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1. Learning Outcomes

After studying this module, you shall be able to

- Appreciate the statistical approach called ensemble method for understanding the properties of a given macroscopic system underlining the need for such an approach
- Define an ensemble characterized by thermodynamic variables such as (E, N, V), (T, N, V) and (μ, N, V) etc.
- Understand the concept of statistical density function or statistical distribution function $\rho(q, p; t)$, link it to the ensemble average of a physical quantity and see its advantage over the equivalent time averaging
- See how knowledge of probability function allows us to calculate average values of a physical quantity.
- Derive Liouville's theorem that the statistical distribution function is constant along the phase trajectory of the system and discuss its significance in statistical physics
- Liouville's theorem as conservation of phase space volume
- Show that ensemble average of any physical quantity is equal to the value one expects to obtain on making an appropriate measurement i.e. time average of a physical quantity is equal to the ensemble average of the same physical quaintity, called erg odic hypothesis.
- Understand the concept of fluctuations, root mean square fluctuation and relative fluctuations for a given physical quantity.
- Prove that relative fluctuation of a physical quantity varies inversely as square root of the number of particles in the system.

2. Introduction

We have already learnt the concept of phase space and its properties in module 10. In this module we introduce an altogether new concept of an ensemble introduced by J W Gibbs in his famous book *Elementary Principles in Statistical Mechanics*. Fully well realizing that in the study of macroscopic systems we are dealing with a situation which can not be approached from point of view of motion of these huge number of particles, J.W. Gibbs introduced this new idea which, without improving on the inherent lack of information about the system, paved way for applying statistical approach to arrive at mean value of a physical quantity via the concept of statistical distribution function or statistical probability density function. To begin with ensemble sounds an obscure abstract concept but later turns out to be an extremely useful one to lay the statistical scaffolding to understand many particle physical systems. We in this module state and prove Liouville's theorem pertaining to probability density function and explore its properties embodied in the theorem. We also explore the statistical meaning of mean value, root mean square fluctuation and relative fluctuations. We wind up our discussion on foundation of ensemble theory by looking at the meaning of ergodicity.

3. Ensemble: An Abstract Useful Concept

Ensemble is a French word meaning a group. In day today conversation we are familiar with the usage of this term applied to a group of musicians in a band forming say Philharmonic Ensemble. In this module we look at this concept as applied to a group of

phase points in phase space representing different microstates of a given macrostate taken together as members of an ensemble of systems as shown in the figure 1 below.
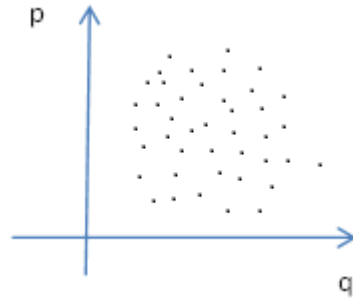

Figure 1 Dots in the picture represent various microstates of a given macrostate forming members of an ensemble

To define precisely, a statistical ensemble is a collection of or a group of large number of exact thought replicas of a given macrostate, with each replica having same state parameters but can find themselves in one of all possible microstates represented by points in phase space for each ensemble.

So in the Gibbs visualization different phase points evolving in time, exploring the allowed phase space can be seen together at the same instant representing members of a group called an ensemble confined to a region in phase space. As time flows each member of this ensemble can acquire any one of the all possible microstates.

4 Statistical (probability) distribution function

What is that characteristic function which can describe this ensemble? First note since we are dealing with a very large number of these systems the points in phase space are very dense we can define their density distribution function $\rho(q, p; t)$, a function which describes how various members of the ensemble are distributed over all allowed microstates at different points of time. So that number of points i.e. macrosystems in the phase space volume $d^{3N}q \, d^{3Np}$ around the point (q,p) of the phase space is $\rho(q, p; t)d^{3N}q \, d^{3Np}$. Therefore, number of systems in the ensemble is given by

$$M = \int \rho(q, p; t)d^{3N}q \, d^{3Np} \tag{1}$$

Also density distribution function helps us to define, the ensemble average $\langle f \rangle$ of a physical quantity $f(q, p)$ which over different members of the ensemble may be different. Therefore, ensemble average $\langle f \rangle$ is defined as

$$\langle f(q, p) \rangle = \frac{\int f(q, p)\rho(q, p; t)d^{3N}q \, d^{3N}p}{\int \rho(q, p; t)d^{3N}q \, d^{3N}p} \tag{2}$$

Here, the integration extends over whole of the phase space, but contribution comes from that region alone where $\rho(q, p; t) \neq 0$.

Since total number of systems in the ensemble do not change with time t, therefore,

$$\frac{d\rho(q, p; t)}{dt} = 0 \tag{3}$$

This implies that

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_\iota + \frac{\partial \rho}{\partial p_i} \dot{p}_\iota \right) \tag{4}$$

Or

$$= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_\iota} \right) \tag{5}$$

Or

$$= \frac{\partial \rho}{\partial t} + [\rho, H] = 0 \tag{6}$$

Where $[\rho, H]$ is a Poisson Bracket.

Two facts are well known

    (i)   If the Poisson Bracket of a physical quantity with Hamiltonian is zero, then that quantity is a constant of motion.

    (ii)   For equilibrium, physical quantities must be independent of time, so if ρ represents an equilibrium system then $\frac{\partial \rho}{\partial t} = 0$.

This implies that $[\rho, H] = 0$ i.e. ρ is a constant of motion. Equation

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0 \tag{7}$$

embodies a theorem called Liouville's theorem. This can be proved equivalently in two ways

(i) The volume element of the phase space remains constant or the phase volume is a constant (invariant) of motion under canonical transformation of the co-ordinates (q, p).

(ii) The movement of phase points treated as steady flow of a gas in the phase space of $6N$ dimensions moves as an incompressible fluid moving in physical space gives

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + [\rho, H] = 0$$

5 Proof of Liouvilles theorem

(i) The volume element of the phase space remains constant or the phase volume is a constant (invariant) of motion under canonical transformation of the co-ordinates (q, p).

Let us consider volume element $d\omega = d^{3N}q \, d^{3N}p = \prod_{i=1}^{3N} dq_i dp_i$ in phase space. As a physical system evolves in time say it is found at point $P(p_i, q_i)$ at time t and is found at some later time t' at another point $P'(p_i', q_i')$, where (p_i', q_i') can be obtained from (p_i, q_i) the initial point, as shown in figure 2.
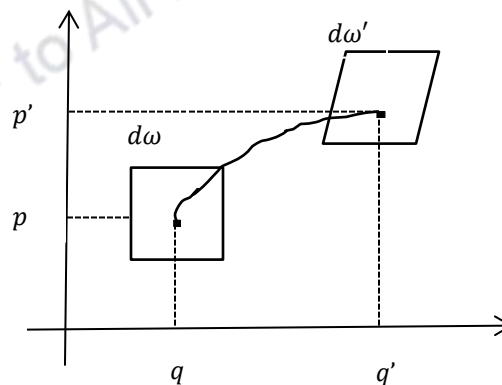

Figure 2 Time evolution of a phase space volume in phase space

This can be achieved in two ways set (p_i', q_i') obtained from (p_i, q_i) by integrating Hamilton's equations of motion. Algebraically this can be represented as

$$p_i' = p_i'(p_i, q_i); q_i' = p_i'(p_i, q_i) \tag{8}$$

Where $i = 1, 2, ... 3N$. Equation (8) is a transformation of the set of variables (p_i, q_i) to (p_i', q_i'). So the volume element of $d\omega$ to the corresponding volume element $d\omega'$ obtained through this transformation is related by an expression

$$d\omega' = \mathbb{J}(t, t')d\omega \qquad (9)$$

Where $\mathbb{J}(t, t')$ is the jacobian determinant of the transformation given below

$$\mathbb{J}(t, t') = \left| \frac{\partial(p_i', q_i')}{\partial(p_i, q_i)} \right| = \begin{vmatrix} \frac{\partial p_1'}{\partial p_1} & \frac{\partial q_1'}{\partial p_1} & \frac{\partial p_2'}{\partial p_1} & \frac{\partial q_2'}{\partial p_1} & ... & ... & \frac{\partial p_{3N}'}{\partial p_1} & \frac{\partial q_{3N}'}{\partial p_1} \\ \frac{\partial p_1'}{\partial q_1} & \frac{\partial q_1'}{\partial q_1} & ... & .... & ... & ... & ... & \\ ... & ... & ... & ... & & & & \\ \frac{\partial p_1'}{\partial p_{3N}} & \frac{\partial q_1'}{\partial p_{3N}} & ... & ... & & & \frac{\partial p_{3N}'}{\partial p_{3N}} & \frac{\partial q_{3N}'}{\partial p_{3N}} \\ \frac{\partial p_1'}{\partial q_{3N}} & \frac{\partial q_1'}{\partial p_{3N}} & ... & ... & ... & ... & \frac{\partial p_{3N}'}{\partial q_{3N}} & \frac{\partial q_{3N}'}{\partial p_{3N}} \end{vmatrix} \qquad (10)$$

To evaluate the various elements of the determinant, let $t' = t$, so that $p_i' = p_i$, $q_i' = q_i$ and, therefore, $\frac{\partial p_i'}{\partial p_k} = \delta_{ik}$, $\frac{\partial p_i'}{\partial q_i} = 0$, $\frac{\partial q_i'}{\partial q_k} = \delta_{ik}$, $\frac{\partial q_i'}{\partial p_k} = 0$, where δ_{ik} is Kronecker delta which is equal to 1 for $i = k$ and zero otherwise. So all the diagonal terms are equal to 1 and all off diagonal elements equal to zero. Therefore, $\mathbb{J}(t, t) = 1$

Let us now go to another instant $t' = t + dt$ and retain only first order terms in dt then, we have after using Hamilton's equations of motion

$$p_i' = p_i + dp_i = p_i + \dot{p}_i \, dt = p_i - \frac{\partial H}{\partial q_i} dt \qquad (11)$$

$$q_i' = q_i + dq_i = q_i + \dot{q}_i \, dt = q_i + \frac{\partial H}{\partial p_i} dt \qquad (12)$$

Differentiating equations (11) and (12), we obtain

$$\frac{\partial p_i'}{\partial p_k} = \delta_{ik} - \frac{\partial^2 H}{\partial p_k \partial q_i} dt \qquad (13)$$

$$\frac{\partial p_i'}{\partial q_k} = -\frac{\partial^2 H}{\partial q_k \partial q_i} dt \qquad (14)$$

$$\frac{\partial q_i'}{\partial p_k} = \frac{\partial^2 H}{\partial p_k \partial p_i} dt \tag{15}$$

$$\frac{\partial q_i'}{\partial q_k} = \delta_{ik} + \frac{\partial^2 H}{\partial q_k \partial p_i} dt \tag{16}$$

So to evaluate the determinant, equation (10), we note that each term containing an off diagonal member contains at least another off diagonal member as a factor. Since all theses members are proportional to dt, these terms are therefore at least of second order in dt and can be neglected while evaluating the determinant. So to this oder, therefore, contribution comes from the diagonal elements

$$\prod \left(1 - \frac{\partial^2 H}{\partial p_k \partial q_k} dt\right)\left(1 + \frac{\partial^2 H}{\partial p_k \partial q_k} dt\right) \tag{17}$$
$$\cong 1 + \sum_k \left(\frac{\partial^2 H}{\partial p_k \partial q_k} - \frac{\partial^2 H}{\partial p_k \partial q_k}\right) = 1$$

Therefore,

$$\mathbb{J}(t, t+dt) = \mathbb{J}(t,t) + \frac{\partial}{\partial t}\mathbb{J}(t'',t)|_{t=t''} dt = 1 \tag{18}$$

And since $\mathbb{J}(t,t) = 1$ we have

$$\frac{\partial}{\partial t}\mathbb{J}(t'',t)|_{t=t''} dt = 0 \tag{19}$$

Let us further consider an arbitrary third time t'' and the corresponding volume element $d\omega''$ at time t''. Then, going from t to t'' and from t'' to t', we have respectively

$$d\omega'' = \mathbb{J}(t, t'')d\omega \tag{20}$$

And

$$d\omega' = \mathbb{J}(t'', t')d\omega'' \tag{21}$$

Therefore,

$$d\omega' = \mathbb{J}(t, t'')\mathbb{J}(t'', t')d\omega = \mathbb{J}(t, t')d\omega \qquad (22)$$

Or

$$\mathbb{J}(t, t') = \mathbb{J}(t, t'')\mathbb{J}(t'', t') \qquad (23)$$

Hence differentiating with respect to final time t' we have

$$\frac{\partial\mathbb{J}(t, t')}{\partial t'} = \mathbb{J}(t, t'') \left(\frac{\partial\mathbb{J}(t'', t')}{\partial t'}\right) \qquad \textbf{(24)}$$

On the right side taking $t'' = t'$, and equation (24) becomes

$$\frac{\partial\mathbb{J}(t, t')}{\partial t'} = \mathbb{J}(t, t') \left(\frac{\partial\mathbb{J}(t'', t')}{\partial t'}\right)\Big|_{t''=t'} \qquad (25)$$

Since equation (19) holds for any time t, it also holds for t', and hence equation (25) implies

$$\frac{\partial\mathbb{J}(t, t')}{\partial t'} = 0 \qquad (26)$$

This relation holds for arbitrary t' and given the intial condition $J(t, t) = 1$, one can on integration get

$$\mathbb{J}(t, t') = 1 \qquad (27)$$

Hence from equation (9) one gets

$$d\omega' = d\omega \qquad (28)$$

This means that the magnitude of the volume element in phase space does not change as it moves along the phase space trajectory.

Furthermore, this result is true for the volume of any closed finite region followed along the phase trajectory. To state it more clearly, to every volume element $d\omega$ within that region at time t, there exists an equal volume element $d\omega'$ within the region R' at time t' obtained from R by equations of motion. This amounts to saying that integrating right

hand side of equation (28) over R corresponds to integrating the left hand side of the equation (28) over R' so that

$$\int_{R'} d\omega' = \int_{R} d\omega \tag{29}$$

Or

$$\Omega' = \Omega \tag{30}$$

Where Ω and Ω' represent the volume contained within R and R' respectively. This is Liouville's theorem which states that phase volume is a constant of motion.

Let us now look at the second way of looking at Liouville's Theorem which is more often used in statistical mechanics with immediately connected with the density distribution function $\rho(q, p; t)$ as stated below.

(ii) The movement of phase points treated as steady flow of a gas in the phase space of $6N$ dimensions moves as an incompressible fluid moving in physical space has

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$$

Physically this means that local density distribution of the phase points in a region as viewed by an observer moving with that region stays constant.

Let us consider an arbitrary volume ω in region of interest in phase space. Let this volume be enclosed by a surface σ as shown in figure 3 below.

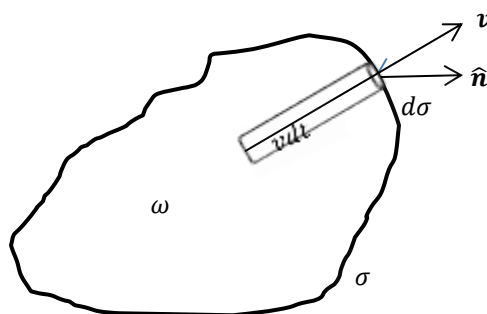
Figure 3   Phase points of a system as a steady flow of a gas in 6N dimensional phase space.

Then the rate of increase of number of representative points in the volume ω is

$$\frac{\partial}{\partial t} \int_\omega \rho \, d\omega \tag{31}$$

Where $d\omega$ is the volume element $d^{3N}q \, d^{3N}p$. The total rate at which the repreresantative points flowing out of the volume ω across the surface σ bounding it is given by

$$\int_\sigma \rho v . \hat{n} d\sigma \tag{32}$$

Where, v is the velocity vetor of the phase points in the region of surface element $d\sigma$, $\hat{n}$ is the unit vector normal to area element $d\sigma$. By Gauss's theorem, surface integral can be written as

$$\int_\omega \nabla . (\rho v) \, d\omega \tag{33}$$

The integrand here in phase space of $6N$ dimensions can be written as

$$\nabla . (\rho v) \equiv \sum_{i=1}^{3N} \left\{ \frac{\partial}{\partial q_i}(\rho \dot{q_i}) + \frac{\partial}{\partial p_i}(\rho \dot{p_i}) \right\} \tag{34}$$

Since the total number of representative points are fixed in phase space, the number of incoming representative points in the volume must remain equal, therefore,

$$\frac{\partial}{\partial t} \int_\omega \rho \, d\omega = - \int_\omega \nabla . (\rho v) \, d\omega \tag{35}$$

i.e.

$$\int_\omega \frac{\partial \rho}{\partial t} + \nabla . (\rho v) \, d\omega = 0 \tag{36}$$

Equation (36) is possible only if the integrand vanishes in the region of concern in phase space. Thus we must have

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$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) = 0 \tag{37}$$

Which is the famous equation of continuity of fluid flow, which in the present context is that of a flow of representative points of the phase space being treated as fluid. Using 34 it can be written equation (37) can be written as

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial \rho}{\partial q_i} \dot{q}_\iota + \frac{\partial \rho}{\partial p_i} \dot{p}_\iota \right\} + \sum_{i=1}^{3N} \rho \left\{ \frac{\partial}{\partial q_i} \dot{q}_\iota + \frac{\partial}{\partial p_i} \dot{p}_\iota \right\} = 0 \tag{38}$$

Since from Hamilton's equations of motion we have

$$\frac{\partial \dot{q}_\iota}{\partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} = \frac{\partial^2 H}{\partial p_i \partial q_i} = -\frac{\partial \dot{p}_\iota}{\partial p_i} \tag{39}$$

Therefore, the third term on right hand side of equation (38) vanishes. And once again using Hamilton's equations of motion $\dot{q}_\iota = \frac{\partial H}{\partial p_i}$ and $\dot{p}_\iota = -\frac{\partial H}{\partial q_i}$, equation (38) becomes

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial \rho}{\partial q_i} \dot{q}_\iota + \frac{\partial \rho}{\partial p_i} \dot{p}_\iota \right\} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right\} = 0 \tag{40}$$

Or

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0 \tag{41}$$

Where, left hand side in equation (40) represents the total derivative $\frac{d\rho}{dt}$ and $[\rho . H]$ is Poission bracket.

Equation (41) embodies the Liouville's theorem.

6 Significance of Liouville's Theorem and Types of Ensembles

Liouville's theorem as seen in equation (40) or (41) has some interesting consequences for arriving at functional dependence of probability distribution functions which we are going to find in later modules and help define different types of ensembles. We have already commented on the significance of the first term $\frac{\partial \rho}{\partial t}$ becoming zero implies a stationary ensemble. For (41) to be zero implies that $[\rho, H] = 0$, which can be made zero in two possible ways:

(i) Since, $[\rho.H] = \sum_{i=1}^{3N}\left\{\frac{\partial\rho}{\partial q_i}\dot{q}_\iota + \frac{\partial\rho}{\partial p_i}\dot{p}_\iota\right\}$, and if ρ is independent of position and momentum co-ordinates, $[\rho.H]$ will be obviously zero. That is

$$\rho(p,q) = constant \tag{42}$$

Over the region of interest for the system under consideration. This further makes calculation of ensemble average defined in equation (2) a simple relation

$$\langle f(q,p)\rangle = \frac{\rho\int f(q,p)d^{3N}q\,d^{3N}p}{\rho\int d^{3N}q\,d^{3N}p} = \frac{\int f(q,p)d^{3N}q\,d^{3N}p}{\int d^{3N}q\,d^{3N}p} \tag{43}$$

$$= \frac{1}{\omega}\int\limits_{\omega} f(q,p)\,d\omega$$

Where ω, denotes volume of region of interest of phase space. This is a restatement of principle of equal apriori probability. That is any representative point in the swarm of points figure 1, is equally likely to be in the nighbourhood of any phase point in the allowed region of interest. The ensemble satisfying equation (42) is called micro-cannonical ensemble.

(ii) An alternative way to satisfy $[\rho.H] = 0$ is to suppose ρ being explicitily dependent on $H(p,q)$ i.e.

$$\rho = \rho\big(H(q,p)\big) \tag{44}$$

This gives us another type of probability distribution functions satisfying equation (41). One of such ensembles is *canonical ensemble* for which

$$\rho\big(H(q,p)\big) \propto e^{-\frac{[H(p,q)]}{kT}} \tag{45}$$

7 Ergodicity Hypothesis: Time Average Versus Ensemble Average

To appreciate this theorem, we must note that for a a given thermodynamic system there are two ways of calculating averages. One way is to study the dynamics of a system over a long period of time and the other is to find average through a statistical description. First type of average is called time average and the second type is called ensemble average. Ergodic Hypothesis requires that both these averages should be equal.

The dynamics of the thermodynamic system is deterministic governed by Hamilton's equations. When we start observing the system at intial time $t = 0$ and let it evolve to time $= \tau$, the state of the system evolves producing a phase trajectory and the Hamilton's equations can be integrated providing $(q, p) = \{q_i(t), p_i(t)\}$ at every instant of time. If we consider a physical quantity $f(q, p)$, we can average over this trajectory and calculate time average defined as

$$< f(q,p) >_\tau = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\infty f(\{q_i(t), p_i(t)\}) dt \qquad (46)$$

Which is not a practical proposition to find all $\{q_i(t), p_i(t)\}$ for a thermodynamic system containing a large number of particles typically of the order of Avagadro's number.

It is important to understand that it is time average which is experimentally observable.

The alternative average called ensemble average, can defined by equation (2)

$$\langle f(q,p) \rangle = \frac{\int f(q,p) \rho(q,p;t) d^{3N}q \, d^{3N}p}{\int \rho(q,p;t) d^{3N}q \, d^{3N}p}$$

Ergodic hypothesis then says that

$$< f(q,p) >_\tau = \langle f(q,p) \rangle \qquad (47)$$

Geometrically speaking, the ergodicity means that phase trajectory passes through all the points through the region of interest defined by the surface $H = E$. A system such as this is called ergodic. The problem with this assertion is that topologically no single phase trajectory can fill all the energy surface, This led to an idea of quasi ergodic hypothesis according to which over a sufficiently long time the phase trajectory for a closed system defined by $H = E$, the phase trajectory comes arbitrarily close to every point on the energy surface and then the time average can be replaced by the ensemble average.

The importance of ergodic hypothesis lies in the fact that it resolves a difficult problem of calculating the mean value of a physical quantity over time by allowing its calculation over a set of exact replicas of the system at a single instant, called ensemble average.

Proof of Ergodic hypothesis:

To prove (47), let us follow plausibility arguments using Liouville's theorem as given below:

According to ergodic hypothesis, since all points on the $H = E$ surface are reached by the phase trajectory of the system, any point on the surface can be taken as a starting point.

This implies that time average $< f(q,p) >_\tau$ is independent of the initial point, any point on the phase trajectory can act as an intial point at time t=0.

Therefore, let us take time average of ensemble average $\langle f(q,p) \rangle$ i.e.

$$\langle\langle f(q,p) \rangle\rangle_\tau \qquad (48)$$

Since according to Liouville's theorem, for a system its ensemble average $\langle f(q,p) \rangle$ is independent of time, therefore,

$$\langle f(q,p) \rangle = \langle\langle f(q,p) \rangle\rangle_\tau = \langle f(q,p) \rangle_\tau \qquad (49)$$

Non Ergodic Systems:

To see the violation of ergodic hypothesis number of situations can be visualized. Suppose there is a rectangular box with perfectly smooth walls containing atoms of an ideal gas arranged to move along straight paths from left to right as shown in the figure 4 below.
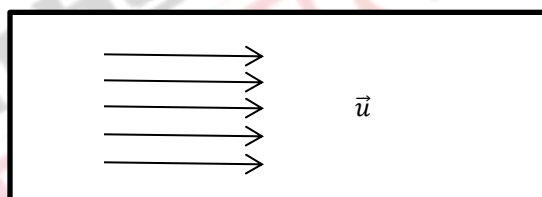

Figure 4 A non-ergodic system

Since walls of the rectangular box are smooth, the atoms of the gas will keep on moving back and forth between the left and right walls and will never pass through any other points in the box, clearly violating the ergodic hypothesis. It must be noted that this is highly improbable situation and a small disturbance can randomize the velocities through collisions.

8 Fluctuation, Root Mean Square Fluctuation and Relative Fluctuation

Furthermore, now we must we aware of the fact that averages of the physical quantities are expected from the measurements yet there is a possibility of deviations or fluctuations occurring from these average values. Study of these fluctuations is of great importance in many phenomenon occurring in nature for example in critical opalescence, Brownian motion etc.

Let us consider a physical quantity f corresponding to a physical system. As time progresses this value varies about its average value as $\Delta f = f - \langle f \rangle$. This variation about

the average or mean value can be both positive an negative and its mean value $\langle \Delta f \rangle = \mathbf{0}$ and, therefore, is not of any significance. A better quantity to define is $(\Delta f)^2$. Interestingly, its average value tends to zero only when $(\Delta f)^2$ tends to zero. $(\Delta f)^2$ can be written as

$$(\Delta f)^2 = (f - \langle f \rangle)^2 = f^2 - 2f\langle f \rangle + \langle f \rangle^2 \tag{50}$$

Let us take the average of both sides we get mean square fluctuation as

$$\langle (\Delta f)^2 \rangle = \langle f^2 \rangle - 2\langle f \rangle\langle f \rangle + \langle f \rangle^2 = \langle f^2 \rangle - \langle f \rangle^2 \tag{51}$$

Which is mean of the square minus square of the mean.

The ratio $\frac{\sqrt{\langle (\Delta f)^2 \rangle}}{\langle f \rangle}$ is called the relative fluctuation. Smaller is the relative fluctuation, less is the proportion of time for which the system remains away from mean value.

Now we shall see that relative fluctuation decreases inversely as the size of the system(i.e. number of partcles) increases.

For this suppose we have a system of N particles. We are interested in a physical quantity (say kinetic energy of the system F) which is an additive quantity corresponding to this physical quantity f_i (say kinetic energy) for each particle i.e.

$$F = \sum_{i=1}^{N} f_i \tag{52}$$

Let us take the average and note that since each particle constituting the system is identical $\langle f_i \rangle$ of every particle is same i.e. say $\langle f \rangle$. Then equation (52) can be written as

$$\langle F \rangle = \sum_{i=1}^{N} \langle f_i \rangle = N \langle f \rangle \tag{53}$$

So now if we calculate the root mean square fluctuation of F from $\langle F \rangle$ and noting that since each $\langle \Delta f_i \rangle = \mathbf{0}$ and $\langle \Delta f_i \Delta f_j \rangle = \langle \Delta f_i \rangle \langle \Delta f_j \rangle = \mathbf{0}$. We have

$$\Delta F = F - \langle F \rangle = \sum_{i=1}^{N} (f_i - \langle f_i \rangle) = \sum_{i=1}^{N} \langle \Delta f_i \rangle \tag{54}$$

Squaring equation (54) and taking average, we get

$$\langle (\Delta F)^2 \rangle = \langle \left(\sum_{i=1}^{N} \langle \Delta f_i \rangle \right)^2 \rangle = \sum_{i=1}^{N} \langle (\Delta f_i)^2 \rangle \tag{55}$$

Again noting that because all the particles are identical each (Δf_i^2) is the same for all particles, therefore,

$$\langle (\Delta F)^2 \rangle = N \langle (\Delta f)^2 \rangle \tag{56}$$

So the relative fluctuation is given by

$$\frac{\sqrt{\langle (\Delta F)^2 \rangle}}{\langle F \rangle} = \frac{\sqrt{N \langle (\Delta f)^2 \rangle}}{N \langle f \rangle} = \frac{1}{\sqrt{N}} \frac{\sqrt{\langle (\Delta f)^2 \rangle}}{\langle f \rangle} \tag{57}$$

Equation (57) tells us that the relative fluctuation of a physical quantity pertaining to a system varies inversely as the square root of the number of particles in a thermodynamical system. In thermodynamical limit it approaches zero.

9 Summary

In this module we have learnt

- About the abstract but useful concept of ensemble for a thermodynamic system which is a collection of exact replicas of a given thermodynamic systems in different possible microstates.
- That an ensemble can be described by a characteristic density distribution function $\rho(q, p; t)$.
- That density distribution function when integrated over relevant phase space volume gives number of systems forming an ensemble.
- That the ensemble average is defined as

$$\langle f(q, p) \rangle = \frac{\int f(q, p) \rho(q, p; t) d^{3N}q \, d^{3N}p}{\int \rho(q, p; t) d^{3N}q \, d^{3N}p}$$

- That for a system in equilibrium statistical distribution function is a constant of motion and is independent of time.
- That Liouville's theorem can be stated and proved in two equivalent ways:

(i)   The volume element of the phase space remains constant or the phase volume is a constant (invariant) of motion under canonical transformation of the co-ordinates (q, p).

(ii)   The movement of phase points treated as steady flow of a gas in the phase space of $6N$ dimensions moves as an incompressible fluid gives

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$$

- That the significance of Liouville's theorem lies in the fact that it provides a way to get probability distribution function as a function of Hamiltonian leading to the defining of micro-canonical and canonical distribution function.
- That ergodic hypothesis provides equivalence between time averages of physical quantities which are experimentally measurable with statistically calculated ensemble averages.
- That Liouville's theorem provides a way to arrive at ergodic hypothesis.
- About the possibility of having a non-ergodic system.
- About the importance of fluctuations in the measurement of a physical quantity and how root mean square fluctuation and relative fluctuation can be calculated.
- That relative fluctuations varies inversely as square root of number of particles constituting the system.

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