

Unit-1: Classical Statistics

Postulates of classical statistical mechanics:

The fundamental Postulates of statistical mechanics are:

1. A gas may be assumed to be consisting of mobile molecules which behave like very small elastic spheres.
2. All the cells in the phase space are of equal volume.
3. All accessible microstates corresponding to possible macrostate are equally probable. This is called the postulate of equal a Priori probability.
4. The equilibrium state of a gas corresponds to the macrostate of maximum probability.
5. The total number of molecules is constant.

Phase space:

Phase space is a concept of multidimensional space in which the coordinates represent the variables required to specify the state of the system, in particular a six-dimensional space incorporating three dimensions of position and three of momentum.

Phase space is a concept which is generalised by combining position space and momentum space. Imagine that a space is represented by six axes, viz., x, y, z, p_x, p_y and p_z axes and a point in space has co-ordinates (x, y, z, p_x, p_y, p_z) . Thus, a point in such six dimensional space represents position as well as momentum and such a space is called phase space. In other words, a combination of the position space and momentum space is known as phase space. For each particle, there are six coordinates and in a system containing n particles, there are $6n$ coordinates giving complete information regarding position and momentum of all the n particles in the phase space for a dynamic system. Phase of the motion of a particle, i.e., position and momentum of the particle can be represented by a point in phase space. Such a point is called phase point corresponding to that particle. Classically, a particle can have definite position x and definite momentum p_x and hence in two dimensional (x, p_x) phase space the state is represented by a point, as shown in Fig. 3.3. A small volume element in phase space is denoted by $d\tau$ and is given by

$$d\tau = dx dy dz dp_x dp_y dp_z$$

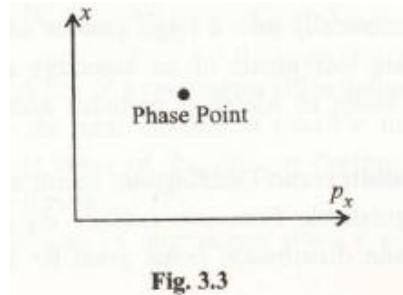


Fig. 3.3

Phase Cells: The phase space can be divided into a large number of cells, each of volume $d\tau$. Such cells are called phase cells. In classical statistics (or Maxwell-Boltzmann statistics) there is no restriction on the volume of the phase cell which may be very small tending to zero also. In Quantum statistics, there is uncertainty. According to Heisenberg's uncertainty principle, we have

$$dx dp_x \geq h$$

$$dy dp_y \geq h$$

$$dz dp_z \geq h$$

So that $d\tau \geq h^3$

Where h is the Planck's constant of action having a value $6.63 \times 10^{-34} \text{ JS}$.

A more detailed analysis shows that

$$d\tau = h^3$$

The value of $h^3 = (6.63 \times 10^{-34})^3 = 2.9 \times 10^{-100} \text{ J}^3 \text{ S}^3$

This is the minimum size of the cell in quantum mechanics. Thus, due to uncertainty principle, a "point" in phase space is in fact a cell of minimum volume h^3 . A point (x, y, z, p_x, p_y, p_z) in phase space specifies that quantum mechanically, the particle lies somewhere in a cell of volume h^3 centred at the point.

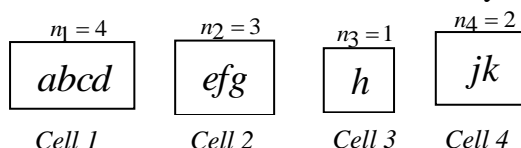
Macrostate and Microstate:

The macrostate of a system refers to its macroscopic properties, such as its temperature, pressure, volume, density or number of particles. A macrostate of the system is defined by the specification of the number of phase point in each phase cell of phase space. (A macrostate is a collection of variables that describe the bulk system such as total internal energy, volume and number of particles if we are talking about a gas for example. It could also describe related concepts which we will encounter later such as temperature, pressure and chemical potential)

A microstate is a huge collection of variables equal to the number of microscopic degrees of freedom in the system. Thus a given macrostate typically corresponds to a huge number of microstates i.e. different microstates can correspond to the same macrostate. A microstate of the system is defined as the specification that at which cell, the which phase point of system belongs temporarily i.e. microstates describes the different possible ways the system can achieve in a particular macrostate. Each possible combination of positions and velocities (momentum) of all molecules refers to a microstate of the system. In other words we may say that in order to define a microstate we must state to which cell each molecule of the system belongs temporarily.

Let there be cell 1, cell 2, cell 3 and cell 4 in phase space. Suppose there are four phase points $abcd$ in cell 1, three phase point efg in cell 2, one phase point h in cell 3 and two phase points jk in cell 4 as shown in figures.

The macrostate of figure is specified by merely giving the phase points $n_1 = 4, n_2 = 3, n_3 = 1, n_4 = 2$ of different cells. This also represents a particular microstate by specifying the positions of phase points $abcd$ in cell 1, efg in cell 2 and so on. Now if the two phase points a and e from different cells are interchanged, then the microstate is changed because the positions of two phase points are changed, while the macrostate remains the same as the number of phase points in cells remains the same. Similarly, with the same macrostate we can consider different microstates. Thus many different microstates may correspond to the same macrostate.



Thus, a microstates change every moment but macrostate does not. For every macrostate there are several microstates. All allowed microstates are equally likely i.e. possibility of each microstate to be at a particular time is equal.

The microstates, which are allowed under given restriction (constrain) are called *accessible microstates*.

e.g.: In the restriction that three molecules a, b, c be distributed in 2 box so that no molecule be outside the box. So the accessible microstate can be (ab, c) , (a, bc) and inaccessible is (a, b) , (a, c) .

One of the most fundamental postulates of statistical mechanics is that all accessible microstates corresponding to a possible macrostate are equally probable.

Ensembles:

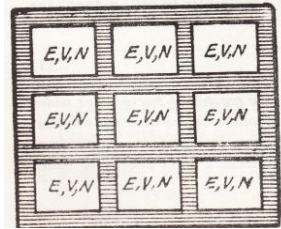
If we have a collection of particles, we shall refer to a single particle as a system and to the collection of particles as a whole as an assembly. The collection of a large number of assemblies is called as an ensemble. The numbers of the ensemble are identical in features (like volume, energy, total number of particles etc.) and are known as element.

Thus an ensemble is defined as a collection of a very large number of assemblies which are essentially independent of one another but which have been made macroscopically as identical as possible. By being macroscopically identical, we mean that each assembly is characterized by the same values of set of macroscopic parameters which uniquely determine the equilibrium state of the assembly.

In an ensemble, the system play the same role as the non-interacting molecules do in a gas. The macroscopic identity of the systems constituting an assembly can be achieved by choosing the same values of some set of macroscopic parameters. These parameters uniquely determine the equilibrium state of the system. Accordingly three types of ensembles i.e., microcanonical, canonical and grand canonical are most widely used.

Microcanonical ensemble:

The microcanonical ensemble is a collection of essentially independent assemblies having the same energy E , volume V , and number N of systems, all the systems are of the same type. The individual assemblies are separated by rigid, impermeable and well insulated walls (Fig. 1) such that the values of E , V and N are not affected by the presence of other systems.



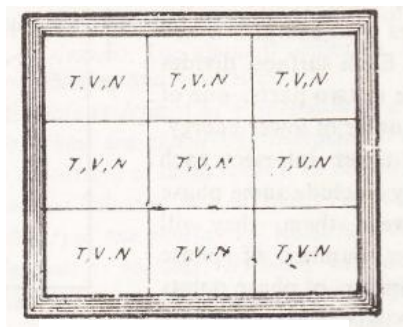
Microcanonical Ensemble

Canonical ensemble:

The canonical ensemble is a collection of essentially independent assemblies having the same temperature T , volume V , and number of identical particles N . To assure ourselves that all the assemblies have the same temperature, we could bring each in thermal contact with a large heat reservoir at temperature T or we could simply bring all of the assemblies in thermal contact with each other.

Fig. 2, represents symbolically a canonical ensemble. The individual assemblies are separated by rigid, impermeable, but diathermic walls. Since energy can be exchanged between the assemblies, they will reach a common temperature.

Thus in canonical ensemble, system can exchange energy but not particles.



Canonical Ensemble

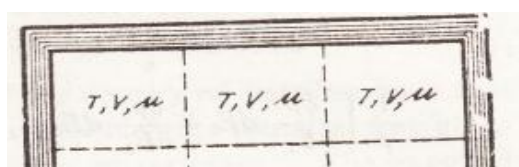
Grand canonical ensemble:

The microcanonical ensemble is a collection of independent assemblies having the same energy E , volume V and number N of system and the canonical ensemble is a collection of independent assemblies having the same temperature T , volume V and number of identical systems N . Thus in going from microcanonical ensemble to canonical ensemble, the condition of constant energy has been relaxed. This simplifies the calculations in thermodynamics where the exchange of energy takes place. Now the next logical step is to abandon the condition of total number of particles. Actually in chemical process this number varies and in various physical problems, e.g., radioactive decay, it is difficult to keep the number of particles constant. Such an ensemble in which exchange of energy as well as of particles takes place with the heat reservoir is known as grand canonical ensemble.

The grand canonical ensemble is a collection of essentially independent assemblies having the same temperature T , volume V and a chemical potential μ .

In the grand canonical ensemble we then effectively have a collection of assemblies, each occupying a separate volume V , but which can exchange energy and molecules as well with each other. Fig.3, represents 1 grand canonical ensemble. The individual assemblies systems are separated by rigid, permeable, diathermic walls.

The grand canonical ensemble will thus correspond to the situation when we know both the average energy and the average number of Particles in assembly, but are otherwise completely ignorant about the state of the system.



Thermodynamic Probability:

A thermodynamic system is taken, having a cylinder and filled with an ideal gas of total number of molecules (N) and they are distributed in (k) energy cells. Let n_1 molecules enter in cell one, n_2 molecules enter in cell two, n_3 molecules enter in cell three and so on ..., n_k molecules enter in cell k . So it is obvious that

$$n_1 + n_2 + n_3 + \dots + n_k = N$$

$$\Rightarrow \sum_{i=1}^k n_i = N \quad \text{--- (1)}$$

The number of ways to distribute n_1 molecule in cell one is

$${}^N C_{n_1} = \frac{N!}{n_1!(N-n_1)!} \quad \text{--- (2)} \quad C = \text{Cell}$$

The no of ways to distribute n_2 molecule in cell two will be

$${}^{N-n_1} C_{n_2} = \frac{(N-n_1)!}{n_2!(N-n_1-n_2)!} \quad \text{--- (3)}$$

The no of ways to distribute n_3 molecule in cell three will be

$${}^{N-n_1-n_2} C_{n_3} = \frac{(N-n_1-n_2)!}{n_3!(N-n_1-n_2-n_3)!} \quad \text{--- (4)}$$

The no of ways to distribute n_k molecules in cell k will be

$$\begin{aligned} {}^{N-n_1-n_2-n_3-\dots-n_{k-1}} C_{n_k} &= \frac{(N-n_1-n_2-n_3-\dots-n_{k-1})!}{n_k!(N-n_1-n_2-n_3-\dots-n_k)!} \\ &= \frac{(N-n_1-n_2-n_3-\dots-n_{k-1})!}{n_k![N-(n_1+n_2+n_3+\dots+n_k)]!} \\ &= \frac{(N-n_1-n_2-n_3-\dots-n_{k-1})!}{n_k![N-N]!} \\ &= \frac{(N-n_1-n_2-n_3-\dots-n_{k-1})!}{n_k! \cdot 0!} \quad \because 0! = 1 \\ &= \frac{(N-n_1-n_2-n_3-\dots-n_{k-1})!}{n_k!} \quad \text{--- (4)} \end{aligned}$$

So, the total chances for such type of molecular distribution in all cells will be

$$\begin{aligned} {}^N C_{n_1} \times {}^{N-n_1} C_{n_2} \times {}^{N-n_1-n_2} C_{n_3} \times \dots \times {}^{N-n_1-n_2-n_3-\dots-n_{k-1}} C_{n_k} \\ = \frac{N!}{n_1!(N-n_1)!} \times \frac{(N-n_1)!}{n_2!(N-n_1-n_2)!} \times \frac{(N-n_1-n_2)!}{n_3!(N-n_1-n_2-n_3)!} \times \dots \times \frac{(N-n_1-n_2-n_3-\dots-n_{k-1})!}{n_k!} \\ = \frac{N!}{n_1! n_2! n_3! \dots n_k!} \quad \text{--- (6)} \end{aligned}$$

Since, the total chance of distribution of N molecules in k cells is known as its thermodynamic probability. It is represented by w or Ω . Therefore,

$$w \text{ or } \Omega = \frac{N!}{n_1! n_2! n_3! \dots n_k!} \Rightarrow w = \frac{N!}{\prod_{i=1}^k n_i!} \quad \text{--- (7)}$$

(Thermodynamic probability: Thermodynamic probability (w) is the number of possible microstates of a particular macrostate.)

Distribution Law:

In practices there are three most probable distribution law are used. They are

1. **Maxwell – Boltzmann distribution law (M-B):** Maxwell Boltzmann statistics is applicable to the identical distinguishable particles of any spin. e.g: molecules of a gas.
2. **Bose – Einstein distribution law (B-E):** Bose Einstein statistics is applied to the identical indistinguishable particles of zero or integral spin. These particles are called Bosons. Example: He-atom at low temperature, Photon, Phonon (energy generated by lattice vibration)
3. **Fermi – Dirac distribution law (F-D):** Fermi Dirac statistics is applicable to identical indistinguishable particles of half integral spin. They obey Pauli's exclusion principle and are called fermions. Example: electrons, Proton, Neutron etc.

Maxwell Boltzmann Distribution Law:

Let us consider a system of N distinguishable molecules of a gas. Suppose n_1 of them have energy E_1 , n_2 have energy E_2 n_i have energy E_i and so on. Thus the entire assembly of molecules can be divided into different energy states with energies $E_1, E_2, E_3, \dots, E_i$ and having $n_1, n_2, n_3, \dots, n_i$ molecules.

- (i) The total number of molecules N is constant. Hence

$$N = n_1 + n_2 + n_3 + \dots + n_i = \text{Constant}$$

$$\therefore \delta N = \delta n_1 + \delta n_2 + \delta n_3 + \dots + \delta n_i = 0$$

$$\Rightarrow \sum_i \delta n_i = 0 \quad \text{----- (1)}$$

- (ii) The total energy E of the gas molecules is constant. Hence

$$E = E_1 n_1 + E_2 n_2 + E_3 n_3 + \dots + E_i n_i = \text{Constant}$$

$$\therefore \delta E = E_1 \delta n_1 + E_2 \delta n_2 + E_3 \delta n_3 + \dots + E_i \delta n_i = 0$$

$$\Rightarrow \sum_i E_i \delta n_i = 0 \quad \text{----- (2)}$$

Suppose there are g_i cells with the energy E_i , the total no of ways in which n_i molecules can have the energy E_i is given by $(g_i)^{n_i}$. Hence the total number of ways in which N molecules can be distributed among the various energies is

$$W_1 = (g_1)^{n_1} (g_2)^{n_2} \dots (g_i)^{n_i}$$

The number of ways in which the groups of $n_1, n_2, n_3, \dots, n_i$ particles can be chosen from N particles is given by

$$W_2 = \frac{N!}{n_1! n_2! n_3! \dots n_i!}$$

Therefore, the number of ways in which N molecules can be distributed among the possible energy level is given by

$$W = W_1 \cdot W_2 = \frac{N!}{n_1! n_2! n_3! \dots n_i!} \cdot (g_1)^{n_1} (g_2)^{n_2} \dots (g_i)^{n_i} \quad \text{----- (3)}$$

Where W is called the thermodynamic probability of the system.

When the gas is in equilibrium then probability is maximum i.e. $\delta W = 0$

Again, When W is maximum, $\log W$ is maximum, i.e. $\delta(\log W) = 0$

Therefore equation (3) becomes

$$\log W = \log N! - \sum \log n_i! + \sum n_i \log g_i$$

By Stirling theorem, $\log n! = n \log n - n$

Therefore,

$$\begin{aligned}\log W &= N \log N - N - \sum n_i \log n_i + \sum n_i + \sum n_i \log g_i \\ \Rightarrow \log W &= N \log N - \sum n_i \log n_i + \sum n_i \log g_i\end{aligned}\quad \text{----- (4)}$$

From equation (4), we have for maximum W

$$\begin{aligned}\Rightarrow \delta \log W &= 0 - \sum n_i \frac{1}{n_i} \delta n_i - \sum \log n_i \delta n_i + \sum \log g_i \delta n_i = 0 \\ \Rightarrow \delta \log W &= - \sum \delta n_i - \sum \log n_i \delta n_i + \sum \log g_i \delta n_i = 0\end{aligned}$$

From equation (1), $\sum_i \delta n_i = 0$

$$- \sum \log n_i \delta n_i + \sum \log g_i \delta n_i = 0 \quad \text{----- (5)}$$

Let us now use the method of Lagrangian undetermined multipliers. For this purpose multiplying equation (1) by $-\alpha$ and equation (2) by $-\beta$ and adding to equation (5), we get

$$\begin{aligned}\sum (-\log n_i + \log g_i - \alpha - \beta E_i) \delta n_i &= 0 \\ \Rightarrow -\log n_i + \log g_i - \alpha - \beta E_i &= 0 \\ \Rightarrow \log n_i &= \log g_i - \alpha - \beta E_i \\ \therefore n_i &= g_i e^{-\alpha} e^{-\beta E_i}\end{aligned}\quad \text{----- (7)}$$

This equation (7) is called M-B statics or distribution law. In terms of temperature,

$$\therefore n_i = g_i e^{-\alpha} e^{-\frac{E_i}{KT}} \quad \text{----- (8)}$$

Where, $\beta = \frac{1}{KT}$, K = Boltzmann constant and T is the absolute temperature.

Limitation of M-B distribution law:

The M-B distribution law has lot of limitations. Some of them are discussed below:

- (i) It is applicable only to an isolated gas of identical molecules in equilibrium, for which the following conditions are satisfied:
 - (a) The mean potential energy due to mutual interaction between the molecules is very small compared to their mean kinetic energy.
 - (b) The gas is dilute, i.e. the number of molecules per unit volume is small, so that the average separation between the molecules is large and hence individual molecules can be distinguished.

Therefore, the important results, such as expression for E , C_V and P , obtained by this method are the same as those derived by applying simple kinetic theory.

- (ii) The expression for the M-B count does not give correct expression for the entropy S of an ideal gas, and thus leads to the Gibbs paradox. To resolve the paradox, the expression must be divided by $N!$.
- (iii) In the expression for entropy of an ideal gas

$$S = Nk \log \left[\frac{2\pi mkT}{h^2} \right]^{\frac{3}{2}} e^{\frac{5}{2}}$$

If we put, $T = 0$, we get,

$$S = Nk \log 0 = \text{negative quantity.} \quad \therefore \log 0 = -\infty$$

Thus, the expression for S does not satisfy the third law of thermodynamics. According to this law, as the temperature of the system approaches the absolute zero, the entropy approaches a constant value S_0 , independent of the system.

- (iv) It cannot be applied to a system of indistinguishable particles. If we apply the M-B distribution law to the thermionic emission, we get the expression for the emission current density

$$J = A_0 T^2 e^{-\frac{\phi}{kT}}$$

Which is not correct. The correct expression which has been verified experimentally is

$$J = A_0 T^2 e^{-\frac{\phi}{kT}}$$

Thermodynamic functions (Entropy) of a Two – Energy levels system: (or Probability distribution and Entropy of a two energy level system)

Let us consider a system of N-independent particles, each of magnetic moment μ that can be parallel or antiparallel in an external magnetic field H . Let $+\varepsilon$ be the energy associated with one orientation and $-\varepsilon$ be the energy associated with another orientation, where $|\varepsilon| = \mu B$.

Let N_+ and N_- be the number of particles of energy $+\varepsilon$ and $-\varepsilon$ respectively, then the total energy of an isolated system is

$$E = N_+\varepsilon - N_-\varepsilon = (N_+ - N_-)\varepsilon = n\varepsilon \quad \text{--- (1)}$$

$$\text{Where, } (N_+ - N_-) = n \quad \text{--- (2)}$$

If total number of particles is N then

$$N = N_+ + N_- \quad \text{--- (3)}$$

Solving equation (2) and (3), we get

$$N_+ = \frac{1}{2}(N + n) \quad \text{and} \quad N_- = \frac{1}{2}(N - n) \quad \text{--- (4)}$$

Now, we want to find out the number of accessible microstates of isolated system having constant energy E . The accessible microstates, according to formula, are given by

$$\Omega(n) = \frac{N!}{N_+! N_-!} \quad \text{--- (5)}$$

$$\Rightarrow \log \Omega = \log N! - \log N_+! - \log N_-!$$

$$\Rightarrow \log \Omega = N \log N - N - N_+ \log N_+ + N_+ - N_- \log N_- + N_-$$

$$\Rightarrow \log \Omega = (N_+ + N_-) \log N - (N_+ + N_-) - N_+ \log N_+ + N_+ - N_- \log N_- + N_-$$

$$\Rightarrow \log \Omega = N_+ \log N + N_- \log N - N_+ - N_- - N_+ \log N_+ + N_+ - N_- \log N_- + N_-$$

$$\Rightarrow \log \Omega = N_+ \log N + N_- \log N - N_+ \log N_+ - N_- \log N_-$$

$$\Rightarrow \log \Omega = N_+ \log \frac{N}{N_+} + N_- \log \frac{N}{N_-}$$

$$\Rightarrow \log \Omega = - \left[N_+ \log \frac{N_+}{N} + N_- \log \frac{N_-}{N} \right]$$

Using equation (4), we get

$$\begin{aligned} \Rightarrow \log \Omega &= - \left[N_+ \log \frac{\frac{1}{2}(N+n)}{N} + N_- \log \frac{\frac{1}{2}(N-n)}{N} \right] \\ \Rightarrow \log \Omega &= - \left[N_+ \log \frac{1}{2} \left(1 + \frac{n}{N} \right) + N_- \log \frac{1}{2} \left(1 - \frac{n}{N} \right) \right] \quad \text{--- (6)} \end{aligned}$$

$$\text{Since, } \log \left(1 \pm \frac{n}{N} \right) = \pm \frac{n}{N} - \frac{n^2}{2N^2} \pm \dots \quad \text{--- (7)}$$

Using equation (7) in (6), we get

$$\Rightarrow \log \Omega = -N_+ \left[\log \frac{1}{2} + \left(\frac{n}{N} - \frac{n^2}{2N^2} \right) \right] - N_- \left[\log \frac{1}{2} + \left(-\frac{n}{N} - \frac{n^2}{2N^2} \right) \right]$$

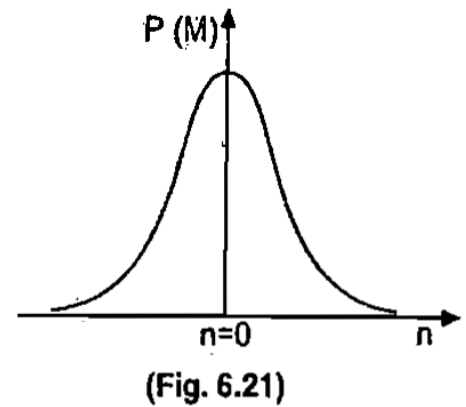
$$\begin{aligned}
\Rightarrow \log \Omega &= -N_+ \log \frac{1}{2} - N_+ \left(\frac{n}{N} - \frac{n^2}{2N^2} \right) - N_- \log \frac{1}{2} - N_- \left(-\frac{n}{N} - \frac{n^2}{2N^2} \right) \\
\Rightarrow \log \Omega &= -(N_+ + N_-) \log \frac{1}{2} - (N_+ + N_-) \left(\frac{n}{N} - \frac{n^2}{2N^2} \right) \\
\Rightarrow \log \Omega &= -N \log \frac{1}{2} - N \left(\frac{n}{N} - \frac{n^2}{2N^2} \right) \\
\Rightarrow \log \Omega &= -N \log \frac{1}{2} - \frac{n^2}{2N} \quad \text{--- (8)}
\end{aligned}$$

As there are only two possible orientations, the probability of each orientation is $\frac{1}{2}$. As the total number of particles is N and then all are independent, therefore the probability of a given sequence of particle is $\left(\frac{1}{2}\right)^N$.

The net magnetic moment = $(N_+ - N_-) \mu = n\mu$

The probability $P(M)$ of the system to possess the net magnetic moment $M = n\mu$ is given by

$$\begin{aligned}
P(M) &= \left(\frac{1}{2}\right)^N \cdot \Omega(n) \\
\Rightarrow P(M) &= \left(\frac{1}{2}\right)^N \cdot \exp[\log \Omega(n)] \\
\Rightarrow P(M) &= \left(\frac{1}{2}\right)^N \cdot \exp \left[-N \log \frac{1}{2} - \frac{n^2}{2N} \right] \\
\Rightarrow P(M) &= \left(\frac{1}{2}\right)^N \cdot \exp \log \left(\frac{1}{2} \right)^{-N} \cdot \exp \left(-\frac{n^2}{2N} \right) \\
\Rightarrow P(M) &= \left(\frac{1}{2}\right)^N \cdot \left(\frac{1}{2} \right)^{-N} \cdot \exp \left(-\frac{n^2}{2N} \right) \\
\Rightarrow P(M) &= e^{-\frac{n^2}{2N}} \quad \text{----- (9)}
\end{aligned}$$



This represents Gaussian distribution, which is symmetrical about the value $n=0$ (fig.6.21). As expected the average value of magnetization in the absence of an external magnetic field is zero. The most probable value is same as the average value. The entropy is given by

$$\begin{aligned}
S &= k \log \Omega \\
\Rightarrow S &= -k \left[N_+ \log \frac{N_+}{N} + N_- \log \frac{N_-}{N} \right] \quad \text{---- (10)}
\end{aligned}$$

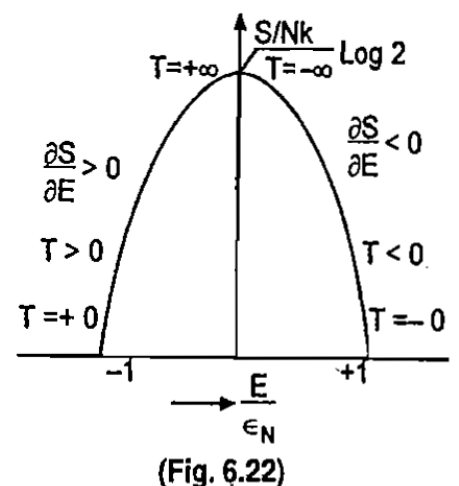
If we use to approximation (8), we get

$$\begin{aligned}
S &= k \log \Omega = -k \left[N \log \frac{1}{2} + \frac{n^2}{2N} \right] \\
\Rightarrow S &= -Nk \left[-\log 2 + \frac{n^2}{2N^2} \right] \quad \text{---- (11)}
\end{aligned}$$

Using equation (1) for n , we get

$$\begin{aligned}
S &= -Nk \left[-\log 2 + \frac{\frac{E^2}{\epsilon^2 N^2}}{2N^2} \right] \\
\Rightarrow S &= -Nk \left[-\log 2 + \frac{1}{2} \left(\frac{E}{\epsilon N} \right)^2 \right] \quad \text{--- (12)}
\end{aligned}$$

$$\Rightarrow \frac{S}{Nk} = \log 2 - \frac{1}{2} \left(\frac{E}{\epsilon N} \right)^2 \quad \text{--- (13)}$$



If we plot a graph of $\frac{S}{Nk}$ versus $\frac{E}{\epsilon N}$ we get, parabola as shown in fig.6.22.

Negative Temperature:

The temperature (T) is defined as the reciprocal of slop of entropy S versus energy E curve i.e.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N}$$

But, $E = n\epsilon$

$$\therefore \frac{1}{T} = \frac{1}{\epsilon} \left(\frac{\partial S}{\partial n} \right)$$

Using equation (10), we get

$$\frac{1}{T} = \frac{1}{\epsilon} \left(\frac{\partial S}{\partial n} \right) = -\frac{k}{\epsilon} \frac{\partial}{\partial n} \left[N_+ \log \frac{N_+}{N} + N_- \log \frac{N_-}{N} \right] \quad \therefore S = -k \left[N_+ \log \frac{N_+}{N} + N_- \log \frac{N_-}{N} \right]$$

Using equation (4) for N_+ and N_- , we get

$$\frac{1}{T} = -\frac{k}{\epsilon} \frac{\partial}{\partial n} \left[\frac{1}{2}(N+n) \log \frac{1}{2} \frac{(N+n)}{N} + \frac{1}{2}(N-n) \log \frac{1}{2} \frac{(N-n)}{N} \right] \quad \therefore N_+ = \frac{1}{2}(N+n) \text{ and } N_- = \frac{1}{2}(N-n)$$

Simplifying, we get

$$\begin{aligned} \frac{1}{T} &= \frac{1}{2} \frac{k}{\epsilon} \log \frac{N-n}{N+n} \\ \Rightarrow \frac{1}{T} &= \frac{1}{2} \frac{k}{\epsilon} \log \frac{N_-}{N_+} \end{aligned}$$

At the conventional absolute zero temperature all the particles are in lower energy state $-\epsilon$.

$$\therefore n = N_+ - N_- = 0 - N = -N \leq 0, \text{ giving } T = +\infty \text{ and } S = 0 \text{ at } E = -N\epsilon.$$

As the temperature is raised, the energy is supplied to system and particles jump from energy state $-\epsilon$ to energy state $+\epsilon$, so the upper level $+\epsilon$ grows at $T > 0$, till we have $n = 0$, giving probability $S' = Nk \log 2$, a state of maximum disorder and $T = +\infty$. If more energy is supplied to system, the upper level becomes more populated than the lower level i.e. $N_+ > N_-$ and so $n > 0$ and we get a decrease in entropy S (more ordered state) and $T < 0$ (negative temperature). Thus the system loses its normal behaviour. Thus the negative temperature T_- corresponds to higher energies than positive temperature T_+ .

For a system to have negative temperature, the following conditions must be satisfied.

- (i) It must have a finite upper limit to the energy spectrum.
- (ii) It must be in thermal equilibrium.
- (iii) It must have negative temperature states isolated from positive temperature state.