

# Supplement to Chapter 2

## REVIEW QUESTIONS

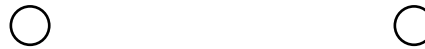
- 2.1 For a spatially uniform ideal gas, how is the velocity distribution  $f(\mathbf{v})$  defined?
- 2.2 Derive the relation  $p = \frac{2}{3}E/V$  for an ideal gas.
- 2.3 In deriving the Maxwell–Boltzmann distribution, how are microstates and macrostates defined?
- 2.4 For a given set of occupation numbers  $N_{kl}$ , how many microstates correspond to that macrostate?
- 2.5 What is the assumption of “equal a priori probability”?
- 2.6 What is the function that must be maximized in the derivation of the Maxwell–Boltzmann distribution?
- 2.7 What are the constraints on the set of variables in the function to be maximized in the previous question?
- 2.8 Describe Lagrange’s procedure for finding the maximum of a function  $F(x, y, z)$  on the constraint surface  $g(x, y, z) = 1$ .
- 2.9 Using the results of Questions 4–8, derive the Maxwell–Boltzmann distribution.
- 2.10 What is the form of the Maxwell–Boltzmann distribution?
- 2.11 For ideal gas particles in an external potential  $U(\mathbf{r})$  that is equal to zero at some location  $\mathbf{r}_o$ , what is the equilibrium particle density?
- 2.12 For a uniform ideal gas of density  $n$ , calculate the normalization constant  $C$  in the Maxwell velocity distribution  $f(\mathbf{v}) = C \exp(-\frac{1}{2}mv^2/kT)$ .
- 2.13 How is the speed distribution  $F(v)$  related to the velocity distribution  $f(\mathbf{v})$ ?
- 2.14 How are the average speed  $\bar{v}$  and  $v_{\text{rms}}$  defined?
- 2.15 For an ideal gas at temperature  $T$ , what is  $v_{\text{rms}}$ ?
- 2.16 How is the mean free path defined?
- 2.17 For a quantum mechanical system of  $N$  particles in a three-dimensional potential  $U(\mathbf{r})$ , what is the Hamiltonian operator?
- 2.18 How are the single-particle energy eigenfunctions defined?
- 2.19 For a system of  $N$  Bose–Einstein particles without interactions, describe the form of the  $N$ -particle energy eigenfunctions.
- 2.20 What are the allowed values for the quantum state occupation numbers  $N_k$  for Bose–Einstein particles?
- 2.21 For a system of  $N$  Fermi–Dirac particles without interactions, describe the form of the  $N$ -particle energy eigenfunctions.
- 2.22 What are the allowed values for the quantum state occupation numbers  $N_k$  for Fermi–Dirac particles?
- 2.23 In deriving the Bose–Einstein and Fermi–Dirac distribution functions, how were microstates and macrostates defined?

- 2.24** How many ways can  $\nu$  fermions be arranged in  $K$  quantum states?
- 2.25** How many Fermi–Dirac microstates are there for a macrostate defined by the bin occupation numbers  $\nu_1, \nu_2, \dots$  if the  $k$ th bin has  $K_k$  states?
- 2.26** Using the result of the previous question, derive the Fermi–Dirac distribution function,  $f_{\text{FD}}(\varepsilon) = (e^{\alpha + \beta\varepsilon} + 1)^{-1}$ .
- 2.27** What is the form of the Bose–Einstein distribution function  $f_{\text{BE}}(\varepsilon)$ ?
- 2.28** For a particle with no external potential in three dimensions, write the Schrödinger energy eigenvalue equation.
- 2.29** For a particle in a cubic box of side  $L$ , what are “periodic boundary conditions”?
- 2.30** What are the eigenfunctions and eigenvalues of the Schrödinger equation for a free particle with periodic boundary conditions?
- 2.31** For a particle in a cubic periodic box of side  $L$ , calculate the number of energy eigenstates with energy less than  $E$ .
- 2.32** Under what condition do the quantum mechanical distribution functions reduce to the Maxwell distribution?

**EXERCISES**

**Exercise 2.1** Draw a realistic picture of the situation in a typical noble gas, say argon, at STP by drawing two spheres with diameters proportional to the “interaction diameters” of argon atoms separated by a distance that is proportional, with the same proportionality constant, to the typical distance between particles, namely  $d = 1/n^{1/3}$ . On the same scale, how large is the mean free path?

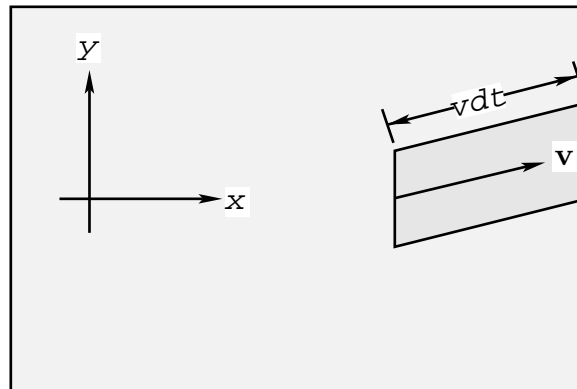
**Fig. S2.1**



**Solution** At STP, the particle density is  $2.7 \times 10^{25} \text{ m}^{-3}$ . Thus  $d = 3.3 \times 10^{-9} \text{ m}$ . The *Handbook of Chemistry and Physics* gives an approximate diameter for Ar, based on crystal structure, of  $3.1 \text{ \AA} = 3.1 \times 10^{-10} \text{ m}$ . Thus the ratio of the atomic diameter to  $d$  is about one to ten.

The mean free path of hard spherical particles is calculated approximately in Problem 2.8 and accurately in Exercises 2.15 through 2.17. It is given by  $\ell = 1/(\sqrt{2} \pi D^2 n)$ , where  $D$  is the diameter of the particles and  $n$  is the particle density. For argon at STP,  $\ell = 8.7 \times 10^{-8}$ . In Fig. S2.1, in which  $d$  is represented by two inches,  $\ell$  would be about 4.4 feet (1.34 m).

**Exercise 2.2** A two-dimensional ideal gas is a collection of noninteracting particles that move on a plane. Suppose a two-dimensional ideal gas of  $N$  particles, with a total energy  $E$ , is confined by one-dimensional “walls” to an area  $A$ . The pressure on a wall is defined as the force per unit length. Show that  $p = E/A$ .



**Fig. S2.2** All the particles with velocity  $\mathbf{v}$  that are in the shaded region will strike the wall within the time interval  $dt$ .

**Solution** Let  $f(v_x, v_y) dv_x dv_y$  be the number of particles per unit area that have velocities in the range  $dv_x dv_y$ . Consider a length  $\ell$  of the container wall, which we assume is in the  $y$  direction. A particle whose velocity is in the range  $dv_x dv_y$  will strike the wall in that length, during the time interval  $dt$ , if it is within the shaded region shown in Fig. S2.2. The area of that region is  $\ell v_x dt$ , and therefore the number of such particles is

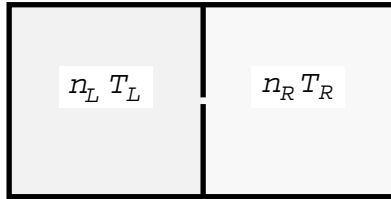
$$dN = \ell v_x dt f(v_x, v_y) dv_x dv_y \tag{S2.1}$$

The momentum delivered to the section of wall by the rebounding particle is  $2mv_x$ . Thus the total rate at

which momentum is being delivered to that section of the wall is

$$\begin{aligned}
 \frac{dP}{dt} &\equiv F = 2\ell m \int_{v_x > 0} f(v_x, v_y) v_x^2 dv_x dv_y \\
 &= \ell m \int f(v_x, v_y) v_x^2 dv_x dv_y \\
 &= \ell \int f(v_x, v_y) \left[ \frac{m}{2} (v_x^2 + v_y^2) \right] dv_x dv_y \\
 &= \ell E/A
 \end{aligned} \tag{S2.2}$$

**Exercise 2.3** Consider two very dilute gases of slightly different densities and temperatures, separated by a thin wall with a small hole in it of area  $A$ . Calculate the rate at which particles and energy are transferred through the hole as a function of the temperature and density differences, to first order in  $\Delta T$  and  $\Delta n$ . (See Fig. S2.3.)



**Fig. S2.3**  $n_L$ ,  $T_L$ ,  $n_R$ , and  $T_R$  are the densities and temperatures of the dilute gases on the two sides.

**Solution** The rate at which particles pass through the hole, from left to right, is

$$R(L \rightarrow R) = An_L (m/2\pi kT_L)^{3/2} \int_{v_x > 0} e^{-mv^2/2kT_L} v_x d^3v \tag{S2.3}$$

Using spherical coordinates with the polar axis in the  $x$  direction

$$\begin{aligned}
 R(L \rightarrow R) &= An_L (m/2\pi kT_L)^{3/2} 2\pi \int_0^{\pi/2} \cos \theta \sin \theta d\theta \int_0^\infty e^{-mv^2/2kT_L} v^3 dv \\
 &= \pi An_L (m/2\pi kT_L)^{3/2} \frac{1}{2} (2kT_L/m)^2 \\
 &= \frac{1}{\sqrt{2\pi}} An_L (kT_L/m)^{1/2} \\
 &= \frac{1}{4} n_L \bar{v}_L A
 \end{aligned} \tag{S2.4}$$

where  $\bar{v}_L$  is the average speed of the particles on the left, given in Eq. (2.30). The rate of transfer of particles from right to left is

$$R(R \rightarrow L) = \frac{An_R T_R^{1/2}}{\sqrt{2\pi m/k}} \tag{S2.5}$$

Assuming that  $n_L = n + \Delta n/2$ ,  $T_L = T + \Delta T/2$ ,  $n_R = n - \Delta n/2$ , and  $T_R = T - \Delta T/2$ , the net rate of particle transfer from left to right is

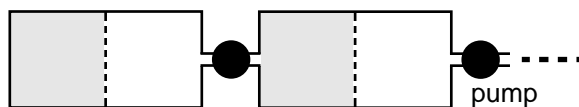
$$\begin{aligned}
 \frac{dN_R}{dt} &= R(L \rightarrow R) - R(R \rightarrow L) \\
 &= \frac{A}{\sqrt{2\pi m/k}} \left[ (n + \Delta n/2)(T + \Delta T/2)^{1/2} \right. \\
 &\quad \left. - (n - \Delta n/2)(T - \Delta T/2)^{1/2} \right] \\
 &\approx \frac{A}{\sqrt{2\pi m/k}} \left( T^{1/2} \Delta n + \frac{1}{2} \frac{n}{T^{1/2}} \Delta T \right)
 \end{aligned} \tag{S2.6}$$

A particle of speed  $v$  that goes through the hole carries an amount of energy  $mv^2/2$ . Therefore the rate at which energy is carried through the hole from left to right can be obtained from Eq. (S2.3) by putting a factor of  $mv^2/2$  in the integrand.

$$\begin{aligned}
 R_E(L \rightarrow R) &= An_L(m/2\pi kT_L)^{3/2} \int_{v_x > 0} e^{-mv^2/2kT_L} (mv^2/2) v_x d^3v \\
 &= \pi m An_L(m/2\pi kT_L)^{3/2} \int_0^{\pi/2} \cos \theta \sin \theta d\theta \cdot \int_0^\infty e^{-mv^2/2kT_L} v^5 dv \\
 &= \frac{1}{2\sqrt{\pi}} m An_L (2kT_L/m)^{3/2} \\
 &= \left(\frac{2k^3}{\pi m}\right)^{1/2} An_L T_L^{3/2}
 \end{aligned} \tag{S2.7}$$

with a similar formula for  $R_E(R \rightarrow L)$ . The net rate of transfer of energy is

$$\begin{aligned}
 \frac{dE_R}{dt} &= \left(\frac{2k^3}{\pi m}\right)^{1/2} A \left[ (n + \Delta n/2)(T + \Delta T/2)^{3/2} - (n - \Delta n/2)(T - \Delta T/2)^{3/2} \right] \\
 &= \left(\frac{2k^3}{\pi m}\right)^{1/2} A (T^{3/2} \Delta n + \frac{3}{2} n T^{1/2} \Delta T)
 \end{aligned} \tag{S2.8}$$



**Fig. S2.4** A series of diffusion chambers, each with many small holes through which the gas diffuses.

**Exercise 2.4** This exercise concerns a simplified model of the process of isotope separation by diffusion. Two chambers are separated by a thin wall containing many small holes, as shown in Fig. S2.4. In the left chamber is a very dilute mixed ideal gas containing a density  $n_A$  of particles of mass  $m_A$  and a density  $n_B$  of particles of mass  $m_B$ . The right chamber is pumped so that its density can be approximated as zero. (a) What is the ratio of the number of  $B$  particles to  $A$  particles in the gas that is being pumped out of the right chamber? (b) Assume that the gas being pumped out of the right chamber is being pumped into the left chamber of a second diffusion stage similar to this one. Assume that the process is repeated for 20 stages, that  $n_A = n_B$  in the initial chamber, and that  $m_A/m_B = 0.8$ . What is  $n_A/n_B$  in the final chamber?

**Solution** (a) According to Eq. (S2.3), the rate at which  $A$  particles pass through the wall is

$$\frac{dN_A}{dt} = \frac{A}{4} \bar{v}_A n_A \tag{S2.9}$$

where  $\bar{v}_A = \sqrt{8kT/\pi m_A}$ . Similarly, the rate at which  $B$  particles pass through the wall is

$$\frac{dN_B}{dt} = \frac{A}{4} \bar{v}_B n_B \tag{S2.10}$$

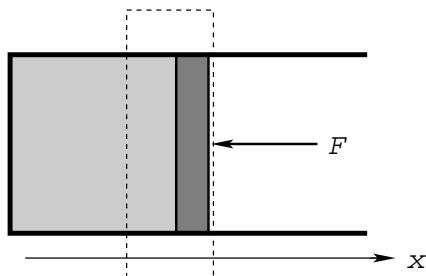
The ratio of the number of  $B$  particles to that of  $A$  particles in the gas extracted from the right chamber is

$$\frac{dN_B/dt}{dN_A/dt} = \frac{\bar{v}_B n_B}{\bar{v}_A n_A} = \left(\frac{m_A}{m_B}\right)^{1/2} \frac{n_B}{n_A} \tag{S2.11}$$

(b) In each stage, the ratio  $n_B/n_A$  is multiplied by the factor  $(m_A/m_B)^{1/2}$ . If  $n_B/n_A$  is initially one, then after 20 stages

$$\frac{n_B}{n_A} = \left(\frac{m_A}{m_B}\right)^{10} = (.8)^{10} = 0.107 \tag{S2.12}$$

**Exercise 2.5** In Section 2.2 we calculated the force per unit area exerted on the walls of a container filled with an ideal gas by assuming that the walls were perfectly smooth, so that each gas particle underwent simple reflection when it hit the wall. When we remember that the walls of a real container are made of atoms that are roughly the same size as the gas particles, it becomes clear that the assumption that the walls are smooth on an atomic scale is completely unrealistic. Assuming that the piston shown in the figure is in equilibrium and taking, as our system, everything within the volume shown by the dashed line in Fig. S2.5, use the momentum conservation law to derive the relation  $p = (2/3)E/V$  without the unrealistic “smooth wall” assumption.



**Fig. S2.5** A cylinder with a movable piston. The system is everything within the dotted lines.

**Solution** Our “system” is everything that is contained in a cylindrical volume that includes the piston plus a certain amount of the gas, to the left of the piston. At the left surface of the system, particles carry momentum into and out of the system. Let us choose our  $x$  axis as shown in Fig. S2.5. Then, because momentum is a conserved quantity, the  $x$  component of the momentum carried into the system by particles entering from the left minus the  $x$  component of the momentum carried out of the system by particles leaving at the left during a time interval  $\Delta t$  must equal the momentum delivered to the system by the force, namely  $F\Delta t$ , if the total momentum of the system is to remain constant. If we take a small area  $\Delta A$  on the imaginary surface that bounds the system on the left, the number of particles entering the system through  $\Delta A$  during time interval  $\Delta t$  that have velocities in the range  $d^3v$ , centered at  $\mathbf{v}$ , is  $[f(\mathbf{v})d^3v]v_x\Delta A\Delta t$ . The  $x$  component of momentum carried into the system by those particles is  $m[f(\mathbf{v})d^3v]v_x^2\Delta A\Delta t$ . The  $x$  momentum carried into the system by all the particles entering through  $\Delta A$  is

$$m\Delta A\Delta t\int_{v_x>0}f(\mathbf{v})v_x^2d^3v \quad (\text{S2.13})$$

The total rate at which particles carry  $x$  momentum into the system at the left is

$$\frac{dP_x(\text{in})}{dt}=mA\int_{v_x>0}f(\mathbf{v})v_x^2d^3v \quad (\text{S2.14})$$

The particles that leave the system at the left carry with them *negative*  $x$  momentum, since their values of  $v_x$  must be negative. The loss of negative  $P_x$  counts as a gain of  $P_x$  by the system. It is easy to see that the rate at which the system gains momentum by the loss of those particles is

$$\frac{dP_x(\text{out})}{dt}=mA\int_{v_x<0}f(\mathbf{v})v_x^2d^3v \quad (\text{S2.15})$$

Combining the two effects, we get

$$\begin{aligned} \frac{dP_x}{dt} &= mA\int f(\mathbf{v})v_x^2d^3v \\ &= \frac{2}{3}A\int f(\mathbf{v})\left(\frac{m}{2}(v_x^2+v_y^2+v_z^2)\right)d^3v \\ &= \frac{2}{3}AE/V \end{aligned} \quad (\text{S2.16})$$

The force delivers negative  $P_x$  to the system at a rate  $F$ . Setting this equal to  $dP_x/dt$  gives the desired result. Notice that, in this analysis, what goes on at the left surface of the piston is a process internal to the system and therefore of no relevance to the conservation of total momentum.

**Exercise 2.6** In computing the pressure by calculating the momentum carried by particles across an imaginary surface, we are ignoring another possible mode of momentum transfer across the surface. That is, that the particles on one side of the surface, without moving across the surface, can exert forces on the particles on the other side, due to the direct interparticle force. In a dense system, such as a liquid, most of the pressure force across any surface is transmitted by interparticle forces rather than by particle transfer. In fact, in a solid, where the particles are not free to move across the surface at all, all the pressure force is transmitted in that way. In order to estimate how much force is transmitted in a dilute gas by interparticle forces, assume that the particles in a gas at STP are distributed randomly with a density  $n$  and have an interparticle potential that depends on the separation of the particles  $r$  as

$$\phi(r) = \phi_o e^{-r^2/a^2} \quad (\text{S2.17})$$

where the range of the potential,  $a = 2 \text{ \AA}$  and  $\phi_o = 1 \text{ eV}$ . Calculate the pressure transmitted by the interparticle force across a surface of area  $A$  and compare it with the kinetic pressure force (the momentum transferred by moving particles).

**Solution** We choose as our surface, dividing the gas into two parts, the surface  $x = 0$ . We calculate the potential energy at a point  $(-x_o, 0, 0)$  to the left of the surface, due to all the particles that lie to the right of the surface. That is

$$\begin{aligned} \phi(-x_o) &= \int_o^\infty dx \int_{-\infty}^\infty dy \int_{-\infty}^\infty dz n \phi_o \exp\left(-\frac{(x+x_o)^2}{a^2} - \frac{y^2}{a^2} - \frac{z^2}{a^2}\right) \\ &= n \phi_o \pi a^2 \int_o^\infty dx e^{-(x+x_o)^2/a^2} \end{aligned} \quad (\text{S2.18})$$

Letting  $u = (x + x_o)/a$ , this can be written as

$$\phi(-x_o) = n \phi_o \pi a^3 \int_{x_o/a}^\infty e^{-u^2} du \quad (\text{S2.19})$$

The force on a particle toward the left, due to all the particles on the right, is

$$F = -\frac{\partial \phi(-x_o)}{\partial x_o} = \pi n \phi_o a^2 e^{-x_o^2/a^2} \quad (\text{S2.20})$$

The total force on all the particles on the left is the integral of  $F$  times the density of particles over all the region on the left. The  $y$  and  $z$  integrals give a factor of  $A$ , the area of the surface separating the two halves. Thus

$$\begin{aligned} F_{\text{total}} &= \pi n^2 \phi_o a^2 A \int_o^\infty e^{-x_o^2/a^2} dx_o \\ &= \pi^{3/2} n^2 \phi_o a^3 A \end{aligned} \quad (\text{S2.21})$$

The pressure exerted by the direct interparticle forces is

$$p_{\text{int}} = \frac{F_{\text{total}}}{A} = \pi^{3/2} n^2 \phi_o a^3 \quad (\text{S2.22})$$

Putting in  $n = n(\text{STP}) = 2.7 \times 10^{25} / \text{m}^3$ ,  $\phi_o = 1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ , and  $a = 2 \times 10^{-10} \text{ m}$ , we get  $p_{\text{int}} = 5.2 \times 10^3 \text{ N/m}^2$ . But, at STP,  $p_{\text{kin}} \approx 10^5 \text{ N/m}^2$ . Thus  $p_{\text{int}}/p_{\text{kin}} = 0.05$ .

**Exercise 2.7** The rate of a certain chemical reaction of the form  $A + A \rightarrow A_2$  in an ideal gas is given by

$$R = \alpha \times \left( \begin{array}{l} \text{the density of pairs of particles with} \\ \text{c.m. kinetic energy greater than } \varepsilon_o \end{array} \right) \quad (\text{S2.23})$$

where  $R$  is the number of reactions per unit volume per second and  $\alpha$  is some constant. Write a one-dimensional integral expression for  $R$  as a function of particle density and temperature.

**Solution** Consider a unit volume of the gas. The number of particles with velocity in the range  $d^3\mathbf{v}$  is  $f(\mathbf{v})d^3\mathbf{v}$ , where  $f(\mathbf{v})$  is the Maxwell velocity distribution function. The number of pairs of particles, where the first particle has velocity in  $d^3\mathbf{v}$  and the second in  $d^3\mathbf{v}'$  is  $f(\mathbf{v})f(\mathbf{v}')d^3\mathbf{v}d^3\mathbf{v}'$ . We must now transform from the absolute velocities of the two particles to center-of-mass and relative velocities, defined by

$$\mathbf{V} = (\mathbf{v} + \mathbf{v}')/2 \quad \text{and} \quad \mathbf{u} = \mathbf{v} - \mathbf{v}' \quad (\text{S2.24})$$

In terms of  $\mathbf{u}$  and  $\mathbf{V}$ , the kinetic energy of the pair is

$$K = \frac{m}{2}(v^2 + v'^2) = \frac{m}{4}u^2 + mV^2 \quad (\text{S2.25})$$

The term involving  $\mathbf{u}$  is called the center-of-mass kinetic energy. Thus

$$K_{\text{cm}} = \frac{m}{4}u^2 \quad (\text{S2.26})$$

The significance of  $K_{\text{cm}}$  is that  $K_{\text{cm}} + \phi(r)$  remains constant while the two particles interact, where  $\phi$  is the interaction potential energy associated with the interaction force between the particles.  $K_{\text{cm}}$  is the energy available in the center-of-mass frame (where the two particles always have equal and opposite velocities) to do work against a repulsive two-particle interaction force.

The number of pairs of particles within the unit volume with  $K_{\text{cm}} > \varepsilon_o$  is therefore

$$N = \frac{1}{2} \int f(\mathbf{v})f(\mathbf{v}')\theta\left(\frac{m}{4}u^2 - \varepsilon_o\right) d^3\mathbf{v}d^3\mathbf{v}' \quad (\text{S2.27})$$

where  $\theta$  is the unit step function. The factor of  $1/2$  is necessary to compensate for the fact that the integral “double counts” the pairs of particles. To see what is meant, let us try to calculate the number of pairs of students in a class whose total ages add up to 39 years. If  $a_x$  is the age of student  $x$  (always an integer), then we might sum the quantity  $\delta(a_x + a_y - 39)$ , where  $\delta(0) = 1$  and  $\delta(n) = 0$  for  $n \neq 0$ , and  $x$  and  $y$  independently take on the values of all the students in the class. But this would count “Mary and John” and “John and Mary” as two pairs although they are really only one.

We must now transform the variables of integration from  $d^3\mathbf{v}d^3\mathbf{v}'$  to  $d^3\mathbf{u}d^3\mathbf{V}$ . Whenever integration variables are changed, one must include the Jacobian determinant of the transformation. According to Eq. (S2.24),  $u_x$  and  $V_x$  are functions of  $v_x$  and  $v'_x$  and similarly for the  $y$  and  $z$  components. The transformation formula is

$$dv_x dv'_x \rightarrow |J| du_x dV_x \quad (\text{S2.28})$$

This is the same transformation that is shown in the Mathematical Appendix to have  $|J| = 1$ . Also

$$f(\mathbf{v})f(\mathbf{v}') = n^2(m/2\pi kT)^3 \exp\left(-\frac{m(v^2 + v'^2)}{2kT}\right) \quad (\text{S2.29})$$

where

$$\frac{m}{2}(v^2 + v'^2) = \frac{m}{4}u^2 + mV^2 \quad (\text{S2.30})$$

Therefore

$$N = \frac{1}{2}n^2(m/2\pi kT)^3 \int e^{-mV^2/kT} d^3V \int \theta\left(\frac{m}{4}u^2 - \varepsilon_o\right) e^{-mu^2/4kT} d^3u \quad (\text{S2.31})$$

The first integral can be done easily

$$I_1 = \int e^{-mV^2/kT} d^3V = (\pi kT/m)^{3/2} \quad (\text{S2.32})$$



The second integral can be reduced to a one-dimensional integral by transforming to spherical coordinates in  $\mathbf{u}$  space.

$$\begin{aligned} I_2 &= \int \theta\left(\frac{m}{4}u^2 - \varepsilon_o\right) e^{-mu^2/4kT} d^3u \\ &= 4\pi \int_{u_o}^{\infty} e^{-mu^2/4kT} u^2 du \end{aligned} \quad (\text{S2.33})$$

where  $u = 2\sqrt{\varepsilon_o/m}$ . Introducing a variable  $x = (m/4kT)^{1/2}u$  with a lower limit,  $x_o = (m/4kT)^{1/2}u_o = \sqrt{\varepsilon_o/kT}$ , we can write  $I_2$  as

$$I_2 = 32\pi \left(\frac{kT}{m}\right)^{3/2} \int_{x_o}^{\infty} e^{-x^2} x^2 dx \quad (\text{S2.34})$$

Putting these expressions for  $I_1$  and  $I_2$  into Eq. (S2.31), we get

$$R = \frac{8\alpha n^2}{\sqrt{2\pi}} \int_{x_o}^{\infty} e^{-x^2} x^2 dx \quad (\text{S2.35})$$

If  $kT$  is much smaller than the activation energy for the reaction  $\varepsilon_o$ , then  $x_o$  is large and, because of the factor of  $\exp(-x^2)$  in the integrand,  $R$  is very small.

**Exercise 2.8** Consider an ideal gas composed mostly of  $A$  particles of mass  $m_A$  but with a low density of  $B$  particles of mass  $m_B$ . If a steady force is applied to the  $B$  particles, but not to the  $A$  particles (one could imagine that only the  $B$  particles carry an electric charge and there is a weak electric field present), then the  $B$  particles will drift through the gas at a speed that is proportional to the force.

$$v = \mu F \quad (\text{S2.36})$$

The proportionality constant  $\mu$  is called the *mobility constant*. Because of the drift, there will be a flux of the  $B$  particles equal to

$$\phi = n_B v = \mu n_B F \quad (\text{S2.37})$$

In the absence of any external force, if the density of  $B$  particles is not uniform (let us say that it depends on the coordinate  $z$ ), then there will be a net flux of the  $B$  particles from the regions of high  $B$  particle density to those of low density. This diffusion of  $B$  particles will eventually bring about a uniform equilibrium state. It is observed that the flux is proportional to the density gradient.

$$\phi = -D \frac{dn_B}{dz} \quad (\text{S2.38})$$

The constant of proportionality  $D$  is called the *diffusion constant*. It is reasonable (and correct) to assume that, if there are both a force and a density gradient, then the net flux is given by the sum of the two terms. Make that assumption and use the equilibrium distribution [Eq. (2.20)] in a gravitational field, to derive a relationship between the mobility constant  $\mu$  and the diffusion constant  $D$ .

**Solution** For a gravitational field pointing in the negative  $z$  direction, the force on a  $B$  particle is  $F_z = -m_B g$ . The flux of  $B$  particles is given by

$$\phi = -\mu n_B m_B g - D \frac{dn_B}{dz} \quad (\text{S2.39})$$

At equilibrium the flux must vanish, giving the following differential equation for the equilibrium distribution.

$$\mu g m_B n_B = -D \frac{dn_B}{dz} \quad (\text{S2.40})$$

This can be written as

$$\frac{d[\log n_B(z)]}{dz} = -\frac{\mu g m_b}{D} \equiv -\frac{1}{h} \quad (\text{S2.41})$$

which has a solution

$$n_B(z) = n_B(0)e^{-z/h} \quad (\text{S2.42})$$

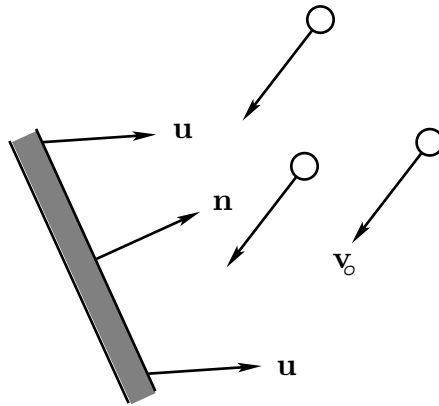
with  $h = D/\mu g m_B$ . But the Maxwell–Boltzmann formula for the scale height is  $h = kT/m_B g$ . Thus we see that, in order for these two formulas to agree, the diffusion constant and the mobility constant must be related by

$$D = \mu kT \quad (\text{S2.43})$$

This formula was first derived by A. Einstein.

The next few exercises involve calculations using single-velocity beams. A single-velocity beam is a shower of particles, all with velocity  $\mathbf{v}_o$ , but distributed randomly throughout space with density  $n_o$ . First, for simplicity, we will consider two-dimensional single-velocity beams.

**Exercise 2.9** In two dimensions, a smooth hard wall has a normal  $\mathbf{n}$  and moves with velocity  $\mathbf{u}$ . A single-velocity beam is being reflected from the wall (Fig. S2.6). What is the force per unit length on the wall?



**Fig. S2.6**  $\mathbf{n}$  is the normal to the wall.  $\mathbf{u}$  is the velocity of the wall.

**Solution** We transform to the inertial frame in which the wall is at rest. In that frame the beam particles have velocity  $\mathbf{v}_o - \mathbf{u}$ . The rate at which they strike a unit length of the wall is equal to their density times the inward normal component of their velocity. That is

$$\text{Rate per length} = -n_o \mathbf{n} \cdot (\mathbf{v}_o - \mathbf{u}) \quad (\text{S2.44})$$

Each particle has a change in momentum equal to  $-2m[\mathbf{n} \cdot (\mathbf{v}_o - \mathbf{u})]\mathbf{n} \equiv \Delta\mathbf{p}$ . The momentum delivered to a unit length of the wall is equal to  $\Delta\mathbf{p}$  times the collision rate. This is defined as the force per unit length on the wall.

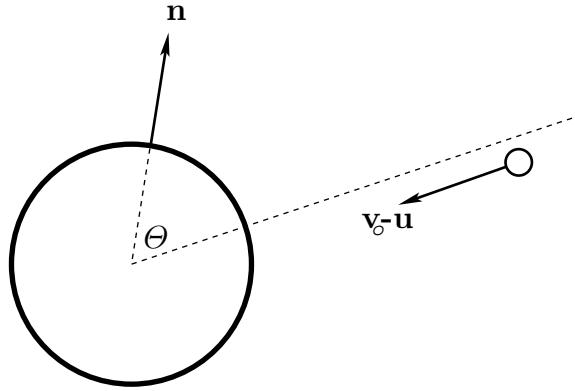
$$\frac{d\mathbf{F}}{d\ell} = -2mn_o[\mathbf{n} \cdot (\mathbf{v}_o - \mathbf{u})]^2 \mathbf{n} \quad (\text{S2.45})$$

As one would expect for a smooth wall, it is a normal force. One should note that this equation is valid only if, in the wall frame, the particles are actually directed at the wall. That is, if

$$\mathbf{n} \cdot (\mathbf{v}_o - \mathbf{u}) < 0 \quad (\text{S2.46})$$

**Exercise 2.10** A heavy smooth hard circular particle of radius  $R$  moves with velocity  $\mathbf{u}$  through a single-velocity beam (Fig. S2.4). What is the net force on the particle?

**Solution** We let  $\theta$  be the angle that a point on the surface of the circle makes with an axis drawn antiparallel to the vector  $\mathbf{v}_o - \mathbf{u}$ . Then  $\mathbf{n}(\theta) \cdot (\mathbf{v}_o - \mathbf{u}) = -|\mathbf{v}_o - \mathbf{u}| \cos \theta$ . The restriction that  $\mathbf{n} \cdot (\mathbf{v}_o - \mathbf{u}) < 0$  says that



**Fig. S2.7** The circle moves with velocity  $\mathbf{u}$  through a single-velocity beam in two dimensions.

we should integrate  $\theta$  from  $-\pi/2$  to  $\pi/2$ .

$$\begin{aligned} \mathbf{F} &= \int_{-\pi/2}^{\pi/2} \frac{d\mathbf{F}}{d\ell} \frac{d\ell}{d\theta} d\theta \\ &= -2mn_o |\mathbf{v}_o - \mathbf{u}|^2 R \int_{-\pi/2}^{\pi/2} \cos^2 \theta \mathbf{n}(\theta) d\theta \end{aligned} \quad (\text{S2.47})$$

Certainly the net force  $\mathbf{F}$  is parallel to  $\mathbf{v}_o - \mathbf{u}$ . Therefore it is sufficient to calculate

$$\begin{aligned} \mathbf{F} \cdot (\mathbf{v}_o - \mathbf{u}) &= 2mn_o |\mathbf{v}_o - \mathbf{u}|^3 R \int_{-\pi/2}^{\pi/2} \cos^3 \theta d\theta \\ &= \frac{8}{3} mRn_o |\mathbf{v}_o - \mathbf{u}|^3 \end{aligned} \quad (\text{S2.48})$$

or

$$\mathbf{F} = \frac{8}{3} mRn_o |\mathbf{v}_o - \mathbf{u}| (\mathbf{v}_o - \mathbf{u}) \quad (\text{S2.49})$$

**Exercise 2.11** A disk moves at a very low velocity  $\mathbf{u} = u\hat{\mathbf{x}}$  through a very dilute two-dimensional ideal gas. Calculate the net force on the disk.

**Solution** The collection of particles with velocities within the range  $d^2v$ , centered at  $\mathbf{v}$ , can be considered as a single-velocity beam with a density  $f(\mathbf{v}) d^2v$ , where  $f(\mathbf{v})$  is the two-dimensional Maxwell distribution function

$$f(v_x, v_y) = n(m/2\pi kT) e^{-mv^2/2kT} \quad (\text{S2.50})$$

The net force on the disk due to those particles is, by Eq. (S2.49),

$$d\mathbf{F} = \frac{8}{3} mRn(m/2\pi kT) e^{-mv^2/2kT} |\mathbf{v} - \mathbf{u}| (\mathbf{v} - \mathbf{u}) d^2v \quad (\text{S2.51})$$

The net force due to all the gas particles is obtained by integrating  $d\mathbf{F}$  over all velocities.

$$\mathbf{F} = \frac{4m^2 Rn}{3\pi kT} \int e^{-mv^2/2kT} |\mathbf{v} - \mathbf{u}| (\mathbf{v} - \mathbf{u}) d^2v \quad (\text{S2.52})$$

We make a transformation to the variable  $\mathbf{V} = \mathbf{v} - \mathbf{u}$  and use the following approximations, which are valid for very small  $\mathbf{u}$ .

$$v^2 = (\mathbf{V} + \mathbf{u})^2 \approx V^2 + 2\mathbf{V} \cdot \mathbf{u} \quad (\text{S2.53})$$

$$e^{-\alpha v^2} \approx e^{-\alpha V^2} e^{-2\alpha \mathbf{V} \cdot \mathbf{u}} \approx e^{-\alpha V^2} (1 - 2\alpha \mathbf{V} \cdot \mathbf{u}) \quad (\text{S2.54})$$

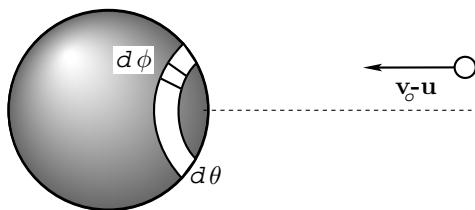
Then

$$\mathbf{F} = \frac{4m^2 Rn}{3\pi kT} \int e^{-mV^2/2kT} \left(1 - \frac{m}{kT} \mathbf{V} \cdot \mathbf{u}\right) |\mathbf{V}| \mathbf{V} d^2V \quad (\text{S2.55})$$

The first term in the parentheses vanishes by symmetry. Since  $\mathbf{u}$  is in the  $x$  direction, it is clear that the net force must have only an  $x$  component. The value of that component is

$$\begin{aligned} F_x &= -\frac{4m^3 Rnu}{3\pi k^2 T^2} \int_0^\infty \int_{-\pi}^\pi e^{-mV^2/2kT} V^4 \cos^2 \theta dV d\theta \\ &= -2Rn\sqrt{2\pi mkT} u \end{aligned} \quad (\text{S2.56})$$

**Exercise 2.12** By reviewing the solution to Exercise 2.9, it is easy to see that Eq. (S2.45) is also valid in three dimensions with the trivial modification that  $d\ell$  must be replaced by an element of area  $dA$  on the wall surface and  $n_o$  is the three-dimensional density of particles in the beam. Use this fact to redo Exercise 2.11 for the case of a heavy hard spherical particle in three dimensions, as shown in Fig. S2.8.



**Fig. S2.8** In three dimensions, a hard sphere moves with velocity  $\mathbf{u}$  through a single-velocity beam.

**Solution** We construct a system of spherical coordinates with the polar axis in a direction opposite to the vector  $\mathbf{v}_o - \mathbf{u}$ . The area on the sphere associated with the range of spherical angles  $d\theta$  and  $d\phi$  is equal to  $dA = R^2 \sin \theta d\theta d\phi$ . The force  $d\mathbf{F}$  imparted to that area by the particles in the single-velocity beam is given by

$$\frac{d\mathbf{F}}{R^2 \sin \theta d\theta d\phi} = -2mn_o [\mathbf{n} \cdot (\mathbf{v}_o - \mathbf{u})]^2 \mathbf{n} \quad (\text{S2.57})$$

Again, as in two dimensions,  $\mathbf{n} \cdot (\mathbf{v}_o - \mathbf{u}) = -|\mathbf{v}_o - \mathbf{u}| \cos \theta$ . The restriction that  $\mathbf{n} \cdot (\mathbf{v}_o - \mathbf{u}) < 0$  restricts  $\theta$  to the range  $0 < \theta < \pi/2$ . Therefore, the total force is given by the integral

$$\mathbf{F} = -2mn_o |\mathbf{v}_o - \mathbf{u}|^2 R^2 \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \cos^2 \theta \sin \theta \mathbf{n}(\theta, \phi) \quad (\text{S2.58})$$

By viewing the process in the rest frame of the sphere, it is obvious that the net force will be in the direction of  $\mathbf{v}_o - \mathbf{u}$ . Thus we need only calculate

$$\begin{aligned} \mathbf{F} \cdot (\mathbf{v}_o - \mathbf{u}) &= -2mn_o |\mathbf{v}_o - \mathbf{u}|^3 R^2 \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos^3 \theta \sin \theta d\theta \\ &= -4\pi mn_o |\mathbf{v}_o - \mathbf{u}|^3 R^2 \left[ \frac{\cos^4 \theta}{4} \right]_0^{\pi/2} \\ &= \pi mn_o R^2 |\mathbf{v}_o - \mathbf{u}|^3 \end{aligned} \quad (\text{S2.59})$$

which implies that

$$\mathbf{F} = \pi mn_o R^2 |\mathbf{v}_o - \mathbf{u}| (\mathbf{v}_o - \mathbf{u}) \quad (\text{S2.60})$$

a result that differs only slightly from the two-dimensional case.

**Exercise 2.13** What is the mobility constant of a hard sphere in a very dilute ideal gas?

**Solution** The mobility constant is the constant  $\mu$  in the equation  $\mathbf{u} = \mu \mathbf{F}$ , relating the steady-state velocity of an object moving through a fluid to the force being exerted on the object. But, for steady-state motion, the

external force must balance the average force that the fluid particles are exerting on the object. Therefore, what we have to calculate is the average force exerted by the particles of a very dilute ideal gas on a sphere moving through the gas at velocity  $\mathbf{u}$ .

We view the gas as being composed of a very large number of single-velocity beams. The collection of all the gas particles with velocities in the element  $d^3v$  forms a single-velocity beam of density  $f(\mathbf{v})d^3v$ . That beam exerts an average force on the sphere of

$$d\mathbf{F} = \pi m R^2 f(\mathbf{v}) d^3v |\mathbf{v} - \mathbf{u}|(\mathbf{v} - \mathbf{u}) \quad (\text{S2.61})$$

The total force on the sphere is

$$\mathbf{F} = \pi m R^2 \int f(\mathbf{v}) |\mathbf{v} - \mathbf{u}|(\mathbf{v} - \mathbf{u}) d^3v \quad (\text{S2.62})$$

It is clear that the net force will be opposed to the velocity of the sphere  $\mathbf{u}$ , so that it is sufficient to calculate

$$\mathbf{F} \cdot \mathbf{u} = \pi m R^2 n (m/2\pi kT)^{3/2} \int e^{-mv^2/2kT} |\mathbf{v} - \mathbf{u}|(\mathbf{v} - \mathbf{u}) \cdot \mathbf{u} d^3v \quad (\text{S2.63})$$

Transforming the variable of integration to the relative velocity  $\mathbf{V} = \mathbf{v} - \mathbf{u}$ , using the approximations

$$e^{-m(\mathbf{V}+\mathbf{u})^2/2kT} \approx e^{-mV^2/2kT} (1 - m\mathbf{V} \cdot \mathbf{u}/kT) \quad (\text{S2.64})$$

and introducing spherical coordinates with the polar axis antiparallel to  $\mathbf{u}$ , we can write the integral for  $\mathbf{F} \cdot \mathbf{u}$  as

$$\begin{aligned} \mathbf{F} \cdot \mathbf{u} = & 2\pi^2 m R^2 n (m/2\pi kT)^{3/2} \int_0^\pi \sin \theta d\theta \\ & \times \int_0^\infty V^2 dV e^{-mV^2/2kT} \left(1 - \frac{m}{kT} uV \cos \theta\right) V^2 u \cos \theta \end{aligned} \quad (\text{S2.65})$$

Because the integral  $\int_0^\pi \cos \theta \sin \theta d\theta = 0$ , the first term in the parentheses vanishes. Thus  $\mathbf{F} \cdot \mathbf{u}$  can be written in terms of the integrals

$$\int_0^\pi \cos^2 \theta \sin \theta d\theta = \frac{2}{3} \quad (\text{S2.66})$$

and

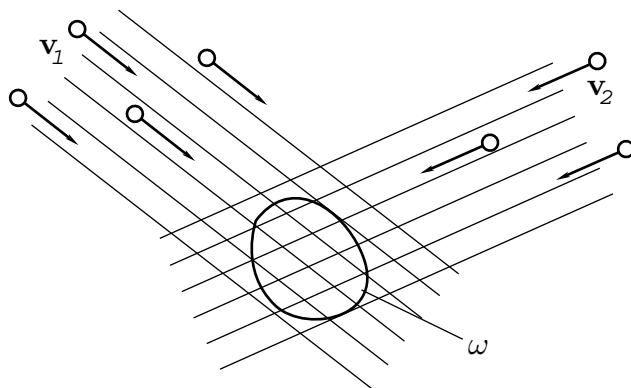
$$\int_0^\infty e^{-mV^2/2kT} V^5 dV = (2kT/m)^3 \quad (\text{S2.67})$$

when this is done, one gets

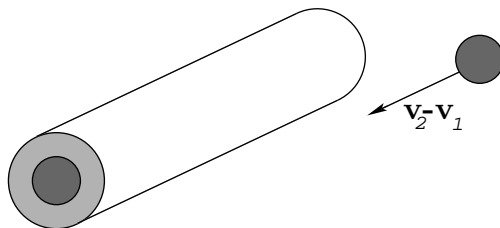
$$\mathbf{F} = -\frac{8}{3} (2\pi m kT)^{1/2} R^2 n \mathbf{u} \quad (\text{S2.68})$$

Note that, from this and Einstein's relation [Eq. (S2.43)], we can get the diffusion constant for hard spheres in a very dilute ideal gas.

$$D = \frac{8}{3} (2\pi m)^{1/2} (kT)^{3/2} R^2 n \quad (\text{S2.69})$$



**Fig. S2.9** At what rate do collisions occur within the volume  $\omega$ ?



**Fig. S2.10** In the frame of the first beam, the particles in the other beam have velocity  $\mathbf{v}_2 - \mathbf{v}_1$ . The length of the cylinder shown is  $|\mathbf{v}_2 - \mathbf{v}_1| dt$ . Its cross-sectional area is  $\pi d^2$ .

**Exercise 2.14** Two single-velocity beams are passing through the same volume  $\omega$ . They have densities  $n_1$  and  $n_2$  and velocities  $\mathbf{v}_1$  and  $\mathbf{v}_2$ . The particles in both beams are hard spheres of diameter  $d$ . At what rate do collisions occur within the volume  $\omega$ ? (See Fig. S2.9.)

**Solution** We observe the situation within the inertial frame of the first beam. Then there is a density  $n_1$  of stationary particles and a density  $n_2$  of particles with velocity  $\mathbf{v}_2 - \mathbf{v}_1$ . The number of stationary particles in  $\omega$  is  $n_1 \omega$ . The probability that one of those stationary particles will be hit within a time interval  $dt$  is equal to the probability that the center of one of the moving particles occupies the cylinder, of volume  $\pi d^2 |\mathbf{v}_2 - \mathbf{v}_1| dt$ , shown in Fig. S2.10. That probability is  $n_2 \pi d^2 |\mathbf{v}_2 - \mathbf{v}_1| dt$ . Thus the number of collisions within  $\omega$  during time interval  $dt$  is

$$dN = \omega n_1 n_2 \pi d^2 |\mathbf{v}_2 - \mathbf{v}_1| dt \quad (\text{S2.70})$$

and the rate of collisions within  $\omega$  is

$$R_{\text{coll}} = \omega n_1 n_2 \pi d^2 |\mathbf{v}_2 - \mathbf{v}_1| \quad (\text{S2.71})$$

Notice that the rate is symmetric with respect to exchange of  $\mathbf{v}_1$  and  $\mathbf{v}_2$ , which shows that we would have obtained the same result by making the calculation in the rest frame of the second beam.

**Exercise 2.15** Within a volume  $\omega$  in an ideal gas of spherical particles of diameter  $d$ , at what rate do collisions occur?

**Solution** Within  $\omega$ , the rate of collisions between pairs of particles, of which one particle has velocity in the range  $d^3 v_1$  and the other has velocity in the range  $d^3 v_2$  is

$$R_{\mathbf{v}_1 \mathbf{v}_2} = \pi \omega d^2 f(\mathbf{v}_1) d^3 v_1 f(\mathbf{v}_2) d^3 v_2 |\mathbf{v}_1 - \mathbf{v}_2| \quad (\text{S2.72})$$

By integrating  $\mathbf{v}_1$  and  $\mathbf{v}_2$  over their full ranges, we obtain twice the total collision rate within  $\omega$  because we count collisions between particles of velocities  $\mathbf{v}$  and  $\mathbf{v}'$  when  $\mathbf{v}_1 = \mathbf{v}$  and  $\mathbf{v}_2 = \mathbf{v}'$  and also when  $\mathbf{v}_1 = \mathbf{v}'$  and  $\mathbf{v}_2 = \mathbf{v}$ . Thus the total collision rate is

$$R = \frac{1}{2} \pi \omega d^2 \int f(\mathbf{v}_1) f(\mathbf{v}_2) |\mathbf{v}_1 - \mathbf{v}_2| d^3 \mathbf{v}_1 d^3 \mathbf{v}_2 \quad (\text{S2.73})$$

We transform to center-of-mass and relative velocities,  $\mathbf{u} = \mathbf{v}_1 - \mathbf{v}_2$  and  $\mathbf{V} = (\mathbf{v}_1 + \mathbf{v}_2)/2$ .

$$\begin{aligned} f(\mathbf{v}_1) f(\mathbf{v}_2) &= n^2 (m/2\pi kT)^3 \exp[-m(v_1^2 + v_2^2)/2kT] \\ &= n^2 (m/2\pi kT)^3 \exp\left[-\left(\frac{m}{4} u^2 + mV^2\right)/kT\right] \end{aligned} \quad (\text{S2.74})$$

With this transformation,

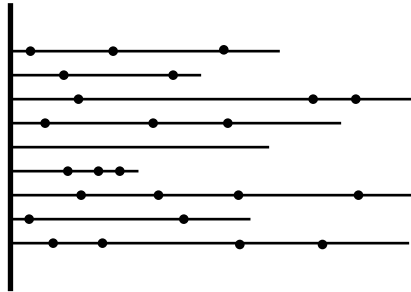
$$\begin{aligned} R &= \frac{1}{2} \pi \omega d^2 n^2 (m/2\pi kT)^3 \int e^{-mV^2/kT} d^3 V \int e^{-mu^2/4kT} |\mathbf{u}| d^3 u \\ &= 2\omega d^2 n^2 \sqrt{\pi kT/m} \end{aligned} \quad (\text{S2.75})$$

**Exercise 2.16** In an ideal gas of density  $n$  at temperature  $T$ , what is the total distance traveled by all the particles within a volume  $\omega$  during one second?

**Solution** The number of particles is  $n\omega$ . Their average speed is  $\bar{v} = \sqrt{8kT/\pi m}$ . Therefore, the total distance traveled by all particles together is

$$s = n\omega\bar{v} = n\omega\sqrt{8kT/\pi m} \tag{S2.76}$$

**Exercise 2.17** Given the results of the previous two exercises, what is the average distance between collisions of a particle in an ideal gas?



**Fig. S2.11** Each line represents the absolute distances traveled by one particle. The dots are points where the particle collided with another particle.

**Solution** Let us imagine that Fig. S2.11 shows a graph of the absolute distances traveled by each of the particles in a volume  $\omega$  in an ideal gas during one second. For each particle, a dot has been drawn at the location of each collision involving that particle. Note that each collision creates two dots on the diagram because it involves two particles. The total length of the lines is  $s = n\omega\sqrt{8kT/\pi m}$ . The total number of dots is  $2R = 4\omega d^2 n^2 \sqrt{\pi kT/m}$ . Therefore, the average distance between dots on the lines (that is, the mean free path of the particles) is

$$\ell = \frac{s}{2R} = \frac{1}{\sqrt{2}\pi d^2 n} \tag{S2.77}$$

**Exercise 2.18** An ideal gas of  $A$  particles contains a low density of  $B$  particles. The diffusion constant for the  $B$  particles, defined in Eq. (S2.38), is  $D$ . Assume that the initial density of the  $B$  particles,  $n(x, 0)$ , depends only on the variable  $x$ . Derive a differential equation, the *diffusion equation*, for  $n(x, t)$ .

**Solution** Consider a cylinder of unit cross-sectional area whose axis is parallel to the  $x$  axis. Let  $N(x_o, t)$  be the total number of  $B$  particles within the cylinder to the left of the plane  $x = x_o$ . By the meaning of the  $B$  particle flux, it is clear that

$$\frac{\partial N(x, t)}{\partial t} = -J(x, t) = D \frac{\partial n(x, t)}{\partial x} \tag{S2.78}$$

where  $J$  is the flux at position  $x$  at time  $t$ . But, by the definition of the particle density, it is also true that  $n(x, t) = \partial N(x, t)/\partial x$ . Differentiating Eq. (S2.78) with respect to  $x$  and using the fact that  $\partial^2 N/\partial x \partial t = \partial n/\partial t$  gives the desired equation.

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \tag{S2.79}$$

**Exercise 2.19** A *Brownian particle* is a particle in a fluid that is large enough to be observed in an ordinary microscope (which means that it must be much larger and heavier than the fluid molecules) but is still small enough that its gradual drift due to the impulses delivered to it by rebounding fluid particles is observable in the same microscope. The thermal motion of a truly macroscopic object is much too small to

be observable. The resultant random drifting motion of such a particle is called *Brownian motion*. Consider a dilute mixture, sometimes called a suspension, of identical Brownian particles in water. Assume that the particles, in water, are known to have a diffusion constant  $D$ . A particle begins at time 0 with  $x$  coordinate 0. What is the probability distribution for its  $x$  coordinate at time  $t$ ?

**Solution** Imagine a system of pure water with a large collection of the Brownian particles randomly distributed over the plane  $x = 0$ . The initial density of Brownian particles would be

$$n(x, 0) = C \delta(x) \quad (\text{S2.80})$$

where  $C$  is some positive constant equal to the two-dimensional density of the particles in the  $y$ - $z$  plane. After time zero, the density of Brownian particles will satisfy the diffusion equation

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n(x, t)}{\partial x^2} \quad (\text{S2.81})$$

We are now faced with a mathematical problem of finding a solution of the diffusion equation that satisfies the initial condition given by Eq. (S2.80). In order to guess the form of the solution, it is best to think about the physics of the Brownian motion process. The particle drifts a noticeable amount during a given time interval because it is being knocked randomly left and right by individually unnoticeable amounts very many times during the time interval. Its final  $x$  displacement is the sum of a very large number of separate  $x$  displacements. It is natural to guess that the probability distribution for an individual particle's  $x$  coordinate will be a Gaussian function of the form predicted by the central limit theorem. The density of particles at time  $t$  will certainly be proportional to the probability density for an individual particle. Therefore we try a solution of the form

$$n(x, t) = C \sqrt{\gamma(t)/\pi} e^{-\gamma(t)x^2} \quad (\text{S2.82})$$

where  $\gamma(t)$  is, as yet, unknown. The square root factor is necessary in order to maintain normalization. Since the particles are conserved, it is necessary that

$$\int_{-\infty}^{\infty} n(x, t) dx = C \int_{-\infty}^{\infty} \delta(x) dx = C \quad (\text{S2.83})$$

Putting this form into the differential equation, we get

$$\begin{aligned} \left(\frac{1}{2}\gamma^{-1/2} - \gamma^{1/2}x^2\right)\frac{d\gamma}{dt} &= -4D\left(\frac{1}{2}\gamma^{3/2} - \gamma^{5/2}x^2\right) \\ &= -4D\left(\frac{1}{2}\gamma^{-1/2} - \gamma^{1/2}x^2\right)\gamma^2 \end{aligned}$$

which would be satisfied if

$$\frac{d\gamma/dt}{\gamma^2} = -\frac{d(1/\gamma)}{dt} = -4D \quad (\text{S2.85})$$

or  $1/\gamma = 4Dt$ . Thus the solution of Eq. (S2.81) is

$$n(x, t) = \frac{C}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \quad (\text{S2.86})$$

The probability density for a single particle differs from the particle density for the ensemble of Brownian particles only by its normalization. Therefore

$$P(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \quad (\text{S2.87})$$

**Historical note:** In the year 1828, the botanist Robert Brown detected, in a suspension of fine pollen grains in water, an irregular “swarming motion.” He attributed it to a somewhat mystical primitive life force. A long period of controversy followed regarding the question of whether the Brownian motion was a genuine effect or was only an artifact of his experiment, due to vibrations of the microscope, currents in the water



caused by evaporation, etc. By 1905, when Einstein’s theoretical explanation and mathematical analysis of the effect appeared, it had been confirmed unambiguously that an irregular diffusive motion with no apparent energy source continued indefinitely within a closed system of small suspended particles. Stimulated by Einstein’s analysis, a number of experimental physicists, but most notably the French physicist Perrin, made detailed quantitative experimental studies of Brownian motion. These studies had two important effects.

1. They completely confirmed the fundamental concept, which was controversial at that time, that heat was simply microscopic kinetic energy.
2. They allowed, using Einstein’s theoretical analysis, a determination, for the first time, of the mass of individual molecules and, from that, of Avogadro’s number.

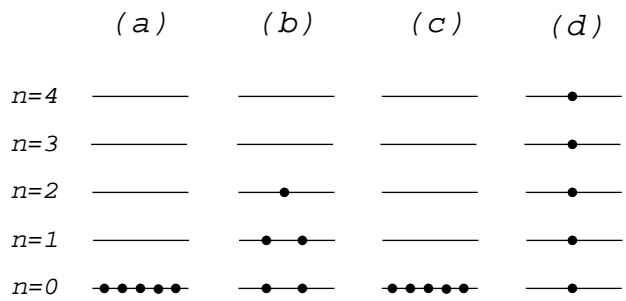
A more recent study (see *Scientific American*, August 1991) has concluded that, with Brown’s experimental techniques, the size and density of pollen grains, and the microscopes available at the time of Brown’s experiments, Brown could not possibly have seen what is now called Brownian motion. What Brown saw really was an artifact of his experimental technique. He has immortalized his name by a lucky fluke!

**Exercise 2.20** A harmonic oscillator potential is a potential of the form  $U(x) = \frac{1}{2}kx^2$ . A single particle of mass  $m$  in a harmonic oscillator potential has quantum mechanical energy levels

$$E_n = \hbar\omega(n + \frac{1}{2}) \tag{S2.88}$$

where  $n = 0, 1, 2, \dots$  and  $\omega = \sqrt{k/m}$ , which is the angular frequency of vibration of a classical particle in the same potential. What is the energy and degeneracy of the ground state of a system of five noninteracting particles in a harmonic oscillator potential in the cases that (a) the particles are spin-0 bosons, (b) the particles are spin- $\frac{1}{2}$  fermions, (c) the particles are spin- $\frac{1}{2}$  bosons, and (d) the particles are spin-0 fermions? Note: cases (c) and (d) are known to be impossible. (See Fig. S2.12.)

**Solution** (a) For bosons, any number of particles may occupy a given single-particle quantum state. The five-particle ground state is obtained by putting all the particles in the single-particle state with quantum number  $n = 0$ . Thus  $E_g = \frac{5}{2}\hbar\omega$ . The ground-state is clearly unique; that is, it has degeneracy one. (b) For spin- $\frac{1}{2}$  fermions, each single-particle state can hold two particles of opposite spin. The spin of the particle in the  $n = 2$  state can be either up or down, giving the five-particle ground state a degeneracy of two. The ground-state energy is  $E_g = 2(\hbar\omega/2) + 2(3\hbar\omega/2) + (5\hbar\omega/2) = 13\hbar\omega/2$ . (c) This has the same energy as case (a), but the number of spin-up particles can vary from 0 to 5, giving the ground state a degeneracy of 6. (d) Only one particle can go into each single-particle state. Thus  $E_g = 25\hbar\omega/2$  and the state is nondegenerate.



**Fig. S2.12** The ground-state configurations in the four cases.

**Exercise 2.21** For particles in a one-dimensional hard-walled box of length  $\pi$ , the single-particle energy eigenstates are  $u_n(x) = \sqrt{2/\pi} \sin(nx)$ , where  $n = 1, 2, \dots$ . If we assume that the particles are bosons, and ignore the problem of normalization, what is the explicit form of the three-particle wave function associated with the occupation numbers  $N_1 = 2, N_2 = 1, N_3 = N_4 = \dots = 0$ ?

**Solution**

$$\psi(x_1, x_2, x_3) = A \sum_{\text{perm}} u_1(x_i)u_1(x_j)u_2(x_k) \tag{S2.89}$$

where  $A$  is a normalization constant and in the sum  $(i, j, k)$  take the values  $(1,2,3)$ ,  $(1,3,2)$ ,  $(3,1,2)$ ,  $(3,2,1)$ ,  $(2,3,1)$ , and  $(2,1,3)$ . The result is

$$\begin{aligned} \psi = & A(\sin(x_1) \sin(x_2) \sin(2x_3) + \sin(x_1) \sin(x_3) \sin(2x_2) \\ & + \sin(x_2) \sin(x_3) \sin(2x_1)) \end{aligned} \quad (\text{S2.90})$$

**Exercise 2.22** For a particle of mass  $m$  in a two-dimensional periodic box of area  $L^2$ : (a) how many single-particle quantum states are there with energies less than  $E$ ? (b) What is the density of single-particle quantum states as a function of energy? (c) If  $m = m_e$ , and  $L = 1$  cm, what is the numerical value of the density of single-particle quantum states?

**Solution** (a) The Schrödinger energy equation for the system is

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) = Eu \quad (\text{S2.91})$$

with the periodic boundary conditions

$$u(0, y) = u(L, y) \quad \text{and} \quad u(x, 0) = u(x, L) \quad (\text{S2.92})$$

The solutions of this equation are plane waves of the form

$$u(x, y) = A \exp[i(k_1 x + k_2 y)] \quad (\text{S2.93})$$

where

$$(k_1, k_2) = \left( \frac{2\pi}{L} K_1, \frac{2\pi}{L} K_2 \right) \quad (\text{S2.94})$$

and  $K_1$  and  $K_2$  are integers. The corresponding energy eigenvalue is

$$E(k_1, k_2) = \frac{\hbar^2(k_1^2 + k_2^2)}{2m} \quad (\text{S2.95})$$

If we plot these allowed wave vectors on a two-dimensional  $\mathbf{k}$  plane, they form a square lattice with a spacing of  $2\pi/L$  (see Fig. 2.5). For a given value of energy  $E$ , the states with energy less than  $E$  all fall within a circle whose radius is  $k = \sqrt{2mE}/\hbar$ . The number of such states is

$$N(E) = \frac{\pi k^2}{(2\pi/L)^2} = \frac{mEL^2}{2\pi\hbar^2} \quad (\text{S2.96})$$

(b) The density of eigenstates is

$$\frac{dN(E)}{dE} = \frac{mL^2}{2\pi\hbar^2} \quad (\text{S2.97})$$

(c) For  $m = m_e$  and  $L = 10^{-2}$  m,  $dN(E)/dE = 1.3 \times 10^{33}$  states/joule.

**Exercise 2.23** 1200 particles are to be distributed among three energy states with energies  $\varepsilon_1 = 1$  eV,  $\varepsilon_2 = 2$  eV, and  $\varepsilon_3 = 3$  eV. Assume that the total energy is 2400 eV and that each possible microstate is equally probable. (a) What is the probability distribution for the number of particles in state 1 if the particles are distinguishable? (b) What is the probability distribution for the number of particles in state 1 if the particles are Bose–Einstein particles?

**Solution** (a) For distinguishable particles, a microstate is defined by giving the energy value of each particle. That is  $E_1, E_2, \dots, E_{1200}$ , where  $E_k$  can be  $\varepsilon_1, \varepsilon_2$ , or  $\varepsilon_3$ . Let  $N_1, N_2$ , and  $N_3$  represent the number of particles in each energy state. The number of microstates with given values of  $N_1, N_2$ , and  $N_3$  is

$$K = \frac{1200!}{N_1!N_2!N_3!} \quad (\text{S2.98})$$

The restriction that  $E = 2400$  eV will be satisfied if and only if  $N_3 = N_1$ . But also,  $N_1 + N_2 + N_3 = 1200$ . Thus only  $N_1$  is independent. For any  $N_1$  between 0 and 600,

$$N_3 = N_1 \quad \text{and} \quad N_2 = 1200 - 2N_1 \tag{S2.99}$$

When we take the restrictions into account, the number of microstates with a given value of  $N_1$  is

$$K(N_1) = \frac{1200!}{(N_1!)^2(1200 - 2N_1)!} \tag{S2.100}$$

To find the most likely value of  $N_1$  we let

$$F(N_1) = \log K(N_1) \approx 1200 \log(1200) - 2N_1 \log N_1 - (1200 - 2N_1) \log(1200 - 2N_1) \tag{S2.101}$$

and set  $dF(N_1)/dN_1 = 0$ , getting

$$-2 \log N_1 + 2 \log(1200 - 2N_1) = 0 \tag{S2.102}$$

or  $(1200 - 2N_1)/N_1 = 1$ , whose solution is  $N_1 = 1200/3 = 400$ .

We will calculate  $P(N_1)/P(400) = \exp[F(N_1) - F(400)]$ . A bit of algebra and use of the expansion,  $\log(1 + \varepsilon) \approx \varepsilon - \varepsilon^2/2$  will show that

$$F(400 + n) - F(400) \approx -3n^2/400 \tag{S2.103}$$

or

$$\frac{P(400 + n)}{P(400)} = e^{-3n^2/400} \tag{S2.104}$$

(b) For Bose–Einstein particles, specifying  $N_1$ ,  $N_2$ , and  $N_3$  completely specifies the 1200-particle quantum state. But Eq. (S2.99) gives  $N_2$  and  $N_3$  in terms of  $N_1$ . For any  $N_1$  between 0 and 600, there is exactly one microstate, and therefore all values of  $N_1$  in that range are equally probable.

**Exercise 2.24** What is the maximum value of the function

$$F(x_1, x_2, \dots, x_{10}) = \sum_{n=1}^{10} n x_n^2 \tag{S2.105}$$

subject to the constraint

$$\sum_{n=1}^{10} x_n = 1 \tag{S2.106}$$

**Solution** Using Lagrange’s method, we look at the function

$$G = \sum_{n=1}^{10} n x_n^2 - \lambda \sum_{n=1}^{10} x_n \tag{S2.107}$$

The unconstrained maximum of  $G$  is given by

$$\frac{\partial G}{\partial x_n} = 2n x_n - \lambda = 0 \tag{S2.108}$$

or  $x_n = \lambda/2n$ . The value of  $\lambda$  is determined by the constraint equation

$$\sum_{n=1}^{10} x_n = \frac{\lambda}{2} \sum_{n=1}^{10} \frac{1}{n} = 1 \tag{S2.109}$$

which gives

$$\lambda = 2 \left( \sum_{n=1}^{10} \frac{1}{n} \right)^{-1} = 0.68283 \quad (\text{S2.110})$$

Then

$$F = \sum_{n=1}^{10} n \left( \frac{\lambda}{2n} \right)^2 = \frac{\lambda^2}{4} \sum_{n=1}^{10} \frac{1}{n} = \frac{\lambda}{2} = 0.341417 \quad (\text{S2.111})$$

**Exercise 2.25** In Exercise 2.22 it was shown that the number of single-particle quantum states of a two-dimensional quantum gas with energies within the interval  $dE$  is equal to  $(mL^2/2\pi\hbar^2) dE$ . (a) What is the spatial density of particles in a two-dimensional Fermi–Dirac gas as an explicit function of temperature and affinity? (b) For particles of electronic mass and  $T = 300$  K, what value of  $\alpha$  will give a density of 1 particle per square Ångström?

**Solution** (a) For given values of  $\alpha$  and  $\beta = 1/kT$ , the average number of particles in a single quantum state of energy  $\varepsilon$  is  $(e^{\alpha+\beta\varepsilon} + 1)^{-1}$ . The number of quantum states in energy interval  $d\varepsilon$  is  $(mL^2/2\pi\hbar^2) d\varepsilon$ . Thus the average number of particles in all quantum states is

$$\begin{aligned} N &= \int_0^\infty \frac{(mL^2/2\pi\hbar^2) d\varepsilon}{e^{\alpha+\beta\varepsilon} + 1} \\ &= \frac{mL^2}{2\pi\hbar^2} \int_0^\infty \frac{e^{-\beta\varepsilon} d\varepsilon}{e^\alpha + e^{-\beta\varepsilon}} \end{aligned} \quad (\text{S2.112})$$

Changing the integration variable to  $x = e^{-\beta\varepsilon}$  and  $dx = -\beta e^{-\beta\varepsilon} d\varepsilon$ , we can write  $N$  as

$$\begin{aligned} N &= \frac{kTmL^2}{2\pi\hbar^2} \int_0^1 \frac{dx}{e^\alpha + x} \\ &= \frac{kTmL^2}{2\pi\hbar^2} \left[ \log(e^\alpha + x) \right]_0^1 \\ &= \frac{kTmL^2}{2\pi\hbar^2} [\log(1 + e^\alpha) - \alpha] \end{aligned} \quad (\text{S2.113})$$

The spatial density of particles is  $N/L^2$ , or

$$n = \frac{mkT}{2\pi\hbar^2} [\log(1 + e^\alpha) - \alpha] \quad (\text{S2.114})$$

(b) Setting  $n = 10^{20}$  particles/m<sup>2</sup> and  $T = 300$  K, we get

$$\log(1 + e^\alpha) - \alpha = 1821 \quad (\text{S2.115})$$

The function on the left becomes large for large negative values of  $\alpha$ . If  $\alpha$  is large and negative, then  $e^\alpha$  is very small and

$$\log(1 + e^\alpha) - \alpha \approx e^\alpha - \alpha \approx -\alpha \quad (\text{S2.116})$$

Therefore,  $\alpha \approx -1821$ .

**Exercise 2.26** What is the density  $n$  as a function of  $T$  and  $\alpha$  if the particles of the previous question are bosons?

**Solution** For Bose–Einstein particles, Eq. (S2.112) must be replaced by

$$\begin{aligned} N &= \frac{mL^2}{2\pi\hbar^2} \int_0^\infty \frac{d\varepsilon}{e^{\alpha+\beta\varepsilon} - 1} \\ &= \frac{mkTL^2}{2\pi\hbar^2} \int_0^1 \frac{dx}{e^\alpha - x} \\ &= \frac{mkTL^2}{2\pi\hbar^2} \left[ -\log(e^\alpha - x) \right]_0^1 \\ &= \frac{mkTL^2}{2\pi\hbar^2} [\alpha - \log(e^\alpha - 1)] \end{aligned} \quad (\text{S2.117})$$

or

$$n = \frac{mkT}{2\pi\hbar^2} [\alpha - \log(e^\alpha - 1)] \quad (\text{S2.118})$$