Statistical Mechanics

Lecture 4

Manoj Kr. Das
Associate Professor
J N College, Boko

Postulates of Classical Statistical Mechanics:

Statistical mechanics is concerned with the properties of matter in equilibrium. The aim of statistical mechanics is to derive all the equilibrium properties of a macroscopic molecular system from the laws of molecular dynamics. Thus it aim to derive not only the general laws of thermodynamics but also the specific thermodynamic functions of a given system. Statistical mechanics doesnot describe how a system approaches equilibrium, nor does it determine whether a system can ever be found to be in equilibrium. It just states what the equilibrium situation is for a given system.

We consider a classical system composed of a large number *N* molecules occupying a large volume *V*. These being enormously large numbers, It would be convenient to consider the system in the limit

$$N \to \infty$$

$$V \to \infty$$

$$\frac{V}{N} = v \to (i)$$

Where the specific volume v is a given finite number.

A state of system is completely and uniquely defined by *3N* canonical coordinates $q_1, q_2, \cdots q_{3N}$ and 3N canonical momenta $p_1, p_2, \cdots p_{3N}$ .These 6N variables are denoted collectively by (p, q) . The dynamics of the system is complexly contained in the $H(p, q)$, from which we may obtained the canonical equations of motion.

$$\frac{\partial H(p,q)}{\partial p_i} = \dot{q_i} \rightarrow (ii)$$

$$\frac{\partial H(p,q)}{\partial q_i} = -\dot{p_i} \rightarrow (iii)$$

Now it is convenient to introduced the *6N*-dimensional Γ–space of the system in which each point represents a state of the system. The locus of all points in Γ–space satisfying the condition $H(p, q) = E$ defines a surface called the energy surface of energy E. As state of the system evolves in time according to equation (ii) & (iii) the representative point traces out a path in Γ–space. This path always stays on the same energy surface because by definition energy is conserved. In case of macroscopic we require that the system has N particles, a volume V and energy laying between the value E and $E + \Delta$.

An infinite number of states satisfy these conditions. Therefore we imagine not of a single system but of an infinite number of copies of same system existing in all possible states satisfying the given conditions. We are actually dealing with one of such system. It is shown by a distribution of points in Γ–space characterized by a density function $\rho(p, q, t)$ defined is such a way that $\rho(p, q, t)\ d^{3N}p\ d^{3N}q =$ Number of points contained in volume element $d^{3N}p\ d^{3N}q$ located at $(p, q,)\ in\ \Gamma$–space at instant t. We restrict our consideration to ensembles whose density function does not depends on time but depends on $(p, q,)$ through Hamiltonian.

That is

$$\rho(p,q) = \rho'[H(p,q)] \rightarrow (iv)$$

Where $\rho'(H)$ is given function of (H)

Again

$$\frac{\partial}{\partial t}\rho(p,q) = 0 \rightarrow (v)$$

Hence the ensemble described by $\rho(p,q)$ is same for all times.

The classical statistical mechanics is found on the postulate of equal a priori probability in which we considered the most probable value and ensemble average which are identical as $N \rightarrow \infty$.

Postulates of Quantum Statistical Mechanics:

We know that nature obey quantum mechanics. In quantum mechanics , an observable of a system is a vector $|\Psi|$ in the same Hilbert space. If $|q\ \rangle$ is an eigen value of the position operator of small particle in the system then $\langle q|\Psi\rangle \equiv \Psi(q)$ the wave function of the system in the$|\Psi\ \rangle$. The wave function furnish the complete description of the state. At any instant of time, the wave function Ψ of a truly isolated system may be expressed as a linear superposition of a complete orthonormal set of stationay wave function $\{\Phi_n\}$ as

$$\Psi = \sum\nolimits_{n} C_n \Phi_n \rightarrow (vi)$$

Where C_n is a complex number and is generally a function of time. The index n states for a set of quantum number, which are eigen values of certain chosen dynamical operators of the system. The square modulus $|C_n|^2$ is the probability that a measurement performed on the system will find it to have the quantum number n. In statistical mechanics we always deal with system that interact with external world. Thus we can regard the system plus external world as a true isolated system.

The wave function Ψ for this whole system will depend on the both the coordinate of the system under consideration and coordinate of the external world. If $\{\Phi_n\}$ denotes the complete set of orthogonal stationary wave functions of the system then Ψ is given by equation *(vi)* and C_n is interpreted as a wave function of the external world. It depends on external world as well as on the time.

Let θ is an operator corresponding to an observable of the system. According to rule of quantum mechanics, the average result of a large number of measurement of the observable is instantaneously given by the expectation value as

$$\frac{(\Psi,\theta(\Psi))}{(\Psi,\Psi)} = \frac{\sum n \sum m (C_n, C_m)\emptyset_n \theta(\emptyset_m)}{\sum n (C_n, C_m)} \rightarrow (vii)$$

Where (C_n, C_m) , the scaler product of the *n*th and *m*th wave function of external world is a function of time. The denominator is identical with (Ψ, Ψ) is independent of time, because the Hamiltonian of the system plus external world is Hermitian. When we actually measure an observable in the laboratory we measure not its instantons value, but a time average. Thus a directly measurable quantity is not equation (vii) , but the following quantity.

$$\langle \theta \rangle \equiv \frac{\overline{\big(\Psi, \theta\,(\Psi)\big)}}{(\Psi, \Psi)}$$

$$\langle \theta \rangle = \frac{\sum_n \sum_m (\overline{C_n, C_m})\, \emptyset_n \theta\ (\emptyset_m)}{\sum_n (\overline{C_n, C_m})} \rightarrow (viii)$$

Where $(\overline{C_n, C_m})$ is the average of (C_n, C_m) over a time interval that is short compared to the resolving time of the measuring apparatus but long compared to molecular time. We also note that $\sum_n (\overline{C_n, C_m})$ is identical with $\sum_n (C_n, C_m)$, because the latter is independent of time.

The postulates of quantum statistical mechanics are postulates concerning the coefficient $(\overline{C_n, C_m})$ where equation $(viii)$ refers to a macroscopic observation of a macroscopic system in thermodynamic equilibrium.

Let us consider a macroscopic system which truly not isolated but interact weakly with external world. Let number of particle in the system is N, volume V, its energy lies in between E and $E + \Delta$. Let H be the Hamiltonian of the system. For a such it is convenient to choose a standard set of complete orthogonal wave function $\{\Phi_n\}$ such that Φ_n is a wave function of N particle contained in volume V and is an eigen function of H with eigen E_n .

$$H\emptyset_n = E_n\emptyset_n \rightarrow (ix)$$

The postulates of a quantum statistical mechanics are the statements of postulate of equal a priori probability as

$$(\overline{C_n, C_m}) = 1 \; if \; E < E_n < E + \Delta \rightarrow (x)$$

$$(\overline{C_n, C_m}) = 0 \;\; otherwise \;\; \rightarrow (xi)$$

And the other one is postulate of Random Phases as

$$(\overline{C_n, C_m}) = 0 \; (n \neq m) \rightarrow (xii)$$

As a consequences of these postulates we may effectively regard the wave function of a system as given by

$$\Psi = \sum_{n} b_n \emptyset_n \rightarrow (xiii)$$

Where

$$|b_n|^2 = 1 \;\; if\; E < E_n < E + \Delta \rightarrow (xiv)$$

$$|b_n|^2 = 0 \;\; otherwise \rightarrow (xv)$$

Where phases of the complex number $\{b_n\}$ are random numbers. In this manner the effect of the external world is taken inti account in an average way.The observed value of an observable associated with the operator θ is then given by

$$\langle\theta\rangle = \frac{\sum_n |b_n|^2 \left(\emptyset_n, \theta(\emptyset_n)\right)}{\sum_n |b_n|^2} \rightarrow (xvi)$$

This should be emphasized that this equation to be effectively valid the system must interact with the external world. The postulate of random phases implies that the state of a system in equilibrium may be regarded as an incoherent superposition of eigen states. It is possible to think of the system as one of the member of an infinite collection of systems, each of which is an eigen state whose wave function $\emptyset_n$. Since these systems do not interfere with one another it is possible to form a mental picture of each system at a time.we may call this mental picture an ensemble.

The postulates of quantum statistical mechanics are to be regarded as working hypotheses whose justification lies in the fact that they lead to results in agreement. Such a point of view is not entirely satisfactory, because these postulates cannot be independent of , and should be derivable from the quantum mechanics of the molecular systems. The postulates of quantum statistical mechanics are more fundamental than the laws of thermodynamics. First the postulates of quantum statistical mechanics not only imply the laws of thermodynamics they also lead to definite formulas for all the thermodynamic functions of a substance. Second they are more directly related to molecular dynamics than are the laws of thermodynamics.

Liouville Theorem:

The dynamical state of a system at some instant of time can be represented by a point in the phase space. This point will not be stationary but will move along a definite trajectory which is determined from equation of motion.

$$\dot{q}_i = \frac{\partial H}{\partial P_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \rightarrow (xvii)$$

Where H is the Hamiltonian and $i = 1,2,3, \dots . f$

As a result of this motion the density ρ of the system in phase space changes with time. To deduce $\frac{\partial \rho}{\partial t}$ at a given point in phase space is Liouville Theorem.

This theorem is primarily concerned with defining a fundamental property of the phase space, the space of position and momenta coordinate in which the system represented by a point moves in time. The consist of two parts-

The first part states conservation of density in phase space i.e. the rate of change of density of phase point in phase space is zero i.e.$\frac{\partial \rho}{\partial t} = 0$

The second part gives the conservation of extension in phase space i.e. $\frac{d}{dt}(dV) = 0$ or the volume at the disposal of a particular number of phase points is conserved throughout the phase space.

Considering any fixed element of volume of phase space located between $q_1 \,\&\, q_1 + \partial q_1 \;\ldots\ldots..q_f \,\&\, q_f + \partial q_f \;\ldots\ldots, p_f \,\&\, p_f + \partial p_f$. The number of system located in the volume $(dq_1 \ldots.dq_f; dp_1 \ldots..dp_f)$ changes as coordinates and momenta of the system vary. In the time dt the change in number of system within the volume of phase space is given by

$$\left(\frac{\partial p}{\partial t}\right) dt(dq_1 \ldots dp_1)$$

This changes is due to number of system in entering and leaving volume in time dt.

The net increase in time dt number of system in this volume of phase space is then obtained by summing the net number of system entering the volume through all the faces labelled by $q_1 \dots q_f$ & $p_1 \dots p_f$. Hence

$$\frac{\partial \rho}{\partial t} dt \partial q_1 \dots \partial q_f . \partial p_1 \dots \partial p_f$$

$$= \sum_{i=1}^{f} \left[\rho \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) + \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \right] dt \partial q_1 \dots \partial q_f \partial p_1 \dots \partial p_f \rightarrow (xviii)$$

$$\Rightarrow \frac{\partial \rho}{\partial t} = - \sum_{i=1}^{f} \left[\rho \left(\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} \right) + \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] \rightarrow (xix)$$

Now $\dot{q}_i = \frac{\partial H}{\partial p_i}$ & $\dot{p}_i = -\frac{\partial H}{\partial q_i}$

Now order of differential is immaterial

$$\sum_{i=1}^{f}\left(\frac{\partial \dot{q}_i}{\partial q_i}+\frac{\partial \dot{p}_i}{\partial p_i}\right)=0 \rightarrow (xx)$$

Therefore

$$\left(\frac{\partial \rho}{\partial t}\right)_{p,\,q}=-\sum_{i=1}^{f}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i+\frac{\partial \rho}{\partial p_i}\dot{p}_i\right)$$

$$\left(\frac{\partial \rho}{\partial t}\right)_{p,\,q}+\sum_{i=1}^{f}\left(\frac{\partial \rho}{\partial qi}\dot{q}_i+\frac{\partial \rho}{\partial pi}\dot{p}_i\right)=0 \rightarrow (xxi)$$

This equation is known as Liouville’s Theorem.

If ρ function of p, q, t and q, p are function of t then

$$\frac{\partial\rho}{\partial t} = \frac{\partial\rho}{\partial t} + \sum_i \frac{\partial\rho}{\partial q_i} \frac{\partial q_i}{\partial t} + \sum_i \frac{\partial\rho}{\partial p_i} \frac{\partial p_i}{\partial t} \rightarrow (xxii)$$

Therefore

$$\frac{\partial\rho}{\partial t} = 0 \rightarrow (xxiii)$$

This is the Principle of Conservation of Density of phase space. Therefore the density of a group of points remains constant along their trajectories in the phase space. If at any time the phase points are distributed uniformly in phase space the will for ever have uniform density.