2-6 Transport Phenomena

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

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

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

$$\rho = \frac{\mathcal{M}}{N_A d^3} \qquad\qquad 2\text{-}38$$

Either N_A or d can be found from a simple measurement of den-

sity if the other is known.[1] If neither is known, they can both be obtained if a second relationship can be found.

The comparison of the predictions of kinetic theory with macroscopic measurements of viscosity and heat conduction provided one of the first estimates of molecular sizes and of Avogadro's number. We shall consider here only the most elementary treatment of kinetic theory of transport phenomena.

An important quantity characterizing molecular collisions is the average distance a molecule travels between collisions. This distance is called the *mean free path*, ℓ. We should expect ℓ to depend inversely on the molecular size and the density of the gas. We can relate ℓ to the number density n and the diameter d as follows.

Mean free path

Consider one molecule moving with speed v through a region of stationary molecules of number density n (Figure 2-17). It will collide with another molecule if the centers are a distance $2r$, or d, apart. In time t the molecule moves a distance vt and collides with every molecule in the cylindrical volume $\pi d^2 vt$. The number of molecules in this volume is $n\pi d^2 vt$. (After each collision, the direction of the molecule changes; thus the path is really a zigzag one.) The total path length divided by the number of collisions is the mean free path:[2]

$$\ell \approx \frac{vt}{n\pi d^2 vt} = \frac{1}{n\pi d^2} \qquad 2\text{-}39$$

The quantity πd^2 is the effective area presented by one molecule of diameter d to another of the same size. This area is called the *collision cross section*, σ. If the molecules are of different size the collision cross section would be $\pi(r_1 + r_2)^2$, where r_1 and r_2 are the radii. In terms of the collision cross section,

Cross section

$$\ell = \frac{1}{n\sigma} \qquad 2\text{-}40$$

Let us now examine the phenomenon of viscosity. Consider a gas between two plates; the upper plate is pulled to the right

[1] The quantity d can now be accurately determined from x-ray diffraction measurements.

[2] Of course, the other molecules are not stationary. If we assume a Maxwell-Boltzmann distribution of velocities, the calculation is considerably more involved, with the result $\ell = 0.707/n\pi d^2$. For our purposes, we may neglect this and other corrections.
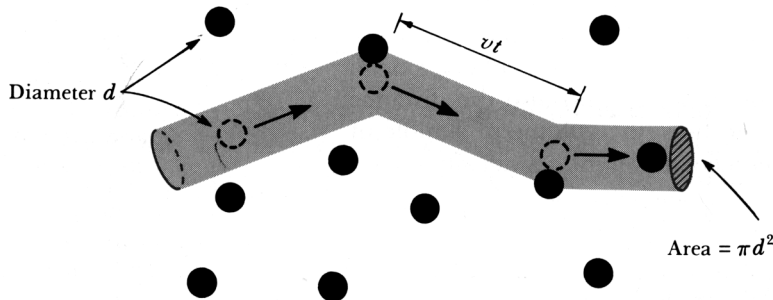

Diameter d

vt

Area $= \pi d^2$

Figure 2-17
Model of a molecule moving in a gas. In time t the molecule with diameter d will collide with any similar molecule whose center is in a cylinder of volume $\pi d^2 vt$, where v is the molecular speed. In this picture all the molecules but one are assumed to be at rest.

with a speed u_0, while the bottom plate is held stationary. It is found that the gas has a net flow to the right, the speed varying with height z from the bottom plate. Essentially, the gas near the top tends to follow the upper plate with speed u_0, whereas that near the bottom tends to remain at rest. The flow velocity $u(z)$ is superimposed on the random, or thermal, velocity of the molecules. A force is necessary to keep the upper plate moving with constant speed and to hold the bottom plate at rest. Evidently there is a drag force, called a *viscous force,* exerted by the gas. The coefficient of viscosity is defined as follows.

Consider a hypothetical plane surface of area A parallel to the plates at a height z_1 above the lower plate, as in Figure 2-18. The gas above this surface exerts a force to the right on the gas below, and of course the gas below exerts an equal but opposite force to the left on the gas above. This force is tangential to the plane and proportional to the area A and to the velocity gradient du/dz. The force per unit area is called the *viscous stress, S.*

$$S = \eta \frac{du}{dz} \qquad \text{2-41}$$

This equation defines the coefficient of viscosity, η.

We shall consider qualitatively the kinetic-theory explanation of the force exerted on the gas below z_1 (shaded region in Figure 2-18). In this theory we consider each molecule to have an average "drift" velocity u to the right (superimposed on its thermal velocity) which is characteristic of the gas velocity u at the point of the last collision of the molecule. Molecules crossing the plane from above bring in x momentum mu_1 and those crossing from below carry away x momentum mu_2. Since the average momentum of those from above is greater than that from below, there is a net transfer of momentum across the plane. The net transfer of momentum across the plane per second per unit area equals the stress exerted on the lower gas. From this model we expect the net rate of transfer of momentum to be proportional to the rate at which molecules cross the plane, which is proportional to the number density n and the mean speed $\bar{v}$. It should also be proportional to the mean free path. For example, for molecules from above, the greater the distance to its last collision, the greater its average momentum mu. A detailed calculation gives for the viscous stress

$$S = \frac{1}{3} n\bar{v}\ell \frac{d(mu)}{dz} = \frac{1}{3} n\bar{v}\ell m \frac{du}{dz} \qquad \text{2-42}$$
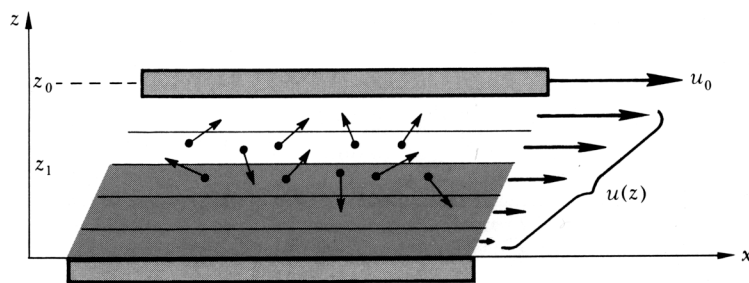

Figure 2-18
Viscous flow of a gas. Because of the relative motion of the plates, the gas between them has a flow velocity that varies from 0 at the bottom plate to u_0 at the top plate. Momentum is transferred from one layer to the other by molecules that cross the boundary.

so the coefficient of viscosity is

$$\eta = \tfrac{1}{3}n\bar{v}\ell m \qquad\qquad 2\text{-}43$$

where m is the mass of the molecule. Substituting $\ell = 1/n\pi d^2$ from Equation 2-39 we have

$$\eta = \frac{1}{3}\frac{m\bar{v}}{\pi d^2} \qquad\qquad 2\text{-}44$$

Note that this expression is independent of density. This surprising result was first pointed out by Maxwell and verified by him experimentally over a wide range of densities. (At extremely low densities, this theory breaks down when the mean free path becomes of the order of the size of the container.) Equation 2-44 also implies that η depends on temperature only through $\bar{v}$, which increases as $T^{1/2}$. The experimental results, so easily understood by a simple kinetic-theory model, that the viscosity of gas is independent of density (and therefore independent of pressure at constant T) and increases with temperature (rather than decreasing, as is the case for liquids), were an important factor in the general acceptance of the kinetic theory in the nineteenth century.

If we write $m = \mathcal{M}/N_A$ for the mass of a molecule, and use the result $\bar{v} = (8RT/\pi\mathcal{M})^{1/2}$ from the Maxwell distribution, we can write for the coefficient of viscosity

$$\eta = \frac{\mathcal{M}}{3\pi N_A d^2}\left(\frac{8RT}{\pi\mathcal{M}}\right)^{1/2} \qquad\qquad 2\text{-}45$$

Loschmidt in 1885 used this result along with Equation 2-38 and measurements of the viscosities of gases and of the densities of solids to obtain the first reliable estimate of N_A and d. (The number N_A is often called "Loschmidt's number" in Europe.) He obtained $d \approx 10^{-10}$ m and $N_A \approx 10 \times 10^{23}$. This is reasonably close to the modern value $N_A = 6.022 \times 10^{23}$.

Table 2-3
Some values of molecular mean free paths, and molecular radii computed from viscosity measurements

Gas	$\eta(15°C)$ (newton-sec/m)	$\ell(15°C, 1\ \text{atm})$ (Å)	r (Å)
He	1.94×10^{-6}	1860	1.09
Ne	31.0	1320	1.30
Ar	22.0	666	1.82
H_2	8.71	1180	1.37
N_2	17.3	628	1.88
O_2	20.0	679	1.80
CO_2	14.5	419	2.30
NH_3	9.7	451	2.22
CH_4	10.8	516	2.07

From J. F. Lee, F. W. Sears, and D. L. Turcotte, *Statistical Thermodynamics*, Reading, Mass.: Addison-Wesley Publishing Company, Inc., 1963.

If we use the modern value of N_A, we can compute the molecular radius[1] from viscosity measurements using Equation 2-44 and the mean free path using Equation 2-39. Table 2-3 lists the results for several gases. From this table we see that molecular radii are about 1 or 2 Å (1 Å = 10^{-10} m), and at normal densities the mean free paths are several hundred times this.

Example 2-7 What is the order of magnitude of the time between collisions for N_A molecules in a gas at standard conditions? Let τ be the time between collisions. The average distance traveled by a molecule in this time is $\ell = v\tau$. Using $\ell \approx 600$ Å = 600×10^{-10} m from Table 2-3, and $v \approx 500$ m/sec from the calculation of v_{rms} in Example 2-1, we have

$$\tau = \frac{\ell}{v} \approx \frac{600 \times 10^{-10} \text{ m}}{500 \text{ m/sec}} \approx 10^{-10} \text{ sec}$$

The collision frequency is of the order of $1/\tau \approx 10^{10}$ collisions per second.

The treatment of heat conduction is similar to that of viscosity except that we consider the transport of molecular energy rather than of momentum. Consider the plates shown in Figure 2-18 to be at rest and at different temperatures. If ΔQ is the heat conducted across area A in time Δt, it is found that ΔQ is proportional to A, Δt, and the temperature gradient dT/dz. The coefficient of heat conduction, K, is defined by

$$\frac{\Delta Q}{A \, \Delta t} = K \frac{dT}{dz} \qquad \text{2-46}$$

We can use the same analysis that we used for viscosity if we replace the momentum mu by the average energy per molecule $\bar{E}$. Molecules crossing the plane from above transport more energy than those from below if the upper plate is at a higher temperature. Equation 2-42 then becomes for the case of heat conduction

$$\frac{\Delta Q}{A \, \Delta t} = \frac{1}{3} n\bar{v}\ell \frac{d\bar{E}}{dz} \qquad \text{2-47}$$

If we multiply the average energy per molecule by N_A, we obtain the energy per mole. Thus $\bar{E}N_A = C_v T$ and

$$\frac{\Delta Q}{A \, \Delta t} = \frac{1}{3} \frac{n\bar{v}\ell C_v}{N_A} \frac{dT}{dz} \qquad \text{2-48}$$

The coefficient of heat conduction is therefore

$$K = \frac{1}{3} \frac{n\bar{v}\ell C_v}{N_A} \qquad \text{2-49}$$

---

[1] It should be pointed out that we are not implying that molecules are spherical. It is the collision cross section that is determined from Equation 2-44. By radius, we mean the quantity related to the collision cross section by $\sigma = \pi d^2 = 4\pi r^2$.

Comparing with Equation 2-43 for η, we have

$$\frac{K}{\eta} = \frac{C_v}{N_A m} = \frac{C_v}{\mathcal{M}}$$

or

$$\frac{K\mathcal{M}}{\eta C_v} = 1 \qquad\qquad\qquad 2\text{-}50$$

The experimental determination of this ratio yields numbers between about 1.5 and 2.5 for most gases. The agreement within a factor of 3 of theory and experiment is another success of the kinetic model, for there is little reason from the macroscopic point of view to suspect heat conduction and viscosity to be simply related. The discrepancy is due to the oversimplification of the theory.

The coefficient of self-diffusion[1] is defined by

$$\frac{\Delta n}{A\,\Delta t} = D\,\frac{dn}{dz} \qquad\qquad\qquad 2\text{-}51$$

where Δn is the number of molecules crossing the plane of area A in time Δt. In this case it is the number of molecules that varies, leading to the transport of molecules. The simple theory gives

$$D = \tfrac{1}{3}\ell v \qquad\qquad\qquad 2\text{-}52$$

We should note that the numerical factors such as the factor $\tfrac{1}{3}$ in the result for the viscosity, heat conduction, and diffusion coefficients come from the simplest kinetic-theory calculations and are often modified by more detailed treatment. In the case of mutual diffusion, or diffusion of large objects through a gas or liquid, this simple mean-free-path treatment is not even an adequate starting point.

Question

8. If we double the number density n, twice as many molecules cross a given area per second. Does this double the rate of heat conduction? Why or why not?

[1] Self-diffusion is the diffusion of molecules into others of the same kind because of a density difference. Restricting the problem to like molecules simplifies the calculations because all the collision cross sections are the same. Experimentally, self-diffusion can be observed by using radioactive-tracer methods to tag certain molecules without changing their collision cross sections.

Optional

2-7   Brownian Motion and the Random-Walk Problem

In 1828 a botanist, Robert Brown, observed an irregular zigzag motion of pollen grains suspended in water. After much experimentation, he concluded that the cause of the motion was not organic, for he observed it in a wide variety of materials. This motion, now called *Brownian motion,* went unexplained for

nearly half a century, until the kinetic theory was developed. (Many thought that the motion was due to convection currents or vibrations transmitted through the liquid.) The true cause of Brownian motion, the irregular bombardment of the grains by the molecules of the suspending fluid, was finally understood at the beginning of the twentieth century. The first complete theory was given by Einstein in 1905. In 1908, Jean Perrin made exhaustive quantitative observations of the paths of many suspended particles of different sizes. From these observations, which were in good agreement with Einstein's theory, Perrin calculated Avogadro's number. Perrin's monumental work finally laid aside all doubts as to the validity of the kinetic theory of matter.

The Brownian motion of suspended particles is similar to the diffusion of molecules, except that the particles are much larger than the molecules. We can get some insight into a number of statistical processes, such as diffusion, Brownian motion, and the combination of errors, by considering a simple statistical problem called the *random-walk problem*. In the one-dimensional version of this problem, a man flips a coin and takes one step forward if the result is heads or one step backward if the result is tails. We are interested in determining how far the man gets from the starting point on the average. Suppose the man takes N steps, each of size unity. After N steps, the man has a displacement x_N from the origin. Since the probabilities of a forward step and a backward step are equal, the average displacement $\bar{x}_N$ will be zero. We shall now show that the rms distance from the origin after N unit steps equals $N^{1/2}$.

After one step the displacement is

$$x_1 = \pm 1$$

Squaring, we obtain $x_1{}^2 = +1$. After two steps, the displacement is

$$x_2 = x_1 \pm 1$$

Squaring, we obtain

$$x_2{}^2 = x_1{}^2 \pm 2x_1 + 1$$

When we take the average, the middle term drops out because $(x_1)_{\text{av}} = 0$. Then

$$(x_2{}^2)_{\text{av}} = (x_1{}^2)_{\text{av}} + 1 = 2$$

If we continue, we find that $(x_3{}^2)_{\text{av}} = (x_2{}^2)_{\text{av}} + 1 = 3$, and so on. Therefore, after N steps we have

$$(x_N{}^2)_{\text{av}} = N \qquad \qquad 2\text{-}53$$

If the step size is ℓ, the above argument gives

$$(x_N{}^2)_{\text{av}} = N\ell^2 \qquad \qquad 2\text{-}54$$

and

$$x_{\text{rms}} = N^{1/2}\ell \qquad \qquad 2\text{-}55$$

This result can be applied to error theory. The probable resulting error due to the combination of a large number, N, of small random errors of size ℓ is given by Equation 2-55. We can also relate this to the problem of self-diffusion by taking N to be the number of collisions made and ℓ to be the mean free path. If the mean speed of the molecules is $\bar{v}$, the number of collisions made in time t is $N = \bar{v}t/\ell$; so

$$(x^2)_{av} = \bar{v}\ell t$$

Thus the mean-square distance is proportional to the time.

Since Brownian motion of a suspended particle is the result of many small irregular movements due to random molecular bombardment, the mean-square distance for this motion is also proportional to the number of collisions made by the particle and therefore to the time.

In 1905 Einstein applied kinetic theory to the calculation of the rms displacement of a large sphere of radius a undergoing Brownian motion in a gas of viscosity η. His result was

$$(x^2)_{av} = \frac{RT}{3\pi\eta a N_A} t \qquad\qquad 2\text{-}56$$
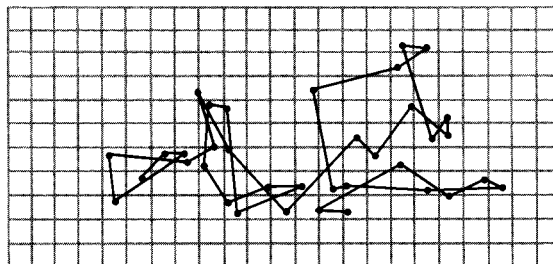
Einstein pointed out that this result could be used to obtain Avogadro's number.

In 1908 Jean Perrin made a series of remarkable measurements of Avogadro's number. In order to use Equation 2-56, he needed a large number of small but visible particles of equal radius a. He found that he could make emulsions of gamboge (prepared from a dried vegetable latex) and mastic which, after several months of separation by centrifuging, contained grains of nearly equal size.[1] In one series of measurements, he watched individual particles as they moved about and recorded their positions at equal time intervals. He verified that the mean-square displacement was proportional to the time and determined N_A. Figure 2-19 is a diagram of the horizontal projections of the positions of a grain with radius 0.53×10^{-6} m observed at intervals of 30 sec. The following quotation is taken from Perrin's Nobel Prize address in 1926.

[1] An interesting account of Perrin's experiments can be found in Jean Perrin, *Atoms*, New York: D. Van Nostrand Company, Inc., 1923.

Figure 2-19
Brownian motion. Points indicate successive positions of a particle observed at 30-sec intervals. The lines between the points are added to indicate the sequence of positions; the particle does not move in straight lines between observations because it is struck by millions of molecules each second. (*From Jean Perrin*, Atoms, *trans. D. Hammick, New York: D. Van Nostrand Company, Inc., 1923.*)

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Wide World Photos

Jean-Baptiste Perrin.

Figure 2-20
Equilibrium height distribution of particles in a gravitational field. The distribution is the same as that given by the law of atmospheres, $n(z) = n_0 e^{-mgz/kT}$. (*This computer-generated plot courtesy of Paul Doherty, Oakland University.*)

These theories can be judged by experiment if we know how to *prepare spherules of a measurable radius.* I was, therefore, in a position to attempt this check as soon as I knew, thanks to Langevin, of the work of Einstein.

I must say that, right at the beginning, Einstein and Smoluchovski had pointed out that the order of magnitude of the Brownian movement seemed to correspond to their predictions. And this approximate agreement gave already much force to the kinetic theory of the phenomenon, at least in broad outline.

It was impossible to say anything more precise so long as spherules of known size had not been prepared. Having such grains, I was able to check Einstein's formulae by seeing whether they led always to the same value for Avogadro's number and whether it was appreciably equal to the value already found.

This is obtained for the displacements by noting on the camera lucida (magnification known) the horizontal projections of the same grain at the beginning and at the end of an interval of time equal to the duration chosen, in such a manner as to measure a large number of displacements, for example, in one minute.

In several series of measurements I varied, with the aid of several collaborators, the size of the grains (in the ratio of 1 to 70,000) as well as the nature of the liquid (water, solutions of sugar or urea, glycerol) and its viscosity (in the ratio of 1 to 125). They gave values between 55×10^{22} and 72×10^{22}, with differences which could be explained by experimental errors. The agreement is such that it is impossible to doubt the correctness of the kinetic theory of the translational Brownian movement.[1]

In another series of measurements, Perrin determined N_A by measuring the density of particles suspended in an emulsion at different heights. If a fluid is in a uniform gravitational field in the negative z direction, the number density is given by the law of atmospheres (Equation 2-37)

$$n(z) = n_0 e^{-mgz/kT} = n_0 e^{-Mgz/RT} \qquad 2\text{-}57$$

where n_0 is the number at $z = 0$. If a visible particle is suspended in the fluid, its tendency to sink because of gravity is counteracted by a tendency to rise because it is struck by more molecules from below than from above (due to the greater density below, as shown by Equation 2-57). The equilibrium distribution of the visible particles is given by Equation 2-57 with $M = N_A m$, where m is the mass of the particle (Figure 2-20). Thus N_A can be determined by measuring the mass of the particles and the number versus height.

Perrin also measured the rotation of particles in a fluid due to bombardment by molecules, and calculated N_A from the theory of rotational Brownian motion given by Einstein.

[1] From *Nobel Prize Lectures: Physics,* Amsterdam and New York: Elsevier Publishing Company, 1964.

Summary

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

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

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

$$\int f(x)\,dx = 1$$

The Maxwell-Boltzmann velocity distribution is

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

and the speed distribution is

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

The Maxwell-Boltzmann energy distribution is

$$F(E) = CE^{1/2} e^{-E/kT}$$

where C is determined by normalization.

The mean translational kinetic energy of gas molecules is $\frac{3}{2}kT$, independent of any characteristics of the molecules. This is an example of the equipartition theorem: there is a mean energy of $\frac{1}{2}kT$ associated with each squared coordinate or momentum in the expression for the energy of a molecule. Molecular speeds are of the order of magnitude of the speed of sound.

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

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