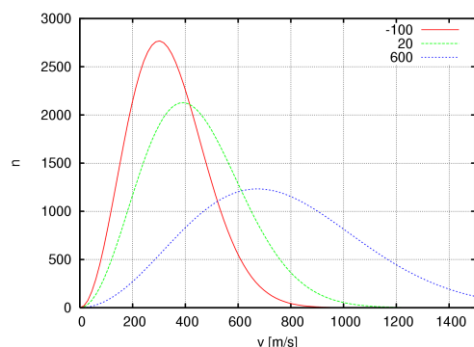


UNIT 13

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.

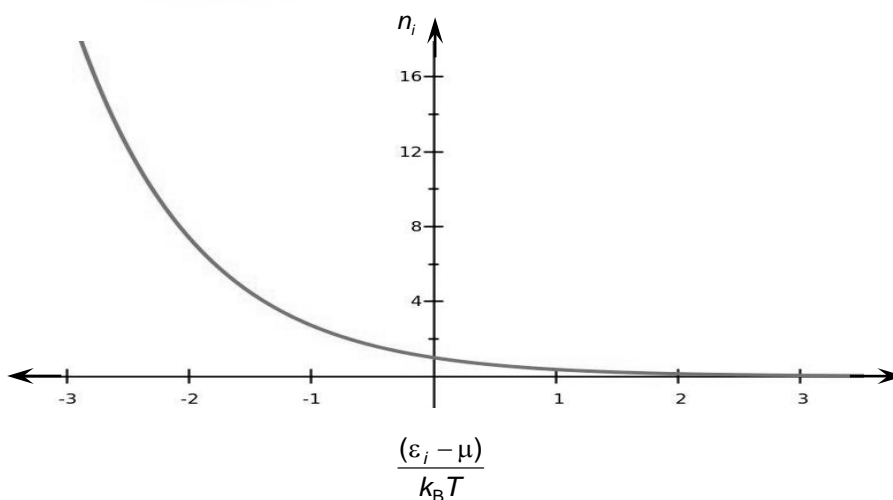


Fig. 13.1: Plot of Maxwell-Boltzmann distribution function as a function of $(\varepsilon_i - \mu) / k_B T$.

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:

$$H = U + pV$$

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

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

we can express the internal energy as

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

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 .