THERMAL AND STATISTICAL PHYSICS

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New Academic Science Limited

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Preface

The present book is designed to meet the requirements of Thermal Physics, also known as Heat and Thermodynamics at undergraduate level. I have been very careful in selecting the topics, laying their sequence and the style of presentation so that students may not afraid of learning new concepts. Realizing the mental state of undergraduate students every attempt has been made to present the material in most elementary and easily digestible form. To this end a sufficient number of examples have been added. Though I have made my best effort in this attempt on the subject while planning the layout of the text and the subject matter, I cannot guess as to how far I have come up to the expectations of esteemed readers, scholars, teachers, learned physicists and students. They have to judge my work critically and pass their constructive criticisms either to me or to the publishers so that my future endeavour be to enlarge and correct mistakes and polish the text in such a way that it becomes more and more object-oriented for the students.

I am thankful to my colleagues, family members and the publishers for their cooperation during writing of the manuscript and its composing and printing. To err is human. Therefore, I hope that in future the readers of this book will help me in correcting any typographical error or conceptual mistake which might have escaped my attention during proof-reading and printing.

In the end, I await the response which this book draws from learned scholars and students.

R.B. Singh

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Thermal Physics

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CHAPTER

Kinetic Theory of Gases

1.1 INTRODUCTION

A vast number of experiments show that heat is a kind of energy associated with molecular motion. In kinetic model, the matter is assumed to be made up of tiny particles called molecules. The molecules move in all possible directions with varying speeds *i.e.,* their motion is completely random. Their speeds increase with rise in temperature of the substance. The molecular kinetic energy is a measure of heat content in a body.

In solids, molecules are closely packed due to intermolecular forces. They cannot move bodily from one place to another. However, they can vibrate about their mean position. For this reason, solids have definite shape and size or volume. In liquids, molecules are at larger distances in comparison to solids and the intermolecular forces are a bit smaller in magnitude. The molecules of liquid cannot leave the liquid but move to anywhere inside it. Liquids have definite volume but not size. In gases, the molecules are at larger distances from each other than those in liquids and the intermolecular forces are very weak. The molecules are free to move anywhere and hence gases have neither definite volume nor any shape. Because gases obey simple laws, the kinetic model of matter was first applied to them. The work of Joule, Bernoulli, Clausius, Maxwell, Boltzmann, James Jean, Lorentz, Rayleigh van der Waals, Planck, Helmholtz, Gibbs etc., laid the foundation of theory of heat over which the modern theory of matter was erected. The present chapter is devoted to the study of kinetic theory of gases.

1.2 FUNDAMENTAL ASSUMPTIONS OF KINETIC THEORY OF IDEAL GASES

The kinetic theory of gases is based on the following assumptions:

(1) A small sample of gas consists of a very large number of molecules. At standard conditions, 1 kilomol of an ideal gas occupies 22.4 m^3 volume and contains $N_A = 6.023 \times 10^{26}$ molecules *i.e.,* 1 cm^3 of gas contains 3×10^{19} molecules.

(2) The molecules of a gas are like hard spheres and are perfectly elastic. The molecular diameter is about 2 or 3×10^{-10} m. The molecules are in continuous motion in all possible directions *i.e.,* there is no preferred direction of motion. Meaning thereby the molecular motion is chaotic in nature.

(3) Not all molecules have the same speed. Their speeds vary from a low value to a very high value. The range of molecular speed is so large that no appreciable error is made in taking the range from zero to infinity.

(4) The collision between any two molecules and between molecule and the wall of the containing vessel are perfectly elastic. When molecules strike the walls of the vessel, they transfer momentum to the wall. The rate of change of momentum suffered by molecules exerts force on the wall. This is origin of pressure of the gas.

(5) The molecules exert no forces among themselves except when they collide. That is, intermolecular forces are assumed to be absent.

(6) The molecules occupy negligible volume in comparison to the volume of the containing vessel.

(7) The duration of collision between the molecules is very small. Between two collisions molecules move in straight lines and the average distance between two collisions is called mean free path.

1.3   MOLECULAR FLUX

Consider an ideal gas consisting of N molecules enclosed in a vessel volume V. The molecules move chaotically in all possible directions with all possible speed from zero to infinity. Let us represent the velocities of the molecules as vectors and call it velocity vectors. These vectors have all possible magnitude and directions. Now transfer the tails of all velocity vectors to a common origin O and imagine a sphere of arbitrary radius r with center at O such that all the velocity vectors intersect the surface of the sphere. The number of points of intersection of velocity vectors with the sphere is equal to the number N of molecules in the gas. The surface density of these points is $N/(4\pi r^2)$. Now consider an element of area dA on the sphere at point (r, θ, ϕ) as shown in the figure. This area is equal to $dA = r^2 \sin\theta \, d\theta \, d\phi$. The number of points on this represents the number of molecules with velocities in the direction between θ and $\theta + d\theta$, and φ and $\varphi + d\varphi$. We denote this number by $dN_{\theta\varphi}$. Thus

$$dN_{\theta\varphi} = \left(\frac{N}{4\pi r^2}\right) dA = \frac{N}{4\pi}\left(\frac{dA}{r^2}\right) = \frac{N}{4\pi}\, d\Omega_{\theta\varphi} = \frac{N}{4\pi}. \sin\theta \, d\theta \, d\varphi \quad ...(1.1)$$

where $d\Omega_{\theta\varphi}$ is the solid angle subtended by area dA at the origin O.

We are interested in finding the number of molecules arriving per second from one side at a unit area of an imaginary surface within the gas. Let dN_v denote the number of molecules whose velocities have magnitude in the range v and $v+dv$ irrespective of their direction of motion and $dN_{\theta\varphi v}$ those molecules moving with speeds between v and $v+dv$ and directions in the angle intervals from θ to $\theta+d\theta$ and from φ to $\varphi + d\varphi$. $dN_{\theta\varphi v}$ is given by

$$dN_{\theta\varphi v} = dN_v.\frac{d\Omega_{\theta\varphi}}{4\pi} = dN_v.\frac{\sin\theta d\theta d\varphi}{4\pi} \quad ...(1.2)$$

Let us first find the number of molecules arriving at an element of surface dS of the vessel towards which $dN_{\theta\varphi v}$ molecules are moving. To this end, we mentally construct a cylinder with area dS as base and $v \, dt$ as length. The volume of this cylinder is

$$dV = (dS \cos\theta) \, (vdt)$$

A fraction $\dfrac{dV}{V}$ of $dN_{\theta\varphi v}$ molecules will strike the surface dS and this number is
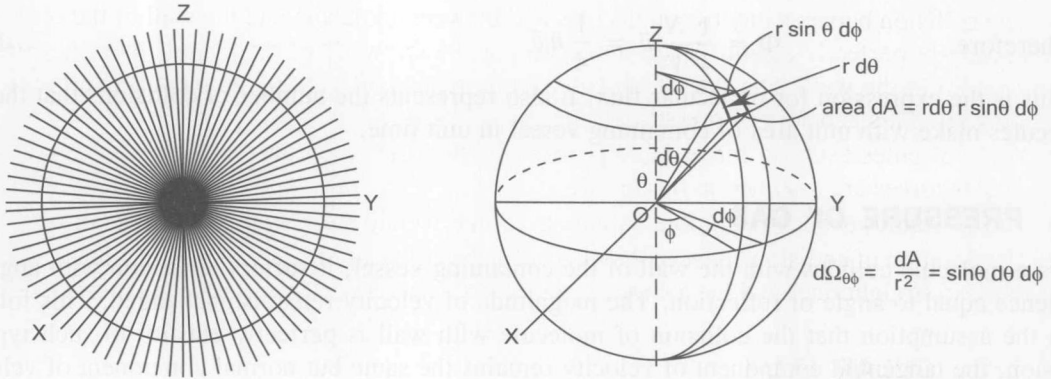
Fig. 1.1.

$$dN_{\theta\varphi v, dS} = dN_{\theta\varphi v}\frac{dV}{V} = dN_v\left(\frac{\sin\theta\, d\theta\, d\varphi}{4\pi}\right)\left(\frac{dS\cos\theta\cdot v dt}{V}\right) \qquad \ldots(1.3)$$
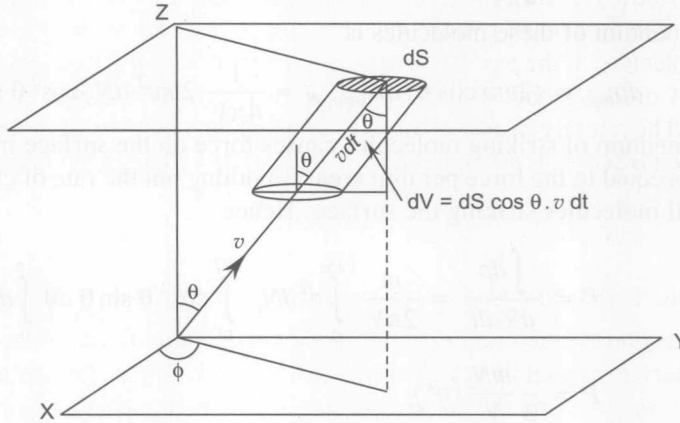

Fig. 1.2.

The number of molecules having speed in the range dv about v and striking unit area in unit time in θ-φ direction is

$$d\Phi_{\theta\varphi v} = \frac{dN_{\theta\varphi v\, dS}}{dS\cdot dt} = \frac{1}{4\pi V}(v dN_v)(\sin\theta\cos\theta\, d\theta)(d\varphi) \qquad \ldots(1.4)$$

The total number of molecules arriving at unit area in unit time from one side is obtained by integrating $d\Phi_{\theta\varphi v}$, within the limits of v from 0 to $v_{\max}$, θ from 0 to $\pi/2$, and φ from 0 to 2π.

$$\Phi = \frac{1}{4\pi V}\int_0^{v_{\max}} v\, dN_v\int_0^{\pi/2}\sin\theta\cos\theta\, d\theta\int_0^{2\pi} d\varphi$$

$$= \frac{1}{4\pi V}\int_0^{v_{\max}} v\, dN_v\left(\frac{1}{2}\right)(2\pi) \qquad \left(\because\ \overline{v} = \frac{\displaystyle\int_0^{v_{\max}} v dN_v}{N}\right)$$