**MSCPH504**

M. Sc. I SEMESTER

Statistical Mechanics
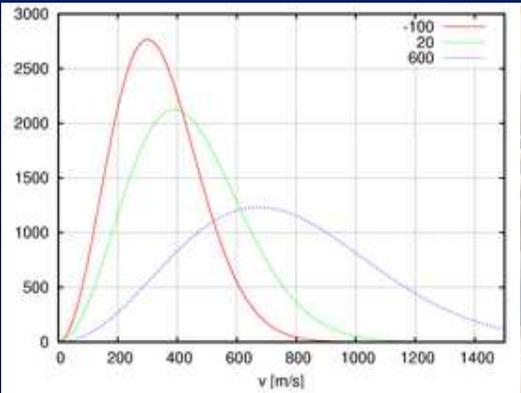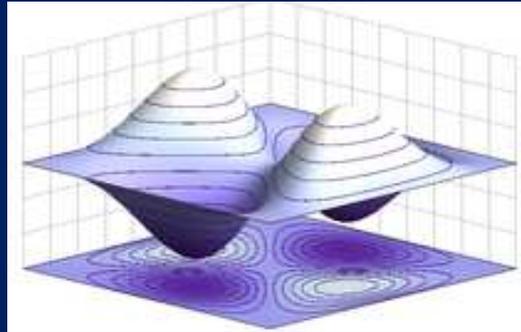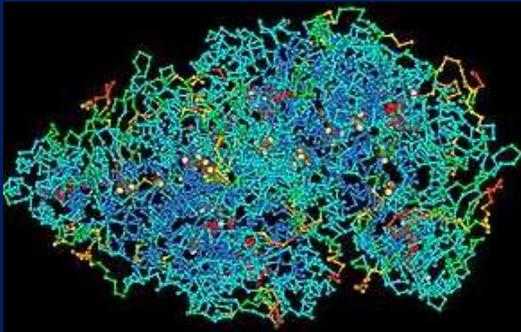
DEPARTMENT OF PHYSICS
SCHOOL OF SCIENCES
UTTARAKHAND OPEN UNIVERSITY

Board of Studies

Department of Physics (School of Sciences)

Unit writing and Editing

Editing

Dr. Kamal Devlal
Department of Physics
School of Sciences, Uttarakhand Open
University

Writing

1. Dr. Mahipal Singh
Department of Physics
R.H. Govt. P.G. College, Kashipur, Uttarakhand
2. Dr. Yogesh Kumar
Department of Physics
Arvino College (University of Delhi)
Delhi
3 Dr. Kishore Thapliyal
 Faculty of Science,
Palacky University, 17. listopadu 12, 771 46 Olomouc,
Czech Republic
4. Dr. Ravi Shankar Kuniyal
Department of Physics, Government Post Graduate
College, Gopeshwar (Chamoli)-246401
5. Dr. Rajesh Mathpal
Department of Physics
School of Sciences, Uttarakhand Open University

Statistical Mechanics

DEPARTMENT OF PHYSICS
SCHOOL OF SCIENCES
UTTARAKHAND OPEN UNIVERSITY
Phone No. 05946-261122, 261123
Toll free No. 18001804025
Fax No. 05946-264232, E. mail info@uou.ac.in
htpp://uou.ac.in

Contents

Course 4: Statistical Mechanics   **Course code: MSCPH504**
                                                       Credit: 3

UNIT 1   Statistical Mechanics at a Glance

Structure

1.1   INTRODUCTION

In our everyday life, we often come across objects in motion.Human beingswere inquisitive to understand the motion in detail since ages. Nowadays, we categorize the branch of physics dealing with these moving bodies as *mechanics*. The motion of objects, we see around us, astronomical objects, etc., which are macroscopic in nature can be defined by the principles of classical mechanics. One of the earliest contributions in the classical mechanics were by Isaac Newton and Gottfried Wilhelm Leibniz, who described the motion of a body under the action of forces. Applicability of classical mechanics is superseded by relativistic mechanics introduced by Albert Einstein for the bodies moving near the speed of light. Similarly, another branch of mechanics developed in the beginning of the last century for the microscopic systems, such as subatomic particles.Therefore, all these developments widened our horizon in understanding of the nature and motion of an object.

In the meantime, our understanding of thermodynamic propertiesdealing with the systems in equilibrium was developed and summarized by the laws of thermodynamics. You may already be familiar with thermodynamics and related basic key terminologies, like the concept of system and surroundings, different types of thermal processes, laws of thermodynamics, state function, state variables and various macroscopic properties (macroscopic properties are the properties of matter as a whole in terms of macroscopic variables,likedensity, volume, temperature, pressure) related through an equation of state. So far these thermodynamic properties for the macroscopic system were not described in terms of its microscopic constituents.Thus, statistical mechanics is that branch of modern physics which deals with physical systems with many degrees of freedom and describes their macroscopic properties in terms of the microscopic properties of the constituent particles.

We understood so far that our treatment of the constituent particles depends upon whether they can individually be described by classical mechanics or quantummechanics. Depending upon that statistical mechanics is broadly studied under two categories namely classical and quantum statistics.The classical statistics is discussed with Maxwell-Boltzmann statistics, whereas quantum statistics can further be categorized as Bose-Einstein and Fermi-Dirac statistics depending upon yet another quantum feature called the spin of the particle. Specifically, all the microscopic particles with integral (half-integral) spin governed by quantum mechanics are studied under Bose-Einstein (Fermi-Dirac) statistics. Therefore, in this book, we will discuss the physical properties of various systems containing a large number of particles (atoms or molecules), comparable to Avogadro number, i.e., 6.022×10^{23}, on the basis of the properties and behavior of the microscopic constituents of those systems. To accomplish this we will be using statistical tools and probability theory as well asthe dynamics of microscopic particles governed by either classical or quantum mechanics.

In this unit, we will discuss various concepts in classical statistical mechanics, like phase space, microscopic and macroscopic variables, the concepts of ensemble, and one of the important principles, i.e., postulate of equal a priori probability. These basic concepts are building blocks of statistical mechanics which are helpful in understanding the forthcoming

units and in discussing quantum statistics. In particular, we want to make a statistical analysis of a large number of collections of identical systems and determine their most probable behavior. In this process, we are not interested in the individual dynamics of a single particle. In statistical mechanics, we average the properties of all the particles to studythe macroscopic bodies they form. For instance, the temperature of a gas is found to be related to the random motion of the gas molecules. The faster they move on average, the higher is the temperature.

1.2 OBJECTIVES

After studying this unit, you should be able to understand-
● Probability
● Probability distribution
● Distinguishable and indistinguishable particles
● Define phase space and phase points
● Ensemble
● Density of states
● Ensemble average or phase space average and time average
● Ergodic hypothesis
● Consequence of ergodic hypothesis as postulate of equal a priori probability

1.3 BASIC CONCEPTS OF STATISTICAL MECHANICS

Statistical mechanics is a branch of science which deals with the most probable behavior of an assembly of particles. There are various examples of such systems, like gases, liquids, solids in different forms, stellar matter, and radiation. In statistical mechanics, one tries to apply the ideas of statistics appropriate to a system containing a large number of particles that are individually described by the laws of mechanics.

At the end of the nineteenth century J. C. Maxwell, L. Boltzmann and J. W. Gibbs established the fundamental pillars of statistical physics. The statistical mechanics started with the Maxwell's kinetic theory of gases. To be specific, the first milestone in statistical physics is J. C. Maxwell's statistical law for distribution of molecular velocities proposed in 1859, which will be discussed in detail in Unit 3. This work inspired L. Boltzmannwho dedicated all his life in developing statistical mechanics. His entropy formula was aptly inscribed on his tombstone. Specifically, he generalized Maxwell's argument and introduced the concept of ensembles, which will be discussed in detail in Unit 4. Although, this branch of mechanics was christened by J. Gibbs in addition to several of his contributions, such as establishing the equivalence of statistical physics and thermodynamics to be discussed in Unit 2. Boltzmann's doctoral student P. Ehrenfestalso contributed significantly in the development of statistical mechanics, alas, both these stalwarts had same tragic demise.Einstein completedour present day understanding of statistical mechanicsby his various theories, like the theory of

fluctuations, diffusion, and Brownian motion. The development ofquantum theory helped in simplifying the principles of statistical physics.

As we have already mentioned, we are going to use probability theory to quantify various notions in statistical physics. Here, we introduce the basic conceptof probability and probability distributionsbecause this serves as an important tool for understanding the behavior of statistical systems.

1.3.1 Probability

Probability is a mathematical concept that deals with calculating the likelihood of a given event's occurrence. Thus, the probability of an event is defined as the ratio of the number of the cases in favor to the total number of possible cases also called sample size.

$$\text{Probability of an event} = \frac{\text{Number of favorable cases}}{\text{Total number of possible cases}} \quad \ldots (1.1)$$

Example 1.1: *Tossing a coin*-when an unbiased coin is tossed, there are two equally probable outcomes, heads (H) or tails (T). Thus, we can say that the probability of the coin landingH up is $\frac{1}{2}$, and the probability of the coin landing T up is $\frac{1}{2}$.

Example 1.2: *Throwing die*- when a fair die is thrown, there are six possible outcomes: 1, 2, 3, 4, 5, and 6. The probability of each of them is $\frac{1}{6}$.

For example, suppose we wish to obtain the probability of getting a "4" on rolling a die. The number of ways it can happen is 1 as there is only one face with a "4" on it, and the total number of possible outcomes is 6 only as there are six faces altogether. So the probability of getting "4"is $\frac{1}{6}$.

Example 1.3: Suppose there are 5 marbles (4 blue and 1 red) in a bag. The probability that a blue marbleis picked can be calculated as:

The number of ways it can happen is 4 for fourblue marbles, and the total number of outcomes is 5 as there are five marbles in total. So the probability is $\frac{4}{5}$.

Self Assessment Question (SAQ) 1: A boxcontains 4 chocolates and 4 icecreams. What is the probability of choosing 1 chocolates?

1.3.2 Basic rules of probability

There are three basic rules of probability distribution, like summation rule, multiplication rule, and conditional probability.

• Summation rule is applicable to mutually exclusive events, i.e., happening of one event excludes the possibility of the happening of the other.

- The multiplication rule is applicable when the probability of occurrence of one event does not affect the probability of occurrence of the other. This rule is also known as joint probability, and the probability of joint occurrence of two independent events is equal to the product of the probabilities of each of the independent events.

- The probability for an event say A to occur conditioned to the fact that another event say B has also occurred is called the conditional probability. This is denoted as $\left(\frac{A}{B}\right)$.

All the three rules discussed above can be better understood by the following examples.

Example 1.4: A card is drawn from a pack of 52 cards. The probability of getting a red ace or a black king can be discussed as

The total number of ways in which the event can occur is N = 52.

We wish to draw a red ace. There are 2 red aces in a pack of 52 cards. Therefore, the number of ways favorable to the first event say $m = 2$.

Thus, the probability of drawing a red ace $p_1 = \frac{m}{N} = \frac{2}{52} = \frac{1}{26}$.

The number of ways in which second event, i.e., drawing a black king may happen say $n = 2$, as there are 2 black kings in the pack of 52 cards.

The probability of drawing a black king $p_2 = \frac{n}{N} = \frac{2}{52} = \frac{1}{26}$.

Notice that both events are mutually exclusive. Therefore, the probability that the card drawn is either a red ace or a black king is

$$P = p_1 + p_2 = \frac{1}{26} + \frac{1}{26} = \frac{2}{26} = \frac{1}{13}.$$

Example 1.5: A bag contains 6 black marbles and 4 blue marbles. Two marbles are drawn from the bag, without replacement. The probability that both marbles are blue may be discussed as

We have 6 black and 4 blue marbles so there are total ten marbles in the bag.

So the probability of the first event, i.e., drawing a blue marble is $p_1 = \frac{4}{10}$.

Now there are nine marbles in the bag, so the probability of the second event, i.e., choosing a blue marble is $p_2 = \frac{3}{9}$.

Hence, the required probability that both the marbles are blue is $p_1 \times p_2 = \frac{4}{10} \times \frac{3}{9} = \frac{12}{90} = \frac{2}{15}$.

Example 1.6: Discuss the probability of drawing two kings from a deck of 52 cards.

First event (say event A) is drawing a king first, and second event (say event B) is drawing a king second.

For the first card the chance of drawing a king is 4 out of 52 as there are 4 kings in a deck of 52 cards. So,

$$P(A) = \frac{4}{52}.$$

After removing a king from the deck the probability of the second card drawn is less likely to be a king as there are only 3 of the 51 cards left are kings. Therefore,

$$\textbf{Probability of event } B \textbf{ given event } A = P\left(\frac{B}{A}\right) = \frac{3}{51}.$$

Probability of event A and event B, i.e., $P(A \cap B)$ = probability of event A, i.e., $P(A)$ times the probability of event B given event A, i.e., $P\left(\frac{B}{A}\right)$. Thus,

$$P(A \cap B) = \frac{4}{52} \times \frac{3}{51} = \frac{12}{2652} = \frac{1}{221}.$$

Hence, the chance of getting 2 kings is 1 in 221.

Example 1.7: Suppose there are 10 marbles (6 blackand 4blue) in a bag as in Example1.5. We randomly select two marbles with replacement from the bag, i.e., once we select the first marble we put it back in the bag and then select the second marble. The probability of getting two blue marbles may be discussed as,

Here, drawing with replacement makes the draws independent of each other, since the color of the first marble drawn does not change the sample size for the second draw.

The chance of drawing a blue marble on the first draw is $\frac{4}{10}$. With the replacement of the first marble the probability of getting a blue marble on the second draw is again $\frac{4}{10}$. Thus, the probability of getting two blue marbles with replacement is $\frac{4}{10} \times \frac{4}{10} = \frac{4}{25}$. Notice the difference between the probability of two blue marbles with replacement and without replacement.

Self Assessment Question (SAQ) 2: What is the probability of drawing a red king and then a black 7 without replacement from a deck of 52 cards?

1.3.3 Probability distribution

In all the examples discussed in the previous subsections, you have a rule which assignsa single real value to each outcome as probability. Notice that this number may vary for different outcomes. Thus, this number is a variableand depends upon the outcome of a random example, and hence, is called random variable.

For example, consider the case of tossing a coin twice in succession. The sample space in this case is S = {HH, HT, TH, TT}. If X denotes the number of heads obtained, then X is a random variable and for each outcome, its value is as X(HH) = 2, X (HT) = 1, X (TH) = 1, X (TT) = 0.More than one random variable can be defined on the same sample space.Thus, these random variables can be used to obtain probability in each case by dividing them with sample size. This mathematical function defines the probability of the occurrence of all the outcomesand as expected the sum of probability in all the cases is unity.

The probability distribution of a random variable can be understood by following example.

Example 1.8: Discuss the probability distribution of the number of aces when two cards are drawn successively with replacement from a well-shuffled deck of 52 cards.

Let the number of aces (random variable) be denoted by X which can take the values 0, 1, or 2. Since the draws are done with replacementthe two draws formindependent experiments.Therefore,

$$P(X = 0) = P \text{ (non ace and non ace)} = P(\text{non ace}) \times P \text{ (non ace)}$$
$$= \frac{48}{52} \times \frac{48}{52} = \frac{144}{169},$$

$$P(X = 1) = P \text{ (ace and non ace or non ace and ace)}$$
$$= P(\text{ace and non ace}) + P \text{ (non ace and ace)}$$
$$= P(\text{ace}) \times P(\text{non ace}) + P(\text{non ace}) \times P(\text{ace})$$
$$= \frac{4}{52} \times \frac{48}{52} + \frac{48}{52} \times \frac{4}{52} = \frac{24}{169},$$

$$P(X = 2) = P \text{ (ace and ace)}$$
$$= \frac{4}{52} \times \frac{4}{52} = \frac{1}{169},$$

Thus, the required probability distribution can be summarized as

X	0	1	2
$P(X)$	$\frac{144}{169}$	$\frac{24}{169}$	$\frac{1}{169}$

Similarly, joint probability distributions are defined over two or more random variables.The probability distribution over one random variable, known as marginal distribution, can be obtained by summation of the joint probability distributions for the rest of the random variables.

Self Assessment Question (SAQ) 3: A pair of dice is thrown thrice. Discuss the probability distribution of the number of doublets.

1.3.4 Distinguishable and indistinguishable particles

Before discussing further, you should know one of the important differences between the classical statistics and the quantum statistics. This difference is directly related to the nature of particles which form the system being considered. In classical statistics, particles are distinguishable whereas in quantum statistics particles are indistinguishable.

Consider Example 1.7 with an additional constraint, i.e., obtain probability that the blue marble drawn in the first round is not the same as in the second round with replacement. In principle, if you keep track of each marble after labeling them with different numbers, you will end up with the same probability as in Example 1.5.This labeling is possible because these marbles, being classical particles,though may have same color, shape, etc., macroscopic properties but have uniquepositions in the bag.Further, assume the marbles in this example are quantum particles. We know that some properties of the subatomic particles are defined as universal constants, suchas mass, charge.Therefore, they are identical in that sense, and

once the marble is replaced in the bag the wavefunction associated with the replaced quantum marble overlaps with that of the remaining marbles in the bag due to spreading of the wavefunction as time progresses.We know that one cannot distinguish overlapping wavefunctionsso the quantum state of the composite system ofquantum marblescan be written as superposition of all the combinations. Therefore, the probability inthis case will be different from the classical particles.For example, in case oftwo indistinguishable quantum particles, quantum state is obtained asthe sum (difference)of two-particle wavefunctionand that obtained by particle exchangewhich is symmetric (antisymmetric). The symmetric (antisymmetric) wavefunction corresponds to bosons (fermions), i.e., quantum particles with integral (half-integral) spin. You can easily verify the significance of Pauli exclusion principlethat two fermions cannot have the same values for all the quantum numbers. We will return to this discussion in forthcoming units, especially Units 7-10.

Suppose you have two distinct particles which are distinguishable, like a Helium-3 atom and a Helium-4 atom. If you switch their positions then the system changes. On the other hand, if two particles are indistinguishable, like two protons then, switching their positions makes no physical change because you do not know whether particles switched at all. The concepts of distinguishable and indistinguishable particles is important in statistical mechanics. Hereafter, for discussing classical statistical mechanics the particles shall be considered as distinguishable and later in quantum statistics you will understand the indistinguishability of particles in detail.

Example 1.9: Let us rearrange all the letter of the word "POTATO" and compute the probability of obtaining words starting with P.

The total number of ways the word "POTATO" can be rearrangedis $N = \frac{6!}{2!2!} = 180$.

There is only 1 possibility for the first letter to be P andthe rest of the five letters can be chosen in 5! ways. Notice that there are two T and O in the word, so effectively there will be only $m = \frac{5!}{2!2!} = 30$unique words.

Thus, the probability of obtaining words starting with P can be written as$P(X) = \frac{m}{N} = \frac{30}{180} = \frac{1}{6}$.

This example shows that a repeated occurrence of letters changes the probability of a favorable outcome.Similarly, distinguishability (indistinguishability) of particlesplays significant role in the computation of probabilities and thus statistics of quantum and classical particles.

1.4 PHASE SPACE

You all know, in a static system the complete position of an object or a point particle in classical mechanics is specified by three Cartesian coordinates. This three dimensional space is known as position space ($r = x, y, z$) and a small volume element in position space is defined as $dV_r = dx\, dy\, dz$. If the system is dynamic then in addition to the position coordinates, we require three components of momenta for the specification of particles in the

system. These three mutually perpendicular momentum coordinates $(p = p_x, p_y, p_z)$constitute momentum space. A small volume element in this space is expressed as$dV_p = dp_x \, dp_y \, dp_z$.

In a similar way, phase space is a scheme for the specification of a system in statistical mechanics. In this, the position of a particle is represented in terms of Cartesian coordinates (x, y, z) and the corresponding momentum (p_x, p_y, p_z) components. Thus, the phase space is a combined position and momentum space. A small volume element in phase space is defined as

$$dV = (dx \, dy \, dz)(dp_x \, dp_y \, dp_z). \dots(1.2)$$

Such a six dimensional space for a single particle or molecule is called phase space or mu-space (μ-space). The phase space is a pure mathematical concept used to describe a single particle. Let us divide the phase space in two dimensional energy sheet as shown in Figure1.1. Further, if we subdivide the range of variables x and p_x into arbitrary small discrete intervals, then the single interval is known as phase cell. The minimum size of the phase cell in classical statistics is equal to the area of thesingle cell, i.e., $dx \, dp_x = h_0 \, (say)$. This $h_0$may be viewed as our experimental limitation in measurement.In the classical scenario, h_0 can be chosen arbitrarily as small as possible.Further, phase cell is the volume occupied by each phase point in the phase space. Hence the value of this elementary volume is equal to $h_0{}^3$. However, in quantum statistics,according to the Heisenberg's uncertainty principle the minimum size(volume) of phase cell in phase spaceis given by h^3,where h is Planck's constant.
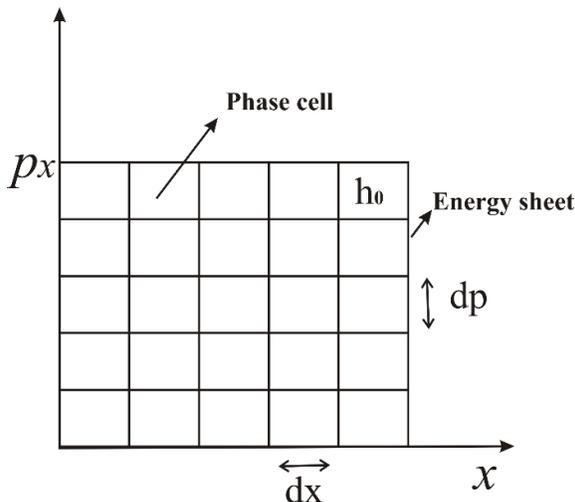

Figure1.1: Two dimensional energy sheet of phase space representing phase cells.

Let us consider a system of N molecules or particles. If each molecule is specified in phase space by $q_1, q_2, q_3 \cdots$ position and $p_1, p_2, p_3 \cdots$momentum coordinates, then for a system of N molecules there will be $6N$ dimensional space, i.e., $3N$ position and $3N$ momentum

coordinates. This space of 6N dimension is called gamma-space or Γ space. In Γ space each point is called a representative point or phase point corresponding to a state of a system of N particles at a particular time.The number of phase points per unit volume of the phase space is called phase density. With the passage of time the representative point traces out a trajectory which gives us a complete dynamics of the system.This trajectory is known as phase space trajectory. It is also important to mention here that a phase space trajectory never intersects itself because if it does so, then the point of intersection would denote two different states at two different times for the same system which is not physically acceptable. In Figure1.2, a random phase space trajectory showing the temporal evolution of systemis depicted. Analogously, the state of the system of N particles can be represented by specifying the state of each particle in six dimensional spaceμ -space (as discussed above). The μ -space is represented by a cloud of N points in a six dimensional space.

Thus, the microscopic state of the complete system is specified by the phase points. These phase points vary with time, and therefore microscopic states of a dynamic system are differentfor each instant of time. Further, for the measurement of macroscopic variables (N, V, P, T, E, etc.) of the whole system we need to calculate the time average of the system of interest. Hence, each phase point represents a separate system with same macroscopic properties, but a different microscopic state.
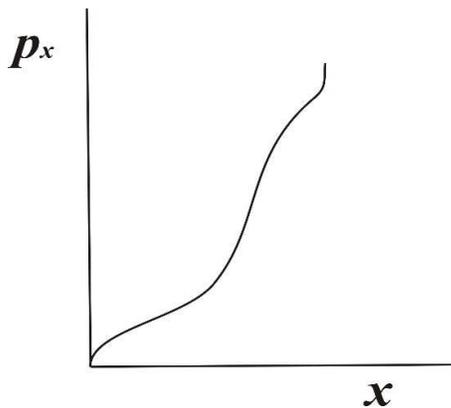
Figure1.2: Random trajectory in phase space.

Example 1.10: Phase space diagram of an oscillator.

Let us consider an oscillatorof mass m and spring constant k with energy

$$E = \frac{p^2}{2m} + \frac{1}{2}kq^2 \quad \text{....(1.3)}$$

We can rewrite this equation as

$$\frac{p^2}{2mE} + \frac{q^2}{\left(\frac{2mE}{k}\right)} = 1 \quad \text{....(1.4)}$$

This represents an ellipse (see Figure1.3) in the $q - p$ plane for constant energy E. This is a phase space diagram of an oscillator. The phase points are lying on the elliptical path with the ellipse whose semi major axis and semi minor axis are $\sqrt{\frac{2E}{k}}$ and $\sqrt{2mE}$, respectively. Thus,

the phase space available to the oscillator having the energy between 0 and E is the area of the ellipse given by $2mE\sqrt{\frac{m}{k}}$.
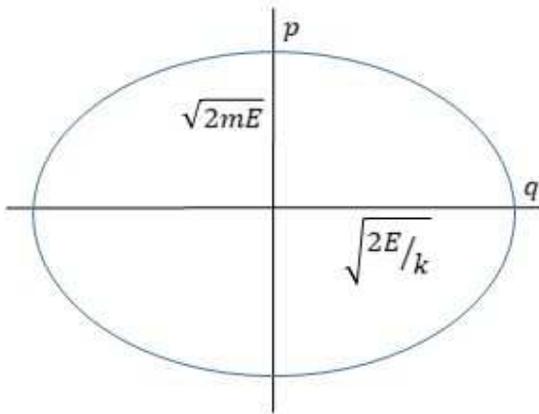
Figure1.3: Phase space diagram of an oscillator.

Self Assessment Question (SAQ) 4: Using the concept of phase space find out the region of states accessible for a particle in an infinite square well potential defined as

$$V(x) = \begin{cases} 0, 0 < x < L \\ \infty, \text{otherwise.} \end{cases}$$

Self Assessment Question (SAQ) 5: Discuss the phase space trajectory of a free particle moving in the positive direction.

1.5 WHAT IS AN ENSEMBLE?

If we are considering a collection of particles with macroscopic properties, like energy, volume, chemical potential, then the collection of such particles is considered as an assembly. Further, this collection of a large number of non-interacting, independent assemblies is known as an ensemble or statistical ensemble. The members of an ensemble are referred to as elements or assemblies. These elements are identical in macroscopic properties, like N, E, V, and differ in their microscopic properties, i.e., elements have different position and momentum coordinates.

In other words, we can say that an ensemble is defined as a collection of a large number of assemblies which are identical in macroscopic properties but differ in microscopic properties. Thus, it can be viewed as numerous copies of a system or a probability distribution defining the state of the system.
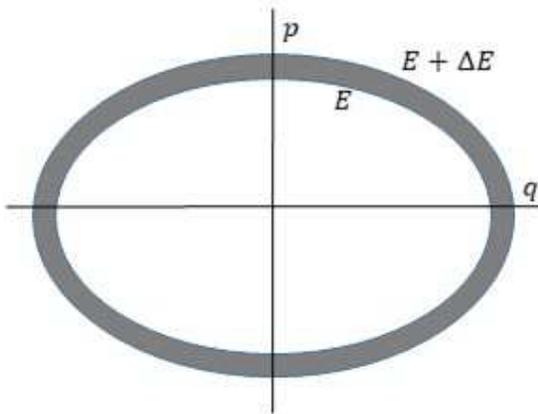
Figure1.4: Phase space diagram of harmonic oscillator with energy between E and $E + \Delta E$ for infinitesimally small ΔE.

For example, consider anotherphase space trajectory of a harmonic oscillator of energy $E + \Delta E$, with infinitesimally small ΔE, represented by an ellipse in Figure1.4. Each point in phase space between the two ellipses represent state of a harmonic oscillator with a constraint that their energy is between$E$and $E + \Delta E$. This ΔE corresponds to our experimental limitation in determining the energy of the system. This hypersurface, whichcorresponds to the collection ofall the phase pointssatisfying the constraint, is phase space distribution or an ensemble.

There are three types of ensembles, namely microcanonical, canonical and grand canonical, which will be discussed in detail in Unit 4. These three categories are specified on the basis of macroscopic constraints.

1.6   DENSITY OF STATES

We have already discussed that the microscopic properties of a system are represented by phase points. The condition of an ensemble at any time can be specified by the density, which describes the distribution of phase points in phase space. The density distribution is often denoted by $\rho = \rho(q,p)$ and is a function of the continuous variables $q$and p. Consequently, the normalization condition for a closed system is$\int \mathrm{d}^{3N} q\, \mathrm{d}^{3N} p\, \rho(q,p) = 1$, where the volume elements are$\mathrm{d}^{3N} q = \mathrm{d}q_1 \dots \mathrm{d}q_m \dots \mathrm{d}q_{3N}$and $\mathrm{d}^{3N} p = \mathrm{d}p_1 \dots \mathrm{d}p_m \dots \mathrm{d}p_{3N}$. Specifically, the density of distribution in phase space gives the number of states per unit volume in a given interval of energy of the phase space. This distribution function is a function of position coordinates and momentum coordinates. The time dependence of ρ may be implicitly governed by the time dependence of q and p. However, ρmay also have an explicit time dependence.

Hence, we can write

$$\rho = \rho(q,p,t). \qquad\qquad \dots (1.5)$$

Therefore, the number of phase points in a small volume element say $d\Gamma = \mathrm{d}^{3N} q\, \mathrm{d}^{3N} p$ is given by

$\delta N = \rho(q,p,t)d\Gamma.$

We will further calculate an expression of density of state for a single particle of mass m with momentum in the range p to $p+dp$ and energy in the range E to $E+dE$, respectively, placed in a phase cell of volume h_0^3 in phase space. The total volume of the phase space is given by

Total volume of phase space $= \int d^3q d^3p = \iiint dq_x dq_y\, dq_z \iiint dp_x\, dp_y dp_z$

$= V \times 4\pi p^2 dp,$ ...(1.6)

where we have used the volume of position space $\iiint dq_x dq_y dq_z - V$, the volume of the momentum space $\iiint dp_x\, dp_y dp_z = 4\pi p^2 dp$.

Thus, we can write the total number of phase cells in the given momentum range as

$n(p)dp = \frac{V \times 4\pi p^2 dp}{h_0^3}.$ ...(1.7)

Using the relation between energy E and momentum p, i.e.,

$E = \frac{p^2}{2m}$ or $p = \sqrt{2mE},$

and therefore,

$dp = \sqrt{\frac{m}{2E}}dE.$

Using this relation in equation (1.7), the total number of phase cells in the energy range E to $E+dE$ is

$n(E)dE = \frac{8\pi m E}{h_0^3}V\sqrt{\frac{m}{2E}}dE$

$= \frac{4\pi V}{h_0^3}\sqrt{2E}m^{3/2}dE.$ ...(1.8)

Hence, the density of state or the total number of phase cells per unit energy range can be obtained as

The total number of phase cells per unit energy range $= \frac{4\pi V\sqrt{2E}m^{3/2}}{h_0^3}$ ...(1.9)

1.7 ERGODIC HYPOTHESIS: Equality of ensemble average and time average

For a large collection of particles we shall consider the average of the variables for discussing the complete system. In the next unit, we will discuss the average values of variables in detail by considering various other aspects of statistical mechanics, like thermodynamic probability, concept of microstates and macrostates.

In general, the ensemble average value of a variable U in an ensemble is calculated as

$\langle U \rangle = \frac{\int U(q,p)\rho(q,p)d^{3N}q\, d^{3N}p}{\int \rho(q,p)d^{3N}q d^{3N}p}.$ ... (1.10)

Here, $U(q,p)$ defines the physical property for different phase points with density of phase points $\rho(q,p)$, which is normalized $\int \rho(q,p)d^{3N}q d^{3N}p = 1$. We have already given an example of ensemble for harmonic oscillator as a hypersurface between two ellipses of energy

E and $E + \Delta E$, respectively.The ensemble average takes into consideration the contribution from each assembly in the ensemble, represented by phase points in the hypersurface,weighed with corresponding probabilitiesin the phase space distribution.

Similarly, the time average of the variable over a complete time period is calculated by the following equation

$$\bar{U} = \lim_{T \to \infty} \left(\frac{1}{T}\right) \int_0^T U(\tau)d\tau. \qquad\qquad \dots (1.11)$$

In case of our example of harmonic oscillator, temporal evolution of a phase point on the elliptical hypersurface traces all the phase pointsbetween energy E and $E + \Delta E$over a long period of time.

Thus, time average in principle takes into consideration the contribution from all the points in the phase space trajectory similarto the ensemble.

Ergodic hypothesis is a connection between both types of averages. It states that the ensemble averages are equivalent to the time averages of any physical quantity to be considered.In other words, this hypothesis says that the ensemble average of any variable is the same as the time average of that variable for the single system.

1.8   POSTULATE OF EQUAL A PRIORI PROBABILITY

In statistical physics, we deal with systems with a very large number of particles and assume that the system exists in an equilibrium state. All the physical properties of such a system can be deduced by knowing the most probable or equilibrium state of the system. In such state, the phase space distribution of the system is independent of time, i.e., the ensemble does not evolve anymore with time.We will discuss the significance of the most probable state in establishing the relation between statistical and thermodynamic quantities in the next unit.

The postulate of equal a priori probability is consistent with the idea of equilibrium and is solely related to the ergodic hypothesis. It states that the probability of finding the phase point for a given system in any region of the phase space is identical with that for any other region of equal extension or volume. Thus, you can assign equal a priori probability to equal volumes in phase space. In other words, for a system in equilibrium, all accessible microstates corresponding to possible macrostates are equally probable. The concept of microstates and macrostates in detail will be discussed in Unit 2.In case of phase space distribution for a harmonic oscillator, as in Figure1.4, all the phase points on the ellipse are equally likely.This priori principle is the fundamental basis of statistical mechanics. The following examples will illustrate this postulate in detail.

Example 1.11: Suppose we pick a card at random from a well shuffled pack of 52 cards. There is nothing that would favor one particular card over the others. Hence, because there are 52 cards, we would expect the probability of picking the ace of spades equal to$\frac{1}{52}$. We could now place some constraints on the system. For instance, we could only count red cards,

in which case the probability of picking the ace of hearts, say, would be $\frac{1}{26}$, by the same reasoning. In both cases, we have used the principle of equal a priori probabilities.

Example 1.12: Let us consider an example from a famous Bollywood flick "Sholay" in which a priori probability for both head and tail on each coin toss is same based on this principle forVeeru, while when he comes to know the secret of the coin his posteriori probability is 1 for head and 0 for tail.

Self Assessment Question (SAQ) 6: By tossing three coins many times check the validity of the postulate of equal a priori probability.

1.9 SUMMARY

In this unit, you have studied the basics of the statistical physics. In particular, this unit focuses on classical statistics. You learned the concepts of phase space and phase points. This concept also helps you to understand the density of states. In this unit, the concept of distinguishability and indistinguishability is also discussed. We understood that the notion of distinguishability (indistinguishability) has a profound impact on the underlying statistics. This is because the statistics involves computation of probabilities and the rules of probability are sensitive to distinguishability (indistinguishability) of the particles. Various other important concepts, like probability, probability distribution, equal a priori principle, are also discussedwith the help of numerical examples. We have briefly introduced the concept of ensemble which will be discussed in detail in Unit 4. All the basics of statistical thermodynamics we have discussed in this unit are very helpful in discussing and understanding many interesting concepts of thermodynamics and statistical physics in the forthcoming units. Many solved examples are given in the unit to make the fundamental concepts clear. Additionally, to check your progress and understanding some self-assessment questions are given at the end of different sections.

We will return to some of the concepts introduced in this unit, like ensembles, equal a priori principle in Units 2-4. The rest of the units of this block (Units 2-3) are dedicated completely to classical statistics, but many of the topics introduced here, which can be easily extended to quantum statistics, are discussed in detail.Dedicated study of ensemble theory and different types of ensembles will be discussed in Block 2, which contains Units 4-6. Further, Block 3 (Units 7-10) is entirely focused on quantum statistics. In the last block, which contains Units 11-12, we will discuss the application part of both classical and quantum statistics by applying the methods of statistical mechanics to some physical situations.

1.10 GLOSSARY

Microscopic properties	*These are defined in terms of microscopic variables, like position and momentum coordinates.*
Macroscopic properties	*These are defined in terms of macroscopic variables, like number of particles N, volume V, temperature T, energy E.*
Phase space	*A scheme for the specification of a system in terms of the position coordinates (x, y, z) and corresponding momentum (p_x, p_y, p_z) components.*
Phase points	*It represents an individual particle in the phase space.*
Density of states	*It tells us about the distribution of phase points in phase space*
Ensemble	*It is a collection of a large number of independent collections of particles.*
Ensemble average	*The value of a variable when averaged over all the states explored within an ensemble.*
Time average	*The value of a variable when averaged over a time period.*
Ergodic hypothesis	*An average over time is equal to an average over all the possible microstates.*
Probability	*A mathematical concept that deals with calculating the likelihood of a given event's occurrence.*
Probability distribution	*A statistical distribution function that describes all the possible values and likelihoods that a random variable can take within a given range.*

1.11 REFERENCES

1. Statistical Mechanics, **S. Prakash,** KedarNath Ram Nath

2. Statistical Mechanics, **R. K. Pathria**, Butterworth-Heinemann, Oxford.

3. Fundamentals of Statistical and Thermal Physics, **F. Reif**, McGraw-Hill.

4. Statistical Mechanics, **K. Huang**, Wiley India.

5. Fundamentals of Statistical Mechanics, **B. B. Laud**, New Age International

1.12 SUGGESTED READINGS

1. Thermodynamics and Statistical mechanics, **W.Greiner, L. Neise** and **H. Stocker,** Springer Science and Business Media

2. Statistical Thermodynamics and Kinetic Theory, **C. E. Hecht**, Freeman, New York.

3. Statistical Mechanics: an Introduction, **D. H. Trevena**, Elsevier.

4. Statistical Physics, **L. D. Landau** and **E. M. Lifshitz**, Elsevier.

1.13 TERMINAL QUESTIONS

1.13.1 Short Answer Type

1. Explain the terms: (i) phase space and (ii) ensemble.

2. Give two examples of phase space trajectories.

3. Define phase cell.

4. What are the basic rules of probability?

5. What is ergodic hypothesis?

6. What do you understand by the density of states?

7. Write down the statement of postulates of equal a priori principle.

1.13.2 Long Answer Type

1. Discuss the probability distribution function with the help of an example.

2. Write notes on:

   (i) Probability, (ii) density of states, and(iii) ensemble average and time average.

3. Discuss the phase space trajectory of a particle of mass m in a gravitational field from a height h attime t.

4. Explain the concept of distinguishability and indistinguishability with the help of an example.

5. Obtain an expression for the total number of phase cells per unit energy range for a single particle in the phase space.

6. With the help of an appropriate example explain the postulate of equal a priori principle.

7. Briefly discuss the connection between ergodic hypothesis and postulates of equal a priori principle.

1.13.3 Numerical Answer Type

1. What is the probability of drawing two queens in succession from a pack of cards?

2. Obtain the probability of drawing an ace three times in a row with replacementfrom a pack of cards.

3.A drawer contains threered paper clips, fourgreen paper clips, and fiveblue paper clips. After taking one paper clip another paper clip is taken from the same drawer without

replacement. What is the probability that the first paper clip is red and the second paper clip is blue?

4.Check the validity of the postulate of equal a priori probability by tossing two coins many times.

1.13.4 Objective Answer Type

1. Phase space is a:

(a) momentum space   (b) configuration space

(c) combinedposition and momentum space   (d) four dimensional Minkowskian space

2. The statistical approach involves the concept of ………….. of distribution.

(a) sum (b) probability

(c) collection(d) particle

3. The value of the probability of an event cannot be:

(a) 1   (b) zero

(c) 1/2   (d) negative

4. What is the probability of getting a sum 9 from two throws of a dice?

(a) 1/8   (b) 1/6

(c) 1/9   (d) 1/12

5. What are the chances that no two boys are sitting together for a photograph if there are 5 girls and 2 boys?

(a) 2/7   (b) 5/7

(c) 4/7   (d) 1/21

6. Ensemble is a set of assemblies of a system, where each individual system may have a:

(a) different microstate but same macrostates (b) different macrostate but same microstate

(c) different macrostate and microstate   (d) same macrostate and microstate

7. Ergodic hypothesis relates the equality of:

(a) phase space and mu space (b) ensemble average and time average of a physical quantity

(c) time average of a physical quantity and density of states (d) ensemble average and density of states

1.14 ANSWERS

1.14.1 Self Assessment Questions (SAQs):

1. There are 4 chocolatesin the box containing total number of 4 chocolates and 4 ice creams,so the probability of getting 1 chocolatesis $\frac{4}{8} = \frac{1}{2}$.

2. There are four card in the pack of cards of each value, with two red and two black.

P (red king) = 2/52. Now we have only 51 cardsand there are still two black 7s in the deck.

P (second card is a black seven) = 2/51.

Therefore, P (red king then black 7)= (2/52) (2/51)=1/663.

3. The probability of rolling a doublet is 1/6 on each throw. It follows that the probability of no doublet on a given throw is 5/6. Therefore,

Probability of zero doublets = (5/6) (5/6) (5/6) = 125/216.

Probability of one doublet = (5/6) (5/6) (1/6)+(5/6) (1/6) (5/6) +(1/6) (5/6) (5/6) = 75/216.

Probability of two doublets = (5/6) (1/6) (1/6) + (1/6) (5/6) (1/6) +(1/6) (1/6) (5/6) = 15/216.

Probability of three doublets = (1/6) (1/6) (1/6) = 1/216.

We can verify that the sum of the probability distribution is (125+75+15+1)/216=216/216=1.

4.As we know that Hamiltonianrepresents the total energy of a system, i.e.,

$$H \text{ or } E = \text{Kinetic energy} + \text{Potential energy.}$$

In the question, for the given range $0 < x < L$, $V=0$. So the Hamiltonian or energy of particle is

$$E = \frac{p^2}{2m}.$$

From this relation we get$p = \pm\sqrt{2mE}$.Hence, the region of states accessible to the particle is shown in dark color.
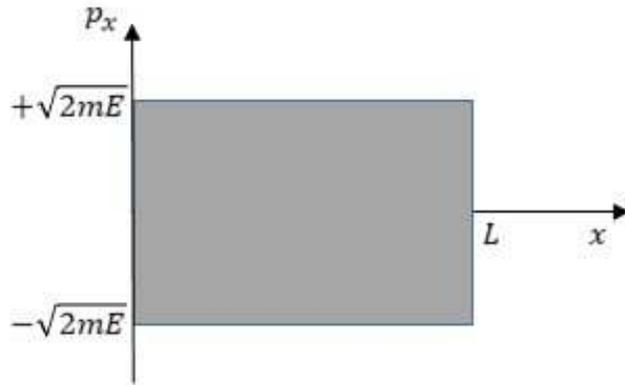
Note that an arbitrary trajectory for the particle will be any random path in the range shown in accessible phase space.

5. A free particle means that there is no potential(V=0) and is thus moving freely. Therefore, the energy of free particle has the form $E = \frac{p^2}{2m}$. Now,we can draw phase space trajectory by similar arguments as in the previous question. The trajectory is shown as
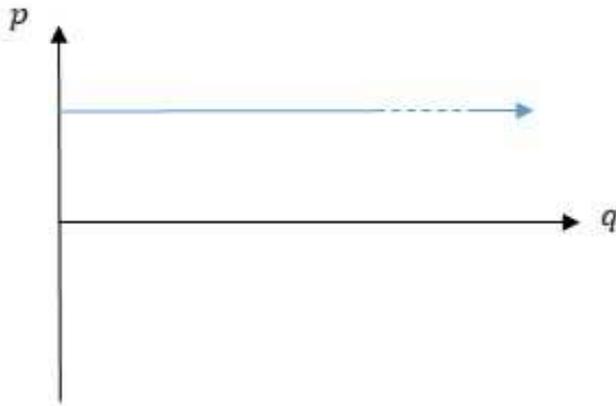
1.14.2 Terminal Questions: Numerical type questions

1. The probability of drawing two queens:

There are 4 queens in the pack of 52 cards, so the probability of drawing 1 queen $= \frac{4}{52}$.

Now only 3 queens left and only 51 cards left in the pack. Therefore, the probability of drawing second queen $= \frac{3}{51}$.

Hence, the probability of drawing two queens in succession is

20

P(two queens in succession) = *P*(first card queen) *P*(second card queen)

$$=\left(\frac{4}{52}\right)\left(\frac{3}{51}\right)=\frac{3}{663}=\frac{1}{221}.$$

2. *P*(Three aces in a row) = *P*(Card 1 is an ace) *P*(card 2 is an ace) *P*(card 3 is an ace).

We are replacing the cards, this means there will always be four aces in the deck of 52 total cards. Hence,

P (Getting an ace) = 4/52.

P (Three aces in a row) = (4/52) (4/52) (4/52)=1/2197.

3. In question it is given that the first paper clip is not replaced. The sample space of the first event is 12 paper clips, but the sample space of the second event is changed it is now 11 paper clips. Both the events are dependent. So,

P(red) = (3/12)

P (blue given red occurred) = (5/11)

P(red then blue) = P(red) P(blue given red occurred) = (3/12) (5/11) = (5/44).

1.14.3 Objective type questions

1. Correct option is (c), combined position and momentum space.

2. Correct option is (b), probability.

3. Correct option is (d), negative.

4. Correct option is (c), 1/9.

5. Correct option is (b), 5/7.

6. Correct option is (a), different microstate but same macrostates.

7. Correct option is (b), ensemble average and time average of a physical quantity.

UNIT 2 Statistical Mechanics and Thermodynamics

Structure

2.1 INTRODUCTION

In the first chapter, you have learnt the basics of statistical mechanics and its role in the modern physics. You already understand that statistical mechanics deals with the most probable behavior of the assembly of a large number of particles, usually comparable to Avogadro number. The dynamics of individual constituent particles may be governed by either classical or quantum mechanics depending upon their properties. You may have been wondering why not we solve the equations of motion for all particles independently to obtain the instantaneous state of the system and study the macroscopic properties forthis state.You probably did not realize the complexity of the task at hand as you would have to solve atleast 10^{23} differential equations. This is not only impractical, we are actually not interested in the states of the individual particles and macroscopic properties of the system only. Therefore, we understand that many copies of the system instatistical ensemble are in different states at any instant of time and thus provide the probability of occurrence in certain state. Thus, it not only simplifies our lives to compute all the macroscopic properties as functions weighed with corresponding probabilities in the phase space distribution, but has application to be discussed in last few units of the book.

We have mentioned in the previous unit that thermodynamics deals with macroscopic properties of the system at equilibrium. We have also mentioned that statistical mechanics is also studied at this stationary state. Equilibrium refers to a state which does not change with time.This state has maximum entropy and is thus most probablecondition for a closed system.Note that this does not mean that the states of the constituent particles is not changing, but their evolution is such that the system remains unchanged macroscopically. As we are going to discuss the connection between statistical and thermodynamic quantities in this unit, we should understand the idea of different types of statistical equilibriumsbefore that. Specifically, we will be discussing thermal, mechanical, and chemical equilibriums.

Thermodynamic properties can be categorized as intensive and extensive properties. The former one is the bulk property and does not depend on the size and nature of material, while in contrast, the latter one is an additive property of the subsystems and increases with size.A few examples of the intensive property are temperature, pressure, chemical potential, density; and extensive property areenthalpy, entropy, internal energy, Gibbs energy. We will discuss these quantities in detail in the present chapter.

We have discussed so far that the macroscopic properties of the system are concerned with the state of the system represented by phase points and remains unchanged with change in the state of the individual particles only. We will discuss the phase points and corresponding properties using terminology of ensemble theory by introducing the idea of macrostate and microstate.

2.2 OBJECTIVES

After studying this unit, you should be able to understand-

●   Concept of statistical equilibrium and its importance in statistical physics
●   Establish a relation between statistical and thermodynamic quantities
●   Microstates and macrostates
●   Liouville's theorem and its applications

2.3 STATISTICAL EQUILIBRIUMS

We are familiar with thermodynamic equilibrium, since our graduation classes. In brief, a system is said to be in thermodynamic equilibrium, if it satisfies all the three requirements of equilibrium, i.e.,thermal, mechanical, and chemical equilibriums. A system is said to be in thermal equilibrium when there is no temperature difference between the system and its surroundings. For mechanical equilibrium there should be no unbalanced forces acting on any part of the system or the system as a whole. While if there is no chemical reaction within the system and there is no movement of any chemical constituent from one part of the system to the other then it represents chemical equilibrium. In Unit 1,we have discussed the postulate of equal a priori principle. This principle states that any arbitrary volume element dV in phase space bounded by a surface and containing a definite number of phase points does not change with time, i.e., equal volumes in phase space. The postulate of equal a priori principle is consistent with the idea of equilibrium.

For a system of the ensemble to be in statistical equilibrium, two conditions should be fulfilled. Firstly the probabilities of finding phase points in various regions of phase space should be independent of time. Secondly the average values of the measurable properties of the system in the ensemble should be independent of time.Therefore, for the system to be in equilibrium, the phase space density should be independent of time. This equilibrium condition is solely related to the Liouville's theorem. In the forthcoming sections, we will prove the equilibrium condition with the help of Liouville's theorem.As we know that any statistical ensemble is defined by the distribution function which characterizes it,the statistical equilibrium is a state in which the probability distribution function of the states remains constant over time. In a similar way, as in the case of thermodynamic equilibrium for an ensemble to be in statistical equilibrium the system should fulfill the condition of thermal, mechanical, and particle equilibrium.

2.4   CONNECTION   BETWEEN   STATISTICAL   AND THERMODYNAMIC QUANTITIES

Statistical mechanics is an experimental and empirical physics. Further, we are familiar with thermodynamic equilibrium. In this equilibrium, there is no net macroscopic flow of matter or energy, either within a system or between systems. Whereas, in statistical equilibrium, the average values of all the physical quantities characterizing the state are independent of time.

Statistical equilibrium plays the same role as thermodynamics equilibrium in thermodynamics.

At equilibrium, in statistical mechanicsprobability is maximum, and in thermodynamics entropy is maximum. We know thatin equilibrium the entropy of a system depends upon the energy of the system (E), number of particles/molecules present in the system (N_i), and the external variables (say x_j), like pressure, volume, etc. Therefore, we can write

$$\sigma = \sigma(E, N_i, x_j).$$

….(2.1)

As we have already mentioned that statistical mechanics and thermodynamics are closely related with each other. This relation between probability and entropy is an important concept in statistical physics. Here, we define statistical temperatureτ, statistical pressureΠ, and statistical chemical potential μ_i to establish this relation. Specifically, the statistical temperature

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial E}\right)_{V,N} \quad …(2.2)$$

is related to the thermodynamic temperature as$\tau = kT$, where k is the Boltzmann's constant. Similarly, statistical pressure

$$\frac{\Pi}{\tau} = \left(\frac{\partial \sigma}{\partial V}\right)_{N,E}, \quad …(2.3)$$

equals to the thermodynamic pressure$\Pi = P$,and statistical chemical potential

$$-\frac{\mu_i}{\tau} = \left(\frac{\partial \sigma}{\partial N_i}\right)_{E,V} \quad\quad …(2.4)$$

are other relevant parameters. Thermal equilibrium states same τ for all parts of the system, while Π is constant for mechanical equilibrium at thermal equilibrium. Due to particle diffusion allowed in particle equilibrium chemical potential is constant at thermal and mechanical equilibrium.

Suppose we make a small insignificant reversible change in the equilibrium condition in such a way that the new system is in equilibrium, too.This can be described as

$$d\sigma = \left(\frac{\partial \sigma}{\partial E}\right) dE + \sum_i \left(\frac{\partial \sigma}{\partial N_i}\right) dN_i + \sum_j \left(\frac{\partial \sigma}{\partial x_j}\right) dx_j. \quad\quad …(2.5)$$

With the help of equations (2.2)-(2.4), we obtained

$$d\sigma = \frac{dE}{\tau} - \frac{1}{\tau}\sum_i \mu_i \, dN_i + \frac{1}{\tau}\sum_j X_j \, dx_j, …(2.6)$$

where$X_j = \tau \frac{\partial \sigma}{\partial x_j}$ is generalized force.After rearrangement we can write

$$dE = \tau \, d\sigma + \sum_i \mu_i \, dN_i - \sum_j X_j \, dx_j, \quad\quad …(2.7)$$

If we assume that the number of particles are fixed and the volume is the only external parameter, i.e.,$dN_i = 0, \; x_i = V$, then from equation (2.7) we get

$$dE = \tau \, d\sigma - \Pi \, dV. \quad\quad …(2.8)$$

The above equation represents the change in the internal energydue to heat exchange and change in external parameters. You should know about the first law of thermodynamics which tells us that the change in the internal energy can be defined in terms of

thermodynamic quantitiesas $dU = TdS - PdV$.Here, S is the thermodynamic entropy.As far as statistical mechanics is concerned, internal energy is the total energy (both kinetic and potential energies) of all the constituentsin the system. Thus, for statistical mechanics we can write$U = E$.On comparing equation (2.8) with the relation in thermodynamics$dE = TdS - PdV$, we have

$$TdS = \tau \, d\sigma. \qquad \ldots(2.9)$$

From this relation we can say that S and τ are proportional to σ and T, respectively. Thus, we can write

$$E = E(\sigma, V) \qquad \ldots(2.10)$$

and we have

$$dE = \left(\frac{\partial E}{\partial \sigma}\right)_V d\sigma + \left(\frac{\partial E}{\partial V}\right)_\sigma dV. \ldots(2.11)$$

It is imperative to mention here that for an ideal gas thepotential energy of the particles vanishesas the non-interacting gas molecules are assumed to be point particles, i.e., the diameter of the particles is negligible in comparison to mean free path,undergoing only elastic collision with each other. Thus, internal energy is just the sum of kinetic energy of all the gas molecules and only depends on the temperature not volume.

Comparing equations (2.8) and (2.11), we get

$$\left(\frac{\partial E}{\partial \sigma}\right)_V = \tau \text{ and } - \left(\frac{\partial E}{\partial V}\right)_\sigma = \Pi. \qquad \ldots(2.12)$$

In a similar way, we can define other thermodynamic potentials which will be useful while discussing different types of ensembles.

Helmholtz Free Energy (F): It definesthe work that can be extracted from a closed system at constant volume and temperature. Mathematically,it is

$$F = E - TS = E - \tau \sigma, \ldots(2.13)$$

which on differentiation gives$dF = dE - \tau d\sigma - \sigma d\tau$. After rearrangement we can write

$$dF = \Pi dV - \sigma d\tau \qquad \ldots(2.14)$$

Independently, we can define

$$F = F(V, \tau) \qquad \ldots(2.15)$$

to obtain

$$dF = \left(\frac{\partial F}{\partial V}\right) dV + \left(\frac{\partial F}{\partial \tau}\right) d\tau. \qquad \ldots(2.16)$$

This allows us to write, on comparing equations (2.14) and (2.16), as

$$\Pi = -\left(\frac{\partial F}{\partial V}\right)_\tau \text{ and } \qquad \sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V.$$

$\ldots(2.17)$

Enthalpy (H): It is the total of the internal energy of the system and the product of pressure and volume. The internal energy of the system is the amount of energy required to bring the system together. It can be described as

$$H = E + PV = E + \Pi V \ldots(2.18)$$

with derivative

$$dH = dE + \Pi dV + V d\Pi = \tau d\sigma + V d\Pi.$$

$\ldots(2.19)$

Further, if we write

$$H = H(\sigma, \Pi)$$

and

$$dH = \left(\frac{\partial H}{\partial \sigma}\right)_\Pi d\sigma + \left(\frac{\partial H}{\partial \Pi}\right)_\sigma d\Pi. \qquad \ldots(2.20)$$

Thus, comparing equations (2.19) and (2.20), we have

$$\tau = \left(\frac{\partial H}{\partial \sigma}\right)_\Pi \text{ and } V = \left(\frac{\partial H}{\partial \Pi}\right)_\sigma. \qquad \ldots(2.21)$$

Gibbs Free Energy (G): It is defined as the maximum reversible work that may be extracted from a system at constant temperature and pressure. Mathematically,

$$G = E - \tau\sigma + \Pi V$$

and its derivative

$$dG = -\sigma d\tau + V d\Pi. \qquad \ldots(2.22)$$

Also, we may write

$$G = G(\tau, \Pi)$$

and thus

$$dG = \left(\frac{\partial G}{\partial \tau}\right)_\Pi d\tau + \left(\frac{\partial G}{\partial \Pi}\right)_\tau d\Pi. \qquad \ldots(2.23)$$

Hence, comparing equations(2.22) and (2.23) we have

$$\sigma = -\left(\frac{\partial G}{\partial \tau}\right)_\Pi \text{ and } V = \left(\frac{\partial G}{\partial \Pi}\right)_\tau. \qquad \ldots(2.24)$$

Therefore, we have established a relation between the statistical quantities, like entropy (σ), temperature (τ), pressure (Π), and thermodynamic quantities, like Helmholtz free energy (F), enthalpy (H), and Gibbs free energy (G).

Self Assessment Question (SAQ) 1: Obtain the change in internal energy as in equation (2.11) for an ideal gas.

Self Assessment Question(SAQ) 2: With the knowledge of thermodynamics discuss the physical significance of Helmholtz free energy and Gibbs free energy.

2.5 MICROSTATES AND MACROSTATES

The aim of statistical mechanics is to serve as a bridge between the microstate and macrostate. Let us understand these two states in detail.

2.5.1 Microstate

We have discussed in the last unit that6Ndimensional Γ space defines the position and momentum of all$N$ particles. Specifically, the state of such a system can be specified by each particle's position q_i and momentum p_i.

The coordinates of this $6N$ dimensional phase space describing the state of the constituent particles of the system are known as microstate.

2.5.2 Macrostate

Suppose we are interested in the macroscopic variable, like energy E of the system, then it will be functions of the microstate, i.e.,

$$E = E(q, p).$$ ...(2.25)

At equilibrium, the value of E is very close to the average or mean value of E. This mean value of the macroscopic quantities specifies the state called macrostate of the system. Thus, the macroscopic state of the system is characterized by the macroscopic properties, like pressure, volume, temperature. More precisely, a microscopic state is simply a point in the phase space while a volume in the phase space represents a macroscopic state as it corresponds to a large number of microstates.

Example 2.1: Consider 1 mol. of He gas at pressure (P) = 1 atm and temperature (T) = 298K. The given pressure and temperature defines one macrostate. Any change in one of the macroscopic properties (say pressure or temperature) corresponds to a different macrostate. For each macrostate, the configuration of each gas particle is the possible microstates.

Here, one should note that a number of different microstates can have the same macrostate.

Example 2.2: Let us distribute three particles a, b, and c in two compartments. The distribution is shown in Table 2.1.

Macrostate	Microstate		
	Description of states		**Number of**
	Compartment 1	Compartment 2	states
(3, 0)	abc	0	1
(2, 1)	ab	c	3
	bc	a	
	ca	b	
(1, 2)	c	ab	3
	a	bc	
	b	ac	
(0, 3)	0	abc	1

Table 2.1: Different possible macrostates and microstates for three particles distributed in two compartments.

From the above table, we can conclude that the system has four macrostates and eight microstates. The macrostates (3,0) and (0,3) has 1 each, and macrostates (2,1) and (1,2) has 3 each microstates, respectively.

Example 2.3: Let us discuss the case of tossing three coins. If we toss them several times, then each of the eight possible outcomes are microstates. One can see in Table 2.2 that the macrostates with only two heads or tails also have three possible microstates. Note that it confirms that there may be more than one microstates corresponding to the same macrostate.

Macrostates	Microstates		
	First coin	Second coin	Third coin
All heads	H	H	H
Two heads	H	H	T
	H	T	H
	T	H	H
Two tails	H	T	T
	T	H	T
	T	T	H
All tails	T	T	T

Table 2.2: All possible macrostates and microstates for the tossing of three coins.

Example 2.4: Suppose there are four particles, say A, B, C, and D, and there are two cells in which these particles are to be distributed. Let us discuss the macrostates and corresponding microstates.

Here, we have four different particles A, B, C, and D, and there are only two cells, namely Cell 1 and Cell 2. In Table 2.3 given below the possible arrangementsare summarized.

Macrostate	Microstate		
	Description of states		Number of states
	Cell 1	Cell 2	

(4, 0)	ABCD	0	1
(0, 4)	0	ABCD	1
(1, 3)	A	BCD	4
	B	ACD	
	C	ABD	
	D	ABC	
(3, 1)	BCD	A	4
	ACD	B	
	ABD	C	
	ABC	D	
(2, 2)	AB	CD	6
	AC	BD	
	AD	BC	
	BC	AD	
	BD	AC	
	CD	AB	

Table 2.3: All the macrostates and microstates of four different particles in two cells.

Therefore, we can conclude that a state of the system which is defined in terms of microscopic variables are called microstates. Here, you should understand that microstates are the states of the constituent particles which gives the complete specification of the system. Whereas the states defined in terms of the macroscopic variables, like *E, V, T* are called macrostates. We also conclude one of the important facts here, i.e.,there are many possible microstates corresponding to a given macrostate.

In statistical mechanics, we also have constraints on a system. These constraints are a set of conditions or say restrictions that must be followed by a system of interest. If we have a system of total number of particles*N*with total energy *E*, then we can represent the constraints in the form of equations known as equations of constraints as$\sum n_i = N = \text{constant}$ and $\sum E_i n_i = E = \text{constant}$. Here, $n_i$is the number of particles in the *i*th cell, and $E_i$is the energy of each particle in the *i*th cell. On the basis of the equations of constraints, we can categorize all the macrostates in two types, one is accessible macrostate and the other one is inaccessible macrostate. Let we discuss an examplebelow which clarifies these two kinds of states.

Example 2.5: Suppose there are two particle J and K, and we wish to distribute them into two compartments say Compartment 1 and Compartment 2. The possible arrangements are shown in Table2.4 given below.

Macrostate	Microstate		
	Description of states		**Number**
	Compartment 1	Compartment 2	**of states**
(2, 0)	JK	0	1
(1, 1)	J	K	2
	K	J	
(0, 2)	0	JK	1

Table 2.4: All the macrostates and microstates for two particles distributed in two compartments.

If we put the constraints that no compartment should remain empty, then the macrostates (2, 0) and (0, 2) are not allowed. Only one macrostate (1, 1) will be there,which results in the decrement of the number of macrostates and microstates. Hence, we conclude that the macrostate which is allowed under the constraint is accessible macrostate, whereas the macrostates which are not allowed under the constraint are inaccessible macrostates. For the above mentioned constraints, i.e., no compartment should be empty, the macrostate (1, 1) is accessible macrostate while (2, 0) and (0, 2) are inaccessible macrostates.

Self AssessmentQuestion (SAQ) 3: Discuss the microstates and macrostates for the distribution of two classical (distinguishable) particles in two compartments.

SelfAssessment Question (SAQ) 4: Consider two coins and toss them many times. Discuss the various possible macrostates and the corresponding microstates.

2.6 LIOUVILLE'S THEOREM

We have studied in the previous unit that each phase point in the phase space represents the state of a system. The representative points in the phase space move along a path known as phase space trajectory. This trajectory is determined from Hamilton's equation of motion. As a result of the motion of the phase points the density of the system in phase space, i.e., phase space density changes with time. Liouville's theorem is helpful in finding the rate of change of phase density at a given point in phase space.

Let us consider an arbitrary volume element in the hyperspace located between q_1 and $q_1 + \delta q_1$, p_1 and $p_1 + \delta p_1$ (see Figure 2.1). The number of phase points or systems in this volume element are given by

$$\delta N = \rho \delta \Gamma. \qquad \qquad \text{...(2.26)}$$

Here, ρ is the phase space density, and $\delta \Gamma$ is the volume element $\delta \Gamma = \delta q_1 \dots \delta q_m \delta p_1 \dots \delta p_m$. The number of phase points entering the volume element through any face will be different from the number of phase points which are leaving the opposite face. This change in the number of phase points per unit time is given by

$$\frac{d}{dt}(\delta N) = \frac{d}{dt}(\rho \, \delta \Gamma) = \dot{\rho} \, \delta \Gamma = \frac{\partial \rho}{\partial t} dt \, \delta q_1 \dots \delta q_m \delta p_1 \dots \delta p_m. \qquad \text{...(2.27)}$$

Further, consider two faces perpendicular to the q axis, located at q_1 and $q_1 + \delta q_1$. The number of phase points entering the element in time dt through the face q_1 are thus $\rho(q, p, t) \dot{q}_1 dt \delta q_2 \dots \delta q_m \delta p_1 \dots \delta p_m$, where $\dot{q}_1$ is velocity in the direction q_1.

Notice that ρ changes in position as well as momentum coordinates. Thus, at the opposite face q_1 changes to $q_1 + \delta q_1$, ρ changes to $\rho + \left(\frac{\partial \rho}{\partial q_1}\right) \delta q_1$, and $\dot{q}_1$ changes to $\dot{q}_1 + \left(\frac{\partial \dot{q}_1}{\partial q_1}\right) \delta q_1$. Thus, the number of phase points leaving the element through face $q_1 + \delta q_1$ are $\left[\rho \dot{q}_1 + \frac{\partial}{\partial q_1}(\rho \dot{q}_1) \delta q_1\right] dt \delta q_2 \dots \delta q_m \delta p_1 \dots \delta p_m$, where higher-order terms are neglected.
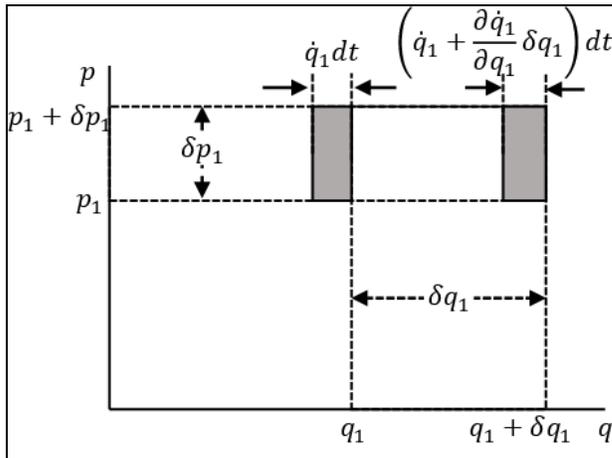
Figure 2.1: Arbitrary volume element in the hyperspace.

Hence, the net number of systems entering the volume element in the direction q_1, i.e., the difference between the number of phase points entering face q_1 and leaving opposite face $q_1 + \delta q_1$, is $-\frac{\partial}{\partial q_1}(\rho \dot{q}_1) \, dt \delta q_1 \dots \delta q_m \delta p_1 \dots \delta p_m$. Similarly, the number of phase points entering the volume element in the direction p_1, i.e., the difference between the number of phase points entering face p_1 and leaving opposite face $p_1 + \delta p_1$, is $-\frac{\partial}{\partial p_1}(\rho \dot{p}_1) \, dt \delta q_1 \dots \delta q_m \delta p_1 \dots \delta p_m$.

Therefore, the net number of phase points entering the volume element through all its faces comes out as

$$\frac{\partial \rho}{\partial t} dt \, \delta q_1 \dots \delta q_m \, \delta p_1 \dots \delta p_m - - \sum_{i=1}^{m} \left[\frac{\partial}{\partial q_i} (\rho \, \dot{q}_i) + \frac{\partial}{\partial p_i} (\rho \, \dot{p}_i) \right] dt \delta q_1 \dots \delta q_m \, \delta p_1 \dots \delta p_m,$$

…(2.28)

which helps us conclude

$$\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{m} \left[\frac{\partial}{\partial q_i} (\rho \, \dot{q}_i) + \frac{\partial}{\partial p_i} (\rho \, \dot{p}_i) \right].$$ …(2.29)

This equation can also be rearranged as

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

…(2.30)

We can further use the Hamilton's equation of motion here, i.e., the quantities

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \text{ and } \dot{p}_i = -\frac{\partial H}{\partial q_i},$$

…(2.31)

and their derivatives

$$\frac{\partial \dot{q}_i}{\partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial^2 H}{\partial q_i \partial p_i}.$$

…(2.32)

Therefore, the first term in the bracket of equation (2.30) vanishes, and we obtain

$$\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{m} \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right].$$ …(2.33)

Here, $\frac{\partial \rho}{\partial t}$ gives the rate of change in phase density at an instant of time. Equation (2.33) is known as Liouville's equation.

Further, we can express equation (2.33) in the form

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{m} \left[\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right] - 0,$$

…(2.34)

or

$$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0.$$

…(2.35)

Here, $\{\rho, H\} = \sum_{i=1}^{m} \left[\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right]$ is Poisson bracket operationdefined for the functions ρ and H. Therefore, the total time derivative of $\rho(q, p, t)$ can be defined as

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0.$$ …(2.36)

This equation tells us that the phase space density is an integral of motion, i.e., the total time derivative of the phase space density vanishes along a phase space trajectory. This is Liouville's theorem in classical statistics.

According to Gibbs $\frac{d\rho}{dt} = 0$ is called the principle of conservation of density in phase space, i.e.,the density of a group of points remains constant along their phase trajectories.Further,

considering equation (2.33) at statistical equilibrium, i.e., $\frac{\partial \rho}{\partial t} = 0$ as ρ is not explicitly dependent on time, it reduces to

$$-\sum_{i=1}^{m}\left[\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right] = 0,$$

which will be satisfied only if $\rho(q,p) = constant$. Thus, phase points are uniformly distributed in the phase space at statistical equilibrium.

As we discussed about the statistical equilibrium in Section 2.3, here we can conclude that ρ is a function of some property of the ensemble which is independent of time. This means that the system of ensemble will be in a statistical equilibrium.

Self Assessment Question (SAQ) 5: We have discussed the Liouville's theorem which represents the conservation of density in the phase space by considering the time derivative of phase density for a volume element in equation (2.27). Similarly, illustrate the conservation of extension of phase space using the time derivative of volume element in equation (2.27).

The Liouville's theorem plays a significant role in statistical mechanics. The theorem is valid for both equilibrium and non-equilibrium systems. Consequently, it is of fundamental importance for the Gibbs formulation of statistical mechanics. In other words, this theorem states that the phase space density remains constant in phase space which suggests that the phase space density gives the probability of finding a system at an instant of time in the phase space.

2.7 SUMMARY

We all are too familiar with equilibrium or say thermal equilibrium, since our graduation classes. The state of equilibrium refers to a state of a system which does not change with time. This unit is solely based on the concept and condition of statistical equilibrium. We have learned about the various conditions required for a system to be in the statistical equilibrium. We also came to know about the role of entropy and probability in thermodynamics and statistical mechanics, respectively. Further, we defined various thermodynamic potentials and establish a relation between the statistical and thermodynamic quantities. Here, in the present unit, we have discussed one of the most important concepts in statistical physics, i.e., the concept of macrostates and microstates with the help of various examples. We can also understand the postulate of equal a priori principle in terms of microstates and macrostates, which will be discussed in detail in the next unit. Specifically, microstates are the representative points in the phase space, and we have already discussed in Unit 1 that these representative points are known as the phase points in the phase space.

Finally, in this unit we came to know about Liouville's theorem which suggests an equal distribution of phase points in the given phase space at statistical equilibrium. This theorem also tells us that if we move with a phase space point as it evolves under the Hamiltonian, the phase space density of the neighbourhood is constant.

2.8 GLOSSARY

Thermal equilibrium	*When the temperature of two or more than two systems is same then this condition is known as thermal equilibrium.*
Mechanical equilibrium	*Two systems are said to be in mechanical equilibrium if their pressures are same.*
Chemical equilibrium	*It is the state in which the chemical activities or concentrations of the reactants and products have no net change over time and also there is no movement of any chemical constituents from one part of the system to the other.*
Thermodynamic equilibrium	*A system is said to be in thermodynamic equilibrium with another system when it achieves all three equilibriums, i.e., thermal, mechanical, and chemical equilibriums.*
Statistical equilibrium	*A system is in statistical equilibrium when the probabilities of finding the phase points in various regions of the phase space and the average values for the measurable properties of the system in the ensemble are independent of time.*
Macrostates	*States which can be represented in terms of macroscopic variable, like pressure P, volume V, number of particles N, temperature T.*
Microstates	*States which can be represented in terms of microscopic variables and phase points in the phase space.*
Liouville's theorem	*It states that the density of particles or phase space density in phase space is constant.*

2.9 REFERENCES

1. Statistical Mechanics, *S. Prakash,* Kedar Nath Ram Nath

2. Statistical Mechanics, *R. K. Pathria*, Butterworth-Heinemann, Oxford.

3. Fundamentals of Statistical and Thermal Physics, *F. Reif*, McGraw-Hill.

4. Statistical Mechanics, *K. Huang*, Wiley India.

5. Fundamentals of Statistical Mechanics, *B. B. Laud*, New Age International

2.10 SUGGESTED READINGS

1. Thermodynamics and Statistical mechanics, *W.Greiner, L. Neise* and *H. Stocker,* Springer Science and Business Media

2. Statistical Thermodynamics and Kinetic Theory, *C. E. Hecht*, Freeman, New York.

3. Statistical Mechanics: an Introduction, *D. H. Trevena*, Elsevier.

4. Statistical Physics, *L. D. Landau* and*E. M. Lifshitz*, Elsevier.

2.11 TERMINAL QUESTIONS

2.11.1 Short Answer Type

1. Explain the term statistical equilibrium.

2. Write down the condition of statistical equilibrium.

3. Define the terms (i) thermodynamic equilibrium and (ii) macrostate and microstate.

4. State the principle of equal a priori principle in terms of microstate and macrostate.

5. Write down the statement of Liouville's theorem.

2.11.2 Long Answer Type

 1. Differentiate between thermodynamic equilibrium and statistical equilibrium.
 2. Discuss the concept of macrostates and microstates in detail. Using an example of two dices rolled simultaneously, write the number of microstates and macrostates.
 3. State and prove Liouville's theorem. Also mention the consequences of Liouville's theorem.

4. Consider three particles which are distributed among three energy levels. Discuss the possible microstates and macrostates of the system.

2.11.3 Numerical Answer Type

1. How many macrostates and microstates are there when a single coin is tossed three times?

2. There are two distinguishable particles to be arranged in three cells. Show the possible arrangements, and discuss the macrostates and microstates in a tabular form.

3. A system has a single particle state with 0, 1, 2, and 3 energy units. Discuss the macrostates and microstates for three distinguishable particles to be distributed in these energy states such that the total energy of the system is 3 units.

4. Discuss the macrostates and microstates for tossing of four coins simultaneously.

2.11.4 Objective Answer Type

1. In general the possible microstates for a given macrostate are:

(a) only 1   (b) Zero

(c) as many as possible   (d) cannot say

2. The relation between the statistical entropy and thermodynamic entropy is given by

(a) $\tau = \frac{k}{T}$ (b) $\tau = kT$

(c) $\tau = \frac{T}{k}$ (d) $\tau = 2kT$

3. Among the following the correct expression for the entropy is

(a) $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$ (b) $\sigma = \left(\frac{\partial F}{\partial \tau}\right)_V$

(c) $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_N$ (d) $\sigma = \left(\frac{\partial F}{\partial \tau}\right)_N$

4. In Liouville's theorem, which of the following physical quantity remains constant along the phase space trajectory:

(a) momentum   (b) phase density

(c) energy   (d) ensemble

5. At statistical equilibrium,Liouville's theorem tells us phase points are ……… distributed in phase space

(a) randomly   (b) uniformly

(c) not uniformly   (d) neither randomly nor uniformly

2.12 ANSWERS
2.12.1 Self-Assessment questions:

1. As we have already mentioned that for an ideal gas $\left(\frac{\partial E}{\partial V}\right)_\sigma = 0$, so we can obtain

$$dE = \left(\frac{\partial E}{\partial \sigma}\right)_V d\sigma.$$

2. If we check or calculate the change in Helmholtz free energy, i.e., ΔF,and change in Gibbs free energyΔG, then it provides us useful information about the system and the process underway. For example, if changes in these quantities vanish,i.e.,$\Delta F = 0$ (at constant temperature and volume) and $\Delta G = 0$ (at constant temperature and pressure), then it represents that the systemis at chemical equilibrium.The minimum value of these free energies represent that the system is in stable condition. The change also tells us about the direction and nature of the process taking place. If at constant temperature and volume,$\Delta F > 0$the process is non-spontaneous, and $\Delta F < 0$corresponds to the spontaneousprocess. Similarly, for $\Delta G > 0$ the process is non-spontaneous (endergonic), while$\Delta G < 0$is signature of the spontaneous (exergonic)process at constant temperature and pressure. All these facts are summarized in the following table.

State function	Mathematical form	Differential equation	Condition for change in free energy	Stable equilibrium measure /Type of process
Helmholtz free energy (*F*)	$F = E - TS$	$dF = -SdT - PdV + \mu dN$	$\Delta F = 0$	System is in equilibrium
			$\Delta F > 0$	Non-spontaneous
			$\Delta F < 0$	Spontaneous

Gibbs free energy (G)	$G = H - TS$	$dG = -SdT + VdP + \mu dN$	$\Delta G = 0$	System is in equilibrium
			$\Delta G > 0$	Non-spontaneous (endergonic)
			$\Delta G < 0$	Spontaneous (exergonic)

3.Different microstates and macrostates for the distribution of two classical (distinguishable) particles in two compartments.

Macrostate	Microstate		
	Description of states		**Number**
	Compartment 1	Compartment 2	**of states**
(2, 0)	a b	0	1
(1, 1)	a	b	2
	b	a	
(0, 2)	0	a b	1

4.Possible macrostates and the corresponding microstates for tossing of two coins.

Macrostate	Microstate		
	Description of states		**Number**
	Coin 1	Coin 2	**of states**
Both heads	H	H	1
Either head or tail	H	T	2
	T	H	
Both tail	T	T	1

5.   Let us consider an elementary volume $\delta\Gamma$ in the phase space, and the phase space density can be assumed uniform throughout the phase space for this very small region. Thus, from equation (2.27) we will have

$$\frac{d}{dt}(\delta N) = \frac{d}{dt}(\rho\,\delta\Gamma) = \frac{d\rho}{dt}\delta\Gamma + \rho\frac{d}{dt}(\delta\Gamma).$$

We know in a given phase space each phase point represents a definite system, which can neither be created nor destroyed. Therefore, $\frac{d}{dt}(\delta N) = 0$, i.e., the number of phase point δN remains fixed. So,

$$\frac{d\rho}{dt}\delta\Gamma + \rho\frac{d}{dt}(\delta\Gamma) = 0.$$

With the help of equation (2.36), the above equation reduces to

$$\frac{d}{dt}(\delta\Gamma) = 0 \text{ or } \delta\Gamma = 0.$$

This shows the conservation of extension in phase space.

2.12.2 Numerical answer type:

1. The macrostates are (three heads, two heads, one head, no head), and the corresponding microstates are (three heads: HHH; two heads: HHT, HTH, THH; one head: HTT, THT, TTH; no head: TTT).

2. Let the particles be R and P

Macrostates	Microstates			Total number of microstates
	Cell 1	Cell 2	Cell 3	
Both in same cell	RP	-	-	3
	-	RP	-	
	-	-	RP	
Both in different cells	R	P	-	6
	P	R	-	
	-	R	P	
	-	P	R	

	R	-	P	
	P	-	R	

3. Consider three particles as J, K, and L, and the energy unit is E.

Macrostates	0E	1E	2E	3E	Total energy	Number of microstates
(2, 0,0, 1)	JK	0	0	L	3E	3
	KL	0	0	J		
	LJ	0	0	K		
(1, 1, 1, 0)	J	K	L	0	3E	6
	J	L	K	0		
	K	L	J	0		
	K	J	L	0		
	L	J	K	0		
	L	K	J	0		
(0, 3, 0, 0)	0	JKL	0	0	3E	1

4. There are five macrostates as (all heads, only one head, two heads, only one tail, and all tails). The possible microstates are (HHHH, TTHT, TTTH, THTT, HTTT, HHTT, HTTH, THHT, THTH, TTHH, HHHT, HHTH, HTHT, HTHH, THHH, TTTT).

2.12.3 Objective answer type:

1. Correct option is (c), as many as possible.

2. Correct option is (b), $\tau = kT$.

3. Correct option is (a), $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$.

4. Correct option is (b), uniformly.

5. Correct option is (d), statistical equilibrium.

UNIT 3   Maxwell-Boltzmann Statistics

Structure

3.1 INTRODUCTION

We have already discussed and understand so farthe basic concepts of statistical mechanics and probability theory. We have further elucidated the relevance of statistical equilibrium in this discussion and stressed on the connection between statistical and thermodynamic quantities.The principle of equal a priori probability and the ergodic hypothesis enable us to compute statistical quantities and understand intensive and extensive thermodynamic properties. We have also discussed that the density of a group of points remains constant along their phase trajectorieswhich is useful in the Gibbs formulation of statistical mechanics. Our basic tools for both classical and quantum statistics are incomplete without the introduction of the idea of macrostates and microstates. Each phase point in the phase space corresponds to a microstate while many such microscopic statesmay have same macroscopic properties and thus macrostate. In the present unit, we will stress on the significance of the number of microstates in each macrostate which is concerned with thermodynamic probability. We will revisit the definition of the most probable state in view of the thermodynamic probability.

We have all the tools required to understand the classical statistics governed by Maxwell-Boltzmann distribution law. We also discuss the nature of particles this type of statistics may be used.We further study Maxwell-Boltzmann distributions of velocity and speedin brief. This gives us significant types of speeds namely, most probable speed, mean speed and root mean square speed. These unique types of speeds have a prominent role in statistical mechanics. Therefore, we will not only obtain their mathematical expressions, we will also discuss their physical relevance with the help of corresponding examples. We conclude this unit, as well as this block, focused on the classical statistics with the principle of equipartition of energy over all the degrees of freedoms.

Here, it is worth stressing thatthe significance of the discussion in the present unit (and this block) is not restricted to classical particles, but many of these basic ideas areeither directly useful or easily extendible to quantum statistics to be discussed in the forthcoming blocks. One more significant example of classical statistics deservesattention here could be interaction between a quantum particle and its environment, which causes decoherence or quantum to classical transition of quantum behavior. To perform this study the environment is modeled as a classical system governed by Maxwell-Boltzmann statistics. There are various physical processes relevant in different branches of physics where the topics discussed in the present unit will be useful. For instance, obtaining Einstein coefficients and, in turn, the idea of laser. To begin with, we start our discussion with thermodynamic probability of macrostates.

3.2 OBJECTIVES

After studying this unit, you should be able to understand-

- Thermodynamic probability
- Most probable state
- Classical distribution law known as Maxwell-Boltzmann distribution law
- Maxwell law of distribution of velocities

- Maxwell speed distribution law
- Principle of equipartition of energy
- Fundamental postulates of statistical mechanics

3.3 THERMODYNAMICAL PROBABILITY

In the previous unit, we have discussed the microstates and macrostates in detail. The number of microstates corresponding to a given macrostate is called its *thermodynamic probability*. Hence, the probability of a macrostate is defined as the ratio of the number of microstates in it to the total number of possible microstates of the system.

$$P_{macro} = \frac{\text{Number of microstates in the macrostate}}{\text{Total number of microstates of the system}}. \qquad \text{…(3.1)}$$

For a given macrostate, the number of microstates is equal to the number of possiblearrangements of various particles. Consider there are *n* particles to be filled in two compartments. Let *r* particles are kept in Compartment 1 and the remaining (*n-r*) are in Compartment 2, thenthe total number of arrangements is given by

$$w(r, n-r) = \binom{n}{r} = \frac{n!}{r!(n-r)!} \dots \text{(3.2)}$$

Here, the notation $\binom{n}{r}$ means we have total*n* particles, and out of these we choose *r*particles

to be filledin one compartment and the remaining in the second compartment.

Thus,*thermodynamic probability*gives the number of microstates in a macrostate (*r, n-r*). Further, if there are *c* compartments, then the total number of microstates of the system is c^n.

Therefore, the probability of macrostate *(r, n-r)*can be computed as

$$P_{(r,n-r)} = \frac{\binom{n}{r}}{c^n}. \qquad \text{…(3.3)}$$

With the help of following examples we can understand the concept of thermodynamic probability and probability.

Example 3.1: Let us distribute three distinguishable particles a, b, and c in two compartments as shown in Table 3.1. The system has four macrostates and eight microstates.

MACROSTATE	MICROSTATES		
	Description of state		Number of states
	Compartment 1	Compartment 2	
(3, 0)	a b c	0	1
(2, 1)	a b	c	3
	b c	a	

	c a	b	
(1, 2)	c	a b	3
	a	b c	
	b	a c	
(0, 3)	0	a b c	1

Table 3.1: Distribution of three distinguishable particles a, b, and c in two compartments.

Thermodynamic probability of macrostate (3, 0) is 1 as there is only one possible microstate corresponding to macrostate (3, 0). Similarly, thermodynamic probability of macrostates (2, 1), (1, 2), and (0, 3) are 3, 3, and 1, respectively.

Example 3.2: Calculate the thermodynamic probability for the case of three coins tossed several times.

In this case, there are eight possible microstates. See Table3.2 below summarizing all these possible outcomes.

Macrostates	**Microstates**			
	First coin	Second coin	Third coin	Number of states
All heads	H	H	H	1
Two heads	H	H	T	3
	H	T	H	
	T	H	H	
Two tails	H	T	T	3
	T	H	T	
	T	T	H	
All tails	T	T	T	1

Table 3.2: All possible outcomes of three coin tosses summarizing all microstates and macrostates.

Now we can discuss the thermodynamic probability of all the macrostates. Thermodynamic probability of both macrostates "All heads" and "All tails" is 1 as there is only one microstate

corresponding to these macrostates.Similarly, thermodynamic probability of macrostate "Two heads" is 3.You can verify that the thermodynamic probability of macrostate "Two tails" is 3.

In Unit 1,we have discussed the postulate of equal a priori principle and stated that it is connected with the concept of microstates and macrostates.Further, in unit 2 we have already discussed this principle in brief. Here, we can verify the validity of this principleusing the following example.

Example 3.3: Let us consider three distinguishable particles, say a, b, and c, in two compartments (see Example 3.1).

With the help of the expression for thermodynamic probability and probability, we can calculate probabilities of different microstates as

Probability of microstate (a b c, 0) corresponding to macrostate (3,0)$= \frac{1}{2^3} = \frac{1}{8}$.

Probability of microstate (a b, c) corresponding to macrostate (2, 1) $= \left(\frac{1}{2^2}\right)\left(\frac{1}{2}\right) = \frac{1}{8}$.

Probability of microstate (a, bc) corresponding to macrostate (1, 2) $= \left(\frac{1}{2}\right)\left(\frac{1}{2^2}\right) = \frac{1}{8}$.

Probability of microstate (0, a b c) corresponding to macrostate (0, 3) $= \frac{1}{2^3} = \frac{1}{8}$.

Thus, we can conclude that the probability of all microstates of the system corresponding to the possible macrostates isequal.

Self Assessment Question (SAQ) 1: Check the validity of the postulate of equal a priori principle by considering the system of four particles a, b, c, and d in two compartments for any two macrostates.

3.3.1 Most probable state: Equilibrium state

In statistical physics, we deal with systems with a very large number of particles and assume that the system exists in an equilibrium state. All the physical properties of such a system can be deduced by knowing the most probable or equilibrium state of the system. Thus, the macrostate having maximum probabilityis termed as the most probable state.

Suppose there is a system of n distinguishable particles distributed in two compartments. Let r particles are kept in Compartment 1, and the remaining $(n-r)$ are in Compartment 2, then the total number of arrangements $= \frac{n!}{r!(n-r)!}$. Therefore, the probability of macrostate$(r,n-r)$ is represented as

$$P_{(r,n-r)} = \frac{n!}{r!(n-r)!}\frac{1}{2^n}.$$

$$\ldots(3.4)$$

The probability will be maximum when $r = \frac{n}{2}$. The maximum value of probability is then given by$P_{max} = \frac{n!}{\frac{n}{2}\left(\frac{n}{2}\right)!}\frac{1}{2^n}$ or

$$P_{max} = \frac{n!}{\left(\frac{n}{2}!\right)^2}\frac{1}{2^n}.$$

$$\ldots(3.5)$$

We will elaborate this idea further using an example.

Example 3.4: A coin is tossed six times. What is the probability of getting (i) all heads, (ii) three heads and three tails, (iii) four heads and two tails?Also calculate the probability of the most probable state.

We have a coin which is tossed six times. Here, we will use equation (3.4). For there are all heads, then $r = 6, (n-r) = 0$. Therefore, $P_{(6,0)} = \frac{1}{2^6}\frac{6!}{6!0!} = \frac{1}{2^6} = \frac{1}{64}$.

    (i) For there are three heads and three tails, then $r = 3, (n-r) = 3$.

        Therefore, $P_{(3,3)} = \frac{1}{2^6}\frac{6!}{3!3!} = \frac{20}{2^6} = \frac{20}{64} = \frac{5}{16}$.

    (ii) For there are four heads and two tails, then $r = 4, (n-r) = 2$.

        Therefore, $P_{(4,2)} = \frac{1}{2^6}\frac{6!}{4!2!} = \frac{15}{2^6} = \frac{15}{64}$.

We have already mentioned that for most probable state $r - \frac{n}{2}$, and thus the result of (ii) corresponds to the most probable state.

3.4 CLASSICAL MAXWELL-BOLTZMANN DISTRIBUTION LAW

The distribution of classical particles is given by Maxwell-Boltzmann distribution law. In general, we have three types of particles. The first kind of particles is identical but distinguishable (like molecules of a gas) and the other two categories have identical but indistinguishable particles with integer or half integer spin (shall be discussed in Block 3 under quantum statistics).

The Maxwell distribution law, we are going to discuss or derive here, tells us about the distribution of energy among the assembly of identical particles.Let us consider a system of a large number of particles or gas molecules (say *N*)with $n_1, n_2, \dots n_i$of them in different compartments(or different energies), namely *1, 2, 3,...i*, respectively.First, we will write the basic assumptions of classical statistics as

(a) The particles or classical particles are identical and distinguishable.

(b) Each energy level or state can be occupied by any number of particles.

(c) The total number of particles in the system is constant the total number of particles

      $\sum_i n_i = N = \text{constant}$ ...(3.6)

or

      $\sum_i \delta n_i = 0.$ ...(3.7)

(d) The total energy of all the particles in the system is also constant

      $\sum_i \varepsilon_i n_i = \text{constant}$

              ...(3.8)

or

    $\sum_i \varepsilon_i \delta n_i = 0,$ ...(3.9)

where ε_i is the energy of the ith particles.

All these N particles are continuously moving in different directions and thus the values of $n_i$skeep changing,maintaining the values which define the state of maximum probability or most probable state. We know that in this equilibrium state the thermodynamic probability(w) is maximum, which can be written in the condition

$$\delta w = 0, \qquad \qquad ...(3.10)$$

where the thermodynamic probability may be written in this case as

$$w = \frac{N!}{n_1!n_2! \dots \dots n_i!}. \qquad \qquad ...(3.11)$$

Taking the logarithm of both the sides, we get

$$\log w = \log N! - \log n_1! - \log n_2! \dots - \log n_i!. \qquad \qquad ...(3.12)$$

Note that the number of molecules is large which allows us to use Striling's approximation (i.e., $\log x! = x \log x - x$) to obtain

$$\log w - N \log N - N - (n_1 \log n_1 - n_1) - (n_2 \log n_2 - n_2) \dots - (n_i \log n_i - n_i)$$
$$= N \log N - N - \sum_i (n_i \log n_i - n_i). \qquad \qquad ...(3.13)$$

Differentiating this equation with respect to$n_1, n_2, \dots n_i$ (keep in mind that the total number of particles N is constant) we obtain

$$\delta \log w = -\sum_i [n_i(\delta \log n_i) + \log n_i \, \delta n_i - \delta n_i] \qquad \qquad ...(3.14)$$

or

$$\sum_i (\log n_i \, \delta n_i) = 0. \qquad \qquad ...(3.15)$$

Equations (3.7), (3.9), and (3.15) are independent of each other and they must be satisfied at any instant. Thus, we apply the Lagrange method of undetermined multiplier, i.e., multiply equation(3.7) by α,equation(3.9) by β, and adding the resultant equations to equation(3.15), we get

$$\sum_i (\log n_i + \alpha + \beta \varepsilon_i) \delta n_i = 0, \qquad \qquad ...(3.16)$$

whereα and β are arbitrary constants independent of n_is.Similarly, all δn_is are independent of each other. Thus, equation (3.16) will be satisfied only when each term in the summation is separately equal to zero, i.e.,

$$\log n_i + \alpha + \beta \varepsilon_i = 0.$$

After rearrangement and simplification,we can rewrite this equation as

$$n_i = \frac{1}{e^{(\alpha + \beta \varepsilon_i)}}. \qquad \qquad ...(3.17)$$

This expression is known as Maxwell-Boltzmann distribution law of particles in classical statistics.Here, the values of two constants α and β may be further evaluated in thenextsubsection.

This distribution law has various important applications, such as in discussing the probability that a given assembly of molecules in equilibrium, and in understanding the equipartition principle in detail. With the help of above distribution law, we will discuss the some important distribution laws in statistical mechanics, i.e., the law of distribution of velocities and speedsof molecules.

3.4.1 Evaluation of constants α and βin Maxwell-Boltzmann distribution law

For evaluating the two constants in Maxwell-Boltzmann distribution law, we assume continuous distribution of energy and can represent equation (3.17) in the following form

$$n(\varepsilon)d\varepsilon = Ce^{-\beta\varepsilon}d\varepsilon, \qquad \qquad …(3.18)$$

where $C = e^{-\alpha}$ and $n(\varepsilon)d\varepsilon$ is the number of molecules with energy between ε and $\varepsilon + d\varepsilon$.

Now consider a system of monoatomic ideal gas of mass m defined in three Cartesian *(x, y, z)* coordinates and three momentum coordinates (p_x, p_y, p_z). Then the number of molecules in volume element $dx\,dy\,dz$with energy in the range ε and $\varepsilon + d\varepsilon$are

$$n(\varepsilon)d\varepsilon dx\,dy\,dz = Ce^{-\beta\varepsilon}dx\,dy\,dz\,d\varepsilon. \qquad \qquad …(3.19)$$

The kinetic energy of these particles ε with velocity components $v_x, v_y,$ and v_z is given by

$$\varepsilon = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right) = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right).$$

Thus, we can write equation (3.19) as

$$n(p)dx\,dy\,dz\,dp_x\,dp_y\,dp_z = Ce^{-\frac{\beta\left(p_x^2 + p_y^2 + p_z^2\right)}{2m}}dx\,dy\,dz\,dp_x\,dp_y\,dp_z. \qquad …(3.20)$$

The total number of molecules can be obtained by integrating it over all the possible values of position and momentum coordinates as

$$N = \int n(p)dx\,dy\,dz\,dp_x\,dp_y\,dp_z = C\int e^{-\frac{\beta\left(p_x^2 + p_y^2 + p_z^2\right)}{2m}}dx\,dy\,dz\,dp_x\,dp_y\,dp_z. \qquad …(3.21)$$

Thus, we can write

$$\frac{1}{C} = \frac{1}{N}\int e^{-\frac{\beta\left(p_x^2 + p_y^2 + p_z^2\right)}{2m}}dx\,dy\,dz\,dp_x\,dp_y\,d\,p_z. \qquad \qquad …(3.22)$$

The integration over coordinate space gives us the total volume $\int dx\,dy\,dz = V$,therefore,

$$\frac{1}{C} = \frac{V}{N}\int e^{-\frac{\beta\left(p_x^2 + p_y^2 + p_z^2\right)}{2m}}dp_x\,dp_y\,d\,p_z. \qquad \qquad …(3.23)$$

Thus, equation (3.23) becomes

$$\frac{1}{C} = \frac{V}{N}\int e^{-\frac{\beta p_x^2}{2m}}dp_x\int e^{-\frac{\beta p_y^2}{2m}}dp_y\int e^{-\frac{\beta p_z^2}{2m}}dp_z.$$

With the help of a standard result

$$\int e^{-at^2}\,dt = \sqrt{\frac{\pi}{a}}$$

we get

$$\frac{1}{C} = \frac{V}{N}\left(\frac{2\pi m}{\beta}\right)^{1/2}\left(\frac{2\pi m}{\beta}\right)^{1/2}\left(\frac{2\pi m}{\beta}\right)^{1/2}$$

or

$$\frac{1}{C} = \frac{V}{N}\left(\frac{2\pi m}{\beta}\right)^{3/2}. \qquad \qquad …(3.24)$$

We know the total energy E of N molecules is

$$E = \int \varepsilon\, n(\varepsilon)d\varepsilon dx\,dy\,dz. \qquad \qquad …(3.25)$$

Using equations (3.19)-(3.20) in equation (3.25), we get

$$E = C \int \frac{(p_x^2 + p_y^2 + p_z^2)}{2m} e^{-\frac{\beta(p_x^2 + p_y^2 + p_z^2)}{2m}} \, dx \, dy \, dz \, dp_x \, dp_y \, dp_z$$

or

$$E = \frac{VC}{2m} \int (p_x^2 + p_y^2 + p_z^2) e^{-\frac{\beta p_x^2}{2m}} e^{-\frac{\beta p_y^2}{2m}} e^{-\frac{\beta p_z^2}{2m}} dp_x \, dp_y \, dp_z . \qquad \qquad \ldots(3.26)$$

As we can write this integration in the following form

$$E = \frac{VC}{2m} \left[\int p_x^2 e^{-\frac{\beta p_x^2}{2m}} e^{-\frac{\beta p_y^2}{2m}} e^{-\frac{\beta p_z^2}{2m}} dp_x \, dp_y \, dp_z + \int p_y^2 e^{-\frac{\beta p_x^2}{2m}} e^{-\frac{\beta p_y^2}{2m}} e^{-\frac{\beta p_z^2}{2m}} dp_x \, dp_y \, dp_z + \right.$$

$$\left. \int p_z^2 e^{-\frac{\beta p_x^2}{2m}} e^{-\frac{\beta p_y^2}{2m}} e^{-\frac{\beta p_z^2}{2m}} dp_x \, dp_y \, dp_z \right]$$
$$\ldots(3.27)$$

which allows us to use the standard result

$$\int t^2 e^{-at^2} \, dt = \frac{1}{2} \sqrt{\frac{\pi}{a^3}}$$

to obtain equation (3.27) as

$$E = \frac{VC}{2m} \left[\frac{m}{\beta} \left(\frac{2\pi m}{\beta} \right)^{3/2} + \frac{m}{\beta} \left(\frac{2\pi m}{\beta} \right)^{3/2} + \frac{m}{\beta} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right]$$

or

$$E = \frac{VC}{2m} \frac{3m}{\beta} \left(\frac{2\pi m}{\beta} \right)^{3/2} . \qquad \qquad \ldots(3.28)$$

With the help of equation (3.24), the expression of energy comes out as

$$E = \frac{3N}{2\beta}. \qquad \qquad \ldots(3.29)$$

For an ideal gas we have

$$E = \frac{3}{2} NkT. \qquad \qquad \ldots(3.30)$$

So on comparing equation (3.29) and equation (3.30), we have

$$\beta = \frac{1}{kT}, \qquad \qquad \ldots(3.31)$$

Now, from equation (3.24), we get

$$\frac{1}{C} = \frac{V}{N} (2\pi mkT)^{\frac{3}{2}} \text{or} \, C = \frac{N}{V} \frac{1}{(2\pi mkT)^{\frac{3}{2}}}$$

or

$$e^{-\alpha} = \frac{N}{V} \frac{1}{(2\pi mkT)^{\frac{3}{2}}}. \qquad \qquad \ldots(3.32)$$

Thus, we can obtain the coefficient as

$$\alpha = \log\left[\frac{V}{N} (2\pi mkT)^{3/2}\right]. \qquad \qquad \ldots(3.33)$$

Thus, on substituting the values of constants α and β the distribution law can be written as

$$n(p) = \frac{N}{V} \frac{1}{(2\pi mkT)^{\frac{3}{2}}} e^{-\frac{p^2}{2mkT}} . \qquad \qquad \ldots(3.34)$$

3.4.1 Maxwell distribution law of velocities

At equilibrium, the Maxwell-Boltzmann distribution law is given by equation (3.17). If we consider the position and momentum in the range x to $x + dx$, y to $y + dy$, z to $z + dz, p_x$ to $p_x + dp_x$, p_y to $p_y + dp_y$, p_z to $p_z + dp_z$, respectively. Thus, the number of molecules in this phase space volume element is proportional to the corresponding volume $dx\,dy\,dz\,dv_x dv_y\,dv_z$.

Therefore, the number of molecules n_i of mass m having energy ε_i in this volume element using equation (3.34) is given by

$$n_i\,dx\,dy\,dz\,dp_x dp_y dp_z = \frac{N}{V}\frac{1}{(2\pi mkT)^{\frac{3}{2}}} e^{-\frac{(p_x^2+p_y^2+p_z^2)}{2mkT}}\,dx\,dy\,dz\,dp_x dp_y dp_z \dots (3.35)$$

In terms of position-velocity coordinates in the range x to $x + dx$, y to $y + dy$, z to $z + dz, v_x$ to $v_x + dv_x$, v_y to $v_y + dv_y$, v_z to $v_z + dv_z$, equation (3.35) can be written using $p_i = mv_i$ as

$$n_i\,dx\,dy\,dz\,dv_x dv_y\,dv_z = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)}\,dx\,dy\,dz\,dv_x dv_y\,dv_z. \quad \dots (3.36)$$

If we further integrate this equation with respect to the position coordinates, we will get the number of molecules having velocity coordinates in the range v_x to $v_x + dv_x$, v_y to $v_y + dv_y$, and v_z to $v_z + dv_z$ as

$$n_i\,dv_x dv_y\,dv_z = N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)}\,dv_x dv_y\,dv_z. \quad \dots (3.37)$$

Therefore, we can obtain the number of molecules having velocity components in the range v_x to $v_x + dv_x$ by integrating this equation with respect to v_y and v_z, which becomes

$$n_i(v_x)dv_x = N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv_x^2}{2kT}}\,dv_x \iint e^{-\frac{m(v_y^2+v_z^2)}{2kT}}\,dv_y\,dv_z$$

$$= N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv_x^2}{2kT}}\,dv_x \int e^{-\frac{mv_y^2}{2kT}}\,dv_y \int e^{-\frac{mv_z^2}{2kT}}\,dv_z$$

$$= N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv_x^2}{2kT}}\,dv_x \left(\sqrt{\frac{2kT}{m}}\right)\left(\sqrt{\frac{2kT}{m}}\right)$$

thatcan be simplified as

$$n_i(v_x)dv_x = N\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}}\,dv_x. \quad \dots (3.38)$$

This equation gives a symmetric distribution of the number of molecules having x-component of velocity in the range v_x and $v_x + dv_x$. Therefore, the probability that a molecule will have x-component of velocity in the range v_x and $v_x + dv_x$ can be represented as

$$P(v_x)dv_x = \frac{n_i(v_x)}{N}dv_x = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}}\,dv_x. \quad \dots (3.39)$$

These two equations, i.e.,equations(3.38) and (3.39), representthe Maxwell distribution law of velocities. In a similar way, we can obtain the expressions for the number of molecules

having x and y component of velocity in the range v_x and $v_x + dv_x$, and v_y and $v_y + dv_y$, respectively.

It is clear from equation(3.39) that the function $P(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}}$ is symmetrically distributed about $v_x = 0$, i.e., $P(-v_x) = P(v_x)$. This can be used to calculate the average value of v_x using Maxwellvelocity distribution to be zero. Further, the maximum of the probability distribution function can be calculated using the first derivative with respect to v_x,

i.e., $\frac{\partial P(v_x)}{\partial v_x} = 0$ or $\frac{\partial}{\partial v_x}\left[\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}}\right] = 0$. Thus, the maximum value of $P(v_x)$ is

$$P_{max}(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}. \qquad ...(3.40)$$

It is clear from this equation that $P_{max}(v_x)$ increases as mass$m$ increases while$T$ decreases.

Example 5: Calculate the velocity componentv_x for which the probability falls to $\frac{1}{e}$ times the maximum value.

The probability distribution function is given by

$$P(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}}.$$

The condition $v_x = 0$ gives the value of maximum probability, i.e.,

$$P_{max}(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}.$$

We are given that

$$P(v_x) = \frac{1}{e}P_{max}(v_x) = \frac{1}{e}\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}.$$

Therefore,

$$\frac{1}{e}\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}}$$

or

$$\frac{1}{e} = e^{-\frac{mv_x^2}{2kT}}.$$

Taking $\log_e$ of both the sides of this equation

$$\log_e e = -\frac{mv_x^2}{2kT}.$$

Using the property$\log_e e = 1$, we obtained

$$v_x = \sqrt{\frac{2kT}{m}}.$$

Hence, this is the value of v_x for which the probability falls to $\frac{1}{e}$ times the maximum value.

Self Assessment Question (SAQ) 2: Calculate the value of velocity componentv_x, for which the probability falls to $\frac{1}{10}$ times the maximum value.

3.4.3 Maxwell speed distribution law

Let us obtain the expression of the speed distribution law from the velocity distribution law given by equation (3.37). This equation represents the Maxwell distribution law for the number of molecules with velocity components in the interval v_x to $v_x + dv_x$, v_y to $v_y + dv_y$, and v_z to $v_z + dv_z$. For the expression of speed distribution, we change the velocity components in terms of the speed of a molecule v and changing it over to polar coordinates, i.e.,

$$v^2 = v_x^2 + v_y^2 + v_z^2 \text{ and } dv_x dv_y dv_z = v^2 \sin\theta \, d\theta \, d\varphi \, dv.$$

Using these values in equation(3.37), we get

$$n_i \, d\theta \, d\varphi \, dv = N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} v^2 \sin\theta \, d\theta \, d\varphi \, dv. \qquad \ldots(3.41)$$

This is the equation for the number of molecules with speeds between v and $v+dv$ in a direction lying within the angular ranges θ and $\theta + d\theta$, and φ and $\varphi + d\varphi$. We can obtain the number of molecules with velocity between v and $v+dv$ (say $F(v)dv$) by integrating over the angular part as

$$F(v)dv = N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} v^2 dv \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\varphi \qquad \ldots(3.42)$$

or

$$F(v)dv = 4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} \, dv. \qquad \ldots(3.43)$$

The function $F(v)dv$ is called the *Maxwell speed distribution function*, and $F(v)$ is called the probability distribution function given by

$$F(v) = 4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}. \qquad \ldots(3.44)$$

Both the velocity and speed distributions have been experimentally verified, too.

Most probable speed (v_p): It is the speed at which distribution has maximum value.

The condition for $F(v)$ to be maximum is $\frac{dF(v)}{dv} = 0$ or $\frac{d}{dv}\left[4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}\right] = 0$. This can be simplified to $4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\left(2v_p - \frac{v_p^3 m}{kT}\right) e^{-\frac{mv^2}{2kT}} = 0$, which gives $2v_p - v_p^3 \frac{m}{kT} = 0$ or

$$v_p = \sqrt{\frac{2kT}{m}}. \qquad \ldots(3.45)$$

This is the most probable speed of molecules.

Mean or average speed (v_{avg} or $\bar{v}$): It is the mean of all the speeds at which the molecules of the gas are moving.Thus, the mean speed is calculated

as$v_{avg} = \frac{1}{n}\int_0^\infty vF(v)dv = \frac{1}{n}4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\int_0^\infty v^3 e^{-\frac{mv^2}{2kT}}dv$or

$v_{avg} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\frac{1}{2}\left(\frac{2kT}{m}\right)^2$,which can be simplified as

$v_{avg} = \sqrt{\frac{8kT}{\pi m}}.$ ...(3.46)

Root mean square speed (v_{rms}): It is the average speed squared of the molecules of the gas. It can be defined as$v_{rms}^2 = \overline{v^2} = \frac{1}{n}\int_0^\infty vF(v)dv$,which can be simplified as

$v_{rms}^2 = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\int_0^\infty v^4 e^{\left(-\frac{mv^2}{2kT}\right)}dv$or $v_{rms}^2 = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\frac{3\sqrt{\pi}}{8}\left(\frac{2kT}{m}\right)^{5/2}$.Thus, we can

compute

$v_{rms} = \sqrt{\frac{3kT}{m}}.$ ...(3.47)

It is clear from equations (3.45)-(3.47) that $v_{rms} > v_{avg} > v_p$(see Figure3.1).
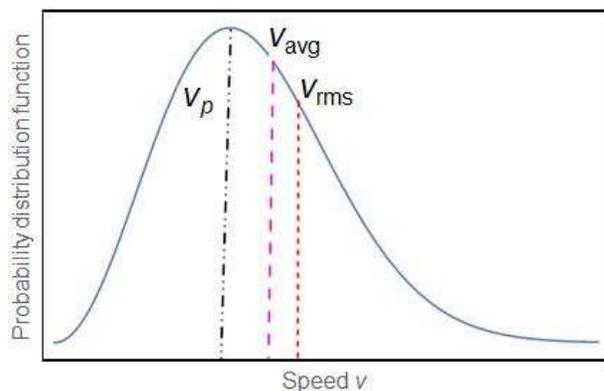
**Figure 3.1:**Speed distribution of gas moleculesdepicting most probable$\left(v_p\right)$, average$\left(v_{avg}\right)$, and root mean square $\left(v_{rms}\right)$speeds.

The variation of the speed distribution with all three types of molecular speeds, i.e., most probable, average, and root mean square speeds,is depicted in Figure3.1. The graph shows how the speeds of molecules are distributed for a gas. The vertical axis of the distribution graph gives the number of molecules per unit speed, and the total area under the entire curve is equal to the total number of the molecules in the given gas. Here, we can also see that the most probable speed is the speed that is most likely to be found for a molecule in a gas.

Example 3.6: Calculate the most probable speed of hydrogen molecule at 27^0C. Use$k = 1.38 \times 10^{-23} JK^{-1}$, mass of hydrogen molecule $= 0.33 \times 10^{-26} kg$.

We have the expression of most probable speed given by equation (3.45).

Using mass of hydrogen molecule $m = 0.33 \times 10^{-26} kg$, $k = 1.38 \times 10^{-23} JK^{-1}$, and temperature $T = 273 + 27 = 300\ K$. From the expression of most probable speed

$$v_p = \sqrt{\frac{2 \times 1.38 \times 10^{-23} \times 300}{0.33 \times 10^{-26}}} = 10^3\sqrt{3.27} = 1.808 km/s.$$

Example 3.7: Calculate the root mean square value of speed of nitrogen molecules (mass of the nitrogen molecule $m = 4.6 \times 10^{-26} kg$) at 27^0C.

With the help of equation (3.47). For given temperature $T = 273 + 27 = 300K$, we can compute

$$v_{rms} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 300}{4.6 \times 10^{-26}}} = 10^3\sqrt{0.270} = 0.5196 km/s.$$

Example 3.8: At what temperature the mean speed of hydrogen molecules will be same as that of oxygen molecules at 35^0C. (Given, the molecular mass of hydrogen molecule is 2 and of oxygen molecule is 32.)

We have the expression of mean speed given by equation (3.46).

For hydrogen molecules, $v_{avg}(H_2) = \sqrt{\frac{8kT_H}{\pi m_H}}$.

While for oxygen molecules, $v_{avg}(O_2) = \sqrt{\frac{8kT_O}{\pi m_O}}$.

Given, $T_O = 273 + 35 = 308K$, $m_H = $ molecular mass $= 2$, $m_O = $ molecular mass $= 32$.

According to the question

$$\sqrt{\frac{8kT_H}{\pi m_H}} = \sqrt{\frac{8kT_O}{\pi m_O}}, \text{ i.e., } \frac{T_H}{2} = \frac{308}{32}, \text{ and thus}$$

$$T_H = 308 \times \frac{2}{32} = 19.25K.$$

Therefore, at $T = 19.25K$ the mean speed of hydrogen molecules will be same as that of oxygen molecules at 35^0C.

Self Assessment Question (SAQ) 3: Calculate the most probable, average, and root mean speed of oxygen molecules at 27^0C. (Given, $k = 1.38 \times 10^{-23} JK^{-1}$, molecular mass of hydrogen molecule is 2 and of oxygen molecule is 32.)

Self Assessment Question (SAQ) 4: Calculate the temperature at which the most probable speed of the molecules of hydrogen gas will be double the most probable speed of oxygen molecules at 300 K. (Given, $k = 1.38 \times 10^{-23} JK^{-1}$, molecular mass of hydrogen molecule $m_H = 2$, and molecular mass of oxygen molecule $m_O = 32$.)

3.5 PRINCIPLE OF EQUIPARTITION OF ENERGY

This principle states that the total kinetic energy of a system in thermal equilibrium at temperature T is equally distributed amongst the various degrees of freedom, and the average kinetic energy associated with each degree of freedom is $\frac{1}{2}kT$, where k is Boltzmann's constant.

With the help of the following discussion, we can understand this principle in more detail. Consider one mole of a monoatomic gas in thermal equilibrium at temperature T and each gas molecule has three degrees of freedom due to its translational motion, i.e.,

$$\frac{1}{2}m\bar{v}^2 - \frac{3}{2}kT, \qquad \qquad ...(3.48)$$

where $\bar{v}^2$ is the mean square velocity of the gas molecules, and m is the mass of the molecule.

If the components of the mean square velocity of the gas molecules along the three axes are $\bar{v_x}^2$, $\bar{v_y}^2$, and $\bar{v_z}^2$, respectively. Then the average energy of a gas molecule will be

$$\frac{1}{2}m\bar{v}^2 = \frac{1}{2}m\bar{v_x}^2 + \frac{1}{2}m\bar{v_y}^2 + \frac{1}{2}m\bar{v_z}^2. \qquad \qquad ...(3.49)$$

From above two equations, i.e., (3.48) and (3.49), we have

$$\frac{1}{2}m\bar{v_x}^2 + \frac{1}{2}m\bar{v_y}^2 + \frac{1}{2}m\bar{v_z}^2 = \frac{3}{2}kT. \qquad \qquad ...(3.50)$$

However, it is clear that the molecular motion is random in nature, and there is no preferred direction of motion. Therefore, the average kinetic energy corresponding to each degree of freedom is same. Thus, we can write

$$\frac{1}{2}m\bar{v_x}^2 = \frac{1}{2}m\bar{v_y}^2 = \frac{1}{2}m\bar{v_z}^2 \qquad \qquad ...(3.51)$$

Hence, from equation(3.50) we can express

$$\frac{1}{2}m\bar{v_x}^2 = \frac{1}{2}m\bar{v_y}^2 = \frac{1}{2}m\bar{v_z}^2 = \frac{1}{2}kT \qquad \qquad ...(3.52)$$

This suggests that the mean kinetic energy per molecule per degree of freedom is $\frac{1}{2}kT$.

Further, if we generalize this discussion for a system of N molecules of monoatomic gas then there are $3N$ number of degrees of freedom, and therefore the total kinetic energy is $3N \times \frac{1}{2}kT$. For example, in case of 10 Helium molecules, there will be 30 degrees of freedom.

Example 3.9: Discuss the principle of equipartition of energy for diatomic gas molecules.
The diatomic gases (like nitrogen, hydrogen, oxygen) have five degrees of freedom (three translational and two rotational). Therefore, the total kinetic energy is $3 \times \frac{1}{2}kT + 2 \times \frac{1}{2}kT - \frac{5}{2}kT$.

Example 3.10: Discuss the principle of equipartition of energy for linear triatomic and non-linear triatomic gas molecules.
The linear triatomic molecule like carbon dioxide has five degrees of freedom (three translational and two rotational). Hence, the total kinetic energy of a linear triatomic molecule is $3 \times \frac{1}{2}kT + 2 \times \frac{1}{2}kT = \frac{5}{2}kT$. However, in case of a non-linear triatomic molecule, like water

molecule, there are six degrees of freedom (three translational and three rotational). Hence, the total kinetic energy of a linear triatomic molecule is $3 \times \frac{1}{2}kT + 3 \times \frac{1}{2}kT = \frac{6}{2}kT = 3kT$.

Example 3.11: The average kinetic energy of a monoatomic gas molecule at a certain temperature is $3.21 \times 10^{-21} J$. Calculate the temperature given that $k = 1.38 \times 10^{-23} JK^{-1}$.

Solution: We know the average kinetic energy of a monoatomic gas is $\frac{3}{2}kT$.

So, $3.21 \times 10^{-21} = \frac{3}{2}kT$,

$$T = \frac{6.42}{4.14} \times 10^{2} K = 155\ K$$

Self Assessment Question (SAQ) 5: What is the total kinetic energy for a hydrogen chloride molecule?

3.6 Classical statistics in brief

We have studied the first three units focused on classical statistical mechanics. Many of the concepts are discussed which are basic building blocks of classical statistical physics. Here, we are in the position of summarizing all these important discussions as follows.

    (i) Any gas under consideration is a collection of a large number of molecules in motion.
    (ii) All the phase cells in a phase space are equal in size.
    (iii) All the accessible microstates corresponding to all possible macrostates are equally probable.
    (iv) The equilibrium state of a gas corresponds to the macrostate of maximum probability.
    (v) The total number of molecules is constant. This is in agreement with the conservation of matter.
    (vi) The total energy of the system is constant. This is in agreement with the conservation of energy.

The conclusion of classical statistics mentioned above will be further helpful in constructing the structure of quantum statistical mechanics and its applications.

3.7 SUMMARY

This unit is solely based on the concept of thermodynamic probability. In this unit, we have learned about the concepts of thermodynamic probability and also calculated it for different cases. Further, with the help of this concept we discussed the distribution of molecules in the classical scenario as Maxwell-Boltzmann distribution law. This law is applicable for only classical particles or molecules. As an application of Maxwell-Boltzmann distribution law, we have obtained the expression for the velocity distribution law. Also, we discussed

Maxwell speed distribution law and defined the various types of speeds namely most probable speed, mean or average speed and root mean square speed. We have further shown that the root mean square speed is maximum and most probable speed is minimum among all three speeds. We also came to know about the principle of equipartition of energy which states that for a system in thermal equilibrium, on the average, an equal amount of energy will be associated with each independent energy state or degree of freedom associated with the system.

As a whole we can say that we are now familiar with all the basics of statistical mechanics after completing this unit including first two units. In the next units, we shall discuss the concepts of ensemble and different types of ensembles in detail.

3.8 GLOSSARY

Thermodynamic probability   *Itis the number of microstates corresponding to a given macrostate.*

Most probable state   *The most probable state is a macrostate with maximum probability.*

Maxwell-Boltzmann   distribution law   *It is a probability distribution in classical statistical mechanics used for discussing the distribution of speed, velocity, and energy of particles at a particular temperature.*

Equipartition principle   *This principle states that energy is shared equally among all the accessible degrees of freedom of a given state.*

Degree of freedom   *It isdefined as the number of independent ways that specify the orientation or dynamics of a system or body, such as translational, rotational and vibrational.*

3.9 REFERENCES

1. Statistical Mechanics, **R. K. Pathria**, Butterworth-Heinemann, Oxford.

2. Statistical Mechanics, **S. Prakash,**KedarNath Ram Nath.

3. Fundamentals of Statistical and Thermal Physics, *F. Reif*, McGraw-Hill.

4. Statistical Mechanics: an Introduction, *D. H. Trevena*, Elsevier.

5. Statistical Physics, *L. D. Landau* and*E. M. Lifshitz*, Elsevier.

3.10 SUGGESTED READINGS

1. Thermodynamics and Statistical Mechanics, *W. Greiner, L. Neise* and *H. Stocker,* Springer Science and Business Media.

2. Statistical and Thermal Physics, *S. Lokanathan* and *R. S. Gambhir*, PHI Learning Private Limited, Delhi.

3. Statistical Mechanics, *K. Huang*, Wiley India.

4. Fundamentals of Statistical Mechanics, *B. B. Laud*, New Age International.

3.11 TERMINAL QUESTIONS

3.11.1Short Answer Type

1. What is thermodynamic probability?
2. What is most probable state?
3. Write down the expression of Maxwell-Boltzmann distribution law.
4. State the principle of equipartition of energy.
5. What is the total kinetic energy for a linear hydrogen cyanide (*HCN*) and non-linear Sulfur dioxide (SO_2)molecules?
6. Write down the expressions for the most probable, average, and root mean square speeds.

3.11.2 Long Answer Type

1. With the help of an example, discuss the difference between probability and thermodynamic probability.

2. Derive the expression of Maxwell-Boltzmann distribution law for the distribution of particles. With the help of distribution law also obtain the Maxwell velocity distribution law?

3. Obtain an expression for speed distribution of particles in classical statistical mechanics. Also deduce the expression for the most probable, average and root mean square speeds.

4. What are the postulates of statistical mechanics?

5. State and prove the principle of equipartition principle.

3.11.3 Numerical Answer Type

1. Calculate the thermodynamic probability of various macrostates corresponding to the distribution of two distinguishable particles into three energy levels 0, E, and 2E.

2. Consider five particles in three compartments and calculate the thermodynamic probability for (i) 4 particles in the first compartment, one in the second, and none in the third compartment, and (ii) All five particles in the first compartment, and none in the second and third compartments.

3. Find out the number of ways of distributing two identical particles in three distinct energy levels according to classical Maxwell-Boltzmann statistics.

4. Find the value of temperature at which the mean speed of hydrogen molecules is double the mean speed of fluorine molecules at *300K*.[Given, $k - 1.38 \times 10^{-23} J K^{-1}$, molecular mass of hydrogen molecule is 2 and of fluorine molecule is 38.]

5.If the most probable speed of nitrogen molecule is *50m/s* at *T K*. Calculate the most probable speed of oxygen molecule at temperature*4T K*. [Given, $k - 1.38 \times 10^{-23} J K^{-1}$, mass of nitrogen molecule $m = 4.6 \times 10^{-26} kg$, mass of oxygen molecule $m = 5.3 \times 10^{-26} kg$]

3.11.4 Objective Answer Type

1. In statistical equilibrium, the thermodynamic probability of a system is

(a) 1   (b) zero

(c)   maximum   (d) minimum but not 1

2. Maxwell-Boltzmann statistics is applicable for

(a) photons   (b) ideal gas

(c) phonons   (d) electrons

3. The value of β in Maxwell-Boltzmann distribution law is

(a) 1

(b) zero

(c) kT

(d) $\frac{1}{kT}$

4. The most probable speed of a gas molecules of mass m at a given temperature T K is proportional to

(a) m

(b) $m^{-\frac{1}{2}}$

(c) $m^{\frac{1}{2}}$

(d) m^0

5. The speed of four particles are 2, 2, 3, and 3, respectively. Their root mean square speed is

(a) $\frac{\sqrt{26}}{2}$

(b) $\frac{\sqrt{26}}{4}$

(c) $\sqrt{26}$ (d) $\frac{1}{\sqrt{26}}$

6. The ratio between the root-mean-square speed, average speed and most probable speed will be

(a) 1.596: 1.732: 1.414

(b) 1: 1.596: 1.414

(c) 1.732 : 1.596: 1.414

(d) 1.596: 1.732: 2.125

3.12 ANSWERS

3.12.1 Self-Assessment questions

1. The two macrostates for the distribution of four distinguishable particles a, b, c, and d in two compartmentsmay be chosen as
Macrostate (0, 4) – One possible microstate (0, a b c d).
Macrostate (1, 3) – Four possible microstates {(a, b c d); (b, c d a); (c, d a b); (d, a b c)}.
Probability of microstate (0, a b c d) corresponding to macrostate (0, 4) = $\left(\frac{1}{2^4}\right) = \frac{1}{16}$.
Probability of microstate (a, b c d) corresponding to macrostate (1, 3) = $\left(\frac{1}{2^1}\right)\left(\frac{1}{2^3}\right) = \frac{1}{16}$.
Probability of microstate (b, c d a) corresponding to macrostate (1, 3) = $\left(\frac{1}{2^1}\right)\left(\frac{1}{2^3}\right) = \frac{1}{16}$.
Probability of microstate (c, d a b) corresponding to macrostate (1, 3) = $\left(\frac{1}{2^1}\right)\left(\frac{1}{2^3}\right) = \frac{1}{16}$.
Probability of microstate (d, a b c) corresponding to macrostate (1, 3) = $\left(\frac{1}{2^1}\right)\left(\frac{1}{2^3}\right) = \frac{1}{16}$.

2. The probability distribution function is given by

$$P(v_x) = \left(\frac{m}{2\pi k T}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}},$$

According to question

$$P(v_x) = \frac{1}{10} P_{max}(v_x) = \frac{1}{10}\left(\frac{m}{2\pi\,kT}\right)^{\frac{1}{2}},$$

$$\frac{1}{10}\left(\frac{m}{2\pi\,k\,T}\right)^{\frac{1}{2}} = \left(\frac{m}{2\pi\,k\,T}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}}$$

or

$$\frac{1}{10} = e^{-\frac{mv_x^2}{2kT}}.$$

Taking $\log_e$ of both the sides of this equation

$$\log_e 10 = -\frac{mv_x^2}{2\,kT}.$$

We obtained

$$v_x = \sqrt{\frac{2\,k\,T}{m}} \times 2.303.$$

3. Use equations (3.45), (3.46) and (3.47).Here temperature is *T= 27+273=300K.*

$$v_p = \sqrt{\frac{2 \times 1.38 \times 10^{-23} \times 300}{5.3 \times 10^{-26}}} = 10^3 \times 0.3952 = 0.3952\ km/s.$$

$$v_{avg} = \sqrt{\frac{8 \times 1.38 \times 10^{-23} \times 300}{3.14 \times 5.3 \times 10^{-26}}} = 10^3 \times 0.446 = 0.446\ km/s.$$

$$v_{rms} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 300}{5.3 \times 10^{-26}}} = 10^3 \times 0.484 = 0.484\ km/s.$$

4. We have the expression of most probable speed given by equation (3.45).

For hydrogen molecules, $v_p(H_2) = \sqrt{\frac{2kT_H}{m_H}}$.

While for oxygen molecules, $v_p(O_2) = \sqrt{\frac{2kT_O}{m_O}}$.

Given, $T_O = 300K$, $m_H = $ molecular mass $= 2$, $m_O = $ molecular mass $= 32$.

According to the question

$$\sqrt{\frac{2kT_H}{m_H}} = 2\sqrt{\frac{2kT_O}{m_O}}, \text{ i.e., } \frac{T_H}{2} = 4 \times \frac{300}{32},$$

and thus

$$T_H = 300 \times \frac{8}{32} = 75K.$$

Therefore, at $T = 75K$ the mean speed of hydrogen molecules will be double as that of oxygen molecules at *300K.*

5. *HCl* is a diatomic molecule having three translational and two rotational degrees of freedom. So, the total kinetic energy of this molecule is

$$3 \times \frac{1}{2}kT + 2 \times \frac{1}{2}kT = \frac{5}{2}kT.$$

3.12.2 Numerical answer type question:

1. Let the two particles are A and B

Macrostates	Microstates			
	0E	E	2E	Number of states
Total energy 0	AB	-	-	1
Total energy E	A	B	-	2
	B	A	-	
Total energy 2E	-	AB	-	3
	A	-	B	
	B	-	A	
Total energy 3E	-	A	B	2
		B	A	
Total energy 4E	-	-	AB	1

As we know that thermodynamic probability is the number of microstates corresponding to a given macrostate. Therefore,

Thermodynamic probability of macrostate "Total energy 0" = 1.
Thermodynamic probability of macrostate "Total energy E" = 2.
Thermodynamic probability of macrostate "Total energy 2E" = 3.
Thermodynamic probability of macrostate "Total energy 3E" = 2.
Thermodynamic probability of macrostate "Total energy 4E" = 1.

2. Let the five particles are a, b, c, d, and e. We can write all the microstates corresponding to the desired macrostates.

Macrostates	Microstates			
	0E	E	2E	Number of states
(4,1,0)	abcd	e	-	5
	abce	d	-	
	abdc	c	-	

	adce	b	-	
	bcde	a	-	
(5,0,0)	abcde	-	-	1

(i) Thermodynamic probability of macrostate (4,1,0) = 5.

(ii) Thermodynamic probability of macrostate (5,0,0) = 1.

3. Let the two particles are P_1 and P_2. According to Maxwell-Boltzmann distribution law a single state can be occupied by an arbitrary number of particles. So, the distribution is given as

Macrostates	Microstates		
	Energy level 1	Energy level 2	Energy level 3
Both in same state	$P_1 P_2$	-	-
	-	$P_1 P_2$	-
	-	-	$P_1 P_2$
Both in different states	P_1	P_2	-
	P_2	P_1	-
	P_1	-	P_2
	P_2	-	P_1
	-	P_1	P_2
		P_2	P_1

4. Use equation (3.46) for calculating T_H. Here, temperature $T_F = 300K$, so

$$\sqrt{\frac{8kT_H}{\pi m_H}} = 2\sqrt{\frac{8kT_F}{\pi m_F}},$$

and thus

$$T_H = \frac{4 \times 2 \times 300}{38} = 63.15K.$$

5. From equation (3.45), for nitrogen molecules we can write

$$(50)^2 = \frac{2kT}{m_N},$$

or

$$T = 2500 \times \frac{m_N}{2k}.$$

Now again with the help of equation (3.45), for oxygen molecule,

$$v_p(\text{oxygen}) = \sqrt{\frac{2k(4T)}{m_O}},$$

Substitute the value of T from the expression of nitrogen in the expression of $v_p(\text{oxygen})$, we get

$$v_p(\text{oxygen}) = \sqrt{\frac{8k}{m_O} \times \frac{2500 \times m_N}{2k}} = \sqrt{8 \times 2500 \times \frac{4.6 \times 10^{-26}}{5.3 \times 10^{-26}}} = 37.26 \ m/s.$$

3.12.3 Objective answer type questions:

1. Correct option is (c), maximum.
2. Correct option is (b), ideal gas.
3. Correct option is (d), $\frac{1}{kT}$.
4. Correct option is (b), $m^{-1/2}$.
5. Correct option is (a), $\frac{\sqrt{26}}{2}$.
6. Correct option is (c), 1.732 : 1.596: 1.414.

UNIT 4   Microcanonical Ensemble

Structure

4.1 INTRODUCTION

We already understand the significance of statistical mechanics in the modern physics. Specifically, its applicability in studying the systems with a large number of constituent particles,where it provides us tool to study the macroscopic properties of the system in terms of the microscopic properties of its particles. We have already learned the basic tools of statistical physics and classical statistics in Block 1.

The statistical analysis of the systemis useful if we consider a probability distribution describing the state of the systemcalled ensemble, which allows us to calculate the average values of the macroscopic properties as a weighed function with the help of probability distribution.Physically, we can consider an ensemble as multiple copies of independent systems with same macroscopic properties but different microscopic states. There are different types of ensembles depending uponthe macroscopic constraints. One of the most significant ensembles describes isolated system, i.e., when the individual assemblies are separated by a rigid, impermeable, and well insulated walls and thus the individual systems cannot exchange energy and particles with each other. The present unit will be focused entirely on this particular type of ensemble, i.e., microcanonical ensemble.

Ourunderstanding of the thermodynamics tells us that entropy or randomness is an extensive property.Therefore, entropy of the systemobtained by mixing two distinct ideal gases increases, whereas if both ideal gases are sameit is a reversible process and entropy should not increase. Mathematically, a contradiction occurs in the latter case as it gives non-zero change in entropy, which is termed asGibbs paradox. This is resolved by dividing the number of microstates, used in obtaining the formula for entropy, by a factor called Gibbs factor. Quantum mechanics providesus an explanation for this factor as the constituent particles or gas molecules are identical.

We will further discuss partition function, which quantifies the number of microstates accessible to the system in a given ensemble.While calculating this function, it becomes important that whether there exist more than one state with the same energy, if so it is referred to asdegeneracy.The partition function providesus a mathematical tool to obtain thermodynamic quantities.Therefore, we will be obtaining partition function and its relation to thermodynamic quantities for microcanonical ensemble. Some of the topics discussed in this unit will be further useful in the next units and understanding the rest of the ensembles, i.e., canonical and grand canonical ensembles. Specifically, we will obtain partition function for canonical and grand canonical ensembles in the next two units and obtain corresponding thermodynamic quantities. Here, we begin with a general discussion of ensemble theory.

4.2 OBJECTIVES

After studying this unit, you should be able to understand-

- Concepts of ensemble
- Microcanonical ensemble

- Entropy of an ideal gas in microcanonical ensemble
- Gibbs paradox and Gibbs factor
- Partition function
- Relation between partition function and various thermodynamic quantities

4.3 ENSEMBLE THEORY

In statistical mechanics, we always deal with a large number of particles. For this kind of a system, it is very difficult to study the precise microscopic details of the system. Therefore, we need to construct the concept of ensembles in which a large number of systems with the same macroscopic properties but different microscopic properties are considered, and the individual system is assumed to evolve from different initial conditions. Therefore, the time evolution of individual system will be different from the other systems. Hence,the ensemble is a collection of copies of identical systems with the same macroscopic but different microscopic properties, and the macroscopic variables are obtained as averages over the system of ensemble.

In statistical mechanics, there are three types of ensembles, namely microcanonical, canonical, and grand canonical, specified on the basis of macroscopic constraints.

4.3.1 Microcanonical ensemble

A collection of essentially independent assemblies with same energy E, volume V, and number of the particles N is known as microcanonical ensemble. The individual assemblies are separated by a rigid, impermeable, and well insulated walls. The macroscopic properties, such as E, V, and N, are not affected by the presence of other systems. In this case, the individual systems cannot exchange energy and particles with each other(see Figure4.1). Here, it should be clear that independent systems essentially satisfy same macroscopic conditions, while the individual system in the ensemble differ in microscopic conditions.
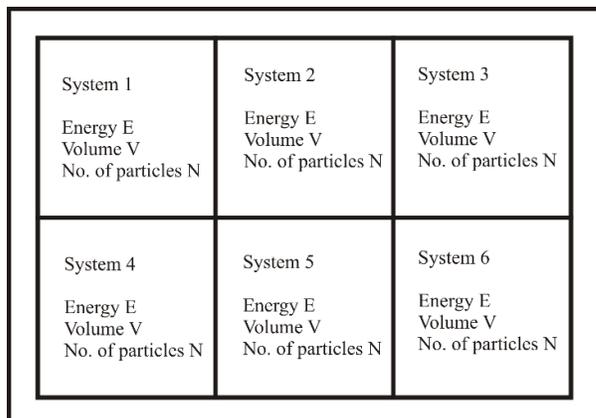

Figure4.1: Pictorial representation of microcanonical ensemble.

4.3.2 Canonical ensemble

A collection of essentially independent assemblies with same temperature T, volume V, and number of the particles N is known as canonical ensemble. The individual assemblies are separated by a rigid, impermeable, and diathermic wall. The macroscopic properties, such as E, V, and N, are not affected by the presence of other systems. Here, the individual systems can exchange energy, but not particles with each other. Since energy can be exchanged between assemblies, one could bring all of the assemblies in thermal contact with each other (see Figure4.2).
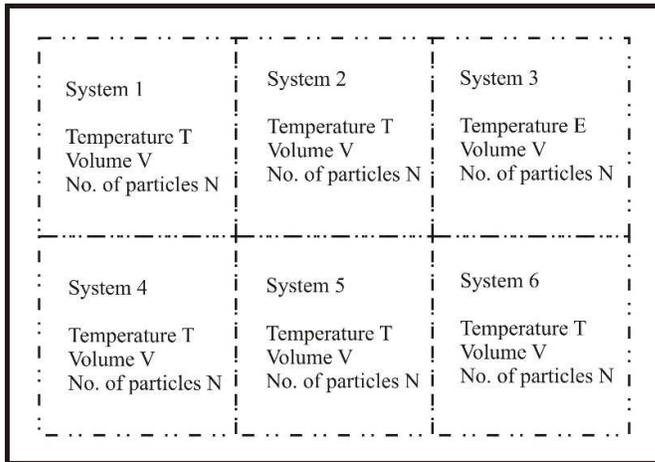
Figure4.2: Pictorial representation of canonical ensemble.

4.3.3 Grand canonical ensemble

The grand canonical ensemble is a collection of essentially independent assemblies having same temperature T, volume V, and chemical potential μ. The individual assemblies are separated by a rigid, permeable, and diathermic wall. In grand canonical ensemble, the assemblies can exchange energy as well as particles with each other (see Figure4.3).
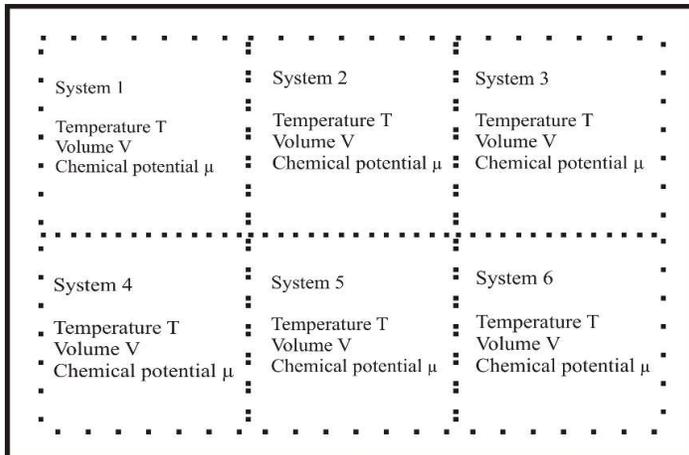
Figure4.3: Pictorial representation of grand canonical ensemble.

We will discuss the microcanonical ensemble in the forthcoming sections of this unit. Whereas, the canonical and grand canonical ensembles shall be discussed in the Units 5 and 6, respectively, in more detail.

It is worth emphasizing here that the three kinds of ensembles mentioned in the previous section are used to obtain different thermodynamics quantities.

Self Assessment Question (SAQ) 1: Discuss how microcanonical, canonical, and grand canonical ensembles are different from each other.

4.4 MICROCANONICAL ENSEMBLE

In the previous section, we have introduced the microcanonical ensemble in brief. The microcanonical ensemble is a system which is totally isolated from its surrounding. Therefore, it describes an isolated system, i.e., a microcanonical ensemble is a collection of multiple copies of the isolated system (seeFigure4.1). In microcanonical ensemble, the Boltzmann entropy relation $S = k \log \Omega$is significant to discuss the thermodynamics of a system.Here, S is a thermodynamic quantity entropy and $\Omega$is a statistical quantity gives the total number of microstates. This serves as a bridge between statistical mechanics and thermodynamics, which shows that entropy is an appropriate thermodynamic function for understanding isolated system of microcanonical ensemble.

4.4.1 Entropy of ideal gas in microcanonical ensemble

We all are familiar with ideal gases since our graduation classes. Here, we briefly discuss what an ideal gas is. It is a gas in which the molecules interact only by elastic collisions and there are no intermolecular attractive forces between the molecules. Ideal gas obeys general gas equation and other gas laws. Further, the internal energy of an ideal gas is solely temperature dependent and is independent of its volume. Therefore, the internal energy is the only average kinetic energy of the molecules of an ideal gas.

Let us calculate the expression for the entropy of an ideal gas in microcanonical ensemble. Suppose there are N particles or molecules of mass m each enclosed in a container of volume V with energy ΔE. The total energy of the system is E. Therefore, the total number of microstates is given by

$$\Omega = \frac{\int \prod_i dx_i dy_i dz_i \int \prod_i dp_{x_i} dp_{y_i} dp_{z_i}}{h^{3N}}.$$

…(4.1)

Here, the integral over the phase space gives the total volume, andthus

$$\Omega = \frac{V^N}{h^{3N}} \int \prod_i dp_{x_i} dp_{y_i} dp_{z_i}.$$

…(4.2)

The integration is left in momentum spaceonly, and the momenta are constrained by relation

$$\Sigma_i \left(\frac{p_{x_i}^2}{2m} + \frac{p_{y_i}^2}{2m} + \frac{p_{z_i}^2}{2m} \right) = E.$$

...(4.3)

Thisrepresents the equation of a *3N*-dimensional hypersphere of radius $\sqrt{2\,m\,E}$.

We assume that the energy is not exactly constant but vary by an amount ΔE, which satisfy$\frac{E}{N} < \Delta E \ll E$. Thus, the momentum space available or accessible for the gas is a thin shell of a *3N*-dimensional hypersphere of radius $\sqrt{2\,m\,E}$ and thickness $\sqrt{\frac{m}{2E}}\Delta E$. Therefore, the surface area of this hypersphere is $\frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!}(2\,m\,E)^{\frac{3N-1}{2}}$. (Here, we use the standard result, the surface area of an*N*-dimensional hypersphere of radius *R*is $\frac{2\pi^{N/2}}{\left(\frac{N}{2}-1\right)}(R)^{\frac{N-1}{2}}$).

Hence, the total number of microstates can becalculated as

$$\Omega = \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!}(2\,m\,E)^{\frac{3N-1}{2}}\sqrt{\frac{m}{2E}}\Delta E$$

or

$$\Omega - \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{\left(\frac{3N}{2}-1\right)!}\frac{\Delta E}{E}.$$

...(4.4)

Further, using the relation$S - k\log\Omega$, the entropy of the gas can now be written as

$$S = k\log\left(\frac{V^N}{h^{3N}} \frac{(2\pi m E)^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!}\frac{\Delta E}{E} \right),$$ ...(4.5)

which can be simplified as

$$S = Nk\log\left(\frac{V}{h^3}(2\pi m E)^{3/2} \right) - k\,\log\left\{ \left(\frac{3N}{2}-1\right)! \right\} + k\,\log\left(\frac{\Delta E}{E}\right).$$

With the help of Stirling formula we can write

$$\log\left\{ \left(\frac{3N}{2}-1\right)! \right\} = \left(\frac{3N}{2}-1\right)\log\left(\frac{3N}{2}-1\right) - \frac{3N}{2}+1 \approx \left(\frac{3N}{2}-1\right)\log\left(\frac{3N}{2}\right) - \frac{3N}{2}+1.$$

Thus, the expression of entropy given by equation (4.5) now reduces as

$$S = Nk\log\left(\frac{V}{h^3}(2\pi m E)^{3/2} \right) + \frac{3Nk}{2} + \left\{ k\log\left(\frac{3N}{2}\right) - k + k\log\left(\frac{\Delta E}{E}\right) \right\}.$$

...(4.6)

In this equation, the terms in the curly bracket are much smaller than the other terms, hence we can neglect them, which results in

$$S = Nk\log\left(V\left(\frac{4\pi m E}{3N h^2}\right)^{\frac{3}{2}} \right) + \frac{3Nk}{2}.$$ ...(4.7)

This is the expression of entropy (thermodynamic) for an ideal gas in the microcanonical ensemble.

We have a relation between thermodynamic entropy and statistical entropy as $S = k\sigma$, where k is Boltzmann's constant, and σ is the statistical entropy. Therefore, the expression of statistical entropy looks like

$$\sigma = N\log\left(V\left(\frac{4\pi m E}{3N h^2}\right)^{\frac{3}{2}}\right) + \frac{3N}{2}. \qquad \qquad \text{...(4.8)}$$

We now establish relation with other thermodynamic quantities.

1.   Internal energy:

From Unit 2, we are familiar with the statistical temperature as

$$\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial E}\right)_{V,N}$$

$$= \frac{\partial}{\partial E}\left[N\log\left(V\left(\frac{4\pi m E}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{3N}{2}\right]$$

$$= \frac{\partial}{\partial E}\left(\frac{3N}{2}\log E\right).$$

We have used the fact that V and N are constant, so the remaining terms vanish.Thus, we get

$$\frac{1}{\tau} = \frac{3N}{2E}$$

or the internal energy as

$$E = \frac{3N}{2}\tau = \frac{3N}{2}kT.$$
$$\text{...(4.9)}$$

2.   Relation between statistical temperature and thermodynamic pressure:

Using the relation introduced in Unit 2, we have

$$\frac{P}{\tau} = \left(\frac{\partial\sigma}{\partial V}\right)_{N,E}$$

$$= \frac{\partial}{\partial V}(N\log V).$$

We have used the fact that E and N are constant here so the remaining terms vanish. Thus, we get the desired relation as

$$\frac{P}{\tau} = \frac{N}{V}$$

or

$$PV = N\tau = NkT. \qquad \qquad \text{...(4.10)}$$

3.   Chemical potential:

We have already discussed in Unit 2 that

$$-\frac{\mu}{\tau} = \left(\frac{\partial\sigma}{\partial N}\right)_{E,V}$$

$$= \frac{\partial}{\partial N}\left[N\log\left(V\left(\frac{4\pi m E}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{3N}{2}\right]$$

$$= \frac{\partial}{\partial N}\left[N\log V + N\log\left(\frac{4\pi mE}{3\,k^2}\right)^{3/2} - N\log N^{3/2} + \frac{3N}{2}\right]$$

$$= \log\left[V\left(\frac{4\pi mE}{3\,h^2}\right)^{3/2}\right].$$

Therefore, the chemical potential can be defined as

$$\frac{\mu}{\tau} = \log\left[\frac{1}{V}\left(\frac{3\,h^2}{4\pi mE}\right)^{3/2}\right]. \qquad \dots(4.11)$$

Example 4.1: If the available volume V of the container of an ideal gas is doubled with no change in the number of molecules N, their mass m, and total energy E, how will the statistical entropy will change?

The new volume is now $2V$ and the total number of molecules are constant. Therefore, the expression of statistical entropy given by equation (4.8) becomes

$$\sigma = N\log\left(2V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{3N}{2}.$$

This means that on increasing the volume by keeping the number of molecules constant the statistical entropy increases.

Self Assessment Question (SAQ) 2: How will the pressure change in Example 4.1 discussed above?

4.5 GIBBS PARADOX

We all are familiar that the mixing of two different gases is an irreversible process which leads to an increase in entropy. The Gibbs paradox involves the contrast between the quantities for mixing two distinct ideal gases and that for mixing of the same ideal gas. Let us consider two different but similar ideal gases in a box of volume V with partition as shown in Figure4.4, at the same temperature and pressure. The ideal gas in Partition 1 (Partition 2) of volume $V_1(V_2)$ contains $N_1(N_2)$ number of gas molecules of mass $m_1(m_2)$ and total energy $E_1(E_2)$. We subsequently remove the partition and allow the gases to mix with each other.

Before mixing, the initial entropy (S_I) of the combined system, using equation (4.7), is the sum of the entropies of the two gases, i.e.,

$$S_I = N_1 k\log\left(V_1\left(\frac{4\pi m_1 E_1}{3N_1 h^2}\right)^{\frac{3}{2}}\right) + \frac{3N_1 k}{2} + N_2 k\log\left(V_2\left(\frac{4\pi m_2 E_2}{3N_2 h^2}\right)^{\frac{3}{2}}\right) + \frac{3N_2 k}{2} \dots(4.12)$$

After mixing, i.e., on the removal of partition, the energy, temperature, and pressure will not change as they are at the same temperature and pressure. Thus, the volume available to both the gases is V. Therefore, the final entropy (S_F) after mixing of gases comes out as

$$S_F = N_1 k\log\left(V\left(\frac{4\pi m_1 E_1}{3N_1 h^2}\right)^{\frac{3}{2}}\right) + \frac{3N_1 k}{2} + N_2 k\log\left(V\left(\frac{4\pi m_2 E_2}{3N_2 h^2}\right)^{\frac{3}{2}}\right) + \frac{3N_2 k}{2}. \qquad \dots(4.13)$$

So the change in entropy is

$$\Delta S = S_F - S_I,$$

i.e.,

$$\Delta S = N_1 k \log\left(\frac{V}{V_1}\right) + N_2 k \log\left(\frac{V}{V_2}\right). \qquad \qquad \ldots(4.14)$$

This shows that there is a change (an increase) in entropy after mixing of the same kind of different gases, which is what we are expecting. This change, i.e., ΔS is called the entropy of mixing.
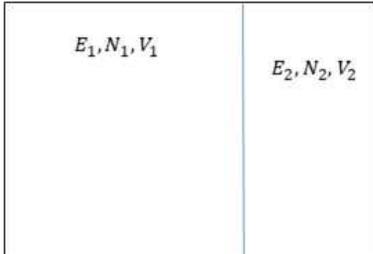

Figure 4.4: Pictorial representation of mixing of two ideal gases.

If we further consider that there is same ideal gas on both sides before removing the partition, then a problem arises. On removing the partition there should be no effect on entropy as the system remains unchanged. However, the expression of change in entropy represented by equation (4.14) yieldsa change in entropy. Let us check this fact in detail. In the case of two identical ideal gases, $\frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{E}{N}$. Therefore, the final entropy is

$$S_F = N_1 k \log\left(V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{3N_1 k}{2} + N_2 k \log\left(V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{3N_2 k}{2}$$

or

$$S_F = (N_1 + N_2) k \log\left(V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{3(N_1 + N_2)k}{2} \quad \ldots(4.15)$$

Here, $N = N_1 + N_2$ is the total number of particles. Thus, equation (4.15) can be simplified as

$$S_F = Nk \log\left(V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}}\right) + \frac{3Nk}{2}. \qquad \qquad \ldots(4.16)$$

We can calculate ΔS, which gives us anon-zero value, i.e., there is a change in the entropy.However, there should be no change in entropy because this is a reversible process, i.e.,after reinserting the partition we are not able to make out if the partition was removed before. This contradiction of mixing of identical gases is known as *Gibbs paradox*.

This paradox can be resolved. Gibbs suggested that while counting the number of microstates for *N* molecules of anideal gas if we multiply the number of microstates by a factor known as *Gibbs factor*, i.e., by $\frac{1}{N!}$, the contradiction disappears.

In this way equation (4.4) in Subsection 4.4.1, takes the following form

$$\Omega = \frac{1}{N! h^{3N}} \frac{V^N (2\pi mE)^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} \frac{\Delta E}{E}. \qquad \qquad \ldots(4.17)$$

Hence, the expression of entropy (see equation (4.5)) takes the form,

$$S = k \log \left(\frac{1}{N!} \frac{V^N}{h^{3N}} \frac{(2\pi mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!} \frac{\Delta E}{E} \right)$$

...(4.18)

Further, on applying the Stirling's approximation in this equation, we get an extra term $-k(N \log N - N)$ in comparison with equation (4.7). Thus, on simplification we obtain the correct form of entropy as

$$S = Nk \log \left(\frac{V}{N} \left(\frac{4\pi mE}{3Nh^2} \right)^{\frac{3}{2}} \right) + \frac{5Nk}{2}.$$

...(4.17)

This equation describes the entropy of a classical ideal gas known as the *Sackur-Tetrode equation*.

Hence, the entropy of two gases before mixing can be described by

$$S_I = N_1 k \log \left(\frac{V_1}{N_1} \left(\frac{4\pi m_1 E_1}{3N_1 h^2} \right)^{\frac{3}{2}} \right) + \frac{5N_1 k}{2} + N_2 k \log \left(\frac{V_2}{N_2} \left(\frac{4\pi m_2 E_2}{3N_2 h^2} \right)^{\frac{3}{2}} \right) + \frac{5N_2 k}{2}.$$

...(4.18)

For two identical ideal gases, $\frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{E}{N}$ and $\frac{V_1}{N_1} = \frac{V_2}{N_2} = \frac{V}{N}$. So equation (4.18) reduces in the following form

$$S_I = N_1 k \log \left(\frac{V}{N} \left(\frac{4\pi mE}{3Nh^2} \right)^{\frac{3}{2}} \right) + \frac{5N_1 k}{2} + N_2 k \log \left(\frac{V}{N} \left(\frac{4\pi mE}{3Nh^2} \right)^{\frac{3}{2}} \right) + \frac{5N_2 k}{2}$$

$$= (N_1 + N_2) k \log \left(\frac{V}{N} \left(\frac{4\pi mE}{3Nh^2} \right)^{\frac{3}{2}} \right) + \frac{5(N_1 + N_2)k}{2}.$$

Thus, the initial entropy of the combined system is

$$S_I = Nk \log \left(\frac{V}{N} \left(\frac{4\pi mE}{3Nh^2} \right)^{\frac{3}{2}} \right) + \frac{5Nk}{2}.$$

...(4.19)

This equation is similar to the equation for the entropy after mixing. So in the case of mixing of identical gases, there is no change in entropy after removing the partition. In a similar way, we can also verify Sakur-Tetrode equation for the case of different types of ideal gases, which gives the same result for the entropy of mixing.

The justification for the Gibbs factor can be provided from the quantum mechanical point of view. Specifically, we know that the particles or atoms or molecules are considered as identical in quantum statistics (discussed in detail in Section 1.3.4). Consider Example 1.9 of Unit 1 and calculate the number of words that can be obtained by rearrangement of a five letter word. It would be $n = 5!$, but what if all the five letters are same (say "aaaaa") then we divide the total number n by 5! to obtain only 1 word after rearrangement, i.e., "aaaaa".

Similarly, we should count the microstates in this case by assuming the particles (gas molecules) are indistinguishable. Therefore, we must divide the number of microstates by $N!$, where N is the number of gas molecules. Thus, Gibbs paradox is resolved by taking into consideration that gas molecules are identical.

Example 4.2: Out of the two cases given below in which case we will encounter Gibbs paradox for mixing of gases?

Case (a): There is an ideal gashelium (oxygen) in Partition 1 (Partition 2) of volume V_1 (V_2) containing N_1 (N_2) number of gas molecules of mass m_1 (m_2) and total energy E_1 (E_2) before mixing.

Case (b): There is an ideal gas helium (helium) in Partition 1 (Partition 2) of volume V_1 (V_2) contains N_1 (N_2) number of gas molecules of mass m_1 (m_1) and total energy E_1 (E_2) before mixing.

In case (b), we have identical gas molecules so due to the indistinguishability of gas molecules we will encounter Gibbs paradox.

4.6 PARTITION FUNCTION AND ITS RELATION WITH THERMODYNAMIC QUANTITIES

First of all, we define partition function, which tells us how many microstates are accessible to the system in a given ensemble. In other words, it is a measure of volume occupied by the system in phase space. Partition function plays a central role in statistical mechanics and is useful in calculating various thermodynamic functions.

Consider an assembly or collection of n_t molecules of an ideal gas in microcanonical ensemble. The Maxwell Boltzmann distribution law can be written as,

$$n_i = e^{-(\alpha+\beta\varepsilon_i)} = C\ e^{-\beta\varepsilon_i},\qquad\qquad\qquad …(4.20)$$

where ε_i is the energy of the ith particles, $C = e^{-\alpha}$ and $\beta = \frac{1}{kT}$. Therefore, the total number of molecules in the given system is

$$N = \sum_i n_i = C \sum_i e^{-\beta\varepsilon_i}$$

or

$$\frac{N}{C} = \sum_i e^{-\beta\varepsilon_i}.\qquad\qquad\qquad …(4.21)$$

Thus, we introduce Z, called as partition function, as

$$Z = \sum_i e^{-\beta\varepsilon_i}.\qquad\qquad\qquad …(4.22)$$

This partition function represented by equation (4.22) tells us how the gas molecules are distributed among various energy states or the particles are partitioned among various energy levels. In a similar way, we will obtain the two different expressions of partition function for the other two types of ensembles, i.e., canonical ensemble in Unit 5 and grand canonical ensemble in Unit 6.

Here, we introduce the term degeneracy, which corresponds to the situation if there are more than one stateor level with the same energy. Taking into consideration the degeneracy of states, the expression of partition function given by equation (4.22) modifies to

$$Z = \sum_i g_i\ e^{-\beta\varepsilon_i},\qquad\qquad\qquad …(4.23)$$

where g_i is the degeneracy factor.

In thermodynamic equilibrium, partition function which is a function of thermodynamic state variables, like volume and temperature, describes the statistical properties of a system.

We will further discuss that various thermodynamic variables can be expressed in terms of the partition function or its derivatives.

    1.   Relation with entropy (S):

For a classical system or classical statistical mechanics the distribution of molecules can be defined by

$$\Omega = \frac{N!}{\prod_i n_i!}. \qquad \qquad \qquad \dots(4.24)$$

Taking the logarithm of both sides of the equation

$$\log \Omega = \log N! - \sum_i \log n_i! \qquad \qquad \dots(4.25)$$

and using Striling's approximation, we can write

$$\log \Omega = N \log N - N - \sum_i [n_i \log n_i - n_i]. \qquad \dots(4.26)$$

Further, we know that the Maxwell Boltzmann distribution law is

$$n_i = e^{-(\alpha + \beta \varepsilon_i)} = e^{-\alpha} e^{-\beta \varepsilon_i} = C e^{-\beta \varepsilon_i}. \qquad \dots(4.27)$$

With the help of equations (4.25) and (4.26), we get

$$\log \Omega = N \log N \quad N \quad \sum_i [n_i \log(C\ e^{-\beta \varepsilon_i}) \quad n_i]$$

$$\dots(4.28)$$

or

$$\log \Omega = N \log N - N - \sum_i n_i \log C + \sum_i n_i \beta \varepsilon_i + \sum_i n_i. \qquad \dots(4.29)$$

In equation (4.28), the last two terms represent the total energy of the molecules and the total number of molecules, respectively, i.e., $\sum_i n_i \beta \varepsilon_i = E$ and $\sum_i n_i = N$.

Therefore, equation (4.28) can be simplified as

$$\log \Omega = N \log N - N - \sum_i n_i \log C + \beta E + N$$

$$= N \log N - N \log C + \beta E$$

$$= N \log \frac{N}{C} + \beta E.$$

Further, using $\frac{N}{C} - Z$, the partition function, we get

$$\log \Omega = N \log Z + \beta E. \qquad \qquad \dots(4.30)$$

Now we know that, the Boltzmann's entropy relation is

$$S = k \log \Omega. \qquad \qquad \qquad \dots(4.31)$$

With the help of equation (4.30), we get

$$S = Nk \log Z + \beta k E$$

or

$$S = Nk \log Z + \frac{E}{T}. \qquad \qquad \dots(4.32)$$

This is the relation between partition function and entropy.

For an ideal gas, $E = \frac{3}{2} NkT$, so

$$S = Nk \log Z + \frac{3}{2} Nk. \qquad \qquad \dots(4.33)$$

This equation gives the entropy of an ideal gas in microcanonical ensemble. As in mechanics, the potential energy of a system tells us about its stability, in a similar way,

entropy gives information about the most stable equilibrium state of the system. Also the entropy difference determines the direction of a change in an isolated system.

2. Relation with Helmholtz free energy (F):

The Helmholtz free energy is defined as

$$F = E - TS, \qquad \qquad \ldots(4.34)$$

which can be obtained using equation (4.31) as

$$F = E - T\left(Nk \, \log Z + \frac{E}{T}\right)$$

or

$$F = -NkT \log Z. \qquad \qquad \ldots(4.35)$$

3. Relation with pressure (P):

Pressure of a gas given by

$$P = \left(\frac{\partial F}{\partial V}\right)_V,$$

and can be obtained in terms of the partition function

$$P = NkT \left[\frac{\partial}{\partial V}(\log Z)\right]_V. \qquad \qquad \ldots(4.36)$$

4. Relation with total energy (E):

The total energy of a system of N particle is given by

$$E = N\bar{E}. \qquad \qquad \ldots(4.37)$$

Here, $\bar{E}$ the average energy per particle is obtained as

$$\bar{E} = \frac{E}{N} = \frac{\sum_i n_i \varepsilon_i}{\sum_i n_i}$$

$$= \frac{\sum_i \varepsilon_i \, C \, e^{-\beta \varepsilon_i}}{\sum_i C \, e^{-\beta \varepsilon_i}}$$

$$= \frac{\sum_i \varepsilon_i \, e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}}.$$

Further, using $Z = \sum_i e^{-\beta \varepsilon_i}$, it becomes

$$\bar{E} = \frac{\sum_i \varepsilon_i e^{-\beta \varepsilon_i}}{Z}. \qquad \qquad \ldots(4.38)$$

For an isothermal-isochoric process, we have

$$\left(\frac{\partial Z}{\partial T}\right)_V = \frac{\sum_i \varepsilon_i \, e^{-\beta \varepsilon_i}}{kT^2}$$

$$kT^2 \left(\frac{\partial Z}{\partial T}\right)_V = \sum_i \varepsilon_i \, e^{-\beta \varepsilon_i}$$

$$= Z\bar{E}$$

or

$$\bar{E} = \frac{kT^2}{Z} \left(\frac{\partial Z}{\partial T}\right)_V,$$

and

$$N\bar{E} = \frac{NkT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_V.$$ ...(4.39)

Thus, the total energy is given by

$$E = N\bar{E} = \frac{NkT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_V$$

or

$$E = NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V.$$ ...(4.40)

This is the relation between total energy and partition function.

5. Relation with enthalpy (H):

The enthalpy is defined as
$$H = E + PV$$
and can be written in terms of the partition function as
$$H = NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + PV.$$ ...(4.41)

6. Relation with Gibbs potential or Gibbs free energy (G):
Gibbs potential is defined as
$$G = H - TS.$$
It can be obtained in terms of partition function as

$$G = NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + PV - T\left(Nk\log Z + \frac{E}{T}\right)$$

$$- NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + PV - NkT\log Z - E$$

$$= NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + PV - NkT\log Z - NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V,$$

which can be simplified as
$$G = PV - NkT\log Z.$$ ...(4.42)

7. Relation with specific heat at constant volume (C_V):

The specific heat at constant volume is defined as
$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$
and using equation (4.38), we obtain
$$C_V = \frac{\partial}{\partial T}\left[NkT^2\left\{\frac{\partial}{\partial T}(\log Z)\right\}_V\right].$$
This can be simplified to
$$C_V = Nk\left[2T\frac{\partial}{\partial T}(\log Z) + T^2\frac{\partial^2}{\partial T^2}(\log Z)\right].$$ ...(4.43)

Thus, we can conclude that if we are able to write a partition function for a given system in microcanonical ensemble we can obtain various thermodynamic quantities of the system.

Example 4.3: Consider a system of N particles with only three possible energy levels 0, ε, and 2ε. Write down the expression of the partition function and average energy per particle for this system by assuming that the particles are following Maxwell Boltzmann statistics.

For the given system of N particles with only three possible energy levels 0, ε, and 2ε. Using equation (4.22) we can directly write the partition function as

$$Z = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$$

Further, from equation (4.38), the average energymay be expressed as

$$\bar{E} = \frac{\varepsilon e^{-\beta\varepsilon} + 2\varepsilon e^{-3\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}},$$

Example 4.4: There are two energy levels 2ε and 3ε with degeneracy 1 and 2 for a system of two particles which follow Maxwell Boltzmann statistics. Calculate the mean energy of the system.

It is given that the particles are following Maxwell Boltzmann distribution law and degeneracy of the lower energy level is 1, whereas degeneracy of the upper energy level is 2. So, we can write partition function using equation (4.23) as

$$Z = e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon},$$

Again, using equation (4.38), we havethe mean energy of the system

$$\bar{E} = \frac{2\varepsilon e^{-2\beta\varepsilon} + 3\varepsilon e^{-3\beta\varepsilon}}{e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}},$$

Self Assessment Question (SAQ) 3: The expression of partition function for a system is given as$Z = e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$. Write down the expression for Helmholtz free energy.

Self Assessment Question (SAQ) 4: Obtain an expression for total energy when the partition function of a system is given by$Z = 2 + e^{-\beta\varepsilon} + 2 e^{-2\beta\varepsilon}$.

4.7 SUMMARY

In this unit, we learned about the concept of ensembles and three types of ensemblesoften used in statistical mechanics.Based on the three different types of macroscopic conditions, these three categories of ensembles are proposed. We also discussed the microcanonical ensemble in detail by considering the system of ideal gases in classical statistics. Yet another important quantity in statistical mechanics, i.e., partition function, is discussed in detail along with its relation with various thermodynamic quantities. The paradoxin deriving entropy due to mixing of ideal gases is discussed as the well-known Gibbs paradox, which can be resolved by dividingthe number of microstates with the Gibbs factor.Quantum mechanics

provides an explanation of the Gibbs factor that it is due to indistinguishabilityof molecules or particles.

This unit was further focused on the system of an ideal gas as we calculated the entropy of ideal gases in microcanonical ensemble. We know the connection between statistical mechanics and thermodynamics is given by the Boltzmann entropy relation.Thus, it is important to calculate entropy in a particular type of ensemble,which helps us to calculate other thermodynamic parameters.

In a similar way, we will discuss the remaining two kinds of ensembles, i.e. canonical and grand canonical ensembles, in Units 5 and 6, respectively. Thus,topics discussed in this unit will also be helpful in understanding the calculations and discussions in the forthcoming units.

4.8 GLOSSARY

Ensemble	*A large number of systems with the same macroscopic properties but different microscopic properties are collectively called an ensemble.*
Microcanonical ensemble	*A collection of essentially independent assemblies with same energy E, volume V, and number of the particles N is known as microcanonical ensemble.*
Entropy	*A thermodynamic quantity which is a measure of the molecular disorder or randomness of a system.*
Gibbs factor	*For the system of indistinguishable particles or molecules we have to multiply the expression of number of microstates by a factor of $\frac{1}{N!}$ known as Gibbs factor.*
Gibbs paradox	*Gibbs paradox involves the contradiction between mixing two ideal gases of a different kind and that of mixing two ideal gases of the same kind.*
Partition function	*This is a function which tells us how the gas molecules are distributed among various energy states or the particles are partitioned among various energy levels.*

4.9 REFERENCES

1. Statistical Mechanics, **R. K. Pathria**, Butterworth-Heinemann, Oxford.

2. Statistical Mechanics, **S. Prakash,** Kedar Nath Ram Nath.

3. Fundamentals of Statistical and Thermal Physics, *F. Reif*, McGraw-Hill.

4. Statistical Mechanics: an Introduction, *D. H. Trevena*, Elsevier.

5. Statistical Physics, *L. D. Landau* and *E. M. Lifshitz*, Elsevier.

4.10 SUGGESTED READINGS

1. Thermodynamics and Statistical Mechanics, *W. Greiner, L. Neise* and *H. Stocker,* Springer Science and Business Media.

2. Statistical and Thermal Physics, *S. Lokanathan* and *R. S. Gambhir*, PHI Learning Private Limited, Delhi.

3. Statistical Mechanics, *K. Huang*, Wiley India.

4. Fundamentals of Statistical Mechanics, *B. B. Laud*, New Age International.

4.11 TERMINAL QUESTIONS

4.11.1 Short Answer Type

1. Define ensemble.

2. With the help of pictorial representation define microcanonical ensemble.

3. What do you understand by partition function?

4. What is the Gibbs paradox?

5. Write down the expression for entropy and Sakur-Tetrode equation after removing Gibbs paradox.

4.11.2   Long Answer Type

1.   Explain in brief the ensemble theory and various types of ensembles in statistical mechanics.
2. What do you understand by ensemble? How the concept of ensemble is utilized to obtain the priorities of a statistical system.
3.   Define partition function for a microcanonical ensemble. Use it to derive expressions for chemical potential, Helmholtz free energy, and Gibbs free energy.

4. Obtain an expression for entropy of an ideal gas in the microcanonical ensemble,and also establish the relation between statistical entropy and various thermodynamic quantities.

5. Discuss the significance of partition function.Subsequently, obtain an expression for the partition function in microcanonical ensemble and also establish its relation with different thermodynamic variables.

6. By considering a system of an ideal gas discuss the Gibbs paradox by deriving an expression for entropy. Obtain an expression for Sakur-Tetrode equation after the removal of Gibbs paradox.

7. Explain Gibbs paradox. How it can be resolved by the concept of indistinguishability of the molecules or particles.

4.11.3 Numerical Answer Type

1. Consider a system of two particles, each of which can be in one of three quantum states of respective energies 0, ε,and 3ε. Obtain an expression for the particle function if the particles obey classical Maxwell Boltzmann statistics.

2. Obtain the expression of Helmholtz free energy by writing partition function for a system of non-interacting classical particles having two energy levels with energies ε and 2ε. The lower level is four fold degenerate and the upper level is doubly degenerate.

3. Calculate the partition function of a single harmonic oscillator with energy levels given by $\left(n + \frac{1}{2}\right)\hbar\omega$.

4. Consider a system of two classical particles, each of which can occupy any of the two energy levels 0 and ε. Write down the expression for the mean energy of the system at temperature T.

5. If a non-interacting system has two energy levels 0 and ε,the lower level is doubly degenerated while that of energy ε is non-degenerate. Write down an expression for partition function of this system. Also calculate the total energy and Gibbs free energy.

4.11.4 Objective Answer Type

1. The individual assemblies of an ensemble in which the macroscopic properties, namely energy, volume, and the number of particles remain same are separated by rigid
    (a) impermeable and insulated wall   (b) permeable and insulated wall
    (c) impermeable and diathermic wall(d) permeable and diathermic wall

2.   In microcanonical ensemble, the individual systems cannot exchange
     (a) particles   (b) energy and particles
     (c) energy   (d) none of these

3.   The correct form of Boltzmann entropy relation is
     (a) $S = \frac{k}{2}\log \Omega$ (b) $S = \frac{1}{k}\log \Omega$
     (c) $S = k \log \Omega$ (d) $S = 2k \log \Omega$

4. The entropy of the assembly of ideal gas molecules in terms of partition function Z is given by
     (a) $S = Nk \, \log Z + \frac{1}{2}Nk$ (b) $S = Nk \, \log Z + \frac{2}{3}Nk$
     (c) $S = Nk \, \log Z$ (d) $S = Nk \, \log Z + \frac{3}{2}Nk$

5.   For removing the Gibbs paradox, one should multiply the expression of number of microstates by a factor of
     (a) $\frac{1}{N!}$ (b) $2N!$
     (c) $\frac{1}{2N!}$ (d) $N!$

4.12   ANSWERS
4.12.1 Self Assessment questions:

1. We can summarize some of the important facts about the microcanonical ensemble in the tabular form given below.

Property	Microcanonical ensemble	Canonical ensemble	Grand canonical ensemble
Macroscopic properties of independent assemblies	Energy E, volume V and number of particles N	Temperature T, volume V and number of particles N	Temperature T, volume V and chemical potential μ
Separation between independent assemblies	Rigid, impermeable and insulated wall	Rigid, impermeable and diathermic wall	Rigid, permeable and diathermic wall
Contact of individual assemblies with each other	Cannot interact	Can interact	Can interact

Macroscopic property that can be exchanged between individual systems	No exchange of energy and particles	Only energy can be exchanged	Both energy and particles can be exchanged
Variation in the number of particles and energy for each assembly	Both remain constant	Number of particles remains constant but not energy	Neither number of particles nor energy remains constant

As we are restricted with microcanonical ensemble in this unit, the expression of partition function is, $Z = \sum_i g_i \, e^{-\beta \varepsilon_i}$in the present case. Further, with the knowledge of the partition function for microcanonical ensemble, we can define various physical quantities in terms of the partition function, like entropy (equation (4.32)), Helmholtz free energy (equation (4.35)), pressure (equation (4.36)), total energy (equation (4.40)), enthalpy (equation (4.41)), Gibbs free energy (equation (4.42)), specific heat (equation (4.43)). Similar expressions for partition function in canonical and grand canonical ensembles will be obtained in the next two units.

2.From equation (4.8), the pressure will remain one-half.

3. The given partition function is,$Z = e^{-\beta \varepsilon} + e^{-2\beta \varepsilon} = e^{-\beta \varepsilon}\left(1 + e^{-\beta \varepsilon}\right)$.

From equation (4.35) we can write
$$F = -NkT \, \log\left[e^{-\beta \varepsilon}\left(1 + e^{-\beta \varepsilon}\right)\right] = -NkT\left[-\beta \varepsilon + \log\left(1 + e^{-\beta \varepsilon}\right)\right]$$

or
$$F = N\varepsilon - NkT \log\left(1 + e^{-\beta \varepsilon}\right).$$

4. With the help of equation (4.40), we can calculate the total energy as
$$E = NkT^2 \left\{ \frac{\partial}{\partial T}\left(\log\left(2 + e^{-\frac{\varepsilon}{kT}} + 2\,e^{-\frac{2\varepsilon}{kT}}\right)\right)\right\},$$

and thus
$$E = NkT^2 \left[\frac{\left(\frac{\varepsilon}{kT^2}\right)e^{-\frac{\varepsilon}{kT}} + 2\left(\frac{2\varepsilon}{kT^2}\right)e^{-\frac{2\varepsilon}{kT}}}{\left(2 + e^{-\frac{\varepsilon}{kT}} + 2\,e^{-\frac{2\varepsilon}{kT}}\right)}\right]$$

or
$$E = N\varepsilon \left[\frac{e^{-\frac{\varepsilon}{kT}} + 4\,e^{-\frac{2\varepsilon}{kT}}}{\left(2 + e^{-\frac{\varepsilon}{kT}} + 2\,e^{-\frac{2\varepsilon}{kT}}\right)}\right],$$

4.12.2 Numerical answer type:

1. It is given that particle (say A and B) obey Maxwell Boltzmann statistics, i.e., any number of particles can occupy a single energy state. The distribution is shown in the table below.

0ε	ε	3ε	Total energy	Degeneracy
AB	-	-	0	1
A B	B A	-	ε	2
-	AB	-	2ε	1
A B	-	B A	3ε	2
-	A B	B A	4ε	2
-	-	AB	6ε	1

Now using the relation given by equation (4.23), we can obtain an expression of partition function as

$$Z = 1 + 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + 2e^{-3\beta\varepsilon} + 2e^{-4\beta\varepsilon} + e^{-6\beta\varepsilon}.$$

2. In question, we have $g_i = 4$ for lower energy level, and $g_i = 2$ for upper energy level. So, with the help of equation (4.23), we can directly write the expression for partition function as

$Z = 4e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon}$. Thus, from equation (4.35) we obtain the expression of Helmholtz free energy as

$$F = -NkT \log\left(4e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon}\right) \text{ or } F = -\frac{N}{\beta}\log\left(4e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon}\right).$$

3. We have $\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega$. Thus, the partition function can be written as

$$Z = \sum_{n=0}^{\infty} e^{-\beta\varepsilon_n} = \sum_{n=0}^{\infty} \exp\left[-\beta\left(n+\frac{1}{2}\right)\hbar\omega\right] = e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n.$$

The summation term is a geometric series, so we can write

$$Z = e^{-\frac{\beta\hbar\omega}{2}} \left(\frac{1}{1-e^{-\beta\hbar\omega}}\right) = \frac{1}{2} \times \frac{1}{\left(\frac{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}}{2}\right)} \text{ and}$$

$$Z = \frac{1}{2 \sinh\left(\frac{\beta\hbar\omega}{2}\right)}.$$

8. Let P and Q be the two particles and the distribution is given below

0ε	ε	Total energy	Degeneracy
PQ	-	0	1
P	Q	ε	2
Q	P		
-	PQ	2ε	1

We can write down the partition function as

$$Z = 1 + 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}.$$

Thereafter, with the help of equation (4.38), we get the expression of mean energy

$$\bar{E} = \frac{\varepsilon\, e^{-\beta\varepsilon}}{1 + 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}.$$

9. According to the question, we can write the partition function
$$Z = 2 + e^{-\beta\varepsilon}.$$

We can use equation (4.40) for calculating the total energy as

$$E = NkT^2 \frac{\partial}{\partial T}\{\log(2 + e^{-\beta\varepsilon})\} = NkT^2 \frac{\partial}{\partial T}\left\{\log\left(2 + e^{-\frac{\varepsilon}{kT}}\right)\right\}$$

$$= NkT^2 \left[\frac{\left(\frac{\varepsilon}{kT^2}\right)e^{-\frac{\varepsilon}{kT}}}{\left(2 + e^{-\frac{\varepsilon}{kT}}\right)}\right]$$

$$= N\varepsilon \frac{e^{-\frac{\varepsilon}{kT}}}{\left(2 + e^{-\frac{\varepsilon}{kT}}\right)}.$$

Further, from equation (4.42), Gibbs free energy can be calculated as

$$G = PV - NkT \log\left(2 + e^{-\frac{\varepsilon}{kT}}\right).$$

4.12.3: Objective answer type:
1. Correct option is (a), impermeable and insulated walls.
2. Correct option is (b), energy and particles.

3. Correct option is (c), $S = k \log \Omega$.

4. Correct option is (d), $S - Nk \log Z + \frac{3}{2} Nk$.

5. Correct option is (a), $\frac{1}{N!}$.

UNIT 5: Canonical Ensemble

Structure:

5.1 Introduction:

The given unit discuss an important ensemble of statistical mechanics, canonical ensemble. Among all ensembles, canonical ensemble is considered as more appropriate. It plays a central role in statistical mechanics. Reasonably it should come first and rest other ensemble (micro-canonical and grand-canonical) should be followed as a special case. In the case of canonical ensemble, system is considered in thermal equilibrium with a heat bath (taken as a closed system).

The partition function is used as an important parameter to solve various thermodynamic quantities for canonical ensemble. Also, this helps to explain energy fluctuations as well. The difficulties and limitations raised by the Boltzmann's statistical mechanics was removed by the Gibb's theory which was based on the ensemble concept. The Boltzmann's method is applicable only for the systems having small number density almost no interactions between particles while Gibb's ensemble theory shows its validity for both the classical and quantum systems.

5.2 Objectives:

Students will understand:

1. Concept of canonical ensemble.
2. Role of partition function.
3. The way to compute the various thermodynamic variables with the help of partition function.
4. Energy fluctuations calculations.
5. The case of Linear Harmonic Oscillator.

5.3   CANONICAL ENSEMBLE: -

It is a collection of essentially independent system having same temperature T. Exchange of energy of ensemble is explained by temperature.

It is similar to partial open system. Ensemble are separated by rigid impermeable but conducting walls.

Here we make walls conducting so energy is going to exchange. The physical quantity which defines the exchange of energy at equilibrium is temperature. The natural variable are [N, V, T].

The energy of this system is variable and can take up values anywhere b/w 0 to ∞.

Let have a subsystem S_1 in S_2 which is a heat reservoir from which we can draw as much heat as we want without changing anything $E_2 >> E_1$.
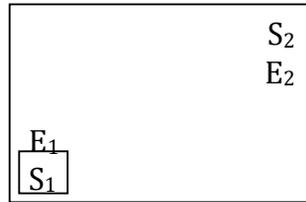
Assuming system is closed then E1 + E2 = Constant

⇒System as a whole is micro-canonical ensemble

∵ $\quad$ $E_1 + E_2 = E = Constant$ $\quad\quad\quad\quad\quad$ .... (1)

Since the reservoir is much layer them the system ∴ any value of E_1 will be a small fraction of E.

$$\frac{E_1}{E} = \frac{E - E_2}{E}$$

$$\Rightarrow \quad \frac{E_1}{E} = \left(1 - \frac{E_2}{E}\right) \ll 1 \quad\quad\quad ....(2)$$

$\quad\quad$ Let the number of states available to the reservoir be Ω_2 (E_2). The larger the number of states available to the reservoir, the larger the probability of the reservoir assuming that particular energy value E_2.

$\quad\quad$ The phase density $\rho(p,q)$ of the subsystem is proportional to the number of microstates available to both reservoirs

$$P(p_1, q_1) \propto \Omega_2(E_2) \quad\quad\quad ...(3)$$

$$\propto \Omega_2 (E - E_1)$$

But the entropy is defined as,

$$S_2 (E - E_1) = K \ln \Omega_2 (E - E_1)$$

As $E_1 \ll E$, hence the above expression is expanded

$$S_2 (E - E_1) \approx S_2 (E) - E_1 \left(\frac{\partial S_2}{\partial E_2}\right)\bigg|_{E_2 = E}$$

$$\approx S_2 (E) - E_1/T \quad\quad\quad \left(\because \frac{\partial S}{\partial E} = \frac{1}{T}\right)$$

$$\Rightarrow K \ln \Omega_2 (E - E_1) = S_2 (E) - E_1/T$$

$$\Rightarrow K \ln \Omega_2 (E - E_1) = \frac{S_2(E)}{k} - \frac{E_1}{kT}$$

using eqn^n (3)

$$\ln \rho(p_1, q_1) \propto \frac{S_2(E)}{k} - \frac{E_1}{kT}$$

$$\Rightarrow \quad \rho(p_1, q_1) \propto \exp.\left[\frac{S_2(E)}{k}\right] * \exp.\left[\frac{-E_1}{kT}\right]$$

If 'H' be the Hamiltonian of the system then,

$$\rho(p_1, q_1) \propto \exp.\left[\frac{-H(p_1, q_i)}{kT}\right]$$

where 'i' is dummy indices

$$\rho(p,q) \propto e^{-H(p,q)/kT} = e^{-\beta H(p,q)}$$

i.e. $\rho(p, q)$ phase density is dependent on exponential term and hence ρ is not a constant. As tempertaure increases, the phase density decreases i.e. all the states in canonical ensemble do not have equal probability.

$$\text{or} \quad \rho(p, q) = A e^{-H(p,q)/kT}$$

The ensemble average <F> of a given physical quantity F(p, q) which may be different for system in different microstates is

$$< F >= \frac{\int f(p,q)\rho(q,p,t) d^{3N}q\, d^{3N}p}{\int \rho(q,p,t) d^{3N}q\, d^{3N}p}$$

This gets reduced to the form:

$$< F >= \int \frac{f(p,q) \exp.(-\beta H) d\omega}{\int \exp.(-\beta H) d\omega}$$

$$\forall \quad \beta = \frac{1}{kT}$$

$d\omega = d^{3N}p\, d^{3N}q$ (volume element of phase density)

Here, denominator specifies the normalization constant or partition function which should be a dimensionless quantity.

To get rid of the dimension of 'dω' we will use the relation

$$\Omega = \frac{d\omega}{\omega_0} = \frac{d\omega}{N! h^{3N}}$$

N! is multiplied as the particles are indistinguishable. This is done for correct Boltzmann counting and is known as Gibb's paradox.

Hence, $< F >= \dfrac{\int f(q,p) e^{-\beta H} d\omega / N! h^{3N}}{\int e^{-\beta H} d\omega / N! h^{3N}}$

Now, the denominator is dimensionless and the expression for partition function is

$$Q_N(V,T) = \frac{1}{N \, h^{3N}} \int e^{-\beta H} d\omega$$

Where, the integration goes over the whole space. Once the partition function is known, it tells us how the states are divided and this makes averages normalised.

5.3.1 Application:-

I.   An Ideal Gas:-

Consider a system of N-identical particles which are non-interacting. The particles confined to a space of volume V and in equilibrium at temperature T.

So, $H(q,p) = \sum_{i=1}^{N} \frac{p_i^2}{2m}$ …(1)

$\Rightarrow$ Partition function in this case is

$$Q_N(V,T) = \frac{1}{N! h^{3N}} \int e^{-\beta/2m} \sum p_i^2 \prod_{i=1}^{N} d^3 q_i d^3 p_i$$

Since potential energy depends only on q so

$$d^3 q_k = V^N$$

$$Q_N = \frac{V^N}{N! \, h^{3N}} \left[\int \exp \left[\frac{-p^2}{2mkT}\right] d^3 p \right]_0^N$$

To find d^{3}p:-

Consider $d^3 x = 4\Pi \, x^2 \, dx$ for spherical coordinates

$$d^3 x = x^2 \sin\theta \, d\theta \, d\dot\varphi \, dx$$

$$\left\{ \begin{array}{l} \because \int \sin\theta d\theta = 2 \, \& \int d\phi = 2\Pi \\ \Rightarrow d^3 x = 2\Pi.2.x^2 dx = 4\Pi \, x^2 dx \end{array} \right\}$$

Replacing d^{3}x by d^{3}p

$$Q_N = \frac{V^H}{N! h^{3N}} \left[\int_0^p e^{\frac{-p^2}{2mkT}} . 4\Pi p^2 dp \right]$$

But 4Π is soild angle

$$I = 4\Pi \int_0^\infty e^{\frac{-p^2}{2mkT}} p^2 dp$$

Let $t = \frac{p^2}{2mkT}$ we get

93

$$I = (4\Pi)(mkT)(2mkT)^{\frac{1}{2}} \int t^{\frac{1}{2}} e^{-t} dt \qquad where \int t^{\frac{1}{2}} e^{-t} dt = \frac{\sqrt{\Pi}}{2}$$

$$I = (4\Pi)(mkT)(2mkT)^{\frac{1}{2}} \times \frac{\sqrt{\Pi}}{2}$$

$$I = (2\Pi mkT)^{\frac{3}{2}}$$

$$Q_N = \frac{V^N}{N! \, h^{3N}} (2\Pi mkT)^{\frac{3N}{2}}$$

$$Q_N = \frac{1}{N!} \left[\frac{V}{h^3} (2\Pi mkT)^{\frac{3}{2}} \right]^N \underline{\hspace{3cm}}(a)$$

To make Q$_N$ dimensionless in more obvious way we introduce De-Broglie wavelength.

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

Now thermal wavelength

$$\lambda_T = \frac{h}{\sqrt{2mkT}}$$

But its correct definition is

$$\lambda_T = \frac{h}{\sqrt{2\Pi mkT}}$$

$$\lambda_T^3 = \frac{h^3}{(2\Pi mkT)^{\frac{3}{2}}}$$

$$Q_N = \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N$$

In above expression, we have all the three variables of canonical ensemble they are (N, V, T)

In 1-D; $$Q_N = \frac{1}{N!} \left(\frac{L}{\lambda_T^3} \right)^N$$

and for distinguishable particle

$$Q_N = \left(\frac{V}{\lambda_T^3} \right)^N$$

Note:- 1. If partition function of electron & proton together but non-interacting is to find than potential energy of e⁻ & potential energy of p.

2. Steps to write partition function:

(a) Write integral over dω

(b) Make it dimensionless

(c)   To make dω dimensionless $\frac{1}{h^{3N}}$ is multiplied

(d)   Check whether system have distinguishable or indistinguishable particles.

(i)   Helmholtz Free Energy: -

Using equ. (a), we write the expression for partition function

$$A\ (N,\ V,\ T) = -\ KT\ \ln Q_N\ (V,\ T)$$

but from equ. (a), $Q_N(V,T) = \frac{1}{N!}\left[\frac{V}{h^3}(2\Pi\ mkT)^{\frac{3}{2}}\right]^N$

$\Rightarrow$ $A(N,\ V,\ T) = -kT\ \ln\left[\frac{1}{N!}\left\{\frac{V}{h^3}(2\Pi\ mkT)^{\frac{3}{2}}\right\}^N\right]$

$$= kT\ \ln N! - NKT\ \ln\left\{\frac{V}{h^3}(2\Pi\ mkT)^{\frac{3}{2}}\right\}$$

Using Stirling formula,

$$= kT\ (N\ \ln N - N) - NKT\ \ln\frac{V}{h^3} - \frac{3}{2}NKT\ \ln(2\Pi\ mkT)$$

$$= NKT\ (\ln N - 1) - NKT\ \ln V + NKT\ \ln h^3 - \frac{3}{2}NKT\ \ln(2\Pi\ mkT)$$

$$= NKT\left[\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\Pi\ mkT}\right)^{\frac{3}{2}}\right\}\ 1\right]$$

or $A\ (V,\ N,\ T) = NKT\left[\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\Pi\ mkT}\right)^{\frac{3}{2}}\right\} - 1\right]$ … (b)

The above expression is helpful to derive rest of thermodynamic parameters.

(ii)   Chemical Potential: -

It can be defined as: -

$$\mu = \left(\frac{\delta A}{\delta N}\right)_{V,T}$$

Using equ. (b)

$$A\ (V,\ N,\ T) = NKT\left[\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\Pi\ mkT}\right)^{\frac{3}{2}}\right\} - 1\right]$$

$$= \text{NKT} \ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\Pi \, mkT} \right)^{\frac{3}{2}} \right\} - NKT$$

$$\left(\frac{\partial A}{\partial N} \right) = \frac{\partial}{\partial N} \left[\text{NKT} \ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\Pi \, mkT} \right)^{\frac{3}{2}} \right\} - \frac{\partial}{\partial N} (NKT) \right]$$

Let us suppose $\quad \ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\Pi \, mkT} \right)^{\frac{3}{2}} \right\} = X$

$$\Rightarrow \qquad \mu = kTX + NKT \left| \frac{\left(\frac{h^2}{2\Pi mkT} \right)^{\frac{3}{2}} \times \frac{1}{V}}{\frac{N}{V} \left(\frac{h^2}{2\Pi mkT} \right)^{\frac{3}{2}}} \right| - kT$$

Or

$$= kT ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\Pi mkT} \right)^{\frac{3}{2}} \right\} + kT - kT$$

$$\mu = kT \ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\Pi mkT} \right)^{\frac{3}{2}} \right\}$$

(iii)   Pressure:-

$$P = - \left(\frac{\partial A}{\partial V} \right)_{N,T}$$

from equ. (a), $\quad A = NKT \left[\ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\Pi \, mkT} \right)^{\frac{3}{2}} \right\} - 1 \right]$

Now, $P = - \frac{\partial}{\partial v} \left[\text{NKT} \left\{ \ln \left(\frac{N}{V} \left(\frac{h^2}{2\Pi \, mkT} \right)^{\frac{3}{2}} \right) \right\} - 1 \right]$

$$= -NKT \frac{\partial}{\partial v} \left[\ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\Pi \, mkT} \right)^{\frac{3}{2}} \right\} \right]$$

$$= -NKT \left[\frac{N \left(\frac{h^2}{2\Pi \, mkT} \right)^{\frac{3}{2}} \times \frac{-1}{V^2}}{\frac{N}{V} \left(\frac{h^2}{2\Pi \, mkT} \right)^{\frac{3}{2}}} \right]$$

$$\Rightarrow \qquad P = \frac{NKT}{V}$$

(iv)   Entropy:-

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}$$

from equ. (a),

$$A = NKT\left[\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\Pi\, mkT}\right)^{\frac{3}{2}}\right\} - 1\right]$$

$$= NKT\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\Pi\, mkT}\right)^{\frac{3}{2}}\right\} - NKT$$

$$-\frac{\partial A}{\partial T} = -\frac{\partial}{\partial T}\left[NKT\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\Pi\, mkT}\right)^{\frac{3}{2}}\right\}\right] + \frac{\partial}{\partial T}(NKT)$$

Let $\frac{N}{V}\left(\frac{h^2}{2\Pi\, mkT}\right)^{\frac{3}{2}} = y$

$\Rightarrow$ $\quad S = \frac{-\partial}{\partial T}[NKT\ln y] + \frac{\partial}{\partial T}(NKT)$

or $\quad = -NK\ln y - NKT\frac{\partial y}{\partial T} + NK$

$$\frac{\partial}{\partial T}\ln y = \frac{\partial}{\partial T}\left[\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\Pi\, mkT}\right)^{\frac{3}{2}}\right\}\right]$$

$$= \left[\frac{\frac{N}{V}\left(\frac{h^2}{2\Pi\, mkT}\right)^{\frac{3}{2}}}{\frac{N}{V}\left(\frac{h^2}{2\Pi\, mkT}\right)^{\frac{3}{2}}} \times \frac{\partial}{\partial T}\left(T^{-\frac{3}{2}}\right)\right]$$

$$= \frac{-\frac{3}{2}T^{\frac{-5}{2}}}{T^{\frac{-3}{2}}} = \frac{-3}{2}\frac{1}{T}$$

$\Rightarrow$ $\quad S = -NK\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\Pi\, mkT}\right)^{\frac{3}{2}}\right\} + \frac{3}{2}NKT + NK$

$$= NK\ln\left\{\frac{V}{N}\left(\frac{2\Pi\, mkT}{h^2}\right)^{\frac{3}{2}}\right\} + \frac{5}{2}NK$$

or $\quad S = NK\left[\ln\left\{\frac{V}{N}\left(\frac{2\Pi\, mkT}{h^2}\right)^{\frac{3}{2}}\right\}\right] + \frac{5}{2}$ $\quad$ … (c)

It is also known as Sackur – Tetrode equation for the entropy.

(v)   Internal Energy:-

It is a function of temperature alone independent on volume & pressure.

$$U = \frac{E}{N} \text{ (Average Energy per system in the Ensemble)}$$

$$U = -\left[\frac{\partial}{\partial \beta}(\ln Q)\right]$$

$$A = -kT \ln Q$$

$$\Rightarrow \quad \ln Q - \frac{-A}{kT} - -\beta A$$

$$\frac{\partial}{\partial \beta}(\beta A) = \frac{\partial}{\partial \beta}(-\ln Q_N)$$

but $\quad Q_N = \frac{1}{N! h^{3N}} \int e^{-\beta H} d\omega$

The Hamiltonian for a canonical ensemble is not conserved (as there is exchange of energy)

$$\Rightarrow \quad \frac{\partial}{\partial \beta}(-\ln Q_N) = \frac{\partial}{\partial \beta}\left[\ln h^{3N} N! - \ln \int e^{-\beta H} d\omega\right]$$

$$= -\frac{\partial}{\partial \beta}\left[\ln \int e^{-\beta H} d\omega\right]$$

$$= \frac{-\int e^{-\beta H}(-H) d\omega}{\int e^{-\beta H} d\omega}$$

Multiplying and dividing by $\frac{1}{h^{3N} N!}$ to make it dimensionless.

$$U = \frac{\int e^{-\beta H} H \, d\omega / h^{3N} N!}{\int e^{-\beta H} d\omega / h^{3N} N!} = < H >$$

$$\Rightarrow \quad <H> = U \text{ (internal energy)}$$

$$U - <H> - \frac{\partial}{\partial \beta}(\beta A) - -\frac{\partial}{\partial \beta}(\ln Q_N)$$

$$U = \frac{\partial}{\partial \beta}(\beta A) = \beta \frac{\partial A}{\partial \beta} + A$$

But $\beta = \frac{1}{kT}$

$$U = \frac{1}{kT} \frac{\partial A}{\partial \left(\frac{1}{kT}\right)} + A$$

$$= \frac{1}{T} \frac{\partial A}{\partial \left(\frac{1}{T}\right)} + A = \frac{1}{T}\left(\frac{\partial A}{-\partial T}\right)|T^2 + A$$

$\Rightarrow$ $\quad U = -T\left(\frac{\partial A}{-\partial T}\right) + A$

but $-\frac{\partial A}{\partial T} = S$

$\Rightarrow$ $\quad U = +TS + A$

or $\quad A = U - TS$

Now substituting the value of 'A' from equ. (b) and 'S' from equ. (c), we get

$$U = NKT\left[\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\Pi m kT}\right)^{\frac{3}{2}} - 1\right\} + NKT\left[\ln\left\{\frac{V}{N}\times\left(\frac{2\Pi m kT}{h^2}\right)^{\frac{3}{2}}\right\} + \frac{5}{2}\right]\right]$$

$$= NKT\ln\left[\frac{N}{V}\left\{\left(\frac{h^2}{2\Pi m kT}\right)^{\frac{3}{2}}\times\frac{V}{N}\left(\frac{2\Pi m kT}{h^2}\right)^{\frac{3}{2}}\right\} + NKT\left(\frac{5}{2}-1\right)\right]$$

$$= NKT\ln(1) + \frac{3}{2}NKT$$

$$= 0 + \frac{3}{2}NKT$$

$\Rightarrow$ $\quad U = \frac{3}{2}NKT$

5.4 Energy Fluctuation in the Canonical Ensemble:

The average of energy is not a good option because positive or negative energies will cancel out each other and total energy will be zero. So to get rid of −ve sign and this problem we take square of energies and find out the average mean square energies.

It is defined as the root mean square deviation & Hamiltonian from its average value <H>

$$(\Delta E)^2 = |(H - < H >)|^2$$

$$=<H^2+<H>^2-2H<H>>$$

$$=<H^2> +<H>^2-2<H><H>$$

$$=<H^2> -<H>^2$$

$$\Delta E = \sqrt{<H^2>-<H>^2} \qquad \ldots(A)$$

We've already proved that

$$<H> = \frac{-\partial}{\partial \beta}(\ln Q_N) \qquad \ldots\ldots(1)$$

By definition

$$<H^2> = \frac{\int H^2 e^{-\beta H} d\omega / h^{3N} N!}{\int e^{-\beta H} d\omega / h^{3N} N!}$$

$$= \frac{1}{h^{3N} N!} \frac{\int H^2 e^{-\beta H} d\omega}{Q_N}$$

$$= \frac{1}{Q_N h^{3N} N!} \int \frac{\partial^2}{\partial \beta^2} e^{-\beta H} d\omega$$

$$= \frac{1}{Q_N} \frac{\partial^2}{\partial \beta^2} \left(\frac{1}{h^{3N} N!} \int e^{-\beta H} d\omega\right)$$

$$<H^2> - \frac{1}{Q_N} \frac{\partial^2}{\partial \beta^2} Q_N \qquad \ldots(2)$$

Combining equ. (1) & (2) as defined by (A)

$$<H^2> + <H>^2$$

Consider,

$$\frac{\partial^2}{\partial \beta^2} \ln Q_N + \frac{1}{Q_N^2}\left(\frac{\partial Q_N}{\partial \beta}\right)^2$$

$$= \frac{\partial}{\partial \beta}\left[\frac{\partial}{\partial \beta} \ln Q_N\right] + \frac{1}{Q_N^2}\left(\frac{\partial Q_N}{\partial \beta}\right)^2$$

$$- \frac{\partial}{\partial \beta}\left[\frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta}\right] + \frac{1}{Q_N^2}\left(\frac{\partial Q_N}{\partial \beta}\right)^2$$

$$= \frac{1}{Q_N^2}\left(\frac{\partial Q_N}{\partial \beta}\right)^2 + \frac{1}{Q_N}\frac{\partial^2 Q_N}{\partial \beta^2} + \frac{1}{Q_N^2}\left(\frac{\partial Q_N}{\partial \beta}\right)^2$$

$$= \frac{1}{Q_N}\frac{\partial^2 Q_N}{\partial \beta^2} = <H^2> \qquad \text{\{Using equ. (2)\}}$$

$$\therefore <H^2> = \frac{\partial^2}{\partial \beta^2} \ln Q_N + \left[\frac{\partial}{\partial \beta}(\ln Q_N)\right]^2 \qquad \qquad \ldots(3)$$

Now using (1) & (3) in equ. (A)

$$(\Delta E)^2 = \frac{\partial^2}{\partial \beta^2} \ln Q_N + \left[\frac{\partial}{\partial \beta}(\ln Q_N)\right]^2 - \left[\frac{\partial}{\partial \beta}(\ln Q_N)\right]^2 = \frac{\partial^2}{\partial \beta^2} \ln Q_N$$

$$= -\frac{\partial}{\partial \beta}\left[\frac{-\partial}{\partial \beta}(\ln Q_N)\right] \qquad \qquad \text{using equ. (1) here,}$$

$$= \frac{-\partial}{\partial \mu} <H>$$

$$= -\frac{\partial E}{\partial \beta}$$

$$= \frac{-\partial E}{\partial \left(\frac{1}{kT}\right)} = kT^2 \left(\frac{\partial E}{\partial T}\right)$$

$$= kT^2 \, C_V$$

$$\Delta E = \sqrt{kT^2 C_V}$$

or $\quad \frac{\Delta E}{E} = \frac{\sqrt{kT^2 C_V}}{E}$

Here, temperature is an intensive quantity. Energy & C_V are extensive quantity. If E ∝N then C_V∝N,

$$\Rightarrow \frac{\Delta E}{E} \times \frac{1}{\sqrt{N}}$$

Here we're dealing with macroscopic system which has number of molecules of as out 10^{24}. The energy fluctuation is of the order 10^{-12}i.e. they are very tiny ∴ we can say that canonical and thermodynamic ensemble are approximately equivalent.

For a perfect gas:-

$$E = \frac{3}{2} NKT$$

$$\frac{\partial E}{\partial T} = C_V = \frac{3}{2} NK$$

$$\Rightarrow \qquad \frac{\Delta E}{E} = \sqrt{\frac{2}{3}} \frac{1}{\sqrt{N}}$$

Here, $\sqrt{\frac{2}{3}}$ is the fudge factor. If this factor doesn't come then result is wrong.

$$\Delta E \propto \frac{1}{\sqrt{N}}$$

5.5 Linear Harmonic Oscillator:-

Classical expression for Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{1}{2}kq^2$$

where,

        k = spring constant

        m = mass of the particle

        q = A cos $(\omega_o t + \phi)$

        $\dot{q} - -A\omega_o \sin(\omega_o t + \phi)$

$\Rightarrow$ $m\dot{q} = p$

        $p = m\dot{q} = -m\omega_o A \sin(\omega_o t + \phi)$

        A = Amplitude of Vibration

        ω_o = Angular frequency of Vibration

        $\omega_o = \sqrt{\frac{k}{m}}$

        $\omega_o^2 = \frac{k}{m} \Rightarrow k = m\omega_o^2$

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_o^2 q^2$$

Since,

Hamiltonian = $Q_N = \sum e^{-\beta E i}$ = Free Energy A(T, V, N) we use above Hamiltonian as,

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_o^2 q^2$$

The partition function for 1-Oscillator is

$$Q_1 = \int_{-\infty}^{\infty} e^{\left[-\beta\left(\frac{p^2}{2m} + \frac{1}{2}m\omega_o^2 q^2\right)\right]} \frac{dq\,dp}{h}$$

Solving integration, we have

$$Q_1 = \frac{1}{h}\left(\frac{2\Pi m}{\beta}\right)^{\frac{1}{2}}\left(\frac{2\Pi}{\beta m \omega_0^2}\right)^{\frac{1}{2}}$$

$$Q_1 = \frac{kT}{\hbar\omega_0}$$

where, $\hbar = \frac{h}{2\Pi}$

For N-independent Oscillator

$$Q_N = (Q_1)^N = \left(\frac{kT}{\hbar\omega_0}\right)^N$$

&other thermodynamic variables,

$$A = NKT \ln\left(\frac{\hbar\omega_0}{kT}\right)$$

$$U = NKT$$

$$S = NK\left[\ln\left(\frac{kT}{\hbar\omega_0}\right) + 1\right]$$

$$\mu = kT \ln\left(\frac{\hbar\omega_2}{kT}\right)$$

The internal energy, U is an example of the general equipartition theorem in which each coordinate or monentum appear as a quadratic term in Hamiltonian such as($\frac{p^2}{2m}, \frac{kq^2}{2}$) contributes $\frac{1}{2}$ to the average energy in case classical:

In 3-Dim space, just replace N by 3N in the above expressions.

\#   For Quantum – Mechanical situation, energy sign values of a 1-Dim harmonic oscillator is given by,

$$e_n = \left[n + \frac{1}{2}\right]\hbar\omega_0; n = 0,1,2 \ldots \ldots \ldots$$

for single-Oscillator partition function

$$Q_1 - \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar w_0}$$

$$= \frac{e^{-\beta\hbar\omega_0/2}}{1 - e^{-\beta\hbar\omega_0}}$$

$$= \frac{1}{2\sinh(\beta\hbar\omega_0/2)}$$

For N-one dimensional Oscillators.

$Q_N = (Q_1)^N$ from which the thermodynamic variables follows as

,

$$Q_N = (Q_1)^N = \frac{2}{[2\sin(\beta\hbar\omega_o/2)]^N}$$

$$= \frac{1}{e^{-\beta\hbar\omega_o/2}} \times \frac{1}{[1 - e^{-\beta\hbar\omega_o}]^N}$$

For the Helmholtz free energy of the system,

$A = NKT \ln [2 \sin h (\beta\hbar\omega_o/2)]$

$$A = N\left[\frac{1}{2}\hbar\omega_o + kT\ln\left(1 - e^{-\beta\hbar\omega_o}\right)\right]$$

$$U = \frac{1}{2}N\hbar\omega_o \coth(\beta\hbar\omega_o/2)$$

$$= N\hbar\omega_o\left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_o} - 1}\right]$$

$$\mu = \frac{A}{N}$$

$P = 0$

$$S = NK\left[\frac{1}{2}\beta\hbar\omega_o \coth\left(\frac{1}{2}\beta\hbar\omega_o\right) - \ln\{2\sinh\left(\frac{1}{2}\beta\hbar\omega_o\right)\}\right]$$

$$- NK\left[\frac{\beta\hbar\omega_o}{e^{\beta\hbar\omega_o} - 1} - \ln\{1 - e^{-\beta\hbar\omega_o}\}\right]$$

& $$C = C_p = C_v = \frac{\partial U}{\partial T} = NK(\beta\hbar\omega_o)^2 \text{cosech}^2\left(\frac{1}{2}\beta\hbar\omega_o\right)$$

$$C = NK(\beta\hbar\omega_o)^2 \frac{e^{\beta\hbar\omega_o}}{(e^{\beta\hbar\omega_o} - 1)^2}$$

For $T \to \infty$, $\beta \to 0$& the exponantials can be expanded, thus we find classical equipartition result $C = NK$.

5.6 Summary:

In the given unit you have studied aboutcanonical ensemble. Out of all the ensembles, canonical ensemble is considered as the most appropriate one. Ideally this ensemble considered as first and rest other ensemble should be followed as a special case. In a given unit, the theory of canonical ensemble is discussed in which the system is considered in thermal equilibrium with a heat bath (taken as a closed system).Here, you have also learnt about the partition function which is used as an important parameter to solve various

thermodynamic quantities for canonical ensemble. An important application of canonical ensemble is highlighted.You have learnt how tocalculatethe energy fluctuations in canonical ensemble. Also, linear harmonic oscillator case discussed as an important example.To check your progress, multiple choice questions and terminal questions are given in the unit.

5.7 Glossary:

Ensemble: It is consisting of a large number of virtual copies of a system, considered all at once, each of which represents a possible state that the real system might be in. Also, a statistical ensemble is a probability distribution for the state of the system.

Density of states: It is the number of microstates or the number of independent quantum states of an N particle system per unit energy range. In other words, the density of states, denoted by g(E), indicates how densely packed quantum states in a particular system. Macroscopically, we can define: the density of states can be treated as a continuous function of the internal energy of the system.

Microstate of a system: The microstate of a system at any time is given by specifying the maximum possible information about the system, e.g. the position and velocity of each molecule. It is a particular quantum state of a system.

Canonical Ensemble: It is a statistical representative of a system in equilibrium (thermal contact) with a heat reservoir (bath) at some fixed temperature. It has a fixed N, V and T but variable E. The system can exchange energy with the heat bath, so that the states of the system will differ in total energy. This is a closed system.

5.8 Terminal Questions:

Q 1. Find the average energy of an ideal classical gas in a canonical ensemble at temperature T.

Q 2. A system in contact witha heat reservoir at temperature T has two accessible energy states with energies 0 and 0.2 eV. If the probability of the system being in the higher energy state is 0.2, find the temperature of the heat reservoir.

Q3. Show that $<(\Delta E)^3> = T^4\left(\frac{\partial C_v}{\partial T}\right) + 2T^3C_v$ at constant volume for a system of canonical ensemble.

Q 4. How does the probability of a microstate of a system in canonical ensemble vary with the energy of state? Show the variation with the help of a graph.

Q 5. Find out the equation of state of an ideal classical gas in canonical ensemble.

Q 6. Show that the mean square fluctuations in the energy of a system in a canonical ensemble is proportional to the heat capacity of the system.

Q 7. Using the method of canonical ensemble. calculate the partition function, average energy and specific heat of a system consisting of N noninteracting quantum harmonic oscillators and show that these expressions do reduce to the corresponding classical results in the appropriate classical limit.

Q 8. Consider non-interacting particles subjected to a harmonic potential. Calculate the canonical partition function

(a) for a single particle

(b) for two distinguishable particles

(c) for two spinless fermions

(d) for two spin-zero bosons

(e) for two spin-1/2 fermions.

Compare the internal energies and entropies in these various cases. Study the limit $T \rightarrow 0$, $T \rightarrow \infty$, and $\hbar = 0$ and interpret the results physically.

Q9. Give an account of Gibb's canonical ensemble.

Q10. Prove that energy fluctuations in canonical ensemble are related to the specific heat.

5.8.1 Some Multiple Choice Questions for Practice:

Q1. A collection of independent ensembles having the same temperature T, volume V and chemical potential μ is known as

(a) microcanonical ensemble   (b) macrocanonical ensemble

(c) canonical ensemble   (d) grand canonical ensemble

Q2. A canonical ensemble provides a model for

(a) an equilibrium system with fixed volume and number of molecules and which exchanges energy with the outside world

(b) an equilibrium isolated system with fixed volume, number of molecules and energy

(c) an equilibrium system with fixed volume and which can exchange energy and matter with the surroundings

(d) a system at constant pressure

Q3. In a Maxwell-Boltzmann system with two states of energies ϵ and 2ϵ, respectively and a degeneracy of 2 for each state, the partition function is

(a) $2e^{-2\epsilon/kT}$

(b) $2e^{-3\epsilon/kT}$

(c) $e^{-\epsilon/kT} + e^{-2\epsilon/kT}$

(d) $2(e^{-\epsilon/kT} + e^{-2\epsilon/kT})$

Q4. An ensemble of systems is in thermal equilibrium with a reservoir for which kT =0.025eV. State A has an energy that is 0.1 eV above that of state B. If it is assumed the systems obey Maxwell-Boltzmann statistics and that the degeneracies of the two states are the same, then the ratio of the number of systems in state A to the number in state B is

(a) $e^{+0.25}$ (b) 1   (c) $e^{-0.25}$ (d) e^{-4}

Q5. Consider a system consisting of two distinguishable particles and having two energy states 0 and ϵ. The partition function of the system is given by

(a) $1+e^{-\beta\epsilon}$ (b) $\frac{1}{1+e^{-\beta\epsilon}}$ (c) $(1+e^{-\beta\epsilon})^2$ (d) $\frac{1}{(1+e^{-\beta\epsilon})^2}$

Q6. The classical statistics is valid under the following condition

(a) $n\lambda_T^3 = 1$ (b) $n\lambda_T^3 = 0$ (c) $n\lambda_T^3 \ll 1$ (d) $n\lambda_T^3 \gg 1$

Q7. The partition function of a single one-dimensional harmonic oscillator is

(a) $\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}$ (b) $\frac{e^{-2\beta h\nu}}{1-e^{-\beta h\nu}}$

(c) $\frac{e^{-\beta h\nu/2}}{1+e^{-\beta h\nu}}$ (d) $\frac{e^{-2\beta h\nu}}{1+e^{-\beta h\nu}}$

Q8. The number of microstates $\Omega(E)$ for an ideal gas of N monoatomic molecules is related to energy as

(a) $\Omega(E) \propto E^{3N/2}$ (b) $\Omega(E) \propto E^{N/2}$ (c) $\Omega(E) \propto E^{N}$ (d) $\Omega \propto E$

Q9. The partition function (Z) of a system of particles is related to average energy <E>

(a)$<E> = \frac{\partial Z}{\partial \beta}$ (b) $<E> = -\frac{\partial Z}{\partial \beta}$ (c) $<E> = \frac{\partial \ln Z}{\partial \beta}$ (d) $<E> = -\frac{\partial \ln Z}{\partial \beta}$

Q10. N distinguishable particles are distributed among three states having energies 0, kBT and 2kBT respectively. If the total equilibrium energy of the system is 151.23 kBT, the number of particles of the system is about

(a) 152   (b) 264   (c) 356   (d) 635

Q11. Which of the following statements is true?
(a) In a micro-canonical ensemble the total no. Of particles N and the energy E are constants while in a canonical ensemble N and temperature are constants.
(b) In a micro-canonical ensemble the total no. Of particles N is constant but the

energy E is variable while in canonical ensemble N and T are constants.
(c) In a macro-canonical ensemble N and E are constants while in a canonical ensemble N and T both vary.
(d) In a micro-canonical ensemble N and E are constants while in a canonical ensemble N is a constant but T varies.

Q12. An isolated system consists of two non-interacting spin (1/2) particles a & b fixed in space& kept in magnetic field b. Find out the total no. of microstates allowed to the system

(a) 2   (b) 4   (c) 3   (d) 0

Q13. What is the total energy of the system when one particles is in spin down state.

(a) 0   (b) $2\mu B$ (c) $-2\mu B$ (d) $4\mu B$

Q14. The partition function of two independent (non-interacting) system i and j is given by
(a) $Z_{ij} = Z_i + Z_j$ (b) $Z_{ij} = Z_i - Z_j$(c) $Z_{ij} = Z_i \times Z_j$ (d) $Z_{ij} = Z_i / Z_j$

Q15. A gas of N non-interacting particles is in thermal equilibrium at temperature T. Each particle can be in any of the possible non-degenerate states of energy 0, 2ε and 4ε.
The average energy per particle of the gas, when $\beta\varepsilon<<1$, is

(a) 2ε (b)3ε (c) $2\varepsilon/3$ (d) ε

Q16. Which of the following are the state functions of a grand canonical ensemble?

(a) E,V,N   (b) T,V,μ (c) T,V,N   (d) E,N,T

Q17. The relative fluctuation in energy of a system in a canonical ensemble is proportional to

(a) 0   (b) N   (c) $N^{1/2}$ (d) $N^{-1/2}$

Q18. In a canonical ensemble at equilibrium, F is

(a) 0   (b) constant   (c) maximum   (d) minimum

Q19. In a monatomic gas, the first excited state is only 1.5 eV above the groundstate, whiletheother excited states are much higher up. The ground state is doubly-degenerate, while the first excited state has a four-fold degeneracy. If now, the gas is heated to a temperature of 7000 K, the fraction of atoms in the excited state will be approximately

(a) 0.07   (b) 0.14   (c) 0.42   (d) 0.3

Q20. A system consists of N weakly interacting subsystems, each with two internal quantum states with energies 0 and ϵ. The internal energy for this system at absolute temperature T is equal to

(a) $N\epsilon e^{-\epsilon/kT}$ (b) 3/2 NKT   (c)$\frac{N\epsilon}{e^{\epsilon/kT}+1}$ (d) $\frac{N\epsilon}{1+e^{-\epsilon/kT}}$

Q21. Consider an ensemble of quantum particles each of which can be in one of two states of energy E_1 and E_2. This system is in equilibrium at temperature T= 300 K. Let N_1 and N_2

denote the average number of particles in the two states. If the ratio N_2/N_1 is $1/e$, the frequency of the radiation corresponding to transition between the two states is approximately

(a) 62×10^9 Hz   (b) 62×10^{11} Hz   (c) 62×10^{13} Hz (d) 62×10^{15} Hz

Q22. Two non-interacting particles are distributed in three distinct states. Let P_c be the probability for both of them in the same state in case particles are distinguishable and P_b the probability for them to be in the same state in case they are indistinguishable bosons. The ratio P_c/P_b is

(a) 3/2   (b) 1   (c) 2/3   (d) 1/3

Q23. An isolated system has N non-interacting particles. If each particle can exist in three states, the entropy of the system according to Boltzmann's prescription is given by

(a) $Nk_B \ln 2$ (b) $Nk_B \ln 3$ (c) $k_B \ln(3N)$ (d) $3k_B \ln(N)$

Q24. The classical statistics is valid under the following condition

(b) $n\lambda_T^3 = 1$ (b) $n\lambda_T^3 = 0$ (c) $n\lambda_T^3 \ll 1$ (d) $n\lambda_T^3 \gg 1$

Q25. The number of microstates $\Omega(E)$ for an ideal gas of N monoatomic molecules is related to energy as

(b) $\Omega(E) \propto E^{3N/2}$ (b) $\Omega(E) \propto E^{N/2}$ (c) $\Omega(E) \propto E^N$ (d) $\Omega \propto E$

Q26. An ensemble is said to be in statistical equilibrium if the phase point density

(a) is zero   (b) varies linearly with time

(c) varies inversely with time   (d) is time independent

5.9 References:

1. Statistical Mechanics by R. K. Pathria
2. Statistical Mechanics by K. Huang
3. Statistical Mechanics by L. D. Landau and E. M. Lifshitz
4. Fundamentals of Statistical and Thermal Physics by E. Reif
5. Thermodynamic, Kinetic Theory and Statistical Thermodynamics by F. W. Sear and G. L. Salinger
6. Statistical Mechanics by GeetaSanon
7. Statistical Mechanics by R. H. Fowler
8. Introductory Statistical Mechanics: R. Bowley and M. Sanchez (Oxford Univ. Press)
9. Statistical Physics: F. Mandl (Wiley)
10. Problems and Solutions on Thermodynamics and Statistical Mechanics: Lim Yung-Kou
    (Sarat Book House)

11. Elementary Statistical Physics by C. Kittel
12. Statistical Mechanics by R. Kubo

5.10 Suggested Readings:

1. Statistical Physics: Berkeley Physics Course, F. Reif, (McGraw-Hill)

2. An Introduction to Statistical Physics: W.G.V. Rosser (Wiley)

3. An Introduction to Thermal Physics: D. Schroeder (Pearson)

4. Concepts in Thermal Physics: Blundell and Blundell (Oxford Univ. press)

5. Statistical and Thermal Physics: Loknathan and Gambhir (PHI)

UNIT 6   GRAND – CANONICAL ENSEMBLE

Structure

6.1 Introduction:

The given unit discuss another important ensemble of statistical mechanics, grand canonical ensemble which allows the subsystem to exchange both energy and number of particles. It plays a central role in statistical mechanics where we need an ensemble having neither energy nor number of particles are fixed. In the case of canonical ensemble, system is considered in thermal equilibrium with a heat bath (taken as a closed system) while grand canonical ensemble is taken in contact with both heat and particle bath (open system).

The partition function is used as an important parameter to solve various thermodynamic quantities for grand canonical ensemble as well. Here, both N and E may take any value from zero and infinity. To know the actual picture,we have explained energy and particle fluctuations. In the grand canonical systems, the distribution function and the phase space both will have dependence on the number of particles in the subsystem so the number of particles plays very crucial role in grand canonical ensemble.

6.2 Objectives:

Students will understand:

6. About grand canonical.
7. Role of G.C. partition function.
8. Ideal gas equation for G.C.E. for a perfect gas
9. Mean Energy for a G.C.E
10. Energy and particle fluctuations in Grand Canonical Ensembles.
11. Comparison of all ensembles.

6.3   GRAND – CANONICAL ENSEMBLE:

It is a large collection of copies of subsystems. For the macroscopic system, the number of copies has to be 10^{24} equivalent to N. The characteristics of grand canonical ensemble are:

(i)   The walls are rigid specified by volume.
(ii)   They are conducting specified by temperature.
(iii)   They are permeable specified by chemical potential.

$$E \neq \text{constant}, T = \text{constant}$$

$$N \neq \text{constant}, \mu = \text{constant}$$

$$V = \text{constant}$$

Therefore,   [V, T, μ] are the controlling variables here.

Let us conrider a subsystem S_1 under study. It is immersed in S_2 where S_2 consists of heat reservoirs and particle reservoirs. Both together form a system S specified by (N, V, T). S_1 & S_2 are kept at same temperature and since T is a defined quantitytherefore both S_1 & S_2 are canonical ensembles.

S_1 has H(p, q, N_1)
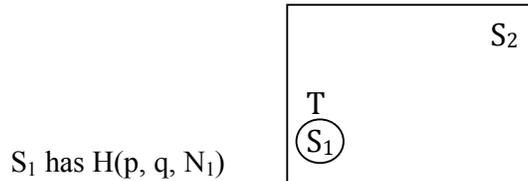
S_2 has H(p_2, Q_2, N_2) are respectively Hamiltonians.

The restrictions here are:-

$N_1 + N_2 = N$ $\qquad$ $S_1 << S_2$

$V_1 + V_2 = V$ $\qquad$ $N_2 >> N_1, V_2 >> V_1$

These are very strong inequalities which are resulted ∵ of reservoir.

$\rho(p_1, q_1, N_1)$ and $\rho(p_2, q_2, N_2)$ are the phase densities of subsystem S_1 & S_2 respectively.

$\rho(p_1, q_1, N_1) \propto$ Probability that there are N_1 particles in volume V_1 with coordinates p_1, q_1, n_1

Since this subsystem is immersed in S_2.∴the $\rho(p_1, q_1, N_1)$ is dependent in the partition function of S_1 & S_2 but how are they related?

They can't be directly multiplied. Since we're not interested in the path of S_2 but the result does not depend upon path. So, we integrate it over the whole space of path.

$$\rho(p_1, q_1, N_1) \propto e^{-\beta H(p_1, q_1, N_1)} \int e^{-\beta H(p_2, q_2, N_2)} \, dp_2 \, dq_2$$

Q_N is the normalisation factor which we obtained for normalised ρ.

To remove this proportional sign we've to do the normalisation ∵ of that we divide it by Q_N.

$$\rho(p_1, q_1, N_1) \propto \frac{e^{-\beta H(p_1, q_1, N_1)}}{Q_N \cdot h^{3N_1} N_1} \cdot \int_{v_2} \frac{e^{-\beta H(p_2, q_2, N_2)}}{h^{3N_2} N_2!} dp_2 \, dq_2$$

$$\propto \frac{e^{-\beta H(p_1, q_1, N_1)}}{h^{3N_1} N_1!} \cdot \frac{Q_{N2}}{Q_N}$$

$$\rho(p_1, q_1, N_1) = \frac{Q_{N2}}{Q_N} \cdot \frac{e^{-\beta H(p_2, q_2, N_2)}}{h^{3N_1} N_1!}$$

$$Q_{N_2}(V_2, T) = e^{-\beta A(N_2, V_2, T)}$$

Since we know that partition function is a dimensionless quantity which can be written as $e^{-\beta A}$

$$Q_N(V, T) = e^{-\beta A(N, V, T)}$$

$$\frac{Q_{N_2}}{Q_N} = e^{-\beta[A(N_2, V_2, T) - A(N, V, T)]} \qquad \qquad \text{...(a)}$$

N >> N$_1$& V >> V$_1$, expand using Taylor's expansion

A (N$_2$, V$_2$, T) = A (N − N$_1$, V − V$_1$, T)

$$= \text{A (N, V, T)} - N_1 \left(\frac{\partial A}{\partial N_2}\right)_{N_2 = N} - V_1 \left(\frac{\partial A}{\partial V_2}\right)_{V_2 = 0}$$

= A(N, V, T) − N$_1\mu$ + V$_1$P

Now equ. (a) becomes,

$$\frac{Q_{N_2}}{Q_N} = e^{-\beta(-N_1\mu + V_2 P)}$$

Now,

$$\rho(p_1, q_1, \mu) = e^{(N_2\beta_2\mu)} \frac{e^{-\beta P V_1 - \beta H(p, q, \mu)}}{N_1! h^{3N_1}}$$

Similarly,

$$\rho(p_1, q_1, N) = \left(e^{\beta\mu}\right)^N \frac{e^{-\beta P V} e^{-\beta H(p, q, N)}}{N_1! h^{3N}}$$

Where $e^{\beta\mu}$ is the quantity which is defining that the ensemble is Grand CanonicalFugacity.

We define $z = e^{\beta\mu}$ as the fugacity which tells us that there's an exchange of matter as well as energy.

Fugacity is the signature of G.C.E.

$$\rho(p_1, q_1, N) = \frac{z^N}{N_1! h^{3N}} e^{-\beta P V - \beta H(p, q, N)}$$

This is the phase density of the system.

According to normalisation condition the phase density integrated over entire space has to be 1.

$$\sum_{n=0}^{\infty} \int \rho(p,q,N)dpdq = 1$$

$$\sum_{n=0}^{\infty} Z^N e^{-\beta PV} \int \frac{e^{\beta u(p,q,N)}}{N!h^{3N}} dpdq = 1$$

$e^{\beta PV} \rightarrow$ This quantity is independent of p, q, N $\therefore$ it can be written outside the summation & integral sign.

$$e^{-\beta PV} \sum z^N Q_N(V,T) = 1$$

$$\sum z^N Q_N(V,T) = e^{\beta PV}$$

6.4 Definition of G.C. partition function:

$$\sum Z^N Q_N(V,T) = -\Xi(Z,V,T)$$

Our G.C.E partition function is the fugacity multiplied by old canonical partition function.

Now,

$$\Xi(Z,V,T) - e^{\beta PV}$$

$$\beta PV = \ln \Xi (Z,V,T) \left\{ \beta = \frac{1}{kT} \right\}$$

$$\frac{PV}{kT} = \ln \Xi (Z,V,T)$$

$$PV = kT \ln \Xi (Z,V,T) \qquad \dots (A)$$

Now, we've the following results

$$ST = kT \ln \Omega \qquad = \qquad \text{Canonical}$$

$$A = -kT \ln Q_N \qquad = \qquad \text{Micro-canonical}$$

$$PV = kT \ln \Xi \qquad = \qquad \text{Grand Canonical}$$

"A partition function helps us to lead the ideal gas equation".

e.g., For a perfect gas

$$\ln \Xi = N \qquad \{\text{dimensionless}\}$$

Using (A),

PV = NKT   Ideal gas equation.

6.5 Deriving the ideal gas equation for G.C.E. for a perfect gas:-

The value of $Q_N = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N$

$$= \frac{1}{N!}\left[\frac{V}{h^3}(2\Pi mkT)\right)^{\frac{3}{2}}]^N$$

∵   for perfect gas, $\lambda = \dfrac{h}{(2\Pi m kT)^{\frac{1}{2}}}$

The G.C. partition function,

$$= \sum_{N=0}^{\infty} Z^N Q_N$$

$$\Xi = \sum_{N=0}^{\infty} \frac{\left[ZV\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right]^N}{N!}$$

By definition, $\sum_{N=0}^{\infty} \frac{x^N}{N!} = \exp(x)$

Hence,

$$\Xi = exp\left[ZV\left(\frac{2\Pi mkT}{h^2}\right)^{\frac{3}{2}}\right]$$

$$\ln \Xi = ZV\left(\frac{2\Pi mkT}{h^2}\right)^{\frac{3}{2}} \qquad \qquad …(1)$$

Wa've found earlier

$$\frac{PV}{kT} = \ln \Xi \qquad \qquad …(2)$$

on equating (1) & (2), we've

$$\frac{PV}{kT} = ZV\left(\frac{2\Pi mkT}{h^2}\right)^{\frac{3}{2}} \qquad \qquad …(3)$$

\#   If our G.C.E. is in equilibrium then there must be some mean of N.

By definition,

$$\langle N \rangle = \frac{\sum_{N=0}^{\infty} N Z^N Q_N (V,T)}{\sum_{N=0}^{\infty} Z^N Q_N (V,T)} \qquad ………(4)$$

$$ln\, \Xi = ln \sum_{N=0}^{\infty} Z^N Q_N$$

Diff. w.r.t. z

$$\frac{\partial}{dz}(ln\, \Xi) = \frac{\sum_{N=0}^{\infty} N Z^{N-1} Q_N}{\sum_{N=0}^{\infty} Z^N Q_N}$$

$$Z\frac{\partial}{dz}(ln\, \Xi) = \frac{\sum_{N=0}^{\infty} N Z^N Q_N}{\sum_{N=0}^{\infty} Z^N Q_N} ------(5)$$

on comparing (4) & (5) we obtain,

$$Z\frac{\partial}{\partial z}(ln\, \Xi) = N \qquad\qquad ...(6)$$

on using (1) in (6) we obtain

$$Z\frac{\partial}{\partial z}\left(ZV \left(\frac{2\Pi mkT}{h^2}\right)^{\frac{3}{2}} \right) = N$$

$$ZV \left(\frac{2\Pi mkT}{h^2}\right)^{\frac{3}{2}} = N -------(7)$$

on substituting (7) equ.in (3) we obtain

$$\frac{PV}{kT} - N$$

Where z is independent of β while Q_N is independent of z

$\Rightarrow$ PV = NKT

This is equation of state for a perfect gas G.C.E.

6.6   Mean Energy for a G.C.E.:-

To prove $<H> = \frac{-\partial}{\partial \beta} ln\, \Xi$

PROOF:-   The mean H is defined by,

$$<H> = \frac{\sum_{N=0}^{\infty} H Z^N Q_N}{\sum_{N=0}^{\infty} Z^N Q_N}$$

We've $ln \Xi = ln \sum_{N=0}^{\infty} Z^N Q_N$

Diff. w.r.t. β

$$\frac{\partial}{\partial \beta}(\ln \Xi) = \frac{\partial}{\partial \beta} \ln \left(\sum_{N=0}^{\infty} Z^N - \frac{1}{h^{3N} N!} \int e^{-\beta H} d\omega\right)$$

$$= \frac{\sum_{N=0}^{\infty} -\frac{H Z^N \int e^{-\beta H} d\omega}{h^{3N} N!}}{\sum_{N=0}^{\infty} Z^N Q_N}$$

$$= \frac{\sum_{N=0}^{\infty} -H Q_N Z^N}{\sum_{N=0}^{\infty} Z^N Q_N} \qquad \qquad ...(9)$$

On comparing eqn^n (8) & (9) we obtain

$$<H> = \frac{-\partial}{\partial \beta}(\ln \Xi)$$

Now, using this relation we can find out the value of mean energy for perfect gas.

$$\frac{\partial}{\partial \beta}(\ln \Xi) = \frac{\partial}{\partial \beta} \ln(\sum_{N=0}^{\infty} Z^N Q_N) \qquad \text{using equ. (1)}$$

$$= \frac{\partial}{\partial \beta}\left[ZV \left(\frac{2\Pi m}{h^2 \beta}\right)^{\frac{5}{2}-1}\right]$$

$$= ZV \left(\frac{2\Pi m}{h^2 \beta}\right)^{\frac{5}{2}} - \frac{3}{2} \beta^{-\frac{5}{2}}$$

$$= -\frac{3}{2} \frac{ZV}{\beta^{\frac{5}{2}}} \left(\frac{2\Pi m}{h^2}\right)^{\frac{3}{2}} \times \frac{\beta}{\beta}$$

$$= -\frac{3N}{2\varrho}$$

$$< H > = \frac{\partial}{\partial \beta} \ln(\Xi)$$

$$< H > = +\frac{3}{2} NKT \qquad \text{It is the energy for on ideal gas}$$

6.7   Particles Fluctuations in Grand CanonicalEnsemble

We have proved that the energy fluctuations are very small for canonical ensembles. We'll prove the same thing for Grand Canonical. Let N(bar) is the total phase density integrated over entire phase volume.

$$\overline{N} = \frac{\sum_{N=0}^{\infty} \int N\rho(p,q,N)dpdq}{\sum_{N=0}^{\infty} \int \rho(p,q,N)dpdq}$$

$$\overline{N} = \sum_{N=0}^{\infty} N \int \rho\, dpdq$$

when we say, $N = \infty$ then

$$\rho(p,q,N) = \frac{z^N e^{-\beta PV} e^{-\beta H}}{N!\, h^{3N}}$$

$$\overline{N} = \sum_{N=0}^{\infty} NZ^N \frac{\int e^{-\beta PV} e^{-\beta H}}{N! h^{3N}} dpdq$$

$$= \sum_{N=0}^{\infty} NZ^N \frac{\int e^{-\beta H} dpdq \,/\, N! h^{3N}}{e^{\beta PV}}$$

$$= \sum_{N=0}^{\infty} NZ^N \frac{Q_N}{e^{\beta PV}} \quad\text{------------(10)}$$

Using (A), we've

$$\frac{PV}{kT} = \ln \Xi$$

$$\Rightarrow \quad \exp\beta PV = \Xi$$

Substitute this in equ. (10)

$$\overline{N} = \sum_{N=0}^{\infty} \frac{NZ^N Q_N}{\Xi}$$

$$\overline{N} = \frac{\sum_{N=0}^{\infty} NZ^N Q_N}{\sum_{N=0}^{\infty} Z^N Q_N} \qquad\qquad ...(11)$$

We define,

$$\Xi(Z,V,T) = \sum_{N=0}^{\infty} Z^N Q_N$$

$$\frac{\partial \Xi}{\partial z} = \sum NZ^{N-1} Q_N$$

$$Z\frac{\partial \Xi}{\partial z} = \sum_{N=0}^{\infty} NZ^N Q_N \qquad\qquad ...(12)$$

Substitute (12) in (11)

$$\overline{N} = \left(Z \frac{\partial \Xi}{\partial Z}\right)/\Xi \qquad \ldots(13)$$

We've expressed average number of particle in terms of Grand Canonical partition function.

Now finding the value for $<N^2>$

$$< N^2 > = \frac{\sum_{N=0}^{\infty} N^2 Z^N Q_N}{\sum_{N=0}^{\infty} Z^N Q_N} \qquad \ldots(14)$$

On Diff. w.r.t.Z, equ. (12) we get

$$\frac{\partial \Xi}{\partial Z} + Z \frac{\partial^2 \Xi}{\partial Z^2} = \sum_{N=0}^{\infty} N^2 Z^{N-1} Q_N$$

$$Z \frac{\partial \Xi}{\partial Z} + Z \frac{\partial^2 \Xi}{\partial Z^2} = \sum_{N=0}^{\infty} N^2 Z^N Q_N \qquad \ldots(15)$$

$$Z\left(\frac{\partial}{\partial Z}\left(Z \frac{\partial \Xi}{\partial Z}\right)\right) = \sum_{N=0}^{\infty} N^2 Z^N Q_N$$

When we Substitute (15) in (14), we obtain

$$< N^2 > = \frac{1}{\Xi}\left(Z \frac{\partial \Xi}{\partial Z} + Z^2 \frac{\partial^2 \Xi}{\partial Z^2}\right) \qquad \ldots(16)$$

Equ. $(16) - [(13)]^2$

$$< N^2 > - < N >^2 = \frac{1}{\Xi}\left(Z \frac{\partial \Xi}{\partial Z} + Z^2 \frac{\partial^2 \Xi}{\partial Z^2}\right) - \frac{Z^2}{\Xi^2}\left(\frac{\partial \Xi}{\partial Z}\right)^2 \qquad \ldots(17)$$

we ought to simplify equ. (17). For this diff. (13) w.r.t.Z again,

$$\frac{\partial}{\partial Z} < N > = \frac{\partial}{\partial Z}\left[\frac{Z\left(\frac{\partial \Xi}{\partial Z}\right)_{V,T}}{\Xi}\right]$$

$$= \frac{\Xi \frac{\partial}{\partial Z}\left[Z\left(\frac{\partial \Xi}{\partial Z}\right)\right] - Z\left(\frac{\partial \Xi}{\partial Z}\right)\left(\frac{\partial \Xi}{\partial Z}\right)}{\Xi^2}$$

$$= \frac{\Xi \frac{\partial \Xi}{\partial Z} + \Xi Z \frac{\partial^2 \Xi}{\partial Z^2} - Z\left(\frac{\partial \Xi}{\partial Z}\right)^2}{\Xi^2}$$

Multiply by z,

$$Z \frac{\partial}{\partial Z} < N > = \frac{1}{\Xi}\left[Z \frac{\partial \Xi}{\partial Z} + Z^2 \frac{\partial^2 \Xi}{\partial Z^2}\right] - \frac{Z^2}{\Xi^2}\left(\frac{\partial \Xi}{\partial Z}\right)^2 \qquad \ldots(18)$$

When we Substitute (18) in (17) we obtain

$$\langle N^2 \rangle - \langle N \rangle^2 = Z\frac{\partial}{\partial Z}\langle N \rangle \qquad \ldots(19)$$

$$Z = e^{\beta\mu} = \text{fugacity}$$

Since we know that exponentials and logarithmic are of dimensionless quantity, this implies that $\beta\mu$ is dimensionless

Z = It is the signature of temperature & exchange of energy.

Equ.(19) in terms of β will be

$$. \langle N^2 \rangle - \langle N \rangle^2 = e^{\beta\mu}\left[\frac{\partial \langle N}{\partial(e^{\beta\mu})}\right]_{V,T}$$

$$= e^{\beta\mu}.\frac{1}{e^{\beta\mu}}.\frac{1}{\beta}\left[\frac{\partial \langle N \rangle}{\partial \mu}\right]_{V,T}$$

$$\langle N^2 \rangle - \langle N \rangle^2 = kT\left[\frac{\partial \langle N \rangle}{\partial \mu}\right]_{V,T}$$

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} = \frac{kT}{\langle N \rangle^2}\left[\frac{\partial \langle N \rangle}{\partial \mu}\right]_{V,T} \qquad \ldots(20)$$

So far, we're doing statistical mechanics. Now we want to go to thermodynamics. In thermodynamics we replace $\langle N \rangle$ by its thermodynamic limit N.

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} - \frac{kT}{N^2}\left[\frac{\partial N}{\partial \mu}\right]_{V,T} \qquad \ldots(21)$$

$\langle N \rangle \sim N$ Here

We've the relation,

$Nd\mu = VdP - SdT$

$$d\mu = \frac{V}{N}dP - \frac{S}{N}dT \qquad \qquad (\frac{V}{N} = v = \text{Specific volume})$$

$$= vdp - \frac{S}{N}dT$$

Diff. adore eqn [n] w.r.t. v

$$\frac{\partial \mu}{\partial v} = v\left(\frac{\partial P}{\partial v}\right)_{N,T}$$

$$\left[\frac{\partial \mu}{\partial\left(\frac{V}{N}\right)}\right]_{T,V} = v\left[\frac{\partial P}{\partial\left(\frac{V}{N}\right)}\right]_{T,V}$$

$$-\frac{N^2}{V}\left(\frac{\partial \mu}{\partial N}\right)_{V,T} = vN\left[\frac{\partial P}{\partial V}\right]_{N,T} \qquad\qquad [V = vN]$$

$$-\frac{N^2}{V}\left(\frac{\partial \mu}{\partial N}\right)_{V,T} = V\left[\frac{\partial P}{\partial V}\right]_{N,T}$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{V,T} = -\frac{V^2}{N^2}\left[\frac{\partial P}{\partial V}\right]_{N,T} \qquad\qquad …(22)$$

Put (22) in (21)

$$\frac{<N^2>-<N>^2}{<N>^2} = \frac{-kT}{V^2}\left[\frac{\partial V}{\partial P}\right]_{N,T}$$

But $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{N,T} = \chi_T$ which is referred to as isothermal compressibility.

Isothermal compressibility is the change in volume w.r.t. pressure keeping temperature and N constant.

Hence,

$$\frac{<N^2>-<N>^2}{<N>^2} = \frac{kT}{N^2}\chi_T$$

The fluctuations of particles for G.C.E. is

$$\sqrt{\frac{<N^2>-<N>^2}{<N>^2}} = \sqrt{\frac{kT\chi_T}{V}} \qquad\qquad …(23)$$

This again shows that particle fluctuation will vary with $\frac{1}{\sqrt{N}}$ times. This result is similar to the result obtained for C.E.

EQUIVALENCE CRITERIA "All the ensembles are equivalent becauseall have very tiny energy fluctuations".

This is equivalence criteria for ensembles.

In equ.(23), χ_T is an intensive parameter.

V is an Extensive parameter.

Determining particle fluctuation for perfect gas:-

For a perfect gas,

PV = NKT

$\Rightarrow$ $V = \frac{NKT}{P}$

To obtain χ_T differentiate above equation,

$$\frac{\partial V}{\partial P} = -\frac{NKT}{P^2}$$

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right) = \frac{NKT}{P.PV}$$

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right) = \frac{1}{P} \text{ for perfect gas}$$

So the fluctuation $= \sqrt{\frac{KT}{V}\cdot\frac{1}{P}} = \frac{1}{\sqrt{N}}$ 　　　　　 …(24)

So for a perfect gas, fluctuations are equal to $\frac{1}{\sqrt{N}}$ ordinarily. But there may be exceptions too like the one which is met in the case of phase transitions.

In these conditions compressibility of a given system can become extremely large as is evident by an almost flattening of isothermal.

The point in P— V Curve where phase of a substance changes from phase 1 to 2 is the critical point. Here $\frac{\partial V}{\partial P}$ is very large. So near the critical point, the fluctuations will be the order of $\frac{1}{N}$.
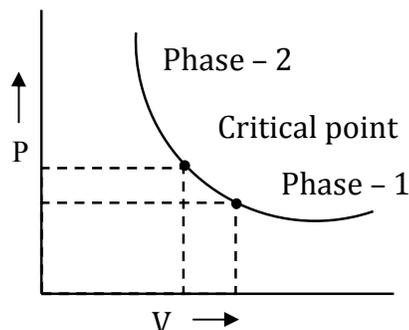
Far away from the critical points, fluctuations are ordinary. The large fluctuations near critical point account for the existence of phenomenon like 'Critical opalescence'.

6.8 Energy Fluctuations in Grand Canonical Ensemble:

The mean value of energy is given by,

$$< H >= \frac{\sum_{N=0}^{\infty} \int H \rho(p,q,N)dpdq}{\sum_{N=0}^{\infty} \int \rho(p,q,N)dpdq}$$

The denominator term as normalisation constant = 1

$$< H >= \sum_{N=0}^{\infty} \int H \rho(p,q,N)dpdq \ldots(25)$$

For G.C.E., the normalised value of

$$\rho(p,q,N) = \frac{Z^N e^{-\beta H}}{N!h^{3N}}/\Xi$$

$$\Xi = \sum_{N=0}^{\infty} Z^N Q_N \qquad \ldots(26)$$

Substitute ρ and Ξ in equ. 25,

$$< H >= \sum_{N=0}^{\infty} \int H \frac{z^N e^{-\beta H}/N!h^{3N} \, dpdq}{\sum Z^N Q_N} \qquad \ldots(27)$$

On differentiating equ. 26 w.r.t. β

$$\frac{\partial \Xi}{\partial \beta} = \sum Z^N \frac{\partial Q_N}{\partial \beta}$$

$$= \sum Z^N \frac{\partial}{\partial \beta} \int \frac{e^{-\beta H}}{N! \, h^{3N}} dpdq$$

$$< H >= \sum_{N=0}^{\infty} \int \frac{-H e^{-\beta H} dpdq}{N!h^{3N}} \qquad \ldots(28)$$

using (28) in (27) we obtain

$$< H >= -\frac{1}{\Xi}\left(\frac{\partial \Xi}{\partial \beta}\right) \qquad \ldots(29)$$

Now finding $<H^2>$

$$< H^2 >- \sum_{N=0}^{\infty} \frac{\int H^2 Z^N e^{-\beta H}/N!h^{3N} \, dpdq}{\Xi}$$

On differentiating equ. (28) again w.r.t. β we get

$$\frac{\partial^2 \Xi}{d\beta^2} = \sum_{N=0}^{\infty} Z^N \int \frac{H^2 e^{-\beta H}}{N!h^{3N}} dpdq$$

This is nothing but N_1 of $<H^2>$. Hence we obtain

$$< H^2 >= \frac{1}{E}\frac{\partial^2 E}{\partial \beta^2} \qquad \qquad \text{...(30)}$$

To find energy fluctuation subtract (30) – (29)²

$$<H^2> - <H>^2 = \frac{1}{E}\frac{\partial^2 E}{\partial \beta^2} - \frac{1}{E^2}\left(\frac{\partial E}{\partial \beta}\right)^2 \qquad \qquad \text{...(31)}$$

This quantity has to be related to a Thermodynamics quantity and since for canonical ensemble ΔE was directly related to C_V. Here too we expect the same relation,

Differentiate (29) w.r.t. β

$$\frac{\partial}{\partial \beta} < H > = \frac{\partial}{\partial \beta}\left(-\frac{1}{E}\left(\frac{\partial E}{\partial \beta}\right)\right)$$

$$= -\frac{1}{E}\frac{\partial^2 E}{\partial \beta^2} + \frac{1}{E^2}\left(\frac{\partial E}{\partial \beta}\right)^2 \qquad \qquad \text{...(31)}$$

On comparing (30) & (31), we've

$$<H^2> - <H>^2 = -\frac{\partial}{\partial \beta^2} < H > \qquad \qquad \text{...(32)}$$

using the result for canonical ensemble,

$$\frac{-\partial}{\partial \beta} < H = kT^2 C_V$$

Here too, we've energy fluctuations,

$$\frac{\Delta E}{E} = \sqrt{\frac{<H^2>-<H>^2}{<H>^2}} = \sqrt{\frac{kT^2 C_V}{E}} \times \frac{1}{\sqrt{N}}$$

So, the energy fluctuations are same for the Canonical & Grand Canonical but only when we're away from the critical point.

6.9   Comparison of Ensembles:

S.No.	MicroCanonical Ensemble	Canonical Ensemble	Grand Canonical Ensemble
1.	Walls are rigid, impermeable & wall	Walls are rigid, impermeable & diathermal	Rigid, permeable & diathermal walls

	insulated.		
2.	Constant parameter are E, V, N	Constant parameter are T, V, N	Constant parameter are T, V, μ
3.	No exchange of energy & particle with surroundings.	Only energy can exchange with surrounding not particle.	Both energy & particle can exchange with surroundings.
4.	ρ (E)=constant	ρ= A exp(-E/kT)	ρ= exp(Ω+Nμ-E/kT)
5.	Thermodynamic state function is S (E, V, N)	Thermodynamic state function is A (T, V, N) or F	Thermodynamic state function is ϕ(T, V, μ) or PV
6.	Partition function is Ω(E, V, N)	Q_N (T, V, N) or Ω	Ξ(T, V, μ)
7.	S = k ln Ω	A = - kT ln Q_N(or Ω)	PV= kT ln Ξ

6.10 Summary:

In the given unit you have discussedanother important ensemble of statistical mechanics, i.e., grand canonical ensemble which allows the subsystem to exchange both energy and number of particles. Here, you focussed on the ensemble where neither energy nor number of particles are fixed. You have also discussed and analysedin the case of grand canonical ensemble the system is taken in contact with both heat and particle bath (open system). Here, in this unit you have discussed the partition function which is used to solve various thermodynamic quantities for grand canonical ensemble. Here, you have analysed both N and E may take any value from zero and infinity. You have also learnt how to computeenergy and particle fluctuations to know the actual picture.Here, in this unit, you have discussed the grand canonical system, the distribution function and the phase space which have dependence on the number of particles in the subsystem so the number of particles plays very crucial role in grand canonical ensemble. At the end, you discussed the comparison of an ensembles. Finally, to check your progress, multiple choice questions and terminal questions are given in the unit.

6.11 Glossary:

Grand Canonical Ensemble: System separated by a rigid, impermeable and diathermal walls.

Partition Function: Indicate that how the gas molecules of an assembly are distributed among the different energy levels.

Fugacity: It refers to the activity or the ability of a gas to expand.It is more convenient to workwith the function $Z = e^{\beta\mu}$ which is called fugacity.

Chemical potential (μ): It is the change in the energy of the system as a result of the change in its number ofparticles, when every other thermodynamical variable that describes the state of thesystem, such as entropy, volume, etc., is kept constant.It has the units of energy/molecule, or otherwise stated, for a single species of particlesin a G.C.E. -∞<μ<0 for bosons and -∞<μ<∞ for fermions.

6.12 Terminal Questions:

Q1. Consider a grand-canonical system in which a state with energy 2kT and 21 particles has a probability of 0.004, while a state with energy 3kT and 20 particles has a probability of 0.002. Find the temperature of the system if it has a chemical potential value -1.15 X 10^{-21} J. Also find out the value of grand partition function of the system.

Q 2. Find the grand partition function of 1 mole of argon gas at 300 K and 1 atm pressure if it has a chemical potential value -0.212.

Q 3. Derive an expression for grand canonical partition function and hence grand canonical distribution.

Q 4. Show that the relative fluctuation in the particle number in a system in grand canonical ensemble is inversely proportional to the square root of mean particle number in the system, N.

Q 5. Consider a grand-canonical system in which a state with energy 2kT and 21 particles has a probability of 0.004, while a state with energy 3kT and 20 particles has a probability of 0.002. Find the temperature of the system if it has a chemical potential value -1.15 X 10^{-21} J. Also find out the value of grand partition function of the system.

Q 6. Find the grand partition function of 1 mole of argon gas at 300 K and 1 atm pressure if it has a chemical potential value -0.212.

Q 7. Derive an expression for grand canonical partition function and hence grand canonical distribution.

Q8. Show that the relative fluctuation in the particle number in a system in grand canonicalensemble is inversely proportional to the square root of mean particle number in the system, N.

Q9. Deduce the equation of state and the entropy of an ideal classical gas in a grand canonical ensemble. Show that the results are the same as obtained in a canonical ensemble. What do you infer from this?

Q10. Obtain the expression for the chemical potential µ (T, P) for an ideal gas of non-relativistic particles in a grand canonical ensemble.

6.12.1 Some Multiple Choice Questions for Practice:

Q1. Which of the following statements is true?
(a) In a micro-canonical ensemble the total no. Of particles N and the energy E are constants while in a canonical ensemble N and temperature are constants.
(b) In a micro-canonical ensemble the total no. Of particles N is constant but the energy E is variable while in canonical ensemble N and T are constants.
(c) In a macro-canonical ensemble N and E are constants while in a canonical ensemble N and T both vary.
(d) In a micro-canonical ensemble N and E are constants while in a canonical ensemble N is a constant but T varies.

Q2. Which of the following are the state functions of a grand canonical ensemble?

(a) E,V,N   (b) T,V,µ   (c) T,V,N   (d) E,N,T

Q3. The chemical potential µ of a system in grand canonical ensemble is

(a) positive   (b) fixed   (c) variable   (d) 0

Q4. The probability of finding subsystem with n atoms of a perfect gas in grand canonical ensemble is ($\bar{n}$ is mean number of atoms present)

(a) $\omega(n) = \frac{1}{n!}(\bar{n})^n \rho^{-\bar{n}}$ (b) $\frac{1}{n!}\rho^{-\bar{n}}$ (c) $(\bar{n})^{n-1}\rho^{-\bar{n}}$ (d) $n_i(\bar{n})^n e^{-\bar{n}}$

Q5. Two examples of G.C.E. are

(a) an ideal gas   (b) a photon gas   (c) radioactive decay   (d) a paramagnetic solid

Q6. Entropy (s) is related to the Grand partition function by the relation

(a) $s = k \ln z$ (b) $s = k \ln z + \frac{E}{T}$ (c) $s = k \ln z + \frac{E}{T} + \frac{\mu N}{T}$ (d) $s = k \ln z + \frac{E}{T} - \frac{\mu N}{T}$

Q6. The probability of a microstate in G.C.E. is proportional to

(a) $\frac{e^{\frac{-E}{kT}}}{z_N}$ (b) $e^{\frac{-E}{kT}}$ (c) $1/\Omega$ (d) $e^{-\beta[E-\mu N]}$

Q7. In grand-canonical ensemble the expression for probability distribution is

(a) $\rho(E) = e^{\left[\frac{\Omega + n\mu - \bar{E}}{kT}\right]}$ (b) $\rho(E) = e^{\left[\frac{\Omega + n - \mu\bar{E}}{kT}\right]}$ (c) $\rho(E) = e^{\left[\frac{\Omega + n - \bar{E}}{\mu kT}\right]}$ (d) $\rho(E) = e^{\left[\frac{\Omega\mu + n - E}{kT}\right]}$

Q8. The grand partition function of a system whose canonical partition function is Z_N is

(a) $z_N e^{\mu N}$ (b) $\sum_N z_N e^{\beta \mu N}$ (c) $\sum_N z_N e^{\beta \mu}$ (d) $\sum_N z_N e^{-\beta E}$

6.13 References:

13. Statistical Mechanics by R. K. Pathria
14. Statistical Mechanics by K. Huang
15. Statistical Mechanics by L. D. Landau and E. M. Lifshitz
16. Fundamentals of Statistical and Thermal Physics by E. Reif
17. Thermodynamic, Kinetic Theory and Statistical Thermodynamics by F. W. Sear and G. L. Salinger
18. Statistical Mechanics by GeetaSanon
19. Statistical Mechanics by R. H. Fowler
20. Introductory Statistical Mechanics: R. Bowley and M. Sanchez (Oxford Univ. Press)
21. Statistical Physics: F. Mandl (Wiley)
22. Problems and Solutions on Thermodynamics and Statistical Mechanic: Lim Yung-Kou (Sarat Book House)
23. Elementary Statistical Physics by C. Kittel
24. Statistical Mechanics by R. Kubo

6.14 Suggested Readings:

1. Statistical Physics: Berkeley Physics Course, F. Reif, (McGraw-Hill)

2. An Introduction to Statistical Physics: W.G.V. Rosser (Wiley)

3. An Introduction to Thermal Physics: D. Schroeder (Pearson)

4. Concepts in Thermal Physics: Blundell and Blundell (Oxford Univ. press)

5. Statistical and Thermal Physics: Loknathan and Gambhir (PHI)

UNIT 7:   QUANTUM STATISTICS

STRUCTURE

7.1 INTRODUCTION

In Maxwell-Boltzmann statistics or Bose – Einstein statistics, there is no restriction on the particles to be present in any energy state. But in case of Fermi-Dirac statistics, applicable to particles like electrons and obeying Pauli Exclusion Principle (no two electrons in an atom have same energy state), only one particle can occupy a single energy state. In Maxwell – Boltzmann statistics Particles are distinguishable and only particles are taken into consideration. In Fermi – Dirac statistics Particles are indistinguishable and quantum states are taken into consideration. In Bose – Einstein statistics Particles are indistinguishable and quantum states are taken into consideration. The most important application of Bose-statistics to electromagnetic radiation in thermal equilibrium, called black body radiation. The deviations from perfect gas behaviour exhibited by Bose Einstein gas is termed as 'gas degeneracy. As the temperature is lowered, beginning at $T = T_0$ the molecules fall rapidly into the ground state. There is a sort of condensation into this state. This phenomenon is known as Bose Einstein Condensation. The temperature T_0 at which the Bose Einstein condensation begins depends upon the density of the gas.

7.2 OBJECTIVES

After studying this unit, you should be able to-

- understand Symmetric and AntisymmetricWavefunctions,
- understand and use Fermi – Dirac Statistics
- understand and use Bose – Einstein Statistics
- understand Ideal Bose Einstein Gas
- understand Gas Degeneracy
- understand Ideal Fermi Dirac Gas
- understand Electron Gas

7.3.   CONSTRUCTION OF SYMMETRIC AND ANTISYMMETRIC WAVEFUNCTIONS:

We know that the number of ways in which the indices can be interchanged will give the number of solutions of the Schrödinger equation of the system. For a two particle system {let the wave functions be [1, s_1: 2,s_2]there will be 2! Solutions, similarly for n particle system there will be n! Solutions. A linear combination of these solutions will be solution of Schrödinger equation.

As an example, we can consider two and three particle functions with 2 and 6solutions respectively. The Schrödinger wave equation for two –particle system is

$$\hat{H}\psi(1,2) = E\psi(1,2) \qquad \qquad \text{…(1)}$$

The two degenerate solutions are $\psi(1,2)$ and $\psi(2,1)$. Now the symmetric wave function will be given by

$$\psi_s = \psi(1,2) + \psi(2,1) \qquad \ldots(2)$$

And ant symmetric function by

$$\psi_a = \psi(1,2) - \psi(2,1), \qquad \ldots(3)$$

Where $\psi(1,2)$ and $\psi(2,1)$ are unnormalized wave functions.

Similarly, in case of three – particle system, there are six ways of exchanging the indices of particles,

$$\psi(1,2,3), \psi(2,3,1), \psi(3,2,1), \psi(1,3,2), \psi(2,1,3) \text{ and } \psi(3,1,2)$$

And the symmetric combinations are

$$\psi_s = \{(\psi(1,2,3) + \psi(2,3,1) + \psi(3,2,1) + \psi(3,1,2) + \psi(2,1,3) + \psi(1,3,2)\}\ldots(4)$$

And antisymmetric combinations are

$$\psi_a = \{\psi(1,2,3) + \psi(2,3,1) + \psi(3,1,2)\} - \{\psi(2,1,3) + \psi(1,3,2) + \psi(3,2,1)\}\ldots(5)$$

Thus, antisymmetric wave function can be built by adding all the functions with even number of interchanges and subtracting the sum of all those with an odd number of interchanges.

The two particles will be distinguishable from each other if the sum of the probabilities of the individual wave functions in two states is equal to the probability derived by the symmetrised wave function i.e., equations (2) and (3).

Thus, $|\psi(1,2)|^2 + |\psi(2,1)|^2 = |\{\psi(1,2) \pm \psi(2,1)\}|^2$

$$= |\psi(1,2)|^2 + |\psi(2,1)|^2 + 2\text{Re}\,\psi(1,2)\psi(2,1) \qquad \ldots(6)$$

Where Re is the real part of $\{2\psi(1,2)\psi(2,1)\}$

This is possible if the overlap of wave functions $\psi(1,2)$ and $\psi(2,1)$ is zero or 2 Re $\{\psi(1,2)\psi(2,1)\}=0$. In the way when the coordinates (space and spin) of two particles are not the same between exchange degenerate functions, the interference term $2\text{Re}\,\psi(1,2)\psi(2,1)$ becomes zero and particle coordinates do not overlap.

7.4. AVERAGE VALUE AND QUANTUM STATISTICS:

The average value of a dynamical quantity (a) in the same ψ is given by

$$\langle a \rangle = \frac{\int \psi^* \hat{A} \psi dq}{\int \psi^* \psi dq} \qquad \ldots(1)$$

Where $\hat{A}$ is the operator corresponding to the dynamical quantity? Remembering that the denominator integral is unity i.e.,

$$\int \psi^* \psi \, dq = 1$$

$\therefore \qquad \langle a \rangle = \int \psi^* \bar{A} \psi \, dq \qquad \qquad \dots(2)$

For example, the average value of the x component of momentum is given by

$$\langle p_x \rangle = \frac{\int \psi^* \left(-\frac{ih}{2\pi} \frac{\partial}{\partial x}\right) \psi \, dx}{\int \psi^* \psi \, dx} \qquad \qquad ..(3)$$

In case of free particle

$$\psi = e^{\{2\pi i \sqrt{(2mE_x)}\}/h\}}$$

$\therefore \qquad \langle p_x \rangle = \sqrt{(2mE_x)} \qquad \qquad \dots(4)$

The symmetric and antisymmetriceigen functions give the following results

$$\langle a_{symm.} \rangle = \int \psi_s^* \bar{A} \psi_s \, dq \qquad \qquad \dots(5)$$

And $\qquad \langle a_{anti} \rangle = \int \psi_a^* \bar{A} \psi_a \, dq$

It is clear from equation (5) that $\langle a_{symm} \rangle$ remains unchanged due to exchange of coordinates of particles because exchange of particles leaves both ψ_s^* and ψ_s unaltered. In case of antisymmetric solution, the exchange of coordinates changes the sign of ψ_a^* and ψ_a and hence the net result is that $\langle a_{anti} \rangle$ remains unaltered. We, therefore, conclude that the exchange of particles leaves the average value unaffected. Therefore; from the quantum mechanical point of view, the similar particles leaves the average value unaffected. Therefore; from the quantum mechanical point of view, the similar particles cannot be distinguished.

7.5. FERMI – DIRAC STATISTICS:

In Maxwell-Boltzmann statistics or Bose – Einstein statistics, there is no restriction on the particles to be present in any energy state. But in case of Fermi-Dirac statistics, applicable to particles like electrons and obeying Pauli Exclusion Principle (no two electrons in an atom have same energy state), only one particle can occupy a single energy state. The distribution of four particles (a,b,c and d) among two cells x and y, each having 4 energy states. Such that there are three particle in cell x while one particle in cell y is shown in fig 4.

In this case there will be $4 \times 4 = 16$ possible distribution.

We consider a general case. This statistics is applied to indistinguishable particles having half integral spin. Though the particles are indistinguishable, the restriction imposed is that only one particle will be occupied by a single cell. The situation of distribution is as follow:

Energy level e_1, e_2, ...,e_i,...........e_k

Degeneracy g_1, g_2, ...,g_i,.....g_k

Occupation no. n_1, n_2,......,n_i,....n_k

So in case of Fermi – Dirac statistics, we have the problem of assigning n_i indistinguishable particles to g_i distinguishable levels under the restriction that only one particle will be occupied by a single level; obviously, g_i must be greater than or equal to n_i, because there must be atleast one elementary wave function available for every element in the group.

Thus in Fermi – Dirac statistics, the conditions are:

(1)   The particles are indistinguishable from each other i.e., there is no restriction between ways in which n_i particles are chosen.
(2)   Each sublevel or cell may contain 0 or one particle. Obviously g_i must be greater than or equal to n_i.
(3)   The sum of energies of all the particles in the different quantum groups, taken together, constitution the total energy of the system.

Now the distribution of n_i particles among the g_i states can be done in the following way:

We easily find that the first particle can be put in any one of the ith level in g_i ways. According to Pauli exclusion principle no more particles can be assigned to that filled state. Thus we are left with $(g_i - 1)$ states in $(g_i - 1)$ ways, and soon. Thus the number of ways in which n_i, particles can be assigned to g_i states is

$g_i(g_i - 1)(g_i - 2)............(g_i - n_i + 1)$,

$$= \frac{g_i!}{(g_i - n_i)!} \qquad \qquad \text{...(1)}$$

The permutations among identical particles do not give distribution, and hence such permutations must be excluded from equation (1), which can be done on dividing it by n_i !. Thus we have the required number as

$$= \frac{g_i!}{n_i!(g_i - n_i)!} \qquad \text{...(2)}$$

The total number of eigen states for whole system is given by

$$G = \prod \frac{g_i}{n_i!(g_i - n_i)!} \qquad \text{...(3)}$$

The probability of the specific state being proportional to G will be

$$\infty = \prod \frac{g_i}{n_i!(g_i - n_i)} \times \text{constant} \qquad \text{...(4)}$$

To obtain the condition of maximum probability, we proceed as follows:

Talking log of equation (4), we have

$$\log_{(i)} = \Sigma_i \{ \log g_i! - \log n_i! - \log(g_i - n_i)! \} + \text{constant} \qquad \qquad \ldots(5)$$

Using stirling approximation, equation (5) reduces to

$$\text{Log (i)} = \Sigma_i \{ (n_i - g_i) \log(g_i - n_i) + g_i \log g_i - n_i \log n_i \} + \text{constant} \qquad \ldots(6)$$

Differentiating equation (6) with respect to n_i, we get

$$\delta \log = \sum \delta(n_i \quad g_i) \log(g_i \quad n_i) \mid g_i \log g_i \quad n_i \log n_i \}$$

$$= \Sigma_i \{ \delta n_i \log(g_i - n_i) + \frac{n_i - g_i}{g_i - n_i}(-\delta n_i) - \delta n_i \log n_i - \frac{n_i}{n_i} \delta n_i \}$$

$$= \Sigma_i -\{ \log n_i - \log(g_i - n_i) \} \delta n_i$$

$$= - \Sigma_i \{ \log \frac{n_i}{(g_i - n_i)} \} \delta n_i$$

$$\qquad \qquad \ldots(7)$$

The condition of maximum probability gives

$$\Sigma_i \left\{ \log \frac{n_i}{(g_i - n_i)} \right\} \delta n_i = 0.$$

$$\qquad \qquad \ldots(8)$$

Introducing the auxiliary conditions,

$$\delta n = \Sigma \, \delta n_i = 0$$

$$\qquad \qquad \ldots(9)$$

$$\delta E = \Sigma \, e_i \, \delta n_i = 0.$$

$$\qquad \qquad \ldots(10)$$

And applying the Lagrange method of undetermined multipliers i.e., multiplying equations (9) by β and adding the resulting expression to equation (8), we have

$$\Sigma_i [\log \frac{n_i}{(g_i - n_i)} + \alpha + \beta \varepsilon i] \, \delta n_i = 0$$

$$\qquad \qquad \ldots(11)$$

Since δn_i s can be treated as arbitrary

$$\text{Log } \frac{n_i}{(g_i - n_i)} = -(\alpha + \beta \varepsilon i)$$

Or $\qquad \qquad \frac{g_i}{n_i} - 1 = e^{(\alpha + \beta e_i)}$

Or $\qquad n_i = \dfrac{g_i}{e^{(\alpha + \beta \varepsilon i)} + 1}$

$\qquad\qquad$ …(12)

This is the most probable distribution according to Fermi – Dirac statistics.

7.6.　　BOSE – EINSTEIN STATISTICS:

In Maxwell-Boltzmann statistics, the particles are distinguishable from each other. Thus if the two particles interchange their positions or energy state, a new state is generated. But in case of Bose – Einstein statistics, the particles are indistinguishable. So the interchange of two particles between two energy states will not produce any new state.

We consider a general case. Suppose the system contains n independent identical particles. Let these particles be divided into quantum groups or levels such that there are n_1, n_2, n_i… number of particle in groups whose approximate constant energies are $\varepsilon_1, \varepsilon_2, \varepsilon_i$ … respectively. n_1, n_2, n_i are the occupation numbers of levels i.e, the numbers of levels i.e, the numbers of levels i.e., the number of particles that are in that level. Again let there be g_i single particle states in the ith level, and we speak of this as the degeneracy or the statistical weight of the ith level. This situation is as follows:

Energy level $\qquad\qquad \varepsilon_1, \varepsilon_2, \dots, \varepsilon_i, \dots \varepsilon_k$

Degeneracies $\qquad\quad g_1, g_2, \dots g_i, \dots g_k$

Occupation no. $\qquad\quad n_1, n_2, \dots n_i, \dots, n_k$

In case of Bose – Einstein statistics, we have the problem of assigning n indistinguishable particles to g_i distinguishable levels when there is no restriction as to the number of particles that can occupy one level. G_i is also termed as density of states function which gives number of one particle states per unit energy range.

Thus in Bose – Einstein statistics, the conditions are:

(1)　　　The particles are indistinguishable from each other so that there is no distinction between the different ways in which n_i particles can be chosen.

(2)　　　Each cell or sublevel of i^{Th} quantum state contains $0, 1, 2 \dots, n_i$ identical particles.

(3)　　　The sum of energies of all particles in the different quantum groups, taken together, constitutes the total energy of the system.

For this distribution, let us imagine a box divided into g_i sections and the particles to be distributed among these sections. The choice that which of the compartments will have the sequence, can be made in g_i ways. Once this has been done, the remaining $(g_i - 1)$ compartments and n_i particles i.e., total particles $(n_i + g_i - 1)$ can be arranged in any order i.e., number of ways of doing this will be equal to $(n_i + g_i - 1)!$. Thus the total number of ways realizing the distribution will be

$$g_i(n_i + g_i - 1)!$$
$$\ldots(1)$$

The particles are indistinguishable and therefore rearrangement of particles will not give rise to any distinguishable arrangement. There are n_i !permutations which correspond to the same configuration, hence term indicated by (1) should be divided by n_i !.

Secondly, the distributions which can be derived from one another by mere permutation of the cells among themselves, does no produce different states, the term (1) should also be divided by g_i!.

We thus obtain the required number of ways as

$$\frac{g_i(n_i + g_i - 1)!}{g_i! n_i!}$$

Or
$$\frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

There will be similar expressions for various other quantum states. Therefore, the total number of ways in which n_1 particles can be assigned to the level with the energy $\varepsilon_1, n_2 \, to \, \varepsilon_2$ ... and so on is given by the product of such expressions as given below:

$$G = \frac{(n_1 + g_1 - 1)!}{n_1!(g_1 - 1)} \cdot \frac{(n_2 + g_2 - 1)!}{n_2!(g_2 - 1)!} \cdots \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)}$$

$$= \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!},$$
$$\ldots(2)$$

According to the postulate of a priori probability of eigen states, we have the probability (i) of the system for occurring with the specified distribution to the total number of eigen states, i.e.,

$$(i) \quad = \sum_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \times constant$$
$$\ldots(3)$$

So to obtain the condition of maximum probability, we proceed as follows:

Taking log of equation (3), we have

$$\log(i) = \sum_i \{(n_i + g_i)\log(n_i + g_i) - \log n_i - g_i \log g_i\} + constant \qquad \ldots(4)$$

Using the Stirling's approximation, equation (4) becomes

$$\log(i) = \sum_i \{(n_i + g_i)\log(n_i + g_i) - \log n_i - g_i \log g_i\} + constant \ldots(5)$$

Here we have neglected 1 in comparison to n_i and g_i as they are very large numbers.

$$\delta \log(i) = \sum_i \delta[n_i + g_i)\log(n_i + g_i) - n_i \log n_i - g_i]$$

$$= \sum \left\{ \delta n_i \log(n_i + g_i) + \frac{(n_i+g_i)}{(n_i+g_i)} \delta n_i - \delta n_i \log n_i - \frac{n_i}{n_i} \delta n_i \right\}$$

$$= \sum 1[\delta n_i \log(n_i + g_i) - \delta n_i \log n_i]$$

$$= -\sum \left[\log \frac{n_i}{(n_i+g_i)} \right] \delta n_i \qquad \ldots (6)$$

The condition of maximum probability gives

$$\sum_i [\log \frac{n_i}{(n_i+g_i)} \delta n_i = 0. \qquad \ldots (7)$$

The auxiliary condition to be satisfied are

$$\delta n = \sum \delta n_i = 0 \qquad \ldots (8)$$

$$\delta E = \sum \varepsilon i \delta n_i = 0. \qquad \ldots (9)$$

Applying the Lagrange method of undetermined multipliers i.e., multiplying equation (8) by α and equation (9) by β, and adding the resulting expressions to equation (7), we get

$$\sum_i \left[\log \frac{n_i}{(n_i+g_i)} + \alpha + \beta \varepsilon i \right] \delta n_i = 0. \qquad \ldots (10)$$

As the variations δn_i are independent of each other,

$$\log \frac{n_i}{(n_i + g_i)} + \alpha + \beta \varepsilon_i = 0$$

or

$$1 + \frac{g_i}{n_i} = e^{\alpha + \beta e_i}$$

$$\frac{g_i}{n_i} = e^{\alpha + \beta e_i} - 1$$

$\therefore$

$$n_i = \frac{g_i}{e^{\alpha + \beta e_i - 1}}.$$

This represents the most probable distribution of the elements among various energy levels for a system obeying Bose – Einstein statistics.

7.7. MAXWELL BOLTZMANN DISTRIBUTION LAW OF VELCOTITIES:

The molecules of a gas do not all move with the same speed due to frequent collisions and so their velocities vary. The manner in which the molecules of a gas are distributed over the possible velocities from zero to very high values was first worked out by Maxwell distribution law. In deriving this law certain assumptions are made which are as follows:

(1)   The gas in an enclosure maintained at a constant temperature assumes a steady state in which it is in thermal equilibrium with its surroundings. In the steady state the density of the gas remains uniform on an average throughout the gas.

(2)   The velocities along the three coordinate axes are independent if each other, i.e, the probability of a molecule along any axis will depend on the velocity along that axis only and not on the other.

(3)   The probability of the velocity of a molecule lying between certain limits is a function of velocity and of the limits considered.

Let u,v,w be the component velocities of a molecule along X, Y, and Z axes, respectively as shown in fig 7. The number of molecules per c.c. having the velocities lying between u and u+du can be denoted by $n_u du$. Obviously, n_u must be some function of u say n f(u) where n is the number of molecules per e.e. and f(u) is a function of u to be determined. The probability that any molecule selected at random will have velocities lying between u and u + du is f(u) du. Hence the probability that molecule may have its velocity simultaneously between u and (u + du), v and (v + du), and w and (w + dw) is

$$F(u)f(v)f(w)du \, dv \, dw.$$

All the molecules whose velocity components lie in the range u and (u + du),v and (v + dv), w and (w + dw) will be contained in the element of volume du dv dw. The chance that a single velocity of value c ends in this volume elements du dv dw is given by the assumption no. (3) as convenience we write the function F(c) as (c^2)

∴ $f(u) \, f(v) \, f(w) \, du \, dv \, dw = (c^2) \, du \, dv \, dw$

Or $f(u) \, f(v) \, f(w) = (c^2) = (u^2 + v^2 + w^2).$
…(2)

Where $c^2 = u^2 + v^2 + w^2.$

The equation (2) determines the nature of distribution law. Differentiating equation (2), we get

$$D \, [f(u) \, f(v) \, f(w)= d[(c^2)]=0.$$

$D[(c^2)] = 0$, because for a particular value of c, (c^2) is constant and its differentiate will be zero.

Differentiating , we get

$$F(u)f(v)f(w) \, du + f(u) \, f(v)f(w)dw+f(u)f(v)f(w)dw = 0$$

Dividing by f(u) f(v) f(w), we get

$$\frac{f(u)}{f(u)} du + \frac{f(v)}{f(v)} dv + \frac{f(w)}{f(w)} dw = 0$$

...(3)

Again $c^2 = u^2 + v^2 + w^2$ on differentiation gives

$$0 = 2u \, dx + 2u \, dv + 2w \, dw$$

Or $0 = \lambda u du + \lambda u \, dv + \lambda w \, dw$

...(4)

Where λ is an arbitrary constant.

Adding equation

$$\left\{ \frac{f(u)}{f(u)} \lambda u \right\} du + \left\{ \frac{f(v)}{f(v)} + \lambda v \right\} dv + \left\{ \frac{f(w)}{f(w)} + \lambda w \right\} dw = 0.$$

...(5)

According to assumption no. (2), the velocity components are independent of each other, hence equation (5) can only be satisfied when each the term is separately equal to zero, i.e.

$$\begin{cases} \left\{ \frac{f(u)}{f(u)} + \lambda u \right\} du = 0 \dots (a) \\ \left\{ \frac{f(u)}{f(u)} + \lambda u \right\} du = 0 \dots (b) \\ \left\{ \frac{f(u)}{f(u)} + \lambda u \right\} du = 0 \dots (a) \end{cases}$$

...(6)

Now integrating equation 6(a), we have

$$\log f(u) = -\frac{\lambda u^2}{2} + \log \log A.$$

Where log A is constant of integration, thus

$$\text{Log} \left\{ \frac{f(u)}{A} \right\} = -\frac{\lambda u^2}{2}$$

Or $f(u) = Ae^{-ku2/2} = Ac^{-u2/u2}$ where $\frac{\lambda}{2} = \frac{1}{\alpha^2}$

..(7)

Similarly, writing for other two components

$$f(v) = Ac^{x^2/u^2}$$

...(8)

$$f(v) = Ac^{-u/a^2}$$

...(9)

From equation (7), (8) and (9), we have

$$F(u), f(v), f(w) = A^3 e^{(u^2+v^2+w^2)/u^2}$$
...(10)

Thus the probability that a molecule has the velocity between u and v + du is given by

$$F(u) \, du = Ac^{u2/a2} \, du$$
...(11)

7.7.1. EVALUATION OF CONSTANTS A AND α : The only problem remains to evaluate the values of the constants A and α interms of known quantities.

Let n be the number of molecules per c.c. of the gas with all possible velocities from - ∞ to + ∞. Then the number of molecules per c.c. with velocity components between u and v + du. v and u + dv and, w and w + dw is n f(u)f(v)f(w) du dv dw. Hence

$$\iiint_{-\infty}^{+\infty} n \, f(u)f(v)f(w) \, du \, dv \, dw = n$$

Or
$$\iiint_{-\infty}^{+\infty} A^3 e^{-(u^2+v^2+w^2)/a^2} \, du \, dv \, dw = 1$$
...(12)

The value of the definite integral $\int_{-\infty}^{+\infty} c^{u^2/a^2} \, du = \sqrt{\pi}.\alpha$

$$A^3 \left(\sqrt{\pi}\right)^3 \alpha^3 = 1$$

Or
$$A = \frac{1}{\alpha\sqrt{\pi}}.$$

In order to consider the value of α, we calculate the pressure extorted by the gas on the walls of the enclosure. Let us consider the case of a molecule moving along X axis with velocity u. the molecule will collide with the surface of the enclosure which is perpendicular to X axis and will be reflected back with velocity – u. the change in the momentum of the molecule will be 2mu. The components v and w do not contribute any thing to the pressure for this surface. We know that the pressure is equal to the change in momentum suffered by the molecules striking per unit area of the wall per second if n_u be the number of molecules per unit volume having velocity u, then the number of impacts on an area ∂t will be n_u u ∂A ∂t. Now the pressure P on the wall, average through the time interval ∂t is given by

$$P \, \partial A \, \partial t = \sum_{u=0}^{\infty} 2mu \times n_u u \, \partial A \, \partial t.$$

Or $\qquad\qquad P = 2m \sum_{0}^{\infty} n_u u^2$

...(13)

The number of molecules per c.c. having velocity components lying between u and v + du is given in accordance with equation (11) by

$$N_u = nf(u) = n \, Ae^{-u^2/u^2}$$

$$= n \frac{1}{\alpha\sqrt{\pi}} e^{-u^2/\alpha^2}$$

...(14)

Substituting the value of n_u from equation (14) in equation (13), we have

$$P = 2m \sum_{0}^{\infty} n \frac{1}{\alpha\sqrt{\pi}} e^{-u^2/\alpha^2} u^2$$

Replacing the sign of summation by integration, we have

$$P = 2m \int_{0}^{\infty} n \frac{1}{\alpha\sqrt{\pi}} e^{-u^2/\alpha^2} u^2 du$$

$$= 2mn. \frac{1}{\alpha\sqrt{\pi}} \int_{0}^{\infty} e^{-u^2/\alpha^2} u^2 du$$

$$= 2mn. \frac{1}{\alpha\sqrt{\pi}} . \frac{1}{4} . \sqrt{\pi} . \sqrt{\alpha^6} = \frac{mn}{2} \alpha^2$$

Because $\int_{0}^{\infty} e^{-u^2/v^2} u^2 du = \frac{1}{4} \sqrt{\pi} \sqrt{\alpha^6}$

We also know that $P = nkT$

∴ $\qquad\qquad nkT = \frac{mn}{2} \alpha^2$

Or $\qquad\qquad \frac{1}{\alpha^2} = \left(\frac{m}{2kT}\right).$

...(15)

Again $\qquad\qquad A = \frac{1}{\alpha\sqrt{\pi}} = \sqrt{\left(\frac{m}{2\pi kT}\right)}$

....(16)

Now, the number of molecules dn having velocity components lying between u and v + du, v and v + dv, w + dw is given by

Dn = n(fu)duf(v)dvf(w)dw

$$= nA^3 e^{-\frac{u^2+v^2+w^2}{\alpha^2 du}} dv \, dw$$

$$= n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp.\left[-\frac{m}{2}(u^2 + v^2 + w^2)/kT\right]du\ dv\ dw$$
…(17)

This is known as Mawell's distribution law of velocities.

7.7.2. NUMBER OF MOLECULES HAVING VELOCITY WITHIN C AND C + DC.

Let us consider that the molecules having velocity within c and c + dc lie between two concentric spheres of radius c and c + dc with a common centre O as shown in fig 8.

The volume of the shaded portion will be

$$\frac{4}{3}\pi[(c + dc)^3 - c^3] = 4\pi c^2 dc$$

On neglecting small terms.

This volume is the same as du dv dw in equation (17). Hence

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp.\left[-\frac{m}{2}(u^2 + v^2 + w^2)/kT\right]4\pi c^2 dc$$
…(18)

This is Maxwell – Boltxmann distribution law for molecular velocities. This can also be put in the following form

$$dn_c = n\frac{1}{\alpha^3\pi^{3/2}}e^{-c^2/\alpha^2}4\pi c^2 dc$$
…(18)

This is Maxwell – Boltzmann distribution law for molecular velocities. This can also be put in the following form.

$$dn_c = n\frac{1}{\alpha^3\pi^{3/2}}e^{-c^2/u^2}A\pi c^2 dc$$

$$dn_c = n\frac{4c^2}{\alpha^3\sqrt{\pi}}e^{-c^2/\alpha^2}dc$$
…(19)

7.7.3. EXPERIMENTAL PROOF OF MAWELL'S DISTRIBUTION LAW FROM THE FINITE BREADTHS IF SPECTRAL LINES:Theoretically s spectral line should have zero breadth and uniform intensity but it is observed that when the spectral line is viewed with the help of high resolving power instruments, it has large number of lines with varying intensity. This phenomenon is direct consequence of the Maxwell's law of distribution of velocities and can be explained as follows:

We know that when atoms or molecules come from high energy levels to low energy levels, they emit spectral lines. If the atoms or molecules were at rest, the frequency emitted by them would have a single frequency. But as the molecules are moving with different velocities, they emit different frequency. When a source emitting radiation is moving away from the observer with components velocity v_0, its wavelength, λ, as observed by the observer, is given by

$$\lambda = \lambda_0\left(1 + \frac{v_0}{c}\right),$$

Where λ_0 the wavelength of radiation corresponding to definite velocity v0 and c is is the velocity of light.

Now the spectral range corresponding to the molecules having velocities in the range d_{vo}, will be

$$d\lambda = \lambda_0\left(\frac{dv_0}{c}\right)$$

...(20)

If I is a vector representing the intensity of the spectral line, then multiplying equation (20) by I, we have

$$I\, d\lambda = I\lambda_0\left(\frac{dv_0}{c}\right)$$

...

(21)

The number of molecules having velocities between v_0 and $v_0 + dv_0$ is given by

$$N\, Ae^{-v_0^2/\alpha^2}.\, dv_0.$$

If y represented the amount of radiation emitted by a single molecules, then the intensity of spectral line will be

$$\gamma n Ae^{-v_0^2/a^2} dv_0.$$

...(22)

From equations (21) and (22), we have

$$I\lambda_0\left(\frac{dv_0}{c}\right) = \gamma n Ae^{-v_0^2/\alpha^2} dv_0.$$

Or

$$\frac{I\lambda_0}{c} = \gamma n\, Ae^{-v_0^2/\alpha^2}$$

$$= \gamma n\, Ae^{-c^2(\lambda-\lambda_0)^2/\lambda^2 0\alpha^2}$$

$$\left[\text{because } v_0 = \left(\frac{\lambda-\lambda_0}{\lambda_0}\right) c \text{ from equation } \lambda = \lambda_0\left(1 + \frac{v_0}{c}\right).\right]$$

Or $\qquad I = \frac{c}{\lambda_0}\gamma nA e^{-c^2(\lambda-\lambda_0)^2/\lambda^2\, 0\alpha^2}$

If $\lambda = \lambda_0$, then $\qquad I = \frac{c}{\lambda_0}\gamma nA = I_0$ = constant representing the intensity

Corresponding to molecules of velocity v_O

Therefore

$I = I_O \exp. \left[\frac{c^2(\lambda-\lambda_v)^2}{\lambda_0^2\alpha^2}\right]$ $\qquad$ ….(23)

If I is plotted as a function of λ, a graph of the form shown I figure 9 is obtained. It is observed from the graph that the intensity is decreasing on both the sides of the maximum. The distance on the wavelength scale in either side where $I = \frac{1}{2}I_o$ is known as half width and is denoted by

When $I = \frac{I_0}{2}$, $\lambda = \lambda_0 + b$ or $\lambda - \lambda_0 = b$

Now from equation (23) we get

$\frac{I_v}{2} = I_C \exp. \left[-\frac{c^2 b^2}{\lambda_0^2\alpha^2}\right]$

Or $\qquad \log_e 2 = -\frac{c^2 b^2}{\lambda_0^2 x^2} = \frac{c^2 h^2 m}{2kT\lambda_0^2}$ as $\frac{1}{\alpha^2} = \left(\frac{m}{2kT}\right)$.

Solving we have

$$B^2 = \frac{(2\log_e 2)kTT\lambda_0^2}{mc^2}$$

Or $\qquad b = \left[\frac{[2\log_e 2]kT\lambda_0^2}{mc^2}\right]^{1/2}$

Or $\qquad \frac{b}{\lambda_0} = \frac{\sqrt{(2\log 2)R^{1/2}}}{c}\sqrt{\left(\frac{T}{A}\right)}$

$\qquad$ ….(24)

Where A is atomic weight

Equation (24) shows that the half width is inversely proportional to the atomic weight i.e, the lighter elements will have greater width. Experimentally it is observed that hydrogen lines are very much broad while spectral lines due to heavy elements like Hg and Cd are quite sharp. This verifies the Maxwell's law of distribution of velocities.

7.8. A COMPARISON OF THE THREE STATISTICS

A comparison of the three statistics:

Maxwell – Boltzmann	Fermi – Dirac	Bose – Einstein
1. Particles are distinguishable and only particles are taken into consideration.	Particles are indistinguishable and quantum states are taken into consideration.	Particles are indistinguishable and quantum states are taken into consideration.
2. There is no restriction on the number of particles in a given state.	Only one particles may be in a given quantum state.	No restriction on the number of particles in a given quantum state.
3. Applicable to ideal gas molecules.		Applicable to photons and symmetrical particles.
4. Volume in six dimensional space is not known.	Applicable to electrons and elementary particles. Volume in phase space is known, (h^3).	
5. Internal energy of ideal gas molecules at absolute zero is taken as zero.		Volume in phase space is know, (h^3).
	Even at absolute zero, the energy is not zero.	The energy at absolute zero is taken to be zero.
6. –	At high temperatures, Fermi distribution approaches Maxwell – Boltzmann distribution. The most probable distribution is given by	At high temperatures, Bose-Einstein distribution approaches Maxwell-Boltzmann distribution. The most probable distribution is given by
7. The most probable distribution is given by $$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta z_i}}$$	$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \varepsilon} - 1}$$	$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \varepsilon_i} + 1}$$

7.9. BLACK BODY RADIATION AND THE PLANCK RADIATION LAW:

The most important application of Bose-statistics to electromagnetic radiation in thermal equilibrium, called black body radiation. In quantum theory, radiant energy occurs in energy packets or photons or light quanta of energy hv/c where v is the frequency and c is the velocity. Photons have zero – rest mass and a spin quantum number of 1: like all particles with spin 1, they obey Bose – Einstein statistics.

Consider a black body radiation chamber of volume V containing radiation in equilibrium with the walls at temperature T. Let U_v dv represent the energy density of radiation of frequency lying between frequencies v and v + dv. The problem is to find out U_v as a function of T. This was first solved by Max Planck through the hypothesis of linear harmonic oscillator possessing discrete energy values.

In the momentum space, particles within a small volume $\alpha_p - \frac{h^3}{V}$ are indistinguishable. It therefore, represents an eigen state. At any instant, all particles, having their momenta between p and p + dp will lie within a cell of volume $4\pi p^2 dp$. Therefore the total number of eigen states is given by

$$G(p)\, dp = \frac{4\pi p^2}{h^3/V}\, dp \qquad \qquad \dots(1)$$

For a photon

$$P = \frac{h}{\lambda} = \frac{hv}{c}$$

$$\therefore \qquad \qquad dp = \frac{hdv}{c} \qquad \qquad \dots(2)$$

Substituting this value of dp in equation (1), we have

$$G(v)dv \;=\; 4\pi V \frac{v^2}{c^3}\, dv. \qquad \qquad \dots(3)$$

There is a duplication of states for the two independent directions of polarization. Therefore

$$G(v)\, dv = 8\pi V \frac{v^2}{c^3}\, dv. \qquad \qquad \dots(4)$$

Equation (4) represents the total number of eigen states lying in the frequency range v and v + dv. Introducing the result in Bose – Einstein distribution law, we get

$$Dn = \frac{g(v)dv}{e^{\alpha+\beta\varepsilon}-1}. \qquad \qquad \dots(5)$$

$$Dn = 8\,\pi V \frac{v^2}{c^3} \frac{dv}{e^{\alpha+\beta\varepsilon}-1}.$$

$$\text{Or} \qquad \frac{dn}{V} = 8\pi \frac{v^2}{c^3} \frac{dv}{e^{\alpha+\beta\varepsilon}-1}. \qquad \qquad \dots(6)$$

The left hand side of equation (6) represents the number of photons per unit volume. Multiplying by h_v, the energy of photon, it gives energy density $U_v dv$ in the specified frequency range substituting $\varepsilon = hv$, we have

$$U_v dv = \frac{8\pi h v^3}{c^3} \frac{d\varepsilon}{e^{\alpha + \beta\varepsilon} - 1}. \qquad \qquad \dots(7)$$

We know that $\beta - \frac{1}{kT}$. Moreover, if we put $\alpha = 0$, equation (7) is just Planck radiation formula, $\alpha = 0$, means, the conditions $\delta n = \sum \delta n_i = 0$ should be dropped.

Every process of emission, in nature, results in the creation of photons and similarly, every absorption process results in the absorption of photons, which may be converted into other forms of energy. Under these conditions, the restriction $\sum \delta n_i = 0$ is no longer applicable. The term α then, does not involve in undermined multiplier and equation (7) reduces to

$$U_v \, dv = \frac{8\pi h v^3}{c^3} \frac{dv}{e^{hv/kT} - 1}, \qquad \qquad \dots(8)$$

Which is Planck's law,

When $hv \ll kT$, the term $(e^{hv/kT} - 1) = hv/kT$ and hence equation (8) can be written as

$$U_v dv = \frac{8\pi kT}{c^3} v^2 dv. \text{ Rayeligh Zean's law,} \qquad \qquad \dots(9)$$

For $hv \gg kT$, equation (8) becomes

$$U_v \, dv = \frac{8\pi kT}{c^3} v^2 dv. \text{ Wien's Law} \qquad \qquad \dots(10)$$

The total energy density is

$$\frac{U}{V} = \frac{8\pi h}{c^3} \int_0^\infty \frac{v^3 dv}{e^{hv/kT} - 1}$$

$$= \frac{8\pi h}{c^3} \left(\frac{kT}{h}\right)^4 \int_0^\infty \frac{x^3 dx}{e^x - 1} \text{on substituting } \frac{hv}{kT} = x$$

$$= \frac{8\pi h}{c^3} \left(\frac{kT}{h}\right)^4 \frac{\pi^4}{15}$$

$$= bT^4 \text{ where } b = \frac{8\pi k^4 \pi^4}{15 c^3 h^3} \qquad \qquad \dots(11)$$

Equation (11) is Stefan – Boltzmann law.

7.10. IDEAL BOSE EINSTEIN GAS

In Bose – Einstein distribution, we consider a system of identical (indistinguishable), independent, no interacting particles of integral spin (bosons) that have symmetrical wave function.

7.11. ENERGY AND PRESSURE OF THE GAS:

Consider a prefect Bose – Einstein gas of n bosons. Let these particles be distribution among states such that there are n_1, n_2, n_3 no of particles In quantum state whose approximate constant energies are e_1, e_2, e_3 respectively.

For a perfect Bose – Einstein gas, consisting of material particles, the formula for the most probable distribution is

$$N_i = \frac{g_i}{e^{\alpha + \beta e_i} - 1}, \qquad \qquad \ldots(1)$$

Where g_i is measure of degeneracy. Since the gas is ideal the interaction between the particles is assumed to be negligible so that the energy may be regarded as entirely translational in character. The results thus obtained will be applicable to a monatomic gas. Equation (1) can be written as

$$N_i = \frac{g_i}{De^{\beta e_i} - 1}. \qquad \qquad \ldots(2)$$

Where; for convenience, we have put $D = e^{\alpha}$.

We know that for particles in a box of 'normal size', the translational energy levels are closely spaced so that we can integrate over phase space instead of summing over particle states. The number of particle states $g(p)dp$ lying between momentum p and $p + dp$ is determined from

$$g(p) - g_{\alpha} \frac{\frac{4\pi}{3} p^3}{h^3 / V},$$

Giving

$$g(p)dp = g_{\alpha} \frac{4\pi V}{h^3} p^3 dp. \qquad \qquad \ldots(3)$$

Where g_1 (=2s +1) is the spin degeneracy factor (arising due to the spin s_1, of the particle).

Equation (2) can now be written as

$$dn(p) - \frac{g(p)dp}{De^{\beta p^2 / 2mn} - 1}$$

$$= g_{\alpha} \frac{4\pi V}{h^3} \cdot \frac{p^3 dp}{De^{\beta e^2 / 2m} - 1}$$

Since $\varepsilon = \frac{p^2}{2m}$, we can write number of particles lying between energy range ϵ and $\epsilon + d\epsilon$ from equation (4), i.e.

$$dn(\epsilon) = g_i \frac{4\pi V}{h^3} \cdot \frac{2m\varepsilon(m/2\epsilon)^{1/2}d\varepsilon}{D\varepsilon^{\epsilon/kT} - 1},$$

Where $\beta = \frac{1}{kT}$ has been substituted

$$dn(\epsilon) - g_i \frac{4\pi m V}{h^3} \sqrt{(2m)} \frac{\varepsilon^{1/2}d\varepsilon}{D\varepsilon^{\epsilon/kT} - 1}$$

Let us put
$$x = \frac{\epsilon}{kT}$$

$$Dx = \frac{d\epsilon}{kT}.$$

So that we express $dn(\epsilon) = g_i \frac{4\pi m V}{h^3} \sqrt{(2m)} \frac{x^{\frac{1}{2}}dx(kT)^{3/2}}{D\epsilon^x - 1}$,

$$= g_x \frac{1}{\sqrt{x}} \left(\frac{2\pi m kT}{h^3} \right)^{3/2} V \frac{x^{1/2}dx}{D\epsilon^x - 1}$$

From thermodynamically properties of diatomic molecules, we note that translational partition function is

$$Z_2 = \left(\frac{2\pi kT}{h^2} \right)^{3/2} V$$

It follow then $dn = \frac{2gZi \, x^{1/2}dx}{\sqrt{\pi} \, D\epsilon^x - 1}$

On integration total number of particles is given by

$$N = \int dn$$

$$= \frac{2gZ_1}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}dn}{D\epsilon^x - 1} \qquad \ldots(6)$$

And energy $\quad E = \int \varepsilon \, dn,$

$$= kT \int x \, dx$$

$$= \frac{2gZi}{\sqrt{\pi}} \cdot kT \int_0^\infty \frac{x^{1/2}dx}{D\epsilon^\epsilon - 1} \qquad \ldots(7)$$

We shall now evaluate the integrals of equation (6) and (7). For a Bose Einstein system α should be positive otherwise the value of

$$n_i = g_i\left(De^{\beta zi} - 1\right)^{-1},$$

Would become negative at sufficiently low energies which is physically unacceptable. When a is positive $D > 1$. The integral of equation (6) is

$$\int_0^\infty \frac{x^{1/2}dx}{De^x - 1} = \int_0^\infty x^{1/2}\frac{e^{-x}}{D}\left(1 - \frac{e^{-x}}{D}\right)^{-1} dx.$$

$$= \int_0^\infty x^{1/2}\frac{e^{-x}}{D}\left(1 + \frac{e^{-x}}{D} + \frac{e^{-2x}}{D^2} + \cdots\right)^{-1} dx$$

$$= \frac{1}{D}\int_0^\infty x^{1/2} e^{-x}dx + \frac{1}{D^2}\int_0^\infty x^{1/2} e^{-2x}dx + \cdots$$

$$= \frac{\sqrt{\pi}}{2D}\left(1 + \frac{1}{2^{\frac{3}{2}}} + \frac{1}{2^{\frac{3}{2}}D} + \cdots\right)$$

And similarly, integral of equation (7) is

$$\int_0^\infty \frac{x^{3/2}dx}{De^x - 1} = \frac{1}{D}\int_0^\infty x^{3/2}e^{2x}dx + \cdots$$

$$= \frac{3}{4}\frac{\sqrt{\pi}}{D}\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{3^{5/2}D^2} + \cdots\right) \quad \cdots(9)$$

Using relation (8), we get from equation (6),

$$n = \frac{g_x Z_1}{D}\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{3^{1/2}D^2} + \cdots\right) \quad \cdots(10)$$

And from equations (9) and (7),

$$E = \frac{3kTgZ1}{2D}\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{3^{5/2}D^2} + \cdots\right)\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{3^{1/2}D^2} + \cdots\right)^{-1} \quad \cdots(11)$$

Substituting value of $g_i Z_I$ from equation (10) in equation (11), we get

$$E = \frac{3nkT}{2}\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{2^{5/2}D^2} + \cdots\right)\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{2^{3/2}D^2} + \cdots\right)^{-1}$$

$$= \frac{3nkT}{2}\left(1 + \frac{1}{2^{3/2}D} + \frac{1}{2^{5/2}D^2} + \cdots\right)\left(1 - \frac{1}{2^{5/2}D} - \frac{1}{3^{5/2}} + \cdots\right)$$

$$= \frac{3nkT}{2}\left(1 + \frac{1}{2^{5/2}D} + \frac{1}{2^{3/2}D^2} + \cdots - \frac{1}{2^{3/2}D} - \frac{1}{3^{3/2}} - \cdots\right)$$

$$= \frac{3nkT}{2}\left[1 + \frac{1}{2^{5/2}D} - \frac{1}{3^{3/2}D^2} - \cdots\right] \qquad \ldots(12)$$

If we take only first term in equation (10) then

$$D = \frac{g_s Z_i}{n},$$

Which, when substituted in equation (12), gives

$$E = \frac{3}{2}nKT\left[1 - \frac{1}{2^{\frac{5}{2}}}\left(\frac{n}{g_s Z_i}\right) - \frac{1}{3^{\frac{5}{2}}}\left(\frac{n}{g_i Z_i}\right)^2 - \cdots\right].$$

For one gram, molecule of the gas, since nk = R, we write energy expression as

$$E = \frac{3}{2}RT\left[1 - \frac{1}{2^{\frac{5}{2}}}\left(\frac{n}{g_s Z_t}\right) - \frac{1}{3^{\frac{5}{2}}}\left(\frac{n}{g_s Z_i}\right)^2 - \cdots\right]$$

$$= \frac{3}{2}RTn. \qquad \ldots(13)$$

Where n has been substituted for bracketed terms.

7.12. GAS DEGENERACY

The pressure of a gas can be calculated from the relation.

$$P = -\left(\frac{\partial E}{\partial V}\right)_S \qquad \ldots(14)$$

Which means, in order to calculate pressure, we must first set up a relation in energy E and volume V.

Let us consider a particle of mass m enclosed in a container of volume abc. The wave function ψ of the particle must satisfy the Schrödinger equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V^*)\psi = 0. \qquad \ldots(15)$$

Where V* (x,y,z) represents the potential energy of the particle which for single particle in the box should be zero. Therefore

$$- \frac{h^2}{8\pi^2 m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \frac{\partial^2 \psi}{\partial x^2} \right) = E\psi. \qquad \dots(16)$$

To solve this equation let us write ψ in terms of variable.

$$\psi = X(x), Y(y), Z(z), \qquad \dots(17)$$

So that this equation (16) assumes the form

$$- \frac{h^2}{8\pi^2 m} \left(\frac{1}{X} \cdot \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \cdot \frac{\partial^2 Y}{\partial Y^2} + \frac{1}{Z} \cdot \frac{\partial^2 Z}{\partial z^2} \right) = E, \qquad \dots(18)$$

Which means

$$- \frac{h^2}{8\pi^2 m} \cdot \frac{1}{X} \cdot \frac{\partial^2 X}{\partial x^2} = E_x$$

$$- \frac{h^2}{8\pi^2 m} \cdot \frac{1}{Y} \cdot \frac{\partial^2 Y}{\partial y^2} = E_y \ \} \qquad \dots(19)$$

$$- \frac{h^2}{8\pi^2 m} \cdot \frac{1}{Z} \cdot \frac{\partial^2 Z}{\partial z^2} = E_Z$$

We consider first equation (19), i.e.,

$$- \frac{h^2}{8\pi^2 m} \cdot \frac{1}{X} \cdot \frac{h^2}{8\pi^2 m} \cdot \frac{\partial^2 X}{\partial x^2} = E_{x'}$$

The general solution of which can be written as

$$X(x) = A \sin(Bx + C), \qquad \dots(20)$$

In which the constant A, B and C are to be determined by the application of boundary conditions.

We know that the probability of finding the particle at any point (x,y,z) is equal to $|\psi(x, y, z)|^2$ at the point. Therefore $|X(x)|^2$, which is a function of x – coordinate only, would determine the probability of the particle being found somewhere along the X- axis. Since the walls (x = 0 and x = a) is equal to zero.

Thus $\qquad\qquad\qquad$ X(x) = 0 at $\begin{matrix} x = 0 \\ x = a \end{matrix}\}$

Applying X(x) = 0 at x = 0, to equation (20), we get

$\qquad\qquad$ 0 = A sin C,

Giving $\qquad\qquad$ sin C = 0 or C = 0.

Now applying X (x) = 0 at x = a to the same equation we find

$$0 = A \sin (Ba + C)$$

Giving

$$Ba + C = r_x\pi, \text{ where } r_x, \text{ is an integer.}$$

Or $$B = \frac{r_x\pi}{a}, \text{ since C is zero.}$$

Therefore equation (20) finally assumes the form

$$X(x) = A \sin \frac{r_x\pi}{a} \qquad \qquad \text{...(21s)}$$

Similarly, for the remaining two equation of relation (19), we can find

$$Y(y) = A \sin \frac{r_y\pi}{a} \qquad \qquad \text{...(21b)}$$

$$Z(z) = A \sin \frac{r_z\pi}{c}. \qquad \qquad \text{...(21c)}$$

Substituting (21a), (21b) and (21c) in equation of relation (19), we find

$$E_x = \frac{r_x^2\pi^2 h^2}{8\pi^2 a^2 m},$$

$$E_y = \frac{r_y^2\pi^2 h^2}{8\pi^2 b^2 m},$$

$$E_z = \frac{r_z^2\pi^2 h^2}{8\pi^2 c^2 m},$$

Giving $$E = E_x + E_y + E_z$$

$$\frac{h^2\pi^2}{8\pi^2 m}, \left(\frac{r_x^2}{a^2} + \frac{r_y^2}{b^2} + \frac{r_x^2}{c^2}\right).$$

If container is cubic, $a = b = c = l$,

So that $$E = \frac{h^2\pi^2}{8\pi^2 m}\left(\frac{r_x^2 + r_y^2 + r_z^2}{l^2}\right).$$

Further for cube of side l, volume is

$$V = l^3$$

So that $$l^2 = V^{2/3}$$

And taking $$r_x^2 + r_y^2 + r_z^2 = r^2. \qquad \qquad \text{...(22)}$$

Thus we have established a relation between energy and volume. Now from equation (14), we obtain the pressure of ideal Bose gas, thus

$$P = -\left(\frac{\partial E}{\partial V}\right)$$

$$= -\frac{\partial}{\partial V}\left(\frac{h^2 \pi^2 r^2}{8\pi^2 m V^{5/3}}\right)$$

$$= \frac{2}{3}\frac{h^2 \pi^2 r^2}{8\pi^2 m V^{5/3}}$$

$$= \frac{2}{3} \cdot \frac{E}{V}$$

Which is in agreement with classical result, Using equation (13), pressure of an ideal Bose gas is

$$P = \frac{2}{3V} \cdot \frac{3}{2} RT \left[1 - \frac{1}{2^{\frac{5}{2}}}\left(\frac{n}{g_s z_i}\right) - \frac{1}{3^{\frac{5}{2}}}\left(\frac{n}{g_s z_i}\right)^2 - \cdots\right]$$

$$= \frac{RT}{V} \cdot n. \qquad \qquad \qquad \qquad \qquad \qquad \dots(23)$$

We find from equation (13) and (23) that there are deviations in energy and pressure from the values for ideal gas behaviour. An additional factor n occurs which can be held responsible for these deviations. The deviations from perfect gas behaviour exhibited by Bose Einstein gas is termed as 'gas degeneracy'. The gas degeneracy is obviously a function of 1/D. Also

$$\frac{1}{D}\frac{n}{g_n z_i}\frac{n}{g_s V}\left(\frac{2\pi m kT}{h^2}\right)^{-3/2} \qquad \qquad \qquad \dots(24)$$

This shows that for particles of small mass at low temperature and small volume or high pressure, the gas degeneracy will be more marked. The deviations due to gas degeneracy are rather small as compared to those due to Van der Waal's forces and that is why it is not possible to observe this effect under normal conditions.

7.12.1. DEGENERACY FOR MOLECULAR HYDROGEN:Molecular hydrogen obeys Bose – Einstein statistics. The boiling temperature of hydrogen at atmosphere pressure is 20.38K which is the lowest temperature at which hydrogen can exist as a gas. For molecular hydrogen.

$$N = 6.02 \times 10^{23}$$

$$M = 2 \times 1.67 \times 10^{-24} \text{ gram.} \quad \text{(Mass of proton)}$$

$$V = 1400 \text{ e.e.} \qquad \qquad \text{(Molar volume)}$$

$$K = 1.38 \times 10^{-16} \text{erg/K}$$

And $\qquad$ h = 6.62 $\times$ 10^{-37} erg. Sec.

Spin statistical weight

$$G_x = (2s + 1)$$

$$= 1 \text{ for paraform}$$

$$= 3 \text{ for orthoform}$$

Taking $\qquad$ $g_x = 1$,

We find that $\qquad$ $\dfrac{1}{D} = \dfrac{6.02 \times 10^{23}}{1 \times 1400} \times \left(\dfrac{2 \times 3.14 \times 2 \times 1.67 \times 10^{-24} \times 1.38 \times 20.38}{6.62 \times 10^{-37} \times 6.62 \times 10^{-37}}\right)^{-1/2}$

$$= 0.84 \times 10^{-2}.$$

So that pressure

$$P = \frac{RT}{V}\left(1 - \frac{1}{2^{\frac{5}{2}}} \times 0.84 \times 10^{-2}\right)$$

$$= \frac{RT}{V}(1 - 1.49 \times 10^{-3}) = 0.99851\frac{RT}{V}.$$

We note that it differs slightly from PV = RT, the perfect gas equation. Further, $\frac{1}{D} = 0.84 \times 10^{-2}$, we conclude that gas degeneracy in the case of molecular hydrogen is small and impossible to be observed.

7.12.2. DEGENERACY FOR HELIUM: Helium also obeys Bose – Einstein statistics. For helium molecular weight is two times that of hydrogen, it can exist in gaseous states at much lower temperatures (the boiling point being 4.2K at atmosphere pressure) and the molar volume is 345e.e. we find

$$\frac{1}{D} = 0.134,$$

Which is appreciable as compared to the case of molecular hydrogen and that is why there is some possibility of observing gas degeneracy in the gas of helium.

7.12.3.   BOSE EINSTEIN CONDENSATION

We have

$$\frac{1}{D} = \frac{1}{g_s V}\left(\frac{2\pi m k T}{h^2}\right)^{-3/2}.$$

We note that at temperature nearing zero i.e, T = 0,1/D will have a large value which means the degeneracy will be more marked. It means the gas will deviate highly form its perfect gas behaviour. The reason is as follows:

While arriving at the Bose – Einstein distribution, we have assumed that, because of the closeness of the energy levels, we could always replace the discrete distribution by a continuous distribution giving.

$$n = \int_0^\infty dn(E)$$

I.e. we have changed summation into integration. As long as the change in occupation number, n_i from state to state is small compared to the number of particles in the state, this is a valid procedure. If, however, the temperature in an ideal Bose gas is lowered to zero, the particles will begin to crowd into a few levels and the above condition will be violated. This means that when we are working at low temperatures, we must be careful in replacing the summation by integration. Now, from equation (5) the number of particles lying between energy range ε and $\varepsilon + d\varepsilon$ is given by

$$dn(\varepsilon) = \frac{g(\varepsilon)d\varepsilon}{De^{\varepsilon/kT} - 1}$$

Where $\qquad g(\varepsilon) - \frac{4\pi m V}{h^3}\sqrt{(2m\varepsilon)}$.

We note that for ground state $\varepsilon = \varepsilon_0 = 0 g(\varepsilon) = 0,$ while actually it should have been unity because there is one state at $\varepsilon = 0.$ Therefore above distribution fails to give the number of states at e = 0, while state, called the ground state, is very important at low temperatures because a large number of particles occupy it at such temperatures. We further note that if e =0, the above distribution holds good ass g (e) = 0. Therefore above distribution can still be applied for all states except ground state which should be treated separately. For a single state, we write

$$n_i = \frac{g_i}{e^{\alpha + \beta\varepsilon_i} - 1}.$$

For ground state $e_1 = e_0 = 0$ and $g_i = 1$. Therefore, number of particles in ground state.

$$n_i \rightarrow n_0 = \frac{1}{e^\alpha - 1}.$$

For ground state $\varepsilon_1 = \varepsilon_0 = 0$ and $g_i = 1$. Therefore, number of particles in ground state

$$n_i \rightarrow n_0 = \frac{1}{e^\alpha - 1}.$$

Therefore, for the total number of particle states we write

$$n = n_0 + \int dn = n_0 + \int g_s \frac{4\pi mV}{H^3} \cdot \frac{\sqrt{(2me)}\, de}{De^{e/kT} - 1}$$

$$= n_0 + \frac{2gZt}{\sqrt{\pi}} \int_0^\infty \frac{x^{\frac{1}{2}} dx}{De^x - 1},$$

From equation (6) Value x is e/kT,

And
$$Z_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V.$$

Further
$$n = n_0 + g_i Z_t\, F_{3/2}\,(a), \qquad \ldots(26)$$

Where
$$F_{2/3}(a) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{De^x - 1}$$

$$= \frac{\sqrt{\pi}}{2D} \times \frac{2}{\sqrt{\pi}} \left(1 + \frac{1}{2^{\frac{5}{2}}D} + \frac{1}{3^{\frac{5}{2}}D^2} + \cdots\right) \qquad \ldots(27)$$

When
$$\alpha = 0, D = e^\alpha = 1,$$

So that
$$F_{2/3}(0) = \frac{2}{\sqrt{\pi}} \cdot \frac{\sqrt{\pi}}{2} \left(1 + \frac{1}{2^{5/2}} + \frac{1}{3^{5/2}} + \cdots\right)$$

$$= 2.612$$

Let $T = T_0$ when $\alpha = 0$ or $D = 1$ so that that from equation (10) we get

$$N = g_i \,(Z_t)_{T-To}\left(1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}}\right)$$

$$= g_s(Z_t)_{t=to}\, F_{3/2}\,(0). \qquad \ldots(29)$$

Therefore
$$g_s(Z_t)_{t-to}\, F._{=3/12}\frac{n}{F_{3/2}(0)}$$

Putting the value g_s from equation (26) in equation (26), we find

$$N = n_0 + n\,\frac{Z_i}{(z_i)_{T-TO}} - \frac{F_{3/2}(a)}{F_{3/2}(0)}$$

$$= n_0 + n\,\frac{\left(\frac{2\pi kT}{H^2}\right)^{3/2} V\, F_{3/2}(a)}{\left(\frac{2\pi kT}{H^2}\right)^{3/2} V\, F_{3/2}(0)}$$

$$= n_o + n\left(\frac{T}{T_o}\right)^{3/2} \frac{F_{1/2}(a)}{F_{1/2}(0)}$$

Or
$$n = n - n_0 + n\left(\frac{T}{T_0}\right)^{3/2} \frac{F3/2(a)}{F3/2(0)}$$

From equation (27), we find that with D > 1. $F_{3/2}(a)$ will have less value than when D = 1, i.e.

$$F_{3/2/}(a) < F_{3/2}(0)$$

When

This means that n given by equation (29) acquires maximum value when a = 0. Thus for a = 0 the maximum number of particles occupying states ground state is given by

$$N = n\left(\frac{T}{T_0}\right)^{3/2}, \text{when } T < T_0 \qquad \dots (30)$$

And the rest of the particles given by

$$N_0 = n - n = n\ [I - T/T_0)^{3/2}]. \qquad \dots (31)$$

When
$$T = T_0$$

Must condense into ground state.

Thus from equation (31) we note that, as the temperature is lowered, beginning at $T = T_0$ the molecules fall rapidly into the ground state. There is a sort of condensation into this state. This phenomenon is known as Bose Einstein Condensation. The temperature T_0 at which the Bose Einstein condensation begins depends upon the density of the gas. If we consider liquid helium to be a gas, we would obtain a value of about 3.14K for T_0.

It is found experimentally that liquid helium does undergo a rather unusual transition at 2.19K below this temperature, the liquid helium displays the properties of a super fluid. It is generally, agreed that this transition in liquid helium is associated with a Bose – Einstein conservation.

For temperatures above T_0 – μ must decrease in order to keep n < (n_0 + n)< n. But if μ becomes significantly different from zero, then n_o becomes very small. We, therefore, assume for temperatures above T_0 that $n_0 = 0$. Therefore for T >T_0

$$N_0 = 0.$$

And
$$n = n = g_i F_{3/2}(a).$$

From equation (29) when $n = n_1$ we find that

$$N = n\left(\frac{T}{T_0}\right)^{3/2} \frac{F_{3/2}(a)}{F_{3/2}(0)}$$

Or $$F_{3/2}(1) = F_{3/2}(0)\left(\frac{T_0}{T}\right)^{3/2} = 2.612\left(\frac{T_0}{T}\right)^{3/2}.$$ ...

(32)

Which when substituted in the expression for n given the total number of particle states equal to

$$N = g_i Z_i \; 3.162 \left(\frac{T_0}{T}\right)^{3/2}$$ ...

(33)

7.13. IDEAL FERMI DIRAC GAS

In Fermi – Dirac distribution, we consider a system of identical, independent, non – intersecting particles sharing a common volume and obeying ant symmetrical statistics so that the spin is half/integral and then according to the Pauli principle, the total wave function is ant symmetrical on interchange of any two particles.

7.14. ENERGY AND PRESSURE OF THE GAS:

Participants of Fermi – Dirac assembly are the particles with half integral spin like electrons, protons and neutrons. The general expression for the most probable distribution in energy for the Fermi – Dirac gas is,

$$N_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + 1},$$

Which, on putting $D = e^{\alpha}$, if of form

$$N_i = \frac{g_i}{De^{\beta \varepsilon_i} + 1}$$ ...

(1)

Since in the denominator factor + 1 occurs, α need not be restricted to positive value only but may assume negative value as well unlike Bose Einstein gas.

The number of one particle states lying between momentum p and p + dp is determined from

$$G_p = g_s \frac{(4\pi/3)p^3}{h^3/V}.$$

Giving $$g_p dp = g_s \frac{(4\pi/3)p^3}{h^3/V}$$ ...

(2)

Where $g_s = (2s + 1)$ is the spin degeneracy factor (Arising due to the spin s_1 of desertions).

Since $\varepsilon = p^2/2m$ and $dp = \frac{1}{2}\sqrt{(2m/\varepsilon)}.d\varepsilon$, the number of states in the energy range between e and (e + de) will be, on using equation (2),

$$G(e)de = g_s = g_s \frac{4\pi V}{h^3} . 2me. \sqrt{(m/2e)}.de,$$

…(3)

Where g (e) is termed as density of states function.

From equation (1) and (3) we get the number of particles in the energy range between e and (e + de), as

$$Dn(e) = g_s \frac{4\pi m V}{h^3} . \sqrt{(2m)} . \frac{e^{1/2}de}{De^{e/kT}+1}$$

…(4)

Where we have substituted $\beta = \frac{1}{kT}$,

. Let us put $\qquad x = e/kT$

And $\qquad dx = de/kT$

Equation (4) then becomes

$$Dn = g_s \frac{4\pi m V}{h^3} \sqrt{(2m)} \frac{x^{1/2}dx(kT)^{3/2}}{De^x+1}$$

$$= g_s. \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m kT}{h^2}\right)^{3/2} . V. \frac{x^{1/2}dx}{De^x+1}$$

From the thermodynamic properties of diametric molecules, we note that translational partition function is

$$Z_i \left(\frac{2\pi kT}{h^2}\right)^{\frac{3}{2}} . V.$$

It follows then

$$dn = \frac{2gZt}{\sqrt{\pi}} \frac{x^{\frac{1}{2}}dx}{De^x + 1}.$$

Therefore total number of particles

$$n = \int dn = \frac{2g_sZt}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}dx}{De^x+1}. \qquad \qquad \text{… (5)}$$

And energy $\qquad \qquad E = \int \varepsilon\, dn = kT \int x\, dx.$

$$= kT. \frac{2gZt}{\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}dx}{De^x+1}, \qquad \qquad \text{… (6)}$$

We shall evaluate the integral in equation (5) and (6) for both values of α, i.e, when a is positive and again when it is negative. When s is positive, D is greater than one and the

condition so obtained is referred to as slight or weak degeneracy. Condition corresponding to a negative i.e, D less than one is referred to as strong degeneracy.

7.14.1. CASE OF SLIGHT DEGENERACY:

For this case, integral in equation (5) can be expressed as

$$\int_0^\infty \frac{x^{\frac{1}{2}} dx}{De^x + 1} = \int_0^\infty x^{\frac{1}{2}} dx . \frac{e^{-x}}{D} \left(1 + \frac{e^{-x}}{D}\right)^{-1}$$

$$= \int_0^\infty x^{\frac{1}{2}} dx \frac{e^{-x}}{D} \left[1 - \frac{e^{-x}}{D} + \frac{e^{-2x}}{D^2} - \cdots\right]$$

$$= \frac{1}{D} \int_0^\infty x^{\frac{1}{2}} e^{-x} dx - \frac{1}{D^2} \int_0^\infty x^{\frac{1}{2}} e^{-2x} dx + \frac{1}{D^3} \int_0^\infty x^{\frac{1}{2}} e^{-3x} dx - \cdots$$

$$= \frac{\sqrt{\pi}}{2D} \left[1 - \frac{1}{2^{\frac{3}{2}} D} + \frac{1}{3^{\frac{3}{2}} D^2} - \cdots\right],$$

So that total number of particles is given by

$$n = \frac{g_s Z_1}{D} \left(1 - \frac{1}{2^{\frac{3}{2}} D} + \frac{1}{3^{\frac{3}{2}} D^2} - \cdots\right)$$

Further the integral in equation (6) can be solved as follows:

$$\int_0^\infty \frac{x^{5/2} dx}{De^x + 1} = \frac{1}{D} \int_0^\infty x^{3/2} e^{-x} dx - \frac{1}{D^2} \int_0^\infty x^{\frac{3}{2}} e^{-2x} dx + \cdots$$

$$= \frac{3\sqrt{\pi}}{4D} \left(1 + \frac{1}{2^{\frac{5}{2}} D} + \frac{1}{3^{\frac{5}{2}} D^2} - \cdots\right)$$

So that the total energy is given by

$$E = \frac{3 g_s Z_t}{4D} kT \left(1 - \frac{1}{2^{\frac{5}{2}} D} + \frac{1}{3^{\frac{5}{2}} D^2} - \cdots\right) \qquad \qquad \dots (8)$$

Putting the value of $g_s Z_t$ from equation (7) into equation (8), we get

$$E = \frac{3}{2} nKT \left(1 - \frac{1}{2^{\frac{5}{2}} D} + \frac{1}{3^{\frac{5}{2}} D^2} - \cdots\right) \left(1 - \frac{1}{2^{\frac{3}{2}} D} + \frac{1}{\frac{33}{2} d}\right)^{-1}$$

$$= \frac{3}{2} nKT \left(1 + \frac{1}{2^{\frac{5}{2}} n} - \frac{1}{3^{\frac{5}{2}} n^2} + \cdots\right),$$

Which assumes the form … (9)

After putting $D = \frac{g_s Z_1}{n}$ from equation (7) which has been approximated only upon the first term of the expansion.

The pressure of the ideal Fermi gas can now be obtained by the relation

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,s}$$

$$= \frac{2E}{V}$$

$$= \frac{nkT}{V}\left[1 + \frac{1}{2^{\frac{5}{2}}}\left(\frac{N}{G_s Z_t}\right) - \frac{1}{3^{\frac{5}{2}}}\left(\frac{n}{g_s Z_T}\right) + \cdots\right],$$ …(10)

In which nk = R, for one note of the ideal Fermi gas.

We infer from equations (9) and (10), that ideal Fermi gas deviates from perfect gas behaviour and this deviation, as we know, is called degeneracy, obviously, degeneracy is a function of $\frac{1}{D}$ or e^{-x}. Smaller is the value of D or greater the value of $\frac{1}{D}$ more marked will be the degeneracy.

7.14.2. CASE OF STRONG DEGENERACY:

When a is large and negative $e^{-a} \gg 1$ or D is much less than one. This increases the value of $\frac{1}{D}$ and hence the degeneracy will become more prominent. Further

$\frac{1}{D} \frac{n}{g_s Z_i}$, From equation (7),

$$= \frac{n}{g_s} \frac{h^s}{(2\pi nkT)^{5/2}v}.$$ … (11)

Which shows that a gas will be highly degenerate at low temperature and high density $\left(\frac{n}{v}\right)$. we shall discuss this case of strong degeneracy at two temperature ranges. Firstly when T = 0 i.e, at absolute zero and secondly when temperature is above absolute zero but degeneracy is still considerably high i.e., D is still less than unity.

(i) **At T = 0:** From equation (11) we note that when T = 0, D = 0, so that equation (5) assumes the form

$N = \frac{2gZt}{\sqrt{\pi}}\int_0^\infty x^{1/2}dx.$

Since D = 0, we can replace the upper limit by 1/D. Therefore

$$N = \frac{2gZ_i}{\sqrt{\pi}} \int_0^\infty x^{1/2} dx = \frac{2gZ_i}{\sqrt{\pi}} \qquad \dots (12)$$

Which gives

$$\frac{1}{D} = \left(\frac{3n\pi^{1/2}}{4g_sZ_t}\right)^{2/3}$$

With

$$Z_t = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V.$$

We find that

$$\frac{1}{D} = \frac{h^2}{2mkT}\left(\frac{3n}{4\pi V g_s}\right)^{2/3}. \qquad \dots (13)$$

Which is a measure of degeneracy of the ideal Fermi gas at T = 0.

From equation (6) we can obtain the energy of the Fermi gas ar absolute zero. Putting E as E_0 and D = 0 in equation (6) we get

$$E_0 = kT. \frac{2gZ_i}{\sqrt{\pi}} \int_0^\infty x^{3/2} dx.$$

Where E_0 is termed as zero point energy of a highly degenerate Fermi gas. Replacing again the upper limit by 1/D and solving the interval, we arrive at.

Which, on using equation (13), becomes

$$E_0 = kT. \frac{2gs}{\sqrt{\pi}} \cdot \frac{2}{5} \left[\frac{h^2}{2mkT}\left(\frac{3n}{4\pi V g_s}\right)^{\frac{2}{3}} \right]^{\frac{5}{2}}$$

$$= kT \frac{2g}{\sqrt{\pi}} \cdot \frac{2}{5} \left[\frac{h^2}{2mkT}\left(\frac{3n}{4\pi V g}\right)^{2/3} \right]^{5/2}$$

$$= \frac{3nh^2}{10m}\left(\frac{3n}{4\pi g_s V}\right)^{2/3} \qquad \dots (14)$$

And the corresponding zero point pressure will be

$$P_0 = \frac{2}{3}\frac{Ev}{V}$$

$$= \frac{n}{V}$$

From equation (14) and (15) we find that a highly degenerate Fermi Dirac gas would have a residual zero point energy and pressure – the so called zero point pressure – even at the absolute zero of the temperature, quite unlike a Bose Eisntein gas where all the particles are condensed to the ground state with e = 0 at T = 0.

7.14.3. EXPRESSION OF E AND P IN TERMS OF FERMI ENERGY E_F:

From equation (3), the total number of energy states lying between 0 and specified value e_f can be obtained as

$$G_f = g_s \frac{2\pi V}{h^3} (2m^3)^{1/2} \int_0^{ef} e^{1/2} de.$$

Or $\qquad G_f = \frac{4\pi V g_s}{3h^3} (2m ef)^{3/2}$ $\qquad\qquad\qquad\qquad …(15a)$

Further, in Fermi Dirac distribution, not more than one particle is to be occupied by a given cell which is also obvious from

$$N_i = \frac{g_i}{De^{\varepsilon/kT}+1}.$$

Which gives $n_i = g_i$ since at T = 0, D = 0.

Therefore taking $g_f = n_i$, we write

$$N = \frac{4\pi V g}{3h^3} (2m ef)^{3/2}$$

Or $\qquad\qquad\qquad e_f = \frac{h^2}{2m} \left(\frac{3n}{4\pi V g} \right)^{2/3}$ $\qquad\qquad …(16)$

Where the quantity e_f is called the Fermi energy and it represents the energy of the highest level filled at T = 0K for the given assembly.

From equation (13) and (16), we find that

$$\frac{1}{D} = \frac{e_f}{kT}, \qquad\qquad\qquad\qquad …(17)$$

And from equation (14) and (16), zero point energy is

$$E_0 = \frac{3\pi h^2}{10m} \cdot \frac{2m e_f}{h^2}$$

$$= \frac{3}{5} n \, ef. \qquad\qquad\qquad\qquad …(19)$$

If we define the Fermi temperature as

$$kT_i = \varepsilon_f$$

Equation (17) becomes

$$\frac{1}{D} = \frac{T}{T}.$$

From which we conclude that gas is degenerate when T $<<T_f$.

(ii) **At T above absolute zero but D << 1:** From eq. (4), the number of particles lying in the energy range between c and (c +de)is

$$dn(e) = g_s \frac{4\pi m V}{h^3} \sqrt{(2m)} \frac{e^{1/2} de}{D e^{e/kT} + 1}$$

We have seen in chapter 6 art 6, 10, that

$$D - e^{\alpha} = -e^{-\beta/kT}$$

$$dn(e) = 3n \left(\frac{4\pi V g_s}{3n}\right) \left(\frac{2m^3}{h^6}\right)^{1/2} \frac{e^{1/2} de}{e^{(e-\mu)kT} + 1}.$$

But from equation (16).

$$E_f = \frac{h^2}{2m} \left(\frac{3n}{4\pi V g_s}\right)^{2/3}$$

Giving $\qquad \left(\frac{4\pi V g_s}{3n}\right) = \left(\frac{2me1}{h^2}\right)^{-3/2}.$

So that $\qquad$ dn (e) $= 3n \left(\frac{2me1}{h^2}\right)^{-3/2} \cdot \left\{\frac{2m^3}{h^6}\right\}^{1/2} \frac{e^{1/2} de}{e^{(e-\mu)kT} + 1}$

$$= \frac{3n}{2 e_1^{3/2} e^{(e-e)kt} + 1} \qquad \text{... (20)}$$

Which gives the total number of particles, as

$$N (e) = \frac{3n}{2 e^{3/2}} \int_0^\infty \frac{e^{1/2} de}{e^{(e-\mu)kT} + 1}. \qquad \text{....(22)}$$

To evaluate the integrals of equations (21) and (22) we should solve the integral of the type

$$I = \int_0^\infty \frac{\emptyset(e) de}{e^{(e-\mu)kT} + 1},$$

Where $\emptyset(\varepsilon)$ is a simple function of e such that $\emptyset(\varepsilon) = 0$ if e = 0. Such integrals can be expanded using the method of Taylor's series expansion i.e,

$$I = \int_0^\infty \frac{\emptyset(\varepsilon) de}{e^{(e-\mu)kT} + 1} = \int_0^\mu \theta(\varepsilon) de + \frac{\pi^2}{6} (kT)^2 (\emptyset')_{e=\mu} + \frac{7\pi^4}{360} (kT)^4 (\theta)_{e=\mu+\cdots} \qquad \text{... (23)}$$

Where $\emptyset, \emptyset,$ etc denote the first, third … differentiate of the function $\emptyset$.we shall confinite ourselves only to the first two terms of the expansion (23).

Observing equation (32), we write

$$\emptyset(e) = e^{1/2}$$

So that and $\int_0^\mu \emptyset(e) de = \frac{2}{3} \mu^{3/2}$}

$$\emptyset(e) = \frac{1}{2} \mu^{-1/2}$$

Therefore we write equation (20) as

$$n = \frac{3n}{2e_f^{3/2}} \left[\int_0^\mu \theta(e)\, de + \frac{\pi^2}{6}(kT)^2 \emptyset \bigg| + \cdots \right]$$

$$n = \frac{3n}{2e_f^{\frac{3}{2}}} \left[\frac{\frac{2}{3}\mu^3}{2} + \frac{\pi^2}{6}(kT)^2 \times \frac{1}{2}\mu^{-\frac{1}{2}} + \cdots \right]$$

Or
$$e_f^{\frac{3}{2}} = \frac{3}{2}\left[\frac{2}{3}\mu^{\frac{3}{2}} + \frac{\pi^2}{12}\mu^{\frac{3}{2}}\left(\frac{kT}{\mu}\right) + \cdots \right]$$

$$= \mu^{\frac{3}{2}}\left[1 + \frac{1}{8}\left(\frac{\pi kT}{\mu}\right)^2 + \cdots \right]^{-\frac{2}{3}}$$

Giving
$$\frac{\mu}{e_f} = \left[1 + \frac{1}{8}\left(\frac{\pi kT}{\mu}\right)^2 + \cdots \right]^{-2/3}$$

$$= 1 - \frac{1}{12}\left(\frac{\pi kT}{\mu}\right)^2 + \ldots \qquad\qquad \ldots (24)$$

Taking into consideration only the first two terms of the expansion. We can write

$$\mu^2 = e_f^2 \left[1 - \frac{1}{12}\left(\frac{\pi kT}{\mu}\right)^2 \right]^2$$

$$= e_f^2 \left[1 - \frac{1}{6}\left(\frac{\pi kT}{\mu}\right)^2 \right]^2$$

Neglecting higher order terms.

Thus
$$\frac{1}{\mu^2} = \frac{1}{e_f^2}\left[1 + \frac{1}{6}\left(\frac{\pi kT}{\mu}\right)^2 \right].$$

We make here a crude approximation by putting $\mu = e_f$ in the second term on right side of above equation

$$\frac{1}{\mu^2} = \frac{1}{e_f^2}\left[1 + \frac{1}{6}\left(\frac{\pi kT}{e_f}\right)^2 \right] \qquad\qquad \ldots$$

(25)

Now putting equation (25) in equation (24), we get

$$\mu = e_f \left[1 - \frac{1}{12}(\pi kT)^2 \frac{1}{e_f^2}\left\{ 1 + + \frac{1}{6}\left(\frac{\pi kT}{e_f}\right)^2 \right\} + \cdots \right]$$

$$= e_f \left[1 - \frac{1}{12} \left\{ \left(\frac{\pi kT}{e_f} \right)^2 \right\} + \cdots \right]$$

$$= ef \left[1 - \frac{1}{12} \left(\frac{\pi kT}{e_f} \right)^2 - \cdots \right] \qquad \ldots (26)$$

Neglecting the higher order terms.

Since equation (22) involves the integral of the same type, we write, using the expansion (23), as

$$E = \frac{3n}{2e_f^{3/2}} \left[\int_0^\mu \emptyset(e) de + \frac{1}{6} (\pi kT)^2 \emptyset'(e) | + \cdots \right]$$

$$\emptyset(e) = e^{1/2}$$

Where $\int_0^\mu \emptyset(e) de = \frac{2}{3} \mu^{3/2}$ }

$$\emptyset'(e) = \frac{1}{2} \mu^{-1/2}$$

So that and

Therefore,
$$E = \frac{3n}{2e_f^{\frac{3}{2}}} \left[\frac{2}{5} \mu^{\frac{5}{2}} + \frac{1}{6} (\pi kT)^2 \frac{3}{2} \mu^{\frac{1}{2}} + \cdots \right]$$

$$= \frac{3n}{5} \left[\frac{\mu}{e_f} \right]^{3/2} \mu \left[1 + \frac{5}{8} \left(\frac{\pi kT}{\mu} \right)^2 - \cdots \right].$$

Putting the value of μ from equation (26) and $\frac{1}{\mu^2}$ from eq. (25), we get

$$= \frac{3}{5} nfe \left[1 \quad \frac{5}{24} \left(\frac{\pi kT}{ef} \right)^2 \right] \times \left[1 \mid \frac{5}{8} \left(\frac{nkt}{et} \right)^2 \mid \cdots \right]$$

$$= \frac{3}{5} nfe \left[1 - \frac{5}{8} \left(\frac{\pi kT}{ef} \right)^2 - 1 + \frac{5}{24} \left(\frac{nkt}{et} \right)^2 + \cdots \right],$$

Leaving from the very beginning, the higher order terms.

Therefore
$$E = \frac{3}{5} nfe \left\{ 1 + \frac{5}{12} \left(\frac{\pi kT}{ef} \right)^2 - \cdots \right\} \qquad \ldots (27)$$

This is the approximate energy of a highly degenerate gas. The corresponding pressure will be

$$p = \frac{2}{3} \cdot \frac{E}{V}$$

$$= \frac{2}{3} \left(\frac{nef}{V} \right) \left[1 + \frac{5}{12} \left(\frac{nkT}{ef} \right)^2 - \cdots \right] \qquad \ldots (28)$$

7.15. THERMODYNAMIC FUNCTION OF DEGENERATE FERMI – DIRAC GAS:

Energy and pressure expressions have already been obtained [equations (27) and (28)].

7.15.1. THERMAL CAPACITY, C_V:
At such low temperatures, the gas will have a thermal capacity given by

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \frac{\partial}{\partial T}\left[\frac{3}{5}nei\left\{1 + \frac{5}{12}\left(\frac{\pi kT}{\epsilon_f}\right)^2 - \cdots\right\}\right]$$

$$= ne_i\left(\frac{\pi k}{\epsilon_f}\right)^2 \frac{T}{2} - \cdots$$

$$= \frac{nT}{2}(nk)\frac{1}{\epsilon_f} - \cdots \qquad\qquad \ldots$$

(1)

We have

$$C_V = \frac{nT}{2}(\pi k)^2 \frac{1}{\frac{h^2}{2m}\left(\frac{3n}{4\pi Vgs}\right)^{2/3}}$$

From equation (2), we infer that heat capacity per particle would be small for large deviation $\left(\frac{n}{V}\right)$ and small particle mass m. If the particles are electrons then equation (2), gives electronic specific heat. We note that it is proportional to the absolute temperature and therefore, at ordinary temperatures, the contribution to the specific heat of metals due to electrons would be negligible as compared to the contribution due to the atoms since atomic specific heat is proportional to T_3 while at very low temperatures electronic specific heat will be significant.

7.15.2. Entropy:
Entropy S. can be obtained from

$$S = \int_o^T \frac{C_V}{T}dT$$

$$- \int_0^T \frac{n\pi^2 mk^2}{h^2}\left(\frac{4\pi Vgs}{3n}\right)^{2/3} T.$$

$$= \frac{n\pi^2 mk^2}{h^2}\left(\frac{4\pi Vgs}{3n}\right)^{\frac{2}{3}} T.$$

Using equation (2), If we use equation (1),

$$S = \int_0^T \left[\frac{nef}{2}\left(\frac{\pi k}{E_f}\right)^2 - \cdots\right]dT$$

$$= \frac{ne_f}{2}\left(\frac{\pi k}{E_f}\right)^2 T - \cdots$$

$$= \left(\frac{ne_f}{T}\right)\left\{\frac{\pi^2}{2}\left(\frac{kT}{e_f}\right)^2 - \cdots\right\} \qquad \ldots(3)$$

7.15.3. HELMHOLTZ FREE ENERGY:

$$F = E - TS$$

$$-\frac{3}{5}M_2\left[1 + \frac{5}{12}\left(\frac{\pi kT}{e_f}\right)^2 - \cdots\right] - T\left(\frac{ne_f}{T}\right)\left\{\frac{\pi^2}{2}\left(\frac{kT}{ef}\right)^2 - \cdots\right\}$$

$$-\frac{3}{5}nei + \frac{1}{4}\left(\frac{\pi kT}{a_f}\right)^2 neif$$

Which is an expression for Helmholtz free energy.

7.16. COMPRESSIBILITY OF FERMI GAS

Here we shall derive an expression for compressibility of Fermi gas at absolute zero. The energy at absolute zero is given by

$$E_0 = \frac{4\pi V (2m)3/2}{h3}$$

$$= \frac{4\pi V (2m)^{\frac{5}{2}}}{H^3}\left(\frac{2}{5}\right)\frac{c5}{2}$$

Now $$P_0 = \frac{2}{3}\frac{E_0}{V} = \frac{16\pi (2m)^{5/2}}{15h^3}\varepsilon^{5/2}$$

$$= \frac{16\pi (2m)^{\frac{5}{2}}}{15 h^3}\left(\frac{n}{v}\right)^{5/3} \qquad \text{(where } h = h/2\pi)$$

So, $$\log P_0 = \log e\left[\frac{3^{2/3}\pi^{4/3}n^2 n^{5/3}}{5m}\right] - \frac{5}{3}\log ev$$

Or $$\frac{\partial \log v}{\partial P_0} = \frac{3}{5}\left[\frac{5m}{3^{\frac{2}{3}}\pi^{\frac{4}{3}}h^2}\left(\frac{n}{V}\right)^{-\frac{5}{3}}\right]$$

Now compressibility is given by

$$-\frac{1}{V}\frac{\partial V}{\partial P_0} = \frac{3}{5}\left[\frac{5m}{3^{\frac{2}{3}}\pi^{\frac{4}{3}}h^2}\left(\frac{h}{V}\right)^{-\frac{5}{3}}\right]$$

It has been observed that the compressibility of alkali metals is close to the compressibility of an electron gas.

7.17. ELECTRON GAS:-

A metal can be considered to be composed of a system of fixed positive nuclei and a number of mobile electrons referred to as electron gas.

To study the properties of an electron gas at low temperatures in the region $T - 0$ we shall revise the earlier discussion. For electrons $s = \frac{1}{2}$ so that $g_z = 2s + 1 = 2$, and therefore from equation

$$e_f = \frac{h^2}{2m}\left(\frac{3n}{4\pi V.2}\right)^{2/3}$$

$$10 \ (=n/V) = \frac{h^2}{8m}\left(\frac{3n}{\pi V}\right)^{2/3}$$

...(1)

$$E_O = \frac{3}{5}nei$$

...(2)

Further, from equations (15a) and (16) of, we get

$$G_f = n_i$$

Which means that in the limit $T - 0$ each one of the states is occupied fully upto the energy level e_f whereas all the states above this energy level are empty.

The degeneracy factor of an electron gas for electrons $m = 9.1 \times 10^{-28}$gm, and $g = 2$, we get

$$\frac{1}{D} = \frac{h^2}{2 \times 9.1 \times 10^{-28}kT}\left(\frac{3n}{8\pi V}\right)^{2/3}$$

Taking a typical metal of atomic weight 100 and density 10 so that volume of gm. Atom be 10e.e. and the number of electrons, assuming one free electrons per atom, is 6.02×10^{23}. Then,

$$\frac{1}{D} = \frac{(6.62 \times 10^{-27})^2}{2 \times 9.1 \times 10^{-28} \times 1.38 \times 10^{-16} \times T}\left(\frac{3 \times 6.02 \times 10^{23}}{8 \times 3.14 \times 10}\right)^{\frac{2}{3}}$$

$$= \frac{10^5}{1.5T},$$

Which means degeneracy is sufficiently high. It shows clearly that for electron gas, the classical statistics is not valid and can be applied only at temperatures of the order of 10^5K (because only then D will approach unity). Therefore at low and other ordinary working temperatures, it is necessary to use Fermi – Dirac statics to study the electron gas in the

metals. At low temperatures electrons contribution to the specific heat of metals is given by equation

$$C_v - \frac{1}{2}nk\pi^2\left(\frac{kT}{ef}\right).$$

But we have

$$D = \frac{kT}{et}.$$

So that
$$C_V = \frac{1}{2}nk\pi^2 D.$$

Using the above value of 1/D, we find that

$$C_V = \frac{1}{2}nk\pi^2 \times 1.5 \times 10^{-5} \times T.$$

Putting
$$nk = R \text{ gas constant}$$

$$= 1.978 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$= 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$\pi^2 = 10.$$

We get electronic specific heat

$$C_V = \frac{1}{2} \times 1.5 \times 10^{-5} \times 2 \times 10 \times T$$

$$= 1.5 \times 10^{-4} \times T \text{ cal/gm. Atom.}$$

Pressure of the electrons gas can be obtained from equation

$$P_0 = \frac{2}{5}\frac{ne_f}{V}$$

$$= \frac{2n}{5V}\frac{h^2}{2m}\left(\frac{3n}{4\pi Vg}\right)^{2/3}$$

$$= \frac{nh^2}{20mv}\left(\frac{3n}{\pi V}\right)^{2/3}, \text{ using } g = 2.$$

For a metal of atomic weight 100 and density

$$P_0 - 10^5 \text{ atoms}$$

Which means at normal temperature, the pressure of the gas is sufficiently high.

7.18. SUMMARY

In this you unit you have learnt about construction of symmetric and antisymmetric wave functions. In this you unit you have learnt about different types of distribution method such as Maxwell-Boltzmann, Bose – Einstein and Fermi-Dirac statistics. You also learnt about different type of particle such as Boson and Fermions. You also learnt about Ideal Bose Einstein Gas and Ideal Fermi Dirac Gas. . You also learnt about Gas Degeneracy as an example for molecular hydrogen and for helium. You also learnt about Compressibility of Fermi Gas and electron gas.

7.19. GLOSSARY

Degeneracy - different states of equal energy

Condensation - change of the physical state of matter from the gas phase into the liquid phase

7.20. TERMINAL QUESTIONS

1. What do you understand by a symmetric and anti-symmetricwave functions?

2. What is gas degeneracy explain it for He atom?

3. Explain the following-

   (i)Bose Einstein statistics   (ii) Electron gas

4. Compare all the three statistics Bose Einstein, Fermi Dirac and Maxwell Boltzmann. Show that at low temperature all the statistics give same result.

5. What do you understand by Fermi Dirac statistics? Find an expression for it?

6. What do you understand by Bose Einstein statistics? Find an expression for it?

7. What do you understand by electrons gas? Show that at normal temperature, the pressure of the gas is sufficiently high.

7.21. REFERENCES

1. Statistical mechanics by R.K. Pathria

2. A textbook of Statistical mechanics by Suresh Chandra and Mohit Kumar Sharma

UNIT 8   PHASE TRANSITIONS

Structure

8.1 INTRODUCTION

In the previous unit, you have studied the quantum statistics of identical particles, symmetric and anti-symmetric wave functions, degeneracy, Bose-Einstein condensation etc. The phase transition is very important term in statistical mechanics. In this unit, you will study about phase transitions, various types of phase transitions, Ising model, Landau's theory, Weiss theory of ferro-magnetism, Virial equation of states etc.In the unit, you will also study the significance of phase transitions.

8.2 OBJECTIVES

After studying this unit, you should be able to-

- understand phase transitions
- understand Ising model
- know about ferro-magnetism

8.3PHASE TRANSTION

In this section, let us know about phase transition. The term phase transition (or phase change) is most commonly used to illustrate transitions between solid, liquid, and gaseousstates of matter, as well as plasma in rare cases. A phase of a thermodynamic system and the states of matter have uniform physical properties. During a phase transition of a given medium, certain properties of the medium change, often discontinuously, as a result of the change of external conditions, such as temperature, pressure, or others. For example, a liquid may become gas upon heating to the boiling point, resulting in an abrupt change in volume. The measurement of the external conditions at which the transformation occurs is termed the phase transition. Phase transitions commonly occur in nature and are used today in many technologies.

Phase transitions occur when the thermodynamic free energy of a system is non-analytic for some choice of thermodynamic variables (cf. phases). This condition generally stems from the interactions of a large number of particles in a system, and does not appear in systems that are too small. It is important to note that phase transitions can occur and are defined for non-thermodynamic systems, where temperature is not a parameter. Examples include: quantum phase transitions, dynamic phase transitions, and topological (structural) phase transitions. In these types of systems other parameters take the place of temperature. For instance, connection probability replaces temperature for percolating networks.

At the phase transition point (for instance, boiling point) the two phases of a substance, liquid and vapor, have identical free energies and therefore are equally likely to exist. Below the boiling point, the liquid is the more stable state of the two, whereas above the gaseous form is preferred.

It is sometimes possible to change the state of a system diabatically (as opposed to adiabatically) in such a way that it can be brought past a phase transition point without undergoing a phase transition. The resulting state is metastable, i.e., less stable than the phase

to which the transition would have occurred, but not unstable either. This occurs in superheating, supercooling, and supersaturation, for example.
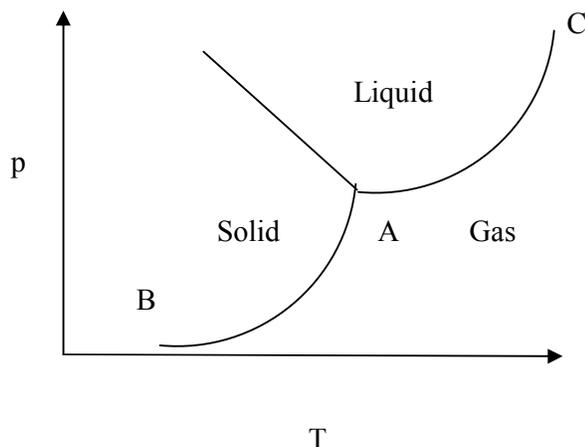

Figure 1: Phase diagram

      Simple substances are capable of existing in phases of three types- solid, liquid and gas. The three lines, in a phase diagram (Figure 1) separating these phases are called phase equilibrium lines. The common point A, where three lines meet, is called 'triple point' at this unique temperature and pressure all three phases can coexist in equilibrium with each other. Point C is the critical point at which liquid gas equilibrium line ends. The change in volume ΔV between liquid and gas has then approached zero; beyond C there is no further phase transition since there exists only one 'fluid phase'

      The following figure 2 shows the curve of constant temperature T for an equation of state $p = p(v, t)$ describing the fluid state of a substance. In the shaded region mixture of two phases can coexist along the horizontal line. If at the given temperature T, the pressure is sufficiently low so that $p < p_1$, the curve gives in, correspondingly, a unique value of v. There exists then a well defined single phase. Here the slope of the curve $\frac{\partial p}{\partial v} \leq 0$ as necessary for the stability condition. Also $|\frac{\partial p}{\partial v}|$ is relatively small so that compressibility of this phase is large as in a case of a gaseous phase.

      If at the given temperature T the pressure is sufficiently high that $p > p_2$, then there exists again a single phase with a unique value of v. The stability condition $\frac{\partial p}{\partial v} \leq 0$ is again satisfied but $|\frac{\partial p}{\partial v}|$ is relatively large so that compressibility of this phase is relatively small as would be the case for a liquid phase.

p

p_2

p_1

O v_1 v_2
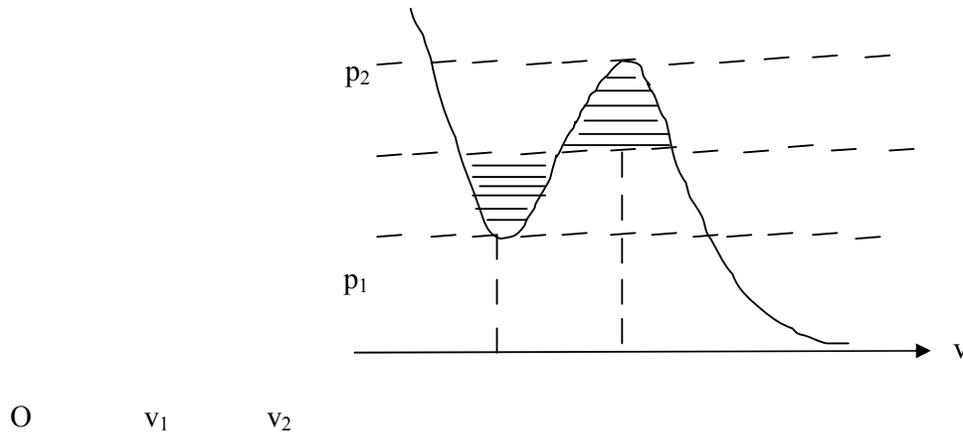
Figure 2: Fluid state representation

For intermediate pressure range $p_1 < p < p_2$. At the given temperature T, there are three values of v for each pressure p. In addition, the stability condition $\frac{\partial p}{\partial v} \leq 0$ is violated in

the region $v_1 < v < v_2$ where curve has positive slope. This is the region where mixture of two phases coexist along the horizontal line.

8.3.1 Classifications of Phase Transitions

Let us discuss the classifications of phase transitions. There are two classifications of phase transitions. Now we shall discuss these phase transitions one by one.

Ehrenfest classification

Paul Ehrenfest classified phase transitions based on the behavior of the thermodynamic free energy as a function of other thermodynamic variables. Under this scheme, phase transitions were labeled by the lowest derivative of the free energy that is discontinuous at the transition. First-order phase transitions exhibit a discontinuity in the first derivative of the free energy with respect to some thermodynamic variable. The various solid/liquid/gas transitions are classified as first-order transitions because they involve a discontinuous change in density, which is the (inverse of the) first derivative of the free energy with respect to pressure. Second-order phase transitions are continuous in the first derivative (the order parameter, which is the first derivative of the free energy with respect to the external field, is continuous across the transition) but exhibit discontinuity in a second derivative of the free energy. These include the ferromagnetic phase transition in materials such as iron, where the magnetization, which is the first derivative of the free energy with respect to the applied magnetic field strength, increases continuously from zero as the temperature is lowered below the Curie temperature. The magnetic susceptibility, the second derivative of the free energy with the field, changes discontinuously. Under the Ehrenfest classification scheme, there could in principle be third, fourth, and higher-order phase transitions.

Though useful, Ehrenfest's classification has been found to be an incomplete method of classifying phase transitions, for it does not take into account the case where a derivative

of free energy diverges (which is only possible in the thermodynamic limit). For instance, in the ferromagnetic transition, the heat capacity diverges to infinity. The same phenomenon is also seen in superconducting phase transition.

Modern classifications

In the modern classification scheme, phase transitions are divided into two broad categories, named similarly to the Ehrenfest classes:

First-order phase transitions are those that involve a latent heat. During such a transition, a system either absorbs or releases a fixed (and typically large) amount of energy per volume. During this process, the temperature of the system will stay constant as heat is added: the system is in a "mixed-phase regime" in which some parts of the system have completed the transition and others have not.[4][5] Familiar examples are the melting of ice or the boiling of water (the water does not instantly turn into vapor, but forms a turbulent mixture of liquid water and vapor bubbles). Imry and Wortis showed that quenched disorder can broaden a first-order transition. That is, the transformation is completed over a finite range of temperatures, but phenomena like supercooling and superheating survive and hysteresis is observed on thermal cycling.

Second-order phase transitions are also called "continuous phase transitions". They are characterized by a divergent susceptibility, an infinite correlation length, and a power law decay of correlations near criticality. Examples of second-order phase transitions are the ferromagnetic transition, superconducting transition (for a Type-I superconductor the phase transition is second-order at zero external field and for a Type-II superconductor the phase transition is second-order for both normal-state—mixed-state and mixed-state—superconducting-state transitions) and the superfluid transition. In contrast to viscosity, thermal expansion and heat capacity of amorphous materials show a relatively sudden change at the glass transition temperature which enables accurate detection using differential scanning calorimetry measurements. Lev Landau gave a phenomenologicaltheory of second-order phase transitions.

Apart from isolated, simple phase transitions, there exist transition lines as well as multicritical points, when varying external parameters like the magnetic field or composition.

Several transitions are known as infinite-order phase transitions. They are continuous but break no symmetries. The most famous example is the Kosterlitz–Thouless transition in the two-dimensional XY model. Many quantum phase transitions, e.g., in two-dimensional electron gases, belong to this class.

The liquid–glass transition is observed in many polymers and other liquids that can be supercooled far below the melting point of the crystalline phase. This is atypical in several respects. It is not a transition between thermodynamic ground states: it is widely believed that the true ground state is always crystalline. Glass is a quenched disorder state, and its entropy, density, and so on, depend on the thermal history. Therefore, the glass transition is primarily a dynamic phenomenon: on cooling a liquid, internal degrees of freedom successively fall out of equilibrium. Some theoretical methods predict an underlying phase transition in the hypothetical limit of infinitely long relaxation times. No direct experimental evidence supports the existence of these transitions.

8.4 Theory of Yang and Lee

In this section, we shall discuss theory of Yang and Lee. This theory is a mathematical description of phase transition which becomes possible because we can characterize a phase transition as the manifestation of a certain singularity or discontinuity in the equation of state-

$$\beta P = \frac{1}{V} \log Z(z,v)$$

$$\frac{1}{v} = \frac{1}{V}.z.\frac{\partial}{\partial z}\log Z\ (z,V) \qquad\qquad .....(1)$$

where $\beta = \frac{1}{kT}$, v the specific volume – a parameter independent of the total volume, V. Z is the grand partition function, z is the fugacity defined by-

$$z \qquad\qquad = \qquad\qquad e^{\beta\mu}$$

.....(2)

It can be made clear that both P and v are analytic functions of z in a region of the complex z-plane that includes the real positive axis. For any finite value of V, there are no real positive roots of the equation Z (z, V) = 0. This means that regarded as a function of complex variable z the zeros of the function Z(z, V) are distributed in the complex z-plane but are never on the positive real axis. But as V increases, number of zeros increases and their positions may move about in the complex z-plane. In the limit as V→ ∞ some of the roots may converge towards the positive real axis. In this limit, the equation of state is given by-

$$\beta P = \lim_{V \to \infty}\left[\frac{1}{V}\log Z(z,V)\right] \qquad\qquad .....(3)$$

$$\frac{1}{v} = \lim_{V \to \infty}\left[\frac{1}{v}z\frac{\partial}{\partial z}\log Z(z,v)\right]$$

We may now hope to find possible singularities in the equation of state that can be identified as phase transitions. Suppose that in the complex z-plane there is a region R which contains a segment of the real positive z-axis and which is free of zeros of Z(z,v) for all V. It is reasonable to expect that as V→∞, the stability condition $\frac{\partial p}{\partial v} \leq 0$ holds. In that case region R represents a single phase. If there are many overlapping regions R, each region may be expected to correspond to a phase of the system. Therefore, to study phase transition, we study the behavior of equation of state as z goes from one R region to another. In this reference, there are two theorems- theorem 1 and theorem 2. Let us discuss these two theorems.

8.4.1 Theorem 1

$\lim_{V \to \infty} \left[\frac{1}{V} \log Z(z,V) \right]$ exists   for all z> 0. This limit is independent of the shape of the volume V and is a continuous, non-decreasing function of z.

It is assumed that as V →∞ the surface area of V increases no faster that $V^{2/3}$.

8.4.2 Theorem 2 (First order Phase Transitions)

This theorem tells about first order phase transition. Let us discuss theorem 2.

Let us consider a region R in the complex z- plane that contains a segment of the positive real axis and contains no root of the equation Z(z, v) = 0 for any V, then for all z in the region R the quantity V^{-1} log Z(z, v) converges uniformly to a limit as V→∞. This limit is an analytic function of z for all z in region R.

Now let us discuss possible behaviors of equation of state consistent with above theorems. Suppose region R includes complete positive z-axis as shown in figure 3. Then the system is always in a single phase and if a phase of the system be defined as the collection of thermodynamic states corresponding to values of zlying in the single region R then P and v in


R

O
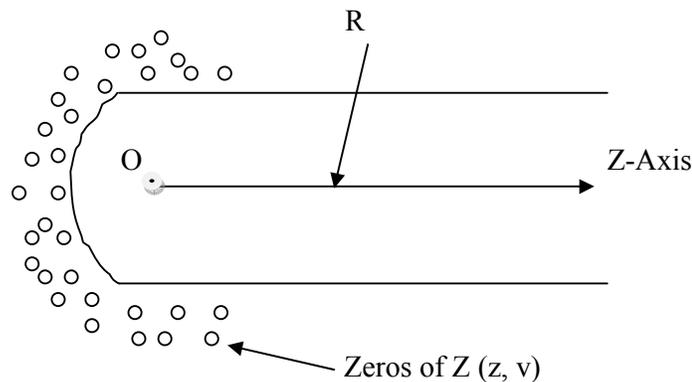
Z-Axis

Zeros of Z (z, v)

Figure 3: Region R that is free of zeros of Z (z, v)

the equation of state can be written as-

$$\beta\, P\,(z) = \lim_{V \to \infty} \frac{1}{V} \log Z\,(z,V) = F_\infty(z) \qquad\qquad .....(4)$$

$$\frac{1}{v(z)} = z\, \frac{\partial F_\infty(z)}{\partial z}$$

On the other hand, if a zero of Z (z, V) approaches the point z_0 on the real positive z-axis as V→∞ then there will be two regions R_1 and R_2 in which theorem 2 holds separately [as

shown in figure (4)]. At z= z_0, P(z) must be continuous though its derivative dP(z)/dz may be discontinuous. An example of such a behavior is shown in figure(5), where for z < z_0 system possesses one phase while for z > z_0, the other phase.


Zeros of Z (z, v)
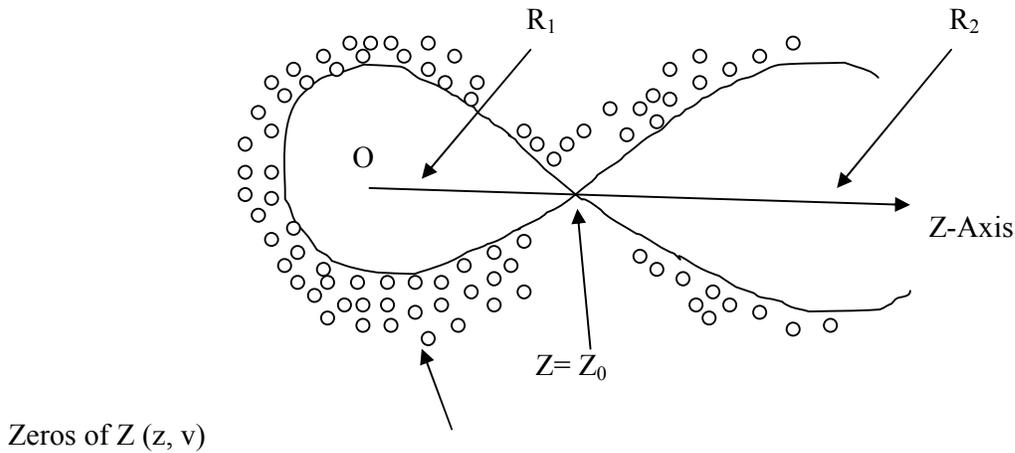
**Figure 4: Two regions R₁ and R₂each free of zones of Z (z, v)**
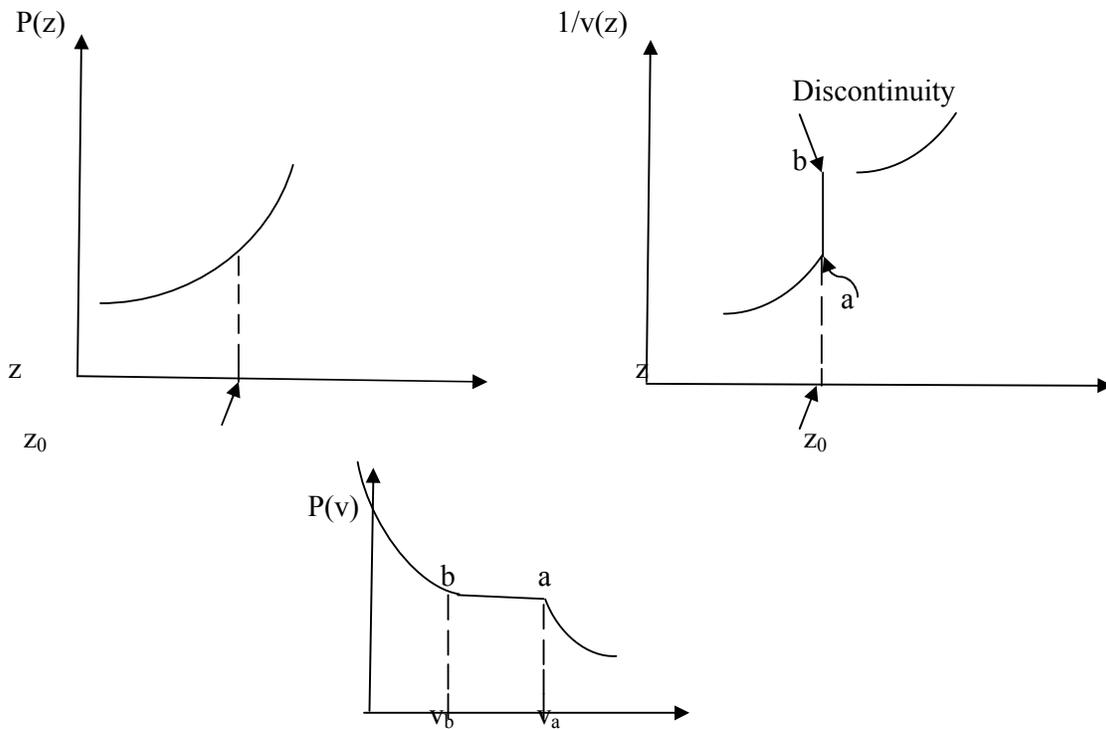
Figure 5: Equation of state of a system with two phases connected by a first order transition

At z = z_0, 1/v(z) is discontinuous. Thus we obtain first order phase transition between two phases (first order derivative is discontinuous at z = z_0). This is shown infigure 5 exhibiting a discontinuity at z = z_0. If dP(z)/dz is continuous at z = z_0 but second derivative $d^2P(z)/dz^2$ is discontinuous then we have second order phase transition. In the next section, we shall study second order phase transitions in detail.

8.5 Second Order Phase Transitions

Now in this section, let us study second order phase transition. If in the above example, dP(z)/dz is continuous at z = z_0 but second derivative $d^2P(z)/dz^2$ is discontinuous then we have second order phase transition. The transition of liquid helium I into helium II for the common isotope of He^4 is a well known example of second order phase transition. The other example of second order phase transition is the transition from non-ferromagnetic state to a ferromagnetic state. When a magnetic material changes its state from a ferromagnetic material to a paramagnetic material, the symmetrical arrangement of the elementary magnetic moments undergoes a discontinuity jump and the symmetry changes. Therefore, the second order phase transitions are usually associated with the abrupt changes in various properties characterizing the symmetry of the body. Thus, we can conclude that phase transition of second is continuous in the sense that the state of the body changes continuously but discontinuous in the sense that symmetry of the body changes discontinuously.

8.6 Ising Model: Phase Transitions of second kind

In this section, we shall study Ising Model and phase transitions of second kind. In phase transition of second kind, the state of the body changes continuously. Let us consider a ferromagnetic substance like iron or nickel. In the absence of any external magnetic field, some of the spins of the atoms become spontaneously polarized in the same direction, below the curie temperature T_c. This generates a macroscopic magnetic field. The spontaneous magnetization, so generated, vanishes if temperature is greater than T_c because then thermal energy makes some of the aligned spins to flip over. In this way, the spinsget oriented at random and no net magnetic field is produced. As the curie temperature is approached from both sides the specific heat of the metal approaches infinity. The transition from non-ferromagnetic state to the ferromagneticstate called the phase transition of second kind is associated with some kind of change in the symmetry of the lattice; for example, in ferromagnetism the symmetry of the spins is involved. In Ising model, the system considered is an array of N fixed points called lattice sites that form an n-dimensional periodic lattice (n = 1, 2, 3). Associated with each lattice site is a spin variable s_i (i=1,2,…….N) which is anumber that is either +1 or -1. There are no other variables. If s_i = +1, the ith state is said to have spin up and s_i = -1, it is said to have spin down. A given set of $\{s_i\}$ specifies a configuration of the whole system whose energy is defined to be –

$$E_I\{s_i\} = - \sum_{<i,j>} \varepsilon_{ij}\, s_i s_i s_j - \mu H \sum_{i=1}^{N} s_i \qquad \text{…..(5)}$$

where the subscript I stands for Ising and the symbol < i, j> denotes a nearest-neighbor pair of spins. There is no distinction between < i, j> and <j, i>. ε_{ij} is the interaction energy and μH is the interaction energy associated with an external magnetic field H. For spontaneous magnetization, H = 0. μ_{ij} and H are given constants. We apply the model to the case is isotopic interaction so that all ε_{ij} have the same value ε. We write for energy-

$$E_I\{s_i\} = - \sum_{<i,j>} \varepsilon\, s_i s_j - \mu H \sum_{i} s_i$$

Or $$E_I\{s_i\} = - \varepsilon \sum_{<i,j>} s_i s_j - \mu H \sum_{i=1}^{N} s_i \qquad \text{…..(6)}$$

The case $\varepsilon > 0$ corresponds to ferromagnetism and the case $\varepsilon < 0$ to anti-ferromagnetism. In the former case neighbouring spins tend to be parallel while in the latter case they tend to be antiparallel. In equation (6), the sum over $<i, j>$ contains $\gamma N/2$ terms where γ is the number of nearest neighbours of any given site (coordination number of the lattice). Thus in the Ising model equation (6), geometry of the lattice enters through γ and interaction energy ε_{ij}.

We consider only the case of $\varepsilon > 0$. The partition function can be written as-

$$Z = \sum_{S_1} \sum_{S_2} \dots \dots \sum_{S_N} e^{-\beta E_I\{S_i\}} \qquad \qquad \dots(7)$$

where each S_i ranges independently over the values ± 1. Hence, there are 2^N terms in the summation. Thermodynamic functions e.g. internal energy, heat capacity can be calculated through Z but it is enormously not easy to calculate the partition function. There are so many approximate methods for this.

8.7 Ising Model: One Dimensional

One-dimensional Ising model is a chain of N spins, each spin interacting only with its two nearest neighbours. Ignoring external magnetic field H, we can write for the energy of the configuration specified by $\{S_1, S_2, S_3, \dots .. S_N\}$ as-

$$E_I \qquad = \qquad - \qquad \varepsilon \qquad \sum_{i=1}^{N} S_i S_{i+1}$$
$$\dots(8)$$

Applying periodic boundary condition,

$$S_{i+1} = S_i$$

The partition function is-

$$Z = \sum_{S_1 = \pm 1} \dots \dots \dots \sum_{S_N = \pm 1} \exp[\beta \varepsilon \sum_{i=1}^{N} S_i S_{i+1}]$$

$$= \qquad \sum_{S_1 = \pm 1} \dots \dots \dots \sum_{S_N = \pm 1} \pi[\cosh \beta \varepsilon + S_i S_{i+1} \sinh \beta \varepsilon]$$
$$\dots(9)$$

where, we have used $\exp(css') = \begin{cases} e^c & (ss' = 1) \\ e^{-c} & (ss' = -1) \end{cases} = (\cosh c + ss' \sinh c)$

which holds because ss' can only be $+1$ or -1. The expansion of products in equation (9) gives a sum of terms, each of which is a product of the form-

(cos   βε)   N^{-S} (sinh   βε)^s (S$_i$ S$_{i+1}$ ………..   S$_j$ S$_{j+1}$)
…..(10)
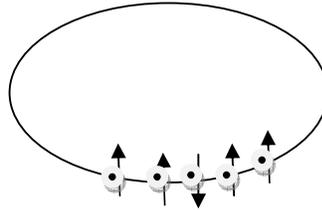
Figure 6: N Ising spins arranged in a ring

Graphically these terms can be displayed by thick (corresponding to factor SS$^{'}$ sinh βε) and thin (corresponding to factor cosh βε) links forming the ring. It can be argued that non-zero terms are the first term (cosh βε)^N and the last term (sinh βε)^N so that-

$$Z = 2^N [(\cosh \beta\varepsilon)^N + (\sinh \beta\varepsilon)^N]$$

$$= 2^N \ (\ \cosh \ \beta\varepsilon)^N \ , \qquad \text{for} \quad N \quad >>1.$$
…..(11)

because cosh βε >>sinh βε for βε = $\frac{\varepsilon}{kT} \neq \infty$ for T ≠0.

Therefore, Helmholtz free energy for the system is written as-

$$F \ = \ -kT \ \log_e Z \ = \ - \ N \ k \ T \ \log_e \left(2 \cosh \frac{\varepsilon}{kT} \right)$$
…..(12)

We can write the energy of the system as-

$$E \ = \ \frac{\varepsilon}{\partial \left(\frac{1}{T} \right)} \left(\frac{F}{T} \right) \ = \ - \ N \ \varepsilon \ \tanh \ \left(\frac{\varepsilon}{kT} \right)$$
…..(13)

Obviously, in this case, there is no transition temperature. Therefore, one dimensional Ising model cannot be ferromagnetic.

8.8 Weiss Theory of Ferro-magnetism

To explain the phenomenon of ferromagnetism, Weiss proposed a hypothetical concept of ferromagnetic domains. He postulated that the neighboring atoms of the ferromagnetic materials, due to certain mutual exchange interactions, form several numbers

of very small regions, called domains. Weiss theory of ferromagnetism is also called domain theory of ferromagnetism. It has following points:

- The domains which are aligned approximately along the direction of the applied magnetic field grow in size at the cost of unfavorably oriented domains, that is, those align opposite to the field direction get reduced. In other words, the domain boundaries move so as to expand the favorable domains.
- Also domains rotate and orient themselves in the direction of the external magnetic field.

In the presence of the weak external field, the magnetization in the material occurs mostly by the process of domain growing, but in the strong magnetic field the material is magnetized mostly by the process of domain alignment. When the magnetic field is removed, the domain boundaries do not recover their original positions and thus, the material is not completely demagnetized, but some residual magnetism remains in it.

When the magnetizing field is weak; the magnetic polarization of the sample changes as a result of motion of domain walls. In this process, domains whose axes are parallel or at a small angle with the magnetic field grow at the expenses of those which are unfavorably oriented [Figure 7 (b)]. This growth is reversible so long as the magnetic field stays very small; if we turn the magnetic field off, the magnetization will return to zero. This part of magnetization curve is marked in figure 7. In this region of field strength, magnetization is not a continuous process but takes place in a series of infinite small discrete steps because of the irregularities in crystal structure which might be due to strains, dislocation, impurities, dirt and imperfections. This can be shown by inserting the sample in a coil connected to an amplifier and loudspeaker, If the magnetic field surrounding the speaker is slowly increased, individual clicks are heard in a speaker which represent small discrete flux-increments. This is known as Barkhausen effect.
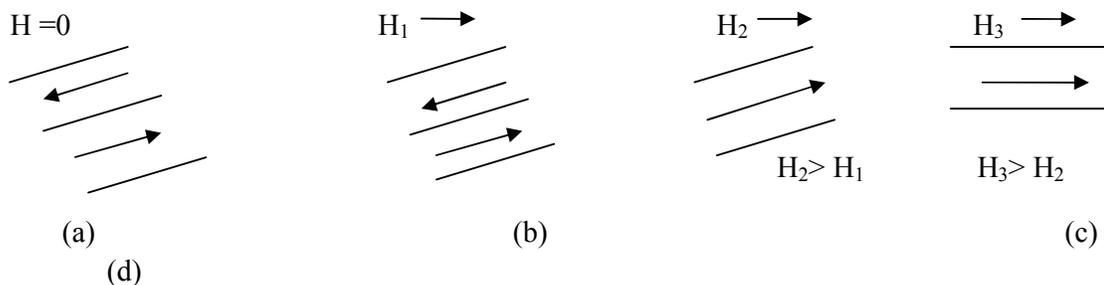

Figure 7: Magnetic domain

The step like nature of the magnetization curve, it viewed on a macroscopic scale, would appear as shown in figure 8.


185
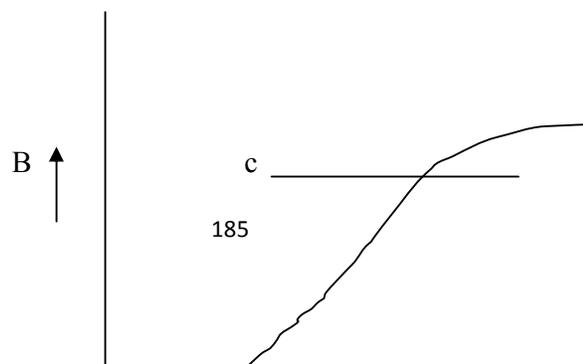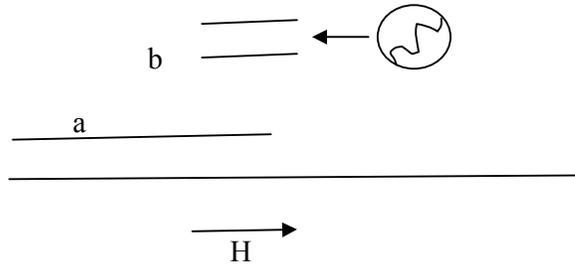
Figure 8: Step-like nature of magnetization curve

Now, let us explain the curve as shown in figure 8. It is obvious from the curve that near the knee of the curve, we have moved all domains walls and magnetized each crystal of the sample in its best direction [figure 7 (c)]. The use of a very powerful magnetic field then causes domain rotation, during which the magnetic polarization assumes a direction parallel to the applied magnetic field as in figure 7 (d) and this accounts for the curve c in figure 8. In this way, the motion of the domain walls accounts for portion of the magnetization curve below the knee of the curve while domain rotation accounts for the portion above the knee. If the applied magnetic field is removed, there is little change in the domain structure so that the magnetization remains quite high until reverse magnetic fields are applied and this accounts for the hysteresis.

Weiss introduced the idea of domains. Weiss assumed that in ferromagnetic substances, there must exist a molecular field produced at any point by all the neighboring molecules which is proportional to the magnetization vector M, i.e.

Molecular field $\propto M$

$$= \alpha\, M$$

In this way, the actual magnetic field acting upon a dipole is the sum of the applied field H and that arising from the presence of neighbouring dipoles i.e. effective magnetizing field may be expressed as-

$$H_i \qquad = \qquad H \qquad + \qquad \alpha \qquad M$$
…..(14)

assuming that the contributions of the neighbouring dipoles to the effective field is proportional to the magnetic polarization. This form of dependence is not self evident but was chosen by Weiss because it leads to the desired form. The factor of proportionality α is known as the molecular field coefficient.

When the molecular field coefficient α is positive, the possibility of spontaneous magnetization of these domains arises even in the absence of external magnetic field. The value of such a spontaneous magnetization due to internal molecular field may be found by putting the external field H to zero in the above relation. This reduction can also determine the condition for spontaneous magnetization.

Since the domains are assumed to obey the general theory of paramagnetism, therefore, we can write-

$$M/M_S = \coth x - 1/x \qquad \text{.....(15)}$$

Where $x = m\ B_i\ /kT = \mu_0\ m\ H_i/\ kT = \mu_0\ m\ (H + \alpha\ M)/\ kT$ .....(16)

$M_S = nm$ represents the saturation value of I, n = total number of molecules or atoms per unit volume of the substance, m = magnetic moment of the atom, k = Boltzmann's constant and rest symbols have their usual meaning.

Since the dipole aligning force $H_i = H + \alpha\ M$ depends partially upon the degree of alignment , any increase in magnetic polarization will result in an increase in the aligning force, which in turn, will result in an increase in the magnetic polarization etc. Thus, magnetization once induced, could occur without the application of an external field. Let us now examine the conditions under which such spontaneous magnetization could take place. When the applied field is zero i.e. $H = 0$ the equation (16) reduces to-

$$x = \mu_0\ m\ \alpha\ M\ /kT = \alpha\ (\mu_0\ M\ M_S)/\ (n\ k\ T) \qquad \text{.....(17)}$$

Since $M_S = n\ m$, therefore equation (17) may be expressed as-

$$M/M_S = (n\ k\ T)\ x\ /\ (\alpha\ \mu_0 M_S^2) \qquad \text{.....(18)}$$

Equations (15) and (18) constitute a pair of equation which may be solved simultaneously for two variables M/M_S and x.

Figure (9) represents the curves corresponding to two equations (15) and (18) ; equation (15) gives the Langevin's curve 1 while equation (18) gives a straight line 2 passing through the origin whose slope is equal to $(n\ k\ T)/\ (\alpha\ \mu_0\ M_S^2)$ and increases with T. These two curves intersect at origin O and at another point A so that solutions of these equations are-

$$M/M_S = 0\ \text{or}\ AP$$

$$\xrightarrow{\hspace{3cm} P \hspace{3cm}}$$

x
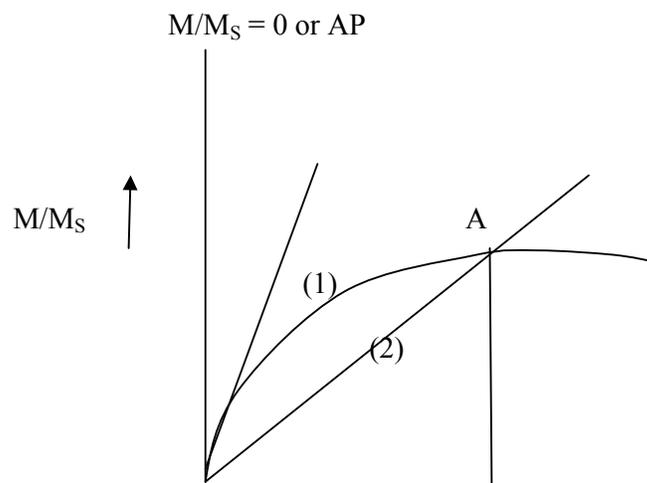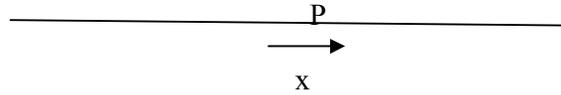
Figure 9: Curves corresponding to equations (15) and (18)

But $M/M_S = 0$ cannot be a true solution, since there is spontaneous magnetization by supposition. Hence, the only correct solution is $M/M_S = AP$ i.e. non-zero point of intersection of two curves. We can conclude that as the slope of the straight line curve (2) increases with T, if this slope coincide or becomes greater than that tangent at the origin to the Langevin curve, then there will not exist a non- zero point of intersection of two curves; hence the spontaneous magnetization will not occur. On the other hand, we know that the slope of the tangent at the origin to the Langevin curve is 1/3, since $M / M_S = x/3$, when x is small. From these considerations, the condition of stable spontaneous $(nkT/ \alpha\mu_0 M_S^2) < 1/3$ magnetization may be expressed as $T < (\alpha\mu_0 M_S^2/ 3nk)$.

But $\alpha\mu_0 M_S^2/ 3nk = \Theta$, the Curie point ; hence $T < \Theta$. Hence, below Curie point Θ a state of magnetization is possible without an applied field. The degree of spontaneous magnetization depends on the temperature approaching the saturation value as the temperature approaches absolute zero, since the non-zero point intersection will take place at-

$M/M_S =1$ for $x = \mu_0 m H_i /k T \rightarrow \infty$ when $T = 0$.

From the relation $\Theta = \alpha\mu_0 M_S^2/ 3n k$, we may note that the absolute value of Θ is greater if the magnetic moment of domains (M_S) and molecular field coefficient α have large values. If Θ is greater, greater will be the transition temperature. Incidentally, the Curie temperature for ferromagnetic elements Fe, Co and Ni are 770^0C, 1131^0 C and 358^0 C respectively. Above the Curie point Θ, the spontaneous magnetization no longer occurs and ferromagnetic properties disappear and the substance becomes paramagnetic.   At temperature, not too near the transition point the Curie-Weiss law is obeyed.

There are some shortcomings of Weiss theory. This theory could not explain why and how internal fields between the molecules of ferromagnetic materials possess such large values and why the linear relationship expressed by Curie-Weiss law breaks near the Curie point.

8.9 Landau's Theory

The **Landau theory** of phase transitions is based on the idea that the free energy can be expanded as a power series in the order parameter m. ... The parameters that are input into the form are also used to plot the temperature dependence of the order parameter, the free energy, the entropy, and the specific heat.

At a first-order phase transition, an order parameter like the magnetization is discontinuous. At a critical point, the magnetization is continuous – as the parameters are tuned closer to the critical point, it gets smaller, becoming zero at the critical point. However,

experiments on the liquid-gas phase transition and on three-dimensional magnets (and exact computations like Onsager and Yang's for the two-dimensional Ising model) both point that even though the magnetization is continuous, its derivative is not. In mathematical language the magnetization is a continuous function, but not analytic. For example, at h → 0+ in the Ising magnet in 3d, the magnetization vanishes as T → Tc from below as-

$$M \propto (Tc - T)^{0.315} \qquad T < Tc, \text{ 3d Ising} \qquad \qquad …..(19)$$

where all evidence suggests that the exponent is not even a rational number. In the two-dimensional Ising model, the exact computations give

$$M \propto (Tc - T)^{1/8} \qquad T < Tc, \text{ 2d Ising} \qquad \qquad …..(20)$$

Even though the exponent is rational, the function is decidedly not analytic. This was (and remains) very strange compared to most of physics. The partition function of any finite system is a continuous function of all the parameters. Thus if any non-analyticity occurs, it must be a property of taking an infinite number of degrees of freedom. We usually take this limit out of necessity – it's not possible to follow 1023 (or for that matter even 100) particles individually, even with a computer. Even Monte Carlo simulations can at best do thousands of particles. Now we're saying that at a critical point, the limit we so desperately need to take is suspect. Since dimensionalanalysis arguments rely on analyticity, these are also suspect. Of course, at the end of the day all formulas are dimensionally consistent. What happens though is that at and near critical points, a hidden parameter is necessary for describing the physics. This 1 parameter arises from the short-distance physics – even if we are interested in describing long-distance physics, critical physics necessarily involves all length scales! To understanding how that happens requires considerable effort – this is why Wilson won a Nobel Prize, and why many others provided essential ingredients. The first major step toward theoretical understanding came from Landau, and his approach is still called today Landau theory, or Landau-Ginzburg theory. Sometimes it is also called GinzburgLandau theory, because the two wrote a paper applying these ideas to superconductivity.

Landau theory is an effective theory for what happens at and near the critical point. The experimental fact that very different systems can have quantitatively identical critical behavior suggests that one does not need to worry about every single detail of the system to understand this behavior. We gave an explicit example of how if we ignored many details of the liquid-gas system, we could obtain a lattice gas that was identical to the Ising model. This provides a suggestion as to why the universality occurs; Landau theory is the first serious attempt to derive a theory that will describe the critical behavior quantitatively. Landau theory only describes the universal behavior of a system; by construction, it cannot for example give non-universal numbers like the value of Tc for a given system. But one of the miracles of critical behavior is that it can give precise results for the universal behavior. It is important to emphasize that Landau's original (genius) idea for an effective theory was and remains completely correct. It's just that the naive computations do not give the right answers. To be precise, in the next section, I will describe how the effective theory can arise

from taking a specific approximation called mean-field theory. This approximation breaks down in low dimensions, for reasons explained by Ginzburg. But one of the beautiful aspects of Landau theory is that it makes deriving the consequences of mean-field theory really easy. The whole point is that the effective theory is independent of the details, so one can just guess what it is based on the symmetries and degrees of freedom of the system. Landau theory is an effective theory of the order parameter. To be precise about it, one first decides what the appropriate order parameter is to describe the phase transition. In one phase, the order parameter is non-vanishing, in another it vanishes. In a ferromagnetic spin system, this very naturally is the magnetization $\vec{M}$. In an antiferromagnetic systems, there are a variety of possibilities, such as the staggered magnetization, which describes a transition away from N´eel order. Another possibility is that no local order parameters change values at a phase transitions. One example of such is known as "topological order", where only non-local order parameters characterize the transition. One of Landau's insights was an easy way to see how the non-analyticity arises. The basic assumption of Landau theory is that at a fixed value of the order parameter, the free energy as a function of the order parameter is analytic, both in the parameters such as J and T, and in the order parameter itself.

8.10 Viril Equation of States

Because the perfect gas law is an imperfect description of a real gas, we can combine the perfect gas law and the compressibility factors of real gases to develop an equation to describe the isotherms of a real gas. This Equation is known as the *Virial Equation of state,* which expresses the deviation from ideality in terms of a power series in the density.

$$\frac{P}{RT} = \rho + B\rho^2 + C\rho^3 + \ldots\ldots\ldots \qquad \ldots(21)$$

where B is the second virial coefficient, Cis called the third virial coefficient, etc.

The second Virial coefficient represents the initial departure from ideal-gas behavior and describes the contribution of the pair-wise potential to the pressure of the gas. The third virial coefficient depends on interactions between three molecules. The jth virial coefficient can be calculated in terms of the interaction of j molecules in a volume V. The second and third Virial coefficients give most of the deviation from ideal $\frac{P}{\rho RT}$ up to 100 atm. It is important to note

that value of the virial coefficients are temperature dependent.

Because $\rho = \frac{n}{V} = \frac{1}{\bar{V}}$ $\qquad \ldots(22)$

We can rearrange the viril equation to-

$$P\bar{V} = RT \left(1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \ldots\ldots\right) \qquad \ldots(23)$$

Or $P\overline{V} = R \; T \; Z$

…..(24)

Where $Z = \left(1 + \frac{B}{\overline{V}} + \frac{C}{\overline{V}^2} + \; \text{………}\right)$

…..(25)

The *virial Equation of state* is a model that attempts to describe the properties of a real gas. If it were a perfect model, the viril equation would give results identical to those of the perfect gas law as the pressure of a gas sample approached zero. For the viril equation to collapse to the perfect gas law, all of the viril coefficients would need to have a value of zero at the same temperature. This is an unlikely occurrence but because the second term in the viril equation $B = \frac{B}{\overline{V}}$ is the largest termin the equation ($\frac{1}{\overline{V}} \ll \frac{1}{\overline{V}^2} \ll \frac{1}{\overline{V}^3} \ll \cdots \; \text{……}$), we can focus on the temperature at which B is zero. This temperature is called the Boyle temperature (T_B) and it is the temperature at which the repulsive forces between the gas molecules exactly balance the attractive forces between the gas molecules. The equation (23) can be written as-

$$P = RT \left\{1 + \frac{B}{RT} P + \frac{C}{(RT)^2} P^2 + \; \text{………}\right\} \qquad …..(26)$$

In which case, $Z = 1 + \frac{B}{RT} P + \frac{C}{(RT)^2} P^2 + \; \text{… …}$

…..(27)

Then, $\frac{dZ}{dP} \to \frac{B}{RT} \; as \; P \to 0$

…..(28)

Example 1: Calculate the pressure exerted by 0.275 moles of N_2 gas in a 0.500 L flask at 273 K using the first two terms of the series of viril equation. The value of B for N_2 at 273 K is – 10.5 cm³/mole.

Solution: Given, V = 0.275 L = 5 × 10⁻⁴ m³

B = - 10.5 cm³/mole = - 1.05 × 10⁻⁵ m³/mole

$V = \frac{V}{n} = \frac{5 \times 10^{-4} m^3}{0.275 \, moles} = 1.82 \times 10^{-3}$ m³/ mole

Now applying equation $P\overline{V} = RT \left(1 + \frac{B}{\overline{V}}\right)$

P × 1.82 × 10⁻³ m³/ mole = 8.3145 Joule/mole K × 273 K $\left(1 - \frac{-1.05 \times 10^{-5} m^3 / moles}{1.82 \times 10^{-3} m^3 / moles}\right)$

Or   P = 1240 k Pa

For a perfect gas, the pressure would be 1250 kPa.

Self Assessment Question (SAQ) 1: Calculate the pressure exerted by 0.35 moles of CO_2 gas in a 0.5 L flask at 273 K. The value of B for CO_2 at 273 K is -149.7 cm^3/mole.

8.11 Summary

In this unit, you have studied about phase transition and its classification. You have studied that during a phase transition of a given medium, certain properties of the medium change, often discontinuously, as a result of the change of external conditions, such as temperature, pressure, or others. You have discussed Ehrenfest and Modern classifications in detail. In the unit, you have also discussed the theory of Yang and Lee, Ising model etc. To explain the phenomenon of ferromagnetism, you have studied Weiss theory of ferro-magnetism in the unit. Weiss postulated that the neighboring atoms of the ferromagnetic materials, due to certain mutual exchange interactions, form several numbers of very small regions, called domains. You have also discussed and analyzed the Landau's theorem and Virial equation of states. The Landau theory of phase transitions is based on the idea that the free energy can be expanded as a power series in the order parameter m. ... The parameters that are input into the form are also used to plot the temperature dependence of the order parameter, the free energy, the entropy, and the specific heat.To present the clear understanding and to make the concepts of the unit clear, some solved examples are given in the unit. To check your progress, self assessment questions (SAQs) and terminal questions are given in the unit.

8.12 Glossary

Generate - create, make, cause

Macroscopic- Visible to naked eye without use of any instrument.

Spontaneous- natural, impulsive

Magnetization- Difference between the ratio of the magnetic induction to the permeability and

the magnetic intensity. It represents departure from randomness of magnetic

domains.

Align- line up, ally

8.13 Terminal Questions

1. What is meant by phase transition? Explain first order and second order phase transitions.

2. What are the phase transitions of first and second kind? Discuss Ising model for phase transitions of second kind.

3. Give a brief account of one-dimensional Ising model.

4. What are phase transitions? How Yang and Lee theory may be used to explain phase transition?

5. Explain Landau theory of phase transitions.

6. Write notes on-

    (a) Virial equation of states   (b) Weiss theory of ferro-magnetism

7. Discuss Weiss's modification to explain the phenomenon of spontaneous magnetization in ferromagnetic substances.

8. Establish Virial equation of states. What are the advantages of this equation of states?

8.15 Answers

Self Assessment Questions (SAQs):

1. Given, $V = 0.5$ L $= 5 \times 10^{-4}$ m^3 , B $= - 149.7$ cm^3/mole $= - 1.497 \times 10^{-4}$ m^3/mole, n $= 0.35$ moles

$$\bar{V} = \frac{V}{n} = \frac{5 \times 10^{-4} m^3}{0.35 \, moles} = 1.42 \times 10^{-3} \, m^3 / \text{ mole}$$

Now applying equation $P\bar{V} = RT \left(1 + \frac{B}{\bar{V}}\right)$

$P \times 1.42 \times 10^{-3}$ m^3/ mole $= 8.3145$ Joule/mole K $\times 273$ K $\left(1 - \frac{-1.497 \times 10^{-4} m^3 / moles}{1.42 \times 10^{-3} m^3 / moles}\right)$

Or   P $= 1420$ k Pa

For a perfect gas, the pressure would be 1420 kPa.

8.16 References
1. Statistical Mechanics; S.L. Gupta, V. Kumar, Pragati Prakashan, Meerut
2. Statistical Mechanics; Satya Prakash, Kedar Nath Ram Nath, Delhi
3. Statistical Mechanics; R K Patharia, Academic Press

8.17 Suggested Readings
1. Elementary Principles in Statistical Mechanics; Josiah Willard Gibbs, Charles Scribner's Sons
2. Course of Theoretical Physics; Lev Landau, Addison-Wesley, Pergamon Press
3. Introduction to Modern Statistical Mechanics; David Chandler, Oxford University Press