

# Introductory Kinetic Theory

Vincenti and Kruger, Introduction to Physical Gas Dynamics, c1965

## 1 INTRODUCTION

We begin our study of physical gas dynamics with a discussion of some of the pertinent problems from the kinetic theory of gases. In kinetic theory a gas is considered as made up at the microscopic level of very small, individual molecules in a state of constant motion. If there is no movement of the gas at the macroscopic level, this motion is regarded as purely random and is accompanied by continual collisions of the molecules with each other and with any surfaces that may be present. The movement of a given molecule is thus to be thought of as a kind of random banging about, with its velocity undergoing frequent and more or less discontinuous changes in both magnitude and direction. Indeed, it is this freedom of motion of the molecules, limited only by collisions, that differentiates a gas from the more ordered situation that exists in a liquid or a solid.

When there is a general macroscopic movement of the gas, as is the usual situation in gas dynamics, the motion of the molecules is not completely random. This statement is, in fact, merely two ways of saying the same thing—the general motion is only a macroscopic reflection of the nonrandomness of the molecular motion. In particular, the familiar flow velocity of continuum gas dynamics is, from the molecular point of view, merely the average velocity of the molecules taken over a volume large enough to contain many molecules but small relative to the dimensions of the flow field. Zero flow velocity, that is, an average molecular velocity of zero, corresponds to random absolute motion of the molecules (i.e., molecules of a given speed have no preferred direction). In a flowing gas the molecular motion, although not random from an absolute point of view, will appear almost so to an observer moving at the local flow velocity. These ideas will be made precise in Chapter IX when we consider

the flow of a nonuniform gas in detail. For the time being we are interested primarily in the properties of the gas as such, and for this a consideration of the random motion is for the most part sufficient.

To make the foregoing ideas quantitative, we must introduce a precise assumption regarding the molecular model, that is, regarding the nature of the molecules and of the forces acting between them. Given such a model and the usual laws of mechanics, it would then be possible, in principle, to trace out the path of each molecule with time, assuming that the initial conditions are known (which, of course, they are not). Such a calculation, though of interest theoretically, would be enormously difficult. Fortunately it is also of little necessity. What we are really concerned with in most practical applications is the gross, bulk behavior of the gas as represented by certain observable quantities such as pressure, temperature, and viscosity, which are manifestations of the molecular motions averaged in space or time. It is the primary task of kinetic theory to relate and "explain" these macroscopic properties in terms of the microscopic characteristics of the molecular model.

The approach to this problem in the present chapter will be deliberately rough and nonrigorous—refinement will come later in Chapter II. The aim here is a qualitative understanding of certain ideas and some feeling for the numerical magnitudes that are involved. The results, however, are essentially correct.

The reader who wants to study kinetic theory more extensively than we shall be able to here will probably enjoy the book by Jeans (1940). His mechanical description (pp. 11–15) of the theory in terms of balls on a billiard table is particularly helpful in fixing the basic ideas. Among the other useful books in the field are those of Kennard (1938), Present (1958), and Loeb (1961). Other references will be given later in Chapter IX.

## 2     MOLECULAR MODEL

Further word on the molecular model is necessary. Aside from the fundamental attribute of mass, a molecule possesses an external force field and an internal structure. The external field is, as a matter of fact, a consequence of the internal structure, that is, of the fact that the molecule consists of one or more atomic nuclei surrounded by orbiting electrons. The somewhat arbitrary concentration of our attention separately on the "outside" and "inside" of the molecules, however, is a useful procedure. (For a discussion of the origin of interatomic and intermolecular forces at a beginning level, see Slater, 1939, Chapter XXII.)

The external force field is generally assumed to be spherically symmetric. This is very nearly true in many cases and to assume otherwise is almost prohibitively difficult. On this basis, the force field can be represented as in Fig. 1, which shows the force  $F$  between two molecules as a function of the distance  $r$  between them. At large distances the true representation (solid curve) shows a weak attractive force that tends to zero as the distance increases. At short distances there is a strong repulsive force that increases rapidly as the orbiting electrons of the two molecules intermingle. At

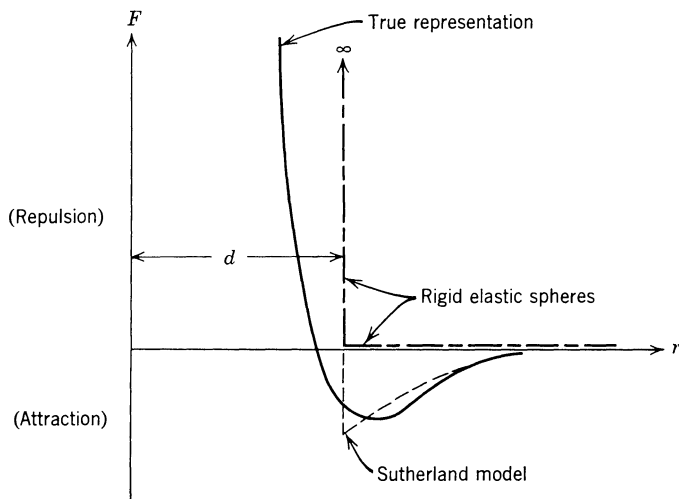


Fig. 1. Intermolecular force  $F$  as a function of the distance  $r$  between two molecules.

some intermediate distance,  $F$  passes through zero. The molecules, if they had no kinetic energy, would remain in equilibrium indefinitely at this distance.

Even with the simplest possible equation for the curve just described, the analysis is complicated. For this reason further approximation is often made. The simplest (Fig. 1) is to regard the molecules as rigid elastic spheres with zero attractive force when apart and an infinite repulsive force at the instant of contact. For like molecules, contact will take place when the distance between the center of the spheres is  $d$ , where  $d$  is the assumed diameter of the spherical molecule. A considerable amount of surprisingly accurate information can be obtained on the basis of this crude model, provided we chose  $d$  to give agreement between the resulting theory and the experimental data for some basic quantity such as viscous stress. Some improvement can be obtained at the expense of further complication by going to the so-called "Sutherland model." This

model supplements the rigid sphere by adding a weak attractive force when the spheres are not in contact. Other models are also possible. One that we shall find useful in Chapter IX dispenses entirely with the idea of solid spheres and assumes a pure repulsive force varying with some inverse power of the intermolecular distance.

The internal structure of the molecules is important primarily for its effect on the energy content of the gas. Being composed of nuclei and electrons that have motion relative to the center of mass of the molecule, the molecules can possess forms of energy (rotation, vibration, etc.) above and beyond that associated with their translational motion. In addition, the internal structure may be expected to affect the collisional interaction of the molecules at short range. Inclusion of the effects of internal structure considerably complicates the kinetic theory.

In the present book the treatment of intermolecular forces in any but the simplest way will be reserved for the discussion of nonequilibrium kinetic theory in Chapters IX and X. The effects of internal structure, at least insofar as the internal energy is concerned, will be taken up in detail in the discussion of equilibrium statistical mechanics in Chapter IV. For the present the molecular model that will be assumed, except for certain digressions, is that of the structureless, perfectly elastic sphere with no attractive forces and with repulsive forces existing only during contact. The characteristics of this "billiard-ball" model are completely specified by giving the mass and diameter of the various types of molecules, the number of each type of molecule per unit volume, and some measure of the speed of the random motion. Our task is to relate the macroscopic properties of the gas to these assumedly given microscopic quantities.

### 3     PRESSURE, TEMPERATURE, AND INTERNAL ENERGY

Consider a gas mixture in a state of equilibrium inside a cubical box. Suppose that the box is at rest so that the molecular motion is purely random. We wish to study the pressure exerted on the walls of the box by this random motion.

For simplicity we assume that the molecules do not collide with each other but only with the walls. We also assume that upon collision with a wall a molecule is reflected specularly (i.e., angle of reflection equals angle of incidence) and with its speed unchanged. It must be emphasized that neither of these assumptions is true; the fate of a given molecule upon collision with the wall is not known, and molecules do in reality collide with each other with great frequency. Intermolecular collisions are, in

fact, the chief mechanism for bringing the gas to its final state of equilibrium. Nevertheless, *once the equilibrium state has been established*, the gas behaves, at least insofar as the pressure is concerned, *as if* the assumptions were correct. This is because the condition of equilibrium requires that in any region the number of molecules of a given species and having velocity closely equal, in both magnitude and direction, to any given value must not vary with time. Thus, in a small region in the vicinity of a given point, for every molecule deflected away from its original velocity by a collision, there will at the same time be another of the same species deflected into this velocity. This molecule can be regarded as carrying on the motion of the original molecule just as if no collision had occurred. Somewhat similar ideas can be applied at the wall. Here the essential fact is that within a gas in equilibrium there can be no preferred direction. That is to say, in any region of the gas the number of molecules of a given species and having velocity closely equal in magnitude to a given value must be the same irrespective of the direction of the velocity. If this requirement is applied in a small region immediately adjacent to the wall, it implies that for every molecule arriving at a small element of the wall, another of the same species will at the same time leave that element with a specularly oriented velocity of equal magnitude. Thus the gas behaves as if a given molecule were reflected specularly and without change of speed.

Under the assumption of no intermolecular collisions and specular, elastic reflection at the walls, the motion of a given molecule is as shown in two-dimensional projection in Fig. 2. The molecule in this purely fictitious situation moves at a constant speed  $C$  irrespective of its direction. When it collides with the wall, its velocity component perpendicular to the wall is reversed whereas that parallel to the wall is unaltered. If coordinate axes  $x_1, x_2, x_3$  are taken along three edges of the box, the magnitudes of the corresponding velocity components thus have fixed values  $|C_1|, |C_2|, |C_3|$ , where  $C_1^2 + C_2^2 + C_3^2 = C^2$ .

The force exerted on a given wall of the box by the molecule depends on the number of collisions with the wall per unit time and on the change in momentum per collision. Let us consider the force on the wall perpendicular to  $Ox_1$  at the right-hand side of the box. If  $l$  is the length of an edge of the box, the time required to traverse the distance between the two walls perpendicular to  $Ox_1$ , irrespective of collisions with other walls, is  $l/|C_1|$ . Since there are two such traverses between each collision with the right-hand wall, the number of collisions per unit time with this wall is therefore  $|C_1|/2l$ . At each such collision, the molecule, having mass  $m$ , suffers a change in  $x_1$ -momentum of amount  $2m|C_1|$ , that is, from  $mC_1$  to  $-mC_1$ . The magnitude of the total change in  $x_1$ -momentum per unit time,

which is equal to the total force exerted on the wall by the molecule, is thus

$$2m |C_1| \times |C_1|/2l = \frac{mC_1^2}{l}.$$

Since the area of the wall is  $l^2$ , the corresponding pressure on the wall is

$$\frac{mC_1^2}{l^3} = \frac{mC_1^2}{V},$$

where  $V = l^3$  is the volume of the box.

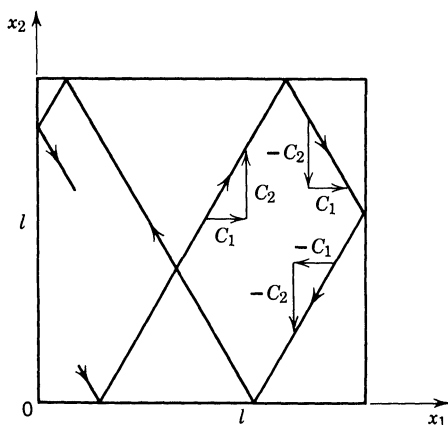


Fig. 2. Projection on the  $x_1, x_2$ -plane of the path of a molecule in a cubical box in the fictitious situation of no intermolecular collisions and specular, elastic reflection at the walls.

Now suppose that the gas mixture consists of a large number of molecules of different mass  $m_a, m_b, m_c, \dots$  moving with speeds  $C_a, C_b, C_c, \dots$ . The total pressure exerted on the wall perpendicular to  $Ox_1$  by all the molecules is then

$$\frac{1}{V} (m_a C_{a1}^2 + m_b C_{b1}^2 + m_c C_{c1}^2 + \dots) = \frac{1}{V} \sum_z m_z C_{z1}^2.$$

But under the assumed conditions of equilibrium the pressure on this wall is the same as on the other walls of the box. Denoting this common pressure by  $p$ , we can therefore equate the foregoing pressure to  $p$  and write

$$p = \frac{1}{V} \sum_z m_z C_{z1}^2.$$

Corresponding equations hold for the pressure calculated on the faces

perpendicular to  $Ox_2$  and  $Ox_3$ . Taking the sum of these equations for the three coordinate directions and dividing by three, we also obtain

$$p = \frac{1}{3V} \sum_z m_z (C_{z_1}^2 + C_{z_2}^2 + C_{z_3}^2) = \frac{1}{3V} \sum_z m_z C_z^2. \quad (3.1)$$

Since the total energy of translation  $E_{tr}$  of the molecules is  $\frac{1}{2} \sum_z m_z C_z^2$ , this equation can be written

$$\boxed{pV = \frac{2}{3} E_{tr}}. \quad (3.2)$$

The same final results will be rederived in Chapter II on the basis of a more realistic analysis.

The foregoing kinetic-theory equation of state can be compared with the empirically derived equation of state for a thermally perfect gas from classical thermodynamics. This is, in one of its forms,

$$pV = \mathcal{N} \hat{R} T,$$

where  $\hat{R}$  is the universal gas constant (i.e., gas constant per mole),<sup>1</sup>  $\mathcal{N}$  is the number of moles of gas in the volume  $V$ , and  $T$  is the gas temperature. We see that the theoretical formula and the empirical equation are identical if we take

$$\boxed{E_{tr} = \frac{3}{2} \mathcal{N} \hat{R} T}. \quad (3.3a)$$

This equation relates the energy of translation of the molecules in kinetic theory to the absolute temperature as defined in classical thermodynamics. The temperature may thus be interpreted as a measure of the molecular energy. Equation (3.3a) is sometimes taken, from a somewhat different point of view (cf. Chapter IX, Sec. 2), as giving a kinetic *definition* of temperature.

The result (3.3a) can be reexpressed in terms of the average kinetic energy per molecule by dividing both sides by the total number  $N$  of molecules. This gives

$$\tilde{e}_{tr} \equiv \frac{E_{tr}}{N} = \frac{3}{2} \times \frac{\mathcal{N}}{N} \hat{R} T = \frac{3}{2} \times \frac{\hat{R}}{\hat{N}} T,$$

where  $\hat{N} = N/\mathcal{N}$  is the number of molecules per mole, which is *Avogadro's number*, another universal constant. The quotient  $\hat{R}/\hat{N}$ , which is in the nature of a "gas constant per molecule," is thus also a universal constant, usually denoted by  $k$  and called the *Boltzmann constant*. We thus write

<sup>1</sup> The value of this and other fundamental physical constants is given in the appendix at the end of the book.

for the average kinetic energy per molecule

$$\bar{\epsilon}_{\text{tr}} = \frac{3}{2}kT. \quad (3.3b)$$

We can also obtain the specific kinetic energy  $e_{\text{tr}}$  per unit mass by dividing both sides of equation (3.3a) by the total mass  $M = \sum_z m_z$ . Noting that the combination  $\mathcal{N}\hat{R}/M$  is the ordinary gas constant  $\hat{R}$  (i.e., gas constant per unit mass), we thus obtain

$$e_{\text{tr}} = \frac{3}{2}RT. \quad (3.3c)$$

Under our assumption that the molecules have no internal structure, the energy of translation constitutes the entire molecular energy of the gas. It can therefore be taken as equal to the internal energy  $e$  of thermodynamics. We thus find for the specific heat at constant volume in the present case

$$c_v = \left( \frac{\partial e}{\partial T} \right)_v = \frac{de_{\text{tr}}}{dT} = \frac{3}{2}R.$$

The specific heat at constant pressure, as given by the thermodynamic relation  $c_p - c_v = R$ , valid for a thermally perfect gas, is

$$c_p = \frac{5}{2}R,$$

and the ratio of specific heats  $\gamma \equiv c_p/c_v$  is therefore

$$\gamma = \frac{5}{3}.$$

Since our assumed gas model has constant specific heats, it is calorically as well as thermally perfect.<sup>2</sup> The calculated value of  $c_v$  is in good agreement with experimental data for monatomic gases at ordinary temperatures. This indicates that our model is a reasonable one for such gases.

The foregoing theory can also be used to obtain an estimate of molecular speeds. For this purpose we return to equation (3.1) and divide both sides by  $M = \sum_z m_z$ . Introducing the mass density  $\rho = M/V$  and a mean-square molecular speed defined by

$$\overline{C^2} \equiv \frac{\sum_z m_z C_z^2}{\sum_z m_z}, \quad (3.4)$$

<sup>2</sup> When a gas is both thermally and calorically perfect, we shall ordinarily describe it by the unmodified term "perfect gas." When we wish to distinguish between thermal perfection (a gas obeying the equation  $pV = \mathcal{N}\hat{R}T$ ) and caloric perfection (a gas with constant specific heats), we shall try to remember to add the adjectives. The reader will recall that a gas can be thermally perfect and calorically imperfect, but not vice versa.



we thus obtain

$$\boxed{\frac{p}{\rho} = \frac{1}{3} \overline{C^2}}. \quad (3.5)$$

This relation allows an estimate of molecular speeds directly from macroscopically measurable quantities. For example, for air<sup>3</sup> at standard conditions (1 atm pressure and 0°C) we have  $p = 1.013 \times 10^6$  dyne/cm<sup>2</sup> and  $\rho = 1.288 \times 10^{-3}$  gm/cm<sup>3</sup>, so that the root-mean-square molecular speed is

$$\sqrt{\overline{C^2}} = \left(3 \frac{p}{\rho}\right)^{1/2} = 4.86 \times 10^4 \text{ cm/sec} = 486 \text{ m/sec.}$$

This is of the same order as the corresponding speed of sound (332 m/sec), which is as would be expected since the molecular motion is the real mechanism underlying the propagation of sound. From equation (3.5) and the equation of state in the form  $p/\rho = RT$ , it follows that the root-mean-square molecular speed, like the speed of sound, is proportional to  $T^{1/2}$ .

Turning our attention to another matter, let us suppose that the gas is composed of numbers of molecules of distinct species A, B, C, etc. Returning again to equation (3.1) we can then write

$$p = \frac{1}{3V} \sum_{\text{species A}} m_A C_A^2 + \frac{1}{3V} \sum_{\text{species B}} m_B C_B^2 + \cdots.$$

Here the summation for a given species Y is understood to be taken over all molecules of that species; the corresponding mass  $m_Y$  is thus a constant but  $C_Y$  varies from molecule to molecule. Now, each term of the foregoing equation has itself the same form as equation (3.1), that is, it can be thought of as constituting a partial pressure  $p_Y$  calculated as if the molecules of that species filled the container by themselves. We can thus write for a mixture of gases

$$\boxed{p = p_A + p_B + \cdots = \sum_Y p_Y}, \quad (3.6)$$

which is recognized as *Dalton's law of partial pressures* for a mixture of

<sup>3</sup> This use of the theory might be questioned on the grounds that air is composed of diatomic molecules that have an effective internal structure. As will be shown in Chapter IV, however, the internal structure does not alter the relationship between pressure and *translational* energy, so that this application of (3.5) is permissible.

perfect gases. The partial pressure is given analogously to equation (3.2) by

$$p_Y V = \frac{2}{3} E_{Y_{tr}}, \quad (3.7)$$

where  $E_{Y_{tr}} = \frac{1}{2} \sum_Y m_Y C_Y^2$  is the total molecular energy of translation of species Y. The corresponding thermodynamic equation here is

$$p_Y V = \mathcal{N}_Y \hat{R} T,$$

where  $\mathcal{N}_Y$  is the number of moles of species Y in the mixture, and the common temperature  $T$  is used since at equilibrium all gases in the mixture must have the same temperature. Comparing the two equations we obtain, as in equation (3.3a),

$$E_{Y_{tr}} = \frac{3}{2} \mathcal{N}_Y \hat{R} T. \quad (3.8a)$$

If we now divide by the total number  $N_Y$  of molecules of species Y and note that  $\hat{N} = N_Y / \mathcal{N}_Y$  is again Avogadro's number, we find for the average translational energy per molecule of species Y

$$\tilde{e}_{Y_{tr}} = \frac{3}{2} k T. \quad (3.8b)$$

The right-hand side of this equation is identical to that of equation (3.3b) for the entire mixture. Equations (3.8b) and (3.3b) thus show that

$$\tilde{e}_{A_{tr}} = \tilde{e}_{B_{tr}} = \cdots = \tilde{e}_{tr}. \quad (3.9)$$

That is to say, *when a number of gases are mixed at the same temperature, the average kinetic energy of their molecules is the same.* It follows that the heavy molecules must move, on the average, slower than the light molecules.

One remark needs to be made. The foregoing development has used our prior thermodynamic knowledge of the equation of state of a thermally perfect gas and of the existence of the universal gas constant and Avogadro's number. The appeal to thermodynamics in this restricted way, however, is not essential and has been used here only for the sake of brevity. An alternative—and perhaps logically preferable—approach is given in Jeans' book (pp. 21–30). Proceeding from considerations of the mechanics of molecular collisions for elastic spheres, one can, with a little work, establish the result of equation (3.9) from mechanical considerations alone and with no reference to thermodynamics. The identification of the average kinetic energy with the thermodynamic temperature [equation (3.8b)] is then made from general thermodynamic considerations of internal energy and entropy without recourse to the equation of state. The equation of state for a thermally perfect gas then follows directly

from the basic kinetic equation (3.2). From this point of view, the thermodynamic form of the equation of state together with Avogadro's law (which is equivalent to the existence of the universal gas constant) emerge as logical deductions from the kinetic approach rather than as independently introduced empirical findings.

Equations (3.3b) and (3.8b) are a special case of the general *principle of equipartition of energy*, which we shall encounter again later. This principle states that *for any part of the molecular energy that can be expressed as the sum of square terms, each such term contributes an average energy of  $\frac{1}{2}kT$  per molecule*. By a "square term" we mean a term that is quadratic in some appropriate variable used to describe the energy. In the kinetic energy of translation, for example, the energy of any molecule can be written in the form  $\frac{1}{2}m(C_1^2 + C_2^2 + C_3^2)$ , which is the sum of three square terms. The average translational energy per molecule is therefore  $\frac{3}{2}kT$  in agreement with (3.3b) and (3.8b). For molecules with internal structure, the total number of square terms may be greater. If the total number of such terms is  $\xi$ , the average molecular energy, now expressed per unit mass rather than per molecule, is given by

$$e = \xi(\frac{1}{2}RT) = \frac{\xi}{2}RT. \quad (3.10)$$

The corresponding specific heats and their ratio  $\gamma$  are then

$$c_v = \frac{\xi}{2}R, \quad c_p = \frac{\xi + 2}{2}R, \quad \gamma = \frac{\xi + 2}{\xi}. \quad (3.11)$$

A given type of molecular energy (rotational, vibrational, etc.) cannot always validly be expressed as a sum of square terms. For this to be possible, the type of energy in question must be "fully excited." The meaning of this term will become apparent when we study the effects of internal structure from the quantum-mechanical point of view (see Chapter IV, Sec. 12). For a diatomic gas such as air there are at ordinary temperatures five square terms, three for translation and two for rotation about the two major axes of the molecule. We thus have in this case  $\xi = 5$  and hence  $\gamma = \frac{7}{5}$ , which is a well-known approximate value for diatomic gases.

The treatment leading up to the basic equation (3.1) is unrealistic in that it assumes specular reflection and a special shape of container and ignores the intermolecular collisions that are a characteristic feature of kinetic theory. It also does not demonstrate that the pressure is the same for all regions on the surface of the container. These objections will be overcome in Chapter II. The results, however, will not be altered.

## 4 MEAN FREE PATH

We now wish to say something about the collisions between molecules, which were ignored in the previous discussion. A concept of fundamental importance here is that of the *mean free path*, which can be defined as the average distance that a molecule travels between successive collisions. We wish in particular to obtain an expression for the mean free path in terms of the quantities that define the gas model.

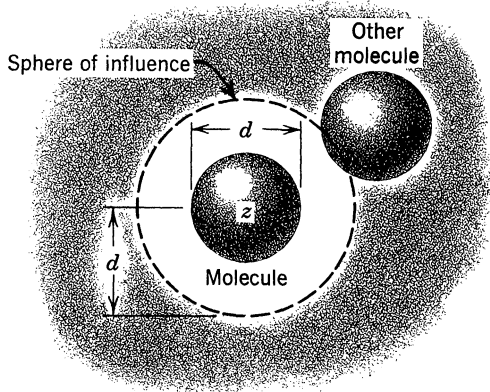


Fig. 3. Sphere of influence of molecule among like molecules.

Let us consider the situation when all of the molecules in an assumed billiard-ball model are of one species and thus have the same diameter  $d$ . A given molecule  $z$  will then suffer a collision whenever the center of  $z$  approaches the distance  $d$  from the center of any other molecule. We may thus imagine  $z$  as carrying with it a *sphere of influence* of radius  $d$  (Fig. 3); a collision will occur whenever the center of another molecule lies on the surface of this sphere of influence.

To make things easy for ourselves, we consider here an oversimplified situation in which  $z$  is moving at a uniform speed equal to the mean molecular speed  $\bar{C}$  [not to be confused with the slightly different root-mean-square speed  $(\bar{C}^2)^{1/2}$ ] and all the other molecules are standing still. The zig-zag path of the molecule and its sphere of influence is then as illustrated in Fig. 4(a), where the molecules with which it collides are indicated by their centers. Ignoring the violation of mechanical principles, imagine that this path is straightened out as shown in Fig. 4(b), with the

centers of the target molecules retaining their position relative to the path of the moving molecule prior to the collision. These centers will then all lie within the straight cylindrical volume swept out by the sphere of influence. Since the molecule is traveling at the uniform speed  $\bar{C}$ , the volume swept out per unit time is obviously  $\pi d^2 \bar{C}$ . If  $n$  denotes the number of molecules per unit volume of gas, the number of centers lying within

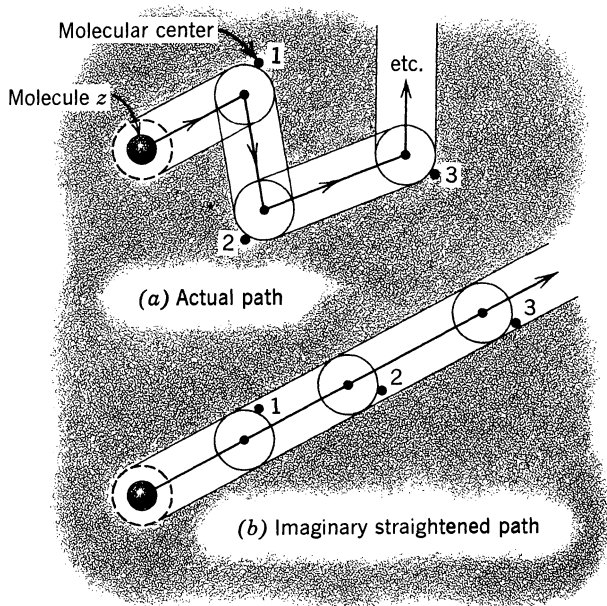


Fig. 4. Path of molecule  $z$  among stationary molecules.

the cylindrical volume is  $\pi d^2 \bar{C} n$ . Since each of these centers corresponds to a collision, this product must also represent the number  $\Theta$  of collisions per unit time for molecule  $z$ , that is,

$$\Theta = \pi d^2 \bar{C} n. \quad (4.1)$$

But the distance traveled by molecule  $z$  per unit time is  $\bar{C}$ . It follows that the average distance traveled per collision, which is the mean free path  $\lambda$ , is

$$\lambda = \frac{\bar{C}}{\Theta} = \frac{1}{\pi d^2 n}. \quad (4.2)$$

In view of the approximations involved, this gives accurately the mean free path for a particle moving with a speed infinitely greater than that of

the other particles. It follows from equation (3.9) that this is approximately the case for a free electron (very small mass) moving in a gas of normal molecular mass.<sup>4</sup> For improved accuracy in purely molecular collisions, the derivation should be modified to account for the motion of the target molecules, and this will be done in Chapter II, Sec. 6. The modified expression for  $\lambda$  turns out to be

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n} \quad (4.3a)$$

The factor  $\sqrt{2}$  in the denominator arises essentially from the fact that the correct speed to use for the evaluation of  $\Theta$  in equation (4.1) is really the mean *relative* speed of the molecules, and this can be shown to be  $\sqrt{2}\bar{C}$ . Equation (4.3a) can also be written in terms of the mass density  $\rho = mn$ , where  $m$  is the mass of the assumedly identical molecules. This gives

$$\lambda = \frac{m}{\sqrt{2} \pi d^2 \rho} \quad (4.3b)$$

Thus for a given value of  $\rho$ , the mean free path for the rigid-sphere model is independent of  $T$  and depends only on the mass and diameter of the molecules.

*Exercise 4.1.* The *Knudsen number*, which plays an important role in low-density flow problems, is defined as the dimensionless ratio  $\lambda/L$ , where  $\lambda$  is the mean free path and  $L$  is some characteristic length of the boundaries. Flow for which  $\lambda/L \geq 1$  is sometimes called free-molecule flow. Consider a sphere 1 foot in diameter traveling through the atmosphere, and take the diameter of the sphere as the characteristic length. Using the results of this section, find the altitude above which free-molecule flow prevails, assuming that the density of the atmosphere is given to a sufficient approximation by

$$\frac{\rho}{\rho_0} = e^{-\alpha H},$$

where  $H$  is the altitude,  $\alpha = 4.25 \times 10^{-5}/\text{ft}$ , and  $\rho_0$  is the sea-level density  $1.23 \times 10^{-3} \text{ gm/cm}^3$ . The molecular quantities required in the calculation can be taken from Sec. 6.

[This problem is intended only as an illustration, and the results should not be taken literally. To obtain correct results it would be necessary to take account of the variation of the effective molecular diameter with temperature (see final paragraphs of Sec. 5) as well as to use a more accurate density-altitude relation.]

<sup>4</sup> In this case, however,  $d$  must be interpreted as the arithmetic mean of the diameters of the electron and molecule, which is very nearly equal to the radius of the molecule.

*Exercise 4.2.* Consider an equilibrium mixture of two species of molecule A and B with different diameters  $d_A$  and  $d_B$ . Using the simplest possible methods, find an expression for the collision frequency  $\Theta_A$  of one A-molecule with all other molecules and for the mean free path  $\lambda_A$  of A-molecules.

## ~~5 TRANSPORT PHENOMENA~~

The phenomena that we have treated so far have had to do with a gas in thermodynamic equilibrium, that is, in which all macroscopic properties are uniform in space and time. When the gas is out of equilibrium by virtue of a nonuniform spatial distribution of some macroscopic quantity (flow velocity, temperature, composition, etc.), additional phenomena arise as a result of the microscopic molecular motion. Very briefly, the molecules in their random thermal movement from one region of the gas to another tend to transport with them the macroscopic properties of the region from which they come. If these macroscopic properties are nonuniform, the molecules thus find themselves out of equilibrium with the properties of the region in which they arrive. The result of these molecular transport processes is the appearance at the macroscopic level of the well-known nonequilibrium phenomena of viscosity, heat conduction, and diffusion. (For a more detailed description of the mechanism of transport processes, see Present, 1958, pp. 38–39.) The situation can be summarized as follows:

Macroscopic Cause	Molecular Transport	Macroscopic Result
Nonuniform flow velocity	Momentum	Viscosity
Nonuniform temperature	Energy	Heat conduction
Nonuniform composition	Mass	Diffusion

For the simplest possible case of nonuniformity in one direction only, macroscopic (i.e., continuum) theory assumes the following relations for the foregoing phenomena, where the symbols are as defined below:

$$\tau = \mu \frac{du_1}{dx_2}, \quad (5.1)$$

$$q = -K \frac{dT}{dx_2}, \quad (5.2)$$

$$\Gamma_A = -D_{AB} \frac{dn_A}{dx_2}. \quad (5.3)$$

Here the nonuniformities are taken to be in the  $x_2$ -direction. In equation (5.1),  $u_1$  is the component of flow velocity in the  $x_1$ -direction (the other components being zero),  $\mu$  is the coefficient of viscosity, and  $\tau$  is the shearing stress. In equation (5.2),  $T$  is the temperature,  $K$  is the coefficient of thermal conductivity, and  $q$  is the heat flow per unit area per unit time, where it is understood that the area is taken normal to the  $x_2$ -axis. In equation (5.3),  $n_A$  is the number density of molecules of species A in an assumed mixture of species A and B,  $D_{AB}$  is the coefficient of diffusion in such a mixture, and  $\Gamma_A$  is the flow of A-molecules per unit area per unit time. We shall now use the methods of kinetic theory in a crude way to

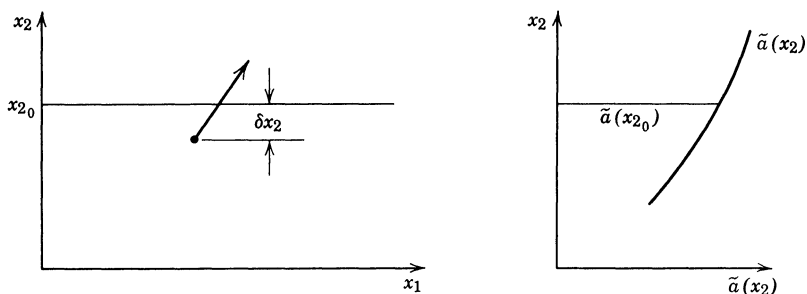


Fig. 5. Assumed situation for calculation of transport properties.

deduce the same equations and to obtain expressions for the transport coefficients. In this we follow essentially the unified treatment given by Present (1958, Chapter 3).

Let  $\tilde{a}(x_2)$  denote some mean molecular quantity (measured per molecule), which varies in the  $x_2$ -direction only (Fig. 5). When a molecule crosses a plane  $x_2 = x_{2_0}$ , it transports a value of  $\tilde{a}$  characteristic mainly of the place at which it made its last collision but dependent to some extent on the location of previous collisions. Let  $\tilde{a}(x_{2_0} - \delta x_2)$  represent the mean value of  $\tilde{a}$  transported in the positive  $x_2$ -direction by a molecule from below  $x_{2_0}$  and  $\tilde{a}(x_{2_0} + \delta x_2)$  the value transported in the negative  $x_2$ -direction by a molecule from above. In a first approximation,  $\delta x_2$  would represent the average distance from the plane to the point at which the molecule made its last collision before crossing; in a higher approximation it will depend on the location of previous collisions and on the nature of the quantity being transported. Whatever the approximation, we may expect that its value is roughly the same as that of the local mean free path. We therefore set  $\delta x_2 = \alpha_{\tilde{a}} \lambda$ , where  $\alpha_{\tilde{a}}$  is a number that is only slightly different from unity and varies somewhat depending on the quantity  $\tilde{a}$  in question. Furthermore, to a first approximation the average number of molecules crossing the plane per unit area per unit time from either above or below



is proportional to  $n\bar{C}$ , where  $n$  is the number density of molecules and  $\bar{C}$  is the average speed of the random molecular motion, both evaluated at  $x_{2_0}$ . This result can be arrived at by dimensional reasoning or by proportion—doubling either  $n$  or  $\bar{C}$  would certainly double the flux of molecules. The net amount of  $\tilde{a}$  transported in the positive  $x_2$ -direction per unit area per unit time, denoted by  $\Lambda_{\tilde{a}}$ , is therefore

$$\Lambda_{\tilde{a}} = \eta n \bar{C} [\tilde{a}(x_{2_0} - \alpha_{\tilde{a}} \lambda) - \tilde{a}(x_{2_0} + \alpha_{\tilde{a}} \lambda)],$$

where  $\eta$  is a constant of proportionality. Expanding  $\tilde{a}$  in a Taylor's series and retaining only first-order terms in  $\lambda$ , we obtain

$$\Lambda_{\tilde{a}} = -\beta_{\tilde{a}} n \bar{C} \lambda \frac{d\tilde{a}}{dx_2}, \quad (5.4)$$

where  $\beta_{\tilde{a}} = 2\eta\alpha_{\tilde{a}}$  is a new constant of proportionality and  $d\tilde{a}/dx_2$  is the gradient of  $\tilde{a}$  evaluated at the plane under consideration. Equation (5.4)

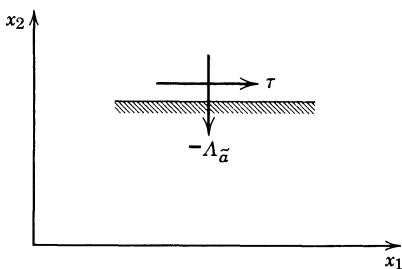


Fig. 6. Correspondence between momentum flux and positive shearing stress.

is the general transport equation. From it three equations equivalent to (5.1) to (5.3) can be obtained as described in the following paragraphs.

(a) Momentum Transport. In this case the quantity being transported is the mean  $x_1$ -momentum of the molecules. Since the mean molecular velocity in a moving fluid is equal to the flow velocity, we have specifically  $\tilde{a} = mu_1(x_2)$ , where  $m$  is the mass of one molecule, all of which are here taken to be alike. The resulting flux of  $\tilde{a}$  (momentum per unit area per unit time) is then equivalent by Newton's law to a shearing stress (force per unit area). In Fig. 6, for example, a net flux of momentum into the material below the plane in question is equivalent to a shearing stress  $\tau$  on that material in the positive  $x_1$ -direction. If this stress is counted as positive in accord with the usual sign convention for shearing stress, a negative flux then corresponds to a positive stress, and we have specifically

$-\Lambda_{\tilde{a}} = \tau$ . Equation (5.4) thus becomes

$$\tau = \beta_{\mu} n m \bar{C} \lambda \frac{du_1}{dx_2} = \beta_{\mu} \rho \bar{C} \lambda \frac{du_1}{dx_2},$$

where we have written  $\beta_{\mu}$  for simplicity. Comparison with the phenomenological equation (5.1) shows that

$$\boxed{\mu = \beta_{\mu} \rho \bar{C} \lambda}. \quad (5.5)$$

We have already seen in equation (4.3b) that  $\lambda$  is inversely proportional to  $\rho$ . It follows that for a given value of  $\bar{C}$ , which like  $(\bar{C}^2)^{1/2}$  is proportional to  $T^{1/2}$ , the value of  $\mu$  is independent of density. This result was first obtained in 1860 by Maxwell, who found it so surprising that he would not rest until he had confirmed it by experiment. Of the dependence on  $T$ , we shall have more to say later.

(b) Energy Transport. Here the quantity being transported is the mean energy of the random and internal motions of the molecules. (We take into account here the internal structure.) We thus have, following equations (3.10) and (3.11),  $\tilde{a} = \tilde{e} = (\xi/2)kT = (\xi/2)mRT = mc_v T$ . The resulting flux  $\Lambda_{\tilde{a}}$  is the heat flow  $q$ . Equation (5.4) thus becomes

$$q = -\beta_K n m \bar{C} \lambda c_v \frac{dT}{dx_2} = -\beta_K \rho \bar{C} \lambda c_v \frac{dT}{dx_2},$$

and comparison with (5.2) shows that

$$\boxed{K = \beta_K \rho \bar{C} \lambda c_v}. \quad (5.6)$$

(c) Mass Transport. Properly speaking, we are concerned here with a mixture of gases, and the quantity being transported is the mass—and with it the identity—of the different species. It will be sufficient for our purposes, however, to continue to deal with a single species. To have something to be transported, we must then imagine that certain of the molecules are “tagged” in some way that distinguishes them from the others without significantly altering their molecular properties. This would be the case, for example, with radioactive tracer molecules. The transport of such tagged molecules through otherwise identical molecules as the result of a concentration gradient is called *self diffusion*. The property being transported is then the identity of the molecule, that is, the probability that it is a tagged molecule. This probability is expressed quantitatively by the fraction  $n_A/n$ , where  $n_A$  is the number density of

tagged molecules, called A-molecules, and  $n$  is the number density of all molecules. We thus have  $\tilde{a} = n_A/n$ . The corresponding flux is taken as  $\Lambda_{\tilde{a}} = \Gamma_A$ , where  $\Gamma_A$  is the net transport of A-molecules per unit area per unit time. Putting these expressions into (5.4) we obtain, on the assumption that the total number of molecules  $n$  is uniform,<sup>5</sup>

$$\Gamma_A = -\beta_D n \bar{C} \lambda \frac{d(n_A/n)}{dx_2} = -\beta_D \bar{C} \lambda \frac{dn_A}{dx_2}.$$

Comparison with equation (5.3) gives

$$\boxed{D_{AA} = \beta_D \bar{C} \lambda}, \quad (5.7)$$

where we have written  $D_{AA}$  for the coefficient of self-diffusion. Equation (5.7) is also a reasonable approximation for the diffusion of one gas through another that is *nearly* identical. This is the situation, for example, with nitrogen and carbon monoxide, which have very similar molecules with nearly the same molecular weight. For the so-called *mutual diffusion* of truly dissimilar molecules, the analysis leading up to equation (5.4) does not apply. In this case we must take account of the fact that the mean free path and mean velocity of the different species are different (see, e.g., Jeans, 1940, Chapter VIII, or Present, 1958, Chapter 4). We shall not attempt to treat this more difficult problem. Further discussion of the motion of mixtures of gases will be given in Chapter IX, Sec. 10.

The precise determination of the constants  $\beta_\mu$ ,  $\beta_K$ , and  $\beta_D$  is a matter of considerable difficulty. To illustrate the results, we shall mention here only the first two of these, and then only very briefly. (For a more complete discussion see Jeans, 1940, Chapters VI and VII. For a treatment of  $\beta_D$  see the same reference, Chapter VIII.) The simplest possible approximation assumes that: (a) the effective slant path of each molecule as regards the value of  $\tilde{a}$  that it transports across  $x_{2_0}$  is exactly  $\lambda$  (i.e., the effect of collisions prior to the one before crossing is negligible), and (b) all molecules have precisely the speed  $\bar{C}$ . This leads to the result that

$$\beta_\mu = \beta_K = \frac{1}{2}. \quad (5.8a)$$

Taking account of the actual distribution of molecular speeds about the mean (cf. Chapter II) reduces the value to

$$\beta_\mu = \beta_K = \frac{1}{3}. \quad (5.8b)$$

Including the effect of previous collisions ("persistence of velocity") increases the effective distance  $\delta x_2$  from which the molecules come and

<sup>5</sup> This corresponds to the assumption that the temperature and pressure are uniform.

thus tends to increase  $\beta_\mu$  and  $\beta_K$  again. In the transport of energy there is also a correlation between the velocity of the molecule and the amount of energy transported (i.e., molecules with high translational energy tend to come from greater distances away from  $x_{2_0}$ ) and this increases  $\beta_K$  still further. The final result of including these and other secondary effects for monatomic gases is that

$$\beta_\mu = 0.499 \cong \frac{1}{2} \quad \text{and} \quad \beta_K \cong \frac{5}{4}. \quad (5.8c)$$

For more complex gases no such simple results are available.

The relation between  $\mu$  and  $K$  implied by equations (5.5) and (5.6) is of interest. Combining these equations we obtain

$$K = \frac{\beta_K}{\beta_\mu} \mu c_v.$$

If the transport of momentum and energy followed the same mechanism [equations (5.8a) or (5.8b)], we would have

$$K = \mu c_v. \quad (5.9a)$$

Owing primarily to the velocity correlation in the transport of energy, we actually obtain [equations (5.8c)]

$$K = \frac{5}{4} \mu c_v = \frac{5}{2} \mu c_v. \quad (5.9b)$$

From this we find for the *Prandtl number*  $\text{Pr} \equiv c_p \mu / K$ , which is an important dimensionless parameter in viscous heat-transfer problems,

$$\text{Pr} = \frac{c_p}{c_v} \times \frac{c_v \mu}{K} = \frac{2}{5} \gamma. \quad (5.10)$$

This checks well with experiment for a monatomic gas ( $\gamma = \frac{5}{3}$  and hence  $\text{Pr} = \frac{2}{3}$ ). For diatomic gases such as air, however, it is known that  $\text{Pr} \cong \frac{3}{4}$  and  $\gamma = \frac{7}{5}$ , and these do not check well with equation (5.10). This is not surprising, since the theoretical values of  $\beta_K$  and  $\beta_\mu$  used in equation (5.9b) were those for a monatomic gas.

A crude method for taking account of the effects of internal structure for polyatomic molecules was suggested by Eucken. His method divides the molecular energy into two parts

$$e = e_{\text{tr}} + e_{\text{int}},$$

where  $e_{\text{tr}}$  is the energy of translational motion and  $e_{\text{int}}$  is the energy associated with the internal structure. We have correspondingly

$$c_v = c_{v_{\text{tr}}} + c_{v_{\text{int}}}. \quad (5.11)$$

The assumption is now made that transport of translational energy involves correlation with the velocity as for a monatomic gas [equation (5.9b)], but that transport of internal energy involves no correlation and is therefore similar to that of momentum [equation (5.9a)]. We write accordingly

$$K = K_{\text{tr}} + K_{\text{int}} = \frac{5}{2}\mu c_{v\text{tr}} + \mu c_{v\text{int}},$$

or, in view of equation (5.11),

$$K = \mu(\frac{3}{2}c_{v\text{tr}} + c_v).$$

Using  $c_{v\text{tr}} = \frac{3}{2}R$ , which follows from equation (3.3c), together with the perfect-gas relation  $c_v = R/(\gamma - 1)$ , we obtain finally for the Prandtl number

$$\text{Pr} = \frac{4\gamma}{9\gamma - 5}. \quad (5.12)$$

This is known as *Eucken's relation*. It gives the same result as the previous relation for a monatomic gas ( $\gamma = \frac{5}{3}$  and  $\text{Pr} = \frac{2}{3}$ ) and is a reasonably good approximation for other gases at ordinary temperatures (e.g., for air  $\gamma = \frac{7}{5}$  and  $\text{Pr} = \frac{2.8}{3.8} = 0.737 \cong \frac{3}{4}$ ).

We close this section with a brief discussion of the effect of temperature on the coefficient of viscosity  $\mu$ . This will serve also to illustrate the effect of the intermolecular forces, which we have up till now ignored. The discussion proceeds from equations (5.5) and (4.3b), which show that for a fixed value of  $m$

$$\mu \sim \bar{C}/d^2. \quad (5.13)$$

Since  $\bar{C}$  is proportional to  $T^{1/2}$  (this will be shown in Chapter II), it follows that for the billiard-ball model we have  $\mu \sim T^{1/2}$ . Actually,  $\mu$  is found to vary more rapidly than this, the difference being due to the variation of the intermolecular force with distance.

Consider, for example, the Sutherland model (Fig. 1), which has a rigid-sphere center surrounded by a weak field of attraction. As two spheres of this kind approach each other their paths are deflected even before the spheres actually strike. From the point of view of an observer fixed relative to a given molecule  $z$ , the path of a colliding molecule is as shown in Fig. 7. As a result of the attractive force, the center of the colliding molecule follows the curved path  $PQR$ , with a collision occurring when the center is at the point  $Q$  on the sphere of influence of  $z$ . The overall change in direction of the molecule as the result of the encounter is the same as if it had followed the straight-line path  $PQ'R$ , with the collision occurring at the point  $Q'$  on some larger, effective sphere of influence. The gross behavior of the spheres with a weak attractive field

is thus equivalent to that of nonattractive spheres of a somewhat larger diameter. The effect of the attractive force can thus be accounted for to a first approximation by replacing  $d$  in relation (5.13) by an effective diameter  $d_{\text{eff}}$ . The larger the relative speed of the molecules, the less time there is for the attractive forces to deflect them and the smaller is  $d_{\text{eff}}$  relative to  $d$ . Detailed analysis of the dynamics of the situation (Loeb,

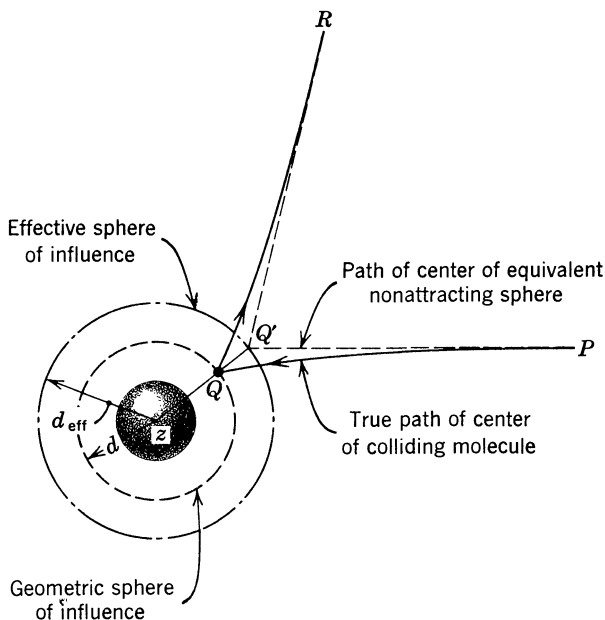


Fig. 7. Collision of two Sutherland molecules as seen by observer fixed relative to molecule  $z$ .

1961, p. 221; Kennard, 1938, p. 154) shows that

$$d_{\text{eff}}^2 = d^2 \left[ 1 + \frac{4}{m} \overline{1/g^2} \int_d^\infty -F(r) dr \right],$$

where  $F(r)$  is the intermolecular force as in Fig. 1 and  $\overline{1/g^2}$  is the mean of  $1/g^2$ , where  $g$  is the relative speed of the molecules. Since it can be shown that  $\overline{1/g^2} \sim 1/T$ , this equation has for a given force field the form

$$d_{\text{eff}}^2 = d^2 \left( 1 + \frac{\chi}{T} \right),$$

where  $\chi$  is a constant that is positive for attractive forces ( $F < 0$ ). Using

$d_{\text{eff}}^2$  in (5.13) in place of  $d^2$  and noting as before that  $\bar{C} \sim T^{1/2}$ , we obtain finally

$$\frac{\mu}{\mu_{\text{ref}}} = \left( \frac{T}{T_{\text{ref}}} \right)^{1/2} \frac{1 + \chi/T_{\text{ref}}}{1 + \chi/T}, \quad (5.14)$$

where  $\mu_{\text{ref}}$  is the coefficient of viscosity at some reference temperature  $T_{\text{ref}}$ . This is *Sutherland's formula*. Although it is still rather crude from a theoretical point of view, it does provide a more rapid variation of  $\mu$  than the simple  $T^{1/2}$ . With the constants determined empirically, it gives accurate results for certain gases such as oxygen and nitrogen and is therefore of considerable practical value.

*Exercise 5.1.* The thickness  $\delta$  of a laminar boundary layer at a given angular position on a circular cylinder of diameter  $D$  varies as  $\delta/D \sim 1/\sqrt{\text{Re}}$ . Here the Reynolds number  $\text{Re}$  is defined by  $\text{Re} \equiv \rho_{\infty} U_{\infty} D / \mu_{\infty}$ , where  $U_{\infty}$  is the flow velocity of the undisturbed stream relative to the cylinder and  $\rho_{\infty}$  and  $\mu_{\infty}$  are the corresponding density and coefficient of viscosity. If  $\lambda_{\infty}$  is the mean free path in the undisturbed stream, find how the ratio  $\lambda_{\infty}/\delta$  varies as a function of  $\text{Re}$  and  $M$ , where  $M$  is the Mach number  $M \equiv U_{\infty}/\sqrt{\gamma RT_{\infty}}$ .

*Exercise 5.2.* In the treatment of energy transport in this section we in effect assumed (by considering only the energy of the random and internal motions) that there was no macroscopic motion of the gas. Consider now a gas with not only a temperature gradient  $dT/dx_2$  but also a gradient of flow velocity  $du_1/dx_2$  as in the treatment of momentum transport. By the mean-free-path methods of this section, show that the flux of molecular energy in the  $x_2$ -direction is now given by

$$\Lambda = -K \frac{dT}{dx_2} - u_1 \mu \frac{du_1}{dx_2} = q - u_1 \tau.$$

The second term on the right is interpreted at the macroscopic level as the work done by the shear stress.

## 6 MOLECULAR MAGNITUDES

We are now in a position to use macroscopic measurements to make an estimate of the magnitudes involved in molecular phenomena. Among the quantities that can be measured macroscopically are  $p$ ,  $\rho$ ,  $\mu$ , and  $\hat{M}$ , where  $\hat{M}$  is the molecular weight (mass per mole). We should like to find the following four quantities that characterize the molecular model:  $m$ ,  $d$ ,  $n$ , and  $\sqrt{\bar{C}^2}$ . Since  $m = \hat{M}/\hat{N}$ , the determination of  $m$  also entails the determination of Avogadro's number  $\hat{N}$ .

We shall consider air, which has the following macroscopic properties at standard conditions of 1 atm and  $0^\circ\text{C}$ :

$$p = 1.013 \times 10^8 \text{ dyne/cm}^2,$$

$$\rho = 1.288 \times 10^{-3} \text{ gm/cm}^3,$$

$$\mu = 1.71 \times 10^{-6} \text{ gm/cm sec.}$$

We shall ignore the fact that air is a mixture of gases, and consider it to be made up of fictitious identical molecules. Since the molecular weights of  $\text{N}_2$  and  $\text{O}_2$  are not very different, this assumption is not far from the truth. On this basis the molecular weight is  $\hat{M} \cong 28.9 \text{ gm/mole}$ .

The root-mean-square molecular speed at the above conditions has already been found following equation (3.5) and is

$$\sqrt{\bar{C}^2} = \left(3 \frac{p}{\rho}\right)^{1/2} \cong 5 \times 10^4 \text{ cm/sec.} \quad (6.1)$$

We can estimate  $d$  and  $\hat{N}$  simultaneously by the following procedure. From equations (5.5) and (5.8c) plus equation (4.3b) we can write

$$\mu = \frac{1}{2} \rho \bar{C} \lambda = \frac{1}{2} \rho \bar{C} \frac{m}{\sqrt{2} \pi d^2 \rho} = \frac{1}{2\sqrt{2} \pi} \times \frac{\hat{M}}{\hat{N}} \times \frac{\bar{C}}{d^2},$$

or, if we take  $\bar{C} \cong \sqrt{\bar{C}^2}$  and  $2\sqrt{2} \pi \cong 9$ ,

$$\hat{N} d^2 \cong \frac{1}{9} \frac{\hat{M} \sqrt{\bar{C}^2}}{\mu}. \quad (6.2)$$

Since the quantities on the right are known, this gives a relation between  $\hat{N}$  and  $d$ . A second relation can be found by going outside kinetic theory and considering the situation in *liquid* air. We assume as a rough estimate that each molecule in the liquid state occupies a cube of side  $d$ . If  $\rho_L$  denotes the density of the liquid state, we then have  $m = \rho_L d^3$  or, since  $m = \hat{M}/\hat{N}$ ,

$$\hat{N} d^3 \cong \frac{\hat{M}}{\rho_L}. \quad (6.3)$$

Dividing (6.3) by (6.2) and substituting the known values of  $\mu$ ,  $\sqrt{\bar{C}^2}$ , and  $\rho_L = 0.86 \text{ gm/cm}^3$ , we find

$$d \cong \frac{9\mu}{\rho_L \sqrt{\bar{C}^2}} \cong \underline{3.7 \times 10^{-8} \text{ cm.}} \quad (6.4)$$

Returning to equation (6.3), we then obtain for Avogadro's number

$$\hat{N} \cong \frac{\hat{M}}{\rho_L d^3} \cong 6.7 \times 10^{23} / \text{mole}$$



The accepted value of this universal constant, from accurate considerations based on measurements of electronic charge, is

$$\hat{N} = \underline{6.02252 \times 10^{23}/\text{mole}}. \quad (6.5)$$

With the foregoing results, we now find for the mass of one molecule

$$m = \hat{M}/\hat{N} \cong \underline{4.80 \times 10^{-23} \text{ gm}},$$

and for the number density

$$n_0 = \frac{\rho}{m} \cong \underline{2.69 \times 10^{19}/\text{cm}^3}. \quad (6.6)$$

This last is the number of molecules per cubic centimeter of air at standard conditions of  $p = 1$  atm and  $T = 0^\circ\text{C}$ . Since the perfect-gas equation can be written  $p = nkT$ , the same number must hold, to the accuracy of perfect-gas theory, for *any* gas at that pressure and temperature. This *standard number density*, which we denote by the addition of the subscript  $( )_0$ , is known also as *Loschmidt's number*.

We have thus found the four quantities that we set out to evaluate. It is also of interest to calculate the average spacing  $\delta$  between molecules. Since the average volume available per molecule is  $1/n_0$ , this is given by

$$\delta = \frac{1}{n_0^{1/3}} \cong 3.3 \times 10^{-7} \text{ cm}.$$

We can also find the mean free path, which is

$$\lambda = \frac{1}{\sqrt{2}\pi n_0 d^2} \cong 6 \times 10^{-6} \text{ cm},$$

and the frequency of collisions per molecule, which is

$$\Theta = \frac{\bar{C}}{\lambda} \cong \frac{\sqrt{\bar{C}^2}}{\lambda} \cong 10^{10}/\text{sec}.$$

It is of interest to compare the various microscopic distances that we have obtained. On the basis of the foregoing results we can write

$$\lambda:\delta:d = 6 \times 10^{-6}:3.3 \times 10^{-7}:3.7 \times 10^{-8} \cong 170:10:1.$$

Thus the mean free path is much greater than the average spacing, which in turn is much greater than the molecular diameter. Since the effective range of intermolecular forces is of the order of the diameter, this justifies the assumption that the gas molecules interact only during some kind of collision process of relatively short duration. This idea is implicit in our entire development of kinetic theory. It remains valid so long as the density is not too high.

The foregoing picture, with its minute distances and astronomical number density, would be fantastic if we were not already accustomed to molecular ideas. Some feeling for the wonder of it may be regained with the following quotation from Jeans (1940, p. 32):

... , a man is known to breathe out about 400 c.c. of air at each breath, so that a single breath of air must contain about  $10^{22}$  molecules. The whole atmosphere of the earth consists of about  $10^{44}$  molecules. Thus one molecule bears the same relation to a breath of air as the latter does to the whole atmosphere of the earth. If we assume that the last breath of, say, Julius Caesar has by now become thoroughly scattered through the atmosphere, then the chances are that each of us inhales one molecule of it with every breath we take. A man's lungs hold about 2000 c.c. of air, so that the chances are that in the lungs of each of us there are about five molecules from the last breath of Julius Caesar.

## References

- Jeans, J., 1940, *An Introduction to the Kinetic Theory of Gases*, Cambridge University Press.
- Kennard, E. H., 1938, *Kinetic Theory of Gases*, McGraw-Hill.
- Loeb, L. B., 1961, *The Kinetic Theory of Gases*, 3rd ed., Dover.
- Present, R. D., 1958, *Kinetic Theory of Gases*, McGraw-Hill.
- Slater, J. C., 1939, *Introduction to Chemical Physics*, McGraw-Hill.