

Block

1

KINETIC THEORY OF GASES

UNIT 1

Ideal and Real Gases

7

UNIT 2

Molecular Velocity Distribution Function

27

UNIT 3

Mean Free Path and Transport Phenomena

55

UNIT 4

Brownian Motion

79

Course Design Committee

Prof. A. K. Ghatak, *Retd.*
IIT Delhi,
New Delhi

Prof. Vijayshri
School of Sciences
IGNOU, New Delhi

Dr. Sanjay Gupta
School of Sciences
IGNOU, New Delhi

Prof. Suresh Garg, *Retd.*
School of Sciences
IGNOU, New Delhi

Prof. Sudip Ranjan Jha
School of Sciences
IGNOU, New Delhi

Dr. Subhalakshmi Lamba
School of Sciences
IGNOU, New Delhi

Prof. S. Gokhale
School of Sciences
IGNOU, New Delhi

Block Preparation Team

Prof. Suresh Garg (*Editor*)
Vice Chancellor
Usha Martin University, Ranchi

Dr. Sanjay Gupta (Units 1-4)
School of Sciences
IGNOU, New Delhi

Units 1 to 4 of this block are based on Block 1 of the course Thermodynamics and Statistical Mechanics (BPHE-106) of the earlier B.Sc. programme of IGNOU. Prof. Shubha Gokhale, School of Sciences, IGNOU had contributed in its preparation.

Course Coordinators: Dr. Sanjay Gupta, Dr. Subhalakshmi Lamba

Block Production Team

Sh. Sunil Kumar
AR (P), IGNOU

Acknowledgement: Shri Gopal Krishan Arora for CRC preparation. The images on pages 7 and 27 are taken from the following URLs: <https://pixabay.com/photos/industry-smoke-chimney-pollution-80956/> (Unit 1) and <https://pixabay.com/photos/astronomy-bright-constellation-dark-1867616/> (Unit 2).

June, 2020

© Indira Gandhi National Open University, 2020

ISBN:

Disclaimer: Any materials adapted from web-based resources in this module are being used for educational purposes only and not for commercial purposes.

All rights reserved. No part of this work may be reproduced in any form, by mimeograph or any other means, without permission in writing from the Copyright holder.

Further information on the Indira Gandhi National Open University courses may be obtained from the University's office at Maidan Garhi, New Delhi-110 068 or the official website of IGNOU at www.ignou.ac.in.

Printed and published on behalf of Indira Gandhi National Open University, New Delhi by Prof. Sujatha Verma, Director, SOS, IGNOU.

Printed at

CONTENTS

Block and Unit Titles	1
Credit page	2
Contents	3
THERMAL PHYSICS AND STATISTICAL MECHANICS: COURSE INTRODUCTION	5
BLOCK 1: Kinetic Theory of Gases	6
<u>Unit 1 Ideal and Real Gases</u>	<u>7</u>
1.1 Introduction	8
1.2 Assumptions of Kinetic Theory	9
1.3 Pressure Exerted by an Ideal Gas	10
1.3.1 Kinetic Interpretation of Temperature	11
1.3.2 Molecular Speeds	13
1.3.3 Deduction of Gas Laws	14
1.4 Deviations from Ideal Gas Behaviour	17
1.5 van der Waals' Equation of State	19
1.5.1 Comparison with Experimental Results	22
1.6 Summary	23
1.7 Terminal Questions	24
1.8 Solutions and Answers	24
<u>Unit 2 Molecular Velocity Distribution Function</u>	<u>27</u>
2.1 Introduction	28
2.2 Maxwell's Distribution Law	29
2.2.1 Assumptions	29
2.2.2 Velocity Distribution Function	30
2.2.3 Distribution Function for Molecular Speeds	34
2.2.4 Determination of Constants <i>A</i> and <i>B</i>	35
2.3 Some Useful Deductions from Maxwell's Law	40
2.3.1 Average Speed	40
2.3.2 Root Mean Square Speed	40
2.3.3 Most Probable Speed	41
2.4 Direct Experimental Verification of Maxwell's Law: Zartman and Ko Experiments	43
2.5 Law of Equipartition of Energy	44
2.5.1 Degree of Freedom	44
2.5.2 Heat Capacity of Gases	46
2.6 Summary	49

2.7	Terminal Questions	50
2.8	Solutions and Answers	50
<u>Unit 3 Mean Free Path and Transport Phenomena</u>		<u>55</u>
3.1	Introduction	56
3.2	Mean Free Path	57
3.2.1	Elementary Derivations	58
3.2.2	Distribution of Free Paths	63
3.3	Transport Phenomena	66
3.3.1	Viscosity: Transport of Momentum	66
3.3.2	Thermal Conductivity: Transport of Energy	69
3.3.3	Diffusion: Transport of Matter	71
3.4	Summary	72
3.5	Terminal Questions	73
3.6	Solutions and Answers	74
<u>Unit 4 Brownian Motion</u>		<u>79</u>
4.1	Introduction	80
4.2	Brownian Motion	81
4.3	Theoretical Analysis	82
4.4	Examples of Brownian Motion	84
4.4.1	Sedimentation	84
4.5	Determination of Avogadro Number	87
4.6	Summary	88
4.7	Terminal Questions	89
4.8	Solutions and Answers	89

Table of Physical Constants

List of Blocks and Units: BPHCT-135

Syllabus: Thermal Physics and Statistical Mechanics (BPHCT-135)

THERMAL PHYSICS AND STATISTICAL MECHANICS : COURSE INTRODUCTION

We know that under normal conditions, matter exists in three states: solids, liquids and gases. To gain knowledge of thermal properties of matter, we begin with understanding of the gaseous state. It marked the beginning of kinetic theory of matter. In Block 1, you will learn kinetic theory of gases, which, in conjunction with the laws of mechanics for individual molecules, helps us to know bulk properties of matter. You will realise that Kinetic theory has great aesthetic elegance.

In its manifestation as heat, energy is intimate to our existence. However, early physicists struggled with questions such as: What is heat? How can we specify the direction of flow of heat? and so on. Our quest to answer these and other related questions is contained in the subject of thermodynamics. This subject developed on phenomenological basis long before we knew the nature or behaviour of elementary constituents of matter such as electrons, atoms or molecules.

There are two distinct approaches to learn this subject. The traditional or classical approach is based on some postulates derived from experience. In our view, as a distance learner, you will find it easier to understand the subject following the formal approach based on postulates, which is illustrated in the second and third blocks of this course. Among others, Joule, Carnot, Clausius, Kelvin, Maxwell, Gibbs and Planck have contributed to the development of this subject.

The classical statistical mechanics evolved out of the efforts of Boltzmann. He supplemented purely statistical methods (considerations of probability) by the laws of (classical) mechanics for a large number of particles making up the system. With the advent of quantum mechanics, this subject got a new shape at the hands of Bose, Einstein, Fermi, Dirac and Fowler. You will learn it in Block 4 of this course.

We have explained some interesting physical phenomena encountered in the nature and certain mathematical concepts and techniques in Appendices of Units 7, 11 and 13 of this course for better understanding. **You will not be examined on the material given in these Appendices.**

In its present state, Thermal Physics is one of the most fascinating courses taught to undergraduate physics students. It finds use in material science, engineering, chemistry, quantum, atomic and molecular physics, spectroscopy and beyond. It provides ample opportunities to develop a sensibility towards nature; it is an essential part of physics education. Therefore, while a simplistic reading will enable you to understand the subject, more thoughtful study will bring extra rewards!

Our best wishes are with you!

BLOCK 1 : KINETIC THEORY OF GASES

In your school classes, you have learnt that Dalton established the law of partial pressures and explained the laws of chemical combination. This work provided much needed impetus to kinetic view point. In 1811, Avogadro's hypothesis was proposed. But it was not until 1859, when Maxwell showed that this result could be derived from kinetic theory, that physicists placed their confidence in this theory. Subsequent growth was due to pioneers like Joule, Clausius, Jeans and van der Waals.

Matter is not continuous in structure and its state is determined by the interplay of thermal energy and intermolecular forces. You will learn that macroscopic properties of gases such as pressure and temperature can be related to its microscopic properties such as speed and mass of its constituent atoms/molecules.

In Unit 1, we have reviewed the basic concepts of the kinetic theory of gases. You will learn how to apply them to obtain various gas laws and kinetic interpretation of temperature. You may be familiar with some of these concepts, but we have included these for the sake of completeness. You will also learn how elementary kinetic theory failed to explain the behaviour of real gases under different temperatures and pressures. A satisfactory explanation was provided by van der Waals. This work was so profound that Boltzmann considered van der Waals as 'Newton of real gases'. We know that gas molecules move randomly with all possible velocities; but it required the genius of Maxwell to derive the distribution function for spread of molecular velocities/speeds. You will learn about it in Unit 2. As a consequence of random motion of molecules, non-equilibrium conditions such as mass motion in a particular direction make a gas to undergo transport processes. You will learn about mean free path, coefficient of viscosity, thermal conductivity and diffusion coefficient in Unit 3.

The direct experimental evidence of molecular motion, which provided this theory a sound pedestal, came in the form of Brownian motion. In Unit 4, we have discussed Brownian motion, and its connection with random motion qualitatively. Physical examples of Brownian motion are also discussed here.

After going through this block, you will realize that kinetic theory has great aesthetic appeal. Very elegant laws governing the gaseous behaviour emerge out of chaotic motion of a large number of molecules. We urge upon you to read the block carefully and work out SAQs as well as TQs. Only then you will enjoy it.



The behaviour of real gases is different from ideal gases. You will learn the differences between these gases when you study this unit. (Picture source:

<https://pixabay.com/photos/industry-smoke-chimney-pollution-80956/>)

UNIT 1

IDEAL AND REAL GASES

Structure

- | | | | |
|-----|---------------------------------------|-----|--------------------------------------|
| 1.1 | Introduction | 1.4 | Deviations from Ideal Gas Behaviour |
| | Expected Learning Outcomes | 1.5 | van der Waals' Equation of State |
| 1.2 | Assumptions of Kinetic Theory | | Comparison with Experimental Results |
| 1.3 | Pressure Exerted by an Ideal Gas | 1.6 | Summary |
| | Kinetic Interpretation of Temperature | 1.7 | Terminal Questions |
| | Molecular Speeds | 1.8 | Solutions and Answers |
| | Deduction of Gas Laws | | |

STUDY GUIDE

In this unit, you will learn basic concepts of kinetic theory of gases and use the expression for pressure to obtain kinetic interpretation of temperature and deduce gas laws. The elementary kinetic theory fails to explain the behaviour of real gases under different temperatures and pressures. This problem was overcome by van der Waals. It is possible that you are familiar with some of these concepts from your +2 physics classes. In that case, you will find it easier to follow the content and begin your journey through this course on a positive note. Therefore, we would like you to refresh your earlier knowledge by referring to your school textbook. Then it will be a perfect launch pad into the core of kinetic theory.

“Life is a relationship between molecules.”

Linus Pauling

1.1 INTRODUCTION



Rudolf Julius Emmanuel Clausius (1822-1888) was a German physicist and mathematician who is considered to be one of the founders of kinetic theory of gases and thermodynamics. Beginning with his famous paper in 1850 entitled "On the mechanical theory of heat", he formulated the statements of first and second laws of thermodynamics. He interpreted the free heat of the system as the kinetic energy of gas molecules.

In your school science curriculum, you have learnt that matter is made up of atoms and a few atoms combine to form a molecule. A molecule is the smallest entity that can exist in free state and exhibit all characteristic properties of a substance. You may recall that these building blocks are identical in size, mass and chemical properties. When Clausius supplemented this hypothesis by laws of mechanics for molecular motion, a new area of knowledge – **the kinetic theory of gases** – was born. You may recall that elementary kinetic theory has been used successfully to explain even large-scale physical phenomena. Some of these include distribution of gases with altitude in the Earth's lower atmosphere and adiabatic lapse rate (which refers to the change in temperature of air as we move upwards), etc.

Broadly speaking, kinetic theory of gases is based on two basic postulates:

(i) Matter is made up of identical molecules, and (ii) thermal energy can be identified with molecular motion. Based on these postulates, a few assumptions are made about the nature of molecules, interactions among them and their movement. To describe this motion, simple laws of mechanics are used. This helps us to obtain elegant explanations of the laws governing the behaviour of ideal gases in equilibrium.

In Sec. 1.2, you will learn the assumptions of kinetic theory of gases. We have given justifications for their appropriateness as far as possible. In Sec. 1.3, you will learn an expression for the pressure exerted by a gas on the walls of a container and use it to correlate temperature with molecular properties. In particular, you will discover that *Absolute Zero* is that temperature at which all molecular motion ceases to exist. You will also apply this to deduce gas laws and calculate the magnitude of molecular speeds for different gases. These help us to explain the observed distribution of gases in our atmosphere. In Sec. 1.4, we have discussed the behaviour of real gases – how van der Waals' equation helps us in explaining their observed properties.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ discuss the basic assumptions of kinetic theory of gases;
- ❖ use the expression for pressure to deduce gas laws;
- ❖ interpret temperature in terms of molecular properties;
- ❖ discuss deviations shown by a real gas from an ideal gas behaviour; and
- ❖ explain how van der Waals' equation of state satisfactorily explains the behaviour of real gases.

To develop understanding of elementary kinetic theory, we first state its basic assumptions as a convenient starting point.

1.2 ASSUMPTIONS OF KINETIC THEORY

The basic assumptions of kinetic theory of ideal gases are:

1. **A gas consists of a very large number of identical molecules.** This assumption is quite justified. The number of molecules in a kilomole is 6.023×10^{26} . (This is commonly known as Avogadro number.) It means that 1 cm^3 of an ideal gas at standard temperature and pressure (STP) contains nearly 3×10^{19} molecules. (This number is almost six billion times the population of the world as of now.)
2. **The gas molecules can be regarded as point masses.** Experiments show that the diameter of a gas molecule is about $2 - 3 \times 10^{-10} \text{ m}$. The distance between any two neighbouring gas molecules at STP, on an average, is about $3 \times 10^{-9} \text{ m}$, which is an order of magnitude bigger than their diameter.
3. **The gas molecules are in a state of constant random motion.** This is shown in Fig. 1.1. (The motion of gas molecules resembles the motion of honeybees disturbed from their hive.) In essence, it means that molecules of an ideal gas can move in all possible directions and all positions are equally probable. The support for this assumption came from Brownian motion.

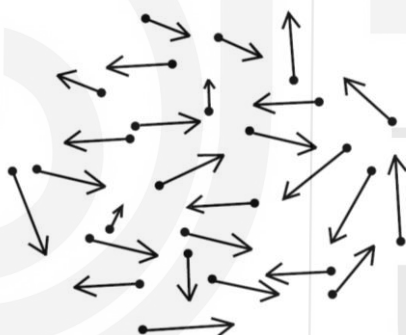


Fig. 1.1: Depiction of random motion of molecules of a gas.

4. **In the absence of any external force field, the molecules are distributed uniformly in the container.** It means that an ideal gas behaves as an isotropic medium. In practice, however, some randomness in the direction of the velocities may arise because of irregularities in the walls of the container.
5. **The molecules of a gas experience force only during collisions.** This assumption implies that there are no intermolecular forces (of mutual attraction) or any forces between the molecules and the walls of the container. That is, molecule of a gas can be thought of as moving about freely unaware of the presence of other molecules. It means that molecules of an ideal gas possess only kinetic energy.
6. **The molecules of a gas behave as perfectly elastic hard spheres.** It means that the molecules undergo perfectly elastic collisions, i.e. they do not deform in collisions among themselves or with the walls of the container.

Standard Temperature and Pressure (STP)

refer to commonly agreed sets of conditions under which experimental measurements are reported.

Internationally, two standards are in use: International Union of Pure and Applied Chemistry (IUPAC) and the National Institute of Standards and Technology (NIST). The IUPAC's standard refers to a temperature of 0°C (273.15 K) and an absolute pressure of 100 kPa (0.986 atm) while NIST's standard is a temperature of 20°C (293.15 K) and an absolute pressure of 101.325 kPa (1 atm). In this course, we shall use IUPAC standards, unless stated otherwise.

7. **The duration of collision is negligible compared to the time interval between successive collisions.**
8. **All molecules do not move with the same speed.** That is, there is a spread of molecular speeds about a mean value. This is depicted in Fig. 1.2. An indirect justification for this assumption lies in the finite width of spectral lines.
9. **All molecules move in a straight line between successive collisions. The authenticity of this assumption was validated by Brown.**

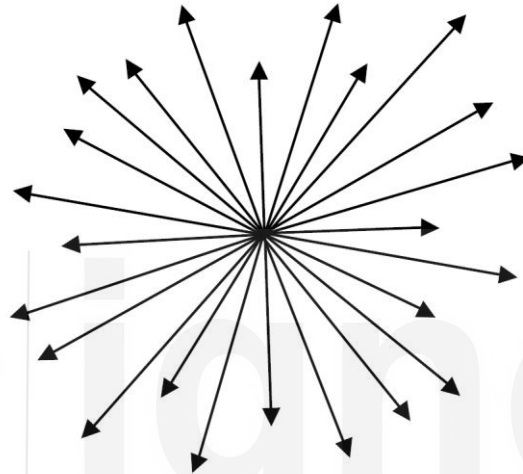


Fig. 1.2: Distribution of molecular velocities at a given temperature.

You now know the basic assumptions of kinetic theory of gases. Using these assumptions, an expression for pressure exerted by the molecules of a gas on the walls of a container can be derived. You must have learnt it in your school physics. So, we will just quote the result and use it to obtain gas laws and some other useful results. The correctness of its various predictions put faith in the kinetic theory model in its initial stages.

You may now like to answer the following SAQ.

***SAQ 1* – Validity of assumptions**

Write down the assumptions which are not justified for real gases.

1.3 PRESSURE EXERTED BY AN IDEAL GAS

Consider μ kilomole of a gas confined in a container (Fig. 1.3). For generality, we denote the total number of molecules in volume V by N . So we can say that there are $n(= N/V)$ molecules per m^3 . We assume that mass of each molecule is m . Since gas molecules are moving randomly with finite speeds, these will collide with the walls of the container and recoil. This will cause change in their momentum. Using Newton's second law of motion, it can be related to force and force exerted per unit area leads to following expression for pressure:

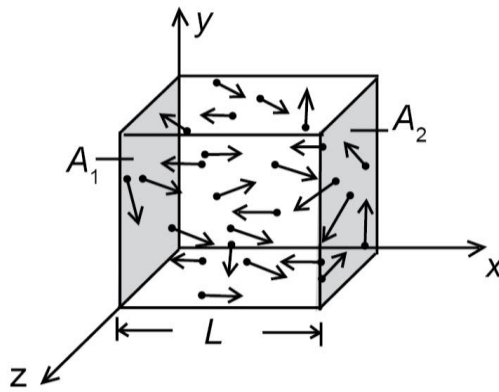


Fig. 1.3: Schematics of motion of molecules of a gas in a cubical container

$$\begin{aligned}
 p &= \frac{1}{3} mn\overline{v^2} \\
 &= \frac{1}{3V} mN\overline{v^2} = \frac{1}{3} \rho \overline{v^2}
 \end{aligned} \quad (1.1)$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

In the instant case,
Mass of gas = mN .

where $n = N/V$ is number density, ρ is density of the gas and $\overline{v^2}$ is mean square speed of gas molecules. This is an important result. You will note that it relates macroscopic properties (p and V) with the microscopic properties (m and v) of individual molecules making up the system. Moreover, it is independent of the shape of container.

Before proceeding further, we summarise the result of this section.

EXPRESSION FOR PRESSURE

The pressure exerted by the molecules of an ideal gas on the walls of the container is given by

$$p = \frac{1}{3} mn\overline{v^2} = \frac{1}{3} \rho \overline{v^2}$$

where m is the mass of a molecule, n is the number of molecules per cubic metre, ρ is the density of the gas and $\overline{v^2}$ is the mean square speed of gas molecules. Note that in this prescription, gas molecules are regarded as randomly moving point masses devoid of inter-molecular forces.



Don't forget!

You will agree that we started from a purely mechanical picture of a gas as a collection of randomly moving molecules. But we have obtained an expression for pressure in terms of the microscopic properties of individual molecules. Let us now discover kinetic interpretation of temperature and learn to use Eq. (1.1) to deduce gas laws.

1.3.1 Kinetic Interpretation of Temperature

To seek kinetic interpretation of temperature, we first rewrite Eq. (1.1) as

$$pV = \frac{2}{3} N \left(\frac{1}{2} m\overline{v^2} \right) = \frac{2}{3} N\epsilon \quad (1.2)$$

where $\varepsilon = \frac{1}{2} m \overline{v^2}$ is average kinetic energy of a gas molecule.

For one mole of a gas, N equals Avogadro's number, N_A . And from ideal gas equation, we recall that

$$pV = \mu RT$$

where $\mu = N/N_A$ is the number of kilomole of the gas, T is absolute temperature and R is *kilomolar gas constant*. Its value is $8314 \text{ J kmol}^{-1} \text{ K}^{-1}$. By combining ideal gas equation with Eq. (1.2), we can connect ε to temperature through the relation

$$\frac{2}{3} \mu N_A \varepsilon = \mu RT$$

or
$$\varepsilon = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} k_B T \quad (1.3)$$

In text books, Boltzmann constant is denoted by k .

$$1.6 \times 10^{-19} \text{ J} = 1 \text{ eV}$$

where $k_B = R/N_A$ is *Boltzmann constant*. Its value is $1.38 \times 10^{-23} \text{ JK}^{-1}$. At 300 K, kinetic energy of a molecule is about $6 \times 10^{-21} \text{ J}$ or 0.04 eV (see SAQ 2). Therefore, even if all this energy could be absorbed in a head-on collision between molecules moving in opposite directions, it is too small to increase the internal energy of either molecule. This justifies why it is reasonable to treat gas molecules as perfect hard spheres.

Note that in arriving at Eq. (1.3), we have connected a purely mechanical quantity – the average kinetic energy of a molecule – to temperature. This is a big step as it relates molecular (microscopic) and macroscopic viewpoints through Boltzmann constant. (In Block 4, you will learn that Boltzmann constant appears in the relation that bridges the statistical and the thermodynamic viewpoints for a system in equilibrium.) This assigns a completely new and deeper meaning to temperature:

- Temperature is linearly proportional to average (kinetic) energy of molecules of an ideal gas.
- At a given temperature, the (kinetic) energy of the molecules of all gases, irrespective of the differences in their masses, will be the same.
- The motion of gas molecules will become more vigorous as temperature increases. However, **at absolute zero of temperature, the gas molecules will be devoid of all motion**. So kinetic theory predicts that at absolute zero, all molecules will behave as if frozen in space. (In Block 4 on Statistical Mechanics, you will learn that due to quantum effects, a few typical systems possess finite energy even at absolute zero.)

Activity 1

We cannot see gas molecules. But to get a feel of increased molecular motion, observe the motion of potassium permanganate (KMnO_4) molecules in water kept in a glass beaker. As you heat water, motion of KMnO_4 molecules will gradually become more and more vigorous.

KINETIC INTERPRETATION OF TEMPERATURE

Temperature is linearly proportional to average (kinetic) energy of molecules. It means that the motion of gas molecules will become more lively as temperature increases. However, at absolute zero, all molecules will behave as if frozen in space, devoid of all motion.



Before proceeding further, you should solve the following SAQ.

SAQ 2 – Average kinetic energy of an ideal gas

Calculate the average kinetic energy of molecules of an ideal gas at STP.

Take $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$.

Do you think that we have developed a reliable model of gaseous state? As a first check of this model, let us use it to calculate the value of molecular speed. Thereafter, we shall calculate some other numbers of physical interests.

1.3.2 Molecular Speeds

To know how fast the molecules in a gas move, we equate expressions for kinetic energy expressed in terms of mean square speed and temperature as

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

so that

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

where $M = mN_A$ is molecular weight of the gas.

The square root of mean square speed is usually denoted as v_{rms} and is called **root mean square speed**. It is given by

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}} \quad (1.4)$$

From this expression we note that v_{rms} is inversely proportional to the molecular weight of a gas. It implies that at a given temperature, lighter gas molecules would move faster. For a few gases found in our atmosphere, the values of v_{rms} at STP are given in Table 1.1.

Table 1.1: Values of v_{rms} for different gases at 273 K

Gas	v_{rms} (ms ⁻¹)	Gas	v_{rms} (ms ⁻¹)
H ₂	1840	O ₂	450
He	1300	Ar	410
H ₂ O	615	CO ₂	393
N ₂	493	Benzene vapour	290
Air	485	Mercury vapour	180

The fact that lighter molecules move faster has an interesting consequence for existence of life on our planet. Gases like hydrogen, helium, nitrogen and water vapour move upward in the Earth's atmosphere, whereas oxygen and carbon dioxide are available near the Earth's surface. This provided an indirect evidence in favour of kinetic theory.

Further, from your school physics, you will recall that an object having radially outward velocity more than 11.2 km s^{-1} can escape from the influence of gravity of Earth. ($v_e = \sqrt{2gR}$, where R is radius of the Earth.) Since no gas molecule has speed greater than v_e , there is little chance of their escaping from the Earth instantaneously. For the Moon, Jupiter and the Sun, the values of escape velocity are 2.3 km s^{-1} , 60 km s^{-1} and 600 km s^{-1} , respectively. This explains why over a period of time, all gases have escaped from the surface of the Moon, whereas even hydrogen is held back by the Sun.

The ever widening ozone holes in the upper atmosphere over the North Arctic as well as Antarctica are together of the size of Australia and pose a serious threat to the existence of life on our planet.

The vertical distribution of gases in our atmosphere can also be used to understand the ill-effects of pollution of air and greenhouse effect caused by gases such as carbon monoxide and nitrogen oxide, which combine with atmospheric oxygen and get converted into carbon dioxide, chlorofluorocarbons (CFCs) and oxides of nitrogen. These chemicals are discharged by vehicular/air traffic, air conditioners and refrigerators in our atmosphere. This highlights why we should plant more trees and push for eco-friendly systems. Moreover, it is important to get our vehicles regularly checked for pollution. (In fact, in metropolitan cities, the central and state governments have made pollution check for all vehicles mandatory. Now-a-days, these agencies are recommending the use of CNG gas. But some experts are of the view that even the use of CNG is not devoid of harmful effects, since benzene vapour tends to stay close to the ground level. The emission standards for vehicles are also being reviewed periodically and Govt proposes to move to Bharat VI compliant vehicles.) In the upper layers of the atmosphere, these gases are breaking up ozone, which is so vital for absorbing ultraviolet radiations and stopping them from entering the biosphere.

The correct prediction of vertical distribution of gases in our atmosphere provided indirect but sound evidence in its favour and boosted the confidence of physicists in it. The next step was to deduce gas laws from the expression for pressure. You will now learn to deduce the gas laws.

1.3.3 Deduction of Gas Laws

By combining Eqs. (1.2) and (1.3) for a given mass of a gas, we can write

$$pV = Nk_B T \quad (1.5)$$

Since the right-hand side in the above relation will remain constant at a fixed temperature, we can write

$$pV = \text{constant} \quad (1.5a)$$

From this result we note that *pressure exerted by a given mass of a gas varies inversely with its volume, when temperature remains constant*. This is **Boyle's law**.

For constant volume, Eq. (1.5) implies that

$$\frac{p}{T} = \text{constant} \quad (1.5b)$$

That is, *at constant volume, pressure exerted by a given mass of a gas is directly proportional to its temperature.* This is **Gay-Lussac's law**.

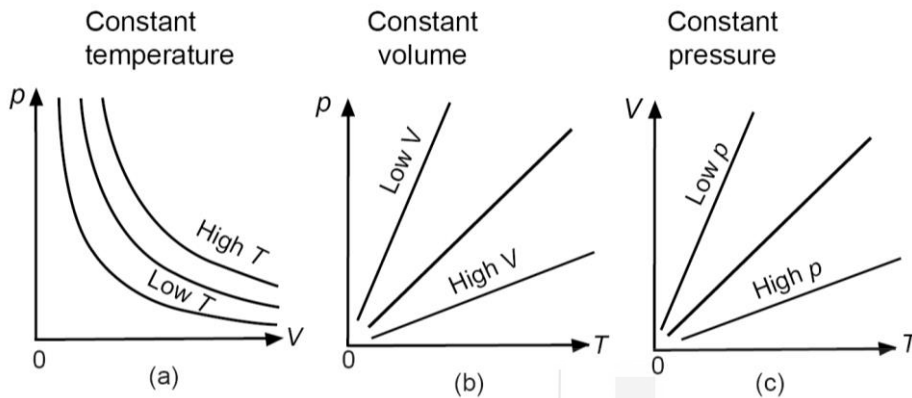


Fig. 1.4: Graphical depiction of a) Boyle's law; b) Gay-Lussac's law; c) Charles' law.

When pressure remains constant, Eq. (1.5) implies that

$$\frac{V}{T} = \text{constant} \quad (1.5c)$$

That is, *the volume of a given mass of a gas changes linearly with temperature.* This is **Charles' law**. Fig. 1.4 illustrates these three laws graphically.

Note that the straight lines in Figs. 1.4b and c seem to merge towards origin. The trend is only indicative, as absolute zero is unattainable. Therefore, these curves can be obtained only for finite values of temperature.

Note that these laws are strictly valid only for ideal gases.

Next, we consider two different gases at the same temperature and pressure. Then, from Eq. (1.1) we can write

$$\begin{aligned} p &= \frac{1}{3} m_1 n_1 \overline{v_1^2} \\ &= \frac{1}{3} m_2 n_2 \overline{v_2^2} \end{aligned} \quad (1.6)$$

where $\overline{v_1^2}$ and $\overline{v_2^2}$ are respectively the mean squared speeds of the molecules of two gases.

Recall that at constant temperature, the mean kinetic energies of both gases will be equal. So, we can write

$$\frac{1}{2} m_1 \overline{v_1^2} = \frac{1}{2} m_2 \overline{v_2^2}$$

On combining this result with Eq. (1.6), we get

$$n_1 = n_2 \quad (1.7)$$

This is mathematical statement of **Avogadro's law**, which states that *at constant temperature and pressure, equal volume of all gases contains the same number of molecules.*

Before proceeding further, you should answer the following SAQ.

SAQ 3 – Gas laws

When we blow air in a balloon, both pressure and volume increase simultaneously. Does it violate Boyle's law? Explain.

To get a feel of these results you should go through the following example carefully.

EXAMPLE 1.1: DENSITY OF A GAS

Calculate the number density of oxygen at $1 \text{ atm} = 1.013 \times 10^5 \text{ Nm}^{-2}$ and $T = 300 \text{ K}$. Also calculate its density using the data given in Table 1.1. Take $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$.

SOLUTION ■ By combining Eq. (1.1) with the equation of state for an ideal gas, we can write

$$p = \frac{1}{3} mn \overline{v^2} = nk_B T$$

so that

$$n = \frac{p}{k_B T}$$

On substituting the given numerical values, we get

$$\begin{aligned} n &= \frac{1.013 \times 10^5 \text{ Nm}^{-2}}{(1.38 \times 10^{-23} \text{ JK}^{-1}) \times (300 \text{ K})} \\ &= \frac{1.013 \times 10^{26}}{4.14} \text{ m}^{-3} = 2.45 \times 10^{25} \text{ m}^{-3} \end{aligned}$$

Using the value of $\overline{v^2}$ given in Table 1.1, we can write

$$\rho = \frac{3p}{\overline{v^2}} = \frac{3 \times 1.013 \times 10^5 \text{ Nm}^{-2}}{(450 \text{ ms}^{-1})^2} = 1.5 \text{ kg m}^{-3}$$

You will agree that motion of extremely large number of molecules can be described in terms of simple laws which can be verified by experiments up to a fairly reasonable degree of correctness. The remarkable elegance of kinetic theory brings out its aesthetic appeal. The success proved an important milestone in the growth of the kinetic theory. However, this theory was put to litmus test when it was applied to real gases.

1.4 DEVIATIONS FROM IDEAL GAS BEHAVIOUR

You now know that ideal gas model is simple and widely applicable. However, it does not hold universally. The concept of ideal gas breaks down for common gases at high pressures and low temperatures. That is, *the ideal gas equation does not apply at high pressures and low temperatures*. Another major drawback of ideal gas model is its inability to predict liquefaction of gases, which is technologically important. You will now definitely like to know the reasons responsible for these limitations. The following paragraphs will serve this purpose.

1. **Regnault's Experiments:** Regnault performed a series of experiments by applying pressure up to 30 atmosphere and varying the temperature from 273 K to 373 K. His results for hydrogen, oxygen, nitrogen and carbon dioxide for $T = 273\text{K}$ and pressure in the range 0-10 atm are shown in Fig. 1.5, where we have plotted pV as a function of p . The straight line (dotted curve) parallel to the p -axis corresponds to a perfect gas. On closely examining the curves, you will note that for real gases:

- The curves are straight lines inclined to the p -axis.
- The product pV increases with p for hydrogen and decreases for nitrogen, oxygen and carbon dioxide.
- All the curves converge to the same point ($2.271 \times 10^3 \text{ J mol}^{-1}$) on the pV -axis at 273 K. This value corresponds to $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ for $T = 273 \text{ K}$. This is the accepted value of Universal gas constant. Therefore, we can say that real gases deviate from perfect gas behaviour, except for $p \rightarrow 0$.

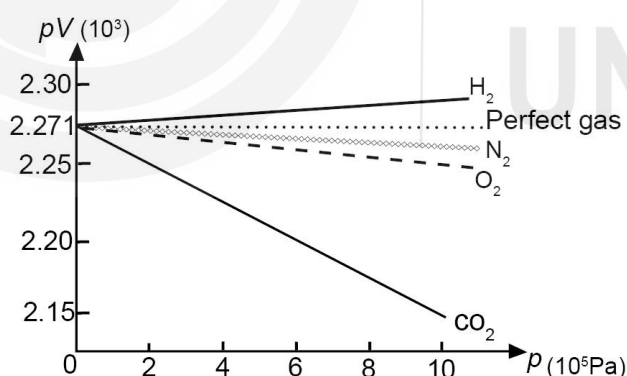


Fig. 1.5: Variation of pV versus p for hydrogen, oxygen, nitrogen and carbon dioxide in the range 0-10 atm. The dotted horizontal line indicates the values for an ideal gas.

2. **Andrews' Experiments:** Andrews carried out detailed experiments on the compressibility of gases while trying to liquefy them. For CO_2 , his results are shown on the p - V diagram at various temperatures in Fig. 1.6. We can draw the following conclusions:

- At 321 K and above, the behaviour of CO_2 resembles that of a perfect gas.

- ii) At 304.4 K, a kink appears in the isotherm. It signifies that CO₂ gas has begun to condense. The point *P* is called point of inflexion.
- iii) At 294.5 K, the kink has spread into a horizontal line. It signifies coexistence of liquid and gaseous phases. Physically, it implies a discontinuous change in the density of the material for a particular range of values of pressure and temperature.
- iv) For $T < 294.5$ K, this trend continues.

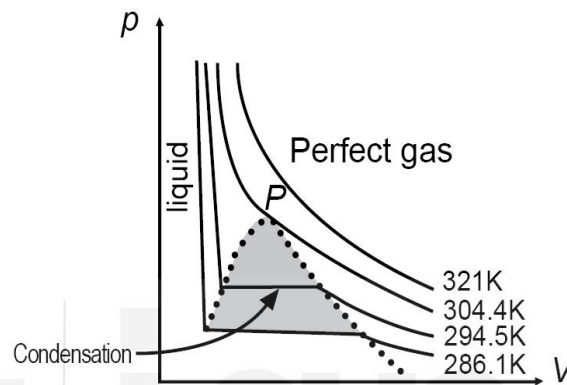


Fig. 1.6: Andrews' curves for CO₂.

The set of values of temperature (T_c) and pressure (p_c) at the point of inflexion are called **critical values**.

You may ask: Are the gaseous and liquid phases identical at this point? Note that the dotted curve in Fig. 1.6 passes through the extremities of horizontal portions of different isotherms indicating vapour state on the right and liquid state on the left. The area within the dotted curve marks co-existence of vapour – liquid phase in equilibrium.

The values of T_c and p_c for some common gases are given in Table 1.2.

You will note that each gas has its characteristic critical temperature and pressure. Furthermore, the pressure required for liquefaction is less for a gas having lower value of critical temperature.

Table 1.2: Critical temperature and pressure for some common gases

Gas	T_c (K)	p_c (10^5 Pa)
He	5.2	2.3
H ₂	33	13
Ar	151	49
O ₂	155	51
CO ₂	304	74
NH ₃	405	113

Critical temperature (T_c): of a gas is defined as that temperature below which the gas can be liquefied by the application of pressure alone. Above the critical temperature, the gas cannot be liquefied howsoever large the applied pressure may be.

Critical pressure (p_c): is the pressure applied to the gas at its critical temperature so that it gets liquefied.

From Fig. 1.6, we can say that

- a) A gas can be liquefied only if it is cooled up to or below its characteristic critical temperature. It is therefore clear that the increase in pV for hydrogen observed by Regnault (Fig. 1.5) arises because its critical temperature is much below the room temperature.
 - b) There exists a continuity of liquid and gaseous states. That is, these are two distinct stages of a continuous physical phenomenon. It means that it is possible to move from the gas to the liquid phase by compressing the gas to a high pressure and then cooling it gradually.
3. Amagat and other experimentalists investigated the behaviour of several gases at various temperatures and up to 3000 atm pressure. Their work lent support to the findings of Regnault and Andrews.

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

REAL GASES

Recap

The work of Andrews, Regnault, Amagat and other experimental physicists on real gases showed that

- Real gases do not obey ideal gas equation of state, except for low pressures.
- It is easier to liquefy a gas at lower temperatures. No liquefaction can occur above critical temperature, however high the pressure may be.
- Compression promotes liquefaction.

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

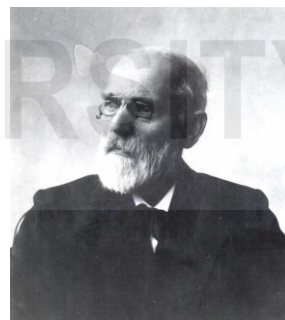
SAQ 4 – Liquefaction of gases

In Table 1.2 we have given values of T_c and p_c for some common gases. Which of these gases cannot be liquefied by compression alone at room temperature?

So far, we have discussed the observed behaviour of a few gases under different conditions of temperature and pressure. A satisfactory theoretical explanation of these results was provided by van der Waals.

1.5 VAN DER WAALS' EQUATION OF STATE

In order to explain experimental results, theoretical physicists revisited the assumptions of elementary kinetic theory with a view to modify the ideal equation of state. Accordingly, several equations of state were put forward to describe the behaviour of real gases. But the most elegant effort in this



Johannes Diderik van der Waals (1837 – 1923) was a Dutch theoretical physicist. He is credited for his equation of state to understand the behaviour of real gases, concept of molecular size and intermolecular forces. He received the Nobel Prize in 1910 for this work.

direction was made by van der Waals. He made reasonable assumptions regarding the size of gas molecules and nature of intermolecular forces. It is therefore pertinent to first know the assumptions made by him.

Assumptions

1. Gas molecules have finite size and behave as incompressible rigid spheres.
2. Gas molecules attract each other with a weak force which is a function of distance between them. (This implies that molecules of a real gas have kinetic as well as potential energies.) However, only nearest neighbour interactions are important.
3. The number of collisions with the walls of the container remain the same for point and finite size molecules.

For one mole of the gas, he obtained the following equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (1.8)$$

This equation is known as **van der Waals' equation of state**. The constants a and b are known as van der Waals' constants. Their values are assumed to depend only on the nature of the gas. For some common gases, we have listed the values of van der Waals' constants in Table 1.3. (a/V^2) is termed as cohesive pressure and arises due to presence of inter-molecular interactions.

Table 1.3: van der Waals' Constants for Some Common Gases

Gas	a ($10^{-6} \text{ atm m}^6 \text{ mol}^{-2}$)	b ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$)
H ₂	0.244	26.6
He	0.034	23.7
N ₂	1.39	39.1
O ₂	1.36	31.8
Ar	1.35	32.2
Ne	0.210	17.1
H ₂ O	5.46	30.5
NH ₃	4.17	37.1
CO ₂	3.59	42.7
CH ₄	2.25	42.8

A p - V diagram is also referred to as an indicator diagram.

For μ moles of the gas, van der Waals' equation takes the form

$$\left(p + \frac{\mu^2 a}{V^2}\right)(V - \mu b) = \mu RT \quad (1.9)$$

Note that for a rarefied gas, $p \gg a/V^2$ and $V \gg \mu b$, van der Waals' equation

reduces to the equation of state for an ideal gas. For a given temperature, plot of Eq. (1.8) on the indicator diagram is shown in Fig. 1.7. The contribution of self-attracting term is shown separately.

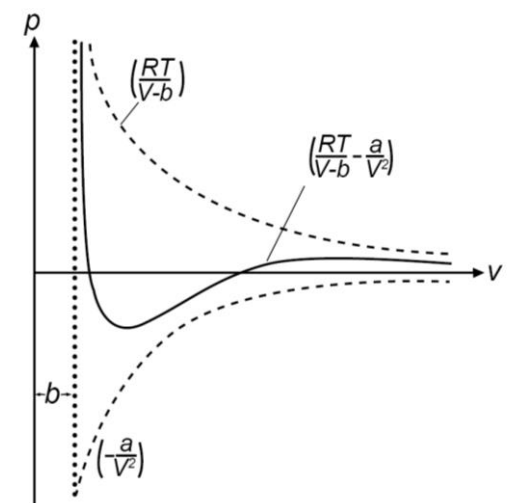


Fig. 1.7: Plot of Eq. (1.8) on p - V diagram.

We now give a solved example. It should give you an idea about the magnitude of various terms occurring in Eq. (1.8). You should go through it carefully.

EXAMPLE 1.2: VAN DER WAALS' EQUATION

One mole of CO_2 occupies 192 cm^3 at 32.5°C and 70 atm . Calculate the pressure exerted by CO_2 molecules, if we assume that it obeys (i) perfect gas equation, and (ii) van der Waals' equation. Given $a = 3.59 \times 10^{-6} \text{ atm m}^6 \text{ mol}^{-2}$, $b = 42.7 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ and $R = 8.2 \times 10^{-5} \text{ atm m}^3 \text{ K}^{-1} \text{ mol}^{-1}$.

SOLUTION ■ Volume of $\text{CO}_2 = 192 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$,
 $T = 273 + 32.5 = 305.5 \text{ K}$

i) In case CO_2 behaves as a perfect gas, we have

$$p = \frac{RT}{V} = \frac{(8.2 \times 10^{-5} \text{ atm m}^3 \text{ K}^{-1} \text{ mol}^{-1}) \times (305.5 \text{ K})}{(192 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})} = 131 \text{ atm}$$

ii) If CO_2 obeys van der Waals equation, the pressure exerted by CO_2 molecules is given by

$$p = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{(8.2 \times 10^{-5} \text{ atm m}^3 \text{ K}^{-1} \text{ mol}^{-1}) \times (305.5 \text{ K})}{(192 \times 10^{-6} - 42.7 \times 10^{-6}) \text{ m}^3 \text{ mol}^{-1}} - \frac{3.59 \times 10^{-6} \text{ atm m}^6 \text{ mol}^{-2}}{(192 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})^2} = 70.4 \text{ atm}$$

You will note that in this case, (a) the pressure calculated for a van der Waals' gas is close to the observed value of 70 atm , and (b) it is much less than that calculated by assuming CO_2 to be an ideal gas. It means that the cohesive pressure and co-volume account for nearly 60.6 atm .

Before proceeding further, we recapitulate what you have learnt about it so far.

Recap

VAN DER WAALS' EQUATION

- van der Waals modified the ideal gas assumptions on the size of molecules and inter-molecular forces.
- Based on these assumptions, for one mole of the gas he obtained the equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

where a and b are constant for a gas.

- b is referred to as **co-volume**.
- Due to intermolecular forces, the pressure exerted by the molecules of a real gas is less than that exerted by an ideal gas. This drop is known as **cohesive pressure**.

1.5.1 Comparison with Experimental Results

We now discuss how van der Waals' equation explains experimental results. To do so, we first rewrite Eq. (1.8) as

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \quad (1.10)$$

In expanded form, this equation can be rewritten as

$$pV^3 - (pb + RT)V^2 + a(V - b) = 0 \quad (1.11)$$

From this we note that:

1. van der Waals' equation is cubic in V . It means that for given values of p and T , V will have three values, which become equal at the point where condensation begins ($T = T_c$).
2. For large values of V , p would be small and van der Waals' equation reduces to an ideal gas equation. On the other hand, when $V \rightarrow b$ for finite temperatures, $p \rightarrow \infty$. Further, V cannot be less than b as this will lead to negative values of p , which is physically unacceptable. Obviously, a gas cannot occupy volume less than that of molecules, which are assumed to be incompressible rigid hard spheres.
3. For CO_2 , the plot of theoretical curves obtained on the basis of van der Waals' equation at various temperatures is shown in Fig. 1.8. Note that the qualitative shape of the curves resembles the experimental isotherms of Andrews (Fig. 1.6). However, there are differences in details, particularly at low temperatures. For instance, van der Waals' equation predicts wave-like pattern in the straight-line region of Andrews' curves obtained for $T \leq 294.5$ K. This is depicted as shaded portion in this figure. For $T = 286.1$ K, the portions AB and FG respectively represent gaseous and liquid states. However, the portion BC represents supersaturated

vapour and portion EF represents a superheated liquid. These correspond to meta-stable states and are not observed in the experimental results obtained by Andrews, which represent only the states of stable equilibrium. The portion CDE of the theoretical curve indicates that as we move from the state of supersaturated vapour towards superheated liquid, the volume and pressure decrease simultaneously. This corresponds to a *collapsible state*, which is unnatural and can never be realised in practice.

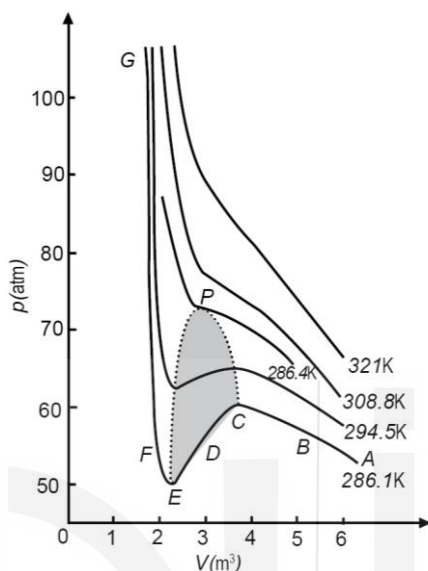


Fig. 1.8: Theoretical isotherms for CO_2 .

We thus find that proper interpretation of van der Waals' curves helps to resolve the apparent discrepancy with observed results.

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

1.6 SUMMARY

Concept	Description
Pressure exerted by gas molecules	<ul style="list-style-type: none"> The pressure exerted by the molecules of a gas on the walls of a container is given by $p = \frac{1}{3} mn\overline{v^2} = \frac{1}{3} \rho \overline{v^2}.$
Root mean square speed	<ul style="list-style-type: none"> The root mean square speed of a gas molecule is given by $v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}}$ <ul style="list-style-type: none"> At absolute zero temperature, gas molecules are devoid of all motion.
Van der Waals' equation for real gases	<ul style="list-style-type: none"> Ideal gas equation fails to explain observed behaviour of real gases, except at low temperatures. van der Waals' equation of state for one mole of a real gas is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

- Here (a / V^2) arises due to the presence of intermolecular interactions and is called cohesive pressure. b is known as co-volume and has its origin in the finite size of the gas molecules.
- van der Waals' equation reduces to perfect gas equation at low pressures.

1.7 TERMINAL QUESTIONS

1. Calculate v_{rms} for helium atoms at 300K. At what temperature will oxygen molecules have the same value of v_{rms} ?
Take $m_{He} = 6.67 \times 10^{-27}$ kg.
2. A cubical box of side 0.1 m contains 3×10^{22} molecules of a gas at 300 K. Calculate the average pressure exerted by it on the walls of the cube.
3. Calculate the temperature at which the root mean square speed of hydrogen and oxygen molecules will be equal to their escape velocities from the Earth's gravitational field. The radius of the Earth is 6400 km.

$$N_A = 6 \times 10^{26} \text{ mol}^{-1}, \quad g = 9.8 \text{ ms}^{-2}, \quad k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

4. Calculate the average kinetic energy of neutrons at 300 K. Take the mass of the neutron as 1.675×10^{-27} kg.
5. 210 g of N_2 gas at 8 atm pressure occupies $24 \times 10^{-3} \text{ m}^3$ of volume. Assuming that the gas obeys van der Waals' equation of state with $a = 1.39 \times 10^{-6} \text{ atm m}^6 \text{ mol}^{-2}$ and $b = 39.1 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$, calculate its temperature.

1.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. The assumptions made about point size of molecules and lack of intermolecular attraction will not be valid for real gases. The equation of state for real gases is more accurately described by van der Waals' equation.
2. We know that the average kinetic energy of a molecule is given by

$$\begin{aligned} \varepsilon &= \frac{3}{2} k_B T = \frac{3}{2} \times (1.38 \times 10^{-23} \text{ JK}^{-1}) \times 300 \text{ K} \\ &= 6.21 \times 10^{-21} \text{ J} = 3.88 \times 10^{-2} \text{ eV} = 39 \text{ meV} \end{aligned}$$

$$\text{since } 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J.}$$

3. Boyle's law is not violated because in this case the mass of the gas does not remain constant inside the balloon.
4. We know that a gas can be liquefied by compression when its temperature is below its critical temperature. So, we cannot liquefy helium, argon, hydrogen and oxygen at room temperature.

Terminal Questions

1. We know that

$$v_{rms}(\text{He}) = \sqrt{\frac{3k_B T}{m_{\text{He}}}}$$

On inserting the numerical data, we get

$$\begin{aligned} v_{rms} &= \sqrt{\frac{3 \times (1.38 \times 10^{-23} \text{ JK}^{-1}) \times (300 \text{ K})}{6.67 \times 10^{-27} \text{ kg}}} \\ &= 1365 \text{ ms}^{-1} \end{aligned}$$

You can also write

$$\begin{aligned} 1 &= \frac{v_{rms}(\text{O}_2)}{v_{rms}(\text{He})} \\ &= \sqrt{\frac{T_{\text{O}_2}}{M_{\text{O}_2}} \times \frac{M_{\text{He}}}{T_{\text{He}}}} \end{aligned}$$

so that the temperature at which the root mean square speed of oxygen will become equal to that of helium is given by

$$\begin{aligned} T_{\text{O}_2} &= \frac{M_{\text{O}_2} T_{\text{He}}}{M_{\text{He}}} = \frac{8 M_{\text{He}} T_{\text{He}}}{M_{\text{He}}} \\ &= 8 T_{\text{He}} = 2400 \text{ K} \end{aligned}$$

2. Here $N = 3 \times 10^{22}$ molecules, $T = 300 \text{ K}$ and $V = 10^{-3} \text{ m}^3$. On inserting these values in the ideal gas equation

$$p = \frac{N}{V} k_B T$$

we get

$$\begin{aligned} p &= \frac{3 \times 10^{22}}{10^{-3} \text{ m}^3} \times (1.38 \times 10^{-23} \text{ JK}^{-1}) \times (300 \text{ K}) \\ &= 1.24 \times 10^5 \text{ Nm}^{-2} \end{aligned}$$

3. The average kinetic energy of a gas molecule of mass m and moving with root mean square speed, v_{rms} is equal to $\frac{1}{2} m \overline{v^2}$ or $\frac{3}{2} k_B T$. We know that the escape velocity from the surface of the Earth is given by

$$v_{es} = \sqrt{2gR_0}$$

where g is acceleration due to gravity and R_0 is the radius of the Earth.

Since kinetic energy of a molecule moving with escape velocity will be equal to $\frac{1}{2} m v_{es}^2$ we can write

$$\frac{3}{2} k_B T = mgR_0$$

so that $T = \frac{2}{3} \frac{mgR_0}{k_B}$

a) For hydrogen molecules

$$T_{\text{H}_2} = \frac{2}{3} \frac{m_{\text{H}_2} g R_0}{k_B}$$

$$\text{Here } m_{H_2} = \frac{2}{N_A} = \frac{2}{6 \times 10^{26}} \text{ kg, } g = 9.8 \text{ ms}^{-1}, R_0 = 6.4 \times 10^6 \text{ m}$$

$$\text{and } k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}.$$

$$\therefore T_{H_2} = \frac{2}{3} \times \left(\frac{2}{6 \times 10^{26}} \text{ kg} \right) \times \left(\frac{(9.8 \text{ ms}^{-2}) \times (6.4 \times 10^6 \text{ m})}{1.38 \times 10^{-23} \text{ JK}^{-1}} \right) = 1.1 \times 10^4 \text{ K}$$

b) For oxygen molecules

$$\begin{aligned} T_{O_2} &= \frac{2}{3} \frac{m_{O_2} g R_0}{k_B} = \frac{2}{3} \times \frac{16 m_{H_2}}{k_B} g R_0 = 16 T_{H_2} \\ &= 1.62 \times 10^5 \text{ K} \end{aligned}$$

4. The average kinetic energy of an ideal gas molecule is given by

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

We consider that assembly of neutrons behaves as an ideal gas.

Therefore, on substituting the values of $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$ and

$T = 300 \text{ K}$, we get

$$\varepsilon = \frac{3 \times 1.38 \times 10^{-23} \times 300}{2} = 6.21 \times 10^{-21} \text{ J} = 0.04 \text{ eV}$$

Such neutrons are known as thermal neutrons and are very effective in inducing fission reaction in isotopes of uranium and plutonium. A controlled fission reaction is used to produce electricity in a nuclear power plant. Nuclear energy also finds important uses in agriculture, industry and medicine, among others.

5. Since mass of the gas taken is 210 g and its molecular weight is 28, the number of moles is $210 \text{ g} / 28 \text{ g} = 7.5$.

Volume of the gas $V = 24 \times 10^{-3} \text{ m}^3$

External pressure $p = 8 \text{ atm}$

Now, van der Waals' equation of state for μ moles reads

$$\left(p + \frac{\mu^2 a}{V^2} \right) (V - \mu b) = \mu R T$$

We rewrite it as

$$T = \frac{1}{\mu R} \left(p + \frac{\mu^2 a}{V^2} \right) (V - \mu b)$$

Substituting various values, we get

$$\begin{aligned} T &= \left(\frac{1}{7.5 \text{ mol} \times (8.2 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1} \text{ K}^{-1})} \right) \times \\ &\quad \left(8 \text{ atm} + \frac{(7.5)^2 \text{ mol}^2 \times (1.39 \times 10^{-6} \text{ atm m}^6 \text{ mol}^{-2})}{(24 \times 10^{-3} \text{ m}^3)^2} \right) \times \\ &\quad (24 \times 10^{-3} \text{ m}^3 - 7.5 \text{ mol} \times 39.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \\ &= 313.2 \text{ K} \end{aligned}$$



UNIT 2

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

- | | | |
|-----|--|---|
| 2.1 | Introduction | Root Mean Square Speed |
| | Expected Learning Outcomes | Most Probable Speed |
| 2.2 | Maxwell's Distribution Law | 2.4 Direct Experimental Verification of Maxwell's Law |
| | Assumptions | 2.5 Law of Equipartition of Energy |
| | Velocity Distribution Function | Degree of Freedom |
| | Distribution Function for Molecular Speeds | Heat Capacity of Gases |
| | Determination of Constants A and B | 2.6 Summary |
| 2.3 | Some Useful Deductions from Maxwell's Law | 2.7 Terminal Questions |
| | Average Speed | 2.8 Solutions and Answers |

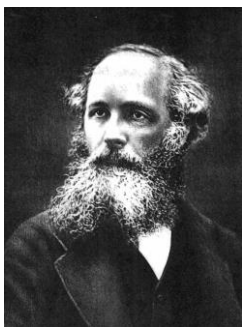
STUDY GUIDE

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



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.

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 ms^{-1} and 461 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.

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 $d\vec{v}$ is an infinitesimal volume element.

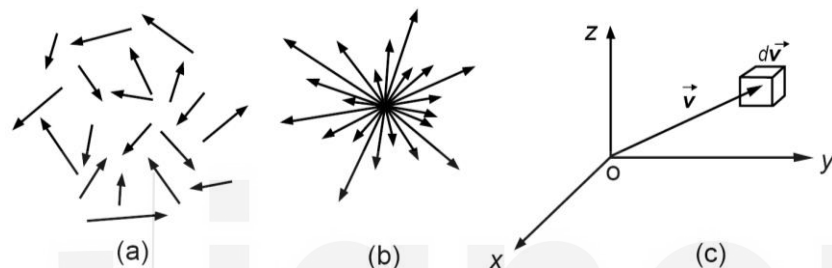


Fig. 2.1: a) Gas molecules in random motion; b) all velocity vectors transferred to a common origin; c) a volume element $d\vec{v}$ in velocity space for a molecule of velocity \vec{v} .

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{v} of a particle by v_x, v_y and v_z . Therefore, in terms of these three rectilinear components, we can write

$$v^2 = v_x^2 + v_y^2 + v_z^2 \quad (2.1)$$

The number of velocity vectors ending in element $d\vec{v} = dv_x dv_y dv_z$ gives the average number of molecules whose velocities lie between given limits \vec{v} and $\vec{v} + d\vec{v}$ 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

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

$$\text{or} \quad dN_{v_x} = Nf(v_x) dv_x \quad (2.2)$$

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, $\frac{dN_{v_x}}{N}$ 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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned} \frac{\partial f(v_x)}{\partial v_x} dv_x f(v_y) f(v_z) + f(v_x) \frac{\partial f(v_y)}{\partial v_y} f(v_z) dv_y \\ + f(v_x) f(v_y) \frac{\partial f(v_z)}{\partial v_z} dv_z = 0 \end{aligned} \quad (2.10)$$

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

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

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

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

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 $2B$. (You will soon realise that the factor 2 with B simplifies mathematical steps.)

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

$$\begin{aligned} \left[\frac{1}{f(v_x)} \frac{\partial f(v_x)}{\partial v_x} + 2Bv_x \right] dv_x + \left[\frac{1}{f(v_y)} \frac{\partial f(v_y)}{\partial v_y} + 2Bv_y \right] dv_y \\ + \left[\frac{1}{f(v_z)} \frac{\partial f(v_z)}{\partial v_z} + 2Bv_z \right] dv_z = 0 \end{aligned} \quad (2.13)$$

We now choose the constant B such that

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

Then Eq. (2.13) reduces to

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

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

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned}
 d^3N_{v_x v_y v_z} &= NA^3 e^{-B(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \\
 &= NA^3 e^{-Bv^2} dv_x dv_y dv_z
 \end{aligned}
 \tag{2.21}$$

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

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

where $d^3v = dv_x dv_y dv_z$ 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.

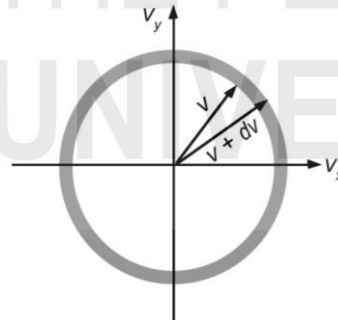


Fig. 2.2: A spherical shell of radius v and thickness dv .

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 $dv_x dv_y dv_z$ in terms of spherical polar coordinates. So we put $dv_x dv_y dv_z = v^2 \sin\theta d\theta d\phi dv$ and replace $d^3N_{v_x v_y v_z}$ 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

$$\begin{aligned}
 dN_v &= \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} NA^3 e^{-Bv^2} v^2 \sin\theta d\theta d\phi dv \\
 &= NA^3 v^2 e^{-Bv^2} [(-\cos\pi + \cos 0) 2\pi] dv = 4\pi NA^3 v^2 e^{-Bv^2} dv
 \end{aligned}
 \tag{2.23}$$

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.

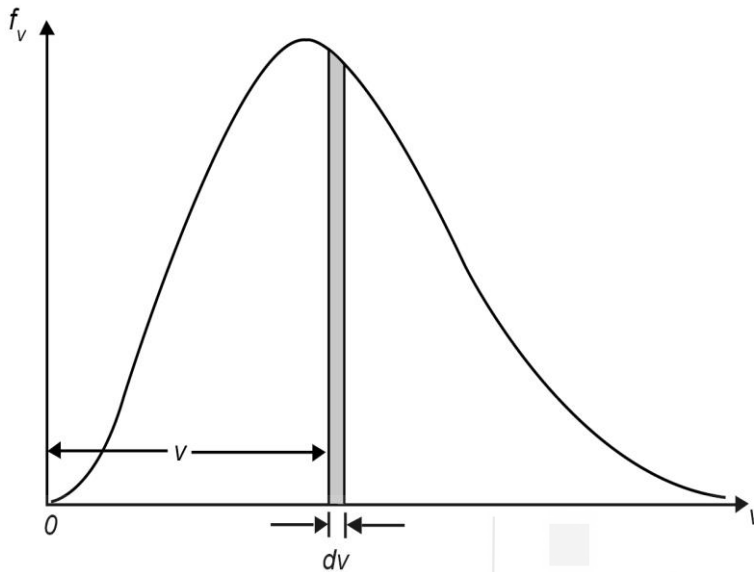


Fig. 2.3: A plot of Maxwellian distribution function versus molecular speed.

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:

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

The value of the integral

$$\int_0^{\infty} e^{-Bv^2} v^n dv = \frac{1}{2B^{(n+1)/2}} \Gamma\left(\frac{n+1}{2}\right)$$

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:

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

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

$$N = 4\pi NA^3 \frac{1}{2B^{3/2}} \int_0^{\infty} e^{-x} x^{1/2} dx \quad (i)$$

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

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

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 :

$$A = \sqrt{B/\pi} \quad (2.26)$$

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

$$\overline{v^2} = \frac{\int_0^{\infty} v^2 dN_v}{\int_0^{\infty} dN_v} \quad (2.27)$$

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

$$\overline{v^2} = \frac{\int_0^{\infty} 4\pi NA^3 e^{-Bv^2} v^2 \cdot v^2 dv}{\int_0^{\infty} 4\pi NA^3 e^{-Bv^2} v^2 dv} = \frac{\int_0^{\infty} v^4 e^{-Bv^2} dv}{\int_0^{\infty} v^2 e^{-Bv^2} dv}$$

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

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

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

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

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

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

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

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

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

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

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, $f_v = \frac{dN_v}{dv}$, 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.

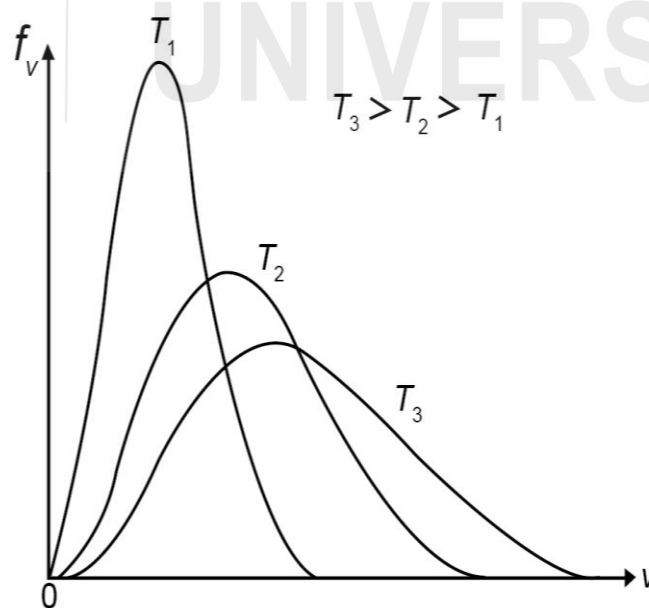


Fig. 2.4: Plots of Maxwellian distribution function versus speed at three different temperatures.

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

EXAMPLE 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 $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$.

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 $dv = 195 - 185 = 10 \text{ ms}^{-1}$ and the mean speed of molecules is

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

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, $m = \frac{32}{6.02 \times 10^{26}} = 5.31 \times 10^{-26} \text{ kg}$

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

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

$$\begin{aligned} dN_v &= 4\pi \times 4.7 \times 10^{24} \left(\frac{5.31 \times 10^{-26} \text{ kg}}{2\pi \times 3.767 \times 10^{-21} \text{ J}} \right)^{3/2} \times \\ & (190 \text{ ms}^{-1})^2 \exp \left(- \frac{(5.31 \times 10^{-26} \text{ kg}) \times (190 \text{ ms}^{-1})^2}{2 \times (3.767 \times 10^{-21} \text{ J})} \right) \times (10 \text{ ms}^{-1}) \\ &= 59.08 \times 10^{27} \times 361 \times (2.245 \times 10^{-6})^{3/2} \exp(-0.2544) \end{aligned}$$

(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_{ms} 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

$$\bar{v} = \frac{\int_0^{\infty} v dN_v}{\int_0^{\infty} dN_v} = \frac{1}{N} \int_0^{\infty} v dN_v \quad (2.32)$$

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

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

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 $x = \frac{mv^2}{k_B T}$ and substituting for $v^3 dv$. You can easily verify

that the integral in Eq. (2.33) has the value $\frac{1}{2(m/2k_B T)^2} \Gamma(2)$.

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

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

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

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

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

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

Hence,

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} \quad (2.35)$$

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

$$\begin{aligned} \frac{df_v}{dv} &= 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{d}{dv} \left[v^2 \exp \left\{ - \left(\frac{mv^2}{2k_B T} \right) \right\} \right] \\ &= C \left\{ 2v \exp \left[- \left(\frac{mv^2}{2k_B T} \right) \right] + v^2 \exp \left[- \left(\frac{mv^2}{2k_B T} \right) \right] \left(- \frac{2mv}{2k_B T} \right) \right\} \quad (2.36) \end{aligned}$$

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

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

We can rewrite it as

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

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

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

or
$$v_p^2 = \frac{2k_B T}{m}$$

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

$$v_p = \sqrt{\frac{2k_B T}{m}} \quad (2.37)$$

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	$v_p(\text{ms}^{-1})$ $= \sqrt{\frac{2k_B T}{m}}$	$\bar{v}(\text{ms}^{-1})$ $= \sqrt{\frac{2.55k_B T}{m}}$	$v_{rms}(\text{ms}^{-1})$ $= \sqrt{\frac{3k_B T}{m}}$
H ₂	1501	1695	1838
H ₂ O	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 $\frac{d^2 f_v}{dv^2} < 0$.

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.

MAXWELL'S DISTRIBUTION LAW OF SPEEDS

Recap

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

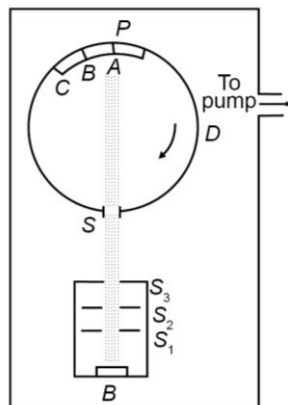


Fig. 2.5: A schematic diagram of the apparatus used by Zartman and Ko to verify Maxwell's law for distribution of molecular speeds.

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.

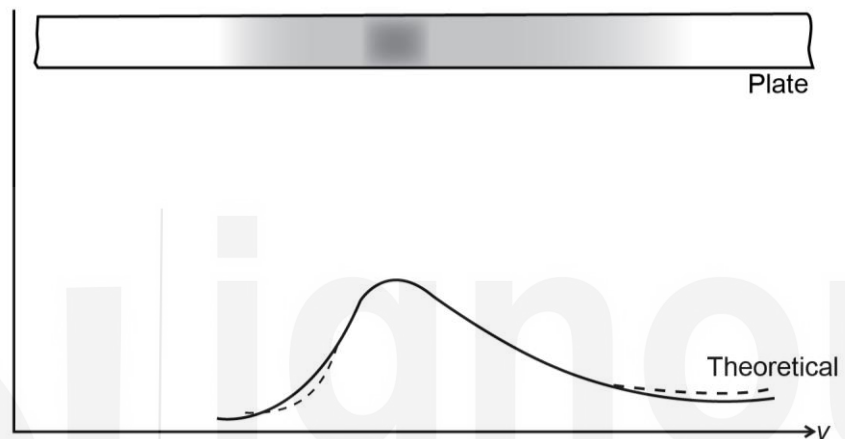


Fig. 2.6: Spread of molecular deposit in the experiment of Zartman and Ko.

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):

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

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 $k_B T / 2$. 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 ($H_2, O_2, N_2 \dots$) 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.)

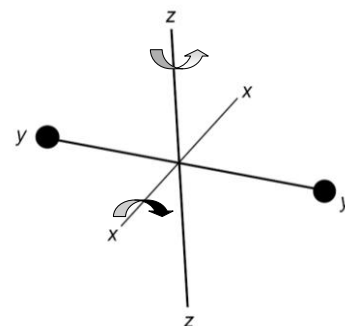


Fig. 2.7: A linear diatomic molecule.

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

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

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

Recap

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.

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

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

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 $\frac{1}{2}m\omega^2x^2$ 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 $k_B T/2$ 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 $k_B T/2$.** (The total energy of such a system will be $f k_B T/2$.) 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 $k_B T/2$.

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 $\text{Jkg}^{-1}\text{K}^{-1}$. For a gas, we define specific heat capacity at constant volume as

$$C_V = \left. \frac{1}{m} \frac{\delta Q}{\Delta T} \right|_V$$

and specific heat capacity at constant pressure as

$$C_p = \left. \frac{1}{m} \frac{\delta Q}{\Delta T} \right|_p$$

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

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 $\text{Jmol}^{-1}\text{K}^{-1}$.

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

$$c_V = \left. \frac{1}{\mu} \frac{\delta Q}{\Delta T} \right|_V$$

and

$$c_p = \left. \frac{1}{\mu} \frac{\delta Q}{\Delta T} \right|_p$$

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

$$u = \frac{f N_A}{2} k_B T = \frac{f}{2} RT \quad (2.39)$$

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

$$c_V = \frac{f}{2} R \quad (2.40)$$

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

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

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

$$\gamma = \frac{c_p}{c_V} = \frac{f+2}{f} \quad (2.42)$$

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

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

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

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

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:

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

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

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

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

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

- 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 $\bar{E} = 2.89 \times 10^{-21} \text{ J}$. 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.

$$\begin{aligned}
 \frac{d^2 f_v}{dv^2} &= \frac{d}{dv} \left(\frac{df_v}{dv} \right) \\
 &= \frac{d}{dv} C \left\{ 2v \exp\left(-\frac{mv^2}{2k_B T}\right) + v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \left(-\frac{2mv}{2k_B T}\right) \right\} \\
 &= C \frac{d}{dv} \left\{ \exp\left(-\frac{mv^2}{2k_B T}\right) \left[2v - \frac{mv^3}{k_B T} \right] \right\} \\
 &= C \left[\exp\left(-\frac{mv^2}{2k_B T}\right) \left[2 - \frac{3mv^2}{2k_B T} \right] + \left(2v - \frac{mv^3}{k_B T} \right) \left(-\frac{2mv}{2k_B T}\right) \exp\left(-\frac{mv^2}{2k_B T}\right) \right] \\
 &= C \exp\left(-\frac{mv^2}{2k_B T}\right) \left(2 - \frac{5mv^2}{k_B T} + \frac{m^2 v^4}{(k_B T)^2} \right)
 \end{aligned}$$

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

$$\begin{aligned} \left. \frac{d^2 f_v}{dv} \right|_{v=v_p} &= C \exp\left(-\frac{m}{2k_B T} \frac{2k_B T}{m}\right) \left(2 - \frac{5m}{k_B T} \frac{2k_B T}{m} + \frac{m^2}{(k_B T)^2} \frac{(2k_B T)^2}{m^2}\right) \\ &= -4C \exp(-1) < 0. \end{aligned}$$

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

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

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

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

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

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

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

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

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

Further, we know that

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

Here m is the mass of helium.

$$m = \frac{4 \times 1.008}{6.023 \times 10^{26}} \text{ kg} = 6.7 \times 10^{-27} \text{ kg}$$

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

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

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):

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

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

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

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

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

$$\begin{aligned} \bar{E}_x &= \frac{m}{2} \int_{-\infty}^{\infty} v_x^2 A \exp(-Bv_x^2) dv_x \\ &= \frac{m}{2} \times 2A \int_0^{\infty} v_x^2 \exp(-Bv_x^2) dv_x \end{aligned} \quad (\text{iii})$$

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

using this result in (iii), we get

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

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

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

On squaring both sides, we get

$$\begin{aligned} 10000 \text{ m}^2\text{s}^{-2} &= \frac{k_B T}{m} (\sqrt{3} - \sqrt{2})^2 \\ &= \frac{k_B T}{m} (1.73 - 1.41)^2 = \frac{0.1 k_B T}{m} \end{aligned}$$

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

For nitrogen

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

$$\begin{aligned} \therefore T &= \frac{(4.65 \times 10^{-26} \text{ kg}) \times 10^4 \text{ m}^2 \text{ s}^{-2}}{0.1 \times (1.38 \times 10^{-23} \text{ JK}^{-1})} \\ &= 337 \text{ K} \end{aligned}$$

5. a) Average velocity

$$\begin{aligned} \bar{v}_x &= \int_{-\infty}^{\infty} v_x f(v_x) dv_x \\ &= A \int_{-\infty}^{\infty} v_x e^{-Bv_x^2} dv_x \end{aligned}$$

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

Hence,

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

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

$$\int_{-\infty}^{\infty} f(v_x) dv_x = A \int_{-\infty}^{\infty} \exp(-Bv_x^2) dv_x = 1 \quad (\text{i})$$

We use the standard integral:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \quad (\text{ii})$$

Using this result in Eq. (i), we get

$$A = \sqrt{\frac{B}{\pi}} \quad (\text{iii})$$

Since $B = \sqrt{\frac{m}{2k_B T}}$, we get

$$A = \sqrt{\frac{m}{2\pi k_B T}} \quad (\text{iv})$$

So that

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

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

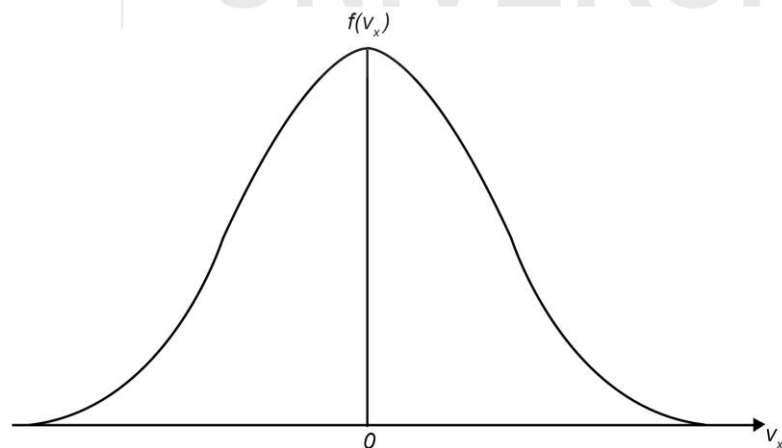
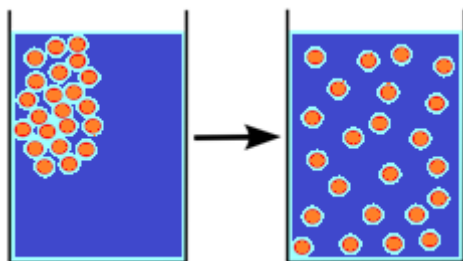


Fig. 2.8: 1-D Maxwell velocity distribution, which is Gaussian centred about $\bar{v}_x = 0$.



Diffusion is a transport phenomenon. You will learn about it in this unit.

MEAN FREE PATH AND TRANSPORT PHENOMENA

Structure

- | | |
|---|---|
| <p>3.1 Introduction
Expected Learning Outcomes</p> <p>3.2 Mean Free Path
Elementary Derivations
Distribution of Free Paths</p> <p>3.3 Transport Phenomena
Viscosity: Transport of Momentum
Thermal Conductivity: Transport of Energy
Diffusion: Transport of Matter</p> | <p>3.4 Summary</p> <p>3.5 Terminal Questions</p> <p>3.6 Solutions and Answers</p> |
|---|---|

STUDY GUIDE

In the previous unit, you have learnt about Maxwell distribution function for molecular speeds and used it to obtain expressions for average speed, most probable speed and root mean square speed. In this unit, you will learn about mean free path and transport phenomena. The study of free paths involves simple concepts of probability, which you have learnt in your school mathematics classes. You are, therefore, advised to refresh your earlier knowledge of probability. Also, you are familiar with the concept of viscosity, diffusion and thermal conductivity. It will be a good idea to revise your school physics about these concepts. This unit is slightly longer but the concepts are simple. Yet we advise you to master sub-topics one at a time. Moreover, if you solve numerical problems given here as also in other texts, you should get extra rewards.

“Atoms and molecules from their very nature can never be made the objects of sensuous contemplations.”

Ernst Mach

3.1 INTRODUCTION

In the previous units you have learnt that molecules of an ideal gas can be considered as point masses, which move randomly with varying speeds. We have seen that even at room temperature, the molecules of a gas, say oxygen, move with very large speeds: $v_{rms} = 480 \text{ ms}^{-1}$. It means that a small amount of scent released in a large room from a vessel should spread throughout the room in no time. But this is not supported by our observation; when we open the lid of a perfume bottle in one corner of the room, the perfume is smelt at the other corner after a considerable time. This apparent paradox led to a serious objection in the early stages of development of kinetic theory of gases. However, this paradox was resolved by Clausius when he argued that **gas molecules have finite size and as they move, they collide with one another leading to increase in diffusion time**. This amounts to modifying the basic assumption about the size of gas molecules.

You may now like to know: What is the average distance travelled by a molecule between successive collisions? What is the mechanism of these collisions? To answer these and such other questions, we use the concept of **mean free path**. We have derived an expression for mean free path in Sec. 3.2 under simplified assumptions. These help us to get a feel of the basic physics. The distribution of free paths is also discussed in this section.

Suppose that a gas moves with a flow velocity towards the right. If its molecules experience velocity gradient in a direction normal to the direction of flow, the gas experiences net transport of momentum across an imaginary plane in the gas along the direction of flow. This is characterised by the **coefficient of viscosity**. You will note that in gases, unlike the case of liquids, random thermal motion associated with gas molecules rather than frictional force between successive layers, gives rise to the phenomenon of viscosity. We will just quote the expression for the coefficient of viscosity in terms of mean free path and discuss its temperature as well as pressure dependence.

When a temperature gradient exists in the body of such a gas in a direction perpendicular to the direction of flow, random motion of gas molecules leads to net transport of thermal energy in the direction of flow. This gives rise to the phenomenon of thermal conduction. This is characterised by **thermal conductivity**. You will learn how to correlate it with the coefficient of viscosity in Sec 3.3.2.

When concentration gradient exists inside a gas normal to the direction of flow, there is net transport of mass in the direction of preferential motion. This is characterised by the **coefficient of diffusion**. You will learn how to express the coefficient of diffusion in terms of mean free path, discuss its temperature dependence and correlate it with coefficient of viscosity in Sec. 3.3.3. These processes (viscosity, thermal conduction and diffusion) are collectively referred to as **transport phenomena**, since we observe net transfer of momentum, energy or matter.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define mean free path and obtain its expressions using elementary derivation;
- ❖ describe the law of free paths;
- ❖ explain the term transport phenomena;
- ❖ discuss physical implications of viscosity of a gas;
- ❖ discuss how thermal conductivity is related to the coefficient of viscosity; and
- ❖ establish the relation between mean free path and coefficient of self-diffusion.

3.2 MEAN FREE PATH

You may recall that in elementary kinetic theory, gas molecules are considered point masses (Assumption 2, Sec. 1.2) and intermolecular collisions are ignored. But as mentioned earlier, to explain the finite time taken by a gaseous mass in an open container to disperse, Clausius assigned a *finite size to gas molecules*. He argued that when a molecule moves within the gas under equilibrium conditions, it necessarily collides with other molecules it encounters in its path and undergoes frequent changes in its direction of motion. This results in a series of zig-zag paths. These are called **free paths**.

The trajectory of a molecule moving with average speed \bar{v} is shown in Fig. 3.1. The concept of mean free path may be visualised if you consider a person shooting aimlessly in a thick forest. The bullets fired by him may eventually hit trees but some will travel farther than others.

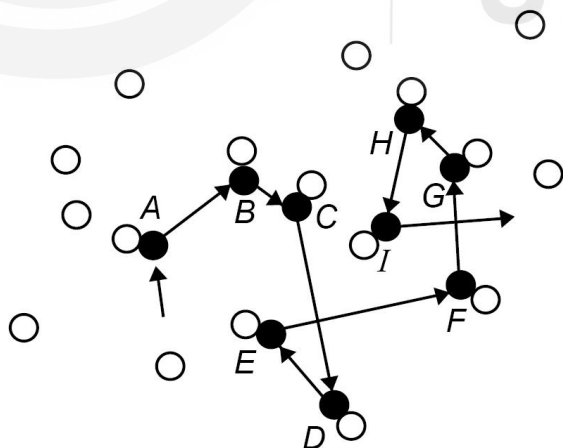


Fig. 3.1: The trajectory of a molecule moving in a gas.

Now carefully examine Fig. 3.1. You will note that free paths are of unequal length; some are short while others are long. The *average length of the free paths is referred to as mean free path*. Thus, **mean free path is the average distance travelled by a molecule between two successive collisions**. We denote it by the symbol λ (pronounce as lambda).

If $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_N$ are the successive free paths traversed by a molecule in time t and N denotes the total number of collisions suffered in this period, we can write

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_N}{N}$$

$$= \frac{\text{total distance travelled}}{\text{total number of collisions}}$$

If \bar{v} is the average speed with which a molecule moves in the body of the gas, then you can write

$$\lambda = \frac{\bar{v} t}{N} \quad (3.1)$$

Under normal conditions, the mean free path of oxygen molecules is about 2×10^{-7} m. This is smaller than the wavelength of visible light, which is in the range 4×10^{-7} m – 6×10^{-7} m. However, mean free path is greater than the average intermolecular separation (3×10^{-9} m).

If $\tau = t/N$ denotes the mean time between two successive collisions, then you can also write

$$\lambda = \bar{v} \tau = \frac{\bar{v}}{P_c} \quad (3.2)$$

Here $P_c = (\tau^{-1})$ denotes the collision frequency, which is a measure of the average number of collisions per second. You may now ask: How can we relate λ to the microscopic properties of a gas? To answer this question, we first make an elementary calculation.

3.2.1 Elementary Derivations

Suppose that a gas consisting of a large number of molecules, each of mass m and diameter d , is in thermal equilibrium. We assume that gas molecules undergo random collisions. Mathematically speaking, we can say that the probability of a molecule suffering a collision in a small interval of time dt is independent of the history of past collisions made by it. As a simple analogy, you can consider that if you throw a dice, the probability of getting a six does not depend on the preceding throw, where a six may or may not have appeared. Similarly, winning or losing toss before a match is independent of earlier results.

From Eq. (3.2), we note that to derive an expression for λ , we must first know the expression for P_c . We shall make this calculation by assuming that only one molecule is in motion. We refer to it as Zeroth order approximation. You will realise that essential physics involved in this phenomenon can be understood well through simple arguments.

Case 1: Zeroth order approximation: Only one molecule in motion

We assume that only one molecule, labelled as A , criss-crosses a sea of other molecules that are at rest. (As such, this is an over-simplification of the actual situation.) You can easily visualise that for a collision to take place, the

centre-to-centre distance between the moving and a stationary molecule should be equal to $2r(=d)$, as shown in Fig. 3.2a.

Note that the centre-to-centre distance at the time of collision between the moving and a stationary molecule will also be equal to the diameter d of a gas molecule, if the stationary molecules were shrunk to geometrical points and the moving molecule is taken to be of radius d (Fig.3.2b). You can visualise this as if the moving molecule carries with it a circular disc of radius d . Therefore, the moving molecule can be thought of as sweeping out a cylinder of cross-sectional area πd^2 and length $\bar{v}t$ in time t . This is illustrated in Fig. 3.2c. During this time, it will collide with all other molecules whose centres lie within a cylinder of volume $\bar{v}t\pi d^2$. You must convince yourself about this before proceeding further.

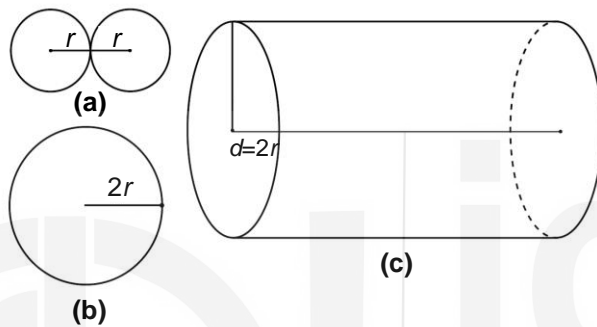


Fig. 3.2: a) Collision of two molecules of radii r : Instantaneous representation; b) equivalent representation of collision in (a) where radius of the moving molecule is increased to $2r$ and the stationary molecule is shrunk to a geometrical point; c) cylindrical volume mapped by the moving molecule of radius $2r$.

If the number of molecules per unit volume is n , the number of molecules contained in the cylinder of volume $\bar{v}t\pi d^2$ will be equal to $\bar{v}t\pi d^2n$. You will agree that this number also equals the number of collisions suffered by the moving molecule in time t .

The collision frequency, which defines the number of collisions per second, is given by

$$P_c = \bar{v} \pi d^2 n = n\sigma \bar{v} \quad (3.3)$$

where $\sigma = \pi d^2$ is known as *microscopic collision cross-section*. It is expressed in m^2 .

Substituting this result in Eq. (3.2), we get

$$\lambda = \frac{\bar{v}}{P_c} = \frac{1}{\pi d^2 n} = \frac{1}{\sigma n} \quad (3.4)$$

The quantity $n\sigma$ is called *macroscopic collision cross-section* and its unit is m^{-1} . Note here that the unit of macroscopic collision cross-section is *reciprocal length*, not an area.

Let us pause for a moment and ask: What is good about the relation contained in Eq. (3.4)? What are its implications? To seek answers to these questions, we note that Eq. (3.4) predicts that mean free path is inversely proportional to the macroscopic collision cross-section or number density and second power of diameter of the molecule. It means that mean free path will

be less for a denser and/or a heavier gas. This is in perfect agreement with common observation and lends support to the basic tenets of kinetic theory. The aesthetic beauty of kinetic theory is in its ability to relate experimentally measurable macroscopic quantity such as mean free path to a microscopic quantity – size of a molecule.

You may now logically ask: What is the typical magnitude of mean free path in a gas at STP? The answer to this question is contained in the following example. You should go through it carefully.

EXAMPLE 3.1: COLLISION CROSS-SECTION

The average speed of hydrogen molecules is 1840 ms^{-1} . The radius of a hydrogen molecule is $1.37 \times 10^{-10} \text{ m}$. Calculate (i) collision cross section, (ii) collision frequency and (iii) mean free path. Take $n = 3 \times 10^{25} \text{ m}^{-3}$.

SOLUTION ■ Since the radius of a hydrogen molecule is $1.37 \times 10^{-10} \text{ m}$ and number density n is $3 \times 10^{25} \text{ m}^{-3}$, we can easily calculate the collision cross-section, collision frequency and mean free path using Eqs. (3.3) and (3.4):

$$(i) \quad \sigma = \pi d^2 = 4\pi (1.37)^2 \times 10^{-20} \text{ m}^2 = 23.6 \times 10^{-20} \text{ m}^2$$

$$(ii) \quad P_c = \pi d^2 n \bar{v} = n \bar{v} \sigma \\ = (3 \times 10^{25} \text{ m}^{-3}) \times (1.84 \times 10^3 \text{ ms}^{-1}) \times (23.6 \times 10^{-20} \text{ m}^2) \\ = 1.3 \times 10^{10} \text{ s}^{-1}$$

$$(iii) \quad \lambda = \frac{1}{n\pi d^2} = \frac{1}{(3 \times 10^{25} \text{ m}^{-3}) \times (23.6 \times 10^{-20} \text{ m}^2)} \\ = 141 \times 10^{-9} \text{ m} = 141 \text{ nm}$$

Note that the number of collisions per second is of the order of 10^{10} , which is a very large number. For this reason, the path of a molecule is made up of so many kinks and zigzags that it is almost impossible to follow its trajectory.

Also note that λ is large compared to intermolecular distance, which is only a few nanometer ($\approx 3 \text{ nm}$).

To ensure that you have grasped the ideas and your progress is satisfactory, we would like you to solve an SAQ before proceeding further.

SAQ 1 – Mean free path

The mean speed of oxygen molecules at room temperature is 450 ms^{-1} . If the radius of an oxygen molecule is 1.8 \AA , calculate σ , P_c , λ , and τ . Take $n = 3 \times 10^{25} \text{ m}^{-3}$.

From ideal gas equation, we know that the pressure exerted by a gas can be expressed in terms of its temperature as

$$p = nk_{\text{B}}T$$

On using this result to substitute for n in Eq. (3.4), the expression for mean free path takes the form

$$\lambda = k_{\text{B}}T / \sigma p \quad (3.5)$$

This result is very interesting; it suggests that mean free path is directly proportional to absolute temperature of a gas and inversely proportional to the pressure exerted by it on the walls of the container. It means that the value of λ will increase as pressure decreases and/or temperature increases. Now suppose we reduce pressure to a very small value using a vacuum pump. According to Eq. (3.5), the mean free path can approach infinity. But in actual practice, this is forbidden by physical considerations. At the most, the value of λ can equal the dimensions of the container.

You will agree that in deriving Eq. (3.4), we made a rather unrealistic assumption that only one molecule moved while other molecules were at rest. But in Unit 2 you have learnt that molecules in a gas move about randomly. Therefore, a better way to represent the actual situation will be to assume that all molecules move with the same speed. When we consider this, Eq. (3.5) modifies to

$$\lambda_{\text{C}} = \frac{3}{4n\sigma} = \frac{0.75}{n\sigma} = 0.75 \frac{k_{\text{B}}T}{p\sigma} \quad (3.6)$$

It may be mentioned here that this result was obtained by Clausius. That is why we have put the subscript C with λ . It shows that mean free path of the molecules in a gas decreases when all molecules are moving.

You will recall that in actual practice, we should have considered Maxwellian distribution of velocities. However, the mathematical calculations are quite involved and it will be sufficient to quote the result. (Those of you who are interested in these details may refer to references given in the Further Readings):

$$\begin{aligned} \lambda_{\text{M}} &= \frac{1}{\sqrt{2} n\sigma} = (0.707) \frac{1}{n\sigma} \\ &= (0.707) \frac{k_{\text{B}}T}{p\sigma} \end{aligned} \quad (3.7)$$

Note that $\frac{\lambda_{\text{M}}}{\lambda_{\text{C}}} = 0.94$.

This result shows that there is a correction of only 6 per cent in the value of mean free path when we go from uniform speed model to Maxwell distribution. You will also note that for point molecules ($d \rightarrow 0$), collision cross-section $\sigma \rightarrow 0$ and mean free path $\lambda \rightarrow \infty$.

Before proceeding further, we would like you to revise what you have learnt so far in this unit.

Recap

MEAN FREE PATH

- The average distance covered by a gas molecule between two successive collisions defines the mean free path.
- The mean free path of a gas molecule when only one molecule moves with speed \bar{v} is given by

$$\lambda = \frac{1}{\pi d^2 n}$$

Now go through the following example carefully to get a feel of the values involved in real situations.

EXAMPLE 3.2: MOLECULAR DIAMETER

A gas is assumed to obey Maxwell's law of distribution of speeds. Calculate the (i) molecular diameter of a gas and (ii) the number of collisions per unit distance if mean free path at STP is 2.85×10^{-7} m. Take $n = 3 \times 10^{25} \text{ m}^{-3}$.

SOLUTION ■ From Eq. (3.7), we can write $\lambda = \frac{1}{\sqrt{2}} \frac{1}{\pi d^2 n}$

(a) To determine d , we rewrite the expression for mean free path as

$$d^2 = \frac{1}{\sqrt{2}} \frac{1}{\pi \lambda n}$$

On substituting the given values in this expression, we get

$$\begin{aligned} d^2 &= \frac{1}{\sqrt{2}} \cdot \frac{1}{3.14} \times \frac{1}{2.85 \times 10^{-7} \text{ m}} \times \frac{1}{3 \times 10^{25} \text{ m}^{-3}} \\ &= \frac{1}{37.96 \times 10^{18}} \text{ m}^2 = 2.63 \times 10^{-20} \text{ m}^2 \end{aligned}$$

so that

$$d = 1.62 \times 10^{-10} \text{ m}$$

Note that the order of magnitude of mean free path is 10^3 times that of molecular diameter.

(b) By definition, the number of collisions per unit distance is reciprocal of the mean free path. Therefore, we can write

$$\begin{aligned} N_c &= \frac{1}{\lambda} = \frac{1}{2.85 \times 10^{-7} \text{ m}} \\ &= 3.51 \times 10^6 \text{ m}^{-1} \end{aligned}$$

To test your understanding, you may like to answer the following SAQ.

SAQ 2 – Pressure and mean free path

The mean free path of the molecules of an ideal gas at 15°C is 6.28×10^{-8} m. If the radius of a gas molecule is 1.88 Å, calculate the pressure exerted by the gas. Also calculate the number of collisions suffered by a molecule in travelling a distance of one metre. Take $k_B = 1.38 \times 10^{-23}$ JK⁻¹.

You now know that molecules undergo collisions very frequently. It means that the distribution of free paths will be spread over a wide range. It is, therefore, interesting to know their distribution. This forms the subject of discussion of the following sub-section.

3.2.2 Distribution of Free Paths

Imagine a person shooting aimlessly in a thick forest. Every bullet eventually hits a tree, but some travel farther than others. This situation is analogous to the flights of gas molecules. We now wish to know the distribution of free paths. To do so, let us consider a molecule at the start of its journey (point O).

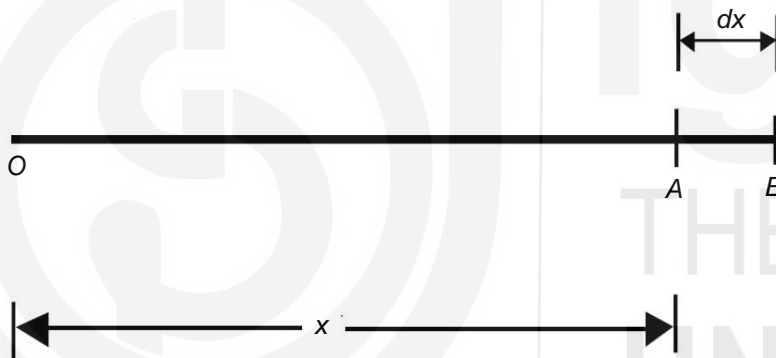


Fig. 3.3: A molecule travels from O to A without colliding with another molecule. It traverses a further distance AB in time dt .

We assume that past history of a molecule does not influence its subsequent motion in any way. Suppose that a molecule moving with average speed \bar{v} , travels a distance $OA = x$ without suffering any collision. The probability of this event will be a function of x . Let us denote it by $f(x)$. The probability that this molecule makes a collision in moving from A to B will be determined by the product of collision frequency and time interval in which it covers the given distance. So, we can take it to be equal to $P_c dt$, where P_c is the collision frequency. Since $dx = \bar{v} dt$, we can write

$$P_c dt = P_c \frac{dx}{\bar{v}} = \frac{dx}{\lambda}$$

where λ is the mean free path defined by Eq.(3.2). Hence, the probability that a molecule traverses a distance dx without making a collision is $\left(1 - \frac{dx}{\lambda}\right)$.

1. If the probability of occurrence of a collision is $p(x)$, the probability of its non-occurrence will be $1 - p(x)$.
2. The probability of occurrence of two mutually exclusive events is multiplicative.

Since motion from O to A and from A to B can be considered as two independent events, we can say that the probability $f(x + dx)$ of this molecule completing its journey from O to B without making any collision is equal to the product of probabilities for individual events. Mathematically, we express it as $f(x)\left(1 - \frac{dx}{\lambda}\right)$. Hence, we can write

$$f(x + dx) = f(x)\left(1 - \frac{dx}{\lambda}\right) \quad (3.8)$$

To simplify this expression, we use Taylor series expansion of $f(x + dx)$ and ignore second and higher order terms in dx . Then we can write

$$f(x + dx) = f(x) + \frac{df(x)}{dx} dx$$

On using this result in Eq. (3.8), we get

$$\frac{df(x)}{dx} = -\frac{f(x)}{\lambda}$$

You can easily integrate it to obtain

$$f(x) = A \exp(-x/\lambda). \quad (3.9)$$

The constant of integration A can be easily evaluated using the fact that $f(0) = 1$. (Physically it means that the particle is yet to move or collide.) This gives $A = 1$. Hence, Eq. (3.9) takes a compact form:

$$f(x) = \exp(-x/\lambda) \quad (3.10)$$

This is the law of *distribution of free paths*. It suggests that the probability of a molecule travelling very large distance without making a collision will be vanishingly small.

If we have a sample of N_0 molecules to start with, only $N_0 \exp(-x/\lambda)$ of these will survive a collision in traversing a distance x . Let this number be denoted by $N(x)$. Then we can write

$$N(x) = N_0 \exp\left(-\frac{x}{\lambda}\right) \quad (3.11)$$

This equation is known as *survival equation*. You will come across similar equations in other areas of physics. For example, radioactive decay obeys the equation $N(x) = N_0 \exp(-\Lambda t)$, where $N(x)$ is the number of atoms which survive disintegration for time t and Λ is disintegration constant.

Now refer to Fig. 3.4. It shows the plot of distribution of free paths as a function of x/λ . Note that the fraction of molecules with free paths larger than λ is only $e^{-1} \approx 0.37$.

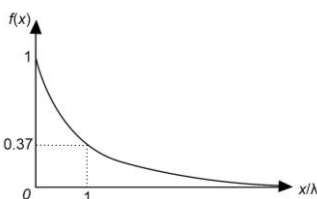


Fig. 3.4: The plot of the survival equation.

We now give a solved example to reinforce our discussion of this section.

EXAMPLE 3.3: SURVIVAL EQUATION

In a sample of 10^4 gas molecules, each molecule is moving with the same speed. Calculate the number of molecules that will continue to travel undeflected after traversing distances of 0.4λ , 0.5λ , λ , 2λ , and 10λ .

SOLUTION ■ The values of $N(x)$ are tabulated below for different distances traversed by the gas molecules and you can readily verify these using Eq. (3.11). To illustrate, for $x = 0.4\lambda$, we can write

$$N(x) = 10^4 e^{-0.4} = 6703$$

$\frac{x}{\lambda}$	0.4	0.5	1	2	10
N	6703	6065	3679	1353	0.4540

You will note that after traversing a distance of λ , 2λ and 10λ , nearly 37%, 13.5% and 0.5% molecule, respectively, will survive a collision.

You may now like to solve an SAQ to assess your understanding.

SAQ 3 – Law of free paths

The mean free path of the molecules of a gas at pressure p and temperature T is 5.2×10^{-8} m. Calculate the probabilities that a molecule will travel 10.4×10^{-8} m without making a collision, if (i) temperature is doubled, (ii) both temperature and pressure are doubled, and (iii) pressure is tripled.

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

LAW OF FREE PATHS

Recap

- The law of distribution of free paths gives the probability that a gas molecule covers a distance x without making a collision:

$$f(x) = \exp(-x/\lambda)$$

- The law of distribution of free paths is supported by experimental results.

So far we confined ourselves to a gaseous system at uniform temperature and pressure in equilibrium so that there is no preferential motion of any kind. This is because the rate of migration of molecules across a given plane in the gas is exactly balanced by an equal number moving in the opposite direction. However, when the entire gas or a part of it moves as a whole in a particular direction, the preferential motion and random molecular motion combine to give rise to a new behaviour. Let us learn about it now.

3.3 TRANSPORT PHENOMENA

We know that each gas molecule has a finite mass and is characterised by random molecular motion. Therefore, it possesses momentum as well as energy. So, while moving from one part of the container to another, it is a potential carrier of these physical quantities under certain peculiar conditions. When a gas is in equilibrium, there is no *net* transport of matter, energy, or momentum. However, when a gas is endowed with macroscopic motion, i.e., the entire gas or a part of it moves as a whole in a particular direction, the following three cases may occur singly or jointly:

- *The different parts of the gas move with different velocities.* This will give rise to relative motion between different layers of the gas. As a result, the faster moving layers in the body of the gas will lose momentum to the slower moving layers. Therefore, *across an imaginary plane, there will be net transport of momentum in the preferential direction.* This results in a frictional force, which is characterised by the *coefficient of viscosity*.

Note that viscosity in gases arises due to the random thermal motion of molecules when it is endowed with macroscopic motion rather than a frictional force between any two adjacent layers, as in the case of liquids.

- *Different parts of a gas are at different temperatures.* In this case, the molecules of the gas will carry *thermal energy* from regions of higher temperature to regions of lower temperature and tend to attain thermal equilibrium. This gives rise to the phenomenon of *thermal conduction*.
- *Different parts of a gas have different concentrations.* The molecules from regions of higher concentration will migrate to the regions of lower concentration resulting in the transport of *mass (matter)*. This leads to the phenomenon of *diffusion*.

We thus find that viscosity, conduction and diffusion are bulk properties of gases signifying transport of momentum, energy and mass, respectively. These are collectively categorised under the title of *transport phenomena*. These processes are of vital importance in physical sciences and find several important applications. We will now discuss these in some detail on the basis of the simple molecular model discussed in the preceding chapters.

3.3.1 Viscosity: Transport of Momentum

In your school physics classes, you have learnt that the property by virtue of which a liquid opposes the motion between adjacent layers is referred to as viscosity. It is quantitatively expressed in terms of the coefficient of viscosity, η . Can you recall its definition? The *coefficient of viscosity is defined as the tangential force per unit area when a unit velocity gradient exists in a direction perpendicular to the direction of motion*. Mathematically, for small velocity gradient we write

$$F = -\eta A \frac{du}{dy} \quad (3.12)$$

Here F denotes the viscous force acting on an area A and du/dy is velocity gradient along the +ve y -direction. The negative sign signifies that the viscous force is directed against the velocity gradient. Note that η has dimensions

$\text{ML}^{-1}\text{T}^{-1}$. Its SI units are $\text{kgm}^{-1}\text{s}^{-1}$. It is also denoted as pascal-second. The CGS unit of η is poise ($= 10^{-1}\text{kgm}^{-1}\text{s}^{-1}$).

Let us consider a gas enclosed between two planes depicted as aa' and bb' in Fig. 3.5 and separated through a distance h . Suppose that the gas is endowed with mass motion from left to right and a positive velocity gradient exists along the y -axis, which is normal to the direction of flow.

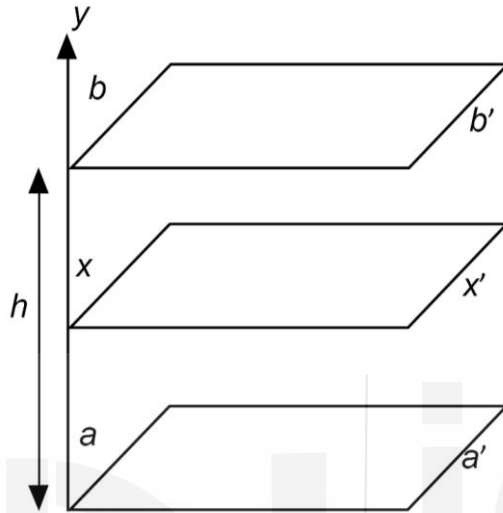


Fig. 3.5: Momentum transport across a plane in a gas having velocity gradient.

Mathematically, the coefficient of viscosity of a gas is given by

$$\eta = \frac{1}{3} mn\bar{v}\lambda = \frac{1}{3} \rho\bar{v}\lambda \quad (3.13)$$

On substituting the expression for λ corresponding to Maxwellian distribution of speeds in Eq. (3.13) from Eq. (3.7), we can express η in terms of σ :

$$\eta_M = \frac{1}{3\sqrt{2}} \frac{m\bar{v}}{\sigma} \quad (3.14)$$

This result provides us a useful way to estimate a microscopic property such as molecular diameter in terms of a macroscopic property such as viscosity η , which is directly measurable. This finding provided remarkable support to elementary kinetic theory.

To be able to discuss pressure and temperature dependence of η , we

substitute for $\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$ from Eq. (2.34) in Eq. (3.14). This gives

$$\eta_M = \frac{2}{3\sigma} \sqrt{\frac{m k_B T}{\pi}} = \frac{0.376}{\sigma} \sqrt{m k_B T} \quad (3.15)$$

Effect of Temperature and Pressure on Viscosity

- From Eq. (3.15) we note that the viscosity of a gas is directly proportional to the square root of absolute temperature. So, if we plot η versus $T^{1/2}$, we should obtain a straight line. However, experiments show that viscosity of a gas increases with temperature at a slightly faster rate than $T^{1/2}$.

The departure from the value 0.5 provides us an opportunity to review the assumptions of elementary kinetic theory.

- According to elementary kinetic theory, the viscosity of a gas is independent of pressure (or n). But in actual practice, pressure independence of η is observed only for a limited range – from a few mm of mercury to a few atmosphere. Experiments show that at very low pressures, viscosity decreases and at very high pressures, viscosity increases.

We can explain these observations as follows:

At very low pressures, intermolecular collisions become rare and as mentioned earlier, the mean free path becomes comparable to the dimensions of the apparatus. However, the number density decreases continuously with pressure. This makes the coefficient of viscosity to decrease as pressure decreases. On the other hand, at very high pressures, the mean free path is comparable to molecular size and the coefficient of viscosity increases with pressure (or n).

We now recapitulate important results of this sub-section.

Recap

COEFFICIENT OF VISCOSITY

- When different parts of a gas endowed with mass motion and its molecules move with different speeds, there is net transport of momentum in the direction of mass motion.
- The coefficient of viscosity of a gas is given by $\eta = \frac{1}{3} mn\bar{v}\lambda = \frac{1}{3} \rho\bar{v}\lambda$.
- Theory predicts that η is independent of pressure but varies as $T^{1/2}$.

EXAMPLE 3.4: COEFFICIENT OF VISCOSITY AND MEAN FREE PATH

The coefficients of viscosity of argon and helium are 22×10^{-6} Pa s and 19×10^{-6} Pa s, respectively. Calculate the mean free paths for these gases, if they are kept under identical conditions.

SOLUTION ■ Since the gases are under identical conditions, n is same for both gases. Then from Eq. (3.13) we can write

$$\frac{\eta_{\text{Ar}}}{\eta_{\text{He}}} = \frac{m_{\text{Ar}} \bar{v}_{\text{Ar}} \lambda_{\text{Ar}}}{m_{\text{He}} \bar{v}_{\text{He}} \lambda_{\text{He}}} \quad (\text{i})$$

Using the relation $\bar{v} = \sqrt{\frac{8k_{\text{B}}T}{\pi m}}$, we can rewrite (i) as

$$\frac{\eta_{\text{Ar}}}{\eta_{\text{He}}} = \sqrt{\frac{m_{\text{Ar}}}{m_{\text{He}}}} \frac{\lambda_{\text{Ar}}}{\lambda_{\text{He}}}$$

On re-arranging terms, we get

$$\frac{\lambda_{\text{Ar}}}{\lambda_{\text{He}}} = \sqrt{\frac{m_{\text{He}}}{m_{\text{Ar}}}} \frac{\eta_{\text{Ar}}}{\eta_{\text{He}}} = \left(\frac{4}{39.9}\right)^{1/2} \left(\frac{22 \times 10^{-6} \text{ Pa s}}{19 \times 10^{-6} \text{ Pa s}}\right) = 0.367$$

EXAMPLE 3.5: COEFFICIENT OF VISCOSITY AND MEAN FREE PATH

The molecules of helium gas move with an average speed of 1200 ms^{-1} . If $\eta = 19 \times 10^{-6} \text{ Pa s}$, calculate the mean free path for helium.

SOLUTION ■ We can rewrite Eq. (3.13) as

$$\lambda = \frac{3\eta}{\rho\bar{v}} = \frac{3\eta V}{M\bar{v}}$$

where M is molecular weight and V is volume occupied by one mole of the gas. On inserting the given numerical values, we get

$$\begin{aligned}\lambda &= \frac{3 \times (19 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}) \times (22.4 \times 10^{-3} \text{ m}^3)}{(4 \times 10^{-3} \text{ kg}) \times (1200 \text{ ms}^{-1})} \\ &= 2.66 \times 10^{-7} \text{ m}\end{aligned}$$

You may now like to solve an SAQ to assess your understanding.

SAQ 4 – Viscosity and molecular dimensions

Calculate the radius of an oxygen molecule, if coefficient of viscosity of oxygen is $19.6 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}$ at 15°C and $\bar{v} = 436 \text{ ms}^{-1}$. Assume that it obeys Maxwellian law of distribution of speeds.

3.3.2 Thermal Conductivity: Transport of Energy

When a gas is endowed with mass motion and a temperature gradient exists between its different layers, a finite amount of energy is transported by gas molecules due to their random motion from regions of higher temperature to regions of lower temperature. As mentioned earlier, this gives rise to the phenomenon of thermal conduction. The rate at which thermal energy is transported across any surface per unit area is characterised in terms of thermal conductivity, K and we can write

$$Q = -K \frac{dT}{dy} \quad (3.16)$$

where (dT/dy) is temperature gradient and temperature of the gas at an imaginary surface xx' within the gas is T .

The expression for thermal conductivity is given by

$$K = \frac{f}{6} n \bar{v} \lambda k_B \quad (3.17)$$

From this equation, we note that thermal conductivity is directly proportional to average molecular speed. Therefore, theory predicts that thermal conductivity

You should not confuse the symbol K used for thermal conductivity with the symbol used for kelvin, the unit of temperature.

is directly proportional to square root of temperature. However, in actual practice, K increases somewhat more rapidly suggesting that when intermolecular forces come into play, they begin to influence energy transport.

Relation Between η and K

When we closely examine the expressions for η and K , we expect some connection between them. It is instructive to ascertain it as both these quantities are physically measurable. Therefore, we divide Eq. (3.17) by Eq. (3.13) and obtain

$$\frac{K}{\eta} = \frac{f}{2} \frac{k_B}{m} = \frac{f}{2} \frac{k_B N_A}{M} = \frac{f}{2} \frac{R}{M} \quad (3.18)$$

where $m = \frac{M}{N_A}$ and M is molecular weight of the substance.

From Unit 2 you will recall that molar heat capacity at constant volume is given by

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

Using this result, we can rewrite Eq. (3.18) as

$$\frac{K}{\eta} = \frac{c_V}{M}$$

or

$$\frac{KM}{\eta c_V} = 1 \quad (3.19)$$

Atomicity of a gas defines the number of atoms in its molecule.

From this result we note that the ratio $(KM/\eta c_V)$ is constant, same for all gases. But experiments show that this ratio is greater than one. A more rigorous calculation shows that this ratio varies between 1.5 and 2.5 and is different for different gases; decreasing with atomicity. There can be several reasons for this difference.

You should now go through the following example carefully.

EXAMPLE 3.6: THERMAL CONDUCTIVITY AND VISCOSITY

The coefficient of viscosity of helium is $18.6 \times 10^{-6} \text{ Nsm}^{-2}$, $M = 4 \text{ kg kmol}^{-1}$ and $c_V = 12.5 \times 10^3 \text{ Jkmol}^{-1} \text{ K}^{-1}$. Calculate the thermal conductivity of helium.

SOLUTION ■ From Eq. (3.19) we can write $K = \frac{\eta c_V}{M}$. On putting the given values, we get

$$\begin{aligned} K &= \frac{(18.6 \times 10^{-6} \text{ Nsm}^{-2}) \times (12.5 \times 10^3 \text{ Jkmol}^{-1} \text{ K}^{-1})}{4 \text{ kg kmol}^{-1}} \\ &= 5.8 \times 10^{-2} \text{ Jm}^{-1} \text{ s}^{-1} \text{ K}^{-1}. \end{aligned}$$

Before proceeding further, we recapitulate important result in this sub-section.

THERMAL CONDUCTIVITY

Recap

- When a temperature gradient exists between different layers of a gas endowed with mass motion, there is net transport of energy from regions of higher temperature to regions of lower temperature. This gives rise to phenomenon of thermal conduction.
- The thermal conductivity of a gas is given by

$$K = \frac{fn\bar{v}}{6} \lambda k_B$$

- In terms of the coefficient of viscosity, we can write $\frac{KM}{\eta c_V} = 1$.

3.3.3 Diffusion: Transport of Matter

Inter-mixing of gases is known as *diffusion*. This phenomenon is responsible for the smell of flowers/scent reaching us. This is also why while sitting in your study room, you can know what is being cooked in the kitchen. It is a direct consequence of random molecular motion when there are inequalities in concentration. Molecules diffuse from regions of higher concentration towards regions of lower concentration. Fig. 3.6a schematically depicts self-diffusion (diffusion of like molecules). Diffusion of unlike molecules is shown in Fig. 3.6b.

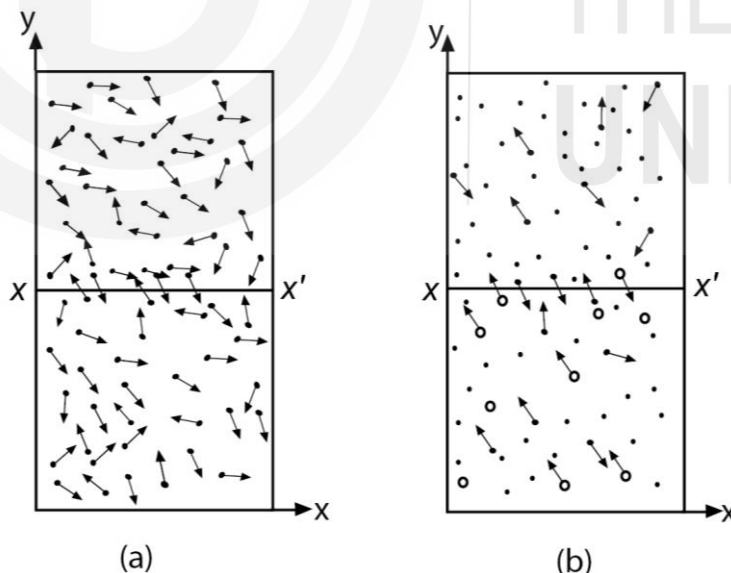


Fig. 3.6: a) Self-diffusion across a barrier; b) Diffusion of unlike molecules.

We describe intermixing of gases in terms of diffusion coefficient, D . If the molecular concentration along a horizontal plane xx' is n and there is positive concentration gradient dn/dy in the vertical plane, the number of particles crossing the given surface per unit area per unit time is given by

$$\Gamma = -D \frac{dn}{dy} \quad (3.20)$$

The concentration of ^{235}U isotope in natural uranium is 0.71%. For power generation in a nuclear power plant, it is desirable to increase its concentration to 2-3%, i.e., above its natural value. Then we say that uranium has been enriched.

The calculation of diffusion coefficient is complicated due to the fact that the rates of diffusion of two gases may not be the same. However, we can understand the essential ideas by considering the diffusion of like molecules, i.e., **self-diffusion**. The diffusion of the isotopes of the same element (say ^{235}U and ^{238}U) is an excellent example of self-diffusion. For self-diffusion, the expression for diffusion coefficients is

$$D = \frac{1}{3} \bar{v} \lambda \quad (3.21)$$

If we now substitute the values of \bar{v} and λ for a Maxwellian gas, we get

$$D = \frac{0.376 (k_B T)^{3/2}}{\sigma \rho \sqrt{m}} \quad (3.22)$$

For air at STP, $\lambda = 100 \text{ nm}$, and $\bar{v} = 450 \text{ m s}^{-1}$. It means that the diffusion coefficient for air is of the order of $10^{-5} \text{ m}^2 \text{ s}^{-1}$. Moreover, Eq. (3.22) implies that diffusion coefficient will vary inversely with pressure and directly with temperature as $T^{3/2}$. The predicted variation with pressure is in agreement with the observed results but the power of T lies between 1.75 and 2. The reason for the more rapid increase with temperature is attributed to the presence of intermolecular forces in real gases. To be precise, it is due to the attractive part of the intermolecular potential.

Relation between D and η

If we combine Eqs. (3.13) and (3.21), we can write

$$\frac{D\rho}{\eta} \equiv \xi = 1 \quad (3.23)$$

Though simple kinetic theory predicts that ξ is constant, equal to one for all gases, its observed value lies between 1.3 and 1.5. It means that simple calculations given here help us to know qualitative behaviour.

We now sum up what you have learnt in this unit.

3.4 SUMMARY

Concept	Description
Mean free path	<ul style="list-style-type: none"> The mean free path is the average distance travelled by a molecule between two successive collisions. If we assume that all but one molecule moves with average speed \bar{v}, the expressions for λ is given by $\lambda = \frac{1}{\pi n d^2} = \frac{1}{n \sigma}$ <p>where n is the molecular number density and σ is the collision cross-section. For a sphere of diameter d, $\sigma = \pi d^2$.</p>

Survival equation

- For a sample of N_0 molecules, the number of molecules which travel a distance x without making any collision is given by **survival equation**:

$$N = N_0 \exp(-x/\lambda)$$

Transport phenomena

- When a gas is endowed with mass motion, random molecular motion can lead to **transport of energy, momentum and mass**, depending on the physical conditions, which lead to the phenomena of **thermal conduction, viscosity and diffusion**, respectively. These are collectively referred to as transport phenomena.

Coefficient of viscosity

- The **coefficient of viscosity** for a gas having velocity gradient is given by

$$\eta = \frac{1}{3} mn\bar{v}\lambda = \frac{1}{3}\rho\bar{v}\lambda$$

where m is molecular mass and \bar{v} is average speed of a molecule.

Thermal conductivity

- The thermal conductivity K is given by

$$K = \frac{f}{6} n\bar{v}\lambda k_B$$

where f denotes the number of degrees of freedom.

- K and η are connected by the relation

$$\frac{KM}{\eta c_V} = 1$$

Coefficient of diffusion

- The coefficient of diffusion D is given by

$$D = \frac{\bar{v}}{3}\lambda$$

3.5 TERMINAL QUESTIONS

1. Calculate the diffusion coefficient of hydrogen molecules at 27°C when pressure is 2 atm. Assume that it behaves as a Maxwellian gas. Take

$$r_{\text{H}_2} = 1.37 \times 10^{-10} \text{ m and } k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

2. Calculate the radius of the nitrogen molecule using the following data:

$$K = 23.7 \times 10^{-3} \text{ Js}^{-1} \text{ m}^{-1} \text{ K}^{-1}, c_V = 29.1 \times 10^3 \text{ Jkmol}^{-1} \text{ K}^{-1} \text{ at } 273 \text{ K}$$

$$M = 28.02 \text{ kg, } N_A = 6.023 \times 10^{26} \text{ and } k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

3. Calculate the mean free path for hydrogen molecules at STP. The diameter of a hydrogen molecule is 2.9 Å. Take $n = 3 \times 10^{25} \text{ molecules m}^{-3}$.

4. The coefficient of viscosity of a gas is $16.6 \times 10^{-6} \text{ N s m}^{-2}$. Calculate the diameter of the gas molecule at STP, when average molecular velocity $\bar{v} = 4.5 \times 10^2 \text{ m s}^{-1}$; number density = $2.7 \times 10^{25} \text{ molecules m}^{-3}$, and molecular weight of nitrogen = 28. Take Avogadro's number = $6.023 \times 10^{23} \text{ mol}^{-1}$.
5. Calculate the thermal conductivity of air using the following data:
 $\bar{v} = 470 \text{ m s}^{-1}$, $\rho = 1.29 \text{ kg m}^{-3}$, $\lambda = 5.6 \times 10^{-8} \text{ m}$, $M = 29$, $\gamma = 1.4$, and $R = 8.31 \text{ kJ mol}^{-1} \text{ K}^{-1}$.

3.6 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. We have

$$\sigma = 4\pi r^2 = 4\pi(1.8 \times 10^{-10} \text{ m})^2 = 40.7 \times 10^{-20} \text{ m}^2$$

$$P_c = n\sigma \bar{v} = (3 \times 10^{25} \text{ m}^{-3}) \times (40.7 \times 10^{-20} \text{ m}^2) \times (450 \text{ m s}^{-1}) \\ = 5.49 \times 10^9 \text{ s}^{-1}$$

$$\tau = P_c^{-1} = 1.8 \times 10^{-10} \text{ s}$$

and
$$\lambda = \frac{1}{(3 \times 10^{25} \text{ m}^{-3}) \times (40.7 \times 10^{-20} \text{ m}^2)} = 82 \text{ nm}$$

2. From Eq. (3.7), we recall that

$$\lambda = \frac{k_B T}{\rho \sigma}$$

$$\text{Here } \sigma = 4\pi r^2 = 4 \times 3.14 \times (1.88 \times 10^{-10} \text{ m})^2 = 44.42 \times 10^{-20} \text{ m}^2$$

On substituting the given values of Boltzmann constant and temperature (in kelvin), we get

$$\rho = \frac{k_B T}{\lambda_M \sigma} = \frac{(1.38 \times 10^{-23} \text{ JK}^{-1}) \times (288 \text{ K})}{(6.28 \times 10^{-8} \text{ m}) \times (44.4 \times 10^{-20} \text{ m}^2)} \\ = 1.43 \times 10^5 \text{ Nm}^{-2}$$

For a Maxwellian gas, the value for ρ will be lower by a factor of $\frac{1}{\sqrt{2}}$.

Hence, its magnitude will be

$$\rho = 1.01 \times 10^5 \text{ Nm}^{-2}.$$

The number of collisions suffered by a molecule per metre of the path

$$N_s = \frac{1}{6.28 \times 10^{-8} \text{ m}} = 16 \times 10^6 \text{ m}^{-1}.$$

3. From Eq. (3.10) we recall that the probability of a molecule travelling a distance x without making a collision is given by $f(x) = \exp\left(-\frac{x}{\lambda}\right)$, where λ is a function of p and T . Here $x = 10.4 \times 10^{-8} \text{ m}$ and

$$\lambda(p, T) = 5.2 \times 10^{-8} \text{ m}$$

i) Using Eq. (3.7) we can write $\lambda(p, 2T) = 2 \times \lambda(p, T) = 10.4 \times 10^{-8} \text{ m}$.

$$\therefore \text{Required probability} = e^{-1} = 0.37$$

ii) $\lambda(2p, 2T) = \lambda(p, T) = 5.2 \times 10^{-8} \text{ m}$

$$\therefore \text{Required probability} = e^{-2} = 0.14$$

iii) $\lambda(3p, T) = \frac{1}{3} \lambda(p, T) = \frac{5.2}{3} \times 10^{-8} \text{ m} = 1.73 \times 10^{-8} \text{ m}$

$$\therefore \text{Required probability} = e^{-6} = 2.48 \times 10^{-3}$$

$$4. \quad m = \frac{32}{6 \times 10^{26}} = 5.33 \times 10^{-26} \text{ kg}$$

From Eq. (3.13) we recall that

$$\eta = \frac{1}{3} \frac{m\bar{v}}{\pi d^2}$$

On re-arrangement, we can write

$$d^2 = \frac{m\bar{v}}{3\pi\eta}$$

On substituting the values of various physical quantities, we get

$$d^2 = \frac{(5.33 \times 10^{-26} \text{ kg}) \times (436 \text{ ms}^{-1})}{3\pi \times (19.6 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1})}$$

Hence,

$$d = \left(\frac{5.33 \times 436}{3\pi \times 19.6} \right)^{1/2} \times 10^{-10} \text{ m}$$

$$= 3.55 \times 10^{-10} \text{ m}$$

$$\text{and } r = 1.77 \times 10^{-10} \text{ m}$$

Terminal Questions

1. From Eq. (3.22), we recall that

$$D = \frac{0.376}{\sigma} \frac{(k_B T)^{3/2}}{p\sqrt{m}}$$

On substituting the given values, we get

$$\begin{aligned}
 D &= \frac{0.376}{(3.1417 \times 4) (1.37 \times 10^{-10} \text{ m})^2} \frac{[(1.38 \times 10^{-23} \text{ JK}^{-1}) \times (300 \text{ K})]^{3/2}}{(2.026 \times 10^5 \text{ Nm}^{-2}) (3.3 \times 10^{-27} \text{ kg})^{1/2}} \\
 &= \frac{0.376}{(23.59 \times 10^{-20} \text{ m}^2)} \frac{266.4 \times 10^{-33} \text{ J}^{3/2}}{(2.026 \times 10^5 \text{ Nm}^{-2}) (5.74 \times 10^{-14} \text{ kg}^{1/2})} \\
 &= 3.56 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}
 \end{aligned}$$

2. We have from Eq. (3.19)

$$K = \frac{\eta c_V}{M} = 0.376 \frac{\sqrt{m}}{\sigma} (k_B T)^{1/2} \frac{c_V}{M} = \frac{0.376}{\sigma} (k_B T)^{1/2} \frac{c_V}{\sqrt{M N_A}}$$

where we have used Eq. (3.15) for η and $m = M/N_A$.

Hence,

$$\begin{aligned}
 \sigma &= 4\pi r^2 = \frac{(0.376)(k_B T)^{1/2} c_V}{K \sqrt{M}} \\
 \text{or } r^2 &= \frac{(0.376)(k_B T)^{1/2} c_V}{4\pi K \sqrt{M}}
 \end{aligned}$$

On substituting the given values, we get

$$\begin{aligned}
 r^2 &= \frac{(0.376)(1.38 \times 10^{-23} \text{ JK}^{-1})^{1/2} \times (273 \text{ K})^{1/2} \times (29.1 \times 10^3 \text{ Jk mol}^{-1} \text{ K}^{-1})}{4\pi \times (23.7 \times 10^{-3} \text{ Jm}^{-1} \text{ s}^{-1} \text{ K}^{-1}) \times [(6.02 \times 10^{26} \text{ kmol}^{-1}) \times (28.02 \text{ kg})]^{1/2}} \\
 &= \frac{671.5 \times 10^{-9}}{3869.0 \times 10^{10}} = 1.74 \times 10^{-20} \text{ m}^2
 \end{aligned}$$

Hence $r = 1.32 \times 10^{-10} \text{ m}$

3. From Eq. (3.7) we recall that $\lambda = \frac{1}{n\sigma}$

Here $\sigma = \pi d^2 = \pi (2.9 \times 10^{-10})^2 \text{ m}^2 = 26.42 \times 10^{-20} \text{ m}^2$

and $n = 3 \times 10^{25} \text{ m}^{-3}$

Hence,

$$\begin{aligned}
 \lambda &= \frac{1}{(3 \times 10^{25} \text{ m}^{-3}) \times (26.42 \times 10^{-20} \text{ m}^2)} \\
 &= 1.26 \times 10^{-7} \text{ m}
 \end{aligned}$$

4. $m = \frac{28 \text{ kg kmol}^{-1}}{6.023 \times 10^{26} \text{ kmol}^{-1}}$

$$= 4.649 \times 10^{-26} \text{ kg}$$

$$\eta = 16.6 \times 10^{-6} \text{ N s m}^{-2}$$

$$\bar{v} = 4.5 \times 10^2 \text{ m s}^{-1}$$

From Eq. (3.13), we can write

$$\lambda = \frac{3\eta}{m\bar{v}}$$

On inserting the values of various physical quantities, we get

$$\lambda = \frac{3 \times (16.6 \times 10^{-6} \text{ N s m}^{-2})}{(4.65 \times 10^{-26} \text{ kg}) \times (2.7 \times 10^{25} \text{ m}^{-3}) \times (4.5 \times 10^2 \text{ m s}^{-1})} = 8.85 \times 10^{-8} \text{ m}$$

Now, the diameter of a gas molecule can be determined by using the

relation $\lambda = \frac{1}{\sqrt{2} \pi d^2 n}$

and rewriting it as

$$d = \left[\frac{1}{\sqrt{2} \pi n \lambda} \right]^{1/2}$$

On substituting the values of n and λ , we get

$$d = \left(\frac{1}{1.414 \times 3.14 \times (2.7 \times 10^{25} \text{ m}^{-3}) \times (8.85 \times 10^{-8} \text{ m})} \right)^{1/2}$$

$$= 3.07 \times 10^{-10} \text{ m}$$

and $r = 1.53 \times 10^{-10} \text{ m}$

Note that the values of radius calculated in TQ 2 and TQ 4 are slightly different. These deviations point to limitations of theory, or values of physical quantities used in two calculations.

5. Using Eq. (3.17), we can write

$$K = \frac{f}{6} n \bar{v} \lambda k_B$$

But we know that $k_B = \frac{R}{N_A}$, therefore we can rewrite the above

expression as

$$K = \frac{f}{6} n \bar{v} \lambda \frac{R}{N_A} \quad (i)$$

You will recall that molar heat capacity

$$c_V = \frac{f}{2}R \quad (\text{ii})$$

Substituting the value of c_V in Eq. (i), we get

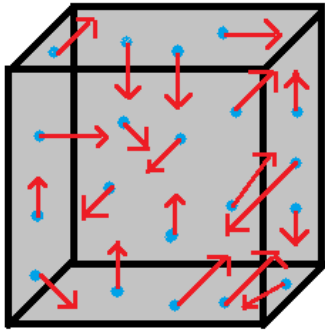
$$\begin{aligned} K &= \frac{c_V}{3} \left(\frac{n}{N_A} \right) \bar{v} \lambda \\ &= \frac{1}{3} \rho \frac{c_V}{M} \bar{v} \lambda \end{aligned} \quad (\text{iii})$$

Since air is primarily a mixture of two diatomic gases (N_2 and O_2),

$$\begin{aligned} c_V &= \frac{5}{2}R = \frac{5}{2} \times 8.31 \times 10^3 \text{ J kmol}^{-1} \text{ K}^{-1} \\ &= \frac{41.55}{2} = 20.78 \times 10^3 \text{ J kmol}^{-1} \text{ K}^{-1} \end{aligned}$$

Now substituting the values of various physical quantities in Eq. (iii), we get the required result:

$$\begin{aligned} K &= \frac{1}{3} \times \frac{(1.29 \text{ kg m}^{-3}) \times (20.78 \times 10^3 \text{ J kmol}^{-1} \text{ K}^{-1}) \times (470 \text{ ms}^{-1}) \times (5.6 \times 10^{-8} \text{ m})}{29 \text{ kg kmol}^{-1}} \\ &= 8.1 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1} \end{aligned}$$



UNIT 4

Brownian motion is continuous and random motion of molecules. You will learn about its importance in kinetic theory in this unit.

BROWNIAN MOTION

Structure

- | | | | |
|-----|-----------------------------|-----|----------------------------------|
| 4.1 | Introduction | 4.5 | Determination of Avogadro Number |
| | Expected Learning Outcomes | 4.6 | Summary |
| 4.2 | Brownian Motion | 4.7 | Terminal Questions |
| 4.3 | Theoretical Analysis | 4.8 | Solutions and Answers |
| 4.4 | Examples of Brownian Motion | | |
| | Sedimentation | | |

STUDY GUIDE

In the previous unit, you have learnt about mean free path, coefficient of viscosity, thermal conductivity and diffusion coefficient. These physical properties helped us to estimate the size of gas molecules in terms of directly measurable quantities. The conformity of theoretical and experimental results provided indirect evidence in favour of kinetic theory. In this unit, you will learn about Brownian motion, which provided the first direct evidence in favour of kinetic theory. For this reason, this concept is extremely important and we have discussed the physics of this phenomenon. However, you should answer the SAQs and TQs, which will help you develop conceptual clarity.

“We cannot solve our problems with the same thinking we used when we created them.”

Albert Einstein

4.1 INTRODUCTION



Robert Brown (1773 – 1858) was a Scottish botanist. He reported the initial observation of continuous random motion of pollen particles in a viscous liquid observed under a microscope. He is also credited with coining the word 'nucleus' in reference to living cells.

In the study of Brownian motion, scientists from three diverse disciplines were involved: Brown, a botanist, observed the phenomena; Einstein, a physicist, provided theoretical explanation and Perrin, a chemist, provided experimental evidence through determination of Avogadro's number. This is an excellent example of unified nature of knowledge.

You now know that elementary kinetic theory successfully explains many observed properties of gases and has great aesthetic appeal; well defined laws are used to describe chaotic motion. Moreover, it helps us to estimate the size of gas molecules in terms of directly measurable quantities fairly well. The agreement between theoretically predicted behaviour with observed results constituted indirect evidence in favour of kinetic theory. However, direct evidence for the *existence of molecules and their motion was lacking* and prominent scientists were reluctant to accept the realities of atoms and molecules.

The first experimental evidence for the existence of molecules and their continuous chaotic motion was provided by Robert Brown while he was observing the motion of particles suspended in a fluid. These suspended particles were seen to move completely haphazardly. This irregular motion was termed **Brownian motion**. The nature of Brownian movements (motion) of suspended particles was seen to depend on the properties of the fluid in which the particles were suspended. In view of its importance, in Sec. 4.2, we review the developments that led to the discovery of Brownian motion.

Albert Einstein explained the phenomenon of Brownian motion theoretically in 1905 in terms of the effects of collisions between fluid molecules and the suspended particles. He argued that although each impact is very small, the net result of a large number of random collisions gives rise to haphazard motion. Einstein quantified this problem by relating the diffusion of particles to the properties of the molecules responsible for collisions. In this way, he related the molecular theory of gases to the observed motion of particles. His predictions were verified by Perrin in 1908. This work convinced everyone about the reality of molecular/atomic nature of matter. Several efforts have been made to generalise Einstein's theory of Brownian motion. In 1908, Langevin re-derived Einstein's formula for mean square displacement by considering the equation of motion of suspended particles. In this unit, we shall not go into mathematical aspects of these effects. In Sec. 4.4, we have discussed examples of Brownian motion and Sec. 4.5 is devoted to the discussion of Perrin's experiments, which provided a convenient method to determine Avogadro number.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ explain the significance of Brownian motion;
- ❖ write expression for the mean square displacement;
- ❖ discuss sedimentation as an example of Brownian motion; and
- ❖ explain how Perrin determined Avogadro's number and discuss its significance for kinetic theory of gases.

4.2 BROWNIAN MOTION

In 1827, Scottish botanist Robert Brown observed the motion of pollen grains suspended in an aqueous solution through a high-power microscope. These pollen grains were seen to exhibit a continuous and completely erratic movement. This irregular motion is termed as **Brownian motion** (Fig. 4.1).

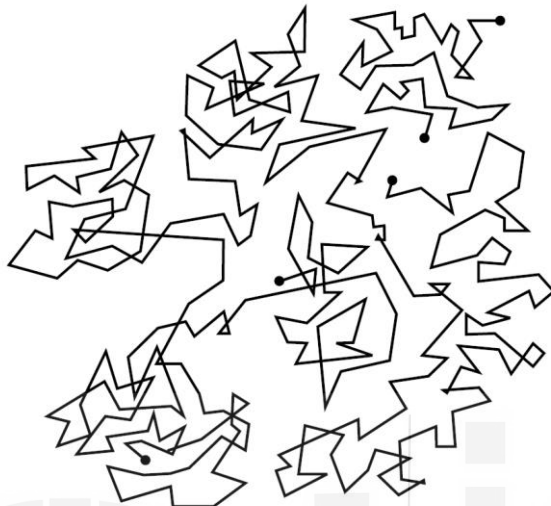


Fig. 4.1: Brownian motion of suspended particles in an aqueous solution.

The observed characteristics of Brownian motion are:

1. The motion is continuous, completely random and irregular.
2. No two particles execute the same motion.
3. Smaller particles execute faster and hence more noticeable motion.
4. The movement is about the same in all directions.
5. The motion is independent of external influences.
6. Smaller the viscosity, faster is the motion.
7. Motion is more rigorous at higher temperatures.

A proper explanation of this phenomenon eluded scientists for a long time. Studies of Guy Williams and other physicists led to the view that Brownian motion arises due to collisions of suspended particles with the molecules of the surrounding fluid. This phenomenon provided a very elegant picture of the gaseous state wherein gas molecules were in random motion and frequently collided against each other. In a way, Brownian motion provided us a mechanism for visualising the behaviour of matter at microscopic scale. Only for this reason, it has been of such great interest to physicists. But it required the genius of Einstein to work out a detailed theory of Brownian motion. Einstein's predictions were found to be precisely correct by the beautiful experiments of Perrin. This also paved the way for accurate determination of molecular masses and convinced everyone of the reality of the molecular nature of matter.

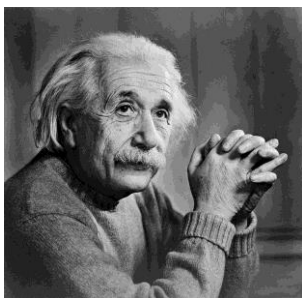
BROWNIAN MOTION

A perpetual, irregular and completely random motion of particles suspended in a viscous solution is known as **Brownian motion**. This phenomenon provides an elegant picture of gaseous state.



SAQ 1 – Brownian motion

State the importance of Brownian motion.



Albert Einstein (1879 – 1955) is regarded as the greatest physicist of 20th century. 1905 was a wonder year for Albert Einstein. He published four very important papers in this year. Each of these papers significantly contributed to enhance our knowledge at that point of time. The diverse topics covered in these papers were photoelectric effect, Brownian motion, special theory of relativity and matter energy equivalence ($E = mc^2$) relation. In 1921, Nobel prize was conferred on him for his work on photoelectric effect. In the paper on Brownian motion, Einstein gave an exact description of the effects of random collisions with the molecules of the liquid on the motion of the suspended particles.

4.3 THEORETICAL ANALYSIS

Einstein's Theory

Einstein gave an exact description of Brownian motion by relating Brownian motion to physical processes. In particular, he considered the effects of random collisions between molecules of the liquid and suspended particles. To quantify this problem, he obtained expressions for diffusion coefficient, D , from the random motion of suspended particles as well as from the osmotic pressure difference in different parts of the solution caused by difference in concentrations of suspended particles (see box below). He then equated these expressions to calculate mean squared displacement of a Brownian particle. We just quote the result without going into mathematical details.

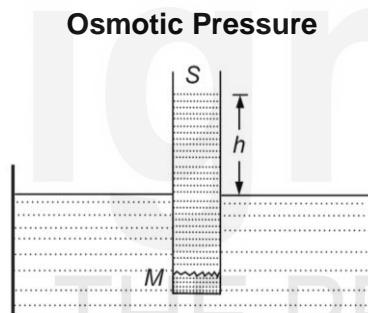


Fig. 4.2: Glass tube with semi-permeable membrane M at its end filled with sugar solution dipped in water.

Osmotic pressure of a solution is the pressure required to prevent osmosis when the solution is separated from pure solvent by a semi-permeable membrane. van't Hoff's law of osmotic pressure states that the osmotic pressure of a dissolved substance in a solution is numerically equal to the pressure which it would exert if it were assumed to behave like a gas having same volume as occupied by the given solution at the same temperature. Suppose we take an open glass tube and cover its one end with a 'semi-permeable membrane' that is permeable to water but not to sugar in solution. Let us fill this tube with a dilute sugar solution and dip it into a beaker of water, as shown in Fig. 4.2 above. We observe that the solution rises to a height above the level of the water.

This means that the solution has a pressure $\rho g h$ higher than that of pure water at the same temperature. This pressure, exerted by the sugar dissolved in solution, is called **osmotic pressure**. For dilute solutions, i.e., in which the number of solute molecules is very small compared to the solvent molecules, van't Hoff established that

$$p_{osmotic} = nk_B T$$

where n is concentration of the solution. That is, for dilute solutions, the osmotic pressure is equal to the pressure which the solute would exert if it were assumed to behave like an ideal gas having the volume and temperature as that of the solution.

$$\ell^2 = \frac{k_B T}{3\pi\eta r_0} \tau = \frac{RT}{N_A} \frac{1}{3\pi\eta r_0} \tau \quad (4.1)$$

This is the famous **Einstein's formula** for mean square displacement of a Brownian particle.

It is instructive to note that Brownian mean square displacement is independent of the mass of particles. Through a brilliant series of experiments, Perrin confirmed this prediction by varying mass through a factor of 15,000. We further note that diffusion of particles is related to molecular motion. Moreover, since ℓ^2 , τ , η and r_0 are measureable quantities, Eq. (4.1) proved a ready tool for determination of Avogadro number. In fact, this equation was verified by Perrin, and was found to be precisely correct. His experiments, therefore, established the existence of molecules beyond any doubt and provided general acceptability to kinetic theory of gases.

You must have realised that Einstein laid greater emphasis on relating Brownian motion to physical processes.

Langevin Theory

A somewhat more elegant explanation was given by Langevin. He assumed that the average force acting on a suspended particle due to molecular bombardment is made up of a frictional and a fluctuating component.

Langevin argued that a suspended particle undergoes, on an average, one collision in about 10^{-21} s with the molecules of the liquid. So the mean free path of the molecules is small compared with the size of the suspended particles. It means that the surrounding medium can be considered continuous. Langevin also assumed that all suspended particles are spherical in shape. Then using Stoke's law and the fact that the direction of motion of each suspended particle changes after each collision, he arrived at Einstein's expression for mean square displacement of Brownian particles.

$$\overline{\Delta(x^2)} = \frac{k_B T}{3\pi\eta r_0} \tau = \frac{RT}{N_A} \frac{1}{3\pi\eta r_0} \tau \quad (4.2)$$

Note that $\overline{\Delta(x^2)}$ is not the actual displacement of Brownian particles. We have to take a snapshot of the suspension at time $t = 0$ and again at time $t = \tau$. Then we measure the component of displacement along any arbitrarily chosen direction, say x-axis, and determine $\Delta(x^2)$ for each particle. A sum over all the $\Delta(x^2)$ and division by the number of particles gives $\overline{\Delta(x^2)}$. In his experiments, Perrin worked with 100 different particles of known size. If we closely re-examine Fig. 4.1 we find that the motion is so complex that an experimentalist may not find it convenient to work with such a large number. However, we can make use of the fact that if one particle is followed for N successive intervals of time (when N is a large number), the motion is almost equivalent to the motion of N particles during a single time interval.

SAQ 2 – Size of a particle

In an experiment with colloidal particles suspended in water at temperature 32°C , the mean square displacement in unit time was found to be $1.8 \times 10^{-6} \text{ cm}^2$. Calculate the value of the radius of a suspended particle.

Take $R = 8.31 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1}$, $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ and $\eta = 0.01 \text{ poise}$.

4.4 EXAMPLES OF BROWNIAN MOTION

We have just now seen that colloidal suspensions in a fluid exhibit Brownian motion. We come across many other interesting examples of Brownian motion. These include sedimentation, diffusion of pollutants or smoke particles in air and Johnson noise in electrical devices. We will discuss sedimentation now.

4.4.1 Sedimentation

From common experience we know that if we take sandy water in a beaker, the sand settles down at the bottom. This natural process is known as sedimentation. It is responsible for automatic cleaning of rainwater stored in ponds and lakes. In sedimentation, the distribution of particles is determined by the influence of gravity and diffusion. Whereas gravity tends to settle them, diffusion brings about homogenisation. (The same is true of pollutants in our atmosphere, which give rise to acid rain, greenhouse effect and climate change.)

To calculate the number of particles at a given height, we consider a shallow box of depth Δz enclosing layers of particles bound at heights z and $z + \Delta z$. Let the pressure on the lower and upper faces be p and $p + \Delta p$ respectively as shown in Fig. 4.3.

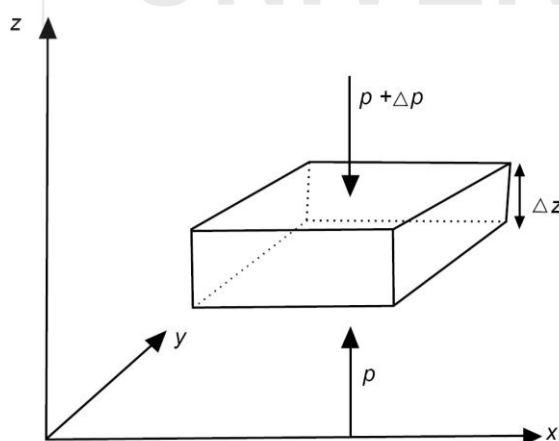


Fig. 4.3: A shallow box of depth Δz and cross-sectional area A . The pressures on the lower and upper faces are assumed to be p and $p + \Delta p$, respectively.

If ρ and g , respectively, denote the density of particles and acceleration due to gravity, the pressure difference between the two surfaces in equilibrium is given by

$$\Delta p = -g\rho\Delta z \quad (4.3)$$

The negative sign signifies that pressure decreases as height increases. If the mass of a single particle is m and number density is n , we can write $\rho = mn$. Then we can rewrite the expression for pressure difference as

$$\Delta p = -gmn\Delta z = -\frac{mgN}{V}\Delta z$$

If we assume that Brownian particles obey gas laws, we can replace V by $\mu RT/p$. This gives

$$\frac{\Delta p}{p} = -\frac{mgN}{\mu RT}\Delta z$$

where μ denotes the number of moles.

This expression can be readily integrated to obtain

$$\ln p = -\frac{mgN}{\mu RT}z + \ln p_0$$

where $\ln p_0$ is constant of integration.

On taking antilog, we get

$$p = p_0 \exp\left(-\frac{mgN}{\mu RT}z\right) \quad (4.4)$$

where $p = p_0$ at $z = 0$. From Unit 1, you may recall that the pressure exerted by the molecules of a gas on the walls of the container is proportional to number density ($p = \frac{1}{3}mnv^2$). Using this result, we can rewrite Eq. (4.4) as

$$n = n_0 \exp\left(-\frac{mgN}{\mu RT}z\right) = n_0 \exp\left(-\frac{mgN_A}{RT}z\right) \quad (4.5)$$

where $N_A = N/\mu$ is Avogadro number.

This result shows that during sedimentation, particle concentration decreases exponentially as height increases. In practice, the suspended particles experience upward buoyant force due to difference in the densities of the solute ρ and the solvent ρ' . As a result, the effective mass of the suspended particles is reduced to

$$m_{eff} = \frac{4\pi}{3}(\rho - \rho')r_0^3 \quad (4.6)$$

where r_0 is the radius of a particle. If $\rho \approx \rho'$, m_{eff} would be substantially small. We now take natural log of both sides of Eq. (4.5) and use the value of m_{eff} given in Eq. (4.6). Then we can write the expression for Avogadro's number in terms of the microscopic properties of the suspended particles:

$$N_A = \frac{3RT}{4\pi r_0^3(\rho - \rho')gz} \ln\left(\frac{n_0}{n}\right) \quad (4.7)$$

Eq. (4.7) suggests that if we study the variation of n with height for fine suspensions, we can conveniently determine Avogadro number. Perrin

A. Avogadro, an Italian scientist, had proposed in 1811 that equal volume of all gases at a given pressure and temperature contains the same number of molecules. The number of molecules in one mole of a gas is known as Avogadro number. We denote it by N_A . Jean Perrin proposed this nomenclature in 1905.

worked with emulsions of gamboge and mastic (resin pigments obtained from trees) and obtained a value very close to the presently accepted value. His results lent support to molecular theory of gases.

In the next section, we will discuss Perrin's work. However, for now, go through the following example.

EXAMPLE 4.1: AVOGADRO'S NUMBER

In an experiment, motion of 49 particles per cm^2 is observed in a layer of gamboge suspended in water at one level and 14 particles per cm^2 in a layer 60 microns higher (1 micron = 10^{-6} m). If the density of gamboge is 1.194 g cm^{-3} and radius of each particle is 0.212 micron, calculate Avogadro number. Take the temperature of the solution as 20°C , $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$, and $g = 9.8 \text{ ms}^{-2}$.

SOLUTION ■ From Eq. (4.7), we have

$$N_A = \frac{3RT}{4\pi r_0^3 (\rho - \rho')gz} \ln\left(\frac{n_0}{n}\right)$$

On substituting the values of various quantities, we get

$$\begin{aligned} N_A &= \frac{3 \times (8.31 \text{ J mol}^{-1} \text{ K}^{-1})}{4 \times 3.14 \times (0.212 \times 10^{-6} \text{ m})^3 \times (1.194 - 1.0) \times 10^3 \text{ kg m}^{-3}} \\ &\quad \times \frac{(293 \text{ K})}{(9.8 \text{ ms}^{-2}) \times (60 \times 10^{-6} \text{ m})} \ln\left(\frac{49}{14}\right) \\ &= \frac{3 \times 8.31 \times 293 \times 1.25}{4 \times 3.14 \times (0.212)^3 \times 0.194 \times 9.8 \times 60} \times 10^{21} \text{ mol}^{-1} \\ &= 6.7 \times 10^{23} \text{ mol}^{-1}. \end{aligned}$$

Let us now recapitulate what we have discussed in this sub-section.

Recap

EXAMPLES OF BROWNIAN MOTION

- Sedimentation and Johnson Noise are two very familiar examples of Brownian motion.
- During sedimentation, particle density decreases exponentially as height increases:

$$n = n_0 \exp\left(-\frac{mgN_A}{RT} z\right)$$

Perrin carried out a series of beautiful experiments on colloidal suspensions to obtain the value of Avogadro number. This work signified a great triumph of molecular theory. For these investigations Perrin was awarded Nobel Prize for Physics in 1926. We now discuss Perrin's experiments.

4.5 DETERMINATION OF AVOGADRO NUMBER

To determine Avogadro number, we have to measure $\overline{x^2}$, the mean square displacement of a Brownian particle. Perrin observed the motion of a single gamboge grain suspended in water at intervals of thirty seconds with the help of a microscope and a camera. To locate the particle, the microscope had in its field of view a series of mutually perpendicular lines, as shown on a graph paper in Fig. 4.4. The projections of successive displacements along the x-axis give a set of values of x from which $\overline{x^2}$ can be calculated.

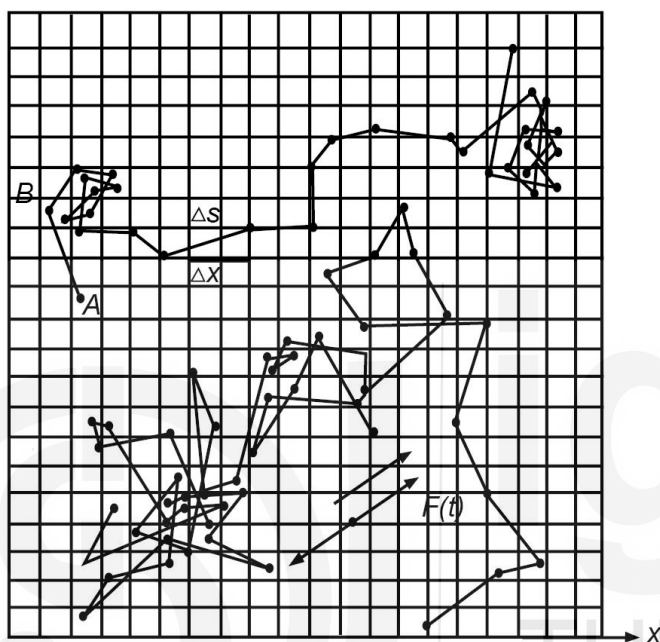


Fig. 4.4: Calculation of $\overline{x^2}$ for a Brownian particle.

It should be realised that the straight-line segments in Fig. 4.4 are in no way a representation of the actual path of the particle. The particle is hit millions of times in a second, and hence, its trajectory has a jagged and irregular structure. For example, if we magnify the part AB of the trajectory, it will appear as shown in Fig. 4.5.

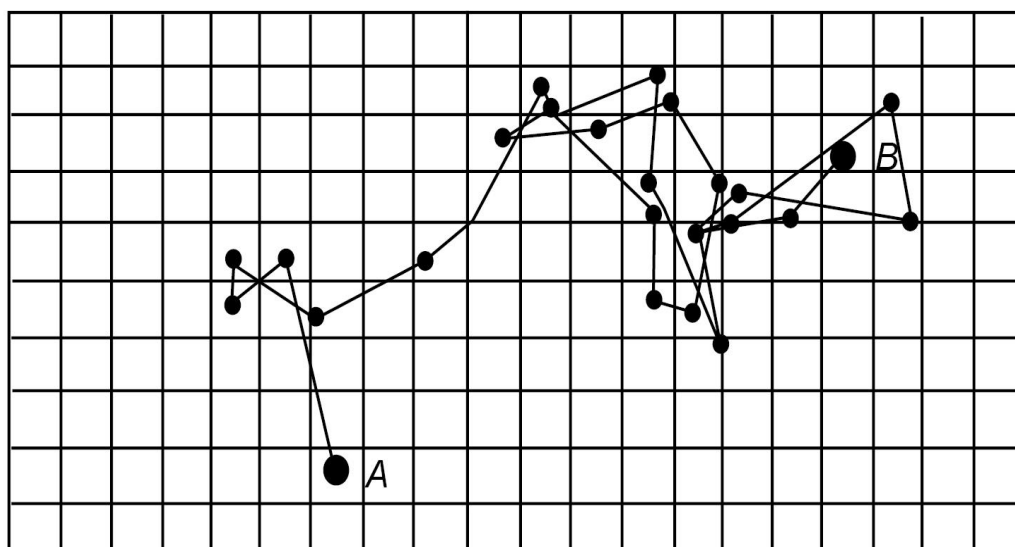


Fig. 4.5: The path AB after magnification.

You may now ask: How could Perrin make such wonderful observations with a simple arrangement? The physical basis of his work was very sound. Perrin derived his argument from the fact that at 300 K, $v_{\text{rms}} = 2 \times 10^{-2} \text{ ms}^{-1}$ for a $2 \times 10^{-7} \text{ m}$ radius grain of gamboge having a mass of about $3 \times 10^{-17} \text{ kg}$ (which is 10^9 times the mass of H_2O molecule). This combination of slow speeds and large size was used by Perrin to observe the motion of suspended particles. It justifies the popular belief that Nature likes simplicity: most natural laws have been unfolded using very simple arguments. (Sir C. V. Raman explained the blue colour of Deep Ocean in terms of scattering of light by H_2O molecules and used a very modest apparatus, to vividly demonstrate it.)

From his measurements, Perrin obtained a value of 6.85×10^{26} molecules kmol^{-1} for Avogadro number, which is fairly close to the currently accepted value of $6.022 \times 10^{26} \text{ kmol}^{-1}$.

From this value of Avogadro number, we can estimate the mass of a molecule. For example, one kilo-mole of nitrogen gas has a mass of 14 kg. Hence, mass of a nitrogen molecule

$$m_{\text{N}_2} = \frac{14 \text{ kg}}{6.02 \times 10^{26}} = 2.32 \times 10^{-26} \text{ kg}$$

Perrin is, therefore, said to be the first person to have weighed the atom with kinetic theory as the tool!

4.6 SUMMARY

Concept	Description
Brownian motion	<ul style="list-style-type: none"> ■ Brownian motion is perpetual and irregular motion of the particles immersed in fluid. It is caused by their continuous bombardment by the surrounding molecules of much smaller size. Sedimentation and Johnson noise are familiar examples of Brownian motion. ■ Brownian motion provided direct experimental evidence in support of kinetic theory of gases.
Einstein's relation	<ul style="list-style-type: none"> ■ Einstein's relation for mean square displacement of a Brownian particle is
	$l^2 = \frac{RT}{N_A} \frac{1}{3\pi\eta r_0} \tau$
Sedimentation	<ul style="list-style-type: none"> ■ The variation of particle concentration with height, z, during sedimentation is given by

$$n = n_0 \exp \left(- \frac{mgN_A}{RT} z \right)$$

Avogadro number

- Perrin determined the value of Avogadro number and used it to determine the mass of nitrogen atom. That is, Perrin weighed the atom with kinetic theory as tool.

4.7 TERMINAL QUESTIONS

1. W. Pospisil observed the motion of soot particles of radius 0.4×10^{-4} cm in a water-glycerine solution with $\eta = 0.0278$ poise at $T = 292$ K. The observed value of $\overline{\Delta x^2}$ was 3.3×10^{-8} cm² for $t = 10$ s. Use this information to calculate Boltzmann constant and hence N_A .
2. The mean kinetic energy of molecules of hydrogen at 0°C is 5.60×10^{-21} J and molar gas constant is 8.31 J mol⁻¹ K⁻¹. Calculate Avogadro's number.
3. A Brownian particle of radius 2.10×10^{-7} m moves in a liquid at 20°C . If the value of RMS displacement in 32 s is 6.5×10^{-6} m, calculate the value of Boltzmann constant. The coefficient of viscosity of the liquid is 1.2×10^{-3} N s m⁻².

4.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. The Brownian motion is the experimental evidence in support of the basic assumption of kinetic theory of a gas that it consists of molecules moving at random.
2. Given $N_A = 6.023 \times 10^{23}$ mol⁻¹, $\eta = 10^{-2}$ poise,
 $T = 32^\circ\text{C} = 32 + 273 = 305$ K, $\tau = 1$ s
 $\overline{\Delta(x^2)} = 1.8 \times 10^{-6}$ cm², $R = 8.31 \times 10^7$ erg mol⁻¹ K⁻¹.

From Eq. (4.2), we recall that

$$\overline{\Delta(x^2)} = \frac{RT}{N_A} \frac{1}{3\pi\eta r_0} \tau$$

On rearranging the terms, we can express r_0 in terms of the given physical parameters:

$$r_0 = \frac{RT}{\overline{\Delta(x^2)} N_A \times 3\pi\eta} \tau$$

On substituting the given values, we get

$$\begin{aligned} r_0 &= \frac{(8.31 \times 10^7 \text{ erg mol}^{-1} \text{K}^{-1}) \times (305 \text{ K}) \times 1 \text{ s}}{(6.023 \times 10^{23} \text{ mol}^{-1}) \times (1.8 \times 10^{-6} \text{ cm}^2) \times (3 \times 3.14 \times 0.01 \text{ dyne cm}^{-2} \text{ s})} \\ &= 2479.53 \times 10^{-10} \text{ cm} = 2.48 \times 10^{-7} \text{ cm} \end{aligned}$$

Terminal Questions

1. We have $\Delta(\overline{x^2}) = \frac{k_B T}{3\pi\eta r_0} \tau$

On rearrangement, we can write

$$k_B = \frac{3\pi\eta r_0}{T\tau} \Delta(\overline{x^2}) = \frac{3\pi \times (0.0278 \text{ poise}) \times (0.4 \times 10^{-4} \text{ cm}) \times 3.3 \times 10^{-8}}{(292 \text{ K}) \times (10 \text{ s})}$$

$$= 1.18 \times 10^{-16} \text{ erg K}^{-1}$$

Using this result, we can write

$$N_A = \frac{R}{k_B} = \frac{8.31 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1}}{1.18 \times 10^{-16} \text{ erg K}^{-1}}$$

$$= 7.04 \times 10^{23} \text{ mol}^{-1}$$

2. Given: $E = 5.60 \times 10^{-21} \text{ J}$, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ and $T = 273 \text{ K}$.

We have

$$E = \frac{3}{2} k_B T \quad \text{(i)}$$

But $k_B = \frac{R}{N_A}$ (ii)

On combining Eqs. (i) and (ii), we get the following expression for energy:

$$E = \frac{3}{2} \left(\frac{R}{N_A} \right) \cdot T$$

$$\Rightarrow N_A = \frac{3RT}{2E} \quad \text{(iii)}$$

On substituting the values in Eq. (iii), we get

$$N_A = \frac{3 \times 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}}{2 \times 5.60 \times 10^{-21} \text{ J}} = 6.08 \times 10^{23} \text{ mol}^{-1}$$

3. From Eq. (4.2), we can write

$$\Delta(\overline{x^2}) = \frac{k_B T}{3\pi\eta r_0} \tau$$

We are given that RMS displacement is $6.5 \times 10^{-6} \text{ m}$,

$\eta = 1.2 \times 10^{-3} \text{ N s m}^{-2}$, and $r_0 = 2.10 \times 10^{-7} \text{ m}$. To use the value of RMS

displacement in the above formula for $\Delta(\overline{x^2})$, we have to calculate its square. Hence, we can write

$$(6.5 \times 10^{-6} \text{ m})^2 = \frac{k_B \times (293 \text{ K}) \times 32 \text{ s} \times 7}{3 \times 22 \times (1.2 \times 10^{-3} \text{ N s m}^{-2}) \times (2.10 \times 10^{-7} \text{ m})}$$

or $k_B = \frac{42.25 \times 10^{-12} \times 166.32 \times 10^{-10} \text{ Nm}}{65632 \text{ K}}$

$$= \frac{7027.02 \times 10^{-22} \text{ J}}{65632 \text{ K}} = 1.07 \times 10^{-23} \text{ JK}^{-1}$$