Unified Theory of Thermal Transport

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1 Transport equation

We consider that the system of phonons are governed by the equation:

$$\frac{\partial\rho(t)}{\partial t} + \frac{i}{\hbar}\left[H_0, \rho(t)\right] = \left.\frac{\partial\rho(t)}{\partial t}\right|_{coll} \tag{1}$$

Define the creation and annhiliation operator a_{qb} and $a^\dagger_{qb}$ with $b = (b, \alpha)$, which is related to phonon creation and annhiliation operator a_{qv} and $a^\dagger_{qv}$ by:

$$a_{qb} = \sum_v e^b_{qv} a_{qv} \tag{2}$$

$$a^\dagger_{qb} = \sum_v e^{*b}_{qv} a^\dagger_{qv} \tag{3}$$

e^b_{qv} gives the transformation between the two set of operators. The Harmonic Hamiltonian written using a_{qb} and $a^\dagger_{qb}$ is:

$$H_0 = \sum_q \sum_{b,b'} \hbar \sqrt{D_q}_{bb'} \left(a^\dagger_{qb} a_{qb'} + \frac{1}{2}\delta_{bb'}\right) \tag{4}$$

$\sqrt{D_q}$ is the square root of matrix D_q with matrix elements $\Phi_{q,bb'}(m_b m_{b'})^{-\frac{1}{2}}$. Taking e^b_{qv} to be the v^{th} orthonormal eigenvector of the Dynamic matrix $D_q e^b_{qv} = \omega^2_{qv} e^b_{qv}$. e^b_{qv} then also is the eigenvector of matrix $\sqrt{D_q}$ with eigenvalue ω_{qv}. We can then recovery the harmonic Hamiltonian in its usual form:

$$H_0 = \sum_{q,v} \hbar\omega_{qv} \left(a^\dagger_{qv} a_{qv} + \frac{1}{2}\right) \tag{5}$$

The one body density matrix $\rho_1(q, q', t)$ is defined as:

$$\rho_1(q, q', t)_{b,b'} = \mathrm{Tr}[\rho(t) a^\dagger_{q'b'} a_{qb}] \tag{6}$$

We insert H_0 into Eq.1 and multiply on both side $a^\dagger_{q'b'} a_{qb}$ and take the trace:

$$\mathrm{Tr}\left[\frac{\partial\rho(t) a^\dagger_{q'b'} a_{qb}}{\partial t}\right] = \frac{\partial\rho_1(q, q', t)_{b,b'}}{\partial t} \tag{7}$$

$$\mathrm{Tr}\left[\left(\frac{\partial\rho(t) a^\dagger_{q'b'} a_{qb}}{\partial t}\right)_{coll}\right] = \left.\frac{\partial\rho_1(q, q', t)_{b,b'}}{\partial t}\right|_{coll} \tag{8}$$

For the term $\mathrm{Tr}\left[\frac{i}{\hbar}\left[H_0,\rho(t)\right]a^{\dagger}_{q'b'}a_{qb}\right]$, we can derive:

$$
\begin{aligned}
& i\sum_{q_1}\sum_{b_1b_2}\sqrt{D_{q_1}}_{b_1b_2}\mathrm{Tr}\left[\rho(a^{\dagger}_{q'b'}a_{qb}a^{\dagger}_{q_1b_1}a_{q_1b_2}-a^{\dagger}_{q_1b_1}a_{q_1b_2}a^{\dagger}_{q'b'}a_{qb})\right] \\
&= i\sum_{q_1}\sum_{b_1b_2}\sqrt{D_{q_1}}_{b_1b_2}\mathrm{Tr}\left[\rho(\delta_{q,q_1}\delta_{b,b_1}a^{\dagger}_{q'b'}a_{q_1b_2}-\delta_{q',q_1}\delta_{b',b_2}a^{\dagger}_{q_1b_1}a_{qb})\right] \\
&= i\left(\sum_{q_1}\sum_{b_1b_2}\sqrt{D_{q_1}}_{b_1b_2}\mathrm{Tr}\left[\rho\delta_{q,q_1}\delta_{b,b_1}a^{\dagger}_{q'b'}a_{q_1b_2}\right]-\sum_{q_1}\sum_{b_1b_2}\sqrt{D_{q_1}}_{b_1b_2}\mathrm{Tr}\left[\rho\delta_{q',q_1}\delta_{b',b_2}a^{\dagger}_{q_1b_1}a_{qb}\right]\right) \\
&= i\left(\sum_{b_2}\sqrt{D_q}_{bb_2}\mathrm{Tr}\left[\rho a^{\dagger}_{q'b'}a_{qb_2}\right]-\sum_{b_1}\sqrt{D_{q'}}_{b_1b'}\mathrm{Tr}\left[\rho a^{\dagger}_{q'b_1}a_{qb}\right]\right) \\
&= i\left(\sum_{b_2}\sqrt{D_q}_{bb_2}\rho_1(q,q',t)_{b_2,b'}-\sum_{b_1}\sqrt{D_{q'}}_{b_1b'}\rho_1(q,q',t)_{b,b_1}\right) \\
&= i\left[\sqrt{D_q}\cdot\rho_1(q,q',t)-\rho_1(q,q',t)\cdot\sqrt{D_{q'}}\right]_{bb'}
\end{aligned}
\tag{9}
$$

So that we obtain the equation:

$$
\frac{\partial\rho_1(q,q',t)_{b,b'}}{\partial t}+i\left[\sqrt{D_q}\cdot\rho_1(q,q',t)-\rho_1(q,q',t)\cdot\sqrt{D_{q'}}\right]_{bb'}=\left.\frac{\partial\rho_1(q,q',t)_{b,b'}}{\partial t}\right|_{coll}
\tag{10}
$$

We perform the Weyl transformation to $\rho_1(q,q',t)_{b,b'}$:

$$
N(R,q,t)_{b,b'}=\sum_{q''}\rho_1(q+q'',q-q'',t)_{b,b'}e^{2iq''R}
\tag{11}
$$

to Eq.10, we will have:

$$
\frac{\partial\rho_1(q+q'',q-q'',t)_{b,b'}}{\partial t}+i\left[\sqrt{D_{q+q''}}\cdot\rho_1(q+q'',q-q'',t)-\rho_1(q+q'',q-q'',t)\cdot\sqrt{D_{q-q''}}\right]_{bb'}
\tag{12}
$$

$$
=\left.\frac{\partial\rho_1(q+q'',q-q'',t)_{b,b'}}{\partial t}\right|_{coll}
\tag{13}
$$

Assume the one particle density $\rho_1(q+q'',q-q'',t)_{b,b'}$ is sharply peaked at q, q'' will be small, we can then replace frequency $\sqrt{D_{q+q''}}$ and $\sqrt{D_{q-q''}}$ by:

$$
\sqrt{D_{q+q''}}=\sqrt{D_q}+\frac{\partial\sqrt{D_q}}{\partial q''}q''
\tag{14}
$$

$$
\sqrt{D_{q-q''}}=\sqrt{D_q}-\frac{\partial\sqrt{D_q}}{\partial q''}q''
\tag{15}
$$

Multiply both side with $e^{2iq''R}$ and integrate, we have:

$$
\begin{aligned}
\frac{\partial N(R,q,t)_{bb'}}{\partial t}&+i\left[\sqrt{D_q}\cdot N(R,q,t)-N(R,q,t)\cdot\sqrt{D_q}\right]_{bb'} \\
&+\frac{1}{2}\left[\nabla_q\sqrt{D_q}\cdot\nabla_R N(R,q,t)+\nabla_R N(R,q,t)\cdot\nabla_q\sqrt{D_q}\right]_{bb'}=\left.\frac{\partial N(R,q,t)_{bb'}}{\partial t}\right|_{coll}
\end{aligned}
\tag{16}
$$

which can be simplified a bit:

$$
\frac{\partial N(R,q,t)_{bb'}}{\partial t}+i\left[\sqrt{D_q},N(R,q,t)\right]_{bb'}+\frac{1}{2}\left\{\nabla_q\sqrt{D_q},\nabla_R N(R,q,t)\right\}_{bb'}=\left.\frac{\partial N(R,q,t)_{bb'}}{\partial t}\right|_{coll}
\tag{17}
$$

Finally, we apply the transformation from (qb) to phonon coordinate (qv), obtaining:

$$
\frac{\partial N(R,q,t)}{\partial t}+i\left[\Omega_q,N(R,q,t)\right]+\frac{1}{2}\left\{V_q,\nabla_R N(R,q,t)\right\}=\left.\frac{\partial N(R,q,t)}{\partial t}\right|_{coll}
\tag{18}
$$

where Ω_q is a diagonal matrix with diagonal element the frequency of phonon mode ω_{qv}, and $V_{qbb'}$ is the velocity matrix containing off-diagonal elements:

$$
V_{q,vv'}=\sum_{bb'}e^{*b}_{qv}(\nabla_q\sqrt{D_q})_{bb'}e^{b'}_{qv'}
\tag{19}
$$

2 Solving the equation

The scattering term on the right of Eq.18 is given:

$$\left.\frac{\partial N(R,q,t)_{vv'}}{\partial t}\right|_{coll} = -(1-\delta_{vv'})\frac{\Gamma_{qv}+\Gamma_{qv'}}{2}N(R,q,t)_{vv'} - \delta_{vv'}\sum_{q''v''}A_{qv,q''v''}(N(R,q'',t)_{v''v''}-\bar{N}_{q''v''}) \tag{20}$$

Γ_{qv} is the phonon linewidth $\Gamma_{qv} = 1/\tau_{qv}$, $\bar{N}_{qv}$ is the equilibrium Bosen distribution. The scattering matrix A is given by:

$$A_{q,q'} = \frac{1}{\tau_q}\delta_{q,q'} - \sum_{q''}\left(\Lambda^{q'}_{q,q''} - \Lambda^{q''}_{q,q'} + \Lambda^{q',q''}_{q}\right) \tag{21}$$

with Λ given by:

$$\Lambda^{q''}_{q,q'} = \frac{\bar{N}_q\bar{N}_{q'}(\bar{N}_{q''}+1)}{\bar{N}_q(\bar{N}_q+1)}L^{q''}_{q,q'} \tag{22}$$

$$\Lambda^{q',q''}_{q} = \frac{\bar{N}_q(\bar{N}_{q'}+1)(\bar{N}_{q''}+1)}{\bar{N}_q(\bar{N}_q+1)}L^{q',q''}_{q} \tag{23}$$

and L is the standard scattering probability of phonon absorption and emission events. We focus on the case of RTA and ignore the second term in Eq.21. Eq.18 is then:

$$\begin{aligned}&\left[\frac{\partial N(R,q,t)}{\partial t} + i\left[\Omega_q, N(R,q,t)\right] + \frac{1}{2}\left\{V_q, \nabla_R N(R,q,t)\right\}\right]_{vv'}\\ &= -(1-\delta_{vv'})\frac{\Gamma_{qv}+\Gamma_{qv'}}{2}N(R,q,t)_{vv'} - \delta_{vv'}A_{qv,qv}(N(R,q,t)_{vv}-\bar{N}_{qv})\end{aligned} \tag{24}$$

We aim to solve the Eq.18 under a temperature field $T_l(R)$, l indicate local temperature as opposed to the equilibrium temperature T. In an steady state, $N(R,q,t)$ will be time independent, we linearize $N(R,q)$ as:

$$N(R,q)_{vv'} = \delta_{vv'}\left[\bar{N}_{qv} + \frac{\partial\bar{N}_{qv}}{\partial T}(T_l(R)-T)\right] + n^{(1)}_{q,vv'}\cdot\nabla T \tag{25}$$

the first term of the right hand side depend only on equilibrium temperature, the second term accounts for the correction due to the local temperature, and the third term is the linear response (vector) correspond to a temperature grident. Putting Eq.25 into Eq.24 and keep only linear term in ∇T, we can write terms on the left side of Eq.24 as:

$$i\left[\Omega_q, N(R,q,t)\right] = i\left(\omega_{qv}n^{(1)}_{q,vv'} - n^{(1)}_{q,vv'}\omega_{qv'}\right)\nabla T \tag{26}$$

$$\frac{1}{2}\left\{V_q, \nabla_R N(R,q,t)\right\} = \frac{1}{2}\left(V_{qvv'}\frac{\partial\bar{N}_{qv'}}{\partial T} + \frac{\partial\bar{N}_{qv}}{\partial T}V_{qvv'}\right)\nabla T \tag{27}$$

Heat flux is given by:

$$\begin{aligned}J(R,t) &= \frac{1}{2NV}\sum_{qv}\hbar\omega_{qv}\left\{V_q, N(R,q,t)\right\}_{vv}\\ &= \frac{1}{2NV}\sum_{qv}\hbar\omega_{qv}\left\{V_q, n^{(1)}_q\right\}_{vv}\nabla T = -\kappa\nabla T\end{aligned} \tag{28}$$

giving the expression for thermal conductivity:

$$\kappa = -\frac{1}{2NV}\sum_{qv}\hbar\omega_{qv}\left\{V_q, n^{(1)}_q\right\}_{vv} \tag{29}$$

We can separate matrix $n^{(1)}_q$ into a diagonal matrix and an off-diagonal matrix whose diagonal element is zero. For the diagonal part, we find:

$$v_{qv}\frac{\partial\bar{N}_{qv}}{\partial T}\nabla T = -A_{qv,qv}n^{(1)}_{q,vv}\nabla T \tag{30}$$

$$n^{(1)}_{q,vv} = -v_{qv}\frac{\partial\bar{N}_{qv}}{\partial T}\tau_{qv} \tag{31}$$

The diagonal part gives the contribution to thermal conductivity:

$$\kappa_{diagonal} = \frac{1}{NV}\sum_{qv}\hbar\omega_{qv}v_{qv}v_{qv}\frac{\partial\bar{N}_{qv}}{\partial T}\tau_{qv} \tag{32}$$

which is the usual expression in RTA formulism. The off diagonal part of matrix $n_q^{(1)}$ is given by:

$$i\left(\omega_{qv}n^{(1)}_{q,vv'} - n^{(1)}_{q,vv'}\omega_{qv'}\right) + \frac{1}{2}\left(V_{qvv'}\frac{\partial\bar{N}_{qv'}}{\partial T} + \frac{\partial\bar{N}_{qv}}{\partial T}V_{qvv'}\right) = -\frac{\Gamma_{qv}+\Gamma_{qv'}}{2}n^{(1)}_{q,vv'} \tag{33}$$

$$n^{(1)}_{q,v\neq v'} = -\frac{\hbar}{k_bT}V_{qvv'}\frac{\omega_{qv}\bar{N}_{qv}(\bar{N}_{qv}+1)+\omega_{qv'}\bar{N}_{qv}(\bar{N}_{qv'}+1)}{2i(\omega_{qv}-\omega_{qv'})+(\Gamma_{qv}+\Gamma_{qv'})} \tag{34}$$

The diagonal part of $n_q^{(1)}$ contribute to thermal conductivity by:

$$\begin{aligned}\kappa_{off-diagonal} = \frac{\hbar^2}{k_bT^2}\frac{1}{NV}\sum_{q}\sum_{v\neq v'}&\frac{\omega_{qv}+\omega_{qv'}}{2}V_{qvv'}V_{qv'v}\\ &\frac{\omega_{qv}\bar{N}_{qv}(\bar{N}_{qv}+1)+\omega_{qv'}\bar{N}_{qv}(\bar{N}_{qv'}+1)}{4(\omega_{qv}-\omega_{qv'})^2+(\Gamma_{qv}+\Gamma_{qv'})^2}(\Gamma_{qv}+\Gamma_{qv'})\end{aligned} \tag{35}$$

The total thermal conductivity is therefore:

$$\kappa = \kappa_{diagonal} + \kappa_{off-diagonal} \tag{36}$$

Appendix A. Wigner function

Define the transformation, called *Weyl transformation* from an operator A to a function $A(x,p)$:

$$\tilde{A}(x,p) = \int e^{-ipy/\hbar} \langle x + \frac{y}{2}|A|x - \frac{y}{2}\rangle dy \tag{37}$$

$$= \int e^{ixu/\hbar} \langle p + \frac{u}{2}|A|p - \frac{u}{2}\rangle du \tag{38}$$

where $\langle x|A|x'\rangle$ and $\langle p|A|p'\rangle$ denotes the matrix element of A in position or momentum base, and both integral give the same expression $\tilde{A}(x,p)$. Suppose the operator A is only a function of x, than the Weyl transformationwill give:

$$\tilde{A} = \int e^{-ipy/\hbar} \langle x + \frac{y}{2}|A|x - \frac{y}{2}\rangle dy \tag{39}$$

$$= \int e^{-ipy/\hbar} \langle x + \frac{y}{2}|A|x - \frac{y}{2}\rangle \delta_{y=0} dy \tag{40}$$

$$= \langle x|A|x\rangle = A(x) \tag{41}$$

The same will be true if an operator is purely a function of momentum p. However, this is not true if an operator is a function of x, p at the same time. It can be shown that:

$$\mathrm{Tr}[AB] = \frac{1}{\hbar} \int \int \tilde{A}(x,p)\tilde{B}(x,p) dx dp \tag{42}$$

define the density operator ρ so that $\mathrm{Tr}[\rho A] = \langle A\rangle$, we thus have:

$$\langle A\rangle = \frac{1}{\hbar} \int \int \tilde{\rho}(x,p)\tilde{A}(x,p) dx dp \tag{43}$$

It is therefore convenient to define a function:

$$W(x,p) = \frac{1}{\hbar} \int e^{-ipy/\hbar} \langle x + \frac{y}{2}|\rho|x - \frac{y}{2}\rangle dy \tag{44}$$

$$= \frac{1}{\hbar} \int e^{ixu/\hbar} \langle p + \frac{u}{2}|\rho|p - \frac{u}{2}\rangle du \tag{45}$$

This is called *Wigner function*. Now, we can find expectation value of an operator by integrating over phase space x, p, similar to classical statistic mechanics:

$$\langle A\rangle = \int \int W(x,p)\tilde{A}(x,p) dx dp \tag{46}$$

Intergrating over one phase space coordinates gives the probability distribution of another:

$$\langle A\rangle(x) = \int W(x,p)\tilde{A}(x,p) dp \tag{47}$$

Wigner function is real and normalized:

$$\int \int W(x,p) dx dp = 1 \tag{48}$$

But it is not always positive, therefore, it cannot be interpreted as a classical probability density.