Chapter 5

The Kinetic Theory of Gases (2)

Topics

Development of the kinetic theory. The pressure according to kinetic theory, $p = \frac{1}{3}nm\overline{v^2}$*. The internal energy of a gas and the ideal gas law. Mixtures of gases, Dalton's law of partial pressures. Heat capacities,* $C_V = \frac{3}{2}nk$*. The number of collisions per second* $J = \frac{1}{4}n\overline{v}$*. Random walks in physics; survival equation and the distribution of free paths, mean free path; random walks. Brownian motion, the determination of* k*.*

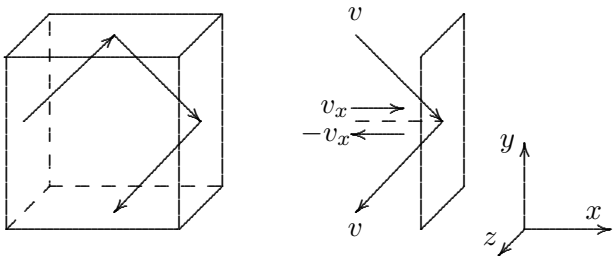
5.1 Calculating the pressure

We now apply the concepts of Chapter 4 to perfect gases. We begin by calculating the pressure exerted by our model gas. This calculation will demonstrate how to tackle calculations of this type in kinetic theory. We consider the behaviour of a small number of *typical* particles and use Newton's laws of mechanics to calculate their behaviour. We then average over all the particles using the distribution functions derived in the Chapter 4.

The *pressure* is the normal force per unit area which arises from the rate of change of momentum per unit area of all the particles striking the wall elastically. Because of collisions, the pressure is *isotropic*, that is, the same in all directions, throughout the volume of the box.

To calculate the pressure we start by considering the impact of a single particle on one wall of the container, say the wall which is in the $y-z$ plane (Figure 5.1). The pressure on the $y-z$ wall is only associated with the change in the x-component of the momentum. The collision with the wall is elastic and the wall does not move. Therefore the x-momentum of the particle changes by $\Delta p_x = 2p_x = 2mv_x$.

Figure 5.1. Illustrating the origin of pressure.



To calculate the rate of change of momentum we need to know the total number of particles hitting the wall per unit time:

- in a time Δt, particles with positive x-components of velocity of v_x which are within a distance $v_x\,\Delta t$ of the wall will reach it;
- the *fraction* of particles with this positive x-component of velocity is $f_1(v_x)\,\mathrm{d}v_x$;
- if the number of particles per unit volume is n, then the number hitting unit area in Δt is $n\,v_x f_1(v_x)\,\mathrm{d}v_x\,\Delta t$.

The change in momentum per unit area due to these collision is therefore

$$\Delta p_x = 2mv_x \times nv_x f_1(v_x)\,\mathrm{d}v_x\,\Delta t. \qquad (5.1)$$

We now average over all the particles by integrating with respect to v_x and identify the pressure as the rate of change of momentum per unit area

$$p = \frac{\Delta p_x}{\Delta t} = 2mn\int_0^\infty v_x^2\, f_1(v_x)\,\mathrm{d}v_x. \qquad (5.2)$$

The limits of this integral are from 0 to ∞ since only positive values of v_x can be included, that is, only particles which will collide with the wall.

We can simplify this result without using the explicit form of the distribution function; since $f_1(v_x)$ is symmetrical about the origin, the integral becomes

$$\int_0^\infty v_x^2\, f_1(v_x)\,\mathrm{d}v_x = \tfrac{1}{2}\int_{-\infty}^\infty v_x^2\, f_1(v_x)\,\mathrm{d}v_x = \tfrac{1}{2}\overline{v_x^2}. \qquad (5.3)$$

Therefore, from (5.2),

$$p = nm\overline{v_x^2}. \tag{5.4}$$

Because the distribution of velocities is isotropic, the pressure is also isotropic. This is entirely consistent with our demonstration in the last chapter that

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \qquad \text{and} \qquad \overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_y^2}. \tag{5.5}$$

Therefore,

$$\overline{v_x^2} = \tfrac{1}{3}\overline{v^2}, \tag{5.6}$$

and so

$$p = \tfrac{1}{3}nm\overline{v^2}. \tag{5.7}$$

This is an important equation – it relates the pressure p to processes occurring at the molecular level.

5.2 The internal energy and the link to the ideal gas law

Energy is stored in the gas and this is referred to as its *internal energy*. According to the present model, the internal energy of our ideal gas is the *kinetic energy of the individual particles*, since there are no long-range forces between the particles or between the particles and the walls of the enclosure. They also have no internal structure. The kinetic energy of a particle with speed v is $\frac{1}{2}mv^2$. We can therefore find the kinetic energy of the particles per unit volume and hence the internal energy per unit volume u, the *energy density*, by averaging over the population. Since the fraction of particles with this speed is $f(v)\,\mathrm{d}v$, we find:

$$u = n\int_0^\infty \tfrac{1}{2}mv^2 f(v)\,dv = \tfrac{1}{2}nm\overline{v^2}. \tag{5.8}$$

The perfect gas law is $p = nkT$, and hence

$$p = \tfrac{1}{3}nm\overline{v^2} = nkT. \tag{5.9}$$

Therefore

$$\tfrac{3}{2}kT = \tfrac{1}{2}m\overline{v^2}, \tag{5.10}$$

and

$$u = \tfrac{1}{2}nm\overline{v^2} = \tfrac{3}{2}nkT. \tag{5.11}$$

Kinetic Theory:
pressure and internal energy

$$p = \tfrac{1}{3}nm\overline{v^2} = nkT,$$

$$u = \tfrac{1}{2}nm\overline{v^2} = \tfrac{3}{2}nkT.$$

However, this is precisely the result for $\frac{1}{2}nm\overline{v^2}$ obtained by calculating $\overline{v^2}$ directly from the distribution function (4.16).

These are key results. Most importantly, we have shown that the internal energy is just a function of the temperature T, consistent with the null result of Joule's experiment, and consistent with our macroscopic equation of state.

5.3 The pressure of a mixture of gases - Dalton's law of partial pressures

Let us modify our simulation of how a gas of particles comes into statistical equilibrium by considering the case of a mixture of two types of particles of masses m_1 and m_2. The outcome of the collision between two particles with momenta

$$\begin{aligned} m_1: &\quad \boldsymbol{p}_1 \equiv [p_{1x}, p_{1y}] \\ m_2: &\quad \boldsymbol{p}_2 \equiv [p_{2x}, p_{2y}] \end{aligned}$$

can be evaluated in exactly the same way as in Section 3.3, but now the particles have different masses. The analysis is left as an exercise for the enthusiast, and is entirely straightforward. The outcome of the collision is that the momentum of particle 1 is

$$\begin{aligned} p''_{1x} = \frac{1}{(m_1+m_2)}[&(m_2 p_{1x} - m_1 p_{2x})\cos\theta \\ &+ (m_2 p_{1y} - m_1 p_{2y})\sin\theta + m_1(p_{1x} + p_{2x})], \end{aligned} \tag{5.12}$$

$$\begin{aligned} p''_{1y} = \frac{1}{(m_1+m_2)}[&-(m_2 p_{1x} - m_1 p_{2x})\sin\theta \\ &+ (m_2 p_{1y} - m_1 p_{2y})\cos\theta + m_1(p_{1y} + p_{2y})]. \end{aligned} \tag{5.13}$$

Similarly, for particle 2,

$$p''_{2x} = \frac{1}{(m_1+m_2)}[(m_1p_{2x} - m_2p_{1x})\cos\theta + (m_1p_{2y} - m_2p_{1y})\sin\theta + m_2(p_{1x} + p_{2x})], \tag{5.14}$$

$$p''_{2y} = \frac{1}{(m_1+m_2)}[-(m_1p_{2x} - m_2p_{1x})\sin\theta + (m_1p_{2y} - m_2p_{1y})\cos\theta + m_2(p_{1y} + p_{2y})]. \tag{5.15}$$

Once again the new components of the momenta depend only upon θ, the rotation angle of the collision in the centre of momentum frame of reference. Therefore, we can set up the same array of cells including the p_x and p_y components in each cell as in the previous simulation, but there are now two different species present (Table 5.1). We divide the array into two halves, all those in one half having masses m_1 and the other half m_2. Again, we ensure that the system has no net momentum and so we have to arrange the initial state of the particles of the gas so that

$$\sum_i p_{xi} = 0, \qquad \sum_i p_{yi} = 0. \tag{5.16}$$

An arbitrary example of the new array is shown in Table 5.1, where the momenta are given integral values.

Table 5.1. An array of p_{xi}, p_{yi} values.

m_1			m_2		
-7 , 7	-6 , 2	-5 , -3	-7 , 7	-6 , 2	-5 , -3
-4 , 6	-3 , 1	-2 , -4	-4 , 6	-3 , 1	-2 , -4
-1 , 5	0 , 0	1 , -5	-1 , 5	0 , 0	1 , -5
2 , 4	3 , -1	4 , -6	2 , 4	3 , -1	4 , -6
5 , 3	6 , -2	7 , -7	5 , 3	6 , -2	7 , -7

The simulation proceeds as follows:

1. Choose any element i of the complete array at random.
2. Choose another element of the complete array at random j.
3. Allow i and j to collide and choose the angle θ at random. The possible collisions which can occur are m_1 with m_1, m_1 with m_2, m_2 with m_1 and m_2 with m_2.
4. Determine the values of $[p''_{1x}, p''_{1y}]$ and $[p''_{2x}, p''_{2y}]$ using the expressions (5.12) to (5.15).
5. Replace the original values of the $[p_{1x}, p_{1y}]$ and $[p_{2x}, p_{2y}]$ by the new $[p''_{1x}, p''_{1y}]$ and $[p''_{2x}, p''_{2y}]$.

6. Choose a new pair of cells at random and repeat the process.

7. Repeat this procedure thousands of times and plot the histogram of velocities of the particles with masses m_1 and m_2 separately.

The results of these simulations are shown in Figure 5.2. It can be seen that the distributions tend very rapidly to gaussian distributions in both the x and y directions for both types of particles, but the standard deviations are in the ratio $(m_1/m_2)^{1/2}$. Thus, under the randomising effect of many collisions, the two sets of particles come into statistical equilibrium with

$$\frac{\sigma_{m_2}}{\sigma_{m_1}} = \left(\frac{m_1}{m_2}\right)^{1/2}$$
$$\tfrac{1}{2}m_1\overline{v_1^2} = \tfrac{1}{2}m_2\overline{v_2^2} \qquad (5.17)$$

Therefore, under the action of random collisions, the particles come into statistical equilibrium at the same temperature T such that

$$\tfrac{1}{2}m_1\overline{v_1^2} = \tfrac{1}{2}m_2\overline{v_2^2} = \tfrac{3}{2}kT. \qquad (5.18)$$

We can now work out the total pressure acting on the walls due to the effects of both types of particles:

$$p = n_1kT + n_2kT = p_1 + p_2, \qquad (5.19)$$

which is *Dalton's law of partial pressures.*

5.4 Heat Capacities

One of the basic properties of all forms of matter is that of *heat capacity.* Heat capacities describe the change in temperature of a substance when it is supplied with a given amount of heat. In general we can write,

$$\Delta Q = C\Delta T, \qquad (5.20)$$

where ΔQ is the heat supplied and ΔT is the resultant temperature change. In the case of gases,

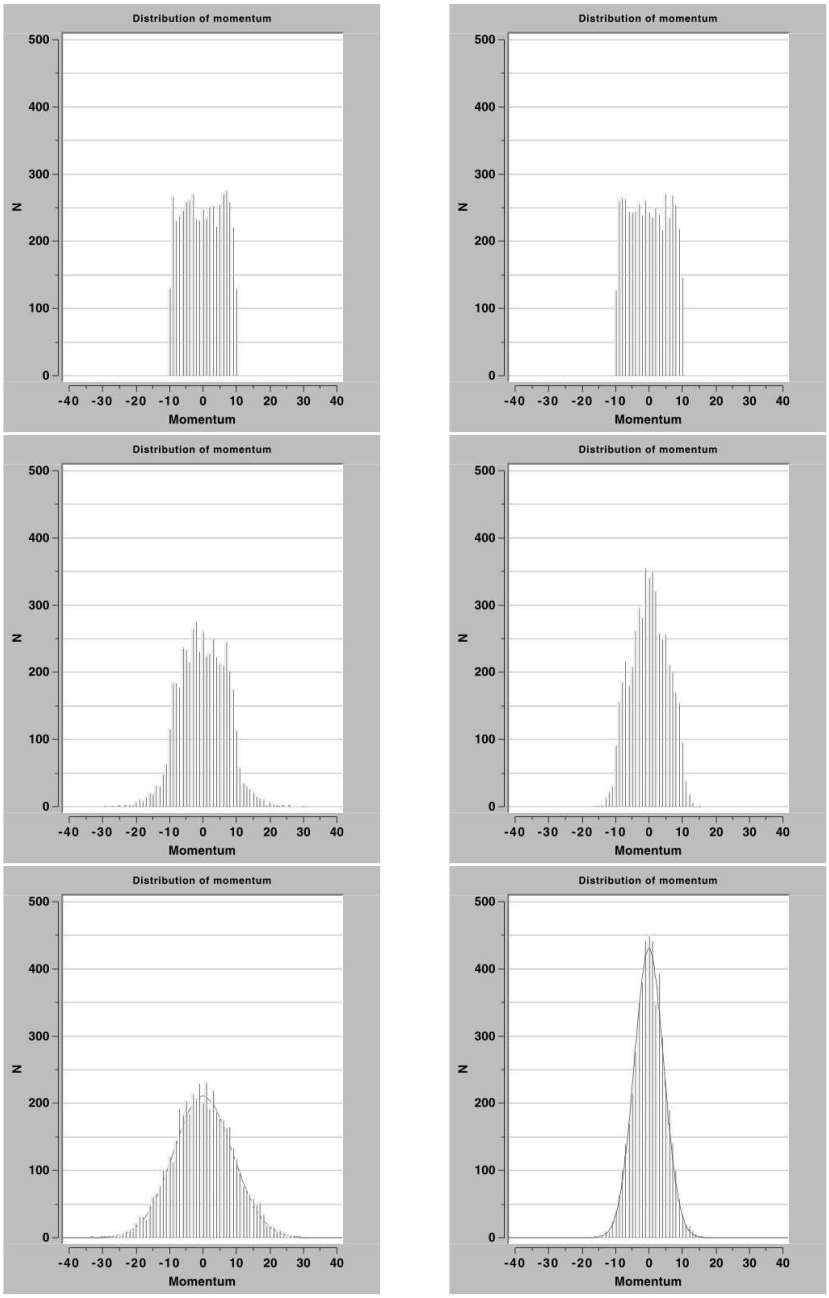


Figure 5.2: The evolution of the momentum distributions for particles of two different masses. The left hand plots are for a particles of mass m and the right hand plots for particles of mass $4m$. Initially (top) all particles have the same momentum distribution. After 10000 collisions the momentum distributions shown in the middle two plots are obtained; a fraction of the lighter particles are beginning to acquire larger velocities. After 50000 collisions both distribution functions have become gaussians (bottom); the width of the distribution for the lighter particles is exactly twice that of the heavier particles indicating that the mean kinetic energy, and hence temperature, is the same for both masses of particles.

there is the complication that the gas can expand on heating if it is not constrained. We therefore define two heat capacities for a gas – the heat capacity per mole if the gas is maintained at constant volume, C_V, and the heat capacity per mole at constant pressure, C_p.

In the latter case, we allow the volume of the enclosing vessel to expand at constant pressure. Clearly work has to be done in this process and so more heat has to be supplied to achieve the same temperature change. Thus, for one mole of any substance, we can define the *molar heat capacities* at constant volume and constant pressure by the expressions:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V, \qquad C_p = \left(\frac{\partial Q}{\partial T}\right)_p. \tag{5.21}$$

One of the objectives of the theory will be to account for the experimentally measured variation of the heat capacities of different gases with temperature, two examples of which are shown in Figure 5.3.

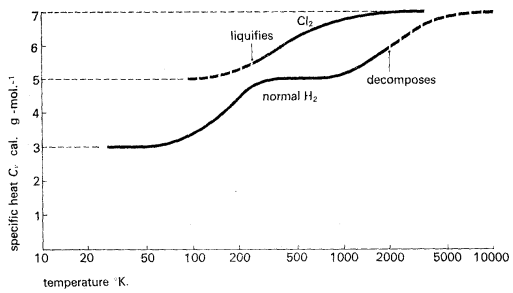


Figure 5.3. The variation of the molar heat capacity at constant volume with temperature for molecular hydrogen and chlorine.

In the same way, it is a challenge to account for the variation of the molar heat capacities of solids with temperature as shown in Figure 5.4 for copper. We will find that we need quantum concepts to explain the detailed form of Figure 5.4.

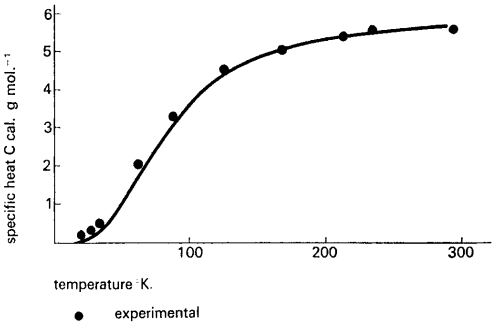


Figure 5.4. The variation of the molar heat capacity with temperature for copper.

Let us make a first attempt to account for at least part of the variation of the heat capacity of gases at constant volume with temperature T on the basis of kinetic theory. If we add or remove energy in the form of heat, we change the internal energy of the gas and also the temperature. The heat capacity at constant volume is

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \tag{5.22}$$

and for one mole of an ideal gas

$$\begin{aligned} C_V &= \left(\frac{\partial Q}{\partial T}\right)_V = \frac{\mathrm{d}U}{\mathrm{d}T} \\ &= \tfrac{3}{2}N_A kT = \tfrac{3}{2}RT. \end{aligned}$$

We can also define a heat capacity per particle which is $c_V = \frac{3}{2}kT$.

Returning to Figure 5.3, we see that at low temperatures, the heat capacity of hydrogen is 3 calories per mole. The gas constant R is 8.31 J K^{-1} mole^{-1} and there are 4.186 Joules per calorie. Therefore, the heat capacity per mole is $(1.5 \times 8.31)/4.186 = 3$ calories per mole, in agreement with the data shown in Figure 5.3 at low temperatures. Indeed, *for all monatomic gases, the heat capacity per particle is* $c_V = \frac{3}{2}kT$. There is, however, much more to be explained about these diagrams, which are for diatomic molecules, and we will deal with these in due course.

5.5 The number of collisions per unit area per second

In our derivation of the pressure of a perfect gas, particles continually hit the walls of the container. We showed that the number of collisions per unit area in time Δt for particles with x velocities in the interval v_x to $v_x + \mathrm{d}v_x$ was given by

$$\Delta N = n v_x f_1(v_x)\,\mathrm{d}v_x\,\Delta t$$

The rate of collisions per unit area, that is, the number of collisions per unit area per unit time, or the *flux density*, is found by integrating over all positive values of v_x,

$$J = \frac{\Delta N}{\Delta t} = n\int_0^\infty v_x f_1(v_x)\,\mathrm{d}v_x$$

where the limits of the integral include only positive velocities as these are the particles which reach the wall. Using (4.12) for the one-dimensional velocity distribution, we can evaluate this integral using the substitution $x = v_x\sqrt{m/2kT}$.

$$\begin{aligned} J &= n\sqrt{\frac{m}{2\pi kT}}\int_0^\infty v_x\,\mathrm{e}^{-mv_x^2/2kT}\,\mathrm{d}v_x, \\ &= n\sqrt{\frac{2kT}{m\pi}}\int_0^\infty x\,\mathrm{e}^{-x^2}\,\mathrm{d}x = n\sqrt{\frac{2kT}{m\pi}}\int_0^\infty \frac{1}{2}\mathrm{e}^{-y}\,\mathrm{d}y, \\ &= \frac{n}{2}\sqrt{\frac{2kT}{m\pi}}. \end{aligned}$$

Now we have already shown that $\overline{v} = \sqrt{8kT/m\pi}$ and so we can rewrite this result in the form

$$J = \tfrac{1}{4}n\overline{v}. \qquad (5.23)$$

Reminder - The One-dimensional Maxwell Distribution

$$f_1(v_x)\,\mathrm{d}v_x = \sqrt{\frac{m}{2\pi kT}}\,\mathrm{e}^{-mv_x^2/2kT}\,\mathrm{d}v_x$$

Although we have worked out this result assuming a Maxwellian distribution of velocities, *it is in fact true for any distribution function* $f_1(v_x)$.

Flux density of particles onto a surface

$$J = \tfrac{1}{4} n \overline{v}$$

5.6 Random walks in Physics

We have emphasised the crucial importance of collisions between particles for the kinetic theory of gases. We need to quantify in more detail the motions of individual particles. The key ideas are:

- the concept of *mean free path*;
- survival probabilities;
- the mathematics of random walks.

These ideas have *very* wide applicability in essentially all aspects of physics and many other subjects.

We consider the particles to be hard spheres with finite diameters a. Some typical values are given in Table 5.2. Although some of the molecules are compounds, they are treated as spheres for the purposes of the calculations which follow.

Table 5.2

Atom or molecule	Symbol	(a/nm)
Argon	Ar	0.340
Carbon dioxide	CO_2	0.390
Nitrogen	N_2	0.375
Oxygen	O_2	0.354

How far do molecules travel before they collide with other molecules? We imagine the gas to consist of a random distribution of n spheres per unit volume, each of diameter a. First, we consider them to be stationary. Now, suppose we choose a molecule at random and that it moves through the gas at speed v. Then, there will be collisions with molecules of the gas, if they lie within a cylinder of radius a about the path of the centre of the molecule, as illustrated in Figure 5.5.

The shaded sphere No. 1 travels at speed v and sweeps out the volume indicated by the cylinder drawn in solid lines. The spheres Nos. 2 and 3 are stationary. There will certainly be a collision with No. 3 and a grazing collision with No. 2. It can be seen that, if the centres of the molecules lie within the dashed cylinder, which has *radius* a, sphere No. 1 will collide with them. Now suppose molecule No. 1 travels a length l through the gas.

The number of molecules which lie within radial distance a of the path, and with which collisions will occur, is $N = \pi a^2 l n$, where n is the number density of molecules. Therefore, the molecule will make one collision with the other molecules when it has travelled a typical distance λ such that $N = 1 = \pi a^2 \lambda n$, that is

$$\lambda = \frac{1}{\sigma n} \qquad \text{where} \qquad \sigma = \pi a^2. \tag{5.24}$$

This is an important formula and provides a definition of the *mean free path* λ of the molecule travelling through the gas. σ is known as the *cross-section* for scattering of the particle.

$$\lambda = \frac{1}{\sigma n}. \tag{5.25}$$

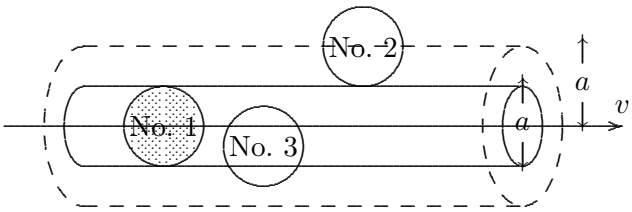
The above calculation has a number of unsatisfactory features. In fact, all the particles are in motion and so it is a crude approximation to assume that the other molecules are stationary. This slightly changes the expression for the cross-section, which is $\sigma = \sqrt{2}\pi a^2$ for a gas which has a Maxwellian distribution of velocities. We will simply write $\lambda = 1/\sigma n$, understanding that the mean-free path will always be given by a suitably defined cross-section σ, so that $\lambda = (\sigma n)^{-1}$ gives the correct expression for the mean free path.

In the same way, we can define a *mean free time* τ between collisions by $\tau = \lambda/\overline{v}$, where $\overline{v}$ is the mean speed of the particles. Some values for the mean speeds, mean free paths and mean free times for the gases listed above at Standard Temperature and Pressure (STP) are listed in Table 5.3. Thus, atoms or molecules are scattered many times per second as they move through a gas under normal atmospheric conditions.

5.7 The Survival Probability and the Distribution of Free Paths

The calculation carried out in the last section tells us the mean distance between collisions, but it does not tell us anything about the *distribution* of the

Figure 5.5. Collision of moving molecule with random stationary molecules.



Mean free path

$$\lambda = \frac{1}{\sigma n}$$

STP means to "standard temperature and pressure". This corresponds to $T = 273$ K and a pressure of 1 standard atmosphere or $p \sim 10^5$ Pa.

Table 5.3

Atom or molecule	Mean speed ($\overline{v}$/m s^{-1})	Mean free path (λ/nm)	Mean free time (τ/ns)
Ar	380	63	0.165
CO_2	362	39	0.108
N_2	454	59	0.130
O_2	425	63	0.149

free paths of particles, in other words, what is the likelihood of the particle having a collision after travelling a certain distance.

Let us analyse the problem in terms of the *survival probability* $p(x)$, meaning the probability that the particle travels a distance x before it collides with another molecule. We can understand the general form of the function. If the particle has travelled no distance, $x = 0$, it cannot have had any collisions at all and so $p(0) = 1$. On the other hand, after a very long path length through the gas, the probability of surviving tends to zero, $p(\infty) \to 0$.

Survival probabilities
The term 'survival' here simply refers to the distance before something happens. A more direct example of this usage is in radioactive decay, where $p(t)$ would mean that the probability that the radioactive nucleus decays after time t. In other words, it really is a survival probability for the nucleus.

In our analysis of the mean free path, we showed that the number of collisions was proportional to l, the distance travelled though the gas. Therefore, the probability of a collision occurring in the elementary distance $\mathrm{d}x$ is proportional to $\mathrm{d}x$ and we write this as $\alpha\,\mathrm{d}x$. Now, $p(x)$ is the probability that the particle survives to distance x without making a collision. Recalling that we multiply probabilities if the events are statistically independent, the probability that the collision occurs in the next small increment of distance $\mathrm{d}x$ is $p(x) \times \alpha\,\mathrm{d}x$. Thus, we can write

If the events A and B are statistically independent, we *multiply* the probabilities,

$$p_{(\mathrm{A\ and\ B})} = p_{\mathrm{A}} p_{\mathrm{B}}$$

$$p(x) - p(x + \mathrm{d}x) = -\frac{\mathrm{d}p}{\mathrm{d}x}\,\mathrm{d}x = p(x)\alpha\,\mathrm{d}x. \quad (5.26)$$

This results in an exponential integral

$$\int_{p(0)}^{p(x)} \frac{\mathrm{d}p}{p} = -\int_0^x \alpha\,\mathrm{d}x. \quad (5.27)$$

Therefore,

$$\ln\left[\frac{p(x)}{p(0)}\right] = -\alpha x, \qquad p(x) = p(0)\exp(-\alpha x),$$
$$p(x) = \exp(-\alpha x), \quad (5.28)$$

since $p(0) = 1$. This is the expression for the probability that the particle travels a distance x before colliding.

Now, let us work out the mean distance which a particle travels before it collides. This is just the *mean free path* λ. The probability that the particle has a collision in the small distance increment $\mathrm{d}x$ is

$p(x)\,\alpha\,\mathrm{d}x$. Therefore, the average distance travelled is

$$\lambda = \int_0^\infty x \times p(x)\alpha\,\mathrm{d}x = \int_0^\infty \alpha x\,\mathrm{e}^{-\alpha x}\,\mathrm{d}x. \quad (5.29)$$

This is a simple integration by parts which gives the result $\lambda = \alpha^{-1}$.

Thus, the survival probability, in the sense that the molecule travels a distance x *without suffering a collision*, is

$$p(x) = \exp\left(-\frac{x}{\lambda}\right), \quad (5.30)$$

where λ is the mean free path. Thus, λ has a much greater significance than simply the average distance travelled before a collision occurs – it also tells us about the *probability distribution of free paths* as well. Notice that the *probability distribution of free paths* $f(x)$ is

$$f(x)\,\mathrm{d}x = p(x)\,\alpha\,\mathrm{d}x = \exp\left(-\frac{x}{\lambda}\right)\,\frac{\mathrm{d}x}{\lambda} \quad (5.31)$$

This type of analysis occurs in many different branches of the physical sciences – for example, exactly the same analysis applies to the decay of radioactive isotopes.

Example: *Check that the probability distribution of free paths is correctly normalised,* $\int_0^\infty f(x)\,\mathrm{d}x = 1$.

$$\int_0^\infty f(x)\,\mathrm{d}x = \int_0^\infty \exp\left(-\frac{x}{\lambda}\right)\,\frac{\mathrm{d}x}{\lambda}$$
$$= \int_0^\infty \exp(-y)\,\mathrm{d}y = 1.$$

Integrating by parts

$$\begin{aligned}\lambda &= \int_0^\infty \alpha x\,\mathrm{e}^{-\alpha x}\,\mathrm{d}x,\\ &= \left[\frac{\alpha x\,\mathrm{e}^{-\alpha x}}{-\alpha}\right]_0^\infty - \int_0^\infty \frac{\alpha\,\mathrm{e}^{-\alpha x}}{-\alpha}\,\mathrm{d}x,\\ &= [0-0] + \int_0^\infty \mathrm{e}^{-\alpha x}\,\mathrm{d}x,\\ &= -\left[\frac{\mathrm{e}^{-\alpha x}}{\alpha}\right]_0^\infty = -\left[0 - \frac{1}{\alpha}\right],\\ &= \frac{1}{\alpha}.\end{aligned}$$

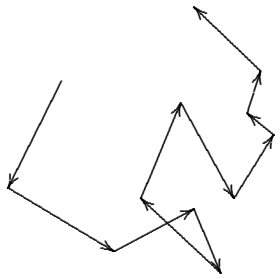
5.8 Random Walks

Let us now work out what happens when particles diffuse through a gas under the influence of collisions between particles. There are two key features of this process.

- There is a *distribution* of free paths between collisions, given by (5.31) and so sometimes there is only a short time between collisions, and sometimes a long time.

- When a collision occurs the velocity vector of the particle changes. As demonstrated by our similation in Chapter 3, it is a very good approximation that the particles lose all memory of their initial directions of motion after one or two collisions. In other words, we can assume that each particle's velocity vector is randomised following each collision. The sort of motion envisaged is illustrated in Figure 5.6.

Figure 5.6. A Random Walk



If we repeat the experiment of determining how far the particle moves away from the origin many, many times and take an average in the x, y and z directions, the average distance must be zero since the particles are just as likely to move in any direction with the same distribution of free paths between collisions. To put it another way, if we start lots of particles off at the origin and allow them to make random walks away from the centre, we would expect them all to drift away from the centre. Although the average displacement is zero, any individual particle will have moved away from the origin.

Let us determine this distance using vectors. We start from the origin and make a vector displacement $\boldsymbol{r}_1$. We then add another vector $\boldsymbol{r}_2$ to $\boldsymbol{r}_1$ so that the displacement from the origin is $\boldsymbol{r}_1 + \boldsymbol{r}_2$. Then we add another vector to $\boldsymbol{r}_3$ to $\boldsymbol{r}_1 + \boldsymbol{r}_2$ to produce a vector $\boldsymbol{r}_1 + \boldsymbol{r}_2 + \boldsymbol{r}_3$ and so on. We see that the total displacement from the origin is the vector sum

$$\boldsymbol{R} = \boldsymbol{r}_1 + \boldsymbol{r}_2 + \boldsymbol{r}_3 + \cdots = \sum_i \boldsymbol{r}_i \qquad (5.32)$$

Let us now work out the length of the vector $\boldsymbol{R}$. We recall that we take the scalar product of $\boldsymbol{R}$ with itself to find the square of its magnitude and so we

find

$$\begin{aligned}|\boldsymbol{R}|^2 &= (\boldsymbol{r}_1 + \boldsymbol{r}_2 + \boldsymbol{r}_3 + \dots) \cdot (\boldsymbol{r}_1 + \boldsymbol{r}_2 + \boldsymbol{r}_3 + \dots) \\ &= |\boldsymbol{r}_1|^2 + |\boldsymbol{r}_2|^2 + |\boldsymbol{r}_3|^2 + \dots \\ &\quad + 2\boldsymbol{r}_1 \cdot \boldsymbol{r}_2 + 2\boldsymbol{r}_1 \cdot \boldsymbol{r}_3 + 2\boldsymbol{r}_2 \cdot \boldsymbol{r}_3 + \dots\end{aligned} \tag{5.33}$$

The term $|\boldsymbol{r}_1|^2 + |\boldsymbol{r}_2|^2 + |\boldsymbol{r}_3|^2 + \dots$ is the sum of the magnitudes of all the individual vectors. The second line of (5.33) contains a very large number of scalar products of pairs of vectors pointing in random directions. Therefore, on average, there will be as many positive as negative scalar products. Furthermore, although the magnitudes of the vectors involved in the scalar products are different, they are all drawn from the same probability distribution (5.31) and therefore, on averaging over a very large number of random displacements, all the scalar products average to zero. We can therefore write

$$|\boldsymbol{R}|^2 = |\boldsymbol{r}_1|^2 + |\boldsymbol{r}_2|^2 + |\boldsymbol{r}_3|^2 + \dots = \sum_i |\boldsymbol{r}_i|^2 \tag{5.34}$$

In other words, the total displacement is the root mean square sum of all the individual displacements. We can write this as

$$|\boldsymbol{R}|^2 = N\overline{r^2} \text{ where } \overline{r^2} = \frac{1}{N}\sum_i |\boldsymbol{r}_i|^2 \tag{5.35}$$

In other words, if $l = (\overline{r^2})^{1/2}$ is the *root mean square displacement*,

$$l^2 = \frac{1}{N}\sum_i |\boldsymbol{r}_i|^2,$$

the typical distance from the origin moved by a particle after N encounters is

$$R = \sqrt{N}l. \tag{5.36}$$

We can show that $l \approx \lambda$, the mean free path. This is the characteristic behaviour found in diffusion processes.

Thus, in a random walk of N steps, the particle diffuses on average a distance $R \approx \sqrt{N}\,\lambda$ from the origin. Let us work out the time dependence of

Relation of l and λ

$$\begin{aligned}l^2 &= \int_0^\infty x^2\, p(x)\,\mathrm{d}x \\ &= \int_0^\infty x^2 \mathrm{e}^{-x/\lambda}\,\mathrm{d}(x/\lambda), \\ &= \lambda^2 \int_0^\infty y^2 \mathrm{e}^{-y}\,\mathrm{d}y,\end{aligned}$$

Now, integrate by parts:

$$= -\lambda^2 \left[y^2\,\mathrm{e}^{-y}\right]_0^\infty + 2\lambda^2 \int_0^\infty y\,\mathrm{e}^{-y}\,\mathrm{d}y,$$

$$l^2 = 2\lambda^2.$$

this diffusion process. We assume that the particles travel with the mean speed $\overline{v}$ between collisions. Therefore, the time to make N collisions is $t = N\lambda/\overline{v}$. Substituting into the above expression for R, we find,

$$R = \sqrt{N}\,\lambda = (\overline{v}t\lambda)^{1/2} \tag{5.37}$$

Thus,

- the distance from the origin increases only as the square root of time;
- the distance depends upon the square root of the average speed. We have shown that, in equilibrium, each particle has the same kinetic energy $\frac{1}{2}mv^2$ and so in this case the distance would be proportional to $m^{-1/4}$. This is a weak dependence, but it proved to be enough to separate the isotopes of radioactive species, if no other process was available. This was the original process by which the fissile isotope uranium-235 was separated from uranium 238. These gaseous diffusion plants were very expensive, requiring huge factories and vast amounts of power.

5.9 Brownian Motion

Let us demonstrate experimentally that these processes actually take place at the microscopic level.

The phenomenon of *Brownian motion* played a key role in the revolution in physics which took place in the first decade of the 20th century. If tiny specks of dust are observed in a liquid such as water, they are observed to move about randomly. In 1905, Einstein showed that this motion is due to random collisions of the molecules of the fluid with the dust particle. Their motions mimic exactly processes happening at the microscopic level and indeed the specks of dust are in thermal equilibrium with the molecules of the fluid.

Einstein's paper is a beautiful analysis of the statistics of the random motion of the particles. He

showed that, in a time interval t, the mean-square displacement of a sphere of radius a is

$$\langle x^2 \rangle = \frac{kTt}{3\pi\eta a} \tag{5.38}$$

where η is the viscosity of the fluid and T the temperature. The key experiments was carried out in 1908 by Jean Perrin. We can repeat his experiment using microspheres, which are identical polythene spheres, all 1 micron in diameter. We can observe random movement of the microspheres and, if we wish, use the typical distance travelled to determine Boltzmann's constant. The experimental arrangement is shown in Figure 5.7. The motion of the microspheres is observed with a CCD camera.

An example of the data from such an experiment using microspheres at room temperature is shown in Table 5.4. This experiment was of great importance because it provided direct evidence for the reality of atoms and molecules. Once Boltzmann's constant $k = 1.38 \times 10^{-23}$ J K^{-1} was determined, it was possible to work out the number of atoms in a mole of gas, knowing the value of the gas constant $R = N_A k$. This was one of the earliest accurate determinations of N_A and was used by Einstein in his other great papers of 1905.

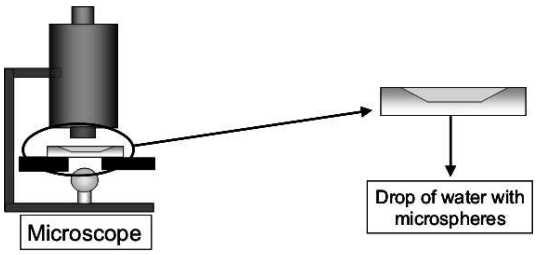


Figure 5.7. Perrin's observation of Brownian motion.

Table 5.4. Determination of Boltzmann's constant	
Temperature	293 K
Time interval	$t = 5$ seconds
Radius of microsphere	$a = 0.545\,\mu$m
Viscosity of water	$\eta = 10^{-3}$ kg m^{-1} s^{-1}
Mean square displacement	5.1 μm^2
Boltzmann's constant	1.8×10^{-23} J K^{-1}.