CHAPTER 4

Gases: background theory

4.1 Introduction

In this chapter, we will develop one of the earliest and most successful theories of matter: the so-called ideal gas theory. This theory envisages a gas as being a collection of molecules whose average *kinetic energy* is so large that the *potential energy* of interaction between the molecules is unable to hold them together. This model will probably be familiar, but just in case it is not, Figure 4.1 shows how one imagines the motion of the molecules in a gas.
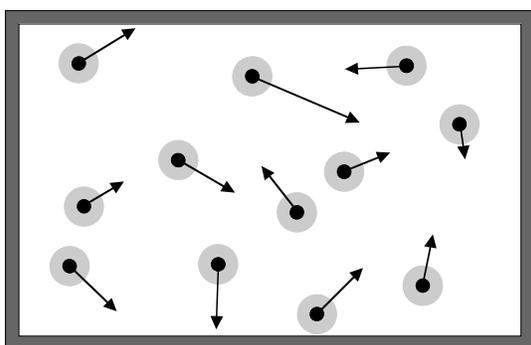

Figure 4.1. A schematic illustration of the motion of molecules in a gas. The molecules are shown as a central darkly-shaded region, where the electron charge density is high, and a peripheral lightly-shaded region. Although there is no electronic charge in this peripheral region, the electric field there will significantly affect the motion of any other molecules that enter that region. Notice that on average, the distance between the molecules is large compared with the extent of their region of influence. The arrows indicate the velocities of the molecules. Notice that the velocities are randomly oriented and that the length of the velocity vectors is varied, indicating that the molecules have a wide range of speeds.

Ideal gas theory tells us some amazing things are happening in the air around us. It predicts that the average speed of the molecules is around 500 m s^{-1} and that molecules collide with every square centimetre of the skin on your body roughly 10^{23} times every second. It also predicts that separation between the molecules is around 3.5 nm compared with the typical separation between molecules in their solid state of around 0.3 nm. As we shall see in Chapter 5, we have every reason to believe these predictions because quantitative explanations of the properties of gases based on the ideal gas model are extraordinarily successful.

§4.2   **The ideal gas model:** Here we outline the basic assumptions of the ideal gas theory. Importantly these assumptions are approximately true for almost every real gas that we will encounter! Then we derive from first principles an equation that relates the density of an ideal gas to its temperature and pressure

§4.3   **Calculating microscopic quantities:** In this section we look at some results which allow us to calculate some microscopic properties of gas.

§4.4   **Beyond the ideal gas equation:** Finally we look at how we can extend the ideal gas theory in order to take account of a more realistic set of assumptions than those we made in §4.2.

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In addition to copies of the figures and tables, you will find animations of several of the important equations in this chapter and a computer program which realistically simulates the dynamics of simple molecules in gases, liquids and solids.

4.2 The ideal gas model

4.2.1 Assumptions

The simplest model of a real gas is known as the ideal or perfect model of a gas. It consists of a list of real properties of molecules that are systematically ignored! The justification for this is that the model is relatively simple and yet has wide range of applicability. It predicts an astoundingly simple expression for the macroscopic properties of any gas, independent of the type of molecules that make up the gas. This universal relationship is summarised in the so-called *ideal gas equation*:

$$PV = zRT \qquad (4.1)$$

where:

P is the pressure of the gas (Pa)
V is the volume of the gas (m^3)
z is the number of moles of the gas under consideration (mol).
T is the absolute temperature (K)
R is the molar gas constant (J K^{-1} mol^{-1})

What we assume :	What we neglect :
The molecules behave as perfect point masses, i.e. they have zero volume.	The molecules have a small, but finite, volume.
The molecules do not interact with each other except instantaneously as they collide.	The molecules of gases do interact with each other.
The collisions between molecules are elastic.	Not much: this is a very good assumption. The only time it is not appropriate is when we discuss electrical conduction through a gas.

These will be our initial assumptions. As we proceed through Chapters 4 and 5 we will see that these assumptions are sufficient to understand many properties of gases. However, we will on occasion need to go beyond some of these basic assumptions.

4.2.2 Derivation of the ideal gas equation

To derive this equation we need to make two connections between microscopic properties of the molecules and the macroscopic properties of the gas.

- First, we will identify the pressure (force per unit area) of a gas against the walls of its container with the average effect of the very large number of collisions of the molecules of the gas with the wall.
- Second, we will identify the temperature of the gas as being proportional to the average energy of molecules in the gas. (We will define this relationship more precisely in the following sections.)

In order to do this, we will first establish a relationship between the *average momentum* and the *average energy* of a gas molecule. Then, because of the identifications above, we will be able to establish a relationship between the pressure of the gas and its temperature.

Step 1: An average molecule, S

We consider z moles of a substance, i.e. zN_A molecules of just one type, each with mass m. We assume that in the gaseous state molecular collisions are relatively infrequent, and that most of a molecule's time is spent 'cruising' between collisions.

Consider a particular molecule, S, representative of all the molecules in the box. S has mass m and velocity $\mathbf{v}$, and thus has momentum $\mathbf{p} = m\mathbf{v}$. S's kinetic energy is given by $KE_S = \frac{1}{2}m\mathbf{v}^2$, and if we express this in terms of the individual components of its velocity v_x, v_y and v_z we find:
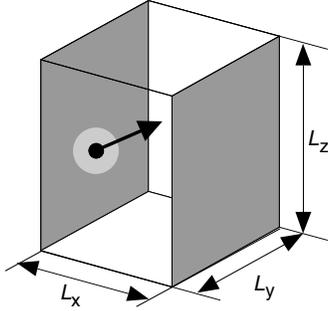
$$KE_S = \tfrac{1}{2}m\mathbf{v} \cdot \mathbf{v}$$
$$KE_S = \tfrac{1}{2}m(v_x, v_y, v_z) \cdot (v_x, v_y, v_z) \qquad (4.2)$$

$$KE_S = \tfrac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \qquad (4.3)$$

Step 2: Hitting the wall of the box

We first of all imagine a limiting case of a low density gas with just one molecule, S, bouncing

Figure 4.2 The molecule S is alone in a box travelling with a kinetic energy which is the same as the *average* kinetic energy of all the molecules that will eventually inhabit the box.

around inside a box of sides L_x, L_y and L_z and volume V (Figure 4.2). The speed of S is chosen such that its kinetic energy KE_S is the same as the average kinetic energy of the molecules with which we will eventually populate the box.

An elastic collision with the wall imparts momentum to the wall. Figure 4.3 (a) and (b) show a molecule before and after such a collision. The *x*-component of the velocity of S causes it to bounce backwards and forwards between the two walls that have been shaded. The *y*- and *z*- components cause it to bounce between the other walls. When it hits a wall it imparts some momentum to the wall. When it leaves the wall and re-enters the interior of the box the wall imparts momentum to it, and so it is subject to a reaction force. Although these forces are tiny, we will eventually populate the box with sufficiently large numbers of molecules so as to make the sum of these forces appreciable.

Figure 4.3 An elastic collision with the wall imparts momentum to the wall. (a) and (b) show a molecule before and after such a collision.

(a)   **(b)**
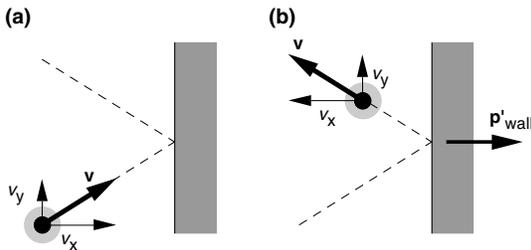
ciable. We will add up the forces that S produces as she bounces around.

Imagine that S's collisions with the walls are simple elastic collisions. If they are, then we are considering an event similar to the one depicted in Figure 4.3. More realistic assumptions concerning the interactions between the gas molecules and the molecules of the walls of the box are considered under *Complication 1* below.

If momentum is conserved, we can analyse the situation by equating momentum before and after the collision. We must consider the momentum both of the wall and the molecule.

Momentum before collision:

$$m\mathbf{v} + \mathbf{p}_{\text{wall}} \qquad (4.4)$$

Momentum after collision:

$$m\mathbf{v}' + \mathbf{p}'_{\text{wall}} \qquad (4.5)$$

Equating momentum before and after the collision, we have:

$$m\mathbf{v} + \mathbf{p}_{\text{wall}} = m\mathbf{v}' + \mathbf{p}'_{\text{wall}} \qquad (4.6)$$

Noting that the initial momentum of the wall is zero ($\mathbf{p}_{\text{wall}} = 0$), we have

$$\mathbf{p}'_{\text{wall}} = m\mathbf{v} - m\mathbf{v}' \qquad (4.7)$$

This means that the momentum imparted to the wall is just the difference between S's initial and final momentum. Imagining this to be an ideal collision, we assume v_y is unchanged by the collision and so there is no change in its *y*-component of momentum, and no force on the wall in the *y*-direction. However its *x*-component of velocity is exactly reversed. The momentum acquired by the wall is thus:

$$\mathbf{p}'_{\text{wall}} = mv_x\hat{\mathbf{x}} - mv'_x\hat{\mathbf{x}} \qquad (4.8)$$

$$\mathbf{p}'_{\text{wall}} = mv_x\hat{\mathbf{x}} - m(-v_x)\hat{\mathbf{x}}$$
$$= 2mv_x\hat{\mathbf{x}} \qquad (4.9)$$
$$= \Delta p_x\hat{\mathbf{x}}$$

So the momentum imparted to the wall is twice

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S's initial momentum. Not surprisingly this momentum transfer will be maximised if S is travelling quickly and has a large mass.

Step 3: Bouncing around in the box
After a collision, S will head off into the box, bounce off the other wall, and eventually return to the same wall for another collision. Notice that in the analysis above, if S collides with the other walls of the box then the x-component of its velocity will be unaffected. Thus we may confine our attention to the one wall we considered in Step 1. How long does it take for S to return to the same wall? If it travels with velocity v_x then it will take L_x / v_x seconds to reach the opposite wall, and a further L_x / v_x seconds to return. It thus makes collisions such as that described in Step 1 every $\Delta t = 2L_x / v_x$ seconds. Thus the average rate at which S imparts momentum to the wall is approximated by:

$$\frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L_x / v_x} = \frac{mv_x^2}{L_x} \qquad (4.10)$$

The rate at which momentum is transferred to the wall is nothing more than the force on the wall (Newton's second law of motion):

$$F = \frac{\Delta p_x}{\Delta t} = \frac{mv_x^2}{L_x} \qquad (4.11)$$

Thus the force per unit area on the wall, i.e. the *pressure* due to S alone, is:

$$P = \frac{F}{Area} = \frac{mv_x^2 \big/ L_x}{L_y L_z} \qquad (4.12)$$
$$= \frac{mv_x^2}{L_x L_y L_z} = \frac{mv_x^2}{V}$$

Comparing this with the formula for S's kinetic energy (Equation 4.3), this is just twice the kinetic energy associated with the x-component of its motion, divided by the volume.

Step 4: Pressure and kinetic energy
Now S is not just any molecule: its speed is chosen such that its kinetic energy is the same as the *average* kinetic energy of the real molecules with
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which we will fill the box in Step 5. Neglecting the small gravitational energy term, there is no difference between the three directions in the box, and so we expect that S's average speed will be the same in each direction. Hence, the kinetic energy associated with motion in each of the three directions will be equal, i.e.

$$\tfrac{1}{2} mv_x^2 = \tfrac{1}{2} mv_y^2 = \tfrac{1}{2} mv_z^2 \qquad (4.13)$$

Notice that because S does not interact with the other molecules it only has kinetic energy; it has no potential energy. So in terms of its total kinetic energy KE_S we expect that the kinetic energy associated with S's motion in the x-direction will be just one third of its total kinetic energy, i.e.

$$\tfrac{1}{2} mv_x^2 = \tfrac{1}{3} KE_S \qquad (4.14)$$

Similar expressions will hold for the energy terms associated with motion in the y- and z-directions. Remembering S's role as an average molecule, we expect the average kinetic energy associated with a molecule moving in the x-direction will be just one third of the average of its total kinetic energy

Now returning to the expression (Equation 4.12) for the pressure that S exerts on the wall perpendicular to the x-direction:

$$P = \frac{mv_x^2}{V} \qquad (4.15)$$

We can rewrite this as:

$$P = 2\frac{\tfrac{1}{2} mv_x^2}{V} = 2\frac{\tfrac{1}{3} KE_S}{V} \qquad (4.16)$$

i.e.

$$P = \frac{2}{3}\frac{KE_S}{V} \qquad (4.17)$$

Or, in words: *the pressure due to a single molecule travelling with a velocity representative of the average kinetic energy of a large number of molecules is just two-thirds of the kinetic energy per unit volume, i.e. two-thirds of the kinetic energy density.*

Step 5: Filling the box

Suppose now the box contains not just one representative molecule, but z moles of ideal gas, i.e. zN_A molecules, where N_A is Avogadro's number. Now if there were two molecules, the pressure would be twice as great. So a first guess would be that if there were zN_A molecules, the pressure on the wall would simply be zN_A times larger:

$$P = zN_A \times \frac{2}{3}\frac{KE_S}{V} \qquad (4.18)$$

In *Complication 2* below, we consider to what extent it is really true that the pressure on the wall will simply be zN_A times larger. In Equation 4.18 we can already see the skeleton of the ideal gas equation emerging. To see this we can rearrange it and compare it with our 'target' equation:

$$PV = zN_A \times \frac{2}{3} KE_S$$
$$PV = zRT \qquad (4.19)$$

Comparing these two equations, we see we need to establish a relationship between the temperature and the average kinetic of a molecule in the gas.

Step 6: Temperature

We now come to a microscopic definition of that familiar macroscopic property, temperature. Temperature is defined as being a quantity proportional to the average energy per degree of freedom (see *Complication 3* for more details).

$$T \propto \frac{\text{Average energy per}}{\text{degree of freedom}} \qquad (4.20)$$

For historical reasons, this relationship is usually written the other way around, and a slightly confusing factor of $\frac{1}{2}$ introduced:

$$\frac{\text{Average energy per}}{\text{degree of freedom}} = \frac{1}{2}k_B T \qquad (4.21)$$

The constant of proportionality is called the *Boltzmann constant* $k_B = 1.38 \times 10^{-23}$ J K^{-1}. Now S has 3 degrees of freedom and so we can now relate the temperature of a gas to the average kinetic energy of its molecules:

$$\tfrac{1}{3} KE_S = \tfrac{1}{2}k_B T \qquad (4.22)$$

In other words, the temperature of the gas is defined in terms of the average kinetic energy per degree of freedom of a gas molecule. If scientific understanding of matter had developed along different lines, it is quite possible that we might not today have a separate unit for temperature, but would measure it directly in joules!

Step 7: The ideal gas equation

Inserting the definition of temperature (Equation 4.22) into the expression for pressure (Equation 4.18), we can eliminate reference to KE_S. We begin with:

$$P = zN_A \times \frac{2}{3}\frac{KE_S}{V} \qquad (4.23)$$

and substitute:

$$KE_S = \tfrac{3}{2}k_B T \qquad (4.24)$$

and hence arrive at:

$$P = zN_A \times \frac{2}{3}\frac{\left[\tfrac{3}{2}k_B T\right]}{V} \qquad (4.25)$$

After cancelling terms and rearranging the equation we find:

$$PV = z\left[N_A k_B\right]T \qquad (4.26)$$

The product of the Boltzmann constant and the Avogadro number is known as the *molar gas constant*, R, which has the value:

$$R = \left[6.023 \times 10^{23} \text{ mol}^{-1}\right]\left[1.38 \times 10^{-23} \text{ J K}^{-1}\right]$$
$$= 8.314 \quad \text{J K}^{-1}\text{ mol}^{-1} \qquad (4.27)$$

We have thus arrived at:

$$PV = zRT \qquad (4.28)$$

This is a predicted relationship between the pressure P, temperature T, and volume V, of z moles of ideal gas material. It is an example of what is called an *equation of state* for a substance: it links the properties that define the state of the substance. We will see that many real gases agree closely with the predictions for an ideal gas.

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Example 4.1

Let's make a rough check of $PV = zRT$ on the nearest gas we have to hand: air. Air is a mixture of $\approx 78.1\%$ N2, 20.1% O_2, 0.9% Ar, 0.03% CO_2 and a variable fraction of typically 0.5% H_2O. *Kaye and Laby* give the measured value of the density of air at 20 °C and 101.3 kPa (typical values) as 1.199 kg m^{-3}. What value does the perfect gas equation (Eq. 4.29) predict?

Rearranging $PV = zRT$, we write the number of moles per unit volume, the molar density z/V, as:

$$\frac{z}{V} = \frac{P}{RT}$$

If the *molar density* of air is z/V, then the *mass density* is Mz/V, where M is molar mass in kilograms. Thus according to perfect gas theory the density of air should be close to:

$$\rho = \frac{Mz}{V} = \frac{MP}{RT}$$

Let us evaluate this formula. If we ignore the minor constituents of air and treat it as a gas with an effective molecular weight given by the average of nitrogen (28), oxygen (16), and argon (40), we have the average molecular weight of air is:

$$M = (78.1\% \text{ of } 28) + (20.1\% \text{ of } 16) + (0.9\% \text{ of } 40)$$
$$= (0.781 \times 28) + (0.201 \times 16) + (0.009 \times 40)$$
$$= 28.66$$

and so the molar mass is $M = 28.66 \times 10^{-3}$ kg. Substituting $T = 293.15$ K, $P = 101.3$ kPa, and $R = 8.314$ JK^{-1} mol^{-1}, we find:

$$\rho = 1.191 \text{ kg m}^{-3}$$

Comparing the theoretical value with the experimental value of 1.199 kg m^{-3}, we can see that the perfect gas equation has predicted the density of air – a complex gas – with an accuracy of around 0.7%. If we had taken account of water vapour, our answer would be even closer to the experimental value. Impressive.

Example 4.2

Use the ideal gas equation to derive an expression for the number density of molecules in a gas and estimate the number density of molecules in a gas at *STP*.

There are a number ways to rearrange the ideal gas equation $PV = zRT$ to make it even more useful. First of all, we start by rearranging this equation for the molar density:

$$\frac{z}{V} = \frac{P}{RT} \text{ mol}^{-1} \text{ m}^{-3}$$

This tells us the number of moles of gas per cubic metre in terms of the pressure and temperature of the gas. Each mole of gas contains the Avogadro number of molecules, so we can write the number density as:

$$n = N_A \frac{z}{V}$$
$$= N_A \frac{P}{RT}$$

As we saw just before Equation 4.29, the molar gas constant is the product $R = N_A k_B$ where k_B is the Boltzmann constant. So we can divide through by N_A to give:

$$n = N_A \frac{P}{[N_A k_B]T}$$
$$= \frac{P}{k_B T}$$

At STP this evaluates to:

$$n = \frac{P}{k_B T} = \frac{1.013 \times 10^5}{1.38 \times 10^{-23} \times 273.15}$$
$$= 2.69 \times 10^{25} \text{ molecules m}^{-3}$$

In some older texts, this number is sometimes referred to as the *Loschmidt number*, being named for the scientist who first estimated this quantity in 1865.

If you skip to Chapter 5, in which the theory is compared with experimental data, you will see that the model can account for many properties of gases with a typical accuracy of around 1%. However, in order to understand some of the experimental results discussed in Chapter 5 it will be necessary to read through §4.3 on *Calculating microscopic quantities*. Alternatively you can read through the *Complications and reservations* section below to find out about the limits of the simplifications and assumptions we have made in our seven-step derivation of $PV = zRT$.

Complications and reservations

Complication 1: Hitting the wall – what really happens?

The collision of a molecule with a wall is really quite a complex process. However, we will see that in terms of the exchange of momentum with the wall, the results of a more sophisticated analysis are identical with those arrived at in Step 1.

The real story is illustrated in Figure 4.4 and goes something like this. Molecules hit the wall, interact electrically with the atoms of the wall and then, in general, stick to wall. While they are on the wall, they can either stay vibrating about some attractive point on the wall, or move around on the surface. Then, typically after a nanosecond or so, they leave the wall and return to the gas. A nanosecond may seem rather short time to you, but in a nanosecond, a typical atom will vibrate around 10,000 times and so a great deal can happen. How can this complex process be approximated by the simple 'bouncing' model outlined in Step 1? The reasoning is as follows:

- Since molecules hit the wall from random directions and leave in random directions then on average there is no net momentum transfer parallel to the plane of the wall. This validates our assumption that on average the y-component of S's momentum is unaffected by the collision process.
- If we look at the initial and final situations, without asking about the details of the reflection process, then we find that the two processes are rather similar. In each case the molecule is first approaching the wall, and

Example 4.3

Suppose we have 1.3 moles of helium gas in a container of volume 1 litre at a temperature of 20 °C. (a) What is the pressure of the gas? (b) If the temperature is changed to 100 °C, but the gas is contained in the same volume, what is the pressure?

(a) Use $PV = zRT$ and substitute:

$V = 1$ litre

$\quad = 10^{-3}$ m^{-3}

$z = 1.3$ mol

$R = 8.31$ J^{-1}K^{-1}mol

$T = 20$ °C

$\quad = 273.15 + 20 \ = 293.15$ K

To find:

$$P = \frac{zRT}{V} = \frac{1.3 \times 8.314 \times 293.15}{10^{-3}}$$

$$= 3.168 \times 10^6 \text{ Pa}$$

or approximately 31 times atmospheric pressure.

(b) Use $PV = zRT$ and substitute:

$V = 1$ litre

$\quad = 10^{-3}$ m^{-3}

$z = 1.3$ mol

$R = 8.31$ J^{-1}K^{-1}mol

$T = 100$ °C

$\quad = 273.15 + 100 \ = 373.15$ K

To find:

$$P = \frac{zRT}{V} = \frac{1.3 \times 8.314 \times 373.15}{10^{-3}}$$

$$= 4.033 \times 10^6 \text{ Pa}$$

or approximately 40 times atmospheric pressure.

(a) (b) (c)

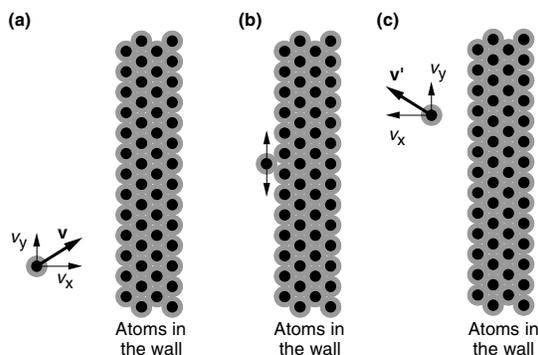Atoms in the wall — Atoms in the wall — Atoms in the wall

Figure 4.4. When a molecule hits a wall, what really happens is that it sticks to the wall for a short while (typically 10^{-12} s), and eventually leaves the wall and rejoins the gas with no 'memory' of the trajectory with which it hit the wall. It sticks to the wall because the wall is made of molecules with which it will have some kind of interaction. The figure shows (a) the approach to the wall, (b) the adsorption on the wall and (c) the escape from the wall. On each molecule, the area shaded grey indicates the region in which the molecule interacts strongly with neighbouring molecules.

then leaving the wall, with a velocity component v_x characteristic of the temperature of the gas and wall. Thus the average momentum transfer is the same in both cases. Thus the *x*-component of momentum imparted to the wall is unaffected by the detailed nature of the collision process.

The fact that S has spent some time on the wall instead of travelling through the box means the average time between its collisions with the wall will be slightly greater than we assumed in Equation 4.10. This will tend to reduce the pressure of a real gas as compared to an ideal gas.

Note that the argument above is only valid when both the walls and the gas are at the same temperature. If this is not so, then S will return to the gas with kinetic energy appropriate to the temperature of the wall and not the temperature of the gas. This is the mechanism by which a gas can be cooled or warmed by contact with a hotter or colder solid surface.

Complication 2: Collisions with other molecules.

While S may be able to bounce around happily from side to side of the container when it is in the box alone, it will not be free to do so when the box is filled with other molecules. Does the analysis break down if S cannot bounce back and hit the wall again after $2L_x / v_x$ seconds? No. However the reason it doesn't is quite subtle.

What happens is that although S does not travel from side to side in the box, the *momentum* that it

Figure 4.5 When there is more than one molecule in the box, a 'representative' molecule can no longer travel freely across the box and bounce from side to side in a time $2L_x/v_x$

Atoms in
the wall
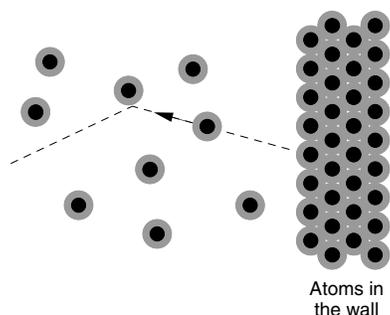
carries does (Figure 4.5). In each collision with another molecule the momentum is conserved, and so the momentum does bounce from side to side of the container. In addition to this there are many other molecules whose momentum is being 'bounced' across the box. In practice this makes calculations rather complicated, but in the end it amounts to exactly the same thing as our simple assumption in Step 1.

Complication 3: Degrees of freedom.

The idea of a degree of freedom is important in statistical mechanics and has already been mentioned in this chapter and in Chapter 2. There are three questions we need to ask in this context:
- What is a degree of freedom?
- What is an *accessible* degree of freedom?
- How is the energy distributed amongst accessible degrees of freedom?

1. What is a degree of freedom?

Colloquially, a *degree of freedom* of a molecule is a 'thing it can do' or a 'way it can possess energy'. Technically this corresponds to an independent 'squared term' in the expression for the energy of a molecule.
- For example, an atom in a gas can move in three dimensions and has kinetic energy associated with each of those possibilities. So it has at least three degrees of freedom:

$$KE = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2 \qquad (4.29)$$

- The same atom in a solid has more possibilities open to it. As it jiggles around it can possess kinetic energy in the same way as a molecule in a gas can, but it also has potential energy. This is stored in the deformation of its 'bonds' with its neighbours as it vibrates. For small displacements from its equilibrium position x_o, y_o, z_o, the potential energy can be written as:

$$PE = \tfrac{1}{2}K_x(x-x_o)^2 + \tfrac{1}{2}K_y(y-y_o)^2 \\ + \tfrac{1}{2}K_z(z-z_o)^2 \qquad (4.30)$$

where K_x, K_y, K_z are the spring constants describing the variation of potential energy with position.

These are the three independent squared terms in Equation 4.28, which correspond to an additional three degrees of freedom.

- A diatomic molecule in a gas has three degrees of freedom associated with its kinetic energy, but may also have kinetic energy of vibration and rotation, and potential energy of vibration, and so has more degrees of freedom than an atom by itself. As a rule of thumb, the more atoms making up a molecule in a gas, then the greater will be the number of degrees of freedom.

2. What is an accessible degree of freedom?

The term *degrees of freedom* refers to things that a molecule *can* do, not to whether it is doing them. Due to the importance of the quantum nature of matter on small scales, some processes cannot take place because an energy gap ΔE separates quantum states in which the process does not occur, from quantum states in which it does occur. If the average energy available to a particular molecule is much less than the energy gap ΔE, then the process will only take place occasionally when (rare) local fluctuations cause the particular molecule's energy to exceed the energy gap.

The average energy per degree of freedom available to a molecule in an environment at temperature T is by definition of Equation 4.22, $\frac{1}{2}k_BT$. If this energy is much less than the energy gap then the process will not take place and the degree of freedom associated with that process is said to be inaccessible. If the temperature increases so that $\frac{1}{2}k_BT$ is much greater than the energy gap, then the process becomes accessible.

The idea of accessibility will be extremely important when we try to understand the heat capacity of gases in §5.3. Indeed, historically the inability of classical theories to explain something as apparently simple as the heat capacity of gases was (according to Lord Kelvin) one of the two outstanding problems remaining for physicists at the end of the nineteenth century.

3. How is the energy distributed amongst accessible degrees of freedom?

It is a fundamental assumption of statistical mechanics that, on average, energy is stored equally in all accessible degrees of freedom. This is a sound assumption, but one which is extremely important.

Consider the example of a molecule which has just the three degrees of freedom of translational motion. It is perhaps not surprising that on average, the kinetic energy associated with each degree of freedom will be equal. The *principle of equipartition of energy* allows us to go one step further by stating that *on average*, the kinetic energy associated with each degree of freedom will *definitely* be equal.

Consider now a molecule with extra accessible degrees of freedom associated, for example, with internal vibration. It is not at all obvious that on average, the energy associated with each translational degree of freedom will be equal to the energy associated with each vibrational degree of freedom. The principle of equipartition of energy allows us to state that *on average*, the energy associated with each accessible degree of freedom will be equal, independent of the type of motion each accessible degree of freedom corresponds to.

What the principle implicitly assumes is that there exists some mechanism for coupling one degree of freedom with another. A molecule travelling through space which never collided or interacted with another molecule would not exchange energy between its degrees of freedom: if it was not vibrating initially it would not spontaneously slow down and start vibrating. However, if it interacts with other molecules then it can exchange energy between its own degrees of freedom and other degrees of freedom on other molecules. We rely on the randomising effect of these interactions to ensure that energy is on average equally distributed amongst all the accessible degrees of freedom. Thus during a collision a molecule which was not vibrating could start vibrating at the expense of energy in another accessible degree of freedom.

Finally we consider degrees of freedom associated with different molecules. Again, collisions or interactions of some kind are an essential assumption of the principle of equipartition of energy. Molecular collisions act to share out energy

equally between different accessible degrees of freedom. If one degree of freedom of a molecule has much more than the average energy associated with a degree of freedom ($\frac{1}{2}k_BT$), then in inter-actions with other molecules, the energy associated with that degree of freedom will tend to be lost to other degrees of freedom which have less than the average energy per degree of freedom.

4.3 Calculating microscopic quantities

To understand some properties of gases we need go no further than the ideal gas theory outlined above. However, in order to understand, for example, the thermal conductivity of gases, we need to develop the theory still further. This development is generally referred to as the *kinetic theory* of an ideal gas. However, we need to go beyond some of the assumptions of the ideal gas model. In particular we need to find out about:

- the size of a gas molecule
- the root mean square speed of a gas molecule
- the mean speed of a gas molecule
- the mean free path of a gas molecule,

These quantities are important for understanding the behaviour of gases. However, unlike P, V and T, the quantities are not directly measurable in a straightforward way.

4.3.1 The size of a gas molecule

In the discussion of the complications of our deri-vation of the ideal gas equation we mentioned the idea of molecular collisions as being important in establishing the averaging of energy amongst de-grees of freedom of the gas molecules. It is clear that molecules must have a finite size in order to collide. However, it is not clear what we mean by 'size' exactly, and how do we represent the 'size' of a molecule which may have a complex shape?

There are many definitions of the 'size' of atoms, slightly differing from one another. In general they refer to a radius within which (say) 90% of the electric charge distribution is found. For mole-cules which are non-spherical, we could specify complex shapes to describe the same criteria. In this chapter however we shall use the idea of an 'effective' cross-sectional area of a molecule. We will specify an 'effective diameter' a such that the chance of collision with a spherical molecule of diameter a is the same as that of colliding with the

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molecule in question. We note that it is possible for a to change with temperature. For example, rotational degrees of freedom may be made acces-sible at high temperatures, which might tend to increase its effective cross-sectional area. Alterna-tively, the average speed of molecules may be-come so high that the region of electrical interac-tion around a molecule no longer affects the tra-jectory of nearby molecules. This would have the effect of reducing the effective cross-sectional area.

4.3.2 The distribution of molecular speeds

Clearly not all molecules in a gas move at the same speed. Even if by some clever contrivance we arranged that all the molecules did have the same speed at some time, things would not stay that way for long. Collisions between the mole-cules would cause one molecule to speed up and another to slow down. It might seem that it would be impossible to say anything about the range of molecular speeds present in a gas. Surprisingly, we can in fact say rather a lot, but only if the gas is in equilibrium at a temperature T. If this is the case, then using an analysis outlined in Appendix A1, we can show that the probability that a mole-cule has a speed between v and $v + dv$ is given by the Maxwell speed distribution $P_M(v)$:

$$P_M(v)dv = \frac{4}{\sqrt{\pi}}\left[\frac{m}{2k_BT}\right]^{3/2} v^2 \exp\left[\frac{-\frac{1}{2}mv^2}{k_BT}\right]dv$$

$$(4.31)$$

The general form of the Maxwell speed distribu-tion curve is illustrated in Figure 4.6, and specific examples are shown in Figures 4.7 and 4.8. Given the Maxwell speed distribution function, one can define three distinct speeds, all similar in order of

magnitude and all characterising the speed distribution curve in slightly different ways. These speeds are:

The average speed	The root mean square speed	The most probable speed
$\bar{v}$	$v_{RMS} = \overline{\left(v^2\right)}^{1/2}$	v_{prob}

In general, either the average speed $\bar{v}$ or the root mean square speed v_{RMS} are the relevant averages. These two speeds differ by about 8%, $\bar{v} = 0.921 v_{RMS}$, and you should take care to the use right one. Special care needs to be taken in expressions in which the speed enters as a 'squared' term. We must distinguish between $\bar{v}^2$ and $\overline{v^2}$: the two are not the same! The most probable speed v_{prob} is the speed marking the peak of the speed distribution curve, but is of no special physical significance: you may now happily forget about it.

4.3.3 The number of molecules hitting unit area per second

There will be several occasions below, for example in considering the thermal conductivity of a gas, when it will prove useful to know how many molecules are crossing a unit area within the gas per second. We can get an estimate of this if we return to situation depicted in Figure 4.2 in our derivation of the ideal gas equation.

The molecule S is alone in a box travelling with a kinetic energy which is the same as the *average* kinetic energy of all the molecules that will eventually inhabit the box. We consider its collisions with the wall of area $A = L_x L_y$. S collides with this wall, bounces off into the box, bounces off the opposite face of the box, and eventually returns to the same wall for another collision. It takes S a time L_x / v_x seconds to reach the opposite wall, and a further L_x / v_x seconds to return: it thus makes collisions with the wall in question every $\Delta t = 2 L_x / v_x$ seconds. Thus the number of collisions with the wall per unit area per second is given by:

$$\begin{array}{l} \text{Number of collisions} \\ \text{per unit area} \\ \text{per second} \end{array} = \frac{1}{A\Delta t} \qquad (4.32)$$

Figure 4.6 The general form of the Maxwell speed distribution curve for a gas (Equation 4.31)
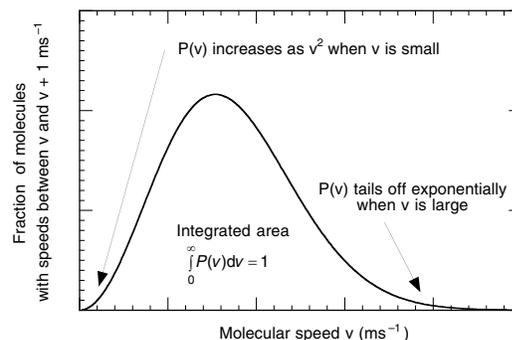
Figure 4.7 Three curves showing the Maxwell distribution of molecular speeds in nitrogen gas and hydrogen. The vertical axis is the probability $P(v)$ that a molecule has a speed between v and $v + 1$ ms^{-1}. Two of the curves show the distribution for nitrogen at temperatures of 100 K and 1000 K. Notice that the peak of the curves shifts to higher speeds at higher temperatures. The third curve is for hydrogen at 100 K. Notice that because of the low mass of hydrogen compared with nitrogen, the curve is similar to the curve for nitrogen at 1000 K.
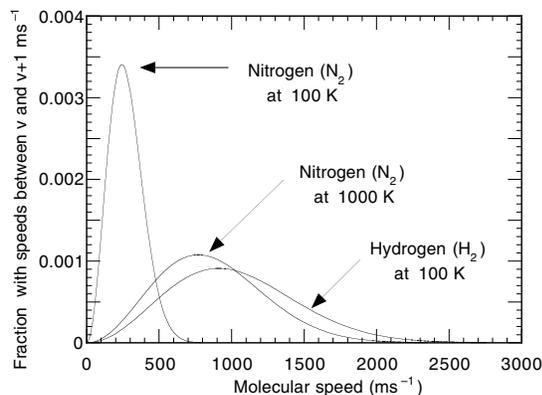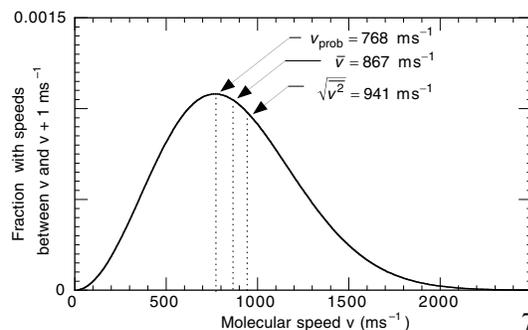

Figure 4.8 Illustration of the special speeds relevant to the Maxwell speed distribution curve. The curve shown refers to nitrogen molecules at a temperature of 1000 K (approximately 730 °C). Notice the three speeds shown are all near the peak of the curve, but differ significantly from each other.

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This can be simplified in several steps as follows:

$$\frac{1}{A\Delta t} = \frac{1}{A[2L_x / v_x]} = \frac{1}{L_y L_z [2L_x / v_x]}$$

$$= \frac{v_x}{2L_x L_y L_z} \qquad (4.33)$$

$$= \frac{v_x}{2V}$$

where I have used the fact that:

$$L_x L_y L_z = V \qquad (4.34)$$

If there are N molecules in the box with an x-velocity similar to that of S, then the number of collisions with the wall per unit area per second is given by:

$$\text{Number of collisions} \atop \text{per unit area} \atop \text{per second} \quad \begin{aligned} &= \frac{1}{2}\frac{Nv_x}{V} \\ &= \frac{1}{2}nv_x \end{aligned} \qquad (4.35)$$

where n is the number density of molecules. Next we notice that in this argument v_x was chosen such that the kinetic energy of S represented the average kinetic energy of the molecules in the box. Thus, in terms of the discussion of the distribution of molecular speeds in the previous section, we can write that:

$$KE_S = \frac{1}{2}m\overline{v^2} \qquad (4.36)$$

Now since:

$$\overline{v^2} = v_x^2 + v_y^2 + v_z^2 \qquad (4.37)$$

we see that $v_x^2 = \frac{1}{3}\overline{v^2}$ and so v_x in equation 4.35 is given by $v_x = \left(\frac{1}{3}\overline{v^2}\right)^{\frac{1}{2}}$. Substituting this value into Equation 4.35 yields our final expression for the number of collisions with the wall per unit area per second:

$$= \frac{1}{2}n\left(\frac{1}{3}\overline{v^2}\right)^{\frac{1}{2}} = \frac{1}{2\sqrt{3}}nv_{RMS} \qquad (4.38)$$

This remarkably simple expression is nearly, but

Example 4.4

What is the probability that a molecule of nitrogen in nitrogen gas at 1000 K has a speed between 750 ms^{-1} and 751 ms^{-1} ?

We need to evaluate Equation 4.32 to find $P_M(v)dv$ with $v = 750$ ms^{-1} and $dv = 1$ ms^{-1}.

$$P_M(v)dv = \frac{4}{\sqrt{\pi}}\left[\frac{m}{2k_B T}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-\frac{1}{2}mv^2}{k_B T}\right]dv$$

From Table 7.2 we find that the mass m of an individual molecule of N$_2$, is $2 \times 14u = 28u$ where $u = 1.661 \times 10^{-27}$ kg. Substituting this into Equation 4.32 along with $T = 1000$ K and remembering that the Boltzmann constant $k_B = 1.38 \times 10^{-23}$ J K^{-1} we arrive at:

$$P_M(750) = \frac{4}{\sqrt{\pi}}\left[\frac{28 \times 1.661 \times 10^{-27}}{2 \times 1.38 \times 10^{-23} \times 1000}\right]^{\frac{3}{2}}(750)^2$$

$$\times \exp\left[\frac{-\frac{1}{2} \times 28 \times 1.661 \times 10^{-27}(750)^2}{1.38 \times 10^{-23} \times 1000}\right]$$

$$= \frac{4}{\sqrt{\pi}}\left[1.685 \times 10^{-6}\right]^{\frac{3}{2}} \times 5.63500 \times \exp[-0.948]$$

$$= \frac{4}{\sqrt{\pi}}2.187 \times 10^{-9} \times 562500 \times \exp[-0.948]$$

And so:

$$P_M(750) = 1.076 \times 10^{-3}$$

This point is near the peak of the 1000 K curve for nitrogen in Figure 4.8.

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not quite, correct. It is an underestimate of the correct value because of our simplified assumption that all molecules move with the same speed. Using a considerably more complicated analysis it can be shown that:

$$\text{Number of collisions} \atop \text{per unit area} \atop \text{per second} \quad = \frac{1}{4}n\overline{v} \qquad (4.39)$$

an answer which exceeds our simple estimate by about 25%. Example 4.6 shows that the number of collisions with the wall per second is *extremely* large. This is important because it allows us to understand how the tiny forces of molecular collisions can add up to the substantial force exerted by a gas on the walls of its container.

Example 4.5

In nitrogen gas at 1000 K, what fraction of molecules have speeds greater than 867 ms^{-1}. You will definitely need to use the following result:

$$\int_{x=867}^{x=\infty} x^{\frac{1}{2}} \exp[-x]\mathrm{d}x = 0.4164$$

The required fraction is the integral of $P(v)\mathrm{d}v$ (Equation 4.32) over the required speed range, which in this case is from $v = 867$ ms^{-1} to $v = \infty$. This is the area under the high-speed end of the Maxwellian speed distribution curve:

$$fraction = \int_{v=867}^{v=\infty} P(v)\mathrm{d}v$$

$$= \int_{v=867}^{v=\infty} \frac{4}{\sqrt{\pi}} \left[\frac{m}{2k_BT}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-\frac{1}{2}mv^2}{k_BT}\right]\mathrm{d}v$$

Now to solve this kind of integral we need to transform into a standard form. To do this we substitute:

$$x = mv^2/2k_BT$$

We also need to find expressions for all the other terms involving v:

$$\frac{\mathrm{d}x}{\mathrm{d}v} = \frac{2mv}{2k_BT} \quad \Rightarrow \quad \mathrm{d}v = \mathrm{d}x\left[\frac{k_BT}{mv}\right]$$

Substituting we find:

$$fraction = \int_{v=867}^{v=\infty} \frac{4}{\sqrt{\pi}} \left[\frac{m}{2k_BT}\right]^{\frac{3}{2}} v^2 \exp\left[\underbrace{\frac{-\frac{1}{2}mv^2}{k_BT}}_{x}\right] \underbrace{\mathrm{d}v}_{\mathrm{d}x\left[\frac{k_BT}{mv}\right]}$$

$$= \int_{v=867}^{v=\infty} \frac{4}{\sqrt{\pi}} \left[\frac{m}{2k_BT}\right]^{\frac{3}{2}} \left[\frac{k_BT}{mv}\right] v^2 \exp[x]\mathrm{d}x$$

$$fraction = \int_{v=867}^{v=\infty} \frac{4}{\sqrt{\pi}} \left[\frac{m}{2k_BT}\right]^{\frac{3}{2}} \left[\frac{k_BT}{m}\right] \underbrace{v}_{\sqrt{\frac{2k_BT}{m}}x^{\frac{1}{2}}} \exp[x]\mathrm{d}x$$

The integral then becomes:

$$= \frac{4}{\sqrt{\pi}} \underbrace{\left[\frac{m}{2k_BT}\right]^{\frac{3}{2}} \left[\frac{k_BT}{m}\right]\sqrt{\frac{2k_BT}{m}}}_{=1} \int_{v=11200}^{v=\infty} x^{\frac{1}{2}} \exp[x]\mathrm{d}x$$

$$= \frac{4}{\sqrt{\pi}} \int_{v=867}^{v=\infty} x^{\frac{1}{2}} \exp[x]\mathrm{d}x$$

where the upper limit x_2 is infinity, and we will work out the value x_1 using $x = mv^2/2k_BT$. We have:

$$x_1 = \frac{28\times1.66\times10^{-27}\times(867)^2}{2\times1.38\times10^{-23}\times1000}$$

$$= 1.266$$

where we have used the fact that a nitrogen molecule has two atoms of nitrogen each of mass $14u$. Substituting for the lower limit of the integral:

$$fraction = 2\sqrt{\frac{1}{\pi}} \int_{x=1.266}^{x=\infty} x^{\frac{1}{2}} \exp[-x]\mathrm{d}x$$

We can now substitute for the standard integral given at the start of the question. Hence:

$$fraction = 2\sqrt{\frac{1}{\pi}} \times 0.4164 = 0.4695$$

Thus around 47% of molecules have speeds greater than 867 ms^{-1}. We can use this kind of analysis to solve problems, such as working out how many molecules of a given type have a speed greater than the escape velocity of the Earth. (Chapter 12: Exercises 4 and 5)

4.3.4 The mean free path of a gas molecule

Collisions between molecules play an important part in the transport of both heat and electricity through a gas. The distance molecules travel before colliding with other molecules is particularly important. On average, a slowly moving molecule travels a considerably shorter distance before colliding than a fast moving molecule. For this reason we define the *mean free path* of a gas molecule, λ_{mfp}, as the average distance a gas molecule travels before colliding with another molecule.

We can fairly easily estimate the average free path for molecules that either move much slower than, or much faster than, the mean speed of a gas molecule. To do this we will treat molecules as hard spheres, and ignore the region of electrical interaction sketched in grey around the molecules in Figures 4.4 and 4.5. We will consider the effect of these interactions briefly at the end of this chapter. Recall that if molecules are not spherical, then the diameter, *a*, represents an average dimension related to the average cross-sectional area that the molecule presents to other molecules.

Example 4.6

Some nitrogen gas is held at a temperature of 1000 K inside a cubical container of dimensions 10 cm ×10 cm ×10 cm at a pressure of one atmosphere. What is the number of collisions per second with each wall of the container?

We use the fact that the number of collisions per unit area per second is $\frac{1}{4}n\bar{v}$.

- The molecular density n can be estimated using the ideal gas equation from the *molar density z/V*.

$$\frac{z}{V} = \frac{P}{RT}$$

Multiplying both side by the Avogadro constant yields an expression for the molecular density.

$$n = \frac{zN_A}{V} = \frac{PN_A}{RT} = \frac{P}{k_B T}$$

where k_B is the Boltzmann constant.

- The mean speed $\bar{v}$ can be evaluated using the Maxwell speed distribution Equation 4.31. However, in this case we can cheat by taking the answer directly from Figure 4.8.

The area of each wall is $0.1 \times 0.1 = 10^{-2}$ m^2, so the number of collisions with each wall is given by:

$$= \frac{1}{4} \times n \times \bar{v} \times A$$

$$= \frac{1}{4}\left[\frac{1.0135 \times 10^5}{1.38 \times 10^{-23} \times 1000}\right] \times 867 \times 10^{-2}$$

$$= 1.6 \times 10^{25}$$

We find the answer is given by 1.6×10^{25} collisions per second. This is an immense number. For comparison, as this book is being prepared for publication in the year 2001, it exceeds by several orders of magnitude the number of clock cycles completed by *every* computer that has *ever* existed!

Average free path of molecules moving much faster than $\bar{v}$

Imagine taking a snapshot of the molecules of gas at some particular time t and concentrating our attention on a particularly fast-moving molecule, M. The situation might look like the one depicted in Figure 4.9.

On average, M travels a distance λ before colliding with another molecule. In the limit of M moving extremely quickly it will be as if the other

Figure 4.9 A method for making an approximation for the mean free path for fast-moving molecules. A molecule travels on average a distance λ before colliding with another molecule. If the other molecules are effectively stationary while M travels through the gas then there must on average be no other molecules whose centres lie within a volume $\pi a^2 \lambda$.
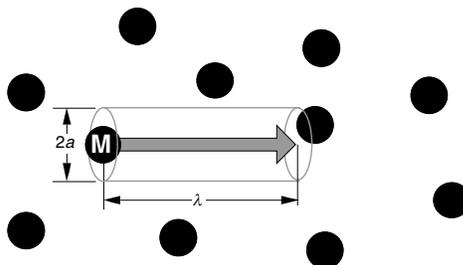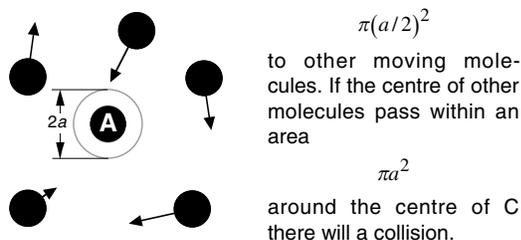

Figure 4.10 A method for making an approximation for the mean free path for slow moving molecules. A stationary molecule C presents a cross-sectional area

$$\pi(a/2)^2$$

to other moving molecules. If the centre of other molecules pass within an area

$$\pi a^2$$

around the centre of C there will a collision.

molecules did not move at all. In this case, there must on average be no other molecules whose centres lie within a cylinder of volume $\pi a^2 \lambda$ where a is the effective diameter of an atom. Since there is just one molecule (M) in a volume $\pi a^2 \lambda$, the number density of molecules n must be given by:

$$n = \frac{1}{\pi a^2 \lambda} \tag{4.40}$$

Rearranging this gives an expression for λ:

$$\lambda = \frac{1}{n\pi a^2} \tag{4.41}$$

This equation is an estimate for the average free path appropriate to fast-moving molecules. The effect of the motion of the other molecules (which

we have neglected entirely above) is difficult to account for quantitatively. However, it can be seen that in general other molecules will be likely to encroach on M's 'free space'. Thus Equation 4.41 represents an overestimate of the average free path appropriate to more typical molecules.

Average free path of molecules moving much slower than $\bar{v}$

Imagine taking a snapshot of the molecules of gas at some particular time t, and concentrate attention on a particularly slow-moving molecule, C. The situation might look like the one depicted in Figure 4.10.

If C were essentially stationary in comparison to the speeds of the other molecules then, as outlined in Figure 4.10, other molecules passing within an area πa^2 around the centre of C would collide. Considering a surface through C's centre we recall from §4.3.3 that the average number of molecules crossing unit area per second is $\frac{1}{4}n\bar{v}$. Thus the average number of molecules per second colliding with C from each of the two sides of the surface is given by:

$$= 2 \times \frac{1}{4}n\bar{v} \times \pi a^2 \qquad (4.42)$$

and so the average time between collisions is:

$$\Delta t = \frac{1}{2 \times \frac{1}{4}n\bar{v} \times \pi a^2} = \frac{2}{\bar{v}n\pi a^2} \qquad (4.43)$$

Now if C is not quite stationary, but moves with a speed v much less than the mean speed $\bar{v}$, then the average distance travelled by C before a collision, (the average free path) will be given by:

$$\lambda = v\Delta t$$
$$= \frac{2}{n\pi a^2}\left(\frac{v}{\bar{v}}\right) \qquad (4.44)$$

The mean free path of all molecules

We have calculated that for slow-moving molecules the average free path is given by Equation 4.44 which corresponds to a molecule being struck by other molecules at a constant average rate. Thus the faster it moves, the further it travels on

Figure 4.11 The variation of the mean free path λ of molecules as a function of the speed of the molecules expressed as fraction of the mean speed in units of $1/n\pi a^2$. The figure indicates the limiting behaviour of λ for low-speed molecules, high-speed molecules, and the average value for all molecules, λ_{mfp}. Also shown is a qualitative indication of the distribution of molecular speeds (Figures 4.6 , 4.7 & 4.8)
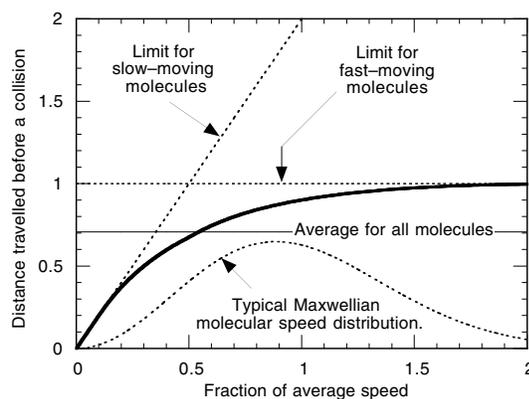
average between collisions. This increase of free path with speed cannot continue indefinitely: a molecule moving so fast that other molecules appear stationary cannot travel an indefinite distance before colliding. As shown above, the limiting average free path is:

$$\lambda = \frac{1}{n\pi a^2} \qquad (4.41)^*$$

Establishing these low and high speed limits has not been too difficult. However, finding the correct expression for the mean free path of all molecules, λ_{mfp}, is rather complex. We will however not be surprised to find (in common with Equations 4.41 and 4.45) that λ_{mfp} is proportional to $1/n\pi a^2$. It is perhaps rather surprising to find that the result of the complex calculation is simply that this factor is multiplied by $1/\sqrt{2} \approx 0.71$, to give:

$$\lambda_{mfp} = \frac{1}{\sqrt{2}n\pi a^2} \qquad (4.45)$$

The slow molecule, fast molecule, and average behaviours are summarised in Figure 4.11.

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Example 4.7

It would be interesting to estimate λ_{mfp} for some typical situations. But how can we estimate the number density of molecules n and the diameter of a molecule a?

First of all we use Example 4.2 to rewrite the perfect gas equation for z moles of gas, Eq. 4.28 $PV = zRT$, as:

$$n = \frac{P}{k_B T} = \frac{10^5}{1.38 \times 10^{-23} \times 293}$$

$$= 2.5 \times 10^{25} \quad \text{molecules m}^{-3}$$

Using a typical value of the spacing between atoms in a solid as an estimate for the molecular diameter $a \approx 0.3$nm, we have:

$$\lambda_{mfp} = \frac{1}{\sqrt{2} n \pi a^2}$$

$$= \frac{1}{\sqrt{2} \times 2.5 \times 10^{25} \times 3.1415 \times \left(0.3 \times 10^{-9}\right)^2}$$

$$\approx 10^{-7} \text{m} \quad \text{i.e. about 100 nm}$$

In the air around us there are approximately 2.5×10^{25} molecules per cubic metre. Thus, the average separation between molecules can be estimated:

$$average \ \ spacing \approx \frac{1}{\sqrt[3]{2.5 \times 10^{25}}}$$

$$\approx 3.4 \times 10^{-9} \quad \text{m}$$

$$\approx 3 \text{ nm}$$

So we find that:

- The average spacing between molecules (3 nm) is approximately 10 times the diameter of a molecule (0.3 nm).
- The molecules travel on average, about 100 nm before colliding with another molecule. This is about 300 times the diameter of a molecule, or 30 times the average separation between molecules.

Thus our initial assumptions (§4.2.1) about our model of a gas are at least consistent with the predictions of the ideal gas theory.

4.4 Beyond the ideal gas model

In this chapter, we have developed a simple model of a gas. The extent to which this has been worthwhile depends on how well the model actually describes the properties of real gas. In Chapter 5 we will consider a variety of experimental data on gases and see to what extent we can understand the real behaviour of gases in terms of the theory developed above. We will find that the answer is, broadly, that the ideal gas model describes real gases well under a wide range of experimental circumstances.

Before moving on to compare the predictions of the ideal gas model with experiment, it is worth considering in what way a more general theory would differ from ideal gas theory. More advanced theories must take account of two key features of molecules that have been ignored (§4.1). These are first, the finite size of the molecules, and second, the interactions between the molecules, which, though weak do have measurable effects.

4.4.1 The Van der Waals equation

The Van der Waals equation of state is an interesting modification of the ideal gas equation. It is derived by considering a gas composed of hard spheres, each with volume v and a binding energy per pair of atoms of Δu. Since the molecules now have a finite volume, we can plausibly argue that the actual volume available for molecules to move in is reduced. This reduction is roughly equivalent to the volume which would be occupied by the hard spheres themselves. Thus we can write for a gas with molar volume V_m:

$$P\left(V_m - b\right) = RT \qquad (4.46)$$

where b is the approximate volume of N_A hard-sphere molecules, i.e. $b \approx N_A v$. A more sophisticated analysis indicates that the volume is in fact reduced by more than just the volume of the molecules and normally we estimate b as:

$$b = 4N_{A}v \qquad (4.47)$$

However, Equation 4.46 has taken no account of the attraction between the molecules. This effect is not modelled quite so realistically in the Van der Waals model of a gas, but some account may be taken by introducing a term of the form:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \qquad (4.48)$$

Van der Waals equation

where the coefficient a is given by:

$$a = \frac{2}{3}N_{A}b\Delta u \qquad (4.49)$$

The additional a/V_m^2 term in Equation 4.48 is small when the molar volume of the gas is large, but becomes significant as the molar volume is reduced. Commonly Equation 4.48 is used to model real gases with the parameters a and b determined experimentally from the small deviations of gases from $PV = RT$. Surprisingly, the Van der Waals Equation not only predicts deviations from ideal gas behaviour, but at small molar volumes and low temperatures, it predicts a region of solid-like behaviour.

4.4.2 The virial equation

Modern theories of gases represent the equation of state of a gas using a so-called *virial expansion*:

$$\begin{aligned} Z &= \frac{PV_m}{RT} \\ &= 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \ldots \end{aligned} \qquad (4.50)$$

The virial expansion

Z is known as the *compression factor* of a gas, and the coefficients $B(T)$, $C(T)$ etc. are known as the *second virial coefficient*, the *third virial coefficient* etc., and are functions of temperature only. The second virial coefficients of many gases are tabulated in *Kaye and Laby*. Notice that if the virial coefficients are taken as zero, then Equation 4.50 is the ideal gas equation. Thus the virial coefficients model deviations from perfect gas behaviour. In general the virial coefficients are determined experimentally, and their values tabulated in reference books such *Kaye and Laby*. However in certain theories of gases, the coefficient $B(T)$ can be understood as arising from interactions between pairs of molecules, and $C(T)$ as arising from interactions between clusters of three molecules. In general knowledge of the second virial coefficient is sufficient to understand the properties of gases at a level of a few parts per million.

Figure 4.12 Molecular interactions are sometimes poorly modelled by the hard sphere approach used in determining the mean free path of a molecule λ_{mfp}. Each of the following cases shows a molecule A colliding with a stationary molecule B.

(a) In the hard sphere approach, A would completely 'miss' B.

(b) This shows the effect of long-range attractive interactions between molecules (grey region). If A is moving slowly, interactions such as this produce quite different results from those envisioned in (a).

(c) This shows how the same collision as in (b) might be affected if molecule A were moving more quickly. Notice the deviation of A's trajectory is less than in (b).
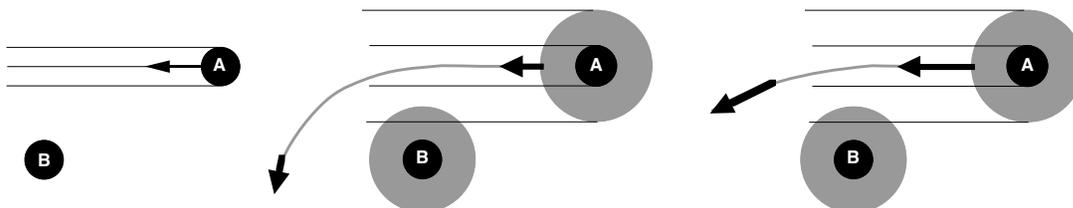
4.4.3 Molecular collisions

Finally, we consider the effect of molecular interactions on molecular collisions. The interactions between molecules are generally weakly attractive at long range (modelled by a grey area around the molecules in Figure 4.12), but repulsive at short range (modelled by the central black area of the molecules in Figure 4.12). Notice that assuming hard-sphere instantaneous-contact collisions will model the collision process correctly in most cases. However, some types of collision, such as those illustrated in Figure 4.12 (b) and (c), are not modelled at all well. The importance of this is that the 'effectiveness' of such collisions is reduced when the average kinetic energy of molecules is much larger than the attractive potential energy between molecules. This leads to a temperature dependence of the apparent average cross-sectional area used to evaluate the mean free path of a molecule.

4.5 Exercises

Exercises marked with a P prefix are 'normal' exercises. Those marked with a C prefix are best solved numerically by using a computer program or spreadsheet. Exercises marked with an E prefix are in general rather more challenging that the P and C exercises. Answers to all the exercises may be downloaded from www.physicsofmatter.com

Some more demanding exercises relating to material in this chapter and others may be found in Chapter 12.

P1. If 4 moles of gas are contained in a chamber of volume 1 litre at around room temperature, what is the pressure inside the container (Equation 4.29)? Is this above or below atmospheric pressure? To what temperature would you have to heat/cool the chamber in order to increase/decrease the pressure to atmospheric pressure?

P2. What is the number density of molecules in (a) air and (b) helium, at room temperature and atmospheric pressure (Example 4.2)?

C3. The probability that a molecule of mass m in a gas at temperature T has a speed between v and $v + dv$ is given by the Maxwell speed distribution curve. Program the formula for Equation 4.32 into a spreadsheet and so reproduce Figure 4.7.

P4. The average number of molecules colliding with unit area of wall per second is $\frac{1}{4}n\bar{v}$ (Equation 4.39). Produce an order of magnitude estimate for this quantity in air at atmospheric pressure and room temperature.

If an atom in the wall of a chamber has an 'area' of approximately 0.3 nm × 0.3 nm exposed to the chamber, estimate the frequency with which this atom is struck by atoms of the gas. To what pressure must the gas be lowered in order to reduce this frequency to 1 collision in 1000 seconds? (See also question P15 at the end of Chapter 3)

P5. By equating the average thermal energy per molecule $1.5k_BT$ with the kinetic energy of a molecule, (Equation 4.26) estimate the average speed of a molecule of argon at atmospheric pressure and room temperature. Assuming that argon molecules have a typical 'effective diameter' of around 0.3 nm, estimate the mean free path of an argon molecule in argon at atmospheric pressure and room temperature (Equation 4.45). Estimate the mean time between collisions and the average number of collisions per second.

P6. Appendix A1 outlines how the Maxwell speed distribution curve may be derived. Write an essay summarising the key stages of the calculation and suggest an experimental method by which the speed distribution curve might be determined.

P7. Academics! (a) You are a professor at Oxford University and a colleague claims that the ideal gas law does not agree well with experiment. Think of an experiment to demonstrate that the gas law is in fact obeyed rather well by most gases. (Hint: Try looking at the next chapter!) (b) Another colleague claims that the ideal gas law agrees well with experiment. Think of an experiment to demonstrate that under some circumstances the gas law breaks down completely.

P8. Measurements are made of the speed of 20 molecules sampled from some argon gas with the following results (in m s^{-1}) :

101.3	308.5	451.7	500.8
126.3	357.5	468.6	503.2
152.0	379.2	478.1	527.9
174.3	379.9	482.1	574.4
304.5	417.0	492.1	867.0

(a) Estimate $\bar{v}$ and v_{RMS} and their ratio. How closely does this result agree with what you might have expected from Figure 4.8

(b) Estimate the temperature and hence the pressure and number density of the gas.

C9. From www.physicsofmatter.com you can download a small program illustrating the dynamics of molecules in 2-dimensions. In the help section of the demo are some suggestions for phenomena you might like to observe. In particular you should set the program going with the option to plot molecular trajectories ON. After a while, switch the MOLECULAR INTERACTIONS off and notice the change in the character of the molecular motions. Write a paragraph summarising your observations.

P10. In Example 4.1 we compared the theoretical density of an air-like mixture of oxygen, nitrogen and argon with experimental values for the density of air. We said that the two estimates would agree more closely if we took account of the presence of water vapour. Let us see if that is right.

The vapour pressure of water (H_2O) at 20 °C is around 2000 Pa (Figure 9.22b). This would be pressure of water vapour if there were liquid water present in the container. However, more typically the vapour pressure would be about half of this value (i.e. 50% relative humidity). Estimate how much this would contribute to the density of air. Does this explain the small discrepancy of Example 4.1?

P11. In the derivation of the ideal gas equation we specifically neglected the effect of gravity. As we shall see in several questions in Chapter 12, this is sometimes not a good approximation. In fact, the pressure of a gas falls with increasing height, z, according to:

$$P = P_o \exp\left[-\frac{mgz}{k_B T} \right]$$

where m is the mass of an individual molecule. Estimate the difference in the pressure between the top and bottom of the room you are in.