CHAPTER 2 The Kinetic Theory of Matter

Objectives

After studying this chapter you should:

1. Know the value of Avogadro’s number and its relation to the unified mass unit.
2. Know the relation between the kinetic energy of the molecules of a gas and the pressure and temperature of the gas.
3. Know the approximate value of kT in eV at room temperature.
4. Be able to state the equipartition theorem and discuss its applications.
5. Know what a distribution function is and how to use it to calculate average values of quantities.
6. Be able to sketch the Maxwell-Boltzmann velocity and speed distribution functions.
7. Be able to calculate average values of various quantities, such as \( v, \) \( v^2, \) \( E_k, \) etc., from the Maxwell-Boltzmann distribution function.
8. Be able to discuss the connection between viscosity, heat conduction, and diffusion based on simple transport theory.

In this chapter we shall study some aspects of kinetic theory, the first successful microscopic model of matter. We shall see how the first estimates and measurements of the size and mass of molecules were made. The introduction to the statistical methods of distribution functions and averages in this chapter should prove valuable in Chapter 6, where the same methods are used in quantum mechanics.

The idea that all matter is composed of tiny particles, or atoms, dates back to the speculations of the Greek philosopher Democritus and his teacher Leucippus about 450 B.C. However, there was little attempt to correlate such speculations with observations of the physical world until the seventeenth century. Pierre Gassendi, in the middle of the seventeenth century, and somewhat later Robert Hooke attempted to explain states of matter and the transitions between them with a model of tiny indestructible solid objects flying in all directions.

In 1662, Robert Boyle published results of his experiments showing that the product of the pressure and volume of a gas remains constant at constant temperature. Isaac Newton in his Principia (1687) showed that Boyle’s law could be derived by assuming the gas to consist of hard static particles that repel each other with a force varying inversely with their separation. The first mathematical derivation of Boyle’s law using a kinetic model was done by Daniel Bernoulli in 1758.

Little more was done along these lines for nearly a hundred years. The nineteenth century saw a rapid development of the kinetic theory of matter by many people, notably Herapath, Waterston, Joule, Clausius, Maxwell, and Boltzmann. A parallel development of the theory of atoms emerged in the beginning of the nineteenth century from attempts to understand the laws of chemistry. To explain the law of definite proportions postulated by J. L. Proust (1754–1826), which states that the elements that make up a chemical compound always combine in the same definite proportions by weight, John Dalton in 1808 assumed that an element consisted of identical indestructible atoms. In the same year, J. L. Gay-Lussac announced the law of combining volumes; when two gases combine to form a third, the ratios of the volumes are ratios of integers. He showed, for example, that whenever hydrogen combined with oxygen to form water vapor, the ratio of the volumes of hydrogen to that of oxygen was 2 to 1 within 0.1 percent accuracy. (It is interesting to note that Dalton did not accept Gay-Lussac’s law because it did not agree with his static atomic model, a model which he thought had been proved by Newton’s derivation of Boyle’s law. Dalton also had data less accurate than Gay-Lussac’s, which showed deviations from ratios of integers.) In 1811 an Italian physicist, Amedeo Avogadro, proposed a remarkable hypothesis which, though not accepted for some time, eventually paved the way for the atomic theory of chemistry. Avogadro assumed that:

1. Particles of a gas were small compared with the distances between them.

2. The particles of elements sometimes consisted of two or more atoms stuck together. These particles he called “molecules” to distinguish them from atoms.

3. Equal volumes of gases at constant temperature and pressure contained equal numbers of molecules.

Using these hypotheses along with the work of Gay-Lussac, Dalton, Proust, and others, Avogadro worked out the composition of molecules and, in particular, found that it was necessary to assume that the molecules of a gas such as hydrogen and oxygen contained two atoms. At first, few scientists believed these hypotheses, primarily because of the difficulty of understanding why, if two oxygen atoms attracted each other to form the molecule \( O_2 \), three or four atoms did not likewise bind together to form \( O_3 \) or \( O_4 \). (This was not completely understood until the development of quantum mechanics.)
2.2 The Pressure of a Gas

Kinetic theory attempts to describe the 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 molecules that make elastic collisions with each other and with the walls of the container.

2. The molecules are separated by distances that are large compared with their diameters, and 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. If we take the \( x \) axis to be perpendicular to the wall, the \( x \) component of momentum of 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 \( 2Nv_x \Delta t \), the number of molecules that hit the wall during this interval.

Let us consider a rectangular container of volume \( V \) with a right wall of area \( A \) (Figure 2.1). Let \( N \) be the number of gas molecules whose \( x \) component of velocity is \( v_x \). The number of molecules hitting the right wall in time \( \Delta t \) is the number within a distance \( v_x \Delta t \) and traveling to the right. Since there are \( N \) such molecules in volume \( V \), the number in the volume \( A \Delta t \) is \( N(\frac{V}{A}) = N \frac{v}{A} \Delta t \). If we assume for the moment that \( v_x \) is positive, the number that hit the right wall in time \( \Delta t \) is

\[
Nv_x \frac{v}{A} \Delta t
\]

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:

\[
I = \left( Nv_x \frac{v}{A} \Delta t \right) \Delta t = \frac{2Nm \Delta v}{v} \Delta t
\]
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 \( \Delta t \). The pressure is this average force divided by the area \( A \). The pressure exerted by these molecules is thus

\[
P = \frac{I}{\Delta t A} = \frac{2N \bar{v}^2 m \bar{v}^2}{V}
\]

The total pressure exerted by all the molecules is obtained by summing over all the \( x \) components of velocity \( \bar{v}_x \) that are positive. Since, on the average, half the molecules will be moving to the right (positive \( v_x \)) and half to the left (negative \( v_x \)) at any time, we can sum over all the molecules and multiply by \( \frac{1}{2} \):

\[
P = \frac{1}{2} \sum P_x = \frac{1}{2} \sum \frac{2N \bar{v}^2 m \bar{v}^2}{V} = \frac{m}{V} \Sigma N (\bar{v}^2)_{av}^x
\]

We can write this in terms of the average value of \( \bar{v}^2 \), defined as

\[
(\bar{v}^2)_{av}^x = \frac{1}{N} \sum N (\bar{v}^2)_{av}^x
\]

where \( N = \Sigma N_i \) is the total number of molecules. Thus we can write for the pressure (on the wall perpendicular to the \( x \) axis),

\[
P = \frac{N m}{V} (\bar{v}^2)_{av}^x \tag{2.3}
\]

If there is no preferred direction of motion of the molecules, \((\bar{v}^2)_{av}^x \) must be the same as \((\bar{v}^2)_{av}^y \) and \((\bar{v}^2)_{av}^z \). The square of the speed is

\[
\bar{v}^2 = \bar{v}^2 + \bar{v}^2 + \bar{v}^2
\]

Hence

\[
(\bar{v}^2)_{av} = (\bar{v}^2)_{av} + (\bar{v}^2)_{av} + (\bar{v}^2)_{av} = 3(\bar{v}^2)_{av}
\]

Thus we can write the pressure in terms of the average speed:

\[
P = \frac{1}{3} \frac{N m}{V} (\bar{v}^2)_{av} = \frac{2}{3} \frac{N}{V} \left( \frac{1}{2} m \bar{v}^2 \right)_{av}
\]

\[
= \frac{1}{2} \frac{N m}{V} \bar{v}^2 = \frac{1}{2} \frac{N}{V} \bar{v}^2
\]

where \( n = N/V \) is called the number density. This result shows that the pressure is proportional to the number of molecules per unit volume and to their average kinetic energy.

If we write \( E_k = \frac{1}{2} m \bar{v}^2 \), the average kinetic energy, we have

\[
PV = \frac{1}{2} N \bar{v}^2 \tag{2.5}
\]

Let us compare this result with the ideal gas relation

\[
P V = n k T
\]

where \( n \) is the number of moles, which is the total number of molecules divided by Avogadro's number

\[
\frac{N}{N_A}
\]

and \( R \) is the gas constant

\[
R = 8.31 J/K-mole = 1.99 \text{cal/K-mole}
\]

We then have

\[
\frac{\nu R T}{2} = \frac{\bar{v} E_k}{2} \tag{2.6}
\]

or

\[
E_k = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} \frac{k T}{n}
\]

where \( k = \frac{R}{N_A} \) is called Boltzmann's constant:

\[
k = 1.381 \times 10^{-23} J/K = 8.617 \times 10^{-5} \text{ eV/K}
\]

The absolute temperature is therefore a measure of 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 enters the 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

\[
E_k = N \bar{v}^2 = \frac{1}{2} n k T = \frac{1}{2} \bar{v} R T
\]

The translational kinetic energy is \( \frac{1}{2} k T \) per molecule or \( \frac{1}{2} n k T \) per mole. At a typical temperature of \( T = 300 K \) (= 81°F), the quantity \( k T \) has the value

\[
k T = 2.585 \times 10^{-2} \text{ eV} 
\]

The mean translational kinetic energy of a gas molecule at room temperature is only a few hundredths of an electron volt. Two important results are obtained from this simple calculation:

1. **Speed of a molecule in a gas.** We do not expect all the molecules in a gas to have the same speed. The distribution of molecular speeds will be discussed in Section 2-5. However, even without knowing this distribution, we can calculate the average speed \( \bar{v} \) and the root-mean-square (rms) speed \( \bar{v}_{rms} \). We have

\[
\bar{v} = \frac{\sqrt{E_k}}{m} = \frac{\sqrt{3 k T}}{N_A m} = \frac{\sqrt{3 R T}}{M}
\]

where \( M \) is the molecular weight. Then

\[
\bar{v}_{rms} = \sqrt{\frac{3 R T}{M}} \tag{2.12}
\]

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 a gas molecule is of the same order of magnitude as the speed of sound in the gas.

2. Heat capacities: The molar heat capacity at constant volume is defined by

\[ C_v = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} \]

where \( \Delta Q \) is the heat input and \( \Delta T \) is the temperature rise for 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 2.9 for 1 mole,

\[ U = N_k k_B T = \frac{3}{2} N R T \]

and

\[ C_v = \frac{3}{2} R = 2.98 \text{ cal/mole} \]

This result agrees well with experiments for monatomic gases such as argon and helium (see Table 2-1, page 51). For other gases, the measured molar heat capacity is greater than this, 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.

**Example 2-1** Calculate the root-mean-square speed of nitrogen molecules at \( T = 300 \) K. We have

\[ M = 28 \text{ g/mole} = 28 \times 10^{-3} \text{ kg/mole} \]

\[ v_{\text{rms}} = \sqrt{\frac{3 \times 8.31 \text{ J/K mole}^{-1} \times 300 \text{ K}}{28 \times 10^{-3} \text{ kg/mole}}} \]

= 517 m/sec

**Questions**

1. Why can we neglect collisions of the molecules with the top, bottom, and sides of the box when calculating the pressure exerted on the end of the box?

2. How does \( \bar{E}_x \) for \( \text{H}_2 \) molecules compare with \( \bar{E}_x \) for \( \text{O}_2 \) 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?

**SECTION 2-5** Equipartition Theorem and Heat Capacities of Gases and Solids

Equation 2-7 can be written

\[ \bar{E}_x = (\bar{mv}_x^2)_{av} = (\bar{mv}_y^2)_{av} + (\bar{mv}_z^2)_{av} \]

\[ = \frac{3}{2} k_B T \]

But since \( (\bar{v}_x^2)_{av} = \bar{v}_y^2 = \bar{v}_z^2 \), we have

\[ (\frac{3}{2} k_B T)_{av} = (\bar{mv}_x^2)_{av} = (\bar{mv}_y^2)_{av} = (\bar{mv}_z^2)_{av} = \frac{3}{2} k_B T \]

**Figure 2-2** Rigid-dumbbell model of a diatomic gas molecule that can translate along the \( x, y, \) or \( z \) axis, and rotate about the \( x' \) or \( y' \) axis. If the spheres are smooth or are points, rotation about the \( z' \) axis can be neglected.

In equilibrium, the kinetic energy is shared equally among the three terms \( \bar{mv}_x^2, \bar{mv}_y^2, \) and \( \bar{mv}_z^2 \). This sharing is the natural consequence of collisions between molecules. Suppose we tried to increase the energy associated with motion in the \( x \) direction, \( \bar{mv}_x^2 \), without affecting the energy associated with the motion in the \( y \) or \( z \) direction. We could do this momentarily by replacing the wall perpendicular to the \( x \) direction with a movable piston. If we compress the gas by moving the piston, a molecule moving toward the piston with \( x \) component of velocity \( v_x \) will rebound with \( v_x' \) of greater magnitude so that the energy associated with motion in the \( x \) direction will be increased, with no change in that associated with motion in the \( y \) or \( z \) directions. But immediately after colliding with the piston, molecules collide with other nearby molecules and a new equilibrium is established with \( \bar{mv}_x^2, \bar{mv}_y^2, \) and \( \bar{mv}_z^2 \) each having the same average value \( \frac{3}{2} k_B T \). (This average value is greater than before—thus the work done on the gas by the moving piston has increased the temperature of the gas.) This sharing of energy is a special case of the **equipartition theorem** which can be derived from statistical mechanics.

We call each coordinate, velocity component, angular-velocity component, etc., that appears squared in the expression for the energy of a molecule a degree of freedom. The equipartition theorem states that

In equilibrium, there is associated with each degree of freedom an average energy of \( \frac{3}{2} k_B T \) per molecule.

As an example of the use of the equipartition theorem, consider a rigid-dumbbell model of a diatomic molecule (Figure 2-2) that can translate in the \( x, y, \) and \( z \) directions and can rotate about axes \( x' \) and \( y' \) through the center of mass and perpendicular to the \( z' \) axis along the line joining the two atoms. The kinetic energy for this rigid-dumbbell-model molecule is then

\[ E_k = \frac{3}{2} k_B T = \bar{mv}_x^2 + \bar{mv}_y^2 + \bar{mv}_z^2 + \frac{3}{2} I_x \omega_x^2 + \frac{3}{2} I_y \omega_y^2 \]

where \( I_x \) and \( I_y \) are the moments of inertia about the \( x' \) and \( y' \) axes.

1. We rule out rotation about the \( z' \) axis of the dumbbell by assuming either that the atoms are points and the moment of inertia about this axis is therefore zero, or that the atoms are hard smooth spheres, in which case rotation about this axis cannot be changed by collisions and therefore does not participate in the exchange of energy. Either of these assumptions also rules out the possibility of rotation of a monatomic molecule.
axes. Since this molecule has 5 degrees of freedom, 3 translational and 2 rotational, the equipartition theorem predicts the average energy to be \( \frac{5}{2} kT \) per molecule. The energy per mole is then \( \frac{5}{2} N_v kT = \frac{5}{2} R T \) and the molar heat capacity at constant volume is \( \frac{5}{2} R \). From the observation that \( C_v \) for both nitrogen and oxygen is about \( \frac{5}{2} R \), Clausius speculated (about 1880) that these gases must be diatomic gases which can rotate about two axes as well as translate.

If a diatomic molecule is not rigid, the atoms can vibrate along the line of separation (Figure 2.3). Then, in addition to the translational energy of the center of mass and rotational energy, there can be vibrational energy. The vibration adds two more squared terms to the energy, one for the potential energy, which is proportional to \( (r - r_0)^2 \), and one for kinetic energy proportional to \( (dr/dt)^2 \), where \( r \) is the separation of the atoms which has the value \( r_0 \) at equilibrium. For a diatomic molecule that is translating, rotating, and vibrating, the equipartition theorem predicts a molar heat capacity of \( (3 + 2 + 2) \frac{5}{2} R \), or \( \frac{5}{2} R \) (Figure 2.4).

Table 2-1 lists experimental values of \( C_v \) for several gases. For all the diatomic molecules except \( \text{Cl}_2 \), these data are consistent with the equipartition-theorem prediction assuming a rigid non-vibrating molecule. The value for \( \text{Cl}_2 \) is about halfway between that predicted for a rigid molecule and that predicted for a vibrating molecule. The situation for molecules with three or more atoms is more complicated and will not be examined in detail here.

It is difficult to understand why the equipartition theorem in conjunction with the point-atom, rigid-dumbbell model is so successful in predicting the molar heat capacity for most diatomic molecules but not for all of them. Why should not diatomic gas molecules vibrate? If the atoms are not points, the moment of inertia about the line joining the atoms is not zero, and there are three terms for rotational energy rather than two. Assuming no vibration, \( C_v \) should be \( \frac{5}{2} R \). This agrees with the measured value for \( \text{Cl}_2 \) but not for the other diatomic gases. Furthermore, monatomic molecules would have three terms for rotational energy


![Figure 2-3](image)

Table 2-1

<table>
<thead>
<tr>
<th>Gas</th>
<th>( C_v ) (cal/mole-deg)</th>
<th>( C_v R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ar} )</td>
<td>2.98</td>
<td>1.50</td>
</tr>
<tr>
<td>( \text{He} )</td>
<td>2.98</td>
<td>1.50</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>4.94</td>
<td>2.49</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>4.87</td>
<td>2.45</td>
</tr>
<tr>
<td>( \text{HCl} )</td>
<td>5.11</td>
<td>2.57</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>4.98</td>
<td>2.49</td>
</tr>
<tr>
<td>( \text{NO} )</td>
<td>5.00</td>
<td>2.51</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>5.04</td>
<td>2.54</td>
</tr>
<tr>
<td>( \text{Cl}_2 )</td>
<td>5.93</td>
<td>2.98</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>6.75</td>
<td>3.40</td>
</tr>
<tr>
<td>( \text{CS}_2 )</td>
<td>9.77</td>
<td>4.92</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>6.08</td>
<td>3.06</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>6.81</td>
<td>3.42</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>7.49</td>
<td>3.76</td>
</tr>
</tbody>
</table>

\( R = 1.987 \text{cal/mole-deg} \)


if the atoms were not points, and \( C_v \) should be \( \frac{5}{2} R \) for these atoms also. Since the average energy is calculated by counting terms, it should not matter how small the atoms are as long as they are not merely points.

In addition to these difficulties, the molar heat capacity is found to depend on temperature, contrary to the predictions from the equipartition theorem. The most spectacular case is that of \( \text{H}_2 \), shown in Figure 2.5. It seems as if at very low temperatures, \( \text{H}_2 \) behaves like a monatomic molecule and does not rotate. At very high temperatures \( \text{H}_2 \) begins to vibrate, but the molecule dissociates before \( C_v \) reaches \( 5.5 R \). Other diatomic gases show similar behavior except that at low temperatures they liquefy before \( C_v \) reaches \( 1.5 R \).

![Figure 2-4](image)

Energy modes of a diatomic molecule. With each of the seven possible motions there is associated an average energy \( \frac{5}{2} kT \), giving a total energy of \( \frac{5}{2} kT \) per molecule.
The equipartition theorem is also useful in understanding the heat capacity of solids. In 1819, Dulong and Petit pointed out that the molar heat capacity of most solids was very nearly equal to 3 cal/K-mole = \( 3R \). This result was used by them to obtain unknown molecular weights from the experimentally determined heat capacities. The Dulong-Petit law is easily derived from the equipartition theorem by assuming that the internal energy of a solid consists of the vibrational energy of the molecules (Figure 2-6). If the force constants in the \( x \), \( y \), and \( z \) directions are \( K_x \), \( K_y \), and \( K_z \), the vibrational energy of each molecule is

\[
E = \frac{1}{2} m u_x^2 + \frac{1}{2} m u_y^2 + \frac{1}{2} m u_z^2 + \frac{1}{2} K_x u_x^2 + \frac{1}{2} K_y u_y^2 + \frac{1}{2} K_z u_z^2
\]

Since there are six squared terms, the average energy per molecule is \( 6k T \), and the total energy of 1 mole is \( 3N_A k T = 3RT \), giving \( C_v = 3R \).

At high temperatures, all solids obey the Dulong-Petit law. For temperatures below some critical value, \( C_v \) drops appreciably below the value of \( 3R \) and approaches zero as \( T \) approaches zero. The critical temperature is characteristic of the solid. It is lower for soft solids such as lead than for hard solids such as diamond. The general temperature dependence of \( C_v \) for solids is shown in Figure 2-7.

The fact that \( C_v \) for metals is not appreciably different from that for insulators is somewhat puzzling. A model of a metal that is moderately successful in describing electrical and heat conduction assumes that approximately one electron per atom is free to move about the metal, colliding with the atoms much as molecules do in a gas. According to the equipartition theorem, this "electron gas" should have an average energy of \( 4kT \) per electron; thus the molar heat capacity should be about \( 5R \) greater for a conductor than for an insulator. Although the molar heat capacity for metals is slightly greater than \( 3R \) at very high temperatures, the difference is much less than the 1.5\( R \) predicted for the contribution of the electron gas.

![Figure 2-5](image_url)

**Figure 2-5**

Temperature dependence of molar heat capacity of \( \beta \). Between about 250 and 1000 K, \( C_v \) is approximately \( 3R \), as predicted by the rigid-dumbbell model. At low temperatures, \( C_v \) is only \( \frac{1}{2} R \), as predicted for a nonrotating molecule. At high temperatures \( C_v \) seems to be approaching \( 3R \), as predicted for a dumbbell model that rotates and vibrates, but the molecule dissociates before this plateau is reached.

![Figure 2-6](image_url)

**Figure 2-6**

Simple model of a solid consisting of atoms connected to each other by springs. The internal energy of the solid then consists of kinetic and potential vibrational energy.

The specific heats was instrumental in the discovery of energy quantization in the beginning of the twentieth century. We shall see in the next chapter how energy quantization provides a basis for the complete understanding of the problems discussed in this section.

**Question**

4. Discuss the effect of molecular collisions on a gas which initially had half its molecules moving to the right and half moving to the left with the same speed \( v \). Assume a random placement of molecules in a box with no initial \( v_x \) or \( v_y \).

**2.4 Distribution Functions**

The calculation of the pressure of a gas gives us interesting information about the average square speed, and therefore the average energies, of the molecules in a gas, but it does not yield any details about the distribution of molecular velocities. Before we consider this problem in Section 2-5, we shall discuss the idea of distribution functions in general, with some elementary examples from common experience. This discussion should prove useful not only in the next section, but also in Chapter 6 where the same methods are applied to the more abstract probability distribution functions of quantum mechanics.

Suppose a teacher gave a 25-point quiz to a large number, \( N \), of students. In order to describe the results of the quiz, he might give the average score or the median score, but this would not be a complete description. For example, if all \( N \) students received 12.5, this is quite a different result than if \( N/2 \) students received 25 and \( N/2 \) received 0, though both results have the same average. A complete description would be to give the number \( n_i \) who received the score \( s_i \) for all scores \( s_i \) between 0 and 25. An alternative would be to divide \( n_i \) by the total number of students, \( N \), to give the fraction of the students, \( f_i = n_i/N \), receiving the score \( s_i \). Both \( n_i \) and \( f_i \) (which depend on the variable \( s \)) are called distribution functions. The fractional distribution, \( f_i \), is
A useful quantity characterizing a distribution is the standard deviation, \( \sigma \), defined by

\[
\sigma = \sqrt{\frac{1}{N} \sum (s_i - \bar{s})^2 f_i}
\]

Note that

\[
\sum (s_i - \bar{s})^2 f_i = \sum s_i^2 f_i + \sum s_i^2 f_i - 2\bar{s} \sum s_i f_i = \bar{s}^2 - \bar{s}
\]

Therefore,

\[
\sigma = (\bar{s}^2 - \bar{s})^{1/2}
\]

The standard deviation measures the spread of the values \( s_i \) about the mean. For most distributions there will be few values that differ from \( \bar{s} \) by more than a few multiples of \( \sigma \). In the case of the normal or Gaussian distribution, common in the theory of errors, about two-thirds of the values will lie within \( \pm \sigma \) of the mean value. A Gaussian distribution is shown in Figure 2-9.

If a student were selected at random from the class and one had to guess his score, the best guess would be the score obtained by the greatest number of students, called the most probable score, \( s_{mp} \). For the distribution in Figure 2-8, \( s_{mp} \) is 16 and the average score, \( \bar{s} \), is 14.17. The root-mean-square score, \( s_{rms} = (\bar{s}^2)^{1/2} \), is 14.9, and the standard deviation, \( \sigma \), is 4.6. Note that 66 percent of the scores for this distribution lie within \( \bar{s} \pm \sigma = 14.17 \pm 4.6 \).

Now consider the case of a continuous distribution. Suppose we wanted to know the distribution of heights of a large number of people. For a finite number \( N \), the number of persons exactly 6 ft tall would be zero. If we assume that height can be determined to any desired accuracy, there is an infinite number of possible heights, and the chance that anybody has a particular exact height is zero. We would therefore divide the heights into intervals \( \Delta h \) (for example, \( \Delta h \) could be 0.1 ft) and ask what fraction of people have heights that fall in any particular interval.
The fraction of lifetimes between \( t \) and \( t + dt \) is \( f(t) \, dt \). The fraction of lifetimes between \( t = 0 \) and \( t = \infty \) must be 1; thus the normalization condition is

\[
\int_0^\infty f(t) \, dt = \int_0^\infty C e^{-\lambda t} \, dt = 1
\]

The integral \( \int_0^\infty e^{-\lambda t} \, dt \) has the value \( \lambda^{-1} \). Then \( C = \lambda \). Because the constant \( C \) is determined by the normalization condition, it is called the \textit{normalization constant}. The mean lifetime is calculated by

\[
\bar{t} = \int_0^\infty t f(t) \, dt = \lambda \int_0^\infty te^{-\lambda t} \, dt = \lambda^{-1}
\]

The mean lifetime is the reciprocal of the decay constant.

\[\text{Question}\]

5. If the distribution function \( f(x) \) is symmetric about the origin, i.e., if \( f(-x) = f(x) \), the mean value of \( x \) is zero. Must the most probable value \( x_m \) also be zero?

\[\text{Example 2-2}\]

The distribution function for lifetimes of radioactive nuclei is given by

\[
f(t) = Ce^{-\lambda t}
\]

where \( \lambda \), called the \textit{decay constant}, depends on the particular kind of nucleus (and the type of radioactivity). Assuming \( \lambda \) is known, find the constant \( C \) and the mean lifetime.

\[\text{Mean or average value}\]

\[
\bar{t} = \int_0^\infty t f(t) \, dt
\]

\[\text{Normalization condition}\]

\[
\int f(t) \, dt = 1
\]

\[\text{The limit on the integration depend on the range of the variable. For this case, \( h \) ranges from 0 to } \infty. \text{ We shall often omit explicit indication of the limits when the range of the variable is clear.}\]

\[\text{The constant } C \text{ is determined by the normalization condition, it is called the \textit{normalization constant}. The mean lifetime is calculated by}\]

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\]

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\[
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\]

\[\text{The limit on the integration depend on the range of the variable. For this case, \( h \) ranges from 0 to } \infty. \text{ We shall often omit explicit indication of the limits when the range of the variable is clear.}\]
Maxwell assumed that the components \( v_x, v_y, \) and \( v_z \) were independent and that, therefore, the probabilities of a molecule having a certain \( v_x, v_y, v_z \) could be factored into the product of the probability of having \( v_x \) times the probability of having \( v_y \) times the probability of having \( v_z \). He also assumed that the distribution could depend only on the speed, i.e., the velocity components could occur only in the combination \( v^2 \). He thus wrote

\[
F(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z) \quad 2.25
\]

where \( f(v_x) \) is the distribution function for \( v_x \) only, i.e., \( f(v_x) \, dv_x \) is the fraction of the total number of molecules which have their \( x \) component of velocity between \( v_x \) and \( v_x + dv_x \).

We shall omit Maxwell's derivation and merely state his result. The form of \( f(v_x) \) is

\[
f(v_x) = C e^{-m v_x^2 / 2kT} \quad 2.24
\]

with similar expressions for \( f(v_y) \) and \( f(v_z) \), where \( C \) is a constant determined by the normalization condition

\[
\int_{-\infty}^{\infty} f(v_x) \, dv_x = \int_{-\infty}^{\infty} C e^{-m v_x^2 / 2kT} \, dv_x = 1 \quad 2.25
\]

We shall need to evaluate integrals of the form

\[
I_n = \int_{v_x}^{\infty} x^n e^{-\lambda x^2} \, dx \quad 2.26
\]

several times in this chapter. Table 2.2, derived in Appendix B, lists \( I_n \) for values of \( n \) from 0 to 5. Using this table to evaluate Equation 2.25 with \( \lambda = m / 2kT \) we find

\[
C = \left( \frac{\lambda}{\pi} \right)^{1/2} = \left( \frac{m}{2\pi kT} \right)^{1/2} \quad 2.27
\]

To avoid having to repeat this rather long phrase, we shall hereafter use the expression "the number in \( dv_x \) at \( v_x \)" or simply "the number in \( dv_x \)."

### Table 2.2

<table>
<thead>
<tr>
<th>( n )</th>
<th>( I_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \frac{1}{\sqrt{\pi}} \lambda^{-1/2} )</td>
</tr>
<tr>
<td>1</td>
<td>( \lambda^{-1} )</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{1}{\sqrt{\pi}} \lambda^{-3/2} )</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{3}{2^{3/2}} \lambda^{-2} )</td>
</tr>
<tr>
<td>4</td>
<td>( \frac{1}{\sqrt{\pi}} \lambda^{-5/2} )</td>
</tr>
<tr>
<td>5</td>
<td>( \lambda^{-3} )</td>
</tr>
</tbody>
</table>

If \( n \) is even:

\[
I_n = \int_{-\infty}^{\infty} x^n e^{-\lambda x^2} \, dx = 2I_n
\]

If \( n \) is odd:

\[
I_n = \int_{-\infty}^{\infty} x^n e^{-\lambda x^2} \, dx = 0
\]

Substituting this result for \( C \) into Equation 2.24 we have

\[
f(v_x) = \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-m v_x^2 / 2kT} \quad 2.28
\]

Figure 2.11 shows a sketch of \( f(v_x) \) versus \( v_x \). Of course, \( f(v_x) \) is symmetric about the origin, \( f(-v_x) = f(v_x) \), so the average of \( v_x \) is zero. As can be seen from the figure, the most probable \( v_x \) is also zero. The complete velocity distribution is

\[
F(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z) = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2) / 2kT} \quad 2.29
\]

**Maxwell velocity distribution**

**Example 2.3** Find the mean value of \( v_x^2 \). We have

\[
(v_x^2)_{av} = \int_{-\infty}^{\infty} v_x^2 f(v_x) \, dv_x
\]

where \( f(v_x) \) is given by Equation 2.24. Writing \( \lambda = m / 2kT \) we have

\[
(v_x^2)_{av} = \int_{-\infty}^{\infty} C v_x^2 e^{-\lambda v_x^2} \, dv_x
\]

\[
= 2C \int_{0}^{\infty} v_x^2 e^{-\lambda v_x^2} \, dv_x
\]

with \( C \) given by Equation 2.27. This integral is of the form \( I_n \) given in Table 2.2 with \( n = 2 \). Then

\[
(v_x^2)_{av} = 2GI_2 = 2 \left( \frac{\lambda}{\pi} \right)^{1/2} \frac{1}{2^{3/2}} \frac{1}{\lambda^{3/2}} \frac{1}{\pi} \lambda^{-1/2}
\]

\[
= \frac{1}{\lambda} \frac{kT}{m}
\]

Note that this agrees with the equipartition theorem

\[
(3kT)_{av} = \frac{1}{2} kT
\]

The velocity distribution can be represented pictorially in what is called velocity space. Imagine the velocity vector of each molecule placed with its tail at the origin of a coordinate system \( v_x, v_y, v_z \) as in Figure 2.12. If we have \( N \) molecules, the
Figure 2.12
Velocity vectors in velocity space. The velocity distribution function gives the fraction of molecular velocities whose vectors end in a cell $d v_x d v_y d v_z$. A simpler representation is shown in Figure 2.13. Here each molecular velocity with components $v_x, v_y$, and $v_z$ is represented by a point in velocity space. The velocity distribution function is the density of points in this space. The density is maximum at the origin since $F(v_x, v_y, v_z)$ has its maximum value there. Note that this density is spherically symmetric in velocity space; i.e., it depends only on the "distance" $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$, which is the molecular speed.

We can now calculate the speed distribution from the velocity distribution. Let $N g(v) dv$ be the number of molecules with speeds between $v$ and $v + dv$. In Figure 2.13 this is just the number of points in a spherical shell between $v$ and $v + dv$. This number is the density $N F(v_x, v_y, v_z) dv_x dv_y dv_z$ times the volume of the shell $4 \pi v^2 dv$. Thus

$$N g(v) dv = N F(v_x, v_y, v_z) 4 \pi v^2 dv$$

or

$$g(v) = 4 \pi \left( \frac{m}{2 \pi kT} \right)^{3/2} v^2 e^{-m v^2/2 kT}$$

2.30 Speed distribution

The speed distribution is sketched in Figure 2.14. The most probable speed $v_m$, the mean speed $\bar{v}$, and the rms speed $v_{rms}$ are indicated in the figure. Although the density function $F$ is a maximum at the origin ($v = 0$), the speed distribution function $g(v)$ approaches zero as $v \rightarrow 0$ because the volume of a spherical shell, $4 \pi v^2 dv$, approaches zero. The factor $4 \pi v^2$ thus shifts the maximum in the function $g(v)$ away from the origin to the value $v = v_m$ indicated in Figure 2.14. At very high speeds, the speed distribution function approaches zero because of the exponential factor $e^{-m v^2/2 kT}$.

Example 2.4 Calculate the mean speed $\bar{v}$. We have

$$\bar{v} = \int_0^\infty v g(v) dv = \int_0^\infty A v^2 e^{-m v^2/2 kT} dv = A I_2$$

with $\lambda = m/2 kT$ as before and $A = 4 \pi (m/2 kT)^{3/2}$. Note that the integration ranges from 0 to $\infty$ rather than from $-\infty$ to $+\infty$ since speed is always positive. Using Table 2.2 for $I_2$ we have

$$\bar{v} = A \frac{\lambda^{-3}}{2} = \frac{1}{2} \frac{A}{4 \pi} \left( \frac{m}{2 \pi kT} \right)^{3/2} \left( \frac{2 kT}{m} \right)^{1/2}$$

2.31

The mean speed is slightly less than $v_{rms} = (3 kT/m)^{1/2}$, as indicated in Figure 2.14. The rms speed can be calculated directly from the speed distribution, or from the equipartition theorem

$$(\bar{v}_2)_{av} = (\bar{v}_x^2)_{av} + (\bar{v}_y^2)_{av} + (\bar{v}_z^2)_{av} = \frac{3 kT}{m}$$

Figure 2.14
Maxwell speed distribution function $g(v)$. The most probable speed $v_m$, the mean speed $\bar{v}$, and the rms speed $v_{rms}$ are indicated.
It is left as an exercise to show that the most probable speed is

\[ v_m = \left( \frac{2kT}{m} \right)^{1/2} \]  

2.32

The energy distribution function, \( F(E) \), is the fraction of molecules with (kinetic) energies between \( E \) and \( E + dE \). We can calculate the energy distribution by noting that

\[ F(E) \; dE = g(v) \; dv \]

with \( E = \frac{1}{2}mv^2 \) and \( dE = mv \; dv \). Thus

\[ v^2 \; dv = \frac{dE}{m} = \left( \frac{2E}{m} \right)^{1/2} \frac{dE}{m} \]

The energy distribution is thus

\[ F(E) \propto E^{1/2}e^{-E/kT} \]  

2.33

The proportionality constant can be determined by the normalization condition.

The first direct measurement of the speed distribution of molecules was made by O. Stern in 1926. Since then, measurements have been made by Zartman and Ko (1930); I. Estermann, O. C. Simpson, and O. Stern (1946); and Miller and Kusch (1955). These experiments employed various methods of selecting a range of speeds of molecules escaping from a small hole in an oven and determining the number of molecules in this range. Zartman and Ko, for example, allowed the beam to pass through a slit in a rotating cylinder and measured the intensity versus position on the collecting plate. In the more recent experiment of Miller and Kusch, illustrated in Figure 2-15, a collimated beam from the oven is aimed at a fixed detector. Most of the beam is stopped by a rotating cylinder. Small helical slits in

The cylinder allow passage of those molecules in a narrow speed range determined by the angular velocity of the cylinder. The Miller and Kusch results are shown in Figure 2-16.

The velocity distribution for molecules in a gas (Equation 2-29) is a special case of the general Maxwell-Boltzmann distribution, which can be derived by the methods of statistical mechanics. Since this distribution is applicable to a wide variety of systems other than gases (for example, atoms in a solid), it will be stated in a more general form here. We consider a system of particles for which the energy \( E \) can be a function of the coordinates \( x, y, z \) and momenta \( p_x, p_y, \) and \( p_z \). The six-dimensional space \( x, y, z, p_x, p_y, p_z \) is called phase space. The probability of a particle being in a cell in phase space of "volume" \( d\tau = dx \; dy \; dz \; dp_x \; dp_y \; dp_z \) is

\[ \int f(x,y,z,p_x,p_y,p_z) \; d\tau = Ce^{-\frac{E}{kT}} \; d\tau \]  

2.34

where the constant \( C \) is determined by the normalization condition

\[ \int Ce^{-\frac{E}{kT}} \; d\tau = 1 \]  

2.35

We can apply this to the case of an ideal gas by writing the energy

\[ E = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \]

1 This distribution also holds if we interpret \( p \) to be angular momentum and the coordinates to be the corresponding angles. For example, \( p_x \) can be the \( x \) component of angular momentum, in which case \( z \) is the angle of rotation \( \phi \).
Since the energy does not depend on \( x, y, \) or \( z \), we can integrate over these coordinates to obtain the total volume of the container \( V \). (This factor will cancel a factor \( 1/V \) in the normalization constant \( C \) given by Equation 2-35.) We are left with a momentum distribution function which is essentially the same as the velocity distribution of Equation 2-29 except for the normalization constants.

We shall see in the next chapters that, in general, the energy of a system is not a continuous variable but takes on only a discrete set of values. (The energy often appears to be continuous because these discrete values are very close together.) It is useful therefore to have a statement of the Maxwell-Boltzmann distribution for the case of discrete energy states.

Given a system of paricles for which the energy has a discrete set of values, the probability of a particle having energy \( E_i \) is

\[
f_i = C g_i e^{-\frac{E_i}{kT}}\]

where the constant \( C \) is determined by the normalization condition and \( g_i \) is called the statistical weight. The statistical weight is the number of quantum states having the same energy value \( E_i \).

In our study of quantum mechanics and atomic physics in Chapters 6 and 7 we shall see how \( g_i \) is determined for various systems.

**Example 2-5 The Law of Atmospheres** Consider an ideal gas in a uniform gravitational field. Find how the density of the gas depends on height above the ground. Let the force of gravity be in the negative \( z \) direction and consider a column of gas of cross-sectional area \( A \). The energy of a gas molecule is then

\[
E = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + mgz = \frac{p^2}{2m} + mgz
\]

where \( p^2 = p_x^2 + p_y^2 + p_z^2 \) and \( mgz \) is the potential energy of a molecule at height \( z \) above the ground.

From Equation 2-34 we have

\[
f(p_x, p_y, p_z, x, y, z) = Ce^{-\frac{p^2}{2mk}} e^{-mgz}\]

Since we are interested only in the dependence on \( z \), we can integrate over the other variables \( dx, dy, dp_x, dp_y, \) and \( dp_z \). The integration merely gives a new normalization constant \( C' \), i.e., the result is equivalent to ignoring these variables. The fraction of the molecules between \( z \) and \( z + dz \) is then

\[
f(z) \, dz = C'e^{-mgz} \, dz
\]

The constant \( C' \) is obtained from the normalization condition

\[
f(z) \, dz = 1.
\]

The result is \( C' = kT/mg \). We see that the density decreases exponentially with distance above the ground. This is known as the law of atmospheres.

**Example 2-6** The first excited state of the hydrogen atom is 10.2 eV above the ground state. What is the ratio of the number of atoms in the first excited state to the number in the ground state at \( T = 300 \) K? We shall see in Chapter 7 that the statistical weights for these states are \( g_1 = 2 \) and \( g_2 = 8 \). The ratio is \( \frac{j_2}{j_1} \), given by Equation 2-36, using \( kT = 0.026 \) eV:

\[
\frac{j_2}{j_1} = \frac{g_2 e^{-\frac{E_2}{kT}}}{g_1 e^{-\frac{E_1}{kT}}} = \frac{g_2}{g_1} e^{\frac{E_1 - E_2}{kT}} = 4 e^{(10.2\text{eV}/0.026\text{eV})} = 4 e^{385} = 10^{121}
\]

We see that because of the great energy difference compared with \( kT \), very few atoms are in the excited state.

**Questions**

6. If we derive the energy distribution for an ideal gas from the general Maxwell-Boltzmann distribution, we obtain a factor \( E^{1/2} \) multiplying \( e^{-E/kT} \). Where does this factor come from?

7. \( H_2 \) molecules can escape so freely from the earth's gravitational field that \( H_2 \) is not found in the earth's atmosphere. Yet the mean speed of \( H_2 \) molecules at ordinary atmospheric temperatures is much less than the escape speed. How then can \( H_2 \) molecules escape?

### 2.6 Transport Phenomena

In the calculation of the pressure exerted by a gas on its container, the use of the molecules was not involved, and we could neglect the collision of the molecules with each other. We shall now consider the phenomena of viscosity, heat conduction, and diffusion, which depend directly on the size of gas molecules and on molecular collisions. The success of the application of kinetic theory to these phenomena provided one of the first convincing demonstrations of its essential validity, and consequently of the existence of molecules.

In the kinetic theory, viscosity involves the transport of momentum; heat conduction involves the transport of kinetic energy, and diffusion involves the transport of the density of the molecules. Molecular collisions play an important role in the transport of these quantities, and the frequency of collisions depends directly on the size of the molecules and the number of molecules per unit volume.

It is not difficult to see that if either Avogadro's number or the size of a molecule is known, the other can be estimated. Consider, for example, a solid in which the molecules are close together. If we assume each molecule to occupy a cube of side \( d \), where \( d \) is the diameter of the molecule and also the distance between the centers of the molecules, the volume of 1 mole of the solid is \( N_d^3 \). If \( M \) is its molecular weight, its density is

\[
\rho = \frac{M}{N_d^3}
\]

Either \( N_d \) or \( d \) can be found from a simple measurement of den-
Summary

The number of molecules in a mole is Avogadro's number $N_A = 6.022 \times 10^{23}$, which is the reciprocal of the unified mass unit expressed in grams.

A simple model assuming that the pressure of a gas is due to collisions of molecules with the walls of a container implies that the mean kinetic energy of the molecules is proportional to the temperature of the gas.

The probability of occurrence of a value of $x$ in the range $dx$ is given by $f(x) \, dx$, where $f(x)$ is the distribution function. Such a function obeys the normalization condition

\[ \int f(x) \, dx = 1 \]

The Maxwell-Boltzmann velocity distribution is

\[ f(v_x,v_y,v_z) = \left( \frac{m}{2 \pi kT} \right)^{3/2} e^{-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}} \]

and the speed distribution is

\[ g(v) = \frac{4 \pi v^2}{(2 \pi kT)^{3/2}} e^{-\frac{mv^2}{2kT}} \]

The Maxwell-Boltzmann energy distribution is

\[ F(E) = C E^{3/2} e^{-\frac{E}{kT}} \]

where $C$ is determined by normalization.

The mean translational kinetic energy of gas molecules is $\frac{3}{2} kT$, independent of any characteristics of the molecules. This is an example of the equipartition theorem: there is a mean energy of $\frac{3}{2} kT$ associated with each squared coordinate or momentum in the expression for the energy of a molecule. Molecular speeds are of the order of magnitude of the speed of sound.

An elementary theory of transport yields similar expressions for the coefficients of viscosity, heat conduction, and diffusion in terms of the molecular density, mean speed, and mean free path between collisions. The mean free path varies inversely with density and with the square of the molecular diameter. In particular, this theory predicts that the coefficient of viscosity is independent of density and is proportional to the square root of the temperature, in agreement with experiment. From this theory, and macroscopic measurements of viscosity, the first estimates of molecular size and Avogadro's number were made.

In the random-walk problem, the rms distance is proportional to the square root of the number of steps. This problem is useful in visualizing the processes of diffusion and Brownian motion. Since the number of molecular collisions is proportional to time, the rms distance for diffusion or Brownian motion is proportional to the square root of the time. Detailed observations of the position of particles in colloidal suspension allowed Perrin to make the first accurate measurements of Avogadro's number and to verify directly and quantitatively the predictions of kinetic theory.

References


2. H. Boorse and L. Motz (eds.), The World of the Atom, New York: Basic Books, Inc., Publishers, 1966. This two-volume, 1875-page work is a collection of original papers translated and edited. Much of the work referred to in this chapter and throughout this text can be found in these volumes. Of particular interest for this chapter are the papers by Boyle, Hooke, Bernoulli, Dalton, Gay-Lussac, Avogadro, Herapath, Brown, Waterston, Joule, and Maxwell.


References 8 and 9 are intermediate-level textbooks.

Exercises

Section 2-1, Avogadro's Number

1. The molecular weight of O$_3$ is 32.0 g/mole. Find the mass of an O$_3$ molecule.

2. The quantity $N_A$ is called the faraday, where $e = 1.60 \times 10^{-19}$ coulomb is the electron charge. Find the number of coulombs in a faraday.

Section 2-2, The Pressure of a Gas

5. What is the SI unit of $(3RT/6)^{1/2}$? Are m/sec.

4. $(a)$ Find the total kinetic energy of translation of 1 mole of N$_2$ molecules at $T = 273$ K. $(b)$ Would your answer be the same, greater, or less for 1 mole of He atoms at the same temperature?
5. (a) Calculate $v_{\text{esc}}$ for H$_2$ at $T = 500$ K. (b) Calculate the temperature $T$ for which $v_{\text{esc}}$ for H$_2$ equals the escape speed of 11.2 km/sec.

6. (a) The ionization energy for hydrogen atoms is 13.6 eV. At what temperature is the average kinetic energy of translation equal to 13.6 eV? (b) What is the average kinetic energy of translation of hydrogen atoms at $T = 10^7$ K, a typical temperature in the interior of the sun?

### Section 2-3, Equipartition Theorem and Heat Capacities of Gases and Solids

7. For an ideal gas, the molar heat capacity at constant pressure $C_p$ is related to that at constant volume $C_v$ by $C_p = C_v + R$. A quantity that is often measured is the ratio $\gamma = C_p/C_v$. Find $C_p$ and $\gamma$ for an ideal gas which consists of (a) spherical atoms that do not rotate, (b) rigid-dumbbell-shaped molecules, (c) nonrigid-dumbbell-shaped molecules that vibrate as well as rotate.

8. The measured value of $\gamma$ for air is 1.4. Which of the models in Exercise 7 best describes air molecules?

9. A monatomic gas is confined to move in two dimensions so that the energy of a molecule is $E_k = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2$. What are $C_v$, $C_p$, and $\gamma$ for this gas? (See Exercise 7.)

10. Use the Dulong-Petit law that $C_p = 3R$ for solids to calculate the specific heat $c_v = C_p/\text{mole}$ for (a) aluminum, $M = 27.0$ g/mole, (b) copper, $M = 65.5$ g/mole, and (c) lead, $M = 207$ g/mole, and compare your results with values given in a handbook.

### Section 2-4, Distribution Functions

11. A class of 50 students was given a 10-point quiz. The grade distribution was:

<table>
<thead>
<tr>
<th>Score</th>
<th>10</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>1</td>
<td>4</td>
<td>8</td>
<td>7</td>
<td>6</td>
<td>5</td>
<td>1</td>
<td>6</td>
<td>6</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Find the mean grade and the standard deviation. Indicate these on a histogram plot of this distribution.

12. The speed of sound is measured in an elementary laboratory by students $A$ and $B$. Each takes nine readings. The data are:

- $A$: 343, 350, 358, 540, 555, 534, 464, 320 m/sec
- $B$: 540, 350, 345, 350, 525, 560, 529, 555, 335 m/sec

Compute the mean value and the standard deviation for each set.

13. The distribution function for some quantity $x$ is given by

$$f(x) = C$$ for $x < a$

where $C$ is a constant.

$$f(x) = 0$$ for $x > a$

Find $A$, $x_{\text{max}}$, and $\sigma$, and indicate these quantities on a sketch of $f(x)$.

14. The distribution function for some positive quantity $x$ is

$$f(x) = A x$$ for $x < x_0$

$$f(x) = 0$$ for $x > x_0$

Find $A$, $x_{\text{max}}$, and $\sigma$. Indicate $A$, $x_{\text{max}}$, and $\sigma$ on a sketch of $f(x)$.

### Section 2-5, The Maxwell-Boltzmann Distribution

15. Neutrons in a reactor have a Maxwell-Boltzmann velocity distribution when they are in thermal equilibrium. Find $v$ and $v_{\text{esc}}$ for neutrons in thermal equilibrium at $T = 300$ K.

16. Show that $g(v)$ (Equation 2-30) has its maximum value at $v = v_m = (2kT/m)^{1/2}$.

17. (a) Show that Equation 2-28 can be written

$$f(v) = 2\pi v^2 e^{-\frac{mv^2}{2kT}}$$

where $v_m = v_{\text{esc}} = (kT/m)^{1/2}$. Consider 1 mole of gas and approximate $\Delta v_x$ by $\Delta v_y = 0.01v_m$. Find the number of molecules in $\Delta v_x$ at $(v_x = 0, v_y = v_z) = v_z = 2v_0$. (c) $v_x = 2v_0$. (e) $v_x = 8v_0$.

18. Calculate the mean value of the reciprocal speed $(1/v)$ from the speed distribution $g(v)$.

19. (a) Show that the velocity distribution function (Equation 2-29) can be written

$$f(v_x,v_y,v_z) = 2\pi v_x v_y v_z e^{-\frac{mv_x^2}{2kT}}$$

where $v_m = (2kT/m)^{1/2}$ is the most probable speed and $v_x = v_x^2 + v_y^2 + v_z^2$. Consider 1 mole of molecules and approximate $\Delta v_x$, $\Delta v_y$, and $\Delta v_z$ by $\Delta v_x = \Delta v_y = \Delta v_z = 0.01v_m$. Find the number of molecules in a cell centered at $(v_x = v_y = v_z = 0, c) = v_x = v_y = v_z = v_m$.

20. Calculate the most probable energy $E_m$ from the energy distribution (Equation 2-33) and indicate it on a sketch of $F(E)$ versus $E$.

21. (a) Show that the speed distribution function can be written

$$g(v) = 4\pi v^2 e^{-\frac{mv^2}{2kT}}$$

where $v_m$ is the most probable speed. Consider 1 mole of molecules and approximate $\Delta v_x$ by $\Delta v_x = 0.01v_m$. Find the number of molecules with speeds in $\Delta v$ at $(v_x = 0, c) = v = v_m$. (c) $v = 2v_m$. (e) $v = 8v_m$.

22. From the absorption spectrum it is determined that about one out of $10^4$ hydrogen atoms in a certain star is in the first excited state, 10.2 eV above the ground state (other excited states can be neglected). What is the temperature of the star? (Take the ratio of statistical weights to be 4, as in Example 5-6.)

23. The first rotational energy state of the H$_2$ molecule ($g_z = 3$) is about $4 \times 10^4$ eV above the lowest energy state ($g_z = 1$). What is the ratio of the numbers of molecules in these two states at room temperature (300 K)?

### Section 2-6, Transport Phenomena

24. One mole of a gas occupies a volume of 22.4 liters = $22.4 \times 10^{-6}$ m$^3$ under standard conditions. Using $N_a L^3$ for this volume, find the order of magnitude of the molecular separation of the molecules $L$. Compare this with the size of the molecules and with their mean free path.

25. Use the known value of $N_a$ to estimate $d$ from Equation 2-38 for (a) aluminum with density 2.7 g/cm$^3$ and molecular weight 27 g/mole, (b) lead with density 11.2 g/cm$^3$ and molecular weight 207 g/mole, (c) copper with density 8.96 g/cm$^3$ and molecular weight 63.5 g/mole.