Quantum free electron theory(Sommerfield)

- Particles of micro dimension like the electrons are studied under quantum physics
- moving electrons inside a solid material can be associated with waves with a wave function ψ(x) in one dimension (ψ(**r**) in 3D)
- Hence its behaviors can be studied with the Schrödinger's equation (1D)

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi(x) = 0$$

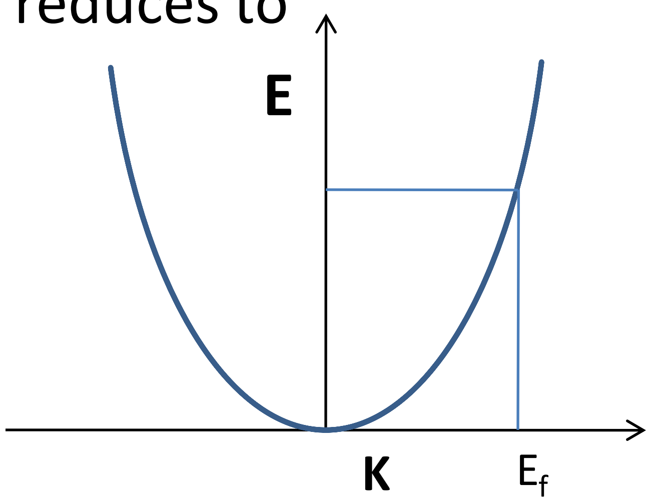
For a free particle V=0, hence the equation reduces to

$$\frac{\partial^2 \psi(x)}{\partial x^2} + k^2 \psi(x) = 0,$$

With

$$k^2 = \frac{2mE}{\hbar^2}$$

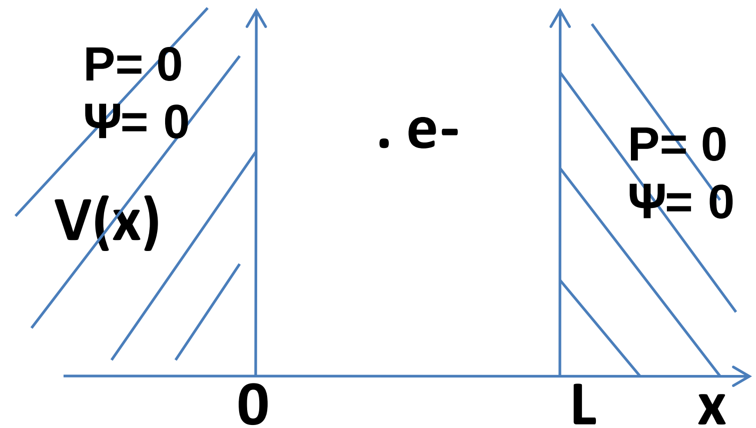
$$or, E = \frac{\hbar^2 k^2}{2m}, \hbar = \frac{h}{2\pi}$$



Sommerfield’s model

- As the freely moving electrons can not escape the surface of the material, they may be treated as particles confined (trapped)in a box
- Hence, **V(x) =0, for 0<x<L**

  = ∞, for x=0 & x=L



Sch’s equation , $$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

Solution of the equation can be obtained as

ψ(x) = A sin kx + B cos kx

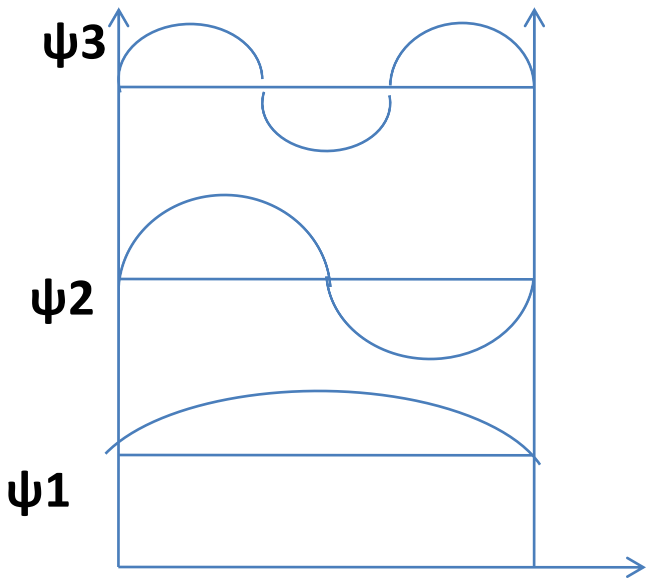
From boundary conditions , at **x=o & x=L , ψ(x)=0,**

we can get **B=0** and **k= ± nπ / L** ,

Putting the normalization condition we get **A=** $\sqrt{\frac{2}{L}}$

- Substituting all the values
- $\Psi_n(x) = (\sqrt{2/L}) \sin n\pi x / L$
- & $E_n(x) = \hbar^2 k^2 / 2m = \hbar^2\pi^2 n^2 / 2m L^2 = h^2 n^2 / 8mL^2$

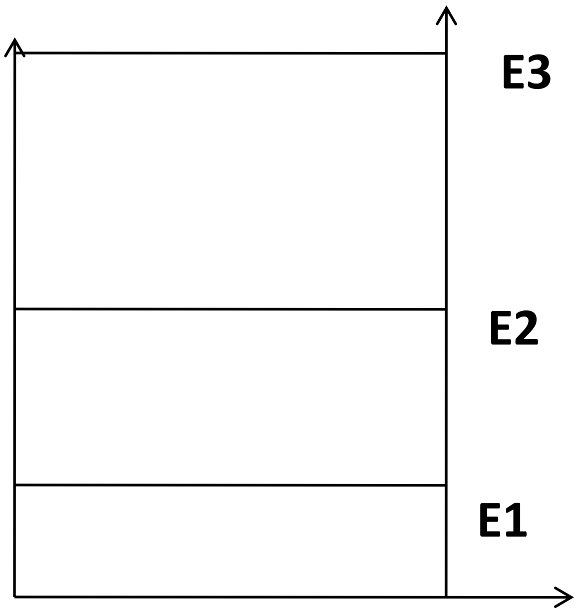
This shows that energy of the electrons inside the material is **quantized** and hence is **<u>discrete</u>**



n=3

n=2

n=1



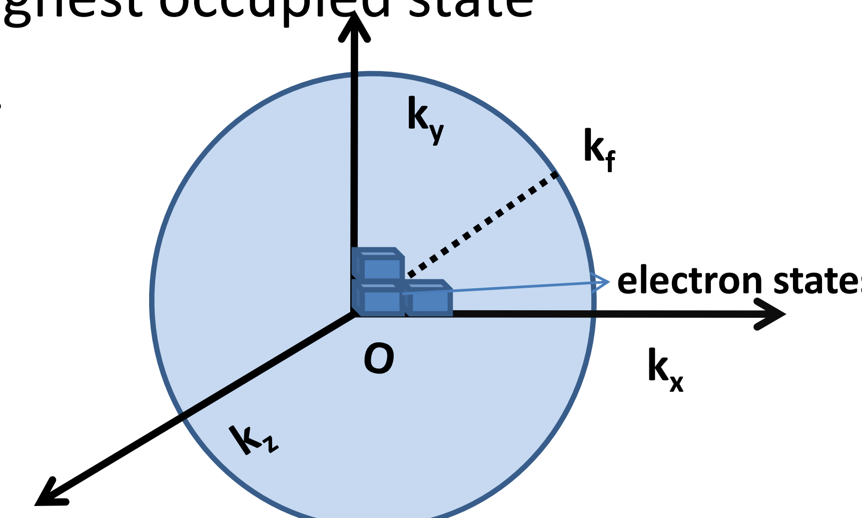
In 3D, $\Psi_n(r) = (\sqrt{8/L^3}) \sin n_x\pi x / L \ \sin n_y\pi y / L \ \sin n_z\pi z / L$

& $E_n(r) = \hbar^2 k^2 / 2m = (n_x^2+n_y^2+n_z^2)\, \hbar^2\pi^2 / 2m L^2$

Fermi Level and Fermi Energy:

- Electrons are fermions or Fermi particles, which obey Pauli's exclusion principle
- At 0K temperature the highest filled energy level is called the "Fermi Level" & the energy possessed by the electrons in that level is "Fermi Energy"
- $$\mathbf{E_f = \hbar^2 k_f^2 / 2m \quad or \quad k_f = (2mE_f / \hbar^2)^{1/2}}$$
- In 3D electrons will fill up the k-space with one state accommodating 2 electrons each (↑↓)
- If N is the total no. of electrons & is large , electrons will occupy a sphere of radius k_f , then highest occupied state

$$n_f = N/2$$



From uncertainty principle

$\Delta x\, \Delta p = h$ or, $\Delta x\, \hbar \Delta k = h$

Or, $L\,(h/2\pi)\,\Delta k = h$ or, $\mathbf{\Delta k = 2\pi / L}$

- state in k-space of radius k_f = $\dfrac{\frac{4\pi k_f^3}{3}}{\left(\frac{2\pi}{L}\right)^3}$

- = $K_f^3 L^3 / 6\pi^2$

- Hence no. of electrons ‘N’ = 2 X ($K_f^3 L^3 / 6\pi^2$)

$$\boxed{\mathbf{N = k_f^3 V / 3\pi^2}}$$

- So, $k_f = \{3\pi^2 (N/V)\}^{1/3}$

$$\boxed{\mathbf{k_f = (3\pi^2 n)^{1/3}}}$$

- where **n** = electron density = N/V = **1/ V** (**k_f^3 V / 3π²**)

- Or, n= $$\boxed{\frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_f^{\frac{3}{2}}}$$

- at 0 K, the fermi energy
- $E_f(0) = \hbar^2 k_f^2 / 2m$
- $= \hbar^2 / 2m \, (3\pi^2 n)^{2/3}$
- $E_f(0) = h^2 / 8m \, (3n/\pi)^{2/3}$

- Fermi velocity $v_f = \hbar k_f / m = \hbar / m \, (3\pi^2 n)^{1/3}$

Density of States: Z(E) = **no. of states per unit energy range per unit volume of the metal**

No. of free electrons within energy value 'E'

= no. of states within the sphere of radius 'k' in k-space

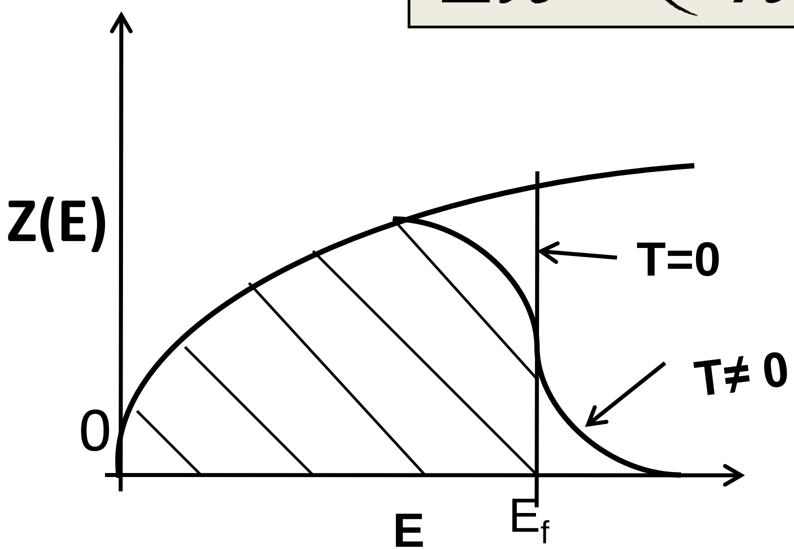
$= N(E) = Vk^3 / 3\pi^2 = V / 3\pi^2 \, (2mE/\hbar^2)^{3/2}$

or , Z(E) =

$$\frac{1}{V}\frac{dN(E)}{dE} = \frac{d}{dE}\left(\frac{k^3}{3\pi^2}\right) = \frac{d}{dE}\left[\frac{1}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{\frac{3}{2}}\right]$$

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

Or, **Z(E)=** $$\frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}}$$



or, **Z(E) α $E^{½}$**

Fermi Dirac distribution function

Distribution of electrons in different energy states is given by Fermi-Dirac statistics.

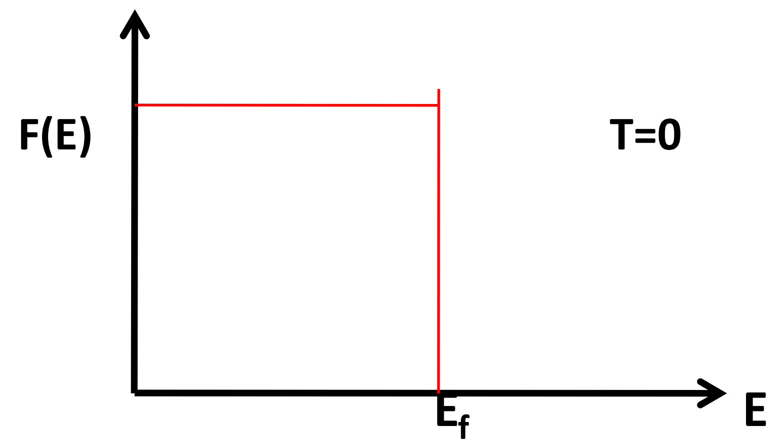
Fermi Dirac distribution function F(E) gives the probability of occupation of an energy level 'E', by an electron at temperature 'T'

- $F(E) = \dfrac{1}{e^{\frac{(E-E_f)}{k_\beta T}} + 1}$

- At T= 0 K

If E < E_f , then F(E)=1

If E > E_f , then F(E)= 0



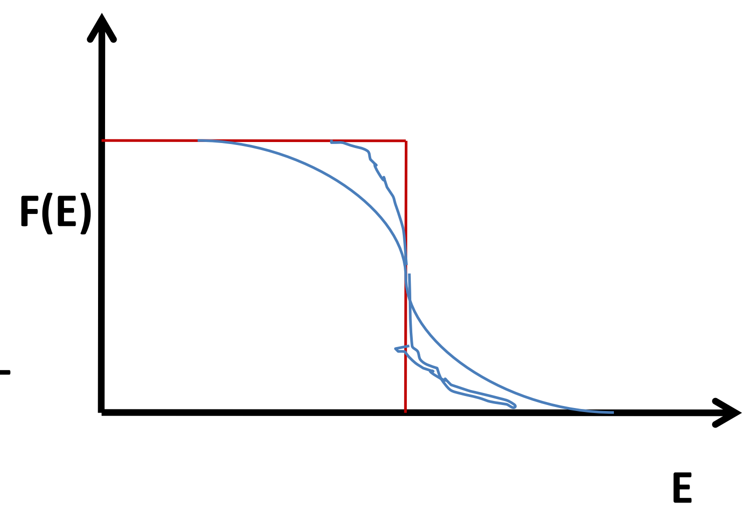
At T > 0 K

Some states below E_f are unoccupied

and some above are occupied

For E= E_f , F(E) = ½

*This is applicable in an energy range $k_\beta T$



- **Average energy of free electrons:**
- Av. Energy = $\dfrac{\text{total energy of all the electrons in the metal}}{\text{no. of electrons per unit volume}}$

$$< E > \; = \frac{\int_0^\infty E.Z(E)F(E)dE}{n}$$

As no. of free electrons per volume, n= $\int_0^\infty Z(E)dE.F(E)$

At T = 0 K : upper limit of integration is E_{f0} and F(E) is 1

$$<E_0> \; = \frac{\int_0^{E_{f0}} E.\frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}}.1.dE}{\frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_f^{\frac{3}{2}}}$$

As n = $\dfrac{1}{3\pi^2}\left(\dfrac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_f^{\frac{3}{2}}$

- $<E_0> = \dfrac{\frac{1}{2} E_{f_o}^{\frac{5}{2}}}{\frac{5}{2} \cdot \frac{1}{3} E_{f_o}^{\frac{3}{2}}}$ or $<E_0> = \mathbf{3/5}\ E_{f0}$

For T > 0 K (In a metal some states above fermi level are occupied at T > 0K)

- $< E_T> = \dfrac{\int_0^{\infty} E . \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} . \frac{1}{e^{\frac{(E-E_f)}{k_\beta T}}+1} dE}{\frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_f^{\frac{3}{2}}}$

$= \quad < E_o > \left[1 + \frac{5\pi^2}{12}\left(\frac{k_\beta T}{E_{f_o}}\right)^2\right]$

- Where, $E_f (T) = \quad E_{f_o}\left[1 - \frac{\pi^2}{12}\left(\frac{k_\beta T}{E_{f_o}}\right)^2\right]$

Specific heat in quantum free electron theory

- In classical theory , Specific heat '**C**' of the electron gas

$$C = \frac{d}{dT}(E) = \frac{d}{dT}\left(\frac{3}{2}k_\beta T\right) = 3/2\ k_\beta$$

- Molar specific heat = **$C = n\,C = 3/2\ n\,k_\beta$**

Hence, thermal conductivity $K = 1/2\ n\,k_\beta\,v_{th}\,\lambda$

$$= 1/3\ C\,v_{th}\,\lambda$$

In quantum theory, av. Energy of a free electron,

$$< E > = \frac{3}{5}E_{f_0}\left[1 + \frac{5\pi^2}{12}\frac{k_\beta{}^2T^2}{E^2{}_{f_0}}\right]$$

For an electron density 'n'

specific heat =

$$\mathbf{C = n\,d<E>/\,dT = \pi^2 n k_\beta{}^2 T / 2E_{f0}}$$

Is found to be agreeing with experimental result

Lorenz no. in quantum free electron theory

So, thermal conductivity

$K = 1/3\ (\pi^2 n k_\beta^2 T / 2E_{f0})\ v_{th}^2 \tau$

$= \pi^2 k_\beta^2 n T\tau / 3m \qquad (\text{as } ½\, m v_{th}^2 = E_{f0})$

So, Weidman – Franz law

$$K/\sigma = \frac{\dfrac{\pi^2 k_\beta^2 n T \tau}{3m}}{\dfrac{n q^2 \tau}{m}}$$

$$= \frac{\pi^2 k_\beta^2}{3q^2} T$$

$$= L\,T$$

In classical theory L = Lorenz no. = $3k_\beta^2 / 2q^2$

In quantum theory $L = \pi^2 k_\beta^2 / 3q^2 = 2.45 \times 10^{-8}\ W\Omega / K^2$

and agrees well with exptl. result