

# Kinetic Theory

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 monoatomic 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.

In this section we will illustrate 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 already have a firm grasp of the *kinetic theory of gases* from an introductory physics or chemistry course, you may omit this CCR unit. However, if it has been a while since you studied kinetic theory, you may want to review this unit, particularly if you are planning to review the CCR derivation of the Boltzmann distribution. In that regard, you may also find it useful to review the CCR unit on distribution functions.

## Basic Assumptions of the Theory

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:

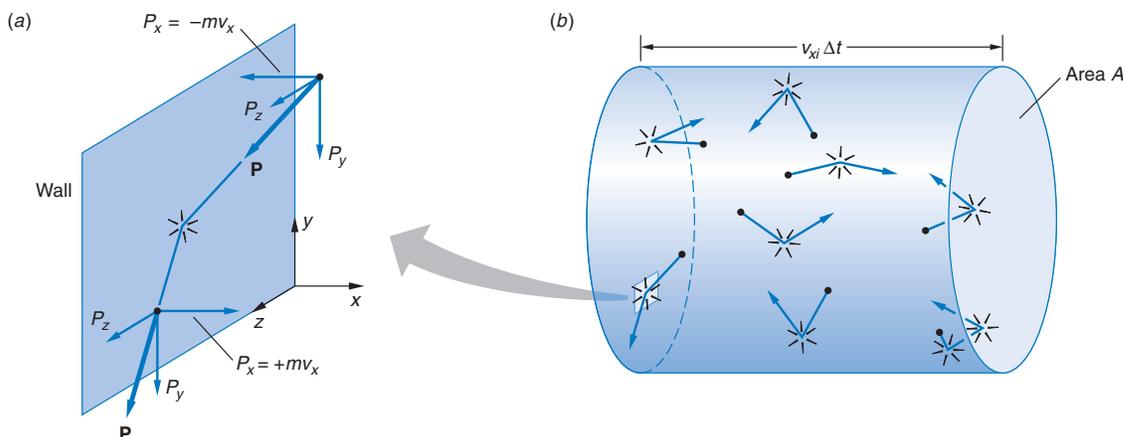
1. The gas consists of a large number,  $N$ , of identical molecules that are separated by distances that are large compared with their diameters. As we will see later in the chapter, this is equivalent to assuming that the particles are distinguishable from one another.

- The molecules make elastic collisions with each other and with the walls of the container, and they are non-interacting, that is, they exert no forces on each other except when they collide.
- 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.

## Kinetic Theory of Gases

For the moment we will ignore the collisions the molecules make with each other. This is not a serious flaw in our calculation because, 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 KT-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  $\Delta t$  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 KT-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  $\Delta t$  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  $\Delta t$ ; the other half will collide with the right end wall during that time. If we use the left end wall as an example, the number hitting the wall during  $\Delta t$  is  $(\frac{1}{2}) \times (\text{number per unit volume}) \times (\text{volume})$ , or



**KT-1** (a) 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  $\Delta t$ , where the length of the cylinder is  $v_{xi} \Delta t$ .

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

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

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

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  $\Delta t$ . 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

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

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

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

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:

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

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  $\overline{E_k} = (mv^2/2)_{\text{av}}$  for the average kinetic energy of a molecule, we have

$$PV = \frac{2}{3} N \overline{E_k} \quad \text{KT-4}$$

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

$$PV = nRT \quad \text{KT-5}$$

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  $N_A$ :

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

where  $R$  is the gas constant:

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

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

$$PV = \frac{2}{3}nN_A\overline{E_k} \quad \text{KT-7}$$

where the product  $N_A\overline{E_k}$  is the average total kinetic energy of one mole. Thus, Equation KT-7 agrees with the kinetic theory prediction, Equation KT-5, provided that

$$N_A\overline{E_k} = \frac{3}{2}RT \quad \text{KT-8}$$

To test if Equation KT-8 is true, 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  $\Delta Q$  is the heat input and  $\Delta T$  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 KT-8,

$$U = N_A\overline{E_k} = \frac{3}{2}RT$$

and

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

This value agrees well with the results of experiments for monatomic gases such as argon and helium (see Table KT-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, that is, kinetic theory. For other gases, the measured molar heat capacity is greater than  $(3/2)R$ , 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 KT-8 implies another extremely interesting prediction, which can be emphasized by writing it as

$$\overline{E_k} = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} kT \quad \text{KT-9}$$

Table KT-1 $C_v$ for some gases at 15°C and 1 atm		
Gas	$C_v$ (cal/mol-deg)	$C_v/R$
Ar	2.98	1.50
He	2.98	1.50
CO	4.94	2.49
H <sub>2</sub>	4.87	2.45
HCl	5.11	2.57
N <sub>2</sub>	4.93	2.49
NO	5.00	2.51
O <sub>2</sub>	5.04	2.54
Cl <sub>2</sub>	5.93	2.98
CO <sub>2</sub>	6.75	3.40
CS <sub>2</sub>	9.77	4.92
H <sub>2</sub> S	6.08	3.06
N <sub>2</sub> O	6.81	3.42
SO <sub>2</sub>	7.49	3.76
$R = 1.987$ cal/mol-deg		

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

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

$$k = 1.382 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K} \quad \text{KT-10}$$

Thus, *the absolute temperature measures the average translational kinetic energy of the molecules.* (We include the word *translational* here because a molecule may have other kinds of kinetic energy, for example, 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

$$E_k = N\overline{E_k} = \frac{3}{2}NkT = \frac{3}{2}nRT$$

The translational kinetic energy is  $(3/2)kT$  per molecule or  $(3/2)RT$  per mole. At a typical temperature of  $T = 300$  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 below.

## An Application of Kinetic Theory

An interesting consequence of Equation KT-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 is discussed in Section 8-1 of the textbook; 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

$$(v^2)_{\text{av}} = \frac{2\overline{E_k}}{m} = \frac{3RT}{N_A m} = \frac{3RT}{M} \quad \text{KT-11}$$

where  $M$  is the *molecular weight*. Then

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

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  $\gamma$  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*.

**EXAMPLE KT-1**  $v_{\text{rms}}$  for  $\text{N}_2$  molecules Calculate the root-mean-square speed of nitrogen molecules at  $T = 300$  K and at  $T = 273$  K.

### SOLUTION

$$M = 28 \text{ g/mol} = 28 \times 10^{-3} \text{ kg/mol.}$$

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 (and the speed of sound) in air is about 5 percent slower in cold weather than on a warm day.

### 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?
3. How does  $v_{\text{rms}}$  for  $\text{H}_2$  molecules compare with  $v_{\text{rms}}$  for  $\text{O}_2$  molecules under standard conditions?
4. How does the speed of sound in He compare with that in  $\text{N}_2$ ?