UNIT- IV

FREE ELECTRON THEORY OF METALS

* The outstanding Properties of Metals

(i) Metals have high electrical and thermal conductivities.

(ii) In the steady state ohm's law is obeyed i.e

$$I \propto E$$

(iii) Resistivity above Debye's temperature is proportional to absolute temperature,

$$\rho \propto T$$

(iv) At low temperatures, the resistivity of the metal is proportional to the fifth power of absolute temperature, i.e $\rho \propto T^5$

(v) For most metals, resistivity is inversely proportional to pressure, $\rho \propto \frac{1}{P}$

(vi) Widemann and Franz's Law: Above Debye's temp. the ratio of thermal and electrical conductivities is proportional to the absolute temperature

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

(vii) superconductivity: At absolute zero, the resistivity tends towards zero.

* Drude-Lorentz Theory

In 1900 Drude made a very good proposal that metals are composed of positive metal ions whose valance electrons are free to move among the ionic array, with the restriction that they are confined to remain within the boundaries of the metals. The metal ions are bounded to the electrons by an electrostatic force of attraction between their positive charges and the negatively charged electron gas. The concentration of electrons in an electron gas is quite large. These electrons are responsible for conduction of electricity through metals. In general, the motion of electrons is random, but in an electric field, the negatively charged electrons stream in the positive field direction and produce a current in the metal. In order to prevent the electrons from accelerating indefinitely it was assumed that they collide elastically with metal ions. This leads to a steady state current which is proportional to an applied voltage and explains the origin of ohm's law.

Based on the Drude's considerations that the electron gas behaves as a perfect gas. H.A. Lorentz postulated in 1909 that the electrons constituting the electron gas obey Maxwell-Boltzmann statistics under equilibrium conditions. The combined ideas of Drude and Lorentz constitute the Drude-Lorentz theory.

The theory has been successfully applied to explain the various properties of metals.

(i) Ohm's law is obeyed, $I \propto E$

(ii) For impure metals, electrical conductivity is inversly proportional to square root of absolute temp.

$$\sigma \propto \frac{1}{\sqrt{T}}$$

(iii) For pure metals, $\sigma \propto 1/T$

(iv) For most metals, resistivity is inversly proportional to pressure, $\rho \propto 1/p$

(v) Widemann-Franz relation is obeyed,

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

* Electrical Conductivity

If free time (i.e. time taken between two successive collision) be τ and velocity along one direction be v, then

$$\tau = \frac{\lambda}{v} \quad \text{-------------} (1)$$

where λ is the mean free path.

If the applied field on the electron of charge $-e$ be E then the equation of motion of electron is

$$m\frac{d^2x}{dt^2} = -eE \qquad \text{or}$$

$$\frac{d^2x}{dt^2} = -\frac{e}{m}E$$

Integrating the above equation we get

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

At $t=0$, $x=0$

$$0 = 0 + C \qquad \therefore \; C = 0$$

Hence $$\frac{dx}{dt} = \dot{x} = -\frac{eE}{m}t$$

Average velocity between two collisions is

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

$$= -\frac{1}{\tau}\left[\frac{eE}{m}\frac{t^2}{2}\right]_0^{\tau}$$

$$= -\frac{1}{\tau}\frac{eE}{m}\frac{\tau^2}{2}$$

$$\bar{\dot{x}} = -\frac{eE}{m}\cdot\frac{\tau}{2} \quad \text{-------------} (2)$$

If I is the current density and n is the number of electrons per unit volume, then we have

$$I = -ne\dot{x}$$

$$= -ne\left[-\frac{eE}{m}\cdot\frac{\tau}{2}\right]$$

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

$$= \frac{1}{2}\,\frac{ne^2E}{m}\,\frac{\lambda}{v} \qquad \left(\because \tau = \frac{\lambda}{v}\right) \text{ -------}$$

Multiplying and dividing by v, we get

$$I = \frac{1}{2}\,\frac{ne^2E}{m}\,\frac{\lambda}{v}\cdot\frac{v}{v} \qquad \text{-------- (3)}$$

since we know that

$$\frac{1}{2}mv^2 = \frac{3}{2}kT \qquad \text{-------------}$$

$$mv^2 = 3kT \qquad \text{--------- (4)}$$

substituting the value of mv^2 from equation (4) in expression (3), we get

$$I = \frac{1}{2}\,\frac{ne^2E\lambda v}{3kT}$$

$$\therefore I = \frac{ne^2E\lambda v}{6kT}$$

∴ ~~$I = ne^2E\lambda$~~

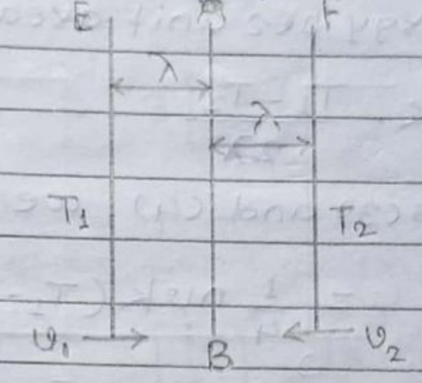
$$I = \frac{ne^2\lambda v}{6kT}\,E$$

or $I = \sigma . E$

where

$$\boxed{\sigma = \frac{ne^2\lambda v}{6kT}} \qquad \text{------------- (5)}$$

* Thermal conductivity



On the basis of kinetic theory, if two temperatures are equal i.e. if $T_1 = T_2$, then there is no transfer of energy.

If $T_1 > T_2$ there is transfer of energy from E to F. Then from E to F the number of electrons per unit area per unit time is $\frac{1}{6} n v$ and each electron has energy $\frac{1}{6} m v_1^2$.

Hence total energy transferred from E to F

$$= \frac{1}{6} n v \cdot \frac{1}{2} m v_1^2$$

$$= \frac{1}{6} n v \cdot \frac{3}{2} k T_1$$

$$= \frac{1}{4} n v k T_1 \quad \text{-----------} \quad (1)$$

Similarly the energy transferred from F to E

$$= \frac{1}{4} n v k T_2 \quad \text{-----------} \quad (2)$$

Hence net energy transferred from E to F per unit area per unit time

$$= \frac{1}{4} n v k T_1 - \frac{1}{4} n v k T_2$$

$$= \frac{1}{4} n v k (T_1 - T_2) \quad \text{---------} \quad (3)$$

If K be the thermal conductivity, then the transfer of energy per unit area per unit time

$$= K \cdot \frac{T_1 - T_2}{2\lambda} \quad \text{-----------} \quad (4)$$

From equations (3) and (4), we get

$$K \cdot \frac{T_1 - T_2}{2\lambda} = \frac{1}{4} n v k (T_1 - T_2)$$

$$\therefore \quad \frac{K}{2\lambda} = \frac{1}{4} n v k$$

$$\therefore \quad \boxed{K = \frac{1}{2} \lambda n v k} \quad \text{-----------} \quad (5)$$

* Widemann-Franz Relation

The ratio of thermal conductivity to electrical conductivity (K/σ) is known as Widemann-Franz relation.

The thermal conductivity is

$$K = \frac{1}{2} \lambda n v k$$

The electrical conductivity is

$$\sigma = \frac{n e^2 \lambda v}{6kT}$$

$$\therefore \quad \frac{K}{\sigma} = \frac{\frac{1}{2} \lambda n v k}{n e^2 \lambda v / 6kT}$$

$$\therefore \quad \frac{K}{\sigma} = \frac{\frac{1}{2} \lambda n v k}{n e^2 \lambda v} \cdot 6kT$$

$$\frac{K}{\sigma} = \frac{1}{2} \frac{k}{e^2} \cdot 6kT$$

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

$$\frac{k}{\sigma} = 3\left[\frac{k}{e}\right]^2 T$$

$$\therefore \frac{k}{\sigma} = LT$$

where $L = 3\left[\frac{k}{e}\right]^2$ is called Lorentz number.

$$\therefore \frac{k}{\sigma T} = L$$

$$\boxed{\therefore \frac{k}{\sigma} \propto T}$$

This is Widemann-Franz relation.

* Sommerfeld's Model

An electron in a metal finds itself in the field of all nuclei and all other electrons. The potential energy for such an electron may be expected to be periodic. In the sommerfeld's model, it is assumed that the free electrons find themselves in a potential which is constant everywhere inside the metal. Since one does not observe electron emission from metals at room temperature because the potential energy of an electron at rest must be lower than that of an electron at rest outside the metal.

In the Sommerfield's model, the free electrons are assumed to be the valance electrons of the composing atoms. Thus the alkali metals are assumed to contain one free electron per atom

consider first an electron limited to remain within a one-dimensional crystal of length L.

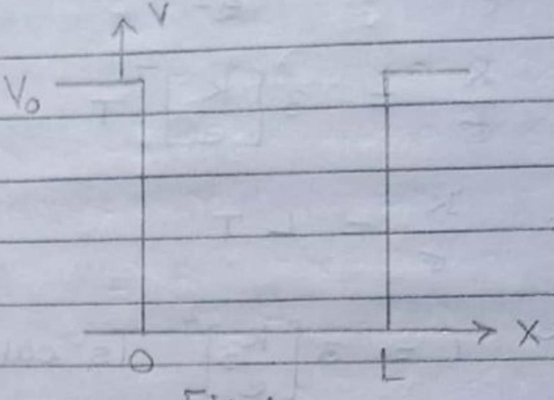


Fig.1

Next assume that the potential energy everywhere within this crystal is constant and is equal to zero. At the two ends of the crystal the electron is prevented from leaving the crystals by a very high potential energy barrier represented by V_0 as in Fig.1.

Since the potential energy inside the crystal is zero, the Schrodinger equation has the form

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

or $$\frac{d^2\psi}{dx^2} + \omega^2\psi = 0 \quad \text{------------ (1)}$$

where $\omega^2 = \frac{2mE}{\hbar^2}$

Its solution is

$$\psi = Ae^{\alpha x} \quad \text{---------- (2)}$$

Differentiating twice eq.(2), we get

$$\frac{d\psi}{dx} = A\alpha e^{\alpha x}$$

$$\therefore \frac{d^2\psi}{dx^2} = A\alpha^2 e^{\alpha x} \quad \text{-------- (3)}$$

put these values from eqn. (2) and (3) in eqn. (1) we have

~~$A\alpha^{2}e^{\alpha x}$~~ + ~~A[illegible]~~

$$A\alpha^2 e^{\alpha x} + A\omega^2 e^{\alpha x} = 0$$

or $$\alpha^2 + \omega^2 = 0$$

or $$\alpha = \pm \omega i$$

$$\therefore \quad \psi = A_1 e^{i\omega x} + B_1 e^{-i\omega x}$$

$$= A_1[\cos\omega x + i\sin\omega x] + B_1[\cos\omega x - i\sin\omega x]$$

$$= (A_1 + B_1)\cos\omega x + i(A_1 - B_1)\sin\omega x$$

$$= C_2\cos\omega x + C_1\sin\omega x$$

$$\therefore \quad \psi = C_2\cos\sqrt{\frac{2mE}{\hbar^2}}\,x + C_1\sin\sqrt{\frac{2mE}{\hbar^2}}\,x \quad ----(4)$$

The values of two constants C_1 and C_2 can be determined by the boundary conditions existing at $x = 0$ and $x = L$.

Consider the form of schrodinger equation on either side of the crystal, i.e. in the regions where the potential energy is very large. Including the potential energy term V_0, the schrodinger equation can be written as

$$\frac{d^2\psi}{dx^2} - \frac{2m(V_0 - E)}{\hbar^2}\psi = 0 \quad -------(5)$$

where $V_0 > E$.

The general solution of this equation for $V_0 > E$ is

$$\psi = e^{\frac{\sqrt{(2m(V_0-E)}}{\hbar}x}\cdot C_3 + e^{-\frac{\sqrt{2m(V_0-E)}}{\hbar}x}\cdot C_4 \quad ------(6)$$

An examination of the solution (4) reveals that as x increases in either a positive or negative sense, the value of the wavefunction also increases. This ~~obsi~~ obviously cannot be possible since this means that the probability of finding the electron outside the crystal increases with increasing distance from the crystal.

consequently $C_3 = 0$ when $x \geq L$
and $C_4 = 0$ when $x \leq 0$

This gives two different solutions,

when $x \geq L$, $\psi = C_4 e^{-\frac{\sqrt{2m(V_0-E)}}{\hbar}x}$ ------ (7)

and when $x \leq 0$, $\psi = C_3 e^{\frac{\sqrt{2m(V_0-E)}}{\hbar}x}$ ------ (8)

It is now possible to consider the boundary conditions that solutions (4), (7) and (8) must satisfy. Since there is finite probability of finding the electron anywhere in space, the wavefunction must be continuous. Similarly, it can be shown that $d\psi/dx$ must be continuous. Consider first that $d\psi/dx$ is continuous at $x = L$.

Differentiating equations (4) and (7)

$$\left(\frac{d\psi}{dx}\right)_{x=L} = C_1 \frac{\sqrt{2mE}}{\hbar} \cos\frac{\sqrt{2mE}}{\hbar}L - C_2 \frac{\sqrt{2mE}}{\hbar} \sin\frac{\sqrt{2mE}}{\hbar}L \quad \text{------ (9)}$$

and

$$\left(\frac{d\psi}{dx}\right)_{x=L} = -\frac{\sqrt{2m(V_0-E)}}{\hbar} C_4 \cdot e^{-\frac{\sqrt{2m(V_0-E)}}{\hbar}L}$$

$$= \frac{\sqrt{2m(V_0-E)}}{\hbar} \psi_{x=L} \quad \text{---------- (10)}$$

As the potential energy at the crystal surface increases, i.e as $V_0 \to \infty$ eqⁿ (10) becomes infinite.

Considering the solution (4) at $x = 0$

$$\psi = 0 = C_1 \sin(0^\circ) + C_2 \cos(0^\circ)$$

$$= C_2 \quad \text{---------- (11)}$$

at $x = L$

$$\psi = 0 = C_1 \sin \frac{\sqrt{2mE}}{\hbar} . L$$

$$\therefore \psi = C_1 \sin \frac{\sqrt{2mE}}{\hbar} L \quad \text{------- (12)}$$

Excluding the trivial solution that C_1 also is zero, the only way that eqⁿ (12) can be ~~classified~~ satisfied is for the sine to be zero

$$\therefore \sin \frac{\sqrt{2mE}}{\hbar} L = 0$$

or

$$\frac{\sqrt{2mE}}{\hbar} L = n\pi \quad \text{------- (13)}$$

where $n = 1, 2, \ldots$

$$\therefore \sqrt{2mE}\, L = n\pi \hbar$$

$$\sqrt{2mE} = \frac{n\pi}{L} \frac{h}{2\pi} \quad \left(\because \hbar = \frac{h}{2\pi}\right)$$

$$\therefore \sqrt{2mE} = \frac{nh}{2L}$$

$$\therefore 2mE = \frac{n^2 h^2}{4L^2}$$

$$\therefore \boxed{E_n = \frac{n^2 h^2}{8mL^2}} \quad \text{------- (14)}$$

the energy can have only the discrete values.

If L is large, the energy levels are spaced closely together

* Electrical conductivity and ohms law

The momentum of a free electron is related to a wave vector by

$$p = \hbar k \qquad \text{-------- (1)}$$

Fermi surface is the surface in K- space seperating occupied and unoccupied states. on free-electron model the states $\varepsilon < \varepsilon_f$ in ground state i.e at $T = 0$ fill a sphere of radius k_F in K-space called the Fermi sphere as in below Fig. 1

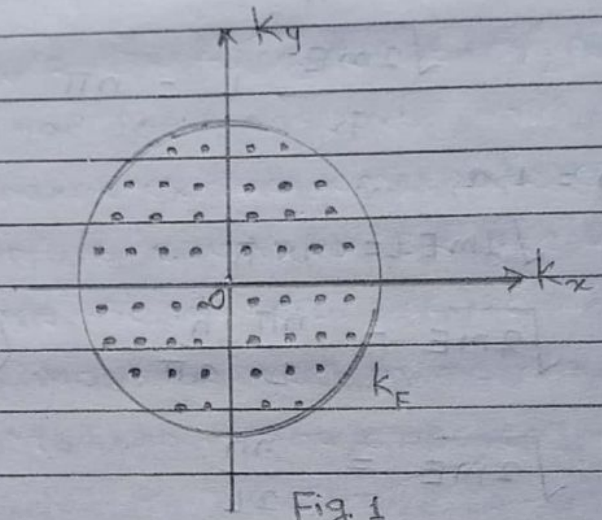


Fig. 1

The net momentum is zero because for every occupied state k there is an occupied state -k, consequently it is not a current-carrying state. In electric field $\bar{E}$ the force on the electron is $\bar{F} = -eE$ so that

$$\bar{F} = \frac{dp}{dt} = \hbar \frac{dk}{dt} = -e\bar{E} \qquad \text{----(2)}$$

In the absence of collisions the Fermi surface in K-space is displaced uniformly by the applied field giving infinite conductivity because this corrosponds to a flow of current as there are more electrons with momentum in the +x direction than in the -x direction. For the force acting for time δt, k vector of every state is increased by

$$\delta k = \frac{F\,\delta t}{\hbar} = -\frac{Ee\,\delta t}{\hbar} \qquad \text{-----}\ (3)$$

If collision time is τ, the displacement of the Fermi sphere in the steady state is given by equation (3). The incremental velocity is

$$\delta v = -\frac{eE\tau}{m} \qquad \text{---------}\ (4)$$

If there are n electrons per unit volume, the electric current density is

~~$J = nq\,\delta v =$~~

$$J = -ne\,\delta v = \frac{ne^2\tau E}{m} \qquad \text{--------}\ (5)$$

This is in the form of ohms law.

The electrical conductivity σ is defined by

$J = \sigma E$ so that

$$\sigma = \frac{ne^2\tau}{m} \qquad \text{----------}\ (6)$$

The electrical resistivity ρ is defined as the reciprocal of conductivity

$$\rho = \frac{1}{\sigma}$$

$$\rho = \frac{1}{\left(\frac{ne^2\tau}{m}\right)}$$

$$\therefore\ \rho = \frac{m}{ne^2\tau} \qquad \text{---------}\ (7)$$

* Electronic specific heat

According to classical free-electron theory, all the valance electrons in a metal can absorb thermal energy. This leads to an electronic contribution to the specific heat of metal of $3/_2 R$ per kilogram atomic weight. Accordingly the total specific heat of metal can be expressed as

$$C_V = C_V\,(\text{atomic}) + C_V\,(\text{electronic})$$

$$C_V = 3R + {}^{3}/_{2} R = {}^{9}/_{2} R \qquad \text{------ (1)}$$

Dulong and Petit observed that the specific heat above the characteristic temperature is the same for all solids and is equal to 3R per kilogram atomic weight. since the larger specific heat is predicted by eq^n(1) is not observed in metals, this constitutes an important flaw in the classical free electron theory.

It is possible to estimate the electronic specific heat by making use of the Fermi distribution function.

In thermal equilibrium, the number of electrons dN within the energy range E and E+dE is given by

$$dN = f(E)\,g(E)\,dE$$

$$= f(E)\,CE^{1/2}\cdot dE$$

$$N = \int dN = \int_0^\infty CE^{1/2}\cdot f(E)\,dE$$

$$N = C\int_0^\infty E^{1/2}\cdot f(E)\,dE \qquad \text{---------- (2)}$$

To energy of the electron

$$\Sigma NE = C\int_0^\infty E\cdot E^{1/2} f(E)\,dE \qquad \text{------ (3)}$$

where $\Sigma NE = N_1E_1 + N_2E_2 + \cdots$

Hence the mean energy

$$\bar{E} = \frac{C}{N}\int_0^{\infty} E^{3/2} f(E)\,dE \quad \text{per electron} \qquad \text{-------} (4)$$

Integrating it by parts, we get

$$\bar{E} = \frac{C}{N}\left[\left\{ f(E)\,\frac{2}{5}E^{5/2}\right\}_0^{\infty} - \int_0^{\infty}\frac{df(E)}{dE}\cdot\frac{2}{5}E^{5/2}\,dE\right] \qquad \text{------} (5)$$

First term is zero because $E = 0$ for lower limit

The average kinetic energy of a free electron as given by the classical mechanics is

$$\bar{E} = \frac{3}{2}k_BT \qquad \text{---------} (6)$$

If the metal contains N free electrons, then the total kinetic energy becomes

$$\bar{E} = N\bar{E}_0 = \frac{3}{2}Nk_BT$$

Hence, the electronic specific heat is

$$C_v = \frac{3}{2}Nk_B \qquad \text{----------} (7)$$

The quantum mechanics suggests that only those electrons contribute to the specific heat which lie within an energy range k_BT below the Fermi level. This happens because when the electron gas is heated upto a temperature T, these electrons aquire energy of the order of k_BT and jump to the empty higher energy states. The deep lying electrons cannot do so because the unfilled energy states are not available to these electrons for excitation. These electrons do not contribute to the specific heat. The number of electrons which contribute to the specific heat is of the order

$$N\left(\frac{k_B T}{E_F}\right) \quad \text{or} \quad N\left(\frac{T}{T_F}\right)$$

where $T_F = \frac{E_F}{k_B}$ is called the Fermi temperature and is defined by equation $E_F = k_B T_F$

Using effective value of N eq? (7) becomes

$$C_v \cong \frac{3}{2} N k_B \left(\frac{T}{T_F}\right) \quad \text{-------} \quad (8)$$

This indicates that C_v is proportional to T and approaches zero as $T \rightarrow 0$.

* Thermionic Emission :

The emission of electrons from the metal surface by the application of heat is called thermionic emission. The escape of electron can happen as a result of applying sufficiently high temperatures or electric field. ~~to supply the~~ Similarly energetic photons or charged particles bombarding the surface may transfer energy to electrons through collisions, resulting in electron emission. Each of these processes is strongly dependent upon the properties of material itself.

The electrical conductivity of metals is the result of electrons within the material which are not definitely attached to any particular molecule. For these free electrons to escape from the surface they must perform certain amount of work to overcome the force of attraction present at the surface. When the kinetic energy is more enough electron will escape from the metal.

As the temperature is increased, the kinetic energy of free electrons in the material is increased At sufficiently high temperature an appreciable number of electrons will have the kinetic energy required to escape through the surface. This results in thermionic emission of electrons.

The number of electrons emitted per unit area of emitting surface is related to absolute temperature T of the emitting material and a quantity W_0 i.e a measure of work that an electron must perform in escaping from the surface, according to the equation

$$I = AT^2 \exp\left(-\frac{W_0}{kT}\right)$$

* Escape of Electrons from a Metal:

A solid metal is a regular pattern of atomic nuclei each surrounded by bound electrons.

Fig. 1 shows the forces acting on several electrons at different positions inside a lattice. The free electrons

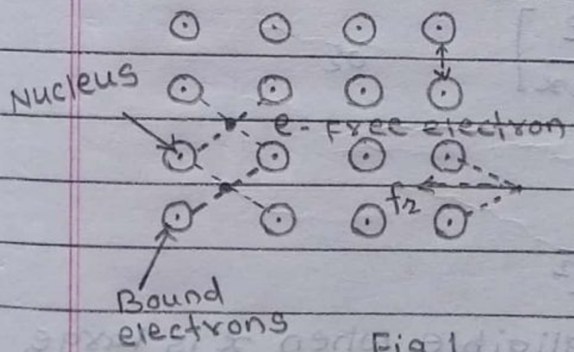


Fig. 1

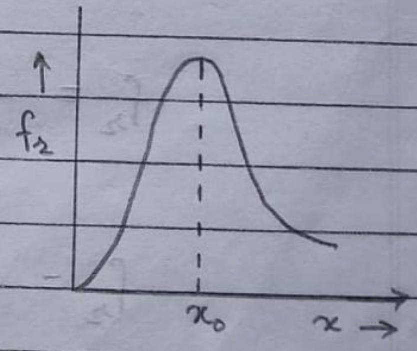


Fig. 2

move through the electric field of ion lattice. on the average the resultant force on the electrons is zero as it moves within the body of metal, but whenever its motion carries the electrons beyond the outer layer of ions it experiences an inward force. To escape from the metal an electron must therefore have a kinetic energy at least equal to the work which it must do against this restraining force. If the inward force has a magnitude f_r at a distance x from the layer of ions, then the condition of electron escape is

$$\frac{1}{2}mv^2 \geq \int_0^\infty f_r \cdot dx$$

The gross work function of metal is therefore

$$W_c = \int_0^\infty f_r \cdot dx$$

The magnitude of the force f_r is zero at $x=0$ but as the electron moves outward from the layer of ions, the force f_r increases with distance x as shown in Fig. 2. The force becomes weaker as the distance increases and becomes zero. It follows that force f_r must pass through a maximum at some distance x_0 beyond which it declines to zero.

The restraining force is then given by

$$f_r = \frac{1}{4\pi k_0}\left[\frac{e}{2x}\right]^2 \quad \text{or}$$

$$f_r = \frac{e^2}{16\pi k_0 x^2}$$

This force becomes negligible when x is large.