

More

Kinetic Theory: A Brief Review

Information concerning the initial motions of each of the atoms of macroscopic systems is not accessible, nor do we have the computational capability even with the largest and fastest computers to apply the laws of motion to each, even if it were; therefore, we resort to statistical methods to determine theoretically the values of observable properties of such systems. Indeed, many of these, such as pressure, temperature, heat capacity, and thermal conductivity, are concepts that are only meaningful for large ensembles of particles since they represent average properties of the constituent particles. In experimental measurements of these quantities it is the response of the *system* that is of interest, not that of the individual particles. In this context it is worth noting that the complexity of such systems is more than just a matter of enormous amounts of quantitative detail. The very complexity of the system can itself result in remarkable features that may seem quite unexpected. For example, if we consider a monatomic gas made up of identical atoms, such as helium or neon, which interact with one another through the known electromagnetic force, this microscopic information provides no hint of the fact that the gas may suddenly condense into a liquid. Yet that is exactly what happens.

This section illustrates how the application of the laws of mechanics to the microscopic constituents of a macroscopic system can, with the aid of statistical techniques, predict the behavior of the system in agreement with experimental observation. If you have a firm grasp of the *kinetic theory of gases* from your introductory physics course, you may omit this section without loss of continuity and go directly to the discussion of the Boltzmann distribution in the chapter. Appendix B2 provides a review of distribution functions, using the distribution of grades in a class of students as an example.

Kinetic theory attempts to describe the macroscopic properties of gases in terms of a microscopic picture of the gas as a collection of particles in motion. The pressure exerted by a gas on the walls of its container is an example of a property that is readily calculated by kinetic theory. The gas exerts a pressure on its container because, as molecules of the gas collide with the walls of the container, they must transfer momentum to the walls. The total change in momentum per second is the force exerted on the walls by the gas. We start by making the following assumptions:

1. The gas consists of a large number N of identical molecules that are separated by distances that are large compared with their diameters. As we will see later in the chapter, this is equivalent to assuming that the particles are distinguishable from one another.
2. The molecules make elastic collisions with each other and with the walls of the container, and they are noninteracting, i.e., they exert no forces on each other except when they collide.
3. In the absence of external forces (we can neglect gravity), there is no preferred position for a molecule in the container, and there is no preferred direction for the velocity vector.

For the moment we shall ignore the collisions the molecules make with each other. This is not a serious flaw in our calculation for, since momentum is conserved, collisions of molecules with one another will not affect the total momentum in any given direction. Let m be the mass of each molecule. Taking the x axis to be perpendicular to the wall in Figure 8-1a, the x component of momentum in a molecule is $-mv_x$ before it hits the wall and $+mv_x$ afterward. The magnitude of the change in momentum of the molecule due to its collision with the wall is $2mv_x$. The total change in the momentum of all the molecules in some time interval Δt is $2mv_x$ times the number that hit the wall during this interval.

Let us consider a gas in an imaginary cylindrical container of volume V with each end wall having area A as illustrated in Figure 8-1b. Let N_i be the number of gas molecules in the container whose x component of velocity is $\pm v_{xi}$ and let the length of the cylinder be $v_{xi} \Delta t$. Thus in a time interval Δt molecules with $\pm v_{xi}$ will travel a distance parallel to the x axis equal to $v_{xi} \Delta t$. Therefore, half of the N_i molecules, those with v_{xi} in the $-x$ direction, will collide with the left end wall in the time interval Δt ; the other half will collide with the right end wall during that time. Using the left end wall as an example, the number hitting the wall during Δt is $(\frac{1}{2}) \times$ (number per unit volume) \times (volume), or

$$\frac{1}{2} \left(\frac{N_i}{V} \right) (A v_{xi} \Delta t)$$

The impulse exerted by the wall on these molecules equals the total change in momentum of these molecules, which is $2mv_{xi}$ times the number that hit:

$$I_i = \left(\frac{N_i v_{xi} A \Delta t}{2V} \right) 2mv_{xi} = \frac{N_i m v_{xi}^2 A \Delta t}{V} \quad \mathbf{8-1}$$

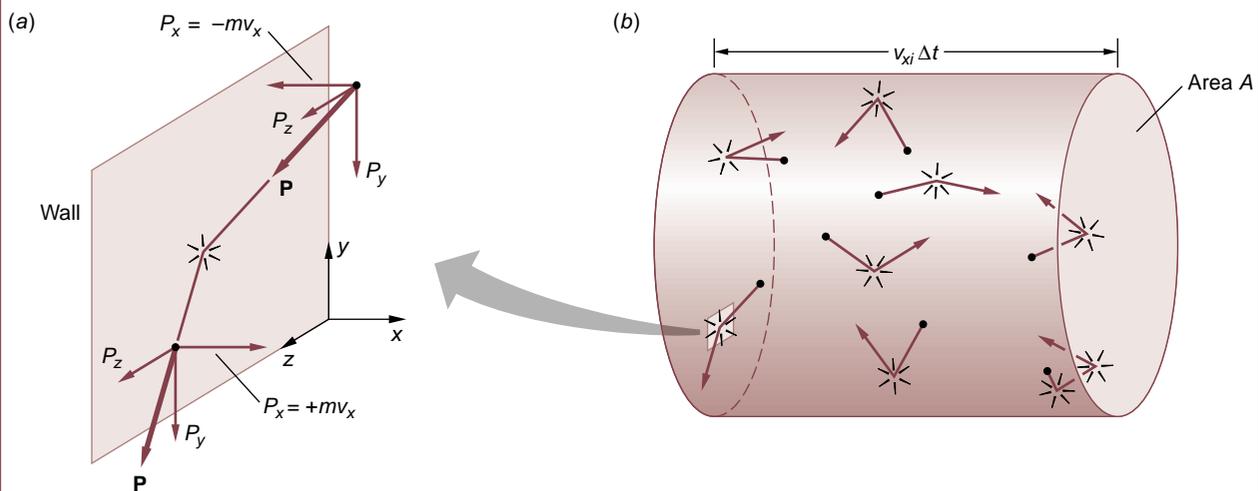


Fig. 8-1 (a) Molecule with momentum \mathbf{p} collides elastically with the wall, the only effect of which is to reverse the direction of the x component p_x while leaving the y and z components unchanged. The molecule undergoes a net change of momentum equal to $2mv_x$. (b) Gas molecules in a cylindrical container colliding with the walls. With the x axis parallel to the cylindrical surface, only those molecules colliding with the ends reverse the directions of their x components of momentum p_{xi} . A molecule starting at the right end with x velocity component v_{xi} will just collide at the left end in time Δt , where the length of the cylinder is $v_{xi} \Delta t$.

This also equals the magnitude of the impulse exerted by these molecules *on* the wall. We obtain the average force exerted by these molecules by dividing the impulse by the time interval Δt . The pressure is this average force divided by the area A . The pressure exerted by these molecules is thus

$$P_i = \frac{I_i}{\Delta t A} = \frac{N_i m v_{xi}^2}{V}$$

The total pressure exerted by all the molecules is obtained by summing over all the x components of velocity v_{xi} that are in the $-x$ direction:

$$P = \sum P_i = \sum \frac{N_i m v_{xi}^2}{V} = \frac{m}{V} \sum N_i v_{xi}^2$$

We can write this in terms of the average value of v_x^2 , defined as

$$(v_x^2)_{\text{av}} = \frac{1}{N} \sum N_i v_{xi}^2$$

where $N = \sum N_i$ is the total number of molecules. Thus, we can write for the pressure on the end walls

$$P = \frac{Nm}{V} (v_x^2)_{\text{av}} \quad \mathbf{8-2}$$

Since there is no preferred direction of motion of the molecules, $(v_x^2)_{\text{av}}$ must be the same as $(v_y^2)_{\text{av}}$ and $(v_z^2)_{\text{av}}$. The square of the speed is

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Hence

$$(v^2)_{\text{av}} = (v_x^2)_{\text{av}} + (v_y^2)_{\text{av}} + (v_z^2)_{\text{av}} = 3(v_x^2)_{\text{av}}$$

Thus we can write the pressure in terms of the average square speed and the kinetic energy:

$$P = \frac{1}{3} \frac{N}{V} m (v^2)_{\text{av}} = \frac{2}{3} \frac{N}{V} \left(\frac{1}{2} m v^2 \right)_{\text{av}} \quad \mathbf{8-3}$$

where N/V is called the number density. This result shows that kinetic theory predicts that the pressure exerted by a gas is proportional to the number of molecules per unit volume and to their average kinetic energy. Writing $\bar{E}_k = \left(\frac{1}{2} m v^2 \right)_{\text{av}}$ for the average kinetic energy of a molecule, we have

$$PV = \frac{2}{3} N \bar{E}_k \quad \mathbf{8-4}$$

To see how well this prediction agrees with experiment, let us compare this result with the ideal-gas law,

$$PV = nRT \quad \mathbf{8-5}$$

an empirical relation where n , the number of moles in the system, is equal to the total number of molecules divided by Avogadro's number N_A :

$$n = \frac{N}{N_A}$$

and R is the gas constant:

$$R = 8.31 \text{ J/K} \cdot \text{mol} = 1.99 \text{ cal/K} \cdot \text{mol} \quad \mathbf{8-6}$$

Equation 8-4 can then be written in terms of n and N_A as

$$PV = \frac{2}{3} n N_A \bar{E}_k \quad \mathbf{8-7}$$

where $N_A \bar{E}_k$ is the average total kinetic energy of one mole. Thus, Equation 8-7 agrees with the ideal-gas law, Equation 8-5, provided that

$$N_A \bar{E}_k = \frac{3}{2} RT \quad \mathbf{8-8}$$

To test Equation 8-8, consider the molar heat capacity at constant volume C_V , which is defined as

$$C_V = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T}$$

where ΔQ is the heat input and ΔT is the temperature rise of 1 mole of a substance. Since no work is done if the volume is constant, the heat input equals the change in internal energy U (from the first law of thermodynamics). Thus

$$C_V = \left(\frac{\partial U}{\partial T} \right)_v$$

If we assume that the total internal energy is *translational* kinetic energy, we have, from Equation 8-8,

$$U = N_A \bar{E}_k = \frac{3}{2} RT$$

and

$$C_V = \frac{\partial(\frac{3}{2} RT)}{\partial T} = \frac{3}{2} R = 2.98 \text{ cal/mol}$$

This value agrees well with the results of experiments for monatomic gases such as argon and helium (see Table 8-1). This agreement is quite remarkable, considering the simple microscopic model of the gas on which it is based, and was an important early success of statistical physics. For other gases, the measured molar heat capacity is greater than $\frac{3}{2} R$, indicating that some of the heat input goes into forms of internal energy other than translational kinetic energy, such as energy of molecular rotation or vibration.

Equation 8-8 implies another extremely interesting prediction, which can be emphasized by writing it as

$$\bar{E}_k = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} kT \quad \mathbf{8-9}$$

where $k = R/N_A$, the gas constant per molecule, is called Boltzmann's constant:

$$k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K} \quad \mathbf{8-10}$$

Thus, the absolute temperature measures the average translational kinetic energy of the molecules. (We include the word *translational* because a molecule may have other kinds of kinetic energy, e.g., rotational or vibrational. Only the translational kinetic energy has entered into our calculation of the pressure exerted on the walls of the container.) The total translational kinetic energy of n moles of a gas containing N molecules is

$$E_k = N \bar{E}_k = \frac{3}{2} N kT = \frac{3}{2} n RT$$

Table 8-1 C_V for some gases at 15°C and 1 atm

Gas	C_V (cal/mol·K)	C_V/R
Ar	2.98	1.50
He	2.98	1.50
CO	4.94	2.49
H ₂	4.87	2.45
HCl	5.11	2.57
N ₂	4.93	2.49
NO	5.00	2.51
O ₂	5.04	2.54
Cl ₂	5.93	2.98
CO ₂	6.75	3.40
CS ₂	9.77	4.92
H ₂ S	6.08	3.06
N ₂ O	6.81	3.42
SO ₂	7.49	3.76

$$R = 1.987 \text{ cal}/(\text{mol}\cdot\text{K})$$

From J. R. Partington and W. G. Shilling, *The Specific Heats of Gases*, Ernest Benn, Ltd., London, 1924.

The translational kinetic energy is $\frac{3}{2}kT$ per molecule or $\frac{3}{2}RT$ per mole. At a typical temperature of $T = 300 \text{ K}$ ($= 81^\circ\text{F}$), the quantity kT has the value

$$kT = 2.585 \times 10^{-2} \text{ eV} \approx \frac{1}{40} \text{ eV}$$

Thus, the mean translational kinetic energy of a gas molecule at room temperature is only a few hundredths of an electron volt. We will discuss this result in more detail later in this section.

Questions

1. Why can we neglect collisions of the molecules with the cylindrical surface of the container when calculating the pressure exerted on the end of the cylinder?
2. How does \overline{E}_k for He molecules compare with \overline{E}_k for Kr molecules under standard conditions?

Another interesting consequence of Equation 8-8 concerns the speed of a molecule in the gas. We do not expect all the molecules in a gas to have the same speed. The distribution of molecular speeds will be discussed later in this section; however, even without knowing this distribution, we can calculate the average square speed $(v^2)_{\text{av}}$ and the root-mean-square (rms) speed $v_{\text{rms}} = [(v^2)_{\text{av}}]^{1/2}$. We have

$$(v^2)_{\text{av}} = \frac{2\overline{E}_k}{m} = \frac{3RT}{N_A m} = \frac{3RT}{M} \quad \mathbf{8-11}$$

Continued

where M is the *molecular weight*. Then

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad \text{8-12}$$

It is not hard to remember the order of magnitude of molecular speeds if we recall that the speed of sound in a gas is given by

$$v_{\text{sound}} = \sqrt{\frac{\gamma RT}{M}}$$

where γ is the ratio of the heat capacity at constant pressure to that at constant volume. (For air, $\gamma = C_p/C_v = 1.4$.) Thus the rms speed of gas molecules is of the same order of magnitude as the speed of sound in the gas.

Questions

3. How does v_{rms} for H_2 molecules compare with v_{rms} for O_2 molecules under standard conditions?
 4. How does the speed of sound in He compare with that in N_2 ?
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Example 8-1 v_{rms} for N_2 molecules

Calculate the root-mean-square speed of nitrogen molecules at $T = 300$ K and at $T = 273$ K.

Solution

$M = 28$ g/mol = 28×10^{-3} kg/mol.

For $T = 300$ K:

$$\begin{aligned} v_{\text{rms}} &= \left(\frac{3 \times 8.31 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 300 \text{ K}}{28 \times 10^{-3} \text{ kg/mol}} \right)^{1/2} \\ &= 517 \text{ m/s} \end{aligned}$$

For $T = 273$ K:

$$\begin{aligned} v_{\text{rms}} &= \left(\frac{3 \times 8.31 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 273 \text{ K}}{28 \times 10^{-3} \text{ kg/mol}} \right)^{1/2} \\ &= 493 \text{ m/s} \end{aligned}$$

Thus, the rms speed of nitrogen molecules in air is about 5 percent slower in cold weather than on a warm day.
