

1. Application of statistical Mechanics

Most objects we care about are fundamentally macroscopic (i.e. consist of many particles). However, the properties of these *macroscopic* objects derive from the *microscopic* nature of its constituent molecules. Statistical mechanics is a means to connect the microscopic and the macroscopic properties. In doing so, many degrees of freedom are *intentionally* thrown away, since there are too many to deal with (indeed, if we have moles of particles, we have many moles of degrees of freedom). Statistical mechanics provides a systematic means to do this.

Statistical mechanics aims at studying the macroscopic parameters of a system in equilibrium from knowledge of the microscopic properties of its constituent particles using the laws of mechanics.

Prediction of statistical physics becomes nearly exact for a system that deals with very large number of particles.

2. Need for Quantum Statistics

Classical statistics due to Maxwell – Boltzmann, explained the energy and velocity distribution of molecules of an ideal gas to a very good degree of accuracy, but failed to explain the observed energy distribution of electrons in the so-called ELECTRON GAS and that of photons in the PHOTON GAS.

In classical statistics the cell size in phase space may be as small as we please. Hence the number of cells in a compartment in the phase space can be made as large as we wish so that it can be much greater than the number of particle n_i in the i^{th} compartment of the phase space. Therefore the occupation index

$$\frac{n_i}{g_i} \ll 1.$$

[Occupation index: The ratio of number of particles to the number of phase cells corresponding to

a compartment or energy interval is occupation index given by $\frac{n_i}{g_i}$ for the i^{th} compartment or state.] In such a case, the probability that a phase cell contains two or more particles is negligible and so the particles can be treated as distinguishable and so the classical statistics can be applicable to them.

But all natural systems obey uncertainty principle and so we cannot choose the size of the phase cell as small as we like. The minimum size of a phase cell is \hbar^3 , so that the number g_i of phase cells is

limited by \hbar^3 and hence the occupation index $\frac{n_i}{g_i}$ cannot be made as small as we like. When the

occupation index $\frac{n_i}{g_i} \sim 1$, the particles cannot be treated as distinguishable and so we cannot apply the classical statistics.

All these have been resolved by the quantum statistics and hence the need.

3. Difference Between Classical and Quantum Statistics

- (1) Classical statistics applies to a system of identical particles, which obey the laws of classical mechanics. Quantum statistics applies to a system of identical particles, which obey the laws of quantum statistics.
- (2) In classical statistics, the volume of an elementary cell in the phase space can be made as small as we please. But in quantum statistics, the minimum size of an elementary cell in the phase is h^3 , where h is the Planck's constant. For f degrees of freedom, this is h^f .
- (3) In classical statistics, since the size of an elementary phase cell can be made as small as we please, the number of cells in a compartment of the phase space can be made as large as we please. So the occupation index is $\frac{n_i}{g_i} \ll 1$. But in quantum statistics, the minimum size of an elementary cell is h^3 . So the number of cells in a compartment cannot be made as large as we wish. In quantum statistics, the number of cells in a compartment is approximately equal to the number of particles in that compartment. So the occupation number is $\frac{n_i}{g_i} \sim 1$.
- (4) In classical statistics, the particles are considered distinguishable, whereas in quantum statistics, they are considered indistinguishable.

3.1 Difference between B.E and F.D statistics

Bose-Einstein Statistics	Fermi-Dirac Statistics
<ol style="list-style-type: none">1. B.E. statistics applies to identical indistinguishable particles which obey laws of quantum mechanics, but are not governed by Pauli's exclusion principle.2. Particles have zero or integral spin and are called Bosons.3. There is no restriction on the number of particles in an elementary cell of phase space.4. Familiar examples are (i) photons in a cavity, (ii) phonons in solids.	<ol style="list-style-type: none">1. F.D. statistics applies to identical indistinguishable particles which obey laws of quantum mechanics and are governed by Pauli's exclusion principle.2. Particles have half integral spin and are called Fermions.3. There can be no particle or only one particle a given cell in phase space.4. Familiar example is (i) free electrons in a metal.

4.1 Fermi distribution at zero and non-zero temperature

For electron, we have $g(\varepsilon) d\varepsilon = 2 \times 2\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} d\varepsilon$

And $\alpha = -\frac{\varepsilon_f}{KT}$, ε_f = fermi energy value.

$$\beta = \frac{1}{KT}$$

Now we introduce, Fermi distribution function,

$$\text{Occupation index, } f(\varepsilon) = \frac{n(\varepsilon)}{g(\varepsilon)} = \frac{\text{the number of electrons per unit energy range in the energy level } \varepsilon}{\text{the number of energy states per unit energy range in the energy level } \varepsilon}$$

According to F-D statistics,

$$\frac{n(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{\alpha + \beta\varepsilon} + 1} = \frac{1}{e^{(\varepsilon - \varepsilon_f)/KT} + 1}$$

Case 1: For values of $\varepsilon < \varepsilon_f$, $T = 0 K$

$$\text{occupation index, } f(\varepsilon) = \frac{n(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{(\varepsilon - \varepsilon_f)/KT} + 1} = \frac{1}{e^{-\alpha} + 1} = 1$$

i.e., all energy states having $\varepsilon < \varepsilon_f$ are each fully occupied by the electrons.

Case 2: For values of $\varepsilon > \varepsilon_f$, $T = 0 K$

$$\text{occupation index, } f(\varepsilon) = \frac{n(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{(\varepsilon - \varepsilon_f)/KT} + 1} = \frac{1}{e^\alpha + 1} = 0$$

i.e., all energy states having $\varepsilon > \varepsilon_f$ are each fully unoccupied by the electrons.

Fermi energy: The energy values up to which all the energy states are full at $T=0K$ and above which all the energy states are empty is known as Fermi energy and denoted by ε_f .

Case 3: For values of $\epsilon = \epsilon_f$, $T > 0K$

$$\text{occupation index, } f(\epsilon) = \frac{n(\epsilon)}{g(\epsilon)} = \frac{1}{e^{(\epsilon - \epsilon_f)/KT} + 1} = \frac{1}{e^0 + 1} = \frac{1}{2}$$

i.e., $T > 0K$, the probability of finding the particle is 50% at the fermi energy level.

So we can define also that the highest energy level at $T > 0K$ upto which probability of finding the electron is 50%

Note: $n(\epsilon) d\epsilon = g(\epsilon) d\epsilon \times f(\epsilon) = 2 \times 2\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} d\epsilon \times \frac{1}{e^{(\epsilon - \epsilon_f)/KT} + 1}$

$$\text{Or, } n(\epsilon) d\epsilon = 4\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} \times \frac{1}{e^{(\epsilon - \epsilon_f)/KT} + 1} d\epsilon$$

So $n(\epsilon)$ is proportional to $\epsilon^{\frac{1}{2}}$ which represents graphically in the figure 2

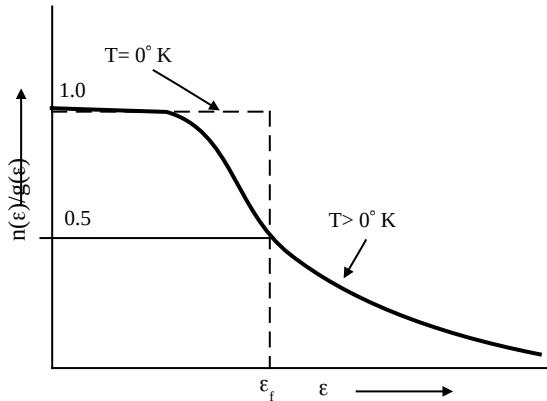


Fig: 1

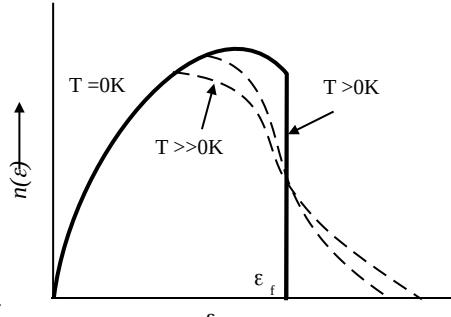


Fig: 2

4.2 Determination of Fermi Energy Level

If a particular metal sample contains n free electrons, we can calculate its Fermi energy ϵ_f at 0K by filling up its energy states with these electrons in order of increasing energy starting from $\epsilon = 0$. The highest energy state to be filled will then have the energy $\epsilon = \epsilon_f$ by definition. We know that each state is limited to one electron (as per pauli's exclusion principle).

Now we if we go on adding all such states up to the highest energy level i.e., ϵ_f at 0K obviously we will get the total number of electrons i.e., n . So mathematically

$$n = \int_0^{\epsilon_f} f(\epsilon) g(\epsilon) d\epsilon = \int_0^{\epsilon_f} g(\epsilon) d\epsilon \quad [\text{at the temperature } 0K, \epsilon < \epsilon_f] \quad \dots (1)$$

as we know that the number of electrons between energy states ϵ to $\epsilon + d\epsilon$ is

$$g(\varepsilon) d\varepsilon = 2 \times 2\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} d\varepsilon$$

Substituting $g(\varepsilon)d\varepsilon$ in (1) we have

$$\begin{aligned} n &= 4\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \int_0^{\varepsilon_f} \varepsilon^{1/2} d\varepsilon \\ n &= 4\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \left(\frac{2}{3} \right) \varepsilon_f^{3/2} \rightarrow \varepsilon_f = \frac{h^2}{2m} \left(\frac{3n}{8\pi V} \right)^{2/3} \end{aligned}$$

Hence it becomes

$$\boxed{\varepsilon_f = \frac{h^2}{2m} \left(\frac{3n_0}{8\pi} \right)^{2/3}} \quad \dots (2)$$

Where n_0 be the number of electrons per unit volume and expression (2) is the value of Fermi energy at 0K.

It is clear from expression (2) that the Fermi energy is independent of the size and volume of the conductor as it only depends upon the number of electrons per unit volume or electron concentration.

4.3 Average and Total Kinetic energy at 0K

If $\bar{\varepsilon}$ is the average kinetic energy per electron at 0K, then

$$\bar{\varepsilon} = \frac{\int_0^{\varepsilon_f} \varepsilon n(\varepsilon) d\varepsilon}{n} = \frac{\int_0^{\varepsilon_f} \varepsilon g(\varepsilon) d\varepsilon}{n}$$

$$\text{Or, } \bar{\varepsilon} = \frac{4\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \int_0^{\varepsilon_f} \varepsilon^{3/2} d\varepsilon}{n}$$

$$\text{Or, } \bar{\varepsilon} = \frac{4\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \left[\frac{2}{5} \varepsilon^{5/2} \right]_0^{\varepsilon_f}}{n} = \frac{4\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \frac{2}{5} \varepsilon_f^{5/2}}{n}$$

$$\text{Or, } \bar{\varepsilon} = \frac{4\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \frac{2}{5} \varepsilon_f^{3/2} \varepsilon_f}{n}$$

$$\bar{\varepsilon} = \frac{4\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \frac{2}{5} \left(\frac{h^2}{2m} \right)^{\frac{3}{2}} \left(\frac{3n}{8\pi V} \right)^{2/3} \varepsilon_f}{n}$$

Hence $\boxed{\bar{\varepsilon} = \frac{3}{5} \varepsilon_f}$

This equation gives the **average energy per electron** at 0K.

So, **total energy** $\boxed{E = n\bar{\varepsilon} = \frac{3}{5}n\varepsilon_f}$

4.4 Fermi velocity and Average velocity of the electron at 0K

Fermi velocity (v_f) is the velocity of electron corresponding to the energy value ε_f .

$$\varepsilon_f = \frac{1}{2}mv_f^2$$

$$v_f^2 = \frac{2\varepsilon_f}{m} = \frac{2}{m} \times \frac{h^2}{2m} \left(\frac{3n_0}{8\pi} \right)^{2/3}$$

$$v_f = \left(\frac{h}{m} \right) \left(\frac{3n_0}{8\pi} \right)^{1/3}$$

If $n(v)dv$ be the number of electrons in the velocity range v to $v+dv$, then the average velocity of an

electron at 0K is $\bar{v}_0 = \frac{1}{n} \int_0^{v_f} v n(v) dv$ where $v_f(0)$ is called the Fermi-velocity at 0K

$$\text{We know } n(\varepsilon)d\varepsilon = g(\varepsilon)d\varepsilon = 2 \times 2\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} d\varepsilon$$

$$\text{Hence } n(v)dv = 2 \times 2\pi V \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \sqrt{\frac{m}{2}} v m v dv = \frac{8\pi V m^3}{h^3} v^2 dv \quad [\varepsilon \text{ are substituted by } v]$$

Now,

$$\bar{v}_0 = \frac{1}{n} \int_0^{v_f} v \times \frac{8\pi V m^3}{h^3} v^2 dv$$

$$\bar{v}_0 = \frac{1}{n} \frac{8\pi V m^3}{h^3} \int_0^{v_f} v^3 dv = \frac{1}{n} \frac{8\pi V m^3}{h^3} \frac{1}{4} v_f^4$$

$$\bar{v}_0 = \frac{1}{n} \frac{8\pi V m^3}{h^3} \frac{1}{4} v_f^3 \times v_f$$

$$\bar{v}_0 = \frac{1}{n} \frac{8\pi V m^3}{h^3} \frac{1}{4} \left(\frac{h}{m} \right)^3 \left(\frac{3n}{8\pi V} \right) \times v_f$$

$$\bar{v}_0 = \frac{3}{4} v_f$$

Thus the average speed of the electron at 0K is $\frac{3}{4}$ th of the fermi velocity.

4.5 Fermi temperature

Fermi temperature (T_f) is the temperature of electron corresponding to the energy value ϵ_f .

$$kT_f = \epsilon_f \rightarrow T_f = \frac{\epsilon_f}{k} \text{ where } k \text{ is the Boltzmann constant.}$$

Typical metal the Fermi energy $\epsilon_f = 5 \text{ eV}$. So $T_f = \frac{5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}} \approx 57971 \text{ Kelvin}$. This high value

suggest that T_f is not a real temperature just a convenient notation used for classical statistics.

5. Application of BE Statistics

5.1 Planck's law of radiation

Planck's law of distribution of energy with wavelength in the case of black body radiations can be derived on the basis of Bose - Einstein statistics. According to classical theory the frequency of this radiation lies continuously between zero and infinity. But it has been observed that these radiations carry energy in discrete units or bundles or quanta. According to quantum theory, radiation of frequency has a quantum

energy h where h is Planck's constant and momentum $p = \frac{h\nu}{c}$ where c is the velocity of light. These

quanta are known as photons and can be treated as particles. The radiations inside the hollow enclosure consist of a very large number of photons of different energies as these have different wavelengths (or frequencies) and can be supposed to form a photon gas. The distribution of energy among these photons inside the enclosure obeys the law of statistics. Since the photons have integral spin angular momentum in

units of $\frac{h}{2\pi}$ they obey BE statistics.

According to Bose - Einstein statistics we may write the distribution of particles in different energy states

$$\text{as } n_i = \frac{g_i}{e^{\epsilon_i/kT} - 1} .$$

To find the number of photons in the frequency interval ν and $\nu + d\nu$ and substituting $\varepsilon_i = \varepsilon = h\nu$ we

have, number of photons in the said frequency interval $n(\nu)d\nu = \frac{g(\nu)d\nu}{e^{h\nu/KT} - 1}$ (1)

In (1) term $g(\nu)$ gives the number of cells in phase space volume lying in the energy interval (compartment) between ν and $\nu + d\nu$. Corresponding momentum $p = \frac{h\nu}{c}$ and $p + dp = \frac{h(\nu + d\nu)}{c}$

The number of cells in the phase space in the momentum interval between p and $p + dp$ is given by

$$g(p)dp = \frac{4\pi V p^2 dp}{h^3}$$

Due to property of polarization of photons i.e., one set of photon has left handed polarization and the other set has right handed polarization. Therefore, the number of cells for both kind of photons, is given by

$$g(p)dp = \frac{2 \times 4\pi V p^2 dp}{h^3} = \frac{8\pi V p^2 dp}{h^3}$$

Substituting the value of $p = \frac{h\nu}{c}$ and $dp = \frac{h}{c}d\nu$ we have

$$g(\nu)d\nu = \frac{8\pi V}{h^3} \frac{h^2 \nu^2}{c^2} \cdot \frac{h d\nu}{c}$$

$$g(\nu)d\nu = \frac{8\pi V}{c^3} \nu^2 d\nu$$

Putting the expression of $g(\nu)$ in the equation (1) we have,

$$n(\nu)d\nu = \frac{8\pi V}{c^3} \nu^2 d\nu \frac{1}{e^{h\nu/KT} - 1}$$

Since each photon has energy $h\nu$, the energy density $E(\nu)d\nu$ defined as the amount of energy per unit

volume lying between the frequencies ν and $\nu + d\nu$ is given by, $\frac{h\nu n(\nu)d\nu}{V}$

$$E(\nu)d\nu = \frac{h\nu n(\nu)d\nu}{V} = \frac{8\pi h\nu^3}{c^3} d\nu \frac{1}{e^{h\nu/KT} - 1}$$

$$E(\nu)d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/KT} - 1} \quad \dots (2)$$

Equation (2) is known as **Planck's law of black body radiation in terms of frequency of radiation**. Planck's law accurately fits in the experimental results regarding the distribution of energy with wavelength in the spectrum due to radiations from black body.

2.17 Fermions & Bosons

(i) The particles which obey F.D statistics are known as **Fermions**.

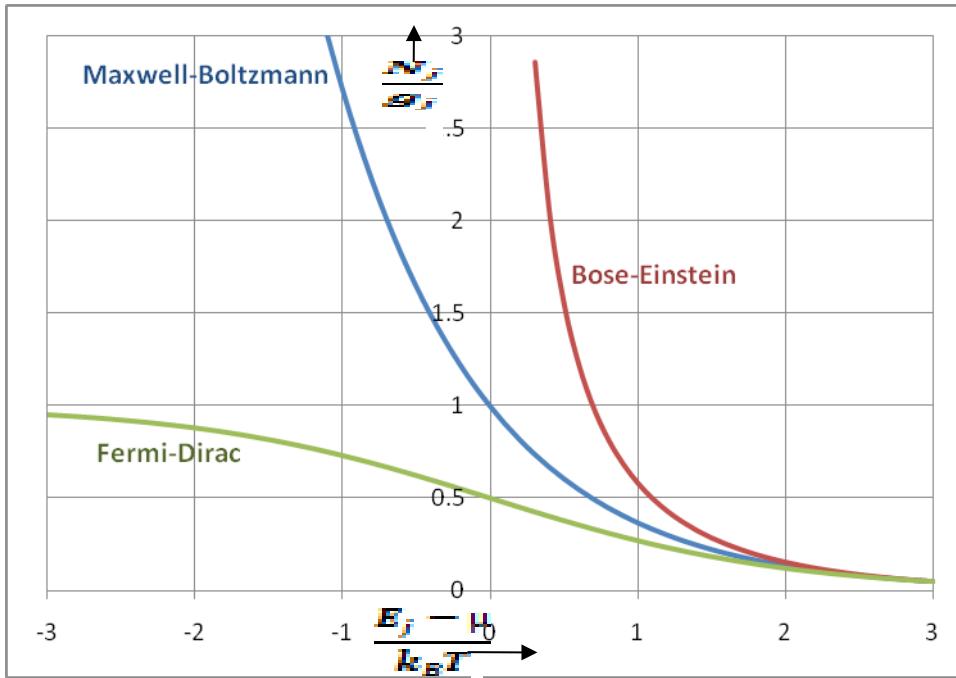
Example: electron, proton, neutron, positron

(ii) The particles which obey B.E statistics are known as **Bosons**.

Example: Photon, π -meson, k-meson.

Category	M.B Statistics	B.E Statistics	F.D Statistics
Nature of particles	Particles are identical but distinguishable <i>example:</i> gas molecules	Particle are identical but distinguishable <i>example:</i> photon particles	Particle are identical but indistinguishable <i>example:</i> electron
Number of particles in a cell	any number of particles can occupy a single phase space cell	any number of particles can occupy a single phase space cell	a phase space cell cannot accommodate more than one particle.
Spin	particles can have any spin.	particles have integral spin and are called Boson	particles have half integral spin and are called Fermions
Energy distributions	$n_i = g_i e^{-\alpha} e^{-\beta \varepsilon_i}$	$n_i = \frac{g_i}{e^{\alpha} e^{-\beta \varepsilon_i} - 1}$	$n_i = \frac{g_i}{e^{\alpha} e^{-\beta \varepsilon_i} + 1}$
Macrostate and Microstate	A macrostate can have more than one microstate	each macrostate has one microstate	each macrostate has one microstate
Wave function	No specification in wave function of the particles.	wave function of a particle can be represented by a anti-symmetric wave function	wave function of a particle can be represented by a anti-symmetric wave function

2.18 Graphical comparision of three statistics



Both the B-E and F-D distributions approach the M-B distribution (i.e. a pure exponential decay) at higher energies with $E_j - \mu > k_B T$. That is, for the levels j with low occupation indices, (i.e., the number of particles N_j significantly lower than the degeneracy g_j) the B-E and F-D distributions begin to ‘behave’ like the M-B distribution with the same decay constant.

Problems

Example 8.6 Evaluate the temperature at which there is one per cent probability that a state, with an energy 0.5 eV above the Fermi energy will be occupied by an electron.

Sol. The FD distribution is $f(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/K_B T} + 1}$

$$\frac{0.01 \times 0.1 \times 800 \times 10^{-3}}{0.01 \times 1.6} = n$$

ϵ_F is the Fermi energy
 K_B = Boltzmann constant
Given $\epsilon = (\epsilon_F + 0.5)$ eV

Thus, $f(\epsilon) = \frac{1}{100} = \frac{1}{1 + e^{0.5/K_B T}}$

or, $0.01 = \frac{1}{1 + e^x}$ where $x = \frac{0.5}{K_B T}$

or, $0.01 + 0.01e^x = 1$

or, $e^x = \frac{0.99}{0.01} = 99$

or, $x = 2.303 \log_{10} 99 = \frac{0.5}{K_B T}$

So, $T = \frac{0.109 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}} = 1264$ K

Example 8.7 Calculate the Fermi energy at 0 K of metallic silver containing one free electron per atom. The density and atomic weight of silver is 10.5 g/cm³ and 108 respectively.

Sol. Fermi energy $\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$

Here $\frac{N}{V} = \frac{6.02 \times 10^{23}}{108} \times 10.5 = 5.9 \times 10^{28} \text{ m}^{-3}$

So, $\epsilon_F = \frac{(6.6 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}} \times \left(\frac{3}{8 \times 3.14} \times 5.9 \times 10^{28} \right)^{2/3}$

$$= 8.8 \times 10^{-19} \text{ Joules} = \frac{8.8 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 5.5 \text{ eV}$$

Example 8.8 The Fermi energy of silver is 5.51 eV (i) What is the average energy of the free electrons in silver at 0 K? (ii) What is the speed of the electron corresponding to the above average energy?

Sol. The average electron energy at 0 K is

$$\bar{\epsilon} = \frac{3}{5} \epsilon_F$$

$$= \frac{3}{5} \times 5.51 = 3.306 \text{ eV}$$

If v is the velocity of the electron, then its kinetic energy

$$\frac{1}{2}mv^2 = 3.306 \times 1.6 \times 10^{-19}$$

or, $v = \left(\frac{2 \times 3.306 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}} \right)^{1/2} \text{ m/s}$

$$= (1.16 \times 10^{12})^{1/2} = 1.08 \times 10^6 \text{ m/s}$$

Example 8.9 Consider a free electron gas at zero degree Kelvin and show that the de Broglie wavelength associated with an electron is given by

$$\lambda_F = 2 \left(\frac{\pi}{3n_0} \right)^{1/3}$$

where n_0 is the number of electrons per c.c. of the gas.

Sol. The momentum (p) of the electrons is given by

$$p = \sqrt{2m\varepsilon_F}$$

$$\text{But } \varepsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

Again, de Broglie wavelength λ_F is given by

$$\lambda_F = \frac{h}{p}$$

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

$$= \sqrt{\left(\frac{8\pi V}{3N} \right)^{2/3}} = 2 \left(\frac{\pi V}{3N} \right)^{1/3}$$

$$= 2 \left(\frac{\pi}{3n_0} \right)^{1/3} \quad \left[\text{where } n_0 = \frac{N}{V} \right]$$

Example 8.10 Estimate the temperature of the sun, if λ_m for the sun is 490 nm.

Sol. From Wien's displacement law of radiation, we know that

$$\lambda_m T = 0.2896$$

$$\text{Here, } T = \frac{0.2896}{\lambda_m} = \frac{0.2896}{490 \times 10^{-9}} \approx 5910 \text{ K}$$

So, the temperature of the sun is 5910 K.

Example 8.11 The Fermi energy for sodium at $T = 0$ K is 3.1 eV. Find its value for aluminum, given that the free electron density in aluminum is approximately 7 times that in sodium.

Sol. $\frac{\text{Electron density in Al}}{\text{Electron density in Na}} = \frac{n_2}{n_1} = 7$

$$\text{For Na, Fermi energy } \epsilon_{F_1} = \frac{\hbar^2}{2m} \left(\frac{3n_1}{8\pi} \right)^{2/3} \quad \dots(1)$$

$$\text{For Al } \epsilon_{F_2} = \frac{\hbar^2}{2m} \left(\frac{3n_2}{8\pi} \right)^{2/3} \quad \dots(2)$$

Dividing Eq. (2) by Eq. (1)

$$\frac{\epsilon_{F_2}}{\epsilon_{F_1}} = \left(\frac{n_2}{n_1} \right)^{2/3} = (7)^{2/3}$$

so,

$$\epsilon_{F_2} = \epsilon_{F_1} \times 7^{2/3} = 3.1 \times 3.66 = 11.35 \text{ eV.}$$

- 3.9 The Fermi energy E for Lithium is 4.72 eV at $T = 0$. Calculate the number of conduction electrons per unit volume in lithium. [CUH 1997]

Solution. The Fermi energy at $T = 0$ K is

$$E_f = \frac{\hbar^2}{8m} \left(\frac{3n}{\pi} \right)^{2/3}.$$

\therefore conduction electrons per unit volume is

$$\begin{aligned} n &= \frac{\pi}{3} \left[\frac{8m}{\hbar^2} E_f \right]^{3/2} = \frac{\pi}{3} \left[\frac{8 \times (9.11 \times 10^{-31}) \times (4.72 \times 1.6 \times 10^{-19})}{(6.62 \times 10^{-34})^2} \right]^{3/2} \\ &= \frac{\pi}{3} \left[\frac{8 \times 9.11 \times 4.72 \times 1.6}{(6.62)^2} \times 10^{18} \right]^{3/2} = 4.66 \times 10^{28} \text{ per cubic metre.} \end{aligned}$$

- 3.10 Three indistinguishable particles (Bosons) are to be distributed in two compartments, the first one having 3 cells and the second one 2 cells. What are the thermodynamic probability for the macro-states (5, 0) and (3, 2).

Solution. The thermodynamic probability

$$W = \prod_{i=1}^k \frac{N_i + g_i - 1}{N_i!},$$

where N_i is the number of particles and g_i is the number of cells.

$$W = \prod_{i=1}^k \frac{(N_i + g_i - 1)}{N_i! (g_i - 1)!} = \frac{(N_1 + g_1 - 1)!}{N_1! (g_1 - 1)!} \times \frac{(N_2 + g_2 - 1)!}{N_2! (g_2 - 1)!}.$$

Now, for the macro-state (5, 0), $N_1 = 5, N_2 = 0, g_1 = 3, g_2 = 4$.

$$\therefore W_{(5,0)} = \frac{(5+3-1)!}{5!(3-1)!} \times \frac{(0+2-1)!}{0!(2-1)!} = \frac{7!}{5!2!} \times \frac{1!}{0!1!} = \frac{7 \times 6 \times 5!}{5!2!} \times 1 = \frac{42}{2} = 21.$$

For the macro-state (3, 2), $N_1 = 3, N_2 = 2, g_1 = 3, g_2 = 2$

$$\therefore W_{(3,2)} = \frac{(3+3-1)!}{3!(3-1)!} \times \frac{(2+2-1)!}{2!(2-1)!} = \frac{5!}{3!2!} \times \frac{3!}{2!1!} = \frac{5 \times 4 \times 3!}{3!2!} \times \frac{3 \times 2!}{2!1!} = 30.$$

- 3.11 Find Fermi energy in copper on the assumption that each copper atom contributes one electron to electron gas. [PU 1991]

Solution. The density of copper = $8.94 \times 10^3 \text{ kg/m}^3$.

Atomic mass of copper = 63.5 amu.

$$\therefore \text{Fermi energy in copper is } E_f = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

Now the number of copper atoms per unit volume

$$n = \frac{N}{V} = \frac{\text{Density of copper}}{\text{Mass of a copper atom}} = \frac{8.94 \times 10^3 \text{ kg/m}^3}{63.5 \times 1.66 \times 10^{-27}} = 8.84 \times 10^{28} \text{ atoms/m}^3 = 8.84 \times 10^{28} \text{ electrons/m}^3.$$

$$\therefore E_f = \frac{(6.63 \times 10^{-34})^2}{2 \times 9.11 \times 10^{-31}} \left[\frac{3 \times 8.48 \times 10^{28}}{8 \times 3.14} \right]^{2/3} \text{ J}$$

$$= 1.13 \times 10^{-18} \text{ J} = 7.04 \text{ eV.}$$

- 3.12 A system has 7 particles arranged in two compartments. The first compartment has 8 cells and the second has 10 cells, all cells are of equal size. Calculate the number of micro-states in the macro-state (3,4) when the particles are fermions. [PU 1993]

Solution. For the fermions obeying FD statistics the thermodynamic probability of the macro-state is given by

$$W(n_1, n_2, \dots, n_k) = \prod_{i=1}^k \frac{g_i!}{N_i!(g_i - N_i)!}.$$

Since in the problem the number of compartments $k = 2$,

$$\therefore W(n_1, n_2) = \frac{g_1!}{N_1!(g_1 - N_1)!} \times \frac{g_2!}{N_2!(g_2 - N_2)!}.$$

Here g_1 = number of cells in the first compartment = 8

and g_2 = number of cells in the second compartment = 10.

Now for the macro-state (3,4), $N_1 = 3$, $N_2 = 4$.

$$\therefore W(3,4) = \frac{8!}{3!(8-3)!} \times \frac{10!}{4!(10-4)!} = \frac{8!}{3!5!} \times \frac{10!}{4!6!} = \frac{8 \times 7 \times 6}{3 \times 2 \times 1} \times \frac{10 \times 9 \times 8 \times 7}{4 \times 3 \times 2 \times 1}$$

$$= 56 \times 210 = 11760.$$

- 3.13 The number of conduction electrons per cc is 24.2×10^{22} in beryllium and 0.91×10^{27} in Cesium. If the Fermi energy of conduction electrons in beryllium is 14.44 eV, calculate that in cesium.[HPU 1991]

Solution. Electrons per cc in beryllium and in cesium is

$$\frac{N}{V} = 24.2 \times 10^{22} \text{ for beryllium}$$

$$\text{and } \frac{N}{V} = 0.91 \times 10^{27} \text{ for cesium.}$$

$$\text{Fermi energy } E_f = \frac{h^2}{2m} \left(\frac{3}{8\pi} \right)^{2/3} \left(\frac{N}{V} \right)^{2/3}.$$

$$\therefore \frac{\text{Fermi energy for beryllium}}{\text{Fermi energy for cesium}} = \frac{\frac{h^2}{2m} \left(\frac{3}{8\pi} \right)^{2/3} \times (24.2 \times 10^{22})^{2/3}}{\frac{h^2}{2m} \left(\frac{3}{8\pi} \right)^{2/3} \times (0.91 \times 10^{27})^{2/3}}.$$

$$\therefore \text{Fermi energy for cesium} = 14.44 \times \left(\frac{0.91}{24.2} \right)^{2/3} = 1.587 \text{ eV.}$$

Carrier Concentration and positions of Fermi Levels in Semiconductor:

In a semiconductor, the conductivity arises due to the mobilities of electrons in the conduction band and holes in the valence band. The electrons and holes are both carriers of charge in semiconductors.

(A) Electron concentrations in Conduction band.

The valence band extends from a lower limit E_{bottom} to the upper limit E_V . The conduction band extends from E_c to an upper limit E_{top} .

According to quantum statistics, the no. of electrons in the energy interval ε to $\varepsilon + d\varepsilon$ in the conduction band can be written as —

$$N(\varepsilon)d\varepsilon = f(\varepsilon)g(\varepsilon)d\varepsilon$$

∴ Total no. of electrons in the conduction band per unit vol^m is —

$$n_e = \int_{E_c}^{E_f} N(\varepsilon)d\varepsilon = \int_{E_c}^{E_f} f(\varepsilon)g(\varepsilon)d\varepsilon$$

$$\text{where, } g(\varepsilon) = 4\pi \left(\frac{2m^*}{h^2}\right)^{3/2} (\varepsilon - E_c)^{1/2} \quad | \quad \text{In conduction band -}$$

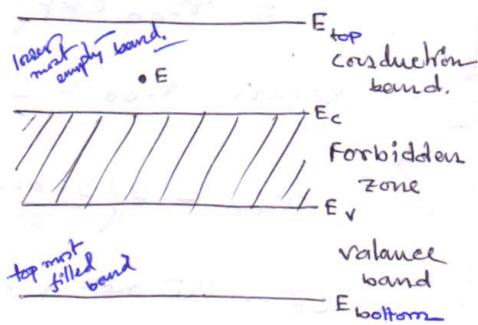
$$\text{and } f(\varepsilon) = \frac{1}{e^{(\varepsilon - E_f)/kT} + 1} \quad | \quad \text{and,}$$

$$E = E_c + \frac{\hbar^2 k^2}{2m^*} \quad | \quad \therefore \frac{\hbar^2 k^2}{2m^*} = E - E_c.$$

Since, E_f is usually midway between E_c and E_v and ε lies in the conduction band above E_c , we have

$$\int E d\varepsilon \gg E_f - 3kT. \Rightarrow (\varepsilon - E_f)/kT \gg 1; \text{ here, } m^* \text{ is the effective mass of electron.}$$

$$\therefore n_e = 4\pi \left(\frac{2m^*}{h^2}\right)^{3/2} \int_{E_c}^{E_f} \frac{(\varepsilon - E_c)^{1/2} d\varepsilon}{e^{(\varepsilon - E_f)/kT}} = 4\pi \left(\frac{2m^*}{h^2}\right)^{3/2} \int_{E_c}^{E_f} e^{-\frac{(\varepsilon - E_f)}{kT}} (\varepsilon - E_c)^{1/2} d\varepsilon$$



$$\text{Let, } y = \frac{(\varepsilon - \varepsilon_c)}{kT} \quad | \quad n_e = 4\pi \left(\frac{2m_e^*}{h^2} \right)^{3/2} \int_{\varepsilon_c}^{\varepsilon_f} e^{\frac{2T - (\varepsilon - \varepsilon_c)}{kT}} \cdot e^{\frac{(\varepsilon_f - \varepsilon_c)}{kT}} \cdot (\varepsilon - \varepsilon_c)^{1/2} d\varepsilon$$

$$dy = \frac{d\varepsilon}{kT}$$

$$= 4\pi \left(\frac{2m_e^*}{h^2} \right)^{3/2} e^{\frac{(\varepsilon_f - \varepsilon_c)}{kT}} \int_{\varepsilon_c}^{\varepsilon_f} e^{\frac{2T - (\varepsilon - \varepsilon_c)}{kT}} \cdot (\varepsilon - \varepsilon_c)^{1/2} d\varepsilon$$

$$\therefore n_e = 4\pi \left(\frac{2m_e^*}{h^2} \right)^{3/2} \cdot (kT)^{3/2} e^{\frac{(\varepsilon_f - \varepsilon_c)}{kT}} \int_0^{\infty} e^{-y} \cdot y^{1/2} dy \quad [\varepsilon_f \rightarrow \infty]$$

$$n_e = 4\pi \left(\frac{2m_e^*}{h^2} \right)^{3/2} (kT)^{3/2} e^{\frac{(\varepsilon_f - \varepsilon_c)}{kT}} \cdot \frac{1}{2} \sqrt{\pi}$$

$$= 2 \left(\frac{2\pi m_e^* k T}{h^2} \right)^{3/2} \cdot \exp\{-(\varepsilon_c - \varepsilon_f)/kT\}$$

$$= n_{e0} \exp\{-(\varepsilon_c - \varepsilon_f)/kT\}.$$

Since, $y^{1/2}$ is a slowly rising function of y while $\exp(-y)$ diminishes rapidly with increasing y , we can replace the upper limit by $y_f = \infty$

$$\text{where, } n_{e0} = 2 \left(\frac{2\pi m_e^* k T}{h^2} \right)^{3/2} \cdot \left(\frac{m_e^*}{m} \right)^{3/2}$$

$$\Gamma(3/2) = \frac{1}{2} \sqrt{\pi}$$

$$n_{e0} = 2 \left(\frac{2\pi m_e^* k T}{h^2} \right)^{3/2} \cdot \left(\frac{m_e^*}{m} \right)^{3/2} T^{3/2}$$

1 m⁴ → mass of an electron in the bound.

n_{e0} → the no. of electrons in the conduction band when $\varepsilon_f = \varepsilon_c$ i.e., Fermi Level rises to the bottom of the conduction band.

$$m^* = \frac{m}{\frac{d^2 E}{d k^2}}$$

⑥ Concentration of holes in the valence band:

Since, holes represent absence of electrons in the valence band, the distribution function in this case measures the probability [1 - f(ε)] for a state of energy ε to be unoccupied. Hence for the holes, we can write –

The total no. of holes is —

$$n_h = \int_{\varepsilon_b}^{\varepsilon_v} N(\varepsilon) d\varepsilon = \int_{\varepsilon_b}^{\varepsilon_v} [1-f(\varepsilon)] g(\varepsilon) d\varepsilon$$

where,

$$g(\varepsilon) = 4\pi \left(\frac{2m_n^*}{h^2} \right)^{3/2} (\varepsilon_v - \varepsilon)^{1/2}$$

In valence band,

$$E = E_v - \frac{\hbar \nu}{2m_n^*}$$

$$\frac{\hbar \nu}{2m_n^*} = E_v - E.$$

$$\text{and } [1-f(\varepsilon)] = 1 - \frac{1}{e^{\frac{(\varepsilon-\varepsilon_f)/kT}{}} + 1} = \frac{e^{(\varepsilon-\varepsilon_f)/kT}}{e^{(\varepsilon-\varepsilon_f)/kT} + 1}$$

Since, $\varepsilon < \varepsilon_v$ and $(\varepsilon-\varepsilon_f)/kT$ is a large negative number, the exponential in the denominator can be neglected so, that $[1-f(\varepsilon)] = e^{(\varepsilon-\varepsilon_f)/kT}$ [If $\varepsilon \leq E_v - 3kT$].

Hence we get,

$$\begin{aligned} n_h &= 4\pi \left(\frac{2m_n^*}{h^2} \right)^{3/2} \int_{\varepsilon_b}^{\varepsilon_v} e^{(\varepsilon-\varepsilon_f)/kT} \cdot (\varepsilon_v - \varepsilon)^{1/2} d\varepsilon \\ &= 4\pi \left(\frac{2m_n^*}{h^2} \right)^{3/2} \cdot \cancel{(y)^{3/2}} \cdot e^{(\varepsilon_v-\varepsilon_f)/kT} \int_{\varepsilon_b}^{\varepsilon_v} e^{(\varepsilon-\varepsilon_f)/kT} \cdot (\varepsilon_v - \varepsilon)^{1/2} d\varepsilon \\ &= 4\pi \left(\frac{2m_n^*}{h^2} \right)^{3/2} \cdot (kT)^{3/2} \cdot e^{(\varepsilon_v-\varepsilon_f)/kT} \cdot \int_{-\infty}^0 e^{-y} \cdot y^{1/2} dy \end{aligned}$$

$$\text{Let, } y = (\varepsilon_v - \varepsilon)/kT \quad \Rightarrow \quad dy = -d\varepsilon/kT$$

$$= 4\pi \left(\frac{2m_n^*}{h^2} \right)^{3/2} (kT)^{3/2} \cdot e^{(\varepsilon_v-\varepsilon_f)/kT} \cdot \int_0^\infty e^{-y} \cdot y^{1/2} dy$$

$$= 4\pi \left(\frac{2m_n^*}{h^2} \right)^{3/2} (kT)^{3/2} \cdot e^{(\varepsilon_v-\varepsilon_f)/kT} \cdot \frac{1}{2} \sqrt{\pi}$$

$$= 2 \left(\frac{2\pi m_n^* k T}{h^2} \right)^{3/2} \exp[-(\varepsilon_f - \varepsilon_v)/kT]$$

$$= n_{h0} \exp[-(\varepsilon_f - \varepsilon_v)/kT]$$

converse, n_{ho} - the no. of holes in the valence band when
 $\epsilon_f = \epsilon_v$; the Fermi level goes down to the top
of the valence band.

$$\therefore n_{ho} = 2 \times \left(\frac{2\pi m^* k}{h^2} \right)^{3/2} \cdot \left(\frac{m^*_h}{m} \right)^{3/2} \cdot T^{3/2}$$

(c) Calculation of ϵ_f :

(i) Intrinsic Semi-conductor

The concentrations of the electrons and holes are equal in this case, so that $n_e = n_h$

$$\therefore m_e^{3/2} \exp(\epsilon_f - \epsilon_c)/kT = m_h^{3/2} \exp(\epsilon_v - \epsilon_f)/kT.$$

$$\exp\left[\frac{\epsilon_f - \epsilon_c - \epsilon_v + \epsilon_f}{kT}\right] = \left(\frac{m_h^*}{m_e^*}\right)^{3/2}$$

$$\Rightarrow \frac{2\epsilon_f - (\epsilon_c + \epsilon_v)}{kT} = \frac{3}{2} \ln\left(\frac{m_h^*}{m_e^*}\right)$$

$$\Rightarrow \boxed{\epsilon_f = \frac{\epsilon_c + \epsilon_v}{2} + \frac{3}{4} kT \ln\left(\frac{m_h^*}{m_e^*}\right)}$$

at $T=0K$, $\epsilon_f = \frac{\epsilon_c + \epsilon_v}{2}$; shows Fermi level is located half-way between the valence and conduction band.

if $m_h^* = m_e^*$, the position of the Fermi level is independent of temperature. In general, $m_h^* > m_e^*$ and the Fermi level is just above the middle and rises slightly with the increase of temperature.

(c) Carrier Concentration in Intrinsic Semiconductor:

For an intrinsic semi-conductor, since -

$$n_e = n_h = n_i \text{ (say),}$$

\therefore the carrier concentration is -

$$n_i = \sqrt{n_e n_h}$$

$$\therefore n_i = \left[2 \times \left(\frac{2\pi m_e^* kT}{h^2} \right)^{3/2} \cdot 2 \times \left(\frac{2\pi m_h^* kT}{h^2} \right)^{3/2} \times \exp \left[(\epsilon_f - \epsilon_c + \epsilon_v - \epsilon_f)/kT \right] \right]^{1/2}$$

$$= 2 \left(\frac{2\pi kT}{h^2} \right)^{3/2} \times (m_e^* m_h^*)^{3/4} \cdot e^{-\epsilon_g/kT} \quad \begin{bmatrix} \epsilon_g = \epsilon_c - \epsilon_v \\ \downarrow \\ \text{band gap energy.} \end{bmatrix}$$

The intrinsic Carrier Concentration is thus independent of the position of the Fermi level. Smaller the band gap, larger is n_i , similarly higher the temperature, larger is n_i .

The intrinsic electron concentration in pure Ge at $T = 300\text{ K}$ is about $n_i = 2.4 \times 10^{19}/\text{m}^3$ whereas the concentration of Ge atoms is $4.4 \times 10^{28}/\text{m}^3$. It indicates that at ordinary temp. only about five covalent bonds per 10^{18} Ge atoms are broken contributing to intrinsic conduction. But for metals like Cu about 10^{28} el./m^3 are available.

N-type Semiconductor

($Z=32$)

Suppose some tetravalent germanium atoms in a germanium crystal are replaced by atoms of some pentavalent element i.e., arsenic ($Z=33$). When an arsenic atom takes the position of a germanium atom in the lattice, it shares four of its valence electrons with the four neighbouring atoms while the fifth electron does not ~~not~~ take part in any bonding. The extra electron is occupying a level (D) in the forbidden zone between the valence (E_V) and conduction band (E_C).

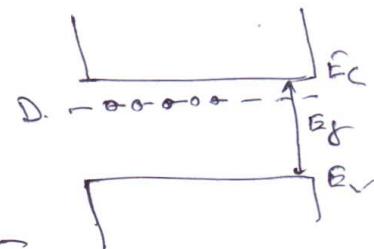
about 0.01 eV below the bottom of conduction band. If an energy amounting to 0.01 eV is given to this electron, it is raised to the conduction band and imparts additional conductivity of the materials.

Since the impurity (arsenic) atoms donate electrons to the material, it is called a donor impurity and the levels that the additional electrons occupy are called donor levels.

It may be noted that when the electron is raised from donor level to the conduction band, a hole is created in the immobile arsenic atom which therefore does not take part in electrical conductivity of the material.

P-type semiconductor

If some germanium atoms are replaced by the atoms of a trivalent impurity i.e., indium ($Z=19$), then the In (indium) atom in the lattice lacks one electron to complete the bonds with its four neighbouring Ge atom. It can thus borrow an electron, so to say from another Ge atom to complete the bond, causing a rupture in the bond of the Ge atom in the lattice.



This corresponds to a hole. The energy required to form the hole is about 0.01 eV.

The appearance of an impurity level (A) about 0.01 eV above the valence band. Because of the small gap between the impurity level and the valence band, some electrons from the valence band are raised to the impurity level even at room temperature. They complete the bonds of the impurity In (indium) atoms and are therefore unable to move in the lattice, so they do not contribute to the conductivity of the materials.

However, the holes that are created in the valence band due to the absence of electrons now contribute to the conductivity of the materials.

Since the impurity atoms accept electrons from the valence band, they are known as acceptor atoms and the corresponding impurity levels as acceptor levels.

Equation of continuity

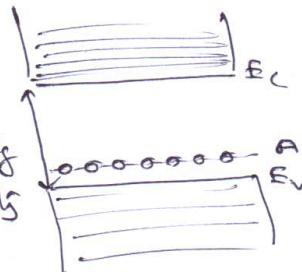
For an extrinsic semiconductor, the sum of the concentrations of the electrons (n_e) and the negatively charged acceptor ions (n_a) must be equal to the sum of the concentration of the positive holes (n_h) and the positively charged donor ions (n_d). This makes the net charge density under equilibrium to be zero —

$$n_e + n_a = n_h + n_d$$

For an n-type semiconductor —

[$n_h \ll n_e$] $n_h = 0$ and $n_a = 0$ so that we have $n_d = n_e$
[$n_d \ll n_n$]

$$\therefore n_d = n_{e0} \exp(E_F - E_d)/kT ; n_{e0} = 2 \left(\frac{2\pi m_e k T}{h^2} \right)^{3/2}$$



$$\therefore \frac{n_{eo}}{n_d} = \exp(+E_c - E_f)/kT$$

$$\Rightarrow kT \ln\left(\frac{n_{eo}}{n_d}\right) = E_c - E_f$$

$$\Rightarrow \boxed{E_f = E_c - kT \ln\left(\frac{n_{eo}}{n_d}\right)}$$

usually, $n_d < n_{eo}$ which gives $E_f < E_c$ i.e., the Fermi level lies in the forbidden zone slightly below the conduction band in an n-type semiconductor.

when, $n_d = n_{eo}$, the Fermi level ~~reaches~~ reaches the bottom of the conduction band.

when n_d becomes larger than n_{eo} , the semiconductor becomes degenerate and behaves like metal.

P-type - semiconductor

In this case, $n_a \gg n_d$ and $n_n \gg n_e$.

$$\therefore n_a = n_n = n_{no} \exp(E_v - E_f)/kT$$

$$\frac{n_{no}}{n_a} = \exp(E_f - E_v)/kT$$

$$\Rightarrow \boxed{E_f = E_v + kT \ln\left(\frac{n_{no}}{n_a}\right)}.$$

usually, $n_a \ll n_{no}$ and E_f lies slightly above the top of the valence band (E_v) and lies in the forbidden zone. when $n_a = n_{no}$, E_f goes down towards E_v and becomes equal to E_v .