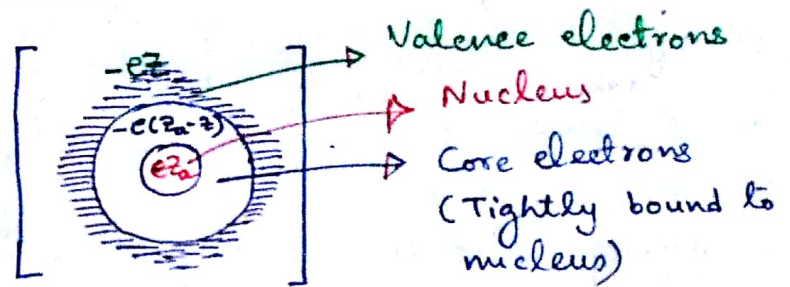
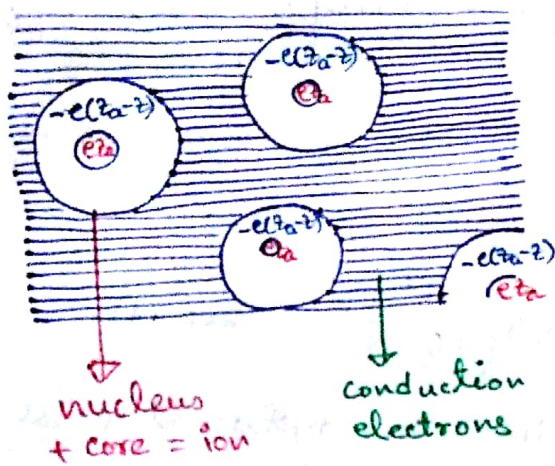


Free Electron Theory of Metals



Draude - Lorentz theory (Classical free electron theory) :

Dense metallic electron gas \rightarrow kinetic theory of neutral dilute gas. collisions of electron with other electron & ions is neglected, and under external field they move in straight line with Newton's law. Electron-electron interaction is neglected (independent electron approximation), electron-ion interaction is also neglected (free electron approximation). Their speed distribution is Maxwellian & their collisions are elastic.

Electric Conductivity

The rms velocity of electron at T is $\bar{v}_{rms} = \sqrt{\frac{3kT}{m}}$ & equation of motion of electron

At steady state $\dot{v} = 0 \Rightarrow$

$$v_d = -\frac{e\tau}{m} E = -\mu E$$

v_d = drift velocity, μ = mobility

Current density $J = -ne v_d$ ($-ne$ = charge/unit volume, n = no. density of conduction electron)

$$= -ne \left(-\frac{e\tau}{m} E \right)$$

$$= \frac{ne^2\tau}{m} E = \sigma E$$

\therefore Electric conductivity $\sigma = \frac{ne^2\tau}{m} \propto n$

$$= \left(\frac{ne}{m} \right) (e\tau) = ne\mu$$

resistivity $\rho = \sigma^{-1} = \frac{1}{ne\mu} = \frac{m}{ne^2\tau}$

In metals, $n \sim \text{constant}$, μ decreases with temperature, so as σ .

In semiconductors, n exponentially increases with temperature, σ increases.

In insulators, $n \sim \text{constant}$, μ increases exponentially \rightarrow dielectric breakdown

Wiedemann-Franz law (metals) $\frac{K}{\sigma} \propto T$, $K = \text{thermal conductivity}$
 $\sigma = \text{electrical}$

Good conductor of electricity are also good conductors of heat & the ratio $\frac{K}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2} = \text{Lorentz number}$

Although free electron theory explains WF law & validates Ohm's law, low temperature behaviour, $\rho \propto T$ etc cannot be obtained.

Sommerfeld's free electron theory

Despite the success of Drude-Lorentz classical electron theory to explain WF law, difficulties were

- Why Debye theory of lattice specific heat that ignores electronic specific heat is accurately "valid" for metals?
- Paramagnetism of metals does "not" obey Curie law ($\chi \propto \frac{1}{T}$) & is independent of temperature. But a gas of electrons, each of which are tiny magnet must exhibit large magnetic susceptibility.
- Hall effect of some divalent metal is positive, meaning that the charge carriers are "positive"!
- Electric resistivity has a temperature variation $\rho = \rho_0(1 + \alpha T)$ that can't be explained from classical electron gas model.
- Certain metals (tin, mercury etc) having poor electrical conductivity becomes superconductor at very low temperature but alkali & noble metals (Ag, Au, Pt etc) do not show superconductivity.

Schrödinger equation for free electron gas in 3D.

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi \quad \text{or} \quad \nabla^2 \psi + \frac{2m}{\hbar^2} E\psi = 0$$

Plane wave solution $\psi(\vec{r}) = A e^{i\vec{k} \cdot \vec{r}}$, $\nabla^2 \psi = -k^2 \psi$.

$$\text{or } -k^2 \psi + \frac{2m}{\hbar^2} E\psi = 0 \quad \text{or} \quad E = \frac{\hbar^2 k^2}{2m}$$

where $k^2 = \left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$, n_x, n_y, n_z integers

because $\psi(\vec{r}) = \psi(\vec{r} + \vec{L})$. Each set of (n_x, n_y, n_z) gives a stationary state of an electron inside the metal. In k-space, number of possible states of integers within k & $k + dk$, each of which gives rise to one state of electron

$$\therefore \int_0^k D(k) dk = \frac{4\pi k^2 dk}{(2\pi/L)^3}$$

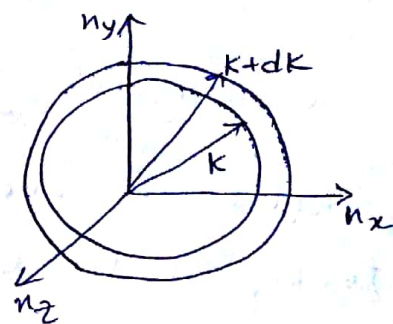
$$= \frac{4\pi L^3}{8\pi^3} \frac{2mE}{\hbar^2} \frac{1}{\hbar} \sqrt{\frac{m}{2}} E^{-1/2} dE$$

$$= L^3 2\pi \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

$$\therefore D(E) = 2\pi \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE \quad [\text{no. of states/unit volume}]$$

$$E = \frac{\hbar^2 k^2}{2m}$$

$$dk = \frac{m dE \hbar}{\hbar^2 \sqrt{2mE}} = \frac{1}{\hbar} \sqrt{\frac{m}{2}} E^{-1/2} dE$$

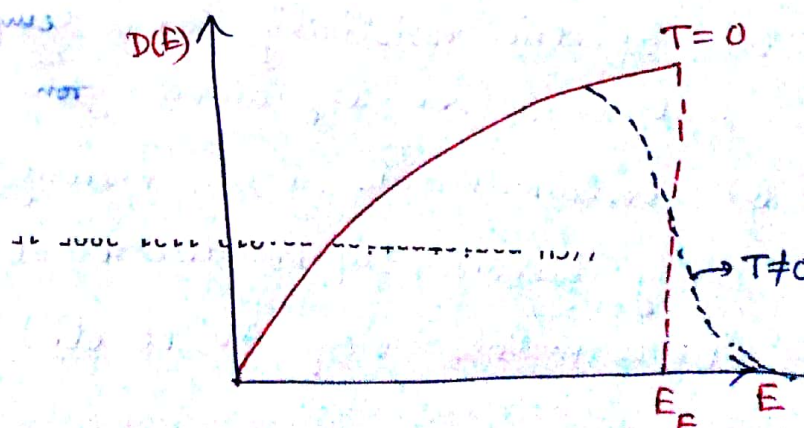


Using Pauli's exclusion principle, since electrons are spin $\pm \frac{1}{2}$ so each energy state will have 2-fold degeneracy.

$$\therefore D(E) = 2 \times 2\pi \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

$$D(E) = 4\pi \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

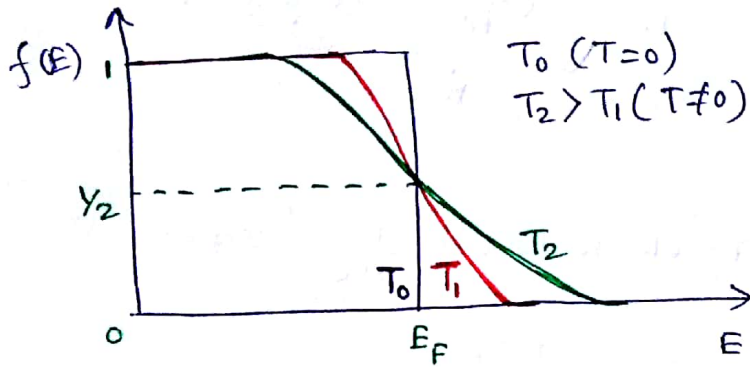
This is valid at $T = 0K$.



At a finite temperature T , the probability that an electron occupies a state with energy E is given by Fermi-Dirac function

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \quad \text{where } E_F = \mu = \frac{\partial G}{\partial N} = \text{chemical potential}$$

at $T=0$, $f(E) = 0$ if $E > E_F$ at $T \neq 0$, $f(E) = \frac{1}{2}$ if $E = E_F$
 $= 1$ if $E < E_F$



at $T=0$, Below Fermi energy all states are filled & above states are empty. at $T \neq 0$, at Fermi energy half of the states are filled.

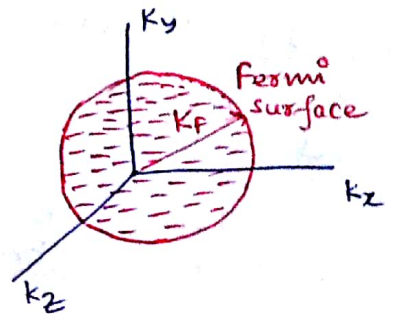
$$E_F = \frac{\hbar^2 K_F^2}{2m} \quad \text{and in } k\text{-space, Fermi-sphere } S_F = 4\pi K_F^2$$

$$\text{Now } \int_0^\infty f(E) D(E) dE = n$$

at $T=0$, $f(E) = 1$ till $E = E_F$

$$\therefore \int_0^{E_F} D(E) dE = n$$

$$\propto 4\pi \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{E_F} E^{1/2} dE = n \quad \propto \boxed{E_F = \frac{\hbar^2}{2m} \left(\frac{3n}{8\pi} \right)^{2/3}} \propto n^{2/3}$$



at $T \neq 0$ for $E_F \gg k_B T$, $E_F(T)$ is given by Sommerfeld equation

$$E_F(T) = E_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right]$$

$$\text{from } E_F = \frac{\hbar^2 K_F^2}{2m}, \quad K_F^2 = \frac{2m}{\hbar^2} \frac{\hbar^2}{2m} \left(\frac{3n}{8\pi} \right)^{2/3} = (3n\pi^2)^{2/3}$$

$$\text{Fermi wave vector } \boxed{K_F = (3\pi^2 n)^{1/3}}$$

$$\text{Fermi velocity } \boxed{v_F = \frac{\hbar K_F}{m} = \frac{\hbar}{m} (3\pi^2 n)^{1/3}}$$

$$E_F = \frac{3}{2} K_B T_F \Rightarrow \text{Fermi temperature } T_F = \frac{2E_F}{3K_B} = \frac{2\hbar^2}{6K_B m} (3\pi^2 n)^{2/3}$$

Substituting values & $n = 10^{22}/\text{cc}$, $T_F \sim 39,000 \text{ K}$.

Average energy of the electron at $T=0\text{K}$ is

$$\begin{aligned} \bar{E} &= \frac{1}{n} \int_0^{E_F} E D(E) dE = \frac{1}{n} 4\pi \left(\frac{2m}{h^2} \right)^{3/2} \int_0^{E_F} E^{3/2} dE \\ &= \frac{4\pi}{n} \left(\frac{2m}{h^2} \right)^{3/2} \frac{2}{5} E_F^{5/2} = \frac{1}{n} 4\pi \left(\frac{2m}{h^2} \right)^{3/2} E_F^{3/2} \frac{2}{3} \frac{5}{5} E_F \end{aligned}$$

$$\boxed{\bar{E} = \frac{3}{5} E_F}$$

Average speed of electron at $T=0\text{K}$ is $\bar{v} = \frac{1}{n} \int_0^{v_F} v dn$

$$\text{Now } v_F = \frac{\hbar}{m} (3\pi^2 n)^{1/3} \quad \therefore \quad n = \frac{1}{3\pi^2} \left(\frac{mv_F}{\hbar} \right)^3$$

If all velocity are below v_F & then $n = \frac{1}{3\pi^2} \left(\frac{m}{\hbar} \right)^3 v^3$

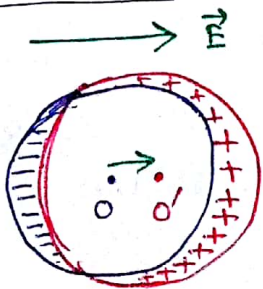
& number density of states between v & $v+dv$ is

$$dn = \frac{1}{3\pi^2} \left(\frac{m}{\hbar} \right)^3 3v^2 dv$$

$$\therefore \bar{v} = \frac{1}{n} \int_0^{v_F} \frac{1}{3\pi^2} \left(\frac{m}{\hbar} \right)^3 3v^3 dv = \frac{1}{n} \frac{1}{3\pi^2} \left(\frac{m}{\hbar} \right)^3 \frac{3}{4} v_F^4$$

$$= \frac{1}{n} \frac{1}{3\pi^2} \left(\frac{m}{\hbar} \right)^3 v_F^3 \frac{3}{4} v_F \quad \therefore \quad \boxed{\bar{v} = \frac{3}{4} v_F}$$

Sommerfeld's free electron theory & conductivity



Concept of Fermi surface $S_F = 4\pi k_F^2$ introduced by Sommerfeld changes the notion of conduction in metals. When an electric field is switched on, movement of the Fermi surface gives a

displacement of the centre of Fermi surface. This displacement is equivalent to creation of electrons on one side & positive charges

on the other. Like each electron have velocity $\vec{v} = \frac{\hbar \vec{k}}{m}$, then equation of motion of each electron in Fermi surface under steady field is $\frac{d\vec{p}}{dt} = \hbar \frac{d\vec{k}}{dt} = e\vec{E}$. So in the absence of any resistive force, the Fermi surface will move at constant rate in k space.

$$\int_{\vec{k}(0)}^{\vec{k}(t)} \hbar d\vec{k} = \int_0^t e\vec{E} dt \quad \therefore \quad \delta\vec{k} = \frac{e\vec{E}}{\hbar} t = \frac{e\vec{E}}{\hbar} \left(\frac{\lambda}{v_F} \right)$$

where λ is mean free path or distance between two ions.

But the collision of electron with impurity ions, imperfection & phonons (lattice vibrations) will create a restoring force.

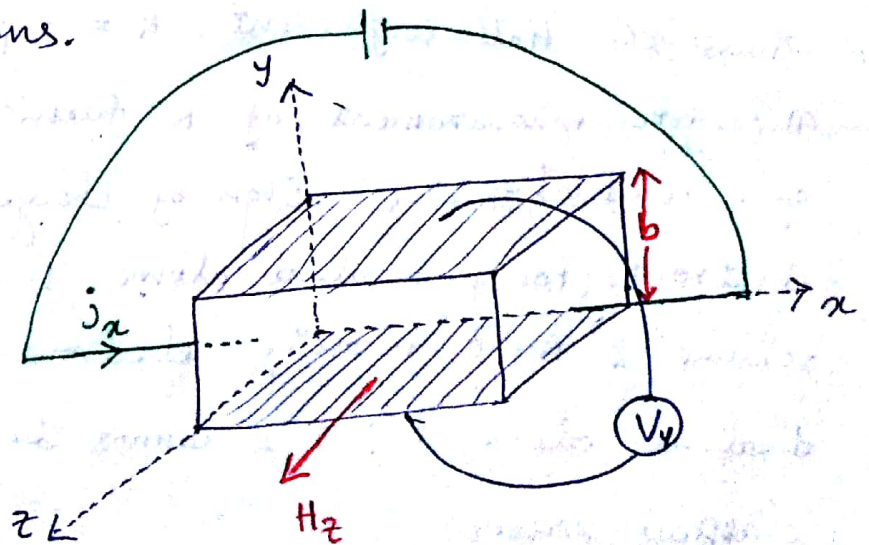
Thus in steady state, $\vec{J} = ne\vec{v}_d$ where $\vec{v}_d = \frac{\hbar \delta\vec{k}}{m}$.

$$= \frac{ne\hbar}{m} \delta\vec{k} = \frac{ne\hbar}{m} \frac{e\vec{E}\lambda}{\hbar v_F} = \frac{ne^2\lambda}{mv_F} \vec{E} = \sigma \vec{E}$$

This expression is identical to Drude's free electron theory but it destroys the notion of classical theory that all free electrons are conduction electrons. In Sommerfeld theory only few electrons that lie in the vicinity of the Fermi surface are the conduction electrons.

Hall effect

In 1879, Hall discovered that if a uniform magnetic field H_z is applied in z -direction normal to the direction of a steady current flow j_x in a rectangular slab, then a transverse electrical potential difference develops in the y direction.



$$V_y \propto j_x$$

$$\propto H_z$$

$$\propto b$$

$$V_y = R j_x H_z b$$

\downarrow Hall voltage \downarrow Hall coefficient \rightarrow Thickness of slab

Hall effect can be explained by simple classical theory. Current flows in x direction & H_z is applied in z direction. Thus the Lorentz force exerted on an electron in the slab is $F_y = -e v_x H_z$ where v_x is uniform drift velocity, so electrons are deflected in y direction. Because electrons are deposited near the surface, a potential difference in y direction is developed until the Hall electric field E_y stops further deflection of electrons.

$$E_y = \frac{V_y}{b} \text{ and the force } F_y = -e E_y = -\frac{e V_y}{b}$$

$$\text{Equating, } -e v_x H_z = -\frac{e V_y}{b} \Rightarrow v_x = \frac{V_y}{b H_z}$$

$$\therefore \text{Current density } j_x = -n e v_x = -n e \frac{V_y}{b H_z}$$

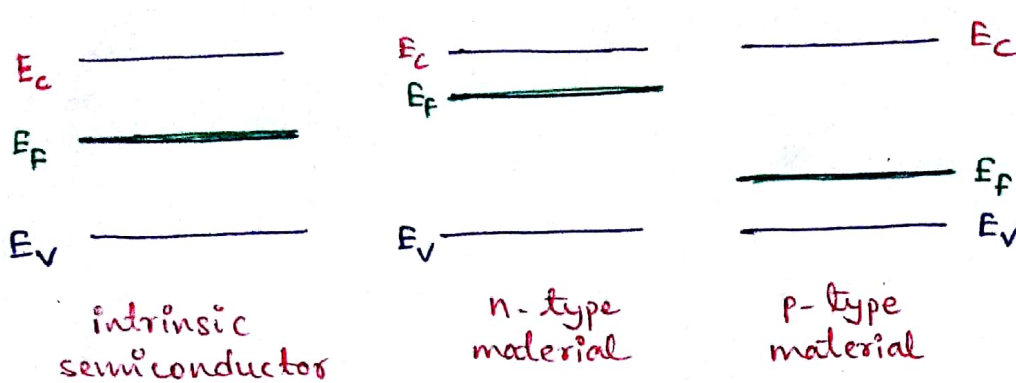
$$\text{or } V_y = \underbrace{\left(-\frac{1}{n e}\right)}_R j_x H_z b$$

Thus the Hall coefficient $R = -\frac{1}{n e}$ is $\propto \frac{1}{n}$ and $-\frac{1}{e}$.

Therefore measurement of R furnishes two important characteristics of a conductor: (1) Sign of charge carrier, (2) density of electrons. For monovalent atoms, n is number of electrons/unit volume & $R < 0$ meaning electrons are carriers. But for certain divalent atoms, $R > 0$ & cannot be explained only by the classical theory.

Read about 1D crystal's density of states, $\bar{E} = \frac{1}{3} E_F$ from any standard book.

Position of Fermi level



For intrinsic semiconductor concentration of electrons in conduction band = concentration of holes in valence band & so E_F lies at middle of band gap.

for n-type material concentration of electrons in conduction band $>$ hole concentration in valence band. E_F lies near to E_C . This is opposite in p-type material & E_F lies near to E_V . Whenever a pN junction diode is formed, barrier potential V_B is $eV_B = E_{F_n} - E_{F_p}$.

HW 1. In Sodium, free electrons per cubic metre are 2.5×10^{28} . Calculate the Fermi energy & Fermi velocity. You can use $h = 6.625 \times 10^{-34}$ Js, $m = 9.1 \times 10^{-31}$ Kg.

2. Consider silver in the metallic state with one free electron per atom. Calculate the Fermi energy. Given density of silver is 10.5 gm/cm^3 & atomic weight 108, $N = 6.02 \times 10^{23} / \text{g atom}$

3. Aluminium metal crystallites form fcc structure. If each atom contributes single electron as free electron & lattice constant a is 4 \AA , treating conduction electrons as free electron Fermi gas, calculate Fermi energy E_F , Fermi vector k_F & total K.E. per unit volume at $T = 0 \text{ K}$.