In stars, the gas molecules undergo intermolecular-collisions and move with all possible speeds. The estimate of these speeds gives us an idea about the nature of molecular distribution as you will learn in this unit. (Picture source: https://pixabay.com/photos/astronomy-bright-constellation-dark-1867616/)

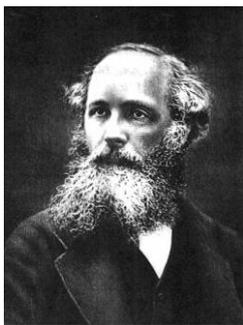# MOLECULAR VELOCITY DISTRIBUTION FUNCTION

Structure

STUDY GUIDE

In the preceding unit, you have learnt kinetic interpretation of temperature, gas laws and van der Waals' equation formulated to explain the behaviour of real gases. In this unit, you will learn to derive Maxwell distribution law for velocities as well as speeds. To follow the mathematical treatment, you should have basic knowledge of probability theory, know how to obtain derivative of a function and evaluate the integral of a function. Moreover, you will have to deal with special functions. However, do not worry. We have included all that you will need in this unit. You should therefore refresh your knowledge of 10+2 mathematics. In order to enhance your understanding of various concepts, you should work out numerical problems and answer questions in SAQs and TQs, which test your analytical abilities and conceptual clarity. This unit may take you a little more time as compared to Unit 1.

"Anyone who thinks the sky is the limit, has limited imagination."

James Clerk Maxwell

2.1 INTRODUCTION

In Unit 1, you have learnt that elementary kinetic theory supports the view that molecules of a gas move randomly in all directions. You may recall that we defined the root mean square speed of all gas molecules, even though there is spread of speeds. In fact, based on Eq. (1.4), Clausius deduced the values of root mean square speeds of nitrogen and oxygen molecules as $493 \, \text{ms}^{-1}$ and $461 \, \text{ms}^{-1}$, respectively. The critics of kinetic theory argued that in a room having dimensions of $3 \text{m} \times 3 \text{m}$, pungent odour should permeate in a fraction of second (0.006 s). But it is well known that invariably it takes up to a minute or so. To explain this discrepancy, Clausius argued that in actual practice, gas molecules have finite size and therefore undergo inter-molecular collisions as they move. (It means that strictly speaking, the assumption made in Unit 1 to depict gas molecule as a point mass is not valid.) As a result, the molecules move in a zig-zag path as they diffuse from one part of a volume to another rather than move in straight lines. He therefore introduced the concept of *mean free path*. (You will learn about it in the next unit.) However, he could not visualise how the molecular velocities were spread.

In his characteristically novel and profound work published in 1860, Maxwell provided the correct answer for the distribution of molecular velocities and introduced statistical concepts in kinetic theory of gases. His theory marked the beginning of a new era in physics; it formed the basis of modern theory of statistical mechanics and led to statistical interpretation of the laws of thermodynamics. Using the theory of probability, Boltzmann put Maxwellian theory on firm mathematical foundations. For this reason, distribution function for molecular velocities is also referred to as **Maxwell-Boltzmann distribution** function. In Sec 2.2, you will learn about Maxwell-Boltzmann distribution function for molecular velocities as well as speeds. This helps us to estimate the number of molecules having velocities/speeds in a particular range.

In Sec. 2.3, you will use Maxwell distribution function for speeds to obtain expressions for average speed, most probable speed and root mean square speed. In science, no theory is accepted till such time that it is directly verified. The first direct proof of Maxwell's law was given by Stern in 1920. His technique was subsequently modified by Zartman and Ko. A detailed discussion of these experiments, with necessary theory will take us too far. However, we outline the experimental procedure in Sec 2.4. For other more elegant methods conducted in the second half-of the 20th century, you may like to refer to Further Readings.

An important result associated with Maxwellian distribution leads us to the law of equipartition of energy. In Sec. 2.5, you will learn about it and its applications to explain temperature dependence of heat capacities of gases.

James Clerk Maxwell (1831-1879) was a celebrated Scottish theoretical physicist and mathematician. Before working on kinetic theory of gases, he had proposed the well-known Maxwell's equations for e. m. fields and brought the entire science of optics under the umbrella of electromagnetism – a classic example of unification of knowledge. This amazing and exciting work brought crowning glory to Maxwell. His work opened flood gates for new research and development in telecommunication.

He is also credited with the creation of the first true colour photograph.

Expected Learning Outcomes

After studying this unit, you should be able to:

❖ derive expression for Maxwell's distribution function for molecular velocities and speeds;

❖ obtain expressions for average speed, most probable speed and root mean square speed using Maxwell's distribution function;

❖ describe direct experimental verification of Maxwell's distribution law;

❖ discuss law of equipartition of energy; and

❖ apply law of equipartition of energy for thermal heat capacities of gases.

2.2 MAXWELL'S DISTRIBUTION LAW

The molecules in a gas are known to be in a state of constant random motion. As a result, these molecules collide against each other as well as against the walls of the container. This results in a continuous change both in magnitude and direction of their velocities. It implies that in a real system, even if all the molecules have the same velocity at a given time, we should expect that molecular collisions will result in a wide distribution of molecular velocities at some later time. You may therefore logically ask: What is the distribution of molecular velocities and how to determine the number of molecules having velocities in a certain range? The answer to this question was first provided by Maxwell.

To derive the expression for distribution function of velocities, Maxwell modified some assumptions of kinetic theory made by Clausius and made a few additional assumptions. We now state these.

2.2.1   Assumptions

1. **The gas molecules move with all possible velocities from zero to infinity**. As such, at STP no molecule can move with infinite or zero velocity. But this assumption helped to simplify mathematical steps without affecting the physics of the system.

2. **There is no mass motion or convection current in the body of the gas**. As long as there is no net force (or pressure gradient) acting on the system, this assumption is quite justified.

3. **The probability that the *x*-velocity component of a molecule, say after a large number of collisions is independent of other two components (in the *y* and *z*-directions)**. This assumption follows from random motion of gas molecules.

4. **The probability that a molecule selected at random has velocity component in the given range is a function purely of the magnitude of velocity component and the width of the interval**.

5. **The gas molecules have no vibrational or rotational energies**. This assumption is quite justified at STP because vibrational and rotational energies remain unchanged when gas molecules undergo collisions.

You will now learn how to derive the expression for Maxwell distribution function for velocities.

2.2.2 Velocity Distribution Function

Suppose that a gas made up of a total of N randomly moving molecules is enclosed in a vessel of an arbitrary shape, as shown in Fig. 2.1a. To each molecule, we attach a vector, which represents its velocity in magnitude and direction. We then transfer these vectors (not the molecules) to a common origin (Fig. 2.1b). To do so, we use the property that *a vector remains unchanged when it is translated parallel to itself*. We represent these molecules on a velocity diagram, as shown in Fig. 2.1c. Here $d\vec{\mathbf{v}}$ is an infinitesimal volume element.
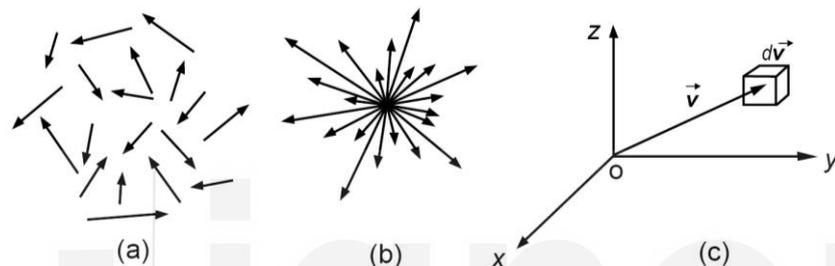
Fig. 2.1: **a) Gas molecules in random motion; b) all velocity vectors transferred to a common origin; c) a volume element $d\vec{\mathbf{v}}$ in velocity space for a molecule of velocity $\vec{\mathbf{v}}$.**

Note that each velocity vector will be defined by the coordinates of its end point. Let us denote the x, y and z components of the velocity $\vec{\mathbf{v}}$ of a particle by v_x, v_y and v_z. Therefore, in terms of these three rectilinear components, we can write

$$v^2 = v_x^2 + v_y^2 + v_z^2 \tag{2.1}$$

The number of velocity vectors ending in element $d\vec{\mathbf{v}} = dv_x\, dv_y\, dv_z$ gives the average number of molecules whose velocities lie between given limits $\vec{\mathbf{v}}$ and $\vec{\mathbf{v}} + d\vec{\mathbf{v}}$ after a large number of collisions among identical molecules. It means that we have to calculate the number of molecules simultaneously having velocity components in the range v_x to $v_x + dv_x$, v_y to $v_y + dv_y$ and v_z to $v_z + dv_z$. Assumption (4) stated in sub-section 2.2.1 implies that the fraction of molecules having velocity components in the range v_x to $v_x + dv_x$ can be expressed as $f(v_x)\, dv_x$. That is

$$\frac{dN_{v_x}}{N} = f(v_x)\, dv_x$$

or $$dN_{v_x} = N f(v_x)\, dv_x \tag{2.2}$$

where dN_{v_x} is the number of molecules having velocity components in the range v_x and $v_x + dv_x$, N is the total number of molecules and f is an unknown function, which we have to determine. Mathematically, the ratio, $\dfrac{dN_{v_x}}{N}$ denotes the probability that a molecule with x-component of velocity lies in the range v_x to $v_x + dv_x$.

The probability of an event is the ratio of the number of favourable outcomes to the total number of outcomes. For example, the probability of getting a head in tossing a coin is one-half.

Proceeding further, we note that existence of velocity component v_x does not in any way affect velocity components v_y and v_z, since these are mutually perpendicular and independent of each other. So the number of molecules having velocity components in the range v_y to $v_y + dv_y$ and v_z to $v_z + dv_z$ are, respectively, given by

$$dN_{v_y} = Nf(v_y)\, dv_y \qquad (2.3)$$

and $$dN_{v_z} = Nf(v_z)\, dv_z \qquad (2.4)$$

Note that we have assumed the same functional dependence in all three cases. It signifies that there is no preferred direction of motion of gas molecules.

Since the three perpendicular components of velocity are independent, we can express the probability for a molecule to simultaneously have velocity components in the range v_x to $v_x + dv_x$, v_y to $v_y + dv_y$ and v_z to $v_z + dv_z$ using the law of compound probabilities. This gives

> According to the law of compound probabilities, for **independent events**, the composite probability is equal to the product of the probabilities of individual events.

$$\frac{d^3N_{v_x v_y v_z}}{N} = f(v_x)f(v_y)f(v_z)\, dv_x\, dv_y\, dv_z \qquad (2.5)$$

Hence, the number of molecules simultaneously having velocity components lying between v_x to $v_x + dv_x$, v_y to $v_y + dv_y$ and v_z to $v_z + dv_z$ is

$$d^3N_{v_x v_y v_z} = Nf(v_x)\, f(v_y)f(v_z)\, dv_x\, dv_y\, dv_z \qquad (2.6)$$

Note that all these $d^3N_{v_x v_y v_z}$ molecules lie in the small volume element $dv_x\, dv_y\, dv_z$. In Fig. 2.1c, one such molecule is depicted as a velocity point. (A point representing a molecule with velocity components in the three coordinate directions is called velocity point.)

Therefore, the density of velocity points, i.e., number density of gas molecules can be expressed as

$$\rho = \frac{d^3N_{v_x v_y v_z}}{dv_x dv_y dv_z} \qquad (2.7)$$

On combining Eqs. (2.6) and (2.7), we can write

$$\rho = Nf(v_x)\, f(v_y)\, f(v_z)$$

Since the velocity space has been assumed to be isotropic, the density of velocity points can be taken as constant. So, we can write

$$Nf(v_x)\, f(v_y)\, f(v_z) = \text{constant} = NJ(\vec{v}) = NF(v^2) \qquad (2.8)$$

where F is some other function. Note that this equation holds for a fixed value of $\vec{v}$, i.e. it is subject to the condition

$$v^2 = v_x^2 + v_y^2 + v_z^2 = \text{constant} \qquad (2.9)$$

Physically it means that after a large number of collisions, the distribution will be isotropic. Therefore, we can take

$$dF(v^2) = 0$$

In terms of dv_x, dv_y and dv_z, we can write Eq. (2.8) as

$$\frac{\partial f(v_x)}{\partial v_x} dv_x f(v_y) f(v_z) + f(v_x) \frac{\partial f(v_y)}{\partial v_y} f(v_z) dv_y$$

$$+ f(v_x) f(v_y) \frac{\partial f(v_z)}{\partial v_z} dv_z = 0 \qquad (2.10)$$

Proceeding further, we divide Eq. (2.10) by $f(v_x)f(v_y)f(v_z)$ and obtain

$$\frac{1}{f(v_x)} \frac{\partial f(v_x)}{\partial v_x} dv_x + \frac{1}{f(v_y)} \frac{\partial f(v_y)}{\partial v_y} dv_y + \frac{1}{f(v_z)} \frac{\partial f(v_z)}{\partial v_z} dv_z = 0 \qquad (2.11)$$

The differential form of Eq. (2.9), which expresses the condition under which v_x, v_y and v_z can vary while $\vec{v}$ remains constant is

$$v_x \, dv_x + v_y \, dv_y + v_z \, dv_z = 0 \qquad (2.12)$$

From this equation it is clear that the differentials dv_x, dv_y and dv_z are not mutually independent; these can take any value but must satisfy Eq. (2.12). To relax this constraint, we use Lagrange's method of undetermined multipliers. In this method, the constraining relation is multiplied by a constant and the resultant expression is added to the constrained equation. In this case, we choose the undetermined multiplier to be 2*B*. (You will soon realise that the factor 2 with *B* simplifies mathematical steps.)

On multiplying Eq. (2.12) by 2*B* and adding the resultant expression to Eq. (2.11), we get

$$\left[\frac{1}{f(v_x)} \frac{\partial f(v_x)}{\partial v_x} + 2Bv_x \right] dv_x + \left[\frac{1}{f(v_y)} \frac{\partial f(v_y)}{\partial v_y} + 2Bv_y \right] dv_y$$

$$+ \left[\frac{1}{f(v_z)} \frac{\partial f(v_z)}{\partial v_z} + 2Bv_z \right] dv_z = 0 \qquad (2.13)$$

We now choose the constant *B* such that

$$\frac{1}{f(v_x)} \frac{\partial f(v_x)}{\partial v_x} + 2Bv_x = 0 \qquad (2.14)$$

Then Eq. (2.13) reduces to

$$\left[\frac{1}{f(v_y)} \frac{\partial f(v_y)}{\partial v_y} + 2Bv_y \right] dv_y + \left[\frac{1}{f(v_z)} \frac{\partial f(v_z)}{\partial v_z} + 2Bv_z \right] dv_z = 0 \qquad (2.15)$$

Of the three variables dv_x, dv_y and dv_z, we can consider dv_y and dv_z to be independent. Then, for finite values of dv_y and dv_z, Eq. (2.13) will be

satisfied if the coefficients of these differentials in Eq. (2.15) vanish separately. This leads us to the equations

$$\frac{1}{f(v_y)}\frac{\partial f(v_y)}{\partial v_y} + 2Bv_y = 0 \tag{2.16}$$

and

$$\frac{1}{f(v_z)}\frac{\partial f(v_z)}{\partial v_z} + 2Bv_z = 0 \tag{2.17}$$

To proceed further, we rewrite Eq. (2.14) as

$$\frac{df(v_x)}{f(v_x)} = -2Bv_x\,dv_x$$

Note that we have replaced '∂' with d because f in the above expression is a function of v_x only.

This equation can be easily integrated to obtain

$$\ln f(v_x) = -\frac{2Bv_x^2}{2} + \ln A$$

where $\ln A$ is an arbitrary constant of integration.

You can rewrite this result as

$$f(v_x) = Ae^{-Bv_x^2} \tag{2.18}$$

where A and B are unknown constants. Note that Lagrange's method of undetermined multipliers has helped us to discover the form of the function f; it is a decaying exponential. But now we will have to deal with two unknown constants (A and B) rather than one unknown function (f). This apparent complexity should not discourage you; it is more difficult to determine an unknown function than two unknown constants.

Note that Eq. (2.18) gives the probability for a molecule having velocity component in the x-direction between v_x and $v_x + dv_x$.

On combining this result with Eq. (2.2) we can express the number of molecules having velocity components in the range v_x to $v_x + dv_x$ as

$$dN_{v_x} = NA\exp(-Bv_x^2)\,dv_x \tag{2.18a}$$

Proceeding further, we note that the differential equations satisfied by $f(v_y)$ and $f(v_z)$ will be similar to that satisfied by $f(v_x)$. Therefore, by analogy, we can write

$$f(v_y) = Ae^{-Bv_y^2} \tag{2.19}$$

and

$$f(v_z) = Ae^{-Bv_z^2} \tag{2.20}$$

On combining Eqs. (2.18), (2.19) and (2.20) with Eq. (2.6), we obtain the required expression for $d^3N_{v_x v_y v_z}$:

$$d^3N_{v_xv_yv_z} = NA^3e^{-B(v_x^2+v_y^2+v_z^2)}dv_xdv_ydv_z$$

$$= NA^3e^{-Bv^2}dv_xdv_ydv_z \tag{2.21}$$

Hence, the probability that a molecule has velocity between $\vec{v}$ and $\vec{v}+d\vec{v}$ is given by

$$\frac{d^3N_{v_xv_yv_z}}{N} = A^3e^{-Bv^2}d^3v \tag{2.22}$$

where $d^3v = dv_xdv_ydv_z$ is three-dimensional element of velocity space.

This expression is referred to as the **Maxwell velocity distribution function**. This result shows that the probability that a molecule has velocity between $\vec{v}$ and $\vec{v}+d\vec{v}$ decreases exponentially with $\vec{v}$.

Usually we are not interested in knowing the molecular distribution for individual velocity components since the distribution has been assumed to be isotropic and gas molecules show no preferential direction of motion. Therefore, it is more desirable to express Eq. (2.21) in other forms. We now discuss distribution function for molecular speeds.

2.2.3 Distribution Function for Molecular Speeds

To obtain the expression for distribution function for molecular speeds, we consider the number of molecules having speeds in the range v to $v+dv$. We can easily calculate this number by considering a spherical shell of radius v and thickness dv, in the velocity space (see Fig. 2.2). The number of velocity vectors ending in such a spherical shell gives the required number.
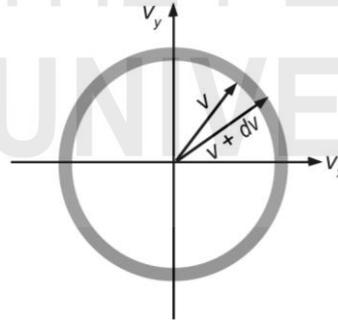

Fig. 2.2: **A spherical shell of radius** v **and thickness** dv**.**

The volume of such a shell in velocity space will be $4\pi v^2\,dv$. In view of the geometry under consideration, it will be more appropriate to express the volume element $dv_xdv_ydv_z$ in terms of spherical polar coordinates. So we put $dv_xdv_ydv_z = v^2\sin\theta\,d\theta\,d\phi\,dv$ and replace $d^3N_{v_xv_yv_z}$ by dN_v. Note that the limits of integration over θ vary from 0 to π and over ϕ from 0 to 2π. This gives

$$dN_v = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} NA^3e^{-Bv^2}v^2\sin\theta\,d\theta\,d\phi\,dv$$

$$= NA^3v^2e^{-Bv^2}[(-\cos\pi+\cos0)\,2\pi]dv = 4\pi NA^3v^2e^{-Bv^2}\,dv \tag{2.23}$$

The ratio, dN_v / dv determines the **Maxwellian distribution** of **molecular speeds**. The qualitative shape of the Maxwellian distribution function as a function of molecular speed is shown in Fig. 2.3.
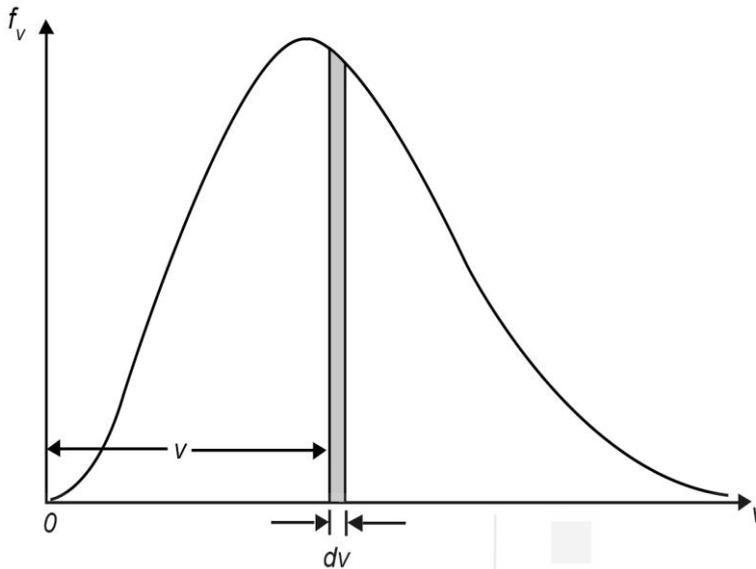

Fig. 2.3: **A plot of Maxwellian distribution function versus molecular speed.**

Note that

- The shape of the curve is determined by the interplay of an increasing quadratic function and a decaying exponential.

- For smaller values of v, the quadratic function dominates and the curve rises. The exponential function begins to become important gradually.

- Beyond a certain value of v, the exponential term begins to dominate and limits the maximum of the curve to a finite value. At that point, the curve shows an inversion and decays exponentially thereafter.

- If we consider a strip of width dv, its area (shown by the shaded part) gives us the number of molecules with speeds between v and $v + dv$. The number of gas molecules with very small and very large speeds is extremely small.

- The area under the curve gives the total number of molecules in the gas.

Note that to relax the constraint expressed by Eq. (2.9), we introduced only one unknown constant ($2B$) but Eq. (2.23) for molecular velocity distribution has two unknowns (A and B). Obviously, we must determine these to obtain the quantitative shape of the distribution curve. Let us do so now.

2.2.4   Determination of Constants A and B

To evaluate the unknown constants A and B, we first make use of the fact that if we integrate Eq. (2.23) for dN_v over all possible values of v from 0 to ∞, we will get the total number of molecules:

$$N = \int dN_v = 4\pi N A^3 \int_0^\infty v^2 e^{-Bv^2} \, dv \qquad (2.24)$$

The value of the integral

$$\int\limits_{0}^{\infty} e^{-Bv^2} v^n dv$$

$$= \frac{1}{2B^{((n+1)/2)}} \Gamma\left(\frac{n+1}{2}\right)$$

where $\Gamma(n)$ is gamma function. Its values for a few values of n are given below:

n	$\Gamma(n)$
$\frac{1}{2}$	$\sqrt{\pi}$
1	1
$\frac{3}{2}$	$\frac{\sqrt{\pi}}{2}$
2	1

Note that at ordinary temperatures, all molecules move with finite speed. Moreover, Einstein's theory of relativity puts the upper limit of v at the speed of light and no material particle can move with infinite speed. And, at speeds comparable to the speed of light, the theory of relativity stipulates that we should include relativistic effects. Therefore, strictly speaking, the limits 0 to ∞ are non-realistic. However, for mathematical simplicity in present discussion, we will work within these limits without any reference to relativistic effects.

To know the total number of molecules, we have to evaluate the integral in Eq. (2.24). We have given the value of a general integral of this type in the margin. You will be required to use it several times in this unit. Therefore, it will be worthwhile to remember it for fast calculations. If you compare the integral in Eq. (2.24) with that given in the margin remark, you can easily identify that $n = 2$ and the integral on the RHS of Eq. (2.24) can be expressed in terms of the gamma function as: $\Gamma\left(\frac{n+1}{2}\right) = \Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2}$ (see table). Using this result in Eq. (2.24), we get an elegant expression for the total number of particles:

$$N = 4\pi NA^3 \frac{1}{2B^{3/2}} \Gamma(3/2) = \frac{4\pi NA^3}{2B^{3/2}} \frac{\sqrt{\pi}}{2} \tag{2.25}$$

Those of you who would like to know how the integral in Eq. (2.24) has been evaluated, we illustrate it now. Change the variable of integration and put $Bv^2 = x$ so that $2Bv\, dv = dx$ or $v\, dv = \frac{1}{2B} dx$ and

$v^2 dv = \frac{1}{2B^{3/2}} x^{1/2} dx$. However, the limits of integration will not change since $x = 0$ for $v = 0$ and $x = \infty$ for $v = \infty$. Hence we can write

$$N = 4\pi NA^3 \frac{1}{2B^{3/2}} \int\limits_{0}^{\infty} e^{-x} x^{1/2} dx \tag{i}$$

The integral in this expression denotes a special function, known as **gamma function**:

$$\Gamma(n) = \int\limits_{0}^{\infty} e^{-x} x^{n-1} dx$$

In this case, $n = 3/2$. Therefore, the integral in (i) is equal to $\Gamma(3/2) = (1/2)\Gamma(1/2) = \sqrt{\pi}/2$. In writing the last step, we have used the relation $\Gamma(n) = (n-1)\Gamma(n-1)$ and $\Gamma(1/2) = \sqrt{\pi}$. (You will learn these special functions in higher level physics.) Hence, the expression for total number of particles in the gas takes a simple form:

$$N = 4\pi NA^3 \frac{1}{2B^{3/2}} \frac{\sqrt{\pi}}{2}$$

On simplification and rearrangement of terms in Eq. (2.25), we can express A in terms of B:

$$A = \sqrt{B/\pi} \tag{2.26}$$

To determine B, we calculate the mean square speed $\overline{v^2}$ of a molecule. It is defined as

$$\overline{v^2} = \frac{\int\limits_0^\infty v^2 dN_v}{\int\limits_0^\infty dN_v} \qquad (2.27)$$

On substituting for dN_v from Eq. (2.23), we can write

$$\overline{v^2} = \frac{\int\limits_0^\infty 4\pi NA^3 e^{-Bv^2} v^2 . v^2 dv}{\int\limits_0^\infty 4\pi NA^3 e^{-Bv^2} v^2 dv} = \frac{\int\limits_0^\infty v^4 e^{-Bv^2} dv}{\int\limits_0^\infty v^2 e^{-Bv^2} dv}$$

By referring to the integral in the margin remark on the previous page, we get

$$\overline{v^2} = \frac{\dfrac{1}{2B^{5/2}}\Gamma(5/2)}{\dfrac{1}{2B^{3/2}}\Gamma(3/2)} = \frac{2B^{3/2}\Gamma(5/2)}{2B^{5/2}\Gamma(3/2)}$$

Since $\Gamma(5/2) = (3/2)\Gamma(3/2)$, the expression for $\overline{v^2}$ simplifies to

$$\overline{v^2} = \frac{3}{2B} \qquad (2.28)$$

In Unit 1, you have learnt that average kinetic energy of a molecule is equal to $(3/2)k_B T$. So we can write

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$$

On combining this result with Eq. (2.28), we get

$$\frac{1}{2}m\,\overline{v^2} = \frac{1}{2}m \cdot \frac{3}{2B} = \frac{3}{2}k_B T$$

so that

$$B = \frac{m}{2k_B T} \qquad (2.29)$$

On substituting this value of B in Eq. (2.26), we obtain the value of constant A:

$$A = \sqrt{\frac{m}{2\pi k_B T}} \qquad (2.30)$$

If we now substitute the values of A and B from Eqs. (2.29) and (2.30), respectively, in Eq. (2.23), we can express the number of molecules in a Maxwellian gas having speeds in the range v to $v + dv$ as

37

$$dN_v = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left[-\left(\frac{mv^2}{2k_B T}\right)\right] dv \qquad (2.31)$$

Let us pause for a while and reflect on the implications of this result. Eq. (2.31) tells us that distribution of molecular speeds is a function of temperature of the gas. Note that at a given temperature

- The probability that a molecule has a speed between v and $v + dv$ is dN_v / N.

- The value of Maxwellian distribution function of molecular speeds, $f_v = \dfrac{dN_v}{dv}$, will be zero for $v = 0$ as well as $v = \infty$. It means that molecular speeds can have only finite values.

- For small molecular speeds, Maxwellian distribution function increases as a quadratic function.

- As magnitude of molecular speed increases, the exponential function, which is a decaying term, starts becoming important. As a result, the Maxwellian distribution function increases initially, attains a maximum value and then decreases exponentially. This is illustrated in Fig. 2.4.

- The Maxwellian distribution curve becomes flatter as temperature increases; the peak value shifts to the right and entire distribution is pushed towards higher speeds because the gas molecules become more energetic.

- The nature of the gas comes into play in determining the shape of the curve through the presence of mass of the molecules.
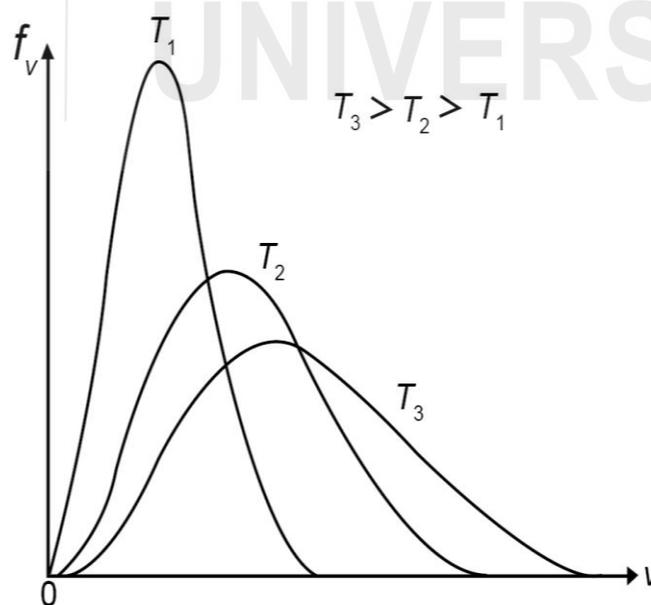
Fig. 2.4: **Plots of Maxwellian distribution function versus speed at three different temperatures.**

To give you an idea about the numbers involved, we would like you to go through the following Example carefully.

$\mathcal{E}$XAMPLE 2.1: MAXWELL DISTRIBUTION FUNCTION

Consider a cubical container having oxygen gas. The velocities of oxygen molecules in this sample have speeds between $185 \, ms^{-1}$ and $195 \, ms^{-1}$ at $0°C$. Calculate (i) the number of molecules in this range, and (ii) the probability that the speed of an oxygen molecule will lie between these values. The mass of oxygen sample is 0.25 kg. Take $k_B = 1.38 \times 10^{-23} \, JK^{-1}$.

Solution ■ From Eq. (2.31) we know that the number of molecules having speeds in the range v to $v + dv$ is given by

$$dN_v = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left[-\left(\frac{mv^2}{2k_B T}\right)\right] dv$$

The interval of speeds under consideration is $dv = 195 - 185 = 10 \, ms^{-1}$ and the mean speed of molecules is

$$v = \frac{195 + 185}{2} = \frac{380}{2} = 190 \, ms^{-1}$$

Recall that 32 kg of oxygen contains 6.02×10^{26} molecules. Hence, the number of molecules in the given sample (0.25 kg) of oxygen is given by

$$N = \frac{0.25 \times 6.02 \times 10^{26}}{32} = 0.047 \times 10^{26}$$

The mass of an oxygen molecule, $m = \dfrac{32}{6.02 \times 10^{26}} = 5.31 \times 10^{-26} \, kg$

At $T = 273 \, K$, $k_B T = (1.38 \times 10^{-23} \, JK^{-1}) \times 273 \, K = 3.767 \times 10^{-21} \, J$

On substituting these values in the expression for dN_v, we get

$$dN_v = 4\pi \times 4.7 \times 10^{24} \left(\frac{5.31 \times 10^{-26} \, kg}{2\pi \times 3.767 \times 10^{-21} \, J}\right)^{3/2} \times$$

$$(190 \, ms^{-1})^2 \exp\left(-\frac{(5.31 \times 10^{-26} \, kg) \times (190 \, ms^{-1})^2}{2 \times (3.767 \times 10^{-21} \, J)}\right) \times (10 \, ms^{-1})$$

$$= 59.08 \times 10^{27} \times 361 \times (2.245 \times 10^{-6})^{3/2} \exp(-0.2544)$$

(i) $dN_v = 21.33 \times 10^{30} \times (3.36 \times 10^{-9}) \times 0.77 = 5.52 \times 10^{22}$ molecules.

(ii)   The probability that the speed of an oxygen molecule lies between the given range is only about 1%:

$$\frac{dN_v}{N} = \frac{5.52 \times 10^{22}}{4.7 \times 10^{24}} = 1.17 \times 10^{-2}$$

2.3 SOME USEFUL DEDUCTIONS FROM MAXWELL'S LAW

Now you know that Maxwell distribution function gives the number of molecules whose speeds lie within a small range. You may recall that molecules of a gas are free to move with all speeds between zero and infinity. Therefore, it should be possible for us to characterise a Maxwellian gas with some average speed, $\bar{v}$. Since Maxwell distribution function comprises two competing functions − an increasing quadratic function and a decaying exponential function − it should be possible to determine the speed at which the function will have maximum value. It is referred to as the most probable speed, v_p. From Unit 1, you may recall that energy of a molecule is defined in terms of mean square speed, $\overline{v^2}$. It will, therefore, be instructive to derive an expression for root mean square speed, v_{rms} for a Maxwellian gas. An estimate of the values of these speeds gives us an idea about the nature of molecular distribution. You will learn how to obtain expressions for these now.

2.3.1 Average Speed

The **average speed** is defined as

$$\bar{v} = \frac{\int_0^\infty v\,dN_v}{\int_0^\infty dN_v} = \frac{1}{N}\int_0^\infty v\,dN_v \tag{2.32}$$

On substituting for dN_v from Eq. (2.31), we get

$$\bar{v} = \frac{1}{N}4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^3 \exp\left[-\left(\frac{mv^2}{2k_B T}\right)\right]dv \tag{2.33}$$

The integral on the RHS of above expression can be evaluated following the steps described in the Box in Sec. 2.2.4. That is, we introduce a change of variable by defining $x = \dfrac{mv^2}{k_B T}$ and substituting for $v^3 dv$. You can easily verify that the integral in Eq. (2.33) has the value $\dfrac{1}{2(m/2k_B T)^2}\Gamma(2)$.

Since $\Gamma(2) = 1$, the expression for average speed simplifies to

$$\bar{v} = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\frac{1}{2\left(\dfrac{m}{2k_B T}\right)^2} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{2.55 k_B T}{m}} \tag{2.34}$$

Let us now obtain the expression for root mean square speed.

2.3.2 Root Mean Square Speed

The **root mean square speed** of a molecule is defined as

$$v_{rms} = \sqrt{\overline{v^2}}$$

From Eq. (2.28), we recall that for a Maxwellian gas, mean square speed is related to constant B. On substituting the value of B from Eq. (2.29), we get

$$\overline{v^2} = \frac{3}{2B} = \frac{3k_BT}{m}$$

Hence,

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m}} \qquad\qquad (2.35)$$

By comparing the expressions for average speed and root mean square

speed given in Eqs. (2.34) and (2.35), you will note that $v_{rms} > \overline{v}$.

2.3.3   Most Probable Speed

Refer to Fig.2.4 again. The speed at which the Maxwellian distribution function f_v exhibits maxima is known as the **most probable speed**. It is denoted by the symbol v_p. To obtain an expression for the most probable speed, we use the elementary knowledge of calculus: **For maxima of a function to occur, the first derivative with respect to the independent variable should be zero and the second derivative less than zero**. Therefore, let us first calculate $\frac{df_v}{dv}$ using Eq. (2.31). This gives

$$\frac{df_v}{dv} = 4\pi N \left(\frac{m}{2\pi k_BT}\right)^{3/2} \frac{d}{dv}\left[v^2 \exp\left\{-\left(\frac{mv^2}{2k_BT}\right)\right\}\right]$$

$$= C\left\{2v\exp\left[-\left(\frac{mv^2}{2k_BT}\right)\right] + v^2\exp\left[-\left(\frac{mv^2}{2k_BT}\right)\right]\left(-\frac{2mv}{2k_BT}\right)\right\} \quad (2.36)$$

We now equate $\frac{df_v}{dv} = 0$ and solve for v. This value will define $v = v_p$. Hence,

we can write

$$2v_p\exp\left[-\left(\frac{mv_p^2}{2k_BT}\right)\right] + v_p^2\exp\left[-\left(\frac{mv_p^2}{2k_BT}\right)\right]\left(-\frac{2mv_p}{2k_BT}\right) = 0$$

We can rewrite it as

$$2v_p\exp\left[-\left(\frac{mv_p^2}{2k_BT}\right)\right]\left[1 - \frac{m}{2k_BT}v_p^2\right] = 0$$

For finite value of v_p, this equality will hold only if

$$1 - \frac{m}{2k_BT}v_p^2 = 0$$

or $$v_p^2 = \frac{2k_BT}{m}$$

Hence, the most probable speed of a molecule in a Maxwellian gas is given by

$$v_p = \sqrt{\frac{2k_BT}{m}} \qquad\qquad (2.37)$$

The numerical values of average speed, root mean square speed and most probable speed calculated for molecules of a few typical gases on the basis of Eqs. (2.34), (2.35) and (2.37), respectively, at STP are given in Table 2.1. You will note that root mean square speed of a molecule of a Maxwellian gas is greater than its average speed, which, in turn, is greater than the most probable speed. You can easily convince yourself that
$v_p : \bar{v} : v_{rms} :: 1 : 1.128 : 1.224$.

Table 2.1: Values of v_p, $\bar{v}$ and v_{rms} for different gases at STP

Gas	$v_p(\text{ms}^{-1})$ $= \sqrt{\dfrac{2k_BT}{m}}$	$\bar{v}(\text{ms}^{-1})$ $= \sqrt{\dfrac{2.55k_BT}{m}}$	$v_{rms}(\text{ms}^{-1})$ $= \sqrt{\dfrac{3k_BT}{m}}$
H_2	1501	1695	1838
H_2O	502	567	615
N_2	403	455	493
Air	396	447	485
O_2	376	425	461
CO_2	321	362	393

On the basis of this discussion on most probable speed, we cannot say very authentically that Eq. (2.37) corresponds to the maximum of the Maxwellian distribution function. Can you argue this out? As mentioned earlier, for v_p to correspond to maximum of the Maxwellian distribution function, the second order derivative should be less than zero. This is a simple exercise of calculus and we will leave it as an SAQ.

SAQ 1 – **Most probable speed**

Calculate the second order derivative of Maxwellian distribution function, substitute the value of most probable speed given by Eq. (2.37) and convince yourself that $\dfrac{d^2 f_v}{dv^2} < 0$.

You may like to solve another SAQ.

SAQ 2 – **Molecular speeds**

Calculate the most probable speed, average speed and the root mean square speed for oxygen molecules at 300K. Given $m_{O_2} = 5.31 \times 10^{-26}$ kg and $k_B = 1.38 \times 10^{-23}$ JK^{-1}.

Let us now revise what you have learnt so far in this unit.

MAXWELL'S DISTRIBUTION LAW OF SPEEDS

- The number of molecules in a Maxwellian gas having speeds in the range v and $v + dv$ is given by

$$d N_v = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left[-\left(\frac{mv^2}{2k_B T}\right)\right] dv$$

- The Maxwellian distribution of molecular speeds is determined by the interplay of an increasing quadratic function and a decaying exponential.

- The Maxwellian distribution is pushed towards higher speeds as temperature increases. However, the peak value of the distribution function f_v corresponding to the most probable speed shifts to the right and is lowered. That is, as temperature increases, the distribution curve becomes flatter and broader.

- The average speed, root mean square speed and most probable speed of molecules in a Maxwellian gas are respectively given by

$$\bar{v} = \sqrt{\frac{2.55\, k_B T}{m}}\ ,\ v_{rms} = \sqrt{\frac{3\, k_B T}{m}}\ \text{and}\ v_p = \sqrt{\frac{2\, k_B T}{m}}$$

So far, we have confined our discussion to distribution of molecular speeds for a Maxwellian gas at finite temperatures. Another physical quantity of interest is the energy of a gas molecule. You may, therefore, like to know the energy distribution of a Maxwellian gas. Let us learn about it now.

2.4 DIRECT EXPERIMENTAL VERIFICATION OF MAXWELL'S LAW: ZARTMAN AND KO EXPERIMENTS

The apparatus used by Zartman and Ko is illustrated in Fig. 2.5. A beam of bismuth molecules, produced in an oven, was collimated by a series of slits S_1, S_2, S_3. A glass plate P fixed inside a cylindrical drum, D, which can be rotated at a high speed about an axis passing through its centre, was used to collect bismuth molecules. (Instead of the plate, a photographic film could also be placed.) The entire apparatus was placed in an evacuated chamber.
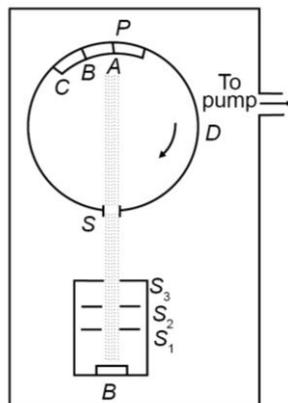

Fig. 2.5: **A schematic diagram of the apparatus used by Zartman and Ko to verify Maxwell's law for distribution of molecular speeds.**

When the drum is stationary, the beam will strike the glass plate at a particular spot, *A*, say. And as the drum is rotated, the molecules will enter it only when the slit *S* crosses the molecular beam. If the rotation is clockwise, the glass plate moves towards the right and the faster moving molecules entering the cylinder will strike it to the left of *A*; the point of impact when the cylinder was stationary. Suppose that the slower molecules reach the plate between *B* and *C*. The density of deposit across the plate gives a measure of the velocity distribution of molecules.

The results obtained by Zartman and Ko are shown in Fig. 2.6. The agreement between theoretical and experimental values was surprisingly good.
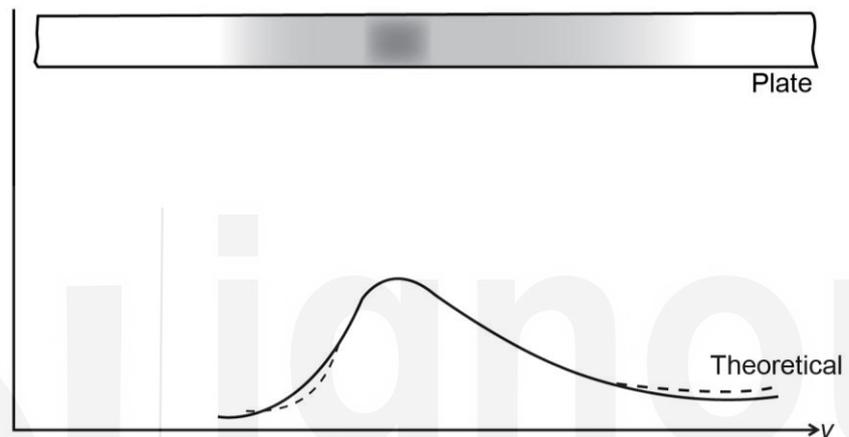

Fig. 2.6: **Spread of molecular deposit in the experiment of Zartman and Ko.**

2.5   LAW OF EQUIPARTITION OF ENERGY

In Sec. 1.3.1, you have learnt that translational kinetic energy of a molecule is given by Eq. (1.3):

$$\varepsilon = \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT$$

We also know that molecular motion is completely random. So, for an isotropic distribution in equilibrium, all three directions are equivalent and translational (kinetic) energy associated with each component of velocity of an ideal (perfect) gas molecule is one-third of its total translational (kinetic) energy; equal to $k_BT/2$. In other words, we can say that *energy is equally partitioned among the three components of velocity.* This is known as the **principle of equipartition of energy** for a monatomic ideal gas. This is an important result of classical physics. And to discuss its applications, we introduce the concept of *degree of freedom* (d.f.).

2.5.1   Degree of Freedom

The degree of freedom of a molecule is defined as the number of independent coordinates required to specify its position in space completely. A point moving along a curved path has only one d.f. Similarly, a house fly moving on a stretched string has only one d.f. This is because we can completely specify its motion/position with only one coordinate. However, when the house fly moves on the floor, the number of its degrees of freedom

increases to two. Similarly, when the housefly flies (in the room), its motion is 3-dimensional and we will require three coordinates (x, y, z) to specify its position. That is, the number of degrees of freedom will be three. How many d.f. does a randomly moving molecule of monatomic gas (like helium, argon, or krypton) have? If you are thinking that it has three translational d.f, you have visualised its motion correctly.

In addition to translational degrees of freedom, a diatomic or a polyatomic molecule has a tendency to rotate (about fixed axes). In another course, you have learnt that we can resolve the angular velocity of a rotating body (molecule in the instant case) along three mutually perpendicular coordinate axes, as shown in Fig. 2.7. So, you may expect a rigid diatomic molecule (H_2, O_2, N_2 …) to have three rotational degrees of freedom. But the moment of inertia of a diatomic molecule about an axis along or parallel to the axis of the molecule (i.e., the line joining the atoms) is very small and no rotation of the molecule as a whole is possible. So, the number of rotational degrees of freedom of a linear diatomic molecule is, in general, only two. That is, a rigid linear diatomic molecule will have a total of five degrees of freedom. (A non-linear molecule like H_2O has 3 rotational degrees of freedom.)
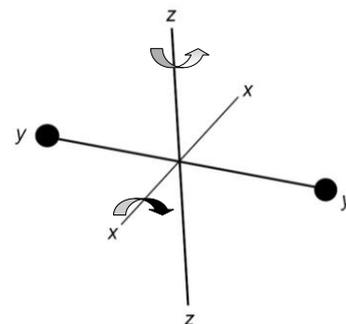

Fig. 2.7: A linear diatomic molecule.

Recap

DEGREE OF FREEDOM

The degree of freedom of a molecule is defined as the number of independent coordinates required to specify its position completely. The number of d.f. can also be defined as the total number of independent squared terms appearing in the expression of energy of a system.

The general formula for the number of degrees of freedom (f) of a molecule can be written as

$$f = 3q - c \qquad (2.38)$$

where q is the number of atoms constituting the molecule and c is the total number of constraints.

For a single atom, $q = 1$ and $c = 0$, since the motion is random, i.e., there is no constraint on its motion. Hence, $f = 3$. For a rigid diatomic molecule ($q = 2$) and the distance between the atoms is fixed so that $c = 1$ and $f = 5$. You will agree that gas molecules do not have a perfectly rigid structure. So, they may even vibrate as a result of intermolecular collisions.

You may now like to know how much energy is associated with a rotational and vibrational degree of freedom. To discover answer to this question, we recall that in case of translational energy, we have seen that the energy associated with each degree of freedom is solely determined by (linear velocity)^2 in each of these independent coordinates and the mean value of the corresponding energy is $k_B T / 2$. The energy of rotation of a body about a specified axis is determined by (angular velocity)^2 and is equal to $I\omega^2 / 2$, where I is moment of inertia about the axis of rotation. So, each of these degrees of freedom has mean rotational energy $k_B T / 2$. Vibrations present a

The number of d.f. can also be defined as the total number of independent squared terms appearing in the expression of energy of a system.

45

special problem. For a harmonic oscillator, the equation of motion for a body of mass m is

$$\frac{d^2x}{dt^2} = -\omega^2 x$$

It has solution of the form

$$x = A\sin\omega t$$

The kinetic energy of the oscillator at any time is $\frac{1}{2}m\left(\frac{dx}{dt}\right)^2$ and the potential energy is $\frac{1}{2}m\omega^2 x^2$ and the sum of kinetic and potential energies is $\frac{1}{2}mA^2\omega^2$ suggesting that total energy is independent of x as well as its first time derivative. Nevertheless, at any instant of time, the kinetic energy is a quadratic function of linear velocity and the potential energy is a quadratic function of displacement. And each of these contributes $k_BT/2$ to mean thermal energy. We may therefore conclude that **every active degree of freedom for which thermal energy of a system is a quadratic function of a variable has associated with it an average thermal energy of $k_BT/2$.** (The total energy of such a system will be $f\,k_BT/2$.) This is the general statement of the principle of **equipartition of energy**. Note that this principle is not valid for systems where energy is a linear function of the variable, as in the case of potential energy due to elevation.

Recap

PRINCIPLE OF EQUIPARTITION OF ENERGY

The thermal energy of a system is equally divided amongst all active degrees of freedom and the mean energy associated with each degree of freedom is $k_BT/2$.

Let us now apply the concept of degree of freedom to discuss the heat capacities of gases.

2.5.2 Heat Capacity of Gases

To begin our discussion, we assume that an amount of heat δQ given to a substance increases its temperature by ΔT. Then **heat capacity** of a substance is given by $\delta Q/\Delta T$. From your +2 classes, you may recall that heat capacity is proportional to the mass of the substance and depends on the temperature. It means that for a given mass of a substance, a different amount of heat may be needed for a unit rise in temperature at different temperatures.

We now define **specific heat capacity** as

$$C = \frac{1}{m}\frac{\delta Q}{\Delta T}$$

where m is the mass in kg. The specific heat capacity of a substance depends on its nature and temperature. It is measured in $Jkg^{-1}K^{-1}$. For a gas, we define specific heat capacity at constant volume as

$$C_V = \frac{1}{m} \frac{\delta Q}{\Delta T}\bigg|_V$$

and specific heat capacity at constant pressure as

$$C_p = \frac{1}{m} \frac{\delta Q}{\Delta T}\bigg|_p$$

If the amount of substance is specified in moles (μ) instead of mass, we define **molar heat capacity** (*c*), which is written as

$$c = \frac{1}{\mu} \frac{\delta Q}{\Delta T}$$

The unit of *c* is $Jmol^{-1}K^{-1}$.

Like specific heat capacity, we will have two types of molar heat capacities for a gas:

$$c_V = \frac{1}{\mu} \frac{\delta Q}{\Delta T}\bigg|_V$$

and

$$c_p = \frac{1}{\mu} \frac{\delta Q}{\Delta T}\bigg|_p$$

Let us consider one mole of a gas. Its total kinetic energy is given by

$$u = N_A \varepsilon$$

If each molecule in the system has *f* degrees of freedom, we can rewrite the expression for energy as

$$u = \frac{f N_A}{2} k_B T = \frac{f}{2} RT \tag{2.39}$$

This equation implies that **molar heat capacity at constant volume,** defined **as the energy required to raise the temperature of one mole of an ideal gas by one kelvin,** is

$$c_V = \frac{f}{2} R \tag{2.40}$$

From your school physics, you know that molar heat capacity at constant pressure $c_p = c_V + R$. (This is known as Mayor's formula). Hence, we can write

$$c_p = \left(\frac{f+2}{2}\right) R \tag{2.41}$$

On combining Eqs. (2.40) and (2.41), we can express the ratio of molar heat capacities at constant pressure and at constant volume as

$$\gamma = \frac{c_p}{c_V} = \frac{f+2}{f} \tag{2.42}$$

In Unit 5, you will learn why we have put δ before *Q* and Δ before *T*.

47

From Eq. (2.42) we note that molecular theory predicts the absolute values as well as the ratio of heat capacities in terms of the degrees of freedom and the gas constant. In particular, it shows that c_V, c_p and γ do not vary with temperature.

Proceeding further, we recall that for monatomic gases, $f = 3$. For a monatomic gas, molar heat capacity at constant volume, molar heat capacity at constant pressure and their ratio are given by

$$c_V = \frac{3}{2}R, \; c_p = \frac{5}{2}R \text{ and } \gamma = \frac{5}{3} = 1.67 \qquad (2.43)$$

This result shows that the value of c_V (or c_p) is same for all monatomic gases. As such, this prediction is fairly well borne out by experiments.

You may now ask: Is this result true even for diatomic molecules? To seek answer to this question, we note that for diatomic molecules, $f = 5$ so that

$$c_V = \frac{5}{2}R, \; c_p = \frac{7}{2}R \text{ and } \gamma = \frac{7}{5} = 1.4 \qquad (2.44)$$

Note that the ratio of molar heat capacities decreases with increasing atomicity of gases. This conclusion is in general conformity with experiments. We can also conclude that for all ideal gases, molar heat capacities and their ratios are independent of temperature. This result of molecular theory is fairly well borne out by observed results. Refer to Table 2.2 where we have listed the values of γ and molar heat capacities (in units of R) for a few typical gases.

Table 2.2: Molar heat capacities at room temperature

Gas	c_p / R	c_v / R	γ
He	2.50	1.51	1.66
Ne	2.50	1.52	1.64
Ar	2.51	1.51	1.67
H_2	3.47	2.47	1.40
O_2	3.53	2.52	1.40
Cl_2	4.07	3.00	1.36
Air	3.50	2.50	1.40

From the above discussion you may get the impression that elementary kinetic theory explains all observed results. This is not true. The first sign of disagreement between theory and experiments came to knowledge when the ratio of heat capacities of different gases at constant pressure and at constant volume was determined from their measured values and used to determine the number of degrees of freedom; the result was not, in general, an exact integer. You will discover answer to this question as you proceed in this course.

Let us now sum up what you have learnt in this unit.

2.6 SUMMARY

Concept	Description

Distribution of molecular velocities

■ The distribution of molecular velocities is given by

$$dN_v = NA^3 e^{-Bv^2} d^3v$$

Maxwell's law

■ The distribution of molecular speeds is given by **Maxwell's law:**

$$dN_v = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\left(\frac{mv^2}{2k_B T}\right)} v^2 dv$$

Root mean square speed, average speed and most probable speed

■ The root mean square speed, the average speed, and the most probable speed are, respectively, given by the expressions:

$$v_{rms} = \sqrt{\frac{3 k_B T}{m}}, \quad \bar{v} = \sqrt{\frac{2.55 k_B T}{m}}, \quad v_p = \sqrt{\frac{2 k_B T}{m}}$$

Note that $v_{rms} > \bar{v} > v_p$.

Average energy of a molecule

■ The average energy of a molecule obeying Maxwell's law is given by

$$\bar{E} = \frac{3}{2} k_B T$$

Law of equipartition of energy

■ The **law of equipartition of energy** states that thermal energy is equally divided amongst various active degrees of freedom of a molecule and its magnitude is $k_B T / 2$.

Molar heat capacities

■ **The molar heat capacity at constant volume, molar heat capacity at constant pressure and their ratio for a monatomic gas** are given by

$$c_V = \frac{3}{2} R, \ c_p = \frac{5}{2} R \text{ and } \gamma = \frac{5}{3} = 1.67$$

■ **The molar heat capacity at constant volume, molar heat capacity at constant pressure and their ratio for a diatomic gas** are given by

$$c_V = \frac{5}{2} R, \ c_p = \frac{7}{2} R \text{ and } \gamma = \frac{7}{5} = 1.4$$

■ **The ratio of molar heat capacities decreases with increasing atomicity of gases and their values are independent of temperature**.

2.7   TERMINAL QUESTIONS

1. Calculate the temperature at which the velocities of nitrogen molecules $v_1 = 400 \text{ ms}^{-1}$ and $v_2 = 800 \text{ ms}^{-1}$ are associated with the same value of Maxwell distribution function f_v.

2. The average energy of helium molecules is $\bar{E} = 2.89 \times 10^{-21}$ J. Calculate their average speed $(\bar{v})$.

3. Obtain the expression for mean translational energy per degree of freedom for the molecules of a Maxwellian gas.

4. Calculate the temperature at which root-mean square speed of nitrogen molecules exceeds their most probable speed by 100 ms^{-1}.

5. a) Prove that for a system of particles in random motion, the average velocity $\bar{v}$ is zero.

    b) Show that the average velocity distribution is a Gaussian centred about zero velocity.

2.8   SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. To prove that the most probable speed corresponds to a maximum of the distribution function, we have to show that the second order derivative of the Maxwell's distribution function is less than zero. So we differentiate Eq. (2.36) with respect to v and substitute $v = v_p$ in the resultant expression.

$$\frac{d^2 f_v}{dv} = \frac{d}{dv}\left(\frac{df_v}{dv}\right)$$

$$= \frac{d}{dv}\, C\left\{2v \exp\left(-\frac{mv^2}{2k_BT}\right) + v^2 \exp\left(-\frac{mv^2}{2k_BT}\right)\left(-\frac{2mv}{2k_BT}\right)\right\}$$

$$= C\frac{d}{dv}\left\{\left[\exp\left(-\frac{mv^2}{2k_BT}\right)\right]\left[2v - \frac{mv^3}{k_BT}\right]\right\}$$

$$= C\left[\exp\left(-\frac{mv^2}{2k_BT}\right)\right]\left[2 - \frac{3mv^2}{2k_BT}\right] + \left(2v - \frac{mv^3}{k_BT}\right)\left(-\frac{2mv}{2k_BT}\right)\exp\left(-\frac{mv^2}{2k_BT}\right)$$

$$= C\exp\left(-\frac{mv^2}{2k_BT}\right)\left(2 - \frac{5mv^2}{k_BT} + \frac{m^2v^4}{(k_BT)^2}\right)$$

On substituting the value of the most probable speed, $v_p = \sqrt{\dfrac{2k_BT}{m}}$ in this expression, we get

$$\frac{d^2 f_v}{dv}\bigg|_{v=v_p} = C \exp\left(-\frac{m}{2k_B T}\frac{2k_B T}{m}\right)\left(2 - \frac{5m}{k_B T}\frac{2k_B T}{m} + \frac{m^2}{(k_B T)^2}\frac{(2k_B T)^2}{m^2}\right)$$

$$= -4C\exp(-1) < 0.$$

2. Let us first calculate the value of $\sqrt{k_B T/m}$ as all the speeds require this value:

$$\frac{k_B T}{m} = \frac{(1.38 \times 10^{-23}\,\text{JK}^{-1}) \times (300\,\text{K})}{5.31 \times 10^{-26}\,\text{kg}} = 7.8 \times 10^4\,\text{m}^2\text{s}^{-2}$$

$$\therefore \quad \sqrt{\frac{k_B T}{m}} = 2.8 \times 10^2\,\text{ms}^{-1}$$

Hence,

$$v_p = \sqrt{2} \times 2.8 \times 10^2\,\text{ms}^{-1} = 395\,\text{ms}^{-1}$$

$$\bar{v} = \sqrt{2.55} \times 2.8 \times 10^2\,\text{ms}^{-1} = 446\,\text{ms}^{-1}$$

$$v_{rms} = \sqrt{3} \times 2.8 \times 10^2\,\text{ms}^{-1} = 484\,\text{ms}^{-1}$$

Terminal Questions

1. Let the temperature at which the two distributions are same be T.
    Then, from Eq. (2.31), we can write

$$f_{v_1} = N\sqrt{\frac{2}{\pi}}\left(\frac{m}{k_B T}\right)^{3/2} e^{\left(\frac{-mv_1^2}{2k_B T}\right)} v_1^2$$

$$f_{v_2} = N\sqrt{\frac{2}{\pi}}\left(\frac{m}{k_B T}\right)^{3/2} e^{\left(\frac{-mv_2^2}{2k_B T}\right)} v_2^2$$

But $f_{v_1} = f_{v_2}$ (given equal values of the Maxwell distribution function)

Therefore,

$$v_1^2\, e^{\left(\frac{-mv_1^2}{2k_B T}\right)} = v_2^2\, e^{\left(\frac{-mv_2^2}{2k_B T}\right)}$$

Taking natural logarithm of both sides and on rearranging the terms, we get

$$\frac{m}{2k_B T}\left(v_2^2 - v_1^2\right) = 2\ln\left(\frac{v_2}{v_1}\right)$$

$$\therefore \quad T = \frac{m\left(v_2^2 - v_1^2\right)}{4k_B \ln\left(\frac{v_2}{v_1}\right)} = \frac{M\left(v_2^2 - v_1^2\right)}{4N_A k_B \ln\left(\frac{v_2}{v_1}\right)}$$

$$= \frac{0.028 \times (48 \times 10^4 \text{ m}^2\text{s}^{-2})}{4 \times 6.02 \times 10^{23} \times (1.38 \times 10^{-23} \text{ JK}^{-1}) \times 0.693}$$

$$T = \frac{1.344 \times 10^4}{23.04} = 583\text{K}$$

2. The average energy is given by

$$\bar{E} = \frac{f}{2} k_B T$$

where f is the number of total degrees of freedom. Helium is a mono-atomic gas, therefore $f = 3$ and hence $\bar{E} = \frac{3}{2} k_B T = 2.89 \times 10^{-21}$J.

Further, we know that

$$\bar{v} = \sqrt{\frac{2.55 \, k_B T}{m}}$$

Here m is the mass of helium.

$$m = \frac{4 \times 1.008}{6.023 \times 10^{267}} \text{kg} = 6.7 \times 10^{-27} \text{ kg}$$

Since $\bar{E} = \frac{3}{2} k_B T$,

$$k_B T = \frac{2}{3} \bar{E} = \frac{2}{3} \times 2.89 \times 10^{-21} \text{ J} = 1.93 \times 10^{-21} \text{ J}$$

Therefore, the average speed is given as

$$\bar{v} = \sqrt{\frac{2.55 \times 1.93 \times 10^{-21} \text{ J}}{6.7 \times 10^{-27} \text{ kg}}} = \sqrt{0.734 \times 10^6} \text{ ms}^{-1}$$

$$\bar{v} = 8.57 \times 10^2 = 857 \text{ms}^{-1}$$

3. If we consider that molecules are moving along the x-axis, their distribution function is given by Eq. (2.18):

$$f(v_x) dv_x = A \exp(-Bv_x^2) dv_x \qquad \text{(i)}$$

where $A = \sqrt{\frac{B}{\pi}}$ and $B = \frac{m}{2k_B T}$.

The average kinetic energy of molecules moving along x-axis is given by

$$\bar{E}_x = \frac{m}{2} \int_{-\infty}^{\infty} v_x^2 \, f(v_x) \, dv_x \qquad \text{(ii)}$$

On substituting for $f(v_x)$ from (i), this expression takes the form

$$\bar{E}_x = \frac{m}{2} \int_{-\infty}^{\infty} v_x^2 \, A \exp(-Bv_x^2) dv_x$$

$$= \frac{m}{2} \times 2A \int_{0}^{\infty} v_x^2 \exp(-Bv_x^2) dv_x \qquad \text{(iii)}$$

The integral on the RHS (with $n = 2$) is equal to $\dfrac{1}{2B^{3/2}} \Gamma_{3/2} = \dfrac{\sqrt{\pi}}{4B^{3/2}}$. On

using this result in (iii), we get

$$\overline{E}_x = \frac{mA\sqrt{\pi}}{4B^{3/2}} = m\left(\frac{m}{2\pi k_B T}\right)^{1/2} \frac{\sqrt{\pi}}{4}\left(\frac{2k_B T}{m}\right)^{3/2} = \frac{k_B T}{2}$$

This result is consistent with the **principle of equipartition of energy**.

4. We know that v_{rms} and v_p for a gas obeying Maxwell's law are

    respectively given by

    $$v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

    and $\quad v_p = \sqrt{\frac{2k_B T}{m}}$

    Here $v_{rms} - v_p = 100 \text{ ms}^{-1} = \sqrt{\dfrac{3k_B T}{m}} - \sqrt{\dfrac{2k_B T}{m}}$

    On squaring both sides, we get

    $$10000 \text{ m}^2\text{s}^{-2} = \frac{k_B T}{m}(\sqrt{3} - \sqrt{2})^2$$

    $$= \frac{k_B T}{m}(1.73 - 1.41)^2 = \frac{0.1 k_B T}{m}$$

    $\therefore \qquad T = \dfrac{m \times 10^4 \text{m}^2 \text{ s}^{-2}}{0.1 k_B}$

    For nitrogen

    $$m = \frac{28 \text{ kg kmol}^{-1}}{6.02 \times 10^{26} \text{kmol}^{-1}} = 4.65 \times 10^{-26} \text{ kg}$$

    $\therefore \qquad T = \dfrac{(4.65 \times 10^{-26} \text{kg}) \times 10^4 \text{m}^2 \text{s}^{-2}}{0.1 \times (1.38 \times 10^{-23} \text{ JK}^{-1})}$

    $\quad = 337 \text{K}$

5. a) Average velocity

    $$\overline{v}_x = \int\limits_{-\infty}^{\infty} v_x f(v_x) dv_x$$

    $$= A \int\limits_{-\infty}^{\infty} v_x e^{-Bv_x^2} dv_x$$

    Since the integral is an odd function of v_x, the integral will be zero.

    Hence,

    $$\overline{v}_x = 0$$

This result is expected for a system of particles in random motion.

b) On integrating both sides of Eq. (2.18) over v_x in the limits $-\infty$ to ∞, and setting the result equal to one, we can write

$$\int\limits_{-\infty}^{\infty} f(v_x)\,dv_x = A \int\limits_{-\infty}^{\infty} \exp\,(-Bv_x^2)\,dv_x = 1 \qquad \text{(i)}$$

We use the standard integral:

$$\int\limits_{-\infty}^{\infty} e^{-\alpha x^2}\,dx = \sqrt{\frac{\pi}{\alpha}} \qquad \text{(ii)}$$

Using this result in Eq. (i), we get
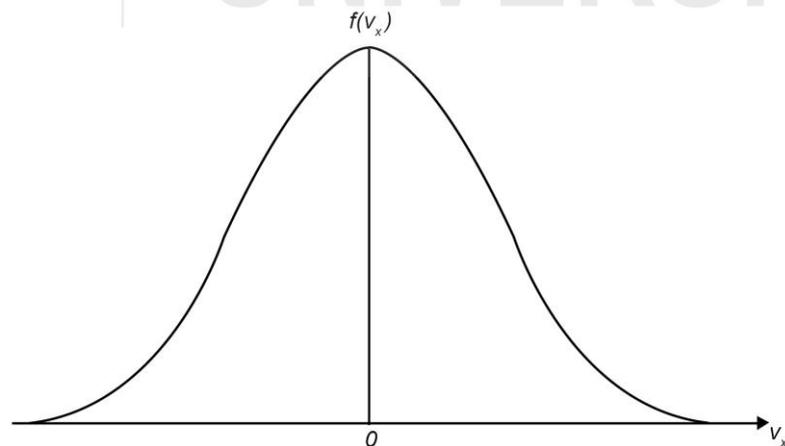
$$A = \sqrt{\frac{B}{\pi}} \qquad \text{(iii)}$$

Since $B = \sqrt{\dfrac{m}{2k_\text{B}T}}$, we get

$$A = \sqrt{\frac{m}{2\pi k_\text{B}T}} \qquad \text{(iv)}$$

So that

$$f(v_x)\,dv_x = \sqrt{\frac{m}{2\pi k_\text{B}T}}\,\exp\left(-\frac{mv_x^2}{2k_\text{B}T}\right)dv_x \qquad \text{(v)}$$

This result shows that the normalised velocity distribution is a Gaussian distribution, centred about mean velocity $\overline{v}_x$, which is zero since there is no preferred direction. It is shown in Fig. 2.8.

Fig. 2.8: **1-D Maxwell velocity distribution, which is Gaussian centred about** $\overline{v}_x = 0$.