

Free Electron theory

Classical free electron theory: Three years after the discovery of electron , in 1900, Drude formulated his theory of electrical and thermal conduction by applying kinetic theory of gases to a metal, considered as a gas of electrons. Later Lorentz modified this theory and hence the classical free electron theory is known as Lorentz-Drude Theory.

- (1) The valence electrons in a solid are free to move anywhere in the metal in a way similar to gas molecules in a container. Therefore, the assembly of free electrons in a metal is called electron gas.
- (2) The electrical and thermal conductivities of the metals is solely due to free electrons.
- (3) The electrons move randomly in all directions with random velocities following the classical Maxwell Boltzmann distribution. The average kinetic energy of a free electron is thus given by

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

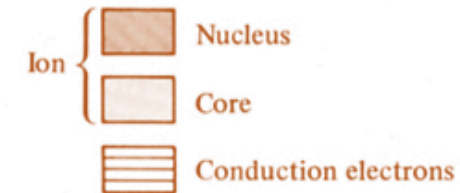
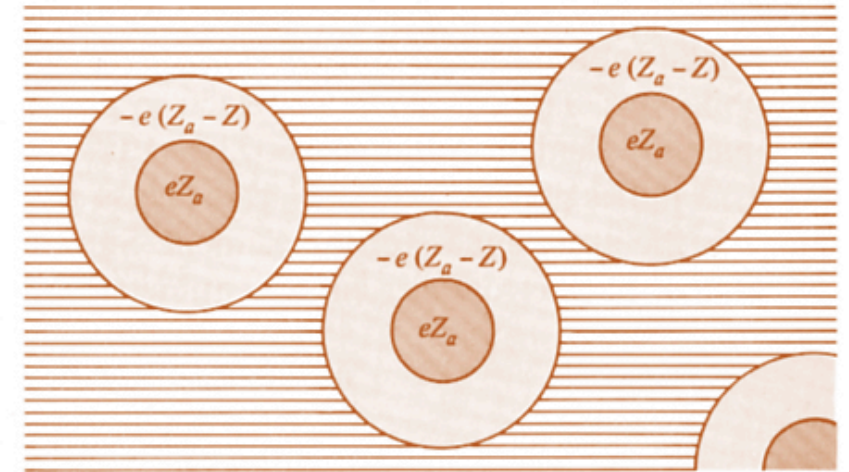
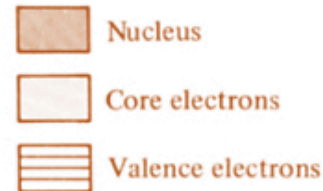
Where k_B is the Boltzmann constant and T is the absolute temperature (in Kelvins).

4. Mobile negatively charged electrons are confined in a metal by attraction to immobile positively charged ions.

Nucleus charge eZ_a

Z valence electrons are weakly bound to the nucleus (participate in chemical reactions)

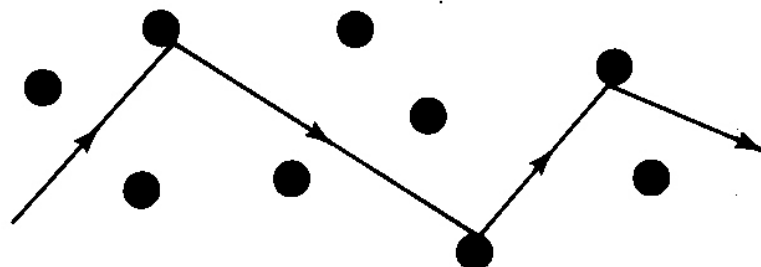
$Z_a - Z$ core electrons are tightly bound to the nucleus (play much less of a role in chemical reactions)



In a metal

- the core electrons remain bound to the nucleus to form the metallic ion
- the valence electrons wander far away from their parent atoms called conduction electrons or electrons

- (5) The free electrons make collisions from time to time with fixed positive ions. Between these collisions, the electron-ion interaction is neglected. This is called free electron approximation. Further electron-electron interaction is also neglected. This is called independent electron approximation.

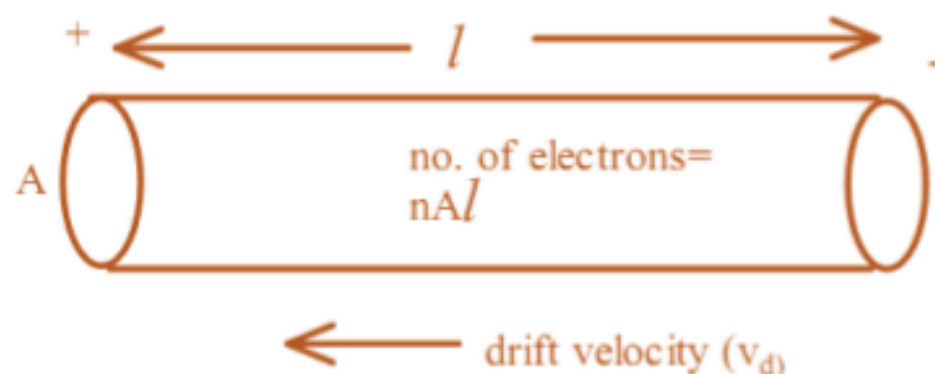


- (6) Collisions in Drude model, as in kinetic theory, are instantaneous events that abruptly alter the velocity of an electron.
- (7) An electron experiences a collision with a probability per unit time $1/\tau$. This means that on the average an electron travels for time τ after it undergoes a collision and before its next collision i.e. the average time between two successive collisions is τ . This time is known as **relaxation time (τ)**. The average distance traversed by a free electron between two successive collisions with positive ions is called the **mean free path (λ)**.

(8) In absence of external electric field, the random motion of free electrons is equally probable in all directions. As a result, there is no net current in the absence of electric field. When an external electric field is applied, the electrons are accelerated in a direction opposite to that of electric field. Hence they acquire an average velocity in a direction opposite to that of electric field which is superimposed over the random motion. This velocity is known as the **drift velocity** (v_d).

Consider a metal wire of cross sectional area ' A ' and length ' l '. If ' n ' is the number of electrons per unit volume, the total number of electrons in the wire is, ' nAl '. Thus total charge associated with these electrons is:

$$Q = -e nAl$$



The time taken by these electrons to emerge out from one end of the wire is:

$$t = l/v_d$$

Hence, current in the wire is:

$$I = Q/t = -en Al / (l / v_d) = -nA v_d e$$

Now, if E is the applied field, the force acting on an electron is $F = -e E = ma$, This gives

$$a = -e E/m$$

Thus the average velocity gained by the electron in the direction opposite to that of the field (in average time τ) is

$$v_d = u + a\tau = 0 + a\tau = a\tau = -eE \tau/m$$



$$v_d = -e E \tau/m$$

Hence, current in the wire is: $I = -n A e (-e E \tau/m) = A E n e^2 \tau/m$

Thus

$$I/A = (n e^2 \tau/m) E$$

Now if V is the potential difference $V = El$ or $E = V/l$

$$I/A = (ne^2 \tau/m) V/l,$$



$$V = Il / (ne^2 \tau/m) A$$

Comparing with Ohm's law, $V = IR$, we get

$$R = \frac{l m}{ne^2 \tau A} = \frac{\rho l}{A} \quad \text{where } \rho = \frac{m}{ne^2 \tau} \text{ is called the resistivity.}$$

Conductivity is given by inverse of resistivity

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

Also the mobility of the charge carrier is given by the velocity per unit applied field;

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

Thus

$$\sigma = ne\mu \text{ or } \rho = \frac{1}{ne\mu}$$

It is clear that for a given temperature, the only factor which varies in metals is 'n' i.e. the number of free electrons per unit volume. Therefore different metals will have different conductivities.

The temperature dependence of conductivity comes from the temperature dependence of relaxation time. As $\sigma = \frac{ne^2\tau}{m}$ and $\tau = \frac{\lambda}{v_0}$, where v_0 is the average velocity due to random

thermal motion which is given by $\frac{1}{2}mv_0^2 = \frac{3}{2}kT$, i.e. $v_0 = \sqrt{\frac{3kT}{m}}$.

$$\sigma = \frac{1}{\rho} = \frac{ne^2\tau}{m} = \frac{ne^2\lambda}{mv_0} = ne^2\lambda\sqrt{\frac{1}{3mkT}}$$

Hence with increase in temperature the conductivity decreases.

Limitations of Classical free electron theory:

1. It was not able to explain the observed temperature dependence of the specific heat. According to free electron theory, the electronic contribution to specific heat is constant, however actually it is directly proportional to temperature T .
2. It cannot explain the temperature independent paramagnetism in metals.
3. It cannot account for the deviation from Weidmann-Franz law at low temperatures.
4. It was not able to explain the temperature and field dependence of the Hall coefficient.
5. It cannot explain the correct temperature dependence (T^{-5} dependence) of the electrical conductivity.
6. The values of mean free path as predicted by the free electron theory are one order less than the observed values.
7. The value of Lorenz number as calculated from free electron theory does not matches with the experimental value.

Sommerfeld's Quantum Theory of Free Electron

Sommerfeld, in 1928, modified the free electron model on the basis of quantum statics. The assumptions are:

- 1) The metal contains a large number of conduction electrons which are completely free, yet are bound to the metal as a whole. Thus a metal is said to be consisting of electron gas. Free electrons in a metal can be described as free particles confined in a box of certain volume. The possible electronic states and the distribution of electrons in these states can thus be determined using quantum mechanics.
- 2) The force between conduction electrons and ion cores are neglected in the free-electron approximation, so that the electron within the metal is treated as free. The total energy of electron is wholly kinetic energy since potential energy is negligible ($V = 0$).
- 3) The electrons are assumed to obey Pauli's exclusion principle and hence they obey quantum Fermi-Dirac statistics rather than classical Maxwell-Boltzmann statistics.

Density of states

Conduction electrons can be considered as moving independently in a square well of finite depth & the edges of the well correspond to the edges of the sample.

Consider a metal with a cubic shape with edge length **L**: Ψ and E can be found by solving the Schrödinger equation:

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

Use periodic boundary conditions & get the Ψ 's as travelling plane waves. For three-dimensional box electron energy,

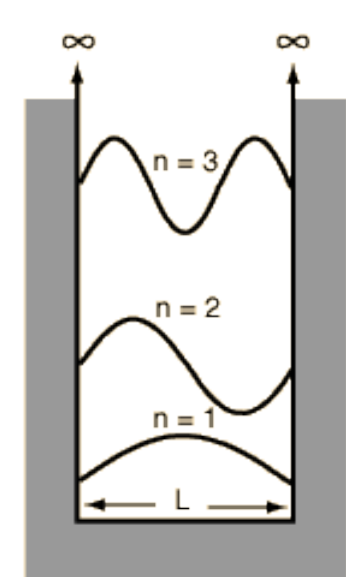
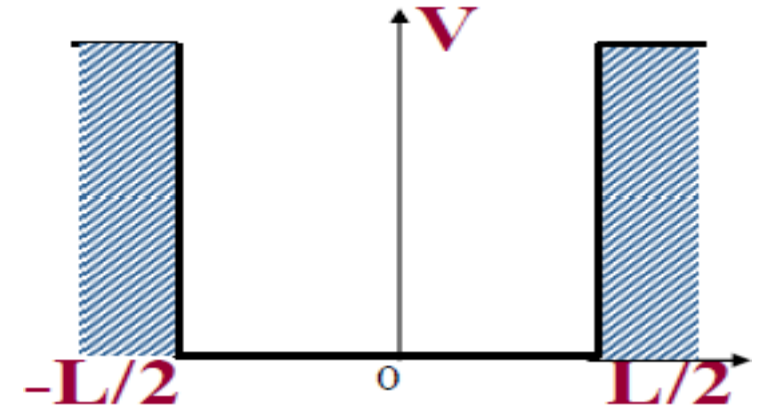
$$E = \frac{(n_1^2 + n_2^2 + n_3^2) \hbar^2}{8mL^2}$$

It is for a cubic solid of length L with the 3 quantum numbers for the 3 axes.

We can replace the 3 quantum numbers by a single value n ,

$$E_n = \frac{n^2 \hbar^2}{8mL^2}$$

For small values of n these energy levels are quantized, but for large values of n the spacing between them are close so that the energy levels can be considered to be continuous.



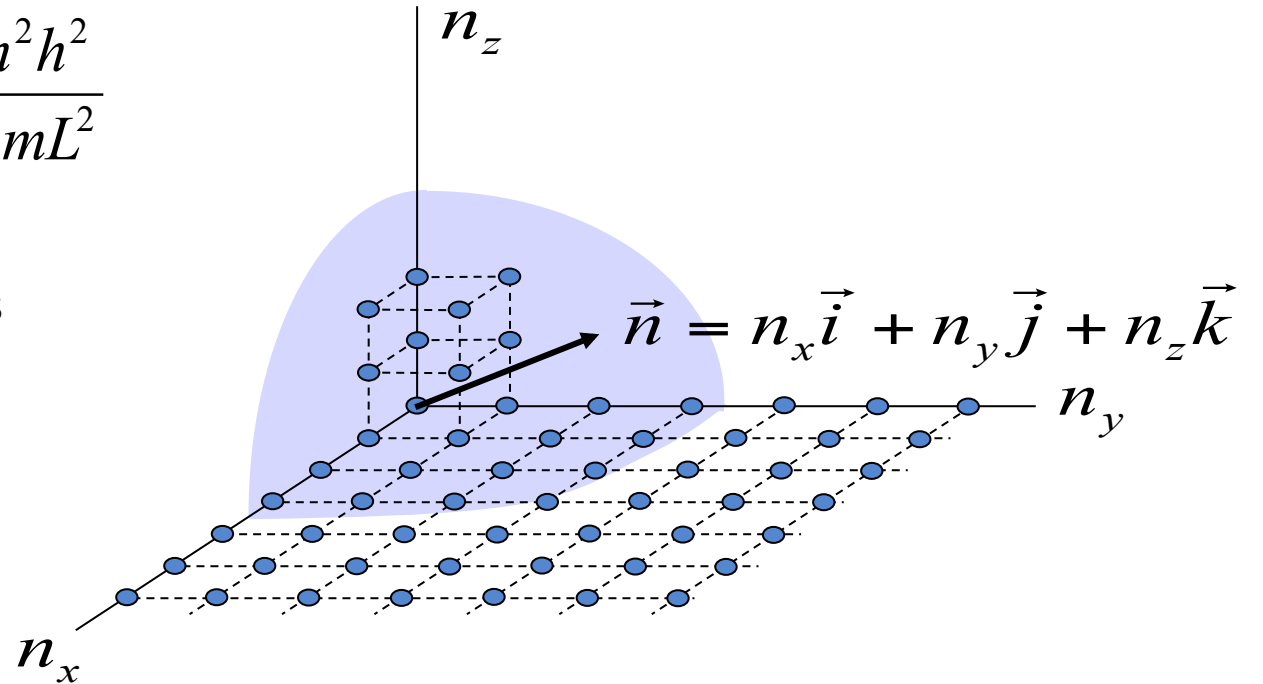
Electron Energy Density

➤ So n represents the radius of a sphere, where the total number of states within the sphere is given by its volume.

$$E = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} \quad \text{Or} \quad E_n = \frac{n^2 h^2}{8mL^2}$$

➤ Hence the total number of 'orbitals' (energy states) is given by the volume of the sphere in the first quadrant

$$\frac{1}{8} \left(\frac{4}{3} \pi n^3 \right) = \frac{1}{6} \pi n^3$$



➤ Since each orbital can take two electrons of opposite spin, the total number of energy states (including spin) is given by

$$= 2 \times \frac{1}{6} \pi n^3 = \frac{1}{3} \pi n^3$$

Electron Energy Density

- We can relate n (quantum number of the electron in the solid) to the energy E using equation

$$E_n = \frac{n^2 h^2}{8mL^2}$$

the total number of states in terms of energy

$$N = \frac{1}{3} \pi n^3 = \frac{1}{3} \pi (8m_e E)^{\frac{3}{2}} \frac{L^3}{h^3}$$

- Dividing by the volume of the cube will give total number of states per unit volume

$$n_s = \frac{N}{L^3} = \left(\frac{8\pi}{3} \right) \frac{(2mE)^{3/2}}{h^3}$$

- The density of states is the differential of the total number of states, so that $g(E)$ is given by

$$g(E) = 8\pi \sqrt{2} \left(\frac{m_e}{h^2} \right)^{\frac{3}{2}} \sqrt{E}$$

The Fermi Energy

The density of states per unit volume for a 3D free electron gas (m is the electron mass):

$$g^{3D}(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}$$

The number of electron per unit volume:

$$n \equiv \frac{N}{V} = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon$$

At $T = 0$, all the states up to $\varepsilon = E_F$ are filled, at $\varepsilon > E_F$ – empty:

$$f(\varepsilon) = \begin{cases} 1, & \varepsilon \leq E_F \\ 0, & \varepsilon > E_F \end{cases}$$

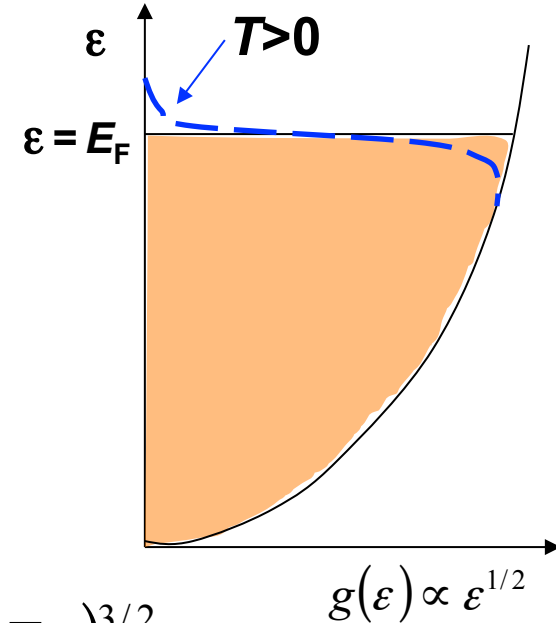
$$n = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon = \int_0^{E_F} g(\varepsilon) d\varepsilon = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{E_F} \sqrt{\varepsilon} d\varepsilon = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} (E_F)^{3/2}$$

Thus Fermi energy of an ideal Fermi gas at $T=0$:

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = \frac{\hbar^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3}$$

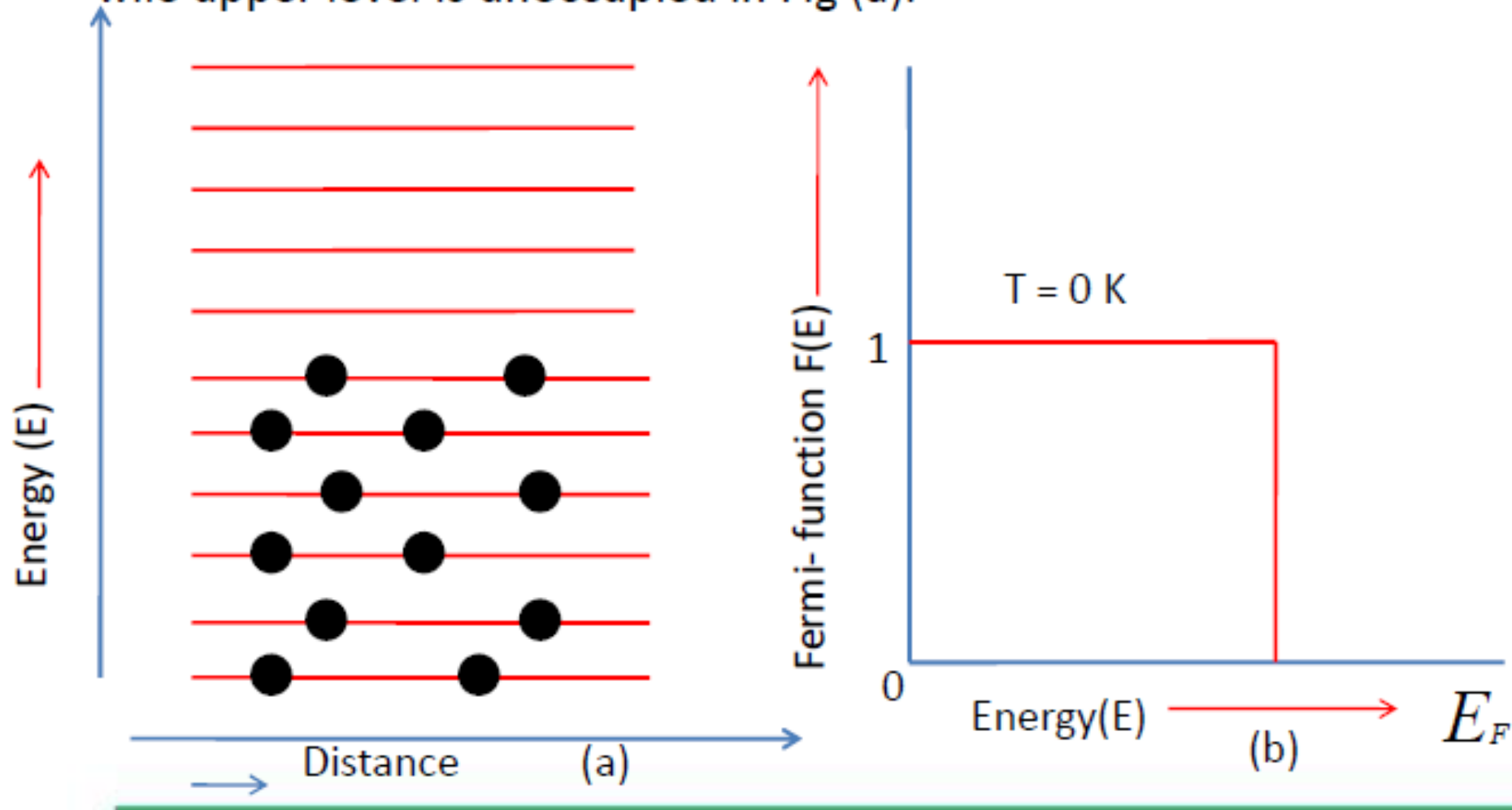
The **total energy** of all electrons in the conduction band (per unit volume):

$$U_0 = \int_0^{E_F} \varepsilon \times g(\varepsilon) d\varepsilon = \frac{3}{5} N E_F$$



It does not provide information whether those states are occupied or not. The occupation is given by the Fermi function and is usually a function of temperature

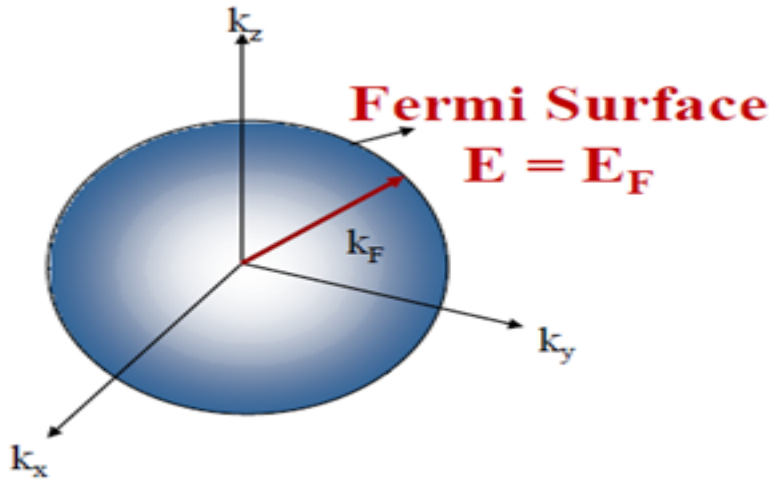
- At $T = 0$ K, lower energy level of conduction band are occupied by electrons while upper level is unoccupied in Fig (a).



Fermi Energy

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = \frac{h^2}{8m} \left(\frac{3}{\pi} \frac{N}{V} \right)^{2/3}$$

The occupied states are inside the **Fermi sphere** in k-space as shown below; the radius is **Fermi wave number k_F** .



$$E_F = \frac{\hbar^2 k_F^2}{2m_e} \text{ and } k_F = \left[\frac{3\pi^2 N}{V} \right]^{1/3}$$

The surface of the Fermi sphere represents the boundary between occupied & unoccupied k states at absolute zero for the free electron gas.

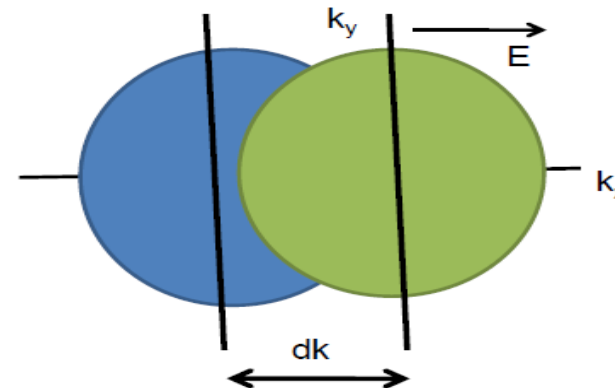
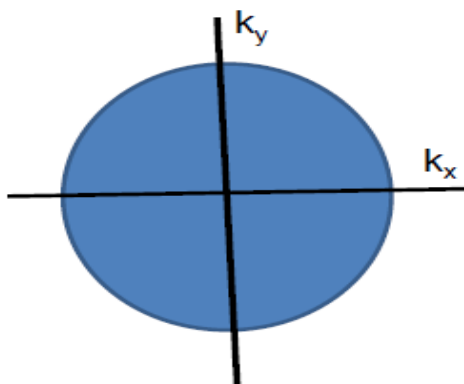
Electrical Conductivity

Equation of motion of an electron with an applied electric and magnetic field.

$$m_e \frac{d\vec{v}}{dt} = -e\vec{E} - e\vec{v} \times \vec{B}$$

1. This is just Newton's law for particles of mass m_e and charge $(-e)$.
2. The use of this classical equation of motion of a particle is to describe the behaviour of electrons in the plane wave states, which extend throughout the crystal. A particle-like entity can be obtained by superposing the plane wave states to form a wave packet.
3. On the basis of free electron model, electron at 0K fill a sphere of radius k_F in the wave number space. It is known as Fermi wave vector. Fermi surface is the surface of maximum energy.
4. On the application of electric field E , each electron acquires a certain additional velocity dv . This is equivalent to the displacement of the Fermi sphere by dk .
5. So, $F = -eE$

Fermi surface in
absence of field



In presence of field

Electrical Conductivity

$$F = -eE = m \frac{dv}{dt} \Rightarrow dv = -\frac{eE}{m} dt$$

This additional velocity is acquired in the characteristic time τ given by

$$dv = -\frac{eE}{m} \tau$$

Current density

$$J = -nedv = \frac{ne^2\tau}{m} E$$

But $\mathbf{J} = \sigma \mathbf{E}$. So the electrical conductivity is

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

Electrical Conductivity

$$\lambda = \frac{h}{p} \Leftrightarrow \frac{2\pi}{k} = \frac{h}{mv}$$

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



$$v_F = \frac{\hbar}{m} \left[\frac{3\pi^2 N}{V} \right]^{1/3}$$

Mean free path $\lambda_F = v_F \tau$, where v_F is the velocity at Fermi surface.

$$\lambda_F = \tau v_F$$
$$\Rightarrow \lambda_F = \frac{\hbar \tau}{m} \left[\frac{3\pi^2 N}{V} \right]^{1/3}$$

Typical values for monovalent Potassium metal

Fermi Energy

$$\varepsilon_F = \frac{\hbar^2}{2m_e} \left(\frac{3\pi^2 N}{V} \right)^{2/3} = 2.12 eV$$

Fermi vector

$$k_F = \left[\frac{3\pi^2 N}{V} \right]^{1/3} = 0.746 \text{ \AA}^{-1}$$

Fermi momentum

$$p_F = \hbar k_F = m_e v_F$$

Fermi velocity

$$v_F = \frac{p_F}{m_e} = 0.86 \times 10^6 \text{ m s}^{-1}$$

Fermi temperature

$$T_F = \frac{E_F}{k_B} = 2.46 \times 10^4 \text{ K}$$

The Fermi Sphere plays an important role in the behavior of metals.

Problem

When the copper atoms form a crystal lattice with the density of atoms of $8.5 \cdot 10^{28} \text{ m}^{-3}$, each atom donates 1 electron in the conduction band.

- (a) Assuming that the effective mass of the conduction electrons is the same as the free electron mass, calculate the Fermi energy. Express your answer in eV.

$$E_F = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} = \frac{(6.6 \cdot 10^{-34})^2}{8 \times 9.1 \cdot 10^{-31}} \left(\frac{3}{\pi} 8.5 \cdot 10^{28} \right)^{2/3} = 1.1 \cdot 10^{-18} \text{ J} = 6.7 \text{ eV}$$

- (b) The electrons participate in the current flow if their energies correspond to the occupancy $n(\varepsilon)$ that is not too close to 1 (no empty states available for the accelerated electrons) and not too small (no electrons to accelerate). At $T=300\text{K}$, calculate the energy interval that is occupied by the electrons that participate in the current flow, assuming that for these electrons the occupancy varies between 0.1 and 0.9.

$$\bar{n}(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - E_F}{k_B T}\right) + 1}$$

$$\frac{1}{\exp\left(\frac{\varepsilon_1 - E_F}{k_B T}\right) + 1} = 0.9 \quad \exp\left(\frac{\varepsilon_1 - E_F}{k_B T}\right) = 9 \quad \varepsilon_1 = E_F + k_B T \ln 9$$

$$\frac{1}{\exp\left(\frac{\varepsilon_2 - E_F}{k_B T}\right) + 1} = 0.1 \quad \exp\left(\frac{\varepsilon_2 - E_F}{k_B T}\right) = \frac{1}{9} \quad \varepsilon_2 = E_F - k_B T \ln 9$$

$$\Delta\varepsilon = 2k_B T \ln 9 = 0.11 \text{ eV}$$