Module – 2
Electrical conductivity

Syllabus: Failures of classical free electron theory- assumptions of quantum free electron theory- Fermi Energy- density of states- Fermi factor- variation of Fermi factor with temperature and energy. Polar and non-polar dielectrics- polarization mechanisms- internal fields in solid dielectrics- Clausius- Mossotti equation, Numerical Problems

Introduction: (Basic Terminologies)

Current density: It is defined as the current flowing per unit area of cross section. The area is held perpendicular to the direction of charge flow.

Current density = Current/ Area

$\Rightarrow \qquad J = \frac{I}{A}$

SI unit of current density is amp/m^2. It is a vector quantity.

The current density varies directly with the applied electric field (E)

$\therefore \qquad J \propto E$

$\Rightarrow \qquad J = \sigma E$

Where, σ is the electrical conductivity of a material.

The Reciprocal of electrical conductivity is called Resistivity, $\rho = \frac{1}{\sigma}$

Drift Velocity:

The average velocity with which electrons drift (displaces) in the presence of electric field is called drift velocity.

Drift velocity = Mean free path/ Mean collision time

$\Rightarrow \qquad v_d = \frac{\lambda}{\tau}$

Mean collision time (τ):

It is the average time taken by the electrons between two successive collisions. It is also called as Relaxation time.

Mean free path (λ): It is the average distance travelled by the electrons between two successive collisions.

Mobility: Mobility is defined as the ratio of drift velocity acquired by the electrons to the applied electric field.

Mobility = drift velocity/ electric field

$\Rightarrow \qquad \mu = \frac{v_d}{E}$

Failures of Classical Free Electron Theory.

The classical free electron theory proposed by Lorentz and Drude was a pioneering effort to explain the electrical and thermal properties of metals using classical mechanics and statistical physics. This theory treats the electrons in a metal as a gas of free non-interacting particles, similar to molecules in an ideal gas. Despite its initial success in explaining some basic electrical properties, the classical free electron theory faced significant limitations and failures.

The following are the failures of Classical free electron theory:

1. Specific heat of solid
2. Temperature dependence of electrical conductivity
3. Dependence of electrical conductivity on electron concentration:

1. Specific heat:

According to classical free electron theory, all the free electrons contribute to molar specific heat at constant volume. Hence the value of specific heat is high. It is given by

$$C_V = \frac{3}{2} R$$

Where, R → Universal Gas constant and C_V is independent of temperature.

But experimentally, the value of specific heat is having less value and C_V depends on temperature and it is given by

$$C_V = 10^{-4} RT$$

Only those free electrons which are close to the Fermi Sphere will contribute to specific heat. Hence this contrary fails Classical free electron theory to explain specific heat of solids.

2. Temperature dependence of electrical conductivity:

According to classical free electron theory, the conductivity σ varies inversely with the square root of temperature.

i.e, $\sigma \, \alpha \, \frac{1}{\sqrt{T}}$

But experimentally, the conductivity σ varies directly with the square root of temperature.

i.e, $\sigma \, \alpha \, \frac{1}{T}$

Hence Classical free electron theory fails to explain dependence of electrical conductivity on temperature

3. Dependence of electrical conductivity on electron concentration:

From classical free electron theory, the conductivity, $\sigma = \frac{ne^2\tau}{m}$

i.e   σ α n (free electron density)

As 'n' increases ,σ also increases. i.e, divalent or trivalent atom should possess more conductivity than mono valent atom. But experimentally, $\sigma_{Cu} > \sigma_{Al}$ even though $n_{Cu} < n_{Al}$.

Hence Classical free electron theory fails to explain dependence of electrical conductivity on electron concentration.

Metal	Conductivity (σ) in $\Omega^{-1}m^{-1}$	Concentration (n) in m^{-3}
Cu	5.88 X 10^7	8.45 x10^{28}
Al	3.65 X 10^7	18.06 x10^{28}

**Quantum Free Electron Theory**

To overcome the failures ofclassical free electron theory, Arnold Sommerfeld proposed quantum free electron theory.

Assumptions of quantum free electron theory.

1. The energy levels of free/conduction electrons are quantized. The allowed energy levels are realized in terms of set of discrete energy levels.
2. The distribution of electrons in various allowed energy levels is according Pauli's exclusion principle. (No free electron can occupy the same energy states - Maximum of two energy levels spin up & spin down).
3. The free electrons are confined to metal by potential barrier at the surface. The potential is constant inside and throughout the metal.
4. The electrostatic force of attraction between the electron and lattice point is neglected.
5. The electrostatic force of repulsion between the electrons is ignored.

Fermi energy (E_F): Fermi energy is defined as the highest energy level that electrons can occupy at absolute zero temperature (0 K) in a solid and the corresponding level is called the The Fermi energy is denoted by E_F.

Explanation: At absolute zero, all energy levels below the Fermi energy are filled with electrons, while those above are empty. At temperatures above absolute zero, electrons can occupy energy levels slightly above the Fermi level due to thermal excitation, but the Fermi level itself remains a reference point.
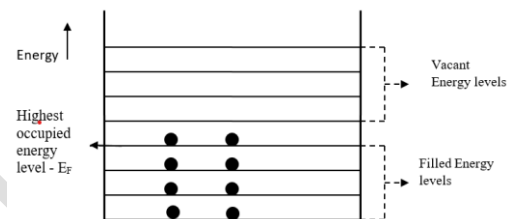
Density of states: $[g(E)dE]$

Definition: The number of possible electron quantum energy states between energy states E & E+dE per unit volume is known as density of states. It is represented by g(E)dE.

It is given by

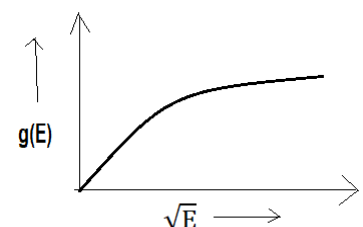$$g(E)dE = \left[\frac{8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3}\right] E^{\frac{1}{2}} dE$$

Where, m$\rightarrow$ mass of electron

h$\rightarrow$ Planck's constant

E$\rightarrow$ Energy state occupied by the electron at temperature T

As per the above equation $g(E) \alpha \sqrt{E}$. The variation of

$g(E)$ vs $\sqrt{E}$ is as shown in the graph

Fermi-Dirac Statistics:

Fermi-Dirac (F-D) statistics is applicable for an assembly of particles which obey Pauli's exclusion principle. The particles are identical, indistinguishable and have half-integral spin (spin 1/2). These particles are called Fermions.

Fermions are those particles which obey Fermi-Dirac Statistics.

Ex: Electrons, Protons etc.

Fermi factor: It is the function which defines the Probability of electrons occupied by the energy states at a given temperature. It is also called as Fermi function.

It is given by,

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

Where, $f(E) \rightarrow$ Fermi factor (Probability of electrons occupying energy state)

$E \rightarrow$ the energy of the state occupied by the electron at the temperature T in K

$E_F \rightarrow$ Fermi energy

$k \rightarrow$ Boltzmann constant

.**Variation of Fermi factor $f(E)$ with temperature T and energy E:**

The Fermi factor is given by the expression

$$f(E) = \frac{1}{e^{\frac{(E-E_F)}{kT}} + 1} \qquad \text{----------------- (1)}$$

Where, $f(E) \rightarrow$ Fermi factor.

$E \rightarrow$ the energy of the state occupied by the electron at the temperature T in K

$E_F \rightarrow$ Fermi energy

$k \rightarrow$ Boltzmann constant

Case (i): For $E < E_F$ at $T = 0\ K$ (Energy levels below the Fermi level):

If $E < E_F$ and at T = 0 K,

Eqn (1) $\Rightarrow$
$$f(E) = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1}$$
$$\therefore \quad f(E) = 1$$

The energy levels lying below the Fermi level are completely occupied at $T = 0\ K$.

Case (ii): For $E > E_F$ at $T = 0\ K$ (Energy levels above the Fermi level):

If $E > E_F$ and at T = 0 K,

Eqn (1) $\Rightarrow$
$$f(E) = \frac{1}{e^{\infty} + 1} = \frac{1}{\infty + 1} = \frac{1}{\infty} = 0$$
$$\therefore \quad f(E) = 0$$

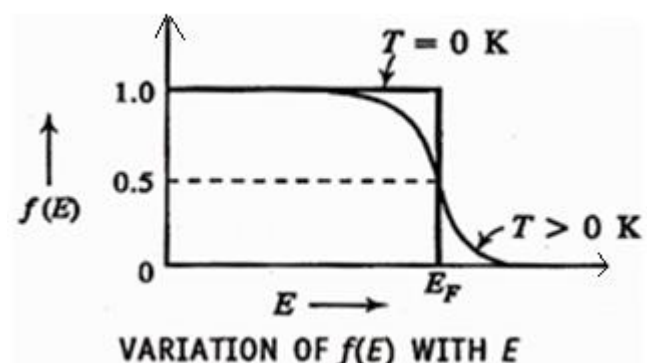The energy levels lying above the Fermi level are unoccupied (empty) at $T = 0\ K$.

Case (iii): For $E = E_F$ at $T > 0\ K$ (Fermi level):

If $E = E_F$ and at T > 0 K,

$$f(E) = \frac{1}{e^{0} + 1} = \frac{1}{1 + 1} = \frac{1}{2}$$
$$\therefore f(E) = \frac{1}{2} = 0.5$$

Only 50 % of electrons being occupied at Fermi level at Temperature T>0 K.

The variation of f(E) with E is shown in the graph for the above three cases..

VARIATION OF $f(E)$ WITH E

DIELECTRIC MATERIAL

Introduction:
Dielectric materials are insulating substances which do not conduct electricity.
These are the insulators which have the ability to get electrically polarized in the presence of electric field.

Ex: Air, Glass, Ceramic, Mica, and various plastics like polyethylene and Teflon. These materials are widely used in capacitors, insulators in electronic devices, and other applications requiring energy storage and insulation.

Electric dipole and dipole moment:

A pair of equal and opposite charges separated by a small distance is called an electric dipole, and the product of the magnitude of one of the charges and the distance of their separation is called the dipole moment (μ).
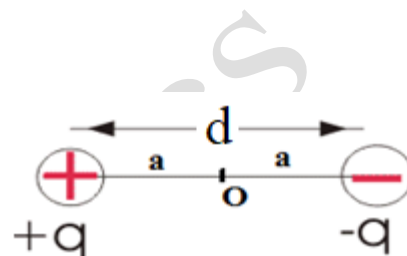
Consider two charges –q and + separated by a distance 2a where "a" is the distance from the center of the dipole to one of the charge as shown figure.
The dipole moment is given by

$$\mu = (2a)q$$

If $2a = d$ then,

$$\mu = qd$$

The SI unit of dipole moment is the coulomb meter (C·m) or Debye (D).

The induced dipole moment (μ) is proportional to the field strength. The larger the field, the greater be the displacement of charges. This leads to larger induced dipole moment. The induced dipole moment can also be written as,

$$\mu = \alpha E$$

Here, α represents the polarizability of the molecule.

Dielectric Polarization (P):
The displacement of electric charges in the atom or molecule of a dielectric under the application of electric field which leads to development of dipole moment is called as polarisation of dielectric.
OR
It is also defined as the dipole moment acquired per unit volume.

Dielectric constant (K or ε_r):
It is also called as Relative permittivity of a medium.
It is defined as the ratio of absolute permittivity of given medium to absolute permittivity of free space.

$$\Rightarrow \qquad K \text{ or } \varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$

For isotropic materials, the electric field strength E and the electric induction or electric displacement D are related by the equation

$$D = \varepsilon_0 \varepsilon_r E$$

Where,

$\varepsilon_0 = 8.854 x 10^{-12} F/m$, is the dielectric constant of vacuum called absolute permittivity which is a constant value.

ε_r has no units and the values are different for different materials.

Ex: ε_r= 1 for Air / Vacuum

ε_r= 5.6 for Pyrex glass

ε_r= 80 for Water

ε_r= 233 for Strontium Titanate.

Relation between polarization and dielectric constant:

The relation between dielectric constant ε_r and polarization P is given by

$$\vec{P} = \varepsilon_0(\varepsilon_r - 1)\vec{E}$$
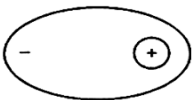
Where,

$\vec{E}$ is the applied electric field strength

$\vec{P}$ is dielectric polarization.

Types of Dielectric materials:

There are two types of Dielectric materials. They are Polar and Non-polar dielectrics.

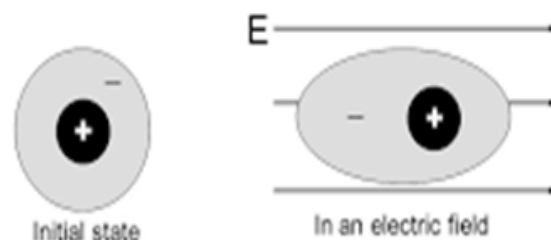| Polar dielectrics	Non-polar dielectrics
• Polar dielectrics are those molecules in which the effective centers of positive and negative charges are separated by a small distance, acts as dipole	• Non- Polar dielectrics are those molecules in which the effective centres of positive and negative charges are coincided/ overlapped. They get separated on applying electric field
• They also called as permanent dipoles	• They also called as Induced dipoles
• Ex: H_2O, HCl, CO_2 etc.	• Ex: N_2, O_2, CO etc.
•	•

Types of Polarization

1. **Electronic or Atomic Polarization:**

In the absence of electric field (E=0), the charges are not separated.

When the electric field (E≠0) is applied, the displacement of electron clouds of atoms or molecules with respect to the heavy fixed nuclei takes place throughout the material. This polarization is known as Electronic polarization.

The Electronic polarizability (α_e) is given by

$$\alpha_e = \frac{\varepsilon_0(\varepsilon_r - 1)}{N}$$

Where, $\varepsilon_r \rightarrow$ Dielectric constant of a non-polar gaseous dielectric.

$N \rightarrow$ Number of atoms per unit volume

$\varepsilon_0 \rightarrow$ Absolute permittivity

Electronic polarization is independent of temperature.

2. Ionic Polarization:

Ionic polarization occurs only in those dielectric materials which possess ionic bonds like in NaCl.

In the absence of electric field ($E_0 = 0$), the ions are uniformly distributed. When the electric field ($E_0 \neq 0$) is applied, then thr adjacent ions of opposite sign undergo displacement, which causes net dipole moment. This leads to shifting of electrons cloud relative to nuclei.
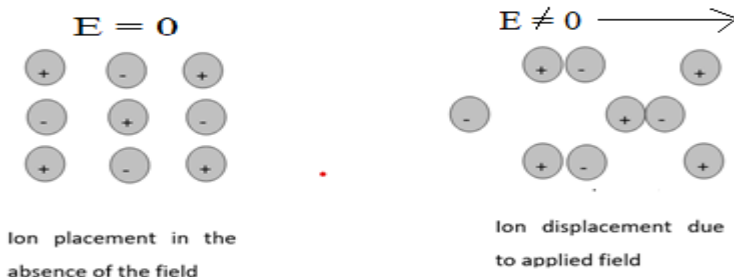
The Ionic polarizability (α_i))is given by $\alpha_i = \frac{e^2}{\omega^2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)$
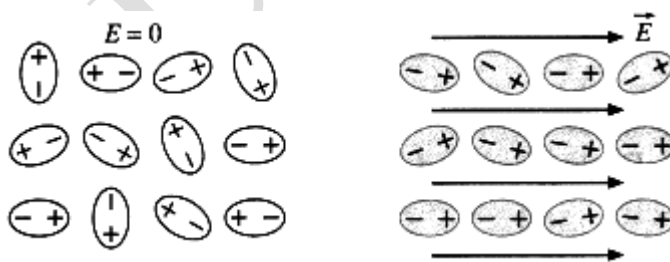
Where, $e \rightarrow$ charge of electron

$\omega \rightarrow$ angular frequency

m_1 & $m_2 \rightarrow$ Mass of cat ion & anion

Ionic polarization is also independent of temperature.

3. Orientation or dipole Polarization:

In the absence of electric field (E=0), the dipoles in a dielectric slab, arranged in a random directions.

Therefore Net field due to all the dipoles is zero.

When the same dielectric slab is placed in an external electric field (E≠0), then the dipoles arranged in a particular direction leads to electric polarisation as shown in the figure.

The Orientation polarizability (α_o) is given by

$$\alpha_o = \frac{\mu^2}{3kT}$$

Where, $\mu \rightarrow$ Dipole moment

$k \rightarrow$ Boltzmann's constant

$T \rightarrow$ Absolute Temperature

Orientation polarization is inversely proportional to temperature and directly proportional to the square of the permanent dipole moment.

4. Space charge or Interface polarization:

In multiphase dielectric materials, where different phases exhibit different resistivities, a specific type of polarization occurs. When an electric field is applied, especially at high temperatures, charges tend to accumulate at the interfaces between phases due to the abrupt change in conductivity at the boundaries. This charge accumulation creates a dipole moment within the low-resistivity phase, as charges of opposite signs gather on opposite sides of the interface.
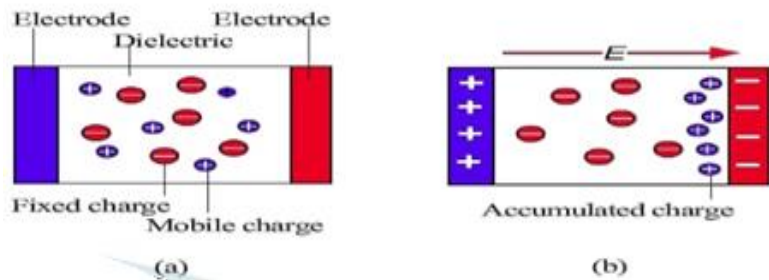
This phenomenon is particularly relevant in non-homogeneous materials such as composites, where the different phases or materials contribute to the overall dielectric behavior.

## Internal Fields Local field or Lorentz' field in Solid dielectrics:

Internal field is also called as local field developed in a dielectric material due to the resultant of two fields. (applied field and field due to all the surrounding dipoles).

When a dielectric material, either solid or liquid is subjected to an external electric field each of the atom develops a dipole moment, and acts as electric dipole and induce its own electric filed. Hence the internal field or the resultant field at any given atom will be the sum of applied electric field and the electric field due to the surrounding dipoles.

$$\therefore E_i = E + E^I$$

Where E_i is the internal field, E is the applied field, E^I is the field due to dipoles.

Expression for the internal field in the case of liquid and solid dielectrics:
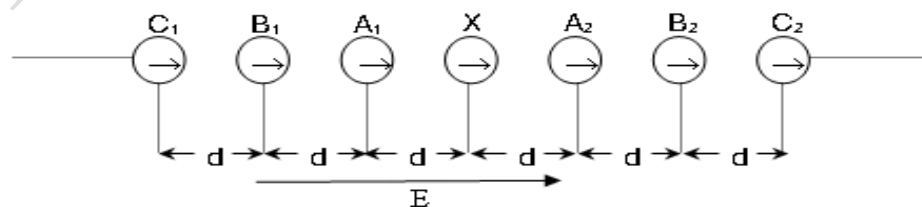
Consider a dielectric material, either liquid or solid kept in an external uniform electric field of strength E. In the material, imagine an array of equidistant atomic dipoles arranged parallel to the direction of the field as shown in figure.

Let the inter-atomic distance be 'd' and the dipole moment of each atom be μ. In the linear array consider a reference atom X. To calculate the total field at X due to all the other dipoles in the array we have to find the electric field at a point due to a dipole

$$E_i = \frac{E}{\left(1 - \frac{1.2\alpha_e}{\pi\varepsilon_0 d^3}\right)}$$

The above expression is the expression for internal field in case of one-dimensional array of atoms in dielectric solids and liquids.

Internal field for three dimensional (3D) array of atoms can be expressed as,

$$E_i = E + \frac{P\gamma}{\varepsilon_0}$$

If the material has cubic lattice then it can be shown that the internal field constant $\gamma = \frac{1}{3}$ in which the internal field is Lorentz field and is given by,

$$E_i = E + \frac{P}{3\varepsilon_0}$$

ClausiusMosotti Equation:

Let us consider a solid dielectric material of dielectric constant ε_r, which exhibits electronic polarizability.

If N number of atoms are present per unit volume of the material and μ be the atomic diploe moment, then we have,

$$\frac{Dipole\,moment}{unit\,volume} = N\mu \qquad \text{--------------------- (1)}$$

But, $\quad \frac{Dipole\,moment}{unit\,volume} = P(Polarization) \qquad \text{---------------------- (2)}$

Put Eqn (2) in (1)

Eqn (1) $\Rightarrow \qquad\qquad P = N\mu \qquad\qquad \text{---------------------- (3)}$

Here, the field experienced by the atom is the internal field E_i. Hence if α_e is the electronic polarizability of the atoms, we can write the equation for μ as,

$$\mu = E_i\alpha_e \qquad \text{---------------------- (4)}$$
$$P = NE_i\alpha_e$$

Eqn (4) $\Rightarrow \qquad E_i = \frac{P}{N\alpha_e} \qquad\qquad \text{---------------------- (5)}$

We know that relation for P as,

$$P = \varepsilon_0(\varepsilon_r - 1)\vec{E}$$
$$\Rightarrow \qquad E = \frac{P}{\varepsilon_0(\varepsilon_r - 1)} \qquad \text{---------------------- (6)}$$

From Lorentz equation, the expression for internal field is given by

$$E_i = E + \frac{P\gamma}{\varepsilon_0} \qquad \text{---------------------- (7)}$$

Substitute equation (5) and (6) in eqn (7)

$$\frac{P}{N\alpha_e} = \frac{P}{\varepsilon_0(\varepsilon_r - 1)} + \frac{P\gamma}{\varepsilon_0}$$

Where the internal field constant $\gamma = \frac{1}{3}$

$$\therefore \frac{1}{N\alpha_e} = \frac{1}{\varepsilon_0(\varepsilon_r - 1)} + \frac{1}{3\varepsilon_0}$$

$$\frac{1}{N\alpha_e} = \frac{\varepsilon_r - 1 + 3}{3\varepsilon_0(\varepsilon_r - 1)}$$

$$\frac{3\varepsilon_0}{N\alpha_e} = \frac{(\varepsilon_r+2)}{(\varepsilon_r-1)}$$

$$\therefore \qquad \frac{N\alpha_e}{3\varepsilon_0} = \frac{(\varepsilon_r-1)}{(\varepsilon_r+2)} \qquad \text{---------------------} (8)$$

The Eqn (8) is the expression for Clausius Mosotti equation and it holds good for crystals of high degree of symmetry. The equation provides a relation between ε_r the dielectric constant which is macroscopically measurable quantity, and α_e the electronic polarizability which is an atomic property (microscopic).

Numerical on Electrical conductivity & Dielectric materials

Solved Numerical:

1. **Find the temperature at which there is 1.0% probability that a state with energy 0.5 eV above Fermi energy will be occupied.**

   Solution: The Fermi distribution function is $f(E) = \dfrac{1}{1+e^{(E-E_F)/KT}}$

   $f(E) = 1.0\% = 0.01$

   $E-E_F = 0.5$ eV $= 0.5 \times 1.6 \times 10^{-19}$ J

   $\therefore$ $E-E_F = 8 \times 10^{-20}$ J

   $k = 1.38 \times 10^{-23}$ J/K

   $\therefore$ $0.01 = \dfrac{1}{1+e^{\left(\frac{8\times10^{-20}}{1.38\times10^{-23}T}\right)}}$

   $1 + e^{\left(\frac{5797.1}{T}\right)} = 100$

   $e^{\left(\frac{5797.1}{T}\right)} = 99$

   $\dfrac{5797.1}{T} = 4.595$

   $\therefore$ $T = 1261.6$ K

2. **Calculate the probability of an electron occupying an energy level 0.02 eV above the fermi level at 200K and 400K in a material.**

   Solution: The Fermi distribution function is $f(E) = \dfrac{1}{1+e^{(E-E_F)/KT}}$

   $E-E_F = 0.02$ eV above the Fermi level

   $k = 1.38 \times 10^{-23}$ J/K $= 8.625 \times 10^{-5}$ eV/K

   For T = 200K,

   $f(E) = \dfrac{1}{1+e^{\left(\frac{0.02}{8.625\times10^{-5}\times200}\right)}}$

   $f(E) = 0.239$

   For T = 400K,

   $f(E) = \dfrac{1}{1+e^{\left(\frac{0.02}{8.625\times10^{-5}\times400}\right)}} = 0.359$

3. **Calculate the probability of an electron occupying an energy level 0.02 eV below the Fermi level and 0.02 eV above the Fermi level at 200K.**

   Solution: For 0.02 eV below the Fermi level

   $E-E_F = -0.02$ eV

   $k = 8.625 \times 10^{-5}$ eV/K

   T = 200K

   $f(E) = \dfrac{1}{1+e^{(E-E_F)/KT}}$

   $f(E) = \dfrac{1}{1+e^{\left(\frac{-0.02}{8.625\times10^{-5}\times200}\right)}}$

   $f(E) = 0.761$

   For 0.02 eV above the Fermi level at 200K

   $E-E_F = 0.02$ eV

$$f(E) = \frac{1}{1+e^{\left(\frac{0.02}{8.625\times10^{-5}\times200}\right)}}$$

$$f(E) = 0.238$$

4. **Calculate the dielectric constant of NaCl, if a NaCl crystal is subjected to an electric field of 1000 V/m and the resulting polarization is 4.3x10^{-8} C/m^2.**

Solution:

Given: E = 1000 V/m

$\qquad$ P = 4.3x10^{-8} C/m^2

$\qquad\qquad$ We know $\qquad P = \varepsilon_0(\varepsilon_r - 1)E$

$$(\varepsilon_r - 1) = \frac{P}{\varepsilon_0 E} = \frac{4.3x10^{-8}}{8.856x10^{-12}\,x10^3} = 4.85$$

$\varepsilon_r = 4.85 + 1 = 5.85$

6. **The dielectric constant of Helium at 0°C is 1.000074. The density of atoms is 2.7x10^{25}/m^3. Calculate the dipole moment induced in each atom when the gas is placed in an electric field of 3x10^4 V/m.**

Solution: Given: ϵ_r =1.000074

$\qquad\qquad$ E = 3x10^{4}V/m

$\qquad\qquad$ N =2.7x10^{25}/m^3

Electronic polarizability, $\alpha_e = \dfrac{\varepsilon_0(\varepsilon_r - 1)}{N} = \dfrac{8.854x10^{-12}\,x(1.000074-1)}{2.7x10^{25}} = 2.4255\,x10^{-41}$

Dipole moment=P $= \alpha_e E = 2.4255\,x10^{-41}\,x3x10^4 = 7.2767\,x10^{-37}\,Cm$

7. **An elemental solid dielectric material has a polarizability 7x10^{-40} Fm^2. Assuming the internal field to be Lorentz field, calculate the dielectric constant for the material if the material has 3x10^{28} atoms/m^3.**

Solution: Given : α_e = 7x10^{-40} Fm^2

$\qquad\qquad$ N =3x10^{28}/m^3

Formula, $\qquad \dfrac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} = \dfrac{N\alpha_e}{3\varepsilon_0}$

$$= \frac{3x10^{28}\,x7x10^{-40}}{3x8.854x10^{-12}} = 0.7906$$

$$(\varepsilon_r - 1) = (\varepsilon_r + 2)x0.7906$$

$$(\varepsilon_r - 1) = (0.7906\varepsilon_r + 2x0.7906)$$

$$\varepsilon_r = 0.7906\varepsilon_r + 1.5812 + 1 = 0.7906\varepsilon_r + 2.5812$$

$$\varepsilon_r(1 - 0.7906) = 2.5812$$

$$\varepsilon_r(0.2094) = 2.5812$$

$$\varepsilon_r = \frac{2.5812}{0.2094} = 12.33$$

Exercise Problems:

1. Calculate the probabilities of an electron occupying an energy level 0.02eV above the Fermi level and that in an energy level 0.02eV below the Fermi level at 312K.

2. Find the probability that an energy level at 0.2eV below Fermi level being occupied at temperatures 300K and 1000K.

3. The Fermi level in potassium is 2.1eV what are the energies for which the probabilities of occupancy at 300K are 0.99, 0.01 and 0.5

4. Find the polarization produced in a crystal by an electric field of strength 500V/mm if it has a dielectric constant of 6.

5. An elemental solid dielectric material has polarizability 7×10^{-40} Fm^2. Assuming the internal field to be Lorentz filed, calculate the dielectric constant for the material if the material has 3×10^{28} atoms/