



Classical and quantum assemblies :

If the systems in an assembly obey classical mechanics then a limitation will be imposed on the energies of the systems only if there is a definite total energy for the assembly.

Also each of these classical systems will be completely distinguishable from every other system in the assembly even if the systems all belong to the same species of particle.

If, on the other hand the systems in the assembly obey quantum mechanics, there will only be certain discrete energy levels which are available to the systems rather than the continuum of energies which are available to the classical systems. For example in the case of the simple harmonic oscillator the only values of energy which the oscillator can take are given by $(n + \frac{1}{2}) h \nu$ where (n) is an integer, (h) is Planck's constant and (ν) is the oscillator frequency.



there are two types of quantum mechanical system - If a system has an angular momentum which is half-integral in units of $(h/2\pi)$ or which is equivalent, has an antisymmetric wave function, then it will obey the Pauli exclusion principle. Such a system (e.g. an electron or Proton) is known as fermion and will be restricted in its occupation of energy states in that no single state can be occupied by more than one such system. On the other hand, a system which has an integral value of angular momentum, and hence a symmetric wave function, will not obey the Pauli exclusion principle. This type of system (e.g. a photon or an alpha particle) is known as a boson and there is no restriction on the number of such systems which may occupy a given energy state.



Maxwell - Boltzmann Statistics :-

The Purpose of Statistical Physics to enable the macroscopic Properties to be described in terms of the microscopic Properties of the molecules without involving the detailed calculation of the individual molecules.

Description of the assemblies - Phase space -
the state of a system is defined by a six-dimensional space (x, y, z, p_x, p_y, p_z) which is termed Phase-space or Γ -space.

$$dV = dx dy dz \Rightarrow \text{an element of volume in Euclidean space}$$

$$d\Gamma = dx dy dz dp_x dp_y dp_z \Rightarrow \text{an element of volume in phase space}$$

the state of an assembly of (N) systems defined in terms of $6N$ coordinates.

$6N$ -dimensional Phase space (Γ_N -space)

$$d\Gamma_{6N} = \prod_{i=1}^{i=N} dx_i dy_i dz_i dp_{x_i} dp_{y_i} dp_{z_i}$$

$$= \prod_{i=1}^N (d\Gamma_i)$$



where $(d\Gamma)_i$ is the volume element of the six-dimensional phase space for the i th system.

Distribution over energies :

The distribution of the systems over the various energies which are available

$$: E_1, E_2, E_3, \dots, E_i, \dots, E_N$$

$$\sum_{i=1}^{i=N} E_i = E_{\text{total}}$$

Consider the energies of the system can be divided into sheets (S), the effective energy of the system in the sheet is (E_s) , the number of energy states available to the systems in the sheet (S) is (g_s) is called the weight of the sheet, or the degeneracy of the sheet.



The distribution of the systems over the various energies is given by specifying the occupation number (n_s) of systems with energy E_s .

The total of the occupation number.

$$\sum_{s=1}^r n_s = N$$

The total energy of the assembly is

$$\sum_{s=1}^r n_s E_s = E_{\text{Total}}$$

* The over all configuration of the assembly for which only the numbers of systems in an energy sheet are specified is sometimes referred to as a macrostate.

* The Particular arrangement of the assembly in which the actual system occupying a given energy state is specified, are



Known as microstate.

Example :

Assume there are four systems, labelled a, b, c and d are distributed over two energy sheets of weight $g=3$ and $g=4$ respectively (distribution over two sheets with two systems in sheet 1 and two system in sheet 2).

Sheet 1 : $g=3$, $n_s=2$

a	b		b	a		a		b	a	d	
---	---	--	---	---	--	---	--	---	---	---	--

Sheet 2 : $g=4$, $n_s=2$

c	d			c		a		a	b	c			a
---	---	--	--	---	--	---	--	---	---	---	--	--	---

Calculate the total number of arrangement (the weight of the configuration) or the total thermodynamics probability W .

Solution:

$$W = N! \prod_s \left(\frac{g_s^{n_s}}{n_s!} \right)$$

$$\therefore W = 4! \prod_s \left[\frac{3^2}{2 \times 1} \times \frac{4^2}{2 \times 1} \right] = 24 \times 36 = 864$$

calculation show that, in the classical case where the systems are completely distinguishable there are (864) possible arrangements corresponding to given configuration.

If the energies of the systems are spread over a total of (r) energy sheets then the distribution may be written in terms of the occupation numbers as follows:

Sheet number	1	2	3	...	s	...	r
Sheet energy	E_1	E_2	E_3	...	E_s	...	E_r
weight of sheet	g_1	g_2	g_3	...	g_s	...	g_r
Occupation number	n_1	n_2	n_3	...	n_s	...	n_r

where the total of the occupation numbers $\sum_{s=1}^r n_s$ is equal to the total number of systems, N .

the energy of the systems in the sheet (s) is ($n_s E_s$) and the total energy of the assembly is $\left(\sum_{s=1}^r n_s E_s \right)$.



Weight of Configuration (w) :

The number of distinct arrangement of the system which all correspond to the particular configuration, (The Probability That an assembly is in the given configuration will be proportional to the weight of the configuration).

$$N - n_1 - n_2 \quad \text{-----} \quad n_3$$

$$N - n_1 \quad \text{-----} \quad n_2$$

$$N \quad \text{-----} \quad n_1$$

$${}^N C_{n_1} = \frac{N!}{n_1! (N - n_1)!} \quad \Rightarrow \text{For the First sheet}$$

$${}^{N-n_1} C_{n_2} = \frac{(N - n_1)!}{n_2! (N - n_1 - n_2)!} \quad \Rightarrow \text{For the 2nd sheet}$$

* The total number of ways of choosing the configuration (for 3 sheets) -



$$W = \left[\frac{N!}{n_1! n_2! n_3!} \right]$$

* in the energy sheet (ϵ_s) there are (g_s) energy states, N_s systems in this sheet may be placed in (g_s) ways of arranging the (N_s) system within the sheet (ϵ_s), the weight of configuration

$$W = \frac{N!}{n_1! n_2! n_3!} (g_1^{n_1}, g_2^{n_2}, \dots, g_s^{n_s})$$

$$W = N! \prod \left[\frac{g_s^{n_s}}{n_s!} \right]$$

Ex: Consider two cells i and j in the phase space and four phase point (a, b, c, d), find the weight configuration.

N_i	4	3	2	1	0
N_j	0	1	2	3	4



$$W = \frac{N!}{\prod N_i!} = \frac{N!}{N_1! N_2! N_3!}$$

$$\textcircled{1} \left. \begin{matrix} N_i = 4 \\ N_j = 0 \end{matrix} \right\} \Rightarrow W_1 = \frac{N!}{N_i! N_j!} = \frac{4!}{4! 0!} = 1$$

N_i	abcd
N_j	0

$$\textcircled{2} \left. \begin{matrix} N_i = 3 \\ N_j = 1 \end{matrix} \right\} \Rightarrow W_2 = \frac{4!}{3! 1!} = 4$$

N_i	abc	bcd	cda	dab
N_j	d	a	b	c

$$\textcircled{3} \left. \begin{matrix} N_i = 2 \\ N_j = 2 \end{matrix} \right\} \Rightarrow W_3 = \frac{4!}{2! 2!} = \boxed{6} \text{ most probable}$$

N_i	ab	bc	cd	da	ac	bd
N_j	cd	ad	ab	bc	bd	ac

$$\textcircled{4} \left. \begin{matrix} N_i = 1 \\ N_j = 3 \end{matrix} \right\} \Rightarrow W_4 = \frac{4!}{1! 3!} = 4$$

N_i	a	b	c	d
N_j	bcd	acd	abd	abc

$$\textcircled{5} \left. \begin{matrix} N_i = 0 \\ N_j = 4 \end{matrix} \right\} \Rightarrow W_5 = \frac{4!}{0! 4!} = 1$$

N_i	0
N_j	abcd

$\therefore$ The total number of possible macrostates = 5

and the total number of possible microstates is:

$$\sum_{k=1}^5 W_k = W_1 + W_2 + W_3 + W_4 + W_5$$

$$= 1 + 4 + 6 + 4 + 1 = 16$$