

Module P7.5 Kinetic theory — an example of microscopic modelling

- 1 [Opening items](#)
 - 1.1 [Module introduction](#)
 - 1.2 [Fast track questions](#)
 - 1.3 [Ready to study?](#)
- 2 [Kinetic theory of ideal gases](#)
 - 2.1 [The ideal gas model](#)
 - 2.2 [The assumptions of the kinetic theory of an ideal gas](#)
 - 2.3 [The molecular basis of temperature, pressure and internal energy](#)
 - 2.4 [Kinetic theory and the ideal gas equation of state](#)
 - 2.5 [Boltzmann's constant](#)
 - 2.6 [Kinetic theory and the internal energies of molecules](#)
 - 2.7 [Kinetic theory and the specific heat of gases](#)
 - 2.8 [The mean free path of an ideal gas molecule](#)
 - 2.9 [Summary of Section 2](#)
- 3 [The Maxwell–Boltzmann speed distribution](#)
 - 3.1 [The distribution of molecular speeds](#)
 - 3.2 [The distribution of molecular kinetic energies](#)
 - 3.3 [Applications and verification of the speed distribution](#)
 - 3.4 [Summary of Section 3](#)
- 4 [A more realistic model of a gas](#)
 - 4.1 [Van der Waals equation of state](#)
 - 4.2 [Excluded volumes](#)
 - 4.3 [Intermolecular forces](#)
- 5 [Closing items](#)
 - 5.1 [Module summary](#)
 - 5.2 [Achievements](#)
 - 5.3 [Exit test](#)

[Exit module](#)

1 Opening items

1.1 Module introduction

Modern physics tries to understand matter at a *microscopic* level, where bulk properties are explained in terms of atoms or molecules behaviour. One such theory is the *kinetic theory* which attempts to explain the bulk properties of gases in terms of a microscopic picture of the motion of atoms and molecules, interacting according to Newton's laws of motion.

It is not feasible to attempt to apply Newton's laws to each atom, since even a small macroscopic system of a few grams involves of the order of 10^{23} atoms. Not only would the mathematical task of solving the equations be impossible, but even a minute uncertainty in the initial position and velocity of each individual atom would, after a very short time, produce a prediction which bore no resemblance to the real situation. To deal with these enormous numbers, we have to use statistical methods that describe the *average* behaviour of the atoms. These statistical methods are based on the idea that the individual motions of atoms are *random*. It is the combination of Newton's laws (to describe the individual atomic behaviour) and statistical reasoning (to describe the average behaviour of many atoms) that makes up the study of kinetic theory.

Section 2 begins the study of kinetic theory by considering an *ideal gas*. This is an ‘idealization’ of a real gas (one to which real gases approximate quite closely) in which the molecules are assumed to be vanishingly small and to interact with each other only during collisions. Using simple statistical ideas the macroscopic properties of the gas such as temperature, pressure, internal energy and specific heat can all be related to average molecular motion and this allows relationships between the macroscopic properties, such as the ideal gas law, to be derived. This section concludes with a discussion of the characteristic distances between collisions, the *mean free path*, and the characteristic time between collisions, the *mean free time*, relating both to molecular size and the *average speed* of the molecules.

Section 3 considers how individual molecular speeds are distributed about the mean molecular speed. This can be characterized in terms of a *probability distribution function*, the *Maxwell–Boltzmann speed distribution function*. This function is quoted and discussed, but its derivation lies beyond the scope of *FLAP*. The discussion of the speed distribution leads to the identification of three characteristic speeds for the distribution — the *most probable speed*, the *average speed* and the *root-mean-squared speed*. The distribution of molecular kinetic energies can then be derived from the speed distribution. This section concludes with brief discussions of the experimental validation of the speed distribution, and some of the *transport processes* in gases, e.g. *diffusion*, *viscosity* and *thermal conduction*.

In Section 4 we consider refinements to the simplest model of the ideal gas so as to describe real gases more accurately. This is done by incorporating molecular *excluded volumes* and *intermolecular forces*. This leads us to the introduction and discussion of the *van der Waals equation of state*.

Study comment Having read the introduction you may feel that you are already familiar with the material covered by this module and that you do not need to study it. If so, try the [*Fast track questions*](#) given in Subsection 1.2. If not, proceed directly to [*Ready to study?*](#) in Subsection 1.3.

1.2 Fast track questions

Study comment Can you answer the following *Fast track questions*?. If you answer the questions successfully you need only glance through the module before looking at the *Module summary* (Subsection 5.1) and the *Achievements* listed in Subsection 5.2. If you are sure that you can meet each of these achievements, try the *Exit test* in Subsection 5.3. If you have difficulty with only one or two of the questions you should follow the guidance given in the answers and read the relevant parts of the module. However, *if you have difficulty with more than two of the Exit questions you are strongly advised to study the whole module.*

Question F1

In the kinetic theory of ideal gases, it can be shown that $PV = \frac{2}{3} N \langle \epsilon_{\text{tran}} \rangle$, where P is the pressure, V the volume, N the total number of atoms or molecules in the gas and $\langle \epsilon_{\text{tran}} \rangle$ the average translational kinetic energy per molecule.

- (a) Explain how this leads to a microscopic definition of absolute temperature.
- (b) Calculate the mean translational kinetic energy per atom for an ideal monatomic gas at 295 K.
(Boltzmann's constant $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$.)
- (c) Calculate the total internal energy of 5.00 moles of a *diatomic* gas with five degrees of freedom at 295 K (the molar gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).
- (d) What is the molar specific heat at constant pressure for this gas?



Question F2

The Maxwell–Boltzmann speed distribution in a gas can be described by the equation:

$$n(v)\Delta v = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp(-mv^2/2kT) \Delta v$$

where m is the atomic mass, k is Boltzmann's constant, T the absolute temperature, N the number of molecules and v the molecular speed.

(a) Explain briefly what this equation represents.

(b) One characteristic of the distribution is the root-mean-squared (rms) speed, given by:

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

If the gas is molecular hydrogen (H_2), one mole of which has a mass of 2.02 g, and the temperature is 250 K, what is the rms speed? (Avogadro's constant $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$, Boltzmann's constant $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$.)

(c) Suppose you have two systems, one consisting of molecular hydrogen and the other of molecular oxygen. If their rms speeds are the same, what can you conclude about the relative temperatures of the two gases?



Question F3

The van der Waals equation of state can be written:

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

where a and b are constants, V_m is the volume per mole of gas, and the remaining variables have their usual meanings.

- (a) Explain briefly the physical interpretation of the terms which make this different from the ideal gas equation of state.
- (b) For a particular gas the constants have values of $a = 2.30 \times 10^{-2} \text{ N m}^4 \text{ mol}^{-2}$ and $b = 2.70 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. If 0.200 moles of the gas have a volume of $1.50 \times 10^{-4} \text{ m}^3$ at a pressure of $5.00 \times 10^6 \text{ Pa}$, what is T ?
- (c) The gas expands at constant temperature to a volume of $4.50 \times 10^{-4} \text{ m}^3$. What is the new pressure in Pa (1 Pa = 1 N m⁻²)?



Study comment Having seen the *Fast track questions* you may feel that it would be wiser to follow the normal route through the module and to proceed directly to [*Ready to study?*](#) in Subsection 1.3.

Alternatively, you may still be sufficiently comfortable with the material covered by the module to proceed directly to the [*Closing items*](#).

1.3 Ready to study?

Study comment In order to study this module you should have a clear understanding of the following terms: absolute temperature, atom, atomic mass, atomic mass unit, conservation of energy, conservation of momentum, density, displacement, elastic collision, force, kinetic energy (translational, rotational and vibrational), mole, molecule, Newton's laws of motion, potential energy, pressure, relative molecular mass, speed, velocity, volume and work. You should be familiar with vectors, vector components and vector addition and also with calculus notation, although the only derivative used is of a quadratic function. Ability to manipulate simple algebraic equations, including exponential functions, is assumed. If you are uncertain about any of these terms, review them by reference to the *Glossary*, which will also indicate where in *FLAP* they are developed. The following *Ready to study question* will allow you to establish whether you need to review some of the topics before embarking on this module.

Question R1

A particle travels from the point $x = 0$ m to $x = 5$ m, where it strikes a wall at 90° to the x -axis and then rebounds to the starting point. It moves at a uniform speed throughout – except for a negligible time at the turnaround. The total travel time is 10 s.

- (a) What is the average speed over the time?
- (b) What is the average velocity over the time?
- (c) If the particle has a mass of 3 kg, what is the average kinetic energy over the time?
- (d) What is the average *magnitude* of its momentum over the time?
- (e) What is the change in momentum during the turnaround?
- (f) If the duration of the collision with the wall is Δt , what is the average force exerted on the wall during the collision?



2 Kinetic theory of ideal gases


2.1 The ideal gas model

The goal of the [kinetic theory](#) of gases is to understand the bulk ([macroscopic](#)) properties of gases in terms of the constituent atoms or molecules—that is, to develop a [microscopic](#) model of these properties. When a physicist develops a model for a phenomenon, the first attempt always involves as much simplification as possible, keeping only the essential physical attributes and minimizing the mathematical complication. Our attempt to understand thermal phenomena at the microscopic level begins with the simplest system. We anticipate that the interactions between gas molecules are much weaker than those between molecules in solids or liquids, because in a gas the molecules are much further apart. We hope that this may allow us to describe the behaviour of gas molecules without having to know or calculate the detailed microscopic forces involved. We will ignore these forces, except when molecules collide, and assume all collisions are [elastic collisions](#), conserving total kinetic energy.

To simplify the model further we will describe real gases without regard to their detailed molecular structure. This approach seems reasonable since we know that the behaviour of many gases approximates that of an ideal gas, characterized by:

the ideal gas equation of state or ideal gas law

$$PV = nRT \quad (1)$$

where P is the pressure, V the volume, n the number of moles of gas  and R the universal molar gas constant of magnitude $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and T is the absolute temperature.

The first task for our microscopic model is to explain this ideal gas equation, i.e. to develop the kinetic theory of an ideal gas. This we will do in Subsection 2.2, but first try the following question.

Question T1

An ideal gas is in a container of volume 2.00 m^3 , with a pressure of $2.00 \times 10^5 \text{ Pa}$ at a temperature of 310 K . (The universal gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.)

- (a) How many moles of the gas are contained?
- (b) If the gas is made up of hydrogen molecules (which have a relative molecular mass of 2.02), what is the density of the gas?
- (c) Suppose the volume of the container increased by a factor of two, with the temperature remaining constant. What would the new pressure be? ☐




2.2 The assumptions of the kinetic theory of an ideal gas

Since the ideal gas equation works well for most real gases, irrespective of whether the molecules are *monatomic* (single atom), *diatomic* (two atoms), or *polyatomic* (more than two atoms), it is likely that an adequate model can be based upon the simplest form of microscopic particle — a point particle.

Study comment From now on we will use the word ‘molecule’ as a general term to describe the constituent particles of all gases, whether they be individual atoms, or diatomic molecules or polyatomic molecules. At some stages we will have to distinguish between these possibilities.

Now we will set out the five basic assumptions on which we can base the simplest microscopic model for gas behaviour — these form the foundation of the kinetic theory model of an ideal gas.

Assumption 1 The ideal gas consists of a large number of identical molecules which are in high speed **random motion**.

Implication Random motion means that the molecules are equally likely to be travelling in any direction. Although individual molecules undergo collisions and change direction frequently, the fact that there is a *large number* of them means that at any time there will be, to a very good approximation, equal numbers travelling in all directions, illustrated schematically in Figure 1. Molecules will also be uniformly distributed in space. 

Later we will discuss more implications of this randomness, but it is the crucial assumption of kinetic theory. We will use this randomness to discuss the properties of the gas in terms of the *average molecule*, which is all we will need to characterize much of the macroscopic behaviour of the gas.

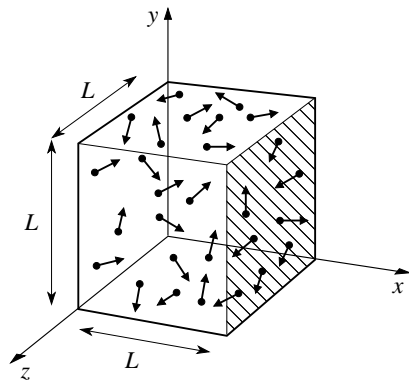


Figure 1 A schematic representation of the gas filled volume used in the kinetic theory calculation of pressure. The box contains N molecules, each with mass m . The direction of molecular motion (shown by the arrows) is random.

Assumption 2 All molecular collisions, whether between molecule and molecule, or between molecule and wall, are elastic.

Implication You might guess that this is so since a gas isolated from external influences maintains its pressure and hence the molecules must maintain their kinetic energy. From this we can assume that kinetic energy must be conserved on a microscopic scale. You may be puzzled why perfectly elastic collisions are assumed between molecules, yet they never occur in the macroscopic world. The reason is that on a microscopic scale the walls also are molecular and these molecules are also in random vibrational motion. Therefore Assumption 2 implies that *on average* a molecule neither gains nor loses kinetic energy when it collides with another molecule — whether it is in the gas or in the wall.

Assumption 3 The molecular motion is governed by Newton's laws of motion.

Implication We know today that [*quantum mechanics*](#) replaces the [*classical mechanics*](#) of Newton's laws at the atomic level, but a classical model still gives many correct insights into the properties of gases. It is fortunate that the assumption that classical physics is applicable turns out to be justified in most of kinetic theory — there are only a few places where quantum mechanics is required, and we will point these out as we come to them.

Assumption 4 The molecules experience only *contact* forces. They interact like hard spheres and this only when they are in contact.

Implication We ignore the presence of long-range forces between the molecules (such as electrical forces). We can be fairly certain that some long-range forces exist, but ignoring them is reasonable if their magnitude is small. This assumption allows us to take the motions of molecules as being along straight lines between collisions.

Assumption 5 The volume occupied by the molecules themselves is very small compared to the volume occupied by the gas as a whole.

Implication This is another way of saying that the molecular diameter is small compared to the average distance between molecules and that the molecules may be treated as particles.

Question T2

(a) Using the ideal gas equation of state (Equation 1)

$$PV = nRT \quad (\text{Eqn 1})$$

calculate the volume occupied by one mole of an ideal gas at $T = 300 \text{ K}$ and at a pressure of $1.00 \times 10^5 \text{ Pa}$.

(b) Using the fact that the number of molecules per mole of gas is given by Avogadro's constant N_A (where $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$), show that [Assumption 5](#) is justified, taking a typical molecule as a sphere of radius $r = 0.2 \text{ nm}$.

(c) What is the number of molecules per unit volume?

(d) If the average separation of the centres of these molecules in the gas is d , estimate d and compare this to the radius of a molecule. \square




2.3 The molecular basis of temperature, pressure and internal energy

Before making detailed calculations let us consider what our model and our common experience qualitatively suggests about the temperature, pressure and internal energy of a gas. In general terms we may expect the internal energy of a system to increase as its temperature rises. For an ideal gas the only form of internal energy possible is the kinetic energy of the translational motion of its molecules. On this basis, we would expect the speed of our molecules to increase as the temperature of the gas increases. While we do not know the precise relationship, we would *expect* to be able to associate the molecular speed in some sense with the temperature, if our kinetic theory model is to make sense.

At the same level of understanding, the pressure exerted by the ideal gas must be the result of the collisions of the molecules with the walls of the container, so we would expect the pressure to increase as we add more molecules to the system or if we increase their speed by raising the temperature. This is in accordance with Equation 1,

$$PV = nRT \qquad \text{(Eqn 1)}$$

the pressure increases as the temperature increases for a fixed volume and a fixed number of moles of a gas. For a fixed temperature and volume, the pressure increases with the number of moles of gas.

On the basis of our simplified ideal gas point particle model, the molecules in the gas can have only translational kinetic energy. We might therefore associate the internal energy of a gas with the average translational kinetic energy per molecule. On the other hand, if the molecules have some internal structure, for instance if they are diatomic or polyatomic, then there could be additional energy associated with the rotational and vibrational motions of molecules. For more complicated molecules, we might expect to associate the internal energy with the average *total* energy per molecule, . even though the temperature and pressure are associated with only translational kinetic energy. These are reasonable extensions to the simplified ideal gas point particle model, which allows no internal structure of the molecules.

These ideas about the molecular basis of temperature, pressure and internal energy are merely qualitative, but it is encouraging that the kinetic theory model seems to be consistent with our understanding of bulk properties at this level. However, for the model to be truly useful, we must be able to use it to make calculations, which in turn requires equations. These will be derived in the next subsection.

2.4 Kinetic theory and the ideal gas equation of state

We will derive the ideal gas equation of state (Equation 1)

$$PV = nRT \quad (\text{Eqn 1})$$

from the assumptions listed in [Subsection 2.2](#), treating the molecules as point particles. We will start by using our kinetic theory model to calculate the pressure. The pressure is the net force exerted on unit area of the wall, so we need to calculate the force exerted by a molecule when it collides with the wall. The force exerted by the molecule on the wall is equal and opposite to the force exerted by the wall on the molecule, so we can work out either. The force on the wall at an impact can be calculated from [Newton's second law](#) as *the rate of change of momentum of the molecule*. We take as our model a cubical box of side L , filled with N molecules each of mass m (see Figure 1). We will calculate the force exerted on the wall at $x = L$, shown by hatching on Figure 1.

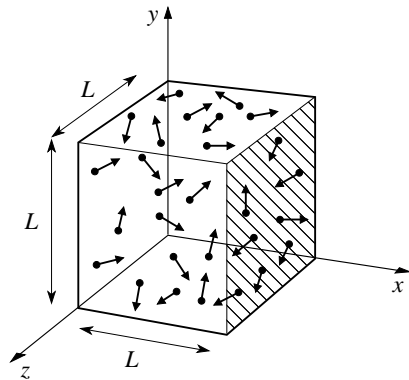



Figure 1 A schematic representation of the gas filled volume used in the kinetic theory calculation of pressure. The box contains N molecules, each with mass m . The direction of molecular motion (shown by the arrows) is random.

Consider a typical molecule with velocity vector $\mathbf{v} = (v_x, v_y, v_z)$. Collisions of this molecule with the chosen wall arise because of the component v_x and after the elastic wall collision v_x is reversed, with v_y and v_z unchanged. Thus, if p_x represents the x -component of the molecule's momentum and Δp_x the change caused by a collision we can write:

$$\text{initial value of } p_x + \Delta p_x = \text{final value of } p_x$$

$$\text{i.e. } mv_x + \Delta p_x = -mv_x$$

$$\text{so } \Delta p_x = -mv_x - (mv_x) = -2mv_x$$

Assuming no further intermolecular collisions, the molecule will return to impact on this wall again after rebounding from the wall at $x = 0$ — a round trip along x of length $2L$ that will require a time $\Delta t = 2L/v_x$. 

The chosen molecule will therefore impact on the chosen wall once in each time interval Δt , and from Newton's second law, the *average* component of force in the x -direction $\langle f_x \rangle$ exerted *by the wall*, is given by the rate of change of momentum of the molecule in the x -direction, $\Delta p_x / \Delta t$,

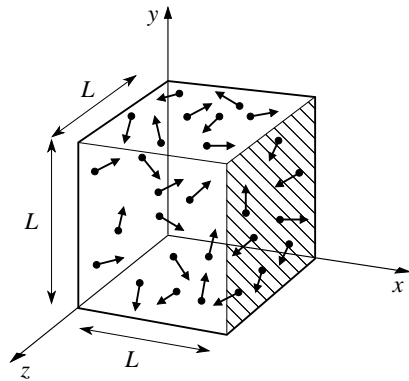


Figure 1 A schematic representation of the gas filled volume used in the kinetic theory calculation of pressure. The box contains N molecules, each with mass m . The direction of molecular motion (shown by the arrows) is random.

$$\text{i.e. } \langle f_x \rangle = \frac{\Delta p_x}{\Delta t} = \frac{-2mv_x}{2L/v_x} = \frac{-mv_x^2}{L}$$

This is the average force exerted by the wall on the molecule; the force exerted by the molecule on the wall will be just the negative of this. The effects of N molecules impacting on this same wall, each molecule with its own v_x component, causes an average force $\langle F_x \rangle$ *exerted on the wall* given by:

$$\langle F_x \rangle = -N\langle f_x \rangle = \frac{Nm}{L} \langle v_x^2 \rangle$$

where $\langle v_x^2 \rangle$ is the average or mean squared v_x component of all the N molecules,

$$\text{i.e. } \langle v_x^2 \rangle = \frac{1}{N} \sum_{i=1}^N v_{x_i}^2 \quad \text{👉}$$

However, we want to know the pressure rather than the force, so we must divide the force by the wall area L^2 .

The total pressure on the wall from the molecules is

$$P_x = \frac{\langle F_x \rangle}{L^2}$$

Substituting for $\langle F_x \rangle$

$$\langle F_x \rangle = -N \langle f_x \rangle = \frac{Nm}{L} \langle v_x^2 \rangle$$

gives us

$$P_x = \frac{Nm}{L^3} \langle v_x^2 \rangle = \frac{Nm}{V} \langle v_x^2 \rangle \quad (2)$$

where V is the volume of the gas. If we now invoke [Assumption 1](#) we see that there is nothing special about our choice of x -axis — we could have reached similar conclusions about P_y and P_z , so:

$$\text{so } P_y = \frac{Nm}{V} \langle v_y^2 \rangle \quad \text{and} \quad P_z = \frac{Nm}{V} \langle v_z^2 \rangle$$

Assumption 1 implies

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \quad (3)$$

Thus $P_x = P_y = P_z = P$, where P is the pressure exerted by the gas, which is equal in all directions.

The velocity components of an individual molecule are related to the speed v by the expression:

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

This relationship also must hold for the *averages* of these components and so the mean-squared speed is:

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle.$$

Equation 3 then gives

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle \quad (4)$$

You may have noticed that we have ignored collisions between molecules as they bounce back and forth between the walls. Surprisingly enough, this omission does not matter. The large number of molecules means that at any one time there will be as many molecules travelling towards the wall as away from it and because the collisions are elastic, the distribution of speeds will not vary with time (this is considered in more detail in Section 3). Thus the *average* effect on the wall will be the same as if the molecules never collided with each other.

Combining Equations 2 and 4

$$P_x = \frac{Nm}{L^3} \langle v_x^2 \rangle = \frac{Nm}{V} \langle v_x^2 \rangle \quad (\text{Eqn 2})$$

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle \quad (\text{Eqn 4})$$

produces our required equation, which relates the macroscopic properties of a gas (on the left-hand side of Equation 5) and the average microscopic quantities (on the right-hand side of Equation 5):

$$PV = \frac{1}{3} Nm \langle v^2 \rangle \quad (5)$$

Here $\langle v^2 \rangle$ is the mean-squared speed of the molecules. The positive square root of this is known as the **root-mean-squared (rms) speed** v_{rms}


$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} \quad (6)$$

So Equation 5 can be written as:

$$PV = \frac{1}{3} Nm v_{\text{rms}}^2$$

We can also write Equation 5

$$PV = \frac{1}{3} Nm \langle v^2 \rangle \quad (\text{Eqn 5})$$

in terms of the *average molecular translational kinetic energy*, $\langle \epsilon_{\text{tran}} \rangle$,  by noting that:

$$\frac{1}{3} m \langle v^2 \rangle = \frac{1}{3} \langle mv^2 \rangle = \frac{2}{3} \langle \frac{1}{2} mv^2 \rangle = \frac{2}{3} \langle \epsilon_{\text{tran}} \rangle$$

Equation 5 then becomes

$$PV = \frac{2}{3} N \langle \epsilon_{\text{tran}} \rangle \quad (7)$$

which relates the product PV to the average translational kinetic energy of the molecules in the gas. This is the result of our kinetic theory model calculation, and that is as far as we can take the equation simply on the basis of kinetic theory.

If you compare Equations 1 and 7,

$$PV = nRT \quad (\text{Eqn 1})$$

$$PV = \frac{2}{3} N \langle \epsilon_{\text{tran}} \rangle \quad (\text{Eqn 7})$$

you will see that the macroscopic ideal gas law and the kinetic theory result imply a particular association between temperature and the mean molecular kinetic energy. This relationship was anticipated qualitatively in Subsection 2.3. The relationship is:

$$PV = nRT = \frac{2}{3} N \langle \epsilon_{\text{tran}} \rangle$$

or, taking the last two parts of the chain and rewriting them slightly we obtain:

$$\langle \epsilon_{\text{tran}} \rangle = \frac{3}{2} \frac{nR}{N} T = \frac{3}{2} \frac{nR}{nN_A} T = \frac{3}{2} \frac{R}{N_A} T \quad (8)$$

where we have written the total number of molecules N in n moles as nN_A , where N_A is [Avogadro's constant](#), the number of molecules in one mole.

Equation 8 relates the macroscopic idea of absolute temperature to the average molecular (microscopic) translational kinetic energy of the molecules

$$T = \frac{2}{3} \frac{N_A}{R} \langle \epsilon_{\text{tran}} \rangle \quad (9)$$

Equation 9 gives us a microscopic definition of [temperature](#) in terms of the average molecular translational kinetic energy $\langle \epsilon_{\text{tran}} \rangle$.

Notice that the average molecular translational kinetic energy is determined *only* by the temperature and is independent of the molecular mass.

2.5 Boltzmann's constant

Equation 8


$$\langle \epsilon_{\text{tran}} \rangle = \frac{3}{2} \frac{nR}{N} T = \frac{3}{2} \frac{nR}{nN_A} T = \frac{3}{2} \frac{R}{N_A} T \quad (\text{Eqn 8})$$

is usually written as

$$\langle \epsilon_{\text{tran}} \rangle = \frac{3}{2} kT \quad (10)$$

where the new constant k , defined by the relationship

$$k = \frac{R}{N_A} \quad (11)$$

is known as **Boltzmann's constant**.  This constant appears frequently in equations relating macroscopic parameters to microscopic phenomena. From Equation 11 it is apparent that one can view k as the gas constant for one *molecule* in contrast with R , as the gas constant for one mole. The currently accepted value for k is $1.380\,662 \times 10^{-23} \text{ J K}^{-1}$, normally rounded to $1.381 \times 10^{-23} \text{ J K}^{-1}$.

We can express the root-mean-squared speed (see Equation 6)

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} \quad (\text{Eqn 6})$$

in terms of Boltzmann's constant using Equations 6 and 10.

$$\langle \epsilon_{\text{tran}} \rangle = \frac{3}{2} kT \quad (\text{Eqn 10})$$

Since m is a constant:

$$\langle \epsilon_{\text{tran}} \rangle = \left\langle \frac{1}{2} m v^2 \right\rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} kT$$

$$\text{i.e.} \quad v_{\text{rms}} = \sqrt{\frac{3kT}{m}} \quad (12)$$

Notice here that the root-mean-squared speed is determined by both the temperature and the molecular mass; this is in contrast to the average molecular kinetic energy which is determined only by the temperature.

Here k has arisen in relating the ideal gas law to kinetic theory. Another way of obtaining Boltzmann's constant is by examining the behaviour of the quantity PV/NT as a function of pressure, as shown in Figure 2. Here we can see that as P approaches zero, the value of PV/NT approaches a single value for a range of simple gases, and that this number is Boltzmann's constant. This is just what we would expect from the ideal gas law since $PV = nRT = nN_A kT$. Thus the ideal gas law can be written as:

$$PV = NkT \quad (13)$$

with $k = PV/NT$.

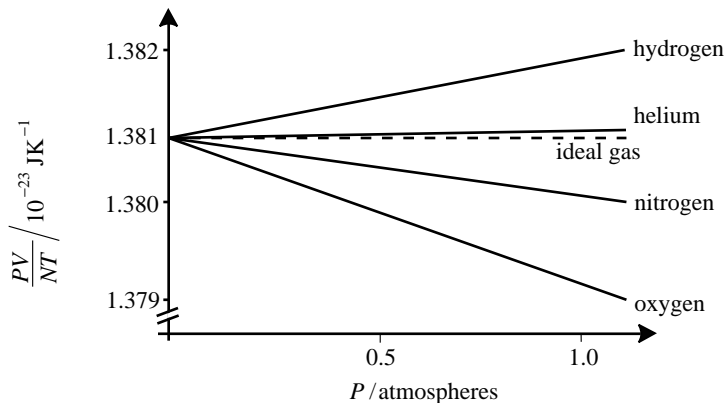


Figure 2 As the pressure falls towards zero, the value of PV/NT for all gases tends toward the ideal gas value, which is Boltzmann's constant k .

Figure 2 also shows how real gases approach ideal gas behaviour at low pressures. As you can see from Figure 2, helium approximates better than others to the ideal gas law, but many more common gases deviate from this by no more than 0.1% even at atmospheric pressure.

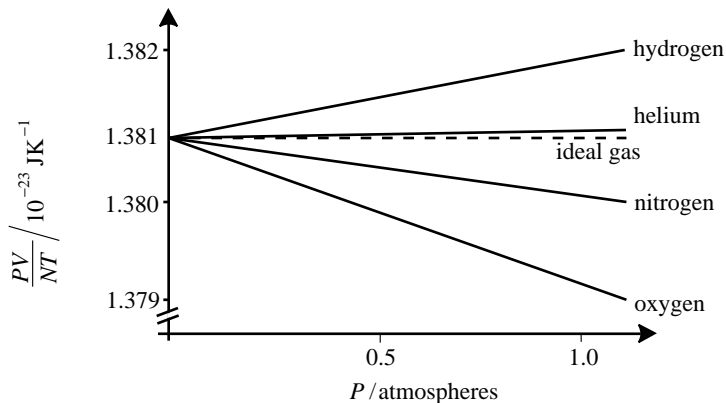


Figure 2 As the pressure falls towards zero, the value of PV/NT for all gases tends toward the ideal gas value, which is Boltzmann's constant k .

Question T3

Calculate an average translational kinetic energy and a root-mean-squared speed for molecules of (a) helium ($m = 6.6 \times 10^{-27}$ kg) and (b) argon ($m = 6.6 \times 10^{-26}$ kg) each at a temperature of 300 K. ☐




Question T4

What gas temperature corresponds to an average molecular translational kinetic energy of 1 electronvolt ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$)?

What would be the root-mean-squared speed for H_2 molecules ($m = 3.3 \times 10^{-27}$ kg) at this temperature? ☐




2.6 Kinetic theory and the internal energies of molecules

We have already shown that the pressure and temperature of an ideal gas are determined by the average translational kinetic energy of the molecules in the gas. If we allow our molecules only to be monatomic hard spheres (as we have done so far), then that is the only significant form the energy can take. However, if we allow for more complex diatomic or polyatomic molecules then energy may also be stored as kinetic and potential energy *within individual molecules* as a molecule can vibrate or rotate about its [centre of mass](#). When energy is added to a sample of such a gas the translational motion of its molecules will increase, but also they may store some of this energy in additional rotational or vibrational motion. The total energy of such a molecule would exceed that due to translational motion alone. 

For the monatomic gas $\langle \epsilon_{\text{tran}} \rangle = \frac{3}{2} kT$ (Eqn 10)


and we assumed that the molecules were free to move in three dimensions, but that they had no internal structure and hence no rotational or vibrational energy. This freedom to move in *three* dimensions can be expressed by saying that the molecules have *three* [degrees of freedom](#). If we were to allow for rotational or vibrational motion then this would give additional degrees of freedom, in which additional energy may be present.

Where there are several degrees of freedom available [statistical mechanics](#)  leads to the result that, on average, the available energy will be shared equally between all degrees of freedom.

The proof of this lies beyond the scope of *FLAP* but it is another manifestation of the assumption of total randomness, and it is known as the *equipartition of energy theorem*.

The [equipartition of energy theorem](#) states that *each* degree of freedom possesses an average energy of $\frac{1}{2} kT$ per molecule.

So, with three degrees of freedom each molecule has an average energy of $3 \times \frac{1}{2} kT = \frac{3}{2} kT$ and this *average total energy per molecule*, $\langle \epsilon_{\text{tot}} \rangle$, is purely translational.

◆ Suppose our molecules are diatomic, with their atoms rigidly connected along a line and are unable to vibrate along this line. We can define two mutually perpendicular axes of rotation at right angles to this line and it can be shown that these count as *two* additional degrees of freedom  (see Figure 3). What is the average *total* energy per molecule in this case?



In general, if a molecule has q degrees of freedom

$$\langle \epsilon_{\text{tot}} \rangle = \frac{q}{2} \frac{R}{N_A} T = \frac{q}{2} kT \quad (14a)$$

$$\text{or} \quad T = \frac{2}{q} \frac{N_A}{R} \langle \epsilon_{\text{tot}} \rangle = \frac{2}{qk} \langle \epsilon_{\text{tot}} \rangle \quad (14b)$$

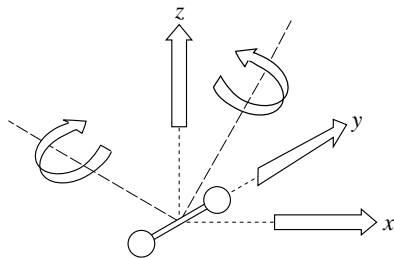


Figure 3 Five independent degrees of freedom (two directions of rotation and three of translation) for a dumbbell-shaped diatomic molecule.

Equation 14b

$$T = \frac{2}{q} \frac{N_A}{R} \langle \epsilon_{\text{tot}} \rangle = \frac{2}{qk} \langle \epsilon_{\text{tot}} \rangle \quad (\text{Eqn 14b})$$

provides an alternative to Equation 9



$$T = \frac{2}{3} \frac{N_A}{R} \langle \epsilon_{\text{tran}} \rangle \quad (\text{Eqn 9})$$

as a microscopic definition of temperature.

We can now relate the *total internal energy*, E_{int} , for the whole molecular system to a key macroscopic parameter, the absolute temperature. For a gas of N molecules with q degrees of freedom, we can write:

$$E_{\text{int}} = N \langle \epsilon_{\text{tot}} \rangle = \frac{q}{2} NkT \quad (15)$$

Question T5



Suppose that you have two gas samples, each of one mole, at the same temperature and pressure. One gas is monatomic and the other is diatomic, with the molecules able to rotate but not vibrate.  If the same amount of energy is added to each sample, which will reach the higher temperature? 



2.7 Kinetic theory and the specific heat of gases

The **specific heat** is defined as the energy required to raise the temperature of a specified amount of material by one degree absolute. Normally the specified amount is 1 kg, with the specific heat measured in units of $\text{J K}^{-1} \text{kg}^{-1}$. We can also define a **molar specific heat**, which has units of $\text{J K}^{-1} \text{mol}^{-1}$, where the specified amount is one mole. From the general definition of specific heat we can define the molar specific heat by the equation:

$$C = \frac{\Delta Q_m}{\Delta T} \quad (16)$$

where C is the molar specific heat, ΔQ_m is the energy supplied per mole of gas, in the form of **heat**,  causing a change in temperature ΔT .  For a gas, the conditions under which the energy is added must be carefully specified, (e.g. at constant pressure, or at constant volume), since this will affect the value of the resulting specific heat. We will consider now what our kinetic theory model for the ideal gas tells us about these specific heats.

First we will consider C_V , the molar specific heat at constant volume. When heat is added to the system, the energy transferred to the gas must increase the energy of the gas molecules. This is all that can happen if the process is at constant volume. For a monatomic ideal gas, we therefore see from Equation 15

$$E_{\text{int}} = N \langle \epsilon_{\text{tot}} \rangle = \frac{q}{2} NkT \quad (\text{Eqn 15})$$

that the increase in internal energy corresponding to a temperature increase ΔT is

$$\Delta E_{\text{int}} = \frac{3}{2} Nk\Delta T = \frac{3}{2} nR\Delta T$$

where n is the number of moles present.

Thus, to cause the temperature rise, the heat that must be supplied per mole is

$$\Delta Q_m = \frac{\Delta E_{\text{int}}}{n} = \frac{3}{2} \frac{Nk\Delta T}{n} = \frac{3}{2} R\Delta T$$

$$\text{so } C_V = \left(\frac{\Delta Q_m}{\Delta T} \right)_V = \frac{3}{2} N_A k = \frac{3}{2} R \quad (17) \quad \text{👉}$$

where R is the gas constant (Equation 11).

$$k = \frac{R}{N_A} \quad (\text{Eqn 11})$$

If we have polyatomic molecules with q degrees of freedom, this is simply generalized to:

$$C_V = \frac{q}{2} N_A k = \frac{q}{2} R \quad (18)$$

We also need to derive an expression for the molar specific heat at constant pressure, C_p . The difference between the two specific heats, in terms of bulk properties, is that for the constant pressure process, the gas will expand as heat is added. This means that part of the energy transferred to the system as heat will be used to do the work of expansion and there will be a correspondingly smaller increase in internal energy than for the constant volume system. Since the internal energy of the ideal gas is proportional to the absolute temperature, there will be a smaller rise in temperature for the same amount of heat transferred, which implies that $C_p > C_V$. We will now try to understand this in terms of our kinetic theory model.

As heat is added to the system, the volume increases to maintain constant pressure. This could be done by having the gas contained in a cylinder with a frictionless piston (see Figure 4), with a fixed reference pressure (say atmospheric pressure) on top of the piston. As the gas in the cylinder is heated, the piston will rise, maintaining constant pressure, so allowing the volume to increase. How can we interpret this microscopically?

In [Subsection 2.4](#) we assumed that the wall of the container was held rigidly in place by external forces, so that the elastic collisions of the molecules caused no recoil of the wall itself. Now we are going to allow the wall of the piston to move in response to the collisions, by making the piston frictionless, so we need to re-analyse the situation. In an elastic collision where both masses are free to move, the energy will be shared out between them. This means that the molecules will, on average, transfer some of their kinetic energy to the recoiling piston as the gas expands and more heat will therefore be required to produce the same rise in temperature, compared to the constant volume case.

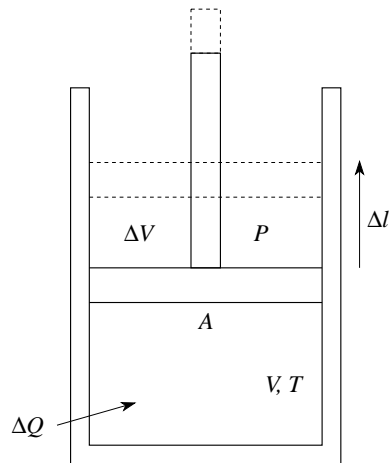


Figure 4 Expansion of a gas under constant pressure conditions.

In Figure 4 the gas initially has volume V , pressure P , temperature T and is contained in a cylinder with a piston of cross-sectional area A . An amount of heat ΔQ is added to the gas, its temperature rises to $(T + \Delta T)$ and it also expands under constant pressure P to volume $(V + \Delta V)$. To raise the piston, the gas must apply an upwards force of magnitude F given by $F = PA$. The gas does work by raising the piston a distance Δl .

This work done by the gas is given by

$$\Delta W = F\Delta l = PA\Delta l = P\Delta V$$

Using the principle of energy conservation:

heat added = change in internal energy of gas + work done by the gas

Thus we obtain the [first law of thermodynamics](#)

$$\Delta Q = \Delta E_{\text{int}} + P\Delta V \quad (19)$$

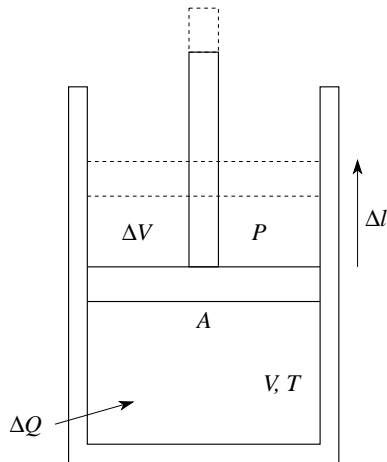


Figure 4 Expansion of a gas under constant pressure conditions.

We can calculate $P\Delta V$ from Equation 1

$$PV = nRT \quad (\text{Eqn 1})$$

by considering the system before and after the expansion. For an ideal gas:

initially $PV = nRT$

and finally $P(V + \Delta V) = nR(T + \Delta T)$

If we subtract these two, we find

$$P\Delta V = nR\Delta T \quad (20)$$

ΔE_{int} for the system can be obtained from Equation 15

$$\Delta E_{\text{int}} = \frac{q}{2} Nk\Delta T = \frac{q}{2} nR\Delta T$$

and using Equation 18 we may write this as

$$\Delta E_{\text{int}} = nC_V\Delta T \quad (21)$$

If we now substitute Equations 20 and 21 into Equation 19


$$P\Delta V = nR\Delta T \quad (\text{Eqn 20})$$

$$\Delta E_{\text{int}} = nC_V\Delta T \quad (\text{Eqn 21})$$

$$\Delta Q = \Delta E_{\text{int}} + P\Delta V \quad (\text{Eqn 19})$$


and divide both sides by n we find that at constant pressure the heat per mole required to raise the temperature by ΔT is

$$\Delta Q_{\text{m}} = C_V\Delta T + R\Delta T = (C_V + R)\Delta T$$

so $C_P = \left(\frac{\Delta Q_{\text{m}}}{\Delta T} \right)_P = C_V + R$ 

i.e. $C_P - C_V = R \quad (22)$

Equation 22 gives the difference in the molar specific heats for an ideal gas. As expected from our earlier discussion, C_P exceeds C_V .

The ratio of the specific heats, C_P/C_V is often written as γ ,  and using Equations 22 and 18

$$C_V = \frac{q}{2} N_A k = \frac{q}{2} R \quad (\text{Eqn 18})$$


$$C_P - C_V = R \quad (\text{Eqn 22})$$

we see that

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{R}{C_V} = 1 + \frac{R}{\frac{q}{2} R} = 1 + \frac{2}{q} \quad (23)$$

Notice that the *difference* between the two specific heats is independent of the number of degrees of freedom q of the molecule, but the two specific heats themselves and their ratio γ depend on q .

Question T6

How would the expression for the specific heat at constant pressure be generalized to the case of a polyatomic molecule with q degrees of freedom? 



We may collect the result from [Question T6](#) into our set of equations by writing, for a gas with q degrees of freedom:

$$C_P = \left(1 + \frac{q}{2}\right)R \quad (24)$$

Question T7

Predict the values of C_V , C_P , $(C_P - C_V)$ and $\gamma = C_P/C_V$ for gases having, (a) three degrees of freedom, (b) five degrees of freedom, (c) seven degrees of freedom. \square




The conclusion from this subsection is that our microscopic kinetic theory model allows the number of degrees of freedom of the molecules in a gas to be inferred from macroscopic measurements of the gas specific heats.

2.8 The mean free path of an ideal gas molecule

In [Subsection 2.4](#), it was claimed that intermolecular collisions did not invalidate the derivation of Equation 5.

$$PV = \frac{1}{3} Nm \langle v^2 \rangle \quad (\text{Eqn 5})$$

However, it is still of interest to know something about the frequency of these collisions and how far molecules travel between them.

The [mean free path](#) λ  of a molecule is defined as the average distance it travels between collisions. We might expect the mean free path to vary strongly with temperature and pressure as these properties determine the speed and the closeness of the molecules, respectively. We can get a feel for the kind of distances involved by thinking about a specific example. Let us consider one mole of a gas at a temperature of 300 K and a pressure of 1.0×10^5 Pa — these were the conditions for the gas in [Question T2](#).

◆ What is the [number density](#) (the number of molecules per unit volume) for molecules under these conditions?



In [Question T2](#) we calculated the average separation between molecules under these conditions as 3.46 nm. You might expect that the mean free path would be very similar to the intermolecular separation — in fact it is considerably different, as we will see in a moment — mainly because it also depends on the *size* of the molecules as well as on their mean separation.

To calculate λ , we need to think about the average volume per molecule. This must also be the volume a molecule will have to sweep through before it makes a collision. A molecule will contact another identical molecule if (assuming they are spherical) the distance between their centres is equal to twice the molecular radius or $2r$ (see Figure 5).

We are only interested in centre-to-centre intermolecular distances, so the situation is equivalent to one where all the other molecules are considered to be points, and our reference molecule has a radius of $2r$.

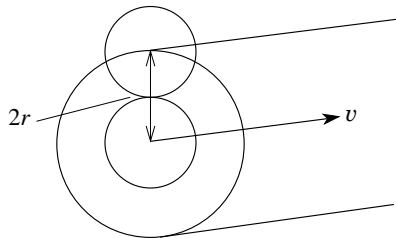



Figure 5 A molecule travelling through the gas sweeps out a volume that is cylindrical, with the axis coinciding with the centre of the molecule.

In a time Δt our reference molecule, assumed to be travelling with the average speed $\langle v \rangle$, sweeps out a volume equal to that of a cylinder of length $\langle v \rangle \Delta t$ and *radius* $2r$. This volume is $\Delta V = \pi(2r)^2 \langle v \rangle \Delta t = 4\pi r^2 \langle v \rangle \Delta t$. All other molecules whose centres lie within this volume will be struck by the reference molecule within the time Δt . This number is $n_\rho \Delta V$ where n_ρ is the number density of the molecules. So, in a time Δt the number of collisions with the reference molecule is $4\pi r^2 n_\rho \langle v \rangle \Delta t$. We can define the **mean collision frequency** f_{coll} (mean number of collisions per second) as

$$f_{\text{coll}} = \frac{\text{mean number of collisions in } \Delta t}{\Delta t} = \frac{4\pi r^2 n_\rho \langle v \rangle \Delta t}{\Delta t} = 4\pi r^2 n_\rho \langle v \rangle \quad (25)$$

The mean time between collisions, or the **mean free time** τ_{coll}  is

$$\tau_{\text{coll}} = \frac{1}{f_{\text{coll}}} = \frac{1}{4\pi r^2 n_\rho \langle v \rangle} \quad (26)$$

and the mean distance between collisions, or the mean free path λ , is

$$\lambda = \langle v \rangle \tau_{\text{coll}} = \frac{1}{4\pi r^2 n_\rho} \quad (27)$$

Notice that the mean free path is independent of the average molecular speed. You may be concerned that this simple calculation has ignored the *effects* of collisions on our calculated volumes. Again we are justified in doing this because of Assumption 1. Since we are concerned with random motion, we only have to use averages. In fact, a more careful calculation, which takes into account the motion of all the molecules, changes these results only by a factor of $\sqrt{2}$, so that for example, the expression for mean free path becomes

$$\lambda = \frac{1}{4\sqrt{2}\pi r^2 n_p} \quad (28)$$

Question T8

Use Equation 28 to calculate the mean free path for the gas discussed in [Question T2](#).

(i.e. an ideal gas at $T = 300$ K and at a pressure of 1.00×10^5 Pa.) ☐



Question T9

In [Question T2](#) we estimated that the average separation between molecules (of diameter 0.4 nm) in this gas was about 3.5 nm (equivalent to 8.75 molecular diameters), but in [Question T8](#) we have calculated a mean free path which is 58 nm (equivalent to 145 molecular diameters). Are these numbers consistent? Give your reasoning. ☐



2.9 Summary of Section 2

The kinetic theory model of an ideal gas is based on Newton's laws and certain simplifying assumptions.

The simplifying assumptions are as follows:

Assumption 1 The ideal gas consists of a large number of identical molecules in high speed random motion.

Assumption 2 All collisions between molecule and molecule, or between molecule and wall, are elastic.

Assumption 3 The individual molecules obey Newton's laws of motion.

Assumption 4 The molecules only experience contact forces. They interact like hard spheres and this only when they touch.

Assumption 5 The volume occupied by the molecules themselves is very small compared to the volume occupied by the gas as a whole.

This model provides a derivation of the ideal gas equation of state ($PV = nRT$) and shows that the absolute temperature can be expressed in terms of the average kinetic energy per molecule

$$T = \frac{2}{3} \frac{N_A}{R} \langle \epsilon_{\text{tran}} \rangle = \frac{2}{3k} \langle \epsilon_{\text{tran}} \rangle \quad (\text{Eqns 9 and 10})$$

Boltzmann's constant is a useful parameter, it is defined by the equation $k = R/N_A$ and can be interpreted as the gas constant per molecule.

The kinetic theory model can be used to derive theoretical expressions for the specific heat of an ideal gas at constant volume and at constant pressure and for the mean free path of a molecule. In a *monatomic* ideal gas

$$C_V = \frac{3R}{2} \quad C_P = \frac{5R}{2} \quad \text{and} \quad \lambda = \frac{1}{4\sqrt{2}\pi r^2 n_p}$$


3 The Maxwell–Boltzmann speed distribution

Study comment This is a rather mathematical and even abstract section. Do not worry too much about the details of the mathematics if you are uncomfortable with them. Concentrate on the basic physical *concepts* of the Maxwell–Boltzmann distribution and on the physical meaning of the equation that characterizes it. The material in Section 4 does not depend on the details of what is described in Section 3.

3.1 The distribution of molecular speeds

So far we have been able to base our discussions on the *average* properties of the molecules, but to understand the detailed behaviour properly, we need to have some idea about how the properties of the molecules vary about the average. In particular, we would like to know the way the speeds of the molecules are spread or distributed around the average speed. Are most of the speeds within a per cent or so of this average or are they spread much wider than this? The distribution of molecular speeds in an ideal gas was first obtained by James Clerk Maxwell (1831–1879), using arguments based on statistical mechanics. This speed distribution is known as the [Maxwell–Boltzmann speed distribution](#). We will make no attempt to derive it here but we will comment on its origins, specify it explicitly and finally explore some of its implications.

The speeds of individual molecules in an ideal gas will be constantly changing as the molecules collide. However, for a given sample of gas at a fixed temperature, containing a given number of molecules, the effect of the collisions is to establish and maintain a particular distribution of speeds—the Maxwell–Boltzmann distribution. This distribution will determine the average number (or proportion) of the molecules that have speeds in any specified range of values. If the actual speeds of the molecules depart from this distribution (as they will) the overall effect of the energy and momentum exchanges that take place in intermolecular collisions will tend to restore the actual speed distribution to that described by the Maxwell–Boltzmann distribution. Thus, the Maxwell–Boltzmann speed distribution represents an average distribution of molecular speeds, about which the true distribution fluctuates.

There are two commonly used methods of specifying the distribution of molecular speeds within a sample of ideal gas. The first is to specify the *number* of molecules in the gas that have speeds in any narrow range between v and $v + \Delta v$. The second is to specify the relative likelihood (i.e. [*probability*](#))  that an individual molecule, chosen at random, will have a speed in the range v to $v + \Delta v$. Though different, these two methods are deeply related since the greater the number of molecules with speed in a given range the greater the likelihood that a randomly chosen molecule will have its speed in that range. We will present these two specifications of the Maxwell–Boltzmann distribution in turn.

Suppose you have a sample of ideal gas at temperature T that consists of N identical molecules of mass m . If the number of molecules that have speeds in the narrow range v to $v + \Delta v$ is represented by the quantity $n(v)\Delta v$ then:

The *Maxwell–Boltzmann speed distribution* can be written as:

$$n(v)\Delta v = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp(-mv^2/2kT) \Delta v \quad (29)$$

where k is Boltzmann's constant.

Note that since $n(v)\Delta v$ represents a *number* of molecules, the quantity $n(v)$ must have the dimensions of (speed)⁻¹, so it might be measured in units of s m⁻¹, and it should be interpreted as the number of molecules *per unit speed interval* with speeds in the range v to $v + \Delta v$.

It follows from Equation 29

$$n(v)\Delta v = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp(-mv^2/2kT) \Delta v \quad (\text{Eqn 29})$$

that, on average, the *fraction* of molecules in the sample with speeds in the range v to $v + \Delta v$ will be $n(v)\Delta v/N$. This fraction, which we will denote by $f(v)\Delta v$ represents the relative likelihood (i.e. *probability*) that a single molecule chosen at random will have its speed in the range v to $v + \Delta v$. Thus:

The Maxwell–Boltzmann speed distribution can also be written as:

$$f(v)\Delta v = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp(-mv^2/2kT) \Delta v \quad (30)$$

In this case the function $f(v)$, which has the dimensions of $1/v$. and could also be measured in units of s m^{-1} , is called the **Maxwell–Boltzmann speed distribution function**

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


Question T10

A probability must be dimensionless, and so the product $f(v)\Delta v$ should have no units. By considering the terms on the right-hand side of Equation 30

$$f(v)\Delta v = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp(-mv^2/2kT) \Delta v \quad (\text{Eqn 30})$$

(apart from the final Δv) verify that $f(v)$ has dimensions of $1/v$, so that this condition is met. \square



Note that this distribution function is *independent of angle*; the direction of motion is irrelevant as it concerns only the *speed*. It is also independent of position, because we have assumed a uniform spatial distribution — which means that the probability of finding a molecule in any particular element of volume is constant . Before we look at the detailed shape of the Maxwell–Boltzmann speed distribution function let us examine Equation 30 qualitatively.

Although the equation looks complicated, let us concentrate first on the exponential ($-mv^2/2kT$) factor. Like any exponent, this must be dimensionless; we can see that this is so since it is the ratio of two energies, $mv^2/2$ and kT , where $mv^2/2$ is the kinetic energy of the molecule with mass m and speed v , while kT is related to the average translational energy per molecule, $3kT/2$. For a molecule which is much slower than average, the kinetic energy is very small compared to kT , and $mv^2/2kT$ is much less than unity.

◆ For this slow molecule, what is the approximate value of the exponential factor, $\exp(-mv^2/2kT)$?
From Equation 30,

$$f(v)\Delta v = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp(-mv^2/2kT) \Delta v \quad (\text{Eqn 30})$$

what then is the approximate form of the speed distribution function $f(v)$ for slow molecules?



We now know the shape of the Maxwell–Boltzmann speed distribution at low speeds.

What happens at high speeds?

◆ From Equation 30, what is the form of the speed distribution function $f(v)$ for molecules whose speed is much higher than the average?



The result of combining the low and high speed behaviours of Equation 30 is that there must be a maximum in the function at some speed, between the quadratic growth regime and the exponential decay regime.

This is illustrated in Figure 6, which shows the shape of the Maxwell–Boltzmann speed distribution function $f(v)$ for a sample of gas at three different temperatures. The important points to notice here are that as the temperature increases the peak in the distribution becomes lower and broader, and occurs at higher speeds.

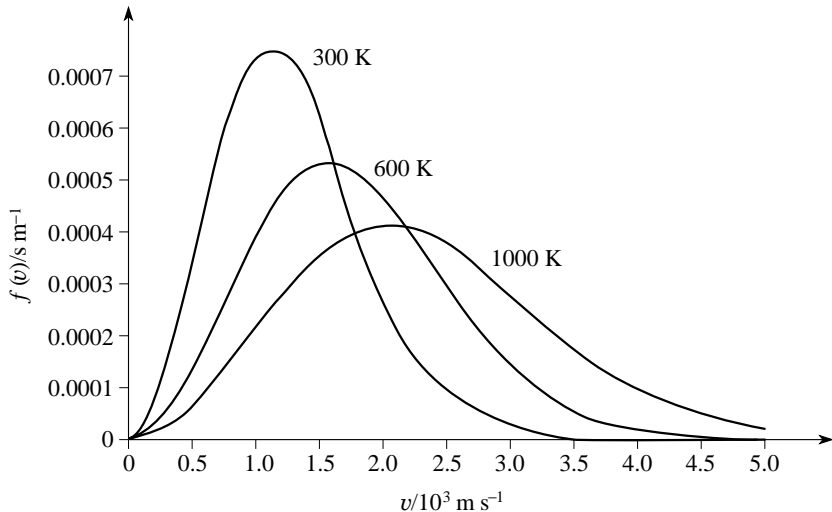



Figure 6 The Maxwell–Boltzmann speed distribution function for a sample of gas at three different temperatures. At higher temperatures, the peak in the distribution function becomes lower, broader, and occurs at a higher speed.

The interpretation of $f(v)\Delta v$ as a probability has an important implication for any graph of $f(v)$ against v , including the graphs in Figure 6.

The area enclosed between any graph of $f(v)$ and the v -axis must be exactly 1 

(in the scale units appropriate to the graph).

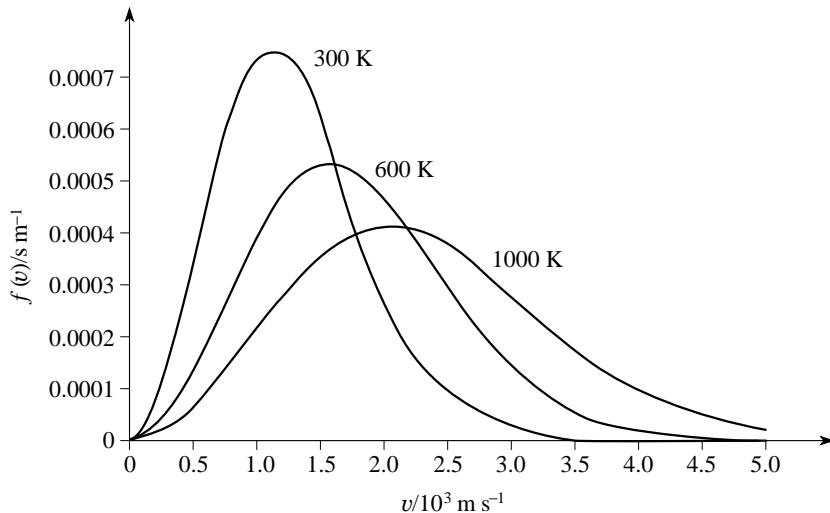


Figure 6 The Maxwell–Boltzmann speed distribution function for a sample of gas at three different temperatures. At higher temperatures, the peak in the distribution function becomes lower, broader, and occurs at a higher speed.

Actually measuring the area under the curves in Figure 6 to verify this would be very time consuming, but you can easily see that it might well be true just by noticing that the 1000 K curve is fairly close to being a triangle with

height $4 \times 10^{-4} \text{ s m}^{-1}$,
base length $5 \times 10^3 \text{ m s}^{-1}$

and hence area

$(4 \times 10^{-4} \text{ s m}^{-1} \times 5 \times 10^3 \text{ m s}^{-1})/2 = 1$.

Keeping this constant area requirement in mind will help you to answer Question T11, which concerns the way the distribution function $f(v)$ changes shape as the temperature parameter T is altered.

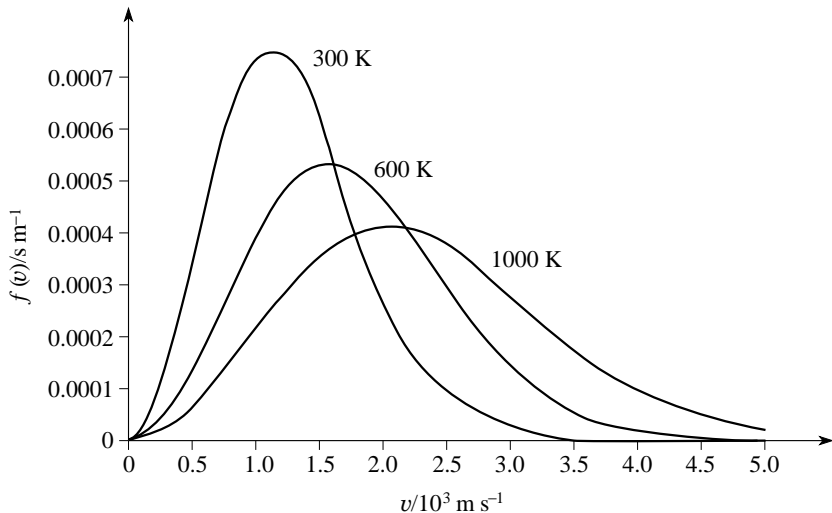


Figure 6 The Maxwell–Boltzmann speed distribution function for a sample of gas at three different temperatures. At higher temperatures, the peak in the distribution function becomes lower, broader, and occurs at a higher speed.

Question T11

Explain qualitatively why the peak in the Maxwell–Boltzmann speed distribution function (Figure 6) becomes lower, broader, and moves to higher speeds as the temperature increases. ☐

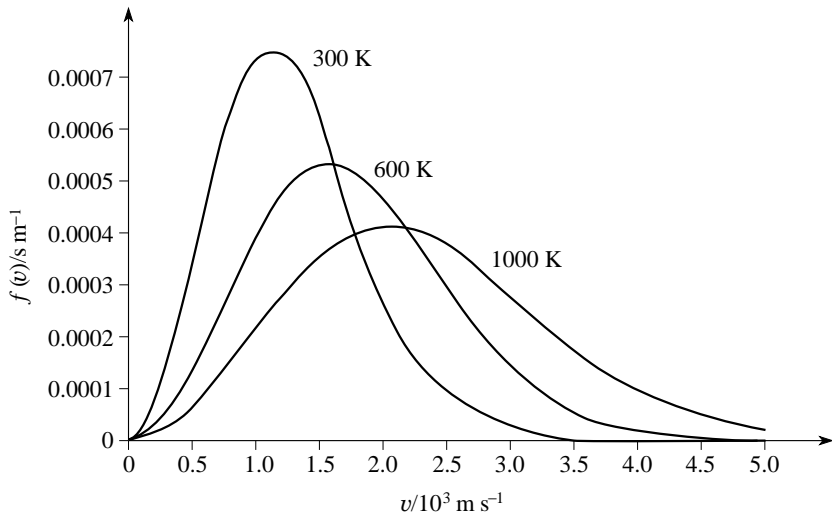



Figure 6 The Maxwell–Boltzmann speed distribution function for a sample of gas at three different temperatures. At higher temperatures, the peak in the distribution function becomes lower, broader, and occurs at a higher speed.

Knowing the Maxwell–Boltzmann distribution function we can answer a variety of questions about an ideal gas. For example, there are at least three characteristic speeds that are likely to be of interest:

- 1 First, and most obviously, we would like to know the speed corresponding to the peak in the distribution — the most common speed. For obvious reasons we will call this the **most probable speed** v_{prob} .
- 2 Second, we would like to know the **average speed** $\langle v \rangle$.
- 3 Finally, because of its significance in the kinetic theory link with the ideal gas law, as shown in [Subsection 2.4](#), we would like to know the *root-mean-squared speed* v_{rms} . This would also allow us to calculate the average kinetic energy per molecule $mv_{\text{rms}}^2/2$.

All of these characteristic speeds  can be calculated from the form of the distribution function implied by (Equation 30)

$$f(v)\Delta v = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp(-mv^2/2kT)\Delta v \quad (\text{Eqn 30})$$

using [*calculus*](#).

Aside The most probable speed comes at the peak of the distribution, which can be found from the point at which the *gradient* of the function becomes zero; using calculus, we find that this corresponds to the speed at which $df(v)/dv = 0$. We must *differentiate* $f(v)$ with respect to v , and set the result equal to zero, and solve the resulting equation to find the appropriate speed $v = v_{\text{prob}}$. The average speed $\langle v \rangle$ is given by the *integral*

$$\langle v \rangle = \int_0^{\infty} v f(v) dv$$

and the root-mean-squared speed v_{rms} may be obtained from

$$v_{\text{rms}}^2 = \int_0^{\infty} v^2 f(v) dv \quad \square$$

We will not present the mathematical details of these calculations for the three characteristic speeds, but the results are as follows:

$$\text{the most probable speed} \quad v_{\text{prob}} = \sqrt{\frac{2kT}{m}} \quad (32)$$

$$\text{the average speed} \quad \langle v \rangle = \sqrt{\frac{8kT}{\pi m}} \quad (33)$$

$$\text{the root-mean-squared speed} \quad v_{\text{rms}} = \sqrt{\frac{3kT}{m}} \quad (\text{Eqn 12})$$

We have already derived the expression for v_{rms} in [Subsection 2.5](#), on the basis of a comparison with the ideal gas law; it is reassuring that this result is also derivable from the Maxwell–Boltzmann speed distribution.

Also, Equation 12

the root-mean-squared speed $v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$ (Eqn 12)

confirms that the average kinetic energy per molecule ($\frac{1}{2}mv_{\text{rms}}^2$) is $3kT/2$, in agreement with Equation 10.

$$\langle \epsilon_{\text{tran}} \rangle = \frac{3}{2} kT \quad (\text{Eqn 10})$$

All three characteristic speeds

the most probable speed $v_{\text{prob}} = \sqrt{\frac{2kT}{m}}$ (Eqn 32)

the average speed $\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$ (Eqn 33)

the root-mean-squared speed $v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$ (Eqn 12)

are proportional to $(T/m)^{1/2}$, but it is apparent from the numerical factors involved that $v_{\text{rms}} > \langle v \rangle > v_{\text{prob}}$.

Figure 7 shows the relationship between v_{prob} , $\langle v \rangle$ and v_{rms} for the Maxwell–Boltzmann speed distribution.

For *any* distribution (where there is a spread of speeds) it is generally true that $v_{\text{rms}} > \langle v \rangle$, but the special results shown in Figure 7 and given by Equations 32, 33 and 12

$$v_{\text{prob}} = \sqrt{\frac{2kT}{m}} \quad (\text{Eqn 32})$$

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} \quad (\text{Eqn 33})$$

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} \quad (\text{Eqn 12})$$

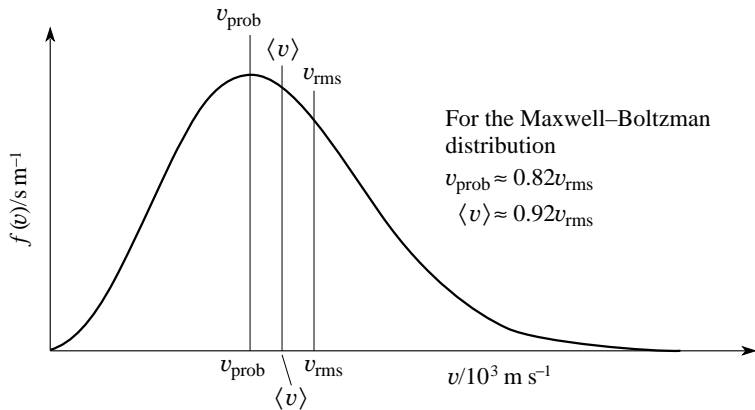



Figure 7 The relationship between v_{prob} , $\langle v \rangle$ and v_{rms} for the Maxwell–Boltzmann speed distribution.


are specific to the Maxwell–Boltzmann speed distribution. These inequalities lead to the interesting point that, for any distribution, the molecule with the average speed is *not* the molecule with the average kinetic energy!

Question T12

Suppose we have a very simple speed distribution involving only five molecules.

In arbitrary units  their speeds are 1, 2, 2, 3 and 4.

Calculate the three characteristic speeds for this distribution (not Maxwell–Boltzmann) and show that $v_{\text{rms}} > \langle v \rangle > v_{\text{prob}}$.

Explain why $v_{\text{rms}} > \langle v \rangle$ is likely to be true for *any* distribution. 



Question T13

Calculate v_{prob} , $\langle v \rangle$ and v_{rms} for helium at a temperature of 300 K. The mass of a helium atom is 6.65×10^{-27} kg.



3.2 The distribution of molecular kinetic energies

We can use the Maxwell–Boltzmann speed distribution to determine how the kinetic energies of the molecules are distributed around the mean kinetic energy, $3kT/2$. A molecule with speed v has translational kinetic energy $\epsilon_{\text{tran}} = mv^2/2$. The number of molecules, $n(v)\Delta v$, having speeds within a narrow range between v and $(v + \Delta v)$ will also have translational kinetic energies in the range ϵ_{tran} to $(\epsilon_{\text{tran}} + \Delta\epsilon_{\text{tran}})$; we will call this number $n_\epsilon(\epsilon_{\text{tran}})\Delta\epsilon_{\text{tran}}$. The numbers in this speed interval and this energy interval are clearly equal, since they are the same molecules.

Therefore we can write

$$n(v)\Delta v = n_\epsilon(\epsilon_{\text{tran}})\Delta\epsilon_{\text{tran}}$$

Using Equation 29

$$n(v)\Delta v = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp(-mv^2/2kT) \Delta v \quad (\text{Eqn 29})$$

and substituting $\epsilon_{\text{tran}} = mv^2/2$ we have

$$n(v)\Delta v = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} \left(\frac{2\epsilon_{\text{tran}}}{m} \right) \exp(-\epsilon_{\text{tran}}/kT) \Delta v = n_\epsilon(\epsilon_{\text{tran}})\Delta\epsilon_{\text{tran}}$$

$$\text{or } n_{\epsilon}(\epsilon_{\text{tran}}) \left(\frac{\Delta \epsilon_{\text{tran}}}{\Delta v} \right) = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} \left(\frac{2\epsilon_{\text{tran}}}{m} \right) \exp(-\epsilon_{\text{tran}}/kT)$$

Finding an explicit formula for $n_{\epsilon}(\epsilon_{\text{tran}})$ in terms of ϵ_{tran} (similar to the expression for $n(v)$ in terms of v implied by Equation 30)

$$f(v)\Delta v = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp(-mv^2/2kT) \Delta v \quad (\text{Eqn 30})$$

requires that we express $(\Delta \epsilon_{\text{tran}}/\Delta v)$ in terms of ϵ_{tran} . This is done by noting that

$$\begin{aligned} \Delta \epsilon_{\text{tran}} &= \frac{1}{2} m(v + \Delta v)^2 - \frac{1}{2} mv^2 = \frac{1}{2} mv^2 + mv\Delta v + \frac{1}{2} m(\Delta v)^2 - \frac{1}{2} mv^2 \\ &= mv(\Delta v) + \frac{1}{2} m(\Delta v)^2 \end{aligned}$$

But, since the speed range is narrow, Δv is small and the term involving $(\Delta v)^2$ can be ignored.

Thus $\Delta \epsilon_{\text{tran}} \approx mv\Delta v$

$$\text{and } \frac{\Delta \epsilon_{\text{tran}}}{\Delta v} \approx mv = \sqrt{2m\epsilon_{\text{tran}}}$$



We therefore have

$$n_{\varepsilon}(\varepsilon_{\text{tran}}) = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} \left(\frac{2\varepsilon_{\text{tran}}}{m} \right) \left(\frac{1}{2m\varepsilon_{\text{tran}}} \right)^{1/2} \exp(-\varepsilon_{\text{tran}}/kT)$$

$$\text{i.e.} \quad n_{\varepsilon}(\varepsilon_{\text{tran}}) = 2\pi N \left(\frac{1}{\pi kT} \right)^{3/2} \varepsilon_{\text{tran}}^{1/2} \exp(-\varepsilon_{\text{tran}}/kT) \quad (34)$$

for the distribution of molecular translational kinetic energy. As before we can use our knowledge of $n_{\varepsilon}(\varepsilon_{\text{tran}})$ to write down a **Maxwell–Boltzmann energy distribution function**, $f_{\varepsilon}(\varepsilon_{\text{tran}}) = n_{\varepsilon}(\varepsilon_{\text{tran}})/N$, such that $f_{\varepsilon}(\varepsilon_{\text{tran}})\Delta\varepsilon_{\text{tran}}$ is the probability that a molecule chosen at random will have energy in the narrow range $\varepsilon_{\text{tran}}$ to $\varepsilon_{\text{tran}} + \Delta\varepsilon_{\text{tran}}$.

Figure 8 shows the energy distribution function for the same three temperatures used for the speed distributions shown in [Figure 6](#).

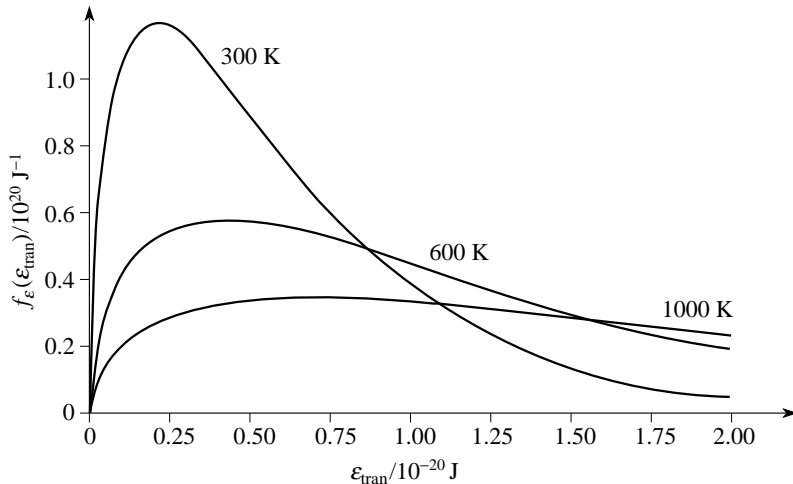


Figure 8 The distribution of molecular kinetic energies associated with the speed distribution. The Maxwell–Boltzmann energy distribution function for a sample of gas at the same three temperatures used for the speed distributions shown in Figure 6.

It is interesting to note
(from Equation 34)

$$n_{\epsilon}(\epsilon_{\text{tran}}) = 2\pi N \left(\frac{1}{\pi kT} \right)^{3/2} \times \\ \epsilon_{\text{tran}}^{1/2} \exp(-\epsilon_{\text{tran}}/kT) \quad (\text{Eqn 34})$$

that *the energy distribution is determined only by the temperature and is independent of the molecular mass*; this extends the observation we made in [Subsection 2.4](#), that the *average* molecular kinetic energy is determined only by the temperature and is independent of the molecular mass. This is in contrast to the average speeds and the distributions over speed which *are* dependent on the molecular masses, as expected from [Subsection 2.5](#).

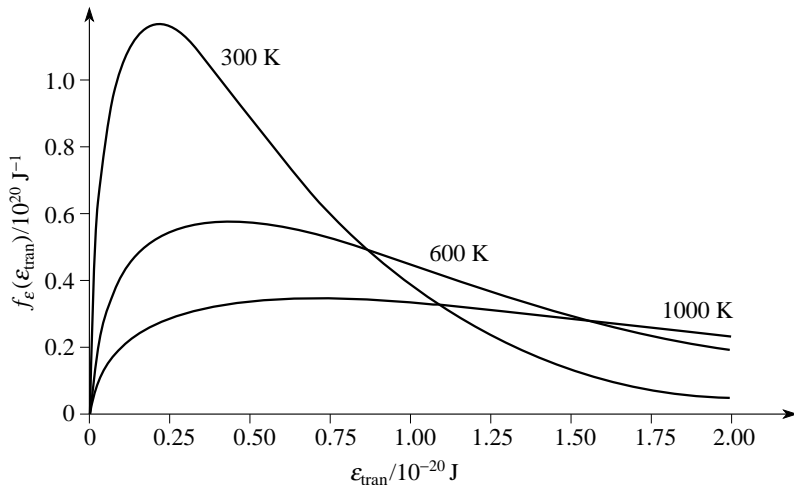



Figure 8 The distribution of molecular kinetic energies associated with the speed distribution. The Maxwell–Boltzmann energy distribution function for a sample of gas at the same three temperatures used for the speed distributions shown in Figure 6.

3.3 Applications and verification of the speed distribution

In [Section 2](#) we were able to relate the microscopic molecular behaviour of a gas to its macroscopic properties of pressure and temperature. This relationship did not involve any particular speed distribution but only required there to be an average molecular translational kinetic energy. In contrast, there are other properties of gases which *do* depend on the details of the speed distribution. Examples of such properties are:

- 1 The inter-mixing of gases (same or different) when there are local differences of concentrations present; this process is called [diffusion](#).
- 2 [Viscosity](#) or gas friction, in which layers of gas in relative motion tend to inter-mix and thereby reduce the relative motion.
- 3 [Thermal conduction](#), when there are temperature gradients present in a gas, in which inter-mixing of gas from the hot and cold regions tends to equalize the average speeds and hence the temperatures in each region.

You will realize that these three properties are related in that they are each controlled by the rate of molecular inter-mixing, or how quickly molecules can find their way from one region to another region of the gas. This rate will be limited due to intermolecular collisions, which slow down the rate of transport. It is perhaps not surprising then that these three properties are collectively known as [transport processes](#). These transport processes can each be predicted assuming the speed distribution and the agreement between the predicted and measured properties then gives strong indirect support for the validity of the Maxwell–Boltzmann speed distribution itself .

The validity of the Maxwell-Boltzmann speed distribution can also be demonstrated from direct measurement of the distribution of molecular speeds in a gas. How can we accomplish this? We cannot measure the speed of individual molecules, so we need to make some measurement that directly depends on their speeds. One method of performing such measurements is shown in Figure 9. We generally begin by taking a container of gas and place a fine slit in the side (termed a nozzle). When molecules from inside strike the slit space they emerge from the slit. If the region beyond the slit is a good vacuum these emerging molecules continue on in the same direction.

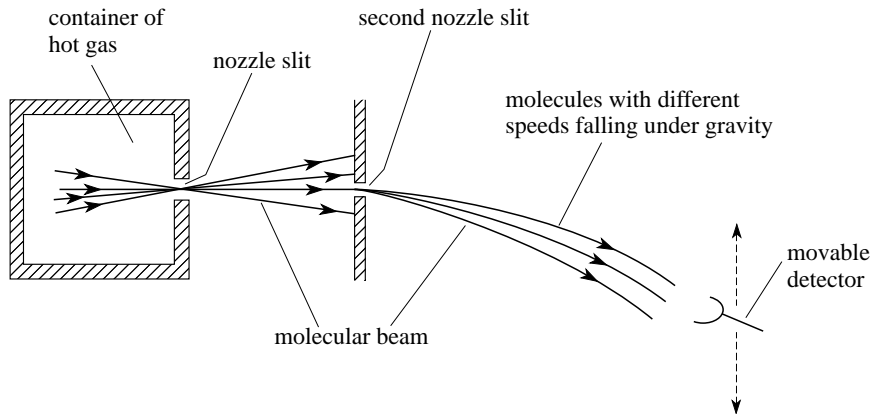



Figure 9 A method of measuring molecular speeds that can be used to demonstrate the Maxwell-Boltzmann speed distribution. The whole apparatus is enclosed in a sealed evacuated chamber.

If we then interpose a second fine slit some distance downstream we will select only those molecules travelling in a particular direction. Such a beam, with a well-defined direction, is called a **molecular beam**.

Molecules in such a molecular beam, when launched horizontally, will tend to fall due to gravity and if the vertical drop to a distant detector is measured this can be related to the time of flight and hence to the molecular speed. Careful interpretation  of the numbers of molecules arriving as a function of the distance dropped confirms the form of the speed distribution, but the details of the method do not concern us here.

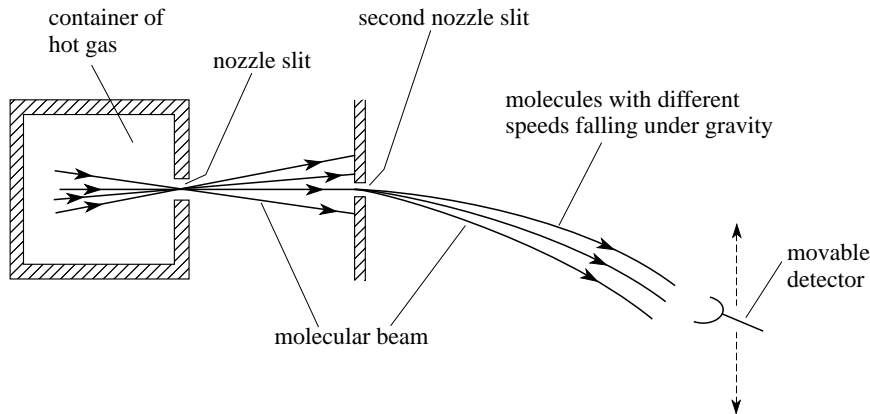


Figure 9 A method of measuring molecular speeds that can be used to demonstrate the Maxwell–Boltzmann speed distribution. The whole apparatus is enclosed in a sealed evacuated chamber.

3.4 Summary of Section 3

The Maxwell–Boltzmann speed distribution for a gas has been introduced but not derived. This distribution gives the numbers of molecules within a narrow speed range as a function of the speed. From this expression it is possible to identify three characteristic speeds for a gas: these are the most probable speed, the average speed and the root-mean-squared speed — arranged in order of increasing magnitude. The distribution of molecular kinetic energies associated with the Maxwell–Boltzmann speed distribution has been derived from the speed distribution and this is seen to be independent of the molecular mass, being determined only by the temperature. Finally, both indirect and direct evidence in support of the Maxwell–Boltzmann speed distribution has been given in terms of transport processes and the speeds in molecular beams, respectively.

4 A more realistic model of a gas

4.1 Van der Waals equation of state

It was discovered through careful measurements in the 19th century that the ideal gas equation of state was only an approximation to the true behaviour of real gases. The Dutch physicist Johannes van der Waals (1837–1923) devised the following generalization to the ideal gas equation of state in order to describe more accurately the behaviour of real gases.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad (35)$$

This is known as [van der Waals equation of state](#).

In this equation, V_m represents the volume per mole; a and b can be regarded as empirical constants, although they have a theoretical interpretation in terms of a kinetic theory model.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad (\text{Eqn 35})$$

The values of a and b vary from one gas to another, as indicated in Table 1. We want to consider briefly what the physical origin of such terms might be in terms of our kinetic theory model of a gas.

Question T14

What should be the dimensions of a and b in order that Equation 35 should be dimensionally consistent? Are the units in Table 1 appropriate? ☐



Table 1 Values of van der Waals constants a and b for various gases.

	$a/10^{-1} \text{ m}^6 \text{ Pa mol}^{-2}$	$b/10^{-5} \text{ m}^3 \text{ mol}^{-1}$
helium (He)	0.035	2.4
nitrogen (N ₂)	1.41	3.91
oxygen (O ₂)	1.38	3.18
xenon (Xe)	4.25	5.10

4.2 Excluded volumes

In [Subsection 2.4](#), in deriving the ideal gas equation of state, we ignored the volume taken up by the gas molecules themselves. Although reasonable, this approximation has repercussions. For example, the ideal gas equation of state implies that the volume of the gas approaches zero when the temperature approaches zero, whereas in reality the minimum volume that the gas can occupy must exceed the total molecular volume.

If we consider the molecules to be perfect spheres of radius r , then on touching, the molecules will be separated by $2r$. This means that the centre of a second molecule will be excluded from a sphere of radius $2r$, whose volume equals $\frac{4}{3}\pi(2r)^3$, which is eight times the individual molecular volume. Thus the [excluded volume per molecule](#) for spheres is *four* times the molecular volume.

For one mole of gas, the total volume excluded by the finite size of the molecules will be $N_A \times 4 \times v_m$, where v_m is the individual molecular volume. We might then predict that the appropriate generalization for the ideal gas would be to replace the volume per mole, V/n , by $(V_m - 4v_m N_A)$. This identifies the constant b in the van der Waals equation of state with $4v_m N_A$.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad (\text{Eqn 35})$$

4.3 Intermolecular forces

We now test our assumption that the long-range forces between molecules are negligible. Figure 10 shows a typical variation in (a) **intermolecular force**, and (b) the corresponding potential energy curves for the interaction between two molecules.


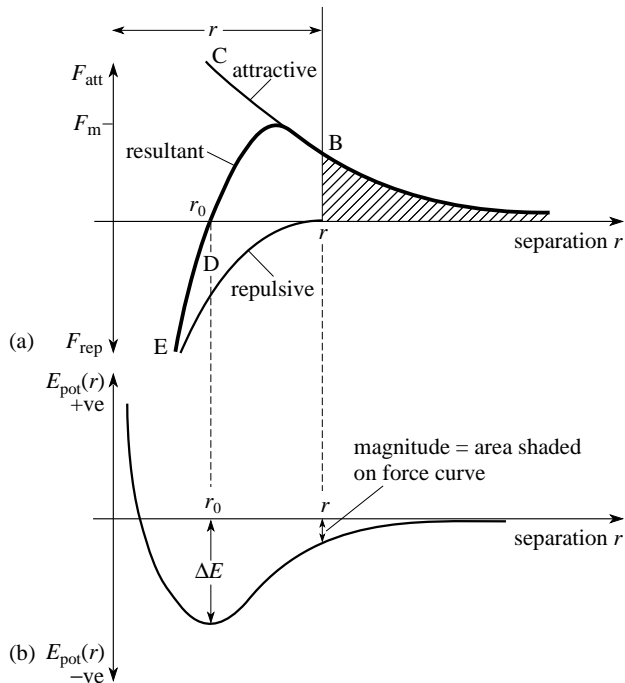
Figure 10a shows that there is a large repulsive force between molecules when they are very close to each other, and a relatively weak attractive force at larger separations .

Figure 10 Typical variation of (a) the intermolecular force and (b) the corresponding potential energy for two molecules separated by a distance r . When the molecules are very close together there is a repulsive force (as at point E), when they are far apart the force is attractive (as at B).




This is to be expected, since we know that most gases will condense to form a liquid if we cool them enough, and this would only happen if there were an attractive force that pulled the molecules together (this was actually van der Waals motivation in deriving his equation). The short-range strong repulsion accounts for the collisional forces and the success of the hard sphere model. What effect will the weak long-range attractive force have on the ideal gas equation of state? Let us consider a single reference molecule as it moves towards a wall.

In the centre of the volume of gas, there will be (*on average*) an equal number of gas molecules on all sides of our reference molecule, so that the net force will be approximately zero. When our reference molecule approaches a wall of the container, there will be more gas molecules on the side away from the wall than on the side toward the wall, and ultimately (just before the collision with the wall) all other gas molecules will be on the side away from the wall. The reference molecule will then feel a weak attraction from the remaining molecules in the gas, which will tend to *reduce its velocity before impact* with the wall and hence reduce the change in momentum on colliding with the wall. This will *reduce the effective pressure* compared with the gas at the same temperature but without such attractive forces.

What form will this reduction take? The reduction in pressure must depend on the size of the attractive force on each molecular impact and on the number of these impacts per second. The force depends on the number of molecules in the gas which are within range, and for a fixed number of molecules (e.g. per mole) this will depend inversely on the volume. Also, for a fixed number of molecules, the rate of molecular impacts depends on the pressure — which also will depend inversely on the volume. These two multiplying factors, each proportional to $1/V_m$, suggest that the effective pressure reduction should be proportional to $1/V_m^2$. Since we have not evaluated any actual forces, we can only say that the pressure should be less by some term proportional to $1/V_m^2$. This effect is reproduced by replacing the term P in the ideal gas equation of state by a term $(P + a/V_m^2)$, as in the van der Waals equation of state, to restore the effective pressure reduction.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad (\text{Eqn 35})$$

Question T15

If there is an appreciable attractive force between the molecules of the gas, there should be a similar attractive force between the gas molecules and the molecules of the containing walls. Consider the effect of this additional force on the molecular encounters with the wall and argue what effect this will have on the pressure exerted on the walls by the gas. 



5 Closing items

5.1 Module summary

- 1 The *macroscopic* or bulk properties of an *ideal gas*, as given by the *ideal gas law*

$$PV = nRT \quad (\text{Eqn 1})$$

can be derived from a simple *microscopic* model of the behaviour of molecules within the gas, based on certain fundamental assumptions. This model is known as the *kinetic theory*.

- 2 The kinetic theory calculation of the pressure due to an ideal gas leads to a form of the equation of state which allows us to associate the average translational kinetic energy per molecule with the absolute temperature. This enables us to give a microscopic interpretation to the macroscopic concept of *temperature*.

$$PV = \frac{2}{3} N \langle \epsilon_{\text{tran}} \rangle \quad (\text{Eqn 7})$$

$$\langle \epsilon_{\text{tran}} \rangle = \frac{3}{2} kT \quad (\text{Eqn 10})$$

where $k = \frac{nR}{N} = \frac{R}{N_A}$ is *Boltzmann's constant*.

- 3 The kinetic theory can also be used to give microscopic interpretations of the internal energy and *specific heats* of gases, in terms of the number of molecular *degrees of freedom* q and the *equipartition of energy theorem*.

$$E_{\text{int}} = \frac{q}{2} NkT \quad (\text{Eqn 15})$$

$$C_V = \frac{q}{2} R \quad \text{and} \quad C_P = \left(1 + \frac{q}{2}\right) R \quad (\text{Eqns 18 and 24})$$

$$\text{so} \quad C_P - C_V = R \quad \text{and} \quad \gamma = \frac{C_P}{C_V} = 1 + \frac{q}{2} \quad (\text{Eqns 22 and 23})$$

- 4 The *mean free path* is the average distance travelled by molecules between collisions. The *mean free time* is the average time between collisions. A value for these, given specified conditions, can also be calculated from kinetic theory.

- 5 The random nature of molecular motion leads to an expression for the distribution of speeds among the gas molecules; this is the Maxwell–Boltzmann speed distribution.

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

The distribution can be characterized in terms of a most probable speed, an average speed and a root-mean-squared speed. The Maxwell–Boltzmann speed distribution has been verified experimentally, indirectly through its effect on transport processes and directly by measuring molecular speeds in a molecular beam.

- 6 The van der Waals equation of state

$$\left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT \quad (\text{Eqn 35})$$

provides a more accurate description of real gases than the ideal gas equation. Its empirically determined parameters can be explained in terms of modifications to the simple kinetic theory, through excluded volumes and intermolecular forces.

5.2 Achievements

Having completed this module, you should be able to:

- A1 Define the terms that are emboldened and flagged in the margins of the module.
- A2 Describe and explain the basic assumptions underpinning the kinetic theory of gases.
- A3 Explain qualitatively how the kinetic theory model of a gas is in accord with the ideal gas equation of state $PV = nRT$.
- A4 Make approximate calculations of mean free paths and mean free times, given appropriate molecular data.
- A5 Carry out simple calculations based on the kinetic theory equation

$$PV = \frac{2}{3} N \langle \epsilon_{\text{tran}} \rangle \quad (\text{Eqn 7})$$

- A6 Recall and explain the significance of the equation

$$\langle \epsilon_{\text{tran}} \rangle = \frac{3}{2} kT \quad (\text{Eqn 10})$$

and use it in calculations.

- A7 Explain the interpretation of the internal energy of a gas in terms of the kinetic theory model and calculate internal energies and specific heats in terms of degrees of freedom for different types of molecules.
- A8 Recall the equation relating v_{rms} to absolute temperature and molecular mass and be able to use it in calculations.
- A9 Explain what is meant by the Maxwell–Boltzmann speed distribution, sketch its form and briefly explain how it may be tested.
- A10 Distinguish between the quantities v_{prob} , $\langle v \rangle$ and v_{rms} for the Maxwell–Boltzmann speed distribution and explain why they differ and how their magnitudes compare (without detailed formulae).
- A11 Describe the physical reasoning behind the modifications to the ideal gas equation of state which lead to the van der Waals equation of state.
- A12 Use the van der Waals equation of state to calculate physical parameters.

Study comment You may now wish to take the [Exit test](#) for this module which tests these Achievements. If you prefer to study the module further before taking this test then return to the [Module contents](#) to review some of the topics.

5.3 Exit test

Study comment Having completed this module, you should be able to answer the following questions each of which tests one or more of the Achievements.

You may need to use the following values in the *Exit test* questions.

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$k = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

Question E1

(A2 and A3) Summarize the key assumptions of the kinetic theory of ideal gases. Explain how the concept of randomness is crucial to the theory.



Question E2

(A4) The mass density of helium gas at a temperature of 273 K and a pressure of 1.01×10^5 Pa is 0.178 kg m^{-3} and the mean free path is found to be 285 nm. The mass of one mole of helium is 4.00 g.

Using the kinetic theory model:

- (a) What is the number density for helium under these conditions?
- (b) What is the effective atomic diameter?



Question E3

(A5 and A6) Fifteen moles of a monatomic ideal gas are at a pressure of 1.8×10^5 Pa in a container of volume 0.25 m^3 .

- (a) What is the temperature of the gas?
- (b) What is the average kinetic energy of a gas molecule?



Question E4

(A7) 2.0 moles of a monatomic ideal gas and 2.0 moles of a diatomic ideal gas (with no vibrational degrees of freedom) are at a common temperature of 300 K. What are the total internal energies of the two gases?



Question E5

(A7 and A8) Normal dry air is composed (by volume) mainly of N_2 (78.08%), O_2 (20.94%), and Ar (0.93%), with a variety of other constituents making up the remaining 0.05%. The mass of one mole of each of these gases is 28.01 g, 32.00 g and 39.95 g, respectively.

(a) At a temperature of 295 K, what are the root-mean-squared speeds of the three main constituents of dry air?

(b) Dry air has a specific heat at constant volume of approximately $20.5 \text{ J mol}^{-1} \text{ K}^{-1}$. If the specific heat of a mixture of gases can be taken as the sum of the specific heats due to each gas, is this consistent with air as a mixture of ideal gases, as above?



Question E6

(A8 and A10) Nitrogen molecules in a container are found to have a root-mean-squared speed of 521 m s^{-1} and a molar mass (i.e. mass per mole) of $28.01 \times 10^{-3} \text{ kg mol}^{-1}$.

- (a) Assuming ideal gas behaviour, what is the temperature of the gas?
- (b) What are the average and most probable speeds for nitrogen molecules in this gas?
- (c) What is the ratio $\langle v^2 \rangle / \langle v \rangle^2$ for this gas? Will this ratio change if the gas is heated?



Question E7

(A9) Briefly *describe* the sort of experimental evidence which supports the Maxwell–Boltzmann speed distribution.



Study comment This is the final *Exit test* question. When you have completed the *Exit test* go back to Subsection 1.2 and try the [*Fast track questions*](#) if you have not already done so.

If you have completed **both** the *Fast track questions* and the *Exit test*, then you have finished the module and may leave it here.

