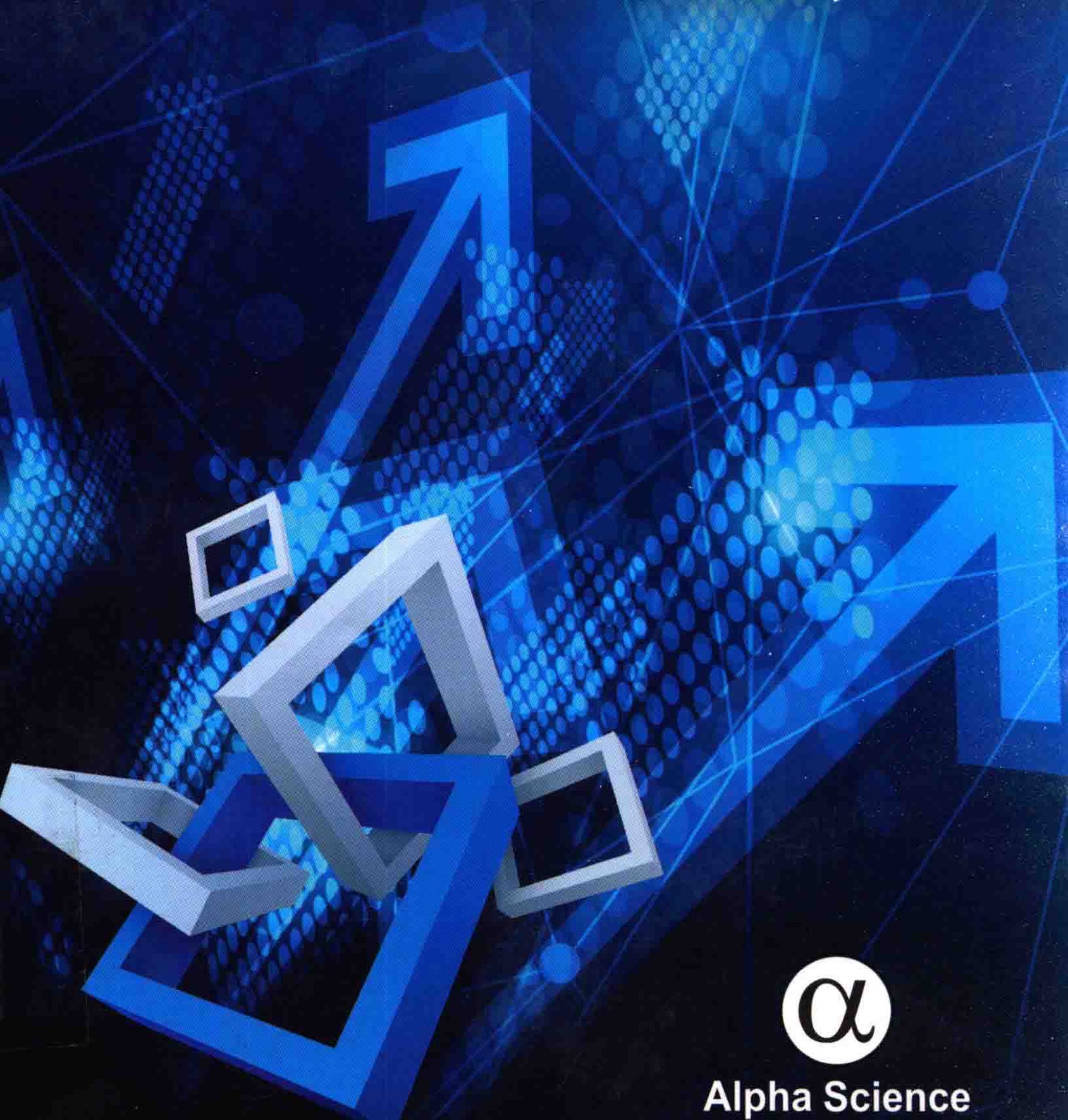
Statistical Mechanics

Madhusudan Jana



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Statistical Mechanics

Dedicated to my
grandfather
who inspired me to
do something good

Preface

Being a teacher of this subject, I have felt a crisis of the students in empowering themselves in the subject through a thorough reading and thereby learning the essence of this branch of physics following a methodical book, keeping in mind the University examination system. I have tried to meet this crisis presenting this book to our beloved UG and PG students. Research is done on the articles which are required for their easy understanding of the subject and to meet the university curriculum. The basic understanding as well as their relation to thermodynamic macroscopic variables are emphasized. All three statistics are developed separately following number of applications to solid state phenomenon and others. The method of ensembles is discussed with sincerity without mathematical complications. Some special topics like Transport phenomenon, Bose-Einstein condensation of liquid Helium, White dwarfs, introductory Ising model and Yang and Lee Theory are given to grow interest to our students into the recent research on the relevant topics. Hope this book will serve most of the requirement for UG and PG students of this discipline. Every suggestion and query will be appreciated for further improvement of this book.

While writing this book, I have consulted a large number of text books and websites. I am grateful to the authors of such books and acknowledge their contribution submissively. Nothing new is written by me, but the presentation is different from others. I would feel grateful if this publication receives the encouraging support and patronage from the concerned students and faculty.

I express heartfelt thanks to my wife Amala who is also a teacher of this subject for inspiring me to publish the work and thoughts for a prestigious organization like Narosa Publishing House in the form of text book. Deep gratitude is also extended to my only daughter Samadrita for sacrificing her leisure time during the preparation of the manuscript.

Last but not the least, I sincerely express my thanks to the publisher and the Managing Director of Narosa Publishing House, Mr. N. K. Mehra whose promptness encouraged me to complete the manuscript in time. Thanks to the entire production team for giving shape of the work in the form of book.

Madhusudan Jana

1

Basics of Statistical Mechanics and its Relation to Thermodynamics

1.1 INTRODUCTION: NEED OF STATISTICAL MECHANICS

All we know that the thermodynamics describes the macroscopic properties of matter phenomenologically with the help of equations of state which are derived empirically. But it consistent with the large universality of thermodynamics, the same laws of thermodynamics hold for different materials. However, this doesn't tell us what makes the thermal conductivity of one material different from the other. It is intuitively obvious that the thermal conductivity of one material is different from the other because microscopically the materials are different. The macroscopic quantities in materials must come from the microscopic properties. For example, the pressure of a gas is due to the collisions of the molecules with a surface of the wall of container, whereas temperature is directly given by the mean kinetic energy of the particles. On the other hand, the microscopic laws of physics describe the behaviour of individual particles with their mutual interaction. We use Newton's equations of motion for classical particles, whereas for quantum particles we use Schrödinger equation. Although microscopic laws describe the performance of particles precisely, they do not tell us how an enormous collection of particles, of the order of 10^{23}, would perform on the average.

It is the task of statistical mechanics to answer this question, particularly how microscopic performance of particles or small constituents, leads to a particular macroscopic property of the material. Thus, statistical mechanics provides a bridge between microscopic physics and thermodynamics.

One may think that microscopic laws describe the physics of one particle, and hence, they should describe the behavior of an assembly of particles (however large). A gas of N classical particles can be described by a group of N numbers of Newtonian coupled equations of motion. A solution of these equations would allow us to know exact position and velocity of each particle at any future time. This information allows us to know the microscopic state (which will be henceforth called *microstate*) of the gas at every instant. Solving these coupled equations methodically is usually not possible. However, one may solve such equations numerically, using computers. However, for a practical situation N is of the order of 10^{23}, and solving such a large number of equations numerically is beyond the capacity of any computer.

One should appreciate that for describing the macroscopic state of the gas, characterised by pressure, volume, temperature (which will be henceforth called *macrostate*), we do not need information on each microscopic detail which these coupled equations could make available. A large number of microstates may correspond to a single macrostate. We would, be interested in knowing the temperature of the gas, and not bother about what a particular atom of the gas is doing every of time. This means, we only need some average macroscopic quantities, and not every microscopic detail. So, solving these coupled differential equations would anyway be an overload, if we are able to solve them. So, we need a theoretically different approach to solve this problem.

In one sentence, thermodynamics is devoted to enlightening relations, sometimes predicted and unpredicted between the macroscopic quantities describing the gross properties of the materials. Statistical Mechanics provides statistically based approaches which fill up the gap between the physics of the individual particles of the materials and the simple thermodynamic laws which explain the macroscopic properties of many-particle systems.

The study of statistical mechanics can be classified mainly in the following categories:

(1) Classical Statistical Mechanics known as	**Maxwell-Boltzmann Statistics**
(2) Quantum Statistical Mechanics known as	**(i) Bose-Einstein Statistics** **(ii) Fermi-Dirac Statistics**

All these three statistics and their applications will be discussed in separate chapters.

1.2 PHASE SPACE

Let us be more specific about the concept of microstates. For a classical system, it is required to know at a time t all generalised coordinates $q_i(t)$ and momenta $p_i(t)$ to uniquely specify the state of motion of the system. Thus, for a mechanical system, we can interpret the set $\{q_i; p_i; i = 1; 2; ... N\}$ as the microstate of this system. For a single particle in one dimension, there is only one position variable x and one momentum variable p_x. If we plot x on the x-axis and p_x on the y-axis, a point on the graph will represent one state of the particle. As the particle moves in time, the point will follow a trajectory. We will call the space described by x and p_x, *phase space* (also called μ-*space*), the point representing a particular value of x and p_x, a *phase point*, and the trajectory followed by the point, the *phase trajectory*. In this particular case, the phase space is 2-dimensional.

Problem Find the phase trajectory of a one-dimensional S.H.O.

Solution: Suppose the Equation of the S.H.O. is given by

$$x = a \sin wt$$

or,
$$\frac{x}{a} = \sin wt$$

Velocity of the particle, $v_x = \frac{dx}{dt} = aw \cos wt$

Momentum, $p_x = maw \cos wt$

or,
$$\frac{p_x}{mwa} = \cos wt$$

Therefore, $\frac{x^2}{a^2} + \frac{p_x^2}{(maw)^2} = 1$

So, the phase trajectory is an ellipse as shown in Fig. 1.1 having semi-major and semi-minor axes as 'a' and 'mwa' respectively.

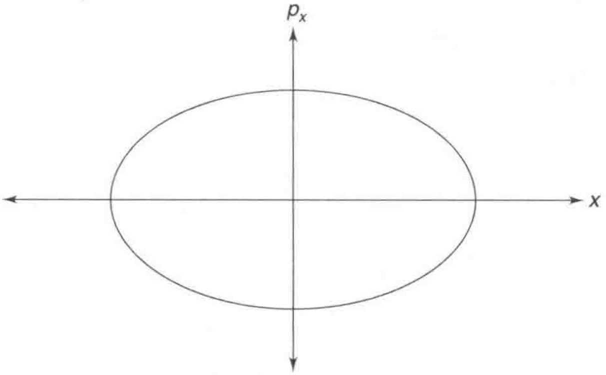


Fig. 1.1 *The phase trajectory of a one-dimensional S.H.O.*

Problem Find the phase trajectory of a particle of mass m and energy E moving along the x-axis in the force free region between two rigid walls at $x = 0$ and $x = L$.

Solution: For motion along +ve x-direction, $p_x = \sqrt{2mE} = \text{constant}$ $\left[\text{as } p_x^2/2m = E\right]$.

Thus, for reverse direction it will be $p_x = -\sqrt{2mE} = \text{constant}$

So, the phase trajectory is the line segment parallel to x-axis as shown in Fig. 1.2 on next page.

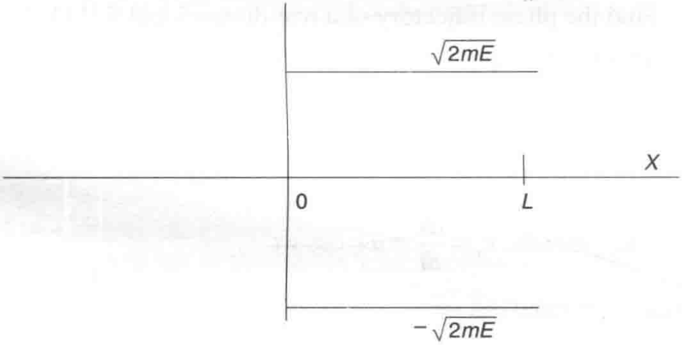


Fig. 1.2 *The phase trajectory of a particle of mass m and energy E*

For a single particle moving in 3-dimensions, 6 co-ordinate axes for x; y; z; p_x; p_y; p_z are needed. For N-particles in 3-dimensions, the phase space will be $6N$-dimensional. Such a $6N$-dimensional space is called Γ-*space*. So, the set $\{q_i\,;\,p_i\}$ can now be understood as a point in a $6N$-dimensional phase space. A point defined by $6N$-coordinates $(x_{11}, x_{21}, x_{31}, \ldots x_{1N}, x_{2N}, x_{3N}, p_{11}, p_{21}, p_{31}, \ldots p_{1N}, p_{2N}, p_{3N})$ in this phase space describes particular value of position and momentum values of all N-particles. Hence, a definite point in this phase space exactly corresponds to one microscopic state of motion of the whole system. The trajectory in phase space is described by Hamilton's equations:

$$\frac{\partial q_i}{\partial t} = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \frac{\partial p_i}{\partial t} = -\frac{\partial H}{\partial q_i}$$

where, the Hamiltonian $H\{q_i(t), p_i(t)\}$ in general, corresponds to the (possibly time-dependent) total energy of the system. In a closed system, in which the Hamiltonian does not depend explicitly on time, the total energy $E = H$ is a conserved quantity. Therefore, the phase trajectory always moves on a constant-energy curve or multi-dimensional surface.

1.3 VOLUME OF AN ELEMENTARY CELL

The phase space can be subdivided into small elements of sides δx, δy and δz and moments δp_x, δp_y, δp_z. The volume of each elementary cell is given by,

$$H = \delta x \cdot \delta y \cdot \delta z \cdot \delta p_x \cdot \delta p_y \cdot \delta p_z.$$

Now, according to Heisenberg's uncertainty principle,

$$\delta x \cdot \delta p_x \sim h$$
$$\delta y \cdot \delta p_y \sim h$$
$$\delta z \cdot \delta p_z \sim h$$

Therefore, $H = h^3$

According to Heisenberg's uncertainty principle, in phase space, the co-ordinates of a particle can be specified only to the extent that the particle under consideration has the position and momentum lying within the element of phase space of volume h^3.

If the system consists of molecules, each having, f degrees of freedom, then the state of each molecule is determined by f generalized co-ordinates $q_1, q_2, ..., q_f$ and f generalised momenta $p_1, p_2, ..., p_f$. In this case, the phase space of each molecule has $2f$ dimensions, and a volume element $d\phi = dq_1 dq_2 ... dq_f \, dp_1 dp_2 ... dp_f$.

1.4 CONCEPT OF ENSEMBLE

Each microstate of a N-particle gas is described by a point in the $6N$-dimensional phase space. So, if we consider all possible microstates which the gas can have, we will have a large collection of points in the phase space. This collection of phase points in the phase space, of all possible microstates of the system, is called an ***ensemble***. So, one can imagine each point in the phase space representing an imaginary replica of the system, each in a different microstate. This set of imaginary copies of the system, each in a different microstate, is referred as an 'ensemble'. When the gas moves randomly in time, in the phase space, it basically goes from one phase point to the next, in a specific succession. Any macroscopic quantity of the gas which we measure, is not measured at once. Rather it is measured over a finite time, which is very long with respect to the time-scale of motion of the particles of the gas. So, the measured quantity is actually the quantity averaged over time.

The basic idea of statistical mechanics is the following. In making a time-average of a quantity, one should basically look at different values the quantity takes, as it travels from one microstate to the other, during its time evolution. And then one should take an average of all the values of the quantity. White taking an average, it is not important what the sequence from one microstate to the other is. One can just take the phase points of the ensemble, over which the system goes, and take the average. So, the time average can be replaced by the average over the whole ensemble.

To enable one to replace time-average by ensemble-average, some conditions have to be fulfilled. Firstly, average over the ensemble implicitly assumes that the system passes all phase points during its time evolution. Secondly, it is also assumed that all microstates are equally likely to be encountered. If the system spends more time in certain microstates, and less time in other microstates, our assumption will breakdown. This assumption corresponds, which is called the 'ergodic hypothesis'. *The ergodic hypothesis states that, over a long period of time, the time spent by a system in some section of the phase space with the same* *energy is proportional to the phase-volume of this section, i.e., all accessible microstates are equiprobable over a long period of time.* Ergodic hypothesis is an important base of statistical mechanics. However, it cannot be proved in general. It is assumed to be true, which finds validation in the fact that statistical mechanics turns out to be a successful theory, in agreement with experimental results.

We consider a thermally insulated isolated system consisting of gas in a box. The system will be subjected to the constraint that the total energy remains constant during any change of time. It can be considered to be in equilibrium when it is left for a long time. Within the system we can assume that it is found with equal probability in each of its accessible microstates. This is nothing but the postulate of equal *a priory probability*. This postulate is at the very strong pillar of statistical mechanics. Now each macrostate can have numerous microstates. There are general ways by which the gas particles can accommodate, by various arrangements of particles and their momenta. So, there are a lot of microstates associated with a single macrostate. Now each microstate is equally probable, but we never actually see a gas occupying the quantity of volume of its container. Why so? It happens because the number of microstates associated with the gas occupying the whole volume are overwhelmingly large, compared to the microstates associated with the gas occupying only partial (say half) volume of the box.

One can get an idea of the numbers concerned in such situations through the following given example. We consider an array of four non-interacting magnetic moments, each of which can only take values + 1 or − 1. Now, assume that each magnetic moment is free to turn over up and down, *i.e.*, + 1 or − 1. We can designate the total magnetic moment of the array to assign a macrostate. There is only one microstate corresponding to the macrostate with total magnetic moment 4, which is nothing but all positive or all in up positions *i.e.*, (+ 1 + 1 + 1 + 1) giving four. Now, we consider the macrostate with total magnetic moment zero, the microstates associated in this case are (+ 1 + 1 − 1 − 1), (− 1 − 1 + 1 + 1), (+ 1 − 1 + 1 − 1), (+1 − 1 − 1 + 1), (− 1 + 1 + 1 − 1), (− 1 + 1 − 1 + 1) in terms of their orientation of magnetic moments. So, there are 6 microstates corresponding to total magnetic moment zero, whereas only one microstate with magnetic moment 4. So, we can easily see that if there were 40 magnetic moments, there would still be only one microstate associated with total magnetic moment 40. However, the number of microstates associated with total magnetic moment zero in that case, will be tremendously large. So, in a system of 40 magnetic moments which are freely orienting up and down, one will almost never see magnetic moment 40, and the magnetic moment will appear to be zero or very small almost all the time.

In the basis of above argument, it can be concluded that equilibrium state is one in which the number of microstates is maximum. In practice, the system will go over all microstates, but it will be mostly found in certain microstates. Three types of ensembles namely, microcanonical, canonical and grand canonical are mostly used. The ***microcanonical ensemble*** is a collection of essentially independent assemblies having the same energy E, volume V, and number of particles N. The ***canonical ensemble*** is a collection of essentially independent assemblies having the same temperature T, volume V, and number of particles N. The ***grand canonical*** ensemble is a collection of essentially independent assemblies having same temperature T, volume V, and a chemical potential μ. The different types of ensemble and the method of ensemble in developing statistical mechanics will be discussed in a separate chapter in detail.

1.5 ENSEMBLE AVERAGE

An ensemble average is the average at a fixed time over all elements in an ensemble. It is difficult to prove the exact equivalence of the ensemble average and the time average over a single system. However, one can hope that the ensemble average would approximate the time average, if the following essential conditions are satisfied:

(i) The system should be a macroscopic system consisting of a large number of molecules/particles ($N \to \infty$) so that we can randomise in a true sense the microscopic variables.

(ii) The number of imagined elements (M) that form the ensemble at one time is large ($M \to \infty$) enough so that they can truly represent the range of states available to actual system over a long period of time ($t \to \infty$). In statistical mechanics, we shall use the terms system and ensemble in the above sense only.

We consider a set of N points distributed arbitrarily along a line. If $x(i)$ is the distance of the i^{th} point from the origin, then the average distance from the origin is given by,

$$\bar{x} = \frac{1}{N}\sum_{i-1}^{N} \boldsymbol{x(i)}$$

The line is now supposed to be divided into cells, and N_i is the number of points in the i^{th} cell located at $x(i)$, then we can write,

$$\bar{x} = \frac{1}{N}\sum_{i} N_i x(\boldsymbol{i})$$

If the distribution is given in the form of a continuous function $N(x)$,

$$\bar{x} = \frac{1}{N}\int_{-\infty}^{+\infty} \boldsymbol{xN(x)dx},$$

And naturally, $$N = \int_{-\infty}^{+\infty} \boldsymbol{N(x)dx}$$

In general, if $F(x)$ is any arbitrary property of the points, then its average value is given by,

$$\overline{F} = \frac{\int_{-\infty}^{+\infty} F(x)N(x)dx}{\int_{-\infty}^{+\infty} N(x)dx}$$

It can be shown that the average over ensemble is same as average over time.

1.6 MICROSCOPIC AND MACROSCOPIC SYSTEMS

What is the distinction between different sizes of the systems that we are going to examine! We shall call a system *microscopic*, if it is of atomic dimensions, or smaller. Where as a system is called *macroscopic* when it is large enough to be visible in the ordinary sense. This is not a precise definition. The precise definition depends on the number of particles in the system, say N. A system is macroscopic if,

$$\frac{1}{\sqrt{N}} \ll 1$$

For example, if we want to keep the statistical error below one percent, then a macroscopic system should contain at least ten thousand particles. Any system containing less than this number of particles would be regarded as essentially microscopic, and, hence, statistical point of view cannot be applied to such a system without intolerable error.

1.7 MACRO AND MICROSTATES

A microstate of an ensemble (a collection of similar, non-interacting, independent, imagined systems is called ensemble by Gibbs) *may be defined by the specification of the individual position of phase points for each system or molecule of the ensemble.* So, each arrangement of specified system or molecules with their representative points in particular cells is called a microstate.

According to gross observable properties, or macroscopic behavior, it is immaterial which particular system or molecules are occupying the specified cells. Therefore, *a macrostate of the ensemble may be defined by the specification of phase point in each cell i.e.*, by specifying the numbers only and overlooking the identities of the system or molecules.

A change of phase points between two cells in phase space shifts the position of unit cell because the microstate changes. But according to macroscopic properties, this exchange makes no difference. Thus, *there may be many different microstates which may correspond to the same macrostate.* This will be more cleare from an example in the following section.

Let there be cell -1, cell -2, cell -3 ... cell $-i$ in phase space. Suppose, there are three phase points $a\ b\ c$ in cell -1, four phase points $d\ e\ f\ g$ in cell -2, two phase points $h\ k$ in and five phase points $r\ s\ t\ u\ v$ in cell $-i$ as shown in Fig. 1.3 below.

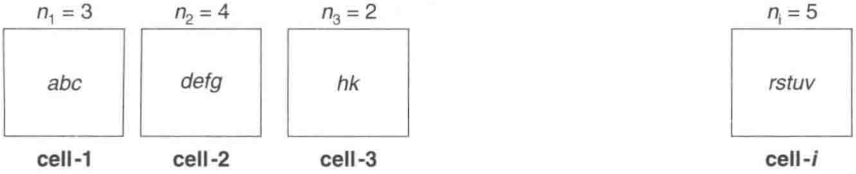


Fig. 1.3

The macrostate in the Fig. 1.3 is specified by merely giving the phase points $n_1 = 3$, $n_2 = 4$, $n_3 = 2$, $n_i = 5$ of different cells. This also represents a particular microstate by specifying the position of phase points *abc* in cell 1, *defg* in cell 2 and so on. Now, if the two phase points a and d from first two cells are interchanged, then the microstate is changed because the positions of two phase points are changed, whereas the macrostate remains the same as the number of phase points in the cells remains the same. Similarly, with the same macrostate we can consider different microstates. Thus, *many different microstates may correspond to the same macrostate.*

1.8 NUMBER OF PHASE CELLS IN A GIVEN ENERGY RANGE

To handle many problems in statistical mechanics, it is necessary to know the number of phase cells in a given energy range. So, we must have an idea about this Suppose, in the energy range 0 to E, the possible values of momentum be from 0 to $p_{\max}$. Now, the space between the momentum range p_x to $p_x + dp_x$, p_y to $p_y + dp_y$ and p_z to $p_z + dp_z$ is equal to $dp_x dp_y dp_z$, which is equal to concentric spherical shell volume between p to $p + dp$.

Therefore, $dp_x dp_y dp_z = 4\pi p^2 dp$ [*see Fig. 2.3 in the next chapter*].

As the total volume of momentum space is a sphere of radius $p_{\max}$, we can write,

$$\iiint dp_x\, dp_y\, dp_z = \frac{4}{3}\pi p_{\max}^3$$

The energy E of a free particle is given by,

$$\frac{p_{\max}^2}{2m} = E$$

Therefore, $\iiint dp_x\, dp_y\, dp_z = \frac{4}{3}\pi\,(2mE)^{3/2}$

Therefore, the volume in phase space $\iiint dx\, dy\, dz\, dp_x\, dp_y\, dp_z = V \frac{4}{3}\pi$ $(2mE)^{3/2}$

Where, $V = \iiint dx\, dy\, dz$ = volume of coordinate space.

Now, since the volume of phase cell is h^3, the number of cells in phase space

$$= V\frac{4}{3}\pi\,(2mE)^{3/2} \times \frac{1}{h^3}$$

Thus, the number of phase cells is proportional to $E^{3/2}$.

1.9 PHASE SPACE DISTRIBUTION FUNCTIONS AND LIOUVILLE'S THEOREM

For an ensemble with many members, each member having a different phase space vector x corresponding to a different microstate, we need a way to tell, how the phase space a vectors of the members in the ensemble will be distributed in the phase space *i.e.*, if we choose to observe one particular member in the ensemble, what is the probability that its phase space vector will be in a small region dx around a point x in the phase space at time t. This probability will be denoted as,

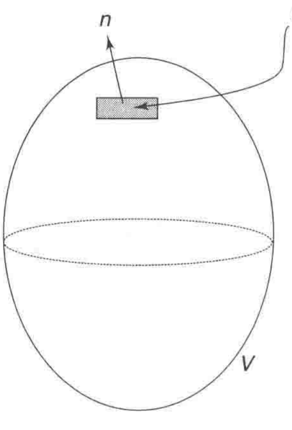
$$f(x, t)dx$$

where, $f(x, t)$ is known as the *phase space probability density* or *phase space distribution function*. It properties are as follows:

$$f(x, t) \geq 0$$

$$\int dx\, f(x, t) = \text{Number of members in the ensemble.}$$

Liouville's Theorem: The total number of systems in the ensemble is a constant. For a given volume V in phase space, this condition requires that the decreasing rate of the number of systems from this region is equal to the flux of systems into the volume. Let $\hat{n}$ be the unit normal vector to the surface of this region.



The flux through the small surface area element, dS is just $\hat{n}\cdot\dot{\mathbf{x}}f(x,t)\,dS$. Then, the total flux of the volume is obtained by integrating this over the entire surface that encloses V:

$$\int dS\,\hat{n}\cdot(\dot{x}f(x,t)) = \int_V \nabla_x\cdot(\dot{x}f(x,t))\,dV$$

which follows from the divergence theorem. ∇_x is the $6N$-dimensional gradient on the phase space.

$$\nabla_x = \left(\frac{\partial}{\partial p_1},\ldots,\frac{\partial}{\partial p_N},\frac{\partial}{\partial q_1},\ldots,\frac{\partial}{\partial p_N}\right)$$

On the other hand, the decreasing rate in the number of systems out of the volume is,

$$-\frac{d}{dt}\int_V dV(x,t) = -\int_V dV\frac{\partial}{\partial t}f(x,t)$$

Equating these two quantities gives,

$$\int_V dV\,\nabla_x\cdot(\dot{x}f(x,t)) = -\int_V dV\frac{\partial}{\partial t}f(x,t)$$

But this result must hold for any arbitrary choice of the volume V, which we may allow to reduce in size to zero so that the result holds locally, and we obtain the local result:

$$\frac{\partial}{\partial t}f(x,t) + \nabla_x\cdot(\dot{x}f(x,t)) = 0$$

But, $$\nabla_x\cdot(\dot{x}f(x,t)) = \dot{x}\cdot\nabla_x f(x,t) + f(x,t)\nabla_x\cdot\dot{x}$$

This equation is similar to an equation for a 'hydrodynamic' surge in the phase space, with $f(x,t)$ playing the role of a density. The quantity $\nabla_x\cdot\dot{x}$, being the divergence of a velocity field, is known as the *phase space compressibility*, and it does not vanish for a general dynamical system. Let us consider the phase space compressibility for a Hamiltonian system, where in,

$$\nabla_x\cdot\dot{x} = \sum_{i=1}^{N}[\nabla_{p_i}\cdot\dot{p}_i + \nabla_{q_i}\cdot\dot{q}_i]$$