

§4. Transport properties of solids

* Classical theory (Drude's theory)

{ electrons as classical particles
 collisions with a relaxation time τ

DC conductivity:

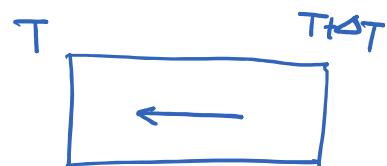
$$\vec{J} = \sigma \vec{E} \quad , \quad \sigma = \frac{n e^2 \tau}{m}$$

- Thermal conductivity

Fourier's law:

$$\vec{J}^q = -k \vec{\nabla} T$$

thermal conductivity



1D case:

$$J^q = -k \frac{dT}{dx}$$

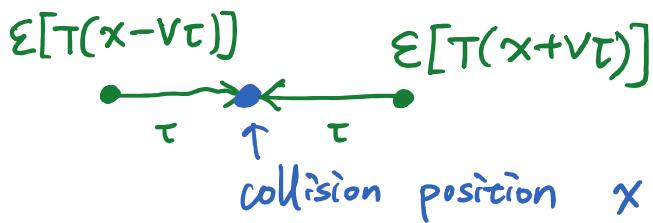


Warmer region: larger electron (average) speed

thermal energy per electron (1D) :

$$\varepsilon(T) = \frac{1}{2}mv^2 = \frac{1}{2}k_B T \quad (3D: \frac{1}{2}mv^2 = \frac{3}{2}k_B T)$$

$\curvearrowleft T \text{ is now position dependent!}$



Energy flow per electron :

$$\varepsilon[T(x-v\tau)] - \varepsilon[T(x+v\tau)]$$

(length: $v\tau$ $v\tau$)

of electrons: $\sum_{\text{from left}}^{\text{from right}} \frac{1}{2}n v\tau$

electron density: $n = \frac{N_e}{L}$

\Rightarrow energy transport within time τ :

$$E^q = \frac{n}{2} v \tau \left(\varepsilon[T(x-v\tau)] - \varepsilon[T(x+v\tau)] \right)$$

\Rightarrow thermal current (energy transport per unit time):

$$J^q = \frac{E^q}{\tau} = \frac{n}{2} v \left(\varepsilon[T(x-v\tau)] - \varepsilon[T(x+v\tau)] \right)$$

Assumption: mean free path $\lambda = v\tau$ small

$$J^q = \frac{1}{2} n v \left(\varepsilon[\tau(x-v\tau)] - \varepsilon[\tau(x+v\tau)] \right)$$

$$= \frac{1}{2} n v \cdot (-2v\tau) \frac{d\varepsilon}{dx}$$

$$= -n v^2 \tau \frac{d\varepsilon}{dT} \cdot \frac{dT}{dx} \quad \leftarrow n \frac{d\varepsilon}{dT} = \frac{N}{L} \frac{d\varepsilon}{dT} = \frac{1}{L} \frac{d\varepsilon}{dT}$$

From 1D to 3D: $= C_v$ (heat capacity)

$$\frac{dT}{dx} \rightarrow \vec{\nabla} T$$

$$\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \frac{1}{3} v^2$$

$$\Rightarrow J^q = \frac{1}{3} v^2 \tau n \frac{d\varepsilon}{dT} \cdot (-\vec{\nabla} T)$$

$$\frac{N}{V} \frac{d\varepsilon}{dT} \stackrel{||}{=} \frac{1}{V} \frac{dE}{dV} = C_V \quad \begin{array}{l} E = N\varepsilon : \text{total} \\ \text{internal energy} \end{array}$$

$$\Rightarrow J^q = k (-\vec{\nabla} T) \quad \begin{array}{l} \text{heat capacity} \end{array}$$

$$\text{with } k = \frac{1}{3} v^2 \tau C_V \quad (\text{thermal conductivity})$$

Wiedemann-Franz law:

$$\frac{k}{\sigma} = \frac{\frac{1}{3} v^2 \tau C_V}{\frac{n e^2 \tau}{m}} = \frac{\frac{1}{3} n v^2 C_V}{n e^2}$$

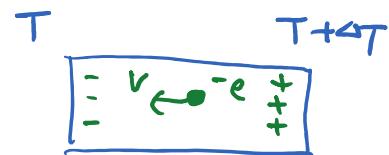
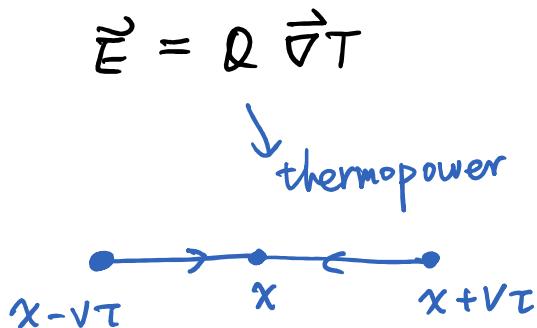
$$C_V = \frac{3}{2} n k_B, \frac{1}{2} m v^2 = \frac{3}{2} k_B T \quad \text{universal!}$$

classical!

$$= \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T$$

- Thermolectric effect

Heat flow generates electric field!



$$\begin{aligned} v^2 &= \frac{1}{2} [v(x-v\tau) - v(x+v\tau)] \\ &= \frac{1}{2} \cdot (-2v\tau) \frac{dv}{dx} \\ &= -v\tau \frac{dv^2}{dx} \\ &= -\frac{1}{2} \tau \frac{dv^2}{dT} \cdot \frac{dT}{dx} \end{aligned}$$

("net" velocity
at position x
due to the
temperature
gradient)

From 1D to 3D: $v_x^2 = v_y^2 = v_z^2 = \frac{1}{3} v^2$

$$\Rightarrow v^2 = -\frac{1}{6} \tau \frac{dv^2}{dT} (\vec{\nabla} T)$$

$$\underbrace{\vec{v}}_{\text{constant}} = -\frac{e \vec{E} \tau}{m}$$

due to the acceleration from thermally generated \vec{E}

Steady state: $\vec{v}^g + \vec{v}^E = 0$

$$\Rightarrow \frac{e\vec{E}\tau}{m} = -\frac{\tau}{6} \frac{dV^2}{dT}(\vec{\nabla}T)$$

$$\vec{E} = -\frac{1}{6} \frac{m}{e} \frac{dV^2}{dT}(\vec{\nabla}T)$$

$$= -\frac{1}{3e} \frac{d}{dT} \left(\frac{3}{2} k_B T \right) (\vec{\nabla}T) \quad \begin{matrix} \text{use } \frac{1}{2} m V^2 = \frac{3}{2} k_B T \\ C_V = \frac{3}{2} n k_B \end{matrix}$$

$$= -\frac{C_V}{3ne} (\vec{\nabla}T)$$

$$\text{thermopower } Q = -\frac{C_V}{3ne}$$

$$C_V = \frac{3}{2} n k_B$$

$$\Rightarrow Q = -\frac{k_B}{2e} \sim 10^{-4} \text{ volt/k}$$

10^2 times larger compared to experiments!

* Sommerfeld's theory

Electron velocity distribution in Drude's theory:

$$f_B(\vec{v}) \propto e^{-\frac{1}{2}mv^2/k_B T}$$



Boltzmann distribution

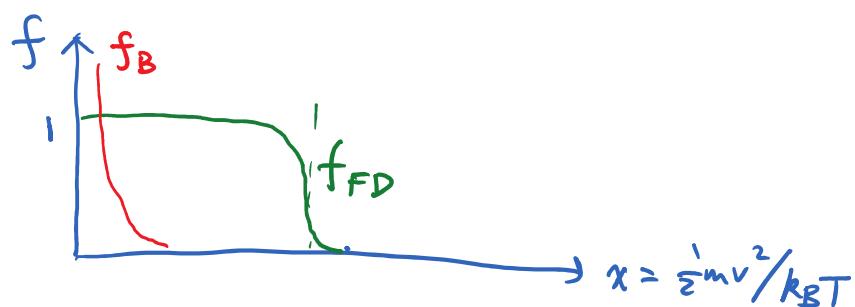
(electrons treated as classical particles)

$$\rightarrow f_{FD}(\vec{v}) \propto \frac{1}{e^{(\frac{1}{2}mv^2 - k_B T_0)/k_B T} + 1}$$



Fermi-Dirac distribution
(Quantum treatment)

$$\int f(\vec{v}) d\vec{v} = n = \frac{N}{V}$$



Sommerfeld's approach:

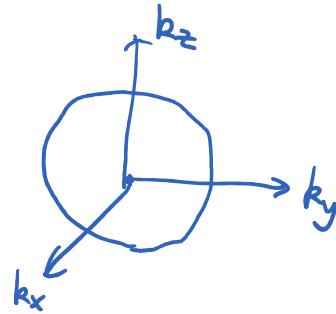
free electron gas + Fermi-Dirac distribution

$$E_{\vec{k}} = \frac{\frac{1}{2} \hbar^2 k^2}{2m}$$

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot \vec{r}}$$

momentum: $\vec{p} = \frac{i}{\hbar} \vec{\nabla}$

$$\Rightarrow \vec{p} \psi_{\vec{k}}(\vec{r}) = \frac{i}{\hbar} \vec{\nabla} \psi_{\vec{k}}(\vec{r}) = \underbrace{\hbar \vec{k}}_{\text{momentum of a single electron}} \psi_{\vec{k}}(\vec{r})$$



velocity: $\vec{v} = \frac{\vec{p}}{m}$

$$\vec{v} \psi_{\vec{k}}(\vec{r}) = \frac{\hbar \vec{k}}{m} \psi_{\vec{k}}(\vec{r})$$

\downarrow velocity of a single electron

Work out $f(\vec{v}) d\vec{v}$ (velocity distribution)

Each \vec{k} point has volume $\frac{(2\pi)^3}{V}$

DOS in \vec{k} -space: $2 \times \frac{1}{(2\pi)^3/V} d\vec{k}$ ($T=0$)

Finite T: $2 \times \frac{V}{(2\pi)^3} f_{FD}(\epsilon_{\vec{k}}) d\vec{k}$

probability of the \vec{k} -point being occupied

$$\vec{v} = \frac{\hbar \vec{k}}{m} \Rightarrow d\vec{k} = \left(\frac{m}{\hbar}\right)^3 d\vec{v}, \quad \epsilon_{\vec{k}} = \frac{\frac{1}{2} \hbar^2 k^2}{2m} = \frac{1}{2} m \vec{v}^2$$

$$\Rightarrow 2 \times \frac{V}{(2\pi)^3} \frac{1}{e^{(\frac{1}{2} m \vec{v}^2 - \mu)/k_B T} + 1} \left(\frac{m}{\hbar}\right)^3 d\vec{v}$$

$$f(\vec{v}) = \frac{m^3 V}{4\pi^3 \hbar^3} \frac{1}{e^{(\frac{1}{2} m \vec{v}^2 - \mu)/k_B T} + 1}$$

Semiclassical description valid?
 electrons treated as wave packets



$$v = \frac{\hbar k_F}{m}$$

$\Delta p \ll \hbar k_F$ only those electrons close to the Fermi energy are important.

uncertainty principle:

$$\Delta x \cdot \Delta p \sim \hbar$$

$$\Rightarrow \Delta x \sim \frac{\hbar}{\Delta p} \gg \frac{1}{k_F} \simeq 10^{-10} \text{ m}$$

\downarrow

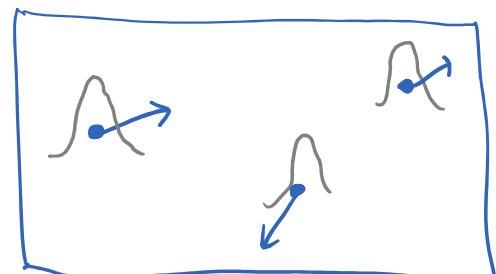
\sim size of a unit cell

Mean free path:

$$l \simeq v_F \tau$$

$\sim 10^{-8} \text{ m}$ $\sim 10^{-14} \text{ s}$

(room temperature)



- 1) size of electron wave packet \gg size of a unit cell
- 2) mean free path \gg ...



Semiclassical treatment valid!

Thermal conductivity:

$$\kappa = \frac{1}{3} v^2 T C_V$$

\downarrow

$$v_F^2 = \frac{2\epsilon_F}{m}$$

$\sim \rightarrow$

$$\frac{\pi^2}{2} n k_B \left(\frac{k_B T}{\epsilon_F} \right) \text{ vs. Drude value } \frac{3}{2} n k_B$$

vs. Drude value $v^2 = \frac{3k_B T}{m}$

$$= \frac{\pi^2}{3} \frac{\tau}{m} n k_B^2 T$$

[see also electron-2.pdf
for the derivation of C_V]

Niedermann - Franz law (Sommerfeld theory)

$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 T$$

$\sim \rightarrow$

$$(\text{Drude value: } \frac{3}{2})$$

much more accurate now!

Thermopower:

$$Q = - \frac{C_V}{3ne} \quad \leftarrow C_V = \frac{\pi^2}{2} n k_B \left(\frac{k_B T}{\epsilon_F} \right)$$

$$= - \frac{1}{6} \frac{k_B}{e} \left(\frac{k_B T}{\epsilon_F} \right)$$

$$\sim - \left(\frac{T}{T_F} \right) \times 10^{-4} \text{ volt/K} \quad \checkmark$$

$\rightarrow 10^2 \text{ K}$
 $\rightarrow 10^4 \text{ K}$