

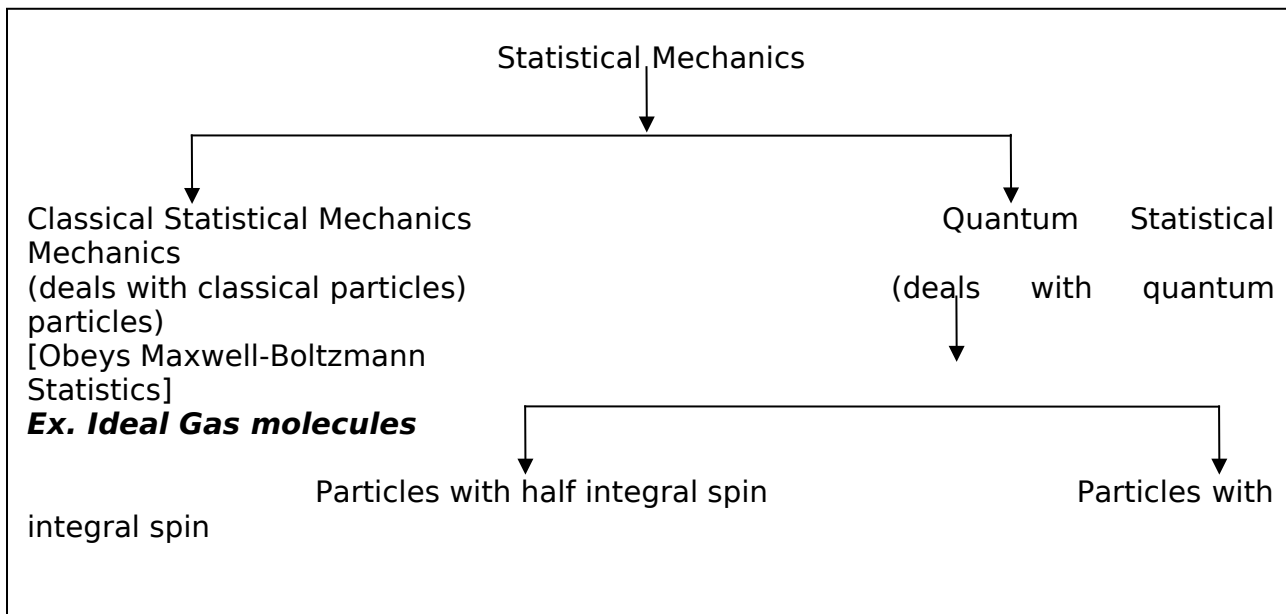
# Statistical Mechanics

## 1. Introduction:

Statistical mechanics deals with the mechanical systems that are in equilibrium or near to one. It is statistical because it makes a statistical prediction of large number of particles of the system. Statistical mechanics is that branch of physics which studies macroscopic systems from a microscopic or molecular point of view. The goal of statistical mechanics is the understanding and prediction of macroscopic phenomena and the calculation of macroscopic properties from the properties of the individual molecules making up the system. Thus the aim of statistical mechanics is to derive the general laws of thermodynamics and all thermodynamic relations for a given system. The main object of statistical physics can be formulated as follows: **“To establish the laws governing the behavior of macroscopic quantity of a system by using the laws governing the behavior of the particles of that system in thermal equilibrium”**. In principle, we should obtain a complete description of the properties of a macroscopic thermodynamic system obeying the laws of classical mechanics, if we could set up and solve the equation of motion for each and every individual particle of the system. But in practice this is not possible on account of a great number of equations we will have to deal with. For example  $1 \text{ cm}^3$  of a gas under normal temperature and pressure contains  $2.7 \times 10^{19}$  molecules. Assuming that each molecule has three degrees of freedom, we will have to set up and solve  $3 \times 2.7 \times 10^{19}$  equations of motion for  $1 \text{ cm}^3$  of the gas. Even if we could solve so many equations the solutions would be in terms of mass, position, velocity, energy of each molecules, etc. and not in terms of thermodynamic variables such as pressure, entropy, etc. thus there is a gap between the results of classical mechanic and thermodynamics. It is the theory of statistical mechanics which provides the link between the mechanical properties and thermodynamical properties of systems.

It has been applied to gases, liquids, solutions, polymers, metals, the electrical properties of matter, DNA and other biological systems, among others. Statistical mechanics basically takes advantage of the fact that molecules are very numerous and average properties of a large number of molecules can be calculated even in the absence of any information about specific molecules.

## 2. Classification of Statistical Mechanics



[Obeys Fermi-Dirac Statistics]  
Einstein Statistics]  
**Ex. Electron, proton, neutron, phonon, deuterons,  $\pi$  He<sup>3+</sup> atom,  $\mu$ -meson, etc. atom etc.**

[Obeys Bose-  
Ex. **Photon, meson, He<sup>4+</sup>**

### 3. Quantum States (Energy States), Energy Levels and Degeneracy:

Some important discussions now follow whose understanding will be critically important for your progress in this class. Each quantum state is defined by a unique set of quantum numbers and a given value of the energy. The energy is a function of one or more of the quantum numbers defining the quantum state. Two examples are cited below to illustrate these points.

Systems	Electron in a Hydrogen atom	Particle of mass $m$ in a cubic box of side $L$
Energy levels	$E_n = -13.6/n^2 \text{ eV}$ <p>where <math>n = 1, 2, 3, \dots</math></p>	<p>where</p> $n_x, n_y, n_z = 1, 2, 3, \dots; i = 1, 2, 3, \dots$
Quantum States	$\{n, l, m_l, s\}$	$\{n_x, n_y, n_z\}$
Degeneracy	$g_n = 2n^2$	$g(E) \propto E^{\frac{1}{2}} \text{ (levels closely spaced)}$

Students, identify the symbols used in the above table. Recall that the degeneracy of an energy level is the number of different quantum states corresponding to that level and always increases with energy as far as we are concerned. Let us take an example as stated below.

**Example:** Write down the possible quantum states corresponding to the first excited state ( $n=2$ ) of the hydrogen atom. Verify that the number of these states is indeed 8.

**Possible electronic states** in a Hydrogen atom

Energy level	$n$	$l$	$m_l$	$m_s$	Energy states
--------------	-----	-----	-------	-------	---------------

2	2	0	0	(+1/2, -1/2)	(2, 0, 0, +1/2); (2, 0, 0, -1/2);
			-1	(+1/2, -1/2)	(2, 1, -1, 1/2); (2, 1, -1, -1/2);
			0	(+1/2, -1/2)	(2, 1, 0, +1/2); (2, 1, 0, -1/2);
			1	(+1/2, -1/2)	(2, 1, 1, +1/2); (2, 1, 1, -1/2)

Further write down the possible quantum states corresponding to the first four energy levels for the particle in a box case. What is the degeneracy of each of these levels? (You will understand the parabolic dependence of the degeneracy on energy later in this course.)

#### 4. Particle of mass $m$ in a cubic box of side $L$

A stationary wave is equivalent to two travelling waves propagating in opposite directions, the waves being reflected and re-reflected at the ends of the string. This is analogous to the motion of a particle moving freely back and forth along a straight line and making elastic collisions at two points separated by the distance  $L$ . The string can vibrate in a steady state in any one of a number of stationary waves, three of which are shown in the figure below. That is, there may be a node  $N$  at each end and antinodes  $A$  at the center, or there may be a node at the center as well as at the ends, with antinodes midway between the nodes and so on as shown.

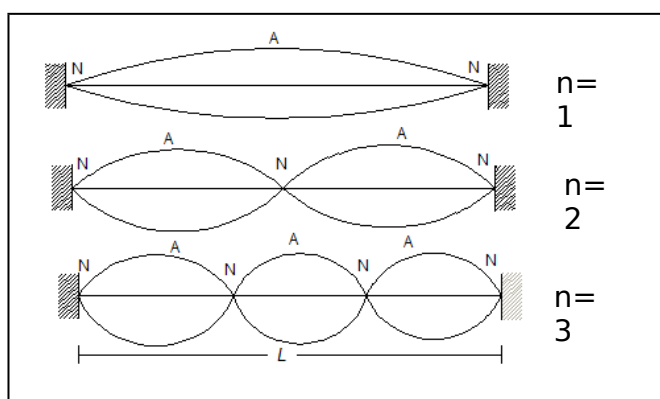


Fig 1. String vibration forms stationary waves

String vibration formation of stationary waves  $\lambda_1 = 2L$ ;  $\lambda_2 = \frac{1}{2}2L$ ;  $\lambda_3 = \frac{1}{3}2L$ ; .....etc; or general,

$\lambda_i = \frac{1}{n_i}2L$ , where  $n_i$  is an integer equal to the number of antinodes and can have some one of the values  $n_i=1,2,3,.....$

According to quantum mechanics, a stationary wave is in fact completely equivalent to such a particle, and the wavelength  $\lambda$  of the stationary wave is related to the momentum  $p$  of the particle through the relation  $p = \frac{h}{\lambda}$ , where  $h$  is a universal constant called Planck's constant.

The momentum of the particle is therefore permitted to have only some one of the set of values

$$p_i = \frac{h}{\lambda_i} = n_i \frac{h}{2L}.$$

If a particle is free to move in any direction within a cubical box of side length  $L$  whose sides are parallel to the  $x$ ,  $y$ ,  $z$  axes of a rectangular coordinates system, the  $x$ ,  $y$ , and  $z$  components of its momentum are permitted to have only the values  $p_x = n_x \frac{h}{2L}$ ,  $p_y = n_y \frac{h}{2L}$ ,  $p_z = n_z \frac{h}{2L}$ , Where  $n_x$ ,  $n_y$ , and  $n_z$  are integers called quantum number, each of which can have some one of the values 1, 2, 3, etc. each set of quantum numbers therefore corresponds to a certain direction of the momentum. Then if  $P_j$  is the resultant momentum corresponding to some set of quantum numbers  $n_x$ ,  $n_y$ , and  $n_z$ ,

$$p_i^2 = p_x^2 + p_y^2 + p_z^2 = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{4L^2};$$

The kinetic energy  $E$  of a particle of mass  $m$ , speed  $v$ , and momentum  $p = mv$

The energy  $E_i$  corresponding to the momentum  $p_i$  is therefore

$$E_i = \frac{p_i^2}{2m} = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8mL^2} = n_i^2 \frac{h^2}{8mL^2}; \text{ where } (n_x^2 + n_y^2 + n_z^2) = n_i^2$$

The values of  $n_x$ ,  $n_y$ , and  $n_z$  are said to define the state of a particle, and the energies corresponding to the different possible values of  $n_i^2$  are the possible energy levels. The energy levels depend only on the values of  $n_i^2$  and not on the individual values of  $n_x$ ,  $n_y$ , and  $n_z$ . In general, a number of different states will have the same energy. The energy level is then said to be degenerate and we shall use the symbol  $g_i$  to designate the degeneracy of level  $i$ , that is the number of states having the same energy  $E_i$ .

	$n_x$	$n_y$	$n_z$	$E$	Energy states	degeneracy
--	-------	-------	-------	-----	---------------	------------

Ground state/lowest energy state	1	1	1	$\frac{3h^2}{8mL^2}$	(1,1,1)	1
1 <sup>st</sup> excited state	2	1	1	$\frac{6h^2}{8mL^2}$	(2,1,1); (1,2,1); (1,1,2);	3
	1	2	1			
	1	1	1			
2 <sup>nd</sup> excited state	2	2	1	$\frac{9h^2}{8mL^2}$	(2,2,1); (2,1,2); (1,2,2);	3
	2	1	2			
	1	2	2			
3 <sup>rd</sup> excited state	1	1	3	$\frac{11h^2}{8mL^2}$	(1,1,3); (1,3,1); (3,1,1);	3
	1	3	1			
	3	1	1			
4 <sup>th</sup> excited state	2	2	2	$\frac{12h^2}{8mL^2}$	(2,2,2)	1

**Important notes on energy levels, quantum states and degeneracy:**

- (i) The concepts of energy levels, quantum states and degeneracy are extremely important in the context of statistical mechanics and MUST be understood by the students. In the above, we have introduced these in the context of essentially single particle quantum mechanical systems. However their definitions remain valid for multi-particle systems such as for electrons in a piece of metal, or in a Si crystal, etc. For example, the quantum state of an electron in the conduction band of a Si crystal may

$$\{n_x, n_y, n_z, s\}$$

be represented by \_\_\_\_\_ as explained in the class. The concerned energy levels here start

$$E_c$$

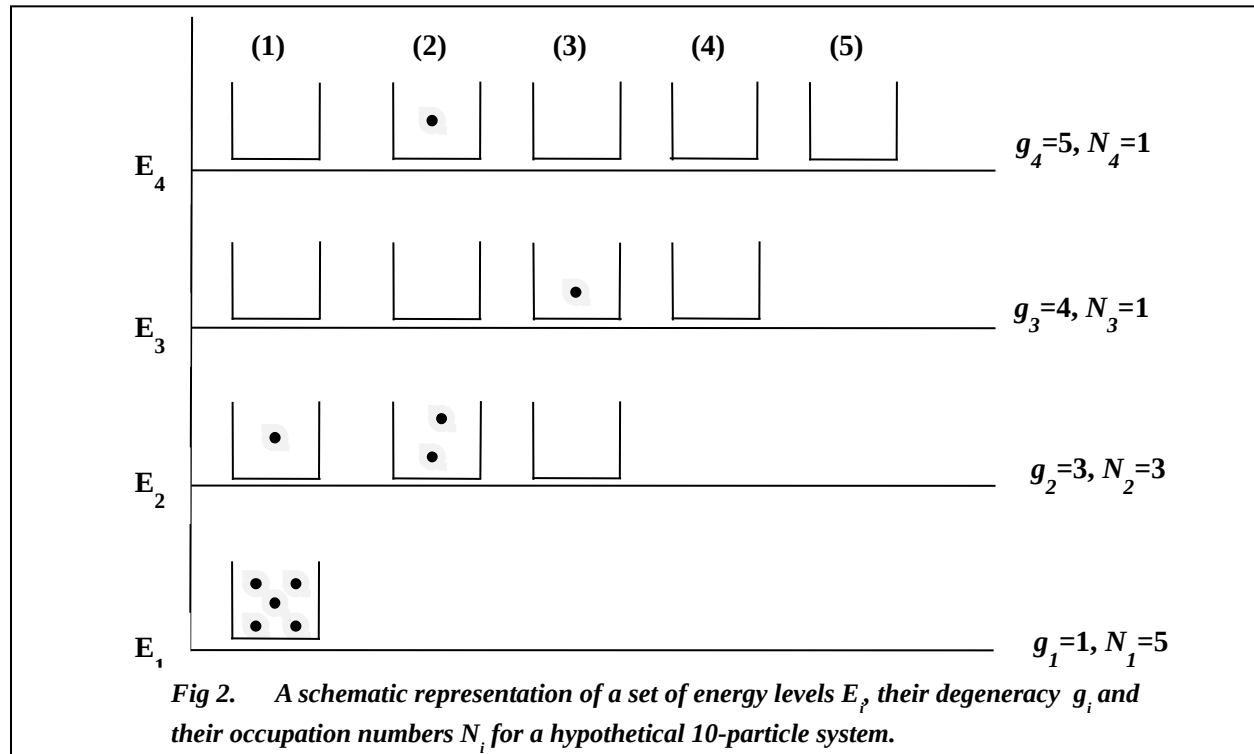
from the bottom of the conduction band (i.e. \_\_\_\_\_).

- (ii) Many or different energy states/quantum states may corresponds to the same energy level. The number of different energy states corresponding to particular energy level is called degeneracy. For non-degenerate energy level,  $g_i=1$ .
- (iii) On a molecular scale, quantum mechanics comes into play. According to the quantum mechanics, the energy of a particle cannot take any arbitrary value or cannot change in a continuous manner. The

particle can exist only in some one of a number of dynamical states having specified energies. The energy is said to be quantized.

## 5. Schematic representation of energy levels, quantum states and degeneracy (of a level)

Following figure shows a schematic representation of the concepts of energy levels, quantum states and degeneracy (of a level). The energy levels are represented by horizontal lines/shelves; the quantum states corresponding to these energies are represented by open boxes on these shelves and the degeneracy of an energy level by the number of boxes on the corresponding shelf. It is important to understand this figure as it will be used to introduce fundamental quantities and ideas in statistical mechanics.



**Discussion:** As discussed in class, the particles in the above system cannot in principle be electrons which must obey the Pauli Exclusion Principle. Each quantum state above is uniquely represented by the pair of i-j. Here energy level index 'i' runs from (1) to (4) and energy states index 'j' runs from (1) to (5) as shown in the figure above. For example, the quantum state (1-1) contains 5 particles and the quantum state (4-2) contains 1 particle. The total number of particles in a system is given by  $N = \sum_i N_i$  where  $N_i$  is the **occupation number** of the level  $i$ .

$$N_1 = 5, N_2 = 3 \quad N = 10$$

**Example:** In the figure 2, , etc. (and ). Further since each particle in energy level  $i$

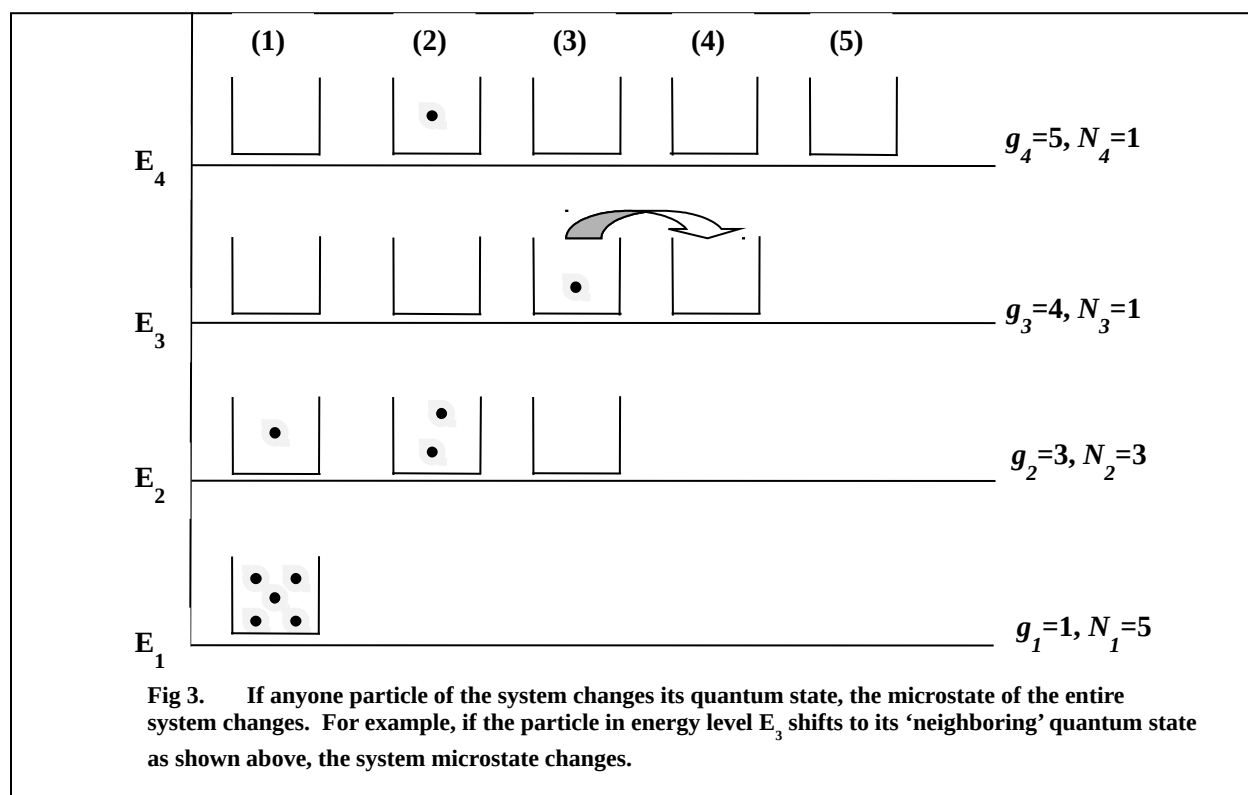
has the energy  $E_i$  irrespective of the quantum state it occupies at that level, the total energy of the system is given by  $E = \sum_i E_i N_i$

## 6. a) Microstates:

**Definition:** A specification of the quantum states of all the particles of a system defines a microstate of the system.

**Explanation:** Since a particle can only be in one quantum state at a time (a student can sit only on one chair at a time), the system taken as a whole can only be in one microstate at a time (students can be distributed among the classroom chairs only one way at a time). Changing the quantum state of any one particle of the system will change the microstate of the system as a whole (if any one student changes his seat, the entire distribution of the students among the chairs changes).

**Example:** In Fig 2, if we shift the particle from the quantum state (3-3) to the state (3-4), the microstate of the system changes as illustrated below in Figure 3.



## b) Macrostates:

**Definition:** A specification of the set of **occupation numbers** of the energy levels of the system defines a **macrostate** of the system. That is, a macrostate is defined by the set of numbers  $(N_1, N_2, N_3, \dots, N_i)$  where  $N_1, N_2, N_3, \dots, N_i$  are the number of particles in the energy levels  $E_1, E_2, E_3, \dots, E_i$  respectively. For example, the macrostate in Figure 1 may be written as  $\{5, 3, 1, 1\}$ .

**Explanation:** The transfer of the particle from one to another quantum state as shown in Fig 3 above results in a **new microstate** as explained above. However since this transfer does not entail any change in

the occupation numbers, **the macrostate remain unchanged** at {5, 3, 1, 1}. There are actually a large number of ways in which these transfers can be made **without** changing the macrostate. However at the end of each transfer, a new microstate comes into existence. (You may want to identify a few more for practice.) In other words, corresponding to a given macrostate, there are a large number of possible microstates. Why have we used the word ‘possible’ here? Because at any given time, the system can be only in one microstate (since each particle can occupy only one quantum state at a time).

**Note :** A microstate of a system can also be defined as a particular distribution of the particles of the system among the available quantum states and energy levels of the system. At a given time, only one such distribution is possible, i.e. the system can be in only one microstate.

**Can we count actual number of possible microstates corresponding to a macrostate ( $N_1, N_2, N_3, \dots, N_i$ ) ?**

The answer is yes. Clearly this number is simply the number of ways in which the particles can be distributed among the available quantum states and energy levels of the system while keeping the occupation number in each energy level a constant. This number is technically known as the thermodynamic probability (about which we will talk more in the next section) of the macrostate and we will calculate it shortly for particles obeying Bose-Einstein, Fermi-Dirac and Maxwell-Boltzmann statistics.

## 7. Thermodynamic Probability

**Background :** We will now consider a system that is **isolated** and **closed**. That is its total energy  $E$  (where  $E = \sum_i E_i N_i$ ) and total number of particles  $N$  (where  $N = \sum_i N_i$ ) are both constants. Clearly then, the distribution of the particles among the quantum states and energy levels of the system must satisfy these conditions. Since each distribution corresponds to a unique microstate (recall that a system can only be in one microstate at a given time) we can say that only those microstates are possible that satisfy the conditions of constant  $E$  and  $N$ . This point will become clear if we first think in terms of macrostates in the context of an isolated and closed system.

Constant values of the total energy  $E$  (with  $E = \sum_i E_i N_i$ ) and total number of particles  $N$  (with ) are possible even if the values of the occupation numbers  $N_i$  of the energy levels are varied. But every time we change these numbers, by definition, we get a new macrostate. In other words, for an isolated and closed system corresponding to a total constant energy  $E$  (and constant  $N$ ), there are a large number of possible macrostates.

**Explanation with example:** To see this, once again consider fig 2. For the sake of simplicity assume that the energies of the levels starting from level 1 are 1eV, 2 eV, 3 eV, and 4 eV respectively. In that case, the total energy of the system as shown in the figure 2 is  $5 \times 1\text{eV} + 3 \times 2\text{eV} + 1 \times 3\text{eV} + 1 \times 4\text{eV} = 18\text{eV}$ . **Now let us isolate the system so that its energy remains constant.**

The macrostate as shown in Fig2 is {5, 3, 1, 1}. However, the macrostate {5, 2, 3, 0} is also allowed as it also corresponds to a total energy of 18eV.





***Can you find out few more macrostates that have this energy ? It is strongly advised that you should .***

**Expression for thermodynamic probability :** Now we know that corresponding to each of these possible macrostates say  $M_k$  (where 'k' is the macrostate index), there are a large number (say  $W_k$ ) of possible microstates corresponding to this macrostate  $M_k$ . The total number of possible microstates of this isolated and closed system (i.e. corresponding to fixed E and N) is then given by  $\sum_k W_k$ . We call this number as  $\Omega$ , that is,

$$\Omega = \sum_k W_k \quad (3)$$

Note that each of these possible  $\Omega$  microstates of the system **MUST** satisfy the conditions of constant E and N as mentioned in the first paragraph of this section.

The fundamental postulate of statistical thermodynamics (also known as the postulate of equal a priori probabilities) states that ***in an isolated and closed system, all the ( $\Omega$ ) possible microstates are equally probable***. The principle of assuming equal probability for the events which are equally likely is known as the principle of equal a priori probability. A priori really means something which exists in our mind prior to and independently of the observation we are going to make. The entire structure of statistical thermodynamics is based on this postulate. There is no direct way of verifying this postulate experimentally. Its justification lies in the experimental verifications of theoretical results derived using this postulate. (For all the possible microstates to be equally probable, there must be a mechanism through which the isolated and closed system changes its microstate from time to time. This indeed occurs because of interactions between the particles of the system.

The number  $W_k$  is known as the thermodynamic probability of the (possible) **macrostate**  $M_k$  of the system. The total number of possible microstates  $\Omega$  is known as the thermodynamic probability of the (isolated and closed) **system**.

### ***For Advanced Learners***

The connection between thermodynamics and statistical mechanics is given by the equation  $S = k_B \ln \Omega$

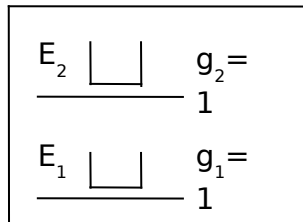
where  $S$  is the entropy and  $k_B$  is the Boltzmann constant. Can you explain why this equation makes

sense? Also can you use this equation and the second law of thermodynamics to get an expression for the absolute temperature in terms of  $\Omega$ ?

## **8. The most probable macrostate (of the isolated and closed system)**

It is simply the macrostate with the highest thermodynamic probability.

**Example: 4** distinguishable particles are distributed in 2 non-degenerate energy levels/compartments/energy states with different energy value. Calculate the possible macrostates and microstates of the system.



Microstates (M)	Energy levels		Microstates (W)
$M_1 (4,0)$	abcd	0	$W_1 = 1$
$M_2 (1,3)$	a	bcd	$W_2 = 4$
	b	acd	
	c	abd	
	d	abc	
$M_3 (2,2)$	ab	cd	$W_3 = 6$
	ac	bd	
	ad	bc	
	bc	ad	
	bd	ac	
	cd	ab	
$M_4 (3,1)$	bcd	a	$W_4 = 4$
	acd	b	
	abd	c	
	abc	d	
$M_5 (0,4)$	0	abcd	$W_5 = 1$

- Total number of microstates  $\Omega = \sum_k W_k = 1+4+6+4+1=16$  [  $C^N = 2^4 = 16$ , C- Number of non degenerate energy level and n- number of distinguishable particle]
- Total number of macrostates = 5
- Probability of any one microstates (p) =  $1/(\text{total number of microstates}) = 1/16$
- Probability of any one macrostate (P) =  $W_k / \Omega$

For example, probability of the macrostate  $M_4 = W_4 / \Omega = 4/16 = 0.25$

- The most probable state of the above system is  $M_3$  ie, (2,2) because the probability of that macrostate  $M_3 = W_3 / \Omega = 6/16 = 0.375$  [ note: particles are equally distributed in two compartment]

## 9. Background Knowledge Required

### Basic Concept of Probability

As a mathematical foundation for statistics, probability theory is essential to many human activities that involve quantitative analysis of large sets of data. Methods of probability theory also apply to descriptions of complex systems given only partial knowledge of their state, as in statistical mechanics. As per the classical definition of probability let a space of elementary events  $E$  be given and this space consists of  $N$  equally likely elementary events, among which there are  $n$  events, favorable for an event  $A$ . Then the number

$$P(A) = \frac{n}{N} = \frac{\text{number of ways which are favourable to the event}}{\text{total number of equally likely possible ways}}$$

is called the probability of an event  $A$ .

### Some examples of Probability calculation

- 1.If a coin is tossed honestly, it will have equal chance of getting a head or a tail. That is the chance of tossing either a head or tail is 1 out of two or the probability of tossing a head or a tail is  $\frac{1}{2}$
- 2.If a dice is thrown honestly, the probability of getting any number will be  $\frac{1}{6}$
- 3.From a deck of cards, if cards are well shuffled, the probability of drawing say, an ace of spades, will be  $\frac{1}{52}$  and the probability of drawing a spades card will be  $\frac{13}{52}$
4. Consider two dice say  $a$  and  $b$ , both having six faces numbered 1 to 6. Total numbered of combination would be  $6 \times 6$  or 36. If these dices are rolled, what is the probability of getting a number 7 ? The possible number of getting a number 7 are:

$a(5) \quad b(2)$   
 $a(2) \quad b(5)$   
 $a(4) \quad b(3)$   
 $a(3) \quad b(4)$   
 $a(1) \quad b(6)$   
 $a(6) \quad b(1)$

Therefore, there are 6 ways of getting number 7 from a pair of dice. Hence the probability of securing number 7 from a pair of dice will be  $\frac{6}{36}$

There is only one way of getting number 12, a(6) b(6), therefore, the probability of getting number 12 will be  $\frac{1}{36}$ .

**(a) Law of multiplication of probabilities:**

The probability that two independent events will occur simultaneously is equal to that the product of the probability of the separate events, or  $p_{12} = p_1 \cdot p_2$  where  $p_{12}$  is the probability that events 1 and 2 will occur simultaneously and  $p_1$  and  $p_2$  are probabilities of occurring of events 1 and 2 respectively.

**Example of law of multiplication of Probability**

**If two identical coins are tossed separately and simultaneously what will be the probability of getting head in both the coins?**

**Solution:**

If a single coin is tossed honestly, it will have equal chance of getting a head or a tail. That is the chance of tossing either a head or tail is 1 out of two or the probability of tossing a head or a tail is  $\frac{1}{2}$ . Now

when two identical coins are tossed then probability of occurrence of head of both will be  $\frac{1}{2} \times \frac{1}{2}$  i.e.  $\frac{1}{4}$ .

This can be verified very simple way as follows. The possible occurrence will be (H H), (H T), (T H), (T T). So total number of trials are 4. Particular event i.e. (H H) occurs once and hence the result.

**(b) Law of addition of probabilities:**

The probability that one of the two (or more) mutually exclusive events will occur is the sum of the probability of their separate occurrence,  $p_1$  and  $p_2$  can be written as  $p_{12} = p_1 + p_2$ .

**Example of law of addition of probability**

**What is the probability that a dice will turn to 4 or an odd number?**

**Solution:**

The chance of getting 4 are 1/6 and the chance of getting an odd number (1,3,5) is 3/6. Both these events are mutually exclusive, since it is 4, it cannot be odd number or vice versa. Hence  $p = 1/6 + 3/6 = 2/3$

**Practics problems**

1. From well shuffled deck of 52 cards, what is the probability that three cards drawn simultaneously are all kings?

- Two six faced dice, each marked 1 to 6 are thrown, calculate the probability that one of the dice shows 6 and the other shows 5.
- A card is drawn from a well shuffled pack of 52 cards. Calculate the probability for this card to be either king or queen.
- A bag containing 5 red balls and 3 white balls. All balls are identical except for the colour. A) If a ball is taken at random from the bag, what is the probability that it is red? B) If the two balls are drawn independently, what is the probability that both are red? C) What is the probability that on two independent drawing one ball is red and one is white.
- A box is divided into 9 equal size compartments. A ball thrown in the box is equally likely to go into any one of these compartment. If 9 balls are thrown. Calculate the probability for a particular compartment to contain a) one particular ball only. B) All the nine balls. C) None of the balls.

**Example 2:**

**Find out the possible number of macro states and microstates if three balls are distributed in two compartments when (i) Balls are distinguishable (ii) Balls are indistinguishable.**

**Solution:**

(i) Since the balls are distinguishable (say they are labelled as a, b, c) each compartment wise distribution can have a number of different arrangements as shown below.

Macrostate	Possible arrangement		Microstates
	Compartment 1	Compartment 2	
(0,3)	0	abc	1
(1,2)	a	bc	3
	b	ca	
	c	ab	
(2,1)	ab	c	3
	ac	b	
	bc	a	
(0,3)	0	abc	1

Possible macrostates are  $(3,0), (1,2), (2,1), (0,3) = 4$  states. Hence the total no of microstates are  $(1 + 3 + 3 + 1) = 8$  states

(ii) When the balls are indistinguishable (say they are labelled as ) each compartment wise distribution will be given as follows

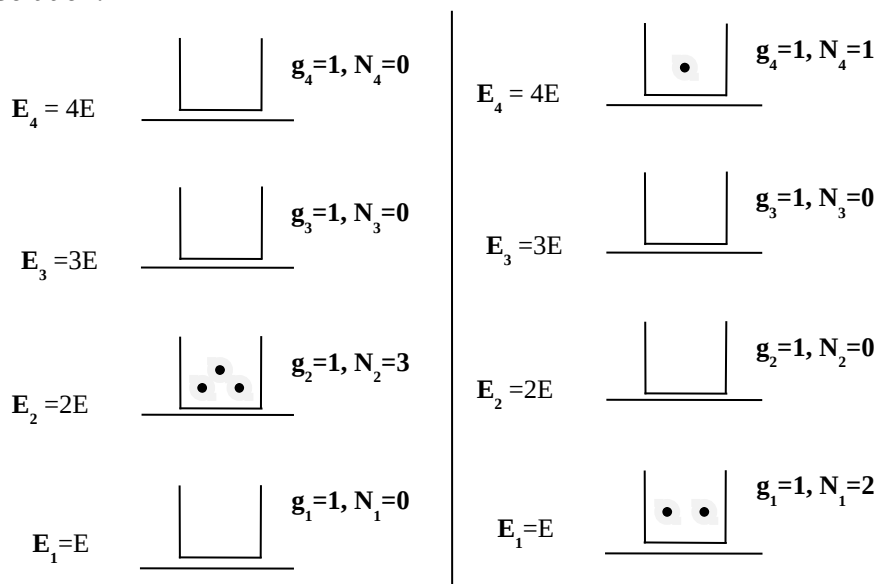
Possible arrangement		Macrostate	Microstates
Compartment 1	Compartment 2		
0	•••	0,3	1
•••	0	3,0	1
••	•	2,1	1
•	••	1,2	1

So the possible number of macrostates are **4** i.e., (0,3), (3,0), (2,1), (1,2) and possible number of microstates are **4**.

**Example 3:**

**3 distinguishable particles each of which can be in one of the  $E$ ,  $2E$ ,  $3E$ ,  $4E$  energy states have total energy  $6E$ . Find all possible numbers of distribution of all particles in the energy states.**

**Solution:**



$$E_4 = 4E \quad \begin{array}{|c|} \hline \\ \hline \end{array} \quad g_4=1, N_4=0$$

$$E_3 = 3E \quad \begin{array}{|c|} \hline \bullet \\ \hline \end{array} \quad g_3=1, N_3=1$$

$$E_2 = 2E \quad \begin{array}{|c|} \hline \bullet \\ \hline \end{array} \quad g_2=1, N_2=1$$

$$E_1 = E \quad \begin{array}{|c|} \hline \bullet \\ \hline \end{array} \quad g_1=1, N_1=1$$

Possible macrostates are = (0,3,0,0); (2,0,0,1); (1,1,1,0)

Macrostates	Possible arrangements				Microstates
(0,3,0,0)	0	abc	0	0	1
(2,0,0,1)	ab	0	0	c	
	ac	0	0	b	
	bc	0	0	a	3
(1,1,1,0)	a	b	c	0	
	a	c	b	0	
	b	a	c	0	
	b	c	a	0	
	c	a	b	0	
	c	b	a	0	

Total number of microstates= 1+3+6=10.

Practice problems:

1. Three distribution particles have a total energy of 9 units. But the particles are restricted to energy levels from 0 to 4. Calculate the numbers the macrostates and microstates.
2. Three distinguishable particles have a total energy of 9 units. But the particles are restricted to energy levels from 0 to 4. Calculate the numbers the macrostates and microstates.



- Three distinguishable particles each of which can be in one of the non-degenerate states with 0, 1, 2, 3 energy of the system have total energy of 3 units. Calculate all possible distribution of all the particles in the system and also find the most probable state of the system.

## 10. Maxwell Boltzmann Distribution

### *The basic postulate of M-B statistics*

- The particles are identical and distinguishable.
- The total number of particles of the system is constant (Closed system)  
 $N = N_1 + N_2 + \dots + N_i = \text{constant}$   
Or,  $\sum_i N_i = \text{constant}$
- The total energy of the system is constant (Isolated system)  
 $E = N_1 E_1 + N_2 E_2 + \dots + N_i E_i = \text{constant}$   
Or,  $\sum_i N_i E_i = \text{constant}$
- The particles don't obey the Pauli's Exclusion Principle.
- The particles don't obey Heisenberg Uncertainty Principle.
- The particles have no spin motion.

$$\{N_1, N_2, N_3, \dots, N_j, \dots\}$$

We will calculate the thermodynamic probability of a macrostate  $\{N_1, N_2, N_3, \dots, N_j, \dots\}$  for a system of particles obeying Maxwell-Boltzmann statistics. That is, we will calculate the number of possible

$$W^{MB} \{N_1, N_2, N_3, \dots, N_j, \dots\}$$

microstates,  $\{N_1, N_2, N_3, \dots, N_j, \dots\}$ , corresponding to this macrostate. Particles are considered to

be **identical** and **distinguishable**, and they do NOT obey the Pauli Exclusion Principle. So each quantum state in the system can have any number of particles.

### **Derivation:**

let us start with a certain distribution of all the particles of the system among the energy levels of the system which is in the macrostate  $\{N_1, N_2, N_3, \dots, N_j, \dots\}$ . Out of a total of  $N$  distinguishable particles,

what is the total number of ways in which  $N_1$  particles can be chosen for level 1,  $N_2$  for level 2,  $N_3$  for level 3, and so on? To begin,

$N_1$  particles can be chosen from  $N$  in  ${}^N C_{N_1}$  ways. Out of the remaining

$N - N_1$  particles,  $N_2$  particles can be chosen in  ${}^{N-N_1} C_{N_2}$  ways, and so on. So the required number of distributions (i.e., the total number of ways to collect in which  $N_1$  particles can be chosen for level 1,

$N_2$  for level 2,  $N_3$  for level 3, and so on) is given by

$${}^N C_{N_1} \times {}^{N-N_1} C_{N_2} \times {}^{N-N_1-N_2} C_{N_3} \times \dots = \frac{N!}{N_1! N_2! N_3! \dots} = \frac{N!}{\prod_j N_j!} \quad (1)$$

Let us consider the energy level  $E_1$  with degeneracy  $g_1$  and number of (distinguishable) particles  $N_1$ . The

first particle can be arranged among the  $g_1$  quantum states in  $g_1$  ways. The second particle can also be

arranged among the  $g_1$  quantum states in  $g_1$  ways (remember the particles do not obey the Pauli Exclusion Principle). So the total number of ways in which the two particles can be arranged among the

$g_1$  quantum states is  $g_1^2$ . For three particles this number will be  $g_1^3$  and so on. Therefore the total number

of ways in which the  $N_1$  distinguishable particles can be arranged among the  $g_1$  quantum states is  $g_1^{N_1}$ .

Therefore following usual arguments, the total number of possible microstates corresponding to this distribution will be:

$$\prod_j g_j^{N_j} \quad (2)$$

From (1) and (2), the total number of possible microstates corresponding to the (i.e. the thermodynamic probability of the) macrostate  $\{N_1, N_2, N_3, \dots, N_j, \dots\}$  for a system of particles obeying Maxwell-Boltzmann statistics is given by,

$$W^{MB} \{N_1, N_2, N_3, \dots, N_j, \dots\} = \frac{N!}{\prod_j N_j!} \times \prod_j g_j^{N_j} = N! \prod_j \frac{g_j^{N_j}}{N_j!}$$

## 11. Quantum Statistics

**Fermi-Dirac Distribution:**

**The basic postulate of F-D statistics**

1. The particles are identical and indistinguishable.
2. The total number of particles of the system is constant (Closed system)  
 $N = N_1 + N_2 + \dots + N_i = \text{constant}$   
Or,  $\sum_i N_i = \text{constant}$
3. The total energy of the system is constant (Isolated system)  
 $E = N_1 E_1 + N_2 E_2 + \dots + N_i E_i = \text{constant}$   
Or,  $\sum_i N_i E_i = \text{constant}$
4. The particles have half integral spin motion.
5. The particles have asymmetric wave function.
6. The particles obey the Pauli's Exclusion Principle.
7. The particles obey Heisenberg Uncertainty Principle.
8. The particles are called Fermions.

We will calculate the thermodynamic probability of a macrostate

$$\{N_1, N_2, N_3, \dots, N_j, \dots\}$$

for a system of particles (fermions) obeying Fermi-Dirac statistics. That is, we will calculate the number of possible microstates,

$$W^{FD}\{N_1, N_2, N_3, \dots, N_j, \dots\}$$

, corresponding to this macrostate for a system of fermions. Fermions are considered to be identical and indistinguishable with half-integral spins and they obey the Pauli Exclusion Principle. So each quantum state in the system can have *at most* one particle.

let us start with a certain distribution of all the particles of the system among the energy levels of the system which is in the macrostate

$$\{N_1, N_2, N_3, \dots, N_j, \dots\}$$

$$N$$

. Out of a total of  $N$  indistinguishable particles, what is the

total number of ways in which  $N_1$  particles can be chosen for level 1,  $N_2$  for

level 2,  $N_3$  for level 3, and so on? To begin,  $N_1$  particles can be chosen from  $N$

in 1 ways. Out of the remaining  $N - N_1$  particles,  $N_2$  particles can be chosen in

1 ways, and so on. So the required number of distributions (i.e., the total

number of ways to collect in which  $N_1$  particles can be chosen for level 1,  $N_2$

$N_3$  for level 2,  $N_3$  for level 3, and so on) is given by

$$1 \times 1 \times 1 \dots \times 1 = 1 \text{ ways.}$$

Consider the energy level  $E_1$  of a system of fermions with degeneracy  $g_1$  and number of particles  $N_1$ .

Recall that the particles are identical and indistinguishable and *do* obey the Pauli Exclusion Principle. The

question is what is the number of possible distributions of these  $N_1$  particles among the  $g_1$  available

quantum states at this level where each quantum state can have at most one particle? Note that because of

$N_1 \leq g_1$  the Pauli Principle, and the required number of possible distributions is simply..

The first particle can be arranged among the  $g_1$  quantum states in  $g_1$  ways. The second particle can be arranged among the  $g_1$  quantum states in  $(g_1 - 1)$  ways (remember the particles obey the Pauli Exclusion Principle). So the total number of ways in which the two particles can be arranged among the  $g_1$  quantum states is  $g_1(g_1 - 1)$ . For three particles this number will be  $g_1(g_1 - 1)(g_1 - 2)$  and so on. Therefore the total number of ways in which the  $N_1$  indistinguishable particles can be arranged among the  $g_1$  quantum states is

$$= \frac{g_1(g_1-1)(g_1-2)\dots\dots(g_1-N_1+1)}{N_1!}$$

[since particles are indistinguishable, the interchange the particles among the energy states will not give the new arrangement]

$$= \frac{g_1(g_1-1)(g_1-2)\dots\dots(g_1-N_1+1)(g_1-N_1)(g_1-N_1-1)\dots\dots 3.2.1}{N_1(g_1-N_1)(g_1-N_1-1)\dots\dots 3.2.1}$$

$$= \frac{g_1!}{N_1!(g_1-N_1)!}$$

Therefore following usual arguments, the total number of possible microstates corresponding to this distribution will be:

$$\prod_j \frac{g_j!}{N_j!(g_j-N_j)!}$$

$$\{N_1, N_2, N_3, \dots, N_j, \dots\}$$

Therefore the thermodynamic probability of the macrostate in Fermi-Dirac (or FD)  
statistics will be given by

$$W^{FD}\{N_1, N_2, N_3, \dots, N_j, \dots\} = \prod_j g_j C_{N_j} = \prod_j \frac{g_j!}{N_j!(g_j - N_j)!}$$

BOSE-Einstein Distribution:

### **The basic postulate of B-E statistics**

1. The particles are identical and indistinguishable.
2. The total number of particles of the system is constant (Closed system)  
 $N = N_1 + N_2 + \dots + N_i = \text{constant}$   
 Or,  $\sum_i N_i = \text{constant}$
3. The total energy of the system is constant (Isolated system)  
 $E = N_1 E_1 + N_2 E_2 + \dots + N_i E_i = \text{constant}$   
 Or,  $\sum_i N_i E_i = \text{constant}$
4. The particles have integral spin motion.
5. The particles have symmetric wave function.
6. The particles don't obey the Pauli's Exclusion Principle.
7. The particles obey Heisenberg Uncertainty Principle.
8. The particles are called Bosons.

We will calculate the thermodynamic probability of a macrostate

$$\{N_1, N_2, N_3, \dots, N_j, \dots\}$$

for a system of particles (Bosons) obeying Bose-Einstein statistics. That is, we will calculate the number of possible microstates,

$$W^{FD}\{N_1, N_2, N_3, \dots, N_j, \dots\}$$

, corresponding to this macrostate for a system of

Bosons. Bosons are considered to be identical and indistinguishable with integral spins and they don't obey the Pauli Exclusion Principle. So there is no restriction to the number of particles which can occupy a particular quantum state in the system.

let us start with a certain distribution of all the particles of the system among the energy levels of the system which is in the macrostate

$$\{N_1, N_2, N_3, \dots, N_j, \dots\}$$

$$N$$

. Out of a total of indistinguishable particles, what is the

$$N_1$$

$$N_2$$

total number of ways in which particles can be chosen for level 1, for

$$N_3$$

$$N_1$$

$$N$$

level 2, for level 3, and so on? To begin, particles can be chosen from

$$N - N_1$$

$$N_2$$

in 1 ways. Out of the remaining particles, particles can be chosen in

1 ways, and so on. So the required number of distributions (i.e., the total

$$N_1$$

$$N_2$$

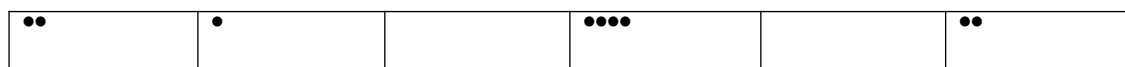
number of ways to collect in which particles can be chosen for level 1,

$$N_3$$

for level 2, for level 3, and so on) is given by

$$1 \times 1 \times 1 \dots \times 1 = 1 \text{ ways.}$$

Now, The number of possible ways in which  $N_1$  particles can be arranged in  $g_1$  energy states at the energy  $E_1$  can be carried out by the fig below in which the different energy states are represented by the different boxes and the particles by the dots.



As can be seen the boxes and the particles are arranged in an entirely arbitrary manner, the only restriction being that we start with the first box at the left and end with box number  $g_1$  on the right. The first box can be chosen in  $g_1$  different ways. Then the remaining  $(g_1 + N_1 - 1)$  entities (the partitions between the boxes plus the

$$(g_1 - N_1 - 1)!$$

particles) can be arranged in ways. However the permutations of the  $g_1$  boxes or of the  $N_1$  particles amongst themselves do not give any new arrangement.

$$(g_1! \times N_1!)$$

So we have divide by to get the total number of ways in which the  $N_1$  particles can be arranged between the  $g_1$  boxes:

$$= \frac{(g_1 + N_1 - 1)!}{g_1! N_1!}$$

Therefore the thermodynamic probability of the macrostate

$$\{N_1, N_2, N_3, \dots, N_j, \dots\}$$

in Bose-Einstein (or BE) statistics will simply be the product of all the above distributions (corresponding to all the energy levels of the system) as explained earlier (see page 1), i.e.,

$$W^{BE} \{N_1, N_2, N_3, \dots, N_j, \dots\} = \prod_j \frac{g_j [(g_j + N_j - 1)!]}{g_j! N_j!}$$

$\prod_j$  represents a product over the index  $j$

where the symbol

## PROBLEMS:

1. Calculate the probability that in tossing a coin 5 times, we get a) 3 heads and 2 tails. B) All heads c) 4 heads and 1 tails.
2. In a system of 14 distinguishable particles distributed in two equally probable halves of a box. Determine the probability of distribution (10, 4); (14, 0); (7, 7).
3. Consider 100 molecules and 10 cells of equal energy. Find In W for a) the most probability distribution b) the least probability distribution.
4. Three distribution particles have a total energy of 9 units. But the particles are restricted to energy levels from 0 to 4. Calculate the numbers the macrostates and microstates.
5. 8 distinguishable particles are distributed in two compartments. The first compartment is divided into 4 cells and the second into 2 cells. Each cell is of equal a priori probability and there is no restriction on the number of particles



that can be contained in each cell. Calculate the thermodynamics probability of a) the most prob. State b) the macrostate (8, 0).

6. Six distinguishable particles are distributed over three non-degenerate levels of energies 0, E and 2E. Calculate the numbers of microstates of the system and the energy of the distribution for which the prob. Is a maximum.
7. 3 distinguishable particles each of which can be in one of the E, 2E, 3E, 4E energy states have total energy 6E. Find all possible numbers of distribution of all particles in the energy states.
8. Three distinguishable particles each of which can be in one of the non-degenerate states with 0, 1, 2, 3 energy of the system have total energy of 3 units. Find the microstates if the particles obey a) M-B, b) F-D, c) B-E statistics.
9. Four particles are distributed into three energy levels having energies 0, E, 3E so that the total energy is 4E. If the levels are degenerate with degeneracy 1, 2, 3 respectively, find out the macrostates and the corresponding microstates for M-B particles and B-E particles.
10. 2 particles are distributed into two energy levels with degeneracy 1, 2 respectively. Find the most probable state of the distribution of the particle in the system, if the particles obey a) M-B, b) F-D, c) B-E Statistics.
11. A system has 7 particles arranged in two compartments. The 1<sup>st</sup> compartment has 8 cells and the second has 10 cells, all cells are of equal size. Calculate the number of microstates in the macrostates (3, 4), when the particles are Fermions and Boson.
12. A system has two particles, each one of them can be in one of three quantum states. Find the possible number of microstates of the system according to the three statistics.

# DISTRIBUTION LAW:

Fermi-Dirac statistics:

$$\sum_i N_i = \text{constant}$$

$$\sum_i E_i N_i = \text{constant}$$

$$W_{F-D} = \prod_i \frac{g_i!}{N_i!(g_i - N_i)!}$$

And

$$\ln W_{F-D} = \sum_i [\ln g_i! - \ln N_i! - \ln(g_i - N_i)!]$$

For most probable state,  $W_{F-D}$  is maximum,

Applying Lagrange's Undermined Multiplier method to maximize the distribution of particles among the energy states in the energy level of the system.....

$$[\ln W_{\max} - \alpha \sum_i N_i - \beta \sum_i E_i N_i] = \text{maximum}$$

$$\text{or, } \frac{d}{dN_i} [\ln W_{\max} - \alpha \sum_i N_i - \beta \sum_i E_i N_i] = 0$$

$$\text{or, } \frac{d}{dN_i} [\sum_i [\ln g_i! - \ln N_i! - \ln(g_i - N_i)!] - \alpha \sum_i N_i - \beta \sum_i E_i N_i] = 0$$

[using Stirling approximation:  $\ln N! = N \ln N - N$ , where  $N$  is very large quantity.]

$$\text{or, } \frac{d}{dN_i} [\sum_i [g_i \ln g_i - g_i - N_i \ln N_i + N_i - (g_i - N_i) \ln (g_i - N_i) + (g_i - N_i) - \alpha \sum_i N_i - \beta \sum_i E_i N_i] = 0$$

$$\text{or, } [-\ln N_i - 1 + 1 + \ln (g_i - N_i) + 1 - 1 - \alpha - \beta E_i] = 0$$

$$\text{or, } \ln \frac{(g_i - N_i)}{N_i} - \alpha - \beta E_i = 0$$

$$\text{or, } \ln \frac{(g_i - N_i)}{N_i} = \alpha + \beta E_i$$

$$\text{or, } \frac{(g_i - N_i)}{N_i} = e^{(\alpha + \beta E_i)}$$

$$\text{or, } \frac{g_i}{N_i} - 1 = e^{(\alpha + \beta E_i)}$$

$$\text{or, } \frac{g_i}{N_i} = e^{(\alpha + \beta E_i)} + 1$$

$$\text{or, } \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} + 1}$$

This is F-D particles distribution law.

By following the same procedure for maximizing the Bose-Einstein and Maxwell-Boltzmann thermodynamic probabilities subject to the constancy of the total number of particles and the total energy, we get the Bose-Einstein and Maxwell-Boltzmann distribution functions respectively as follows:

$$\frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} - 1}, \text{ for } B - E \text{ statistics}$$

And,

$$\frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)}}, \text{ for } M - B \text{ statistics}$$

Similarly, we can write,

$$\text{for, } M - B \text{ statistics, } \frac{N(E)}{g(E)} = \frac{1}{e^{(\alpha + \beta E)}}$$

$$\text{or, } N(E)dE = \frac{g(E)dE}{e^{(\alpha + \beta E)}}$$

$$\text{for, } F - D \text{ statistics, } \frac{N(E)}{g(E)} = \frac{1}{e^{(\alpha + \beta E)} + 1}$$

$$\text{or, } N(E)dE = \frac{g(E)dE}{e^{(\alpha + \beta E)} + 1}$$

$$\text{for, } B - E \text{ statistics, } \frac{N(E)}{g(E)} = \frac{1}{e^{(\alpha + \beta E)} - 1}$$

$$\text{or, } N(E)dE = \frac{g(E)dE}{e^{(\alpha + \beta E)} - 1}$$

Here the undetermined multipliers are  $\alpha$  and  $\beta$ .

$N(E)dE$ =The number of particles in the energy range  $E$  to  $E+dE$

$G(E)dE$ = The number of energy states in the energy range  $E$  to  $E+dE$

## Density of States: [g(E)]

Density of states is defined as the number of energy states per unit energy per unit volume in the range E to (E+dE).

### PHASE SPACE

A complete specification of the state of the motion of any particle of the system is determined by six coordinates: three position coordinates (x, y, z) and three momentum coordinate ( $p_x$ ,  $p_y$ ,  $p_z$ ). Such a position-momentum coordinate's space is known as phase space.

For single particle, phase space will have 6 dimensions. Such six-dimensional space is called the  **$\mu$ -phase space**.

Each particle has its own phase space. Therefore, if there are N particles constituting a system and if each has three degrees of freedom, the phase space of the system will have 6N dimensions. Such phase space is called the  **$\Gamma$ -phase space**.

We consider, the phase space is divided into a large number of cells/energy states of equal size.

For 2D phase space,

The area of each cell/energy state is  $dx.dp_x=h$  (For quantum mechanical system, we can write using Heisenberg's uncertainty relation the minimum possible value of  $dx.dp_x \approx h$ , where  $h$  is planck's constant)

For 6D phase space,  
The volume of each cell/energy state is-----

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

[where  $x, y, z, p_x, p_y, p_z$  are the coordinates of a point in phase space]

So, the finite volume of the phase space available for a particle is

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

$$\text{Or, } \tau = \iiint \iiint dx dy dz dp_x dp_y dp_z$$

So, minimum size or volume of a unit cell for a quantum mechanical system

$$d\tau = dx dy dz dp_x dp_y dp_z \approx h^3$$

Now, the number of cells/energy states in the phase space corresponding to momentum  $p$  to  $p+dp$  is

$$g(p)dp = \frac{\text{volume in phase space having momentum between } p \text{ to } p + dp}{h^3}$$

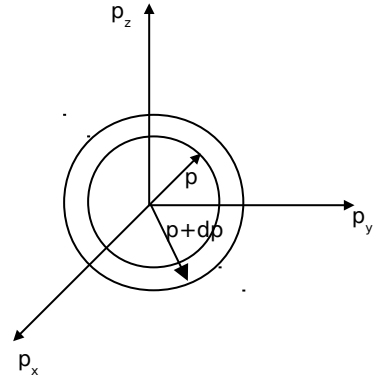
Or, 
$$g(p)dp = \frac{\iiint dxdydz \iiint dp_x dp_y dp_z}{h^3}$$

Now, the volume of the system of particles  $V = \iiint dxdydz$

Hence 
$$g(p)dp = \frac{V \iiint dp_x dp_y dp_z}{h^3} \quad \dots (1)$$

To evaluate the volume of the system  $\iiint dp_x dp_y dp_z$  in momentum space corresponding to momentum interval  $p$  to  $p+dp$ , we construct a sphere of radius  $p$  such that all the points lying on the sphere have a momentum  $p$  and it is given by the equation  $p^2 = p_x^2 + p_y^2 + p_z^2 = 2mE$ , where  $E$  is the energy of the particle of mass  $m$ .

We further draw another concentric sphere of radius  $p+dp$ .



The volume enclosed by the spherical shell between two spheres of radius  $p$  and  $p+dp$  is given by

$$\iiint dp_x dp_y dp_z = \text{area of the sphere of radius } p \times \text{thickness of the cell}$$

Or, 
$$\iiint dp_x dp_y dp_z = 4\pi p^2 dp \quad \dots (2)$$

Substituting (2) in (1) we have, 
$$g(p)dp = \frac{V 4\pi p^2 dp}{h^3}$$

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

or, 
$$\rightarrow \text{Density of states in terms of momentum} \dots (3)$$

Under non-relativistic case since  $\frac{p^2}{2m} = \epsilon \quad \therefore p = \sqrt{2m\epsilon}$

Differentiating  $p^2 = 2m\epsilon$  we get  $2pdp = 2m d\epsilon$  or,  $pdp = m d\epsilon$

Substituting the value of  $p$  and  $pdp$  in (3) we have

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

Or, 
$$\rightarrow \text{Density of states in terms of}$$

**energy**

### Calculation of $\beta$ , the multiplier constant:

Details of the calculations will not be given (interested students are of course welcome to contact me) and we will straightway write down the results:

$$\beta = \frac{1}{k_B T}$$

,  $k_B$  – the Boltzmann constant

### **MAXWELL-BOLTZMANN STATISTICS**

$$N(E)dE = e^{-\alpha} e^{-\beta E} g(E) dE$$

$$\text{Now, } N = \int_0^{\infty} N(E) dE = \int_0^{\infty} e^{-\alpha} e^{-\beta E} g(E) dE$$

$$\text{or, } e^{-\alpha} = \frac{N}{\int_0^{\infty} e^{-\beta E} g(E) dE}$$

$$\text{or, } e^{-\alpha} = \frac{N}{\int_0^{\infty} e^{\frac{-E}{k_B T}} 2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} dE}$$

$$\text{or, } e^{-\alpha} = \frac{N}{2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^{\infty} e^{\frac{-E}{k_B T}} E^{\frac{1}{2}} dE}$$

,

$$\frac{E}{k_B T} = x, E = k_B T x, \text{ or, } dE = k_B T dx$$

Let,

$$\text{or, } e^{-\alpha} = \frac{N}{2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} (k_B T)^{\frac{3}{2}} \int_0^{\infty} e^{-x} x^{\frac{1}{2}} dx} \quad \int_0^{\infty} e^{-x} x^{\frac{1}{2}} dx = \frac{1}{2} \sqrt{\pi}$$

,

$$\text{or, } e^{-\alpha} = \frac{N}{2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} (k_B T)^{\frac{3}{2}} \frac{1}{2} \sqrt{\pi}}$$

$$\text{or, } e^{-\alpha} = \frac{N}{V \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}}$$

The total energy of the gas molecules at a particular temperature,

$$E = \int_0^{\infty} E N(E) dE$$

$$\text{or, } E = \int_0^{\infty} E e^{-\alpha} e^{-\beta E} g(E) dE$$

$$\text{or, } E = \int_0^{\infty} E \frac{N}{V \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}} e^{\frac{-E}{k_B T}} 2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} dE$$

$$\text{or, } E = \frac{2\pi N}{(\pi k_B T)^{\frac{3}{2}}} \int_0^{\infty} E e^{\frac{-E}{k_B T}} E^{\frac{1}{2}} dE$$

$$\text{or, } E = \frac{2\pi N}{(\pi k_B T)^{\frac{3}{2}}} \int_0^{\infty} e^{\frac{-E}{k_B T}} E^{\frac{3}{2}} dE$$

$$\frac{E}{k_B T} = x, E = k_B T x, \text{ or, } dE = k_B T dx$$

Let,

$$\text{or, } E = \frac{2\pi N}{(\pi k_B T)^{\frac{3}{2}}} (k_B T)^{\frac{5}{2}} \int_0^{\infty} e^{-x} x^{\frac{3}{2}} dx$$



$$\text{or, } E = \frac{2\pi N}{(\pi k_B T)^{\frac{3}{2}}} (k_B T)^{\frac{5}{2}} \frac{3}{2} \frac{1}{2} \sqrt{\pi}$$

$$\text{or, } E = \frac{3}{2} k_B T$$

N

The average energy of the gas molecules at a given temperature is.....

$$\text{or, } E = \frac{3}{2} k_B T$$

The average energy per degrees of freedom of the gas molecules at a given temperature is

$$E = \frac{1}{2} k_B T$$

, (Equi-partition energy law)

### Maxwell-Boltzmann Velocity Distribution law

$$N(E)dE = e^{-\alpha} e^{-\beta E} g(E)dE$$

$$\text{or, } N(E)dE = \frac{N}{V \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}}} e^{\frac{-E}{k_B T}} 2\pi V \left( \frac{2m}{h^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} dE$$

$$\text{or, } N(E)dE = \frac{2\pi N}{(\pi k_B T)^{\frac{3}{2}}} \int_0^{\infty} e^{\frac{-E}{k_B T}} E^{\frac{1}{2}} dE$$

$$E = \frac{1}{2} m v^2, \text{ or, } dE = m v dv$$

$$\text{or, } N(v)dv = \frac{2\pi N}{(\pi k_B T)^{\frac{3}{2}}} \int_0^{\infty} e^{\frac{-m v^2}{2 k_B T}} \frac{1}{\sqrt{2}} m^{\frac{1}{2}} v m v dv$$

$$\text{or, } N(v)dv = \frac{\sqrt{2\pi N m^{\frac{3}{2}}}}{(\pi k_B T)^{\frac{3}{2}}} \int_0^{\infty} e^{\frac{-m v^2}{2 k_B T}} v^2 dv$$

Now,

$$v_{avg} = \frac{\int_0^{\infty} v N(v) dv}{N}$$

$$or, \quad v_{avg} = \frac{\sqrt{2\pi Nm^{\frac{3}{2}}} \int_0^{\infty} v e^{\frac{-mv^2}{2k_B T}} v^2 dv}{(\pi k_B T)^{\frac{3}{2}} N}$$

$$\frac{mv^2}{2k_B T} = x, or, mv dv = k_B T dx$$

Let,

$$or, \quad v_{avg} = \frac{\sqrt{2\pi m^{\frac{3}{2}}} \frac{2k_B T}{m} \frac{k_B T}{m} \int_0^{\infty} e^{-x} x dx}{(\pi k_B T)^{\frac{3}{2}}}$$

$$or, \quad v_{avg} = \frac{\sqrt{2\pi m^{\frac{3}{2}}} \frac{2k_B T}{m} \frac{k_B T}{m} \times 1}{(\pi k_B T)^{\frac{3}{2}}}$$

$$or, \quad v_{avg} = \sqrt{\frac{8k_B T}{\pi m}}$$

$$Now, \quad v_{r.m.s} = \frac{\int_0^{\infty} v^2 N(v) dv}{N} = \sqrt{\frac{3k_B T}{m}}$$

### **Most probable speed**

$$N(v) = \frac{\sqrt{2\pi Nm^{\frac{3}{2}}}}{(\pi k_B T)^{\frac{3}{2}}} e^{\frac{-mv^2}{2k_B T}} v^2$$

Where,  $N(v)$  = number of particles per unit velocity range in between  $v$  to  $v+dv$ .

$$\ln[N(v)] = \ln \left[ \frac{\sqrt{2\pi Nm^{\frac{3}{2}}}}{(\pi k_B T)^{\frac{3}{2}}} \right] + 2 \ln v - \frac{mv^2}{2k_B T}$$

Taking derivative both side with respect to  $v$

$$\frac{1}{N(v)} \frac{d[N(v)]}{dv} = 0 + \frac{2}{v} - \frac{mv}{k_B T}$$

$$\text{or, } \frac{d[N(v)]}{dv} = N(v) \left[ \frac{2}{v} - \frac{mv}{k_B T} \right]$$

At the most probable speed  $v = v_p$ , the number of molecules  $N(v)$  is maximum,

$$\frac{d[N(v)]}{dv} = 0$$

$$\text{or, } \frac{mv}{k_B T} = \frac{2}{v}$$

$$\text{or, } v_p = \sqrt{\frac{2k_B T}{m}}$$