TWO

THE KINETIC THEORY OF MATTER

In this chapter we shall study some aspects of kinetic theory, the first successful microscopic model of matter. We shall see how the first estimates and measurements were made of the size and number of molecules. The introduction to the statistical methods of distribution functions and averages in this chapter should prove valuable in Chapter 6, where the same methods are used in quantum mechanics.

The idea that all matter is composed of tiny particles, or atoms, dates back to the speculations of the Greek philosopher Democrites and his teacher Leucippus about 450 B.C. There was little attempt to correlate such speculations with observations of the physical world, however, until the seventeenth and eighteenth centuries. Pierre Gassendi, in the middle of the seventeenth century, and somewhat later Robert Hooke (now well known for his experiments with springs), attempted to explain the states of matter and transitions between them with a model of tiny indestructible solid objects flying in all directions.

In 1662, Robert Boyle published results of his experiments that showed that the product of the pressure and volume of a gas remains constant at constant temperature. Isaac Newton in his *Principia* (1687) showed that Boyle's law could be derived by assuming the gas to consist of hard *static* particles which repel each other with a force varying inversely with their separation. The first mathematical derivation of Boyle's law using a *kinetic* model was done by D. Bernoulli in 1738. Little more was done along these lines for nearly a century.

The nineteenth century saw a rapid development of the kinetic theory of matter by many people, notably Herapath, Waterston, Joule, Clausius, Maxwell, and Boltzmann. A parallel development of the theory of atoms took place in the beginning of the nineteenth century from attempts to understand the laws of chemistry. John Dalton in 1808 assumed that an element consisted of identical indestructible atoms to explain the law of definite proportions postulated by J. L. Proust (1754–1826); elements that make up a chemical compound always combine in the same definite proportions by weight. In the same year (1808), Joseph L. Gay-Lussac announced the law of combining volumes; when two gases combine to form a third, the ratios of the volumes are ratios of integers. He showed, for example, that when hydrogen combined with oxygen to form water vapor, the ratio of the volume of hydrogen to that of oxygen was 2 to 1 within 0.1 percent accuracy. (It is interesting to note that Dalton did not believe Gay-Lussac's law because it did not agree with his static atomic model, a model which he thought had been proved by Newton's derivation of Boyle's law. Dalton also had data less accurate than Gay-Lussac's; it showed deviations from ratios of integers.) In 1811 an Italian physicist, Amedeo Avogadro, proposed a remarkable hypothesis which, though not accepted for some time, eventually paved the way for the understanding of the atomic theory of chemistry. Avogadro assumed that:

1. Particles of a gas were small compared with the distances between them.
2. The particles of elements sometimes consisted of two or more atoms stuck together. These particles he called molecules to distinguish them from atoms.
3. Equal volumes of gases at constant temperature and pressure contained equal numbers of molecules.

Using these hypotheses along with the work of Gay-Lussac, Dalton, Proust, and others, Avogadro could work out the composition of molecules, and in particular he found that it was necessary to assume that the molecules of a gas such as hydrogen and oxygen contained two atoms. At first, few scientists believed these hypotheses, mainly because of the difficulty of understanding why, if two oxygen atoms attracted each other to form the molecule O_2, three or four atoms did not bind together. (This was not completely understood until the development of quantum mechanics.)

Avogadro's hypotheses were not really accepted until the latter half of the nineteenth century. It is interesting to note that he had no knowledge of the magnitude of the number of molecules in a given volume of gas, only that the number was very large. The first calculation of this number was done by Loschmidt in 1865 from the kinetic theory of gases.[1] We do not have the space in this brief introduction to go into more detail concerning the fascinating history of the discovery of the atomic theory of chemistry. The interested reader is referred to the excellent discussion in Ref. 1, on which much of this introduction is based. We shall investigate some of the important ideas of the kinetic theory developed in the latter part of the nineteenth century. Before we undertake this study, we need to understand the use of distribution functions.

2·1
DISTRIBUTION FUNCTIONS

Suppose a teacher gave a 25-point quiz to a large number, N, of students. In order to describe the results of the quiz, he might give the average score or the median score, but this would not be a complete description. For example, if all N students received 12.5, this is a quite different result than if $N/2$ students received 25 and $N/2$ received 0, though both results have the same average. A complete description would be to give the number n_i who received the score s_i for all scores s_i between 0 and 25. An alternative would be to divide n_i by the total number of students, N, to give the fraction of the students, $f_i = n_i/N$, receiving the score s_i. Either of the two functions of s_i, n_i or f_i, is called a *distribution function*. The fractional distribution, f_i, is slightly more convenient to use. The probability that one of the N students selected at random received the score s_i equals the number of students that received that score, $n_i = Nf_i$, divided by the total number N; thus this probability equals the distribution function f_i. Note that

$$\sum_{i=1}^{N} f_i = \sum_i \frac{n_i}{N} = \frac{1}{N}\sum_i n_i$$

and since

$$\sum_i n_i = N$$

we have

$$\sum_i f_i = 1 \tag{2-1}$$

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[1] This number is often called *Loschmidt's number*, particularly in Europe.

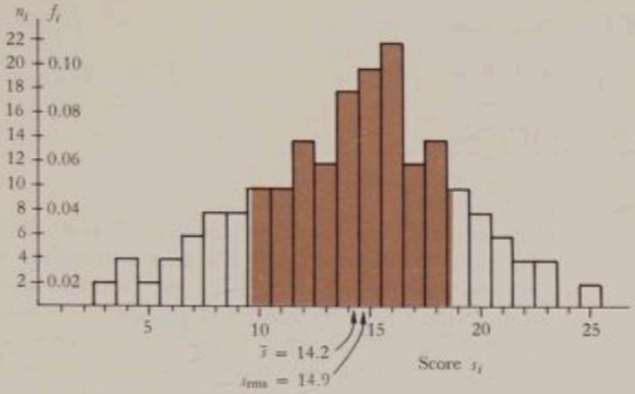

figure 2–1 *Grade distribution for a 25-point quiz given to 200 students;* n_i *is the number and* $f_i = n_i/N$ *is the fraction of the number of students receiving the score* s_i. *The average score* $\bar{s}$ *and root-mean-square score* $s_{\rm rms}$ *are indicated. The shaded area indicates the scores between* $\bar{s} - \sigma$ *and* $\bar{s} + \sigma$, *where* σ *is the standard deviation, which for this distribution is 4.6.*

Equation (2–1) is called the *normalization condition* for fractional-distribution functions. A possible distribution function for a 25-point quiz is shown in Figure 2–1.

To find the average score, all the scores are added and the result is divided by N. Since each score s_i was obtained by $n_i = Nf_i$ students, this procedure is equivalent to

$$\bar{s} = \frac{1}{N}\sum_i s_i n_i = \sum_i s_i f_i \tag{2-2}$$

We shall take Eq. (2–2) for the definition of the average score $\bar{s}$. Similarly, the average of any function $g(s)$ is defined by

$$\overline{g(s)} = \sum_i g(s_i) f_i \tag{2-3}$$

In particular, the average square score is often useful:

$$\overline{s^2} = \sum_i s_i^2 f_i$$

A particularly useful quantity characterizing a distribution is the standard deviation, σ, defined by

$$\sigma = \left[\sum_i (s_i - \bar{s})^2 f_i\right]^{1/2} \tag{2-4}$$

Note that

$$\sum_i (s_i - \bar{s})^2 f_i = \sum_i s_i^2 f_i + \bar{s}^2 \sum_i f_i - 2\bar{s} \sum_i s_i f_i = \overline{s^2} - \bar{s}^2$$

Therefore,

$$\sigma = (\overline{s^2} - \bar{s}^2)^{1/2} \tag{2-5}$$

The standard deviation is an important measure of the spread of the values s_i about the mean. For most distributions there will be few values s_i that differ from $\bar{s}$ by more than one or two multiples of σ. In the case of the normal or gaussian distribution, common in the theory of errors, about two-thirds of the values will lie within $\pm\sigma$ of the mean value. A gaussian distribution is shown in Figure 2-2.

If a student were selected at random from the class and one had to guess his score, the best guess would be the score obtained by the greatest number of students, called the *most probable score*, s_m. For the distribution in Figure 2-1, s_m is 16 and the average score, $\bar{s}$, is 14.2. The root-mean-square score, $s_{\text{rms}} = (\overline{s^2})^{1/2}$, is 14.9, and the standard deviation, σ, is 4.6. Note that 66 percent of the scores for this distribution lie within $s \pm \sigma = 14.2 \pm 4.6$. We shall now consider the problem of continuous distributions.

Suppose we wanted to know the distribution of heights of a large number of people. For a finite number N, the number of persons *exactly* 6 ft tall would be zero. If we assume that height can be determined to any desired accuracy, there is an infinite number of possible heights; thus the chance that anybody has a particular height is zero. We therefore divide the heights into intervals Δh (for example, Δh could be 0.1 ft) and ask what fraction of people have heights in any particular interval. This number depends on the size of the interval. We define the distribution function $f(h)$ as the fraction of the number of people with heights in a particular interval divided by the size of the interval. Thus for N people, $Nf(h)\,\Delta h$ is the number of people with height in the interval between h and $h + \Delta h$. A possible height-distribution function is plotted in Figure 2-3. The fraction of people with heights in a particular interval is just the area of the rectangle $\Delta h \times f(h)$. The total area represents the sum of all fractions; thus it must equal 1. If N is very large, we can choose Δh very small and still have $f(h)$ vary only slightly between intervals. The histogram $f(h)$ versus h approaches a smooth curve as $N \to \infty$ and $\Delta h \to 0$. In most practical cases, the number of objects N is extremely large, and the intervals can be taken as small as measurement allows. The distribution functions $f(h)$ are usually considered to be continuous functions, intervals are written dh, and the sums are replaced by integrals. For example, if $f(h)$ is a continuous function, the average height $\bar{h}$ is[2]

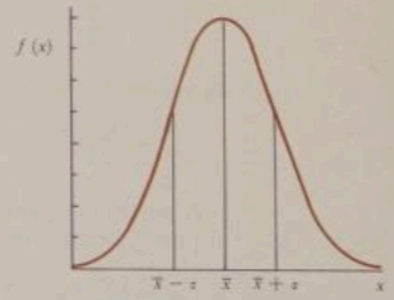

figure 2-2

Gaussian or normal-distribution curve. The curve is symmetrical about the mean $\bar{x}$, which is also the most probable value. Sixty-eight percent of the area under the curve is within one standard deviation of the mean. This curve describes the distribution of random errors in many experimental situations.

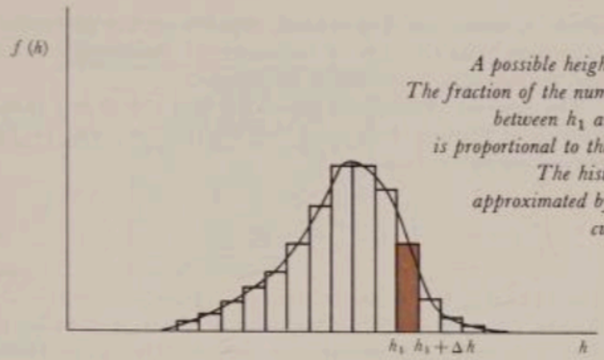

figure 2-3

A possible height distribution. The fraction of the number of heights between h_1 and $h_1 + \Delta h_1$ is proportional to the shaded area. The histogram can be approximated by a continuous curve as shown.

$$\bar{h} = \int h f(h)\, dh \tag{2-6}$$

and the normalization condition expressing the fact that the sum of all fractions is 1 is

$$\int f(h)\, dh = 1 \tag{2-7}$$

Example 2-1 The distribution function for lifetimes of radioactive nuclei is given by

$$f(t) = Ce^{-\lambda t} \tag{2-8}$$

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[2] The limits on the integration depend on the range of the variable. For this case, h ranges from 0 to ∞. We shall often omit the explicit indication of the limits when the range of the variable is clear.

where λ, called the *decay constant*, depends on the particular kind of nucleus (and the type of radioactivity). Assuming λ is known, find the constant C and the mean lifetime.

The fraction of lifetimes between t and $t + dt$ is $f(t)\,dt$. The fraction of lifetimes between $t = 0$ and $t = \infty$ must be 1; thus the normalization condition is

$$\int_0^\infty f(t)\,dt = \int_0^\infty Ce^{-\lambda t}\,dt = 1 \tag{2-9}$$

The integral $\int_0^\infty e^{-\lambda t}\,dt$ has the value λ^{-1}; thus $C\lambda^{-1} = 1$, or $C = \lambda$. Because the constant C is determined by the normalization condition, it is called the *normalization constant*. The mean lifetime is calculated by

$$\bar{t} = \int_0^\infty tf(t)\,dt = \lambda\int_0^\infty te^{-\lambda t}\,dt = \lambda^{-1}$$

Thus the mean lifetime is the reciprocal of the decay constant.

*

2·2
PRESSURE OF A GAS

We are now ready to calculate the pressure exerted by a gas on the walls of a container. We make the following assumptions:

1. The gas consists of a large number, N, of molecules that make elastic collisions with each other and with the walls of the container.
2. The molecules are separated by distances large compared with their diameters, and they exert no forces on each other except when they collide.
3. In the absence of external forces (we can neglect gravity), there is no preferred position for a molecule in the container, and there is no preferred direction for the velocity vector.

For the moment, we shall neglect the collisions the molecules make with each other. To simplify the discussion, we shall consider a rectangular box of length L along the x direction and of side area A. Let $f(v_x)$ be the distribution function for the x component of velocity; that is, $Nf(v_x)\,dv_x$ is the number of molecules with x component of velocity between v_x and $v_x + dv_x$. To avoid using this rather long phrase over and over, we shall hereafter use the expression "the number in dv_x at v_x" or sometimes merely "the number in dv_x." In a short time interval, dt, these molecules will hit the right end if they are within $\ell = v_x\,dt$ of that end, i.e., if they are in the shaded region of Figure 2-4. These molecules may have any y and z components of velocity. They may hit the top or side of the box first, for such a collision, if elastic as assumed, will not affect the motion in the x direction. The number of molecules in the shaded region in Figure 2-4 is

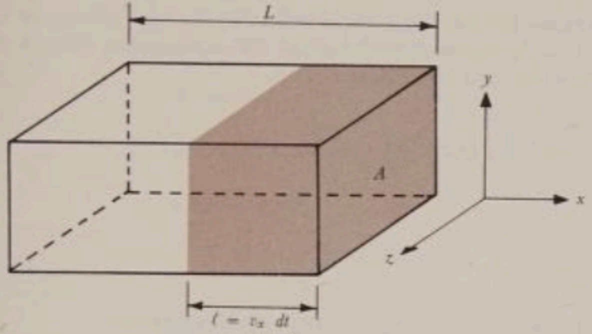

figure 2-4 *Molecules that are within $\ell = v_x\,dt$ of the end of the box will hit the end in time dt.*

$$N\frac{\ell A}{V} = nAv_x\,dt \tag{2-10}$$

where V is the volume of the container and n is the number density defined by $n = N/V$. Multiplying $nAv_x\,dt$ by the fraction of these molecules with v_x in the interval dv_x gives the number of molecules with this x component of velocity which hit the end in time dt. This number is

$$nAv_x\,dt\,f(v_x)\,dv_x$$

Upon hitting the end, each molecule has its x component of momentum changed from $+mv_x$ to $-mv_x$, a total change of $2mv_x$ to the left. The force exerted by the wall on the molecule is dp/dt, and by Newton's law of action and reaction, each molecule exerts an equal force outward on the wall. The total force exerted by these molecules is thus

$$\begin{aligned} F_v &= nAv_x\,dt\,f(v_x)\,dv_x\frac{2mv_x}{dt} \\ &= 2Anmv_x^{\,2}f(v_x)\,dv_x \end{aligned}$$

The pressure on the right wall of the box exerted by molecules with x components of velocity in the interval dv_x is this force divided by the area. We get the total pressure by summing over all the molecules moving to the right:

$$P = 2nm\int_0^\infty v_x^{\,2}f(v_x)\,dv_x \tag{2-11}$$

Though we do not know the distribution function, $f(v_x)$, we do know that $f(-v_x) = f(+v_x)$ by our assumption that there is no preferred direction for velocities. Then

$$\int_0^{\infty} v_x^2 f(v_x)\, dv_x = \tfrac{1}{2}\int_{-\infty}^{+\infty} v_x^2 f(v_x)\, dv_x = \tfrac{1}{2}\overline{v_x^2}$$

Thus

$$P = nm\overline{v_x^2} \tag{2–12}$$

The assumption of random directions also implies that

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \tfrac{1}{3}\overline{v^2}$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$. We can thus write Eq. (2–12) as

$$P = \tfrac{1}{3}nm\overline{v^2} \tag{2–13}$$

This equation can be written in several other interesting forms. Noting that the average kinetic energy of translation is

$$\overline{E}_k = \tfrac{1}{2}m\overline{v^2}$$

and $n = N/V$, we can write

$$PV = \tfrac{2}{3}N\overline{E}_k = \tfrac{2}{3}U \tag{2–14}$$

where $U = N\overline{E}_k$ is the total kinetic energy for all N molecules in the box.

Note that Eqs. (2–13) and (2–14) do not depend on the form of the distribution functions $f(v_x)$ or $f(v)$, since only the average values of v_x^2 and v^2 enter the calculation. Any assumed distribution will, of course, give the same result. For example, the assumption is sometimes made that all molecules move with the same speed, u, with one-sixth of them moving to the right along the x axis. This assumption is hardly likely; however, the result is the same. We can see that ignoring molecular collisions is not critical to the argument, for since momentum is conserved, collisions will not affect the total momentum in any given direction.

We can now compare our result with the ideal gas relation

$$PV = \nu RT \tag{2–15}$$

where ν is the number of moles and R is the gas constant, $R = 1.99$ cal/°K-mole $= 8.31$ J/°K-mole.

The total number of molecules, N, is related to the number of moles through Avogadro's number:

$$N = \nu N_A \tag{2–16}$$

Comparing Eqs. (2–14) and (2–15), we have

$$\begin{aligned} \nu RT &= \tfrac{2}{3}N\overline{E}_k \\ \overline{E}_k &= \frac{3}{2}\frac{R}{N_A}T = \frac{3}{2}kT \end{aligned} \tag{2–17}$$

where $k \equiv R/N_A$ is called *Boltzmann's constant.*

$$k = 1.38 \times 10^{-23}\ \text{J/°K} = 8.63 \times 10^{-5}\ \text{eV/°K}$$

At $T = 300$°K,

$$kT = 2.59 \times 10^{-2}\ \text{eV} \approx \tfrac{1}{40}\ \text{eV}$$

Thus at room temperature the mean kinetic energy of gas molecules is only a few hundredths of an electron volt. There are two important results we can obtain from this simple calculation:

1. *Speed of a molecule in a gas.* Without knowing $f(v)$ or even $\bar{v}$, we can get an idea of the size of molecular speeds from

$$\overline{v^2} = \frac{2E_k}{m} = \frac{3RT}{N_A m} = \frac{3RT}{\mathfrak{M}} \tag{2–18}$$

where $\mathfrak{M} = N_A m$ is the mass of 1 mole. (This is commonly called the *molecular weight.*) Thus the rms speed is

$$v_{\text{rms}} = \left(\frac{3RT}{\mathfrak{M}}\right)^{1/2} \tag{2–19}$$

It is not hard to remember the order of magnitude of molecular speeds if we recall that the speed of sound in air is given by

$$v_{\text{sound}} = \left(\frac{\gamma RT}{\mathfrak{M}}\right)^{1/2}$$

where γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume:

$$\gamma = \frac{c_p}{c_v} = 1.4 \text{ for air}$$

Example 2–2 Calculate the root-mean-square speed of nitrogen molecules at $T = 300°\text{K}$. We have

$$\mathfrak{M} = 28 \text{ g/mole} = 28 \times 10^{-3} \text{ kg/mole}$$

$$v_{\text{rms}} = \left(\frac{3 \times 8.31 \text{ J°K}^{-1} \text{ mole}^{-1} \times 300°\text{K}}{28 \times 10^{-3} \text{ kg mole}^{-1}}\right)^{1/2} = 517 \text{ m/sec}$$

*

2. *Heat capacities.* The molar heat capacity at constant volume is defined by

$$C_v = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}$$

where ΔQ is the heat input and ΔT is the temperature rise for 1 mole of a substance. Since no work is done if the volume is constant, the heat input equals the change in internal energy U. Thus

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \tag{2–20}$$

If we assume that the total internal energy is *translational* kinetic energy, we have from Eq. (2–17) for 1 mole,

$$U = N_A \bar{E}_k = \tfrac{3}{2} RT$$

and

$$C_v = \tfrac{3}{2} R = 2.98 \text{ cal/mole}$$

This result agrees well with experiments for monatomic gases such as argon and helium (see Table 2–2, page 81). For other gases, the measured molar heat capacity is greater than this, indicating that the heat input goes into internal energy, other than translational kinetic energy, such as energy of rotation or vibration.

2·3 THE MAXWELL-BOLTZMANN DISTRIBUTION

The distribution function for molecular velocities was first obtained by Maxwell in 1859. The problem can be stated as follows: Given N molecules of a gas confined to some volume V, let the number with velocity components v_x in dv_x, v_y in dv_y, and v_z in dv_z be $NF(v_x,v_y,v_z)\, dv_x\, dv_y\, dv_z$. What is the form of $F(v_x,v_y,v_z)$ when the gas is in equilibrium at temperature T?

Some insight to this problem can be gained by examining some simple distributions to see if they are possible solutions. Consider the distribution — all molecules moving with the same speed, one-sixth of them in the positive x direction, one-sixth in the negative x direction, one-sixth in the positive y direction, etc. Place the molecules at random positions in the box at time zero. It is obvious that the molecules will collide and that many of the collisions will not be head-on collisions; thus their velocities will change and the original distribution will not persist. If we assume some model such as hard spheres for the molecules, we can calculate (statistically) what collisions will take place knowing the original distribution. The equilibrium distribution is the one that remains unchanged by the collisions determined by the distribution.

Maxwell assumed that the components v_x, v_y, and v_z were independent and that, therefore, the probabilities of a molecule having a certain v_x, v_y, v_z could be factored into the product of the probability of having v_x times the probability of having v_y times the probability of having v_z. He also assumed that the distribution could depend only on the speed, i.e., the velocity components could occur only in the combination $v_x^2 + v_y^2 + v_z^2$. His derivation is given below.[3]

"Prop. IV. To find the average number of particles whose velocities lie between given limits, after a great number of collisions among a great number of particles.

"Let N be the whole number of particles. Let x, y, z be the components of the velocity of each particle in three rectangular directions, and let the number of particles for which x lies between x and $x + dx$, be $Nf(x)\, dx$, where $f(x)$ is a function of x to be determined.

"The number of particles for which y lies between y and $y + dy$ will be $Nf(y)\, dy$, and the number for which z lies between z and $z + dz$ will be $Nf(z)\, dz$ where f always stands for the same function.

"Now the existence of the velocity x does not in any way affect that of the velocities y or z, since these are all at right angles to each other and independent, so that the number of particles whose velocity lies between x and $x + dx$, and also between y and $y + dy$, and also between z and $z + dz$, is

$$Nf(x)f(y)f(z)\, dx\, dy\, dz$$

"If we suppose the N particles to start from the origin at the same instant, then this will be the number in the element of volume (dx,dy,dz) after unit of time, and the number referred to unit volume will be

$$Nf(x)f(y)f(z)$$

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[3] Quoted from "Illustrations of the Dynamical Theory of Gases," by J. C. Maxwell, in *Scientific Papers*, edited by W. Niven, Hermann & Cie, Paris, 1927, and Dover Publications, Inc., New York, 1952. Maxwell's use of x, y, and z for the velocity components which we designate by the symbols v_x, v_y, and v_z may cause some confusion.

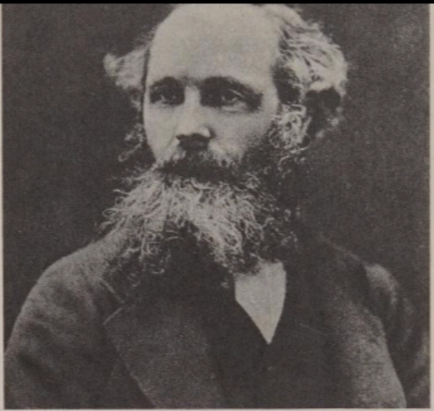

figure 2–5

James Clerk Maxwell. (Courtesy of Culver Pictures, Inc.)

"But the directions of the coordinate are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is,

$$f(x)f(y)f(z) = \phi(x^2 + y^2 + z^2)$$

Solving this functional equation,[4] we find

$$f(x) = Ce^{Ax^2} \qquad \phi(r^2) = C^3e^{Ar^2}$$

"If we make A positive, the number of particles will increase with the velocity, and we should find the whole number of particles infinite. We therefore make A negative and equal to $-1/a^2$ so that the number between x and $x + dx$ is

$$NCe^{-x^2/a^2}\,dx$$

Integrating from $x = -\infty$ to $x = +\infty$, we find the whole number of particles,

$$NCa\sqrt{\pi} = N$$

$$C = \frac{1}{a\sqrt{\pi}}$$

$f(x)$ is therefore

$$\frac{1}{a\sqrt{\pi}}\,e^{-x^2/a^2}$$

whence we may draw the following conclusions. . . ."

We shall use a notation slightly more convenient than that in the quotation above. Let $\lambda = 1/a^2$. The distribution function for v_x is then

$$f(v_x) = Ce^{-\lambda v_x^2} \tag{2–21}$$

The constant C is determined by the normalization condition

$$\int_{-\infty}^{\infty} f(v_x)\,dv_x = \int_{-\infty}^{\infty} Ce^{-\lambda v_x^2}\,dv_x = 1 \tag{2–22}$$

We shall need to evaluate integrals of the form

$$I_n = \int_0^{\infty} x^n e^{-\lambda x^2}\,dx \tag{2–23}$$

several times in this chapter. Table 2–1, derived in Appendix B, lists I_n for values of n from 0 to 5. Using this table to evaluate Eq. (2–18), we find

$$C = \left(\frac{\lambda}{\pi}\right)^{1/2}$$

table 2–1 *Values of the integral* $I_n = \int_0^{\infty} x^n e^{-\lambda x^2}\,dx$ *for* $n = 0$ *to* $n = 5$.

n	I_n
0	$\frac{1}{2}\sqrt{\pi/\lambda}$
1	$1/2\lambda$
2	$\frac{1}{4}\sqrt{\pi/\lambda^3}$
3	$1/2\lambda^2$
4	$\frac{3}{8}\sqrt{\pi/\lambda^5}$
5	$1/\lambda^3$

If n is even, $\displaystyle\int_{-\infty}^{\infty} x^n e^{-\lambda x^2}\,dx = 2I_n$

If n is odd, $\displaystyle\int_{-\infty}^{\infty} x^n e^{-\lambda x^2}\,dx = 0$

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[4] Solving this functional equation is not trivial, but the result is easy to check. The mathematical details of solution do not add much clarity to this derivation. The interested reader is referred to pages 41 to 48 in Ref. 8 for a more detailed treatment.

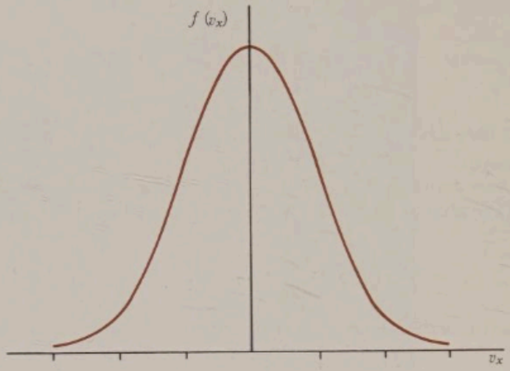


figure 2–6 *The distribution function $f(v_x)$ for the x component of velocity. This is a gaussian curve, given by Eq. (2–25).*

The constant λ can be determined by calculating $\overline{v_x^2}$:

$$\overline{v_x^2} = \int_{-\infty}^{+\infty} v_x^2 f(v_x)\, dv_x = \int_{-\infty}^{+\infty} v_x^2 C e^{-\lambda v_x^2}\, dv_x = 2CI_2$$

$$= 2\left(\frac{\lambda}{\pi}\right)^{1/2} \frac{1}{4}\left(\frac{\pi}{\lambda^3}\right)^{1/2}$$

Thus $\overline{v_x^2} = \frac{1}{2}\lambda^{-1}$. Comparing with Eq. (2–18),

$$\overline{v_x^2} = \tfrac{1}{3}\overline{v^2} = \frac{2}{3}\frac{\bar{E}_k}{m} = \frac{kT}{m}$$

We find

$$\lambda = \frac{m}{2kT} \qquad (2\text{–}24)$$

Thus the complete distribution function $f(v_x)$ is

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} \qquad (2\text{–}25)$$

Figure 2–6 shows a sketch of $f(v_x)$ versus v_x. Of course, $f(v_x)$ is symmetrical about the origin, $f(v_x) = f(-v_x)$; thus the average of v_x is zero. As can be seen from the figure, the most probable

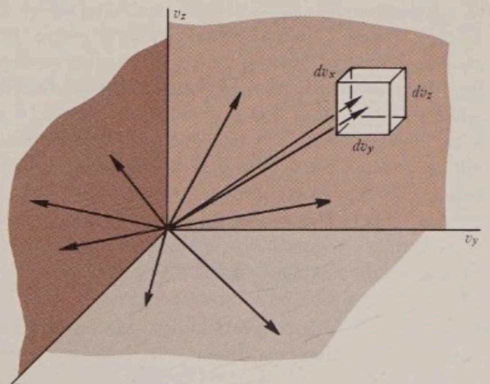
v_x is also zero. The complete velocity distribution is thus

$$F(v_x,v_y,v_z) = f(v_x)f(v_y)f(v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2kT} \qquad (2\text{–}26)$$

We can calculate the *speed* distribution from the velocity distribution. Let $g(v)\, dv$ be the fraction of molecules with speeds v in the range dv. The difference between $F(v_x,v_y,v_z)$ and $g(v)$ can be seen most easily by examining what is called *velocity space*. Imagine the velocity vector of each molecule placed with its tail at the origin of the coordinate system v_x, v_y, v_z. (See Figure 2–7). $F(v_x,v_y,v_z)\, dv_x\, dv_y\, dv_z$ is the fraction of these vectors whose tips end in the "volume" element $dv_x\, dv_y\, dv_z$. On the other hand, $g(v)\, dv$ is the fraction whose tips end in the "volume" element between the sphere of radius v and one of radius $v + dv$. We could also represent each molecular velocity by a point at the tip of the vector in the velocity space shown in Figure 2–7. Then $F(v_x,v_y,v_z)$ is the density of points in this space. Since this density depends only on the "distance" $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$, the number of points between v and $v + dv$ is just the density times the "volume" of the spherical shell of thickness dv, or

$$g(v)\, dv = 4\pi v^2\, dv F(v_x,v_y,v_z) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\, dv \qquad (2\text{–}27)$$

figure 2–7 *Velocity vectors in velocity space. Each molecular velocity can be represented by a point in velocity space at the tip of the velocity vector. The velocity distribution function $NF(v_x,v_y,v_z)$ is the number of points per unit volume $dv_x\, dv_y\, dv_z$, where N is the number of molecules.*



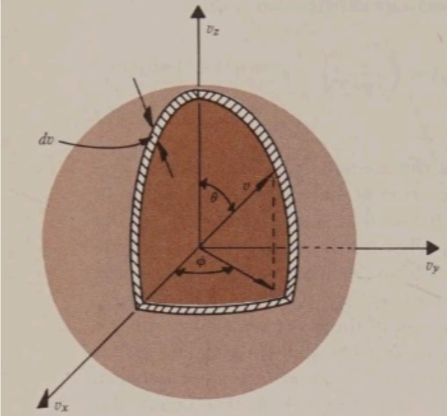


figure 2–8

One octant of a spherical shell in velocity space. The volume of the entire spherical shell is $4\pi v^2\,dv$. The speed distribution $Ng(v)$ is the number of points per unit length dv in the spherical shell.

The speed-distribution function $g(v)$ is sketched in Figure 2–9.

The mean speed is

$$\bar{v} = \int_0^\infty vg(v)\,dv = \left(\frac{8kT}{\pi m}\right)^{1/2} \tag{2–28}$$

It is left as an exercise to show that the most probable speed is

$$v_m = \left(\frac{2kT}{m}\right)^{1/2} \tag{2–29}$$

The energy-distribution function, $F(E)\,dE$, is the fraction of molecules with energies between E and $E + dE$. We can calculate the energy distribution by noting that

$$F(E)\,dE = g(v)\,dv$$

with $E = \frac{1}{2}mv^2$ and $dE = mv\,dv$. Thus

$$v^2\,dv = \frac{v\,dE}{m} = \left(\frac{2E}{m}\right)^{1/2}\frac{dE}{m}$$

The energy distribution is thus

$$F(E)\,dE \propto E^{1/2}e^{-E/kT}\,dE \tag{2–30}$$

The proportionality constant can be determined by the normalization condition.

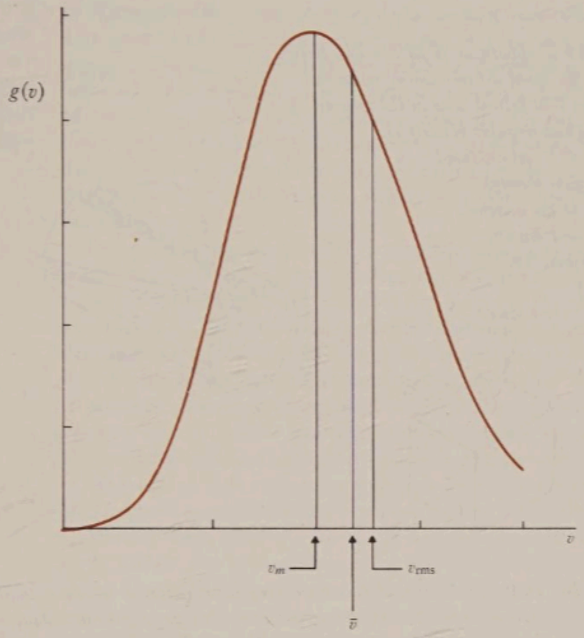


figure 2–9 *Maxwell's speed distribution $g(v)$. The most probable speed v_m, the mean speed $\bar{v}$, and the rms speed v_{rms} are indicated.*

The first direct measurement of the speed distribution of molecules was made by O. Stern in 1926. Since then, measurements have been made by Zartman and Ko (1930); I. Estermann, O. C. Simpson, and O. Stern (1946); and Miller and Kusch (1955). These experiments employed various methods of selecting a range of speeds of molecules escaping from a small hole in an oven and determining the number of molecules in this range. Zartman and Ko, for example, allowed the beam to pass through a slit in a rotating cylinder and measured the intensity versus position on the collecting plate. In the more recent experiment of Miller and Kusch, illustrated in Figure 2–10, a collimated beam from the oven is aimed at a fixed detector. Most of the beam is stopped by a rotating cylinder. Small helical slits in the cylinder allow passage of those molecules in a narrow speed range determined by the angular velocity of the cylinder. The Miller and Kusch results are shown in Figure 2–11.

figure 2–10

Schematic sketch of apparatus of Miller and Kusch for measuring the speed distribution of molecules. Only one of the 720 helical slits in the cylinder is shown. For a given angular velocity ω, only molecules of a certain speed from the oven pass through the helical slit to the detector. [From Miller and Kusch, Physical Review, **99,** *1314* (*1955*).]

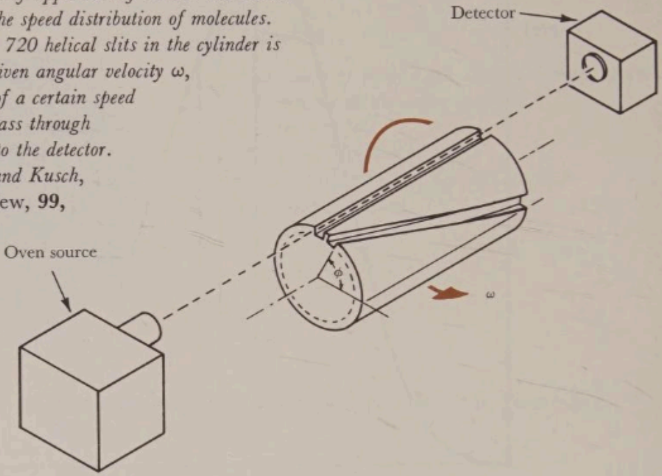


figure 2–11 *Data of Miller and Kusch showing distribution of speeds of thallium atoms from an oven. The data have been corrected to give the distribution inside the oven. The solid curve is that predicted by the Maxwell speed distribution. [From Miller and Kusch,* Physical Review, **99,** *1314* (*1955*).]