

Electronic structure

Free electron gas

Phonons only account partial properties of crystals. To account many other properties, such as electrical conduction, we need to include electrons.

As we indicated from the beginning, the total Hamiltonian for condensed matter system

$$\hat{H} = \sum_n \frac{\hat{p}_n^2}{2M_n} + \frac{1}{2} \sum_{n \neq n'} \frac{q_n q_{n'}}{|\vec{r}_n - \vec{r}_{n'}|}$$

Where summation over both atoms/ions and electrons.

In reality, total # of $n \sim 10^{23}$ but our ability (by using computers) can only deal with

10-20 particles! Hence, to explain electronic

properties associated with crystals, approximations

must be made.

In the simplest model, one assumes that each atom contributes Z conduction electrons

and becomes Z^+ . Electrons are treated.

Classically, This is the Drude model

The Drude model

of ^{conduction} electrons is usually measured by

$n = \frac{N}{V}$ $N = \# \text{ of electrons}$

$\frac{V}{N} = \frac{1}{n} = \frac{4\pi}{3} r_s^3$

$r_s = \text{radius of sphere}$

whose volume = volume per electron

Usual metal (alkali)

$n \sim 10^{22} - 10^{23} \text{ cm}^{-3}$

$\frac{r_s}{a_0} \sim 2-3$ $a_0 = \text{Bohr radius} = 0.529 \text{ \AA}$



example: $\text{Na} \rightarrow \text{Na}^+ + e^-$
 Alkali metal \uparrow conduction electron
 Diagram: $e^- \rightarrow$ and $e^- \rightarrow$ above three '+' signs, with a double-headed arrow below labeled 1.83 \AA .

Nobel metals, Cu, Ag, Au
 $\rightarrow \text{Cu}^+ + e^-$

Drude applied kinetic theory to the conduction electrons by assuming electrons move in a static ionic background classically.

(i) interaction with ions : collisions
 , instantaneously happen , neglect ion-e attraction

(ii) neglect e-e interaction :
 between collisions , governed by Newton's law

$m \frac{d\vec{v}}{dt} = (-e) (\vec{E} + \vec{v} \times \vec{B})$

(iii) electron experiences a collision with

the probability = $\frac{1}{\tau}$ per unit time

During dt , $P = \frac{dt}{\tau}$

τ = relaxation time, $l = \langle v \rangle \tau$ = mean free path

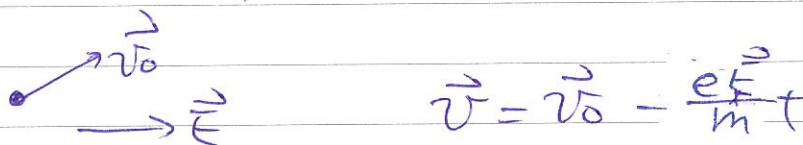
(Simplest Drude model, τ is independent of electron's speed & position.)

(iv) thermalization: after collisions, electron's velocity is totally random, not related to its previous velocity (before collision) in any way.

But speed has to be consistent with local temperature. $T \uparrow$, $v \uparrow$

DC electrical conductivity of a metal

In the Drude model, electrons get accelerated by \vec{E} after collision:



$$\vec{v} = \vec{v}_0 - \frac{e\vec{E}}{m}t$$

$\therefore \tau$ = average collision time, $\vec{v}_{\text{ave}} = \vec{v}_0 - \frac{e\vec{E}}{m}\tau$

As we shall see, experiments show $\langle v \rangle$

is actually almost temperature independent!

real $\langle v \rangle$ is much larger $\sim 10 \times 10^7$ cm/sec

Furthermore, ℓ can be much larger

in some cases, ℓ can even go to $10^8 \text{ \AA}!$

AC electric conductivity of a metal

The Drude model also predicts AC electric

conductivity $\sigma(\omega)$ that can be measured by optical methods.

At $t+dt$, fraction of electrons that do

not collide = $1 - \frac{dt}{\tau}$

These electrons acquire an 'additional

momentum $\vec{p}(t) dt$ $\vec{F}(t) = \text{force}$

\therefore If $\vec{p}(t) = \overbrace{\text{average}}^{\text{average}}$ momentum of electron at t ,

$$\vec{p}(t+dt) = \frac{dt}{\tau} \times \langle \vec{p}_0 \rangle + \left(1 - \frac{dt}{\tau}\right) (\vec{p}(t) + \vec{F}(t) dt)$$

no collision
= 0

$$\therefore \vec{p}(t+dt) = \vec{p}(t) - \frac{dt}{\tau} \vec{p}(t) + \vec{F}(t) dt$$

Each electron has different \vec{v}_0 , therefore

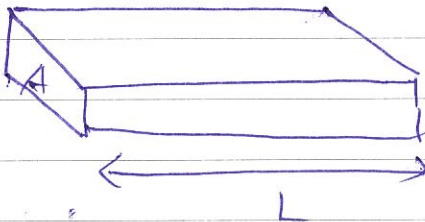
$$\vec{j} = n(-e) \langle \vec{v}_{ave} \rangle$$

$$= n(-e) \left(\frac{-e\tau}{m} \vec{E} \right) = \frac{ne^2\tau}{m} \vec{E} = \Delta \vec{E}$$

\uparrow
 $\langle \vec{v}_0 \rangle = 0$

$$\therefore \Delta = \frac{ne^2\tau}{m}, \quad \rho = \frac{1}{\Delta} = \frac{m}{ne^2\tau} \quad \dots \textcircled{1}$$

ρ is measured by $V = IR$



$$\vec{E} = \rho \vec{j}$$

$$V = EL = \rho L j = \rho L \frac{IA}{A} = \frac{\rho L}{A} I$$

$$R = \rho \frac{L}{A} \quad [\text{ohm}]$$

In the Drude model, τ (ρ) is unknown. However, given measured ρ & n , one can deduce

τ and then $\lambda = \langle v \rangle \tau$ by using

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

Expts. $\tau \sim 10^{-14} \text{ sec} - 10^{-15} \text{ sec}$

$$\left(\frac{0.22}{\rho} \left(\frac{ks}{ao} \right)^3 \times 10^{-14} \text{ sec} \right)$$

$\langle v \rangle \approx 10^7 \text{ cm/sec}$ at room temperature

$\lambda \sim 10^{-8} \text{ m} \approx \text{interatomic spacing}$

$$\therefore \frac{d\vec{p}}{dt} = -\frac{\vec{p}(t)}{\tau} + \vec{f}(t)$$

$$\text{For } \vec{f}(t) = (-e)\vec{E}(t),$$

$$(i\omega)\vec{p}(\omega) = -\frac{1}{\tau}\vec{p}(\omega) - e\vec{E}(\omega)$$

$$\therefore \vec{p}(\omega) = \frac{-e\vec{E}(\omega)}{\frac{1}{\tau} - i\omega}$$

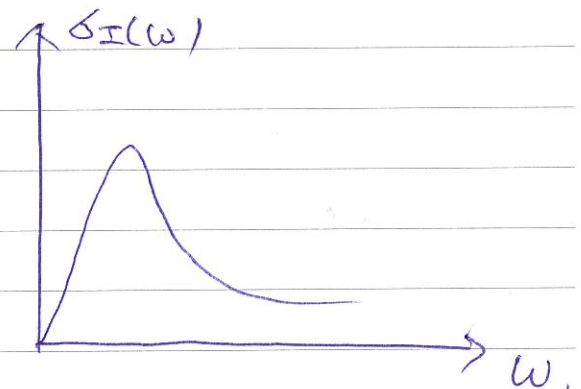
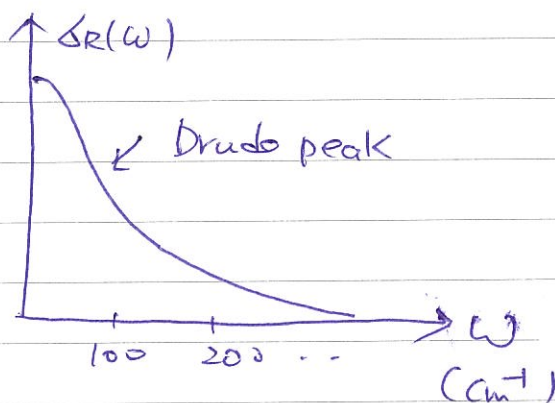
$$\therefore \vec{J}(t) = \frac{n(-e)}{m}\vec{p}(t), \quad \therefore \vec{J}(\omega) = -\frac{ne\vec{p}(\omega)}{m}$$

$$= \frac{ne^2\vec{E}(\omega)}{\frac{1}{\tau} - i\omega} \equiv \sigma(\omega)\vec{E}(\omega)$$

$$\therefore \sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau} \quad \sigma_0 = \frac{ne^2\tau}{m}$$

$$\sigma_R(\omega) = \frac{\sigma_0}{1 + \omega^2\tau^2} \quad \left(\int_0^\infty \sigma_R(\omega) d\omega = \frac{\pi ne^2\tau}{2m} \right)$$

$$\sigma_I(\omega) = \frac{\omega\tau\sigma_0}{1 + \omega^2\tau^2}$$



The Drude peak is a character of metal.

It is often exhibited in optical measurement in

which measurement of dielectric constant $\epsilon(\omega)$

is done.

Using Maxwell's equations,

$$\nabla \times (\nabla \times \vec{E}) = \nabla \times \left(-\frac{1}{c} \frac{d\vec{H}}{dt} \right)$$

$$\Rightarrow \nabla^2 \vec{E} = \frac{i\omega}{c} \nabla \times \vec{H} \quad \text{--- (2)}$$

$$\because \nabla \times \vec{H} = \frac{4\pi}{c} \vec{J} + \frac{1}{c} \frac{d\vec{D}}{dt}$$

$$\therefore \nabla \times \vec{H} = \frac{4\pi\sigma(\omega)}{c} \vec{E} - \frac{i\omega}{c} \vec{E}$$

$$\text{(2)} \Rightarrow -\nabla^2 \vec{E} = \frac{\omega^2}{c^2} \left(1 + \frac{4\pi i\sigma}{\omega} \right) \vec{E} \equiv \frac{\omega^2}{c^2} \epsilon(\omega) \vec{E}$$

$$\therefore \epsilon(\omega) = 1 + \frac{4\pi i\sigma(\omega)}{\omega}$$

By measuring reflectance and transmission, one can deduce $\epsilon(\omega)$ and hence $\sigma(\omega)$

(optical conductivity) in the optical frequency regime.

The AC Drude model neglects spatial variations and Lorentz force: $\frac{e\hbar}{c} \nabla \times \vec{H}$.

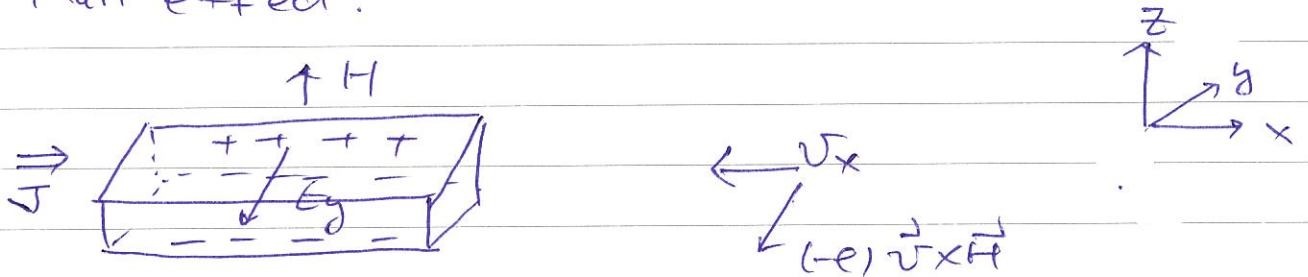
Hence it is valid only when $\lambda \gg \ell$

The neglect of Lorentz force, however,

is valid as $\frac{v}{c}$ makes it smaller than \vec{E} !

Hall effect & magneto resistance

In the presence of a static magnetic field, Drude also predicts metals have Hall effect.



magneto resistivity : $\rho(H) \equiv \frac{E_x}{J_x}$

Hall coefficient : $R_H = \frac{E_y}{J_x H}$ ($J_y = 0$, steady)

$$\vec{f} = -e \left(\vec{E} + \frac{\vec{p}}{mc} \times \vec{H} \right)$$

$$\therefore \frac{d\vec{p}}{dt} = (-e) \left(\vec{E} + \frac{1}{mc} \vec{p} \times \vec{H} \right) - \frac{1}{\tau} \vec{p}$$

Steady state : $\frac{d\vec{p}}{dt} = 0$

$$0 = -eE_x - \omega_c p_y - \frac{1}{\tau} p_x$$

$$0 = -eE_y + \omega_c p_x - \frac{1}{\tau} p_y$$

$$\omega_c = \frac{eH}{mc}$$

= cyclotron frequency

$$\times \left(\frac{he^2}{m} \right)$$

$$\Rightarrow \sigma_0 E_x = \tau \omega_c J_y + J_x$$

$$\sigma_0 E_y = -\tau \omega_c J_x + J_y$$

, $\sigma_0 = \text{Drude DC}$

$$\text{Conductivity} = \frac{ne^2 \tau}{m}$$

$$\vec{E} = \vec{\rho} \cdot \vec{j}, \quad \vec{\rho} = \begin{pmatrix} \frac{1}{\sigma_0} & \frac{\omega c z}{\sigma_0} \\ -\frac{\omega c z}{\sigma_0} & \frac{1}{\sigma_0} \end{pmatrix}$$

$$\vec{j} = \vec{\sigma} \cdot \vec{E}, \quad \vec{\sigma} = \vec{\rho}^{-1} = \frac{\sigma_0}{H(\omega c z)^2} \begin{pmatrix} 1 & -\omega c z \\ \omega c z & 1 \end{pmatrix}$$

$$j_y = 0, \quad \rho(H) = \frac{1}{\sigma_0}$$

$$R_H = \frac{E_y}{j_x H} = \frac{-\omega c z}{\sigma_0 H} = -\frac{1}{nec}$$

\therefore Both $\rho(H)$ & R_H are independent of H .

In general, however, R_H (expt.) depends on $\rho(H)$

H . (for instance, quantum Hall effect.)

Wiedemann-Franz empirical law

In the Drude model, $\sigma = \frac{ne^2\tau}{m}$

but it also predicts that for thermal conductivity, $\kappa = \frac{1}{3} e v C_v$ $l = \langle v \rangle \tau$

$$\therefore \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \quad = \frac{1}{3} \tau v^2 C_v$$

$$\langle v \rangle = \frac{\sqrt{\frac{3}{2} k_B T}}{\sqrt{m}} = \sqrt{\frac{3}{2} k_B T / m}$$

$$\frac{\kappa}{\sigma} = \frac{\frac{1}{3} v^2 C_v}{\frac{ne^2\tau}{m}} = \frac{\frac{1}{3} m v^2 C_v}{ne^2\tau} = \frac{\frac{2}{3} \times \frac{3}{2} k_B T \cdot \frac{3}{2} n k_B}{ne^2\tau}$$

$$= \frac{3}{2} \left(\frac{k_B}{e}\right)^2 \frac{1}{T} \therefore \frac{\kappa}{\sigma T} = \frac{3}{2} \left(\frac{k_B}{e}\right)^2$$

$$= 1.11 \times 10^8 \text{ watt-ohm/k}^2$$

This seems to explain the empirical

Wiedemann - Franz Law : $\frac{\kappa}{\sigma T} \approx \text{const.}$

	273K	313	
Li	2.22	2.43	(10^8 watt-ohm/ K^2)
Na	2.12		
K	2.23		
Rb	2.42		
Cu	2.20	2.29	
Pb	2.64	2.53	
Al	2.14	2.19	
Fe	2.61	2.88	
Zn	2.28	2.30	

Drude originally predicted $\frac{\kappa}{\sigma T} = 2.22 \times 10^8$ (watt-ohm/ K^2) due to an error, but the prediction $\frac{\kappa}{\sigma T} \approx T$ -independent seems to be correct.

However, the result is based on $C_V = \frac{3}{2} n k_B$ for relations and this was not found in specific heat measurement at room temperature

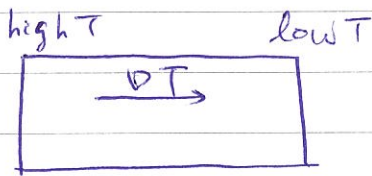
Then, how would it be possible for $\frac{\kappa}{\sigma T} \approx T$ -independent?

It turns that two errors cancel out from each other so that $\frac{\kappa}{\sigma T}$ is roughly correct:
room temperature : $C_V \approx \frac{1}{1.5} \times \frac{3}{2} n k_B$

$v^2 \approx \frac{1}{1.5} \langle v^2 \rangle_{\text{classical}}$

Thermal power

As we have seen, when a temperature gradient ΔT is applied, electrons will tend to move from high T to low T . This is often done in an open circuit.



However, since electrons carry charges, eventually charges will be accumulated so that

an electric field \vec{E} opposite to ΔT is

built. $\vec{E} = \alpha \Delta T$ $\alpha \equiv$ thermal power, (the Seebeck effect) (thermo electric effect)

To estimate α , we note that at x , the

velocity due to temperature gradient is

$$v_{\theta} = \frac{1}{2} (v_x(x-vz) - v_x(x+vz))$$

$$\begin{array}{c} \leftarrow \frac{1}{2} \rightarrow \frac{1}{2} \quad \leftarrow \frac{1}{2} \rightarrow \frac{1}{2} \\ \underbrace{\hspace{10em}} \\ v_z \quad x \quad v_z \end{array}$$

$$= -v_z \frac{dv_x}{dx}$$

$$= -z \frac{d}{dx} \frac{1}{2} v_x^2$$

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

$$\therefore v_{\theta} = -\frac{z}{6} \frac{d}{dx} v^2 \Rightarrow -\frac{z}{6} \frac{dv^2}{dT} \Delta T$$

On the other hand, the velocity due to the acceleration of \vec{E} , is $\vec{v}_E = -\frac{e\vec{E}z}{m}$

$$\therefore \vec{v}_{\theta} + \vec{v}_E = 0 \text{ in equilibrium} \quad \therefore \vec{E} = \left[\frac{-1}{3e} \frac{d}{dT} \left(\frac{1}{2} m v^2 \right) \right] \Delta T$$

$$\theta = \frac{1}{3e} \frac{d}{dT} \left(\frac{1}{2} m v^2 \right) = -\frac{Cv}{3ne}$$

In the Drude model, $Cv = \frac{3}{2} nk_B$

$$\therefore \theta = -\frac{k_B}{2e} = -0.43 \times 10^{-4} \text{ volt/K}$$

Which is 100 smaller than experimental value at room temperature!

In this case, unlike $\frac{k}{\delta T}$, the error is not cancelled!

Failures of classical theory

(i) ρ can be as large as 10^8 a
while $\rho \sim A^0$ in the Drude model

(ii) $\frac{k}{\delta T}$ is not correct
value of

(iii) heat capacity, $\rho \sim \frac{1}{100}$ expt value
(room temperature)

The question is then: how could electrons contribute to electric conduction but not to heat capacity?

The Sommerfeld theory of metals

An obvious extension of the Drude theory is to include quantum statistics. In resolving the issue of specific heat for crystals, we have seen that quantization (phonons) is essential to explain why C_v is not $\frac{3}{2}k_B$.

For the same reason, one expects that including quantum nature of electrons may resolve some issues based on classical of the Drude model mechanics.

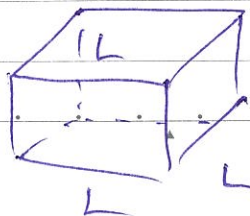
In the Sommerfeld theory of metals, one replaces the Boltzmann distribution

$$e^{-\beta \frac{mv^2}{2}} \text{ by}$$

$$f(\epsilon) = \frac{1}{e^{\frac{\epsilon - \mu}{k_B T}} + 1} \quad \text{and assumes}$$

that electrons are otherwise free.

Therefore, electrons are considered in a box of $L \times L \times L$ (or $L \times L$ in 2D, L in 1D) in which they move freely.



Since except Pauli exclusion principle, electrons do not interact. One refers it as free electron gas.

Electronic states:

The wavefunction of an electron $\psi(\vec{r})$ satisfies

$$\frac{\hbar^2}{2m} \nabla^2 \psi = \epsilon \psi(\vec{r})$$

$$\therefore \psi(\vec{r}) = A e^{i\vec{r}\cdot\vec{k}} \quad \text{with} \quad \epsilon = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

For real systems, realistic solutions are

$$\psi(\vec{r}) = A \sin k_x x \sin k_y y \sin k_z z$$

$$\text{So that } \psi(0, y, z) = \psi(L, y, z) = 0$$

$$\psi(x, 0, z) = \psi(x, L, z) = 0$$

$$\psi(x, y, 0) = \psi(x, y, L) = 0$$

These are known as open boundary conditions.

Hence

$$\sin k_x L = 0$$

$$\sin k_y L = 0$$

$$\sin k_z L = 0$$

$$k_x L = l\pi$$

$$k_y L = m\pi$$

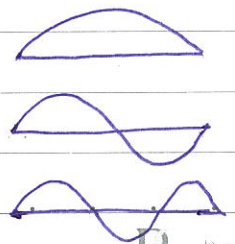
$$k_z L = n\pi$$

$$l, m, n,$$

$$= 1, 2, 3, \dots$$

$$\epsilon = \frac{\hbar^2 (\pi)^2}{2m L^2} (l^2 + m^2 + n^2)$$

These solutions represent standing waves

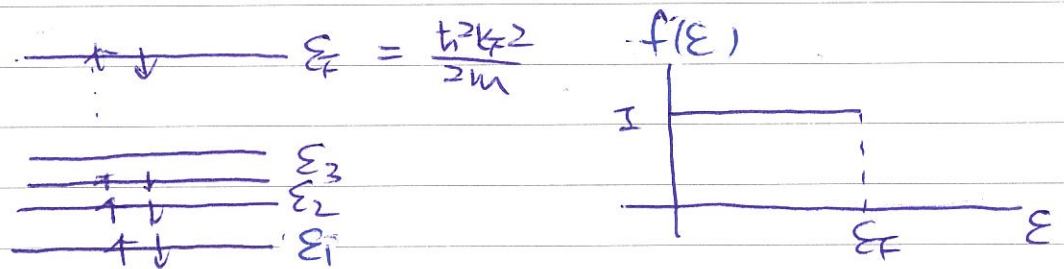


Each level can accommodate two electrons for

$$m_s = \pm 1/2 \quad (\text{spin } \uparrow \text{ and } \downarrow)$$

Therefore, at $T=0$, electrons fill up to an energy E_F , called Fermi energy.

with $E_F = \frac{\hbar^2 k_F^2}{2m}$, $k_F =$ Fermi wave number
 $\lambda_F =$ " " length

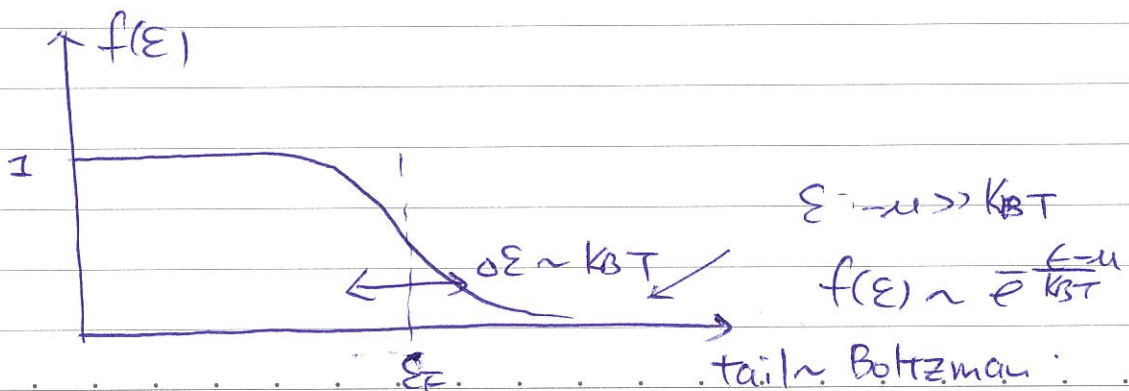


It's clear that as # of electrons (density n of electrons) goes up, k_F goes up!

For finite temperatures, the distribution $f(E)$ becomes the Fermi-Dirac distribution

$$f(E) = \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1}$$

$$\mu = \mu(T) \rightarrow E_F \quad \text{as } T \rightarrow 0$$



In general, the contribution from the boundaries $\sim O(L^2)$.

In the limit $L \rightarrow \infty$, $\frac{O(L^2)}{L^3} \rightarrow 0$. Therefore,

the boundary condition does not affect bulk properties. One can choose convenient

boundary conditions.

The periodic boundary condition is often adopted for this purpose. One requires

$$\psi(x+L, y, z) = \psi(x, y, z)$$

$$\psi(x, y+L, z) = \psi(x, y, z)$$

$$\psi(x, y, z+L) = \psi(x, y, z)$$

$$\psi = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \quad V = L \times L \times L = L^3, \quad L = Na$$

So that $\int_V |\psi|^2 d^3r = 1$

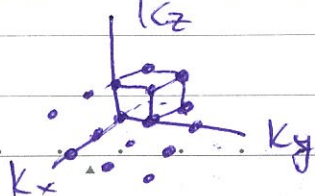
BC. $e^{ik_x L} = 1, \quad e^{ik_y L} = 1, \quad e^{ik_z L} = 1$

$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}$$

$$n_x, n_y, n_z = 0, 1, 2, \dots, N-1, \quad \epsilon_k = \frac{\hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

\therefore In the k space, allowed (k_x, k_y, k_z) form a

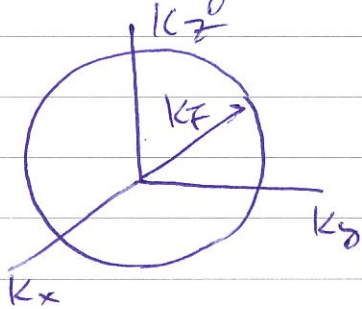
lattice with unit cell = $(\Delta k) = \left(\frac{2\pi}{L}\right)^3$



\therefore # of allowed k per volume V .

$$k \text{ space} = \frac{V}{8\pi^3}$$

For large V , E_F can be estimated



$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

$$2 \cdot \frac{4\pi}{3} k_F^3 \cdot \frac{V}{8\pi^3} = N$$

$$\therefore \frac{k_F^3}{3\pi^2} = \frac{N}{V} = n \quad \left\{ \begin{array}{l} k_F \propto n^{1/3} \quad 3D \\ k_F = (2\pi n)^{1/2} \quad 2D \\ k_F = \frac{\pi}{2} n \quad 1D \end{array} \right.$$

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} (3\pi^2 n)^{2/3}$$

$$\frac{V}{N} = \frac{1}{n} = \frac{4\pi r_s^3}{3}, \quad k_F = \frac{1.9}{r_s}$$

Normally, one defines

$$E_F = k_B T_F$$

↑

Fermi temperature

$$T_F \sim 10^4 \text{ K (1eV.) (e.g. Li, } 5.48 \times 10^4 \text{ K}$$

$$\text{Na, } 3.75 \times 10^4 \text{ K)}$$

$$v_F \sim 10^8 \frac{\text{cm}}{\text{sec}} \quad (100 \times 10^6 \text{ cm/sec in the Drude model!)$$

The increase of v_F is obviously due to

Fermi-Dirac distribution! (Fermi statistics)

In addition to E_F & v_F , one can find

the total energy.

One notes that $\therefore \Delta^3 \vec{k} = \frac{(2\pi)^3}{V}$ $\therefore \frac{(2\pi)^3}{V} \Delta^3 \vec{k} = 1$

For any $F(\vec{k})$

$$\sum_{\vec{k}} F(\vec{k}) = \frac{V}{(2\pi)^3} \sum_{\vec{k}} F(\vec{k}) \Delta^3 \vec{k}$$

$$\therefore \frac{1}{V} \sum_{\vec{k}} F(\vec{k}) = \int_{V \rightarrow \infty} \frac{d^3 \vec{k}}{(2\pi)^3} F(\vec{k})$$

i.e. $\sum_{\vec{k}} F(\vec{k})$ is extensive

For example, $E = 2 \sum_{\vec{k} < k_F} \frac{\hbar^2 k^2}{2m}$

$$\frac{E}{V} = \frac{1}{4\pi^3} \int_{\vec{k} < k_F} d^3 \vec{k} \frac{\hbar^2 k^2}{2m}$$

$$= \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}$$

$$\frac{N}{V} = 2 \int_{\vec{k} < k_F} \frac{d^3 \vec{k}}{(2\pi)^3} = \frac{k_F^3}{3\pi^2}$$

$$\therefore \frac{E}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} E_F$$

\therefore energy per electron = $\frac{3}{5} k_B T_F$ $T_F \sim 10^4 \text{K}$

in contrast to classical result $\langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} k_B T$

From E , one can calculate pressure

$$P = -\left(\frac{\partial E}{\partial V}\right)_N = -\frac{3}{5} \left(\frac{\partial E_F}{\partial V}\right)_N N$$

$$\therefore E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V}\right)^{2/3}$$

$$\left(\frac{\partial E_F}{\partial V}\right)_N = -\frac{2}{3} \frac{E_F}{V}$$

$$\therefore P = \frac{2}{5} \frac{N}{V} E_F = \frac{2}{3} \frac{E}{V}$$

Therefore, unlike classical electrons, in which

$P=0$ ($PV=NR$) at $T=0$, electrons

are fermions and $P \neq 0$ at $T=0$.

This pressure is a character of fermions and is responsible for existence of white Dwarf stars & neutron stars.

To analyze electron gases at finite T ,

it's convenient to introduce the quantity

density of states (DOS)

$$D(E) = \sum_{\substack{\uparrow \\ \downarrow}} \sum_{\mathbf{k}} \delta(E - E_{\mathbf{k}}) = \frac{2V}{(2\pi)^d} \int d^d \mathbf{k} \delta(E - E_{\mathbf{k}})$$

\uparrow
Spin $\uparrow +$ Spin \downarrow

To calculate $D(E)$, one can also calculate

$$N(E) = \int_{-\infty}^E D(E') dE' \quad (\# \text{ of states } \leq E)$$

$$= \frac{2V}{(2\pi)^d} \int_{\frac{\hbar^2 k^2}{2m} \leq E} d^d k \quad (k < \sqrt{\frac{2mE}{\hbar^2}}), \quad D(E) = \frac{dN(E)}{dE}$$

For $d=3$,

$$N(E) = \frac{2V}{(2\pi)^3} \times \frac{4\pi}{3} \left(\sqrt{\frac{2mE}{\hbar^2}} \right)^3$$

$$= \frac{V}{3\pi^2} \left(\frac{2mE}{\hbar^2} \right)^{3/2}$$

$$\therefore D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} = \frac{3V}{2E_F} \left(\frac{E}{E_F} \right)^{1/2}$$

Similarly, $d=2$,

$$N(E) = \frac{2V}{(2\pi)^2} \pi \times \frac{2mE}{\hbar^2} = \frac{mV}{\pi \hbar^2} E$$

$$\therefore D(E) = \frac{dN}{dE} = \frac{mV}{\pi \hbar^2} = \text{constant}, \quad V = \text{Area}$$

$d=1$

$$N(E) = \frac{2V}{(2\pi)} \times 2 \times \sqrt{\frac{2mE}{\hbar^2}}$$

$$= \frac{2V}{\pi} \left(\frac{2m}{\hbar^2} \right)^{1/2} E^{1/2}$$

$$D(E) = \frac{dN}{dE} = \frac{V}{\pi} \left(\frac{2m}{\hbar^2} \right)^{1/2} E^{-1/2}$$

For $T \neq 0$ $\mu = \mu(T) \neq E_F$

$$E = 2 \sum_K \epsilon_K f(\epsilon_K), \quad f(\epsilon) = \frac{1}{e^{\frac{\epsilon - \mu}{k_B T}} + 1}$$

$$= \int d\epsilon \left[2 \sum_K \delta(\epsilon - \epsilon_K) \right] \epsilon f(\epsilon)$$

$$= \int_{-\infty}^{\infty} d\epsilon \epsilon D(\epsilon) f(\epsilon)$$

$$u \equiv \frac{E}{N} = \int_{-\infty}^{\infty} d\epsilon \epsilon g(\epsilon) f(\epsilon)$$

$$g(\epsilon) \equiv \frac{D(\epsilon)}{V} = \frac{m}{h^2 \pi^2} \sqrt{\frac{2m\epsilon}{h^2}} = \frac{3}{2} \frac{n}{\epsilon_F} \left(\frac{\epsilon}{\epsilon_F}\right)^{\frac{1}{2}} \quad \epsilon > 0$$

$$= 0$$

$$\epsilon < 0$$

Similarly,

$$n = \frac{N}{V} = \int_{-\infty}^{\infty} \epsilon g(\epsilon) f(\epsilon) d\epsilon$$

Therefore, one needs to calculate

$$\int_{-\infty}^{\infty} H(\epsilon) f(\epsilon) d\epsilon \quad \text{--- (3)}$$

where $H(\epsilon)$ is a smooth function near

$$\epsilon = \mu.$$

Since $T=0$, $\mu = \epsilon_F \approx 10^4 \text{ K}$, room temperature

$\sim 300 \text{ K} \ll T_F$, one expects $\epsilon_F \sim \mu$ the

deviation is $(\frac{T}{T_F})^2$. The method for systematical

calculation of the correction is the

Sommerfeld expansion:

$$K(\epsilon) \equiv \int_{-\infty}^{\epsilon} H(\epsilon') d\epsilon'$$

$$\int_{-\infty}^{\infty} H(\epsilon) f(\epsilon) d\epsilon = \int_{-\infty}^{\infty} f(\epsilon) dK(\epsilon)$$

$$= K(\epsilon) f(\epsilon) \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} K(\epsilon) \frac{df}{d\epsilon} d\epsilon$$

$$f(\infty) \rightarrow 0, \quad K(-\infty) = 0$$

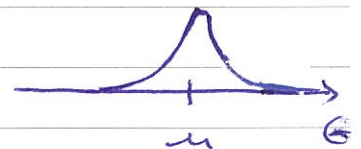
$$\frac{df}{d\epsilon} \neq 0 \text{ only for } |\epsilon - \mu| \lesssim k_B T.$$

\therefore One may expand

$$K(\epsilon) = K(\mu) + \sum_{n=1}^{\infty} \frac{(\epsilon - \mu)^n}{n!} \left. \frac{d^n K(\epsilon)}{d\epsilon^n} \right|_{\epsilon = \mu}$$

$$\therefore \int_{-\infty}^{\infty} \frac{df}{d\epsilon} d\epsilon = -1 \Rightarrow \text{1st term} = K(\mu) = \int_{-\infty}^{\mu} H(\epsilon) d\epsilon$$

$$\frac{df}{d\epsilon} = \text{even function of } \epsilon - \mu$$



\therefore only $n = \text{even}$ contributors

$$\text{Hence } \int_{-\infty}^{\infty} H(\epsilon) f(\epsilon) d\epsilon$$

$$= \int_{-\infty}^{\mu} H(\epsilon) d\epsilon + \sum_{n=1}^{\infty} \left[\int_{-\infty}^{\infty} \frac{(\epsilon - \mu)^{2n}}{(2n)!} \left(\frac{df}{d\epsilon} \right) d\epsilon \right] \left. \frac{d^{2n-1}}{d\epsilon^{2n-1}} H(\epsilon) \right|_{\epsilon = \mu}$$

$$\text{Set } \frac{\epsilon - \mu}{k_B T} = x, \quad \therefore \frac{df}{d\epsilon} = \left(-\frac{d}{dx} \frac{1}{e^x + 1} \right) \times k_B T$$

$$\therefore \int_{-\infty}^{\infty} H(\epsilon) f(\epsilon) d\epsilon = \int_{-\infty}^{\mu} H(\epsilon) d\epsilon + \sum_{n=1}^{\infty} C_n (k_B T)^{2n} \left. \frac{d^{2n-1}}{d\epsilon^{2n-1}} H(\epsilon) \right|_{\epsilon = \mu}$$

$$a_n = \int_{-\infty}^{\infty} \frac{x^{2n}}{(2n)!} \left(-\frac{d}{dx} \frac{1}{e^x + 1} \right) dx$$

$$= 2 \left(1 - \frac{1}{2^{2n}} + \frac{1}{3^{2n}} - \frac{1}{4^{2n}} + \frac{1}{5^{2n}} - \dots \right)$$

$$= \left(2 - \frac{1}{2^{2(n-1)}} \right) \zeta(2n)$$

$$\zeta(n) = 1 + \frac{1}{2^n} + \frac{1}{3^n} + \frac{1}{4^n} + \dots \quad (\text{Riemann zeta function})$$

$$a_1 = \zeta(1) = \frac{\pi^2}{6}$$

$$\therefore u = \int_0^u \epsilon g(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 [u g(u)]' + o(T^4) \quad \text{--- (4)}$$

$$n = \int_0^u g(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 g'(u) + o(T^4) \quad \text{--- (5)}$$

$$\therefore \int_0^{\epsilon_F} g(\epsilon) d\epsilon = n \quad (T=0)$$

$$\therefore \text{(5) implies } u - \epsilon_F = o(T^2)$$

$$\therefore \text{(5)} \Rightarrow \underbrace{\int_{\epsilon_F}^u g(\epsilon) d\epsilon}_n + \frac{\pi^2}{6} (k_B T)^2 g'(u) + o(T^4) = 0$$

$$(u - \epsilon_F) g(\epsilon_F) + o(T^4)$$

$$\therefore (u - \epsilon_F) g(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\epsilon_F) + o(T^4) = 0$$

$$u = \epsilon_F - \frac{\pi^2}{6} (k_B T)^2 \frac{g'(\epsilon_F)}{g(\epsilon_F)} = \epsilon_F \left[1 - \frac{1}{3} \left(\frac{\pi k_B T}{2\epsilon_F} \right)^2 \right] \quad \text{--- (6)}$$

Similarly, eq. (4) implies

$$u = \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon + \int_{\epsilon_F}^{\mu} \epsilon g(\epsilon) d\epsilon \quad \begin{matrix} \rightarrow \epsilon_F (\mu - \epsilon_F) g(\epsilon_F) \\ + O(T^4) \end{matrix}$$

$$+ \frac{\pi^2}{6} (k_B T)^2 [\epsilon_F g'(\epsilon_F) + g(\epsilon_F)] + O(T^4)$$

$$= u_0 + \epsilon_F [(\mu - \epsilon_F) g(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\epsilon_F)]$$

$$+ \frac{\pi^2}{6} (k_B T)^2 g(\epsilon_F) + O(T^4)$$

$$\rightarrow u_0 + \frac{\pi^2}{6} (k_B T)^2 g(\epsilon_F) + O(T^4)$$

eq (6)

$$\therefore C_V = \left(\frac{du}{dT} \right)_N = \frac{\pi^2}{6} k_B^2 T g(\epsilon_F) \quad \begin{matrix} \rightarrow \frac{3}{2} \frac{n}{\epsilon_F} \end{matrix}$$

$$= \frac{\pi^2}{2} \left(\frac{k_B T}{\epsilon_F} \right) n k_B = \frac{\pi^2}{2} \left(\frac{T}{T_F} \right) n k_B$$

$$\therefore \frac{C_V}{C_V^{\text{classical}}} = \frac{\frac{\pi^2}{2} \left(\frac{k_B T}{\epsilon_F} \right) n k_B}{3/2} \sim 10^{-2}, \quad \frac{\equiv \delta T}{\uparrow}$$

$$\delta = \frac{\pi^2}{2} \frac{n k_B}{T_F}$$

linear in T

(i) specific heat

Including the contribution from the lattice, one

has $C_V = \delta T + AT^3$ ← electronic ← ionic ($\propto \omega^2 \propto k^3$)

high T. . . dominated by phonons. . . In a few T. δT dominates.

Experimentally, it is found that alkali metals

& noble metals (Cu, Ag, Au) are reasonably well described by free electron theory.

C_V is linear in T but $\frac{\delta_{\text{expt}}}{\delta_{\text{free}}} \neq 1$.

Since $k_B T_F = E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$,

the difference can be attributed to

the correction of mass: $\gamma = \frac{\pi^2 M k_B}{2 T_F}$

$$\frac{m_{\text{eff}}}{m} = \frac{\delta_{\text{expt}}}{\delta_{\text{free}}}$$

The difference is due to several factors neglected in the Sommerfeld theory:

- (i) periodic potential in crystals
- (ii) electron-phonon interaction
- (iii) electron-electron "

In real materials, the ratio $\frac{m_{\text{eff}}}{m}$ can be as large as 1000. Such as Heavy fermions

materials: $U\text{Be}_{13}$, CeAl_3 , CeCu_2Si_2 .

In addition to the linear T behavior of C_V ,

the Sommerfeld theory also predicts

(ii) mean free path

Since most free electrons are near $E = E_F$,

$$\therefore v \sim v_F, \quad l \sim v_F \tau$$

$$v_F \sim 10^8 \text{ cm/sec}, \quad \therefore l \sim 100 \text{ } l_{\text{classical}} \\ (\text{ } 100 \text{ } v_{\text{classical}} \sim 10^6 \text{ cm/sec})$$

(iii) thermal conductivity

$$K_{\text{electron}} = \frac{1}{3} C_V l v_F \\ = \frac{1}{3} C_V v_F^2 \tau$$

$$C_V = \frac{\pi^2}{2} \frac{n k_B}{T_F} T, \quad v_F^2 = \frac{2 E_F}{m}$$

$$\sigma = \frac{n e^2 \tau}{m}$$

$$\therefore \frac{K}{\sigma T} = \frac{\frac{2}{3} \frac{E_F \tau}{m} \frac{\pi^2}{2} \frac{n k_B T}{T_F}}{\frac{n e^2 \tau}{m}} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2$$

$$= 2.44 \times 10^{-8} \text{ watt-ohm/K}^2$$

\sim expt. value! (Drude = 1.11×10^{-8})

(iv) temperature dependent of ρ in free electron gas

In the free electron gases, resistivity ρ

is mainly due to scattering of electrons by impurities or phonons.

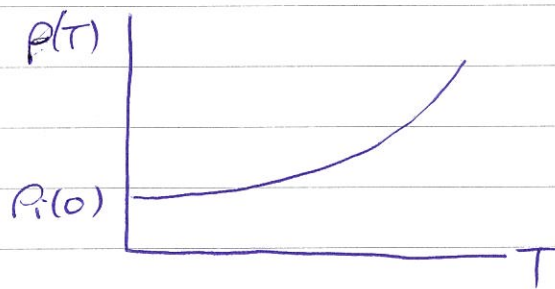
Experimentally, it is found empirically that

when concentration of impurities is low,

$$\rho = \rho_L + \rho_i \quad \rho_i \approx \text{contribution from impurities}$$

$$\rho_L \approx \text{ " " " phonons}$$

This is the Matthiessen's rule



$\rho_i \approx T$ -independent

$\rho_L = T$ -dependent

This can be also stated by

$$\frac{1}{\tau} = \frac{1}{\tau_L} + \frac{1}{\tau_i} \quad \therefore \text{scattering due to}$$

\uparrow
probability
of scattering

impurities & phonons are
additive.

$\rho - \rho_i(0)$ is caused by phonons.

$$(i) \text{ For } T \gg \theta_D, \quad n(\epsilon) = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \approx \frac{k_B T}{\hbar\omega}$$

$$\therefore \frac{1}{\tau} \propto n(\epsilon) \propto T \quad \therefore \rho(T) \propto T$$

(ii) $T \ll \Theta_D$

As we have seen,

$$N_{ph} = \frac{3V}{2\pi^2 c^3} \int_0^{\omega_D} \omega^3 \frac{d\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

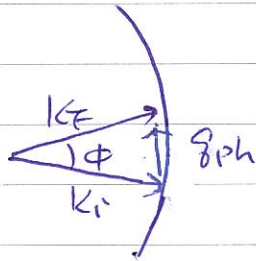
$$= \frac{3V}{2\pi^2 c^3} \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\frac{\hbar\omega_D}{k_B T}} \frac{x^3 dx}{e^x - 1}$$

$$\sim T^3 \int_0^\infty \frac{x^3 dx}{e^x - 1} \propto T^3$$

$$\therefore \frac{1}{\tau} \propto T^3$$

Only electrons $|\epsilon - \epsilon_F| \leq k_B T$ contribute transport \checkmark ~~only $\hbar\omega \approx k_B T$ contributes~~ During scattering, electron's

$$\vec{k} = \vec{k}_i \rightarrow \vec{k}_f \quad \text{with } |\vec{k}_i| \approx |\vec{k}_f| \approx k_F$$



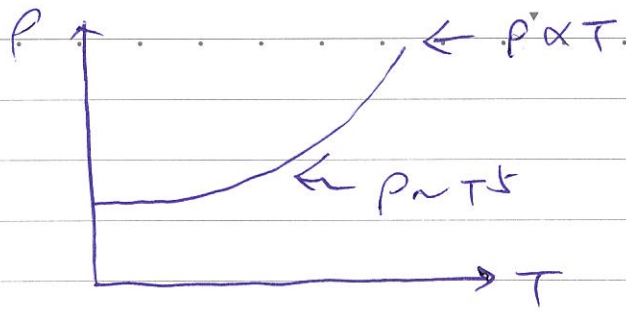
\therefore Each scattering degrades the forward momentum by $1 - \cos\phi \approx \frac{\phi^2}{2} \sim \left(\frac{g_{ph}}{k_F}\right)^2$

\therefore The effectiveness of each scattering = $\left(\frac{g_{ph}}{k_F}\right)^2$

$\therefore \rho \sim$ Scattering frequency \times effectiveness

$$\sim T^3 \left(\frac{g_{ph}}{k_F}\right)^2 \sim T^5$$

(This is the Bloch T^5 law)



In reality, there are other competitions which are not considered in the free electron model.

(Such as $e-e$ interaction ...)

The observed $\rho(T)$ does not follow the above T -dependence exactly.

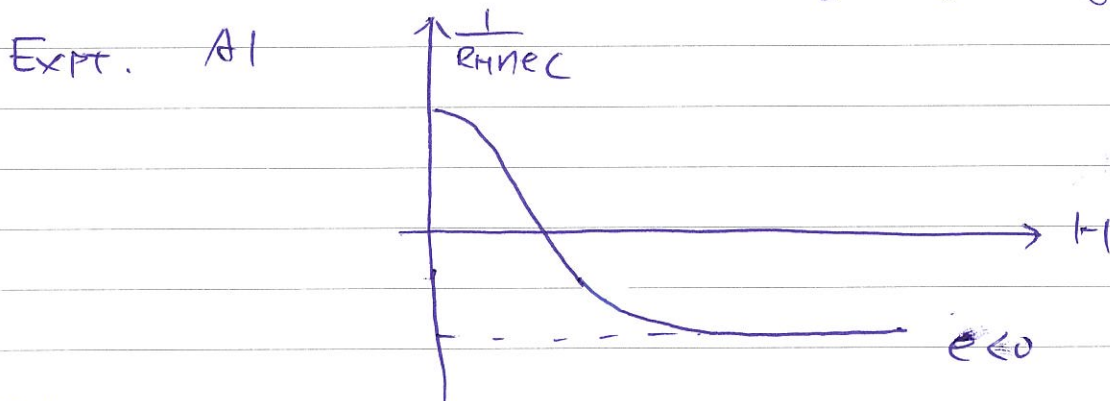
Failures of free electron model

(1) The Hall coefficient

$$R_H = \frac{-1}{nec} \quad \text{independent of } T \text{ \& } H$$

Only Alkali metals are close to $R_H = \frac{-1}{nec}$

Some metals even exhibit change sign of R_H .



(2) Magneto resistance : $R(H)$ depends on H
most of time!

(3) Why is ℓ so long?

Even though after taking quantum nature into consideration, $\ell \sim 100 \ell_{\text{classical}}$. The mean free path is still considerably smaller than what is observed in expts.

In expts, ℓ can be as large as $1 \mu\text{m}$!

(4) The Wiedeman-Franz law is actually obeyed only at high (room) temperature & very low (a few K) temperature.

In between, $\frac{\kappa}{\sigma T}$ is T-dependent.

(5) The most important failure is that the free electron model fails to distinguish metals, insulators, semiconductors, ...

good metals: $\rho \sim 10^{-10} \text{ ohm-cm}$
 " insulators: $\rho \sim 10^{22} \text{ ohm-cm}$ } differ by 10^{32} ohm-cm !

We need a more realistic model of electrons in crystals!