Equations for phonon drag

WH

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1 Boltzmann equation

We can write out the Boltzmann transport equation for both electrons and phonons as:

$$v_{nk}\frac{\partial f^0_{nk}}{\partial T}\nabla T - ev_{nk}\frac{\partial f^0_{nk}}{\partial \varepsilon}\nabla\phi = -\frac{df_{nk}}{\tau^{ext}_{nk}} + \left(\frac{\partial f_{nk}}{\partial t}\right)_{e-p} \tag{1}$$

$$v_{qs}\frac{\partial n^0_{qs}}{\partial T}\nabla T = -\frac{dn_{qs}}{\tau^{ext}_{qs}} + \left(\frac{\partial n_{qs}}{\partial t}\right)_{e-p} \tag{2}$$

where k, α indicate electron wavevector and band, ϕ is the external electrical potential, $\tau*$ indicate the relaxation time apart from electron-phonon interaction. The equilibrium distribution function is given by:

$$f^0_{nk} = \frac{1}{e^{(\varepsilon_{nk}-\mu)/k_B T}+1} \tag{3}$$

$$f^0_{qs} = \frac{1}{e^{\hbar\omega_{qs}/k_B T}-1} \tag{4}$$

2 Linearized transport equation

2.1 Electronic part

We now consider the term $\left(\frac{\partial f_{n,k}}{\partial t}\right)_{e-p}$. It can be written out to be

$$\left(\frac{\partial f_k}{\partial t}\right)_{e-p} = \sum_{q,k'}\left\{-\Gamma^{k'}_{k,q} + \Gamma^{k,q}_{k'} - \Gamma^{k',q}_{k} + \Gamma^{k}_{k',q}\right\} \tag{5}$$

where Γ^f_i denotes the transition rate from initial state i to final state j. Using the result in the Appendix, we have:

$$\begin{aligned}-\Gamma^{k'}_{k,q} + \Gamma^{k,q}_{k'} = \frac{2\pi}{\hbar}&|g^{SE}(k,k',q)|^2\delta(\varepsilon_{nk}+\hbar\omega_{q,s}-\varepsilon_{n'k'})\delta(k+q-k')\\ &\{-f_{nk}(1-f_{n'k'})n_{q,s} + f_{n'k'}(1-f_{nk})(n_{q,s}+1)\}\end{aligned} \tag{6}$$

$$\begin{aligned}-\Gamma^{k',q}_{k} + \Gamma^{k}_{k',q} = \frac{2\pi}{\hbar}&|g^{SE}(k,k',-q)|^2\delta(\varepsilon_{nk}-\hbar\omega_{q,s}-\varepsilon_{n'k'})\delta(k-q-k')\\ &\{-f_{nk}(1-f_{n'k'})(n_{q,s}+1) + f_{n'k'}(1-f_{nk})n_{q,s}\}\end{aligned} \tag{7}$$

with the term $g^{SE}(k,k',q)$ given as:

$$g^{SE}(k,k',q) = \frac{1}{N_e}\sum_{\kappa,R_p}\sum_{mm'R}\left(\frac{\hbar}{2N_q\omega_{q,s}m_\kappa}\right)^{1/2} U_{m'n'}(k')U^\dagger_{mn}(k)e^{\kappa}_{q,s}e^{ikR+iqR_p}\langle m'0|\partial_{\kappa,R_p}V|mR\rangle \tag{8}$$

changing the dummy index in the summation of Eq.5 from q to $-q$ in the last two term, we have:

$$\begin{aligned}\left(\frac{\partial f_k}{\partial t}\right)_{e-p} = \frac{2\pi}{\hbar}\sum_{q,k'}&|g^{SE}(k,k',q)|^2\delta(k+q-k')\\ &\{[-f_{nk}(1-f_{n'k'})n_{q,s} + f_{n'k'}(1-f_{nk})(n_{q,s}+1)]\,\delta(\varepsilon_{nk}+\hbar\omega_{q,s}-\varepsilon_{n'k'})\\ &+[-f_{nk}(1-f_{n'k'})(n_{-q,s}+1) + f_{n'k'}(1-f_{nk})n_{-q,s}]\,\delta(\varepsilon_{nk}-\hbar\omega_{q,s}-\varepsilon_{n'k'})\}\end{aligned} \tag{9}$$

The term in the square bracket can be linearized to first order with $f_k = f_k^0 + df_k$ and $n_q = n_q^0 + dn_q$ to be:

$$
\begin{aligned}
&-f_k(1-f_{k'})n_q + f_{k'}(1-f_k)(n_q+1) \\
&\quad \to -\left(f_{k'}^0 + n_q^0\right) df_k + \left(1 + n_q^0 - f_k^0\right) df_{k'} + \left(f_{k'}^0 - f_k^0\right) dn_q \qquad (10)\\
&-f_k(1-f_{k'})(n_{-q}+1) + f_{k'}(1-f_k)n_{-q} \\
&\quad \to -\left(n_q^0 + 1 - f_{k'}^0\right) df_k + \left(n_q^0 + f_k^0\right) df_{k'} + \left(f_{k'}^0 - f_k^0\right) dn_{-q} \qquad (11)\\
& \qquad (12)
\end{aligned}
$$

we ignore the terms linear in dn_k', so that we can write Eq.9 into two part:

$$\frac{1}{\tau_{nk}^{ph}} = \frac{2\pi}{\hbar}\sum_{q,k'} |g^{SE}(k,k',q)|^2 \delta(k+q-k') \left\{ \left(f_{k'}^0 + n_q^0\right)\delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'}) + \left(n_q^0 + 1 - f_{k'}^0\right)\delta(\varepsilon_{nk} - \hbar\omega_{q,s} - \varepsilon_{n'k'}) \right\} \tag{13}$$

$$
\begin{aligned}
D_{nk} &= \frac{2\pi}{\hbar}\sum_{q,k'} |g^{SE}(k,k',q)|^2 \delta(k+q-k') \left(f_{k'}^0 - f_k^0\right) \{\delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'})dn_q + \delta(\varepsilon_{nk} - \hbar\omega_{q,s} - \varepsilon_{n'k'})dn_{-q}\} \\
&= \sum_{q,k'} \Pi_{k,k',q} \{\delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'})dn_q + \delta(\varepsilon_{nk} - \hbar\omega_{q,s} - \varepsilon_{n'k'})dn_{-q}\}
\end{aligned} \tag{14}
$$

where the final equation is introduced for simplicity.

$$\left(\frac{\partial f_k}{\partial t}\right)_{e-p} = -\frac{df_{nk}}{\tau_{nk}^{ph}} + \sum_{q,k'} \Pi_{k,k',q} \{\delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'})dn_q + \delta(\varepsilon_{nk} - \hbar\omega_{q,s} - \varepsilon_{n'k'})dn_{-q}\} \tag{15}$$

2.2 Phonon lifetime

for the term $\left(\frac{\partial n_{qs}}{\partial t}\right)_{e-p}$ in Eq.2, we count the scattering in and out process:

$$
\begin{aligned}
\left(\frac{\partial n_{qs}}{\partial t}\right)_{e-p} &= \frac{1}{2}\sum_{k,k'} \left\{ -\Gamma_{k,q}^{k'} - \Gamma_{k',q}^{k} + \Gamma_{k'}^{k,q} + \Gamma_{k}^{k',q} \right\} \\
&= \frac{1}{2}\sum_{k,k'} 2\left\{ -\Gamma_{k,q}^{k'} + \Gamma_{k'}^{k,q} \right\} = \sum_{k,k'} \left\{ -\Gamma_{k,q}^{k'} + \Gamma_{k'}^{k,q} \right\}
\end{aligned} \tag{16}
$$

where the the initial 1/2 take care of the double counting of k, k', and the second equality comes by exchanging the dummy index in the summation. Using Eq.6 that we already obtained, we have:

$$
\begin{aligned}
\left(\frac{\partial n_{qs}}{\partial t}\right)_{e-p} = \frac{2\pi}{\hbar}\sum_{k,k'} &|g^{SE}(k,k',q)|^2 \delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'})\delta(k+q-k') \\
&\{-f_{nk}(1-f_{n'k'})n_{q,s} + f_{n'k'}(1-f_{nk})(n_{q,s}+1)\}
\end{aligned} \tag{17}
$$

keeping only to linear part in dn_{qs} and using the relationship $(\partial n_{qs}/\partial t)_{e-p} = -dn_{qs}/\tau_{q,s}^{e-p}$, we have:

$$\frac{1}{\tau_{q,s}^{e-p}} = \frac{2\pi}{\hbar}\sum_{k,k'} |g^{SE}(k,k',q)|^2 \delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'})\delta(k+q-k')(f_k - f_{k'}) \tag{18}$$

3 Transport properties

the charge and energy current can be expressed as:

$$Q^i = \frac{e}{N_k\Omega}\sum_{n,k} f_{nk}v_{nk}^i = \sigma E - \zeta\nabla T \tag{19}$$

$$J_{ele}^i = \frac{1}{N_k\Omega}\sum_{n,k} (\varepsilon_{nk} - \mu) f_{nk}v_{nk}^i \tag{20}$$

where Ω is the volume of the unit cell. We consider the external temperature gradient ∇T and ignoring the effect of electron-phonon interaction on in the phonon Boltzmann equation Eq.2, we have the phonon off equilibrium part:

$$dn_{q,s} = -\sum_j \left(\frac{\partial n^0_{q,s}}{\partial T}\right) \tau_{q,s} v^j_{q,s} (\nabla T)^j = \sum_j \phi^j_{q,s} (\nabla T)^j \tag{21}$$

with $\phi^j_{q,s}$ defined as:

$$\phi^j_{q,s} = -\left(\frac{\partial n^0_{q,s}}{\partial T}\right) \tau_{q,s} v^j_{q,s} \tag{22}$$

where the lifetime is given by the $1/\tau_{q,s} = 1/\tau^{ext}_{q,s} + 1/\tau^{e-p}_{q,s}$. The electronic transport equation now becomes:

$$v_{n,k} \frac{\partial f^0_{n,k}}{\partial T} \nabla T = -\left(\frac{1}{\tau^{ext}_{nk}} + \frac{1}{\tau^{ph}_{nk}}\right) df_{nk} + \sum_{q,k'} \Pi_{k,k',q} \left\{\delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'}) dn_q + \delta(\varepsilon_{nk} - \hbar\omega_{q,s} - \varepsilon_{n'k'}) dn_{-q}\right\} \tag{23}$$

now define:

$$\frac{1}{\tau^*_k} = \frac{1}{\tau^{ext}_k} + \frac{1}{\tau^{ph}_k} \tag{24}$$

we have for ζ as a tensor:

$$\zeta_{ij} = \frac{e}{N_k \Omega} \sum_k v^i_k \tau^*_k \left[v^j_k \frac{\partial f^0_{n,k}}{\partial T} - \sum_{q,k'} \Pi_{k,k',q} \left\{ \delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'}) \phi^j_{q,s} + \delta(\varepsilon_{nk} - \hbar\omega_{q,s} - \varepsilon_{n'k'}) \phi^j_{-q,s} \right\} \right] \tag{25}$$

electrical conductivity tensor σ_{ij} is given by:

$$\sigma_{i,j} = \frac{e^2}{N_k \Omega} \sum_k \left(-\frac{\partial f^0_k}{\partial \varepsilon}\right) \tau_k v^i_k v^j_k \tag{26}$$

Seebeck coefficient is given by:

$$S = \zeta/\sigma \tag{27}$$

Appendix A

3.1 Derivation of electron-phonon vertex elements

We consider linear approximation of the perturbation to the potential energy:

$$V_{perturb} = \sum_{\kappa,R_p} \partial_{\kappa,R_p} V \cdot \eta_{\kappa,R_p} \tag{28}$$

where η_{κ,R_p} is the atomic displacement of the κ^{th} atom in R_p^{th} cell, this is given in the form of phonon creation and annihilation operator:

$$\eta_{\kappa,R_p} = \sum_{q,s} \left(\frac{\hbar}{2N_q \omega_{q,s} m_\kappa} \right)^{1/2} e^\kappa_{q,s} e^{iqR_p} (a_{q,s} + a^\dagger_{-q,s}) \tag{29}$$

where $e_{q,s}$ is the phonon eigenvector.

Absorption process Consider the transition of electronic state n, k to n', k', while absorb a phonon q, s. The vertex element of such a process is denoted by $g^{k'}_{k,q}$ and is given by:

$$\begin{aligned} g^{k'}_{k,q} &= \langle f|V_{perturb}|i\rangle \\ &= \langle n_{q,s} - 1; n'k'| \sum_{\kappa,R_p} \partial_{\kappa,R_p} V \cdot \eta_{\kappa,R_p} |n_{q,s}; nk\rangle \end{aligned} \tag{30}$$

where $|n_q; k\rangle = |n_q\rangle|k\rangle$ because of the Born approximation. the creation and annihilation operater act on the phonon states to give:

$$\langle n_{q,s} - 1|(a_{q',s'} + a^\dagger_{-q',s'})|n_{q,s}\rangle = \sqrt{n_{q,s}}\delta_{qq',ss'} \tag{31}$$

so that we now have:

$$g^{k'}_{k,q} = \sum_{\kappa,R_p} \left(\frac{\hbar}{2N_q \omega_{q,s} m_\kappa} \right)^{1/2} e^\kappa_{q,s} e^{iqR_p} \langle n'k'|\partial_{\kappa,R_p} V|nk\rangle \sqrt{n_{q,s}} \tag{32}$$

using the Wannier transformation:

$$|nk\rangle = \frac{1}{N_e} \sum_{mR} e^{ikR} U^\dagger_{mn}(k)|mR\rangle \tag{33}$$

we can write:

$$\langle n'k'|\partial_{\kappa,R_p} V|nk\rangle = \frac{1}{N_e^2} \sum_{m'R'} \sum_{mR} e^{ikR - ik'R'} U_{m'n'}(k') U^\dagger_{mn}(k) \langle m'R'|\partial_{\kappa,R_p} V|mR\rangle \tag{34}$$

putting Eq.34 into Eq.32 and using the relationship:

$$\begin{aligned} \sum_{R'} e^{ikR + iqR_p - ik'R'} &= \sum_{R'} e^{ik(R-R') + iq(R_p - R')} e^{i(k+q-k')R'} & (35) \\ &= e^{ik(R-R') + iq(R_p - R')} N_e \delta(k + q - k') & (36) \end{aligned}$$

choosing $R' = 0$ gives

$$g^{k'}_{k,q} = \frac{\sqrt{n_{q,s}}}{N_e} \sum_{\kappa,R_p} \sum_{mm'R} \left(\frac{\hbar}{2N_q \omega_{q,s} m_\kappa} \right)^{1/2} U_{m'n'}(k') U^\dagger_{mn}(k) e^\kappa_{q,s} e^{ikR + iqR_p} \langle m'0|\partial_{\kappa,R_p} V|mR\rangle \delta(k + q - k') \tag{37}$$

The transition probability is given by *Fermi golden rule* as:

$$\Gamma^{k'}_{k,q} = \frac{2\pi}{\hbar} |g^{k'}_{k,q}|^2 f_{nk}(1 - f_{n'k'}) \delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'}) \tag{38}$$

where the momentum conservation and phonon distribution function $n_{q,s}$ is contained in $|g^{k'}_{k,q}|^2$.

Emission process Now consider the transition of electronic state n, k to n', k' but emitt a phonon q, s. we denote vertex element as $g^{k',q}_k$ and is given by

$$g^{k'}_{k,q} = \langle n_{q,s} + 1; n'k'| \sum_{\kappa,R_p} \partial_{\kappa,R_p} V \cdot \eta_{\kappa,R_p} |n_{q,s}; nk\rangle \tag{39}$$

we can change the dummy index of Eq.29 so that we have:

$$\begin{aligned}
\eta_{\kappa,R_p} &= \sum_{q,s} \left(\frac{\hbar}{2N_q \omega_{q,s} m_\kappa} \right)^{1/2} e^{\kappa}_{q,s} e^{iqR_p} (a_{q,s} + a^{\dagger}_{-q,s}) \\
&= \sum_{-q,s} \left(\frac{\hbar}{2N_q \omega_{q,s} m_\kappa} \right)^{1/2} e^{\kappa}_{-q,s} e^{-iqR_p} (a_{-q,s} + a^{\dagger}_{q,s}) \\
&= \sum_{q,s} \left(\frac{\hbar}{2N_q \omega_{q,s} m_\kappa} \right)^{1/2} e^{\kappa}_{-q,s} e^{-iqR_p} (a_{-q,s} + a^{\dagger}_{q,s}) \qquad (40)
\end{aligned}$$

putting Eq.40 into Eq.39 and applying the Wannier transformation, we find:

$$g_k^{k',q} = \frac{\sqrt{n_{q,s}+1}}{N_e} \sum_{\kappa,R_p} \sum_{mm'R} \left(\frac{\hbar}{2N_q \omega_{q,s} m_\kappa} \right)^{1/2} U_{m'n'}(k') U^{\dagger}_{mn}(k) e^{\kappa}_{-q,s} e^{ikR-iqR_p} \langle m'0|\partial_{\kappa,R_p} V|mR\rangle \delta(k-q-k') \tag{41}$$

and the transition probability is given by:

$$\Gamma_k^{k',q} = \frac{2\pi}{\hbar} |g_k^{k',q}|^2 f_{nk}(1-f_{n'k'}) \delta(\varepsilon_{nk} - \hbar\omega_{q,s} - \varepsilon_{n'k'}) \tag{42}$$

Now define $g^{SE}(k,k',q)$ as:

$$g^{SE}(k,k',q) = \frac{1}{N_e} \sum_{\kappa,R_p} \sum_{mm'R} \left(\frac{\hbar}{2N_q \omega_{q,s} m_\kappa} \right)^{1/2} U_{m'n'}(k') U^{\dagger}_{mn}(k) e^{\kappa}_{q,s} e^{ikR+iqR_p} \langle m'0|\partial_{\kappa,R_p} V|mR\rangle \tag{43}$$

we can write $g_k^{k',q}$ and $g_{k,q}^{k'}$ by:

$$g_{k,q}^{k'} = \sqrt{n_{q,s}} g^{SE}(k,k',q) \delta(k+q-k') \tag{44}$$

$$g_k^{k',q} = \sqrt{n_{q,s}+1} g^{SE}(k,k',-q) \delta(k-q-k') \tag{45}$$

so that

$$\Gamma_{k,q}^{k'} = \frac{2\pi}{\hbar} |g^{SE}(k,k',q)|^2 f_{nk}(1-f_{n'k'}) n_{q,s} \delta(k+q-k') \delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'}) \tag{46}$$

$$\Gamma_k^{k',q} = \frac{2\pi}{\hbar} |g^{SE}(k,k',-q)|^2 f_{nk}(1-f_{n'k'}) (n_{q,s}+1) \delta(k-q-k') \delta(\varepsilon_{nk} - \hbar\omega_{q,s} - \varepsilon_{n'k'}) \tag{47}$$

Appendix B

Adaptive smearing

For the delta function in Eq.13 and Eq.14, we can replace it with gaussian functions.

$$g(x) = \frac{1}{\sqrt{2\pi}\sigma} exp\left(-\frac{(x-\mu)^2}{2\sigma^2} \right) \tag{48}$$

The smearing width is related to the mean squre deviation of energy in $\hbar\omega_{q,s} + \varepsilon_{n',k'}$ and $-\hbar\omega_{q,s} + \varepsilon_{n',k'}$ with respect to the uncertainty in q With the requirement that $k' = k + q$, we find, for the two delta function:

$$\delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'}) : \quad \frac{d(-\hbar\omega_{q,s} + \varepsilon_{n',k'})}{dq} = \frac{d\varepsilon_{n'k'}}{dk'} \frac{dk'}{dq} - \frac{d\hbar\omega_{q,s}}{dq} = v_{n'k'} - v_{q,s} \tag{49}$$

$$\delta(\varepsilon_{nk} - \hbar\omega_{q,s} - \varepsilon_{n'k'}) : \quad \frac{d(\hbar\omega_{q,s} + \varepsilon_{n',k'})}{dq} = \frac{d\varepsilon_{n'k'}}{dk'} \frac{dk'}{dq} + \frac{d\hbar\omega_{q,s}}{dq} = v_{n'k'} + v_{q,s} \tag{50}$$

(51)

and the smearing width σ is given by:

$$\sigma_w = \frac{1}{\sqrt{12}} \sqrt{\sum_{\mu} \left[\sum_{\alpha} (v^{\alpha}_{n'k'} \pm v^{\alpha}_{q,s}) \frac{Q^{\alpha}_{\mu}}{N_{q,\mu}} \right]^2} \tag{52}$$

where α is the cartesian direction and μ is the direction along reciprocal lattice vector.

Adaptive smearing in phonon selfenergy

For phonon selfenergy, we find a delta function $\delta(\varepsilon_{nk} + \hbar\omega_{q,s} - \varepsilon_{n'k'})\delta(k + q - k')$. This give the expression for smearing width

$$\sigma_w = \frac{1}{\sqrt{12}} \sqrt{\sum_{\mu} \left[\sum_{\alpha} (v^{\alpha}_{n'k'} - v^{\alpha}_{n,k}) \frac{Q^{\alpha}_{\mu}}{N_{q,\mu}} \right]^2} \tag{53}$$