

Sommerfeld Theory of Metals

- For two decades the Drude Model stood w/ some glaring inaccuracies
- in 1926, the development of FD-stats (Fermi-Dirac statistics) was published
 - ↳ since e^- 's are fermions, this may be appropriate for the FEM!
- Sommerfeld 1927 → applied FD stats to Drude Model!

- this application only changes a couple of parameters:

- 1) typical e^- speeds: v_0
- 2) heat capacity: C_V

- Results that don't depend on v_0 or C_V do not change! i.e. σ_0 , R_H , $\sigma(\omega)$.

DC cond.

Hall coeff.

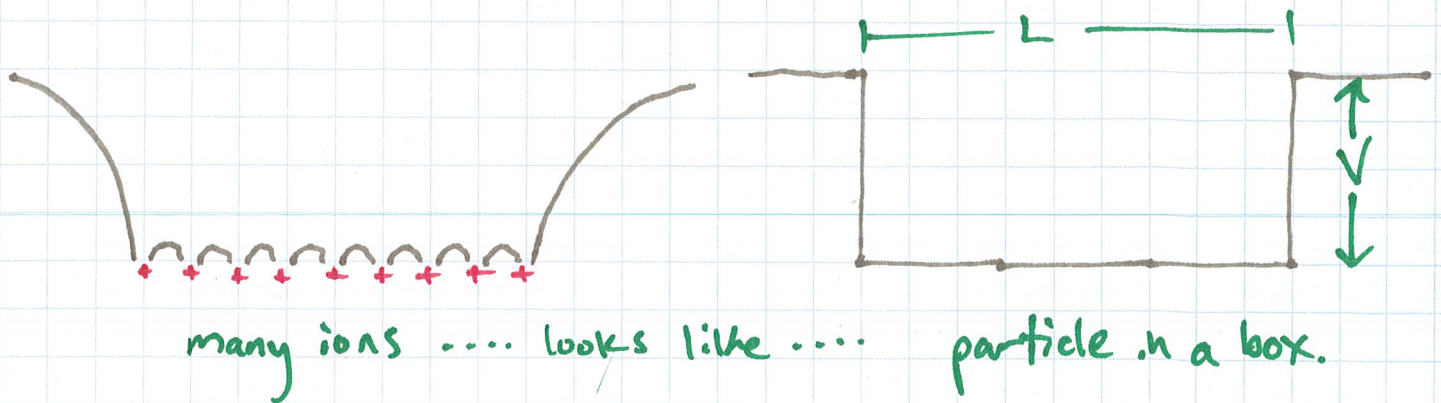
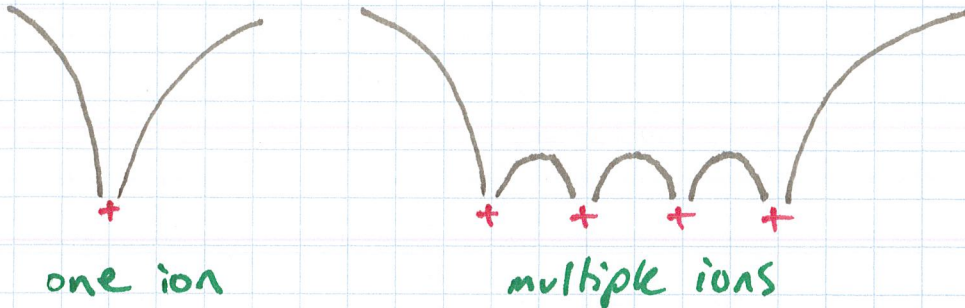
AC cond.

- Additionally QM was developed significantly during this time → is QM approach needed?

↳ we will take this opportunity to begin a QM treatment of the solid.

→ introduce terminology & parameters which are relevant.

Consider Coulomb potential: $V(r) = \frac{1}{4\pi\epsilon_0} \frac{qQ}{r}$



Schrödinger's Eqn.

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r) = [E - V(r)] \psi(r)$$

- inside the metal take $V=0$ (Free electron)

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi$$

Solutions:
 eigen function $\psi_k = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}$
 eigen value $\rightarrow E_k = \frac{\hbar^2 k^2}{2m}$

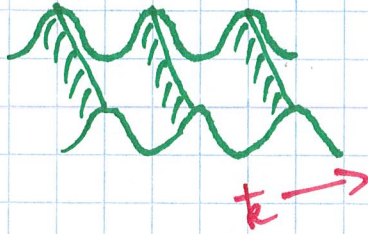
$V =$ volume of box
 $\sim L^3$

$$\int |\psi|^2 dr = 1$$

Recall that:

$$e^{i\vec{k}\cdot\vec{r}}$$

represents a plane wave
in \vec{k} direction



Consider the momentum operator: (From QM)

$$\vec{p} = -i\hbar\vec{\nabla}$$

$$\therefore \vec{p}\psi(r) = -i\hbar\vec{\nabla}\psi(r) = \hbar\vec{k}\psi(r)$$

↑ operator ↑ eigenvalue

$\therefore \psi(r)$ is also a momentum eigenstate w
eigenvalue $\hbar\vec{k}$

$$\therefore \vec{p} = \hbar\vec{k}$$

$\psi(r)$ is plane wave w energy: $E = \frac{\hbar^2 k^2}{2m}$

& momentum: $\vec{p} = \hbar\vec{k}$

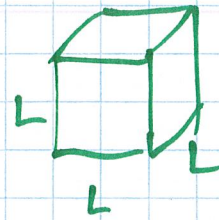
$\psi_{\vec{k}}(r)$ is a set of single \vec{E} solutions:

Apply Boundary Conditions:

→ we are not interested (for now) in surface effects

→ "infinite crystal"

Periodic Boundary Conditions:



$$V = L \times L \times L$$

$$\begin{aligned} \therefore \psi(x, y, z) &= \psi(x+L, y, z) \\ &= \psi(x, y+L, z) \\ &= \psi(x, y, z+L) \end{aligned}$$

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

$$\therefore \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot (x, y, z)} = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot (x+L, y, z)}$$

dot prod $\Rightarrow e^{ik_x x} = e^{ik_x(x+L)}$

$$\therefore e^{ik_x L} = 1$$

$$\therefore k_x L = 2\pi n_x, \quad n_x = 0, \pm 1, \pm 2, \dots$$

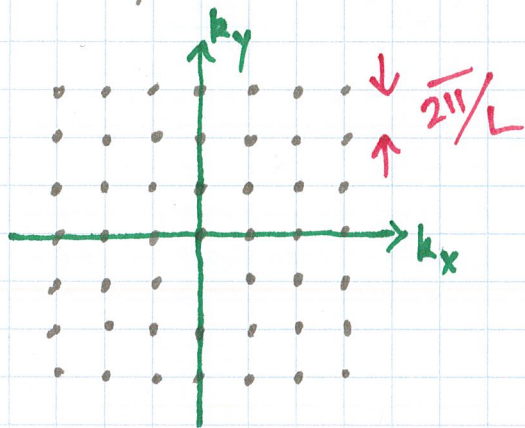
$$\therefore k_x = \frac{2\pi}{L} n_x$$

Likewise: $k_y = \frac{2\pi}{L} n_y$

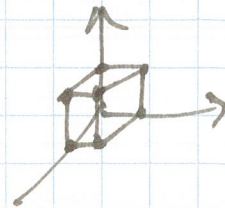
$$k_z = \frac{2\pi}{L} n_z$$

k_i are quantized!

In 2-D, the allowed k 's:



In 3-D these are cubes or rectangular prisms.



This visualization is called k -space
or momentum-space

→ get used to it!

$\psi_{\vec{k}}(r)$, w the \vec{k} 's quantized, form set of allowed single \vec{e} wavefunctions.

- Notice that each $\vec{k} = (k_x, k_y, k_z)$ has an associated k -space volume of:

$$\frac{2\pi}{L} \times \frac{2\pi}{L} \times \frac{2\pi}{L} = \frac{8\pi^3}{V}$$

k -space density:
 $\frac{V}{8\pi^3}$

What is the ground state of our system?

i.e. $T=0$

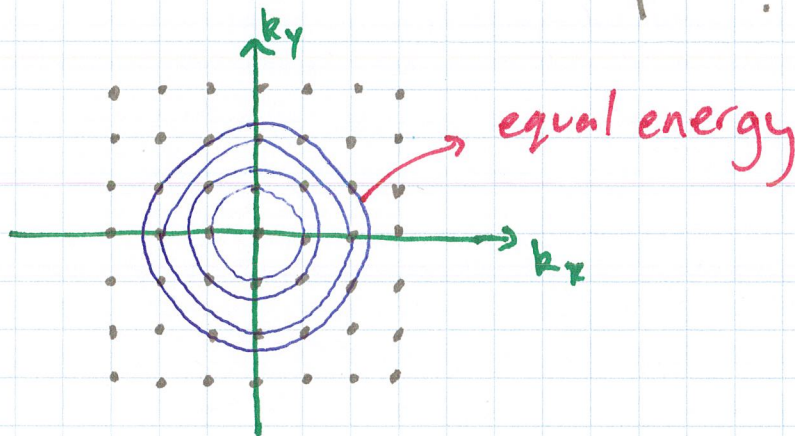
$N = \#$ conduction e^- 's
(total)

This involves filling the allowed levels w/ N e^- 's starting w/ the lowest energy k : $k=0$.

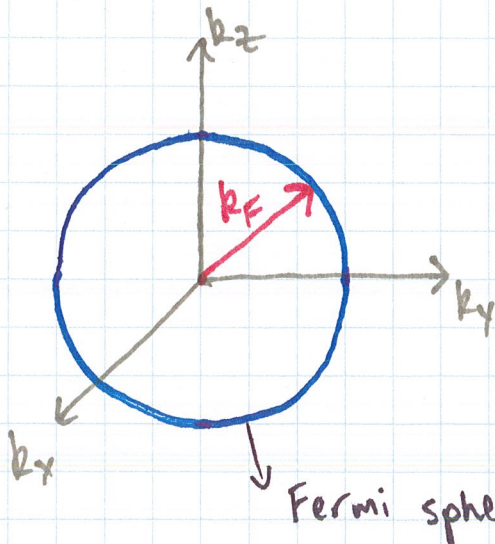
BUT: Pauli exclusion principle:

each state can only hold 2 e^- 's: spin \uparrow
spin \downarrow

What does this look like in k -space?



In 3-D this is a sphere



Fill until all N e^- 's are accounted for.

Define: $k_F \rightarrow$ Fermi wavevector

\sim radius of sphere in k -space
whos volume contains all filled
states

Fermi sphere/surface

Volume of sphere w radius k_F :

$$\frac{4}{3} \pi k_F^3$$

k-space state density is: $\frac{V}{8\pi^3}$ $\xrightarrow{V \rightarrow \text{real space volume}}$

\therefore # states in Fermi-sphere: $\left(\frac{4}{3} \pi k_F^3\right) \left(\frac{V}{8\pi^3}\right)$

Each state can hold 2- e^- 's (Pauli EP).

$$\therefore N = 2 \cdot \left(\frac{4}{3} \pi k_F^3\right) \left(\frac{V}{8\pi^3}\right)$$

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

$$\text{or } n = \frac{N}{V} = \frac{k_F^3}{3\pi^2} \Rightarrow \bar{e} \text{ density}$$

$$\therefore k_F = (3\pi^2 n)^{1/3}$$

Important terms:

k_F - Fermi wavevector - \vec{k} of highest occupied state @ $T=0$.

E_F - Fermi energy - $\frac{\hbar^2 k_F^2}{2m}$

p_F - Fermi momentum - $\hbar k_F$

v_F - Fermi velocity - $\frac{p_F}{m} = \frac{\hbar k_F}{m}$ - speed of most energetic e^- 's

$$T_F - \text{Fermi temperature} - k_B T_F = E_F \Rightarrow T_F = \frac{E_F}{k_B}$$

See Table 2.1 for typical values:

$$k_F \sim 1 \text{ \AA}^{-1}$$

$$E_F \sim 1-15 \text{ eV} \rightarrow \text{Binding energy of H is } 13.6 \text{ eV}$$

$$v_F \sim 10^6 \text{ m/s} \rightarrow 10 \times \text{'s faster than classical est. (@ room temp.)}$$

$$T_F \sim 10^5 \text{ K} \rightarrow \text{Note W melts @ } 3695 \text{ K}$$

\Rightarrow see Aside on distribution function.

What is the ground state energy of our system?

We must add up the energies of occupied states, i.e. up to k_F (or E_F):

$$U = 2 \sum_{\substack{\mathbf{k} \\ \leq k_F}} \frac{\hbar^2 k^2}{2m}$$

This $\sum_{\mathbf{k}}$ can be expressed as an integral:

Consider our k -space density: # states / k -volume

$$\frac{V}{8\pi^3} \Rightarrow \Delta k = \frac{8\pi^3}{V} \Rightarrow \text{volume per } k\text{-space state.}$$

$$\therefore \frac{V}{8\pi^3} \Delta k \equiv 1$$

Aside:

What does the occupancy function look like for the g.s.?

$f(\epsilon_i) \rightarrow$ expected # of particles in single \bar{e} state with energy ϵ_i

\rightarrow sometimes written as \bar{n} .

\rightarrow also, "carrier distribution" function

From PEP, we started @ $\vec{k}=0$ ($\epsilon=0$) and filled each single \bar{e} state up to k_F (ϵ_F).

$$\therefore f(\epsilon_i) = \begin{cases} 1, & \epsilon(k) < \epsilon_F \\ 0, & \epsilon(k) > \epsilon_F \end{cases}$$



\rightarrow step function @ $\epsilon = \epsilon_F$, Fermi energy.

\rightarrow looks like Fermi-Dirac distribution, perhaps in some extreme limit.....

\rightarrow clear that ϵ_F is the cost for adding or removing an \bar{e} from the system.... more stat. mech.

Take any 'smooth' function of \mathbf{k} : $F(\mathbf{k})$

$$\sum_{\mathbf{k}} F(\mathbf{k}) = \frac{V}{8\pi^3} \sum_{\mathbf{k}} F(\mathbf{k}) \Delta\mathbf{k} \quad \Rightarrow \text{multiply by "1"}$$

In limit that $\Delta\mathbf{k} \rightarrow 0$ or $V \rightarrow \infty$:

$$\lim_{V \rightarrow \infty} \frac{1}{V} \sum_{\mathbf{k}} F(\mathbf{k}) = \frac{1}{8\pi^3} \int F(\mathbf{k}) d^3\mathbf{k}$$

Back to total g.s. energy: E

$$U = 2 \sum_{\mathbf{k} \leq k_F} \frac{\hbar^2 \mathbf{k}^2}{2m} = 2 \frac{V}{8\pi^3} \frac{\hbar^2}{2m} \int_0^{k_F} k^2 d^3\mathbf{k}$$

$d^3\mathbf{k} = 4\pi k^2 dk$

$$\therefore U = \frac{V}{\pi^2} \frac{\hbar^2}{2m} \int_0^{k_F} k^4 dk$$

$$U = \frac{V}{5\pi^2} \frac{\hbar^2}{2m} k_F^5$$

note: $u = \frac{U}{V}$

Recall: $N = \frac{V}{3\pi^2} k_F^3$

\therefore Energy per particle \rightarrow
(avq. in g.s.)

$$\frac{U}{N} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} = \frac{3}{5} \epsilon_F$$

The average particle velocity can be estimated from $\frac{E}{V}$:

$$\text{note: } E = \frac{\hbar^2 k^2}{2m} = \frac{\bar{p}^2}{2m} = \frac{1}{2} m \bar{v}^2$$

$$\frac{E}{V} = \frac{1}{2} m v_0^2 = \frac{3}{5} E_F$$

$$\therefore v_0 = \sqrt{\frac{3}{5} \frac{2}{m} E_F}$$

$$\text{OR } v_0 = \sqrt{\frac{3}{5}} v_F \Rightarrow \sqrt{\frac{3}{5}} \approx 0.775$$

Often $v_0 \approx v_F$ is used for estimates/calculations.

$v_F \approx 10^6 \text{ m/s} \approx 10 \times$'s classical estimate @ room temp!

Note that this estimate is @ $T=0$! Classically @ $T=0$, $v_0=0$. This is a significant departure from classical theory.

Density of States (DOS):

$D(\epsilon)$ or $g(\epsilon)$ or $N(\epsilon) \rightarrow$ the # of allowed single \bar{e} states @ a given energy.

Definition:

$$D(\epsilon) = \frac{1}{V} \sum_i^N \delta(\epsilon - \epsilon_{k_i})$$

Scale to Volume
Count # of states

DOS can also be defined as:

$$D(\epsilon) = \frac{d\Omega_k(\epsilon)}{d\epsilon} \quad \Omega_k \rightarrow \text{k-space volume.}$$

Calculate $D(\epsilon)$:

$$D(\epsilon) = \frac{1}{V} \sum_i \delta(\epsilon - \epsilon_{k_i})$$

↑ sum over all states.

$$= \frac{2}{V} \sum_k \delta(\epsilon - \epsilon_k)$$

↘ sum over allowed k 's

2 \bar{e} 's per k .

using $\frac{1}{V} \sum_k F(k) = \int \frac{d^3k}{8\pi^3} F(k)$

$$\therefore D(\epsilon) = \frac{1}{4\pi^3} \int \delta(\epsilon - \epsilon_k) d^3k \quad \rightarrow d^3k = 4\pi k^2 dk$$

$$\text{since } \epsilon = \frac{\hbar^2 k^2}{2m}, \quad d\epsilon = \frac{2\hbar^2 k}{2m} dk.$$

$$\therefore d^3k = 4\pi k^2 dk = \frac{4\pi k^2 m}{\hbar^2} d\epsilon$$

$$\therefore D(\epsilon) = \frac{m}{\pi^2 \hbar^2} \int k \delta(\epsilon - \epsilon_k) d\epsilon$$

$$k = \sqrt{\frac{2m\epsilon}{\hbar^2}}$$

$$\therefore D(\epsilon) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m}{\hbar^2}} \int \sqrt{\epsilon} \delta(\epsilon - \epsilon_k) d\epsilon$$

@ each $\epsilon = \epsilon_k$, integral yields $\sqrt{\epsilon_k}$

\therefore assuming a virtually continuous k -space, i.e. large N :

$$D(\epsilon) = \frac{m}{\pi^2 \hbar^3} \sqrt{2m\epsilon} \quad \rightarrow \text{dropped } k \text{ label.}$$

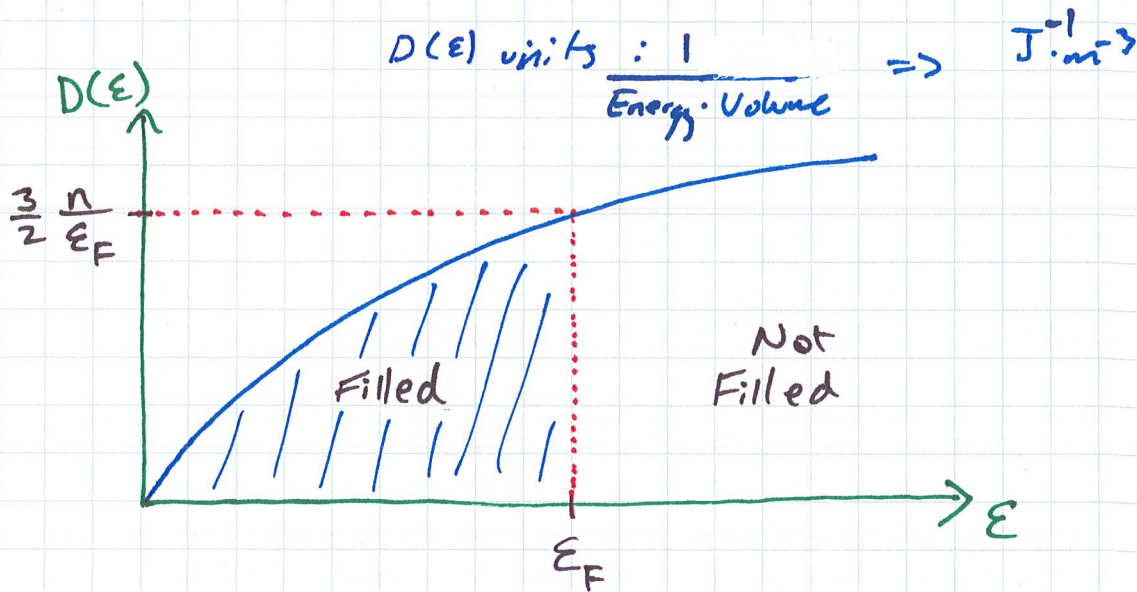
Through some subs:

$$D(\epsilon) = \frac{3}{2} \frac{N}{\epsilon_F} \sqrt{\frac{\epsilon}{\epsilon_F}}$$

Note:

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

$$D(\epsilon) = D(\epsilon_F) \sqrt{\frac{\epsilon}{\epsilon_F}}$$



Quantum Free \bar{e} (Sommerfeld) @ finite temperatures

→ moving to $T > 0$ means \bar{e} will fill our single \bar{e} allowed states in a slightly different manner

Grand canonical ensemble:

→ expected single-state occupancy $\langle N_i \rangle \Rightarrow (f(\epsilon_k))$

$$\langle N_i \rangle = k_B T \frac{1}{Z} \left(\frac{\partial Z}{\partial \mu} \right)_{V, T}$$

$\mu \rightarrow$ chemical potential

$Z \rightarrow$ partition function