Macroscopic system:
Any system that is large enough to be observable using our senses are known
as a macroscopic system. Examples: A gas enclosed in a cylinder, a liquid in a
vessel & a solid of definite dimension. The state of a macroscopic system is
represented by macroscopic parameters like pressure, volume, temperature,
entropy, electrical resistivity and so on. When the macroscopic parameters of an
isolated system do not change with time, the system is said to be in equilibrium.

Microscopic system:
A system of atomic dimension or of a size unobservable with our senses is
known as microscopic system. In a microscopic system there are a large number
of minute particles positioned randomly and moving with random momentum. Thus,
position and momentum of individual particles are known as microscopic
parameters. Since a large number of particles constitute the assembly, or an
ensemble, they possess unpredictable parameters. The theory of probability is used
to predict the behaviour of constituent microstates of the system.

Statistical Mechanics:
Statistical mechanics is the study of macroscopic parameters of a system in
equilibrium from knowledge of the microscopic properties of its constituent
particles using the law of mechanics. The statistical mechanics uses probability
theory to correlate macroscopic parameters to the microscopic parameters.

Statistical mechanics is divided into two branches.
(1) Classical Statistics or Newtonian Statistics: It uses predictable behaviour of
microscopic particles to relate macroscopic parameters to microscopic parameters.
(2) Quantum Statistics: It uses unpredictable behaviour of indistinguishable
microscopic particles to relate macroscopic parameters to microscopic parameters.
Quantum statistics is divided into (a) Bose-Einstein Statistics & (b) Fermi-Dirac
Statistics.

Statistical ideas in physics:
Statistical theories are used in physics in the explanation of macroscopic
phenomenon. It is used in Newtonian mechanics as well as quantum mechanics. In
Newtonian statistics predictable behaviour of microscopic parameters are used and
in quantum statistics unpredictable behaviour of microscopic parameters are used.

Examples
1. Kinetic theory of gases:
In kinetic theory, the behaviour of gas molecules is predicted using
assumptions on the behaviour of gas molecules. It assumes that the volume of the
gas molecule is negligibly small compared to the volume of the container and the
molecules move randomly with random velocities. The molecules can have velocities
varying from zero to maximum value at some instant or other as it undergoes
collision with the other molecules. Due to this reason the average velocity of each
and every molecule can have the same value. It predicts that in general one third of
the molecules move with an average velocity in a particular direction and hit the
wall of the container and transfers its momentum to the wall and exerts a force on
the wall of the container and hence a force per unit area known as the pressure of

Statistical Physics:  [8 hours]
Statistical ideas in physics, Phase space, derivation of statistical
equilibrium, Maxwell – Boltzmann, Bose – Einstein and Fermi – Dirac
distribution function and their comparison.
the gas. In kinetic theory, pressure is related to volume and also temperature. Thus macroscopic parameters pressure, volume and temperature of gas in a container are determined using the predictable parameters of the molecules of the gas in the container such as its position and momentum. In statistical ideas applied to Newtonian mechanics, predictable behaviour of millions of millions of particles is used in arriving at the macroscopic parameters of the gaseous system.

2. Radio-activity:

In radio-activity, alpha, beta and gamma particles are emitted from a radioactive element. In this case, we cannot predict out of millions of atoms of the radio-active sample which atom exactly emitted alpha particle or beta particle or gamma particle. After the emission of alpha or beta particle, the nuclear transformation takes place and the resulting nuclei are known as daughter nuclei. The radio-activity is a continuous process. The number of radio-active atoms reduces exactly to half its number after a time equal to half life of radioactive sample. For example, 1 gram of radioactive radium reduces to half gram of radioactive radium after 1600 years. This is macroscopic observation of physicists. As 1 gram of radium contains millions of millions of atoms and out of which any half of them must have disintegrated in 1600 years, the phenomenon can not be understood by any predictable behaviour of the atoms responsible for radioactive emission. Statistical mechanics uses statistical laws governing radioactive disintegration of radium atoms as a group.

3. Intensity of spectral lines emitted by hydrogen atom:

The spectra of hydrogen atom consists of hundreds of spectral lines divided in to five spectral series and they are (1) Lymann series in UV region, (2) Balmer series in visible region, (3) Paschen series, (4) Bracket series and (5) Pfund series in IR region. The intensity of spectral lines in any series has a maximum value for one particular line known as band head and decreases in intensity as we move towards the other end of the spectral band.

We know that according to Bohr’s theory of hydrogen atom, the electron cannot revolve in hydrogen in a shell of any radius, but in a shell for which angular momentum is quantized. This predicts that electron can be in any one of the shells depending on the energy it possess. If it possesses least possible energy, it will be in the lowest K shell. If it absorbs energy it can be in any one of the outer shells L, M, N, etc, depending on the energy it gains form external agency. At any point of time we can not exactly predict the shell in which the electron of a particular hydrogen atom is present. When the atom is cooled, it jumps back to any one of the lower shell with the emission of radiation of energy exactly equal to energy difference of the two shells. When it undergoes the downward jump, there is again unpredictability in its jump as it can jump to any one of the lower shells.

Statistical mechanics uses the overall behaviour of the group of hydrogen gas molecules in arriving at the probability of a group of atoms in a particular shell in arriving at the a relation between intensity of spectral lines and the probability of downward transition in hydrogen atom.

In the study of statistical physics calculation of probabilities plays an important role in arriving at a relation between macroscopic and microscopic properties. It is discussed in the following topic.

Calculation of probabilities:

Let us assume that we have to distribute N identical particles in n containers such that there is N1 number of particles in the first, N2 number of particles in the second, N3 number of particles in the third, and so on. To find the number of ways
this can be done, we begin with two containers. N particles are to be distributed in these two containers such that the first contains $N_1$ particles and the second contains the remaining $N_2 = (N - N_1)$ particles. The number of such distributions is clearly given by,

$$^NC_{N_1} = \frac{N!}{N_1!(N - N_1)!} = \frac{N!}{N_1!N_2!} \quad \cdots (1)$$

Let us assume that the second container is partitioned into two chambers containing $n_1$ and $n_2$ particles. Then $n_1 + n_2 = N_2 = N - N_1 \quad \cdots (2)$

The number of independent ways of obtaining the above distribution in the chambers of the second container is

$$^N_C_{n_1} = \frac{N_2!}{n_1!(N_2 - n_1)!} = \frac{N_2!}{n_1!n_2!} \quad \cdots (3)$$

This may be visualized as the system consisting of three chambers such that the first chamber contains $N_1$ particles, the second contains $n_1$ particles and the third contains $n_2$ particles. The total number of ways this arrangement can be achieved is given by the product,

$$^NC_{N_1} \times ^N_C_{n_1} = \frac{N!}{N_1!N_2!} \times \frac{N_2!}{n_1!n_2!} = \frac{N!}{N_1!n_1!n_2!} \quad \cdots \quad \cdots (4)$$

This is due to the reason that for each arrangement given by equation 1, there are $^N_C_{n_1}$ ways of arranging particles in the second and third containers.

We can subdivide the third container into two chambers as before and proceed in a similar way to cover the case of all the n containers. Finally if the chambers contain $N_1$, $n_2=N_2$, $N_3$ . . . . $N_n$ particles, then the total number of ways of achieving this arrangement is given by the formula,

$$W = \frac{N!}{N_1!N_2! \times N_3! \times \ldots \times N_n!} = \frac{N!}{\prod_{i=1}^{n} N_i!} \quad \cdots \quad (5)$$

Where $\prod_{i=1}^{n}$ indicates the extended product.

Now, the mathematical probability of an event is defined as the ratio of the actual number of cases in which the event occurs to the total number of cases. Thus the probability of distribution of $N_1$, $N_2$, . . . . $N_n$ particles in containers 1, 2' . . . . n will be obtained by dividing W by the total number of ways of arranging N particles among n containers considering all possible distributions. This latter factor is $n^N$, as each particle can be arranged in n ways. Thus probability of this particular distribution is given by,

$$P_r = \frac{W}{n^N} = \frac{N!}{\prod_{i=1}^{n} N_i!} \times n^{-N} \quad \cdots \quad (6)$$

**CLASSICAL STATISTICS**

Classical Statistics is also known as Maxwell – Boltzmann Statistics. This is due to the reason that it originated from Maxwell’s law of distribution of molecular velocities and Boltzmann theorem relating entropy and probability. Hence a brief review of these basic ideas is necessary.
Maxwell Distribution of Molecular Velocities:

According to kinetic theory of matter, a gas consists of a very large number of rigid and perfectly elastic material particles called molecules. All the molecules have the same mass and move freely within the vessel containing the gas. When the molecules move in all direction, collide with one another and hence the molecules acquire all possible velocities ranging from $-\infty$ to $+\infty$. Maxwell conceived the idea that at a given temperature, when the gas is in a state of thermal equilibrium, there should be a law according to which the molecular velocities can be grouped in spite of their apparent random and chaotic motion. He was able to derive the law of distribution of molecular velocities by the application of elementary ideas of probability as follows.

Considering the case of mono atomic gas and that the molecular density is unaffected by molecular motion and collisions. It is possible that $N_1$ molecules have velocities lying between $u \& u+du$, $v \& v + du$ and $w \& w+dw$. The value of $N_1$ is given by

$$N_1 = N f(u,v,w)du dv dw \quad \cdots (1)$$

Where, $N$ is the total number of molecules in unit volume. Equation (1) is known as Maxwell’s law of distribution of molecular velocities. It is expressed in the following form

$$N_1 = N \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} d\tau \quad \cdots \quad (2)$$

Where $k$ is Boltzmann constant & $d\tau = du dv dw$ is the volume element in velocity space containing $N_1$ number of molecules, $a = \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}}$ & $b = \frac{1}{2kT}$ and ‘c’ is root mean square velocity of the molecules.

Comparing equations (1), (2) & (3), the distribution function for molecular velocities is given by,

$$f(u,v,w) = a e^{-bmc^2} = \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left( \frac{-mc^2}{2kT} \right) \quad \cdots (4)$$

Boltzmann theorem on entropy and probability:

A gas at a definite temperature and pressure is considered to be in a macroscopic equilibrium state. But the constituent molecules are in incessant motion of random and chaotic nature, so that the microscopic state of a gas is continually changing. When, it is not in a state of macroscopic equilibrium, its state changes until equilibrium is established. This process involves naturally an increase in the number of possible microscopic states. Thus it is evident that an equilibrium macroscopic state has maximum number of microscopic states in equilibrium.

On the other hand, according to second law of thermodynamics stated by Carnot, the entropy of a system always tends towards a maximum and maximum entropy corresponds to a state of maximum disorder and hence a statistical condition of maximum probability.

Due to this reason, Boltzmann concluded that there must be a relation between the thermodynamic entropy, which has always a maximum value in the case of equilibrium, and the maximum probability of dynamical equilibrium state. If $S$ is the entropy of an isolated system and $W$ is the number of possible micro
states through which the system passes in a given macroscopic state, both \( S \) and \( W \) tend to increase to maximum value and according to Boltzmann’s idea \( S \) is a function of \( W \). Therefore,

\[
S = f(W) \quad - - (5)
\]

In equation (5) \( W \) is called thermodynamic probability of the system. In order to understand the nature of this function, let us consider two separate systems having entropies \( S_1 \) and \( S_2 \) and thermodynamic probability \( W_1 \) and \( W_2 \), Then,

\[
S_1 = f(W_1) \quad \text{&} \quad S_2 = f(W_2)
\]

The total entropy of the system is \( S_1 + S_2 = f(W_1) + f(W_2) \)

The total thermodynamic probability of the two systems taken together is \( W_1W_2 \) and hence, \( f(W_1W_2) = f(W_1) + f(W_2) = S_1 + S_2 \)

If this relation should be true, then, \( f(W) \) must be a logarithmic function of \( W \). Therefore,

\[
W \log W = \frac{S}{K} 
\]

Hence \( S \) and \( W \) are related by \( W \log W = \frac{S}{K} \), where \( K \) is a constant of proportionality.

**Phase space:**

Phase space is a six dimensional space to represent the position and momentum of particles in a microscopic system. The microscopic particles forming an ensemble possess random position and random momentum. Both these values change for each and every particles due to collision and the number of particles possessing any particular momentum values has a constant value according to statistical principles. The position and momentum of the particles can be represented in a six dimensional space known as phase space consisting of 3 position co-ordinate values and 3 momentum co-ordinate values. Any point in such a phase space represents both the position and momentum of a particle. A small elemental volume of phase space is represented by \( [dx dy dz \times dp_x dp_y dp_z = h^3] \). The number of particles in this small elemental volume \( h^3 \) is given by

\[
dn = f(x,y,z,p_x,p_y,p_z)dx dy dz dp_x dp_y dp_z, \quad - - - (1)
\]

In this relation, \( dn \) represents the number of particles having coordinates between \( x \) and \( (x+dx) \), \( y \) and \( (y+dy) \) \& \( z \) and \( (z+dz) \) and momentum values \( p_x \) and \( (p_x+dp_x) \), \( p_y \) and \( (p_y+dp_y) \) \& \( p_z \) and \( (p_z+dp_z) \) and the function \( f \) defines the distribution of particles in phase space of six dimention.

**Maxwell-Boltzmann Distribution function:**

Let \( N \) be the total number of particles in an ensemble. Also let \( N_1, N_2 \ldots \ldots N_n \) be the number of particles with energies \( E_1, E_2 \ldots \ldots E_n \) respectively and \( g_i \) be the number of quantum states for the energy level \( E_i \). The quantity \( g_i \) is called the degeneracy of the energy level \( E_i \). Since, the total number of particles of an isolated system is constant and the total energy of the system is also a constant, we can write,

\[
N = \sum_{i=1}^{n} N_i = Cons \tan t \quad - - - (1)
\]

& \[ E = \sum_{i=1}^{n} N_i E_i = Cons \tan t \quad - - - (2) \]

\[
\therefore \delta N = \sum_{i=1}^{n} \delta N_i = 0 \quad - - - (3)
\]

\[
\delta E = \sum_{i=1}^{n} E_i \delta N_i = 0 \quad - - - (4)
\]
If the particles are identifiable, the number of ways in which the groups of \( N_1, N_2 \ldots \ldots N_n \) particles can be chosen from N particles is given by the equation,

\[
W_i = \frac{N!}{N_i!} \cdot \ldots \cdot (5)
\]

Now, \( N_1 \) particles are to be accommodated in \( g_i \) states, each of which has the same a priori probability of being occupied. Each of the \( N_i \) particles may thus occupy any of the \( g_i \) states. The number of ways in which \( N_i \) particles are arranged in \( g_i \) states is therefore given by \( g_i^{N_i} \). Considering the different values of ‘\( i \)’, the total number of arrangements will be,

\[
w_2 = \prod_{i=1}^{n} (g_i)^{N_i} \cdot \ldots \cdot (6)
\]

The required number of ways \( W \) is obtained by taking the product of \( W_1 \) and \( W_2 \). Thus,

\[
w = w_1w_2 = \frac{N!}{N_i!} \prod_{i=1}^{n} (g_i)^{N_i} = N! \prod_{i=1}^{n} \frac{(g_i)^{N_i}}{N_i!} \cdot \ldots \cdot (7)
\]

The quantity \( W \) is called the thermodynamic probability for the system. It is related to entropy of the system by

\[
S = K \log W = K \log \left[ \frac{N! \prod_{i=1}^{n} (g_i)^{N_i}}{N!} \right]
\]

\[
S = K \log W = K \left[ \log N! + \sum_{i=1}^{n} (\log g_i^{N_i} - \log N_i!) \right]
\]

\[
S = K \log W = K \left[ \log N! + \sum_{i=1}^{n} N_i \log g_i - \log N_i! \right] \cdot \ldots \cdot (8)
\]

Using sterling theorem, \( \log N! = N \log N - N \) Equation (8) can be modified as follows

\[
S = K \log W = K \left[ N \log N - N + \sum_{i=1}^{n} N_i \log g_i - \sum_{i=1}^{n} (N_i \log N_i - N_i) \right]
\]

\[
S = K \log W = K \left[ N \log N - N + \sum_{i=1}^{n} N_i \log g_i - \sum_{i=1}^{n} N_i \log N_i + \sum_{i=1}^{n} N_i \right]
\]

\[
S = K \log W = K \left[ N \log N - N + \sum_{i=1}^{n} N_i \log g_i - \sum_{i=1}^{n} N_i \log N_i + N \right]
\]

\[
S = K \log W = K \left[ N \log N + \sum_{i=1}^{n} N_i \log g_i - \sum_{i=1}^{n} N_i \log N_i \right] \cdot \ldots \cdot (9)
\]

For an equilibrium state the entropy always tend to a maximum value and for maximum \( S \), \( dS = K \log W = 0 \cdot \ldots \cdot (10) \)

Now from equation (9) and (10) it follows that,

\[
dS = d(K \log W) = K \left[ \frac{n}{d} \sum_{i=1}^{n} N_i \log g_i - \sum_{i=1}^{n} N_i \log N_i \right] = 0
\]

\[
\Rightarrow K \left[ \frac{n}{d} \sum_{i=1}^{n} N_i \log g_i - \frac{n}{d} \sum_{i=1}^{n} N_i \log N_i \right] = 0
\]

\[
\Rightarrow \left[ \sum_{i=1}^{n} \log g_i \times dN_i \right] - \left( \sum_{i=1}^{n} N_i \times \frac{dN_i}{N_i} + \sum_{i=1}^{n} \log N_i \times dN_i \right) = 0
\]

\[
\Rightarrow \left[ \sum_{i=1}^{n} \log g_i \times dN_i \right] - \left( \sum_{i=1}^{n} N_i \right) - \sum_{i=1}^{n} \log N_i \times dN_i = 0
\]
Using equation (3), we can write,
\[ \Rightarrow \sum_{i=1}^{n} \log (g_{i}) \delta N_{i} - \sum_{i=1}^{n} \log (N_{i}) \delta N_{i} - \sum_{i=1}^{n} \delta N_{i} = 0 \quad \cdots (12) \]

Using Lagrange's method of undetermined multipliers (constants), we can multiply equation (3) by (-α) and equation (4) by (-β) and add the resulting equation to equation (13),
\[ \sum_{i=1}^{n} (\log (g_{i}) - \log (N_{i}) - \alpha - \beta E_{i}) \delta N_{i} = 0 \quad \cdots (14) \]

Since the variations are quite arbitrary, we can write,
\[ \log \left( \frac{g_{i}}{N_{i}} \right) = \alpha + \beta E_{i} \quad \Rightarrow \quad \frac{g_{i}}{N_{i}} = e^{\alpha + \beta E_{i}} \]
Re-arranging the equation we get,
\[ f(E_{i}) = \frac{N_{i}}{g_{i}} = e^{-\alpha - \beta E_{i}} = \frac{1}{e^{(\alpha + \beta E_{i})}} \quad \cdots (15) \]

The quantity \( f(E_{i}) \), defined by the ratio of the number of particles \( N_{i} \) distributed in \( g_{i} \) states to the number of states \( g_{i} \), is called the distribution function. It gives the average number of particles per quantum state of the system.

The distribution function defined by equation (15) is known as the Maxwell-Boltzmann distribution function.

The number of particles \( N_{i} \) in a particular energy state \( E_{i} \) is given by,
\[ N_{i} = \frac{g_{i}}{e^{(\alpha + \beta E_{i})}} = (g_{i} e^{-\alpha}) e^{-\beta E_{i}} \quad \cdots (16) \]

Thus, the number of particles having energy \( E_{i} \) is proportional to \( e^{-\beta E_{i}} = e^{\frac{E_{i}}{kT}} \),
where \( \beta = \frac{1}{kT} \) and \( k \) is Boltzmann constant and \( T \) is absolute temperature of the system.

**Evaluation of the constants \( \alpha \) & \( \beta \):**

If the energy distribution among molecules is continuous, then the number of molecules with energies between \( \varepsilon \) and \( (\varepsilon + d\varepsilon) \) is given by
\[ n(\varepsilon) d\varepsilon = g(\varepsilon) e^{\alpha} e^{-\beta \varepsilon} d\varepsilon \quad \cdots (17) \]

Where \( g(\varepsilon) d\varepsilon \) is the number of energy states between \( \varepsilon \) and \( (\varepsilon + d\varepsilon) \)

Equation (18) in momentum form is written as,
\[ n(p)dp = g(p)e^{-\alpha} e^{-\frac{\beta p^2}{2m}} dp \quad \cdots (18) \]

Where \( g(p)dp \) is a priori probability that a molecule has momentum between \( p \) & \( (p+dp) \). This is equal to the number of cells in phase space in which the molecules may exist. As each cell in phase space has an infinitesimal volume \( h^3 \), we can write,
\[ g(p)dp = \iiint \frac{dxdydzdp,dp_x,dp_y,dp_z}{h^3} = \frac{V \times 4\pi p^2dp}{h^3} \quad \cdots (19) \]

Substituting for \( g(p)dp \) in equation (18), we get,

\[ n(p)dp = \frac{4\pi p^2V}{h^3} e^{-\frac{p^2}{2m}} \int p^2 \times e^{-\frac{\beta p^2}{2m}} dp \quad \cdots (20) \]

Integrating equation (20) between the limits 0 to \( \infty \), we get the total number of particles \( N \).

\[ \therefore N = \int_0^\infty n(p)dp = \frac{4\pi V}{h^3} e^{-\frac{1}{4\beta}} \int_0^\infty \frac{2m}{\beta} \left( \frac{\beta}{2m} \right)^{\frac{1}{2}} \pi \int_0^\infty \frac{2m}{\beta} \left( \frac{\beta}{2m} \right)^{\frac{1}{2}} \]

Using the standard integral, \( \int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4} \left( \frac{\pi}{a^3} \right)^{\frac{1}{2}} \), we can write,

\[ N = \int_0^\infty n(p)dp = \left[ \frac{4\pi V}{h^3} e^{-\frac{1}{4\beta}} \right] \int_0^\infty \frac{2m}{\beta} \left( \frac{\beta}{2m} \right)^{\frac{1}{2}} \pi \int_0^\infty \frac{2m}{\beta} \left( \frac{\beta}{2m} \right)^{\frac{1}{2}} \]

\[ e^{-\frac{1}{4\beta}} = \left( \frac{Nh^3}{V} \right)^{\frac{1}{4}} \left( \frac{\beta}{2\pi m} \right)^{\frac{3}{4}} \cdots (21) \]

Substituting for \( e^{\frac{1}{4\beta}} \) in equation (20), we get,

\[ n(p)dp = \frac{4\pi p^2V}{h^3} \left( \frac{Nh^3}{V} \frac{\beta}{2\pi m} \right)^{\frac{3}{4}} e^{-\frac{\beta p^2}{2m}} \int_0^\infty \frac{2m}{\beta} \left( \frac{\beta}{2m} \right)^{\frac{1}{2}} \pi \int_0^\infty \frac{2m}{\beta} \left( \frac{\beta}{2m} \right)^{\frac{1}{2}} \]

To evaluate \( \beta \):

\[ \therefore \epsilon = \frac{p^2}{2m} \text{ or } p^2 = 2m\epsilon \therefore dp = \frac{mde}{p} = \frac{mde}{\sqrt{2m\epsilon}} \]

Equation (22) in energy form is given by,

\[ n(\epsilon)d\epsilon = 4\pi N \left( \frac{\beta}{2\pi m} \right)^{\frac{3}{2}} \times 2m\epsilon \times e^{-\frac{\beta\epsilon}{2m}} \frac{mde}{\sqrt{2m\epsilon}} \]

\[ n(\epsilon)d\epsilon = 2N \frac{\beta^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \times \epsilon^{\frac{3}{2}} \times e^{-\frac{\beta\epsilon}{2m}} d\epsilon \cdots (23) \]

The total energy is given by,

\[ E = \int_0^\infty \epsilon \times n(\epsilon)d\epsilon = 2N \frac{\beta^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \times \int_0^\infty \epsilon^{\frac{3}{2}} \times e^{-\frac{\beta\epsilon}{2m}} d\epsilon \]
Using the standard integral 
\[ \int_0^\infty x^{\frac{3}{2}} e^{-ax^2} \, dx = \frac{3}{4} a^{\frac{1}{2}} \left( \frac{\pi}{a} \right)^{\frac{1}{2}} \]
we can write,

\[ E = 2N \frac{\beta^{\frac{3}{2}}}{\pi^{\frac{1}{2}}} \times \frac{3}{4} \frac{1}{(\beta^2)} \left( \frac{\pi}{\beta} \right)^{\frac{1}{2}} = \frac{3}{2} \times \frac{N}{\beta} \cdot \cdot \cdot (24) \]

But, according to kinetic theory of gases, 
\[ E = \frac{3}{2} N kT \cdot \cdot \cdot (25) \]

Comparing equations (24) and (25), we get, 
\[ \beta = \frac{1}{kT} \cdot \cdot \cdot (26) \]

Substituting for \( \beta \) in equation (23), we get,

\[ n(\varepsilon) d\varepsilon = 2\pi N \frac{1}{(\pi kT)^{\frac{1}{2}}} \times e^{\varepsilon^{\frac{1}{2}}} \times e^{-\frac{\varepsilon}{2kT}} d\varepsilon \quad \cdot \cdot \cdot (27) \]

Equation (27) is known as Maxwell–Boltzmann distribution law in complete form and it gives the number of molecules having their energies between \( \varepsilon \) and \( (\varepsilon+d\varepsilon) \).

Maxwell–Boltzmann distribution law can be expressed in momentum form by substituting \( \varepsilon = \frac{p^2}{2m} \) and \( \varepsilon = \frac{p}{m} dp \) in equation (27) and the resulting equation is given by,

\[ n(p) dp = \frac{\sqrt{2} \pi N}{(\pi mkT)^{\frac{1}{2}}} \times p^2 \times e^{-\frac{p^2}{2mkT}} dp \quad \cdot \cdot \cdot (28) \]

Maxwell–Boltzmann distribution law can be expressed in velocity form by substituting \( p = mv \) & \( dp = m \, dv \) in equation (29) and the resulting equation is,

\[ n(v) dv = \frac{\sqrt{2} \pi N}{(\pi kT)^{\frac{1}{2}}} \times v^2 \times e^{-\frac{mv^2}{2kT}} dv \quad \cdot \cdot \cdot (29) \]

###
Quantum Statistics

Quantum statistics is used to relate macroscopic parameters to microscopic parameters using unpredictable behaviour of indistinguishable microscopic particles. Quantum statistics is divided into (a) Bose-Einstein Statistics & (b) Fermi-Dirac Statistics.

Bose – Einstein distribution function:

Bose-Einstein distribution function gives the method of distributing N indistinguishable particles with out any restriction on the number of particles in any particular degenerate energy level.

Consider a system consisting of N indistinguishable particles. Let these particles be distributed into different energy states such that there are \( n_1 \) particles in the energy state 1 with energy \( \varepsilon_1 \), \( n_2 \) particles in the energy state 2 with energy \( \varepsilon_2 \), \( n_3 \) particles in the energy state 3 with energy \( \varepsilon_3 \) and so on, \( n_i \) particles in the energy state \( i^{th} \) with energy \( \varepsilon_i \). Let \( g_i \) be the degeneracy (number of states with the same energy) of the \( i^{th} \) state of energy \( \varepsilon_i \).

Now let us consider the number of different ways of distributing \( n_i \) indistinguishable particles in ‘g’ cells. This situation is similar to distributing \( n_i \) indistinguishable particles in a box of \( g_i \) compartments, with out any restriction to the number of particles in any compartments. To carry out this distribution, let us consider a series of \( n_i \) white balls and \((g_i - 1)\) black balls placed in a line. The \((g_i - 1)\) black balls may be regarded as separating a total of ‘g’ cells.

For example, if we want to distribute 25 white balls [indistinguishable particles] in to \( g_i = 8 \) cells, then, the number of partitions between the cells will be \((g_i - 1) = 8 - 1 = 7\) (black balls). Further, white balls are distributed into different cells as shown in the following figure (1).

Now, there are \((25+7)!\) ways of arranging 25 white balls and 7 black balls to have the above distribution. Out of these 7! Permutations of black balls and 25! Permutations of white balls amongst themselves will not produce any new configurations (because both black and white balls are indistinguishable).

Thus the number of possible different arrangements of 25 white balls in 8 cells is given by, \( \frac{(25+7)!}{25! \times 7!} \).

Generalizing this idea, the number of possible arrangements of \( n_i \) indistinguishable particles in \( g_i \) cells [having \((g_i - 1)\) partitions] is given by, \( \frac{(n_i + g_i - 1)!}{n_i! \times (g_i - 1)!} \)

Therefore, the number of ways \( W \) in which all \( N \) particles are distributed among different states is given by,

\[
W = \prod_{i=1}^{\infty} \frac{(n_i + g_i - 1)!}{n_i! \times (g_i - 1)!} \quad \ldots \ldots \quad (1)
\]

Since \((n_i + g_i) > > 1\) and \( g_i > > 1\), we can neglect 1 compared to other terms in equation (1) and hence, equation (1) can be written as, \( W = \prod_{i=1}^{\infty} \frac{(n_i + g_i)!}{n_i! \times g_i!} \quad \ldots \ldots \quad (2)\)
Taking Logarithm of equation (2), we get,
\[
\log W = \sum_{i=1}^{\infty} \left[ \log(n_i + g_i)! - \log n_i! - \log g_i! \right] - \cdot - (3)
\]
Using Sterling formula, \( \log n! = n \log n - n \) in the above equation, we get,
\[
\log W = \sum_{i=1}^{\infty} \left[ (n_i + g_i) \log(n_i + g_i) - n_i \log n_i + n_i - g_i \log g_i + g_i \right]
\]
\[
\log W = \sum_{i=1}^{\infty} \left[ (n_i + g_i) \log(n_i + g_i) - n_i \log n_i - g_i \log g_i, \right] - - (4)
\]
The condition for most probable configuration is that small changes \( \delta n_i \) in any individual number \( n_i \) does not affect the value of \( W \).
Thus, \( \delta W = 0 \) or \( \delta (\log W) = 0 \) - - (5)
Taking partial differentiation of equation (4), we get,
\[
\delta \log W = \sum_{i=1}^{\infty} \delta \left[ (n_i + g_i) \log(n_i + g_i) \right] - \sum_{i=1}^{\infty} \delta [n_i \log n_i] - \sum_{i=1}^{\infty} \delta [g_i \log g_i] - - (6)
\]
Since, \( g_i \) is constant the last term in equation (6) reduces to zero. Thus, from equations (5) & (6) we can write,
\[
\delta \log W = \sum_{i=1}^{\infty} \left[ \log(n_i + g_i) \delta n_i + (n_i + g_i) \left( \frac{\delta n_i}{n_i + g_i} \right) - \log n_i \delta n_i - n_i \left( \frac{\delta n_i}{n_i} \right) \right] = 0
\]
\[
\text{Or,} \quad \sum_{i=1}^{\infty} \left[ \log(n_i + g_i) \delta n_i + \delta n_i - \log n_i \delta n_i - \delta n_i \right] = 0
\]
\[
\text{Or,} \quad \sum_{i=1}^{\infty} \left[ \log(n_i + g_i) - \log n_i \right] \delta n_i = 0 - - (7)
\]
Since total number of particles \( N \) and the total energy of all particles in equilibrium is a constant, we can write,
\[
\delta N = \sum_{i=1}^{\infty} \delta n_i = 0 - - - - (8) \quad \text{&} \quad \delta \sum_{i=1}^{\infty} n_i \epsilon_i = \sum_{i=1}^{\infty} \epsilon_i \delta n_i = 0 - - - - (9)
\]
Using Lagrange’s method of un-determined multipliers, we can multiply equation (8) by \( -\alpha \) and equation (9) by \( -\beta \) and adding the resulting equations to equation (7), we get,
\[
\sum_{i=1}^{\infty} \left[ \log(n_i + g_i) - \log n_i - \alpha - \beta \epsilon_i \right] \delta n_i = 0
\]
Since \( \delta n_i \) is not zero the terms in the bracket is zero for each and every value of \( i \). Therefore, we get,
\[
\log \left( \frac{n_i + g_i}{n_i} \right) = \alpha + \beta \epsilon_i \quad \& \quad \text{hence,} \quad \frac{n_i + g_i}{n_i} = e^{\alpha + \beta \epsilon_i}
\]
\[
\text{Or,} \quad 1 + \frac{g_i}{n_i} = e^{\alpha + \beta \epsilon_i} \quad \text{Or,} \quad \frac{g_i}{n_i} = e^{\alpha + \beta \epsilon_i} - 1
\]
\[
n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} - 1} - - - - (10)
\]
But, \( \beta = \frac{1}{kT} \), where \( k \) is Boltzmann constant and hence, we get,
\[
n_i = \frac{g_i}{e^{\frac{\alpha + \epsilon_i}{kT}} - 1} - - - - (11)
\]
Equation (11) gives the most probable distribution of the particles among various energy levels for a system of particles obeying Bose-Einstein Statistics.

**Application of Bose-Einstein Statistics to derive Planck’s radiation formula for radiation density:**

The radiation emitted from the cavity of an opaque material is known as Black Body radiation. Let V be the volume of the cavity and it contains a large number of indistinguishable photons of various frequencies. The photons are the example for Bosons and they do not obey Pauli’s exclusion principle and obey Bose-Einstein distribution function. According to Bose-Einstein distribution function, the number of photons having an energy $\varepsilon_i$ is given by,

$$ n_i = \frac{g_i}{e^{\varepsilon_i/kT} - 1} \quad \cdots (1) $$

In deriving this equation, it is assumed that $\sum \delta n_i = 0$ \& $\alpha \sum \delta n_i = 0$. In the cavity, the number of photons is not a constant due to their continuous absorption and re-emission from the walls of the cavity and hence $\sum \delta n_i \neq 0$ and hence $\alpha$ must be zero in the above equation. [To satisfy the condition $\alpha \sum \delta n_i = 0$] Therefore equation (1) reduces to the form,

$$ n_i = \frac{g_i}{e^{\varepsilon_i/kT} - 1} \quad \cdots (2) $$

If we consider the distribution of photons in a small interval of frequency lying between $\gamma$ \& $(\gamma + d\gamma)$ in the cavity at absolute temperature T, then the number of photons in this range of frequency range is given by,

$$ n(\gamma)d\gamma = \frac{g(\gamma)d\gamma}{e^{\gamma/kT} - 1} \quad \cdots (3) $$

Where $g(\gamma)d\gamma$ is known as the density of energy states between $\gamma$ \& $(\gamma + d\gamma)$ and its value can be calculated as follows.

The number of photons between the momentum range $p$ and $(p+dp)$ is given by,

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

Equation (4) contains the term 2 because the photons can have two different direction of circular polarization. Also, in the case of photons, $p = \frac{h\gamma}{c}$ and $dp = \frac{h}{c} d\gamma$

Hence, $p^2 dp = \left(\frac{h\gamma}{c}\right)^2 \frac{h}{c} d\gamma = \frac{h^3 \gamma^2}{c^3} d\gamma$. Substituting these values in equation (4), we get,

$$ g(\gamma)d\gamma = \left(\frac{8 \pi V}{h^3}\right) \frac{h^3 \gamma^2}{c^3} d\gamma = \frac{8 \pi V \gamma^2}{c^3} d\gamma $$

Substituting the value of $g(\gamma)d\gamma$ in equation (3), we get,

$$ n(\gamma)d\gamma = \left(\frac{8 \pi V}{c^3}\right) \times \frac{\gamma^2 d\gamma}{e^{\gamma/kT} - 1} \quad \cdots (5) $$

The corresponding energy density per unit volume is given by,

---

MBR, VSC, Bellary
\[
\varepsilon(\gamma) d\gamma = \frac{h\gamma}{V} \times n(\gamma) d\gamma = \frac{8\pi h\gamma^3}{e^3} \frac{d\gamma}{\exp\left(\frac{h\gamma}{kT}\right)-1}
\]

Equation (6) is the famous Planck’s radiation formula for the energy density of radiation emitted from a black body.

**Fermi – Dirac distribution function:**

Fermi – Dirac Statistics is applicable to indistinguishable particles obeying Pauli’s exclusion principle. Thus, Fermi – Dirac statistics imposes the condition that individual states which are available to the particles can be occupied at the most by a single particle. The particles which obey this statistics are known as Fermions.

Consider the distribution of \( n_i \) particles in \( g_i \) cells having same energy \( \varepsilon_i \). In this case \((g_i > n_i)\) as there must be at least one cell available for each particle. According to F – D Statistics, one particle can occupy only a single cell and as there are \( n_i \) particles, only \( n_i \) cells will be occupied by these particles and the remaining \((g_i - n_i)\) cells remain vacant or empty. The \( g_i \) cells can be re-arranged in \( g_i! \) ways. As the particles are indistinguishable and all the occupied cells are similar, hence \( n_i! \) of filled cells does not give rise to any new configuration. Thus, the number of distinguishable arrangements of particles among the cells in given by the formula,

\[
\frac{g_i!}{n_i!(g_i - n_i)!}
\]

The probability of the entire distribution of particles is given by,

\[
W = \prod_{i=1}^{n} \left[ \frac{g_i!}{n_i!(g_i - n_i)!} \right] - - - (1)
\]

Taking natural logarithm of equation (1), we get,

\[
\log W = \sum_{i=1}^{n} [\log (g_i!) - \log (n_i!) - \log (g_i! - n_i)!] - - - (2)
\]

Using Sterling formula, \((\log n! = n \log n - n)\) in equation (2), we get,

\[
\log W = \sum_{i=1}^{n} [g_i \log (g_i) - g_i - n_i \log (n_i) + n_i - (g_i - n_i) \log (g_i - n_i) + (g_i - n_i)]
\]

Or, \[
\log W = \sum_{i=1}^{n} [g_i \log (g_i) - n_i \log (n_i) - (g_i - n_i) \log (g_i - n_i)] - - - (3)
\]

For this distribution to have maximum probability, small changes in \( \delta n_i \) should not alter the value of \( W \) or \( \log W \) and hence \( \delta W = 0 \) or \( \delta[\log W] = 0 \)

\[
\therefore \delta (\log W) = \sum_{i=1}^{n} \delta\left[ g_i \log (g_i) - n_i \log (n_i) - (g_i - n_i) \log (g_i - n_i) \right] = 0
\]

\[
\Rightarrow \sum_{i=1}^{n} \left[ 0 - \delta n_i \log (n_i) - n_i \left( \frac{\delta n_i}{n_i} \right) - (g_i - n_i) \log (g_i - n_i) - (g_i - n_i) \left( \frac{-\delta n_i}{g_i - n_i} \right) \right] = 0
\]

\[
\Rightarrow \sum_{i=1}^{n} \left[ - \delta n_i \log (n_i) - \delta n_i + (\delta n_i) \log (g_i - n_i) + \delta n_i \right] = 0
\]

\[
\Rightarrow \sum_{i=1}^{n} \left[ - \log (n_i) + \log (g_i - n_i) \right] \delta n_i = 0 - - - (4)
\]

Taking in to account conservation of particles and total energy of the entire system, we get,

\[
\delta N = \sum_{i=1}^{n} \delta n_i = 0 - - - (5)
\]
\[ \delta \sum_i n_i \varepsilon_i = \sum_i \varepsilon_i \delta n_i = 0 \quad (6) \]

Using Lagrange's method of undetermined multipliers, we can multiply equation (5) by \((-\alpha)\) and equation (6) by \((-\beta)\) and adding the resulting equation to (4), we get,
\[ \sum_i \left[ -\log(n_i) + \log(g_i - n_i) - \alpha - \beta \varepsilon_i \right] \delta n_i = 0 \quad (7) \]

Since \( \delta n_i \neq 0 \), the quantity in the brackets must vanish for each value of \('i'. Therefore, we get,
\[ \log \left( \frac{g_i - n_i}{n_i} \right) - \alpha - \beta \varepsilon_i = 0 \quad \Rightarrow \quad \log \left( \frac{g_i - n_i}{n_i} \right) = \alpha + \beta \varepsilon_i \quad \Rightarrow \quad \frac{g_i - n_i}{n_i} = e^{\alpha + \beta \varepsilon_i} \quad \Rightarrow \quad \frac{g_i}{n_i} - 1 = e^{\alpha + \beta \varepsilon_i} \quad \Rightarrow \quad \frac{g_i}{n_i} = e^{\alpha + \beta \varepsilon_i} + 1 \quad \therefore \quad n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + 1} \quad (8) \]

Since \( \beta = \frac{1}{kT} \), hence we can write, \( \therefore \quad n_i = \frac{g_i}{\exp\left( \alpha + \frac{\varepsilon_i}{kT} \right) + 1} \quad (9) \)

Equation (9) is known as Fermi–Dirac distribution law.

**Application to derive Fermi–Dirac distribution law:**

Consider free electron gas in a metal in thermal equilibrium at absolute zero. The electrons are considered to be indistinguishable particles and as they have spin half, they are known as Fermions and hence they obey Fermi–Dirac statistics. At absolute zero, the electrons are in their lowest possible energy levels and hence the energy levels having values from zero to a certain maximum value \( \varepsilon_f \) known as Fermi energy are occupied and the energy levels above \( \varepsilon_f \) are empty.

According to Fermi–Dirac distribution law, the number of particles having their energy between \( \varepsilon \) and \((\varepsilon + d\varepsilon)\) is given by,
\[ n(\varepsilon) d\varepsilon = \frac{g(\varepsilon) d\varepsilon}{\exp\left( \alpha + \frac{\varepsilon}{kT} \right) + 1} = g(\varepsilon) d\varepsilon \ f(\varepsilon) \quad (10) \]

Where, \( f(\varepsilon) = \frac{1}{\exp\left( \alpha + \frac{\varepsilon}{kT} \right) + 1} \quad (11) \) is known as Fermi distribution function.

For a system of electrons enclosed in a volume \( V \), we have,
\[ g(\varepsilon) d\varepsilon = \frac{2 \times 4 \pi \ p^2 dp \times V}{h^3} \quad (12) \]

Equation (12) contains the term 2, because, electrons in a Fermi gas have two spin states.

From equations (10) and (12), we get, \( n(\varepsilon) d\varepsilon = \frac{8 \pi \ p^2 dp \times V}{h^3} \times f(\varepsilon) \).

The total number of electrons in the system is given by,
\[ N = \int_{\varepsilon_f}^{\infty} n(\varepsilon) d\varepsilon = \int_{\varepsilon_f}^{\infty} \frac{8 \pi \ p^2 dp \times V}{h^3} \times f(\varepsilon) = \frac{8 \pi V}{h^3} \int_{\varepsilon_f}^{\infty} p^2 dp \times f(\varepsilon) \quad (13) \]

At absolute zero, \( f(\varepsilon) = 1 \ for \ \varepsilon < \varepsilon_f \ and \ f(\varepsilon) = 0 \ for \ \varepsilon > \varepsilon_f \) and hence equation (13) can be written as,
\[ N = \frac{8\pi V}{h^3} \int_{\varepsilon=0}^{\varepsilon_f} p^2 dp = \frac{8\pi V}{h^3} \times \left( \frac{p^3}{3} \right)^{\varepsilon=\varepsilon_f} \quad - - - (14) \]

But, \( p^2 = 2m\varepsilon \) & \( p = \sqrt{2m\varepsilon} \) and hence, \( N = \frac{8\pi V}{h^3} \times \left( \frac{(2m\varepsilon)^{3/2}}{3} \right)^{\varepsilon=\varepsilon_f} = \frac{8\pi V}{h^3} \times \frac{(2m\varepsilon_f)^{3/2}}{3} \)

\[ 3N \ h^3 = 8\pi V \times (2m)^{3/2} \times (\varepsilon_f)^{3/2} : \varepsilon_f = \left[ \frac{3N \ h^3}{8\pi V \times (2m)^{3/2}} \right]^{3/2} = \frac{h^2}{2m} \times \left( \frac{3n}{8\pi} \right)^{3/2} - - - (15) \]

Where \( n = N/V \) is the density of electrons [number of electrons per unit volume] in the free electron gas. Equation (15) gives the relation for Fermi energy of electron gas at absolute zero.

### Comparison between the three Statistics

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Maxwell - Boltzmann</th>
<th>Fermi - Dirac</th>
<th>Bose - Einstein</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Particles are distinguishable and only particles are taken into consideration</td>
<td>Particles are indistinguishable and quantum states are taken into consideration</td>
<td>Particles are indistinguishable and quantum states are taken into consideration</td>
</tr>
<tr>
<td>2</td>
<td>There is no restriction on the number of particles in a given state</td>
<td>Only one particle may be in a given quantum state</td>
<td>No restriction on the number of particles in a given quantum state.</td>
</tr>
<tr>
<td>3</td>
<td>Applicable to ideal gas molecules</td>
<td>Applicable to electrons and elementary particles</td>
<td>Applicable to photons and symmetrical particles.</td>
</tr>
<tr>
<td>4</td>
<td>Internal energy of ideal gas molecules at absolute zero is taken as zero.</td>
<td>Even at absolute zero, the energy is not zero.</td>
<td>The energy at absolute zero is taken to be zero.</td>
</tr>
<tr>
<td>5</td>
<td>- - -</td>
<td>At high temperature, Fermi distribution approaches Maxwell – Boltzmann distribution.</td>
<td>At high temperature, Bose – Einstein distribution approaches Maxwell – Boltzmann distribution.</td>
</tr>
<tr>
<td>6</td>
<td>The most probable distribution is given by, ( \frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \varepsilon_i}} )</td>
<td>The most probable distribution is given by, ( \frac{n_i}{g_i} = \frac{1}{[e^{\alpha + \beta \varepsilon_i} - 1]} )</td>
<td>The most probable distribution is given by, ( \frac{n_i}{g_i} = \frac{1}{[e^{\alpha + \beta \varepsilon_i} + 1]} )</td>
</tr>
</tbody>
</table>