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
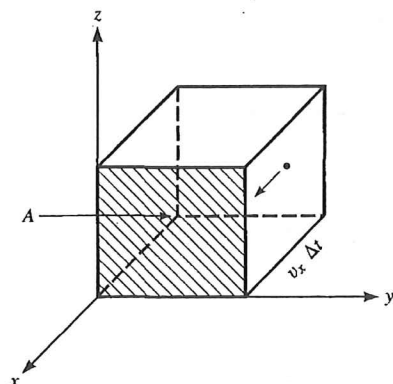
■ Figure 1.1

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 $n N_A / V$, 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 $\mathbf{v}^2 = \mathbf{v} \cdot \mathbf{v} = v^2$.

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

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

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:

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

or, more generally for any observable quantity,

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

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

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

The quantity $|\psi(x)|^2\,dx$ 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 $4\pi r^2\,dr$. 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

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

or

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

so that

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

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

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

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,

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

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

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

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:

$$\int_{-\infty}^{\infty} F(v_x)\,dv_x = 1. \tag{1.24}$$

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

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

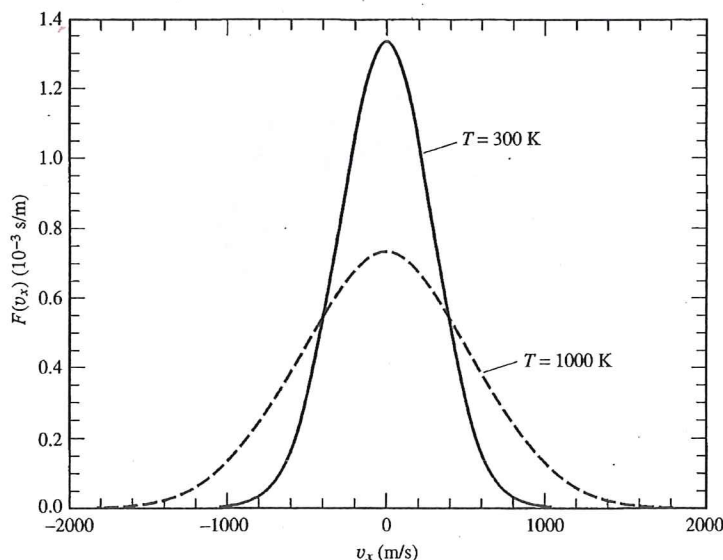where the integral was evaluated using **Table 1.1**. The solution is then $K = (\kappa/\pi)^{1/2}$.

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

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

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

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

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, $v = |v|$, 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]

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[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.

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

$$<v> = \int_0^\infty vF(v)\,dv$$

(1.32)

$$= \int_0^\infty v4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv = \left(\frac{8kT}{\pi m}\right)^{1/2},$$

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):

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

(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 $P(Q)\,dQ$ as the velocity distribution function given in **equation 1.31,** we see that we need to integrate $vF(v)\,dv$ from limits $v = 0$ to $v = \infty$.

Solution $$<v> = \int_0^\infty vF(v)\,dv = \int_0^\infty 4\pi v^3 \left(\frac{a^3}{\pi^{3/2}}\right) \exp(-a^2v^2)\,dv$$

(1.34)

$$= \frac{4}{\sqrt{\pi}} \int_0^\infty a^3 v^3 \exp(-a^2v^2)\,dv,$$

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

$$\frac{4}{a\sqrt{\pi}} \int_0^\infty x^3 \exp(-x^2)\,dx = \frac{4}{a\sqrt{\pi}} \frac{1}{2}$$

(1.35)

$$= \frac{2}{\sqrt{\pi}} \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{8kT}{\pi m}\right)^{1/2},$$

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
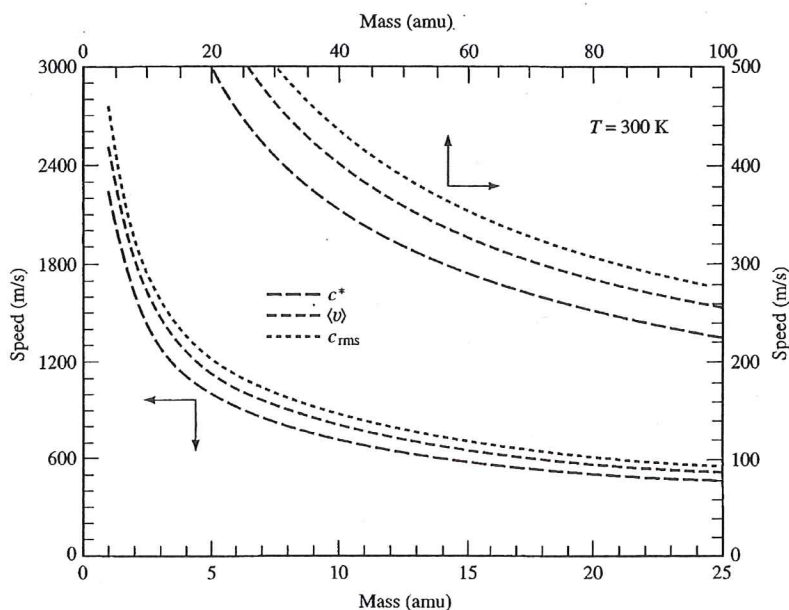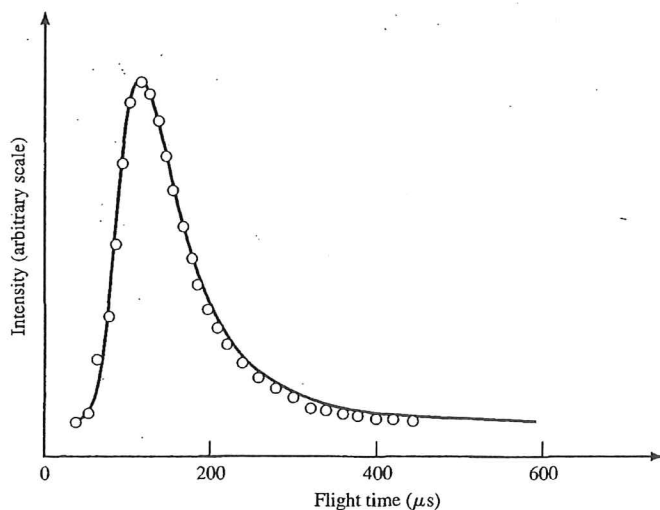
Figure 1.6

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 1.8

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 $<\epsilon> = 3kT/2$ (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
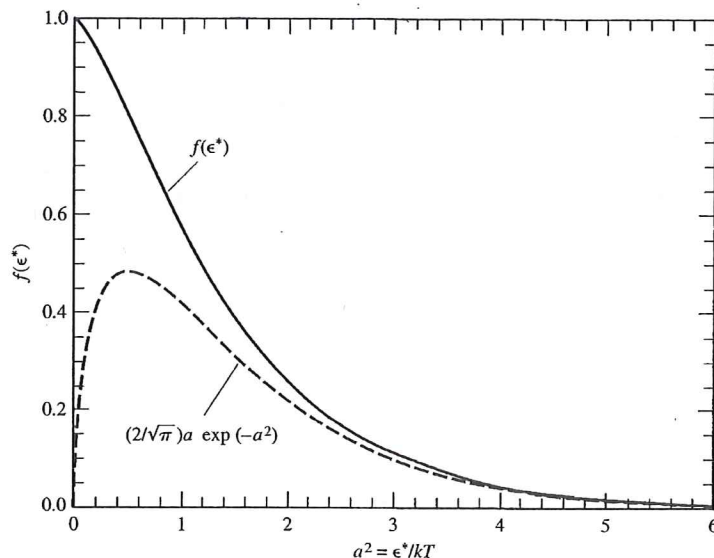
Figure 1.10

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 $\text{erfc}(a)$ 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
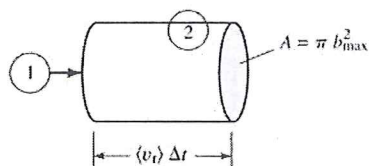
Figure 1.12

Molecule 1 sweeps out a cylinder of area πb_{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.[i] 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

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

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

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

where b_{max}^2 has been replaced by d^2 since $r_1 + r_2 = 2r_1 = d$. The quantity πb_{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:

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

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

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

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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[i]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.

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 atm)(6.02 × 10^{23} molec/mole)/[(0.082 L atm mol^{-1} K^{-1})(300 K)] = 2.45 × 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^*(NO) = n^*(O_3) = (0.2 × 10^{-6})(2.45 × 10^{22}) = 4.9 × 10^{15} molec/L. The average relative velocity is $\langle v_r \rangle = (8kT/\pi\mu)^{1/2} = $ [8(1.38 × 10^{-23} J K^{-1})(300 K)(6.02 × 10^{23} amu/g)(1000 g/kg)/ $(\pi(48 × 30/78)$ amu)]$^{1/2}$= 586 m/s. The average diameter is (300 + 375 pm)/2 = 337.5 pm. Then $Z_{12} = \pi$(337.5 × 10^{-12} m)^2 (586 m/s)(4.9 × 10^{15} molec/L)^2(1 L/10^{-3} m^3)^2 = 5.0 × 10^{21} collisions s^{-1} 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 $\langle v \rangle$ in meters per second by the collision number Z_1 in collisions per second, we obtain the mean free path in meters per collision:

$$\lambda = \frac{\langle v \rangle}{Z_1} = \frac{\langle v \rangle}{\pi d^2 \sqrt{2} \langle v \rangle n_1^*}$$

$$= \frac{1}{\sqrt{2}\, \pi d^2 n_1^*} \quad\quad\quad (1.47)$$

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 $\langle v_r \rangle$, **equation 1.43** to calculate Z_1, and **equation 1.47** to calculate λ.

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

$$\langle v_r \rangle = \left\{ \frac{8(1.38 × 10^{-23}\text{ J K}^{-1})(300\text{ K})(6.02 × 10^{23}\text{ amu/g})(1000\text{ g/kg})}{(3.1415 × 14\text{ amu})} \right\}^{1/2} \quad (1.48)$$

$$= 673 \text{ m/s.}$$

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

$$\frac{df(z)}{dz} \frac{dz}{da} = f'(a)f(b). \tag{1.51}$$

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

$$\frac{df(z)}{dz} \frac{dz}{db} = f(a)f'(b). \tag{1.52}$$

Since $z = a + b$, $dz/da = dz/db = 1$. Consequently,

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

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:

$$\frac{f'(a)}{f(a)} = \pm\kappa \qquad \frac{f'(b)}{f(b)} = \pm\kappa. \tag{1.55}$$
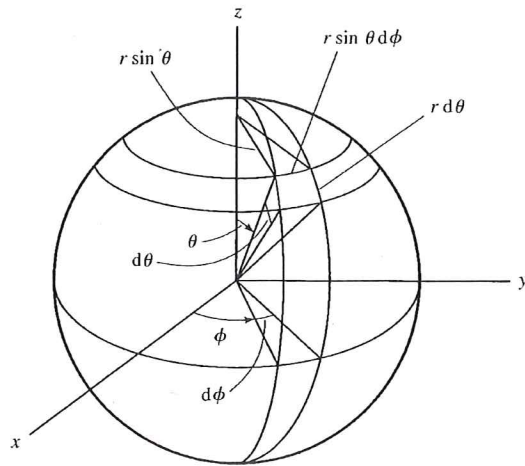
Figure 1.15

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, $r\,d\theta$, times the arc length on the latitude, $r\sin\theta\,d\phi$. Thus, the volume element is $dV = r^2\sin\theta\,d\theta\,d\phi\,dr$.

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*:

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

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

$$\frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2}\,du + \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2}\,du = \text{erf}(x) + \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2}\,du$$

$$= \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-u^2}\,du = 1. \tag{1.59}$$
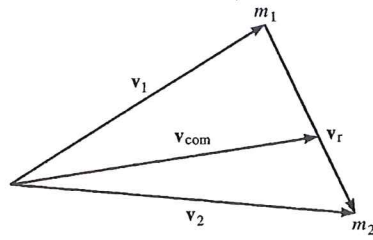
Figure 1.17

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 $M\mathbf{v}_{com}$. Because we assume that no external forces are acting on the system, $\mathbf{F} = M\mathbf{a}_{com} = (d\mathbf{p}_{com}/dt) = 0$, 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

$$\mathbf{v}_2 - \mathbf{v}_{com} = \left(\frac{m_1}{M} + \frac{m_2}{M}\right)\mathbf{v}_2 - \mathbf{v}_{com}$$

(1.62)

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

However,

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

(1.63)

so that

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

Consequently,

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

(1.64)

$$= \frac{m_1}{M}\mathbf{v}_r.$$

In a similar way, we find that

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

(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.

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 $(0.326 \text{ s}^3 \text{ m}^{-3})v_x^3 + (\pi \text{ s}^9 \text{ m}^{-9})v_x^9$. 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 $\int u \, dv = (uv)|_{\text{limits}} - \int v \, du$, where the notation $|_{\text{limits}}$ 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 $<v_r> = (8kT/\pi\mu)^{1/2}$, where μ, the reduced mass, is defined as $\mu \equiv m_1m_2/(m_1 + m_2)$.

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 $m/(2kT) = 5.62 \times 10^{-6}$ 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 $k(T)$.