

Therefore,

$$\begin{aligned}
 \log \Omega(N, n) &\approx (n + N) \left[\log n + \frac{N}{n} \right] - n \log n - N \log N \\
 &\approx N \log n + (n + N) \frac{N}{n} - N \log N \\
 &\approx N \log \left(\frac{n}{N} \right) + N + \frac{N^2}{n} \\
 &\approx N \log \left(\frac{n}{N} \right) + N
 \end{aligned}$$

where in each step, we've made use of the fact that $n \gg N$ to eliminate small terms. Finally, we have the desired result:

$$\Omega(N, n) = e^N \left(\frac{n}{N} \right)^N \text{ for } n \gg N \quad (65)$$

You should be able to work out the corresponding low temperature limit ($n \ll N$). Hint: Even though we require $n \ll N$, we still have $n \gg 1$.

9.9 The Thermodynamic Limit

In this section we bring two Einstein solids into contact as before and explore the form of the multiplicity function in the high temperature limit define in the previous section. The point of this section is to quantify the statement that the most probable macrostate is the one in which the two systems are in thermal equilibrium.

Using the high-temperature expression for the multiplicity function of a single ES, we can model the composite consisting of two ES's each with N oscillators:

$$\Omega = \Omega_1 \Omega_2 \approx e^{2N} \left(\frac{n_1}{N} \right)^N \left(\frac{n_2}{N} \right)^N$$

Now, to explore what this function looks like near its peak, let's define the following parameters

$$\begin{aligned}
 n &\equiv n_1 + n_2 \\
 n_1 &\equiv \frac{n}{2} + x \\
 n_2 &\equiv \frac{n}{2} - x
 \end{aligned}$$

The latter two relations define x - the distance that each of the solids' energy macrostate is from the "thermal equilibrium point" $n/2$ (the peak of the function $\Omega(N, n)$ at a given N). In terms of x , Ω takes the form

$$\begin{aligned}
 \Omega(N, x) &= \frac{1}{N^{2N}} \left[\left(\frac{n}{2} + x \right)^N \left(\frac{n}{2} - x \right)^N \right] e^{2N} \\
 &= \left(\frac{e}{N} \right)^{2N} \left[\left(\frac{n}{2} \right)^2 - x^2 \right]^N \quad (\text{using } (a+x)(a-x) = a^2 - x^2)
 \end{aligned}$$

Now we can evaluate the logarithm of Ω , apply our approximation tricks, and then exponentiate to get Ω back:

$$\log \Omega = 2N \log \left(\frac{e}{N} \right) + N \log \left[\left(\frac{n}{2} \right)^2 - x^2 \right]$$

Now, let's work on the second term above:

$$\begin{aligned}
 \log \left[\left(\frac{n}{2} \right)^2 - x^2 \right] &= \left[\left(\frac{n}{2} \right)^2 \left(1 - \left(\frac{2x}{n} \right)^2 \right) \right] \\
 &= \log \left(\frac{n}{2} \right)^2 + \log \left[1 - \left(\frac{2x}{n} \right)^2 \right] \\
 &\approx \log \left(\frac{n}{2} \right)^2 - \left(\frac{2x}{n} \right)^2 \quad (\text{using the first term of the Taylor expansion of the log function: } \log(1 - \epsilon) \approx -\epsilon)
 \end{aligned}$$

Exponentiating both sides, we have

$$\begin{aligned}\Omega(N, x) &\approx \frac{e^{2N}}{N^{2N}} \exp N \left[\log \left(\frac{n}{2} \right)^2 - \left(\frac{2x}{n} \right)^2 \right] \\ &\approx \frac{e^{2N}}{N^{2N}} \left(\frac{n}{2} \right)^{2N} e^{-N(2x/n)^2}\end{aligned}$$

Since, we should regard N as a fixed constant, we can recast Ω as a function of n and x :

$$\Omega(x, n) \approx \Omega_{\max} e^{-N(2x/n)^2} \quad (66)$$

The text illustrates how sharply peaked this Gaussian function is. There is just (almost) no chance that the system will be found in any other state but the state at the peak of the Ω distribution.

10 Multiplicity of an Ideal Gas

Calculating the multiplicity of an Einstein Solid was relatively straight forward. In an upcoming chapter, we will learn about the *partition function* which will allow us to circumvent the actual calculation of the multiplicity function. This is a good thing, because it is almost always impossible to directly calculate it. One of the few other systems for which the multiplicity is easily calculated is the ideal gas.

Imagine a single molecule in a 3-D volume V . What does Ω_1 depend on?

- the more physical positions for the molecule to be in, the larger the multiplicity:

$$\Rightarrow \Omega_1 \propto V$$

- the more momentum states the molecule is allowed to have, the larger the multiplicity:

$$\Rightarrow \Omega_1 \propto V_p$$

where V_p is the “volume” of available momentum space.

What does this last volume represent? The kinetic energy of a single particle is

$$U_1 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2).$$

This defines the surface of a sphere with coordinate p_x , p_y , and p_z . The radius of the sphere is $\sqrt{2mU}$. Since all momentum triplets must satisfy this constraint, we can imagine that the allowed values of momentum exist on the surface of a sphere of radius $\sqrt{2mU}$.

But, how many values of the momentum can exist on the momentum sphere? Here, I refer you to the text, because I have nothing to add or subtract from the arguments on page 69-70 for the calculation of the number of allowed momenta living on our p -sphere. The result of Schroeder’s analysis is that the multiplicity function of a single particle gas in a volume V is:

$$\Omega_1 = \frac{VV_p}{h^3}$$

where $h = 6.63 \times 10^{-34} \text{ J sec.}$ is Planck’s Constant. You really need to read the appendix on basic quantum mechanics if you don’t understand where the h comes from.

Now, V_p is actually the *area* of the momentum sphere of radius $\sqrt{2mU}$. The surface area of a sphere is $4\pi R^2$, so

$$V_p = 4\pi(\sqrt{2mU})^2 = 8\pi mU$$

If there were two particles in the gas (each of mass m), we should find

$$\Omega_2 = \frac{1}{2} \left(\frac{V}{h^3} \right)^2 \times (\text{area of 2-particle momentum “hypersphere”}).$$

A two particle gas has a total energy of

$$U_2 = \frac{1}{2m}(p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2).$$

U_2 defines the surface of a six-dimensional hypersphere. Clearly, we can generalize to an N -particle gas:

$$\Omega_N = \frac{1}{N!} \frac{V^N V_p^N}{h^{3N}}$$

The area of the relevant N -particle momentum hypersphere has $3N$ dimensions. How do you compute the surface area of a $6N$ -dimensional sphere?? Appendix B has the answer. And the answer is that the area of a d -dimensional hypersphere of radius R is

$$A_d = C_d R^{d-1}$$

where C_d is a constant given by

$$C_d = \frac{2\pi^{d/2}}{\Gamma(\frac{d}{2})}.$$

The Γ function is defined by

$$\Gamma(n+1) = \int_0^\infty x^n e^{-x} dx = n!.$$

The Γ function is a generalization of the factorial function that works even when the argument is not an integer. Using this definition you can see that the constants for the first few “spheres” are $C_1 = 1$, $C_2 = 2\pi$, and $C_3 = 4\pi$. So, what’s the area of a four-dimensional sphere? Work it out to get the somewhat interesting result $A_4 = 2\pi^2 R^3$.

Applying the formula for the area of a hypersphere to the multiplicity of an ideal gas, we first need to find the area of the $d = 3N$ -dimensional momentum hypersphere:

$$A_{3N} = \frac{2\pi^{3N/2}}{\Gamma(\frac{3N}{2})} \times (2mU)^{\frac{3N}{2}-1}$$

Now, $\Gamma(3N/2) = (3N/2 - 1)! \approx (3N/2)!$, and we can replace the exponent of $(2mU)$: $3N/2 - 1 \approx 3N/2$. So, we have:

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(\frac{3N}{2})!} (2mU)^{3N/2} \quad (67)$$

You should work out the equivalent multiplicity function for a gas confined to a two-dimensional “volume” (prob. 2.26) and find

$$\Omega_N^{2d} = \left(\frac{1}{N!}\right)^2 \left(\frac{2mA\pi U}{h^2}\right)^N$$

10.1 Interacting Systems

In analogy to the derivation of the total multiplicity function for two Einstein Solids in contact, we can write the multiplicity function for two containers of N gas particles in thermal contact as

$$\Omega_{total} = \Omega_A \Omega_B = [f(N)]^2 (V_A V_B)^N (U_A U_B)^{3N/2}$$

with $f(N)$ shorthand for the complicated function of N that appears in the multiplicity function for the ideal gas. Working in analogy with the Einstein Solid problem, you can determine that the peak of Ω_{total} has width $(V_A + V_B)/\sqrt{N}$. Again, we find a sharp peak that represents all the microstates corresponding to thermal equilibrium. There is just no chance (almost literally) that the composite gas will be found in any state other than thermal equilibrium.

This is the fundamental result of statistical mechanics:

Any large system in equilibrium will be found in the macrostate with the greatest multiplicity

11 Entropy

The statement above is essentially a statement of the Second Law of Thermodynamics. All this talk about multiplicity has really been about entropy. It turns out to be more convenient to work with the logarithm of large numbers (the logarithm of huge numbers are not huge at all: $\log e^{100} = 100$). So, entropy is defined as the log of the multiplicity:

$$S = k \ln \Omega \quad (68)$$

Check out Boltzmann's headstone - he had this engraved on it. The factor of k is a historical artifact that allows us to define the temperature according to:

$$T^{-1} \equiv \frac{\partial S}{\partial U}$$

Example: The entropy of an Einstein Solid: Recall that the multiplicity is $\Omega(N, n) = (en/N)^N$ when $n \gg N$. The entropy is therefore $S = kN[1 + \log(n/N)]$. e.g., if $N = 10^{22}$ and $n = 10^{24}$, we have $S \approx 0.77J/K$.

Example: Ideal Gas: The book works out the famous Sakur-Tetrode equation for the entropy of an ideal monatomic gas. The derivation starts with the multiplicity function

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(\frac{3N}{2})!} (2mU)^{3N/2}$$

. A few applications of the product and sum rules for logarithms and an couple applications of Stirling's Approximation, and we get the Sakur-Tetrode result:

$$S(U, V, N) = Nk \left[\log \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right] \quad (69)$$

where m is the mass of a single atom in the gas.

It seems that most entropy calculations result in a leading term of Nk . This allows us to make a quick estimate of the entropy of anything.

Example: Find the entropy of your textbook. Let's say the book has a total mass of 1 kg. This is about 100 moles of carbon (why?) So, the number of particles making up the book is $N \approx N_A \times 100 \approx 10^{26}$. Therefore, the entropy of the book is approximately $Nk = 10^3 J/K$. Exercise for the reader: calculate the entropy of your roommate. Explain this calculation to your roommate.

11.1 Calculating Changes in Entropy

- Change in entropy when an ideal gas expands from V_1 to V_2 with N and U fixed:

$$\Delta S = Nk \left[\log \left[\frac{V_2}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right] - Nk \left[\log \left[\frac{V_1}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right] = Nk \log \frac{V_2}{V_1}$$

- Change in entropy when a monatomic ideal gas is heated from T_1 to T_2 at constant V, N : Here, we need to use $U = (3/2)NkT$ for the energy of a monatomic ideal gas. We can rewrite the ST equation in terms of T and compute ΔS :

$$\Delta S = Nk \left[\log \left[\frac{V}{N} \left(\frac{4\pi m(\frac{3}{2}NkT_2)}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right] - Nk \left[\log \left[\frac{V}{N} \left(\frac{4\pi m(\frac{3}{2}NkT_1)}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right] = \frac{3}{2} Nk \log \frac{T_2}{T_1}.$$

- In many introductory textbooks, the entropy change for quasistatic, isothermal expansion of an ideal gas is reported to be

$$\Delta S = \frac{Q}{T}$$

Where does this come from? From the first example above, we know that the ΔS associated with a quasistatic, isothermal expansion of an ideal gas is given by $\Delta S = kN \log(V_2/V_1)$. The heat input during an isothermal process is $Q = -W$ (by the first law of thermodynamics). So,

$$Q = -W = + \int_{V_1}^{V_2} \frac{NkT}{V} dV = NkT \log \frac{V_2}{V_1}$$

Comparing $\frac{Q}{T}$ with the original calculation for ΔS , we see that they are identical $\rightarrow \Delta S = Q/T$ for an isothermal, quasistatic expansion (or compression). Note that this formula *only applies to isothermal processes*. If you consider free expansion of a gas, then $Q = 0$ and $\Delta S \neq Q/T$.

- Change in entropy when 1 mol of air is heated from a temperature of 300K to 301K:

$$\Delta S = \frac{3}{2} Nk \log \frac{T_2}{T_1} = \frac{3}{2} nR \log \frac{T_2}{T_1} \quad (70)$$

$$= \frac{3}{2} (1 \text{ mol}) (8.31 \text{ J/mol-K}) \log \frac{301}{300} \quad (71)$$

$$= 0.042 \text{ J/K} \quad (72)$$

11.2 Entropy of a black hole

This is problem 2.42 on page 84 of the text. We went over in general in class. Here are the specifics of the problem.

(a) By dimensional analysis, the radius must be proportional to GM/c^2 .

(b) Ordinarily, the entropy of a system is of the same order as the number of particles in the system. If we take a system of N particles and compress it to form a black hole, the second law requires that when we're done, the entropy of the black hole is still at least of order N . But since the end result is the same whether we start with a lot of particles or a few (with the same total mass), the final entropy must in fact be of the order of the *maximum* N , the largest possible number of particles that it could have been formed from.

(c) Suppose we start with N photons, each of which has a wavelength equal to the size of the black hole: $\lambda = GM/c^2$. Each photon has an energy $E = hc/\lambda$, and the total energy of all of them must equal Mc^2 :

$$Mc^2 = NE = \frac{Nhc}{\lambda} = \frac{Nhc^3}{GM}.$$

Solving for N gives

$$N = \frac{GM^2}{hc},$$

and so the entropy in conventional units must be of order

$$S \sim \frac{GM^2 k}{hc}.$$

(d) For a one-solar mass black hole,

$$\frac{S}{k} = 1.06 \times 10^{77}; \quad S = 1.5 \times 10^{54} J/K.$$

This is an enormous entropy. For comparison, an ordinary star like the sun contains something like 10^{57} particles, so its entropy is something like $10^{57}k$. To equal the entropy of a single one-solar-mass black hole, you would need 10^{20} ordinary stars or enough to populate a billion (10^9) Milky Way galaxies. Furthermore, since the entropy of a black hole is proportional to the square of its mass, a million-solar mass black hole (as may exist at the center of our galaxy) would have a trillion times the entropy of a one-solar-mass black hole.