CHEMICAL KINETICS AND REACTION DYNAMICS

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Kinetic Theory of Gases

1

Chapter Outline

1.1 INTRODUCTION

The overall objective of this chapter is to understand macroscopic properties such as pressure and temperature on a microscopic level. We will find that the pressure of an ideal gas can be understood by applying Newton's law to the microscopic motion of the molecules making up the gas and that a comparison between the Newtonian prediction and the ideal gas law can provide a function that describes the distribution of molecular velocities. This distribution function can in turn be used to learn about the frequency of molecular collisions. Since molecules can react only as fast as they collide with one another, the collision frequency provides an upper limit on the reaction rate.

The outline of the discussion is as follows. By applying Newton's laws to the molecular motion we will find that the product of the pressure and the volume is proportional to the average of the square of the molecular velocity, $<v^2>$, or equivalently to the average molecular translational energy ϵ. In order for this result to be consistent with the observed ideal gas law, the temperature T of the gas must also be proportional to $<v^2>$ or $<\epsilon>$. We will then consider in detail how to determine the average of the square of the velocity from a distribution of velocities, and we will use the proportionality of T with $<v^2>$ to determine the Maxwell-Boltzmann distribution of speeds. This distribution, $F(v)\,dv$, tells us the number of molecules with speeds between v and $v + dv$. The speed distribution is closely related to the distribution of molecular energies, $G(\epsilon)\,d\epsilon$. Finally, we will use the velocity distribution to calculate the number of collisions Z that a molecule makes with other molecules in the gas per unit time. Since in later chapters we will argue that a reaction between two molecules requires that they collide, the collision rate Z provides an upper limit to the rate of a reaction. A related quantity λ is the average distance a molecule travels between collisions or the *mean free path.*

The history of the kinetic theory of gases is a checkered one, and serves to dispel the impression that science always proceeds along a straight and logical path.[a] In 1662 Boyle found that for a specified quantity of gas held at a fixed temperature the product of the pressure and the volume was a constant. Daniel Bernoulli derived this law in 1738 by applying Newton's equations of motion to the molecules comprising the gas, but his work appears to have been ignored for more than a century.[b] A school teacher in Bombay, India, named John James Waterston submitted a paper to the Royal Society in 1845 outlining many of the concepts that underlie our current understanding of gases. His paper was rejected as "nothing but nonsense, unfit even for reading before the Society." Bernoulli's contribution was rediscovered in 1859, and several decades later in 1892, after Joule (1848) and Clausius (1857) had put forth similar ideas, Lord Rayleigh found Waterston's manuscript in the Royal Society archives. It was subsequently published in *Philosophical Transactions.* Maxwell (*Illustrations of Dynamical Theory of Gases,* 1859–1860) and Boltzmann (*Vorlesungen über Gastheorie,* 1896–1898) expanded the theory into its current form.

1.2 PRESSURE OF AN IDEAL GAS

We start with the basic premise that the pressure exerted by a gas on the wall of a container is due to collisions of molecules with the wall. Since the number of molecules in the container is large, the number colliding with the wall per unit time is large enough so that fluctuations in the pressure due to the individual collisions are immeasurably small in comparison to the total pressure. The first step in the calculation is to apply Newton's laws to the molecules to show that the product of the pressure and the volume is proportional to the average of the square of the molecular velocity, $<v^2>$.

Consider molecules with a velocity component v_x in the x direction and a mass m. Let the molecules strike a wall of area A located in the z-y plane, as shown in **Figure 1.1.** We would first like to know how many molecules strike the wall in a time Δt, where Δt is short compared to the time between molecular collisions. The distance along the x axis that a molecule travels in the time Δt is simply $v_x \Delta t$, so that all molecules located in the volume $Av_x\Delta t$ and moving toward the wall will strike it. Let n^* be the number of molecules per unit volume. Since one half of the molecules will be moving toward the wall in the $+x$ direction while the other half will be moving in the $-x$ direction, the number of molecules which will strike the wall in the time Δt is $\frac{1}{2}n^*Av_x\Delta t$.

The force on the wall due to the collision of a molecule with the wall is given by Newton's law: $F = ma = m\,\mathrm{d}v/\mathrm{d}t = \mathrm{d}(mv)/\mathrm{d}t$, and integration yields $F\Delta t = \Delta(mv)$. If a molecule rebounds elastically (without losing energy) when it hits the wall, its momentum is changed from $+mv_x$ to $-mv_x$, so that the total momentum change is $\Delta(mv) = 2mv_x$. Consequently, $F\Delta t = 2mv_x$ for one molecular collision, and $F\Delta t = (\frac{1}{2}n^*Av_x\Delta t)(2mv_x)$ for the total number of collisions. Canceling Δt from both sides and recognizing that the pressure is the force per unit area, $p = F/A$, we obtain $p = n^*mv_x^2$.

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[a] The history of the kinetic theory of gases is outlined by E. Mendoza, *Physics Today* 14, 36–39 (1961).

[b] A translation of this paper has appeared in *The World of Mathematics,* J. R. Newman, Ed., Vol. 2 (Simon and Schuster, New York, 1956), p. 774.

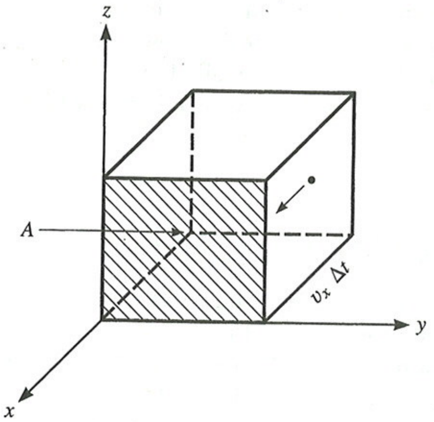

Figure 1.1

All the molecules in the box that are moving toward the z-y plane will strike the wall.

Of course, not all molecules will be traveling with the same velocity v_x. We will learn below how to characterize the distribution of molecular velocities, but for now let us simply assume that the pressure will be proportional to the average of the square of the velocity in the x direction, $p = n^* m \langle v_x^2 \rangle$.[c] The total velocity of an individual molecule most likely contains other components along y and z. Since $\mathbf{v} = \hat{i}v_x + \hat{j}v_y + \hat{k}v_z$,[d] where $\hat{i}$, $\hat{j}$, and $\hat{k}$ are unit vectors in the x, y, and z directions, respectively, $\mathbf{v}^2 = v_x^2 + v_y^2 + v_z^2$ and $\langle \mathbf{v}^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$. In an isotropic gas the motion of the molecules is random, so there is no reason for the velocity in one particular direction to differ from that in any other direction. Consequently, $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \langle v^2 \rangle /3$. When we combine this result with the calculation above for the pressure, we obtain

$$p = \frac{1}{3} n^* m \langle v^2 \rangle. \tag{1.1}$$

Of course, n^* in **equation 1.1** is the number of molecules per unit volume and can be rewritten as nN_A/V, where N_A is Avogadro's number and n is the number of moles. The result is

$$pV = \frac{1}{3} n N_A m \langle v^2 \rangle. \tag{1.2}$$

Since the average kinetic energy of the molecules is $\langle \epsilon \rangle = \frac{1}{2} m \langle v^2 \rangle$, another way to write **equation 1.2** is

$$pV = \frac{2}{3} n N_A \langle \epsilon \rangle. \tag{1.3}$$

Equations 1.2 and **1.3** bear a close resemblance to the ideal gas law, $pV = nRT$. The ideal gas law tells us that the product of p and V will be constant if the temperature is constant, while **equations 1.2** and **1.3** tell us that the product will be constant if $\langle v^2 \rangle$ or $\langle \epsilon \rangle$ is constant. The physical basis for the constancy of pV with $\langle v^2 \rangle$ or $\langle \epsilon \rangle$ is clear from our previous discussion. If the volume is

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[c] In this text, as in many others, we will use the notation $\langle x \rangle$ or $\bar{x}$ to mean "the average value of x."

[d] Throughout the text we will use **boldface** symbols to indicate vector quantities and normal weight symbols to indicate scalar quantities. Thus, $v = |\mathbf{v}|$. Note that $\mathbf{v}^2 = \mathbf{v} \cdot \mathbf{v} = v^2$.

increased while the number, energy, and velocity of the molecules remain constant, then a longer time will be required for the molecules to reach the walls; there will thus be fewer collisions in a given time, and the pressure will decrease. To identify **equation 1.3** with the ideal gas law, we need to consider in more detail the relationship between temperature and energy.

1.3 TEMPERATURE AND ENERGY

Consider two types of molecule in contact with one another. Let the average energy of the first type be $<\epsilon>_1$ and that of the second type be $<\epsilon>_2$. If $<\epsilon>_1$ is greater than $<\epsilon>_2$, then when molecules of type 1 collide with those of type 2, energy will be transferred from the former to the latter. This energy transfer is a form of heat flow. From a macroscopic point of view, as heat flows the temperature of a system of the type 1 molecules will decrease, while that of the type 2 molecules will increase. Only when $<\epsilon>_1 = <\epsilon>_2$ will the temperatures of the two macroscopic systems be the same. In mathematical terms, we see that $T_1 = T_2$ when $<\epsilon>_1 = <\epsilon>_2$ and that $T_1 > T_2$ when $<\epsilon>_1 > <\epsilon>_2$. Consequently, there must be a correspondence between $<\epsilon>$ and T so that the latter is some function of the former: $T = T(<\epsilon>)$.

The functional form of the dependence of T on $<\epsilon>$ cannot be determined solely from kinetic theory, since the temperature scale can be chosen in many possible ways. In fact, one way to define the temperature is through the ideal gas law: $T = pV/(nR)$. Experimentally, this corresponds to measuring the temperature either by measuring the volume of an ideal gas held at constant pressure or by measuring the pressure of an ideal gas held at constant volume. Division of both sides of **equation 1.3** by nR and use of the ideal gas relation gives us the result

$$T = \frac{pV}{nR} = \frac{2}{3}\frac{N_A}{R}<\epsilon>, \tag{1.4}$$

$$<\epsilon> = \frac{3}{2}kT, \tag{1.5}$$

where k, known as Boltzmann's constant, is defined as R/N_A. Note that since $<\epsilon> = \frac{1}{2}m<v^2>$,

$$<v^2> = \frac{3kT}{m}. \tag{1.6}$$

example 1.1

Calculation of Average Energies and Squared Velocities

Objective Calculate the average molecular energy, $<\epsilon>$, and the average squared velocity, $<v^2>$, for a nitrogen molecule at $T = 300$ K.

Method Use **equations 1.5** and **1.6** with $m = (28 \text{ g/mole})(1 \text{ kg}/1000 \text{ g})/(N_A \text{ molecule/mole})$ and $k = 1.38 \times 10^{-23}$ J/K.

Solution $<\epsilon> = 3kT/2 = 3(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})/2 = 6.21 \times 10^{-21}$ J.

$$<v^2> = \frac{3kT}{m}$$

$$= 3\frac{(1.38 \times 10^{-23}\ \mathrm{J/K})(300\ \mathrm{K})}{[(28/6.02 \times 10^{26})]}$$

$$= 2.67 \times 10^5\ (\mathrm{m/s})^2 = (516\ \mathrm{m/s})^2.$$

To summarize the discussion so far, we have seen from **equation 1.2** that pV is proportional to $<v^2>$ and that the ideal gas law is obtained if we take the definition of temperature to be that embodied in **equation 1.5.** Since $<\epsilon> = \frac{1}{2}m<v^2>$, both temperature and pV are proportional to the average of the square of the velocity. The use of an average recognizes that not all the molecules will be moving with the same velocity. In the next few sections we consider the *distribution* of molecular speeds. But first we must consider what we mean by a distribution.

1.4 DISTRIBUTIONS, MEAN VALUES, AND DISTRIBUTION FUNCTIONS

Suppose that five students take a chemistry examination for which the possible grades are integers in the range from 0 to 100. Let their scores be $S_1 = 68$, $S_2 = 76$, $S_3 = 83$, $S_4 = 91$, and $S_5 = 97$. The average score for the examination is then

$$<S> = \frac{S_1 + S_2 + S_3 + S_4 + S_5}{N_T} = \frac{1}{N_T}\sum_{i=1}^{N_T} S_i, \tag{1.7}$$

where $N_T = 5$ is the number of students. In this case, the average is easily calculated to be 83.

Now suppose that the class had 500 students rather than 5. Of course, the average grade could be calculated in a manner similar to that in **equation 1.7** with an index i running from 1 to $N_T = 500$. However, another method will be instructive. Clearly, if the examination is still graded to one-point accuracy, it is certain that more than one student will receive the same score. Suppose that, instead of summing over the students, represented by the index i in **equation 1.7,** we form the average by summing over the scores themselves, which range in integer possibilities from $j = 0$ to 100. In this case, to obtain the average, we must weight each score S_j by the number of students who obtained that score, N_j:

$$<S> = \frac{1}{N_T}\sum_{j=0}^{100} S_j N_j. \tag{1.8}$$

Note that the definition of N_j requires that $\Sigma N_j = N_T$. The factor $1/N_T$ in **equation 1.8** is included for normalization, since, for example, if all the students happened to get the same score $S_j = S$ then

$$<S> = \frac{1}{N_T}\sum_j S_j N_j = \frac{S}{N_T}\sum_j N_j = S. \tag{1.9}$$

Now let us define the probability of obtaining score S_j as the fraction of students receiving that score:

$$P_j = \frac{N_j}{N_T}. \tag{1.10}$$

Then another way to write **equation 1.8** is

$$<S> = \sum_j S_j P_j, \tag{1.11}$$

where $\Sigma_j P_j = 1$ from normalization.

Equation 1.11 provides an alternative to **equation 1.7** for finding the average score for the class. Furthermore, we can generalize **equation 1.11** to provide a method for finding the average of *any* quantity,

$$<Q> = \sum_j P_j Q_j, \tag{1.12}$$

where P_j is the probability of finding the jth result.

example 1.2

Calculating Averages from Probabilities

Objective Find the average throw for a pair of dice.

Method Each die is independent, so the average of the sum of the throws will be twice the average of the throw for one die. Use **equation 1.12** to find the average throw for one die.

Solution The probability for each of the six outcomes, 1–6, is the same, namely, 1/6. Factoring this out of the sum gives $<T> = (1/6)\ \Sigma\ T_i$, where $T_i = 1,2,3,4,5,6$ for $i = 1$–6. The sum is 21, so that the average throw for one die is $<T> = 21/6 = 3.5$. For the sum of two dice, the average would thus be 7.

The method can be extended to calculate more complicated averages. Let $f(Q_j)$ be some arbitrary function of the observation Q_j. Then the average value of the function $f(Q)$ is given by

$$<f(Q)> = \sum_j P_j f(Q_j). \tag{1.13}$$

For example, if Q were the square of a score, then

$$<S^2> = \sum_j P_j S^2. \tag{1.14}$$

Suppose now that the examination is a very good one, indeed, and that the talented instructor can grade it not just to one-point accuracy (a remarkable achievement in itself!) but to an accuracy of dS, where dS is a very small fraction of a point. Let $P(S)$ dS be the probability that a score will fall in the range between S and S + dS, and let dS become infinitesimally small. The fundamental theorems of calculus tell us that we can convert the sum in **equation 1.11** to the integral

$$<S> = \int P(S) S\ \mathrm{d}S, \tag{1.15}$$

or, more generally for any observable quantity,

$$<Q> = \int P(Q)Q\,\mathrm{d}Q. \tag{1.16}$$

Equation 1.16 will form the basis for much of our further work. The probability function $P(Q)$ is sometimes called a *distribution function,* and the range of the integral is over all values of Q where the probability is nonzero. Note that normalization of the probability requires

$$\int P(Q)\,\mathrm{d}Q = 1. \tag{1.17}$$

The quantity $|\psi(x)|^2\,\mathrm{d}x$ is simply a specific example of a distribution function. Although knowledge of quantum mechanics is not necessary to solve it, you may recognize a connection to the particle in the box in Problem 1.7, which like **Example 1.3** is an exercise with distribution functions.

example 1.3

Determining Distribution Functions

Objective Bees like honey. A sphere of radius r_0 is coated with honey and hanging in a tree. Bees are attracted to the honey such that the average number of bees per unit volume is given by Kr^{-5}, where K is a constant and r is the distance from the center of the sphere. Derive the normalized distribution function for the bees. They can be at any distance from the honey, but they cannot be inside the sphere. Using this distribution, calculate the average distance of a bee from the center of the sphere.

Method First we need to find the normalization constant K by applying **equation 1.17,** recalling that we have a three-dimensional problem and that in spherical coordinates the volume element for a problem that does not depend on the angles is $4\pi r^2\,\mathrm{d}r$. Then, to evaluate the average, we apply **equation 1.16.**

Solution Recall that, by hypothesis, there is no probability for the bees being at $r < r_0$, so that the range of integration is from r_0 to infinity. To determine K we require

$$\int_{r_0}^{\infty} (Kr^{-5})\,4\pi r^2\,\mathrm{d}r = 1, \tag{1.18}$$

or

$$4\pi K \int_{r_0}^{\infty} r^{-3}\,\mathrm{d}r = 1 = 4\pi K\left(-\frac{r^{-2}}{2}\right)\Bigg|_{r_0}^{\infty} = \frac{4\pi K}{2r_0^2}, \tag{1.19}$$

so that

$$K = \frac{r_0^2}{2\pi}.$$

Having determined the normalization constant, we now calculate the average distance:

$$
\begin{aligned}
<r> &= \int_{r_0}^{\infty} r\left(\frac{r_0^2}{2\pi}\right) r^{-5} 4\pi r^2 \, \mathrm{d}r \\
&= 2r_0^2 \int_{r_0}^{\infty} r^{-2} \, \mathrm{d}r \qquad \textbf{(1.20)} \\
&= 2r_0^2 (-r^{-1}) \Big|_{r_0}^{\infty} = 2r_0^2 \frac{1}{r_0} = 2r_0.
\end{aligned}
$$

1.5 THE MAXWELL DISTRIBUTION OF SPEEDS

We turn now to the distribution of molecular speeds. We will denote the probability of finding v_x in the range from v_x to $v_x + dv_x$, v_y in the range from v_y to $v_y + dv_y$, and v_z in the range from v_z to $v_z + dv_z$ by $F(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z$. The object of this section is to determine the function $F(v_x, v_y, v_z)$. There are four main points in the derivation:

1. In each direction, the velocity distribution must be an even function of v.
2. The velocity distribution in any particular direction is independent from and uncorrelated with the distributions in orthogonal directions.
3. The average of the square of the velocity $<v^2>$ obtained using the distribution function should agree with the value required by the ideal gas law: $<v^2> = 3kT/m$.
4. The three-dimensional velocity distribution depends only on the magnitude of v (i.e., the speed) and not on the direction.

We now examine these four points in detail.

1.5.1 The Velocity Distribution Must Be an Even Function of *v*

Consider the velocities v_x of molecules contained in a box. The number of molecules moving in the positive x direction must be equal to the number of molecules moving in the negative x direction. This conclusion is easily seen by examining the consequences of the contrary assumption. If the number of molecules moving in each direction were not the same, then the pressure on one side of the box would be greater than on the other. Aside from violating experimental evidence that the pressure is the same wherever it is measured in a closed system, our common observation is that the box does not spontaneously move in either the positive or negative x direction, as would be likely if the pressures were substantially different. We conclude that the distribution function for the velocity in the x direction, or more generally in any arbitrary direction, must be symmetric; i.e., $F(v_x) = F(-v_x)$. Functions possessing the property that $f(x) = f(-x)$ are called *even functions*, while those having the property that $f(x) = -f(-x)$ are called *odd functions*. We can ensure that $F(v_x)$ be an even function by requiring that the distribution function depend on the square of the velocity: $F(v_x) = f(v_x^2)$. As shown in Section 1.5.3, this condition is also in accord with the Boltzmann distribution law.[e]

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[e] Other even functions, for example, $F = f(v_x^4)$ would be mathematically acceptable, but would not satisfy the requirement of Section 1.5.3.

1.5.2 The Velocity Distributions Are Independent and Uncorrelated

We now consider the relationship between the distribution of x-axis velocities and y- or z-axis velocities. In short, there should be no relationship. The three components of the velocity are independent of one another since the velocities are uncorrelated. An analogy might be helpful. Consider the probability of tossing three honest coins and getting "heads" on each. Because the tosses t_i are independent, uncorrelated events, the joint probability for a throw of three heads, $P(t_1 = \text{heads}, t_2 = \text{heads}, t_3 = \text{heads})$, is simply equal to the product of the probabilities for the three individual events, $P(t_1 = \text{heads}) \times P(t_2 = \text{heads}) \times P(t_3 = \text{heads}) = \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$. In a similar way, because the x-, y-, and z-axis velocities are independent and uncorrelated, we can write that

$$F(v_x, v_y, v_z) = F(v_x)F(v_y)F(v_z). \qquad \textbf{(1.21)}$$

We can now use the conclusion of the previous section. We can write, for example, that $F(v_x) = f(v_x^2)$ and similarly for the other directions. Consequently,

$$F(v_x, v_y, v_z) = F(v_x)F(v_y)F(v_z) = f(v_x^2)f(v_y^2)f(v_z^2). \qquad \textbf{(1.22)}$$

What functional form has the property that $f(a + b + c) = f(a)f(b)f(c)$? A little thought leads to the exponential form, since $\exp(a + b + c) = e^a e^b e^c$. It can be shown, in fact, that the exponential is the *only* form having this property (see Appendix 1.1), so that we can write

$$F(v_x) = f(v_x^2) = K\exp(\pm\kappa v_x^2), \qquad \textbf{(1.23)}$$

where K and κ are constants to be determined. Note that although κ can appear mathematically with either a plus or a minus sign, we must require the minus sign on physical grounds because we know from common experience that the probability of very high velocities should be small.

The constant K can be determined from normalization since, using **equation 1.17,** the total probability that v_x lies somewhere in the range from $-\infty$ to $+\infty$ should be unity:

$$\int_{-\infty}^{\infty} F(v_x)\,\mathrm{d}v_x = 1. \qquad \textbf{(1.24)}$$

Substitution of **equation 1.23** into **equation 1.24** leads to the equation

$$1 = K\int_{-\infty}^{\infty} \exp(-\kappa v_x^2)\,\mathrm{d}v_x = K\left(\frac{\pi}{\kappa}\right)^{1/2}, \qquad \textbf{(1.25)}$$

where the integral was evaluated using **Table 1.1.** The solution is then $K = (\kappa/\pi)^{1/2}$.

1.5.3 $<v^2>$ Should Agree with the Ideal Gas Law

The constant κ is determined by requiring $<v^2>$ to be equal to $3kT/m$, as in **equation 1.6.** From **equation 1.16** we find

$$<v_x^2> = \int_{-\infty}^{\infty} v_x^2 F(v_x)\,\mathrm{d}v_x = \left(\frac{\kappa}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} v_x^2 \exp(-\kappa v_x^2)\,\mathrm{d}v_x. \qquad \textbf{(1.26)}$$

The integral is a standard one listed in **Table 1.1,** and using its value we find that

$$<v_x^2> = \frac{1}{2}\left(\frac{\kappa}{\pi}\right)^{1/2}\left(\frac{\pi}{\kappa^3}\right)^{1/2} = \frac{1}{2\kappa}. \qquad \textbf{(1.27)}$$

TABLE 1.1 Integrals of Use in the Kinetic Theory of Gases

$$\int_{-\infty}^{\infty} x^{2n}e^{-\beta x^2}\,\mathrm{d}x = 2\int_0^{\infty} x^{2n}e^{-\beta x^2}\,\mathrm{d}x \qquad \int_{-\infty}^{\infty} x^{2n+1}e^{-\beta x^2}\,\mathrm{d}x = 0$$

$$\int_0^{\infty} e^{-\beta x^2}\,\mathrm{d}x = \tfrac{1}{2}\sqrt{\pi}\beta^{-1/2} \qquad \int_0^{\infty} xe^{-\beta x^2}\,\mathrm{d}x = \tfrac{1}{2}\beta^{-1}$$

$$\int_0^{\infty} x^2e^{-\beta x^2}\,\mathrm{d}x = \tfrac{1}{2}\sqrt{\pi}\tfrac{1}{2}\beta^{-3/2} \qquad \int_0^{\infty} x^3e^{-\beta x^2}\,dx = \tfrac{1}{2}\beta^{-2}$$

$$\int_0^{\infty} x^4e^{-\beta x^2}\,\mathrm{d}x = \tfrac{1}{2}\sqrt{\pi}\tfrac{3}{4}\beta^{-5/2} \qquad \int_0^{\infty} x^5e^{-\beta x^2}\,\mathrm{d}x = \beta^{-3}$$

$$\int_0^{\infty} x^{2n}e^{-\beta x^2}\,\mathrm{d}x = \tfrac{1}{2}\sqrt{\pi}\,\frac{(2n)!\beta^{-(n+1/2)}}{2^{2n}n!} \qquad \int_0^{\infty} x^{2n+1}e^{-\beta x^2}\,\mathrm{d}x = \tfrac{1}{2}(n!)\beta^{-(n+1)}$$

As a consequence, the average of the square of the total speed, $<v^2> = <v_x^2> + <v_y^2> + <v_z^2> = 3<v_x^2>$, is simply

$$<v^2> = \frac{3}{2\kappa}. \tag{1.28}$$

From **equation 1.6** we have that $<v^2> = 3kT/m$ for agreement with the ideal gas law, so that $3kT/m = 3/(2\kappa)$, or $\kappa = m/(2kT)$. The complete one-dimensional distribution function is thus

$$F(v_x)\,\mathrm{d}v_x = \left(\frac{m}{2\pi kT}\right)^{1/2}\exp\left(-\frac{1}{2}\frac{mv_x^2}{kT}\right)\mathrm{d}v_x. \tag{1.29}$$

This equation is known as the *one-dimensional Maxwell-Boltzmann distribution for molecular velocities.* Plots of $F(v_x)$ are shown in **Figure 1.2.**

Note that **equation 1.29** is consistent with the Boltzmann distribution law, which states that the probability of finding a system with energy ϵ is proportional to $\exp(-\epsilon/kT)$. Since $\epsilon_x = \frac{1}{2}mv_x^2$ is equal to the translational energy of the molecule in the x direction, the probability of finding a molecule with an energy ϵ_x should be proportional to $\exp(-\epsilon_x/kT)$, as it is in **equation 1.29.** In Section 1.5.1 we ensured $F(v_x)$ to be even by choosing it to depend on the square of the velocity, $F(v_x) = f(v_x^2)$. Had we chosen some other even function, say $F(v_x) = f(v_x^4)$, the final expression for the one-dimensional distribution would not have agreed with the Boltzmann distribution law.

Equation 1.29 provides the distribution of velocities in one dimension. In three dimensions, because $F(v_x,v_y,v_z) = F(v_x)F(v_y)F(v_z)$, and because $v^2 = v_x^2 + v_y^2 + v_z^2$, we find that the probability that the velocity will have components v_x between v_x and $v_x + \mathrm{d}v_x$, v_y between v_y and $v_y + \mathrm{d}v_y$, and v_z between v_z and $v_z + \mathrm{d}v_z$ is given by

$$\begin{aligned} F(v_x,v_y,v_z)\,\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z &= F(v_x)F(v_y)F(v_z)\,\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \\ &= \left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z. \end{aligned} \tag{1.30}$$

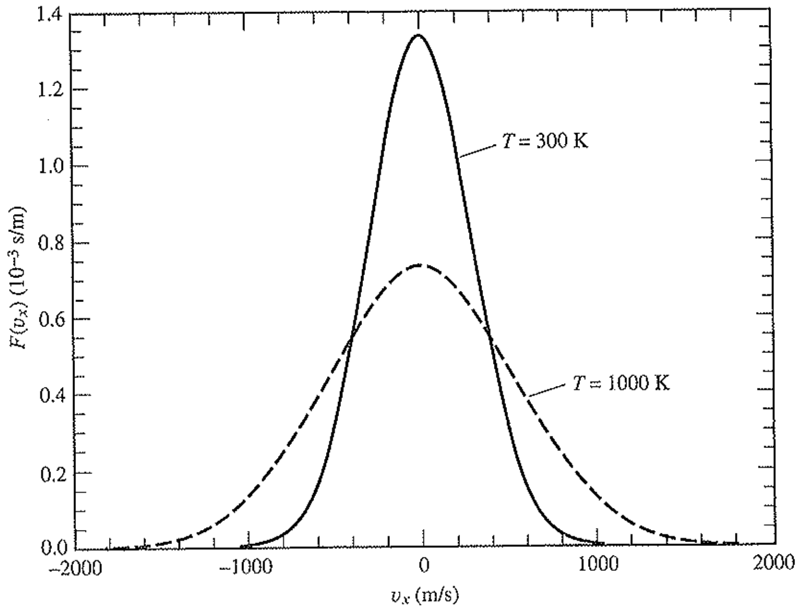


Figure 1.2

One-dimensional velocity distribution for a mass of 28 amu and two temperatures.

1.5.4 The Distribution Depends Only on the Speed

Note that the right-hand side of **equation 1.30** depends on v^2 and not on the directional property of **v**. When we have a function that depends only on the length of the velocity vector, $v = |\mathbf{v}|$, and not on its direction, we can be more precise by saying that the function depends on the *speed* and not on the *velocity*. Since $F(v_x, v_y, v_z) = f(v^2)$ depends on the speed, it is often more convenient to know the probability that molecules have a speed in a particular range than to know the probability that their velocity vectors will terminate in a particular volume. As shown in **Figure 1.3**, the probability that the speed will be between v and $v + dv$ is simply the probability that velocity vectors will terminate within the volume of a spherical shell between the radius v and the radius $v + dv$. The volume of this shell is $dv_x\, dv_y\, dv_z = 4\pi v^2\, dv$, so that the probability that speed will be in the desired range is[f]

---

[f] An alternate method for obtaining **equation 1.31** is to note that $dv_x\, dv_y\, dv_z$ can be written as $v^2 \sin\theta\, d\theta\, d\phi\, dv$ in spherical coordinates (see Appendix 1.2) and then to integrate over the angular coordinates. Since the distribution does not depend on the angular coordinates, the integrals over $d\theta$ and $d\phi$ simply give 4π and we are left with the factor $v^2\, dv$.

$$F(v)\, dv = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} v^2\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)\sin\theta\, dv\, d\theta\, d\phi$$

$$= \int_{\phi=0}^{2\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta\, d\theta\, v^2\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right) dv$$

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

A more complete description of spherical coordinates is found in Appendix 1.2.

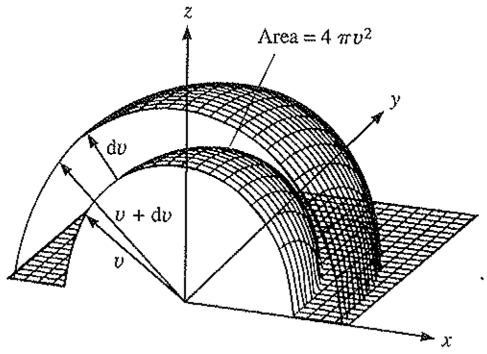


Figure 1.3

The shell between v and $v + \mathrm{d}v$ has a volume of $4\pi v^2\,\mathrm{d}v$. The thickness of the shell here is exaggerated for clarity.

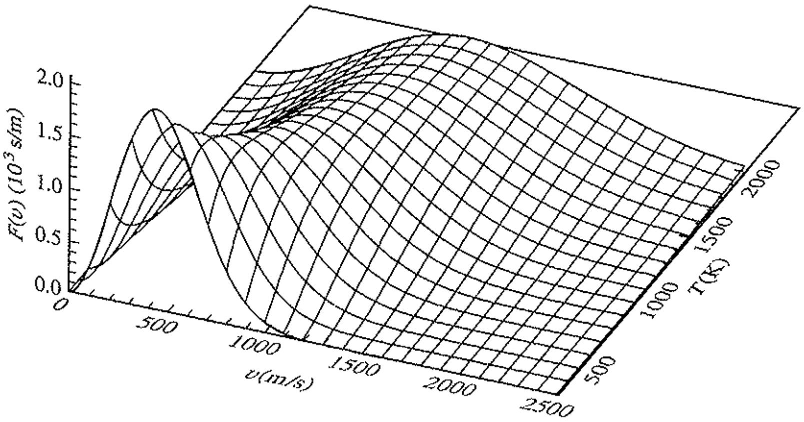


Figure 1.4

Maxwell-Boltzmann speed distribution as a function of temperature for a mass of 28 amu.

$$F(v)\,\mathrm{d}v = 4\pi v^2\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)\mathrm{d}v. \tag{1.31}$$

By analogy to **equation 1.29,** we will call **equation 1.31** the *Maxwell-Boltzmann speed distribution.* Speed distributions as a function of temperature are shown in **Figure 1.4.**

We often characterize the speed distribution by a single parameter, for example, the temperature. Equivalently, we could specify one of several types of "average" speed, each of which is related to the temperature. One such average is called the *root-mean-squared* (rms) speed and can be calculated from **equation**

1.6: $c_{\mathrm{rms}} \equiv <v^2>^{1/2} = (3kT/m)^{1/2}$. Another speed is the *mean* speed defined by using **equation 1.16** to calculate $<v>$:

$$\begin{aligned} <v> &= \int_0^\infty vF(v)\,\mathrm{d}v \\ &= \int_0^\infty v4\pi v^2\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)\mathrm{d}v = \left(\frac{8kT}{\pi m}\right)^{1/2}, \end{aligned} \tag{1.32}$$

where the integral was evaluated using **Table 1.1** as described in detail in **Example 1.4.** Finally, the distribution might also be characterized by the *most probable* speed, c^*, the speed at which the distribution function has a maximum (Problem 1.8):

$$c^* = \left(\frac{2kT}{m}\right)^{1/2}. \tag{1.33}$$

example 1.4

Using the Speed Distribution

Objective The speed distribution can be used to determine averages. For example, find the average speed, $<v>$.

Method Once one has the normalized distribution function, **equation 1.16** gives the method for finding the average of any quantity. Identifying Q as the velocity and $P(Q)\,\mathrm{d}Q$ as the velocity distribution function given in **equation 1.31,** we see that we need to integrate $vF(v)\,\mathrm{d}v$ from limits $v = 0$ to $v = \infty$.

Solution

$$\begin{aligned} <v> &= \int_0^\infty vF(v)\,\mathrm{d}v = \int_0^\infty 4\pi v^3\left(\frac{a^3}{\pi^{3/2}}\right)\exp(-a^2v^2)\,\mathrm{d}v \\ &= \frac{4}{\sqrt{\pi}}\int_0^\infty a^3v^3\exp(-a^2v^2)\,\mathrm{d}v, \end{aligned} \tag{1.34}$$

where $a \equiv (m/2kT)^{1/2}$. We now transform variables by letting $x \equiv av$. The limits will remain unchanged, and $\mathrm{d}v = \mathrm{d}x/a$. Thus the integral in **equation 1.34** becomes

$$\begin{aligned} \frac{4}{a\sqrt{\pi}}\int_0^\infty x^3\exp(-x^2)\,\mathrm{d}x &= \frac{4}{a\sqrt{\pi}}\frac{1}{2} \\ &= \frac{2}{\sqrt{\pi}}\left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{8kT}{\pi m}\right)^{1/2}, \end{aligned} \tag{1.35}$$

where we have used **Table 1.1** to evaluate the integral.

The molecular speed is related to the speed of sound, since sound vibrations cannot travel faster than the molecules causing the pressure waves. For example, in **Example 1.5** we find that the most probable speed for O_2 is 322 m/s, while the

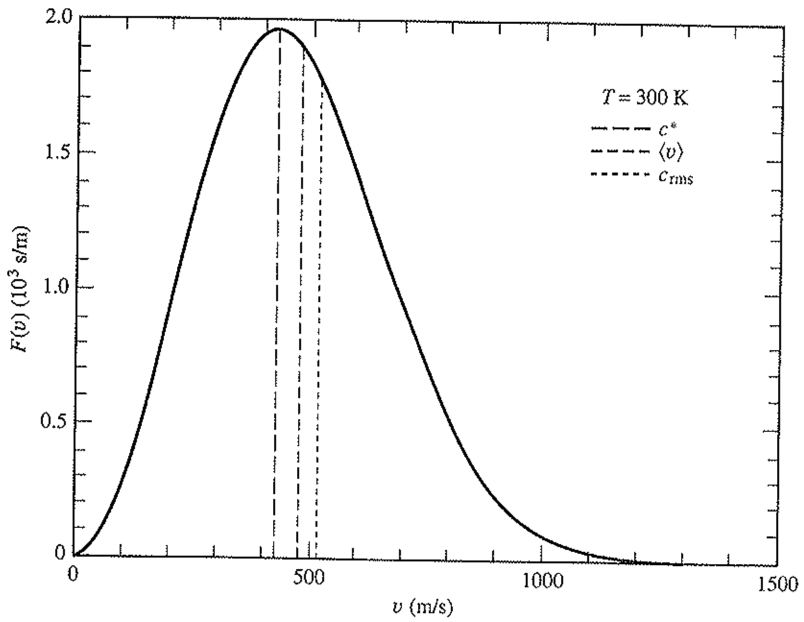


Figure 1.5

Maxwell-Boltzmann speed distribution for a mass of 28 amu and a temperature of 300 K. The vertical lines mark c^*, $<v>$, and c_{rms}.

speed of sound in O_2 is measured to be 330 m/s. For an ideal gas the speed of sound can be shown to be $(\gamma kT/m)^{1/2}$, where γ is the ratio of heat capacities, $\gamma = C_p/C_V$. The *Mach number* is defined as the ratio of the speed of an object in a medium to the speed of sound through the same medium, so that when an aircraft "breaks the sound barrier" (or exceeds "Mach 1") it is actually traveling faster than the speed of the molecules in the medium.

Figure 1.5 shows the shape of the distribution function for $T = 300$ K and the locations of the variously defined speeds.

example 1.5

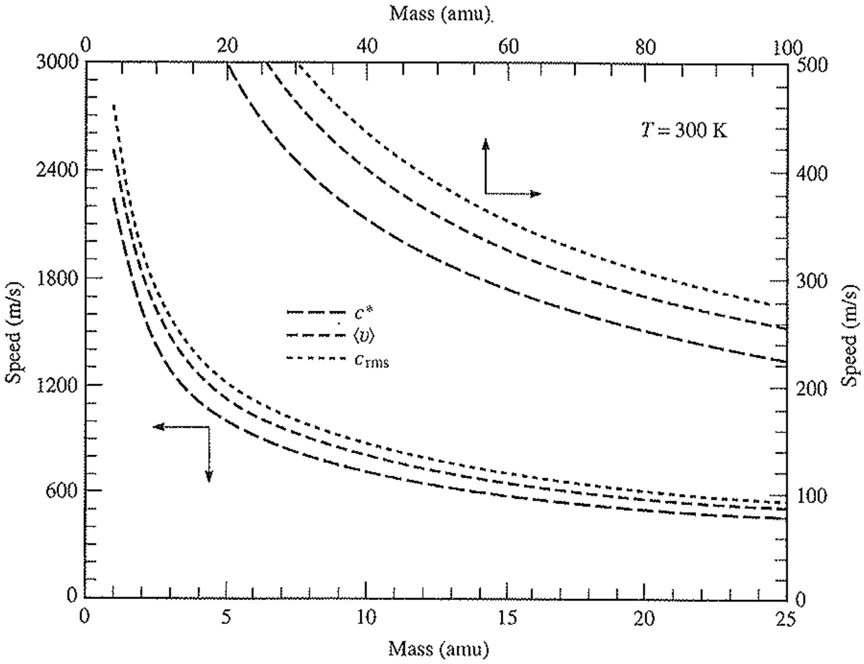
Comparison of the Most Probable Speeds for Oxygen and Helium

Objective Compare the most probable speed for O_2 to that for He at 200 K.

Method Use **equation 1.33** with $T = 200$ K and $m = 2$ amu or $m = 32$ amu. Note that the relative speeds should be proportional to $m^{-1/2}$.

Solution $c^*(\text{He}) = (2kT/m)^{1/2} = [2(1.38 \times 10^{-23}\ \text{J K}^{-1})(200\ \text{K})(6.02 \times 10^{23}\ \text{amu/g})(1000\ \text{g/kg})/(2\ \text{amu})]^{1/2} = 1290$ m/s. A similar calculation substituting 32 amu for 2 amu gives $c^*(O_2) = 322$ m/s.

Comment The escape velocity from the Earth's gravitational field is roughly $v_e = 1.1 \times 10^4$ m/s, only about 10 times the most probable speed for helium. Because the velocity distribution shifts so strongly toward high velocities as the mass decreases, the fraction of helium



■ **Figure 1.6**

Various average speeds as a function of mass for $T = 300$ K.

atoms having speeds in excess of v_e, while minuscule (about 10^{-31}), is still 10^{475} times larger than the fraction of oxygen molecules having speeds in excess of v_e! As a consequence, the composition of the atmosphere is changing; much of the helium released during the lifetime of the planet has already escaped into space. A plot of various speeds as a function of mass for $T = 300$ K is shown in **Figure 1.6.**

1.5.5 Experimental Measurement of the Maxwell Distribution of Speeds

Experimental verification of the Maxwell-Boltzmann speed distribution can be made by direct measurement using the apparatus of **Figure 1.7.** Two versions of the measurement are shown. In **Figure 1.7a,** slits (S) define a beam of molecules moving in a particular direction after effusing from an oven (O). Those that reach the detector (D) must successfully have traversed a slotted, multiwheel chopper by traveling a distance d while the chopper rotated through an angle ϕ. In effect, the chopper selects a small slice from the velocity distribution and passes it to the detector. The speed distribution is then measured by recording the integrated detector signal for each cycle of the chopper as a function of the angular speed of the chopper.

A somewhat more modern technique, illustrated in **Figure 1.7b,** clocks the time it takes for molecules to travel a fixed distance. A very short pulse of molecules leaves the chopper at time $t = 0$. Because these molecules have a distribution of speeds, they spread out in space as they travel toward the detector, which records as a function of time the signal due to molecules arriving a distance L from the chopper.

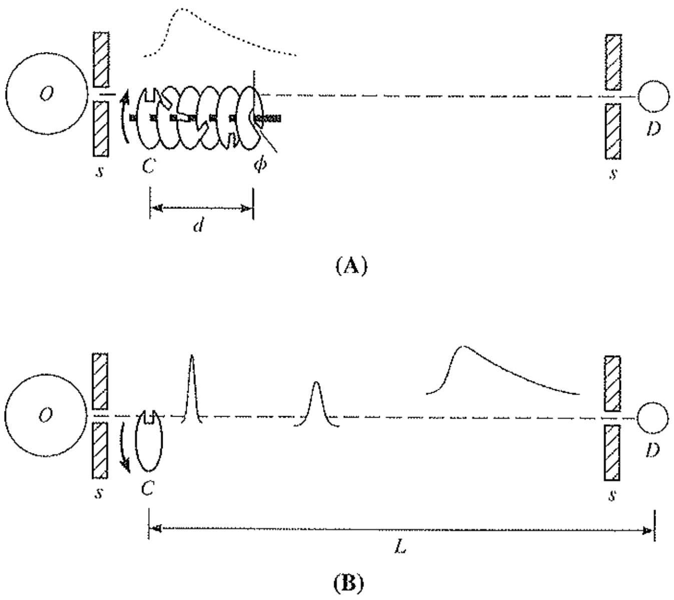


Figure 1.7

Two methods for measuring the Maxwell-Boltzmann speed distribution.

Analysis of the detector signal from this second experiment is instructive, since it introduces the concept of *flux*. Recall that the distribution $F(v)\,\mathrm{d}v$ gives the fraction of molecules with speeds in the range from v to $v + \mathrm{d}v$; it is dimensionless. If the number density of molecules is n^*, then $n^*F(v)\,\mathrm{d}v$ will be the number of molecules per unit volume with speeds in the specified range. The *flux* of molecules is defined as the number of molecules crossing a unit area per unit time. It is equal to the density of molecules times their velocity: flux (number/m^2/s) = density (number/m^3) × velocity (m/s).[g] Thus, the flux J of molecules with speeds between v and $v + \mathrm{d}v$ is

$$J\,\mathrm{d}v = vn^*F(v)\,\mathrm{d}v. \tag{1.36}$$

We will consider the flux in more detail in Section 4.3.2 and make extensive use of it in Chapter 4.

We now return to the speed measurement. Most detectors actually measure the number of molecules in a particular volume during a particular time duration. For example, the detector might measure current after ionizing those molecules that enter a volume defined by a cross-sectional area of A and a length ℓ. Because molecules with high velocity traverse the distance ℓ in less time than molecules with low velocity, the detection sensitivity is proportional to $1/v$. The detector signal $S(t)$ is thus proportional to $JA\ell\,\mathrm{d}v/v$, or to $n^*A\ell F(v)\,\mathrm{d}v$, where n^* is the number density of molecules in the oven. Assuming that a very narrow pulse of molecules is emitted from the chopper, the speed measured at a particular time t is simply $v = L/t$. We must now transform the velocity distribution from a speed distribution to a time distribution. Note that $\mathrm{d}v = \mathrm{d}(L/t) = -L\,\mathrm{d}t/t^2$, and recall from **equation 1.31** that $F(v)\,\mathrm{d}v \propto v^2\exp(-\beta v^2)\,\mathrm{d}v \propto (1/t^2)\exp(-\beta L^2/t^2)(L/t^2)$. We thus find that $S(t) \propto t^{-4}\exp(-\beta L^2/t^2)$. **Figure 1.8** displays an arrival time distribution of helium measured

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[g] Strictly speaking, the flux, **J**, is a vector, since the magnitude of the flux may be different in different directions. Here, since the direction of the flux is clear, we will use just its magnitude, J.

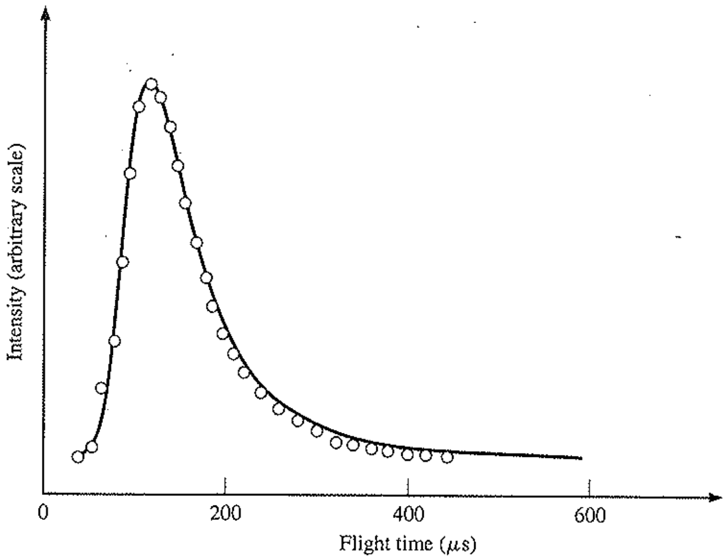

Figure 1.8

Time-of-flight measurements: intensity as a function of flight time.
From J. F. C. Wang and H. Y. Wachman, as illustrated in F. O. Goodman and H. Y. Wachman, *Dynamics of Gas-Surface Scattering* (Academic Press, New York, 1976). Figure from "Molecular Beams" in DYNAMICS OF GAS-SURFACE SCATTERING by F. O. Goodman and H. Y. Wachmann, copyright © 1976 by Academic Press, reproduced by permission of the publisher. All rights or reproduction in any form reserved.

using this "time-of-flight" technique. The open circles are the detector signal, while the smooth line is a fit to the data of a function of the form expected for $S(t)$. The best fit parameter gives a temperature of 300 K.

1.6 ENERGY DISTRIBUTIONS

It is sometimes interesting to know the distribution of molecular energies rather than velocities. Of course, these two distributions must be related since the molecular translational energy ϵ is equal to $\frac{1}{2}mv^2$. Noting that this factor occurs in the exponent of **equation 1.31** and that $d\epsilon = mv\,dv = (2m\epsilon)^{1/2}\,dv$, we can convert velocities to energies in **equation 1.31** to obtain

$$\begin{aligned} G(\epsilon)\,d\epsilon &= 4\pi\left(\frac{2\epsilon}{m}\right)\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{\epsilon}{kT}\right)\frac{d\epsilon}{\sqrt{2m\epsilon}} \\ &= 2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\sqrt{\epsilon}\exp\left(-\frac{\epsilon}{kT}\right)d\epsilon. \end{aligned} \tag{1.37}$$

The function $G(\epsilon)\,d\epsilon$ tells us the fraction of molecules which have energies in the range between ϵ and $\epsilon + d\epsilon$. Plots of $G(\epsilon)$ are shown in **Figure 1.9.**

The distribution function $G(\epsilon)$ can be used to calculate the average of any function of ϵ using the relationship of **equation 1.16.** In particular, it can be shown as expected that $\langle\epsilon\rangle = 3kT/2$ (see Problem 1.9).

Let us pause here to make a connection with thermodynamics. In the case of an ideal monatomic gas, there are no contributions to the energy of the gas from internal degrees of freedom such as rotation or vibration, and there is normally very

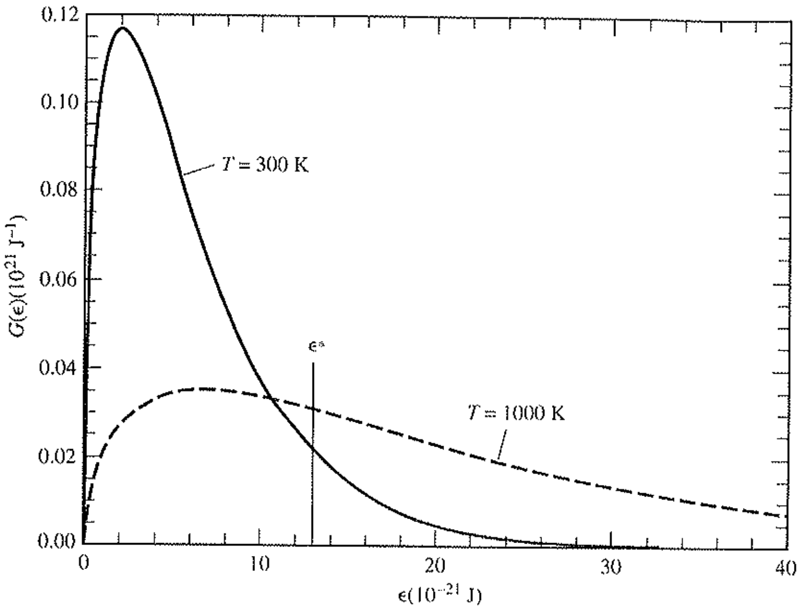

Figure 1.9

Energy distributions for two different temperatures. The fraction of molecules for the 300 K distribution having energy in excess of ϵ^* is shown in the shaded region.

little contribution to the energy from excitation of electronic degrees of freedom. Consequently, the average energy U of n moles of a monatomic gas is simply nN_A times the average energy of one molecule of the gas, or

$$U = nN_A\frac{3}{2}kT = \frac{3}{2}nRT. \tag{1.38}$$

Note that the heat capacity at constant volume is defined as $C_V = (\partial U/\partial T)_V$, so that for an ideal monatomic gas we find that

$$C_V = \frac{3}{2}nR. \tag{1.39}$$

This result is an example of the *equipartition principle,* which states that each term in the expression of the molecular energy that is quadratic in a particular coordinate contributes $\frac{1}{2}kT$ to the average kinetic energy and $\frac{1}{2}R$ to the molar heat capacity. Since there are three quadratic terms in the three-dimensional translational energy expression, the molar heat capacity of a monatomic gas should be $3R/2$.

It is sometimes useful to know what fraction of molecules has an energy greater than or equal to a certain value ϵ^*. In principle, the energy distribution $G(\epsilon)$ should be able to provide this information, since the fraction of molecules having energy in the desired range is simply the integral of $G(\epsilon)\,d\epsilon$ from ϵ^* to infinity, as shown by the hatched region in **Figure 1.9.** In practice, the mathematics are somewhat cumbersome, but the result is reasonable. Let $f(\epsilon^*)$ be the fraction of molecules with kinetic energy equal to or greater than ϵ^*. This fraction is given by the integral

$$f(\epsilon^*) = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\int_{\epsilon^*}^{\infty}\sqrt{\epsilon}\exp\left(-\frac{\epsilon}{kT}\right)d\epsilon. \tag{1.40}$$

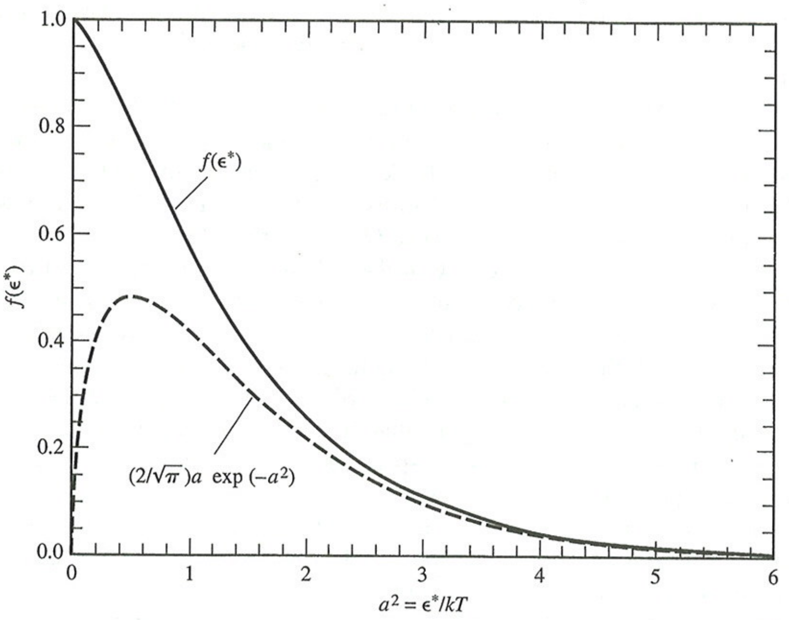

Figure 1.10

The fraction of molecules having energy in excess of ϵ^* as a function of ϵ^*/kT.

Problem 1.10 shows that this integral is given by

$$f(\epsilon^*) = \frac{2}{\sqrt{\pi}}ae^{-a^2} + \text{erfc}(a), \tag{1.41}$$

where $a = (\epsilon^*/kT)^{1/2}$ and erfc(a) is the co-error function defined in Appendix 1.3. A plot of $f(\epsilon^*)$ as a function of ϵ^*/kT is shown in **Figure 1.10.** Note that for $\epsilon^* > 3kT$, the function $f(\epsilon^*)$ is nearly equal to the first term in **equation 1.41,** $2\sqrt{(\epsilon^*/\pi kT)}\exp(-\epsilon^*/kT)$, shown by the dashed line in the figure. Thus, the fraction of molecules with energy greater than ϵ^* falls off as $\sqrt{\epsilon^*}\exp(-\epsilon^*/kT)$, provided that $\epsilon^* > 3kT$.

1.7 COLLISIONS: MEAN FREE PATH AND COLLISION NUMBER

One of the goals of this chapter is to derive an expression for the number of collisions that molecules of type 1 make with molecules of type 2 in a given time. We will argue later that this collision rate provides an upper limit to the reaction rate, since the two species must have a close encounter to react.

The principal properties of the collision rate can be easily appreciated by anyone who has ice skated at a local rink. Imagine two groups of skaters, some rather sedate adults and some rambunctious 13-year-old kids. If there is only one kid and one adult in the rink, then the likelihood that they will collide is small, but as the number of either adults or kids in the rink increases, so does the rate at which collisions will occur. The collision rate is proportional to the number of possible kid-adult pairs, which is proportional to the number density of adults times the number density of kids.

But the collision rate depends on other factors as well. If all the skaters follow the rules and skate counterclockwise around the rink at the same speed, then there will be no collisions. More often, the kids will skate at much faster or slower speeds, and they will rarely move uniformly. The rate at which they collide with the adults is proportional to the *relative speed* between the adults and kids.

Finally, consider the dependence of the collision rate on the size of the adults and kids. People are typically about 40 cm wide. What would be the effect of increasing or decreasing this diameter by a factor of 10? If the diameter were decreased to 4 cm, the number of collisions would go down dramatically; if the diameter were increased to 4 m, it would be difficult to move around the rink at all. Thus, simple considerations suggest that the collision rate between molecules should be proportional to the relative speed of the molecules, to their size, and to the number of possible collision pairs.

Let us assume that the average of the magnitude of the relative velocity between molecules of types 1 and 2 is $<v_r>$ and that the molecules behave like hard spheres; there are no attractive forces between them, and they bounce off one another like billiard balls when they collide.[h] Let the quantity b, shown in **Figure 1.11,** be defined as the distance of a line perpendicular to the each of the initial velocities of two colliding molecules, one of type 1 and the other of type 2. This distance is often referred to as the *impact parameter.* If the radii of the two molecules are r_1 and r_2, then, as shown in **Figure 1.11,** a "collision" will occur if the two molecules approach one another so that their centers are within the distance $b_{\text{max}} \equiv r_1 + r_2$. Thus, b_{max} is the maximum value of the impact parameter for which a collision can occur. From the point of view of one type of molecule striking a molecule of the other type, the target area for a collision is then equal to $\pi(r_1 + r_2)^2 = \pi b_{\text{max}}^2$.

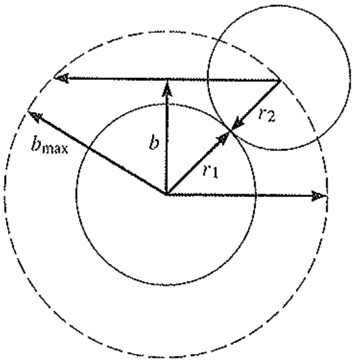

Figure 1.11

A collision will occur if the impact parameter is less than b_{max}, the sum of the two molecular radii.

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[h] We consider only the *relative* velocity between the molecules. Appendix 1.4 shows that the *total* velocity of each molecule can be written as a vector sum of the velocity of the center of mass of the pair of molecules and the relative velocity of the molecule with respect to the center of mass. The forces between molecules depend on the relative distance between them and do not change the velocity of their center of mass, which must be conserved during the collision.

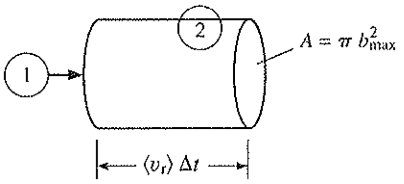

Figure 1.12

Molecule 1 sweeps out a cylinder of area $\pi b_{\max}^2$. Any molecule of type 2 whose center is within the cylinder will be struck.

Consider a molecule of type 1 moving through a gas with a speed equal to the average magnitude of the relative velocity $<v_r>$. **Figure 1.12** shows that any molecule of type 2 located in a cylinder of volume $\pi b_{\max}^2 <v_r> \Delta t$ will then be struck in the time Δt.[1] If the density of molecules of type 2 is n_2^*, then the number of collisions one molecule of type 1 will experience with molecules of type 2 per unit time is

$$Z_2 = \pi b_{\max}^2 <v_r> n_2^*. \qquad \textbf{(1.42)}$$

Of course, for a molecule of type 1 moving through other molecules of the same type,

$$Z_1 = \pi b_{\max}^2 <v_r> n_1^* = \pi d^2 <v_r> n_1^*, \qquad \textbf{(1.43)}$$

where $b_{\max}^2$ has been replaced by d^2 since $r_1 + r_2 = 2r_1 = d$. The quantity $\pi b_{\max}^2$ is known as the hard-sphere collision cross section. Cross sections are generally given the symbol σ.

Equation 1.42 gives the number of collisions per unit time of one molecule of type 1 with a density n_2^* of molecules of type 2. The *total* number of collisions of molecules of type 1 with those of type 2 per unit time and per unit volume is found simply by multiplying by the density of type 1 molecules:

$$Z_{12} = Z_2 n_1^* = \pi b_{\max}^2 <v_r> n_1^* n_2^*. \qquad \textbf{(1.44)}$$

Note that the product $n_1^* n_2^*$ is simply proportional to the total number of pairs of collision partners.

By a similar argument, if there were only one type of molecule, the number of collisions per unit time per unit volume is given by

$$Z_{11} = \frac{1}{2} Z_1 n_1^* = \frac{1}{2} \pi b_{\max}^2 <v_r> (n_1^*)^2. \qquad \textbf{(1.45)}$$

The factor of $\frac{1}{2}$ is introduced for the following reason. The collision rate should be proportional to the number of pairs of collision partners. If there are n molecules, then the number of pairs is $n(n - 1)/2$, since each molecule can pair with $n - 1$ others and the factor of 2 in the denominator corrects for having counted each pair twice. If n is a large number, then we can approximate $n(n - 1)$ as n^2, and since the number of molecules is proportional to the number density, we see that the number of pairs goes as $(n_1^*)^2/2$.

It remains for us to determine the value of the relative speed, averaged over the possible angles of collision and averaged over the speed distribution for each molecule. One way to arrive quickly at the answer for a very specific case is shown in

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[1] Because of the collisions, the molecule under consideration will actually travel along a zigzag path, but the volume swept out per unit time will be the same.

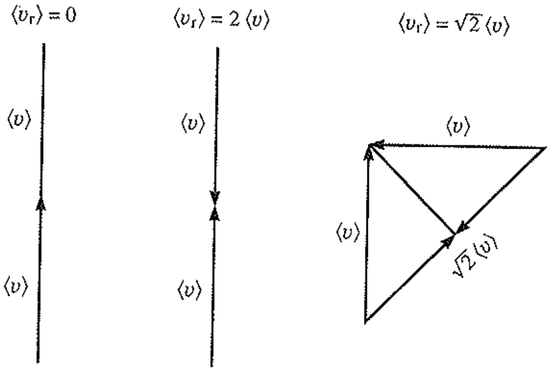

Figure 1.13

In a hypothetical collision where two molecules each have a speed equal to the average $<v>$, the relative velocity between two molecules, averaged over all collision directions, is $\sqrt{2}<v>$.

Figure 1.13. Suppose that the two types of molecules have the same mass, m. Let us assume for the moment that we can accomplish the average of the speed distribution by assuming that the two molecules each have a speed equal to the average of their distribution. Since the two molecules are assumed to have the same mass (and temperature), they will also have the same average speed, $<v>$. We now consider the average over collision angles. If the molecules are traveling in the same direction, then the relative velocity between them will have zero magnitude, $v_r = 0$, while if they are traveling in opposite directions along the same line the relative velocity will have a magnitude of $v_r = 2<v>$. Suppose that they are traveling at right angles to one another. In that case, which is representative of the average angle of collision, the relative velocity will have a magnitude of $v_r = <v_r> = \sqrt{2}<v>$. Recalling from **equation 1.32** that $<v> = (8kT/\pi m)^{1/2}$, we find that

$$\begin{aligned} <v_r> &= \sqrt{2}<v> \\ &= \sqrt{2}\left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8kT}{\pi(m/2)}\right)^{1/2} = \left(\frac{8kT}{\pi\mu}\right)^{1/2}, \end{aligned} \quad \textbf{(1.46)}$$

where we have introduced the *reduced mass*, μ, defined as $\mu = m_1m_2/(m_1 + m_2)$. When the masses m_1 and m_2 are the same, $\mu = m^2/2m = m/2$. If the masses are different, then the mean velocities will not be the same, and the simple analysis of **Figure 1.13** is not adequate. However, as shown for the general case in Appendix 1.4 and Problem 1.12, the result for $<v_r>$ is the same as that given in **equation 1.46.** The appendix also shows why the definition of μ as $m_1m_2/(m_1 + m_2)$ is a useful one.

example 1.6

The Collision Rate of NO with O_3

Objective Find the collision rate of NO with O_3 at 300 K if the abundances at 1 atm total pressure are each 0.2 ppm and if the molecular diameters are 300 and 375 pm, respectively. Reactive collisions between these two species are important in photochemical smog formation.

Method Use **equation 1.44,** remembering to convert the abundances to number densities at 300 K and calculating the average relative velocity by use of **equation 1.46.**

Solution First find the total number density n^* at 1 atm: $n^* = (n/V)N_A = (p/RT)N_A = (1\text{ atm})(6.02 \times 10^{23}\text{ molec/mole})/[(0.082\text{ L atm mol}^{-1}\text{ K}^{-1})(300\text{ K})] = 2.45 \times 10^{22}$ molec/L. Next determine the number densities of NO and O_3, each being the total density times 0.2×10^{-6}: $n^*(\text{NO}) = n^*(O_3) = (0.2 \times 10^{-6})(2.45 \times 10^{22}) = 4.9 \times 10^{15}$ molec/L. The average relative velocity is $<v_r> = (8kT/\pi\mu)^{1/2} = [8(1.38 \times 10^{-23}\text{ J K}^{-1})(300\text{ K})(6.02 \times 10^{23}\text{ amu/g})(1000\text{ g/kg})/(\pi(48 \times 30/78)\text{ amu})]^{1/2} = 586$ m/s. The average diameter is $(300 + 375\text{ pm})/2 = 337.5$ pm. Then $Z_{12} = \pi(337.5 \times 10^{-12}\text{ m})^2(586\text{ m/s})(4.9 \times 10^{15}\text{ molec/L})^2(1\text{ L}/10^{-3}\text{ m}^3)^2 = 5.0 \times 10^{21}$ collisions $\text{s}^{-1}\text{ m}^{-3}$. If every collision resulted in a reaction, this would be the number of reactions per unit second per cubic meter.

A quantity related to Z_1 is the *mean free path*, λ. This is the average distance a molecule travels before colliding with another molecule. If we divide the average speed $<v>$ in meters per second by the collision number Z_1 in collisions per second, we obtain the mean free path in meters per collision:

$$\lambda = \frac{<v>}{Z_1} = \frac{<v>}{\pi d^2\sqrt{2}<v>n_1^*} = \frac{1}{\sqrt{2}\,\pi d^2 n_1^*}. \tag{1.47}$$

Note that the mean free path is inversely proportional to pressure. The mean free path will be important in Chapter 4, where we will see that the transport of heat, momentum, and matter are all proportional to the distance traveled between collisions.

example 1.7

The Mean Free Path of Nitrogen

Objective Find Z_1 and the mean free path of N_2 at 300 K and 1 atm given that the molecular diameter is 218 pm.

Method Use **equation 1.46** to calculate $<v_r>$, **equation 1.43** to calculate Z_1, and **equation 1.47** to calculate λ.

Solution We start by calculating $<v_r> = (8kT/\pi\mu)^{1/2}$, where $\mu = 28 \times 28/(28 + 28) = 14$ amu.

$$<v_r> = \left\{\frac{8(1.38 \times 10^{-23}\text{ J K}^{-1})(300\text{ K})(6.02 \times 10^{23}\text{ amu/g})(1000\text{ g/kg})}{(3.1415 \times 14\text{ amu})}\right\}^{1/2} = 673\text{ m/s}. \tag{1.48}$$

Next, we calculate Z_1 noting that the density

$$n_1^* = \frac{p}{RT} = \frac{(1\ \text{atm})(6.02 \times 10^{23}\ \text{molec/mole})}{(0.082\ \text{L atm mole}^{-1}\ \text{K}^{-1})(10^{-3}\ \text{m}^3/\text{L})(300\ \text{K})}$$

$$= 2.45 \times 10^{25}\ \text{molec/m}^3. \qquad \textbf{(1.49)}$$

Then, $Z_1 = \pi(218 \times 10^{-12}\ \text{m})^2(673\ \text{m/s})(2.45 \times 10^{25}\ \text{molec/m}^3) = 2.46 \times 10^9$ collision/s. Finally, $<v_r>/(\sqrt{2}Z_1) = (673\ \text{m/s})/(\sqrt{2} \times 2.46 \times 10^9\ \text{collision/s}) = 1.93 \times 10^{-7}\ \text{m}$.

1.8 SUMMARY

By considering the pressure exerted by ideal gas molecules on a wall, we determined that, for agreement with the observed ideal gas law, the average energy of a molecule must be given by

$$<\epsilon> = \frac{3}{2}kT. \qquad \textbf{(1.5)}$$

To learn how to perform averages, we discussed distribution functions of a continuous variable. The average of some observable quantity Q was found to be given by

$$<Q> = \int P(Q)Q\,dQ, \qquad \textbf{(1.16)}$$

where $P(Q)$ is the distribution function for the quantity Q. We then made the following observations about the molecular speed distribution: (1) the speed distribution must be an even function of v, (2) the speed distribution in any particular direction is independent from and uncorrelated with that in orthogonal directions, (3) the value of $<v^2>$ must be equal to $3kT/m$ to agree with the ideal gas law, and (4) the distribution depends only on the magnitude of v. These four considerations allowed us to determine the Maxwell-Boltzmann distribution of speeds:

$$F(v)\,dv = 4\pi v^2\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv. \qquad \textbf{(1.31)}$$

Calculations using this distribution gave us an equation for the average speed of a molecule,

$$<v> = \left(\frac{8kT}{\pi m}\right)^{1/2}, \qquad \textbf{(1.32)}$$

and the most probable speed,

$$c^*\left(\frac{2kT}{m}\right)^{1/2}. \qquad \textbf{(1.33)}$$

A simple transformation of variables in the speed distribution led to the Maxwell-Boltzmann energy distribution:

$$G(\epsilon)\,d\epsilon = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2} \sqrt{\epsilon}\,\exp\left(-\frac{\epsilon}{kT}\right) d\epsilon. \qquad \textbf{(1.37)}$$

Finally, for molecules behaving as hard spheres, we determined the collision rate,

$$Z_1 = \pi b_{\text{max}}^2 <v_r> n_1^*, \qquad \textbf{(1.42)}$$

the relative velocity,

$$<v_r> = \sqrt{2}<v> = \left(\frac{8kT}{\pi\mu}\right)^{1/2}, \tag{1.46}$$

and the mean free path,

$$\lambda = \frac{<v>}{Z_1} = \frac{1}{\sqrt{2}\pi d^2 n_1^*}. \tag{1.47}$$

These concepts form the basis for further investigation into transport properties and chemical reaction kinetics.

appendix 1.1

The Functional Form of the Velocity Distribution

We demonstrate in this appendix that the exponential form used in **equation 1.23** is the only function that satisfies the equation $f(a + b + c) = f(a)f(b)f(c)$. Consider first the simpler equation

$$f(z) = f(a)f(b), \tag{1.50}$$

where $z = a + b$. Taking the derivative of both sides of **equation 1.50** with respect to a we obtain

$$\frac{\mathrm{d}f(z)}{\mathrm{d}z}\frac{\mathrm{d}z}{\mathrm{d}a} = f'(a)f(b). \tag{1.51}$$

On the other hand, taking the derivative of both sides of **equation 1.50** with respect to b, we obtain

$$\frac{\mathrm{d}f(z)}{\mathrm{d}z}\frac{\mathrm{d}z}{\mathrm{d}b} = f(a)f'(b). \tag{1.52}$$

Since $z = a + b$, $\mathrm{d}z/\mathrm{d}a = \mathrm{d}z/\mathrm{d}b = 1$. Consequently,

$$\frac{\mathrm{d}f(z)}{\mathrm{d}z} = f'(a)f(b) = f(a)f'(b). \tag{1.53}$$

Division of both sides of the right-hand equality by $f(a)f(b)$ yields

$$\frac{f'(a)}{f(a)} = \frac{f'(b)}{f(b)}. \tag{1.54}$$

Now the left-hand side of **equation 1.54** depends only on a, while the right-hand side depends only on b. Since a and b are independent variables, the only way that **equation 1.54** can be true is if each side of the equation is equal to a constant, $\pm\kappa$, where κ is defined as nonnegative:

$$\frac{f'(a)}{f(a)} = \pm\kappa \qquad \frac{f'(b)}{f(b)} = \pm\kappa. \tag{1.55}$$

Solution of these differential equations using x to represent either a or b leads to

$$\frac{f'(x)}{f(x)} = \pm\kappa \qquad \text{or} \qquad \frac{\mathrm{d}f(x)}{f(x)} = \pm\kappa\,\mathrm{d}x. \tag{1.56}$$

Integration shows that

$$f(x) = Ke^{\pm\kappa x}, \tag{1.57}$$

where K is related to the constant of integration. **Equation 1.23** is obtained by replacing x with v_x^2.

appendix 1.2

Spherical Coordinates

Many problems in physical chemistry can be solved more easily using spherical rather than Cartesian coordinates. In this coordinate system, as shown in **Figure 1.14,** a point P is located by its distance r from the origin, the angle θ between the z axis and the line from the point to the origin, and the angle ϕ between the x axis and the line between the origin and a projection of the point onto the x-y plane. Any point can be described by a value of r between 0 and ∞, a value of θ between 0 and π, and a value of ϕ between 0 and 2π. The Cartesian coordinates are related to the spherical ones by the following relationships: $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, and $z = r \cos\theta$.

The volume element in spherical coordinates can be calculated with the help of **Figure 1.15.** As the variable θ is increased for fixed r, the position of the point described by (r,θ,ϕ) moves along a longitudinal line on the surface of a sphere, while if ϕ is increased at fixed r, the position of the point moves along a latitudinal line. Starting at a point located at (r,θ,ϕ), if r is increased by dr, θ is increased by dθ, and ϕ is increased by dϕ, then the volume increase is the surface area on the

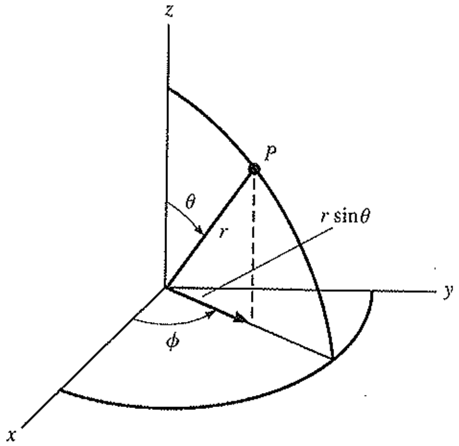

Figure 1.14

Spherical coordinates.

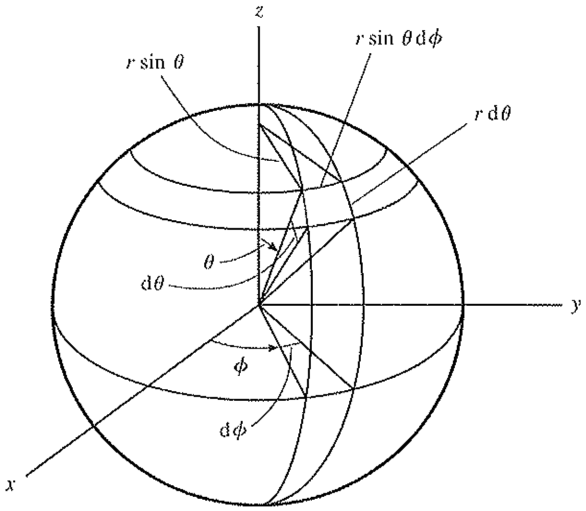

Figure 1.15

The volume element in spherical coordinates.

sphere times the thickness dr (for clarity, the thickness dr is not shown in the diagram). The surface area is given by the arc length on the longitude, $r\,\mathrm{d}\theta$, times the arc length on the latitude, $r \sin\theta\,\mathrm{d}\phi$. Thus, the volume element is $\mathrm{d}V = r^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}r$.

appendix 1.3

The Error Function and Co-Error Function

It often occurs that we need to evaluate integrals of the form of those listed in **Table 1.1** but for limits less than the range of 0 to infinity. For such evaluations it is useful to define the *error function*:

$$\mathrm{erf}(x) \equiv \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2}\,\mathrm{d}u. \tag{1.58}$$

From **Table 1.1** we see that for $x = \infty$, the value of the integral is $\sqrt{\pi}/2$, so that $\mathrm{erf}(\infty) = 1$. Note that if we "complement" the error function by $2/\sqrt{\pi}$ times the integral from x to ∞, we should get unity:

$$\begin{aligned} \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2}\,\mathrm{d}u + \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2}\,\mathrm{d}u &= \mathrm{erf}(x) + \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2}\,\mathrm{d}u \\ &= \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-u^2}\,\mathrm{d}u = 1. \end{aligned} \tag{1.59}$$

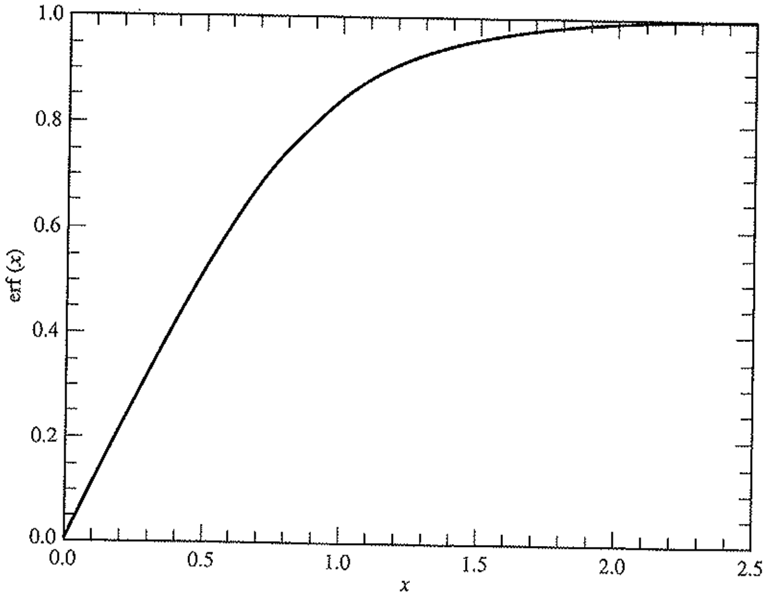

Figure 1.16

Values of the error function.

Consequently, it is also useful to define the co-error function, erfc(x), as the complement to the error function:

$$\operatorname{erfc}(x) \equiv 1 - \operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-u^2}\, \mathrm{d}u. \tag{1.60}$$

Tables of the error function and co-error function are available, but the pervasive use of computers has made them all but obsolete. For calculational purposes, the integrand in **equation 1.58** or **equation 1.60** can be expanded using a series,

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{n!\,(2n+1)}, \tag{1.61}$$

and then the integration can be performed term by term. **Figure 1.16** plots erf(x) as a function of x.

appendix 1.4

The Center-of-Mass Frame

We show in this appendix that the total kinetic energy of two particles of velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ is given by $\frac{1}{2}\mu v_r^2 + \frac{1}{2}Mv_{\text{com}}^2$, where $\mathbf{v}_r = \mathbf{v}_2 - \mathbf{v}_1$, and where $\mathbf{v}_{\text{com}}$, the vector describing the velocity of the center of mass, is defined by the equation $(m_1 + m_2)\mathbf{v}_{\text{com}} = m_1\mathbf{v}_1 + m_2\mathbf{v}_2$, and $M \equiv m_1 + m_2$. **Figure 1.17** shows the vector relationships.

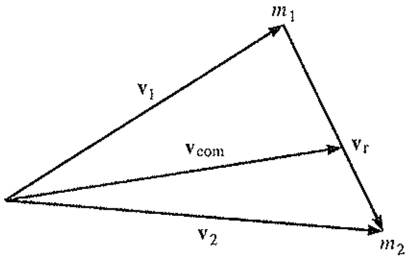

Figure 1.17

Vector diagram for center-of-mass conversion.

The virtue of this transformation is that the total momentum of the system $\mathbf{p} = m_1\mathbf{v}_1 + m_2\mathbf{v}_2$ is also equal to the momentum of the center of mass, defined as $M\mathbf{v}_{\text{com}}$. Because we assume that no external forces are acting on the system, $\mathbf{F} = M\mathbf{a}_{\text{com}} = (d\mathbf{p}_{\text{com}}/dt) = 0$, so that the momentum of the center of mass does not change during the interaction between the two particles.

Note that since $(m_1/M) + (m_2/M) = 1$ we can write

$$\begin{aligned}\mathbf{v}_2 - \mathbf{v}_{\text{com}} &= \left(\frac{m_1}{M} + \frac{m_2}{M}\right)\mathbf{v}_2 - \mathbf{v}_{\text{com}} \\ &= \frac{m_1}{M}\mathbf{v}_2 + \frac{m_2}{M}\mathbf{v}_2 - \mathbf{v}_{\text{com}}.\end{aligned} \tag{1.62}$$

However,

$$m_1\mathbf{v}_1 + m_2\mathbf{v}_2 = M\mathbf{v}_{\text{com}}, \tag{1.63}$$

so that

$$-\frac{m_1\mathbf{v}_1}{M} = \frac{m_2\mathbf{v}_2}{M} - \mathbf{v}_{\text{com}}.$$

Consequently,

$$\begin{aligned}\mathbf{v}_2 - \mathbf{v}_{\text{com}} &= \frac{m_1}{M}\mathbf{v}_2 - \frac{m_1}{M}\mathbf{v}_1 \\ &= \frac{m_1}{M}\mathbf{v}_r.\end{aligned} \tag{1.64}$$

In a similar way, we find that

$$\mathbf{v}_{\text{com}} - \mathbf{v}_1 = \frac{m_2}{M}\mathbf{v}_r. \tag{1.65}$$

We now note an important point, that the velocities of the particles with respect to the center of mass are just given by the two pieces of the vector $\mathbf{v}_r$: $\mathbf{u}_1 = -(m_2/M)\mathbf{v}_r$, and $\mathbf{u}_2 = (m_1/M)\mathbf{v}_r$, as shown in **Figure 1.18.** Note also that in the moving frame of the center of mass, there is no net momentum for the particles; that is, $m_1\mathbf{u}_1 + m_2\mathbf{u}_2 = 0$. This important property enables us to calculate the velocity of one particle in the center-of-mass frame given just the mass and the velocity of the other particle.

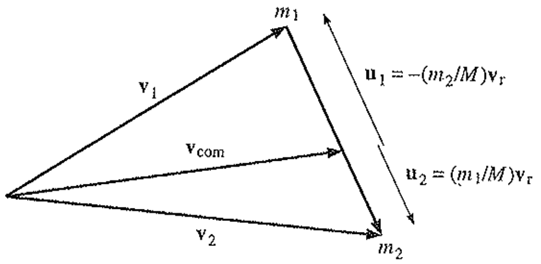

Figure 1.18

Vector diagram for center-of-mass conversion, showing the relative velocities in the center-of-mass frame for the two particles.

We can rearrange **equations 1.64** and **1.65** to get

$$\begin{aligned}\mathbf{v}_{\text{com}} - \frac{m_2}{M}\mathbf{v}_r &= \mathbf{v}_1,\\ \mathbf{v}_{\text{com}} + \frac{m_1}{M}\mathbf{v}_r &= \mathbf{v}_2.\end{aligned} \tag{1.66}$$

The total energy is then

$$\begin{aligned}\frac{1}{2}m_1\mathbf{v}_1^2 + \frac{1}{2}m_2\mathbf{v}_2^2 &= \frac{1}{2}m_1\left(\mathbf{v}_{\text{com}} - \frac{m_2}{M}\mathbf{v}_r\right)^2 + \frac{1}{2}m_2\left(\mathbf{v}_{\text{com}} + \frac{m_1}{M}\mathbf{v}_r\right)^2\\ &= \frac{1}{2}m_1\mathbf{v}_{\text{com}}^2 - \frac{2m_1m_2}{2M}\mathbf{v}_r\cdot\mathbf{v}_{\text{com}} + \frac{m_1m_2^2}{2M^2}\mathbf{v}_r^2\\ &\quad + \frac{1}{2}m_2\mathbf{v}_{\text{com}}^2 + \frac{2m_2m_1}{2M}\mathbf{v}_r\cdot\mathbf{v}_{\text{com}} + \frac{m_2m_1^2}{2M^2}\mathbf{v}_r^2\\ &= \frac{1}{2}M\mathbf{v}_{\text{com}}^2 + \frac{m_1m_2M}{2M^2}\mathbf{v}_r^2\\ &= \frac{1}{2}Mv_{\text{com}}^2 + \frac{1}{2}\mu v_r^2.\end{aligned} \tag{1.67}$$

It will often be useful to consider collisions in the center-of-mass frame. For example, we will make extensive use of this view in talking about molecular scattering in Section 8.4. Problem 1.12 shows how this result can be used to calculate the average relative velocity.

suggested readings

G. G. Hammes, *Principles of Chemical Kinetics* (Academic Press, New York, 1978).

W. Kauzmann, *Kinetic Theory of Gases*, Vol. 1, *Thermal Properties of Matter*, (Benjamin, Reading, MA, 1966)

E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1938).

R. D. Present, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1958).

R. E. Weston, Jr., and H. A. Schwarz, *Chemical Kinetics* (Prentice-Hall, Englewood Cliffs, NJ, 1972).

problems

1.1 Molecules all of mass m and speed v exert a pressure p on the walls of a vessel. If half the molecules are replaced by ones of another type all with mass $\frac{1}{2}m$ and speed $2v$, will the pressure (a) increase, (b) decrease, (c) remain constant?

1.2 Suppose the probability of obtaining a score between 0 and 100 on an exam increases monotonically between 0 and 1.00. Is the average score on the exam (a) greater than 50, (b) equal to 50, (c) less than 50?

1.3 Suppose some property q of a gas is proportional to $(0.326\ \mathrm{s^3\ m^{-3}})v_x^3 + (\pi\ \mathrm{s^9\ m^{-9}})v_x^9$. What is the average value of q?

1.4 Without referring to any formula, decide whether at constant density the mean free path (a) increases, (b) decreases, or (c) stays constant with increasing temperature and explain your answer.

1.5 Consider a deck of cards. With aces valued at one and jacks, queens, and kings valued at 11, 12, and 13, respectively, calculate the average value of a card drawn at random from a full deck.

1.6 The distribution of the grades S (where $0 \leq S \leq 100$) for a class containing a large number of students is given by the continuous function $P(S) = K(50 - |S - 50|)$, where $|x|$ is the absolute value of x and K is a normalization constant. Determine the normalization constant and find out what fraction of the students received grades greater than or equal to 90.

1.7 A pair of dancers is waltzing on a one-dimensional dance floor of length L. Since they tend to avoid the walls, the probability of finding them at a position x between walls at $x = 0$ and $x = L$ is proportional to $\sin^2(\pi x/L)$. What is the normalized distribution function for the position of the waltzers? Using this distribution function, calculate the most probable position for the waltzers. Calculate the average position of the waltzers. (*Hint:* The integral of $y \sin^2 y\, dy$ is $[y^2/4] - [(y \sin 2y)/4] - [(\cos 2y)/8]$; this is also the probability for finding a particle in a box at a particular position.)

1.8 By setting the derivative of the formula for the Maxwell-Boltzmann speed distribution equal to zero, show that the speed at which the distribution has its maximum is given by **equation 1.33.**

1.9 Show using **equations 1.16** and **1.37** that the average molecular energy is $3kT/2$.

1.10 Prove **equation 1.41** from **equation 1.40.** Integration can be accomplished by making the following change of variable. Let $\epsilon = kTx^2$, so that $d\epsilon = kT\, d(x^2)$ and $\epsilon^{1/2} = (kT)^{1/2}x$. Substitute these into **equation 1.40** and integrate by parts, recalling that since $d(uv) = u\, dv + v\, du$, then $\int d(uv) = \int u dv + \int v du$, so that $\int u dv = (uv)\big|_{\text{limits}} - \int v du$, where the notation $\big|_{\text{limits}}$ indicates that the product (uv) should be evaluated at the limits used for the integrals.

1.11 The Maxwell-Boltzmann distribution may not be quite valid! Calculate the fraction of N_2 molecules having speeds in excess of the speed of light.

1.12 The object of this problem is to show more rigorously that $\langle v_r \rangle = (8kT/\pi\mu)^{1/2}$, where μ, the reduced mass, is defined as $\mu \equiv m_1m_2/(m_1 + m_2)$.

We have already learned in Appendix 1.4 that the total kinetic energy of two particles is given by $\frac{1}{2}\mu v_r^2 + \frac{1}{2}Mv_{\text{com}}^2$, where $\mathbf{v}_r = \mathbf{v}_2 - \mathbf{v}_1$ and $\mathbf{v}_{\text{com}}$, the center-of-mass velocity vector, is defined by the equation $(m_1 + m_2)\mathbf{v}_{\text{com}} = m_1\mathbf{v}_1 + m_2\mathbf{v}_2$, and $M \equiv m_1 + m_2$.

a. Consider the probability of finding two molecules, one with velocity $\mathbf{v}_1$ and one with velocity $\mathbf{v}_2$. Using **equation 1.30,** we see that this probability is given by

$$F(v_{1x})F(v_{1y})F(v_{1z})F(v_{2x})F(v_{2y})F(v_{2z})\,dv_{1x}\,dv_{1y}\,dv_{1z}\,dv_{2x}\,dv_{2y}\,dv_{2z}$$
$$= \left(\frac{m_1}{2\pi kT}\right)^{3/2}\left(\frac{m_2}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m_1\mathbf{v}_1^2}{2kT}\right)\exp\left(-\frac{m_2\mathbf{v}_2^2}{2kT}\right)$$
$$\times\, dv_{1x}\,dv_{1y}\,dv_{1z}\,dv_{2x}\,dv_{2y}\,dv_{2z}.$$

Use the result from Appendix 1.4 to show that this probability can also be written as

$$F(v_{rx})F(v_{ry})F(v_{rz})F(v_{\text{com}x})F(v_{\text{com}y})F(v_{\text{com}z})$$
$$\times\, dv_{rx}\,dv_{ry}\,dv_{rz}\,dv_{\text{com}x}\,dv_{\text{com}y}\,dv_{\text{com}z}$$
$$= \left(\frac{m_1}{2\pi kT}\right)^{3/2}\left(\frac{m_2}{2\pi kT}\right)^{3/2}\exp\left(-\frac{M\mathbf{v}_{\text{com}}^2}{2kT}\right)\exp\left(-\frac{\mu\mathbf{v}_r^2}{2kT}\right)$$
$$\times\, dv_{rx}\,dv_{ry}\,dv_{rz}\,dv_{\text{com}x}\,dv_{\text{com}y}\,dv_{\text{com}z}.$$

b. Now transform the Cartesian coordinates to spherical ones and show by integration over all coordinates that the average relative velocity $<v_r>$ is given by $(8kT/\pi\mu)^{1/2}$.

1.13 What is the ratio of the probability of finding a molecule moving with the average speed to the probability of finding a molecule moving with three times the average speed? How does this ratio depend on the temperature?

1.14 You are caught without an umbrella in the rain and wish to get to your dorm, 1 km away, in the driest possible condition. Should you walk or run? To answer this question, calculate the ratio of the rain drop collisions with your body under the two conditions. Assume that the cross section is independent of direction (i.e., that you are spherical), that you run at 8 m/s, you walk at 3 m/s, and that the rainfall is constant with a velocity of, say, 15 m/s.

1.15 Calculate the root-mean-squared deviation of the speed from its mean value: $[<(v - <v>)^2>]^{1/2}$.

1.16 Find $<v^4>$ for a gas of molecular weight M at temperature T.

1.17 A very expensive gas is sold by the molecule, and the price is proportional to the velocity of the individual molecule: price in \$ $= v/<v>$. If I buy a bulb of these gaseous molecules, what is the average price per molecule, and does the price depend on the temperature of the bulb?

1.18 In a group of molecules all traveling in the positive z direction, what is the probability that a molecule will be found with a z-component speed between 400 and 401 m/s if $m/(2kT) = 5.62 \times 10^{-6}\ \mathrm{s^2/m^2}$? (*Hint:* You need to find and normalize a one-dimensional distribution function first!)

1.19 We will see in Chapter 3, **equation 3.4**, that the rate constant for a reaction as a function of temperature is given by the average of $\sigma(\epsilon_r)v_r$ over the thermal energy distribution $G(\epsilon_r)$, where $\epsilon_r = \frac{1}{2}mv_r^2$ and $\sigma(\epsilon_r)$ is the energy-dependent cross section for the reaction. The thermal relative kinetic energy distribution $G(\epsilon_r)$ has the same functional form as the kinetic energy distribution $G(\epsilon)$ given in **equation 1.37,** except that all energies $\epsilon = \frac{1}{2}mv^2$ are replaced by relative kinetic energies $\epsilon_r = \frac{1}{2}\mu v_r^2$.

a. Suppose that for a particular reaction $\sigma(\epsilon_r) = c\epsilon_r^2$, where c is a constant. Calculate $k(T)$.

b. Suppose that for another reaction $\sigma(\epsilon_r) = c/\epsilon_r$; calculate $k(T)$.

4

Transport Properties

Chapter Outline

4.1 INTRODUCTION

The goal of this chapter is to understand such properties as thermal conductivity, viscosity, and diffusion on a microscopic level. For gases, we can attain this understanding by application of the kinetic theory developed in the last chapter. Although an exact treatment is mathematically cumbersome, simple physical ideas can be used to derive approximate formulas that have the correct dependence on molecular parameters and differ from the exact formulas only by numerical constants of order unity. Thus, our approach focuses on the underlying physics of the process rather than on obtaining exact results.

The outline of the approach is as follows. After briefly discussing the general functional form of the transport equations, we will make four simplifying assumptions that will enable us to easily apply kinetic theory to transport phenomena in gases. The basic theme is that the properties transported, namely, energy, momentum, or concentration, are carried by the motions of molecules. We know something about this motion from our discussions of the Maxwell-Boltzmann distribution. The first step in a general treatment of transport is to calculate the flux of molecules, i.e., the number of molecules that cross an area per unit time. The second step is to calculate how far the molecules travel in a particular direction between collisions. This distance is clearly related to the mean free path, but it is slightly different.

The third step is to combine these two results to calculate a transport equation for an arbitrary property carried by the gas molecules. We will see that the transport always moves the property in a direction opposite to a gradient, or spatial derivative, in the property, and that the proportionality constant is related to the mean velocity of the molecules, the mean free path, and other properties of the molecules. For gradients that are independent of time, it is then relatively straightforward to apply the general equation in turn to thermal conductivity, where energy is transported; to viscosity, where momentum is transported; and to diffusion, where the molecules themselves are transported. For gradients that are not constant in time, the treatment is somewhat more complex but can again be understood using a simple model, as shown in the final section of this chapter.

4.2 THE FUNCTIONAL FORM OF THE TRANSPORT EQUATIONS

The principal features of all transport equations can be appreciated by considering the flow of a liquid through a tube. **Figure 4.1** displays the important parameters. For the liquid under consideration and for a particular choice of diameter, the tube has an inherent conductivity C. Suppose that a pressure differential $\Delta p = p_2 - p_1 > 0$ is placed across the tube so as to force the liquid to flow from left to right. We expect from common experience that the rate of liquid volume that crosses a unit area oriented perpendicular to the flow will depend linearly on both the pressure differential and the conductivity. The flow of a quantity per unit time per unit area is called the *flux* and has dimensions of (quantity) $\mathrm{s}^{-1}\,\mathrm{m}^{-2}$. In this case, the quantity is the volume of liquid and the linear proportionalities can be expressed by the equation

$$J_z = -C\frac{\partial p}{\partial z}, \qquad \textbf{(4.1)}$$

an equation known as Poiseuille's law. In the example above, $\partial p/\partial z$ is simply $-\Delta p/\ell$ and is called the *gradient* of the pressure. Strictly speaking, since the gradient can have different values in different directions, **equation 4.1** should be written in vector form: $\mathbf{J} = -C\nabla p$, where ∇ is the vector $\mathbf{i}\partial/\partial x + \mathbf{j}\partial/\partial y + \mathbf{k}\partial/\partial z$ and **i**, **j**, and **k** are unit vectors in the x, y, and z directions, respectively. To keep the notation simple, we will focus on the z component of the flux, while remembering that similar equations can be written for the other directions. Note in **equation 4.1** that the gradient $\partial p/\partial z$ is negative since the pressure decreases as z increases, but that the flux is positive because of the negative sign incorporated in **equation 4.1.**

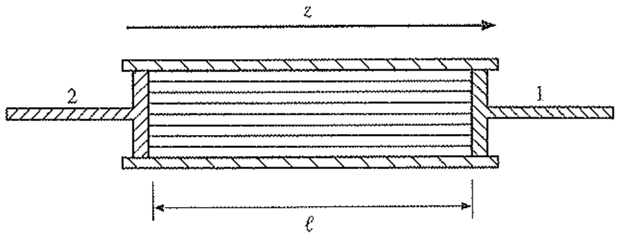

Figure 4.1

The flow of liquid through a tube.

TABLE 4.1 Transport Equations

Quantity Transported	Equation	Name
Fluid	$J_z = -C(\partial p/\partial z)$	Poiseuille's law
Heat (thermal conductivity)	$J_z = -\kappa(\partial T/\partial z)$	Fourier's law
Momentum	$J_z = -\eta(\partial v_x/\partial z)$	Viscosity
Particles (diffusion)	$J_z = -D(\partial n^*/\partial z)$	Fick's law
Electrical charge	$J_z = -(1/\rho)(\partial\phi/\partial z)$	Ohm's law

From dimensional analysis we see that the units of the conductivity C are volume $\mathrm{s}^{-1}\ \mathrm{m}^{-1}$ pressure^{-1}. While we note here that C is inversely proportional to the viscosity, we defer discussion of the relationship between the conductivity and molecular properties until Section 4.5.

All transport equations have the form of **equation 4.1;** the only differences involve the form of the gradient and the quantity that flows counter to the gradient. The examples of greatest interest are described in **Table 4.1.**

In the case of thermal conductivity, the quantity carried is heat or energy, and it is carried in the direction opposite to the temperature gradient; i.e., heat flows in the positive z direction if the temperature decreases as z increases. The proportionality constant, κ, is called the coefficient of thermal conductivity. Similarly, in the case of diffusion, the quantity carried is the particle itself, and it is carried counter to a density gradient. The proportionality constant, D, is called the diffusion coefficient. Viscosity is at first a bit confusing. The quantity carried is the x component of momentum, but it is carried in the z direction against a gradient of momentum, as discussed in detail in Section 4.5. The proportionality constant is called the viscosity coefficient. Ohm's law concerns the transport of electricity through a conductor against a gradient in electrical potential, as discussed in **Example 4.1.**

example 4.1

Ohm's Law

Objective Determine Ohm's law for the flux of electrons through a wire, given that its conductivity is $1/\rho$ (ρ is called the resistivity) and that the potential decrease across the wire is V volts per m. Show that the result leads to the common form of Ohm's law: $V = IR$.

Method The charge flux will have the units of charge per cross-sectional area of the wire per second. It should be proportional to the conductivity of the wire and to the gradient of the electrical potential that pushes the electrons along the wire.

Solution Since the electrons flow from a region of high potential ϕ to one of low potential, the gradient in the direction of flow is negative; the potential decreases with increasing z, where z is the direction of electron flow. Assuming a linear variation in voltage across the wire, the gradient is thus $\partial\phi/\partial z = -V/\ell$, where ℓ is the length of the wire. The flux of electrons is thus $J_z = -(1/\rho)(\partial\phi/\partial z)$. Writing the flux of electrons as the current, I, per unit area and substituting for the gradient, we obtain $I/A = V/\rho\ell$, or $V = IR$, where $R = \rho\ell/A$ is the resistance of the wire.

Comment The units of I are amperes (one coulomb of charge per second), while the units of R are ohms. A 1-volt drop in potential across a resistance of one ohm causes a current flow of 1 ampere. The units of the resistivity, ρ, are ohm m.

4.3 THE MICROSCOPIC BASIS FOR THE TRANSPORT LAWS

4.3.1 Simplifying Assumptions

It is clear from **Table 4.1** that the transport laws all have the same basic form, namely that the flux of some quantity is proportional to and in the opposite direction of a gradient. In the case of transport in gases, the explanation of this common form is based on the kinetic theory outlined in Chapter 1. As realized very early by Maxwell and by Boltzmann and later expanded by Enskog and by Chapman,[a] the property transported by the flux must be transported by the individual particles comprising the gas, namely, by molecules subject to the Maxwell-Boltzmann distribution law. In the case of thermal conductivity, the property carried is the energy, $\epsilon = mv^2/2$. In the case of viscosity, the property carried is the momentum mv_x. Diffusion involves the flux of the molecules themselves. While a rigorous theory of transport properties involves both complicated mathematics and physics, the basic form of the answer can be derived from kinetic theory and a few simple assumptions. We will follow this latter route, recognizing that while we expect to capture the basic taste of the argument, the seasoning of our dishes may not be perfect. Most of the equations we derive will show the correct dependence on molecular parameters but will have numerical factors that are not quite correct.

We make the following simplifying assumptions: (1) the molecules behave as rigid spheres with no attractive forces; (2) they all travel with the same speed, equal to the average speed $\langle v \rangle$, and traverse the same distance, equal to the mean free path λ, between collisions; (3) the molecules taken collectively have an isotropic angular distribution; and (4) each collision results in complete equilibrium with respect to the interchange of the property q which is being transported.

The first assumption is obviously a drastic oversimplification, since we know that it is the forces, both attractive and repulsive, between gas molecules that account for the deviations from ideal gas behavior. The second assumption is more than merely a matter of convenience. It is certainly easier to deal with the average behavior rather than performing each calculation as a function of velocity and finally integrating over the velocity distribution. But this procedure hides the fact that some of the properties we want to transport depend on velocity, $q = q(v)$, so that the rate of transport of this

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[a] D. Enskog, *Kungliga Svenska Vetenskapsakademiens Handlingar* **63,** No. 4 (1922) (in German); S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases* (Cambridge University Press, Cambridge, England, 1939).

property is proportional to $vq(v)$. By considering only the average velocity we are in effect replacing $<vq(v)>$ by $<v><q(v)>$, an approximation whose accuracy depends on the exact nature of the distributions. The third assumption turns out to be particularly weak. When molecules collide, they do not completely forget their original direction of motion, so their motion in the presence of a gradient is not likely to be isotropic. The approximation ignores the fact that the gradient affects the velocity distribution. The fourth assumption is likewise a source of error. It may be true for transfer of infinitesimal amounts of the property q per collision, but it will certainly fail when the gradients become large. In view of these approximations, it should be no surprise that the derivations below will introduce incorrect numerical factors. Nonetheless, the essential physical picture is unchanged by these approximations; the property q is carried by molecules whose motions over a wide range of conditions are not too different from those predicted by kinetic theory.

We begin by considering gradients that are stable in time; i.e., gradients that are established by some external means so that the transport of heat, momentum, or concentration does not change the gradient with time. For example, we might hold the ends of a tube of gas at fixed, but different, temperatures by using two large heat baths. Heat would then be transferred through the gas from one bath to another without appreciably changing the gradient.

In the remainder of this section we will first develop an equation for the molecular flux. We will then use this equation to determine two quantities: the flux of a property through a plane and the vertical distance between planes where collisions have occurred. We will finally develop a general flux equation that can be used in subsequent sections to relate the coefficients of thermal conductivity, viscosity, and diffusion to molecular properties such as diameter, speed, heat capacity, and mass.

4.3.2 The Molecular Flux

The first step in a microscopic explanation for transport properties is to recognize that, if molecules are carrying the quantity in question across a unit area in a unit time, we need to know the rate at which the molecules themselves cross the area. **Equation 1.30** and **Figure 4.2** can help in this exercise. How many molecules cross the area A in the indicated plane per unit time? We treat the problem in spherical coordinates,

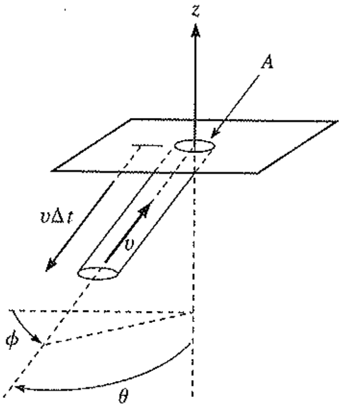

Figure 4.2

The flux of molecules through a plane.

where v ranges from 0 to ∞, θ from 0 to π, and ϕ from 0 to 2π. The relationship between spherical and Cartesian coordinates is discussed in Appendix 1.2. Consider for each possible value of v, θ, and ϕ a cylinder of slant height $v\Delta t$ tilted at angles θ and ϕ with respect to the z axis, where the slant height is chosen so that all molecules within the cylinder with velocities centered on v, θ, and ϕ will cross area A in the time Δt. The volume of the cylinder depends both on the slant height, $v\Delta t$, and on $\cos\theta$: $V = Av\Delta t\cos\theta$. The number of molecules crossing A in Δt is then given simply as the number of molecules in the cylindrical volume times the probability that a molecule will have a velocity v centered on angles θ and ϕ. The number of molecules in the volume is $n^*V = n^*Av\Delta t\cos\theta$, while the probability of having the given velocity is $(m/2\pi kT)^{3/2} \times \exp(-mv^2/2kT)v^2\sin\theta\, d\theta\, d\phi\, dv$.[b] Thus,

$$\text{number} = n^*Av\Delta t\cos\theta\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)v^2\sin\theta\, d\theta\, d\phi\, dv. \quad \textbf{(4.2)}$$

The number of molecules in the cylinder with velocities centered on (v,θ,ϕ) that cross a unit area of the plane in a unit time is then the flux distribution function:

$$\begin{aligned} J(v,\theta,\phi)v^2\sin\theta\, d\theta\, d\phi\, dv &= \frac{\text{number}}{A\Delta t} \\ &= n^*v^3\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)\cos\theta\sin\theta\, d\theta\, d\phi\, dv. \end{aligned} \quad \textbf{(4.3)}$$

Equation 4.3 is evidently a distribution function giving the probability that a molecule with a speed in the range $v \to v + dv$ and direction in the range $\theta \to \theta + d\theta$, $\phi \to \phi + d\phi$ will pass through the plane in a unit time. We can use it to calculate two important quantities.

We would first like to know the flux of molecules J_z that cross the plane from below regardless of their velocity and direction. To find this quantity, we simply need to integrate **equation 4.3** over all the variables, but the range of integration for θ should be from 0 to $\pi/2$ (see **Figure 4.2**) since we want only those molecules moving upward through the plane. Thus,

$$J_z = n^*\int_0^\infty\int_0^{2\pi}\int_0^{\pi/2} v^3\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)\cos\theta\sin\theta\, d\theta\, d\phi\, dv. \quad \textbf{(4.4)}$$

The integration over v (with an additional factor of 4π) was performed in **equation 1.31:** the answer here is simply $1/(4\pi<v>)$. The integration over ϕ gives a factor of 2π. Thus,

$$\begin{aligned} J_z &= n^*\frac{1}{4\pi}<v>2\pi\int_0^{\pi/2}\cos\theta\sin\theta\, d\theta \\ &= n^*\frac{1}{2}<v>\int_0^{\pi/2}\sin\theta\, d(\sin\theta) = n^*\frac{1}{2}<v>\left[\frac{\sin^2\theta}{2}\right]_0^{\pi/2}, \end{aligned} \quad \textbf{(4.5)}$$

or

---

[b] Note that integration of the probability over the angles would give a factor of 4π, so that the probability would be identical to that given in **equation 1.31.**

$$J_z = \frac{1}{4} n^* \langle v \rangle, \tag{4.6}$$

where we recall from Chapter 1 that $\langle v \rangle = (8kT/\pi m)^{1/2}$, where m is the mass of the gas molecules. This important equation gives the flux of molecules in a particular direction. Of course, for an isotropic gas, the flux of molecules has the same value in any direction, a conclusion that is clear from the fact that the right-hand side of **equation 4.6** does not depend on direction.

Suppose now that the molecules each carry an amount q of some property. Then the flux of that property will be simply the flux of molecules times the amount of the property each carries. In particular, for the $+z$ direction,

$$J_z = \frac{1}{4} \langle v \rangle n^* q. \tag{4.7}$$

4.3.3 The Vertical Distance between Collisions

The next question we consider is the distance in the z direction traveled by the average molecule between collisions. Although the total average distance is the mean free path λ, the distance in the z direction will be somewhat shorter, since molecules with positive z component velocities move at a variety of angles θ with respect to the z axis. The second result that we will derive from **equation 4.3** is that the average z distance between collision planes is $2\lambda/3$.

Let the slant length of the cylinder in **Figure 4.2** be $v\Delta t = \langle v \rangle / Z_1 = \lambda$. Then the vertical distance between the indicated plane and the plane in which the molecule last had its collision is $\lambda \cos\theta$. We wish to find the average of this quantity. Since **equation 4.3** gives the flux probability, the average of $\lambda \cos\theta$ will simply be

$$\begin{aligned} \langle \lambda \cos\theta \rangle &= \frac{\int \lambda \cos\theta \, J(v,\theta,\phi)\, d\tau}{\int J(v,\theta,\phi)\, d\tau} \\ &= \lambda \frac{\int_0^{\pi/2} \cos^2\theta \sin\theta \, d\theta}{\int_0^{\pi/2} \cos\theta \sin\theta \, d\theta} = \lambda \frac{\left[\dfrac{\cos^3\theta}{3}\right]_0^{\pi/2}}{\left[\dfrac{\cos^2\theta}{2}\right]_0^{\pi/2}} = \frac{2}{3}\lambda, \end{aligned} \tag{4.8}$$

where the volume element abbreviated as $d\tau$ is equal to $v^2 \sin\theta \, d\theta \, d\phi \, dv$ and where the integral in the denominator is used for normalization. Consequently, we see that the average distance traveled in the z direction between collisions is $2\lambda/3$.

4.3.4 The General Flux Equation

To calculate the flux of the property q it is convenient to consider a plane located perpendicular to the direction of the gradient. Let the gradient be in the z direction, and let the plane be located at the arbitrary position z_0. As shown schematically in **Figure 4.3,** we calculate the net flux into the plane at z_0 as the flux due to the

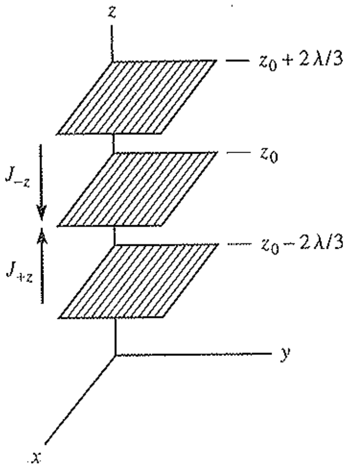

Figure 4.3

Transport between layers separated by the mean free path.

upward motion of molecules that made their last collision in the plane at $z_0 - 2\lambda/3$ and due to the downward motion of molecules that made their last collision in the plane at $z_0 + 2\lambda/3$. From **equation 4.7,** the flux from a plane at z is given by $J_z = \frac{1}{4}n^*q<v>$, where n^*, q, and $<v>$ are evaluated at the position z. While assumption 2 enables us to treat $<v>$ as constant, in principle both n^* and q can vary between planes. Introducing temporarily the notation $\rho_q(z)$ as n^*q evaluated at location z, the upward flux of the property q is then given by $J_{+z} = \frac{1}{4}<v>\rho_q(z_0 - 2\lambda/3)$, where $\rho_q(z_0 - 2\lambda/3)$ is the value of $\rho_q = n^*q$ for upward traveling molecules that had their last collision in the plane at $z_0 - 2\lambda/3$. Similarly, the downward flux of the property is given by $J_{-z} = \frac{1}{4}<v>\rho_q(z_0 + 2\lambda/3)$. The net flux in the upward direction is then

$$\begin{aligned} J_z &= J_{+z} - J_{-z} \\ &= \frac{1}{4}<v>\left[\rho_q\left(z_0 - \frac{2\lambda}{3}\right) - \rho_q\left(z_0 + \frac{2\lambda}{3}\right)\right]. \end{aligned} \tag{4.9}$$

If the gradient is constant or if its change is small over dimensions corresponding to the mean free path, then we may approximate $\rho_q(z_0 \pm 2\lambda/3)$ by the first two terms in a Taylor series expansion about the position z_0:[c]

$$\rho_q\left(z_0 \pm \frac{2\lambda}{3}\right) \approx \rho_q(z_0) \pm \frac{2\lambda}{3}\left(\frac{\partial \rho_q}{\partial z}\right). \tag{4.10}$$

Substitution of **equation 4.10** into **equation 4.9** and replacement of ρ_q by n^*q yields

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[c] The Taylor series expansion for $y(x_0 + \Delta x)$ is given as $y(x_0 + \Delta x) = y(x_0) + \Delta x(dy/dx) + \frac{1}{2}(\Delta x)^2(d^2y/dx^2) + \cdots$, where the derivatives are evaluated at $x = x_0$. If (dy/dx) is nearly constant over the range of Δx, then (d^2y/dx^2) will be small and only the first few terms in the expansion will be needed.

$$J_z = \frac{1}{4}<v>\left[-\frac{4\lambda}{3}\left(\frac{\partial(n^*q)}{\partial z}\right)\right]$$
$$= -\frac{1}{3}<v>\lambda\frac{\partial(n^*q)}{\partial z}. \quad \textbf{(4.11)}$$

Equation 4.11 will form the basis for much of our further discussion. At this point it is worthwhile to make two comments. First, the result does not depend on having a gradient that is independent of position. If the gradient is constant everywhere in space, then **equations 4.10** and **4.11** are exact, but even if the gradient changes as a function of position, **equation 4.11** will give an excellent approximation to the flux through the plane at z_0 as long as the change in the gradient is small over distances within roughly one mean free path of z_0. Second, **equation 4.11** suggests that a nonzero flux will result from either a gradient in the molecular density, n^*, or a gradient in the property q, or both. In our discussions of thermal conductivity and viscosity below, we will assume that there is no net movement of the molecules; that only the property $q = \epsilon$ for thermal conductivity or $q = mv_x$ for viscosity changes with position. In this case, since the number density does not change with position, we see that $\partial(n^*q) = n^*\partial q$. In the case of diffusion, however, the property in flux is the number density itself, so $q = 1$ and $\partial(n^*q) = \partial n^*$.

4.4 THERMAL CONDUCTIVITY

A fundamental observation in the development of the second law of thermodynamics is that heat flows from a hot body to a cold one. The phenomenological description of this flow was discussed in Section 4.2 and is embodied in the equation called Fourier's law: $J_z = -\kappa(\partial T/\partial z)$, where J_z is the flux of heat (energy) in the z direction and κ is the coefficient of thermal conductivity. Since the units of the flux are energy per area per time, we see that Fourier's law has dimensions (J m^{-2} s^{-1}) = κ (K m^{-1}), or that the dimensions of κ are (J m^{-2} s^{-1})/(K m^{-1}) = J m^{-1} s^{-1} K^{-1}.[d] Since 1 J of energy per second is also equal to 1 watt of power, alternative units for κ are W m^{-1} K^{-1}. **Table 4.2** gives some values for κ.

TABLE 4.2 Thermal Conductivity Coefficients, κ, for Various Substances at 273 K and 1 atm

Substance	κ (J m^{-1} s^{-1} K^{-1})
Cu	400
Fe	80
He	0.144
Ar	0.0162
N_2	0.0237
H_2	0.174
O_2	0.0240
CO_2	0.0142
CH_4	0.0300

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[d] Kappa, κ, is used here for the thermal conductivity coefficient and should not be confused with the isothermal compressibility coefficient, which sometimes also uses this symbol.

example 4.2

The Heat Flow through Fiberglass Insulation

Objective Calculate the rate of heat loss through a wall insulated with fiberglass. Let the wall be 3 m × 4 m, ignore the conductivity of any other wall materials, and take the thickness of the insulation to be 15 cm, the temperature difference between the inside and outside of the wall to be 10 K, and the coefficient of thermal conductivity for fiberglass to be 5×10^{-2} W m^{-1} K^{-1}.

Method According to Fourier's law, the flux of energy is given by $J_z = -\kappa(\partial T/\partial z)$. The flux is the heat per unit time, so that the total heat loss in watts (joules per second) is the area times the flux: AJ_z.

Solution The gradient is $-(10\ \text{K})/0.15\ \text{m})$, so that the total heat loss is $(3\ \text{m} \times 4\ \text{m})(5 \times 10^{-2}\ \text{W m}^{-1}\ \text{s}^{-1})(10\ \text{K})/(0.15\ \text{m}) = 40\ \text{W}$.

Of course, thermal conductivity is not the only method for heat transport. Heat is also transferred by radiation, as from the sun to Earth, or by convection, as in winds that move weather fronts. In our consideration of thermal conductivity, we will separate these processes and analyze the flow of heat (energy) in the absence of net movement of either photons or matter. To be sure, even in conduction the heat is transported by the movement of particles, usually by the motion of molecules, but, in metals, also by the motion of electrons. However, we will assume that there is no *net* molecular motion in conductivity. Thus, the conducted heat moves like the baton in a relay race; it is passed from one particle to another. This view is true, and the macroscopic equations valid, for heat flow through solids, liquids, or gases. In the latter case, however, we can easily come to a microscopic understanding of the coefficient of thermal conductivity.

The kinetic theory that we have developed describes the collisions that provide the opportunity for gases to exchange energy, so that **equation 4.11** should predict the essential features of thermal conductivity in gases, subject to the simplifying assumptions made in the last section. The property transported by the molecules is their energy, ϵ, and by assumption 4, this energy is equilibrated at every collision. If we assume no net motion of the molecules, then $\partial(n^*q) = n^*\partial q$. If the energy per mole is $q = U/N_A = \epsilon$, **equation 4.11** then becomes

$$J_z = -\frac{1}{3}n^*\lambda\langle v\rangle\left(\frac{\partial\epsilon}{\partial z}\right). \tag{4.12}$$

Recalling from Chapter 1, Section 1.6, that $(\partial U/\partial T)_V = C_V$, the constant volume molar heat capacity, we write the gradient $(\partial\epsilon/\partial z)$ as

$$\begin{aligned}\frac{\partial\epsilon}{\partial z} &= \frac{1}{N_A}\frac{\partial U}{\partial z}\\ &= \frac{1}{N_A}\frac{\partial U}{\partial T}\frac{\partial T}{\partial z}\\ &= \frac{C_V}{N_A}\frac{\partial T}{\partial z}.\end{aligned} \tag{4.13}$$

Thus,

$$J_z = -\frac{1}{3}n^*\lambda\langle v\rangle\frac{C_V}{N_A}\left(\frac{\partial T}{\partial z}\right). \tag{4.14}$$

Comparison of **equation 4.14** with Fourier's law yields

$$\kappa = \frac{1}{3}n^*\lambda\langle v\rangle\frac{C_V}{N_A}. \tag{4.15}$$

This expression for the thermal conductivity coefficient may be simplified by using **equation 1.47,** repeated here for use with a single component so that $n_2^* = n^*$ and $b_{max} = d$, the molecular diameter:

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n^*}. \tag{4.16}$$

Substitution of **equation 4.16** into **equation 4.15** yields

$$\kappa = \frac{\langle v\rangle C_V}{3\sqrt{2}\pi d^2 N_A}. \tag{4.17}$$

Note that the result for κ is independent of pressure because the n^* dependence in the general expression for the flux and the $1/n^*$ dependence of the mean free path exactly cancel one another. A qualitative explanation for the cancellation is that, while there are fewer molecules crossing a given area per unit time at low pressure, they travel a longer distance between collisions. Although it is found experimentally that κ is independent of pressure over most pressures of interest, this independence breaks down at very high pressures where the molecules no longer behave like an ideal gas and at very low pressures where the mean free path reaches macroscopic dimensions. In the latter case, truncation of the Taylor expansion used in **equation 4.10** is no longer valid after two terms. At extremely low pressures, the mean free path is limited only by collision at the cold surface or the hot surface, and the thermal conductivity coefficient is then directly proportional to n^*.

It is important to comment that the heat capacity for a real molecule is larger than that for a monatomic ideal gas: $C_V > 3R/2$. The reason, of course, is that real molecules have rotational and vibrational degrees of freedom in addition to translational ones. While many vibrational motions are of high enough frequency not to contribute to the heat capacity, the rotational degrees of freedom contribute R per mole for diatomic molecules and $3R/2$ per mole for polyatomic ones.

example 4.3

The Thermal Conductivity Coefficient of N_2 at 273 K and 1 atm

Objective Estimate the thermal conductivity coefficient of N_2 at 1 atm and 273 K, given that the molecular diameter of N_2 is 370 pm.

Method Use **equation 4.17** recalling that $C_V \approx 5R/2$.

Solution First calculate $\langle v\rangle = (8kT/\pi m)^{1/2}$:

$$<v> = (8kT/\pi m)^{1/2}$$

$$= \left\{\frac{8(1.38 \times 10^{-23}\ \mathrm{J\ K^{-1}})(273\ \mathrm{K})(6.02 \times 10^{23}\ \mathrm{amu/g})(1000\ \mathrm{g/kg})}{[3.1415\ (28\ \mathrm{amu})]}\right\}^{1/2}$$

$$= 454\ \mathrm{m/s} \qquad \textbf{(4.18)}$$

Then evaluate $C_V = 5R/2 = 5(8.314\ \mathrm{J\ mol^{-1}\ K^{-1}})/2 = 20.8\ \mathrm{J\ mol^{-1}\ K^{-1}}$.
Finally,

$$\kappa = \frac{(454\ \mathrm{m/s})(20.8\ \mathrm{J/mol})}{3\sqrt{2}\pi(6.02 \times 10^{23}\ \mathrm{molec/mol})(370 \times 10^{-12}\ \mathrm{m})^2} \qquad \textbf{(4.19)}$$

$$= 8.59 \times 10^{-3}\ \mathrm{J\ m^{-1}\ s^{-1}\ K^{-1}}.$$

Comment Note that the information that the pressure is 1 atm is irrelevant to the solution. Since we used approximations in arriving at **equation 4.17** and in evaluating the heat capacity, the answer is not exactly equal to the measured value listed in **Table 4.2.**

4.5 VISCOSITY

Most people are familiar with the viscous drag of water impeding a swimmer or air impeding a plane. What are the causes of these forces and how can we understand them at a molecular level? Consider two plates of area A separated by a distance in the z direction and immersed in a fluid, as shown in **Figure 4.4.** If the upper plate is drawn through the fluid with a velocity v_x while the lower plate is stationary, then there will be a force exerted on the lower plate in the x direction due to the frictional

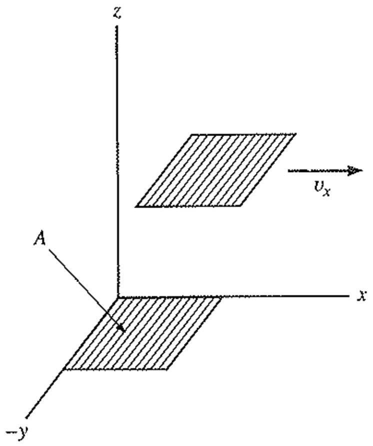

Figure 4.4

The viscous force on a stationary plate exerted by a moving one.

drag of the fluid; an equivalent force in the negative x direction will have to be applied to hold the lower plate stationary. The force transmitted downward to the stationary plate will be proportional to the area A and is given by Newton's law of viscosity: $F_x = -\eta A(\partial v_x/\partial z)$, where the constant η is called the coefficient of viscosity. From Newton's law we recall that $F = ma = dp/dt$, where p is the momentum, so that the force transferred per unit area is the same as momentum transferred per unit time per unit area, or momentum flux. Thus, the gradient in velocity (or the proportional gradient in momentum) between the two plates causes a flux of momentum that is transmitted by the fluid. Note that, while the momentum and force are in the x direction, the *flux* of momentum is in the z direction: $J_z = F_x/A = -\eta(\partial v_x/\partial z)$.

The units of the flux are momentum per second per area or, equivalently, force per area, so that the flux equation has dimensions (force/area) = η (distance/time)/distance. Thus, the units of η are (force/area)/(1/time) or N m^{-2} s. A pascal of pressure is also a N m^{-2}, so that equivalent units for η are Pa s. In older texts, one often encounters the cgs unit for η called a poise; 1 poise = 1 dyne cm^{-2} s = 1 gm cm^{-1} s^{-1} = 0.1 N m^{-2} s.

Table 4.3 provides some viscosity coefficient data for a few materials. Note that both liquids and gases obey the macroscopic viscosity equation. We will focus first on gases and return to the frictional forces in liquids later in this chapter.

In the case of gases and under the assumptions listed in Section 4.3.1, the transfer of momentum must be described by the general flux **equation 4.11,** with $q = mv_x$. We again assume that there is no net transport of molecules, so that $\partial(n^*q) = n^*\partial q$. Substitution of $q = mv_x$ leads to

$$J_z = -\frac{1}{3}n^*<v>\lambda m\left(\frac{\partial v_x}{\partial z}\right), \qquad \textbf{(4.20)}$$

so that

$$\eta = \frac{1}{3}n^*<v>\lambda m. \qquad \textbf{(4.21)}$$

Note that since λ is proportional to $1/n^*$, the viscosity coefficient will be independent of pressure. This prediction was one of the early triumphs of the kinetic theory

TABLE 4.3 **Viscosity Coefficients at 273 K for Various Substances**

Substance	η **(Pa s)**
Glycerol	0.95
Olive oil	0.08
Water, liquid, 298 K	0.9×10^{-3}
He	18.8×10^{-6}
H_2	8.4×10^{-6}
Ar	22.2×10^{-6}
O_2	19.2×10^{-6}
CO_2	13.8×10^{-6}
N_2	16.6×10^{-6}
NH_3	9.2×10^{-6}
CH_4	10.3×10^{-6}

of gases. An alternative formulation of **equation 4.21** recognizes that the density ρ is equal to the product of the number density n^* and the mass m, so that

$$\eta = \frac{1}{3}\rho\langle v\rangle\lambda. \tag{4.22}$$

Again, while the numerical factors in these equations are incorrect, the functional form is correct. However, little is gained by using the correct hard-sphere numbers since real molecules do not behave like hard spheres.

Equations 4.21 and **4.22** provide a convenient method for estimation of molecular diameters. Substitution of **equation 4.16** into **equation 4.21,** for example, leads to

$$\eta = \frac{\frac{1}{3}n^*\langle v\rangle m}{\sqrt{2}\pi d^2 n^*}, \tag{4.23}$$

or

$$d = \left(\frac{\langle v\rangle m}{3\sqrt{2}\pi\eta}\right)^{1/2}. \tag{4.24}$$

Example 4.4 illustrates this calculation.

example 4.4

Finding Molecular Diameters from Viscosity Coefficients

Objective Given that the viscosity coefficient for argon at 298 K is 22.2×10^{-6} Pa s, calculate its molecular diameter.

Method Use **equation 4.24** after calculating $\langle v\rangle$.

Solution First, calculate $\langle v\rangle = (8kT/\pi m)^{1/2}$:

$$\begin{aligned}\langle v\rangle &= (8kT/\pi m)^{1/2}\\ &= \left[\frac{8(1.38\times10^{-23}\ \text{J K}^{-1})(298\ \text{K})(6.02\times10^{23}\ \text{amu/g})(1000\ \text{g/kg})}{(\pi 40\ \text{amu})}\right]^{1/2}\\ &= 397\ \text{m/s}.\end{aligned} \tag{4.25}$$

Then calculate d:

$$\begin{aligned}d &= \left[\frac{\langle v\rangle m}{(3\sqrt{2}\pi\eta)}\right]^{1/2}\\ &= \left[\frac{(397\ \text{m/s})(40\ \text{amu})}{3\sqrt{2}\pi(6.02\times10^{23}\ \text{amu/g})(1000\ \text{g/kg})(22.2\times10^{-6}\ \text{N s m}^{-2})}\right]^{1/2}\\ &= 299\ \text{pm}.\end{aligned} \tag{4.26}$$

Although there are other methods for measuring the viscosity coefficient of a fluid, one convenient technique is to determine the volume of the fluid that passes by a unit area of a tubing per unit time; i.e., the volume flux. We have already seen in the opening section of this chapter that this flux is proportional to the product of the pressure gradient and a conductivity coefficient: $J_z = -C(\partial p/\partial z)$, where C depends on the nature of the fluid and the size of the tubing. The dependence on the nature of the fluid comes about because, while the fluid has a finite velocity in the center of the tube, the molecules in contact with the edges of the tube must have zero velocity. Consequently, C should be inversely proportional to the viscosity coefficient of the fluid. A detailed calculation shows that $C = a^2/8\eta$, where a is the radius of the tube. The volume of liquid passing through the tube per unit time is given simply by the volume flux times the area of the tube: $J_zA = \mathrm{d}V/\mathrm{d}t = -CA(\partial p/\partial z) = -(\pi a^4/8\eta)(\partial p/\partial z)$. This last expression, whose complete derivation is given in Appendix 4.1, is perhaps the most useful form of the *Poiseuille formula* describing the laminar flow of a liquid:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{\pi a^4}{8\eta}\left(\frac{\partial p}{\partial z}\right). \tag{4.27}$$

It enables determination of the viscosity coefficient from a measurement of the rate of volume change. An alternative form of the Poiseuille formula is obtained by multiplying both sides of **equation 4.27** by the liquid's density, ρ:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -\frac{\pi a^4 \rho}{8\eta}\left(\frac{\partial p}{\partial z}\right). \tag{4.28}$$

example 4.5

Using the Poiseuille Formula

Objective Find the viscosity coefficient of a liquid flowing through a tube 0.1 cm in radius and 50 cm in length. When the pressure drop across the tube is 0.1 atm, the volume of liquid emerging from the tube is 1 $\mathrm{cm^3/s}$.

Method Since we know the flow rate and the pressure gradient, we can use Poiseuille's formula, **equation 4.27,** to calculate the viscosity coefficient.

Solution The flow rate is $\mathrm{d}V/\mathrm{d}t = 1\ \mathrm{cm^3\ s^{-1}} = 10^{-6}\ \mathrm{m^3\ s^{-1}}$. The pressure gradient is (0.1 atm)/(0.50 m) = 0.2 atm $\mathrm{m^{-1}}$. Then from the Poiseuille formula, η is

$$\begin{aligned}\eta &= \frac{(\pi r^4/8)(\partial p/\partial z)}{(\mathrm{d}V/\mathrm{d}t)}\\ &= \frac{\pi(0.001\ \mathrm{m})^4(0.2\ \mathrm{atm/m})(101.3\times10^3\ \mathrm{Pa/1\ atm})}{8(10^{-6}\ \mathrm{m^3\ s^{-1}})} \qquad (4.29)\\ &= 7.96\times10^{-3}\ \mathrm{Pa\ s}.\end{aligned}$$

The liquid might very well be olive oil (See **Table 4.3**).

While **equations 4.27** and **4.28** are useful for liquids, where the density is rather insensitive to pressure, for gases the density changes dramatically with pressure: $\rho = Mp/RT$, where M is the molecular weight of the gas. Substitution for ρ and recognition that $n = m/M$ gives

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{\pi a^4}{8\eta RT}\left(p\frac{\partial p}{\partial z}\right). \tag{4.30}$$

Because the number of moles of gas crossing any area per unit time, $\mathrm{d}n/\mathrm{d}t$, is constant, it must also be true that $p(\mathrm{d}p/\mathrm{d}z)$ is a constant. If we call the constant B, then $p\ \mathrm{d}p = B\mathrm{d}z$. Integration gives $p^2 = 2Bz + C$. Applying this equation to pressures p_1 at z_1 and p_2 at z_2 yields two equations: $p_1^2 = 2Bz_1 + C$ and $p_2^2 = 2Bz_2 + C$, where C is a constant of integration. Subtraction gives $B = (p_2^2 - p_1^2)/2(z_2 - z_1)$, so that for gases

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{\pi r^4}{16\eta RT}\left(\frac{p_2^2 - p_1^2}{z_2 - z_1}\right). \tag{4.31}$$

4.6 DIFFUSION

Anyone whose nose is in working order can attest to the fact that diffusion is an important process. The kitchen smells that woke us in the morning as children or the fragrance from an opened bottle of perfume reach us even if there are no convective currents in a room. The mixing process is spontaneous, but the rate of interdiffusion of two substances has yet to be discussed. Experimental observation shows that diffusion in fluids against a gradient obeys Fick's law, whose form is by now quite familiar: $J_z = -D(\partial n^*/\partial z)$, where J_z is the flux of molecules, $(\partial n^*/\partial z)$ is the gradient in number density, and D is the diffusion coefficient. Dimensionally, the equation is (number time^{-1} area^{-1}) = $D \times$ (number/volume)/distance, so that the dimensions of D are thus distance^2 per unit time, or m^2 s^{-1}. Because the diffusion of one substance into another can depend on the properties of each substance, it will be useful to add subscripts to D. Let D_{12} be the coefficient describing the diffusion of type 1 into molecules of type 2 and let D_{11} be the diffusion coefficient for diffusion of molecules of type 1 into other molecules of the same type. One might well wonder how the latter coefficient could be measured; indeed, it cannot. But D_{11} can be approached quite closely by studying the diffusion of one isotope of a substance in another isotope of the same substance. **Table 4.4** lists some typical diffusion coefficients.

TABLE 4.4 Diffusion Coefficients at 273 K and 1 atm for Various Substances

Substances	D_{11} or D_{12} (m^2 s^{-1})
H_2–H_2	1.5×10^{-4}
O_2–O_2	1.9×10^{-5}
N_2–N_2	1.5×10^{-5}
CO_2–CO_2	1.0×10^{-5}
Xe–Xe	5.0×10^{-6}
O_2–N_2	1.8×10^{-5}
O_2–CO_2	1.4×10^{-5}

example 4.6

The Number of O_2 Molecules Crossing an Area per Second While Diffusing through N_2

Objective Find the number of O_2 molecules diffusing through N_2 molecules and crossing a 0.2 m^2 area at 273 K if the concentration gradient is 40 torr per centimeter and the diffusion coefficient is that given in **Table 4.4.**

Method Use the diffusion equation, $J_z = -D(\partial n^*/\partial z)$, to calculate the flux. The number crossing the given area is then the flux times the area.

Solution The diffusion coefficient for O_2–N_2 is $D = 1.8 \times 10^{-5}\ \mathrm{m^2\ s^{-1}}$. Since $p = nRT/V$, we can convert the pressure gradient to a number density gradient by dividing the pressure by RT. The gradient is thus calculated to be

$$\frac{\partial n^*}{\partial z}$$

$$= \frac{(40\ \mathrm{torr/cm})(1\ \mathrm{atm}/760\ \mathrm{torr})(100\ \mathrm{cm/m})(6.02 \times 10^{23}\ \mathrm{molecules\ mole^{-1}})(10^3\ \mathrm{L}/1\ \mathrm{m^3})}{(0.082\ \mathrm{L\ atm\ mole^{-1}\ K^{-1}})(273\ \mathrm{K})}$$

$$= 1.42 \times 10^{26}\ (\mathrm{molecules/m^3})\ \mathrm{m^{-1}}. \tag{4.32}$$

Thus, the flux is

$$J_z = -(1.8 \times 10^{-5}\ \mathrm{m^2\,s^{-1}})[1.42 \times 10^{26}\ (\mathrm{molecules/m^3})\ \mathrm{m^{-1}}]$$

$$= -2.55 \times 10^{21}\ \mathrm{molecules\ s^{-1}\ m^{-2}}. \tag{4.33}$$

The number crossing the area of 0.2 m^2 per unit time is then the flux times the area, or $(0.2\ \mathrm{m^2})(2.55 \times 10^{21}\ \mathrm{molecules\ s^{-1}\ m^{-2}}) = 5.10 \times 10^{20}$ molecules/s.

Like thermal conductivity and viscosity, diffusion in gases can be understood by the application of kinetic theory. In this case, however, we must focus on the motion of the molecules themselves. Because their number density changes with position we cannot bring n^* out of the differential $\partial(n^*q)$ in **equation 4.11,** and because it is the molecules themselves that are being transported, $q = 1$ and the flux is the flux of molecules. **Equation 4.11** then becomes

$$J_z = -\frac{1}{3}<v>\lambda\left(\frac{\partial n^*}{\partial z}\right), \tag{4.34}$$

and comparison with Fick's first law, $J_z = -D(\partial n^*/\partial z)$, shows that

$$D = \frac{1}{3}<v>\lambda. \tag{4.35}$$

As might be expected from the severity of the approximations made in Section 4.3.1, the numerical factor in **equation 4.35** is incorrect, even for hard spheres, but our understanding of the underlying science is enhanced little by correcting it. It is worth noting, however, that the value of the mean free path depends on whether we are considering the diffusion of a molecule of type 1 into other molecules of type 1 or into molecules of another type, 2. For so-called *self-diffusion,* the mean free path is given by **equation 4.16,** since this equation describes how far a molecule travels before colliding with another of the same type. For one molecule of type 1 diffusing through molecules of type 2, however, we must review the derivation of presented in Section 1.7 just prior to **equation 1.47.** If the mean free path for a type 1 molecule in molecules of the same type is $\lambda = \bar{c}/Z_1$, then the mean free path for a type 1 molecule in molecules of type 2 should be $\lambda = \bar{c}/Z_2 = \bar{c}/[\pi b_{\max}^2 v_r n_2^*]$. Note that although the calculation of $\bar{c}$ involves the mass of molecules of type 1, the calculation of v_r involves the reduced mass. Furthermore, $b_{\max}$ is the average of the diameters of molecules of type 1 and 2. Thus, the mean free path will depend on the properties of both types of molecules. In real systems, molecules of type 1 will diffuse both through others of the same type and through those of type 2, so that the mean free path is somewhat more complicated than that in either of the above calculations; it depends inversely on the total number density, not just on the number density of type 2 molecules.

example 4.7

Calculating the Diffusion Coefficient for N_2

Objective Approximate the diffusion coefficient of N_2 in N_2 at 300 K and 1 atm given that the molecular diameter is 218 pm (see Example 1.7).

Method Use **equation 4.35,** noting that under these conditions we have calculated in Example 1.7 the mean free path of N_2 as 3.87×10^{-7} m and the average velocity as 673 m/s.

Solution $D = (1/3)v\lambda = (1/3)(673\ \text{m/s})(3.87 \times 10^{-7}\ \text{m}) = 8.68 \times 10^{-5}\ \text{m}^2\ \text{s}^{-1}$.

Comment That this value is higher than that listed in **Table 4.4** is due only partly to the fact that v and λ are higher at 300 K than at 273 K. Because we have made several simplifying approximations, **equation 4.35** is not expected to be numerically accurate.

4.7 TIME-DEPENDENT TRANSPORT

We have assumed in the preceding sections that the gradient of temperature, momentum, or concentration was steady in time. For example, in the case of diffusion we see from $J_z = -D(\partial n^*/\partial z)$ that if the gradient of concentration is steady in time then the flux of particles will also be steady. We now address the situation in which the gradient changes in time, as it might, for example, if a drop of one material were introduced into another or if heat were momentarily applied to one end of a rod of conductive material. In both cases we see that the gradient is large immediately after the perturbation, but that the diffusion of molecules or the flow of heat tends to cause the gradient to diminish as time progresses.

To be able to describe these processes, we introduce a notation that recognizes that the flux can depend both on position and on time, $J = J(z,t)$. The time dependent flux can be related to the gradient by considering two surfaces of area A separated by a distance Δz, as shown in **Figure 4.5.** Suppose that molecules are diffusing in the positive z direction. What is the change of concentration in the volume $A\Delta z$ per unit time? The concentration is increased by the number of molecules that flow into the volume from below. Because $J(z,t)$ is the number of molecules per unit time per unit area that cross the plane located at z, the change in concentration is given by $J(z,t)$ times A divided by the volume: $\partial n^*(z,t)/\partial t = J(z,t)A/A\Delta z = J(z,t)/\Delta z$, where the dependence of n^* on z and t is made clear by the notation $n^*(z,t)$. Similarly, the concentration is decreased by the molecules that flow out of the volume to regions above; the change is given by $\partial n^*(z,t)/\partial t = -J(z + \Delta z, t)A/A\Delta z = -J(z + \Delta z, t)/\Delta z$. Thus, the net rate of concentration change is

$$\frac{\partial n^*(z,t)}{\partial t} = \frac{J(z,t) - J(z + \Delta z, t)}{\Delta z} \tag{4.36}$$

In the limit when Δz is very small, the quantity on the right-hand side of **equation 4.36** is simply $-\partial J(z,t)/\partial z$, so that

$$\frac{\partial n^*(z,t)}{\partial t} = -\frac{\partial J(z,t)}{\partial z}. \tag{4.37}$$

At any time t, however, the flux is related to the number density gradient, as we have seen in the previous section:

$$J(z,t) = -D\frac{\partial n^*(z,t)}{\partial z}. \tag{4.38}$$

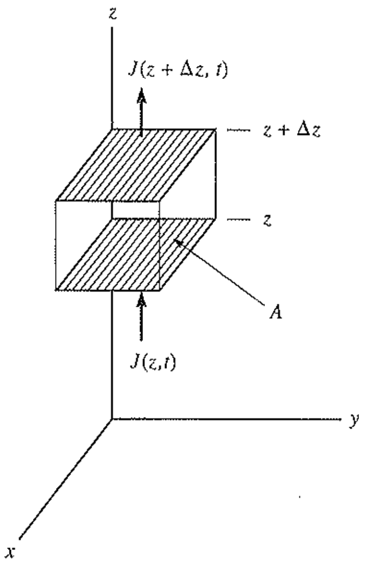

Figure 4.5

The change in flux with time.

If we take the partial derivative of both sides of **equation 4.38** with respect to z, we obtain

$$\frac{\partial J(z,t)}{\partial z} = -D\frac{\partial^2}{\partial z^2}n^*(z,t). \tag{4.39}$$

Finally, using **equation 4.37** we see that **equation 4.39** can be rewritten as

$$\frac{\partial n^*(z,t)}{\partial t} = D\frac{\partial^2}{\partial z^2}n^*(z,t). \tag{4.40}$$

Equation 4.40 is known as the *time-dependent diffusion equation* or as Fick's second law.

Consider the diffusion of N molecules that start at $z = z_0$ at $t = 0$ in the cross-sectional area A of a tube of infinite length. How will this distribution change in space as a function of time? The solution to **equation 4.40,** as shown in Problem 4.16, is

$$n^*(z,t) = \frac{N}{A}\frac{1}{2\sqrt{\pi Dt}}\exp\left[-\frac{(z-z_0)^2}{4Dt}\right]. \tag{4.41}$$

Figure 4.6 displays the concentration profile predicted by **equation 4.41** for different values of Dt. With increasing time, the concentration spreads over larger distances. In fact, if we normalize the right-hand side of **equation 4.41** (which amounts to multiplication by A/N) we will obtain a function that gives the probability that a molecule will be found at a position z at a time t. This function is thus a distribution function for the position at a particular time, and we can use it to calculate average positions. Of course, because the distribution function is symmetric around z_0, the average distance that a molecule has traveled from that position after a time t is zero.

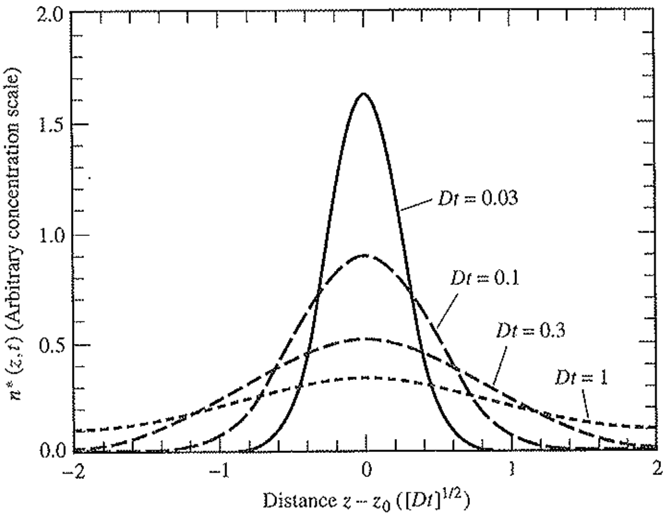

Figure 4.6

Plot of $n^*(z,t)$ following diffusion from a starting condition where all molecules are at $z = 0$ at $t = 0$.

It is useful, however, to calculate the root-mean-squared distance, $z_{\text{rms}} = <(z - z_0)^2>^{1/2}$. Using **Table 1.1** to evaluate the integral, this distance is given by

$$\begin{aligned}[z_{\text{rms}}]^2 &= \int_{-\infty}^{\infty} (z - z_0)^2 \frac{1}{2\sqrt{\pi D t}} \exp\left[-\frac{(z - z_0)^2}{4Dt}\right] dz \\ &= \frac{1}{2\sqrt{\pi D t}} 2\frac{1}{4}\sqrt{\pi}(4Dt)^{3/2} \qquad \textbf{(4.42)} \\ &= 2Dt,\end{aligned}$$

so that

$$z_{\text{rms}} = (2Dt)^{1/2}. \qquad \textbf{(4.43)}$$

We thus see that the root-mean-squared distance that a molecule diffuses is proportional to the square root of the diffusion coefficient and to the square root of the time.

example 4.8

The rms Distance Traveled by a Molecule in a Day

Objective Find the rms distance that a molecule of naphthalene travels by diffusion in 1 day through the atmosphere assuming the diffusion coefficient is 1.5×10^{-6} m^2 s^{-1}. Naphthalene is the principal component in moth balls.

Method Use **example 4.43,** but recognize that this is a three-dimensional problem and not merely a one-dimensional one.

Solution Note that the square of the distance from the center of a three-dimensional object is $r^2 = x^2 + y^2 + z^2$, so that $<r^2> = <x^2> + <y^2> + <z^2> = 3<z^2>$. One day is (24 hr)(60 min/hr)(60 s/min) $= 8.64 \times 10^4$ s. Thus $(z_{\text{rms}})^2 = (2Dt)$ or $(r_{\text{rms}})^2 = (6Dt) = [6(1.5 \times 10^{-6}\ \text{m}^2\ \text{s}^{-1})(8.64 \times 10^4\ \text{s})] = 0.78\ \text{m}^2$ or $r_{\text{rms}} = 0.88$ m.

Comment Note that molecules do not travel far in a day by diffusion. Convection is more often the mode of transport.

We can gain some physical insight into diffusion by considering a process known as the *one-dimensional random walk.* Consider a molecule constrained to move in the z direction in steps of length ℓ, and suppose that after each step the molecule has no memory of which direction it traveled in previous steps; its choice of direction for the next step is completely random. On average, what will be the root-mean-squared position of the molecule with respect to its original position after it has taken N steps?

While this problem can be solved mathematically in closed form, the solution is somewhat complex (see Problem 4.18). It is far easier to write a simple computer program to predict the position. Given a position of z_i after the ith step, the position after the $(i + 1)$th step is given by

$$z_{i+1} = z_i + \ell\,\text{sign}[\text{RND}(\,) - 0.5], \qquad \textbf{(4.44)}$$

where RND( ) is a random number between 0 and 1 and sign[ ] is a function that is equal to +1 if the argument is nonnegative and −1 otherwise.

Figure 4.7 displays the results of six random walks starting at a position z_0. Note that the positions of the particles spread out with increasing number of steps. If we run, say, 1000 trajectories we can compute an accurate average for the root-mean-squared displacement from z_0 as a function of the number of steps. This average for a typical calculation is shown in **Figure 4.8,** which demonstrates that the root-mean-squared displacement in units of ℓ is equal to the square root of the number of steps.

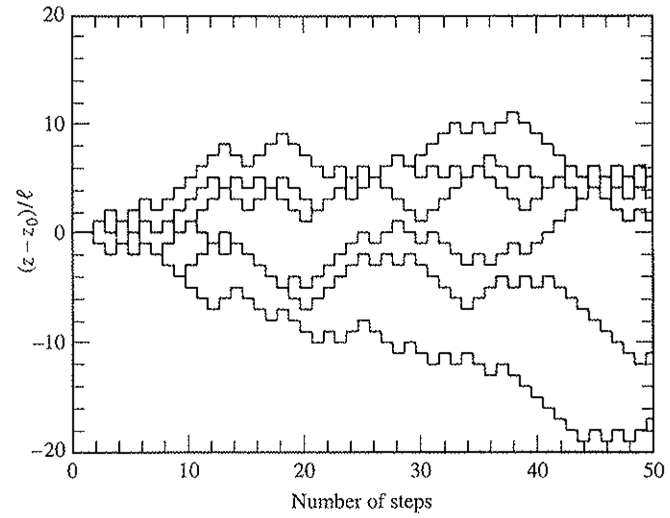

Figure 4.7

Random walks: the position as a function of the number of steps for six one-dimensional random walks.

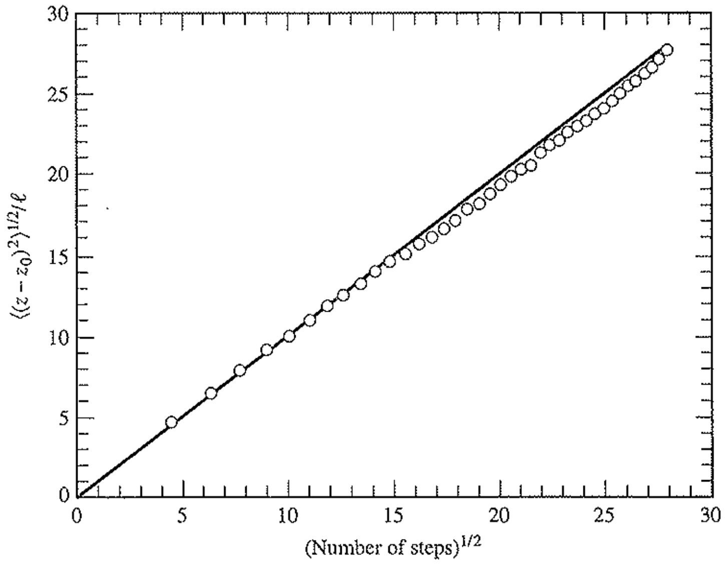

Figure 4.8

Root-mean-squared distance traveled as a function of the square root of the number of steps for a one-dimensional random walk.

What we learn from this computer experiment (or from the more rigorous closed-form solution derived in Problem 4.18) is that molecular diffusion is just like a random walk in one dimension. Let the total time for N steps be equal to N times the average time per step, τ: $t = N\tau$ or $N = t/\tau$. The observation from our computer experiment is that $(z_{\rm rms})^2 = N\ell^2$, or $(z_{\rm rms})^2 = \ell(\ell/\tau)t$. The expression

$$z_{\rm rms} = (\ell^2 t/\tau)^{1/2} \tag{4.45}$$

is known as the *Einstein-Smoluchowski* equation.[e] We can interpret it as follows. Note that $\ell/\tau = <v>$, the average velocity, so that $z_{\rm rms} = [\ell<v>t]^{1/2}$. If we take the step size in the z direction to be that calculated in **equation 4.8,** we find that $z_{\rm rms} = [(2/3)\lambda<v>t]^{1/2}$, or, using **equation 4.35,** $z_{\rm rms} = [2Dt]^{1/2}$. This last equation is exactly what we have calculated in **equation 4.43.**

In retrospect, it should come as no surprise that the one-dimensional random walk agrees with our diffusion calculation. Assumption 4 in Section 4.3.1 made the approximation that complete equilibrium is attained after every collision. When applied to the motion of molecules, this assumption means that there should be no preferential direction for the velocity after any collision. Thus, the assumption that leads to **equation 4.43** and the assumption of a random walk are equivalent. Both are slightly in error when compared to the real situation, but both capture the essential physical situation.

4.8 SUMMARY

By assuming that the motion of molecules is responsible for the transport of properties such as heat, momentum, and concentration in gases, we have found how the constants κ, η, and D in the flux equations for these properties depend on microscopic molecular properties. The relationships were found by making four simplifying assumptions in Section 4.3.1 and by treating the motion of molecules using the kinetic theory developed in Chapter 1. We found that the flux of molecules across a surface is given by

$$J_z = \frac{1}{4} n^* <v> \tag{4.6}$$

and that the average vertical distance between collisions is $2\lambda/3$. Armed with these equations, we showed that when the gradient is constant in time, the flux of a property q in the vertical direction is given by

$$J_z = -\frac{1}{3} <v> \lambda \frac{\partial(n^* q)}{\partial z}. \tag{4.11}$$

Use of this equation with q equal to ϵ, p_x, or 1 gave equations for the following coefficients:

Thermal Conductivity:

$$\kappa = \frac{1}{3} n^* \lambda <v> \frac{C_{\rm V}}{N_{\rm A}} = \frac{<v> C_{\rm V}}{3\sqrt{2}\pi d^2 N_{\rm A}}, \tag{4.17}$$

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[e] A. Einstein, *Ann. d. Physik* **17,** 549 (1905); **19,** 371 (1906); M. v. Smoluchowski, *Ann. d. Physik* **21,** 756 (1906).

Viscosity:

$$\eta = \frac{1}{3} n^* <v> \lambda m, \tag{4.21}$$

and *Diffusion:*

$$D = \frac{1}{3} <v> \lambda. \tag{4.35}$$

It is important to remember that, although these equations capture the essential features of transport properties, the numerical coefficients are not quite correct. Those seeking more accurate formulas are referred to one of the texts listed in the reading list at the end of this chapter.

When the gradient is not constant in time we found, using diffusion as an example, that the derivative of the quantity with time was proportional to the second derivative of the quantity in space:

$$\frac{\partial n^*(z,t)}{\partial t} = D \frac{\partial^2}{\partial z^2} n^*(z,t). \tag{4.40}$$

For a starting condition in which all the molecules have a specified z component at time zero, the root-mean-squared distance traveled as a function of time is given by

$$z_{\text{rms}} = (2Dt)^{1/2}. \tag{4.43}$$

Diffusion of molecules in a gas is analogous to a one-dimensional random walk.

appendix 4.1

The Poiseuille Formula

Consider the flow of a fluid through a cylindrical tube of radius a whose axis is coincident with the x direction and which is subject to a pressure gradient along its length. The velocity of the fluid will be a function of the radial position r from the center of the tube. Molecules at $r = a$ will be in contact with the surface of the tube and will have zero velocity in the x direction, while those in the center of the tube at $r = 0$ will have the largest velocity. The volume V of fluid passing a cross-sectional area of the tube per unit time is given by integrating the area of coaxially concentric shells of thickness dr times the velocity in each shell:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \int_0^a v_x(r)(2\pi r)\,\mathrm{d}r, \tag{4.46}$$

where $2\pi r\,\mathrm{d}r$ is the area of the shell and $v_x(r)$ is the velocity in the x direction as a function of r. To perform the integration, we first need to determine $v_x(r)$.

To evaluate the radial dependence of the velocity, consider a small cylindrical volume element of the fluid coaxial with the x axis, as shown in **Figure 4.9.** The cross-sectional area of the cylinder is πr^2, and the length is dx. The pressure on the left side of the volume is p, while that on the right side is $p - \mathrm{d}p$. When the pressure differential is constant in time, the velocity of the fluid through the cylinder will be constant; its acceleration will be zero. From Newton's law, zero acceleration

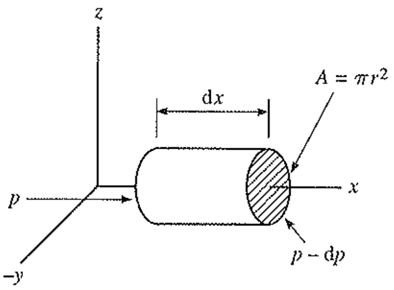

Figure 4.9

The force due to the pressure differential is equal and opposite to the force due to the viscous drag.

means that the total force on the fluid is zero. A fluid in the volume will thus accelerate its flow in the $+x$ direction until the force in the $-x$ direction due to its viscous drag is exactly equal to the force due to the pressure differential. The force due to the pressure differential is the area times dp: $F_{+x} = \pi r^2\, dp$. The force in the $-x$ direction can be calculated from the flux of momentum in the r direction, $J_r = -\eta(\partial v_x/\partial r)$, so that $F_{-x} = J_r A = -\eta(\partial v_x/\partial r)2\pi r\, dx$, where $A = 2\pi r\, dx$ is the surface area of the outside of the cylinder. Thus

$$\pi r^2\, dp = -\eta 2\pi r dx \frac{\partial v_x}{\partial r},$$

$$\frac{\partial v_x}{\partial r} = -\frac{r}{2\eta}\frac{dp}{dx}. \tag{4.47}$$

This equation can be integrated to give

$$v_x = -\frac{r^2}{4\eta}\frac{dp}{dx} + C, \tag{4.48}$$

where C, the constant of integration, can be evaluated by the boundary condition that the velocity is zero at the wall of the cylinder: $v_x(a) = 0$. The result is

$$v_x = -\frac{a^2 - r^2}{4\eta}\frac{dp}{dx}. \tag{4.49}$$

Figure 4.10 shows the velocity distribution predicted by **equation 4.49.**

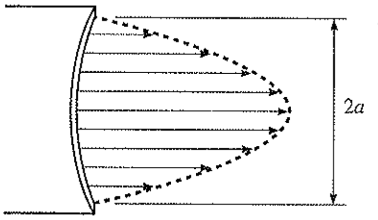

Figure 4.10

The velocity distribution of a fluid in a cylindrical tube.

We now substitute **equation 4.49** into **equation 4.46** and integrate:

$$\begin{aligned}\frac{\mathrm{d}V}{\mathrm{d}t} &= \int_0^a \frac{a^2 - r^2}{4\eta}\frac{\mathrm{d}p}{\mathrm{d}x}(2\pi r)\,\mathrm{d}r \\ &= \frac{2\pi}{4\eta}\frac{\mathrm{d}p}{\mathrm{d}x}\left[\frac{a^2r^2}{2} - \frac{r^4}{4}\right]_0^a \qquad \textbf{(4.50)} \\ &= \frac{\pi a^4}{8\eta}\frac{\mathrm{d}p}{\mathrm{d}x}.\end{aligned}$$

This last equation is simply the Poiseuille formula given in **equation 4.27** with the pressure gradient in the x direction rather than the z direction.

suggested readings

R. S. Berry, S. A. Rice, and J. Ross, *Physical Chemistry* (Wiley, New York, 1980).

J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

W. Kauzmann, *Kinetic Theory of Gases* (W. A. Benjamin, New York, 1967).

E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1938).

L. B. Loeb, *The Kinetic Theory of Gases* 3rd ed. (Dover, New York, 1961).

F. R. W. McCourt, J. J. M. Beenakker, W. E. Köhler, and I. Kuscer, *Non-equilibrium Phenomena in Polyatomic Gases* (Clarendon Press, Oxford, 1990), Chapter 6.

R. D. Present, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1958).

problems

4.1 The coefficient of viscosity does not depend on the number of molecules per unit volume. Explain why not.

4.2 The transport coefficients κ, η, and D all increase as the square root of the temperature, and decrease as the square of the average molecular diameter. Explain why without reference to any formula. Of the three transport coefficients, κ and D vary as $1\sqrt{m}$, whereas η varies as $\sqrt{m}$. Why?

4.3 The rate of a certain surface catalyzed reaction is proportional to the rate at which molecules hit the surface. The rate will increase with an increase in which of the following properties? (a) the mass of the molecules, (b) the velocity of the molecules, (c) the heat capacity of the molecules, (d) the number density of the molecules, (e) the area of the surface.

4.4 Consider a thought experiment in which horses are transported by molecules and suppose that the number of horses is proportional to the number of bushels of oats: $H = kO$. The transport coefficient relating the flux of horses to the gradient of oats depends on which of the following parameters? (a) the weight of the horse, (b) the velocity of the molecule, (c) the proportionality constant k, (d) the mean free path, (e) the speed of the horse.

4.5 Why is the coefficient of thermal conductivity larger for helium than that for argon? Why is the coefficient of thermal conductivity for N_2 larger than that for argon?

4.6 The viscosity coefficient of O_2 is greater than that of CO_2. Which molecule has the greater molecular diameter?

4.7 How does the root-mean-squared distance traveled by a diffusing molecule vary with temperature? (a) not at all, (b) increases (c) decreases. How does it vary with pressure? (a) not at all, (b) increases, (c) decreases.

4.8 Two bugs each execute a one-dimensional random walk with the same step size, but the second bug takes steps twice as often as the first. After a given time the second bug will be (a) twice as far from the origin as the first, (b) $\sqrt{2}$ times as far, (c) the same distance.

4.9 In a tube of infinite length, consider the diffusion of molecules that start at $z = z_0$ at $t = t_0$. The concentration of molecules at a location different than z_0 (a) increases monotonically with time, (b) stays the same, (c) decreases monotonically, (d) increases then decreases, or (e) decreases then increases.

4.10 If thermal conductivity is independent of number density, why is it advantageous to evacuate the region between the walls of a dewar flask?

4.11 The thermal conductivity of silver is about 4 J K^{-1} cm^{-1} s^{-1}. Calculate the heat flow in watts through a silver disk 0.1 cm in thickness and having 2 cm^2 area if the temperature difference between the two sides of the disk is 10 K.

4.12 The heat capacity of N_2 is about 20 J K^{-1} mol^{-1} and its diffusion coefficient is 1.5×10^{-5} m^2 s^{-1}. How much heat will be conducted in 1 s across a 1-cm space between two parallel plates 2 m^2 in area if the plates differ in temperature by 5 K and the space between the plates is filled with nitrogen at 1 atm and 300 K? You may assume that the ideal gas law holds under these conditions.

4.13
a. Calculate the coefficient of thermal conductivity for nitrogen at 303 K. Assume that πd^2 for N_2 is 7×10^{-20} m^2 and $C_{vm} = (5/2)R$.
b. In a double glazed window the panes are separated by 5 cm. What is the rate of heat transfer in watts from a warm room at 323 K to the cold exterior at 283 K through a window of area 1 m^2? Assume that air has the coefficient of thermal conductivity calculated in part (a).
c. To approximately what pressure in torr would one have to evacuate the space between the two windows before κ would be decreased appreciably for the value calculated in part (a)?

4.14 The self-diffusion coefficient of CO is $D = 1.75 \times 10^{-5}$ m^2 s^{-1} at 273 K and 1 atm. The density of CO under these conditions is 1.25 kg m^{-3}. Calculate the molecular diameter.

4.15 The heat capacity of N_2 is 20.9 J K^{-1} mol^{-1}, and its viscosity at room temperature is 1.7×10^{-4} poise (1 poise = 1 g cm^{-1} s^{-1}). How much heat will be conducted in 1 s across a 1-mm space between two parallel plates 10 cm × 10 cm in size if the plates differ in temperature by 5 K and if the space between the plates is filled with N_2 at 1 atm?

4.16 Show by direct differentiation that **equation 4.41** is the solution to **equation 4.40.**

4.17 Write and test a computer program to verify the general result, presented in **Figure 4.8,** that the root-mean-squared distance traveled in a one-dimensional random walk is proportional to the square root of the number of steps.

4.18 The computer experiment on the random walk showed that the root-mean-squared distance traveled in a random walk is proportional to the square root of the number of steps taken. This result can be shown more rigorously by consideration of the following problem.

a. Suppose a drunken sailor leaves a bar at closing time and executes a one-dimensional random walk in the z direction along the sidewalk. Enumerate all the possible sequences of steps for which, after six steps each of length ℓ, she could be at distances -6ℓ, -4ℓ, -2ℓ, 0, 2ℓ, 4ℓ, or 6ℓ from the doorway of the bar.

b. Show that the probabilities obtained in part (a) agree with the following formula, which can be used to calculate the absolute value of the sailor's distance from the bar:

$$P(z) = \frac{n!}{[1/2(n+s)]!\,[1/2(n-s)]!\,2^n},$$

where n is the number of steps, $s = z/\ell$, and $N! = N(N-1)(N-2)\ldots(1)$.

c. A very accurate approximation to $N!$ for large N is given by *Stirling's approximation:*

$$\ln N! = \left(N + \frac{1}{2}\right)\ln N - N + \ln(2\pi)^{1/2}$$

Use this approximation to show that

$$P(z) = \left(\frac{2}{\pi n}\right)^{1/2} \exp\left(-\frac{s^2}{2n}\right).$$

[*Hint:* You will need to approximate $\ln(1+x) \approx x - x^2/2$.]

d. Substitute $s = z/\ell$, and let the number of steps n be given by the total time divided by the time per step: $n = t/\tau$, to show that

$$P(z,t) = \left(\frac{2\tau}{\pi t}\right)^{1/2} \exp\left(-\frac{z^2\tau}{2t\ell^2}\right).$$

e. Finally, compare the above equation with **equation 4.41,** letting $z_0 = 0$, to derive the Einstein-Smoluchowski relationship, **equation 4.45.**