velocity u. The above equation shows that it is of the same form as that for absolute velocities, but with the replacement either $m \to m/2$ or $v \to u/\sqrt{2}$:

$$Ce^{-\beta m v^2/2} \to Ce^{-\beta m u^2/4}.$$

This gives the origin of the factor $\sqrt{2}$. In particular, we see from equation 16.6 that the average relative speed would be

$$\bar{u} = \sqrt{2}\,\bar{v} = \sqrt{\frac{16kT}{\pi m}} \tag{16.16}$$

E   Transport processes

A property that is unevenly distributed will become more uniform as the random thermal motions of the molecules cause mixing.[3] The rate of this diffusive transport depends on average molecular speeds and the mean free path. The faster and the farther the molecules go, the more quickly the mixing progresses.

We call Q the property's density and define the x direction as the direction in which it varies, so that $Q = Q(x)$. Here we list three familiar examples of these "transport processes," along with the corresponding property whose density varies.

- In *molecular diffusion*   the density of molecules of type i varies with x:

$$Q(x) = \rho_i(x). \tag{16.17a}$$

- In *thermal conduction*   the density of the thermal energy (i.e., the density of the particles times the average thermal energy of each) varies with x:

$$Q(x) = \rho\left[\frac{\nu}{2}kT(x)\right]. \tag{16.17b}$$

- In *viscous flow*   the momentum density of flow in the y direction varies with x:

$$Q(x) = \rho m \bar{v}_y(x). \tag{16.17c}$$

E.1   One speed and one dimension

We begin by looking at the flux for the case where all particles move with the same speed v in the x direction half going in the $+x$ direction and the other half in the $-x$ direction. Once we get this result, we will then average it over all speeds and all directions.

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[3] If some property of the gas varies from one region to the next, then the gas is not in equilibrium. Nonetheless, we can safely use the tools of equilibrium thermodynamics as long as the relative variations are small on the scale of the molecular separations (10^{-8} to 10^{-9} m in a typical gas).
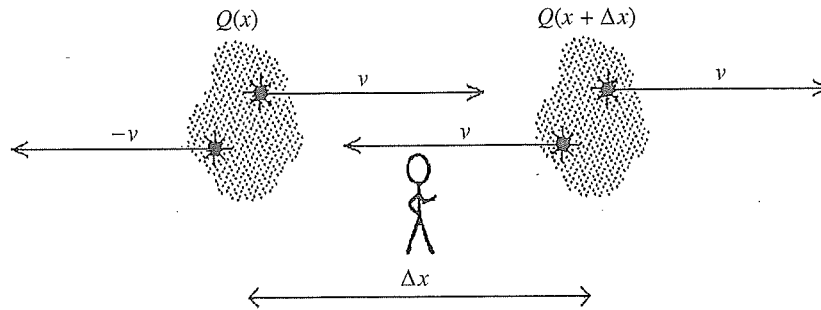
Figure 16.5 Suppose that all molecules are moving in the x direction with velocities $\pm v$, and that we are microscopic observers standing between positions x and $x + \Delta x$, watching the molecules pass by. The density of the property is $Q(x)$ to our left and $Q(x + \Delta x)$ to our right. In each of these regions, only half the particles are moving towards us, so they carry only half the property Q from that region. So the flux from our left is $Q(x)v/2$, and that from our right is $-Q(x + \Delta x)v/2$.

We will imagine that we are microscopic observers, midway between points x and $x + \Delta x$, where the property's densities are $Q(x)$ and $Q(x + \Delta x)$, respectively (Figure 16.5). In both regions only half of the particles are coming towards us (the other half are going away from us) and so the flux (density times velocity) past us of the property from each direction is given by

$$\text{flux from left} = +\frac{Q(x)}{2}v, \qquad \text{flux from right} = -\frac{Q(x + \Delta x)}{2}v.$$

The sum of these two gives the *net* flux of this property past us:

$$\text{net flux} = -\frac{v}{2}\left[Q(x + \Delta x) - Q(x)\right] = -\frac{v}{2}\frac{dQ}{dx}\Delta x.$$

But how do we decide upon the distance "Δx"? To answer this question we observe that molecules entering a new region generally require more than one collision each, on average, in order to either completely acquire or deliver the property for that region. For this reason, the distance Δx would be some small number n of mean free paths ($\Delta x = n\bar{l}$), and the preceding equation would become

$$\text{net flux} = -\frac{n\bar{l}v}{2}\frac{dQ}{dx}. \tag{16.18}$$

E.2   All speeds and all directions

In a real gas the particles are moving with a distribution of speeds and in all directions. The x-components of a particle's mean free path and velocity are given by

$$\bar{l}_x = \bar{l}\cos\theta, \qquad v_x = v\cos\theta,$$

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where θ is the angle that its direction of motion makes with the x-axis. So, for real gases we need to replace the product $\bar{l}v$ in equation 16.18 by $\bar{l}_x v_x$ and average over all speeds and all directions. For those particles coming from the left[4] we would have

$$\bar{l}v \rightarrow (\bar{l}_x v_x)_{\text{ave}} = \int\limits_0^\infty P(v)\mathrm{d}v \frac{1}{2\pi} \int\limits_{\phi=0}^{2\pi} \int\limits_{\theta=0}^{\pi/2} \sin\theta \, \mathrm{d}\theta \mathrm{d}\phi \, v\bar{l}\cos^2\theta,$$

Where the first integral is over speed and the second and third are over angle. Because $\bar{l}$ is independent of both the speed and the angle (equation 16.13) and v is independent of the angle, the right-hand side breaks into three factors:

$$(l_x v_x)_{\text{ave}} = \bar{l}\left[\int\limits_0^\infty P(v)v\mathrm{d}v\right]\left[\frac{1}{2\pi}\int\limits_{\phi=0}^{2\pi}\int\limits_{\theta=0}^{\pi/2}\sin\theta \, \mathrm{d}\theta\mathrm{d}\phi \, \cos^2\theta\right] = \bar{l}[\bar{v}]\left[\frac{1}{3}\right],$$

where $\bar{l}$ and $\bar{v}$ are given by equations 16.13 and 16.6, respectively. We put this result for $(\bar{l}_x v_x)_{\text{ave}}$ into equation 16.18 to get the "diffusion equation,"

$$\text{net flux of } Q = J_x = -\frac{n\bar{l}\,\bar{v}}{6}\frac{\mathrm{d}Q}{\mathrm{d}x}. \tag{16.19}$$

We note that the main features of this result are common sense. First, the minus sign indicates that the net transport is in the direction opposite to the gradient. Diffusion takes things from higher concentrations toward lower concentrations, and not vice versa. Second, the factors that are the particles' average speed and the mean free path tell us that the faster and farther the particles move, the faster diffusion progresses.

For each of the equations 16.17a–c, we group all constants together, and the diffusion equation takes on the following form.

• *Molecular diffusion*

$$J_x = -D\frac{\mathrm{d}\rho_i}{\mathrm{d}x}, \qquad \text{where the "diffusion constant" is} \quad D = \frac{n\bar{l}\bar{v}}{6}. \tag{16.20a}$$

• *Thermal conduction*

$$J_x = -K\frac{\mathrm{d}T}{\mathrm{d}x}, \qquad \text{where the "thermal conductivity" is} \quad K = \frac{n\bar{l}\,\bar{v}}{6}\rho\frac{v}{2}k. \tag{16.20b}$$

• *Viscous flow*

$$J_x = -\eta\frac{\mathrm{d}v_y}{\mathrm{d}x}, \qquad \text{where the "coefficient of viscosity" is} \quad \eta = \frac{n\bar{l}\bar{v}}{6}\rho m. \tag{16.20c}$$

In the last equation, the momentum flux is called the "stress" and it measures the sideways "drag" or "viscous" force between neighboring layers of a fluid

[4] For those coming from the right, the θ integral goes from $\pi/2$ to π, and we get the same answer.
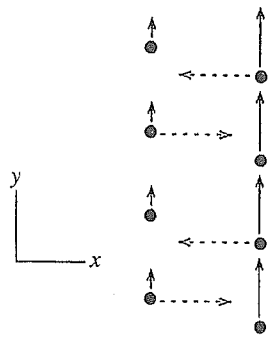
Figure 16.6 The two columns of dots represent two neighboring layers of a fluid that are flowing in the y direction at different speeds. The broken-line arrows indicate diffusion of the molecules in the x direction. Particles diffusing to the left carry more y momentum than those diffusing to the right. This mixing makes the fluid on the left speed up and that on the right slow down. That is, the diffusion causes each layer to exert a viscous drag on the other.

(Figure 16.6). It has the units of pressure (force/area), but it differs in that the force is parallel to the area rather than perpendicular to it.

E.3 Conserved properties

Generalizing from one to three dimensions, we can write all the above processes as

$$\mathbf{J} = -D \, \nabla Q \qquad \text{(diffusion equation)}, \qquad (16.21)$$

where Q is the density of the diffusing property and D is the appropriate diffusion constant. If this property is conserved (as are particles, energy, and momentum, for example) then it must satisfy the continuity equation (equation 12.17)

$$\frac{\partial Q}{\partial t} = -\nabla \cdot \mathbf{J} \qquad \text{(continuity equation)},$$

which states that the change in concentration of the property inside any volume is equal to the difference between the rate at which it enters and leaves (subsection 12E.5).

Taking the divergence of equation 16.21, using this expression for $\nabla \cdot \mathbf{J}$ in the continuity equation above, and then dividing by D gives the generalized form of the "heat equation" (equations 12.20 and 12.21):

$$\nabla^2 Q = \frac{1}{D} \frac{\partial Q}{\partial t} \qquad \text{(heat equation)}, \qquad (16.22)$$

whose solution was given in equation 12.23. Namely, if the property varies in the x direction and its concentration at time $t = 0$ is given by $Q(x, t = 0) = f(x)$ then its concentration at any later time is given by

$$Q(x, t) = \int_{-\infty}^{\infty} f(x') \left(\frac{1}{\sqrt{4\pi Dt}} e^{-(x-x')^2/4Dt} \right) dx'. \qquad (16.23)$$

The first order "diffusion equation" 16.21 states that things diffuse from higher to lower concentrations (**J** is *backwards* to the gradient), and the second order "heat equation" 16.22 states that concentrations even out, decreasing near local maxima ($\partial Q/\partial t < 0$ when $\nabla^2 Q < 0$) and increasing near local minima ($\partial Q/\partial t > 0$ when $\nabla^2 Q > 0$).

Summary of Sections B–E

Using the probability distribution for molecular speeds 16.5′ we find the following. The mean values of the speed and speed squared for a particle in a gas are (equations 16.6, 16.7)

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}, \qquad \bar{v^2} = \frac{3kT}{m}.$$

The flux of particles moving in any direction and the rate at which the gas particles exit an opening of area A in their container (ρ is the particle density) are (equations 16.9, 16.10)

$$J_x = \rho\sqrt{\frac{kT}{2\pi m}}, \qquad \frac{dN}{dt} = -\frac{N}{V}\sqrt{\frac{kT}{2\pi m}}A.$$

The collision frequency and the mean free path (σ is the collisional cross section and equals $4\pi R^2$, where R is the effective molecular radius) are (equations 16.12, 16.13)

$$\nu_c = \sqrt{2}\rho\sigma\bar{v}, \qquad \bar{l} = \bar{v}\left(\frac{1}{\nu_c}\right) = \frac{1}{\sqrt{2}\rho\sigma}.$$

The average relative speed ($\bar{u}$) and absolute speed ($\bar{v}$) of a system of colliding particles are related by (equation 16.16)

$$\bar{u} = \sqrt{2}\,\bar{v}.$$

If Q is the density of some property of the gas that varies from one region to the next, it will even out as the random thermal motions of the molecules cause mixing. If we define the x direction to be the direction in which Q varies, then the net flux of this property past a point is given by the diffusion equation (equation 16.19)

$$J_x = -\frac{n\bar{l}\bar{v}}{6}\frac{dQ}{dx},$$

where the average speed and mean free path are given by equations 16.6 and 16.13, respectively, and where n is a measure of the number of collisions required to transfer the property. Applications include the following important processes (equations 16.20a–c).

- *Molecular diffusion*

$$J_x = -D\frac{d\rho_i}{dx}, \qquad \text{where the diffusion constant is} \quad D = \frac{n\bar{l}\bar{v}}{6}.$$

- *Thermal conduction*

$$J_x = -K\frac{dT}{dx}, \qquad \text{where the thermal conductivity is} \quad K = \frac{n\bar{l}\bar{v}}{6}\rho\frac{v}{2}k.$$

- *Viscous flow*

$$J_x = -\eta\frac{dv_y}{dx}, \qquad \text{where the coefficient of viscosity is} \quad \eta = \frac{n\bar{l}\bar{v}}{6}\rho m.$$

The generalization of the diffusion equation to all directions for the density Q of any property is (equation 16.21)

$$\mathbf{J} = -D\nabla Q \qquad \text{(diffusion equation)},$$

where D is the appropriate diffusion constant. When combined with the continuity equation for conserved properties, it gives (equation 16.23)

$$\nabla^2 Q = \frac{1}{D}\frac{\partial Q}{\partial t} \qquad \text{(heat equation)},$$

which we have encountered before, at the end of Chapter 12.

Problems

For many of these problems, it will be helpful to consult the table of standard integrals in Appendix E.

Section A

1. The probability that the x-component of velocity of a molecule lies in a certain range is 0.3, that the y-component lies in a certain range is 0.2, and that it the z-component lies in a certain range is 0.1. What is the probability that all three components lie in the prescribed ranges?

2. For motion in one dimension and in terms of m, k, T, for what value of the momentum will the probability be half as large as the probability for a molecule to stand still?

3. Suppose that you invest half of your money in each of two businesses. Each business has a 10% chance of failing. What is the probability that (a) both will fail, (b) neither will fail?

4. Starting with $P(\mathbf{p})d^3 p = \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta p^2/2m} d^3 p$, derive $P(\mathbf{v})d^3 v$ by replacing p with mv.

5. The probability that the x-component of a molecule's velocity lies in the range dv_x is given by equation 16.3'. Check that the normalization is correct by integrating this probability distribution over all v_x.

6. According to equation 16.3', the distribution in v_x for particles in a gas is a Gaussian distribution. (See Section 3B.) The molecular mass is m and the temperature is T.
   (a) What is the standard deviation for the x-velocities of these particles?
   (b) the coefficient for a Gaussian distribution is $1/\sqrt{2\pi}\sigma$. Is the coefficient obtained in this way the same as that in equation 16.3'?
   (c) Since the distribution is centered around $v_x = 0$, the square of the standard deviation is equal to the mean value of v_x^2. What is the mean value of $(1/2)mv_x^2$?

7. Check the normalization of the expression 16.4' for $P(\mathbf{v})d^3 v$, by expressing $d^3 v$ in spherical coordinates and then integrating over all values of these coordinates.