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Unit III → Part - I

Free Electron Theory

Classical free electron theory of metals
or

Drude-Lorentz theory of metals

Drude and Lorentz proposed this theory in 1900.
According to this theory the metals ~~contain~~ containing the free electrons obey the laws of classical mechanics.

Assumptions in classical free electron theory

- (1) The valence electrons of atoms are free to move about the whole volume of the metal.
- (2) The free electrons move in random direction and collide with either positive ions or other free electrons.
- (3) All the collisions are elastic in nature.
- (4) The momentum of free electrons obeys the laws of the classical kinetic theory of gases.
- (5) The electron velocities in a metal obey classical Maxwell-Boltzman distribution of velocities.

- (6) When the electric field is applied to the metal, the free electrons are accelerated in the direction opposite to the direction of applied electric field.
- (7) The mutual repulsion among the electrons is ignored.
- (8) In the absence of the field, the energy associated with an electron at temp. T is given by $\frac{3}{2}kT$.

Success of classical Free electron theory

- (1) It verifies Ohm's Law.
- (2) It explains Electrical Conductivity of metals.
- (3) It explains Thermal Conductivity of metals.
- (4) It derives Wiedemann-Franz law.

1) Drawbacks of classical free electron theory

- (1) It could not explain photoelectric effect, Compton effect and black body radiation.
- (2) Electrical conductivity of semiconductor and insulator could not be explained.
- (3) Wiedemann-Franz law ($\frac{Ic}{\sigma T} = \text{constant}$) is not applicable at low temp.
- (4) This theory could not explain resistivity of metals at very low and very high temp.
- (5) The phenomenon of superconductivity could not be explained by this theory.
- (6) The properties of semiconductor could not be explained.
- (7) It could not explain why some solids behave as good conductors while others are insulators.

Classical free electron theory

Electrical Conductivity →

Drude Theory of Conduction →

The classical free electron theory was proposed by Drude and Lorentz. According to this theory the electrons are moving freely and randomly. When electric field is applied the free electrons gets accelerated.

When an electric field E is applied between the two ends of a metal of area of cross section A

Force acting on the electron in the electric field = eE

$$F = ma$$

$$\Rightarrow a = \frac{F}{m} = \frac{eE}{m}$$

The average velocity (drift velocity) acquired by the electrons by the application of electric field, is

$$V_d = a\tau$$

τ = Mean Collision time

$$\Rightarrow V_d = \frac{eET}{m}$$

$$\tau = \frac{d}{\bar{c}} \rightarrow \text{mean Collision time}$$

Where $\bar{c} = \text{Root mean square speed}$,
 $d = \text{Mean free path}$.

$$\Rightarrow V_d = \frac{eE}{m \bar{c}} \quad (2)$$

The relation between current and drift velocity

$$i = neA V_d$$

$$\text{and } j = \frac{i}{A}$$

$$\text{or } j = neV_d \quad (3)$$

Put V_d from (2) in (3)

$$j = \frac{n e^2 A E}{m \bar{c}}$$

$$\text{Now } j = \sigma E$$

$$\Rightarrow \sigma = \frac{j}{E}$$

$$\Rightarrow \boxed{\sigma = \frac{n e^2 d}{m \bar{c}}} \quad \text{where } \bar{c} = \sqrt{\frac{3kT}{m}}$$

Verification of ohm's law

We know, current density $j = \frac{I}{A}$

$$\text{or } I = j A$$

$$I = \sigma E A \quad (j = \sigma E)$$

$$I = \sigma \left(\frac{V}{l} \right) A \quad (E = \frac{V}{l})$$

$$\Rightarrow I = \frac{V}{\rho l} A \quad (\sigma = \frac{1}{\rho})$$

$$\Rightarrow I = \frac{A}{\rho l} V \quad \left\{ R = \rho \frac{l}{A} \right\}$$

$$\Rightarrow I = \frac{V}{R}$$

$$\therefore \boxed{V = IR}$$

Ohm's law is verified.

Thermal Conductivity (K)

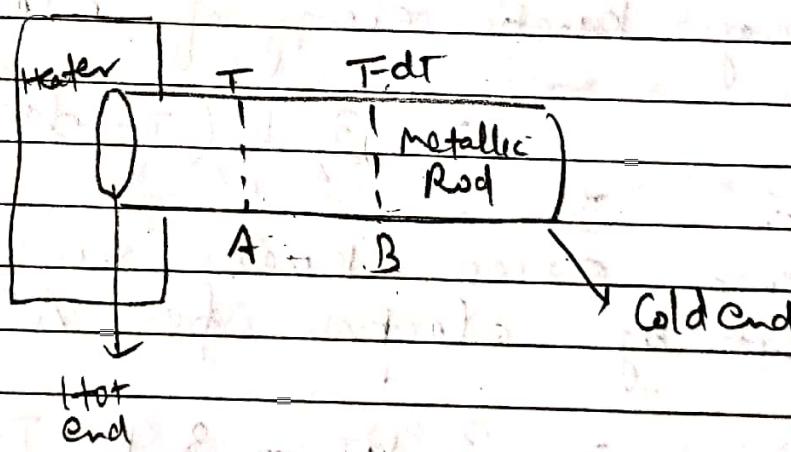
Thermal Conductivity of a metal is defined as the amount of heat (Q) conducted per unit time (t) through the material having unit area of cross-section (A) maintaining at unit temp. gradient ($\frac{dT}{dx}$)

$$K = - \frac{Q}{dT/dx}$$

$$\therefore Q = -K \frac{dT}{dx}$$

$K \rightarrow$ Thermal conductivity

$Q \rightarrow$ Amount of heat energy



Consider a uniform metallic rod containing free electrons. One end is heated using a heater.

Let A and B be the two cross-sections of temperature T and $T - dT$ separated by a distance of mean free path (r)

Heat flow from hot end A
to cold end B.

During the collision the electrons near A lose their kinetic energy and electrons near B gain the energy.

At point A:

$$\text{Average kinetic energy of electron} = \frac{3}{2} kT \quad (1)$$

Where k is Boltzmann's constant.

At point B:

Average kinetic energy of electron

$$= \frac{3}{2} k(T - dT) \quad (2)$$

Hence excess kinetic energy carried out by electron from A to B.

$$= \frac{3}{2} kT - \frac{3}{2} k(T - dT)$$

$$= \frac{3}{2} k dT \quad (3)$$

Let us assume that the electrons will flow in all 6 directions with equal probabilities. If n

is the free electron density and v is the thermal velocity then,

the number of electrons carrying unit area per unit time from A to B = $\frac{1}{6} nv$ — (4)

Excess Energy Carried from A to B

$$= \frac{1}{6} nv \times \frac{3}{2} k dT$$

$$= \frac{1}{4} nv k dT — (5)$$

Similarly the deficiency of energy carried from B to A

$$= -\frac{1}{4} nv k dT — (6)$$

Hence net energy transferred from A to B per unit area per unit time

$$Q = \frac{1}{4} nv k dT - \left(-\frac{1}{4} nv k dT \right)$$

$$\therefore Q = \frac{1}{2} nv k dT — (7)$$

$$\text{We know } Q = k \cdot \left(\frac{dT}{A} \right) — (8) (\because dA = A)$$

Comparing eq. (7) and (8)

$$k \cdot \frac{dT}{A} = \frac{1}{2} nv k dT$$

$$\Rightarrow k = \frac{1}{2} nv k_A — (9)$$

Now $\sigma = T^{\alpha}$

Put in (P)

$$K = \frac{1}{2} n e^2 k T$$

Wiedmann - Franz law

The ratio between the thermal conductivity and the electrical conductivity of a metal is directly proportional to absolute temp. of the metal

From classical theory

$$\sigma = \frac{n e^2 T}{m} \quad \text{--- (1)}$$

$$\text{and } K = \frac{1}{2} n e^2 k T \quad \text{--- (2)}$$

$$\text{Now } \frac{K}{\sigma} = \frac{\frac{1}{2} n e^2 k T}{\frac{n e^2 T}{m}} = \frac{k T}{\frac{T}{m}}$$

$$\Rightarrow \frac{K}{\sigma} = \frac{1}{2} m e^2 \frac{k}{e^2}$$

$$\text{Now } \frac{1}{2} m e^2 = \frac{3}{2} k T$$

$$\Rightarrow \frac{K}{\sigma} = \frac{3}{2} k T \frac{k}{e^2} = \frac{3}{2} \frac{k^2}{e^2} T$$

$$\Rightarrow \frac{K}{\sigma} = L T$$

Lorentz number

or $\frac{K}{\sigma} = \text{Constant}$

Wiedmann - Franz law

Quantum Theory of Free Electrons;

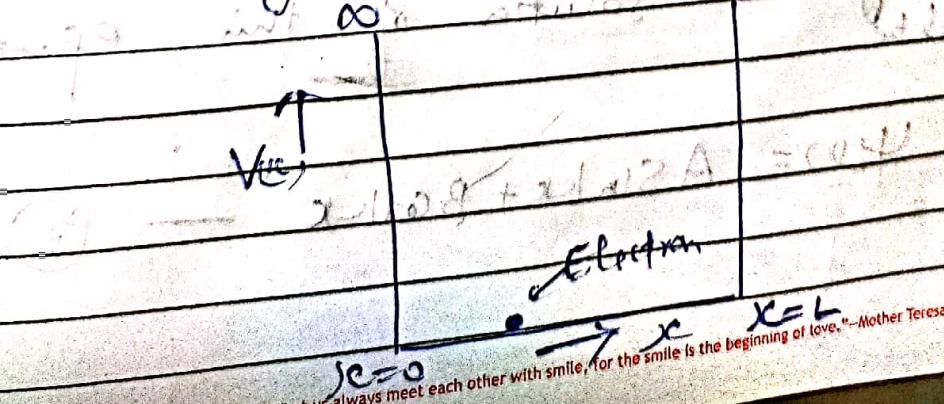
Sommerfeld modified Drude's classical theory by considering quantum concepts like Pauli Exclusion Principle. He treated the problem by using Fermi-Dirac statistics.

Free electron gas in 1-dimensional potential energy box →

In Sommerfeld's theory, it is assumed that free electrons experience constant potential everywhere inside the metal. As there occurs no electron emission from the metals at room temperature, so, it is considered that potential energy of electron inside metal is lower than that of an electron just outside the metal.

Hence metal's surface acts as sharp potential energy barrier of infinite potential energy due to which no electron leaves the metal.

Fig shows one dimensional potential energy box bounded by potential barrier of infinite height.



"Let us always meet each other with smile, for the smile is the beginning of love." - Mother Teresa

We have

$$V(x) = 0 \quad \text{for } x < L$$

$$V(x) = \infty \quad \text{for } x > L$$

Let $\Psi_n(x)$ is the wavefunction associated with the electron.

Now we will solve Schrodinger wave equation for electron which will be

$$\frac{d^2\Psi_n(x)}{dx^2} + \frac{2m}{\hbar^2} E_n \Psi_n(x) = 0 \quad \text{inside the box, } V = 0$$

$$\frac{d^2\Psi_n(x)}{dx^2} + k^2 \Psi_n(x) = 0 \quad (1) \quad \text{where } k^2 = \frac{2mE_n}{\hbar^2}$$

$$\text{Where } k^2 = \frac{2mE_n}{\hbar^2} \quad (2)$$

Here E_n is the total energy of electron in n th energy state.

The general solution of this equation will be

$$\Psi_n(x) = A \sin kx + B \cos kx \quad (3)$$

Now since electron is bounded by infinitely high potential energy barriers at $x=0$ and $x=L$

Wave function must vanish at boundaries

$$\psi_n(0) = 0 \text{ and } \psi_n(L) = 0$$

For $x=0$ eq. (3) becomes

$$\psi_n(0) = A \sin(0) + B \cos(0)$$

$$\text{Hence } B = 0$$

$$\text{Also } \psi_n(L) = 0$$

$$\text{So } \psi_n(L) = A \sin(kL)$$

$$\text{or } 0 = A \sin(kL)$$

$$\text{or } \sin(kL) = 0$$

$$\text{or } k = \frac{n\pi}{L} \quad (4)$$

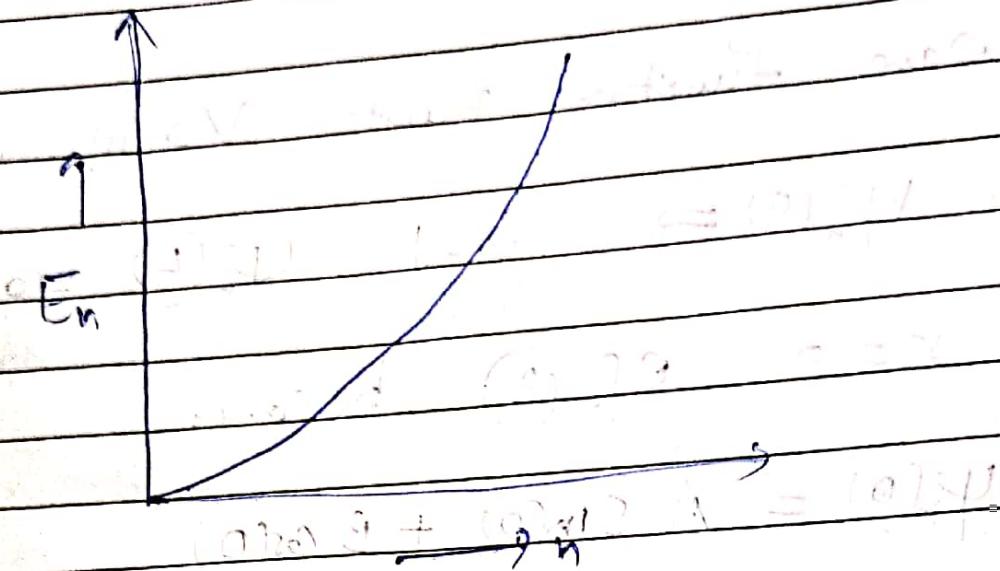
From eq. (2) and (4)

$$\frac{n^2 \pi^2}{L^2} = \frac{2m E_n}{\hbar^2}$$

$$\Rightarrow E_n = \frac{n^2 \pi^2 \hbar^2}{2m L^2} \quad (5)$$

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clearly $E_n \propto n^2$



(1) Energy spectrum consists of discrete energy levels by $E_n \propto n^2$

$$E_n \propto n^2 \Rightarrow E_n = \alpha n^2$$

(2) It also shows that Energy is quadratic function of Quantum number n

(3) Spacing between energy levels is determined by values of n_1 and n_2 . It decreases with increase in L.

Fermi-Dirac Distribution Function.

In Fermi-Dirac distribution all the particles in the system are indistinguishable and it obeys Pauli's exclusion principle (ie not more than two electrons can occupy the same energy level) on filling the particles with the energy levels.

This is mainly applicable for fermions [Fermions are the particles with odd half integral spin ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$)]

According to Fermi-Dirac distribution, the probability of occupying an Energy level E_i is

$$f(E_i) = \frac{1}{e^{\frac{E_i - E_F}{kT}} + 1} \quad (1)$$

Where E_F is Fermi Energy

Fermi Energy \rightarrow Energy of the highest occupied level

The energy of the highest occupied level is referred to as Fermi level.

The Fermi energy is denoted by E_F

In equation (1)

E_i is the energy of i^{th} level.

E_F is the energy of Fermi level

k is Boltzmann constant.

T is absolute temperature.

$f(E_i)$ is the Fermi function.

The highest filled level, which separates the filled and empty levels at 0K is known as the Fermi levels. And the energy corresponding to this level is called Fermi Energy (E_F).

At 0K, the Fermi energy E_F is represented by E_F .

As the temperature of the metal is increased from 0K to T_K , then those electrons which are present up to the depth of $k_B T$ from Fermi energy may take thermal energies equal to $k_B T$.

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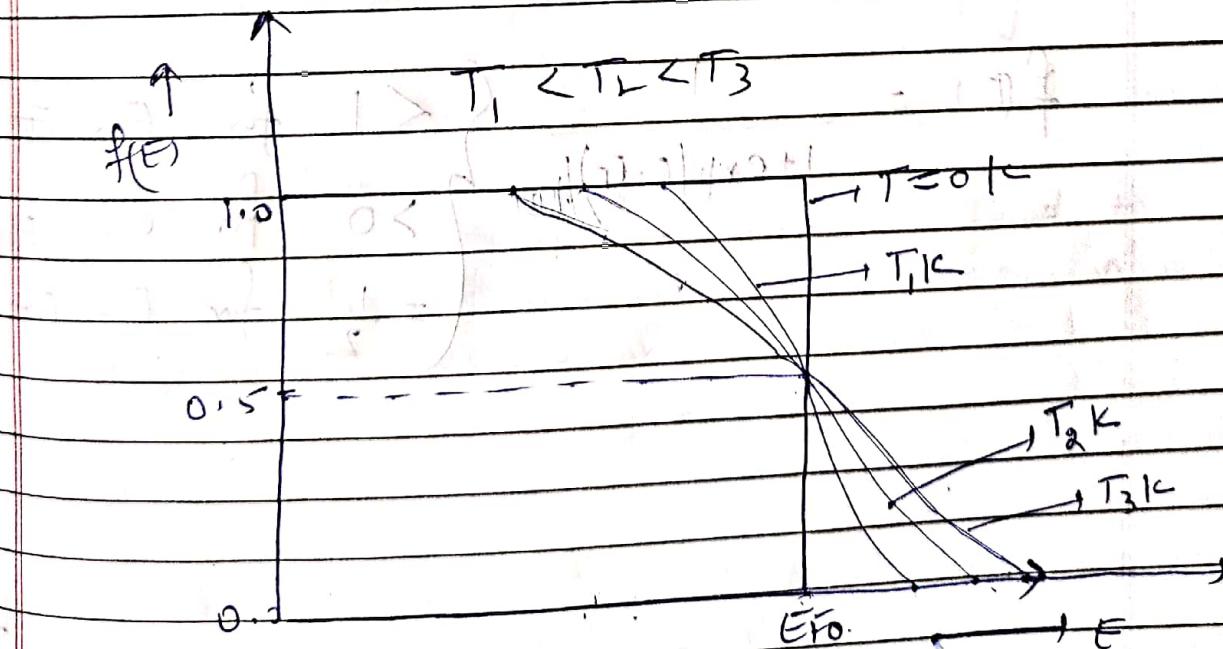
and occupy higher energy levels, whereas the electrons present in the lower energy levels ie below $k_B T$ from Fermi level, will not take thermal energies because they will not find vacant electron states.

The probability that a particular quantum state at energy E is filled with electrons is given by Fermi-Dirac distribution function

$$f(E) = \frac{1}{1 + e^{(E - E_F)/k_B T}} \quad (1)$$

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

The graph between $f(E)$ and E at different temperatures $0^\circ K, T_1 K, T_2 K, T_3 K$ is shown below



\Rightarrow At $T = 0 \text{ K}$

$$f(E) = \frac{1}{1 + \exp((E - E_F)/k_B T)} = \begin{cases} 1 & \text{for } E < E_F \\ 0 & \text{for } E > E_F \end{cases}$$

The curve has step-like character with $f(E) = 1$ for energies below E_F and zero for energies above E_F .

This represents that all the energies (states) below E_F are filled with electrons and above E_F are empty.

\Rightarrow At $T > 0 \text{ K}$

$$f(E) = \frac{1}{1 + \exp((E - E_F)/k_B T)} = \begin{cases} < 1 & \text{for } E < E_F \\ > 0 & \text{for } E > E_F \\ = \frac{1}{2} & \text{for } E = E_F \end{cases}$$

As the temperature is raised from absolute zero to $T_1 K$, the distribution curve begins to depart from step-like function and tails off smoothly to zero.

Again with a further increase in temp. to $T_2 K$ and to $T_3 K$, the departure and tailing of the curves increases. This indicates that more and more electrons may occupy higher energy states with an increase of temperature and a consequence the number of vacancies below the fermi level increases in the same proportion.

At non-zero temperatures, all the curves pass through a point whose $F(E) = \frac{1}{2}$ at $E = E_F$. So E_F lies half way between the filled and empty states.

* $S_{K,T}$ is the amount of heat required to increase the thermodynamic entropy of a system.

Density of states.

It is the total number of available energy states per unit energy range corresponding to energy E.

In three dimensions crystal is considered as a cube of edge L inside which potential energy is zero. Now wavefunction associated with electron is given by Schrödinger wave equation

$$\nabla^2 \psi(\vec{r}) + \frac{2mE_n}{\hbar^2} \psi(\vec{r}) = 0$$

Solving above equation, the admissible energy values are

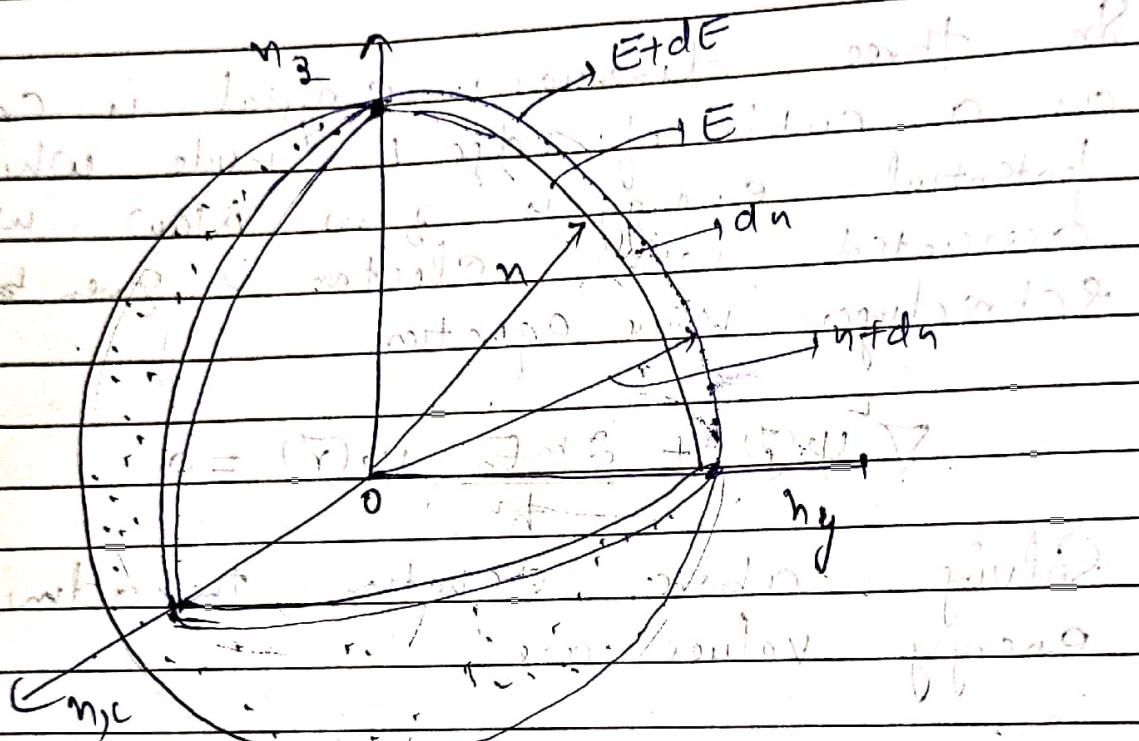
$$E_{n_x, n_y, n_z} = \frac{n_x^2 h^2}{8mL^2} + \frac{n_y^2 h^2}{8mL^2} + \frac{n_z^2 h^2}{8mL^2} \quad (1)$$

Where n_x, n_y, n_z is a set of positive integers which define the energy state.

The number of states with a particular Energy E, depends on combinations of numbers n_x, n_y, n_z which results in unique value of n .

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Construct n -space of points. Each point with integral values of coordinates n_x, n_y, n_z represents one energy state as shown in diagram.



Draw a radius vector r from origin to a point (n_x, n_y, n_z) . All the points on the surface of sphere of radius r will have same energy.

Hence number of states available with in the sphere of radius r will be given by

$$= \frac{\text{Volume of sphere in } n\text{-space}}{\text{Volume of a single state in } n\text{-space}}$$

$$= \frac{1}{8} \left(\frac{4}{3} \pi n^3 \right)$$

↳ Volume of single state
means for $n_x = n_y = n_z = 1$
Volume becomes 1

$$= \frac{1}{8} \cdot \frac{4}{3} \pi n^3 \quad (2)$$

[Three dimensional
Coordinate system inside
the sphere contributes
 $\frac{1}{8}$ th]

Similarly number of states in the energy range ΔE of radius $(n+dn)$ will be

$$= \frac{1}{8} \left[\frac{4}{3} \pi (n+dn)^3 - n^3 \right] \quad (3)$$

Hence number of states in the energy range dE is given by

$$D(E) dE = \frac{1}{8} \left[\frac{4\pi}{3} (n+dn)^3 - n^3 \right]$$

$$D(E) dE = \frac{\pi}{6} 3n^2 dn = \frac{11}{2} n^2 dn \quad (4)$$

by Neglecting dn^2 and dn^3 .

Where $D(E)$ is density of states.

Now we have

$$E = \frac{n^2 h^2}{8m c^2}$$

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$$\text{or } n^2 = \frac{8mL^2}{h^2} E \quad \rightarrow (5)$$

Differentiating this equation

$$2ndn = \frac{8mL^2}{h^2} dE \quad (\cancel{\text{Multiplying by } 2})$$

or we can write

$$n = \left(\frac{8mL^2}{h^2} E \right)^{\frac{1}{2}} \quad (6)$$

$$\text{or } dn = \frac{1}{2} \left(\frac{8mL^2}{h^2} \right)^{\frac{1}{2}} \frac{dE}{E^{\frac{1}{2}}} \quad \rightarrow (6)$$

Put the values of n^2 and dn from
 (5) and (6) in eq. (4) we get

$$D(E)dE = D_2 \left(\frac{8mL^2}{h^2} E \right)^{\frac{1}{2}} \left(\frac{8mL^2}{h^2} E^{\frac{1}{2}} \right)^{\frac{1}{2}} \frac{dE}{E^{\frac{1}{2}}}$$

$$\text{or } D(E)dE = D_2 \left(\frac{8mL^2}{h^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} dE \quad (7)$$

It must be remembered that Pauli Exclusion Principle allows two electrons in each energy state. So Number of quantum states actually available are

$$D(E) dE = \frac{2\pi \times 10^{-16} (8m_e)^{\frac{3}{2}}}{h^2} E^{\frac{1}{2}} dE$$

$$\text{Volume } V = D_2 \left(\frac{8m_e}{h^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} dE$$

$$\text{Now } V = L^3$$

$$\Rightarrow D(E) dE = D_2 \left(\frac{8m_e}{h^2} \right)^{\frac{3}{2}} V E^{\frac{1}{2}} dE$$

~~Now we have~~

$$\Rightarrow \boxed{D(E) dE = D_2 \left(\frac{8m_e}{h^2} \right)^{\frac{3}{2}} V E^{\frac{1}{2}}}$$

$$D(E) = \frac{1}{V} \int_0^{\infty} D_2 \left(\frac{8m_e}{h^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} dE$$

$$= \frac{1}{V} \cdot \frac{1}{2} \left(\frac{8m_e}{h^2} \right)^{\frac{3}{2}} \int_0^{\infty} E^{\frac{3}{2}} dE$$

$$= \frac{1}{V} \cdot \frac{1}{2} \left(\frac{8m_e}{h^2} \right)^{\frac{3}{2}} \cdot \frac{2}{5} E^{\frac{5}{2}} \Big|_0^{\infty}$$

$$= \frac{1}{V} \cdot \frac{1}{5} \left(\frac{8m_e}{h^2} \right)^{\frac{3}{2}} E^{\frac{5}{2}}$$

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Fermi Energy

The highest filled level which separates the filled and empty levels at 0K is known as Fermi level, and the energy corresponding to this level is called Fermi Energy (E_F). At 0K E_F is represented as E_{FO} .

Let $D(E)$ is the density of states at energy E . Then total number of states in the interval dE will be $D(E) dE$.

Let $f(E)$ is the Fermi function of the states corresponding to energy E .

Then total number of electrons corresponding to energy E in the energy interval (dE) will be given as

$$N(E) d(E) = f(E) D(E) dE \quad \text{--- (1)}$$

Also we know

$$D(E) = \frac{8\sqrt{2} \pi V m^{\frac{3}{2}} E^{\frac{1}{2}}}{h^3} \quad \text{--- (2)}$$

and $f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$ (3)

Put ② and ③ in ① we get

$$N(E) dE = \frac{8\sqrt{2}\pi V m^{\frac{3}{2}}}{h^3} \frac{E^{\frac{1}{2}} dE}{1 + e^{(E-E_F)/kT}} \quad (4)$$

Therefore total number of electrons say N in the free electron gas is calculating as

Q.

$$N = \int_0^{\infty} N(E) dE = \int_0^{\infty} f(E) D(E) dE$$

$$\text{or } N = \int_0^{E_F} D(E) dE + \int_{E_F}^{\infty} D(E) dE = 0$$

Since At $T=0K$, we have $f(E)=0$ for $E > E_F$
 $f(E)=1$ for $E < E_F$

$$\text{or } N = \int_0^{E_F} D(E) dE$$

$$\begin{aligned} N &= \frac{8\sqrt{2}\pi V m^{\frac{3}{2}}}{h^3} \int_0^{E_F} E^{\frac{1}{2}} dE \\ &= \frac{8\sqrt{2}\pi V m^{\frac{3}{2}}}{h^3} \left[\frac{E^{\frac{3}{2}}}{\frac{3}{2}} \right]_0^{E_F} \left(\frac{2}{3} \right) \end{aligned}$$

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$$\Rightarrow N = \frac{8\sqrt{2}\pi V m^{\frac{3}{2}}}{h^3} (\bar{E}_{F0})^{\frac{3}{2}} \cdot \frac{2}{3}$$

$$\Rightarrow N = \frac{2}{3} \left[\frac{8\sqrt{2}\pi V m^{\frac{3}{2}}}{h^3} \right] \bar{E}_{F0}^{\frac{3}{2}} \quad \text{--- (5)}$$

Now total number of electrons per unit Volume of metal i.e. density of electrons in free electron gas is

$$n = \frac{kN}{V} = \frac{2}{3} \left[\frac{8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} \right] (\bar{E}_{F0})^{\frac{3}{2}}$$

$$n = \frac{16\sqrt{2}\pi m^{\frac{3}{2}}}{3h^3} \bar{E}_{F0}^{\frac{3}{2}}$$

$$\Rightarrow \bar{E}_{F0}^{\frac{3}{2}} = \frac{3nh^3}{16\sqrt{2}\pi m^{\frac{3}{2}}}$$

$$\Rightarrow \boxed{\bar{E}_{F0} = \left(\frac{3n}{\pi} \right)^{\frac{2}{3}} \frac{h^2}{8m}}$$

Thermionic Emission

5.9 THERMIONIC EMISSION

The phenomenon of emission of electrons from the surface of a metal when the metal is heated is known as thermionic emission. According to quantum theory of free electrons in metals, all the energy states upto fermi level are filled at absolute zero and height of potential barrier is considered infinitely large. If potential energy outside the metal were really infinite, then no electron emission will occur at any temperature. Therefore, at absolute zero, it is now considered that:

- (i) height of potential energy barrier is finite equal to $E_F + \phi$ (V_B , potential barrier energy) as shown in the diagram 5.9.

- (ii) all the levels upto fermi-level are filled and the energy states above fermi level are empty.
- (iii) electrons can not escape from the surface of metal at zero temperature ($T = 0^\circ\text{K}$)
- (iv) Potential energy inside the metal is considered zero (uniform) throughout.

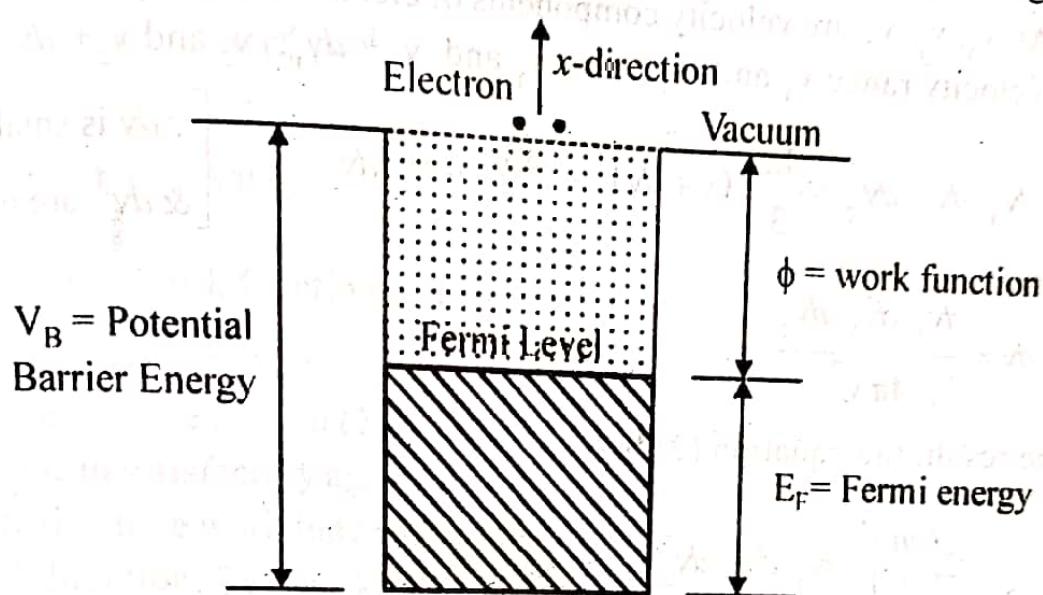


Fig. 5.9 Suitable diagram for thermionic emission at absolute zero of temperature (i.e. $T = 0 \text{ K}$)

Here, work function (ϕ) is the minimum energy required to remove an electron from the Fermi level to the vacuum just outside the metal surface.

Normally, electron emission is not observed from metals even at the ordinary temperatures. When the metal is heated and heat energy greater than ($E_F + \phi$) is supplied, only then, electrons are observed to be emitted from the metal surface. This process is called thermionic emission.