

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 Δt . 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 Δt 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 Δx and Δy , which are, respectively, the changes in the x and the y coordinates of the particle between successive observations. Because Δx and Δy 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, $[(\Delta x)^2]_{\text{av}}$ and $[(\Delta y)^2]_{\text{av}}$, which are inherently positive.

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

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

Here η (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

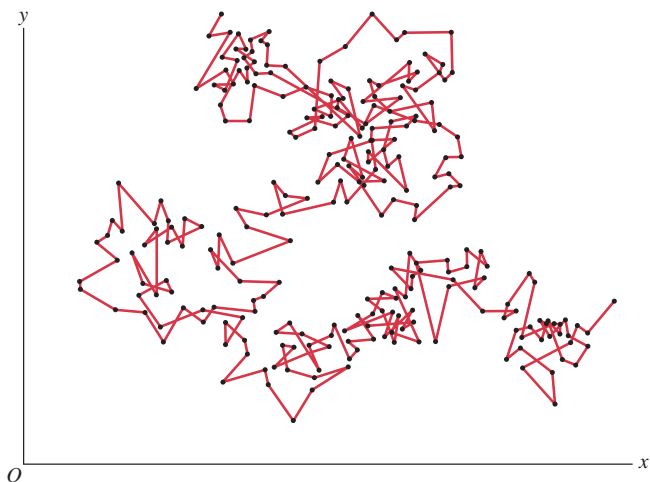


FIGURE 22-1. The Brownian motion of a tiny particle of gum resin of radius about $3\mu\text{m}$. The dots, which are connected by straight lines, mark the positions of the particle at 30-s intervals. The path of the particles is an example of a *fractal*, a curve for which any small section resembles 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 $[(\Delta x)^2]_{\text{av}}$ 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 (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 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 $+2mv_x$.

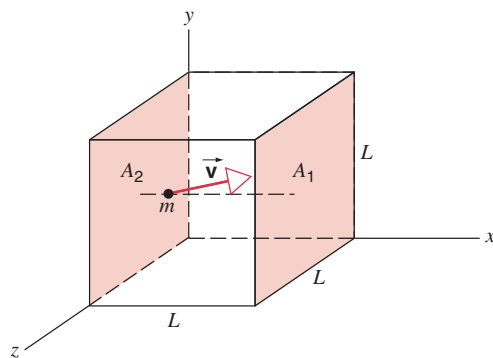


FIGURE 22-2. A cubical box of edge L containing an ideal gas. A molecule of the gas is shown moving with velocity \vec{v} toward side A_1 .

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

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

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 ρ . Thus $m/L^3 = \rho/N$, and

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

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 $(v_x^2)_{\text{av}} = \frac{1}{3}(v^2)_{\text{av}}$, so that Eq. 22-7 becomes

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

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 $(v^2)_{\text{av}}$ 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

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

In Eq. 22-8 we relate a macroscopic quantity (the pressure p) to an average value of a microscopic quantity, that is, to $(v^2)_{\text{av}}$ 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 ρ of $8.99 \times 10^{-2} \text{ kg/m}^3$.

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

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

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, $1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$.

(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 $2L/v_{\text{rms}}$ and the rate at which it strikes that face is the inverse of this, or $v_{\text{rms}}/2L$. 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 $(\frac{1}{3}N)(v_{\text{rms}}/2L)$. From Table 22-1 we see that v_{rms} for oxygen at 300 K is 483 m/s. Thus

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

A more rigorous analysis, taking into account the varying speeds and directions of the molecules, yields 2.8×10^{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}U (0.7% abundance) and practically nonfissionable ^{238}U (99.3%). (a) In 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}U to those containing ^{238}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}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}U reaches 3%? This abundance is typical of the enrichment of ^{235}U needed for the uranium fuel in fission reactors.

Solution (a) Consider two samples of UF_6 gas, identical except that one contains only ^{235}U and the other only ^{238}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

$$\text{ratio after 1 pass} = 0.00705 \times 1.0043 = 0.00708.$$

(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* λ . 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.

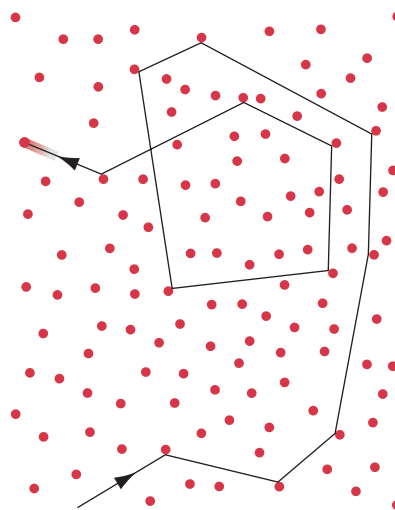


FIGURE 22-3. A molecule traveling through a gas, colliding with other molecules in its path. Of course, the other molecules are themselves moving and experiencing collisions.

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 πd^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 .

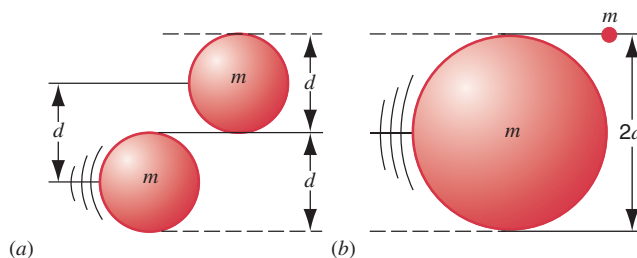


FIGURE 22-4. (a) A collision occurs when the centers of two molecules come within a distance d of each other, where d is the molecular diameter. (b) An equivalent but more convenient representation is to think of the moving molecule as having a diameter $2d$, all other molecules being points.

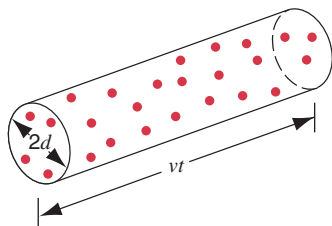


FIGURE 22-5. A molecule with an equivalent diameter $2d$ (as in Fig. 22-4b) traveling with speed v sweeps out a cylinder of base area πd^2 and length vt in a time t . The number of collisions suffered by the molecule in this time is equal to the number of molecules (regarded as points) that lie within 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 λ 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° and 60° , then $0 \leq v_{\text{rel}} \leq v$. If the angle is between 60° and 180° (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° to 180° than in the range of 0° to 60° . 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 (λ 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 3.4×10^{-9} m. This is about 11 molecular diameters. In one mean free path λ 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

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

On average, every nitrogen molecule makes more than 5 billion collisions per second!

22-4 THE DISTRIBUTION OF MOLECULAR SPEEDS

We can calculate v_{rms} , the root-mean-square speed of the molecules of an ideal gas, using Eq. 22-9. However, suppose we want to know how the speeds of the molecules are distributed about this average. It is not likely that the molecules would all have this same speed, because collisions between molecules would soon upset this situation. Speeds either close to zero or very much greater than v_{rms} are also relatively unlikely; such speeds would require a sequence of preferential collisions that would be very improbable in a condition of thermal equilibrium.

The Scottish physicist James Clerk Maxwell (1831–1879) first solved the problem of the distribution of speeds in a gas containing a large number of molecules. The *Maxwell speed distribution*—as it is called—for a sample of gas at temperature T containing N molecules, each of mass m , is

$$N(v) = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}. \quad (22-14)$$

Figure 22-6 shows a plot of this equation for molecules of oxygen at room temperature.

The interpretation of $N(v)$ in Eq. 22-14 is that the (dimensionless) product $N(v) dv$ gives the number of molecules having speeds in the range v to $v + dv$. Graphically, this product for $v = 600$ m/s is represented in Fig. 22-6 as the shaded area of the narrow vertical strip located at that speed.

Avoid the temptation to interpret $N(v)$ as “the number of molecules having a speed v .” This interpretation is meaningless because, although the number of molecules may be

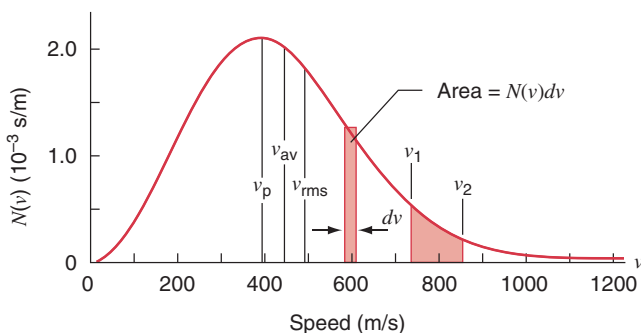


FIGURE 22-6. The Maxwell speed distribution for the molecules of a gas. The plotted curve is characteristic of oxygen molecules at $T = 300$ K. The number of molecules with speeds in any interval dv is $N(v)dv$, indicated by the narrow shaded strip. The number with speeds between any limits v_1 and v_2 is given by the area under the curve between those limits.

large, it cannot be infinite but the number of available speeds is infinite; they cannot be matched up on a one-to-one basis. The probability that a molecule has a precisely stated speed, such as 600.34326759 . . . m/s, is exactly zero. However, the number of molecules whose speeds lie in a narrow range such as 600 m/s to 602 m/s has a definite nonzero value.

If we add up (integrate) the numbers of molecules in each differential speed range dv from $v = 0$ to $v \rightarrow \infty$, we must obtain N , the total number in the system. That is, it must be true that

$$N = \int_0^{\infty} N(v) dv. \quad (22-15)$$

Note that the integral in Eq. 22-15 can be interpreted as the total area under the speed distribution curve of Fig. 22-6. The number of molecules whose speeds lie between any given values, such as v_1 and v_2 , is equal to the area under the speed distribution curve between those limits.

As the temperature increases, the average speed of the molecules increases, so the speed distribution curve must become broader. Because the area under the distribution curve (which is the total number of molecules) remains the same, the distribution curve must also flatten as the temperature rises. Figure 22-7 shows how the speed distribution curve for oxygen molecules at $T = 80$ K is both broadened and flattened as the temperature is increased to 300 K.

The distribution of speeds of molecules in a liquid resembles that of Fig. 22-6. This distribution allows us to understand why water in a saucer will eventually evaporate completely. The speed needed for a molecule of water to

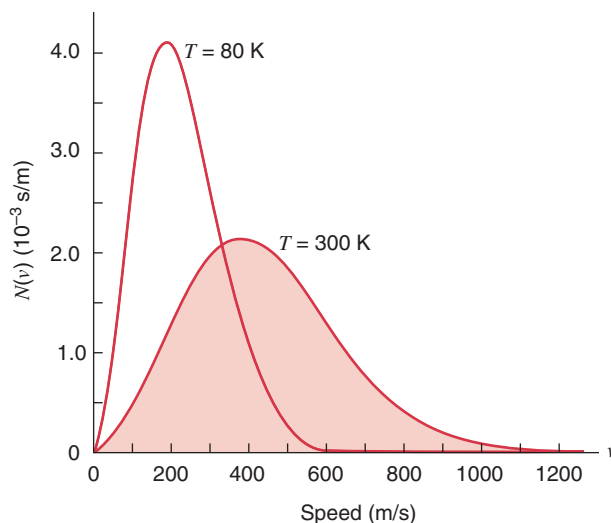


FIGURE 22-7. A comparison of the Maxwell speed distribution for oxygen molecules at two different temperatures. The molecules in general have lower average speeds at the lower temperatures, although both distributions cover the entire range of speeds. The areas of the two distributions are equal, because the total number of molecules is the same in both cases.

escape from the water surface would be very far out indeed on the tail of a distribution curve like that of Fig. 22-6. Only a very small number of molecules would have speeds above this threshold. The escape of these few energetic molecules reduces the average kinetic energy of the remaining molecules, leaving the water at a lower temperature. This explains why evaporation is a cooling process. If the saucer is not thermally isolated from its surroundings, however, energy will flow into the water from these surroundings, maintaining the water in thermal equilibrium with its environment. Energy will flow into the water as heat to compensate for the energy carried away by the escaping “fast” molecules; this process will continue until there is no more water.

Equation 22-14 also shows that the distribution of molecular speeds depends on the mass of the molecule as well as on the temperature. At any given temperature, the smaller the mass of a molecule, the faster it moves. Thus hydrogen is more likely to escape from the Earth’s upper atmosphere than oxygen or nitrogen.

Consequences of the Speed Distribution

We can obtain much useful information from Eq. 22-14, the speed distribution equation.

1. The most probable speed v_p . This quantity is the speed at which $N(v)$ of Eq. 22-14 has its maximum value. We find it by requiring that $dN/dv = 0$ and solving for v . As you should verify, the result proves to be

$$v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}. \quad (22-16)$$

Here we have made the substitutions $k = R/N_A$ (see Eq. 21-17) and $m = M/N_A$ (see Eq. 22-2).

2. The average speed v_{av} . To find the average speed of the molecules, we add up all the individual speeds and divide by the number of molecules. This is most simply done by summing the products of the speed v in each speed interval and the number $N(v) dv$ in that interval. Thus

$$v_{av} = \frac{1}{N} \int_0^{\infty} vN(v) dv. \quad (22-17)$$

The next step is to substitute for $N(v)$ from Eq. 22-14 and evaluate the integral. The result is

$$v_{av} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}. \quad (22-18)$$

3. The root-mean square speed v_{rms} . We encountered this quantity earlier, in Eq. 22-9. To find it from the speed distribution equation we proceed as above except that we find the average value of v^2 (rather than the average value of v). This leads, after another integration, to

$$(v^2)_{av} = \frac{1}{N} \int_0^{\infty} v^2 N(v) dv = \frac{3kT}{m}. \quad (22-19)$$

The root-mean-square speed is the square root of this quantity, or

$$v_{rms} = \sqrt{(v^2)_{av}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}. \quad (22-20)$$

4. The average translational kinetic energy per molecule K_{trans} . Note first that, because we assume that our ideal gas is monatomic, translational kinetic energy is the only kind of energy that the molecules can have. An essentially point molecule cannot have energy of rotation, and we assume that there are no changes in the internal energies of the molecules.

To find K_{trans} , we must first find the total translational kinetic energy of the set of N molecules and then divide by N . The total energy K is

$$\begin{aligned} K &= \frac{1}{2}m(v_1^2 + v_2^2 + \cdots + v_N^2) \\ &= \frac{1}{2}mN \frac{(v_1^2 + v_2^2 + \cdots + v_N^2)}{N} \\ &= \frac{1}{2}mNv_{rms}^2. \end{aligned}$$

Replacing v_{rms}^2 from Eq. 22-20 and dividing by N , the total number of molecules, leads to

$$K_{trans} = \frac{3}{2}kT. \quad (22-21)$$

We will have more to say about this important relation in Chapter 23.

5. The ideal gas law. We have derived two equations for v_{rms} , the root-mean-square velocity of the molecules, Eq. 22-9 and Eq. 22-20. Setting these equations equal yields

$$v_{rms}^2 = \frac{3p}{\rho} = \frac{3RT}{M}.$$

The density ρ can be written as nM/V . With this substitution the above equality reduces to $pV = nRT$. Thus we have recovered the ideal gas law from our investigation into the molecular speeds.

Experimental Verification of the Maxwell Speed Distribution

Maxwell derived his speed distribution law (Eq. 22-14) in 1860. At that early date it was not possible to check this law by direct measurement and it was not until about 1920 that the first attempts were made. However, techniques improved rapidly and, in 1955, R. C. Miller and P. Kusch of Columbia University provided a high-precision experimental verification of Maxwell’s prediction.

Their apparatus is illustrated in Fig. 22-8. The walls of oven O , containing some thallium metal, were heated, in one set of experiments, to a uniform temperature of 870 ± 4 K. At this temperature thallium vapor, at a pressure of 3.2×10^{-3} torr, fills the oven. Some molecules of thallium vapor escape from slit S into the highly evacuated space outside the oven, falling on the rotating cylinder R .

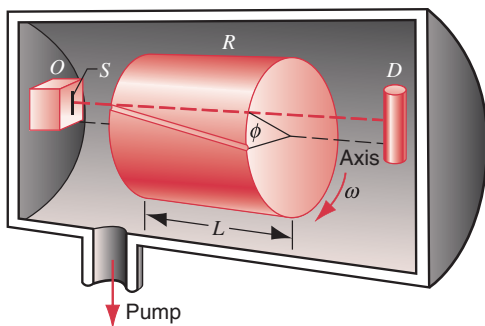


FIGURE 22-8. Apparatus used by Miller and Kusch to verify the Maxwell speed distribution. A beam of thallium molecules leaves the oven O through the slit S , travels through the helical groove in the rotating cylinder R , and strikes the detector D . The angular velocity ω of the cylinder can be varied so that molecules of differing speeds will pass through the cylinder.

This cylinder, of length L , has about 700 helical grooves cut into it, only one of which is shown in Fig. 22-8. For a given angular speed ω of the cylinder, only molecules of a sharply defined speed v can pass along the grooves without striking the walls. The speed v can be found from

$$\text{time of travel along the groove} = \frac{L}{v} = \frac{\phi}{\omega}$$

or

$$v = \frac{L\omega}{\phi},$$

in which ϕ (see Fig. 22-8) is the angular displacement between the entrance and the exit of a helical groove. Thus the rotating cylinder is a *velocity selector*, in which the speed is selected by the (controllable) angular speed ω . The beam intensity is recorded by detector D as a function of the selected speed v . Figure 22-9 shows the remarkable agreement between theory (the solid line) and experiment (the open and filled circles) for thallium vapor.

The distribution of speeds in the *beam* (as distinguished from the distribution of speeds in the *oven*) is not proportional to $v^2 e^{-mv^2/2kT}$, as in Eq. 22-14, but to $v^3 e^{-mv^2/2kT}$. Consider a group of molecules in the oven whose speeds lie within a certain small range v_1 to $v_1 + \delta v$, where v_1 is less than the most probable speed v_p . We can always find another equal speed interval δv , extending from v_2 to $v_2 + \delta v$, where v_2 , which will be greater than v_p , is chosen so that the two speed intervals contain the same number of molecules. However, more molecules in the higher interval than in the lower will escape from slit S to form the beam, because molecules in the higher interval “bombard” the slit with a greater frequency, by precisely the factor v_2/v_1 . Thus, other things being equal, fast molecules are favored in escaping from the oven, just in proportion to their speeds, and the molecules in the beam have a v^3 rather than a v^2 distribution. This effect is included in the theoretical curve of Fig. 22-9.

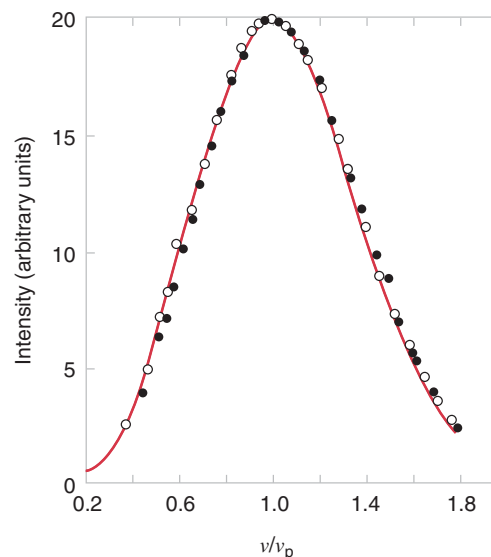


FIGURE 22-9. The results of the experiment to verify the Maxwell speed distribution. The open circles show data taken with the oven temperature at $T = 870$ K, and the filled circles show data at $T = 944$ K. When the distributions are plotted against v/v_p , the two distributions should be identical. The solid curve is the Maxwell distribution. The data agree remarkably well with the curve.

SAMPLE PROBLEM 22-5. The speeds of ten particles in m/s are 0, 1.0, 2.0, 3.0, 3.0, 3.0, 4.0, 4.0, 5.0, and 6.0. Find (a) the average speed, (b) the root-mean-square speed, and (c) the most probable speed of these particles.

Solution (a) The average speed is found from

$$\begin{aligned} v_{\text{av}} &= \frac{1}{N} \sum_{n=1}^N v_n = \frac{1}{10} [0 + 1.0 + 2.0 + 3.0 + 3.0 \\ &\quad + 3.0 + 4.0 + 4.0 + 5.0 + 6.0] \\ &= 3.1 \text{ m/s.} \end{aligned}$$

(b) The mean-square speed is the average value of v^2 :

$$\begin{aligned} (v^2)_{\text{av}} &= \frac{1}{N} \sum_{n=1}^N v_n^2 = \frac{1}{10} [0 + (1.0)^2 + (2.0)^2 + (3.0)^2 + (3.0)^2 \\ &\quad + (3.0)^2 + (4.0)^2 + (4.0)^2 + (5.0)^2 + (6.0)^2] \\ &= 12.5 \text{ m}^2/\text{s}^2, \end{aligned}$$

and the root-mean-square speed is

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{av}}} = \sqrt{12.5 \text{ m}^2/\text{s}^2} = 3.5 \text{ m/s.}$$

(c) Of the ten particles, three have speeds of 3.0 m/s, two have speeds of 4.0 m/s, and each of the other five has a different speed. Hence the most probable speed v_p of a particle is

$$v_p = 3.0 \text{ m/s.}$$

SAMPLE PROBLEM 22-6. A container filled with N molecules of oxygen gas is maintained at 300 K. What fraction of the molecules has speeds in the range 599–601 m/s? The molar mass M of oxygen is 0.032 kg/mol.

Solution This speed interval δv ($= 2$ m/s) is so small that we can treat it as a differential dv . The number of molecules in this interval is $N(v)dv$, and the fraction in that interval is $f = N(v)dv/N$, where $N(v)$ is to be evaluated at $v = 600$ m/s, the midpoint of the range; see the narrow shaded strip in Fig. 22-6. Using Eq. 22-14 with the substitution $m/k = M/R$, we find the fraction

$$f = \frac{N(v) dv}{N} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT} dv.$$

Substituting the given numerical values yields

$$f = 2.6 \times 10^{-3} \text{ or } 0.26\%.$$

At room temperature, 0.26% of the oxygen molecules have speeds that lie in the narrow range between 599 and 601 m/s. If the shaded strip of Fig. 22-6 were drawn to the scale of this problem, it would be a very thin strip indeed.

SAMPLE PROBLEM 22-7. Calculate (a) the most probable speed, (b) the average speed, and (c) the rms speed for oxygen molecules at $T = 300$ K.

Solution (a) From Eq. 22-16 we have

$$v_p = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{(2)(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{0.032 \text{ kg/mol}}} = 395 \text{ m/s}.$$

(b) From Eq. 22-18 we have

$$v_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{(8)(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{(\pi)(0.032 \text{ kg/mol})}} = 445 \text{ m/s}.$$

(c) From Eq. 22-20 we have

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{(3)(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{0.032 \text{ kg/mol}}} = 483 \text{ m/s}.$$

From the equations we have used note that, for any gas at a given temperature,

$$v_p : v_{av} : v_{rms} = 1 : 1.128 : 1.225.$$

22-5 THE DISTRIBUTION OF MOLECULAR ENERGIES

An alternative description of the motion of molecules can be obtained if we look for the distribution in *energy* rather than in speed. That is, we seek the distribution $N(E)$, such that $N(E)dE$ gives the number of molecules with energies between E and $E + dE$.

This problem was first solved by Maxwell. We derive the result, called the *Maxwell–Boltzmann energy distribution*, in the special case that translational kinetic energy is the only form of energy that a molecule can have.

Let us consider again the situation of Sample Problem 22-6, in which we obtained the fraction of oxygen molecules having speeds between 599 and 601 m/s. We found that 0.26% of the molecules in a container at a temperature of 300 K have speeds in that range. An oxygen molecule with a speed of 599 m/s has a kinetic energy of $9.54 \times$

10^{-21} J, and one with a speed of 601 m/s has a kinetic energy of 9.60×10^{-21} J. What fraction of the oxygen molecules has kinetic energies in the range of 9.54×10^{-21} to 9.60×10^{-21} J?

A bit of thought should convince you that this fraction must also be 0.26%. It makes no difference whether we count the molecules by their speeds or by their kinetic energies; as long as we set the lower and upper limits of the interval to have corresponding speeds and kinetic energies, we count the same number of molecules between the limits. That is, the number with kinetic energies between E and $E + dE$ is the same as the number with speeds between v and $v + dv$. Mathematically, we express this conclusion as

$$N(E) dE = N(v) dv, \quad (22-22)$$

or

$$N(E) = N(v) \frac{dv}{dE}. \quad (22-23)$$

Since the energy is only kinetic, we must have $E = \frac{1}{2}mv^2$ or $v = \sqrt{2E/m}$, and thus

$$\frac{dv}{dE} = \sqrt{\frac{2}{m}} \left(\frac{1}{2} E^{-1/2} \right). \quad (22-24)$$

Substituting Eqs. 22-14 and 22-24 into Eq. 22-23, we obtain

$$N(E) = \frac{2N}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} E^{1/2} e^{-E/kT}. \quad (22-25)$$

Equation 22-25 is the *Maxwell–Boltzmann energy distribution*. In deriving this result, we have assumed that the gas molecules can have only translational kinetic energy. This distribution therefore applies only to a monatomic gas. In the case of gases with more complex molecules, other factors (such as rotational kinetic energy) will be present in Eq. 22-25. The factor $e^{-E/kT}$, however, is a general feature of the Maxwell–Boltzmann energy distribution that is present no matter what the form of the energy E . This factor which is generally known as the *Boltzmann factor*, is often taken as a rough estimate of the relative probability for a particle to have an energy E in a collection of particles characterized by a temperature T .

Using Eq. 22-25, we can calculate the fraction of the gas molecules having energies between E and $E + dE$, which is given by $N(E)dE/N$. As before, N is the total number of molecules, which is determined from

$$N = \int_0^{\infty} N(E) dE. \quad (22-26)$$

One interesting feature of the Maxwell–Boltzmann energy distribution is that it is precisely the same for any gas at a given temperature, no matter what the mass of the molecules (in contrast to the Maxwell speed distribution, Eq. 22-14, in which the mass appears explicitly). Even a “gas” of electrons, to the extent they can be treated as classical particles, has the same energy distribution as a gas of heavy

atoms. The effect of increasing the mass m by some factor is to reduce v^2 by the same factor, so that the product mv^2 , and thus the kinetic energy, remains the same.

For a simple application of the Boltzmann factor, consider a long, gas-filled vertical container with its bottom resting on the Earth's surface. We'll assume that the gas in the container is in thermal equilibrium at a uniform temperature T . A molecule at a height y above the bottom has energy $E_0 + mgy$, where E_0 is the energy of a similar molecule at the bottom of the container. Using the Boltzmann factor $e^{-E/kT}$, we can deduce that the number of molecules at height y is, compared with the number at $y = 0$,

$$\frac{N(y)}{N(0)} = \frac{e^{-(E_0 + mgy)/kT}}{e^{-E_0/kT}} \quad (22-27)$$

or

$$N(y) = N_0 e^{-mgy/kT} \quad (22-28)$$

where $N_0 = N(0)$. With $kT = pV/N$ from the ideal gas law, the factor m/kT in the exponent can be written as $mN/pV = \rho/p$, where ρ is the density of the gas. Because we have assumed the gas to be at a uniform temperature, we must have $\rho/p = \rho_0/p_0$, with ρ_0 and p_0 being the values of the density and pressure at the Earth's surface. Furthermore, because the number of molecules in a small volume element at any height is proportional to the density at that height, which is in turn proportional to the pressure, we can write Eq. 22-28 as

$$p(y) = p_0 e^{-mgy/kT} = p_0 e^{-gyp_0/p_0}. \quad (22-29)$$

Equation 22-29 is identical with Eq. 15-12 for the pressure in the atmosphere as a function of the height above the Earth's surface. We also derived Eq. 15-12 under the assumption of a uniform temperature for the atmosphere, and it is comforting that the dynamic approach used in Chapter 15 and the present statistical approach give the same result.

SAMPLE PROBLEM 22-8. Find (a) the average energy and (b) the most probable energy of a gas in thermal equilibrium at temperature T .

(a) The average energy E_{av} can be written, in analogy with Eq. 22-17, as

$$E_{\text{av}} = \frac{1}{N} \int_0^{\infty} E N(E) dE.$$

Substituting Eq. 22-25, we obtain

$$E_{\text{av}} = \frac{2}{\sqrt{\pi}(kT)^{3/2}} \int_0^{\infty} E^{3/2} e^{-E/kT} dE. \quad (22-30)$$

To evaluate this integral, make the substitution $x^2 = E/kT$ and convert it to a standard form for a definite integral given in Appendix I. The result, which you should verify, is

$$E_{\text{av}} = \frac{3}{2} kT \quad (22-31)$$

a result that agrees precisely with Eq. 22-21 for this case in which we have assumed kinetic energy to be the only type of energy that the gas molecules may have.

(b) To find the most probable energy, we take the derivative of Eq. 22-25, set the result equal to zero, and solve for the energy. The result, which you should derive, is

$$E_p = \frac{1}{2} kT.$$

Note that this is *not* equal to $\frac{1}{2}mv_p^2$, which gives an energy of kT . Can you explain why the energy corresponding to the most probable speed is not the most probable energy?

22-6 EQUATIONS OF STATE FOR REAL GASES

The equation of state for an ideal gas holds well enough for real gases at sufficiently low densities. However, it does not hold *exactly* for real gases at *any* density and departs more and more the greater the density. There is much interest in finding an equation of state that describes real gases over a range of densities. We discuss two of the many approaches.

The Virial Expansion

Our first approach to an equation of state for a real gas is to write

$$pV = nRT \left[1 + B_1 \frac{n}{V} + B_2 \left(\frac{n}{V} \right)^2 + \cdots \right], \quad (22-32)$$

in which B_1, B_2, \dots , called *virial coefficients*, are functions of temperature and grow successively smaller as the series progresses. It is clear that, at small molar densities ($n/V \rightarrow 0$), this equation of state reduces to the ideal gas law. This must be the case for all equations of state for gases because the ideal gas law holds in the limit of low densities. The virial coefficients must be found empirically, by fitting Eq. 22-32 to experimental data.

The van der Waals Equation of State

This equation, proposed in 1873 by the Dutch physicist Johannes Diderik van der Waals (1837–1923), is

$$\left(p + \frac{an^2}{V^2} \right) (V - nb) = nRT, \quad (22-33)$$

in which a and b are constants whose values must be obtained by experiment. Comparison of Eq. 22-33 with the ideal gas law ($pV = nRT$) suggests that van der Waals (who received the 1910 Nobel Prize for his work) arrived at his equation by correcting perceived points of failure in the ideal gas law. That is indeed the case. Note that if the constants a and b are put equal to zero (or if we allow the molar density n/V to become very small), Eq. 22-33 reduces to the ideal gas law. We now investigate the line of reasoning that led to the terms containing these constants.

The Volume Correction. In Section 22-1 we assumed (property 3) that the volume occupied by the molecules of an ideal gas is negligible. This is not quite true for real gases. Let us regard each molecule of a real gas as a hard sphere of diameter d . Two such molecules cannot approach each other so close that the distance between their centers would be less than d (Fig. 22-10). The “free volume” per mole available for one molecule is therefore decreased by the volume of a hemisphere of radius d centered on the other molecule. If we estimate d as 2.5×10^{-10} m (a typical molecular diameter), then we can find an approximate value of b of

$$b = \frac{1}{2}N_A\left(\frac{4}{3}\pi d^3\right) = 2 \times 10^{-5} \text{ m}^3/\text{mol}.$$

The factor of $\frac{1}{2}$ comes about because, as two molecules approach each other, the volume within which they interact is not a full sphere but the hemisphere facing the direction of approach. Under standard conditions of temperature and pressure the molar density n/V of an ideal gas is 45 mol/m^3 . Thus $bn/V \approx 0.0009$ or about 0.1%; under these conditions, the volume correction b is relatively small.

The Pressure Correction. In Section 22-1 (property 4) we assumed that the molecules of an ideal gas exert forces on each other only during collisions. That is also not quite true for real gases. A molecule in the body of the gas would experience no net force due to the forces exerted on it by the surrounding molecules; that is, these forces would balance out to zero. However, that is not true for a molecule located near the wall of the containing vessel, as in Fig. 22-11. Such a molecule would experience a net force of attraction away from the wall because of its interaction with the nearby molecules that are within the range of the attractive force that it exerts. Thus the pressure measured at the wall is somewhat less than what we may call the true pressure that exists in the body of the gas.

The reduction in pressure owing to the collisions of molecule C with the wall is proportional to the number of molecules in the hemisphere within the range R of its at-

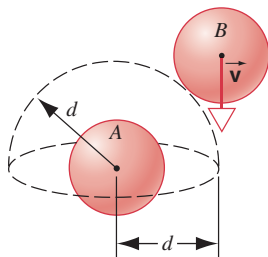


FIGURE 22-10. If molecules of a gas are considered to behave like hard spheres, then the center of molecule B is not permitted to move within the hemisphere of radius d centered on molecule A . Here d is the diameter of a molecule. The free volume available for molecule B is reduced by the volume of such a hemisphere centered on each molecule of the gas.

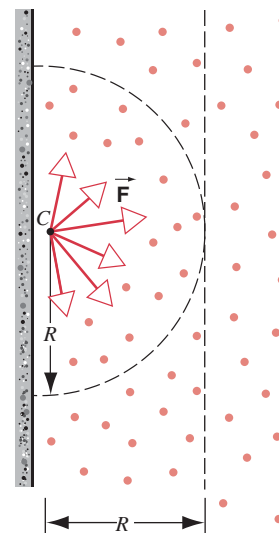


FIGURE 22-11. A gas molecule C (here considered to be a point) near the wall of the container experiences a net force away from the wall due to the attraction of the surrounding molecules within the range R of the force between molecules. The net pressure on the walls of the container is reduced by all such molecules within a distance R of the walls.

tractive force and thus to the number of molecules per unit volume or, alternatively, to n/V . The net effect due to *all* the molecules that strike the wall (C is a typical member of this group) is also proportional to the number of molecules per unit volume or to n/V . The total reduction in pressure is proportional to the product of these two quantities, or $(n/V)^2$.

That is, if we triple the number of molecules in a given container, molecule C will experience three times the unbalanced force. In the entire gas there will be three times as many molecules like C . The overall pressure reduction thus increases ninefold. If p in Eq. 22-33 is to be the measured pressure, we must increase it by a term proportional to $(n/V)^2$ —that is, by an^2/V^2 —to obtain the “true” pressure.

Figure 22-12 compares a pV plot of an ideal gas at various temperatures with a plot of Eq. 22-33 for carbon dioxide gas. Note that the deviation from ideal behavior occurs primarily at high pressures and low temperatures. For CO_2 at 264 K, the graph contains a region of positive slope, indicating that as we decrease the volume in this region the pressure also decreases. Since this behavior is contrary to expectations for a gas, it suggests that some of the CO_2 is condensing to a liquid, leaving less of it in the gaseous state. The van der Waals equation thus suggests the existence of mixtures of different phases, which the ideal gas model cannot do. If we were to compress a sample of CO_2 , we would find that the actual $T = 264$ K graph would not follow the curve shown in Fig. 22-12b, but instead would follow the dashed horizontal segment AB in that figure.

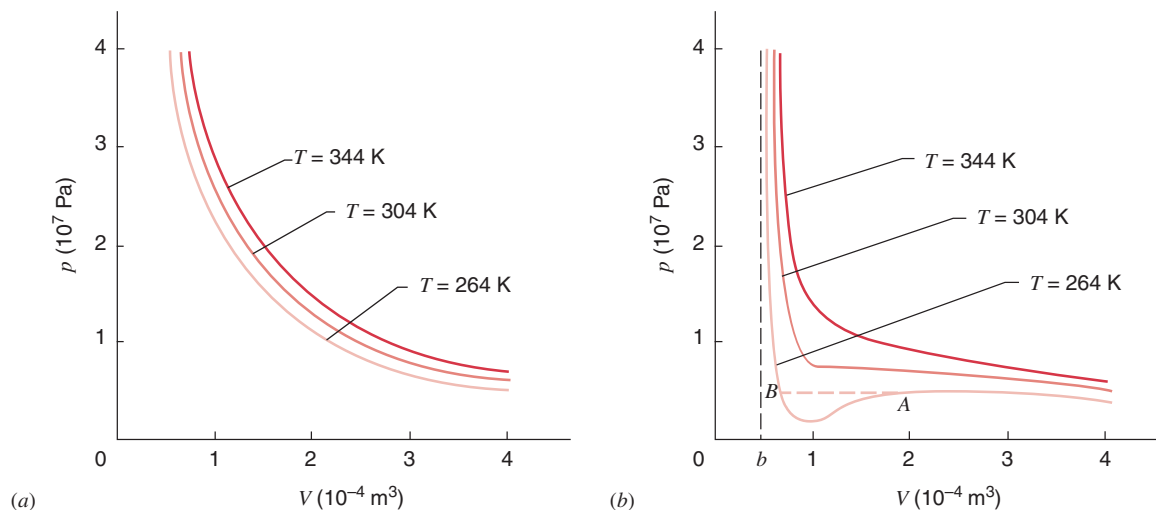


FIGURE 22-12. pV graphs for one mole of (a) an ideal gas and (b) CO_2 determined from the van der Waals equation. Note that at large volume, the ideal and van der Waals graphs behave similarly. As the temperature is raised, the van der Waals graphs behave more like those of the ideal gas. Note also that, as the pressure becomes very large, the volume approaches the value of b , as Eq. 22-33 requires, rather than the value of zero, as the ideal gas equation of state would predict. The dashed line AB shows a more realistic representation of the behavior at $T = 264$ K. As the gas is compressed from A , some of the gas condenses into a liquid, and the pressure remains constant.

SAMPLE PROBLEM 22-9. For oxygen the van der Waals coefficients have been measured to be $a = 0.138 \text{ J} \cdot \text{m}^3/\text{mol}^2$ and $b = 3.18 \times 10^{-5} \text{ m}^3/\text{mol}$. Assume that 1.00 mol of oxygen at $T = 50 \text{ K}$ is confined to a box of volume 0.0224 m^3 . What pressure does the gas exert according to (a) the ideal gas law and (b) the van der Waals equation?

Solution (a) The ideal gas law yields

$$p = \frac{nRT}{V} = \frac{(1.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(50 \text{ K})}{0.0224 \text{ m}^3} \\ = 1.85 \times 10^4 \text{ Pa} = 0.184 \text{ atm.}$$

(b) The pressure and the volume correction terms in the van der Waals equation (Eq. 22-33) are

$$\frac{an^2}{V^2} = \frac{(0.138 \text{ J} \cdot \text{m}^3/\text{mol}^2)(1.00 \text{ mol})^2}{(0.0224 \text{ m}^3)^2} = 275 \text{ Pa}$$

and

$$b = 3.18 \times 10^{-5} \text{ m}^3/\text{mol.}$$

Substituting these quantities into the van der Waals equation and solving that equation for p yields

$$p = 1.83 \times 10^4 \text{ Pa} = 0.181 \text{ atm.}$$

For oxygen under these conditions the ideal gas law and the van der Waals equation yield results that are within 2% of each other. Note that the pressure correction term is only $(275 \text{ Pa})/(1.83 \times 10^4 \text{ Pa})$ or about 1.5%. The volume correction bn/V is only $(3.18 \times 10^{-5} \text{ m}^3/\text{mol})(1.00 \text{ mol})/(0.0224 \text{ m}^3)$ or about 0.14%. For lower temperatures, as the gas moves in the direction of liquifaction, the van der Waals equation will better agree with experiment than will the ideal gas law.

22-7 THE INTERMOLECULAR FORCES (Optional)

Forces between molecules are of electromagnetic origin. All molecules contain electric charges in motion. These molecules are electrically neutral in the sense that the negative charge of the electrons is equal and opposite to the positive charge of the nuclei. This does not mean, however, that molecules do not interact electrically. For example, when two molecules approach each other, the charges on each are disturbed and depart slightly from their usual positions in such a way that the average distance between opposite charges in the two molecules is a little smaller than that between like charges. Hence an attractive intermolecular force results. This internal rearrangement takes place only when molecules are fairly close together, so that these forces act only over short distances; they are short-range forces. If the molecules come very close together, so that their outer charges begin to overlap, the intermolecular force becomes repulsive. The molecules repel each other because there is no way for a molecule to rearrange itself internally to prevent repulsion of the adjacent external electrons. It is this repulsion on contact that accounts for the billiard-ball character of molecular collisions in gases. If it were not for this repulsion, molecules would move right through each other instead of rebounding on collision.

Let us assume that molecules are approximately spherically symmetrical. Then we can describe intermolecular forces graphically by plotting the mutual potential energy of two molecules, U , as a function of distance r between their centers. The force F acting on each molecule is related to the potential energy U by $F = -dU/dr$. In Fig. 22-13a we

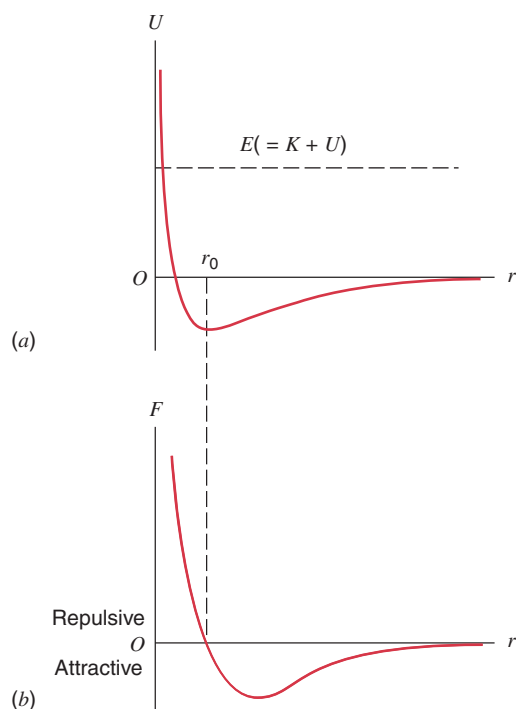


FIGURE 22-13. (a) The mutual potential energy U of two molecules as a function of their separation distance r . The mechanical energy E is indicated by the horizontal line. (b) The radial force between the molecules, given by $-dU/dr$, corresponding to this potential energy. The potential energy is a minimum at the equilibrium separation r_0 , at which point the force is zero.

plot a typical $U(r)$. Here we can imagine one molecule to be fixed at O . Then the other molecule is repelled from O when the slope of U is negative and is attracted to O when the slope is positive. At r_0 no force acts between the molecules; the slope is zero there. In Fig. 22-13b we plot the mutual force $F(r)$ corresponding to this potential energy function. The line E in Fig. 22-13a represents the mechanical energy of the colliding molecules. The intersection of $U(r)$ with this line is a “turning point” of the motion (see Section 12-5). The separation of the centers of two molecules at the turning point is the distance of closest approach. The separation distance at which the mutual potential energy is zero may be taken as the approximate distance of closest approach in a low-energy collision and hence as the diameter of the molecule. For simple molecules the diameter is about $2.5 \times$

10^{-10} m. The distance r_0 at which the potential is a minimum (the equilibrium point) is about 3.5×10^{-10} m for simple molecules, and the force and potential energy approach zero as r increases to about 10^{-9} m, or about 4 diameters. The molecular force thus has a very short range. Of course, different molecules have different sizes and internal arrangement of charges so that intermolecular forces vary from one molecule to another. However, they always show the qualitative behavior indicated in Fig. 22-13.

In a solid, molecules vibrate about the equilibrium position r_0 . Their total energy E is negative—that is, lying below the horizontal axis in Fig. 22-13a. The molecules do not have enough energy to escape from the potential valley (that is, from the attractive binding force). The centers of vibration O are more or less fixed in a solid. In a liquid the molecules have greater vibrational energy about centers that are free to move but that remain about the same distance from one another. Molecules have their greatest kinetic energy in the gaseous state. In a gas the average distance between the molecules is considerably greater than the effective range of intermolecular forces, and the molecules move in straight lines between collisions. Maxwell discusses the relation between the kinetic theory model of a gas and the intermolecular forces as follows: “Instead of saying that the particles are hard, spherical, and elastic, we may if we please say that the particles are centers of force, of which the action is insensible except at a certain small distance, when it suddenly appears as a repulsive force of very great intensity. It is evident that either assumption will lead to the same results.”

It is interesting to compare the measured intermolecular forces with the gravitational force of attraction between molecules. If we choose a separation distance of 4×10^{-10} m, for example, the force between two helium atoms is about 6×10^{-13} N. The gravitational force at that separation is about 7×10^{-42} N, smaller than the intermolecular force by a factor of 10^{29} ! This is a typical result and shows that gravitation is negligible in intermolecular forces.

Although the intermolecular forces appear to be small by ordinary standards, we must remember that the mass of a molecule is so small (about 10^{-26} kg) that these forces can impart instantaneous accelerations of the order of 10^{15} m/s² (10^{14} g). These accelerations may last for only a very short time, of course, because one molecule can very quickly move out of the range of influence of the other. ■

MULTIPLE CHOICE

22-1 The Atomic Nature of Matter

- Which *two* of the following cases do *not* correspond to the behavior of an ideal gas?
 - A molecule loses kinetic energy when it collides elastically with another molecule.
 - There is a potential energy associated with the interaction between molecules.
 - Collisions can change the internal energy of molecules.
 - The speed of a molecule is unchanged after a collision with the walls of the container.
- The gas in a closed container consists of a mixture of helium and krypton. This mixture can be treated as an ideal gas if it is assumed that the helium and krypton atoms have the same average

(A) mass.	(B) speed.
(C) momentum.	(D) kinetic energy.

22-2 A Molecular View of Pressure

- Where does the factor of “3” come from in Eq. 22-9?
 - It is an approximation for π .
 - It is found from comparing the units of pressure and density.
 - It is related to the number of spatial dimensions.
 - It arises from integrating v^2 to find the average.

22-3 The Mean Free Path

- (a) At approximately what density, in molecules/m³, does the mean free path of nitrogen molecules equal the size of a room (≈ 3 m)?
 - 10^{23} molecules/m³
 - 10^{20} molecules/m³
 - 10^{18} molecules/m³
 - 10^9 molecules/m³
 (b) Assuming that room temperature is 300 K, what is the approximate pressure?
 - 10^{-1} atm
 - 10^{-2} atm
 - 10^{-5} atm
 - 10^{-7} atm
- The density of gas in a bell jar is kept constant while varying the temperature. If the temperature is doubled, then the mean free path will
 - double.
 - remain the same.
 - decrease by half.
- In a fixed amount of gas, how would the mean free path be affected if
 - the density of the gas is doubled?
 - the mean molecular speed is doubled?
 - both the density and mean molecular speed are doubled?
 - The mean free path will also double.
 - The mean free path will remain the same.
 - The mean free path will decrease by one-half.
 - The mean free path will decrease to one-fourth its original value.

22-4 The Distribution of Molecular Speeds

- Rank v_p , v_{av} , and v_{rms} from highest to lowest at $T = 350$ K for hydrogen molecules.
 - $v_{rms} > v_p > v_{av}$
 - $v_{rms} > v_{av} > v_p$
 - $v_{av} > v_{rms} > v_p$
 - $v_p > v_{av} > v_{rms}$
- The root-mean-square speed of molecules in still air at room temperature is closest to
 - walking speed (2 m/s).
 - the speed of a fast car (30 m/s).
 - the speed of a supersonic airplane (500 m/s).
 - escape speed from Earth (1.1×10^4 m/s).
 - the speed of light (3×10^8 m/s).

- Which of the following speeds divides the molecules in a gas in thermal equilibrium so that half have speeds faster, and half have speeds slower?
 - v_p
 - v_{av}
 - v_{rms}
 - None of the above.
- Which of the following speeds corresponds to a molecule with the average kinetic energy?
 - v_p
 - v_{av}
 - v_{rms}
 - None of the above.
- Consider the distribution of speeds shown in Fig. 22-14. Which is the correct ordering for the speeds?
 - $v_{rms} < v_{av} < v_p$
 - $v_{rms} < v_p < v_{av}$
 - $v_{av} < v_{rms} < v_p$
 - $v_{av} < v_p < v_{rms}$
 - $v_p < v_{av} < v_{rms}$

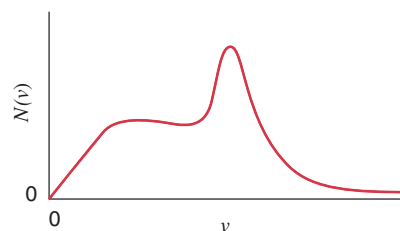


FIGURE 22-14. Multiple-choice question 11.

22-5 The Distribution of Molecular Energies

22-6 Equations of State for Real Gases

- A certain (fictitious!) gas is found to obey the van der Waals equation exactly. The volume of the gas is changed from $V_i = 1000nb$ to $V_f = 2000nb$. Assume that a is small compared to pV^2/n^2 , but not negligible. If the change in volume occurred at constant pressure, then
 - T_f is slightly more than $2T_i$.
 - T_f is slightly less than $2T_i$.
 - T_f is exactly equal to $2T_i$.
 - The answer depends on the value of an^2/pV^2 .
- A plasma is a gas consisting of charged particles. If all the particles have the same charge, then the forces between the particles will be repulsive at all distances. What would be the sign of a in the van der Waals equation for this type of gas?
 - Positive
 - Negative
 - The sign would depend on the sign of the charges in the plasma.
 - There would be no sign, since the van der Waals equation applies only for attractive forces.

22-7 Intermolecular Forces

QUESTIONS

- In kinetic theory we assume that the number of molecules in a gas is large. Real gases behave like an ideal gas at low densities. Are these statements contradictory? If not, what conclusion can you draw from them?
- We have assumed that the walls of the container are elastic for molecular collisions. Actually, the walls may be inelastic. Why does this make no difference as long as the walls are at the same temperature as the gas?
- We have assumed that the force exerted by molecules on the wall of a container is steady in time. How is this justified?
- We know that a stone will fall to the ground if we release it. We put no constraint on molecules of the air, yet they do not all fall to the ground. Why not?
- How is the speed of sound related to the gas variables in the kinetic theory model?

6. Why doesn't the Earth's atmosphere leak away? At the top of the atmosphere atoms will occasionally be headed out with a speed exceeding the escape speed. Isn't it just a matter of time?
7. Titan, one of Saturn's many moons, has an atmosphere, but our own Moon does not. What is the explanation?
8. How, if at all, would you expect the composition of the air to change with altitude?
9. Would a gas whose molecules were true geometric points obey the ideal gas law?
10. Why do molecules not travel in perfectly straight lines between collisions and what effect, easily observable in the laboratory, occurs as a result?
11. Suppose we want to obtain ^{238}U instead of ^{235}U as the end product of a diffusion process. Would we use the same process? If not, explain how the separation process would have to be modified.
12. Considering the diffusion of gases into each other, can you draw an analogy to a large jostling crowd with many "collisions" on a large inclined plane with a slope of a few degrees?
13. Would you expect real molecules to be spherically symmetrical? If not, how would the potential energy function of Fig. 22-13 change?
14. Although real gases can be liquefied, an ideal gas cannot be. Explain.
15. Show that as the volume per mole of a gas increases, the van der Waals equation tends to the equation of state of an ideal gas.
16. Consider the case in which the mean free path is greater than the longest straight line in a vessel. Is this a perfect vacuum for a molecule in this vessel?
17. List effective ways of increasing the number of molecular collisions per unit time in a gas.
18. Give a qualitative explanation of the connection between the mean free path of ammonia molecules in air and the time it takes to smell the ammonia when a bottle is opened across the room.
19. If molecules are not spherical, what meaning can we give to d in Eq. 22-13 for the mean free path? In which gases would the molecules act most nearly like rigid spheres?
20. In what sense is the mean free path a macroscopic property of a gas rather than a microscopic one?
21. Since the actual force between molecules depends on the distance between them, forces can cause deflections even when molecules are far from "contact" with one another. Furthermore, the deflection caused should depend on how long a time these forces act and hence on the relative speed of the molecules. (a) Would you then expect the measured mean free path to depend on temperature, even though the density remains constant? (b) If so, would you expect λ to increase or

decrease with temperature? (c) How does this dependence enter into Eq. 22-13?

22. When a can of mixed nuts is shaken, why does the largest nut generally end up on the surface, even if it is denser than the others?
23. Justify qualitatively the statement that, in a mixture of molecules of different kinds in complete equilibrium, each kind of molecule has the same Maxwellian distribution in speed that it would have if the other kinds were not present.
24. A gas consists of N particles. Explain why $v_{\text{rms}} \geq v_{\text{av}}$ regardless of the distribution of speeds.
25. What observation is good evidence that not all molecules of a body are moving with the same speed at a given temperature?
26. The fraction of molecules within a given range δv of the rms speed decreases as the temperature of a gas rises. Explain.
27. Figure 22-15 shows the distribution of the x component of the velocities of the molecules in a container at a fixed temperature. (a) The distribution is symmetrical about $v_x = 0$; make this plausible. (b) What does the total area under the curve represent? (c) How would the distribution change with an increase in temperature? (d) What is the most probable value of v_x ? (e) Is the most probable speed equal to zero? Explain.

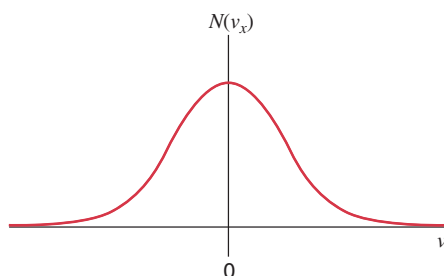


FIGURE 22-15. Question 27.

28. The slit system in Fig. 22-8 selects only those molecules moving in the $+x$ direction. Does this destroy the validity of the experiment as a measure of the distribution of speeds of molecules moving in all directions?
29. List examples of the Brownian motion in physical phenomena.
30. A golf ball is suspended from the ceiling by a long thread. Explain in detail why its Brownian motion is not readily apparent.
31. Let ρ_n be the number of molecules per unit volume in a gas. If we define ρ_n for a very small volume in a gas—say, one equal to 10 times the volume of an atom—then ρ_n fluctuates with time through the range of values zero to some maximum value. How then can we justify a statement that ρ_n has a definite value at every point in a gas?

EXERCISES

22-1 The Atomic Nature of Matter

1. Gold has a molar (atomic) mass of 197 g/mol. Consider a 2.56-g sample of pure gold vapor. (a) Calculate the number of moles of gold present. (b) How many atoms of gold are present?

2. (a) Find the number of molecules in 1.00 m^3 of air at 20.0°C and at a pressure of 1.00 atm. (b) What is the mass of this volume of air? Assume that 75% of the molecules are nitrogen (N_2) and 25% are oxygen (O_2).

- A steel tank contains 315 g of ammonia gas (NH_3) at an absolute pressure of 1.35×10^6 Pa and temperature 77.0°C . (a) What is the volume of the tank? (b) The tank is checked later when the temperature has dropped to 22.0°C and the absolute pressure has fallen to 8.68×10^5 Pa. How many grams of gas leaked out of the tank?
- (a) Consider 1.00 mol of an ideal gas at 285 K and 1.00 atm pressure. Imagine that the molecules are for the most part evenly spaced at the centers of identical cubes. Using Avogadro's constant and taking the diameter of a molecule to be 3.00×10^{-8} cm, find the length of an edge of such a cube and calculate the ratio of this length to the diameter of a molecule. The edge length is an estimate of the distance between molecules in the gas. (b) Now consider a mole of water having a volume of 18 cm^3 . Again imagine the molecules to be evenly spaced at the centers of identical cubes and repeat the calculation in (a).
- Consider a sample of argon gas at 35.0°C and 1.22 atm pressure. Suppose that the radius of a (spherical) argon atom is 0.710×10^{-10} m. Calculate the fraction of the container volume actually occupied by atoms.

22-2 A Molecular View of Pressure

- The mass of the H_2 molecule is 3.3×10^{-24} g. If 1.6×10^{23} hydrogen molecules per second strike 2.0 cm^2 of wall at an angle of 55° with the normal when moving with a speed of 1.0×10^5 cm/s, what pressure do they exert on the wall?
- At 44.0°C and 1.23×10^{-2} atm the density of a gas is 1.32×10^{-5} g/cm³. (a) Find v_{rms} for the gas molecules. (b) Using the ideal gas law, find the number of moles per unit volume (molar density) of the gas. (c) By combining the results of (a) and (b), find the molar mass of the gas and identify it.
- A cylindrical container of length 56.0 cm and diameter 12.5 cm holds 0.350 moles of nitrogen gas at a pressure of 2.05 atm. Find the rms speed of the nitrogen molecules.

22-3 Mean Free Path

- At standard temperature and pressure (0°C and 1.00 atm) the mean free path in helium gas is 285 nm. Determine (a) the number of molecules per cubic meter and (b) the effective diameter of the helium atoms.
- At 2500 km above the Earth's surface the density is about $1.0 \text{ molecule/cm}^3$. (a) What mean free path is predicted by Eq. 22-13 and (b) what is its significance under these conditions? Assume a molecular diameter of 2.0×10^{-8} cm.
- At what frequency would the wavelength of sound be on the order of the mean free path in nitrogen at 1.02 atm pressure and 18.0°C ? Take the diameter of the nitrogen molecule to be 315 pm.
- In a certain particle accelerator the protons travel around a circular path of diameter 23.5 m in a chamber of 1.10×10^{-6} mm Hg pressure and 295 K temperature. (a) Calculate the number of gas molecules per cubic meter at this pressure. (b) What is the mean free path of the gas molecules under these conditions if the molecular diameter is 2.20×10^{-8} cm?
- In Sample Problem 22-4, at what temperature is the average rate of collision equal to $6.0 \times 10^9 \text{ s}^{-1}$? The pressure remains unchanged.

22-4 The Distribution of Molecular Speeds

- The speeds of a group of ten molecules are 2.0, 3.0, 4.0, . . . , 11 km/s. (a) Find the average speed of the group. (b) Calculate the root-mean-square speed of the group.

- (a) Ten particles are moving with the following speeds: four at 200 m/s, two at 500 m/s, and four at 600 m/s. Calculate the average and root-mean-square speeds. Is $v_{\text{rms}} > v_{\text{av}}$? (b) Make up your own speed distribution for the ten particles and show that $v_{\text{rms}} \geq v_{\text{av}}$ for your distribution. (c) Under what condition (if any) does $v_{\text{rms}} = v_{\text{av}}$?
- Calculate the root-mean-square speed of ammonia (NH_3) molecules at 56.0°C . An atom of nitrogen has a mass of 2.33×10^{-26} kg and an atom of hydrogen has a mass of 1.67×10^{-27} kg.
- The temperature in interstellar space is 2.7 K. Find the root-mean-square speed of hydrogen molecules at this temperature. (See Table 22-1.)
- Verify Eq. 22-16 by evaluating $dN(v)/dv = 0$ and solving for v .
- Evaluate the integral in Eq. 22-17 to verify Eq. 22-18.
- Evaluate the integral in Eq. 22-19 to verify that $(v^2)_{\text{av}} = 3kT/m$.
- Calculate the root-mean-square speed of smoke particles of mass 5.2×10^{-14} g in air at 14°C and 1.07 atm pressure.
- At what temperature do the atoms of helium gas have the same rms speed as the molecules of hydrogen gas at 26.0°C ?
- (a) Compute the temperatures at which the rms speed is equal to the speed of escape from the surface of the Earth for molecular hydrogen and for molecular oxygen. (b) Do the same for the Moon, assuming the gravitational acceleration on its surface to be 0.16g. (c) The temperature high in the Earth's upper atmosphere is about 1000 K. Would you expect to find much hydrogen there? Much oxygen?
- You are given the following group of particles (N_n represents the number of particles that have a speed v_n):

N_n	v_n (km/s)
2	1.0
4	2.0
6	3.0
8	4.0
2	5.0

- (a) Compute the average speed v_{av} . (b) Compute the root-mean-square speed v_{rms} . (c) Among the five speeds shown, which is the most probable speed v_p for the entire group?
- In the apparatus of Miller and Kusch (see Fig. 22-8) the length L of the rotating cylinder is 20.4 cm and the angle ϕ is 0.0841 rad. What rotational speed corresponds to a selected speed v of 212 m/s?
- It is found that the most probable speed of molecules in a gas at temperature T_2 is the same as the rms speed of the molecules in this gas when its temperature is T_1 . Calculate T_2/T_1 .
- Show that, for atoms of mass m emerging as a beam from a small opening in an oven of temperature T , the most probable speed is $v_p = \sqrt{3kT/m}$.
- An atom of germanium (diameter = 246 pm) escapes from a furnace ($T = 4220$ K) with the root-mean-square speed into a chamber containing atoms of cold argon (diameter = 300 pm) at a density of 4.13×10^{19} atoms/cm³. (a) What is the speed of the germanium atom? (b) If the germanium atom and an argon atom collide, what is the closest distance be-

tween their centers, considering each as spherical? (c) Find the initial collision frequency experienced by the germanium atom.

22-5 The Distribution of Molecular Energies

- Calculate the fraction of particles in a gas moving with translational kinetic energy between $0.01kT$ and $0.03kT$. (Hint: For $E \ll kT$, the term $e^{-E/kT}$ in Eq. 22-25 can be replaced with $1 - E/kT$. Why?)
- Find the fraction of particles in a gas having translational kinetic energies within a range $0.02kT$ centered on the most probable energy E_p . (Hint: In this region, $N(E) \approx \text{constant}$. Why?)

PROBLEMS

- At 0°C and 1.000 atm pressure the densities of air, oxygen, and nitrogen are, respectively, 1.293 kg/m^3 , 1.429 kg/m^3 , and 1.250 kg/m^3 . Calculate the fraction by mass of nitrogen in the air from these data, assuming only these two gases to be present.
- Dalton's law states that when mixtures of gases having no chemical interaction are present together in a vessel, the pressure exerted by each constituent at a given temperature is the same as it would exert if it alone filled the whole vessel, and that the total pressure is equal to the sum of the partial pressures of each gas. Derive this law from kinetic theory, using Eq. 22-8.
- A container encloses two ideal gases. Two moles of the first gas are present, with molar mass M_1 . Molecules of the second gas have a molar mass $M_2 = 3M_1$, and 0.5 mol of this gas is present. What fraction of the total pressure on the container wall is attributable to the second gas? (Hint: See Problem 2.)
- Calculate the mean free path for 35 spherical jelly beans in a jar that is vigorously shaken. The volume of the jar is 1.0 L and the diameter of a jelly bean is 1.0 cm.
- The mean free path A of the molecules of a gas may be determined from measurements (for example, from measurement of the viscosity of the gas). At 20.0°C and 75.0 cm Hg pressure such measurements yield values of $\lambda(\text{argon}) = 9.90 \times 10^{-6} \text{ cm}$ and $\lambda(\text{nitrogen}) = 27.5 \times 10^{-6} \text{ cm}$. (a) Find the ratio of the effective cross-section diameters of argon to nitrogen. (b) What would be the value of the mean free path of argon at 20.0°C and 15.0 cm Hg? (c) What would be the value of the mean free path of argon at -40.0°C and 75.0 cm Hg?
- The probability that a gas molecule will travel a distance between r and $r + dr$ before colliding with another molecule is given by $Ae^{-cr}dr$, where A and c are constants. By setting the average distance of travel to be equal to the mean free path, find A and c in terms of the number of molecules N and the mean free path λ .
- Two containers are at the same temperature. The first contains gas at pressure p_1 whose molecules have mass m_1 with a root-mean-square speed $v_{\text{rms},1}$. The second contains molecules of mass m_2 at pressure $2p_1$ that have an average speed $v_{\text{av},2} = 2v_{\text{rms},1}$. Find the ratio $m_1:m_2$ of the masses of their molecules.
- A gas, not necessarily in thermal equilibrium, consists of N particles. The speed distribution is not necessarily Maxwell-

22-6 Equations of State for Real Gases

- Estimate the van der Waals constant b for H_2O knowing that one kilogram of water has a volume of 0.001 m^3 . The molar mass of water is 18 g/mol .
- The value of the van der Waals constant b for oxygen is $32 \text{ cm}^3/\text{mol}$. Compute the diameter of an O_2 molecule.
- Show that the constant a in the van der Waals equation can be written in units of

$$\frac{\text{energy per particle}}{\text{particle density}}$$

22-7 Intermolecular Forces

lian. (a) Show that $v_{\text{rms}} \geq v_{\text{av}}$ regardless of the distribution of speeds. (b) When would the equality hold?

- Figure 22-16 shows a hypothetical speed distribution of N gas molecules with $N(v) = Cv^2$ for $0 < v < v_0$ and $N(v) = 0$ for $v > v_0$. Find (a) an expression for C in terms of N and v_0 , (b) the average speed of the particles, and (c) the rms speed of the particles.

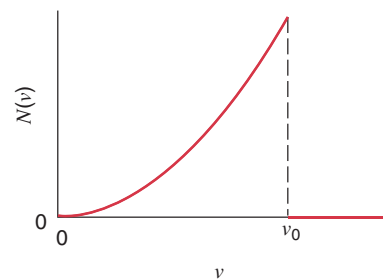


FIGURE 22-16. Problem 9.

- A gas of N particles has the hypothetical speed distribution shown in Fig. 22-17 [$N(v) = 0$ for $v > 2v_0$]. (a) Express a in terms of N and v_0 . (b) How many of the particles have speeds between $1.50v_0$ and $2.00v_0$? (c) Express the average speed of the particles in terms of v_0 . (d) Find v_{rms} .

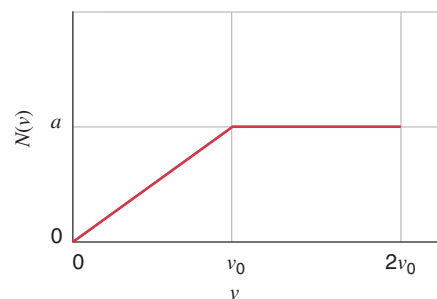


FIGURE 22-17. Problem 10.

- For a gas in which all molecules travel with the same speed v_{av} , show that $v_{\text{rel}} = \frac{4}{3}v_{\text{av}}$ rather than $\sqrt{2}v_{\text{av}}$ (which is the result obtained when we consider the actual distribution of molecular speeds). See Eq. 22-13.

12. The Sun is a huge ball of hot ideal gas. The glow surrounding the Sun in the ultraviolet image shown in Fig. 22-18 is the corona—the atmosphere of the Sun. Its temperature and pressure are 2.0×10^6 K and 0.030 Pa. Calculate the rms speed of free electrons in the corona.

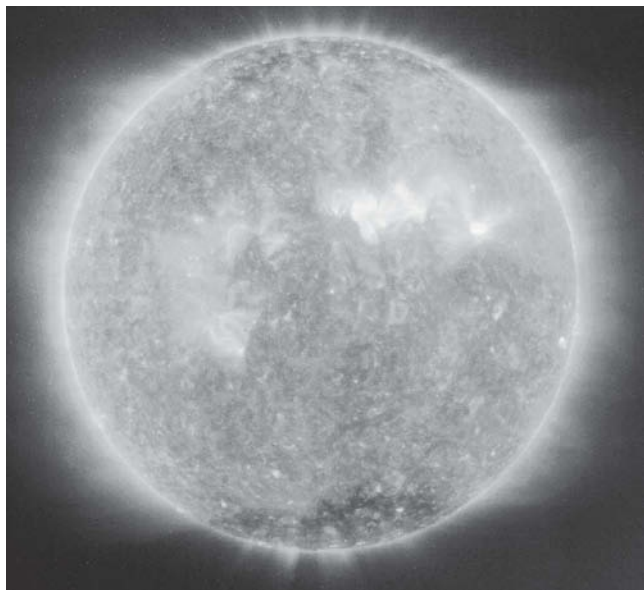


FIGURE 22-18. Problem 12.

13. Consider a gas at temperature T occupying a volume V to consist of a mixture of atoms—namely, N_a atoms of mass m_a each having an rms speed v_a and N_b atoms of mass m_b each having an rms speed v_b . (a) Give an expression for the total pressure exerted by the gas. (b) Suppose now that $N_a = N_b$

and that the different atoms combine at constant volume to form molecules of mass $m_a + m_b$. Once the temperature returns to its original value, what would be the ratio of the pressure after combination to the pressure before?

14. Find *all* of the virial coefficients for a gas that obeys the van der Waals equation of state.
15. The envelope and basket of a hot-air balloon have a combined mass of 249 kg, and the envelope has a capacity of 2180 m^3 . When fully inflated, what should be the temperature of the enclosed air to give the balloon a lifting capacity of 272 kg (in addition to its own mass)? Assume that the surrounding air, at 18.0°C , has a density of 1.22 kg/m^3 .
16. Very small solid particles, called grains, exist in interstellar space. They are continually bombarded by hydrogen atoms of the surrounding interstellar gas. As a result of these collisions, the grains execute Brownian movement in both translation and rotation. Assume that the grains are uniform spheres of diameter $4.0 \times 10^{-6} \text{ cm}$ and density 1.0 g/cm^3 , and that the temperature of the gas is 100 K. Find (a) The root-mean-square speed of the grains between collisions and (b) the approximate rate (rev/s) at which the grains are spinning. (Assume that the average translational kinetic energy and average rotational kinetic energy are equal.)
17. As Fig. 22-11 suggests, if the intermolecular forces are large enough, the measured pressure p of a gas that obeys the van der Waals equation of state could be zero. (a) For what value of the volume per mole would this occur? (Hint: There are two solutions; find them both and interpret them.) (b) Show that there is a maximum temperature for zero pressure to occur, and find this maximum temperature in terms of the a and b parameters in the van der Waals equation. (c) Assuming that oxygen obeys the van der Waals equation with $a = 0.138 \text{ J} \cdot \text{m}^3/\text{mol}^2$ and $b = 3.18 \times 10^{-5} \text{ m}^3/\text{mol}$, find the maximum temperature for which $p = 0$ for oxygen and compare this value with the normal boiling point of oxygen.

COMPUTER PROBLEMS

1. Write a program to simulate the random walk of a particle. The particle starts at the origin, and can then take a step with Δx and Δy increments assigned randomly between -1 and 1 . (a) Allow the particle to “walk” through 200 steps, and graph the motion as was done in Fig. 22-1. Choose the scale of the graph to just fit the data. (b) Allow the particle to walk through 2000 steps, but this time plot the position of the particle only at the end of each 10 steps. Again, choose the scale of the graph to just fit the data. (c) Repeat, but now allow the particle to walk through 20,000 steps, and only plot the position at the end of each 100 steps. Compare the three graphs.

How does the size of the graph grow with the number of steps? Do the graphs look similar? If the graphs were shuffled, would you be able to tell which was which?

2. Consider a van der Waals gas with $a = 0.10 \text{ J} \cdot \text{m}^3/\text{mol}^2$ and $b = 1.0 \times 10^{-4} \text{ m}^3/\text{mol}$. (a) Find the temperature T_{cr} , pressure p_{cr} , and volume V_{cr} where $\partial p/\partial V = 0$ and $\partial^2 p/\partial V^2 = 0$. (b) Graph the pressure along isotherms as a function of volume for $0.80T_{\text{cr}}$, $0.85T_{\text{cr}}$, $0.90T_{\text{cr}}$, $0.95T_{\text{cr}}$, $1.00T_{\text{cr}}$, $1.05T_{\text{cr}}$, and $1.10T_{\text{cr}}$. The graphs should extend from $V = 0$ to $V = 5V_{\text{cr}}$. (c) What is physically significant about the T_{cr} isotherm?