

Elementary kinetic theory of transport processes

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IN THE preceding chapters our concern has been almost exclusively with equilibrium situations. General statistical arguments were quite sufficient to treat problems of this sort, and there was no need to investigate in detail the interaction processes which bring about the equilibrium. Many problems of great physical interest deal, however, with nonequilibrium situations.

Consider, for example, the case where the two ends of a copper rod are maintained at different temperatures. This is *not* an equilibrium situation, since the entire bar would then be at the same temperature. Instead, energy in the form of heat flows through the bar from the high- to the low-temperature end, the rate of this energy transfer being measured by the "thermal conductivity" of the copper bar. A calculation of the coefficient of thermal conductivity thus requires a more detailed consideration of the nonequilibrium processes whereby energy is transported from one end of the bar to the other. Calculations of this sort can become quite complicated, even in the rather simple case of ideal gases which we shall treat in these next chapters. It is therefore very valuable to develop simple approximate methods which yield physical insight into basic mechanisms, which elucidate the main features of phenomena in a semiquantitative way, and which can be extended to the discussion of more complicated cases where more rigorous methods might become hopelessly complex. Indeed, it is very often found that simple approximate calculations of this sort lead to the correct dependence of all significant parameters, like temperature and pressure, and to numerical values which differ by no more than 50 percent from the results of rigorous calculations based on the solution of complicated integrodifferential equations. In this chapter, therefore, we shall begin by discussing some of the simplest approximate methods for dealing with nonequilibrium processes. Although we shall treat the case of dilute gases, the same methods are useful in more advanced work, e.g., in discussing transport processes in solids in terms of "dilute gases" of electrons, "phonons" (quantized sound waves with particlelike properties), or "magnons" (quantized waves of magnetization).

In a gas, molecules interact with each other through collisions. If such a gas is initially not in an equilibrium situation, these collisions are also responsible for bringing about the ultimate equilibrium situation where a Maxwell-Boltzmann velocity distribution prevails. We shall discuss the case of a gas which is *dilute*. The problem is then relatively simple because of the following features:

a. Each molecule spends a relatively large fraction of its time at distances far from other molecules so that it does not interact with them. In short, the time *between* collisions is much greater than the time involved *in* a collision.

b. The probability of *more* than two molecules coming close enough to each other at any time so as to interact with each other *simultaneously* is negligibly small compared to the probability of only two molecules coming sufficiently close to another to interact. In short, triple collisions occur very rarely compared to two-particle collisions. Thus the analysis of collisions can be reduced to the relatively simply mechanical problem of only *two* interacting particles.

c. The mean de Broglie wavelength of molecules is small compared to the mean separation between molecules. The behavior of a molecule between collisions can then be described adequately by the motion of a wave packet or classical particle trajectory, even though a quantum-mechanical calculation may be necessary to derive the scattering cross section describing a collision between two molecules.

Finally, it is worth adding a very general comment about the distinction between equilibrium and steady-state situations. An *isolated* system is said to be in equilibrium when none of its parameters depends on the time. It is, however, also possible to have a nonequilibrium situation where a system A , which is *not* isolated, is maintained in such a way that all of its parameters are time-independent. The system A is then said to be in a "steady state," but this situation is not one of equilibrium, since the combined isolated system $A^{(0)}$ consisting of A and its surroundings is not in equilibrium, i.e., since the parameters of A' vary in time.

Example Consider a copper rod A connecting two heat reservoirs B_1 and B_2 at different temperatures T_1 and T_2 . A steady-state situation would be one where the temperatures T_1 and T_2 at the two ends of the rod are maintained constant and where one has waited a sufficiently long time so that the local temperature in each macroscopically small region of the rod has attained a constant value. If B_1 and B_2 are sufficiently large, the temperatures T_1 and T_2 will vary very slowly, despite the transfer of heat from one reservoir to the other; but B_1 and B_2 are certainly not in equilibrium, and their temperatures will gradually change and reach equality if one waits long enough to attain the final equilibrium situation. Similarly, if one constantly does work on one reservoir and uses a refrigerator on the other reservoir to keep their respective temperatures strictly constant, the environment of A is most certainly not in equilibrium.

12·1 Collision time

Consider a molecule with velocity v . Let

$$P(t) = \left. \begin{array}{l} \text{the probability that such a molecule survives a time} \\ t \text{ without suffering a collision.} \end{array} \right\} \quad (12·1·1)$$

Of course $P(0) = 1$, since a molecule has no chance of colliding in a time $t \rightarrow 0$, i.e., it certainly manages to survive for a vanishingly short time. On the other hand, $P(t)$ decreases as the time t increases, since a molecule is constantly exposed to the danger of suffering a collision; hence its probability of surviving a time t without suffering such a fate decreases as time goes on. Finally, $P(t) \rightarrow 0$ at $t \rightarrow \infty$. (The situation is similar to one very familiar to all of us; being constantly exposed to the vicissitudes of disease and accident, each one of us must die sooner or later.) The net result is that a plot of $P(t)$ versus t must have the shape indicated in Fig. 12·1·1.

To describe the collisions, let

$$w dt = \left. \begin{array}{l} \text{the probability that a molecule suffers a collision} \\ \text{between time } t \text{ and } t + dt. \end{array} \right\} \quad (12·1·2)$$

The quantity w is thus the probability per unit time that a molecule suffers a collision, or the "collision rate." We shall assume that the probability w is *independent* of the past history of the molecule; i.e., it does not matter when the molecule suffered its last collision. In general w may, however, depend on the speed v of the particular molecule under consideration, so that $w = w(v)$.

Knowing the collision probability w , it is possible to calculate the survival probability $P(t)$. This can be done by noting that [the probability that a molecule survives a time $t + dt$ without suffering a collision] must be equal to [the probability that this molecule survives a time t without suffering a collision] multiplied by [the probability that it does not suffer a collision in the

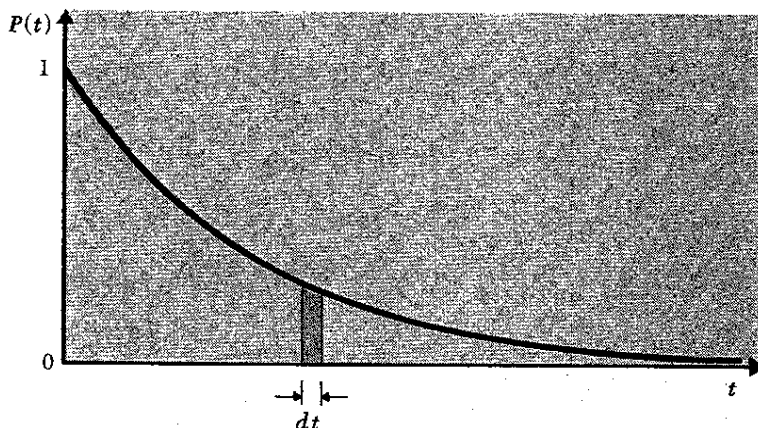


Fig. 12·1·1 Probability $P(t)$ of surviving a time t without suffering a collision. (The shaded area represents the probability $\mathcal{O}(t) dt$ of suffering a collision in the time interval between t and $t + dt$ after surviving a time t without collisions.)

subsequent time interval between t and $t + dt$]. In symbols, this statement becomes

$$P(t + dt) = P(t)(1 - w dt) \quad (12 \cdot 1 \cdot 3)$$

Hence

$$P(t) + \frac{dP}{dt} dt = P(t) - P(t)w dt$$

or

$$\frac{1}{P} \frac{dP}{dt} = -w \quad (12 \cdot 1 \cdot 4)$$

Between collisions (i.e., in a time of the order of w^{-1}) the speed v of a molecule does not change at all; or, if the molecule is subject to external forces due to gravity or electromagnetic fields, its speed changes usually only by a relatively small amount in the short time w^{-1} . Hence the probability w , even if it is a function of v , can ordinarily be considered essentially a constant independent of time. The integration of (12·1·4) is then immediate and gives

$$\ln P = -wt + \text{constant}$$

or

$$P = C e^{-wt}$$

Here the constant of integration C can be determined by the condition that $P(0) = 1$. Thus one obtains $C = 1$ and

$$P(t) = e^{-wt} \quad (12 \cdot 1 \cdot 5)$$

Multiplication of (12·1·1) by (12·1·2) gives then

$$\left. \begin{array}{l} \mathcal{P}(t) dt = \text{the probability that a molecule, after surviving} \\ \text{without collisions for a time } t, \text{ suffers a collision in the time} \\ \text{interval between } t \text{ and } t + dt. \end{array} \right\} \quad (12 \cdot 1 \cdot 6)$$

Thus

$$\mathcal{P}(t) dt = e^{-wt} w dt \quad (12 \cdot 1 \cdot 7)$$

Remark One could also find $\mathcal{P}(t) dt$ by arguing that it must be equal to [the probability of surviving a time t] minus [the probability of surviving a time $t + dt$].

$$\text{Thus} \quad \mathcal{P}(t) dt = P(t) - P(t + dt) = -\frac{dP}{dt} dt$$

By using (12·1·5), this yields again the relation (12·1·7).

The probability (12·1·7) should be properly normalized in the sense that

$$\int_0^{\infty} \mathcal{P}(t) dt = 1 \quad (12 \cdot 1 \cdot 8)$$

This asserts simply that there is probability unity that a molecule collides at some time. Indeed, by (12·1·7), one finds

$$\int_0^{\infty} e^{-wt} w dt = \int_0^{\infty} e^{-y} dy = 1$$

so that the normalization condition (12·1·8) is verified.

Let $\tau \equiv \bar{t}$ be the mean time between collisions. This is also called the "collision time" or "relaxation time" of the molecule. By (12·1·7) one can write

$$\begin{aligned}\tau \equiv \bar{t} &= \int_0^{\infty} \mathcal{P}(t) dt \\ &= \int_0^{\infty} e^{-wt} w dt \\ &= \frac{1}{w} \int_0^{\infty} e^{-y} dy = \frac{1}{w}\end{aligned}$$

since the integral is of the type evaluated in (A·3·3). Thus

$$\tau = \frac{1}{w} \quad (12·1·9)$$

and (12·1·7) can equally well be written in the form

$$\blacktriangleright \quad \mathcal{P}(t) dt = e^{-t/\tau} \frac{dt}{\tau} \quad (12·1·10)$$

Since in general $w = w(v)$, τ may depend on the speed v of the molecule. The mean distance traveled by such a molecule between collisions is called the "mean free path" l of the molecule. One has thus

$$l(v) = v \tau(v) \quad (12·1·11)$$

A gas of molecules can then conveniently be characterized by the average collision time, or the average mean free path, of the molecules traveling with a mean speed \bar{v} .

Remark If w depends on the speed v and the latter *does* change appreciably in times of the order of w^{-1} , then w on the right side of (12·1·4) becomes a function of the time t . The integration would then give, instead of (12·1·7),

$$\mathcal{P}(t) dt = \left\{ \exp \left[- \int_0^t w(t') dt' \right] \right\} w(t) dt \quad (12·1·12)$$

Remarks on the similarity to a game of chance The problem of molecular collisions formulated in the preceding paragraphs is similar to a simple game of chance. The molecule in danger of a collision is analogous to a man who keeps on throwing a die in a game where he has to pay \$100 whenever the throw of the die results in the "fatal event" of a 6 landing uppermost. (The game of Russian roulette described in Problem 1.5, might be a more bloody analogue.) Let

p = the probability that the fatal event occurs in a given trial.

This probability p is assumed to be independent of the past history of occurrence of fatal events. Then

$q \equiv 1 - p$ = the probability that the fatal event does *not* occur in a given trial.

The probability P_n of surviving n trials without a fatal event is thus given by

$$P_n = (1 - p)^n \quad (12 \cdot 1 \cdot 13)$$

The probability \mathcal{P}_n of surviving $(n - 1)$ trials without a fatal event and then suffering the fatal event at the n th trial is then

$$\mathcal{P}_n = (1 - p)^{n-1}p = q^{n-1}p \quad (12 \cdot 1 \cdot 14)$$

This probability is properly normalized so that the probability of suffering the fatal event at *some time* is unity, i.e.,

$$\sum_{n=1}^{\infty} \mathcal{P}_n = 1 \quad (12 \cdot 1 \cdot 15)$$

This can be verified by using (12 · 1 · 14); thus

$$\sum_{n=1}^{\infty} \mathcal{P}_n = \sum_{n=1}^{\infty} q^{n-1}p = p(1 + q + q^2 + \cdots)$$

By summing the geometric series, we obtain properly

$$\sum_{n=1}^{\infty} \mathcal{P}_n = \frac{p}{1 - q} = \frac{p}{p} = 1$$

The mean number of trials is given by

$$\bar{n} = \sum_{n=1}^{\infty} \mathcal{P}_n n = \sum_{n=1}^{\infty} q^{n-1}pn = \frac{p}{q} \sum_{n=1}^{\infty} q^n \quad (12 \cdot 1 \cdot 16)$$

By considering q as an arbitrary parameter one can write

$$\begin{aligned} \sum_{n=1}^{\infty} q^n n &= q \frac{\partial}{\partial q} \sum_{n=1}^{\infty} q^n \\ &= q \frac{\partial}{\partial q} \left(\frac{q}{1 - q} \right) \\ &= q \frac{(1 - q) + q}{(1 - q)^2} = \frac{q}{(1 - q)^2} \end{aligned}$$

Hence (12 · 1 · 16) becomes, putting $q = 1 - p$,

$$\bar{n} = \frac{p}{(1 - q)^2} = \frac{p}{p^2} = \frac{1}{p} \quad (12 \cdot 1 \cdot 17)$$

All these results are analogous to those obtained in discussing a molecule. To make the correspondence exact, consider time to be divided into fixed infinitesimal intervals of magnitude dt . Each such interval represents a "trial" for the molecule in its game of chance. The fatal event is, of course, the suffering of a collision. In terms of the collision rate w of (12 · 1 · 2), the probability p is then given by

$$p = w dt \quad (12 \cdot 1 \cdot 18)$$

Furthermore, the number of trials experienced by a molecule in a time t is given by

$$n = \frac{t}{dt} \quad (12.1.19)$$

Note that as $dt \rightarrow 0$, $p \rightarrow 0$ and $n \rightarrow \infty$ in such a way that

$$pn = wt \quad (12.1.20)$$

By (12.1.13) the survival probability is then given by

$$P(t) = (1 - p)^n$$

Since $p \ll 1$, this can be approximated by writing

$$\ln P = n \ln(1 - p) \approx -np$$

Hence

$$P(t) = e^{-np} = e^{-wt} \quad (12.1.21)$$

where we have used (12.1.20). Thus we regain (12.1.5).

Similarly, one obtains by (12.1.14)

$$\mathcal{G}(t) dt = (1 - p)^{n-1} p = e^{-wt} w dt \quad (12.1.22)$$

which agrees with (12.1.7). Finally (12.1.19) gives

$$\bar{t} = \bar{n} dt$$

which becomes, by (12.1.17),

$$\tau = \frac{1}{p} dt = \frac{dt}{w dt} = \frac{1}{w} \quad (12.1.23)$$

and agrees thus with (12.1.9).

12.2 Collision time and scattering cross section

Scattering cross section An encounter (or collision) between two particles is described in terms of a "scattering cross section" which can be computed by the laws of mechanics if the interaction potential between the particles is known. Consider two particles of respective masses m_1 and m_2 . Denote their respective position vectors by \mathbf{r}_1 and \mathbf{r}_2 , and their respective velocities by \mathbf{v}_1 and \mathbf{v}_2 . View the situation from a frame of reference fixed with respect to particle 2; the motion of particle 1 relative to 2 is then described by the relative position vector $\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2$, and the relative velocity $\mathbf{V} = \mathbf{v}_1 - \mathbf{v}_2$. In this frame of reference where the "target" particle 2 is at rest, consider that there is a uniform flux of \mathfrak{F}_1 type 1 particles per unit area per unit time incident with relative velocity \mathbf{V} on the target particle 2. As a result of the scattering process a number $d\mathcal{N}$ of particles of type 1 will emerge per unit time at large distances from the target particle with final velocity in the range between \mathbf{V}' and $\mathbf{V}' + d\mathbf{V}'$. This defines a small solid angle range $d\Omega'$ about the direction $\hat{\mathbf{V}}' \equiv \mathbf{V}'/|\mathbf{V}'|$ of the scattered beam. (If the collision process is elastic so that

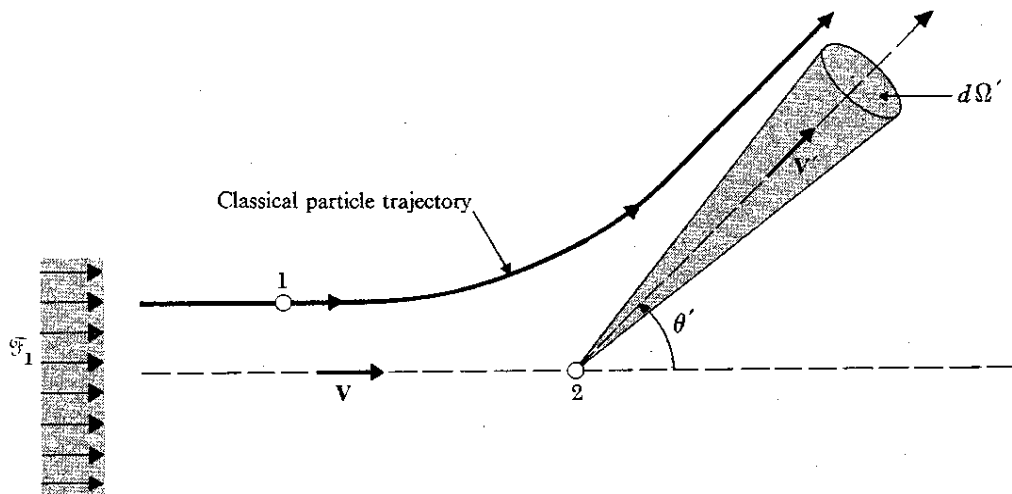


Fig. 12·2·1 Scattering process viewed from the frame of reference where the target particle 2 is at rest.

energy is conserved, $|V'| = |V|$.) This number $d\mathcal{N}$ is proportional to the incident flux \mathcal{F}_1 and to the solid angle $d\Omega'$. One can then write

$$d\mathcal{N} = \mathcal{F}_1 \sigma d\Omega' \quad (12\cdot2\cdot1)$$

where the factor of proportionality σ is called the “differential scattering cross section.” It depends in general on the magnitude V of the relative velocity of the incident particle and on the particular direction \hat{V}' (specified by the polar angle θ' and azimuthal angle φ') of the scattered beam relative to the incident direction V . This differential scattering cross section $\sigma = \sigma(V; \hat{V}')$ can be computed by classical or quantum mechanics if the interaction potential between the particles is known. Note that σ has the dimensions of an area, since the flux \mathcal{F}_1 is expressed per unit area.

The total number \mathcal{N} of particles scattered per unit time in all directions is obtained by integrating (12·2·1) over all solid angles. Thus

$$\mathcal{N} = \int_{\Omega'} \mathcal{F}_1 \sigma d\Omega' \equiv \mathcal{F}_1 \sigma_0 \quad (12\cdot2\cdot2)$$

where

$$\sigma_0(V) = \int_{\Omega'} \sigma(V; \hat{V}') d\Omega' \quad (12\cdot2\cdot3)$$

is called the “total scattering cross section.” In general σ_0 depends on the relative speed V of the incident particles.

The calculation of scattering cross sections for various types of forces between particles is a problem discussed in courses on mechanics. Let us here recall only briefly the very simple result obtained in classical mechanics for the total scattering cross section between two “hard spheres” of respective radii a_1 and a_2 . (This means that the interaction potential $V(R)$ between the particles is a function of the distance R between their centers such that $V(R) = 0$ when $R > (a_1 + a_2)$ and $V(R) \rightarrow \infty$ when $R < (a_1 + a_2)$.) The relative initial motion of the two spheres is indicated in Fig. 12·2·2. Note that scattering takes place only if the distance b (called the “impact parameter”) is such that $b < (a_1 + a_2)$. Hence, out of an incident flux of \mathcal{F}_1 particles per

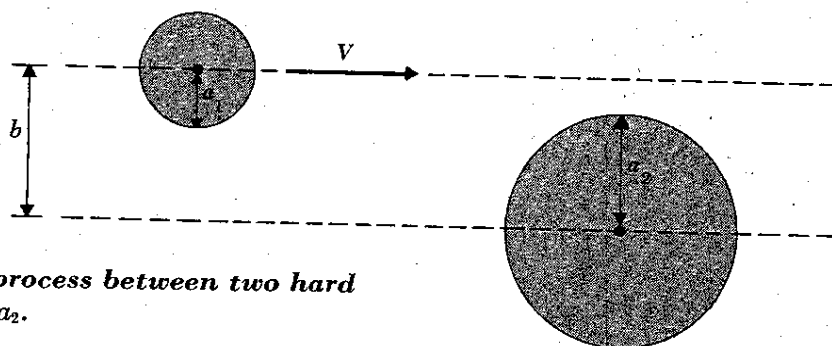


Fig. 12·2·2 Collision process between two hard spheres of radii a_1 and a_2 .

unit area per unit time, only that fraction of particles incident on the circular area $\pi(a_1 + a_2)^2$ is scattered. By the definition (12·2·2) one thus obtains for the total scattering cross section between two hard spheres

$$\sigma_0 = \frac{\mathfrak{N}}{\mathfrak{F}_1} = \pi(a_1 + a_2)^2 \quad (12\cdot2\cdot4)$$

If the two particles are identical, this reduces simply to

$$\sigma_0 = \pi d^2 \quad (12\cdot2\cdot5)$$

where $d = 2a$ is the diameter of the spherical particle.

Relation between collision time and scattering cross section If the scattering cross section σ for collisions between molecules is known, one can readily find the probability τ^{-1} per unit time that a given molecule in a gas suffers a collision. We shall give the argument in simplified fashion without being too careful about the rigorous way of taking various averages.

Consider a gas consisting of only a single kind of molecule. Denote the mean number of molecules per unit volume by n . Let \bar{v} be the mean speed of these molecules, \bar{V} their mean *relative* speed, and σ_0 their mean total scattering cross section at this speed. Focus attention on the particular type of molecules (say those of velocity near v_1) whose collision rate τ^{-1} we wish to calculate, and let n_1 denote the number of such molecules per unit volume. Consider now how this type of molecule (call it type 1) is scattered by all the molecules in an

Type-1 molecules

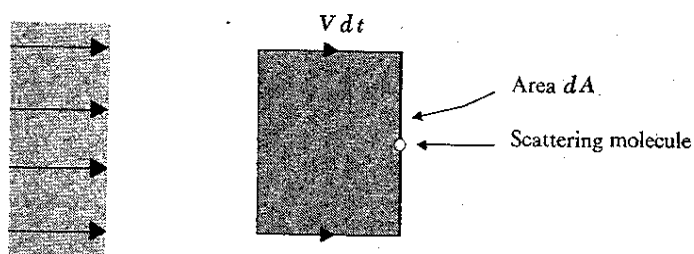


Fig. 12·2·3 If there are n_1 molecules per unit volume with relative velocity near V , all of these contained in the volume $(V dt dA)$ collide with the area dA in time dt and thus constitute a flux $n_1 V$ incident upon the scattering molecule.

element of volume d^3r of the gas. The relative flux of type 1 molecules incident on any *one* molecule in d^3r is given by the familiar argument as

$$\mathcal{F}_1 = \frac{n_1(\bar{V} dt dA)}{dt dA} = n_1\bar{V} \quad (12\cdot2\cdot6)$$

By (12·2·2) a number $n_1\bar{V}\sigma_0$ of these incident molecules is then scattered per unit time in all possible directions by this *one* target molecule. The total number of type 1 molecules scattered by *all* the molecules in d^3r is then given by

$$(n_1\bar{V}\sigma_0)(n d^3r)$$

Dividing this by the number $n_1 d^3r$ of type 1 molecules in the element of volume under consideration, one then obtains the collision probability $w = \tau^{-1}$ per unit time for one molecule of this type. Hence

$$\tau^{-1} = \bar{V}\sigma_0 n \quad (12\cdot2\cdot7)$$

The collision probability is thus enhanced by a large density of molecules, a large molecular speed, and a large scattering cross section.

***Remark** This calculation can readily be made rigorous by careful averaging. Let $f(v) d^3v$ be the mean number of molecules per unit volume with velocity in the range between v and $v + dv$. (In the equilibrium situation envisaged here this is just the Maxwell velocity distribution.) We wish to calculate the collision probability $\tau^{-1}(v_1)$ for a molecule with velocity between v_1 and $v_1 + dv_1$. The relative flux of these molecules with respect to a molecule of velocity v is given by $[f(v_1) d^3v_1 V]$ where $V = |v_1 - v|$. Multiplying this by the differential scattering cross section $\sigma(V; \hat{V}')$, and integrating over all solid angles $d\Omega'$ corresponding to the various directions of scattering \hat{V}' , gives then the total number of molecules scattered by *one* molecule in the volume d^3r . One then has to integrate over all the scattering molecules in d^3r , and to divide by the number of molecules with velocity near v_1 in this volume. Thus

$$\tau^{-1}(v_1) = \frac{\int_v \int_{\Omega'} [f(v_1) d^3v_1 V] \sigma(V; \hat{V}') d\Omega' [f(v) d^3v d^3r]}{f(v_1) d^3v_1 d^3r}$$

or

$$\tau^{-1}(v_1) = \int_v \int_{\Omega'} V \sigma(V; \hat{V}') f(v) d\Omega' d^3v \quad (12\cdot2\cdot8)$$

Equation (12·2·7) yields for the average mean free path l defined in (12·1·11) the result

$$l = \tau\bar{v} = \frac{\bar{v}}{\bar{V}} \frac{1}{n\sigma_0} \quad (12\cdot2\cdot9)$$

Here the ratio (\bar{v}/\bar{V}) of mean speed to mean relative speed is close to unity. Actually \bar{V} is somewhat larger than \bar{v} . The following simple argument makes

this clear. Consider two different molecules with velocities v_1 and v_2 . Their relative velocity is then given by

$$V = v_1 - v_2$$

Hence
$$V^2 = v_1^2 + v_2^2 - 2v_1 \cdot v_2 \quad (12.2.10)$$

If one takes the average of both sides of this equation, $\overline{v_1 \cdot v_2} = 0$, since the cosine of the angle between v_1 and v_2 is as likely to be positive as negative for molecules moving in random directions. Thus (12.2.10) becomes

$$\overline{V^2} = \overline{v_1^2} + \overline{v_2^2}$$

Neglecting the distinction between root-mean-square and mean values, this can be written

$$\bar{V} \approx \sqrt{\bar{v}_1^2 + \bar{v}_2^2} \quad (12.2.11)$$

When the molecules in the gas are all identical, $\bar{v}_1 = \bar{v}_2$ and (12.2.11) becomes

$$\bar{V} \approx \sqrt{2} \bar{v} \quad (12.2.12)$$

Then (12.2.9) becomes

$$l \approx \frac{1}{\sqrt{2} n \sigma_0} \quad (12.2.13)$$

Although this fact is not too interesting, it may be remarked parenthetically that a suitable average of (12.2.8) over the Maxwell velocity distribution yields for hard-sphere collisions precisely the result (12.2.13).

It is of interest to estimate the mean free path for a typical gas at room temperature ($\approx 300^\circ\text{K}$) and atmospheric pressure (10^6 dynes cm^{-2}). The number density n can be calculated from the equation of state. Thus

$$n = \frac{\bar{p}}{kT} = \frac{10^6}{(1.4 \times 10^{-16})(300)} = 2.4 \times 10^{19} \text{ molecules/cm}^3$$

A typical molecular diameter d might be 2×10^{-8} cm. Hence (12.2.5) gives $\sigma_0 \approx \pi(2 \times 10^{-8})^2 \approx 12 \times 10^{-16}$ cm^2 and (12.2.13) yields the estimate

$$l \approx 3 \times 10^{-5} \text{ cm} \quad (12.2.14)$$

Thus

$$l \gg d \quad (12.2.15)$$

so that our approximations based on relatively infrequent encounters between molecules are justified. If the gas is nitrogen, the mean speed of a N_2 molecule is, by (7.10.19), of the order of $\bar{v} \approx 5 \times 10^4$ cm/sec. Its mean time τ between collisions is then roughly $\tau \approx l/\bar{v} \approx 6 \times 10^{-10}$ sec. Thus its collision rate is $\tau^{-1} \approx 2 \times 10^9$ sec^{-1} , which is a frequency in the microwave region of the electromagnetic spectrum.

12.3 Viscosity

Definition of the coefficient of viscosity Consider a fluid (liquid or gas). Imagine in this fluid some plane with its normal pointing along the z direction.

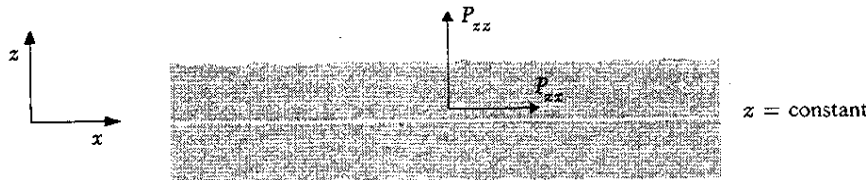


Fig. 12·3·1 A plane $z = \text{constant}$ in a fluid. The fluid below the plane exerts a force P_z on the fluid above it.

Then the fluid below this plane (i.e., on the side of smaller z) exerts a mean force P_z per unit area (or “stress”) on the fluid above the plane. Conversely, it follows by Newton’s third law that the fluid above the plane exerts a stress $-P_z$ on the fluid below the plane.

The mean force per unit area normal to the plane, i.e., the z component of P_z , measures just the mean pressure \bar{p} in the fluid; to be precise, $P_{zz} = \bar{p}$. When the fluid is in equilibrium, so that it is at rest or moving with *uniform* velocity throughout, then there is no mean component of stress *parallel* to the plane. Thus $P_{zx} = 0$. Note that the quantity P_{zx} is labeled by two indices, the first of them designating the orientation of the plane and the second the component of the force exerted across this plane.*

Consider now a nonequilibrium situation where the liquid does *not* move with the same velocity throughout. To be specific, consider the case where the fluid has a constant mean velocity u_x in the x direction, the magnitude of u_x depending on z so that $u_x = u_x(z)$. This kind of situation could be produced if the fluid is enclosed between two plates a distance L apart, the plate at $z = 0$ being stationary and the plate at $z = L$ moving in the x direction with constant velocity u_0 . The layers of fluid adjacent to the plates assume, to a good approximation, the velocities of the plates, so that there is no relative velocity of slip between the fluid and the plates. Layers of fluid between the plates have then different mean velocities u_x varying in magnitude between 0 and u_0 . In this case the fluid exerts a tangential force on the moving plate, tending to slow it down so as to restore the equilibrium situation.

More generally, any layer of fluid below a plane $z = \text{constant}$ exerts a tangential stress P_{zx} on the fluid above it. We already saw that $P_{zx} = 0$ in the equilibrium situation where $u_x(z)$ does *not* depend on z . In the present nonequilibrium case where $\partial u_x / \partial z \neq 0$ one expects, therefore, that P_{zx} should

* The quantity $P_{\alpha\gamma}$ (where α and γ can denote x , y , or z) is called the “pressure tensor.”

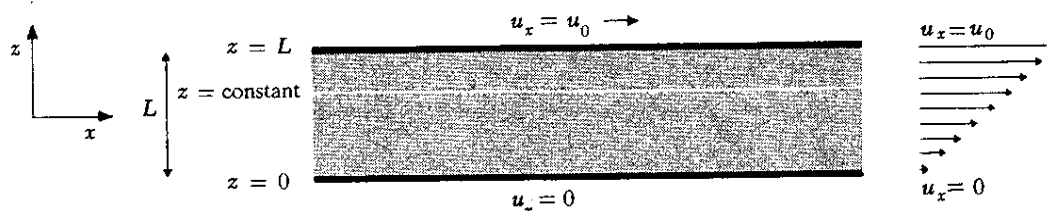


Fig. 12·3·2 A fluid contained between two plates. The lower plate is at rest while the upper one moves with velocity u_0 ; there thus exists a velocity gradient ($\partial u_x / \partial z$) in the fluid.

be some function of derivatives of u_x with respect to z such that it vanishes when u_x is independent of z . But if $\partial u_x / \partial z$ is assumed to be relatively small, the leading term in a power-series expansion of this function should be an adequate approximation, i.e., one expects a linear relation of the form

$$P_{zx} = -\eta \frac{\partial u_x}{\partial z} \quad (12 \cdot 3 \cdot 1)$$

Here the constant of proportionality η is called the "coefficient of viscosity." If u_x increases with increasing z , then the fluid below the plane tends to slow down the fluid above the plane and thus exerts on it a force in the $-x$ direction. That is, if $\partial u_x / \partial z > 0$, then $P_{zx} < 0$. Hence the minus sign was introduced explicitly in (12·3·1) so as to make the coefficient η a positive quantity. The cgs unit of η is, by (12·3·1), that of $\text{gm cm}^{-1} \text{sec}^{-1}$. (It is also commonly called a "poise" in honor of the physicist Poiseuille.) The proportionality implied by (12·3·1) between the stress P_{zx} and the velocity gradient $\partial u_x / \partial z$ is experimentally well satisfied by liquids and gases if the velocity gradient is not too large.

Note the various forces which act in the x direction in Fig. 12·3·2. The fluid below the plane $z = \text{constant}$ exerts a force P_{zx} per unit area on the fluid above it. Since the fluid between this plane and the plate at $z = L$ moves without acceleration, this plate must exert a force $-P_{zx}$ per unit area on the fluid adjacent to it. By Newton's third law, the fluid must then also exert on the plate at $z = L$ a force per unit area $+P_{zx}$, given by (12·3·1).

Calculation of the coefficient of viscosity for a dilute gas In the simple case of a dilute gas, the coefficient of viscosity can be calculated fairly readily on the basis of microscopic considerations of kinetic theory. Suppose that the mean fluid velocity component u_x (which is assumed to be very small compared to the mean thermal speed of the molecules) is a function of z . How does the stress P_{zx} come about in this situation? The qualitative reason is that in Fig. 12·3·2 molecules above the plane $z = \text{constant}$ have a somewhat larger x component of momentum than molecules below this plane. As molecules cross back and forth across this plane they carry this x component of momentum with them. Hence the gas below the plane gains momentum in the x direction from the molecules coming from above the plane; conversely, the gas above the plane loses momentum in the x direction by virtue of the molecules arriving from below the plane. Since the rate of change of momentum of a system is, by Newton's second law, equal to the force acting on the system, it follows that the gas above the plane is acted on by a force due to the gas below the plane. More precisely,

$$P_{zx} = \left. \begin{array}{l} \text{mean increase, per unit time and per unit area of the} \\ \text{plane, of the } x \text{ component of momentum of the gas above the} \\ \text{plane due to the net transport of momentum by molecules} \\ \text{crossing this plane.} \end{array} \right\} \quad (12 \cdot 3 \cdot 2)$$

Remark An analogy may make this mechanism of viscosity by momentum transfer clearer. Suppose two railroad trains move side by side along parallel tracks, the speed of one train being greater than that of the other. Imagine that workers on each train constantly pick up sandbags from their train and throw them onto the other train. Then there is a transfer of momentum between the trains so that the slower train tends to be accelerated and the faster train to be decelerated.

Let us now give an approximate simple calculation of the coefficient of viscosity. If there are n molecules per unit volume, roughly one-third of them have velocities along the z direction. Half of these, or $\frac{1}{6}n$ molecules per unit volume, have mean velocity \bar{v} in the $+z$ direction; the other half have a mean velocity \bar{v} in the $-z$ direction. On the average there are, therefore, $(\frac{1}{6}n\bar{v})$ molecules which in unit time cross a unit area of the plane $z = \text{constant}$ from below; similarly, there are $(\frac{1}{6}n\bar{v})$ molecules which in unit time cross a unit area of this plane from above. But molecules which cross the plane from below have, on the average, experienced their last collision at a distance l ($l = \text{mean free path}$) below the plane. Since the mean velocity $u_x = u_x(z)$ is a function of z , the molecules at this position $(z - l)$ had on the average a mean x component of velocity $u_x(z - l)$. Thus each such molecule of mass m transports across the plane a mean x component of momentum $[mu_x(z - l)]$. Hence one concludes that

$$\left. \begin{array}{l} \text{The mean } x \text{ component of momentum transported per unit} \\ \text{time per unit area across the plane in the } \textit{upward} \text{ direction} = \\ (\frac{1}{6}n\bar{v})[mu_x(z - l)]. \end{array} \right\} \quad (12\cdot3\cdot3)$$

$$\left. \begin{array}{l} \text{Similarly, the mean } x \text{ component of momentum transported} \\ \text{per unit time per unit area across the plane in the } \textit{downward} \\ \text{direction} = (\frac{1}{6}n\bar{v})[mu_x(z + l)]. \end{array} \right\} \quad (12\cdot3\cdot4)$$

By subtracting (12·3·4) from (12·3·3) one obtains the *net* molecular transport of x component of momentum per unit time per unit area from below to above the plane, i.e., the stress P_{zx} described in (12·3·2). Thus

$$P_{zx} = (\frac{1}{6}n\bar{v})[mu_x(z - l)] - (\frac{1}{6}n\bar{v})[mu_x(z + l)]$$

or

$$P_{zx} = \frac{1}{6}n\bar{v}m[u_x(z - l) - u_x(z + l)] \quad (12\cdot3\cdot5)$$

Here $u_x(z)$ can be expanded in Taylor's series and higher-order terms can be neglected, since the velocity gradient $\partial u_x / \partial z$ is assumed to be small (i.e., small

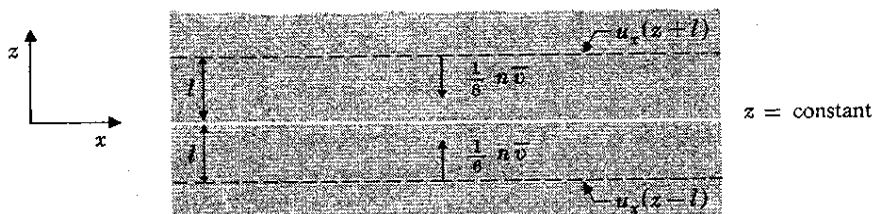


Fig. 12·3·3 Momentum transport by molecules crossing a plane.

enough that the mean velocity u_x does not vary appreciably over a distance of the order of l . Thus

$$u_x(z + l) = u_x(z) + \frac{\partial u_x}{\partial z} l \dots$$

$$u_x(z - l) = u_x(z) - \frac{\partial u_x}{\partial z} l \dots$$

Hence
$$P_{zx} = \frac{1}{6} n \bar{v} m \left(-2 \frac{\partial u_x}{\partial z} l \right) \equiv -\eta \frac{\partial u_x}{\partial z} \quad (12.3.6)$$

where

▶
$$\eta = \frac{1}{3} n \bar{v} m l \quad (12.3.7)$$

Thus P_{zx} is indeed proportional to the velocity gradient $\partial u_x / \partial z$ (as expected by (12.3.1)), and (12.3.7) provides an explicit approximate expression for the viscosity coefficient η in terms of the microscopic parameters characterizing the molecules of the gas.

Our calculation has been very simplified and careless about the exact way various quantities ought to be averaged. Hence the factor $\frac{1}{3}$ in (12.3.7) is not to be trusted too much; the constant of proportionality given by a more careful calculation might be somewhat different. On the other hand, the essential dependence of η on the parameters n , \bar{v} , m , and l ought to be correct.

Discussion The result (12.3.7) leads to some interesting predictions. By (12.2.13)

$$l \approx \frac{1}{\sqrt{2} n \sigma_0} \quad (12.3.8)$$

Thus the factor n cancels in (12.3.7), and one obtains

$$\eta = \frac{1}{3} \frac{m}{\sqrt{2} \sigma_0} \bar{v} \quad (12.3.9)$$

But the mean molecular speed, given by (7.10.13) as*

$$\bar{v} = \sqrt{\frac{8 k T}{\pi m}} \quad (12.3.10)$$

depends only on the temperature but not on the gas density n . Hence (12.3.9) is *independent* of the gas density n , or equivalently, of the gas pressure $\bar{p} = nkT$.

This is a remarkable result. It asserts that in the situation illustrated in Fig. 12.3.2, the viscous retarding force exerted by the gas on the moving upper plate is the same whether the pressure of the gas between the two plates is, for example, equal to 1 mm Hg or is increased to 1000 mm Hg. At first sight such a conclusion seems strange, since a naïve intuition might lead one

* In the approximate calculations of this chapter one could just as well replace the mean speed \bar{v} by the rms speed $\sqrt{3kT/m}$ obtained from the equipartition theorem.

to expect that the tangential force transmitted by the gas should be proportional to the number of gas molecules present. The paradox is resolved by noting that if the number of gas molecules is doubled, there are indeed twice as many molecules available to transport momentum from one plate to the other; but the mean free path of each molecule is then also halved, so that it can transport this momentum only half as effectively. Thus the net rate of momentum transfer is left unchanged. The fact that the viscosity η of a gas at a given temperature is independent of its density was first derived by Maxwell in 1860 and was confirmed by him experimentally.

It is clear, however, that this result cannot hold over an arbitrarily large density range of the gas. Indeed, we made two assumptions in deriving the relation (12·3·7):

1. We assumed that the gas is sufficiently dilute that there is negligible probability that *more* than two molecules come simultaneously so close together as to interact appreciably among themselves. Thus we were allowed to consider only two-particle collisions. This assumption is justified if the density n of the gas is sufficiently low so that

$$l \gg d \quad (12\cdot3\cdot11)$$

where $d \approx \sqrt{\sigma_0}$ is a measure of the molecular diameter.

2. On the other hand, we assumed that the gas is dense enough that the molecules collide predominantly with other molecules rather than with the walls of the container. This assumption implies that n is sufficiently large that

$$l \ll L \quad (12\cdot3\cdot12)$$

where L is a measure of the smallest linear dimension of the containing vessel (e.g., L is the spacing between the plates in Fig. 12·3·2).

If the gas is made so dilute that the condition (12·3·12) is violated, then the viscosity η must decrease, since in the limiting case when $n \rightarrow 0$ (perfect vacuum) the tangential force on the moving plate in Fig. 12·3·2 must clearly go to zero. (Indeed, in this limit the mean free path l in (12·3·7) must approach the container dimension L .) Note, however, that the range of densities where both (12·3·11) and (12·3·12) are simultaneously satisfied is quite large, because $L \gg d$ in usual macroscopic experiments. Thus the coefficient of viscosity η of a gas is independent of its pressure over a very considerable range.

Remark The foregoing comments can be made somewhat more quantitative. The *total* probability per unit time τ_0^{-1} that a molecule suffers a collision can be written as the sum of two probabilities

$$\tau_0^{-1} = \tau^{-1} + \tau_w^{-1} \quad (12\cdot3\cdot13)$$

where τ^{-1} is the probability per unit time that the molecule collides with other molecules and τ_w^{-1} is the probability per unit time that the molecule collides with the walls of the container. But by (12·2·7)

$$\tau^{-1} = \bar{V}n\sigma_0 = \frac{\bar{v}}{l} \tag{12·3·14}$$

where $l \approx (\sqrt{2} n\sigma_0)^{-1}$ is the mean free path due to collisions with other molecules. On the other hand, the mean time τ_w required to cross the smallest dimension L of the container is of the order of L/\bar{v} so that

$$\tau_w^{-1} \approx \frac{\bar{v}}{L} \tag{12·3·15}$$

Hence (12·3·13) gives for the resultant mean free path $l_0 \equiv \tau_0\bar{v}$ the relation

$$\frac{1}{l_0} = \frac{1}{l} + \frac{1}{L} \approx \sqrt{2} n\sigma_0 + \frac{1}{L} \tag{12·3·16}$$

It is this value of l_0 which should be used in (12·3·7) if approximate account is to be taken of collisions with the walls. When the density n becomes sufficiently small, $l_0 \rightarrow L$ and $\eta \propto n$. It should be pointed out, however, that in the very low density limit where $l \gg L$ (a gas satisfying this condition is called a "Knudsen gas") the concept of coefficient of viscosity tends to lose its meaning. The reason is that molecular collisions with the walls are then of overwhelming importance so that geometrical factors involving the shape of the container have to be considered in detail.

Let us now discuss the temperature dependence of η . If the scattering of molecules is similar to that of hard spheres, then the cross section σ_0 is by (12·2·5) a number independent of T . Then it follows by (12·3·9) that the temperature dependence of η is the same as that of \bar{v} ; i.e., for hard-sphere scattering,

$$\eta \propto T^{1/2} \tag{12·3·17}$$

More generally, $\sigma_0 = \sigma_0(\bar{V})$ depends on the mean relative speed of the molecules. Since $\bar{V} \propto T^{1/2}$, σ_0 becomes then also temperature dependent. The result is that η tends to vary with temperature more rapidly than in (12·3·17), somewhat more like $T^{0.7}$. This can be qualitatively understood since there exists not only a repulsive but also a longer-range attractive interaction between the molecules. This latter interaction tends to increase the scattering probability of a molecule and becomes more effective at low temperatures, where the molecules have low velocities and are thus more readily deflected. Hence the scattering cross section σ_0 tends to *decrease* with increasing temperature. As T increases, the viscosity $\eta \propto T^{1/2}/\sigma_0$ tends, therefore, to increase with temperature more rapidly than $T^{1/2}$.

Note that the viscosity of a gas *increases* as the temperature is raised. This behavior is quite different from that of the viscosity of liquids, which generally *decreases* rapidly with increasing temperature. The reason is that in a liquid, where molecules are close together, momentum transfer across a

plane occurs by direct forces between molecules on adjacent sides of the plane as well as by virtue of their motion across this plane.

Finally we estimate the magnitude of η . Since the mean pressure of the gas is, by (7·13·1), approximately given by $\bar{p} = \frac{1}{3}nm\bar{v}^2$, the expression (12·3·7) can be written as

$$\eta = \frac{\bar{p}}{\bar{v}} l = \frac{\bar{p}}{\bar{v}/l} \quad (12·3·18)$$

In words this says that the coefficient of viscosity is of such a magnitude that it would give rise to a stress equal to the gas pressure in the presence of a velocity gradient equal to the mean molecular speed divided by the mean free path. For air at atmospheric pressure (10^6 dynes cm^{-2}) and room temperature (300°K) one has approximately $\bar{v} \approx 5 \times 10^4$ cm sec^{-1} and $l \approx 3 \times 10^{-5}$ cm . Hence (12·3·18) gives as an order-of-magnitude estimate

$$\eta \approx 10^6 / (1.7 \times 10^9) = 6 \times 10^{-4} \text{ gm cm}^{-1} \text{ sec}^{-1}$$

The measured value of η for N_2 gas at this temperature is 1.78×10^{-4} $\text{gm cm}^{-1} \text{sec}^{-1}$.

For purposes of later comparisons with more exact calculations, we can combine (12·3·9) and (12·3·10) to obtain the following explicit expression for η obtained by our simple theory:

$$\eta = \frac{2}{3\sqrt{\pi}} \frac{\sqrt{mkT}}{\sigma_0} = 0.377 \frac{\sqrt{mkT}}{\sigma_0} \quad (12·3·19)$$

12·4 Thermal conductivity

Definition of the coefficient of thermal conductivity Consider a substance in which the temperature is *not* uniform throughout. In particular, imagine that the temperature T is a function of the z coordinate so that $T = T(z)$. Then the substance is certainly not in a state of equilibrium. As a result, energy in the form of heat flows from the region of higher to that of lower temperature. Let

$$\left. \begin{array}{l} \mathcal{Q}_z = \text{the heat crossing unit area of a plane (in the } z \text{ direction)} \\ \text{normal to the plane) per unit time.} \end{array} \right\} \quad (12·4·1)$$

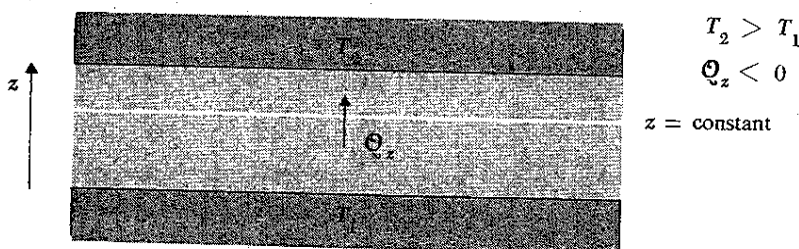


Fig. 12·4·1 A substance in thermal contact with two heat reservoirs at constant temperatures T_1 and T_2 . If $T_2 > T_1$, heat flows in the $-z$ direction from the region of higher to that of lower temperature.

The quantity Q_z is called the "heat flux" in the z direction. If the temperature were uniform, $Q_z = 0$. If it is not uniform, one expects that Q_z should to good approximation be proportional to the temperature gradient $\partial T/\partial z$ if the latter is not too large. Thus one can write

$$\blacktriangleright \quad Q_z = -\kappa \frac{\partial T}{\partial z} \quad (12.4.2)$$

The constant of proportionality κ is called the "coefficient of thermal conductivity" of the substance. Since heat flows from the region of higher to that of lower temperature, $Q_z < 0$ if $\partial T/\partial z > 0$. The minus sign was introduced explicitly in (12.4.2) so as to make κ a positive quantity. The relation (12.4.2) is found to be well obeyed in practically all gases, liquids, and isotropic solids.

Calculation of the coefficient of thermal conductivity for a dilute gas

In the simple case of a dilute gas the coefficient of thermal conductivity can be readily calculated by simple microscopic arguments similar to those used in discussing the viscosity of a gas. Consider a plane $z = \text{constant}$ in the gas where $T = T(z)$. The mechanism of heat transport is due to the fact that molecules cross this plane from above and below. But if $\partial T/\partial z > 0$, a molecule coming from above has a mean energy $\bar{\epsilon}(T)$ which is larger than that of a molecule coming from below. Thus there results a net transport of energy from the region above the plane to that below it. More quantitatively, there are again roughly $\frac{1}{6}n\bar{v}$ molecules which in unit time cross unit area of this plane from below and an equal number of molecules which cross it from above.* Here n is the mean number of molecules per unit volume at the plane $z = \text{constant}$, and \bar{v} is their mean speed. Now molecules which cross this plane from below have, on the average, experienced their last collision at a distance l ($l = \text{mean free path}$) below the plane. But the mean energy $\bar{\epsilon}$ of a molecule is a function of T and, since $T = T(z)$ in the present case, consequently a function of z so that $\bar{\epsilon} = \bar{\epsilon}(z)$. Hence the molecules crossing the plane from below carry with them a mean energy $\bar{\epsilon}(z - l)$ corresponding to the

* Since the thermal conductivity of a gas is measured under steady-state conditions where there is no convective motion of the gas, the number of molecules crossing unit area of any plane per second from one side must always be equal to the number of molecules crossing the plane in the opposite direction. It is therefore unnecessary in this simple discussion to worry about the fact that the temperature gradient causes n and \bar{v} to be slightly different above and below the plane. (Such questions can be investigated more carefully by the methods of the next chapters.)

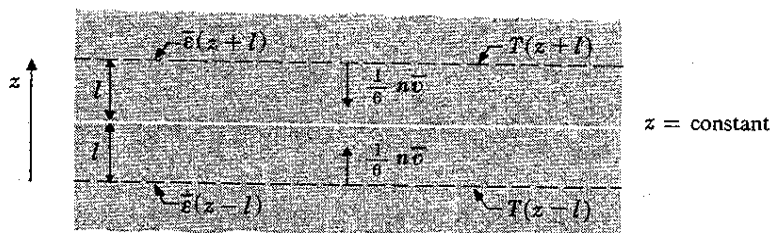


Fig. 12.4.2 Energy transport by molecules crossing a plane.

mean energy assumed by them at their last collision at the position $(z - l)$. Thus one obtains

$$\left. \begin{array}{l} \text{Mean energy transported per unit time per unit area across} \\ \text{the plane from below} = \frac{1}{6}n\bar{v}\bar{\epsilon}(z - l). \end{array} \right\} \quad (12\cdot4\cdot3)$$

Similarly, in considering molecules coming from above the plane where they suffered their last collision at $(z + l)$, one obtains

$$\left. \begin{array}{l} \text{Mean energy transported per unit time per unit area across} \\ \text{the plane from above} = \frac{1}{6}n\bar{v}\bar{\epsilon}(z + l). \end{array} \right\} \quad (12\cdot4\cdot4)$$

By subtracting (12·4·4) from (12·4·3) one then obtains the *net* flux of energy Q_z crossing the plane from below in the $+z$ direction

$$\begin{aligned} Q_z &= \frac{1}{6}n\bar{v}\{\bar{\epsilon}(z - l) - \bar{\epsilon}(z + l)\} \\ &= \frac{1}{6}n\bar{v}\left\{\left[\bar{\epsilon}(z) - l\frac{\partial\bar{\epsilon}}{\partial z}\right] - \left[\bar{\epsilon}(z) + l\frac{\partial\bar{\epsilon}}{\partial z}\right]\right\} \\ \text{or} \quad Q_z &= \frac{1}{6}n\bar{v}\left(-2l\frac{\partial\bar{\epsilon}}{\partial z}\right) = -\frac{1}{3}n\bar{v}l\frac{\partial\bar{\epsilon}}{\partial T}\frac{\partial T}{\partial z} \end{aligned} \quad (12\cdot4\cdot5)$$

since $\bar{\epsilon}$ depends on z through the temperature T . Let us introduce the abbreviation

$$c \equiv \frac{\partial\bar{\epsilon}}{\partial T} \quad (12\cdot4\cdot6)$$

which is the specific heat per *molecule*. Then (12·4·5) becomes

$$Q_z = -\kappa\frac{\partial T}{\partial z} \quad (12\cdot4\cdot7)$$

where

$$\kappa = \frac{1}{3}n\bar{v}cl \quad (12\cdot4\cdot8)$$

The relation (12·4·7) shows that Q_z is indeed proportional to the temperature gradient (as expected by (12·4·2)), and (12·4·8) provides an explicit expression for the thermal conductivity κ of the gas in terms of fundamental molecular quantities.

Once again the precise factor $\frac{1}{3}$ in (12·4·8) is not to be trusted too much in this simplified calculation, but the dependence on the other parameters ought to be correct. Since $l \propto n^{-1}$, the density n again cancels; i.e., using (12·3·8), the thermal conductivity (12·4·8) becomes

$$\kappa = \frac{1}{3}\sqrt{2}\sigma_0\bar{v}c \quad (12\cdot4\cdot9)$$

which is *independent* of the pressure of the gas. This result is due to the same reasons mentioned in connection with the similar property of the viscosity coefficient η and is again valid in a density range where $d \ll l \ll L$.

Note that for a monatomic gas the equipartition theorem gives $\bar{\epsilon} = \frac{3}{2}kT$ so that the specific heat per molecule is simply given by $c = \frac{3}{2}k$.

Since $\bar{v} \propto T^{1/2}$ and since c is usually temperature independent, (12·4·9) gives for hard-sphere interaction between molecules

$$\kappa \propto T^{1/2} \quad (12·4·10)$$

More generally, σ_0 also tends to vary with the temperature in the manner discussed in the last section in connection with the viscosity. As a result, κ increases again somewhat more rapidly with increasing temperature than is indicated by (12·4·10).

An estimate of the order of magnitude of κ for a gas at room temperature can readily be obtained by substituting typical numbers into (12·4·8). A representative value is the measured thermal conductivity of argon at 273°K, namely $\kappa = 1.65 \times 10^{-4}$ watts cm^{-1} deg^{-1} .

By using the result (12·3·10) for \bar{v} , the approximate expression (12·4·9) for the thermal conductivity becomes explicitly

$$\kappa = \frac{2}{3} \frac{c}{\sqrt{\pi} \sigma_0} \sqrt{\frac{kT}{m}} \quad (12·4·11)$$

Finally, comparison between the expressions (12·4·8) for the thermal conductivity κ and (12·3·7) for the viscosity η shows that these are quite similar in form. Indeed, one obtains for their ratio the relation

$$\frac{\kappa}{\eta} = \frac{c}{m} \quad (12·4·12)$$

Equivalently, multiplying both numerator and denominator by Avogadro's number N_a ,

$$\frac{\kappa}{\eta} = \frac{c_V}{\mu} \quad (12·4·13)$$

where $c_V = N_a c$ is the molar specific heat of the gas at constant volume and where $\mu = N_a m$ is its molecular weight. Thus there exists a very simple relation between the two transport coefficients κ and η , a relation which can readily be checked experimentally. One finds that the ratio $(\kappa/\eta)(c/m)^{-1}$ lies somewhere in the range between 1.3 and 2.5 instead of being unity as predicted by (12·4·12). In view of the very simplified nature of the arguments leading to these expressions for η and κ , there is greater justification for being pleased by the extent of agreement with experiment than there is cause for surprise at the discrepancy. Indeed, part of the latter is readily explained by the mere fact that our calculation did not take into account effects due to the distribution of molecular velocities. Thus faster molecules cross a given plane more frequently than slower ones. In the case of thermal conductivity these faster molecules also transport more kinetic energy; but in the case of viscosity they do not carry any greater mean x component of momentum. Thus the ratio κ/η should be increased to a value larger than that given by (12·4·12).

* *Application to nonclassical gases* It is worth pointing out that the simple considerations of this section are applicable to a much wider class of physical situations. Consider, for example, the thermal conductivity of a

metal. Heat in such a metal is predominantly transported by the conduction electrons. The latter would travel through a perfect periodic crystal lattice without being scattered (since the electrons have wave properties in a quantum description). They do, however, get scattered because every metal contains some impurities or other lattice imperfections, and because at a finite temperature the lattice vibrates (i.e., the perfect periodicity of the lattice is then disturbed by thermally excited sound waves, or phonons, traveling through the lattice).

In order to apply (12·4·8) to the conduction electrons which form a highly degenerate Fermi-Dirac gas, we note first that only those electrons lying within a range of the order of kT around the Fermi energy μ , i.e., only the fraction kT/μ of electrons which contribute to the electronic specific heat (an amount $\frac{3}{2}k$ per electron) contribute to the thermal conductivity κ . Hence the product nc in (12·4·8) involves only these effective electrons; thus it becomes approximately $n(kT/\mu)(\frac{3}{2}k)$, i.e., it is proportional to T . All these electrons move nearly with the Fermi velocity v_F ; thus $\bar{v} \approx v_F$ in (12·4·8), and this is essentially temperature independent. If the temperature is low enough, the number n_p of thermally excited phonons per unit volume becomes sufficiently small compared to the number n_i of impurities per unit volume that impurity scattering of the electrons is predominant. But since n_i is a fixed number independent of T , the electron mean free path $l \propto n_i^{-1}$ is independent of T (assuming the electron-impurity scattering cross section to be essentially constant). Hence (12·4·8) predicts that, for impurity scattering,

$$\kappa_i \propto T \quad (12\cdot4\cdot14)$$

This proportionality is experimentally found to be well satisfied for metals (and alloys, which are, of course, very impure) at sufficiently low temperatures.

At higher temperatures, scattering by phonons becomes predominant. If the temperature is still sufficiently low that all thermally excited phonons (or lattice vibrations) have large wavelengths compared to the interatomic spacing (i.e., if T is still appreciably less than the Debye temperature of Sec. 10·2), then the problem is quite analogous to that of photons, and the mean number of phonons per unit volume $n_p \propto T^3$ (see (10·2·27)). Hence the electron mean free path due to collision with phonons is given by $l \propto n_p^{-1} \propto T^{-3}$ (assuming an essentially constant electron-phonon scattering cross section). The temperature dependence of κ in (12·4·8) then becomes, for phonon scattering,

$$\kappa_p \propto T \left(\frac{1}{T^3} \right) \propto \frac{1}{T^2} \quad (12\cdot4\cdot15)$$

More generally, the electrons are scattered independently by both impurities and phonons at the same time. Hence the thermal resistivities (i.e., the reciprocals of the respective conductivities) due to these processes simply add. The resultant thermal conductivity κ must then be given by a relation of the form

$$\frac{1}{\kappa} = \frac{1}{\kappa_i} + \frac{1}{\kappa_p} = \frac{a}{T} + bT^2 \quad (12\cdot4\cdot16)$$

where κ_i and κ_p are given by (12.4.14) and (12.4.15), and where a and b are two constants. The temperature dependence (12.4.16), with its characteristic maximum as a function of T , is experimentally well verified.

Let us finally consider the thermal conductivity of an insulating solid at low temperatures. Since there are no conduction electrons, the thermal conductivity is low and is entirely due to heat transport by lattice vibrations, i.e., by phonons. In order to apply (12.4.8) to these phonons, we note that $n_p \propto T^3$ if T is sufficiently low. The speed \bar{v} of a phonon is the velocity of sound, which is essentially temperature-independent. The mean energy $\bar{\epsilon}$ of a phonon is of the order of kT , so that $c = \partial\bar{\epsilon}/\partial T$ is of the order k and temperature-independent. If T is sufficiently low, the mean free path of a phonon is essentially limited by scattering from the boundaries of the specimen; thus l is of the order of the specimen dimensions and therefore temperature-independent. Hence one obtains for an insulator at low temperature simply

$$\kappa \propto T^3 \quad (12.4.17)$$

This temperature dependence is experimentally found to be approximately correct.

12.5 Self-diffusion

Definition of the coefficient of self-diffusion Consider a substance consisting of similar molecules, but assume that a certain number of these molecules are labeled in some way. For example, some of the molecules might be labeled by the fact that their nuclei are radioactive. Let n_1 be the mean number of labeled molecules per unit volume. In an equilibrium situation the labeled molecules would be distributed uniformly throughout the available volume, so that n_1 is independent of position. Now suppose that their distribution is not uniform, so that n_1 does depend on position, e.g., $n_1 = n_1(z)$, even though the total mean number n of molecules per unit volume remains constant. (This constancy guarantees that there is no mass motion of the whole substance.) This is not an equilibrium situation and thus there will be a motion of labeled molecules tending to increase the entropy, i.e., tending to make the concentration n_1 more nearly uniform. Let the flux of labeled molecules be denoted by J , i.e., let

$$J_z = \left. \begin{array}{l} \text{the mean number of labeled molecules crossing unit} \\ \text{area of a plane (in the } z \text{ direction normal to the plane) per} \\ \text{unit time.} \end{array} \right\} \quad (12.5.1)$$

If n_1 were uniform, $J_z = 0$. If n_1 is not uniform one expects that J_z should to good approximation be proportional to the concentration gradient of labeled molecules. Thus one can write

$$J_z = -D \frac{\partial n_1}{\partial z} \quad (12.5.2)$$

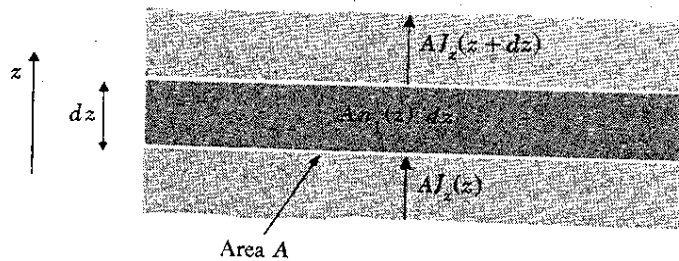


Fig. 12·5·1 Diagram illustrating the conservation of the number of molecules during diffusion.

The constant of proportionality D is called the “coefficient of self-diffusion” of the substance. If $\partial n_1/\partial z > 0$, the flow of labeled particles is in the $-z$ direction so as to equalize the concentration, i.e., $J_z < 0$. Hence the minus sign was introduced explicitly in (12·5·2) to make D a positive quantity. The relation (12·5·2) is found to describe quite adequately the self-diffusion* of molecules in gases, liquids, or isotropic solids.

It is useful to point out that the quantity n_1 satisfies, by virtue of the relation (12·5·2), a simple differential equation. Consider a one-dimensional problem where $n_1(z, t)$ is the mean number of labeled molecules per unit volume located at time t near the position z . Focus attention on a slab of substance of thickness dz and of area A . Since the total number of labeled molecules is conserved, one can make the statement that the [increase per unit time in the number of labeled molecules contained within the slab] must be equal to [the number of labeled molecules entering the slab per unit time through its surface at z] minus [the number of labeled molecules leaving the slab per unit time through its surface at $z + dz$]. In symbols,

$$\frac{\partial}{\partial t} (n_1 A dz) = AJ_z(z) - AJ_z(z + dz)$$

or

$$\frac{\partial n_1}{\partial t} dz = J_z(z) - \left[J_z(z) + \frac{\partial J_z}{\partial z} dz \right]$$

Thus

$$\frac{\partial n_1}{\partial t} = - \frac{\partial J_z}{\partial z} \quad (12·5·3)$$

This equation expresses just the conservation of the number of labeled molecules. Using the relation (12·5·2), this becomes

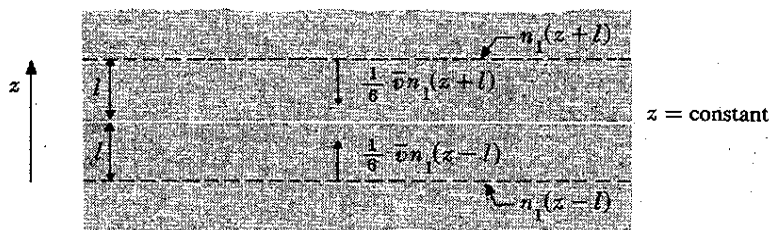
$$\frac{\partial n_1}{\partial t} = D \frac{\partial^2 n_1}{\partial z^2} \quad (12·5·4)$$

This is the desired partial differential equation, the “diffusion equation,” satisfied by $n_1(z, t)$.

Calculation of the coefficient of self-diffusion for a dilute gas In the simple case of a dilute gas, the coefficient of self-diffusion can readily be calculated by mean-free-path arguments similar to those used in the last two sections. Consider a plane $z = \text{constant}$ in the gas. The mean number of

* One speaks of *self-diffusion* if the diffusing molecules are, except for being labeled, identical to the remaining molecules of the substance. The more general and complicated situation would be that of *mutual diffusion* where the molecules are *unlike*, e.g., the diffusion of He molecules in argon gas.

Fig. 12.5.2 Transport of labeled molecules across a plane.



labeled molecules which in unit time cross a unit area of this plane from below is equal to $\frac{1}{6}\bar{v}n_1(z-l)$; the mean number of labeled molecules which in unit time cross a unit area of this plane from above is $\frac{1}{6}\bar{v}n_1(z+l)$. Hence one obtains for the net flux of labeled molecules crossing the plane from below in the $+z$ direction

$$\begin{aligned} J_z &= \frac{1}{6}\bar{v}n_1(z-l) - \frac{1}{6}\bar{v}n_1(z+l) \\ &= \frac{1}{6}\bar{v}[n_1(z-l) - n_1(z+l)] = \frac{1}{6}\bar{v}\left(-2\frac{\partial n_1}{\partial z}l\right) \end{aligned}$$

or
$$J_z = -D\frac{\partial n_1}{\partial z} \quad (12.5.5)$$

where

▶
$$D = \frac{1}{3}\bar{v}l \quad (12.5.6)$$

Thus (12.5.5) shows explicitly that J_z is proportional to the concentration gradient (in accordance with the general relation (12.5.2)), and (12.5.6) gives an approximate expression for the coefficient of self-diffusion in terms of fundamental molecular quantities.

To express D in more explicit form one need only use the relations

$$l = \frac{1}{\sqrt{2}n\sigma_0} = \frac{1}{\sqrt{2}\sigma_0}\frac{kT}{\bar{p}} \quad (12.5.7)$$

and
$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \quad (12.5.8)$$

Thus
$$D = \frac{2}{3}\frac{1}{\sqrt{\pi}}\frac{1}{\bar{p}\sigma_0}\sqrt{\frac{(kT)^3}{m}} \quad (12.5.9)$$

Hence the coefficient of self-diffusion D does depend on the pressure of the gas. At a fixed temperature T ,

$$D \propto \frac{1}{n} \propto \frac{1}{\bar{p}} \quad (12.5.10)$$

Also at a fixed pressure,

$$D \propto T^{\frac{3}{2}} \quad (12.5.11)$$

if the scattering is like that between hard spheres so that σ_0 is a constant independent of T .

By virtue of (12.5.6), the order of magnitude of D at room temperature and atmospheric pressure is $\frac{1}{3}\bar{v}l \approx \frac{1}{3}(5 \times 10^4)(3 \times 10^{-5}) \approx 0.5 \text{ cm}^2 \text{ sec}^{-1}$. The experimentally measured value for N_2 gas at 273°K and 1 atmosphere pressure is $0.185 \text{ cm}^2 \text{ sec}^{-1}$.

Comparison between (12·5·6) and the coefficient of viscosity η in (12·3·7) yields the relation

$$\frac{D}{\eta} = \frac{1}{nm} = \frac{1}{\rho} \quad (12·5·12)$$

where ρ is the mass density of the gas. Experimentally, one finds that the ratio $(D\rho/\eta)$ lies in the range between 1.3 and 1.5 instead of being unity as predicted by (12·5·12). In view of the crude nature of our simple calculations this extent of agreement between theory and experiment can be regarded as quite satisfactory.

Diffusion regarded as a random walk problem It is possible to look upon the diffusion problem as a random walk executed by the labeled molecule. Assume that successive displacements suffered by the molecule between collisions are statistically independent and denote by ζ_i the z component of the i th displacement of the molecule. If the molecule starts at $z = 0$, the z component of its position vector after a total of N displacements is then given by

$$z = \sum_{i=1}^N \zeta_i \quad (12·5·13)$$

We calculate mean values as in Sec. 1·9. By virtue of the random direction of each displacement, $\bar{\zeta}_i = 0$ so that $\bar{z} = 0$. On the other hand, one obtains for the dispersion

$$\bar{z}^2 = \sum_i \bar{\zeta}_i^2 + \sum_{i \neq j} \sum_j \bar{\zeta}_i \bar{\zeta}_j \quad (12·5·14)$$

Now, by virtue of the statistical independence, $\bar{\zeta}_i \bar{\zeta}_j = \bar{\zeta}_i \bar{\zeta}_j = 0$ so that (12·5·14) reduces simply to

$$\bar{z}^2 = N\bar{\zeta}^2 \quad (12·5·15)$$

The mean-square displacement $\bar{\zeta}^2$ per step can readily be computed. The z component of this displacement in time t is $\zeta = v_z t$. Hence

$$\bar{\zeta}^2 = \bar{v}_z^2 t^2$$

But, by symmetry, $\bar{v}_z^2 = \frac{1}{3}\bar{v}^2$. Furthermore, one has by (12·1·10)

$$\bar{t}^2 = \int_0^\infty e^{-t/\tau} \frac{dt}{\tau} \cdot t^2 = \tau^2 \int_0^\infty e^{-u} u^2 du = 2\tau^2$$

Hence

$$\bar{\zeta}^2 = \frac{2}{3}\bar{v}^2\tau^2 \quad (12·5·16)$$

Since each displacement between collisions requires a mean time τ , the total number N of displacements suffered in a time t is equal to t/τ . Hence (12·5·15) yields for the mean-square z component of displacement of a molecule in time t the result

$$\bar{z}^2(t) = \left(\frac{2}{3}\bar{v}^2\tau\right) t \quad (12·5·17)$$

On the other hand, one can also calculate the mean-square displacement $\bar{z}^2(t)$ by purely macroscopic reasoning based on the diffusion equation (12·5·4).

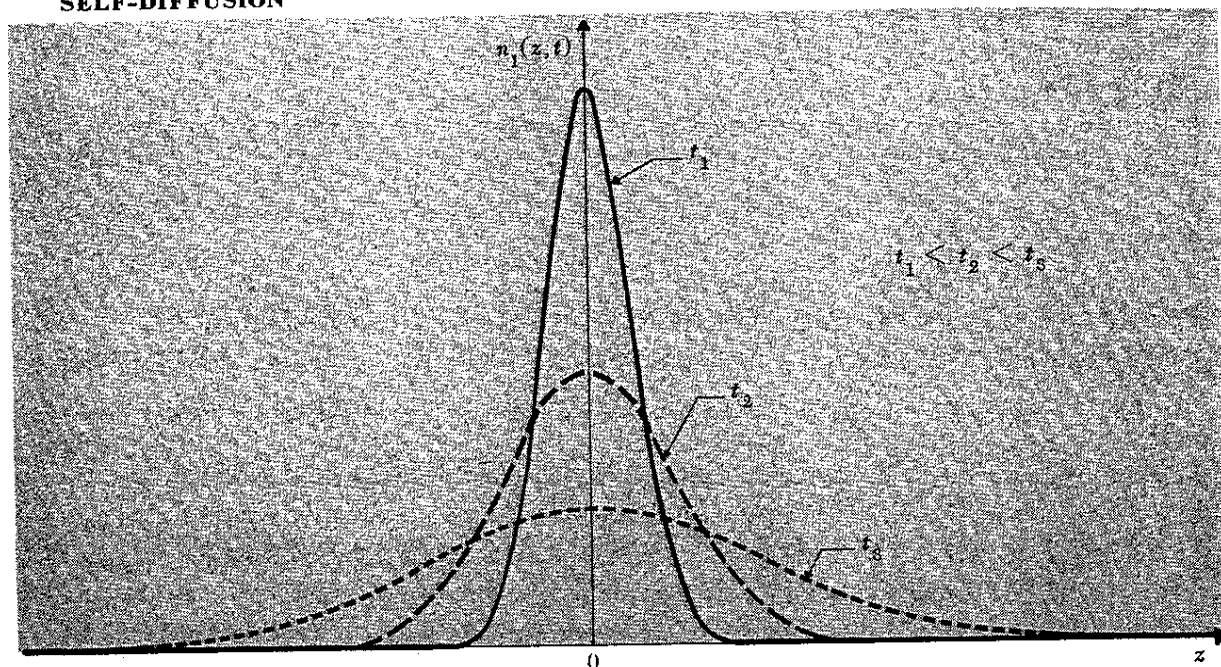


Fig. 12.5.3 The number density $n_1(z, t)$ as a function of z at various times t after molecules are introduced at time $t = 0$ near the plane $z = 0$. The areas under all the curves are the same and equal to the total number N_1 of labeled molecules.

Imagine that a total of N_1 labeled molecules per unit area are introduced at time $t = 0$ in an infinitesimally thick slab near $z = 0$. The molecules then proceed to diffuse (see Fig. 12.5.3). Conservation of the total number of labeled molecules requires that

$$\int_{-\infty}^{\infty} n_1(z, t) dz = N_1 \quad (12.5.18)$$

at all times. By definition one also has

$$\overline{z^2(t)} = \frac{1}{N_1} \int_{-\infty}^{\infty} z^2 n_1(z, t) dz \quad (12.5.19)$$

To find how $\overline{z^2}$ depends on t , multiply the diffusion equation (12.5.4) by z^2 and integrate over z . This yields

$$\int_{-\infty}^{\infty} z^2 \frac{\partial n_1}{\partial t} dz = D \int_{-\infty}^{\infty} z^2 \frac{\partial^2 n_1}{\partial z^2} dz \quad (12.5.20)$$

The left side gives, by (12.5.19),

$$\int_{-\infty}^{\infty} z^2 \frac{\partial n_1}{\partial t} dz = \frac{\partial}{\partial t} \int_{-\infty}^{\infty} z^2 n_1 dz = N_1 \frac{\partial}{\partial t} (\overline{z^2})$$

The right side of (12.5.20) can be simplified by successive integrations by part

$$\begin{aligned} \int_{-\infty}^{\infty} z^2 \frac{\partial^2 n_1}{\partial z^2} dz &= \left[z^2 \frac{\partial n_1}{\partial z} \right]_{-\infty}^{\infty} - 2 \int_{-\infty}^{\infty} z \frac{\partial n_1}{\partial z} dz \\ &= 0 - 2[zn_1]_{-\infty}^{\infty} + 2 \int_{-\infty}^{\infty} n_1 dz \\ &= 0 + 2N_1 \end{aligned}$$

since n_1 and $(\partial n_1/\partial z) \rightarrow 0$ as $|z| \rightarrow \infty$. Thus (12·5·20) becomes

$$\frac{\partial}{\partial t} (\overline{z^2}) = 2D \quad (12·5·21)$$

or

$$\overline{z^2} = 2Dt \quad (12·5·22)$$

where the constant of integration has been set equal to zero, since $\overline{z^2} = 0$ for $t = 0$ by virtue of the initial condition that all molecules start at $z = 0$.

By comparing (12·5·22) with the random walk result (12·5·17) one obtains

$$D = \frac{1}{3} \overline{v^2} \tau \quad (12·5·23)$$

or

$$D = \frac{1}{3} \overline{v} l \quad (12·5·24)$$

if one neglects the distinction between $\overline{v^2}$ and \overline{v}^2 and sets $\overline{v} \tau = l$. Thus one regains the result (12·5·6).

12 · 6 Electrical conductivity

Consider a system (liquid, solid, or gas) containing charged particles which are free to move. If a small uniform electric field \mathcal{E} is applied in the z direction, a nonequilibrium situation results in which an electric current density j_z is set up in this direction. By definition

$$j_z = \left. \begin{array}{l} \text{the mean electric charge crossing a unit area (perpen-} \\ \text{dicular to the } z \text{ direction) per unit time.} \end{array} \right\} \quad (12·6·1)$$

If the electric field \mathcal{E} is sufficiently small, one expects that

$$j_z = \sigma_{el} \mathcal{E} \quad (12·6·2)$$

where the constant of proportionality σ_{el} is called the “electrical conductivity” of the system. The relation (12·6·2) is called “Ohm’s law.”

Consider now a dilute gas of particles having mass m and charge e and interacting with some other system of particles by which they can get scattered with collision time τ . A particularly simple case would be that of a relatively small number of ions (or electrons) in a gas where these ions are predominantly scattered by collisions with the neutral gas molecules.

Remark Another example would be that of the conduction electrons in a metal where the electrons are scattered by the atoms of the solid. This case involves, however, some subtleties by virtue of the Fermi-Dirac statistics obeyed by the electrons. It will be considered more specifically in Chapter 13.

When an electric field \mathcal{E} is applied in the z direction, it gives rise to a mean z component of velocity \overline{v}_z of the charged particles. The mean number of such

particles crossing a unit area (perpendicular to the z direction) per unit time is then given by $n\bar{v}_z$ if n is the mean number of charged particles per unit volume. Since each particle carries a charge e , one thus obtains

$$j_z = ne\bar{v}_z \quad (12.6.3)$$

It only remains to calculate \bar{v}_z . Let us measure time from the instant $t = 0$ immediately after the particle's last collision. The equation of motion of the particle between this collision and the next one is

$$m \frac{dv_z}{dt} = e\mathcal{E}$$

Hence
$$v_z = \frac{e\mathcal{E}}{m} t + v_z(0) \quad (12.6.4)$$

In order to calculate the mean value \bar{v}_z , we assume that as a result of each collision the particle is, at least on the average, restored to thermal equilibrium; its velocity $v(0)$ has then random direction and $\bar{v}_z(0) = 0$ irrespective of the particle's past history before that collision.* Taking the mean value of (12.6.4) over all possible times t between collisions, as given by the probability (12.1.10), we then obtain

$$\bar{v}_z = \frac{e\mathcal{E}}{m} \bar{t} = \frac{e}{m} \int_0^\infty e^{-t/\tau} \frac{dt}{\tau} t = \frac{e\mathcal{E}}{m} \tau \quad (12.6.5)$$

that is, we have just used the familiar result that the mean time \bar{t} between collisions is equal to τ . We have also treated the collision probability τ^{-1} per unit time as a constant, even though it may depend on the particle speed. This is justified because the electric field \mathcal{E} was assumed to be sufficiently small that the increment in the particle's speed produced by \mathcal{E} between successive collisions is negligibly small compared to the thermal speed of the particles.

By using (12.6.5) in (12.6.3), one obtains

$$j_z = \frac{ne^2}{m} \tau \mathcal{E} \quad (12.6.6)$$

or

$$j_z = \sigma_{el} \mathcal{E} \quad (12.6.7)$$

where

$$\sigma_{el} = \frac{ne^2}{m} \tau \quad (12.6.8)$$

Thus j_z is indeed proportional to \mathcal{E} (as expected by (12.6.2)) and (12.6.8) provides an explicit expression for the electrical conductivity σ_{el} in terms of microscopic parameters of the gas.

If the conductivity is due to a relatively small number of ions in a gas, the collisions limiting the mean free path are predominantly those between

* One can expect this to be a very good approximation if the charged particle suffers collisions with particles of much larger mass. Otherwise the charged particle retains after each collision some memory of the z component of velocity it had before that collision. For the time being we neglect corrections due to such "persistence-of-velocity" effects.

ions and neutral gas molecules.* Suppose that the total scattering cross section of an ion by a molecule is σ_{im} and that there are, per unit volume, n_1 molecules of mass $m_1 \gg m$. The thermal speed of the ions is then much greater than that of the molecules, and the mean relative speed of an ion-molecule encounter is simply the mean ion speed \bar{v} . Thus the collision rate of an ion is approximately equal to

$$\tau^{-1} \approx n_1 \bar{v} \sigma_{im} = n_1 \left(\frac{8kT}{\pi m} \right)^{1/2} \sigma_{im}$$

and

$$\sigma_{el} \approx \sqrt{\frac{\pi}{8}} \frac{ne^2}{n_1 \sigma_{im} \sqrt{mkT}} \quad (12.6.9)$$

SUGGESTIONS FOR SUPPLEMENTARY READING

- R. D. Present: "Kinetic Theory of Gases," chap. 3, McGraw-Hill Book Company, New York, 1958. (See also secs. 8.1-8.2 on collision dynamics.)
 J. F. Lee, F. W. Sears, and D. L. Turcotte: "Statistical Thermodynamics," chap. 4, Addison-Wesley Publishing Company, Reading, Mass., 1963.
 C. Kittel: "Introduction to Solid State Physics," 2d ed., pp. 138-153, John Wiley & Sons, Inc., New York, 1956. (Applications to the thermal conductivity of solids.)

PROBLEMS

- 12.1** A large number of throws are made with a single die.
 (a) What is the mean number of throws between the appearances of a six?
 At any stage of the process what is the mean number of throws
 (b) before the next appearance of a six;
 (c) since the last appearance of a six?
- 12.2** Let l denote the mean free path of a molecule in a gas. Suppose that such a molecule has just suffered a collision. What is the mean distance
 (a) it travels before it suffers the next collision;
 (b) it has traveled since it suffered the last collision?
 (c) What is the mean distance traveled by the molecule between two successive collisions?
- 12.3** An ion of mass m and electric charge e is moving in a dilute gas of molecules with which it collides. The mean time between collisions suffered by the ion is τ . Suppose that a uniform electric field \mathcal{E} is applied in the x direction.
 (a) What is the mean distance \bar{x} (in the direction of \mathcal{E}) which the ion travels between collisions if it starts out with zero x component of velocity after each collision?
 (b) In what fraction of cases does the ion travel a distance x less than \bar{x} ?
- 12.4** Calculate the differential scattering cross section σ for the scattering of a hard

* Actually, even if ion-ion collisions occurred frequently, they would not affect the electrical conductivity, since the colliding ions would, effectively, simply exchange roles in carrying the electric current. This will be shown in greater detail in Sec. 14.6.