

Equilibrium Kinetic Theory

Vincenti and Kruger, Introduction to Physical Gas Dynamics, c1965

1 INTRODUCTION

The mean-free-path methods of Chapter I are as far as we shall go for the present in our discussion of nonequilibrium kinetic theory. We shall return to nonequilibrium theory and transport processes in a more rigorous way in Chapters IX and X. For the time being we restrict our attention to a more detailed and rigorous consideration of the equilibrium state. In this chapter in particular, we shall (1) give a more rigorous discussion of the equation of state of a perfect gas, (2) look into the distribution of molecular velocities and the resulting implications with regard to molecular collisions and the mean free path, and (3) examine the conditions of equilibrium of a reacting gas mixture from the kinetic point of view. Some of the results, although obtained from equilibrium ideas, will also be useful later in certain nonequilibrium situations.

2 VELOCITY DISTRIBUTION FUNCTION

All molecules of a gas do not move with the same velocity, nor does the velocity of a given molecule remain constant with time. For a detailed and rigorous discussion of kinetic theory, we must have some statistical way of specifying this fact. This is provided by the *velocity distribution function*.

The distribution function is a general concept in statistics, and there can be distribution functions for all sorts of quantities. We shall introduce the velocity distribution function by analogy to a kind of distribution function with which the student is presumably familiar but which he may not have recognized as such. This is the mass density ρ in a nonuniform density field.

To begin, let us consider a gas uniformly distributed throughout a container of volume V . We consider all the molecules to be alike of mass m and suppose that there are N of these molecules. The mass density of the gas is thus

$$\rho = m \frac{N}{V} = mn, \quad (2.1)$$

where $n = N/V$ is the corresponding number density. Since the gas is uniformly distributed, ρ and n each have the same value for all subvolumes of V , provided these volumes contain a sufficient number of molecules.

If the gas is *nonuniformly* distributed in the container, we introduce the idea of a *local* mass density $\rho(x_1, x_2, x_3) = \rho(x_i)$. Here x_i is shorthand notation for the position *vector* with Cartesian components x_1, x_2, x_3 (Fig. 1); this type of notation will be used for vectors throughout the book. To relate the familiar macroscopic idea of a local density to microscopic molecular ideas,

Fig. 1. Volume element in physical space.

we proceed as follows. Let ΔN be the number of molecules contained in the volume ΔV_x located between x_1 and $x_1 + \Delta x_1$, x_2 and $x_2 + \Delta x_2$, x_3 and $x_3 + \Delta x_3$. We then have, analogous to (2.1),

$$\rho(x_i) = \lim_{\Delta V_x \rightarrow 0} m \frac{\Delta N}{\Delta V_x} = m \lim_{\Delta V_x \rightarrow 0} \frac{\Delta N}{\Delta V_x} = mn(x_i). \quad (2.2)$$

Here the limit is taken to mean that ΔV_x approaches zero on the scale of the container but remains large on the scale of the molecular spacing. Thus ΔV_x is given a macroscopic interpretation even in the limit. Since the molecular spacing is normally very tiny (see Chapter I, Sec. 6), this is a valid procedure except for gases so rarefied as to be of little practical interest. The local number density $n(x_i) = \lim (\Delta N/\Delta V_x)$ in equation (2.2) gives the number of molecules per unit volume as a function of position. It is thus a measure of the distribution of molecules with regard to position in space—in short, it is a *position distribution function*. If we know this function, the number of molecules dN in the macroscopically infinitesimal element $dV_x = dx_1 dx_2 dx_3$ located at the position x_i is then

$$dN = n(x_i) dV_x. \quad (2.3a)$$

This will be the case so long as the dimensions of the subvolumes are large compared with the average spacing between the molecules. Since $\rho(x_i)$ is proportional to $n(x_i)$ by (2.2), the local mass density may also be looked on as a position distribution function, the only difference being that it applies to mass rather than to molecular number. Knowing this distribution function, we can find the mass dM in an infinitesimal volume located at x_i from the relation

$$dM = \rho(x_i) dV_x, \quad (2.3b)$$

a procedure that is presumably familiar. Generally—and loosely—speaking, a distribution function gives the concentration of some quantity per unit “volume” as a function of position in some sort of “space.” To find the amount of that quantity in an infinitesimal volume located at a given position in that space, we merely proceed as in equations (2.3), that is, we multiply the distribution function by the infinitesimal element of volume.

Although $n(x_i)$ can be taken as the position distribution function for molecules, it is sometimes convenient to define a normalized quantity $\omega(x_i) = n(x_i)/N$, and speak of this function $\omega(x_i)$ as the distribution function. The number of molecules located in the volume dV_x is then

$$dN = N\omega(x_i) dV_x. \quad (2.4)$$

The fractional number of molecules within the volume is thus $\omega(x_i) dV_x$. This can also be interpreted as the probability that a molecule chosen at random will lie within the given volume. Since the total number of molecules in V is N , $\omega(x_i)$ is subject to the condition that

$$\int_V N\omega(x_i) dV_x = N,$$

or

$$\int_V \omega(x_i) dV_x = 1, \quad (2.5)$$

where the integration is taken over the volume V .

The foregoing illustrates what we mean by a distribution function. We are interested here, however, not in the spatial distribution of molecules in a nonuniform gas but in the distribution of molecular velocities in a spatially uniform gas.

We return therefore to a consideration of the uniform gas of N molecules in the volume V . At every instant, each of the N molecules will have a velocity that can be completely specified by its three Cartesian components C_1, C_2, C_3 . The molecule can thus be represented uniquely by a point in a Cartesian space having the velocity components as coordinates

(Fig. 2). In this so-called *velocity space* the molecule is thus represented by a point located at the end of the velocity vector C_i laid off from the origin. The entire gas in the volume V is represented correspondingly by a cloud of N points in this space. The situation is thus analogous to (but definitely different from) the distribution of the molecules themselves in physical

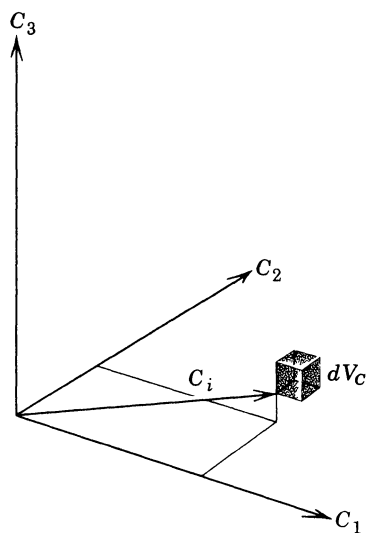


Fig. 2. Volume element in velocity space.

space. As before, a local point density $F(C_i)$ —points per unit “volume,” analogous to $n(x_i)$ —can be introduced. It is defined such that the number of molecular points whose coordinates in velocity space lie in the element of volume $dV_C = dC_1 dC_2 dC_3$ located between C_1 and $C_1 + dC_1$, C_2 and $C_2 + dC_2$, and C_3 and $C_3 + dC_3$ is equal to $F(C_i) dV_C$. Since each point represents a molecule, this also gives the number of molecules for which the velocity components lie between the same limits, or equivalently, for which the velocity vectors end inside the volume dV_C . The function $F(C_i)$ is referred to as a *velocity distribution function*. As before, it is sometimes convenient to replace $F(C_i)$ by a normalized distribution function, defined by $f(C_i) \equiv F(C_i)/N$. The num-

ber of molecules whose components of velocity lie in the range C_1 to $C_1 + dC_1$, C_2 to $C_2 + dC_2$, and C_3 to $C_3 + dC_3$ is then

$$\boxed{dN = Nf(C_i) dV_C}, \quad (2.6a)$$

or, in terms of the number density $n = N/V$,

$$dn = nf(C_i) dV_C. \quad (2.6b)$$

The probability of any given molecule having velocity components within the specified range is $f(C_i) dV_C$. Since all the N molecules must lie somewhere in the velocity space, $f(C_i)$ is subject to the condition

$$\int_{-\infty}^{\infty} Nf(C_i) dV_C = N,$$

or

$$\boxed{\int_{-\infty}^{\infty} f(C_i) dV_C = 1}, \quad (2.7)$$

where the integration extends over all of velocity space, that is, from $-\infty$ to ∞ for each velocity component.

In the work that follows we shall often want to take averages of quantities that depend on the velocity of the molecule. Let $Q = Q(C_i)$ be any quantity (measured per molecule) that is a function of the velocity. The average value of Q for the whole assembly of N molecules is then

$$\bar{Q} = \frac{\int_N Q dN}{N} = \frac{\int_{-\infty}^{\infty} Q(C_i) N f(C_i) dV_C}{N},$$

or

$$\boxed{\bar{Q} = \int_{-\infty}^{\infty} Q f dV_C}, \quad (2.8)$$

where the functional notation is omitted for brevity.

Throughout this book we shall work with the normalized distribution function, which we have denoted by $f(C_i)$. Some authors prefer to write their equations in terms of the non-normalized function, which we have called $F(C_i)$, but use the symbol $f(C_i)$ to denote this latter function. Their equations are readily obtained from ours by formally replacing $f(C_i)$ in our equations by $f(C_i)/N$ or $f(C_i)/n$.

3 EQUATION OF STATE FOR A PERFECT GAS

With the aid of the distribution function we can now give a derivation of the perfect-gas law that does not depend on the special assumptions used in the earlier analysis. For simplicity, we assume here that all molecules are alike and thus have the same mass m .

We consider a locally planar element dS of a fixed, solid wall and choose an x_1, x_2, x_3 coordinate system with the x_3 -axis normal to the element as shown in Fig. 3. Molecules will strike and leave dS in various directions, depending on the direction of the velocity vector of the particular molecule. We assume that each molecule that strikes the element is brought to rest in the positive x_3 -direction and then emitted with a component of motion in the negative direction. The molecule loses momentum normal to the wall in being brought to rest and gains negative momentum in being emitted. Each such change in momentum is accompanied by a force on the wall, and this force will fluctuate with time. In a gas at equilibrium the time average of the force, measured per unit area, is the pressure of the gas.

In calculating the force in this instance we make no supposition about the nature of the reflection for a given molecule. In particular, we dispense with the unrealistic assumption, made in Sec. 3 of the preceding chapter, that the reflection is specular and without change in speed. This can be done by considering the incoming and outgoing molecules in two separate groups.

We look first at the incoming molecules, that is, at molecules with positive values of C_3 . Of these, let us consider to begin with only those with

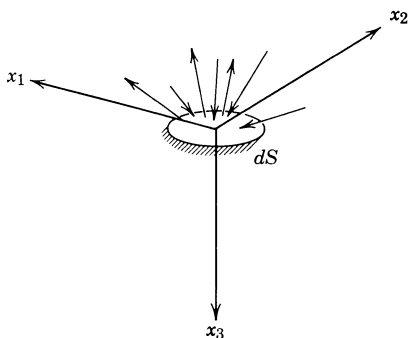


Fig. 3. Element of wall and coordinate system.

velocities infinitesimally close to a specific velocity vector C_i . We consider, in other words, a special class of incoming molecules with velocity components in the range C_1, C_2, C_3 to $C_1 + dC_1, C_2 + dC_2, C_3 + dC_3$, where C_1, C_2, C_3 have given numerical values. We speak of these as “molecules of class C_i .” All classes will be accounted for later by integration. The molecules of class C_i that strike dS in an interval of time dt will be those that, at the beginning of the interval, are contained in the slant cylinder with base dS and surface elements parallel to C_i and of length $C dt$ (Fig. 4). Molecules belonging to the class C_i but lying outside the cylinder obviously cannot reach dS in the interval dt ; by the same token, all molecules of class C_i that lie inside the cylinder must reach dS in the stated interval.¹

¹ In making these statements we have ignored the effect of molecular collisions inside the slant cylinder. This is justified if we take dt small enough that the distance $C dt$ is small compared with the mean free path. In a sufficiently dilute gas the molecular spacing is sufficiently small compared with the mean free path that this can be done and a large number of molecules still retained in the cylinder. The neglect of collisions can also be argued on equilibrium grounds—that is, at equilibrium as many molecules are knocked into the given class in time dt as are knocked out of it. We prefer the first argument, however, since we shall want to apply certain of the resulting expressions to nonequilibrium situations in Chapter IX.

Molecules of other classes, of course, will also reach dS in time dt , but we are for the time being not interested in these. Now, the altitude of the cylinder in question is $C_3 dt$, and its volume is therefore $C_3 dt dS$. Furthermore, by expression (2.6b), the number of molecules of class C_i per unit volume in the physical space is $nf(C_i) dC_1 dC_2 dC_3$. The number of molecules of class C_i striking dS in the interval dt is therefore $nC_3 f(C_i) dC_1 dC_2 dC_3 dS dt$, and the flux of such molecules (number per

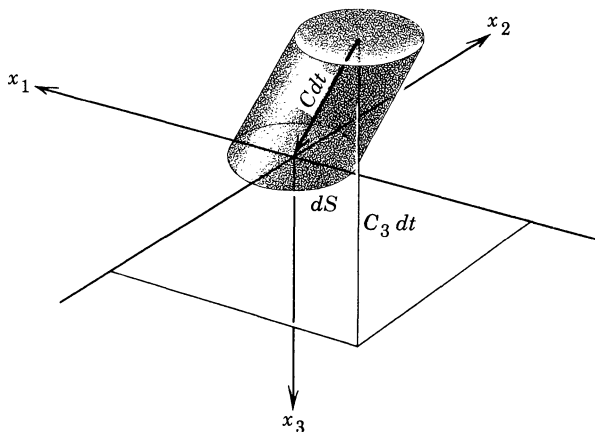


Fig. 4. Slant cylinder containing molecules of class C_i that strike dS in time dt .

unit area per unit time) arriving at dS is correspondingly

$$nC_3 f(C_i) dC_1 dC_2 dC_3. \quad (3.1)$$

To obtain the flux of molecules arriving at an element of area perpendicular to the x_1 - or x_2 -axes we need merely replace C_3 ahead of f by C_1 or C_2 . Expressions of this kind will have considerable use later. If dS is regarded as an open area rather than a wall, expression (3.1) also gives the flux of molecules of class C_i through that area.

The calculation of the normal stress (normal force per unit area) on dS due to the incoming molecules is now simple. Since each such molecule loses normal momentum in the amount mC_3 when it strikes the wall, the total normal momentum lost by incoming molecules of class C_i per unit area per unit time is

$$nmC_3^2 f(C_i) dC_1 dC_2 dC_3.$$

The normal stress σ_I exerted on dS by all incoming molecules is equal to the total loss of normal momentum for all such molecules. This is found by integrating over all classes of incoming molecules as follows:

$$\sigma_I = nm \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty C_3^2 f(C_i) dC_1 dC_2 dC_3.$$

The integration with respect to C_1 and C_2 extends from $-\infty$ to ∞ . That with respect to C_3 extends only from 0 to ∞ , as is appropriate for incoming molecules.

The foregoing arguments can be repeated with regard to outgoing molecules. We thus find for the normal stress σ_O exerted on dS by all such molecules

$$\sigma_O = nm \int_{-\infty}^0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_3^2 f(C_i) dC_1 dC_2 dC_3.$$

Here the integration with respect to C_3 extends from $-\infty$ to 0 since outgoing molecules have negative values of C_3 .

The complete normal stress σ on the wall is the sum of σ_I and σ_O . We thus have

$$\begin{aligned} \sigma &= nm \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_3^2 f(C_i) dC_1 dC_2 dC_3 \\ &\quad + nm \int_{-\infty}^0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_3^2 f(C_i) dC_1 dC_2 dC_3 \\ &= nm \int_{-\infty}^{\infty} C_3^2 f dV_C \end{aligned}$$

or, in view of equation (2.8),

$$\sigma = nm \overline{C_3^2}.$$

No assumption of equilibrium has been made in the development to this point. The foregoing expressions thus hold whether the gas is in equilibrium or not.

We now assume the gas to be in equilibrium, that is, there are no gradients of temperature or mean velocity. It is implicit, of course, that the wall is also in equilibrium with the gas, that is, that it has the same temperature. Since the container is at rest, the molecular velocity C_i must now be entirely random. Under these conditions every direction is statistically like every other direction; or, as stated in Chapter I, Sec. 3, no direction is preferred. We must thus have, in particular, $\overline{C_1^2} = \overline{C_2^2} = \overline{C_3^2}$. But since $C^2 = C_1^2 + C_2^2 + C_3^2$, it follows that

$$\overline{C^2} = \overline{C_1^2} + \overline{C_2^2} + \overline{C_3^2} = 3\overline{C_3^2}. \quad (3.2)$$

Since at equilibrium the normal stress on the wall is equal to the pressure p of the gas, we can thus write finally, with $\rho = nm$,

$$\boxed{\frac{p}{\rho} = \frac{1}{3} \overline{C^2}}. \quad (3.3)$$

This is identical to equation (I 3.5), which was obtained from cruder arguments. The results based on the earlier equation, or on the equivalent equation (I 3.2), thus follow as before.

The foregoing result can be interpreted directly in terms of the pressure in the interior of the gas if we define the normal stress as the momentum transport per unit area per unit time across an imaginary element dS within the gas. The stress σ_I is now interpreted as arising from the flux of momentum through dS in one direction and σ_O from the flux in the opposite direction. The pressure p at equilibrium then follows as before.

Throughout this section we have assumed, as justified by the calculations at the end of Chapter I, that the molecules experience a force only during an actual collision. In other words, we assume that the average spacing of the molecules is much greater than the range of the intermolecular forces. As a result the molecules cannot, so to speak, "reach out" across the element dS in the interior of the gas and exert a force on the molecules on the other side. The only way they can exert such a force is to actually pass through dS and undergo a collision. It is thus reasonable to define the pressure at equilibrium solely in terms of a momentum flux. This is crucial to the kinetic-theory derivation of the perfect-gas equation of state. If the density is high enough that the molecular spacing is at all comparable to the range of the intermolecular forces, then the so-called "van der Waals forces" become important and the definition of pressure and the resulting equation of state must be modified accordingly (see Jeans, 1940, Chapter III).

Note that we have nowhere in this section made the explicit assumption that the molecules collide according to the billiard-ball model. All that we have really assumed is that there exists some sort of loosely defined collision process of relatively short duration (cf. Chapter IX, Sec. 3). The perfect-gas result thus corresponds, not to the billiard-ball model alone, but to any gas provided it is sufficiently dilute.

4 MAXWELLIAN DISTRIBUTION—CONDITION FOR EQUILIBRIUM

The result of equation (3.3) was obtained without finding the form of $f(C_i)$. To proceed further we can no longer ignore this question.

As first published by Maxwell in 1860, the velocity distribution function for a gas at equilibrium is

$$f(C_i) = f(C_1, C_2, C_3) = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left[-\frac{m}{2kT} (C_1^2 + C_2^2 + C_3^2) \right].$$

Unfortunately, the establishment of this formula by kinetic theory represents a pedagogical dilemma in an elementary discussion. The simple treatments, such as that used by Maxwell himself, are lacking in rigor and physical content; the rigorous treatment devised by Boltzmann, although instructive physically, is long and complicated. We shall give here an abbreviated discussion that follows the general approach of the rigorous treatment but cites some of the details without proof. The proof of these details is provided later in Chapter IX. An alternative derivation by the entirely different methods of statistical mechanics is also given in Chapter IV. With molecular-beam techniques, the distribution of molecular velocities can be measured directly and is found to be in excellent agreement with the above formula. The Maxwellian distribution can thus, if we wish, be taken as a fundamental physical law that requires no theoretical proof. From this point of view, the present treatment could be regarded as a kind of plausibility argument.

Our argument proceeds from a consideration of the rate of change of the number of molecules in a given class C_i as the result of collisions. Each time a molecule of this class collides with another molecule, its velocity is changed and it is removed from the class. Such collisions thus tend to deplete the molecules in the class in question. Conversely, when a collision between two molecules occurs such that one of them emerges with the velocity C_i , a molecule is added to the class. Such collisions act to replenish the number of molecules of the class C_i . At equilibrium the net change from the two types of collisions must be zero, and this fact can be used to find the distribution function.

To make these ideas explicit, we consider first a general collision between two molecules of arbitrary classes U_i and Y_i , that is, with velocity components in the respective ranges U_1, U_2, U_3 to $U_1 + dU_1, U_2 + dU_2, U_3 + dU_3$ and Y_1, Y_2, Y_3 to $Y_1 + dY_1, Y_2 + dY_2, Y_3 + dY_3$. The relative-velocity vector of the molecule of class Y_i relative to the molecule of class U_i will be denoted by g_i . It has the magnitude

$$g = [(Y_1 - U_1)^2 + (Y_2 - U_2)^2 + (Y_3 - U_3)^2]^{1/2}. \quad (4.1)$$

Let us temporarily take a molecule of class U_i as the focus of attention. If we assume a billiard-ball model, we can then say, as in Chapter I, Sec. 4, that at the instant of impact the center of the molecule of class Y_i must lie on the sphere of influence of radius d about the center of the molecule of class U_i (Fig. 5). To completely specify the collision, however, it is also necessary to give the direction of the line connecting the centers of the two molecules at the instant of impact, the so-called *line of centers*. Two angles are required for this purpose. A convenient choice for one of these is the acute angle ψ between the line of centers and the line of the vector

g_i . These two lines define a plane, which we call the *plane of the collision*. The direction of the line of centers is then completely specified if we specify the orientation of this plane. This we do by taking as our second angle the angle ϵ that the plane makes with some arbitrary reference plane parallel to g_i .

We now ask: What is the frequency of collisions occurring between molecules of classes U_i and Y_i and such that the direction of the line of

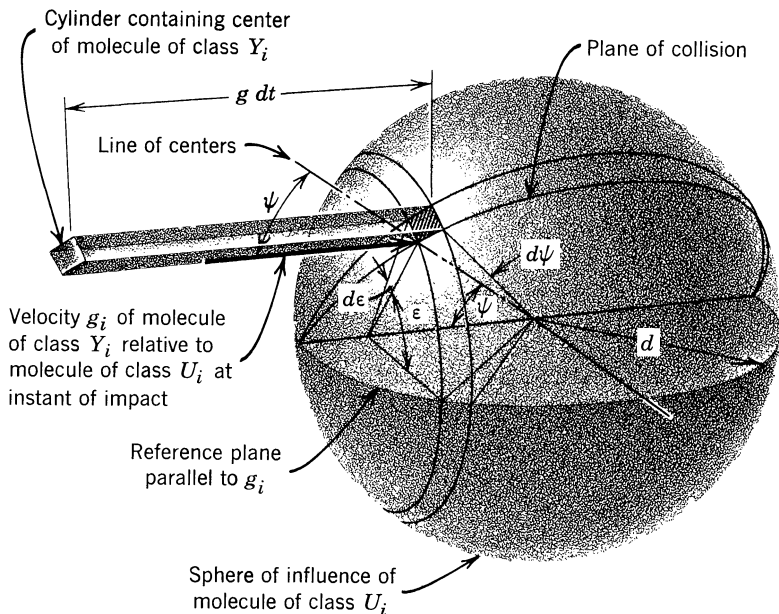


Fig. 5. Construction for calculation of collision rate between molecules of classes U_i and Y_i .

centers lies in the range ψ, ϵ to $\psi + d\psi, \epsilon + d\epsilon$? At the instant of this particular type of collision the center of the molecule of class Y_i must lie on the small rectangle cut out on the sphere of influence of the molecule of class U_i by the angles $d\psi$ and $d\epsilon$ (Fig. 5). The area of this rectangle is $d^2 \sin \psi d\psi d\epsilon$. If such a collision is to occur within a small interval of time dt , then at the beginning of that interval the molecule of class Y_i must lie within a slant cylinder based on the small rectangle and having surface elements parallel to g_i and of length $g dt$. Since the altitude of this cylinder is $g dt \cos \psi$, the volume of the cylinder is $d^2 \sin \psi \cos \psi d\psi d\epsilon g dt$. Now, a cylinder of this kind can be associated with each of the molecules of class U_i . These are present in a unit volume of gas in the number $n f(U_i) dV_U$, where n is the number density of molecules in physical space

and dV_U is, as before, the volume element $dU_1 dU_2 dU_3$ in velocity space. It follows that the total volume of the slant cylinders associated with all the molecules of class U_i taken together is

$$n d^2f(U_i)g \sin \psi \cos \psi d\psi d\epsilon dV_U dt.$$

The number of molecules of class Y_i having centers within this collection of cylinders can be found by multiplying the foregoing expression by the number of molecules of class Y_i per unit volume, which is $nf(Y_i) dV_Y$. Since each of these molecules satisfies the conditions for a collision, we thus find for the number of collisions of the specified type per unit volume of gas per unit time

$$n^2 d^2f(U_i)f(Y_i)g \sin \psi \cos \psi d\psi d\epsilon dV_U dV_Y. \quad (4.2)$$

This is the answer to the question posed at the beginning of the paragraph.

We now wish to apply this formula to the collisions that deplete and replenish the particular class C_i that was originally under discussion. In doing this we shall pair off a specific type of depleting collision with a corresponding type of replenishing collision in a special way. As the typical depleting collision we take those collisions that occur between molecules of the given class C_i and some other specific class Z_i and that have their line of centers in a specified range ψ, ϵ to $\psi + d\psi, \epsilon + d\epsilon$. The two molecules entering such a collision do so with initial velocities C_i and Z_i and leave with final velocities denoted respectively by C'_i and Z'_i . We shall see from detailed consideration of collision dynamics in Chapter IX, Sec. 7 that if C_i, Z_i, ψ , and ϵ are given, then C'_i and Z'_i are completely determined. This is because the four conservation equations (one for energy and three for momentum) plus the two quantities ψ and ϵ give, in effect, six relations for the determination of the six components of C'_i and Z'_i . We can write accordingly that

$$C'_i = C'_i(C_i, Z_i, \psi, \epsilon) \quad \text{and} \quad Z'_i = Z'_i(C_i, Z_i, \psi, \epsilon). \quad (4.3)$$

We now consider the *inverse collision* to the foregoing. The inverse to a given collision is by definition a collision having (a) initial velocities equal to the final velocities of the given collision and (b) the same direction of the line of centers. The inverse to the foregoing collision thus has initial velocities C'_i and Z'_i and the same direction of the line of centers as before. As will be seen from the detailed considerations of collision dynamics in Chapter IX, the final velocities of the molecules leaving this inverse collision are then precisely C_i and Z_i . That is to say, an inverse collision reproduces the velocities at which the molecules entered the corresponding original

collision. An example of a collision and its inverse is shown in Fig. 6.² Since the inverse collision here produces a molecule with velocity C_i , it constitutes a replenishing collision in the sense originally discussed. The reason for pairing a given type of depleting collision with the inverse replenishing collision is that the initial velocities of the latter can then be expressed in terms of the initial velocities of the former [cf. equations (4.3)]. As will be seen, this facilitates the integration necessary to determine the net change in the number of molecules in the class C_i as the result of all possible depleting and replenishing collisions.

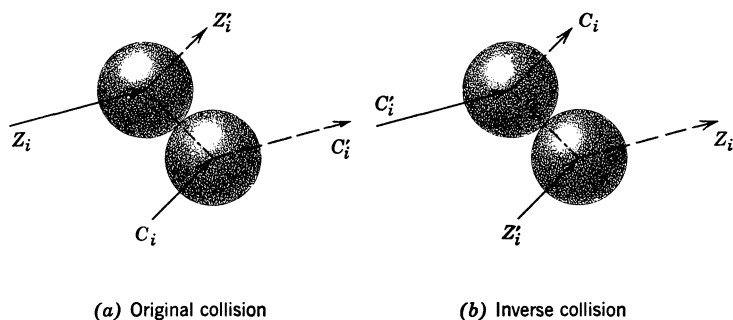


Fig. 6. Example of a collision and its inverse.

We now apply expression (4.2) to the types of collisions just discussed, which are illustrated in terms of relative velocity in Fig. 7. The diagram is drawn here from the point of view of an observer fixed relative to the molecule of class C_i or C'_i . By reference to Fig. 5 and expression (4.2), we write at once for the number of depleting collisions per unit volume per unit time

$$n^2 d^2 f(C_i) f(Z_i) g \sin \psi \cos \psi d\psi d\epsilon dV_C dV_Z.$$

Since each depleting collision removes one molecule from the class C_i , this also gives the rate of removal of molecules by collisions of the given type. To treat the inverse replenishing collisions we note that the relative velocity g'_i leaving the depleting collision lies in the plane of the collision. Furthermore it has a magnitude g' equal to the magnitude g of the incoming velocity and makes an angle ψ' with the line of centers equal to the incoming angle ψ . For the present billiard-ball model, we shall take the truth of the foregoing statements as reasonably obvious; they can be

² Note that an inverse collision is not the same as a *reverse* collision, in which the final velocities of the original collision are reversed and the molecules retrace their original paths. In a reverse collision here the initial velocities would be $-C'_i$ and $-Z'_i$ and the final velocities $-C_i$ and $-Z_i$.

demonstrated precisely from the later considerations of Chapter IX, Sec. 7. Now, for the inverse replenishing collision the velocity entering the collision must also be g'_i . Since the line of centers is the same for the two collisions, it follows that this velocity must again lie in the plane of the original collision, that is, the plane of collision for the original and inverse collisions is identical in the present frame of reference. The orientation of this plane is still specified by the same angle ϵ as originally defined. It

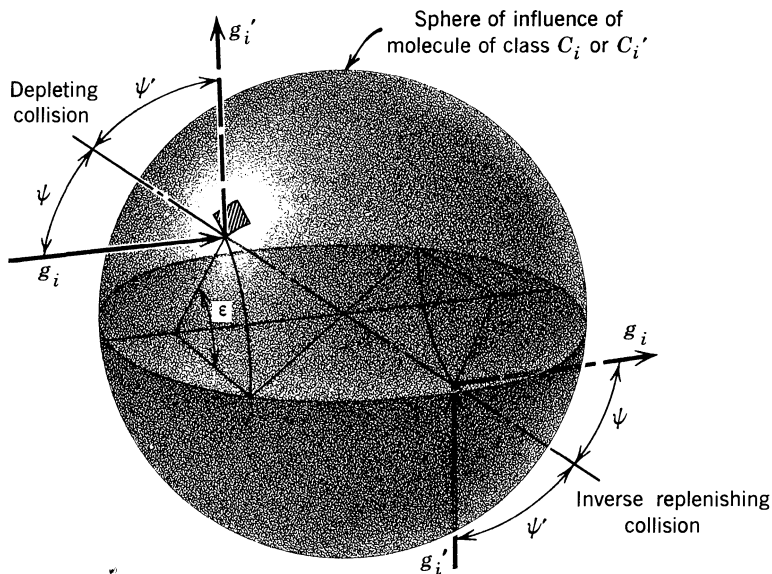


Fig. 7. Details of depleting collision and inverse replenishing collision in terms of relative velocities.

is thus easy to see that (4.2) can be applied to the inverse replenishing collisions with the same $d\epsilon$ as before. Making this application, we thus write for the number of such collisions per unit volume per unit time

$$n^2 d^2 f(C'_i) f(Z'_i) g' \sin \psi' \cos \psi' d\psi' d\epsilon dV_{C'} dV_{Z'}.$$

Each such collision restores one molecule to the class C_i . Subtracting the first of the foregoing expressions from the second and making use of the aforementioned fact that $g' = g$ and $\psi' = \psi$, we then obtain the following expression for the net rate of change of the number of molecules of class C_i per unit volume of gas as a result of a given type of depleting collision and its inverse:

$$n^2 d^2 [f(C'_i) f(Z'_i) dV_{C'} dV_{Z'} - f(C_i) f(Z_i) dV_{C_i} dV_{Z_i}] g \sin \psi \cos \psi d\psi d\epsilon. \quad (4.4)$$

To find the total effect of all collisions on the number of molecules in class C_i , expression (4.4) must be integrated over all types of depleting collisions, that is, over all values of Z_i for a fixed C_i and over all values of ψ and ϵ . The replenishing collisions are automatically taken care of in this process, since they have been paired off with the depleting collisions.³ To actually carry out the integration of the first term in the square brackets it would be necessary to transform the variables of integration from C'_i and Z'_i to Z_i , ψ , and ϵ . This can be done for the arguments of the functions f by direct substitution from the relations of the form (4.3). The transformation of the differential product $dV_{C'} dV_{Z'} = dC'_1 dC'_2 dC'_3 dZ'_1 dZ'_2 dZ'_3$ can also be carried out on the basis of these relations; again the details will be left to Chapter IX, Sec. 7. As it turns out, we obtain simply $dV_{C'} dV_{Z'} = dV_C dV_Z$. (This is a special case of an important general dynamic result known as *Liouville's theorem*.) With these substitutions the limits of integration are then from 0 to $\pi/2$ for ψ and from 0 to 2π for ϵ (see Fig. 5) and over all of velocity space for Z_i . The result gives the total rate of change of the number of molecules in the given class C_i per unit volume of gas as the result of collisions. Since the number of such molecules is $nf(C_i) dV_C$, this quantity can also be written

$$\left\{ \frac{\partial [nf(C_i) dV_C]}{\partial t} \right\}_{\text{coll}} = \left\{ \frac{\partial [nf(C_i)]}{\partial t} \right\}_{\text{coll}} dV_C.$$

Equating the two expressions and cancelling the common differential dV_C , we obtain finally

$$\left\{ \frac{\partial}{\partial t} [nf(C_i)] \right\}_{\text{coll}} = \int_{-\infty}^{\infty} \int_0^{2\pi} \int_0^{\pi/2} n^2 d^2 [f(C'_i)f(Z'_i) - f(C_i)f(Z_i)] g \sin \psi \cos \psi d\psi d\epsilon dV_Z, \quad (4.5)$$

where it is understood that C'_i and Z'_i are given by equations of the form (4.3). This expression will play an important role in the development of nonequilibrium kinetic theory in Chapter IX.

For the time being we are interested only in a gas in equilibrium. In this situation the number of molecules in every velocity class must be constant, that is, $\{\partial [nf(C_i)]/\partial t\}_{\text{coll}} = 0$ for all C_i . Equation (4.5) shows that this will be the case if f is such that

$$f(C'_i)f(Z'_i) - f(C_i)f(Z_i) = 0. \quad (4.6)$$

³ It is apparent that this accounts for *all* replenishing collisions. If there were others, their inverse would be a depleting collision and these are in fact all taken care of in the integration.

As far as we can tell at the moment, this is only a *sufficient* condition for equilibrium. The vanishing of the integral in (4.5) does not demand the vanishing of the integrand but only the cancellation of positive and negative contributions to the integral from different parts of the region of integration. It will be shown in Chapter IX, Sec. 4, however, that (4.6) is also a *necessary* condition for equilibrium, that is, that it is the *only* condition under which the integral will vanish. This shows that in equilibrium it is not enough for the overall effect of all collision processes to be zero; it is necessary that each detailed process and its inverse be individually in balance.

The foregoing is a special instance of the *principle of detailed balancing*, which we shall have occasion to use in several places later. The principle in its general form is a result of quantum theory, and it can be formulated precisely only within the framework of that theory (see Heitler, 1954, pp. 412–414 or Wu and Ohmura, 1962, pp. 423–424). For purposes of this book it may be taken as requiring that in a system at equilibrium each individual molecular process and its inverse proceed, on the average, at the same rate. By the inverse of a given process we mean in each case the process that differs from the given one by interchange of the initial and final conditions. The principle does not, in fact, apply with absolute generality (see preceding references). The exceptions, however, are of no concern in the processes with which we deal.

To arrive at equation (4.5) and thence the condition (4.6), we have for simplicity assumed a billiard-ball model. As will be explained in Chapter IX, Sec. 3, however, a collision integral with form similar to (4.5) and containing the same bracketed terms can be obtained for any type of molecule with a spherically symmetrical force field. The condition (4.6) thus applies to any dilute gas whose molecules satisfy this requirement.

5 MAXWELLIAN DISTRIBUTION—FINAL RESULTS

The problem of finding the velocity distribution function for a gas in equilibrium is now reduced to that of finding a function f that satisfies equation (4.6). This could be done with formal mathematical methods, but it is easier to proceed from our knowledge of mechanics. To do this we take the logarithm of (4.6) and write

$$\ln f(C'_i) + \ln f(Z'_i) = \ln f(C_i) + \ln f(Z_i). \quad (5.1)$$

Since a collision changes C_i, Z_i to C'_i, Z'_i , this equation states that there is a certain function $\ln f$ of the molecular velocity such that the sum of that

function for the two molecules in a collision is the same both before and after the collision. From mechanics we know four functions of velocity that have this property: the energy $\frac{1}{2}m(C_1^2 + C_2^2 + C_3^2)$ and the three components of momentum mC_1 , mC_2 , mC_3 . Any linear combination of these four quantities will also have the required property, and it can be shown that this is the most general function of which this is so (see, e.g., Kennard, 1938, pp. 42–45). The general solution of equation (5.1) and hence of equation (4.6) is therefore

$$\ln f(C_i) = b \frac{m}{2} (C_1^2 + C_2^2 + C_3^2) + a_1 m C_1 + a_2 m C_2 + a_3 m C_3 + a_4,$$

where b and the a 's are constants. That this is in fact a solution can be verified by substitution into (5.1) and use of the conservation equations of mechanics. The foregoing solution can also be written

$$\ln f(C_i) = b \frac{m}{2} [(C_1 - \alpha_1)^2 + (C_2 - \alpha_2)^2 + (C_3 - \alpha_3)^2] + \alpha_4,$$

or finally

$$f(C_i) = A \exp \left\{ -\beta \frac{m}{2} [(C_1 - \alpha_1)^2 + (C_2 - \alpha_2)^2 + (C_3 - \alpha_3)^2] \right\}, \quad (5.2)$$

where A , β , α_1 , α_2 , and α_3 are new constants. The minus sign is used with β in anticipation of the conditions on A and β that will be satisfied later.

The constants in (5.2) can be evaluated with the aid of known conditions on C_i and $f(C_i)$. We note first that $(C_1 - \alpha_1)$ occurs in (5.2) only through its square. Thus corresponding positive and negative values of this quantity occur with equal probability and its average value must obviously be zero, that is, $\overline{C_1 - \alpha_1} = \overline{C_1} - \alpha_1 = 0$. It follows that $\alpha_1 = \overline{\alpha_1} = \overline{C_1}$, that is, α_1 is equal to the average value of C_1 . But for our equilibrium system at rest, the velocity C_i is random and we have $\overline{C_1} = 0$. We therefore obtain $\alpha_1 = 0$, with a similar result for α_2 and α_3 . Equation (5.2) thus reduces to

$$f(C_i) = A \exp \left[-\beta \frac{m}{2} (C_1^2 + C_2^2 + C_3^2) \right]. \quad (5.3)$$

To find the remaining constants A and β , we first obtain a relationship between the two by putting (5.3) into equation (2.7), which requires that

$\int_{-\infty}^{\infty} f(C_i) dV_C = 1$. This gives

$$A \int_{-\infty}^{\infty} e^{-\beta(m/2)C_1^2} dC_1 \int_{-\infty}^{\infty} e^{-\beta(m/2)C_2^2} dC_2 \int_{-\infty}^{\infty} e^{-\beta(m/2)C_3^2} dC_3 = 1.$$

The integral here is one of a general form that will appear often; it is treated in the appendix at the rear of the book. Using the results given

there, we find for the typical integral

$$\int_{-\infty}^{\infty} e^{-\beta(m/2)z^2} dz = \left(\frac{2\pi}{\beta m}\right)^{1/2},$$

and hence from the foregoing equation we have

$$A = \left(\frac{\beta m}{2\pi}\right)^{3/2}. \quad (5.4)$$

With this relationship, we can now find β by calculating $\overline{C_3^2}$, which is already known from equations (3.2) and (3.3) to be equal to $\overline{C^2}/3 = p/\rho = RT = (k/m)T$. Using equation (2.8), substituting from (5.3) and (5.4), and evaluating the integrals from the results in the appendix, we find

$$\begin{aligned} \overline{C_3^2} &= \int_{-\infty}^{\infty} C_3^2 f(C_i) dV_C \\ &= \left(\frac{\beta m}{2\pi}\right)^{3/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C_3^2 e^{-\beta(m/2)(C_1^2 + C_2^2 + C_3^2)} dC_1 dC_2 dC_3 = \frac{1}{\beta m}. \end{aligned} \quad (5.5)$$

Equating this result to $(k/m)T$ gives β finally as

$$\beta = \frac{1}{kT}. \quad (5.6)$$

The value of A follows from (5.4) and is

$$A = \left(\frac{m}{2\pi kT}\right)^{3/2}. \quad (5.7)$$

With these values of A and β , equation (5.3) becomes finally

$$\boxed{f(C_i) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp \left[-\frac{m}{2kT} (C_1^2 + C_2^2 + C_3^2) \right]}. \quad (5.8)$$

This is the famous *Maxwellian distribution* cited at the beginning of the preceding section. If we define

$$\Phi(C_1) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp \left[-\frac{m}{2kT} C_1^2 \right] \quad (5.9)$$

and similarly for the other directions, the probability that a given molecule chosen at random will have velocity in the range C_1, C_2, C_3 to $C_1 + dC_1, C_2 + dC_2, C_3 + dC_3$ is

$$f(C_i) dC_1 dC_2 dC_3 = \Phi(C_1) dC_1 \times \Phi(C_2) dC_2 \times \Phi(C_3) dC_3.$$

The right-hand side of this expression is the product of three independent probabilities, each of which gives the probability that the molecule will have a component of velocity in a specified range in *one* of the coordinate directions. Each of the probabilities is independent of the components in the other directions. (This had been assumed by Maxwell.) The distribution function for a single component as given by (5.9) has the form of Gauss's error-distribution curve. This is illustrated in Fig. 8, which

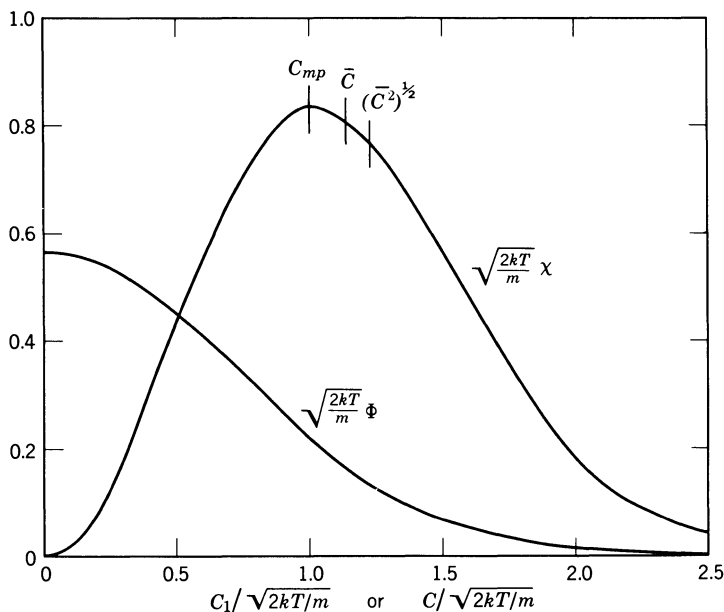


Fig. 8. Distribution functions $\Phi(C_1)$ and $\chi(C)$.

gives a plot of the dimensionless quantity $\sqrt{2kT/m} \Phi(C_1)$ versus the dimensionless velocity $C_1/\sqrt{2kT/m}$. In a dimensional plot of Φ versus C_1 , an increase in T for fixed m would cause the distribution to widen and the peak to lower. The opposite would be true for an increase in m for fixed T .

It is also useful to know the distribution of the magnitude C of the velocity vector (i.e., the speed) without regard to direction. To obtain this we first transform the expression

$$f(C_i) dC_1 dC_2 dC_3 = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-(m/2kT)(C_1^2 + C_2^2 + C_3^2)} dC_1 dC_2 dC_3$$

into spherical polar coordinates in velocity space (Fig. 9). The “volume”

element on the right then becomes $dC_1 dC_2 dC_3 = (C d\phi) (C \sin \phi d\theta) dC = C^2 \sin \phi d\phi d\theta dC$, and $C_1^2 + C_2^2 + C_3^2$ is replaced by C^2 . Redefining the left-hand side, we thus obtain the following expression for the probability that a given molecule has velocity in the range C, ϕ, θ to $C + dC, \phi + d\phi, \theta + d\theta$:

$$f(C, \phi, \theta) dC d\phi d\theta = \left(\frac{m}{2\pi kT} \right)^{3/2} C^2 e^{-(m/2kT)C^2} \sin \phi d\phi d\theta dC.$$

By integrating over all values of ϕ and θ we find for the probability that a

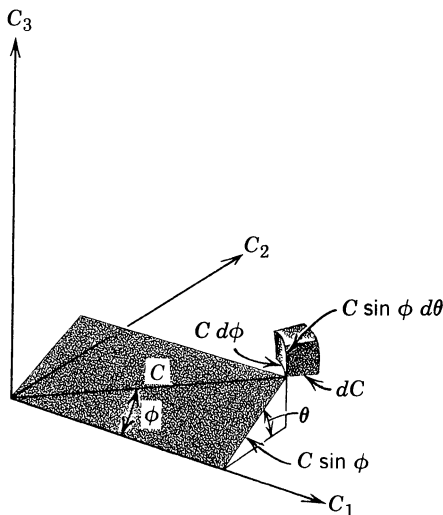


Fig. 9. Polar coordinates and volume element in velocity space.

given molecule has speed between C and $C + dC$ regardless of direction

$$\chi(C) dC = \int_0^\pi \sin \phi d\phi \int_0^{2\pi} d\theta \left(\frac{m}{2\pi kT} \right)^{3/2} C^2 e^{-(m/2kT)C^2} dC,$$

whence we obtain

$$\boxed{\chi(C) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} C^2 e^{-(m/2kT)C^2}}. \quad (5.10)$$

The speed distribution function $\chi(C)$ has the form shown in Fig. 8.

Certain special speeds that can be evaluated with the aid of $\chi(C)$ are of interest:

1. The most probable speed, as determined by the position of the maximum of the distribution curve, is easily found by differentiation and

is

$$C_{mp} = \left(\frac{2kT}{m} \right)^{1/2}. \quad (5.11)$$

2. The average speed \bar{C} is obtained from

$$\bar{C} = \int_0^\infty C \chi(C) dC.$$

Using the integrals from the appendix we find

$$\bar{C} = \frac{2}{\pi^{1/2}} \left(\frac{2kT}{m} \right)^{1/2} \cong 1.13 C_{mp}. \quad (5.12)$$

3. The root-mean-square speed is obtained from

$$\overline{C^2} = \int_0^\infty C^2 \chi(C) dC,$$

and turns out to be

$$(\overline{C^2})^{1/2} = \left(\frac{3kT}{m} \right)^{1/2} \cong 1.22 C_{mp}. \quad (5.13)$$

This is equivalent to the earlier result of equation (3.3) as it should be.

The position of the foregoing speeds in relation to the curve for $\chi(C)$ is indicated on Fig. 8. They can also be compared with the speed of sound given by $a = (\gamma kT/m)^{1/2}$. For a monatomic gas ($\gamma = \frac{5}{3}$), this gives $a \cong 0.91 C_{mp}$. The speed of sound is thus of the same order of magnitude as the previous molecular speeds. The value of all these speeds increases as T increases and decreases as m increases.

Exercise 5.1. A perfect gas containing a single species of molecular weight \bar{M} is enclosed in a container at equilibrium at pressure p and temperature T . The gas escapes into vacuum through a small circular hole of area A in the wall of the container. Assume the following ideal conditions: (1) The wall of the container is negligibly thick and is planar in the vicinity of the hole. (2) The diameter of the hole is appreciably smaller than the mean free path, but considerably larger than the molecular diameter.

(a) Show that the number of molecules escaping from the hole per unit area per unit time is given by $n\bar{C}/4$.

(b) Obtain an expression for the rate of mass outflow in terms of (and only of) p , T , \bar{M} , A , and \hat{R} .

(c) Show that the mean kinetic energy of the escaping molecules is greater than that of the molecules inside the container in the ratio 4/3. Can you give a physical explanation of this result?

Exercise 5.2. Consider a gas of molecules of mass m at equilibrium at temperature T . Let C_t be the magnitude of the component of molecular velocity parallel to one of the coordinate planes in physical space.

(a) Obtain an expression for the fraction of molecules with C_t in the range C_t to $C_t + dC_t$. Check that the integration of this expression over all molecules gives unity.

(b) Show that

$$\frac{(C_t)_{mp}}{C_{mp}} = \left(\frac{1}{2}\right)^{1/2}, \quad \frac{\bar{C}_t}{C} = \frac{\pi}{4}, \quad \left(\frac{\overline{C_t^2}}{C^2}\right)^{1/2} = \left(\frac{2}{3}\right)^{1/2}.$$

Exercise 5.3. Consider again a gas of molecules of mass m at equilibrium at temperature T .

(a) Obtain an expression for the fraction of molecules having kinetic energy $\epsilon \equiv \frac{1}{2}mC^2$ in the range ϵ to $\epsilon + d\epsilon$.

(b) Show that $\epsilon_{mp} = \frac{1}{2}kT$ and $\bar{\epsilon} = \frac{3}{2}kT$.

(c) If the error function (a tabulated function) is defined by

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-z^2} dz,$$

show that the fraction of molecules with kinetic energy equal to or greater than a specified value ϵ is given by

$$1 + \frac{2}{\sqrt{\pi}} \sqrt{\frac{\epsilon}{kT}} e^{-\epsilon/kT} - \operatorname{erf} \left(\sqrt{\frac{\epsilon}{kT}} \right).$$

(d) What percentage of the total kinetic energy of molecular motion is possessed by the molecules that have an individual kinetic energy less than one-tenth of the average kinetic energy? (Do not attempt to evaluate any integrals in closed form. Use a suitable infinite series instead and retain only the first two terms.)

Ans.: 0.24%.

6 COLLISION RATE AND MEAN FREE PATH

We are now in a position to make an improved calculation of the frequency of molecular collisions and of the length of the mean free path. The results will be of particular use when we take up the collision theory of chemical reaction rates in Chapter VII. With this in mind, we shall generalize the work somewhat here by considering collisions between two different molecular species A and B of a gas mixture. (The mixture may also contain other species, but that will not concern us for the moment.) We assume once again the billiard-ball model, to which the formulas of this section are as they stand specifically restricted.

Expression (4.2) for the frequency of collisions between billiard-ball molecules of classes U_i and Y_i is easily generalized to collisions between different species. The development is fairly obvious, and we leave the details to the student. In the generalized expression, $f(U_i)$ is replaced by

$f_A(C_i)$, where f_A is the distribution function for molecules of species A and C_i now denotes any velocity for molecules of this particular species. The function $f(Y_i)$ is similarly replaced by $f_B(Z_i)$, where Z_i is now the velocity for molecules of species B. In place of the common diameter d , we obtain the average diameter $d_{AB} \equiv (d_A + d_B)/2$, where d_A and d_B are the diameters of the molecules of the two species. The result is the following expression for the frequency of collisions per unit volume of gas between molecules of species A of class C_i and molecules of species B of class Z_i :

$$n_A n_B d_{AB}^2 f_A(C_i) f_B(Z_i) g \sin \psi \cos \psi d\psi d\varepsilon dV_C dV_Z. \quad (6.1)$$

Here n_A and n_B are the number density of molecules of the two species, and g is the relative speed

$$g = [(Z_1 - C_1)^2 + (Z_2 - C_2)^2 + (Z_3 - C_3)^2]^{1/2}. \quad (6.2)$$

Expression (6.1) becomes identical to expression (4.2) when only a single species is present. Although we shall not go into the details here, it can be shown (see Jeans, 1940, pp. 114–115) that in a mixture of gases each species individually follows a Maxwellian distribution at the common equilibrium temperature of the mixture. Replacing the f 's by means of equation (5.8) we thus obtain in place of (6.1)

$$n_A n_B \frac{(m_A m_B)^{3/2}}{(2\pi kT)^3} d_{AB}^2 g e^{-(1/2kT)(m_A C^2 + m_B Z^2)} \times \sin \psi \cos \psi d\psi d\varepsilon dC_1 dC_2 dC_3 dZ_1 dZ_2 dZ_3, \quad (6.3)$$

where $C^2 = C_1^2 + C_2^2 + C_3^2$ and $Z^2 = Z_1^2 + Z_2^2 + Z_3^2$ and the volume elements dV_C and dV_Z in velocity space have been written out explicitly.

We now want to find the total frequency of collisions between molecules of species A and B. For this it is necessary to integrate expression (6.3) over all directions of the line of centers and over all velocity classes for both species. The integration with respect to ψ and ε , which defines the direction of the line of centers, is trivial and could be carried out immediately; we choose to defer it, however, since some of the intermediate expressions will be of use in later work. The integration with respect to the velocity classes, on the other hand, is difficult because of the appearance of the components of C_i and Z_i in a complicated way in g .

To circumvent this difficulty, we transform the variables of integration from the components of velocity of the molecules themselves to the components of the relative velocity and of the velocity of the center of mass. The x_1 -component of the velocity g_i of molecule B relative to molecule A is

$$g_1 = Z_1 - C_1, \quad (6.4)$$

and similarly for the other components. The x_1 -coordinate of the center of mass of the molecule pair is

$$x_{c_1} = \frac{m_A x_{A_1} + m_B x_{B_1}}{m_A + m_B},$$

from which it follows by differentiation that the x_1 -component of the velocity W_i of the center of mass is

$$W_1 = \frac{m_A C_1 + m_B Z_1}{m_A + m_B}. \quad (6.5)$$

From equations (6.4) and (6.5) we easily obtain

$$C_1 = W_1 - \frac{m_B}{m_A + m_B} g_1, \quad Z_1 = W_1 + \frac{m_A}{m_A + m_B} g_1. \quad (6.6)$$

These and the corresponding equations in the other coordinate directions give the desired transformation. By means of these equations we can write

$$m_A C_1^2 + m_B Z_1^2 = (m_A + m_B) W_1^2 + \frac{m_A m_B}{m_A + m_B} g_1^2.$$

Combining equations of this type for each component and defining the *reduced mass*

$$m_{AB}^* \equiv \frac{m_A m_B}{m_A + m_B}, \quad (6.7)$$

we obtain for the sum appearing in the exponential factor of (6.3)

$$\frac{1}{2} m_A C^2 + \frac{1}{2} m_B Z^2 = \frac{1}{2} (m_A + m_B) W^2 + \frac{1}{2} m_{AB}^* g^2. \quad (6.8)$$

To transform the differentials we have, for the x_1 -direction,

$$dC_1 dZ_1 = \frac{\partial(C_1, Z_1)}{\partial(W_1, g_1)} dW_1 dg_1, \quad (6.9)$$

where the Jacobian of the transformation is found from (6.6) as

$$\frac{\partial(C_1, Z_1)}{\partial(W_1, g_1)} = \begin{vmatrix} \frac{\partial C_1}{\partial W_1} & \frac{\partial C_1}{\partial g_1} \\ \frac{\partial Z_1}{\partial W_1} & \frac{\partial Z_1}{\partial g_1} \end{vmatrix} = \begin{vmatrix} 1 & -\frac{m_B}{m_A + m_B} \\ 1 & \frac{m_A}{m_A + m_B} \end{vmatrix} = 1. \quad (6.10)$$

Corresponding results hold for the other directions. With these relations, the expression (6.3) can be rewritten

$$n_A n_B \frac{(m_A m_B)^{3/2}}{(2\pi kT)^3} d_{AB}^2 g \exp \left\{ -\frac{1}{2kT} [(m_A + m_B) W^2 + m_{AB}^* g^2] \right\} \\ \times \sin \psi \cos \psi d\psi d\epsilon dW_1 dW_2 dW_3 dg_1 dg_2 dg_3. \quad (6.11)$$

The next step is to transform the “volume” elements in each of the new velocity spaces W_i and g_i from Cartesian to spherical coordinates by the relations (cf. Sec. 5)

$$\begin{aligned} dW_1 dW_2 dW_3 &= W^2 \sin \phi_W d\phi_W d\theta_W dW, \\ dg_1 dg_2 dg_3 &= g^2 \sin \phi_g d\phi_g d\theta_g dg. \end{aligned} \quad (6.12)$$

With this transformation, the required integrations can be readily carried out, since the expression to be integrated now has the form of a product of functions of the individual variables of integration.

The integration will first be made over all possible velocities of the center of mass. To do this we integrate with respect to ϕ_W , θ_W , and W from, respectively, 0 to π , 0 to 2π , and 0 to ∞ . (The integration with respect to W requires the use of one of the integrals in the appendix.) This leads finally to the expression

$$n_A n_B \left(\frac{m_{AB}^*}{2\pi kT} \right)^{3/2} d_{AB}^2 g^3 e^{-(m_{AB}^*/2kT)g^2} \sin \phi_g \sin \psi \cos \psi d\psi d\epsilon d\phi_g d\theta_g dg. \quad (6.13)$$

To obtain all possible velocities of the center of mass we have obviously had to take account of all possible absolute velocities of both species of molecule. The foregoing integration thus, in effect, encompasses all possible velocities of both species. The expression (6.13) is therefore to be interpreted as giving the frequency of collisions per unit volume of gas between *all* molecules of species A and *all* molecules of species B and such that the relative velocity is in the range g , ϕ_g , θ_g to $g + dg$, $\phi_g + d\phi_g$, $\theta_g + d\theta_g$, and the direction of the line of centers in the range ψ , ϵ to $\psi + d\psi$, $\epsilon + d\epsilon$. By “all” molecules of a given species we mean all classes of absolute velocity of that species. This is in contrast to the limited classes of velocity accounted for in the original expression (6.1).

We now take account of all possible directions (but not magnitudes) of the relative velocity by integrating with respect to ϕ_g from 0 to π and with respect to θ_g from 0 to 2π . To obtain an expression that we shall need later, we also take partial account of the possible directions of the line of centers by integrating with respect to ϵ over its range from 0 to 2π . We thus obtain the following expression for the frequency of collisions per unit volume of gas between all molecules of species A and all molecules of species B and such that the relative speed is in the range g to $g + dg$ and the line of centers lies in the angular range ψ to $\psi + d\psi$ measured from the direction of the relative motion:

$$8\pi^2 n_A n_B \left(\frac{m_{AB}^*}{2\pi kT} \right)^{3/2} d_{AB}^2 g^3 e^{-(m_{AB}^*/2kT)g^2} \sin \psi \cos \psi d\psi dg. \quad (6.14)$$

This expression will be used in the development of the collision theory of chemical reaction rates in Chapter VII.

Finally, we can find the total frequency of collisions per unit volume of gas between molecules of species A and B by integrating with respect to ψ from 0 to $\pi/2$ and with respect to g from 0 to ∞ . This so-called *bimolecular collision rate*, denoted by Z_{AB} , comes out to be

$$Z_{AB} = n_A n_B d_{AB}^2 \left(\frac{8\pi kT}{m_{AB}^*} \right)^{1/2}. \quad (6.15a)$$

Equation (6.15a) as it stands cannot be used to obtain the mutual collision rate within a given species A by formally replacing B with A. In performing the integrations necessary to obtain the foregoing results from the original expression (6.1) we have, as already pointed out, summed over all velocity classes of both collision partners. If we consider two specific velocity classes U_i and Y_i with no regard as to which species is associated with which velocity, a collision between molecules with these velocities will appear in the summation twice, once with $C_i = U_i$, $Z_i = Y_i$ and once with $C_i = Y_i$, $Z_i = U_i$. In collisions of unlike molecules these are two distinct cases. In collisions of like molecules, however, they are identical, that is, interchanging the molecules between the velocity classes does not provide a different collision. This is illustrated in Fig. 10, where in (b) only the artifice of different intensities of shading for the two collision partners allows us to recognize that an interchange has been made; without this artifice the interchange is unrecognizable and therefore meaningless. If we had carried through the foregoing analysis for like molecules we would thus have counted each collision twice. To obtain the collision rate within a given species we must therefore divide the integrated results by 2. The same formulas can be made to serve for both cases if we write the bimolecular collision rate (6.15a), for example, as

$$Z_{AB} = \frac{n_A n_B}{\sigma} d_{AB}^2 \left(\frac{8\pi kT}{m_{AB}^*} \right)^{1/2}, \quad (6.15b)$$

where σ is a symmetry factor that is 1 for unlike molecules ($B \not\equiv A$) and 2 for like molecules ($B \equiv A$). It should be noted that the reduced mass m_{AB}^* does not go over into the molecular mass when the results are applied to like molecules. Instead we have $m_{AA}^* = m_A m_A / (m_A + m_A) = m_A / 2$. Exercise 6.2 gives an application of the ideas of this paragraph and may be helpful in understanding them.

The foregoing results can be used to find the mean free path as follows. Each collision included in Z_{AB} in equation (6.15a) terminates one free

path for one species of molecule—say A—by collision with another species—say B. The formula (6.15b) with $\sigma = 1$ can thus be interpreted as also giving the number of free paths of the n_A molecules of species A per unit volume of gas that are terminated per unit time through collisions with species B. In the case of like molecules, however, each collision terminates *two* free paths for molecules of the given species. To find the number of free paths terminated per unit time by the n_A molecules of

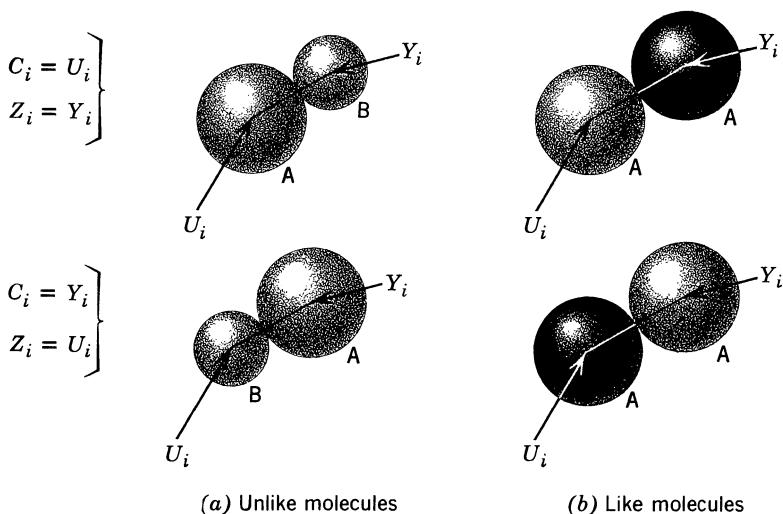


Fig. 10. Interchange of collision partners for unlike and like molecules.

species A through collisions with other molecules of the same species, we must therefore multiply the right-hand side of equation (6.15b) by 2. This has the effect of canceling the factor $\sigma = 2$ introduced in the formula when $A \equiv B$. The end result is thus the same in either case. We can therefore write the common expression

$$n_A n_Y d_{AY}^2 \left(\frac{8\pi kT}{m_{AY}^*} \right)^{1/2}$$

for the number of free paths terminated by n_A molecules of species A per unit volume of gas through collisions with some species Y, and this is correct whether Y is species A itself or some other species. The number of free paths terminated per unit time by one of the molecules out of the n_A

can be found by dividing the foregoing result by n_A and is

$$\Theta_{AY} = n_Y d_{AY}^2 \left(\frac{8\pi kT}{m_{AY}^*} \right)^{1/2}.$$

Since this equation holds for any target species Y, the number of free paths terminated per unit time by one molecule of species A through collisions with all species in a complex mixture can be found by summation and is

$$\Theta_A = \sum_Y \Theta_{AY} = \sqrt{8\pi kT} \sum_Y \frac{n_Y d_{AY}^2}{\sqrt{m_{AY}^*}} = \sqrt{8\pi kT} \sum_Y n_Y d_{AY}^2 \sqrt{\frac{1}{m_A} + \frac{1}{m_Y}},$$

where the summation extends over all species in the mixture. Now, the average distance traveled by a molecule of species A per unit time is [see equation (5.12)]

$$\bar{C}_A = \sqrt{8kT/\pi m_A}.$$

It follows that the average distance traveled between each termination of a free path, which is the mean free path for molecules of species A, is

$$\lambda_A = \frac{\bar{C}_A}{\Theta_A} = \frac{1}{\pi \sum_Y n_Y d_{AY}^2 \sqrt{1 + (m_A/m_Y)}}. \quad (6.16)$$

When there is only a single species present this reduces to

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n},$$

which was cited without proof as equation (I 4.3a).

Exercise 6.1. Measurements made in argon (molecular weight $\cong 40$) at a temperature of 300°K and a mass density of 2×10^{-3} gm/cm³ give a coefficient of viscosity of 2100×10^{-7} gm/cm sec. (These values are not strictly correct, having been altered slightly to facilitate the numerical work.) Calculate the rate of collision between pairs of argon molecules. *Ans.:* 1.14×10^{29} /cm³sec.

Exercise 6.2. (a) Consider a gas consisting of a single molecular species with mass m , diameter d , number density n , and temperature T . Write the expression for the rate Z of bimolecular collisions per unit volume.

(b) Consider a gas made up of two molecular species A and B with mass m_A and m_B , diameter d_A and d_B , and number density n_A and n_B , also at the temperature T . Obtain an expression for the *total* rate Z of bimolecular collisions of *all kinds* per unit volume.

(c) Show that the result of (b) reduces to that of (a) if the two species are made identical and the total number density is unaltered.

Exercise 6.3. This exercise will serve to review many of the ideas and procedures of Chapters I and II. Consider a gas whose molecules are flat discs

sliding on a frictionless plane (e.g., poker chips sliding on a frictionless billiard table). Assume that the molecules exhibit those properties of the familiar billiard-ball model that are consistent with their two-dimensional motion. Supposing that the gas obeys the equation of state $p/\rho = RT$, where now p is the force per unit *length* and ρ is the density per unit *area*, find the following:

(a) The relation connecting p , ρ , and \bar{C}^2 using the methods of Chapter I, Sec. 3. Check whether the principle of equipartition of energy holds.

(b) An approximate expression for the mean free path, using the methods of Chapter I, Sec. 4.

(c) The velocity distribution function at equilibrium. (Use either the arguments of Chapter II, Secs. 4 and 5, or the *functional form* of the three-dimensional distribution function plus some suitable reasoning.) Find \bar{C} and \bar{C}^2 and compare with the results of (a).

(d) The bimolecular collision rate for unlike molecules, using the method of this section. Compute the mean free path λ when there is only one species present, and compare with the result of (b).

7 CHEMICAL EQUILIBRIUM AND THE LAW OF MASS ACTION

In the foregoing sections we have supposed that any gas mixtures with which we were concerned were chemically inert, so that no changes in molecular structure took place upon collision. In this section we consider briefly the conditions of equilibrium in a chemically reacting mixture of gases from the kinetic point of view. We shall later treat the same problem more extensively with entirely different methods.

To fix our ideas we take up the problem here in terms of a specific reaction, namely, that for the decomposition of hydrogen iodide. The chemical formula, or *chemical equation*, that describes this reaction is



The numbers that precede the chemical symbols and that "balance" the equation are called the *stoichiometric coefficients*. The equation expresses the fact that 2 molecules (or moles) of HI must disappear for every molecule (or mole) each of H_2 and I_2 that appears. In any system in equilibrium both the forward (\rightarrow) and the backward (\leftarrow) reactions go on simultaneously and continuously. The seemingly constant state of equilibrium represents a dynamic balance between the forward and backward directions. On a time-averaged basis, there are definite proportions of the various species in the equilibrium mixture, and we wish to know what these proportions are.

For a gas reaction to take place, a minimum requirement is that the reacting molecules must be in collision with each other. It is often

necessary further that the molecules have considerably more than the average amount of energy, but this latter requirement need not concern us for the time being. Let us consider first the forward reaction. For decomposition of the HI to occur, there must be a bimolecular collision between two HI molecules. We assume that in a certain fraction of these collisions, which fraction may depend on the temperature, a reaction will occur. The number of reacting collisions per unit volume per unit time is therefore proportional to the corresponding rate of bimolecular collisions. Using equation (6.15b) for this collision rate, we can thus write

$$\left. \begin{array}{l} \text{number of decomposing collisions} \\ \text{per unit volume per unit time} \end{array} \right\} = k_f(T)n_{\text{HI}}^2, \quad (7.2)$$

where $k_f(T)$ is a coefficient depending on the temperature and the physical properties of the molecules. That this expression must depend on the square of the number density of HI molecules can also be argued directly on elementary grounds: If we double the number of HI molecules we plainly double the chance that one will be found at the point where the collision will take place, and furthermore we double the chance that, if one is there, another will be there also.

For the formation of HI (i.e., the backward reaction) to take place, there must be a bimolecular collision between a hydrogen and an iodine molecule. On the same assumptions as before regarding reacting collisions, we can write, again with the aid of equation (6.15b),

$$\left. \begin{array}{l} \text{number of forming collisions} \\ \text{per unit volume per unit time} \end{array} \right\} = k_b(T)n_{\text{H}_2}n_{\text{I}_2}, \quad (7.3)$$

where $k_b(T)$ is the coefficient appropriate to the backward reaction.

For equilibrium to be maintained, the number of decomposing collisions (7.2) must just equal the number of forming collisions (7.3). Equating the two expressions, we find the following condition for the particular values of the number densities at equilibrium, denoted by asterisks:

$$\frac{n_{\text{H}_2}^* n_{\text{I}_2}^*}{n_{\text{HI}}^{*2}} = \frac{k_f(T)}{k_b(T)} \equiv K(T). \quad (7.4)$$

This is a special case of the famous *law of mass action* first formulated in 1867 by the Norwegian scientists Guldberg and Waage. It is more often written in terms of the *concentration* in moles per unit volume, denoted for any arbitrary species Y by [Y]. Since $n_Y = \hat{N}[\text{Y}]$, where \hat{N} is Avogadro's number, we have in these terms

$$\frac{[\text{H}_2]^* [\text{I}_2]^*}{[\text{HI}]^{*2}} = K_r(T). \quad (7.5)$$

Here $K_c(T)$ is the *equilibrium constant* for concentrations. It is called a "constant" because reaction equilibrium is often studied experimentally at a fixed temperature; actually it is a function of T .

Equation (7.5) is not sufficient in itself to provide a solution for the three quantities $[H_2]^*$, $[I_2]^*$, and $[HI]^*$. We require two additional equations, which are given in this case by the fact that the reaction cannot change the total number of hydrogen and iodine atoms in the system. The equations expressing this fact are

$$\begin{aligned} [HI]^* + 2[H_2]^* &= \frac{n_H}{\hat{N}}, \\ [HI]^* + 2[I_2]^* &= \frac{n_I}{\hat{N}}, \end{aligned} \quad (7.6)$$

where n_H and n_I are the number of hydrogen and iodine atoms per unit volume irrespective of whether they are present in the pure species or in the hydrogen iodide. Their value presumably would be known or calculable from the given conditions in any particular problem.

From the foregoing equations we can find, for example, the effect on the equilibrium of adding—say— H_2 at constant temperature and volume. If the H_2 did not react, then the left-hand side of (7.5) would increase, which would violate the equation at constant T . The only way that the equality can be maintained is for some of the added H_2 to react with the I_2 already present to form additional HI . This will reduce $[H_2]$ and $[I_2]$ and increase $[HI]$ until the equality (7.5) is satisfied. Such changes are seen to be compatible (as indeed they must) with equations (7.6), where n_H would have been increased by the addition of H_2 while n_I remained unchanged.

Equation (7.5) can be rewritten in terms of the equilibrium partial pressures p_Y^* instead of the concentrations by means of the relation

$$p_Y^* = n_Y^* kT = [Y]^* \hat{R}T,$$

which assumes that each gas in the mixture behaves as a perfect gas. The result, which is typical of a form often encountered, is

$$\frac{p_{H_2}^* p_{I_2}^*}{p_{HI}^{*2}} = K_c(T) = K_p(T). \quad (7.7)$$

Other equivalent forms can be obtained, but we shall not go into them here. Equation (7.5) can also be extended without difficulty to more complex chemical reactions involving a greater number of chemical species. We shall defer this, however, until the next chapter, where we take up an alternative derivation by the methods of chemical thermodynamics.

The foregoing derivation does not give us an expression for the function $K_c(T)$. Indeed the derivation of such an expression by purely kinetic methods is impossible, since such a derivation would require knowledge of the probability that a given collision will result in a reaction, and such knowledge is not available on purely theoretical grounds. Fortunately, conditions of equilibrium can be treated by other, more powerful methods that are capable of giving more complete results within their own restricted sphere. We address ourselves to these methods in the next two chapters.

Exercise 7.1. Consider a unit volume containing a mixture of gaseous hydrogen and iodine reacting according to the chemical equation (7.1). The equilibrium composition at $T = 675^\circ\text{K}$ was measured by chemical methods and found to consist of 9.664 mole⁻ of HI, 0.168 moles of H_2 , and 0.168 moles of I_2 . If we add one mole of I_2 to the mixture keeping the volume and temperature constant, what will be the composition after equilibrium is reestablished?

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