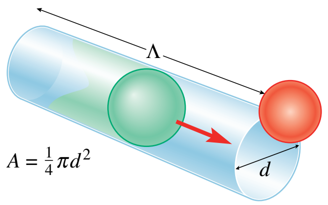

Figure 13.17 A molecule (green) of diameter d moves an average distance Λ before colliding with another molecule (red). The volume of space swept out while moving this distance is the volume of a cylinder of length Λ and cross-sectional area $A = \frac{1}{4}\pi d^2$.

CHAPTER 13

Mean Free Path

In a simplified model of collisions between molecules in a gas, imagine a molecule of diameter d. Its cross-sectional area is

$$A = \pi r^2 = \tfrac{1}{4}\pi d^2 \qquad \text{(13-27)}$$

As the molecule moves in a straight line, it sweeps out a cylindrical volume of space (Fig. 13.17). Once the volume it has swept out equals V/N, the total volume divided by the number of molecules, it has "used up" its own space and begins to infringe on the space "belonging" to another molecule—which means that a collision is imminent. Thus, a collision occurs when

$$\text{Volume} = A\Lambda \approx V/N \qquad \text{(13-28)}$$

or

$$\Lambda \approx \frac{1}{\frac{1}{4}\pi d^2\,(N/V)} \qquad \text{(13-29)}$$

This simplified calculation is correct except for the dimensionless constant of proportionality; a detailed calculation yields

Mean free path:

$$\Lambda = \frac{1}{\sqrt{2}\,\pi d^2\,(N/V)} \qquad \text{(13-25)}$$

Example 13.10

Collisions per Second for N_2 at 20°C and 1 atm

Estimate the average number of collisions per second that each N_2 molecule undergoes in air at room temperature and atmospheric pressure. The diameter of an N_2 molecule is 0.3 nm.

Strategy First find the mean free path. The average time between collisions is the time it takes to travel that distance at the average molecular speed. For the purposes of this estimate, we can use the rms speed instead of the average speed—the rms speed is only 9% higher.

Solution Use the ideal gas law to find the number density:

$$PV = NkT$$

$$\frac{N}{V} = \frac{P}{kT} = \frac{1.01 \times 10^5\ \text{Pa}}{1.38 \times 10^{-23}\ \text{J/K} \times 293\ \text{K}} = 2.50 \times 10^{25}\ \text{m}^{-3}$$

The mean free path is then

$$\Lambda = \frac{1}{\sqrt{2}\,\pi d^2\,(N/V)}$$
$$= \frac{1}{\sqrt{2}\pi \times (3 \times 10^{-10}\ \text{m})^2 \times 2.50 \times 10^{25}\ \text{m}^{-3}}$$
$$= 1 \times 10^{-7}\ \text{m} = 0.1\ \mu\text{m}$$

An estimate of the average time between collisions is the time it takes to travel a distance Λ at speed v_{rms}. In Example 13.7, we found the rms speed of O_2 molecules at 293 K to be 478 m/s. The rms speed of N_2 molecules at that temperature is somewhat higher since the molecular mass of N_2 is smaller (28 u, as opposed to 32 u for O_2). Since average speed is inversely proportional to the square root of molecular mass,

continued on next page

Example 13.10 continued

the difference is insignificant for our estimate. Therefore, taking $v_{\mathrm{rms}} \approx 500$ m/s, the average time between collisions is

$$\langle t \rangle = \frac{\Lambda}{v_{\mathrm{rms}}} \approx \frac{1 \times 10^{-7}\ \mathrm{m}}{500\ \mathrm{m/s}} = 2 \times 10^{-10}\ \mathrm{s} = 0.2\ \mathrm{ns}$$

This is the average time per collision, so the number of collisions per second is

$$\frac{1}{\langle t \rangle} = 5 \times 10^{9}\ \mathrm{s}^{-1}$$

Each molecule collides about 5×10^9 times per second.

Discussion Note that the mean free path is larger than the average distance between a molecule and its nearest neighbor. At room temperature and atmospheric pressure, the latter distance is about 4 nm; the mean free path is 25 times larger. We should suspect an error if we found the mean free path to be comparable to or smaller than the distance between a molecule and its *nearest* neighbor—since only occasionally does a molecule collide with a nearest neighbor.

Practice Problem 13.10 Mean Free Path of a Hydrogen Atom in Space

Intergalactic space is nearly a vacuum: there is on average approximately one hydrogen atom per cubic centimeter. The diameter of a hydrogen atom is about 0.1 nm. (a) Estimate the mean free path of a hydrogen atom under these conditions. (b) Find the rms speed of the hydrogen atoms at temperature 2.7 K. (c) Use (a) and (b) to estimate the average time between collisions in years.

Answers to Practice Problems

13.10 (a) 2×10^{10} km $\approx 100 \times$ the Earth-Sun distance!; (b) 260 m/s; (c) 2000 yr