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Chapter One
Kinetic Theory of Gases

Table of Contents

Chapter 1	Kinetic Theory of Gases	1-3
1.1	Introduction	1-3
1.2	Pressure of an Ideal Gas	1-4
1.3	Temperature and Energy	1-6
1.4	Distributions, Mean Values and Distribution Functions	1-7
1.5	The Maxwell Distribution of Speeds	1-12
1.5.1	The speed distribution must be an even function of v	1-13
1.5.2	The speed distributions are independent and uncorrelated.	1-13
1.5.3	$\langle v^2 \rangle$ should agree with the ideal gas law.	1-15
1.5.4	The distribution depends only on the speed.	1-18
1.5.5	Experimental Measurement of the Maxwell Distribution of Speeds	1-24
1.6	Energy Distributions	1-26
1.7	Collisions: Mean Free Path and Collision Number	1-30
1.8	Summary	1-36
Appendix 1.1	The Functional Form of the Velocity Distribution	1-39
Appendix 1.2	Spherical Coordinates	1-40
Appendix 1.3	The Error Function and Co-Error Function	1-41
Appendix 1.4	The Center-of-Mass Frame	1-43
Suggested Reading	1-46
Chapter 1	Problems	1-47

Chapter 1 Kinetic Theory of Gases

1.1 Introduction

The overall objective of this chapter is to understand macroscopic properties such as pressure and temperature on a microscopic level. We will find that the pressure of an ideal gas can be understood by applying Newton's law to the microscopic motion of the molecules making up the gas and that a comparison between the Newtonian prediction and the ideal gas law can provide a function which describes the distribution of molecular velocities. This distribution function can in turn be used to learn about the frequency of molecular collisions. Since molecules can react only as fast as they collide with one another, the collision frequency provides an upper limit on the reaction rate.

The outline of the discussion is as follows. By applying Newton's laws to the molecular motion we will find that the product of the pressure and the volume is proportional to the average of the square of the molecular velocity, $\langle v^2 \rangle$, or equivalently to the average molecular translational energy $\langle \epsilon \rangle$. In order for this result to be consistent with the observed ideal gas law, the temperature T of the gas must also be proportional to $\langle v^2 \rangle$ or $\langle \epsilon \rangle$. We will then consider in detail how to determine the average of the square of the velocity from a distribution of velocities, and we will use the proportionality of T with $\langle v^2 \rangle$ to determine the Maxwell-Boltzmann distribution of speeds. This distribution, $F(v)dv$, tells us the number of molecules with speeds between v and $v+dv$. The speed distribution is closely related to the distribution of molecular energies, $G(\epsilon)d\epsilon$. Finally, we will use the velocity distribution to calculate the number of collisions Z that a molecule makes with other molecules in the gas per unit time. Since in later chapters we will argue that a reaction between two molecules requires that they collide, the collision rate Z provides an upper limit to the rate of a reaction. A related quantity λ is the average distance a molecule travels between collisions or the *mean free path*.

The history of the kinetic theory of gases is a checkered one, and serves to dispel the impression that science always proceeds along a straight and logical path.^a In 1662 Boyle found that for a specified quantity of gas held at a fixed temperature the product of the pressure and the volume was a constant. Daniel Bernoulli derived this law in 1738 by applying Newton's equations of motion to the molecules comprising the gas, but his work appears to have been ignored for more than a century.^b A school teacher in Bombay, India named John James Waterston submitted a paper to the Royal Society in 1845 outlining many of the concepts that underlie our current understanding of gases. His paper was rejected as "nothing but nonsense, unfit even for reading before the Society." Bernoulli's contribution was rediscovered in 1859, and several decades later in 1892, after Joule (1848) and Clausius (1857)

^aThe history of the kinetic theory of gases is outlined by E. Mendoza, *Physics Today*, **14**, 36-39 (1961).

^bA translation of this paper has appeared in *The World of Mathematics*, J. R. Newman, ed., Volume 2 (Simon and Schuster, New York, 1956), p. 774.

had put forth similar ideas, Lord Rayleigh found Waterston's manuscript in the Royal Society archives. It was subsequently published in *Philosophical Transactions*. Maxwell (*Illustrations of Dynamical Theory of Gases*, 1859-1860) and Boltzmann (*Vorlesungen über Gastheorie*, 1896-1898) expanded the theory into its current form.

1.2 Pressure of an Ideal Gas

We start with the basic premise that the pressure exerted by a gas on the wall of a container is due to collisions of molecules with the wall. Since the number of molecules in the container is large, the number colliding with the wall per unit time is large enough so that fluctuations in the pressure due to the individual collisions are immeasurably small in comparison to the total pressure. The first step in the calculation is to apply Newton's laws to the molecules in order to show that the product of the pressure and the volume is proportional to the average of the square of the molecular velocity, $\langle v^2 \rangle$.

Consider molecules with a velocity component v_x in the x direction and a mass m . Let the molecules strike a wall of area A located in the z - y plane, as shown in **Figure 1.1**. We would first like to know how many molecules strike the wall in a time Δt , where Δt is short compared to the time between molecular collisions. The distance along the x axis that a molecule travels in the time Δt is simply $v_x \Delta t$, so that all molecules located in the volume $Av_x \Delta t$ and moving toward the wall will strike it. Let n^* be the number of molecules per unit volume. Since one half of the molecules will be moving toward the wall in the $+x$ direction while the other half will be moving in the $-x$ direction, the number of molecules which will strike the wall in the time Δt is $\frac{1}{2}n^*Av_x\Delta t$.

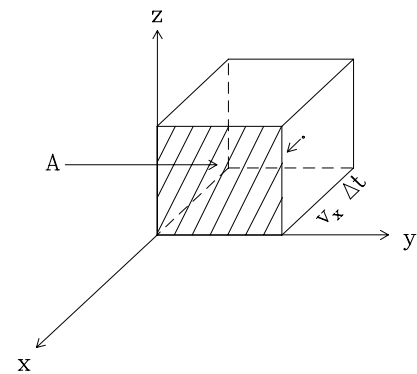


Figure 1.1 All the molecules in the box that are moving toward the z - y plane will strike the wall.

The force on the wall due to the collision of a molecule with the wall is given by Newton's Law: $F = ma = mdv/dt = d(mv)/dt$, and integration yields $F\Delta t = \Delta(mv)$. If a molecule rebounds elastically (without losing energy) when it hits the wall, its momentum is changed from $+mv_x$ to $-mv_x$, so that the total momentum change is $\Delta(mv) = 2mv_x$. Consequently, $F\Delta t = 2mv_x$ for one molecular collision, and $F\Delta t = (\frac{1}{2}n^*Av_x\Delta t)(2mv_x)$ for the total number of collisions. Canceling Δt from both sides and recognizing that the pressure is the force per unit area, $p = F/A$, we obtain $p = n^*mv_x^2$.

Of course, not all molecules will be traveling with the same velocity v_x . We will learn below how to characterize the distribution of molecular velocities, but for now let us simply assume that the pressure will be proportional to the average of the square of the velocity in

the x direction, $p = n^* m \langle v_x^2 \rangle$.^c The total velocity of an individual molecule most likely contains other components along y and z . Since $\mathbf{v} = \hat{i}v_x + \hat{j}v_y + \hat{k}v_z$,^d where \hat{i} , \hat{j} , and \hat{k} are unit vectors in the x , y , and z directions, respectively, $\mathbf{v}^2 = v_x^2 + v_y^2 + v_z^2$ and $\langle \mathbf{v}^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$. In an isotropic gas the motion of the molecules is random, so there is no reason for the velocity in one particular direction to differ from that in any other direction. Consequently, $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \langle v^2 \rangle / 3$. When we combine this result with the calculation above for the pressure, we obtain

$$p = \frac{1}{3} n^* m \langle v^2 \rangle. \quad (1.1)$$

Of course, n^* in (1.1) is the number of molecules per unit volume and can be rewritten as nN_A/V , where N_A is Avogadro's number and n is the number of moles. The result is

$$pV = \frac{1}{3} n N_A m \langle v^2 \rangle. \quad (1.2)$$

Since the average kinetic energy of the molecules is $\langle \epsilon \rangle = \frac{1}{2} m \langle v^2 \rangle$, another way to write (1.2) is

$$pV = \frac{2}{3} n N_A \langle \epsilon \rangle. \quad (1.3)$$

Equations (1.2) and (1.3) bear a close resemblance to the ideal gas law, $pV = nRT$. The ideal gas law tells us that the product of p and V will be constant if the temperature is constant, while (1.2) and (1.3) tell us that the product will be constant if $\langle v^2 \rangle$ or $\langle \epsilon \rangle$ is constant. The physical basis for the constancy of pV with $\langle v^2 \rangle$ or $\langle \epsilon \rangle$ is clear from our previous discussion. If the volume is increased while the number, energy, and velocity of the molecules remain constant, then a longer time will be required for the molecules to reach the walls; there will thus be fewer collisions in a given time, and the pressure will decrease. To identify (1.3) with the ideal gas law, we need to consider in more detail the relationship between temperature and energy.

^cIn this text, as in many others, we will use the notation $\langle x \rangle$ or \bar{x} to mean "the average value of x ."

^dThroughout the text we will use **boldface** symbols to indicate vector quantities and normal weight symbols to indicate scalar quantities. Thus, $v = |\mathbf{v}|$. Note that $\mathbf{v}^2 = \mathbf{v} \cdot \mathbf{v} = v^2$.

1.3 Temperature and Energy

Consider two types of molecule in contact with one another. Let the average energy of the first type be $\langle \epsilon \rangle_1$ and that of the second type be $\langle \epsilon \rangle_2$. If $\langle \epsilon \rangle_1$ is greater than $\langle \epsilon \rangle_2$, then when molecules of type 1 collide with those of type 2, energy will be transferred from the former to the latter. This energy transfer is a form of heat flow. From a macroscopic point of view, as heat flows the temperature of a system of the type 1 molecules will decrease, while that of the type 2 molecules will increase. Only when $\langle \epsilon \rangle_1 = \langle \epsilon \rangle_2$ will the temperatures of the two macroscopic systems be the same. In mathematical terms, we see that $T_1 = T_2$ when $\langle \epsilon \rangle_1 = \langle \epsilon \rangle_2$ and that $T_1 > T_2$ when $\langle \epsilon \rangle_1 > \langle \epsilon \rangle_2$. Consequently, there must be a correspondence between $\langle \epsilon \rangle$ and T so that the latter is some function of the former: $T = T(\langle \epsilon \rangle)$.

The functional form of the dependence of T on $\langle \epsilon \rangle$ cannot be determined solely from kinetic theory, since the temperature scale may be chosen in many possible ways. In fact, one way to define the temperature is through the ideal gas law: $T = pV/(nR)$. Experimentally, this corresponds to measuring the temperature either by measuring the volume of an ideal gas held at constant pressure or by measuring the pressure of an ideal gas held at constant volume. Division of both sides of (1.3) by nR and use of the ideal gas relation gives us the result

$$T = \frac{pV}{nR} = \frac{2}{3} \frac{N_A}{R} \langle \epsilon \rangle, \quad (1.4)$$

or

$$\langle \epsilon \rangle = \frac{3}{2} kT, \quad (1.5)$$

where k , known as Boltzmann's constant, is defined as R/N_A . Note that since $\langle \epsilon \rangle = \frac{1}{2}m\langle v^2 \rangle$,

$$\langle v^2 \rangle = \frac{3kT}{m}. \quad (1.6)$$

Example 1.1 Calculation of average energies and squared velocities

<i>Objective</i>	Calculate the average molecular energy, $\langle \epsilon \rangle$, and the average squared velocity, $\langle v^2 \rangle$, for a nitrogen molecule at $T=300$ K.
<i>Method</i>	Use (1.5) and (1.6) with $m = (28 \text{ gm/mole}) (1 \text{ kg}/1000 \text{ gm}) / (N_A \text{ molecule/mole})$ and $k=1.38 \times 10^{-23} \text{ J/K}$.
<i>Solution</i>	$\langle \epsilon \rangle = 3kT/2 = 3 (1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})/2 = 6.21 \times 10^{-21} \text{ J}.$ $\langle v^2 \rangle = 3kT/m = 3(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K}) / [(28/6.02 \times 10^{26})] = 2.67 \times 10^5 \text{ (m/s)}^2 = (516 \text{ m/s})^2.$

To summarize the discussion so far, we have seen from (1.2) that pV is proportional to $\langle v^2 \rangle$ and that the ideal gas law is obtained if we take the definition of temperature to be that embodied in (1.5). Since $\langle \epsilon \rangle = \frac{1}{2} m \langle v^2 \rangle$, both temperature and pV are proportional to the average of the square of the velocity. The use of an average recognizes that not all the molecules will be moving with the same velocity. In the next few sections we consider the *distribution* of molecular speeds. But first we must consider what we mean by a distribution.

1.4 Distributions, Mean Values and Distribution Functions

Suppose that five students take a chemistry examination for which the possible grades are integers in the range from 0 to 100. Let their scores be $S_1=68, S_2=76, S_3=83, S_4=91, S_5=97$. The average score for the examination is then

$$\langle S \rangle = (S_1 + S_2 + S_3 + S_4 + S_5) / N_T = \frac{1}{N_T} \sum_{i=1}^{N_T} S_i \quad (1.7)$$

where $N_T = 5$ is the number of students. In this case the average is easily calculated to be 83.

Now suppose that the class had 500 students rather than 5. Of course, the average grade could be calculated in a manner similar to that in (1.7) with an index i running from 1 to $N_T = 500$. However, another method will be instructive. Clearly, if the examination is still graded to one point accuracy, it is certain that more than one student will receive the same score. Suppose that, instead of summing over the students, represented by the index i in (1.7), we form the average by summing over the scores themselves, which range in integer possibili-

ties from $j=0$ to 100. In this case, to obtain the average, we must weight each score S_j by the number of students who obtained that score, N_j :

$$\langle S \rangle = \frac{1}{N_T} \sum_{j=0}^{100} S_j N_j \quad (1.8)$$

Note that the definition of N_j requires that $\sum N_j = N_T$. The factor $1/N_T$ in (1.8) is included for normalization, since, for example, if all the students happened to get the same score $S_j = S$ then

$$\langle S \rangle = \frac{1}{N_T} \sum_j S_j N_j = \frac{S}{N_T} \sum_j N_j = S. \quad (1.9)$$

Now let us define the probability of obtaining score S_j as the fraction of students receiving that score:

$$P_j = \frac{N_j}{N_T}. \quad (1.10)$$

Then another way to write (1.8) is

$$\langle S \rangle = \sum_j S_j P_j, \quad (1.11)$$

where $\sum_j P_j = 1$ from normalization.

Equation (1.11) provides an alternative to (1.7) for finding the average score for the class. Furthermore, we can generalize (1.11) to provide a method for finding the average of *any* quantity,

$$\langle Q \rangle = \sum_j P_j Q_j, \quad (1.12)$$

where P_j is the probability of finding the j^{th} result.

Example 1.2 Calculating Averages from Probabilities

<i>Objective</i>	Find the average throw for a pair of dice.
<i>Method</i>	Each die is independent, so the average of the sum of the throws will be twice the average of the throw for one die. Use (1.12) to find the average throw for one die.
<i>Solution</i>	The probability for each of the six outcomes, 1-6, is the same, namely 1/6. Factoring this out of the sum gives $\langle T \rangle = (1/6) \sum T_i$, where $T_i = 1, 2, 3, 4, 5, 6$ for $i=1-6$. The sum is 21, so that the average throw for one die is $\langle T \rangle = 21/6 = 3.5$. For the sum of two dice, the average would thus be 7.

The method can be extended to calculate more complicated averages. Let $f(Q_j)$ be some arbitrary function of the observation Q_j . Then the average value of the function $f(Q)$ is given by

$$\langle f(Q) \rangle = \sum_j P_j f(Q_j). \quad (1.13)$$

For example, if Q were the square of a score, then

$$\langle S^2 \rangle = \sum_j P_j S_j^2. \quad (1.14)$$

Suppose now that the examination is a very good one, indeed, and that the talented instructor can grade it not just to one point accuracy (a remarkable achievement in itself!) but to an accuracy of dS , where dS is a very small fraction of a point. Let $P(S)dS$ be the probability that a score will fall in the range between S and $S+dS$, and let dS become infinitesimally small. The fundamental theorems of calculus tell us that we can convert the sum in (1.11) to the integral

$$\langle S \rangle = \int P(S) S dS, \quad (1.15)$$

or, more generally for any observable quantity,

$$\langle Q \rangle = \int P(Q) Q dQ. \quad (1.16)$$

Equation (1.16) will form the basis for much of our further work. The probability function $P(Q)$ is sometimes called a *distribution function*, and the range of the integral is over all values of Q where the probability is non-zero. Note that normalization of the probability requires

$$\int P(Q) dQ = 1. \quad (1.17)$$

The quantity $|\psi(x)|^2 dx$ is simply a specific example of a distribution function. Although knowledge of quantum mechanics is not necessary to solve it, you may recognize a connection to the particle in the box in Problem 1.7, which like **Example 1.3** is an exercise with distribution functions.

Example 1.3 Determining distribution functions

<i>Objective</i>	Bees like honey. A sphere of radius r_0 is coated with honey and hanging in a tree. Bees are attracted to the honey such that the average number of bees per unit volume is given by Kr^{-5} , where K is a constant and r is the distance from the center of the sphere. Derive the normalized distribution function for the bees. They can be at any distance from the honey, but they cannot be inside the sphere. Using this distribution, calculate the average distance of a bee from the center of the sphere.
<i>Method</i>	First we need to find the normalization constant K by applying (1.17), recalling that we have a three-dimensional problem and that in spherical coordinates the volume element for a problem that does not depend on the angles is $4\pi r^2 dr$. Then, to evaluate the average, we apply (1.16).
<i>Solution</i>	Recall that, by hypothesis, there is no probability for the bees being at $r < r_0$, so that the range of integration is from r_0 to infinity. To determine K we require

$$\int_{r_0}^{\infty} (Kr^{-5}) 4\pi r^2 dr = 1, \quad (1.18)$$

or,

$$4\pi K \int_{r_0}^{\infty} r^{-3} dr = 1 =$$

$$4\pi K \left(-\frac{r^{-2}}{2} \right) \Bigg|_{r_0}^{\infty} = \frac{4\pi K}{2r_0^2}, \quad (1.19)$$

so that

$$K = \frac{r_0^2}{2\pi}.$$

Having determined the normalization constant, we now calculate the average distance:

$$\begin{aligned}
 \langle r \rangle &= \int_{r_0}^{\infty} r \left(\frac{r_0^2}{2\pi} \right) r^{-5} 4\pi r^2 dr = \\
 &2r_0^2 \int_{r_0}^{\infty} r^{-2} dr = \qquad \qquad \qquad (1.20) \\
 &2r_0^2 (-r^{-1}) \Big|_{r_0}^{\infty} = 2r_0^2 (1/r_0) = 2r_0
 \end{aligned}$$

1.5 The Maxwell Distribution of Speeds

We turn now to the distribution of molecular speeds. We will denote the probability of finding v_x in the range from v_x to v_x+dv_x , v_y in the range from v_y to v_y+dv_y , and v_z in the range from v_z to v_z+dv_z by $F(v_x, v_y, v_z)dv_x dv_y dv_z$. The object of this section is to determine the function $F(v_x, v_y, v_z)$. There are four main points in the derivation:

- 1) In each direction, the speed distribution must be an even function of v ,
- 2) The speed distribution in any particular direction is independent from and uncorrelated with the distributions in orthogonal directions,
- 3) The average of the square of the velocity $\langle v^2 \rangle$ obtained using the distribution function should agree with the value required by the ideal gas law: $\langle v^2 \rangle = 3kT/m$, and
- 4) The three-dimensional velocity distribution depends only on the magnitude of v (*i.e.*, the speed) and not on the direction.

We now examine these four points in detail.

1.5.1 The speed distribution must be an even function of v .

Consider the velocities v_x of molecules contained in a box. The number of molecules moving in the positive x direction must be equal to the number of molecules moving in the negative x direction. This conclusion is easily seen by examining the consequences of the contrary assumption. If the number of molecules moving in each direction were not the same, then the pressure on one side of the box would be greater than on the other. Aside from violating experimental evidence that the pressure is the same wherever it is measured in a closed system, our common observation is that the box does not spontaneously move in either the positive or negative x direction, as would be likely if the pressures were substantially different. We conclude that the distribution function for the velocity in the x direction, or more generally in any arbitrary direction, must be symmetric; *i.e.*, $F(v_x) = F(-v_x)$. Functions possessing the property that $f(x) = f(-x)$ are called *even functions*, while those having the property that $f(x) = -f(-x)$ are called *odd functions*. We can ensure that $F(v_x)$ be an even function by requiring that the distribution function depend on the square of the velocity: $F(v_x) = f(v_x^2)$. As shown in the Section 1.5.3, this condition is also in accord with the Boltzmann distribution law.^e

1.5.2 The speed distributions are independent and uncorrelated.

We now consider the relationship between the distribution of x -axis speeds and y - or z -axis speeds. In short, there should be no relationship. The three components of the velocity are independent of one another since the velocities are uncorrelated. An analogy might be helpful. Consider the probability of tossing three honest coins and getting "heads" on each. Because the tosses t_i are independent, uncorrelated events, the joint probability for a throw of three heads, $P(t_1=heads, t_2=heads, t_3=heads)$, is simply equal to the product of the probabilities for the three individual events, $P(t_1=heads) \times P(t_2=heads) \times P(t_3=heads) = \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$. In a similar way, because the x -, y -, and z -axis velocities are independent and uncorrelated, we can write that

^eOther even functions, for example $F = f(v_x^4)$ would be mathematically acceptable, but would not satisfy the requirement of Section 1.5.3.

$$F(v_x, v_y, v_z) = F(v_x)F(v_y)F(v_z) . \quad (1.21)$$

We now use the conclusion of the previous section. We can write, for example, that $F(v_x)=f(v_x^2)$ and similarly for the other directions. Consequently,

$$\begin{aligned} F(v_x, v_y, v_z) &= F(v_x)F(v_y)F(v_z) = \\ &f(v_x^2)f(v_y^2)f(v_z^2) . \end{aligned} \quad (1.22)$$

What functional form has the property that $f(a+b+c) = f(a)f(b)f(c)$? A little thought leads to the exponential form, since $\exp(a+b+c) = e^a e^b e^c$. It can be shown, in fact, that the exponential is the *only* form having this property (see Appendix 1.1), so that we can write

$$F(v_x) = f(v_x^2) = K \exp(\pm \kappa v_x^2), \quad (1.23)$$

where K and κ are constants to be determined. Note that although κ can appear mathematically with either a plus or a minus sign, we must require the minus sign on physical grounds because we know from common experience that the probability of very high velocities should be small.

The constant K can be determined from normalization since, using (1.17), the total probability that v_x lies somewhere in the range from $-\infty$ to $+\infty$ should be unity:

$$\int_{-\infty}^{\infty} F(v_x) dv_x = 1. \quad (1.24)$$

Substitution of (1.23) into (1.24) leads to the equation

$$1 = K \int_{-\infty}^{\infty} \exp(-\kappa v_x^2) dv_x = K \left(\frac{\pi}{\kappa} \right)^{\frac{1}{2}}, \quad (1.25)$$

where the integral was evaluated using **Table 1.1**. The solution is then $K=(\kappa/\pi)^{1/2}$.

1.5.3 $\langle v^2 \rangle$ should agree with the ideal gas law.

The constant κ is determined by requiring $\langle v^2 \rangle$ to be equal to $3kT/m$, as in (1.6). From (1.16) we find

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 F(v_x) dv_x = \left(\frac{\kappa}{\pi} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} v_x^2 \exp(-\kappa v_x^2) dv_x. \quad (1.26)$$

The integral is a standard one listed in **Table 1.1**, and using its value we find that

$$\langle v_x^2 \rangle = \frac{1}{2} \left(\frac{\kappa}{\pi} \right)^{\frac{1}{2}} \left(\frac{\pi}{\kappa^3} \right)^{\frac{1}{2}} = \frac{1}{2\kappa}. \quad (1.27)$$

As a consequence, the average of the square of the total speed, $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\langle v_x^2 \rangle$, is simply

$$\langle v^2 \rangle = \frac{3}{2\kappa}. \quad (1.28)$$

From (1.6) we have that $\langle v^2 \rangle = 3kT/m$ for agreement with the ideal gas law, so that $3kT/m = 3/(2\kappa)$, or $\kappa = m/(2kT)$. The complete one-dimensional distribution function is thus

$$F(v_x)dv_x = \left(\frac{m}{2\pi kT} \right)^{\frac{1}{2}} \exp\left(-\frac{1}{2} \frac{mv_x^2}{kT} \right) dv_x. \quad (1.29)$$

This equation is known as the *One-Dimensional Maxwell-Boltzmann distribution for molecular speeds*. Plots of $F(v_x)$ are shown in **Figure 1.2**.

Table 1.1 Integrals of use in the kinetic theory of gases

$$\begin{array}{ll}
 \int_{-\infty}^{\infty} x^{2n} e^{-\beta x^2} dx = 2 \int_0^{\infty} x^{2n} e^{-\beta x^2} dx & \int_{-\infty}^{\infty} x^{2n+1} e^{-\beta x^2} dx = 0 \\
 \int_0^{\infty} e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\pi} \beta^{-\frac{1}{2}} & \int_0^{\infty} x e^{-\beta x^2} dx = \frac{1}{2} \beta^{-1} \\
 \int_0^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\pi} \frac{1}{2} \beta^{-\frac{3}{2}} & \int_0^{\infty} x^3 e^{-\beta x^2} dx = \frac{1}{2} \beta^{-2} \\
 \int_0^{\infty} x^4 e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\pi} \frac{3}{4} \beta^{-\frac{5}{2}} & \int_0^{\infty} x^5 e^{-\beta x^2} dx = \beta^{-3} \\
 \int_0^{\infty} x^{2n} e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\pi} \frac{(2n)! \beta^{-(n+1/2)}}{2^{2n} n!} & \int_0^{\infty} x^{2n+1} e^{-\beta x^2} dx = \frac{1}{2} (n!) \beta^{-(n+1)}
 \end{array}$$

Note that **(1.29)** is consistent with the Boltzmann Distribution Law, which states that the probability of finding a system with energy ϵ is proportional to $\exp(-\epsilon/kT)$. Since $\epsilon_x = \frac{1}{2} m v_x^2$ is equal to the translational energy of the molecule in the x direction, the probability of finding a molecule with an energy ϵ_x should be proportional to $\exp(-\epsilon_x/kT)$, as it is in **(1.29)**. In Section 1.5.1 we ensured $F(v_x)$ to be even by choosing it to depend on the square of the velocity, $F(v_x) = f(v_x^2)$. Had we chosen some other even function, say $F(v_x) = f(v_x^4)$, the final expression for the one-dimensional distribution would not have agreed with the Boltzmann Distribution Law.

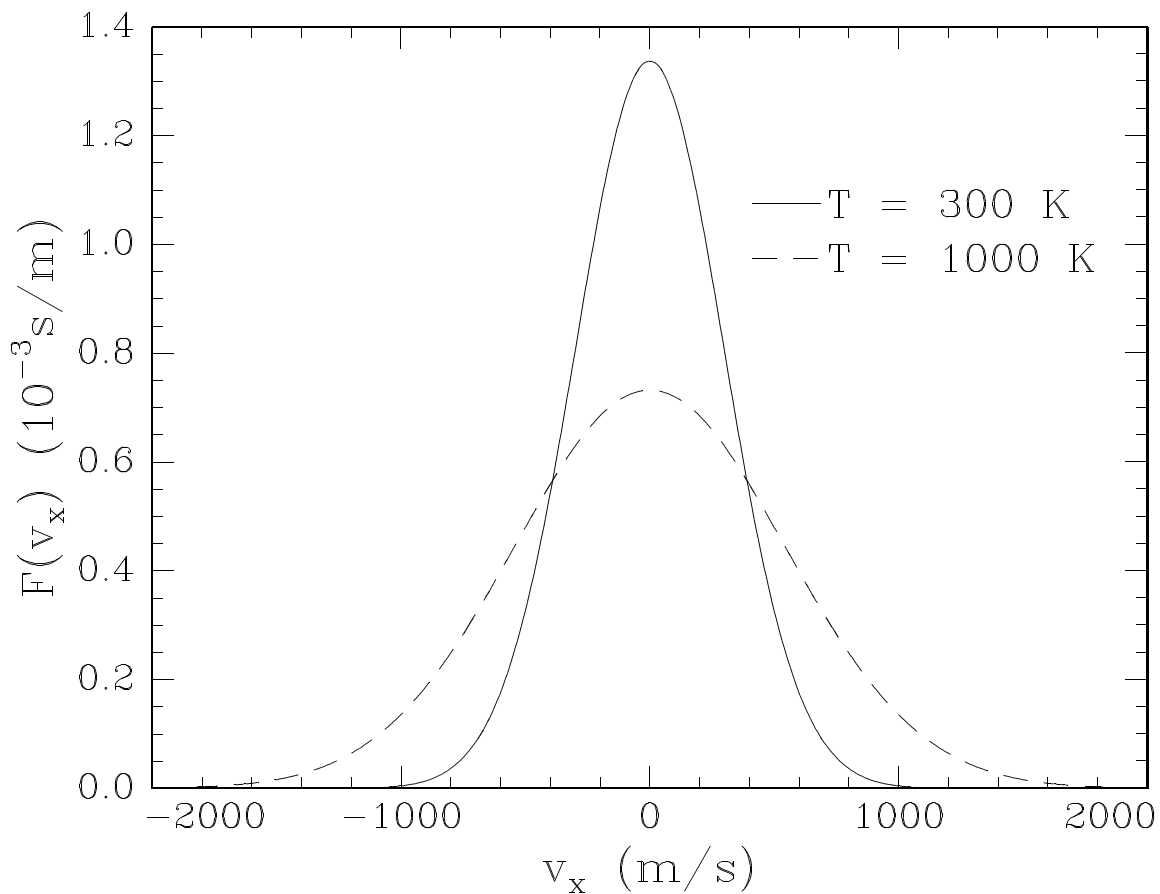


Figure 1.2 One dimensional velocity distribution for a mass of 28 amu and two temperatures.

Equation (1.29) provides the distribution of velocities in one dimension. In three dimensions, because $F(v_x, v_y, v_z) = F(v_x)F(v_y)F(v_z)$, and because $v^2 = v_x^2 + v_y^2 + v_z^2$, we find that the probability that the velocity will have components v_x between v_x and v_x+dv_x , v_y between v_y and v_y+dv_y , and v_z between v_z and v_z+dv_z is given by

$$F(v_x, v_y, v_z) dv_x dv_y dv_z = F(v_x)F(v_y)F(v_z) dv_x dv_y dv_z =$$

$$\left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT} \right) dv_x dv_y dv_z. \quad (1.30)$$

1.5.4 The distribution depends only on the speed.

Note that the right-hand side of (1.30) depends on v^2 and not on the directional property of \mathbf{v} . When we have a function that depends only on the length of the velocity vector, $v = |\mathbf{v}|$, and not on its direction, we can be more precise by saying that the function depends on the *speed* and not on the *velocity*. Since $F(v_x, v_y, v_z) = f(v^2)$ depends on the speed, it is often more convenient to know the probability that molecules have a speed in a particular range than to know the probability that their velocity vectors will terminate in a particular volume. As shown in **Figure 1.3**, the probability that the speed will be between v and $v+dv$ is simply the probability that velocity vectors will terminate within the volume of a spherical shell between the radius v and the radius $v+dv$. The volume of this shell is $dv_x dv_y dv_z = 4\pi v^2 dv$, so that the probability that speed will be in the desired range is^f

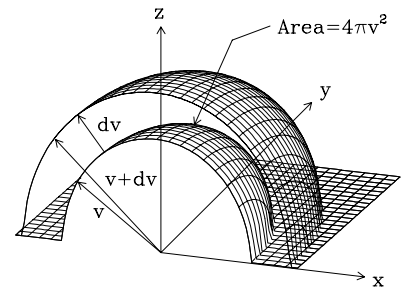


Figure 1.3 The shell between v and $v+dv$ has a volume of $4\pi v^2 dv$. The thickness of the shell is here exaggerated for clarity.

^fAn alternate method for obtaining (1.31) is to note that $dv_x dv_y dv_z$ can be written as $v^2 \sin\theta dv d\theta d\phi$ in spherical coordinates (see Appendix 1.2) and then to integrate over the angular coordinates. Since the distribution does not depend on the angular coordinates, the integrals over $d\theta$ and $d\phi$ simply give 4π and we are left with the factor $v^2 dv$.

$$F(v)dv = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} v^2 \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mv^2}{2kT} \right) \sin\theta dv d\theta d\phi$$

$$= \int_{\phi=0}^{2\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta d\theta v^2 \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mv^2}{2kT} \right) \sin\theta dv d\theta d\phi$$

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

$$F(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT} \right) dv. \quad (1.31)$$

By analogy to (1.29), we will call (1.31) the *Maxwell-Boltzmann speed distribution*. Speed distributions as a function of temperature are shown in **Figure 1.4**.

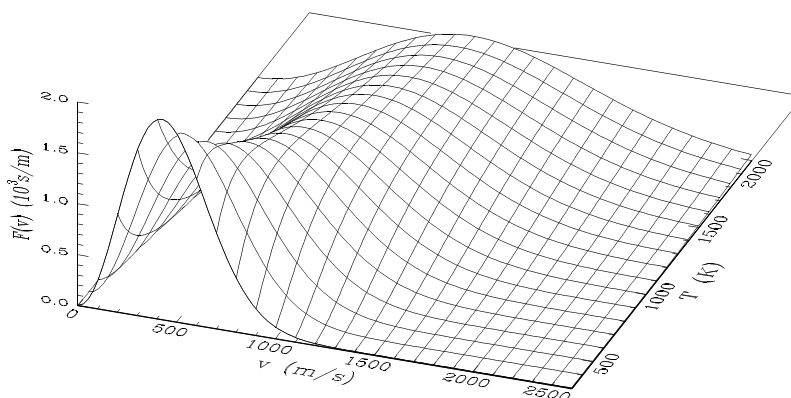


Figure 1.4 Maxwell-Boltzmann speed distribution as a function of temperature for a mass of 28 amu.

We often characterize the speed distribution by a single parameter, for example the temperature. Equivalently, we could specify one of several types of "average" speed, each of which is related to the temperature. One such average is called the *root-mean squared* speed and can be calculated from (1.6): $c_{rms} \equiv \langle v^2 \rangle^{1/2} = (3kT/m)^{1/2}$. Another speed in the *mean* speed defined by using (1.16) to calculate $\langle v \rangle$:

A more complete description of spherical coordinates is found in Appendix 1.2.

$$\begin{aligned} \langle v \rangle &= \int_0^{\infty} v F(v) dv = \\ & \int_0^{\infty} 4\pi v^2 \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT} \right) dv = \left(\frac{8kT}{\pi m} \right)^{\frac{1}{2}}, \end{aligned} \quad (1.32)$$

where the integral was evaluated using **Table 1.1** as described in detail in **Example 1.4**. Finally, the distribution might also be characterized by the *most probable* speed, c^* , the speed at which the distribution function has a maximum (Problem 1.8):

$$c^* = \left(\frac{2kT}{m} \right)^{\frac{1}{2}}. \quad (1.33)$$

The molecular speed is related to the speed of sound, since sound vibrations cannot travel faster than the molecules causing the pressure waves. For example, in **Example 1.5** we find that the most probable speed for O_2 is 322 m/s, while the speed of sound in O_2 is measured to be 330 m/s. For an ideal gas the speed of sound can be shown to be $(\gamma kT/m)^{1/2}$ where γ is the ratio of heat capacities, $\gamma = C_p/C_v$. The *Mach Number* is defined as the ratio of the speed of an object in a medium to the speed of sound through the same medium, so that when an aircraft "breaks the sound barrier" (or exceeds "Mach 1") it is actually traveling faster than the speed of the molecules in the medium.

Figure 1.5 shows the shape of the distribution function for $T=300$ K and the locations of the variously defined speeds.

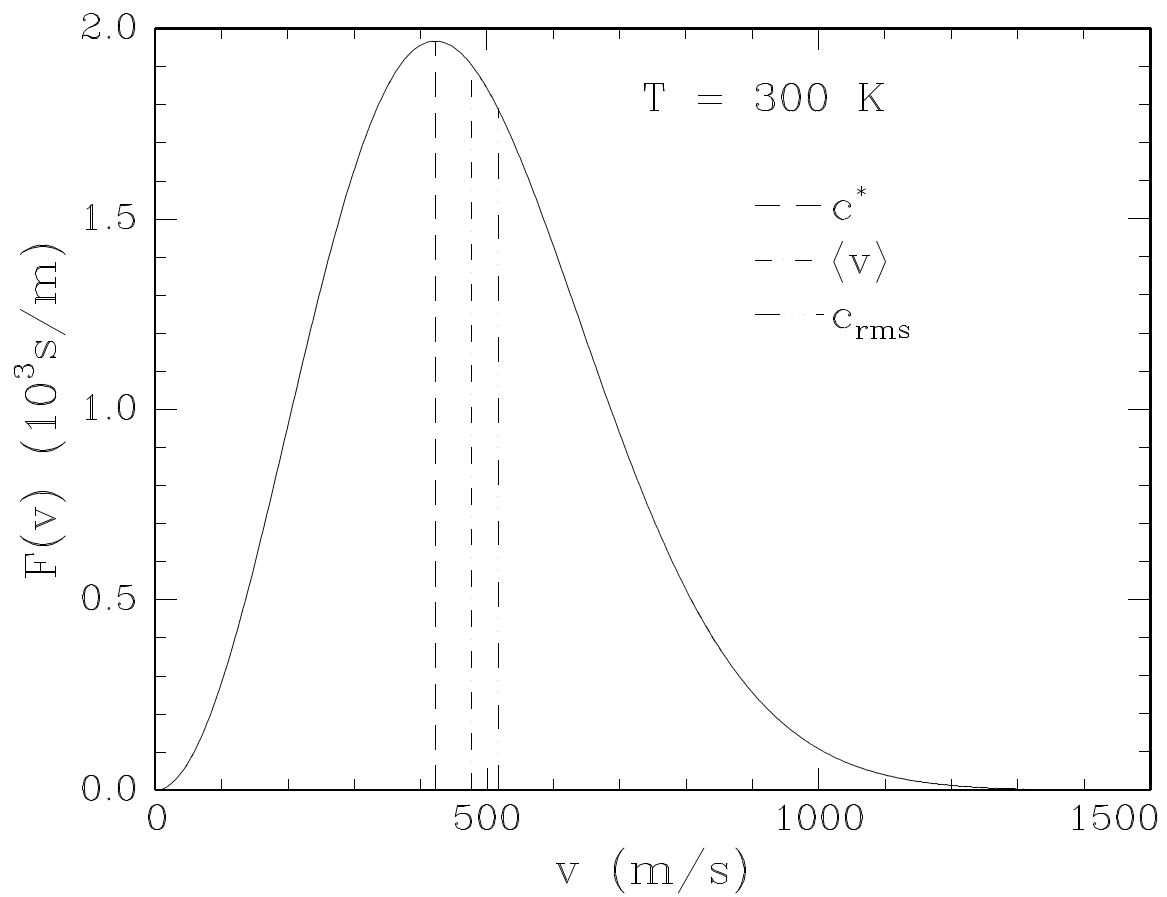


Figure 1.5 Maxwell-Boltzmann speed distribution for a mass of 28 amu and a temperature of 300 K. The vertical lines mark c^* , $\langle v \rangle$, and c_{rms} .

Example 1.4 Using the speed distribution

<i>Objective</i>	The speed distribution can be used to determine averages. For example, find the average speed, $\langle v \rangle$.
<i>Method</i>	Once one has the normalized distribution function, (1.16) gives the method for finding the average of any quantity. Identifying Q as the velocity and $P(Q)dQ$ as the velocity distribution function given in (1.31) , we see that we need to integrate $vF(v)dv$ from limits $v=0$ to $v=\infty$.

$$\begin{aligned}
 \langle v \rangle &= \int_0^{\infty} vF(v)dv = \int_0^{\infty} 4\pi v^3 \left(\frac{a^3}{\pi^{3/2}} \right) \exp(-a^2v^2)dv \\
 &= \frac{4}{\sqrt{\pi}} \int_0^{\infty} a^3 v^3 \exp(-a^2v^2)dv,
 \end{aligned}
 \tag{1.34}$$

where $a \equiv (m/2kT)^{1/2}$. We now transform variables by letting $x \equiv av$. The limits will remain unchanged, and $dv = dx/a$. Thus the integral in **(1.34)** becomes

$$\begin{aligned}
 &\frac{4}{a\sqrt{\pi}} \int_0^{\infty} x^3 \exp(-x^2)dx \\
 &= \frac{4}{a\sqrt{\pi}} \frac{1}{2} = \frac{2}{\sqrt{\pi}} \left(\frac{2kT}{m} \right)^{1/2} = \left(\frac{8kT}{\pi m} \right)^{1/2},
 \end{aligned}
 \tag{1.35}$$

where we have used **Table 1.1** to evaluate the integral.

Example 1.5 Comparison of the most probable speeds for oxygen and helium

<i>Objective</i>	Compare the most probable speed for O ₂ to that for He at 200 K.
<i>Method</i>	Use (1.33) with T=200 K and m=2 amu or m=32 amu. Note that the relative speeds should be proportional to $m^{-1/2}$.
<i>Solution</i>	$c^*(\text{He}) = (2kT/m)^{1/2} = [2(1.38 \times 10^{-23} \text{ J K}^{-1})(200 \text{ K})(6.02 \times 10^{23} \text{ amu/gm})(1000 \text{ gm/kg})/(2 \text{ amu})]^{1/2} = 1290 \text{ m/s}$. A similar calculation substituting 32 amu for 2 amu gives $c^*(\text{O}_2) = 322 \text{ m/s}$.
<i>Comment</i>	The escape velocity from the earth's gravitational field is roughly $v_e = 1.1 \times 10^4 \text{ m/s}$, only about ten times the most probable speed for helium. Because the velocity distribution shifts so strongly toward high velocities as the mass decreases, the fraction of helium atoms having speeds in excess of v_e , while minuscule (about 10^{-31}), is still 10^{475} times larger than the fraction of oxygen molecules having speeds in excess of v_e ! As a consequence, the composition of the atmosphere is changing; much of the helium released during the lifetime of the planet has already escaped into space. A plot of various speeds as a function of mass for T=300 K is shown in Figure 1.6 .

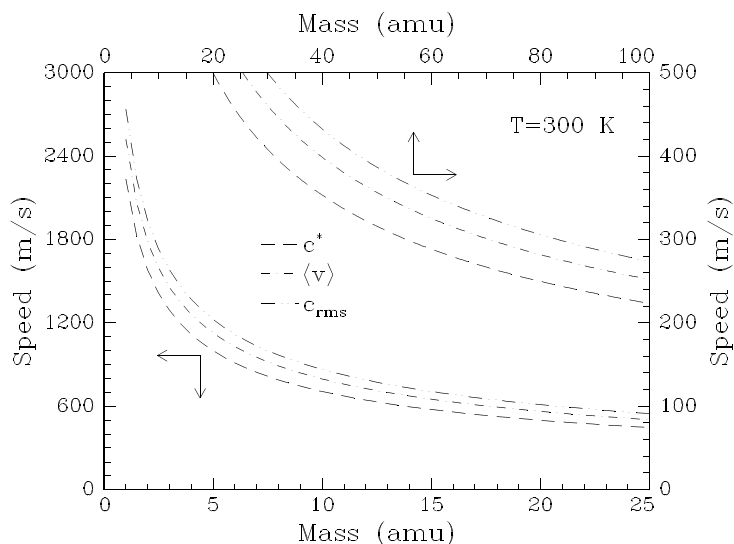


Figure 1.6 Various average speeds as a function of mass for $T=300\text{ K}$.

1.5.5 Experimental Measurement of the Maxwell Distribution of Speeds

Experimental verification of the Maxwell-Boltzmann speed distribution can be made by direct measurement using the apparatus of **Figure 1.7**. Two versions of the measurement are shown. In **Figure 1.7a**, slits (S) define a beam of molecules moving in a particular direction after effusing from an oven (O). Those that reach the detector (D) must successfully have traversed a slotted, multi-wheel chopper by traveling a distance d while the chopper rotated through an angle ϕ . In effect, the chopper selects a small slice from the velocity distribution and passes it to the detector. The speed distribution is then measured by recording the integrated detector signal for each cycle of the chopper as a function of the angular speed of the chopper.

A somewhat more modern technique, illustrated in **Figure 1.7b**, clocks the time it takes for molecules to travel a fixed distance. A very short pulse of molecules leaves the chopper at time $t=0$. Because these molecules have a distribution of speeds, they spread out in space as they travel toward the detector, which records as a function of time the signal due to molecules arriving a distance L from the chopper.

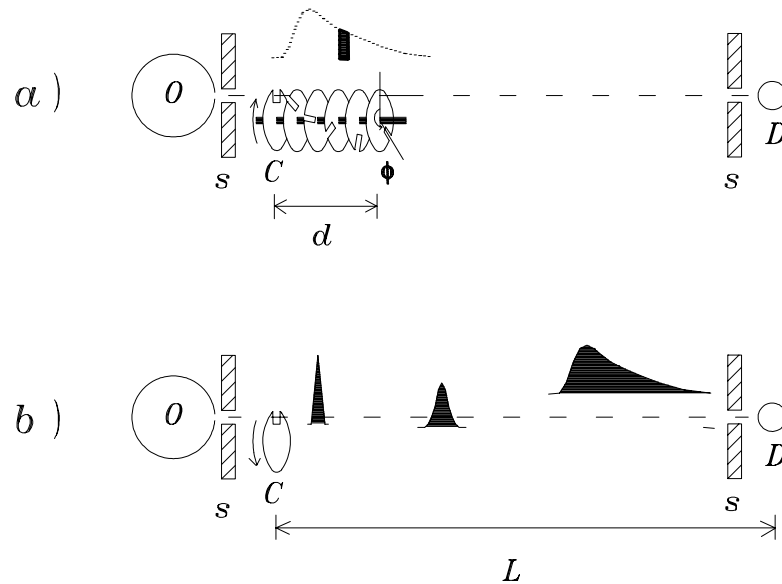


Figure 1.7 Two methods for measuring the Maxwell-Boltzmann speed distribution.

Analysis of the detector signal from this second experiment is instructive, since it introduces the concept of *flux*. Recall that the distribution $F(v)dv$ gives the fraction of molecules with speeds in the range from v to $v+dv$; it is dimensionless. If the number density of molecules is n^* , then $n^*F(v)dv$ will be the number of molecules per unit volume with speeds in the specified range. The *flux* of molecules is defined as the number of molecules crossing a unit area per unit time. It is equal to the density of molecules times their velocity: flux (number/m² s) = density (number/m³) × velocity (m/s).^g Thus, the flux J of molecules with speeds between v and $v + dv$ is

$$J dv = v n^* F(v) dv. \tag{1.36}$$

^gStrictly speaking, the flux, \mathbf{J} , is a vector, since the magnitude of the flux may be different in different directions. Here, since the direction of the flux is clear, we will use just its magnitude, J .

We will consider the flux in more detail in Section 4.3.2 and make extensive use of it in Chapter 4.

We now return to the speed measurement. Most detectors actually measure the number of molecules in a particular volume during a particular time duration. For example, the detector might measure current after ionizing those molecules that enter a volume defined by a cross-sectional area of A and a length ℓ . Because molecules with high velocity traverse the distance ℓ in less time than molecules with low velocity, the detection sensitivity is proportional to $1/v$. The detector signal $S(t)$ is thus proportional to $JA\ell dv/v$, or to $n^*A\ell F(v)dv$, where n^* is the number density of molecules in the oven. Assuming that a very narrow pulse of molecules is emitted from the chopper, the speed measured at a particular time t is simply $v = L/t$. We must now transform the velocity distribution from a speed distribution to a time distribution. Note that $dv = d(L/t) = -Ldt/t^2$ and recall from (1.31) that $F(v)dv \propto v^2 \exp(-\beta v^2)dv \propto (1/t^2) \exp(-\beta L^2/t^2)(L/t^2)$. We thus find that $S(t) \propto t^{-4} \exp(-\beta L^2/t^2)$. **Figure 1.8** displays a arrival time distribution of helium measured using this "time-of-flight" technique. The open circles are the detector signal, while the smooth line is a fit to the data of a function of the form expected for $S(t)$. The best fit parameter gives a temperature of 300 K.

1.6 Energy Distributions

It is sometimes interesting to know the distribution of molecular energies rather than velocities. Of course, these two distributions must be related since the molecular translational energy ϵ is equal to $\frac{1}{2}mv^2$. Noting that this factor occurs in the exponent of equation (1.31) and that $d\epsilon = mv dv = (2m\epsilon)^{1/2}d\epsilon$, we can convert velocities to energies in (1.31) to obtain

$$\begin{aligned}
 G(\epsilon)d\epsilon &= 4\pi \left(\frac{2\epsilon}{m} \right) \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left(-\frac{\epsilon}{kT} \right) \frac{d\epsilon}{\sqrt{2m\epsilon}} \\
 &= 2\pi \left(\frac{1}{\pi kT} \right)^{\frac{3}{2}} \sqrt{\epsilon} \exp\left(-\frac{\epsilon}{kT} \right) d\epsilon.
 \end{aligned}
 \tag{1.37}$$

The function $G(\epsilon)d\epsilon$ tells us the fraction of molecules which have energies in the range between ϵ and $\epsilon+d\epsilon$. Plots of $G(\epsilon)$ are shown in **Figure 1.9**.

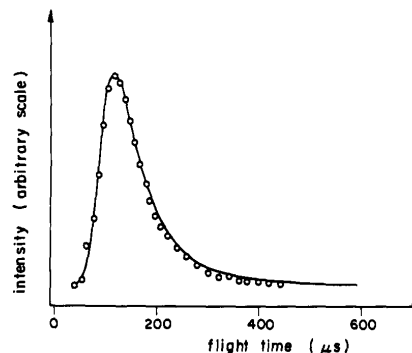


Figure 1.8 Time-of-flight measurement: intensity as a function of flight time. [from J. F. C. Wang and H. Y. Wachman, as illustrated in F. O. Goodman and H. Y. Wachman, *Dynamics of Gas-Surface Scattering*, (Academic Press, New York, 1976)]

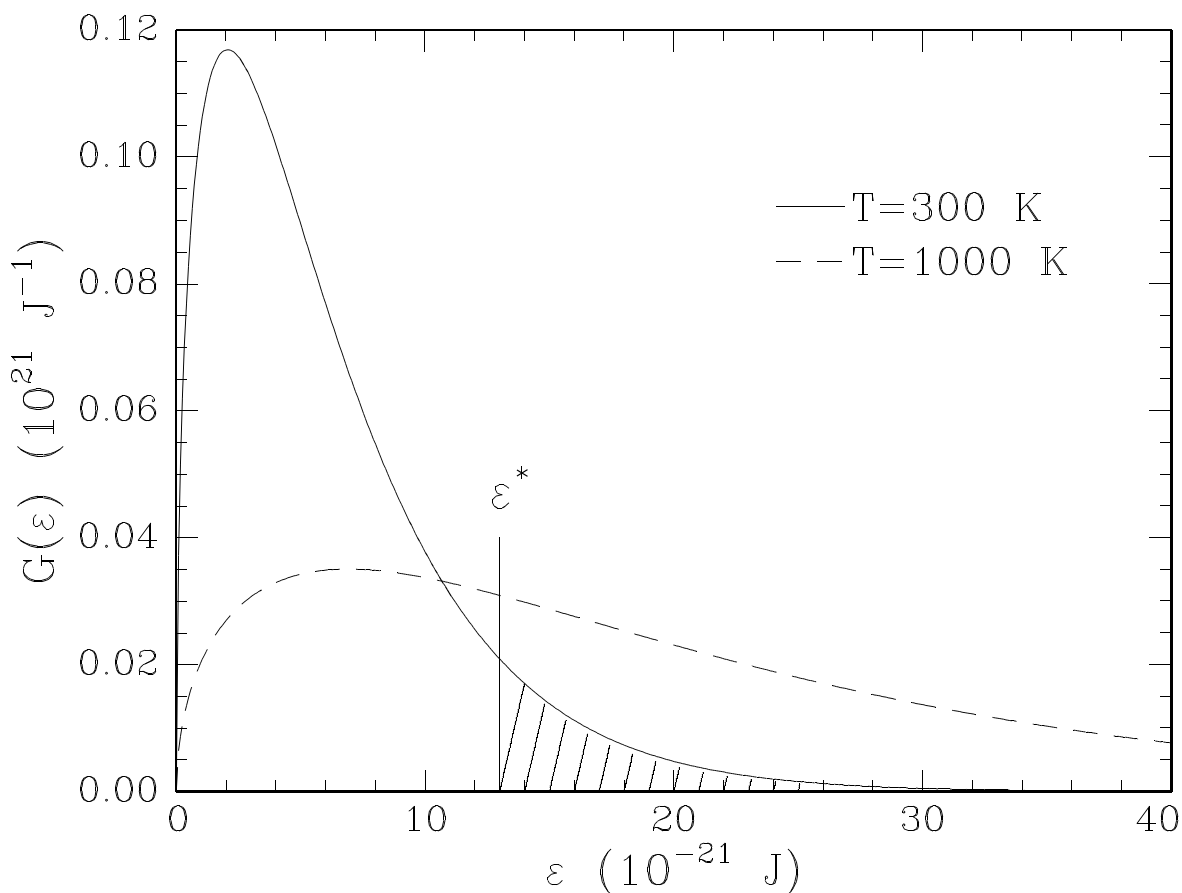


Figure 1.9 Energy distributions for two different temperatures. The fraction of molecules for the 300 K distribution having energy in excess of ϵ^* is shown in the hatched region.

The distribution function $G(\epsilon)$ can be used to calculate the average of any function of ϵ using the relationship (1.16). In particular, it can be shown as expected that $\langle \epsilon \rangle = 3kT/2$ (see Problem 1.9).

Let us pause here to make a connection with thermodynamics. In the case of an ideal monatomic gas, there are no contributions to the energy of the gas from internal degrees of freedom such as rotation or vibration, and there is normally very little contribution to the energy from excitation of electronic degrees of freedom. Consequently, the average energy U of n moles of a monatomic gas is simply nN_A times the average energy of one molecule of the gas, or

$$U = nN_A \frac{3}{2} kT = \frac{3}{2} nRT. \quad (1.38)$$

Note that the heat capacity at constant volume is defined as $C_V = (\partial U / \partial T)_V$, so that for an ideal monatomic gas we find that

$$C_V = \frac{3}{2} nR. \quad (1.39)$$

This result is an example of the Equipartition Principle, which states that each term in the expression of the molecular energy that is quadratic in a particular coordinate contributes $\frac{1}{2}kT$ to the average kinetic energy and $\frac{1}{2}R$ to the molar heat capacity. Since there are three quadratic terms in the three-dimensional translational energy expression, the molar heat capacity of a monatomic gas should be $3R/2$.

It is sometimes useful to know what fraction of molecules has an energy greater than or equal to a certain value ϵ^* . In principle, the energy distribution $G(\epsilon)$ should be able to provide this information, since the fraction of molecules having energy in the desired range is simply the integral of $G(\epsilon)d\epsilon$ from ϵ^* to infinity, as shown by the hatched region in **Figure 1.9**. In practice, the mathematics are somewhat cumbersome, but the result is reasonable. Let $f(\epsilon^*)$ be the fraction of molecules with kinetic energy equal to or greater than ϵ^* . This fraction is given by the integral

$$f(\epsilon^*) = 2\pi \left(\frac{1}{\pi kT} \right)^{\frac{3}{2}} \int_{\epsilon^*}^{\infty} \sqrt{\epsilon} \exp(-\epsilon/kT) d\epsilon. \quad (1.40)$$

Problem 1.10 shows that this integral is given by

$$f(\epsilon^*) = \frac{2}{\sqrt{\pi}} a e^{-a^2} + \operatorname{erfc}(a), \quad (1.41)$$

where $a = (\epsilon^*/kT)^{1/2}$ and $\operatorname{erfc}(a)$ is the co-error function defined in Appendix 1.3. A plot of $f(\epsilon^*)$ as a function of ϵ^*/kT is shown in **Figure 1.10**. Note that for $\epsilon^* > 3kT$, the function $f(\epsilon^*)$ is nearly equal to the first term in (1.41), $2\sqrt{\epsilon^*/\pi kT} \exp(-\epsilon^*/kT)$, shown by the dashed line in the figure. Thus, the fraction of molecules with energy greater than ϵ^* falls off as $\sqrt{\epsilon^*} \exp(-\epsilon^*/kT)$, provided that $\epsilon^* > 3kT$.

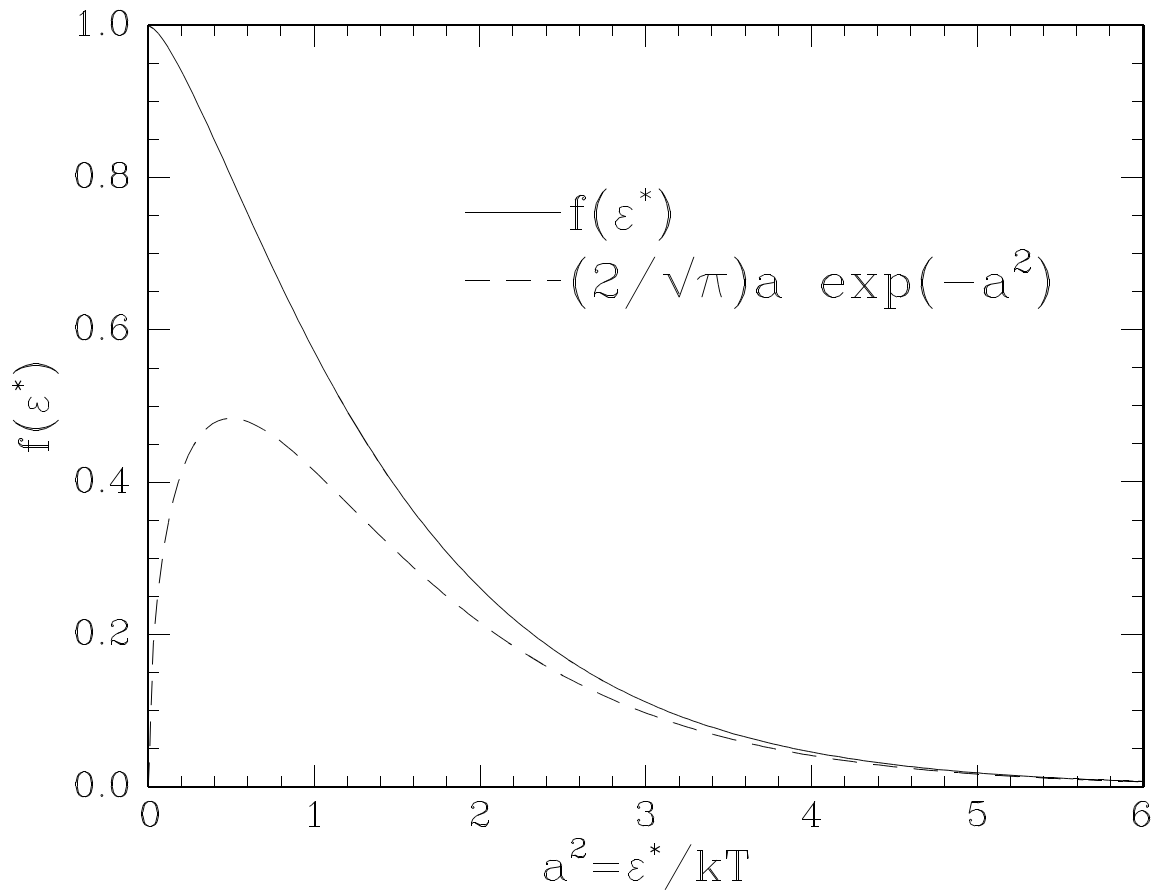


Figure 1.10 The fraction of molecules having energy in excess of ϵ^* as a function of ϵ^*/kT .

1.7 Collisions: Mean Free Path and Collision Number

One of the goals of this chapter is to derive an expression for the number of collisions that molecules of type 1 make with molecules of type 2 in a given time. We will argue later that this collision rate provides an upper limit to the reaction rate, since the two species must have a close encounter to react.

The principal properties of the collision rate can be easily appreciated by anyone who has ice skated at a local rink. Imagine two groups of skaters, some rather sedate adults and some rambunctious 13-year-old kids. If there is only one kid and one adult in the rink, then the likelihood that they will collide is small, but as the number of either adults or kids in the rink increases, so does the rate at which collisions will occur. The collision rate is proportional to the number of possible kid-adult pairs, which is proportional to the number density of adults times the number density of kids.

But the collision rate depends on other factors as well. If all the skaters follow the rules and skate counterclockwise around the rink at the same speed, then there will be no collisions. More often, the kids will skate at much faster or slower speeds, and they will rarely move uniformly. The rate at which they collide with the adults is proportional to the *relative speed* between the adults and kids.

Finally, consider the dependence of the collision rate on the size of the adults and kids. People are typically about 40 cm wide. What would be the effect of increasing or decreasing this diameter by a factor of ten? If the diameter were decreased to 4 cm, the number of collisions would go down dramatically; if the diameter were increased to 4 meters, it would be difficult to move around the rink at all. Thus, simple considerations suggest that the collision rate between molecules should be proportional to the relative speed of the molecules, to their size, and to the number of possible collision pairs.

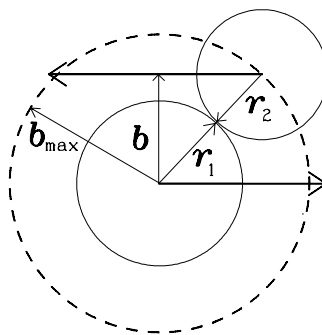


Figure 1.11 A collision will occur if the impact parameter is less than b_{\max} , the sum of the two molecular radii.

Let us assume that the average of the magnitude of the relative velocity between molecules of types 1 and 2 is $\langle v_r \rangle$ and that the molecules behave like hard spheres; there are no attractive forces between them, and they bounce off one another like billiard balls when they collide.^h Let the quantity b , shown in **Figure 1.11**, be defined as the distance of a line perpendicular to the each of the initial velocities of two colliding molecules, one of type 1 and the other of type 2. This distance is often referred to as the *impact parameter*. If the radii of the two molecules are r_1 and r_2 , then, as shown in **Figure 1.11**, a "collision" will occur if the two molecules approach one another so that their centers are within the distance $b_{\max} \equiv r_1 + r_2$. Thus, b_{\max} is the maximum value of the impact parameter for which a collision can occur. From the point of view of one type of molecule striking a molecule of the other type, the target area for a collision is then equal to $\pi(r_1 + r_2)^2 = \pi b_{\max}^2$.

Consider a molecule of type 1 moving through a gas with a speed equal to the average magnitude of the relative velocity, $\langle v_r \rangle$. **Figure 1.12** shows that any molecule of type 2 located in a cylinder of volume $\pi b_{\max}^2 \langle v_r \rangle \Delta t$ will then be struck in the time Δt .ⁱ If the density of molecules of type 2 is n_2^* , then the number of collisions one molecule of type 1 will experience with molecules of type 2 per unit time is

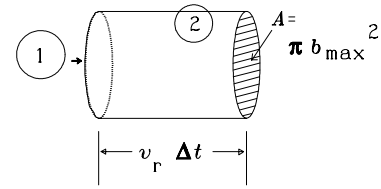


Figure 1.12 Molecule 1 sweeps out a cylinder of area πb_{\max}^2 . Any molecule of type 2 whose center is within this cylinder will be struck.

$$Z_2 = \pi b_{\max}^2 \langle v_r \rangle n_2^* \quad (1.42)$$

Of course, for a molecule of type 1 moving through other molecules of the same type,

$$Z_1 = \pi b_{\max}^2 \langle v_r \rangle n_1^* = \pi d^2 \langle v_r \rangle n_1^* \quad (1.43)$$

^hWe consider only the *relative* velocity between the molecules. Appendix 1.4 shows that the *total* velocity of each molecule can be written as a vector sum of the velocity of the center-of-mass of the pair of molecules and the relative velocity of the molecule with respect to the center of mass. The forces between molecules depend on the relative distance between them and do not change the velocity of their center of mass, which must be conserved during the collision.

ⁱBecause of the collisions, the molecule under consideration will actually travel along a zig-zag path, but the volume swept out per unit time will be the same.

where b_{\max}^2 had been replaced by d^2 since $r_1+r_2 = 2r_1 = d$. The quantity πb_{\max}^2 is known as the hard-sphere collision cross section. Cross sections are generally given the symbol σ .

Equation (1.42) gives the number of collisions per unit time of one molecule of type 1 with a density n_2^* of molecules of type 2. The *total* number of collisions of molecules of type 1 with those of type 2 per unit time and per unit volume is found simply by multiplying by the density of type 1 molecules:

$$\begin{aligned} Z_{12} &= Z_2 n_1^* = \\ &\pi b_{\max}^2 \langle v_r \rangle n_1^* n_2^* . \end{aligned} \tag{1.44}$$

Note that the product $n_1^* n_2^*$ is simply proportional to the total number of pairs of collision partners.

By a similar argument, if there were only one type of molecule, the number of collisions per unit time per unit volume is given by

$$Z_{11} = \frac{1}{2} Z_1 n_1^* = \frac{1}{2} \pi b_{\max}^2 \langle v_r \rangle (n_1^*)^2 . \tag{1.45}$$

The factor of $\frac{1}{2}$ is introduced for the following reason. The collision rate should be proportional to the number of pairs of collision partners. If there are n molecules, then the number of pairs is $n(n-1)/2$, since each molecule can pair with $n-1$ others and the factor of 2 in the denominator corrects for having counted each pair twice. If n is a large number, then we can approximate $n(n-1)$ as n^2 , and since the number of molecules is proportional to the number density, we see that the number of pairs goes as $(n_1^*)^2/2$.

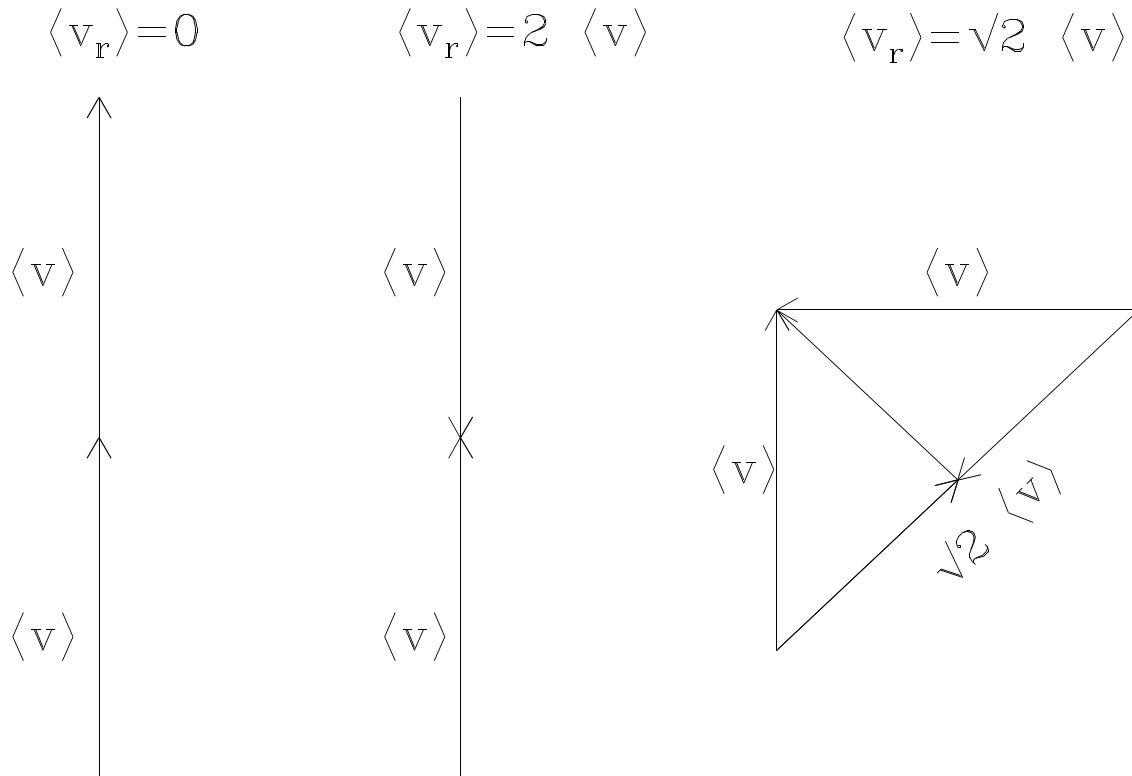


Figure 1.13 In a hypothetical collision where two molecules each have a speed equal to the average $\langle v \rangle$, the relative velocity between two molecules, averaged over all collision directions, is $\sqrt{2} \langle v \rangle$.

It remains for us to determine the value of the relative speed, averaged over the possible angles of collision and averaged over the speed distribution for each molecule. One way to arrive quickly at the answer for a very specific case is shown in **Figure 1.13**. Suppose that the two types of molecules have the same mass, m . Let us assume for the moment that we can accomplish the average of the speed distribution by assuming that the two molecules each have a speed equal to the average of their distribution. Since the two molecules are assumed to have the same mass (and temperature), they will also have the same average speed, $\langle v \rangle$. We now consider the average over collision angles. If the molecules are traveling in the same direction, then the relative velocity between them will have zero magnitude, $v_r = 0$, while if they are traveling in opposite directions along the same line the relative velocity

will have a magnitude of $v_r = 2 \langle v \rangle$. Suppose that they are traveling at right angles to one another. In that case, which is representative of the average angle of collision, the relative velocity will have a magnitude of $v_r = \langle v_r \rangle = \sqrt{2} \langle v \rangle$. Recalling from (1.32) that $\langle v \rangle = (8kT/\pi m)^{1/2}$, we find that

$$\begin{aligned} \langle v_r \rangle &= \sqrt{2} \langle v \rangle \\ &= \sqrt{2} \left(\frac{8kT}{\pi m} \right)^{1/2} = \left(\frac{8kT}{\pi \frac{m}{2}} \right)^{1/2} = \left(\frac{8kT}{\pi \mu} \right)^{1/2}, \end{aligned} \quad (1.46)$$

where we have introduced the *reduced mass*, μ , defined as $\mu = m_1 m_2 / (m_1 + m_2)$. When the masses m_1 and m_2 are the same, $\mu = m^2 / 2m = m/2$. If the masses are different, then the mean velocities will not be the same, and the simple analysis of **Figure 1.13** is not adequate. However, as shown for the general case in 1.4 and Problem 1.12, the result for $\langle v_r \rangle$ is the same as that given in (1.46). The Appendix also shows why the definition of μ as $[m_1 m_2 / (m_1 + m_2)]$ is a useful one.

Example 1.6 The collision rate of NO with O₃

<i>Objective</i>	Find the collision rate of NO with O ₃ at 300 K if the abundances at 1 atm total pressure are each 0.2 ppm and if the molecular diameters are 300 and 375 pm, respectively. Reactive collisions between these two species are important in photochemical smog formation.
<i>Method</i>	Use (1.44), remembering to convert the abundances to number densities at 300 K and calculating the average relative velocity by use of (1.46).
<i>Solution</i>	First find the total number density n^* at 1 atm: $n^* = (n/V)N_A = (p/RT)N_A = (1 \text{ atm})(6.02 \times 10^{23} \text{ molec/mole}) / [(0.082 \text{ l atm mol}^{-1} \text{ K}^{-1})(300 \text{ K})] = 2.45 \times 10^{22} \text{ molec/l}$. Next determine the number densities of NO and O ₃ , each being the total density times 0.2×10^{-6} : $n^*(\text{NO}) = n^*(\text{O}_3) = (0.2 \times 10^{-6})(2.45 \times 10^{22}) = 4.9 \times 10^{15} \text{ molec/l}$. The average relative velocity is $\langle v_r \rangle = (8kT/\pi\mu)^{1/2} = [8(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})(6.02 \times 10^{23} \text{ amu/gm})(1000 \text{ gm/kg}) / (\pi(48 \times 30/78) \text{ amu})]^{1/2} = 586 \text{ m/s}$. The average diameter is $(300 + 375 \text{ pm})/2 = 337.5 \text{ pm}$. Then $Z_{12} = \pi(337.5 \times 10^{-12} \text{ m})^2(586 \text{ m/s})(4.9 \times 10^{15} \text{ molec/l})^2(1 \text{ l} / 10^{-3} \text{ m}^3)^2 = 5.0 \times 10^{21} \text{ collisions s}^{-1} \text{ m}^{-3}$. If every collision resulted in a reaction, this would be the number of reactions per unit second per cubic meter.

A quantity related to Z_1 is the *mean free path*, λ . This is the average distance a molecule travels before colliding with another molecule. If we divide the average speed $\langle v \rangle$ in m/s by the collision number Z_1 in collision/s, we obtain the mean free path in m/collision:

$$\begin{aligned}\lambda &= \frac{\langle v \rangle}{Z_1} = \frac{\langle v \rangle}{\pi d^2 \sqrt{2} \langle v \rangle n_1^*} \\ &= \frac{1}{\sqrt{2} \pi d^2 n_1^*}.\end{aligned}\tag{1.47}$$

Note that the mean free path is inversely proportional to pressure. The mean free path will be important in Chapter 4, where we will see that the transport of heat, momentum, and matter are all proportional to the distance traveled between collisions.

Example 1.7 The mean free path of nitrogen

<i>Objective</i>	Find Z_1 and the mean free path of N_2 at 300 K and 1 atm given that the molecular diameter is 218 pm.
<i>Method</i>	Use (1.46) to calculate $\langle v_r \rangle$, (1.43) to calculate Z_1 , and (1.47) to calculate λ .
<i>Solution</i>	We start by calculating $\langle v_r \rangle = (8kT/\pi\mu)^{1/2}$, where $\mu = 28*28/(28+28) = 14$ amu.

$$\begin{aligned}\langle v_r \rangle &= \left\{ \frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})(6.02 \times 10^{23} \text{ amu/gm})(1000 \text{ gm/kg})}{(3.1415 \times 14 \text{ amu})} \right\}^{1/2} \\ &= 673 \text{ m/s}.\end{aligned}\tag{1.48}$$

Next, we calculate Z_1 noting that the density

$$\begin{aligned}
 n_1^* &= p/(RT) = \frac{(1 \text{ atm})(6.02 \times 10^{23} \text{ molec/mole})}{(0.082 \ell \text{ atm mole}^{-1} \text{ K}^{-1})(10^{-3} \text{ m}^3/\ell)(300 \text{ K})} \\
 &= 2.45 \times 10^{25} \text{ molec/m}^3 .
 \end{aligned}
 \tag{1.49}$$

Then, $Z_1 = \pi (218 \times 10^{-12} \text{ m})^2 (673 \text{ m/s}) (2.45 \times 10^{25} \text{ molec/m}^3) = 2.46 \times 10^9 \text{ collision/s}$.

Finally, $\lambda = \langle v \rangle / Z_1 = \langle v_r \rangle / (\sqrt{2} Z_1) = (673 \text{ m/s}) / (\sqrt{2} \times 2.46 \times 10^9 \text{ collision/s}) = 1.93 \times 10^{-7} \text{ m}$.

1.8 Summary

By considering the pressure exerted by ideal gas molecules on a wall, we determined that, for agreement with the observed ideal gas law, the average energy of a molecule must be given by

$$\langle \epsilon \rangle = \frac{3}{2} kT.
 \tag{1.5}$$

In order to learn how to perform averages, we discussed distribution functions of a continuous variable. The average of some observable quantity Q was found to be given by

$$\langle Q \rangle = \int P(Q) Q \, dQ,
 \tag{1.16}$$

where $P(Q)$ is the distribution function for the quantity Q . We then made the following observations about the molecular speed distribution: 1) the speed distribution must be an even function of v , 2) the speed distribution in any particular direction is independent from and uncorrelated with that in orthogonal directions, 3) the value of $\langle v^2 \rangle$ must be equal to $3kT/m$ to agree with the ideal gas law, and 4) the distribution depends only on the magnitude of v . These four considerations allowed us to determine the Maxwell-Boltzmann distribution of speeds:

$$F(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT} \right) dv. \quad (1.31)$$

Calculations using this distribution gave us an equation for the average speed of a molecule,

$$\langle v \rangle = \left(\frac{8kT}{\pi m} \right)^{\frac{1}{2}}, \quad (1.32)$$

and the most probable speed,

$$c^* = \left(\frac{2kT}{m} \right)^{\frac{1}{2}}. \quad (1.33)$$

A simple transformation of variables in the speed distribution led to the Maxwell-Boltzmann energy distribution:

$$G(\epsilon)d\epsilon = 2\pi \left(\frac{1}{\pi kT} \right)^{\frac{3}{2}} \sqrt{\epsilon} \exp\left(-\frac{\epsilon}{kT} \right) d\epsilon. \quad (1.37)$$

Finally, for molecules behaving as hard spheres, we determined the collision rate,

$$Z_1 = \pi b_{\max}^2 \langle v_r \rangle n_1^*, \quad (1.42)$$

the relative velocity,

$$\langle v_r \rangle = \sqrt{2} \langle v \rangle = \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}}, \quad (1.46)$$

and the mean free path,

$$\lambda = \frac{\bar{c}}{Z_1} = \frac{1}{\sqrt{2} \pi d^2 n_1^*}. \quad (1.47)$$

These concepts form the basis for further investigation into transport properties and chemical reaction kinetics.

Appendices, Chapter 1

Appendix 1.1 The Functional Form of the Velocity Distribution

We demonstrate in this Appendix that the exponential form used in (1.23) is the only function which satisfies the equation $f(a+b+c) = f(a)f(b)f(c)$. Consider first the simpler equation

$$f(z) = f(a)f(b), \quad (\text{A1.1})$$

where $z = a+b$. Taking the derivative of both sides of (A1.1) with respect to a we obtain

$$\frac{df(z)}{dz} \frac{dz}{da} = f'(a)f(b). \quad (\text{A1.2})$$

On the other hand, taking the derivative of both sides of (A1.1) with respect to b we obtain

$$\frac{df(z)}{dz} \frac{dz}{db} = f(a)f'(b). \quad (\text{A1.3})$$

Since $z = a+b$, $dz/da = dz/db = 1$. Consequently,

$$\frac{df(z)}{dz} = f'(a)f(b) = f(a)f'(b). \quad (\text{A1.4})$$

Division of both sides of the right-hand equality by $f(a)f(b)$ yields

$$\frac{f'(a)}{f(a)} = \frac{f'(b)}{f(b)}. \quad (\text{A1.5})$$

Now the left-hand side of (A1.5) depends only on a , while the right-hand side depends only on b . Since a and b are independent variables, the only way that (A1.5) can be true is if each side of the equation is equal to a constant, $\pm\kappa$, where κ is defined as non-negative:

$$\frac{f'(a)}{f(a)} = \pm\kappa \quad \frac{f'(b)}{f(b)} = \pm\kappa. \quad (\text{A1.6})$$

Solution of these differential equations using x to represent either a or b leads to

$$\frac{f'(x)}{f(x)} = \pm\kappa \quad \text{or} \quad \frac{df(x)}{f(x)} = \pm\kappa dx. \quad (\text{A1.7})$$

Integration shows that

$$f(x) = K e^{\pm\kappa x}, \quad (\text{A1.8})$$

where K is related to the constant of integration. Equation (1.23) is obtained by replacing x with v_x^2 .

Appendix 1.2 Spherical Coordinates

Many problems in physical chemistry can be solved more easily using spherical rather than Cartesian coordinates. In this coordinate system, as shown in **Figure 1.14**, a point P is located by its distance r from the origin, the angle θ between the z axis and the line from the point to the origin, and the angle ϕ between the x axis and the line between the origin and a projection of the point onto the x - y plane. Any point can be described by a value of r between 0 and ∞ , a value of θ between 0 and π , and a value of ϕ between 0 and 2π . The Cartesian coordinates are related to the spherical ones by the following relationships: $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, and $z = r\cos\theta$.

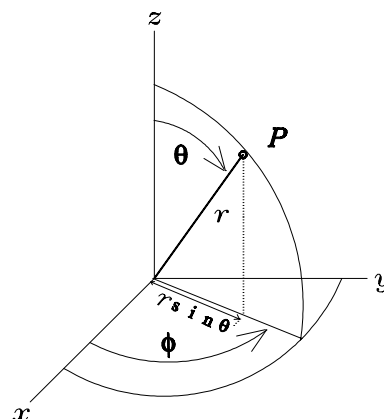


Figure 1.14 Spherical coordinates

The volume element in spherical coordinates can be calculated with the help of **Figure 1.15**. As the variable θ is increased for fixed r , the position of the point described by (r, θ, ϕ) moves along a longitudinal line on the surface of a sphere, while if ϕ is increased at fixed r , the position of the point moves along a latitudinal line. Starting at a point located at (r, θ, ϕ) , if r is increased by dr , θ is increased by $d\theta$, and ϕ is increased by $d\phi$, then the volume increase is the surface area on the sphere times the thickness dr (for clarity, the thickness dr is not shown in the diagram). The surface area is given by the arc length on the longitude, $r d\theta$, times the arc length on the latitude, $r \sin\theta d\phi$. Thus, the volume element is $dV = r^2 \sin\theta d\theta d\phi dr$.

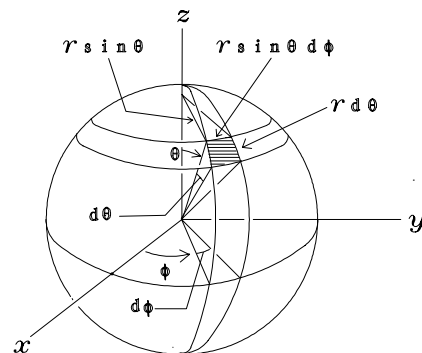


Figure 1.15 The volume element in spherical coordinates

Appendix 1.3 The Error Function and Co-Error Function

It often occurs that we need to evaluate integrals of the form of those listed in **Table 1.1** but for limits less than the range of 0 to infinity. For such evaluations it is useful to define the *error function*:

$$\operatorname{erf}(x) \equiv \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du. \quad (\text{A1.38})$$

From **Table 1.1** we see that for $x=\infty$, the value of the integral is $\sqrt{\pi}/2$, so that $\operatorname{erf}(\infty)=1$. Note that if we "complement" the error function by $2/\sqrt{\pi}$ times the integral from x to ∞ , we should get unity:

$$\begin{aligned} \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du + \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2} du &= \\ \operatorname{erf}(x) + \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2} du &= \\ \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-u^2} du &= 1. \end{aligned} \quad (\text{A1.39})$$

Consequently, it is also useful to define the co-error function, $\operatorname{erfc}(x)$, as the complement to the error function:

$$\operatorname{erfc}(x) \equiv 1 - \operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2} du. \quad (\text{A1.40})$$

Tables of the error function and co-error function are available, but the pervasive use of computers has made them all but obsolete. For calculational purposes, the integrand in **(A1.38)** or **(A1.40)** can be expanded using a series,

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{n!(2n+1)}, \quad (\text{A1.41})$$

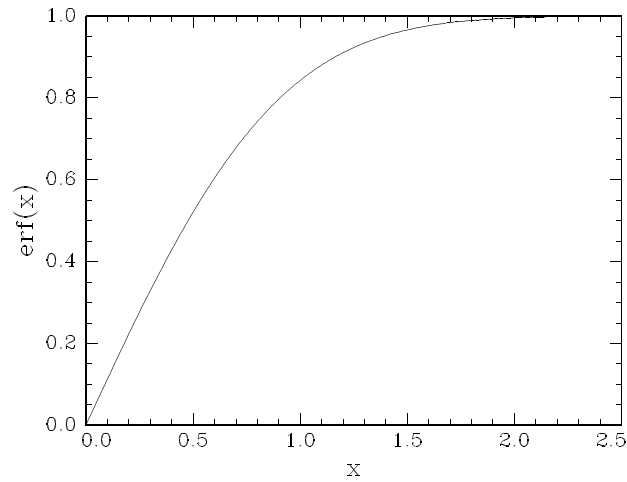


Figure 1.16 Values of the error function

and then the integration can be performed term by term. **Figure 1.16** plots $\text{erf}(x)$ as a function of x .

Appendix 1.4 The Center-of-Mass Frame

We show in this appendix that the total kinetic energy of two particles of velocities \mathbf{v}_1 and \mathbf{v}_2 , is given by $\frac{1}{2}\mu v_r^2 + \frac{1}{2}M v_{\text{com}}^2$, where $\mathbf{v}_r = \mathbf{v}_2 - \mathbf{v}_1$, where \mathbf{v}_{com} , the vector describing the velocity of the center-of-mass, is defined by the equation $(m_1 + m_2)\mathbf{v}_{\text{com}} = m_1\mathbf{v}_1 + m_2\mathbf{v}_2$, and $M \equiv m_1 + m_2$.

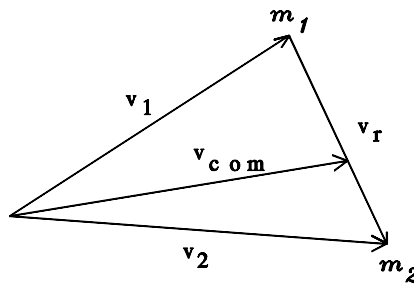


Figure 1.17 Vector diagram for center of mass conversion

Figure 1.17 shows the vector relationships.

The virtue of this transformation is that the total momentum of the system $\mathbf{p} = m_1\mathbf{v}_1 + m_2\mathbf{v}_2$ is also equal to the momentum of the center of mass, defined as $M\mathbf{v}_{\text{com}}$. Because we assume that no external forces are acting on the system, $\mathbf{F} = M\mathbf{a}_{\text{com}} = M(d\mathbf{p}_{\text{com}}/dt) = 0$, so that the momentum of the center of mass does not change during the interaction between the two particles.

Note that since $(m_1/M) + (m_2/M) = 1$ we can write

$$\begin{aligned} \mathbf{v}_2 - \mathbf{v}_{\text{com}} &= \left(\frac{m_1}{M} + \frac{m_2}{M} \right) \mathbf{v}_2 - \mathbf{v}_{\text{com}} \\ &= \frac{m_1}{M} \mathbf{v}_2 + \frac{m_2}{M} \mathbf{v}_2 - \mathbf{v}_{\text{com}} . \end{aligned} \tag{A1.42}$$

However,

$$m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 = M \mathbf{v}_{\text{com}}; \text{ so that}$$

$$-\frac{m_1 \mathbf{v}_1}{M} = \frac{m_2 \mathbf{v}_2}{M} - \mathbf{v}_{\text{com}}. \quad (\text{A1.43})$$

Consequently,

$$\begin{aligned} \mathbf{v}_2 - \mathbf{v}_{\text{com}} &= \frac{m_1}{M} \mathbf{v}_2 - \frac{m_1}{M} \mathbf{v}_1 \\ &= \frac{m_1}{M} \mathbf{v}_r. \end{aligned} \quad (\text{A1.44})$$

In a similar way, we find that

$$\mathbf{v}_{\text{com}} - \mathbf{v}_1 = \frac{m_2}{M} \mathbf{v}_r. \quad (\text{A1.45})$$

We now note an important point, that the velocities of the particles with respect to the center of mass are just given by the two pieces of the vector \mathbf{v}_r : $\mathbf{u}_1 = -(m_2/M)\mathbf{v}_r$, and $\mathbf{u}_2 = (m_1/M)\mathbf{v}_r$, as shown in **Figure 1.18**. Note also that in the moving frame of the center of mass, there is no net momentum for the particles, that is $m_1 \mathbf{u}_1 + m_2 \mathbf{u}_2 = 0$. This important property allows us to calculate the velocity of one particle in the center-of-mass frame given just the masses and the velocity of the other particle.

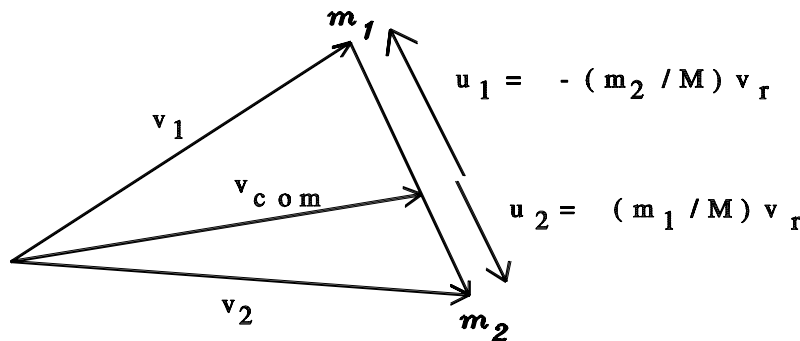


Figure 1.18 Vector diagram for center of mass conversion, showing the relative velocities in the center-of-mass frame for the two particles

We can rearrange (A1.44) and (A1.45) to get

$$\mathbf{v}_{\text{com}} - \frac{m_2}{M}\mathbf{v}_r = \mathbf{v}_1$$

(A1.46)

$$\mathbf{v}_{\text{com}} + \frac{m_1}{M}\mathbf{v}_r = \mathbf{v}_2$$

The total energy is then

$$\begin{aligned} & \frac{1}{2}m_1\mathbf{v}_1^2 + \frac{1}{2}m_2\mathbf{v}_2^2 = \\ & \frac{1}{2}m_1\left(\mathbf{v}_{\text{com}} - \frac{m_2}{M}\mathbf{v}_r\right)^2 + \frac{1}{2}m_2\left(\mathbf{v}_{\text{com}} + \frac{m_1}{M}\mathbf{v}_r\right)^2 \\ & = \frac{1}{2}m_1\mathbf{v}_{\text{com}}^2 - \frac{2m_1m_2}{2M}\mathbf{v}_r \cdot \mathbf{v}_{\text{com}} + \frac{m_1m_2^2}{2M^2}\mathbf{v}_r^2 \\ & \quad + \frac{1}{2}m_2\mathbf{v}_{\text{com}}^2 + \frac{2m_2m_1}{2M}\mathbf{v}_r \cdot \mathbf{v}_{\text{com}} + \frac{m_2m_1^2}{2M^2}\mathbf{v}_r^2 \\ & = \frac{1}{2}M\mathbf{v}_{\text{com}}^2 + \frac{m_1m_2M}{2M^2}\mathbf{v}_r^2 \\ & = \frac{1}{2}Mv_{\text{com}}^2 + \frac{1}{2}\mu v_r^2 \end{aligned}$$

(A1.47)

It will often be useful to consider collisions in the center of mass frame. For example, we will make extensive use of this view in talking about molecular scattering in Section 8.4. Problem 1.12 shows how this result can be used to calculate the average relative velocity.

Suggested Reading

G. G. Hammes, *Principles of Chemical Kinetics*, (Academic Press, New York, 1978).

W. Kauzmann, *Kinetic Theory of Gases (Thermal Properties of Matter, Vol I)*, (Benjamin, Reading, MA, 1966)

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Chapter 1 Problems

- 1.1 Molecules all of mass m and speed v exert a pressure p on the walls of a vessel. If half the molecules are replaced by ones of another type all with mass $\frac{1}{2}m$ and speed $2v$, will the pressure (a) increase, (b) decrease, (c) remain constant?
- 1.2 Suppose the probability of obtaining a score between 0 and 100 on an exam increases monotonically between 0 and 1.00. The average score on the exam is (a) greater than 50, (b) equal to 50, (c) less than 50?
- 1.3 Suppose some property q of a gas is proportional to $(.326 \text{ s}^3 \text{ m}^{-3})v_x^3 + (\pi \text{ s}^9 \text{ m}^{-9})v_x^9$. What is the average value of q ?
- 1.4 Without referring to any formula, decide whether at constant density the mean free path (a) increases, (b) decreases, (c) or stays constant with increasing temperature and explain your answer.
- 1.5 Consider a deck of cards. With aces valued at one and jacks, queens, and kings valued at 11, 12, and 13, respectively, calculate the average value of a card drawn at random from a full deck.
- 1.6 The distribution of the grades S (where $0 \leq S \leq 100$) for a class containing a large number of students is given by the continuous function $P(S) = K(50 - |S-50|)$, where $|x|$ is the absolute value of x and K is a normalization constant. Determine the normalization constant and find out what fraction of the students received grades greater than or equal to 90.
- 1.7 A pair of dancers is waltzing on a one-dimensional dance floor of length L . Since they tend to avoid the walls, the probability of finding them at a position x between walls at $x = 0$ and $x = L$ is proportional to $\sin^2(\pi x/L)$. What is the normalized distribution function for the position of the waltzers? (*Hint*: the integral of $y \sin^2 y$ dy is $[y^2/4] -$

$[(y \sin 2y)/4] - [(\cos 2y)/8]$; this is also the probability for finding a particle in a box at a particular position)

Using this distribution function, calculate the most probable position for the waltzers.

Calculate the average position of the waltzers.

- 1.8** By setting the derivative of the formula for the Maxwell-Boltzmann speed distribution equal to zero, show that the speed at which the distribution has its maximum is given by **(1.33)**.
- 1.9** Show using Equations **(1.12)** and **(1.37)** that the average molecular energy is $3kT/2$.
- 1.10** Prove **(1.41)** from **(1.40)**. Integration can be accomplished by making the following change of variable. Let $\epsilon = kTx^2$, so that $d\epsilon = kTdx^2$ and $\epsilon^{1/2} = (kT)^{1/2}x$. Substitute these into **(1.40)** and integrate by parts, recalling that since $d(uv) = u dv + v du$, then $\int d(uv) = \int u dv + \int v du$, so that $\int u dv = (uv) \Big|_{\text{limits}} - \int v du$, where the notation $\Big|_{\text{limits}}$ indicates that the product (uv) should be evaluated at the limits used for the integrals.
- 1.11** The Maxwell-Boltzmann distribution may not be quite valid! Calculate the fraction of N_2 molecules having speeds in excess of the speed of light.

1.12 The object of this problem is to show more rigorously that $\langle v_r \rangle = (8kT/\pi\mu)^{1/2}$, where μ , the reduced mass, is defined as $\mu \equiv m_1 m_2 / (m_1 + m_2)$. We have already learned in Appendix 1.4 that the total kinetic energy of two particles is given by $\frac{1}{2}\mu v_r^2 + \frac{1}{2}M v_{com}^2$, where $\mathbf{v}_r = \mathbf{v}_2 - \mathbf{v}_1$ and \mathbf{v}_{com} , the center-of-mass velocity vector, is defined by the equation $(m_1 + m_2)\mathbf{v}_{com} = m_1\mathbf{v}_1 + m_2\mathbf{v}_2$, and $M \equiv m_1 + m_2$.

a) Consider the probability of finding two molecules, one with velocity \mathbf{v}_1 and one with velocity \mathbf{v}_2 . Using (1.30) we see that this probability is given by

$$F(v_{1x})F(v_{1y})F(v_{1z})F(v_{2x})F(v_{2y})F(v_{2z})dv_{1x}dv_{1y}dv_{1z}dv_{2x}dv_{2y}dv_{2z} =$$

$$\left(\frac{m_1}{2\pi kT}\right)^{\frac{3}{2}} \left(\frac{m_2}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{m_1 \mathbf{v}_1^2}{2kT}\right) \exp\left(-\frac{m_2 \mathbf{v}_2^2}{2kT}\right) \times$$

$$dv_{1x}dv_{1y}dv_{1z}dv_{2x}dv_{2y}dv_{2z}.$$

Use the result from Appendix 1.4 to show that this probability can also be written as

$$F(v_{rx})F(v_{ry})F(v_{rz})F(v_{comx})F(v_{comy})F(v_{comz}) \times$$

$$dv_{rx}dv_{ry}dv_{rz}dv_{comx}dv_{comy}dv_{comz} =$$

$$\left(\frac{m_1}{2\pi kT}\right)^{\frac{3}{2}} \left(\frac{m_2}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{M \mathbf{v}_{com}^2}{2kT}\right) \exp\left(-\frac{\mu \mathbf{v}_r^2}{2kT}\right) \times$$

$$dv_{rx}dv_{ry}dv_{rz}dv_{comx}dv_{comy}dv_{comz}.$$

b) Now transform the Cartesian coordinates to spherical ones and show by integration over all coordinates that the average relative velocity $\langle v_r \rangle$ is given by $(8kT/\pi\mu)^{1/2}$.

1.13 What is the ratio of the probability of finding a molecule moving with the average speed to the probability of finding a molecule moving with three times the average speed?

How does this ratio depend on the temperature?

1.14 You are caught without an umbrella in the rain and wish to get to your dorm, 1 km away, in the driest possible condition. Should you walk or run? In order to answer this question, calculate the ratio of the rain drop collisions with your body under the two

conditions. Assume that the cross section is independent of direction (i.e., that you are spherical), that you run at 8 m/s, you walk at 3 m/s, and that the rainfall is constant with a velocity of, say, 15 m/s.

- 1.15** Calculate the root mean squared deviation of the speed from its mean value: $[\langle(v-\langle v \rangle)^2 \rangle]^{1/2}$.
- 1.16** Find $\langle v^4 \rangle$ for a gas of molecular weight M at temperature T .
- 1.17** A very expensive gas is sold by the molecule, and the price is proportional to the velocity of the individual molecule: price in \$ = $v/\langle v \rangle$. If I buy a bulb of these gaseous molecules, what is the average price per molecule, and does the price depend on the temperature of the bulb?
- 1.18** In a group of molecules all traveling in the positive z direction, what is the probability that a molecule will be found with an z -component speed between 400 and 401 m/s if $m/(2kT) = 5.62 \times 10^{-6} \text{ s}^2/\text{m}^2$? [Hint: you need to find and normalize a one dimensional distribution function first!]
- 1.19** We will see in Chapter 3, equation (3.4), that the rate constant for a reaction as a function of temperature is given by the average of $\sigma(\epsilon_r) v_r$ over the thermal energy distribution $G(\epsilon_r)$, where $\epsilon_r = \frac{1}{2}mv_r^2$ and $\sigma(\epsilon_r)$ is the energy dependent cross section for the reaction. The thermal relative kinetic energy distribution $G(\epsilon_r)$ has the same functional form as the kinetic energy distribution $G(\epsilon)$ given in (1.37), except that all energies $\epsilon = (1/2)mv^2$ are replaced by relative kinetic energies $\epsilon_r = (1/2)\mu v_r^2$.
- (a) Suppose that for a particular reaction $\sigma(\epsilon_r) = c\epsilon_r^2$, where c is a constant. Calculate $k(T)$.
- (b) Suppose that for another reaction $\sigma(\epsilon_r) = c/\epsilon_r$; calculate $k(T)$.

Index

Average	1-8
Bernoulli	1-3
Boltzmann	1-4
constant	1-6
distribution law	1-16
Boyle	1-3
Clausius	1-3
Co-error function	1-41
Collision	
mean free path	1-30
number	1-30
rate	1-34
Cross section	
hard-sphere	1-32
Distribution	
energy	1-26
function	1-7
functional form of velocity	1-39
of speeds, Maxwell	1-12
Energy	
average	1-27
kinetic	1-5
Error function	1-41
co-error	1-29
Ideal Gas	
ideal gas law	1-5
Joule	1-3
Kinetic Theory of Gases	1-3
Mach Number	1-20
Mass	
reduced	1-34
Maxwell	1-4
distribution of speeds	1-12
distribution, experimental measurement	1-24
Mean free path	1-3, 1-30, 1-35
Momentum	1-4
Newton	1-3
Pressure	
ideal gas	1-4
Rayleigh	1-4
Reduced mass	1-34
Sound	
speed of	1-20
Speed	

mean	1-19
most probable	1-20
root-mean squared	1-19
Temperature	
and energy	1-6
Time-of-flight technique	1-24
Velocity	
relative	1-34
Waterston	1-3

External References

Section 4.3.2	1-26
Chapter 4	1-26
Chapter 4	1-35
Section 8.4	1-45