**Figure 1B.1** The pressure of a gas arises from the impact of its molecules on the walls. In an elastic collision of a molecule with a wall perpendicular to the x-axis, the x-component of velocity is reversed but the y- and z-components are unchanged.

by the number of molecules that reach the wall during the interval.

Because a molecule with velocity component v_x can travel a distance $v_x\Delta t$ along the x-axis in an interval Δt, all the molecules within a distance $v_x\Delta t$ of the wall will strike it if they are travelling towards it (Fig. 1B.2). It follows that if the wall has area A, then all the particles in a volume $A \times v_x\Delta t$ will reach the wall (if they are travelling towards it). The number density of particles is nN_A/V, where n is the total amount of molecules in the container of volume V and N_A is Avogadro's constant, so the number of molecules in the volume $Av_x\Delta t$ is $(nN_A/V)\times Av_x\Delta t$.

At any instant, half the particles are moving to the right and half are moving to the left. Therefore, the average number of collisions with the wall during the interval Δt is $\frac{1}{2}nN_AAv_x\Delta t/V$. The total momentum change in that interval is the product of this number and the change $2mv_x$:

$$\text{Momentum change} = \frac{nN_AAv_x\Delta t}{2V}\times 2mv_x$$

$$= \frac{n\overbrace{mN_A}^{M}Av_x^2\Delta t}{V} = \frac{nMAv_x^2\Delta t}{V}$$
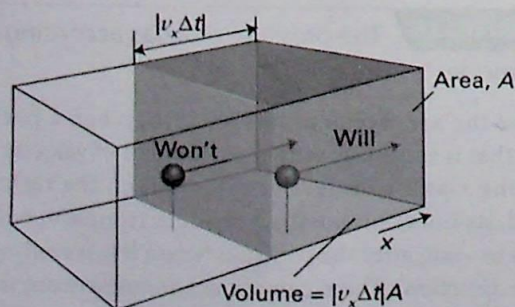
Figure 1B.2 A molecule will reach the wall on the right within an interval Δt if it is within a distance $v_x\Delta t$ of the wall and travelling to the right.

Next, to find the force, we calculate the rate of change of momentum, which is this change of momentum divided by the interval Δt during which it occurs:

$$\text{Rate of change of momentum} = \frac{nMAv_x^2}{V}$$

This rate of change of momentum is equal to the force (by Newton's second law of motion). It follows that the pressure the force divided by the area, is

$$\text{Pressure} = \frac{nMv_x^2}{V}$$

Not all the molecules travel with the same velocity, so the detected pressure, p, is the average (denoted $\langle...\rangle$) of the quantity just calculated:

$$p = \frac{nM\langle v_x^2\rangle}{V}$$

This expression already resembles the perfect gas equation of state.

To write an expression for the pressure in terms of the root-mean-square speed, v_{rms}, we begin by writing the speed of a single molecule, v, as $v^2 = v_x^2 + v_y^2 + v_z^2$. Because the root-mean-square speed is defined as $v_{rms} = \langle v^2\rangle^{1/2}$, it follows that

$$v_{rms}^2 = \langle v^2\rangle = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle$$

However, because the molecules are moving randomly, all three averages are the same. It follows that $v_{rms}^2 = \langle 3v_x^2\rangle$. Equation 1B.1 follows immediately by substituting $\langle v_x^2\rangle = \frac{1}{3}\langle v_{rms}^2\rangle$ into $p = nM\langle v_x^2\rangle/V$.

Equation 1B.1 is one of the key results of the kinetic model. We see that, if the root-mean-square speed of the molecules depends only on the temperature, then at constant temperature

$$pV = \text{constant}$$

which is the content of Boyle's law. Moreover, for eqn 1B.1 to be the equation of state of a perfect gas, its right-hand side must equal to nRT. It follows that the root-mean-square speed of the molecules in a gas at a temperature T must be

$$v_{rms} = \left(\frac{3RT}{M}\right)^{1/2} \qquad \textit{Perfect gas}\quad \text{RMS speed}\quad \text{(1B}$$

Brief illustration 1B.1   Molecular speeds

For N_2 molecules at 25 °C, we use $M = 28.02\,\text{g mol}^{-1}$, then

$$v_{rms} = \left\{\frac{3\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298\,\text{K})}{0.02802\,\text{kg mol}^{-1}}\right\}^{1/2} = 515\,\text{ms}^{-1}$$

Shortly we shall encounter the mean speed, v_{mean}, and the most probable speed v_{mp}; they are, respectively,

$$v_{mean} = \left(\frac{8}{3\pi}\right)^{1/2} v_{rms} = 0.921... \times (515\,ms^{-1}) = 475\,ms^{-1}$$

$$v_{mp} = \left(\frac{2}{3}\right)^{1/2} v_{rms} = 0.816... \times (515\,ms^{-1}) = 420\,ms^{-1}$$

Self-test 1B.1 Evaluate the root-mean-square speed of H_2 molecules at 25 °C.

Answer: 1.92 km s⁻¹

(b) The Maxwell–Boltzmann distribution of speeds

Equation 1B.2 is an expression for the mean square speed of molecules. However, in an actual gas the speeds of individual molecules span a wide range, and the collisions in the gas continually redistribute the speeds among the molecules. Before a collision, a molecule may be travelling rapidly, but after a collision it may be accelerated to a very high speed, only to be slowed again by the next collision. The fraction of molecules that have speeds in the range v to $v+dv$ is proportional to the width of the range, and is written $f(v)dv$, where $f(v)$ is called the **distribution of speeds**. Note that, in common with other distribution functions, $f(v)$ acquires physical significance only after it is multiplied by the range of speeds of interest. In the following *Justification* we show that the fraction of molecules that have a speed in the range v to $v+dv$ is $f(v)dv$, where

$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT} \quad \text{Perfect gas} \quad \boxed{\text{Maxwell–Boltzmann distribution}} \quad (1B.4)$$

The function $f(v)$ is called the **Maxwell–Boltzmann distribution of speeds**.

Justification 1B.2 The Maxwell–Boltzmann distribution of speeds

The Boltzmann distribution (*Foundations* B) implies that the fraction of molecules with velocity components v_x, v_y, and v_z is proportional to an exponential function of their kinetic energy: $f(v) = Ke^{-\varepsilon/kT}$, where K is a constant of proportionality. The kinetic energy is

$$\varepsilon = \tfrac{1}{2} m v_x^2 + \tfrac{1}{2} m v_y^2 + \tfrac{1}{2} m v_z^2$$

Therefore, we can use the relation $a^{x+y+z} = a^x a^y a^z$ to write

$$f(v) = Ke^{-(mv_x^2 + mv_y^2 + mv_z^2)/2kT} = Ke^{-mv_x^2/2kT} e^{-mv_y^2/2kT} e^{-mv_z^2/2kT}$$

The distribution factorizes into three terms, and we can write $f(v) = f(v_x) f(v_y) f(v_z)$ and $K = K_x K_y K_z$, with

$$f(v_x) = K_x e^{-mv_x^2/2kT}$$

and likewise for the other two axes.

To determine the constant K_x, we note that a molecule must have a velocity component somewhere in the range $-\infty < v_x < \infty$, so

$$\int_{-\infty}^{\infty} f(v_x)\,dv_x = 1$$

Substitution of the expression for $f(v_x)$ then gives

$$1 = K_x \int_{-\infty}^{\infty} e^{-mv_x^2/2kT}\,dv_x \overset{\text{Integral G.1}}{=} K_x \left(\frac{2\pi kT}{m}\right)^{1/2}$$

Therefore, $K_x = (m/2\pi kT)^{1/2}$ and at this stage we can write

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} \quad (1B.5)$$

The probability that a molecule has a velocity in the range v_x to v_x+dv_x, v_y to v_y+dv_y, v_z to v_z+dv_z, is therefore

$$f(v_x)f(v_y)f(v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv_x^2/2kT} e^{-mv_y^2/2kT} e^{-mv_z^2/2kT} \times dv_x dv_y dv_z$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} dv_x dv_y dv_z$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$.

To evaluate the probability that the molecules have a speed in the range v to $v+dv$ regardless of direction we think of the three velocity components as defining three coordinates in 'velocity space', with the same properties as ordinary space except that the coordinates are labelled (v_x, v_y, v_z) instead of (x,y,z). Just as the volume element in ordinary space is $dx\,dy\,dz$, so the volume element in velocity space is $dv_x dv_y dv_z$. The sum of all the volume elements in ordinary space that lie at a distance r from the centre is the volume of a spherical shell of radius r and thickness dr. That volume is the product of its surface area, $4\pi r^2$, and its thickness dr, and is therefore $4\pi r^2 dr$. Similarly, the analogous volume in velocity space is the volume of a shell of radius v and thickness dv, namely $4\pi v^2 dv$ (Fig. 1B.3). Now, because $f(v_x)f(v_y)f(v_z)$, the term in blue in the last equation, depends only on v^2, and has the same value everywhere in a shell of radius v, the total probability of the molecules possessing a speed in the range v to $v+dv$ is the product of the term in blue and the volume of the
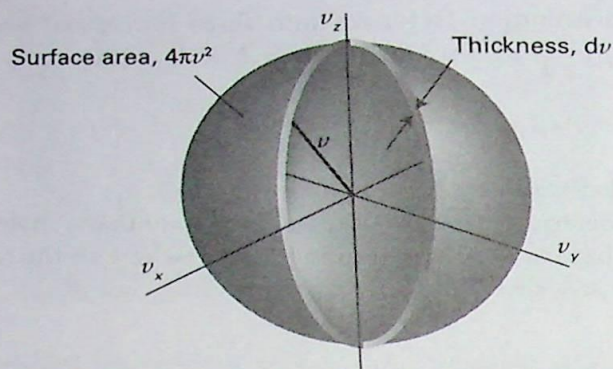
Figure 1B.3 To evaluate the probability that a molecule has a speed in the range v to $v+dv$, we evaluate the total probability that the molecule will have a speed that is anywhere on the surface of a sphere of radius $v=(v_x^2+v_y^2+v_z^2)^{1/2}$ by summing the probabilities that it is in a volume element $dv_x dv_y dv_z$ at a distance v from the origin.

shell of radius v and thickness dv. If this probability is written $f(v)dv$, it follows that

$$f(v)dv = 4\pi v^2 dv \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}$$

and $f(v)$ itself, after minor rearrangement, is

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

Because $m/k = M/R$, this expression is eqn 1B.4.

The important features of the Maxwell–Boltzmann distribution are as follows (and are shown pictorially in Fig. 1B.4):

- Equation 1B.4 includes a decaying exponential function (more specifically, a Gaussian function). Its presence implies that the fraction of molecules with very high speeds will be very small because e^{-x^2} becomes very small when x is large.
- The factor $M/2RT$ multiplying v^2 in the exponent is large when the molar mass, M, is large, so the exponential factor goes most rapidly towards zero when M is large. That is, heavy molecules are unlikely to be found with very high speeds.
- The opposite is true when the temperature, T, is high: then the factor $M/2RT$ in the exponent is small, so the exponential factor falls towards zero relatively slowly as v increases. In other words, a greater fraction of the molecules can be expected to have high speeds at high temperatures than at low temperatures.
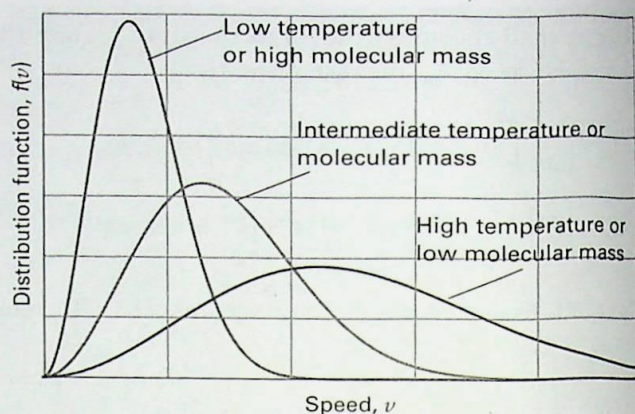
Figure 1B.4 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increase with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

- A factor v^2 (the term before the e) multiplies the exponential. This factor goes to zero as v goes to zero, so the fraction of molecules with very low speeds will also be very small whatever their mass.
- The remaining factors (the term in parentheses in eqn 1B.4 and the 4π) simply ensure that, when we sum the fractions over the entire range of speeds from zero to infinity, then we get 1.

The Maxwell distribution has been verified experimenta For example, molecular speeds can be measured directly w a velocity selector (Fig. 1B.5). The spinning discs have slits tl permit the passage of only those molecules moving throu them at the appropriate speed, and the number of molecu can be determined by collecting them at a detector.
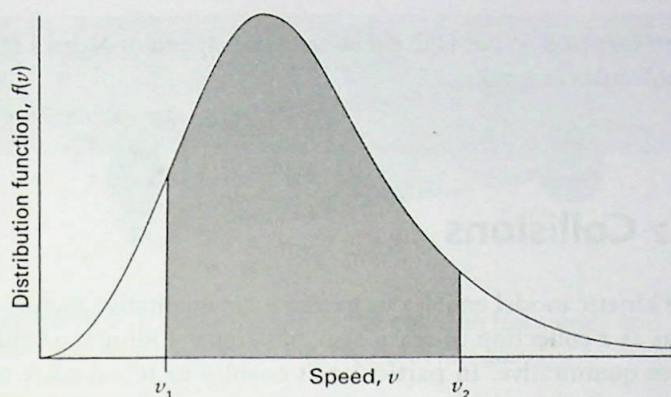
(c) Mean values

Once we have the Maxwell–Boltzmann distribution, we c calculate the mean value of any power of the speed by eva ating the appropriate integral. For instance, to evaluate t
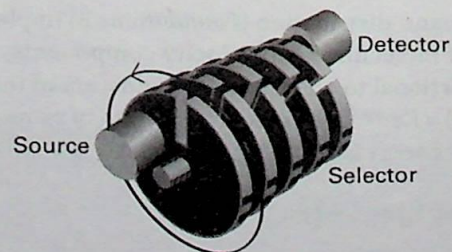
Figure 1B.5 A velocity selector. Only molecules travelling at speeds within a narrow range pass through the succession of slits as they rotate into position.

Figure 1B.6 To calculate the probability that a molecule will have a speed in the range v_1 to v_2, we integrate the distribution between those two limits; the integral is equal to the area of the curve between the limits, as shown shaded here.

fraction of molecules in the range v_1 to v_2 we evaluate the integral:

$$F(v_1, v_2) = \int_{v_1}^{v_2} f(v)\,dv \tag{1B.6}$$

This integral is the area under the graph of f as a function of v and, except in special cases, has to be evaluated numerically by using mathematical software (Fig. 1B.6). To evaluate the average value of v^n we calculate

$$\langle v^n \rangle = \int_0^\infty v^n f(v)\,dv \tag{1B.7}$$

In particular, integration with $n=2$ results in eqn 1B.3 for the mean square speed $\langle v^2 \rangle$ of the molecules at a temperature T. We can conclude that the root-mean-square speed of the molecules of a gas is proportional to the square root of the temperature and inversely proportional to the square root of the molar mass. That is, the higher the temperature, the higher the root-mean-square speed of the molecules, and, at a given temperature, heavy molecules travel more slowly than light molecules. Sound waves are pressure waves, and for them to propagate the molecules of the gas must move to form regions of high and low pressure. Therefore, we should expect the root-mean-square speeds of molecules to be comparable to the speed of sound in air ($340\ \mathrm{m\,s^{-1}}$). As we have seen, the root-mean-square speed of N_2 molecules, for instance, is $515\ \mathrm{m\,s^{-1}}$ at 298 K.

Example 1B.1 Calculating the mean speed of molecules in a gas

Calculate the mean speed, v_{mean}, of N_2 molecules in air at 25 °C.

Method The mean speed is obtained by evaluating the integral

$$v_{mean} = \int_0^\infty v f(v)\,dv$$

with $f(v)$ given in eqn 1B.4. Either use mathematical software or use the standard integrals in the *Resource section*.

Answer The integral required is

$$v_{mean} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2kT}\,dv$$

$$\overset{\text{Integral G.4}}{=} 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \times \frac{1}{2}\left(\frac{2RT}{M}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

Substitution of the data then gives

$$v_{mean} = \left(\frac{8\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})}{\pi\times(28.02\times10^{-3}\ \mathrm{kg\,mol^{-1}})}\right)^{1/2} = 475\ \mathrm{m\,s^{-1}}$$

We have used $1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$ (the difference from the earlier value of 474 is due to rounding effects in that calculation; this value is more accurate).

Self-test 1B.2 Evaluate the root-mean-square speed of the molecules by integration. Use mathematical software or use a standard integral in the *Resource section*.

Answer: $v_{rms} = (3RT/M)^{1/2} = 515\ \mathrm{m\,s^{-1}}$

As shown in *Example* 1B.1, we can use the Maxwell–Boltzmann distribution to evaluate the **mean speed**, v_{mean}, of the molecules in a gas:

$$v_{mean} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8}{3\pi}\right)^{1/2} v_{rms} \qquad \begin{array}{l}\textit{Perfect}\\ \textit{gas}\end{array}\ \begin{array}{l}\text{Mean}\\ \text{speed}\end{array} \tag{1B.8}$$

We can identify the **most probable speed**, v_{mp}, from the location of the peak of the distribution:

$$v_{mp} = \left(\frac{2RT}{M}\right)^{1/2} = \left(\frac{2}{3}\right)^{1/2} v_{rms} \qquad \begin{array}{l}\textit{Perfect}\\ \textit{gas}\end{array}\ \begin{array}{l}\text{Most}\\ \text{probable}\\ \text{speed}\end{array} \tag{1B.9}$$

The location of the peak of the distribution is found by differentiating $f(v)$ with respect to v and looking for the value of v at which the derivative is zero (other than at $v=0$ and $v=\infty$); see Problem 1B.3. Figure 1B.7 summarizes these results and some numerical values were calculated in *Brief illustration* 1B.1.

The **mean relative speed**, v_{rel}, the mean speed with which one molecule approaches another of the same kind, can also be calculated from the distribution:

$$v_{rel} = 2^{1/2} v_{mean} \qquad \begin{array}{l}\textit{Perfect gas,}\\ \textit{identical}\\ \textit{molecules}\end{array}\ \begin{array}{l}\text{Mean}\\ \text{relative}\\ \text{speed}\end{array} \tag{1B.10a}$$
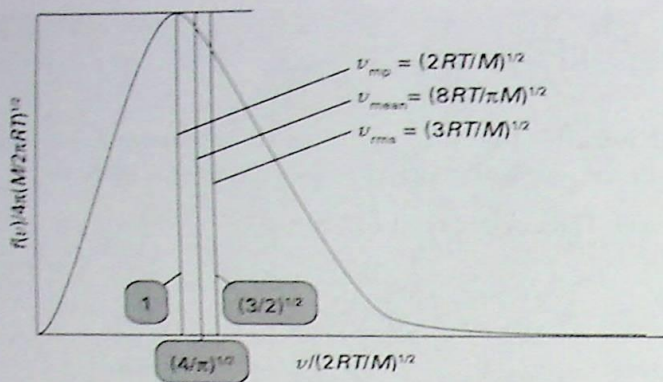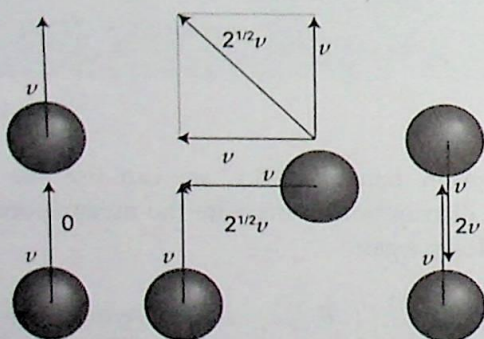
Figure 1B.7 A summary of the conclusions that can be deduced form the Maxwell distribution for molecules of molar mass M at a temperature T: v_{mp} is the most probable speed, v_{mean} is the mean speed, and v_{rms} is the root-mean-square speed.

This result is much harder to derive, but the diagram in Fig. 1B.8 should help to show that it is plausible. For the relative mean speed of two dissimilar molecules of masses m_A and m_B:

$$v_{rel} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \qquad \mu = \frac{m_A m_B}{m_A + m_B} \qquad \begin{array}{l}\textit{Perfect}\\ \textit{gas}\end{array} \quad \begin{array}{l}\text{Mean}\\ \text{relative}\\ \text{speed}\end{array} \quad (1B.10b)$$

Figure 1B.8 A simplified version of the argument to show that the mean relative speed of molecules in a gas is related to the mean speed. When the molecules are moving in the same direction, the mean relative speed is zero; it is $2v$ when the molecules are approaching each other. A typical mean direction of approach is from the side, and the mean speed of approach is then $2^{1/2}v$. The last direction of approach is the most characteristic, so the mean speed of approach can be expected to be about $2^{1/2}v$. This value is confirmed by more detailed calculation.

Brief illustration 1B.2 Relative molecular speeds

We have already seen (in *Brief illustration* 1B.1) that the rms speed of N_2 molecules at 25 °C is 515 m s^{-1}. It follows from eqn 1B.10a that their relative mean speed is

$$v_{rel} = 2^{1/2} \times (515\,ms^{-1}) = 728\,ms^{-1}$$

Self-test 1B.3 What is the relative mean speed of N_2 and ▮ molecules in a gas at 25 °C?

Answer: 1.83 km▮

1B.2 Collisions

The kinetic model enables us to make the qualitative pictur▮ a gas as a collection of ceaselessly moving, colliding molec▮ more quantitative. In particular, it enables us to calculate ▮ frequency with which molecular collisions occur and the ▮ tance a molecule travels on average between collisions.

(a) The collision frequency

Although the kinetic-molecular theory assumes that the m▮ ecules are point-like, we can count a 'hit' whenever the cen▮ of two molecules come within a distance d of each other, wh▮ d, the collision diameter, is of the order of the actual diamet▮ of the molecules (for impenetrable hard spheres d is the dia▮ eter). As we show in the following *Justification*, we can use ▮ kinetic model to deduce that the collision frequency, z, ▮ number of collisions made by one molecule divided by the ti▮ interval during which the collisions are counted, when th▮ are N molecules in a volume V is

$$z = \sigma v_{rel} \mathcal{N} \qquad \textit{Perfect gas} \quad \boxed{\text{Collision frequency}} \quad (1B.1▮$$

with $\mathcal{N} = N/V$, the number density, and v_{rel} given by eqn 1B. The area $\sigma = \pi d^2$ is called the **collision cross-section** of the m▮ ecules. Some typical collision cross-sections are given in Ta▮ 1B.1. In terms of the pressure (as is also shown in the follow▮ *Justification*),

$$z = \frac{\sigma v_{rel} p}{kT} \qquad \textit{Perfect gas} \quad \boxed{\text{Collision frequency}} \quad (1B.1▮$$

**Table 1B.1*** Collision cross-sections, σ/nm^2

	σ/nm^2
C_6H_6	0.88
CO_2	0.52
He	0.21
N_2	0.43

* More values are given in the *Resource section*.

Justification 1B.3 The collision frequency according to the kinetic model

Consider the positions of all the molecules except one ▮ be frozen. Then note what happens as one mobile molecu▮ travels through the gas with a mean relative speed v_{rel} for
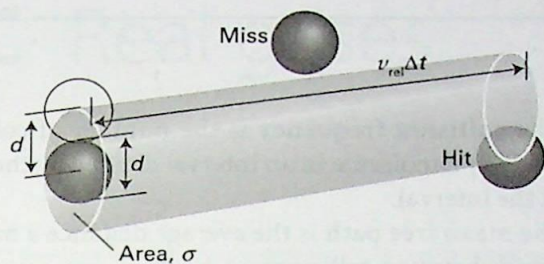
Figure 1B.9 The calculation of the collision frequency and the mean free path in the kinetic theory of gases.

time Δt. In doing so it sweeps out a 'collision tube' of cross-sectional area $\sigma = \pi d^2$ and length $v_{rel}\Delta t$ and therefore of volume $\sigma v_{rel}\Delta t$ (Fig. 1B.9). The number of stationary molecules with centres inside the collision tube is given by the volume of the tube multiplied by the number density $\mathcal{N} = N/V$, and is $\mathcal{N}\sigma v_{rel}\Delta t$. The number of hits scored in the interval Δt is equal to this number, so the number of collisions divided by the time interval is $\mathcal{N}\sigma v_{rel}$, which is eqn 1B.11a. The expression in terms of the pressure of the gas is obtained by using the perfect gas equation to write

$$\mathcal{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{nN_A}{nRT/p} = \frac{p}{kT}$$

Equation 1B.11a shows that, at constant volume, the collision frequency increases with increasing temperature. Equation 1B.11b shows that, at constant temperature, the collision frequency is proportional to the pressure. Such a proportionality is plausible because the greater the pressure, the greater the number density of molecules in the sample, and the rate at which they encounter one another is greater even though their average speed remains the same.

Brief illustration 1B.3 Molecular collisions

For an N_2 molecule in a sample at 1.00 atm (101 kPa) and 25 °C, from Brief illustration 1B.2 we know that $v_{rel} = 728\,\text{m s}^{-1}$. Therefore, from eqn 1B.11b, and taking $\sigma = 0.45\,\text{nm}^2$ (corresponding to $0.45 \times 10^{-18}\,\text{m}^2$) from Table 1B.1,

$$z = \frac{(0.43 \times 10^{-18}\,\text{m}^2) \times (728\,\text{m s}^{-1}) \times (1.01 \times 10^5\,\text{Pa})}{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298\,\text{K})}$$

$$= 7.7 \times 10^9\,\text{s}^{-1}$$

so a given molecule collides about 8×10^9 times each second. We are beginning to appreciate the timescale of events in gases.

Self-test 1B.4 Evaluate the collision frequency between H_2 molecules in a gas under the same conditions.

Answer: $4.1 \times 10^9\,\text{s}^{-1}$

(b) The mean free path

Once we have the collision frequency, we can calculate the mean free path, λ (lambda), the average distance a molecule travels between collisions. If a molecule collides with a frequency z, it spends a time $1/z$ in free flight between collisions, and therefore travels a distance $(1/z)v_{rel}$. It follows that the mean free path is

$$\lambda = \frac{v_{rel}}{z} \qquad \text{Perfect gas} \quad \text{Mean free path} \quad \text{(1B.12)}$$

Substitution of the expression for z in eqn 1B.11b gives

$$\lambda = \frac{kT}{\sigma p} \qquad \text{Perfect gas} \quad \text{Mean free path} \quad \text{(1B.13)}$$

Doubling the pressure reduces the mean free path by half.

Brief illustration 1B.4 The mean free path

In Brief illustration 1B.2 we noted that $v_{rel} = 728\,\text{m s}^{-1}$ for N_2 molecules at 25 °C, and in Brief illustration 1B.3 that $z = 7.7 \times 10^9\,\text{s}^{-1}$ when the pressure is 1.00 atm. Under these circumstances, the mean free path of N_2 molecules is

$$\lambda = \frac{728\,\text{m s}^{-1}}{7.7 \times 10^9\,\text{s}^{-1}} = 9.5 \times 10^{-8}\,\text{m}$$

or 95 nm, about 10^3 molecular diameters.

Self-test 1B.5 Evaluate the mean free path of benzene molecules at 25 °C in a sample where the pressure is 0.10 atm.

Answer: 460 nm

Although the temperature appears in eqn 1B.13, in a sample of constant volume, the pressure is proportional to T, so T/p remains constant when the temperature is increased. Therefore, the mean free path is independent of the temperature in a sample of gas in a container of fixed volume: the distance between collisions is determined by the number of molecules present in the given volume, not by the speed at which they travel.

In summary, a typical gas (N_2 or O_2) at 1 atm and 25 °C can be thought of as a collection of molecules travelling with a mean speed of about 500 m s^{-1}. Each molecule makes a collision within about 1 ns, and between collisions it travels about 10^3 molecular diameters. The kinetic model of gases is valid and the gas behaves nearly perfectly if the diameter of the molecules is much smaller than the mean free path ($d \ll \lambda$), for then the molecules spend most of their time far from one another.

Checklist of concepts

☐ 1. The **kinetic model** of a gas considers only the contribution to the energy from the kinetic energies of the molecules.

☐ 2. Important results from the model include expressions for the pressure and the **root-mean-square speed**.

☐ 3. The Maxwell–Boltzmann distribution of speeds gives the fraction of molecules that have speeds in a specified range.

☐ 4. The **collision frequency** is the number of coll is made by a molecule in an interval divided by the lle of the interval.

☐ 5. The **mean free path** is the average distance a mole travels between collisions.

Checklist of equations

Property	Equation	Comment	Equation number
Pressure of a perfect gas from the kinetic model	$pV = \frac{1}{3} n M v_{rms}^2$	Kinetic model	1B.1
Maxwell–Boltzmann distribution of speeds	$f(v) = 4\pi (M/2\pi RT)^{3/2} v^2 e^{-Mv^2/2RT}$		1B.4
Root-mean-square speed in a perfect gas	$v_{rms} = (3RT/M)^{1/2}$		1B.3
Mean speed in a perfect gas	$v_{mean} = (8RT/\pi M)^{1/2}$		1B.8
Most probable speed in a perfect gas	$v_{mp} = (2RT/M)^{1/2}$		1B.9
Mean relative speed in a perfect gas	$v_{rel} = (8kT/\pi\mu)^{1/2}$ $\mu = m_A m_B/(m_A + m_B)$		1B.10
The collision frequency in a perfect gas	$z = \sigma v_{rel} p/kT,\ \sigma = \pi d^2$		1B.11
Mean free path in a perfect gas	$\lambda = v_{rel}/z$		1B.12

1C Real gases

Contents

➤ **Why do you need to know this material?**

Actual gases, so-called 'real gases', differ from perfect gases and it is important to be able to discuss their properties. Moreover, the deviations from perfect behaviour give insight into the nature of the interactions between molecules. Accounting for these interactions is also an introduction to the technique of model building in physical chemistry.

➤ **What is the key idea?**

Attractions and repulsions between gas molecules account for modifications to the isotherms of a gas and account for critical behaviour.

➤ **What do you need to know already?**

This Topic builds on and extends the discussion of perfect gases in Topic 1A. The principal mathematical technique employed is differentiation to identify a point of inflexion of a curve.

Real gases do not obey the perfect gas law exactly except in the limit of $p \to 0$. Deviations from the law are particularly important at high pressures and low temperatures, especially when a gas is on the point of condensing to liquid.

1C.1 Deviations from perfect behaviour

Real gases show deviations from the perfect gas law because molecules interact with one another. A point to keep in mind is that repulsive forces between molecules assist expansion and attractive forces assist compression.

Repulsive forces are significant only when molecules are almost in contact: they are short-range interactions, even on a scale measured in molecular diameters (Fig. 1C.1). Because they are short-range interactions, repulsions can be expected to be important only when the average separation of the molecules is small. This is the case at high pressure, when many molecules occupy a small volume. On the other hand, attractive intermolecular forces have a relatively long range and are effective over several molecular diameters. They are important when the molecules are fairly close together but not necessarily touching (at the intermediate separations in Fig. 1C.1).
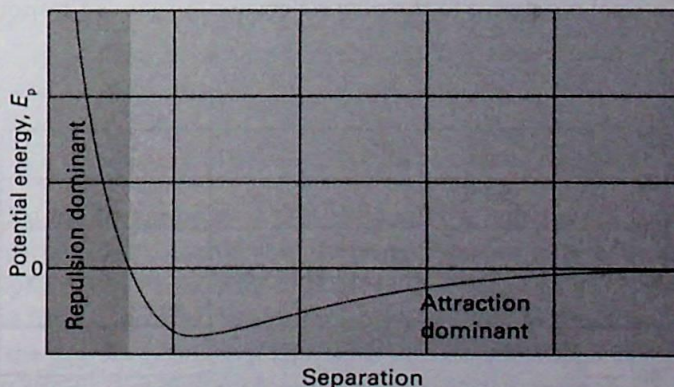
Figure 1C.1 The variation of the potential energy of two molecules on their separation. High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative, the attractive interactions dominate. At large separations (on the right) the potential energy is zero and there is no interaction between the molecules.