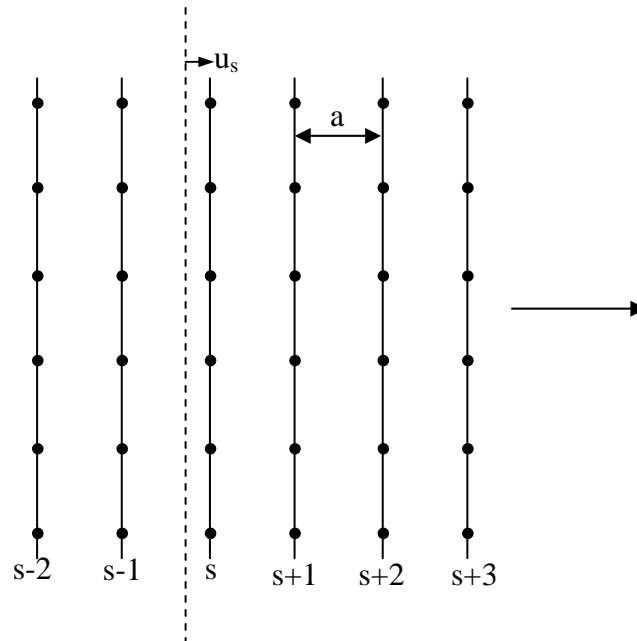


Chapter 6. Review of phonons and thermal properties

I. Phonons

1. The lattice will vibrate more as temperature is raised. This is equivalent to say more phonons are produced by the higher temperature.
2. Consider “harmonic” oscillation of a lattice in one direction:



3. The displacement of the s -th plane is u_s . For harmonic wave, it is given as

$$u_s = Ae^{i(ksa - \omega t)}$$

k is the wave vector and ω is the frequency.

Note that $u_{s+1} = e^{ika} u_s$.

4. If C is the spring constant, u_s is the solution of the equation of motion:

$$M \frac{d^2}{dt^2} u_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s)$$

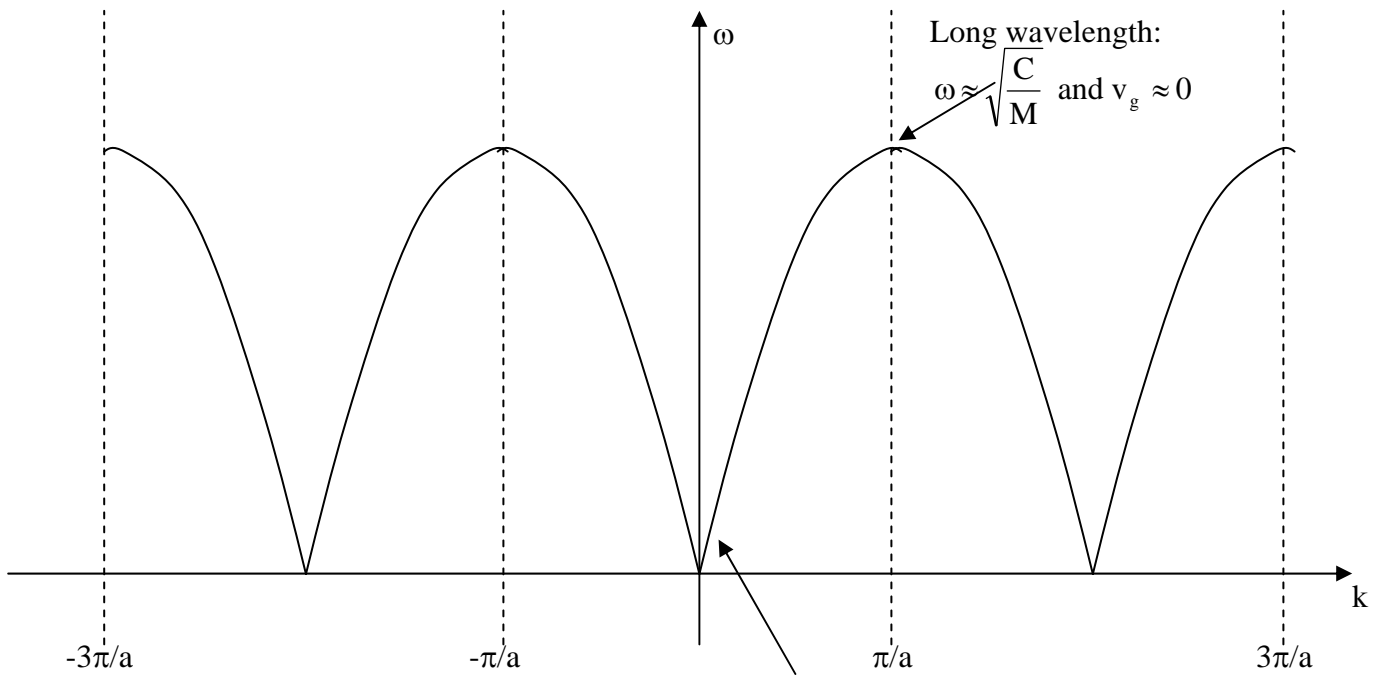
5. As a result, k and ω are not independent of each other. They follow the *dispersion relation*:

$$\omega = \sqrt{\frac{4C}{M}} \left| \sin \frac{1}{2} ka \right| \quad \text{for } -\frac{\pi}{a} \leq k < \frac{\pi}{a}$$

This dispersion relationship has to be periodic in the reciprocal space, i.e.,

$$\omega(k + 2n\pi/a) = \omega(k)$$

The solution (or *normal mode or state*) is determined by the value of k . k can be considered as the “name” of the solution.



Short wavelength, linear dispersion:

$$\omega \approx \sqrt{\frac{C}{M}}|ka| \text{ and } v_g \approx a\sqrt{\frac{C}{M}}$$

6. For small k ,

$$\omega \approx \sqrt{\frac{C}{M}}|ka|$$

7. Group velocity of the waves is given by

$$v_g = \frac{d\omega}{dk} = \sqrt{\frac{C}{M}}a \left| \cos \frac{1}{2}ka \right|$$

For *small k* , or *long wavelength*, $v_g \approx a\sqrt{\frac{C}{M}}$

For *large k* , or *short wavelength*, $v_g \approx 0$.

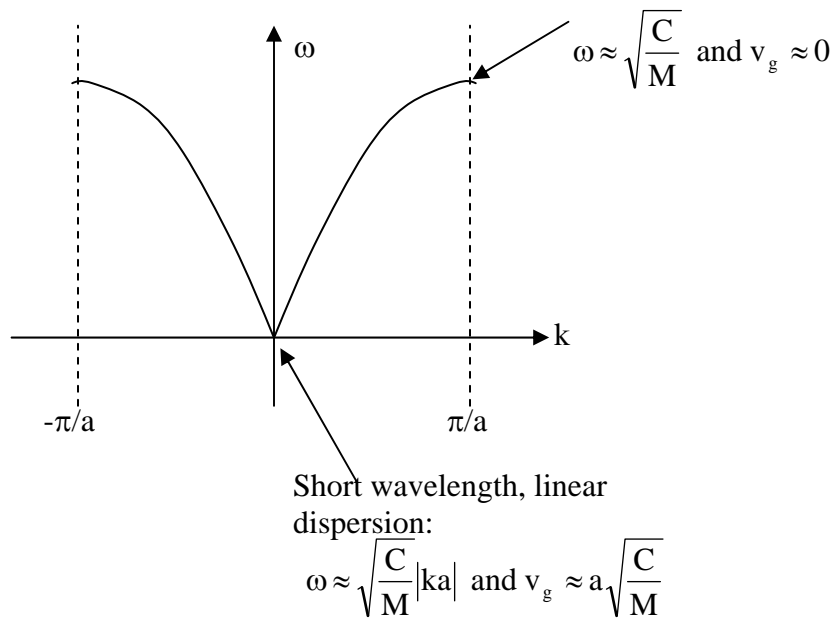
9. Zone boundary:

Consider two states k and $k+2\pi/a$, we know from above discussion that these two states have the same ω (i.e. energy) and they represent exactly the same solution since

$$u_s\left(k + \frac{2\pi}{a}\right) = Ae^{i\left(k + \frac{2\pi}{a}\right)sa - i\omega t} = Ae^{i(ksa - \omega t)} e^{i2s\pi} = u_s(k)$$

Therefore any state outside the *first Brillouin zone* (i.e. $k < -\pi/a$ or $k > \pi/a$) is redundant because it represents the same state within the first Brillouin zone.

Hence for phonon, we need only to focus at the first Brillouin zone:

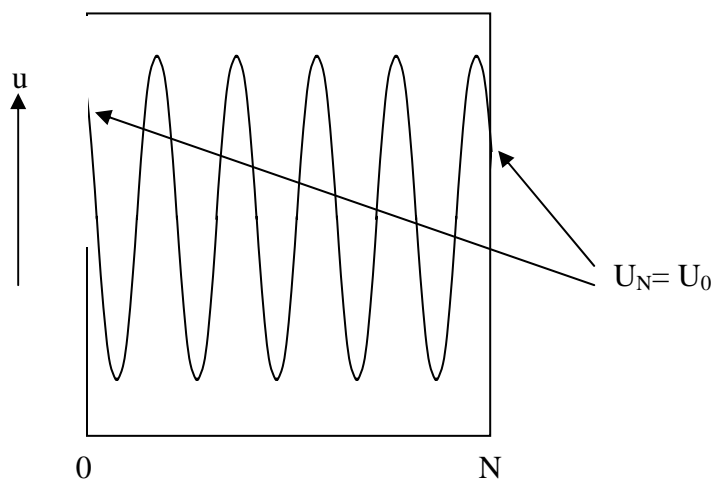


8. In solving the equations of motion, we often introduce the *periodic boundary condition*:

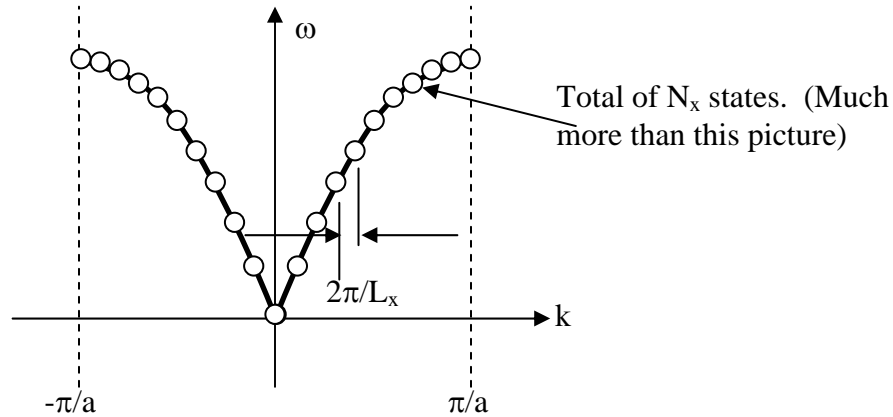
If there are N_x planes along the x direction, then we require

$$\begin{aligned}
 u_{N_x+i} &= u_i \quad (\text{in particular, } u_{N_x} = u_0) \Rightarrow Ae^{i(kN_x a - \omega t)} = Ae^{i[k(0)a - \omega t]} \\
 &\Rightarrow e^{ikN_x a} = 1 \\
 &\Rightarrow kN_x a = 2n_x \pi \\
 &\Rightarrow k = \frac{2\pi}{a} \left(\frac{n_x}{N_x} \right) \quad n_x = -\frac{N_x}{2}, \dots, -1, 0, 1, \dots, \frac{N_x}{2} \\
 &\Rightarrow k = \text{zond size } \frac{2\pi}{a} \times \text{scale facot } \frac{n_x}{N_x}
 \end{aligned}$$

Periodic boundary condition is introduced so that it makes more physical sense to prevent reflection at the surfaces (though not necessary):

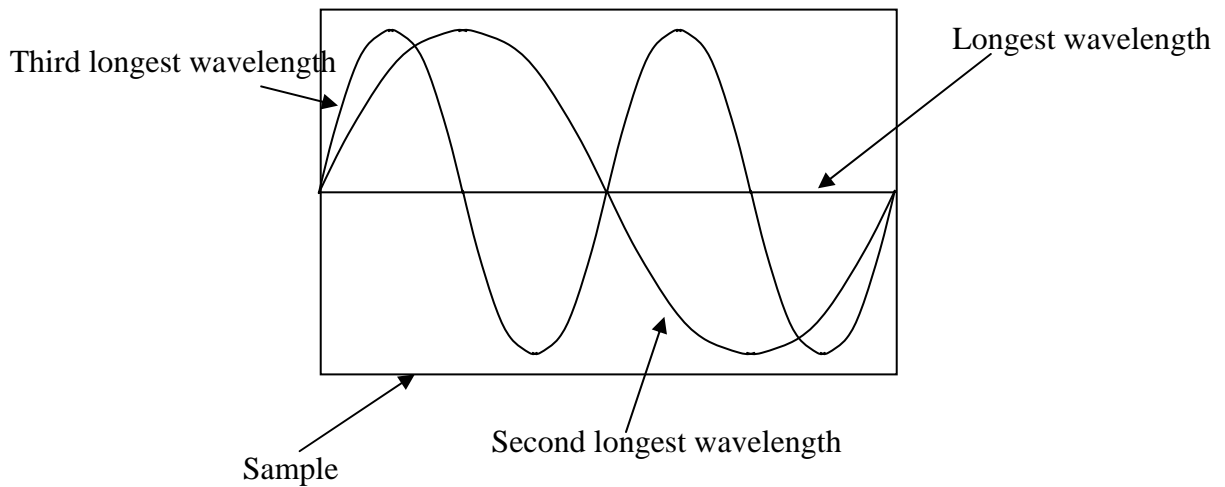


9. Total number of state = N_x . Size per state in reciprocal space $\Delta k_x = 2\pi/N_x a = 2\pi/L_x$ where L_x is the sample length along the x-direction. This correspond to the uncertainty principle $\Delta x \Delta k = 2\pi$. There are a total of N_x equally spaces states in the first Brillouing zone:

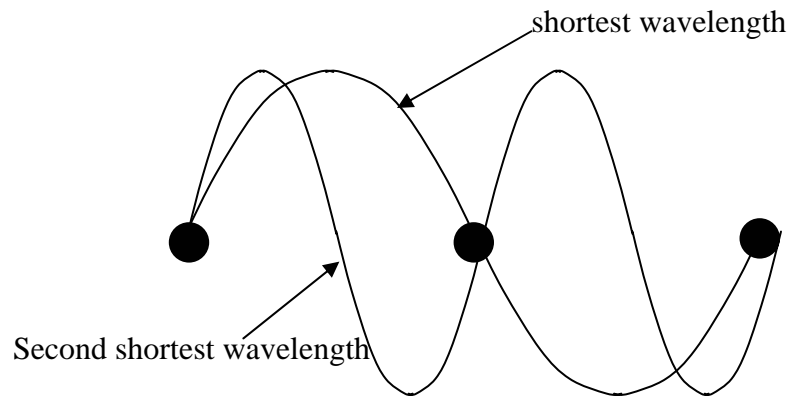


For the same material (i.e. a), note that the large the sample size (L), the number of states N will increase. The zone size ($2\pi/a$) will remain the same in and the states will be more compact ($2\pi/L$) together.

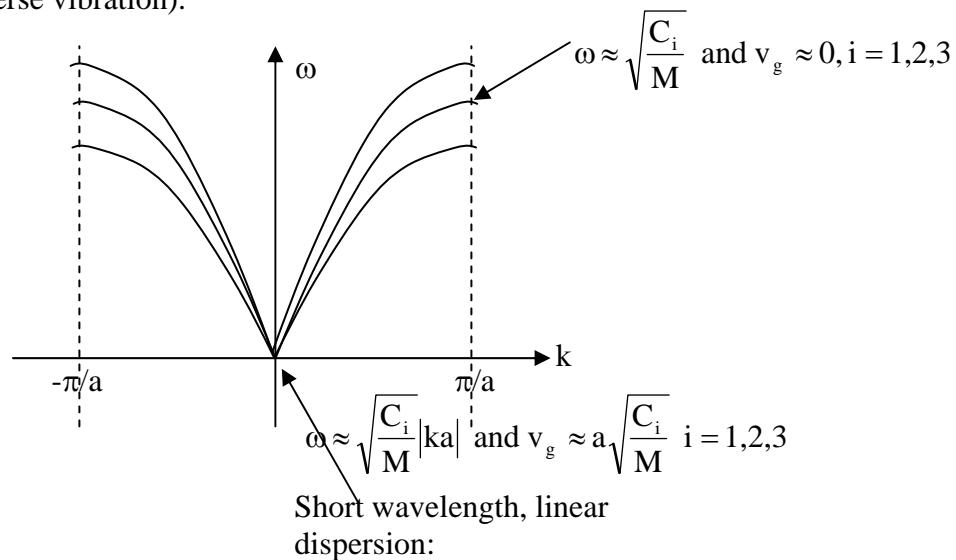
8. The states at the origin (mostly at the center of the Brillouin zone) have the smallest k and the $k=0$ state corresponds to an infinite long wavelength (i.e. dc). The next smallest k is $2\pi/L$, this correspond to a wavelength of L .



The states at the zone boundary have the largest k and shortest wavelengths. The largest k is π/a and this corresponds to a wavelength of $2a$. The next largest k is $\pi/a - 2\pi/L$, this corresponds to a wavelength of $2aL/(L-2a) \approx 2a$. Note the approximation. It is not necessary for the vibrational mode to “match” with the lattice poitns.



10. For three dimensional case, there are extra degree of freedom for the vibration. As a result, there will be three phonon branches (one for longitudinal vibration and two for transverse vibration).



We can also think of a particular “branch” as a scalar field in the reciprocal space -- each \mathbf{k} has a number attached to it representing the value of ω . Different states with the same value of ω can be joined together with a contour (a surface), or constant ω surface.

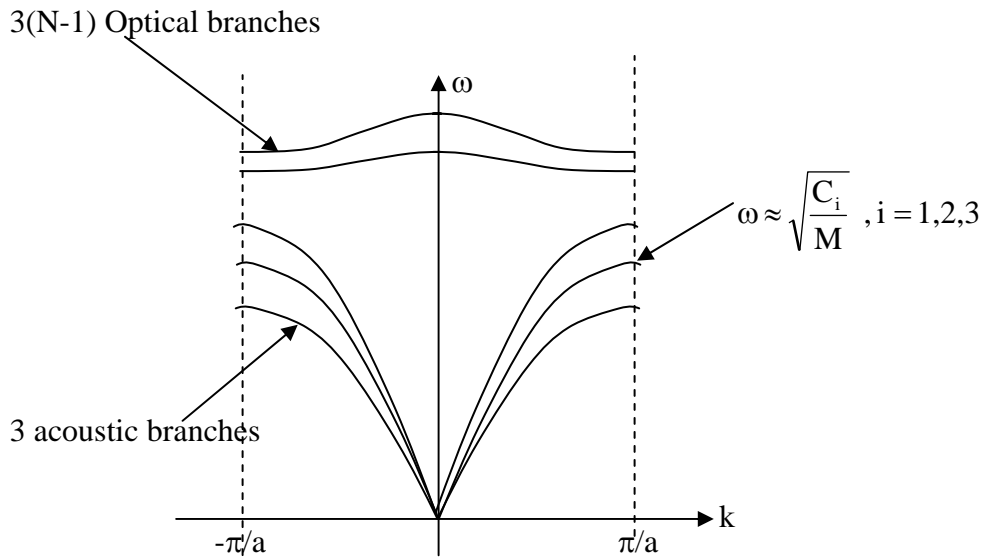
11. For each of the branch in the three dimension case:

$$\text{Total number of states} = N_1 N_2 N_3 = N \text{ (total lattice point in the sample)}$$

$$\therefore \text{Total number of states in all three branches} = 3N$$

$$\text{Volume per state} = \frac{2\pi}{L_x} \frac{2\pi}{L_y} \frac{2\pi}{L_z} = \frac{8\pi}{V} \quad (V = \text{volume of sample})$$

13. If the lattice has basis, there will be more degree of freedom. The vibration of the lattice as discussed above causes the acoustic branch. The vibration of the atoms within a basis causes the optical branch.



Optical branches are relative flat, and at a higher energy than the acoustic branches. There are always three acoustic branches, one for each dimension. If there are N atoms in the basis, there will be $3(N-1)$ optical branches, $(N-1)$ for each dimension.

II. Meaning of phonons

1. For simplicity, consider one dimension with only acoustic branches. We know there are N solutions for the vibration of the s -th plane:

$$\mathbf{u}_{s,i} = e^{i(k_i s a - \omega_i t)} \quad i = 1, 2, \dots, N$$

2. These solution form a complete orthonormal sets. In other words, no matter how complicated is the vibration of the s -th plane over time (of period T), we can always express it as a linear combination of normal mode by Fourier transformation.

$$\mathbf{u}_s(t) = \sum_i A_i(\omega) e^{i(k_i s a - \omega_i t)} \quad i = 1, 2, \dots, N$$

$$A_i(\omega) = \frac{1}{T} \int_0^T \mathbf{u}_s(t) e^{-i(k_i s a - \omega_i t)} dt$$

3. Note that $\mathbf{u}_{s,i} = e^{i(k_i s a - \omega_i t)}$ has group velocity and can be considered as the “plane wave” of a particle. This particle is a phonon. $A_i(\omega)$ is proportional to the number of phonons with frequency ω_i .

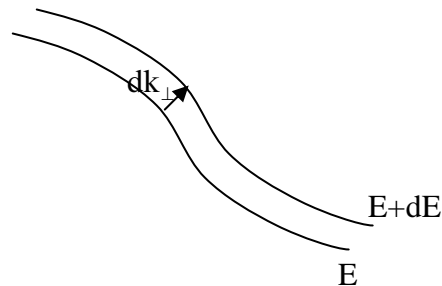
4. Energy of a phonon is given by $\hbar\omega$.

III. Density of states

1. Density of states is defined as the number of states available per unit volume per unit energy.
2. Density of states can be measured experimentally.
3. Density of state can also be considered as a mathematical devices to calculate physical quantities that have to be summed over all reciprocal lattice points.

$$\sum_{\vec{k}} f(\vec{k}) = \int f(E) dE$$

4. k-space:



In three dimensional case,

$$\text{Volume per state in reciprocal space} = \frac{8\pi^3}{V}$$

Consider above constant energy contour, if $D(E)$ = density of state at energy E .

$$D(E)dE = \oint_s \frac{dS dk_{\perp}}{\left(\frac{8\pi^3}{V}\right)} = \frac{V}{8\pi^3} \oint_s dS \frac{dE}{|\nabla_{\vec{k}}(E)|} \quad (dE = |\nabla_{\vec{k}}(E)| dk_{\perp})$$

$$\Rightarrow D(E) = \frac{V}{8\pi^3} \oint_s \frac{dS}{|\nabla_{\vec{k}}(E)|}$$

IV. Specific heat of a lattice

V. Specific heat of electrons

VI. Thermal conductivity of lattice

VII. Boltzmann equation in electric fields and temperature gradients

1. Define distribution function $f(\mathbf{r}, \mathbf{k}, t)$ as the probability density such that $f(\mathbf{r}, \mathbf{k}, t) d^3r d^3k / 4\pi^3$ is the probability for an electron to be found in the volume element $d^3r d^3k$ around point (\mathbf{r}, \mathbf{k}) in the *phase space*.

At *thermodynamic equilibrium*, $f(\mathbf{r}, \mathbf{k}, t) = f_0(\mathbf{r}, \mathbf{k})$. $f_0(\mathbf{r}, \mathbf{k})$ is simply the *local* Fermi-Dirac distribution

$$f_0(\bar{\mathbf{k}}) = \frac{1}{e^{(E(\bar{\mathbf{k}}) - \mu(\bar{\mathbf{r}})) / k_B T(\bar{\mathbf{r}})} + 1}$$

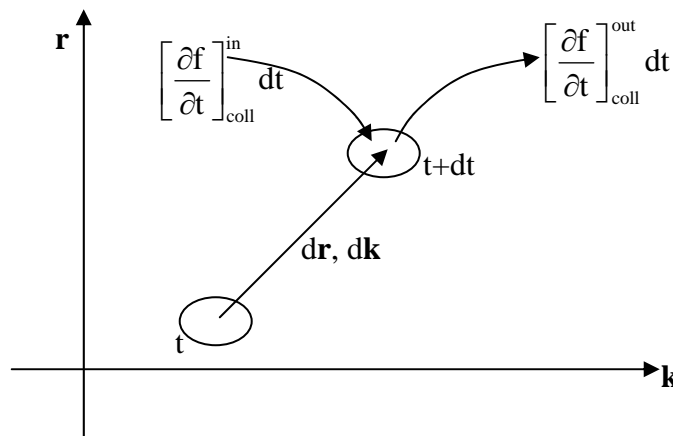
2. According to semi-classical theory, an electron will evolve from point (\mathbf{r}, \mathbf{k}) to $(\mathbf{r} + \bar{\mathbf{v}}_k dt, \mathbf{k} + (\bar{\mathbf{F}}/\hbar) dt)$ at time $t+dt$. \mathbf{V}_k and \mathbf{F} are given by

$$\bar{\mathbf{v}}_k = \frac{1}{\hbar} \frac{\partial E(\bar{\mathbf{k}})}{\partial \bar{\mathbf{k}}} \quad \text{and} \quad \mathbf{F} = \frac{d(\hbar \bar{\mathbf{k}})}{dt}$$

3. Liouville theorem states that the volume in phase space is conserved by the semi-classical equation of motion. In other words, $f(\mathbf{r}, \mathbf{k}, t) = \text{constant}$ if there is no collision.

$$f(\bar{\mathbf{r}} + \bar{\mathbf{v}}_k dt, \bar{\mathbf{k}} + (\bar{\mathbf{F}}/\hbar) dt, t + dt) = f(\bar{\mathbf{r}}, \bar{\mathbf{k}}, t) \Rightarrow \frac{d}{dt} f(\bar{\mathbf{r}}, \bar{\mathbf{k}}, t) = 0$$

3. If there is collision, f is not conserved any more.



$$\begin{aligned}
\therefore \frac{d}{dt} f(\bar{\mathbf{r}}, \bar{\mathbf{k}}, t) &= \left[\frac{\partial f}{\partial t} \right]_{\text{coll}}^{\text{in}} - \left[\frac{\partial f}{\partial t} \right]_{\text{coll}}^{\text{out}} = \left[\frac{\partial f}{\partial t} \right]_{\text{coll}} \\
\Rightarrow \frac{\partial f}{\partial \bar{\mathbf{r}}} \cdot \frac{\partial \bar{\mathbf{r}}}{\partial t} + \frac{\partial f}{\partial \bar{\mathbf{k}}} \cdot \frac{\partial \bar{\mathbf{k}}}{\partial t} + \frac{\partial f}{\partial t} &= \left[\frac{\partial f}{\partial t} \right]_{\text{coll}} \\
\Rightarrow \frac{\partial f}{\partial \bar{\mathbf{r}}} \cdot \bar{\mathbf{v}} + \frac{\partial f}{\partial \bar{\mathbf{k}}} \cdot \frac{\bar{\mathbf{F}}}{\hbar} + \frac{\partial f}{\partial t} &= \left[\frac{\partial f}{\partial t} \right]_{\text{coll}} \quad \text{or} \quad \nabla_{\bar{\mathbf{r}}} f \cdot \bar{\mathbf{v}} + \nabla_{\bar{\mathbf{k}}} f \cdot \frac{\bar{\mathbf{F}}}{\hbar} + \frac{\partial f}{\partial t} = \left[\frac{\partial f}{\partial t} \right]_{\text{coll}}
\end{aligned}$$

This is the Boltzmann transport equation. It is clear that this approach will fail to work in scale dimension less than the de Broglie wavelength.

4. Linear response provides an estimation on $\left[\frac{\partial f}{\partial t} \right]_{\text{coll}}$ that if the deviation of f is small:

$$\left[\frac{\partial f}{\partial t} \right]_{\text{coll}} = - \frac{f - f_0}{\tau}$$

τ is the relaxation time, the average time between collisions. Boltzmann equation becomes:

$$\frac{\partial f}{\partial \bar{\mathbf{r}}} \cdot \bar{\mathbf{v}} + \frac{\partial f}{\partial \bar{\mathbf{k}}} \cdot \frac{\bar{\mathbf{F}}}{\hbar} + \frac{\partial f}{\partial t} = \left[\frac{\partial f}{\partial t} \right]_{\text{coll}} = - \frac{f - f_0}{\tau}$$

Note:

If the external force \mathbf{F} is suddenly removed in a homogeneous system ($\partial f / \partial \mathbf{r} = 0$),

$$\frac{\partial f}{\partial t} = - \frac{f - f_0}{\tau} \Rightarrow f(\bar{\mathbf{k}}, t) = f_0 + (f(\bar{\mathbf{k}}, t=0) - f_0) e^{-t/\tau}$$

The distribution function moves to its equilibrium value f_0 with time constant τ .

5. Transport can occur either in form of electron current density \mathbf{J} or energy flux density \mathbf{U} :

$$\begin{aligned}
\bar{\mathbf{J}}(\bar{\mathbf{r}}, t) &= \frac{1}{4\pi^3} \int (-e) \bar{\mathbf{v}}_{\bar{\mathbf{k}}} f d^3 \bar{\mathbf{k}} \\
\bar{\mathbf{U}}(\bar{\mathbf{r}}, t) &= \frac{1}{4\pi^3} \int E_{\bar{\mathbf{k}}} \bar{\mathbf{v}}_{\bar{\mathbf{k}}} f d^3 \bar{\mathbf{k}}
\end{aligned}$$

6.

$$\begin{aligned}
 \text{For } f_0(\bar{\mathbf{k}}, \bar{\mathbf{r}}) &= \frac{1}{e^{(E(\bar{\mathbf{k}}) - \mu(\bar{\mathbf{r}}))/k_B T(\bar{\mathbf{r}})} + 1} \\
 \frac{\partial f_0}{\partial \bar{\mathbf{r}}} &= \frac{\partial f_0}{\partial(E(\bar{\mathbf{k}}) - \mu(\bar{\mathbf{r}}))/k_B T(\bar{\mathbf{r}})} \frac{\partial(E(\bar{\mathbf{k}}) - \mu(\bar{\mathbf{r}}))/k_B T(\bar{\mathbf{r}})}{\partial \bar{\mathbf{r}}} \\
 &= \frac{\partial f_0}{\partial E} \left[-\frac{E}{T} \frac{\partial T}{\partial \bar{\mathbf{r}}} - T \frac{\partial \mu}{\partial \bar{\mathbf{r}}} \frac{1}{T} \right] \\
 \frac{\partial f_0}{\partial \bar{\mathbf{k}}} &= \frac{\partial f_0}{\partial(E(\bar{\mathbf{k}}) - \mu(\bar{\mathbf{r}}))/k_B T(\bar{\mathbf{r}})} \frac{\partial(E(\bar{\mathbf{k}}) - \mu(\bar{\mathbf{r}}))/k_B T(\bar{\mathbf{r}})}{\partial \bar{\mathbf{k}}} \\
 &= \frac{\partial f_0}{\partial E} \left[\frac{\partial E}{\partial \bar{\mathbf{k}}} \right] \\
 &= \hbar \bar{\mathbf{v}}_{\bar{\mathbf{k}}} \frac{\partial f_0}{\partial E}
 \end{aligned}$$

7. Boltzmann equation in *stationary* electric field and temperature gradient:

$$\begin{aligned}
 \frac{\partial f}{\partial \bar{\mathbf{r}}} \cdot \bar{\mathbf{v}} + \frac{\partial f}{\partial \bar{\mathbf{k}}} \cdot \frac{(-e)\bar{\mathbf{E}}}{\hbar} + \frac{\partial f}{\partial t} &= \left[\frac{\partial f}{\partial t} \right] = -\frac{f - f_0}{\tau} \\
 \Rightarrow \frac{\partial f_0}{\partial E} \left[-\frac{E}{T} \frac{\partial T}{\partial \bar{\mathbf{r}}} - T \frac{\partial \mu}{\partial \bar{\mathbf{r}}} \frac{1}{T} \right] \cdot \bar{\mathbf{v}}_{\bar{\mathbf{k}}} + \hbar \frac{\partial f_0}{\partial E} \bar{\mathbf{v}}_{\bar{\mathbf{k}}} \cdot \frac{(-e)\bar{\mathbf{E}}}{\hbar} &= -\frac{f - f_0}{\tau} \\
 \Rightarrow \left(\frac{\partial f_0}{\partial E} \right) \tau \left[-\frac{E}{T} \frac{\partial T}{\partial \bar{\mathbf{r}}} - T \frac{\partial \mu}{\partial \bar{\mathbf{r}}} \frac{1}{T} \right] \cdot \bar{\mathbf{v}}_{\bar{\mathbf{k}}} + \hbar \tau \frac{\partial f_0}{\partial E} \bar{\mathbf{v}}_{\bar{\mathbf{k}}} \cdot \frac{(-e)\bar{\mathbf{E}}}{\hbar} &= -\delta f \\
 \Rightarrow \left(\frac{\partial f_0}{\partial E} \right) \tau \left[-T \frac{\partial \mu}{\partial \bar{\mathbf{r}}} \frac{1}{T} + (-e)\bar{\mathbf{E}} \right] \cdot \bar{\mathbf{v}}_{\bar{\mathbf{k}}} + \left(-\frac{\partial f_0}{\partial E} \right) \tau \left(\frac{E}{T} \frac{\partial T}{\partial \bar{\mathbf{r}}} \right) \cdot \bar{\mathbf{v}}_{\bar{\mathbf{k}}} &= -\delta f \\
 \Rightarrow \delta f = \left(-\frac{\partial f_0}{\partial E} \right) \tau \left[-e\bar{\mathbf{E}} - T \nabla_{\bar{\mathbf{r}}} \frac{\mu}{T} \right] \cdot \bar{\mathbf{v}}_{\bar{\mathbf{k}}} + \left(-\frac{\partial f_0}{\partial E} \right) \tau (-E) \left(\frac{\nabla_{\bar{\mathbf{r}}} T}{T} \right) \cdot \bar{\mathbf{v}}_{\bar{\mathbf{k}}}
 \end{aligned}$$

8. From this we can calculate the current and energy flux density:

$$\begin{aligned}
\bar{J}(\bar{r}, t) &= \frac{1}{4\pi^3} \int (-e)\bar{v}_{\bar{k}} f d^3\bar{k} \\
&= \frac{1}{4\pi^3} \int (-e)\bar{v}_{\bar{k}} \left\{ \left(-\frac{\partial f_0}{\partial E} \right) \tau \left[-e\bar{E} - T\nabla_{\bar{r}} \frac{\mu}{T} \right] \cdot \bar{v}_{\bar{k}} + \left(-\frac{\partial f_0}{\partial E} \right) \tau(-E) \left(\frac{\nabla_{\bar{r}} T}{T} \right) \cdot \bar{v}_{\bar{k}} \right\} d^3\bar{k} \\
&= \underbrace{\left[\frac{1}{4\pi^3} \int \tau \bar{v}_{\bar{k}}^2 \left(-\frac{\partial f_0}{\partial E} \right) d^3\bar{k} \right]}_{K_0} \left[e^2 \bar{E} + T\nabla_{\bar{r}} \frac{\mu}{T} \right] + \underbrace{\left[\frac{1}{4\pi^3} \int \tau \left(-\frac{\partial f_0}{\partial E} \right) \bar{v}_{\bar{k}}^2 E d^3\bar{k} \right]}_{K_1} \left[e \frac{\nabla_{\bar{r}} T}{T} \right] \\
&= eK_0 \left[e\bar{E} + T\nabla_{\bar{r}} \frac{\mu}{T} \right] + eK_1 \left[\frac{\nabla_{\bar{r}} T}{T} \right] \\
\bar{U}(\bar{r}, t) &= \frac{1}{4\pi^3} \int E_{\bar{k}} \bar{v}_{\bar{k}} \left\{ \left(-\frac{\partial f_0}{\partial E} \right) \tau \left[-e\bar{E} - T\nabla_{\bar{r}} \frac{\mu}{T} \right] \cdot \bar{v}_{\bar{k}} + \left(-\frac{\partial f_0}{\partial E} \right) \tau(-E) \left(\frac{\nabla_{\bar{r}} T}{T} \right) \cdot \bar{v}_{\bar{k}} \right\} d^3\bar{k} \\
&= - \underbrace{\left[\frac{1}{4\pi^3} \int \tau \left(-\frac{\partial f_0}{\partial E} \right) \bar{v}_{\bar{k}}^2 E d^3\bar{k} \right]}_{K_1} \left[e\bar{E} + T\nabla_{\bar{r}} \frac{\mu}{T} \right] - \underbrace{\left[\frac{1}{4\pi^3} \int \tau \left(-\frac{\partial f_0}{\partial E} \right) \bar{v}_{\bar{k}}^2 E^2 d^3\bar{k} \right]}_{K_2} \left[e \frac{\nabla_{\bar{r}} T}{T} \right] \\
&= -K_1 \left[e\bar{E} + T\nabla_{\bar{r}} \frac{\mu}{T} \right] - K_2 \left[\frac{\nabla_{\bar{r}} T}{T} \right]
\end{aligned}$$

Kinetic coefficients :

$$K_n = \frac{1}{4\pi^3} \int \tau \left(-\frac{\partial f_0}{\partial E} \right) \bar{v}_{\bar{k}}^2 E^n d^3\bar{k} \quad n = 0, 1, 2$$

Integrate over constant energy surface,

$$\begin{aligned}
K_n &= \frac{1}{4\pi^3} \int \tau \left(-\frac{\partial f_0}{\partial E} \right) \bar{v}_{\bar{k}}^2 E^n d^3\bar{k} \\
&= \frac{1}{4\pi^3} \int \left(-\frac{\partial f_0}{\partial E} \right) E^n dE \int_{E=\text{const.}} \frac{\tau \bar{v}_{\bar{k}}^2}{|\nabla_{\bar{k}} E(\bar{k})|} dS
\end{aligned}$$

Approximate $\langle \bar{v}_{\bar{k}}^2 \rangle = \frac{1}{3} v^2$

$$\begin{aligned}
K_n &= \frac{1}{12\pi^3} \int \left(-\frac{\partial f_0}{\partial E} \right) E^n dE \int_{E=\text{const.}} \frac{\tau v^2}{|\nabla_{\bar{k}} E(\bar{k})|} dS \\
&= \frac{1}{12\pi^3} \int \left(-\frac{\partial f_0}{\partial E} \right) E^n dE \int_{E=\text{const.}} \frac{\tau v}{\hbar} dS \quad (\nabla_{\bar{k}} E(\bar{k}) = \hbar v)
\end{aligned}$$

Define $\sigma(E) = \frac{e^2}{12\pi^3 \hbar} \int_{E=\text{const.}} \tau v dS$

Then $e^2 K_n = \int \left(-\frac{\partial f_0}{\partial E} \right) E^n \sigma(E) dE$

Note that $\sigma(E_F)$ is the standard conductivity of a metal.

Integration can be done by *Sommerfeld expansion*. For any function $G(E)$:

$$\int_0^{\infty} \left(-\frac{\partial f_0}{\partial E} \right) G(E) dE = G(\mu) + \frac{\pi^2}{6} k_B^2 T^2 \left(\frac{d^2 G}{dE^2} \right)_{E=\mu} + O(T^4)$$

With $G(E)=E^n \sigma(E)$ we have

$$e^2 K_n = \int \left(-\frac{\partial f_0}{\partial E} \right) E^n \sigma(E) dE = \mu^n \sigma(\mu) + \frac{\pi^2}{6} k_B^2 T^2 \left(n \mu^{n-1} \sigma(\mu) + \mu^n \frac{d^n \sigma}{dE} \Big|_{E=\mu} \right)$$

$$e^2 K_0 = \sigma(\mu) + \frac{\pi^2}{6} k_B^2 T^2 \sigma''(\mu)$$

$$e^2 K_1 = \mu \sigma(\mu) + \frac{\pi^2}{6} k_B^2 T^2 [2\sigma'(\mu) + \mu \sigma''(\mu)]$$

$$e^2 K_2 = \mu \sigma(\mu) + \frac{\pi^2}{6} k_B^2 T^2 [2\sigma(\mu) + 4\mu \sigma'(\mu) + \mu^2 \sigma''(\mu)]$$

With this, J and U can be rewritten as follow:

$$\begin{aligned} \bar{J}(\bar{r}, t) &= eK_0 \left[e\bar{E} + T \nabla_{\bar{r}} \frac{\mu}{T} \right] + eK_1 \left[\frac{\nabla_{\bar{r}} T}{T} \right] \\ &= e^2 K_0 \left[\bar{E} + \frac{T}{e} \nabla_{\bar{r}} \frac{\mu}{T} - \frac{K_1}{(-e)K_0} \frac{\nabla_{\bar{r}} T}{T} \right] \\ &= e^2 K_0 \left[\bar{E} + \frac{1}{e} \nabla_{\bar{r}} \mu - \frac{\mu}{eT^2} \nabla_{\bar{r}} T - \frac{K_1}{(-e)K_0} \frac{\nabla_{\bar{r}} T}{T} \right] \\ &= e^2 K_0 \left[\bar{E} + \frac{1}{e} \nabla_{\bar{r}} \mu - S(T) \nabla_{\bar{r}} T \right] \end{aligned}$$

In first approximation,

$$\bar{J}(\bar{r}, t) = \sigma \left[\bar{E} + \frac{1}{e} \nabla_{\bar{r}} \mu - S(T) \nabla_{\bar{r}} T \right]$$

$$S(T) = \frac{1}{(-e)T} \left(\frac{K_1}{K_0} - \mu \right) = \frac{1}{(-e)T} \left(\frac{\mu\sigma(\mu) + \frac{\pi^2}{6} k_B^2 T^2 [2\sigma'(\mu) + \mu\sigma''(\mu)]}{\sigma(\mu) + \frac{\pi^2}{6} k_B^2 T^2 \sigma''(\mu)} - \mu \right)$$

$$\approx \frac{1}{(-e)T} \left(\frac{\frac{\pi^2}{6} k_B^2 T^2 \cdot 2\sigma'(\mu)}{\sigma(\mu)} \right) = \frac{\pi^2}{3} \frac{k_B^2 T}{(-e)} \left(\frac{\sigma'(\mu)}{\sigma(\mu)} \right)$$

$$\text{or } \frac{K_1}{K_0} = \underbrace{\mu}_{\text{1st order}} - \underbrace{eTS(T)}_{\text{2nd order}}$$

$S(T)$ is known as the *thermoelectric power* or *Seebeck coefficient*.

9. $S(T)$ can be either positive or negative, depends on the sign of $d\sigma/dE$ at the Fermi energy μ . If $\sigma(E) = CE^p$ ($p=3/2$ for free electron gas),

$$\frac{\sigma'(\mu)}{\sigma(\mu)} \approx \frac{1}{\mu} = \frac{1}{k_B T_F}$$

$$S(T) \approx \frac{k_B^2 T}{(-e)} \left(\frac{\sigma'(\mu)}{\sigma(\mu)} \right) = -\frac{k_B}{e} \left(\frac{T}{T_F} \right)$$

If $T \sim 300\text{K}$, $T_F \sim 100\text{T}$, $k_B/e = 0.48 \times 10^{-4} \text{ V/K}$ we expect a thermoelectric power of the order of 10^{-6} V/K .

10.

$$\begin{aligned} \bar{U}(\vec{r}, t) &= -K_1 \left[e\bar{E} + T\nabla_{\vec{r}} \frac{\mu}{T} \right] - K_2 \left[\frac{\nabla_{\vec{r}} T}{T} \right] \\ &= \frac{K_1}{(-e)K_0} \left[eK_0 \left(e\bar{E} + T\nabla_{\vec{r}} \frac{\mu}{T} \right) \right] - K_2 \left[\frac{\nabla_{\vec{r}} T}{T} \right] \\ &= \frac{K_1}{(-e)K_0} \left[eK_0 \left(e\bar{E} + T\nabla_{\vec{r}} \frac{\mu}{T} \right) + eK_1 \left[\frac{\nabla_{\vec{r}} T}{T} \right] \right] - \frac{eK_1^2}{(-e)K_0} \left[\frac{\nabla_{\vec{r}} T}{T} \right] - K_2 \left[\frac{\nabla_{\vec{r}} T}{T} \right] \\ &= \frac{K_1}{(-e)K_0} \bar{J}(\vec{r}, t) - \frac{1}{T} \left(K_2 - \frac{K_1^2}{K_0} \right) \nabla_{\vec{r}} T \\ &= \frac{K_1}{(-e)K_0} \bar{J}(\vec{r}, t) - k_e \nabla_{\vec{r}} T \\ &\approx \left[-\frac{\mu}{e} + TS(T) \right] \bar{J}(\vec{r}, t) - k_e \nabla_{\vec{r}} T \end{aligned}$$

$$\begin{aligned}
k_e &= \frac{1}{T} \left(K_2 - \frac{K_1^2}{K_0} \right) = \frac{1}{Te^2} \left(\frac{\mu\sigma(\mu) + \frac{\pi^2}{6} k_B^2 T^2 [2\sigma(\mu) + 4\mu\sigma'(\mu) + \mu^2\sigma''(\mu)]}{(\mu\sigma(\mu) + \frac{\pi^2}{6} k_B^2 T^2 [2\sigma'(\mu) + \mu\sigma''(\mu)])^2} \right. \\
&\quad \left. - \frac{\sigma(\mu) + \frac{\pi^2}{6} k_B^2 T^2 \sigma''(\mu)}{\sigma(\mu) + \frac{\pi^2}{6} k_B^2 T^2 \sigma''(\mu)} \right) \\
&= \frac{1}{Te^2} \left(\frac{\pi^2}{6} k_B^2 T^2 \cdot 2\sigma(\mu) \right) \\
&= \frac{\pi^2}{3} \frac{k_B^2}{e^2} T \sigma(\mu)
\end{aligned}$$

K_e is called the *electron thermal conductivity*.

11. Summary:

$$\begin{aligned}
\bar{J}(\bar{r}, t) &= \sigma \left[\bar{E} + \frac{1}{e} \nabla_{\bar{r}} \mu - S(T) \nabla_{\bar{r}} T \right] \\
\bar{U}(\bar{r}, t) &= \left[-\frac{\mu}{e} + TS(T) \right] \bar{J}(\bar{r}, t) - k_e \nabla_{\bar{r}} T
\end{aligned}$$

VIII. Thermal conductivity of electrons

1. Boltzmann equation:

$$\begin{aligned}
\bar{J}(\bar{r}, t) &= e^2 K_0 \left[\bar{E} + \frac{1}{e} \nabla_{\bar{r}} \mu - S(T) \nabla_{\bar{r}} T \right] \\
\bar{U}(\bar{r}, t) &= \frac{K_1}{(-e)K_0} \bar{J}(\bar{r}, t) - k_e \nabla_{\bar{r}} T
\end{aligned}$$

2. Consider a metal in the presence of a uniform temperature gradient ∇T and in open circuit condition, so that $\bar{J}=0$. Above equation reduces to

$$\bar{U}(\bar{r}, t) = -k_e \nabla_{\bar{r}} T$$

Note that the energy flows in direction opposite to ∇T .

3. Wiedemann-Franz law: The ratio of electron thermal conductivity to electrical conductivity is proportional to T .

$$\begin{aligned}
k_e &= \frac{\pi^2}{3} \frac{k_B^2}{e^2} T \sigma(\mu) \Rightarrow \frac{k_e}{\sigma(\mu)} = \frac{\pi^2}{3} \frac{k_B^2}{e^2} T \\
\text{or Lorentz number} &= \frac{k_e}{T \sigma(\mu)} = \frac{\pi^2}{3} \frac{k_B^2}{e^2}
\end{aligned}$$

4. Note that Lorentz number is a universal number, independent from the material, temperature and relaxation time. Its justification is based on the transport equations. The most vulnerable point of the transport equations is the linear response approximation of the collision time, which gives rise to the relaxation time. The approximation is justified above the Debye temperature, where the electron-phonon scattering is the dominant process. It is also justified at low temperatures, where impurity scattering is dominant. In both temperature regimes, the ratio $k_e/k\sigma_0$ is approximately the same for all metals, At intermediate temperatures, significant deviations may occur.

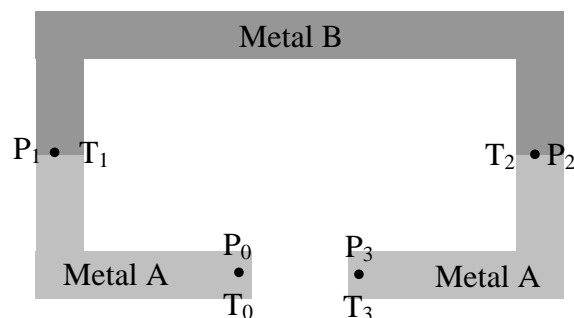
IX. Seebeck or thermocouple effect

1. Similar to the conditions in the previous discussion on thermal conductivity, consider a metal in the presence of a uniform temperature gradient ∇T and in open circuit condition, so that $\mathbf{J}=0$.

2. Instead of paying attention to the energy flux flow \mathbf{U} , we will investigate the electric field \mathbf{E} set up under the condition. Boltzmann equation:

$$\begin{aligned}\bar{\mathbf{J}}(\bar{\mathbf{r}}, t) &= e^2 \mathbf{K}_0 \left[\bar{\mathbf{E}} + \frac{1}{e} \nabla_{\bar{\mathbf{r}}} \mu - S(T) \nabla_{\bar{\mathbf{r}}} T \right] \\ \bar{\mathbf{U}}(\bar{\mathbf{r}}, t) &= \frac{\mathbf{K}_1}{(-e)\mathbf{K}_0} \bar{\mathbf{J}}(\bar{\mathbf{r}}, t) - k_e \nabla_{\bar{\mathbf{r}}} T \\ \bar{\mathbf{J}}(\bar{\mathbf{r}}, t) = 0 &\Rightarrow \bar{\mathbf{E}} + \frac{1}{e} \nabla_{\bar{\mathbf{r}}} \mu - S(T) \nabla_{\bar{\mathbf{r}}} T = 0 \\ &\Rightarrow \bar{\mathbf{E}} = -\frac{1}{e} \nabla_{\bar{\mathbf{r}}} \mu + S(T) \nabla_{\bar{\mathbf{r}}} T\end{aligned}$$

3. Consider the following circuit with two junctions maintained at two different temperatures T_1 and T_2 , hence setting up a temperature gradient along metal B.



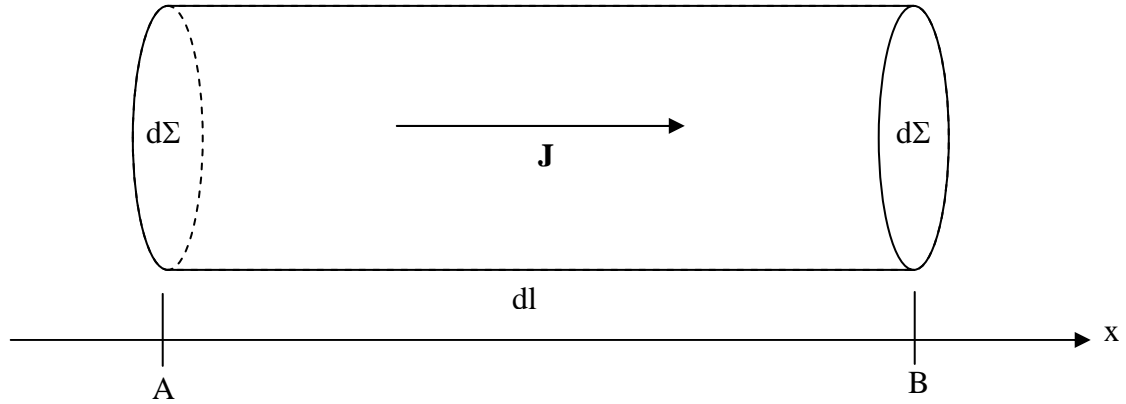
+4. Assume P_0 and P_3 are kept at the same temperature so that $T_0 = T_3$.

$$\begin{aligned}
 \vec{E} = -\frac{1}{e}\nabla_{\vec{r}}\mu + S(T)\nabla_{\vec{r}}T &\Rightarrow \int_{P_0}^{P_3} \vec{E} \cdot d\vec{\ell} = - \int_{P_0}^{P_3} \frac{1}{e}\nabla_{\vec{r}}\mu \cdot d\vec{\ell} + \int_{P_0}^{P_3} S(T)\nabla_{\vec{r}}T \cdot d\vec{\ell} \\
 &\Rightarrow -(V_3 - V_0) = \underbrace{-[\mu]_{P_0}^{P_3}}_{=0 \text{ because } T_0=T_3} + \int_{P_0}^{P_3} S(T)dT \\
 &\Rightarrow V_3 - V_0 = - \int_{T_0}^{T_3} S(T)dT \\
 &\Rightarrow V_3 - V_0 = - \left[\int_{T_0}^{T_1} S_A(T)dT + \int_{T_1}^{T_2} S_B(T)dT + \int_{T_2}^{T_3} S_A(T)dT \right] \\
 &\Rightarrow V_3 - V_0 = - \left[\int_{T_0}^{T_1} S_A(T)dT + \int_{T_1}^{T_2} S_B(T)dT + \int_{T_2}^{T_0} S_A(T)dT \right] \\
 &\Rightarrow V_3 - V_0 = - \left[\int_{T_2}^{T_1} S_A(T)dT + \int_{T_1}^{T_2} S_B(T)dT \right] \\
 &\Rightarrow V_3 - V_0 = \left[\int_{T_1}^{T_2} S_A(T)dT - \int_{T_1}^{T_2} S_B(T)dT \right]
 \end{aligned}$$

5. If $S_A(T)$ of metal A is known, $S_B(T)$ can be measured from $V_3 - V_1$ (potential difference between points P_3 and P_1) by varying T_2 with respect to T_1 . Alternatively, if both $S_A(T)$ and $S_B(T)$ are known, T_2 (with respect to T_1) can be measured from $V_3 - V_1$.

X. Thompson effect

1. If now there is an electric current flow (in the presence of a temperature gradient), heat is released or absorbed because of the mismatch in \mathbf{J} and \mathbf{U} .
2. In contrary to Joule heating, heat can be released or absorbed depending on the *direction* of current flow.
3. If a current J is flowing from point A at temperature T_A to point B $T_B (=T_A + dT)$.



Assume constant temperature when $x \leq x_A$ and $x \geq x_B$ so that $\nabla T = 0$ at points A and B (but not for points within the element).

Boltzmann equation:

$$\bar{U}_A = \frac{K_1(T_A)}{(-e)K_0(T_A)} \bar{J} \quad (\nabla_{\vec{r}} T = 0 \text{ at points A and B})$$

$$\bar{U}_B = \frac{K_1(T_B)}{(-e)K_0(T_B)} \bar{J}$$

4. If dU is the energy accumulated in time dT ,

$$\frac{dU}{dt d\Sigma} = \bar{U}_A - \bar{U}_B = \left[-\frac{K_1(T_A)}{eK_0(T_A)} \bar{J} + \frac{K_1(T_B)}{eK_0(T_B)} \bar{J} \right]$$

5. First law of thermodynamics:

$$dU = dQ - dW$$

dW is the work done by the current and it is given by:

$$\bar{\mathbf{J}}(\bar{\mathbf{r}}, t) = \sigma \left[\bar{\mathbf{E}} + \frac{1}{e} \nabla_{\bar{\mathbf{r}}} \mu - S(T) \nabla_{\bar{\mathbf{r}}} T \right] \Rightarrow \bar{\mathbf{E}} = \frac{\bar{\mathbf{J}}}{\sigma} - \frac{1}{e} \nabla_{\bar{\mathbf{r}}} \mu + S(T) \nabla_{\bar{\mathbf{r}}} T$$

$$\begin{aligned} \frac{dW}{dt d\Sigma} &= \int_A^B \bar{\mathbf{J}} \cdot \bar{\mathbf{E}} d\ell = \int_A^B \mathbf{J} \left[\frac{\mathbf{J}}{\sigma} - \frac{1}{e} \nabla_{\bar{\mathbf{r}}} \mu + S(T) \nabla_{\bar{\mathbf{r}}} T \right] d\ell \\ &= \frac{J^2}{\sigma} d\ell - \frac{J}{e} (\mu_B - \mu_A) + J \int_{T_A}^{T_B} S(T) dT \end{aligned}$$

Disregard the Joule heating $\frac{J^2}{\sigma} d\ell$

$$\begin{aligned} \frac{dQ}{dt d\Sigma} &= dU + dW = \left[-\frac{K_1(T_A)}{eK_0(T_A)} \bar{\mathbf{J}} + \frac{K_1(T_B)}{eK_0(T_B)} \bar{\mathbf{J}} \right] + \left[-\frac{J}{e} (\mu_B - \mu_A) + J \int_{T_A}^{T_B} S(T) dT \right] \\ &= \left[-\frac{K_1(T_A)}{eK_0(T_A)} + \frac{\mu_A}{e} \right] \mathbf{J} - \left[-\frac{K_1(T_B)}{eK_0(T_B)} + \frac{\mu_B}{e} \right] \mathbf{J} + J \int_{T_A}^{T_B} S(T) dT \end{aligned}$$

$$S(T) = \frac{1}{(-e)T} \left(\frac{K_1}{K_0} - \mu \right) \Rightarrow -\frac{K_1}{eK_0} + \frac{\mu}{e} = TS(T)$$

$$\therefore \frac{dQ}{dt d\Sigma} = [T_A S_A(T_A) - T_B S_B(T_A)] J + J \int_{T_A}^{T_B} S(T) dT$$

Integration by parts :

$$\frac{dQ}{dt d\Sigma} = -J \int_{S_A}^{S_B} T dS = -J \int_{T_A}^{T_B} T \frac{dS}{dT} dT$$

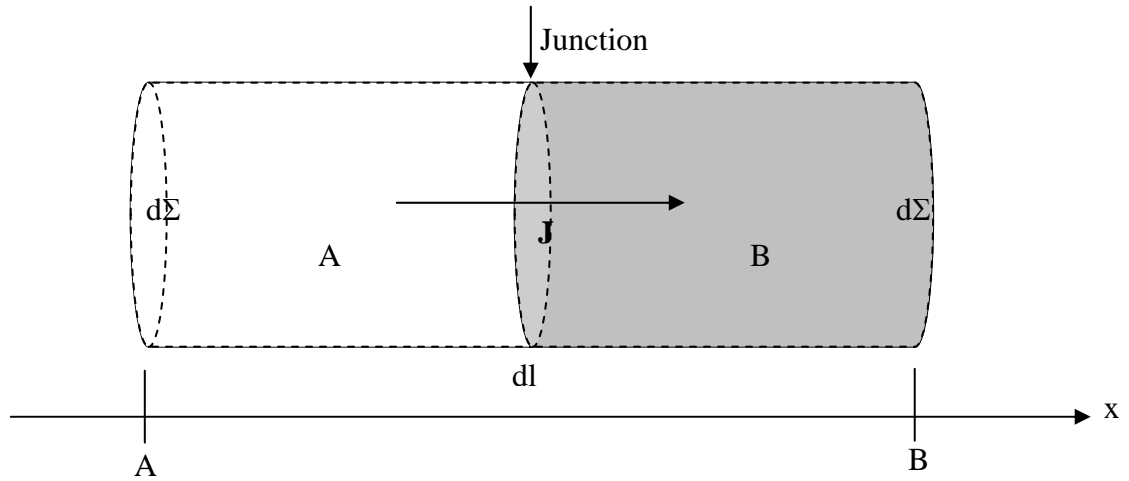
Define Thompson coefficient $K_{\text{Thompson}}(T) = T \frac{dS}{dT}$

$$\frac{dQ}{dt d\Sigma} = -J \int_T^{T_B} K_{\text{Thompson}}(T) dT$$

XI. Peltier effect

1. Thompson effect can be used for cooling. This is not practical because dS/dT (of K_{Thompson}) is too small. ΔS can be large if it is the difference between two different materials (i.e. across a junction). Thompson effect across a junction is called the Peltier effect.

2.



For simplicity, assume the temperature is constant

$$\therefore \frac{dQ}{dt d\Sigma} = -J \int_{T_A}^{T_B} T \frac{dS}{dT} dT = -J [TS_B - TS_A]$$

Define Peltier coefficient $\Pi_A(T) = TS_A(T)$ and $\Pi_B(T) = TS_B(T)$

$$\frac{dQ}{dt d\Sigma} = -J [\Pi_B - \Pi_A]$$

3. For materials to be practical usable in Peltier junction, they need to have large Peltier coefficient Π (or thermoelectric power S), but a low thermal conductivity K_e .

XII. Drift and diffusion current

1. We now consider the current due to the electric field (i.e. no temperature gradient, $\nabla T=0$):

$$\bar{J}(\bar{r}, t) = \sigma \left[\bar{E} + \frac{1}{e} \nabla_{\bar{r}} \mu - S(T) \nabla_{\bar{r}} T \right] \Rightarrow \bar{J}(\bar{r}, t) = \sigma \left[\bar{E} + \frac{1}{e} \nabla_{\bar{r}} \mu \right]$$

2. The first term $\bar{J}_{\text{Drift}}(\bar{r}, t) = \sigma [\bar{E}]$ is called the *drift current*, which is essentially the “ohmic term” described by the Drude model.

3. The second term $\bar{J}_{\text{Diffuse}}(\bar{r}, t) = \frac{\sigma}{e} \nabla_{\bar{r}} \mu$ is the *diffusion current*.

4. Free electron model:

$$\sigma = \frac{ne^2\tau}{m^*}$$

$$\begin{aligned} \mu = E_F = \frac{\hbar^2}{2m^*} (3\pi^2 n)^{2/3} &\Rightarrow d\mu = \frac{\hbar^2}{3m^*} (3\pi^2)^{2/3} n^{1/2} dn \\ &\Rightarrow \frac{\nabla\mu}{\mu} = \frac{\frac{\hbar^2}{3m^*} (3\pi^2)^{2/3} n^{1/2} \nabla n}{\frac{\hbar^2}{2m^*} (3\pi^2 n)^{2/3}} = \frac{2}{3} \frac{\nabla n}{n} \end{aligned}$$

$$\begin{aligned} \bar{\mathbf{J}}(\bar{\mathbf{r}}, t) = \sigma \left[\bar{\mathbf{E}} + \frac{1}{e} \nabla_{\bar{\mathbf{r}}} \mu \right] &\Rightarrow \bar{\mathbf{J}}(\bar{\mathbf{r}}, t) = \sigma \left[\bar{\mathbf{E}} + \frac{2E_F}{3e} \frac{\nabla n}{n} \right] \\ &\Rightarrow \bar{\mathbf{J}}(\bar{\mathbf{r}}, t) = ne\mu_e \bar{\mathbf{E}} + eD \nabla n \end{aligned}$$

μ_e is the electron mobility and $\mu_e = \frac{\sigma}{ne}$

D is the diffusion constant and $D = \frac{2E_F \sigma}{3e^2 n} = \frac{2E_F \mu_e}{3e}$

5. For non-degenerate free electron gas that follows Boltzmann distribution (which is *not* correct),

$$E_F = \frac{3}{2} k_B T$$

$$D = \frac{k_B T}{e} \mu_e \quad (\text{Einstein relation})$$