Chapter 4

The Kinetic Theory of Gases (1)

Topics

Motivation and assumptions for a kinetic theory of gases. Joule expansion. The role of collisions. Probabilities and how to combine them. The velocity distribution in 1- and 3D. Normalisation. The Maxwell-Boltzmann distribution. Mean energy in one and three dimensions.

4.1 Introduction

In the preceding sections we have discussed why we need a statistical description of complex physical systems. *Ideal gases* are the simplest systems to which we can apply our statistical description. In this Chapter and the next, we will develop the *kinetic theory of gases* and examine some of its consequences. The aim is to explain the *macroscopic properties* of gases, described in Section 1.3, in terms of molecular motions.

4.2 Motivation and Assumptions for a Kinetic Theory of Gases

The kinetic theory of gases is a splendid example of *model building in physics*. We find all the features of the best physical theories: the need to follow up clues in setting up the framework of the model, the need to understand clearly the simplifying assumptions on which the model is based and then the confrontation of the theory with the experimental evidence. At each stage, we need to assess the successes and failures of the model and consider carefully which successes are so compelling that the model must be along the correct general lines. Alternatively, the failures may be so serious that some new physical insight is needed to resolve the inconsistencies with the experimental evidence – it is all there in the kinetic theory of gases.

4.2.1 Clues: Joule expansion and the Earth's atmosphere

The starting point for the kinetic theory is the attempt to build a model for a gas based on the motions of individual atoms or molecules. We will often refer to gases as consisting of particles and it is to be understood that 'particle' may refer to an 'atom or molecule'.

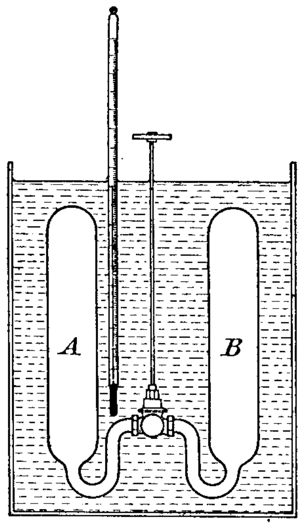


Figure 4.1. Joule's apparatus for investigating the internal work done by a gas during expansion. The dry air in volume A was initially at 22 atmospheres and B was evacuated.

What was not clear in the early 19th century was the nature of the attractive or repulsive forces acting *between* atoms or molecules. Important clues were provided by the great experiments of James Joule. One of his experiments concerned the expansion of gases from a smaller to a large volume (Fig. 4.1). The volume A was filled with dry air and the volume B evacuated. On opening the valve, no temperature change in the thermometer reading in the surrounding heat bath could be detected, although he could have detected a change as small as 0.003 K. Suppose there were significant forces between the molecules of the gas. Then, when the gas expanded from A to (A + B), work would to be done either on or by the gas, resulting in a temperature change of the water. The null result of Joule's experiment meant that the forces between the atoms or molecules of the gas must be very weak indeed. To a first approximation, we can set them equal to zero (but see footnote).

Footnote
A footnote to this story is that, if very sensitive measurements are made, small changes in temperature can be measured, particularly if the gas is close to those temperatures and pressures at which the gas can change state. These small temperature changes provide information about the weak intermolecular forces in the gas. This phenomenon is known as the *Joule-Kelvin* or *Joule-Thomson effect.*

This completes what we need to define a *perfect gas*. A perfect gas has the following properties:

1. Its equation of state is $pV = NkT$;
2. No heat is liberated or absorbed in a Joule expansion.

The second clue is that the Earth's atmosphere exists and so the atoms and molecules of the gas must be in motion, since otherwise they would all fall to Earth, which would be very bad news.

Definition of a Perfect or Ideal Gas

1. Its equation of state is $pV = NkT$;
2. No heat is liberated or absorbed in a Joule expansion.

4.2.2 Assumptions Underlying the Kinetic Theory of Gases

The basic postulates of the model are as follows:

- Gases consist of particles, atoms or molecules, in motion. Each particle has kinetic energy $\frac{1}{2}mv^2$ and the velocities of the particles are in random directions.
- The particles are modelled as solid spheres, with very small, but finite, diameters a.
- The long-range forces between atoms are weak, being undetectable in a Joule expansion and are taken to be zero. The atoms can, however, collide with each other and with the walls of the containing vessel and when they do so they collide *elastically*, meaning that there is no loss of kinetic energy in each collision.
- The origin of the pressure on the walls of a vessel is the force per unit area due to the elastic collisions of enormous numbers of particles of the gas with the walls.
- The temperature is related to the average kinetic energy of the molecules of the gas. If we do work on the gas, we increase the kinetic energy of the particles.

Historical note: The key concept of the origin of pressure was published by Waterston in Edinburgh in 1843, 14 years before Clausius. Waterston's paper was sent to the Royal Society in 1845, but was rejected for publication by a harsh referee. Waterston's key contribution was only published by Lord Rayleigh in 1892, eight years after Waterston's death.

4.3 The Distribution of Velocities in a Perfect Gas

The evolution of the velocity distribution of the particles of a gas from an arbitrary initial distribution of velocities to a *normal* or *gaussian* distribution was demonstrated by the simulations in the last Chapter. The distribution is gaussian in both the x and y directions of that two-dimensional simulation and we would have obtained the same result if we had repeated it in three-dimensions. The key point was that, once the gaussian distribution is established, the velocity distribution in each direction remain unchanged, however long we let the simulation run. In other words, the average properties of the gas are constant; in particular, the mean energy of the particles in three-dimensions must be a constant. This energy can only be in the form of the kinetic energy of the particles, since there are no long-range forces between the particles. Therefore, it must be the case that, in thermal equilibrium:

$$\tfrac{1}{2}m\overline{v^2} = \text{constant}. \tag{4.1}$$

The main points to note are:

- Once equilibrium is established, the directions of velocity vectors are randomised by collisions and therefore the final state of the gas can be characterised by the gaussian distribution of particle velocities in the x, y and z directions and each particle by the speed v.
- The only energy term is the kinetic energy per particle $\frac{1}{2}mv^2$.

4.3.1 The 1-dimensional distribution function.

We can now relate the form of the distribution function to the Boltzmann distribution. We have already two vital clues. The first is that, empirically, from the simulations, we see that the one-dimension distribution is of the form

$$\begin{aligned} \mathrm{d}f_1(v_x) &\propto \exp\left(-\alpha v_x^2\right)\,\mathrm{d}v_x & (4.2)\\ &\propto \exp\left(-\alpha' E_x\right)\,\mathrm{d}v_x, & (4.3)\end{aligned}$$

since the only energy in the problem is the kinetic energy of the particle in the x-direction.

The second is that we know that the probability of an energy state being occupied in thermal equilibrium at temperature T is proportional to $\exp(-E/kT)$. It follows that the one-dimensional velocity distribution at temperature T must be

$$\mathrm{d}f_1(v_x) \propto \exp\left(-E/kT\right)\,\mathrm{d}v_x = \exp\left(-mv_x^2/2kT\right)\,\mathrm{d}v_x. \tag{4.4}$$

This is the *one-dimensional Maxwell distribution* which we have been seeking.

4.3.2 Probabilities and How to Combine Them

Let us revise the theory of combining probabilities. If we study some *event*, such as tossing a coin, in which we may or may not get a particular *outcome* A, such as getting a 'head', the *probability* p_{A} of A means the *expected fraction* of events in which A occurs.

We can mean two things by this 'expected fraction'. We can make a *theoretical* analysis. If we toss a *symmetrical* coin, the expected fractions of 'heads' and 'tails' must be equal and so each must be $\frac{1}{2}$. Alternatively, we can use the idea of *statistical convergence*: if we consider an increasingly large number of events, the fraction actually observed should approach the 'expected fraction'. Thus if we examine N events, and outcome A happens n_{A} times, we can define the probability p_{A} of A as

$$p_{\mathrm{A}} = n_{\mathrm{A}}/N \tag{4.5}$$

in the limit when N is very large.

- **Adding probabilities**

  When different outcomes are *alternatives*, we *add* their probabilities. For example, if we throw a die, in $\frac{1}{6}$ of the throws we get a 'three', and in *another* $\frac{1}{6}$ of the throws we get a 'five'. Therefore, in $\frac{1}{3}$ of the throws, we shall obtain either a 'three' or a 'five'. Thus

  $$p_{(\mathrm{A\ or\ B})} = p_{\mathrm{A}} + p_{\mathrm{B}}, \tag{4.6}$$

  if A and B are alternatives.

- **Multiplying probabilities**

  We are often interested in two outcomes A and B which can both happen in the same trial. For example, what is the probability that the next person to come into the room might be over 6 ft tall *and* blue-eyed? If 40% of people have blue eyes, and 10% of people are over 6 ft, what is the probability that the next person will be over 6 ft *and* blue-eyed? The answer depends on whether height and eye-colour are *statistically independent*. If they are, then to find the probability of obtaining both at once, we must *multiply* the probabilities: of the 40% who are blue-eyed, 10% will be over 6 ft and so 4% will be blue-eyed *and* over 6 ft. Thus

$$p_{(\mathrm{A\,and\,B})} = p_{\mathrm{A}} p_{\mathrm{B}} \tag{4.7}$$

4.3.3 The Three-dimensional Velocity Distribution

We can now extend the arguments which led to the one-dimensional Maxwell distribution to three dimensions. We need to determine the probability that the particles have components of velocity in the narrow range v_x to $v_x + \mathrm{d}v_x$, v_y to $v_y + \mathrm{d}v_y$, and v_z to $v_z + \mathrm{d}v_z$. We know the answer for each direction independently. Now, because of the randoming effects of the collision, these distributions are statistically independent and so the joint probability of find the particle with velocity in the range v_x to $v_x + \mathrm{d}v_x$, v_y to $v_y + \mathrm{d}v_y$, and v_z to $v_z + \mathrm{d}v_z$ is

$$\begin{aligned} f(v_x, v_y, v_z)\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z &= f_1(v_x)\,f_1(v_y)\,f_1(v_z)\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z \\ &\propto \exp\left(-mv_x^2/2kT\right)\,\mathrm{d}v_x \\ &\times \exp\left(-mv_y^2/2kT\right)\,\mathrm{d}v_y \\ &\times \exp\left(-mv_z^2/2kT\right)\,\mathrm{d}v_z, \qquad (4.8) \\ &= \exp\left[-m(v_x^2 + v_y^2 + v_z^2)/2kT\right]\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z \qquad (4.9) \end{aligned}$$

Therefore,

$$f(v)\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z \propto \exp\left(-mv^2/2kT\right)\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z, \tag{4.10}$$

since $v^2 = v_x^2 + v_y^2 + v_z^2$. The combination $\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$ defines an *element of volume in velocity space.*

Notation
We will use the convention that the one-dimensional velocity distribution will be written $f_1(v_x), f_1(v_y)$ and $f_1(v_z)$. The three-dimensional distribution for the speeds of the particles will be written $f(v)$. The probabilities associated with the Boltzmann factor will be written $p(E)$.

4.4 Normalisation of the Velocity Distributions

We have only one final step to determine the complete one- and three-dimensional probability distributions. We need to ensure that the total probability of finding the particle with some velocity in one or three dimensions is unity.

4.4.1 The One-dimensional Velocity Distribution

Taking the one-dimensional distribution first, this means that

$$\int_{-\infty}^{\infty} \mathrm{d}f_1(v_x) = A \int_{-\infty}^{\infty} \exp\left(-mv_x^2/2kT\right)\,\mathrm{d}v_x = 1. \tag{4.11}$$

Example: *Normalising the one-dimensional velocity distribution*
To find the normalisation constant A, we use the standard integral (see Maths Handbook)

$$\int_{-\infty}^{\infty} \mathrm{e}^{-x^2}\,\mathrm{d}x = \sqrt{\pi}.$$

We require

$$A \int_{-\infty}^{\infty} \mathrm{e}^{-mv_x^2/2kT}\,\mathrm{d}v_x = 1.$$

We transform the integral to standard form by substituting $x = v_x\sqrt{m/2kT}$. Then, remembering to substitute for the $\mathrm{d}v_x$ as well, we obtain

$$A\left(\frac{2kT}{m}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} e^{-x^2}\,dx = 1,$$

and solving gives $A = \sqrt{m/2\pi kT}$.

Hence, the one-dimensional velocity distribution function is as follows:

$$f_1(v_x) = \sqrt{\frac{m}{2\pi kT}}\, \mathrm{e}^{-mv_x^2/2kT} \qquad (4.12)$$

This expression is called the *Maxwell distribution of one-component velocity* and is shown in Figure 4.2. As we have discussed, this distribution has the form of the normal curve, a gaussian, and is symmetrical about the origin. The other components of velocity are distributed in the same way.

Let us use the function to determine the mean kinetic energy of a particle in the x-direction.

Example: *Calculate mean kinetic energy of one component of the velocity*
We calculate $\frac{1}{2}m\overline{v_x^2}$, that is,

$$\begin{aligned}\overline{v_x^2} &= \int_{-\infty}^{\infty} v_x^2\, f_1(v_x)\,\mathrm{d}v_x \\ &= \sqrt{\frac{m}{2\pi kT}} \int_{-\infty}^{\infty} v_x^2\, \mathrm{e}^{-mv_x^2/2kT}\,\mathrm{d}v_x\end{aligned}$$

We transform this integral to a standard form by setting $x = v_x \times \sqrt{m/2kT}$, then

$$\begin{aligned}\overline{v_x^2} &= \sqrt{\frac{m}{2\pi kT}} \left(\frac{2kT}{m}\right)^{3/2} \int_{-\infty}^{\infty} x^2\, \mathrm{e}^{-x^2}\,\mathrm{d}x \\ &= \sqrt{\frac{m}{2\pi kT}} \left(\frac{2kT}{m}\right)^{3/2} \times \frac{1}{2}\sqrt{\pi} \\ &= \frac{kT}{m}\end{aligned}$$

Therefore $\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}kT$

This is an important result – the average energy of one component of velocity is $\frac{1}{2}kT$. The same result must be true in the v_y and v_z directions as well. Thus,

$$\tfrac{1}{2}m\overline{v_x^2} = \tfrac{1}{2}m\overline{v_y^2} = \tfrac{1}{2}m\overline{v_z^2} = \tfrac{1}{2}kT. \qquad (4.13)$$

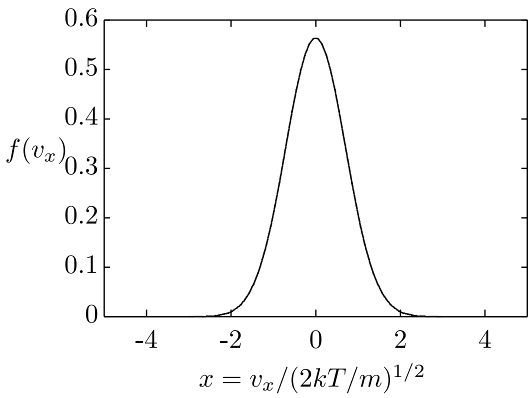
The One-dimensional Maxwell Distribution

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

Figure 4.2. One dimensional velocity distribution function

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

$$v_x = -\infty \to \infty$$



Note See the hint on page 10 of Chapter 2 for determining $\int_{-\infty}^{\infty} x^2\,\mathrm{e}^{-x^2}\,\mathrm{d}x$.

Example: *Show that* $\overline{v_x} = 0$
The mean x-component of velocity is given by

$$\overline{v_x} = \int_{-\infty}^{\infty} v_x f_1(v_x)\, dv_x = 0$$

since v_x is an odd function and $f_1(v_x)$ is even.

4.4.2 Distribution Function for the Speed - the Three-dimensional Maxwell Distribution

We have argued that the answer should only depend on the speed and so, to complete our analysis, we need to re-write our result for the normalised three-dimensional velocity distribution

$$f(v)\, \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z = \left(\frac{m}{2\pi kT}\right)^{3/2} \mathrm{e}^{-mv^2/2kT}\, \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z, \tag{4.14}$$

in terms of the speed v alone.

To find the distribution function in terms of v we note that there are many different combinations of velocity which give the same speed v. In the language of statistical physics, there is a degeneracy $g(v)\,\mathrm{d}v$. To find the probability of a given speed irrespective of the direction of the velocity, we must sum the volumes $\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$ in velocity space which all have the same speed; these form the region of velocity space in a narrow spherical shell between v and $v + dv$ where $v^2 = v_x^2 + v_y^2 + v_z^2$ – one octant of this spherical shell is shown in Figure 4.3. The complete shell has a volume $4\pi v^2 dv$ and so the corresponding distribution function is $f_1(v_x)\, f_1(v_y)\, f_1(v_z)\, 4\pi v^2\, \mathrm{d}v$. Therefore,

$$f(v)\, \mathrm{d}v = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2\, \mathrm{e}^{-mv^2/2kT}\, \mathrm{d}v. \tag{4.15}$$

The expression (4.15) is the *Maxwell-Boltzmann* distribution for the speeds of the particles and is shown in Figure 4.4.

In a similar fashion to our calculation for $\frac{1}{2}m\overline{v_x^2}$, we

Figure 4.3. Summing over all the vectors with magnitude v to $v + \mathrm{d}v$.

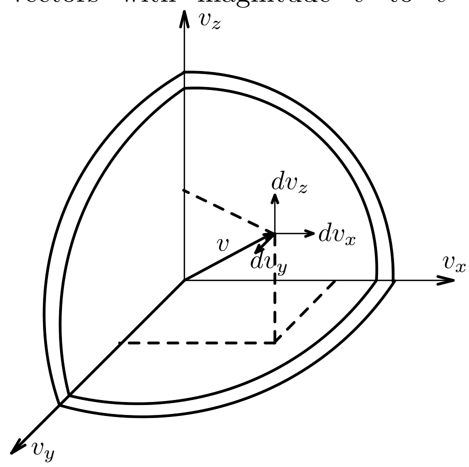
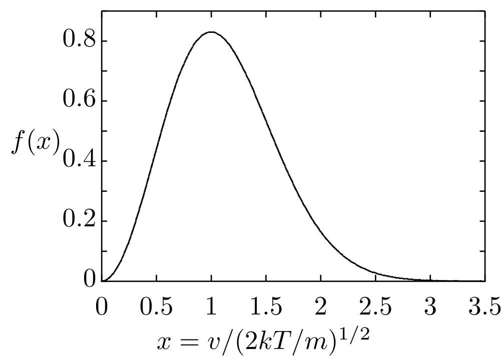


Figure 4.4. The Maxwell-Boltzmann distribution

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



The Maxwell-Boltzmann Distribution

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

can show that (see problem sheet):

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}kT \tag{4.16}$$

$$\overline{v} = \sqrt{\frac{8kT}{\pi m}} \tag{4.17}$$

Therefore, we find that

$$\tfrac{1}{2}m\overline{v_x^2} + \tfrac{1}{2}m\overline{v_y^2} + \tfrac{1}{2}m\overline{v_z^2} = \tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}kT. \tag{4.18}$$

Properties of the Maxwell-Boltmann Distribution

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}kT$$
$$\overline{v} = \sqrt{\frac{8kT}{\pi m}}$$

4.5 Summary

The *Maxwell Distribution*, or the *Maxwell-Boltzmann Distribution*, has the form

$$f(v)\,\mathrm{d}v = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right)\mathrm{d}v$$
$$= \underbrace{\left(\frac{m}{2\pi kT}\right)^{3/2}}_{\substack{\text{normalisation}\\ \text{constant}}} \times \underbrace{\exp\left(-\frac{mv^2}{2kT}\right)}_{\substack{\text{Boltzmann}\\ \text{factor}}} \times \underbrace{4\pi v^2\,\mathrm{d}v}_{\substack{\text{volume of}\\ \text{velocity space}}}$$

We have split up the expression into three parts.

- The *normalisation constant*

$$\left(\frac{m}{2\pi kT}\right)^{3/2} \tag{4.19}$$

  ensures that the integral over all velocities v is unity.

- The *Boltzmann factor*

$$p(E_i) \propto \exp\left(-\frac{E_i}{kT}\right) \tag{4.20}$$

  with $E_i = \frac{1}{2}mv^2$ describes the probability that a state of energy E_i will be occupied.

- The number of available states for particles with velocities between v and $v + \mathrm{d}v$ in velocity space,

$$g(v)\,\mathrm{d}v = 4\pi v^2\,\mathrm{d}v, \tag{4.21}$$

  describes the *degeneracy* of the state E_i, the total number of different ways of obtaining a total velocity $|\boldsymbol{v}|$.

Our next task is to apply these results to understand the properties of perfect gases.