METALS: DRUDE MODEL AND CONDUCTIVITY

ELECTRON THEORY OF METALS

The electron theory has been developed in three stages:

1:- **The Classical Free Electron Theory:**

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

2:- **The Quantum Free Electron Theory:**

Sommerfeld developed this theory during 1928. According to this theory, free electrons obey quantum laws.

3:- **The Band Theory or Zone Theory:**

Bloch stated this theory in 1928. According to this theory, the free electrons move in a periodic field provided by lattice. This theory is also called " Band theory of solids". The concept of hole, origin of band gap and effective mass of electrons are special features of this theory or Zone theory of metals

The Classical Free Electron Theory of Metals

The free electron theory is based on the following assumptions:

a. **In metals, there are a large number of free electrons moving freely within the metals. The electrons revolve around the nucleus in an atom.**

b. **The free electrons are assumed to behave like gas molecules, obeying the laws of kinetic theory of gases. The mean kinetic energy of free electron is equal to that of gas molecules at the same temperature.**

c. **Electric conduction is due to motion of free electrons only. The +ve ion cores are at the fixed positions. The free electrons undergo incessant collisions with the ion core.**

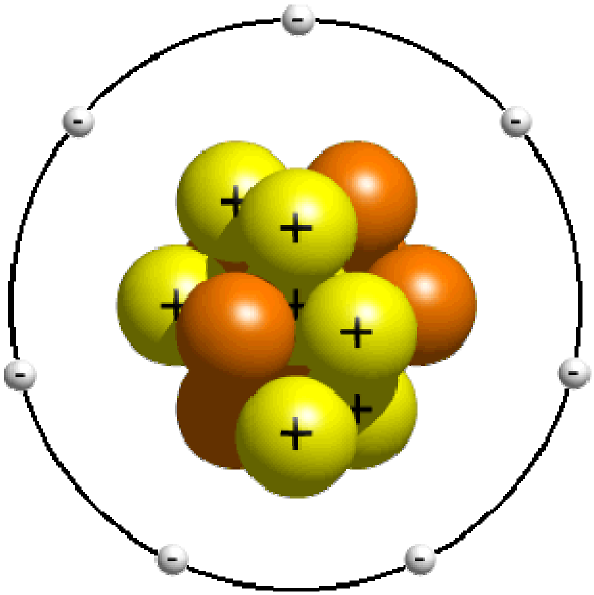
d. The electric field due to the ion cores in constant through the metal (i.e., the free electrons move in a completely uniform potential field due to fixed in the lattice.). The repulsion between the electrons is negligible.

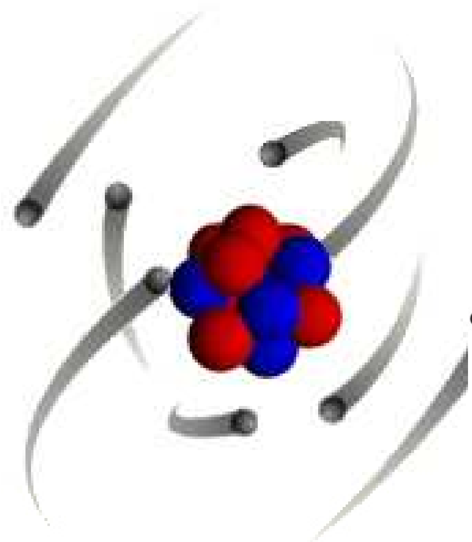
e. When an electric field is applied to the metals, the free electrons are accelerated in the direction opposite to the direction of applied electric field.

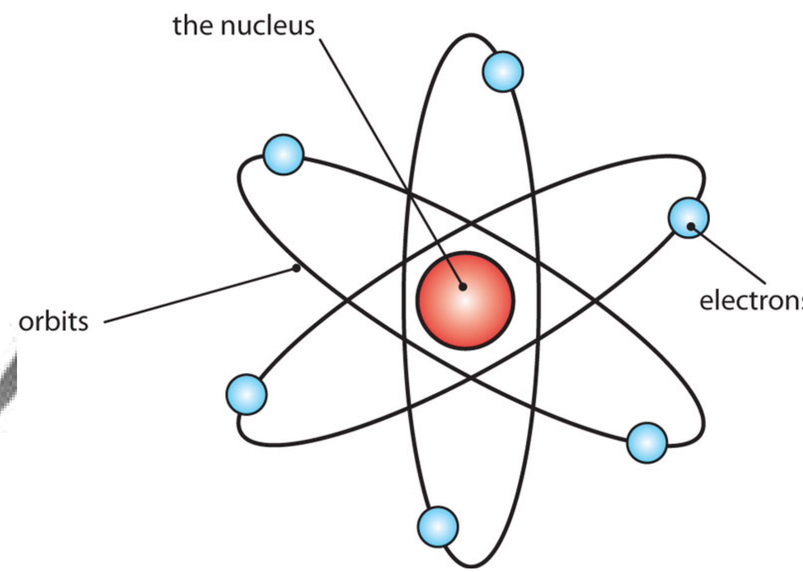
By the end of this section you should be able to:

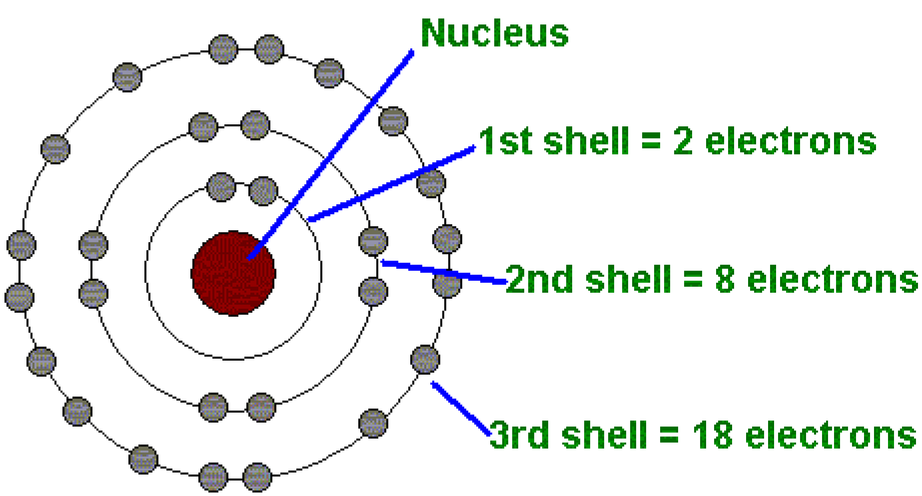
- **Understand the basics of the Drude model**
- **Determine the valence electrons of an atom**
- **Determine the density of conduction electrons**
- **Calculate the electrical conductivity of a metal**
- **Estimate and interpret the relaxation time**

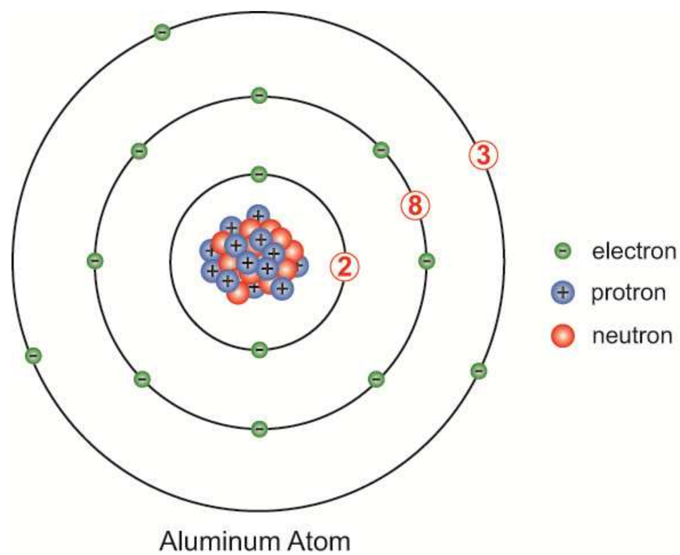
Models of Atoms



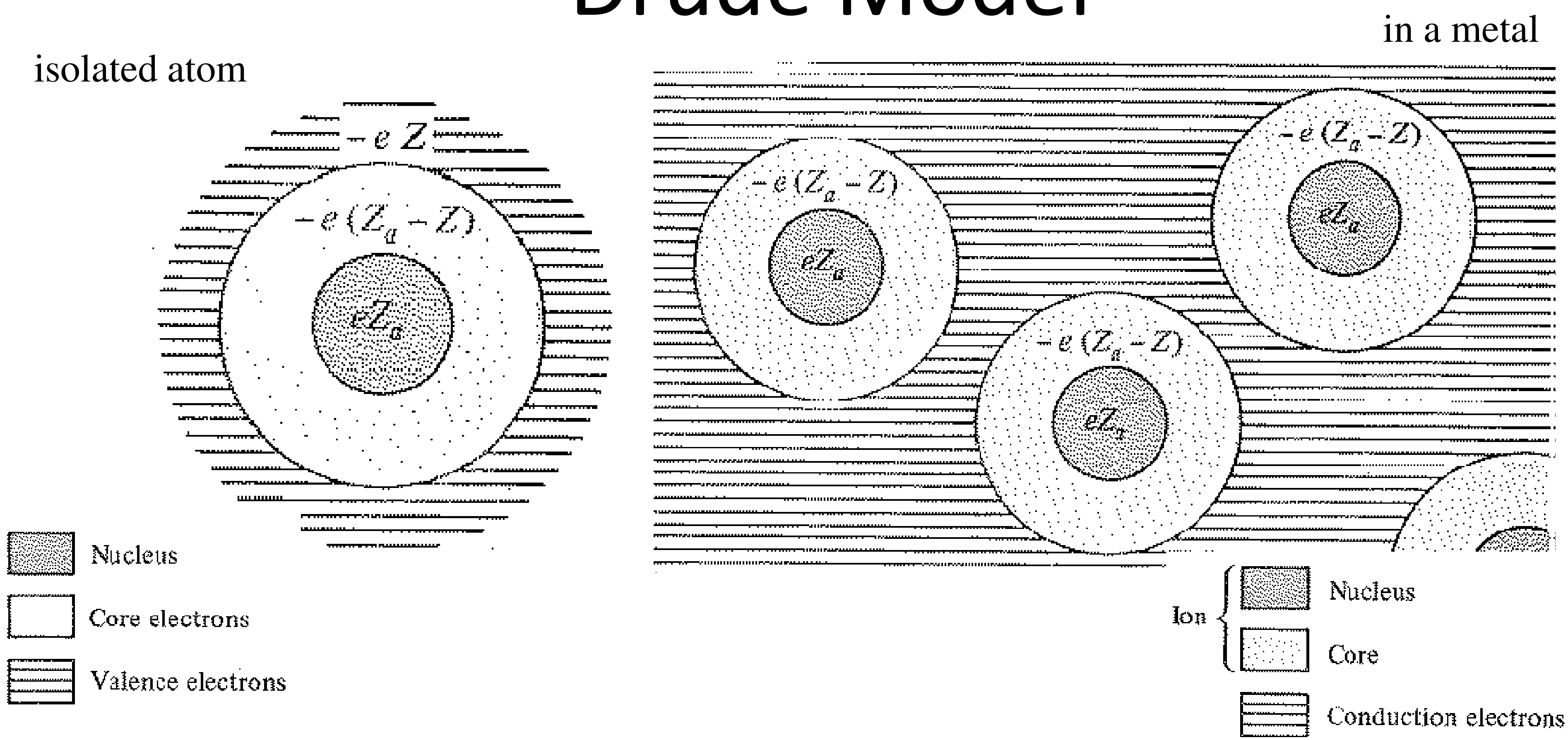








Drude Model



Z valence electrons are weakly bound to the nucleus (participate in reactions)
$Z_a - Z$ core electrons are tightly bound to the nucleus (less of a role)

In a metal, the core electrons remain bound to the nucleus to form the metallic ion Valence electrons wander away from their parent atoms, called conduction electrons

- According to this

Free Electron Model **(FEM)**,

the valence electrons are responsible for the conduction of electricity, & for this reason these electrons are called

"Conduction Electrons".

- As an example, consider **Sodium (Na).** The **electron configuration** of the **Free Na Atom** is:

Core Electrons (tightly bound) → $1s^2\ 2s^2\ 2p^6\ 3s^1$ ← **Valence Electrons (loosely bound)**

- The **outer electron in the third atomic shell** **(n = 3, ℓ = 0)** ***is the electron which is responsible for the physical & chemical properties of Na.***

How to find Valence electrons?

What is the valency of iron, atomic Number 26?

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

Number of outer electrons = 6

Iron would like to suck up other electrons to fill the shell, so it has a valence of 4 when elemental.

Valence vs. Oxidization

Fe: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

Number of outer electrons = 6

The removal of a valance electron leaves a positively charged ion.

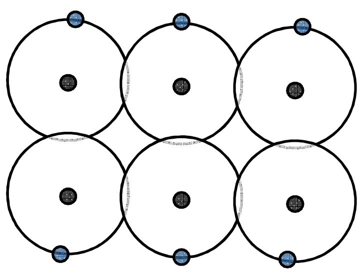
COMPOUND	FORMULA	VALENCE	OXIDATION STATE
Hydrogen chloride	HCl	H=1 Cl=1	H=+1 Cl=−1
Perchloric acid *	$HClO_4$	H=1 Cl=7 O=2	H=+1 Cl=+7 O=−2
Sodium hydride	NaH	Na=1 H=1	Na=+1 H=−1
Ferrous oxide **	FeO	Fe=2 O=2	Fe=+2 O=−2
Ferric oxide **	Fe_2O_3	Fe=3 O=2	Fe=+3 O=−2

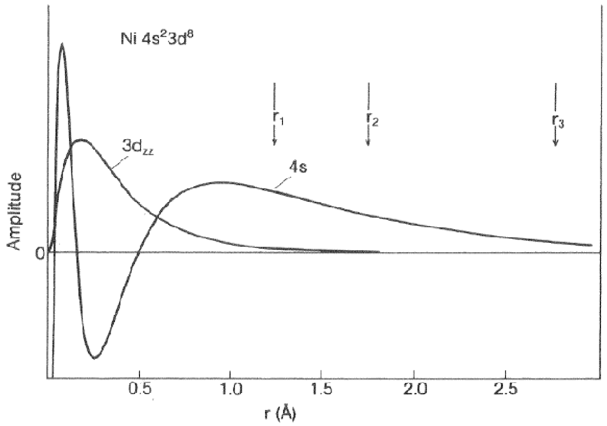
$_8$O: 1s2 2s2 2p4 often steals two e^-s -> O^{2-}

Note: oxidization state (e.g. 2- in O) is not the valence, but can be used in combination with the original valence to find the new valence

How the mobile electrons become mobile?

When we bring Na atoms together to form a Na metal, the orbitals overlap slightly and the





valance electrons become no longer attached to a particular ion, but belong to both.

A valance electron really belongs to the whole crystal, since it can move readily from one ion to its neighbour and so on.

Electron Density $n = N/V$

- 6.022×10^{23} atoms per mole
- Multiply by number of valence electrons
- Convert moles to cm^3 (using mass density ρ_m and atomic mass A)

$$n = N/V = 6.022 \times 10^{23}\, Z\, \rho_m / A$$

Effective Radius

density of conduction electrons in metals ~10^{22} – 10^{23} cm^{-3}

r_s – measure of electronic density = radius of a sphere whose volume is equal to the volume per electron

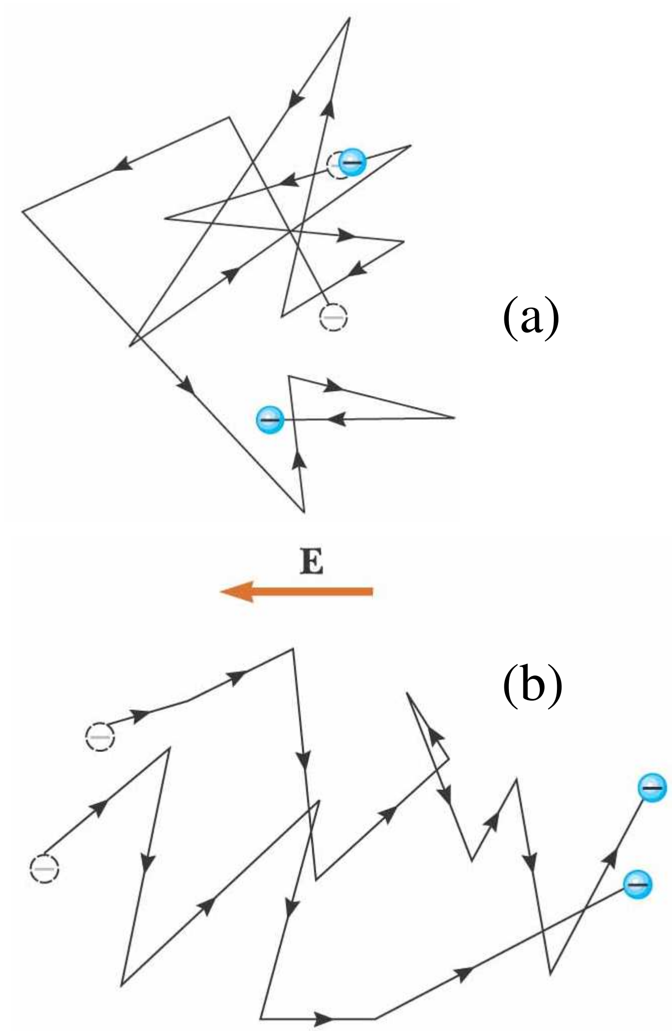
$$\frac{4\pi r_s^3}{3} = \frac{V}{N} = \frac{1}{n} \qquad r_s = \left(\frac{3}{4\pi n}\right)^{1/3} \sim \frac{1}{n^{1/3}}$$

← mean inter-electron spacing

in metals $r_s \sim 1 - 3$ Å (1 Å= 10^{-8} cm) $\qquad r_s/a_0 \sim 2 - 6$

$$a_0 = \frac{\hbar^2}{me^2} = 0.529 \text{ Å}$$ **– Bohr radius**

A model for electrical conduction



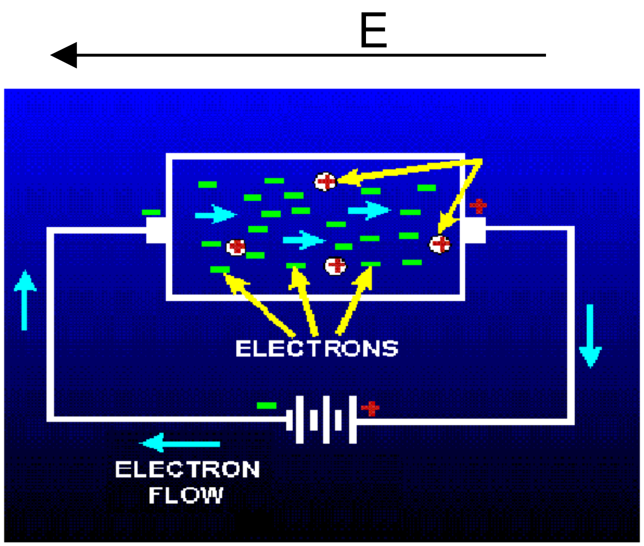
(a)

(b)

Drude model in 1900

- **In the absence of an electric field, the conduction electrons move in random directions through the conductor with average speeds ~ 10^6 m/s. The drift velocity of the free electrons is zero. There is no current in the conductor since there is no net flow of charge.**
- **When an electric field is applied, in addition to the random motion, the free electrons drift slowly (v_d ~ 10^{-4} m/s) in a direction opposite that of the electric field.**

Ohm's Law



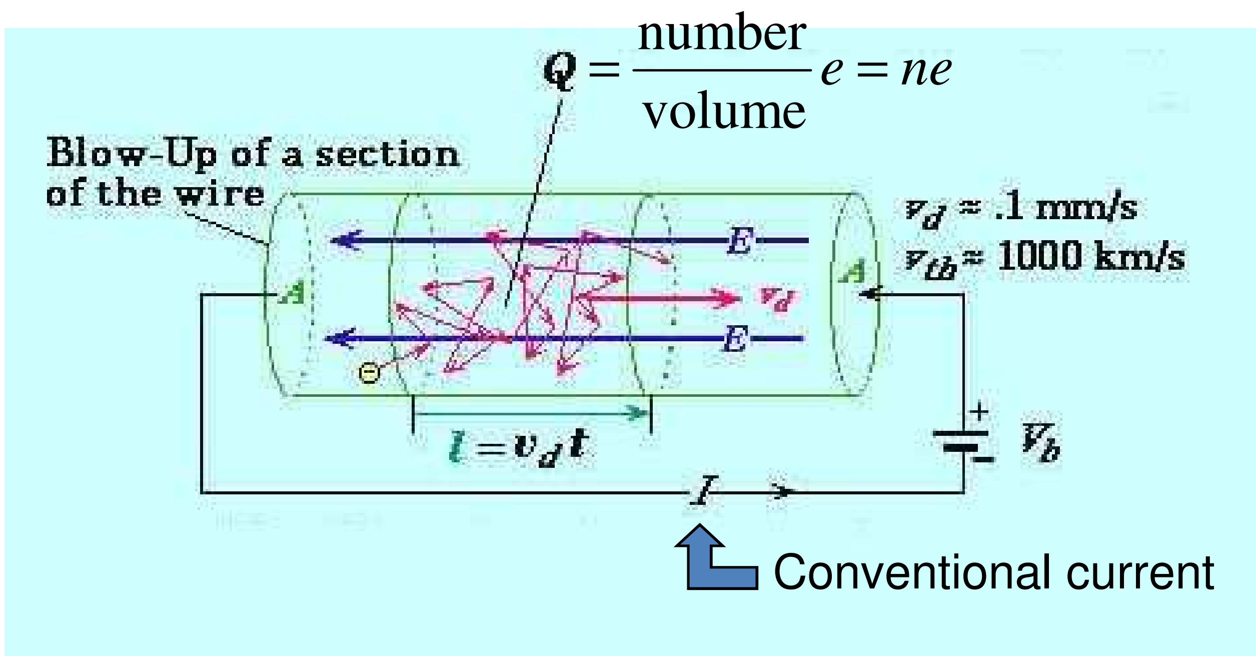
Experimental observation: $V \propto I$

$$V = RI$$
$$= \rho \frac{L}{A} I$$
$$= \rho L \frac{I}{A} = \rho L j$$

$$\frac{V}{L} = \rho j$$
$$E = \rho j$$

or $j = \sigma E$

Ohm's Law: Free Electron Model



$$j = nev_d$$

The electric field accelerates each electron for an average time τ before it collides with an ion core.

Ohm's Law: Free Electron Model

$$F = eE = ma$$

$$= m\frac{v_d}{\tau}$$

$$\Rightarrow\ v_d = \frac{eE\tau}{m}$$

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

σ

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

Ohm's Law: Free Electron Model

If electrons behave like a gas…

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

The mean free time is related to this average speed…

$$\tau = \frac{\ell}{\langle v \rangle} \approx \frac{a}{\langle v \rangle}$$

typical value
About 10^{-14} s

Then,

$$\sigma = \frac{1}{\rho} = \frac{ne^2 a}{m}\sqrt{\frac{\pi m}{8k_B T}}$$

Wiedemann-Franz Law (1853)

	Electrical	Thermal
Conductivities	$\sigma = \frac{ne^2\ell}{m\langle v\rangle}$	$\kappa = \frac{1}{2} n\langle v\rangle \ell k_B$

where $\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}}$

$$\Rightarrow \quad \frac{\kappa}{\sigma} = \frac{4k_B{}^2T}{\pi e^2}$$

Lorentz number (Incorrect!!)

Wiedemann-Franz Law (1853)

(Ludwig) Lorenz Number
(derived via quantum mechanical treatment)

$$L = \frac{\kappa}{\sigma}\frac{1}{T} = \frac{\pi^2 k_B{}^2}{3e^2} = 2.45\times10^{-8}\ \frac{\mathrm{W}\cdot\Omega}{\mathrm{K}^2}$$

Lorenz number in 10^-8 Watt ohm/K^2		
Metal	273K	373K
Ag	2.31	2.37
Au	2.35	2.40
Cd	2.42	2.43
Cu	2.23	2.33
Ir	2.49	2.49
Mo	2.61	2.79
Pb	2.47	2.56
Pt	2.51	2.60
Sn	2.52	2.49
W	3.04	3.20
Zn	2.31	2.33

Please Recall:

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

The average distance traveled by an electron between two successive collisions in the presence of applied electric field is known a mean free path (λ).

The average time between collisions is given by

$\tau =$ *mean free path/ rms velocity of the electron*

$$\tau = \frac{\lambda}{\bar{c}} \quad \text{----------- (b)}$$

The rms velocity, according to the kinetic theory of gases is given by

$$\bar{c} = \sqrt{\frac{3kT}{m}} \quad \text{----------- (c)}$$

From the equation (a), (b), and (c)

$$\sigma = \frac{ne^2\lambda}{\sqrt{3mkT}} \qquad \text{------ (d)}$$

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

From the eqn. (d), According to classical free electron theory, the electrical conductivity is inversely proportional to square root of absolute temperature.

Relaxation time:-

Under the influence of an external electric field, free electrons attain a directional steady state drift velocity of motion.

If the field is turned off, the steady state velocity is decreasing exponentially. Such a process tends to restore equilibrium, this is called relaxation process.

Drift velocity after the cut off of applied electric field

$$m\frac{dv_d}{dt} = -m\frac{v_d}{\tau} \qquad \text{---------} \ (1)$$

$$\frac{dv_d}{dt} = -\frac{v_d}{\tau}$$

$$\frac{1}{v_d}dv_d = -\frac{1}{\tau}dt$$

$$v_d(t) = v_d(0)\exp(-t/\tau) \quad \text{--------} \ (2)$$

At t=0; $v_d(0)$ is steady state drift velocity, when E is cut off

Let $t = \tau$;

$$v_d(t) = \frac{v_d(0)}{e} \quad \text{————————} \ (3)$$

Relaxation time can be defined as the time taken for the drift velocity to decay to 1/e of its initial vale.

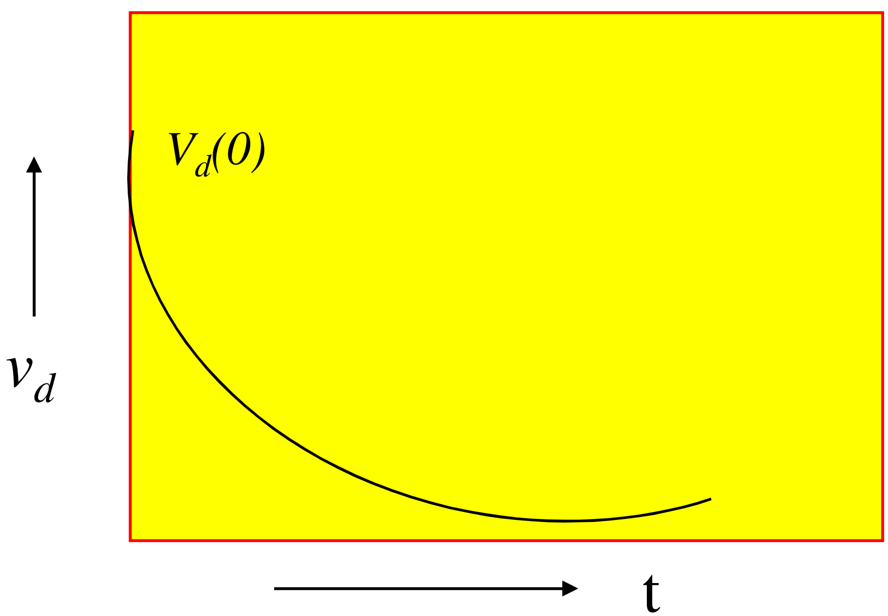


Fig. Relaxation of electron after electric field is cut off

Please also derive the following relation

$$P(t) = P(0)\exp(-t/\tau)$$

Mobility

Mobility of the electron μ is defined as the steady state drift velocity v_d per unit electric field

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

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

$$\sigma = ne\mu$$

Resistivity

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

σ depends on n and μ. These two quantities depends on temperature.

Success of Classical free electron theory:

1. It verifies Ohm's Law.

2. It explains the electrical and thermal conductivities of metals.

3. It sucessfully derives Wiedeman – Franz Law (i.e., The relation between electrical and thermal conductivities).

4. It explains Optical properties of metals in well manner.

Drawbacks of Classical Free electron theory:

- The phenomena such as Photoelectric effect, Crompton effect and the black body radiation couldn't be explained by classical free electron theory.

- Electrical conductivity couldn't explained with temperature using this model. Electrical conductivity is inversely proportional to temperature T, while theory predicts that it is inversely proportional to square root of temperature T.

- $K/(\sigma T)$ is constant according to this theory, where σ is conductivity, K is the thermal conductivity. But it is not constant.

- **According to this theory the value of the electronic specific heat is equal to (3/2)R, But actually it is about 0.01R only, where R is the universal gas constant.**

- **The theoretical value of paramagnetic susceptibility is greater than the experimental value. Ferromagnetism cannot be explained by this theory.**