(i) By definition $\mu_1 = (N_1/N_A)$ and $\mu_2 = (N_2/N_A)$ where N_1 and N_2 are the number of molecules of 1 and 2, and N_A is the Avogadro's number. Therefore, $(N_1/N_2) = (\mu_1 / \mu_2) = 3/2$.

(ii) We can also write $\mu_1 = (m_1/M_1)$ and $\mu_2 = (m_2/M_2)$ where m_1 and m_2 are the masses of 1 and 2; and M_1 and M_2 are their molecular masses. (Both m_1 and M_1; as well as m_2 and M_2 should be expressed in the same units). If ρ_1 and ρ_2 are the mass densities of 1 and 2 respectively, we have

$$\frac{\rho_1}{\rho_2} = \frac{m_1 / V}{m_2 / V} = \frac{m_1}{m_2} = \frac{\mu_1}{\mu_2}\frac{M_1}{M_2}$$

$$= \frac{3}{2}\frac{20.2}{32.0} = 0.947$$ ◀

13.4 KINETIC THEORY OF AN IDEAL GAS

Kinetic theory of gases is based on the molecular picture of matter. A given amount of gas is a collection of a large number of molecules (typically of the order of Avogadro's number) that are in incessant random motion. At ordinary pressure and temperature, the average distance between molecules is a factor of 10 or more than the typical size of a molecule (2 Å). Thus the interaction between the molecules is negligible and we can assume that they move freely in straight lines according to Newton's first law. However, occasionally, they come close to each other, experience intermolecular forces and their velocities change. These interactions are called collisions. The molecules collide incessantly against each other or with the walls and change their velocities. The collisions are considered to be elastic. We can derive an expression for the pressure of a gas based on the kinetic theory.

We begin with the idea that molecules of a gas are in incessant random motion, colliding against one another and with the walls of the container. All collisions between molecules among themselves or between molecules and the walls are elastic. This implies that total kinetic energy is conserved. The total momentum is conserved as usual.

13.4.1 Pressure of an Ideal Gas

Consider a gas enclosed in a cube of side l. Take the axes to be parallel to the sides of the cube, as shown in Fig. 13.4. A molecule with velocity
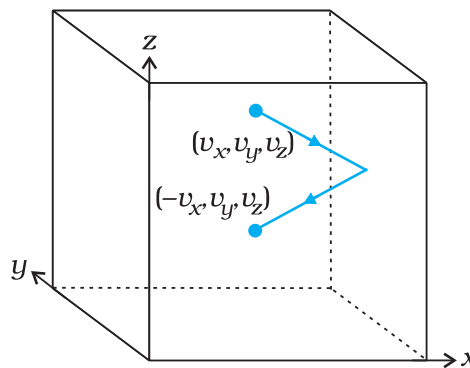

Fig. 13.4 *Elastic collision of a gas molecule with the wall of the container.*

(v_x, v_y, v_z) hits the planar wall parallel to yz-plane of area $A (= l^2)$. Since the collision is elastic, the molecule rebounds with the same velocity; its y and z components of velocity do not change in the collision but the x-component reverses sign. That is, the velocity after collision is $(-v_x, v_y, v_z)$. The change in momentum of the molecule is : $-mv_x - (mv_x) = -2mv_x$. By the principle of conservation of momentum, the momentum imparted to the wall in the collision = $2mv_x$.

To calculate the force (and pressure) on the wall, we need to calculate momentum imparted to the wall per unit time. In a small time interval Δt, a molecule with x-component of velocity v_x will hit the wall if it is within the distance $v_x \Delta t$ from the wall. That is, all molecules within the volume $Av_x \Delta t$ only can hit the wall in time Δt. But, on the average, half of these are moving towards the wall and the other half away from the wall. Thus the number of molecules with velocity (v_x, v_y, v_z) hitting the wall in time Δt is $\frac{1}{2} A v_x \Delta t\, n$ where n is the number of molecules per unit volume. The total momentum transferred to the wall by these molecules in time Δt is :

$$Q = (2mv_x)\left(\frac{1}{2}\, n A v_x \Delta t\right) \qquad (13.10)$$

The force on the wall is the rate of momentum transfer $Q/\Delta t$ and pressure is force per unit area :

$$P = Q /(A \Delta t) = n m v_x^2 \qquad (3.11)$$

Actually, all molecules in a gas do not have the same velocity; there is a distribution in velocities. The above equation therefore, stands for pressure due to the group of molecules with speed v_x in the x-direction and n stands for the number density of that group of molecules. The

total pressure is obtained by summing over the contribution due to all groups:

$$P = n \, m \, \overline{v_x^2} \qquad (13.12)$$

where $\overline{v_x^2}$ is the average of $v_x{}^2$. Now the gas is isotropic, i.e. there is no preferred direction of velocity of the molecules in the vessel. Therefore, by symmetry,

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

$$= (1/3) \, [\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}] = (1/3) \, \overline{v^2} \qquad (13.13)$$

where v is the speed and $\overline{v^2}$ denotes the mean of the squared speed. Thus

$$P = (1/3) \, n \, m \, \overline{v^2} \qquad (13.14)$$

Some remarks on this derivation. First, though we choose the container to be a cube, the shape of the vessel really is immaterial. For a vessel of arbitrary shape, we can always choose a small infinitesimal (planar) area and carry through the steps above. Notice that both A and Δt do not appear in the final result. By Pascal's law, given in Ch. 10, pressure in one portion of the gas in equilibrium is the same as anywhere else. Second, we have ignored any collisions in the derivation. Though this assumption is difficult to justify rigorously, we can qualitatively see that it will not lead to erroneous results. The number of molecules hitting the wall in time Δt was found to be $n \, Av_x \, \Delta t$. Now the collisions are random and the gas is in a steady state. Thus, if a molecule with velocity (v_x, v_y, v_z) acquires a different velocity due to collision with some molecule, there will always be some other molecule with a different initial velocity which after a collision acquires the velocity (v_x, v_y, v_z). If this were not so, the distribution of velocities would not remain steady. In any case we are finding $\overline{v_x^2}$. Thus, on the whole, molecular collisions (if they are not too frequent and the time spent in a collision is negligible compared to time between collisions) will not affect the calculation above.

13.4.2 Kinetic Interpretation of Temperature

Equation (13.14) can be written as

$$PV = (1/3) \, nV \, m \, \overline{v^2} \qquad (13.15a)$$

Founders of Kinetic Theory of Gases
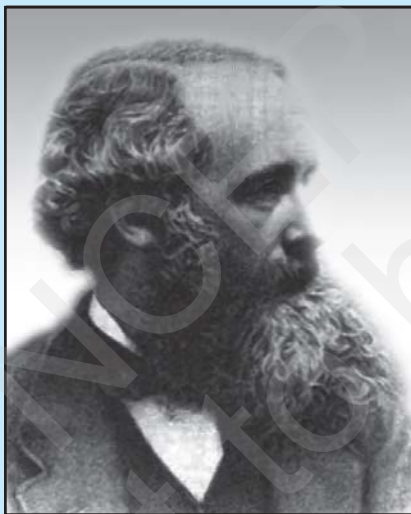
James Clerk Maxwell (1831 – 1879), born in Edinburgh, Scotland, was among the greatest physicists of the nineteenth century. He derived the thermal velocity distribution of molecules in a gas and was among the first to obtain reliable estimates of molecular parameters from measurable quantities like viscosity, etc. Maxwell's greatest achievement was the unification of the laws of electricity and magnetism (discovered by Coulomb, Oersted, Ampere and Faraday) into a consistent set of equations now called Maxwell's equations. From these he arrived at the most important conclusion that light is an electromagnetic wave. Interestingly, Maxwell did not agree with the idea (strongly suggested by the Faraday's laws of electrolysis) that electricity was particulate in nature.

Ludwig Boltzmann (1844 – 1906) born in Vienna, Austria, worked on the kinetic theory of gases independently of Maxwell. A firm advocate of atomism, that is basic to kinetic theory, Boltzmann provided a statistical interpretation of the Second Law of thermodynamics and the concept of entropy. He is regarded as one of the founders of classical statistical mechanics. The proportionality constant connecting energy and temperature in kinetic theory is known as Boltzmann's constant in his honour.
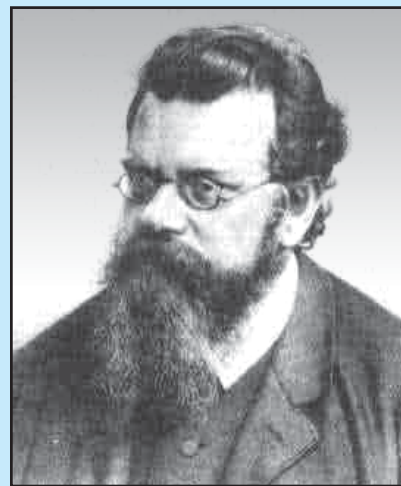
$PV = (2/3) N x \; m \overline{v^2}$ (13.15b)

where $N (= nV)$ is the number of molecules in the sample.

The quantity in the bracket is the average translational kinetic energy of the molecules in the gas. Since the internal energy E of an ideal gas is purely kinetic*,

$E = N \; (1/2) \; m \; \overline{v^2}$ (13.16)

Equation (13.15) then gives :

$PV = (2/3) E$ (13.17)

We are now ready for a kinetic interpretation of temperature. Combining Eq. (13.17) with the ideal gas Eq. (13.3), we get

$E = (3/2) \; k_B NT$ (13.18)

or $E/N = \overline{m v^2} = (3/2) k_B T$ (13.19)

i.e., the average kinetic energy of a molecule is proportional to the absolute temperature of the gas; it is independent of pressure, volume or the nature of the ideal gas. This is a fundamental result relating temperature, a macroscopic measurable parameter of a gas (a thermodynamic variable as it is called) to a molecular quantity, namely the average kinetic energy of a molecule. The two domains are connected by the Boltzmann constant. We note in passing that Eq. (13.18) tells us that internal energy of an ideal gas depends only on temperature, not on pressure or volume. With this interpretation of temperature, kinetic theory of an ideal gas is completely consistent with the ideal gas equation and the various gas laws based on it.

For a mixture of non-reactive ideal gases, the total pressure gets contribution from each gas in the mixture. Equation (13.14) becomes

$P = (1/3) [n_1 m_1 \overline{v_1^2} + n_2 m_2 \overline{v_2^2} + \dots]$ (13.20)

In equilibrium, the average kinetic energy of the molecules of different gases will be equal. That is,

$m_1 \overline{v_1^2} = m_2 \overline{v_2^2} = (3/2) k_B T$

so that

$P = (n_1 + n_2 + \dots) k_B T$ (13.21)

which is Dalton's law of partial pressures.

From Eq. (13.19), we can get an idea of the typical speed of molecules in a gas. At a temperature $T = 300$ K, the mean square speed of a molecule in nitrogen gas is :

$m \; \dfrac{M_{N_2}}{N_A} \; \dfrac{28}{6.02 \; 10^{26}} \; 4.65 \; 10^{-26}$ kg.

$\overline{v^2} = 3 k_B T / m = (516)^2$ m²s⁻²

The square root of $\overline{v^2}$ is known as root mean square (rms) speed and is denoted by v_{rms},

(We can also write $\overline{v^2}$ as $<v^2>$.)

$v_{rms} = 516$ m s⁻¹

The speed is of the order of the speed of sound in air. It follows from Eq. (13.19) that at the same temperature, lighter molecules have greater rms speed.

> **Example 13.5** A flask contains argon and chlorine in the ratio of 2:1 by mass. The temperature of the mixture is 27 °C. Obtain the ratio of (i) average kinetic energy per molecule, and (ii) root mean square speed v_{rms} of the molecules of the two gases. Atomic mass of argon = 39.9 u; Molecular mass of chlorine = 70.9 u.

Answer The important point to remember is that the average kinetic energy (per molecule) of any (ideal) gas (be it monatomic like argon, diatomic like chlorine or polyatomic) is always equal to (3/2) $k_B T$. It depends only on temperature, and is independent of the nature of the gas.

(i) Since argon and chlorine both have the same temperature in the flask, the ratio of average kinetic energy (per molecule) of the two gases is 1:1.

(ii) Now $m v_{rms}^2$ = average kinetic energy per molecule = (3/2)) $k_B T$ where m is the mass of a molecule of the gas. Therefore,

$$\dfrac{\mathbf{v}_{rms\;Ar}^2}{\mathbf{v}_{rms\;Cl}^2} \; \dfrac{m_{Cl}}{m_{Ar}} \; \dfrac{M_{Cl}}{M_{Ar}} = \dfrac{70.9}{39.9} = 1.77$$

where M denotes the molecular mass of the gas. (For argon, a molecule is just an atom of argon.) Taking square root of both sides,

$$\dfrac{\mathbf{v}_{rms\;Ar}}{\mathbf{v}_{rms\;Cl}} = 1.33$$

You should note that the composition of the mixture by mass is quite irrelevant to the above

---

* *E denotes the translational part of the internal energy U that may include energies due to other degrees of freedom also. See section 13.5.*

Maxwell Distribution Function

In a given mass of gas, the velocities of all molecules are not the same, even when bulk parameters like pressure, volume and temperature are fixed. Collisions change the direction and the speed of molecules. However in a state of equilibrium, the distribution of speeds is constant or fixed.

Distributions are very important and useful when dealing with systems containing large number of objects. As an example consider the ages of different persons in a city. It is not feasible to deal with the age of each individual. We can divide the people into groups: children up to age 20 years, adults between ages of 20 and 60, old people above 60. If we want more detailed information we can choose smaller intervals, 0-1, 1-2,..., 99-100 of age groups. When the size of the interval becomes smaller, say half year, the number of persons in the interval will also reduce, roughly half the original number in the one year interval. The number of persons $dN(x)$ in the age interval x and $x+dx$ is proportional to dx or $dN(x) = n_x\,dx$. We have used n_x to denote the number of persons at the value of x.
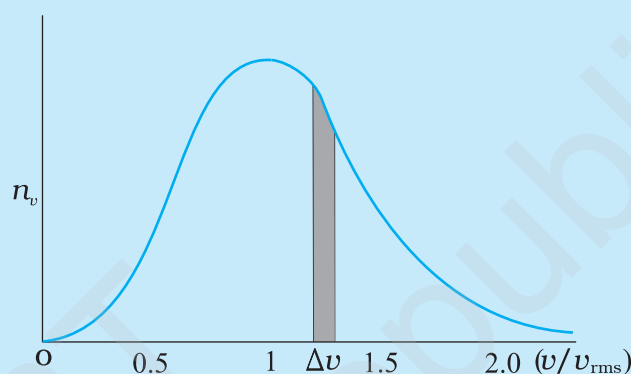
Maxwell distribution of molecular speeds

In a similar way the molecular speed distribution gives the number of molecules between the speeds v and $v+dv$. $dN(v) = 4p\,N\,a^3 e^{-bv^2} v^2\,dv = n_v dv$. This is called Maxwell distribution. The plot of n_v against v is shown in the figure. The fraction of the molecules with speeds v and $v+dv$ is equal to the area of the strip shown. The average of any quantity like v^2 is defined by the integral $<v^2> = (1/N)\int v^2\,dN(v) = \overset{.}{A}(3k_B T/m)$ which agrees with the result derived from more elementary considerations.

---

calculation. Any other proportion by mass of argon and chlorine would give the same answers to (i) and (ii), provided the temperature remains unaltered. ◄

► **Example 13.6** Uranium has two isotopes of masses 235 and 238 units. If both are present in Uranium hexafluoride gas which would have the larger average speed ? If atomic mass of fluorine is 19 units, estimate the percentage difference in speeds at any temperature.

Answer At a fixed temperature the average energy $= \tfrac{1}{2} m <v^2>$ is constant. So smaller the mass of the molecule, faster will be the speed. The ratio of speeds is inversely proportional to the square root of the ratio of the masses. The masses are 349 and 352 units. So

$v_{349} / v_{352} = (352/349)^{1/2} = 1.0044$.

Hence difference $\dfrac{V}{V} = 0.44$ %.

[^{235}U is the isotope needed for nuclear fission. To separate it from the more abundant isotope ^{238}U, the mixture is surrounded by a porous cylinder. The porous cylinder must be thick and narrow, so that the molecule wanders through individually, colliding with the walls of the long pore. The faster molecule will leak out more than

the slower one and so there is more of the lighter molecule (enrichment) outside the porous cylinder (Fig. 13.5). The method is not very efficient and has to be repeated several times for sufficient enrichment.]. ◄

When gases diffuse, their rate of diffusion is inversely proportional to square root of the masses (see Exercise 13.12). Can you guess the explanation from the above answer?
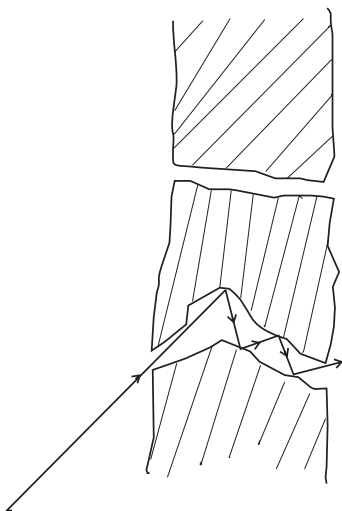

Fig. 13.5 *Molecules going through a porous wall.*

> **Example 13.7** (a) When a molecule (or an elastic ball) hits a (massive) wall, it rebounds with the same speed. When a ball hits a massive bat held firmly, the same thing happens. However, when the bat is moving towards the ball, the ball rebounds with a different speed. Does the ball move faster or slower? (Ch.6 will refresh your memory on elastic collisions.)
>
> (b) When gas in a cylinder is compressed by pushing in a piston, its temperature rises. Guess at an explanation of this in terms of kinetic theory using (a) above.
>
> (c) What happens when a compressed gas pushes a piston out and expands. What would you observe ?
>
> (d) Sachin Tendulkar uses a heavy cricket bat while playing. Does it help him in anyway ?

Answer (a) Let the speed of the ball be u relative to the wicket behind the bat. If the bat is moving towards the ball with a speed V relative to the wicket, then the relative speed of the ball to bat is $V + u$ towards the bat. When the ball rebounds (after hitting the massive bat) its speed, relative to bat, is $V + u$ moving away from the bat. So relative to the wicket the speed of the rebounding ball is $V + (V + u) = 2V + u$, moving away from the wicket. So the ball speeds up after the collision with the bat. The rebound speed will be less than u if the bat is not massive. For a molecule this would imply an increase in temperature.

You should be able to answer (b) (c) and (d) based on the answer to (a).

(Hint: Note the correspondence, piston→ bat, cylinder → wicket, molecule → ball.) ◄

13.5 LAW OF EQUIPARTITION OF ENERGY

The kinetic energy of a single molecule is

$$\epsilon_t \qquad \frac{1}{2}mv_x^2 \qquad \frac{1}{2}mv_y^2 \qquad \frac{1}{2}mv_z^2 \qquad (13.22)$$

For a gas in thermal equilibrium at temperature T the average value of energy denoted by $<\epsilon_t>$ is

$$\langle \epsilon_t \rangle \quad \left\langle \frac{1}{2}mv_x^2 \right\rangle \quad \left\langle \frac{1}{2}mv_y^2 \right\rangle \quad \left\langle \frac{1}{2}mv_z^2 \right\rangle \quad \frac{3}{2}k_BT \quad (13.23)$$

Since there is no preferred direction, Eq. (13.23) implies

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle \quad \frac{1}{2}k_BT \;,\left\langle \frac{1}{2}mv_y^2 \right\rangle \quad \frac{1}{2}k_BT\;,$$

$$\left\langle \frac{1}{2}mv_z^2 \right\rangle \quad \frac{1}{2}k_BT \qquad (13.24)$$

A molecule free to move in space needs three coordinates to specify its location. If it is constrained to move in a plane it needs two;and if constrained to move along a line, it needs just one coordinate to locate it. This can also be expressed in another way. We say that it has one degree of freedom for motion in a line, two for motion in a plane and three for motion in space. Motion of a body as a whole from one point to another is called translation. Thus, a molecule free to move in space has three translational degrees of freedom. Each translational degree of freedom contributes a term that contains square of some variable of motion, e.g., mv_x^2 and similar terms in v_y and v_z. In, Eq. (13.24) we see that in thermal equilibrium, the average of each such term is k_BT .

Molecules of a monatomic gas like argon have only translational degrees of freedom. But what about a diatomic gas such as O_2 or N_2? A molecule of O_2 has three translational degrees of freedom. But in addition it can also rotate about its centre of mass. Figure 13.6 shows the two independent axes of rotation 1 and 2, normal to the axis joining the two oxygen atoms about which the molecule can rotate*. The molecule thus has two rotational degrees of freedom, each of which contributes a term to the total energy consisting of translational energy ϵ_t and rotational energy ϵ_r.

$$\epsilon_t \ \epsilon_r \quad \frac{1}{2}mv_x^2 \ \frac{1}{2}mv_y^2 \ \frac{1}{2}mv_z^2 \ \frac{1}{2}I_1\omega_1^2 \ \frac{1}{2}I_2\omega_2^2 \quad (13.25)$$
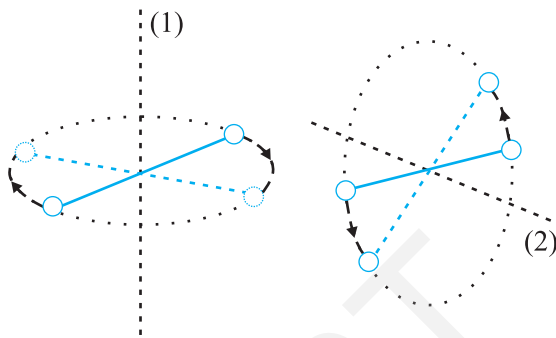

Fig. 13.6 *The two independent axes of rotation of a diatomic molecule*

where ω_1 and ω_2 are the angular speeds about the axes 1 and 2 and I_1, I_2 are the corresponding moments of inertia. Note that each rotational degree of freedom contributes a term to the energy that contains square of a rotational variable of motion.

We have assumed above that the O_2 molecule is a 'rigid rotator', i.e. the molecule does not vibrate. This assumption, though found to be true (at moderate temperatures) for O_2, is not always valid. Molecules like CO even at moderate temperatures have a mode of vibration, i.e. its atoms oscillate along the interatomic axis like a one-dimensional oscillator, and contribute a vibrational energy term ε_v to the total energy:

$$\varepsilon_v \quad \frac{1}{2}m\left(\frac{dy}{dt}\right)^2 \ \frac{1}{2}ky^2$$

---

* *Rotation along the line joining the atoms has very small moment of inertia and does not come into play for quantum mechanical reasons. See end of section 13.6.*

$$\epsilon_t \quad \epsilon_r \quad \epsilon_v \qquad (13.26)$$

where k is the force constant of the oscillator and y the vibrational co-ordinate.

Once again the vibrational energy terms in Eq. (13.26) contain squared terms of vibrational variables of motion y and dy/dt.

At this point, notice an important feature in Eq.(13.26). While each translational and rotational degree of freedom has contributed only one 'squared term' in Eq.(13.26), one vibrational mode contributes two 'squared terms' : kinetic and potential energies.

Each quadratic term occurring in the expression for energy is a mode of absorption of energy by the molecule. We have seen that in thermal equilibrium at absolute temperature T, for each translational mode of motion, the average energy is $\frac{1}{2}k_BT$. A most elegant principle of classical statistical mechanics (first proved by Maxwell) states that this is so for each mode of energy: translational, rotational and vibrational. That is, in equilibrium, the total energy is equally distributed in all possible energy modes, with each mode having an average energy equal to $\frac{1}{2}k_BT$. This is known as the **law of equipartition of energy**. Accordingly, each translational and rotational degree of freedom of a molecule contributes $\frac{1}{2}k_BT$ to the energy while each vibrational frequency contributes $2 \times \frac{1}{2}k_BT = k_BT$, since a vibrational mode has both kinetic and potential energy modes.

The proof of the law of equipartition of energy is beyond the scope of this book. Here we shall apply the law to predict the specific heats of gases theoretically. Later we shall also discuss briefly, the application to specific heat of solids.

13.6 SPECIFIC HEAT CAPACITY

13.6.1 Monatomic Gases

The molecule of a monatomic gas has only three translational degrees of freedom. Thus, the average energy of a molecule at temperature T is $(3/2)k_BT$. The total internal energy of a mole of such a gas is