

APh105c
Homework 2
Due Date: Friday, April 14, 2006

“There is plenty of room at the top. It’s the middle that’s crowded. Be great!” -The guy at Idyllwild

Reading: Read pgs. 105-119 and chap. 27 of Dill and Bromberg.

1. A Feeling for the Numbers: Cataclysms, China and Defects.

I have been doing some fun reading lately, but as usual, I am always struck by the *numbers*. In this problem you will consider a couple of striking examples just for fun and to get a feel for energy.

(a) I have been reading an amazing book by Simon Conway Morris called **Life’s Solution**. Simon Conway Morris, by the way, is one of the heroes of Stephen Jay Gould’s book called **Wonderful Life** which is the story of the Burgess Shale, the most important fossil find in history. Here is what Gould has to say on the Burgess Shale: “Without hesitation or ambiguity, and fully mindful of such paleontological wonders as large dinosaurs and African apemen, I state that the invertebrates of the Burgess Shale, found high in the Canadian Rockies in Yoho National Park, on the eastern border of British Columbia, are the world’s most important animal fossils.” Anyway, after his famous work (while a graduate student, just like you!!), Morris has gone on to think deeply on many topics and **Life’s Solution** tackles one of the great wonders, namely, the origins of life. One of his concerns in making his argument is the extent to which meteorites and comets might have hit the Earth and sterilized it. He says: “What happens when something very big hits the Earth? The amount of energy released is enormous, so great in fact that the heat generated was probably sufficient to evaporate the entire world ocean.” He continues “It is estimated that during the later bombardments the Earth may have been pounded by five or so of these monster impacts, each capable of evaporating the ocean and presumably sterilizing the surface.” Your task in this problem is to do the math and make some estimates to check out

Morris' claims. First, get a sense of the size and speeds of meteorites and comets and work out their kinetic energy. Then figure out how much energy it would take to boil off the oceans and compare the numbers. The bottom line is that this is an open-ended question and you need to make it your own. One avenue of interest would be to figure out how much water would get boiled off as a function of size of the impacting body.

(b) Last week on my flight home from Singapore I read the international edition of Newsweek which had a feature article on why Russia is frightened by China and in particular, on the way in which Siberia is becoming increasingly dominated by Chinese immigrants. The claim is that it is all tied to the energy needs of China. (By the way, to get an interesting take on this, see <http://www-personal.umich.edu/~mejn/cartograms/>). The article claimed that the annual energy budget of China is 40 billion kilowatt hours. Find a way to present this number in some sort of way that makes more sense. For example, tell me how many gallons of gasoline does this correspond to for each citizen of China. Compare this number to the amount of energy in the form of sunlight that falls on China each year (here you will have to look up some numbers - I think it is called the "solar constant").

(c) Figure out how many gold atoms there are in a typical wedding ring. Then, assume that one out of every 10^9 sites has a vacancy (i.e. a point defect). Work out the contribution to the overall free energy coming from configurational entropy by using the same entropy considerations we used in class for Langmuir adsorption, namely,

$$\Omega(n_{vac}; N) = \frac{N!}{n_{vac}!(N - n_{vac})!}, \quad (1)$$

where n_{vac} is the number of vacancies and N is the total number of lattice sites. Now, assume that through a temperature change that the number of vacancies is reduced by a factor of 10 - how much does the entropy change on a per atom basis?

2. A Feeling for the Numbers: Tired Out in the Tour de France.

(Thanks to Prof. Phil Nelson, UPenn Physics for this one.) A bicycle rider in the Tour de France eats a lot. If his total daily food intake were burned it

would liberate about 8000kcal of heat. Over the three or four weeks of the race, his weight change is negligible, less than 1%. Thus his energy input and output must balance. Let's first look at the mechanical work done by the racer. A bicycle is incredibly efficient so the energy lost to internal friction, even including the tires, is negligible. The expenditure against air drag, on the other hand, is significant and amounts to 10MJ per day. Each day the rider races for 6 hours.

(a) Compute the power dissipated in the form of drag. Next, compare the 8000kcal input to the 10MJ of work done. Something's missing! Part of the missing energy is associated with our basic energy requirements even when we are just sitting still - if you like, you can comment on this part of the energy budget as well. Could the remainder of the missing energy be accounted for by the altitude change in a hard days racing? (Note: go to http://www.letour.fr/2006/TDF/presentation/us/profil_10.html and go to the "dynamic profile" for one of the mountain stages and figure out how much altitude gain the riders had that day - does it account for the missing energy or not?) Report the altitude gain they would need in order to explain this energy difference in units of the height of Mt. Everest.

Regardless of how you answered part (a), there are many days in the tour that are more or less flat (though they would really poop us out if we rode them), and hence we must look elsewhere to see where the missing energy went. We have so far neglected another part of the energy equation, namely, the rider gives off heat. Some of this heat is radiated. Some goes to warm up the air he breathes in. But by far the greatest share of energy is related to the water that the rider drinks.

(b) The energy needed to vaporize water is 2.3kJ/gm (note that there is some temperature dependence here and this value is for about 20 degrees centigrade). How much water would a rider have to drink in order for the excess energy found in part (a) to be used in vaporizing the water? Report your result in liters and then comment on whether or not this makes sense relative to how much a rider drinks per race (around 14 liters!). The process of energy extraction from the food is roughly 25% efficient, that means that much of that 8000kcal of energy is liberated as heat and as such has to be managed by the body. Anyway, the basic idea is that there is a latent heat

of vaporization required for the evaporation associated with sweating and we provide this heat to the water. Hence, energy is conveyed from our bodies to fuel this vaporization process and thereby, is carried away.

(c) Finally, let's revisit the 10MJ of mechanical work done by the rider each day. The wind drag is a force $F_{drag} = -Bv^2$, where B is a constant measured in a wind tunnel to be 1.5kg/m. If we simplify the problem by supposing that the speed over the course of a race is a constant, what is that speed and is it reasonable? In particular, once again go to the Tour de France website and look at the distance of some stage and then the time taken to go that distance. Choose a flat stage early on in the race. (Note from RP: Like in the problem on the first homework, we are examining drag, but this time using the more sensible drag law associated with higher Reynolds numbers than the Stokes flow result we used last time).

3. A Feeling for the Numbers: Comparing Multiplicities.

We have discussed the idea that entropy is a way to reckon the number of ways of realizing a given macrostate. To hone our intuition concerning that claim, this problem attempts to estimate the difference in the number of microstates when comparing water in solid, liquid and gaseous forms. Here is the idea. We know that

$$S_{gas} - S_{liquid} = k_B \ln \frac{\Omega_{gas}}{\Omega_{liquid}}. \quad (2)$$

From the macroscopic definition of entropy as $dS = dQ/T$ (which we will discuss more as time goes on), we can make an estimate of the ratios of multiplicities by noting that boiling of water takes place at fixed T at 373 K.

(a) Consider a cubic centimeter of water and use the result that the heat needed to boil water (the latent heat of vaporization) is given by $Q_{vaporization} = 40.66$ kJ/mole (from Schroeder and appropriate for 100 degrees centigrade) or 0.42 eV/molecule (from Baierlein) (check my numbers) to estimate the ratio of multiplicities of water and water vapor for this number of molecules. Write your result as 10 to some power. If we think of multiplicities in terms

of an ideal gas at fixed T , then

$$\frac{\Omega_1}{\Omega_2} = \left(\frac{V_1}{V_2}\right)^N. \quad (3)$$

What volume change would one need to account for the liquid/vapor multiplicity ratio? Does this make sense (RP: I didn't check this point)? What I am asking you to do is to compare your numerical result and the result you get by using the ratio of volumes - which one is larger and why, what does it all mean?

(b) Estimate the difference in the number of microstates when comparing water in solid (ice) and liquid forms. We know that

$$S_{liquid} - S_{ice} = k_B \ln \frac{\Omega_{liquid}}{\Omega_{ice}}. \quad (4)$$

We can make an estimate of the ratios of multiplicities by noting that melting of ice takes place at fixed T at 273 K. Consider a typical ice cube of something like 18cm^3 volume and use the result that the heat needed to melt ice is given by $Q_{melt} = 3.34 \times 10^5 \text{J/kg}$ or $0.062 \text{ eV/molecule}$ (check my numbers) to estimate the ratio of multiplicities of water and ice for this number of molecules. Write your result as 10 to some power. If we think of multiplicities in terms of an ideal gas at fixed T , then

$$\frac{\Omega_1}{\Omega_2} = \left(\frac{V_1}{V_2}\right)^N. \quad (5)$$

What volume change would one need to account for the solid/liquid multiplicity ratio? Does this make sense?

(c) Explain the results for both parts (a) and (b) in terms of the ratio

$$\frac{\Omega_1}{\Omega_2} = \left(\frac{V_1}{V_2}\right)^N. \quad (6)$$

In particular, explain why this isn't the whole story and try to evaluate the discrepancy between your result and the real entropy change (think bonding). Clearly, the case where this volume ratio is NOT the right way to go is in the liquid/solid transition. Give a cogent argument as to why this isn't the right

idea and then try to make an argument as to the origins of the liquid/solid entropy difference for water. In particular, try this out. In ice, assume there is just one configuration which corresponds to the hydrogen bonding network which is fixed. Now for water, assume that each water molecule can point in one of six orientations (see page 580 of Dill and Bromberg, this will help) when in the liquid state and use this to try and make an estimate of the configurational entropy change resulting from melting. Note that even this is not the whole story since there is the momentum space part of the story to consider as well. Part (c) is open-ended and calls for you to do some thinking and analysis.

(d) In this problem, you have worked out ratios of multiplicities. In class, I discussed the Stirling approximation and the fact that our results are incredibly tolerant of error. Let's pursue that in more detail. We have found that the typical types of multiplicities for a system like a gas are of order $\Omega \approx \exp(10^{25})$. Now, let's say we are off by a factor of 10^{1000} in our estimate of the multiplicities, namely, $\Omega = 10^{1000} \exp(10^{25})$. Show that the difference in our evaluation of the entropy is utterly negligible whether we use the first or second of these results for the multiplicity. This is the error tolerance that permits us to use the Stirling approximation so casually!

4. Stirling Approximation Revisited.

In class we noted the usefulness of the Stirling approximation in a variety of different settings. The goal of the present problem is to work through a more sophisticated treatment of this approximation than the simple heuristic argument given in class. Our basic task is to find useful representations of $n!$ since terms of the form $\ln n!$ arise often in reasoning about entropy.

(a) Begin by showing that

$$n! = \int_0^\infty x^n e^{-x} dx. \quad (7)$$

To demonstrate this, use repeated integration by parts. In particular, demonstrate the recurrence relation

$$\int_0^\infty x^n e^{-x} dx = n \int_0^\infty x^{n-1} e^{-x} dx, \quad (8)$$

and then argue that repeated application of this relation leads to the desired result.

(b) Begin by making some plots of the integrand $x^n e^{-x}$ for various values of n and make some observations about the peak width and height of this integrand. We are interested now in finding the value of x for which this function is a maximum. The idea is that we will then expand about that maximum. To carry out this step, consider $\ln(x^n e^{-x})$ and find its maximum - argue why it is okay to use the logarithm of the original function as a surrogate for the function itself - that is, show that the maxima of both the function and its logarithm are at the same x . Also, argue why it might be a good idea to use the logarithm of the integrand rather than the integrand itself as the basis of our analysis. Call the value of x for which this function is maximized x_0 . Now expand the logarithm about x_0 . In particular, examine

$$\ln((x_0 + \delta)^n e^{-(x_0 + \delta)}) = n \ln(x_0 + \delta) - (x_0 + \delta) \quad (9)$$

and expand to second order in δ . Exponentiate your result and you should now have an approximation to the original integrand which is good in the neighborhood of x_0 . Plug this back into the integral (be careful with limits of integration) and by showing that it is acceptable to send the lower limit of integration to $-\infty$, show that

$$n! \approx n^n e^{-n} \int_{-\infty}^{\infty} e^{-\frac{\delta^2}{2n}} d\delta. \quad (10)$$

Evaluate the integral and show that in this approximation

$$n! = n^n e^{-n} (2\pi n)^{1/2}. \quad (11)$$

Also, take the logarithm of this result and make an argument as to why we can get away with dropping the discussion of the $(2\pi n)^{1/2}$ term.

(c) We talked in class about the typical values that are in play when contemplating real thermodynamic systems. Consider the case of 1 cm^3 of Al with one out of every million sites vacant. Work out what we have called N_A and N for this case and compute the entropy and then estimate the errors you have made by virtue of using the Stirling approximation.

5. Ideal Gas and Lagrange Multipliers.

In class I used the ideal gas to demonstrate that the Lagrange multiplier associated with the average energy in our information theoretic derivation of the canonical ensemble was indeed $1/k_B T$. In this problem, I want you to repeat that derivation start to finish, but this time instead of using the classical treatment of the gas (i.e. we summed over positions and momenta) use the quantum mechanical description of the ideal gas and sum over the energy eigenvalues in order to obtain Z . Make sure you give all details and that you demonstrate that the Lagrange multiplier is $1/k_B T$ once again. In particular, here are some of the highlights that you must cover in your derivation.

(a) Write the energy states of the ideal gas in terms of the eigenvalues for the particle in a box.

(b) Like I did in class, write the partition function in the form

$$Z_{tot} = \frac{Z_1^N}{N!}. \quad (12)$$

Show that Z_1 is a product of three sums from 1 to ∞ .

(c) Here is where I want you to be most careful. Show that you can replace those sums with integrals and evaluate those integrals. You must be crystal clear about how you turn the sum into an integral. Show that the resulting single particle partition function is of the form $Z_1 = V/\lambda_{th}^3$, where as I showed in class

$$\lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}. \quad (13)$$

(d) Now show that the Lagrange multiplier in our information-theoretic derivation of the canonical ensemble is really $1/k_B T$.

(e) Now, let's use the partition function for something. In particular, compute the Helmholtz free energy ($F = -k_B T \ln Z$), the entropy $S = -(\partial F / \partial T)_{V,N}$ (show that this yields the classic Sackur-Tetrode equation)

and the chemical potential for the ideal gas, $\mu = (\partial F / \partial N)_{T,V}$.

6. Fluctuations in Thermodynamics.

In class I argued that the partition function is the *analytical engine* of statistical mechanics and is the basis of computing many of the key consequences of our statistical mechanical analysis. In this problem you will work out some of the key results that we need when thinking about thermodynamics.

(a) Show that

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z. \quad (14)$$

I want you to show this by using the formal definition of the average as $\langle E \rangle = \sum_n p(E_n) E_n$.

(b) Now derive a similar formula for $\langle E^2 \rangle$ in terms of derivatives of $\ln Z$.

7. Properties of the Missing Information.

In class I made a lot of noise about the function "missing information" $MI(\{p_i\})$. In this problem we will examine several features of this function.

(a) Consider the case in which there are n outcomes. Show that MI increases anytime we make two of the probabilities more equal, when maintaining the probabilities of all of the other outcomes. Begin by showing that

$$P_1 + P_2 = 1 - \sum_{j=3}^n P_j = C. \quad (15)$$

Then show that

$$MI = -(P_1 \ln P_1 + (C - P_1) \ln (C - P_1) + \sum_{j=3}^n P_j \ln P_j). \quad (16)$$

To examine how the missing information (MI) changes as we vary P_1 take the derivative of MI with respect to P_1 holding P_3, P_4, \dots, P_n fixed. Show that

you can write the result as

$$\frac{dMI}{dP_1} = -\ln \frac{P_1}{P_2}. \quad (17)$$

Show that this implies in turn that if we make the small increment ΔP_1 in P_1 then the change in the missing information is

$$\Delta MI = \frac{dMI}{dP_1} \Delta P_1 = -\ln \frac{P_1}{P_2} \Delta P_1. \quad (18)$$

Now, consider two cases, $P_1 < P_2$ and $P_2 < P_1$ and then work out the change in MI by choosing an appropriate ΔP_1 . Does it increase as expected?