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Molecules in motion: the kinetic theory of gases

Learning objectives

After careful study of this chapter you should be able to:

(1) Specify the *kinetic theory* model of a perfect gas, Introduction.

(2) Use the kinetic theory to calculate the *pressure* exerted by a perfect gas, eqn (26.1.2).

(3) Define the *mean value* of discrete, eqn (26.1.6), and continuous, eqn (26.1.7), distributions.

(4) Derive and use the *Maxwell–Boltzmann distribution of velocities*, eqn (26.1.8), and the *Maxwell distribution of speeds*, eqn (26.1.9) and Example 26.1.

(5) Calculate the *mean speed*, eqn (26.1.10), the *r.m.s. speed*, eqn (26.1.11), and the *most probable speed*, eqn (26.1.12), of particles in a gas.

(6) Define *collision cross-section*, Section 26.2(a), and calculate the *collision frequency*, eqns (26.2.2) and (26.2.5) and Example 26.2, and the *mean free path*, eqn (26.2.6) and Example 26.3, of particles in a gas.

(7) Calculate the frequency of collisions with a surface, eqn (26.2.9).

(8) Explain the term *transport property* and define *flux*, Section 26.3(a).

(9) State *Fick's First Law* of diffusion, eqn (26.3.1).

(10) Calculate the *rate of effusion* of a gas through a hole, eqn (26.3.4), state and justify *Graham's Law*, and use *Knudsen's method* to measure vapour pressure, Example 26.4.

(11) Derive Fick's Law and calculate the *diffusion coefficient* of a perfect gas, eqn (26.3.6).

(12) Calculate the *thermal conductivity* of a gas, eqn (26.3.11) and Example 26.5, and account for its properties.

(13) Calculate the *viscosity* of a gas, eqn (26.3.13), and account for its properties.

(14) Describe how gas viscosities are measured, Section 26.3(e) and Example 26.6.

Introduction

We saw in the Introduction (Section 0.2(e)) that the *kinetic theory*, in which the particles are assumed to move freely, allows us to calculate a number of properties of a perfect gas. That brief outline is the starting point of this chapter, and should be reviewed. We sharpen the argument in this chapter, and go on to find expressions for some of the more interesting properties of gases.

The kinetic theory is based on three assumptions:

(1) The gas consists of a swarm of particles of mass m and diameter d in continual random motion.

(2) The size of the particles is negligible (in the sense that their diameters are much smaller than the average distance travelled between collisions).

(3) The particles do not interact, except that they make perfectly elastic collisions when the separation of their centres is equal to d.

An 'elastic collision' means that the total translational kinetic energy of a pair is the same before and after a collision: no energy is transferred to their rotational or vibrational modes.

The collisions ensure that the particles constantly change their speed and direction. The *collision frequency* (symbol: z) is the average number of collisions per unit time made by a single particle. The *mean free path* (symbol: λ) is the average distance a particle travels between collisions. This means that Assumption 2 can be expressed as $d \ll \lambda$. It should be noted that since any mechanical property can be expressed as a combination of quantities with dimensions of mass, length, and time, and that since m, λ, and $1/z$ are quantities with these dimensions, once they have been calculated we can find expressions for any mechanical property of a gas by forming suitable combinations.

26.1 The basic calculations

There are two basic calculations in kinetic theory: one leads to an expression for the pressure, the other to an expression for the distribution of velocities of the particles.

26.1 (a) The pressure of a gas

Pressure is force per unit area. The kinetic theory accounts for the steady pressure exerted by a gas in terms of collisions of the particles with the walls of the container (but this is an inessential simplification: the pressure can be defined and calculated in the absence of walls). These collisions are so numerous that the walls experience a virtually constant force.

Consider the system in Fig. 26.1. When a particle of mass m collides with the shaded wall its component of momentum parallel to the x-axis changes from mv_x to $-mv_x$, its other components remaining unchanged. The momentum therefore changes by $2|mv_x|$ on each collision. The number of collisions in an interval Δt is equal to the number of particles able to reach the wall in that time. Since a particle with velocity component v_x can travel a distance $|v_x|\Delta t$ in a time Δt, all the particles within a distance $|v_x|\Delta t$ of the wall will strike it if they are travelling towards it. If the wall has area A, all the particles in a volume $A|v_x|\Delta t$ will reach the wall (if they are

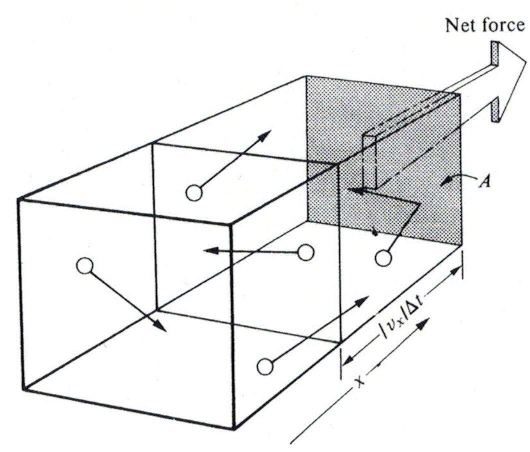

Fig. 26.1. The calculation of the pressure of a gas considers the total force exerted on the shaded wall by the colliding particles. In an interval Δt, all particles within the volume $A\,|v_x|\,\Delta t$ and moving towards the wall strike it and undergo a reversal of their x-component of momentum.

travelling towards it). If the number of particles per unit volume (the *number density*) is $\mathcal{N}$, the number in the volume $A|v_x|t$ is $\mathcal{N}A|v_x|\Delta t$. On average, half these particles are moving to the right, and half are moving to the left, and so the average number of collisions with the wall during the interval Δt is $\frac{1}{2}A|v_x|\mathcal{N}\Delta t$. The total momentum change in that interval is the product of this number and the change $2m|v_x|$:

$$\textit{Momentum change} = \{\tfrac{1}{2}\mathcal{N}A|v_x|\Delta t\}\{2m|v_x|\} = m\mathcal{N}Av_x^2\Delta t.$$

The *rate of momentum change* is therefore $m\mathcal{N}Av_x^2$. The rate of change of momenum is equal to the *force* (by Newton's Law), and so the force exerted by the gas on the wall is $m\mathcal{N}Av_x^2$. It follows that the *pressure*, the force per unit area, is $m\mathcal{N}v_x^2$.

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

$$p = m\mathcal{N}\langle v_x^2\rangle.$$

Since the particles are moving randomly, the average of v_x^2 is the same as the average of the corresponding quantities in the y and z directions. Furthermore, since $v^2 = v_x^2 + v_y^2 + v_z^2$, the *mean square speed* (symbol: c^2) of the particles is

$$c^2 = \langle v^2\rangle = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle = 3\langle v_x^2\rangle. \qquad (26.1.1)$$

The square root of this quantity is the *root mean square speed* (symbol: c; $c = \langle v^2\rangle^{\frac{1}{2}}$). Therefore,

$$p = \tfrac{1}{3}\mathcal{N}mc^2. \qquad (26.1.2)^\circ$$

This is one of the key equations of kinetic theory. (The convention in Parts 1 and 2 is that a superscript ° signifies a perfect gas; by extension it now also means a result stemming from kinetic theory.)

The number density is equal to N/V, where N is the total number of particles present in the volume V. Then, since $N = nN_A$, where N_A is Avogadro's constant,

$$pV = \tfrac{1}{3}nN_Amc^2. \qquad (26.1.3)^\circ$$

Since we know that a perfect gas satisfies the equation of state $pV = nRT$, we can conclude at once that

$$c = \{3kT/m\}^{\frac{1}{2}}, \qquad (26.1.4)^\circ$$

and so obtain an explicit expression for the root mean square speed of the particles at any temperature.

26.1 (b) Mean values and distributions

The expression for c gives only a mean value; in the gas the particles move with a variety of different speeds. In this section we derive the *Maxwell distribution*, which gives the probability that particles have any given speed.

Suppose we want the *mean value* (symbol: $\langle X\rangle$) of a property X which may take any of the values $X_1, X_2, \ldots, X_z$ (these are the possible *outcomes* of the observation), and in a series of N measurements we find that X_1 occurs N_1 times, X_2 occurs N_2 times, and so on. Then the mean value is