

Block

4

STATISTICAL MECHANICS

UNIT 12

Basic Concepts of Statistical Mechanics **103**

UNIT 13

Classical Statistics **119**

UNIT 14

Quantum Statistics **139**

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CONTENTS

Block and Unit Titles	97
Credit page	98
Contents	99
BLOCK 4: Statistical Mechanics	101
<u>Unit 12 Basic Concepts of Statistical Mechanics</u>	<u>103</u>
12.1 Introduction	104
12.2 Elementary Probability Theory	104
12.2.1 Basic Terminology	105
12.2.2 Permutations and Combinations	106
12.2.3 Distribution of Random Variables	107
12.3 Description of a System in Equilibrium	110
12.3.1 Basic Concepts	110
12.4 Entropy and Probability	114
12.4.1 Statistical Interpretation of Entropy	116
12.5 Summary	116
12.6 Terminal Questions	117
12.7 Solutions and Answers	117
<u>Unit 13 Classical Statistics</u>	<u>119</u>
13.1 Introduction	120
13.2 Maxwell-Boltzmann Distribution Function	120
13.2.1 Evaluation of Lagrange Multipliers: The Partition Function	123
13.2.2 Expressing Thermodynamic Variables in Terms of Partition Function	126
13.3 Partition Function of a Monatomic Gas	126
13.3.1 Single Particle Partition Function	127
13.3.2 Degeneracy Parameter	129
13.3.3 N -particle Partition Function	130
13.4 Summary	132
13.5 Terminal Questions	133
13.6 Solutions and Answers	134
Appendix 13A: Method of Lagrange Multipliers	138
<u>Unit 14 Quantum Statistics</u>	<u>139</u>
14.1 Introduction	140
14.2 Need for Quantum Statistics	141
14.2.1 Blackbody Radiation	141
14.2.2 Heat Capacity of Solids	142

14.2.3 Classification of particles	144
14.3 Bose-Einstein Distribution Function	147
14.4 Fermi-Dirac Distribution Function	150
14.5 Comparison of Different Distributions	153
14.6 Applications of Bose-Einstein Statistics	154
14.6.1 Bose's Derivation of Planck's Law	154
14.7 Applications of Fermi-Dirac Statistics	156
14.7.1 Fermi Energy	156
14.7.2 Electronic Heat Capacity	160
14.8 Summary	161
14.9 Terminal Questions	162
14.10 Solutions and Answers	162
Further Readings	165
Table of Physical Constants	166
List of Blocks and Units: BPHCT-135	167
Syllabus: Thermal Physics and Statistical Mechanics (BPHCT-135)	168

BLOCK 4 : STATISTICAL MECHANICS

So far you have learnt how to describe the properties of matter on the basis of thermodynamics and kinetic theory of gases. You must have realized that thermodynamics is essentially an empirical science based on everyday experiences. You will agree that these laws give us no information about the processes at work at the microscopic level. But the kinetic theory of gases, discussed in Block 1, was the first attempt to understand the properties of macroscopic systems from the microscopic point of view. Did you note that some very elegant laws stemmed out of the molecular chaos?

Statistical mechanics is a more profound and realistic approach for understanding the observed behaviour of matter (or radiation). The laws of mechanics are coupled with statistical methods. So, to enable you to master the techniques of statistical mechanics, we have discussed key probabilistic concepts in Unit 12. The concept of phase space, entropy and its statistical interpretation have also been introduced here.

In Unit 13, we use the definition of the equilibrium state of an isolated system as the most probable state and derive the expression for the thermodynamic probability. From it, we derive the expression for the Maxwell-Boltzmann distribution function. We introduce the concept of the partition function and study how all thermodynamic functions may be derived from it.

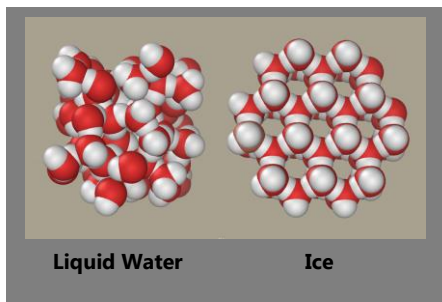
Classical statistics fails to explain the behaviour of an assembly of photons or liquid helium or conduction electrons in metals, particularly at low temperatures. Specifically, the existence of zero point energy and Bose-Einstein condensation – two remarkable phenomena – remain completely unexplained in the tenets of classical physics. These are quantum effects and the likes of Bose, Einstein, Fermi, Dirac, Fowler and Planck have immensely contributed to explain these. In Unit 14, you will study the methods of quantum statistics and their applications.

We hope that you will enjoy studying this block.

We wish you success.



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UNIT 12

Which of these systems do you think would have greater entropy? This unit will help you answer this question.

BASIC CONCEPTS OF STATISTICAL MECHANICS

Structure

- | | |
|--|--|
| <p>12.1 Introduction
Expected Learning Outcomes</p> <p>12.2 Elementary Probability Theory
Basic Terminology
Permutations and Combinations
Distribution of Random Variables</p> | <p>12.3 Description of a System in Equilibrium
Basic Concepts</p> <p>12.4 Entropy and Probability
Statistical Interpretation of Entropy</p> <p>12.5 Summary</p> <p>12.6 Terminal Questions</p> <p>12.7 Solutions and Answers</p> |
|--|--|

STUDY GUIDE

In this unit, you will learn how to use methods of statistics to understand the probable behaviour of a physical system. For this, a clear understanding of the basic concepts of probability is extremely important. You may be familiar with some of these concepts from your school mathematics curriculum. We strongly advise you to refresh your knowledge of probability and statistics before you start studying this block. However, for the sake of completeness, we have also included some important concepts here.

You will also be using differential calculus and at times you may find some mathematical steps somewhat involved. But do not worry; we give you enough time to grasp the ideas. Moreover, several examples and SAQs given in the text should help you maintain an easy pace. We hope you will enjoy studying this unit, which is a prelude to core statistical mechanics.

“Statistical physics and thermodynamics together form a unit. All the concepts and quantities of thermodynamics follow most naturally, simply and rigorously from the concepts of statistical physics.”

Lev Landau

12.1 INTRODUCTION

In the preceding two blocks, you have learnt how to describe the properties of matter on the basis of thermodynamics. You must have realised that the laws of thermodynamics provide us with extremely powerful methods to develop meaningful relations between macroscopic variables, such as pressure, volume, internal energy, entropy and temperature of a system. In this block on Statistical Mechanics, we will deal with directly observable macroscopic properties without any reference to microscopic structure of the constituents of the system.

Statistical mechanics uses the concepts of probability theory and therefore, a clear understanding of the basic concepts of probability is extremely important. For brevity and completeness, we have introduced elementary concepts of probability theory in Sec. 12.2. To describe the behaviour of a system of a large number of particles elegantly, we use the concepts of phase space, macrostate, microstate and thermodynamic probability. These are discussed in Sec. 12.3. In Sec.12.4, you will learn how to establish Boltzmann relation. It tells us that the entropy of a system is proportional to logarithm of its thermodynamic probability, where the proportionality constant is called the Boltzmann constant. This has fundamental significance and provides a connection between thermodynamics and statistical mechanics.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ explain the terms phase space, macrostate and microstate;
- ❖ establish Boltzmann entropy relation $S = k_B \ln W$; and
- ❖ discuss the statistical interpretation of entropy.

12.2 ELEMENTARY PROBABILITY THEORY

The idea of probability is very common in our daily life. Suppose we have to organise a cricket match on a particular day, say in July, which falls in the rainy season in India. We wonder if it will rain on that day. Similarly, the enthusiasts would guess whether their team will win. We can say that there is a chance of shower on that day or there is little chance of a better team, say A , to lose. What do we mean by chance in these cases?

If we examine the meteorological data for 93 days of July spread over three years, and it has rained on 65 days, then we can say that there is a 65 out of 93 chance of rain on a July day. Mathematically, the probability of rain on a July day is $65/93$, which is nearly 0.7. We could get better estimates of probability if we could study the data for more days, say 500 or 1000. In fact, in statistical mechanics, which deals with systems having very large number of particles, we calculate the average of a physical quantity of interest and connect it with the experimentally observed value. So, to refresh your

knowledge of basic concepts of probability theory, we start by discussing basic terminology.

12.2.1 Basic Terminology

In the example considered above, 'rain on a July day (R)' and 'no rain on a July day (NR)' are two possible weather conditions and represent two events. We denote the probabilities of their occurring as $P(R)$ and $P(NR)$. Suppose that an event E can occur with N possible outcomes that are mutually exclusive and equally likely. Let n of these outcomes be favourable to the event. Then, the probability that event E will occur is $P(E) = n/N$. It also means that the event does not occur at $N - n$ times and the probability of the event not occurring $P(E')$ is

$$P(E') = \frac{N-n}{N} = 1 - P(E)$$

Note that $P(E) + P(E') = 1$. That is, either E or E' would occur and the sum of the probabilities of an event occurring and not occurring is unity. The probability of an event which is certain is one.

To illustrate this point further, let us consider that we roll a dice. Obviously, the probability of getting 1 is $1/6$ and the probability of not getting 1 is $5/6$. This clearly shows that the sum of the probabilities of getting 1 and not getting 1 is unity.

Now suppose that E_1 and E_2 are two events. The probability that E_2 occurs, given that E_1 has occurred already is called *conditional probability* of E_2 for given E_1 . It is written as $P(E_2 | E_1)$. However, if the occurrence (or non-occurrence) of E_1 does not influence the occurrence of E_2 , then $P(E_2 | E_1) = P(E_2)$; and we say that E_1 and E_2 are independent events. If E_1 denotes dense fog on a route and E_2 denotes a train on that route running late, then occurrence of E_1 does influence the occurrence of E_2 and these events are said to be dependent.

The probability of two events E_1 and E_2 happening together is called *compound probability*. It is denoted as $P(E_1, E_2)$ for the compound event (E_1, E_2) . When E_1 and E_2 are unrelated, $P(E_1, E_2) = P(E_1)P(E_2)$.

Multiplication rule: If an event can occur in m ways and another independent event can occur in n ways, then the events can occur jointly in $m \times n$ ways.

This is illustrated in the following examples.

EXAMPLE 12.1: PROBABILITY OF INDEPENDENT EVENTS

When a coin is tossed, there is equal chance of getting a head (H) or a tail (T). If we toss two coins, calculate the probability of getting (a) two heads; and (b) at least one head.

SOLUTION ■ Tossing the first coin can have two possible outcomes, a

head or a tail. Tossing the second coin will also have the same two outcomes. Moreover, these two events are independent. So, we can say that four possible outcomes – HH, HT, TH and TT – can occur with equal probability.

a) Note that two heads appear only in the first outcome. So, the

probability of getting two heads is $\frac{1}{4} \left(= \frac{1}{2} \times \frac{1}{2} \right)$.

b) At least one head appears in three outcomes. Therefore, the

probability of getting at least one head is $\frac{3}{4} \left[= \left(\frac{1}{4} \right) + \left(\frac{1}{4} \right) + \left(\frac{1}{4} \right) \right]$.

EXAMPLE 12.2: MULTIPLICATION RULE

When a fair dice is rolled, there is equal chance of getting any one of its six faces. When two fair dice are rolled, calculate the probability that both will show six.

SOLUTION ■ Since a fair dice has equal chances of having one, two, three, four, five or six dots on the top, the probability that the first dice will show six is $\frac{1}{6}$. Similarly, the probability of the second dice showing six is

$\frac{1}{6}$. Since these two events are unrelated, the compound probability that both dice will show six is $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$.

Two events are said to be *mutually exclusive* when the occurrence of one excludes the other. For instance, 'rain on a July day' and 'no rain on a July day' are mutually exclusive.

12.2.2 Permutations and Combinations

A **permutation** is an arrangement of a number of distinguishable objects chosen from a group in a definite order. For example, suppose three persons A, B and C are to be seated on two chairs. The chairs can be occupied in six ways as AB, BA, AC, CA, BC, CB . Each of these ways is a permutation.

The **number of permutations** of n objects taken r at a time is $\frac{n!}{(n-r)!}$.

It is denoted by the symbol ${}^n P_r$.

A **combination** is an arrangement of distinguishable objects out of a group, without regards to the order of selection. Two persons can be selected from A, B and C in only three ways: AB, BC and CA . Each of these is a combination.

The **number of combinations** of r objects chosen out of n is $\frac{n!}{(n-r)! r!}$.

We denote this as ${}^n C_r$.

$n! = n(n-1)(n-2)(n-3) \dots 3.2.1$ and should be read as n factorial.

These are binomial coefficients and occur in the expansion

$$(x+y)^n = {}^n C_0 x^n + {}^n C_1 x^{n-1} y + {}^n C_2 x^{n-2} y^2 + \dots + {}^n C_n y^n$$

$$= \sum_{r=0}^n {}^n C_r x^{n-r} y^r \quad (12.1)$$

where n and r are integers.

We would now like you to go through the following examples.

EXAMPLE 12.3: PERMUTATIONS

In a classroom six vacant chairs with numbers are available and eight students want to attend a class. If only one student sits in each chair, in how many ways can the chairs be occupied by the students?

SOLUTION ■ The required number is

$${}^8 P_6 = \frac{8!}{(8-6)!} = \frac{8!}{2!} = 20160$$

EXAMPLE 12.4: COMBINATIONS

In a party, the host asks four guests out of a total of ten to sit at her table. In how many ways can she choose the four?

SOLUTION ■ The required number is

$${}^{10} C_4 = \frac{10!}{(10-4)! 4!} = \frac{10!}{6! 4!} = \frac{10 \times 9 \times 8 \times 7}{4 \times 3 \times 2 \times 1} = 210$$

12.2.3 Distribution of Random Variables

When a variable associated with a statistical experiment can assume a number of values, each with a distinct probability, it is called a **random variable**. In a statistical experiment of throwing two dice, the sum of the numbers of dots shown on top of the dice is a random variable. The number of combinations giving rise to sums of 2, 3, 4, ..., 12, etc. are, respectively, 1, 2, 3, 4, 5, 6, 5, 4, 3, 2 and 1 giving a total of 36 combinations. These are listed in Table 12.1. The probabilities of getting 2, 3, 4 etc. are therefore, $1/36$, $1/18$, $1/12$, $1/9$, $5/36$, $1/6$, $5/36$, $1/9$, $1/12$, $1/18$ and $1/36$, respectively. In general, if a variable x takes values $x_1, x_2, x_3 \dots x_n$ with probabilities $f(x_1), f(x_2), f(x_3), \dots, f(x_n)$, i.e., if $P(x = x_i) = f(x_i)$, $i = 1$ to n , then $f(x)$ is called the **probability distribution** of x . It satisfies the following properties:

i) $0 \leq f(x_i) \leq 1$, i.e., $f(x)$ lies between 0 and 1, and (12.2a)

ii) $\sum_1^n f(x_i) = 1$, which is the normalisation condition. (12.2b)

Table 12.1: Outcomes of throw of two dice

Sum	Combinations
2	(1,1)
3	(1,2) (2,1)
4	(1,3), (3,1), (2,2)
5	(1,4), (4,1), (2,3) (3,2)
6	(1,5), (5,1), (2,4) (4,2) (3,3)
7	(1,6), (6,1), (2,5) (5,2) (3,4) (4,3)
8	(2,6), (6,2), (3,5) (5,3) (4,4)
9	(3,6), (6,3), (4,5) (5,4)
10	(4,6), (6,4), (5,5)
11	(5,6) (6,5)
12	(6,6)

The summation sign in condition (ii) above is valid only for discrete distributions pertaining to the events having distinct resultant values. For example, sum of number of dots shown by two dice will refer to integer values only between 2 and 12.

Now consider the distribution of weights of students in a school class. Here, the value of weight can be any number in a certain range, say, a to b , and will follow a continuous distribution. In the case of continuous distribution, the normalisation condition takes the following form:

$$\int_a^b f(x)dx = 1 \quad (12.3)$$

when x can have any value between a and b . If there is no fixed range of values taken by the variable, the integration is carried out between $-\infty$ and $+\infty$.

Once we know the distribution function of the variables in a system, we can use it to determine values of system parameters like average, standard deviation and variance. Let us now quickly review the relations representing these parameters.

Suppose that the variable x takes the set of values $x_1, x_2, x_3, \dots, x_n$ with probabilities $f(x_1), f(x_2), f(x_3) \dots f(x_n)$, respectively. Let x_i be the value of the variable of i th element of this distribution. Then the *average value* or *expectation value* of that variable is given by

$$\langle x \rangle = \bar{x} = \sum_{i=1}^n x_i f(x_i) \quad (12.4)$$

For a continuous variable, the average is defined as

$$\langle x \rangle = \bar{x} = \int_{-\infty}^{\infty} x f(x) dx \quad (12.5)$$

The square of the deviation of the value of the variable from the expectation value is expressed as the *variance* of the system and is defined as

$$\text{Var}(x) = \langle (x - \bar{x})^2 \rangle = \langle x^2 \rangle - 2\langle x \rangle \bar{x} + \bar{x}^2 = \langle x^2 \rangle - \bar{x}^2 \quad (12.6)$$

$$\text{where } \langle x^2 \rangle = \sum_{i=1}^n x_i^2 f(x_i).$$

The positive value of the square root of variance is termed as *standard deviation*. This parameter is important because it gives us an estimate of the width of distribution.

It may be mentioned here that though probability theory arose out of simple dice games, its applications span a wide variety of situations and disciplines like physics, medicine, agriculture, biology, military, industrial engineering and other walks of life. For example, it is widely used in insurance sector. Have you ever thought how life insurance companies fix the premium to be paid by

the policy holders? They collect data on the average life expectancy of different age-groups in a country and use probability theory before fixing the premium. Similarly, predictions of poll surveys also use principles of probability theory.

In physics, we can use probability theory to predict the behaviour of a system. From the kinetic theory of gases, you know that when a system consists of a large number of identical particles, the observed behaviour of an individual element can be used to predict the behaviour of the entire system. In statistical mechanics, the probable behaviour of individual elements can be obtained from the observed properties of the entire system.

In the following sections, we elaborate upon this vital link between the behaviour of the elements of a physical system and the properties of the system as a whole. But before proceeding further, you may like to attempt an SAQ.

SAQ 1 – Expectation value

The velocities of gas molecules enclosed in a container follow the function $f(v) = Av^2e^{-v^2}$. Obtain the expectation value of velocity, if v varies from 0 to ∞ .

Let us now summarise the basic terminology used in statistics and discussed in this section.

BASIC TERMINOLOGY IN STATISTICS

Recap

- Permutation represents the number of ways in which we can make ordered choices of r out of n distinguishable objects: ${}^n P_r = \frac{n!}{(n-r)!}$
- Combination represents the number of ways in which we can make choices of r out of n distinguishable objects without bothering about their order: ${}^n C_r = \frac{n!}{(n-r)! r!}$
- Probability distribution of a random variable x satisfies the conditions:

$$0 \leq f(x_i) \leq 1 \quad \text{and} \quad \sum_1^n f(x_i) = 1$$

- Expectation values of x for discrete and continuous distributions are given by, respectively,

$$\langle x \rangle = \bar{x} = \sum_{i=1}^n x_i f(x_i) \quad \text{and} \quad \langle x \rangle = \bar{x} = \int_{-\infty}^{\infty} x f(x) dx$$

- Variance of x is defined as: $\text{Var}(x) = \langle (x - \bar{x})^2 \rangle = \langle x^2 \rangle - (\bar{x})^2$

12.3 DESCRIPTION OF A SYSTEM IN EQUILIBRIUM

Consider a gas of N molecules occupying volume V at a temperature T . Suppose that we know the positions and velocities of all the particles at a given instant of time. Then by solving Newton's equations of motion for all particles individually, it should be possible to determine how the system evolves. But N is a very large number ($\sim 10^{26}$ for one kmol). Hence, calculations, though possible in principle, will be extremely cumbersome. Even the present-day supercomputing machines will take time to solve them.

Due to such complications we prefer to give thermodynamic description of a system at macroscopic level, without referring to its microscopic details. A major advance in this direction was made by Gibbs (1839-1903). He coined the name **statistical mechanics** for the branch of physics which deals statistically with systems consisting of a large number of particles. Instead of looking at each individual molecule, we treat the collection as a whole and try to compute average properties. Statistical mechanics is not just restricted to molecules but can also be applied to quantum particles like photons.

We begin by discussing how a system can be described mathematically.

12.3.1 Basic Concepts

We know that the position of an object in a plane, such as an ant on a table, can be specified completely by giving its Cartesian coordinates (x, y) with respect to a set of Cartesian axes. (It is like specifying the latitude and longitude of a place on a map.) Similarly, the position of an object in space, like a bird flying in a garden, can be described by the (x, y, z) coordinates.

Let us consider the motion of a particle along a straight line (Fig. 12.1a). The mechanical state of the particle at any instant is given by its position x from a fixed point O on the straight line and its velocity $v_x = \frac{dx}{dt}$ at that instant.

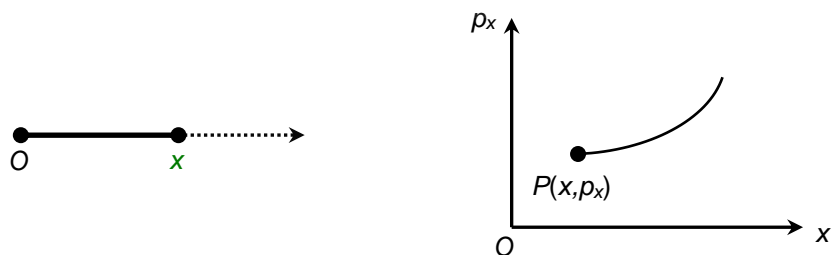


Fig. 12.1: a) Motion of a particle along a straight line; b) phase space for one-dimensional motion.

In your higher classes you will study in Classical Mechanics that the position and momentum of an object form a pair of canonically conjugate variables.

However, it is more desirable to work with momentum $p_x (= mv_x)$ instead of velocity (see margin remark). And the state of the particle at any instant is completely specified classically at a particular instant if its position and momentum are known. It may be represented by a point P on a two dimensional hypothetical space, whose coordinate axes are x and p_x (Fig. 12.1b). The space so defined is called the **phase space** of the system, P is called the **phase point** and such a representation is called a *phase space*

diagram. With the passage of time, the point P traces out a certain trajectory in the phase space. In the phase space diagram, the state of the particle is referred to as the *phase*, and the trajectory as the *phase path*.

When a particle moves in space, we need three position coordinates (x, y, z) and three components of momentum (p_x, p_y, p_z) . In other words, we require six numerical quantities (x, y, z, p_x, p_y, p_z) to specify the state of a particle in space at a particular instant and we have to define a 6-D phase space. (Fig. 12.2 only gives a symbolic representation of such a space.) It is referred to as the μ -space. The state of translational motion of a molecule at any instant is completely specified by a representative point in this hypothetical space.

If we divide the phase space into small six-dimensional cells of sides $\Delta x, \Delta y, \Delta z, \Delta p_x, \Delta p_y, \Delta p_z$, the volume of each of these cells is

$$\Delta H = \Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z \quad (12.7)$$

These considerations can be easily extended to a N particles such as molecules of a gas moving in space. To specify the state of these molecules in 6-D space, we need $6N$ coordinates; $3N$ for positions and $3N$ for momenta:

$$(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N) \text{ and } (p_{1x}, p_{1y}, p_{1z}, p_{2x}, p_{2y}, p_{2z}, \dots, p_{Nx}, p_{Ny}, p_{Nz})$$

However, for ease in writing, it is customary to use generalised coordinates, $(q_1, q_2, \dots, q_{3N})$ and $(p_1, p_2, \dots, p_{3N})$ to denote positions and momenta, respectively. Then the state of the system is given by a point $(q_1, q_2, \dots, q_{3N}, p_1, p_2, \dots, p_{3N})$ in $6N$ -dimensional phase space. Note that position and momentum change with time. So, all these points may undergo extremely complicated motions in this space.

Note that the notion of phase space provides geometrical framework to statistical mechanics and helps to minimise abstraction. You will agree that it is not possible to draw such a space and for this reason, phase space should be considered a purely mathematical concept.

SAQ 2 – Phase space

Suppose that N molecules of hydrogen are free to move in free space. These molecules have two rotational degrees of freedom also. What will be the dimensions of the phase space?

Suppose that this N -particle system is confined to a volume V and the total internal energy of the system is U . By describing the system in terms of the macroscopic quantities N, V, U we are giving what is known as a **coarse-grained** description of the system. In other words, the triplet (N, V, U) defines a macrostate of the system. But in statistical mechanics, we intend to derive the **macroscopic** properties from the knowledge of the constituents of the system. To achieve this end, we proceed as follows:

We divide the phase space into small elements or 'cells' of volume (refer to Fig. 12.3):

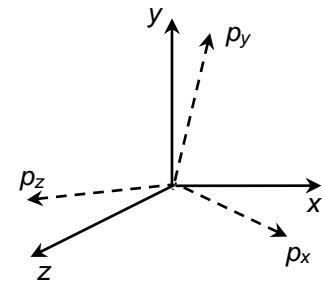


Fig. 12.2: Symbolic representation of μ -space.

Γ -space

When we consider the phase space for entire system (comprising N particles) this $6N$ -dimensional space is referred to as gamma (Γ) space.

$$\Delta\Gamma = \Delta q_1 \Delta q_2 \dots \Delta q_{3N} \Delta p_1 \Delta p_2 \Delta p_{3N} = \prod_i^{3N} \Delta q_i \Delta p_i \quad (12.8)$$

where the symbol \prod_i^{3N} signifies product of all terms from $i = 1$ to $i = 3N$.

For the simple case of a single particle moving in a straight line, we can write $\Delta\Gamma = \Delta q \Delta p$. This is shown in Fig. 12.3.

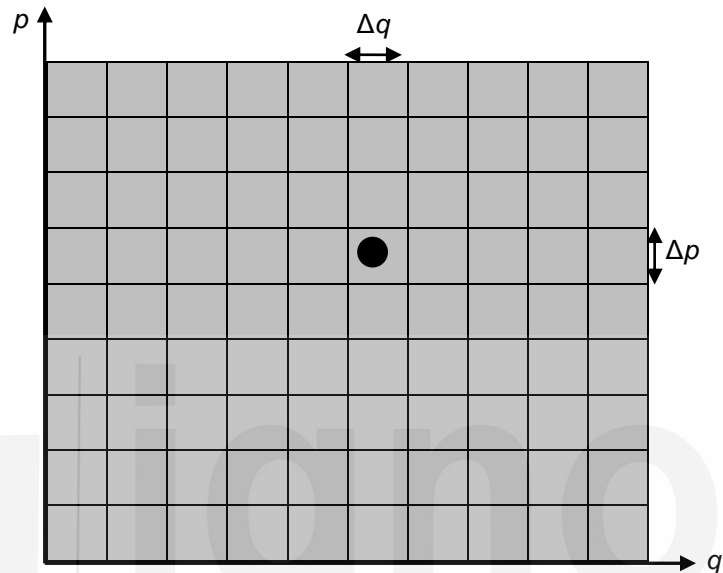


Fig. 12.3: Two-dimensional phase space divided into cells of ‘volume’ $\Delta q \Delta p$. • is the phase point representing a particle

Imagine the cells to be numbered 1, 2, ... and let n_1, n_2, \dots denote the populations of the various cells. In other words, there are n_1 phase points occupying cell 1, n_2 occupying cell 2, and so on. Any phase point will lie in one of the cells. If we specify the **number** of phase points in each cell, we define a **macrostate** of the system. But specification of exactly *which* particles are in which particular cell, defines a **microstate**. Obviously, many different microstates can correspond to the same macrostate. We illustrate this by a simple example.

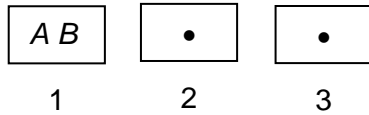
EXAMPLE 12.5: MACROSTATES AND MICROSTATES

Suppose there are three cells in phase space labelled 1, 2, 3, and two particles, A and B. Enumerate the different macrostates and the microstates corresponding to each of them.

SOLUTION ■ There are six possible macrostates:

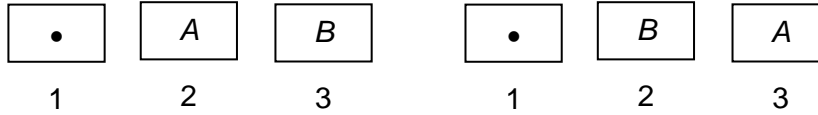
cells	(i)	(ii)	(iii)	(iv)	(v)	(vi)
1	AB	0	0	0	A	A
2	0	AB	0	A	0	B
3	0	0	AB	B	B	0

For macrostate (i), there is only one possible microstate, viz



Similar remarks apply to macrostate (ii) and (iii).

Corresponding to macrostate (iv), two microstates are possible:



Similarly, two microstates correspond to each of macrostate (v) and (vi). Hence, in all we have 9 microstates when particles are distinguishable. You can check yourself that if the particles were indistinguishable, there would be only 6 microstates.

You may now like to answer an SAQ.

SAQ 3 – Macrostates and microstates

Suppose two indistinguishable particles are to be placed in four cells. Enumerate the possible macrostates and the corresponding microstates.

Before proceeding further, let us revise what you have learnt in this section.

MACROSTATES AND MICROSTATES

Recap

- Phase space is a hypothetical space depicting the position and momentum of a particle. For an N particle system, the phase space has $6N$ dimensions. It provides a geometrical framework to statistical mechanics.
- Macrostate can be described by specifying the quantities determined by macroscopic measurements.
- Microstate of a system describes the minute details about the particles occupying the cells in phase space.

In statistical mechanics, we always seek the number of microstates corresponding to a given macrostate (N, V, U). It is called **thermodynamic probability** or **statistical weight** of the macrostate and is denoted by $W(N, V, U)$. You will agree that W can assume a very large value; the minimum value being one. The question now arises: Is it related to any thermodynamic variable? In fact, yes, and the variable is entropy. You will observe that the relation between the entropy S and the thermodynamic probability W provides a bridge between microscopic and macroscopic view points and forms the basis of entire statistical mechanics. You will now learn how to establish this relation.

12.4 ENTROPY AND PROBABILITY

In Unit 9, you have learnt that entropy characterises disorder in a system. Since equilibrium is the most disordered state (because we lose all information about the initial conditions, except the conserved variables), the entropy of a system in equilibrium is maximum. From the discussion so far, we can also say that equilibrium is the most probable state. That is, at equilibrium both entropy and thermodynamic probability tend to be maximum and there seems to exist some connection between them. Mathematically, we express it as

$$S = f(W) \quad (12.9)$$

The nature of the function f is unknown at this stage but we shall soon establish it. Let us now consider two completely independent systems having entropies S_1 and S_2 . We know that entropy is an extensive (additive) quantity. This means that the entropy of the combined system will be the sum of the entropies of individual systems:

$$S = S_1 + S_2 \quad (12.10)$$

On the other hand, if W_1 and W_2 are probabilities of the individual systems, the probability of the combined system is equal to the product of probabilities of individual systems, since these are independent. Then we can write

$$W = W_1 \times W_2 \quad (12.11)$$

Physically, we can say that for every microstate of one system, the other system can exist in any one of its possible microstates.

We now determine the form of the function f using the information provided by Eqs. (12.10) and (12.11). We expect the function f to be such that S increases with W and translates a product into a sum. Mathematically, we can write

$$S_1 + S_2 = f(W_1) + f(W_2) = f(W_1W_2) \quad (12.12)$$

Proceeding further, we take partial derivatives of both sides of Eq. (12.12) with respect to W_1 keeping W_2 fixed:

$$\left(\frac{\partial f(W_1)}{\partial W_1} \right)_{W_2} + \left(\frac{\partial f(W_2)}{\partial W_1} \right)_{W_2} = \left(\frac{\partial f(W_1W_2)}{\partial W_1} \right)_{W_2} \quad (12.13)$$

Since $f(W_1)$ is a function of only W_1 , its partial derivative with respect to W_1 will be equal to its total derivative. Therefore, the first term on the left-hand side of Eq. (12.13) can be expressed as

$$\left(\frac{\partial f(W_1)}{\partial W_1} \right)_{W_2} = \frac{df(W_1)}{dW_1} \quad (12.14)$$

The partial derivative of $f(W_2)$ with respect to W_1 is zero, since it does not depend on W_1 . Therefore, the second term on the left-hand side of Eq.(12.14) drops out.

The partial derivative of $f(W_1W_2)$ with respect to W_1 , is equal to the total derivative of $f(W_1W_2)$ with respect to its argument, multiplied by the partial

derivative of its argument with respect to W_1 , which is simply the constant W_2 .

Thus, we can write

$$\left[\frac{\partial f(W_1, W_2)}{\partial W_1} \right]_{W_2} = \frac{df(W_1, W_2)}{d(W_1 W_2)} \frac{\partial(W_1 W_2)}{\partial W_1} = W_2 \frac{df(W_1 W_2)}{d(W_1 W_2)} = W_2 f'(W_1 W_2) \quad (12.15)$$

where we have denoted the derivative of $f(W_1 W_2)$ with respect to its argument $W_1 W_2$ by $f'(W_1 W_2)$. On combining Eqs. (12.14) and (12.15) with Eq. (12.13), we get

$$\frac{df(W_1)}{dW_1} = W_2 f'(W_1 W_2) \quad (12.16)$$

Similarly, we differentiate Eq. (12.12) with respect to W_2 , keeping W_1 fixed. Following the same line of reasoning, we can show that

$$\frac{df(W_2)}{dW_2} = W_1 f'(W_1 W_2) \quad (12.17)$$

We now multiply Eq. (12.16) by W_1 , and Eq. (12.17) by W_2 . This gives

$$W_1 \frac{df(W_1)}{dW_1} = W_2 \frac{df(W_2)}{dW_2} = W_1 W_2 f'(W_1 W_2)$$

Note that in this expression, the first term is a function of only W_1 and the second term is a function of only W_2 . Hence, we can write

$$W_1 \frac{df(W_1)}{dW_1} = W_2 \frac{df(W_2)}{dW_2} = \text{constant, say } k \quad (12.18)$$

We can readily integrate it to obtain

$$f(W_1) = k \ln W_1 + C_1 \quad (12.19a)$$

$$\text{and } f(W_2) = k \ln W_2 + C_2 \quad (12.19b)$$

where C_1 and C_2 are constants of integration. In general, we can write

$$f(W) = S = k \ln W + C \quad (12.20)$$

Note that the function f is logarithmic and constant k is same for all systems. This relation was derived by Boltzmann but he did not determine the nature of the constants k and C . Subsequently, Planck used the fact that at absolute zero, the entropy is zero and $W = 1$ so that the constant C can be taken to be zero. Moreover, he identified W as thermodynamic probability. The constant k was identified as Boltzmann constant k_B , which has value $1.38 \times 10^{-23} \text{ JK}^{-1}$. Hence, Eq. (12.20) can now be rewritten as

$$S = k_B \ln W \quad (12.21)$$

Eq. (12.21) is called *Boltzmann relation* and is one of the most fundamental relations of statistical mechanics. It states that the entropy of a system is proportional to the logarithm of its thermodynamic probability. Statistically speaking, the universe always tends to change towards a more probable



Ludwig Eduard Boltzmann (1844 – 1906), an Austrian physicist, was famous for his contributions to the field of statistical mechanics; the most significant being applications of probability theory to understand the behaviour of molecular systems. He was one of the most important advocates of atomic theory when it was still in its nascent stages. The relation $S = k \ln W$ is engraved on his resting place in the central cemetery in Vienna, Austria.

(Picture source: https://commons.wikimedia.org/wiki/File:Boltzmann_10566.jpg.)

state. It may be mentioned here that Eq. (12.21) opened the way for a more direct and elegant application of the techniques of probability theory to study widely diverse systems and obtain their thermodynamic properties. You may now like to answer an SAQ.

SAQ 4 – Thermodynamic probability and entropy

Two systems have thermodynamic probabilities of 1.5×10^{28} and 2.0×10^{27} , respectively. Calculate the total thermodynamic probability, when these two systems interact with each other. Also calculate the entropies of individual systems as well as their composite system and verify Boltzmann relation.

Let us summarise the important result of this section.

Recap

BOLTZMANN RELATION

The relation $S = k_B \ln W$ connects thermodynamic probability and entropy. Effectively, it correlates statistical mechanics with thermodynamics

12.4.1 Statistical Interpretation of Entropy

Statistically speaking, the entropy of a system consisting of a very large number of particles is proportional to the natural logarithm of the total number of microstates available to the system. Therefore, if only one microstate is available to an assembly, we have $W = 1$, and $\ln W = 0 = S$. The state of each particle can be uniquely specified and the system is said to be perfectly ordered. However, if more than one energy states become available to the system, $W > 1$ and $S > 0$. It means that the system has become disordered and we cannot specify the state of each particle uniquely. Therefore, thermodynamic probability (or entropy) of a system may be construed as a measure of disorder in the system.

The statistical interpretation of entropy helps us to gain greater insight into the meaning of absolute zero. In Unit 10, you have learnt Planck's statement of the third law of thermodynamics. It states that the equilibrium entropies of all systems tend to zero as temperature approaches absolute zero, i. e., $S \rightarrow 0$ as $T \rightarrow 0$. Therefore, we can say that a system in equilibrium is perfectly ordered at absolute zero. Let us now summarize what you have learnt in this unit.

12.5 SUMMARY

Concept

Description

Phase space

- Phase space is a purely mathematical device, which provides some sort of geometrical framework to statistical mechanics and minimises abstraction.

Macrostate

- The macrostate of a system is that state which can be described by specifying only those quantities which can be determined by macroscopic measurement, without any reference whatsoever to the microscopic details.

Microstate

- Microstate of a system describes the minutest details of the cells occupied by the constituent particles.

Boltzmann relation

- Entropy and thermodynamic probability are connected through Boltzmann relation $S = k_B \ln W$, where k_B is Boltzmann constant.

12.6 TERMINAL QUESTIONS

1. Draw the phase space for a linear harmonic oscillator.
2. Draw the phase space for a particle having energy E and constrained to move in one dimension in the range $[0, L]$.

12.7 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. It is given that $f(v) = Av^2e^{-v^2}$

$$\text{Expectation value is } \langle v \rangle = \int_0^{\infty} vf(v)dv \quad (i)$$

Substituting the expression for $f(v)$ in Eq. (i), we get,

$$\langle v \rangle = \int_0^{\infty} Av^3e^{-v^2} dv \quad (ii)$$

If we substitute $v^2 = x$ and $2vdv = dx$ in Eq. (ii), we get

$$\langle v \rangle = A \int_0^{\infty} xe^{-x} dx = \Gamma(2) = 1 \text{ (read the margin remark)}$$

Hence, $\langle v \rangle = A$.

2. The total number of degrees of freedom for a particle moving in space and having two rotational degrees of freedom will be $3+2=5$. Therefore, the phase space will be $10N$ dimensional.
3. The possible macrostates are:

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)
n_1	2	0	0	0	1	1	0	1	0	0
n_2	0	2	0	0	1	0	0	0	1	1
n_3	0	0	2	0	0	1	1	0	1	0
n_4	0	0	0	2	0	0	1	1	0	1

For the above listed 10 macrostates, there is only one microstate associated with each macrostate.

4. Thermodynamic probability of first system, $W_1 = 1.5 \times 10^{28}$

Thermodynamic probability of second system, $W_2 = 2.0 \times 10^{27}$

The gamma function is defined as follows:

$$\Gamma(n) = \int_0^{\infty} x^{n-1} e^{-x} dx = (n-1)!$$

The thermodynamic probability of the composite system,

$$W = W_1 W_2 = 5 \times 10^{28} \times 2.0 \times 10^{27} = 3.0 \times 10^{55}$$

Now, entropy of the first system,

$$\begin{aligned} S_1 &= k_B \ln W_1 = k_B \times 2.303 \times \log_{10} W_1 \\ &= k_B \times 2.303 \times \log_{10}(1.5 \times 10^{28}) = 64.88 k_B \end{aligned}$$

Similarly, entropy of the second system,

$$\begin{aligned} S_2 &= k_B \ln W_2 = k_B \times 2.303 \times \log_{10} W_2 \\ &= k_B \times 2.303 \times \log_{10}(2.0 \times 10^{27}) = 62.86 k_B \end{aligned}$$

Entropy of the composite system,

$$\begin{aligned} S_0 &= k_B \ln W = k_B \times 2.303 \times \log_{10} W \\ &= k_B \times 2.303 \times \log_{10}(3.0 \times 10^{55}) = 127.74 k_B \end{aligned}$$

$$\text{Also, } S_0 = S_1 + S_2 = 64.88 k_B + 62.86 k_B = 127.74 k_B$$

So, we discover that Boltzmann's relation is verified.

Terminal Questions

1. We know that the equation of motion of a linear harmonic oscillator is

$$\frac{d^2q}{dt^2} = -kq$$

where k is the spring constant. The solutions of this equation are:

$$q = A \cos(\omega t + \phi), \tag{i}$$

where A is the amplitude, $\omega = \sqrt{\frac{k}{m}}$, m being the mass and ϕ being the phase. The total energy $E = \frac{1}{2} m \omega^2 A^2$.

$$\text{Also, } p = m \frac{dq}{dt} = -mA \omega \sin(\omega t + \phi) \tag{ii}$$

$$\text{From (i) and (ii), we have } \frac{q^2}{A^2} + \frac{p^2}{m^2 \omega^2 A^2} = 1$$

$$\text{or } \frac{q^2}{\left(\frac{2E}{m\omega^2}\right)} + \frac{p^2}{2mE} = 1 \tag{iii}$$

$$\text{Hence, the phase space is an ellipse with area} = \pi \sqrt{\frac{2E}{m\omega^2}} \sqrt{2mE} = \frac{2\pi E}{\omega}$$

This is shown in Fig. 12.4.

2 Let us consider a particle moving in one dimension and confined to the interval $[0, L]$. Its energy is given by

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

where p is the momentum. If E is fixed, p can have values $\sqrt{2mE}$ and $-\sqrt{2mE}$. In practice, a system is never completely isolated. Then the energy may lie between E and $E + dE$ and p would lie in a small range around $\pm\sqrt{2mE}$, as shown in Fig.12.5.

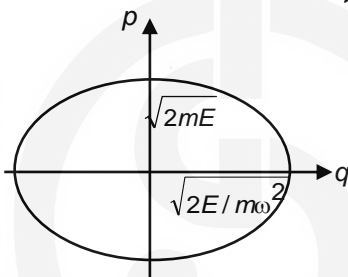


Fig. 12.4: Phase space of a linear harmonic oscillator.

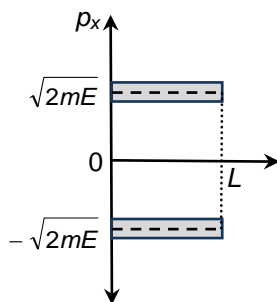
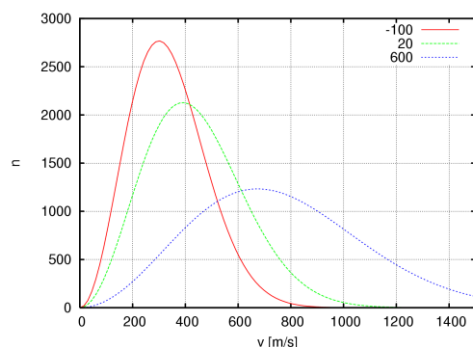


Fig. 12.5: Phase space of a particle moving in x direction.

UNIT 13

CLASSICAL STATISTICS



The Maxwell-Boltzmann distribution function can be used to derive the distribution of speeds in an ideal gas. Here you see the distribution of particle speeds for 10^6 oxygen particles at -100 , 20 and 600°C .

Structure

- 13.1 Introduction
 - Expected Learning Outcomes
- 13.2 Maxwell-Boltzmann Distribution Function
 - Evaluation of Lagrange Multipliers:
 - The Partition Function
 - Expressing Thermodynamic Variables in Terms of Partition Function
- 13.3 Partition Function of a Monatomic Gas
 - Single-Particle Partition Function
 - Degeneracy Parameter
 - N -particle Partition Function
- 13.4 Summary
- 13.5 Terminal Questions
- 13.6 Solutions and Answers
- Appendix 13A: Method of Lagrange Multipliers

STUDY GUIDE

In this unit, you will learn how to use methods of statistics to understand the probable behaviour of the elements of a physical system. For this, you will also be required to use differential and integral calculus. Though some mathematical steps would be somewhat involved, you need not worry; we have solved all steps and given enough time to grasp the ideas to help you progress through the unit. However, if you work these out yourself, you will appreciate the subject better. Moreover, you will gain greater confidence in your analytical capacities and satisfaction in your learning. We, therefore, advise you to revise your prior knowledge of integral and differential calculus. Moreover, solved examples and SAQs given in the unit should help you learn it better. We believe that you will enjoy this unit more, if you answer SAQs and TQs on your own.

“The whole is simpler than the sum of its parts.”

J. W. Gibbs

13.1 INTRODUCTION

From Unit 9, you may recall that the equilibrium state of a system is a state of maximum entropy. Statistically speaking, it is the most probable state of an isolated system. Using this correlation, we derive an expression for thermodynamic probability, W in Sec. 13.2. Then we maximise W to obtain expression for Maxwell-Boltzmann distribution function for an equilibrium state. You will discover that the distribution function contains two unknown constants. To determine these constants, we perform sum over all states and introduce what we call the **partition function**, Z .

The partition function is just a mathematical device and it derives its importance from the fact that all thermodynamic functions – pressure, internal energy, entropy, Helmholtz and Gibbs free energies – of a system obeying Maxwell-Boltzmann statistics can be expressed in terms of Z or its partial derivatives. You will therefore agree that to apply the methods of statistics to a system of interest, it is important to learn to evaluate Z . We illustrate this in Sec 13.3 for a monatomic gas of non-interacting particles.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ obtain thermodynamic probability for a system obeying Maxwell-Boltzmann statistics;
- ❖ maximise thermodynamic probability to obtain the expression for distribution function;
- ❖ express the thermodynamic functions of a gas in terms of the partition function;
- ❖ evaluate single particle partition function and establish Maxwell-Boltzmann distribution law; and
- ❖ obtain expressions for thermodynamic functions of a gas.

13.2 MAXWELL-BOLTZMANN DISTRIBUTION FUNCTION

Consider an ideal monatomic gas made up of N particles enclosed in volume V and having total internal energy U . The state of the system at any time t is represented by a point in a $6N$ -dimensional phase space. This means that every particle is associated with six-dimensional phase space, also called the μ -space. (μ stands for the first letter of molecule.) The particles are moving independent of each other and the contributions of individual particles remain separate.

To give a microscopic description of the system, we divide the μ -space into cells of volume h^3 . Recall that in classical statistics, we can choose h as small as we like. Each particle will be found to occupy a cell in this network.

Suppose the cells are numbered 1, 2, ... Let the energy of a particle in the i th cell be denoted by ε_i and the number of particles in the i th cell be n_i . Then, we have

$$N = \sum_i n_i \quad (13.1a)$$

and
$$U = \sum_i n_i \varepsilon_i \quad (13.1b)$$

The macrostate defined by (N, V, U) can be realised in a number of different ways. In order to proceed with our argument, we advance the hypothesis that all microstates are equally probable. In other words, equal phase elements in phase space are associated with equal probabilities. It corresponds to the assumption that the faces of a dice are equally probable. This hypothesis is known as the **postulate of equal a priori probabilities**.

The thermodynamic probability W is simply the number of ways of placing N distinguishable objects in cells such that there are n_1 objects in the first cell, n_2 in the second, and so on. This number is given by

$$W = \frac{N!}{n_1! n_2! \dots} = \frac{N!}{\prod_{i=1} n_i!} \quad (13.2)$$

where $\prod_{i=1} n_i!$ denotes the product of $n_i!$ for all values of i .

We can easily prove this result by noting that there are ${}^N C_{n_1}$ number of ways of choosing n_1 objects that are to be placed in the first cell. Then we will be left with $(N - n_1)$ objects. Out of these $(N - n_1)$ objects, there are ${}^{N-n_1} C_{n_2}$ ways of choosing n_2 objects to be placed in the second cell. We can continue in this fashion till all objects are placed in given cells. Then the total number of ways

$$\begin{aligned} W &= {}^N C_{n_1} {}^{N-n_1} C_{n_2} {}^{N-n_1-n_2} C_{n_3} \dots 1 \\ &= \frac{N!}{(N-n_1)! n_1!} \cdot \frac{(N-n_1)!}{(N-n_1-n_2)! n_2!} \cdot \frac{(N-n_1-n_2)!}{(N-n_1-n_2-n_3)! n_3!} \dots = \frac{N!}{n_1! n_2! \dots} \end{aligned}$$

Symbolically, we write this as $\binom{N}{n_1, n_2, \dots}$ and call it a **multi-nominal**

coefficient.

We know that equilibrium corresponds to the maximum of the thermodynamic probability W . Since $S = k_B \ln W$, it is more appropriate to work with $\ln W$ rather than W itself. (Since $\ln W$ is monotonically increasing function of W , its extreme points will coincide with those of W .) Then, Eq. (13.2) gives

$$\ln W = \ln N! - \sum_i \ln n_i! \quad (13.3)$$

For most systems of practical interest, N is a very large number. By the same reasoning, most of the n_i 's will be sufficiently large so that we can simplify Eq. 13.3 relation using Stirling's formula:

$$\ln x! = x(\ln x - 1)$$

For small n_j , $\ln n_j!$ will be small and hence not of any consequence.

Proceeding further, we insert Stirling's formula in Eq. (13.3). This gives

$$\begin{aligned}\ln W &= (N \ln N - N) - \sum_i (n_j \ln n_j - n_j) \\ &= N \ln N - \sum_i n_j \ln n_j\end{aligned}$$

since $\sum_i n_j = N$.

You would recall that we set our goal to determine the set (n_j) which maximises $\ln W$. The condition for maximum probability is

$$\delta \ln W = 0$$

We now calculate a small change in $\ln W$ and equate it to zero. This gives

$$\delta \ln W = -\sum_i n_j \delta(\ln n_j) - \sum_i (\ln n_j) \delta n_j = 0 \quad (13.4)$$

This expression has been derived by assuming that N and U are constant. So, we can write

$$\delta N = \sum_i \delta n_j = 0 \quad (13.5a)$$

and

$$\delta U = \sum_i \epsilon_j \delta n_j = 0 \quad (13.5b)$$

Eq. (13.5a) implies that the first term on the R.H.S. of Eq. (13.4) is zero:

$$\sum_i n_j \delta(\ln n_j) = \sum_i n_j (1/n_j) \delta n_j = \sum_i \delta n_j = 0$$

Then Eq. (13.4) reduces to

$$\sum_i \ln n_j \delta n_j = 0 \quad (13.6)$$

To accommodate the condition embodied in Eqs. (13.5a and b), we employ the method of Lagrange multipliers (study the Appendix 13A to this unit). We multiply Eq. (13.5a) by α and Eq. (13.5b) by β . The result so obtained is added to Eq. (13.6). This leads to the relation

$$\sum_i (\ln n_j + \alpha + \beta \epsilon_j) \delta n_j = 0 \quad (13.7)$$

Since the variations δn_j are arbitrary, this relation will hold only if the coefficient of each term vanishes. Hence, we must have

$$\ln n_j + \alpha + \beta \epsilon_j = 0$$

By re-arranging terms in this expression and then taking antilog of both sides, we can write

$$n_j = e^{-\alpha - \beta \epsilon_j} = A e^{-\beta \epsilon_j} = \frac{1}{A^{-1}} e^{-\beta \epsilon_j} \quad (13.8)$$

where

$$A = \exp(-\alpha) \quad (13.9)$$

A is known as the degeneracy parameter. It determines the extent to which the behaviour of a system deviates from that of an ideal gas. You will discover in the next section that $A \ll 1$ corresponds to classical regime.

Eq. (13.8) constitutes what is called the **Maxwell-Boltzmann distribution**. Note that the distribution given by Eq. (13.8) contains two unknown Lagrange multipliers α and β . To derive meaningful physics, we must evaluate these in terms of known quantities.

13.2.1 Evaluation of Lagrange Multipliers: The Partition Function

The constant α (or A) is determined using the normalization condition. The probability that the cell corresponding to energy ε_i is occupied is given by Eq. (13.8) with A defined by Eq. (13.9). Since $\sum_i n_i = N$, we can write

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

or
$$\frac{A}{N} \sum_i e^{-\beta\varepsilon_i} = 1$$

If we now define the sum $\sum_i \exp(-\beta\varepsilon_i)$, as the **single-particle partition function** and denote it by Z , then we can write

$$Z = \sum_i e^{-\beta\varepsilon_i} \quad (13.10)$$

the Lagrange multiplier α or degeneracy parameter A can be expressed as

$$\exp(-\alpha) = A = \frac{N}{Z} \quad (13.11)$$

It may be mentioned here that the nomenclature partition function is due to Darwin and Fowler. Planck called $\sum_i e^{-\beta\varepsilon_i}$ Zustandssumme (sum over states)

and denoted it by Z . (We shall follow Planck's notation here.)

It is pertinent to mention here that partition function occupies a pivotal position in statistical mechanics as all thermodynamic functions can be written in terms of it. But before we do so, it is important to realise that partition function is characteristic of a discrete spectrum, though energy is taken to be continuous in classical physics. However, when energy levels are very closely spaced, even the discrete sum becomes a continuum and it is possible to replace summation by integration.

In terms of the partition function, we can rewrite Eq. (13.8) as

$$n_i = \frac{N}{Z} e^{-\beta\varepsilon_i} = \frac{1}{A^{-1}} e^{-\beta\varepsilon_i} \quad (13.12)$$

Note that so far, we have not evaluated constant β .

To this end, we substitute for n_i from Eq. (13.12) in Eq. (13.3). This gives

$$\begin{aligned}\ln W &= N \ln N - \sum_i n_i (\ln N - \ln Z - \beta \varepsilon_i) \\ &= N \ln N - N \ln N + N \ln Z + \beta U\end{aligned}$$

The first two terms on the right-hand side of this expression cancel out and it simplifies to

$$\ln W = N \ln Z + \beta U \quad (13.13)$$

Now using Boltzmann entropy relation, we can write

$$S = k_B \ln W = N k_B \ln Z + \beta k_B U \quad (13.14)$$

We use this relation to introduce the concept of temperature by relating entropy and internal energy of a system:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V = N k_B \left(\frac{\partial \ln Z}{\partial U} \right)_V + k_B U \left(\frac{\partial \beta}{\partial U} \right)_V + \beta k_B$$

On carrying out the partial differentiation in the first term, we get

$$\frac{1}{T} = \frac{N k_B}{Z} \left(\frac{\partial Z}{\partial U} \right)_V + \beta k_B + k_B U \left(\frac{\partial \beta}{\partial U} \right)_V$$

We rewrite the first term on the right-hand side as a product of two terms. Then this expression takes the form

$$\frac{1}{T} = \frac{N k_B}{Z} \left(\frac{\partial Z}{\partial \beta} \right)_V \left(\frac{\partial \beta}{\partial U} \right)_V + \beta k_B + k_B U \left(\frac{\partial \beta}{\partial U} \right)_V \quad (13.15)$$

Using Eq. (13.10), we can write

$$\left(\frac{\partial Z}{\partial \beta} \right)_V = - \sum_i \varepsilon_i \exp(-\beta \varepsilon_i) \quad (13.16)$$

On substituting for n_i from Eq. (13.12) in Eq. (13.1b), we get

$$U = \sum_i n_i \varepsilon_i = \frac{N}{Z} \sum_i \varepsilon_i \exp(-\beta \varepsilon_i)$$

so that
$$\sum_i \varepsilon_i \exp(-\beta \varepsilon_i) = \frac{UZ}{N}$$

On combining this result with Eq. (13.16), we get

$$\left(\frac{\partial Z}{\partial \beta} \right)_V = - \frac{UZ}{N} \quad (13.17)$$

On substituting this result in Eq. (13.15), we get

$$\frac{1}{T} = - \frac{N k_B}{Z} \frac{UZ}{N} \left(\frac{\partial \beta}{\partial U} \right)_V + \beta k_B + k_B U \left(\frac{\partial \beta}{\partial U} \right)_V$$

Note that the first and the third terms on the RHS of this expression cancel out and we get

$$\beta = \frac{1}{k_B T} \quad (13.18)$$

Now that we have evaluated both Lagrange multipliers, we can rewrite Eq. (13.8) describing Maxwell-Boltzmann distribution as

$$n_i = \frac{1}{\exp(\alpha + \beta\varepsilon_i)} = \frac{1}{\exp[(\varepsilon_i - \mu) / k_B T]} \quad (13.19)$$

Where the chemical potential μ is defined in terms of the degeneracy parameter A through the relation $A = \exp(-\alpha) = \exp\left(\frac{\mu}{k_B T}\right)$. Before

proceeding further, you may like to recapitulate important results obtained in this section.

MAXWELL-BOLTZMANN DISTRIBUTION

Recap

- In Maxwell-Boltzmann statistics, we distribute *distinguishable* non-interacting/weakly interacting particles in various cells.
- There is no limit on the number of particles that can occupy a particular cell.
- The thermodynamic probability W is simply the number of ways of placing N distinguishable objects in cells such that there are n_1 objects in the first cell, n_2 in the second, and so on:

$$W = \frac{N!}{n_1! n_2! \dots} = \frac{N!}{\prod_{i=1} n_i!}$$

- The Maxwell-Boltzmann distribution law is

$$n_i = \frac{1}{\exp(\alpha + \beta\varepsilon_i)} = \frac{1}{\exp[(\varepsilon_i - \mu) / k_B T]}$$

where the chemical potential μ is defined from $A = \exp(\mu / k_B T)$.

A plot of n_i versus $(\varepsilon_i - \mu) / k_B T$ is shown in Fig. 13.1. As may be noted, the distribution function approaches zero at higher energies. This is in conformity with the pattern obtained using kinetic theory of gases.

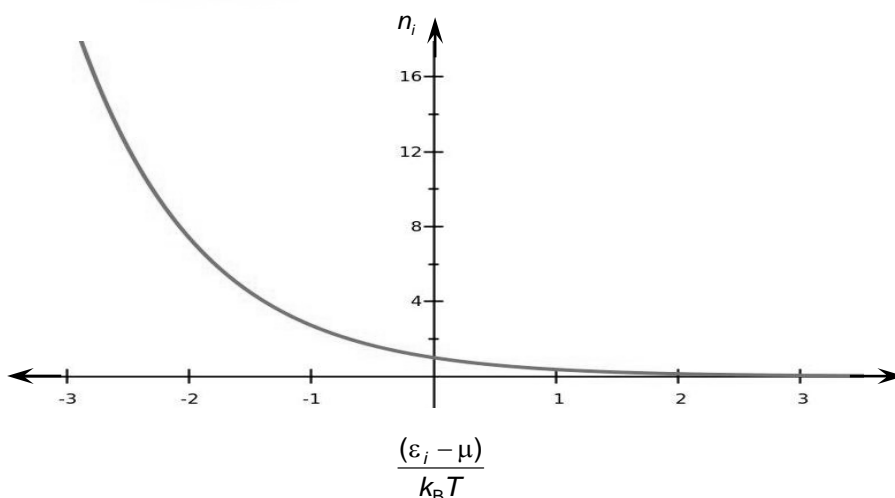


Fig. 13.1: Plot of Maxwell-Boltzmann distribution function as a function of $(\varepsilon_i - \mu) / k_B T$.

To illustrate the utility of the partition function in understanding the thermodynamic behaviour of a system, we now express thermodynamic functions in terms of Z .

13.2.2 Expressing Thermodynamic Variables in Terms of Partition Function

To express thermodynamic quantities in terms of partition function, we begin by considering Eq. (13.14). On substituting the value of β in terms of temperature, we can express entropy as

$$S = Nk_B \ln Z + \frac{U}{T} \quad (13.21)$$

Now, we express internal energy U in terms of Z . For this, we calculate the partial derivative of the partition function with respect to temperature at constant volume and write

$$\left(\frac{\partial Z}{\partial T}\right)_V = \left(\frac{\partial Z}{\partial \beta}\right)_V \left(\frac{\partial \beta}{\partial T}\right)_V$$

On substituting for $\left(\frac{\partial Z}{\partial \beta}\right)_V$ from Eq. (13.17) and noting that $\left(\frac{\partial \beta}{\partial T}\right)_V = -\frac{1}{k_B T^2}$, we get

$$\left(\frac{\partial Z}{\partial T}\right)_V = -\frac{ZU}{N} \times \left(-\frac{1}{k_B T^2}\right) = \frac{U}{k_B T^2} \frac{Z}{N}$$

Hence, the expression for internal energy of a system in terms of the single particle partition function is obtained by inverting this relation:

$$U = Nk_B T^2 \frac{1}{Z} \left(\frac{\partial Z}{\partial T}\right)_V = Nk_B T^2 \frac{\partial}{\partial T} \ln Z \quad (13.22)$$

We now express the Helmholtz free energy F in terms of the partition function. For this, we invert Eq. (13.21) for entropy:

$$F = U - TS = -Nk_B T \ln Z \quad (13.23)$$

In Unit 10 you have learnt that for an isothermal process, the pressure exerted by a gas is related to the Helmholtz free energy (Eq. (10.5)):

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_B T}{Z} \left(\frac{\partial Z}{\partial V}\right)_T \quad (13.24)$$

You now know how thermodynamic functions are related to the partition function Z . To illustrate the utility of partition function in understanding the thermodynamic behaviour of a system, we now evaluate it for a monatomic gas and then express thermodynamic functions in terms of it.

13.3 PARTITION FUNCTION OF A MONATOMIC GAS

Consider an ideal monatomic gas consisting of N identical particles, each of mass m , occupying a volume V and moving randomly. As such, these particles should be treated as indistinguishable.

We now obtain the partition function of this system. Since molecules of an ideal monatomic gas do not interact among themselves, except at the instant of collision, it is reasonable to assume that

- there is no potential energy due to inter-atomic interactions; and
- at moderate temperatures, we have to consider only translational motion of molecules.

Let us first consider single particle partition function.

13.3.1 Single-Particle Partition Function

The energy of a particle in the i^{th} cell is given by

$$\varepsilon_i = \frac{p_i^2}{2m} \quad (13.25a)$$

and the single-particle partition function is given by

$$Z_1 = \sum_i e^{-\beta\varepsilon_i} = \sum_i \exp\left(-\frac{\beta p_i^2}{2m}\right) \quad (13.25b)$$

Note that the subscript 1 with Z signifies that we are considering single particle partition function.

Since the particle has only translational degrees of freedom, classically speaking, energy can be treated as a continuous variable. Then we can replace summation by integration in Eq. (13.25b) and rewrite it as

$$Z_1 = \int \exp\left(-\frac{\beta p^2}{2m}\right) dp \quad (13.26)$$

The probability that a molecule has momentum between p and $p + dp$ is equal to the number of cells in 6-D phase space within which such a molecule may exist. If each cell has volume H , the single particle partition function can be written as

$$Z_1 = \frac{1}{H} \iiint dx dy dz \iiint \exp\left[-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)\right] dp_x dp_y dp_z \quad (13.27)$$

Note that the limits of integration over momentum coordinates vary from $-\infty$ to ∞ .

Proceeding further, we note that integration over space variables gives V so that the expression for single particle partition function simplifies to

$$Z_1 = \frac{V}{H} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \exp\left(-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)\right) \quad (13.28)$$

Note that all the three integrals are identical and it will be sufficient to evaluate only one of them.

Let us, therefore, consider

$$I_x = \int_{-\infty}^{\infty} \exp\left(-\frac{\beta p_x^2}{2m}\right) dp_x$$

We rewrite it as

$$I_x = \int_{-\infty}^0 \exp\left(-\frac{\beta p_x^2}{2m}\right) dp_x + \int_0^{\infty} \exp\left(-\frac{\beta p_x^2}{2m}\right) dp_x \quad (13.29)$$

If we now put $p_x = -q$ in the first integral. Then $dp_x = -dq$ and the limits of integration change to $(\infty, 0)$. We absorb the minus sign in changing the limits of integration to $(0, \infty)$. So, you can easily convince yourself that both the integrals in Eq. (13.29) will be identical and we can write

$$I_x = 2 \int_0^{\infty} \exp\left(-\frac{\beta p_x^2}{2m}\right) dp_x \quad (13.30)$$

To evaluate this integral, we introduce a change of variable by defining

$$\xi = \frac{\beta p_x^2}{2m} \text{ so that } p_x dp_x = \frac{m}{\beta} d\xi \text{ and } dp_x = \sqrt{\frac{m}{2\beta}} \xi^{-1/2} d\xi. \text{ Hence, the integral}$$

in Eq. (13.30) takes the form

$$I_x = \sqrt{\frac{2m}{\beta}} \int_0^{\infty} \exp(-\xi) \xi^{-1/2} d\xi \quad (13.31)$$

This is a standard gamma function integral of order $(1/2)$ (see Unit 1) and has the value $\sqrt{\pi}$ so that

$$I_x = \int_{-\infty}^{\infty} \exp\left(-\frac{\beta p_x^2}{2m}\right) dp_x = \sqrt{\frac{2m\pi}{\beta}} = \sqrt{2m\pi k_B T} \quad (13.32)$$

We will obtain the same values for integrals over dp_y and dp_z . On using these results in Eq. (13.28), we get a compact expression for single-particle partition function:

$$Z_1 = \frac{V}{H} \left(\frac{2m\pi}{\beta}\right)^{3/2} = \frac{V}{H} (2m\pi k_B T)^{3/2}$$

If we take volume of a cell $H = h^3$, the expression for partition function takes the form

$$Z_1 = Z = \frac{V}{h^3} (2m\pi k_B T)^{3/2} \quad (13.33)$$

This equation gives the partition function for a single particle in μ -space.

Before proceeding further, you may like to answer an SAQ to test your understanding.

SAQ 1 – Thermodynamic functions for single particle

Using the expression for single-particle partition function, derive expressions for entropy and pressure.

While deriving expression for Maxwell-Boltzmann distribution function, we introduced the concept of degeneracy parameter A . Let us now discover its physical meaning and significance.

13.3.2 Degeneracy Parameter

The degeneracy parameter A is defined as

$$A = \exp(-\alpha) = \frac{N}{Z}$$

On substituting for Z from Eq. (13.33) for a single particle, we get

$$A = \frac{nh^3}{(2\pi mk_B T)^{3/2}} \quad (13.34)$$

where $n = N/V$. Note that in this expression, T occurs in the denominator and n occurs in the numerator. It means that at high temperatures and/or low densities, A will be small. A system for which degeneracy parameter is low is said to be non-degenerate. Let us now relate degeneracy parameter to physically measurable quantities – deBroglie wavelength λ_{dB} and

inter-particle distance – by noting that $\lambda_{dB} = \frac{h}{p}$. Since $\frac{p^2}{2m} = k_B T$, the

deBroglie wavelength can be expressed as

$$\lambda_{dB} = \frac{h}{\sqrt{2mk_B T}} \quad (13.35)$$

Also, we can express mean inter-particle distance r_0 as $r_0 = \left(\frac{V}{N}\right)^{1/3} = \frac{1}{n^{1/3}}$.

On combining Eqs. (13.34) and (13.35), we get

$$A = \pi^{-3/2} \left(\frac{\lambda_{dB}}{r_0}\right)^3 \quad (13.36)$$

Note that degeneracy parameter is directly proportional to the third power of deBroglie wavelength and inversely proportional to the third power of inter-particle distance. So when deBroglie wavelength is very small compared to inter-particle distance r_0 or $n\lambda_{dB}^3 \ll 1$, we will get $A \ll 1$. The

Maxwell-Boltzmann statistics is then said to hold good. It means that A **essentially signifies deviation of a system from an classical behaviour.**

Let us recapitulate the important results obtained in this section.

SINGLE-PARTICLE PARTITION FUNCTION

Recap

- The single-particle partition function confined in volume V is given by

$$Z_1 = \frac{V}{h^3} (2m\pi k_B T)^{3/2}$$

- In terms of temperature and number density, the degeneracy parameter is given by $A = \frac{nh^3}{(2\pi mk_B T)^{3/2}}$.

In terms of de Broglie wavelength and inter-particle distance, we can write

$$A = \pi^{-3/2} \left(\frac{\lambda_{dB}}{r_0}\right)^3. \text{ When } \lambda_{dB} \ll r_0 \text{ or } n\lambda_{dB}^3 \ll 1, A \ll 1 \text{ and we are}$$

working in the classical regime. And results based on Maxwell-Boltzmann statistics will hold good.

13.3.3 *N*-particle Partition Function

The *N*-particle partition function is given by

$$Z_N = \sum_{j=1}^N e^{-\beta E_j}$$

where

$$E_j = \varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_N.$$

In expanded form, we can write

$$\begin{aligned} Z_N &= \sum_{j=1}^N e^{-\beta(\varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_N)} \\ &= \sum_{j=1}^N (e^{-\beta\varepsilon_1})(e^{-\beta\varepsilon_2}) \dots (e^{-\beta\varepsilon_N}) \end{aligned}$$

Within the framework of classical statistics, we assume that these particles are distinguishable and independent. So, we can rewrite it in a compact form as

$$Z_N = \left(\sum_i e^{-\beta\varepsilon_i} \right)^N = Z^N$$

We know that Eq. (13.33) gives us single particle partition function. For a monatomic gas made up of *N* distinguishable and non-interacting particles, we can write partition function as (see Margin Remark):

$$Z_N = Z_1^N = V^N \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \quad (13.37)$$

We now use this expression for the partition function for an ideal gas made up of *N*-particles to obtain various thermodynamic functions. You will recall that all thermodynamic functions can be expressed in terms of the partition function. [Refer to Eqs. (13.21 to 13.24). In these equations, *Z* refers to single-particle partition function. However, when we use Eq. (13.37), we have to drop *N* occurring with single particle expressions.]

Proceeding with the calculation of thermodynamic functions, we take natural log on both sides of Eq. (13.37). This gives

$$\ln Z_N = N \ln V + \frac{3N}{2} \ln \left(\frac{2\pi m}{h^2} \right) + \frac{3N}{2} \ln(k_B T) \quad (13.38)$$

If we now define $U = k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{N,V}$. We note that the first two terms on the right-hand side of Eq. (13.38) are independent of *T* and will not contribute to the expression of internal energy. Hence, for an *N*-particle gaseous system we can write:

$$\left(\frac{\partial \ln Z}{\partial T} \right)_{N,V} = \frac{3N}{2T}$$

$$\text{so that } U = k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{N,V} = \frac{3}{2} N k_B T = \frac{3}{2} n R T \quad (13.39)$$

where *n* denotes the number of moles of the gas and *R* is universal gas constant.

The energy per molecule is given by

$$\varepsilon = \frac{U}{N} = \frac{3}{2} k_B T$$

This result agrees with that obtained on the basis of kinetic theory for a monatomic gas having three degrees of translational freedom. At 300K, the average energy of an ideal gas molecule is

$$\varepsilon = \frac{3}{2} \times (1.38 \times 10^{-23} \text{ JK}^{-1}) \times 300\text{K} = 6.21 \times 10^{-21} \text{ J} = 0.039 \text{ eV}$$

The heat capacity at constant volume is, by definition

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Using Eq. (13.39), we can write

$$C_V = \frac{3}{2} Nk_B = \frac{3}{2} nR \quad (13.40)$$

In Block 1, you have learnt that the heat capacity of a monatomic gas is independent of temperature as well as the nature of the gas.

Similarly, pressure in terms of N -particle partition function is defined as:

$$p = k_B T \left(\frac{\partial \ln Z_N}{\partial V} \right)_{T,N}$$

Hence, from Eq. (13.38), it readily follows that

$$\left(\frac{\partial \ln Z_N}{\partial V} \right)_{T,N} = \frac{N}{V}$$

And the expression for pressure takes the form

$$p = \frac{Nk_B T}{V} \quad (13.41)$$

Do you recognise this equation? It is the equation of state of an ideal gas. It is important to note here that neither thermodynamics nor kinetic theory of gases enabled us to establish its exact form. It means that a natural explanation of molecular chaos lies in statistical arguments, which are more profound.

On combining this result with Eq. (13.39), we can write

$$p = \frac{2U}{3V} \quad (13.42)$$

That is, the average pressure is two-third of energy density.

Similarly, Helmholtz free energy is given by

$$F = -k_B T \ln Z_N = -Nk_B T \ln \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right] \quad (13.43)$$

The entropy and the partition function of an N -particle system are connected by the relation:

$$S = k_B \ln Z_N + \frac{U}{T}$$

On substituting for $\ln Z_N$ and U from Eqs. (13.38) and (13.39), respectively, we get

$$S(T, V, N) = Nk_B \left[\ln(VT^{3/2}) + \frac{3}{2} \ln(k_B) + \frac{3}{2} \ln\left(\frac{2\pi m}{h^2}\right) \right] + \frac{3}{2} Nk_B \quad (13.44)$$

In your higher classes, you will learn that this expression for entropy leads to **Gibbs paradox**:

The entropy of a system does not behave as an extensive variable and is not a function of the thermodynamic state alone.

That is, we can manage to change entropy of a system by extraneous factors.

Sackur and Tetrode showed that Gibbs paradox arises because within the framework of classical statistics, identical particles were treated as distinguishable.

We summarise important results of this section.

Recap

THERMODYNAMIC VARIABLES OF A GAS

- $U = \frac{3}{2} Nk_B T = \frac{3}{2} nRT$
- $F = -k_B T \ln Z_N = -Nk_B T \ln \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right]$
- $C_V = \frac{3}{2} Nk_B = \frac{3}{2} nR$
- $p = \frac{Nk_B T}{V}$
- $S(T, V, N) = Nk_B \left[\ln(VT^{3/2}) + \frac{3}{2} \ln(k_B) + \frac{3}{2} \ln \left(\frac{2\pi m}{h^2} \right) \right] + \frac{3}{2} Nk_B$

Recap

GIBB'S PARADOX

For a system obeying Maxwell-Boltzmann statistics, entropy of mixing for self-diffusion shows the same increase in entropy as for inter-mixing of two different gases. This unrealistic situation is referred to as Gibbs's Paradox. It arises because in classical statistics, gas molecules are considered distinguishable.

Let us now summarise what you have learnt in this unit.

13.4 SUMMARY

Concept	Description
Thermodynamic probability of distribution in various energy groups	<ul style="list-style-type: none"> ■ The thermodynamic probability of distributing N distinguishable particles into various energy groups is given by $W = \frac{N!}{\prod_i n_i!}$
Most probable state	<ul style="list-style-type: none"> ■ For determining the most probable state, $\ln W$ rather than W is maximised, since the latter is a very large number and inconvenient to handle.
Most probable distribution	<ul style="list-style-type: none"> ■ The most probable distribution of particles among various energy levels of a Maxwellian system is given by

$$n_i = \frac{1}{\exp[(\varepsilon_i - \mu)/k_B T]}$$

where μ is known as the chemical potential.

Single-particle partition function

- Single-particle partition function for a system of N distinguishable particles distributed in non-degenerate levels is given by

$$Z = \sum_{i=1}^N \exp(-\beta\varepsilon_i)$$

Degeneracy parameter

- The degeneracy parameter A is given by

$$A = \frac{N}{Z} = \exp\left(\frac{\mu}{k_B T}\right)$$

Thermodynamic parameters and partition function

- For a non-degenerate thermodynamic system made up of N identical and non-interacting particles enclosed in volume V , the thermodynamic parameters are related to Z as

$$U = Nk_B T^2 \frac{\partial}{\partial T} (\ln Z)$$

$$S = Nk_B \ln Z + \frac{U}{T}$$

$$F = -Nk_B T \ln Z$$

and

$$p = \frac{Nk_B T}{Z} \left(\frac{\partial Z}{\partial V} \right)_T$$

Partition function of an ideal monatomic gas

- The partition function of an ideal monatomic gas made up of N identical particles is given by

$$Z_N = \frac{V^N}{h^{3N}} (2\pi m k_B T)^{3N/2}$$

The internal energy $U = \frac{3}{2} nRT$ and heat capacity $C_V = \frac{3}{2} nR$.

Entropy of an ideal monatomic gas

- The entropy of an ideal monatomic gas is given by

$$S = Nk_B \ln \left[V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} e^{3/2} \right]$$

13.5 TERMINAL QUESTIONS

- Consider a system of N particles and a phase space consisting of only two levels with energies 0 and ε ($\varepsilon > 0$), respectively. Calculate the partition function and the internal energy.
- Show that

$$\text{i) } H = \frac{N}{\beta} \left[\left(\frac{\partial \ln Z}{\partial \ln T} \right)_{V,N} + \left(\frac{\partial \ln Z}{\partial \ln V} \right)_{T,N} \right] \text{ and}$$

$$\text{ii) } G = -\frac{N}{\beta} \left[\ln Z - \left(\frac{\partial \ln Z}{\partial \ln V} \right)_{T,N} \right]$$

3. N particles obey the Maxwell-Boltzmann (M-B) distribution. They are distributed among three states with energies $E_1 = 0$, $E_2 = k_B T$ and $E_3 = 3k_B T$. If the equilibrium energy of the system is $2000k_B T$, calculate the total number of particles, N .
4. Consider a system of N classical linear harmonic oscillators. Calculate (i) the partition function, (ii) the free energy, (iii) entropy, (iv) C_V and C_p .
5. Consider a classical ideal gas consisting of N particles. The energy ε of a particle is given by $\varepsilon = cp$, where c is a constant and p is the magnitude of the momentum. Calculate (i) the partition function of the system, (ii) internal energy, and (iii) C_V .
6. Consider a classical linear oscillator with

$$\varepsilon = \frac{p^2}{2m} + bx^4,$$

where b is a constant. Assuming that the oscillator is in thermal equilibrium with a heat reservoir at temperature T , calculate (i) the mean kinetic energy, (ii) the mean potential energy, and (iii) C_V for an assembly of N such oscillators.

13.6 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. For single particle, we can write from Eq. (13.21):

$$S = k_B \ln Z + \frac{U}{T} \quad \text{with} \quad U = k_B T^2 \frac{\partial}{\partial T} \ln Z$$

On substituting the value of Z from Eq. (13.33), we get

$$\begin{aligned} S &= k_B \ln \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right] + \frac{3}{2} \frac{k_B T}{T} \\ &= k_B \ln \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} e^{3/2} \right] \end{aligned}$$

Similarly, from Eq. (13.24), we recall that $p = \frac{k_B T}{Z} \left(\frac{\partial Z}{\partial V} \right)_T$

On substituting the value of Z from Eq. (14.33) as before, we get

$$= \frac{k_B T}{\frac{V}{h^3} (2\pi m k_B T)^{3/2}} \frac{(2\pi m k_B T)^{3/2}}{h^3} = \frac{k_B T}{V}$$

Terminal Questions

1. It is given that $E_2 = \varepsilon$ and $E_1 = 0$.

$$\text{We have } Z = \sum_i e^{-E_i/k_B T} = 1 + e^{-\theta/T} \text{ with } \theta = \frac{\varepsilon}{k_B}.$$

The occupation numbers are

$$n_1 = \frac{N}{Z} = \frac{N}{1 + e^{-\theta/T}}$$

$$n_2 = \frac{Ne^{-\theta/T}}{Z} = \frac{Ne^{-\theta/T}}{1 + e^{-\theta/T}}$$

$$\therefore U = n_1 E_1 + n_2 E_2 = \frac{N\varepsilon e^{-\theta/T}}{1 + e^{-\theta/T}}$$

For very low temperature ($T \ll \theta$), and we have $n_1 \cong N$, $n_2 = 0$. At very high temperatures ($T \gg \theta$), and hence, $n_1 \cong \frac{N}{2}$, $n_2 \cong \frac{N}{2}$. You will note that for normal temperatures

$$\frac{n_2}{n_1} = e^{-\theta/T} < 1$$

2. i) In Unit 10 you have learnt that the enthalpy H can be expressed in terms of thermodynamic properties as:

$$H = U + pV$$

$$\text{From Eq. (13.43) we have } U = Nk_B T^2 \left. \frac{\partial \ln Z}{\partial T} \right|_V$$

$$\text{Rewriting } \left. \frac{\partial \ln Z}{\partial T} \right|_V = \left[\frac{\partial \ln Z}{\partial \ln T} \frac{\partial \ln T}{\partial T} \right]_V = \frac{1}{T} \left. \frac{\partial \ln Z}{\partial \ln T} \right|_V \text{ and using } \beta = \frac{1}{k_B T}$$

we can express the internal energy as

$$U = Nk_B T^2 \left(\frac{1}{T} \left. \frac{\partial \ln Z}{\partial \ln T} \right|_V \right) = \frac{N}{\beta} \left. \frac{\partial \ln Z}{\partial \ln T} \right|_V$$

From Eq. (13.24), we have

$$p = Nk_B T \left(\frac{\partial \ln Z}{\partial V} \right)_T = Nk_B T \left(\frac{\partial \ln Z}{\partial \ln V} \frac{\partial \ln V}{\partial V} \right)_T = \frac{Nk_B T}{V} \left(\frac{\partial \ln Z}{\partial \ln V} \right)_T = \frac{N}{\beta V} \left(\frac{\partial \ln Z}{\partial \ln V} \right)_T$$

Hence,

$$H = U + pV = \frac{N}{\beta} \left(\left. \frac{\partial \ln Z}{\partial \ln T} \right|_V + \left. \frac{\partial \ln Z}{\partial \ln V} \right|_T \right)$$

- ii) Gibbs free energy $G = U - TS + pV = F + pV$

$$\text{From Eq. (13.40) we have } F = U - TS = -Nk_B T \ln Z = -\frac{N}{\beta} \ln Z$$

$$\text{and we know that } pV = V \frac{Nk_B T}{V} \left(\frac{\partial \ln Z}{\partial \ln V} \right)_T = \frac{N}{\beta} \left(\frac{\partial \ln Z}{\partial \ln V} \right)_T$$

$$\text{Hence, } G = -\frac{N}{\beta} \ln Z + \frac{N}{\beta} \frac{\partial \ln Z}{\partial \ln V} = -\frac{N}{\beta} \left(\ln Z - \frac{\partial \ln Z}{\partial \ln V} \right)$$

$$3. \text{ We have } N = N_1 + N_2 + N_3 \text{ and } E = N_1 E_1 + N_2 E_2 + N_3 E_3$$

Hence, we can write

$$2000 k_B T = N_1(0) + N_2 k_B T + N_3 3k_B T$$

$$2000 = N_2 + 3N_3 \quad (i)$$

$$\text{Also, } N_1 : N_2 : N_3 :: \exp(-E_1 / k_B T) : \exp(-E_2 / k_B T) : \exp(-E_3 / k_B T)$$

$$\text{i.e., } N_1 : N_2 : N_3 :: 1 : \exp(-1) : \exp(-3)$$

$$\text{or } \frac{N_1}{1} = \frac{N_2}{e^{-1}} = \frac{N_3}{e^{-3}} = \text{constant (say) } B$$

$$\text{Hence, } N_1 = B, N_2 = \frac{B}{e} \text{ and } N_3 = \frac{B}{e^3}$$

$$\text{From (i) we have } 2000 = N_2 + 3N_3 = \frac{B}{e} + \frac{3B}{e^3}$$

$$\text{Hence, } B = \frac{2000}{e^{-1} + 3e^{-3}} = \frac{2000}{0.3679 + 0.1493} = \frac{2000}{0.5172} = 3867$$

$$\text{i.e., } N_1 = 3867, N_2 = \frac{3867}{e} = 1423 \text{ and } N_3 = \frac{3867}{e^3} = 193$$

Hence, the total number of particles $N = 5483$.

$$4. \text{ The partition function is given by } Z = \frac{1}{\beta \hbar \omega}$$

Assuming the oscillators to be indistinguishable, we have

$$Z_N = (\beta \hbar \omega)^{-N}$$

$$\text{The free energy } F = -Nk_B T \ln Z = Nk_B T \ln \left(\frac{\hbar \omega}{k_B T} \right)$$

$$S = -\left(\frac{\partial F}{\partial T} \right)_V = Nk_B \left[-\ln \left(\frac{\hbar \omega}{k_B T} \right) + 1 \right] = Nk_B \left[\ln \left(\frac{k_B T}{\hbar \omega} \right) + 1 \right]$$

$$U = F + TS = Nk_B T$$

$$C_V = Nk_B T, \quad p = -\left(\frac{\partial F}{\partial V} \right)_T = 0$$

$$H = U + pV = Nk_B T, \quad C_p = C_p = \left(\frac{\partial H}{\partial T} \right)_p = Nk_B$$

5. We have

$$Z = \frac{V}{h^3} \iiint e^{-\beta cp} dp_x dp_y dp_z$$

In terms of spherical polar coordinates, we can rewrite the volume element as (see the margin remark for evaluation of the integral):

$$Z = \frac{V}{h^3} 4\pi \int_0^\infty e^{-\beta cp} p^2 dp = \frac{8\pi V (k_B T)^3}{(ch)^3}$$

Hence,
$$Z_N = \left[\frac{8\pi V (k_B T)^3}{(ch)^3} \right]^N$$

$$\begin{aligned} \therefore U &= Nk_B T^2 \frac{\partial}{\partial T} (\ln Z) = Nk_B T^2 \frac{\partial}{\partial T} \left[\ln \left(\frac{8\pi V k_B^3}{(ch)^3} \right) + 3 \ln T \right] \\ &= 3Nk_B T \end{aligned}$$

and

$$C_V = 3Nk_B$$

6. The mean kinetic energy is:

$$\bar{E} = \frac{\int e^{-\beta p^2/2m} \left(\frac{p^2}{2m} \right) dp}{\int e^{-\beta p^2/2m} dp} = -\frac{\partial}{\partial \beta} \ln \left(\int e^{-\beta p^2/2m} dp \right)$$

We have

$$I = \int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp$$

By putting $\frac{\beta p^2}{2m} = x$, we find that (read the margin remark):

$$dp = \sqrt{\frac{m}{2\beta}} \frac{1}{\sqrt{x}} dx$$

so that
$$I = 2 \int_0^\infty e^{-x} \frac{1}{\sqrt{x}} \sqrt{\frac{m}{2\beta}} dx$$

or
$$I = \sqrt{\frac{2m\pi}{\beta}} \quad \left(\because \int_0^\infty x^{-1/2} e^{-x} dx = \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \right)$$

To evaluate the integral in the expression for Z , we introduce a new variable by defining

$$x = \beta cp$$

with
$$\beta = \frac{1}{k_B T}$$

$$dp = \frac{dx}{\beta c}$$

and

$$p^2 dp = \frac{x^2 dx}{(\beta c)^3}$$

$$\therefore I = \frac{1}{(\beta c)^3} \int_0^\infty e^{-x} x^2 dx$$

$$= \frac{\Gamma(3)}{(\beta c)^3} = \frac{2}{(\beta c)^3}$$

APPENDIX 13A: THE METHOD OF LAGRANGE MULTIPLIERS

You are familiar with the problem of finding maxima and minima of functions. Many a time, we are required to obtain these extreme values subject to certain conditions or constraints. We came across this problem in Sec. 13.2, where we had to maximise thermodynamic probability subject to the conditions that the number of particles and energy are fixed. This problem is solved using an elegant technique called the **method of undetermined multipliers** due to French analyst Lagrange.

Suppose we wish to know the extrema of the function $f(x, y)$. For this, we have to simultaneously solve equations

$$\frac{\partial f}{\partial x} = 0 \quad \text{and} \quad \frac{\partial f}{\partial y} = 0 \quad (13A.1)$$

The resulting pair (or pairs) of values of x and y specify the point (or points) at which f has a maximum, minimum, or point of inflection. Now suppose that there is an auxiliary condition

$$g(x, y) = 0 \quad (13A.2)$$

In principle, we can eliminate one of the variables. However, in practice, this may not always be possible. So, we proceed as follows:

$$\text{Eq. (13A.1) gives us } \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = 0 \quad (13A.3)$$

From Eq. (13A.2), we can write

$$dg = \left(\frac{\partial g}{\partial x}\right)_y dx + \left(\frac{\partial g}{\partial y}\right)_x dy = 0 \quad (13A.4)$$

Multiplying Eq. (13A.4) by λ and adding to Eq. (13A.3) yields

$$\left(\frac{\partial f}{\partial x}\right) + \lambda \left(\frac{\partial g}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) + \lambda \left(\frac{\partial g}{\partial y}\right) dy = 0$$

where we have dropped subscripts x and y .

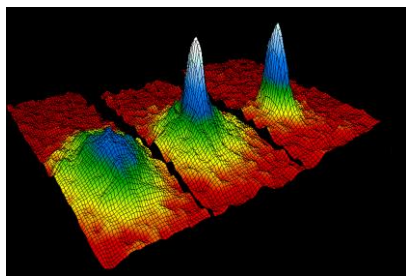
Since x and y are independent, we have

$$\left(\frac{\partial f}{\partial x}\right) + \lambda \left(\frac{\partial g}{\partial x}\right) = 0$$

$$\text{and} \quad \left(\frac{\partial f}{\partial y}\right) + \lambda \left(\frac{\partial g}{\partial y}\right) = 0 \quad (13A.5)$$

These equations are solved simultaneously to know the values of x , y and λ .

UNIT 14



A gas of particles with integer spins obeying Bose-Einstein statistics, when cooled to a very low temperature becomes a Bose-Einstein Condensate.

QUANTUM STATISTICS

Structure

- | | | | |
|------|---------------------------------------|-------|--|
| 14.1 | Introduction | 14.6 | Applications of Bose-Einstein Statistics |
| | Expected Learning Outcomes | | Bose's Derivation of Planck's Law |
| 14.2 | Need for Quantum Statistics | 14.7 | Applications of Fermi-Dirac Statistics |
| | Blackbody Radiation | | Fermi Energy |
| | Heat Capacity of Solids | | Electronic Heat Capacity |
| | Classification of Particles | 14.8 | Summary |
| 14.3 | Bose-Einstein Distribution Function | 14.9 | Terminal Questions |
| 14.4 | Fermi-Dirac Distribution Function | 14.10 | Solutions and Answers |
| 14.5 | Comparison of Different Distributions | | |

STUDY GUIDE

In Unit 13, you have learnt how to evaluate the partition function and thermodynamic functions of a monatomic gas obeying Maxwell-Boltzmann statistics. This exercise required knowledge of elementary differential and integral calculus. However, in this unit, you will apply the basic knowledge of permutations and combinations (Unit 12) to establish distribution functions for Bose-Einstein and Fermi-Dirac systems. You will then study the behaviour of a photon gas using Bose-Einstein statistics. The behaviour of Fermi-Dirac systems at low temperatures will be discussed with particular reference to zero point energy and electronic heat capacity in metals. The mathematics in this unit is somewhat involved and you are advised to refresh your earlier knowledge before starting this unit. Keep pen/pencil with you to solve intermediate steps yourself. Phase out your study and go section by section. Then you will enjoy learning it.

"To see something which nobody else has seen before is thrilling and deeply satisfying. These are the moments when you want to be a scientist."

**Wolfgang
Ketterle**

14.1 INTRODUCTION

In the previous units of this block, you have learnt how to apply statistical methods to study thermodynamic behaviour of systems made up of large number of non-interacting particles. But classical statistics failed to resolve the problem of blackbody radiation.

Also, satisfactory explanation of temperature variation of heat capacity of solids eluded it. Moreover, the concept of zero point energy was completely alien to classical statistics. Similarly, to understand the behaviour of conduction electrons in metals, we have to resort to quantum statistics. Therefore, we begin by discussing need for quantum statistics in Sec. 14.2.

In quantum statistics, we deal with two types of statistics: Bose-Einstein (B-E) statistics and Fermi-Dirac (F-D) statistics depending on the spin of the particles making up the system. Particles with integral spin are called bosons and those with half-integral spins are known as fermions. While fermions obey Pauli Exclusion Principle, no such restriction applies to bosons. Conforming to this condition, we have obtained expressions for distribution functions for B-E and F-D systems in Sec. 14.3 and 14.4, respectively.

You will note that in spite of fundamental difference, the expressions for distribution functions show remarkable similarity. Further, as compared to Maxwell-Boltzmann distribution (Sec. 13.5), the distribution of bosons is skewed towards lower energy states whereas the distribution of fermions is skewed towards higher energy states.

In Sec. 14.6, we have applied B-E statistics to blackbody radiation. We give Bose's derivation of Planck's law, without any reference whatsoever to classical ideas.

In Sec. 14.7, we have discussed applications of F-D statistics. You will learn that an F-D system is quite alive even at absolute zero. We have obtained expression for Fermi energy and given a brief account of temperature variation of heat capacity of metals based on F-D statistics.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ point out inadequacies of classical statistics and discuss need for quantum statistics;
- ❖ obtain expressions for the Bose-Einstein and Fermi-Dirac distribution functions;
- ❖ starting from BE distribution function, obtain expression for Planck's law;
- ❖ explain the concept of zero point energy; and
- ❖ obtain an expression for heat capacity of electrons at low temperatures.

14.2 NEED FOR QUANTUM STATISTICS

In classical statistics, we assume that it is possible to simultaneously determine the position and momentum coordinates of a gaseous particle as precisely as we like. It means that these particles are distinguishable and can be labelled. But this is not true in practice. Heisenberg's uncertainty principle forbids determination of the position (q) and the momentum (p) of a particle simultaneously with infinite precision. If the uncertainties in the measurements of q and p are Δq and Δp , respectively, the product $\Delta q \Delta p$ cannot be made less than $\hbar/2$:

$$\Delta q \Delta p \geq \hbar/2 \quad (14.1)$$

where $\hbar = h/2\pi$ and $h (= 6.62 \times 10^{-34} \text{ Js})$ is Planck's constant. It implies that when we study the behaviour of an assembly of identical particles statistically, we should treat it as a collection of **indistinguishable** particles. Further, blackbody radiation deserves a unique place in physics because it gave birth to quantum theory. You have learnt about it in detail in Unit 11. But here we will recapitulate some important ideas/results.

14.2.1 Blackbody Radiation

We know that when a body is heated, it emits electromagnetic waves from its surface in all directions. The spectrum of radiated frequencies ranges from 0 to ∞ . When such thermal radiation is contained inside a hollow cavity whose walls are opaque to it and maintained at a constant temperature, we expect that in the interior, radiation will have exactly the same spectral distribution as that of blackbody radiation. In other words, the energy distribution over various wavelengths should be a function of temperature, independent of the shape and size of the cavity (Fig. 14.1a). A small opening in one of the walls enables us to experimentally study the nature of emerging radiation. In fact, such experiments were carried out by a large number of scientists in the period of 1895-1900. We may make particular mention of Rubens and Kurlbaum. The results of their experiments established beyond doubt the inability of classical theories to reproduce experimental results. Fig.14.1b shows the experimental curves for the energy density u_λ at three different temperatures.

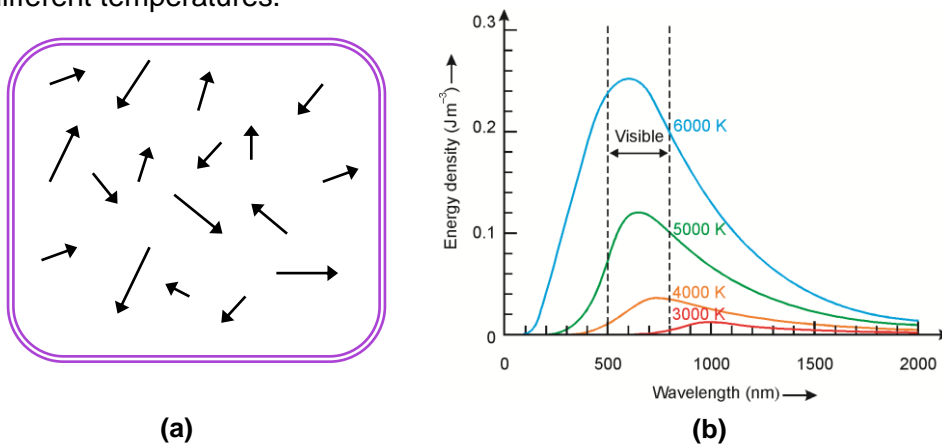


Fig. 14.1: a) The electromagnetic radiation inside an oven is treated as a photon gas in equilibrium with the oven walls; b) Spectral distribution of energy in blackbody radiation.

As discussed in Unit 11, Lord Rayleigh and Sir James Jeans studied the problem using the ideas of classical physics and arrived at **Rayleigh-Jeans law** for $u_\nu d\nu$ [Eq. (11.8)].

You may recall that for small values of ν , it reproduced the experimental curves rather well. However, for $\nu \rightarrow \infty$, Rayleigh-Jeans law showed a serious flaw; it predicted that the total energy density would be infinite. This unphysical situation was termed **ultraviolet catastrophe** by P. Ehrenfest (Fig. 14.2).

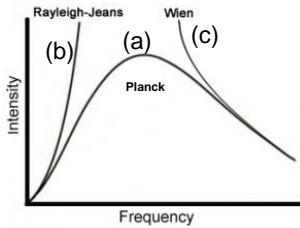


Fig. 14.2

Wien carried out thermodynamic analysis of blackbody radiation spectrum and successfully explained the qualitative features of experimental results at high frequencies (Fig. 14.2). Though it seemed acceptable, it proved completely inadequate at low frequencies. That is, classical theories failed to explain the observed spectrum of blackbody radiation satisfactorily for all frequencies and serious doubts were expressed about the applicability of the principle of equipartition of energy to blackbody radiation.

At this stage, Max Planck rejected classical theories and conjectured that emission and absorption of radiation are discontinuous processes. On December 14, 1900, he declared in a paper presented to the German Physical Society that the only way to derive the correct blackbody radiation formula was to postulate that

- exchange of energy between matter (walls) and radiation (cavity) could take place only in bundles of a certain quantity of energy; and
- the quantum of exchange is directly proportional to its frequency. That is, the energy of an oscillator having frequency ν could only be an integral multiple of $h\nu$, where h is a constant.

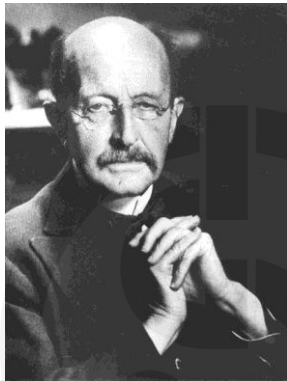
These postulates marked a fundamental departure from then existing ideas. On the basis of his hypothesis that each oscillator can possess only discrete energies; $0, h\nu, 2h\nu, \dots$ and oscillators of energy ϵ_n at a temperature T and by assuming that Maxwell-Boltzmann statistics holds good, Planck arrived at his **law** of blackbody radiation:

$$u_\nu d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \quad (14.2)$$

It reproduced experimental curves of Fig.14.1b beautifully. It is pertinent to mention here that Planck's hypothesis of quantisation of energy gave birth to a new branch of physics – Quantum Physics. However, Planck's law is said to be semi-classical. Do you know the reason? It is because he used Rayleigh's results for calculating the number of modes and Maxwell-Boltzmann statistics for distribution of energies.

14.2.2 Heat Capacity of Solids

You have studied that solids behave as a collection of independent harmonic oscillators and energy associated with one mole of a substance is equal to



Max Karl Ernst Ludwig Planck, (1858 – 1947) was a German theoretical physicist. He is regarded as the originator of the quantum theory which revolutionized our understanding of atomic and subatomic processes. The Nobel Prize in Physics was conferred on him in 1918 for postulating energy quanta, which helped in explaining the black body radiation.

$3N_A k_B T$, where N_A is Avogadro's number. From the definition of constant volume heat capacity, we can write

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3N_A k_B = 3R = 24.9 \text{ J mol}^{-1} \text{ K}^{-1} \quad (14.3a)$$

In other words, constant volume heat capacity is constant ($= 3R$) for all substances and at all temperatures. This is the famous **Dulong and Petit's law**.

Now refer to Fig. 14.3. You will note that experimental data is at complete variance with this law and deviations, particularly in the low temperature region, are very striking.

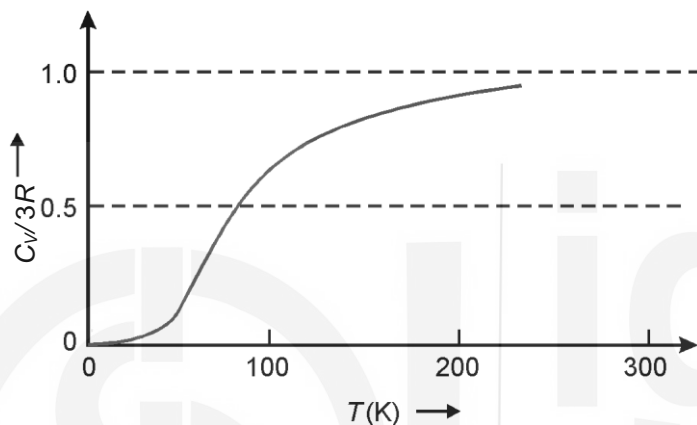


Fig. 14.3: Temperature variation of constant volume heat capacity of a solid.

A qualitative theoretical explanation of experimental results was attempted by Einstein using Planck's ideas on quantisation of energy. That is, following Planck, Einstein discarded the law of equipartition of energy. Instead, he assumed that each atom vibrates with the same angular frequency ω_E and the motion of any atom is independent of the motion of its neighbours.

He obtained the following expression for the heat capacity:

$$C_V = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2} \quad (14.3b)$$

Here ω_E is Einstein's frequency and $\theta_E = \hbar\omega_E / k_B$ is known as Einstein temperature. Einstein could reproduce only the general features of the experimentally observed curve (Fig. 14.4). However, there was disagreement in details, particularly at low temperatures.

Debye (1912) refined Einstein's model and suggested that it would be more appropriate to consider a spectrum of vibration frequencies, particularly at low temperatures. In this way, he showed that at low temperatures, the constant volume heat capacity varies as third power of temperature. This is known as Debye T^3 -law. His results were in excellent agreement with experiments in the entire temperature range.

You may now like to revise important results obtained in this section.

Recap

TOWARDS QUANTUM THEORY

- Indistinguishability of particles and uncertainty in the simultaneous determination of position and momentum are basic premises of quantum statistics.
- Spectral distribution of blackbody radiation and temperature dependence of constant volume heat capacity, particularly at low temperatures, cannot be explained on the basis of classical ideas.
- Planck postulated that exchange of energy between matter and radiation takes place only in bundles of a certain quantity of energy and the quantum of exchange is directly proportional to frequency.
- Einstein and Debye used quantisation of vibrational energy to explain the behaviour of heat capacity of solids at low temperatures.

14.2.3 Classification of Particles

You will recall that according to Heisenberg's uncertainty principle, the particles making up a system should not be treated as distinguishable. The detailed consequences of this concept can be understood fully only after a thorough understanding of the principles of quantum mechanics, which you will study in detail in the fifth semester of this programme. For the present, it is sufficient to know that:

- Simultaneous determination of position and momentum of a particle cannot be accomplished to infinite precision. Instead, uncertainties Δp and Δq in these quantities are subject to $\Delta q \Delta p \sim h$. That is, **the volume of a cell in phase space cannot be arbitrarily small**. In fact, the smallest volume of a cell should be taken as h^3 .
- In quantum statistics, identical particles are treated as indistinguishable. It means that permutation of particles does not lead to a different state. This has profound consequences.
- All known elementary particles can be classified into two categories on the basis of their spin:
 - Particles having integral spin ($0, \hbar, 2\hbar, \dots$) obey Bose-Einstein statistics and are termed **bosons**. This applies to photons, pions, ^4He , etc. The number of bosons that can occupy a given quantum-state has no restriction.
 - Particles with half-integral spin $\frac{\hbar}{2}, \frac{3\hbar}{2}, \dots$ are termed **fermions** and obey the Fermi-Dirac statistics. Particles like electrons, protons, neutrons, muons, etc. belong to this category.

Fermions tend to avoid one another!

The number of fermions in a quantum state is determined by Pauli's Exclusion Principle. For example, there cannot be more than two electrons in the same quantum state having all four quantum numbers the same. You are familiar with the implications of this principle in

electronic configuration of elements in the Periodic Table. In general, the number of fermions in a quantum state is limited to $(2s + 1)$, where $s\hbar$ is the spin angular momentum of the fermion.

You should now test your understanding by answering the following SAQ.

SAQ 1 – Classification of particles

Helium has two isotopes, viz., ${}^3\text{He}$ and ${}^4\text{He}$. Classify these as fermions and bosons. Justify your conclusion.

To illustrate the consequences of indistinguishability, let us consider the following simple example.

Suppose we have a system consisting of only two particles A and B and three quantum states, $i = 1, 2, 3$. According to Maxwell-Boltzmann statistics, these can be distributed in nine ways, which are tabulated below:

Distribution ↓	States →		
	1	2	3
1	AB	–	–
2	–	AB	–
3	–	–	AB
4	A	B	–
5	B	A	–
6	A	–	B
7	B	–	A
8	–	A	B
9	–	B	A

That is, we have 3^2 possibilities. It is straightforward to show that if we have N_i particles to be distributed among g_i states, the total number of ways is $g_i^{N_i}$. (It is pertinent to mention here that for convenience, we considered $g_i = 1$ for M-B statistics.)

In the case of quantum statistics, we cannot distinguish A from B . However, in Bose-Einstein distribution, there is no restriction on the number of particles that can occupy a given state. So, there are only six possibilities:

Distribution ↓	States →		
	1	2	3
1	AA	–	–
2	–	AA	–
3	–	–	AA
4	A	A	–
5	A	–	A
6	–	A	A

In general, the result is $(N_i+g_i-1)C_{N_i}$. This can be proved in several ways. We shall do it using a simple, yet interesting method.

Suppose we want to distribute N_i indistinguishable particles among g_i cells. Imagine the N_i particles, denoted by dots and arranged in a row, as shown in Fig. 14.4a. The cell boundaries are denoted by $(g_i + 1)$ vertical bars. For example, when $g_i = 5$ and $N_i = 10$, a typical distribution is shown in Fig. 14.4b.

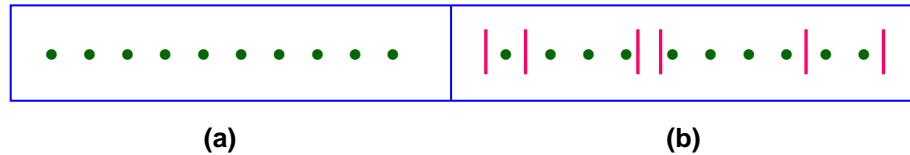


Fig. 14.4: a) N_i particles arranged along a line; b) a possible distribution for $N_i = 10$ and $g_i = 5$.

There is one particle in the first cell, three in the second, none in the third, four in the fourth, and two in the fifth. The total number of dots and bars is $(g_i + 1 + N_i)$. Since the two end positions in such a diagram would always be occupied by bars, the required number of distributions W is equal to the number of ways of choosing N_i positions for the particles from $(N_i + g_i + 1 - 2)$, i.e. $(N_i + g_i - 1)$ positions. Hence,

$$W = (N_i+g_i-1)C_{N_i} \tag{14.4}$$

If we now put $N_i = 2$ and $g_i = 3$, we get $W = {}^4C_2 = 6$, which reproduces the earlier result.

In the case of Fermi-Dirac statistics, there can, at best, be only one particle per cell and we necessarily have $n_i < g_i$. Of course, for particles of spin $s\hbar$, the number of possibilities has to be multiplied by the factor $(2s + 1)$. For the system under consideration, we have just three possibilities as shown below:

Distribution ↓	States →		
	1	2	3
1	A	A	–
2	A	–	A
3	–	A	A

If we now define a parameter r as

$$r = \frac{\text{Probability that two particles are found in the same state}}{\text{Probability that the particles are found in different states}}$$

we have $r_{MB} = \frac{3/9}{6/9} = \frac{1}{2}$, $r_{BE} = \frac{3/6}{3/6} = 1$, and $r_{FD} = 0$

These values of r illustrate a striking difference between these three statistics. You should note that $r_{FD} = 0$ because of the Pauli's principle. On the other hand, r_{BE} is greater than r_{MB} . It signifies that bosons have a greater tendency to bunch together; even more than the classical particles.

Before proceeding further, we will like you to know about Prof. S. N. Bose, who is best known for his work on radiation theory.



Prof. Satyendra Nath Bose (1894-1974) was born on 1st January 1894 in Calcutta (now Kolkata). After matriculation in 1909, he joined Presidency College, Calcutta. He topped his B.Sc. and M. Sc. examinations with specializations in mixed (applied) mathematics. After completing his M.Sc., Bose joined the University of Calcutta, as a research scholar in 1916 and started his

studies in the theory of relativity and got interested in the work of Albert Einstein. Since many of his papers were in German, Bose took up to translate them to English for the benefit of all. He was well versed in Bengali, English, French, German and Sanskrit. Apart from science, his interests ranged from poetry to classical music.

In 1924, Bose derived Planck's law of quantum radiation without any reference to classical physics. This was a very fundamental work in the field of quantum statistics. He sent the manuscript of this paper to Einstein, who immediately recognized the importance of his work. Einstein translated this paper in German and sent it for publication to the prestigious *Zeitschrift für Physik* journal on behalf of Bose. Subsequently, Einstein extended the work of Bose to material particles. This led to the birth of Bose-Einstein (B-E) statistics. The particles obeying this statistics are called **bosons**. This name was coined by renowned scientist Paul Dirac to commemorate the great contribution of Bose to the field of quantum statistics.

Bose was nominated National Professor by the Government of India in 1958. In the same year, he was also elected the Fellow of Royal Society.

In 2012, a new particle, popularly known as God particle and responsible for attributing mass to matter, was named Higgs Boson. It was produced in the Large Hadron Collider near Geneva, Switzerland. It is expected to answer how the universe was formed.

We are now equipped with necessary tools to theoretically understand the behavior of quantum particles. The first step in this is to obtain distribution functions for them. You will now learn to obtain expressions for Bose-Einstein distribution function.

14.3 BOSE-EINSTEIN DISTRIBUTION FUNCTION

Consider a system of N non-interacting bosons occupying volume V and sharing energy U . Suppose that the energy levels of the system are very closely spaced so that we can bracket them into groups. We will refer to these as energy cells. This is depicted schematically in Fig. 14.5.

We assume that the number of levels (g_i) in the i^{th} cell is significantly greater than one ($g_i \gg 1$). It is still reasonable to talk about the energy of the levels in the i^{th} cell as ϵ_i , since they are very close to each other. Let W_i denote the number of ways in which N_i particles can be distributed amongst the g_i levels of the i^{th} cell. This number is available to us from Eq. (14.4).

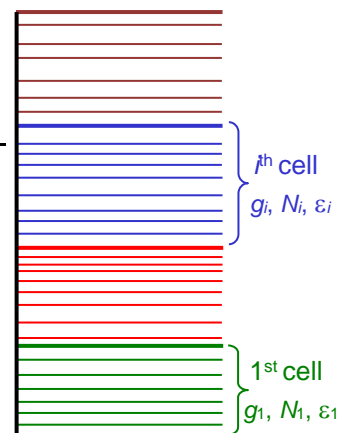


Fig. 14.5: Energy levels of a system bracketed into cells.

Note that this formalism bears close resemblance to M-B statistics but now we have to deal with identical particles. So, rules for counting the states change. In the instant case, we can write

$$W_i = (N_i + g_i - 1) C_{N_i} = \frac{(g_i + N_i - 1)!}{N_i! (g_i - 1)!} \quad (14.5)$$

Recall that the number of ways in which we can put N_1 particles in g_1 levels, N_2 particles in g_2 levels, ..., N_i particles in g_i levels defines thermodynamic probability. Let us denote it by $W(N_1, N_2, \dots, N_i, \dots) = W(\{N\})$. Then we can write

$$W[\{N\}] = \prod_i W_i = \prod_i \frac{(g_i + N_i - 1)!}{N_i! (g_i - 1)!} \quad (14.6)$$

To obtain the expression for distribution function, we have to maximise W subject to the conditions that total number of particles and total energy of the system are constant:

$$\sum_i N_i = N \quad (14.7a)$$

and

$$\sum_i N_i \varepsilon_i = U \quad (14.7b)$$

Following the arguments mentioned in Unit 13, we maximise $\ln W$ rather than W . So, we rewrite Eq. (14.6) as

$$\ln W = \sum_i [\ln(g_i + N_i - 1)! - \ln(g_i - 1)! - \ln N_i!]$$

To extract meaningful information from this expression, we use Stirling's formula and write:

$$\ln W = \sum_i [(g_i + N_i - 1) \ln(g_i + N_i - 1) - (g_i + N_i - 1) - (g_i - 1) \ln(g_i - 1) + (g_i - 1) - N_i \ln N_i + N_i]$$

Note that second term on the RHS cancels out with the fourth and sixth terms. On simplification, this expression reduces to

$$\ln W = \sum_i [(g_i + N_i - 1) \ln(g_i + N_i - 1) - (g_i - 1) \ln(g_i - 1) - N_i \ln N_i]$$

Since N_i and g_i are much greater than one, we can ignore one from all the three terms in the RHS of above expression and write

$$\ln W = \sum_i [(g_i + N_i) \ln(g_i + N_i) - g_i \ln g_i - N_i \ln N_i] \quad (14.8)$$

To maximise $\ln W$, we put $\delta(\ln W) = 0$. Note that g_i is a constant. On using this condition, Eq. (14.8) takes the form

$$\delta \ln W = \sum_i \left[(g_i + N_i) \frac{1}{(g_i + N_i)} \delta N_i + \ln(g_i + N_i) \delta N_i - N_i \frac{1}{N_i} \delta N_i - (\ln N_i) \delta N_i \right] = 0$$

Note that the first and third terms on the RHS cancel out and this equation takes a compact form:

$$\sum_i [\ln N_i - \ln(g_i + N_i)] \delta N_i = 0 \quad (14.9)$$

Recall that Eq. (14.9) is subject to the constraints that N and U are fixed. We can, therefore, rewrite Eqs. (14.7a and b) as

$$\delta N = \sum_i \delta N_i = 0 \quad (14.10a)$$

$$\text{and} \quad \delta U = \sum_i \varepsilon_i \delta N_i = 0 \quad (14.10b)$$

To incorporate the conditions embedded in Eqs. (14.10 a and b) into Eq. (14.9), we use Lagrange's method of undetermined multipliers. As before, we multiply Eqs. (14.10a and b) by α and β , respectively, and add to Eq. (14.9). This leads us to the expression

$$\sum_i [\ln N_i - \ln(g_i + N_i) + \alpha + \beta \varepsilon_i] \delta N_i = 0 \quad (14.11)$$

As in classical statistics, we use the fact that variations δN_i are arbitrary and cannot be zero. Therefore, for Eq. (14.11) to be satisfied, the coefficient of each term in this equation must vanish identically. Hence, we must have

$$\ln\left(\frac{N_i}{g_i + N_i}\right) = -\alpha - \beta \varepsilon_i \Rightarrow \frac{1}{1 + \frac{g_i}{N_i}} = \exp(-\alpha - \beta \varepsilon_i) \Rightarrow \frac{g_i}{N_i} = \exp(\alpha + \beta \varepsilon_i) - 1$$

$$\text{or} \quad \frac{N_i}{g_i} = \frac{1}{\exp(\alpha + \beta \varepsilon_i) - 1} \quad (14.12)$$

As before, we put $e^{-\alpha}$ equal to A , the degeneracy parameter. Then Eq. (14.12) can be written as

$$\frac{N_i}{g_i} = \frac{1}{A^{-1} \exp(\beta \varepsilon_i) - 1} \quad (14.13)$$

Recall that chemical potential (μ) is defined through the relation

$$A = e^{-\alpha} = e^{\beta \mu} \quad (14.14)$$

In terms of chemical potential, we can rewrite Eq. (14.12) as

$$\frac{N_i}{g_i} = f_{\text{BE}}(\varepsilon_i) = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] - 1} \quad (14.15)$$

If we treat energy as a continuous variable, the number of particles with energy ε will be given by

$$\frac{N(\varepsilon)}{g(\varepsilon)} \equiv f_{\text{BE}}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] - 1} \quad (14.16)$$

This relation is known as **Bose-Einstein distribution function**.

We now summarise the important results of this section.

Recap

BOSE-EINSTEIN DISTRIBUTION FUNCTION

- In Bose-Einstein distribution, there is no restriction on the number of particles that can occupy a given state.
- The ways in which N particles can be distributed in M cells is

$$W[N] = \prod_{i=1}^M W_i = \prod_i \frac{(g_i + N_i - 1)!}{N_i! (g_i - 1)!}$$

where i^{th} cell contains N_i particles distributed in g_i levels.

- The Bose-Einstein distribution function for the particles with energy ε is given by

$$f_{\text{BE}}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] - 1}$$

where μ denotes chemical potential.

We now proceed to obtain the Fermi-Dirac distribution function.

14.4 FERMI-DIRAC DISTRIBUTION FUNCTION

To obtain expression for Fermi-Dirac distribution function, we note that fermions obey Pauli's principle and not more than one particle (ignoring spin) can occupy the same energy level. Hence, the number of ways in which we can distribute N_i particles into g_i levels is given by ${}^{g_i}C_{N_i}$ with $N_i < g_i$. The total number of ways in which we can put N particles into various levels are

$$W[\{N\}] = \prod_i {}^{g_i}C_{N_i} = \prod_i \frac{g_i!}{(g_i - N_i)! N_i!} \quad (14.17)$$

As in the case of Bose-Einstein statistics, this distribution is also subject to the conditions that total number of particles in the system and the energy of the system remain constant. That is,

$$\delta N = \sum \delta N_i = 0 \quad (14.18a)$$

and
$$\delta U = \sum \delta N_i \varepsilon_i = 0 \quad (14.18b)$$

As before, we maximise $\ln W$ and set $\delta \ln W = 0$. So on taking logarithm of both sides of Eq. (14.17), we obtain

$$\ln W = \sum_i [\ln g_i! - \ln (g_i - N_i)! - \ln N_i!] \quad (14.19)$$

Using Stirling's approximation, we write

$$\begin{aligned} \ln W = \sum_i [g_i \ln g_i - g_i - (g_i - N_i) \ln (g_i - N_i) + (g_i - N_i) \\ - N_i \ln N_i + N_i] = \sum_i [g_i \ln g_i - (g_i - N_i) \ln (g_i - N_i) - N_i \ln N_i] \end{aligned}$$

Note that g_i are constant. Therefore, while differentiating this expression, we get

$$\delta \ln W = \sum_i \left[(N_i - g_i) \frac{1}{(g_i - N_i)} (-\delta N_i) + \delta N_i \ln(g_i - N_i) - N_i \frac{1}{N_i} \delta N_i - \ln N_i \delta N_i \right]$$

Note that the first and the third terms on the RHS of this expression cancel out. Then it simplifies to

$$\delta \ln W = \sum_i [\ln(g_i - N_i) - \ln(N_i)] \delta N_i$$

On equating $\delta \ln W$ to zero, we can write

$$\sum_i [\ln(N_i) - \ln(g_i - N_i)] \delta N_i = 0 \quad (14.20)$$

This expression is subject to the conditions specified in Eqs. (14.18a and b).

To incorporate these and obtain a general expression for most probable distribution, we use Lagrange's method of undetermined multipliers.

Therefore, we multiply Eq. (14.18a) by α , Eq. (14.18b) by β and add to Eq. (14.20). This gives

$$\sum_i [\ln(N_i) - \ln(g_i - N_i) + \alpha + \beta \varepsilon_i] \delta N_i = 0$$

Since δN_i are arbitrary and can be varied independently, we can set the coefficient of each δN_i equal to zero. This gives

$$\ln \left(\frac{N_i}{g_i - N_i} \right) = -\alpha - \beta \varepsilon_i \Rightarrow \frac{1}{\frac{g_i}{N_i} - 1} = \exp(-\alpha - \beta \varepsilon_i) \Rightarrow \frac{g_i}{N_i} = \exp(\alpha + \beta \varepsilon_i) + 1$$

or

$$\frac{N_i}{g_i} \equiv f_{FD}(\varepsilon_i) = \frac{1}{\exp[\alpha + \beta \varepsilon_i] + 1} = \frac{1}{A^{-1} \exp(\beta \varepsilon_i) + 1} = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] + 1} \quad (14.21)$$

where μ defines chemical potential with $A = e^{-\alpha} = e^{\beta \mu}$. Eq. (14.21) is the desired expression for **Fermi-Dirac distribution function**. For continuous distribution, the Fermi-Dirac distribution function $f_{FD}(\varepsilon)$ can be expressed as

$$f_{FD}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1} \quad (14.22)$$

Note that at $T = 0$ ($\beta = \infty$), the exponent in Eq. (14.22) becomes $-\infty$ for $\varepsilon < \mu$, whereas for $\varepsilon > \mu$, the exponent becomes $+\infty$. We can, therefore, rewrite it as

$$f_{FD}(\varepsilon) = \begin{cases} 1 & \text{for } \varepsilon < \mu \\ 0 & \text{for } \varepsilon > \mu \end{cases} \quad (14.23)$$

Mathematically speaking, $f_{FD}(\epsilon)$ defines a step-function. Physically, it implies that at absolute zero, all levels are occupied up to certain energy, but energy states above it, are empty. This energy is known as *Fermi energy*. We denote it as ϵ_F . This is shown in curve (i) of Fig. 14.6. Curve (ii) shows the effect of raising the temperature. The curve develops a tail, which is symmetrical about $\epsilon = \epsilon_F$. Moreover, at ϵ_F , $f_{FD}(\epsilon) = 0.5$.

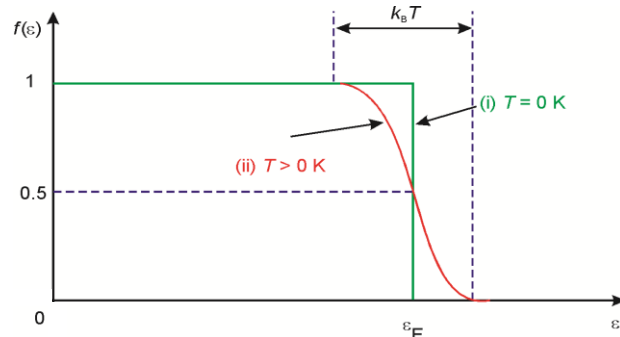


Fig. 14.6: Plot of Fermi function versus energy at different temperatures.

At a finite temperature ($T > 0$), fermions shift to higher energies. However, the width of this region is of the order of $k_B T$. Normally deviations observed from the step-function are important only for those values of ϵ for which $[\beta(\epsilon - \mu)]$ is of the order of unity. At higher energies, the exponential term dominates and the F-D distribution function is given by Eq. (14.23).

On the basis of this discussion, we can say that thermal reshuffling of the particles is confined to $k_B T$ around $\epsilon = \epsilon_F$. This means that the number of electrons which contribute to thermal properties is proportional to linear power of temperature. Even at room temperature, the product $k_B T$ is quite small; and hence, the major proportion of distribution is not influenced significantly by rise in temperature. Let us sum up important points of this section.

Recap

FERMI-DIRAC DISTRIBUTION FUNCTION

- In F-D statistics, the number of levels g_i is always greater than the number of particles N_i .
- The ways in which N particles can be distributed in M cells is

$$W[N] = \prod_{i=1}^M W_i = \prod_i \frac{g_i !}{N_i!(g_i - N_i) !}$$

where i^{th} cell contains N_i particles distributed in g_i levels.

- The Fermi-Dirac distribution function for particles with energy ϵ is:

$$f_{FD}(\epsilon) = \frac{1}{\exp[\beta(\epsilon - \mu)] + 1}$$

where μ denotes chemical potential.

- At absolute zero, F-D distribution is a step-function. At higher temperature, fermions shift to higher energy in the range of $k_B T$ around Fermi energy ϵ_F with $f_{FD}(\epsilon_F) = 0.5$.

Before proceeding further, you may like to answer an SAQ.

SAQ 2 – Limiting case of B-E and F-D distributions

Show that in the high energy range, Bose- Einstein as well as Fermi-Dirac distribution reduce to Maxwell-Boltzmann distribution.

Now that we have obtained distribution functions for classical as well as quantum systems, it would be instructive to compare these and get an idea about how particles obeying different statistics behave.

14.5 COMPARISON OF DIFFERENT DISTRIBUTIONS

To compare how different statistics behave, we re-write the expressions for M-B, B-E and F-D distribution functions:

$$f_{MB}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)]}$$

$$f_{BE}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] - 1}$$

$$f_{FD}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1}$$

A closer examination of these expressions reveals that in spite of the vast differences in the assumptions used to arrive at these expressions, they have deceptively similar appearance. In fact, you can combine them into just one expression as

$$f(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + \kappa} \quad (14.24)$$

where $\kappa = \begin{cases} 0 & \text{M - B distribution} \\ +1 & \text{F - D distribution} \\ -1 & \text{B - E distribution} \end{cases}$

This logically raises the question: What is the significance of the constant κ in describing the behaviour of a system?

To learn about the enormous consequences of κ , refer to Fig. 14.7, which depicts the distribution functions corresponding to M-B, F-D and B-E statistics.

Note that as compared to M-B distribution, the distribution of bosons is skewed towards lower energy states, whereas fermions are skewed towards higher energy states.

It means that bosons prefer to occupy lower energy states, i.e., live together.

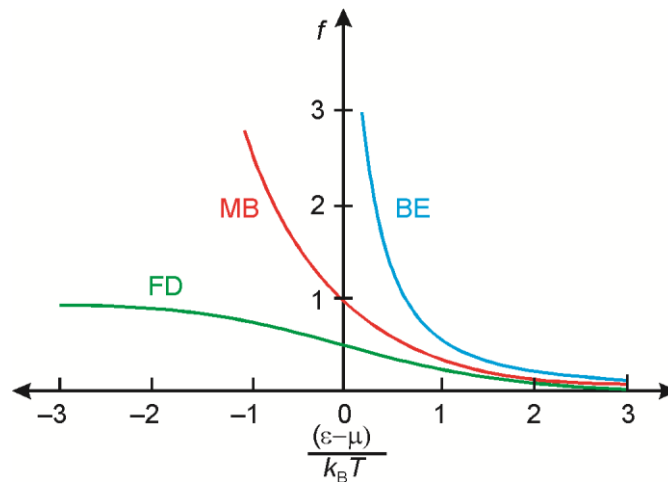


Fig. 14.7: Plot of B-E, F-D and M-B distribution functions as a function of $(\varepsilon - \mu) / k_B T$. Each system is at the same temperature and has the same number of particles.

In the next two sections, we study some applications of B-E and F-D statistics.

14.6 APPLICATIONS OF BOSE-EINSTEIN STATISTICS

You now know that the spectral distribution of blackbody radiation was first successfully explained by Planck. Though Planck was not convinced of the physical basis of his derivation, Bose derived Planck's law of radiation on the basis of quantum statistics. Einstein extended his ideas to the case of material particles obeying Bose statistics. We begin our discussion with Bose's derivation of Planck's law.

14.6.1 Bose's Derivation of Planck's Law

To begin with, we assume that electromagnetic radiation is enclosed in a cavity of volume V at temperature T . From quantum mechanical point of view, radiation in the cavity can be considered as a collection of photons of different frequencies moving randomly with speed of light. Note that photons of same frequency are indistinguishable and behave as a system of non-interacting particles.

The energy of a photon of frequency ν is taken to be $h\nu$. Moreover, photons have zero rest mass and spin \hbar . Further, atoms can emit or absorb photons and the total number of photons is not constant. It means that an assembly of photons is subject to only one constraint, namely $U = \text{constant}$. This essentially means that in Eq. (14.15), we need only one Lagrange multiplier β , i.e., $\alpha = 0$ or $A = 1$. Then Eq. (14.15) can be written as

$$\frac{N_\nu}{g_\nu} = \frac{1}{e^{\beta h\nu} - 1} \quad (14.25)$$

Let $g_\nu d\nu$ denote the number of quantum states between frequencies ν and $\nu + d\nu$. We can derive the expression for $g_\nu d\nu$ using the principles of quantum mechanics. However, we can obtain the same result using a simple

argument as well. Let us first calculate the number of quantum states in the momentum range p to $p + dp$ and denote it as $g_p dp$. The volume of phase space occupied by a particle in a box of volume V and having momentum between p and $p + dp$ is $V d^3 p$. In spherical polar coordinates, $d^3 p = (p^2 dp \sin \theta d\theta d\phi)$ and integration over θ and ϕ gives 4π . If each cell has volume h^3 , we get

$$g_p dp = \frac{4\pi p^2 dp}{h^3} V \quad (14.26a)$$

From de Broglie's relation between momentum and frequency (or

wavelength), we have $p = \frac{h}{\lambda} = \frac{h\nu}{c}$ and $p^2 dp = \left(\frac{h}{c}\right)^3 \nu^2 d\nu$.

On substituting this result in Eq. (14.26a), we can write the number of quantum states in the frequency range ν to $\nu + d\nu$ as

$$g_\nu d\nu = \frac{4\pi V}{c^3} \nu^2 d\nu \quad (14.26b)$$

Since photons can have two types of polarization, we multiply this by a factor of 2 to obtain

$$g_\nu d\nu = \frac{8\pi V}{c^3} \nu^2 d\nu \quad (14.27)$$

On using this result in Eq. (14.25), we get the expression for the number of particles in the frequency range ν to $\nu + d\nu$:

$$N_\nu = \frac{8\pi V}{c^3} \frac{\nu^2 d\nu}{e^{\beta h\nu} - 1} \quad (14.28)$$

If $E_\nu d\nu$ denotes the energy corresponding to the frequency range ν to $\nu + d\nu$, we can write

$$E_\nu d\nu = N_\nu h\nu = \frac{8\pi h V}{c^3} \frac{\nu^3 d\nu}{e^{\beta h\nu} - 1}$$

Note that $E_\nu d\nu$ is a function of volume and therefore depends on the size of the cavity.

So, instead of total energy corresponding to a particular range of frequencies, we prefer energy density. If we represent energy density by $u_\nu d\nu$, we can write

$$u_\nu d\nu = \frac{E_\nu d\nu}{V} = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{\exp(h\nu / k_B T) - 1} \quad (14.29)$$

Do you recognise this equation? It is identical to Eq. (14.2) and is a mathematical statement of Planck's law. Note that Bose treated electromagnetic radiation as a system of indistinguishable particles and used methods of statistics to understand their behaviour.

Before proceeding further, let us recapitulate the important result obtained in this section.

Recap

QUANTUM MECHANICAL DERIVATION OF PLANCK'S LAW

By treating electromagnetic radiation as a system of indistinguishable particles, Bose derived the expression for the energy density as

$$u_\nu d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{\exp(h\nu / k_B T) - 1}$$

14.7 APPLICATIONS OF FERMI-DIRAC STATISTICS

The energy of an F-D system at absolute zero is called **Fermi energy**. As such, it signifies the highest energy level occupied by a fermion at absolute zero. You will now learn how to obtain an expression for Fermi energy.

14.7.1 Fermi Energy

Consider a system of N fermions enclosed in a volume V . According to Pauli's exclusion principle, only one fermion can be accommodated in a given state. You have already learnt that the highest energy possessed by a fermion at absolute zero is known as **Fermi energy**. We will denote it by the symbol ε_F .

To derive an expression for ε_F , we must first know the density of quantum states of a particle with momentum in the interval \vec{p} and $\vec{p} + d\vec{p}$. From Eq. (14.26a), we recall that this number is $\frac{4\pi V}{h^3} p^2 dp$. Since an electron has two independent spin states, the multiplicity factor ($= 2s + 1$) will be equal to 2, since $s = 1/2$. So the required density of quantum states is $\frac{8\pi V}{h^3} p^2 dp$.

Hence, the total number of particles is given by

$$N = \frac{8\pi V}{h^3} \int_0^\infty f_{FD} p^2 dp \quad (14.30)$$

From Eq. (14.23) we recall that

$$f_{FD}(\varepsilon) = \begin{cases} 1 & \text{for } \varepsilon < \mu \\ 0 & \text{for } \varepsilon > \mu \end{cases}$$

We denote the highest momentum at $T = 0$ corresponding to $\varepsilon = \mu$ by p_F .

Then, the upper limit of integration in the integral in Eq. (14.30) changes from ∞ to p_F and we can write

$$N = \frac{8\pi V}{h^3} \int_0^{p_F} p^2 dp \quad (14.31a)$$

$$= \frac{8\pi V}{h^3} \frac{p_F^3}{3} \quad (14.31b)$$

We invert this relation to obtain the expression for **Fermi momentum**, p_F :

$$p_F = \left(\frac{3N}{8\pi V} \right)^{1/3} h \quad (14.32)$$

This result implies that if we draw a sphere with radius p_F , all the particles will be inside the sphere at absolute zero.

This defines the *Fermi surface*. In the case of alkali and noble atoms, the surface is spherical in shape. In other cases, the shape can be quite complicated.

The energy corresponding to the highest occupied energy level at absolute zero is called **Fermi energy**. It is given by

$$\varepsilon_F = \frac{p_F^2}{2m} = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \quad (14.33)$$

Now we define *Fermi temperature*, T_F , through the relation

$$T_F = \frac{\varepsilon_F}{k_B} \quad (14.34)$$

In Table 14.1, we have listed values of Fermi energy as well as Fermi temperature for some typical metals.

Note that ε_F varies from 1.58 eV to 14.3 eV; being minimum for cesium and maximum for beryllium.

The corresponding Fermi temperatures are of the order $10^4\text{K} - 10^5\text{K}$.

Table 14.1: Values of Fermi energy and Fermi temperature for typical metals

Metal	Fermi energy (eV)	Fermi Temperature $\times 10^4$ (K)
Cesium	1.58	1.84
Sodium	3.24	3.77
Calcium	4.69	5.44
Lithium	4.74	5.51
Silver	5.49	6.38
Gold	5.53	6.42
Copper	7.00	8.16
Iron	11.1	13.0
Aluminium	11.7	13.6
Beryllium	14.3	16.6

You should now go through the following example carefully.

EXAMPLE 14.1: FERMI ENERGY

- a) 4.2×10^{21} electrons are confined in a box of volume 1 cm^3 . Calculate their Fermi wavelength and Fermi energy.
- b) The electrons in the box are replaced by neutrons. How will Fermi wavelength and Fermi energy change? Take $m_e = 9.1 \times 10^{-28} \text{ g}$, $m_n = 1.67 \times 10^{-24} \text{ g}$ and $h = 6.62 \times 10^{-27} \text{ erg s}$.

SOLUTION ■ a) From Eq. (14.33), we know that Fermi energy of electrons is given by:

$$\varepsilon_F = \frac{p_F^2}{2m} = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \Rightarrow p_F^2 = \frac{h^2}{4} \left(\frac{3N}{\pi V} \right)^{2/3}$$

On raising the power of both sides by $3/2$, we can write:

$$p_F^3 = \frac{h^3}{8} \left(\frac{3N}{\pi V} \right)$$

Now, Fermi wavelength can be expressed as:

$$\lambda_F = \frac{h}{p_F} = \left(\frac{8\pi V}{3N} \right)^{1/3}$$

Note that Fermi wavelength is independent of mass of the fermions.

On substituting the given values, we get

$$\lambda_F = \left(\frac{8 \times 3.1417 \times 1 \text{ cm}^3}{3 \times 4.2 \times 10^{21}} \right)^{1/3} = (1.995 \times 10^{-21})^{1/3} \text{ cm} = 1.26 \times 10^{-7} \text{ cm}$$

The Fermi energy of electrons can be expressed in terms of Fermi wavelength as

$$\begin{aligned} \varepsilon_F &= \frac{p_F^2}{2m} = \frac{1}{2m} \left(\frac{h}{\lambda_F} \right)^2 = \frac{1}{(2 \times 9.1 \times 10^{-28} \text{ g})} \left(\frac{6.62 \times 10^{-27} \text{ erg s}}{1.26 \times 10^{-7} \text{ cm}} \right)^2 \\ &= 1.52 \times 10^{-12} \text{ erg} \end{aligned}$$

- b) Since Fermi wavelength is independent of mass of the particles making up the system, it is not affected when electrons are replaced by neutrons. However, Fermi energy will be equal to

$$\begin{aligned} \left(\frac{m_e}{m_n} \right) \varepsilon_F &= (\varepsilon_F)_{\text{neutron}} = \left(\frac{9.1 \times 10^{-28} \text{ g}}{1.67 \times 10^{-24} \text{ g}} \right) \times 1.52 \times 10^{-12} \text{ erg} \\ &= 8.28 \times 10^{-16} \text{ erg} = 5.18 \times 10^{-4} \text{ eV} \end{aligned}$$

SAQ 3 – Fermi energy

Calculate ε_F for copper, if $\frac{N}{V} = 8.53 \times 10^{22}$ electrons cm^{-3} . Take the mass of electron = 9.1×10^{-28} g and $h = 6.62 \times 10^{-27}$ erg s.

Zero Point Energy

When a fermion system is in the ground state, all the energy states below the Fermi energy are occupied whereas all the states above Fermi energy are empty. In such a case, the **zero point energy** of a fermion system is obtained by using the relation

$$E_0 = N\varepsilon = N \left(\frac{p^2}{2m} \right)$$

On substituting for N from Eq. (14.31a) and integrating the resultant expression in the range 0 to p_F in the momentum space, we get

$$\begin{aligned} E_0 &= \frac{8\pi V}{h^3} \int_0^{p_F} \frac{p^2}{2m} p^2 dp = \frac{8\pi V}{h^3} \frac{p_F^5}{10m} \\ &= \frac{8\pi V}{5h^3} p_F^3 \varepsilon_F \end{aligned}$$

On combining this result with Eq. (14.31b), we obtain the expression for zero point energy of a fermion system:

$$E_0 = \frac{3}{5} N\varepsilon_F \quad (14.35)$$

The mean energy per fermion at absolute zero is given by

$$\bar{\varepsilon} = \frac{E_0}{N} = \frac{3}{5} \varepsilon_F \quad (14.36)$$

For conduction electrons in copper

$$\bar{\varepsilon} = \frac{3}{5} \times (7.0 \text{ eV}) = 4.2 \text{ eV}$$

This energy corresponds to several thousand kelvin to which an electron, if treated classically, would have to be raised. This shows that unlike a classical particle, a fermion has appreciable energy even at absolute zero!

This justifies our statement that a fermion system is quite alive even at absolute zero.

This is a quantum effect arising out of the Pauli's exclusion principle and brings out the inadequacy of classical statistics in describing the behaviour of electrons at temperatures far below their Fermi temperature ($T \ll T_F$).

Now you may ask: Is it true for pressure also? To learn the answer to this question, you should solve the following SAQ.

SAQ 4 – Pressure exerted by a fermion system

The pressure exerted by a fermion system at absolute zero is equal to $\frac{2}{5} \left(\frac{N}{V} \right) \varepsilon_F$. Using the data obtained in SAQ 3, calculate the pressure exerted by the electrons in a copper wire.

On working out SAQ 4, you will realise that the pressure exerted by electrons in a copper wire comes out to be huge; of the order of 10^5 atm. Do we feel such an enormous pressure when we hold a copper wire in our hand? If not, why? It is because this pressure is counter-balanced by Coulomb attraction of electrons by ions.

Before proceeding further, let us recapitulate what we have learnt in this section.

Recap

FERMI ENERGY

- The maximum energy possessed by fermions at absolute zero is known as Fermi energy. It is given by

$$\varepsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

- Typical values of Fermi energy of metals range from 2 to 15 eV. The corresponding Fermi temperatures are about 10^4 to 10^5 K.
- Electron gas in a metal exerts extremely high pressure ($\sim 10^5$ atm), which is balanced by the Coulomb forces within the material.

We have so far considered an F-D system at absolute zero. Such a system is said to be completely degenerate. You may like to know how thermodynamic properties such as heat capacity and entropy of a F-D system vary with temperature. For simplicity, we confine our discussion to the behaviour of electrons. You will recall that for $T \ll T_F$, f_D does not differ much from the value at $T = 0$ K. Now, for conduction electrons in metals, T_F is of the order of 10^4 to 10^5 K. This means that conduction electrons are in extremely degenerate state even under normal conditions and very few of them are free to move. As such, most of the electrons in a metal are tightly bound in low lying states and do not contribute to conduction.

We will refrain from discussing the behaviour of electrons in metals in detail. However, very simple arguments can be used to understand the heat capacity of metals. You will learn it now.

14.7.2 Electronic Heat Capacity

In Sec 14.2, you have learnt that in the classical regime, the correct explanation of temperature variation of heat capacity of metals, particularly at low values, puzzled physicists for quite some time. The underlying reason is

that electrons are fermions and obey F-D statistics. The electronic heat capacity varies linearly at low temperatures. In fact, heat capacity of a metal is a sum of two parts: (i) an electronic contribution, which is proportional to T and dominates at low temperatures and (ii) the lattice contribution, which is proportional to T^3 and dominates at room temperature and above:

$$C_V = aT + bT^3 \quad (14.37)$$

Experiments show that the contribution of electronic heat capacity is about 1% of the total.

Let us now summarise what you have learnt in this unit.

14.8 SUMMARY

Concept

Description

Bose-Einstein distribution function

- The **Bose-Einstein distribution** function is given by

$$\frac{N_i}{g_i} = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] - 1}$$

For continuous distribution, we can write

$$f_{BE} = \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{\exp[\beta(\varepsilon - \mu)] - 1}$$

Fermi-Dirac distribution function

- The **Fermi-Dirac distribution** function is given by

$$\frac{N_i}{g_i} = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] + 1}$$

For continuous distribution, we can write

$$f_{FD}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1}$$

Spectral energy density as per Planck's law for blackbody radiation

- According to **Planck's law** of blackbody radiation, the spectral energy density is given by

$$u_\nu d\nu = \left(\frac{8\pi h}{c^3}\right) \frac{\nu^3}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} d\nu$$

Fermi energy

- The **Fermi energy** of a fermion is given by:

$$\varepsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V}\right)^{2/3}$$

Pressure exerted by F-D gas at $T = 0$ K

- The pressure exerted by F-D gas at $T = 0$ K is:

$$p_F = \frac{2}{5} \left(\frac{N}{V}\right) \varepsilon_F$$

Electronic heat capacity

- The electronic contribution to the heat capacity of a metal is given by

$$C_V = aT + bT^3$$

14.9 TERMINAL QUESTIONS

1. Explain on the basis of statistical mechanics the reason for different properties observed in case of liquid ^3He and liquid ^4He .
2. Estimate the deviation in the value of heat capacity C_V from the value predicted by the Dulong-Petit's law for a metallic sample kept at its Einstein temperature.
3. Three particles are to be distributed in 4 states. Calculate the number of ways this distribution can be done if the particles obey (i) M-B, (ii) B-E and (iii) F-D statistics.
4. Calculate the Fermi energy and Fermi temperature for:
 - i) liquid ^3He assuming that each atom occupies 63 \AA^3 volume and mass of ^3He is equivalent to mass of 3 protons; and
 - ii) electrons in a white dwarf star consisting of completely ionized He atoms with density $\rho = 10^7 \text{ g cm}^{-3}$ and number density 10^{30} electrons per cm^3 .
5. The number density of gold atoms is $5.9 \times 10^{28} \text{ atoms m}^{-3}$. Each atom contributes one free electron for conduction. Examine, whether the electron gas is strongly degenerate at room temperature.

14.10 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. A particle consisting of an odd number of Fermi particles is a fermion and a particle consisting of an even number of Fermi particles is a boson. ^3He consists of two protons, one neutron, and two electrons. Hence, it consists of five particles of spin $\frac{1}{2}$, and is a fermion. ^4He consists of two protons, two neutrons and two electrons. Hence, it consists of six fermions and is a boson.
2. In the high energy region, we can write $\epsilon \gg \mu$, so that $\beta(\epsilon - \mu) \gg 1$ and then we can ignore unity in comparison to the exponential function in [Eqs. (14.16) and (14.22)]. Then Bose-Einstein as well as Fermi-Dirac distribution functions reduce to Maxwell-Boltzmann distribution function.
3. We have

$$\epsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

On substituting the given values in the expression of ϵ_F , we get

$$\varepsilon_F = \frac{(6.62 \times 10^{-27} \text{ erg s})^2}{2 \times 9.1 \times 10^{-28} \text{ g}} \left(\frac{3}{8\pi} \times 8.53 \times 10^{22} \text{ cm}^{-3} \right)^{2/3} = 11.31 \times 10^{-12} \text{ erg}$$

By using the relation $1 \text{ erg} = 6.24 \times 10^{11} \text{ eV}$, we can express the Fermi energy in the units of electron volts as 7.1 eV.

4. From SAQ 3, we know that for copper, $\frac{N}{V} = 8.53 \times 10^{28} \text{ electrons m}^{-3}$ and $\varepsilon_F = 11.31 \times 10^{-19} \text{ J}$. Substituting these values in the given expression, we get pressure = $\frac{2}{5} \left(\frac{N}{V} \right) \varepsilon_F = 3.86 \times 10^{10} \text{ N m}^{-2} = 3.86 \times 10^5 \text{ atm}$.

Terminal Questions

1. ^3He and ^4He , the two stable isotopes of helium, have markedly different behaviour at low temperatures. The ^4He atom (comprising of two protons, two neutrons and two electrons) has integral spin and is governed by Bose-Einstein statistics. At about 2.18 K and $p \sim 1 \text{ atm}$, it undergoes λ -transition, which was explained by F. London as Bose-Einstein condensation. Above the λ -transition temperature, it behaves like a regular, "normal" fluid. However, below the λ -transition temperature, helium behaves as a super-fluid characterized by zero viscosity.
2. For $T = \theta_E$, Eq. (14.3b) implies that

$$\begin{aligned} C_V &= 3R \left(\frac{\theta_E}{\theta_E} \right)^2 \frac{\exp(\theta_E / \theta_E)}{[\exp(\theta_E / \theta_E) - 1]^2} \\ &= 3R \frac{e}{(e-1)^2} = 3R \frac{2.718}{(2.718-1)^2} = 3R(0.92) \end{aligned}$$

Hence, the deviation from the value predicted by Dulong-Petit's law is $\Delta C_V = 3R(1 - 0.92) = 0.24R$

3. i) For M-B statistics, the particles are distinguishable. Hence, the number of ways are $4^3 = 64$.
- ii) For B-E statistics, the particles are indistinguishable and any number of them can occupy the same state.

Hence, the number of ways they can be distributed are:

$${}^{3+4-1}C_3 = \frac{6!}{3!3!} = 20$$

- iii) For F-D statistics, the particles are indistinguishable and maximum only one particle can occupy any state. The number of ways are:

$${}^4C_3 = \frac{4!}{3!1!} = 4$$

4. We have

$$\varepsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

$$\text{and } T_F = \frac{\varepsilon_F}{k_B} = \frac{h^2}{2m k_B} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

i) For liquid ${}^3\text{He}$, $\frac{V}{N} = 63 \text{ \AA}^3 \text{ atom}^{-1} = 63 \times 10^{-24} \text{ cm}^3 \text{ atom}^{-1}$

$$\therefore \frac{N}{V} = \frac{10^{24}}{63} = 1.59 \times 10^{22} \text{ atom cm}^{-3}$$

$$m = 3 \times \text{mass of proton} = 3 \times 1.67 \times 10^{-24} \text{ g} = 5.01 \times 10^{-24} \text{ g}$$

$$\therefore \varepsilon_F = \frac{(6.62 \times 10^{-27} \text{ erg s})^2}{2 \times 5.01 \times 10^{-24} \text{ g}} \left(\frac{3}{8\pi} \times 15.9 \times 10^{21} \text{ cm}^{-3} \right)^{2/3}$$

$$= 6.71 \times 10^{-16} \text{ erg}$$

$$= 6.71 \times 10^{-16} \times 6.24 \times 10^{11} \text{ eV} = 0.42 \text{ meV}$$

$$\text{This yields, } T_F = \frac{\varepsilon_F}{k_B} = \frac{6.71 \times 10^{-16} \text{ erg}}{1.38 \times 10^{-16} \text{ erg K}^{-1}} = 4.9 \text{ K}$$

ii) For white dwarfs $\rho = 10^7 \text{ g cm}^{-3}$ and $\frac{N}{V} = 10^{30} \text{ cm}^{-3}$

$$\therefore \varepsilon_F = \frac{(6.63 \times 10^{-27} \text{ erg s})^2}{2 \times 9.1 \times 10^{-28} \text{ g}} \left(\frac{3}{8\pi} \times 10^{30} \text{ cm}^{-3} \right)^{2/3}$$

$$= 5.84 \times 10^{-7} \text{ erg} = \frac{5.84 \times 10^{-7} \text{ erg}}{1.6 \times 10^{-12} \text{ erg eV}^{-1}} = 0.36 \text{ MeV}$$

$$\text{and Fermi temperature} = \frac{5.85 \times 10^{-7} \text{ erg}}{1.38 \times 10^{-16} \text{ erg K}^{-1}} = 4.23 \times 10^9 \text{ K}$$

5. To obtain the Fermi temperature, we first calculate the Fermi energy of gold.

$$\varepsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

Substituting the values of the various terms,

$$\varepsilon_F = \frac{(6.62 \times 10^{-34} \text{ J s})^2}{2 \times 9.1 \times 10^{-31} \text{ kg}} \left(\frac{3}{8\pi} \times 5.9 \times 10^{26} \text{ m}^{-3} \right)^{2/3}$$

$$= 8.85 \times 10^{-19} \text{ J} (= 5.53 \text{ eV})$$

Now, the Fermi temperature is related to Fermi energy with the relation

$$T_F = \frac{\varepsilon_F}{k_B}$$

$$= \frac{8.85 \times 10^{-19} \text{ J}}{1.38 \times 10^{-23} \text{ JK}^{-1}} = 6.41 \times 10^4 \text{ K}$$

Since the Fermi temperature for gold is far greater than the room temperature, the electron gas in the gold sample is strongly degenerate.

FURTHER READINGS

1. **Thermal Physics: Kinetic Theory, Thermodynamics and Statistical Mechanics** by Garg, S.C., Bansal, R.M. and Ghosh, C.K., McGraw Hill Education (India) Pvt. Ltd., 2nd Edition, Seventh Reprint (2018).
2. **A Treatise on Heat** by Saha, M.N. and Srivastava, B.N., The Indian Press, 5th Edition (1969).



TABLE OF PHYSICAL CONSTANTS

Symbol	Quantity	Value
c	Speed of light in vacuum	$3.00 \times 10^8 \text{ ms}^{-1}$
μ_0	Permeability of free space	$1.26 \times 10^{-6} \text{ NA}^{-2}$
ϵ_0	Permittivity of free space	$8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
$1/4\pi\epsilon_0$		$8.99 \times 10^9 \text{ Nm}^2 \text{ C}^{-2}$
e	Charge of the proton	$1.60 \times 10^{-19} \text{ C}$
$-e$	Charge of the electron	$-1.60 \times 10^{-19} \text{ C}$
h	Planck's constant	$6.63 \times 10^{-34} \text{ Js}$
\hbar	$h / 2\pi$	$1.05 \times 10^{-34} \text{ Js}$
m_e	Electron rest mass	$9.11 \times 10^{-31} \text{ kg}$
$-e / m_e$	Electron charge to mass ratio	$-1.76 \times 10^{11} \text{ Ckg}^{-1}$
m_p	Proton rest mass	$1.67 \times 10^{-27} \text{ kg (1 amu)}$
m_n	Neutron rest mass	$1.68 \times 10^{-27} \text{ kg}$
a_0	Bohr radius	$5.29 \times 10^{-11} \text{ m}$
N_A	Avogadro constant	$6.02 \times 10^{23} \text{ mol}^{-1}$
R	Universal gas constant	$8.31 \text{ Jmol}^{-1} \text{ K}^{-1}$
k_B	Boltzmann constant	$1.38 \times 10^{-23} \text{ J K}^{-1}$
G	Universal gravitational constant	$6.67 \times 10^{-11} \text{ Nm}^2 \text{ kg}^{-2}$

LIST OF BLOCKS AND UNITS: BPHCT-135

BLOCK 1: KINETIC THEORY OF GASES

- Unit 1 Ideal and Real Gases
- Unit 2 Molecular Velocity Distribution Function
- Unit 3 Mean Free Path and Transport Phenomena
- Unit 4 Brownian Motion

BLOCK 2: THE ZEROth AND THE FIRST LAWS OF THERMODYNAMICS

- Unit 5 Thermodynamic Description of a System
- Unit 6 The Zeroth Law
- Unit 7 The First Law and its Applications

BLOCK 3: SECOND AND THIRD LAWS OF THERMODYNAMICS

- Unit 8 Carnot Cycle
- Unit 9 Entropy and the Laws of Thermodynamics
- Unit 10 The Thermodynamic Potentials
- Unit 11 Theory of Radiation

BLOCK 4: STATISTICAL MECHANICS

- Unit 12 Basic Concepts of Statistical Mechanics
- Unit 13 Classical Statistics
- Unit 14 Quantum Statistics

SYLLABUS: THERMAL PHYSICS AND STATISTICAL MECHANICS (BPHCT-135)

4 Credits

Kinetic Theory of Gases: Expression for pressure (no derivation), kinetic interpretation of temperature and derivation of gas laws, real gases (van der Waals equation, qualitative discussion). Derivation of Maxwell's law of distribution of velocities and its experimental verification, expression for average speed (\bar{v}), most probable speed (v_p), and root mean square (v_{rms}), law of equipartition of energy (no derivation) and its applications to specific heat of gases, monoatomic and diatomic gases. Mean free path (zeroth order). Transport phenomena, viscosity, conduction and diffusion (discussion of physical implications only, no derivation). Brownian motion (no derivation) and its significance, sedimentation, Perrin's experiment.

The Zeroth Law and The First Law of Thermodynamics: Boundaries, variables, processes (reversible and irreversible), graphical description. Statement of zeroth law, introduction of concept of temperature, applications of the zeroth law. Compressibility and expansion coefficient. First law of thermodynamics, statement, parametric form, mathematical form (integral and differential), relation between c_p and c_v , work done during isothermal and adiabatic processes, velocity of sound.

The Second and Third Law of Thermodynamics: Heat engines, conversion of heat into work, Carnot cycle, efficiency of a Carnot engine, Carnot theorem, Kelvin-Planck and Clausius statements of second law of thermodynamics, equivalence of Kelvin-Planck and Clausius statements. Entropy, second law and entropy, entropy changes in reversible and irreversible processes, entropy-temperature diagram, statement and consequences of the third law of thermodynamics (unattainability of absolute zero temperature, etc.). Thermodynamic potentials, enthalpy, Gibbs, Helmholtz and internal energy functions, Maxwell's relations and their applications, Clausius-Clapeyron equation, Joule Thomson effect, TdS equations. Black body radiation, spectral distribution, concept of energy density, derivation of Planck's law, deduction of laws of radiation (Wien's distribution law, Rayleigh-Jeans law, Stefan Boltzmann law and Wien's displacement law).

Statistical Mechanics: Phase space, macrostate and microstate, entropy and thermodynamics probability, distribution function. Maxwell-Boltzmann law, partition function of a monoatomic gas and deduction of thermodynamic functions. Need for quantum statistics, Bose-Einstein distribution function, Bose-Einstein photon gas, Fermi-Dirac distribution function, strongly degenerate Fermi system, Fermi energy, electronic heat capacity, comparison of the three statistics.