\rangle\otimes\left\langle D^A\right\rangle\right)_{l_2l_7l_8l_9}\Lambda_{l_8l_9l_3l_6} && (7.518)\\
L_{l_2l_7}\delta_{l_2l_3}\delta_{l_7l_6} &= \Lambda_{l_2l_7l_3l_6} - L_{l_2l_7}\sum_{l_8l_9}\left(\left\langle D^R\right\rangle\otimes\left\langle D^A\right\rangle\right)_{l_2l_7l_8l_9}\Lambda_{l_8l_9l_3l_6} && (7.519)\\
L_{l_2l_7}\delta_{l_2l_3}\delta_{l_7l_6} &= \sum_{l_8l_9}\left(\delta_{l_8l_2}\delta_{l_9l_7} - L_{l_2l_7}\left(\left\langle D^R\right\rangle\otimes\left\langle D^A\right\rangle\right)_{l_2l_7l_8l_9}\right)\Lambda_{l_8l_9l_3l_6} && (7.520)\\
&\quad|\quad \text{divide by } L_{l_2l_7} \text{ which is diagonal}\\
\delta_{l_2l_3}\delta_{l_7l_6} &= \sum_{l_8l_9}\left((L^{-1})_{l_2l_7}\delta_{l_8l_2}\delta_{l_9l_7} - \left(\left\langle D^R\right\rangle\otimes\left\langle D^A\right\rangle\right)_{l_2l_7l_8l_9}\right)\Lambda_{l_8l_9l_3l_6} && (7.521)\\
&\quad|\quad \text{this is familar when compared with}\\
&\quad|\quad \sum_{l_2\gamma}\left(M(l)\omega^2\delta_{\alpha\gamma}\delta_{ll_2} - \Phi_{l\alpha l_2\gamma}\right)G_{l_2\gamma l'\beta} = \delta_{\alpha\beta}\delta_{ll'} \Rightarrow G = (M\otimes\mathbb{I} - \Phi)^{-1}\\
&\quad|\quad \text{similarly we get,}\\
\Lambda &= \left(L^{-1}\otimes\mathbb{I} - \left(\left\langle D^R\right\rangle\otimes\left\langle D^A\right\rangle\right)\right)^{-1} && (7.522)
\end{aligned}$$

Since we have 3 distinct types of renormalized locators σ, $\sigma_{L/R}$ and $\tilde{\sigma}$ then we can simply define L to be their sum (note that the locators are diagonal in site indices).

$$L_{l_2l_7} = \sigma_{l_2l_7} + (\sigma_{L/R})_{l_2l_7} + \tilde{\sigma}_{l_2l_7} \tag{7.523}$$

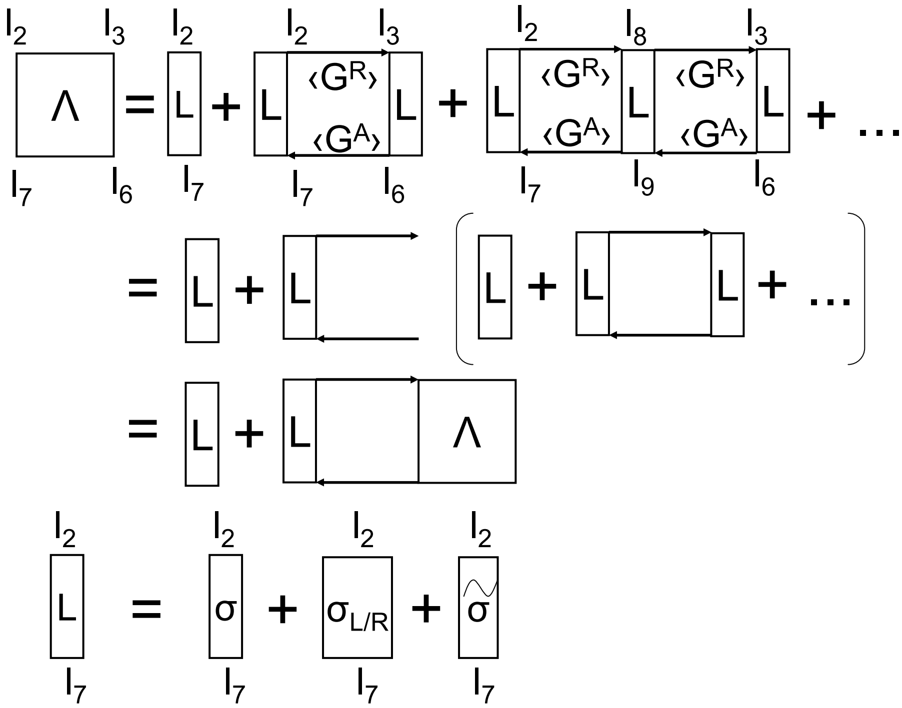


Figure 7.20: Diagrammatics of ladder summation.

7.8 Mass & Force constant Disorder : Mookerjee Theory

7.8.1 Preliminary: Augmented Space Formalism for Configuration Averaging

The main reference is [Alam2004]. As usual, we define a binary alloy with host atoms A and defect atoms B with occupation probability c_A and c_B respectively. Of course $c_A + c_B = 1$. Here we only aim to provide a simple justification for the augmented space theorem and therafter use it as a set of rules. For the rigorous mathematical formulation, see [Mookerjee1973a] and [Mookerjee1973b].

The idea is simple to state: A "configuration" vector space is defined and it is augmented to quantities which contain randomness (eg mass matrix and spring constant matrix). Then the configuration average of that quantity is a certain ground state expectation value.

We define 2 (configuration) states

$$|A\rangle_c\ , \quad |B\rangle_c \tag{7.524}$$

and assume that they are orthonormal. We also define occupation operators $\hat{\eta}_A$ and $\hat{\eta}_B$ which act on the states as follows,

$$\begin{aligned}
\hat{\eta}_A|A\rangle_c &= |A\rangle_c \qquad \text{eigenvalue 1} && (7.525)\\
\hat{\eta}_B|A\rangle_c &= 0 \qquad \text{eigenvalue 0} && (7.526)\\
\hat{\eta}_A|B\rangle_c &= 0 \qquad \text{eigenvalue 0} && (7.527)\\
\hat{\eta}_B|B\rangle_c &= |B\rangle_c \qquad \text{eigenvalue 1} && (7.528)
\end{aligned}$$

An operator representation is

$$\hat{\eta}_A = |A\rangle_{cc}\langle A| \quad , \quad \hat{\eta}_B = |B\rangle_{cc}\langle B| \tag{7.529}$$

Now consider a rotated basis in configuration vector space,

$$|0\rangle_c \equiv \sqrt{c_A}|A\rangle_c + \sqrt{c_B}|B\rangle_c \tag{7.530}$$
$$|1\rangle_c \equiv \sqrt{c_B}|A\rangle_c - \sqrt{c_A}|B\rangle_c \tag{7.531}$$

In the literature, $|0\rangle_c$ is called the average state and $|1\rangle_c$ is called the fluctuation state. Invert and write (using $c_A + c_B = 1$)

$$|A\rangle_c = \sqrt{c_A}|0\rangle_c + \sqrt{c_B}|1\rangle_c \tag{7.532}$$
$$|B\rangle_c = \sqrt{c_B}|0\rangle_c - \sqrt{c_A}|1\rangle_c \tag{7.533}$$

Then rewrite the operators $\hat{\eta}_A$ and $\hat{\eta}_B$,

$$\hat{\eta}_A = |A\rangle_{cc}\langle A| = |0\rangle_c c_{A c}\langle 0| + \sqrt{c_A c_B}\,(|0\rangle_{cc}\langle 1| + |1\rangle_{cc}\langle 0|) + |1\rangle_c c_{B c}\langle 1| \tag{7.534}$$

$$= \begin{array}{c c} & \begin{array}{cc} |0\rangle_c & |1\rangle_c \end{array} \\ \begin{array}{c} {}_c\langle 0| \\ {}_c\langle 1| \end{array} & \begin{pmatrix} c_A & \sqrt{c_A c_B} \\ \sqrt{c_A c_B} & c_B \end{pmatrix} \end{array} \tag{7.535}$$

$$\hat{\eta}_B = |B\rangle_{cc}\langle B| = |0\rangle_c c_{B c}\langle 0| - \sqrt{c_A c_B}\,(|0\rangle_{cc}\langle 1| + |1\rangle_{cc}\langle 0|) + |1\rangle_c c_{A c}\langle 1| \tag{7.536}$$

$$= \begin{array}{c c} & \begin{array}{cc} |0\rangle_c & |1\rangle_c \end{array} \\ \begin{array}{c} {}_c\langle 0| \\ {}_c\langle 1| \end{array} & \begin{pmatrix} c_B & -\sqrt{c_A c_B} \\ -\sqrt{c_A c_B} & c_A \end{pmatrix} \end{array} \tag{7.537}$$

Now consider a quantity which is random and it is written in the occupation number form:

$$f = f_A \eta_A + f_B \eta_B \tag{7.538}$$

We augment it with the configuration space by "quantizing" the occupation numbers into occupation operators.

$$f^{\text{AUG}} \equiv f_A \hat{\eta}_A + f_B \hat{\eta}_B \tag{7.539}$$

Consider the expectation value,

$${}_c\langle 0|f^{\text{AUG}}|0\rangle_c = f_{A c}\langle 0|\hat{\eta}_A|0\rangle_c + f_{B c}\langle 0|\hat{\eta}_B|0\rangle_c \tag{7.540}$$
$$= f_A c_A + f_B c_B \tag{7.541}$$

Hence the (ground state) expectation value of the augmented quantity f^{AUG} gives the correct configuration average of f. This is a special (and simple) example of a diagonal quantity. Again we refer to the rigorous proof in [Mookerjee1973a] and [Mookerjee1973b] for calculating configuration averages of off-diagonal random quantities.

Summary of augmented space formalism (ASF):

1. Augment by "quantizing" the random quantities with the operators (in the $|0\rangle_c$ and $|1\rangle_c$ basis)

$$\hat{\eta}_A = \begin{pmatrix} c_A & \sqrt{c_A c_B} \\ \sqrt{c_A c_B} & c_B \end{pmatrix} \quad , \quad \hat{\eta}_B = \begin{pmatrix} c_B & -\sqrt{c_A c_B} \\ -\sqrt{c_A c_B} & c_A \end{pmatrix} \tag{7.542}$$

2. We have to augment every site. So we write

$$|0\rangle_c\ , \quad |1\rangle_c \longrightarrow |0_l\rangle_c\ , \quad |1_l\rangle_c \tag{7.543}$$

to denote basis for site l.

3. The configuration average is calculated by

$$\langle D_{ll'} \rangle_c = {}_c\langle 0_1 \dots 0_N | D_{ll'}^{\text{AUG}} | 0_1 \dots 0_N \rangle_c \tag{7.544}$$

7.8.2 Mookerjee's Augmented Space Recursion (ASR) Method

7.8.2.1 Augmenting the Mass Matrix and the Force Constant Matrix

The main reference is [Alam2004]. For a monograph style, see [Yussouff1987]. We first need to augment the random harmonic Hamiltonian. We shall develop the general theory by considering the special case of $N = 3$ sites.

There are 8 basis states for the configuration vector space.

$$|0_1 0_2 0_3\rangle_c\ , \quad |0_1 0_2 1_3\rangle_c\ , \quad |0_1 1_2 0_3\rangle_c\ , \quad |0_1 1_2 1_3\rangle_c\ , \quad |1_1 0_2 0_3\rangle_c\ , \quad |1_1 0_2 1_3\rangle_c\ , \quad |1_1 1_2 0_3\rangle_c\ , \quad |1_1 1_2 1_3\rangle_c$$

First we augment the mass matrix

$$M = \begin{pmatrix} M_{11} & 0 & 0 \\ 0 & M_{22} & 0 \\ 0 & 0 & M_{33} \end{pmatrix} \to M^{\text{AUG}} = \begin{pmatrix} (M_{11})_{8\times 8} & 0_{8\times 8} & 0_{8\times 8} \\ 0_{8\times 8} & (M_{22})_{8\times 8} & 0_{8\times 8} \\ 0_{8\times 8} & 0_{8\times 8} & (M_{33})_{8\times 8} \end{pmatrix} \tag{7.545}$$

$$M_{11} = M_A \eta_{1A} + M_B \eta_{1B} \to (M_{11})_{8\times 8} = M_A \hat{\eta}_{1A} + M_B \hat{\eta}_{1B} \tag{7.546}$$
$$M_{22} = M_A \eta_{2A} + M_B \eta_{2B} \to (M_{22})_{8\times 8} = M_A \hat{\eta}_{2A} + M_B \hat{\eta}_{2B} \tag{7.547}$$
$$M_{33} = M_A \eta_{3A} + M_B \eta_{3B} \to (M_{33})_{8\times 8} = M_A \hat{\eta}_{3A} + M_B \hat{\eta}_{3B} \tag{7.548}$$

$$\hat{\eta}_{1A} = \begin{pmatrix} c_A & \sqrt{c_A c_B} \\ \sqrt{c_A c_B} & c_B \end{pmatrix}^{(1)} \otimes \mathbb{I}_{2\times 2}^{(2)} \otimes \mathbb{I}_{2\times 2}^{(3)} \tag{7.549}$$

$$\hat{\eta}_{1B} = \begin{pmatrix} c_B & -\sqrt{c_A c_B} \\ -\sqrt{c_A c_B} & c_A \end{pmatrix}^{(1)} \otimes \mathbb{I}_{2\times 2}^{(2)} \otimes \mathbb{I}_{2\times 2}^{(3)} \tag{7.550}$$

$$\hat{\eta}_{2A} = \mathbb{I}_{2\times 2}^{(1)} \otimes \begin{pmatrix} c_A & \sqrt{c_A c_B} \\ \sqrt{c_A c_B} & c_B \end{pmatrix}^{(2)} \otimes \mathbb{I}_{2\times 2}^{(3)} \tag{7.551}$$

$$\hat{\eta}_{2B} = \mathbb{I}_{2\times 2}^{(1)} \otimes \begin{pmatrix} c_B & -\sqrt{c_A c_B} \\ -\sqrt{c_A c_B} & c_A \end{pmatrix}^{(2)} \otimes \mathbb{I}_{2\times 2}^{(3)} \tag{7.552}$$

$$\hat{\eta}_{3A} = \mathbb{I}_{2\times 2}^{(1)} \otimes \mathbb{I}_{2\times 2}^{(2)} \otimes \begin{pmatrix} c_A & \sqrt{c_A c_B} \\ \sqrt{c_A c_B} & c_B \end{pmatrix}^{(3)} \tag{7.553}$$

$$\hat{\eta}_{3B} = \mathbb{I}^{(1)}_{2\times 2} \otimes \mathbb{I}^{(2)}_{2\times 2} \otimes \begin{pmatrix} c_B & -\sqrt{c_A c_B} \\ -\sqrt{c_A c_B} & c_A \end{pmatrix}^{(3)} \tag{7.554}$$

We shall write the augmented matrices in terms of projection operators instead of writing large matrices. Example,

$$\hat{\eta}_{1A} = [|0_1\rangle_c c_{Ac}\langle 0_1| + \sqrt{c_A c_B}\,(|0_1\rangle_{cc}\langle 1_1| + |1_1\rangle_{cc}\langle 0_1|) + |1_1\rangle_c c_{Bc}\langle 1_1|] \otimes \mathbb{I}_{4\times 4} \tag{7.555}$$

$$\hat{\eta}_{1B} = [|0_1\rangle_c c_{Bc}\langle 0_1| - \sqrt{c_A c_B}\,(|0_1\rangle_{cc}\langle 1_1| + |1_1\rangle_{cc}\langle 0_1|) + |1_1\rangle_c c_{Ac}\langle 1_1|] \otimes \mathbb{I}_{4\times 4} \tag{7.556}$$

$$\begin{aligned}
(M_{11})_{8\times 8} &= [|0_1\rangle_c (M_A c_A + M_B c_B)_c\langle 0_1| + (M_A - M_B)\sqrt{c_A c_B}\,(|0_1\rangle_{cc}\langle 1_1| + |1_1\rangle_{cc}\langle 0_1|) \\
&\quad + |1_1\rangle_c (M_A c_B + M_B c_A)_c\langle 1_1|] \otimes \mathbb{I}_{4\times 4} && (7.557)\\
&\quad |\ \text{use the notations } \bar{M} \equiv M_A c_A + M_B c_B \text{ and } M_A c_B + M_B c_A = \bar{M} + (c_B - c_A)(M_A - M_B) \\
&= \big[|0_1\rangle_c \bar{M}_c\langle 0_1| + (M_A - M_B)\sqrt{c_A c_B}\,(|0_1\rangle_{cc} 1_1| + |1_1\rangle_{cc}\langle 0_1|) \\
&\quad + |1_1\rangle_c \bar{M}_c\langle 1_1| + |1_1\rangle_c (c_B - c_A)(M_A - M_B)_c\langle 1_1|\big] \otimes \mathbb{I}_{4\times 4} && (7.558)\\
&= \bar{M}\,[|0_1\rangle_{cc}\langle 0_1| + |1_1\rangle_{cc}\langle 1_1|] \otimes \mathbb{I}_{4\times 4} \\
&\quad + (M_A - M_B)\,[(c_B - c_A)|1_1\rangle_{cc}\langle 1_1| \otimes \mathbb{I}_{4\times 4} + \sqrt{c_A c_B}\,(|0_1\rangle_{cc}\langle 1_1| + |1_1\rangle_{cc}\langle 0_1|) \otimes \mathbb{I}_{4\times 4}] && (7.559)\\
&= \bar{M}\mathbb{I}_{8\times 8} + (M_A - M_B)\,[(c_B - c_A)|1_1\rangle_{cc}\langle 1_1| + \sqrt{c_A c_B}\,(|0_1\rangle_{cc}\langle 1_1| + |1_1\rangle_{cc}\langle 0_1|)] \otimes \mathbb{I}_{4\times 4} && (7.560)
\end{aligned}$$

In very similar ways, $(M_{22})_{8\times 8}$ and $(M_{33})_{8\times 8}$ are written explicitly as,

$$\begin{aligned}
(M_{22})_{8\times 8} &= \bar{M}\mathbb{I}_{8\times 8} + \mathbb{I}_{2\times 2} \otimes (M_A - M_B)\,[(c_B - c_A)|1_2\rangle_{cc}\langle 1_2| + \sqrt{c_A c_B}\,(|0_2\rangle_{cc}\langle 1_2| + |1_2\rangle_{cc}\langle 0_2|)] \otimes \mathbb{I}_{2\times 2} \\
(M_{33})_{8\times 8} &= \bar{M}\mathbb{I}_{8\times 8} + \mathbb{I}_{4\times 4} \otimes (M_A - M_B)\,[(c_B - c_A)|1_3\rangle_{cc}\langle 1_3| + \sqrt{c_A c_B}\,(|0_3\rangle_{cc}\langle 1_3| + |1_3\rangle_{cc}\langle 0_3|)]
\end{aligned}$$

Recall that the whole augmented mass matrix looks like this

$$M^{\text{AUG}} = \sum_{l=1}^{3} |l\rangle\langle l| \otimes (M_{ll})_{8\times 8} \tag{7.561}$$

Finally we can write down the general N-site augmented mass matrix

$$\begin{aligned}
M^{\text{AUG}} &= \sum_{l=1}^{N} |l\rangle\langle l| \otimes (M_{ll})_{2^N\times 2^N} && (7.562)\\
&= \bar{M}\mathbb{I}_{N\times N} \otimes \mathbb{I}_{2^N\times 2^N} \\
&\quad + (M_A - M_B) \sum_{l=1}^{N} |l\rangle\langle l| \otimes \mathbb{I}^{(1)}_{2\times 2} \otimes \cdots \otimes \mathbb{I}^{(l-1)}_{2\times 2} \\
&\quad \otimes [(c_B - c_A)|1_l\rangle_{cc}\langle 1_l| + \sqrt{c_A c_B}\,(|0_l\rangle_{cc}\langle 1_l| + |1_l\rangle_{cc}\langle 0_l|)] \otimes \mathbb{I}^{(l+1)}_{2\times 2} \otimes \cdots \otimes \mathbb{I}^{(N)}_{2\times 2} && (7.563)\\
&\equiv \bar{M}\mathbb{I}_{N\times N} \otimes \mathbb{I}_{2^N\times 2^N} + M' && (7.564)
\end{aligned}$$

The definition in the last line is only for a footnote later.

Now we proceed to augment the force constant matrix. Again we take the simple $N = 3$ case first.

$$\Phi = \begin{pmatrix} \Phi_{11} & \Phi_{12} & 0 \\ \Phi_{21} & \Phi_{22} & \Phi_{23} \\ 0 & \Phi_{32} & \Phi_{33} \end{pmatrix} \tag{7.565}$$

The occupation numbers are associated as follows,

$$\Phi_{ll'} = \Phi_{ll'}^{AA}\eta_{lA}\eta_{l'A} + \Phi_{ll'}^{AB}\eta_{lA}\eta_{l'B} + \Phi_{ll'}^{BA}\eta_{lB}\eta_{l'A} + \Phi_{ll'}^{BB}\eta_{lB}\eta_{l'B} \tag{7.566}$$

We augment it $\Phi_{ll'} \to (\Phi_{ll'})_{8\times 8}$

$$\Phi^{\mathrm{AUG}} = \begin{pmatrix} (\Phi_{11})_{8\times8} & (\Phi_{12})_{8\times8} & 0_{8\times8} \\ (\Phi_{21})_{8\times8} & (\Phi_{22})_{8\times8} & (\Phi_{23})_{8\times8} \\ 0_{8\times8} & (\Phi_{32})_{8\times8} & (\Phi_{33})_{8\times8} \end{pmatrix} \tag{7.567}$$

We define some notation to shorten expressions later

$$\bar{\Phi}_{ll'} \equiv \Phi_{ll'}^{AA}c_A^2 + \Phi_{ll'}^{AB}c_Ac_B + \Phi_{ll'}^{BA}c_Bc_A + \Phi_{ll'}^{BB}c_B^2 \tag{7.568}$$

$$\Phi_{ll'}^{(1)} \equiv \Phi_{ll'}^{AA}c_A - \Phi_{ll'}^{AB}c_A + \Phi_{ll'}^{BA}c_B - \Phi_{ll'}^{BB}c_B \tag{7.569}$$

$$\Phi_{ll'}^{(2)} \equiv \Phi_{ll'}^{AA} + \Phi_{ll'}^{BB} - \Phi_{ll'}^{AB} - \Phi_{ll'}^{BA} \tag{7.570}$$

We write the augmented Φ_{12}

$$(\Phi_{12})_{8\times8} = \Phi_{12}^{AA}\hat{\eta}_{1A}\hat{\eta}_{2A} + \Phi_{12}^{AB}\hat{\eta}_{1A}\hat{\eta}_{2B} + \Phi_{12}^{BA}\hat{\eta}_{1B}\hat{\eta}_{2A} + \Phi_{12}^{BB}\hat{\eta}_{1B}\hat{\eta}_{2B} \tag{7.571}$$

$$\begin{aligned} = {} & \Phi_{12}^{AA}\begin{pmatrix} c_A & \sqrt{c_Ac_B} \\ \sqrt{c_Ac_B} & c_B \end{pmatrix} \otimes \begin{pmatrix} c_A & \sqrt{c_Ac_B} \\ \sqrt{c_Ac_B} & c_B \end{pmatrix} \otimes \mathbb{I}_{2\times2} \\ & +\Phi_{12}^{AB}\begin{pmatrix} c_A & \sqrt{c_Ac_B} \\ \sqrt{c_Ac_B} & c_B \end{pmatrix} \otimes \begin{pmatrix} c_B & -\sqrt{c_Ac_B} \\ -\sqrt{c_Ac_B} & c_A \end{pmatrix} \otimes \mathbb{I}_{2\times2} \\ & +\Phi_{12}^{BA}\begin{pmatrix} c_B & -\sqrt{c_Ac_B} \\ -\sqrt{c_Ac_B} & c_A \end{pmatrix} \otimes \begin{pmatrix} c_A & \sqrt{c_Ac_B} \\ \sqrt{c_Ac_B} & c_B \end{pmatrix} \otimes \mathbb{I}_{2\times2} \\ & +\Phi_{12}^{BB}\begin{pmatrix} c_B & -\sqrt{c_Ac_B} \\ -\sqrt{c_Ac_B} & c_A \end{pmatrix} \otimes \begin{pmatrix} c_B & -\sqrt{c_Ac_B} \\ -\sqrt{c_Ac_B} & c_A \end{pmatrix} \otimes \mathbb{I}_{2\times2} \end{aligned} \tag{7.572}$$

$$= \begin{pmatrix} \Phi_{12}^{AA}c_A^2 + \Phi_{12}^{AB}c_Ac_B + \Phi_{12}^{BA}c_Ac_B + \Phi_{12}^{BB}c_B^2 & (\Phi_{12}^{AA} - \Phi_{12}^{AB})c_A\sqrt{c_Ac_B} + c_B\sqrt{c_Ac_B}(\Phi_{12}^{BA} - \Phi_{12}^{BB}) & (\Phi_{12}^{AA}c_A + \Phi_{12}^{AB}c_B - \Phi_{12}^{BA}c_A - \Phi_{12}^{BB}c_B)\sqrt{c_Ac_B} & c_Ac_B(\Phi_{12}^{AA} - \Phi_{12}^{AB} - \Phi_{12}^{BA} + \Phi_{12}^{BB}) \\ (\Phi_{12}^{AA} - \Phi_{12}^{AB})c_A\sqrt{c_Ac_B} + c_B\sqrt{c_Ac_B}(\Phi_{12}^{BA} - \Phi_{12}^{BB}) & \Phi_{12}^{AA}c_Ac_B + \Phi_{12}^{AB}c_A^2 + \Phi_{12}^{BA}c_B^2 + \Phi_{12}^{BB}c_Ac_B & c_Ac_B(\Phi_{12}^{AA} - \Phi_{12}^{AB} - \Phi_{12}^{BA} + \Phi_{12}^{BB}) & \sqrt{c_Ac_B}(\Phi_{12}^{AA}c_B + \Phi_{12}^{AB}c_A - \Phi_{12}^{BA}c_B - \Phi_{12}^{BB}c_A) \\ (\Phi_{12}^{AA}c_A + \Phi_{12}^{AB}c_B - \Phi_{12}^{BA}c_A - \Phi_{12}^{BB}c_B)\sqrt{c_Ac_B} & c_Ac_B(\Phi_{12}^{AA} - \Phi_{12}^{AB} - \Phi_{12}^{BA} + \Phi_{12}^{BB}) & \Phi_{12}^{AA}c_Ac_B + \Phi_{12}^{AB}c_B^2 + \Phi_{12}^{BA}c_A^2 + \Phi_{12}^{BB}c_Ac_B & \sqrt{c_Ac_B}(\Phi_{12}^{AA}c_B - \Phi_{12}^{AB}c_B + \Phi_{12}^{BA}c_A - \Phi_{12}^{BB}c_A) \\ c_Ac_B(\Phi_{12}^{AA} - \Phi_{12}^{AB} - \Phi_{12}^{BA} + \Phi_{12}^{BB}) & \sqrt{c_Ac_B}(\Phi_{12}^{AA}c_B + \Phi_{12}^{AB}c_A - \Phi_{12}^{BA}c_B - \Phi_{12}^{BB}c_A) & \sqrt{c_Ac_B}(\Phi_{12}^{AA}c_B - \Phi_{12}^{AB}c_B + \Phi_{12}^{BA}c_A - \Phi_{12}^{BB}c_A) & \Phi_{12}^{AA}c_B^2 + \Phi_{12}^{AB}c_Ac_B + \Phi_{12}^{BA}c_Ac_B + \Phi_{12}^{BB}c_A^2 \end{pmatrix} \otimes \mathbb{I}_{2\times2} \tag{7.573}$$

| use the notations defined above

$$
= \begin{pmatrix}
\bar{\Phi}_{12} & \Phi_{12}^{(1)}\sqrt{c_A c_B} & \Phi_{12}^{(1)}\sqrt{c_A c_B} & \Phi_{12}^{(2)} c_A c_B \\
\Phi_{12}^{(1)}\sqrt{c_A c_B} & \bar{\Phi}_{12} + \Phi_{12}^{(1)}(c_B - c_A) & \Phi_{12}^{(2)} c_A c_B & \sqrt{c_A c_B}\left(\Phi_{12}^{(2)}(c_B - c_A) + \Phi_{12}^{(1)}\right) \\
\Phi_{12}^{(1)}\sqrt{c_A c_B} & \Phi_{12}^{(2)} c_A c_B & \bar{\Phi}_{12} + \Phi_{12}^{(1)}(c_B - c_A) & \sqrt{c_A c_B}\left(\Phi_{12}^{(2)}(c_B - c_A) + \Phi_{12}^{(1)}\right) \\
\Phi_{12}^{(2)} c_A c_B & \sqrt{c_A c_B}\left(\Phi_{12}^{(2)}(c_B - c_A) + \Phi_{12}^{(1)}\right) & \sqrt{c_A c_B}\left(\Phi_{12}^{(2)}(c_B - c_A) + \Phi_{12}^{(1)}\right) & \bar{\Phi}_{12} + \Phi_{12}^{(1)}(c_B - c_A) + \Phi_{12}^{(2)}(c_B - c_A)^2
\end{pmatrix} \otimes \mathbb{I}_{2\times 2} \tag{7.574}
$$

We digress to show how the above matrix elements are obtained.

$$
\begin{aligned}
& \text{Element row 2 column 2} \\
= \ & \Phi_{12}^{AA} c_A c_B + \Phi_{12}^{AB} c_A^2 + \Phi_{12}^{BA} c_B^2 + \Phi_{12}^{BB} c_A c_B && (7.575) \\
= \ & \bar{\Phi}_{12} + \Phi_{12}^{AA} c_A c_B + \Phi_{12}^{AB} c_A^2 + \Phi_{12}^{BA} c_B^2 + \Phi_{12}^{BB} c_A c_B \\
& -\Phi_{12}^{AA} c_A^2 - \Phi_{12}^{AB} c_A c_B - \Phi_{12}^{BA} c_A c_B - \Phi_{12}^{BB} c_B^2 && (7.576) \\
= \ & \bar{\Phi}_{12} + \Phi_{12}^{AA}(c_A c_B - c_A^2) + \Phi_{12}^{AB}(c_A^2 - 2c_A c_B + c_B^2) + \Phi_{12}^{BB}(c_A c_B - c_B^2) && (7.577) \\
= \ & \bar{\Phi}_{12} + \left[\Phi_{12}^{AA} c_A + \Phi_{12}^{AB}(c_B - c_A) - \Phi_{12}^{BB} c_B\right](c_B - c_A) && (7.578) \\
= \ & \bar{\Phi}_{12} + \Phi_{12}^{(1)}(c_B - c_A) && (7.579)
\end{aligned}
$$

To rewrite the even more complicated matrix elemenbts, we invert the linear equations,

$$
\begin{pmatrix} \bar{\Phi} \\ \Phi^{(1)} \\ \Phi^{(2)} \end{pmatrix} = \begin{pmatrix} c_A^2 & 2c_A c_B & c_B^2 \\ c_A & c_B - c_A & -c_B \\ 1 & -2 & 1 \end{pmatrix} \begin{pmatrix} \Phi^{AA} \\ \Phi^{AB} \\ \Phi^{BB} \end{pmatrix} \tag{7.580}
$$

$$
\begin{aligned}
\Rightarrow \begin{pmatrix} \Phi^{AA} \\ \Phi^{AB} \\ \Phi^{BB} \end{pmatrix} &= \frac{1}{(c_A + c_B)^2} \begin{pmatrix} 1 & 2c_B & c_B^2 \\ 1 & c_B - c_A & -c_A c_B \\ 1 & -2c_A & c_A^2 \end{pmatrix} \begin{pmatrix} \bar{\Phi} \\ \Phi^{(1)} \\ \Phi^{(2)} \end{pmatrix} \\
&= \begin{pmatrix} \bar{\Phi} & 2c_B \Phi^{(1)} & c_B^2 \Phi^{(2)} \\ \bar{\Phi} & (c_B - c_A)\Phi^{(1)} & -c_A c_B \Phi^{(2)} \\ \bar{\Phi} & -2c_A \Phi^{(1)} & c_A^2 \Phi^{(2)} \end{pmatrix} && (7.581)
\end{aligned}
$$

Of course, we use $c_A + c_B = 1$ throughout. And now we rewrite the other matrix elements.

$$
\begin{aligned}
& \text{Element row 3 column 4} \\
= \ & \sqrt{c_A c_B}\left(\Phi_{12}^{AA} c_B + \Phi_{12}^{AB} c_A - \Phi_{12}^{BA} c_B - \Phi_{12}^{BB} c_A\right) && (7.582) \\
= \ & \sqrt{c_A c_B}\Big(\bar{\Phi}_{12} c_B + 2c_B^2 \Phi_{12}^{(1)} + c_B^3 \Phi_{12}^{(2)} + (c_A - c_B)\bar{\Phi}_{12} - (c_B - c_A)^2 \Phi_{12}^{(1)} \\
& -c_A c_B (c_A - c_B)\Phi_{12}^{(2)} - c_A \bar{\Phi}_{12} + 2c_A^2 \Phi_{12}^{(1)} - c_A^3 \Phi_{12}^{(2)}\Big) && (7.583) \\
= \ & \sqrt{c_A c_B}\left((c_A + c_B)^2 \Phi_{12}^{(1)} + \Phi_{12}^{(2)}(c_A + c_B)^2 (c_B - c_A)\right) && (7.584) \\
| \ & \text{use } c_A + c_B = 1 \\
= \ & \sqrt{c_A c_B}\left(\Phi_{12}^{(1)} + (c_B - c_A)\Phi_{12}^{(2)}\right) && (7.585)
\end{aligned}
$$

$$\begin{aligned}
& \text{Element row 4 column 4} \\
= \;& \Phi_{12}^{AA}c_B^2 + \Phi_{12}^{AB}c_Ac_B + \Phi_{12}^{BA}c_Ac_B + \Phi_{12}^{BB}c_A^2 && (7.586)\\
= \;& \bar{\Phi}^{12}c_B^2 + 2c_B^3\Phi_{12}^{(1)} + c_B^4\Phi_{12}^{(2)} + 2c_Ac_B\bar{\Phi}_{12} + 2c_Ac_B(c_B - c_A)\Phi_{12}^{(1)} \\
& -2c_A^2c_B^2\Phi_{12}^{(2)} + \bar{\Phi}_{12}c_A^2 - 2c_A^3\Phi_{12}^{(1)} + c_A^4\Phi_{12}^{(2)} && (7.587)\\
= \;& \bar{\Phi}_{12} + 2\Phi_{12}^{(1)}(c_B - c_A)(c_A + c_B)^2 + \Phi_{12}^{(2)}(c_B - c_A)^2(c_A + c_B)^2 && (7.588)\\
| \;& \text{use } c_A + c_B = 1 \\
= \;& \bar{\Phi}_{12} + 2\Phi_{12}^{(1)}(c_B - c_A) + \Phi_{12}^{(2)}(c_B - c_A)^2 && (7.589)
\end{aligned}$$

Just like for the mass matrix, we want to write it in terms of projectors so that we can generalize it to the N site case.

We first work out the arrangement of the basis for reference. We denote $|0\rangle_c \to |\uparrow\rangle$ and $|1\rangle_c \to |\downarrow\rangle$.

$$\begin{aligned}
& \begin{pmatrix} |0_1\rangle_{cc}\langle 0_1| & |1_1\rangle_{cc}\langle 0_1| \\ |0_1\rangle_{cc}\langle 1_1| & |1_1\rangle_{cc}\langle 1_1| \end{pmatrix} \otimes \begin{pmatrix} |0_2\rangle_{cc}\langle 0_2| & |1_2\rangle_{cc}\langle 0_2| \\ |0_2\rangle_{cc}\langle 1_2| & |1_2\rangle_{cc}\langle 1_2| \end{pmatrix} \otimes \mathbb{I}_{2\times 2}^{(3)} \\
\equiv \;& \begin{pmatrix} P_{\uparrow_1} & P_{\downarrow_1\uparrow_1} \\ P_{\uparrow_1\downarrow_1} & P_{\downarrow_1} \end{pmatrix} \otimes \begin{pmatrix} P_{\uparrow_2} & P_{\downarrow_2\uparrow_2} \\ P_{\uparrow_2\downarrow_2} & P_{\downarrow_2} \end{pmatrix} \otimes \mathbb{I}_{2\times 2}^{(3)} && (7.590)\\
= \;& \begin{pmatrix} P_{\uparrow_1}\otimes P_{\uparrow_2} & P_{\uparrow_1}\otimes P_{\downarrow_2\uparrow_2} & P_{\downarrow_1\uparrow_1}\otimes P_{\uparrow_2} & P_{\downarrow_1\uparrow_1}\otimes P_{\downarrow_2\uparrow_2} \\ P_{\uparrow_1}\otimes P_{\uparrow_2\downarrow_2} & P_{\uparrow_1}\otimes P_{\downarrow_2} & P_{\downarrow_1\uparrow_1}\otimes P_{\uparrow_2\downarrow_2} & P_{\downarrow_1\uparrow_1}\otimes P_{\downarrow_2} \\ P_{\uparrow_1\downarrow_1}\otimes P_{\uparrow_2} & P_{\uparrow_1\downarrow_1}\otimes P_{\downarrow_2\uparrow_2} & P_{\downarrow_1}\otimes P_{\uparrow_2} & P_{\downarrow_1}\otimes P_{\downarrow_2\uparrow_2} \\ P_{\uparrow_1\downarrow_1}\otimes P_{\uparrow_2\downarrow_2} & P_{\uparrow_1\downarrow_1}\otimes P_{\downarrow_2} & P_{\downarrow_1}\otimes P_{\uparrow_2\downarrow_2} & P_{\downarrow_1}\otimes P_{\downarrow_2} \end{pmatrix} \otimes \mathbb{I}_{2\times 2}^{(3)} && (7.591)
\end{aligned}$$

We continue rewriting $(\Phi_{12})_{8\times 8}$ in terms of these projectors. Grouping similar terms,

$$\begin{aligned}
(\Phi_{12})_{8\times 8} = \;& \big[\bar{\Phi}_{12}\left(P_{\uparrow_1}\otimes P_{\uparrow_2} + P_{\uparrow_1}\otimes P_{\downarrow_2} + P_{\downarrow_1}\otimes P_{\uparrow_2} + P_{\downarrow_1}\otimes P_{\downarrow_2}\right) \\
& +\Phi_{12}^{(1)}\sqrt{c_Ac_B}\,(P_{\uparrow_1}\otimes P_{\downarrow_2\uparrow_2} + P_{\downarrow_1\uparrow_1}\otimes P_{\uparrow_2} + P_{\uparrow_1}\otimes P_{\uparrow_2\downarrow_2} + P_{\uparrow_1\downarrow_1}\otimes P_{\uparrow_2} + P_{\downarrow_1\uparrow_1}\otimes P_{\downarrow_2} \\
& +P_{\downarrow_1}\otimes P_{\downarrow_2\uparrow_2} + P_{\uparrow_1\downarrow_1}\otimes P_{\downarrow_2} + P_{\downarrow_1}\otimes P_{\uparrow_2\downarrow_2}) \\
& +\Phi_{12}^{(1)}(c_B - c_A)\left(P_{\uparrow_1}\otimes P_{\downarrow_2} + P_{\downarrow_1}\otimes P_{\uparrow_2} + 2P_{\downarrow_1}\otimes P_{\downarrow_2}\right) \\
& +\Phi_{12}^{(2)}c_Ac_B\left(P_{\downarrow_1\uparrow_1}\otimes P_{\downarrow_2\uparrow_2} + P_{\downarrow_1\uparrow_1}\otimes P_{\uparrow_2\downarrow_2} + P_{\uparrow_1\downarrow_1}\otimes P_{\downarrow_2\uparrow_2} + P_{\uparrow_1\downarrow_1}\otimes P_{\uparrow_2\downarrow_2}\right) \\
& +\Phi_{12}^{(2)}(c_B - c_A)\sqrt{c_Ac_B}\left(P_{\downarrow_1\uparrow_1}\otimes P_{\downarrow_2} + P_{\downarrow_1}\otimes P_{\downarrow_2\uparrow_2} + P_{\uparrow_1\downarrow_1}\otimes P_{\downarrow_2} + P_{\downarrow_1}\otimes P_{\uparrow_2\downarrow_2}\right) \\
& +\Phi_{12}^{(2)}(c_B - c_A)^2\left(P_{\downarrow_1}\otimes P_{\downarrow_2}\right)\big] \otimes \mathbb{I}_{2\times 2}^{(3)} && (7.592)\\
| \;& \text{denote } T_{\uparrow_2\downarrow_2} = P_{\uparrow_2\downarrow_2} + P_{\downarrow_2\uparrow_2} \\
= \;& \bar{\Phi}_{12}\mathbb{I}_{4\times 4}\otimes\mathbb{I}_{2\times 2} + \Phi_{12}^{(1)}\sqrt{c_Ac_B}\left(P_{\uparrow_1}\otimes T_{\uparrow_2\downarrow_2} + T_{\uparrow_1\downarrow_1}\otimes P_{\uparrow_2} + T_{\uparrow_1\downarrow_1}\otimes P_{\downarrow_2} + P_{\downarrow_1}\otimes T_{\uparrow_2\downarrow_2}\right)\otimes\mathbb{I}_{2\times 2} \\
& +\Phi_{12}^{(1)}(c_B - c_A)\left(P_{\uparrow_1}\otimes P_{\downarrow_2} + P_{\downarrow_1}\otimes P_{\uparrow_2} + 2P_{\downarrow_1}\otimes P_{\downarrow_2}\right)\otimes\mathbb{I}_{2\times 2} \\
& +\Phi_{12}^{(2)}c_Ac_B\left(P_{\downarrow_1\uparrow_1}\otimes T_{\uparrow_2\downarrow_2} + P_{\uparrow_1\downarrow_1}\otimes T_{\uparrow_2\downarrow_2}\right)\otimes\mathbb{I}_{2\times 2} \\
& +\Phi_{12}^{(2)}(c_B - c_A)\sqrt{c_Ac_B}\left(P_{\downarrow_1}\otimes T_{\uparrow_2\downarrow_2} + T_{\uparrow_1\downarrow_1}\otimes P_{\downarrow_2}\right)\otimes\mathbb{I}_{2\times 2} \\
& +\Phi_{12}^{(2)}(c_B - c_A)^2\left(P_{\downarrow_1}\otimes P_{\downarrow_2}\right)\otimes\mathbb{I}_{2\times 2} && (7.593)\\
| \;& \text{further note that } P_{\uparrow_2} + P_{\downarrow_2} = \mathbb{I}_{2\times 2}^{(2)} \\
= \;& \bar{\Phi}_{12}\mathbb{I}_{8\times 8} + \Phi_{12}^{(1)}\sqrt{c_Ac_B}\left[\mathbb{I}_{2\times 2}^{(1)}\otimes T_{\uparrow_2\downarrow_2} + T_{\uparrow_1\downarrow_1}\otimes\mathbb{I}_{2\times 2}^{(2)}\right]\otimes\mathbb{I}_{2\times 2}^{(3)} \\
& +\Phi_{12}^{(1)}(c_B - c_A)\left[P_{\downarrow_1}\otimes\mathbb{I}_{2\times 2}^{(2)} + \mathbb{I}_{2\times 2}^{(1)}\otimes P_{\downarrow_2}\right]\otimes\mathbb{I}_{2\times 2}^{(3)} \\
& +\Phi_{12}^{(2)}c_Ac_B\left[T_{\uparrow_1\downarrow_1}\otimes T_{\uparrow_2\downarrow_2}\right]\otimes\mathbb{I}_{2\times 2}^{(3)}
\end{aligned}$$

$$+\Phi_{12}^{(2)}(c_B-c_A)\sqrt{c_Ac_B}\left[P_{\downarrow_1}\otimes T_{\uparrow_2\downarrow_2}+T_{\uparrow_1\downarrow_1}\otimes P_{\downarrow_2}\right]\otimes\mathbb{I}_{2\times 2}^{(3)}$$
$$+\Phi_{12}^{(2)}(c_B-c_A)^2\left(P_{\downarrow_1}\otimes P_{\downarrow_2}\right)\otimes\mathbb{I}_{2\times 2}^{(3)} \tag{7.594}$$

Other off-diagonal force constant terms are augmented similarly.[10] The diagonal force constant terms are obtained by using the sum-rule

$$\Phi_{ll}=-\sum_{l'(\neq l)}\Phi_{ll'} \tag{7.595}$$

where the sum is over the nearest neighbors. The sum-rule is thus built into the theory.

The general form of the off-diagonal terms are,

$$\begin{aligned}
\Phi_{ll'(l'\neq l)}^{\mathrm{AUG}} &= \bar{\Phi}_{ll'}\mathbb{I}_{2^N\times 2^N}\\
&\quad+\Phi_{ll'}^{(1)}(c_B-c_A)\mathbb{I}_{2\times 2}^{(1)}\otimes\cdots\otimes\left(P_{\downarrow_l}\otimes\mathbb{I}_{2\times 2}^{(l')}+\mathbb{I}_{2\times 2}^{(l)}\otimes P_{\downarrow_{l'}}\right)\otimes\cdots\otimes\mathbb{I}_{2\times 2}^{(N)}\\
&\quad+\Phi_{ll'}^{(1)}\sqrt{c_Ac_B}\mathbb{I}_{2\times 2}^{(1)}\otimes\cdots\otimes\left(\mathbb{I}_{2\times 2}^{(l)}\otimes T_{\uparrow_{l'}\downarrow_{l'}}+T_{\uparrow_l\uparrow_l}\otimes\mathbb{I}_{2\times 2}^{(l')}\right)\otimes\cdots\otimes\mathbb{I}_{2\times 2}^{(N)}\\
&\quad+\Phi_{ll'}^{(2)}(c_B-c_A)^2\mathbb{I}_{2\times 2}^{(1)}\otimes\cdots\otimes\left(P_{\downarrow_l}\otimes P_{\downarrow_{l'}}\right)\otimes\cdots\otimes\mathbb{I}_{2\times 2}^{(N)}\\
&\quad+\Phi_{ll'}^{(2)}(c_B-c_A)\sqrt{c_Ac_B}\mathbb{I}_{2\times 2}^{(1)}\otimes\cdots\otimes\left(P_{\downarrow_l}\otimes T_{\uparrow_{l'}\downarrow_{l'}}+T_{\uparrow_l\downarrow_l}\otimes P_{\downarrow_{l'}}\right)\otimes\cdots\otimes\mathbb{I}_{2\times 2}^{(N)}\\
&\quad+\Phi_{ll'}^{(2)}c_Ac_B\mathbb{I}_{2\times 2}^{(1)}\otimes\cdots\otimes\left(T_{\uparrow_l\downarrow_l}\otimes T_{\uparrow_{l'}\downarrow_{l'}}\right)\otimes\cdots\otimes\mathbb{I}_{2\times 2}^{(N)} &(7.596)\\
&\quad\Big|\ \text{use a condensed notation}\\
&\equiv \bar{\Phi}_{ll'}\mathbb{I}_{2^N\times 2^N}+\Psi_{ll'(l'\neq l)} &(7.597)
\end{aligned}$$

Using the sum-rule, the (augmented) diagonal term is taken to be as

$$\begin{aligned}
\Phi_{ll}^{\mathrm{AUG}} &= -\sum_{l'(\neq l)}\Phi_{ll'(l'\neq l)}^{\mathrm{AUG}} &(7.598)\\
&= -\sum_{l'(\neq l)}\bar{\Phi}_{ll'}\mathbb{I}_{2^N\times 2^N}-\sum_{l'(\neq l)}\Psi_{ll'(l'\neq l)} &(7.599)
\end{aligned}$$

Now that the relevant operators are augmented, the next step will be to calculate the configuration averaged Green's function. Recall, under the augmented space formalism, the configuration averaged Green's function is

$$\begin{aligned}
\langle D_{ll'}\rangle_c &= {}_c\langle 0_1\ldots 0_N|D_{ll'}^{\mathrm{AUG}}|0_1\ldots 0_N\rangle_c &(7.600)\\
&= {}_c\langle 0_1\ldots 0_N|\left(M^{\mathrm{AUG}}\omega^2-\Phi^{\mathrm{AUG}}\right)^{-1}|0_1\ldots 0_N\rangle_c &(7.601)
\end{aligned}$$

Of course, $\langle D_{ll'}\rangle_c$ cannot be calculated exactly even in this formalism. We will work towards a recursion method and solve $\langle D_{ll'}\rangle_c$ recursively. [11]

We need a bit more arrangement before we can apply Haydock's recursion method. We need to "get

[10] I did not check these terms. The pattern of the terms should be convincing. I will be quoting the results off Mookerjee's paper.

[11] Perturbation theory could be possible at this stage as well. Here we propose a possible starting point. First we write the full augmented force constant matrix explicitly.

$$\begin{aligned}
\Phi_{ll'}^{\mathrm{AUG}} &= \Phi_{ll}^{\mathrm{AUG}}+\Phi_{ll'(l'\neq l)}^{\mathrm{AUG}} &(7.602)\\
&= -\sum_{l'(\neq l)}\bar{\Phi}_{ll'}\mathbb{I}_{2^N\times 2^N}-\sum_{l'(\neq l)}\Psi_{ll'(l'\neq l)}+\bar{\Phi}_{ll'}\mathbb{I}_{2^N\times 2^N}+\Psi_{ll'(l'\neq l)} &(7.603)
\end{aligned}$$

rid" of the mass matrix.

$$\begin{aligned}
\langle D_{ll'}\rangle_c &= {}_c\langle 0_1\dots 0_N|\left(M^{\text{AUG}}\omega^2-\Phi^{\text{AUG}}\right)^{-1}|0_1\dots 0_N\rangle_c && (7.609)\\
&\mid\quad \text{since } M^{\text{AUG}} \text{ is diagonal, } M^{\text{AUG}-\frac{1}{2}} \text{ is well defined}\\
&= {}_c\langle 0_1\dots 0_N|M^{\text{AUG}-\frac{1}{2}}\left(\omega^2\mathbb{I}_{N\times N}\otimes\mathbb{I}_{2^N\times 2^N}-M^{\text{AUG}-\frac{1}{2}}\Phi^{\text{AUG}}M^{\text{AUG}-\frac{1}{2}}\right)^{-1}M^{\text{AUG}-\frac{1}{2}}|0_1\dots 0_N\rangle_c && (7.610)
\end{aligned}$$

Just to be explicit, the expression of $M^{\text{AUG}-\frac{1}{2}}$ is shown here.

$$\begin{aligned}
M^{\text{AUG}-\frac{1}{2}} &= \left(M_A^{-\frac{1}{2}}c_A+M_B^{-\frac{1}{2}}c_B\right)\mathbb{I}_{N\times N}\otimes\mathbb{I}_{2^N\times 2^N}\\
&\quad+\left(M_A^{-\frac{1}{2}}-M_B^{-\frac{1}{2}}\right)\sum_{l=1}^{N}|l\rangle\langle l|\otimes\mathbb{I}^{(1)}_{2\times 2}\otimes\cdots\otimes\mathbb{I}^{(l-1)}_{2\times 2}\\
&\quad\otimes\left[(c_B-c_A)|1_l\rangle_{cc}\langle 1_l|+\sqrt{c_Ac_B}\left(|0_l\rangle_{cc}\langle 1_l|+|1_l\rangle_{cc}\langle 0_l|\right)\right]\otimes\mathbb{I}^{(l+1)}_{2\times 2}\otimes\cdots\otimes\mathbb{I}^{(N)}_{2\times 2} && (7.611)
\end{aligned}$$

We need to know the action of $M^{\text{AUG}-\frac{1}{2}}$ on $|0_1\dots 0_N\rangle_c$ so that the mass matrix can be "removed". We start with the special case,

$$\begin{aligned}
&M_{11}^{\text{AUG}-\frac{1}{2}}|0_1\dots 0_N\rangle_c\\
=&\left[\left(M_A^{-\frac{1}{2}}c_A+M_B^{-\frac{1}{2}}c_B\right)+\left(M_A^{-\frac{1}{2}}-M_B^{-\frac{1}{2}}\right)(c_B-c_A)|1_1\rangle_{cc}\langle 1_1|\right.\\
&\left.+\sqrt{c_Ac_B}\left(M_A^{-\frac{1}{2}}-M_B^{-\frac{1}{2}}\right)\left(|0_1\rangle_{cc}\langle 1_1|+|1_1\rangle_{cc}\langle 0_1|\right)\right]|0_1\dots 0_N\rangle_c && (7.612)\\
&\mid\quad \text{only the first and third terms are nonzero}\\
=&\left(M_A^{-\frac{1}{2}}c_A+M_B^{-\frac{1}{2}}c_B\right)|0_1\dots 0_N\rangle_c+\sqrt{c_Ac_B}\left(M_A^{-\frac{1}{2}}-M_B^{-\frac{1}{2}}\right)|1_10_2\dots 0_N\rangle_c && (7.613)
\end{aligned}$$

$$\begin{aligned}
&= \bar{\Phi}_{ll'}\mathbb{I}_{2^N\times 2^N}-\sum_{l'(\neq l)}\bar{\Phi}_{ll'}\mathbb{I}_{2^N\times 2^N}+\Psi_{ll'(l'\neq l)}-\sum_{l'(\neq l)}\Psi_{ll'(l'\neq l)} && (7.604)\\
&\mid\quad \text{the first 2 terms are diagonal in configuration space}\\
&\equiv \langle\Phi\rangle_c+\Psi_{ll'(l'\neq l)}-\sum_{l'(\neq l)}\Psi_{ll'(l'\neq l)} && (7.605)
\end{aligned}$$

Then we can write,

$$\begin{aligned}
D_{ll'}^{\text{AUG}} &= \left(M^{\text{AUG}}\omega^2-\Phi^{\text{AUG}}\right)^{-1} && (7.606)\\
&= \left(\left(\bar{M}+M'\right)\omega^2-\langle\Phi\rangle_c-\left(\Psi_{ll'(l'\neq l)}-\sum_{l'(\neq l)}\Psi_{ll'(l'\neq l)}\right)\right)^{-1} && (7.607)\\
&\mid\quad \text{define } D^{\text{VCA}-1}\equiv\bar{M}\omega^2-\langle\Phi\rangle_c\\
&\mid\quad \text{define } -M'\omega^2+\Psi_{ll'(l'\neq l)}-\sum_{l'(\neq l)}\Psi_{ll'(l'\neq l)}\equiv\mathcal{D}\\
&= \left(D^{\text{VCA}-1}-\mathcal{D}\right)^{-1} && (7.608)
\end{aligned}$$

So we can choose D^{VCA} as the unperturbed Green's function and $\mathcal{D}$ is the "self energy".

Therefore we can deduce the general result

$$\begin{aligned} M^{\mathrm{AUG}-\frac{1}{2}}|0_1\dots 0_N\rangle_c &= \left(M_A^{-\frac{1}{2}}c_A + M_B^{-\frac{1}{2}}c_B\right)|0_1\dots 0_N\rangle_c \\ &\quad +\sqrt{c_Ac_B}\left(M_A^{-\frac{1}{2}} - M_B^{-\frac{1}{2}}\right)\sum_l |0_1\dots 1_l\dots 0_N\rangle_c && (7.614) \\ &\equiv |1) && (7.615) \end{aligned}$$

where $|1)$ denotes an unnormalized ket. We will use its normalized version $|1\rangle \equiv |1)/\sqrt{(1|1)}$. [12] Back to the configuration averaged Green's function,

$$\begin{aligned} \langle D_{ll'}\rangle_c &= {}_c\langle 0_1\dots 0_N|M^{\mathrm{AUG}-\frac{1}{2}}\left(\omega^2\mathbb{I}_{N2^N\times N2^N} - M^{\mathrm{AUG}-\frac{1}{2}}\Phi^{\mathrm{AUG}}M^{\mathrm{AUG}-\frac{1}{2}}\right)^{-1}M^{\mathrm{AUG}-\frac{1}{2}}|0_1\dots 0_N\rangle_c && (7.618) \\ &= (1|\left(\omega^2\mathbb{I}_{N2^N\times N2^N} - M^{\mathrm{AUG}-\frac{1}{2}}\Phi^{\mathrm{AUG}}M^{\mathrm{AUG}-\frac{1}{2}}\right)^{-1}|1) && (7.619) \\ &= \langle 1|\sqrt{(1|1)}\left(\omega^2\mathbb{I}_{N2^N\times N2^N} - M^{\mathrm{AUG}-\frac{1}{2}}\Phi^{\mathrm{AUG}}M^{\mathrm{AUG}-\frac{1}{2}}\right)^{-1}\sqrt{(1|1)}|1\rangle && (7.620) \\ &= \langle 1|\left(\frac{\omega^2}{(1|1)}\mathbb{I}_{N2^N\times N2^N} - \frac{M^{\mathrm{AUG}-\frac{1}{2}}}{\sqrt{(1|1)}}\Phi^{\mathrm{AUG}}\frac{M^{\mathrm{AUG}-\frac{1}{2}}}{\sqrt{(1|1)}}\right)^{-1}|1\rangle && (7.621) \\ &\quad | \quad \text{denote } \omega'^2 \equiv \frac{\omega^2}{(1|1)} \text{ and } \frac{M^{\mathrm{AUG}-\frac{1}{2}}}{\sqrt{(1|1)}}\Phi^{\mathrm{AUG}}\frac{M^{\mathrm{AUG}-\frac{1}{2}}}{\sqrt{(1|1)}} \equiv \Phi^{\mathrm{eff}} \\ &= \langle 1|\left(\omega'^2\mathbb{I}_{N2^N\times N2^N} - \Phi^{\mathrm{eff}}\right)^{-1}|1\rangle && (7.622) \end{aligned}$$

To put this expression into a continued fraction form, we need to define a basis. Consider this non-orthogonal set ($|\phi_n)$ kets are unnormalized),

$$\left\{|1\rangle, \Phi^{\mathrm{eff}}|1\rangle, \Phi^{\mathrm{eff}}|\phi_2), \dots\right\} \tag{7.623}$$

We carry out Gram-Schmidt orthogonalization for this set (without normalizing it). First is $\Phi^{\mathrm{eff}}|1\rangle$,

$$\begin{aligned} |\phi_2) &= \Phi^{\mathrm{eff}}|1\rangle - |1\rangle\langle 1|\Phi^{\mathrm{eff}}|1\rangle && (7.624) \\ &\quad | \quad \text{denote } a_1 \equiv \langle 1|\Phi^{\mathrm{eff}}|1\rangle \\ &= \Phi^{\mathrm{eff}}|1\rangle - |1\rangle a_1 && (7.625) \end{aligned}$$

[12] The magnitude is

$$\begin{aligned} (1|1) &= \left[\left(M_A^{-\frac{1}{2}}c_A + M_B^{-\frac{1}{2}}c_B\right){}_c\langle 0_1\dots 0_N| + \sqrt{c_Ac_B}\left(M_A^{-\frac{1}{2}} - M_B^{-\frac{1}{2}}\right)\sum_{l_1}{}_c\langle 0_1\dots 1_{l_1}\dots 0_N|\right] \\ &\quad \times\left[\left(M_A^{-\frac{1}{2}}c_A + M_B^{-\frac{1}{2}}c_B\right)|0_1\dots 0_N\rangle_c + \sqrt{c_Ac_B}\left(M_A^{-\frac{1}{2}} - M_B^{-\frac{1}{2}}\right)\sum_{l_2}|0_1\dots 1_{l_2}\dots 0_N\rangle_c\right] && (7.616) \\ &\quad | \quad \text{use the orthogonality of the states} \\ &= \left(M_A^{-\frac{1}{2}}c_A + M_B^{-\frac{1}{2}}c_B\right)^2 + N\left(\sqrt{c_Ac_B}\left(M_A^{-\frac{1}{2}} - M_B^{-\frac{1}{2}}\right)\right)^2 && (7.617) \end{aligned}$$

Next is $\Phi^{\text{eff}}|\phi_2)$,

$$\begin{aligned}
|\phi_3) &= \Phi^{\text{eff}}|\phi_2) - |1\rangle\langle 1|\Phi^{\text{eff}}|\phi_2) - |\phi_2\rangle\langle\phi_2|\Phi^{\text{eff}}|\phi_2) && (7.626)\\
&\mid \quad \text{where } \langle\phi_2| = \frac{(\phi_2|}{\sqrt{(\phi_2|\phi_2)}}\\
&\mid \quad \text{denote } b_2^2 \equiv \langle 1|\Phi^{\text{eff}}|\phi_2)\\
&= \Phi^{\text{eff}}|\phi_2) - |1\rangle b_2^2 - |\phi_2)\frac{(\phi_2|\Phi^{\text{eff}}|\phi_2)}{(\phi_2|\phi_2)} && (7.627)\\
&\mid \quad \text{denote } a_2 \equiv \frac{(\phi_2|\Phi^{\text{eff}}|\phi_2)}{(\phi_2|\phi_2)}\\
&= \Phi^{\text{eff}}|\phi_2) - |\phi_2)a_2 - |1\rangle b_2^2 && (7.628)
\end{aligned}$$

Next is $\Phi^{\text{eff}}|\phi_3)$

$$\begin{aligned}
|\phi_4) &= \Phi^{\text{eff}}|\phi_3) - |1\rangle\langle 1|\Phi^{\text{eff}}|\phi_3) - |\phi_2\rangle\langle\phi_2|\Phi^{\text{eff}}|\phi_3) - |\phi_3\rangle\langle\phi_3|\Phi^{\text{eff}}|\phi_3) && (7.629)\\
&\mid \quad \text{recall } \langle 1|\Phi^{\text{eff}} = (\phi_2| + a_1\langle 1| \text{ and both are orthogonal to } |\phi_3)\\
&= \Phi^{\text{eff}}|\phi_3) - |\phi_2)\frac{(\phi_2|\Phi^{\text{eff}}|\phi_3)}{(\phi_2|\phi_2)} - |\phi_3)\frac{(\phi_3|\Phi^{\text{eff}}|\phi_3)}{(\phi_3|\phi_3)} && (7.630)\\
&\mid \quad \text{define } b_3^2 \equiv \frac{(\phi_2|\Phi^{\text{eff}}|\phi_3)}{(\phi_2|\phi_2)} \text{ and } a_3 \equiv \frac{(\phi_3|\Phi^{\text{eff}}|\phi_3)}{(\phi_3|\phi_3)}\\
&= \Phi^{\text{eff}}|\phi_3) - |\phi_3)a_3 - |\phi_2)b_3^2 && (7.631)
\end{aligned}$$

In general,

$$\boxed{\begin{aligned}
&|\phi_{n+1}) = \Phi^{\text{eff}}|\phi_n) - |\phi_v)a_n - |\phi_{n-1})b_n^2 && (7.632)\\
&a_n = \frac{(\phi_n|\Phi^{\text{eff}}|\phi_n)}{(\phi_n|\phi_n)} \quad , \quad b_n^2 = \frac{(\phi_{n-1}|\Phi^{\text{eff}}|\phi_n)}{(\phi_{n-1}|\phi_{n-1})} && (7.633)
\end{aligned}}$$

Thus in this basis, Φ^{eff} is a tridiagonal matrix.

$$\Phi^{\text{eff}} = \begin{array}{c} \\ \langle 1| \\ \langle\phi_2| \\ \langle\phi_3| \\ \langle\phi_4| \\ \vdots \end{array} \begin{array}{c} \begin{array}{ccccc} |1\rangle & |\phi_2\rangle & |\phi_3\rangle & |\phi_4\rangle & \cdots \end{array} \\ \begin{pmatrix} a_1 & b_2^2 & & & \\ 1 & a_2 & b_3^2 & & \\ & 1 & a_3 & b_4^2 & \\ & & 1 & a_4 & b_5^2 \\ & & & & \ddots \end{pmatrix} \end{array} \tag{7.634}$$

$$\omega'^2\mathbb{I} - \Phi^{\text{eff}} = \begin{pmatrix} \omega'^2 - a_1 & -b_2^2 & & & \\ -1 & \omega'^2 - a_2 & -b_3^2 & & \\ & -1 & \omega'^2 - a_3 & -b_4^2 & \\ & & -1 & \omega'^2 - a_4 & -b_5^2 \\ & & & & \ddots \end{pmatrix} \tag{7.635}$$

Denote the determinant of the whole matrix be D_0, and the determinant without the first row and first column be D_1 and the determinant without the first 2 rows and first 2 columns be D_2 and so on. Then we have a simple form for the configuration averaged Green's function.

$$\langle D_{ll'} \rangle_c = \langle 1 | \left(\omega'^2 \mathbb{I} - \Phi^{\text{eff}} \right)^{-1} | 1 \rangle = \frac{D_1}{D_0} = \frac{1}{D_0/D_1} \tag{7.636}$$

It seems like we are left with evaluating D_0 and D_1. Use Laplace expansion for D_0,

$$\begin{aligned} D_0 &= (\omega'^2 - a_1) D_1 - (-1) \begin{vmatrix} -b_2^2 & 0 \\ -1 & \ddots \end{vmatrix} & (7.637) \\ & \quad | \quad \text{expand the first row of the determinant} \\ &= (\omega'^2 - a_1) D_1 - b_2^2 D_2 & (7.638) \end{aligned}$$

The general pattern in the Laplace expansion is thus clear,

$$D_n = (\omega'^2 - a_{n+1}) D_{n+1} - b_{n+2}^2 D_{n+2} \tag{7.639}$$

So,

$$\begin{aligned} \langle D_{ll'} \rangle_c &= \frac{1}{\omega'^2 - a_1 - \frac{b_2^2}{D_1/D_2}} & (7.640) \\ & \quad | \quad \text{continuing, we get a continued fraction} \\ &= \cfrac{1}{\omega'^2 - a_1 - \cfrac{b_2^2}{\omega'^2 - a_2 - \cfrac{b_3^2}{\omega'^2 - a_3 - \cfrac{b_4^2}{\vdots}}}} & (7.641) \\ & \quad | \quad \text{in practice, a terminator function is introduced} \\ &= \cfrac{1}{\omega'^2 - a_1 - \cfrac{b_2^2}{\cfrac{\vdots}{\omega'^2 - a_n - b_{n+1}^2 T(\omega'^2)}}} & (7.642) \end{aligned}$$

$$\boxed{\langle D_{ll'} \rangle_c = \cfrac{1}{\omega'^2 - a_1 - \cfrac{b_2^2}{\cfrac{\vdots}{\omega'^2 - a_n - b_{n+1}^2 T(\omega'^2)}}}} \tag{7.643}$$

The terminator can be calculated from the asymptotic values of the coefficients.

$$\begin{aligned} T(\omega'^2) &= \frac{1}{\omega'^2 - a_{n+1} - \frac{b_{n+2}^2}{\vdots}} & (7.644) \\ & \quad | \quad \text{let } a \text{ and } b \text{ be the asymptotic values of the respective coefficients} \\ &= \frac{1}{\omega'^2 - a - b T(\omega'^2)} & (7.645) \end{aligned}$$

The solution of the quadratic equation is simply,

$$\boxed{T(\omega'^2) = \frac{1}{2b^2}\left[(\omega'^2 - a) \pm \sqrt{(\omega'^2 - a)^2 - 4b^2}\right]} \tag{7.646}$$

[Beer & Pettifor Terminator] The reference is [Beer1984]. Suppose all the coefficients are real, then the spectrum which is related to $\Im\langle D_{ll'}\rangle_c^{\mathrm{R\ or\ A}}$ is only coming from $T(\omega'^2)$. So we look at the condition where $T(\omega'^2)$ has an imaginary part. This means,

$$(\omega'^2 - a)^2 - 4b^2 < 0 \Longrightarrow a - 2b < \omega'^2 < a + 2b \tag{7.647}$$

The width of this band (of delta functions) is $4b$.

The physical condition that Beer and Pettifor impose on a and b is that, no delta function will be outside the band. So we simply put the first and last delta functions at the bands limits ($a \pm 2b$) itself. That means, we demand the Green's function to diverge (due to the delta functions) at both band limits $a - 2b$ and $a + 2b$.

We substitute the band limits into the Green's function

$$\langle D_{ll'}(\omega'^2 = a \pm 2b)\rangle_c = \cfrac{1}{a \pm 2b - a_1 - \cfrac{b_2^2}{a \pm 2b - a_2 - \cfrac{b_3^2}{\vdots}}} \tag{7.648}$$

$|$ suppose it is terminated at step n

$$= \cfrac{1/2}{\pm b - \frac{a_1 - a}{2} - \cfrac{b_2^2/4}{\pm b - \frac{a_2 - a}{2} - \cfrac{b_3^2/4}{\cfrac{\vdots}{\cfrac{b_n^2/2}{\pm b - (a_n - a)}}}}} \tag{7.649}$$

$|$ write back into a (finite) tridiagonal matrix form

$$= \langle 1| \begin{pmatrix} \pm b - \frac{a_1 - a}{2} & b_2/2 & 0 & & 0 \\ b_2/2 & \pm b - \frac{a_2 - a}{2} & b_3/2 & & 0 \\ \vdots & \vdots & \vdots & \ddots & 0 \\ & & & & b_n/\sqrt{2} \\ 0 & 0 & 0 & b_n/\sqrt{2} & \pm b - (a_n - a) \end{pmatrix}^{-1} |1\rangle$$

$$= \langle 1| \left[\pm b\mathbb{I} - \begin{pmatrix} \frac{a_1 - a}{2} & b_2/2 & & \\ b_2/2 & \frac{a_2 - a}{2} & & \\ & & \ddots & \\ & & & b_n/\sqrt{2} \\ & & b_n\sqrt{2} & a_n - a \end{pmatrix} \right]^{-1} |1\rangle \tag{7.650}$$

The expression in the square brackets is of the form of an eigenvalue problem (i.e. $b\mathbb{I} - \hat{H}$). Hence for a given a, the eigenvalues of $\hat{H}$ cause $(b\mathbb{I} - \hat{H})^{-1}$ to diverge.

We denote the eigenvalues as $\tilde{b}$ and arrange them as $\tilde{b}_{\max} \ldots \tilde{b}_{\min}$. $\tilde{b}_{\max}$ is where no delta function splits off the top of the band. $\tilde{b}_{\min}$ is where no delta function splits off the bottom of the band.

Algorithm to calculate the Beer & Pettifor terminator,

1. Choose $a = a_n$ or $a = \frac{1}{n}\sum_{i=1}^{n} a_i$.
2. Find the eigenvalues of the above finite tridiagonal matrix $\hat{H}$. Extract the largest eigenvalue $\tilde{b}_{\rm max}$ and the smallest eigenvalue $\tilde{b}_{\rm min}$. If $\tilde{b}_{\rm max} \neq |\tilde{b}_{\rm min}|$ then change a to
$$a_{\rm new} = a_{\rm old} + \tilde{b}_{\rm max} + \tilde{b}_{\rm min} \tag{7.651}$$
3. Repeat until $\tilde{b}_{\rm max} + \tilde{b}_{\rm min} = 0$.
4. Construct the terminator function $T(\omega'^2)$ using the final value of a and the final value of $b \stackrel{!}{=} \tilde{b}_{\rm max}$.

[Luchini and Nex Interpolation Scheme] If there are spurious structures when the Beer and Pettifor terminator is used, then a linear interpolation scheme by Luchini and Nex in [Luchini1987] that modifies the calculation of the terminator, appears to improve the numerical results.

The scheme is as follows,

$$a'_n \ , \ b'_n = \begin{cases} a_n \ , \ b_n & n < n_1 \\ \frac{a_n(N-n)+a(n-n_1)}{N-n_1} \ , \ \frac{b_n(N-n)+b(n-n_1)}{N-n_1} & n_1 \leq n \leq N \\ a \ , \ b & n > N \end{cases} \tag{7.652}$$

We give an example to illustrate the scheme. Suppose we want to terminate the continued fraction at $N = 20$, and we calculate the terminator cofficients a and b using the Beer and Pettifor method. We can start the interpolation scheme say at $n_1 = 15$. Thus for coefficients $n = 1$ to $n = 14$, we calculate them via the recusion scheme (1st line above). Coefficients $n = 15$ to $n = 20$ are calculated via the interpolation scheme (2nd line above). The terminator coefficients a and b are calculated via the Beer and Pettifor method (3rd line above).

This completes the calculation of the configuration averaged 1-particle Green's function using Mookerjee's augmented space recursion (ASR) method. For Mookerjee's numerical implementation, see [Banerjee2009].

7.9 Mass & Force constant Disorder : ICPA Theory

[Literature] The main reference is [Ghosh2002] and for a conference proceedings version see [Thorpe1982]. The references [Diehl1979a], [Diehl1979b], [Diehl1979c] and [Kaplan1980] preceed the main reference. The reference [Alam2007] compares the previous Mookerjee theory and the present ICPA.

Recall that Mookerjee's ASR method evaluates the ground state expectation value using Haydock's recusion scheme. Here, ICPA is doing the same thing of evaluating the ground state expectation value of the augmented matrix but by a different set of steps: partition the augmented matrix, restrict only to the "single fluctuation subspace" basis then derive self consistent equations to solve for the ground state expectation value.

[Partitioning the Augmented Matrix] We use the $N = 3$ augmented matrix to illustrate the concepts and then we will give the general N-site expression.

Rearrange the configuration space basis in the augmented matrix into the form (we drop the subscript

c in the basis to save space),

$$\begin{aligned}
& A^{\mathrm{AUG}}(\text{which is } 8\times 8 \text{ in size}) \\
= & \left(\begin{array}{c|cccc}
\langle 0_1 0_2 0_3|A^{\mathrm{AUG}}|0_1 0_2 0_3\rangle & \langle 0_1 0_2 0_3|A^{\mathrm{AUG}}|1_1 0_2 0_3\rangle & \langle 0_1 0_2 0_3|A^{\mathrm{AUG}}|0_1 1_2 0_3\rangle & \langle 0_1 0_2 0_3|A^{\mathrm{AUG}}|0_1 0_2 1_3\rangle & \cdots \\
\hline
\langle 1_1 0_2 0_3|A^{\mathrm{AUG}}|0_1 0_2 0_3\rangle & \langle 1_1 0_2 0_3|A^{\mathrm{AUG}}|1_1 0_2 0_3\rangle & \langle 1_1 0_2 0_3|A^{\mathrm{AUG}}|0_1 1_2 0_3\rangle & \langle 1_1 0_2 0_3|A^{\mathrm{AUG}}|0_1 0_2 1_3\rangle & \cdots \\
\langle 0_1 1_2 0_3|A^{\mathrm{AUG}}|0_1 0_2 0_3\rangle & \langle 0_1 1_2 0_3|A^{\mathrm{AUG}}|1_1 0_2 0_3\rangle & \langle 0_1 1_2 0_3|A^{\mathrm{AUG}}|0_1 1_2 0_3\rangle & \langle 0_1 1_2 0_3|A^{\mathrm{AUG}}|0_1 0_2 1_3\rangle & \cdots \\
\langle 0_1 0_2 1_3|A^{\mathrm{AUG}}|0_1 0_2 0_3\rangle & \langle 0_1 0_2 1_3|A^{\mathrm{AUG}}|1_1 0_2 0_3\rangle & \langle 0_1 0_2 1_3|A^{\mathrm{AUG}}|0_1 1_2 0_3\rangle & \langle 0_1 0_2 1_3|A^{\mathrm{AUG}}|0_1 0_2 1_3\rangle & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{array}\right) \\
| & \text{ we have thus partitioned into 4 blocks, and we denote them as} \\
= & \begin{pmatrix} \langle A\rangle_c & A' \\ A'^{\dagger} & \tilde{A} \end{pmatrix} \qquad (7.653)
\end{aligned}$$

The notation $\langle A\rangle_c = {}_c\langle 0_1 0_2 0_3|A^{\mathrm{AUG}}|0_1 0_2 0_3\rangle_c$ is from Augmented Space Formalism (ASF). If we define the projector $P \equiv |0_1 0_2 0_3\rangle_{cc}\langle 0_1 0_2 0_3|$ then each block can be written as,

$$\begin{aligned}
\Rightarrow \langle A\rangle_c &= PA^{\mathrm{AUG}}P && (7.654)\\
\Rightarrow A' &= PA^{\mathrm{AUG}}(\mathbb{I}-P) && (7.655)\\
\Rightarrow A'^{\dagger} &= (\mathbb{I}-P)A^{\mathrm{AUG}}P && (7.656)\\
\Rightarrow \tilde{A} &= (\mathbb{I}-P)A^{\mathrm{AUG}}(\mathbb{I}-P) && (7.657)
\end{aligned}$$

[“Single Fluctuation Subspace”] This is not a true subspace, it is really an approximation. We will only keep the 4×4 matrix elements written explicitly in A^{AUG} above (i.e. all the elements denoted as $\cdots$ and $\vdots$ are discarded). These elements only involve states with single fluctuations $|0_1\ldots 1_i\ldots 0_N\rangle_c$. We denote the smaller augmented matrix by $A^{\mathrm{AUG}}_{\mathrm{SUB}}$. The general N-site expressions (in configuration space dimension) are,

$$\begin{aligned}
A^{\mathrm{AUG}} &= \begin{pmatrix} \langle A\rangle_{c,1\times 1} & A'_{1\times(2^N-1)} \\ A'^{\dagger}_{(2^N-1)\times 1} & \tilde{A}_{(2^N-1)\times(2^N-1)} \end{pmatrix}_{2^N\times 2^N} && (7.658)\\
A^{\mathrm{AUG}}_{\mathrm{SUB}} &= \begin{pmatrix} \langle A\rangle_{c,1\times 1} & A'_{1\times N} \\ A'^{\dagger}_{N\times 1} & \tilde{A}_{N\times N} \end{pmatrix}_{(N+1)\times(N+1)} && (7.659)
\end{aligned}$$

where there is one ground state $|0_1\ldots 0_N\rangle_c$ and N single fluctuation states $|0_1\ldots 1_i\ldots 0_N\rangle_c$.

We need to define notation for the matrix elements in $A^{\mathrm{AUG}}_{\mathrm{SUB}}$ as we will work with the matrix elements later.

$$\begin{aligned}
{}_c\langle 0_1\ldots 0_N|A^{\mathrm{AUG}}_{ll'}|0_1\ldots 0_N\rangle_c &= \langle A_{ll'}\rangle_c && (7.660)\\
{}_c\langle 0_1\ldots 0_N|A^{\mathrm{AUG}}_{ll'}|0_1\ldots 1_i\ldots 0_N\rangle_c &\equiv A'^{(i)}_{ll'} && (7.661)\\
{}_c\langle 0_1\ldots 1_i\ldots 0_N|A^{\mathrm{AUG}}_{ll'}|0_1\ldots 0_N\rangle_c &\equiv A'^{\dagger(i)}_{ll'} && (7.662)\\
{}_c\langle 0_1\ldots 1_i\ldots 0_N|A^{\mathrm{AUG}}_{ll'}|0_1\ldots 1_{i'}\ldots 0_N\rangle_c &\equiv \tilde{A}^{(ii')}_{ll'} && (7.663)\\
& && (7.664)
\end{aligned}$$

The first line is already standard notation. The second and third line denotes a fluctuation around site i and the fourth line denotes fluctuations around sites i and i'.

Now we are ready to tackle the actual problem on calculating the configuration averaged phonon

Green's function.

$$D^{\text{AUG}} = \begin{pmatrix} \langle D\rangle_c & D' \\ D'^{\dagger} & \tilde{D} \end{pmatrix} \equiv \begin{pmatrix} \langle K\rangle_c & K' \\ K'^{\dagger} & \tilde{K} \end{pmatrix}^{-1} = \begin{pmatrix} \langle M\rangle_c\omega^2 - \langle\Phi\rangle_c & M'\omega^2 - \Phi' \\ M'^{\dagger}\omega^2 - \Phi'^{\dagger} & \tilde{M}\omega^2 - \tilde{\Phi} \end{pmatrix}^{-1} \tag{7.665}$$

where $\langle D\rangle_c$ is the quantity we are after. We carry out the block matrix inverse,

$$A^{\text{AUG}-1} = \begin{pmatrix} (\langle A\rangle_c - A'\tilde{A}^{-1}A'^{\dagger})^{-1} & -(\tilde{A}A'^{-1}\langle A\rangle_c - A'^{\dagger})^{-1} \\ -(\langle A\rangle_c A'^{\dagger-1}\tilde{A} - A')^{-1} & (\tilde{A} - A'^{\dagger}\langle A\rangle_c^{-1}A')^{-1} \end{pmatrix} \tag{7.666}$$

The top left block gives

$$\langle D\rangle_c = \left[\langle K\rangle_c - K'\tilde{K}^{-1}K'^{\dagger}\right]^{-1} \tag{7.667}$$

$|$ write in the explicit expressions for $\langle K\rangle_c$ and $\tilde{K}$

$$= \left[\langle M\rangle_c\omega^2 - \langle\Phi\rangle_c - K'(\tilde{M}\omega^2 - \tilde{\Phi})^{-1}K'^{\dagger}\right]^{-1} \tag{7.668}$$

$|$ define $D^{\text{VCA}-1} \equiv \langle M\rangle_c\omega^2 - \langle\Phi\rangle_c$ then add and subtract $D^{\text{VCA}-1}$

$$= \left[D^{\text{VCA}-1} - K'(D^{\text{VCA}-1} - \langle M\rangle_c\omega^2 - \langle\Phi\rangle_c + \tilde{M}\omega^2 - \tilde{\Phi})^{-1}K'^{\dagger}\right]^{-1} \tag{7.669}$$

$$\equiv \left[D^{\text{VCA}-1} - K'FK'^{\dagger}\right]^{-1} \tag{7.670}$$

So we can treat D^{VCA} as the "free" part, then the self energy of this problem is

$$\Sigma \equiv K'FK'^{\dagger} \tag{7.671}$$

$$\text{and} \quad F \equiv \left(D^{\text{VCA}-1} - \langle M\rangle_c\omega^2 - \langle\Phi\rangle_c + \tilde{M}\omega^2 - \tilde{\Phi}\right)^{-1} \tag{7.672}$$

$$\equiv \left(D^{\text{VCA}-1} - \tilde{V}\right)^{-1} \tag{7.673}$$

$$\text{where} \quad \tilde{V} \equiv \left(\langle M\rangle_c - \tilde{M}\right)\omega^2 - \left(\langle\Phi\rangle_c - \tilde{\Phi}\right) \tag{7.674}$$

We can interprete $\tilde{V}$ as a perturbation to the virtual crystal medium, and F causes itineration of fluctuations in the virtual crystal medium. Everything is exact and now we will restrict the theory to only single fluctuation states. Let's write out the matrix elements explicitly (restricted to only single fluctuation states now)

$$\Sigma = K'FK'^{\dagger} \Rightarrow \Sigma_{ll'} = \sum_{i_1 i_2}\sum_{l_1 l_2} K'^{(i_1)}_{ll_1} F^{(i_1 i_2)}_{l_1 l_2} K'^{\dagger(i_2)}_{l_2 l'} \tag{7.675}$$

Note that F itself has the form of a Dyson equation

$$F = \left(D^{\text{VCA}-1} - \tilde{V}\right)^{-1} \Rightarrow F = D^{\text{VCA}} + D^{\text{VCA}}\tilde{V}F \tag{7.676}$$

Showing only fluctuation site indices, (D^{VCA} has no "fluctuations")

$$F^{(i_1 i_2)} = D^{\text{VCA}}\left(\delta^{i_1 i_2} + \sum_{i_3}\tilde{V}^{i_1 i_3}F^{i_3 i_2}\right) \tag{7.677}$$

Now we can further interprete that $K'^{\dagger(i_2)}$ "creates" a fluctuation at site i_2 and $F^{i_1 i_2}$ itinerates it to site i_1 and $K'^{\dagger(i_1)}$ "destroys" the fluctuation at site i_1.

The equations are not self consistent. Just like in CPA, we need a condition to impose so that we can get self consistent equations. We want to use this self consistency cycle: F determines Σ, Σ determines D and D determines F. We shall seek inspiration from CPA by looking at a typical CPA self energy diagram where the "nested" part contains all kinds of self energy diagrams which represents scattering at sites other than site i.

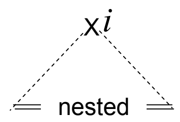


Figure 7.21: *A typical CPA self energy diagram.*

We will now implement the idea in a similar way in ICPA by defining a restricted (or conditional) self energy.

$$\Sigma^{(i)}_{ll'} \equiv \sum_{i_1 i_2 (\neq i)} K'^{(i_1)}_{ll_1} F^{(i_1 i_2)}_{l_1 l_2} K'^{\dagger(i_2)}_{l_2 l'} \tag{7.678}$$

The self energy $\Sigma^{(i)}$ is defined to have scattering at sites other than site i. To form a closed set of equations, we modify the 2 Dyson's equations and write

$$F^{(ii')} = D^{(i)} \left(\delta^{(ii')} + \sum_{i_1} \tilde{V}^{(ii_1)} F^{(i_1 i')} \right) \tag{7.679}$$

$$D^{(i)} = \left(D^{\mathrm{VCA}-1} - \Sigma^{(i)} \right)^{-1} \tag{7.680}$$

These 3 self consistent equations run in the as-mentioned self consistent cycle: $D^{(i)}$ (perhaps starting with $D^{(i)} = D^{\mathrm{VCA}}$) determines $F^{(ii')}$ then $F^{(ii')}$ determines $\Sigma^{(i)}$ and $\Sigma^{(i)}$ determines $D^{(i)}$.

We list the general outline for solving $\langle D \rangle_c$ in this self consistent framework:

1. Solve for $F^{(ii')}$ by using the above 3 equations. The converged $F^{(ii')}$ is what we want.
2. Substitute $F^{(ii')}$ into $\Sigma_{ll'} = \sum_{i_1 i_2} \sum_{l_1 l_2} K'^{(i_1)}_{ll_1} F^{(i_1 i_2)}_{l_1 l_2} K'^{\dagger(i_2)}_{l_2 l'}$ to get $\Sigma_{ll'}$.
3. Substitute $\Sigma_{ll'}$ into $\langle D_{ll'} \rangle_c = \left(D^{\mathrm{VCA}-1} - \Sigma \right)^{-1}$ to finally get the configuration averaged Green's function.

See the proof that $\langle D \rangle_c$ is analytic in [Kaplan1980] Appendix A.

It is very important to note that augmented space quantities are translational invariant since each site has the same configuration space augmented to it. Thus the most efficient way of handling these quantities is to solve them for each point in reciprocal space within the Brillouin zone.

The final part is to modify the self consistency cycle in light of the fact that the restricted sum in $\Sigma^{(i)}$ may be difficult to carry out. So the idea is to bring $\langle D \rangle_c$ into the self consistency cycle creating a (slight) simplification.

We manipulate,

$$D^{(i)} = \left(D^{\mathrm{VCA}-1} - \Sigma^{(i)}\right)^{-1} \tag{7.681}$$

$$| \quad \text{use } \langle D\rangle_c = \left(D^{\mathrm{VCA}-1} - \Sigma\right)^{-1}$$

$$= \left(\langle D\rangle_c^{-1} + (\Sigma - \Sigma^{(i)})\right)^{-1} \tag{7.682}$$

Recall that the meaning of $\Sigma^{(i)}$ is about all sorts of scattering that does not involve site i, then the meaning of $\Sigma - \Sigma^{(i)}$ is about all sorts of scattering that only involves site i. This is the simplification that we are seeking. We break up (or project) $\Sigma - \Sigma^{(i)}$ according to scattering contributions.

$$\Sigma - \Sigma^{(i)} = \sum_{i_1 i_2} K^{'(i_1)} F^{(i_1 i_2)} K^{'\dagger(i_2)} - \sum_{i_3 i_4 (\neq i)} K^{'(i_3)} F^{(i_3 i_4)} K^{'\dagger(i_4)} \tag{7.683}$$

$$| \quad \text{many terms cancel and we are left with}$$

$$= \sum_{i_1} \left[K^{'(i)} F^{(i i_1)} K^{'\dagger(i_1)} + K^{'(i_1)} F^{(i_1 i)} K^{'\dagger(i)}\right] - K^{'(i)} F^{(ii)} K^{'\dagger(i)} \tag{7.684}$$

The first term represents a scattering that starts at site i and ends at i_1. The second term represents a scattering that starts at i_1 and ends at i. The third term removes the overcounting when $i_1 = i$. See [Kaplan1980] eqn (3.12) for a projection operator implementation of this idea (which we will use very soon). We use a block matrix decomposition to arrange the different scattering contributions. Note that these quantities are 1×1 in configuration space.

$$A \equiv \begin{pmatrix} A_1 & A_3 \\ A_3^\dagger & A_2 \end{pmatrix} \tag{7.685}$$

A_1 denotes scattering that starts at site i and ends at site i.
A_2 denotes scattering that neither starts at site i nor ends at site i.
A_3 denotes scattering that starts at site i and ends at site $i_1 (\neq i)$.
$A_3^\dagger$ denotes scattering that starts at site $i_1 (\neq i)$ and ends at site i.

So the self energy in this decomposition is [13]

$$\Sigma - \Sigma^{(i)} = \begin{pmatrix} \Sigma_1 & \Sigma_3 \\ \Sigma_3^\dagger & 0 \end{pmatrix} \tag{7.690}$$

[13] Take a 3-site example and let the reference site i = site 1.

$$\Sigma - \Sigma^{(i)} = K^{'(1)} F^{(11)} K^{'\dagger(1)} + K^{'(1)} F^{(12)} K^{'\dagger(2)} + K^{'(1)} F^{(13)} K^{'\dagger(3)} + K^{'(2)} F^{(21)} K^{'\dagger(2)} + K^{'(3)} F^{(31)} K^{'\dagger(1)} \tag{7.686}$$

Based on the meanings of Σ_1, Σ_3 and $\Sigma_3^\dagger$, they are

$$\Sigma_1 = K^{'(1)} F^{(11)} K^{'\dagger(1)} \tag{7.687}$$

$$\Sigma_3 = K^{'(1)} F^{(12)} K^{'\dagger(2)} + K^{'(1)} F^{(13)} K^{'\dagger(3)} = \sum_{i_1} K^{'(1)} F^{(1 i_1)} K^{'\dagger(i_1)} - K^{'(1)} F^{(11)} K^{'\dagger(1)} = \sum_{i_1} K^{'(1)} F^{(1 i_1)} K^{'\dagger(i_1)} - \Sigma_1 \tag{7.688}$$

$$\Sigma_3^\dagger = \sum_{i_1} K^{'(i_1)} F^{(i_1 1)} K^{'\dagger(1)} - \Sigma_1 \tag{7.689}$$

where $\Sigma_2 = 0$ by construction. We decompose $D^{(i)}$ and $\langle D\rangle_c$ as well.

$$D^{(i)} \equiv \begin{pmatrix} D_1^{(i)} & D_3^{(i)} \\ D_3^{(i)\dagger} & D_2^{(i)} \end{pmatrix}, \quad \langle D\rangle_c \equiv \begin{pmatrix} \langle D\rangle_1 & \langle D\rangle_3 \\ \langle D\rangle_3^\dagger & \langle D\rangle_2 \end{pmatrix} \tag{7.691}$$

Recall the earlier equation,

$$\begin{aligned}
D^{(i)} &= \left(\langle D\rangle_c^{-1} + (\Sigma - \Sigma^{(i)})\right)^{-1} && (7.692)\\
D^{(i)-1}\langle D\rangle_c &= \mathbb{I} + (\Sigma - \Sigma^{(i)})\langle D\rangle_c && (7.693)\\
\langle D\rangle_c^{-1} D^{(i)} &= \left(\mathbb{I} + (\Sigma - \Sigma^{(i)})\langle D\rangle_c\right)^{-1} && (7.694)\\
D^{(i)} &= \langle D\rangle_c \left(\mathbb{I} + (\Sigma - \Sigma^{(i)})\langle D\rangle_c\right)^{-1} && (7.695)\\
&= \langle D\rangle_c \left[\mathbb{I} + \begin{pmatrix} \Sigma_1 & \Sigma_3 \\ \Sigma_3^\dagger & 0 \end{pmatrix}\begin{pmatrix} \langle D\rangle_1 & \langle D\rangle_3 \\ \langle D\rangle_3^\dagger & \langle D\rangle_2 \end{pmatrix}\right]^{-1} && (7.696)\\
&= \langle D\rangle_c \begin{pmatrix} 1 + \Sigma_1\langle D\rangle_1 + \Sigma_3\langle D\rangle_3^\dagger & \Sigma_1\langle D\rangle_3 + \Sigma_3\langle D\rangle_2 \\ \Sigma_3^\dagger\langle D\rangle_1 & 1 + \Sigma_3^\dagger\langle D\rangle_3 \end{pmatrix}^{-1} && (7.697)
\end{aligned}$$

Next, we perform the block matrix inverse,

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} (A - BD^{-1}C)^{-1} & -(DB^{-1}A - C)^{-1})^{-1} \\ -(AC^{-1}D - B)^{-1} & (D - CA^{-1}B)^{-1} \end{pmatrix} \tag{7.698}$$

The top left block $D_1^{(i)}$ is

$$\begin{aligned}
D_1^{(i)} &= \langle D\rangle_1 \left(1 + \Sigma_1\langle D\rangle_1 + \Sigma_3\langle D\rangle_3^\dagger - (\Sigma_1\langle D\rangle_3 + \Sigma_3\langle D\rangle_2)(1 + \Sigma_3^\dagger\langle D\rangle_3)^{-1}(\Sigma_3^\dagger\langle D\rangle_1)\right)^{-1} \\
&\quad -\langle D\rangle_3 \left((1 + \Sigma_1\langle D\rangle_1 + \Sigma_3\langle D\rangle_3^\dagger)(\Sigma_3^\dagger\langle D\rangle_1)^{-1}(1 + \Sigma_3^\dagger\langle D\rangle_3) - (\Sigma_1\langle D\rangle_3 + \Sigma_3\langle D\rangle_2)\right)^{-1} && (7.699)\\
&\quad | \quad \text{rewrite into common denominator} \\
&= \left(\langle D\rangle_1 - \langle D\rangle_3(1 + \Sigma_3^\dagger\langle D\rangle_3)^{-1}(\Sigma_3^\dagger\langle D\rangle_1)\right) \\
&\quad \times \left[1 + \Sigma_1\langle D\rangle_1 + \Sigma_3\langle D\rangle_3^\dagger - (\Sigma_1\langle D\rangle_3 + \Sigma_3\langle D\rangle_2)(1 + \Sigma_3^\dagger\langle D\rangle_3)^{-1}(\Sigma_3^\dagger\langle D\rangle_1)\right]^{-1} && (7.700)
\end{aligned}$$

We can further simplify the numerator and the denominator,

$$\begin{aligned}
\text{Numerator} &\equiv \bar{X} && (7.701)\\
&= \langle D\rangle_1 - \langle D\rangle_3(1 + \Sigma_3^\dagger\langle D\rangle_3)^{-1}\Sigma_3^\dagger\langle D\rangle_1 && (7.702)\\
&= \left(1 - \langle D\rangle_3(1 + \Sigma_3^\dagger\langle D\rangle_3)^{-1}\Sigma_3^\dagger\right)\langle D\rangle_1 && (7.703)\\
&\quad | \quad \text{expand the infinite geometric progression (GP) } (1 + \Sigma_3^\dagger\langle D\rangle_3)^{-1} \\
&= \left(1 - \langle D\rangle_3(1 - \Sigma_3^\dagger\langle D\rangle_3 + \Sigma_3^\dagger\langle D\rangle_3\Sigma_3^\dagger\langle D\rangle_3 - \cdots)\Sigma_3^\dagger\right)\langle D\rangle_1 && (7.704)\\
&= \left(1 - \langle D\rangle_3\Sigma_3^\dagger + \langle D\rangle_3\Sigma_3^\dagger\langle D\rangle_3\Sigma_3^\dagger - \langle D\rangle_3\Sigma_3^\dagger\langle D\rangle_3\Sigma_3^\dagger\langle D\rangle_3\Sigma_3^\dagger + \cdots\right)\langle D\rangle_1 && (7.705)\\
&\quad | \quad \text{resum the geometric progression (GP)} \\
&= \left(1 + \langle D\rangle_3\Sigma_3^\dagger\right)^{-1}\langle D\rangle_1 && (7.706)
\end{aligned}$$

$$\begin{aligned}
\text{Denominator} &= 1+\Sigma_1\langle D\rangle_1+\Sigma_3\langle D\rangle_3^\dagger-(\Sigma_1\langle D\rangle_3+\Sigma_3\langle D\rangle_2)(1+\Sigma_3^\dagger\langle D\rangle_3)^{-1}(\Sigma_3^\dagger\langle D\rangle_1) && (7.707)\\
&= 1+\Sigma_1\langle D\rangle_1+\Sigma_3\langle D\rangle_3^\dagger-(\Sigma_1\langle D\rangle_3)(1+\Sigma_3^\dagger\langle D\rangle_3)^{-1}(\Sigma_3^\dagger\langle D\rangle_1)\\
&\quad -(\Sigma_3\langle D\rangle_2)(1+\Sigma_3^\dagger\langle D\rangle_3)^{-1}(\Sigma_3^\dagger\langle D\rangle_1) && (7.708)\\
&= 1+\Sigma_1\langle D\rangle_1-\Sigma_1\langle D\rangle_3(1+\Sigma_3^\dagger\langle D\rangle_3)^{-1}\Sigma_3^\dagger\langle D\rangle_1\\
&\quad +\Sigma_3\left(\langle D\rangle_3^\dagger-\langle D\rangle_2(1+\Sigma_3^\dagger\langle D\rangle_3)^{-1}\Sigma_3^\dagger\langle D\rangle_1\right) && (7.709)\\
&= 1+\Sigma_1(1-\langle D\rangle_3(1+\Sigma_3^\dagger\langle D\rangle_3)^{-1}\Sigma_3^\dagger)\langle D\rangle_1\\
&\quad +\Sigma_3(\langle D\rangle_3^\dagger-\langle D\rangle_2(1+\Sigma_3^\dagger\langle D\rangle_3)^{-1}\Sigma_3^\dagger\langle D\rangle_1) && (7.710)\\
&= 1+\Sigma_1\bar{X}+\Sigma_3\left(\langle D\rangle_3^\dagger-\langle D\rangle_2(1+\Sigma_3^\dagger\langle D\rangle_3)^{-1}\Sigma_3^\dagger\langle D\rangle_1\right) && (7.711)\\
&| \quad \text{we have } (1+\Sigma_3^\dagger\langle D\rangle_3)^{-1}\Sigma_3^\dagger=\Sigma_3^\dagger(1+\langle D\rangle_3\Sigma_3^\dagger)^{-1} \text{ when we expand GP and resum}\\
&= 1+\Sigma_1\bar{X}+\Sigma_3\langle D\rangle_3^\dagger-\Sigma_3\langle D\rangle_2\Sigma_3^\dagger(1+\langle D\rangle_3\Sigma_3^\dagger)^{-1}\langle D\rangle_1 && (7.712)\\
&= 1+(\Sigma_1-\Sigma_3\langle D\rangle_2\Sigma_3^\dagger)\bar{X}+\Sigma_3\langle D\rangle_3^\dagger && (7.713)
\end{aligned}$$

The top left block is thus written as

$$D_1^{(i)} = \bar{X}\left(1+(\Sigma_1-\Sigma_3\langle D\rangle_2\Sigma_3^\dagger)\bar{X}+\Sigma_3\langle D\rangle_3^\dagger\right)^{-1} \quad (7.714)$$

where $\bar{X}=\left(1+\langle D\rangle_3\Sigma_3^\dagger\right)^{-1}\langle D\rangle_1$. In the expression of $D_1^{(i)}$, we have terms $\langle D\rangle_1$, Σ_1, $\langle D\rangle_3\Sigma_3^\dagger$ and $\Sigma_3\langle D\rangle_2\Sigma_3^\dagger$. We write them out explicitly,

$$\begin{aligned}
\langle D\rangle_c &= \langle D\rangle_1+\langle D\rangle_3+\langle D\rangle_3^\dagger+\langle D\rangle_2 && (7.715)\\
\Sigma_1 &= K'^{(i)}F^{(ii)}K'^{\dagger(i)} && (7.716)
\end{aligned}$$

To write out the other 2 terms, it is easiest to use the projector notation. We will carry out the manipulation symbolically. The projector P denotes scattering that starts at site i and ends at site i.

$$A_1\equiv PAP \quad , \quad A_3\equiv PA(1-P) \quad , \quad A_3^\dagger\equiv(1-P)AP \quad , \quad A_2\equiv(1-P)A(1-P) \quad (7.717)$$

So, using the usual properties of projectors,

$$\begin{aligned}
\langle D\rangle_3\Sigma_3^\dagger &= P\langle D\rangle_c(1-P)(1-P)(\Sigma-\Sigma^{(i)})P && (7.718)\\
&= P\langle D\rangle_c(1-P)(\Sigma-\Sigma^{(i)})P && (7.719)\\
&= P\langle D\rangle_c(\Sigma-\Sigma^{(i)})P-P\langle D\rangle_cP(\Sigma-\Sigma^{(i)})P && (7.720)\\
&= P\langle D\rangle_c(\Sigma-\Sigma^{(i)})P-\langle D\rangle_1\Sigma_1 && (7.721)
\end{aligned}$$

$$\begin{aligned}
\Sigma_3\langle D\rangle_2\Sigma_3^\dagger &= P(\Sigma-\Sigma^{(i)})(1-P)(1-P)\langle D\rangle_c(1-P)(1-P)(\Sigma-\Sigma^{(i)})P && (7.722)\\
&= P(\Sigma-\Sigma^{(i)})\langle D\rangle_c(\Sigma-\Sigma^{(i)})P-P(\Sigma-\Sigma^{(i)})\langle D\rangle_cP(\Sigma-\Sigma^{(i)})P\\
&\quad -P(\Sigma-\Sigma^{(i)})P\langle D\rangle_c(\Sigma-\Sigma^{(i)})P+P(\Sigma-\Sigma^{(i)})P\langle D\rangle_cP(\Sigma-\Sigma^{(i)})P && (7.723)\\
&= P(\Sigma-\Sigma^{(i)})\langle D\rangle_c(\Sigma-\Sigma^{(i)})P-P(\Sigma-\Sigma^{(i)})\langle D\rangle_cP\Sigma_1-\Sigma_1P\langle D\rangle_c(\Sigma-\Sigma^{(i)})P\\
&\quad +\Sigma_1\langle D\rangle_1\Sigma_1 && (7.724)\\
&| \quad \text{from above we have } P\langle D\rangle_c(\Sigma-\Sigma^{(i)})P=\langle D\rangle_3\Sigma_3^\dagger+\langle D\rangle_1\Sigma_1\\
&| \quad \text{it is thus easy to derive } P(\Sigma-\Sigma^{(i)})\langle D\rangle_cP=\Sigma_3\langle D\rangle_3^\dagger+\Sigma_1\langle D\rangle_1
\end{aligned}$$

$$
\begin{aligned}
&= P(\Sigma - \Sigma^{(i)})\langle D\rangle_c(\Sigma - \Sigma^{(i)})P - (\Sigma_3\langle D\rangle_3^\dagger + \Sigma_1\langle D\rangle_1)\Sigma_1 - \Sigma_1(\langle D\rangle_3\Sigma_3^\dagger + \langle D\rangle_1\Sigma_1) \\
&\quad +\Sigma_1\langle D\rangle_1\Sigma_1 \qquad (7.725)\\
&= P(\Sigma - \Sigma^{(i)})\langle D\rangle_c(\Sigma - \Sigma^{(i)})P - \left(\Sigma_3\langle D\rangle_3^\dagger\Sigma_1 + \Sigma_1\langle D\rangle_3\Sigma_3^\dagger + \Sigma_1\langle D\rangle_1\Sigma_1\right) \qquad (7.726)
\end{aligned}
$$

We will now state the modified self consistency cycle. It must be noted that the quantities have space translational invariance so working in reciprocal space is beneficial. A further simplification in calculation is to take a nearest neighbor approximation where the "sum over sites" is now a "sum over nearest neighbors" only.

1. The input quantities are $D^{(i)} = D^{\mathrm{VCA}}$ (or some other guess), K', $K'^\dagger$ and $\tilde{V}$. Please see the appendix of [Ghosh2002] for an explicit example.

2. Solve for F using $F = \left(D^{(i)} - \tilde{V}\right)^{-1}$.

3. Substitute F into $\Sigma = \sum_{i_1 i_2} K'^{(i_1)}F^{(i_1 i_2)}K'^{\dagger(i_2)}$ to get Σ. The scattering contributions (or projections) Σ_1, Σ_3 and $\Sigma_3^\dagger$ are obtained as well.

4. Substitute Σ into $\langle D\rangle_c = \left(D^{\mathrm{VCA}-1} - \Sigma\right)^{-1}$ gives $\langle D\rangle_c$. Real space $\langle D\rangle_c$ and reciprocal space $\langle D\rangle_c$ are both calculated. The scattering contributions (or projections) $\langle D\rangle_1$, $\langle D\rangle_3$, $\langle D\rangle_3^\dagger$ and $\langle D\rangle_2$ are obtained as well.

5. Calculate $D^{(i)} = \bar{X}\left(1 + (\Sigma_1 - \Sigma_3\langle D\rangle_3\langle D\rangle_2\Sigma_3^\dagger)\bar{X} + \Sigma_3\langle D\rangle_3^\dagger\right)^{-1}$ with

$$
\begin{aligned}
\bar{X} &= \left(1 + \langle D\rangle_3\Sigma_3^\dagger\right)^{-1}\langle D\rangle_1 \\
\langle D\rangle_3\Sigma_3^\dagger &= P\langle D\rangle_c(\Sigma - \Sigma^{(i)})P - \langle D\rangle_1\Sigma_1 \\
\Sigma_3\langle D\rangle_2\Sigma_3^\dagger &= P(\Sigma - \Sigma^{(i)})\langle D\rangle_c(\Sigma - \Sigma^{(i)})P - \left(\Sigma_3\langle D\rangle_3^\dagger\Sigma_1 + \Sigma_1\langle D\rangle_3\Sigma_3^\dagger + \Sigma_1\langle D\rangle_1\Sigma_1\right)
\end{aligned}
$$

6. If convergence is not achieved, then set $D_1^{(i)} = D^{(i)}$ in step (1) and iterate.

This marks the end of the chapter on disordered lattices. An array of theories that deals with more and more realistic disordered systems are given. It must be emphasized that these are bulk theories and how applicable they are to finite nanosystems is not clear. Thus further progress is needed in 2 directions; bring in theories that include SRO and carry out detailed numerical simulations of all these theories on finite systems. See the last chapter on further discussion for extensions on this area.

Chapter 8

Conclusions

In this concluding chapter, we shall collect the results in this thesis and put together the big picture of what this thesis is trying to achieve. Again, an enumerated form is chosen to convey maximum clarity.

8.0.1 NEGF

1. A complete and systematic exposition of NEGF is given and it is shown to give rise to 3 transport-related developments, namely, Landauer-like theory, kinetic theory and linear response theory. It should also be obvious that NEGF is much more general than just in the development of transport theories.

2. NEGF provided systematic methods to include interactions into Landauer theory which was diffcult to include interactions as it was conventionally formulated in the quantum mechanical scattering picture. Similarly, NEGF provided systematic methods to include interactions into the calculation of noise.

3. NEGF also provided systematic methods to include correlations into kinetic theory which was devoid of correlations as it was conventionally formulated via the notion of collisions.

4. The derivation of GKBA allows causality of lowest order to be restored to the quantum kinetic equations. This is a fruitful direction for the electronic quantum kinetic equations as shown in the appendix but was a failure for the phononic quantum kinetic equations. The failure appears, at first sight, to be due to the incompatibility between phonon number non-conserving phonon-phonon interaction and causality.

8.0.2 Reduced Density Matrix with Stochastic Unravelling

1. Recall that this method is given to serve as an alternative to cross-check with the results from NEGF.

2. There are issues that need to be resolved in this formalism. The main ones are: choice of model for baths, choice of initial states for the stochastic differential equations and numerical stability problems.

8.0.3 Anharmonicity

1. (Lowest order) Anharmonic corrections in Landauer theory are derived easily within NEGF. Transient terms due to anharmonicity are clearly shown and can be investigated.

2. (Lowest order) Anharmonic corrections to noise are derived easily within NEGF but the resulting expression is too complicated to make sense out of it.

3. NEGF allows the rewriting of the anharmonicity perturbation into its most sophisticated form: Hedin-like self consistent equations. This gives the possibility of carrying out (numerically) highly sophisticated renormalizations so that strongly interacting problems can be probed. This set of equations when iterated, generates conserving (self consistent) self energy approximations.

4. Anharmonic correlation corrections to the kinetic theory are calculated. In addition, correlation corrections to entropy (in Chapter 3), energy and momentum balance equations are derived.

5. Second sound excitation is a collective effect (characterized by the drift distribution) due to overwhelming N-processes. The chapter gave the standard treatment on its dissipation due to U-processes. The chapter also gave methods for including correlations into the understanding of second sound. This understanding is important for elucidating the mechanisms of diffusive transport. More precisely, we need to know how collisions and correlations evolve the initial distribution to the drift distribution and how they dampen and dissipate second sound to bring the drift distribution to the equilibrium distribution. Unfortunately, the methods shown in the chapter seem too complicated to proceed with this investigation as future work.

8.0.4 Electron-Phonon Interaction

1. An electronic quantum kinetic equation with all orders of correlation and lowest order in causal correction (GKBA) is derived. This is the Barker-Ferry equation. A particular form of correlation known as the intracollisional field effect can be investigated with this equation.

2. NEGF allows the rewriting of the electron-phonon perturbation into its most sophisticated form: Hedin-like self consistent equations. This gives the possibility of carrying out (numerically) highly sophisticated renormalizations so that strongly interacting problems can be probed. An added bonus is that the Born-Oppenheimer decoupling is avoided in this formulation. This set of equations when iterated, generates conserving (self consistent) self energy approximations.

8.0.5 Disordered Systems

1. Coherent Potential Approximation (CPA) for mass disordered systems allows the configuration averaged Landauer ballistic transmission function to calculated without further approximations. Thus, a high concentration of mass disorder can be considered in the Landauer formalism. Its effects are worked out in the published paper [NiMLL2011].

2. Having mass disorder only is unrealistic and so various leading theories of (high concentrations of) mass & force constant disorder are presented to allow more realistic calculations of disordered nanosystems. Cross-checking between these theories can also be done.

Chapter 9

Future Work

In this chapter, we mention extensions beyond the results given in this thesis. The extensions are grouped by the relevant topics/chapters.

9.0.6 NEGF

1. The direct numerical attack on the Kadanoff-Baym equations is very promising although it requires large scale computational resources. However once the Green's functions can be solved directly, there is no need for developments (and extra approximations) like QKE, we simply get the physical quantity that we want from the Green's functions. In the references mentioned in the section on Kadanoff-Baym equations, it appears that the numerical results are physically sensible and obey conservation laws. Hence numerical work in this direction would give rather rigorous results.

2. The DC ballistic noise (associated with energy current) is the Satio & Dhar expression. The immediate extension is thus to solve for the AC ballistic noise which should be at least solvable numerically.

3. The third (DC) cummulant can be calculated in a brute force manner similar to the noise calculation. The use of such a calculation is to clarify ambiguity in the definition of the generating functional for ballisitc systems. Various definitions relying on different measurement techniques gives the same first 2 cummulants. The third (DC) cummulant calculated by NEGF does not require any measurement technique whatsoever.

4. The reasons for the failure to construct GKB ansatz for interacting phonons needs to be investigated more carefully. The essential benefit of GKB ansatz over KB ansatz is that GKB ansatz constructs the causality struture properly. Thus it is desirable to construct quantum kinetic equations using GKB ansatz.

9.0.7 Anharmonicity

1. Anharmonic corrections to the Landauer ballistic current can be calculated for particular models. The explicit formulae has been given in that chapter. Numerical work should be the way to go.

2. Anharmonic corrections to (DC) noise is a much bigger venture.

3. Phonon-phonon Hedin-like equations could be attacked directly using numerics instead of using these equations to iterate and generate self consistent self energies.

4. The iterated self consistent self energies could be used in the calculation of interacting Landauer current and interacting (DC) noise. This thesis only briefly mentioned such a calculation, there is much more to do. Again, the main tool should be numerics.

5. Mingo's (numerical) iteration method is certainly an interesting method because it goes beyond (single mode) relaxation time results and almost all the results of kinetic theory are (single mode) relaxation time results.

6. If it can be shown how an initial distribution evolves via phonon Boltzmann equation to the drift distribution, we would gain a much better understanding of how N-processes redistributes phonon distributions.

7. The dissipative hydrodynamic equations could be numerically solved and perhaps more physics can be found in the regime where N-processes $>>$ U-processes.

9.0.8 Electron-Phonon Interaction

1. Solving of the electron-phonon Hedin-like equations is certainly interesting to see how the usual electron-phonon theory with Born-Oppenheimer approximation and hence has the uncontrolled double counting problem affects the accuracy of electron-phonon theories. A starting point could be the article by R. van Leeuwen and E.K.U. Gross titled "Multicomponent Density Functional Theory" in "Time-Dependent Functional Theory" (Springer Lecture Notes in Physics vol 706 2006).

9.0.9 Disordered Systems

1. In small systems, disorder cannot really be regarded as dilute. Thus, theories that deal with high concentrations of disorder in increasing complexity are given in the chapter. Serious numerical work needs to be done to compare the given methods and see which disorder theory works well for finite and small systems.

2. Also, in small systems, it is probable that the disorder sites or clusters are "close enough" that they interact via some kind of short range order (SRO). So disorder theories that includes SRO should be investigated as well. Some references that utilise methods with line with those in this thesis and include SRO are [Rowlands2009], [Rowlands2003] and [Rahaman2009].

9.0.10 Topics in Appendices

1. In NEGF for electrons, quantum kinetic theory is actually well structured. It is gauge invariant, GKB ansatz works which means the causal structure is well defined and gradient expansion is applicable so correlations can be investigated "perturbatively". So it is very worth trying to solve these electronic QKE via more theoretical and numerical considerations.

Part III

Appendices

Appendix A

Basics

A.1 Quantum Dynamics

References are not needed here as this is standard material in Quantum Mechanics.

Let's just put the point straight. A "dynamical" picture consists of 2 parts, the operator(s) and the state (or density matrix). The 3 different pictures come about simply because we can "allocate" the temporal evolution operator U (a) completely to the state (Schrodinger picture), (b) completely to the operator (Heisenberg picture), or (c) partially to the operator and partially to the state (Interaction picture).

This freedom of "allocation" exists because the observable quantity is the time-dependent expectation value which is not affected by this "allocation".

A.1.1 Schrodinger Picture

As mentioned, this is the case where all the temporal evolution is "allocated" to the state or density matrix, thus this is the usual version of quantum mechanics,

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle$$

The operators in this picture are constant in time and all the time evolution is on the state. The time evolution of the physical expectation value can thus be written as,

$$\langle A(t_0)\rangle = \langle\psi(t_0)|A(t_0)|\psi(t_0)\rangle \quad (A.1)$$
$$\langle A(t)\rangle = \langle\psi(t)|A(t_0)|\psi(t)\rangle \quad (A.2)$$

where $A(t_0)$ is an arbitrary operator and time t_0 is a reference time when all the 3 pictures coincide.

We define the evolution operator as,

$$|\psi(t)\rangle \equiv U(t,t_0)|\psi(t_0)\rangle \quad (A.3)$$

Using Schrodinger equation, we get the differential equation for $U(t,t_0)$.

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle &= H(t)|\psi(t)\rangle && (A.4)\\ i\hbar\frac{\partial}{\partial t}U(t,t_0)|\psi(t_0)\rangle &= H(t)U(t,t_0)|\psi(t_0)\rangle && (A.5)\\ \Rightarrow i\hbar\frac{\partial}{\partial t}U(t,t_0) &= H(t)U(t,t_0) && (A.6)\end{aligned}$$

where $H(t) = H_0 + V(t)$.

A formal integration with identity as intitial condition, gives,

$$U(t,t_0) = \mathbb{I} - \frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')U(t',t_0) \tag{A.7}$$

and we can write it into the formal expression,

$$U(t,t_0) = Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')} \tag{A.8}$$

where T is the time ordering operator. For a time independent Hamiltonian (or $V(t) = 0$) then we have [1]

$$U(t,t_0) = e^{-\frac{i}{\hbar}H_0(t-t_0)} \tag{A.9}$$

A.1.2 Heisenberg Picture

As mentioned earlier, this is the case where all the temporal evolution is “allocated” to the operators.

$$\begin{aligned}
\langle A(t)\rangle &= \langle\psi(t_0)|U(t,t_0)^\dagger A(t_0)U(t,t_0)|\psi(t_0)\rangle && \text{(A.10)}\\
A_H(t) &\equiv U(t,t_0)^\dagger A(t_0)U(t,t_0) && \text{(A.11)}\\
&= \left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')}\right)^\dagger A(t_0)\left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')}\right) && \text{(A.12)}
\end{aligned}$$

We differentiate to get the differential equation for $A_H(t)$ (recall that $i\hbar\frac{\partial}{\partial t}U(t,t_0) = H(t)U(t,t_0)$)

$$\begin{aligned}
\frac{d}{dt}A_H(t) &= \frac{i}{\hbar}U(t,t_0)^\dagger H(t_0)A(t_0)U(t,t_0) - \frac{i}{\hbar}U(t,t_0)^\dagger A(t_0)H(t_0)U(t,t_0) + \frac{\partial A_H(t)}{\partial t} && \text{(A.13)}\\
&\mid\ \text{The last term is nonzero when } A_H(t) \text{ depends on time parametrically.}\\
&\mid\ \text{Insert } U(t,t_0)U(t,t_0)^\dagger \text{ between } H(t_0)A(t_0) \text{ and } A(t_0)H(t_0)\\
&\mid\ \text{Define } H_H(t) \equiv U(t,t_0)^\dagger H(t_0)U(t,t_0)\\
&= \frac{i}{\hbar}\left(H_H(t)A_H(t) - A_H(t)H_H(t)\right) + \frac{\partial A_H(t)}{\partial t} && \text{(A.14)}\\
&= \frac{i}{\hbar}\left[H_H(t), A_H(t)\right]_- + \frac{\partial A_H(t)}{\partial t} && \text{(A.15)}
\end{aligned}$$

$[\ldots,\ldots]_-$ stands for the commutator. For the particular case of $A_H(t) = H_H(t)$, we have

$$\frac{d}{dt}H_H(t) = \frac{\partial}{\partial t}H_H(t)$$

which means that the time dependence of the Hamiltonian is only through its parametric time dependence.

---

[1] $U(t,t_0)$ satisfies these properties

- $U(t,t) = \mathbb{I}$
- $U(t_2,t_1) = (U(t_1,t_2))^{-1}$
- $U(t_1,t_2)U(t_2,t_3) = U(t_1,t_3) \qquad \text{for} \qquad t_1 > t_2 > t_3$

When $V(t) = 0$, $H = H_0$ is time independent, we have the familiar expression,

$$\begin{aligned} A_H(t) &= U(t,t_0)^\dagger A(t_0) U(t,t_0) && \text{(A.16)} \\ &= A_{H_0}(t) && \text{(A.17)} \\ &= e^{\frac{i}{\hbar}H_0(t-t_0)} A(t_0) e^{-\frac{i}{\hbar}H_0(t-t_0)} && \text{(A.18)} \end{aligned}$$

A.1.3 Interaction Picture

As mentioned, this is the case where the "allocation" of the temporal evolution is partial between the operators and states depending on how the Hamiltonian is "split". Thus there is actually an infinite "number" of interaction pictures in some sense. A typical use is where there is a time dependent Hamiltonian $H(t) = H_0 + V(t)$, and if solutions for H_0 are known, then it is better to use the Interaction picture to "split off" $V(t)$ as a perturbation.

We define an operator in Interaction picture as follows,

$$A_{H_0}(t) \equiv e^{\frac{i}{\hbar}H_0(t-t_0)} A(t_0) e^{-\frac{i}{\hbar}H_0(t-t_0)} \tag{A.19}$$

and the corresponding differential equation is,

$$\frac{d}{dt} A_{H_0}(t) = -\frac{i}{\hbar}\left[A_{H_0}(t), H_0\right]_- + \frac{\partial A_{H_0}(t)}{\partial t} \tag{A.20}$$

It is the same as Heisenberg operators when $V(t) = 0$.

The Interaction state is defined as

$$|\psi_{H_0}(t)\rangle \equiv e^{\frac{i}{\hbar}H_0(t-t_0)} |\psi(t)\rangle \tag{A.21}$$

We can see that the physical expectation value is unchanged in Interaction picture.

$$\begin{aligned} \langle A(t)\rangle &= \langle \psi_{H_0}(t)|A_{H_0}(t)|\psi_{H_0}(t)\rangle && \text{(A.22)} \\ &= \langle \psi(t)|e^{-\frac{i}{\hbar}H_0(t-t_0)} e^{\frac{i}{\hbar}H_0(t-t_0)} A(t_0) e^{-\frac{i}{\hbar}H_0(t-t_0)} e^{\frac{i}{\hbar}H_0(t-t_0)}|\psi(t)\rangle && \text{(A.23)} \\ &= \langle \psi(t)|A(t_0)|\psi(t)\rangle && \text{(A.24)} \end{aligned}$$

We define the interaction evolution operator as

$$|\psi_{H_0}(t)\rangle \equiv U_{H_0}(t,t_1)|\psi_{H_0}(t_1)\rangle \tag{A.25}$$

We change back to Schrodinger picture,

$$\begin{aligned} e^{\frac{i}{\hbar}H_0(t-t_0)}|\psi(t)\rangle &= U_{H_0}(t,t_1) e^{\frac{i}{\hbar}H_0(t_1-t_0)}|\psi(t_1)\rangle && \text{(A.26)} \\ e^{\frac{i}{\hbar}H_0(t-t_0)} U(t,t_1)|\psi(t_1)\rangle &= U_{H_0}(t,t_1) e^{\frac{i}{\hbar}H_0(t_1-t_0)}|\psi(t_1)\rangle && \text{(A.27)} \\ \Rightarrow U_{H_0}(t,t_1) &= e^{\frac{i}{\hbar}H_0(t-t_0)} U(t,t_1) e^{-\frac{i}{\hbar}H_0(t_1-t_0)} && \text{(A.28)} \end{aligned}$$

We write a differential equation for the evolution of the Interaction state.

$$\begin{aligned} i\hbar\frac{d}{dt}|\psi_{H_0}(t)\rangle &= i\hbar\frac{d}{dt} U_{H_0}(t,t_1)|\psi_{H_0}(t_1)\rangle && \text{(A.29)} \\ &= i\hbar\left(\frac{i}{\hbar}H_0 U_{H_0}(t,t_1) + \frac{1}{i\hbar} e^{\frac{i}{\hbar}H_0(t-t_0)} H(t_1) e^{-\frac{i}{\hbar}H_0(t-t_0)} U_{H_0}(t,t_1)\right)|\psi_{H_0}(t_1)\rangle && \text{(A.30)} \end{aligned}$$

$$= \left(-H_0 + e^{\frac{i}{\hbar}H_0(t-t_0)}(H_0 + V(t_1))e^{-\frac{i}{\hbar}H_0(t-t_0)}\right)|\psi_{H_0}(t)\rangle \tag{A.31}$$
$$= V_{H_0}(t)|\psi_{H_0}(t)\rangle \tag{A.32}$$

This is the main motivation for constructing the Interaction picture. The evolution of the Interaction state only depends on the "difficult" part of the problem, $V(t)$. Similar to the derivation of the differential equation of the Schrodinger evolution operator, we get,

$$i\hbar\frac{d}{dt}U_{H_0}(t,t_0) = V_{H_0}(t)U_{H_0}(t,t_0) \tag{A.33}$$

and the formal solution is

$$U_{H_0}(t,t_0) = Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' V_{H_0}(t')} \tag{A.34}$$

[Dyson's Identity:] Dyson's identity is the identity that relates temporal evolution Heisenberg operators and temporal evolution Interaction operators. To get this identity, we relate the operators in Heisenberg picture and the operators in Interaction picture. From Heisenberg picture,

$$\langle A(t)\rangle = \langle\psi(t_0)|A_H(t)|\psi(t_0)\rangle \tag{A.35}$$
$$| \quad \text{use } |\psi_{H_0}(t_0)\rangle = |\psi(t_0)\rangle$$
$$= \langle\psi_{H_0}(t_0)|A_H(t)|\psi_{H_0}(t_0)\rangle \tag{A.36}$$
$$\tag{A.37}$$

From Interaction picture,

$$\langle A(t)\rangle = \langle\psi_{H_0}(t_0)|U_{H_0}(t,t_0)^\dagger A(t)U_{H_0}(t,t_0)|\psi_{H_0}(t_0)\rangle \tag{A.38}$$

Comparing gives,

$$\Rightarrow A_H(t) = U_{H_0}(t,t_0)^\dagger A_{H_0}(t)U_{H_0}(t,t_0) \tag{A.39}$$

In NEGF perturbation theory, we will use the Hamiltonian in the form $H(t) = H_0 + H_{\text{int}} + V(t)$ where only $V(t)$ is time dependent.

$$A_H(t) = \left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')}\right)^\dagger A(t_0)\left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')}\right) \tag{A.40}$$

$$\begin{aligned}\text{And,}\quad A_H(t) &= U_{H_0}(t,t_0)^\dagger A_{H_0}(t)U_{H_0}(t,t_0)\\ &= \bar{T}e^{\frac{i}{\hbar}\int_{t_0}^{t} dt' V_{H_0+H_{\text{int}}}(t')}e^{\frac{i}{\hbar}(H_0+H_{\text{int}})(t-t_0)}A(t_0)e^{-\frac{i}{\hbar}(H_0+H_{\text{int}})(t-t_0)}Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' V_{H_0+H_{\text{int}}}(t')}\end{aligned} \tag{A.41}$$

Comparing gives the Dyson's identity,

$$\boxed{\begin{aligned} Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')} &= e^{-\frac{i}{\hbar}(H_0+H_{\text{int}})(t-t_0)}\left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' V_{H_0+H_{\text{int}}}(t')}\right) & \text{(A.42)}\\ \left(Te^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')}\right)^\dagger &= \left(\bar{T}e^{\frac{i}{\hbar}\int_{t_0}^{t} dt' V_{H_0+H_{\text{int}}}(t')}\right)e^{\frac{i}{\hbar}(H_0+H_{\text{int}})(t-t_0)} & \text{(A.43)}\end{aligned}}$$

where $\bar{T}$ is the anti-time ordering operator.[2]

A.2 Basic Lattice Dynamics

Here we follow [Callaway1991], [Kwok1968] and [Gruevich1986].

We start by constructing the Hamiltonian. The location of the kth atom in cell l is given by the vector

$$\vec{R} = \vec{R}_l + \vec{R}_k$$

Let the displacement of that atom be denoted by $\vec{u}$ and its components are denoted as $u_{lk\alpha}$. Now we can write the total kinetic energy of the solid as,

$$T = \frac{1}{2}\sum_{lk\alpha} m_k \dot{u}^2_{lk\alpha} \tag{A.44}$$

where m_k is the mass of the kth atom. Let the potential energy by denoted by Φ and the potential at equilibrium be $\Phi^{(0)}$. We can expand Φ as a Taylor series in the displacements

$$\Phi = \Phi^{(0)} + \sum_{lk\alpha} \Phi^{(1)}_{lk\alpha} u_{lk\alpha} + \frac{1}{2}\sum_{l_1k_1\alpha_1}\sum_{l_2k_2\alpha_2} u_{l_1k_1\alpha_1}\Phi^{(2)}_{l_1k_1\alpha_1l_2k_2\alpha_2} u_{l_2k_2\alpha_2} + \dots \tag{A.45}$$

$$\text{where } \Phi^{(1)}_{lk\alpha} = \left.\frac{\partial \Phi}{\partial u_{lk\alpha}}\right|_{\vec{u}=0} \tag{A.46}$$

$$\text{where } \Phi^{(2)}_{l_1k_1\alpha_1l_2k_2\alpha_2} = \left.\frac{\partial^2 \Phi}{\partial u_{l_1k_1\alpha_1}\partial u_{l_2k_2\alpha_2}}\right|_{\vec{u}=0} \tag{A.47}$$

We will now take the harmonic approximation so that we can define the collective excitation called phonons. The Hamiltonian in the harmonic approximation is thus

$$H = \frac{1}{2}\sum_{lk\alpha} m_k \dot{u}^2_{lk\alpha} + \frac{1}{2}\sum_{l_1k_1\alpha_1}\sum_{l_2k_2\alpha_2} u_{l_1k_1\alpha_1}\Phi^{(2)}_{l_1k_1\alpha_1l_2k_2\alpha_2} u_{l_2k_2\alpha_2} \tag{A.48}$$

where we note that $\Phi^{(0)}$ is a constant and is absorbed as a shift in the Hamiltonian while $\Phi^{(1)}_{lk\alpha} = 0$ since we are expanding around the minimum of the potential Φ (the so-called Born-Oppenheimer energy surface).

A.2.1 Normal modes and Normal coordinates

First we establish the dynamical matrix and the normal modes eigenvalue equation. In the above form, we can define the Lagrangian and get the equations of motion using Euler-Lagrange equations.

$$m_k \ddot{u}_{lk\alpha} = -\sum_{l_1k_1\alpha_1} \Phi^{(2)}_{lk\alpha l_1k_1\alpha_1} u_{l_1k_1\alpha_1} \tag{A.49}$$

We seek a periodic solution of the form

$$u_{lk\alpha} = \frac{1}{\sqrt{Nm_k}}\sum_{j\vec{q}} \epsilon_{k\alpha}(j\vec{q}) Q_{j\vec{q}}\, e^{-i\omega t} e^{i\vec{q}\cdot l} \tag{A.50}$$

[2]It should be noted that the Matsubara imaginary time version of this identity is called the Kubo's identity.

where N is the number of cells. We substitute this solution into the equations of motion and obtain

$$
\begin{aligned}
-\frac{m_k}{\sqrt{Nm_k}}\omega^2 \sum_{j\vec{q}} \epsilon_{k\alpha}(j\vec{q})Q_{j\vec{q}}\, e^{-i\omega t}e^{i\vec{q}\cdot l} &= -\sum_{l_1k_1\alpha_1}\sum_{j_1\vec{q}_1} \frac{1}{\sqrt{Nm_{k_1}}}\Phi^{(2)}_{lk\alpha l_1k_1\alpha_1}\epsilon_{k_1\alpha_1}(j_1\vec{q}_1)Q_{j_1\vec{q}_1}e^{-i\omega t}e^{i\vec{q}_1\cdot l_1} \\
\omega^2 \sum_{j\vec{q}} \epsilon_{k\alpha}(j\vec{q})Q_{j\vec{q}}\, e^{i\vec{q}\cdot l} &= \sum_{l_1k_1\alpha_1}\sum_{j_1\vec{q}_1} \frac{1}{\sqrt{m_km_{k_1}}}\Phi^{(2)}_{lk\alpha l_1k_1\alpha_1}\epsilon_{k_1\alpha_1}(j_1\vec{q}_1)Q_{j_1\vec{q}_1}e^{i\vec{q}_1\cdot l}e^{i\vec{q}_1\cdot(l_1-l)}
\end{aligned}
$$

Since $\Phi^{(2)}$ is a function of $l_1 - l$ only we can define the dynamical matrix as,

$$D_{k\alpha k_1\alpha_1}(\vec{q}_1) \equiv \frac{1}{\sqrt{m_km_{k_1}}}\sum_{l_1}\Phi^{(2)}_{lk\alpha l_1k_1\alpha_1}e^{-i\vec{q}_1\cdot(l-l_1)} \tag{A.51}$$

then

$$\omega^2 \sum_{j\vec{q}} \epsilon_{k\alpha}(j\vec{q})Q_{j\vec{q}}e^{i\vec{q}\cdot l} = \sum_{k_1\alpha_1}\sum_{j_1\vec{q}_1}\epsilon_{k_1\alpha_1}(j_1\vec{q}_1)Q_{j_1\vec{q}_1}e^{i\vec{q}_1\cdot l}D_{k\alpha k_1\alpha_1}(\vec{q}_1) \tag{A.52}$$

rename $j_1\vec{q}_1 \to j\vec{q}$, then we can compare term by term in the $j\vec{q}$ sum,

$$\omega^2\epsilon_{k\alpha}(j\vec{q}) = \sum_{k_1\alpha_1} D_{k\alpha k_1\alpha_1}(\vec{q})\epsilon_{k_1\alpha_1}(j\vec{q}) \tag{A.53}$$

We relabel the eigenvalues (normal mode frequencies) ω^2 as $\omega^2 \to \omega_0^2(j\vec{q})$. There are $\dim(l) \times \dim(k)$ number of eigenvalues. (dim stands for number of dimensions.)

$$\omega_0^2(j\vec{q})\epsilon_{k\alpha}(j\vec{q}) = \sum_{k_1\alpha_1} D_{k\alpha k_1\alpha_1}(\vec{q})\epsilon_{k_1\alpha_1}(j\vec{q}) \tag{A.54}$$

We consider some properties of the dynamical matrix. First we note that the dynamical matrix is hermitian

$$
\begin{aligned}
D^*_{k\alpha k_1\alpha_1}(\vec{q}) &= \frac{1}{\sqrt{m_km_{k_1}}}\sum_{l_1}\Phi^{(2)}_{lk\alpha l_1k_1\alpha_1}e^{i\vec{q}_1\cdot(l-l_1)} && \text{(A.55)} \\
&\quad | \quad \text{use the commutativity of partial derivatives in } \Phi^{(2)}. \\
&= \frac{1}{\sqrt{m_km_{k_1}}}\sum_{l_1}\Phi^{(2)}_{l_1k_1\alpha_1lk\alpha}e^{-i\vec{q}_1\cdot(l_1-1)} && \text{(A.56)} \\
&= D_{k_1\alpha_1k\alpha}(\vec{q}) && \text{(A.57)}
\end{aligned}
$$

Thus the eigenvalues $\omega_0^2(j\vec{q})$ are real,

$$\omega_0^2(j\vec{q}) = \omega_0^2(j,-\vec{q}) \tag{A.58}$$

The polarization eigenvectors are thus part of the unitary matrix that diagonalizes $D_{k\alpha k_a\alpha_1}(\vec{q})$, so they are orthonormal and complete.

$$
\begin{aligned}
\text{Orthonormality} &: \sum_{k\alpha}\epsilon^*_{k\alpha}(j\vec{q})\epsilon_{k\alpha}(j_1\vec{q}) = \delta_{jj_1} \\
\text{Completeness} &: \sum_{j}\epsilon^*_{k\alpha}(j\vec{q})\epsilon_{k_1\alpha_1}(j\vec{q}) = \delta_{kk_1}\delta_{\alpha\alpha_1}
\end{aligned}
\tag{A.59}
$$

Taking the complex conjugate of the eigenvalue equation,

$$\omega_0^2(j\vec{q})\epsilon^*_{k\alpha}(j\vec{q}) = \sum_{k_1\alpha_1} D^*_{k\alpha k_1\alpha_1}(\vec{q})\epsilon^*_{k_1\alpha_1}(j\vec{q}) \tag{A.60}$$

$$= \sum_{k_1\alpha_1} D_{k_1\alpha_1 k\alpha}(\vec{q})\epsilon^*_{k_1\alpha_1}(j\vec{q}) \tag{A.61}$$

we compare with $\vec{q} \to -\vec{q}$,

$$\omega_0^2(j,-\vec{q})\epsilon_{k\alpha}(j,-\vec{q}) = \sum_{k_1\alpha_1} D_{k\alpha k_1\alpha_1}(-\vec{q})\epsilon_{k_1\alpha_1}(j,-\vec{q}) \tag{A.62}$$

$$= \omega_0^2(j\vec{q})\epsilon(j,-\vec{q}) \tag{A.63}$$

$$= \sum_{k_1\alpha_1} D_{k_1\alpha_1 k\alpha}(\vec{q})\epsilon_{k_1\alpha_1}(j,-\vec{q}) \tag{A.64}$$

$$\therefore\ \epsilon^*_{k\alpha}(j\vec{q}) = \epsilon_{k\alpha}(j,-\vec{q}) \text{ up to a factor chosen as 1.} \tag{A.65}$$

A.2.2 Classification of modes into acoustic & optical modes

There are $\dim(l)$ of eigenvalues $\omega_0 \to 0$ as $\vec{q} \to 0$ and they are classified as acoustic modes. We show this by setting $\vec{q} \to 0$ in the eigenvalue equation.

$$\omega_0^2(j0)\epsilon_{k\alpha} = \sum_{k_1\alpha_1} D_{k\alpha k_1\alpha_1}(0)\epsilon_{k_1\alpha_1}(j0) \tag{A.66}$$

$$= \sum_{l_1k_1\alpha_1} \frac{1}{\sqrt{m_k m_{k_1}}}\Phi^{(2)}_{lk\alpha l_1k_1\alpha_1}\epsilon_{k_1\alpha_1(j0)} \tag{A.67}$$

Suppose for each α, $\epsilon_{k_1\alpha_1}(j0)/\sqrt{m_{k_1}}$ is independent of k_1 then we can take it out the sum, leaving $\sum_{l_1k_1}\Phi^{(2)}_{lk\alpha l_1k_1\alpha_1} = 0$ due to force constant sum rule. Thus for each $\alpha_1 \in \dim(l)$ we get $\omega_0 = 0$ when $\vec{q} \to 0$. All the particles in the cell are moving in parallel with equal amplitudes.[3]

The remaining modes $\dim(l) \times \dim(k) - \dim(l)$ are called optical modes. We take the example of $\dim(k) = 2$ particles in the cell to illustrate this. We use the notation $+, -$ to denote the 2 particles. Using the orthonormality relation,

$$\sum_{k\alpha}\epsilon^*_{k\alpha}(j\vec{q})\epsilon_{k\alpha}(j_1\vec{q}) = \delta_{jj_1} \tag{A.68}$$

take $\vec{q} \to 0$ and write in vector notation, $|$

$$\vec{\epsilon}_+(j0)\cdot\vec{\epsilon}_+(j_10) + \vec{\epsilon}_-(j0)\cdot\vec{\epsilon}_-(j_10) = 0 \tag{A.69}$$

For $\vec{q} \to 0$, in the acoustic branch we can get the relationship

$$\frac{\vec{\epsilon}_+(j0)}{\sqrt{m_+}} = \frac{\vec{\epsilon}_-(j0)}{\sqrt{m_-}} \tag{A.70}$$

since the 2 atoms in the cell move with equal amplitudes. We substitute this relationship into the above

[3] Be reminded that this classification only makes sense for long wavelength ($\vec{q} \to 0$) as the argument has shown. For short wavelength, there is no pure acoustic or pure optical modes.

long wavelength orthonormality relation.

$$\Rightarrow \quad \vec{\epsilon}_+(j0)\cdot\vec{\epsilon}_+(j_10) + \vec{\epsilon}_-(j0)\cdot\sqrt{\frac{m_-}{m_+}}\vec{\epsilon}_+(j_10) \;=\; 0 \tag{A.71}$$

$$\vec{\epsilon}_+(j_10)\cdot\left(\vec{\epsilon}_+(j0) + \sqrt{\frac{m_-}{m_+}}\vec{\epsilon}_-(j0)\right) \;=\; 0 \tag{A.72}$$

$$\sqrt{m_+}\vec{\epsilon}_+(j0) + \sqrt{m_-}\vec{\epsilon}_-(j0) \;=\; 0 \tag{A.73}$$

Note that this means (since $\vec{\epsilon} \propto \vec{u}$) the 2 ions in the cell vibrates out of phase with each other. The centre of mass remains fixed. A dipole is created and this can interact with external electric fields, that's the reason for the name optical modes.

A.2.3 Quantum Theory and 3 choices of Quantum Variables

Recall

$$u_{lk\alpha} \;=\; \frac{1}{\sqrt{Nm_k}}\sum_{j\vec{q}}\epsilon_{k\alpha}(j\vec{q})Q_{j\vec{q}}\,e^{-i\omega t}e^{i\vec{q}\cdot l} \tag{A.74}$$

$$\equiv \; \frac{1}{\sqrt{Nm_k}}\sum_{j\vec{q}}\epsilon_{k\alpha}(j\vec{q})Q_{j\vec{q}}\,(t)e^{i\vec{q}\cdot l} \tag{A.75}$$

$Q_{j\vec{q}}\,(t)$ are called normal coordinates and now we rewrite the dynamics in terms of these coordinates. We start with the kinetic energy term

$$T \;=\; \frac{1}{2}\sum_{lk\alpha} m_k\frac{1}{Nm_k}\sum_{j_1\vec{q}_1}\sum_{j_2\vec{q}_2}\epsilon_{k\alpha}(j_1\vec{q}_1)\dot{Q}_{j_1\vec{q}_1}(t)e^{i\vec{q}_1\cdot l}\epsilon_{k\alpha}(j_2\vec{q}_2)\dot{Q}_{j_2\vec{q}_2}(t)e^{i\vec{q}_2\cdot l} \tag{A.76}$$

$$= \; \frac{1}{2}\sum_{k\alpha}\frac{1}{N}\sum_{j_1\vec{q}_1}\sum_{j_2\vec{q}_2}\epsilon_{k\alpha}(j_1\vec{q}_1)\epsilon_{k_\alpha}(j_2\vec{q}_2)\dot{Q}_{j_1\vec{q}_1}(t)\dot{Q}_{j_2\vec{q}_2}(t)\sum_l e^{i(\vec{q}_1+\vec{q}_2)\cdot l} \tag{A.77}$$

$$|\quad \text{use} \sum_l e^{i(\vec{q}_1+\vec{q}_2)\cdot l} = N\delta_{\vec{q}_1,-\vec{q}_2}.$$

$$= \; \frac{1}{2}\sum_{j_1j_2\vec{q}_1}\sum_{k\alpha}\epsilon_{k\alpha}(j_1\vec{q}_1)\epsilon_{k\alpha}(j_2,-\vec{q}_1)\dot{Q}_{j_1\vec{q}_1}(t)\dot{Q}_{j_2,-\vec{q}_1}(t) \tag{A.78}$$

$$|\quad \text{use } \epsilon_{k\alpha}(j_2,-\vec{q}_1) = \epsilon^*_{k\alpha}(j_2\vec{q}_1) \text{ and use the orthonormality relation}$$

$$= \; \frac{1}{2}\sum_{j_1j_2\vec{q}_1}\delta_{j_1j_2}\dot{Q}_{j_1\vec{q}_1}(t)\dot{Q}_{j_2,-\vec{q}_1}(t) \tag{A.79}$$

$$= \; \frac{1}{2}\sum_{j_1\vec{q}_1}\dot{Q}_{j_1\vec{q}_1}(t)\dot{Q}_{j_1,-\vec{q}_1}(t) \tag{A.80}$$

And for the potential energy term,

$$V \;=\; \frac{1}{2}\sum_{l_1k_1\alpha_1}\sum_{l_2k_2\alpha_2}\frac{1}{N\sqrt{m_{k_1}}m_{k_2}}\sum_{j_1\vec{q}_1}\sum_{j_2\vec{q}_2}\epsilon_{k_1\alpha_1}(j_1\vec{q}_1)Q_{j_1\vec{q}_1}(t)e^{i\vec{q}_1\cdot l_1}\Phi^{(2)}_{l_1k_1\alpha_1l_2k_2\alpha_2}\epsilon_{k_2\alpha_2}(j_2\vec{q}_2)Q_{j_2\vec{q}_2}(t)e^{i\vec{q}_2\cdot l_2}$$

$$|\quad \text{write } e^{i\vec{q}_2\cdot l_2} = e^{i\vec{q}_2\cdot l_1}e^{-i\vec{q}_2\cdot(l_1-l_2)} \text{ and use the definition of the dynamical matrix.}$$

$$= \; \frac{1}{2}\sum_{l_1k_1\alpha_1}\sum_{k_2\alpha_2}\frac{\sqrt{m_{k_1}m_{k_2}}}{N\sqrt{m_{k_1}m_{k_2}}}\sum_{j_1\vec{q}_1}\sum_{j_2\vec{q}_2}\epsilon_{k_1\alpha_1}(j_1\vec{q}_1)Q_{j_1\vec{q}_1}(t)D_{k_1\alpha_1k_2\alpha_2}(\vec{q}_2)\epsilon_{k_2\alpha_2}(j_2\vec{q}_2)Q_{j_2\vec{q}_2}e^{i(\vec{q}_1+\vec{q}_2)\cdot l_1}$$

$$\Big| \quad \text{use the relation } \sum_{l_1} e^{i(\vec{q}_1+\vec{q}_2)\cdot l_1} = N\delta_{\vec{q}_1,-\vec{q}_2}$$

$$= \frac{1}{2}\sum_{k_1\alpha_1 k_2\alpha_2}\sum_{j_1 j_2 \vec{q}_1} \epsilon_{k_1\alpha_1}(j_1\vec{q}_1)Q_{j_1\vec{q}_1}(t)D_{k_1\alpha_1 k_2\alpha_2}(-\vec{q}_1)\epsilon_{k_2\alpha_2}(j_2,-\vec{q}_1)Q_{j_2,-\vec{q}_1}(t) \tag{A.81}$$

$$\Big| \quad \text{use the eigenvalue equation, } \sum_{k_2\alpha_2} D_{k_1\alpha_1 k_2\alpha_2}(-\vec{q}_1)\epsilon_{k_2\alpha_2}(j_2,-\vec{q}_1) = \omega_0^2(j_2,-\vec{q}_1)\epsilon_{k_1\alpha_1}(j_2,-\vec{q}_1)$$

$$= \frac{1}{2}\sum_{k_1\alpha_1}\sum_{j_1 j_2 \vec{q}_1} Q_{j_1\vec{q}_1}(t)Q_{j_2,-\vec{q}_1}(t)\epsilon_{k_1\alpha_1}(j_1\vec{q}_1)\omega_0^2(j_2\vec{q}_1)\epsilon^*_{k_1\alpha_1}(j_2\vec{q}_1) \tag{A.82}$$

$$\Big| \quad \text{use the completeness relation } \sum_{k_1\alpha_1} \epsilon_{k_1\alpha_1}(j_1\vec{q}_1)\epsilon^*_{k_1 alpha_1}(j_2\vec{q}_1) = \delta_{j_1 j_2}.$$

$$= \frac{1}{2}\sum_{j_1\vec{q}_1} Q_{j_1\vec{q}_1}(t)Q_{j_1,-\vec{q}_1}(t)\omega_0^2(j_1\vec{q}_1) \tag{A.83}$$

We define the conjugate momenta

$$P_{j_1\vec{q}_1}(t) \equiv \frac{\partial L}{\partial \dot{Q}^*_{j_1\vec{q}_1}(t)} \tag{A.84}$$

$$\Big| \quad \text{where } L = T - V.$$

$$= \dot{Q}_{j_1\vec{q}_1}(t) \tag{A.85}$$

$$P^*_{j_1\vec{q}_1}(t) = \dot{Q}^*_{j_1\vec{q}_1}(t) = \dot{Q}_{j_1,-\vec{q}_1}(t) \tag{A.86}$$

The Hamiltonian is a set of decoupled oscillators.

$$H = \frac{1}{2}\sum_{j_1\vec{q}_1} P_{j_1\vec{q}_1}(t)P^*_{j_1\vec{q}_1}(t) + \frac{1}{2}\sum_{j_1\vec{q}_1}\omega_0^2(j_1\vec{q}_1)Q_{j_1\vec{q}_1}(t)Q^*_{j_1\vec{q}_1}(t) \tag{A.87}$$

In these coordinates, we will now go over to quantum theory. We define the operators and the commutation relations,

$$\left[Q^\dagger_{j\vec{q}}, P_{j'\vec{q}\,'}\right]_- = i\hbar\delta_{\vec{q}\vec{q}\,'}\delta_{jj'} \text{ within 1BZ} \tag{A.88}$$

$$\left[Q^\dagger_{j\vec{q}}, P_{j'\vec{q}\,'}\right]_- = i\hbar\delta_{jj'}\sum_{\vec{g}}\delta_{\vec{q},\vec{q}+\vec{g}} \text{ outside 1BZ} \tag{A.89}$$

where $\vec{g}$ is the reciprocal space translation vector. The Hermitian conjugate equations are,

$$\left[Q_{j\vec{q}}, P^\dagger_{j'\vec{q}\,'}\right]_- = -i\hbar\delta_{\vec{q}\vec{q}\,'}\delta_{jj'} \tag{A.90}$$

The vanishing commutators are

$$\left[Q_{j\vec{q}}, Q^\dagger_{j'\vec{q}\,'}\right]_- = 0 = \left[P_{j\vec{q}}, P^\dagger_{j'\vec{q}\,'}\right]_- \tag{A.91}$$

Similar to the simple harmonic oscillator in quantum mechanics, we introduce the bosonic operators,

$$Q_{j\vec{q}} \equiv \sqrt{\frac{\hbar}{2\omega_0(j\vec{q})}}\left(a_{j\vec{q}} + a^\dagger_{j,-\vec{q}}\right) \tag{A.92}$$

$$P_{j\vec{q}} \equiv \frac{1}{i}\sqrt{\frac{\hbar\omega_0(j\vec{q})}{2}}\left(a_{j\vec{q}} - a^\dagger_{j,-\vec{q}}\right) \tag{A.93}$$

These definitions fit the classical to quantum relationship

$$Q_{j\vec{q}} = Q^\dagger_{j,-\vec{q}} \text{ and } P_{j\vec{q}} = P^\dagger_{j,-\vec{q}} \tag{A.94}$$

Using the normal mode variables commutation relations, we get,

$$\left[a_{j\vec{q}}\,, a^\dagger_{j'\vec{q}\,'}\right]_- = \delta_{jj'}\delta_{\vec{q}\vec{q}\,'} \tag{A.95}$$

$$\left[a_{j\vec{q}}\,, a_{j'\vec{q}\,'}\right]_- = 0 = \left[a^\dagger_{j\vec{q}}\,, a^\dagger_{j'\vec{q}\,'}\right]_- \tag{A.96}$$

The Hamiltonian in the bosonic variables is

$$H = \sum_{j\vec{q}} \hbar\omega_0(j\vec{q})\left(a^\dagger_{j\vec{q}}\, a_{j\vec{q}} + \frac{1}{2}\right) \tag{A.97}$$

Finally we relate to the displacement variables

$$u_{lk\alpha} = \frac{1}{\sqrt{Nm_k}}\sum_{j\vec{q}} \epsilon_{k\alpha}(j\vec{q})\sqrt{\frac{\hbar}{2\omega_0(j\vec{q})}}\left(a_{j\vec{q}} + a^\dagger_{j,-\vec{q}}\right)e^{i\vec{q}\cdot l} \tag{A.98}$$

$$= \sum_{j\vec{q}}\sqrt{\frac{\hbar}{2Nm_k\omega_0(j\vec{q})}}\epsilon_{k\alpha}(j\vec{q})\left(a_{j\vec{q}} + a^\dagger_{j,-\vec{q}}\right)e^{i\vec{q}\cdot l} \tag{A.99}$$

This relation is analogous to the relation between momentum field operators to spatial field operators. We work out the commutation relations,

$$\left[m_k\dot{u}_{lk\alpha}\,, u_{l'k'\alpha'}\right]_-$$

$$= \left[m_k\frac{1}{\sqrt{Nm_k}}\sum_{j_1\vec{q}_1}\epsilon_{k\alpha}(j_1\vec{q}_1)\dot{Q}_{j_1\vec{q}_1}e^{i\vec{q}_1\cdot l}, \frac{1}{\sqrt{Nm'_k}}\sum_{j_2\vec{q}_2}\epsilon_{k'\alpha'}(j_2\vec{q}_2)\dot{Q}_{j_2\vec{q}_2}e^{i\vec{q}_2\cdot l'}\right]_- \tag{A.100}$$

$|$ change the $\vec{q}$ sum to $-\vec{q}$, and recall $\dot{Q}_{j_1,-\vec{q}_1} = P^\dagger_{j_1\vec{q}_1}$

$$= \sqrt{\frac{i\hbar}{N}}\sum_{j_1,-\vec{q}_1}\epsilon^*_{k\alpha}(j_1\vec{q}_1)e^{-i\vec{q}_1\cdot l}\frac{1}{\sqrt{Nm'_k}}\sum_{j_2\vec{q}_2}\epsilon_{k'\alpha'}(j_2\vec{q}_2)e^{i\vec{q}_2\cdot l'}\left[P^\dagger_{j_1\vec{q}_1}, Q_{j_2\vec{q}_2}\right]_- \tag{A.101}$$

$|$ the commutator, $\left[P^\dagger_{j_1\vec{q}_1}, Q_{j_2\vec{q}_2}\right]_- = i\hbar\delta_{\vec{q}_1\vec{q}_2}\delta_{j_1j_2}$

$$= \frac{i\hbar}{N}\sqrt{\frac{m_k}{m'_k}}\sum_{j_1,-\vec{q}_1}\epsilon^*_{k\alpha}(j_1\vec{q}_1)\epsilon_{k'\alpha'}(j_1\vec{q}_1)e^{i\vec{q}\cdot(l'-l)} \tag{A.102}$$

$|$ use $\sum_{j_1}\epsilon^*_{k\alpha}(j_1\vec{q}_1)\epsilon_{k'\alpha'}(j_1\vec{q}_1) = \delta_{kk'}\delta_{\alpha\alpha'}$ and $\sum_{\vec{q}_1}e^{i\vec{q}_1\cdot(l'-l)} = N\delta_{ll'}$

$$= i\hbar\delta_{ll'}\delta_{kk'}\delta_{\alpha\alpha'} \tag{A.103}$$

As a closing, I would like to mention some related topics that are worth studying if I had more time. They are: elastic theory and point and space group theory on lattice dynamics.

Appendix B

T $\neq$ 0 Equilibrium Matsubara Field Theory

B.1 Perturbation Expression as a limiting case from NEGF

Here we follow [Bruus2004] chapter 11.

The purpose of this appendix is twofold; (a) to lay out the mathematical tools to handle the $T \neq 0$ equilibrium interacting field theory on the Matsubara contour c_M (b) we can actually use Langreth's theorem as a trick in equilibrium theory to get the answer without going over to imaginary times and without evaluating Matsubara frequency sums.

For the equilibrium formalism (before switching on $V(t)$ at t_0), we have an interacting but time independent Hamiltonian,

$$H = H_0 + H_{\text{int}} \tag{B.1}$$

Note that Wick's theorem and cancellation of disconnected diagrams is already proven for the more general case of contours $c_K + c_M$ in NEGF.

Now we can simply copy over the perturbation expression (3.22) from NEGF and set $V(t) = 0$ and restrict the field operators to c_M, the c_K part becomes identity. Using generic symbols ψ, $\psi^\dagger$ for field operators and G for both fermionic and bosonic Green's function, we carry out this reduction to get the so-called Matsubara Green's function.

$$\begin{aligned}
& G(1,1') \\
= \;& -\frac{i}{\hbar}\frac{\operatorname{Tr}\left(e^{-\beta H_0} T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K+c_M} d\tau (H_{\text{int}})_{H_0}(\tau)} e^{-\frac{i}{\hbar}\int_{c_K} d\tau V_{H_0}(\tau)} \psi_{H_0}(t_1)\psi^\dagger_{H_0}(t_{1'})\right)\right)}{\operatorname{Tr}\left(e^{-\beta H_0} T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K+c_M} d\tau (H_{\text{int}})_{H_0}(\tau)} e^{-\frac{i}{\hbar}\int_{c_K} d\tau V_{H_0}(\tau)}\right)\right)} \qquad \text{(B.2)} \\
& \mid \;\; \text{set } V = 0 \text{ and so its } S\text{-matrix becomes unity} \\
= \;& -\frac{i}{\hbar}\frac{\operatorname{Tr}\left(e^{-\beta H_0} T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K+c_M} d\tau (H_{\text{int}})_{H_0}(\tau)} \psi_{H_0}(t_1)\psi^\dagger_{H_0}(t_{1'})\right)\right)}{\operatorname{Tr}\left(e^{-\beta H_0} T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K+c_M} d\tau (H_{\text{int}})_{H_0}(\tau)}\right)\right)} \qquad \text{(B.3)} \\
& \mid \;\; \text{restrict } t_1,\, t_{1'} \text{ to } c_M, \text{ i.e. } t_1 = t_0 - i\hbar\tau_1^M \text{ and } t_{1'} = t_0 - i\hbar\tau_{1'}^M \\
& \mid \;\; \text{the Keldysh contour } c_K \text{ part factorizes} \\
= \;& -\frac{i}{\hbar}\frac{\operatorname{Tr}\left(e^{-\beta H_0} T_{c_M}\left(e^{-\frac{i}{\hbar}\int_{c_M} d\tau^M (H_{\text{int}})_{H_0}(\tau)} \psi_{H_0}(t_0 - i\hbar\tau_1^M)\psi^\dagger_{H_0}(t_0 - i\hbar\tau_{1'}^M)\right) T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau (H_{\text{int}})_{H_0}(\tau)}\right)\right)}{\operatorname{Tr}\left(e^{-\beta H_0} T_{c_M}\left(e^{-\frac{i}{\hbar}\int_{c_M} d\tau^M (H_{\text{int}})_{H_0}(\tau)}\right)\right)\left(T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau (H_{\text{int}})_{H_0}(\tau)}\right)\right)}
\end{aligned}$$

| the factorized part $T_{c_K}\left(e^{-\frac{i}{\hbar}\int_{c_K} d\tau (H_{\rm int})_{H_0}(\tau)}\right)$ is unity

| this is the Matsubara Green's function (up to factors)

$$\begin{aligned} & G^M(\vec{r}_1, \vec{r}_{1'}, t_0 - i\hbar\tau_1^M, t_0 - i\hbar\tau_{1'}^M) \\ \equiv\ & -\frac{i}{\hbar}\frac{\mathrm{Tr}\left[e^{-\beta H_0}T_{c_M}\left(e^{-\frac{i}{\hbar}\int_{c_M} d\tau^M (H_{\rm int})_{H_0}(\tau)}\psi_{H_0}(t_0 - i\hbar\tau_1^M)\psi^\dagger_{H_0}(t_0 - i\hbar\tau_{1'}^M)\right)\right]}{\mathrm{Tr}\left[e^{-\beta H_0}T_{c_M}\left(e^{-\frac{i}{\hbar}\int_{c_M} d\tau^M (H_{\rm int})_{H_0}(\tau)}\right)\right]} \end{aligned} \tag{B.4}$$

This is the same as [Mahan2000] eqn (3.183). The factors differ because of the definitions. We go back to Heisenberg operators to facilitate the proofs of some properties of this Green's function.

$$G^M(1,1') = G^M(\vec{r}_1, \vec{r}_{1'}, t_0 - i\hbar\tau_1^M, t_0 - i\hbar\tau_{1'}^M) \tag{B.5}$$

$$= -\frac{i}{\hbar}\frac{\mathrm{Tr}\left[e^{-\beta(H_0+H_{\rm int})}T\left(\psi_H(t_0 - i\hbar\tau_1^M)\psi_H^\dagger(t_0 - i\hbar\tau_{1'}^M)\right)\right]}{\mathrm{Tr}\left[e^{-\beta(H_0+H_{\rm int})}\right]} \tag{B.6}$$

Now we will use the above expression to show that indeed G^M satisfies the properties of the usual Matsubara Green's functions. Note that $t_0 - i\hbar\tau^M$ is real time, thus τ^M is pure imaginary (it actually has units of energy^{-1} which is the same as β) and that reconciles with the usual definition of pure imaginary Matusubara time.

B.2 Properties of Matsubara Functions

There are 2 important properties that we need to show

1. G^M is a function of time difference only. This means that t_0 is arbitrary and unphysical which is obviously the case for equilibrium problems (but not for transients in NEGF where t_0 does appear).

$$G^M(\vec{r}_1, \vec{r}_{1'}, t_0 - i\hbar\tau_1^M, t_0 - i\hbar_{1'}^M) = G^M(\vec{r}_1, \vec{r}_{1'}, t_0 - i\hbar\tau_1^M - (t_0 - i\hbar\tau_{1'}^M)) \tag{B.7}$$

$$= G^M(\vec{r}_1, \vec{r}_{1'}, -i\hbar(\tau_1^M - \tau_{1'}^M)) \tag{B.8}$$

$$\equiv G^M(\vec{r}_1, \vec{r}_{1'}, \tau_1^M - \tau_{1'}^M) \tag{B.9}$$

2. Kubo-Martin-Schwinger (KMS) boundary conditions. This is the condition that whatever perturbative solution of the Green's function is solved, it must obey KMS because it is a mathematical identity obeyed by the exact Green's function.

$$G^M(\vec{r}_1, \vec{r}_{1'}, \tau_1^M - \tau_{1'}^M) = \pm G^M(\vec{r}_1, \vec{r}_{1'}, \tau_1^M - \tau_{1'}^M + \beta) \tag{B.10}$$

$$| \quad \text{where } + \text{ is for bosons, } - \text{ is for fermions} \tag{B.11}$$

<u>Proof of the first property</u>

$$G^M(\vec{r}_1, \vec{r}_{1'}, t_0 - i\hbar\tau_1^M, t_0 - \hbar\tau_{1'}^M) \tag{B.12}$$

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\left\langle T\left(\psi_H(t_0 - i\hbar\tau_1^M)\psi_H^\dagger(t_0 - i\hbar\tau_{1'}^M)\right)\right\rangle \tag{B.13}$$

$$= \theta((t_0 - i\hbar\tau_1^M) - (t_0 - i\hbar\tau_{1'}^M))\left\langle\psi_H(t_0 - i\hbar\tau_1^M)\psi_H^\dagger(t_0 - i\hbar\tau_{1'}^M)\right\rangle$$

$$\pm\theta((t_0 - i\hbar\tau_{1'}^M) - (t_0 - i\hbar\tau_1^M)\left\langle \psi_H^\dagger(t_0 - i\hbar\tau_{1'}^M)\psi_H(t_0 - i\hbar\tau_1^M)\right\rangle \tag{B.14}$$

| where $+$ is for bosons, $-$ is for fermions.

We shall consider each term seperately,

First term, $t_0 - i\hbar\tau_1^M > t_0 - i\hbar\tau_{1'}^M$,

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{\frac{i}{\hbar}H(t_0-i\hbar\tau_1^M)}\psi(t_0)e^{-\frac{i}{\hbar}H(t_0-i\hbar\tau_1^M)}e^{\frac{i}{\hbar}H(t_0-i\hbar\tau_{1'}^M)}\psi^\dagger(t_0)e^{-\frac{i}{\hbar}H(t_0-i\hbar\tau_{1'}^M)}\right]$$

| use trace cyclicity and commute $e^{-\beta H}e^{\frac{i}{\hbar}H(\ldots)}$

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{\frac{i}{\hbar}H(t_0-i\hbar\tau_1^M-t_0+i\hbar\tau_{1'}^M)}\psi(t_0)e^{-\frac{i}{\hbar}H(t_0-i\hbar\tau_1^M-t_0+i\hbar\tau_{1'}^M)}\psi^\dagger(t_0)\right] \tag{B.15}$$

$$= G^M(\vec{r}_1, \vec{r}_{1'}, t_0 - i\hbar\tau_1^M - t_0 + i\hbar\tau_{1'}^M, 0) \tag{B.16}$$

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{(\tau_1^M-\tau_{1'}^M)H}\psi(t_0)e^{-(\tau_1^M-\tau_{1'}^M)H}\psi^\dagger(t_0)\right] \tag{B.17}$$

$$= G^M(\vec{r}_1, \vec{r}_{1'}, \tau_1^M - \tau_{1'}^M, 0) \tag{B.18}$$

| using trace cyclicity in a different way, we get,

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}\psi(t_0)e^{\frac{i}{\hbar}H(-t_0+i\hbar\tau_1^M+t_0-i\hbar\tau_{1'}^M)}\psi^\dagger(t_0)e^{-\frac{i}{\hbar}H(-t_0+i\hbar\tau_1^M+t_0-i\hbar\tau_{1'}^M)}\right] \tag{B.19}$$

$$= G^M(\vec{r}_1, \vec{r}_{1'}, 0, t_0 - i\hbar\tau_{1'}^M - t_0 + i\hbar\tau_1^M) \tag{B.20}$$

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}\psi(t_0)e^{(\tau_{1'}^M-\tau_1^M)H}\psi^\dagger(t_0)e^{-(\tau_{1'}^M-\tau_1^M)H}\right] \tag{B.21}$$

$$= G^M(\vec{r}_1, \vec{r}_{1'}, 0, \tau_{1'}^M - \tau_1^M) \tag{B.22}$$

Second term, $t_0 - i\hbar\tau_{1'}^M > t_0 - i\hbar\tau_1^M$,

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{\frac{i}{\hbar}H(t_0-i\hbar\tau_{1'}^M)}\psi^\dagger(t_0)e^{-\frac{i}{\hbar}H(t_0-i\hbar\tau_{1'}^M)}e^{\frac{i}{\hbar}H(t_0-i\hbar\tau_1^M)}\psi(t_0)e^{-\frac{i}{\hbar}H(t_0-i\hbar\tau_1^M)}\right]$$

| use trace cyclicity and commute $e^{-\beta H}e^{\frac{i}{\hbar}H(\ldots)}$

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{\frac{i}{\hbar}H(t_0-i\hbar\tau_{1'}^M-t_0+i\hbar\tau_1^M)}\psi^\dagger(t_0)e^{-\frac{i}{\hbar}H(t_0-i\hbar\tau_{1'}^M-t_0+i\hbar\tau_1^M)}\psi(t_0)\right] \tag{B.23}$$

$$= G^M(\vec{r}_1, \vec{r}_{1'}, 0, t_0 - i\hbar\tau_{1'}^M - t_0 + i\hbar\tau_1^M) \tag{B.24}$$

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{(\tau_{1'}^M-\tau_1^M)H}\psi^\dagger(t_0)e^{-(\tau_{1'}^M-\tau_1^M)H}\psi(t_0)\right] \tag{B.25}$$

$$= G^M(\vec{r}_1, \vec{r}_{1'}, 0, \tau_{1'}^M - \tau_1^M) \tag{B.26}$$

| using trace cyclicity in a different way, we get,

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}\psi^\dagger(t_0)e^{\frac{i}{\hbar}H(-t_0+i\hbar\tau_{1'}^M+t_0-i\hbar\tau_1^M)}\psi(t_0)e^{-\frac{i}{\hbar}H(-t_0+i\hbar\tau_{1'}^M+t_0-i\hbar\tau_1^M)}\right] \tag{B.27}$$

$$= G^M(\vec{r}_1, \vec{r}_{1'}, t_0 - i\hbar\tau_1^M - t_0 + i\hbar\tau_{1'}^M, 0) \tag{B.28}$$

$$= -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}\psi^\dagger(t_0)e^{(\tau_1^M-\tau_{1'}^M)H}\psi(t_0)e^{-(\tau_1^M-\tau_{1'}^M)H}\right] \tag{B.29}$$

$$= G^M(\vec{r}_1, \vec{r}_{1'}, \tau_1^M - \tau_{1'}^M, 0) \tag{B.30}$$

Proof of the second property

First case: we let $\tau_{1'}^M = \beta$ and since $t_0 - i\hbar\beta$ is the "largest time", we take only the second term where $t_0 - i\hbar\beta > t_0 - i\hbar\tau_1^M$.

$$\begin{aligned}
& G^M(\vec{r}_1, \vec{r}_{1'}, \tau_1^M - \beta, 0) \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}\psi^\dagger(t_0)e^{(\tau_1^M-\beta)H}\psi(t_0)e^{-(\tau_1^M-\beta)H}\right] && \text{(B.31)} \\
| \;& \text{use trace cyclicity and commute } e^{\tau H}e^{-\beta H} \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[\psi^\dagger(t_0)e^{\tau_1^M H}e^{-\beta H}\psi(t_0)e^{-\tau_1^M H}\right] && \text{(B.32)} \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{\tau_1^M H}\psi(t_0)e^{-\tau_1^M H}\psi^\dagger(t_0)\right] && \text{(B.33)} \\
| \;& \text{form back the Heisenberg picture} \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{\frac{i}{\hbar}H(t_0-i\hbar\tau_1^M)}\psi(t_0)e^{-\frac{i}{\hbar}H(t_0-i\hbar\tau_1^M)}e^{\frac{i}{\hbar}H(t_0-i\hbar 0)}\psi^\dagger(t_0)e^{-\frac{i}{\hbar}H(t_0-i\hbar 0)}\right] && \text{(B.34)} \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}\psi_H(t_0-i\hbar\tau_1^M)\psi_H^\dagger(t_0-i\hbar 0)\right] && \text{(B.35)} \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}(\pm)\mathrm{Tr}\left[e^{-\beta H}\psi_H^\dagger(t_0-i\hbar 0)\psi_H(t_0-i\hbar\tau_1^M)\right] && \text{(B.36)} \\
| \;& \text{where } + \text{ is for bosons, } - \text{ is for fermions} \\
= \;& \pm G^M(\vec{r}_1, \vec{r}_{1'}, t_0 - i\hbar\tau_1^M - t_0 + i\hbar 0, 0) && \text{(B.37)} \\
= \;& \pm G^M(\vec{r}_1, \vec{r}_{1'}, \tau_1^M - 0, 0) && \text{(B.38)}
\end{aligned}$$

Second case: we let $\tau_1^M = \beta$ and since $t_0 - i\hbar\beta$ is the "largest time", we take only the first term where $t_0 - i\hbar\beta > t_0 - i\hbar\tau_{1'}^M$.

$$\begin{aligned}
& G^M(\vec{r}_1, \vec{r}_{1'}, \beta - \tau_{1'}^M, 0) \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{(\beta-\tau_{1'}^M)H}\psi(t_0)e^{-(\beta-\tau_{1'}^M)H}\psi^\dagger(t_0)\right] && \text{(B.39)} \\
| \;& \text{use trace cyclicity and commute } e^{\tau H}e^{-\beta H} \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\tau_{1'}^M H}\psi(t_0)e^{\tau_{1'}^M H}e^{-\beta H}\psi^\dagger(t_0)\right] && \text{(B.40)} \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{\tau_{1'}^M H}\psi^\dagger(t_0)e^{-\tau_{1'}^M H}\psi(t_0)\right] && \text{(B.41)} \\
| \;& \text{form back the Heisenberg picture} \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}e^{\frac{i}{\hbar}H(t_0-i\hbar\tau_{1'}^M)}\psi^\dagger(t_0)e^{-\frac{i}{\hbar}H(t_0-i\hbar\tau_{1'}^M)}e^{\frac{i}{\hbar}H(t_0-i\hbar 0)}\psi(t_0)e^{-\frac{i}{\hbar}H(t_0-i\hbar 0)}\right] && \text{(B.42)} \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}\mathrm{Tr}\left[e^{-\beta H}\psi_H^\dagger(t_0-i\hbar\tau_{1'}^M)\psi_H(t_0-i\hbar 0)\right] && \text{(B.43)} \\
= \;& -\frac{i}{\hbar}\frac{1}{\mathrm{Tr}(e^{-\beta H})}(\pm)\mathrm{Tr}\left[e^{-\beta H}\psi_H(t_0-i\hbar 0)\psi_H^\dagger(t_0-i\hbar\tau_{1'}^M)\right] && \text{(B.44)} \\
| \;& \text{where } + \text{ is for bosons, } - \text{ is for fermions} \\
= \;& \pm G^M(\vec{r}_1, \vec{r}_{1'}, t_0 - i\hbar 0 - t_0 + i\hbar\tau_{1'}^M, 0) && \text{(B.45)} \\
= \;& \pm G^M(\vec{r}_1, \vec{r}_{1'}, 0 - \tau_{1'}^M, 0) && \text{(B.46)}
\end{aligned}$$

Since G^M obeys periodic (for bosons) or antiperiodic (for fermions) boundary conditions with period β, we can expand G^M as a Fourier series.[1]

$$G^M(\omega_n) \equiv \frac{1}{2}\int_{-\beta}^{\beta} d\tau^M e^{i\hbar\omega_n\tau^M} G^M(\tau^M) = \begin{cases} \omega_n = \omega_n^B = \frac{2n\pi}{\beta\hbar} \text{ for bosons} \\ \omega_n = \omega_n^F = \frac{(2n+1)\pi}{\beta\hbar} \text{ for fermions} \end{cases} \tag{B.47}$$

The Fourier inverse is defined as

$$G^M(\tau^M) = \frac{1}{\beta}\sum_{n=-\infty}^{\infty} e^{-i\hbar\omega_n\tau^M} G^M(\omega_n) \tag{B.48}$$

Finally we derive a further relation,

$$\begin{aligned}
G^M(\omega_n) &= \frac{1}{2}\int_{-\beta}^{\beta} d\tau^M e^{i\hbar\omega_n\tau^M} G^M(\tau^M) && \text{(B.49)}\\
&= \frac{1}{2}\int_{0}^{\beta} e^{i\hbar\omega_n\tau^M} G^M(\tau^M) + \frac{1}{2}\int_{-\beta}^{0} d\tau^M e^{i\hbar\omega_n\tau^M} G^M(\tau^M) && \text{(B.50)}\\
&| \quad \text{shift the second term from } \tau^M \text{ to } \tau^M - \beta \\
&= \frac{1}{2}\int_{0}^{\beta} d\tau^M e^{i\hbar\omega_n\tau^M} G^M(\tau^M) + \frac{1}{2}\int_{0}^{\beta} d\tau^M e^{i\hbar\omega_n(\tau^M-\beta)} G^M(\tau^M-\beta) && \text{(B.51)}\\
&| \quad \text{use the periodic/antiperiodic property, } G^M(\tau^M-\beta) = \pm G^M(\tau^M) \\
&= \frac{1}{2}\int_{0}^{\beta} d\tau^M e^{i\hbar\omega_n\tau^M} G^M(\tau^M) \pm \frac{1}{2}e^{-i\hbar\omega_n\beta}\int_{0}^{\beta} d\tau^M e^{i\hbar\omega_n\tau^M} G^M(\tau^M) && \text{(B.52)}\\
&= \frac{1}{2}(1 \pm e^{-i\hbar\omega_n\beta})\int_{0}^{\beta} d\tau^M e^{i\hbar\omega_n\tau^M} G^M(\tau^M) && \text{(B.53)}\\
&| \quad \text{substitute the expressions of the bosonic Matsubara frequencies} \\
&| \quad \text{and the fermionic Matsubara frequencies} \\
&= \int_{0}^{\beta} d\tau^M e^{i\hbar\omega_n\tau^M} G^M(\tau^M) && \text{(B.54)}
\end{aligned}$$

B.3 Connection to the physical Green's functions

So much for mathematical tricks, $G^M(\omega_n)$ is not physical and so we now need to relate it to the physical ones like $G^{R,A}(\omega)$ or $G^{R,A}(t)$. We will show how to relate the Matsubara Green's function to the retarded Green's function and then to the advanced Green's function by using the Lehmann representation for both bosons and fermions. For the retarded Green's function, we have,

$$\begin{aligned}
G^R(\omega) &= \int dt e^{i\omega t} G^R(t) && \text{(B.55)}\\
&= -\frac{i}{\hbar}\int dt e^{i\omega t}\theta(t)\frac{\mathrm{Tr}\left(e^{-\beta H}\left[\psi_H(t), \psi_H^\dagger(0)\right]_\pm\right)}{\mathrm{Tr}\left(e^{-\beta H}\right)} && \text{(B.56)}\\
&| \quad - \text{ for bosons and } + \text{ for fermions}
\end{aligned}$$

[1] Actually, working in Fourier Series and solving the Fourier component pertubatively ensures that KMS is obeyed. In most of the literature, $\hbar$ is set as 1, so my expressions here may look strange.

$$
\begin{aligned}
& \mid \text{ use the Fourier reprsentation of the step function } \theta(t) = \frac{i}{2\pi}\int d\omega \frac{e^{-i\omega t}}{\omega + i\eta} \\
& \mid \text{ insert a complete set for the trace and between the operators} \\
= \; & \frac{1}{2\pi\hbar}\frac{1}{Z}\int dt \int d\omega' \frac{e^{i(\omega-\omega')t}}{\omega' + i\eta} \\
& \times \left[\sum_{nn'} \langle n|e^{-\beta H}\psi_H(t)|n'\rangle\langle n'|\psi_H^\dagger(0)|n\rangle \pm \sum_{nn'}\langle n'|e^{-\beta H}\psi_H^\dagger(t)|n\rangle\langle n|\psi_H^\dagger(0)|n'\rangle\right] \qquad (B.57) \\
= \; & \frac{1}{2\pi\hbar}\frac{1}{Z}\int dt \int d\omega' \sum_{nn'} \frac{e^{i(\omega-\omega')t}}{\omega' + i\eta}\Big[e^{-\beta E_n} e^{\frac{i}{\hbar}tE_n} e^{-\frac{i}{\hbar}tE_{n'}} \langle n|\psi(0)|n'\rangle\langle n'|\psi^\dagger(0)|n\rangle \\
& \pm e^{-\beta E_{n'}} e^{\frac{i}{\hbar}tE_n} e^{-\frac{i}{\hbar}tE_{n'}} \langle n'|\psi^\dagger(0)|n\rangle\langle n|\psi(0)|n'\rangle\Big] \qquad (B.58) \\
& \mid \text{ note the representation } \frac{1}{2\pi}\int dt e^{i\omega t} = \delta(\omega) \text{ then evaluate the delta function} \\
= \; & \frac{1}{\hbar}\frac{1}{Z}\sum_{nn'} \frac{\langle n|\psi(0)|n'\rangle\langle n'|\psi^\dagger(0)|n\rangle}{\omega + \frac{E_n}{\hbar} - \frac{E_{n'}}{\hbar} + i\eta}\left(e^{-\beta E_n} - (\pm)e^{-\beta E_{n'}}\right) \qquad (B.59) \\
& \mid \text{ where the } - \text{ in the second term in the round brackets is due to commuting } \psi \text{ and } \psi^\dagger.
\end{aligned}
$$

The Lehmann representation for the Matsubara Green's function is

$$
\begin{aligned}
& \text{Take case 1 where } t_0 - i\hbar\tau_1^M > t_0 - i\hbar\tau_{1'}^M \\
= \; & G^M(\vec{r}_1, \vec{r}_{1'}, \tau_1^M - \tau_{1'}^M, 0) \qquad (B.60) \\
= \; & -\frac{i}{\hbar}\frac{1}{Z}\mathrm{Tr}\left[e^{-\beta H} e^{(\tau_1^M - \tau_{1'}^M)H}\psi(t_0) e^{-(\tau_1^M - \tau_{1'}^M)H}\psi^\dagger(t_0)\right] \qquad (B.61) \\
& \mid \text{ denote } \tau_1^M - \tau_{1'}^M = \tau^M \text{ and insert complete sets of states} \\
= \; & -\frac{i}{\hbar}\frac{1}{Z}\sum_{nn'}\langle n|e^{-\beta H} e^{\tau^M H}\psi(t_0)|n'\rangle\langle n'|e^{-\tau^M H}\psi^\dagger(t_0)|n\rangle \qquad (B.62) \\
= \; & -\frac{i}{\hbar}\frac{1}{Z}\sum_{nn'} e^{-\beta E_n} e^{\tau^M(E_n - E_{n'})}\langle n|\psi(t_0)|n'\rangle\langle n'|\psi^\dagger(t_0)|n\rangle \qquad (B.63)
\end{aligned}
$$

We Fourier transform to the Matsubara frequency domain,

$$
\begin{aligned}
G^M(\omega_m) = \; & \int_0^\beta d\tau^M e^{i\hbar\omega_m\tau^M} G^M(\tau^M, 0) \qquad (B.64) \\
= \; & -\frac{i}{\hbar}\frac{1}{Z}\sum_{nn'}\int_0^\beta d\tau^M e^{\tau^M(i\hbar\omega_m + E_n - E_{n'})} e^{-\beta E_n}\langle n|\psi(t_0)|n'\rangle\langle n'|\psi^\dagger(t_0)|n\rangle \qquad (B.65) \\
& \mid \text{ evaluate the } \tau^M \text{ integral} \qquad (B.66) \\
= \; & -\frac{i}{\hbar}\frac{1}{Z}\sum_{nn'} e^{-\beta E_n}\frac{\langle n|\psi(t_0)|n'\rangle\langle n'|\psi^\dagger(t_0)|n\rangle}{i\hbar\omega_m + E_n - E_{n'}}\left(e^{i\hbar\omega_m\beta} e^{\beta(E_n - E_{n'})} - 1\right) \qquad (B.67) \\
& \mid \text{ recall that } e^{i\hbar\omega_m\beta} = \pm 1 \text{ where } + \text{ is for bosons, } - \text{ is for fermions} \qquad (B.68) \\
= \; & \frac{i}{\hbar}\frac{1}{Z}\sum_{nn'}\frac{\langle n|\psi(t_0)|n'\rangle\langle n'|\psi^\dagger(t_0)|n\rangle}{i\hbar\omega_m + E_n - E_{n'}}\left(e^{-\beta E_n} - (\pm)e^{-\beta E_{n'}}\right) \qquad (B.69)
\end{aligned}
$$

Thus they are connected by analytic continuation,

$$G^R(\omega) = -i\hbar G^M(i\omega_m \to \omega + i\eta) \tag{B.70}$$

The extra factor is because my definition of G^M is different from the usual one. Note that this is only true when $G^M(i\omega_m)$ is analytic in the upper half plane of the complex plane.

Since the advanced function only differs in $\omega + i\eta \to \omega - i\eta$ thus we immediately get the relation,

$$G^A(\omega) = -i\hbar G^M(i\omega_m \to \omega - i\eta) \tag{B.71}$$

which is only true when $G^M(i\omega_m)$ is analytic in the lower half of the complex plane.

B.4 Evaluation of Matsubara sums

B.4.1 From frequency summations to contour integrations

From perturbation theory when we need to evaluate Feynman diagrams, we typically encounter Matsubara frequency summations (instead of the usual integrations). The issue is, how to evaluate such Fourier sums? The general form of such summations can be written as

$$\begin{aligned}
S^F(\tau^M) &= \frac{1}{\beta\hbar}\sum_{i\omega_n^F} g(i\omega_n^F)e^{i\hbar\omega_n^F\tau^M} && \text{(B.72)}\\
&\quad | \quad \text{where } \omega_n^F \text{ is the fermionic Matsubara frequency} \\
S^B(\tau^M) &= \frac{1}{\beta\hbar}\sum_{i\omega_n^B} g(i\omega_n^B)e^{i\hbar\omega_n^B\tau^M} && \text{(B.73)}\\
&\quad | \quad \text{where } \omega_n^B \text{ is the bosonic Matsubara frequency}
\end{aligned}$$

In this subsection, we show how to write such sums into contour integrals and thereby make use of residue theorem to evaluate the sums. Subsequent subsections cover more general cases and an explicit example is given later.

First we investigate 2 functions, $n_F(z)$ and $n_B(z)$ which have poles at $z = i\omega_n^F$ and $z = i\omega_n^B$ respectively. [2]

$$n_F(z) = \frac{1}{e^{\beta\hbar z}+1} \qquad \text{poles at } z = \frac{i(2n+1)\pi}{\beta\hbar} \tag{B.74}$$

$$n_B(z) = \frac{1}{e^{\beta\hbar z}-1} \qquad \text{poles at } z = \frac{i(2n)\pi}{\beta\hbar} \tag{B.75}$$

Here we make a quick digression to calculate the residue at each pole,

$$\begin{aligned}
\mathrm{Res}_{z=i\omega_n^F}\left[n_F(z)\right] &= \lim_{z\to i\omega_n^F}\frac{z - i\omega_n^F}{e^{\beta\hbar z}+1} && \text{(B.76)}\\
&\quad | \quad \text{let } z - i\omega_n^F = \delta \\
&= \lim_{\delta\to 0}\frac{\delta}{e^{\beta\hbar(z - i\omega_n^F + i\omega_n^F)}+1} && \text{(B.77)}\\
&= \lim_{\delta\to 0}\frac{\delta}{e^{i\hbar\omega_n^F\beta}e^{\beta\hbar\delta}+1} && \text{(B.78)}
\end{aligned}$$

[2] All factors of $\hbar$ is to make z have the same dimension as frequency.

$$
\begin{aligned}
& \quad | \quad \text{use l' hospital rule} \\
& = \lim_{\delta \to 0} \frac{1}{\beta\hbar(e^{\beta\hbar\delta} e^{\beta\hbar i\omega_n^F})} && \text{(B.79)} \\
& \quad | \quad \text{use } e^{\beta\hbar\delta} = 1 \text{ because } \delta = 0 \text{ and } e^{\beta\hbar i\omega_n^F} = -1 \\
& = -\frac{1}{\beta\hbar} && \text{(B.80)}
\end{aligned}
$$

Then similarly for bosonic Matsubara frequencies,

$$
\mathrm{Res}_{z=i\omega_n^B}\left[n_B(z)\right] = \lim_{z \to i\omega_n^B} \frac{z - i\omega_n^B}{e^{\beta\hbar z} - 1} = +\frac{1}{\beta\hbar} \tag{B.81}
$$

Now we shall evaluate contour integrals that enclose 1 pole but does not enclose the singularities of $g(z)$. The results are,

$$
\oint_{1 \text{ pole}} dz n_F(z) g(z) = 2\pi i \mathrm{Res}_{z=i\omega_n^F}\left[n_F(z) g(i\omega_n^F)\right] = -\frac{2\pi i}{\beta\hbar} g(i\omega_n^F) \tag{B.82}
$$

$$
\oint_{1 \text{ pole}} dz n_B(z) g(z) = 2\pi i \mathrm{Res}_{z=i\omega_n^B}\left[n_B(z) g(i\omega_n^B)\right] = +\frac{2\pi i}{\beta\hbar} g(i\omega_n^B) \tag{B.83}
$$

And for contours that enclose all the points $z = i\omega_n^F$ and $z = i\omega_n^B$ with $g(z)$ being analytic, we can now write the sum into complex contour integrals (whose evaluation is simply done by Residue theorem),

$$
S^F(\tau^M) = \frac{1}{\beta\hbar} \sum_{i\omega_n^F} g(i\omega_n^F) e^{i\hbar\omega_n^F \tau^M} \quad \to \quad S^F(\tau^M) = -\int_c \frac{dz}{2\pi i} n_F(z) g(z) e^{\hbar z \tau^M} \tag{B.84}
$$

$$
S^B(\tau^M) = \frac{1}{\beta\hbar} \sum_{i\omega_n^B} g(i\omega_n^B) e^{i\hbar\omega_n^B \tau^M} \quad \to \quad S^B(\tau^M) = +\int_c \frac{dz}{2\pi i} n_B(z) g(z) e^{\hbar z \tau^M} \tag{B.85}
$$

which we can see by expanding $e^{\hbar z \tau^M}$ and carrying out the integral for each term then resum the series.

B.4.2 Summation over functions with simple poles

Consider the case where $g_0(z)$ has a number of known simple poles, say

$$
g_0(z) = \prod_j \frac{1}{z - z_j} \tag{B.86}
$$

then the sum to evaluate

$$
S_0^F(\tau^M) = \frac{1}{\beta\hbar} \sum_{i\omega_n^F} g_0(i\omega_n^F) e^{i\hbar\omega_n^F \tau^M} \ , \ \tau^M > 0 \tag{B.87}
$$

We take the contour $C_\infty : z = Re^{i\theta}$, $R \to \infty$,
The integral is zero for both the upper half plane and the lower half plane.
Considerations for the kernel,

$$
n_F(z) e^{\hbar z \tau^M} = \frac{e^{\hbar z \tau^M}}{e^{\beta\hbar z} + 1} \propto \begin{cases} e^{\hbar(\tau^M - \beta)\Re z} \to 0 \ \text{ for } \Re z > 0 \\ e^{\hbar \tau^M \Re z} \to 0 \ \text{ for } \Re z < 0 \end{cases} \tag{B.88}
$$

Hence we seperate the integral as,

$$\begin{aligned} 0 &= \int_{C_\infty} \frac{dz}{2\pi i} n_F(z) g_0(z) e^{\hbar z \tau^M} && \text{(B.89)} \\ &= -\frac{1}{\beta\hbar} \sum_{i\omega_n^F} g_0(i\omega_n^F) e^{i\hbar\omega_n^F \tau^M} + \sum_j \text{Res}_{z=z_j} \left[g_0(z)\right] n_F(z_j) e^{\hbar z_j \tau^M} && \text{(B.90)} \\ &| \quad \text{where the first term } (-S_0^F) \text{ is due to the contribution of the poles of } n_F \\ &| \quad \text{where the second term is due to the poles of } g_0(z) \\ \therefore S_0^F &= \sum_j \text{Res}_{z=z_j} \left[g_0(z_j)\right] n_F(z_j) e^{\hbar z_j \tau^M} && \text{(B.91)} \end{aligned}$$

Similarly for bosons we get,

$$\frac{1}{\beta\hbar} \sum_{i\omega_n^B} g_0(i\omega_n^B) e^{i\hbar\omega_n^B \tau^M} = S_0^B(\tau^M) = -\sum_j \text{Res}_{z=z_j} \left[g_0(z)\right] n_B(z_j) e^{\hbar z_j \tau^M} \tag{B.92}$$

B.4.3 Summation over functions with known branch cuts

Note that the poles of the ordered Green's function are on the real axis, so the ordered Green's function are analytic everywhere except on the real axis.

Now consider the sum,

$$S(\tau^M) = \frac{1}{\beta\hbar} \sum_{i\omega_n} g(i\omega_n) e^{i\hbar\omega_n \tau^M} \ , \ \tau^M > 0 \tag{B.93}$$

where $g(z)$ is not analytic on the real axis. We thus choose the contour shown in the diagram.

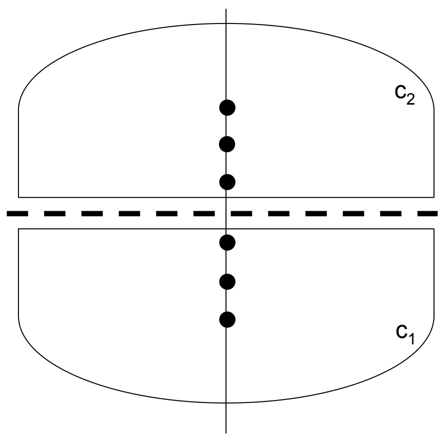


Figure B.1: *The contour used for Matsubara sum with known branch cut. The real axis is a branch cut. The black dots are the poles of n_F. The horizontal part of path c_1 is $z - \epsilon - i\eta$. The horizontal part of path c_2 is $z - \epsilon + i\eta$. Only the horizontal parts contribute when $|z| \to \infty$.*

So the contribution of the contour is

$$S(\tau^M) = -\int_{c_1+c_2} \frac{dz}{2\pi i} n_F g(z) e^{\hbar z \tau^M} \tag{B.94}$$

$$= -\frac{1}{2\pi i}\int_{-\infty}^{\infty} d\epsilon \;\; n_F(\epsilon)\left[g(\epsilon+i\eta)-g(\epsilon-i\eta)\right]e^{\hbar\epsilon\tau^M} \tag{B.95}$$

| if g is the ordered Green's function then $g(\epsilon - i\eta) = g(\epsilon + i\eta)^*$

$$= -\frac{1}{2\pi i}\int_{-\infty}^{\infty} d\epsilon \;\; n_F(\epsilon)2i\Im[g(\epsilon+i\eta)]e^{\hbar\epsilon\tau^M} \tag{B.96}$$

| the $g(\epsilon + i\eta)$ is essentially like G^R

| and spectral function $A(\epsilon) = -2\Im G^R(\epsilon)$

$$= \int_{-\infty}^{\infty}\frac{d\epsilon}{2\pi}n_F(\epsilon)A(\epsilon)e^{\hbar\epsilon\tau^M} \tag{B.97}$$

B.5 An Example comparing Matsubara Field Theory and NEGF: Electron-Phonon Self Energy

This section covers the 2nd purpose of the chapter: to show that Langreth's theorem can serve as a nice trick to bypass the use of Matsubara frequencies and Matsubara sums. We illustrate with the problem of evaluating the retarded electron-phonon self energy. Here we follow [Haug2007] pg 73.

B.5.1 NEGF Treatment

To use the trick, we pretend to use NEGF for an equilibrium problem. Recall the NEGF Hamiltonian consists of $H_0 + H_{\text{int}} + V(t)$. So we let H_0 be the "free" parts of the electrons and the phonons. Let $H_{\text{int}} = 0$. Let $V(t) = H^{(el-ph)}$ and so we only have Keldysh contour c_K for this problem.

The lowest order self energy in contour time is [3]

$$\Sigma^{(el-ph)}_{n_1\sigma_1 j_1}(\vec{k}_1,\tau_1\tau_2) = i\hbar\sum_{\vec{q}_1}\left|M_{\vec{q}_1}\right|^2 G^{(0)}_{n_1,\vec{k}_1-\vec{q}_1,\sigma_1,n_1,\vec{k}_1-\vec{q}_1,\sigma_1}(\tau_1,\tau_2)D^{(0)}_{j_1\vec{q}_1 j_1\vec{q}_1}(\tau_1,\tau_2) \tag{B.98}$$

Use Langreth's theorem to get the retarded self energy for this example. Note that this is the parallel multiplication case. The phonon Green's function, $D^{(0)}$ here is the "Q, Q" version.

$$\Sigma^{(el-ph)R}_{n_1\sigma_1 j_1}(\vec{k}_1,t_1-t_2)$$

$$= i\hbar\sum_{\vec{q}_1}\left|M_{\vec{q}_1}\right|^2\theta(t_1-t_2)\left[G^{(0)>}D^{(0)>} - G^{(0)<}D^{(0)<}\right] \tag{B.99}$$

| make the following symbolic manipulations using $C^R = \theta(C^> - C^<)$ and $\theta^2 = \theta$

| $\theta(G^>D^> - G^<D^<) = (G^R + \theta G^<)(D^R + \theta D^<) + (G^R - \theta G^>)D^<$

$$= i\hbar\sum_{\vec{q}_1}\left|M_{\vec{q}_1}\right|^2\left[G^{(0)<}D^{(0)R} + G^{(0)R}D^{(0)<} + G^{(0)R}D^{(0)R}\right](t_1-t_2) \tag{B.100}$$

| substitute the relevant expressions from the appendix of equilibrium expressions

$$= -\sum_{\vec{q}_1}\left|M_{\vec{q}_1}\right|^2$$

$$\times\left[f^{eq}_{n_1,\vec{k}_1-\vec{q}_1,\sigma_1}e^{-\frac{i}{\hbar}\epsilon_{n_1,\vec{k}_1-\vec{q}_1}(t_1-t_2)}\left(-\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\right)\theta(t_1-t_2)\left(e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)} - e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right)\right.$$

$$+\theta(t_1-t_2)e^{-\frac{i}{\hbar}\epsilon_{n_1,\vec{k}_1-\vec{q}_1}(t_1-t_2)}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left(\left(N^{eq}_{j_1\vec{q}_1}+1\right)e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)} + N^{eq}_{j_1\vec{q}_1}e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right)$$

[3] The notations are as follows: n-electronic band index, $\vec{k}$-electronic wave-vector, σ-electronic spin, j-phonon branch index and $\vec{q}$-phonon wave-vector.

$$+\theta(t_1-t_2)e^{-\frac{i}{\hbar}\epsilon_{n_1,\vec{k}_1-\vec{q}_1}(t_1-t_2)}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\theta(t_1-t_2)\left(e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)}-e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right)\Bigg] \tag{B.101}$$

$$= -\sum_{\vec{q}_1}\theta(t_1-t_2)\left|M_{\vec{q}_1}\right|^2\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left[\left(N^{eq}_{j_1\vec{q}_1}-f^{eq}_{n_1,\vec{k}_1-\vec{q}_1,\sigma_1}+1\right)e^{-i\left(\frac{\epsilon_{n_1,\vec{k}_1-\vec{q}_1}}{\hbar}+\omega_{j_1\vec{q}_1}\right)(t_1-t_2)}\right.$$

$$\left.+\left(N^{eq}_{j_1\vec{q}_1}+1+f^{eq}_{n_1,\vec{k}_1-\vec{q}_1,\sigma_1}-1\right)e^{-i\left(\frac{\epsilon_{n_1,\vec{k}_1-\vec{q}_1}}{\hbar}-\omega_{j_1\vec{q}_1}\right)(t_1-t_2)}\right] \tag{B.102}$$

Now we Fourier transform the expression and we add a small positive η for convergence of the integral (or think of η as coming from the Fourier representation of the temporal step function).

$$\Sigma^{(el-ph)R}_{n_1\sigma_1j_1}(\vec{k}_1,\omega) = \int_{-\infty}^{\infty}d(t_1-t_2)e^{i\omega(t_1-t_2)}\Sigma^{(el-ph)R}_{n_1\sigma_1j_1}(\vec{k}_1,t_1-t_2) \tag{B.103}$$

| simply evaluate the integral

$$= -\sum_{\vec{q}_1}\left|M_{\vec{q}_1}\right|^2\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left(\frac{N^{eq}_{j_1\vec{q}_1}-f^{eq}_{n_1,\vec{k}_1-\vec{q}_1,\sigma_1}+1}{\omega-\omega_{j_1\vec{q}_1}-\frac{\epsilon_{n_1,\vec{k}_1-\vec{q}_1}}{\hbar}+i\eta}+\frac{N^{eq}_{j_1\vec{q}_1}+f^{eq}_{n_1,\vec{k}_1-\vec{q}_1,\sigma_1}}{\omega+\omega_{j_1\vec{q}_1}-\frac{\epsilon_{n_1,\vec{k}_1-\vec{q}_1}}{\hbar}+i\eta}\right) \tag{B.104}$$

B.5.2 Matsubara Treatment

We follow [Mahan2000] section 3.5. The lowest order self energy diagram (from the $T \neq 0$ Feynman diagram rules) is

$$\Sigma^{(el-ph)M}_{n,\sigma,j}(\vec{k},i\omega^F_n) = \frac{1}{\beta\hbar}\sum_{\vec{q}}\sum_{i\omega^B_m}\left|M_{\vec{q}}\right|^2 D^{(0)M}_j(\vec{q},i\omega^B_m)G^{(0)M}_{n,\sigma}(\vec{k}-\vec{q},i\omega^F_n+i\omega^B_m) \tag{B.105}$$

where a bosonic Matsubara sum must be done and where $D^{(0)M}_j$ is the a, $a^\dagger$ version and the $G^{(0)M}_{n,\sigma}$ is the c, $c^\dagger$ version. The explicit expressions for $D^{(0)M}_j$ and $G^{(0)M}_{n,\sigma}$ are,

$$D^{(0)M}_j(\vec{q},i\omega^B_m) = \frac{2\omega_{j\vec{q}}}{(i\omega^B_m)^2-\omega^2_{j\vec{q}}} \tag{B.106}$$

$$G^{(0)M}_{n,\sigma}(\vec{k}-\vec{q},i\omega^F_n-i\omega^B_m) = \frac{1}{i\omega^F_n+i\omega^B_m-\frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} \tag{B.107}$$

$$\Sigma^{(el-ph)M}_{n,\sigma,j}(\vec{k},i\omega^F_n) = \frac{1}{\beta\hbar}\sum_{\vec{q}}\sum_{i\omega^B_m}\left|M_{\vec{q}}\right|^2\frac{2\omega_{j\vec{q}}}{(i\omega^B_m)^2-\omega^2_{j\vec{q}}}\frac{1}{i\omega^F_n+i\omega^B_m-\frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} \tag{B.108}$$

$$= -\sum_{\vec{q}}\left|M_{\vec{q}}\right|^2\left(-\frac{1}{\beta\hbar}\sum_{i\omega^B_m}\frac{2\omega_{j\vec{q}}}{(i\omega^B_m)^2-\omega^2_{j\vec{q}}}\frac{1}{i\omega^F_n+i\omega^B_m-\frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}}e^{i\hbar\omega^B_m(\tau^M=0)}\right) \tag{B.109}$$

| the function before the exponential has 3 known simple poles

| terms in round brackets mark the case in section B.4.2

| and so we apply the result of the Matsubara sum

$$= -\sum_{\vec{q}}\left|M_{\vec{q}}\right|^2\sum_{i=1}^{3}\mathrm{Res}_{z=z_i}\left[\frac{2\omega_{j\vec{q}}}{z^2-\omega^2_{j\vec{q}}}\frac{1}{i\omega^F_n+z-\frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}}\right]n_B(z_i) \tag{B.110}$$

$$
\begin{aligned}
& \quad | \quad \text{we change notation from } n_B \text{ to } N^{eq} \text{ to reconcile notation} \\
= & \; -\sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 \sum_{i=1}^{3} N^{eq}(z_i) \mathrm{Res}_{z=z_i} \left[\frac{2\omega_{j\vec{q}}}{(z-\omega_{j\vec{q}})(z+\omega_{j\vec{q}})} \frac{1}{i\omega_n^F + z - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} \right]
\end{aligned}
$$

We evaluate each of the 3 residues.

$$
\begin{aligned}
\text{Residue at } z_i = \omega_{j\vec{q}} &= N^{eq}(\omega_{j\vec{q}}) \mathrm{Res}_{z=\omega_{j\vec{q}}} \frac{2\omega_{j\vec{q}}}{\omega_{j\vec{q}} + \omega_{j\vec{q}}} \frac{1}{i\omega_n^F + \omega_{j\vec{q}} - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} && \text{(B.111)} \\
&= \frac{N^{eq}_{j\vec{q}}}{i\omega_n^F + \omega_{j\vec{q}} - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} && \text{(B.112)}
\end{aligned}
$$

$$
\begin{aligned}
\text{Residue at } z_i = -\omega_{j\vec{q}} &= N^{eq}(-\omega_{j\vec{q}}) \mathrm{Res}_{z=-\omega_{j\vec{q}}} \frac{2\omega_{j\vec{q}}}{-\omega_{j\vec{q}} - \omega_{j\vec{q}}} \frac{1}{i\omega_n^F - \omega_{j\vec{q}} - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} && \text{(B.113)} \\
& \quad | \quad \text{note that } N^{eq}(-\omega_{j\vec{q}}) = -(N^{eq}(\omega_{j\vec{q}}) + 1) \\
&= \frac{N^{eq}_{j\vec{q}} + 1}{i\omega_n^F - \omega_{j\vec{q}} - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} && \text{(B.114)}
\end{aligned}
$$

$$
\begin{aligned}
& \text{Residue at } z_i = \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar} - i\omega_n^F \\
= & \; N^{eq}\left(\frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar} - i\omega_n^F\right) \mathrm{Res}_{z=\frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar} - i\omega_n^F} \frac{2\omega_{j\vec{q}}}{\left(\frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar} - i\omega_n^F\right)^2 - \omega_{j\vec{q}}^2} && \text{(B.115)} \\
| & \quad \text{note that } N^{eq}\left(\frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar} - i\omega_n^F\right) = \left(e^{\beta\hbar\left(\frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar} - i\omega_n^F\right)} - 1\right)^{-1} = -\left(e^{\beta\epsilon_{n,\vec{k}-\vec{q}}} + 1\right)^{-1} = -f^{eq}_{n,\vec{k}-\vec{q}} \\
| & \quad \text{where we used } e^{-\beta\hbar i\omega_n^F} = -1 = e^{\beta\hbar i\omega_n^F} \\
= & \; \frac{-2\omega_{j\vec{q}} f^{eq}_{n,\vec{k}-\vec{q}}}{\left(i\omega_n^F - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}\right)^2 - \omega_{j\vec{q}}^2} && \text{(B.116)} \\
| & \quad \text{we write it into partial fractions} \\
= & \; \frac{f^{eq}_{n,\vec{k}-\vec{q}}}{i\omega_n^F - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar} + \omega_{\vec{q}}} - \frac{f^{eq}_{n,\vec{k}-\vec{q}}}{i\omega_n^F - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar} - \omega_{j\vec{q}}} && \text{(B.117)}
\end{aligned}
$$

So, the final expression of the equilibrium electron-phonon self energy in (fermionic) Matsubara frequency is

$$
\Sigma^{(el-ph)M}_{n,\sigma,j}(\vec{k}, i\omega_n^F) = -\sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 \left(\frac{N^{eq}_{j\vec{q}} + 1 - f^{eq}_{n,\vec{k}-\vec{q}}}{i\omega_n^F - \omega_{\vec{q}} - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} + \frac{N^{eq}_{j\vec{q}} + f^{eq}_{n,\vec{k}-\vec{q}}}{i\omega_n^F + \omega_{j\vec{q}} - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} \right) \quad \text{(B.118)}
$$

We carry out analytical continuation to real frequencies so that we get the physical retarded self energy.

$$
\begin{aligned}
i\omega_n^F & \overset{\text{retarded}}{\longrightarrow} \omega + i\eta && \text{(B.119)} \\
\Sigma^{(el-ph)R}_{n,\sigma,j}(\vec{k}, \omega) &= -\sum_{\vec{q}} \left|M_{\vec{q}}\right|^2 \left(\frac{N^{eq}_{j\vec{q}} + 1 - f^{eq}_{n,\vec{k}-\vec{q}}}{\omega + i\eta - \omega_{j\vec{q}} - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} + \frac{N^{eq}_{j\vec{q}} + f^{eq}_{n,\vec{k}-\vec{q}}}{\omega + i\eta + \omega_{j\vec{q}} - \frac{\epsilon_{n,\vec{k}-\vec{q}}}{\hbar}} \right) && \text{(B.120)}
\end{aligned}
$$

The discrepancy of the prefactor with the NEGF treatment, is due to the fact that different non-interacting phonon Green's functions are used. The 2 non-interacting phonon Green's function differ by that prefactor, i.e. $Q_{j\vec{q}} = \sqrt{\frac{\hbar}{2\omega_{j\vec{q}}}}\left(a^\dagger_{j,-\vec{q}} + a_{j\vec{q}}\right)$.

Lastly, in some literature, people compare Matsubara Field theory and NEGF which by now should be obvious that Matsubara Field theory is within NEGF. For a time dependent Hamiltonian only NEGF works. For a time independent Hamiltonian we can use the tricks of NEGF (as shown here) to allow us to circumvent Matsubara frequencies and Matsubara sums (analytic continuation is the easy part actually).

Appendix C

Collection of Non-Interacting ("Free") Green's functions

We supply these expressions because they are the most common building blocks in perturbation theory. Here, we provide both electron and phonon Green's functions expressions in both the time domain and in the frequency domain. The time domain expressions are useful in non-steady state theories and the frequency domain expressions are useful in steady state considerations.

C.1 Electron Green's Functions

C.1.1 In Time Domain

The Hamiltonian in momentum variables is

$$H_0 = \sum_{n\vec{k}\sigma} \epsilon_{n\vec{k}} c^{\dagger}_{n\vec{k}\sigma} c_{n\vec{k}\sigma} \tag{C.1}$$

where n is the band index, $\vec{k}$ is the momentum index, and σ is the spin index.

The Heisenberg equation of motion is solved directly. (t_0 is an initial time, and the label on field operator c is really redundant)

$$c_{n\vec{k}\sigma H_0}(t) = e^{\frac{i}{\hbar}H_0(t-t_0} c_{n\vec{k}\sigma}(t_0) e^{-\frac{i}{\hbar}H_0(t-t_0)} \tag{C.2}$$

$$\begin{aligned}
\frac{d}{dt} c_{n_1\vec{k}_1\sigma_1 H_0}(t) &= e^{\frac{i}{\hbar}H_0(t-t_0)} \frac{i}{\hbar} \left[H_0, c_{n_1\vec{k}_1\sigma_1}(t_0) \right]_- e^{-\frac{i}{\hbar}H_0(t-t_0)} && \text{(C.3)} \\
&= e^{\frac{i}{\hbar}H_0(t-t_0)} \frac{i}{\hbar} \left[\sum_{n\vec{k}\sigma} \epsilon_{n\vec{k}} c^{\dagger}_{n\vec{k}\sigma} c_{n\vec{k}\sigma}, c_{n_1\vec{k}_1\sigma_1}(t_0) \right]_- e^{-\frac{i}{\hbar}H_0(t-t_0)} && \text{(C.4)} \\
& \mid \quad \text{use identity to change to anticommutators, } [A, CD]_- = [C, A]_+ D - C[D, A]_+ \\
& \mid \quad \text{and recall the canonical relation } [c_{n_1\vec{k}_1\sigma_1}, c^{\dagger}_{n_2\vec{k}_2\sigma_2}]_+ = \delta_{n_1 n_2} \delta_{\vec{k}_1\vec{k}_2} \delta_{\sigma_1\sigma_2} \\
&= -\frac{i}{\hbar} \epsilon_{n_1\vec{k}_1} c_{n_1\vec{k}_1\sigma_1 H_0}(t) && \text{(C.5)}
\end{aligned}$$

This is immediately integrated to get

$$c_{n_1\vec{k}_1\sigma_1 H_0}(t) = e^{-\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1}(t-t_0)} c_{n_1\vec{k}_1\sigma_1}(t_0) \tag{C.6}$$

Take the Hermitian conjugate and we get

$$c^{\dagger}_{n_1\vec{k}_1\sigma_1 H_0}(t) = e^{\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1}(t-t_0)} c^{\dagger}_{n_1\vec{k}_1\sigma_1}(t_0) \tag{C.7}$$

We define the statistical average to be

$$\langle A_{H_0}(t)\rangle = \frac{\mathrm{Tr}\left(e^{-\beta H_0} A_{H_0}(t)\right)}{\mathrm{Tr} e^{-\beta H_0}} \tag{C.8}$$

and now we can define and solve the Green's function directly using the solution of the equations of motion.

We start with the time-ordered Green's function

$$\begin{aligned}
& G^{(0)t}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t-t') \\
= \;& -\frac{i}{\hbar}\left[\theta(t-t')\left\langle c_{n_1\vec{k}_1\sigma_1 H_0}(t) c^{\dagger}_{n_2\vec{k}_2\sigma_2 H_0}(t')\right\rangle - \theta(t'-t)\left\langle c^{\dagger}_{n_2\vec{k}_2\sigma_2 H_0}(t') c_{n_1\vec{k}_1\sigma_1 H_0}(t)\right\rangle\right] && \text{(C.9)} \\
| \;& \text{simply use the solutions} \\
= \;& -\frac{i}{\hbar}\left[\theta(t-t')\left\langle c_{n_1\vec{k}_1\sigma_1}(t_0) c^{\dagger}_{n_2\vec{k}_2\sigma_2}(t_0)\right\rangle e^{-\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1} t} e^{\frac{i}{\hbar}\epsilon_{n_2\vec{k}_2} t'}\right. \\
& \left. -\theta(t'-t)\left\langle c^{\dagger}_{n_2\vec{k}_2\sigma_2}(t_0) c_{n_1\vec{k}_1\sigma_1}(t_0)\right\rangle e^{-\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1} t} e^{\frac{i}{\hbar}\epsilon_{n_2\vec{k}_2} t'}\right] && \text{(C.10)} \\
| \;& \text{Note that } \left\langle c^{\dagger}_{n_2\vec{k}_2\sigma_2} c_{n_1\vec{k}_1\sigma_1}\right\rangle = \langle n_{n_1\vec{k}_1\sigma_1}\rangle \delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \equiv f^{eq}_{n_1\vec{k}_1\sigma_1}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \\
| \;& \text{where } f^{eq} \text{ is the Fermi-Dirac distribution} \\
| \;& \text{use equal time anticommutation relations to get } \left\langle c_{n_1\vec{k}_1\sigma_1} c^{\dagger}_{n_2\vec{k}_2\sigma_2}\right\rangle = \left(1 - f^{eq}_{n_1\vec{k}_1\sigma_1}\right)\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \\
= \;& -\frac{i}{\hbar}\left(\theta(t-t')\left(1 - f^{eq}_{n_1\vec{k}_1\sigma_1}\right) - \theta(t'-t) f^{eq}_{n_1\vec{k}_1\sigma_1}\right) e^{-\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1}(t-t')}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} && \text{(C.11)}
\end{aligned}$$

The imaginary time Green's function (note that my definition is slightly different from the usual literature), which is found by setting $t_1 = t_0 - i\hbar\tau_1^M$ and $t_2 = t_0 - i\hbar\tau_2^M$.

$$\begin{aligned}
& G^{(0)M}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(\tau_1^M - \tau_2^M) \\
= \;& G^{(0)T}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t_1 - t_2 = -i\hbar(\tau_1^M - \tau_2^M)) && \text{(C.12)} \\
= \;& -\frac{i}{\hbar}\left(\theta(-i\hbar(\tau_1^M - \tau_2^M))\left(1 - f^{eq}_{n_1\vec{k}_1\sigma_1}\right) - \theta(-i\hbar(\tau_2^M - \tau_1^M)) f^{eq}_{n_1\vec{k}_1\sigma_1}\right) e^{-\epsilon_{n_1\vec{k}_1}(\tau_1^M - \tau_2^M)}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} && \text{(C.13)}
\end{aligned}$$

The next Green's function to calculate is the lesser Green's function.

$$\begin{aligned}
G^{(0)<}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t-t') &= +\frac{i}{\hbar}\left\langle c^{\dagger}_{n_2\vec{k}_2\sigma_2}(t') c_{n_1\vec{k}_1\sigma_1}(t)\right\rangle && \text{(C.14)} \\
&= +\frac{i}{\hbar} f^{eq}_{n_1\vec{k}_1\sigma_1} e^{-\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1}(t-t')}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} && \text{(C.15)}
\end{aligned}$$

Greater Green's function

$$\begin{aligned}
G^{(0)>}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t-t') &= -\frac{i}{\hbar}\left\langle c_{n_1\vec{k}_1\sigma_1}(t) c^{\dagger}_{n_2\vec{k}_2\sigma_2}(t')\right\rangle && \text{(C.16)} \\
&= -\frac{i}{\hbar}\left(1 - f^{eq}_{n_1\vec{k}_1\sigma_1}\right) e^{-\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1}(t-t')}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} && \text{(C.17)}
\end{aligned}$$

Retarded Green's function

$$G^{(0)R}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t-t') = \theta(t-t')\left(G^{(0)>}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t-t') - G^{(0)<}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t-t')\right) \tag{C.18}$$

$$= -\frac{i}{\hbar}\theta(t-t')e^{-\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1}(t-t')}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \tag{C.19}$$

Advanced Green's function

$$G^{(0)A}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t-t') = \theta(t'-t)\left(G^{(0)<}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t-t') - G^{(0)>}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t-t')\right) \tag{C.20}$$

$$= \frac{i}{\hbar}\theta(t'-t)e^{-\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1}(t-t')}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \tag{C.21}$$

The (real space) field operator version of the Green's functions can be built up based on these momentum Green's functions. Simply use the (second-quantization) relation between the variables.

$$\psi_{H\sigma_1}(\vec{r}_1 t_1) = \frac{1}{\sqrt{V}}\sum_{n_1\vec{k}_1}\mathcal{U}_{n_1\vec{k}_1}(\vec{r}_1)e^{i\vec{k}_1\cdot\vec{r}_1}c_{Hn_1\vec{k}_1\sigma_1}(t_1) \tag{C.22}$$

where $\mathcal{U}$ is the Bloch function. One can also take the plane-wave approximation (simply let the Bloch function be 1).

$$\psi_{H\sigma_1}(\vec{r}_1 t_1) = \frac{1}{\sqrt{V}}\sum_{n_1\vec{k}_1}e^{i\vec{k}_1\cdot\vec{r}_1}c_{Hn_1\vec{k}_1\sigma_1}(t_1) \tag{C.23}$$

Take the Hermitian conjuate of the relations to get the corresponding relations of the conjugate variables.

C.1.2 In Frequency Domain

The Fourier transform is defined as

$$G(\omega) = \int_{-\infty}^{\infty} d(t-t')e^{i\omega(t-t')}G(t-t') \tag{C.24}$$

First we calculate the time-ordered Green's function.

$$G^{(0)t}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(\omega)$$

$$= \int_{-\infty}^{\infty} d(t-t')e^{i\omega(t-t')}G^{(0)t}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t-t') \tag{C.25}$$

| use the integral representation of the step function, $\theta(t) = \frac{i}{2\pi}\int d\omega' \frac{e^{-i\omega' t}}{\omega' + i\eta}$

$$= -\frac{i}{\hbar}\left(\int_0^{\infty} d(t-t')e^{i\left(\omega - \frac{\epsilon_{n_1\vec{k}_1}}{\hbar} + i\eta\right)(t-t')}\left(1 - f^{eq}_{n_1\vec{k}_1\sigma_1}\right)\right.$$

$$\left. - \int_{-\infty}^{0} d(t-t')e^{i\left(\omega - \frac{\epsilon_{n_1\vec{k}_1}}{\hbar} - i\eta\right)(t-t')}f^{eq}_{n_1\vec{k}_1\sigma_1}\right)\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \tag{C.26}$$

| taking $\eta \to 0$ at the end of the frequency calculation is implicit

| simply carry out the integrals

$$= -\frac{i}{\hbar}\left(-\frac{1-f^{eq}_{n_1\vec{k}_1\sigma_1}}{\omega-\frac{\epsilon_{n_1\vec{k}_1}}{\hbar}+i\eta}-\frac{f^{eq}_{n_1\vec{k}_1\sigma_1}}{\omega-\frac{\epsilon_{n_1\vec{k}_1}}{\hbar}-i\eta}\right)\delta_{n_1n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \tag{C.27}$$

Second is the (fermionic) Matsubara frequency Green's function. Note that Matsubara frequency index n and electronic band index n_1 are unrelated.

$$G^{(0)M}_{n_1\vec{k}_1\sigma_1n_2\vec{k}_2\sigma_2}(i\omega^F_n)$$

$$= \int_0^\beta d\tau^M e^{i\hbar\omega^F_n\tau^M}G^{(0)M}_{n_1\vec{k}_1\sigma_1n_2\vec{k}_2\sigma_2}(\tau^M_1-\tau^M_2=\tau^M) \tag{C.28}$$

$$= -\frac{i}{\hbar}\int_0^\beta d\tau^M e^{(i\hbar\omega^F_n-\epsilon_{n_1\vec{k}_1})\tau^M}\left(\theta(-i\hbar\tau^M)\left(1-f^{eq}_{n_1\vec{k}_1\sigma_1}\right)-\theta(i\hbar\tau^M)f^{eq}_{n_1\vec{k}_1\sigma_1}\right)\delta_{n_1n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2}$$

| the second step function is actually made of $\tau^M_2-\tau^M_1=-\tau^M$ and so

| note that $\int_0^\beta d\tau^M\theta(-\tau^M)=0$

$$= -\frac{i}{\hbar}\frac{1-f^{eq}_{n_1\vec{k}_1\sigma_1}}{i\hbar\omega^F_n-\epsilon_{n_1\vec{k}_1}}\left[e^{(i\hbar\omega^F_n-\epsilon_{n_1\vec{k}_1})\tau^M}\right]_0^\beta \tag{C.29}$$

| use $e^{i\hbar\omega^F_n\beta}=-1$

$$= -\frac{i}{\hbar}\frac{1-f^{eq}_{n_1\vec{k}_1\sigma_1}}{i\hbar\omega^F_n-\epsilon_{n_1\vec{k}_1}}\left(-e^{-\beta\epsilon_{n_1\vec{k}_1}}-1\right) \tag{C.30}$$

| use the explicit form of f^{eq}

$$= \frac{i}{\hbar}\frac{\left(1-\left(e^{\beta\epsilon_{n_1\vec{k}_1}}+1\right)^{-1}\right)\left(e^{-\beta\epsilon_{n_1\vec{k}_1}}+1\right)}{i\hbar\omega^F_n-\epsilon_{n_1\vec{k}_1}} \tag{C.31}$$

$$= \frac{i}{\hbar}\frac{1}{i\hbar\omega^F_n-\epsilon_{n_1\vec{k}_1}} \tag{C.32}$$

Next is the lesser Green's function.

$$G^{(0)<}_{n_1\vec{k}_1\sigma_1n_2\vec{k}_2\sigma_2}(\omega) = \int_{-\infty}^{\infty}d(t_1-t_2)e^{i\omega(t_1-t_2)}G^{(0)<}_{n_1\vec{k}_1\sigma_1n_2\vec{k}_2\sigma_2}(t_1-t_2) \tag{C.33}$$

$$= \frac{i}{\hbar}f^{eq}_{n_1\vec{k}_1\sigma_1}\delta_{n_1n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2}\int_{-\infty}^{\infty}d(t_1-t_2)e^{i\left(\omega-\frac{\epsilon_{n_1\vec{k}_1}}{\hbar}\right)(t_1-t_2)} \tag{C.34}$$

| use the representation $\frac{1}{2\pi}\int dte^{i\omega t}=\delta(\omega)$

$$= \frac{i}{\hbar}f^{eq}_{n_1\vec{k}_1\sigma_1}2\pi\delta\left(\omega-\frac{\epsilon_{n_1\vec{k}_1}}{\hbar}\right)\delta_{n_1n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \tag{C.35}$$

The greater Green's function.

$$G^{(0)>}_{n_1\vec{k}_1\sigma_1n_2\vec{k}_2\sigma_2}(\omega) = -\frac{i}{\hbar}\left(1-f^{eq}_{n_1\vec{k}_1\sigma_1}\right)2\pi\delta\left(\omega-\frac{\epsilon_{n_1\vec{k}_1}}{\hbar}\right)\delta_{n_1n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \tag{C.36}$$

The retarded Green's function.

$$G^{(0)R}_{n_1\vec{k}_1\sigma_1n_2\vec{k}_2\sigma_2}(\omega) = \int_{-\infty}^{\infty}d(t_1-t_2)e^{i\omega(t_1-t_2)}G^{(0)R}_{n_1\vec{k}_1\sigma_1n_2\vec{k}_2\sigma_2}(t_1-t_2) \tag{C.37}$$

$$\begin{aligned}
&\quad | \quad \text{use the step function integral representation } \theta(t) = \frac{i}{2\pi}\int d\omega \frac{e^{-i\omega t}}{\omega + i\eta} \\
&= -\frac{i}{\hbar}\int_{-\infty}^{\infty} d(t_1 - t_2)\frac{i}{2\pi}\int d\omega' \frac{1}{\omega' + i\eta} e^{i\left(\omega - \omega' - \frac{\epsilon_{n_1\vec{k}_1}}{\hbar}\right)(t_1 - t_2)} \delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \quad (C.38) \\
&\quad | \quad \text{use the delta representation to get } \delta\left(\omega - \omega' - \frac{\epsilon_{n_1\vec{k}_1}}{\hbar}\right) \text{ and evaluate } \int d\omega' \\
&= \frac{1}{\hbar}\frac{1}{\omega - \frac{\epsilon_{n_1\vec{k}_1}}{\hbar} + i\eta}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \quad (C.39)
\end{aligned}$$

The advanced Green’s function.

$$G^{(0)A}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(\omega) = \frac{1}{\hbar}\frac{1}{\omega - \frac{\epsilon_{n_1\vec{k}_1}}{\hbar} - i\eta}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \quad (C.40)$$

and indeed $-i\hbar G^M(i\omega_n^F \to \omega + i\eta) = G^R(\omega)$ and $-i\hbar G^M(i\omega_n^F \to \omega - i\eta) = G^A(\omega)$.

C.2 Electron Spectral Functions

C.2.1 In Time Domain

$$\begin{aligned}
A^{(0)}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t_1 - t_2) &\equiv i\left(G^{(0)R}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t_1 - t_2) - G^{(0)A}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(t_1 - t_2)\right) \quad (C.41) \\
&= \frac{1}{\hbar}\left(\theta(t_1 - t_2) + \theta(t_2 - t_1)\right) e^{-\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1}(t_1 - t_2)}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \quad (C.42) \\
&= \frac{1}{\hbar}e^{-\frac{i}{\hbar}\epsilon_{n_1\vec{k}_1}(t_1 - t_2)}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \quad (C.43)
\end{aligned}$$

C.2.2 In Frequency Domain

$$\begin{aligned}
A^{(0)}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(\omega) &\equiv i\left(G^{(0)R}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(\omega) - G^{(0)A}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(\omega)\right) \quad (C.44) \\
&= \frac{i}{\hbar}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2}\left(\frac{1}{\omega - \frac{\epsilon_{n_1\vec{k}_1}}{\hbar} + i\eta} - \frac{1}{\omega - \frac{\epsilon_{n_1\vec{k}_1}}{\hbar} - i\eta}\right) \quad (C.45) \\
&\quad | \quad \text{use identity } \frac{1}{x + i\epsilon} = \mathcal{P}\left(\frac{1}{x}\right) - i\pi\delta(x) \\
&= \frac{i}{\hbar}\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2}\left(-i2\pi\delta\left(\omega - \frac{\epsilon_{n_1\vec{k}_1}}{\hbar}\right)\right) \quad (C.46)
\end{aligned}$$

We can double check with the other relation.

$$\begin{aligned}
A^{(0)}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(\omega) &\equiv i\left(G^{(0)>}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(\omega) - G^{(0)<}_{n_1\vec{k}_1\sigma_1 n_2\vec{k}_2\sigma_2}(\omega)\right) \quad (C.47) \\
&= \frac{1}{\hbar}2\pi\delta\left(\omega - \frac{\epsilon_{n_1\vec{k}_1}}{\hbar}\right)\delta_{n_1 n_2}\delta_{\vec{k}_1\vec{k}_2}\delta_{\sigma_1\sigma_2} \quad (C.48)
\end{aligned}$$

C.3 Phonon Green's Functions

There are 3 types of phonon variables: a and $a^\dagger$, Q, and u and they are related as will be shown later. All time domain and frequency domain expressions will be calculated.

C.3.1 In Time Domain

C.3.1.1 "a, $a^\dagger$" operators

Now we calculate the Green's functions for non-interacting (free) phonons. Again the equation of motion can be solved exactly which enables the exact form to written. We start with the a, $a^\dagger$ Green's functions and build up the Q, Q Green's functions and u, u Green's functions.

The Hamiltonian is

$$H_0 = \sum_{j\vec{q}} \hbar\omega_{j\vec{q}} \left(a^\dagger_{j\vec{q}}\, a_{j\vec{q}} + \frac{1}{2} \right) \tag{C.49}$$

We solve the Heisenberg's equations of motion directly. (Again the argument t_0 is redundant.)

$$a_{H_0 j_1\vec{q}_1}(t) = e^{\frac{i}{\hbar}H_0(t-t_0)} a_{j_1\vec{q}_1}(t_0) e^{-\frac{i}{\hbar}H_0(t-t_0)} \tag{C.50}$$

$$\begin{aligned}
\frac{d}{dt} a_{H_0 j_1\vec{q}_1}(t) &= e^{\frac{i}{\hbar}H_0(t-t_0)} \frac{i}{\hbar} \left[H_0, a_{j_1\vec{q}_1}(t_0) \right]_- e^{-\frac{i}{\hbar}H_0(t-t_0)} && \text{(C.51)} \\
&\mid \quad \text{use canonical commutator } [a, a^\dagger]_- = \mathbb{I} \\
&= -i\omega_{j_1\vec{q}_1} a_{H_0 j_1\vec{q}_1}(t) && \text{(C.52)}
\end{aligned}$$

We immediately integrate to get,

$$a_{H_0 j_1\vec{q}_1}(t) = e^{-i\omega_{j_1\vec{q}_1}(t-t_0)} a_{j_1\vec{q}_1}(t_0) \tag{C.53}$$

Taking Hermitian conjugate gives

$$a^\dagger_{H_0 j_1\vec{q}_1}(t) = e^{i\omega_{j_1\vec{q}_1}(t-t_0)} a^\dagger_{j_1\vec{q}_1}(t_0) \tag{C.54}$$

Now we can define and calculate the Green's functions in time domain.

The time ordered Green's function,

$$\begin{aligned}
D^{(0)t}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2) &= -\frac{i}{\hbar} \left\langle T \left(a_{H_0 j_1\vec{q}_1}(t_1) a^\dagger_{H_0 j_2\vec{q}_2}(t_2) \right) \right\rangle && \text{(C.55)} \\
&= -\frac{i}{\hbar} \left(\theta(t_1 - t_2) \left\langle a_{H_0 j_1\vec{q}_1}(t_1) a^\dagger_{H_0 j_2\vec{q}_2}(t_2) \right\rangle + \theta(t_2 - t_1) \left\langle a^\dagger_{H_0 j_2\vec{q}_2}(t_2) a_{H_0 j_1\vec{q}_1}(t_1) \right\rangle \right) \\
&\mid \quad \text{use the solutions} \\
&= -\frac{i}{\hbar} \left(\theta(t_1 - t_2) \left\langle a_{j_1\vec{q}_1}(t_0) a^\dagger_{j_2\vec{q}_2}(t_0) \right\rangle e^{-i\omega_{j_1\vec{q}_1}(t_1-t_0)} e^{i\omega_{j_2\vec{q}_2}(t_2-t_0)} \right. \\
&\quad \left. + \theta(t_2 - t_1) \left\langle a^\dagger_{j_2\vec{q}_2}(t_0) a_{j_1\vec{q}_1}(t_0) \right\rangle e^{-i\omega_{j_1\vec{q}_1}(t_1-t_0)} e^{i\omega_{j_2\vec{q}_2}(t_2-t_0)} \right) && \text{(C.56)} \\
&\mid \quad \text{use } \langle a^\dagger_{j_2\vec{q}_2} a_{j_1\vec{q}_1} \rangle = \langle n_{j_1\vec{q}_1} \rangle \delta_{j_1 j_2} \delta_{\vec{q}_1\vec{q}_2} \equiv N^{eq}_{j_1\vec{q}_1} \delta_{j_1 j_2} \delta_{\vec{q}_1\vec{q}_2} \\
&\mid \quad \text{and use } [a, a^\dagger]_- = \mathbb{I} \\
&= -\frac{i}{\hbar} \left(\theta(t_1 - t_2) \left(1 + N^{eq}_{j_1\vec{q}_1} \right) + \theta(t_2 - t_1) N^{eq}_{j_1\vec{q}_1} \right) e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)} \delta_{j_1 j_2} \delta_{\vec{q}_1\vec{q}_2} && \text{(C.57)}
\end{aligned}$$

The imaginary time Green's function (with $t_1 = t_0 - i\hbar\tau_1^M$ and $t_2 = t_0 - i\hbar\tau_2^M$)

$$\begin{aligned} & D^{(0)M}_{j_1\vec{q}_1 j_2\vec{q}_2}(\tau_1^M - \tau_2^M) \\ = \;& D^{(0)t}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2 = -i\hbar(\tau_1^M - \tau_2^M)) && \text{(C.58)} \\ = \;& -\frac{i}{\hbar}\left(\theta(-i\hbar(\tau_1^M - \tau_2^M))\left(1 + N^{eq}_{j_1\vec{q}_1}\right) + \theta(-i\hbar(\tau_2^M - \tau_1^M))N^{eq}_{j_1\vec{q}_1}\right) e^{-\hbar\omega_{j_1\vec{q}_1}(\tau_1^M - \tau_2^M)}\delta_{j_1 j_2}\delta_{\vec{q}_1\vec{q}_2} && \text{(C.59)} \end{aligned}$$

The lesser Green's function

$$\begin{aligned} D^{(0)<}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2) &= -\frac{i}{\hbar}\left\langle a^\dagger_{H_0 j_2\vec{q}_2}(t_2) a_{H_0 j_1\vec{q}_1}(t_1)\right\rangle && \text{(C.60)} \\ & \quad | \quad \text{read off from } D^{(0)T} \\ &= -\frac{i}{\hbar}N^{eq}_{j_1\vec{q}_1} e^{-i\omega_{j_1\vec{q}_1}(t_1 - t_2)}\delta_{j_1 j_2}\delta_{\vec{q}_1\vec{q}_2} && \text{(C.61)} \end{aligned}$$

The greater Green's function

$$\begin{aligned} D^{(0)>}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2) &= -\frac{i}{\hbar}\left\langle a_{H_0 j_1\vec{q}_1}(t_1) a^\dagger_{H_0 j_2\vec{q}_2}(t_2)\right\rangle && \text{(C.62)} \\ & \quad | \quad \text{read off from } D^{(0)T} \\ &= -\frac{i}{\hbar}\left(1 + N^{eq}_{j_1\vec{q}_1}\right) e^{-i\omega_{j_1\vec{q}_1}(t_1 - t_2)}\delta_{j_1 j_2}\delta_{\vec{q}_1\vec{q}_2} && \text{(C.63)} \end{aligned}$$

The retarded Green's function

$$\begin{aligned} D^{(0)R}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2) &= \theta(t_1 - t_2)\left(D^{(0)>}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2) - D^{(0)<}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2)\right) && \text{(C.64)} \\ &= -\frac{i}{\hbar}\theta(t_1 - t_2) e^{-i\omega_{j_1\vec{q}_1}(t_1 - t_2)}\delta_{j_1 j_2}\delta_{\vec{q}_1\vec{q}_2} && \text{(C.65)} \end{aligned}$$

The advanced Green's function

$$\begin{aligned} D^{(0)A}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2) &= \theta(t_2 - t_1)\left(D^{(0)<}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2) - D^{(0)>}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2)\right) && \text{(C.66)} \\ &= \frac{i}{\hbar}\theta(t_2 - t_1) e^{-i\omega_{j_1\vec{q}_1}(t_1 - t_2)}\delta_{j_1 j_2}\delta_{\vec{q}_1\vec{q}_2} && \text{(C.67)} \end{aligned}$$

C.3.1.2 "Q, Q" operators

The relationship between the 2 operators is

$$Q_{j\vec{q}} = \sqrt{\frac{\hbar}{2\omega_{j\vec{q}}}}\left(a^\dagger_{j,-\vec{q}} + a_{j\vec{q}}\right) \quad \text{(C.68)}$$

and we will simply construct "QQ" Green's functions from "$aa^\dagger$" ones. The first one is the time ordered Green's function

$$\begin{aligned} & D^{(0)t}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1 - t_2) \\ = \;& -\frac{i}{\hbar}\left\langle T\left(Q_{H_0 j_1\vec{q}_1}(t_1) Q_{H_0 j_2\vec{q}_2}(t_2)\right)\right\rangle && \text{(C.69)} \\ = \;& -\frac{i}{\hbar}\left(\theta(t_1 - t_2)\left\langle Q_{H_0 j_1\vec{q}_1}(t_1) Q_{H_0 j_2\vec{q}_2}(t_2)\right\rangle + \theta(t_2 - t_1)\left\langle Q_{H_0 j_2\vec{q}_2}(t_2) Q_{H_0 j_1\vec{q}_1}(t_1)\right\rangle\right) && \text{(C.70)} \end{aligned}$$

$$
\begin{aligned}
&= -\frac{i}{\hbar}\frac{\hbar}{2\sqrt{\omega_{j_1\vec{q}_1}\omega_{j_2\vec{q}_2}}}\left(\theta(t_1-t_2)\left(\left\langle a_{H0j_1\vec{q}_1}(t_1)a^\dagger_{H0j_2,-\vec{q}_2}(t_2)\right\rangle + \left\langle a^\dagger_{H0j_1,-\vec{q}_1}(t_1)a_{H0j_2\vec{q}_2}(t_2)\right\rangle\right)\right.\\
&\quad \left.+\theta(t_2-t_1)\left(\left\langle a_{H0j_2\vec{q}_2}(t_2)a^\dagger_{H0j_1,-\vec{q}_1}(t_1)\right\rangle + \left\langle a^\dagger_{H0j_2,-\vec{q}_2}(t_2)a_{H0j_1\vec{q}_1}(t_1)\right\rangle\right)\right) \qquad \text{(C.71)}\\
&\quad | \quad \text{with terms } \langle aa\rangle = 0 = \langle a^\dagger a^\dagger\rangle\\
&\quad | \quad \text{use the solutions and the canonical commutator}\\
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left(\theta(t_1-t_2)\left(\left(N^{eq}_{j_1\vec{q}_2}+1\right)e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)} + N^{eq}_{j_1\vec{q}_1}e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right)\right.\\
&\quad \left.+\theta(t_2-t_1)\left(\left(N^{eq}_{j_1\vec{q}_1}+1\right)e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)} + N^{eq}_{j_1\vec{q}_1}e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right)\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \qquad \text{(C.72)}
\end{aligned}
$$

The imaginary time Green's function (with $t_1-t_2=-i\hbar(\tau_1^M-\tau_2^M)$)

$$
\begin{aligned}
&D^{(0)M}_{j_1\vec{q}_1j_2\vec{q}_2}(\tau_1^M-\tau_2^M)\\
&= D^{(0)t}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2=-i\hbar(\tau_1^M-\tau_2^M)) \qquad \text{(C.73)}\\
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left(\theta(-i\hbar(\tau_1^M-\tau_2^M))\left(\left(N^{eq}_{j_1\vec{q}_2}+1\right)e^{-\hbar\omega_{j_1\vec{q}_1}(\tau_1^M-\tau_2^M)} + N^{eq}_{j_1\vec{q}_1}e^{\hbar\omega_{j_1\vec{q}_1}(\tau_1^M-\tau_2^M)}\right)\right.\\
&\quad \left.+\theta(-i\hbar(\tau_2^M-\tau_1^M))\left(\left(N^{eq}_{j_1\vec{q}_1}+1\right)e^{\hbar\omega_{j_1\vec{q}_1}(\tau_1^M-\tau_2^M)} + N^{eq}_{j_1\vec{q}_1}e^{-\hbar\omega_{j_1\vec{q}_1}(\tau_1^M-\tau_2^M)}\right)\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2}\\
&\qquad \text{(C.74)}
\end{aligned}
$$

The lesser Green's function

$$
\begin{aligned}
D^{(0)<}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) &= -\frac{i}{\hbar}\left\langle Q_{H0j_2\vec{q}_2}(t_2)Q_{H0j_1\vec{q}_1}(t_1)\right\rangle \qquad \text{(C.75)}\\
&\quad | \quad \text{read off from } D^{(0)t}\\
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left(\left(N^{eq}_{j_1\vec{q}_1}+1\right)e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)} + N^{eq}_{j_1\vec{q}_1}e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2}\\
&\qquad \text{(C.76)}
\end{aligned}
$$

The greater Green's function

$$
\begin{aligned}
D^{(0)>}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) &= -\frac{i}{\hbar}\left\langle Q_{H0j_1\vec{q}_1}(t_1)Q_{H0j_2\vec{q}_2}(t_2)\right\rangle \qquad \text{(C.77)}\\
&\quad | \quad \text{read off from } D^{(0)t}\\
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left(\left(N^{eq}_{j_1\vec{q}_1}+1\right)e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)} + N^{eq}_{j_1\vec{q}_1}e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2}\\
&\qquad \text{(C.78)}
\end{aligned}
$$

The retarded Green's function

$$
\begin{aligned}
D^{(0)R}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) &= \theta(t_1-t_2)\left(D^{(0)>}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) - D^{(0)<}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2)\right) \qquad \text{(C.79)}\\
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\theta(t_1-t_2)\left(e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)} - e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \qquad \text{(C.80)}
\end{aligned}
$$

The advanced Green's function

$$
D^{(0)A}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) = \theta(t_2-t_1)\left(D^{(0)<}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) - D^{(0)>}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2)\right) \qquad \text{(C.81)}
$$

$$= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\theta(t_2-t_1)\left(e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)} - e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \tag{C.82}$$

C.3.1.3 "u, u" operators

The relationship between u and Q variables is

$$\begin{aligned} u_{l_1k_1\alpha_1} &= \frac{1}{\sqrt{Nm_k}}\sum_{j_1\vec{q}_1}\epsilon_{k_1\alpha_1}(j_1\vec{q}_1)e^{i\vec{q}_1\cdot l_1}Q_{j_1\vec{q}_1} && \text{(C.83)}\\ &\quad\mid\ \text{we define the shorthand } R^{j_1\vec{q}_1}_{l_1k_1\alpha_1}\\ &= \sum_{j_1\vec{q}_1}R^{j_1\vec{q}_1}_{l_1k_1\alpha_1}Q_{j_1\vec{q}_1} && \text{(C.84)}\end{aligned}$$

And in the Heisenberg picture

$$u_{Hl_1k_1\alpha_1} = \sum_{j_1\vec{q}_1}R^{j_1\vec{q}_1}_{l_1k_1\alpha_1}Q_{Hj_1\vec{q}_1} \tag{C.85}$$

All the "u,u" Green's functions are related to the "Q,Q" Green's functions via

$$D^{(0)t,M,<,>,R,A}_{l_1k_1\alpha_1l_2k_2\alpha_2}(t_1-t_2) = \sum_{j_1\vec{q}_1j_2\vec{q}_2}R^{j_1\vec{q}_1}_{l_1k_1\alpha_1}R^{j_2\vec{q}_2}_{l_2k_2\alpha_2}D^{(0)t,M,<,>,R,A}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) \tag{C.86}$$

C.3.2 In Frequency Domain

C.3.2.1 "a, $a^\dagger$" operators

The time-ordered Green's function:

$$\begin{aligned} D^{(0)t}_{j_1\vec{q}_1j_2\vec{q}_2}(\omega) &= \int d(t_1-t_2)e^{i\omega(t_1-t_2)}D^{(0)t}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) && \text{(C.87)}\\ &\quad\mid\ \text{use the integral representation of the step function } \theta(t) = \frac{i}{2\pi}\int d\omega'\frac{e^{-i\omega' t}}{\omega'+i\eta}\\ &= -\frac{i}{\hbar}\left\{\frac{i}{2\pi}\int d\omega'\frac{e^{-i(\omega'-\omega+\omega_{j_1\vec{q}_1})(t_1-t_2)}}{\omega'+i\eta}\left(1+N^{eq}_{j_1\vec{q}_1}\right)\right.\\ &\quad\left.+\int d(t_1-t_2)\frac{i}{2\pi}\int d\omega'\frac{e^{i(\omega'+\omega-\omega_{j_1\vec{q}_1})(t_1-t_2)}}{\omega'+i\eta}N^{eq}_{j_1\vec{q}_1}\right\}\delta_{j_1j_2}\delta_{\vec{q}_1,\vec{q}_2} && \text{(C.88)}\\ &\quad\mid\ \text{use integral representation of delta function } \delta(\omega) = \frac{1}{2\pi}\int dte^{i\omega t}\\ &= \frac{1}{\hbar}\left(\frac{1+N^{eq}_{j_1\vec{q}_1}}{\omega-\omega_{j_1\vec{q}_1}+i\eta} - \frac{N^{eq}_{j_1\vec{q}_1}}{\omega-\omega_{j_1\vec{q}_1}-i\eta}\right)\delta_{j_1j_2}\delta_{\vec{q}_1,\vec{q}_2} && \text{(C.89)}\end{aligned}$$

The (Matsubara) imaginary time Green's function:

$$\begin{aligned} D^{(0)M}_{j_1\vec{q}_1j_2\vec{q}_2}(i\omega^B_n) &= \int_0^\beta d\tau^M e^{i\hbar\omega^B_n\tau^M}D^{(0)M}_{j_1\vec{q}_1j_2\vec{q}_2}(\tau^M_1-\tau^M_2=\tau^M) && \text{(C.90)}\\ &= -\frac{i}{\hbar}\int_0^\beta d\tau^M e^{(i\hbar\omega^B_n-\hbar\omega_{j_1\vec{q}_1})\tau^M}\left(\theta(-i\hbar\tau^M)\left(1+N^{eq}_{j_1\vec{q}_1}\right)+\theta(-i\hbar(-\tau^M))N^{eq}_{j_1\vec{q}_1}\right)\delta_{j_1j_2}\delta_{\vec{q}_1,\vec{q}_2}\end{aligned}$$

$$
\begin{aligned}
& \quad | \quad \text{note that } \int_0^\beta d\tau^M \theta(-\tau^M) = 0 \\
&= -\frac{i}{\hbar} \frac{1+N^{eq}_{j_1\vec{q}_1}}{i\hbar\omega_n^B - \hbar\omega_{j_1\vec{q}_1}} \left[e^{(i\hbar\omega_n^B - \hbar\omega_{j_1\vec{q}_1})\tau^M} \right]_0^\beta && \text{(C.91)} \\
& \quad | \quad \text{use } e^{i\hbar\omega_n^B\beta} = 1 \\
&= -\frac{i}{\hbar} \frac{1+N^{eq}_{j_1\vec{q}_1}}{i\hbar\omega_n^B - \hbar\omega_{j_1\vec{q}_1}} \left[e^{-\hbar\beta\omega_{j_1\vec{q}_1}} - 1 \right] && \text{(C.92)} \\
& \quad | \quad \text{use the explicit form } N^{eq}_{j_1\vec{q}_1} = \left(e^{\beta\hbar\omega_{j_1\vec{q}_1}} - 1 \right)^{-1} \\
&= \frac{i}{\hbar} \frac{1}{\hbar} \frac{1}{i\omega_n^B - \omega_{j_1\vec{q}_1}} && \text{(C.93)}
\end{aligned}
$$

The lesser Green's function:

$$
\begin{aligned}
D^{(0)<}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega) &= \int d(t_1-t_2) e^{i\omega(t_1-t_2)} D^{(0)<}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1-t_2) && \text{(C.94)} \\
&= -\frac{i}{\hbar} N^{eq}_{j_1\vec{q}_1} \int d(t_1-t_2) e^{i(\omega-\omega_{j_1\vec{q}_1})(t_1-t_2)} \delta_{j_1j_2}\delta_{\vec{q}_1,\vec{q}_2} && \text{(C.95)} \\
&= -\frac{i}{\hbar} N^{eq}_{j_1\vec{q}_1} 2\pi\delta(\omega-\omega_{j_1\vec{q}_1}) \delta_{j_1j_2}\delta_{\vec{q}_1,\vec{q}_2} && \text{(C.96)}
\end{aligned}
$$

The greater Green's function:

$$
D^{(0)>}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega) = -\frac{i}{\hbar} \left(1 + N^{eq}_{j_1\vec{q}_1} \right) 2\pi\delta(\omega-\omega_{j_1\vec{q}_1}) \delta_{j_1j_2}\delta_{\vec{q}_1,\vec{q}_2} \quad \text{(C.97)}
$$

The retarded Green's function:

$$
\begin{aligned}
D^{(0)R}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega) &= \int d(t_1-t_2) e^{i\omega(t_1-t_2)} D^{(0)R}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1-t_2) && \text{(C.98)} \\
&= -\frac{i}{\hbar} \int d(t_1-t_2) \int d\omega' \frac{i}{2\pi} \frac{e^{-i(\omega'-\omega+\omega_{j_1\vec{q}_1})(t_1-t_2)}}{\omega'+i\eta} \delta_{j_1j_2}\delta_{\vec{q}_1,\vec{q}_2} && \text{(C.99)} \\
&= \frac{1}{\hbar} \frac{1}{\omega-\omega_{j_1\vec{q}_1}+i\eta} \delta_{j_1j_2}\delta_{\vec{q}_1,\vec{q}_2} && \text{(C.100)}
\end{aligned}
$$

We see the expected relationship: $-i\hbar D^{(0)M}_{j_1\vec{q}_1 j_2\vec{q}_2}(i\omega_n^B \to \omega + i\eta) = D^{(0)R}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega)$.

The advanced Green's function:

$$
D^{(0)A}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega) = \frac{1}{\hbar} \frac{1}{\omega-\omega_{j_1\vec{q}_1}-i\eta} \delta_{j_1j_2}\delta_{\vec{q}_1,\vec{q}_2} \quad \text{(C.101)}
$$

And we see the expected relationship: $-i\hbar D^{(0)M}_{j_1\vec{q}_1 j_2\vec{q}_2}(i\omega_n^B \to \omega - i\eta) = D^{(0)A}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega)$.

C.3.2.2 "Q, Q" operators

The time ordered Green's function is

$$
\begin{aligned}
D^{(0)t}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega) &= \int d(t_1-t_2) e^{i\omega(t_1-t_2)} D^{(0)t}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1-t_2) && \text{(C.102)} \\
& \quad | \quad \text{use the integral representation of step function } \theta(t) = \frac{i}{2\pi} \int d\omega' \frac{e^{-i\omega' t}}{\omega'+i\eta}
\end{aligned}
$$

$$
\begin{aligned}
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\frac{i}{2\pi}\int d(t_1-t_2)d\omega' \\
&\times\left[\left(N^{eq}_{j_1\vec{q}_1}+1\right)\frac{e^{-i(\omega'-\omega+\omega_{j_1\vec{q}_1})(t_1-t_2))}}{\omega'+i\eta}+N^{eq}_{j_1\vec{q}_1}\frac{e^{-i(\omega'-\omega-\omega_{j_1\vec{q}_1})(t_1-t_2)}}{\omega'+i\eta}\right. \\
&\left.+\left(N^{eq}_{j_1\vec{q}_1}+1\right)\frac{e^{i(\omega'+\omega+\omega_{j_1\vec{q}_1})(t_1-t_2)}}{\omega'+i\eta}+N^{eq}_{j_1\vec{q}_1}\frac{e^{i(\omega'+\omega-\omega_{j_1\vec{q}_1})(t_1-t_2)}}{\omega'+i\eta}\right]\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \\
&= \frac{1}{2\omega_{j_1\vec{q}_1}}\left[\left(N^{eq}_{j_1\vec{q}_1}+1\right)\left(\frac{1}{\omega+i\eta-\omega_{j_1\vec{q}_1}}-\frac{1}{\omega-\eta+\omega_{j_1\vec{q}_1}}\right)\right. \\
&\left.+N^{eq}_{j_1\vec{q}_1}\left(\frac{1}{\omega+i\eta+\omega_{j_1\vec{q}_1}}-\frac{1}{\omega-i\eta-\omega_{j_1\vec{q}_1}}\right)\right]\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \qquad \text{(C.103)}
\end{aligned}
$$

The (Matsubara) imaginary time Green's function is

$$
\begin{aligned}
D^{(0)M}_{j_1\vec{q}_1j_2\vec{q}_2}(i\omega_n^B) &= \int_0^\beta d\tau^M e^{i\hbar\omega_n^B\tau^M}D^{(0)M}_{j_1\vec{q}_1j_2\vec{q}_2}(\tau_1^M-\tau_2^M=\tau^M) \qquad \text{(C.104)} \\
&\quad | \quad \text{as previously used, } \int_0^\beta d\tau^M\theta(-\tau^M)=0 \\
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left(\left(N^{eq}_{j_1\vec{q}_1}+1\right)\int_0^\beta d\tau^M e^{(i\hbar\omega_n^B-\hbar\omega_{j_1\vec{q}_1})\tau^M}\right. \\
&\quad\left.+N^{eq}_{j_1\vec{q}_1}\int_0^\beta d\tau^M e^{(i\hbar\omega_n^B+\hbar\omega_{j_1\vec{q}_1})\tau^M}\right)\delta_{j_1\vec{q}_2}\delta_{\vec{q}_1,-\vec{q}_2} \qquad \text{(C.105)} \\
&\quad | \quad \text{evaluate the integrals and use } e^{i\hbar\omega_n^B\beta}=1 \text{ for bosons} \\
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left(\frac{\left(N^{eq}_{j_1\vec{q}_1}+1\right)\left(e^{-\beta\hbar\omega_{j_1\vec{q}_1}}-1\right)}{i\hbar\omega_n^B-\hbar\omega_{j_1\vec{q}_1}}+\frac{N^{eq}_{j_1\vec{q}_1}\left(e^{\beta\hbar\omega_{j_1\vec{q}_1}}-1\right)}{i\hbar\omega_n^B+\hbar\omega_{j_1\vec{q}_1}}\right)\delta_{j_1h_2}\delta_{\vec{q}_1,-\vec{q}_2} \\
&\quad | \quad \text{use explicit form } N^{eq}_{j_1\vec{q}_1}=\left(e^{\beta\hbar\omega_{j_1\vec{q}_1}}-1\right)^{-1} \\
&= \frac{i}{\hbar}\frac{1}{(i\omega_n^B)^2-\omega^2_{j_1\vec{q}_1}}\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \qquad \text{(C.106)}
\end{aligned}
$$

The lesser Green's function is

$$
\begin{aligned}
D^{(0)<}_{j_1\vec{q}_1j_2\vec{q}_2}(\omega) &= \int d(t_1-t_2)e^{i\omega(t_1-t_2)}D^{(0)<}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) \qquad \text{(C.107)} \\
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\int d(t_1-t_2)\left[\left(N^{eq}_{j_1\vec{q}_1}+1\right)e^{i(\omega+\omega_{j_1\vec{q}_1})(t_1-t_2))}+N^{eq}_{j_1\vec{q}_1}e^{i(\omega-\omega_{j_1\vec{q}_1})(t_1-t_2)}\right]\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \\
&\quad | \quad \text{use the integral representation of the delta function} \\
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left(2\pi\left(N^{eq}_{j_1\vec{q}_1}+1\right)\delta(\omega+\omega_{j_1\vec{q}_1})+2\pi N^{eq}_{j_1\vec{q}_1}\delta(\omega-\omega_{j_1\vec{q}_1})\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \qquad \text{(C.108)}
\end{aligned}
$$

The greater Green's function is

$$
D^{(0)>}_{j_1\vec{q}_1j_2\vec{q}_2}(\omega) = -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\left(2\pi\left(N^{eq}_{j_1\vec{q}_1}+1\right)\delta(\omega-\omega_{j_1\vec{q}_1}+2\pi N^{eq}_{j_1\vec{q}_1}\delta(\omega+\omega_{j_1\vec{q}_1})\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \qquad \text{(C.109)}
$$

The retarded Green’s function is

$$\begin{aligned}
D^{(0)R}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega) &= \int d(t_1-t_2)e^{i\omega(t_1-t_2)}D^{(0)R}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1-t_2) &\text{(C.110)}\\
&\quad |\ \text{use the integral representation of the step function}\\
&= -\frac{i}{\hbar}\frac{\hbar}{2\omega_{j_1\vec{q}_1}}\int d(t_1-t_2)d\omega'\frac{i}{2\pi}\left(\frac{e^{i(\omega-\omega'-\omega_{j_1\vec{q}_1})(t_1-t_2)}}{\omega'+i\eta}-\frac{e^{i(\omega-\omega'-\omega_{j_1\vec{q}_1})(t_1-t_2)}}{\omega'+i\eta}\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2}\\
&\quad |\ \text{use the integral representation of the delta function}\\
&= \frac{1}{(\omega+i\eta)^2-\omega^2_{j_1\vec{q}_1}}\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} &\text{(C.111)}
\end{aligned}$$

and we see the expected relationship $-i\hbar D^{(0)M}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega_n^B\to\omega+i\eta)=D^{(0)R}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega)$.

The advanced Green’s function is

$$D^{(0)A}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega) = \frac{1}{(\omega-i\eta)^2-\omega^2_{j_1\vec{q}_1}}\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \qquad \text{(C.112)}$$

and we see the expected relationship $-i\hbar D^{(0)M}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega_n^B\to\omega-i\eta)=D^{(0)A}_{j_1\vec{q}_1 j_2\vec{q}_2}(\omega)$.

C.3.2.3 “u, u” operators

All the “u,u” Green’s functions are related to the “Q,Q” Green’s functions via

$$D^{(0)t,M,<,>,R,A}_{l_1k_1\alpha_1l_2k_2\alpha_2}(\omega) = \sum_{j_1\vec{q}_1j_2\vec{q}_2} R^{j_1\vec{q}_1}_{l_1k_1\alpha_1}R^{j_2\vec{q}_2}_{l_2k_2\alpha_2}D^{(0)t,M,<,>,R,A}_{j_1\vec{q}_1j_2\vec{q}_2}(\omega) \qquad \text{(C.113)}$$

C.4 Phonon Spectral Functions

C.4.1 In Time Domain

C.4.1.1 “a, $a^\dagger$” operators

Here we simply use the defintion of spectral function and substitute in the relevant expressions.

$$\begin{aligned}
A^{(0)}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1-t_2) &= i\left(D^{(0)>}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1-t_2)-D^{(0)<}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1-t_2)\right) &\text{(C.114)}\\
&= \frac{1}{\hbar}e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)}\delta_{j_1j_2}\delta_{\vec{q}_1\vec{q}_2} &\text{(C.115)}
\end{aligned}$$

C.4.1.2 “Q, Q” operators

$$\begin{aligned}
A^{(0)}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1-t_2) &= i\left(D^{(0)>}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1-t_2)-D^{(0)<}_{j_1\vec{q}_1 j_2\vec{q}_2}(t_1-t_2)\right) &\text{(C.116)}\\
&= \frac{1}{2\omega_{j_1\vec{q}_1}}\left(e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)}-e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} &\text{(C.117)}
\end{aligned}$$

C.4.1.3 "u, u" operators

$$A^{(0)}_{l_1k_1\alpha_1l_2k_2\alpha_2}(t_1-t_2) = \sum_{j_1\vec{q}_1j_2\vec{q}_2} R^{j_1\vec{q}_1}_{l_1k_1\alpha_1} R^{j_2\vec{q}_2}_{l_2k_2\alpha_2} A^{(0)}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) \quad (C.118)$$

$$= \sum_{j_1\vec{q}_1} \frac{1}{2\omega_{j_1\vec{q}_1}} R^{j_1\vec{q}_1}_{l_1k_1\alpha_1} R^{j_1,-\vec{q}_1}_{l_2k_2\alpha_2} \left(e^{-i\omega_{j_1\vec{q}_1}(t_1-t_2)} - e^{i\omega_{j_1\vec{q}_1}(t_1-t_2)}\right) \quad (C.119)$$

C.4.2 In Frequency Domain

C.4.2.1 "a, $a^\dagger$" operators

We simply Fourier transform the time domain expressions.

$$A^{(0)}_{j_1\vec{q}_1j_2\vec{q}_2}(\omega) = \int_{-\infty}^{\infty} d(t_1-t_2) e^{i\omega(t_1-t_2)} A^{(0)}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) \quad (C.120)$$

$$| \quad \text{we get a delta function } 2\pi\delta(\omega-\omega_{j_1\vec{q}_1})$$

$$= \frac{2\pi}{\hbar}\delta_{j_1j_2}\delta_{\vec{q}_1\vec{q}_2}\delta(\omega-\omega_{j_1\vec{q}_1}) \quad (C.121)$$

C.4.2.2 "Q, Q" operators

$$A^{(0)}_{j_1\vec{q}_1j_2\vec{q}_2}(\omega) = \int_{-\infty}^{\infty} d(t_1-t_2) e^{i\omega(t_1-t_2)} A^{(0)}_{j_1\vec{q}_1j_2\vec{q}_2}(t_1-t_2) \quad (C.122)$$

$$= \frac{2\pi}{2\omega_{j_1\vec{q}_1}} \left(\delta(\omega-\omega_{j_1\vec{q}_1}) - \delta(\omega+\omega_{j_1\vec{q}_1})\right) \delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \quad (C.123)$$

It satisfies the 2 bosonic sum rules:[1]

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} A^{(0)}_{j_1\vec{q}_1j_2\vec{q}_2}(\omega) = \frac{2\pi}{2\omega_{j_1\vec{q}_1}}(1-1)\delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} = 0 \quad (C.124)$$

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega A^{(0)}_{j_1\vec{q}_1j_2\vec{q}_2}(\omega) = \delta_{j_1j_2}\delta_{\vec{q}_1,-\vec{q}_2} \quad (C.125)$$

C.4.2.3 "u, u" operators

$$A^{(0)}_{l_1k_1\alpha_1l_2k_2\alpha_2}(\omega) = \sum_{j_1\vec{q}_1} \frac{2\pi}{2\omega_{j_1\vec{q}_1}} R^{j_1\vec{q}_1}_{l_1k_1\alpha_1} R^{j_1,-\vec{q}_1}_{l_2k_2\alpha_2} \left(\delta(\omega-\omega_{j_1\vec{q}_1}) - \delta(\omega+\omega_{j_1\vec{q}_1})\right) \quad (C.126)$$

[1] Do note that for phonons, a better definition of the spectral function is $\omega A(\omega)$ instead of $A(\omega)$ as $A(\omega)$ is an odd function of ω. This can be seen that the second sum rule is actually the usual one for, say, electrons.

Appendix D

NEGF for electrons

[Appendix Introduction and Roadmap:] We enumerate this introduction for easy reading.

1. This appendix on NEGF for electrons is included to show the corresponding development for electrons. This provides a comparison with the main text which is concentrated on phonons.
2. NEGF is actually much more developed for electrons and there are "nicer" properties because Coulomb interaction is particle conserving. The long range interaction of Coulomb interaction presents a different type of difficulty for electrons.
3. Firstly, NEGF is stated for electrons as the machinery for phonons obviously works for electrons. The only changes are the use of fermionic 2nd quantized field operators and the resulting sign changes due to fermion statistics.
4. Secondly, the electron-electron Hedin-like equations are stated as a special case of the electron-phonon Hedin-like equations. Thus in this thesis, a total of 3 types of interaction have been converted to Hedin-like equations that generate (Φ-derivable) conserving self energy approximations.
5. With regards to the 3 transport related developments, the Landauer-like theory is very very similar to the phonon case and so we simply stated the results for electrons. The linear response theory is briefly treated at the end of the chapter. The kinetic theory is the one that has a long but elegant development.
6. For kinetic theory of electrons, the derivation to pre-QKE follows the same as that for phonons. However we have external electric and magnetic fields in this theory because they interact with the charge of the electron. The correct theory must thus be gauge invariant. This is achieved by modifying the Fourier Transform. Then GKB ansatz (with fields) are found and applied to turn pre-QKE to QKE and the final kinetic equation which is quantum mechanical, gauge invariant and casual is obtained.

D.1 Foundations

D.1.1 Expression for Perturbation

For electrons, the definition involves the fermionic field operators ψ and $\psi^\dagger$ and the rest of the working is actually the same as that for phonons. The Hamiltonian for NEGF is of the general notation,

$$H(t) = H_0 + H_{\text{int}} + \theta(t - t_0)V(t) \tag{D.1}$$

The perturbation expression is similar.

$$
\begin{aligned}
& G(\vec{r}_1, t_1, \vec{r}_{1'}, t_{1'}) \\
= \; & G(1, 1') && \text{(D.2)} \\
| \; & \text{where } 1 \equiv \vec{r}_1, t_1 \\
= \; & -\frac{i}{\hbar} \frac{\mathrm{Tr}\left(e^{-\beta(H_0+H_{\mathrm{int}})} T(\psi_H(1)\psi_H^\dagger(1'))\right)}{\mathrm{Tr}(e^{-\beta(H_0+H_{\mathrm{int}})})} && \text{(D.3)} \\
\equiv \; & -\frac{i}{\hbar}\langle T(\psi_H(1)\psi_H^\dagger(1'))\rangle && \text{(D.4)} \\
| \; & \text{where } T \text{ is some time ordering operator which will be clear in the last step} \\
| \; & \psi_H \text{ and } \psi_H^\dagger \text{ are the fermionic field operators in the Heisenberg picture.} \\
| \; & \text{go through the same procedure \& the perturbation expression is} \\
= \; & -\frac{i}{\hbar} \frac{\mathrm{Tr}\left(e^{-\beta H_0} T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K+c_M} d\tau (H_{\mathrm{int}})_{H_0}(\tau)} e^{-\frac{i}{\hbar}\int_{c_K} d\tau V_{H_0}(\tau)} \psi_{H_0}(1)\psi_{H_0}^\dagger(1')\right)\right)}{\mathrm{Tr}\left(e^{-\beta H_0} T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K+c_M} d\tau (H_{\mathrm{int}})_{H_0}(\tau)} e^{-\frac{i}{\hbar}\int_{c_K} d\tau V_{H_0}(\tau)}\right)\right)} && \text{(D.5)}
\end{aligned}
$$

This is the final form which is very similar to the what we derived for the phonons earlier. The contour to be used for perturbation is again the Keldysh contour c_K with the Matsubara contour c_M. We define the perturbation expression as the so-called contour-ordered Green's function,

$$
\begin{aligned}
G(1,1') &= -\frac{i}{\hbar} \frac{\mathrm{Tr}\left(e^{-\beta H_0} T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K+c_M} d\tau (H_{\mathrm{int}})_{H_0}(\tau)} e^{-\frac{i}{\hbar}\int_{c_K} d\tau V_{H_0}(\tau)} \psi_{H_0}(1)\psi_{H_0}^\dagger(1')\right)\right)}{\mathrm{Tr}\left(e^{-\beta H_0} T_{c_K+c_M}\left(e^{-\frac{i}{\hbar}\int_{c_K+c_M} d\tau (H_{\mathrm{int}})_{H_0}(\tau)} e^{-\frac{i}{\hbar}\int_{c_K} d\tau V_{H_0}(\tau)}\right)\right)} && \text{(D.6)} \\
&\equiv -\frac{i}{\hbar}\langle T_{c_K+c_M}(\psi_H(1)\psi_H^\dagger(1'))\rangle && \text{(D.7)}
\end{aligned}
$$

D.1.2 Definitions of Green's functions

There are also 7 Green's functions for the electrons, (the notation $1 \equiv \vec{r}_1 t_1$ is used, spin indices are suppressed)

$$
G(1,2) = \begin{cases}
G^t(1,2) & t_1, t_2 \in \overrightarrow{c_K} \\
G^>(1,2) & t_1 \in \overleftarrow{c_K}, t_2 \in \overrightarrow{c_K}, \Rightarrow t_1 > t_2 \\
G^<(1,2) & t_1 \in \overrightarrow{c_K}, t_2 \in \overleftarrow{c_K}, \Rightarrow t_1 < t_2 \\
G^{\bar{t}}(1,2) & t_1, t_2 \in \overleftarrow{c_K} \\
G^{\urcorner}(t_1, \tau_2^M) & t_1 \in c_K, \tau_2^M \in c_M \\
G^{\ulcorner}(\tau_1^M, t_2) & \tau_1^M \in c_M, t_2 \in c_K \\
G^M(\tau_1^M, \tau_2^M) & \tau_1^M, \tau_2^M \in c_M
\end{cases} \tag{D.8}
$$

The explicit expressions for the first 4 (real time) Green functions are,
Time-ordered Green function

$$
\begin{aligned}
G^t(1,2) &= -\frac{i}{\hbar}\langle T(\psi_H(1)\psi_H^\dagger(2))\rangle && \text{(D.9)} \\
&= -\frac{i}{\hbar}\theta(t_1-t_2)\langle \psi_H(1)\psi_H^\dagger(2)\rangle + \frac{i}{\hbar}\theta(t_2-t_1)\langle \psi_H^\dagger(2)\psi_H(1)\rangle && \text{(D.10)}
\end{aligned}
$$

Greater Green function

$$G^{>}(1,2) = -\frac{i}{\hbar}\langle \psi_H(1)\psi_H^\dagger(2)\rangle \tag{D.11}$$

Lesser Green function [1]

$$G^{<}(1,2) = +\frac{i}{\hbar}\langle \psi_H^\dagger(2)\psi_H(1)\rangle \tag{D.12}$$

Anti-time ordered Green function

$$\begin{aligned} G^{\bar{t}}(1,2) &= -\frac{i}{\hbar}\langle \tilde{T}(\psi_H(1)\psi_H^\dagger(2))\rangle & \text{(D.13)}\\ &= -\frac{i}{\hbar}\theta(t_2-t_1)\langle \psi_H(1)\psi_H^\dagger(2)\rangle + \frac{i}{\hbar}\theta(t_1-t_2)\langle \psi_H^\dagger(2)\psi_H(1)\rangle & \text{(D.14)}\end{aligned}$$

Immediately we see a relation (using $\theta(t_1-t_2)+\theta(t_2-t_1)=1$)

$$G^t + G^{\bar{t}} = G^{<} + G^{>} \tag{D.15}$$

Thus are only 3 linearly independent Green's functions in non-equilibrium systems. We define 3 more Green's function for later considerations.

Advanced Green's function

$$\begin{aligned} G^A(1,2) &= \frac{i}{\hbar}\theta(t_2-t_1)\langle [\psi_H(1),\psi_H^\dagger(2)]_+\rangle & \text{(D.16)}\\ &= \theta(t_2-t_1)(G^{<}(1,2)-G^{>}(1,2)) & \text{(D.17)}\end{aligned}$$

Retarded Green's function

$$\begin{aligned} G^R(1,2) &= -\frac{i}{\hbar}\theta(t_1-t_2)\langle [\psi_H(1),\psi_H^\dagger(2)]_+\rangle & \text{(D.18)}\\ &= \theta(t_1-t_2)(G^{>}(1,2)-G^{<}(1,2)) & \text{(D.19)}\end{aligned}$$

Keldysh Green's function

$$G^K(1,2) = G^{>}(1,2) + G^{<}(1,2) \tag{D.20}$$

where $[\ ,\ ]_+$ represents the anti-commutator.

D.1.3 BBGKY Hierarchy of equations of motion

D.1.3.1 Electron-Electron (Coulomb) Interaction Case

We follow [Leeuwen2005] in this section. Here we consider the case of electrons experiencing Coulomb interaction in the presence of time dependent external fields introduced via a vector potential $\vec{A}(\vec{r}t)$ and a scalar potential $V(\vec{r}t)$. The external fields will be switched on at t_0.

[1] A simple way to think about the sign in the definition of $G^{<}$ is as follows, usually a Green's function is defined in the order $\psi(t)\psi^\dagger(t')$ and for $G^{<}$, we have $t' > t$ and we need to order the later quantity to the left, i.e. $\psi^\dagger(t')\psi(t)$ and further recalling that at equal time they anticommute, so a negative sign is inserted for consistency. (No sign change is needed for bosons)

The Hamiltonian in second quantized form with field operator chosen as variables,

$$\begin{aligned} H(t) &= \int d\vec{r} \sum_{\sigma} \psi^{\dagger}_{\sigma}(\vec{r}) h(\vec{r}t) \psi_{\sigma}(\vec{r}) \\ &+ \frac{1}{2} \int \int d\vec{r}_1 d\vec{r}_2 \sum_{\sigma_1\sigma_2} \psi^{\dagger}_{\sigma_1}(\vec{r}_1) \psi^{\dagger}_{\sigma_2}(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_{\sigma_2}(\vec{r}_2) \psi_{\sigma_1}(\vec{r}_1) \qquad \text{(D.21)} \\ \text{where } h(\vec{r}t) &= \frac{1}{2} \left(-i\hbar \nabla_{\vec{r}} + \vec{A}(\vec{r}t)\theta(t-t_0) \right)^2 + V(\vec{r}t)\theta(t-t_0) - \mu \qquad \text{(D.22)} \end{aligned}$$

where μ is the chemical potential.

The relationships between the field operators and the (band) ladder operators are as follows (in Heisenberg picture and contour time τ),

$$\psi_{H\sigma}(\vec{r}\tau) = \sum_{n,\vec{k}} \frac{1}{\sqrt{V}} \mathcal{U}_{n\vec{k}}(\vec{r}) c_{Hn\vec{k}\sigma}(\tau) \qquad \text{(D.23)}$$

$$\psi^{\dagger}_{H\sigma}(\vec{r}\tau) = \sum_{n,\vec{k}} \frac{1}{\sqrt{V}} \mathcal{U}^{*}_{n\vec{k}}(\vec{r}) c^{\dagger}_{Hn\vec{k}\sigma}(\tau) \qquad \text{(D.24)}$$

where $\mathcal{U}_{n\vec{k}}(\vec{r})$ is the Bloch function for momentum $\vec{k}$, band n. We can define contour ordered Green's function based on each variable.

$$G_{\sigma\sigma'}(\vec{r}\tau\vec{r}\,'\tau') \equiv -\frac{i}{\hbar} \left\langle T_{c_K+c_M} \left(\psi_{H\sigma}(\vec{r}\tau) \psi^{\dagger}_{H\sigma'}(\vec{r}\,'\tau') \right) \right\rangle \qquad \text{(D.25)}$$

$$G_{n\vec{k}\sigma n'\vec{k}'\sigma'}(\tau\tau') \equiv -\frac{i}{\hbar} \left\langle T_{c_K+c_M} \left(c_{Hn\vec{k}\sigma}(\tau) c^{\dagger}_{Hn'\vec{k}'\sigma'}(\tau') \right) \right\rangle \qquad \text{(D.26)}$$

We will only use the field operator defined version for the remaining discussion.

[Derivation of the "left" BBGKY equation and the "right" BBGKY equation] We start with the Heisenberg equations of motion for the field operators.

$$i\hbar \frac{\partial}{\partial \tau} \psi_{H\sigma}(\vec{r}\tau) = \Big[\psi_{H\sigma}(\vec{r}\tau), H_H(\tau) \Big]_- \qquad \text{(D.27)}$$

$$\text{and also,} \quad i\hbar \frac{\partial}{\partial \tau} \psi^{\dagger}_{H\sigma}(\vec{r}\tau) = \Big[\psi^{\dagger}_{H\sigma}(\vec{r}\tau), H_H(\tau) \Big]_- \qquad \text{(D.28)}$$

$$\begin{aligned} i\hbar \frac{\partial}{\partial \tau} \psi_{H\sigma}(\vec{r}\tau) &= \Big[\psi_{H\sigma}(\vec{r}\tau), H_H(\tau) \Big]_- \qquad \text{(D.29)} \\ &= \left[\psi_{H\sigma}(\vec{r}\tau), \int d\vec{r}_1 \sum_{\sigma_1} \psi^{\dagger}_{H\sigma_1}(\vec{r}_1\tau) h(\vec{r}_1\tau) \psi_{H\sigma_1}(\vec{r}_1\tau) \right]_- \\ &+ \left[\psi_{H\sigma}(\vec{r}\tau), \frac{1}{2} \int \int d\vec{r}_1 d\vec{r}_2 \sum_{\sigma_1\sigma_2} \psi^{\dagger}_{H\sigma_1}(\vec{r}_1\tau) \psi^{\dagger}_{H\sigma_2}(\vec{r}_2\tau) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_{H\sigma_2}(\vec{r}_2\tau) \psi_{H\sigma_1}(\vec{r}_1\tau) \right]_- \\ & \qquad \text{(D.30)} \end{aligned}$$

Use the anti-commutator identity $[A, CD]_{-} = [C, A]_{+} D - C [D, A]_{+}$ and calculate term by term.

$$\begin{aligned}
\text{First term} &= \int d\vec{r}_1 \sum_{\sigma_1} \left[\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau), \psi_{H\sigma}(\vec{r}\tau)\right]_+ h(\vec{r}_1\tau)\psi_{H\sigma_1}(\vec{r}_1\tau) && \text{(D.31)}\\
&= \int d\vec{r}_1 \sum_{\sigma_1} \delta_{\sigma_1\sigma}\delta(\vec{r}-\vec{r}_1) h(\vec{r}_1\tau)\psi_{H\sigma_1}(\vec{r}_1\tau) && \text{(D.32)}\\
&= h(\vec{r}\tau)\psi_{H\sigma}(\vec{r}\tau) && \text{(D.33)}
\end{aligned}$$

$$\begin{aligned}
& \text{Second Term}\\
= \;& \frac{1}{2}\int\int d\vec{r}_1\vec{r}_2 \sum_{\sigma_1\sigma_2} \left[\psi_{H\sigma}(\vec{r}\tau), \psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\right]_+ \psi^\dagger_{H\sigma_2}(\vec{r}_2\tau)\frac{1}{|\vec{r}_1-\vec{r}_2|}\psi_{H\sigma_2}(\vec{r}_2\tau)\psi_{H\sigma_1}(\vec{r}_1\tau)\\
& -\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\left[\psi_{H\sigma}(\vec{r}\tau), \psi^\dagger_{H\sigma_2}(\vec{r}_2\tau)\frac{1}{|\vec{r}_1-\vec{r}_2|}\psi_{H\sigma_2}(\vec{r}_2\tau)\psi_{H\sigma_1}(\vec{r}_1\tau)\right]_+ && \text{(D.34)}\\
| \;& \text{Evaluate the first line using the anti-commutator identity}\\
= \;& \frac{1}{2}\int d\vec{r}_2 \sum_{\sigma_2} \psi^\dagger_{H\sigma_2}(\vec{r}_2\tau)\frac{1}{|\vec{r}_1-\vec{r}_2|}\psi_{H\sigma_2}(\vec{r}_2\tau)\psi_{H\sigma}(\vec{r}\tau)\\
& -\frac{1}{2}\int\int d\vec{r}_1 d\vec{r}_2 \left(\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\left[\psi_{H\sigma}(\vec{r}\tau), \psi^\dagger_{H\sigma_2}(\vec{r}_2\tau)\right]_+ \frac{1}{|\vec{r}_1-\vec{r}_2|}\psi_{H\sigma_2}(\vec{r}_2\tau)\psi_{H\sigma_1}(\vec{r}_1\tau)\right.\\
& \left. +\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\psi^\dagger_{H\sigma_2}(\vec{r}_2\tau)\left[\psi_{H\sigma}(\vec{r}\tau), \frac{1}{|\vec{r}_1-\vec{r}_2|}\psi_{H\sigma_2}(\vec{r}_2\tau)\psi_{H\sigma_1}(\vec{r}_1\tau)\right]_-\right) && \text{(D.35)}\\
| \;& \text{the last line is zero using the anti-commutator identity}\\
| \;& \text{and the fermionic anti-commutator relations}\\
= \;& \frac{1}{2}\int d\vec{r}_2 \sum_{\sigma_2} \psi^\dagger_{H\sigma_2}(\vec{r}_2\tau)\frac{1}{|\vec{r}_1-\vec{r}_2|}\psi_{H\sigma_2}(\vec{r}_2\tau)\psi_{H\sigma}(\vec{r}\tau)\\
& -\frac{1}{2}\int d\vec{r}_1 \sum_{\sigma_1} \psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\frac{1}{|\vec{r}_1-\vec{r}_2|}\psi_{H\sigma}(\vec{r}\tau)\psi_{H\sigma_1}(\vec{r}_1\tau) && \text{(D.36)}\\
| \;& \text{commute } \psi_{H\sigma}(\vec{r}\tau)\psi_{H\sigma_1}(\vec{r}_1\tau) = -\psi_{H\sigma_1}(\vec{r}_1\tau)\psi_{H\sigma}(\vec{r}\tau) \text{ and rename indices}\\
= \;& \int d\vec{r}_1 \sum_{\sigma_1} \psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\frac{1}{|\vec{r}_1-\vec{r}_2|}\psi_{H\sigma_1}(\vec{r}_1\tau)\psi_{H\sigma}(\vec{r}\tau) && \text{(D.37)}
\end{aligned}$$

The final expression is

$$\left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)\psi_{H\sigma}(\vec{r}\tau) = \int d\vec{r}_1 \sum_{\sigma_1} \frac{1}{|\vec{r}-\vec{r}_1|}\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\psi_{H\sigma_1}(\vec{r}_1\tau)\psi_{H\sigma}(\vec{r}\tau) \tag{D.38}$$

The equation of motion of the adjoint field operator is found similarly as (or simply take the adjoint),

$$\left(i\hbar\frac{\partial}{\partial\tau} + h(\vec{r}\tau)\right)\psi^\dagger_{H\sigma}(\vec{r}\tau) = -\int d\vec{r}_1 \sum_{\sigma_1} \frac{1}{|\vec{r}-\vec{r}_1|}\psi^\dagger_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\psi_{H\sigma_1}(\vec{r}_1\tau) \tag{D.39}$$

We will now use the compact notation $\vec{r}_i\tau_i \equiv i$ and we insert $\delta(\tau-\tau_i)$ and $\int d\tau_1$, the 2 equations become,

$$i\hbar\frac{\partial}{\partial\tau}\psi_{H\sigma}(\vec{r}\tau) = h(\vec{r}\tau)\psi_{H\sigma}(\vec{r}\tau) + \int d1 \sum_{\sigma_1} \frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}\psi^\dagger_{H\sigma_1}(1)\psi_{H\sigma_1}(1)\psi_{H\sigma}(\vec{r}\tau) \tag{D.40}$$

$$i\hbar\frac{\partial}{\partial\tau}\psi^\dagger_{H\sigma}(\vec{r}\tau) = -h(\vec{r}\tau)\psi^\dagger_{H\sigma}(\vec{r}\tau) - \int d1 \sum_{\sigma_1} \frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}\psi^\dagger_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma_1}(1)\psi_{H\sigma_1}(1) \tag{D.41}$$

The notation $\int d1 = \int d\tau_1 \int d\vec{r}_1 \sum_{\sigma_1}$. Note that all the above are in the usual real time. I am only using contour time notation to prepare the expressions for NEGF. The above derivation is the usual Heisenberg quantum mechanics.

Now we can calculate the time derivative (and later, the equations of motion) of the contour ordered Green's function (now, contour time is necessary and $\int d\tau = \int_{c_K+c_M} d\tau$),

$$
\begin{aligned}
& i\hbar\frac{\partial}{\partial\tau}G_{\sigma\sigma'}(\vec{r}\tau\vec{r}\,'\tau') \\
= \; & i\hbar\frac{\partial}{\partial\tau}\left(-\frac{i}{\hbar}\right)\left\langle T_{c_K+c_M}\left(\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\right)\right\rangle && \text{(D.42)}\\
= \; & \frac{\partial}{\partial\tau}\left(\theta(\tau-\tau')\left\langle\left(\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\right)\right\rangle - \theta(\tau'-\tau)\left\langle\left(\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\psi_{H\sigma}(\vec{r}\tau)\right)\right\rangle\right) && \text{(D.43)}\\
= \; & \delta(\tau-\tau')\left(\left\langle\left(\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\right)\right\rangle + \left\langle\left(\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\psi_{H\sigma}(\vec{r}\tau)\right)\right\rangle\right) \\
& +\left(-\frac{i}{\hbar}\right)\left(\theta(\tau-\tau')\left\langle\left(i\hbar\frac{\partial}{\partial\tau}\psi_{H\sigma}(\vec{r}\tau)\right)\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\right\rangle - \theta(\tau'-\tau)\left\langle\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\left(i\hbar\frac{\partial}{\partial\tau}\psi_{H\sigma}(\vec{r}\tau)\right)\right\rangle\right) \\
| \; & \text{for first line we use equal time time anti-commutation relations} \\
| \; & \text{for second line we use equations of motion} \\
= \; & \delta(\tau-\tau')\delta(\vec{r}-\vec{r}\,')\delta_{\sigma\sigma'} \\
& +\left(-\frac{i}{\hbar}\right)\left(\theta(\tau-\tau')h(\vec{r}\tau)\left\langle\left(\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\right)\right\rangle - \theta(\tau'-\tau)h(\vec{r}\tau)\left\langle\left(\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\psi_{H\sigma}(\vec{r}\tau)\right)\right\rangle\right. && \text{(D.44)}\\
& +\theta(\tau-\tau')\int d1\sum_{\sigma_1}\frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}\left\langle\left(\psi^\dagger_{H\sigma_1}(1)\psi_{H\sigma_1}(1)\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\right)\right\rangle \\
& \left.-\theta(\tau'-\tau)\int d1\sum_{\sigma_1}\frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}\left\langle\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\psi^\dagger_{H\sigma_1}(1)\psi_{H\sigma_1}(1)\psi_{H\sigma}(\vec{r}\tau)\right\rangle\right) && \text{(D.45)}\\
| \; & \text{define the density } \psi^\dagger_{H\sigma_1}(1)\psi_{H\sigma_1}(1) \equiv n_H(1) \\
= \; & \delta(\tau-\tau')\delta(\vec{r}-\vec{r}\,')\delta_{\sigma\sigma'} + h(\vec{r}\tau)G_{\sigma\sigma'}(\vec{r}\tau\vec{r}\,'\tau') \\
& -\frac{i}{\hbar}\int d1\sum_{\sigma_1}\frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}\left\{\theta(\tau-\tau')\left\langle n_H(1)\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\right\rangle\right. \\
& \left.-\theta(\tau'-\tau)\left\langle\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')n_H(1)\psi_{H\sigma}(\vec{r}\tau)\right\rangle\right\} && \text{(D.46)}
\end{aligned}
$$

Now we follow [Gross1991] pg 184 and rewrite the second line.

$$
\begin{aligned}
& \left\{\theta(\tau-\tau')\left\langle n_H(1)\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\right\rangle - \theta(\tau'-\tau)\left(\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')n_H(1)\psi_{H\sigma}(\vec{r}\tau)\right\rangle\right\}_{\tau_1=\tau} \\
| \; & \text{the restriction appears due to the delta function} \\
= \; & \left\langle T_{c_K+c_M}\left(n_H(1)\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}\,'\tau')\right)\right\rangle_{\tau_1=\tau} && \text{(D.47)}
\end{aligned}
$$

$$
\begin{aligned}
&| \quad \text{time ordering of 3 terms will give 6 terms but here there are only 2 terms due to the restriction} \\
&= \left\langle T_{c_K+c_M}\left(\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau_1)\psi_{H\sigma_1}(\vec{r}_1\tau_1)\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right)\right\rangle_{\tau_1=\tau} \qquad \text{(D.48)} \\
&| \quad \text{to write it into a 2-particle Green's function expression, we need to shift } \psi^\dagger_{H\sigma_1}(\vec{r}_1\tau_1) \\
&| \quad \text{this shift uses the property of the time-ordering operator, its not anti-commutation!} \\
&= \lim_{\tau_2\to\tau^+}\left\langle T_{c_K+c_M}\left(\psi_{H\sigma_1}(\vec{r}\tau)\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau_2)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right)\right\rangle \qquad \text{(D.49)} \\
&| \quad \text{anticommute the first 2 field operators, rename } \tau_2 \text{ to } \tau_1 \\
&= -\lim_{\tau_1\to\tau^+}\left\langle T_{c_K+c_M}\left(\psi_{H\sigma}(\vec{r}\tau)\psi_{H\sigma_1}(\vec{r}_1\tau)\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau_1)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right)\right\rangle \qquad \text{(D.50)} \\
&| \quad \text{recall the definition of 2-particle Green's function} \\
&| \quad G_{\sigma_1\sigma_2\sigma_3\sigma_4}(\vec{r}_1\tau_1\vec{r}_2\tau_2\vec{r}_3\tau_3\vec{r}_4\tau_4) = \frac{(-i)^2}{\hbar}\left\langle T_{c_K+c_M}\left(\psi_{H\sigma_1}(\vec{r}_1\tau_1)\psi_{H\sigma_2}(\vec{r}_2\tau_2)\psi^\dagger_{H\sigma_3}(\vec{r}_3\tau_3)\psi^\dagger_{H\sigma_4}(\vec{r}_4\tau_4)\right)\right\rangle \\
&= -(i\hbar)^2 G_{\sigma\sigma_1\sigma_1\sigma'}(\vec{r}\tau\vec{r}_1\tau\vec{r}_1\tau^+\vec{r}'\tau') \qquad \text{(D.51)}
\end{aligned}
$$

So the equation is finally written into the (left) BBGKY hierarchy form for Coulomb interaction.

$$
\begin{aligned}
&\left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)G_{\sigma\sigma'}(\vec{r}\tau\vec{r}'\tau') \\
&= \delta(\tau-\tau')\delta(\vec{r}-\vec{r}')\delta_{\sigma\sigma'} - i\int d1\sum_{\sigma_1}\frac{\delta(\tau^+-\tau_1)}{|\vec{r}-\vec{r}_1|}G_{\sigma\sigma_1\sigma_1\sigma'}(\vec{r}\tau\vec{r}_1\tau_1\vec{r}_1\tau_1^+\vec{r}'\tau')
\end{aligned} \tag{D.52}
$$

The right BBGKY hierarchy equation is then,

$$
\begin{aligned}
&\left(-i\hbar\frac{\partial}{\partial\tau'} - h(\vec{r}'\tau')\right)G_{\sigma\sigma'}(\vec{r}\tau\vec{r}'\tau') \\
&= \delta(\tau-\tau')\delta(\vec{r}-\vec{r}')\delta_{\sigma\sigma'} - i\int d1\sum_{\sigma_1}\frac{\delta(\tau'^+-\tau_1)}{|\vec{r}'-\vec{r}_1|}G_{\sigma\sigma_1\sigma_1\sigma'}(\vec{r}\tau\vec{r}_1\tau_1\vec{r}_1\tau_1^+\vec{r}'\tau')
\end{aligned} \tag{D.53}
$$

[Derivation of Dyson's Equation] Now we want to derive the Dyson's equations from the BBGKY equations. We define the self energy as follows,

$$
-i\int d1\sum_{\sigma_1}\frac{\delta(\tau^+-\tau_1)}{|\vec{r}-\vec{r}_1|}G_{\sigma\sigma_1\sigma_1\sigma'}(\vec{r}\tau\vec{r}_1\tau_1\vec{r}_1\tau_1^+\vec{r}'\tau') \equiv \int d1\sum_{\sigma_1}\Sigma_{\sigma\sigma_1}(\vec{r}\tau\vec{r}_1\tau_1)G_{\sigma_1\sigma'}(\vec{r}_1\tau_1\vec{r}'\tau') \tag{D.54}
$$

$$
-i\int d1\sum_{\sigma_1}\frac{\delta(\tau'^+-\tau_1)}{|\vec{r}'-\vec{r}_1|}G_{\sigma\sigma_1\sigma_1\sigma'}(\vec{r}\tau\vec{r}_1\tau_1\vec{r}_1\tau_1^+\vec{r}'\tau') \equiv \int d1\sum_{\sigma_1}G_{\sigma\sigma_1}(\vec{r}\tau\vec{r}_1\tau_1)\Sigma^\dagger_{\sigma_1\sigma'}(\vec{r}_1\tau_1\vec{r}'\tau') \tag{D.55}
$$

Now we need to show that $\Sigma = \Sigma^\dagger$.
First we simplify the notation by defining,

$$
\hat{i}_H(1) \equiv \int d2\sum_{\sigma_2}\frac{\delta(\tau_1-\tau_2)}{|\vec{r}_1-\vec{r}_2|}\psi^\dagger_{H\sigma_2}(2)\psi_{H\sigma_2}(2)\psi_{H\sigma_1}(1) \tag{D.56}
$$

$$
\hat{i}^\dagger_H(1) \equiv \int d2\sum_{\sigma_2}\frac{\delta(\tau_1-\tau_2)}{|\vec{r}_1-\vec{r}_2|}\psi^\dagger_{H\sigma_1}(1)\psi^\dagger_{H\sigma_2}(2)\psi_{H\sigma_2}(2) \tag{D.57}
$$

Now the equations of motion look simpler,

$$i\hbar\frac{\partial}{\partial\tau}\psi_{H\sigma}(\vec{r}\tau) = h(\vec{r}\tau)\psi_{H\sigma}(\vec{r}\tau) + \hat{i}_H(\vec{r}\tau) \Longrightarrow \left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)\psi_{H\sigma}(\vec{r}\tau) = \hat{i}_H(\vec{r}\tau) \tag{D.58}$$

$$i\hbar\frac{\partial}{\partial\tau}\psi^\dagger_{H\sigma}(\vec{r}\tau) = -h(\vec{r}\tau)\psi^\dagger_{H\sigma}(\vec{r}\tau) - \hat{i}^\dagger_H(\vec{r}\tau) \Longrightarrow \left(-i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)\psi^\dagger_{H\sigma}(\vec{r}\tau) = \hat{i}^\dagger_H(\vec{r}\tau) \tag{D.59}$$

We rewrite the equations of motion for the Green's function into the $\hat{i}_H$ notation. For the left equation,

$$\begin{aligned}
&\left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)G_{\sigma\sigma'}(\vec{r}\tau\vec{r}'\tau') \\
=\ & \delta(\tau-\tau')\delta(\vec{r}-\vec{r}')\delta_{\sigma\sigma'} \\
&-\frac{i}{\hbar}\int d1\sum_{\sigma_1}\frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}\left\langle T_{c_K+c_M}\left(\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau_1)\psi_{H\sigma_1}(\vec{r}_1\tau_1)\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right)\right\rangle \quad (D.60)\\
=\ & \delta(\tau-\tau')\delta(\vec{r}-\vec{r}')\delta_{\sigma\sigma'} - \frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(\hat{i}_H(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right)\right\rangle \quad (D.61)
\end{aligned}$$

and for the right equation,

$$\left(-i\hbar\frac{\partial}{\partial\tau'} - h(\vec{r}'\tau')\right)G_{\sigma\sigma'}(\vec{r}\tau\vec{r}'\tau') = \delta(\tau-\tau')\delta(\vec{r}-\vec{r}')\delta_{\sigma\sigma'} - \frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(\psi^\dagger_{H\sigma}(\vec{r}\tau)\hat{i}^\dagger_H(\vec{r}'\tau')\right)\right\rangle \tag{D.62}$$

Based on the earlier definition of self energy we can write,

$$\int d1\sum_{\sigma_1}\Sigma_{\sigma\sigma_1}(\vec{r}\tau\vec{r}_1\tau_1)G_{\sigma_1\sigma'}(\vec{r}_1\tau_1\vec{r}'\tau') = -\frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(\hat{i}_H(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right)\right\rangle \tag{D.63}$$

$$\int d1\sum_{\sigma_1}G_{\sigma\sigma_1}(\vec{r}\tau\vec{r}_1\tau_1)\Sigma^\dagger_{\sigma_1\sigma'}(\vec{r}_1\tau_1\vec{r}'\tau') = -\frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(\psi_{H\sigma}(\vec{r}\tau)\hat{i}^\dagger_H(\vec{r}'\tau')\right)\right\rangle \tag{D.64}$$

With this explicit form, we can now check that Σ and $\Sigma^\dagger$ are the same. We proceed by acting $\left(-i\hbar\frac{\partial}{\partial\tau'} - h(\vec{r}'\tau')\right)$ on the first equation.

$$\begin{aligned}
&\text{LHS of first equation} \\
=\ & \left(-i\hbar\frac{\partial}{\partial\tau'} - h(\vec{r}'\tau')\right)\int d1\sum_{\sigma_1}\Sigma_{\sigma\sigma_1}(\vec{r}\tau\vec{r}_1\tau_1)G_{\sigma_1\sigma'}(\vec{r}_1\tau_1\vec{r}'\tau') \quad (D.65)\\
|\ & \text{ use right Dyson's equation on the term } \left(-i\hbar\frac{\partial}{\partial\tau'} - h(\vec{r}'\tau')\right)G_{\sigma_1\sigma'}(\vec{r}_1\tau_1\vec{r}'\tau') \\
=\ & \int d1\sum_{\sigma_1}\Sigma_{\sigma\sigma_1}(\vec{r}\tau\vec{r}_1\tau_1)\delta(\tau_1-\tau')\delta(\vec{r}_1-\vec{r}')\delta_{\sigma_1\sigma'} \\
&+\int d1\sum_{\sigma_1}\Sigma_{\sigma\sigma_1}(\vec{r}\tau\vec{r}_1\tau_1)\int d2\sum_{\sigma_2}G_{\sigma_1\sigma_2}(\vec{r}_1\tau_1\vec{r}_2\tau_2\Sigma^\dagger_{\sigma_2\sigma'}(\vec{r}_2\tau_2\vec{r}'\tau') \quad (D.66)\\
=\ & \Sigma_{\sigma\sigma'}(\vec{r}\tau\vec{r}'\tau') + \int d1d2\sum_{\sigma_1\sigma_2}\Sigma_{\sigma\sigma_1}(\vec{r}\tau\vec{r}_1\tau_1)G_{\sigma_1\sigma_2}(\vec{r}_1\tau_1\vec{r}_2\tau_2)\Sigma^\dagger_{\sigma_2\sigma'}(\vec{r}_2\tau_2\vec{r}'\tau') \quad (D.67)
\end{aligned}$$

RHS of first equation

$$= \left(-i\hbar\frac{\partial}{\partial\tau'} - h(\vec{r}'\tau')\right)\left(-\frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(\hat{i}_H(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right)\right\rangle\right) \quad (D.68)$$

$$= -\frac{i}{\hbar}\left(-i\hbar\frac{\partial}{\partial\tau'} - h(\vec{r}'\tau')\right)\left(\theta(\tau-\tau')\left\langle\hat{i}_H(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right\rangle - \theta(\tau'-\tau)\left\langle\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\hat{i}_H(\vec{r}\tau)\right\rangle\right) \quad (D.69)$$

$| \quad$ use equation of motion, $\left(-i\hbar\frac{\partial}{\partial\tau'} - h(\vec{r}'\tau')\right)\psi^\dagger_{H\sigma'}(\vec{r}'\tau') = \hat{i}^\dagger_H(\vec{r}'\tau')$

$$\begin{aligned}
= \;& \delta(\tau-\tau')\left(\left\langle\hat{i}_H(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right\rangle + \left\langle\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\hat{i}_H(\vec{r}\tau)\right\rangle\right) \\
& -\frac{i}{\hbar}\left(\theta(\tau-\tau')\left\langle\hat{i}_H(\vec{r}\tau)\left(-i\hbar\frac{\partial}{\partial\tau'} - h(\vec{r}'\tau')\right)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right\rangle\right. \\
& \left.-\theta(\tau'-\tau)\left\langle\left(-i\hbar\frac{\partial}{\partial\tau'} - h(\vec{r}'\tau')\right)\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\hat{i}_H(\vec{r}\tau)\right\rangle\right) \quad (D.70)
\end{aligned}$$

$$= \delta(\tau-\tau')\left\langle\left[\hat{i}_H(\vec{r}\tau), \psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right]_+\right\rangle - \frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(\hat{i}_H(\vec{r}\tau)\hat{i}^\dagger_H(\vec{r}'\tau')\right)\right\rangle \quad (D.71)$$

The first equation becomes

$$\begin{aligned}
& \Sigma_{\sigma\sigma'}(\vec{r}\tau\vec{r}'\tau') + \int d1d2\sum_{\sigma_1\sigma_2}\Sigma_{\sigma\sigma_1}(\vec{r}\tau,1)G_{\sigma_1\sigma_2}(1,2)\Sigma^\dagger_{\sigma_2\sigma'}(2,\vec{r}'\tau') \\
= \;& \delta(\tau-\tau')\left\langle\left[\hat{i}_H(\vec{r}\tau), \psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right]_+\right\rangle - \frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(\hat{i}_H(\vec{r}\tau)\hat{i}^\dagger_H(\vec{r}'\tau')\right)\right\rangle \quad (D.72)
\end{aligned}$$

Now act $\left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)$ on the second equation.

LHS of second equation

$$= \left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)\int d1\sum_{\sigma_1}G_{\sigma\sigma_1}(\vec{r}\tau\vec{r}_1\tau_1)\Sigma^\dagger_{\sigma_1\sigma'}(\vec{r}_1\tau_1\vec{r}'\tau') \quad (D.73)$$

$| \quad$ use left Dyson's equation on the term $\left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)G_{\sigma\sigma_1}(\vec{r}\tau\vec{r}_1\tau_1)$

$$\begin{aligned}
= \;& \int d1\sum_{\sigma_1}\Sigma^\dagger_{\sigma_1\sigma'}(\vec{r}_1\tau_1\vec{r}'\tau')\delta(\tau-\tau_1)\delta(\vec{r}-\vec{r}_1)\delta_{\sigma\sigma_1} \\
& + \int d1\sum_{\sigma_1}\int d2\sum_{\sigma_2}\Sigma_{\sigma\sigma_2}(\vec{r}\tau\vec{r}_2\tau_2)G_{\sigma_2\sigma_1}(\vec{r}_2\tau_2\vec{r}_1\tau_1\Sigma^\dagger_{\sigma_1\sigma'}(\vec{r}_1\tau_1\vec{r}'\tau') \quad (D.74)
\end{aligned}$$

$$= \Sigma^\dagger_{\sigma\sigma'}(\vec{r}\tau\vec{r}'\tau') + \int d1d2\sum_{\sigma_1\sigma_2}\Sigma_{\sigma\sigma_1}(\vec{r}\tau,1)G_{\sigma_1\sigma_2}(1,2)\Sigma^\dagger_{\sigma_2\sigma'}(2,\vec{r}'\tau') \quad (D.75)$$

RHS of second equation

$$= \left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)\left(-\frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(\psi_{H\sigma}(\vec{r}\tau)\hat{i}^\dagger_H(\vec{r}'\tau')\right)\right\rangle\right) \quad (D.76)$$

$$= -\frac{i}{\hbar}\left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)\left(\theta(\tau-\tau')\left\langle\psi_{H\sigma}(\vec{r}\tau)\hat{i}^\dagger_H(\vec{r}'\tau')\right\rangle - \theta(\tau'-\tau)\left\langle\hat{i}^\dagger_H(\vec{r}'\tau')\psi_{H\sigma}(\vec{r}\tau)\right\rangle\right) \quad (D.77)$$

$| \quad$ use equation of motion, $\left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)\psi_{H\sigma}(\vec{r}\tau) = \hat{i}_H(\vec{r}\tau)$

$$= \delta(\tau-\tau')\left\langle\left[\psi_{H\sigma}(\vec{r}\tau), \hat{i}^\dagger_H(\vec{r}'\tau')\right]_+\right\rangle - \frac{i}{\hbar}\left(\theta(\tau-\tau')\left\langle\left(i\hbar\frac{\partial}{\partial\tau} - h(\vec{r}\tau)\right)\psi_{H\sigma}(\vec{r}\tau)\hat{i}^\dagger_H(\vec{r}'\tau')\right\rangle\right.$$

$$-\theta(\tau'-\tau)\left\langle \hat{i}^\dagger_H(\vec{r}'\tau')\left(i\hbar\frac{\partial}{\partial\tau}-h(\vec{r}\tau)\right)\psi_{H\sigma}(\vec{r}\tau)\right\rangle\Bigg) \tag{D.78}$$

$$= \delta(\tau-\tau')\left\langle\left[\psi_{H\sigma}(\vec{r}\tau),\hat{i}^\dagger_H(\vec{r}'\tau')\right]_+\right\rangle - \frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(\hat{i}_H(\vec{r}\tau)\hat{i}^\dagger_H(\vec{r}'\tau')\right)\right\rangle \tag{D.79}$$

The second equation becomes

$$\Sigma^\dagger_{\sigma\sigma'}(\vec{r}\tau\vec{r}'\tau') + \int d1d2\sum_{\sigma_1\sigma_2}\Sigma_{\sigma\sigma_1}(\vec{r}\tau,1)G_{\sigma_1\sigma_2}(1,2)\Sigma^\dagger_{\sigma_2\sigma'}(2,\vec{r}'\tau')$$

$$= \delta(\tau-\tau')\left\langle\left[\psi_{H\sigma}(\vec{r}\tau),\hat{i}^\dagger_H(\vec{r}'\tau')\right]_+\right\rangle - \frac{i}{\hbar}\left\langle T_{c_K+c_M}\left(\hat{i}_H(\vec{r}\tau)\hat{i}^\dagger_H(\vec{r}'\tau')\right)\right\rangle \tag{D.80}$$

We subtract the 2 equations and get,

$$\Sigma_{\sigma\sigma'}(\vec{r}\tau\vec{r}'\tau') - \Sigma^\dagger_{\sigma\sigma'}(\vec{r}\tau\vec{r}'\tau') = \delta(\tau-\tau')\left\langle\left[\hat{i}_H(\vec{r}\tau),\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right]_+\right\rangle - \delta(\tau-\tau')\left\langle\left[\psi_{H\sigma}(\vec{r}\tau),\hat{i}^\dagger_H(\vec{r}'\tau')\right]_+\right\rangle$$

Due to the delta function, we only need to check the equal time terms to prove that the self energies are the same. We will use the equal time anti-commutation relations to do it.

$$\left[\hat{i}_H(\vec{r}\tau),\psi^\dagger_{H\sigma'}(\vec{r}'\tau')\right]_+$$

$$= \int d1\sum_{\sigma_1}\frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}\left[\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau_1\psi_{H\sigma_1}(\vec{r}_1\tau_1)\psi_{H\sigma}(\vec{r}\tau),\psi^\dagger_{H\sigma'}(\vec{r}'\tau)\right]_+ \tag{D.81}$$

| expand the anti-commutator

$$= \int d1\sum_{\sigma_1}\frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}$$

$$\times\left(\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau_1\psi_{H\sigma_1}(\vec{r}_1\tau_1)\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}'\tau)+\psi^\dagger_{H\sigma'}(\vec{r}'\tau)\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau_1\psi_{H\sigma_1}(\vec{r}_1\tau_1)\psi_{H\sigma}(\vec{r}\tau)\right) \tag{D.82}$$

| all times are the same, we can anti-commute any pair

| 2nd term is of the correct form, 1st term needs anti-commutation

| anti-commute $\psi_{H\sigma}(\vec{r}\tau)$ 2 steps to the left, then anti-commute $\psi^\dagger_{H\sigma'}(\vec{r}'\tau)$ 2 steps left

$$= \int d1\sum_{\sigma_1}\frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}$$

$$\times\left(\psi_{H\sigma}(\vec{r}\tau)\psi^\dagger_{H\sigma'}(\vec{r}'\tau)\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)+\psi^\dagger_{H\sigma'}(\vec{r}'\tau)\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau_1\psi_{H\sigma_1}(\vec{r}_1\tau_1)\psi_{H\sigma}(\vec{r}\tau)\right) \tag{D.83}$$

$$= \int d1\sum_{\sigma_1}\frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}\left[\psi_{H\sigma}(\vec{r}\tau),\psi^\dagger_{H\sigma'}(\vec{r}'\tau)\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\psi^\dagger_{H\sigma_1}(\vec{r}_1\tau)\right]_+ \tag{D.84}$$

$$= \int d1\sum_{\sigma_1}\frac{\delta(\tau-\tau_1)}{|\vec{r}-\vec{r}_1|}\left[\psi_{H\sigma}(\vec{r}\tau),\psi^\dagger_{H\sigma'}(\vec{r}'\tau)\psi^\dagger_{H\sigma_1}(1)\psi^\dagger_{H\sigma_1}(1)\right]_+ \tag{D.85}$$

$$= \left[\psi_{H\sigma}(\vec{r}\tau),\hat{i}^\dagger_H(\vec{r}'\tau)\right]_+ \tag{D.86}$$

Hence $\Sigma = \Sigma^\dagger$ which means we can write the left and right Dyson's equations with the same self energy.

$$\boxed{\begin{aligned}\left(i\hbar\frac{\partial}{\partial\tau}-h(\vec{r}\tau)\right)G_{\sigma\sigma'} &= \delta(\tau-\tau')\delta(\vec{r}-\vec{r}')\delta_{\sigma\sigma'}+\int d1\sum_{\sigma_1}\Sigma_{\sigma\sigma_1}(\vec{r}\tau,1)G_{\sigma_1\sigma'}(1,\vec{r}'\tau') \quad (D.87)\\ \left(-i\hbar\frac{\partial}{\partial\tau'}-h(\vec{r}'\tau')\right)G_{\sigma\sigma'} &= \delta(\tau-\tau')\delta(\vec{r}-\vec{r}')\delta_{\sigma\sigma'}+\int d1\sum_{\sigma_1}G_{\sigma\sigma_1}(\vec{r}\tau,1)\Sigma_{\sigma_1\sigma'}(1,\vec{r}'\tau') \quad (D.88)\end{aligned}}$$

Note that the equal time singular part (or time local part) of the self energy will be denoted as Σ^{HF} (if they are used) following Kadanoff and Baym. But Σ^{HF} can always be absorbed into $h(\vec{r}\tau)$ and we will take it that way.

D.1.4 Derivation of Kadanoff-Baym (KB) Equations

Simply put: KB equations are simply the real time versions of the (left and right) Dyson's equations. Langreth's theorem is applied to the Dyson's equations to get the KB equations. The KB equations are the ones that numerical evaluation can be done. Again, we denote $\vec{r}_1 t_1 \equiv 1$.

1. Green's function: $G^<$

$$\begin{aligned}&\left(i\hbar\frac{\partial}{\partial t}-h(\vec{r}t)\right)G^<_{\sigma\sigma'}(\vec{r}t\vec{r}'t')\\ =&\int d1\sum_{\sigma_1}\Sigma^R_{\sigma\sigma_1}(\vec{r}t,1)G^<_{\sigma_1\sigma'}(1,\vec{r}'t')+\int d1\sum_{\sigma_1}\Sigma^<_{\sigma\sigma_1}(\vec{r}t,1)G^A_{\sigma_1\sigma'}(1,\vec{r}'t')\\ &+\int d\vec{r}_1\int_{t_0}^{t_0-i\beta\hbar}dt_1\sum_{\sigma_1}\Sigma^{\urcorner}_{\sigma\sigma_1}(\vec{r}t,\vec{r}_1t_1)G^{\ulcorner}_{\sigma_1\sigma'}(\vec{r}_1t_1,\vec{r}'t') \qquad (D.89)\\ |\;&\text{ on Matsubara contour, we rewrite }\int_{t_0}^{t_0-i\beta\hbar}dt_1A(t_1)=\int_0^\beta d\tau^M A(t_0-i\hbar\tau^M)\\ =&\int d1\sum_{\sigma_1}\Sigma^R_{\sigma\sigma_1}(\vec{r}t,1)G^<_{\sigma_1\sigma'}(1,\vec{r}'t')+\int d1\sum_{\sigma_1}\Sigma^<_{\sigma\sigma_1}(\vec{r}t,1)G^A_{\sigma_1\sigma'}(1,\vec{r}'t')\\ &+\int d\vec{r}_1\int_0^\beta d\tau_1^M\sum_{\sigma_1}\Sigma^{\urcorner}_{\sigma\sigma_1}(\vec{r}t,\vec{r}_1,t_0-i\hbar\tau_1^M)G^{\ulcorner}_{\sigma_1\sigma'}(\vec{r}_1,t_0-i\hbar\tau_1^M,\vec{r}'t') \qquad (D.90)\end{aligned}$$

2. Green's function: $G^>$

$$\begin{aligned}&\left(i\hbar\frac{\partial}{\partial t}-h(\vec{r}t)\right)G^>_{\sigma\sigma'}(\vec{r}t\vec{r}'t')\\ =&\int d1\sum_{\sigma_1}\Sigma^R_{\sigma\sigma_1}(\vec{r}t,1)G^>_{\sigma_1\sigma'}(1,\vec{r}'t')+\int d1\sum_{\sigma_1}\Sigma^>_{\sigma\sigma_1}(\vec{r}t,1)G^A_{\sigma_1\sigma'}(1,\vec{r}'t')\\ &+\int d\vec{r}_1\int_0^\beta d\tau_1^M\sum_{\sigma_1}\Sigma^{\urcorner}_{\sigma\sigma_1}(\vec{r}t,\vec{r}_1,t_0-i\hbar\tau_1^M)G^{\ulcorner}_{\sigma_1\sigma'}(\vec{r}_1,t_0-i\hbar\tau_1^M,\vec{r}'t') \qquad (D.91)\end{aligned}$$

3. Green's function: $G^{\urcorner}$

$$\left(i\hbar\frac{\partial}{\partial t}-h(\vec{r}t)\right)G^{\urcorner}_{\sigma\sigma'}(\vec{r}t\vec{r}',t_0-i\hbar\tau^{M'})$$

$$= \int d1 \sum_{\sigma_1} \Sigma^R_{\sigma\sigma_1}(\vec{r}t, 1) G^{\urcorner}_{\sigma_1\sigma'}(1, \vec{r}', t_0 - i\hbar\tau^{M'})$$
$$+ \int d\vec{r}_1 \int_0^\beta d\tau_1^M \sum_{\sigma_1} \Sigma^{\urcorner}_{\sigma\sigma_1}(\vec{r}t, \vec{r}_1, t_0 - i\hbar\tau_1^M) G^M_{\sigma_1\sigma'}(\vec{r}_1, t_0 - i\hbar\tau_1^M, \vec{r}', t_0 - i\hbar\tau^{M'}) \quad (D.92)$$

4. Green's function: G^M

$$\left(i\hbar\frac{\partial}{\partial(t_0 - i\hbar\tau^M)} - h(\vec{r}, t_0 - i\hbar\tau^M)\right) G^M_{\sigma\sigma'}(\vec{r}, t_0 - i\hbar\tau^M, \vec{r}', t_0 - i\hbar\tau^{M'})$$
$$= \delta((t_0 - i\hbar\tau^M) - (t_0 - i\hbar\tau^{M'}))\delta(\vec{r} - \vec{r}')\delta_{\sigma\sigma'}$$
$$+ \int d\vec{r}_1 \int_0^\beta d\tau_1^M \sum_{\sigma_1} \Sigma^M_{\sigma\sigma_1}(\vec{r}, t_0 - i\hbar\tau^M, \vec{r}_1, t_0 - i\hbar\tau_1^M) G^M_{\sigma_1\sigma'}(\vec{r}_1, t_0 - i\hbar\tau_1^M, \vec{r}', t_0 - i\hbar\tau^{M'}) \quad (D.93)$$

Notice that the left equation for $G^{\ulcorner}$ is not needed as it will be specified as an initial condition later.

We now derive 4 (right) Kadanoff-Baym equations from the (right) Dyson equation by applying Langreth's theorem.

1. Green's function: $G^<$

$$\left(-i\hbar\frac{\partial}{\partial t'} - h(\vec{r}'t')\right) G^<_{\sigma\sigma'}(\vec{r}t\vec{r}'t')$$
$$= \int d1 \sum_{\sigma_1} G^R_{\sigma\sigma_1}(\vec{r}t, 1)\Sigma^<_{\sigma_1\sigma'}(1, \vec{r}'t') + \int d1 \sum_{\sigma_1} G^<_{\sigma\sigma_1}(\vec{r}t, 1)\Sigma^A_{\sigma_1\sigma'}(1, \vec{r}'t')$$
$$+ \int d\vec{r}_1 \int_0^\beta d\tau_1^M \sum_{\sigma_1} G^{\urcorner}_{\sigma\sigma_1}(\vec{r}t, \vec{r}_1, t_0 - i\hbar\tau_1^M)\Sigma^{\ulcorner}_{\sigma_1\sigma'}(\vec{r}_1, t_0 - i\hbar\tau_1^M, \vec{r}'t') \quad (D.94)$$

2. Green's function: $G^>$

$$\left(-i\hbar\frac{\partial}{\partial t'} - h(\vec{r}'t')\right) G^>_{\sigma\sigma'}(\vec{r}t\vec{r}'t')$$
$$= \int d1 \sum_{\sigma_1} G^R_{\sigma\sigma_1}(\vec{r}t, 1)\Sigma^>_{\sigma_1\sigma'}(1, \vec{r}'t') + \int d1 \sum_{\sigma_1} G^>_{\sigma\sigma_1}(\vec{r}t, 1)\Sigma^A_{\sigma_1\sigma'}(1, \vec{r}'t')$$
$$+ \int d\vec{r}_1 \int_0^\beta d\tau_1^M \sum_{\sigma_1} G^{\urcorner}_{\sigma\sigma_1}(\vec{r}t, \vec{r}_1, t_0 - i\hbar\tau_1^M)\Sigma^{\ulcorner}_{\sigma_1\sigma'}(\vec{r}_1, t_0 - i\hbar\tau_1^M, \vec{r}'t') \quad (D.95)$$

3. Green's function: $G^{\ulcorner}$

$$\left(-i\hbar\frac{\partial}{\partial t'} - h(\vec{r}'t')\right) G^{\ulcorner}_{\sigma\sigma'}(\vec{r}, t_0 - i\hbar\tau^M, \vec{r}'t')$$
$$= \int d1 \sum_{\sigma_1} G^{\ulcorner}_{\sigma\sigma_1}(\vec{r}, t_0 - i\hbar\tau^M, 1)\Sigma^A_{\sigma_1\sigma'}(1, \vec{r}'t')$$
$$+ \int d\vec{r}_1 \int_0^\beta d\tau_1^M \sum_{\sigma_1} G^M_{\sigma\sigma_1}(\vec{r}, t_0 - i\hbar\tau^M, \vec{r}_1, t_0 - i\hbar\tau_1^M)\Sigma^{\ulcorner}_{\sigma_1\sigma'}(\vec{r}_1, t_0 - i\hbar\tau_1^M, \vec{r}', t') \quad (D.96)$$

4. Green's function: G^M

$$\begin{aligned}
&\left(-i\hbar\frac{\partial}{\partial(t_0-i\hbar\tau^{M'})}-h(\vec{r}',t_0-i\hbar\tau^{M'})\right)G^M_{\sigma\sigma'}(\vec{r},t_0-i\hbar\tau^M,\vec{r}',t_0-i\hbar\tau^{M'})\\
=\;&\delta((t_0-i\hbar\tau^M)-(t_0-i\hbar\tau^{M'}))\delta(\vec{r}-\vec{r}')\delta_{\sigma\sigma'}\\
&+\int d\vec{r}_1\int_0^\beta d\tau_1^M\sum_{\sigma_1}\Sigma^M_{\sigma\sigma_1}(\vec{r},t_0-i\hbar\tau^M,\vec{r}_1,t_0-i\hbar\tau_1^M)G^M_{\sigma_1\sigma'}(\vec{r}_1,t_0-i\hbar\tau_1^M,\vec{r}',t_0-i\hbar\tau^{M'})
\end{aligned}\tag{D.97}$$

Notice that the right equation for $G^{\urcorner}$ is not needed as it will be specified as an initial condition later.

[Relations between electron Green's functions] We follow [Stan2009]. There are some symmetry relations between the Green's functions and thereby specify the independent quantities to be calculated in Kandanoff-Baym equations.

From the definition of the electronic Green's functions, we get

$$G^<_{\sigma\sigma'}(\vec{r}t\vec{r}'t')^\dagger=\left(-\frac{i}{\hbar}\langle\psi^\dagger_{H\sigma'}(\vec{r}'t')\psi_{H\sigma}(\vec{r}t)\rangle\right)^\dagger=\frac{i}{\hbar}\langle\psi^\dagger_{H\sigma}(\vec{r}t)\psi_{H\sigma'}(\vec{r}'t')\rangle=-G^<_{\sigma'\sigma}(\vec{r}'t'\vec{r}t)\tag{D.98}$$

Similarly,

$$G^>_{\sigma\sigma'}(\vec{r}t\vec{r}'t')^\dagger\;=\;-G^>_{\sigma'\sigma}(\vec{r}'t'\vec{r}t)\tag{D.99}$$

Also,

$$\begin{aligned}
&G^{\urcorner}_{\sigma\sigma'}(\vec{r}t,\vec{r}',t_0-i\hbar(\beta-\tau^M))^\dagger\\
=\;&\left(-\frac{i}{\hbar}\langle\psi^\dagger_{H\sigma'}(\vec{r}',t_0-i\hbar(\beta-\tau^M))\psi_{H\sigma}(\vec{r}t)\rangle\right)^\dagger &\text{(D.100)}\\
|\;\;&\text{note that the first } H=H_0+H_{\text{int}} \text{ and the second } H=H_0+H_{\text{int}}+V(t)\\
=\;&\left(-\frac{i}{\hbar}\frac{1}{Z}\text{Tr}\left[e^{-\beta(H_0+H_{\text{int}})}e^{\frac{i}{\hbar}(H_0+H_{\text{int}})(t_0-i\hbar(\beta-\tau^M)-t_0)}\psi^\dagger_{\sigma'}(\vec{r}'t_0)e^{-\frac{i}{\hbar}(H_0+H_{\text{int}})(t_0-i\hbar(\beta-\tau^M)-t_0)}\right.\right.\\
&\left.\left.\times\left(Te^{\frac{i}{\hbar}\int dtH(t)}\right)\psi_\sigma(\vec{r}t_0)\left(Te^{-\frac{i}{\hbar}\int dtH(t)}\right)\right]\right)^\dagger &\text{(D.101)}\\
=\;&\left(\frac{i}{\hbar}\frac{1}{Z}\text{Tr}\left[e^{-\beta(H_0+H_{\text{int}})}e^{\beta(H_0+H_{\text{int}})}\psi^\dagger_{H\sigma'}(\vec{r}'.t_0+i\hbar\tau^M)e^{-\beta(H_0+H_{\text{int}})}\psi_{H\sigma}(\vec{r}t)\right]\right)^\dagger &\text{(D.102)}\\
|\;\;&\text{use trace cyclicity}\\
=\;&\left(-\frac{i}{\hbar}\frac{1}{Z}\text{Tr}\left[e^{-\beta(H_0+H_{\text{int}})}\psi_{H\sigma}(\vec{r}t)\psi^\dagger_{H\sigma'}(\vec{r}',t_0+i\hbar\tau^M)\right]\right)^\dagger &\text{(D.103)}\\
=\;&\frac{i}{\hbar}\frac{1}{Z}\text{Tr}\left[e^{-\beta(H_0+H_{\text{int}})}\psi_{H\sigma'}(\vec{r}',t_0-i\hbar\tau^M)\psi^\dagger_{H\sigma}(\vec{r}t)\right] &\text{(D.104)}\\
=\;&G^{\ulcorner}_{\sigma'\sigma}(\vec{r}',t_0-i\hbar\tau^M,\vec{r}t) &\text{(D.105)}
\end{aligned}$$

There are also similar relations for the Coulomb self energies which we shall not dig into. Refer to [Stan2009] equations (29) and (31) for details.

[Boundary Conditions for Kadanoff-Baym equations:] The conditions that connect the Green's functions defined in various parts of the contour are given here. These conditions will serve as "initial conditions" for some of the Kadanoff-Baym equations.

The imaginary time evolution is done by the Matsubara Green's functions and it provides the "initial conditions" for the real time evolution of $>$, $<$, $\urcorner$ and $\ulcorner$ components.

For $\urcorner$ and $\ulcorner$,

$$
\begin{aligned}
G^{\urcorner}_{\sigma\sigma'}(\vec{r}, t_0, \vec{r}', t_0 - i\hbar\tau^M) &= G^M_{\sigma\sigma'}(\vec{r}, t_0 - i\hbar 0, \vec{r}', t_0 - i\hbar\tau^M) && \text{(D.106)} \\
G^{\ulcorner}_{\sigma\sigma'}(\vec{r}, t_0 - i\hbar\tau^M, \vec{r}', t_0) &= G^M_{\sigma\sigma'}(\vec{r}, t_0 - i\hbar\tau^M, \vec{r}', t_0 - i\hbar 0) && \text{(D.107)}
\end{aligned}
$$

For $<$ and $>$,

$$
\begin{aligned}
G^{<}_{\sigma\sigma'}(\vec{r}t_0\vec{r}'t_0) &= G^M_{\sigma\sigma'}(\vec{r}, t_0 - i\hbar 0, \vec{r}', t_0 - i\hbar 0^+) && \text{(D.108)} \\
G^{>}_{\sigma\sigma'}(\vec{r}t_0\vec{r}'t_0) &= G^M_{\sigma\sigma'}(\vec{r}, t_0 - i\hbar 0^+, \vec{r}, t_0 - i\hbar 0) && \text{(D.109)}
\end{aligned}
$$

D.2 Φ-Derivable Conserving Approximations for e-e Interaction

This section is about the Hedin's equations for Coulomb interaction. The Hedin's equations generate the self consistent self energies for the Coulomb interaction.

We simply derive the Coulomb Hedin's equations by removing the phonon part (i.e set $D = 0$) of the Electron-Phonon Hedin's equations.

$$
\begin{aligned}
\Sigma_{\sigma_1\sigma_2}(1,2) &= \frac{i}{\hbar}\int d3d4 \sum_{\sigma_3} G_{\sigma_1\sigma_3}(1,3)W(\vec{r}_1 t_1^+, 4)\Gamma_{\sigma_3\sigma_2}(32,4) && \text{(D.110)} \\
\text{where} \quad W_e &= w\left(\mathbb{I} - P_e w\right)^{-1} && \text{(D.111)} \\
P_e(1,2) &= -i\sum_{\sigma_1}\int d3d4 \sum_{\sigma_3\sigma_4} G_{\sigma_1\sigma_3}(1,3)G_{\sigma_4\sigma_1}(4,1)\Gamma_{\sigma_3\sigma_4}(34,2) && \text{(D.112)} \\
\Gamma_{\sigma_1\sigma_2}(12,3) &= \delta_{\sigma_1\sigma_2}\delta(1-2)\delta(1-3) \\
&\quad + \int d4d5d6d7 \sum_{\sigma_4\sigma_5\sigma_6\sigma_7} \frac{\delta\Sigma_{\sigma_1\sigma_2}(1,2)}{\delta G_{\sigma_4\sigma_5}(4,5)} G_{\sigma_4\sigma_6}(4,6)G_{\sigma_7\sigma_5}(7,5)\Gamma_{\sigma_6\sigma_7}(67,3) && \text{(D.113)}
\end{aligned}
$$

The left and right Dyson's equations are included in this set. These are the equations (13.19a-d) in [Hedin1970]. Taking the first term in Γ (which is the delta function) we get the first self consistent self energy known as the "GW approximation".[2] To generate the "lower" self energies like the (self consistent) Hartree-Fock approximation, we simply do not consider the renormalization of w to W, i.e. ignore P_e.

The Hedin's equations generate self consistent skeleton diagrams and it was known that self consistent skeleton diagrams generated from the Luttinger-Ward functional Φ are conserving approximations (e.g GW approximation).[3] The relationships between Φ and Σ are as follows (n is the number of interaction w lines):

$$
\begin{aligned}
\Sigma(1,2) &= \frac{\delta\Phi}{\delta G(2,1)} && \text{(D.114)} \\
\text{and,} \quad \Phi[G] &= \sum_n \frac{1}{2n}\int d1d2\Sigma^{(n)}(1,2)G(2,1^+) && \text{(D.115)}
\end{aligned}
$$

[2] Or more correctly, the "GW approximation" set of equations.

[3] First, do not confuse Φ with the inter-ionic potential Φ used in other chapters of the thesis. Second, I do not have a formal proof that the set of (self consistent) skeleton diagrams generated by Hedin's equations and the set of (self consistent) skeleton diagrams generated by Luttinger-Ward functional Φ is the same set. An intuitive guess is that, there is only 1 set of (self consistent) skeleton diagrams!

One can think, diagrammatically, that the first equation means we take a full G line to close the Σ diagrams to construct Φ. The second equation represents the opposite where a Σ diagram is obtained from a Φ diagram by removing a full G line. The factor $\frac{1}{2n}$ is a combinatorical factor. We show the diagrams of Φ and its corresponding Σ diagrams for Coulomb interaction in the figure.

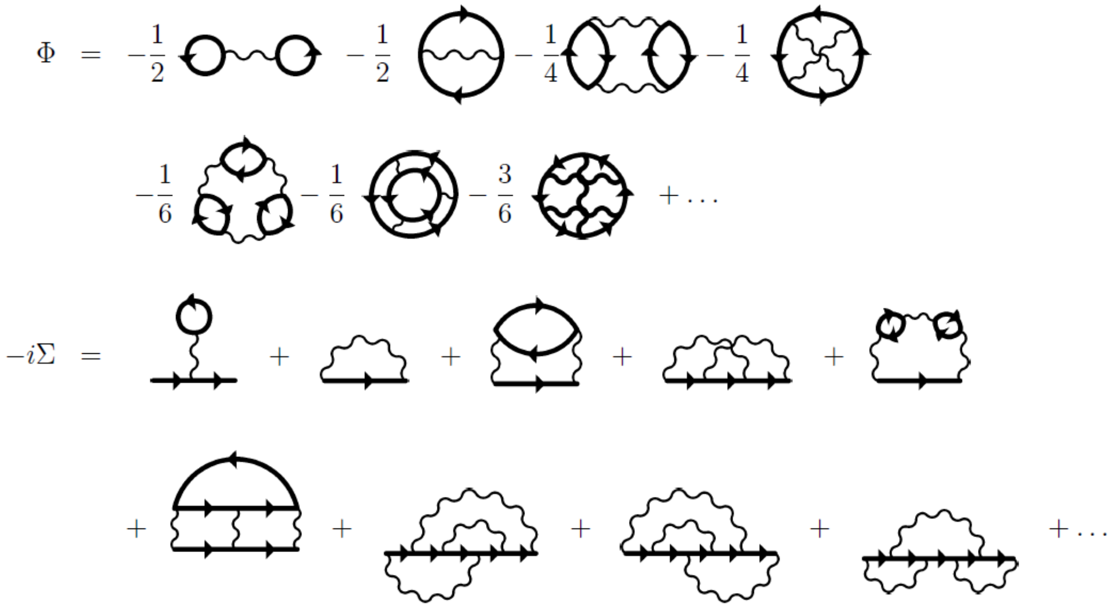


Figure D.1: Φ *diagrams and their corresponding* Σ *diagrams taken from fig 6.1 in [Leeuwen2005]. The thick line is the full G and the wavy line is w. The first 2 diagrams of* Σ *make the (self consistent) Hartree-Fock approximation. The next 2 diagrams of* Σ *make the (self consistent) second Born approximation.*

I can't provide the proofs here, hence I shall state some appropriate references. The Luttinger-Ward functional is derived in [Luttinger1960]. The Baym conserving approximation scheme is from his famous article in [Baym1962]. A modern treatment and the main reference for this section is [Leeuwen2005].

D.3 From NEGF to Landauer-like Equations

The phonon versions derived in the chapter on NEGF are "engineered" from the electron versions actually. Thus, here, we will simply state the (steady state) electron versions which are equations (4.113), (4.114) and (4.124) in [DiVentra2008].

The full interacting Landauer-like formula for particle current:[4]

$$I = 2\frac{ie}{2\hbar}\int \frac{d\omega}{2\pi}\mathrm{Tr}\left\{\left(\Gamma^{(L)}-\Gamma^{(R)}\right)G^{<}(\omega)+\left(f^{eq(L)}\Gamma^{(L)}-f^{eq(R)}\Gamma^{(R)}\right)\left(G^R-G^A\right)\right\} \quad \text{(D.116)}$$

The proportional coupling Landauer-like formula for particle current:

$$I = 2\frac{ie}{\hbar}\int \frac{d\omega}{2\pi}\left(f^{eq(L)}-f^{eq(R)}\right)\mathrm{Tr}\left\{\frac{\Gamma^{(L)}\Gamma^{(R)}}{\Gamma^{(L)}+\Gamma^{(R)}}\left(G^R-G^A\right)\right\} \quad \text{(D.117)}$$

[4]The factor of 2 comes from spin and so the interaction cannot involve spin processes.

The ballistic (non-interacting) Landauer-like for particle current:

$$I = \frac{e}{\pi\hbar}\int d\omega \left(f^{eq(L)} - f^{eq(R)}\right) \mathrm{Tr}\left\{\Gamma^{(R)} G^R \Gamma^{(L)} G^A\right\} \tag{D.118}$$

D.4 From NEGF to QKE

D.4.1 Pre-QKE

D.4.1.1 Wigner Coordinates, Gradient Expansion

We follow [Kadanoff1962] chapter 9. We start with the left and right Dyson's equations and after applying Langreth's theorem to get the lesser and greater quantities (spin indices are omitted and initial terms, $\ulcorner$, $\urcorner$ and M are dropped).

$$\begin{aligned}
\left(i\hbar\frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m}\nabla^2_{\vec{r}_1} - h(\vec{r}_1, t_1)\right) G^<(\vec{r}_1 t_1 \vec{r}_2 t_2) &= \int_t \left(\Sigma^R G^< + \Sigma^< G^R\right)(\vec{r}_1 t_1 \vec{r}_2 t_2) && \text{(D.119)}\\
\left(-i\hbar\frac{\partial}{\partial t_2} + \frac{\hbar^2}{2m}\nabla^2_{\vec{r}_2} - h(\vec{r}_2, t_2)\right) G^<(\vec{r}_1 t_1 \vec{r}_2 t_2) &= \int_t \left(G^R \Sigma^< + G^< \Sigma^A\right)(\vec{r}_1 t_1 \vec{r}_2 t_2) && \text{(D.120)}
\end{aligned}$$

We subtract them to get,

$$\begin{aligned}
&\left(i\hbar\frac{\partial}{\partial t_1} + i\hbar\frac{\partial}{\partial t_2} + \frac{\hbar^2}{2m}\nabla^2_{\vec{r}_1} - \frac{\hbar^2}{2m}\nabla^2_{\vec{r}_2} - h(\vec{r}_1, t_1 + h(\vec{r}_2, t_2)\right) G^<(\vec{r}_1 t_1 \vec{r}_2 t_2) && \text{(D.121)}\\
&= \int_t \left(\Sigma^R G^< + \Sigma^< G^R - G^R\Sigma^< - G^<\Sigma^A\right)(\vec{r}_1 t_1 \vec{r}_2 t_2) && \text{(D.122)}
\end{aligned}$$

Define Wigner coordinates

$$\begin{aligned}
\text{centre coordinates:}\quad & \vec{r}^{\,+} = \frac{\vec{r}_1 + \vec{r}_2}{2}, \quad t^+ = \frac{t_1 + t_2}{2} && \text{(D.123)}\\
\text{relative coordinates:}\quad & \vec{r}^{\,-} = \vec{r}_1 - \vec{r}_2, \quad t^- = t_1 - t_2 && \text{(D.124)}\\
\text{inverse:}\quad & \vec{r}_1 = \vec{r}^{\,+} + \frac{1}{2}\vec{r}^{\,-}, \quad \vec{r}_2 = \vec{r}^{\,+} - \frac{1}{2}\vec{r}^{\,-} && \text{(D.125)}\\
& t_1 = t^+ + \frac{1}{2}t^-, \quad t_2 = t^+ - \frac{1}{2}t^- && \text{(D.126)}
\end{aligned}$$

For the LHS, we will now carry out the coordinate transformation.

$$\begin{aligned}
\text{LHS First term} &= \frac{\partial}{\partial t_1} + \frac{\partial}{\partial t_2} && \text{(D.127)}\\
&= \frac{\partial t^+}{\partial t_1}\frac{\partial}{\partial t^+} + \frac{\partial t^-}{\partial t_1}\frac{\partial}{\partial t_-} + \frac{\partial t^+}{\partial t_2}\frac{\partial}{\partial t^+} + \frac{\partial t^-}{\partial t_2}\frac{\partial}{\partial t^-} && \text{(D.128)}\\
&= \frac{1}{2}\frac{\partial}{\partial t^+} + \frac{\partial}{\partial t^-} + \frac{1}{2}\frac{\partial}{\partial t^+} - \frac{\partial}{\partial t^-} && \text{(D.129)}\\
&= \frac{\partial}{\partial t^+} && \text{(D.130)}
\end{aligned}$$

$$\begin{aligned}
\text{LHS Second term} &= \nabla^2_{\vec{r}_1} - \nabla^2_{\vec{r}_2} && \text{(D.131)}\\
&\mid \ \text{we write in the partial differential forms for simplicity} && \text{(D.132)}
\end{aligned}$$

$$
\begin{aligned}
&= \frac{\partial^2}{\partial \vec{r}_1^2} - \frac{\partial^2}{\partial \vec{r}_2^2} && \text{(D.133)}\\
&= \frac{\partial}{\partial \vec{r}_1}\left(\frac{\partial \vec{r}^{\,+}}{\partial \vec{r}_1}\frac{\partial}{\partial \vec{r}^{\,+}} + \frac{\partial \vec{r}^{\,-}}{\partial \vec{r}_1}\frac{\partial}{\partial \vec{r}^{\,-}}\right) - \frac{\partial}{\partial \vec{r}_2}\left(\frac{\partial \vec{r}^{\,+}}{\partial \vec{r}_2}\frac{\partial}{\partial \vec{r}^{\,+}} + \frac{\partial \vec{r}^{\,-}}{\partial \vec{r}_2}\frac{\partial}{\partial \vec{r}^{\,-}}\right) && \text{(D.134)}\\
&= \frac{\partial}{\partial \vec{r}_1}\left(\frac{1}{2}\frac{\partial}{\partial \vec{r}^{\,+}} + \frac{\partial}{\partial \vec{r}^{\,-}}\right) - \frac{\partial}{\partial \vec{r}_2}\left(\frac{1}{2}\frac{\partial}{\partial \vec{r}^{\,+}} - \frac{\partial}{\partial \vec{r}^{\,-}}\right) && \text{(D.135)}\\
&= \left(\frac{1}{2}\frac{\partial}{\partial \vec{r}^{\,+}} + \frac{\partial}{\partial \vec{r}^{\,-}}\right)^2 - \left(\frac{1}{2}\frac{\partial}{\partial \vec{r}^{\,+}} - \frac{\partial}{\partial \vec{r}^{\,-}}\right)^2 && \text{(D.136)}\\
&= 2\frac{\partial}{\partial \vec{r}^{\,+}}\frac{\partial}{\partial \vec{r}^{\,-}} && \text{(D.137)}\\
&= 2\nabla_{\vec{r}^{\,+}} \cdot \nabla_{\vec{r}^{\,-}} && \text{(D.138)}
\end{aligned}
$$

$$
\begin{aligned}
\text{LHS Third term} &= -h(\vec{r}_1 t_1) + h(\vec{r}_2 t_2) && \text{(D.139)}\\
&= -h(\vec{r}^{\,+} + \tfrac{1}{2}\vec{r}^{\,-}, t^+ + \tfrac{1}{2}t^-) + h(\vec{r}^{\,+} - \tfrac{1}{2}\vec{r}^{\,-}, t^+ - \tfrac{1}{2}t^-)\\
&\mid \ \text{Taylor expand to first order}\\
&\approx -\left(1 + \frac{1}{2}\vec{r}^{\,-}\cdot\nabla_{\vec{r}^{\,+}} + \frac{1}{2}t^-\frac{\partial}{\partial t^+}\right)h(\vec{r}^{\,+}t^+) + \left(1 - \frac{1}{2}\vec{r}^{\,-}\cdot\nabla_{\vec{r}^{\,+}} - \frac{1}{2}t^-\frac{\partial}{\partial t^+}\right)h(\vec{r}^{\,+}t^+)\\
&= -\left(\vec{r}^{\,-}\cdot\nabla_{\vec{r}^{\,+}} + t^-\frac{\partial}{\partial t^+}\right)h(\vec{r}^{\,+}t^+) && \text{(D.140)}
\end{aligned}
$$

The LHS is now,

$$
\left(i\hbar\frac{\partial}{\partial t^+} + \frac{\hbar^2}{m}\nabla_{\vec{r}^{\,+}}\cdot\nabla_{\vec{r}^{\,-}} - \left(\vec{r}^{\,-}\cdot\nabla_{\vec{r}^{\,+}} + t^-\frac{\partial}{\partial t^+}\right)h(\vec{r}^{\,+}t^+)\right)G^<(\vec{r}^{\,-}t^-\vec{r}^{\,+}t^+) \tag{D.141}
$$

Define the Fourier transform of $\vec{r}^{\,-}$ and t^-, [5]

$$
G^<(\vec{p}\omega\vec{r}^{\,+}t^+) = \int d\vec{r}^{\,-}dt^- e^{-i\frac{\vec{p}}{\hbar}\cdot\vec{r}^{\,-}+i\omega t^-}G^<(\vec{r}^{\,-}t^-\vec{r}^{\,+}t^+) \tag{D.142}
$$

and we apply its inverse to the LHS

$$
\begin{aligned}
\text{LHS} &= \left(i\hbar\frac{\partial}{\partial t^+} + \frac{\hbar^2}{m}\nabla_{\vec{r}^{\,+}}\cdot\nabla_{\vec{r}^{\,-}} - \left(\vec{r}^{\,-}\cdot\nabla_{\vec{r}^{\,+}} + t^-\frac{\partial}{\partial t^+}\right)h(\vec{r}^{\,+}t^+)\right)\\
&\quad\times\int\frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{i\frac{\vec{p}}{\hbar}\cdot\vec{r}^{\,-}-i\omega t^-}G^<(\vec{p}\omega\vec{r}^{\,+}t^+) && \text{(D.143)}\\
&= \int\frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}\left(i\hbar\frac{\partial}{\partial t^+} + \frac{\hbar^2}{m}\frac{i}{\hbar}\vec{p}\cdot\nabla_{\vec{r}^{\,+}}\right)e^{i\frac{\vec{p}}{\hbar}\cdot\vec{r}^{\,-}-i\omega t^-}G^<(\vec{p}\omega\vec{r}^{\,+}t^+)\\
&\quad-\left(\vec{r}^{\,-}\cdot\nabla_{\vec{r}^{\,+}}h(\vec{r}^{\,+}t^+)\right)e^{i\frac{\vec{p}}{\hbar}\cdot\vec{r}^{\,-}-i\omega t^-}G^<(\vec{p}\omega\vec{r}^{\,+}t^+) - \left(t^-\frac{\partial}{\partial t^+}h(\vec{r}^{\,+}t^+)\right)e^{i\frac{\vec{p}}{\hbar}\cdot\vec{r}^{\,-}-i\omega t^-}G^<(\vec{p}\omega\vec{r}^{\,+}t^+)\\
&\mid \ \text{write } \left(\vec{r}^{\,-}\cdot\nabla_{\vec{r}^{\,+}}h\right)e^{i\frac{\vec{p}}{\hbar}\cdot\vec{r}^{\,-}-i\omega t^-}G^< = \frac{\hbar}{i}\left(\nabla_{\vec{r}^{\,+}}h\right)\cdot\left(\nabla_{\vec{p}}e^{i\frac{\vec{p}}{\hbar}\cdot\vec{r}^{\,-}-i\omega t^-}\right)G^<\\
&\mid \ \text{then integrate by parts for } \vec{p} \text{ and drop the surface term}\\
&\mid \ \text{to get } i\hbar e^{i\frac{\vec{p}}{\hbar}\cdot\vec{r}^{\,-}-i\omega t^-}\left(\nabla_{\vec{r}^{\,+}}h\right)\cdot\left(\nabla_{\vec{p}}G^<\right)
\end{aligned}
$$

[5] This fails when the external disturbance involves electromagnetic fields. Gauge invariance is spolit and a compatible Fourier transform is needed. This is done in the next section.

$$\begin{aligned}
& \mid \quad \text{do the same for the last term} \\
= & \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{i\frac{\vec{p}}{\hbar}\cdot\vec{r}^{\,-}-i\omega t^-} \\
& i\hbar\left(\frac{\partial}{\partial t^+}+\frac{\vec{p}}{m}\cdot\nabla_{\vec{r}^{\,+}}-\left(\nabla_{\vec{r}^{\,+}}h(\vec{r}^{\,+}t^+)\right)\cdot\nabla_{\vec{p}}+\left(\frac{\partial}{\partial t^+}h(\vec{r}^{\,+}t^+)\right)\frac{\partial}{\partial\hbar\omega}\right)G^<(\vec{p}\omega\vec{r}^{\,+}t^+) \qquad \text{(D.144)}
\end{aligned}$$

Now for RHS, we will expand to first order in gradient. Here we refer to the derivation in the chapter on NEGF since most of the steps are similar and it is the simpler case here. We will quote some explicit expressions.

$$\begin{aligned}
& \text{RHS of pre-QKE} \\
= & \int_{t_0\to-\infty}^{\infty}dt_3\int d\vec{r}_3\left(\Sigma^R(\vec{r}_1t_1\vec{r}_3t_3)G^<(\vec{r}_3t_3\vec{r}_2t_2)+\Sigma^<(\vec{r}_1t_1\vec{r}_3t_3)G^R(\vec{r}_3t_3\vec{r}_2t_2)\right. \\
& \left.-G^R(\vec{r}_1t_1\vec{r}_3t_3)\Sigma^<(\vec{r}_3t_3\vec{r}_2t_2)-G^<(\vec{r}_1t_1\vec{r}_3t_3)\Sigma^A(\vec{r}_3t_3\vec{r}_2t_2)\right) \qquad \text{(D.145)} \\
& \mid \quad \text{write the retarded and advanced functions into the lesser and greater functions} \\
= & \int_{t_0\to-\infty}^{t_1}dt_3\int d\vec{r}_3\left(\Sigma^>-\Sigma^<\right)(\vec{r}_1t_1\vec{r}_3t_3)G^<(\vec{r}_3t_3\vec{r}_2t_2) \\
& +\int_{t_0\to-\infty}^{t_2}dt_3\int d\vec{r}_3\Sigma^<(\vec{r}_1t_1\vec{r}_3t_3)\left(G^<-G^>\right)(\vec{r}_3t_3\vec{r}_2t_2) \\
& -\int_{t_0\to-\infty}^{t_1}dt_3\int d\vec{r}_3\left(G^>-G^<\right)(\vec{r}_1t_1\vec{r}_3t_3)\Sigma^<(\vec{r}_3t_3\vec{r}_2t_2) \\
& -\int_{t_0\to-\infty}^{t_2}dt_3\int d\vec{r}_3G^<(\vec{r}_1t_1\vec{r}_3t_3)\left(\Sigma^<-\Sigma^>\right)(\vec{r}_3t_3\vec{r}_2t_2) \qquad \text{(D.146)}
\end{aligned}$$

The subsequent steps will be to change them into Wigner coordinates as defined earlier and gradient expand to first order. Then extract the Fourier component based on the Fourier transform defined earlier. The result is,

$$\begin{aligned}
& \text{Fourier component of RHS (up to first order)} \\
= & \Sigma^>(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)G^<(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)-G^>(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)\Sigma^<(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) \\
& +\frac{\hbar}{i}\left[\tilde{\sigma},G^<\right]_{GPB}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)-\frac{\hbar}{i}\left[\tilde{b},\Sigma^<\right]_{GPB}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) \qquad \text{(D.147)}
\end{aligned}$$

where $\tilde{\sigma}$ and $\tilde{b}$ are the Fourier components of

$$\tilde{\sigma}(\vec{r}^{\,-}t^-\vec{r}^{\,+}t^+) \equiv \frac{t^-}{|t^-|}\frac{1}{2}\left(\Sigma^>-\Sigma^<\right)(\vec{r}^{\,-}t^-\vec{r}^{\,+}t^+) \qquad \text{(D.148)}$$

$$\tilde{b}(\vec{r}^{\,-}t^-\vec{r}^{\,+}t^+) \equiv \frac{t^-}{|t^-|}\frac{1}{2}\left(G^>-G^<\right)(\vec{r}^{\,-}t^-\vec{r}^{\,+}t^+) \qquad \text{(D.149)}$$

respectively. The generalized Poisson bracket is defined as

$$\begin{aligned}
& [X,Y]_{GPB}(\vec{p}\omega\vec{r}^{\,+}t^+) \\
\equiv & \frac{\partial X(\vec{p}\omega\vec{r}^{\,+}t^+)}{\partial\omega}\frac{\partial Y(\vec{p}\omega\vec{r}^{\,+}t^+)}{\partial t^+}-\frac{\partial X(\vec{p}\omega\vec{r}^{\,+}t^+)}{\partial t^+}\frac{\partial Y(\vec{p}\omega\vec{r}^{\,+}t^+)}{\partial\omega} \\
& -\left(\nabla_{\vec{p}}X(\vec{p}\omega\vec{r}^{\,+}t^+)\right)\cdot\left(\nabla_{\vec{r}^{\,+}}Y(\vec{p}\omega\vec{r}^{\,+}t^+)\right)+\left(\nabla_{\vec{r}^{\,+}}X(\vec{p}\omega\vec{r}^{\,+}t^+)\right)\cdot\left(\nabla_{\vec{p}}Y(\vec{r}\omega\vec{r}^{\,+}t^+)\right) \qquad \text{(D.150)}
\end{aligned}$$

From the chapter on NEGF, it is obvious that $\tilde{\sigma}(\vec{p}\omega\vec{r}^{\,+}t^+)$ and $\tilde{b}(\vec{p}\omega\vec{r}^{\,+}t^+)$ take on similar forms as their phonon counterparts, they are

$$
\begin{aligned}
\tilde{b}(\vec{p}\omega\vec{r}^{\,+}t^+) &= \mathcal{P}\int\frac{d\omega'}{2\pi}\frac{A(\vec{p}\omega'\vec{r}^{\,+}t^+)}{\omega-\omega'} && \text{(D.151)}\\
&\quad\mid\ \text{with analogy to Kramers-Kronig relations, we may write}\\
&= \Re G^{\text{R or A}}(\vec{p}\omega\vec{r}^{\,+}t^+) && \text{(D.152)}\\
\tilde{\sigma}(\vec{p}\omega\vec{r}^{\,+}t^+) &= \mathcal{P}\int\frac{d\omega'}{2\pi}\frac{\Gamma(\vec{p}\omega'\vec{r}^{\,+}t^+)}{\omega-\omega'} && \text{(D.153)}\\
&\quad\mid\ \text{with analogy to Kramers-Kronig relations, we may write}\\
&= \Re\Sigma^{\text{R or A}}(\vec{p}\omega\vec{r}^{\,+}t^+) && \text{(D.154)}
\end{aligned}
$$

We note that actually the LHS can be written into a generalized Poisson bracket form. We check backwards.

$$
\begin{aligned}
\text{LHS} &= \frac{\partial G^<}{\partial t^+}+\frac{\vec{p}}{m}\cdot\left(\nabla_{\vec{r}^{\,+}}G^<\right)-\left(\nabla_{\vec{r}^{\,+}}h\right)\cdot\left(\nabla_{\vec{p}}G^<\right)+\frac{\partial h}{\partial t^+}\frac{\partial G^<}{\partial\omega} && \text{(D.155)}\\
&\quad\mid\ \text{we postulate that it has the following form}\\
&= \frac{\partial ?}{\partial\omega}\frac{\partial G^<}{\partial t^+}-\frac{\partial ?}{\partial t^+}\frac{\partial G^<}{\partial\omega}+\left(\nabla_{\vec{r}^{\,+}}?\right)\cdot\left(\nabla_{\vec{p}}G^<\right)-\left(\nabla_{\vec{r}^{\,+}}G^<\right)\cdot\left(\nabla_{\vec{p}}?\right) && \text{(D.156)}\\
&\quad\mid\ \text{so, by inspection, } \frac{\partial ?}{\partial\omega}=1,\ \frac{\partial ?}{\partial t^+}=-\frac{\partial h}{\partial t^+},\ \nabla_{\vec{r}^{\,+}}?=-\nabla_{\vec{r}^{\,+}}h \text{ and } \nabla_{\vec{p}}?=-\frac{\vec{p}}{m}\\
&\quad\mid\ \text{we guess that } ?=\omega-\frac{\vec{p}^2}{2m}-h(\vec{r}^{\,+}t^+)=G^{(0)-1}(\vec{p}\omega\vec{r}^{\,+}t^+)-h(\vec{r}^{\,+}t^+)\\
&= \left[G^{(0)-1}(\vec{p}\omega\vec{r}^{\,+}t^+)-h(\vec{r}^{\,+}t^+),G^<(\vec{p}\omega\vec{r}^{\,+}t^+)\right]_{GPB} && \text{(D.157)}
\end{aligned}
$$

The final expression for pre-QKE to first order in gradient expansion is

$$
\boxed{
\begin{aligned}
& i\hbar\left[G^{(0)-1}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)-h(\vec{r}_1^{\,+}t_1^+),G^<(\vec{p}_1\omega\vec{r}_1^{\,+}t_1^+)\right]_{GPB}\\
=\ & \Sigma^>(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)G^<(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)-G^>(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)\Sigma^<(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)\\
& +\frac{\hbar}{i}\left[\Re\Sigma^{\text{R or A}},G^<\right]_{GPB}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)-\frac{\hbar}{i}\left[\Re G^{\text{R or A}},\Sigma^<\right]_{GPB}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)
\end{aligned}
} \qquad \text{(D.158)}
$$

As noted by Baym in the reference, the 3rd term on RHS can be "transferred" to LHS.

We can now compare with the expression derived in KB equations (3.350) and come up with a receipe to "short circuit" the gradient expansion derivation and the receipe allows higher orders of gradient expansion to be deduced easily. The receipe is (operators E and F are dummy labels)

- Drop the terms "initial"
- For anticommutators, $\int_t\frac{1}{2}\left[E,F\right]_+\longrightarrow E(\vec{p}\omega\vec{r}^{\,+}t^+)F(\vec{p}\omega\vec{r}^{\,+}t^+)$
- For commutators, in first order gradient expansion, $\int_t[E,F]_-\longrightarrow[E,F]_{GPB}(\vec{p}\omega\vec{r}^{\,+}t^+)$
- For commutators, in all orders of gradient expansion (except the zeroth order), $\int_t[E,F]_-\longrightarrow\exp\left(\frac{i}{2}\left(\frac{\partial^E}{\partial\omega}\frac{\partial^F}{\partial t^+}-\frac{\partial^E}{\partial t^+}\frac{\partial^F}{\partial\omega}-\nabla^E_{\vec{p}}\cdot\nabla^F_{\vec{r}^{\,+}}+\nabla^E_{\vec{r}^{\,+}}\cdot\nabla^F_{\vec{p}}\right)\right)E(\vec{p}\omega\vec{r}^{\,+}t^+)F(\vec{p}\omega\vec{r}^{\,+}t^+)$

D.4.1.2 Gauge Invariant Fourier Transform

If the driving field $h(\vec{r}t)$ is an electromagnetic field (introduced through its scalar and/or vector potential) then we realize the usual Fourier transform is not gauge invariant. We follow [Haug2007] chapter

7 and introduce gauge invariant Fourier transforms and fix the pre-QKE.

Gauge invariant quantities are denoted as $G^{(GI)}$. We construct these quantities by modifying the Fourier transform.

$$G^{(GI)}(\vec{p}\omega\vec{r}^{\,+}t^{+}) = \int d\vec{r}^{\,-}dt^{-}e^{\frac{i}{\hbar}W}G(\vec{r}^{\,-}t^{-}\vec{r}^{\,+}t^{+}) \tag{D.159}$$

where (q is the charge of the particle)

$$W = \int_{-1/2}^{1/2} d\lambda \left(t^{-}\left(\hbar\omega + q\phi(\vec{r}^{\,+}+\lambda\vec{r}^{\,-}, t^{+}+\lambda t^{-})\right) - \vec{r}^{\,-}\cdot\left(\vec{p}+q\vec{A}(\vec{r}^{\,+}+\lambda\vec{r}^{\,-}, t^{+}+\lambda t^{-})\right)\right) \tag{D.160}$$

For one-time, one-space quantities, their coordinates are simply the same as their "center coordinates". Thus Maxwell's equations in Wigner coordinates is the same as usual.

$$\vec{E}(\vec{r}^{\,+}t^{+}) = -\nabla_{\vec{r}^{\,+}}\phi(\vec{r}^{\,+}t^{+}) - \frac{\partial}{\partial t^{+}}\vec{A}(\vec{r}^{\,+}t^{+}) \tag{D.161}$$

$$\vec{B}(\vec{r}^{\,+}t^{+}) = \nabla_{\vec{r}^{\,+}}\times\vec{A}(\vec{r}^{\,+}t^{+}) \tag{D.162}$$

Now we gauge transform [6] $G^{(GI)}$ and check that the form of W given above is correct.

$$\begin{aligned}
& G^{(GI)'}(\vec{p}\omega\vec{r}^{\,+}t^{+}) \\
= & \int d\vec{r}^{\,-}\int dt^{-}e^{\frac{i}{\hbar}W'}G'(\vec{r}^{\,-}t^{-}\vec{r}^{\,+}t^{+}) && \text{(D.165)} \\
| & \quad \text{recall that } G(t_1t_2)\propto\langle T(\psi_H(t_1)\psi_H^{\dagger}(t_2))\rangle = \langle T(\psi_H(t^{+}+\tfrac{1}{2}t^{-})\psi_H^{\dagger}(t^{+}-\tfrac{1}{2}t^{-}))\rangle \\
| & \quad \text{recall the second quantization relations } \psi=\textstyle\sum(\text{wave function})c \text{ and } \psi^{\dagger}=\textstyle\sum(\text{wave function})^{*}c^{\dagger} \\
| & \quad \text{recall gauge transformations of wavefunctions,} \\
| & \quad (\text{wave function})\rightarrow(\text{wave function})e^{iq\chi} \text{ and } (\text{wave function})^{*}\rightarrow(\text{wave function})^{*}e^{-iq\chi} \\
= & \int d\vec{r}^{\,-}\int dt^{-}e^{\frac{i}{\hbar}(W+\Delta W)}G(\vec{r}^{\,-}t^{-}\vec{r}^{\,+}t^{+})e^{iq\chi(\vec{r}^{\,+}+\frac{1}{2}\vec{r}^{\,-},t^{+}+\frac{1}{2}t^{-})}e^{-iq\chi(\vec{r}^{\,+}+\frac{1}{2}\vec{r}^{\,-},t^{+}+\frac{1}{2}t^{-})} && \text{(D.166)}
\end{aligned}$$

where

$$\begin{aligned}
W' &= \int_{-1/2}^{1/2} d\lambda\left[t^{-}\left(\hbar\omega+q\phi'\right)-\vec{r}^{\,-}\cdot\left(\vec{p}+q\vec{A}'\right)\right] && \text{(D.167)} \\
&= W + \int_{-1/2}^{1/2} d\lambda\left[t^{-}\left(-q\frac{\partial}{\partial(t^{+}+\lambda t^{-})}\chi(\vec{r}^{\,+}+\lambda\vec{r}^{\,-},t^{+}+\lambda t^{-})\right)\right. \\
&\qquad \left. -\vec{r}^{\,-}\cdot q\nabla_{(\vec{r}^{\,+}+\lambda\vec{r}^{\,-})}\chi(\vec{r}^{\,+}+\lambda\vec{r}^{\,-},t^{+}+\lambda t^{-})\right] && \text{(D.168)} \\
&| \quad \text{Let } \vec{r}^{\,+}+\lambda\vec{r}^{\,-}=\vec{r}_1,\ \vec{r}^{\,+}-\lambda\vec{r}^{\,-}=\vec{r}_2 \text{ then } \vec{r}^{\,-}=\frac{1}{2\lambda}(\vec{r}_1-\vec{r}_2)
\end{aligned}$$

[6] A reminder of gauge transformations,

$$\vec{A}(\vec{r}t) \rightarrow \vec{A}'(\vec{r}t) = \vec{A}(\vec{r}t)+\nabla_{\vec{r}}\chi(\vec{r}t) \tag{D.163}$$

$$\phi(\vec{r}t) \rightarrow \phi'(\vec{r}t) = \phi(\vec{r}t)-\frac{\partial}{\partial t}\chi(\vec{r}t) \tag{D.164}$$

$$\begin{aligned}
&= W - q\int_{-1/2}^{1/2} d\lambda \left(t^{-}\frac{\partial}{\partial t_1}\chi(\vec{r}_1 t_1) + \vec{r}^{\,-}\cdot\nabla_{\vec{r}_1}\chi(\vec{r}_1 t_1)\right) && \text{(D.169)}\\
&\mid \quad \text{treat } \lambda \text{ as a function of 4 variables, } \lambda(\vec{r}_1\vec{r}_2 t_1 t_2)\\
&\mid \quad \text{then we can write } t_{-}\frac{\partial}{\partial t_1} = \frac{\partial t_1}{\partial \lambda}\frac{\partial}{\partial t_1} \text{ where } t_1 = t^{+}+\lambda t^{-}\\
&\mid \quad \text{then we can write } \vec{r}^{\,-}\cdot\nabla_{\vec{r}_1} = \frac{\partial \vec{r}_1}{\partial\lambda}\nabla_{\vec{r}_1} \text{ where } \vec{r}_1 = \vec{r}^{\,+}+\lambda\vec{r}^{\,-}\\
&\mid \quad \text{we get a total derivative in the end}\\
&= W - q\int_{-1/2}^{1/2} d\lambda \frac{d}{d\lambda}\chi(\vec{r}_1 t_1) && \text{(D.170)}\\
&= W - q\int_{-1/2}^{1/2} d\lambda \frac{d}{d\lambda}\chi(\vec{r}^{\,+}+\lambda\vec{r}^{\,-}, t^{+}+\lambda t^{-}) && \text{(D.171)}\\
&= W - q\chi(\vec{r}^{\,+}+\tfrac{1}{2}\vec{r}^{\,-}, t^{+}+\tfrac{1}{2}t^{-}) + q\chi(\vec{r}^{\,+}-\tfrac{1}{2}\vec{r}^{\,-}, t^{+}-\tfrac{1}{2}t^{-}) && \text{(D.172)}
\end{aligned}$$

which cancels the phases coming from G and we thus get $G^{(GI)'}(\vec{p}\omega\vec{r}^{\,+}t^{+}) = G^{(GI)}(\vec{p}\omega\vec{r}^{\,+}t^{+})$.

Thus for electrons driven by electromagnetic fields, kinetic equations must be constructed with the gauge invariant Green's functions $G^{(GI)}$.

Now let's work out the driving terms (LHS) of the kinetic equations for various configurations of electric fields and magnetic fields.

D.4.1.3 Gauge Invariant Driving Term (LHS) for constant $\vec{E}$ and $\vec{B}$

[Driving by Constant $\vec{E}$:] First we calculate the case where a constant $\vec{E}$ drives the system and we work out the LHS of the kinetic equation in different gauges just to illustrate the gauge invariant construction. Then we extend it and work out the case where a constant $\vec{E}$ and a constant $\vec{B}$ drives the system.

If we use the gauge $\phi(\vec{r}^{\,+}+\lambda\vec{r}^{\,-}, t^{+}+\lambda t^{-}) = -\vec{r}^{\,+}\cdot\vec{E}$ then the modified Fourier transform to use is

$$G^{(GI)}(\vec{p}\omega\vec{r}^{\,+}t^{+}) = \int dt^{-}d\vec{r}^{\,-}e^{\frac{i}{\hbar}W}G^{(\phi)}(\vec{r}^{\,-}t^{-}\vec{r}^{\,+}t^{+}) \tag{D.173}$$

where

$$\begin{aligned}
W &= \int_{-1/2}^{1/2} d\lambda \left(t^{-}(\hbar\omega + q(-\vec{r}^{\,+}\cdot\vec{E})) - \vec{r}^{\,-}\cdot\vec{p}\right) && \text{(D.174)}\\
&\mid \quad \text{the integral is trivial } \frac{1}{2} - \left(-\frac{1}{2}\right) = 1\\
&= t^{-}(\hbar\omega - q\vec{E}\cdot\vec{r}^{\,+}) - \vec{p}\cdot\vec{r}^{\,-} && \text{(D.175)}\\
G^{(GI)}(\vec{p}\omega\vec{r}^{\,+}t^{+}) &= \int dt^{-}d\vec{r}^{\,-}e^{\frac{i}{\hbar}(\hbar\omega - q\vec{E}\cdot\vec{r}^{\,+})t^{-} - \frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}}G^{(\phi)}(\vec{r}^{\,-}t^{-}\vec{r}^{\,+}t^{+}) && \text{(D.176)}
\end{aligned}$$

If we use the vector potential gauge, $\vec{A}(\vec{r}^{\,+}+\lambda\vec{r}^{\,-}, t^{+}+\lambda t^{-}) = -t^{+}\vec{E}$ then the modified Fourier transform is

$$G^{(GI)}(\vec{p}\omega\vec{r}^{\,+}t^{+}) = \int dt^{-}d\vec{r}^{\,-}e^{\frac{i}{\hbar}W}G^{(\vec{A})}(\vec{r}^{\,-}t^{-}\vec{r}^{\,+}t^{+}) \tag{D.177}$$

where

$$
\begin{aligned}
W &= \int_{-1/2}^{1/2} d\lambda \left(t^- \hbar\omega - \vec{r}^{\,-} \cdot (\vec{p} - q\vec{E}t^+) \right) && \text{(D.178)}\\
&\quad | \ \text{the integral is trivial } \frac{1}{2} - \left(-\frac{1}{2}\right) = 1 \\
&= \hbar\omega t^- - (\vec{p} - q\vec{E}t^+) \cdot \vec{r}^{\,-} && \text{(D.179)}\\
G^{(GI)}(\vec{p}\omega\vec{r}^{\,+}t^+) &= \int dt^- d\vec{r}^{\,-} e^{i\omega t^- - \frac{i}{\hbar}(\vec{p}-q\vec{E}t^+)\cdot\vec{r}^{\,-}} G^{(\vec{A})}(\vec{r}^{\,-}t^-\vec{r}^{\,+}t^+) && \text{(D.180)}
\end{aligned}
$$

Now that we have the expressions for the Fourier transform in two different gauges for the same constant $\vec{E}$ applied to the system, we can now construct the proper (LHS) driving term for the gauge invariant Green's function.

We start with the case of the scalar potential gauge [7]. Recall the form of the LHS after it has been written into Wigner coordinates to first order gradient exapansion.

$$
\begin{aligned}
\text{LHS} &= \left(i\hbar\frac{\partial}{\partial t^+} + \frac{\hbar^2}{m}\nabla_{\vec{r}^{\,+}} \cdot \nabla_{\vec{r}^{\,-}} - \left(\vec{r}^{\,-} \cdot \nabla_{\vec{r}^{\,+}} + t^- \frac{\partial}{\partial t^+} \right) h(\vec{r}^{\,+}t^+) \right) G^<(\vec{r}^{\,-}t^-\vec{r}^{\,+}t^+) && \text{(D.184)}\\
&\quad | \ \text{in the scalar potential gauge, } h(\vec{r}t) = q\phi(\vec{r}) = -q\vec{r}\cdot\vec{E} \\
&= \left(i\hbar\frac{\partial}{\partial t^+} + \frac{\hbar^2}{m}\nabla_{\vec{r}^{\,+}} \cdot \nabla_{\vec{r}^{\,-}} + q\vec{r}^{\,-} \cdot \vec{E} \right) G^{(\phi)<}(\vec{r}^{\,-}t^-\vec{r}^{\,+}t^+) && \text{(D.185)}
\end{aligned}
$$

Now we employ the modified Fourier transform (for scalar potential).

$$
\begin{aligned}
\text{LHS} &= \left(i\hbar\frac{\partial}{\partial t^+} + \frac{\hbar^2}{m}\nabla_{\vec{r}^{\,+}} \cdot \nabla_{\vec{r}^{\,-}} + q\vec{r}^{\,-} \cdot \vec{E} \right) \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi} e^{-\frac{i}{\hbar}(\hbar\omega - q\vec{E}\cdot\vec{r}^{\,+})t^- + \frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \\
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi} \left(e^{-\frac{i}{\hbar}(\hbar\omega - q\vec{E}\cdot\vec{r}^{\,+})t^- + \frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} \left(i\hbar\frac{\partial}{\partial t^+} \right) G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \right.\\
&\quad + e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} \left(\frac{\hbar^2}{m}\frac{i}{\hbar}\vec{p}\cdot\nabla_{\vec{r}^{\,+}} \right) e^{-\frac{i}{\hbar}(\hbar\omega - q\vec{E}\cdot\vec{r}^{\,+})t^-} G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \\
&\quad \left. + e^{-\frac{i}{\hbar}(\hbar\omega - q\vec{E}\cdot\vec{r}^{\,+})t^-} \left(q\vec{E}\cdot\frac{\hbar}{i}\left(\nabla_{\vec{p}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} \right) \right) G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \right) && \text{(D.186)}\\
&\quad | \ \text{for 3rd line, integrate by parts to get,} \\
&\quad | \ \left(\nabla_{\vec{p}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} \right) G^{(GI)<} = \nabla_{\vec{p}}\left(e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} G^{(GI)<} \right) - e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} \left(\nabla_{\vec{p}} G^{(GI)<} \right) \text{ and drop surface term} \\
&\quad | \ \text{for 2nd line, use product rule} \\
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi} \left(e^{-\frac{i}{\hbar}(\hbar\omega - q\vec{E}\cdot\vec{r}^{\,+})t^- + \frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} \left(i\hbar\frac{\partial}{\partial t^+} \right) G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \right.
\end{aligned}
$$

[7] The full Hamiltonian (in position representation) is

$$
\begin{aligned}
H &= \frac{1}{2m}\left(\vec{p} + q\vec{A} \right)^2 + q\phi && \text{(D.181)}\\
&\quad | \ \text{in position representation} && \text{(D.182)}\\
&= \frac{1}{2m}\left(\frac{\hbar}{i}\nabla + q\vec{A} \right)^2 + q\phi = -\frac{\hbar^2}{2m}\nabla^2 + \frac{i\hbar q}{m}\vec{A}\cdot\nabla + \frac{i\hbar q}{2m}(\nabla\cdot\vec{A}) + \frac{q^2}{2m}\vec{A}^2 + q\phi && \text{(D.183)}
\end{aligned}
$$

This case is simply where $\vec{A} = 0$.

$$+e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}}\left(\frac{\hbar^2}{m}\left(\frac{i}{\hbar}\right)^2\vec{p}\cdot q\vec{E}t^-e^{-\frac{i}{\hbar}(\hbar\omega-q\vec{E}\cdot\vec{r}^{\,+})t^-}+e^{-\frac{i}{\hbar}(\hbar\omega-q\vec{E}\cdot\vec{r}^{\,+})t^-}\frac{\hbar^2}{m}\frac{i}{\hbar}\vec{p}\cdot\nabla_{\vec{r}^{\,+}}\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)$$
$$+e^{-\frac{i}{\hbar}(\hbar\omega-q\vec{E}\cdot\vec{r}^{\,+})t^-+\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}}\left(\frac{\hbar}{i}q\vec{E}\cdot\nabla_{\vec{p}}\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)\Bigg) \tag{D.187}$$

| for 2nd line first term, we write $t^-e^{-\frac{i}{\hbar}(\hbar\omega-q\vec{E}\cdot\vec{r}^{\,+})t^-}=e^{-\frac{i}{\hbar}(-q\vec{E}\cdot\vec{r}^{\,+})t^-}i\frac{\partial}{\partial\omega}e^{-i\omega t^-}$

| then integrate by parts and drop surface term

$$= \int\frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{-\frac{i}{\hbar}(\hbar\omega-q\vec{E}\cdot\vec{r}^{\,+})t^-+\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}}$$
$$\times\left(i\hbar\frac{\partial}{\partial t^+}+\frac{iq}{m}\vec{p}\cdot\vec{E}\frac{\partial}{\partial\omega}+\frac{i\hbar}{m}\vec{p}\cdot\nabla_{\vec{r}^{\,+}}+i\hbar q\vec{E}\cdot\nabla_{\vec{p}}\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \tag{D.188}$$
$$= \int\frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{-\frac{i}{\hbar}(\hbar\omega-q\vec{E}\cdot\vec{r}^{\,+})t^-+\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}}$$
$$\times\left(i\hbar\frac{\partial}{\partial t^+}+\frac{i\hbar}{m}\vec{p}\cdot\nabla_{\vec{r}^{\,+}}+i\hbar q\vec{E}\cdot\left(\nabla_{\vec{p}}+\frac{\vec{p}}{m\hbar}\frac{\partial}{\partial\omega}\right)\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \tag{D.189}$$

Thus the LHS to use when the electrons are driven by a constant $\vec{E}$ is

$$\text{LHS for constant }\vec{E}\text{:}\boxed{\left(i\hbar\frac{\partial}{\partial t^+}+\frac{i\hbar}{m}\vec{p}\cdot\nabla_{\vec{r}^{\,+}}+i\hbar q\vec{E}\cdot\left(\nabla_{\vec{p}}+\frac{\vec{p}}{m\hbar}\frac{\partial}{\partial\omega}\right)\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)} \tag{D.190}$$

[Driving by constant $\vec{E}$ and by constant $\vec{B}$:] We will now carry out the full derivation where the LHS is driven by a constant $\vec{E}$ and a constant $\vec{B}$ introduced via a vector potential. When the final expression is obtained, the reader can set $\vec{B}=0$ and see that the same driving term as above will be obtained.

The vector potential for constant $\vec{E}$ and constant $\vec{B}$ is as follows,

$$\vec{A}(\vec{r},t)=-t\vec{E}-\frac{1}{d}\vec{r}\times\vec{B} \tag{D.191}$$

where d =number of dimensions $=\nabla_{\vec{r}}\cdot\vec{r}$. [8] We quickly verify the vector potential using the Maxwell's equations.

$$\vec{E} = -\nabla\phi-\frac{\partial}{\partial t}\vec{A}=-\frac{\partial}{\partial t}(-t\vec{E})=\vec{E} \tag{D.192}$$
$$\vec{B} = \nabla\times\vec{A}=-\frac{1}{d}\left(\nabla_{\vec{r}}\times\left(\vec{r}\times\vec{B}\right)\right)=-\frac{1}{d}\left[\left(\nabla_{\vec{r}}\cdot\vec{B}\right)\vec{r}-\left(\nabla_{\vec{r}}\cdot\vec{r}\right)\vec{B}\right] \tag{D.193}$$

| with $\nabla_{\vec{r}}\cdot\vec{B}=0$ and $\nabla_{\vec{r}}\cdot\vec{r}=d$

$$= \vec{B} \tag{D.194}$$

The gauge invariant Fourier transform to use in this case is,

$$G^{(GI)}(\vec{p}\omega\vec{r}^{+}t^{+})=\int dt^-d\vec{r}^{\,-}e^{i\omega t^-}e^{-\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{+}\times\vec{B}\right)\cdot\vec{r}^{\,-}}G^{(\vec{A})}(\vec{r}^{\,-}t^-\vec{r}^{+}t^+) \tag{D.195}$$

[8] $d=3$ since we are usually working in 3-dimensions. $d=2$ when we deal with Hall geometries and Landau levels.

$$
\begin{aligned}
H(\text{without KE term}) &= h(\vec{r},t) && \text{(D.196)}\\
&= \frac{i\hbar q}{m}\vec{A}\cdot\nabla_{\vec{r}} + \frac{i\hbar q}{2m}\left(\nabla_{\vec{r}}\cdot\vec{A}\right) + \frac{q^2}{2m}\vec{A}^2 + q\phi && \text{(D.197)}\\
&\mid\ \text{we have } \phi=0,\ \vec{A}=-t\vec{E}-\frac{1}{d}\vec{r}\times\vec{B} \text{ and } \nabla_{\vec{r}}\cdot\vec{E}=0 \text{ (no source)}\\
&= \frac{i\hbar q}{m}(-t)\vec{E}\cdot\nabla + \frac{q^2}{2m}(-t\vec{E})^2\\
&\quad -\frac{i\hbar q}{m}\frac{1}{d}(\vec{r}\times\vec{B})\cdot\nabla_{\vec{r}} - \frac{i\hbar q}{2m}\frac{1}{d}\left(\nabla_{\vec{r}}\cdot(\vec{r}\times\vec{B})\right) + \frac{q^2}{2m}\frac{1}{d^2}(\vec{r}\times\vec{B})^2 && \text{(D.198)}\\
&\mid\ \text{use vector identity, } \nabla_{\vec{r}}\cdot(\vec{r}\times\vec{B}) = \vec{B}\cdot(\nabla_{\vec{r}}\times\vec{r}) - \vec{r}\cdot(\nabla_{\vec{r}}\times\vec{B})\\
&\mid\ \text{then } \nabla_{\vec{r}}\times\vec{r}=0 \text{ and } \nabla_{\vec{r}}\times\vec{B}=0^{9}\\
&= -\frac{i\hbar q}{m}t\vec{E}\cdot\nabla + \frac{q^2t^2}{2m}\vec{E}^2 - \frac{i\hbar q}{md}(\vec{r}\times\vec{B})\cdot\nabla_{\vec{r}} + \frac{q^2}{2md^2}(\vec{r}\times\vec{B})^2 && \text{(D.199)}
\end{aligned}
$$

The subtraction of the external field in pre-QKE is of the form, (here we cannot say that the external field is hermitian)

$$
\begin{aligned}
-h(\vec{r}_1t_1)+h^\dagger(\vec{r}_2t_2) &= \frac{i\hbar q}{m}t_1\vec{E}\cdot\nabla_{\vec{r}_1} - \frac{q^2t_1^2}{2m}\vec{E}^2 + \frac{i\hbar q}{m}t_2\vec{E}\cdot\nabla_{\vec{r}_2} + \frac{q^2t_2^2}{2m}\vec{E}^2\\
&\quad +\frac{i\hbar q}{md}(\vec{r}_1\times\vec{B})\cdot\nabla_{\vec{r}_1} - \frac{q^2}{2md^2}(\vec{r}_1\times\vec{B})^2 + \frac{i\hbar q}{md}(\vec{r}_2\times\vec{B})\cdot\nabla_{\vec{r}_2} - \frac{q^2}{2md^2}(\vec{r}_2\times\vec{B})^2\\
&\mid\ \text{write } \vec{r}_1=\vec{r}^{\,+}+\frac{1}{2}\vec{r}^{\,-} \text{ and } \vec{r}_2=\vec{r}^{\,+}-\frac{1}{2}\vec{r}^{\,-}\\
&= \frac{i\hbar q}{m}\vec{E}\cdot(t_1\nabla_{\vec{r}_1}+t_2\nabla_{\vec{r}_2}) - \frac{q^2}{2m}\vec{E}^2(t_1^2-t_2^2)\\
&\quad +\frac{i\hbar q}{md}\left((\vec{r}^{\,+}\times\vec{B})\cdot(\nabla_{\vec{r}_1}+\nabla_{\vec{r}_2}) + \frac{1}{2}(\vec{r}^{\,-}\times\vec{B})\cdot(\nabla_{\vec{r}_1}-\nabla_{\vec{r}_2})\right)\\
&\quad -\frac{q^2}{2md^2}\Bigg[((\vec{r}^{\,+}\times\vec{B})+\frac{1}{2}(\vec{r}^{\,-}\times\vec{B}))\cdot((\vec{r}^{\,+}\times\vec{B})+\frac{1}{2}(\vec{r}^{\,-}\times\vec{B}))\\
&\quad -((\vec{r}^{\,+}\times\vec{B})-\frac{1}{2}(\vec{r}^{\,-}\times\vec{B}))\cdot((\vec{r}^{\,+}\times\vec{B})-\frac{1}{2}(\vec{r}^{\,-}\times\vec{B}))\Bigg] && \text{(D.200)}\\
&\mid\ \text{change to Wigner coordinates, } t_1=t^+ + \frac{1}{2}t^- \text{ and } t_2=t^+-\frac{1}{2}t^-\\
&= \frac{i\hbar q}{m}\vec{E}\cdot\left(t^+(\nabla_{\vec{r}_1}+\nabla_{\vec{r}_2}) + \frac{1}{2}t^-(\nabla_{\vec{r}_1}-\nabla_{\vec{r}_2})\right) - \frac{q^2}{2m}\vec{E}^2t^-t^+\\
&\quad +\frac{i\hbar q}{md}\left((\vec{r}^{\,+}\times\vec{B})\cdot(\nabla_{\vec{r}_1}+\nabla_{\vec{r}_2}) + \frac{1}{2}(\vec{r}^{\,-}\times\vec{B})\cdot(\nabla_{\vec{r}_1}-\nabla_{\vec{r}_2})\right)\\
&\quad -\frac{q^2}{md^2}(\vec{r}^{\,+}\times\vec{B})\cdot(\vec{r}^{\,-}\times\vec{B}) && \text{(D.201)}\\
&\mid\ \text{change to Wigner coordinates, } \nabla_{\vec{r}_1}-\nabla_{\vec{r}_2}=2\nabla_{\vec{r}^{\,-}} \text{ and } \nabla_{\vec{r}_1}+\nabla_{\vec{r}_2}=\nabla_{\vec{r}^{\,+}}\\
&= \frac{i\hbar q}{m}\vec{E}\cdot\left(t^+\nabla_{\vec{r}^{\,+}}+t^-\nabla_{\vec{r}^{\,-}}\right) - \frac{q^2}{m}\vec{E}^2t^-t^+\\
&\quad +\frac{i\hbar q}{md}\left((\vec{r}^{\,+}\times\vec{B})\cdot\nabla_{\vec{r}^+} + (\vec{r}^{\,-}\times\vec{B})\cdot\nabla_{\vec{r}^{\,-}}\right) - \frac{q^2}{md^2}(\vec{r}^{\,+}\times\vec{B})\cdot(\vec{r}^{\,-}\times\vec{B})
\end{aligned}
$$

[9] $\nabla_{\vec{r}}\times\vec{B}=0$ from Maxwell's equation since there are no sources and a constant field causes no induction. Hope the argument is correct.

Now we substitute this expression into LHS of pre-QKE and use the Fourier transform modified for the vector potential.

$$\begin{aligned}
\text{LHS} &= \Bigg(i\hbar\frac{\partial}{\partial t^+} + \frac{\hbar^2}{m}\nabla_{\vec r^+}\cdot\nabla_{\vec r^-} + \frac{i\hbar q}{m}\vec E\cdot\left(t^-\nabla_{\vec r^-} + t^+\nabla_{\vec r^+}\right) - \frac{q^2}{m}t^+t^-\vec E^2 \\
&\quad + \frac{i\hbar q}{md}\left((\vec r^+\times\vec B)\cdot\nabla_{\vec r^+} + (\vec r^-\times\vec B)\cdot\nabla_{\vec r^-}\right) - \frac{q^2}{md^2}(\vec r^+\times\vec B)\cdot(\vec r^-\times\vec B)\Bigg) G^{(\vec A)<}(\vec r^-t^-\vec r^+t^+) \\
&= \Bigg(i\hbar\frac{\partial}{\partial t^+} + \frac{\hbar^2}{m}\nabla_{\vec r^+}\cdot\nabla_{\vec r^-} + \frac{i\hbar q}{m}\vec E\cdot\left(t^-\nabla_{\vec r^-} + t^+\nabla_{\vec r^+}\right) - \frac{q^2}{m}t^+t^-\vec E^2 \\
&\quad + \frac{i\hbar q}{md}\left((\vec r^+\times\vec B)\cdot\nabla_{\vec r^+} + (\vec r^-\times\vec B)\cdot\nabla_{\vec r^-}\right) - \frac{q^2}{md^2}(\vec r^+\times\vec B)\cdot(\vec r^-\times\vec B)\Bigg) \\
&\quad \times\int\frac{d\vec p}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{-i\omega t^- + \frac{i}{\hbar}\left(\vec p - q\vec Et^+ - \frac{q}{d}\vec r^+\times\vec B\right)\cdot\vec r^-} G^{(GI)<}(\vec p\omega\vec r^+t^+)
\end{aligned} \tag{D.202}$$

Since the expressions are quite complicated, we shall work them out term by term.

$$\text{First term} = \int\frac{d\vec p}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}\left(i\hbar\frac{\partial}{\partial t^+}\right)e^{-i\omega t^- + \frac{i}{\hbar}\left(\vec p - q\vec Et^+ - \frac{q}{d}\vec r^+\times\vec B\right)\cdot\vec r^-} G^{(GI)<}(\vec p\omega\vec r^+t^+) \tag{D.203}$$

$$\begin{aligned}
&= \int\frac{d\vec p}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{-i\omega t^- + \frac{i}{\hbar}\left(\vec p - q\vec Et^+ - \frac{q}{d}\vec r^+\times\vec B\right)\cdot\vec r^-} \\
&\quad \times\left(i\hbar\left(-\frac{i}{\hbar}q\vec E\cdot\vec r^-\right) + i\hbar\frac{\partial}{\partial t^+}\right)G^{(GI)<}(\vec p\omega\vec r^+t^+)
\end{aligned} \tag{D.204}$$

| write $\vec r^- e^{\frac{i}{\hbar}\vec p\cdot\vec r^-} = \frac{\hbar}{i}(\nabla_{\vec p}e^{\frac{i}{\hbar}\vec p\cdot\vec r^-})$ and integrate by parts then drop surface term

| essentially we have the "replacement" $\vec r^- \to -\frac{\hbar}{i}\nabla_{\vec p} = i\hbar\nabla_{\vec p}$

$$= \int\frac{d\vec p}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{-i\omega t^- + \frac{i}{\hbar}\left(\vec p - q\vec Et^+ - \frac{q}{d}\vec r^+\times\vec B\right)\cdot\vec r^-}\left(i\hbar q\vec E\cdot\nabla_{\vec p} + i\hbar\frac{\partial}{\partial t^+}\right)G^{(GI)<}(\vec p\omega\vec r^+t^+)$$

$$\begin{aligned}
\text{Second term} &= \int\frac{d\vec p}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}\left(\frac{\hbar^2}{m}\nabla_{\vec r^+}\cdot\nabla_{\vec r^-}\right)e^{-i\omega t^- + \frac{i}{\hbar}\left(\vec p - q\vec Et^+ - \frac{q}{d}\vec r^+\times\vec B\right)\cdot\vec r^-} G^{(GI)<}(\vec p\omega\vec r^+t^+) \\
&= \int\frac{d\vec p}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{-i\omega t^-} \\
&\quad \times\frac{\hbar^2}{m}\nabla_{\vec r^+}\cdot\left(\frac{i}{\hbar}\left(\vec p - q\vec Et^+ - \frac{q}{d}\vec r^+\times\vec B\right)e^{\frac{i}{\hbar}\left(\vec p - q\vec Et^+ - \frac{q}{d}\vec r^+\times\vec B\right)\cdot\vec r^-}G^{(GI)<}(\vec p\omega\vec r^+t^+)\right)
\end{aligned}$$

| use vector identity $\nabla\cdot(\psi\vec A) = \psi\nabla\cdot\vec A + \vec A\cdot\nabla\psi$ where ψ is a scalar function

$$\begin{aligned}
&= \int\frac{d\vec p}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{-i\omega t^-}\frac{\hbar^2}{m} \\
&\quad \times\Bigg[e^{\frac{i}{\hbar}\left(\vec p - q\vec Et^+ - \frac{q}{d}\vec r^+\times\vec B\right)\cdot\vec r^-}G^{(GI)<}(\vec p\omega\vec r^+t^+)\left(-\frac{i}{\hbar}\frac{q}{d}\nabla_{\vec r^+}\cdot(\vec r^+\times\vec B)\right) \\
&\quad + \frac{i}{\hbar}\left(\vec p - q\vec Et^+ - \frac{q}{d}\vec r^+\times\vec B\right)\cdot\left(\nabla_{\vec r^+}e^{\frac{i}{\hbar}\left(\vec p - q\vec Et^+ - \frac{q}{d}\vec r^+\times\vec B\right)\cdot\vec r^-}G^{(GI)<}(\vec p\omega\vec r^+t^+)\right)\Bigg]
\end{aligned}$$

| the first term is zero as we shown $\nabla\cdot(\vec r\times\vec B)$

| write $\vec r^+\times\vec B\cdot\vec r^- = \vec B\times\vec r^-\cdot\vec r^+$

$$
\begin{aligned}
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{-i\omega t^-}\frac{\hbar^2}{m}e^{\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad\times\left[\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\left(\left(-\frac{i}{\hbar}\frac{q}{d}\vec{B}\times\vec{r}^{\,-}\right)+\nabla_{\vec{r}^{\,+}}\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)\right] \\
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{-i\omega t^-}e^{\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad\left[\frac{q}{md}\vec{p}\cdot(\vec{B}\times\vec{r}^{\,-})-\frac{q^2}{md}t^+\vec{E}\cdot(\vec{B}\times\vec{r}^{\,-})-\frac{q}{md^2}(\vec{r}^{\,+}\times\vec{B})\cdot(\vec{B}\times\vec{r}^{\,-})\right. \\
&\quad\left.+\frac{i\hbar}{m}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}(\vec{r}^{\,+}\times\vec{B})\right)\cdot\nabla_{\vec{r}^{\,+}}\right]G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)
\end{aligned}
\tag{D.205}
$$

$$
\text{Third term} = \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}\left(\frac{i\hbar q}{m}\vec{E}\cdot t^-\nabla_{\vec{r}^{\,-}}\right)e^{i\omega t^-+\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}}G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)
$$

$$
= \int d\vec{p}d\omega e^{i\omega t^-+i(\vec{p}-q\vec{E}t^+)\cdot\vec{r}^{\,-}}\left(-qt^-\vec{E}\cdot i(\vec{p}-q\vec{E}t^+)\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \tag{D.206}
$$

$$
\begin{aligned}
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{i\omega t^-+\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad\times\frac{i\hbar q}{m}t^-\vec{E}\cdot\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)
\end{aligned}
\tag{D.207}
$$

$$
\begin{aligned}
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{i\omega t^-+\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad\times\left(-\frac{q}{m}t^-\vec{E}\cdot\vec{p}+\frac{q^2}{m}t^+t^-\vec{E}^2+\frac{q^2}{md}t^-\vec{E}\cdot(\vec{r}^{\,+}\times\vec{B})\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)
\end{aligned}
\tag{D.208}
$$

$$
\text{Fourth term} = \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}\left(\frac{i\hbar q}{m}\vec{E}\cdot t^+\nabla_{\vec{r}^{\,+}}\right)e^{i\omega t^-+\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}}G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)
$$

$| \quad$ write $\vec{r}^{\,+}\times\vec{B}\cdot\vec{r}^{\,-}=\vec{B}\times\vec{r}^{\,-}\cdot\vec{r}^{\,+}$

$$
\begin{aligned}
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{i\omega t^-+\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad\times\left(\frac{i\hbar q}{m}t^+\vec{E}\cdot\left(-\frac{i}{\hbar}\frac{q}{d}\vec{B}\times\vec{r}^{\,-}\right)+\frac{i\hbar q}{m}t^+\vec{E}\cdot\nabla_{\vec{r}^{\,+}}\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)
\end{aligned}
\tag{D.209}
$$

$$
\begin{aligned}
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{i\omega t^-+\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad\times\left(\frac{q^2}{m}t^+\vec{E}\cdot\left(\vec{B}\times\vec{r}^{\,-}\right)+\frac{i\hbar q}{m}t^+\vec{E}\cdot\nabla_{\vec{r}^{\,+}}\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)
\end{aligned}
\tag{D.210}
$$

$$
\text{Sixth term} = \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}\left(\frac{i\hbar q}{md}(\vec{r}^{\,+}\times\vec{B})\cdot\nabla_{\vec{r}^{\,+}}\right)e^{i\omega t^-+\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}}G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)
$$

$| \quad$ write $\vec{r}^{\,+}\times\vec{B}\cdot\vec{r}^{\,-}=\vec{B}\times\vec{r}^{\,-}\cdot\vec{r}^{\,+}$

$$
\begin{aligned}
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}e^{i\omega t^-+\frac{i}{\hbar}\left(\vec{p}-q\vec{E}t^+-\frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad\times\left(\frac{i\hbar q}{md}(\vec{r}^{\,+}\times\vec{B})\cdot\left(-\frac{i}{\hbar}\frac{q}{d}\vec{B}\times\vec{r}^{\,-}\right)+\frac{i\hbar q}{md}(\vec{r}^{\,+}\times\vec{B})\cdot\nabla_{\vec{r}^{\,+}}\right)G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)
\end{aligned}
\tag{D.211}
$$

$$
\begin{aligned}
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi} e^{i\omega t^- + \frac{i}{\hbar}\left(\vec{p} - q\vec{E}t^+ - \frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad \times \left(\frac{q^2}{md^2}(\vec{r}^{\,+}\times\vec{B})\cdot(\vec{B}\times\vec{r}^{\,-}) + \frac{i\hbar q}{md}(\vec{r}^{\,+}\times\vec{B})\cdot\nabla_{\vec{r}^{\,+}}\right) G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \qquad \text{(D.212)}
\end{aligned}
$$

Seventh term

$$
\begin{aligned}
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi}\left(\frac{i\hbar q}{md}(\vec{r}\times\vec{B})\cdot\nabla_{\vec{r}^{\,-}}\right) e^{i\omega t^- + \frac{i}{\hbar}\left(\vec{p} - q\vec{E}t^+ - \frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \qquad \text{(D.213)} \\
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi} e^{i\omega t^- + \frac{i}{\hbar}\left(\vec{p} - q\vec{E}t^+ - \frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad \times \left(\frac{i\hbar q}{md}(\vec{r}^{\,-}\times\vec{B})\cdot\left(\frac{i}{\hbar}\left(\vec{p} - q\vec{E}t^+ - \frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\right)\right) G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \qquad \text{(D.214)} \\
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi} e^{i\omega t^- + \frac{i}{\hbar}\left(\vec{p} - q\vec{E}t^+ - \frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad \times \left(-\frac{q}{md}(\vec{r}^{\,-}\times\vec{B})\cdot\vec{p} + \frac{q^2}{md}(\vec{r}^{\,-}\times\vec{B})\cdot\vec{E}t^+ + \frac{q^2}{md}(\vec{r}^{\,-}\times\vec{B})\cdot(\vec{r}^{\,+}\times\vec{B})\right) G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+)
\end{aligned}
$$

So, we can now put all the terms together and many will cancel. Then we extract the (gauge invariant) Fourier component.

$$
\begin{aligned}
\text{LHS} &= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi} e^{i\omega t^- + \frac{i}{\hbar}\left(\vec{p} - q\vec{E}t^+ - \frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad \times \left(i\hbar\frac{\partial}{\partial t^+} + i\hbar q\vec{E}\cdot\nabla_{\vec{p}} + \frac{q}{md}\vec{p}\cdot(\vec{B}\times\vec{r}^{\,-}) - \frac{q^2}{md}t^+\vec{E}\cdot(\vec{B}\times\vec{r}^{\,-}) + \frac{i\hbar}{m}\vec{p}\cdot\nabla_{\vec{r}^{\,+}}\right. \\
&\quad \left. -\frac{q}{m}t^-\vec{E}\cdot\vec{p} + \frac{q^2}{md}t^-\vec{E}\cdot(\vec{r}^{\,+}\times\vec{B}) - \frac{q}{md}(\vec{r}^{\,-}\times\vec{B})\cdot\vec{p}\right) G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \qquad \text{(D.215)} \\
&\mid \quad \text{write } t^- e^{-i\omega t^-} = \frac{1}{-i}\frac{\partial}{\partial\omega}e^{-i\omega t^-}\text{, then integrate by parts and drop surface term} \\
&\mid \quad \text{effectively } t^- \to \frac{1}{i}\frac{\partial}{\partial\omega} \\
&\mid \quad \text{write } \vec{r}^{\,-} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} = \frac{\hbar}{i}\nabla_{\vec{p}}e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}}\text{, then integrate by parts and drop surface term} \\
&\mid \quad \text{effectively } \vec{r}^{\,-} \to -\frac{\hbar}{i}\nabla_{\vec{p}} = i\hbar\nabla_{\vec{p}} \\
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi} e^{i\omega t^- + \frac{i}{\hbar}\left(\vec{p} - q\vec{E}t^+ - \frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad \times \left(i\hbar\frac{\partial}{\partial t^+} + \frac{i\hbar}{m}\vec{p}\cdot\nabla_{\vec{r}^{\,+}} + i\hbar q\vec{E}\cdot\nabla_{\vec{p}} + \frac{iq}{m}\vec{E}\cdot\vec{p}\frac{\partial}{\partial\omega} + \frac{2i\hbar q}{md}\vec{p}\cdot(\vec{B}\times\nabla_{\vec{p}})\right. \\
&\quad \left. -\frac{i\hbar q^2}{md}t^+\vec{E}\cdot(\vec{B}\times\nabla_{\vec{p}}) + \frac{q^2}{md}\frac{1}{i}\vec{E}\cdot(\vec{r}^{\,+}\times\vec{B})\frac{\partial}{\partial\omega}\right) G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \qquad \text{(D.216)} \\
&= \int \frac{d\vec{p}}{(2\pi\hbar)^3}\frac{d\omega}{2\pi} e^{i\omega t^- + \frac{i}{\hbar}\left(\vec{p} - q\vec{E}t^+ - \frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\cdot\vec{r}^{\,-}} \\
&\quad \times \left(i\hbar\frac{\partial}{\partial t^+} + \frac{i\hbar}{m}\vec{p}\cdot\nabla_{\vec{r}^{\,+}} + i\hbar q\vec{E}\cdot\nabla_{\vec{p}} + \frac{iq}{m}\vec{E}\cdot\left(\vec{p} - \frac{q}{d}\vec{r}^{\,+}\times\vec{B}\right)\frac{\partial}{\partial\omega}\right. \\
&\quad \left. +\frac{i\hbar q}{md}\vec{p}\cdot(\vec{B}\times\nabla_{\vec{p}}) + \frac{i\hbar q}{md}\left(\vec{p} - qt^+\vec{E}\right)\cdot(\vec{B}\times\nabla_{\vec{p}})\right) G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) \qquad \text{(D.217)}
\end{aligned}
$$

$$
\begin{aligned}
& \text{Gauge Invariant LHS for constant } \vec{E} \text{ and constant } \vec{B} \\
= & \left(i\hbar\frac{\partial}{\partial t^+} + \frac{i\hbar}{m}\vec{p}\cdot\nabla_{\vec{r}^+} + i\hbar q\vec{E}\cdot\nabla_{\vec{p}} + \frac{iq}{m}\vec{E}\cdot\left(\vec{p} - \frac{q}{d}\vec{r}^+\times\vec{B}\right)\frac{\partial}{\partial\omega} \right. \\
& \left. + \frac{i\hbar q}{md}\vec{p}\cdot(\vec{B}\times\nabla_{\vec{p}}) + \frac{i\hbar q}{md}\left(\vec{p} - qt^+\vec{E}\right)\cdot(\vec{B}\times\nabla_{\vec{p}}) \right) G^{(GI)<}(\vec{p}\omega\vec{r}^+t^+) \qquad \text{(D.218)}
\end{aligned}
$$

It is obvious that when we set $\vec{B} = 0$ in the above expression, we get the same gauge invariant LHS for constant $\vec{E}$ introduced by a scalar potential. We need to turn LHS from pre-QKE form to QKE form, i.e. from $G^{(GI)}$ to f^W. Recall the definition of Wigner function,

$$
\frac{i}{\hbar}f^W(\vec{p}\vec{r}^+t^+) = G^{(GI)<}(\vec{p}t^-\vec{r}^+t^+)|_{t^-=0} = \int\frac{d\omega}{2\pi}e^{-i\omega t^-}G^{(GI)<}(\vec{p}\omega\vec{r}^+t^+)\bigg|_{t^-=0} \qquad \text{(D.219)}
$$

So we perform the temporal Fourier transform on LHS

$$
\begin{aligned}
\text{LHS} = & \int\frac{d\omega}{2\pi}e^{-i\omega t^-}\left(i\hbar\frac{\partial}{\partial t^+} + \frac{i\hbar}{m}\vec{p}\cdot\nabla_{\vec{r}^+} + i\hbar q\vec{E}\cdot\nabla_{\vec{p}} + \frac{iq}{m}\vec{E}\cdot\left(\vec{p} - \frac{q}{d}\vec{r}^+\times\vec{B}\right)\frac{\partial}{\partial\omega} \right. \\
& \left. + \frac{i\hbar q}{md}\vec{p}\cdot(\vec{B}\times\nabla_{\vec{p}}) + \frac{i\hbar q}{md}\left(\vec{p} - qt^+\vec{E}\right)\cdot(\vec{B}\times\nabla_{\vec{p}}) \right) G^{(GI)<}(\vec{p}\omega\vec{r}^+t^+)\bigg|_{t^-=0} \qquad \text{(D.220)} \\
& \mid \quad \text{only the } \frac{\partial}{\partial\omega} \text{ term is affected} \\
& \mid \quad \text{write } e^{-i\omega t^-}\frac{\partial}{\partial\omega}G^{(GI)} = \frac{\partial}{\partial\omega}\left(e^{-i\omega t^-}G^{(GI)}\right) - \left(\frac{\partial}{\partial\omega}e^{-i\omega t^-}\right)G^{(GI)} \\
& \mid \quad \text{drop surface term and with } t^- = 0\text{, the second term} = 0 \\
= & \left(i\hbar\frac{\partial}{\partial t^+} + \frac{i\hbar}{m}\vec{p}\cdot\nabla_{\vec{r}^+} + i\hbar q\vec{E}\cdot\nabla_{\vec{p}} + \frac{i\hbar q}{md}\vec{p}\cdot(\vec{B}\times\nabla_{\vec{p}}) + \frac{i\hbar q}{md}\left(\vec{p} - qt^+\vec{E}\right)\cdot(\vec{B}\times\nabla_{\vec{p}}) \right) \\
& \times G^{(GI)<}(\vec{p}, t^- = 0, \vec{r}^+t^+) \qquad \text{(D.221)} \\
& \mid \quad \text{now write } \frac{i}{\hbar}f^W = G^{(GI)<}(t^- = 0) \\
= & -\left(\frac{\partial}{\partial t^+} + \frac{\vec{p}}{m}\cdot\nabla_{\vec{r}^+} + q\vec{E}\cdot\nabla_{\vec{p}} + \frac{q}{md}\vec{p}\cdot(\vec{B}\times\nabla_{\vec{p}}) + \frac{q}{md}\left(\vec{p} - qt^+\vec{E}\right)\cdot(\vec{B}\times\nabla_{\vec{p}}) \right) f^W(\vec{p}\vec{r}^+t^+) \\
& \qquad \text{(D.222)}
\end{aligned}
$$

This is the final LHS in QKE form for constant $\vec{E}$ and constant $\vec{B}$ (introduced via the vector potential which does not matter). We make some remarks

1. For RHS, the step $t^- = 0$ must also be carried out. However, the RHS remains in pre-QKE form (i.e. $G^{(GI)}$ remains in the RHS). Then GKBA is required to turn RHS into QKE form (i.e. only f^W appears).
2. If only one type of field is applied to the system, just set the other field to zero.
3. For homogenous systems, we drop terms with $\vec{r}^+$ and drop the argument $\vec{r}^+$.
4. For steady state considerations, we drop terms with t^+ and drop the argument t^+.

D.4.1.4 Gauge Invariant Collision Integral (RHS) for constant $\vec{E}$ and $\vec{B}$:

The RHS is more complicated, thus we can only gives expressions for special cases: either it is resctricted to the spatially homogenous case or it is gradient expanded.

D.4.1.4.1 Full collision integral (but restricted to spatially homogenous case) The full collision integral is

$$\text{RHS} = \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \left(\Sigma^R G^< + \Sigma^< G^A - G^R \Sigma^< - G^< \Sigma^A\right)(\vec{r}_1 t_1 \vec{r}_3 t_3)(\vec{r}_3 t_3 \vec{r}_2 t_2) \quad \text{(D.223)}$$

We define a simplified notation

$$I(\vec{r}_1 t_1 \vec{r}_2 t_2) = \int dt_3 \int d\vec{r}_3 X(\vec{r}_1 - \vec{r}_3, t_1 - t_3, \tfrac{\vec{r}_1+\vec{r}_3}{2}, \tfrac{t_1+t_3}{2}) Y(\vec{r}_3 - \vec{r}_2, t_3 - t_2, \tfrac{\vec{r}_3+\vec{r}_2}{2}, \tfrac{t_3+t_2}{2}) \quad \text{(D.224)}$$

To proceed, we have to assume spatial homogenity (drop $\vec{r}^{\,+}$) otherwise most of the subsequent working will not go through. We go over to Wigner coordinates,

$$I(\vec{r}_1^{\,-} t_1^- t_1^+) = \int dt_3 \int d\vec{r}_3 X(\vec{r}_1 - \vec{r}_3, t_1 - t_3, \tfrac{t_1+t_3}{2}) Y(\vec{r}_3 - \vec{r}_2, t_3 - t_2, \tfrac{t_3+t_2}{2}) \quad \text{(D.225)}$$

The gauge invariant inverse Fourier Transform (for constant $\vec{E}$) to use is,

$$G^{(\vec{A})}(\vec{r}^{\,-} t^- t^+) = \int \frac{d\vec{p}}{(2\pi\hbar)^3} \int \frac{d\omega}{2\pi} e^{-i\omega t^-} e^{\frac{i}{\hbar}(\vec{p} - q\vec{E}t^+)\cdot\vec{r}^{\,-}} G^{(GI)}(\vec{p}\omega t^+) \quad \text{(D.226)}$$

$$\begin{aligned}
I(\vec{r}_1^{\,-} t_1^- t_1^+) &= \int dt_3 \int d\vec{r}_3 \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_1}{2\pi} e^{-i\omega_1(t_1-t_3)} e^{\frac{i}{\hbar}(\vec{p}_1 - q\vec{E}\frac{t_1+t_3}{2})\cdot(\vec{r}_1 - \vec{r}_3)} X(\vec{p}_1, \omega_1, \tfrac{t_1+t_3}{2}) \\
&\quad \times \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} e^{-i\omega_2 t^-} e^{\frac{i}{\hbar}(\vec{p}_2 - q\vec{E}\frac{t_3+t_2}{2})\cdot(\vec{r}_3 - \vec{r}_2)} Y(\vec{p}_2, \omega_2, \tfrac{t_3+t_2}{2}) \qquad \text{(D.227)} \\
&= \int dt_3 \int d\vec{r}_3 \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} e^{-i\omega_1(t_1-t_2)} e^{-i\omega_2(t_3-t_2)} \\
&\quad \times e^{\frac{i}{\hbar}(\vec{p}_1 - q\vec{E}\frac{t_1+t_3}{2})\cdot\vec{r}_1} e^{\frac{i}{\hbar}(\vec{p}_2 - q\vec{E}\frac{t_3+t_2}{2})\cdot\vec{r}_2} \\
&\quad \times e^{\frac{i}{\hbar}(\vec{p}_2 - q\vec{E}\frac{t_3+t_2}{2} - \vec{p}_1 + q\vec{E}\frac{t_1+t_3}{2})\cdot\vec{r}_3} X(\vec{p}_1, \omega_1, \tfrac{t_1+t_3}{2}) Y(\vec{p}_2, \omega_2, \tfrac{t_3+t_2}{2}) \qquad \text{(D.228)} \\
&\quad | \ \text{carry out the integral } \int d\vec{r}_3 \text{ and get } \delta(\vec{p}_2 - \vec{p}_1 + \tfrac{1}{2}q\vec{E}t_1^-) \text{ where } t_1^- = t_1 - t_2 \\
&\quad | \ \text{then evaluate integral } \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
&= \int dt_3 \frac{d\vec{p}_1}{(2\pi\hbar)^3} \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} e^{-i\omega_1(t_1-t_3)} e^{-i\omega_2(t_3-t_2)} e^{\frac{i}{\hbar}(\vec{p}_1 - q\vec{E}\frac{t_1+t_3}{2})\cdot(\vec{r}_1 - \vec{r}_2)} \\
&\quad \times X(\vec{p}_1, \omega_1, \tfrac{t_1+t_3}{2}) Y(\vec{p}_2, \omega_2, \tfrac{t_3+t_2}{2}) \qquad \text{(D.229)} \\
&\quad | \ \text{write frequencies back to time} \\
&= \int dt_3 \frac{d\vec{p}_1}{(2\pi\hbar)^3} e^{\frac{i}{\hbar}(\vec{p}_1 - q\vec{E}\frac{t_1+t_3}{2})\cdot(\vec{r}_1 - \vec{r}_2)} X(\vec{p}_1, t_1 - t_3, \tfrac{t_1+t_3}{2}) Y(\vec{p}_2, t_3 - t_2, \tfrac{t_3+t_2}{2}) \qquad \text{(D.230)}
\end{aligned}$$

Now we Fourier transform the expression $I(\vec{r}_1^{\,-} t_1^- t_1^+)$.

$$\begin{aligned}
I(\vec{p}\omega t_1^+) &= \int d\vec{r}_1^{\,-} \int dt_1^- e^{i\omega t_1^-} e^{-\frac{i}{\hbar}(\vec{p} - q\vec{E}t_1^+)\cdot\vec{r}_1^{\,-}} I(\vec{r}_1^{\,-} t_1^- t_1^+) \qquad \text{(D.231)} \\
&= \int d\vec{r}_1^{\,-} dt_1^- dt_3 \frac{d\vec{p}_1}{(2\pi\hbar)^3} e^{\frac{i}{\hbar}(\vec{p}_1 - q\vec{E}\frac{t_1+t_3}{2} - \vec{p} + q\vec{E}t_1^+)\cdot\vec{r}_1} e^{i\omega t_1^-} \\
&\quad \times X(\vec{p}_1, t_1 - t_3, \tfrac{t_1+t_3}{2}) Y(\vec{p}_2, t_3 - t_2, \tfrac{t_3+t_2}{2}) \qquad \text{(D.232)}
\end{aligned}$$

$$\begin{aligned}
& | \quad \text{carry out } \int d\vec{r}_1^{\,-} \text{ to get } \delta(\vec{p}_1 - \vec{p} - q\vec{E}\tfrac{t_3-t_2}{2}) \text{ then carry out } \int d\vec{p}_1 \\
= & \int dt_1^- dt_3 e^{i\omega t_1^-} X(\vec{p} + q\vec{E}\tfrac{t_3-t_2}{2}, t_1 - t_3, \tfrac{t_1+t_3}{2}) Y(\vec{p} + q\vec{E}\tfrac{t_3-t_1}{2}, t_3 - t_2, \tfrac{t_3+t_2}{2}) \quad \text{(D.233)} \\
& | \quad \text{write } t_1 = t_1^+ + \frac{1}{2}t_1^- \text{ and } t_2 = t_1^+ - \frac{1}{2}t_1^- \\
= & \int dt_1^- dt_3 e^{i\omega t_1^-} X\left(\vec{p} + q\vec{E}(\tfrac{t_3}{2} - \tfrac{t_1^+}{2} + \tfrac{t_1^-}{4})), t_1^+ + \tfrac{t_1^-}{2} - t_3, \tfrac{t_1^+}{2} + \tfrac{1}{2}(t_3 + \tfrac{t_1^-}{2})\right) \\
& \times Y\left(\vec{p} + q\vec{E}(\tfrac{t_3}{2} - \tfrac{t_1^+}{2} - \tfrac{t_1^-}{4}), -t_1^+ + \tfrac{t_1^-}{2} + t_3, \tfrac{t_1^+}{2} + \tfrac{1}{2}(t_3 - \tfrac{t_1^-}{2})\right) \quad \text{(D.234)}
\end{aligned}$$

This is equation (7.19) in [Haug2007].

D.4.1.4.2 Zeroth order gradient expansion collision integral The zeroth order gradient terms are

$$\begin{aligned}
& \text{Zeroth Order Collision Integral} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r} \left[\left(\Sigma^> - \Sigma^<\right) G^< - \left(G^> - G^<\right)\Sigma^<\right](\vec{r}_1^{\,-} - \vec{r}_3, t_1^- - t_3, \vec{r}_1^{\,+}, t_1^+)(\vec{r}_3 t_3 \vec{r}_1^{\,+} t_1^+) \quad \text{(D.235)} \\
| \; & \text{in vector potential gauge, we change notation} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r} \\
& \times \left[\left(\Sigma^{(\vec{A})>} - \Sigma^{(\vec{A})<}\right) G^{(\vec{A})<} - \left(G^{(\vec{A})>} - G^{(\vec{A})<}\right)\Sigma^{(\vec{A})<}\right](\vec{r}_1^{\,-} - \vec{r}_3, t_1^- - t_3, \vec{r}_1^{\,+}, t_1^+)(\vec{r}_3 t_3 \vec{r}_1^{\,+} t_1^+) \\
& \text{(D.236)}
\end{aligned}$$

In general, we handle the term,

$$\begin{aligned}
& \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 X^{(\vec{A})}(\vec{r}_1^{\,-} - \vec{r}_3, t_1^- - t_3, \vec{r}_1^{\,+}, t_1^+) Y^{(\vec{A})}(\vec{r}_3 t_3 \vec{r}_1^{\,+} t_1^+) \\
| \; & \text{introduce the inverse (gauge invariant) Fourier transform} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \\
& \times \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+} \times \vec{B})\cdot(\vec{r}_1^{\,-} - \vec{r}_3)} X^{(GI)}(\vec{p}_1 \omega_1 \vec{r}_1^{\,+} t_1^+) \\
& \times \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}(\vec{p}_2 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+} \times \vec{B})\cdot\vec{r}_3} Y^{(GI)}(\vec{p}_2 \omega_2 \vec{r}_1^{\,+} t_1^+) \quad \text{(D.237)} \\
| \; & \text{perform } \int dt_3 \text{ to get } \delta(\omega_1 - \omega_2) \text{, then evaluate } \int d\omega_2 \\
= & \int d\vec{r}_3 \int \frac{d\omega}{2\pi} \frac{d\vec{p}_1}{(2\pi\hbar)^3} \frac{d\vec{p}_2}{(2\pi\hbar)^3} e^{\frac{i}{\hbar}(\vec{p}_2 - \vec{p}_1)\cdot\vec{r}_3} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+} \times \vec{B}\right)\cdot\vec{r}_1^{\,-}} e^{-i\omega_1 t_1^-} \\
& \times X^{(GI)}(\vec{p}_1 \omega_1 \vec{r}_1^{\,+} t_1^+) Y^{(GI)}(\vec{p}_2 \omega_1 \vec{r}_1^{\,+} t_1^+) \quad \text{(D.238)} \\
| \; & \text{carry out } \int d\vec{r}_3 \text{ to get } \delta(\vec{p}_2 - \vec{p}_1) \text{ and evaluate } \int d\vec{p}_2 \\
= & \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} e^{-i\omega_1 t_1^-} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+} \times \vec{B}\right)\cdot\vec{r}_1^{\,-}} X^{(GI)}(\vec{p}_1 \omega_1 \vec{r}_1^{\,+} t_1^+) Y^{(GI)}(\vec{p}_1 \omega_1 \vec{r}_1^{\,+} t_1^+) \text{(D.239)}
\end{aligned}$$

$$\text{Fourier Component} = X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)Y^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) \tag{D.240}$$

This expression is the same as before. Thus the zeroth order collision integral is already gauge invariant. We shall simply just rewrite it with the explicit notation of "(GI)".

$$\begin{aligned}
&\text{Fourier component of the zeroth order collision integral} \\
=\;& \Sigma^>(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)G^<(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) - G^>(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)\Sigma^<(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) && \text{(D.241)} \\
=\;& \Sigma^{(GI)>}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)G^{(GI)<}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) - G^{(GI)>}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)\Sigma^{(GI)<}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) && \text{(D.242)}
\end{aligned}$$

D.4.1.4.3 First order gradient expansion collision integral The first order terms represent correlations between the particles. It turns out that the fields $\vec{E}$ and $\vec{B}$ appear in the first order, indicating that the fields are part of the correlations in between collisions. This is known in the literature as the "intra-collisional field effect". Recall the first order collision integral,

$$\begin{aligned}
&\text{First order collision integral} \\
=\;& \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \left(\vec{r}_3\cdot\nabla_{\vec{r}_1} + t_3\frac{\partial}{\partial t_1^+} - \left(\vec{r}_1^{\,-}-\vec{r}_3\right)\cdot\nabla_{\vec{r}_1^{\,+\prime}} - \left(t_1^- - t_3\right)\frac{\partial}{\partial t_1^{+\prime}}\right) \\
&\times \left(\tilde{\sigma}G^< - \tilde{b}\Sigma^<\right)(\vec{r}_1^{\,-}-\vec{r}_3, t_1^- - t_3, \vec{r}_1^{\,+}, t_1^+)(\vec{r}_3 t_3 \vec{r}_1^{\,+\prime} t_1^{+\prime})\Big|_{\vec{r}_1^{\,+\prime}=\vec{r}_1^{\,+}, t_1^{+\prime}=t_1^+} && \text{(D.243)} \\
&|\quad \text{in vector potential gauge, we change notation} \\
=\;& \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \left(\vec{r}_3\cdot\nabla_{\vec{r}_1} + t_3\frac{\partial}{\partial t_1^+} - \left(\vec{r}_1^{\,-}-\vec{r}_3\right)\cdot\nabla_{\vec{r}_1^{\,+\prime}} - \left(t_1^- - t_3\right)\frac{\partial}{\partial t_1^{+\prime}}\right) \\
&\times \left(\tilde{\sigma}^{(\vec{A})}G^{(\vec{A})<} - \tilde{b}^{(\vec{A})}\Sigma^{(\vec{A})<}\right)(\vec{r}_1^{\,-}-\vec{r}_3, t_1^- - t_3, \vec{r}_1^{\,+}, t_1^+)(\vec{r}_3 t_3 \vec{r}_1^{\,+\prime} t_1^{+\prime})\Big|_{\vec{r}_1^{\,+\prime}=\vec{r}_1^{\,+}, t_1^{+\prime}=t_1^+} && \text{(D.244)}
\end{aligned}$$

In general, we handle the term,

$$\begin{aligned}
&\text{First order collision integral} \\
=\;& \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \left(\vec{r}_3\cdot\nabla_{\vec{r}_1} + t_3\frac{\partial}{\partial t_1^+} - \left(\vec{r}_1^{\,-}-\vec{r}_3\right)\cdot\nabla_{\vec{r}_1^{\,+\prime}} - \left(t_1^- - t_3\right)\frac{\partial}{\partial t_1^{+\prime}}\right) \\
&\times X^{(\vec{A})}(\vec{r}_1^{\,-}-\vec{r}_3, t_1^- - t_3, \vec{r}_1^{\,+}, t_1^+)Y^{(\vec{A})}(\vec{r}_3 t_3 \vec{r}_1^{\,+\prime} t_1^{+\prime})\Big|_{\vec{r}_1^{\,+\prime}=\vec{r}_1^{\,+}, t_1^{+\prime}=t_1^+} && \text{(D.245)} \\
&|\quad \text{introduce the inverse (gauge invariant) Fourier transform} \\
=\;& \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \left(\vec{r}_3\cdot\nabla_{\vec{r}_1} + t_3\frac{\partial}{\partial t_1^+} - \left(\vec{r}_1^{\,-}-\vec{r}_3\right)\cdot\nabla_{\vec{r}_1^{\,+\prime}} - \left(t_1^- - t_3\right)\frac{\partial}{\partial t_1^{+\prime}}\right) \\
&\times \int\frac{d\omega_1}{2\pi}\int\frac{d\vec{p}_1}{(2\pi\hbar)^3} e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) \\
&\times \int\frac{d\omega_1}{2\pi}\int\frac{d\vec{p}_2}{(2\pi\hbar)^3} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+\prime} - \frac{q}{d}\vec{r}_1^{\,+\prime}\times\vec{B}\right)\cdot\vec{r}_3} Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+\prime}t_1^{+\prime})\Big|_{\vec{r}_1^{\,+\prime}=\vec{r}_1^{\,+}, t_1^{+\prime}=t_1^+} && \text{(D.246)} \\
=\;& \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int\frac{d\omega_1}{2\pi}\int\frac{d\vec{p}_1}{(2\pi\hbar)^3}\int\frac{d\omega_2}{2\pi}\int\frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
&\times \left(\vec{r}_3\cdot\nabla_{\vec{r}_1} + t_3\frac{\partial}{\partial t_1^+} - \left(\vec{r}_1^{\,-}-\vec{r}_3\right)\cdot\nabla_{\vec{r}_1^{\,+\prime}} - \left(t_1^- - t_3\right)\frac{\partial}{\partial t_1^{+\prime}}\right) \\
&\times e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+\prime} - \frac{q}{d}\vec{r}_1^{\,+\prime}\times\vec{B}\right)\cdot\vec{r}_3}
\end{aligned}$$

$$\times X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+} \tag{D.247}$$

Due to the complexity, we will deal with the above term by term.

$$\begin{aligned}
& \text{First term} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times \left(\vec{r}_3 \cdot \nabla_{\vec{r}_1^{\,+}}\right) e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} \\
& \times X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+} \qquad \text{(D.248)} \\
| \quad & \text{use vector identity } e^{\frac{i}{\hbar}\left(-\frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} = e^{-\frac{i}{\hbar}\frac{q}{d}\left(\vec{B}\times(\vec{r}_1^{\,-}-\vec{r}_3)\right)\cdot\vec{r}_1^{\,+}} \text{ then take derivative } \nabla_{\vec{r}_1^{\,+}} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} \\
& \times \vec{r}_3 \cdot \left(-\frac{i}{\hbar}\frac{q}{d}\vec{B}\times(\vec{r}_1^{\,-}-\vec{r}_3) + \nabla_{\vec{r}_1^{\,+}}\right) X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+} \qquad \text{(D.249)} \\
| \quad & \text{write } \vec{r}_3 \cdot \left(\vec{B}\times(\vec{r}_1^{\,-}-\vec{r}_3)\right) = \vec{B}\cdot(\vec{r}_1^{\,-}-\vec{r}_3)\times\vec{r}_3 \\
| \quad & \text{write } e^{\frac{i}{\hbar}\vec{p}_2\cdot\vec{r}_3}\vec{r}_3 = \frac{\hbar}{i}\nabla_{\vec{p}_2} e^{\frac{i}{\hbar}\vec{p}_2\cdot\vec{r}_3} \text{ then integrate by parts and drop surface term} \\
| \quad & \frac{\hbar}{i}\left(\nabla_{\vec{p}_2} e^{\frac{i}{\hbar}\vec{p}_2\cdot\vec{r}_3}\right) X^{(GI)}Y^{(GI)} = \frac{\hbar}{i}\nabla_{\vec{p}_2}\left(e^{\frac{i}{\hbar}\vec{p}_2\cdot\vec{r}_3}X^{(GI)}Y^{(GI)}\right) - \frac{\hbar}{i}e^{\frac{i}{\hbar}\vec{p}_2\cdot\vec{r}_3}\nabla_{\vec{p}_2}\left(X^{(GI)}Y^{(GI)}\right) \\
| \quad & \text{essentially } \vec{r}_3 \to -\frac{\hbar}{i}\nabla_{\vec{p}_2} \text{ and } \vec{r}_1^{\,-}-\vec{r}_3 \to -\frac{\hbar}{i}\nabla_{\vec{p}_1} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} \\
& \times \left(-\frac{\hbar}{i}\frac{q}{d}\vec{B}\cdot\nabla_{\vec{p}_1}\times\nabla_{\vec{p}_2} - \frac{\hbar}{i}\nabla_{\vec{p}_2}\cdot\nabla_{\vec{r}_1^{\,+}}\right) X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+} \qquad \text{(D.250)}
\end{aligned}$$

$$\begin{aligned}
& \text{Second term} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times \left(t_3\frac{\partial}{\partial t_1^+}\right) e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} \\
& \times X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+} \qquad \text{(D.251)} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} \\
& \times t_3\left(-\frac{i}{\hbar}q\vec{E}\cdot(\vec{r}_1^{\,-}-\vec{r}_3) + \frac{\partial}{\partial t_1^+}\right) X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+} \qquad \text{(D.252)} \\
| \quad & \text{write } e^{-i\omega_2 t_3}t_3 = \frac{1}{-i}\frac{\partial}{\partial\omega_2}e^{-i\omega_2 t_3} \text{ then integrate by parts and drop surface term}
\end{aligned}$$

$$
\begin{aligned}
| & \quad \text{essentially } t_3 \rightarrow \frac{1}{i}\frac{\partial}{\partial \omega_2}, \text{ write also } \vec{r}_1^{\,-} - \vec{r}_3 \rightarrow -\frac{\hbar}{i}\nabla_{\vec{p}_1} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} \\
& \times \left(\frac{1}{i} q\vec{E}\cdot\nabla_{\vec{p}_1}\frac{\partial}{\partial\omega_2} + \frac{1}{i}\frac{\partial}{\partial\omega_2}\frac{\partial}{\partial t_1^+}\right) X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+}
\end{aligned} \tag{D.253}
$$

Third term

$$
\begin{aligned}
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times \left((\vec{r}_1^{\,-} - \vec{r}_3)\cdot\nabla_{\vec{r}_1^{\,+'}}\right) e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} \\
& \times X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+}
\end{aligned} \tag{D.254}
$$

$$
\begin{aligned}
| & \quad \text{use vector identity } e^{\frac{i}{\hbar}\left(-\frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} = e^{-\frac{i}{\hbar}\frac{q}{d}(\vec{B}\times\vec{r}_3)\cdot\vec{r}_1^{\,+'}} \text{ then carry out the derivative } \nabla_{\vec{r}_1^{\,+'}} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} \\
& \times (\vec{r}_1^{\,-} - \vec{r}_3)\cdot\left(-\frac{i}{\hbar}\frac{q}{d}\vec{B}\times\vec{r}_3 + \nabla_{\vec{r}_1^{\,+'}}\right) X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+}
\end{aligned} \tag{D.255}
$$

$$
\begin{aligned}
| & \quad \text{write } (\vec{r}_1^{\,-} - \vec{r}_3)\cdot\vec{B}\times\vec{r}_3 = \vec{B}\cdot\vec{r}_3\times(\vec{r}_1^{\,-} - \vec{r}_3) \\
| & \quad \text{then “replace” } \vec{r}_3 \rightarrow -\frac{\hbar}{i}\nabla_{\vec{p}_2} \text{ and } \vec{r}_1^{\,-} - \vec{r}_3 \rightarrow -\frac{\hbar}{i}\nabla_{\vec{p}_1} \\
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} \\
& \times \left(\frac{\hbar}{i}\frac{q}{d}\vec{B}\cdot\nabla_{\vec{p}_1}\times\nabla_{\vec{p}_2} - \frac{\hbar}{i}\nabla_{\vec{p}_1}\cdot\nabla_{\vec{r}_1^{\,+'}}\right) X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+}
\end{aligned} \tag{D.256}
$$

Fourth term

$$
\begin{aligned}
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times \left((t_1^- - t_3)\frac{\partial}{\partial t_1^{+'}}\right) e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3} \\
& \times X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+) Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+}
\end{aligned} \tag{D.257}
$$

$$
\begin{aligned}
= & \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi} \int \frac{d\vec{p}_1}{(2\pi\hbar)^3} \int \frac{d\omega_2}{2\pi} \int \frac{d\vec{p}_2}{(2\pi\hbar)^3} \\
& \times e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3}
\end{aligned}
$$

$$\times (t_1^- - t_3)\left(-\frac{i}{\hbar}q\vec{E}\cdot\vec{r}_3 + \frac{\partial}{\partial t_1^{+'}}\right) X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+} \quad \text{(D.258)}$$

| then "replace" $t_1^- - t_3 \to \frac{1}{i}\frac{\partial}{\partial\omega_1}$ and $\vec{r}_3 \to -\frac{\hbar}{i}\nabla_{\vec{p}_2}$

$$= \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi}\int\frac{d\vec{p}_1}{(2\pi\hbar)^3}\int\frac{d\omega_2}{2\pi}\int\frac{d\vec{p}_2}{(2\pi\hbar)^3}$$
$$\times e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3}$$
$$\times\left(\frac{1}{i}q\vec{E}\cdot\nabla_{\vec{p}_2}\frac{\partial}{\partial\omega_1} + \frac{1}{i}\frac{\partial}{\partial\omega_1}\frac{\partial}{\partial t_1^{+'}}\right) X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+} \quad \text{(D.259)}$$

First order collision integral

$$= \int_{-\infty}^{\infty} dt_3 \int d\vec{r}_3 \int \frac{d\omega_1}{2\pi}\int\frac{d\vec{p}_1}{(2\pi\hbar)^3}\int\frac{d\omega_2}{2\pi}\int\frac{d\vec{p}_2}{(2\pi\hbar)^3}$$
$$\times e^{-i\omega_1(t_1^- - t_3)} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot(\vec{r}_1^{\,-}-\vec{r}_3)} e^{-i\omega_2 t_3} e^{\frac{i}{\hbar}\left(\vec{p}_2 - q\vec{E}t_1^{+'} - \frac{q}{d}\vec{r}_1^{\,+'}\times\vec{B}\right)\cdot\vec{r}_3}$$
$$\times\frac{\hbar}{i}\left(-\frac{q}{d}\vec{B}\cdot\nabla_{\vec{p}_1}\times\nabla_{\vec{p}_2} - \nabla_{\vec{p}_2}\cdot\nabla_{\vec{r}_1^{\,+}} + q\vec{E}\cdot\nabla_{\vec{p}_1}\frac{\partial}{\hbar\partial\omega_2} + \frac{\partial}{\hbar\partial\omega_2}\frac{\partial}{\partial t_1^+} - \frac{q}{d}\vec{B}\cdot\nabla_{\vec{p}_1}\times\nabla_{\vec{p}_2}\right.$$
$$\left.+\nabla_{\vec{p}_1}\cdot\nabla_{\vec{r}_1^{\,+'}} - q\vec{E}\cdot\nabla_{\vec{p}_2}\frac{\partial}{\hbar\partial\omega_1} - \frac{\partial}{\hbar\partial\omega_1}\frac{\partial}{\partial t_1^{+'}}\right) X^{(GI)}(\vec{p}_1\omega_1\vec{r}_1^{\,+}t_1^+)Y^{(GI)}(\vec{p}_2\omega_2\vec{r}_1^{\,+'}t_1^{+'})\Big|_{\vec{r}_1^{\,+'}=\vec{r}_1^{\,+},t_1^{+'}=t_1^+} \quad \text{(D.260)}$$

| put $X^{(GI)}$ and $Y^{(GI)}$ into their respective differentials, the limit $\vec{r}_1^{\,+'} = \vec{r}_1^{\,+}$ and $t_1^{+'} = t_1^+$ is trivial

| carry out $\int dt_3$ and $\int d\vec{r}_3$ to get $\delta(\omega_1 - \omega_2)$ and $\delta(\vec{p}_1 - \vec{p}_2)$ respectively

| use the definition of the generalised Poisson bracket

$$= \int\frac{d\omega_1}{2\pi}\int\frac{d\vec{p}_1}{(2\pi\hbar)^3} e^{-i\omega_1 t_1^-} e^{\frac{i}{\hbar}\left(\vec{p}_1 - q\vec{E}t_1^+ - \frac{q}{d}\vec{r}_1^{\,+}\times\vec{B}\right)\cdot\vec{r}_1^{\,-}}\left(\frac{\hbar}{i}\right)\left(-\left[X^{(GI)}, Y^{(GI)}\right]_{GPB}\right.$$
$$\left.-q\vec{E}\cdot\left(\frac{\partial X^{(GI)}}{\hbar\partial\omega_1}(\nabla_{\vec{p}_1}Y^{(GI)}) - (\nabla_{\vec{p}_1}X^{(GI)})\frac{\partial Y^{(GI)}}{\hbar\partial\omega_1}\right) - \frac{2q}{d}\vec{B}\cdot(\nabla_{\vec{p}_1}X^{(GI)})\times(\nabla_{\vec{p}_1}Y^{(GI)})\right) \quad \text{(D.261)}$$

Fourier component of the first order collision integral

$$= \left(\frac{\hbar}{i}\right)\left(-\left[\tilde{\sigma}^{(GI)}, G^{(GI)<}\right]_{GPB} - q\vec{E}\cdot\left(\frac{\partial\tilde{\sigma}^{(GI)}}{\hbar\partial\omega_1}(\nabla_{\vec{p}_1}G^{(GI)<}) - (\nabla_{\vec{p}_1}\tilde{\sigma}^{(GI)})\frac{\partial G^{(GI)<}}{\hbar\partial\omega_1}\right)\right.$$
$$\left.-\frac{2q}{d}\vec{B}\cdot(\nabla_{\vec{p}_1}\tilde{\sigma}^{(GI)})\times(\nabla_{\vec{p}_1}G^{(GI)<})\right)$$
$$-\left(\frac{\hbar}{i}\right)\left(-\left[\tilde{b}^{(GI)}, \Sigma^{(GI)<}\right]_{GPB} - q\vec{E}\cdot\left(\frac{\partial\tilde{b}^{(GI)}}{\hbar\partial\omega_1}(\nabla_{\vec{p}_1}\Sigma^{(GI)<}) - (\nabla_{\vec{p}_1}\tilde{b}^{(GI)})\frac{\partial\Sigma^{(GI)<}}{\hbar\partial\omega_1}\right)\right.$$
$$\left.-\frac{2q}{d}\vec{B}\cdot(\nabla_{\vec{p}_1}\tilde{b}^{(GI)})\times(\nabla_{\vec{p}_1}\Sigma^{(GI)<})\right) \quad \text{(D.262)}$$

Notice that the fields only appear from the first order onwards and recall that the gradient expansion is an expansion about the correlations between the particles. This implies that the fields are now mixed into the correlations between the particles. This is known as the "intracollisional field effect" in the literature. These extra terms can also be seen in [Kita2010] equation (6.10).

D.4.1.5 Problems with KB ansatz

In the chapter on NEGF, we developed the KB ansatz and derived phonon Boltzmann equation from it. Exactly the same thing can be done and the electron Boltzmann equation can be derived. We started with casual quantum field theory but ended up with Boltzmann equation which is non-causal. See [Haug2007] pg 95 for more details. Thus the question is, can we have an ansatz to reduce the (gauge invariant) Green's function in pre-QKE to the distribution function while preserving some form of causality (and obeys gauge invariance and allows gradient expansion)?

The answer is the Generalized Kadanoff-Baym (GKB) ansatz. The ground-breaking paper is [Lipavsky1986] and the important review paper [Spicka2005]. Here we follow [Haug2007] section 8.2 for a simple derivation.

D.4.1.6 Generalized Kadanoff-Baym Ansatz

D.4.1.6.1 Systematic "expansion" about the time diagonal We will show how it is possible to systematically the 2-time function about its time diagonal part.[10] We start by defining auxiliary functions (we only keep time labels here)

$$\begin{aligned} G^{R<}(t_1t_2) &\equiv \theta(t_1-t_2)G^{<}(t_1t_2) && \text{(D.263)} \\ G^{R>}(t_1t_2) &\equiv \theta(t_1-t_2)G^{>}(t_1t_2) && \text{(D.264)} \\ G^{A<}(t_1t_2) &\equiv \theta(t_2-t_1)G^{<}(t_1t_2) && \text{(D.265)} \\ G^{A>}(t_1t_2) &\equiv \theta(t_2-t_1)G^{>}(t_1t_2) && \text{(D.266)} \end{aligned}$$

Convolve G^{R-1} from the left of $G^{R<}$

$$\begin{aligned} & \int dt_3 G^{R-1}(t_1t_3)G^{R<}(t_3t_2) \\ = & \int dt_3 \left(G^{(0)R-1}(t_1t_3) - \Sigma^R(t_1t_3)\right) G^{R<}(t_3t_2) && \text{(D.267)} \\ = & \int dt_3 \left(\left(i\frac{\partial}{\partial t_1} - \epsilon_{\vec{k}_1}\right)\delta(t_1-t_3) - \Sigma^R(t_1t_3)\right) G^{R<}(t_3t_2) && \text{(D.268)} \\ | & \quad \text{use the definition } G^{R<}(t_1t_2) = \theta(t_1-t_2)G^{<}(t_1t_2) \\ = & \int dt_3 \left(i\frac{\partial}{\partial t_1}\left(\theta(t_3-t_1)G^{<}(t_3t_2)\delta(t_1-t_3)\right) - \epsilon_{\vec{k}_1}\delta(t_1-t_3)G^{R<}(t_3t_2) - \Sigma^R(t_1t_3)G^{R<}(t_3t_2)\right) \\ = & \; i\frac{\partial}{\partial t_1}\left(\theta(t_1-t_2)G^{<}(t_1t_2)\right) - \theta(t_1-t_2)\epsilon_{\vec{k}_1}G^{<}(t_1t_2) - \int dt_3\Sigma^R(t_1t_3)\theta(t_3-t_2)G^{<}(t_3t_2) && \text{(D.269)} \\ = & \; i\delta(t_1-t_2)G^{<}(t_1t_2) + i\theta(t_1-t_2)\frac{\partial}{\partial t_1}G^{<}(t_1t_2) - \theta(t_1-t_2)\epsilon_{\vec{k}_1}G^{<}(t_1t_2) \\ & - \int_{t_2}^{t_1} dt_3\Sigma^R(t_1t_3)G^{<}(t_3t_2) && \text{(D.270)} \\ = & \; i\delta(t_1-t_2)G^{<}(t_1t_2) + \theta(t_1-t_2)\left(\left(i\frac{\partial}{\partial t_1} - \epsilon_{\vec{k}_1}\right)G^{<}(t_1t_2) - \int_{t_2}^{t_1} dt_3\Sigma^R(t_1t_3)G^{<}(t_3t_2)\right) && \text{(D.271)} \end{aligned}$$

The first term is the time diagonal term and that gives the Wigner distribution function, $i\delta(t_1 -$

[10] This is a mathematical exercise. Whether there are physical justifications to say that time off-diagonal terms can be dropped, depends on the particular application.

$t_2)G^<(t_1t_2) = -\delta(t_1-t_2)f^W(t_2)$. We rewrite Keldysh equation,

$$\begin{aligned}
G^< &= G^R\Sigma^<G^A && \text{(D.272)}\\
\Rightarrow G^{R-1}G^< &= \Sigma^<G^A && \text{(D.273)}\\
\left(i\frac{\partial}{\partial t_1}-\epsilon_{\vec{k}_1}-\int_{t_0}^{t_1}dt_1\Sigma^R(t_1t_3)\right)G^<(t_3t_2) &= \int_{t_0}^{t_2}dt_3\Sigma^<(t_1t_3)G^A(t_3t_2) && \text{(D.274)}\\
&\mid\ \text{rewrite}\int_{t_0}^{t_1}=\int_{t_0}^{t_2}+\int_{t_2}^{t_1}\\
\left(i\frac{\partial}{\partial t_1}-\epsilon_{\vec{k}_1}-\int_{t_2}^{t_1}dt_1\Sigma^R(t_1t_3)\right)G^<(t_3t_2) &= \int_{t_0}^{t_2}dt_3\left(\Sigma^R(t_1t_3)G^<(t_3t_2)+\Sigma^<(t_1t_3)G^A(t_3t_2)\right)
\end{aligned}$$

This is substituted into $\int dt_3G^{R-1}G^{R<}$ to get,

$$\int dt_3G^{R-1}G^{R<} = i\delta(t_1-t_2)G^<(t_1t_2)+\theta(t_1-t_2)\int_{t_0}^{t_2}dt_3\left(\Sigma^R(t_1t_3)G^<(t_3t_2)+\Sigma^<(t_1t_3)G^A(t_3t_2)\right)$$

Convolve G^R on both sides so that only $G^{R<}$ is left on LHS.

$$\begin{aligned}
G^{R<}(t_1t_2) &= i\int dt_4G^R(t_1t_4)\delta(t_4-t_2)G^<(t_4t_2)\\
&\quad+\int_{t_2}^{t_1}dt_4\int_{t_0}^{t_2}dt_3G^R(t_1t_4)\left(\Sigma^R(t_4t_3)G^<(t_3t_2)+\Sigma^<(t_4t_3)G^A(t_3t_2)\right)\\
&= iG^R(t_1t_2)G^<(t_2t_2)\\
&\quad+\int_{t_2}^{t_1}dt_4\int_{t_0}^{t_2}dt_3\left(G^R(t_1t_4)\Sigma^R(t_4t_3)G^<(t_3t_2)+G^R(t_1t_4)\Sigma^<(t_4t_3)G^A(t_3t_2)\right)
\end{aligned}$$

We repeat for $G^{A<}$ and get,

$$\begin{aligned}
G^{A<}(t_1t_2) &= -iG^<(t_1t_1)G^A(t_1t_2)\\
&\quad+\int_{t_1}^{t_2}dt_4\int_{t_0}^{t_1}dt_3\left(G^<(t_1t_3)\Sigma^A(t_3t_4)G^A(t_4t_2)+G^R(t_1t_3)\Sigma^<(t_3t_4)G^A(t_4t_2)\right)
\end{aligned}$$

With these 2 terms, we can reconstruct $G^<$,

$$\begin{aligned}
G^<(t_1t_2) &= G^{R<}+G^{A<} && \text{(D.275)}\\
&= iG^R(t_1t_2)G^<(t_2t_2)-iG^<(t_1t_1)G^A(t_1t_2)\\
&\quad-\int_{t_1}^{t_2}dt_4\int_{t_0}^{t_2}dt_3\left(G^R(t_1t_4)\Sigma^R(t_4t_3)G^<(t_3t_2)+G^R(t_1t_4)\Sigma^<(t_4t_3)G^A(t_3t_2)\right)\\
&\quad+\int_{t_1}^{t_2}dt_4\int_{t_0}^{t_1}dt_3\left(G^<(t_1t_3)\Sigma^A(t_3t_4)G^A(t_4t_2)+G^R(t_1t_3)\Sigma^<(t_3t_4)G^A(t_4t_2)\right) && \text{(D.276)}
\end{aligned}$$

This results in an infinite series when we iterate $G^<$ from second term onwards. Usually only the first term is kept and its validity is justified by saying that the interaction is weak. This can be seen as the self energy terms enter only from the second term onwards. Thus the lowest order GKB ansatz can be written as

$$\boxed{G^<(t_1t_2)\approx -G^R(t_1t_2)f^W(t_2t_2)+f^W(t_1t_1)G^A(t_1t_2)} \tag{D.277}$$

The $G^>$ component is constructed by calculating the equal time commutator to see the difference between $G^<$ and $G^>$ on the time diagonal.

D.4.1.6.2 GKB ansatz For Electrons in constant $\vec{E}$ and constant $\vec{B}$: We will deal with constant $\vec{E}$ and later we see that the constant $\vec{B}$ field can be incooperated into the result trivally. From the zeroth order terms in the time diagonal expansion, we put back the $\vec{r}^{\,+}$ argument and change notation in view of the vector potential gauge used.

$$\begin{aligned} G^{(GI)<}(\vec{p},\vec{r}^{\,+},t_1,t_2) &= iG^{(GI)R}(\vec{p},\vec{r}^{\,+},t_1,t_2)G^{(GI)<}(\vec{p},\vec{r}^{\,+},t_2,t_2) \\ &\quad -iG^{(GI)<}(\vec{p},\vec{r}^{\,+},t_1,t_1)G^{(GI)A}(\vec{p},\vec{r}^{\,+},t_1,t_2) \end{aligned} \tag{D.278}$$

Going to Wigner time coordinates is tricky for $G^{(GI)<}(\vec{p},\vec{r}^{\,+},t_2,t_2)$ and $G^{(GI)<}(\vec{p},\vec{r}^{\,+},t_1,t_1)$ and we need to handle them seperately from the other terms. We start by considering the gauge invariant Fourier transform.

$$G^{(GI)<}(\vec{p}\omega\vec{r}^{\,+}t^+) = \int dt^- d\vec{r}^{\,-} e^{i\omega t_1^-} e^{-\frac{i}{\hbar}(\vec{p}-q\vec{E}t_1^+)\cdot\vec{r}^{\,-}} G^{(\vec{A})<}(\vec{r}^{\,-}t_1^-\vec{r}^{\,+}t_1^+) \tag{D.279}$$

| reverse the temporal Fourier transform

$$G^{(GI)<}(\vec{p}\vec{r}^{\,+}t_1^-t^+) = \int d\vec{r}^{\,-} e^{i\omega t_1^-} e^{-\frac{i}{\hbar}(\vec{p}-q\vec{E}t_1^+)\cdot\vec{r}^{\,-}} G^{(\vec{A})<}(\vec{r}^{\,-}t_1^-\vec{r}^{\,+}t_1^+) \tag{D.280}$$

| reverse the Wigner time transformation

$$G^{(GI)<}(\vec{p}\vec{r}^{\,+}t_1t_2) = \int d\vec{r}^{\,-} e^{i\omega t_1^-} e^{-\frac{i}{\hbar}(\vec{p}-q\vec{E}\frac{t_1+t_2}{2})\cdot\vec{r}^{\,-}} G^{(\vec{A})<}(\vec{r}^{\,-}\vec{r}^{\,+}t_1t_2) \tag{D.281}$$

| now set $t_1 = t_2$

$$G^{(GI)<}(\vec{p},\vec{r}^{\,+},t_2,t_2) = \int d\vec{r}^{\,-} e^{-\frac{i}{\hbar}(\vec{p}-q\vec{E}t_2)\cdot\vec{r}^{\,-}} G^{(\vec{A})<}(\vec{r}^{\,-},\vec{r}^{\,+},t_2,t_2) \tag{D.282}$$

| LHS is the term that we want to tackle

| RHS gives the expression to carry out the Wigner time transformation

$$G^{(GI)<}(\vec{p},\vec{r}^{\,+},0,\tfrac{t_2+t_2}{2}) = \int d\vec{r}^{\,-} e^{-\frac{i}{\hbar}(\vec{p}-q\vec{E}t_2)\cdot\vec{r}^{\,-}} G^{(\vec{A})<}(\vec{r}^{\,-},\vec{r}^{\,+},0,\tfrac{t_2+t_2}{2}) \tag{D.283}$$

| write $t_2 = t_1^+ - \dfrac{1}{2}t_1^-$

$$G^{(GI)<}(\vec{p},\vec{r}^{\,+},0,t_1^+ - \tfrac{1}{2}t_1^-) = \int d\vec{r}^{\,-} e^{-\frac{i}{\hbar}(\vec{p}-q\vec{E}(t_1^+-\frac{1}{2}t_1^-))\cdot\vec{r}^{\,-}} G^{(\vec{A})<}(\vec{r}^{\,-},\vec{r}^{\,+},0,t_1^+ - \tfrac{1}{2}t_1^-) \tag{D.284}$$

| take the steady state condition and thus drop t_1^+

| and drop the "center of time" argument

$$G^{(GI)<}(\vec{p},\vec{r}^{\,+},0) = \int d\vec{r}^{\,-} e^{-\frac{i}{\hbar}(\vec{p}+q\vec{E}\frac{1}{2}t_1^-)\cdot\vec{r}^{\,-}} G^{(\vec{A})<}(\vec{r}^{\,-},\vec{r}^{\,+},0) \tag{D.285}$$

Now compare with the usual definition of f^W [11]

$$\begin{aligned}
G^<(\vec{p}, t^- = 0, \vec{r}^{\,+}, t^+) &\equiv \frac{i}{\hbar} f^W(\vec{p}\vec{r}^{\,+}t^+) = \int d\vec{r}^{\,-} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} G^<(\vec{r}^{\,-}, t^- = 0, \vec{r}^{\,+}, t^+) \quad (D.291)\\
&\mid \text{ take steady state condition}\\
G^<(\vec{p}, t^- = 0, \vec{r}^{\,+}) &= \frac{i}{\hbar} f^W(\vec{p}\vec{r}^{\,+}) = \int d\vec{r}^{\,-} e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}^{\,-}} G^<(\vec{r}^{\,-}, t^- = 0, \vec{r}^{\,+}) \quad (D.292)
\end{aligned}$$

Thus for the (constant $\vec{E}$) gauge invariant version, it is just a "shifted momentum" modification to the Wigner function.

$$\begin{aligned}
G^{(GI)<}(\vec{p}, \vec{r}^{\,+}, t_2, t_2) &= G^{(GI)<}(\vec{p}, \vec{r}^{\,+}, 0) \equiv \frac{i}{\hbar} f^W(\vec{p} + \tfrac{1}{2}q\vec{E}t_1^-, \vec{r}^{\,+}) \quad (D.293)\\
&= \int d\vec{r}^{\,-} e^{-\frac{i}{\hbar}(\vec{p}+\frac{1}{2}q\vec{E}t_1^-)\cdot\vec{r}^{\,-}} G^{(\vec{A})<}(\vec{r}^{\,-}, \vec{r}^{\,+}, 0) \quad (D.294)
\end{aligned}$$

It can be easily deduced that

$$\begin{aligned}
G^{(GI)<}(\vec{p}, \vec{r}^{\,+}, t_1, t_1) &= G^{(GI)<}(\vec{p}, \vec{r}^{\,+}, 0) \equiv \frac{i}{\hbar} f^W(\vec{p} - \tfrac{1}{2}q\vec{E}t_1^-, \vec{r}^{\,+}) \quad (D.295)\\
&= \int d\vec{r}^{\,-} e^{-\frac{i}{\hbar}(\vec{p}-\frac{1}{2}q\vec{E}t_1^-)\cdot\vec{r}^{\,-}} G^{(\vec{A})<}(\vec{r}^{\,-}, \vec{r}^{\,+}, 0) \quad (D.296)
\end{aligned}$$

We can now reconstruct $G^{(GI)<}(\vec{p}, \vec{r}^{\,+}, t_1, t_2)$

$$\begin{aligned}
G^{(GI)<}(\vec{p}, \vec{r}^{\,+}, t_1, t_2) &= iG^{(GI)R}(\vec{p}, \vec{r}^{\,+}, t_1, t_2)G^{(GI)<}(\vec{p}, \vec{r}^{\,+}, t_2, t_2)\\
&\quad -iG^{(GI)<}(\vec{p}, \vec{r}^{\,+}, t_1, t_1)G^{(GI)A}(\vec{p}, \vec{r}^{\,+}, t_1, t_2) \quad (D.297)\\
&\mid \text{ go over to Wigner time coordinates}\\
&\mid \text{ which is trivial for LHS, } G^{(GI)R} \text{ and } G^{(GI)A}\\
&\mid \text{ we impose the steady state condition}\\
G^{(GI)<}(\vec{p}, t_1^-, \vec{r}^{\,+}) &= iG^{(GI)R}(\vec{p}, t_1^-, \vec{r}^{\,+}) i f^W(\vec{p} + \tfrac{1}{2}q\vec{E}t_1^-, \vec{r}^{\,+})\\
&\quad -i^2 f^W(\vec{p} - \tfrac{1}{2}q\vec{E}t_1^-, \vec{r}^{\,+})G^{(GI)A}(\vec{p}, t_1^-, \vec{r}^{\,+}) \quad (D.298)\\
&\mid \text{ recall the definition of the spectral function } A = i(G^R - G^A)\\
&\mid \text{ recall the step function in the definitions of } G^R \text{ and } G^A \text{ then,}\\
&\mid \; A(\vec{p}, t_1^- > 0, \vec{r}^{\,+}) = iG^{(GI)R}(\vec{p}, t_1^-, \vec{r}^{\,+})
\end{aligned}$$

[11] From the equal time anticommutation relation,

$$\begin{aligned}
\left[\psi(t), \psi^\dagger(t)\right]_+ &= \mathbf{1} \quad (D.286)\\
\psi(t)\psi^\dagger(t) + \psi^\dagger(t)\psi(t) &= \mathbf{1} \quad (D.287)\\
&\mid \text{ take statistical average}\\
\langle\psi(t)\psi^\dagger(t)\rangle + \langle\psi^\dagger(t)\psi(t)\rangle &= \mathbf{1} \quad (D.288)\\
&\mid \text{ recall } G^< = \frac{i}{\hbar}\langle\psi^\dagger\psi\rangle \text{ and } G^> = -\frac{i}{\hbar}\langle\psi\psi^\dagger\rangle\\
\Rightarrow i\hbar(G^> - G^<) &= \mathbf{1} \quad (D.289)\\
&\mid \text{ insert } G^< = \frac{i}{\hbar} f^W\\
G^> &= -\frac{i}{\hbar}(\mathbf{1} - f^W) \quad (D.290)
\end{aligned}$$

$$
\begin{aligned}
& \mid \quad A(\vec{p}, t_1^- < 0, \vec{r}^{\,+}) = -iG^{(GI)A}(\vec{p}, t_1^-, \vec{r}^{\,+}) \\
= \; & iA(\vec{p}, t_1^- > 0, \vec{r}^{\,+}) f^W(\vec{p} + \tfrac{1}{2} q\vec{E}|t_1^-|, \vec{r}^{\,+}) \\
& + i f^W(\vec{p} + \tfrac{1}{2} q\vec{E}|t_1^-|, \vec{r}^{\,+}) A(\vec{p}, t_1^- < 0, \vec{r}^{\,+}) \qquad \text{(D.299)} \\
= \; & iA(\vec{p}, t_1^-, \vec{r}^{\,+}) f^W(\vec{p} + \tfrac{1}{2} q\vec{E}|t_1^-|, \vec{r}^{\,+}) \qquad \text{(D.300)}
\end{aligned}
$$

See [Haug2007] equation (8.19) for the time dependent $\vec{E}$ GKBA (introduced via the vector potential). To include the constant magnetic field, we realise that the Fourier kernel $e^{-\frac{i}{\hbar}(\vec{p} - q\vec{E}t^+ - \frac{q}{d}\vec{r}^{\,+} \times \vec{B}) \cdot \vec{r}^{\,-}}$ which involves only spatial variables in the magnetic field related term. Spatial variables are not involved in the time diagonal expansion, thus we only get another trivial "momentum shift".

$$
\begin{aligned}
G^{(GI)<}(\vec{p}, t_1^-, \vec{r}^{\,+}) &= iA(\vec{p}, t_1^-, \vec{r}^{\,+}) f^W(\vec{p} + \tfrac{1}{2} q\vec{E}|t_1^-| - \tfrac{q}{d}\vec{r}^{\,+} \times \vec{B}, \vec{r}^{\,+}) && \text{(D.301)} \\
G^{(GI)>}(\vec{p}, t_1^-, \vec{r}^{\,+}) &= -iA(\vec{p}, t_1^-, \vec{r}^{\,+}) \left(1 - f^W(\vec{p} + \tfrac{1}{2} q\vec{E}|t_1^-| - \tfrac{q}{d}\vec{r}^{\,+} \times \vec{B}, \vec{r}^{\,+})\right) && \text{(D.302)}
\end{aligned}
$$

where the second GKBA is obtained via the relation $i(G^> - G^<) = A$. This is the final result. We see that (even in steady state) the momentum, time and space variables have been mixed up. This could mean interesting quantum effects but it makes the quantum kinetic equations (QKE) very difficult to handle.

D.5 Summary and Receipe of QKE

Here we want to write some kind of receipe for QKE so that people can quickly construct the QKE they want and it also serves as a summary for this appendix.

1. Choose a LHS. Various choices for the driving are: mechanical driving or (time dependent or time independent) electromagnetic fields driving. Various choices of approximations for LHS are: full distribution or linearized distribution. Various choices of conditions are: spatial homogenity or temporal steady state.

2. Choose a matching RHS. Decide whether to use the full collision integral (which only works with spatially homogenous systems) or use the gradient expanded ones. Then decide how many orders of gradient expansion should be kept.

3. Choose a self consistent self energy for RHS from the Hedin's equations according to the interaction the researcher is interested in.

4. Choose a matching GKB ansatz and the pre-QKE becomes QKE.

For an example of such an implementation of the receipe, refer to the section on the QKE treatment of electron-phonon interaction.

D.6 From NEGF to Linear Response Theory

The derivation has already been given in the chapter on NEGF. Here we will just apply the linear response formula to electronic transport, i.e. calculate electrical conductivity.

D.6.1 Application: Electrical Conductivity

Here we follow [Bruus2004] chapter 6. The time-dependent Hamiltonian with electromagnetic driving fields (introduced by scalar and vector potentials) is

$$V(t) = -\int d\vec{r}\rho(\vec{r})\phi(\vec{r},t) + \int d\vec{r}\vec{J}(\vec{r})\cdot\vec{A}(\vec{r},t) \tag{D.303}$$

where $\rho(\vec{r})$ and $\vec{J}(\vec{r})$ are treated as operators and $\phi(\vec{r},t)$ and $\vec{A}(\vec{r},t)$ are treated as functions with parametric time dependence.

We first write the retarded response function in the Kubo correlator form. Choose a gauge such that the Hamiltonian becomes

$$V(t) = \int d\vec{r}\rho(\vec{r})\phi(\vec{r}) \tag{D.304}$$

$$\text{and let} \quad \hat{V} = \rho(\vec{r}) \quad , \quad f(t) = \phi(\vec{r},t) \tag{D.305}$$

Following the procedure, we first take the time derivative.

$$\begin{aligned}
\frac{dV(t)}{dt} &= \int d\vec{r}\phi(\vec{r},t)\frac{d\rho(\vec{r})}{dt} && \text{(D.306)}\\
&\quad | \quad \text{use (operator) continuity equation, } \frac{d\rho}{dt} + \nabla_{\vec{r}}\cdot\vec{J}(\vec{r}) = 0 \\
&= -\int d\vec{r}\phi(\vec{r},t)\left(\nabla_{\vec{r}}\cdot\vec{J}(\vec{r})\right) && \text{(D.307)}\\
&\quad | \quad \text{integrate by parts and drop the surface term} \\
&= \int d\vec{r}\vec{J}(\vec{r})\cdot\nabla_{\vec{r}}\phi(\vec{r},t) && \text{(D.308)}\\
&\quad | \quad \text{use Maxwell's equation, } -\nabla_{\vec{r}}\phi(\vec{r},t) = \vec{E}(\vec{r},t) \\
&= -\int d\vec{r}\vec{E}(\vec{r},t)\cdot\vec{J}(\vec{r},t) && \text{(D.309)}
\end{aligned}$$

So, $\dot{\hat{V}} = \vec{J}(\vec{r})$ and we choose operator A to be $\vec{J}$ and now we can write the linear response formula for electrical conductivity. [12]

$$\begin{aligned}
\delta\langle\vec{J}(\vec{r},t)\rangle &= \langle\vec{J}(\vec{r},t)\rangle && \text{(D.310)}\\
&\quad | \quad \text{since there is no current when no field is applied} \\
&= -\int_{-\infty}^{\infty} dt_1 \int d\vec{r}_1 \overleftrightarrow{\chi}^R_{A=\vec{J},\dot{\hat{V}}=\vec{J}}(\vec{r}-\vec{r}_1, t-t_1)\vec{E}(\vec{r}_1,t_1) && \text{(D.311)}
\end{aligned}$$

Taking spatial and temporal Fourier transforms, we get the Ohm's law form,

$$\langle\vec{J}(\vec{q},\omega)\rangle = -\overleftrightarrow{\chi}^R_{\vec{J}\vec{J}}(\vec{q},\omega)\vec{E}(\vec{q},\omega) \tag{D.312}$$

Thus the electrical conductivity $\overleftrightarrow{\sigma}$ is simply

$$\sigma_{\alpha\beta}(\vec{q},\omega) = -\chi^R_{\vec{J}\vec{J},\alpha\beta}(\vec{q},\omega) \tag{D.313}$$

[12] Note that all these manipulations are done so that the linear response formula looks like the transport law we are interested in. In this case, the transport law of interest is Ohm's law.

$$\begin{aligned}
&= \int d(\vec{r}-\vec{r}_1)e^{-i\vec{q}\cdot(\vec{r}-\vec{r}_1)} \lim_{\epsilon\to 0^+}\int d(t-t_1)e^{(i\omega-\epsilon)(t-t_1)} \\
&\quad \times \int_0^\beta d\tau^M \left\langle J_{\beta,H_0+H_{\rm int}}(\vec{r}_1, t_1 - i\hbar\tau^M) J_{\alpha,H_0+H_{\rm int}}(\vec{r},t)\right\rangle \qquad \text{(D.314)}\\
&\quad | \ \text{introduce } \frac{1}{V}\int d\vec{r} = 1 \\
&\quad | \ \text{assuming spatial translational invariance, we can rename } (\vec{r},\vec{r}-\vec{r}_1)\to(\vec{r},\vec{r}_1)\\
&= \frac{1}{V}\int d\vec{r}\int d(\vec{r}-\vec{r}_1)e^{-i\vec{q}\cdot\vec{r}}e^{i\vec{q}\cdot\vec{r}_1} \lim_{\epsilon\to 0^+}\int d(t-t_1)e^{(i\omega-\epsilon)(t-t_1)}\\
&\quad \times \int_0^\beta d\tau^M \left\langle J_{\beta,H_0+H_{\rm int}}(\vec{r}_1, t_1 - i\hbar\tau^M) J_{\alpha,H_0+H_{\rm int}}(\vec{r},t)\right\rangle \qquad \text{(D.315)}\\
&= \frac{1}{V}\lim_{\epsilon\to 0^+}\int_0^\infty d(t-t_1)e^{(i\omega-\epsilon)(t-t_1)}\int_0^\beta d\tau^M \left\langle J_{\beta,H_0+H_{\rm int}}(-\vec{q}, t_1 - i\hbar\tau^M) J_{\alpha,H_0+H_{\rm int}}(\vec{q},t)\right\rangle\\
&\quad | \ \text{now we can write the average explicitly in terms of } (t-t_1) \text{ \& rename } t-t_1\to t\\
&= \frac{1}{V}\lim_{\epsilon\to 0^+}\int_0^\infty dt e^{(i\omega-\epsilon)t}\int_0^\beta d\tau^M \left\langle J_{\beta,H_0+H_{\rm int}}(-\vec{q}, -i\hbar\tau^M) J_{\alpha,H_0+H_{\rm int}}(\vec{q},t)\right\rangle \qquad \text{(D.316)}
\end{aligned}$$

This is our final result in Kubo correlator form. [13]

We want to write the commutator version. Choose a gauge such that $V(t)$ becomes

$$V(t) = \int d\vec{r}\vec{J}(\vec{r})\cdot\vec{A}(\vec{r},t) \qquad \text{(D.317)}$$

where the current operator $\vec{J}$ is to be substituted for $\hat{V}$, the function $f(t)$ to be the vector potential $\vec{A}$ and choose operator A as $\vec{J}$. The linear response formula is now written as (again, we take no current when $V(t)=0$)

$$\langle \vec{J}(\vec{r},t)\rangle = \int_{-\infty}^{\infty} dt_1 \int d\vec{r}_1 \overleftrightarrow{\chi}^R_{A=\vec{J},\hat{V}=\vec{J}}(\vec{r}-\vec{r}_1, t-t_1)\vec{A}(\vec{r}_1,t_1) \qquad \text{(D.318)}$$

We want to write it so that it looks like Ohm's law so that we can identify the electrical conductivity expression. To this end, we take the spatial and temporal Fourier transforms and use Maxwell's equation, $\vec{A}(\vec{q},\omega) = \frac{1}{i\omega}\vec{E}(\vec{q},\omega)$.

$$\langle \vec{J}(\vec{q},\omega)\rangle = \overleftrightarrow{\chi}^R_{\vec{J}\vec{J}}(\vec{q},\omega)\frac{1}{i\omega}\vec{E}(\vec{q},\omega) \qquad \text{(D.319)}$$

Thus the electrical conductivity is simply identified as

$$\begin{aligned}
\sigma_{\alpha\beta}(\vec{q},\omega) &= \frac{1}{i\omega}\chi^R_{\vec{J}\vec{J},\alpha\beta}(\vec{q},\omega) \qquad \text{(D.320)}\\
&= \frac{1}{i\omega}\frac{-i}{\hbar}\int d(\vec{r}-\vec{r}_1)e^{-i\vec{q}\cdot(\vec{r}-\vec{r}_1)}\lim_{\epsilon\to 0^+}\int_0^\infty dt e^{(i\omega-\epsilon)t}\left\langle [J_{\alpha,H_0+H_{\rm int}}(\vec{r},t), J_\beta(\vec{r}_1)]_-\right\rangle \qquad \text{(D.321)}\\
&\quad | \ \text{use the same trick where we insert } \frac{1}{V}\int d\vec{r} = 1 \text{ and rename } (\vec{r},\vec{r}-\vec{r}_1)\to(\vec{r},\vec{r}_1)\\
&= \frac{-1}{\hbar\omega V}\lim_{\epsilon\to 0^+}\int_0^\infty e^{(i\omega-\epsilon)t}\left\langle [J_{\alpha,H_0+H_{\rm int}}(\vec{q},t), J_\beta(-\vec{q})]_-\right\rangle \qquad \text{(D.322)}
\end{aligned}$$

[13] In some references, Laplace transform is used early in the derivation and the results are the same. Now we can see that Laplace transform is a compact way of accounting for the retarded response, i.e causality. One may also think of the the ϵ as coming from the Fourier representation of the time step function in χ.

The other commutator version is simply

$$\sigma_{\alpha\beta}(\vec{q},\omega) = \frac{2}{i\hbar\omega V}\lim_{\epsilon\to 0^+}\int_0^\infty dt e^{(i\omega-\epsilon)t}\Im\left\langle J_{\alpha,H_0+H_{\rm int}}(\vec{q},t)J_\beta(-\vec{q})\right\rangle \tag{D.323}$$

Appendix E

Proofs

E.1 Subjecting the Phonon self energy to the Φ-Deriviability condition

One must read the famous paper by Baym in [Baym1962]. The Φ-derivability condition amounts to the satisfaction of 4 conservation laws (in the electronic case). In terms of diagrams, it amounts a certain symmetry in the vertex. The check is at the level of Feynman diagrams, so these are the contour time self energies. Thus by visual inspection of the diagrams, we expect the terms type 1,2,3 do not satisfy the diagram symmetry and hence do not satisfy the conservation condition. We checked 2 versions of the self energy; the general version from the iteration of the Hedin-like equations and the sign-assigned version. All times are contour times, I apologize for using the notation t here. The Φ-derivability condition comes from the "curl" condition of the self energy,

$$\frac{\delta\Sigma(1,2)}{\delta D(4,3)} = \frac{\delta\Sigma(3,4)}{\delta D(2,1)} \tag{E.1}$$

E.1.1 $V^{(4ph)}$ Term (Yes)

Version 1: General Self Energy

The self energy is (in the abbreviated notation, as an argument $1 \equiv j_1\vec{q}_1 t_1$ and as a subscript $1 \equiv j_1\vec{q}_1$)

$$\Sigma(1,2) = -\frac{1}{2}\frac{\hbar}{i}\sum_{56}\tilde{V}^{(4ph)}_{1562}D_{56}(t_1t_2)\delta(t_1-t_2) \tag{E.2}$$

$$\Sigma(3,4) = -\frac{1}{2}\frac{\hbar}{i}\sum_{56}\tilde{V}^{(4ph)}_{3564}D_{56}(t_3t_4)\delta(t_3-t_4) \tag{E.3}$$

$$\begin{aligned}
\text{LHS} &= \frac{\delta\Sigma(1,2)}{\delta D(4,3)} && \text{(E.4)}\\
&= -\frac{1}{2}\frac{\hbar}{i}\sum_{56}\tilde{V}^{(4ph)}_{1562}\frac{\delta D_{56}(t_1t_2)}{\delta D_{43}(t_4t_3)}\delta(t_1-t_2) && \text{(E.5)}\\
&= -\frac{1}{2}\frac{\hbar}{i}\sum_{56}\tilde{V}^{(4ph)}_{1562}\delta_{54}\delta_{63}\delta(t_1-t_4)\delta(t_2-t_3)\delta(t_1-t_2) && \text{(E.6)}\\
&= -\frac{1}{2}\frac{\hbar}{i}\tilde{V}^{(4ph)}_{1432}\delta(t_1-t_4)\delta(t_2-t_3)\delta(t_1-t_2) && \text{(E.7)}
\end{aligned}$$

$$\begin{aligned}
\text{RHS} &= \frac{\delta\Sigma(3,4)}{\delta D(2,1)} && \text{(E.8)}\\
&= -\frac{1}{2}\frac{\hbar}{i}\sum_{56}\tilde{V}^{(4ph)}_{3564}\delta_{52}\delta_{61}\delta(t_3-t_2)\delta(t_4-t_1)\delta(t_3-t_4) && \text{(E.9)}\\
&= -\frac{1}{2}\frac{\hbar}{i}\tilde{V}^{(4ph)}_{3214}\delta(t_1-t_4)\delta(t_2-t_3)\delta(t_3-t_4) && \text{(E.10)}\\
&| \quad \text{the (contour) time delta function leads } \delta(t_3-t_4) \text{ to } \delta(t_1-t_2)\\
&| \quad \text{use symmetry } \tilde{V}^{(4ph)}_{3214} = \tilde{V}^{(4ph)}_{1432}\\
&= \text{LHS} && \text{(E.11)}
\end{aligned}$$

Version 2: Sign-assigned Self Energy

$$\Sigma(1,2) = -\frac{1}{2}\frac{\hbar}{i}\sum_{56}\tilde{V}^{(4ph)}_{\bar{1}5\bar{6}2}D_{56}(t_1t_2)\delta(t_1-t_2) \tag{E.12}$$

$$\Sigma(3,4) = -\frac{1}{2}\frac{\hbar}{i}\sum_{56}\tilde{V}^{(4ph)}_{\bar{3}5\bar{6}4}D_{56}(t_3t_4)\delta(t_3-t_4) \tag{E.13}$$

$$\begin{aligned}
\text{LHS} &= \frac{\delta\Sigma(1,2)}{\delta D(4,3)} && \text{(E.14)}\\
&= -\frac{1}{2}\frac{\hbar}{i}\sum_{56}\tilde{V}^{(4ph)}_{\bar{1}5\bar{6}2}\frac{\delta D_{56}(t_1t_2)}{\delta D_{43}(t_4t_3)}\delta(t_1-t_2) && \text{(E.15)}\\
&= -\frac{1}{2}\frac{\hbar}{i}\tilde{V}^{(4ph)}_{\bar{1}4\bar{3}2}\delta(t_1-t_4)\delta(t_2-t_3)\delta(t_1-t_2) && \text{(E.16)}
\end{aligned}$$

$$\begin{aligned}
\text{RHS} &= \frac{\delta\Sigma(3,4)}{\delta D(2,1)} && \text{(E.17)}\\
&= -\frac{1}{2}\frac{\hbar}{i}\sum_{56}\tilde{V}^{(4ph)}_{\bar{3}5\bar{6}4}\frac{\delta D_{56}(t_3t_4)}{\delta D_{21}(t_2t_1)}\delta(t_3-t_4) && \text{(E.18)}\\
&= -\frac{1}{2}\frac{\hbar}{i}\tilde{V}^{(4ph)}_{\bar{3}2\bar{1}4}\delta(t_3-t_2)\delta(t_4-t_1)\delta(t_3-t_4) && \text{(E.19)}\\
&| \quad \text{use the symmetry of } \tilde{V}^{(4ph)}_{\bar{3}2\bar{1}4}\\
&= \frac{1}{2}\frac{\hbar}{i}\tilde{V}^{(4ph)}_{\bar{1}4\bar{3}2}\delta(t_1-t_4)\delta(t_2-t_3)\delta(t_3-t_4) && \text{(E.20)}\\
&| \quad \text{the (contour) time delta function leads } \delta(t_3-t_4) \text{ to } \delta(t_1-t_2)\\
&= \text{LHS} && \text{(E.21)}
\end{aligned}$$

E.1.2 $V^{(3ph)^2}$ Term (Yes)

Version 1: General Self Energy

The self energy is

$$\Sigma(1,2) = \frac{1}{2}\frac{\hbar}{i}\sum_{5678}\tilde{V}^{(3ph)}_{156}\tilde{V}^{(3ph)}_{782}D_{57}(t_1t_2)D_{86}(t_2t_1) \tag{E.22}$$

$$\Sigma(3,4) = \frac{1}{2}\frac{\hbar}{i}\sum_{5678}\tilde{V}^{(3ph)}_{356}\tilde{V}^{(3ph)}_{784}D_{57}(t_3t_4)D_{86}(t_4t_3) \tag{E.23}$$

$$\begin{aligned}
\text{LHS} &= \frac{\delta\Sigma(1,2)}{\delta D(4,3)} && \text{(E.24)}\\
&= \frac{1}{2}\frac{\hbar}{i}\sum_{5678}\tilde{V}^{(3ph)}_{156}\tilde{V}^{(3ph)}_{782}\left(\frac{\delta D_{57}(t_1t_2)}{\delta D_{43}(t_4t_3)}D_{86}(t_2t_1)+D_{57}(t_1t_2)\frac{\delta D_{86}(t_2t_1)}{\delta D_{43}(t_4t_3)}\right) && \text{(E.25)}\\
&= \frac{1}{2}\frac{\hbar}{i}\sum_{5678}\tilde{V}^{(3ph)}_{156}\tilde{V}^{(3ph)}_{782}\\
&\quad\times(\delta_{54}\delta_{73}\delta(t_1-t_4)\delta(t_2-t_3)D_{86}(t_2t_1)+D_{57}(t_1t_2)\delta_{84}\delta_{63}\delta(t_2-t_4)\delta(t_1-t_3)) && \text{(E.26)}\\
&= \frac{1}{2}\frac{\hbar}{i}\sum_{68}\tilde{V}^{(3ph)}_{146}\tilde{V}^{(3ph)}_{382}D_{86}(t_2t_1)\delta(t_1-t_4)\delta(t_2-t_3)\\
&\quad+\frac{1}{2}\frac{\hbar}{i}\sum_{57}\tilde{V}^{(3ph)}_{153}\tilde{V}^{(3ph)}_{742}D_{57}(t_1t_2)\delta(t_2-t_4)\delta(t_1-t_3) && \text{(E.27)}
\end{aligned}$$

$$\begin{aligned}
\text{RHS} &= \frac{1}{2}\frac{\hbar}{i}\sum_{5678}\tilde{V}^{(3ph)}_{356}\tilde{V}^{(3ph)}_{784}\\
&\quad\times(\delta_{52}\delta_{71}\delta(t_3-t_2)\delta(t_4-t_1)D_{86}(t_4t_3)+D_{57}(t_3t_4)\delta_{82}\delta_{61}\delta(t_4-t_2)\delta(t_3-t_1)) && \text{(E.28)}\\
&= \frac{1}{2}\frac{\hbar}{i}\sum_{68}\tilde{V}^{(3ph)}_{326}\tilde{V}^{(3ph)}_{184}D_{86}(t_4t_3)\delta(t_3-t_2)\delta(t_4-t_1) && \text{(E.29)}\\
&\quad+\frac{1}{2}\frac{\hbar}{i}\sum_{57}\tilde{V}^{(3ph)}_{351}\tilde{V}^{(3ph)}_{724}D_{57}(t_3t_4)\delta(t_4-t_2)\delta(t_3-t_1) && \text{(E.30)}\\
&\mid\quad \text{rename } 6\leftrightarrow 8 \text{ in the first term}\\
&\mid\quad \text{the second term is the same using the symmetry of } \tilde{V}^{(4ph)} \text{ and that of the delta functions}\\
&= \frac{1}{2}\frac{\hbar}{i}\sum_{68}\tilde{V}^{(3ph)}_{328}\tilde{V}^{(3ph)}_{164}D_{68}(t_4t_3)\delta(t_3-t_2)\delta(t_4-t_1) && \text{(E.31)}\\
&\quad+\frac{1}{2}\frac{\hbar}{i}\sum_{57}\tilde{V}^{(3ph)}_{153}\tilde{V}^{(3ph)}_{742}D_{57}(t_1t_2)\delta(t_2-t_4)\delta(t_1-t_3) && \text{(E.32)}\\
&\mid\quad \text{use } D_{68}(t_4t_3)=D_{86}(t_3t_4) \text{ and use the (contour time) delta functions}\\
&= \text{LHS} && \text{(E.33)}
\end{aligned}$$

Version 2: Sign-assigned Self Energy
The paired momenta are $(\vec{q}_1,\vec{q}_2)$, $(\vec{q}_5,\vec{q}_7)$ and $(\vec{q}_8,\vec{q}_6)$.

$$\Sigma(1,2) = \frac{1}{2}\frac{\hbar}{i}\sum_{5678}\tilde{V}^{(3ph)}_{\bar{1}56}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}2}D_{57}(t_1t_2)D_{86}(t_2t_1) \tag{E.34}$$

$$\Sigma(3,4) = \frac{1}{2}\frac{\hbar}{i}\sum_{5678}\tilde{V}^{(3ph)}_{\bar{3}56}\tilde{V}^{(3ph)}_{\bar{7}\bar{8}4}D_{57}(t_3t_4)D_{86}(t_4t_3) \tag{E.35}$$

$$\text{LHS} = \frac{1}{2}\frac{\hbar}{i}\sum_{68}\tilde{V}^{(3ph)}_{\bar{1}46}\tilde{V}^{(3ph)}_{\bar{3}\bar{8}2}D_{86}(t_2t_1)\delta(t_1-t_4)\delta(t_2-t_3)$$

$$+\frac{1}{2}\frac{\hbar}{i}\sum_{57}\tilde{V}^{(3ph)}_{\bar{1}53}\tilde{V}^{(3ph)}_{\bar{7}\bar{4}2}D_{57}(t_1t_2)\delta(t_2-t_4)\delta(t_1-t_3) \tag{E.36}$$

$$\begin{aligned}
\text{RHS} &= \frac{1}{2}\frac{\hbar}{i}\sum_{68}\tilde{V}^{(3ph)}_{\bar{3}26}\tilde{V}^{(3ph)}_{\bar{1}\bar{8}4}D_{68}(t_4t_3)\delta(t_3-t_2)\delta(t_4-t_1) \\
&\quad +\frac{1}{2}\frac{\hbar}{i}\sum_{57}\tilde{V}^{(3ph)}_{\bar{3}51}\tilde{V}^{(3ph)}_{\bar{7}\bar{2}4}D_{57}(t_3t_4)\delta(t_4-t_2)\delta(t_3-t_1) &\text{(E.37)} \\
&\quad | \quad \text{rename } 6 \leftrightarrow 8 \text{ in the first term then write } D_{68}(t_4t_3) = D_{86}(t_3t_4) \\
&= \frac{1}{2}\frac{\hbar}{i}\sum_{68}\tilde{V}^{(3ph)}_{\bar{3}26}\tilde{V}^{(3ph)}_{\bar{1}\bar{8}4}D_{86}(t_3t_4)\delta(t_3-t_2)\delta(t_4-t_1) \\
&\quad +\frac{1}{2}\frac{\hbar}{i}\sum_{57}\tilde{V}^{(3ph)}_{\bar{3}51}\tilde{V}^{(3ph)}_{\bar{7}\bar{2}4}D_{57}(t_3t_4)\delta(t_4-t_2)\delta(t_3-t_1) &\text{(E.38)} \\
&\quad | \quad \text{interchange the signs of } \vec{q}_8 \text{ and } \vec{q}_6 \text{ so that } \tilde{V}^{(3ph)}_{\bar{3}26}\tilde{V}^{(3ph)}_{\bar{1}\bar{8}4} = \tilde{V}^{(3ph)}_{\bar{3}2\bar{8}}\tilde{V}^{(3ph)}_{\bar{1}64} \\
&\quad | \quad \text{interchange the signs of } \vec{q}_3 \text{ and } \vec{q}_4 \text{ as well as } \vec{q}_1 \text{ and } \vec{q}_2 \text{ so that } \tilde{V}^{(3ph)}_{\bar{3}51}\tilde{V}^{(3ph)}_{\bar{7}\bar{2}4} = \tilde{V}^{(3ph)}_{35\bar{1}}\tilde{V}^{(3ph)}_{\bar{7}2\bar{4}} \\
&= \text{LHS} &\text{(E.39)}
\end{aligned}$$

E.1.3 $V^{(3ph)^2}V^{(4ph)}$ Type-1 Term (No)

Version 1: General Self Energy

$$\Sigma(1,2) = \frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,9,10,11,12}\int dt_7\tilde{V}^{(3ph)}_{1,5,6}\tilde{V}^{(3ph)}_{7,9,10}\tilde{V}^{(4ph)}_{11,12,8,2}D_{5,7}(t_1t_7)D_{9,11}(t_7t_2)D_{12,10}(t_2t_7)D_{8,6}(t_2t_1)$$

$$\Sigma(3,4) = \frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,9,10,11,12}\int dt_7\tilde{V}^{(3ph)}_{3,5,6}\tilde{V}^{(3ph)}_{7,9,10}\tilde{V}^{(4ph)}_{11,12,8,4}D_{5,7}(t_3t_7)D_{9,11}(t_7t_4)D_{12,10}(t_4t_7)D_{8,6}(t_4t_3)$$

$$\begin{aligned}
&\text{LHS} \\
&= \frac{\delta\Sigma(1,2)}{\delta D(4,3)} &\text{(E.40)} \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,9,10,11,12}\int dt_7\tilde{V}^{(3ph)}_{1,5,6}\tilde{V}^{(3ph)}_{7,9,10}\tilde{V}^{(4ph)}_{11,12,8,2} \\
&\quad \times\left(\frac{\delta D_{5,7}(t_1t_7)}{\delta D_{43}(t_4t_3)}D_{9,11}(t_7t_2)D_{12,10}(t_2t_7)D_{8,6}(t_2t_1)+D_{5,7}(t_1t_7)\frac{\delta D_{9,11}(t_7t_2)}{\delta D_{43}(t_4t_3)}D_{12,10}(t_2t_7)D_{8,6}(t_2t_1)\right. \\
&\quad \left.+D_{5,7}(t_1t_7)D_{9,11}(t_7t_2)\frac{\delta D_{12,10}(t_2t_7)}{\delta D_{43}(t_4t_3)}D_{8,6}(t_2t_1)+D_{5,7}(t_1t_7)D_{9,11}(t_7t_2)D_{12,10}(t_2t_7)\frac{\delta D_{8,6}(t_2t_1)}{\delta D_{43}(t_4t_3)}\right) &\text{(E.41)} \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{6,8,9,10,11,12}\tilde{V}^{(3ph)}_{1,4,6}\tilde{V}^{(3ph)}_{3,9,10}\tilde{V}^{(4ph)}_{11,12,8,2}D_{9,11}(t_3t_2)D_{12,10}(t_2t_3)D_{8,6}(t_2t_1)\delta(t_1-t_4) \\
&\quad +\frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,10,12}\tilde{V}^{(3ph)}_{1,5,6}\tilde{V}^{(3ph)}_{7,4,10}\tilde{V}^{(4ph)}_{3,12,8,2}D_{5,7}(t_1t_4)D_{12,10}(t_2t_4)D_{8,6}(t_2t_1)\delta(t_2-t_3) \\
&\quad +\frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,9,11}\tilde{V}^{(3ph)}_{1,5,6}\tilde{V}^{(3ph)}_{7,9,3}\tilde{V}^{(4ph)}_{11,4,8,2}D_{5,7}(t_1t_3)D_{9,11}(t_3t_2)D_{8,6}(t_2t_1)\delta(t_2-t_4)
\end{aligned}$$

$$+\frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,7,9,10,11,12} \int dt_7 \tilde{V}^{(3ph)}_{1,5,3} \tilde{V}^{(3ph)}_{7,9,10} \tilde{V}^{(4ph)}_{11,12,4,2} D_{5,7}(t_1t_7) D_{9,11}(t_7t_4) D_{12,10}(t_2t_7) \delta(t_2-t_4)\delta(t_1-t_3)$$

$$\begin{aligned}
& \text{RHS} \\
= & \frac{\delta\Sigma(3,4)}{\delta D(2,1)} \qquad \text{(E.42)} \\
= & \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12} \int dt_7 \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(3ph)}_{7,9,10} \tilde{V}^{(4ph)}_{11,12,8,4} \\
& \times \left(\frac{\delta D_{5,7}(t_3t_7)}{\delta D_{21}(t_2t_1)} D_{9,11}(t_7t_4) D_{12,10}(t_4t_7) D_{8,6}(t_4t_3) + D_{5,7}(t_3t_7) \frac{\delta D_{9,11}(t_7t_4)}{\delta D_{21}(t_2t_1)} D_{12,10}(t_4t_7) D_{8,6}(t_4t_3) \right. \\
& \left. + D_{5,7}(t_3t_7) D_{9,11}(t_7t_4) \frac{\delta D_{12,10}(t_4t_7)}{\delta D_{21}(t_2t_1)} D_{8,6}(t_4t_3) + D_{5,7}(t_3t_7) D_{9,11}(t_7t_4) D_{12,10}(t_4t_7) \frac{\delta D_{8,6}(t_4t_3)}{\delta D_{21}(t_2t_1)} \right) \text{(E.43)} \\
= & \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{6,8,9,10,11,12} \tilde{V}^{(3ph)}_{3,2,6} \tilde{V}^{(3ph)}_{1,9,10} \tilde{V}^{(4ph)}_{11,12,8,4} D_{9,11}(t_1t_4) D_{12,10}(t_4t_1) D_{8,6}(t_4t_3) \delta(t_3-t_2) \\
& + \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,10,12} \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(3ph)}_{7,2,10} \tilde{V}^{(4ph)}_{1,12,8,4} D_{5,7}(t_3t_2) D_{12,10}(t_4t_2) D_{8,6}(t_4t_3) \delta(t_4-t_1) \\
& + \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,11} \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(3ph)}_{7,9,1} \tilde{V}^{(4ph)}_{11,2,8,4} D_{5,7}(t_3t_1) D_{9,11}(t_1t_4) D_{8,6}(t_4t_3) \delta(t_4-t_2) \\
& + \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,7,9,10,11,12} \int dt_7 \tilde{V}^{(3ph)}_{3,5,1} \tilde{V}^{(3ph)}_{7,9,10} \tilde{V}^{(4ph)}_{11,12,2,4} D_{5,7}(t_3t_7) D_{9,11}(t_7t_4) D_{12,10}(t_4t_7) \delta(t_4-t_2)\delta(t_3-t_1)
\end{aligned}$$

Hence the fourth line of LHS and RHS matches. However, the curl condition is not satisfied by noticing that in LHS, the external index 4 appears in $\tilde{V}^{(3ph)}$ and in RHS, the external index 4 appears in $\tilde{V}^{(4ph)}$.

E.1.4 $V^{(3ph)^2}V^{(4ph)}$ Type-2 Term (No)

The same situation in Type-1 term appears here, thus the curl condition is not satisfied.

E.1.5 $V^{(3ph)^2}V^{(4ph)}$ Type-3 Term (No)

Type-3 term is different from Type-1 and Type-2 terms, so we need to check the curl condition explicitly.

Version 1: General Self Energy

$$\begin{aligned}
\Sigma(1,2) &= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12} \int dt_7 \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(4ph)}_{7,8,9,10} \tilde{V}^{(3ph)}_{11,12,2} D_{5,7}(t_1t_7) D_{9,11}(t_7t_2) D_{12,10}(t_2t_7) D_{8,6}(t_7t_1) \\
\Sigma(3,4) &= \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12} \int dt_7 \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(4ph)}_{7,8,9,10} \tilde{V}^{(3ph)}_{11,12,4} D_{5,7}(t_3t_7) D_{9,11}(t_7t_4) D_{12,10}(t_4t_7) D_{8,6}(t_7t_3)
\end{aligned}$$

$$\begin{aligned}
& \text{LHS} \\
= & \frac{\delta\Sigma(1,2)}{\delta D(4,3)} \qquad \text{(E.44)}
\end{aligned}$$

$$
\begin{aligned}
= & \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12} \int dt_7 \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(4ph)}_{7,8,9,10} \tilde{V}^{(3ph)}_{11,12,2} \\
& \times \left(\frac{\delta D_{5,7}(t_1 t_7)}{\delta D_{43}(t_4 t_3)} D_{9,11}(t_7 t_2) D_{12,10}(t_2 t_7) D_{8,6}(t_7 t_1) + D_{5,7}(t_1 t_7) \frac{\delta D_{9,11}(t_7 t_2)}{\delta D_{43}(t_4 t_3)} D_{12,10}(t_2 t_7) D_{8,6}(t_7 t_1) \right. \\
& \left. + D_{5,7}(t_1 t_7) D_{9,11}(t_7 t_2) \frac{\delta D_{12,10}(t_2 t_7)}{\delta D_{43}(t_4 t_3)} D_{8,6}(t_7 t_1) + D_{5,7}(t_1 t_7) D_{9,11}(t_7 t_2) D_{12,10}(t_2 t_7) \frac{\delta D_{8,6}(t_7 t_1)}{\delta D_{43}(t_4 t_3)} \right) \\
= & \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{6,8,9,10,11,12} \tilde{V}^{(3ph)}_{1,4,6} \tilde{V}^{(4ph)}_{3,8,9,10} \tilde{V}^{(3ph)}_{11,12,2} D_{9,11}(t_3 t_2) D_{12,10}(t_2 t_3) D_{8,6}(t_3 t_1) \delta(t_1 - t_4) \\
& + \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,10,12} \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(4ph)}_{7,8,4,10} \tilde{V}^{(3ph)}_{3,12,2} D_{5,7}(t_1 t_4) D_{12,10}(t_2 t_4) D_{8,6}(t_4 t_1) \delta(t_2 - t_3) \\
& + \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,11} \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(4ph)}_{7,8,9,3} \tilde{V}^{(3ph)}_{11,4,2} D_{5,7}(t_1 t_3) D_{9,11}(t_3 t_2) D_{8,6}(t_3 t_1) \delta(t_2 - t_4) \\
& + \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{5,7,9,10,11,12} \tilde{V}^{(3ph)}_{1,5,3} \tilde{V}^{(4ph)}_{7,4,9,10} \tilde{V}^{(3ph)}_{11,12,2} D_{5,7}(t_1 t_4) D_{9,11}(t_4 t_2) D_{12,10}(t_2 t_4) \delta(t_1 - t_3)
\end{aligned} \tag{E.45}
$$

$$
\begin{aligned}
& \text{RHS} \\
= & \frac{\delta \Sigma(3,4)}{\delta D(2,1)}
\end{aligned} \tag{E.46}
$$

$$
\begin{aligned}
= & \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12} \int dt_7 \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(4ph)}_{7,8,9,10} \tilde{V}^{(3ph)}_{11,12,4} \\
& \times \left(\frac{\delta D_{5,7}(t_3 t_7)}{\delta D_{21}(t_2 t_1)} D_{9,11}(t_7 t_4) D_{12,10}(t_4 t_7) D_{8,6}(t_7 t_3) + D_{5,7}(t_3 t_7) \frac{\delta D_{9,11}(t_7 t_4)}{\delta D_{21}(t_2 t_1)} D_{12,10}(t_4 t_7) D_{8,6}(t_7 t_3) \right. \\
& \left. + D_{5,7}(t_3 t_7) D_{9,11}(t_7 t_4) \frac{\delta D_{12,10}(t_4 t_7)}{\delta D_{21}(t_2 t_1)} D_{8,6}(t_7 t_3) + D_{5,7}(t_3 t_7) D_{9,11}(t_7 t_4) D_{12,10}(t_4 t_7) \frac{\delta D_{8,6}(t_7 t_3)}{\delta D_{21}(t_2 t_1)} \right) \\
= & \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{6,8,9,10,11,12} \tilde{V}^{(3ph)}_{3,2,6} \tilde{V}^{(4ph)}_{1,8,9,10} \tilde{V}^{(3ph)}_{11,12,4} D_{9,11}(t_1 t_4) D_{12,10}(t_4 t_1) D_{8,6}(t_1 t_3) \delta(t_3 - t_2) \\
& + \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,10,12} \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(4ph)}_{7,8,2,10} \tilde{V}^{(3ph)}_{1,12,4} D_{5,7}(t_3 t_2) D_{12,10}(t_4 t_2) D_{8,6}(t_2 t_3) \delta(t_4 - t_1) \\
& + \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,11} \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(4ph)}_{7,8,9,1} \tilde{V}^{(3ph)}_{11,2,4} D_{5,7}(t_3 t_1) D_{9,11}(t_1 t_4) D_{8,6}(t_1 t_3) \delta(t_4 - t_2) \\
& + \frac{1}{4}\left(\frac{\hbar}{i}\right)^2 \sum_{5,7,9,10,11,12} \tilde{V}^{(3ph)}_{3,5,1} \tilde{V}^{(4ph)}_{7,2,9,10} \tilde{V}^{(3ph)}_{11,12,4} D_{5,7}(t_3 t_2) D_{9,11}(t_2 t_4) D_{12,10}(t_4 t_2) \delta(t_3 - t_1)
\end{aligned} \tag{E.47}
$$

Note that indices $1, 2, 3, 4$ are all "external indices" and some external indices are in the coupling constant $\tilde{V}^{(4ph)}$ on LHS but in $\tilde{V}^{(3ph)}$ in the corresponding term on RHS. The corresponding term is identified by looking at the time delta functions. Hence they don't match even after renaming indices.

E.1.6 $V^{(4ph)^2}$ Term (Yes)

Version 1: General self energy

$$\Sigma(1,2) = -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10} \tilde{V}^{(4ph)}_{1567}\tilde{V}^{(4ph)}_{8,9,10,2} D_{87}(t_2t_1)D_{59}(t_1t_2)D_{10,6}(t_2t_1) \tag{E.48}$$

$$\Sigma(3,4) = -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10} \tilde{V}^{(4ph)}_{3567}\tilde{V}^{(4ph)}_{8,9,10,4} D_{87}(t_4t_3)D_{59}(t_3t_4)D_{10,6}(t_4t_3) \tag{E.49}$$

$$\begin{aligned}
\text{LHS} &= -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10} \tilde{V}^{(4ph)}_{1567}\tilde{V}^{(4ph)}_{8,9,10,2}\left(\frac{\delta D_{87}(t_2t_1)}{\delta D_{43}(t_4t_3)}D_{59}(t_1t_2)D_{10,6}(t_2t_1)\right. \\
&\quad \left. +D_{87}(t_2t_1)\frac{\delta D_{59}(t_1t_2)}{\delta D_{43}(t_4t_3)}D_{10,6}(t_2t_1) + D_{87}(t_1t_1)D_{59}(t_1t_2)\frac{\delta D_{10,6}(t_2t_1)}{\delta D_{43}(t_4t_3)}\right) \qquad (E.50)\\
&= -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,9,10} \tilde{V}^{(4ph)}_{1563}\tilde{V}^{(4ph)}_{4,9,10,2} D_{59}(t_1t_2)D_{10,6}(t_2t_1)\delta(t_2-t_4)\delta(t_1-t_3) \\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{6,7,8,10} \tilde{V}^{(4ph)}_{1467}\tilde{V}^{(4ph)}_{8,3,10,2} D_{87}(t_2t_1)D_{10,6}(t_2t_1)\delta(t_1-t_4)\delta(t_2-t_3) \\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{5,7,8,9} \tilde{V}^{(4ph)}_{1537}\tilde{V}^{(4ph)}_{8,9,4,2} D_{87}(t_2t_1)D_{59}(t_1t_2)\delta(t_2-t_4)\delta(t_1-t_3) \qquad (E.51)
\end{aligned}$$

$$\begin{aligned}
\text{RHS} &= \frac{\delta\Sigma(3,4)}{\delta D(2,1)} \qquad (E.52)\\
&= \frac{\delta}{\delta D(2,1)}\left(-\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{56789,10} \tilde{V}^{(4ph)}_{3567}\tilde{V}^{(4ph)}_{89,10,4} D_{87}(t_4t_3)D_{59}(t_3t_4)D_{10,6}(t_4t_3)\right) \qquad (E.53)\\
&= -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{56789,10} \tilde{V}^{(4ph)}_{3567}\tilde{V}^{(4ph)}_{89,10,4}\left(\frac{\delta D_{87}(t_4t_3)}{\delta D_{21}(t_2t_1)}D_{59}(t_3t_4)D_{10,6}(t_4t_3)\right. \\
&\quad \left. +D_{87}(t_4t_3)\frac{\delta D_{59}(t_3t_4)}{\delta D_{21}(t_2t_1)}D_{10,6}(t_4t_3) + D_{87}(t_4t_3)D_{59}(t_3t_4)\frac{\delta D_{10,6}(t_4t_3)}{\delta D_{21}(t_2t_1)}\right) \qquad (E.54)\\
&= -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{569,10} \tilde{V}^{(4ph)}_{3561}\tilde{V}^{(4ph)}_{29,10,4} D_{59}(t_3t_4)D_{10,6}(t_4t_3)\delta(t_4-t_2)\delta(t_3-t_1) \\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{678,10} \tilde{V}^{(4ph)}_{3267}\tilde{V}^{(4ph)}_{81,10,4} D_{87}(t_4t_3)D_{10,6}(t_4t_3)\delta(t_3-t_2)\delta(t_4-t_1) \\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{5789} \tilde{V}^{(4ph)}_{3517}\tilde{V}^{(4ph)}_{8924} D_{87}(t_4t_3)D_{59}(t_3t_4)\delta(t_4-t_2)\delta(t_3-t_1) \qquad (E.55)\\
&\quad |\quad \text{rename } 6\leftrightarrow 10,\ 8\leftrightarrow 7 \text{ in the second line}\\
&= -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{569,10} \tilde{V}^{(4ph)}_{3561}\tilde{V}^{(4ph)}_{29,10,4} D_{59}(t_3t_4)D_{10,6}(t_4t_3)\delta(t_4-t_2)\delta(t_3-t_1) \\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2 \sum_{678,10} \tilde{V}^{(4ph)}_{32,10,8}\tilde{V}^{(4ph)}_{7164} D_{78}(t_4t_3)D_{6,10}(t_4t_3)\delta(t_3-t_2)\delta(t_4-t_1)
\end{aligned}$$

$$-\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{5789}\tilde{V}^{(4ph)}_{3517}\tilde{V}^{(4ph)}_{8924}D_{87}(t_4t_3)D_{59}(t_3t_4)\delta(t_4-t_2)\delta(t_3-t_1) \tag{E.56}$$

$|$ use $D_{78}(t_4t_3)=D_{87}(t_3t_4)$, $D_{6,10}(t_4t_3)=D_{10,6}(t_3t_4)$

$$\begin{aligned}
&= -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{569,10}\tilde{V}^{(4ph)}_{3561}\tilde{V}^{(4ph)}_{29,10,4}D_{59}(t_3t_4)D_{10,6}(t_4t_3)\delta(t_4-t_2)\delta(t_3-t_1)\\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{678,10}\tilde{V}^{(4ph)}_{32,10,8}\tilde{V}^{(4ph)}_{7164}D_{87}(t_3t_4)D_{10,6}(t_3t_4)\delta(t_3-t_2)\delta(t_4-t_1)\\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{5789}\tilde{V}^{(4ph)}_{3517}\tilde{V}^{(4ph)}_{8924}D_{87}(t_4t_3)D_{59}(t_3t_4)\delta(t_4-t_2)\delta(t_3-t_1) \qquad \text{(E.57)}\\
&= \text{LHS} \qquad \text{(E.58)}
\end{aligned}$$

Version 2: Sign-assigned Self Energy
The paired momenta are $(\vec{q}_1,\vec{q}_2)$, $(\vec{q}_8,\vec{q}_7)$, $(\vec{q}_5,\vec{q}_9)$, $(\vec{q}_{10},\vec{q}_6)$ and $(\vec{q}_3,\vec{q}_4)$.

$$\Sigma(1,2) = -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,9,10}\tilde{V}^{(4ph)}_{\bar{1}567}\tilde{V}^{(4ph)}_{\bar{8},\bar{9},\bar{10},2}D_{87}(t_2t_1)D_{59}(t_1t_2)D_{10,6}(t_2t_1) \tag{E.59}$$

$$\Sigma(3,4) = -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,9,10}\tilde{V}^{(4ph)}_{\bar{3}567}\tilde{V}^{(4ph)}_{\bar{8},\bar{9},\bar{10},4}D_{87}(t_4t_3)D_{59}(t_3t_4)D_{10,6}(t_4t_3) \tag{E.60}$$

$$\text{LHS} = \frac{\delta\Sigma(1,2)}{\delta D(4,3)} \tag{E.61}$$

$$\begin{aligned}
&= -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,9,10}\tilde{V}^{(4ph)}_{\bar{1}563}\tilde{V}^{(4ph)}_{\bar{4},\bar{9},\bar{10},2}D_{59}(t_1t_2)D_{10,6}(t_2t_1)\delta(t_2-t_4)\delta(t_1-t_3)\\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{6,7,8,10}\tilde{V}^{(4ph)}_{\bar{1}467}\tilde{V}^{(4ph)}_{\bar{8},\bar{3},\bar{10},2}D_{87}(t_2t_1)D_{10,6}(t_2t_1)\delta(t_1-t_4)\delta(t_2-t_3)\\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{5,7,8,9}\tilde{V}^{(4ph)}_{\bar{1}537}\tilde{V}^{(4ph)}_{\bar{8},\bar{9},\bar{4},2}D_{87}(t_2t_1)D_{59}(t_1t_2)\delta(t_2-t_4)\delta(t_1-t_3) \qquad \text{(E.62)}
\end{aligned}$$

$$\text{RHS} = \frac{\delta\Sigma(3,4)}{\delta D(2,1)} \tag{E.63}$$

$$\begin{aligned}
&= -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,9,10}\tilde{V}^{(4ph)}_{\bar{3}561}\tilde{V}^{(4ph)}_{\bar{2},\bar{9},\bar{10},4}D_{59}(t_3t_4)D_{10,6}(t_4t_3)\delta(t_4-t_2)\delta(t_3-t_1)\\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{6,7,8,10}\tilde{V}^{(4ph)}_{\bar{3}267}\tilde{V}^{(4ph)}_{\bar{8},\bar{1},\bar{10},4}D_{87}(t_4t_3)D_{10,6}(t_4t_3)\delta(t_3-t_2)\delta(t_4-t_1)\\
&\quad -\frac{1}{3!}\left(\frac{\hbar}{i}\right)^2\sum_{5,7,8,9}\tilde{V}^{(4ph)}_{\bar{3}517}\tilde{V}^{(4ph)}_{\bar{8},\bar{9},\bar{2},4}D_{87}(t_4t_3)D_{59}(t_3t_4)\delta(t_4-t_2)\delta(t_3-t_1) \qquad \text{(E.64)}
\end{aligned}$$

$|$ use the pairing $(\vec{q}_1,\vec{q}_2)$ and $(\vec{q}_3,\vec{q}_4)$ to change signs in the momenta and first line matches
$|$ use the pairing $(\vec{q}_1,\vec{q}_2)$ and $(\vec{q}_3,\vec{q}_4)$ to change signs in the momenta and third line matches
$|$ rename $6\leftrightarrow 10$ and $8\leftrightarrow 7$ in the second line

$$
\begin{aligned}
&| \quad \text{use } D_{78}(t_4t_3) = D_{87}(t_3t_4) \text{ and } D_{6,10}(t_4t_3) = D_{10,6}(t_3t_4) \text{ in second line} \\
&| \quad \text{use the pairing } (\vec{q}_8, \vec{q}_7) \text{ and } (\vec{q}_{10}, \vec{q}_6) \text{ to change signs in the momenta and second line matches} \\
&= \quad \text{LHS} \qquad \text{(E.65)}
\end{aligned}
$$

E.1.7 $V^{(3ph)^4}$ Term (Yes)

Version 1: General Self Energy

$$
\begin{aligned}
\Sigma(1,2) &= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12,13,14} \int dt_7 dt_8 \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(3ph)}_{7,9,10} \tilde{V}^{(3ph)}_{11,12,8} \tilde{V}^{(3ph)}_{13,14,2} \\
&\quad \times D_{57}(t_1t_7) D_{9,13}(t_7t_2) D_{14,11}(t_2t_8) D_{12,10}(t_8t_7) D_{86}(t_8t_1) \qquad \text{(E.66)} \\
\Sigma(3,4) &= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12,13,14} \int dt_7 dt_8 \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(3ph)}_{7,9,10} \tilde{V}^{(3ph)}_{11,12,8} \tilde{V}^{(3ph)}_{13,14,4} \\
&\quad \times D_{57}(t_3t_7) D_{9,13}(t_7t_4) D_{14,11}(t_4t_8) D_{12,10}(t_8t_7) D_{86}(t_8t_3) \qquad \text{(E.67)} \\
& \qquad \text{(E.68)}
\end{aligned}
$$

$$
\begin{aligned}
\text{LHS} &= \frac{\delta\Sigma(1,2)}{\delta D(4,3)} \qquad \text{(E.69)} \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12,13,14} \int dt_7 dt_8 \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(3ph)}_{7,9,10} \tilde{V}^{(3ph)}_{11,12,8} \tilde{V}^{(3ph)}_{13,14,2} \\
&\quad \times \Bigg(\frac{\delta D_{57}(t_1t_7)}{\delta D_{43}(t_4t_3)} D_{9,13}(t_7t_2) D_{14,11}(t_2t_8) D_{12,10}(t_8t_7) D_{86}(t_8t_1) \\
&\quad + D_{57}(t_1t_7) \frac{\delta D_{9,13}(t_7t_2)}{\delta D_{43}(t_4t_3)} D_{14,11}(t_2t_8) D_{12,10}(t_8t_7) D_{86}(t_8t_1) \\
&\quad + D_{57}(t_1t_7) D_{9,13}(t_7t_2) \frac{\delta D_{14,11}(t_2t_8)}{\delta D_{43}(t_4t_3)} D_{12,10}(t_8t_7) D_{86}(t_8t_1) \\
&\quad + D_{57}(t_1t_7) D_{9,13}(t_7t_2) D_{14,11}(t_2t_8) \frac{\delta D_{12,10}(t_8t_7)}{\delta D_{43}(t_4t_3)} D_{86}(t_8t_1) \\
&\quad + D_{57}(t_1t_7) D_{9,13}(t_7t_2) D_{14,11}(t_2t_8) D_{12,10}(t_8t_7) \frac{\delta D_{86}(t_8t_1)}{\delta D_{43}(t_4t_3)} \Bigg) \qquad \text{(E.70)} \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{6,8,9,10,11,12,13,14} \int dt_8 \tilde{V}^{(3ph)}_{1,4,6} \tilde{V}^{(3ph)}_{3,9,10} \tilde{V}^{(3ph)}_{11,12,8} \tilde{V}^{(3ph)}_{13,14,2} \\
&\quad \times D_{9,13}(t_3t_2) D_{14,11}(t_2t_8) D_{12,10}(t_8t_3) D_{86}(t_8t_1) \delta(t_1 - t_4) \qquad \text{(E.71)} \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,10,11,12,14} \int dt_8 \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(3ph)}_{7,4,10} \tilde{V}^{(3ph)}_{11,12,8} \tilde{V}^{(3ph)}_{3,14,2} \\
&\quad \times D_{5,7}(t_1t_4) D_{14,11}(t_2t_8) D_{12,10}(t_8t_4) D_{86}(t_8t_1) \delta(t_2 - t_3) \qquad \text{(E.72)} \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,12,13} \int dt_7 \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(3ph)}_{7,9,10} \tilde{V}^{(3ph)}_{3,12,8} \tilde{V}^{(3ph)}_{13,4,2} \\
&\quad \times D_{5,7}(t_1t_7) D_{9,13}(t_7t_2) D_{12,10}(t_3t_7) D_{86}(t_3t_1) \delta(t_2 - t_4) \qquad \text{(E.73)} \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,11,13,14} \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(3ph)}_{7,9,3} \tilde{V}^{(3ph)}_{11,4,8} \tilde{V}^{(3ph)}_{13,14,2}
\end{aligned}
$$

$$\times D_{5,7}(t_1t_3)D_{9,13}(t_3t_2)D_{14,11}(t_2t_4)D_{86}(t_4t_1) \tag{E.74}$$

$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,7,9,10,11,12,13,14} \int dt_7 \tilde{V}^{(3ph)}_{1,5,3}\tilde{V}^{(3ph)}_{7,9,10}\tilde{V}^{(3ph)}_{11,12,4}\tilde{V}^{(3ph)}_{13,14,2}$$

$$\times D_{5,7}(t_1t_7)D_{9,13}(t_7t_2)D_{14,11}(t_2t_4)D_{12,10}(t_4t_7)\delta(t_1-t_3) \tag{E.75}$$

$$\text{RHS} = \frac{\delta\Sigma(3,4)}{\delta D(2,1)} \tag{E.76}$$

$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12,13,14} \int dt_7 dt_8 \tilde{V}^{(3ph)}_{3,5,6}\tilde{V}^{(3ph)}_{7,9,10}\tilde{V}^{(3ph)}_{11,12,8}\tilde{V}^{(3ph)}_{13,14,4} \tag{E.77}$$

$$\times\left(\frac{\delta D_{57}(t_3t_7)}{\delta D_{21}(t_2t_1)}D_{9,13}(t_7t_4)D_{14,11}(t_4t_8)D_{12,10}(t_8t_7)D_{86}(t_8t_3)\right.$$

$$+D_{57}(t_3t_7)\frac{\delta D_{9,13}(t_7t_4)}{\delta D_{21}(t_2t_1)}D_{14,11}(t_4t_8)D_{12,10}(t_8t_7)D_{86}(t_8t_3)$$

$$+D_{57}(t_3t_7)D_{9,13}(t_7t_4)\frac{\delta D_{14,11}(t_4t_8)}{\delta D_{21}(t_2t_1)}D_{12,10}(t_8t_7)D_{86}(t_8t_3)$$

$$+D_{57}(t_3t_7)D_{9,13}(t_7t_4)D_{14,11}(t_4t_8)\frac{\delta D_{12,10}(t_8t_7)}{\delta D_{21}(t_2t_1)}D_{86}(t_8t_3)$$

$$\left.+D_{57}(t_3t_7)D_{9,13}(t_7t_4)D_{14,11}(t_4t_8)D_{12,10}(t_8t_7)\frac{\delta D_{86}(t_8t_3)}{\delta D_{21}(t_2t_1)}\right) \tag{E.78}$$

$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{6,8,9,10,11,12,13,14} \int dt_8 \tilde{V}^{(3ph)}_{3,2,6}\tilde{V}^{(3ph)}_{1,9,10}\tilde{V}^{(3ph)}_{11,12,8}\tilde{V}^{(3ph)}_{13,14,4}$$

$$\times D_{9,13}(t_1t_4)D_{14,11}(t_4t_8)D_{12,10}(t_8t_1)D_{86}(t_8t_3)\delta(t_3-t_2) \tag{E.79}$$

$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,10,11,12,14} \int dt_8 \tilde{V}^{(3ph)}_{3,5,6}\tilde{V}^{(3ph)}_{7,2,10}\tilde{V}^{(3ph)}_{11,12,8}\tilde{V}^{(3ph)}_{1,14,4}$$

$$\times D_{5,7}(t_3t_2)D_{14,11}(t_4t_8)D_{12,10}(t_8t_2)D_{86}(t_8t_3)\delta(t_4-t_1) \tag{E.80}$$

$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,12,13} \int dt_7 \tilde{V}^{(3ph)}_{3,5,6}\tilde{V}^{(3ph)}_{7,9,10}\tilde{V}^{(3ph)}_{1,12,8}\tilde{V}^{(3ph)}_{13,2,4}$$

$$\times D_{5,7}(t_3t_7)D_{9,13}(t_7t_4)D_{12,10}(t_1t_7)D_{86}(t_1t_3)\delta(t_4-t_2) \tag{E.81}$$

$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,11,13,14} \tilde{V}^{(3ph)}_{3,5,6}\tilde{V}^{(3ph)}_{7,9,1}\tilde{V}^{(3ph)}_{11,2,8}\tilde{V}^{(3ph)}_{13,14,2}$$

$$\times D_{5,7}(t_3t_1)D_{9,13}(t_1t_4)D_{14,11}(t_4t_2)D_{86}(t_2t_3) \tag{E.82}$$

$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,7,9,10,11,12,13,14} \int dt_7 \tilde{V}^{(3ph)}_{3,5,1}\tilde{V}^{(3ph)}_{7,9,10}\tilde{V}^{(3ph)}_{11,12,2}\tilde{V}^{(3ph)}_{13,14,4}$$

$$\times D_{5,7}(t_3t_7)D_{9,13}(t_7t_4)D_{14,11}(t_4t_2)D_{12,10}(t_2t_7)\delta(t_3-t_1) \tag{E.83}$$

RHS first line (expected to match with LHS second line)

$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{6,8,9,10,11,12,13,14} \int dt_8 \tilde{V}^{(3ph)}_{1,9,10}\tilde{V}^{(3ph)}_{13,14,4}\tilde{V}^{(3ph)}_{11,12,8}\tilde{V}^{(3ph)}_{3,2,6}$$

$$\times D_{9,13}(t_1t_4)D_{14,11}(t_4t_8)D_{12,10}(t_8t_1)D_{86}(t_8t_3)\delta(t_3-t_2) \tag{E.84}$$

$$\begin{aligned}
&\mid\quad \text{rename } 9,10 \to 5,6,\ 13,14 \to 7,10 \text{ and } 6 \to 14 \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{14,8,5,6,11,12,7,10} \int dt_8 \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(3ph)}_{7,10,4} \tilde{V}^{(3ph)}_{11,12,8} \tilde{V}^{(3ph)}_{3,2,14} \\
&\quad \times D_{57}(t_1 t_4) D_{10,11}(t_4 t_8) D_{12,6}(t_8 t_1) D_{8,14}(t_8 t_3) \delta(t_3 - t_2) \qquad \text{(E.85)} \\
&\mid\quad \text{write } D_{8,14}(t_8 t_3) = D_{14,8}(t_3 t_8),\ D_{10,11}(t_4 t_8) = D_{11,10}(t_8 t_4) \\
&\mid\quad \text{rename } 11 \to 12,\ 8 \to 11 \text{ and } 12 \to 8 \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,10,11,12,14} \int dt_8 \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(3ph)}_{7,10,4} \tilde{V}^{(3ph)}_{12,8,11} \tilde{V}^{(3ph)}_{3,2,14} \\
&\quad \times D_{57}(t_1 t_4) D_{12,10}(t_8 t_4) D_{86}(t_8 t_1) D_{14,11}(t_3 t_8) \delta(t_3 - t_2) \qquad \text{(E.86)} \\
&= \text{LHS second line} \qquad \text{(E.87)}
\end{aligned}$$

RHS second line (expected to match with LHS first line)

$$\begin{aligned}
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,10,11,12,14} \int dt_8 \tilde{V}^{(3ph)}_{1,14,4} \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(3ph)}_{11,12,8} \tilde{V}^{(3ph)}_{7,2,10} \\
&\quad \times D_{5,7}(t_3 t_2) D_{14,11}(t_4 t_8) D_{12,10}(t_8 t_2) D_{86}(t_8 t_3) \delta(t_4 - t_1) \qquad \text{(E.88)} \\
&\mid\quad \text{rename } 14 \to 6,\ 5,6 \to 9,10,\ 7,10 \to 13,14,\ 8 \to 12,\ 12 \to 11 \text{ and } 11 \to 8 \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{9,10,13,12,14,8,11,6} \int dt_8 \tilde{V}^{(3ph)}_{1,6,4} \tilde{V}^{(3ph)}_{3,9,10} \tilde{V}^{(3ph)}_{8,11,12} \tilde{V}^{(3ph)}_{13,2,14} \\
&\quad \times D_{9,13}(t_3 t_2) D_{68}(t_4 t_8) D_{11,14}(t_8 t_2) D_{12,10}(t_8 t_3) \delta(t_4 - t_1) \qquad \text{(E.89)} \\
&\mid\quad \text{write } D_{11,14}(t_8 t_2) = D_{14,11}(t_2 t_8) \text{ and } D_{68}(t_4 t_8) = D_{86}(t_8 t_4) \\
&= \text{LHS first line} \qquad \text{(E.90)}
\end{aligned}$$

RHS third line (expected to match with LHS third line)

$$\begin{aligned}
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,12,13} \int dt_7 \tilde{V}^{(3ph)}_{1,12,8} \tilde{V}^{(3ph)}_{7,9,10} \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(3ph)}_{13,2,4} \\
&\quad \times D_{5,7}(t_3 t_7) D_{9,13}(t_7 t_4) D_{12,10}(t_1 t_7) D_{86}(t_1 t_3) \delta(t_4 - t_2) \qquad \text{(E.91)} \\
&\mid\quad \text{rename } 12,8 \to 5,6,\ 10 \to 7,\ 6 \to 8,\ 5 \to 12 \text{ and } 7 \to 10 \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{12,8,10,6,9,7,5,13} \int dt_7 \tilde{V}^{(3ph)}_{1,5,6} \tilde{V}^{(3ph)}_{10,9,7} \tilde{V}^{(3ph)}_{3,12,8} \tilde{V}^{(3ph)}_{13,2,4} \\
&\quad \times D_{12,10}(t_3 t_7) D_{9,13}(t_7 t_4) D_{5,7}(t_1 t_7) D_{68}(t_1 t_3) \delta(t_4 - t_2) \qquad \text{(E.92)} \\
&\mid\quad \text{write } D_{68}(t_1 t_3) = D_{86}(t_3 t_1) \\
&= \text{LHS third line} \qquad \text{(E.93)}
\end{aligned}$$

RHS fourth line (expected to match with LHS fourth line)

$$\begin{aligned}
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,11,13,14} \tilde{V}^{(3ph)}_{7,9,1} \tilde{V}^{(3ph)}_{3,5,6} \tilde{V}^{(3ph)}_{13,14,2} \tilde{V}^{(3ph)}_{11,2,8} \\
&\quad \times D_{5,7}(t_3 t_1) D_{9,13}(t_1 t_4) D_{14,11}(t_4 t_2) D_{86}(t_2 t_3) \qquad \text{(E.94)} \\
&\mid\quad \text{rename } 7,9 \to 5,6 \text{ and } 13,14 \to 8,11
\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{7,9,5,13,6,14,8,11} \tilde{V}^{(3ph)}_{5,6,1}\tilde{V}^{(3ph)}_{3,7,9}\tilde{V}^{(3ph)}_{8,11,4}\tilde{V}^{(3ph)}_{14,2,13} \\
&\quad \times D_{75}(t_3t_1)D_{68}(t_1t_4)D_{11,14}(t_4t_2)D_{13,9}(t_2t_3) && \text{(E.95)}\\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,11,13,14} \tilde{V}^{(3ph)}_{5,6,1}\tilde{V}^{(3ph)}_{3,7,9}\tilde{V}^{(3ph)}_{8,11,4}\tilde{V}^{(3ph)}_{14,2,13} \\
&\quad \times D_{57}(t_1t_3)D_{9,13}(t_3t_2)D_{14,11}(t_2t_4)D_{8,6}(t_4t_1) && \text{(E.96)}\\
&= \text{LHS fourth line} && \text{(E.97)}
\end{aligned}$$

RHS fifth line (expected to match with LHS fifth line)

$$\begin{aligned}
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,7,9,10,11,12,13,14} \int dt_7 \tilde{V}^{(3ph)}_{1,5,3}\tilde{V}^{(3ph)}_{7,9,10}\tilde{V}^{(3ph)}_{13,14,4}\tilde{V}^{(3ph)}_{11,12,2} \\
&\quad \times D_{5,7}(t_3t_7)D_{9,13}(t_7t_4)D_{14,11}(t_4t_2)D_{12,10}(t_2t_7)\delta(t_3-t_1) && \text{(E.98)}\\
&| \quad \text{rename } 14 \leftrightarrow 11,\ 12 \leftrightarrow 13 \text{ and } 10 \leftrightarrow 9 \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,7,10,9,14,13,12,11} \int dt_7 \tilde{V}^{(3ph)}_{1,5,3}\tilde{V}^{(3ph)}_{7,10,9}\tilde{V}^{(3ph)}_{12,11,4}\tilde{V}^{(3ph)}_{14,13,2} \\
&\quad \times D_{5,7}(t_3t_7)D_{10,12}(t_7t_4)D_{11,14}(t_4t_2)D_{13,9}(t_2t_7)\delta(t_3-t_1) && \text{(E.99)}\\
&| \quad \text{write } D_{10,12}(t_7t_4) = D_{12,10}(t_4t_7),\ D_{11,14}(t_4t_2) = D_{14,11}(t_2t_4) \text{ and } D_{13,9}(t_2t_7) = D_{9,13}(t_7t_2) \\
&= \text{LHS fifth line} && \text{(E.100)}
\end{aligned}$$

Hence the curl condition is satisfied.

Version 2: Sign-assigned Self Energy
Paired momenta are $(\vec{q}_1,\vec{q}_2)$, $(\vec{q}_5,\vec{q}_7)$, $(\vec{q}_9,\vec{q}_{13})$, $(\vec{q}_{14},\vec{q}_{11})$, $(\vec{q}_{12},\vec{q}_{10})$ and $(\vec{q}_8,\vec{q}_6)$

$$\begin{aligned}
\Sigma(1,2) &= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12,13,14} \int dt_7 dt_8 \tilde{V}^{(3ph)}_{\bar{1},5,6}\tilde{V}^{(3ph)}_{\bar{7},9,10}\tilde{V}^{(3ph)}_{11,\bar{12},\bar{8}}\tilde{V}^{(3ph)}_{\bar{13},\bar{14},2} \\
&\quad \times D_{57}(t_1t_7)D_{9,13}(t_7t_2)D_{14,11}(t_2t_8)D_{12,10}(t_8t_7)D_{86}(t_8t_1) && \text{(E.101)}\\
\Sigma(3,4) &= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,11,12,13,14} \int dt_7 dt_8 \tilde{V}^{(3ph)}_{\bar{3},5,6}\tilde{V}^{(3ph)}_{\bar{7},9,10}\tilde{V}^{(3ph)}_{11,\bar{12},\bar{8}}\tilde{V}^{(3ph)}_{\bar{13},\bar{14},4} \\
&\quad \times D_{57}(t_3t_7)D_{9,13}(t_7t_4)D_{14,11}(t_4t_8)D_{12,10}(t_8t_7)D_{86}(t_8t_3) && \text{(E.102)}
\end{aligned}$$

$$\begin{aligned}
\text{LHS} &= \frac{\delta\Sigma(1,2)}{\delta D(4,3)} && \text{(E.103)}\\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{6,8,9,10,11,12,13,14} \int dt_8 \tilde{V}^{(3ph)}_{\bar{1},4,6}\tilde{V}^{(3ph)}_{\bar{3},9,10}\tilde{V}^{(3ph)}_{11,\bar{12},\bar{8}}\tilde{V}^{(3ph)}_{\bar{13},\bar{14},2} \\
&\quad \times D_{9,13}(t_3t_2)D_{14,11}(t_2t_8)D_{12,10}(t_8t_3)D_{86}(t_8t_1)\delta(t_1-t_4) \\
&\quad + \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,10,11,12,14} \int dt_8 \tilde{V}^{(3ph)}_{\bar{1},5,6}\tilde{V}^{(3ph)}_{\bar{7},4,10}\tilde{V}^{(3ph)}_{11,\bar{12},\bar{8}}\tilde{V}^{(3ph)}_{\bar{3},\bar{14},2} \\
&\quad \times D_{5,7}(t_1t_4)D_{14,11}(t_2t_8)D_{12,10}(t_8t_4)D_{86}(t_8t_1)\delta(t_2-t_3) \\
&\quad + \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,12,13} \int dt_7 \tilde{V}^{(3ph)}_{\bar{1},5,6}\tilde{V}^{(3ph)}_{\bar{7},9,10}\tilde{V}^{(3ph)}_{3,\bar{12},\bar{8}}\tilde{V}^{(3ph)}_{\bar{13},\bar{4},2}
\end{aligned}$$

$$\times D_{5,7}(t_1t_7)D_{9,13}(t_7t_2)D_{12,10}(t_3t_7)D_{86}(t_3t_1)\delta(t_2-t_4)$$
$$+\frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,9,11,13,14}\tilde{V}^{(3ph)}_{\bar{1},5,6}\tilde{V}^{(3ph)}_{\bar{7},9,3}\tilde{V}^{(3ph)}_{11,\bar{4},\bar{8}}\tilde{V}^{(3ph)}_{\bar{13},\bar{14},2}$$
$$\times D_{5,7}(t_1t_3)D_{9,13}(t_3t_2)D_{14,11}(t_2t_4)D_{86}(t_4t_1)$$
$$+\frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,7,9,10,11,12,13,14}\int dt_7\tilde{V}^{(3ph)}_{\bar{1},5,3}\tilde{V}^{(3ph)}_{\bar{7},9,10}\tilde{V}^{(3ph)}_{11,\bar{12},\bar{4}}\tilde{V}^{(3ph)}_{\bar{13},\bar{14},2}$$
$$\times D_{5,7}(t_1t_7)D_{9,13}(t_7t_2)D_{14,11}(t_2t_4)D_{12,10}(t_4t_7)\delta(t_1-t_3) \quad \text{(E.104)}$$

$$\text{RHS} = \frac{\delta\Sigma(3,4)}{\delta D(2,1)} \quad \text{(E.105)}$$
$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{6,8,9,10,11,12,13,14}\int dt_8\tilde{V}^{(3ph)}_{\bar{3},2,6}\tilde{V}^{(3ph)}_{\bar{1},9,10}\tilde{V}^{(3ph)}_{11,\bar{12},\bar{8}}\tilde{V}^{(3ph)}_{\bar{13},\bar{14},4}$$
$$\times D_{9,13}(t_1t_4)D_{14,11}(t_4t_8)D_{12,10}(t_8t_1)D_{86}(t_8t_3)\delta(t_3-t_2)$$
$$+\frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,10,11,12,14}\int dt_8\tilde{V}^{(3ph)}_{\bar{3},5,6}\tilde{V}^{(3ph)}_{\bar{7},2,10}\tilde{V}^{(3ph)}_{11,\bar{12},\bar{8}}\tilde{V}^{(3ph)}_{\bar{1},\bar{14},4}$$
$$\times D_{5,7}(t_3t_2)D_{14,11}(t_4t_8)D_{12,10}(t_8t_2)D_{86}(t_8t_3)\delta(t_4-t_1)$$
$$+\frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,9,10,12,13}\int dt_7\tilde{V}^{(3ph)}_{\bar{3},5,6}\tilde{V}^{(3ph)}_{\bar{7},9,10}\tilde{V}^{(3ph)}_{1,\bar{12},\bar{8}}\tilde{V}^{(3ph)}_{\bar{13},\bar{2},4}$$
$$\times D_{5,7}(t_3t_7)D_{9,13}(t_7t_4)D_{12,10}(t_1t_7)D_{86}(t_1t_3)\delta(t_4-t_2)$$
$$+\frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,9,11,13,14}\tilde{V}^{(3ph)}_{\bar{3},5,6}\tilde{V}^{(3ph)}_{\bar{7},9,1}\tilde{V}^{(3ph)}_{11,\bar{2},\bar{8}}\tilde{V}^{(3ph)}_{\bar{13},\bar{14},2}$$
$$\times D_{5,7}(t_3t_1)D_{9,13}(t_1t_4)D_{14,11}(t_4t_2)D_{86}(t_2t_3)$$
$$+\frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,7,9,10,11,12,13,14}\int dt_7\tilde{V}^{(3ph)}_{\bar{3},5,1}\tilde{V}^{(3ph)}_{\bar{7},9,10}\tilde{V}^{(3ph)}_{11,\bar{12},\bar{2}}\tilde{V}^{(3ph)}_{\bar{13},\bar{14},4}$$
$$\times D_{5,7}(t_3t_7)D_{9,13}(t_7t_4)D_{14,11}(t_4t_2)D_{12,10}(t_2t_7)\delta(t_3-t_1) \quad \text{(E.106)}$$

RHS first line (expected to match with LHS second line)

| follow earlier to rename $9,10\to 5,6$, $13,14\to 7,10$ and $6\to 14$

$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{14,8,5,6,11,12,7,10}\int dt_8\tilde{V}^{(3ph)}_{\bar{3},2,14}\tilde{V}^{(3ph)}_{\bar{1},5,6}\tilde{V}^{(3ph)}_{11,\bar{12},\bar{8}}\tilde{V}^{(3ph)}_{\bar{7},\bar{10},4}$$
$$\times D_{5,7}(t_1t_4)D_{10,11}(t_4t_8)D_{12,6}(t_8t_1)D_{8,14}(t_8t_3)\delta(t_3-t_2) \quad \text{(E.107)}$$

| write $D_{8,14}(t_8t_3)=D_{14,8}(t_3t_8)$ and $D_{10,11}(t_4t_8)=D_{11,10}(t_8t_4)$

| then rename $11\to 12$, $8\to 11$ and $12\to 8$

$$= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2\sum_{5,6,7,8,10,11,12,14}\int dt_8\tilde{V}^{(3ph)}_{\bar{3},2,14}\tilde{V}^{(3ph)}_{\bar{1},5,6}\tilde{V}^{(3ph)}_{12,\bar{8},\bar{11}}\tilde{V}^{(3ph)}_{\bar{7},\bar{10},4}$$
$$\times D_{5,7}(t_1t_4)D_{12,10}(t_8t_4)D_{8,6}(t_8t_1)D_{14,11}(t_3t_8)\delta(t_3-t_2) \quad \text{(E.108)}$$

| use the pairing $(\vec{q}_{10},\vec{q}_{12})$ and $(\vec{q}_{14},\vec{q}_{11})$ to change signs

$=$ LHS second line (E.109)

RHS second line (expected to match with LHS first line)

$$
\begin{aligned}
&| \quad \text{follow earlier to rename } 14 \to 6,\ 5,6 \to 9,10,\ 7,10 \to 13,14,\ 8 \to 12,\ 12 \to 11 \text{ and } 11 \to 8 \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{9,10,13,12,14,8,11,6} \int dt_8 \tilde{V}^{(3ph)}_{\bar{3},9,10} \tilde{V}^{(3ph)}_{\bar{1}\bar{3},2,14} \tilde{V}^{(3ph)}_{8,\bar{1}\bar{1},12} \tilde{V}^{(3ph)}_{\bar{1},\bar{6},4} \\
&\quad \times D_{9,13}(t_3t_2) D_{68}(t_4t_8) D_{11,14}(t_8t_2) D_{12,10}(t_8t_3)\delta(t_4-t_1) \qquad \text{(E.110)} \\
&| \quad \text{write } D_{11,14}(t_8t_2) = D_{14,11}(t_2t_8) \text{ and } D_{68}(t_4t_8) = D_{86}(t_8t_4) \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{6,8,9,10,11,12,13,14} \int dt_8 \tilde{V}^{(3ph)}_{\bar{3},9,10} \tilde{V}^{(3ph)}_{\bar{1}\bar{3},2,14} \tilde{V}^{(3ph)}_{8,\bar{1}\bar{1},12} \tilde{V}^{(3ph)}_{\bar{1},\bar{6},4} \\
&\quad \times D_{9,13}(t_3t_2) D_{86}(t_8t_4) D_{14,11}(t_2t_8) D_{12,10}(t_8t_3)\delta(t_4-t_1) \qquad \text{(E.111)} \\
&| \quad \text{use the pairing } (\vec{q}_6,\vec{q}_8) \text{ and } (\vec{q}_{11},\vec{q}_{14}) \text{ to change signs} \\
&= \text{LHS first line} \qquad \text{(E.112)}
\end{aligned}
$$

RHS third line (expected to match with LHS third line)

$$
\begin{aligned}
&| \quad \text{rename } 12,8 \to 5,6,\ 10 \to 7,\ 6 \to 8,\ 5 \to 12 \text{ and } 7 \to 10 \\
&| \quad \text{then write } D_{68}(t_1t_3) = D_{86}(t_3t_1) \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,10,12,13} \int dt_7 \tilde{V}^{(3ph)}_{\bar{3},12,8} \tilde{V}^{(3ph)}_{\bar{1}\bar{0},9,7} \tilde{V}^{(3ph)}_{1,\bar{5},\bar{6}} \tilde{V}^{(3ph)}_{\bar{1}\bar{3},\bar{2},4} \\
&\quad \times D_{12,10}(t_3t_7) D_{9,13}(t_7t_4) D_{5,7}(t_1t_7) D_{86}(t_3t_1)\delta(t_4-t_2) \qquad \text{(E.113)} \\
&| \quad \text{use the pairings } (\vec{q}_5,\vec{q}_7),\ (\vec{q}_6,\vec{q}_8),\ (\vec{q}_{10},\vec{q}_{12}),\ (\vec{q}_3,\vec{q}_4) \text{ and } (\vec{q}_1,\vec{q}_2) \text{ to change signs} \\
&= \text{LHS third line} \qquad \text{(E.114)}
\end{aligned}
$$

RHS fourth line (expected to match with LHS fourth line)

$$
\begin{aligned}
&| \quad \text{rename } 7,9 \leftrightarrow 5,6,\ 13,14 \leftrightarrow 8,11 \\
&| \quad \text{then swop all indices in all the Green's functions, } D \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,6,7,8,9,11,13,14} \tilde{V}^{(3ph)}_{\bar{3},7,9} \tilde{V}^{(3ph)}_{\bar{5},6,1} \tilde{V}^{(3ph)}_{14,\bar{2},\bar{1}\bar{3}} \tilde{V}^{(3ph)}_{\bar{8},\bar{1}\bar{1},4} \\
&\quad \times D_{5,7}(t_1t_3) D_{9,13}(t_3t_2) D_{14,11}(t_2t_4) D_{86}(t_4t_1) \qquad \text{(E.115)} \\
&| \quad \text{use the pairings } (\vec{q}_1,\vec{q}_2),\ (\vec{q}_5,\vec{q}_7),\ (\vec{q}_3,\vec{q}_4),\ (\vec{q}_{11},\vec{q}_{14}) \text{ and } (\vec{q}_{13},\vec{q}_9) \text{ to change signs} \\
&= \text{LHS fourth line} \qquad \text{(E.116)}
\end{aligned}
$$

RHS fifth line (expected to match with LHS fifth line)

$$
\begin{aligned}
&| \quad \text{rename } 14 \leftrightarrow 11,\ 12 \leftrightarrow 13,\ 10 \leftrightarrow 9 \\
&| \quad \text{then write } D_{10,12}(t_7t_4) = D_{12,10}(t_4t_7),\ D_{11,14}(t_4t_2) = D_{14,11}(t_2t_4) \text{ and } D_{13,9}(t_2t_7) = D_{9,13}(t_7t_2) \\
&= \frac{1}{2}\left(\frac{\hbar}{i}\right)^2 \sum_{5,7,9,10,11,12,13,14} \int dt_7 \tilde{V}^{(3ph)}_{\bar{3},5,1} \tilde{V}^{(3ph)}_{\bar{7},10,9} \tilde{V}^{(3ph)}_{14,\bar{1}\bar{3},\bar{2}} \tilde{V}^{(3ph)}_{\bar{1}\bar{2},\bar{1}\bar{1},4} \\
&\quad \times D_{5,7}(t_3t_7) D_{12,10}(t_4t_7) D_{14,11}(t_2t_4) D_{9,13}(t_7t_2)\delta(t_3-t_1) \qquad \text{(E.117)} \\
&| \quad \text{use the pairings } (\vec{q}_1,\vec{q}_2),\ (\vec{q}_3,\vec{q}_4) \text{ and } (\vec{q}_{11},\vec{q}_{14)} \text{ to change signs} \\
&= \text{LHS fifth line} \qquad \text{(E.118)}
\end{aligned}
$$

Some concluding comments are

1. Indeed the satisfaction of the curl condition amounts to certain symmetries of the vertex parts.
2. The 3 cross terms do not satisfy the curl condition and it can be seen from the Feynman diagrams that the vertex parts are not symmetric.
3. $V^{(3ph)^4}$ term satisfies the curl condition as the ladder vertex correction has the required symmetry.
4. Thus there is no Φ-derivability for certain diagrams of the combined 3-phonon and 4-phonon interaction, though there may be Φ-derivability for each interaction seperately. Perhaps the reason is just like that for electron-phonon interaction. There are 2 systems where energy can distribute. In this case the "2 systems" are the 3-phonon system and the 4-phonon system. And just like in electron-phonon interaction, to get conservation, we need pairs of diagrams to take into account the total energy in the 2 systems which is conserved.

E.2 Subjecting the Phonon self energy to the Landauer Energy Current Conservation Sum rule

E.2.1 $V^{(3ph)^2}$ Term

The Landauer energy conservation sum rule is,

$$0 = \int \frac{d\omega}{2\pi}\hbar\omega \sum_{1,2} \left(\Sigma_{12}^{(C)<}(\omega) D_{21}^{(C)>} - \Sigma_{12}^{(C)>}(\omega) D_{21}^{(C)<}(\omega)\right) \tag{E.119}$$

We drop the central device superscript label (C) from now on. First establish an identity, $D_{21}^{>}(-\omega) = D_{12}^{<}(\omega)$

$$\begin{aligned}
D_{21}^{>}(-\omega) &= \int dt e^{i(-\omega)t} D_{21}^{>}(t) && \text{(E.120)}\\
&= \int dt e^{i\omega(-t)} D_{21}^{>}(t) && \text{(E.121)}\\
&\mid \quad \text{rename } t \to -t \text{ so } \int_{-\infty}^{\infty} dt \to \int_{-\infty}^{\infty} dt \\
&= dt e^{i\omega t} D_{21}^{>}(-t) && \text{(E.122)}\\
&\mid \quad \text{compare the 3 expressions at steady state: } D_{21}^{>}(t) = D_{21}^{>}(t_1 - t_2) = -\frac{i}{\hbar}\langle u_2(t_1)u_1(t_2)\rangle \\
&\mid \quad D_{21}^{>}(-t) = D_{21}^{>}(t_2 - t_1) = -\frac{i}{\hbar}\langle u_2(t_2)u_1(t_1)\rangle \\
&\mid \quad D_{12}^{<}(t) = D_{12}^{<}(t_1 - t_2) = -\frac{i}{\hbar}\langle u_2(t_2)u_1(t_1)\rangle \text{ so } D_{12}^{<}(t) = D_{21}^{>}(-t) \\
&= \int dt e^{i\omega t} D_{12}^{<}(t) && \text{(E.123)}\\
&= D_{12}^{<}(\omega) && \text{(E.124)}
\end{aligned}$$

Now we check this sum rule for the self energy $\tilde{V}^{(3ph)^2}$ which has been checked for conservation by kinetic theory and by Baym's Φ-derivability condition earlier in this appendix.

The self consistent self energy is

$$\Sigma_{12}^{\gtrless}(t_1t_2) = \frac{1}{2}\frac{\hbar}{i}\sum_{3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D_{35}^{\gtrless}(t_1t_2)D_{64}^{\lessgtr}(t_2t_1) \tag{E.125}$$

We have assumed steady state so we can Fourier transform to the frequency domain.

$$\begin{aligned}\Sigma_{12}^{>}(\omega) &= \int d(t_1-t_2)e^{i\omega(t_1-t_2)}\Sigma_{12}^{>}(t_1-t_2) &\text{(E.126)}\\ &\mid\ \text{write the Green's functions into Fourier form } D_{35}^{>}(\omega_1) \text{ and } D_{64}^{<}(\omega_2)\\ &= \frac{1}{2}\frac{\hbar}{i}\sum_{3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}\int\frac{d\omega_1}{2\pi}\int\frac{d\omega_2}{2\pi}\int d(t_1-t_2)e^{i(\omega-\omega_1+\omega_2)(t_1-t_2)}D_{35}^{>}(\omega_1)D_{64}^{<}(\omega_2)\\ &\mid\ \text{use representation of delta function } \frac{1}{2\pi}\int dte^{i\omega t}=\delta(\omega) \text{ then evaluate } \int d\omega_2\\ &= \frac{1}{2}\frac{\hbar}{i}\sum_{3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}\int\frac{d\omega_1}{2\pi}D_{35}^{>}(\omega_1)D_{64}^{<}(\omega_1-\omega) &\text{(E.127)}\end{aligned}$$

The other self energy is

$$\Sigma_{12}^{<}(\omega) = \frac{1}{2}\frac{\hbar}{i}\sum_{3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}\int\frac{d\omega_1}{2\pi}D_{35}^{<}(\omega_1)D_{64}^{>}(\omega_1-\omega) \tag{E.128}$$

$$\begin{aligned}&\text{First term of sum rule}\\ &= \int\frac{d\omega}{2\pi}\hbar\omega\sum_{1,2}\Sigma_{12}^{<}(\omega)D_{21}^{>}(\omega) &\text{(E.129)}\\ &= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D_{35}^{<}(\omega_1)D_{64}^{>}(\omega_1-\omega)D_{21}^{>}(\omega)\hbar\omega &\text{(E.130)}\end{aligned}$$

$$\begin{aligned}&\text{Second term of sum rule}\\ &= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D_{35}^{>}(\omega_1)D_{64}^{<}(\omega_1-\omega)D_{21}^{<}(\omega)\hbar\omega &\text{(E.131)}\\ &\mid\ \text{rename } \omega\to-\omega \text{ and } \omega_1\to-\omega_1\\ &= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D_{35}^{>}(-\omega_1)D_{64}^{<}(-(\omega_1-\omega))D_{21}^{<}(-\omega)\hbar(-\omega) &\text{(E.132)}\\ &\mid\ \text{use } D_{12}^{<}(\omega)=D_{21}^{>}(-\omega)\\ &= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D_{53}^{<}(\omega_1)D_{46}^{>}(\omega_1-\omega)D_{12}^{>}(\omega)\hbar(-\omega) &\text{(E.133)}\\ &\mid\ \text{rename } 3\leftrightarrow5,\ 4\leftrightarrow6 \text{ and } 1\leftrightarrow2\\ &= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}\tilde{V}^{(3ph)}_{\bar{2}56}\tilde{V}^{(3ph)}_{\bar{3}\bar{4}1}D_{35}^{<}(\omega_1)D_{64}^{>}(\omega_1-\omega)D_{21}^{>}(\omega)\hbar(-\omega) &\text{(E.134)}\end{aligned}$$

The Sum Rule

$$= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}\left(\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}+\tilde{V}^{(3ph)}_{\bar{2}56}\tilde{V}^{(3ph)}_{\bar{3}\bar{4}1}\right)(\hbar\omega)D^{<}_{35}(\omega_1)D^{>}_{64}(\omega_1-\omega)D^{>}_{21}(\omega)$$

| the coefficients are complex conjugates of each other

$$= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}2\Re\left(\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}\right)(\hbar\omega)D^{<}_{35}(\omega_1)D^{>}_{64}(\omega_1-\omega)D^{>}_{21}(\omega) \tag{E.135}$$

$$\neq 0 \tag{E.136}$$

Hence the sum rule is not satisfied. We try again following the slightly different approach in [Lu2007] between equations (B5) and (B6).

Second term of sum rule

$$= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D^{>}_{35}(\omega_1)D^{<}_{64}(\omega_1-\omega)D^{<}_{21}(\omega)\hbar\omega \tag{E.137}$$

| rename $\omega \to -\omega$

$$= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D^{>}_{35}(\omega_1)D^{<}_{64}(\omega_1+\omega)D^{<}_{21}(-\omega)\hbar(-\omega) \tag{E.138}$$

| use $D^{<}_{21}(-\omega) = D^{>}_{12}(\omega)$ then shift $\omega_1 \to \omega_1 - \omega$

$$= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}\tilde{V}^{(3ph)}_{\bar{1}34}\tilde{V}^{(3ph)}_{\bar{5}\bar{6}2}D^{>}_{35}(\omega_1-\omega)D^{<}_{64}(\omega_1)D^{<}_{12}(\omega)\hbar(-\omega) \tag{E.139}$$

| rename $3 \leftrightarrow 6$, $4 \leftrightarrow 5$ and $1 \leftrightarrow 2$

$$= \frac{1}{2}\frac{\hbar}{i}\int\frac{d\omega}{2\pi}\int\frac{d\omega_1}{2\pi}\sum_{1,2,3,4,5,6}\tilde{V}^{(3ph)}_{\bar{2}65}\tilde{V}^{(3ph)}_{\bar{4}\bar{3}1}D^{>}_{64}(\omega_1-\omega)D^{<}_{35}(\omega_1)D^{<}_{21}(\omega)\hbar(-\omega) \tag{E.140}$$

and we get exactly the same expression as the first approach hence the sum rule is not satisfied.

So what is the problem? I suspect the sum rule for energy current is somehow incorrect. Looking back at the derivation of the sum rule in the chapter on NEGF (mostly phonons), we realize that the frequency integral plays no part in the derivation but definitely plays a part in the final sum rule expression. We display the role of the frequency integral by decomposing the expression, [1]

$$\mathrm{Tr}\left(\Sigma^{<}(\omega)D^{>}(\omega)-\Sigma^{>}(\omega)D^{<}(\omega)\right) = \text{"odd in } \omega \text{ part"} + \text{" even in } \omega \text{ part"} \tag{E.142}$$

Then with the frequency integral

$$\int\frac{d\omega}{2\pi}\hbar\omega\text{"odd in } \omega \text{ part"} + \int\frac{d\omega}{2\pi}\hbar\omega\text{"even in } \omega \text{ part"} \tag{E.143}$$

The second integral is zero whatever the even part is because we recall odd × even = odd and odd integrals are zero. The first integral is nonzero and is the expression we got earlier. So for the sum rule to hold, $\mathrm{Tr}(\Sigma^{<}D^{>} - \Sigma^{>}D^{<})$ must be even in ω, there is no odd (in ω) part.

It is interesting to note that the particle current conservation rule sum rule which is derived in

[1] Recall the standard way to decompose a function into even-odd parts is

$$f(x) = \underbrace{\frac{1}{2}\left[f(x)+f(-x)\right]}_{\text{even part}} + \underbrace{\frac{1}{2}\left[f(x)-f(-x)\right]}_{\text{odd part}} \tag{E.141}$$

essentially the same way says a different story. This is equation (12.34) in [Haug2007]

$$0 = \int \frac{d\omega}{2\pi} \mathrm{Tr} \left(\Sigma^{(C)<}(\omega) G^{(C)>}(\omega) - \Sigma^{(C)>}(\omega) G^{(C)<}(\omega) \right) \tag{E.144}$$

and the sum rule holds when $\mathrm{Tr}(\ldots)$ is odd in ω and has no even (in ω) part.

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