

MAXWELL-BOLTZMANN LAW OF DISTRIBUTION OF VELOCITIES IN AN IDEAL GAS

According to kinetic theory, each gas is made up of molecules. The molecules in a gas move continuously in all the possible directions in a random manner and they collide with themselves as well as with the walls of the container. In each collision, the speed and direction of motion of the molecules changes i.e., velocities change and it is quite probable to get molecules of any possible velocity at any instant. Maxwell and Boltzmann arrived at a statistical law for the distribution of velocities amongst the molecules of the gas. Following assumptions were made:

- (i) Velocities can range between $-\infty$ and $+\infty$.
- (ii) In each volume element, the average number of molecules per unit volume remains the same at any instant.
- (iii) In each volume element, the velocity of molecules can have each possible magnitude and direction whose distribution neither depends on the position of volume element nor depends on the molecular collisions.
- (iv) In the steady state, the number of molecules in different ranges of velocity remains constant at a constant temperature although the velocity of each independent molecule can vary.

Consider a perfect gas enclosed in a vessel of volume V at an absolute temperature T . Let the number of molecules per unit volume be N . A molecule whose speed at any instant is C and has the velocity components v_x, v_y, v_z , then

$$C^2 = v_x^2 + v_y^2 + v_z^2 \quad (1)$$

We can now consider a velocity space having v_x, v_y, v_z as axes and velocity distribution functions $f(v_x), f(v_y)$ and $f(v_z)$ such that $f(v_x)$ is independent of v_y and v_z and $f(v_y)$ is independent of v_x and v_z ; and $f(v_z)$ is independent of v_x and v_y (Fig. 2.3).

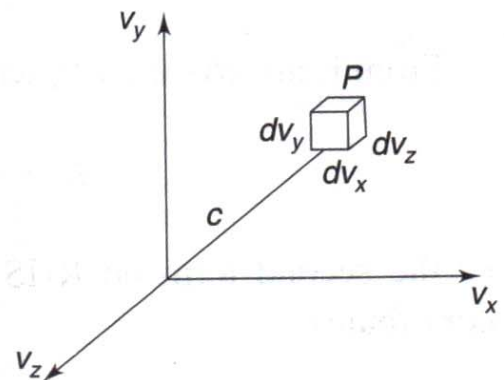


Fig. 2.3

We are to find the number of molecules whose velocity components are in the range v_x and $v_x + dv_x$, v_y and $v_y + dv_y$ and v_z and $v_z + dv_z$. Obviously, such molecules are represented by a parallelopiped in the vicinity of point $p(v_x, v_y, v_z)$ and having sides dv_x, dv_y, dv_z .

Let $Nf(v_x) dv_x$ = number of gas molecules in the velocity range v_x and $v_x + dv_x$. Similarly, we have $Nf(v_y) dv_y$ and $Nf(v_z) dv_z$. Then, the number of molecules with velocity components in the range v_x and $v_x + dv_x$, v_y and $v_y + dv_y$ and v_z and $v_z + dv_z$ will be

$$dN = Nf(v_x) Nf(v_y) Nf(v_z) dv_x dv_y dv_z \quad (2)$$

A molecule of a monatomic gas has only the translational motion for which the number of degrees of freedom is 3, hence to describe its state we need to consider a 6 dimensional phase space in which volume of each phase cell is h^3 where h is Planck's constant. In this phase space, the number of phase cells in the volume element $dx dy dz dp_x dp_y dp_z$ in between the position coordinates $x, x + dx; y, y + dy; z, z + dz$ and momentum coordinates $p_x, p_x + dp_x; p_y, p_y + dp_y; p_z, p_z + dp_z$ is

$$g = \frac{dx dy dz dp_x dp_y dp_z}{h^3} \quad (3)$$

and translational energy of the molecule is

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \equiv \frac{p^2}{2m} \quad (4)$$

Now, the probability P of finding the molecules in a given volume element of phase space is

$$P \propto g e^{-\beta E}$$

where

$$\beta = \frac{1}{kT} \quad (k = \text{Boltzmann constant}).$$

or

$$P \propto \frac{dx dy dz dp_x dp_y dp_z}{h^3} \times e^{-p^2/(2mkT)} \quad (5)$$

Hence, the probability of finding the molecules in the momentum range $p_x, p_x + dp_x; p_y, p_y + dp_y; p_z, p_z + dp_z$ inside the entire vessel will be

$$P(p)dp = \frac{CV}{h^3} e^{-(p_x^2 + p_y^2 + p_z^2)/(2mkT)} dp_x dp_y dp_z \quad (6)$$

$$(\because \iiint dx dy dz = V)$$

C is a constant of proportionality.

The constant C is determined as follows, we have

$$\int_{-\infty}^{+\infty} P(p) dp = 1$$

or
$$\iiint \frac{CV}{h^3} e^{-(p_x^2 + p_y^2 + p_z^2)/(2mkT)} dp_x dp_y dp_z = 1$$

or
$$\frac{CV}{h^3} \int_{-\infty}^{+\infty} e^{-p_x^2/(2mkT)} dp_x \int_{-\infty}^{+\infty} e^{-p_y^2/(2mkT)} dp_y \int_{-\infty}^{+\infty} e^{-p_z^2/(2mkT)} dp_z = 1$$

From the standard integral

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}},$$

we get

$$\begin{aligned} \int_{-\infty}^{+\infty} e^{-p_x^2/(2mkT)} dp_x &= \int_{-\infty}^{+\infty} e^{-p_y^2/(2mkT)} dp_y = \int_{-\infty}^{+\infty} e^{-p_z^2/(2mkT)} dp_z \\ &= \sqrt{\frac{\pi}{(1/2mkT)}} = \sqrt{2\pi mkT} \end{aligned}$$

$$\therefore C = \frac{h^3}{V(2\pi mkT)^{3/2}} \quad (7)$$

Substituting the value of constant C in Eqn. (6) we get

$$P(p)dp = \left(\frac{1}{2\pi mkT}\right)^{3/2} e^{-(p_x^2 + p_y^2 + p_z^2)/(2mkT)} dp_x dp_y dp_z \quad (8)$$

Substituting $p_x = mv_x$, $p_y = mv_y$, $p_z = mv_z$, we have

$$dp_x dp_y dp_z = m^3 dv_x dv_y dv_z$$

Then from Eqn. (8) we have the probability of finding the molecules in the velocity range (v_x, v_y, v_z) to $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$ as

$$\begin{aligned} f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z &= \left(\frac{1}{2\pi mkT}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/(2kT)} \times m^3 dv_x dv_y dv_z \\ &= \left(\frac{m^2}{2\pi mkT}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/(2kT)} dv_x dv_y dv_z \end{aligned} \quad (9)$$

$$\therefore dN = N \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/(2kT)} dv_x dv_y dv_z \quad (10)$$

This is the Maxwell Boltzmann law of distribution of velocities.

The number of molecules with x -component of velocity in the range 0 to v_x is

$$N(v_x) = N \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/(2kT)}$$

Similarly

$$N(v_y) = N \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_y^2/(2kT)}$$

and

$$N(v_z) = N \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_z^2/(2kT)}$$

2.9.1 Discussion on velocity Distribution Function

We can draw following conclusions from the above equation:

- (i) Since $N_{(-v_x)} = N_{(v_x)}$
therefore a graph plotted for $N_{(v_x)}$ vs. v_x is symmetrical about the $N_{(v_x)}$ axis (Fig. 2.4).
- (ii) When $v_x = 0$, $N_{(v_x)} = \text{maximum}$. Thus the number of molecules with zero velocity is maximum. In other words, the most probably velocity $(v_x)_m = 0$ and

$$|N_{(v_x)}|_{\max} = \left(\frac{m}{2\pi kT} \right)^{1/2} N$$

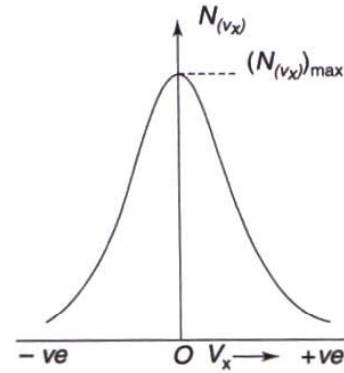


Fig. 2.4 Plot between $N_{(v_x)}$ and v_x

As v_x increases, the value of $N_{(v_x)}$ decreases exponentially. At $v_x = \infty$, $N_{(v_x)} = 0$.

- (iii) The number of molecules is $1/e$ times the number of molecules at $v_x = 0$ when

$$N_{(v_x)} = \frac{1}{e} |N_{(v_x)}|_{\max}$$

$$\text{or} \quad N \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/(2kT)} = \frac{1}{e} \left(\frac{m}{2\pi kT} \right)^{1/2} N$$

$$\text{or} \quad e^{-mv_x^2/(2kT)} = e^{-1}$$

$$\text{or} \quad v_x = \pm \sqrt{2kT/m}$$

- (iv) On increasing the temperature of gas, the number of molecules at the maximum probably velocity $v_x = 0$ decreases and the exponential fall

becomes slow, i.e., distribution curve spreads (Fig. 2.5).

- (v) The velocity distribution is different for different gases even at the same temperature. On increasing the mass of molecule (e.g., for a heavier gas), the number of molecules corresponding to maximum probable velocity $v_x = 0$ increases and the exponential fall becomes rapid i.e., the distribution curve contracts.
- (vi) Average value of v_x is

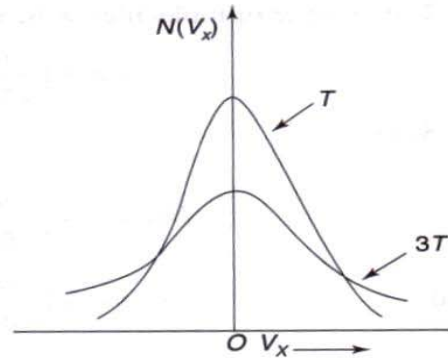


Fig. 2.5 Velocity distribution curve at two different temperatures

$$\begin{aligned}\bar{v}_x \text{ or } \langle v_x \rangle &= \frac{\text{Area enclosed by } N_{(v_x)} \text{ vs. } v_x \text{ curve with } v_x \text{ axis}}{\text{Total number of molecules}} \\ &= \frac{\int_{-\infty}^{+\infty} v_x N_{(v_x)} dv_x}{N} \\ &= \frac{\int_{-\infty}^{+\infty} v_x N \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/(2kT)} dv_x}{N} \\ &= \left(\frac{m}{2\pi kT} \right)^{1/2} \int_{-\infty}^{+\infty} v_x e^{-mv_x^2/(2kT)} dv_x\end{aligned}$$

But we have standard integral

$$\int_{-\infty}^{+\infty} x e^{-\alpha x^2} dx = 0$$

$$\therefore \langle v_x \rangle = 0$$

Similarly $\langle v_y \rangle = 0$ and $\langle v_z \rangle = 0$

- (vii) Root Mean Square Value of v_x

We know that

$$(v_x)_{\text{rms}} = \sqrt{\langle v_x^2 \rangle}$$

$$\text{But } \langle v_x^2 \rangle = \frac{\int_{-\infty}^{+\infty} v_x^2 N_{(v_x)} dv_x}{N}$$

or
$$\langle v_x^2 \rangle = \frac{\int_{-\infty}^{+\infty} v_x^2 N \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/(2kT)} dv_x}{N}$$

$$= \left(\frac{m}{2\pi kT} \right)^{1/2} \int_{-\infty}^{+\infty} e^{-mv_x^2/(2kT)} v_x^2 dv_x$$

But, we have standard integral,

$$\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2\alpha} \sqrt{\pi/\alpha}$$

Hence
$$\int_{-\infty}^{+\infty} v_x^2 e^{-mv_x^2/(2kT)} dv_x = \frac{1}{2 \left(\frac{m}{2kT} \right)} \sqrt{\frac{\pi}{m/(2kT)}}$$

$$\begin{aligned} \langle v_x^2 \rangle &= \left(\frac{m}{2\pi kT} \right)^{1/2} \times \frac{1}{2 \left(\frac{m}{2kT} \right)} \sqrt{\frac{\pi}{m/(2kT)}} \\ &= \frac{kT}{m} \end{aligned}$$

$$\Rightarrow (v_x)_{\text{rms}} = \sqrt{kT/m}$$

Similarly,

$$(v_y)_{\text{rms}} = \sqrt{kT/m};$$

$$(v_z)_{\text{rms}} = \sqrt{kT/m}.$$

2.9.2 Maxwell-Boltzmann Law of Distribution of Speeds

Let c be the speed of the molecule which has v_x, v_y, v_z as its velocity components. Then

$$c^2 = v_x^2 + v_y^2 + v_z^2 \quad (1)$$

From the law of distribution of velocity

$$dN = N \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/(2kT)} dv_x dv_y dv_z$$

where $dv_x dv_y dv_z$ represents volume element in the velocity space. Since Eqn. (1) is the equation of a sphere (of radius c) we may use spherical polar coordinates.

Then

$$dv_x dv_y dv_z = c^2 dc \sin \theta d\theta d\phi$$

and total volume of the shell between c and $c + dc$ is

$$\begin{aligned} &= \int_0^\pi c^2 dc \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= 2\pi c^2 dc (-\cos \theta)_0^\pi = 4\pi c^2 dc \end{aligned}$$

Consequently, the number of molecules with speeds in the range c and $c + dc$ is

$$N_{(c)} dc = N \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/(2kT)} 4\pi c^2 dc$$

or
$$N_{(c)} dc = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-mc^2/(2kT)} dc$$

or
$$N_{(c)} = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-mc^2/(2kT)}$$

This is the Maxwell Boltzmann's speed distribution function.

Most Probable Speed c_m

It is the speed corresponding to which the number of molecules is maximum ($= N_{(c)}$) i.e.,

At $c = c_m$, $|N_{(c)}| = \text{maximum}$

or
$$\frac{d}{dc} N_{(c)}|_{c=c_m} = 0$$

or
$$\frac{d}{dc} \left\{ 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-mc^2/(2kT)} \right\}_{c=c_m} = 0$$

or
$$4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} \left\{ 2c e^{-mc^2/(2kT)} + c^2 e^{-mc^2/(2kT)} \left(-\frac{2mc}{2kT} \right) \right\}_{c=c_m} = 0$$

or
$$\left(1 - \frac{mc^2}{2kT} \right)_{c=c_m} = 0$$

$\therefore c_m = \sqrt{\frac{2kT}{m}}$ (2)

Speed Distribution Function

When $c = 0$, $N_{(c)} = 0$ i.e., in translational motion, no molecule has the zero speed. For lower values of c , the term c^2 is more effective than $e^{-mc^2/(2kT)}$ therefore as

c increases, the number of molecules corresponding to it increases and for $c = c_m$, the number of molecules is maximum. On further increasing c , the term $e^{-mc^2/(2kT)}$ becomes more pronounced, and so, $N_{(c)}$ then decreases exponentially with c . At $c = \infty$, $N_{(c)} = 0$ (Fig. 2.6).

Number of Molecules Corresponding to Maximum Probable Speed $(N_{(c)})_{\max}$

At $c = c_m = \sqrt{2kT/m}$

$$(N_{(c)})_{\max} = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} \left(\frac{2kT}{m} \right) e^{m2kT/(m2kT)}$$

$$\text{or } (N_{(c)})_{\max} = 4N \sqrt{\frac{m}{2\pi kT}} e^{-1} \quad (3)$$

As the temperature of gas increases, the maximum probable speed c_m increases, but the number of molecules corresponding to it decreases. The exponential fall of $N_{(c)}$ with c becomes slow. But the area enclosed by the curve (with c -axis) remains the same i.e., the distribution curve spreads (Fig. 2.7).

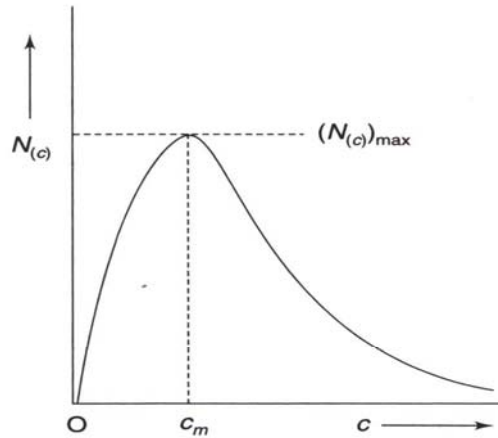


Fig. 2.6 Maxwell Boltzmann speed distribution function

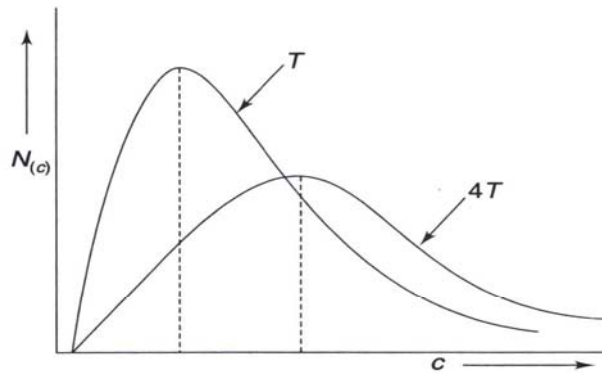


Fig. 2.7 Speed distribution curve at two different temperatures

Mean or Average Speed

$$\langle c \rangle = \frac{\int_0^{\infty} c N_{(c)} dc}{N}$$

Substituting the value of $N_{(c)}$, we get

$$\begin{aligned}\langle c \rangle &= \frac{1}{N} \int_0^{\infty} c \times 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-mc^2/(2kT)} dc \\ &= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} c^3 e^{-mc^2/(2kT)} dc\end{aligned}$$

But from standard integral,

$$\int_0^{\infty} x^3 e^{-\alpha x^2} dx = \frac{1}{2\alpha^2}$$

Hence,

$$\int_0^{\infty} c^3 e^{-mc^2/(2kT)} dc = \frac{1}{2 \left(\frac{m}{2kT} \right)^2}$$

\therefore

$$\langle c \rangle = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{1}{2 \left(\frac{m}{2kT} \right)^2}$$

or

$$\langle c \rangle = \sqrt{\frac{8kT}{m\pi}} \quad (4)$$

Root Mean Square Speed $\sqrt{\langle c^2 \rangle}$

$$\begin{aligned}\langle c^2 \rangle &= \frac{\int_0^{\infty} c^2 N_{(c)} dc}{N} \\ &= \frac{1}{N} \int_0^{\infty} c^2 \times 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-mc^2/(2kT)} dc \\ &= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} c^4 e^{-mc^2/(2kT)} dc\end{aligned}$$

Now, from the standard integral

$$\int_0^{\infty} x^4 e^{-\alpha x^2} dx = \frac{3}{8\alpha^2} \sqrt{\frac{\pi}{\alpha}}$$

we get

$$\int_0^{\infty} c^4 e^{-mc^2/(2kT)} dc = \frac{3}{8 \left(\frac{m}{2kT} \right)^2} \sqrt{\frac{\pi}{\left(\frac{m}{2kT} \right)}}$$

$$= \frac{3kT}{m}$$

$$\therefore c_{rms} = \sqrt{\langle c^2 \rangle} = \sqrt{3kT/m} \quad (5)$$

Relation Between the Most Probable Speed, Average Speed and R.M.S. Speed

Most probable speed

$$c_m = \sqrt{2kT/m}$$

Average speed

$$c_{av} \equiv \langle c \rangle = \sqrt{8kT/m\pi}$$

R.M.S. speed

$$c_{rms} \equiv \sqrt{\langle c^2 \rangle} = \sqrt{3kT/m}$$

Hence,

$$\frac{c_m}{\sqrt{2}} = \frac{c_{av}}{\sqrt{8/\pi}} = \frac{c_{rms}}{\sqrt{3}} = \frac{kT}{m} \quad (6)$$

2.12 MEAN FREE PATH

If molecules were geometrical points, they would not collide at all. Molecules, however, are not points. They are more like hard elastic spheres. Therefore, collisions occur.

If we could observe a single molecule travelling through a gas, its path would look something like that shown in Fig. 2.12. Between collisions the molecule moves freely with a constant speed along a straight line.

The distance between two successive collisions, for example $\lambda_{2,3}$, is called a *free path*. The average length of these free paths is called the *mean free path* λ . If $\lambda_{1,2}, \lambda_{2,3}, \dots$, etc. are the values of successive free paths,

$$\lambda_{1,2} + \lambda_{2,3} + \dots + \lambda_{v-1,v} + \lambda_{v,v+1} = \bar{c}t \quad (1)$$

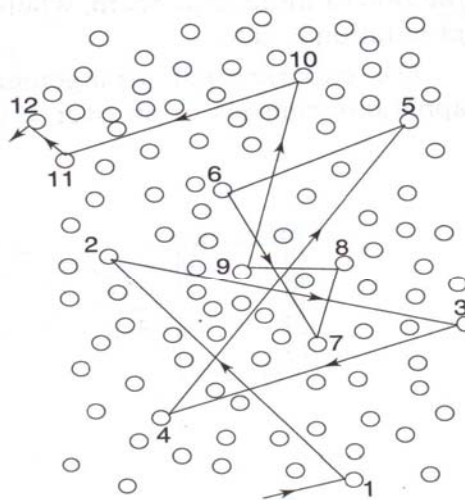


Fig. 2.12 Path of a molecule

where \bar{c} is the mean speed of the molecule and t the total time in covering the free paths, then

$$\lambda \equiv \frac{\lambda_{1,2} + \lambda_{2,3} + \dots + \lambda_{v,v+1}}{v} = \frac{\bar{c}t}{v} \quad (2)$$

Here v is the *number of collisions* suffered in time t .

Let d be the diameter of a hard sphere molecule. Any other molecule B , whose centre is within a distance d from the molecule A under consideration, will collide with A , Fig. 2.13. In other words, a collision occurs whenever the centre of another molecule comes within the 'sphere of influence' of radius d drawn around the centre of A . For our simplest model we assume that only A moves and all the other gas molecules are instantaneously at rest.

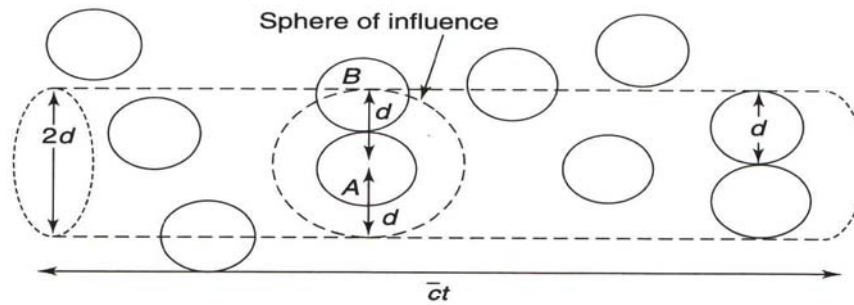


Fig. 2.13 Number of molecular collisions

If A is moving with the average speed \bar{c} , its 'sphere of influence' sweeps out in time t a cylinder of base πd^2 and length $\bar{c}t$. The quantity πd^2 is called the *collision cross section* of the hard sphere model. If n_v is the number of molecules per unit volume, this cylinder will contain $(\pi d^2 \bar{c}t) n_v$ molecules. Therefore, in all A experiences $v = \pi d^2 \bar{c}t n_v$ collisions and its mean free path is

$$\lambda = \frac{\bar{c}t}{v} = \frac{\bar{c}t}{\pi d^2 \bar{c}t n_v} = \frac{1}{\pi d^2 n_v} \quad (3)$$

In deriving Eqn. (3), we have assumed that A collides with other stationary molecules. Actually, all the molecules are moving. Consequently, we should write $v = \pi d^2 \bar{c}_{rel} t n_v$, where \bar{c}_{rel} is the mean relative speed of A with respect to other molecules.

A detailed calculation, taking into account the actual speed distribution of the molecules, yields $\bar{c}_{rel} = \sqrt{2}\bar{c}$. In a simple picture, the origin of the factor $\sqrt{2}$ can be seen by considering the relative velocities of two molecules at the point of collision, Fig. 2.14. The extreme cases are the head-on collision (a) and the grazing collision (b). The average case appears to be the 90° collision (c), for which $\bar{c}_{rel} = \sqrt{2}\bar{c}$. Therefore, Eqn. (3) becomes

$$\lambda = \frac{\bar{c}t}{v} = \frac{\bar{c}}{\pi d^2 \bar{c}_{rel} n_v}$$

$$= \frac{1}{\sqrt{2} \pi d^2 n_v} = \frac{0.707}{\pi d^2 n_v} \quad (4)$$

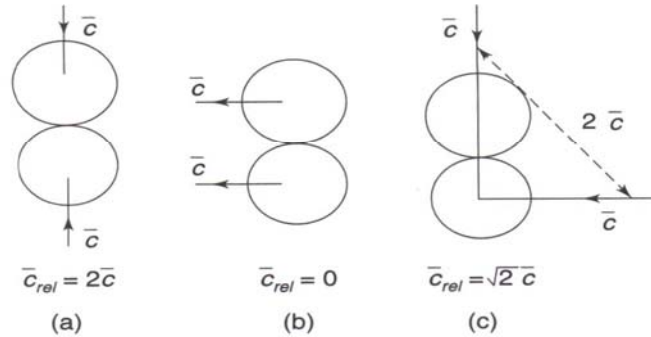


Fig. 2.14 Relative speeds: (a) head-on collision, (b) grazing collision, and (c) right-angle collision

We have $p = n_v kT$. Hence, λ can be expressed as

$$\lambda = \frac{kT}{\sqrt{2} \pi d^2 p} \quad (5)$$

Using $n_v = 3 \times 10^{19}$ molecules/cm³ at NTP and $d = 2 \times 10^{-8}$ cm, we find $\lambda = 2 \times 10^{-5}$ cm which is slightly smaller than the wavelength of visible light. Thus, at sea level ($p = 760$ mm-Hg) $\lambda \sim 10^{-5}$ cm for air molecules. At 100 km above the earth (10^{-3} mm-Hg $\approx 10^{-6}$ atm) $\lambda = 100$ cm.

2.13 TRANSPORT PHENOMENA

In problems like viscosity, heat conduction, or diffusion one is interested in the transport of something (like momentum, thermal energy, or mass) from one part of a gas to another. For this reason they are called transport phenomena.

The transport of momentum, for example, can be understood with the help of the following analogy. Consider two trains 1 and 2 moving along parallel tracks in same direction but at different speeds, Fig. 2.15. As they pass one another suppose some passengers start jumping from 1 to 2 and from 2 to 1. Suppose $v_1 < v_2$ and all passengers have equal mass μ . Then the jump $2 \rightarrow 1$ is from the more rapidly moving train to the slower one and therefore transports momentum of amount $+\mu(v_2 - v_1)$ in one jump. This tends to speed up the slower train 1 when the passenger lands upon it from 2. The jump $1 \rightarrow 2$ from the slower train to the faster train, on the other hand, tends to slow down 2.

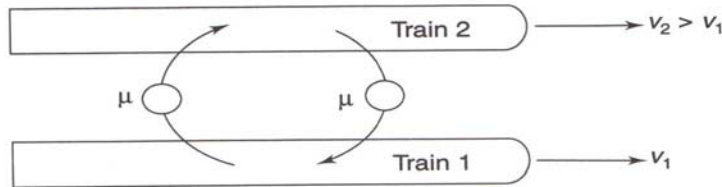


Fig. 2.15 Exchange of momentum

If n pairs of passengers are exchanged per unit time between the two trains, there will be an average force $+\mu (v_2 - v_1) n$ tending to speed up train 1 and an average force $-\mu (v_2 - v_1) n$ tending to slow down train 2. A distant observer who is unable to see the exchange of passengers will feel that this result is due to some frictional drag between the trains.

The mechanism by which one layer of flowing gas exerts a viscous drag on an adjacent layer is exactly similar, the gas molecules taking the role of the exchanged passengers.

2.14 GAS VISCOSITY

Consider a gas at constant temperature, moving in the x -direction with a velocity which increases with z . We know that (i) a molecule changes in velocity only on collision, and (ii) it moves on an average a distance λ before it undergoes collision. Therefore, the motion of the gas can be regarded to occur in parallel layers such that adjacent layers with different velocities are separated by a distance λ , Fig. 2.16.

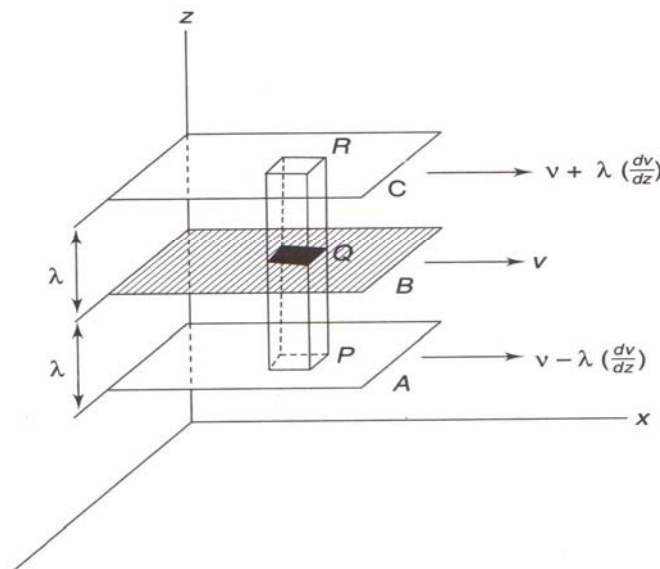


Fig. 2.16 Motion of a gas in layers

Let B be an arbitrary layer with a uniform velocity v in the x -direction and a velocity gradient dv/dz . Then the layer C above it has a flow velocity $v + \lambda(dv/dz)$ and the layer A below it has a flow velocity $v - \lambda(dv/dz)$.

For simplicity, we assume:

- (a) that the flow velocity v is very small compared with the mean velocity \bar{c} of the gas molecules due to their random motion, and
- (b) that all molecules which reach B have travelled exactly a distance λ with the mean speed \bar{c} since their last collision took place.

A molecule of mass μ reaching layer B from layer C brings horizontal momentum

$$p_x^{(C)} = \mu \left(v + \lambda \frac{dv}{dz} \right) \quad (1)$$

A molecule reaching B from A brings horizontal momentum

$$p_x^{(A)} = \mu \left(v - \lambda \frac{dv}{dz} \right) \quad (2)$$

For molecules, moving at random, all directions are equally possible. On average, *one-third* of all the molecules will be moving parallel to each of the three coordinate axes. Moreover, on average, the number of molecules moving in any one direction of given *sign* will be *one-sixth* of the total number.

Draw a cylinder RQ of height λ and unit area of cross-section between the layers C and B , Fig. 2.15. Its volume is λ and contains $n_v \lambda$ molecules, where n_v is the number of molecules per unit volume. Of these $\frac{1}{6} n_v \lambda$ are moving downward with a speed \bar{c} . Molecules will take time λ/\bar{c} to travel from R to Q . In this time all the molecules moving downward in the cylinder RQ will cross the unit area Q . That is, the number of molecules crossing Q in downward direction in one second is

$$\frac{\frac{1}{6} n_v \lambda}{\lambda/\bar{c}} = \frac{1}{6} n_v \bar{c} \quad (3)$$

The same number will cross Q in the upward direction as can be evaluated by drawing the cylinder PQ between the layers A and B .

The layer B itself will also discharge $\frac{1}{6} n_v \bar{c}$ molecules per second per unit area towards both A and C layers. The resultant behaviour is summarized in Table 2.1.

Table 2.1 Molecules crossing unit area Q in the layer B per second.

	Number	Horizontal momentum
Entering from layer C	$\frac{1}{6} n_v \bar{c}$	$\mu \left(v + \lambda \frac{dv}{dz} \right) \frac{1}{6} n_v \bar{c}$
Entering from layer A	$\frac{1}{6} n_v \bar{c}$	$\mu \left(v - \lambda \frac{dv}{dz} \right) \frac{1}{6} n_v \bar{c}$
Leaving from layer B upwards	$\frac{1}{6} n_v \bar{c}$	$\mu v \frac{1}{6} n_v \bar{c}$
Leaving from layer B downwards	$\frac{1}{6} n_v \bar{c}$	$\mu v \frac{1}{6} n_v \bar{c}$
Net addition to layer B	0	0

We find that there is no accumulation of molecules or momentum in layer B . However, there is a transport of momentum per unit area per second through the layer B in the downward direction given by

$$p_x^{(C)} - p_x^{(A)} \times \frac{1}{6} n_v \bar{c} = \frac{1}{3} \mu n_v \bar{c} \lambda \frac{dv}{dz} \equiv F \quad (4)$$

This horizontal momentum per second is a horizontal force which is transmitted through the gas to the top moving surface. In other words, this horizontal momentum per unit area per second is equivalent to the shearing (tangential) stress F .

The defining equation of viscosity is

$$F = \eta \frac{dv}{dz}$$

where η is the *coefficient of viscosity*. By comparison, we have

$$\eta = \frac{1}{3} \mu n_v \bar{c} \lambda = \frac{1}{3} \rho \bar{c} \lambda \quad (5)$$

Since $\lambda = (\sqrt{2} \pi n_v d^2)^{-1}$, we can write

$$\eta = \frac{\mu \bar{c}}{\sqrt{2} \pi d^2} \quad (6)$$

This relations can be used to compute molecular diameters, since μ , \bar{c} and η can all be measured (or calculated).

From Eqn. (6), we conclude that the viscosity of a gas is proportional to \bar{c} , that is to $T^{1/2}$, and is independent of n_v , that is, of the pressure. Both these conclusions are in good agreement with experiments. Deviations occur at very low pressures

when λ becomes comparable to the dimension of the container (λ cannot increase further by reduction of n_v or pressure).

2.15 THERMAL CONDUCTIVITY

In this case the temperature T of a gas increases in the z -direction. The situation can be experimentally realized by confining a gas between parallel walls, one of which is at a higher temperature.

The temperature gradient is dT/dz . We again have layers separated by distance λ . We can draw a figure similar to Fig. 2.16 or its simplified version shown in Fig. 2.17. The heat flow per second per unit area across the layer B is

$$Q = K \frac{dT}{dz}$$

where K is the *thermal conductivity coefficient*.

We assume that in a gas heat conduction is due to the transport of thermal energy. The transport of mean thermal energy per unit area per unit time into plane B from planes C and A is

$$Q^{(C)} = \mu c_v \left(T + \lambda \frac{dT}{dz} \right) \frac{1}{6} n_v \bar{c} \text{ from the upper layer } C$$

$$Q^{(A)} = \mu c_v \left(T - \lambda \frac{dT}{dz} \right) \frac{1}{6} n_v \bar{c} \text{ from the lower layer } A$$

where c_v is the specific heat at constant volume per unit mass. The net transport of thermal energy through the layer B per unit area per unit time is

$$Q = Q^{(C)} - Q^{(A)} = \frac{1}{3} n_v \bar{c} \lambda \mu c_v \frac{dT}{dz}$$

By comparison we see that the thermal conductivity is given by

$$K = \frac{1}{3} \mu n_v \bar{c} \lambda c_v = \frac{1}{3} \rho c \lambda c_v \quad (7)$$

Since $\lambda \propto 1/\rho$, K , like η , is independent of pressure and increases with temperature.

From Eqns. (5) and (7), one obtains

$$\frac{K}{\eta} = c_v \quad (8)$$

Experimentally also it is found that $K/\eta c_v$ is a constant, although its value is different from unity. The observed ratio is between 1.4 and 2.5 for a very wide range of gases, even though the individual quantities K , η , c_v vary much more.

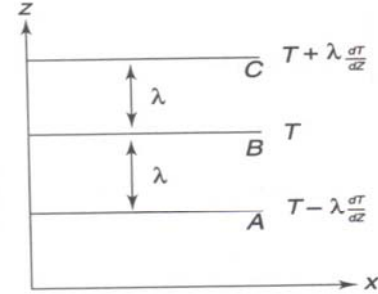


Fig. 2.17 Model for transport of thermal energy

2.16 GAS SELF DIFFUSION

Suppose we have a concentration gradient in a gas. The molecules will move from the more concentrated to the less concentrated regions so that the property being transported is simply the gas molecules themselves.

Let n_v be the number of molecules per unit volume and dn_v/dz the concentration gradient at the layer B , Fig. 2.18. The net number of molecules transported across B per unit area and per unit time is

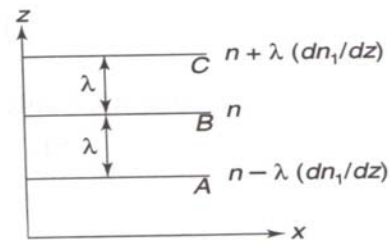


Fig. 2.18 Concentration layers

$$\begin{aligned} n_v^{(C)} - n_v^{(A)} &= \frac{1}{6} \left(n_v + \lambda \frac{dn_v}{dz} \right) \bar{c} - \frac{1}{6} \left(n_v - \lambda \frac{dn_v}{dz} \right) \bar{c} \\ &= \frac{1}{3} \lambda \bar{c} \frac{dn_v}{dz} \equiv \Gamma \end{aligned}$$

The basic law of diffusion, due to Fick, is

$$\Gamma = D \frac{dn_v}{dz}$$

where D is the *coefficient of self diffusion*. Therefore

$$D = \frac{1}{3} \lambda \bar{c} = \frac{1}{3} \left(\frac{1}{\pi d^2 n_v} \right) \bar{c} \quad (9)$$

For air at NTP; $d = 2.5 \text{ \AA}$, $\lambda = 1000 \text{ \AA}$, $\bar{c} = 45000 \text{ cm sec}^{-1}$. This gives D to be of the order of 1 molecule per cm^2 per unit concentration gradient.

From Eqns. (5) and (9), we have

$$\frac{\eta}{D} = \rho \quad (10)$$

Thus, the single kinetic theory establishes general correlations between diverse phenomena such as viscosity, thermal conductivity and self diffusion.

The results of mean free path treatments of the transport processes studied are summarized in Table 2.2.

Table 2.2 Comparison of transport processes.

Process	Transfer of	Result	cgs units of coefficient
Viscosity	Momentum, $\mu \bar{c}$	$\eta = \frac{1}{3} \rho \bar{c} \lambda$	$\text{g cm}^{-1} \text{sec}^{-1}$
Thermal conductivity	Kinetic energy, $\frac{1}{2} \mu \bar{c}^2$	$K = \frac{1}{3} \rho \bar{c} \lambda c_v$	$\text{erg cm}^{-1} \text{sec}^{-1} \text{degree}^{-1}$
Diffusion	Mass, μ	$D = \frac{1}{3} \rho \bar{c}$	$\text{cm}^2 \text{sec}^{-1}$