

**CHAPTER****22**

## MOLECULAR PROPERTIES OF GASES

**I**

*n Section 21-5 we introduced the ideal gas law, which is expressed in terms of pressure, volume, and temperature. When we deal with such large-scale, measurable properties of gases, we are taking what we describe as a macroscopic approach to the subject. The ideal gas law says nothing about the fact that gases—and indeed matter of all kinds—are made up of particles, which may be atoms or molecules.*

*In this chapter we take a microscopic approach and seek to account for the macroscopic properties of a gas in terms of the properties of its molecules. Our plan is to follow the motion of a representative molecule and then average this behavior over all the molecules that make up the system. If the number of molecules is very large—and it usually is—such averages give sharply defined quantities. The formal name for the approach we are taking is the kinetic theory of gases, the word “kinetic” suggesting that we are dealing with particles that are in motion.*

### **22-1 THE ATOMIC NATURE OF MATTER**

Today no informed person doubts that all matter is made up of atoms. It may come as a surprise to learn that universal acceptance of the existence of atoms by the scientific community did not occur until the early 1900s. There were many earlier speculations about the atomic nature of matter, dating back to the ancient Greeks, but none were sufficiently firmly supported by experiment to exclude other points of view. Today the hypothesis that atoms exist is so essential to our understanding of the nature of the world around us that the Nobel laureate physicist Richard Feynman could write: “If all scientific knowledge were to be destroyed, I would hope that the knowledge that atoms exist might be spared.”

The modern trail to belief in atoms can be said to have started in 1828 when the Scottish botanist Robert Brown observed through his microscope that tiny grains of pollen suspended in water underwent ceaseless random motion. We now call this phenomenon *Brownian motion*. Brown

also noted that this same “dancing” motion occurred when particles of finely powdered coal, glass, rocks, and various minerals were suspended in a fluid. The motion seemed to be—and indeed proved to be—a fundamental property of matter.

In 1905, Einstein (unaware of Brown’s report of his observations) predicted that the effect should occur and presented it as direct evidence that the fluid in which the particle is suspended is made up of atoms. A particle suspended in a fluid is bombarded on all sides by the atoms of the fluid, which are in constant motion of thermal agitation. Let  $N$  be the average number of particle–atom collisions on any one side of the particle during a short time interval  $\Delta t$ . On average, the same number of collisions will occur on the other side of the particle. However, because the collisions occur randomly, there will be fluctuations about this average on each side. Thus in any particular interval  $\Delta t$  there will be slightly more collisions on one side of the particle than on the other. These random unbalances occur in three dimensions so the bombarded particle, which typically is many orders of magnitude more massive than the

atoms that bombard it, jitters about in the erratic manner that characterizes Brownian motion.

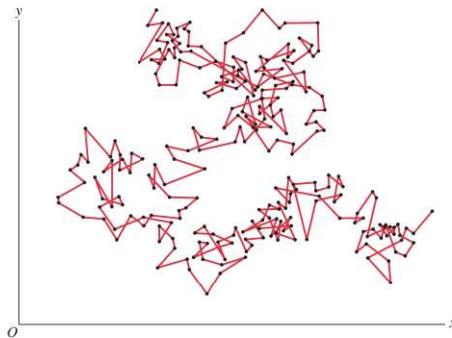
A few years after Einstein's analysis of Brownian motion, the French physical chemist Jean Baptiste Perrin (1870–1942) made quantitative measurements of the effect. Figure 22-1 shows a sample of his data. It displays the Brownian motion of a tiny particle of gum resin suspended in water and viewed through a microscope. Perrin measured the  $x$ ,  $y$  coordinates of the moving particle every 30 s and marked the particle's position with a dot on a graph. (The straight line segments in Fig. 22-1 were drawn simply to connect the dots; the particle does not follow these lines but moves in the same erratic fashion that characterizes the figure as a whole.)

The quantities that can be directly measured from the so-called *random walk* pattern of Fig. 22-1 are  $\Delta x$  and  $\Delta y$ , which are, respectively, the changes in the  $x$  and the  $y$  coordinates of the particle between successive observations. Because  $\Delta x$  and  $\Delta y$  can be either positive or negative, their average value over many measurements is zero. The significant parameters are the average values of the *squares* of these quantities,  $[(\Delta x)^2]_{av}$  and  $[(\Delta y)^2]_{av}$ , which are inherently positive.

Einstein derived the following expression for  $[(\Delta x)^2]_{av}$  if the bombarded particle is a sphere of radius  $a$  suspended in a gas:

$$[(\Delta x)^2]_{av} = \frac{RT}{3\pi\eta a N_A} \Delta t. \quad (22-1)$$

Here  $\eta$  (Greek "eta") is a measure of the viscosity of the gas (see Section 16-6). This quantity enters because, when the suspended particle is given a "kick" because of an unbalance in the atomic bombardment, the particle is slowed



**FIGURE 22-1.** The Brownian motion of a tiny particle of gum resin of radius about  $3\mu\text{m}$ . The dots, which are connected by straight lines, mark the positions of the particle at 30-s intervals. The path of the particles is an example of a *fractal*, a curve for which any small section resembles the curve as a whole. For example, if we take any short 30-s segment and view it in smaller intervals, perhaps 0.1 s, the plot of the motion in that single 30-s segment would be similar to the entire figure.

down by friction-like viscous forces.  $R$  in Eq. 22-1 is the molar gas constant,  $T$  is the Kelvin temperature, and  $N_A$  is the Avogadro constant.

If  $N_A$  were much larger than it actually is, the extent of the Brownian motion would be reduced because the collision rates would be more closely equal on opposite sides of the suspended particle. On the other hand, if  $N_A$  were much smaller than it actually is, the Brownian magnitude would be increased. Thus, with  $[(\Delta x)^2]_{av}$  measured, Eq. 22-1 can be used to deduce  $N_A$ . After collecting much data, of which Fig. 22-1 is a small sample, Perrin found  $N_A \approx 6 \times 10^{23}$  molecules/mol, which agreed with results obtained at that time by other methods. For this work, which was so compelling a confirmation of the existence of atoms, Perrin received the 1926 Nobel Prize in physics. In his 1913 book, *Atoms*, Perrin wrote enthusiastically about his Brownian motion observations: "The atomic theory has triumphed. Until recently still numerous, its adversaries, at last overcome, now renounce one after another their misgivings . . ."

### Properties of the Ideal Gas

In Section 21-5 we described the macroscopic properties of the ideal gas and showed that they were related by the ideal gas law ( $pV = nRT$ ). Now that we have shown the evidence that matter is really made up of atoms, let us look in a little more detail at the atomic or microscopic properties of the ideal gas. In most of the remaining sections of this chapter we will rely on the ideal gas as our thermodynamic system of choice.

**1. The ideal gas consists of particles, which are in random motion and obey Newton's laws of motion.** These particles may be single atoms or groups of atoms. In either case, we will refer to the particles as "molecules." The molecules move in all directions and with a wide range of speeds.

**2. The total number of molecules is "large."** When a molecule rebounds from the wall of its container, it delivers momentum to it. We assume that the number of molecules is so large that the rate at which momentum is delivered to any area  $A$  of the container wall is essentially constant.

**3. The volume occupied by the molecules is a negligibly small fraction of the volume occupied by the gas.** We know that when a gas condenses to liquid form, the volume of the liquid is much smaller than that of the gas. Thus molecules are "small" and our assumption is plausible.

**4. No forces act on a molecule except during a collision, either with the container walls or with another molecule.** If we follow a particular molecule, it moves in a zigzag path consisting of straight-line segments with constant velocity between impulsive encounters.

**5. All collisions are (i) elastic and (ii) of negligible duration.** Part (i) tells us that the total kinetic energy of the molecules is a constant. Part (ii) tells us that the total potential energy of the molecules (which can only come into play during a collision) is negligible.

In the ideal gas model, we take all molecules of a gas of a particular type to be identical and thus to have identical masses. The mass of a molecule is determined by adding the masses of the atoms that make up the molecule. Atomic masses (in units of u), which are often given on a periodic chart of the elements, can be found in Appendix D. For example, the mass of a molecule of sulfur dioxide ( $\text{SO}_2$ ) is given in terms of the atomic masses of sulfur and oxygen as

$$m = m(\text{S}) + 2m(\text{O}) = 32.1 \text{ u} + 2(16.0 \text{ u}) = 64.1 \text{ u}.$$

Instead of the number of molecules  $N$ , it is often more convenient to describe the amount of a gas in terms of the number of moles  $n$ ; the relationship between these two equivalent measures of the quantity of gas was given in Eq. 21-15,  $N = nN_A$ , where  $N_A$  is the Avogadro constant with a value of  $N_A = 6.02 \times 10^{23}$  molecules/mol.

The mass of a mole of any substance, called the *molar mass*  $M$ , is simply the mass of one molecule times the number of molecules per mole, or

$$M = mN_A. \quad (22-2)$$

The molar mass, measured in grams, is numerically equal to the molecular mass, measured in u. Thus the molar mass of  $\text{SO}_2$  is  $M = 64.1 \text{ g/mol} = 0.0641 \text{ kg/mol}$ .

In the rest of this chapter we show how the analysis of a gas as a collection of molecules that behave according to Newton's laws gives us a connection between its macroscopic thermodynamic properties and such microscopic properties as the average molecular speed or the average distance a molecule travels between collisions.

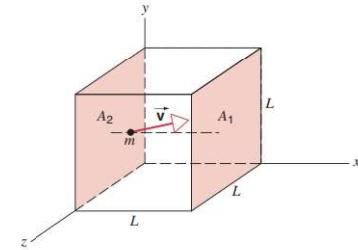
## 22-2 A MOLECULAR VIEW OF PRESSURE

In this section we associate the pressure exerted by a gas on the walls of its container with the constant bombardment of those walls by the molecules of the gas, a point of view perhaps first advanced by the Swiss scientist Daniel Bernoulli (1700–1782) in 1738. We will take the ideal gas as our system and will derive an expression for the pressure it exerts in terms of the properties of the molecules that make it up.

Consider  $N$  molecules of an ideal gas confined within a cubical box of edge length  $L$ , as in Fig. 22-2. Call the faces at right angles to the  $x$  axis  $A_1$  and  $A_2$ , each of area  $L^2$ . Let us focus our attention on a single molecule of mass  $m$ , whose velocity  $\vec{v}$  we can resolve into components  $v_x$ ,  $v_y$ , and  $v_z$ . When this molecule strikes face  $A_1$ , it rebounds with its  $x$  component of velocity reversed, because all collisions are assumed to be elastic; that is,  $v_x \rightarrow -v_x$ . There is no effect on  $v_y$  or  $v_z$ , so that the change in the molecule's momentum has only an  $x$  component, given by

$$\begin{aligned} \text{final momentum} - \text{initial momentum} &= \\ -mv_x - (mv_x) &= -2mv_x. \end{aligned} \quad (22-3)$$

Because the total momentum is conserved in the collision, the momentum imparted to  $A_1$  is  $+2mv_x$ .



**FIGURE 22-2.** A cubical box of edge  $L$  containing an ideal gas. A molecule of the gas is shown moving with velocity  $\vec{v}$  toward side  $A_1$ .

Suppose that this molecule reaches  $A_2$  without striking any other molecule on the way. The time required to cross the cube is  $L/v_x$ . (If the molecule strikes one of the other faces of the box on the way to  $A_2$ , the  $x$  component of its velocity does not change, nor does the transit time.) At  $A_2$  it again has its  $x$  component of velocity reversed and returns to  $A_1$ . Assuming there are no collisions with other molecules, the round trip takes a time  $2L/v_x$ , which is the time between collisions with  $A_1$ . The average impulsive force exerted by this molecule on  $A_1$  is the transferred momentum divided by the time interval between transfers, or

$$F_x = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}. \quad (22-4)$$

To obtain the *total* force on  $A_1$ —that is, the rate at which momentum is imparted to  $A_1$  by *all* the gas molecules—we must sum the quantity  $mv_x^2/L$  for all the molecules. Then, to find the pressure, we divide this force by the area of  $A_1$ —namely,  $L^2$ . The pressure is therefore

$$\begin{aligned} p &= \frac{1}{L^2} \frac{mv_{1x}^2 + mv_{2x}^2 + \dots}{L} \\ &= \frac{m}{L^3} (v_{1x}^2 + v_{2x}^2 + \dots), \end{aligned} \quad (22-5)$$

where  $v_{1x}$  is the  $x$  component of the velocity of molecule 1,  $v_{2x}$  is that of molecule 2, and so on. If  $N$  is the total number of molecules in the container, then  $Nm$  is the total mass and  $Nm/L^3$  is the density  $\rho$ . Thus  $m/L^3 = \rho/N$ , and

$$p = \rho \left( \frac{v_{1x}^2 + v_{2x}^2 + \dots}{N} \right). \quad (22-6)$$

The quantity in parentheses in Eq. 22-6 is the average value of  $v_x^2$  for all the molecules in the container, which we represent by  $(v_x^2)_{\text{av}}$ . Then

$$p = \rho(v_x^2)_{\text{av}}. \quad (22-7)$$

For any molecule,  $v^2 = v_x^2 + v_y^2 + v_z^2$ . Because we have many molecules and because they are moving entirely at random, the average values of  $v_x^2$ ,  $v_y^2$ , and  $v_z^2$  are equal, and the value of each is exactly one-third the average value of

$v^2$ . There is no preference among the molecules for motion along any one of the three axes. Hence  $(v_x^2)_{av} = \frac{1}{3}(v^2)_{av}$ , so that Eq. 22-7 becomes

$$p = \frac{1}{3}\rho(v^2)_{av}. \quad (22-8)$$

Although we derived this result by neglecting collisions between molecules, the result is true even when we consider collisions. Because of the exchange of velocities in an elastic collision between identical particles, there will always be a molecule that collides with  $A_2$  with momentum  $mv_x$  corresponding to the molecule that left  $A_1$  with this same momentum. Also, the time spent during collisions is negligible compared to the time spent between collisions. Hence our neglect of collisions is merely a convenient device for calculation. Similarly, we could have chosen a container of any shape: the cube merely simplifies the calculation. Although we have calculated the pressure exerted only on the side  $A_1$ , it follows from Pascal's law that the pressure is the same on all sides and everywhere in the interior. (This is true only if the density of the gas is uniform. In a large sample of gas, gravitational effects might be significant, and we should take into account the varying density. See Section 15-3 and Problem 19 of Chapter 21.)

The square root of  $(v^2)_{av}$  is called the *root-mean-square* speed of the molecules and is a useful measure of average molecular speed. Using Eq. 22-8, we can calculate the root-mean-square speed from measured values of the pressure and density of the gas. Thus

$$v_{rms} \equiv \sqrt{(v^2)_{av}} = \sqrt{\frac{3p}{\rho}}. \quad (22-9)$$

In Eq. 22-8 we relate a macroscopic quantity (the pressure  $p$ ) to an average value of a microscopic quantity, that is, to  $(v^2)_{av}$  or  $v_{rms}^2$ .

**SAMPLE PROBLEM 22-1.** Calculate the root-mean-square speed of hydrogen molecules at 0.00°C and 1.00 atm pressure, assuming hydrogen to be an ideal gas. Under these conditions hydrogen has a density  $\rho$  of  $8.99 \times 10^{-2}$  kg/m<sup>3</sup>.

**Solution** Since  $p = 1.00 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$ ,

$$v_{rms} = \sqrt{\frac{3p}{\rho}} = \sqrt{\frac{3(1.01 \times 10^5 \text{ Pa})}{8.99 \times 10^{-2} \text{ kg/m}^3}} = 1840 \text{ m/s.}$$

This is equal to 4120 mi/h, or just slightly more than a mile per second.

Table 22-1 gives the results of similar calculations for some selected gases at room temperature. The values of  $v_{rms}$  in that table refer to the speeds of the molecules between collisions. Because of these collisions, gas molecules are continuously changing direction and do not move very rapidly in any selected direction. This contrast between intercollision speeds and outward diffusion speeds is sometimes said to account for the noticeable time lag between

**TABLE 22-1** Some Molecular Speeds at Room Temperature (300 K)

Gas	Molecular Mass $m$ (u)	$v_{rms}$ (m/s)
Hydrogen	2.0	1920
Helium	4.0	1370
Water vapor	18.0	645
Nitrogen	28.0	517
Oxygen	32.0	483
Carbon dioxide	44.0	412
Sulfur dioxide	64.1	342

opening a perfume bottle at one end of a room and smelling perfume at the other end. However, the fact that one smells perfume at all can be shown to be due to unavoidable convection currents in the air of the room. If these currents could be eliminated, the time lag would be very much greater indeed. The diffusion speed of one gas into another is very much less than the rms speed of the diffusing molecules.

**SAMPLE PROBLEM 22-2.** The cubical box of Fig. 22-2 is 10 cm on edge and contains oxygen at a pressure of 1.0 atm and a temperature  $T = 300 \text{ K}$ . (a) How many moles of oxygen are in the box? (b) How many molecules? (c) At what approximate rate do oxygen molecules strike one face of the box? (Hint: For simplicity, assume that the molecules all move with the same speed  $v_{rms}$ , that they do not collide with each other, and that one-third of them move back and forth between each pair of opposing faces of the cube.)

**Solution** (a) Solving the ideal gas equation (Eq. 21-17) for  $n$ , the number of moles, we obtain

$$n = \frac{pV}{RT} = \frac{(1.01 \times 10^5 \text{ Pa})(0.10 \text{ m}^3)}{(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})} = 0.041 \text{ mol.}$$

Here we have replaced  $V$  by  $L^3$  and used the fact that, in SI units, 1 atm =  $1.01 \times 10^5$  Pa.

(b) The number of molecules follows from Eq. 21-15:

$$N = nN_A = (0.041 \text{ mol})(6.02 \times 10^{23} \text{ molecules/mol}) = 2.5 \times 10^{22} \text{ molecules.}$$

(c) Consider the back-and-forth motion of a single molecule. Its average time between collisions on a particular face is  $2L/v_{rms}$  and the rate at which it strikes that face is the inverse of this, or  $v_{rms}/2L$ . If the box contains  $N$  molecules, on our assumption  $\frac{1}{3}N$  of them are doing the same thing. So the total rate at which molecules hit the face in question is  $(\frac{1}{3}N)(v_{rms}/2L)$ . From Table 22-1 we see that  $v_{rms}$  for oxygen at 300 K is 483 m/s. Thus

$$\begin{aligned} \text{Rate} &\approx \frac{Nv_{rms}}{6L} = \frac{(2.5 \times 10^{22} \text{ molecules})(483 \text{ m/s})}{(6)(0.1 \text{ m})} \\ &= 2.0 \times 10^{25} \text{ collisions/s.} \end{aligned}$$

A more rigorous analysis, taking into account the varying speeds and directions of the molecules, yields  $2.8 \times 10^{25}$  collisions/s. Thus our approximate answer is not too far removed from the correct answer. In solving problems in physics, we often make

grossly simplifying assumptions if we seek only an approximate answer.

**SAMPLE PROBLEM 22-3.** Natural uranium consists primarily of two isotopes, fissionable  $^{235}\text{U}$  (0.7% abundance) and practically nonfissionable  $^{238}\text{U}$  (99.3%). (a) In  $\text{UF}_6$  (uranium hexafluoride) gas containing a natural mixture of these two isotopes at a common temperature  $T$ , calculate the ratio of the rms speed of the gas molecules containing  $^{235}\text{U}$  to those containing  $^{238}\text{U}$ . (b) If this gas is passed through a porous barrier, the faster molecules emerge first, and the resulting abundances of the two kinds of gas molecules on the far side of the barrier are proportional to their rms speeds. What will be the relative abundance of gas molecules containing  $^{235}\text{U}$  after the passage of the gas through such a barrier? (c) How many times must the gas be passed through such a barrier before the abundance of  $^{235}\text{U}$  reaches 3%? This abundance is typical of the enrichment of  $^{235}\text{U}$  needed for the uranium fuel in fission reactors.

**Solution** (a) Consider two samples of  $\text{UF}_6$  gas, identical except that one contains only  $^{235}\text{U}$  and the other only  $^{238}\text{U}$ . The molecular masses of  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$  are  $m(235) = 235 \text{ u} + 6(19 \text{ u}) = 349 \text{ u}$  and  $m(238) = 238 \text{ u} + 6(19 \text{ u}) = 352 \text{ u}$ . The ratio of densities—all other factors being equal—is the ratio of the molecular masses so, from Eq. 22-9,

$$\frac{v_{\text{rms}}(235)}{v_{\text{rms}}(238)} = \sqrt{\frac{m(238)}{m(235)}} = \sqrt{\frac{352 \text{ u}}{349 \text{ u}}} = 1.0043.$$

(b) The relative abundance of the two kinds of gas molecules in the mixed gas sample is the same as the relative abundance of the uranium isotopes they contain. On entering the barrier this ratio is  $0.007/0.993 = 0.00705$ . On our assumption, passage through the barrier increases this ratio by the factor calculated in (a), so

$$\text{ratio after 1 pass} = 0.00705 \times 1.0043 = 0.00707.$$

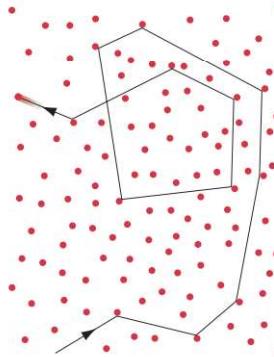
(c) The gas entering the first barrier has an isotope ratio, calculated in (b), of 0.00705. After passage through a barrier  $n$  times, we wish the isotope ratio of the emerging gas to be  $0.030/0.97 = 0.03093$ . There is an increase in this ratio of 1.0043 at each passage, so

$$(1.0043)^n (0.00705) = 0.03093.$$

If we solve this relationship for  $n$  (by taking logarithms) we find  $n \approx 350$ .

## 22-3 THE MEAN FREE PATH

Suppose that we could follow the zigzag path (Fig. 22-3) of a typical molecule in a gas as it moves around, colliding with other molecules. In particular, let us measure the straight-line distance our chosen molecule travels between collisions and find its average value. We call this quantity the molecule's *mean free path*  $\lambda$ . Because our chosen molecule is not "special," all molecules of the gas have the same mean free path. Of course, we cannot follow a single molecule and make these measurements, but in this section we will calculate the outcome of such measurements.



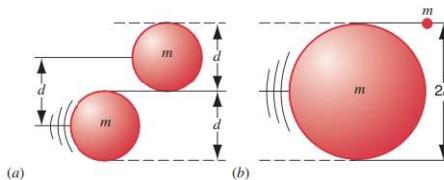
**FIGURE 22-3.** A molecule traveling through a gas, colliding with other molecules in its path. Of course, the other molecules are themselves moving and experiencing collisions.

Consider the molecules of a gas to be spheres of diameter  $d$ . A collision will take place when the centers of two such molecules approach within a distance  $d$  of each other. An equivalent description of collisions made by any chosen molecule is to regard that molecule as having a diameter  $2d$  and all other molecules as point particles; see Fig. 22-4.

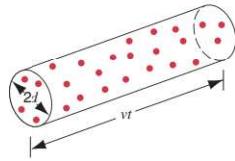
Let us temporarily assume that our molecule of diameter  $2d$  exerts no forces on the point molecules among which it moves. In time  $t$  our "fat" molecule would sweep out a cylinder of cross-sectional area  $\pi d^2$ , length  $L_{\text{cyl}} = vt$  (where  $v$  is the speed of the molecule), and volume  $V_{\text{cyl}} = \text{area} \times \text{length} = (\pi d^2)(vt)$ . Let the volume of the box within which the gas is confined be  $V$  and let the box contain  $N$  molecules. The number of (point) molecules in the cylinder of Fig. 22-5 is then

$$N_{\text{cyl}} = N \frac{V_{\text{cyl}}}{V} = \frac{N\pi d^2 vt}{V}. \quad (22-10)$$

Since our moving molecule and the point molecules *do* exert forces on each other, this number is also the number of collisions experienced by our moving molecule in time  $t$ .



**FIGURE 22-4.** (a) A collision occurs when the centers of two molecules come within a distance  $d$  of each other, where  $d$  is the molecular diameter. (b) An equivalent but more convenient representation is to think of the moving molecule as having a diameter  $2d$ , all other molecules being points.



**FIGURE 22-5.** A molecule with an equivalent diameter  $2d$  (as in Fig. 22-4b) traveling with speed  $v$  sweeps out a cylinder of base area  $\pi d^2$  and length  $vt$  in a time  $t$ . The number of collisions suffered by the molecule in this time is equal to the number of molecules (regarded as points) that lie within the cylinder. In actuality, this cylinder would be bent many times as the direction of the molecule's path is changed by collisions; for convenience that path has been straightened.

The cylinder of Fig. 22-5 is, in fact, a broken one, changing direction with every collision.

The mean free path  $\lambda$  is the total distance covered by the moving molecule in time  $t$  divided by the number of collisions that it makes in that time, or

$$\lambda = \frac{L_{\text{cyl}}}{N_{\text{cyl}}} = \frac{vtV}{N\pi d^2 vt} = \frac{V}{N\pi d^2}. \quad (22-11)$$

As Eq. 21-13 shows, we can write the ideal gas law in the form  $pV = NkT$ , in which  $k$  is the Boltzmann constant. From this equation,  $V/N = kT/p$  and Eq. 22-11 becomes

$$\lambda = \frac{kT}{\pi d^2 p}. \quad (22-12)$$

Equation 22-12 is based on the assumption of a single moving molecule hitting stationary targets. Actually, the molecule that we are following hits moving targets. When all molecules are moving, the two  $v$ 's in Eq. 22-11 are not the same and thus do not cancel. The  $v$  in the numerator ( $= v_{\text{av}}$ ) is the average molecular speed measured with respect to the box in which the gas is contained. The  $v$  in the denominator ( $= v_{\text{rel}}$ ) is the average relative speed with respect to the other molecules. It is this relative speed that determines the collision rate.

We can see qualitatively that  $v_{\text{rel}} > v_{\text{av}}$  as follows. Two molecules of speed  $v$  moving toward each other have  $v_{\text{rel}} = 2v$ , which is greater than  $v$ . You can easily show that two molecules moving at right angles to each other have  $v_{\text{rel}} = \sqrt{2}v$ , which is also greater than  $v$ . Two molecules moving with speed  $v$  in the same direction have  $v_{\text{rel}} = 0$ , which, of course, is less than  $v$ . If the angle between the velocities of the colliding molecules (assuming them to have the same speed) is between  $0^\circ$  and  $60^\circ$ , then  $0 \leq v_{\text{rel}} \leq v$ . If the angle is between  $60^\circ$  and  $180^\circ$  (the latter corresponding to a head-on collision), then  $v \leq v_{\text{rel}} \leq 2v$ . Because the collisions are random, there is a greater probability that the collision angle will be in the range of  $60^\circ$  to  $180^\circ$  than in the range of  $0^\circ$  to  $60^\circ$ . Thus the relative speed will on the average be greater than  $v$ .

A similar conclusion holds on the average if the molecules have a distribution of different speeds. A full calculation, taking into account the actual speed distribution of the molecules, gives  $v_{\text{rel}} = \sqrt{2} v_{\text{av}}$ . As a result, Eq. 22-12 becomes

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 p} \quad (\text{mean free path}). \quad (22-13)$$

This equation relates two microscopic quantities ( $\lambda$  and  $d$ ) to two macroscopic quantities ( $p$  and  $T$ ).

For air molecules at sea level,  $\lambda \approx 10^{-7}$  m or  $0.1 \mu\text{m}$ . At an altitude of 100 km, the density of air has dropped to such an extent that  $\lambda \approx 16$  cm. At 300 km,  $\lambda \approx 20$  km. In much scientific and industrial work it is necessary to pump the air out of a sealed container, producing a vacuum. Once the pressure has been reduced to the extent that the mean free path calculated from Eq. 22-13 exceeds the dimensions of the container, the concept of mean free path loses its significance; at that stage molecules collide more often with the container walls than with each other.

The ability of gases to conduct heat, the viscosity of gases, and the rate at which gases diffuse from regions of high concentration to regions of lower concentration are matters of considerable interest, both in science and in industry. All are proportional to the mean free path of the gas molecules. Designers of high-energy particle accelerators, such as those at CERN and Fermilab, go to great lengths to remove as much air as possible from the huge circular rings around which the accelerating particles must circulate thousands of times without colliding with a residual air molecule.

**SAMPLE PROBLEM 22-4.** What are (a) the mean free path and (b) the average collision rate for nitrogen at room temperature ( $T = 300$  K) and atmospheric pressure ( $p = 1.01 \times 10^5$  Pa)? A nitrogen molecule has an effective diameter of  $d = 3.15 \times 10^{-10}$  m and, for the conditions stated, an average speed  $v_{\text{av}} = 478$  m/s.

**Solution** (a) From Eq. 22-13,

$$\begin{aligned} \lambda &= \frac{kT}{\sqrt{2}\pi d^2 p} = \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{(\sqrt{2}\pi)(3.15 \times 10^{-10} \text{ m})^2(1.01 \times 10^5 \text{ Pa})} \\ &= 9.3 \times 10^{-8} \text{ m.} \end{aligned}$$

This is about 300 molecular diameters. On average, the distance between molecules in a gas is equal to the cube root of the volume occupied by a single molecule or  $(V/N)^{1/3}$ . From Eq. 21-13 ( $pV = NkT$ ), we can write this as  $(kT/p)^{1/3}$ , which proves to be about  $3.4 \times 10^{-9}$  m. This is about 11 molecular diameters. In one mean free path  $\lambda$  a given molecule will pass about 27 other molecules before experiencing a collision.

(b) The average collision rate is the average speed divided by the mean free path, or

$$\begin{aligned} \text{rate} &= \frac{v_{\text{av}}}{\lambda} = \frac{478 \text{ m/s}}{9.3 \times 10^{-8} \text{ m/collision}} \\ &= 5.1 \times 10^9 \text{ collisions/second} \end{aligned}$$