# 43

# Diffusion



## 43–1 Collisions between molecules

We have considered so far only the molecular motions in a gas which is in thermal equilibrium. We want now to discuss what happens when things are near, but not exactly in, equilibrium. In a situation far from equilibrium, things are extremely complicated, but in a situation very close to equilibrium we can easily work out what happens. To see what happens, we must, however, return to the kinetic theory. Statistical mechanics and thermodynamics deal with the equilibrium situation, but away from equilibrium we can only analyze what occurs atom by atom, so to speak.

As a simple example of a nonequilibrium circumstance, we shall consider the diffusion of ions in a gas. Suppose that in a gas there is a relatively small concentration of ions—electrically charged molecules. If we put an electric field on the gas, then each ion will have a force on it which is different from the forces on the neutral molecules of the gas. If there were no other molecules present, an ion would have a constant acceleration until it reached the wall of the container. But because of the presence of the other molecules, it cannot do that; its velocity increases only until it collides with a molecule and loses its momentum. It starts again to pick up more speed, but then it loses its momentum again. The net effect is that an ion works its way along an erratic path, but with a net motion in the direction of the electric force. We shall see that the ion has an average "drift" with a mean speed which is proportional to the electric field—the stronger the field, the faster it goes. While the field is on, and while the ion is moving along, it is, of course, *not* in thermal equilibrium, it is trying to get to equilibrium, which is to be sitting at the end of the container. By means of the kinetic theory we can compute the drift velocity.

It turns out that with our present mathematical abilities we cannot really compute *precisely* what will happen, but we can obtain approximate results which exhibit all the essential features. We can find out how things will vary with pressure, with temperature, and so on, but it will not be possible to get precisely the correct numerical factors in front of all the terms. We shall, therefore, in our derivations, not worry about the precise value of numerical factors. They can be obtained only by a very much more sophisticated mathematical treatment.

Before we consider what happens in nonequilibrium situations, we shall need to look a little closer at what goes on in a gas in thermal equilibrium. We shall need to know, for example, what the average time between successive collisions of a molecule is.

Any molecule experiences a sequence of collisions with other molecules—in a random way, of course. A particular molecule will, in a long period of time $T$, have a certain number, $N$, of hits. If we double the length of time, there will be twice as many hits. So the number of collisions is proportional to the time $T$. We would like to write it this way:

$$N = T/\tau \tag{43.1}$$

We have written the constant of proportionality as $1/\tau$, where $\tau$ will have the dimensions of a time. The constant $\tau$ is the average time between collisions. Suppose, for example, that in an hour there are 60 collisions; then $\tau$ is one minute. We would say that $\tau$ (one minute) is the *average time* between the collisions.

We may often wish to ask the following question: "What is the *chance* that a molecule will experience a collision during the next *small interval* of time $dt$?" The answer, we may intuitively understand, is $dt/\tau$. But let us try to make a more

convincing argument. Suppose that there were a very large number $N$ of molecules. How many will have collisions in the next interval of time $dt$? If there is equilibrium, nothing is changing *on the average* with time. So $N$ molecules waiting the time $dt$ will have the same number of collisions as *one* molecule waiting for the time $N\,dt$. That number we know is $N\,dt/\tau$. So the number of hits of $N$ molecules is $N\,dt/\tau$ in a time $dt$, and the chance, or probability, of a hit for any one molecule is just $1/N$ as large, or $(1/N)(N\,dt/\tau) = dt/\tau$, as we guessed above. That is to say, the fraction of the molecules which will suffer a collision in the time $dt$ is $dt/\tau$. To take an example, if $\tau$ is one minute, then in one second the fraction of particles which will suffer collisions is 1/60. What this means, of course, is that 1/60 of the molecules happen to be close enough to what they are going to hit next that *their* collisions will occur in the next minute.

When we say that $\tau$, the mean time between collisions, is one minute, we do not mean that all the collisions will occur at times separated by exactly one minute. A particular particle does not have a collision, wait one minute, and then have another collision. The times between successive collisions are quite variable. We will not need it for our later work here, but we may make a small diversion to answer the question: "What *are* the times between collisions?" We know that for the case above, the *average* time is one minute, but we might like to know, for example, what is the chance that we get no collision for *two* minutes?

We shall find the answer to the general question: "What is the probability that a molecule will go for a time $t$ without having a collision?" At some arbitrary instant—that we call $t = 0$—we begin to watch a particular molecule. What is the chance that it gets by until $t$ without colliding with another molecule? To compute the probability, we observe what is happening to all $N_0$ molecules in a container. After we have waited a time $t$, some of them will have had collisions. We let $N(t)$ be the number that have *not* had collisions up to the time $t$. $N(t)$ is, of course, less than $N_0$. We can find $N(t)$ because we know how it changes with time. If we know that $N(t)$ molecules have got by until $t$, then $N(t + dt)$, the number which get by until $t + dt$, is *less* than $N(t)$ by the number that have collisions in $dt$. The number that collide in $dt$ we have written above in terms of the mean time $\tau$ as $dN = N(t)\,dt/\tau$. We have the equation

$$N(t + dt) = N(t) - N(t)\frac{dt}{\tau}. \tag{43.2}$$

The quantity on the left-hand side, $N(t + dt)$, can be written, according to the definitions of calculus, as $N(t) + (dN/dt)\,dt$. Making this substitution, Eq. (43.2) yields

$$\frac{dN(t)}{dt} = -\frac{N(t)}{\tau}. \tag{43.3}$$

The number that are being lost in the interval $dt$ is proportional to the number that are present, and inversely proportional to the mean life $\tau$. Equation (43.3) is easily integrated if we rewrite it as

$$\frac{dN(t)}{N(t)} = -\frac{dt}{\tau}. \tag{43.4}$$

Each side is a perfect differential, so the integral is

$$\ln N(t) = -t/\tau + (\text{a constant}), \tag{43.5}$$

which says the same thing as

$$N(t) = (\text{constant})e^{-t/\tau}. \tag{43.6}$$

We know that the constant must be just $N_0$, the total number of molecules present, since all of them start at $t = 0$ to wait for their "next" collision. We can write our result as

$$N(t) = N_0 e^{-t/\tau}. \tag{43.7}$$

If we wish the *probability* of no collision, $P(t)$, we can get it by dividing $N(t)$ by $N_0$, so

$$P(t) = e^{-t/\tau}. \tag{43.8}$$

Our result is: the probability that a particular molecule survives a time $t$ without a collision is $e^{-t/\tau}$, where $\tau$ is the mean time between collisions. The probability starts out at 1 (or certainty) for $t = 0$, and gets less as $t$ gets bigger and bigger. The probability that the molecule avoids a collision for a time equal to $\tau$ is $e^{-1} = 0.37\ldots$ The chance is less than one-half that it will have a greater than average time between collisions. That is all right, because there are enough molecules which go collision-free for times much *longer* than the mean time before colliding, so that the average time can still be $\tau$.

We originally defined $\tau$ as the average time *between* collisions. The result we have obtained in Eq. (43.7) also says that the mean time from an *arbitrary* starting instant to the *next* collision is *also* $\tau$. We can demonstrate this somewhat surprising fact in the following way. The number of molecules which experience their *next* collision in the interval $dt$ at the time $t$ after an arbitrarily chosen starting time is $N(t)\,dt/\tau$. Their "time until the next collision" is, of course, just $t$. The "average time until the next collision" is obtained in the usual way:

$$\text{Average time until the next collision} = \frac{1}{N_0}\int_0^\infty t\,\frac{N(t)\,dt}{\tau}.$$

Using $N(t)$ obtained in (43.7) and evaluating the integral, we find indeed that $\tau$ is the average time from *any* instant until the next collision.

### 43–2 The mean free path

Another way of describing the molecular collisions is to talk not about the *time* between collisions, but about *how far* the particle moves between collisions. If we say that the average time between collisions is $\tau$, and that the molecules have a mean velocity $v$, we can expect that the average *distance* between collisions, which we shall call $l$, is just the product of $\tau$ and $v$. This distance between collisions is usually called the *mean free path:*

$$\text{Mean free path } l = \tau v. \tag{43.9}$$

In this chapter we shall be a little careless about *what kind of average* we mean in any particular case. The various possible averages—the mean, the root-mean-square, etc.—are all nearly equal and differ by factors which are near to one. Since a detailed analysis is required to obtain the correct numerical factors anyway, we need not worry about which average is required at any particular point. We may also warn the reader that the algebraic symbols we are using for some of the physical quantities (e.g., $l$ for the mean free path) do not follow a generally accepted convention, mainly because there is no general agreement.

Just as the chance that a molecule will have a collision in a short time $dt$ is equal to $dt/\tau$, the chance that it will have a collision in going a distance $dx$ is $dx/l$. Following the same line of argument used above, the reader can show that the probability that a molecule will go at least the distance $x$ before having its next collision is $e^{-x/l}$.

The average distance a molecule goes before colliding with another molecule—the mean free path $l$—will depend on how many molecules there are around and on the "size" of the molecules, i.e., how big a target they represent. The effective "size" of a target in a collision we usually describe by a "collision cross section," the same idea that is used in nuclear physics, or in light-scattering problems.

Consider a moving particle which travels a distance $dx$ through a gas which has $n_0$ scatterers (molecules) per unit volume (Fig. 43–1). If we look at each unit of area perpendicular to the direction of motion of our selected particle, we will find there $n_0\,dx$ molecules. If each one presents an effective collision area or, as it is usually called, "collision cross section," $\sigma_c$, then the total area covered by the scatterers is $\sigma_c n_0\,dx$.

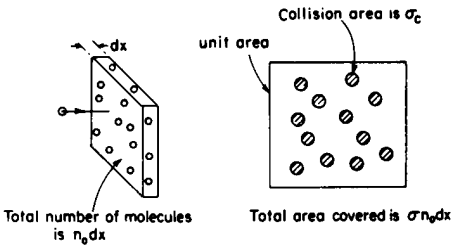


Fig. 43–1. Collision cross section.

By "collision cross section" we mean the area within which the center of our particle must be located if it is to collide with a particular molecule. If molecules were little spheres (a classical picture) we would expect that $\sigma_c = \pi(r_1 + r_2)^2$, where $r_1$ and $r_2$ are the radii of the two colliding objects. The chance that our particle will have a collision is the ratio of the area covered by scattering molecules to the total area, which we have taken to be one. So the probability of a collision in going a distance $dx$ is just $\sigma_c n_0\, dx$:

$$\text{Chance of a collision in } dx = \sigma_c n_0\, dx. \tag{43.10}$$

We have seen above that the chance of a collision in $dx$ can also be written in terms of the mean free path $l$ as $dx/l$. Comparing this with (43.10), we can relate the mean free path to the collision cross section:

$$\frac{1}{l} = \sigma_c n_0, \tag{43.11}$$

which is easier to remember if we write it as

$$\sigma_c n_0 l = 1. \tag{43.12}$$

This formula can be thought of as saying that there should be one collision, on the average, when the particle goes through a distance $l$ in which the scattering molecules *could* just cover the total area. In a cylindrical volume of length $l$ and a base of unit area, there are $n_0 l$ scatterers; if each one has an area $\sigma_c$ the total area covered is $n_0 l \sigma_c$, which is just one unit of area. The whole area is *not* covered, of course, because some molecules are partly hidden behind others. That is why some molecules go farther than $l$ before having a collision. It is only *on the average* that the molecules have a collision by the time they go the distance $l$. From measurements of the mean free path $l$ we can determine the scattering cross section $\sigma_c$, and compare the result with calculations based on a detailed theory of atomic structure. But that is a different subject! So we return to the problem of nonequilibrium states.

### 43–3 The drift speed

We want to describe what happens to a molecule, or several molecules, which are different in some way from the large majority of the molecules in a gas. We shall refer to the "majority" molecules as the "background" molecules, and we shall call the molecules which are different from the background molecules "special" molecules or, for short, the *S*-molecules. A molecule could be special for any number of reasons: It might be heavier than the background molecules. It might be a different chemical. It might have an electric charge—i.e., be an ion in a background of uncharged molecules. Because of their different masses or charges the *S*-molecules may have forces on them which are different from the forces on the background molecules. By considering what happens to these *S*-molecules we can understand the basic effects which come into play in a similar way in many different phenomena. To list a few: the diffusion of gases, electric currents in batteries, sedimentation, centrifugal separation, etc.

We begin by concentrating on the basic process: an *S*-molecule in a background gas is acted on by some specific force **F** (which might be, e.g., gravitational or electrical) and *in addition* by the not-so-specific forces due to collisions with the background molecules. We would like to describe the *general* behavior of the *S*-molecule. What happens to it, *in detail*, is that it darts around hither and yon as it collides over and over again with other molecules. But if we watch it carefully we see that it does make some net progress in the direction of the force **F**. We say that there is a *drift* superposed on its random motion. We would like to know what the speed of its drift is—its *drift velocity*—due to the force **F**.

If we start to observe an *S*-molecule at some instant we may expect that it is somewhere between two collisions. In addition to the velocity it was left with after its last collision it is picking up some velocity component due to the force **F**. In a

short time (on the average, in a time $\tau$) it will experience a collision and start out on a new piece of its trajectory. It will have a new starting velocity, but the same acceleration from **F**.

To keep things simple for the moment, we shall suppose that after each collision our *S*-molecule gets a completely "fresh" start. That is, that it keeps no remembrance of its past acceleration by **F**. This might be a reasonable assumption if our *S*-molecule were much lighter than the background molecules, but it is certainly not valid in general. We shall discuss later an improved assumption.

For the moment, then, our assumption is that the *S*-molecule leaves each collision with a velocity which may be in any direction with equal likelihood. The starting velocity will take it equally in all directions and will not contribute to any net motion, so we shall not worry further about its initial velocity after a collision. In addition to its random motion, each *S*-molecule will have, at any moment, an additional velocity in the direction of the force **F**, which it has picked up *since* its last collision. What is the *average* value of *this* part of the velocity? It is just the acceleration $\mathbf{F}/m$ (where $m$ is the mass of the *S*-molecule) times the *average* time *since* the last collision. Now the average time *since* the *last* collision must be the same as the average time *until* the *next* collision, which we have called $\tau$, above. The *average* velocity from **F**, of course, is just what is called the drift velocity, so we have the relation

$$v_{\text{drift}} = \frac{F\tau}{m}. \tag{43.13}$$

This basic relation is the heart of our subject. There may be some complication in determining what $\tau$ is, but the basic process is defined by Eq. (43.13).

You will notice that the drift velocity is *proportional* to the force. There is, unfortunately, no generally used name for the constant of proportionality. Different names have been used for each different kind of force. If in an electrical problem the force is written as the charge times the electric field, $\mathbf{F} = q\mathbf{E}$, then the constant of proportionality between the velocity and the electric field **E** is usually called the "mobility." In spite of the possibility of some confusion, *we* shall use the term *mobility* for the ratio of the drift velocity to the force for *any* force. We write

$$v_{\text{drift}} = \mu F \tag{43.14}$$

in general, and we shall call $\mu$ the mobility. We have from Eq. (43.13) that

$$\mu = \tau/m. \tag{43.15}$$

The mobility is proportional to the mean time between collisions (there are fewer collisions to slow it down) and inversely proportional to the mass (more inertia means less speed picked up between collisions).

To get the correct numerical coefficient in Eq. (43.13), which is correct as given, takes some care. Without intending to confuse, we should still point out that the arguments have a subtlety which can be appreciated only by a careful and detailed study. To illustrate that there are difficulties, in spite of appearances, we shall make over again the argument which led to Eq. (43.13) in a reasonable *but erroneous* way (and the way one will find in many textbooks!).

We might have said: The mean time between collisions is $\tau$. After a collision the particle starts out with a random velocity, but it picks up an additional velocity between collisions, which is equal to the acceleration times the time. Since it takes the time $\tau$ to arrive at the *next* collision it gets there with the velocity $(F/m)\tau$. At the beginning of the collision it had zero velocity. So between the two collisions it has, on the average, a velocity one-half of the final velocity, so the mean drift velocity is $\frac{1}{2}F\tau/m$. (Wrong!) This result is wrong and the result in Eq. (43.13) is right, although the arguments may sound equally satisfactory. The reason the second result is wrong is somewhat subtle, and has to do with the following: The argument is made as though all collisions were separated by the mean time $\tau$. The fact is that some times are shorter and others are longer than the mean. Short times occur *more often* but make *less* contribution to the drift velocity because they have less

chance "to really get going." If one takes proper account of the *distribution* of free times between collisions, one can show that there should not be the factor $\frac{1}{2}$ that was obtained from the second argument. The error was made in trying to relate by a simple argument the *average final* velocity to the average velocity itself. This relationship is not simple, so it is best to concentrate on what is wanted: the average velocity itself. The first argument we gave determines the average velocity directly—and correctly! But we can perhaps see now why we shall not in general try to get all of the correct numerical coefficients in our elementary derivations!

We return now to our simplifying assumption that each collision knocks out all memory of the past motion—that a fresh start is made after each collision. Suppose our $S$-molecule is a heavy object in a background of lighter molecules. Then our $S$-molecule will not lose its "forward" momentum in each collision. It would take several collisions before its motion was "randomized" again. We should assume, instead, that at each collision—in each time $\tau$ on the average —it loses a certain fraction of its momentum. We shall not work out the details, but just state that the result is equivalent to replacing $\tau$, the average collision time, by a new—and longer—$\tau$ which corresponds to the average "forgetting time," i.e., the average time to forget its forward momentum. With such an interpretation of $\tau$ we can use our formula (43.15) for situations which are not quite as simple as we first assumed.

### 43–4 Ionic conductivity

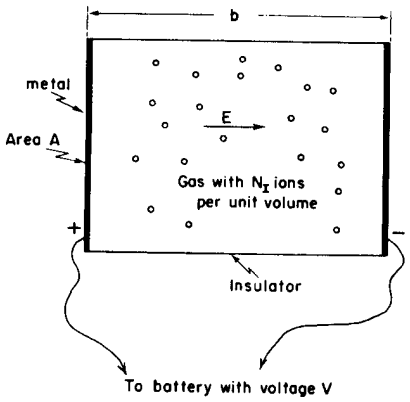


Fig. 43–2. Electric current from an ionized gas.

We now apply our results to a special case. Suppose we have a gas in a vessel in which there are also some ions—atoms or molecules with a net electric charge. We show the situation schematically in Fig. 43–2. If two opposite walls of the container are metallic plates, we can connect them to the terminals of a battery and thereby produce an electric field in the gas. The electric field will result in a force on the ions, so they will begin to drift toward one or the other of the plates. An electric current will be induced, and the gas with its ions will behave like a resistor. By computing the ion flow from the drift velocity we can compute the resistance. We ask, specifically: How does the flow of electric current depend on the voltage difference $V$ that we apply across the two plates?

We consider the case that our container is a rectangular box of length $b$ and cross-sectional area $A$ (Fig. 43–2). If the potential difference, or voltage, from one plate to the other is $V$, the electric field $E$ between the plates is $V/b$. (The electric potential is the work done in carrying a unit charge from one plate to the other. The force on a unit charge is $\mathbf{E}$. If $\mathbf{E}$ is the same everywhere between the plates, which is a good enough approximation for now, the work done on a unit charge is just $Eb$, so $V = Eb$.) The special force on an ion of the gas is $q\mathbf{E}$, where $q$ is the charge on the ion. The drift velocity of the ion is then $\mu$ times this force, or

$$v_{\text{drift}} = \mu F = \mu qE = \mu q \frac{V}{b}. \tag{43.16}$$

An electric current $I$ is the flow of charge in a unit time. The electric current to one of the plates is given by the total charge of the ions which arrive at the plate in a unit of time. If the ions drift toward the plate with the velocity $v_{\text{drift}}$, then those which are within a distance $(v_{\text{drift}} \cdot T)$ will arrive at the plate in the time $T$. If there are $n_i$ ions per unit volume, the number which reach the plate in the time $T$ is $(n_i \cdot A \cdot v_{\text{drift}} \cdot T)$. Each ion carries the charge $q$, so we have that

$$\text{Charge collected in } T = qn_iAv_{\text{drift}}T. \tag{43.17}$$

The current $I$ is the charge collected in $T$ divided by $T$, so

$$I = qn_iAv_{\text{drift}}. \tag{43.18}$$

Substituting $v_{\text{drift}}$ from (43.16), we have

$$I = \mu q^2 n_i \frac{A}{b} V. \tag{43.19}$$

We find that the current is proportional to the voltage, which is just the form of Ohm's law, and the resistance $R$ is the inverse of the proportionality constant:

$$\frac{1}{R} = \mu q^2 n_i \frac{A}{b}. \tag{43.20}$$

We have a relation between the resistance and the molecular properties $n_i$, $q$, and $\mu$, which depends in turn on $m$ and $\tau$. If we know $n_i$ and $q$ from atomic measurements, a measurement of $R$ could be used to determine $\mu$, and from $\mu$ also $\tau$.

### 43–5 Molecular diffusion

We turn now to a different kind of problem, and a different kind of analysis: the theory of diffusion. Suppose that we have a container of gas in thermal equilibrium, and that we introduce a small amount of a different kind of gas at some place in the container. We shall call the original gas the "background" gas and the new one the "special" gas. The special gas will start to spread out through the whole container, but it will spread slowly because of the presence of the background gas. This slow spreading-out process is called *diffusion*. The diffusion is controlled mainly by the molecules of the special gas getting knocked about by the molecules of the background gas. After a large number of collisions, the special molecules end up spread out more or less evenly throughout the whole volume. We must be careful *not* to confuse diffusion of a gas with the gross transport that may occur due to convection currents. Most commonly, the mixing of two gases occurs by a combination of convection and diffusion. We are interested now only in the case that there are *no "wind" currents*. The gas is spreading only by molecular motions, by diffusion. We wish to compute how fast diffusion takes place.

We now compute the *net flow* of molecules of the "special" gas due to the molecular motions. There will be a net flow only when there is some nonuniform distribution of the molecules, otherwise all of the molecular motions would average to give no net flow. Let us consider first the flow in the $x$-direction. To find the flow, we consider an imaginary plane surface perpendicular to the $x$-axis and count the number of special molecules that cross this plane. To obtain the net flow, we must count as positive those molecules which cross in the direction of positive $x$ and *subtract* from this number the number which cross in the negative $x$-direction. As we have seen many times, the number which cross a surface area in a time $\Delta T$ is given by the number which start the interval $\Delta T$ in a volume which extends the distance $v\,\Delta T$ from the plane. (Note that $v$, here, is the actual molecular velocity, not the drift velocity.)

We shall simplify our algebra by giving our surface one unit of area. Then the number of special molecules which pass from left to right (taking the $+x$-direction to the right) is $n_- v\,\Delta T$, where $n_-$ is the number of special molecules per unit volume to the left (within a factor of 2 or so, but we are ignoring such factors!). The number which cross from right to left is, similarly, $n_+ v\,\Delta T$, where $n_+$ is the number density of special molecules on the right-hand side of the plane. If we call the molecular current $J$, by which we mean the net flow of molecules per unit area per unit time, we have

$$J = \frac{n_- v\,\Delta T - n_+ v\,\Delta T}{\Delta T}, \tag{43.21}$$

or

$$J = (n_- - n_+)v. \tag{43.22}$$

What shall we use for $n_-$ and $n_+$? When we say "the density on the left," how *far* to the left do we mean? We should choose the density at the place from which the molecules started their "flight," because the number which *start* such

trips is determined by the number present at that place. So by $n_-$ we should mean the density a distance to the left equal to the mean free path $l$, and by $n_+$, the density at the distance $l$ to the right of our imaginary surface.

It is convenient to consider that the distribution of our special molecules in space is described by a continuous function of $x$, $y$, and $z$ which we shall call $n_a$. By $n_a(x, y, z)$ we mean the number density of special molecules in a small volume element centered on $(x, y, z)$. In terms of $n_a$ we can express the difference $(n_+ - n_-)$ as

$$(n_+ - n_-) = \frac{dn_a}{dx}\,\Delta x = \frac{dn_a}{dx}\cdot 2l. \tag{43.23}$$

Substituting this result in Eq. (43.22) and neglecting the factor of 2, we get

$$J_x = -lv\,\frac{dn_a}{dx}. \tag{43.24}$$

We have found that the flow of special molecules is proportional to the derivative of the density, or to what is sometimes called the "gradient" of the density.

It is clear that we have made several rough approximations. Besides various factors of two we have left out, we have used $v$ where we should have used $v_x$, and we have assumed that $n_+$ and $n_-$ refer to places at the perpendicular distance $l$ from our surface, whereas for those molecules which do not travel perpendicular to the surface element, $l$ should correspond to the *slant* distance from the surface. All of these refinements can be made; the result of a more careful analysis shows that the right-hand side of Eq. (43.24) should be multiplied by 1/3. So a better answer is

$$J_x = -\frac{lv}{3}\,\frac{dn_a}{dx}. \tag{43.25}$$

Similar equations can be written for the currents in the $y$- and $z$-directions.

The current $J_x$ and the density gradient $dn_a/dx$ can be measured by macroscopic observations. Their experimentally determined ratio is called the "diffusion coefficient," $D$. That is,

$$J_x = -D\,\frac{dn_a}{dx}. \tag{43.26}$$

We have been able to show that for a gas we expect

$$D = \tfrac{1}{3}lv. \tag{43.27}$$

So far in this chapter we have considered two distinct processes: *mobility*, the drift of molecules due to "outside" forces; and *diffusion*, the spreading determined only by the internal forces, the random collisions. There is, however, a relation between them, since they both depend basically on the thermal motions, and the mean free path $l$ appears in both calculations.

If, in Eq. (43.25), we substitute $l = v\tau$ and $\tau = \mu m$, we have

$$J_x = -\tfrac{1}{3}mv^2\mu\,\frac{dn_a}{dx}. \tag{43.28}$$

But $mv^2$ depends only on the temperature. We recall that

$$\tfrac{1}{2}mv^2 = \tfrac{3}{2}kT, \tag{43.29}$$

so

$$J_x = -\mu kT\,\frac{dn_a}{dx}. \tag{43.30}$$

We find that $D$, the *diffusion* coefficient, is just $kT$ times $\mu$, the *mobility* coefficient:

$$D = \mu kT. \tag{43.31}$$

And it turns out that the numerical coefficient in (43.31) is exactly right—no extra factors have to be thrown in to adjust for our rough assumptions. We can show,

in fact, that (43.31) must *always* be correct—even in complicated situations (for example, the case of a suspension in a liquid) where the details of our simple calculations would not apply at all.

To show that (43.31) must be correct in general, we shall derive it in a different way, using only our basic principles of statistical mechanics. Imagine a situation in which there is a gradient of "special" molecules, and we have a diffusion current proportional to the density gradient, according to Eq. (43.26). We now apply a force field in the $x$-direction, so that each special molecule feels the force $F$. According to the *definition* of the mobility $\mu$ there will be a drift velocity given by

$$v_{\text{drift}} = \mu F. \tag{43.32}$$

By our usual arguments, the *drift current* (the *net* number of molecules which pass a unit of area in a unit of time) will be

$$J_{\text{drift}} = n_a v_{\text{drift}}, \tag{43.33}$$

or

$$J_{\text{drift}} = n_a \mu F. \tag{43.34}$$

We now *adjust* the force $F$ so that the drift current due to $F$ just *balances* the diffusion, so that there is *no net flow* of our special molecules. We have $J_x + J_{\text{drift}} = 0$, or

$$D \frac{dn_a}{dx} = n_a \mu F. \tag{43.35}$$

Under the "balance" conditions we find a steady (with time) gradient of density given by

$$\frac{dn_a}{dx} = \frac{n_a \mu F}{D}. \tag{43.36}$$

But notice! We are describing an *equilibrium* condition, so our *equilibrium* laws of statistical mechanics apply. According to these laws the probability of finding a molecule at the coordinate $x$ is proportional to $e^{-U/kT}$, where $U$ is the potential energy. In terms of the number density $n_a$, this means that

$$n_a = n_0 e^{-U/kT}. \tag{43.37}$$

If we differentiate (43.37) with respect to $x$, we find

$$\frac{dn_a}{dx} = -n_0 e^{-U/kT} \cdot \frac{1}{kT} \frac{dU}{dx}, \tag{43.38}$$

or

$$\frac{dn_a}{dx} = -\frac{n_a}{kT} \frac{dU}{dx}. \tag{43.39}$$

In our situation, since the force $F$ is in the $x$-direction, the potential energy $U$ is just $-Fx$, and $-dU/dx = F$. Equation (43.39) then gives

$$\frac{dn_a}{dx} = \frac{n_a F}{kT}. \tag{43.40}$$

[This is just exactly Eq. (40.2), from which we deduced $e^{-U/kT}$ in the first place, so we have come in a circle]. Comparing (43.40) with (43.36), we get exactly Eq. (43.31). We have shown that Eq. (43.31), which gives the diffusion current in terms of the mobility, has the correct coefficient and is very generally true. Mobility and diffusion are intimately connected. This relation was first deduced by Einstein.

### 43–6 Thermal conductivity

The methods of the kinetic theory that we have been using above can be used also to compute the *thermal conductivity* of a gas. If the gas at the top of a container is hotter than the gas at the bottom, heat will flow from the top to the bottom. (We think of the top being hotter because otherwise convection currents would be

set up and the problem would no longer be one of heat *conduction*.) The transfer of heat from the hotter gas to the colder gas is by the diffusion of the "hot" molecules—those with more energy—downward and the diffusion of the "cold" molecules upward. To compute the flow of thermal energy we can ask about the energy carried downward across an element of area by the downward-moving molecules, and about the energy carried upward across the surface by the upward-moving molecules. The difference will give us the net downward flow of energy.

The thermal conductivity $\kappa$ is defined as the ratio of the rate at which thermal energy is carried across a unit surface area, to the temperature gradient:

$$\frac{1}{A}\frac{dQ}{dt} = -\kappa\frac{dT}{dz}. \tag{43.41}$$

Since the details of the calculations are quite similar to those we have done above in considering the flow of electric current in an ionized gas, we shall leave it as an exercise for the reader to show that

$$\kappa = \frac{knlv}{\gamma - 1}, \tag{43.42}$$

where $(\gamma - 1)kT$ is the average energy of a molecule at the temperature $T$.

If we use our relation $nl\sigma_c = 1$, the heat conductivity can be written as

$$\kappa = \frac{1}{\gamma - 1}\frac{kv}{\sigma_c}. \tag{43.43}$$

We have a rather surprising result. We know that the average velocity of gas molecules depends on the temperature but *not on the density*. We expect $\sigma_c$ to depend only on the *size* of the molecules. So our simple result says that the thermal conductivity $\kappa$ (and therefore the *rate* of flow of heat in any particular circumstance) is independent of the *density* of the gas! The change in the number of "carriers" of energy with a change in density is just compensated by the larger distance the "carriers" can go between collisions.

One may ask: "Is the heat flow independent of the gas density in the limit as the density goes to zero? When there is no gas at all?" Certainly not! The formula (43.43) was derived, as were all the others in this chapter, under the assumption that the mean free path between collisions is much smaller than any of the dimensions of the container. Whenever the gas density is so low that a molecule has a fair chance of crossing from one wall of its container to the other without having a collision, none of the calculations of this chapter apply. We must in such cases go back to kinetic theory and calculate again the details of what will occur.