Electronic properties of solids - Quantum Theory

Lecture 13

CHM 637

Chemistry & Physics of Materials

Varadharajan Srinivasan
Dept. Of Chemistry
IISER Bhopal

Lecture Plan

- Sommerfeld Model
- Tightbinding Approach

Sommerfeld Model

Assume that valence electrons are free in the metal.

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2$$

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

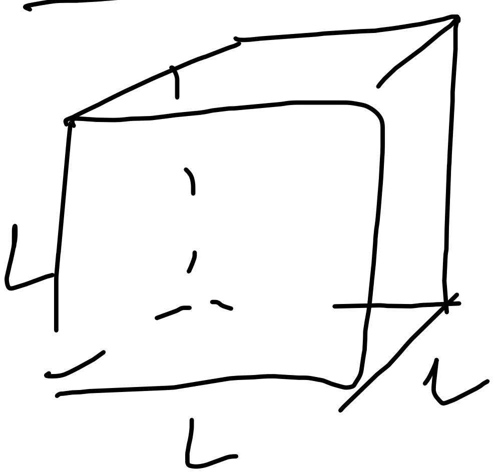
$\hookrightarrow \alpha(\sigma)$
$\beta(\sigma)$

$$\vec{k} = k_x \hat{i} + k_y \hat{j} + k_z \hat{k}.$$

$$\hat{\vec{p}}\,\psi_{\vec{k},s} = \frac{\hbar}{i}\vec{\nabla}\psi_{\vec{k},s} = \hbar\vec{k}\left(\psi_{\vec{k},s}\right)$$

$\Rightarrow \hbar\vec{k} \rightarrow$ momentum of the electron in the state $\psi_{\vec{k},s}$

Born von-Karman Boundary condition



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

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

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

Applying these boundary conditions to $\psi_{\vec{k},s}$

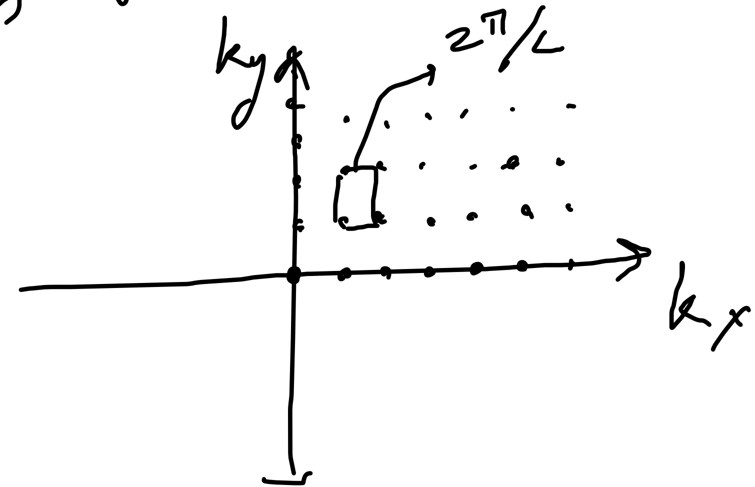
$$\Rightarrow \quad k_x = \frac{2\pi n_x}{L}$$

$$k_y = \frac{2\pi n_y}{L} \qquad n_x, n_y, n_z = 0, 1, 2, \ldots$$

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

If $L \to \infty$ then spacing between adjacent k-pts vanishes.

vol. occupied by any 1 k-pt. $= \left(2\pi/L\right)^3 = \frac{8\pi^3}{V}$



No. of k-pts in a unit vol. of reciprocal space $= V/8\pi^3$

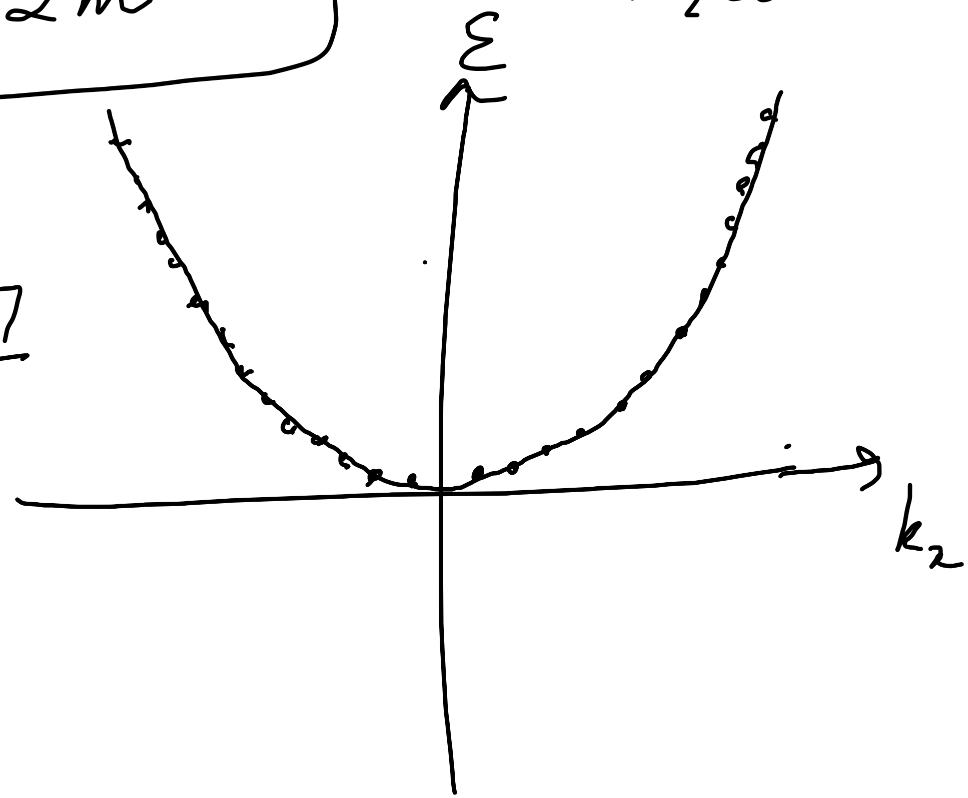
$$\boxed{\varepsilon_{\vec{k}}(\vec{k}) = \frac{\hbar^2 k^2}{2m}}$$

Dispersion relation

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

$$\vec{v} = \frac{\hbar\vec{k}}{m}$$

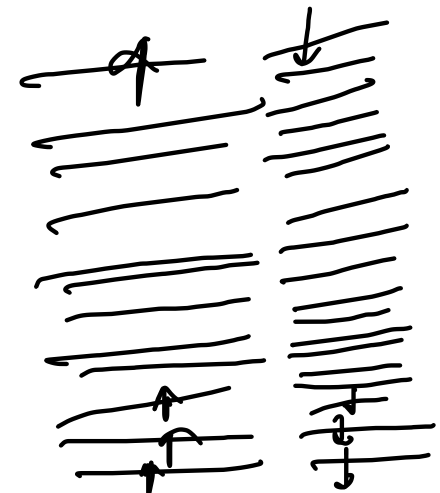
$$k = \frac{2\pi}{\lambda}$$



Pauli Exclusion Principle →

No state can have more than 1 electron

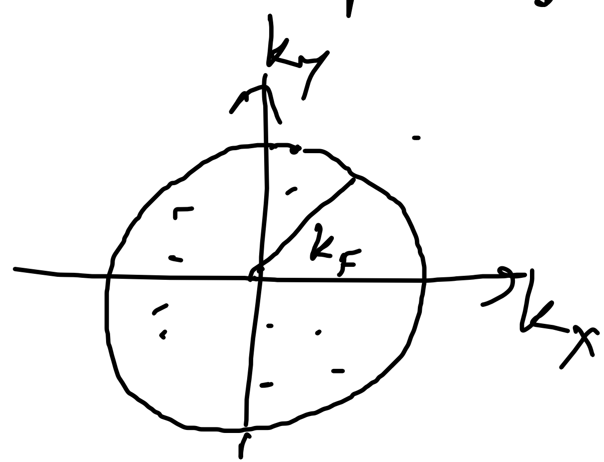
$\psi_{\vec{k}, s} \longrightarrow$ spin-orbital



$\therefore \quad \varepsilon \equiv \varepsilon(|\vec{k}|) \Rightarrow$

there are huge degeneracies in the system.

$N \rightarrow$ no. of electrons



No. of allowed k-pts w/in the sphere of radius k_F $= \dfrac{\frac{4}{3}\pi k_F^3}{8\pi^3/V} = \dfrac{V}{6\pi^2} k_F^3$

No. of occupied state $= 2 \times \dfrac{V}{6\pi^2} k_F^3 = \dfrac{V}{3\pi^2} k_F^3 = N$

$$\Rightarrow \boxed{k_F = \left(3\pi^2 \underbrace{n}_{N/V}\right)^{1/3}}$$

Fermi wavevector

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} \longrightarrow \text{Fermi energy}$$

$$v_F = \frac{\hbar k_F}{m} , \quad \frac{4}{3}\pi r_s^3 = 1/n$$

$$\frac{4.20}{(r_s/a_0)} \times 10^8 \text{ cm/s} \quad (\sim 1\% \text{ of } c) \qquad k_F = \frac{1.92}{r_s}$$

In typical metals, $\varepsilon_F \sim 1.5$ to 15 eV

Fermi level $\longrightarrow$ the energy that separates occupied & unoccupied levels

$$U = 2 \times \sum_{\vec{k}:\, k<k_F} \varepsilon(\vec{k}) = 2 \times \sum_{\vec{k}} f_{\vec{k}}\, \varepsilon(\vec{k})$$

$$f_{\vec{k}} = \begin{cases} 1 & \varepsilon(\vec{k}) < \varepsilon_F \\ 0 & \varepsilon(\vec{k}) > \varepsilon_F \end{cases} \quad @\ 0K$$

$$\Theta\left(\varepsilon(\vec{k}) - \varepsilon_F\right)$$

$$\lim_{V\to\infty} \frac{1}{V} \sum_{\vec{k}} \longrightarrow \int \frac{d^3k}{8\pi^3}$$

$$\frac{U}{V} = \underbrace{2}_{\text{spin}} \times \int \frac{d^3k}{8\pi^3} \, \frac{\hbar^2 k^2}{2m} \, \Theta\left(\varepsilon(k) - \varepsilon_F\right)$$

$$= 2 \times 4\pi \int_0^{k_F} k^2 \, dk \, \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 k_F^5}{10 m \pi^2}$$

$$\boxed{U/N = \frac{3}{5} \varepsilon_F} \equiv \frac{3}{5} k_B \underbrace{T_F}_{\text{Fermi Temperature}}$$

At finite temperature:

$f_{\vec{k},s}$ = probability of there being an electron in the particular state $(\vec{k},s)$

$$f_{\vec{k},s} = \frac{1}{e^{(\varepsilon_s(\vec{k})-\mu)/k_BT}+1} \rightarrow \text{Fermi-Dirac distribution function}$$

$\mu \rightarrow$ chemical potential

$\mu(T=0) = \varepsilon_F$

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_BT}+1}$$

Average energy density

$$u = \frac{U}{V} = 2\int \frac{d^3k}{8\pi^3}\, \varepsilon(\vec{k})\, f(\varepsilon(\vec{k}))$$

$$= \int_0^\infty d\varepsilon\, \underline{\underline{g(\varepsilon)}}\, f(\varepsilon)\, \varepsilon$$

$g(\varepsilon)\, d\varepsilon = \frac{1}{V} \times$ no. of free electron levels in the range ε to $\varepsilon + d\varepsilon$

density of states

$$g(\varepsilon) = \begin{cases} \dfrac{m}{\hbar^2 \pi^2} \sqrt{\dfrac{2m\varepsilon}{\hbar^2}} , & \varepsilon > 0 \\ 0 , & \varepsilon < 0 \end{cases}$$

$$\frac{3}{2} \frac{n}{\varepsilon_F} \left(\frac{\varepsilon}{\varepsilon_F}\right)^{1/2}$$

$$g(\varepsilon) \sim \varepsilon^{1/2} .$$

$$n = \int_0^\infty d\varepsilon \, g(\varepsilon) f(\varepsilon) \longrightarrow \text{fixes } \mu$$

It can be shown that at temperature T

$$u = \frac{U}{V} = u_0 + \frac{\pi^2}{6}(k_B T)^2 \underline{g}(\varepsilon_F)$$

$$\mu = \varepsilon_F\left[1 - \frac{1}{3}\left(\frac{\pi k_B T}{2\varepsilon_F}\right)^2\right]$$

$\Rightarrow$ volume specific heat capacity from conduction electrons

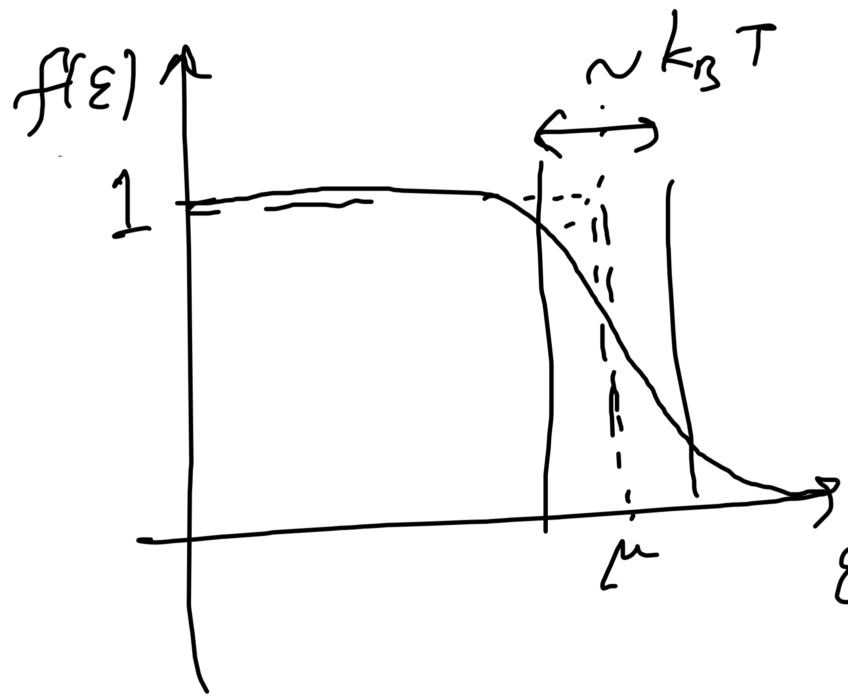
$$c_V = \left(\frac{\partial u}{\partial T}\right)_n = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B$$

$$= \pi^2 \underbrace{\left(\frac{k_B T}{\varepsilon_F}\right)} \times \overline{\left(\frac{3}{2} n k_B\right)}$$

The effect of F-D statistics is to reduce C_V by a factor $\sim \left(\frac{k_B T}{\mathcal{E}_F}\right) \propto T$

and even at room temp. is about

10^{-2}.



$$u \approx g(\mathcal{E}_F) \times (k_B T) \times k_B T$$

$$\sim T^2$$

$$\Rightarrow C_V = \frac{du}{dT} \propto T.$$

By Debye Theory, $C_V^{ion} \sim T^3$

$$C_V^{metal} = \gamma T + A T^3$$

$$\frac{C_V}{T} = \gamma + A T^2$$

plot $C_V/_T$ vs T then γ can be obtd. by extrapolation to 0 K.

$$\gamma = \frac{\pi^2}{2}\left(\frac{k_B^2}{\varepsilon_F}\right) n = \left(\frac{\pi^2 k_B^2 n}{\hbar^2 k_F^2}\right) m$$

$$\gamma \propto m$$

Li:

$$\gamma^{\text{observed}} = 4.2 \times 10^{-4} \ \text{cal-mol}^{-1}\text{-K}^{-2}$$

$$\gamma^{\text{th}} = 1.8 \times 10^{-4} \ \text{"}$$

$$\frac{m^*}{m} = \frac{\gamma^{\text{obsv}}}{\gamma^{\text{th}}} = 2.3$$

Mean free path: $\quad l = v\tau = v_F \tau$

$$1/\rho = \frac{ne^2\tau}{m}. \qquad l = \frac{(r_s/a_0)^2}{\rho_\mu} \times 92\,\text{Å}$$

$\rho_\mu \rightarrow \mu\Omega\,\text{cm}$

$\Rightarrow \sim 100\,\text{Å}$ @ R.T.

Thermal Conductivity :

$$K = \frac{1}{3} v^2 \tau C_v$$

$$v^2 \longrightarrow v_F^2 = 2\varepsilon_F/m$$

$$C_v = \frac{\pi^2}{2}\left(\frac{k_B^2}{\varepsilon_F}\right) n T, \quad \tau = \frac{m\sigma}{ne^2}$$

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

compares well to expt

$$\boxed{\frac{K}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2} = 2.44 \times 10^{-8} \; W\text{-}\Omega/K^2$$

Thermopower:

$$Q = -\frac{1}{3en} \times c_v$$

$$= -\frac{\pi^2}{6} \times \left(\frac{k_B}{e}\right)\left(\frac{k_B T}{\varepsilon_F}\right)$$

$$= -1.42 \times \left(\frac{k_B T}{\varepsilon_F}\right) \times 10^{-4} \ V/K.$$

which is smaller than Drude's estimate by a factor $O\left(\frac{k_B T}{\varepsilon_F}\right) \sim 0.01$