

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

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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

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

$$= \sum_{r=0}^n {}^n C_r x^{n-r} y^r \tag{12.1}$$

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

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

Table 12.1: Outcomes of throw of two dice

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)

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.

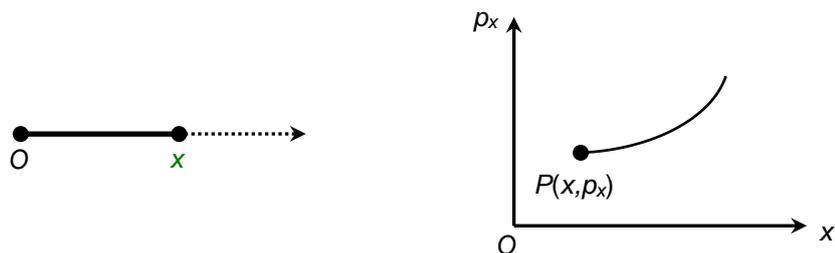


Fig. 12.1: a) Motion of a particle along a straight line; b) phase space for one-dimensional motion.

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):

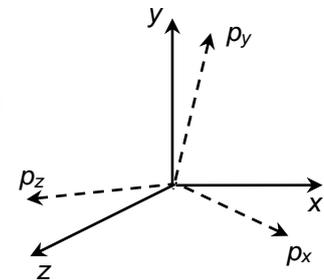


Fig. 12.2: Symbolic representation of μ -space.

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.

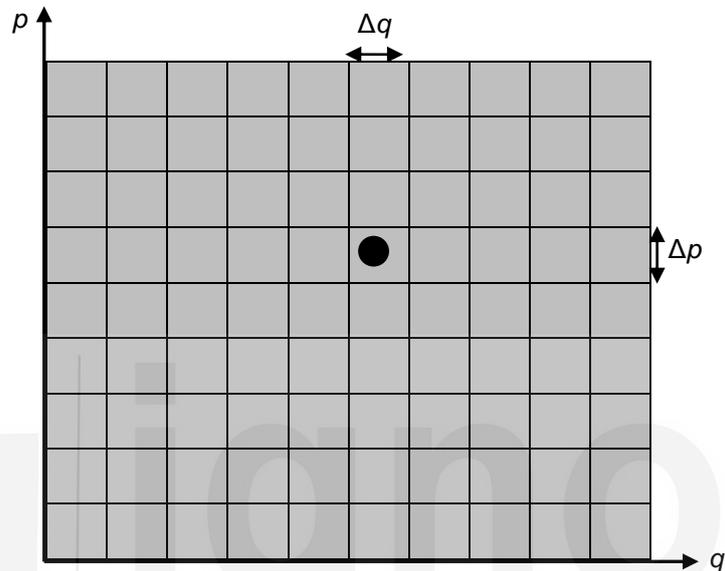


Fig. 12.3: Two-dimensional phase space divided into cells of ‘volume’ $\Delta q \Delta p$. • is the phase point representing a particle

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.

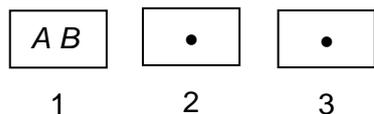
EXAMPLE 12.5: MACROSTATES AND MICROSTATES

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:

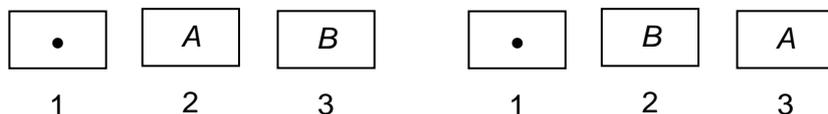
cells	(i)	(ii)	(iii)	(iv)	(v)	(vi)
1	AB	0	0	0	A	A
2	0	AB	0	A	0	B
3	0	0	AB	B	B	0

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 $f(v) = Av^2e^{-v^2}$

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

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

$$\langle v \rangle = \int_0^\infty Av^3e^{-v^2} dv$$
 (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, $\langle v \rangle = A$.

The gamma function is defined as follows:

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

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 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,

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

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 $E = \frac{1}{2} m \omega^2 A^2$.

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

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

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

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.

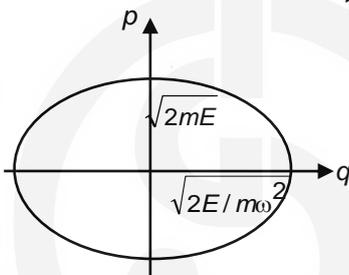


Fig. 12.4: Phase space of a linear harmonic oscillator.

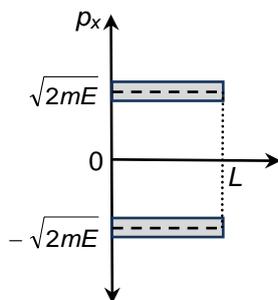


Fig. 12.5: Phase space of a particle moving in x direction.