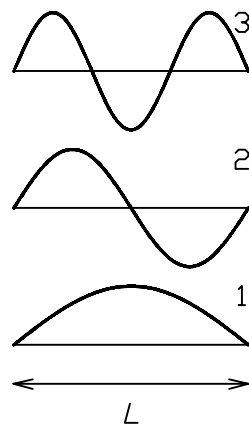


## States of a Particle in a Box.

In order to count states, we will use quantum mechanics to ensure that we have discrete states and energy levels. Let's consider a single particle which is confined to a cubical box of dimensions  $L \times L \times L$ . You might think that this is artificial and wonder how the physics could depend on the size of a box a particle is in? It is artificial and it's a trick to make the math easier. Once a box is big enough, the physics doesn't depend on the size of the box, and the physics we deduce must not depend in any critical way on the box size when we take the limit of a very big box. (Of course, the volume of a system is one of the extensive parameters that describes the system and it's OK for the volume to enter in a manner like it does in the ideal gas law!) In what follows, we'll ignore rotational and internal energy of the particles and drop the "tran" subscript.

As you probably know, particles are described by wave functions in quantum mechanics. The de Broglie relation between wavelength ( $\lambda$ ) and momentum ( $P$ ) is  $P = h/\lambda$ , where  $h$  is Planck's constant. The wave function for a particle in a box must be zero at the walls of the box (otherwise the particle might be found right at the wall). In one dimension, suitable wave functions are  $\psi(x) \propto \sin(n_x \pi x/L)$  where  $0 \leq x \leq L$  and  $n_x$  is an integer. This amounts to fitting an integer number of half wavelengths into the box. (If you recall the Bohr model of the atom, the idea there is to fit an integral number of wavelengths in the electron's orbit.) The momentum is  $P_x = \pm n_x h/2L = \pm n_x \hbar \pi/L$ . The  $\pm$  sign on the momentum indicates that the wave function is a standing wave that is a superposition of travelling waves moving in both directions. The first three wave functions are shown in the figure. In three dimensions, we have



$$\psi(x, y, z) \propto \sin(n_x \pi x/L) \sin(n_y \pi y/L) \sin(n_z \pi z/L),$$

which corresponds to fitting standing waves in all three directions in the box. The momentum is

$$\mathbf{P} = \frac{\pi \hbar}{L} (\pm n_x, \pm n_y, \pm n_z).$$

The energy is

$$E = \frac{P^2}{2m} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2).$$

Now we are getting close to being able to count states. Consider a three dimensional coordinate system with axes  $n_x$ ,  $n_y$ ,  $n_z$  (regarded as continuous variables). There is a state at each lattice point ( $n_x$ ,  $n_y$ ,  $n_z$  integers) in the octant where all are non-negative. Because  $\hbar$  is so small, and also because we usually deal with a large number of particles, we will be concerned with energies where the quantum numbers (the  $n$ 's) are large. How

many states are there with energy  $< E$ ? Answer:

$$N(< E) = \frac{1}{8} \frac{4\pi}{3} \left( \sqrt{\frac{E}{\pi^2 \hbar^2 / 2mL^2}} \right)^3 .$$

This is just the volume of an octant of a sphere with radius given by the square root above. It's the number of states because each state (lattice point) occupies unit volume. For a large number of states, we don't care about the small errors made at the surface of the sphere. The number of states with energy less than  $E$  is the integral of the density of states,  $n(E)$ ,

$$N(< E) = \int_0^E n(E') dE' ,$$

where  $E'$  is the dummy variable of integration. Differentiate both sides with respect to  $E$  using the previous result for  $N(< E)$ ,

$$n(E) = 2\pi\sqrt{E} \left( \frac{\sqrt{2mL}}{2\pi\hbar} \right)^3 .$$

Recall that when we discussed the Maxwell distribution, we concluded that the density of states had to be proportional to  $\sqrt{E}$  in order to give the Maxwell distribution. Sure enough that's what we get. All the other factors get absorbed into the overall normalization constant.

It will be instructive to work out a numerical value for the number of states for a typical case. So let's suppose that  $E = 3kT/2$  where  $T = 273$  K and the volume  $L^3 = 22 \times 10^3$  cm<sup>3</sup>. That is, we consider an energy and volume corresponding to the average energy and molar volume of a gas at standard temperature and pressure. For  $m$  we'll use a mass corresponding to an N<sub>2</sub> molecule. The result is about  $4 \times 10^{30}$  states, more than a million times Avogadro's number.

We have been working out the states for one particle in a box. If we have more than one particle in the box, and they are non-interacting, then the same set of states is available to each particle. If the particles are weakly interacting, then these states are a first approximation to the actual states and we will usually just ignore the interactions when it comes to counting states. With this approximation, and with a mole of particles in the box, we've found that less than one in a million of the available states are occupied.

## Partition Function for a Single Particle in a Box

We can use the same states we've just discussed to evaluate the partition function for a single particle in a box. We have

$$Z(\tau) = \sum_{n_x, n_y, n_z} \exp\left(-\frac{\pi^2 \hbar^2}{2mL^2\tau} (n_x^2 + n_y^2 + n_z^2)\right).$$

We will make a negligibly small error by converting the sums to integrals,

$$\begin{aligned} Z(\tau) &= \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \exp\left(-\frac{\pi^2 \hbar^2}{2mL^2\tau} (n_x^2 + n_y^2 + n_z^2)\right), \\ &= \left(\frac{\sqrt{2m\tau}}{\pi\hbar}\right)^3 L^3 \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz \exp(-x^2 - y^2 - z^2), \\ &\quad \text{(rescaling variables)} \\ &= \frac{1}{8} 4\pi \left(\frac{\sqrt{2m\tau}}{\pi\hbar}\right)^3 L^3 \int_0^\infty dr r^2 e^{-r^2}, \\ &\quad \text{(changing to spherical coordinates and integrating over angles)} \\ &= \frac{1}{8} 4\pi \left(\frac{\sqrt{2m\tau}}{\pi\hbar}\right)^3 V \frac{1}{2} \Gamma\left(\frac{3}{2}\right), \\ &= \frac{V}{(2\pi\hbar^2/m\tau)^{3/2}} \quad (\Gamma(3/2) = \sqrt{\pi}/2), \\ &= n_Q V. \end{aligned}$$

The volume of the system is  $V = L^3$  and the quantity that occurs in the last line,  $n_Q$  has the dimensions of an inverse volume or a number per unit volume.  $m\tau$  is the square of a typical momentum. So  $\hbar^2/m\tau \sim \lambda^2$ , and the volume associated with  $n_Q$  is roughly a cube of the de Broglie wavelength. This is roughly the smallest volume in which you can confine the particle (given its energy) and still be consistent with the uncertainty principle. K&K call  $n_Q$  the *quantum concentration*. A concentration is just a number per unit volume, and  $n_Q$  can be thought of as the concentration that separates the classical (lower concentrations) and quantum (higher concentrations) domains. For a typical gas at STP, the actual concentration  $n = N/V$  is much less than the quantum concentration (by the same factor as the ratio of the number of states to the number of molecules we calculated earlier), so the gas can be treated classically.

Partition Function for  $N$  Particles in a Box

If we have  $N$  non-interacting particles in our box, all with the same mass, then (see the homework) the partition function for the composite system is just the product of the partition functions for the individual systems,

$$Z_N(\tau) = Z_1(\tau)^N \quad \text{wrong!}$$

where  $Z_N$  is the  $N$ -particle partition function and  $Z_1$  is the 1-particle partition function calculated in the previous section.

Why is this wrong? Recall that the partition function is the sum of Boltzmann factors over all the states of the composite system. Writing  $Z_N$  as a product includes terms corresponding to molecule A with energy  $E_a$  and molecule B with energy  $E_b$  and vice versa: molecule A with  $E_b$  and molecule B with  $E_a$ . However, these are not different composite states if molecules A and B are indistinguishable! The product overcounts the composite states. Any given Boltzmann factor appears in the sum roughly  $N!$  times more than it should because there are roughly  $N!$  permutations of the molecules among the single particle states that give the same composite state.

Why “roughly?” Answer, if there are two or more particles in the same single particle state, then the correction for indistinguishability (what a word!) is not required. However, we’ve already seen that for typical low density gasses, less than one in a million single particle states will be occupied, so it’s quite safe to ignore occupancies greater than 1. (If this becomes a bad approximation, other quantum effects enter as well, so we need to do something different, anyway!)

To correct the product, we just divide by  $N!$ ,

$$Z_N(\tau) = \frac{1}{N!} Z_1^N = \frac{1}{N!} (n_Q V)^N .$$

To find the energy, we use

$$\begin{aligned} \langle U \rangle &= \tau^2 \frac{\partial}{\partial \tau} \log Z_N , \\ &= \tau^2 \frac{\partial}{\partial \tau} (-\log N! + N \log n_Q + N \log V) , \\ &= \tau^2 \frac{\partial}{\partial \tau} (N \log n_Q) , \\ &\quad \text{(derivatives of } N! \text{ and } \log V \text{ give 0)} \\ &= \tau^2 \frac{\partial}{\partial \tau} \left( N \log \left( \frac{m\tau}{2\pi\hbar^2} \right)^{3/2} \right) , \\ &= \frac{3}{2} N \tau , \end{aligned}$$

which expresses the energy of an ideal gas in terms of the temperature. We've obtained this result before, using the Maxwell distribution. Note that our correction for overcounting of the microstates does not appear in the result.

In lecture 6, we noted that

$$p = - \left( \frac{\partial U}{\partial V} \right)_{\sigma, N} ,$$

and we remarked that keeping the entropy constant while changing the volume of a system means keeping the probability of each microstate constant. The average energy is

$$\langle E \rangle = \sum_s E_s P(E_s) ,$$

and keeping the probabilities of the microstates constant means that  $P(E_s)$  doesn't change. Thus, changing the volume at constant entropy changes the energy through changes in energies of the individual states. For each single particle state,

$$E_s \propto \frac{1}{L^2} \propto V^{-2/3} ,$$

which means

$$\frac{dU}{U} = \frac{dE_s}{E_s} = -\frac{2}{3} \frac{dV}{V} ,$$

all at constant  $\sigma$ . Then the pressure is

$$p = - \left( \frac{\partial U}{\partial V} \right)_{\sigma, N} = \frac{2}{3} \frac{U}{V} .$$

Again, this is a result we've seen before.

## Helmholtz Free Energy

Recall the expression for the conservation of energy,

$$dU = \tau d\sigma - p dV ,$$

where we have omitted the chemical potential term, since we won't be contemplating changing the number of particles at the moment.

If we have a system whose temperature is fixed by thermal contact with a heat bath, it is convenient to eliminate the differential in the entropy in favor of a differential in the temperature. For this we use a Legendre transformation—exactly the same kind of transformation used in classical mechanics to go from the Lagrangian, a function of coordinates and velocities, to the Hamiltonian, a function of coordinates and momenta.

Define the Helmholtz free energy by

$$F = U - \tau\sigma .$$

Not all authors use the symbol  $F$  for this quantity—I believe some use  $A$  and there may be others. In any case,

$$dF = dU - \tau d\sigma - \sigma d\tau = \tau d\sigma - p dV - \tau d\sigma - \sigma d\tau = -\sigma d\tau - p dV .$$

If a system is placed in contact with a heat bath and its volume is fixed, then its free energy is an extremum. As it turns out, the extremum is a minimum. To show this, we show that when the entropy of the system plus reservoir is a maximum (so equilibrium is established), the free energy is a minimum.

$$\begin{aligned} \sigma &= \sigma_r(U - U_s) + \sigma_s(U_s) , \\ &= \sigma_r(U) - U_s(\partial\sigma_r/\partial U) + \cdots + \sigma_s(U_s) , \\ &= \sigma_r(U) - U_s/\tau + \sigma_s(U_s) , \\ &= \sigma_r(U) - (U_s - \tau\sigma_s(U_s))/\tau , \\ &= \sigma_r(U) - F_s/\tau . \end{aligned}$$

In the above, the subscripts  $r$  and  $s$  refer to the reservoir and system and  $U$  is the fixed total energy shared by the reservoir and system. Note that unlike our derivation of the Boltzmann factor, the system here need not be so small that it can be considered to be in a single state—it can be a macroscopic composite system. However, it should be much smaller than the reservoir so that  $U_s \ll U$ . Also, the partial derivatives above occur at fixed volume and particle number. Since  $\sigma_r(U)$  is just a number, and  $\tau$  is fixed, maximizing  $\sigma$  requires minimizing  $F$ .

From  $dF = -\sigma d\tau - p dV$ , we see

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V \quad \text{and} \quad p = -\left(\frac{\partial F}{\partial V}\right)_\tau .$$

Substituting  $F = U - \tau\sigma$  in the right equation above,

$$p = -\left(\frac{\partial U}{\partial V}\right)_\tau + \tau \left(\frac{\partial \sigma}{\partial V}\right)_\tau .$$

This shows that at fixed temperature, if a system can lower its energy by expanding, then it generates a “force,” pressure, that will create an expansion. This is probably intuitive, since we are used to the idea that the equilibrium state is a minimum energy state. If the system can increase its entropy (at fixed temperature) by expanding, this too, generates a “force” to create an expansion.

Note that

$$\left(\frac{\partial \sigma}{\partial V}\right)_\tau = -\frac{\partial^2 F}{\partial V \partial \tau} = -\frac{\partial^2 F}{\partial \tau \partial V} = \left(\frac{\partial p}{\partial \tau}\right)_V .$$

The outer equality in this line is called a Maxwell relation. These occur often in thermodynamics and result from the fact that many thermodynamic parameters are first derivatives of the same thermodynamic “potential,” such as the free energy in this case.

### The Free Energy and the Partition Function

Consider  $F = U - \tau\sigma$  and  $\sigma = -(\partial F/\partial \tau)_V$ . Putting these together, we have

$$\begin{aligned} U &= F + \tau\sigma , \\ &= F - \tau \left(\frac{\partial F}{\partial \tau}\right)_V , \\ &= -\tau^2 \frac{\partial(F/\tau)}{\partial \tau} . \end{aligned}$$

Recall the expression for energy in terms of the partition function

$$U = \tau^2 \frac{\partial \log Z}{\partial \tau} .$$

Comparing with the above, we see

$$\frac{F}{\tau} = -\log Z + C ,$$

where  $C$  is a constant independent of  $\tau$ . In fact, the constant must be zero in order to give the correct entropy as  $\tau \rightarrow 0$ . If  $\tau$  is sufficiently small, only the lowest energy ( $E_0$ ) state enters the partition function. If it occurs  $g_0$  different ways, then  $\log Z \rightarrow \log g_0 - E_0/\tau$  and  $\sigma = -\partial F/\partial\tau \rightarrow \partial(\tau \log g_0 - E_0 - \tau C)/\partial\tau = \log g_0 - C$ . So  $C = 0$  in order that the entropy have the correct zero point. Then

$$F = -\tau \log Z \quad \text{or} \quad Z = e^{-F/\tau} .$$

Remembering that the Boltzmann factor is normalized by the partition function to yield a probability, we have

$$P(E_s) = \frac{e^{-E_s/\tau}}{Z} = e^{(F - E_s)/\tau} .$$

Just for fun, let's apply some of these results using the partition function for the ideal gas we derived earlier.

$$\begin{aligned} F &= -\tau \log Z , \\ &= -\tau \log((n_Q V)^N / N!) , \\ &= -\tau(N \log n_Q + N \log V - N \log N + N) \quad (\text{Stirling's approx.}) , \\ &= -\tau N \log \left[ (m\tau/2\pi\hbar^2)^{3/2} (V/N) \right] - \tau N . \end{aligned}$$

With  $p = -\partial F/\partial V$ , we have

$$p = \tau N/V ,$$

the ideal gas law again. For the entropy,  $\sigma = -\partial F/\partial\tau$ ,

$$\begin{aligned} \sigma &= N \log(n_Q V/N) + (3/2)N + N , \\ &= N \left( \log \frac{n_Q}{n} + \frac{5}{2} \right) , \end{aligned}$$

where  $n = N/V$  is the concentration. This called the Sackur-Tetrode formula. Note that if one considers the change in entropy between two states of an ideal gas,

$$\sigma_f - \sigma_i = \frac{3}{2} N \log \frac{\tau_f}{\tau_i} + N \log \frac{V_f}{V_i} ,$$

a classical result which doesn't contain Planck's constant. However, to set the zero point and get an "absolute" entropy, Planck's constant does enter since it determines the spacing between states and their total number. The overcounting correction does not make any difference in the pressure above, but it does enter the entropy—as might have been expected. A final note is that these expressions for an ideal gas do not apply in the limit  $\tau \rightarrow 0$ . (Why?)