

Drude assumed classical Maxwell-Boltzmann distribution

Sommerfeld: Drude + Fermi-Dirac distribution

Distribution function

"Fermi function"

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

Chemical potential

Quantum theory of electron gas N electrons
volume V

x independent

- ⇒ ① Find energy levels for single electron
 ② Fill up levels according to Pauli principle

Schrödinger eq.
$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(\vec{r}) = E \Psi(\vec{r})$$

Avoid surface complications

⇒ Periodic boundary conditions (Born-von Karman)

$$\Psi(x+L) = \Psi(x) \quad \text{etc.}$$

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

$$\Rightarrow E(\vec{k}) = \frac{\hbar^2 k^2}{2m}$$

Momentum operator $\hat{p} = -i\hbar \nabla \Rightarrow$ Eigenvalue
 $\vec{p} = \hbar \vec{k}$

$$\vec{p} = m\vec{v} \Rightarrow \vec{v} = \frac{\hbar \vec{k}}{m}, \quad E = \frac{p^2}{2m} = \frac{m v^2}{2}$$

Plane wave $\Rightarrow \vec{k}$ wave vector with $\lambda = \frac{2\pi}{k}$

Boundary conditions

$$\psi(x+L) = \psi(x) \Rightarrow e^{ik_x L} = 1$$

$$k_x \cdot L = n \cdot 2\pi$$

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

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

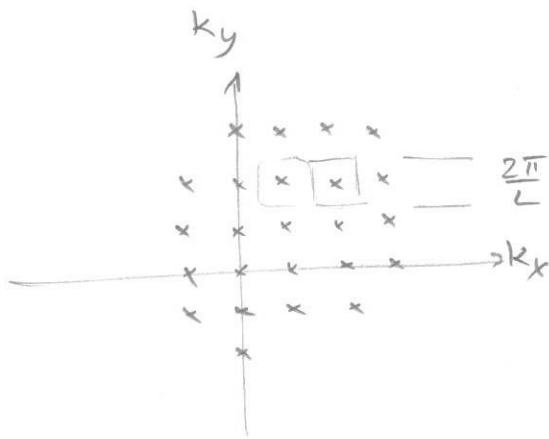
$$k_z = \frac{2\pi n_z}{L}$$

$$n_i = 0, \pm 1, \pm 2, \dots$$

"Allowed k-points"

Any state can then be formed by superposition

$$\psi = \sum_{\vec{k}} A_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$



Number of points per volume

in "k-space" =

$$= \frac{1}{(2\pi/L)^3} = \frac{V}{8\pi^3}$$

$\vec{v} \sim \vec{k} \Rightarrow$ velocity space

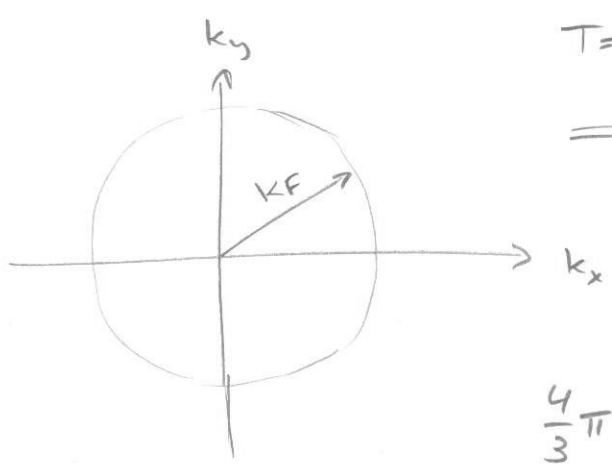
$E \sim k^2 \Rightarrow$ energy increases as sphere

Pauli principle

Two electrons cannot have the same set of quantum numbers.

\Rightarrow Max 2 electrons (spin up, down) per \vec{k} -point.

Fermi sphere : Contains all electrons at $T=0$



$T=0 \Rightarrow$ lowest energy states occupied

\Rightarrow Fermi sphere, radius k_F

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad \text{Fermi energy (defined at } \underline{T=0})$$

$$\underbrace{\frac{4}{3}\pi k_F^3}_{\text{Volume}} \cdot \underbrace{2 \cdot \frac{V}{8\pi^3}}_{\text{points per volume}} = N$$

States per point

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

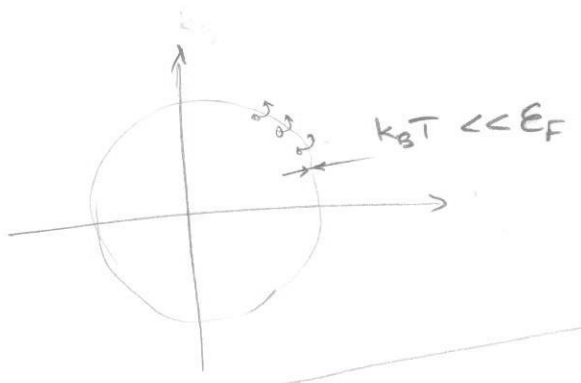
$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

Metals have $E_F \sim 2-10 \text{ eV} \gg k_B T \sim 25 \text{ meV}$

Fermi velocity $v_F = \frac{\hbar k_F}{m}$

Fermi temperature $k_B T_F = E_F$

$T > 0$: Thermal excitation



Thermal excitation limited to energies $\sim k_B T$ around E_F

\rightarrow P.5

$$T=0 : \langle E \rangle = \left(\sum_{k < k_F} 2 \cdot \frac{\hbar^2 k^2}{2m} \right) / N = \frac{2}{N} \sum_{k < k_F} \frac{\hbar^2 k^2}{2m} =$$

$$\left\{ d^3k = \frac{8\pi^3}{V} \right\} = \frac{2}{N} \cdot \left(\frac{V}{8\pi^3} \right) \cdot \int_{k < k_F} \frac{\hbar^2 k^2}{2m} d^3k = \frac{V}{8\pi^3 N} \int_{k < k_F} \frac{\hbar^2 k^4}{2m} dk =$$

$$= \frac{1}{\pi^2 n} \frac{\hbar^2 k_F^5}{10m} = \left\{ n = \frac{k_F^3}{3\pi^2} \right\} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} E_F$$

Density of states

Def. $D(E)dE$ = number of states with energy between E and $E+dE$

$$D(E)dE = 2 \cdot \underbrace{\frac{V}{8\pi^3}}_{\substack{\text{number} \\ \text{of points} \\ \text{per volume}}} \cdot \underbrace{4\pi k^2 dk}_{\text{spherical shell volume}}$$

spin up / down

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow dE = \frac{\hbar^2}{m} k dk, \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

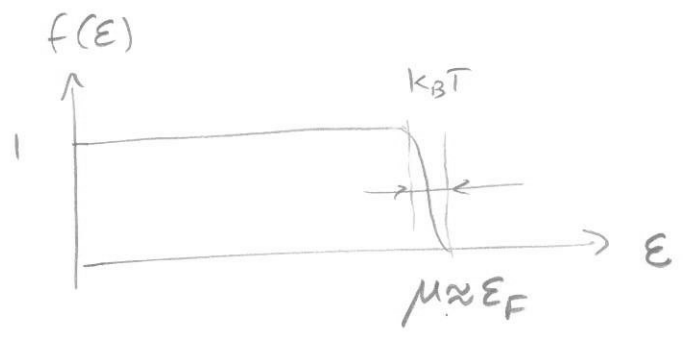
$$D(E)dE = \frac{V}{\pi^2} \underbrace{\frac{2mE}{\hbar^2}}_{k^2} \underbrace{\frac{m}{\hbar^2} \cdot \frac{\hbar}{\sqrt{2mE}}}_{dk} dE = \frac{V}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \sqrt{E} dE$$

$$D(E) \sim \sqrt{E}$$

T=0 : $N = \int_0^{E_F} D(E) dE$ $f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$

T>0 : $N = \int_0^{\infty} D(E) f(E) dE$ \hookrightarrow Fermi-Dirac distrib.

T→0 : $f(E) \rightarrow \begin{cases} 1 & E < E_F \\ 0 & E > E_F \end{cases} \Rightarrow \mu \rightarrow E_F$



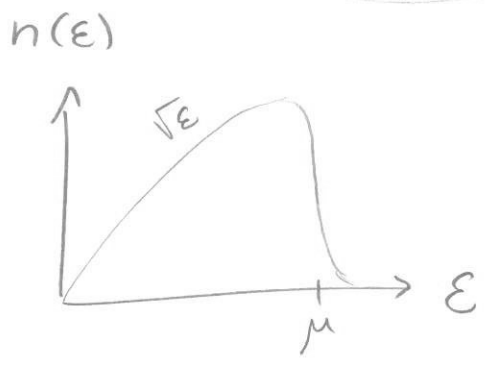
$$N(\epsilon) d\epsilon = f(\epsilon) \cdot D(\epsilon) d\epsilon$$

Defines μ :

$$N = \int_0^{\infty} N(\epsilon) d\epsilon = \int_0^{\infty} f(\epsilon) D(\epsilon) d\epsilon$$

$$g(\epsilon) = \frac{D(\epsilon)}{V} \Rightarrow n(\epsilon) d\epsilon = f(\epsilon) g(\epsilon) d\epsilon$$

Also $D(\epsilon) d\epsilon = D(k) dk$



Thermal excitation:

Estimate of heat capacity

A surface layer with $\Delta\epsilon \sim k_B T$ excited

Number of active electrons ; $D(\epsilon_F) \cdot \underbrace{k_B T}_{\text{"d}\epsilon"}$

With a classical contribution of $\frac{1}{2} k_B T$ per degree of freedom

$$\Rightarrow \text{Active internal energy } U_{\text{active}} = D(\epsilon_F) k_B T \cdot \frac{3}{2} k_B T$$

$$C_v = \frac{dU}{dT} = 3 D(\epsilon_F) k_B^2 T$$

$$C_v = \frac{1}{V} \frac{dU}{dT} = 3 g(\epsilon_F) k_B^2 T$$

more exact:

$$C_v = \frac{\pi^2}{3} g(\epsilon_F) k_B^2 T$$

$$U = \frac{1}{V} C = \int_0^\infty \epsilon \cdot g(\epsilon) f(\epsilon) d\epsilon$$

$$n = \frac{1}{V} Z = \int_0^\infty g(\epsilon) f(\epsilon) d\epsilon \stackrel{\text{Also}}{=} \int_0^{\epsilon_F} g(\epsilon) d\epsilon$$

Sommerfeld expansion / integration technique:

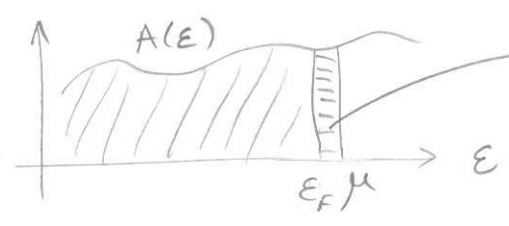
$$\int_0^\infty A(\epsilon) f(\epsilon) d\epsilon \approx \int_0^\mu A(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 A'(\mu)$$

$$n = \int_0^\mu g(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\mu)$$

small correction $\sim (k_B T)^2$

$\Rightarrow \mu$ close to ϵ_F

$$\int_0^\mu A(\epsilon) d\epsilon = \int_0^{\epsilon_F} A(\epsilon) d\epsilon + (\mu - \epsilon_F) A(\epsilon_F)$$



Difference between integrals

$\mu \approx \epsilon_F$
in this term

$$\Rightarrow n = \underbrace{\int_0^{\epsilon_F} g(\epsilon) d\epsilon}_n + (\mu - \epsilon_F) g(\epsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\epsilon_F)$$

$$\Rightarrow \mu - \epsilon_F = - \frac{\pi^2}{6} (k_B T)^2 \frac{g'(\epsilon_F)}{g(\epsilon_F)}$$

Difference between μ and ϵ_F

More proper determination of specific heat:

(7)

$$\begin{aligned}
 U &= \int_0^{\infty} \epsilon \cdot g(\epsilon) f(\epsilon) d\epsilon = \\
 &= \int_0^{\mu} \epsilon \cdot g(\epsilon) d\epsilon + \left. \frac{\pi^2}{6} (k_B T)^2 \frac{d}{d\epsilon} (\epsilon \cdot g(\epsilon)) \right|_{\epsilon_F} = \\
 &= \int_0^{\epsilon_F} \epsilon \cdot g(\epsilon) d\epsilon + \underbrace{(\mu - \epsilon_F) \cdot \epsilon_F \cdot g(\epsilon_F)}_{\mu - \epsilon_F = -\frac{\pi^2}{6} (k_B T)^2 \frac{g'(\epsilon_F)}{g(\epsilon_F)}} + \frac{\pi^2}{6} (k_B T)^2 g(\epsilon_F) + \\
 &\quad + \frac{\pi^2}{6} (k_B T)^2 \epsilon_F \cdot g'(\epsilon_F)
 \end{aligned}$$

$$\Rightarrow U = \underbrace{\int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon}_{U_0} + \frac{\pi^2}{6} (k_B T)^2 g(\epsilon_F)$$

$$c_v = \frac{dU}{dT} = 0 + \frac{\pi^2}{3} k_B^2 T g(\epsilon_F)$$

$$g(\epsilon_F) = \frac{1}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \sqrt{\epsilon_F}, \quad \epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

$$\Rightarrow g(\epsilon_F) = \frac{1}{2\pi^2} \cdot \frac{2m}{\hbar^2} (3\pi^2 n)^{1/3}$$

$$\Rightarrow c_v = \frac{m}{3\hbar^2} (3\pi^2 n)^{1/3} k_B^2 T \cdot \frac{\epsilon_F}{\epsilon_F} =$$

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

small factor \rightarrow gives temp. dependence!

Compare classical: $c_v = \frac{3}{2} n k_B$

Before we had $l = v \cdot \tau$

now v typically v_F for active electrons

$\Rightarrow \boxed{l = v_F \tau}$

Revisit thermal conductivity

$K = \frac{1}{3} C_v l v \Rightarrow K = \frac{1}{3} C_v l v_F = \frac{1}{3} C_v v_F^2 \tau$
 $\frac{\pi^2}{2} n k_B \left(\frac{k_B T}{E_F} \right) \quad \downarrow \quad \frac{2 E_F}{m}$

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

Lorenz number $L = \frac{K}{\sigma T} = \frac{\pi^2}{3} \frac{k_B^2}{e^2}$
 $\sigma = \frac{ne^2 \tau}{m}$

So Drude assumed $v^2 \sim k_B T \sim T$
 $C_v \sim n k_B \sim \text{const}$
 but Sommerfeld showed $v^2 \sim v_F^2 \sim \text{const} \gg k_B T$
 $C_v \sim \gamma \cdot T \sim T \ll n k_B$

Revisit thermopower

$\vec{E} = - \frac{C_v}{3ne} \vec{\nabla} T = \left\{ \text{Sommerfeld} \right\}_{C_v} = - \frac{\pi^2}{6} \frac{k_B}{e} \left(\frac{k_B T}{E_F} \right) \vec{\nabla} T$
 Q

Still problem with sign

With numbers

$Q = -1.42 \cdot \left(\frac{k_B T}{E_F} \right) \cdot 10^{-4} \text{ V/K} \sim \underline{\underline{\mu\text{V/K}}}$
 $\frac{25 \text{ meV}}{5 \text{ eV}}$

Problems with the free electron model

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- 1) Sign of Hall coefficient
 - Also magnetic field dependence for some metals
- 2) Magnetoresistance $\neq 0$
 - Sample preparation
 - Orientation
 - Some materials

} Strong effects
- 3) Sign of thermoelectric field
- 4) Wiedemann-Franz law
 - Deviations at intermediate temperatures
- 5) Temperature dependence of resistivity
- 6) Frequency dependence in optical properties
 - Reflectivity
 - Color of Au, Cu

7) Specific heat

$$C_{\text{isolators}} \approx C_{\text{metals}} \gg \gamma T$$

$$C_{\text{metal}} = \gamma T + C_{\text{isolator}}$$

not in agreement
for Fe, Mn, Bi, Sb

Look at ion lattice



and see what we can resolve/effects that appear