Equations for phonon drag

WH

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1 The coupled equations

Boltzmann equation enable us to reduce the $6N$ phase space of a N particles distribution to a one-particle distribution function f_1. In this case, we say that "f_1 captures all we really need to know about a system" The most general form of the Boltzmann euqation, for a distribution in equilibrium is:

$$\frac{\partial f_1}{\partial t} = \frac{\partial H_1}{\partial r_i}\frac{\partial f_1}{\partial p_i} - \frac{\partial H_1}{\partial p_i}\frac{\partial f_1}{\partial r_i} + \left(\frac{\partial f_1}{\partial t}\right)_{coll} = 0 \tag{1}$$

with the summation implied for cartesian directions i. For an electron in an electric field ϕ, we have:

$$\frac{\partial H_1}{\partial r_i} = e\frac{\partial \phi}{\partial r_i}; \frac{\partial H_1}{\partial p_i} = v_i \tag{2}$$

Including the temperature gredient, we have:

$$v_i\frac{\partial f_1}{\partial r_i} - e\frac{\partial f_1}{\partial p_i}\frac{\partial \phi}{\partial r_i} = \left(\frac{\partial f_1}{\partial t}\right)_{coll} \tag{3}$$

$$v_i\frac{\partial f_1}{\partial T}\nabla T - ev_i\frac{\partial f_1}{\partial \varepsilon}\nabla \phi = \left(\frac{\partial f_1}{\partial t}\right)_{coll} \tag{4}$$

with

$$\frac{\partial f_1}{\partial r_i} = \frac{\partial f_1}{\partial T}\frac{\partial T}{\partial r_i} \tag{5}$$

$$\frac{\partial f_1}{\partial p_i} = \frac{\partial f_1}{\partial E}\frac{\partial E}{\partial p_i} = \frac{\partial f_1}{\partial E}v_i \tag{6}$$

and gradient as a vector:

$$\nabla A = \left(\frac{\partial A}{\partial x}, \frac{\partial A}{\partial y}, \frac{\partial A}{\partial z}\right) \tag{7}$$

We separate the collision term of electrons into two parts, one with phonons, one without phonons as:

$$\left(\frac{\partial f_1}{\partial t}\right)_{coll} = -\frac{f_1 - f_1^0}{\tau_e *} + \left(\frac{\partial f_1}{\partial t}\right)_{e-p} \tag{8}$$

with the local equilibrium of electrons and phonon given by the distribution function, the states of electrons and phonons are indicated by $\alpha, k, \uparrow$ and λ, q:

$$f^0_{\alpha,k,\uparrow} = \frac{1}{e^{(\varepsilon_{\alpha,k,\uparrow} - \mu)/k_B T} + 1} \tag{9}$$

$$n^0_{\lambda,q} = \frac{1}{e^{\hbar\omega_{\lambda,q}/k_B T} - 1} \tag{10}$$

for phonon, we also write its Boltzmann equation, since it only response to the temperature gredient:

$$v\frac{\partial n_1}{\partial T}\nabla T = \left(\frac{\partial n_1}{\partial t}\right)_{coll} = -\frac{n_1 - n_1^0}{\tau_{ph} *} + \left(\frac{\partial n_1}{\partial t}\right)_{e-p} \tag{11}$$

for the collision without electron-phonon interaction, the term $\tau_e *$ and $\tau_{ph} *$ can be mode dependent and includes

- τ_e* can include electron-impurity sacttering.
- $\tau_{ph}*$ includes phonon-phonon and impurity-phonon.

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In summery, we obtained two coupled equations, with band index α, λ and wave vector k and q:

$$v_\alpha(k)\frac{\partial f_{\alpha,k,\uparrow}}{\partial T}\nabla T - ev_{\alpha,k,\uparrow}\frac{\partial f_{\alpha,k,\uparrow}}{\partial \varepsilon}\nabla\phi = -\frac{f_{\alpha,k,\uparrow} - f^0_{\alpha,k,\uparrow}}{\tau_{\alpha,k,\uparrow}} + \left(\frac{\partial f_{\alpha,k,\uparrow}}{\partial t}\right)_{e-p} \tag{12}$$

$$v_{\lambda,q}\frac{\partial n_{\lambda,q}}{\partial T}\nabla T = -\frac{n_{\lambda,q} - n^0_{\lambda,q}}{\tau_{\lambda,q}*} + \left(\frac{\partial n_{\lambda,q}}{\partial t}\right)_{e-p} \tag{13}$$

2 Electron-phonon interaction

In the Born approximation, the electron feels the extra potential of the ionic displacement, and is scattered by this potential. we can define the electron-phonon matrix element $g_{\alpha,\beta,\lambda}(k,k',q)$ scattering an electron from (α,k) to (β,k') by a phonon (λ,q). The value of $|g|^2$ in the following text is given by:

$$g^2 = \frac{\hbar}{2m_0\omega_{\lambda,q}}|\langle\beta,k',\uparrow|\partial_{\lambda,q}V|\alpha,k,\uparrow\rangle|^2 \tag{14}$$

We classify the scattering even into 4 different kinds and write, with the delta function denoting both the momemtum conservation as well as the energy conservation requirement.

Table 1: Four distinct scattering event

F_1	phonon emission	$(\alpha,k,\uparrow)\to(\lambda,q)+(\beta,k',\uparrow)$	$f_{\alpha,k,\uparrow}(1-f_{\beta,k',\uparrow})(n_{\lambda,q}+1)\vert g\vert^2\delta(k-k'-q)$
F_2	phonon absorption	$(\alpha,k,\uparrow)+(\lambda,q)\to(\beta,k',\uparrow)$	$f_{\alpha,k,\uparrow}(1-f_{\beta,k',\uparrow})(n_{\lambda,q})\vert g\vert^2\delta(k+q-k')$
F_3	phonon emission	$(\beta,k',\uparrow)\to(\lambda,q)+(\alpha,k,\uparrow)$	$f_{\beta,k',\uparrow}(1-f_{\alpha,k,\uparrow})(n_{\lambda,q}+1)\vert g\vert^2\delta(k+q-k')$
F_4	phonon absorption	$(\beta,k',\uparrow)+(\lambda,q)\to(\alpha,k,\uparrow)$	$f_{\beta,k',\uparrow}(1-f_{\alpha,k,\uparrow})(n_{\lambda,q})\vert g\vert^2\delta(k-k'-q)$

We note that spin is conserved in the scattering event so that the spin of the two electronic state $\alpha,k,\uparrow$ and $\beta,k',\uparrow$ should have the same spin. In other words, the two spin channels are independent to each other.

For an arbitrary electronic state $\alpha,k,\uparrow$, the rate of change of its distribution function due to electron-phonon interaction is given by

$$\left(\frac{\partial f_{\alpha,k,\uparrow}}{\partial t}\right)_{e-ph} = \frac{1}{N_q}\frac{2\pi}{\hbar}\sum_{\beta,k',\uparrow,\lambda,q}(-F_1 - F_2 + F_3 + F_4) \tag{15}$$

For phonon, we have, from a single spin channel:

$$\left(\frac{\partial n_{\lambda,q}}{\partial t}\right)_{e-ph} = \frac{1}{2}\frac{1}{N_k}\frac{2\pi}{\hbar}\sum_{\alpha,k,\uparrow,\beta,k',\uparrow}(F_1 - F_2 + F_3 - F_4) \tag{16}$$

We note that the summation over electronic state $\alpha,k,\uparrow$ and $\beta,k',\uparrow$ are double counted, therefore we have the leading $\frac{1}{2}$ to take care of this. But the summation of the F_1 term is exactly the same as F_3 if we change the summation index. Therefore we can reduce the equation to:

$$\left(\frac{\partial n_{\lambda,q}}{\partial t}\right)_{e-ph} = \frac{1}{N_k}\frac{2\pi}{\hbar}\sum_{\alpha,k,\uparrow,\beta,k',\uparrow}(F_1 - F_2) \tag{17}$$

Furthermore, taking account of the spin degeneracy(sum up the spin up and down contribution), we would have

$$\left(\frac{\partial n_{\lambda,q}}{\partial t}\right)_{e-ph} = \frac{2}{N_k}\frac{2\pi}{\hbar}\sum_{\alpha,k,\uparrow,\beta,k',\uparrow}(F_1 - F_2) \tag{18}$$

To linearize the equation for both electron part and phonon part, we write the distribution function

$$f_{\alpha,k,\uparrow} = f^0_{\alpha,k,\uparrow} + \Delta f_{\alpha,k,\uparrow} \tag{19}$$

$$f_{\beta,k',\uparrow} = f^0_{\beta,k',\uparrow} + \Delta f_{\beta,k',\uparrow} \tag{20}$$

$$n_{\lambda,q} = n^0_{\lambda,q} + \Delta n_{\lambda,q} \tag{21}$$

We try to find the parts in $(\partial f_{\alpha,k,\uparrow}/\partial t)_{e-ph}$ and $(\partial n_{\lambda,q}/\partial t)_{e-ph}$ that is linear in $\Delta f_{\alpha,k,\uparrow}$ and $\Delta n_{\lambda,q}$. To do this, we simply replace the distribution function in equation.15 and 18 to their Δ counterpart. As an example, equation.15 linearized in terms of $\Delta f_{\alpha,k,\uparrow}$ is given by:

$$\begin{aligned} -F_1 + F_4 &= \left[-\Delta f_{\alpha,k,\uparrow}(1-f_{\beta,k',\uparrow})(n_{\lambda,q}+1) + f_{\beta,k',\uparrow}(-\Delta f_{\alpha,k,\uparrow})n_{\lambda,q}\right]|g|^2\delta(k-k'-q) \\ &= -(n_{\lambda,q}+1-f_{\beta,k',\uparrow})|g|^2\delta(k-k'-q)\Delta f_{\alpha,k,\uparrow} \qquad (22) \\ -F_2 + F_3 &= \left[-\Delta f_{\alpha,k,\uparrow}(1-f_{\beta,k',\uparrow})(n_{\lambda,q}) + f_{\beta,k',\uparrow}(-\Delta f_{\alpha,k,\uparrow})(n_{\lambda,q}+1)\right]|g|^2\delta(k+q-k') \\ &= -(n_{\lambda,q}+f_{\beta,k',\uparrow})|g|^2\delta(k+q-k')\Delta f_{\alpha,k,\uparrow} \qquad (23) \end{aligned}$$

so that when we sum them together, we obtain(note that $\Delta f_{\alpha,k,\uparrow}$ can now be pulled outside of the summation)

$$\left(\frac{\partial f_{\alpha,k,\uparrow}}{\partial t}\right)_{e-ph} = -\frac{1}{N_q}\frac{2\pi}{\hbar}\sum_{\beta,k',\uparrow,\lambda,q}\left[(n_{\lambda,q}+1-f_{\beta,k',\uparrow})|g|^2\delta(k-k'-q) + (n_{\lambda,q}+f_{\beta,k',\uparrow})|g|^2\delta(k+q-k')\right]\Delta f_{\alpha,k,\uparrow} \tag{24}$$

Using the same method, we write the linearized part in terms of other two variation in distribution:

$$\left(\frac{\partial f_{\alpha,k,\uparrow}}{\partial t}\right)_{e-ph} = \frac{1}{N_q}\frac{2\pi}{\hbar}\sum_{\beta,k',\uparrow,\lambda,q}\left[\left\{(f_{\alpha,k,\uparrow}+n_{\lambda,q})|g|^2\delta(k-k'-q) + (n_{\lambda,q}+1-f_{\alpha,k,\uparrow})|g|^2\delta(k+q-k')\right\}\Delta f_{\beta,k',\uparrow}\right] \tag{25}$$

$$\left(\frac{\partial f_{\alpha,k,\uparrow}}{\partial t}\right)_{e-ph} = \frac{1}{N_q}\frac{2\pi}{\hbar}\sum_{\beta,k',\uparrow,\lambda,q}\left[\left\{(f_{\beta,k',\uparrow}-f_{\alpha,k,\uparrow})|g|^2\delta(k-k'-q) + (f_{\beta,k',\uparrow}-f_{\alpha,k,\uparrow})|g|^2\delta(k+q-k')\right\}\Delta n_{\lambda,q}\right] \tag{26}$$

The relaxation time due to the electron-phonon interaction is given by:

$$-\frac{\Delta f_{\alpha,k,\uparrow}}{\tau_{\alpha,k,\uparrow}} = \left(\frac{\partial f_{\alpha,k,\uparrow}}{\partial t}\right)_{e-ph} \tag{27}$$

i.e. the linear coefficient of $\Delta f_{\alpha,k,\uparrow}$. Therefore, we obtain:

$$\frac{1}{\tau_{\alpha,k,\uparrow}} = \frac{1}{N_q}\frac{2\pi}{\hbar}\sum_{\beta,k',\uparrow,\lambda,q}\left[(n_{\lambda,q}+1-f_{\beta,k',\uparrow})|g|^2\delta(k-k'-q) + (n_{\lambda,q}+f_{\beta,k',\uparrow})|g|^2\delta(k+q-k')\right] \tag{28}$$

Which is the same equation as relaxation time from the self-energy approximation, see equation.8 of the paper *EPW:Electron-phonon coupling, Computer Physics Communication*. The relaxation time is given by:

$$\frac{1}{\tau_{\alpha,k,\uparrow}(\omega,T)} = 2\Sigma''_{\alpha,k,\uparrow}(\omega,T) \tag{29}$$

and the change from k-space summation and integration is given by:

$$\int_{BZ}\frac{dq}{\Omega_{BZ}} \Rightarrow \frac{1}{N_q}\sum_q \tag{30}$$

Linearizing the phonon scattering rate, we have:

$$\left(\frac{\partial n_{\lambda,q}}{\partial t}\right)_{e-ph} = \frac{2}{N_k}\frac{2\pi}{\hbar}\sum_{\alpha,k,\uparrow,\beta,k',\uparrow}\left[f_{\alpha,k,\uparrow}(1-f_{\beta,k',\uparrow})(n_{\lambda,q}+1)|g|^2\delta(k-k'-q) - f_{\alpha,k,\uparrow}(1-f_{\beta,k',\uparrow})(n_{\lambda,q})|g|^2\delta(k+q-k')\right] \tag{31}$$

Noting that the second part can be rewrite by changing the index $(\alpha,k,\uparrow)\to(\beta,k',\uparrow)$ and vice versa:

$$f_{\alpha,k,\uparrow}(1-f_{\beta,k',\uparrow})(n_{\lambda,q})|g|^2\delta(k+q-k') \Rightarrow f_{\beta,k',\uparrow}(1-f_{\alpha,k,\uparrow})(n_{\lambda,q})|g|^2\delta(k-k'-q) \tag{32}$$

We have, to linear part:

$$\begin{aligned} \left(\frac{\partial n_{\lambda,q}}{\partial t}\right)_{e-ph} &= \frac{4\pi}{N_k\hbar}\sum_{\alpha,k,\uparrow,\beta,k',\uparrow}\left\{(n_{\lambda,q}+1-f_{\beta,k',\uparrow})|g|^2\delta(k-k'-q)\Delta f_{\alpha,k,\uparrow} - (f_{\alpha,k,\uparrow}+n_{\lambda,q})|g|^2\delta(k-k'-q)\Delta f_{\beta,k',\uparrow}\right\} \\ &\quad + \frac{4\pi}{N_k\hbar}\left\{\sum_{\alpha,k,\uparrow,\beta,k',\uparrow}(f_{\alpha,k,\uparrow}-f_{\beta,k',\uparrow})|g|^2\delta(k-k'-q)\right\}\Delta n_{\lambda,q} \end{aligned} \tag{33}$$

We are able to write the phonon relaxation:

$$\frac{1}{\tau_{\lambda,q}} = \frac{4\pi}{N_k\hbar}\sum_{\alpha,k,\uparrow,\beta,k',\uparrow}(f_{\beta,k',\uparrow}-f_{\alpha,k,\uparrow})|g|^2\delta(k-k'-q) \tag{34}$$

notice the sign of the relaxation time, we should have $f_{\beta,k',\uparrow} > f_{\alpha,k,\uparrow}$, which is true since from the delta function $\delta(k-k'-q)$, state $(\beta,k',\uparrow)$ should have a lower energy. This equation is comparable to equation.9 of *EPW:Electron-phonon coupling*.

As a temporary summary, we write down the linearized parts as:

$$\left(\frac{\partial f_{\alpha,k,\uparrow}}{\partial t}\right)_{e-ph} = -\frac{\Delta f_{\alpha,k,\uparrow}}{\tau_{\alpha,k,\uparrow}} + \sum_{\beta,k',\uparrow,\lambda,q}[\mathit{\Gamma}_{\beta,k',\uparrow}(\alpha,k,\uparrow,\lambda,q)\Delta f_{\beta,k',\uparrow} + \mathit{\Gamma}_{\lambda,q}(\alpha,k,\uparrow,\beta,k',\uparrow)\Delta n_{\lambda,q}] \tag{35}$$

$$\left(\frac{\partial n_{\lambda,q}}{\partial t}\right)_{e-p} = -\frac{\Delta n_{\lambda,q}}{\tau_{\lambda,q}} + \sum_{\alpha,k,\uparrow,\beta,k',\uparrow}[\mathit{\Xi}_{\alpha,k,\uparrow}(\beta,k',\uparrow,\lambda,q)\Delta f_{\alpha,k,\uparrow} + \mathit{\Xi}_{\beta,k',\uparrow}(\alpha,k,\uparrow,\lambda,q)\Delta f_{\beta,k',\uparrow}] \tag{36}$$

notice here that the electronic part equation.35 is only for single spin channel while the second equation for the phonon already take into account the spin degeneracy, the $\uparrow$ in the thus only mean a single state, in equation.36. With the relaxation time already defined above and the $\mathit{\Xi}$ and $\mathit{\Gamma}$ defined as:

$$\mathit{\Gamma}_{\beta,k',\uparrow}(\alpha,k,\uparrow,\lambda,q) = \frac{1}{N_q}\frac{2\pi}{\hbar}\left\{(f_{\alpha,k,\uparrow}+n_{\lambda,q})|g|^2\delta(k-k'-q) + (n_{\lambda,q}+1-f_{\alpha,k,\uparrow})|g|^2\delta(k+q-k')\right\} \tag{37}$$

$$\mathit{\Gamma}_{\lambda,q}\alpha,k,\uparrow,\beta,k',\uparrow = \frac{1}{N_q}\frac{2\pi}{\hbar}\left\{(f_{\beta,k',\uparrow}-f_{\alpha,k,\uparrow})|g|^2\delta(k-k'-q) + (f_{\beta,k',\uparrow}-f_{\alpha,k,\uparrow})|g|^2\delta(k+q-k')\right\} \tag{38}$$

$$\mathit{\Xi}_{\alpha,k,\uparrow}(\beta,k',\uparrow,\lambda,q) = \frac{4\pi}{N_k\hbar}(n_{\lambda,q}+1-f_{\beta,k',\uparrow})|g|^2\delta(k-k'-q) \tag{39}$$

$$\mathit{\Xi}_{\beta,k',\uparrow}(\alpha,k,\uparrow,\lambda,q) = -\frac{4\pi}{N_k\hbar}(f_{\alpha,k,\uparrow}+n_{\lambda,q})|g|^2\delta(k-k'-q) \tag{40}$$

Putting the terms $(\partial f_{\alpha,k,\uparrow}/\partial t)_{e-ph}$ and $(\partial n_{\lambda,q}/\partial t)_{e-ph}$ in equation.35 and 36 back into the coupled transport equation.12 and 13. We would then obtain the necessary equation to solve the phonon drag problem.

3 Seebeck in the uncoupled case

We start with the general linear relationship between current flow and the field, following mainly the notation of the paper *"Transpor coefficients from first-principles calculations, PRB, 2003"*. The general linear current response to an applied temperature gradient and a electric field is given by:

$$J_c = \sigma E - \zeta\nabla T \tag{41}$$

$$J_q = T\zeta E - \kappa_0\nabla T \tag{42}$$

with J_c the charge current, J_q the thermal current, σ and κ can be recognized to be the electric conductivity and the total thermal conductivity. In the matrix form, we have:

$$\begin{pmatrix} J_c \\ J_q \end{pmatrix} = \begin{pmatrix} \sigma & -\zeta \\ T\zeta & -\kappa_0 \end{pmatrix}\begin{pmatrix} E \\ \nabla T \end{pmatrix} \tag{43}$$

Each currents are vectors with element i,j,k correspond to three cartesian directions, the same is true for the gradient of the field we consider here. Note that the electric field is given from the electric potential by $E = -\nabla\phi$. The transport properties σ, ζ and κ are corresponding tensors so that, for example:

$$J_{c,i} = \sum_j \sigma_{ij}E_j \tag{44}$$

according to the above definition, we find the Seebeck coefficients and the Peltier coefficients to be:

$$S = \frac{\zeta}{\sigma} \tag{45}$$

$$\Pi = \frac{T\zeta}{\sigma} \tag{46}$$

$$\pi = TS \tag{47}$$

The final equation is the Kelvin equation. The current flow J_c is solely due to electrons while the heat flow is from both electrons and phonons. We have:

$$J_{c,i,\uparrow} = \frac{e}{N_k\Omega}\sum_{\alpha,k,\uparrow} f_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,i} \tag{48}$$

$$J_{q,ele,i,\uparrow} = \frac{1}{N_k\Omega}\sum_{\alpha,k,\uparrow}(\varepsilon_{\alpha,k,\uparrow}-\mu) f_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,i} \tag{49}$$

$$J_{q,phonon,i} = \frac{1}{N_q\Omega}\sum_{\lambda,q}\hbar\omega_{\lambda,q}n_{\lambda,q}v_{\lambda,q,i} \tag{50}$$

where Ω is the volumn of the unit cell. Dividing the $N_{k(q)}\Omega$ term is necessary because the these properties are defined as "density" and we should note that $N_{k(q)}\Omega$ term is simply the volumn of the finite system that we are concerning with. N_k gives the number of unit cells in the system.

We can consider two cases:

- Starting with $\nabla T = 0$ and $E \neq 0$. This correspond to the Peltier effect.
- Starting with $\nabla T \neq 0$ and $E = 0$. This correspond to the process of Seebeck effect.

We start by first deriving the transport equation of decoupled equations in the Peltier case, the off-equilibrium electron distribution, given by (the equilibrium part of the distribution sum up to zero):

$$\Delta f_{\alpha,k,\uparrow} = e\sum_j\left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial\varepsilon}\right)\tau_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,j}E_j \tag{51}$$

where we explicitly written down the summation. the electric current flow is given by equation.48 as:

$$J_{c,i} = 2J_{c,i,\uparrow} = \frac{2e^2}{N_k\Omega}\sum_j\sum_{\alpha,k,\uparrow}\left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial\varepsilon}\right)\tau_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,i}v_{\alpha,k,\uparrow,j}E_j \tag{52}$$

$$J_{c,i} = \sum_j \sigma_{ij}E_j \tag{53}$$

with $J_{c,i}$ now denote the total current of both spin channel by the factor of 2 and giving the result for σ:

$$\sigma_{ij} = \frac{2e^2}{N_k\Omega}\sum_{\alpha,k,\uparrow}\left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial\varepsilon}\right)\tau_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,i}v_{\alpha,k,\uparrow,j} \tag{54}$$

Since the electron and phonon are decoupled, phonon do not respond to the electric field. All the heat flow is due to electrons, and thus we have, from equation.49:

$$J_{q,ele,i} = \frac{2e}{N_k\Omega}\sum_j\sum_{\alpha,k,\uparrow}(\varepsilon_{\alpha,k,\uparrow}-\mu)\left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial\varepsilon}\right)\tau_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,i}v_{\alpha,k,\uparrow,j}E_j \tag{55}$$

$$J_{q,i} = T\sum_j \zeta_{ij}E_j \tag{56}$$

$$\tag{57}$$

finally giving:

$$\zeta_{ij} = \frac{2e}{N_k\Omega T}\sum_{\alpha,k,\uparrow}(\varepsilon_{\alpha,k,\uparrow}-\mu)\left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial\varepsilon}\right)\tau_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,i}v_{\alpha,k,\uparrow,j} \tag{58}$$

the Seebeck coefficients are thus given by:

$$S_{ij} = \left[\frac{2e}{N_k\Omega T}\sum_{\alpha,k,\uparrow}(\varepsilon_{\alpha,k,\uparrow}-\mu)\left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial\varepsilon}\right)\tau_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,i}v_{\alpha,k,\uparrow,j}\right]/\sigma \tag{59}$$

in which the division should be interpreted as matrix operation.

In the Seebeck picture, $E = 0$ and electrons are driven by the thermal gradient ∇T:

$$\Delta f_{\alpha,k,\uparrow} = -\sum_j \left(\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial T} \right) \tau_{\alpha,k,\uparrow} v_{\alpha,k,\uparrow,j} (\nabla T)_j \tag{60}$$

the electric conductivity is still given by equation.54. Now we consider:

$$J_{c,i} = -\frac{2e}{N_k \Omega} \sum_j \sum_{\alpha,k,\uparrow} \left(\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial T} \right) \tau_{\alpha,k,\uparrow} v_{\alpha,k,\uparrow,i} v_{\alpha,k,\uparrow,j} (\nabla T)_j \tag{61}$$

$$J_{c,i} = -\sum_j \zeta_{ij} (\nabla T)_j \tag{62}$$

finally, we have:

$$\zeta_{ij} = \frac{2e}{N_k \Omega} \sum_{\alpha,k,\uparrow} \left(\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial T} \right) \tau_{\alpha,k,\uparrow} v_{\alpha,k,\uparrow,i} v_{\alpha,k,\uparrow,j} \tag{63}$$

The two equations of ζ (58 and 63) are the same, obeying the Kelvin relation. This can be seen, with $\varepsilon' = (\varepsilon_{\alpha,k,\uparrow} - \mu)/k_B T$ by:

$$\frac{\partial f_k}{\partial T} = \frac{\partial f_k}{\partial \varepsilon'} \frac{\partial \varepsilon'}{\partial T} = \frac{\partial f_k}{\partial \varepsilon'} \left(-\frac{\varepsilon_{\alpha,k,\uparrow} - \mu}{k_B T^2} \right) \tag{64}$$

$$\frac{\partial f_k}{\partial \varepsilon} = \frac{\partial f_k}{\partial \varepsilon'} \frac{\partial \varepsilon'}{\partial \varepsilon} = \frac{\partial f_k}{\partial \varepsilon'} \left(\frac{1}{k_B T} \right) \tag{65}$$

$$\tag{66}$$

so that we find:

$$\frac{\partial f_k}{\partial T} = \frac{\partial f_k}{\partial \varepsilon} \left(-\frac{\varepsilon_{\alpha,k,\uparrow} - \mu}{T} \right) \tag{67}$$

Placing the above relation into equation.63, we can recover the results in equation.58. Thus the Seebeck coefficient calculated from the ζ function and σ is the same.

4 Seebeck in the coupled case

Now we consider the transport equation when electron and phonon systems are coupled by the $e - ph$ interaction, as discussed before. The coupled equations are the set 12 and 13.

We still start with the Peltier case with $\nabla T = 0$. Electric field is applied to drive the coupled electron-phonon system. Off-equilibrium phonons are only because of the electron-phonon interaction. We make the following approximation to the coupled transport equation:

- In the electron equation.35, the $\Delta f_{\beta,k',\uparrow}$ term is small and can be ignored.
- The term due to the non-equilibrium phonon is also small in equation.35 so that $\Delta n_{\lambda,q}$ is also insignificant.

The electron transport equation 35 are now decoupled from the phonon one. We can obtain the electronic part of the heat flow and the elctric conductivity:

$$\sigma_{ij} = \frac{2e^2}{N_k \Omega} \sum_{\alpha,k,\uparrow} \left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial \varepsilon} \right) \tau_{\alpha,k,\uparrow} v_{\alpha,k,\uparrow,i} v_{\alpha,k,\uparrow,j} \tag{68}$$

$$J_{q,ele,i} = \frac{2e}{N_k \Omega} \sum_j \sum_{\alpha,k,\uparrow} (\varepsilon_{\alpha,k,\uparrow} - \mu) \left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial \varepsilon} \right) \tau_{\alpha,k,\uparrow} v_{\alpha,k,\uparrow,i} v_{\alpha,k,\uparrow,j} E_j \tag{69}$$

$$\tag{70}$$

for phonons, we have, from equation.12 and 35:

$$\Delta n_{\lambda,q} = \tau_{\lambda,q,tot} \sum_{\alpha,k,\beta,k'} [\Xi_{\alpha,k} \Delta f_{\alpha,k,\uparrow} + \Xi_{\beta,k'} \Delta f_{\beta,k',\uparrow}] \tag{71}$$

$$\tau_{\lambda,q,tot} = \tau_{\lambda,q,others} + \tau_{\lambda,q,e-ph} \tag{72}$$

where the index in function Ξ is omitted for simplicity. The phonon heat flow is thus:

$$\begin{aligned} J_{q,phonon,i} = &\sum_j \frac{e}{N_q \Omega} \sum_{\lambda,q} \hbar\omega_{\lambda,q} \tau_{\lambda,q} v_{\lambda,q,i} \\ &\sum_{\alpha,k,\uparrow,\beta,k',\uparrow} \left[\Xi_{\alpha,k} \left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial \varepsilon} \right) \tau_{\alpha,k,\uparrow} v_{\alpha,k,\uparrow,j} + \Xi_{\beta,k'} \left(-\frac{\partial f^0_{\beta,k',\uparrow}}{\partial \varepsilon} \right) \tau_{\beta,k',\uparrow} v_{\beta,k',\uparrow,j} \right] E_j \end{aligned} \tag{73}$$

the total heat flow is given by:

$$J_{q,i} = J_{q,ele,i} + J_{q,phonon,i} \tag{74}$$

corresponding to

$$J_{q,i} = T \sum_j \zeta_{ij} E_j \tag{75}$$

We obtain the ζ function:

$$\zeta_{ij} = \frac{2e}{N_k \Omega T} \sum_{\alpha,k,\uparrow} (\varepsilon_{\alpha,k,\uparrow} - \mu) \left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial \varepsilon} \right) \tau_{\alpha,k,\uparrow} v_{\alpha,k,\uparrow,i} v_{\alpha,k,\uparrow,j} \tag{76}$$

$$+\frac{e}{N_q \Omega T} \sum_{\lambda,q} \sum_{\alpha,k,\beta,k'} \hbar\omega_{\lambda,q} \tau_{\lambda,q} v_{\lambda,q,i} \left[\Xi_{\alpha,k} \left(-\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial \varepsilon} \right) \tau_{\alpha,k,\uparrow} v_{\alpha,k,\uparrow,j} + \Xi_{\beta,k'} \left(-\frac{\partial f^0_{\beta,k',\uparrow}}{\partial \varepsilon} \right) \tau_{\beta,k',\uparrow} v_{\beta,k',\uparrow,j} \right] \tag{77}$$

The Seebeck coefficient is thus given by the matrix operation:

$$S = \zeta / \sigma \tag{78}$$

From the Seebeck picture, we consider the following:

- Term $\Delta f_{\alpha,k,\uparrow}$ and $\Delta f_{\beta,k',\uparrow}$ in the phonon equation.36 are in-significant and thus ignored. Thus the phonons are decoupled from the electron equation.
- In the electron equation.35, the $\Delta f_{\beta,k',\uparrow}$ term is small and can be ignored.

from this picture, we first obtain the off-equilibrium phonon:

$$\Delta n_{\lambda,q} = -\sum_j \left(\frac{\partial n^0_{\lambda,q}}{\partial T} \right) \tau_{\lambda,q} v_{\lambda,q,j} (\nabla T)_j \tag{79}$$

The electrons themself are affected by the temperature gradient, and also the electron phonon interaction. We have

$$v_{\alpha,k,\uparrow} \frac{\partial f^0_{\alpha,k,\uparrow}}{\partial T} \nabla T = -\frac{f_{\alpha,k,\uparrow} - f^0_{\alpha,k,\uparrow}}{\tau_{\alpha,k}} + \sum_{\beta,k',\uparrow,\lambda,q} \Gamma_{\lambda,q} \Delta n_{\lambda,q} \tag{80}$$

We have the off-equilibrium electron distribution:

$$\Delta f_{\alpha,k,\uparrow} = -\sum_j \tau_{\alpha,k,\uparrow} \left[\sum_{\beta,k',\lambda,q} \Gamma_{\lambda,q} \left(\frac{\partial n^0_{\lambda,q}}{\partial T} \right) \tau_{\lambda,q} v_{\lambda,q,j} + v_{\alpha,k,\uparrow,j} \frac{\partial f^0_{\alpha,k,\uparrow}}{\partial T} \right] (\nabla T)_j \tag{81}$$

the electron current is thus given by from equation.48 as

$$J_{c,i} = -\sum_j \zeta_{ij} (\nabla T)_j \tag{82}$$

$$= -\frac{2e}{N_k \Omega} \sum_j \left[\sum_{\alpha,k,\uparrow} \sum_{\beta,k',\uparrow,\lambda,q} v_{\alpha,k,\uparrow,i} \tau_{\alpha,k,\uparrow} \Gamma_{\lambda,q} \left(\frac{\partial n^0_{\lambda,q}}{\partial T} \right) \tau_{\lambda,q} v_{\lambda,q,j} + \sum_{\alpha,k,\uparrow} \left(\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial T} \right) \tau_{\alpha,k,\uparrow} v_{\alpha,k,\uparrow,i} v_{\alpha,k,\uparrow,j} \right] (\nabla T)_j \tag{83}$$

We re-organize and recognize that the ζ function to be:

$$\zeta_{ij} = \frac{2e}{N_k\Omega}\left[\sum_{\alpha,k,\uparrow}\left(\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial T}\right)\tau_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,i}v_{\alpha,k,\uparrow,j} + \sum_{\alpha,k,\uparrow}\sum_{\beta,k',\lambda,q} v_{\alpha,k,\uparrow,i}\tau_{\alpha,k,\uparrow}\mathit{\Gamma}_{\lambda,q}\left(\frac{\partial n^0_{\lambda,q}}{\partial T}\right)\tau_{\lambda,q}v_{\lambda,q,j}\right] \tag{84}$$

Seebeck coefficient is given by the ζ and σ, as:

$$S_{ij} = \frac{2e}{N_k\Omega\sigma}\left[\sum_{\alpha,k,\uparrow}\left(\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial T}\right)\tau_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,i}v_{\alpha,k,\uparrow,j} + \sum_{\alpha,k,\uparrow}\sum_{\beta,k',\lambda,q} v_{\alpha,k,\uparrow,i}\tau_{\alpha,k,\uparrow}\mathit{\Gamma}_{\lambda,q}\left(\frac{\partial n^0_{\lambda,q}}{\partial T}\right)\tau_{\lambda,q}v_{\lambda,q,j}\right] \tag{85}$$

Rewriting the equation for calculation

We implement the Seebeck picture in the calculation. In the code, we iterate all the q points first, inside each q-point iteration, we iterate over the electronic states $\alpha, k, \uparrow$ and $\beta, k', \uparrow$ of interest. In the ζ_{ij} function above, the first part depends straight-forwardly on electronic properties only (τ given by electron-phonon interaction) and is simple to implemented in the transport coefficient calculation routine. The second part:

$$\sum_{\alpha,k,\uparrow}\sum_{\beta,k',\lambda,q} v_{\alpha,k,\uparrow,i}\tau_{\alpha,k,\uparrow}\mathit{\Gamma}_{\lambda,q}\left(\frac{\partial n^0_{\lambda,q}}{\partial T}\right)\tau_{\lambda,q}v_{\lambda,q,j} \tag{86}$$

requires two part that need to be calculated: $\tau_{\lambda,q}$ and coefficient $\mathit{\Gamma}_{\lambda,q}$. We can rewrite this part to:

$$\sum_{\alpha,k,\uparrow} v_{\alpha,k,\uparrow,i}\tau_{\alpha,k,\uparrow}\left[\sum_{\lambda,q}\sum_{\beta,k',\uparrow}\mathit{\Gamma}_{\lambda,q}\left(\frac{\partial n^0_{\lambda,q}}{\partial T}\right)\tau_{\lambda,q}v_{\lambda,q,j}\right] \tag{87}$$

now the terms in the bracket is summed over $\beta, k', \uparrow$ and λ, q, and therefore can be indexed by $\alpha, k, \uparrow$ only. The calculation of the bracket term is thus procede almost the same as the calculation of electron life time.

Now, ζ can be written as:

$$\zeta_{ij} = \frac{2e}{N_k\Omega}\sum_{\alpha,k,\uparrow}\tau_{\alpha,k,\uparrow}v_{\alpha,k,\uparrow,i}\left[\left(\frac{\partial f^0_{\alpha,k,\uparrow}}{\partial T}\right)v_{\alpha,k,\uparrow,j} + \sum_{\beta,k',\lambda,q}\mathit{\Gamma}_{\lambda,q}\left(\frac{\partial n^0_{\lambda,q}}{\partial T}\right)\tau_{\lambda,q}v_{\lambda,q,j}\right] \tag{88}$$

with the two terms in the square bracket is the off-equilibrium electron distribution because of the temperature gradient (diffusive) and the phonon drag part.

Usage of atomic units

Hartree units are named after the physicist Douglas Hartree[1], in this unit *the numerical values of the following four fundamental physical constants are all unity by definition.* They are:

- **Reduced Planck Constant** $\hbar = 1$ (unit of action)
- **Elementary charge** $e = 1$ (unit of charge)
- **Bohr radius** $a_0 = 1$ (unit of length)
- **Electron mass** $m_e = 1$ (unit of mass)

Each unit in this system can be expressed as a product of powers of four physical constants *without a multiplying constant.* Therefore, they are consistent units, meaning that given any mathematical expression, if all the values are in atomic unit, the result will come out as atomic unit without the need for conversion. The derived units in atomic unit system are converted to SI unit by replacing the value of those constants (the constants are used as units).

Table 2: Defining constants

Symbol	**Definition**	**Value in SI units**
$\hbar$	$\hbar$	$1.054571 \times 10^{-34} J \cdot s$
e	e	$1.602176 \times 10^{-19} C$
a_0	$4\pi\epsilon_0\hbar^2/(m_e e^2)$	$5.291772 \times 10^{-11} m$
m_e	m_e	$9.109383 \times 10^{-31} kg$
E_h	$\hbar^2/(m_e a_0^2)$	$\hbar^2/(m_e a_0^2)$

5 Unit conversion

As an example, the speed of light in atomic unit of velocity is approximately 137.036, The atomic unit of velocity is expressed by the constants $a_0 E_h/\hbar$, which is converted to SI unit by $a_0 E_h/\hbar = 2.187 \times 10^6 m/s$, and therefore $137.036 \times 2.187 \times 10^6 = 2.99 \times 10^8 m/s$

Table 3: Derived atomic units

Atomic unit of	**Expression**	**Value in SI**
Action	$\hbar$	$1.054 \times 10^{-34} J \cdot s$
Charge	e	$1.602 \times 10^{-19} C$
Charge Density	e/a_0^3	$1.081 \times 10^12 C \cdot m^{-3}$
Current	$eE_h/\hbar$	$6.623 \times 10^{-3} A$
Electric Field	$E_h/(ea_0)$	$5.142 \times 10^11 V/m$
Electric Potential	E_h/e	$27.211 V$
Electric Dipole moment	ea_0	$8.478 \times 10^{-30} C \cdot m$
Energy	E_h	$4.359 \times 10^{-18} J$
Force	E_h/a_0	$8.238 \times 10^{-8} N$
Length	a_0	$5.291 \times 10^{-11} m$
Magnetic Dipole Moment	$e\hbar/m_e$	$1.854 \times 10^{-23} J/T$
Mass	m_e	$9.109 \times 10^{-31} kg$
Momentum	$\hbar/a_0$	$1.992 \times 10^{-24} kg \cdot m/s$
Permitivity	$e^2/(a_0 E_h)$	$1.112 \times 10^{-10} F/m$
Time	$\hbar/E_h$	$2.418 \times 10^{-17} s$
Pressure	E_h/a_0^3	$2.942 \times 10^{13} Pa$
Velocity	$a_0 E_h/\hbar$	$2.187 \times 10^6 m/s$

[1] the reference of this note is Wikipedia