Reading assignment. Schroeder, section **2.6**.

1   Multiplicity of the ideal gas

Our evaluation of the numbers of microstates corresponding to each macrostate of the two-state paramagnet and the Einstein model of a crystal were based on simple combinatorial arguments that worked well in the context of quantization of the constituent states of those systems. Now we want to take a look at the classical ideal gas, which appears to be fundamentally different in that the states of classical particles are specified by continuous position and momentum variables. That turns out not to be too much of a barrier, so it is possible to calculate the probability distribution of the macrostates of a system with continuous parameters defining the microstates—one merely has to resort to integration instead of summation. However, the result turns out to be inconsistent with a quantum mechanical analysis of the system, even when the classical limit of the quantum system is taken. Essentially, there is a macroscopically measurable effect due to quantization on the microscopic level, much as the macroscopically measurable spectrum of black-body radiation was found by Planck more than a century ago to require the assumption of microscopic quantization of electromagnetic mode energies. Thus, we will be forced either to quantize the ideal gas or to resort to some hand waving or some difficult mathematics in order to graft on at the end the bits needed for consistency with quantum mechanics. Since quantum systems are so much easier to handle statistically, we'll take the former approach.

Recall that the ideal gas is a collection of essentially independent particles— if they interact with each other, other than through point collisions, then the presence of some of the particles will influence the states of other particles. We don't want to deal with that added complexity at this stage. Furthermore, we'll assume the gas is sufficiently dilute that we won't have to think about whether any of the particles have significant likelihood of attempting to occupy the same single-particle state. If that were the case, we would have to take into consideration whether the particles were bosons or fermions, that is, whether the multiparticle states (the microstates) were required to have wave functions that were symmetric or antisymmetric under particle interchange. That's a problem we'll handle some time in the future.

Finally, we'll assume the gas is monatomic—it has no internal degrees of freedom to be considered.

1.1   Quantization of free-particle states

This requires only the simplest of quantum mechanics, the particle-in-a-box problem, but we'll do it with a bit of a twist that may not be so familiar.

Let's begin by laying out the conditions for the quantum problem of an ideal gas:

- No external interactions—$V(\mathbf{r}) = 0$

- No interparticle interactions (ideal gas, independent particles)

- "Confinement" to a large, but finite-sized box. This is traditionally done by using an infinite potential at the boundaries of the box, leading to a boundary condition that requires the wave functions to vanish at and outside the boundaries. For a single particle in one dimension, this boundary condition can be written:

$$\psi\left(|x| \geq \frac{L}{2}\right) = 0\,, \tag{1}$$

  assuming the box is centered at the origin and has width L, which we take to be of macroscopic proportions. This scheme turns out to be a bit inconvenient for us, mainly because the reflecting walls complicate the counting of states a bit. Instead, we'll make the walls effectively transparent, eliminating the confining potential while using periodic boundary conditions:

$$\psi(x, y, z) = \psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L)\,, \tag{2}$$

  for a cubic box of side L. Essentially, this amounts to wrapping opposing surfaces around to meet each other. In two dimensions, this would take a rectangular box into a torus, but in three dimensions it would be topologically impossible to construct an actual container that satisfies periodic boundary conditions. Nevertheless, we'll find it mathematically convenient.

The time-independent Schrödinger equation for a single particle then looks like

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = E\psi(\mathbf{r})\,, \tag{3}$$

and its solutions are plane waves:

$$\psi(\mathbf{r}) = \left(\frac{1}{L}\right)^{3/2} e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}\,, \tag{4}$$

where $\mathbf{p}$ is the particle's momentum, $E = p^2/2m$, and we've omitted the time dependence.

Now, if the particle were completely free, $\mathbf{p}$ could take on any vector value. But we are imposing periodic boundary conditions, and this restricts the possible values of $\mathbf{p}$ to a discrete set. To see how this happens, consider an arbitrary spatial translation by a multiple of the box:

$$\mathbf{R} = (n_1\hat{\mathbf{x}} + n_2\hat{\mathbf{y}} + n_3\hat{\mathbf{z}})L\,, \tag{5}$$

where the n_i are integers, possibly negative. The periodic boundary conditions require that

$$\psi(\mathbf{r} + \mathbf{R}) = \psi(\mathbf{r}) \tag{6}$$

for any choice of the n_i. Thus (ignoring the normalization constant):

$$\underbrace{e^{\frac{i}{\hbar}\mathbf{P}\cdot(\mathbf{r}+\mathbf{R})}}_{\psi(\mathbf{r}+\mathbf{R})} = \underbrace{e^{\frac{i}{\hbar}\mathbf{P}\cdot\mathbf{r}}}_{\psi(\mathbf{r})} \times \underbrace{e^{\frac{i}{\hbar}\mathbf{P}\cdot\mathbf{R}}}_{\text{must be 1}} . \tag{7}$$

This implies that

$$\frac{1}{\hbar}\mathbf{p} \cdot \mathbf{R} = 2\pi n, \ n \text{ some integer}, \tag{8}$$

which in turn implies that

$$n_1 p_x + n_2 p_y + n_3 p_z = \frac{2\pi}{L}n\hbar. \tag{9}$$

The only way this can hold for all values of n_1, n_2, and n_3 is if

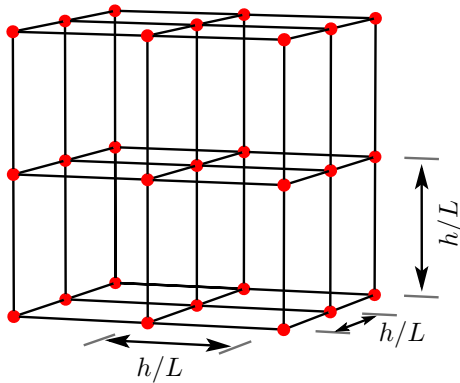$$p_x = \frac{2\pi}{L}\hbar K_x \tag{10}$$

$$p_y = \frac{2\pi}{L}\hbar K_y \tag{11}$$

$$p_z = \frac{2\pi}{L}\hbar K_z , \tag{12}$$

where the K_i are integers, possibly negative. Thus, the values of $\mathbf{p}$ form a discrete, cubic lattice in momentum space, with lattice constant

$$\frac{2\pi}{L}\hbar = \frac{h}{L} : \tag{13}$$

This gives us the key to counting the states. For each lattice point in the momentum-space grid, there is a momentum state that the particle could

occupy. That is, the constituent (or single-particle) states are eigenstates of momentum, with the momentum being one of the points on that lattice.

Since we envision the gas being isolated, the energy must be fixed, which also fixes the magnitude of the momentum of the particle:

$$U = \frac{p^2}{2m} = \frac{h^3}{V}\left(K_x^2 + K_y^2 + K_z^2\right), \tag{14}$$

where $V = L^3$ is the volume of the physical container holding the particle. This means the values of the three integers K_i specifying the state of the particle are constrained by the fixed energy in such a way that the allowed set of points in the momentum-space lattice must lie on the surface of a sphere of radius $p = \sqrt{2mU}$ in momentum space.

Now if V, hence L, is macroscopic in size, then h/L is an extremely tiny momentum spacing on the scale of the momenta of typical gas particles at room temperature. So we must envision a sphere in momentum space that encloses a huge number of finely spaced grid points representing a huge number of states. On that scale, the points on the momentum-space lattice look almost like a continuum. Each unit cell of the lattice, corresponding to a single momentum state has "volume"

$$V_{p,\,\text{cell}} = \frac{h^3}{V} \tag{15}$$

in momentum space. To count the number of momenta having the allowed energy, we merely need to compute the volume of a thin spherical shell of radius $\sqrt{2mU}$ and divide that by the volume per allowed momentum point:

$$\text{Number of allowed momenta} = \frac{\text{volume of shell in momentum space}}{V_{p,\,\text{cell}}}$$
$$= \frac{V_{p,\,\text{shell}}}{V_{p,\,\text{cell}}}. \tag{16}$$

If there were two particles in one dimension, the specification of a microstate of the system would require two momentum coordinates, one for each particle, and the possible momenta would form a square lattice in two dimensions, one for each particle. Each lattice point then specifies the single-particle momentum states of *both* particles. The "sphere" defining the states allowed by the fixed-energy constraint would just be a circle with radius $\sqrt{2mU}$. The combination of the momenta of the two particles into a single two-dimensional momentum space reflects the fact that the energy constraint applies to the sum of the energies of the particles, so that the total can be distributed in many ways between them.

The generalization to many particles in three dimensions is then clear. The momentum space has $3N$ dimensions, the volume of each unit cell in the lattice of possible momenta is

$$V_{p,\,\text{cell}} = \frac{h^{3N}}{V^N}, \tag{17}$$

and the shell defining the states allowed by the energy constraint lives in a $3N$-dimensional space. For macroscopic systems N is of order 10^{23}, so we're going to have to deal with a lot of dimensions in order to count the states.

The solution to our problem requires evaluation of the volume $V_{p,\,\mathrm{shell}}$ of a thin shell of given radius, say $r = \sqrt{2mU}$, in a large number of dimensions, say $n = 3N$. That volume is the surface area $A_{p,\,\mathrm{shell}}$ multiplied by some small thickness, which we needn't bother to specify for now. The surface-area calculation is conveniently done by calculating the volume of the bounding sphere $V_{p,\,\mathrm{sphere}}$ in momentum space, then differentiating the result with respect to radius.

The volume of an n-dimensional sphere can be calculated as follows. First, we express the volume of interest in terms of an integral over all of the n-dimensional space, with an integrand that is one inside the sphere and zero outside. The condition for being inside the sphere is conveniently expressed as

$$\sum_{i=1}^{n} x_i^2 < r^2 \,, \tag{18}$$

so the integrand is conveniently expressed in terms of a unit step function:

$$V_n(r) = \int \theta\left(r^2 - \sum_{i=1}^{n} x_i^2\right) d^n x \,, \tag{19}$$

where

$$\theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \,. \end{cases} \tag{20}$$

Next we reduce the calculation to that of the volume of a unit sphere in n dimensions:

$$\begin{aligned} V_n(r) &= \int \theta\left(r^2 - \sum_{i=1}^{n} x_i^2\right) d^n x \\ &= \int \theta\left[1 - \sum_{i=1}^{n} \left(\frac{x_i}{r}\right)^2\right] d^n x \\ &= r^n \underbrace{\int \theta\left(1 - \sum_i y_i^2\right) d^n y,}_{V_n(1)\ (\text{unit sphere})} \end{aligned} \tag{21}$$

where we've made use of the fact that $\theta(rx) = \theta(x)$, and we've made the substitution $y_i = x_i/r$, so that $dx_i = r\,dy_i$. Now the volume element $d^n y$ in n dimensional spherical coordinates is not quite obvious, so we resort to a little trickery to evaluate the integral. We know that the derivative of a

5

unit step function is just a delta function:

$$\frac{d\theta(x)}{dx} = \delta(x) \tag{22}$$

and that δ functions are easy to integrate. So we differentiate $V_n(r)$ with respect to r:

$$\frac{d}{dr} \int \theta \left(r^2 - \sum_i x_i^2 \right) d^n x = \frac{d}{dr} [r^n V_n(1)], \tag{23}$$

which yields

$$\int 2r\delta \left(r^2 - \sum_i x_i^2 \right) d^n x = nr^{n-1} V_n(1). \tag{24}$$

This, by the way, is precisely the surface area we seek, so once we find the volume $V_n(1)$ of a unit sphere, it's a simple matter to find either the surface area or the volume of the sphere of radius r.

It's easy to integrate on the one-dimensional variable r because of the δ function, so we multiply this by a factor that will yield easy integrals on the x_i after integration on r: e^{-r^2}. Then we have

$$\underbrace{\int \int_0^\infty \delta \left(r^2 - \sum_i x_i^2 \right) e^{-r^2} \underbrace{2r \, dr}_{d(r^2)} \, d^n x}_{e^{-\sum_i x_i^2} = \prod_i e^{-x_i^2}} = nV_n(1) \int_0^\infty r^{n-1} e^{-r^2} \, dr$$

$$= nV_n(1) \frac{1}{2} \underbrace{\int_0^\infty (r^2)^{(n-2)/2} e^{-r^2} \underbrace{2r \, dr}_{d(r^2)}}_{\Gamma\left(\frac{n}{2}\right)} . \tag{25}$$

This reduces to:

$$\underbrace{\left(\int_{-\infty}^\infty e^{-x^2} \, dx \right)^n}_{\sqrt{\pi}} = V_n(1) \underbrace{\frac{n}{2}\Gamma\left(\frac{n}{2}\right)}_{\Gamma\left(\frac{n}{2}+1\right)} , \tag{26}$$

from which we immediately obtain the volume of the unit sphere

$$V_n(1) = \frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2}+1\right)} . \tag{27}$$

This gives us all we need to find the volume of the n-dimensional sphere of radius r:

$$V_n(r) = r^n V_n(1) = r^n \frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2}+1\right)} \tag{28}$$

and the surface area:

$$A_n(r) = nr^{n-1}V_n(1)$$

$$= nr^{n-1}\frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2}+1\right)} \qquad (29)$$

$$= r^{n-1}\frac{2\pi^{n/2}}{\Gamma\left(\frac{n}{2}\right)}.$$

Exercise. Show that for the familiar cases $n = 3$, $n = 2$, and $n = 1$, the expression we've derived for the volume of an n-dimensional sphere gives the expected result. This may be useful:

$$\Gamma\left(\frac{1}{2}\right) = \left(-\frac{1}{2}\right)! = \int_0^\infty t^{-1/2}e^{-t}dt$$

$$= 2\int_0^\infty e^{-x^2}dx \qquad (30)$$

$$= \sqrt{\pi},$$

where I've used the substitution $t = x^2$ to obtain the form on the second line.

Now let's put our results back into the expression for the number of allowed momenta. The number of dimensions is $n = 3N$, and we'll denote the thickness of the thin shell in the $3N$-dimensional momentum space by ϵ_p. Then we have

$$\text{Number of allowed momenta} = \frac{V_{p,\,\text{shell}}}{V_{p,\,\text{cell}}}$$

$$= \frac{V^N}{h^{3N}}\,\epsilon_p A_{p,\,\text{shell}} \qquad (31)$$

$$= \epsilon_p\frac{V^N}{h^{3N}}(2mU)^{(3N-1)/2}\frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}.$$

But this isn't yet the correct number of microstates of the gas in the macrostate characterized by the total energy U. The missing piece is that the atoms are indistinguishable. Given any particular set of occupied single-atom momentum states, that set being represented by a single point in the $3N$-dimensional momentum-space lattice, we could perform any permutation of the N atoms among those single-particle states to obtain an identical microstate that is represented by a different lattice point. Thus, the number of distinct microstates is the number of allowed momenta divided by $N!$, the number of permutations of the atoms among those states:

$$\Omega = \epsilon_p\frac{V^N}{N!\,h^{3N}}(2mU)^{(3N-1)/2}\frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}. \qquad (32)$$

That correction factor accounts for the fact that there are $N!$ different points in the $3N$-dimensional lattice that differ only in the interchange of some of the particles and thus really represent the same microstate.