Lecture Notes of B.Sc.(HONS.) PHYSICS ,Part-III, Paper -VI

By: Sonu Rani,
Assistant Professor ,
Department of Physics ,MMC,P.U.

TOPIC:-------Fundamentals of Statistical Mechanics and Ensemble

<u>What is Statistical Mechanics</u>: Statistical mechanics is the branch of science which establishes the interpretation of macroscopic behaviour of a system in terms of its microscopic properties. It is not concerned with the actual motion of individual particles of the system but gives average or most probable properties of system. Larger the number of particles more correct are statistical prediction. It is suitable for systems having large degree of freedom. This method is based on statistical methods, probability theory and microscopic laws.

<u>Relation between Thermodynamics and Statistical Mechanics:</u>

Thermodynamics entropy of system has maximum value when system is in equilibrium and statistical probability is also maximum in equilibrium. Therefore there is close relationship between entropy and probability ⇒ $S=K \ln \Omega$. This equation in the basic of statistical mechanics, where K⇒ Boltzmann constant (1.38×10^{-23} J/k) that establishes correspondence of statistical entropy of Boltzmann to thermodynamics entropy of Clausius.

Examples of macroscopic objects:-

1. For finding pressure, temperature, density etc. of bottle of water, molecules of water are microscopic and bottle of water is macroscopic object.
2. Atom is macroscopic object and electrons, protons, neutrons are microscopic objects.
3. Polymer is macrostate and monomers are microstates.

4. Society is a macroscopic object and men, women, children are microscopic objects.

Statistical Mechanics says that if you know the properties of microscopic objects we can predict the behaviour of macroscopic object.

<u>Phase Space:</u> In classical mechanics the state of system of particle at any time is specified by knowledge of position and momentum. For a single particle it has three position(x,y,z) and three momentum $(v_{x,,}v_{y,,}v_{z)}$ i.e. 6 coordinates. Therefore we can imagine 6D space in which $dx\ dy\ dz\ dp_x\ dp_y\ dp_z$ is an element of volume and the position of a point particle in this space will be described by a set of 6 coordinates x,y,z,p_x,p_y,p_z. This 6 dimensional space for a single particle is called **phase space**. The dimension of phase space depends upon the degree of freedom of system. The instantaneous state of a particle in a phase space is represented by a point known as **phase point**. The number of phase point per unit volume is called **phase density** of these points. An element of volume in this space is termed as cell.

<u>Ensemble:</u> A system is defined as a collection of number of a large no. of macroscopically identical but essentially independent Systems. By the term macroscopically identical we mean that each of the systems constituting an ensemble satisfies the same macroscopic conditions example, volume, energy, pressure, total number of particles etc. By the term independent system we mean that the system constituting an ensemble are mutually non-interacting. In an ensemble the system plays the same role as the non-interacting molecules do in a gas. The macroscopic identity of the systems constituting an ensemble may be achieved by choosing the same values of some set of macroscopic parameters which uniquely determined the equilibrium state of the system. Accordingly there may be many types of ensemble out of them the most widely used are the Microcanonical, Canonical and Grand Canonical ensemble.

Microcanonical Ensemble: It is the collection of a large number of essentially independent systems having the same energy E, volume V, and the number of particles N. For simplicity we assume that all the particles are identical. The individual systems of a microcanonical ensemble are separated by rigid, impermeable and well insulated walls as shown in Fig.(1) such that the values of E ,V and N for a particular system are not affected by the presence of other systems.

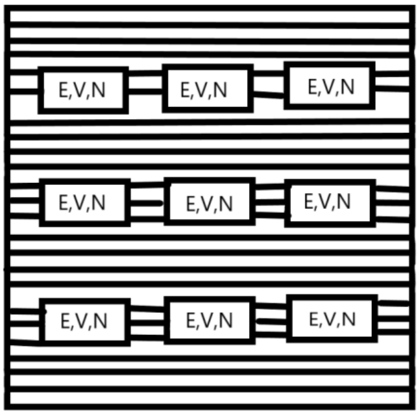

Fig.(1)

Canonical Ensemble: It is the collection of a large number of essentially independent systems having the same temperature T, volume V and the same number of identical particles N. The equality of temperature of all the systems can be achieved by bringing each in thermal contact with a large heat reservoir at constant temperature T or bringing all of the systems in thermal contact with one another. The individual systems of a Canonical ensemble are separated by rigid, impermeable but conducting walls as shown in Fig.(2). As the separating walls are conducting, heat can be exchanged between the systems. As a result all the systems will arrive at the common temperature capital T.

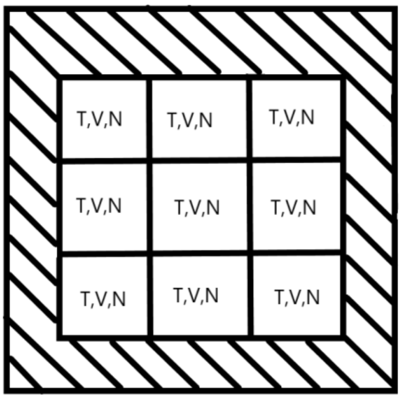

Fig.(2)

Grand Canonical Ensemble: It is the collection of a large number of essentially independent systems having the same temperature T, volume V and chemical potential μ. The individual systems of a grand canonical ensemble are separated by rigid, permeable and conducting walls as shown in Fig.(3). As the separating walls are conducting and permeable, the exchange of heat energy as well as that are particles between the systems takes place in such a way that all the systems arrive at common temperature T and chemical potential μ.

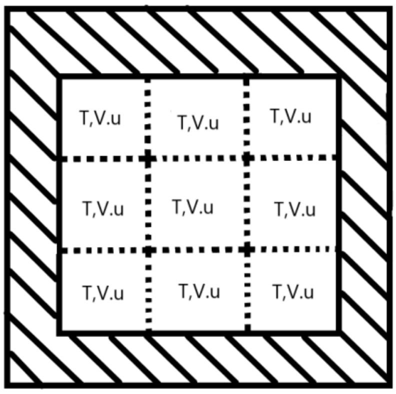

Fig.(3)

As the instantaneous state of any system of f Degree of freedom can be completely specified by the position of a suitable point, called the phase point or representative points in the 2f dimensional phase space. Therefore an ensemble being the collection of a large number of microscopically independent systems, will appear as a dust cloud made up of large number of phase points in the phase space. The change in the phase that is in position coordinate and momenta of any system can be represented by a curve or phase line in the phase space. Then the behaviour of an ensemble in the course of time can be represented by a large number of trajectories or phase lines in the phase space or the streaming motion of the dust cloud as the trajectories are described by the points according to the laws of mechanics.

It is easier to compute the behaviour of a suitable chosen ensemble than to study the behaviour of any particular system. By the knowledge of the behaviour of the ensemble we can predict the probable behaviour of the system under consideration.

<u>Equal a Priori Probability</u>: (fundamental assumption of statistical mechanics)

Each microstates corresponding to a given microstate (Total energy) is equally probable. Hence we conclude that events such as the spontaneous compression of gas or spontaneous conduction of heat from a cold body to hot body are not impossible but they are so improbable that they never occur.

Postulate of equal a priori probability: " The probability of finding the phase point for a given system in any one region of phase space is identical with that any other region of equal extension or volume. This postulate is known as the postulate of equal a priori probability."

According to the principle of conservation of density in the phase space ,the density of a group of phase points remains constant along their trajectories in the phase space. If at any time the phase points are distributed uniformly in the phase space ,phase points move in such a way that they will have uniform density of phase points at all times.