19 Sep 2017

Fermi - Golden rule

Let consider a general quantum-mechanical system

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

where we assume $\hat{H}_1$ is small and will be treated as a perturbation. And $\hat{H}_0$ is a solvable problem. As an example, we are thinking of the electron - phonon system where

$$\hat{H}_0 = c^\dagger H c + u^T K u + \frac{1}{2} p^2, \qquad p = \dot{u}$$

is free electron + free phonon and

$$\hat{H}_1 = c^\dagger \vec{M} c \cdot \vec{u} = \sum_{jkl} M^l_{jk} c^\dagger_j c_k u_l$$

is the electron-phonon interaction, which is assumed small. How small is small? According to Peierls, it should be such that $\hbar/\tau \ll k_B T$.

Note that $u_j \equiv \sqrt{M_j}\,(R_j - R_j^0)$ has extra $\sqrt{\text{mass}}$ so that $\sqrt{K}$ has units of frequency ω. c, $c^\dagger$ is dimensionless. H is single particles (spinless) Hamiltonian

We give a quick derivation of the Fermi-golden rule and emphasize the conceptual underpinning.

Let imagine that there is no interaction at $t < 0$ so $\hat{H} = \hat{H}_0$, $\hat{H}_1 = 0$ and the problem is solved, given the eigen state $|i\rangle$ with Eigenvalue E_i such that

$$\hat{H}_0 |i\rangle = E_i |i\rangle$$

We turn on the interaction $\hat{H}_1$ for a duration T so $\hat{H}_1(t)$ has the form

Due to the disturbance of $\hat{H}_1(t)$ the system cannot stay in the initial state $|i\rangle$ but will make a transition to other states $|i'\rangle$. After $t > T$ the transition stop and we are interested in the transition probability $|\langle f|i\rangle|^2$.

Let the wave function be $\psi(t) = \sum_n C_n(t)|n\rangle \rightarrow \begin{pmatrix} C_0 \\ C_1 \\ C_2 \\ \vdots \end{pmatrix}$

we assume for $t \leq 0$, $C_n = \begin{cases} e^{-\frac{i}{\hbar}E_i t} & \text{if } n = i \\ 0 & \text{otherwise.} \end{cases}$ i is a particularly fixed state

we ask what is $C_n(t)$ for $t > T$.

Since for $t > T$ $|n\rangle$ is again the eigenstate of $\hat{H}_0$

$|C_n(t)|^2 = P_n$ is independent of time.

We need to solve the Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = (\hat{H}_0 + \hat{H}_1)\psi$$

with the special initial condition $C_n = \delta_{ni}$ at $t=0$

Put the expansion in $|n\rangle$, we get

$$i\hbar \sum_n \dot{C}_n(t)|n\rangle = \sum_n C_n(t) E_n |n\rangle + \sum_n C_n(t) \hat{H}_1 |n\rangle$$

Multiply by $\langle m|$ from left, we get using $\langle m|n\rangle = \delta_{mn}$

$$i\hbar \dot{C}_m(t) = E_m C_m(t) + \sum_n H'_{mn} C_n(t)$$

where $H'_{mn} \equiv \langle m|\hat{H}_1|n\rangle$

If $H'_{mn} = 0$ $\quad i\hbar \dot{C}_m = E_m C \rightarrow C_m = A_m e^{-\frac{i}{\hbar} E_m t}$

$|C_m| = \text{const}$ in time t

Put this form back to the full equation assume A_m is a function of time

$$i\hbar \dot{C}_m = i\hbar \dot{A}_m e^{-\frac{i}{\hbar} E_m t} + A_m E_m e^{-\frac{i}{\hbar} E_m t} =$$

$$E_m A_m e^{-\frac{i}{\hbar} E_m t} + \sum_n H'_{mn} e^{-\frac{i}{\hbar} E_n t} \underbrace{A_n}_{C_n}$$

Divide the $e^{-\frac{i}{\hbar} E_m t}$ factor to the right. we get (interaction picture equation)

$$i\hbar \dot{A}_m = \sum_n H'_{mn} e^{-\frac{i}{\hbar}(E_n - E_m)t} A_n$$

integrate from time $t = 0$ to time $t > T$, since $H'(t)$ is steps

we get

$$\int_0^t \dot{A}_m dt = A_m(t) - A_m(0) = \frac{1}{i\hbar} \sum_n \int_0^T H'_{mn} e^{+\frac{i}{\hbar}(E_m - E_n)t} A_n(t)\, dt$$

$A_m(0) \rightarrow \delta_{mi}$

Let focus on one particular state f. if the final state $f \neq i$

then $$A_f(t) = \frac{1}{i\hbar} \sum_n \int_0^T H'_{fn} e^{\frac{i}{\hbar}(E_f - E_n)t} A_n(t)$$

Since H' is 1st order small, we can replace $A_n(t)$ by its zero order value. Or if not, we can do Dyson-like expansion in H', i.e. H', and $H'H'$, $H'H'H'$, etc. In any case the lowest order result is to take $A_n = \delta_{ni}$ on the right-hand side we get

$$A_f(t) = \frac{1}{i\hbar} \int_0^T H'_{fi} e^{\frac{i}{\hbar}(E_f - E_i)t} dt$$

The transition probability is $P_{f \leftarrow i} = |C_f|^2 = |A_{fi}|^2$

The time integral can be done

$$A_{fi} = \frac{1}{i\hbar} H'_{fi} \frac{e^{\frac{i}{\hbar}(E_f - E_i)T} - 1}{\left(\frac{+i}{\hbar}\right)(E_f - E_i)}$$

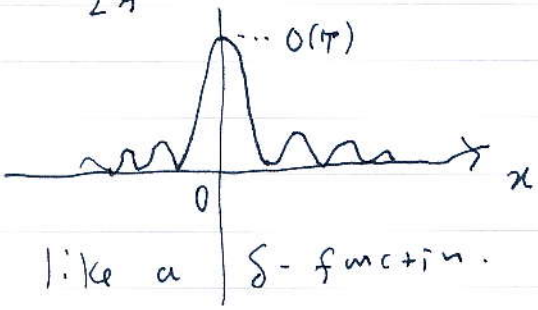
$$P_{f \leftarrow i} = |A_{fi}|^2 = |H'_{fi}|^2 \cdot \frac{4 \cdot \sin^2\left(\frac{(E_f - E_i)T}{\hbar\, 2}\right)}{(E_f - E_i)^2}$$

The transition $P_{f \leftarrow i}$, by definition must be bounded, $0 \leq P_{f \leftarrow i} \leq 1$. however, if H'_{fi} is not small this expression seems to break this bound. In fact we must require $|H'_{fi}|^2 T$ is finite (as $T \to \infty$). in order for the first order perturbation theory to be valid.

We are not interested in the total transition probability P but the transition rate

$$W_{fi} = \frac{P_{f \leftarrow i}}{T} = |H'_{fi}|^2 \frac{4 \sin^2\left(\frac{(E_f - E_i)T}{2\hbar}\right)}{(E_f - E_i)^2 T}$$

Let $x = \frac{E_f - E_i}{2\hbar}$ the factor is $\frac{\sin^2(xT)}{\hbar^2 \cdot x^2 T}$. It looks like



as $T \to \infty$ this function behave like a δ-function. in fact $xT = y$

We need to know $\int_{-\infty}^{+\infty} \frac{\sin^2(xT)}{x^2 T} dx \overset{?}{=} \int_{-\infty}^{+\infty} \frac{\sin^2(y)}{y^2} dy = \pi$

so for $T \to \infty$ $\frac{\sin^2(xT)}{x^2 T} = \pi \delta(x)$ $\qquad \delta(x) = \delta\left(\frac{E_f - E_i}{2\hbar}\right) = 2\hbar\, \delta(E_f - E_i)$

So finally we get the fermi-golden rule

$$W_{fi} = \frac{P_{f \leftarrow i}}{T} = \frac{2\pi}{\hbar} \cdot |\langle f | \hat{H}_1 | i \rangle|^2 \delta(E_f - E_i)$$

Units of / dimension of W_{fi} is 1/time.

The eigen state of $\hat{H}_0$

Assuming we have diagonalized single particle Hamiltn
$H \to \varepsilon_k$ and the dynamic matrix $K \to \omega_q$

so that we can write

$$\hat{H}_0 = \sum_k \varepsilon_k c_k^\dagger c_k + \sum_q \hbar\omega_q \left(a_q^\dagger a_q + \frac{1}{2}\right)$$

for system with periodicity $k \equiv (n, \vec{K})$ n: band, $\vec{K} \in 1BZ$

and similarly $q \equiv (\lambda, \vec{q})$
λ: branch index

For systems without periodicity, they are just some labelling of quantum states. we can not separate them nicely as band/branch + lattice moment label.

For a concrete calculation, we need to know the exact relationship of real space variables to diagonal variables.

For example, if we have only one degree per unit cell, then

$$C_k = \frac{1}{\sqrt{N}} \sum_j C_j e^{-i\vec{k}\cdot\vec{R}_j}$$

N total # of unit cell.

The relation is just a Fourier transform, note we need the $\frac{1}{\sqrt{N}}$ factor.

For phonon it is

$$u_\ell = \frac{1}{\sqrt{N}} \sum_q \sqrt{\frac{\hbar}{2\omega_q}} \epsilon_{q\lambda} a_q e^{i\vec{q}\cdot\vec{R}_\ell} + \text{h.c.}$$

ϵ is the eigen vector of the dynamic matrix $D(\vec{q})$ (not K) properly orthonormalized, we need the h.c. hermitian conjugate, so that u_ℓ is hermitian. both u_ℓ and ϵ are vector indexed in a unit cell.

If we have one atom per cell, u_ℓ and ϵ are 3D vector in 3D space. if we have 2 atoms per cell, like graphe. then u_ℓ and ϵ are 6-dimensional vectors. and the index ℓ label the cell only.

Some book/paper use more complicated labelling such as $u_\ell^{i\alpha}$ ℓ : cell, i : which atom, α x, y or z

I combine $(i\alpha)$ as a single vector $\vec{u}_\ell$ (also omit $\rightarrow$)

With the above transform $C_j \rightarrow C_k$

$u_\ell \rightarrow a_q$

We can obtain transformed M matrix

$$M^{\ell}_{jk} \rightarrow M^{q}_{xx'}$$

Diagonalize H

Assuming periodicity so that $H \rightarrow H^{jj'}_{\ell\ell'}$ is a function of $\ell - \ell'$ only ℓ is vector labelling the unit cell so $H_{\ell\ell'}$ is $s \times s$ matrix s: # of degree of freedom per cell. Let define

$$H(\vec{k}) \equiv \sum_{\ell} H_{\ell\ell'} e^{-i\vec{k}\cdot(\vec{R}_\ell - \vec{R}_{\ell'})}$$ is $s \times s$ matrix

due to periodicity the result of the sum is independent of ℓ'. where $\vec{R}_\ell = \sum_i \ell_i \vec{a}_i$ is lattice vector $\ell_i \in \mathbb{Z}$. are integers.

Let $H(\vec{k}) e_{n\vec{k}} = \varepsilon_{n\vec{k}} e_{n\vec{k}}$

various eigenvalues are labelled by band index n for each parameters $\vec{k}$. We assume $e^{+}_{n} e_{n'} = \delta_{nn'}$

Then the transformation is given by

$$C_\ell = \frac{1}{\sqrt{N}} \sum_K C_K e_K e^{i \vec{k} \cdot \vec{R}_\ell}$$

N: total number of cells.

where $C_\ell = \begin{pmatrix} C_\ell^1 \\ C_\ell^2 \\ \vdots \\ C_\ell^s \end{pmatrix}$ is a vector of dimension s: s # of degree per cell.

e_K is also vector of dimension s. $H(\vec{k})$ is $s \times s$.

$$H(\vec{k}) e_K = \varepsilon_K e_K$$

$K \equiv (n, \vec{k})$ included band index.

One can check this indeed work in the sense we can get diagonal form $\sum_K \varepsilon_K c_K^+ c_K$ for real space form $C^+ H C$

$$= \sum_{\ell \ell' ; j j'} C_{\ell j}^+ H_{\ell \ell'}^{j j'} C_{\ell' j'}$$

ℓ label the cell
j label the degree inside the cell
e.g. differ basis / spin.

For the phonon degrees of freedom we can combine the h.c. term as

$$u_\ell = \frac{1}{\sqrt{N}} \sum_q \sqrt{\frac{\hbar}{2\omega_q}} \left(\epsilon(q) a_q e^{-i \vec{q} \cdot \vec{R}_\ell} + \text{h.c.} \right)$$

$$= \sum_q \sqrt{\frac{\hbar}{2\omega_q N}} \left(\epsilon(q) a_q e^{i \vec{q} \cdot \vec{R}_\ell} + \epsilon^*(q) a_q^+ e^{-i \vec{q} \cdot \vec{R}_\ell} \right)$$

We can define or chose $\epsilon(q)$ such that $\epsilon^*(q) = \epsilon(-q)$.

Since $q = (\lambda, \vec{q})$ $-q$ means $(\lambda, -\vec{q})$. i.e. the minus sign apply to the wave vector only. Now for the 2nd term, we make a change of variable $q \to -q$, but we assume $\omega_{-q} = \omega_q$ is even in $\vec{q}$ so

$$\sqrt{\frac{\hbar}{2\omega_q N}} \epsilon^*(q) a_q^+ e^{-i \vec{q} \cdot \vec{R}_\ell} \to \sqrt{\frac{\hbar}{2\omega_q N}} \epsilon(q) a_{-q}^+ e^{i \vec{q} \cdot \vec{R}_\ell}$$

$q \to -q$

Note the factor $\sqrt{\frac{\hbar}{\omega}}$ has dimension $\sqrt{\text{mass} \times \text{length}} = \sqrt{M \cdot L}$

Thus we have the following standard form

$$u_\ell = \sum_q \sqrt{\frac{\hbar}{2\omega_q N}} \left(\epsilon(q)\, e^{i \vec{q} \cdot \vec{R}_\ell} \right) \left(a_q + a^+_{-q} \right)$$

Now the interaction term can be written as

$$C^+ \vec{M} C \cdot \vec{u} = \sum_{jk\ell} M^{\ell}_{jk}\, C^+_j C_k\, u_\ell$$

$$= \sum_{\substack{\ell \ell' \ell'' \\ j j' j''}} M^{\ell'' j''}_{\ell j\, \ell' j'}\, C^+_{\ell j}\, C_{\ell' j'}\, u^{j''}_{\ell''}$$

ℓ unit cell
j degree in cell

$$= \sum_{\substack{\ell \ell' \ell'' \\ j j' j'' \\ k k' q}} M^{\ell'' j''}_{\ell j\, \ell' j'} \left(\frac{1}{\sqrt{N}} \right)^3 \left(e^{j''}_{k} \right)^* e^{-i \vec{k} \cdot \vec{R}_\ell}\, e^{j'}_{k'}\, e^{i \vec{k}' \cdot \vec{R}_{\ell'}} \sqrt{\frac{\hbar}{2\omega_q}}\, \epsilon^{j''}(q)\, e^{i \vec{q} \cdot \vec{R}_{\ell''}}\, C^+_k C_{k'} \left(a_q + a^+_{-q} \right)$$

We assume M is lattice translationally invariant so

$$M^{\ell''}_{\ell\, \ell'} = M^{\ell'' - \ell'}_{\ell - \ell',\, 0} \quad \text{is a function of two variables} = M^{\Delta \ell''}_{\Delta \ell',\, 0}$$

$$\Delta \ell'' = \ell'' - \ell' \qquad \Delta \ell' = \ell - \ell'$$

Let use $\Delta \ell''$, $\Delta \ell'$, and ℓ' as summation variables

then

$$\sum_{\ell \ell' \ell''} M^{\ell''}_{\ell\, \ell'}\, e^{-i \vec{k} \cdot \vec{R}_\ell + i \vec{k}' \cdot \vec{R}_{\ell'} + i \vec{q} \cdot \vec{R}_{\ell''}}$$

$$= \sum_{\Delta \ell\, \Delta \ell'',\, \ell'} M^{\Delta \ell''}_{\Delta \ell,\, 0}\, e^{-i \vec{k} \cdot \vec{R}_{\Delta \ell} + i \vec{q} \cdot \vec{R}_{\Delta \ell''} + i \left(\vec{k}' - \vec{k} + \vec{q} \right) \cdot \vec{R}_{\ell'}}$$

$$\vec{R}_{\Delta \ell} = \vec{R}_\ell - \vec{R}_{\ell'}$$

$$= \sum_{\Delta \ell\, \Delta \ell''} M^{\Delta \ell''}_{\Delta \ell,\, 0}\, e^{-i \vec{k} \cdot \vec{R}_{\Delta \ell} + i \vec{q} \cdot \vec{R}_{\Delta \ell''}} \cdot N\, \delta\left(\vec{k}' - \vec{k} + \vec{q} \right)$$

Summing over ℓ' we get Kronecker δ mod $\vec{G}$ where $\vec{G}$ is reciprocal lattice vectors i.e. $\delta(\vec{k}' - \vec{k} + \vec{q}) = \begin{cases} 1 & \text{if } \vec{k}' - \vec{k} + \vec{q} = \vec{G} \\ 0 & \text{other} \end{cases}$

$\vec{k}$ $\vec{k}'$, $\vec{q}$ are considered discrete.

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Putting the j index back we get

$$C^+ \vec{M} C \cdot \vec{u} = \sum_{\substack{\Delta\ell \, \Delta\ell'' \\ \kappa \, \kappa' \, q}} M^{\Delta\ell'' \, j''}_{\Delta\ell j, \, 0 j'} e^{-i\vec{K}\cdot\vec{R}_{\Delta\ell} + i\vec{q}\cdot\vec{R}_{\Delta\ell''}} \frac{1}{\sqrt{N}} \delta(\vec{K}' - \vec{K} + \vec{q}) \; j \, j' \, j''$$

$$* \left(e^{j}_{\kappa}\right)^* e^{j'}_{\kappa'} \epsilon^{j''}(q) \sqrt{\frac{\hbar}{2\omega_q}} \cdot C^+_{\kappa} C_{\kappa'} \left(a_q + a^+_{-q}\right)$$

$$= \frac{1}{\sqrt{N}} \sum_{\kappa \kappa' q} g^{q}_{\kappa \kappa'} \, \delta(\vec{K}' - \vec{K} + \vec{q}) \, C^+_{\kappa} C_{\kappa'} \left(a_q + a^+_{-q}\right)$$

g is like M but in Fourier space, due to the Kronecker δ q is defined only for $\vec{K}' = \vec{K} - \vec{q} + \vec{G}$

we left the factor $\frac{1}{\sqrt{N}}$ outside g. Obviously g need to have the dimension of energy.

$$g^{q}_{\kappa \kappa'} \equiv \sum_{\substack{\ell \, \ell'' \\ j \, j' \, j''}} M^{\ell'' j''}_{\ell j, \, 0 j'} e^{-i\vec{K}\cdot\vec{R}_{\ell} + i\vec{q}\cdot\vec{R}_{\ell''}} \left(e^{j}_{\kappa}\right)^* e^{j'}_{\kappa'} \epsilon^{j''}(q)$$

↑ all space related index are summed

All space related indices are transformed by the eigenvectors into mode space.

$\kappa = (n \vec{K})$

$\kappa' = (n' \vec{K}')$

$q = (\lambda, \vec{q})$

In order to define the distributions f and N for electrons and phonons, we take a brief look of the operators and states. The properties of the states are uniquely determined by the commutation relations for bosons

$$a_q \, a^+_{q'} - a^+_{q'} \, a_q = \delta_{qq'}$$

$$a_q \, a_{q'} - a_{q'} \, a_q = 0 \qquad a^+_q \, a^+_{q'} - a^+_{q'} \, a^+_q = 0$$

Focus on one particles quantum number q we have

$$a|n\rangle = \sqrt{n}\,|n-1\rangle \qquad a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle$$

and $$a^\dagger a|n\rangle = n|n\rangle \qquad n = 0, 1, 2, \cdots$$

For fermion we have

$$C_k C_{k'}^\dagger + C_{k'}^\dagger C_k = \delta_{kk'} \qquad C_k C_{k'} + C_{k'} C_k = 0$$
$$C_k^\dagger C_{k'}^\dagger + C_{k'}^\dagger C_k^\dagger = 0$$

Due to Pauli exclusion, $C^2 = 0$, we can have only two possibilities $|0\rangle$ and $|1\rangle$

we can demand $$C^\dagger C|n\rangle = n|n\rangle \qquad n = 0, 1$$

and $$C|n\rangle = \sqrt{n}\,|n-1\rangle \rightarrow C|0\rangle = 0,\quad C|1\rangle = |0\rangle$$

$$C^\dagger|n\rangle = \sqrt{1-n}\,|n+1\rangle \longrightarrow \begin{cases} C^\dagger|0\rangle = |1\rangle \\ C^\dagger|1\rangle = 0 \end{cases}$$

For multiple particle state, since the operators are anti-commute a sign convention is needed when operator acts on state so we expect extra sign ± 1 in front of these formulas. However, the transition rate depends only on the modulus so we don't care.

What I mean above is if $\psi = C_1^\dagger C_2^\dagger|0\rangle = |1,1\rangle$

The position of the operators matters. $C_2^\dagger C_1^\dagger|0\rangle = -C_1^\dagger C_2^\dagger|0\rangle = -\psi$
$= -|1,1\rangle$

We now define

$$f_k \equiv \langle C_k^\dagger C_k\rangle = Tr(\rho(t)\, C_k^\dagger C_k) \qquad \text{similarly } N = \langle a_q^\dagger a_q\rangle$$

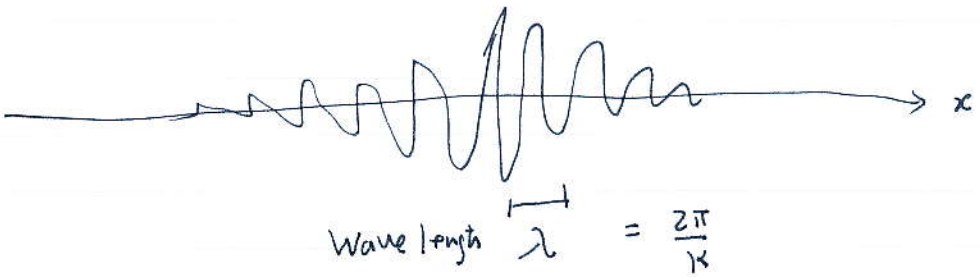
here operator & density matrix will be in Schrödinger picture. This is not quite right, as in Boltzmann equation we expect f a function of k, t, $\vec{r}$. But there is no $\vec{r}$ dependence here.

To make a more rigorous definition we need to consider the Green's function

$$-i\hbar G^{<}_{KK'}(t,t') \equiv \langle C^{\dagger}_{K'}(t') C_{K}(t) \rangle$$

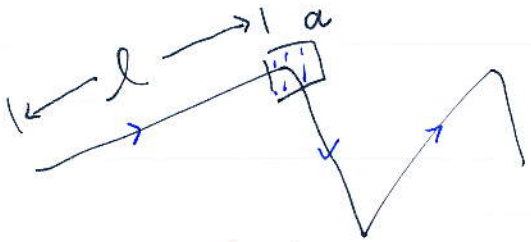
perform a Wigner transform to $\vec{K}$ and $\vec{K}'$, t and t' fast variables $\frac{\vec{K}+\vec{K}'}{2}$ is keep and slow variables $\Delta\vec{K} = \vec{K}' - \vec{K}$ is Fourier transformed back to $\vec{r}$. time is identified with $\frac{t+t'}{2}$. And we don't transform $t'-t$ back to frequency as there is no ω in Boltzmann equation.

This is very complicated, see, eg. Kadanoff + Baym, "Quantum statistical Mechanics" 1962. We will interprete the meanis of f_K intuitively by says the $\vec{K}$ represents the wave vector of a wave packet so it does has a location $\vec{r}$ (to f)



In this sense, we can say $C^{\dagger}_{K} C_{K}$ is also for the wave packet at location $\vec{r}$. Fortunately in Boltzmann equation, the collision happen involving only one fixed location $\vec{r}$.

A fundamental assumption is Boltzmann equation is the separation of scale.



$l \gg a$

l: mean free path

a: range of interaction

or $\tau \gg \tau_0$

τ_0 time needed to change course!

Following the usual argument we write

$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} + \vec{v}\cdot\frac{\partial f}{\partial \vec{r}} + \vec{F}\cdot\frac{\partial f}{\partial \hbar\vec{k}} = \left(\frac{\partial f}{\partial t}\right)_{coll}$$

$$\frac{DN}{Dt} = \frac{\partial N}{\partial t} + \dot{\vec{r}}\cdot\frac{\partial N}{\partial \vec{r}} + \hbar\dot{\vec{q}}\,\frac{\partial N}{\partial \hbar\vec{q}} = \left(\frac{\partial N}{\partial t}\right)_{coll}$$

here electron velocity $\vec{v} = \frac{\partial \varepsilon_k}{\partial \hbar\vec{k}}$ is computed by the electron dispersion relation. $\vec{F} = (-e)\vec{E}$ is Coulomb force assuming no magnetic field. For phonon

$\dot{\vec{r}} = \frac{\partial\, \hbar\omega_q}{\partial \hbar\vec{q}} = \frac{\partial \omega_q}{\partial \vec{q}}$ is phonon group velocity.

$\hbar\dot{\vec{q}}$ is 0, but if lattice gets disturbed / stressed, this is the lattice distortion force, see book by Gurevich "Transport in phonon Systems" 1988.

For simplicity of notation we have defined (t: time)

$$f \equiv f_k(t\,\vec{r}) = f_{n\vec{k}}(t,\vec{r})$$

(n: band, $\vec{k}$: wave, $\vec{r}$: space)

and similarly $N \equiv f_q(t\,\vec{r}) = N_{\lambda\vec{q}}(t,\vec{r})$

There is something slightly inconsistent in the derivation of the electron-phonon Boltzmann equations. On the left-hand side, we have the total derivative operator

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \dot{\vec{r}}\cdot\frac{\partial}{\partial \vec{r}} + \dot{\vec{p}}\cdot\frac{\partial}{\partial \vec{p}} \qquad (\vec{p} = \hbar\vec{k} \text{ or } \hbar\vec{q})$$

Clearly, this is a classical picture since we talk about position $\vec{r}$ and momentum $\vec{p} = \hbar\vec{k}$ simultaneously. This is exactly Boltzmann had

in his 1872 work for dilute gases. However, on the right-hand side for the collisn terms $\left(\frac{\partial}{\partial t}\right)_{colli}$ we will use quantum mechanics, and take the wave vector $\vec{k}$ as sharply defined quantity quantized in a big box of volume $V = L^3$, with L order cm. ie. a macroscopic lays system. In the usual Boltzmann calculation, the discretness of $\vec{k}$ is ignored and we also convert $\sum_{\vec{k}} \to V \int \frac{d^3\vec{k}}{(2\pi)^3}$ in the end.

The consequence of this treatment is that the waves are not localized at all, it is a plane wave (for both electrn & phonon) $\psi_{\vec{k}} \propto e^{i\vec{k}\cdot\vec{r}}$ and $|\psi_k| = \text{const}$ independ of $\vec{r}$ so it is not at all a wave packet.

However, after the transitin rate is found and expressed as a functional of f and N, we reinsert the $\vec{r}$ dependence back. so after all, the Boltzmann equatin is a equatin for f and N as a functin of $t, \vec{r}$ and k (wq).

This makes sense only if the variatin of f or N over $\vec{r}$ are at the macroscopic scale while the wave with wavelength λ are at microscopic scale.

Since we assume the perturbatin $\hat{H}_1$ is small, the states are very well characterized by the eigenstats of $\hat{H}_0$ $|n\rangle$. Thus we assume the density matrix for a short period of time takes the following form

$$\hat{\rho}(t) = \sum_n P_n(t) |n\rangle\langle n|$$

This is not the most general density matrix as we don't have cross terms $|n\rangle\langle m|$ $m \neq n$.

This form of density matrix means we can focus on a particular pure quantum state $|n\rangle$, the eigen state of $\hat{H}_0$, $\hat{H}_0|n\rangle = E_n|n\rangle$, and compute f (or N) by ensamble average

$$f = Tr(\hat{\rho} C_k^+ C_k) = \sum_n P_n(t) \langle n| C_k^+ C_k |n\rangle$$

Since we are interested how f varies due to collision to compute $\left(\frac{\partial f}{\partial t}\right)_{colli}$ we focus the effect of interaction on the state labelled by k, i.e. consider

$$\langle f | \hat{H}_1 | i \rangle$$

here $|i\rangle = |\cdots n_k \cdots\rangle$ $n_k = 0, 1$ or $0, 1, 2, 3, \cdots$ for boson

Since we take trace in the end, we don't care too much as what are the other states denoted by $\cdots$.

Since $\hat{H}_1$ takes the form $\sum_{k\, k'\, q} \cdots C_k^+ C_{k'} (a_q + a_{-q}^+)$

The effect of $\hat{H}_1$ acting on $|i\rangle$ is a state of superposition of origin eigen state $|n\rangle$ i.e.

$$\hat{H}_1 |i\rangle = \sum_n d_n |n\rangle$$

d_n is some complex amplitude. After the collision the state is again characterized by the eigen state of $\hat{H}_0$ so the final state $\langle f|$ is some $\langle m|$

since $\langle m|n\rangle = \delta_{mn}$ we get $\langle f| H_1 |i\rangle = \text{some } d_i$

We assume different $C_k^+ C_{k'} a_q$ does not produce same state $|n\rangle$.

true for electron - electron scattering

since different operator term $c^\dagger c\, a$ or $c^\dagger c\, a^\dagger$ does not give same state, we do not have interference terms.

The point is the transition probability is proportional to

$$\sum_m \left| \langle m | \hat{H}_1 | n \rangle \right|^2$$ for each possible m

and there is no interfere term.

Based on this understanding, we ask the following two questions. 1) if we are in a state with n_k given, how it can be changed? This reduce f. 2) what state can make a transition to the state k. This increase f.

consider $|i\rangle = |\cdots \underbrace{n_k}_{\text{electron}} \cdots n_{k'} \cdots \underbrace{n_q}_{\text{phonon}} \cdots\rangle$

Such state will be destroyed by

$$\frac{1}{\sqrt{N}} \sum_{q k'} \underbrace{g^q_{k'k}}_{\text{swapped } k \leftrightarrow k' \text{ from page 129}} \delta(\vec{k} - \vec{k}' + \vec{q})\, c^\dagger_{k'} c_k\, a_q$$

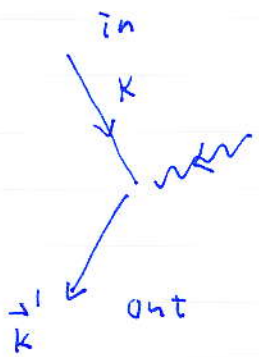
acting on $|i\rangle$ produces

$$\frac{1}{\sqrt{N}} \sum_{q k'} g^q_{k'k} \delta(\vec{k} - \vec{k}' + \vec{q}) \sqrt{n_k} \cdot \sqrt{1 - n_{k'}} \cdot \sqrt{n_q} \, |\cdots n_k - 1 \cdots n_{k'} + 1 \cdots n_q - 1 \cdots\rangle$$

Thus the probability is sum of modulus squared i.e.

$$\frac{1}{N} \sum_{q k'} \left| g^q_{k'k} \right|^2 \delta(\vec{k} - \vec{k}' + \vec{q})\, n_k (1 - n_{k'})\, n_q$$

$\delta^2 = \delta$ with diagram



We note n_k $n_{k'}$ $= 0, 1$ and $n_q = 0, 1, 2, \ldots$ are discrete variables. To go to the Boltzmann continous variable f and N we need to perform an ensemble average, ie. still need to do statistical mechanics

$$\langle \ldots \rangle = \mathrm{Tr}(\rho \ldots)$$

$$\langle n_k (1-n_{k'}) n_q \rangle$$

However, we don't know to calulate this average unless we make a "mean-field" type approximation ie. we assume

$$\langle n_k (1-n_{k'}) n_q \rangle = \langle n_k \rangle \langle 1 - n_{k'} \rangle \langle n_q \rangle$$
$$= f (1-f') N$$

here we use the short-hand notation

$$f \equiv \langle n_k \rangle$$
$$f' \equiv \langle n_{k'} \rangle$$
$$N \equiv \langle n_q \rangle$$

Note that these averages are in nonequilibrium state depends on t as well as $\vec{r}$.

Applying the Fermi-golden rule,

$$\frac{2\pi}{\hbar} \left| \langle f | \hat{H}_1 | i \rangle \right|^2 \delta(E_f - E_i)$$

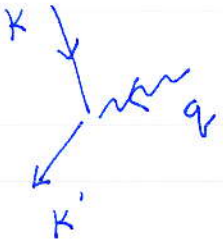
E is total energy of the system

we need to multiply by the $\frac{2\pi}{\hbar}$ factor and energy conservation $\leftarrow$ Dirac-δ function Note that with fixed k k', q the energy change $\Delta E = E_f - E_i$ is fixed not a fluctuating quantity, The averages only affect f not energy. k is destroyed and k' is created, and one phonon of $\hbar\omega_q$ is decreased

So we get $\Delta E = \varepsilon_{k'} - \varepsilon_k - \hbar\omega_q$

Thus this process gives the final collision term contribution as

$$-\frac{2\pi}{\hbar}\frac{1}{N}\sum_{k'q}\left|g^{q}_{k'k}\right|^2 \delta(\vec{k}-\vec{k}'+\vec{q})\,\delta(\varepsilon_{k'}-\varepsilon_{k}-\hbar\omega_q) * f_k(1-f_{k'})N_q$$



Kroneker δ — Dirac-δ — omitted.

Since we also need ω_{-q} and N_{-q} let put the subscript back

$$-\frac{2\pi}{\hbar}\frac{1}{N}\sum_{k'q}\left|g^{q}_{k'k}\right|^2 \delta(\vec{k}'-\vec{k}-\vec{q})\,\delta(\varepsilon_{k'}-\varepsilon_{k}-\hbar\omega_q) f_k(1-f_{k'})N_q$$

create k', destroy k

over $\vec{q}$ and put $\vec{q} = \vec{k}'-\vec{k}+\vec{G}$ Of course we can eliminate summation But I put/prefer δ-function as well also need $q \equiv (\lambda \vec{q})$. This form is more symmetric.

The phonon emission term due to $c^{+}_{k'} c_k a^{+}_{-q}$ is obtained by replacing $N_q \to N_{-q}+1$

$$-\hbar\omega_q \to +\hbar\omega_{-q}$$

$a^{+}|n\rangle = \sqrt{n+1}\,|n+1\rangle$ because

No change to $\delta(\vec{k}'-\vec{k}-\vec{q})$

So $$-\frac{2\pi}{\hbar}\frac{1}{N}\sum\left|g^{q}_{k'k}\right|^2 \delta(\vec{k}'-\vec{k}-\vec{q})\,\delta(\varepsilon_{k'}-\varepsilon_{k}+\hbar\omega_{-q}) f_k(1-f_{k'})(N_{-q}+1)$$

where $-q \equiv (\lambda, -\vec{q})$

Combined the two scattering out terms we write

$$-\frac{2\pi}{\hbar}\frac{1}{N}\sum_{k'q}\left|g^{q}_{k'k}\right|^2 \delta(\vec{k}'-\vec{k}-\vec{q})\, f_k(1-f_{k'})\left[N_q\,\delta(\varepsilon_{k'}-\varepsilon_{k}-\hbar\omega_q) + (N_{-q}+1)\,\delta(\varepsilon_{k'}-\varepsilon_{k}+\hbar\omega_{-q})\right]$$

N-factor is absorbing

$N+1$ is emitting

at $T=0$ we can emit but no absorb.

22 Aug 2017

We now consider the "scattering-in" processes which increases f. This is given by creating a state k and destroy another state k', absorbing or emitting a phonon at the same time at momentum $\pm q$. Mathematically, this is coming from the term

$$\frac{1}{\sqrt{N}} g^{q}_{kk'} \delta(\vec{k} - \vec{k}' + \vec{q}) \, c^{\dagger}_{k} c_{k'} a_{q} \quad \text{or} \quad a^{\dagger}_{-q}$$

see page 129.

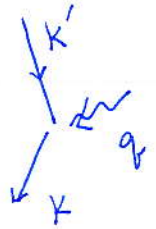
$$|i\rangle$$

$$c^{\dagger}_{k} c_{k'} a_{q} | \cdots n_k \cdots n_{k'} \cdots n_q \rangle$$

$$= \sqrt{1-n_k}\sqrt{n_{k'}}\sqrt{n_q} | \cdots n_k+1 \cdots n_{k'}-1 \cdots n_q - 1 \cdots \rangle$$

$$|f\rangle$$

Take the final state $|f\rangle$ as shown we get the transition rate



$$\left| \langle f | g \, c^{\dagger}_{k} c_{k'} a_{q} | i \rangle \right|^2 = \frac{1}{N} |g^{q}_{kk'}|^2 (1-n_k) n_{k'} n_q \cdot \delta(\vec{k}' - \vec{k} + \vec{q})$$

We then do statistical mechanical argument assuming again

$$\langle (1-n_k) n_{k'} n_q \rangle \approx (1-f_k) f_{k'} N_q$$

Multiply by $\frac{2\pi}{\hbar}$ and energy conservation Dirac-δ we get

$$+ \frac{2\pi}{\hbar N} \sum_{q k'} |g^{q}_{kk'}|^2 \delta(\vec{k}' - \vec{k} + \vec{q}) (1-f_k) f_{k'} N_q \delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_q)$$

The phonon emission process term is obtained by replacing

$$N_q \to N_{-q} + 1$$

$$\hbar\omega_q \to -\hbar\omega_{-q}$$

else everything is the same

we get

$$\frac{2\pi}{\hbar N} \sum_{q k'} |g^{q}_{kk'}|^2 \delta(\vec{k}' - \vec{k} + \vec{q}) (1-f_k) f_{k'} (N_{-q}+1) \delta(\varepsilon_k - \varepsilon_{k'} + \hbar\omega_{-q})$$

Combine the two terms we can write

$$+\frac{2\pi}{\hbar N}\sum_{q k'} |g^q_{k k'}|^2 \delta(\vec{k}-\vec{k}'-\vec{q})(1-f_k) f_{k'} \left(N_q \delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_q) + (N_{-q}+1)\delta(\varepsilon_k - \varepsilon_{k'} + \hbar\omega_{-q}) \right)$$

Let's define

$$S_{k k'} \equiv \frac{2\pi}{\hbar}\sum_q |g^q_{k k'}|^2 \delta(\vec{k}-\vec{k}'-\vec{q}) \left(N_q \delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_q) + (N_{-q}+1)\delta(\varepsilon_k - \varepsilon_{k'} + \hbar\omega_{-q}) \right)$$

as "Scattering" rate for $k \leftarrow k'$

$\Delta E = E_f - E_i$

then we can write the collision term more compactly as

$$\left(\frac{\partial f}{\partial t}\right)_{colli} = \frac{1}{N}\sum_{k'} \left(S_{k k'}(1-f_k) f_{k'} - S_{k' k}(1-f_{k'}) f_k \right)$$

Note that S is not symmetric because it still depends on N.

But need to know the symmetry for g. Since $\hat{H}_1 = c^\dagger \vec{M} c \cdot \vec{u}$ must be a hermitian operator we see M^ℓ_{jk} must be hermitian matrix for each fixed ℓ

$$\hat{H}_1 = \sum_{jk\ell} c^\dagger_j M^\ell_{jk} c_k u_\ell$$

$$(\hat{H}_1)^\dagger = \vec{H}_1 = \sum_{jk\ell} (c^\dagger_j M^\ell_{jk} c_k u_\ell)^\dagger = \sum_{jk\ell} u^\dagger_\ell c^\dagger_k (c^\dagger_j)^\dagger (M^\ell_{jk})^*$$

$$= \sum_{jk\ell} c^\dagger_k (M^\ell_{jk})^* c_j u_\ell \qquad u^\dagger_\ell = u_\ell$$

swap $k \leftrightarrow j$

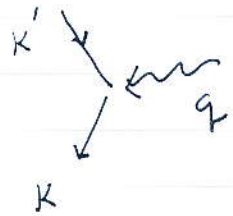
So $M^{\ell\,*}_{kj} = M^\ell_{jk}$

The implication of hermicity of M is that

$$(g^q_{k k'})^* = g^{-q}_{k' k}$$

note in addition to swap $k \leftrightarrow k'$ we also need $q \to -q$.

Phonon collision term $\left(\frac{\partial N_q}{\partial t}\right)_{colli}$ as we have ignored phonon - phonon interaction, this term involves only electron scattering to phonon, causing phonon number to increase or decrease



absorb a phonon decrease phonon count

$$c_k^+ c_{k'} a_q^+ | \cdots \; n_q \cdots \rangle$$

$$= \sqrt{1-n_k}\sqrt{n_{k'}}\sqrt{n_q}\,| \cdots \; n_q - 1 \cdots \rangle$$

This is the same as that on page 141 - 145 except now q is fixed ($\frac{D N_q}{Dt}$ of left hand side) but k' and k is the summation variable so we get

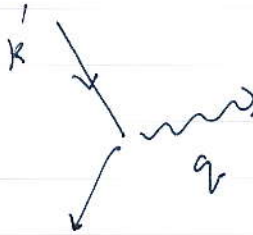
$$\left(\frac{\partial N_q}{\partial t}\right)_{colli} = -\frac{2\pi}{\hbar N}\sum_{k k'} |g_{kk'}^{q}|^2 \delta(\vec{k}' - \vec{k} + \vec{q})(1-f_k) f_{k'} \Big[N_q \cdot \delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_q) \Big]$$

$$+ \text{absorption process}$$

If collision causes emission of phonon in state q it causes an increase in phonon count N_q so we need the term $\frac{1}{\sqrt{N}}\sum g_{kk'}^{-q} c_k^+ c_{k'} a_q^+ \delta(\vec{k} - \vec{k}' - \vec{q})$

Here we have flipped the sign for q as we are interested in state q not -q. This gives

$$+\frac{2\pi}{\hbar N}\sum_{k k'} |g_{kk'}^{-q}|^2 \delta(\vec{k}' - \vec{k} - \vec{q})(1-f_k) f_{k'} \Big[(N_q + 1) \delta(\varepsilon_k - \varepsilon_{k'} + \hbar\omega_q) \Big]$$



emitting of phonon

since $g_{kk'}^{-q} = g_{k'k}^{q\,*}$ $\quad |g^*| = |g|$

We can combine the two δ- functions to get

by swaping $k \leftrightarrow k'$ both of them dummy summation index

$$\left(\frac{\partial N_q}{\partial t}\right)_{colli} = \frac{2\pi}{\hbar N}\sum_{kk'} |g^q_{kk'}|^2 \delta(\vec{k}'-\vec{k}+\vec{q})\,\delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_q) \times \left[(1-f_{k'})f_k(N_q+1) - (1-f_k)f_{k'}N_q\right]$$

We now have the explicit Boltzmann eqn, combining the left side $\frac{D}{Dt}$ expressions on page 135.

i.e. $$\frac{\partial f_k}{\partial t} + \vec{v}_k \cdot \frac{\partial f_k}{\partial \vec{r}} + \vec{F}\cdot\frac{\partial f_k}{\partial \hbar\vec{k}} = \left(\frac{\partial f_k}{\partial t}\right)_{colli}$$

$$\frac{\partial N_q}{\partial t} + \frac{\partial \omega_q}{\partial \vec{q}}\cdot\frac{\partial N}{\partial \vec{r}} = \left(\frac{\partial N_q}{\partial t}\right)_{colli}$$

we assume $\hbar\dot{\vec{q}} = 0$. We check if we get $0=0$ in thermodynamical equilibrium. If the system is in statistical mechanical equilibrium. it should not depends on time t and space $\vec{r}$, so

$$f_k(t,\vec{r}) \equiv f_k^0 \text{ only} \quad \text{similarly for } N_q$$

External force $\vec{F}=0$ so we ignore left side $=0$.
We check the collision terms are zero if

$$f_k = f_k^0 = \frac{1}{e^{\beta(\varepsilon_k - \mu)}+1} \qquad N_q = N_q^0 = \frac{1}{e^{\beta\hbar\omega_q}-1}$$

Indeed we have the identity

$$(1-f^0_{k'})f^0_k(N^0_q+1) = (1-f^0_k)f^0_{k'}N^0_q \quad \text{if} \begin{cases} \vec{k}'+\vec{q} = \vec{k}+\vec{G} \\ \varepsilon_{k'} = \varepsilon_k + \hbar\omega_q \end{cases}$$

so $\left(\frac{\partial N_q}{\partial t}\right)^0_{colli} = 0$. For electron, we have detailed balance when system is in equilibrium i.e.

$$S^0_{kk'}(1-f^0_k)f^0_{k'} = S^0_{k'k}(1-f^0_{k'})f^0_k$$

So $\left(\frac{\partial f}{\partial t}\right)^0_{colli} = 0$. please go throw the math to check explicitly.

Ok we go thrum the math, omit 0 and use $f \equiv f_k^0$ $f' \equiv f_{k'}^0$ $N = N_q^0$ for simplicity $\omega = \omega_q$

$$(1-f')f(N+1) = \left(1 - \frac{1}{e^{\beta(\varepsilon'-\mu)}+1}\right)\frac{1}{e^{\beta(\varepsilon-\mu)}+1}\left(\frac{e^{\beta\hbar\omega}}{e^{\beta\hbar\omega}-1}\right)$$

$$= \frac{e^{\beta(\varepsilon'-\mu)}\, e^{\beta\hbar\omega}}{(e^{\beta(\varepsilon'-\mu)}+1)(e^{\beta(\varepsilon-\mu)}+1)(e^{\beta\hbar\omega}-1)}$$

energy conservation $\varepsilon = \varepsilon' + \hbar\omega$

$$= \frac{e^{\beta(\varepsilon - \mu)}}{(e^{\beta(\varepsilon'-\mu)}+1)(e^{\beta(\varepsilon-\mu)}+1)(e^{\beta\hbar\omega}-1)} = \frac{e^{(\mu-\varepsilon)\beta}}{(e^{\beta(\varepsilon'-\mu)}+1)(e^{\beta(\varepsilon-\mu)}+1)(1-e^{-\beta\hbar\omega})}$$

$= f'(1-f)\cdot N$ ✓ checked

□ I left the detailed balance equation for $S^0_{kk'}$ as a student exercise.

Conservation laws

Having derived Boltzmann equations. Let's ask some general questions before attempt to solve it.

(1) particle number conservation.

Clearly boson number N is not conserved because it can be created or destroyed. The electron numbers must be conserved

$$N_e = \frac{1}{V}\int_V d\vec{r} \sum_K f_k \qquad K \equiv (n, \vec{k})$$

$d\vec{r} = dxdydz$ in 3D.

This is the total # of electrons assuming we have a finite box of volume V Note $\sum_{\vec{k}} = \frac{V}{(2\pi)^3}\int d\vec{k}$

so $n_n(t,\vec{r}) = \frac{1}{(2\pi)^3}\int d\vec{k}\, f_{n\vec{k}}$ is electron density in mode n (branch).

$\sum f$

We check if $\frac{dN_e}{dt} \overset{?}{=} 0$

$$\frac{dN_e}{dt} = \frac{1}{V}\int d\vec{r} \sum_k \frac{df_k}{dt}$$

Since f_k is a function of t and $\vec{r}$ and $\vec{r}$ is integration variable here what does $\frac{d}{dt}$ mean here?

More slowly

$$N_e = \frac{1}{V}\int d\vec{r} \sum_k f_k(t, \vec{r})$$

Both $\vec{r}$ and k is summed/integrated, so we must have $N_e \equiv N_e(t)$ is a function of time only

$$\frac{dN_e}{dt} = \frac{1}{V}\int d\vec{r} \sum_k \frac{\partial f_k}{\partial t} = \frac{1}{V}\int d\vec{r} \sum_k \left[-\vec{v}_k \cdot \frac{\partial f_k}{\partial \vec{r}} - \vec{F}\cdot\frac{\partial f_k}{\partial \hbar\vec{k}} + \left(\frac{\partial f_k}{\partial t}\right)_{colli} \right]$$

stream term

$\vec{v}_k = \frac{\partial \varepsilon_{\vec{k}}}{\partial \hbar \vec{k}}$ is indepent of $\vec{r}$

$\vec{F}$ may depends on $\vec{r}$ but indpt of $\vec{k}$

The stream term can be written as $\sum_{\mu=1}^{6} \frac{\partial (v_\mu f)}{\partial x_\mu}$

$x_\mu = (x\ y\ z\ P_x\ P_y\ P_z)$, $v_\mu = \dot{x}_\mu$ $\quad \mu = 1,2,3,4,5,6$

In any event, the Boltzmann equation can be written in the form

$$\frac{\partial f}{\partial t} + \sum_\mu \frac{\partial}{\partial x_\mu}(v_\mu f) = \left(\frac{\partial f}{\partial t}\right)_{colli}$$

Using the divergence theorem, volume integration in $\vec{r}$ and $\vec{k}$ can only get a surface contribution for $\vec{k}$ the surface in at $\pm\infty$ of $f \to 0$. for $\vec{r}$ outside box there is no particles. the stream term has no contribution We get

$$\frac{dN_e}{dt} = \frac{1}{V}\int d\vec{r} \sum_k \left(\frac{\partial f_k}{\partial t}\right)_{colli}$$

Since the collision term does not depends on $\vec{r}$ explicit, we can show a stronger conservation.

conservation of electron number occurs point-wise

i.e. $\sum_k \left(\frac{\partial f_k}{\partial t}\right)_{coll} = 0$ for all $\vec{r}$ so $\frac{dN_e}{dt} = \int d\vec{r} \cdot 0 = 0$

from page 149

$$\sum_k \left(\frac{\partial f_k}{\partial t}\right)_{coll_i} = \sum_k \left[\frac{1}{N} \sum_{k'} \left(S_{kk'} (1-f_k) f_{k'} - S_{k'k} (1-f_{k'}) f_k \right) \right]$$

Now both k and k' are dummy summation variable we can swap the 2nd term $k \leftrightarrow k'$. Then two terms cancel, we get 0.

(2) conservation of momentum. Since $\vec{k}$ and $\vec{q}$ are lattice momentum, one need $\vec{G}$ in lattice momentum conservation, e.g. $\vec{k}' - \vec{k} + \vec{q} = \vec{G}$

so $\vec{P} = \sum_k \hbar \vec{k} f_k + \sum_q \hbar \vec{q} N_q$ is not a conserved quantity

If this quantity is conserved or nearly so, it means the scattering is too weak to establish thermal equilibrium in long time. If momentum does become a conserved quantity, then we expect the equilibrium distribution f^0 and N^0 would depend on it. E.g.

$$f^0 = \frac{1}{e^{\beta(\varepsilon - \vec{u}\cdot\vec{k} - \mu)} + 1}$$

where β, $\vec{u}$, μ characterize the equilibrium states. But for electron-phonon system this is not the case.

(3) Energy conservation

Hamiltonian system conserves total energy. Our electron phonon system is a Hamiltonian system so energy is conserved. More precisely $\frac{d\hat{H}}{dt} = \frac{1}{i\hbar}[\hat{H}, \hat{H}] = 0$

And the statistical-mechanical average

$$\langle H \rangle = \text{const}$$

But $\hat{H} = \hat{H}_0 + \hat{H}_1$ $\qquad \hat{H}_0 = \hat{H}_e + \hat{H}_p$

$$= \sum_k \varepsilon_k c_k^+ c_k + \sum_q \hbar\omega_q \left(a_q^+ a_q + \tfrac{1}{2}\right)$$

While $\frac{d}{dt}\hat{H} = 0$

$$\frac{d}{dt}\hat{H}_0 = \frac{1}{i\hbar}[\hat{H}_0, \hat{H}] = \frac{1}{i\hbar}[\hat{H}_0, \hat{H}_1] \neq 0$$

so the free particles part, $\hat{H}_0$ is not a conserved quantity only the total energy, including the contribution from the interaction, is a conserved quantity.

However, in the Boltzmann treatment of the dynamics we assume $\hat{H}_1$ is infinitesimally small, i.e. we take the limit $\hat{H}_1 \to 0$. So when consider energy only the free partile part ε_k and $\hbar\omega_q$ is take into account and interactin energy is not considered at all. This shows the intrinsic limitation of Boltzmann approach.

We now demonstrate that the free particle total energy E is a conserved quantity

$$E = \frac{1}{V}\int d\vec{r}\left(\sum_k \varepsilon_k f_k + \sum_q \hbar\omega_q N_q\right)$$

Since $k \equiv (n\vec{k})$ we sum over all $\vec{k}$ in the 1st Brillouin zone for all branch n.

$$\frac{dE}{dt} = \frac{1}{V}\int d\vec{r}\left(\sum_k \varepsilon_k \frac{\partial f}{\partial t} + \sum_q \hbar\omega_q \frac{\partial N_q}{\partial t}\right)$$

We can change $\frac{\partial f}{\partial t}$ to $\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}$ and similaly fr N_q because the stream term conserve energy. $\varepsilon_k \frac{\partial f}{\partial \vec{r}} = \frac{\partial}{\partial \vec{r}}\cdot(\vec{v}\varepsilon f)$ is a divegence so no problem. What about $\varepsilon_k \vec{F}\cdot\frac{\partial f}{\partial \hbar\vec{k}}$ term? OF course we cannot! Since ε_k is function of $\vec{k}$

The physical meanig is clear. If we apply an external force $\vec{F}$, the force do work, total energy is not conserved, so we must set $\vec{F} = 0$ in order to compute $\frac{dE}{dt}$.

So when there is no external disterbance we get

$$\frac{dE}{dt} = \frac{1}{V}\int d\vec{r}\left(\sum_k \varepsilon_k \left(\frac{\partial f}{\partial t}\right)_{colli} + \sum_q \hbar\omega_q \left(\frac{\partial N_q}{\partial t}\right)_{colli}\right)$$

since we don't have explicit $\vec{r}$ dependence in the collism intgrl, this also means that conservatin of energy is "point-wise" i.e. the integrand is 0 for each $\vec{r}$.

$$\left[\sum_k \varepsilon_k \left(\frac{\partial f}{\partial t}\right)_{colli} + \sum_q \hbar\omega_q \left(\frac{\partial N_q}{\partial t}\right)_{colli}\right] \cdot N$$

$$= \sum_{kk'} \varepsilon_k \left(S_{kk'}(1-f_k) f_{k'} - S_{k'k}(1-f_{k'}) f_k \right)$$

$$+ \sum_{kk'q} \hbar\omega_q \frac{2\pi}{\hbar} |g^q_{kk'}|^2 \delta(\vec{k}'-\vec{k}+\vec{q}) \delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_q)$$

$$\times \left[(1-f_{k'}) f_k (N_q + 1) - (1-f_k) f_{k'} N_q \right]$$

we need to show this is 0.

Put $S_{kk'}$ expressin back, use simplifying notatins

$$f \equiv f_k \qquad f' \equiv f_{k'} \qquad N = N_q \qquad \bar{N} = N_{-q}$$

$$\varepsilon = \varepsilon_k \qquad \varepsilon_{k'} = \varepsilon' \qquad \hbar\omega_q = \omega$$

and we sum over all k, k', and q

$$= \frac{2\pi}{\hbar} \sum_{kk'q} \varepsilon \Big(|g^q_{kk'}|^2 \delta(\vec{k}-\vec{k}'-\vec{q}) \big(N \delta(\varepsilon - \varepsilon' - \hbar\omega) + (\bar{N}+1)\delta(\varepsilon - \varepsilon' + \hbar\bar{\omega}) \big) (f-1) f'$$

$$- |g^q_{k'k}|^2 \delta(\vec{k}'-\vec{k}-\vec{q}) \big(N \delta(\varepsilon' - \varepsilon - \hbar\omega) + (\bar{N}+1)\delta(\varepsilon' - \varepsilon + \hbar\bar{\omega}) \big) (1-f') f \Big) + \hbar\omega_q \text{ term}$$

Since all $k\, k'\, q$ are dummy summatin variable we can do $k \leftrightarrow k'$.

For the terms involving $\bar{N} \equiv N_{-q}$ we do simultaneous

$q \to -q$, $\kappa \leftrightarrow \kappa'$ then $|g^{q}_{\kappa\kappa'}|^2 = |g^{-q}_{\kappa'\kappa}|^2 = |g^{q\,*}_{\kappa\kappa'}|^2 = |g^{q}_{\kappa\kappa'}|^2$

is invariant so $|g|^2$ becomes a common factor, we have (as well as the two δ-functions)

$$\sum_{\kappa\kappa' q} |g^{q}_{\kappa\kappa'}|^2 \Big\{ \delta(\vec{\kappa}-\vec{\kappa}'-\vec{q})\,\delta(\varepsilon-\varepsilon'-m\nu)\; f'(f-1)N\,\varepsilon\,(m\nu+\varepsilon-\varepsilon')\,\delta(\vec{\beta}+\vec{\kappa}-\vec{\kappa}')\,\delta$$
$$f(f'-1)(1+N)\,\varepsilon'\,(m\nu+\varepsilon-\varepsilon')\,\delta(\vec{\beta}+\vec{\kappa}-\vec{\kappa}')\,\delta \;-$$
$$f'(f-1)\,N\,\varepsilon'\,(m\nu-\varepsilon'+\varepsilon)\,\delta(\vec{\beta}-\vec{\kappa}'+\vec{\kappa})\,\delta \;-$$
$$f(f'-1)\,(1+N)\,\varepsilon\,(m\nu+\varepsilon-\varepsilon')\,\delta(\vec{\beta}+\vec{\kappa}-\vec{\kappa}')\,\delta \;-$$
$$f(f'-1)\,(1+N)\,m\nu\,(m\nu-\varepsilon'+\varepsilon)\,\delta(\vec{\beta}+\vec{\kappa}-\vec{\kappa}')\,\delta \;+$$
$$\Big\{ f'(f-1)\cdot N\cdot m\nu\,(m\nu-\varepsilon'+\varepsilon)\,\delta(\vec{\beta}+\vec{\kappa}-\vec{\kappa}')\,\delta \;-$$

Combine the δ-functions which we the same
$0 \equiv (m\nu-\varepsilon'+\varepsilon)\,\delta\cdot(m\nu-\varepsilon'+\varepsilon)$

All factors are same we get

$$= \sum_{\kappa\kappa' q} |g^{q}_{\kappa\kappa'}|^2 \Big\{ \delta(\vec{\kappa}-\vec{\kappa}'-\vec{q})\,\delta(m\nu-\varepsilon'+\varepsilon) \Big[f'(f-1)N\,\varepsilon + \cdots$$

$$\Big[f(f-1)(1+N)\,\varepsilon' + f'(f'-1)N\,\varepsilon \Big]\,(m\nu+\varepsilon'-\varepsilon)\,\delta(\vec{\beta}+\vec{\kappa}'-\vec{\kappa})\,\delta -$$
$$\Big\}$$

Simplify a bit of the 1st line we get

$$= \sum_{\kappa\kappa' q} |g^{q}_{\kappa\kappa'}|^2 \Big\{ \delta(\vec{\kappa}-\vec{\kappa}'-\vec{q})\,\delta(m\nu-\varepsilon'+\varepsilon) \Big[f'(f-1)N\,\varepsilon + \cdots$$

$$\Big[f(f-1)(1+N)\,\varepsilon' + f'(f'-1)N\,\varepsilon \Big]\,(m\nu+\varepsilon'-\varepsilon)\,\delta(\vec{\beta}+\vec{\kappa}'-\vec{\kappa})\,\delta -$$
$$\Big\}$$

we have used $\varepsilon = \varepsilon' + m\nu$ in the 1st line.

We see they don't cancell unless we do a swap $\kappa \leftrightarrow \kappa'$ again assume $|g^{q}_{\kappa\kappa'}|^2 = |g^{q}_{\kappa'\kappa}|^2$

Since $g^{q\,*}_{\kappa\kappa'} = g^{-q}_{\kappa'\kappa}$ so $|g^{q}_{\kappa\kappa'}|^2 = |g^{-q}_{\kappa'\kappa}|^2$ we need flip sign for q. Unless g is even in q and flip sign

So I can prove $\frac{dE}{dt} = 0$. ~~is true only if~~

I assume $|g^{q}_{xx'}|^2$ is an even function of q.

However, due to the moment conservation δ-function $g^{q}_{xx'}$ is not really three variables but only a function of $\vec{x}, \vec{x}'$ taken $\vec{q}$ as follow the moment conservation if so since $|g^{q}_{kk'}|^2 = |g^{-q}_{k'k}|^2$ we can say it is even in $\vec{q}$ already ?

There is still puzzling aspect I'm not very happy with !!

error in page 165 corrected!

H-theorem / entropy production

It is one of the great achievement of Boltzmann to prove the H-theorem, which gives a mechanical interpretation of thermodynamic entropy.

In the context of electron-phonon system, we define

$$H = \frac{1}{V}\int d\vec{r} \left\{ \sum_k \left(f \ln f + (1-f)\ln(1-f) \right) + \sum_q \left(N \ln N - (N+1)\ln(N+1) \right) \right\}$$

such that the entropy is $S = -k_B H$. The problem is to show that $\frac{dH}{dt} \leq 0$. entropy always increases

$-H$ always decreases.

$$\frac{dH}{dt} = \frac{1}{V}\int d\vec{r} \left\{ \sum_k \frac{\partial}{\partial t}\left(f\ln f + (1-f)\ln(1-f) \right) + \sum_q \frac{\partial}{\partial t}\left\{ N\ln N - (N+1)\ln(N+1) \right\} \right.$$

$$\frac{\partial}{\partial t} f\ln f = \frac{\partial f}{\partial t}\ln f + f\cdot\frac{1}{f}\frac{\partial f}{\partial t} = (1+\ln f)\frac{\partial f}{\partial t}$$

$$\frac{\partial (1-f)\ln(1-f)}{\partial t} = -\frac{\partial f}{\partial t}\ln(1-f) + (1-f)\frac{1}{(1-f)}\left(-\frac{\partial f}{\partial t}\right) = \left(-1 - \ln(1-f)\right)\frac{\partial f}{\partial t}$$

so $\sum_\kappa$ term is $\sum_\kappa \ln\left(\frac{f}{1-f}\right)\cdot\left(\frac{\partial f}{\partial t}\right)$

$$\frac{\partial}{\partial t}(N+1)\ln(N+1) = \partial t(1+1)\frac{\partial N}{\partial t} + \frac{\partial N}{\partial t}$$

$\sum_q$ term is $\left(1+\ln N - \ln(N+1) - 1\right)\frac{\partial N}{\partial t} = \left(\ln\frac{N}{N+1}\right)\frac{\partial N}{\partial t}$

we can write

$$\frac{dH}{dt} = \frac{1}{V}\int d\vec{r}\left\{\sum_\kappa \left(\ln\frac{f}{1-f}\right)\frac{\partial f}{\partial t} + \sum_q \left(\ln\frac{N}{N+1}\right)\cdot\frac{\partial N}{\partial t}\right\}$$

Again $\frac{\partial f}{\partial t}$ = stream term + collision term. the stream term vanish. by the same reasm that we can write as divergence.

e.g. $\frac{\partial}{\partial \vec{r}}(f\ln f) = (1+\ln f)\frac{\partial f}{\partial \vec{r}}$ so we can identically $\frac{\partial f}{\partial t}$ as $\left(\frac{\partial f}{\partial t}\right)_{coll}$ Substitute the explicit expression for the collision integral, we focus on the sum

$$\sum_{\kappa\kappa' q}\Big[\left(\ln\frac{f}{1-f}\right)\Big(|g^q_{\kappa\kappa'}|^2\delta(\vec{\kappa}-\vec{\kappa}'-\vec{q})\big(N\delta(\varepsilon-\varepsilon'-\hbar\omega) + (\bar{N}+1)\delta(\varepsilon-\varepsilon'+\hbar\omega)\big)f'(1-f) - |g^q_{\kappa'\kappa}|^2\delta(\vec{\kappa}'-\vec{\kappa}-\vec{q})\big(N\delta(\varepsilon'-\varepsilon-\hbar\omega) + (\bar{N}+1)\delta(\varepsilon'-\varepsilon+\hbar\omega)\big)f(1-f')\Big)$$

$$+\left(\ln\frac{N}{N+1}\right)\cdot\Big(|g^q_{\kappa'\kappa}|^2\delta(\vec{\kappa}'-\vec{\kappa}+\vec{q})\delta(\varepsilon-\varepsilon'-\hbar\omega)\big((1-f')f(N+1) - (1-f)f'N\big)\Big)\Big]$$

We now apply the same trick as in computing $\frac{dE}{dt}$, by swap $\kappa\leftrightarrow\kappa'$, and $q\to -q$ and assuming $|g|^2$ is invariant under such transformation of the dummy summation variables of κ, κ' and q. By proper swap, we can show $|g|^2\delta(\vec{\kappa}-\vec{\kappa}'-\vec{q})\delta(\varepsilon-\varepsilon'-\hbar\omega)$ is a common factor of all the 6 terms.

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Using the dummy variable swapping technique we obtain something similar to that of page 165,

$$\frac{dH}{dt} = \frac{2\pi}{N\hbar}\int d\vec{r} \sum_{kk'q} \left\{ |g^q_{kk'}|^2 \delta(\vec{k}-\vec{k}'-\vec{q}) \, \delta(\varepsilon-\varepsilon'-\hbar\omega) \right.$$

$$\left[N(1-f)f' \ln\frac{f}{1-f} \right. \qquad + (N+1)(1-f')f \ln\frac{f'}{1-f'}$$

$$\xrightarrow{q\to -q} \quad \xrightarrow{k\leftrightarrow k'}$$

$$- N(1-f)f' \ln\frac{f'}{1-f'} \qquad - (N+1)(1-f')f \ln\frac{f}{1-f}$$

$$\xrightarrow{k\leftrightarrow k'} \qquad \xrightarrow{q\to -q} \quad \text{no change}$$

$$- (N)(1-f)f' \ln\frac{N}{N+1} \qquad \left. + (N+1)(-f')f \ln\frac{N}{N+1} \right]$$

Simplify the terms inside the square brackets $[\cdots]$ we get

$$[\cdots] = N(1-f)f' \ln\left[\frac{f}{1-f}\cdot\frac{1-f'}{f'}\cdot\frac{N+1}{N}\right]$$

$$+ (N+1)f(1-f')\ln\left[\frac{1-f}{f}\cdot\frac{f'}{1-f'}\cdot\frac{N}{N+1}\right]$$

$$= \left[N(1-f)f' - (N+1)f(1-f')\right]\ln\left[\frac{f}{1-f}\cdot\frac{1-f'}{f'}\cdot\frac{N+1}{N}\right]$$

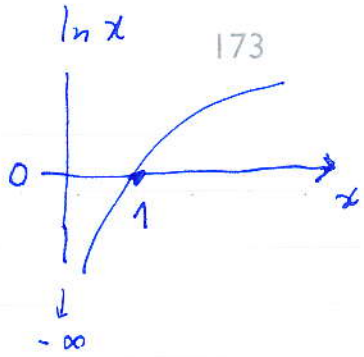
If the system is in equilibrium, we have the identity of page 153, ie.

$$(1-f')f(N+1) = (1-f)f'N \qquad (\text{with } \varepsilon = \varepsilon'+\hbar\omega)$$

we get $0\cdot\ln 1 = 0$. If system is not in equilibrium we don't have this identity so $\frac{dH}{dt} \neq 0$, but define

$$A = N(1-f)f', \qquad B = (N+1)f(1-f')$$

then $[\cdots] = (A-B)\ln\frac{B}{A}$ clearly $A \geq 0$, $B \geq 0$



If $B > A > 0$ then $\ln \frac{B}{A} > 0$

so $(A-B) < 0$ & $(A-B)\ln\frac{B}{A} < 0$

But if $0 < B < A$ then $\ln \frac{B}{A} < 0$

but $A - B > 0$ so $(A-B)\ln\frac{B}{A} < 0$

So for all possible choices of values of A and B we have

$$(A-B)\ln\frac{B}{A} \leq 0$$

Thus, we have proved the H-theorem $\frac{dH}{dt} \leq 0$

H can only decrease with time, Boltzmann equation does not have time reversal symmetry.

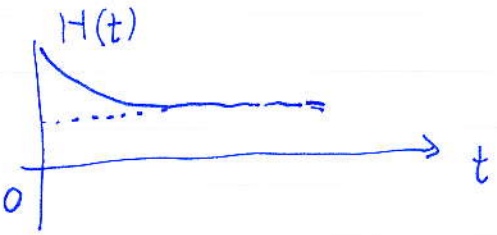
When $t \to -t$ $\quad \frac{\partial f}{\partial t} + \sum_\mu \frac{\partial}{\partial x^\mu} v^\mu f = \left(\frac{\partial f}{\partial t}\right)_{coll.}$

left side change sign $t \to -t$

$v \to -v$

$p \to -p$

But right side does not change sign. → time has a direction.



Linearized Boltzmann equation

The Boltzmann equation is valid for any driven field $\vec{F}$ but the definition of transport coefficients like conductivity and Seebeck coefficient are defined only in the linear response regime. I.e. $\vec{F}$ and temperature gradient are 1st order small. Thus we only need to know small deviation from equilibrium $f = f^0 + y$

To obtain the single-mode relaxation time, the straight forward

$$f = f^\circ + y$$
$$N = N^\circ + z$$

where y and z are small, is a good variable to using since we are looking for $\left(\frac{\partial f}{\partial t}\right)_{coll} = -\frac{f-f^\circ}{\tau} = -\frac{y}{\tau}$.

But to solve the Boltzmann equation explicitly, the following new variables makes the equations simpler see, eg. B. P. Allen (see also R.E. Peierls page 127)

$$f = f^\circ - \frac{\partial f^\circ}{\partial \varepsilon}\phi \qquad \phi, \psi \text{ small}$$
$$N = N^\circ - \frac{\partial N^\circ}{\partial(\hbar\omega)}\psi$$

We note the identity

$$-\frac{\partial f^\circ}{\partial \varepsilon} = \beta f^\circ(1-f^\circ) \qquad f^\circ = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}$$
$$-\frac{\partial N^\circ}{\partial \hbar\omega} = \beta N^\circ(1+N^\circ) \qquad N^\circ = \frac{1}{e^{\beta\hbar\omega}-1}$$

We plug the small expansion forms into the collision terms $\left(\frac{\partial f}{\partial t}\right)_{colli}$ and $\left(\frac{\partial N}{\partial t}\right)_{colli}$ expand them, the 0-th order cancells exactly and we keep only up to linear order, to obtain result.

To compute the linearized form of the collision terms, we essentially compute small variation of it. So we can apply Newton-Leibniz rule, ie.

$$\delta(abc) = (\delta a)bc + a(\delta b)c + ab\delta c.$$

where a or b or c is one of the terms in $\left(\frac{\partial f}{\partial t}\right)_{coll}$ or $\left(\frac{\partial N}{\partial t}\right)_{colli}$

From page 149 this gives

$$\delta\left(\frac{\partial f}{\partial t}\right)_{colli} = \frac{1}{N}\sum_{k'}\Big(\delta S_{kk'}(1-f_k)f_{k'} + S_{kk'}(\delta f_k)f_{k'} + S_{kk'}(1-f_k)\delta f_{k'}$$

After taking the variation we set $f \equiv f^0 \quad N \equiv N^0$
but for notation simplicity, we omit the superscript 0.

$$\delta S_{kk'} = \frac{2\pi}{\hbar} \sum_q |g^q_{kk'}|^2 \delta(\vec{k} - \vec{k}' - \vec{q}) \Big(\delta N \, \delta(\varepsilon - \varepsilon' - \hbar\omega) + \delta \bar{N} \, \delta(\varepsilon - \varepsilon' + \hbar\bar{\omega}) \Big)$$

$$\bar{N} \equiv N_{-q} \qquad \bar{\omega} = \omega_{-q}$$

Let regroup the terms according to δf $\delta f'$ and δN
using $\delta f = + \beta f(1-f)\phi \qquad \delta N = \beta N(N+1)\psi$

$$\delta\left(\frac{\partial f}{\partial t}\right)_{colli} = \frac{1}{N} \sum_{k'} \Big(-S_{kk'} f' \beta f(1-f)\phi - S_{k'k}(1-f')\beta f(1-f)\phi + S_{kk'}(1-f)\beta f'(1-f')\phi' + S_{k'k} f \beta f'(1-f')\phi' \Big) + \delta N \text{ term}$$

Note that in the above S is S^0 so it satisfies the detailed balance condition of page 153

$$S_{kk'}(1-f)f' = S_{k'k}(1-f')f \equiv P_{kk'} = P_{k'k}$$

one define it as $P_{kk'}$ which is symmetric in kk'
we can simplify as

$$\delta\left(\frac{\partial f}{\partial t}\right)_{colli} = \frac{1}{N}\beta \sum_{k'} P_{kk'}(\phi' - \phi) + \delta N \text{ term}$$

δN contribution is

$$\delta S_{kk'}(1-f)f' - \delta S_{k'k}(1-f')f$$

$$= \frac{2\pi}{\hbar N} \sum_{q\,k'} |g^q_{kk'}|^2 \delta(\vec{k} - \vec{k}' - \vec{q}) \Big(\delta(\varepsilon - \varepsilon' - \hbar\omega)\beta N(N+1)\psi + \delta(\varepsilon - \varepsilon' + \hbar\bar{\omega})\beta\bar{N}(\bar{N}+1)\bar{\psi} \Big)(1-f')f'$$

$$- \frac{2\pi}{\hbar N} \sum_{q\,k'} |g^q_{k'k}|^2 \delta(\vec{k}' - \vec{k} - \vec{q}) \Big(\delta(\varepsilon' - \varepsilon - \hbar\omega)\beta N(N+1)\psi + \delta(\varepsilon' - \varepsilon + \hbar\bar{\omega})\beta\bar{N}(\bar{N}+1)\bar{\psi} \Big)(1-f')f$$

For the bar terms $\bar{N} = N_{-q}$ since q is dummy summation variable we can do $q \to -q$ then

$$|g^{q}_{k k'}|^2 \Rightarrow |g^{-q}_{k k'}|^2 = |g^{q\,*}_{k' k}|^2 = |g^{q}_{k' k}|^2$$

The factor can be group as $P_{kk'}$

$$P_{kk'} = S_{kk'}(1-f)f'$$

$$= \frac{2\pi}{\hbar}\sum_q \Big[|g^{q}_{kk'}|^2 \delta(\vec{k}-\vec{k}'-\vec{q})\,\delta(\varepsilon-\varepsilon'-\hbar\omega)\, N (1-f) f' + |g^{q}_{k'k}|^2 \delta(\vec{k}-\vec{k}'+\vec{q})\,\delta(\varepsilon-\varepsilon'+\hbar\omega)\,(N+1)(1-f)f' \Big]$$

def

$$\equiv \sum_q P^{q}_{kk'}$$

← the summation contain only one term because of Kronecker $\delta(\vec{k}-\vec{k}'\pm\vec{q})$

One can check the following identity is true

if $\varepsilon = \varepsilon' + \hbar\omega$ then $N(f'-f) = (1-f')f$

if $\varepsilon = \varepsilon' - \hbar\omega$ $(N+1)(f-f') = (1-f')f$

I see to get a min sign error somewhere. Ignore this possible error, my guess it that the final result for the collision term can be written as (which sign is correct?)

? $$\delta\left(\frac{\partial f}{\partial t}\right)_{coll} = \frac{\beta}{N}\sum_{k'q} P^{q}_{kk'}(\phi' - \phi \pm \psi)$$

WRONG! both $\pm\psi$ exist ↑ check back later

↖ we have both term with diffrent coeffcient!!

The linear term for the phonon part is, from pg 153,

$$\delta\left(\frac{\partial f_q}{\partial t}\right)_{coll} = \frac{2\pi}{\hbar N}\sum_{kk'} |g^{q}_{kk'}|^2 \delta(\vec{k}'-\vec{k}+\vec{q})\,\delta(\varepsilon-\varepsilon'-\hbar\omega) \times \Big[-\delta f' \cdot f\,(N+1) + (1-f')\,\delta f\,(N+1) + (1-f')f\,\delta N + \delta f\, f' N - (1-f)\,\delta f' N - (1-f)f'\delta N \Big]$$

Substitute $\delta f = \beta f(1-f)\phi$, $\delta N = \beta N(N+1)\psi$

we can simplify as

$$[\cdots] = -\delta f'\left(f(N+1) + (1-f)N\right) + \delta f\left((1-f')(N+1) + f'N\right) + \delta N\left((1-f')f - (1-f)f'\right)$$

$$= -\delta f'(f+N) + \delta f(1-f'+N) + \delta N(f-f')$$

$$= \beta\left[-f'(1-f')(f+N)\phi' + f(1-f)(1-f'+N)\phi + N(N+1)(f-f')\psi\right]$$

Because of the δ function for energy conservation we have $\varepsilon = \varepsilon' + \hbar\omega$

We can show the following relation is true

$$(1-f)(N+1-f') = (N+1)(1-f')$$

$$f'(N+f) = (N+1)f$$

$$N(f'-f) = (1-f')f$$

where $f \equiv f_k$, $f' \equiv f_{k'}$, $N \equiv N_q$ always, $\varepsilon = \varepsilon_k$, $\varepsilon' = \varepsilon_{k'}$, $\omega = \omega_q$

the square brade term simplify as

$$[\cdots] = \beta f(1-f')(N+1)\left[-\phi' + \phi - \psi\right]$$

So

$$\delta\left(\frac{\partial N_q}{\partial t}\right)_{\text{colli}} = \frac{2\pi\beta}{\hbar N}\sum_{kk'}\left|g^q_{kk'}\right|^2 \delta(\vec{k}-\vec{k}'-\vec{q})\,\delta(\varepsilon-\varepsilon'-\hbar\omega) * (N+1)f(1-f')\left[-\phi'+\phi-\psi\right]$$

Having obtained the linearized collision term, we can now make the Single-Mode-Relaxation-time approximation (SMRTA)

We ignore the off-diagonal contribution and only the diagonal ones i.e. $\left(\frac{\partial f}{\partial t}\right)_{\text{colli}} \approx -\frac{\gamma}{\tau} = -\frac{f-f_0}{\tau}$

24 Aug 2017

Similarly $\left(\frac{\partial N}{\partial t}\right)_{coll} = -\frac{N-N^0}{\tau_p} = -\frac{z}{\tau_p}$

For electron, since $\left(\frac{\partial f}{\partial t}\right)_{coli} \approx -\frac{\beta}{N}\sum_{k'} P_{kk'}\,\phi$

$$= -\frac{\beta}{N}\sum_{k'} S_{k'k}(1-f')f\,\phi$$

$$f - f_0 = -\frac{\partial f^0}{\partial \epsilon}\phi = y$$

$$= \beta f^0(1-f^0)\phi = y$$

$$= -\frac{\beta}{N}\sum_{k'} S_{k'k}\frac{(1-f')f\,y}{\beta f(1-f)}$$

$$= -\frac{1}{N}\sum_{k'} S_{k'k}\left(\frac{1-f'}{1-f}\right) y$$

This gives $\frac{1}{\tau_i} = \frac{1}{N}\sum_{k'} S_{k'k}\frac{1-f'}{1-f}$ which is standard form

and agrees with imginary part of self energy $\frac{\hbar}{2\tau} = -\mathrm{Im}\Sigma^r$.

Note that $S_{k'k}$ is the transition from k to k'.

Similarly we can obtain the phonon relaxation time approximation due to electrons as

$$\frac{1}{\tau_p} = \frac{2\pi}{\hbar N}\sum_{kk'} |g^q_{kk'}|^2 \delta(\vec{k}-\vec{k}'-\vec{q})\,\delta(\epsilon-\epsilon'-\hbar\omega)\frac{f(1-f')}{N}$$

$\frac{2\pi}{\hbar N}$: # of unit cell

$\frac{f(1-f')}{N}$: Bose or Planck function

Note $\frac{f(1-f')}{N} = f'-f$

How does the magnitude of electron relaxation time compare to phonon τ v.s. τ_p which is larger!

The result for δN contribution to the collision term is not ~~correlation~~ correct, we need split the absorption process from the emission process.

$$P^q = P^q(+1) + P^q(-1) = \sum P^q_{kk'}(\sigma)$$

From page 179 let define

$$P^{q}_{kk'}(+1) = \frac{2\pi}{\hbar} |g^{q}_{kk'}|^2 \delta(\vec{k}-\vec{k}'-\vec{q}) \delta(\varepsilon-\varepsilon'-\hbar\omega) N(1-f) f'$$

$$P^{q}_{kk'}(-1) = \frac{2\pi}{\hbar} |g^{q}_{k'k}|^2 \delta(\vec{k}-\vec{k}'+\vec{q}) \delta(\varepsilon-\varepsilon'+\hbar\omega) (N+1)(1-f) f'$$

then $P^{q}_{kk'} = P^{q}_{kk'}(+1) + P^{q}_{kk'}(-1)$

we also have the symmetry $P^{q}_{k'k}(-1) = P^{q}_{kk'}(+1)$

Then the linearized collision term is

$$\delta\left(\frac{\partial f}{\partial t}\right)_{coll} = \frac{\beta}{N} \sum_{k'q\sigma} P^{q}_{kk'}(\sigma) (\phi' - \phi + \sigma\psi)$$

$\sigma = \pm 1$

and we can write for phonon collision term as

$$\delta\left(\frac{\partial N}{\partial t}\right)_{coll} = \frac{\beta}{N} \sum_{kk'} P^{q}_{kk'}(+1) (-\phi' + \phi - \psi)$$

---

remember our shorthand notation $\phi \equiv \phi_k$ $\phi' \equiv \phi_{k'}$ $\psi \equiv \psi_q$

$f \equiv f_k$ $f' \equiv f_{k'}$ $N \equiv N_q$

Having worked out the linearized form of the collision term, we now look at the left side of the Boltzmann equation. On the left side, we use local equilibrium approximation, ie. we assume

$$f = \frac{1}{e^{\beta(\vec{r})(\varepsilon-\mu)}+1}, \qquad N = \frac{1}{e^{\beta(\vec{r})(\hbar\omega)}-1}$$

before taking the derivative and then set to f^0 and N^0 after the derivative is taken. i.e.

$$\frac{\partial f}{\partial \vec{r}} \approx \frac{\partial f}{\partial \beta}\bigg|_{\beta \equiv \text{const}} \frac{\partial \beta(\vec{r})}{\partial \vec{r}} = \frac{\partial f}{\partial(\beta(\varepsilon-\mu))} \frac{\partial(\beta(\varepsilon-\mu))}{\partial \beta} \left(-\frac{1}{k_B T^2}\right) \vec{\nabla} T$$

$\beta = \frac{1}{k_B T}$

$$\frac{\partial f}{\partial \vec{r}} = -\frac{\partial f}{\partial \varepsilon}\bigg|_{eq} \frac{\vec{\nabla} T}{T}\cdot(\varepsilon-\mu) \quad \text{ie. } f = f^0 \text{ here}$$

Similarly $\dfrac{\partial N}{\partial \vec{r}} = -\dfrac{\partial N}{\partial \varepsilon}\bigg|_0 \dfrac{\varepsilon}{T}\vec{\nabla} T$

$$\frac{\partial f}{\partial \vec{k}} = \frac{\partial f}{\partial \varepsilon}\frac{\partial \varepsilon}{\partial \vec{k}} = \vec{v}\frac{\partial f}{\partial \varepsilon} \qquad \text{where } \vec{v} = \frac{\partial \varepsilon}{\partial(\hbar\vec{k})} \text{ is}$$

electron group velocity.

Putting these terms together the linearized Boltzmann equations are

$$\frac{\partial f}{\partial t} + \left(-\frac{\partial f}{\partial \varepsilon}\right)(\varepsilon-\mu)\,\vec{v}\cdot\frac{\vec{\nabla} T}{T} + \underbrace{(-e)\vec{E}}_{\vec{F}}\cdot\vec{v}\,\frac{\partial f}{\partial \varepsilon} = S\left(\frac{\partial f}{\partial t}\right)_{coll}$$

$$\frac{\partial N}{\partial t} + \left(-\frac{\partial N}{\partial \varepsilon}\right)\varepsilon\,\vec{v}_q\cdot\frac{\vec{\nabla} T}{T} = S\left(\frac{\partial N}{\partial t}\right)_{coll}$$

$\vec{v}_q = \dfrac{\partial \omega_q}{\partial \vec{q}}$ is phonon group velocity. We are interested in steady state so we drop the $\frac{\partial f}{\partial t}$ and $\frac{\partial N}{\partial t}$ terms.

In many applications such as ZT calculations we assume phonons are in equilibrium. so $N = N^0$ and $\psi = 0$

why this is a valid assumption?

typical electron relaxation time is 10^{-13} s

phonon is much slower of order 10^{-10} s

I do not understand Peierls argument the due to phonon - phonon interaction phonons are in equilibrium is a good one. Assume that is the case, then we focus only on electron drop the phonon degree ψ in the 'end here.

For simplicity, we assume both $\vec{E}$ and $\vec{\nabla}T$ are in the same direction $\hat{z}$ so

$$\vec{v}\cdot\vec{\nabla}T = v_z \frac{\partial T}{\partial z} \qquad \vec{v}\cdot\vec{E} = v_z E$$

then the linearized Boltzmann equation for electron is

$$\left(-\frac{\partial f}{\partial \varepsilon}\right)\left(\left(\frac{\varepsilon-\mu}{T}\right)\frac{\partial T}{\partial z} + eE\right)v_z = \frac{\beta}{N}\sum_{k'q} P^q_{kk'}(\phi'-\phi)$$

$\| \quad \beta f(1-f)$. Let use $P_{kk'} = S_{kk'}(1-f)f'$ form

$\sum_q P^q_{kk'} = P_{kk'}$ we see we can cancel the $\beta(1-f)$ factor so

$v_z \equiv v_k^z$ depends on k

$\varepsilon \equiv \varepsilon_k$

$$\left(\frac{\varepsilon-\mu}{T}\cdot\frac{\partial T}{\partial z} + eE\right)v_z = \frac{1}{N}\sum_{k'} S_{kk'}\frac{f'}{f}(\phi'-\phi)$$

Note also $S_{kk'}\frac{f'}{f} = S_{k'k}\frac{1-f'}{1-f}$ from detailed balance relation. page 153

Let introduce a new variable, τ, in the spirit of Sarbello (J. phys. F: Metal phys. 4, 503 (1974))

ie. Let $\phi = -\left(eEv_z + \frac{\varepsilon-\mu}{T}\frac{\partial T}{\partial z}v_z\right)\tau$

i.e. $\phi_k = -\left(eEv_k^z + \frac{\varepsilon_k-\mu}{T}\frac{\partial T}{\partial z}v_k^z\right)\tau_k = \phi$

and $\phi_{k'} = \phi' = -\left(eE + \frac{\varepsilon_{k'}-\mu}{T}\frac{\partial T}{\partial z}\right)v_{k'}^z\tau_{k'}$

both $\tau, v_z, \varepsilon, \phi$ are function of $k \equiv (n,\vec{k})$

Putting this ansatz in, , divides the $\left(\frac{\varepsilon-\mu}{T}\frac{\partial T}{\partial z} + eE\right)v_z$ to the right side we get

$$1 = \frac{1}{N}\sum_{k'} S_{kk'}\frac{f'}{f}\left(\tau - \frac{v'_z\left(eE + \left(\frac{\varepsilon'-\mu}{T}\right)\frac{\partial T}{\partial z}\right)\tau'}{v_z\left(eE + \frac{\varepsilon_k-\mu}{T}\frac{\partial T}{\partial z}\right)}\right)$$

So we get, divide by τ out

$$\frac{1}{\tau} = \frac{1}{N}\sum_{k'} S_{kk'} \frac{f'}{f}\left[1 - \left(\frac{eE + \frac{(\varepsilon'-\mu)}{T}\frac{dT}{dz}}{eE + \frac{(\varepsilon-\mu)}{T}\frac{dT}{dz}}\right)\frac{v_z'\tau'}{v_z\tau}\right]$$

This does not look like Sarbello's original equation unless scattering is elastic, $\varepsilon = \varepsilon'$ or $\frac{dT}{dz} = 0$.

This is strange as τ depends on E and $\frac{dT}{dz}$ explicitly contrary to our assumption that transport coefficient is defined in linear response.

However if take the $\frac{dT}{dz} = 0$, $E \neq 0$

or $\frac{dT}{dz} \neq 0$ but $E = 0$, then the result is

~~then same independent~~ different

$$\frac{dT}{dz} = 0 \quad \Rightarrow \quad \frac{1}{\tau_E} = \frac{1}{N}\sum_{k'} S_{kk'} \frac{f'}{f}\left(1 - \frac{v_z'\tau_E'}{v_z\tau_E}\right)$$

$$\text{if } E = 0 \quad \Rightarrow \quad \frac{1}{\tau_T} = \frac{1}{N}\sum_{k'} S_{kk'} \frac{f'}{f}\left(1 - \frac{(\varepsilon'-\mu)}{(\varepsilon-\mu)}\frac{v_z'\tau_T'}{v_z\tau_T}\right)$$

Note the equations are different!

Since formally we have a linear system

$$A\phi = b \qquad \phi = \phi_1 + \phi_2$$

if $b = b_1 + b_2$, then if $A\phi_1 = b_1$ $\rightarrow$ then

$A\phi_2 = b_2$ $\quad A(\phi_1 + \phi_2) = b_1 + b_2$

So the solution must be linear in E & ∇T. The above nonlinear apparence perhaps is only a superficial solution method effect. Nonlinear dependence is not correct!

To resolve apparent contradiction we can write the solution in two form.

$$\phi = -eE v_z \tau_E - \left(\frac{1}{T}\right)(\varepsilon-\mu)\frac{\partial T}{\partial z} v_z \tau_T \qquad (1)$$

$$\text{or} \quad = -\left(eE v_z + \left(\frac{1}{T}\right)(\varepsilon-\mu)\frac{\partial T}{\partial z} v_z\right)\tau \qquad (2)$$

The first form is linear in E and $\frac{\partial T}{\partial z}$ explicitly, but the 2nd form is not. But the two forms must be equal and can be proved to be equal.

The 1st form is preferred. We need to define two relaxation time; one for E field driven, one for temperature driven then the electron current is

$$j = \rho v$$

$$j_e^z = \sum_k (-e) v^z f = \frac{1}{V}\sum_k (-e) v^z \left(-\frac{\partial f}{\partial \varepsilon}\phi\right)$$

$$= \frac{1}{V}\sum_k e v^z \left(-\frac{\partial f}{\partial \varepsilon}\right)\left(eE v_z \tau_E + \left(\frac{1}{T}\right)\frac{\partial T}{\partial z} v_z \tau_T\right)$$

$$= e^2 \frac{1}{V}\sum_k (v^z)^2 \tau_E \left(-\frac{\partial f}{\partial \varepsilon}\right)E + \frac{1}{V}\frac{e}{T}\sum_k (v_z)^2 \tau_T (\varepsilon-\mu)\left(-\frac{\partial f}{\partial \varepsilon}\right)\frac{\partial T}{\partial z}$$

different τ

$f = f^0 - \frac{\partial f^0}{\partial \varepsilon}\phi$ The result agrees with the usual Boltzmann equation formula except we need different τ for the two terms. Note that τ is not an approximation, but an exact result, following the argument of Sondheimer.

So these results are really exact result since we have solved the Boltzmann equation exactly!

The Seebeck coefficient is given by setting $j_e^z = 0$

$$\text{or} \quad S = +\frac{E}{\partial T/\partial z} = \frac{-\sum_k (v_z)^2 \tau_T (\varepsilon-\mu)\left(-\frac{\partial f}{\partial \varepsilon}\right)}{eT\sum_k (v)^2 \tau_E \left(-\frac{\partial f}{\partial \varepsilon}\right)}$$

If we use constant relaxation time approximation then the Seebeck coeffient S is independ of the relaxation time $\tau = \tau_E = \tau_T$. But in the current theory, since in general, there is no good reason for $\tau_E = \tau_T$, they don't cancel, and Seebeck coefficient does depends on the relaxation times.

If we really have solution of ϕ in the form given by Eq (1) on page 193, i.e. $\phi = -eE v_z \tau_E - \frac{(\varepsilon-\mu)}{T}\frac{dT}{dz} v_z \tau_T$ then we run into big problem — Onsager relation is violated.

The heat current of the electron is

$$j_Q = \frac{1}{V}\sum_k (\varepsilon-\mu) v^2 f = \frac{1}{V}\sum_k (\varepsilon-\mu) v^2 \left(-\frac{\partial f_0}{\partial \varepsilon}\right)(\phi)$$

$$= \frac{1}{V}\sum_k (-e)(\varepsilon-\mu) v_z^2 \tau_E \left(\frac{\partial f_0}{\partial \varepsilon}\right) E + \frac{1}{V}\sum_k -(\varepsilon-\mu)^2 (v_z)^2 \tau_T \left(\frac{\partial f_0}{\partial \varepsilon}\right)\frac{1}{T}\frac{dT}{dz}$$

Let introduce $L_n^x \equiv \frac{1}{V}\sum_k (\varepsilon-\mu)^n v_z^2 \tau_x \left(-\frac{\partial f_0}{\partial \varepsilon}\right)$

where x is either empty ($L_n \to \tau$) or E or T $\quad n = 0, 1, 2$

With this short-hand notation we can write

$$j_e = e^2 L_0^E E + e L_1^T \frac{1}{T}\frac{dT}{dz}$$

$$j_Q = -e L_1^E E - L_2^T \frac{1}{T}\frac{dT}{dz}$$

Onsager relation means $L_1^T = L_1^E$, since in gen $\tau_E \neq \tau_T$ it seems onsager relation is violated. But since Onsager relation is from a fundamental symmetry

consideration (time reversed symmetry). Its violation is wrong. Does this mean my solution is wrong??

Impact of dimensionality to relaxation time

Intuitively low dimension has much less possible scattering channels and high dimension more channels to scatters so I expect $\frac{1}{\tau}$ small in $d=1$

large in $d=3$

i.e. It is harder in 1d to relax so τ is long in 1D.

Why this is not true?

To answer this question approximately, let look at the SMRTA expression for relaxation time (page 149)

$$\frac{1}{\tau} = \frac{1}{N}\sum_{k'} S^{\circ}_{kk'}\frac{f'}{f} = \frac{1}{N}\sum_{k'q}\frac{2\pi}{\hbar}\left|g^{q}_{kk'}\right|^2\delta(\vec{k}-\vec{k}'-\vec{q})\times$$

$$\left[N_q\,\delta(\varepsilon-\varepsilon'-\hbar\omega) + (N_{-q}+1)\,\delta(\varepsilon-\varepsilon'+\hbar\omega)\right]\frac{f'}{f}$$

shorthand notation

$\omega \equiv \omega_q$

$f \equiv f_k$

$f' \equiv f_{k'}$

$N \equiv N_q$

$\tau \equiv \tau_k$

We note when $\varepsilon = \varepsilon' + \hbar\omega$ $\quad 1+N-f' = N\frac{f'}{f}$

and when $\varepsilon = \varepsilon' - \hbar\omega$

and in equilm $N_q \equiv N_{-q} = N$ $\quad N+f' = (N+1)\frac{f'}{f}$

We can write as

$$\frac{1}{\tau} = \frac{1}{N}\sum_{k'q}\frac{2\pi}{\hbar}\left|g^{q}_{kk'}\right|^2\delta(\vec{k}-\vec{k}'-\vec{q})\left[(1+N-f')\,\delta(\varepsilon-\varepsilon'-\hbar\omega) + (N+f')\,\delta(\varepsilon-\varepsilon'+\hbar\omega)\right]$$

This form is numerically better as we might cause a divergent if $f\to 0$ the other form. Since $|f'|\le 1$

Let assume temperature is high such that $N \gg 1$ for all relevant q we approximate $N+f' \propto \frac{1}{\beta\hbar\omega} \approx 1+N-f'$

Since $N = \frac{1}{e^{\beta\hbar\omega}-1} = \frac{1}{1+\beta\hbar\omega+\cdots-1} \approx \frac{1}{\beta\hbar\omega} = \frac{k_B T}{\hbar\omega}$ valid if T large

Let consider a hypercubic lattice of lattice spacings a, in d-dimensions with parabolic dispersion

$$\varepsilon_k = \frac{\hbar^2 \vec{k}^2}{2m}$$

We assume each site has only one state so there is no mode index $k \equiv \vec{k}$, $q \equiv \vec{q}$ etc.

We assume phonon is accoustic with dispersion relation

$$\omega_q = c|\vec{q}| \qquad c: \text{sound velocity.}$$

For $g^q_{kk'}$ we use the deformation potential formula.

$$g^{\vec{q}}_{\vec{k}\vec{k}'} = -i\sqrt{\frac{\hbar}{2M\omega_q}} \cdot |q| V_0 \qquad \text{(Giustino Eq (21)}$$

↗ no mode indices — we assume $V_0 = \text{const.}$ So $|g|^2 \propto |q|$

$V_0 \to E_{1,k} = \frac{\partial \varepsilon_k}{\partial \text{in}}$ may be $\vec{k}$ dependent or $(\vec{n}\vec{k}) = k$ dependent

for simplicity we take it independent of $\vec{k}$.

So $|g^q_{\vec{k}\vec{k}}|^2 = \frac{\hbar}{2Mc|q|} |q|^2 V_0^2$

We have approximate equation

$$\frac{1}{\tau} = \frac{1}{N}\sum_{k'q} \frac{2\pi}{\hbar} \underbrace{\frac{\hbar}{2Mc|q|}}_{\omega_q} |q|^2 V_0^2 \underbrace{\frac{k_B T}{\hbar c|q|}}_{\omega_q} \delta(\vec{k}-\vec{k}'-\vec{q}) \left(\delta(\varepsilon-\varepsilon'-\hbar\omega_q) + \delta(\varepsilon-\varepsilon'+\hbar\omega_q)\right)$$

$|q|$ factors cancelled exactly

$$\frac{1}{\tau} = \frac{1}{N}\sum_{k'q} \frac{\pi V_0^2}{Mc^2\hbar} k_B T\, \delta(\vec{k}-\vec{k}'-\vec{q}) \left(\delta(\varepsilon-\varepsilon'-\hbar\omega) + \delta(\varepsilon-\varepsilon'+\hbar\omega)\right)$$

$$= \frac{1}{N}\sum_{k'} \frac{\pi V_0^2 (k_B T)}{Mc^2\hbar} \left[\delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_{\vec{k}-\vec{k}'}) + \delta(\varepsilon_k - \varepsilon_{k'} + \hbar\omega_{k-k'})\right]$$

$$\sum = \left(\frac{aL}{2\pi}\right)^d \int d\vec{k}$$

$N = L^d$ # of unit cell

Convert the summation of $\vec{k}$ in the 1st BZ into an integral

we get

$$\frac{1}{\tau} = \frac{a^d}{(2\pi)^d} \int d\vec{k}'^d \, \frac{\pi V_0^2 (k_B T)}{M c^2 \hbar} \delta(\varepsilon_k - \varepsilon_{k'} \mp \hbar\omega_{|\vec{k}-\vec{k}'|})$$

↑ two terms

$$= \frac{a^d}{(2\pi)^d} \frac{\pi V_0^2 (k_B T)}{M c^2 \hbar} \int d\vec{k}'^d \left[\delta(\varepsilon_k - \varepsilon_{k'} - \hbar\omega_{|k-k'|}) + \delta(\varepsilon_k - \varepsilon_{k'} + \hbar\omega_{|k-k'|}) \right]$$

If $\hbar\omega$ is small compare to $\Delta\varepsilon$, we can just ignore this

so $$\frac{1}{\tau_k} = 2\pi \frac{V_0^2 (k_B T)}{M c^2 \hbar} D(\varepsilon_k)$$

where $D(\varepsilon) \equiv \frac{a^d}{(2\pi)^d} \int d\vec{k}'^d \, \delta(\varepsilon - \varepsilon_{k'})$ is density of state per unit cell. $\int D(\varepsilon) \, d\varepsilon = 1$

The density of state can be evaluate analytically

$$D(\varepsilon) = \frac{a^d}{(2\pi)^d} \int_0^\infty S_d \, k^{d-1} dk \, \delta(\varepsilon' - \varepsilon)$$

$$= \frac{a^d}{(2\pi)^d} S_d \int_v^\infty \left(\frac{2m\varepsilon'}{\hbar^2}\right)^{\frac{d-2}{2}} \frac{m}{\hbar^2} d\varepsilon' \, \delta(\varepsilon' - \varepsilon)$$

$$= \frac{a^d}{(2\pi)^d} S_d \frac{m}{\hbar^2} \left(\frac{2m\varepsilon}{\hbar^2}\right)^{\frac{d-2}{2}}$$

$\frac{\hbar^2 k^2}{2m} = \varepsilon'$

$S_1 = 2$

$S_2 = 2\pi$

$S_3 = 4\pi$

$\frac{\hbar^2 k \, dk}{m} = d\varepsilon'$

dimens d	1	2	3
$D(\varepsilon)$	$\frac{1}{\pi}\sqrt{\frac{ma^2}{2\hbar^2\varepsilon}}$	$\frac{ma^2}{2\pi\hbar^2}$	$\frac{1}{2\pi^2}\left(\frac{ma^2}{\hbar^2}\right)^{3/2}\sqrt{2\varepsilon}$

Let define $\varepsilon_0 \equiv \frac{2\hbar^2}{ma^2}$ which is energy we can rewrite as

	$\frac{1}{\pi}\sqrt{\frac{1}{2}\frac{\varepsilon_0}{\varepsilon}}$	$\frac{1}{\pi}\cdot\frac{1}{\varepsilon_0}$	$\frac{1}{\pi^2}\sqrt{\frac{\varepsilon}{\varepsilon_0^3}}$

We can make some numerical estimates

since $\frac{\hbar^2}{m a_0^2} = 27.2\ eV = 1\ hartree$

if $a = 3\ \text{Å} \approx 6\, a_0$ $\quad \varepsilon_0 = \frac{2 \times 27}{36}\ eV \approx 1.5\ eV$

Electron energy are of order eV (Al 11 eV) this means indeed $D(\varepsilon) \sim 1\ (eV)^{-1}$ in all dimensions so we can say roughly $\frac{1}{\tau}$ is the same in all dimensions.

Typical $\frac{\hbar}{\tau} \sim \frac{V_0^2 (k_B T)}{Mc^2} D(\varepsilon)$

$k_B T = k_B\, 300\,K = 0.03\ eV$ $\quad D(\varepsilon) \approx 1\ (eV)^{-1}$

$Mc^2 = \frac{10 \times 1.6 \times 10^{-27}\ kg\ (10^4\ m/s)^2}{1.6 \times 10^{-19}\ J/eV} = 0.001\ eV$

typical $V_0 = 1\ eV$

so $\frac{\hbar}{\tau} \sim \frac{0.03}{0.001} \approx 30\ eV$ ← wrong too large why?

Note 1 eV is corresponds to $6.6 \times 10^{-16}\ s$

typical $\tau \sim 10^{-13}\ s$ so we expect $\frac{\hbar}{\tau} = 0.001\ eV$

$\approx 1\ meV$

Last topic — momentum conservation

We still need to check if $\frac{d\vec{P}}{dt} \stackrel{?}{=} 0$ answer is NOT 0.

$$\vec{P} = \frac{1}{V} \int d^3r \left(\sum_{K \in 1BZ} \hbar \vec{K} f_K + \sum_q \hbar \vec{q} N_q \right)$$

$K \equiv (n, \vec{K})$

$q \equiv (\lambda, \vec{q})$

↑ sum over lattice momenta as well as modes n and λ

See also page 159 on discussion.

Using the same argument as for energy conservation or for H-theorem, the stream terms does not contribute.
Of course we assume no external force $\vec{F}$, otherwise momentum cannot be conserved. We get

$$\frac{d\vec{P}}{dt} = \frac{1}{V}\int d\vec{r}\left(\sum_k \hbar\vec{k}\frac{\partial f}{\partial t} + \sum_q \hbar\vec{q}\frac{\partial N}{\partial t}\right) = \frac{1}{V}\int d\vec{r}\left(\sum_k \hbar\vec{k}\left(\frac{\partial f}{\partial t}\right)_{coll.} + \sum_q \hbar\vec{q}\left(\frac{\partial N}{\partial t}\right)_{coll.}\right)$$

Focus on the integrand of $d\vec{r}$ we have

$$\sum_k \hbar\vec{k}\left(\frac{\partial f}{\partial t}\right)_{coll.} + \sum_q \hbar\vec{q}\left(\frac{\partial N}{\partial t}\right)_{coll.}$$

$= \sum_k \hbar\vec{k}\left[\sum_{k'q} \cdots\right]$ use exactly same technique as pge 195 except ε is $\hbar\vec{k}$ now we get

$$= \sum_{kk'q} |g^q_{kk'}|^2 \Big\{ \delta(\vec{k}-\vec{k}'-\vec{q})\,\delta(\varepsilon-\varepsilon'-\hbar\omega)\,(\hbar\vec{k})\, N(1-f)f' \\ - \delta(\vec{k}'-\vec{k}+\vec{q})\,\delta(\varepsilon'-\varepsilon+\hbar\omega)\,(\hbar\vec{k}')\,(N+1)(1-f')f \\ - \delta(\vec{k}'-\vec{k}-\vec{q})\,\delta(\varepsilon'-\varepsilon-\hbar\omega)\,(\hbar\vec{k}')\,N(1-f')f \\ - \delta(\vec{k}-\vec{k}'+\vec{q})\,\delta(\varepsilon-\varepsilon'+\hbar\omega)\,(\hbar\vec{k})\,(N+1)(1-f)f' \\ + \delta(\vec{k}-\vec{k}'+\vec{q})\,\delta(\varepsilon-\varepsilon'-\hbar\omega)\,(\hbar\vec{q})\,N(1-f)f' \\ - \delta(\vec{k}'-\vec{k}+\vec{q})\,\delta(\varepsilon'-\varepsilon-\hbar\omega)\,(\hbar\vec{q})\,(N+1)(1-f')f \Big\}$$

combine the term with same pre factor

$$= \sum_{kk'q} |g^q_{kk'}|^2 \Big\{ \delta(\vec{k}-\vec{k}'-\vec{q})\,\delta(\varepsilon-\varepsilon'-\hbar\omega)\Big[\\ \hbar\Big[\vec{k}\big(N(1-f)f' - (N+1)(1-f')f\big) \\ -\vec{k}'\big(N(1-f)f' - (N+1)(1-f')f\big) \\ -\vec{q}\big(N(1-f)f' - (N+1)(1-f')f\big)\Big]\Big]$$

all same form

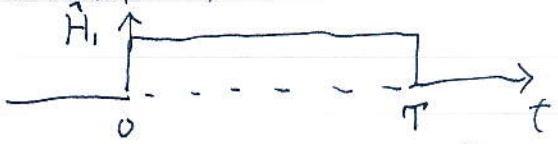
so we get $(\vec{k}-\vec{k}'-\vec{q})\,\delta(\vec{k}-\vec{k}'-\vec{q})$ as a factor

However $\delta(\vec{k}-\vec{k}'-\vec{q})$ is $\vec{k}-\vec{k}'-\vec{q}=\vec{G}$ so $\frac{d\vec{P}}{dt}\neq 0$.

We cannot conclude $\vec{k}-\vec{k}'-\vec{q}=0$. i.e.

Sunday 27 Aug 2017

Summary — starting from page 113 we derive the Fermi-golden rule by asking, if we start in a fixed, pure quantum eigen state of $\hat{H}_0$, $|i\rangle$, what states it goes to, if $\hat{H}_1$, the small perturbation, is turned on for a duration of T.



time

Note that $|i\rangle$ is many-particles states, no single particle one state label by a single k and q. $k \equiv (n, \vec{k})$, $q \equiv (\lambda, \vec{q})$.).

We then derive the Boltzmann equation using the Fermi-golden rule. We then ask, what is conserved by the Boltzmann equation? It is the total electron number N_e, (page 155) and the free particle energy E associated with $\hat{H}_0$. Not the total energy associated with $\hat{H}$. i.e. we treat $\hat{H}' \to 0$. This is consistent with a proper use of the Fermi-golden rule.

We linearized the Boltzmann equations and solve it. I can only solve it (still formally) only when $N \equiv N^0$, $\Psi = 0$ i.e. assume that phonons are in thermal equilibrium. If I have not made a math error or incorrect physical assumption, we need two relaxation times τ_E, τ_T associated with an external electric field $\vec{E}$, and temperature gradient $\vec{\nabla} T$. However, a big trouble is that such solutions violated Onsager reciprocal relation, Why?

Finally, lattice momentum $\vec{P}$ is not a conserved quantity. If this were not the case, then the standard Planck distribution N^0 and Fermi-Dirac distribution f^0 are wrong!

Refs: R.E. Peierls "Quantum Theory of Solids" 1955; H. Smith & H. H Jensen, "Transport phenomena" 1989

31 Aug 2017

We obtain pair of linearized Boltzmann equations given on page 185

$$\frac{\partial f}{\partial t} + \left(\frac{\partial \varepsilon}{\partial p}\right)\left[eE v_z + \frac{L}{m-3} z_p \Omega (m-3)\right] = \begin{cases} \\ \end{cases}$$

$$\frac{N}{\beta} \sum_{k' q \sigma = \pm} P^q_{kk'}(\sigma)\,(\phi' - \phi + \sigma\psi)$$

$$\frac{\partial N_\varepsilon}{\partial t} - \left(\frac{\partial N_\varepsilon}{\partial \varepsilon}\right) \frac{L}{m_q} \omega_q v_{qz} \frac{\partial p}{\partial z} = \frac{N}{\beta} \sum_{kk'} P^q_{kk'}(+1)\,(-\phi' + \phi - \psi)$$

consider steady states $\frac{\partial f}{\partial t} = \frac{\partial N_\varepsilon}{\partial t} = 0$.

We ask the following question. Is $\psi \equiv 0$ consistent for the 2nd equation? Since ϕ satisfies the first eq

$$eE v_z + \frac{L}{m-3} z_p \Omega \frac{\partial p}{\partial z} = \frac{1}{N} \sum_{k' q \sigma} \frac{P^q_{kk'}(\sigma)}{f(1-f)} (\phi' - \phi)$$

We also simultaneously need to satisfy the 2nd equation

$$\frac{L}{m_q \omega_q} v_{qz} \frac{\partial p}{\partial z} = \frac{1}{N} \sum_{kk'} \frac{P^q_{kk'}(+1)}{N_q (N_q + 1)} (\phi' - \phi) \quad ?$$

k k' are summation variables

$$\sum_{kk'} P^q_{kk'}(+1)\,\phi_{k'} - \sum_{kk'} P^q_{kk'}(+1)\,\phi_k$$

$$= \sum_{kk'} P^q_{k'k}(+1)\,\phi_k - \sum P^q_{kk'}(+1)\,\phi_k$$

$$= \sum_{kk'} \left(P^q_{k'k}(+1) - P^q_{kk'}(+1) \right) \phi_k = \sum_{kk'} \left(P^q_{kk'}(-1) - P^q_{kk'}(+1) \right) \phi_k$$

This is like to ask ϕ satisfy a set of linear equations of the form $b^q = A^q \phi$ for each q and fixed vector ϕ. (b^q vector, A^q matrix) which is impossible.

i.e. assuming $\psi \equiv 0$ is inconsistent with the pair of Boltzmann equations for electrons & phonons.

Since phonons are in equilibrium, it makes no sense to have a driven temperature gradient for phonons. So we must assume the left hand side $= 0$ ie $\hbar\omega \frac{d\pi}{dz} = 0$

so the condition now becomes

$$\sum_{kk'} \left(P^{q}_{kk'}(-1) - P^{q}_{kk'}(+1) \right) \phi_k = 0 \quad \text{for all } q$$

From page 185, we note $P(-1) - P(+1) \neq 0$
For the case of high temperature $N+1 \approx N$ and if $\varepsilon - \varepsilon'$ compared to $\hbar\omega$ $\hbar\omega$ is small, this expression is approximately 0, ie. $\sum_{kk'} 0 \cdot \phi_k \approx 0$ is approximately true. But the above equation is not true, $\sum_{kk'} (P - P)\, \phi_k \neq 0$, for any actually parameters.

I think I have demonstrated rather convincingly that the assumption that the phonons are in thermal equilibrium with $N = N^0$, $\psi = 0$, is inconsistent with the pair of Boltzmann equations.

This is because both electrons and phonons degrees of freedom in $\hat{H} = c^\dagger H c + \frac{1}{2}(p^2 + u^T K u) + \sum_{jk} M^{\ell}_{jk} c^\dagger_j c_k u_\ell$ are dynamic variables. They are coupled together. Assuming one in equilibrium and the other not is wrong. We need to treat them on equal footing.

To resolve the difficulty of the violation of the Onsager relation, we need to consider three external drives; the external electric field E, the temperature different / gradient to the electrons, and the temperature gradient to the phonon. When the system is out of equilibrium, there is no good reason to assume that the two temperatures are the same, so we have $T = T_e$ for electrons and T_p for phonons. The most general (Onsager) linear response takes the form (see Smith & Jensen sec. 1.12)

$$J_i = \sum_{k=1}^{3} L_{ik} F_k \qquad i = 1, 2, 3$$

or in matrix form

$$\begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ L_{21} & L_{22} & L_{23} \\ L_{31} & L_{32} & L_{33} \end{pmatrix} \begin{pmatrix} F_1 \\ F_2 \\ F_3 \end{pmatrix}$$

Here J_1 = electric current density $= \frac{Q}{At}$ = charge per unit time unit area

J_2 = electron heat current density $= \frac{\text{Joule}}{m^2\,\text{sec}} = \frac{W}{m^2}$

J_3 = phonon heat current $= W/m^2$

J_i are called generalized currents. F_k is a generalized Force. We take $F_1 = E$ electric field,

$$F_2 = -\frac{1}{T_e}\frac{dT_e}{dz} \quad \text{and} \quad F_3 = -\frac{1}{T_p}\frac{dT_p}{dz}.$$

Why we have a minus sign here and divide by $\frac{1}{T}$? To answer this ~~question~~ question, we need entropy production.

Given the definition of J_i, F_i is defined correctly if $\frac{dS}{dt} = c \sum_{i=1}^{3} J_i F_i$ where c is any function of the "thermodynamic" variables.

Compare with j_e and j_q on page 195 for the usual case of single relaxation time τ and L_n we see for the two driven forces E and $-\frac{1}{T}\frac{dT}{dz}$ we get

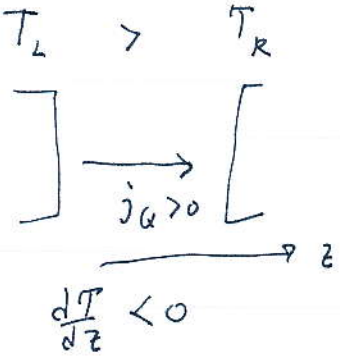
$$L_{11} = e^2 L_0, \qquad L_{12} = -e L_1$$

$$L_{21} = -e L_1 \qquad L_{22} = +L_2$$

(electron charge is $-e$, $e>0$)

We see $L_{12} = L_{21}$, Onsager relation is true and the corresponding entropy production is

$$\frac{dS}{dt} \propto j_e E + j_Q\left(-\frac{1}{T}\frac{dT}{dz}\right) \geq 0$$



Since if left is hot, right cold, then heat flows from hot to cold, $j_Q > 0$, $\frac{dT}{dz} < 0$ and $j_Q\left(-\frac{1}{T}\frac{dT}{dz}\right) > 0$. The minus sign is correct.

Nonequilibrium process always increase entropy, consistent with 2nd law of thermodynamics.

$j_e E$ is joule heating (per unit volume) units is Watts/m^3 = Joule/sec m^3 = $\frac{W}{m^3}$

units for $j_Q\left(-\frac{1}{T}\frac{dT}{dz}\right) = \frac{W}{m^2}\frac{1}{dz} = \frac{W}{m^3}$

so the units of $[j_e E] = \left[j_Q - \frac{dT}{dT\,dz}\right]$ is comparable.

Obviously to get entropy we need to divide by T so the entropy production per unit volume is

$$\frac{dS}{dt} = \frac{j_e E}{T} - \frac{j_Q}{T^2}\frac{dT}{dz}$$ as an equality.

For the more general 3×3 case, we expect

$L_{ik} = L_{ki}$ (no magnetic field) This means the last colum and both row are related i.e.

Onsager relation implies

$$L = \begin{pmatrix} L_{11} & c & a \\ c & L_{22} & b \\ a & b & L_{33} \end{pmatrix}$$

out of 9 entries we should have only 6 independent coefficients

Let take $F_1 \neq 0$ $F_2 \neq 0$, but $F_3 = -\frac{1}{T}\frac{dT_h}{dz} = 0$ then

$$J = \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = \begin{pmatrix} L_{11} & c & a \\ c & L_{22} & b \\ a & b & L_{33} \end{pmatrix} \begin{pmatrix} E \\ -\frac{1}{T}\frac{dT}{dz} \\ 0 \end{pmatrix}$$

here $T = T_e$

we get

$$\begin{cases} J_1 = L_{11}E + c\left(-\frac{1}{T}\frac{dT}{dz}\right) \\ J_2 = cE - L_{22}\frac{1}{T}\frac{dT}{dz} \\ J_3 = aE - b\frac{1}{T}\frac{dT}{dz} \end{cases}$$

When there is no temperate drive to the phonon $\frac{dT_p}{dz} = 0$ we still have Onsager symmetry in the sense $L_{12} = L_{21}$. But we also have an unexpected phonon current due to the drag effect.

What is Seebeck effect? we get electron current to 0

$$J_1 = 0 = L_{11}E + c\left(-\frac{1}{T}\frac{dT}{dz}\right) + a\left(-\frac{1}{T_p}\frac{dT_p}{dz}\right)$$

How to define the seebeck coffient? should we get $dT_p = 0$? if so $S = \frac{E}{dT/dz} = -\frac{c}{T L_{11}}$

If instead we see electron & phonon are in equilibrium so $dT = dT_h$ then $S' = -\frac{(c+a)}{T L_{11}}$. Which versus S or S' is actually measured experimentally.

Whatever is a correct definition of the Seebeck coefficient S, when L is 3x3, now let give a formal proof of the Onsager relation $L_{ik} = L_{ki}$ following the steps of Smith & Jensen, "Transport phenomena", page 60 - 63.

To begin with we write the linearized Boltzmann equation in a more formal notation as

$$F_1 X_1 + F_2 X_2 + F_3 X_3 = H(\Phi)$$

since the two Boltzmann equations are coupled through the linearized collision terms $\delta\left(\frac{\partial f}{\partial t}\right)_{coll}$, $\delta\left(\frac{\partial N}{\partial t}\right)_{coll}$ we have combined the two equations into one single one. The linear operator H acting on both electrons & phonon space. Here we define $\Phi = \begin{pmatrix} \phi \\ \psi \end{pmatrix} = \begin{pmatrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_k \\ \vdots \\ \psi_q \end{pmatrix}$ is a column vector by listing all the ϕ and ψ variables index by k and q.

We define $F_1 = E$, $F_2 = -\frac{1}{T_e}\frac{dT_e}{dz}$, $F_3 = -\frac{1}{T_p}\frac{dT_p}{dz}$ as used in the $J_i = \sum_{k=1}^{3} L_{ik} F_k$ form.

ie. F_i are the same driven generalized force as in discussion the Onsager reciprocal relation.

X_1, X_2, X_3 are column vectors of same dimension of Φ. (F_i is just a number). The point is that to define X_i in such a way so that H is a positive-definite symmetric matrix. The positive part is not important, the important part is that it need to be symmetric so that eigenvalues

Indeed, by noting the important relation

$$P^{q}_{kk'}(+1) = P^{q}_{k'k}(-1)$$ See page 185

we can identify the symmetric H matrix by putting

$$\begin{pmatrix} \delta\left(\frac{\partial f}{\partial t}\right)_{coll.} \\ \delta\left(\frac{\partial N}{\partial t}\right)_{coll} \end{pmatrix} = H \begin{pmatrix} \phi \\ \psi \end{pmatrix} = \begin{matrix} \\ k \\ q \end{matrix} \overset{\begin{matrix} k' & q \end{matrix}}{\begin{pmatrix} \cdots & \vdots & \\ & \ddots & 0 \\ & 0 & \ddots \end{pmatrix}} \begin{pmatrix} \phi_{k'} \\ \psi_{q} \end{pmatrix}$$

we find 2 x 2 blocks where the $k\,k'$ block is

$$H_{kk'} = \begin{cases} \frac{\beta}{N} P_{kk'} & \text{if } k \neq k' \quad P_{kk'} = P_{k'k} \text{ is symmetric} \\ \frac{\beta}{N}\left(P_{kk} - \sum_{k'} P_{kk'}\right) & k \text{ th diagonal is different} \end{cases}$$

and $$H_{kq} = H_{qk} = \frac{\beta}{N}\sum_{k'}\left(P^{q}_{kk'}(+1) - P^{q}_{kk'}(-1)\right)$$ is symmetric

and $$H_{qq'} = \delta_{qq'}\left(-\sum_{kk'} P^{q}_{kk'}(+1)\right)\frac{\beta}{N}$$ is diagonal in q only.

Indeed we can check the kq block and qk block is related by matrix transpose. Detail left as a student exercise.

So $$H = H^{T}$$ is correct.

Since we have identified the right-hand side of Boltzmann equations $\begin{bmatrix} \delta\left(\frac{\partial f}{\partial t}\right)_{coll} \\ \delta\left(\frac{\partial N}{\partial t}\right)_{coll} \end{bmatrix}$ as $H\begin{pmatrix}\phi\\ \psi\end{pmatrix}$ $\quad \vec{\zeta}_i = \begin{pmatrix}\phi\\ \psi\end{pmatrix}$

as a matrix times a vector, the driven forces $F_1 = E$, $F_2 = -\frac{1}{T}\frac{dT}{dz}$ $\quad F_3 = -\frac{1}{T_p}\frac{dT_p}{dt}$. the vectors X_i is uniquely determined. They are.

$$X_1 = \begin{bmatrix} \beta(f(1-f)v_z e \\ 0 \end{bmatrix}, \quad X_2 = \begin{bmatrix} -\beta f(1-f)v_z (\varepsilon-\mu) \\ 0 \end{bmatrix}, \quad X_3 = \begin{bmatrix} 0 \\ -\beta\hbar N(N+1)v_q^z \hbar\omega \end{bmatrix}$$

In general X_i is of the Form $X_i \equiv \begin{pmatrix} X_k \\ Y_q \end{pmatrix}$ the top half index by $k \equiv (n\vec{k})$, button half index by $q \equiv (\lambda \vec{q})$ so the Boltzman equation is

$$F_1 X_1 + F_2 X_2 + F_3 X_3 = H \underline{\Gamma} = H \begin{pmatrix} \phi \\ \psi \end{pmatrix}$$

[Since both X_i and H contains β, we could canal the β.] but we don't

If H is not singular and has inverse, the solution is immediate (at least formally) we get

$$\underline{\Gamma} = \begin{pmatrix} \phi \\ \psi \end{pmatrix} = H^{-1} X_1 F_1 + H^{-1} X_2 F_2 + H^{-1} X_3 F_3$$

F_i is just a number.

From this solution we can compute J_i

$f = f_0 - \frac{\partial f}{\partial \varepsilon}\phi$

$$J_1 = \frac{1}{V}\sum_k (-e) v^z f = \frac{1}{V}\sum_k (-e) v^z \left(-\frac{\partial f}{\partial \varepsilon}\phi\right)$$

$$= \frac{1}{V}\sum_k (-e)\beta f_0(1-f_0) v^z \phi = -X_1^T \underline{\Gamma} \frac{1}{V} = (\cdots 0) \begin{pmatrix} \phi \\ \psi \end{pmatrix}$$

vector form

similarly

$$J_2 = \frac{1}{V}\sum_k (\varepsilon-\mu) v^z f = \frac{1}{V}\sum_k (\varepsilon-\mu) v^z \beta f_0(1-f_0)\phi$$

$$= -\frac{1}{V} X_2^T \underline{\Gamma}$$

and finally $J_3 = \frac{1}{V}\sum_q \hbar\omega v^z N = \frac{1}{V}\sum_q \hbar\omega v_q^z \beta N_0(N+1)\psi$

$$= -\frac{1}{V} X_3^T \underline{\Gamma}$$

Here superscript T stands for matrix transpose.

We see we can write the currents in an elegant form

$$J_i = -\frac{1}{V} X_i^T \begin{bmatrix} 2 \\ \lfloor 1 \end{bmatrix} = -\frac{1}{V} \sum_{K=1}^{3} X_i^T H^{-1} X_K F_K \qquad i = 1,2,3$$

From this the Onsager coefficients are given as

$$L_{iK} = -\frac{1}{V} X_i^T H^{-1} X_K$$

since H is symmetric $\left(X_i^T H^{-1} X_K\right)^T = X_K^T \left(H^{-1}\right)^T \left(X_i^T\right)^T$

$X_i = \begin{pmatrix} | \\ | \end{pmatrix}$ is colum $X_i^T = (\cdots)$ is row L_{iK} is just a number (1×1 matrix) $\left(H^{-1}\right)^T = \left(H^T\right)^{-1} = H^{-1}$ so $L_{iK} = L_{Ki}$. Onsager relation is proved.

However, the existence of inverse for H is wrong. In fact, we can show $\det(H) = 0$, and H is rank 2 deficient and the null space of H is two dimensional. i.e. there exists two dimensional subspace X, such that $HX = 0$.

However the above proof still more or less works, if H^{-1} is interpreted as pseudo inverse in a subspace orthogonal to the null space. So the proof does go through.

We now show the two-dimensional null space of H, i.e. all of x such that $Hx = 0$, is due to two conservation laws, particles number conservation of the electrons, and energy conservation of total energy. The set of all x such that $Hx = 0$,

clearly form a vector space since

1) if $H x = 0$, $H(\alpha x) = \alpha H x = 0$
since H is linear

2) if $H x = 0$ and $H y = 0$ $\quad H(x+y) = (Hx) + (Hy) = 0$

so the set $\alpha x + \beta y$, α, β are real numbers, consistent with the definition of vector space [or linear space].

We have derived the two conservation laws on pages 155-167. Here, we need the linearized form.

The particle number conservation is

$$0 = \frac{dN_e}{dt} = \sum_k \delta\left(\frac{\partial f}{\partial t}\right)_{coll} = \frac{\beta}{N} \sum_{kk'q\sigma} P^{kk'}_{q}(\sigma)\,(\phi' - \phi + \sigma\psi)$$

ignore constant here

This is, of course an identity.

consider a particle vector $x_0 = \begin{pmatrix} 1 \\ 1 \\ 1 \\ \vdots \\ 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$ } k part
} q part

then the above equation is equivalent to

$$x_0^T H \vec{\Sigma}_1 = 0$$

This is true for any choice of $\vec{\Sigma}_1$ since it is an identity due to the property of P. We must have a vector equation

$x_0^T H = 0 \Rightarrow$ transpose $H^T = H$ we get $H x_0 = 0$

This is one of the dimension of null space. Since any $H(\chi x_0) = 0$. We say x_0 is a collision invariant.

Similarly we take $x_1 = \begin{pmatrix} \varepsilon \\ \hbar\omega \end{pmatrix} = \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \vdots \\ \varepsilon_k \\ \vdots \\ \hbar\omega_1 \\ \vdots \\ \hbar\omega_q \end{pmatrix}$ because $\frac{dE}{dt} = \sum \varepsilon \left(\frac{\partial f}{\partial t}\right) = 0$

We also see $x_1^T H \vec{\Sigma}_1 = 0$ $\vec{\Sigma}_1$ is arbitrary so

$x_1^T H = 0$ or $H x_1 = 0$. x_1 is also a collision invariant.

We thus have identified two vectors X_0 and X_1 corresponding to particle number and energy which span the null space. $H X_i = 0 \quad i = 0, 1$

this means, if we diagonalized H, we have at least two eigen values of H which are 0

$$H \to \text{diagonal} \begin{pmatrix} 0 & & \\ & 0 & \\ & & \lambda_1 \end{pmatrix} \qquad \lambda_2 \neq 0$$

Hopefully the rest is not zero. In fact, it cannot be 0 since here X_0, X_1 are assumed to be the only conserved quantity. The other quantity orthogonal to the null space must decay.

The pseudo inverse is obtained by $\begin{pmatrix} 0 & & \\ & 0 & \\ & & \frac{1}{\lambda_1} \end{pmatrix}$ then transform back.

In solving the linearized Boltzmann equation

$$b = \sum_{i=1}^{3} F_i X_i = H \vec{I}$$ we must assume the b vector must be orthogonal to the null space. If this is not the case, then b will have some components of X_0 or X_1. Putting the equation in the eigenbasis of H it is like

$$\begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 & & & & \\ & 0 & & & \\ & & \lambda_2 & & \\ & & & \lambda_3 & \\ & & & & \ddots \end{pmatrix} \begin{pmatrix} d_0 \\ d_1 \\ \vdots \\ \vdots \end{pmatrix}$$

If $b \perp (\alpha X_0 + \beta X_1)$ is false, or $b = c_0 X_0 + c_1 X_1 + \cdots$ with $c_0 \neq 0$ or $c_1 \neq 0$, then we get $0 \neq c_0 = 0$ which is inconsistent, and the linear equation has no solution. As long as b and $\vec{I}$ stay away from null space of H and be othogonal to it,

then H behaves as if it has inverse. i.e. in the restrictive space = full space of H − null space. H does have inverse, and the proof for onsager reciprocal relation ~~whotes~~ holds.

To verify the thermodynamic forces are correctly defined we need to check that the entropy production is proportional to

$$\sum_{i=1}^{3} F_i J_i .$$

See page 215.

[Why this is so? I don't understand]. We have

$$J_i = -\frac{1}{V} X_i^T \vec{I} \qquad \text{so} \quad \sum_i F_i J_i = -\frac{1}{V} \sum_i F_i X_i^T \vec{I}$$

X_i is vector J_i, F_i are number

The Boltzmann equation is $\sum_i F_i X_i = H\vec{I}$, transpose we get

$$\sum_{i=1}^{3} F_i J_i = -\frac{1}{V} \vec{I}^T H \vec{I}$$

We need to compare this quadratic form with the full formula of entropy production on page 171 when linearized. Entropy production per unit volume is

$$\frac{dS}{dt} = \frac{k_B}{V|N} \sum_{kk'q} \frac{2\pi}{\hbar} |g^q_{kk'}|^2 \delta(\vec{k} - \vec{k}' - \vec{q}) \delta(\varepsilon - \varepsilon' - \hbar\omega) \left[(B - A) \ln \frac{B}{A} \right] \geq 0$$

$$A = N(1-f)f' \qquad B = (N+1)f(1-f')$$

$-\frac{1}{V}\vec{I}^T H \vec{I}$ is for linearized for N so we need to expand in ϕ and ψ to 2nd order. 0-th order is 0 by detailed balance. 1st order must be 0 since $\frac{dS}{dt}$ cannot change sign

$$\delta A = \delta N\,(1-f)f' + Nf'(-\delta f) + N(1-f)\,\delta f'$$

(set at $f^0 f_i'$ and N^0)

$$\delta B = \delta N\, f(1-f') + (N+1)(1-f')\,\delta f + (N+1)f(-\delta f')$$

The 1st order linear term is

$$\delta\left((B-A)\ln\frac{B}{A}\right) = (\delta B - \delta A)\ln\frac{B}{A} + (B-A)\left[\frac{\delta B}{B} - \frac{\delta A}{A}\right]$$

$= 0$ This is because after taken variation we set A & B to equilibrium values which has detailed balance $A \equiv B$.

at equilibrium. $\ln\frac{B}{A} = \ln 1 = 0$, $B - A = 0$

So the order small in q, ψ is 0.

So $\frac{dS}{dt}$ must also be quadratic. We need to show, up to some constant, it is $-\vec{\xi}^T H \vec{\xi}$.

We take the 2nd order variation which is equivalent to take 2nd order derivatives.

$$\delta^2 A = \delta N f'(-\delta f) + \delta N(1-f)\delta f' - f'\delta N\delta f - N\delta f'\delta f$$
$$+ (1-f)\delta N\delta f' - N\delta f\delta f'$$

NO use

$$\delta^2 B = (1-f')\delta N\delta f - f\delta N\delta f' + (1-f')\delta N\delta f - (N+1)\delta f'\delta f$$
$$- f\delta N\delta f' - (N+1)\delta f\delta f'$$

$$\delta^2 B - \delta^2 A = 2\left(\delta N\delta f - \delta N\delta f' - \delta f\delta f'\right)$$

$$\delta^2\left((B-A)\ln\frac{B}{A}\right) = \left(\delta^2 B - \delta^2 A\right)\ln\frac{B}{A} + (\delta B - \delta A)\left[\frac{\delta B}{B} - \frac{\delta A}{A}\right]$$

$\ln\frac{B}{A} = 0$ because $B = A$ in eq.

At eq $A = B$ $\quad + (B-A)\left[-\frac{\delta B}{B^2}\delta B + \frac{\delta A}{A^2}\delta A\right]$

$(B-A) = 0$

so the only nonvanish term is $(\delta B - \delta A)\left(\delta(B) - \delta A\right)\frac{1}{A}$

$A = N(1-f)f'$

$$\delta B - \delta A = (f - f')\delta N + (N+1-f')\delta f + (-f-N)\delta f'$$

square this, we get 9 terms. This is getting complicated.

here f, f', N are equilibrium values ie f^0, f'^0, N^0.

$$\delta N = \beta N(N+1)\psi$$

Focusing the $(\delta N)^2$ term we get

$$\frac{1}{A}\left[(f-f')\delta N\right]^2 = \frac{1}{A}\left[(f-f')\cdot N(N+1)\right]^2 \beta^2 \psi^2$$

using the relation $N(f'-f) = (1-f')f$ and define below $A = B$ (see page 181

$B = (N+1)f(1-f')$ we find this to be equal

$$\frac{1}{A}\left[(f-f')N(N+1)\right]^2 = \frac{1}{A}\left[(1-f')f(N+1)\right]^2 = A$$

$A = N(1-f)f'$

we have for the ψ^2 terms contribution to $\frac{dS}{dt}$

$$\frac{dS}{dt} = \frac{k_B}{VN}\sum_{kk'q} \beta^2 \frac{2\pi}{\hbar} |g^q_{k-k'}|^2 \delta(\vec{k}-\vec{k}'-\vec{q})\,\delta(\varepsilon-\varepsilon'-\hbar\omega)\, N(1-f)f'\psi^2 + \cdots$$

$$= \frac{k_B \beta^2}{VN}\sum_{kk'q} p^q_{kk'}(+1)\psi^2 + \cdots$$

This agree with the ψ^2 term in $-\frac{1}{V}\vec{\psi}^T H \vec{\psi}$ if set a constant $k_B\beta$ Since $H_{qq} = -\frac{\beta}{N}\sum_{kk'} p^q_{kk'}(+1)$

ie we can show we have proved that

$$\frac{dS}{dt} = k_B\beta\left(-\frac{1}{V}\vec{\psi}^T H \vec{\psi}\right) \geq 0$$

H is negative definite

We still need to verify the kk' sector and kq sector. It is very tedious, but can be done, and hopefully the above claim is correct! $k_B\beta = \frac{1}{T}$.

Having understand the linear response Onsager coefficients, its symmetry, and its relation to entropy production we need to see how to actully compute L_{ik}.

The inverse method by $L_{ik} = -\frac{1}{V} X_i^T H^{-1} X_k$ is a NO, NO. Since we need factor out the null space and the matrix size of H is simply too large to invere!

Sunday 3 Sep 2017

How to determine the Onsager coefficient L_{ik} then?

Since $J_i = \sum_{k=1}^{3} L_{ik} F_k$, $i=1,2,3$

and Boltzmann equation is linear, we can determine the 3×3 matrix elements one column at a time.

$$L = \begin{pmatrix} L_{11} & \cdots & \\ L_{21} & & \\ L_{31} & \cdots & L_{33} \end{pmatrix}.$$ If we set $F_1 = 1$ (in some units)

$F_2 = 0$

$F_3 = 0$

then $$J = \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & \cdots \\ L_{21} & L_{22} & \\ L_{31} & \cdots & L_{33} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} L_{11} \\ L_{21} \\ L_{31} \end{pmatrix}$$

i.e. $J_i = L_{i1}$ $i=1,2,3$ the currents are same as L. The Boltzmann equation is then

$$F_1 X_1 = H\textcircled{H}_1 \qquad (\text{since } F_2 = F_3 = 0)$$

or $$X_1 = H\textcircled{H}_1, \qquad (F_1 = 1)$$

Since $(-H)$ is a sparse matrix (due to $\delta(\varepsilon-\varepsilon'-\hbar\omega)$), symmetric, & positive definite, the conjugate gradient (CG) method for large matrices seems to me the best method. See, e.g. J. R. Shewchuk "An introduction to the conjugate gradient method Without the agonizing Pain", or "Numerical Recipes": W.H. Press, et al. Chap 10.

CG method: Starting with some good guess, say $\tilde{\textcircled{H}}$ $\perp$ to null space of H, we want to solve $X = H\textcircled{H}$.

We do the following iterations

$d_0 = r_0 = X - H\tilde{\textcircled{H}}$ is the initial residue.

compute $\alpha_i = r_i^T r_i / d_i^T (H d_i)$

$i = 0, 1, 2, \ldots$

β_i, α_i is a scalar

Do
$$\begin{cases} \textcircled{H}_{i+1} = \textcircled{H}_i + \alpha_i d_i \\ r_{i+1} = r_i - \alpha_i (H d_i) \\ \beta_{i+1} = r_{i+1}^T r_{i+1} / r_i^T r_i \\ d_{i+1} = r_{i+1} + \beta_{i+1} d_i \end{cases}$$

time consuming part is to compute

$$Hd = \begin{pmatrix} \delta\left(\frac{\partial d_k}{\partial t}\right)_{coll} \\ \delta\left(\frac{\partial d_q}{\partial t}\right)_{coll} \end{pmatrix}$$

i.e. the right-side of Boltzmann equation.

Conjugate gradient method is guarantee to converge in exact N steps where N is the dimension of $\textcircled{H}$ or X or r_i or d_i.

However this is still too large. $N \sim (30)^3 = 3 \times 10^4$!

Successive Over-relaxation (SOR) method

For the equation $X = H \underline{\vec{2}}$

we do
$$\underline{\vec{2}}_i^{(k+1)} = (1-\omega)\underline{\vec{2}}_i^{(k)} + \frac{\omega}{H_{ii}}\left(X_i - \sum_{j<i} H_{ij}\underline{\vec{2}}_j^{(k+1)} - \sum_{j>i} H_{ij}\underline{\vec{2}}_j^{(k)}\right)$$

here $0 < \omega < 2$ the superscript (k) is for iteration number, subscript for vector components.

If $\omega = 1$ we obtained Gauss-Seidel method. If the middle term is $\underline{\vec{2}}^{(k)}$ instead of $\underline{\vec{2}}^{(k+1)}$ we get Jacobi simple iteration method. (also $\omega = 1$).

over relaxation means $1 < \omega < 2$.

How to choose the initial value $\underline{\vec{2}}^{(0)}$? $\underline{\vec{2}} = \begin{pmatrix} \phi \\ \psi \end{pmatrix}$

If $F_2 = F_3 = 0$, $F_1 = 1$, we take ϕ given by SMRTA (Single mode relaxation approximation) for ψ we solve for the diagonal: ie. $\psi_q = \frac{\beta}{N}\left(\sum_{KK'} P^q_{KK'}(+1)(\phi - \phi')\right) / \sum_{KK'} P^q_{KK'}(+1)$

For $F_1 = 0$, $F_2 = 1$, $F_3 = 0$, we work out a good guess analogously.

In any case we need to make sure $\vec{\underline{z}}^{(0)} \perp \chi_0, \chi_1$ where $H\chi_i = 0$ are null space vectors.

Once the solution associated with $F_i = 1$, is found as $\vec{\underline{z}}_i$, then the currents and Onsager coefficients are neatly given by

$k = 0, 1, 3 \quad J_k = L_{ki} = -\frac{1}{V} \chi_k^T \vec{\underline{z}}_i$ for fixed i $F_i = 1$, other $F_j = 0$ $j \neq i$

We do this three times, for $i=1$, or 2, or 3.

Should we divide the $-\frac{\partial f}{\partial \varepsilon}$, $-\frac{\partial N}{\partial \hbar\omega}$ factor out in H, or keep it as it is?

Note that for anisotropic systems, the results depends on the choice of choosing direction $\hat{z}$ through v_z.

check that $L_{11} = -\frac{1}{V} \chi_1^T \vec{\underline{z}}_1$ has the correct units of conductivity $j = \sigma E = L_{11} E$ $\vec{k}$ spacings $\rightarrow \Delta k = \frac{2\pi}{L}$, $L^3 = V$

$\left[\frac{1}{V}\right] = L^{-3}$ length cube inverse

$[\chi_1] = \left[\beta f(1-f) v_z e\right] = \left[\frac{ve}{mv^2}\right] = \left[\frac{e}{mv}\right] = \left[\frac{ve}{\varepsilon}\right]$

β is inverse energy

$[\vec{\underline{z}}_1] = ? = [\varphi] = [mv^2] =$ energy wrong

since $f = f^0 - \frac{\partial f^0}{\partial \varepsilon} \varphi$ $[f] = 1$, so $[\varphi] = [\varepsilon]$

so $[L_{11}] = \frac{1}{L^3} \frac{ve}{\varepsilon} \cdot \varepsilon$

$\vec{\underline{z}}_1$ is obtained by $F_1 \chi_1 = H \vec{\underline{z}}_1$ or $\chi_1 = H \vec{\underline{z}}_1 / F_1$

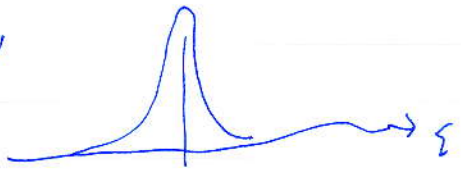
so $[\vec{\underline{z}}_1] = \left[\frac{\varphi}{F_1}\right] = \left[\frac{\varepsilon}{E}\right] =$ energy / E field

so $[L_{11}] = \frac{1}{L^3} \cdot \frac{ve}{\varepsilon} \cdot \frac{\varepsilon}{E} = \frac{1}{L^3} \frac{ve^2}{eE} = \left[\frac{ve^2}{L^3 \cdot F}\right]$ F = force $= m \frac{dv}{d\tau}$

$= \left[\frac{ve^2}{L^3 mv} \tau\right] = \left[\frac{n}{m} e \tau\right] = [\sigma]$ this is correct!

The $\delta(\varepsilon - \varepsilon' - \hbar\omega)$ in $P^{q}_{\kappa\kappa'}(\sigma)$.

The usual method is replace δ by a gaussian.



It seems to me one need very fine grid to converge. probably it is better to do this semi-analytically, i.e. approximate $\varepsilon - \varepsilon' \mp \hbar\omega$ as a plane in $\vec{k}$ space and integrate over the plane exactly. I already had code to do search a thing, plane intersecting a cube.

Summary — to handle electron-phonon interacting systems correctly, one needs a 3×3 matrix L. $J = L \cdot F$. with $F = \begin{pmatrix} E \\ -\frac{dT}{T dz} \\ -\frac{dT_p}{T_p dz} \end{pmatrix}$. Only in this frame would we have the correct Onsager reciprocal relation. Assuming that phonons are in thermal equilibrium is inconsistent with the fact that electron-phonon scatterings are inelastic. We need 3×3 L for phonon drag.

The Boltzmann equation in the form $F_i X_i = H$ (H) $i = 1, 2, 3$ can be solved by some of the standard iteration methods, such as CG (conjugate gradient) or SOR (successive over-relaxation) method.

The Onsager coefficient is given easily by inner products, $L_{ki} = -\frac{1}{V} X_k^T \Gamma_2 \Gamma_i$ here V is total volume associated with Brillouin zone discretization.