2 FREE ELECTRON THEORY OF METALS

2.1. INTRODUCTION

A number of physical properties of metals like thermal conductivity, electrical conductivity, specific heat, magnetic susceptibility etc. can be explained on the basis of free electron theory. This theory was first developed by Drude and Lorentz by applying classical laws of physics but it could not explain the heat capacity and the paramagnetic susceptibility of the conduction electrons though it explained properties like Ohm's law and metallic luster etc.

The difficulties occurred in classical theory were removed by using statistics. Firstly, we discuss classical theory in brief and then the quantum theory as developed by Sommerfield.

2.2. FREE ELECTRON GAS MODEL (DRUDE-LORENTZ CLASSICAL THEORY)

It was suggested by P. Drude in 1900, that the metal crystals consist of positive ion cores with their valence electrons (also known as conduction electrons since these are responsible for the conduction of electricity in metals) free to move among these positive metal ions (cores). The Coulomb's force of attraction between these positive ions and negatively charged electrons do not allow these free electrons to leave the metal surface. The potential field due to these ion cores is supposed to be uniform and hence potential energy of electrons may be taken as constant, which is taken to be zero for convenience. Hence, we have to deal only with the kinetic energy of the electrons. The mutual repulsion between the electron is neglected.

It has been suggested that the free electrons in the metal behave like those of atoms or molecules in a perfect gas. Hence, these electrons are sometimes known as *free electrons gas or fermi gas or free electron cloud.*

However, this fermi gas differs from ordinary gas in the following ways :

(*i*) Fermi gas is constituted by electrons which are charged particles while the atoms or molecules which constitute ordinary gas are neutral.

(*ii*) The concentration of electrons in fermi gas is large 10^{29} per m^3 as compared with concentration of atoms or molecules of ordinary gas (10^{25} per m^3).

In 1909, Lorentz suggested that this free electron gas like perfect gas obeys Maxwell-Boltzmann statistics. Hence, the classical theory is also known as *Drude-Lorentz theory.*

Let us first give a look at the experimental facts which must be explained satisfactorily by any theory.

(*i*) Ohm's law is obeyed by all metallic conductors.

(*ii*) High electrical and thermal conductivity.

(*iii*) The specific resistivity (ρ) of metals at room temperature is of the order of 10^{-5} ohm cm.

(*iv*) Above Debye temperature

$$\rho \propto T$$

(*v*) At low temperature (but > 20 K),

$$\rho \propto T^5$$

(*vi*) The resistivity varies in presence of magnetic field. The effect is known as Magneto resistance.

(*vii*) For most metals $\rho \propto \frac{1}{P}$, where P is pressure.

(*viii*) According to Matthiessen's rule, for metals containing small amounts of impurity,

$$\rho = \rho_0 + \rho(T)$$

where ρ_0 is constant and increase with impurity content and $\rho(T)$ is temperature dependent part of resistivity.

(*ix*) Above Debye temperature, the ratio of thermal (K) to electrical (σ) conductivity is proportional to T.

$$\frac{K}{\sigma} \propto T \text{ (Wiedemann-Franz law)}$$

where the constant of proportionality is nearly same for all the metals.

(*x*) At 0 K, most of metals show the phenomenon of super conductivity.

On the basis of free electron theory following properties of solids have been explained.

(i) Electrical conductivity

It is defined as the quantity of electricity that flows in unit time per unit area of cross-section of the conductor per unit potential gradient.

According to free electron theory, in a solid the electrons move freely. If E is the applied electric field, then the acceleration of an electron having charge '*e*' is given by

$$a = \frac{d^2x}{dt^2} = \frac{eE}{m} \qquad \text{... (2.1)}$$

If λ is the mean free path of electrons, then the relaxation time τ between two successive collisions is given by

$$\tau = \frac{\lambda}{v} \qquad \text{... (2.2)}$$

Integrating eq. 2.1, we get

$$\frac{dx}{dt} = \frac{eE}{m}t + C$$

At $t = 0, \frac{dx}{dt} = 0$

$$C = 0$$

Hence $$\frac{dx}{dt} = v = \frac{eE}{m}t$$

So average velocity between two successive collisions

$$\bar{v} = \frac{1}{\tau}\int_0^{\tau}\frac{eE}{m}t\,dt = \frac{eE}{\tau m}\int_0^{\tau}t\,dt$$

$$= \frac{eE}{\tau m}\,\frac{\tau^2}{2}$$

or $$\bar{v} = \frac{eE\lambda}{2m}$$

Putting the value of τ from eq. 2.2, we get

$$\bar{v} = \frac{eE\lambda}{2mv}$$

Since $\frac{1}{2}mv^2 = \frac{3}{2}k_B T$ (T is absolute temperature and k is Boltzmann constant)

So $mv = \frac{3k_B T}{v}$

So $\bar{v} = \frac{eE\lambda v}{6k_B T}$

If n is number density of electrons in the conductor, then the current density i is given by

$$i = ne\bar{v}$$

or $$i = \frac{ne^2 E\lambda v}{6k_B T} \quad \ldots (2.3)$$

If q charge is flowing through a conductor of cross-section area A in time t, then

$$q = \sigma AEt$$

or $$\frac{q}{t} = \sigma AE$$

or $$i = \sigma AE$$

or $$\sigma = \frac{i}{AE} \quad \ldots (2.4)$$

For unit area of cross-section $\sigma = \frac{i}{E}$

Using eq. (2.3)

$$\sigma = \frac{ne^2\lambda v}{6k_B TA}$$

This expression shows that different conductivities of different materials are due to different number of free electrons.

(ii) Ohm's law

From eq. (2.4) we have $\sigma E = \frac{i}{A}$

or $\sigma E = J$

or $J = \sigma E \quad \ldots (2.5)$

This is microscopic form of Ohm's law.

(iii) Thermal conductivity

We know that if there is no temperature difference between two points in a specimen i.e. $T_1 = T_2$, there is no transfer of energy. So to discuss the thermal conductivity of metals, we suppose that a temperature gradient exists across the specimen instead of voltage gradient, hence the transport of thermal energy takes place due to this gradient.

If we consider the specimen in the form of a metallic rod having two ends namely A and B and the end A is at higher temperature than B, then the conduction of heat from A to B takes place by electrons. In collision, the electrons near A loose their kinetic energy while the electrons near B gain the energy.

The amount of heat Q passing through a cross-section of the rod per unit area per second is given by :

$$Q = \frac{1}{3}nv\lambda\frac{dE}{dt} \quad \ldots (2.6)$$

where λ = mean free path

v = velocity of electrons

n = number density of free electrons

From kinetic theory of gases

$$E = \frac{3}{2}k_B T$$

$$\frac{dE}{dt} = \frac{3}{2}k_B \frac{dT}{dt}$$

$$\therefore \quad Q = \frac{1}{2}nv\lambda k_B \frac{dT}{dt}$$

Hence

$$K\frac{dT}{dt} = \frac{1}{2}nv\lambda k_B \frac{dT}{dt} \qquad \left[\because Q = K\frac{dT}{dt}\right]$$

or

$$K = \frac{1}{2}nv\lambda k_B \qquad \ldots (2.7)$$

or

This value of K is verified experimentally and the free electrons theory is found to be successful to explain thermal conductivity.

(iv) Wiedemann-Franz relation

Wiedemann and Franz in 1853 discovered that all good electrical conductors are also good thermal conductors and the ratio of thermal conductivity to the electrical conductivity at any temperature (but not too low temperature) is constant for all metals.

$$\frac{K}{\sigma} = \text{constant}$$

i.e.,

Using eqs. (2.7) and (2.3), we get

$$\frac{K}{\sigma} = \frac{\frac{1}{2}nv\lambda k_B . 6k_B T}{ne^2\lambda v}$$

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

$$\frac{K}{\sigma} \propto T.$$

or

This is Wiedemann-Franz relation.

(v) Lustre and Opacity of metals

When electromagnetic radiations fall on a metal, it produces forced oscillations in the free electrons having the same velocity as that of electromagnetic radiations. Thus, the energy of incident radiations is absorbed by free electrons and the metal appears opaque. The excited electron on returning to its initial state emits photon having the same energy as is absorbed initially. This energy is given out in the form of visible light in all directions, but only the light rays directed towards the metal surface can get through. Hence, the metal appears to reflect virtually all the light that is incident on it, giving it the characteristic metallic lustre.

(vi) Success of free eletron theory

The free electron theory explained

(*i*) Electrical conductivity
(*ii*) Ohm's law
(*iii*) Thermal conductivity
(*iv*) Wiedemann-Franz law
(*v*) Complete opacity of metals and their high lustre.

Failure of the theory

(*i*) It does not explain the heat capacity of materials.
(*ii*) It fails to explain the paramagnetic susceptibility of the conduction electrons.
(*iii*) It is unable to explain that why metals prefer certain structures.

(*iv*) It does not explain the occurrence of long mean free paths (of the order of centimetre) a low temperature.

(*v*) This theory does not explain the temperature variation of electrical resistivity because th theory predicts the variation of resistivity as $\sqrt{T}$, which actually is linear.

(*vi*) It does not explain why some crystals are metallic.

2.3. SOMMERFIELD'S QUANTUM THEORY

We have seen that the classical theory of free electron gas could not explain many experiment facts. In the development of classical theory Maxwell-Boltzmann statistics was used. According t this, electrons were considered as distinguishable particles and hence metal was considered simpl a box of field electrons.

Sommerfield in 1928, suggested that electron gas should be treated quantum mechanically i the light of Pauli's exclusion principle which states that *no two particles can have all the quantu numbers identical*. He used Fermi-Dirac statistics rather than Maxwell-Boltzmann statistics an succeeded in explaining many experimental facts. We first consider the possible energy states i one dimension and then extend the idea to three dimensional case.

2.4. FREE ELECTRON GAS IN ONE DIMENSIONAL BOX

Consider an electron of mass m confined to move in one dimensional rectangular box of lengt L. *i.e.*, The electron moves along a straight line say along X-axis let the walls of the box be rigid elastic and non-potentiable. Let the electron can travel along X-axis between $x = \sigma$ and $x = L$.

The potential V is defined as

$$V = \begin{cases} 0 \text{ for } 0 < x < L \\ \infty \text{ for } x < 0 \text{ and } x > L \end{cases}$$

The Schrodinger's wave equation for the wave function of the electron moving along a straight line may be written as

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

For free electron inside the box $V = 0$, so the above equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

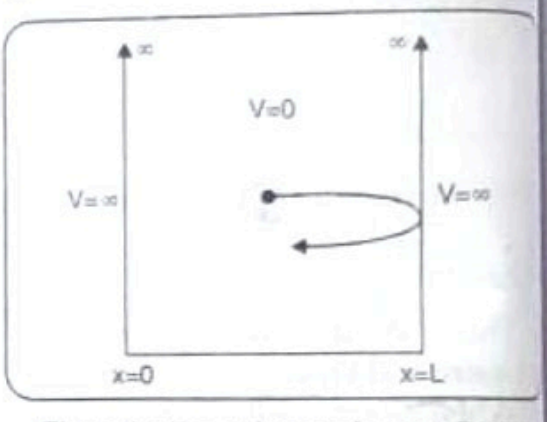

Fig. 2.1 : Free electron in non-dimensional box bounded by infinite potentialbarrier

where E is the kinetic energy of the electron

or
$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \ldots (2.8)$$

where
$$k^2 = \frac{2mE}{\hbar^2} \quad \ldots (2.9)$$

The general solution of eq. (2.8) may be written as

$$\psi(x) = Be^{ikx} + Ce^{-ikx}. \quad \ldots (2.10)$$

where A and B are the constants to be determined by the boundary conditions.

Boundary Conditions

The wave function $\psi = 0$ at $x = 0$ and at $x = L$

(i) At $x = 0$, $\psi = 0$, So eq. (2.10) becomes

$$B + C = 0$$

$$C = -B \quad \text{... (2.11)}$$

or

So eq. (2.10) becomes ... (2.12)

$$\psi = B e^{ikx} - B e^{-ikx} = B [e^{ikx} - e^{-ikx}]$$

$$= 2iB \left(\frac{e^{ikx} - e^{-ikx}}{2i} \right)$$

$$\psi = 2iB \sin kx,$$

or

$$= A \sin kx, \quad \text{... (2.13)}$$

$$A = 2iB$$

where

(ii) At $x = L$, $\psi = 0$, So, eq. (2.13) becomes

$$0 = A \sin kL$$

$$\sin kL = 0$$

or

$$kL = n\pi, (n = 0, 1, 2, ...)$$

or

$$k = \frac{n\pi}{L}$$

or

$$k^2 = \frac{n^2\pi^2}{L^2} \quad \text{...(2.14)}$$

or

For nth state eq. (2.13) becomes

$$\psi_n = A \sin \frac{\pi n x}{L} \quad \text{... (2.15)}$$

Using eq. (2.9), we get

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

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

or

Since E depends on n, so let us denote the energy of the electron by E_n. So, the above equation can be written as

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \quad \text{... (2.16)}$$

Thus we see from eq. (2.15) and (2.16) that wave function exists only for integral values of n and corresponding energy levels are also quantised. The number n is called the quantum number. We find that the lowest energy is obtained when $n = 1$ from eq. (2.16), we have

$$E_1 = \frac{\hbar^2\pi^2}{2mL^2}$$

i.e.

$$E_n = n^2 E_1 \quad \text{... (2.17)}$$

Let us find the spacing between the energy levels

$$E_{n+1} - E_n = (n+1)^2 E_n - n^2 E_1 = (2n+1) E_1$$

Energy level diagram is shown in Fig. (2.2)

It is also obvious that the spacing between levels depends upon the length (L) of the box as well as on the value of 'n', the quantum number. The spacing between energy levels is important only when L is of the order of atomic dimensions.

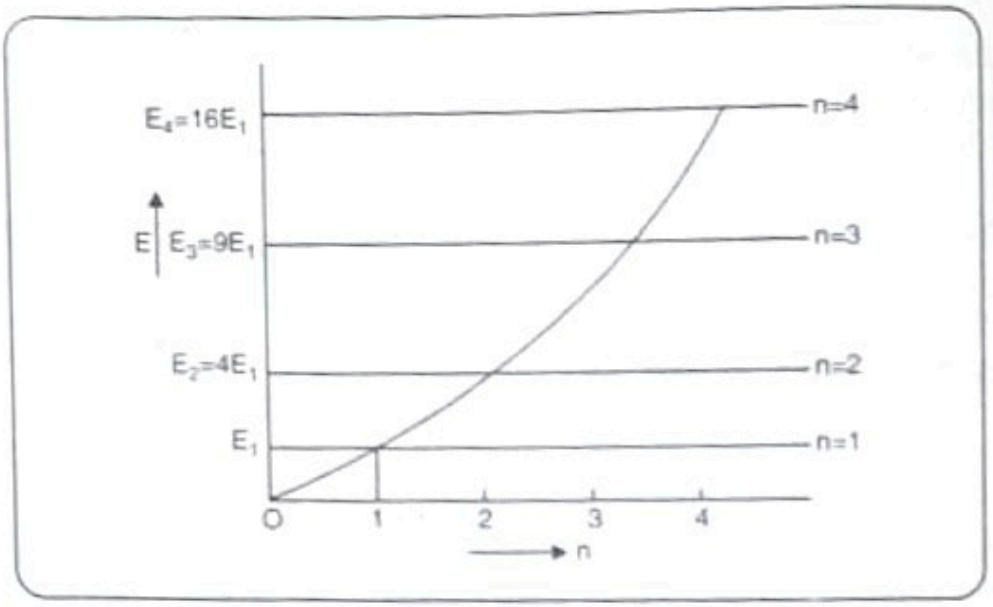

Fig. 2.2 : Energy level diagram of a particle in one dimensional box.

The constant A in eq. (2.15) can be calculated by applying normalising condition *i.e.*, the probability of finding the electron in whole space is unity.

$$\therefore \quad \int_0^L \psi_n^* \psi_n dx = 1$$

$$A^2 \int_0^L \sin^2 (n\pi x/L)\, dx = 1$$

$$\frac{A^2}{2} \int_0^L \left(1 - \cos \frac{2n\pi x}{L}\right) dx = 1$$

or $$\frac{A^2}{2} \int_0^L dx - \left[\int_0^L \omega x \frac{2n\pi x}{L} dx\right] = 1$$

or $$\frac{A^2}{2}[L-0] = 1$$

or $$A^2 = \frac{2}{L}$$

or $$A = \sqrt{\frac{2}{L}}$$

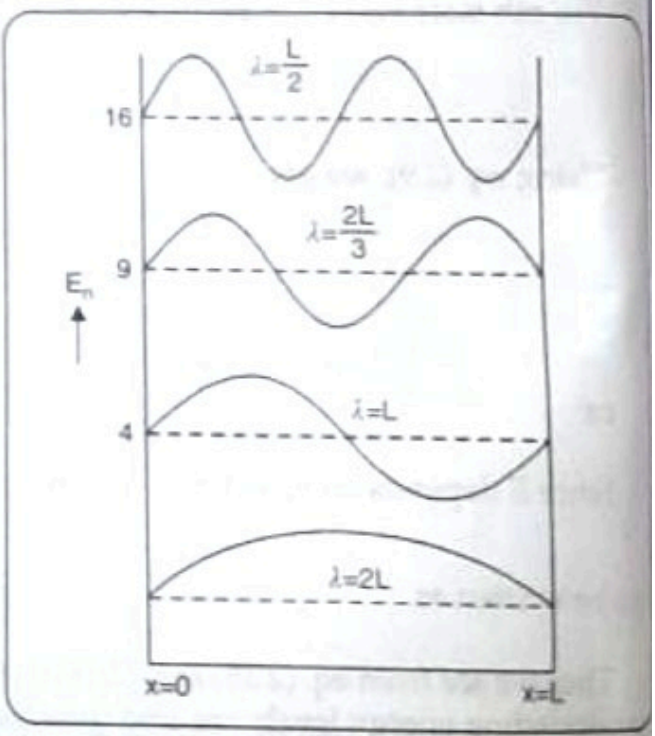

Fig. 2.3 : First four wave functions and energy levels for e^- in one dimensional box.

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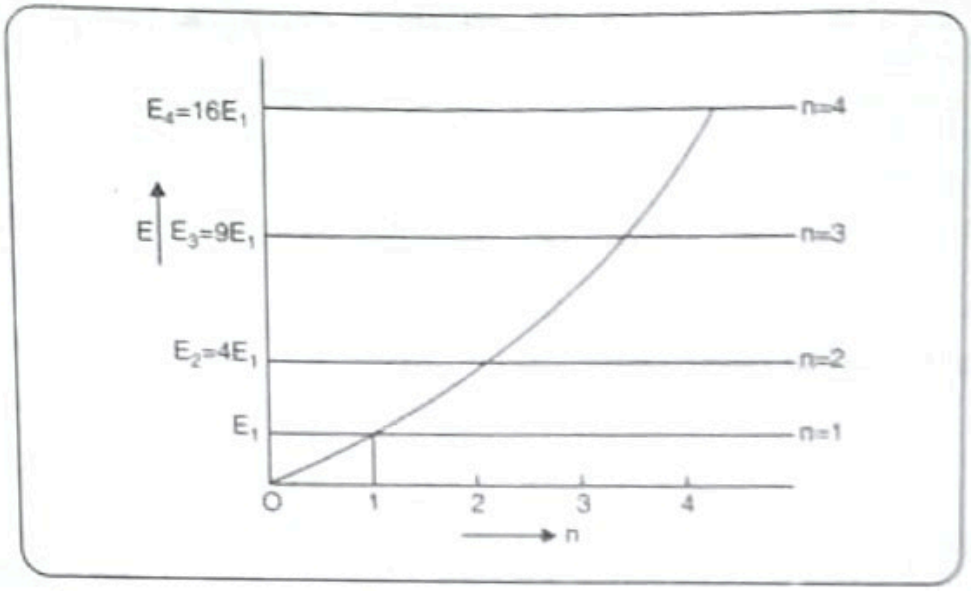

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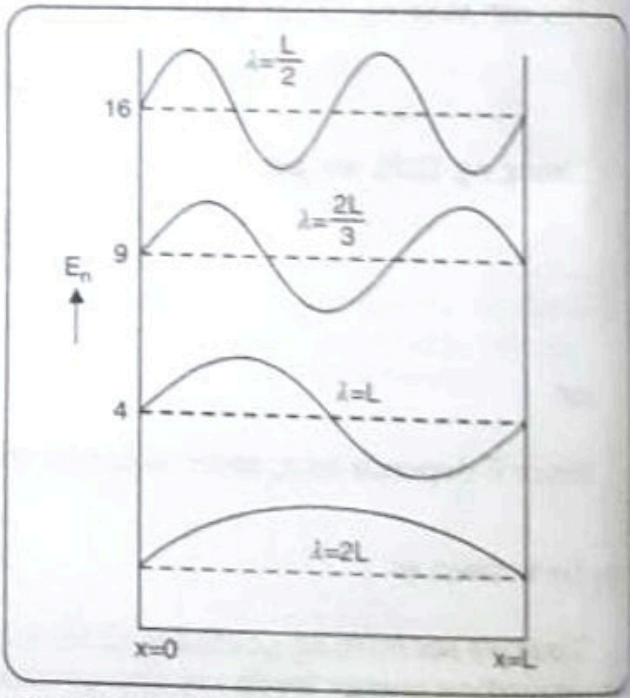


Fig. 2.3 : First four wave functions and energy levels for e^- in one dimensional box.

Hence, eq. (2.15) becomes

$$\psi_n = \sqrt{\frac{2}{L}} \sin(n\pi x/L) \quad \ldots (2.18)$$

First four *i.e.*, for $n = 1, 2, 3, 4$, wave functions are represented in Fig. (2.3).

(i) Fermi energy

Let us now see how N electrons could be distributed on this one dimensional line.

Electrons are indistinguishable particles and obey Pauli's exclusion principle which states that no two electrons can have all the four quantum numbers identical. That is, each quantum state can be occupied at the most by one electron. (These quantum states are referred to as orbitals in case of atoms) but there may be more than one quantum states *i.e.* having the same energy, such states are known as *degenerate* quantum states (orbitals). In a linear solid, there are two quantum numbers of a conduction electron orbital *i.e.* n (= 1, 2, 3, ... etc.) and spin s $(= \pm \frac{1}{2})$. This means that for each value of n, s can have two values depending upon the orientation of electrons. Hence, every orbital or quantum state n can accommodate two electrons one with spin up (↑) and other with spin down (↓). In other words each energy level is doubly degenerate. If there are nine electrons of course some having spin up and others having spin down. Then in the ground state of the system these could be accommodated in five levels with $n = 1, 2, 3, 4, 5$. First four levels accommodating one pair of electrons (with spin up and down) each and the fifth level accommodating the unpaired last electron. That is, the states with $n > 5$ are empty.

Let n_F denotes the uppermost filled energy level, and if there are N electrons (assumed even), we can write

$$n_F = N/2 \quad \ldots (2.19)$$

Since each level can accommodate a pair of electrons. Here n_F is the quantum number representing the uppermost filled energy level. The uppermost filled energy level at absolute zero is known as *Fermi level* and the energy value corresponding to this level is known as *Femi energy*, E_F.

Hence eq. (2.16) gives for $n = n_F$

$$E_F = \frac{\hbar^2}{2m}\left(\frac{\pi n_F}{L}\right)^2 \quad \ldots (2.20)$$

Hence, eqs. (2.19) and (2.20) gives

$$E_F = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2 \quad \ldots (2.21)$$

It is clear from above that energy of the top electrons depends upon number of electrons (N) and size of the box (L). Thus, for N/L = 1 electrons/angstrom = 10^{10} electrons/m, we have from eq. (2.21)

$$E_F = 9.6 \text{ eV}$$

Thus to accommodate 10^{10} electrons/m, the energy of uppermost electron must be 9.6 eV.

(ii) Total energy

The total energy E_0 of the entire system can be calculated by summing up the individual energies E_1, E_2, E_3 ... etc. between energy levels corresponding to $n = 1$ to $n_F = N/2$. Therefore,

$$E_0 = 2\sum_{n=1}^{N/2} E_n$$

Here the factor 2 comes into picture since each level accommodates two electrons with equal energies. Here by using eq. (2.16), we get.

$$E_0 = \frac{\hbar^2\pi^2}{2mL^2}\sum_{n=1}^{N/2} n^2 \qquad \text{... (2.22)}$$

As we know

$$\sum_{n=1}^{x} n^2 = \frac{1}{6}x(2x^2 + 3x + 1)$$

$$= \frac{1}{3}x^3 \text{ for } x \geq 1$$

So
$$\sum_{n=1}^{N/2} n^2 = \frac{1}{3}\left(\frac{N}{2}\right)^3$$

Hence eq. (2.22) becomes

$$E_0 = 2\frac{\hbar^2\pi^2}{2mL^2}\frac{1}{3}\left(\frac{N}{2}\right)^3$$

$$E_0 = \frac{1}{3}\frac{\hbar^2}{2m}\left[\frac{N\pi}{2L}\right]^2 N$$

Making use of eq. (2.21), we get

$$E_0 = \frac{1}{3}NE_F \qquad \text{... (2.23)}$$

Thus, *we find that for one dimensional problem, the average (kinetic) energy in the ground state is one third of that of the fermi energy.*

(iii) The density of states [D (E)]

The density of states is defined as the number of electronic or quantum states per unit energy range and is usually denoted by D (E). Therefore,

$$D(E) = \frac{dn}{dE}, \qquad \text{... (2.24)}$$

where dn is the number of quantum states present in the energy range between E to E + dE. Since each quantum state contains two electrons, actual density of states is twice the value given in eq. (2.24), i.e.

$$D(E) = 2\frac{dn}{dE}, \qquad \text{... (2.25)}$$

Now according to eq. (2.16),

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

$$\therefore \quad \frac{dE}{dn} = \frac{\hbar^2}{2m}2\left(\frac{nx}{L}\right).\frac{\pi}{L}$$

$$= \frac{\hbar^2\pi^2 n}{mL^2}$$

So
$$\frac{dn}{dE} = \frac{mL^3}{\hbar^2\pi^2 n}$$

$$\therefore \quad D(E) = 2\frac{dn}{dE} = \frac{2mL^2}{\hbar^2\pi^2}\cdot\frac{1}{n} \qquad \text{... (2.26)}$$

Again from eq. (2.16), we get

$$\frac{1}{n} = \left[\frac{\hbar^2\pi^2}{2mL^2E}\right]^{1/2}$$

or
$$\frac{1}{n} = \frac{\hbar\pi}{L}\left[\frac{1}{2mE}\right]^{1/2} \qquad \text{... (2.27)}$$

Putting eq. (2.27) in eq. (2.26), we get

$$D(E) = \frac{2mL^2}{\hbar^2\pi^2}\cdot\frac{\hbar\pi}{L}\left[\frac{1}{2mE}\right]^{1/2}$$

$$D(E) = \frac{L}{\hbar\pi}\,[2m/E]^{1/2} \quad \text{....(2.28)}$$

This result is shown plotted in Fig. 2.4.

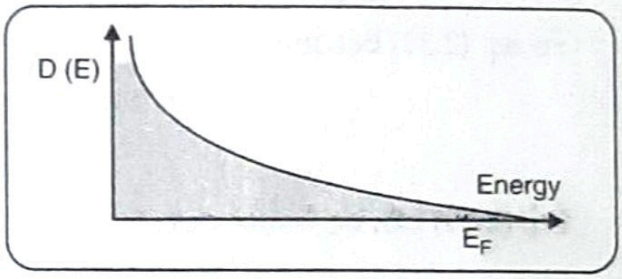


Fig. 2.4 : Density of states as a function of energy for one dimensional line.

It shows that all the states upto Fermi level E_F are filled at 0K.

2.5. FREE ELECTRON GAS IN THREE DIMENSIONS

Let us now consider the free electron gas in three dimensional crystal assumed to be in the shape of a cubical box of edge L. It is also assumed that potential inside the box is zero and outside it is infinitely large.

Schrodinger wave equation for a free particle in three dimensions is given as

$$V^2\psi + \frac{2mE}{\hbar^2}\psi = 0 \qquad \text{... (2.29)}$$

or
$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi + k^2\psi = 0 \qquad \text{.. (2.30)}$$

where
$$k^2 = \frac{2mE}{\hbar^2} \qquad \text{.. (2.31)}$$

where E is the total energy of the electron.

The general solution of eq. (2.30) is of the type

$$\psi = A\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right).\sin\left(\frac{n_z\pi z}{L}\right)$$

or
$$\psi = A\sin k_x x.\sin k_y y.\sin k_z z \qquad \text{.. (2.32)}$$

where $$k_x = \frac{n_x \pi}{L}, ky = \frac{n_y \pi}{L}, k_z = \frac{n_z \pi}{L} \quad \text{-- (2.33)}$$

When n_x, n_y and n_z are positive integers and the solution represents a standing wave. The value of A is determined by normalising the wavefunction over the volume.

i.e., $$\int_V \psi^* \psi dV = 1$$

or $$A^2 \int_0^L \int_0^L \int_0^L \sin^2 k_x x . \sin^2 k_y y . \sin^2 k_z z \, dx \, dy dz = 1$$

or $$A^2 \frac{L}{2} \cdot \frac{L}{2} \cdot \frac{L}{2} = 1$$

or $$A = \sqrt{\frac{8}{L^3}} \quad \text{-- (2.34)}$$

So eq. (2.32) becomes

$$\psi = \sqrt{\frac{8}{L^3}} \sin k_x x . \sin k_y y . \sin k_z z \quad \text{-- (2.35)}$$

Eq. (2.31) can be written as

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2}$$

Hence, $$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \quad \text{-- (2.36)}$$

or $$E = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

or $$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \quad \text{-- (2.37)}$$

where $$n^2 = n_x^2 + n_y^2 + n_z^2$$

Periodic boundary conditions.

We have considered a cubical box of edge L but in case of a crystal there are infinitely many such boxes stacked together, which means that the wave function must satisfy the periodic boundary conditions *i.e.*, they are periodic with a period L. Hence.

$$\psi(x + L, y, z) = \psi (x, y + L, z) = \psi (x, y, z + L) = \psi (x, y, z) \quad \text{-- (2.38)}$$

Wave function satisfying the free particle Schrodinger equation (2.29) and the periodicity condition (2.38) are of the form of a travelling plane wave

$$\psi (r) = A \exp (i \vec{k} . \vec{r})$$

or $$\psi (r) = A \exp [i (k_x x + k_y y + k_z z)] \quad \text{-- (2.39)}$$

Applying the periodic boundary conditions (2.38) to eq. (2.39), we get

$$\exp[i(k_x x + k_y y + k_z z)] = \exp[i(k_x x + k_x L + k_y y + k_z z)]$$

$$\exp(ik_x L) = 1$$

$\therefore$ which means that k_x can have only the values given below

$$k_x = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L} \ldots \pm\frac{2p\pi}{L}$$

and k_y and k_z have similar values as k_x. That is any component of k is of the form $2p\pi/L$, where p is an integer. The components of k *i.e.* k_x, k_y and k_z along with spin s are the quantum numbers of the problem.

The value of normalising constant A is given as

$$\int_0^L \int_0^L \int_0^L A^2 \exp[i(\vec{k}\cdot\vec{r})]\exp[-i(\vec{k}\cdot\vec{r})]dx\,dy\,dz = 1$$

$$A^2 L \times L \times L = 1$$

or

$$A^2 L^3 = 1$$

$$A^2 = \frac{1}{L^3} = \frac{1}{V}$$

$$A = \left(\frac{1}{V}\right)^{1/2}$$

Hence, normalised wave function is given as

$$\psi(r) = V^{-1/2} \exp[i(\vec{k}.\vec{r})] \quad \ldots (2.40)$$

2.6. FERMI DIRAC STATISTICS AND ELECTRONIC DISTRIBUTION IN SOLIDS

As discussed in the case of one dimensional distribution of N electrons that according to Pauli's exclusion principle no two electrons can have all the quantum numbers identical. The quantum numbers in three dimensional cases are k_x, k_y, k_z and s. Since s can have two values *i.e.*, + 1/2 and -1/2, hence each energy level with given k_x, k_y and k_z can accommodate two electrons one with spin up and other with spin down. Hence, N electrons require N/2 energy levels, where N is assumed to be even. It is also assumed that the system is in its ground state i.e. at absolute zero. The (N/2)th level which is also referred to as n_F and is known as Fermi level. It divides the filled and empty levels. The energy corresponding to Fermi level n_F is called Fermi energy F_0. According to classical theory all the electrons in a metal can have the same energy, so that, at 0 K, they all condense into the lowest available energy. But when quantum statistics is applied we find that these electrons occupy states between the energy values 0 and E_{F0}.

Fermi has shown that the probability of occupancy of a particular quantum state is given as

$$f(E) = \frac{1}{\exp[(E - E_F)/kT] + 1} \quad \ldots (2.41)$$

where $f(E)$ is known as *Fermi factor or Fermi function*. E is the energy of the given state and E_F is the Fermi energy at temperature T. The function (2.41) is plotted in Fig. (2.5) for various values of T.

Let us consider the behaviour of Fermi factor at different temperatures.

(*a*) At T = 0 K, the exponential term when $E < E_{F0}$ approaches zero as $e^{-\infty} = 0$ and we get $f(E) = 1$

when $E > E_{F0}$, we get $f(E) = 0$

The meaning of $f(E) = 1$ for $E < E_{F0}$ is that all the quantum states are occupied and all the states having $E > E_{F0}$ are empty at 0 K.

It is observed that E_{F0} is of the order of several electron volts.

(*b*) When $kT << E_F$ it is found that kT is small as compared with E_F for all metals below their melting points (kT at room temperature is only 0.03 eV), we also find that at $E = E_F$, $f(E) = \frac{1}{2}$. Hence the meaning of E_F is that, at the Fermi level the probability of occupation is fifty percent. The plot for T_1 and T_2 (> 0) temperatures is also shown in Fig. (2.5). The value of $f(E)$ is still practically unity.

For energies above E_F, the Fermi distribution becomes identical with that of Boltzmann distribution. The meaning of this is that all the states below E_F are not filled and hence all the states above E_F are not empty for a temperature T_1 or T_2 (> 0).

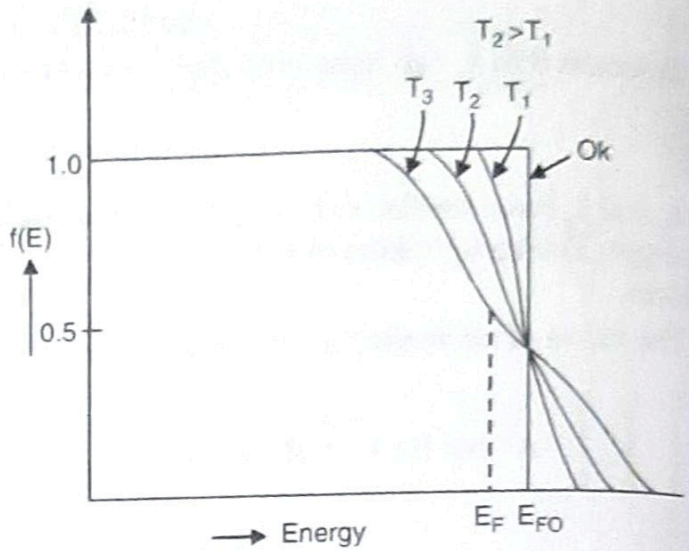


Fig. 2.5 : Plot of fermi factor vs energy of states

Hence, we find that at $E = E_F$ the value of $f(E) = \frac{1}{2}$ which implies that E_F is a level which lies half way between the filled and empty levels. E_F is a function of temperature and the relation between E_F and E_{F0} is given as

$$E_F = E_{F0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{F0}}\right)^2\right] \quad \ldots (2.42)$$

(*c*) At very high temperatures when $kT \to E_F$, the relation (2.42) does not remain valid and the entire distribution becomes Maxwell-Boltzmann. This is shown for temp. T_3 in the Fig. (2.5).

2.7. THE FERMI ENERGY E_{F0}

The Fermi energy E_{F0} is the energy which corresponds to the Fermi level, below which all the quantum states (levels) are filled and above will be empty at 0 K. This level is denoted by n_F (k_F the wave vector). Now each level is determined by the quantum numbers k_x, k_y and k_z and each level is occupied by two electrons, one having spin up and the other having spin down. In ground state of a system of N free electrons the occupied levels may be represented as points inside a sphere in k space or n space. The energy at the surface of the sphere is the Fermi energy which is given as from eq. (2.37).

$$E_{F0} = \frac{\hbar^2\pi^2 n_F^2}{2mL^2} \quad \ldots (2.43)$$

We now find the number of points in n space represented by n_F. Now each point occupies on the average a unit volume in the integer space and volume of the positive octant is $\frac{1}{8}\left(\frac{4}{3}\pi n_F^3\right)$ and

Hence number of points in the octant is also $\frac{1}{8}\left(\frac{4}{3}\pi n_F^3\right)$. When we consider spin of electrons, the number of points becomes twice this number.

If N is the density (i.e. number per unit volume) then in the box there are total NL^3 electrons. Hence,

$$NL^3 = 2\left(\frac{1}{8}\right)\left(\frac{4}{3}\pi n_F^3\right)$$

$$= \frac{1}{3}\pi n_F^3 \quad \text{.. (2.44)}$$

$$\therefore \quad \frac{n_F}{L} = \left(\frac{3N}{\pi}\right)^{1/3}$$

Eq. (2.43) becomes

$$E_{F0} = \hbar^2 \frac{\pi^2}{2m}\left(\frac{3N}{\pi}\right)^{2/3}$$

$$= \frac{\hbar^2}{2m}(3\pi^2 N)^{2/3} \quad \text{.. (2.45)}$$

Hence, we find that the Fermi energy is function of the density of electrons. We also conclude that even at absolute zero, electrons have some finite energy.

2.8. DENSITY OF AVAILABLE ELECTRONIC STATES D (E)

Now we are interested to find an expression for the number of allowed (available) states per unit volume in an energy range between E and E + dE.

The density of state D (E) is obtained from the fact that all the energy states below fermi energy are occupied and the total number of states must be equal to the total number of electrons.

$$\int_0^{E_F} D(E)\, dE = N \quad \text{.. (2.46)}$$

From eq. (2.45), we get

$$N = \frac{1}{3\pi^2}\left[\frac{2mE_F}{\hbar^2}\right]^{3/2} \quad \text{.. (2.47)}$$

Therefore,

$$\int_0^{E_F} DE\ dE = \frac{1}{3\pi^2}\left[\frac{2mE_F}{\hbar^2}\right]^{3/2}$$

Expressing the integral as infinite integral, we get

$$\therefore \quad D(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \quad \text{.. (2.48)}$$

According to this expression the variation of D(E) with E is parabolic and is shown in Fig. (2.6) Another way of expressing result (2.48) is as given ahead.

From eq. (2.47),

$$\ln N = \frac{3}{2} \ln E_F + \text{const.}$$

$$\frac{1}{N}\frac{dN}{dE_F} = \frac{3}{2}\frac{1}{E_F}$$

Hence $$D(E_F) = \frac{dN}{dE_F} = \frac{3N}{2E_F} \quad ...(2.49)$$

Thus, we find that the number of states per unit energy range per unit volume at the Fermi energy is just the total number of conduction electrons divided by the Fermi energy.

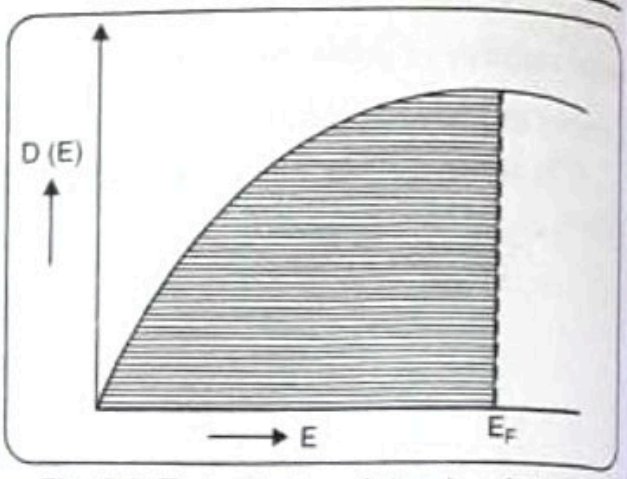


Fig. 2.6. The variation of density of states function D(E) with energy E for three dim. case

Density of filled electronic states.

The density of filled electron states N (E) at a particular temperature and between the energy E and E + *d* E is given as,

$$N(E)\, dE = D(E)\, f(E)\, d\,E \quad ... (2.50)$$

where *f*(E) is the Fermi factor.

The difference between N(E) and D(E) is that; D(E) measures the number of states at a given energy and N(E) measures the number of particles actually having a given energy.

Average kinetic energy E_0

Average kinetic energy $\bar{E}_0$ is calculated as

$$\bar{E}_0 = \frac{\int_0^{E_{F0}} ED(E)\, dE}{\int_0^{E_{F0}} D(E) dE} = \frac{1}{N}\int_0^{E_{F0}} E\, D(E)\, dE \quad ... (2.51)$$

Substituting the value of D(E) from eq. (2.48), we get

$$\bar{E}_0 = \frac{1}{N}\frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{E_{F0}} E^{3/2} dE$$

$$= \frac{1}{2\pi^2 N}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{2E_{F0}^{5/2}}{5}$$

Substituting for E_{F0} from eq. (2.45), we get

$$\bar{E}_0 = \frac{3}{5} E_{F0}$$

SOLVED EXAMPLES

Example 2.1. *Metallic silver has 1 free electron per atom. Find the fermi energy if density of silver is 10.5 g cm^{-3} and atomic weight is 1.08 gm atom.* **(H.P.U. 2000)**

Solution.

Since $$E_F = \frac{\hbar^2}{8m}\left[\frac{3N}{\pi V}\right]^{2/3}$$

We know that density, $d = \frac{M}{V}$

or $$V = \frac{M}{d} = \frac{108}{10.5\times10^{6}}\,m^3$$

Hence $$E_F = \frac{(6.625\times10^{-34})^2}{8\times9.1\times10^{-31}}\left[\frac{3\times6.023\times10^{23}\times10.5\times10^{6}}{3.142\times108}\right]^{2/3}$$

$$= 8.8\times10^{-19}\ J$$

$$= \frac{8.8\times10^{-19}}{1.6\times10^{-19}}\,eV \qquad [\because\ 1\,eV = 1.6\times10^{-19}\ J]$$

$$= 5.5\ eV$$

Example 2.2. *Find the energies of the six lowest energy levels of a particle in a cubical box. Which of the levels are degenerate ?*

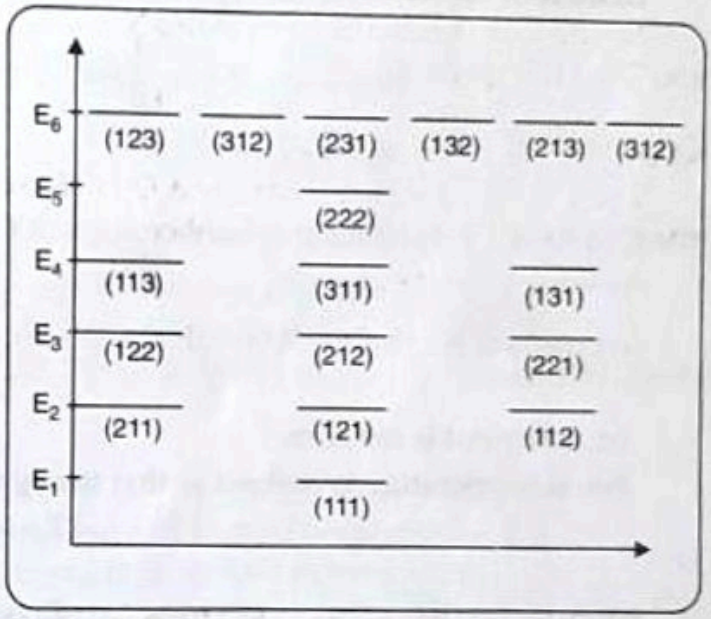
Solution. We know that energy for a cubical box of edge L is given as

$$E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

Now first six states are given by quantum numbers (n_x, n_y, n_z) (1,1,1), (1,1,2), (1,2,2) (1,1,3),(2,2,2), (1,2,3) energies corresponding to these quantum numbers can be calculated from the above expression and we find

$E_{111} = 3\,E$, $E_{112} = 6E$, $E_{122} = 9E$,

$E_{113} = 11E$, $E_{222} = 12E$, $E_{123} = 14E$



where $$E = \hbar^2\frac{\pi^2}{2mL^2}$$

Hence, we find that E_1, E_5 are non-degenerate, E_2, E_3 and E_4 are three fold degenerate and E_6 is six fold degenerate.

Example 2.3. *The fermi energy of silver is 5.51. eV. (a) What is the average energy of the free electrons in silver at 0 K ? (b) What temperature is necessary for the average molecular energy in an ideal gas to have this value ? (c) What is the speed of electrons with this energy ? Given* $K = 1.38\times10^{-23}\ J\,K^{-1}$.

(H.P.U. 2008)

Solution. (*a*) As we know, average electron energy

$$\bar{E}_0 = \frac{3}{5}EF_0 = \frac{3}{5}\times5.51$$

$$\bar{E}_0 = 3.306\ eV$$

(b) For an ideal gas, average molecular energy at temperature T, is given as

$$\bar{E}_0 = \frac{3}{5}\,kT$$

$$T = \frac{2}{3}\left[\frac{\bar{E}_0}{k}\right] = \frac{2}{3}\times\frac{3.306\ eV\times1.6\times10^{-19}\ J/eV}{1.38\times10^{-23}\ J/K}$$

(c) Let v be velocity of electron, then kinetic energy

$$\frac{1}{2}mv^2 = \bar{E}_0$$

$$v = \frac{\sqrt{2E_0}}{m} = \left[\frac{2\times3.306\times1.6\times10^{-19}}{9.1\times10^{-31}}\right]^{1/2}$$

$$= 1.3 \times 10^6 \text{ m/sec}$$

Example 2.4. *Calculations of Fermi energy for some monovalent elements yield the following results.*

Metal	*Cu*	*Li*	*Rb*	*Cs*	*Ag*	*K*
E_F *(eV)*	*7.04*	*4.72*	*1.82*	*1.53*	*5.51*	*2.12*

If the fermi velocity of an electron in one of the metals of the above series is 0.73 × 10⁶ m/s, identify the metal and also calculate the fermi temperature.

Solution. We have

$$\frac{1}{2} m V_F^2 = E_F$$

$$E_F = \frac{1}{2} \times 9.1 \times 10^{-31} \times (0.73 \times 10^6)^2$$

$$= 2.42 \times 10^{-19} \text{ J}$$

$$= \frac{2.42\times10^{-19}}{1.6\times10^{-19}} eV = 1.51 \, eV = 1.53 \, eV$$

i.e., the metal is caesium.

Fermi temperature is defined as that temperature at which

$$kT_F = E_F$$

$$\therefore \quad T_F = \frac{E_F}{k} = \frac{2.42\times10^{-19}\text{J}}{1.38\times10^{-23}\text{J/K}} = 1.75\times10^4\text{K}$$

Example 2.5. *The Fermi energy in silver is 5.51 eV. Find (i) the average energy of the free electrons in silver at 0K. (ii) At what temperature a classical free particle like an ideal gas molecule will have this kinetic energy ? Given $k = 1.38 \times 10^{-23} JK^{-1}$.*

Solution.

(*i*) Given $E_{F0} = 5.51 \, e\,V$

Since $\bar{E}_0 = \frac{3}{5} E_{F0}$

$$\bar{E}_0 = \frac{3}{5} \times 5.51 = 3.306 \, eV$$

(*ii*) The kinetic energy of calssical particle at kelvin temperature $T = \frac{3}{2} kT$

i.e., $E_{F0} = kT$

or $T = \frac{2}{3k} E_{F0}$

or $$T = \frac{2\times3.306\times1.6\times10^{-19}}{3\times1.38\times10^{-23}} \quad (\because 1\,eV = 1.6\times10^{-19}\,J)$$

or $$T = 2.55\times10^{4}\,K$$

MULTIPLE CHOICE QUESTIONS

1. *Wiedemann-Frenz law gives the relationship between :*
   (a) thermal conductivity and electrical polarisability
   (b) thermal conductivity and electrical susceptibility
   (c) electrical conductivity and electrical polarisability
   (d) thermal conductivity and electrical conductivity.
2. *At 0K, all the states above fermi level E_F are :*
   (a) empty (b) completely filled
   (c) partially filled.
3. *The average kinetic energy of electron in the ground states in one dimension is :*
   (a) $\frac{1}{3}$ of fermi energy (b) $\frac{1}{4}$ of that fermi energy
   (c) $\frac{1}{2}$ of the fermi energy (d) equal to that of fermi energy. *(H.P.U. 2007)*
4. *In Drude-Lorentz's theory for the free electron gas, the statistics used was :*
   (a) Maxwell- Boltzmann statistics (b) Fermi-Dirac statistics
   (c) Bose-Einstein statistics (d) None of the above. *(H.P.U. 2009)*
5. *At 0K fermi level lies :*
   (a) Above top of the valence band E_v
   (b) Below the bottom of conduction band E
   (c) Midway between the top of the valence band and bottom of conduction band.
6. *The average kinetic energy of electron in the ground state, in three dimensions, is :* *(H.P.U. 2001 S, 2006)*
   (a) $\frac{3}{5}$ of fermi energy (b) $\frac{2}{5}$ of fermi energy
   (c) $\frac{1}{5}$ of fermi energy (d) equal to that of fermi energy.
7. *Free electron Fermi gas consists of :*
   (a) bound and non-interacting electrons
   (b) free and non-interacting electrons
   (c) bound and interacting electrons
   (d) free and interacting electrons.
8. *In Sommerfield model of electron :*
   (a) the potential is taken constant inside the metal
   (b) the potential is taken variable inside the metal
   (c) the potential is taken infinite inside the metal
   (d) potential has no role inside the metal

ANSWERS

1. *(d)* **2.** *(a)* **3.** *(a)* **4.** *(a)* **5.** *(c)* **6.** *(a)* **7.** *(b)* **8.** *(a)*