APh105c
Homework 1
Due Date: Friday, April 7, 2006

"There is no calculation that is not worth doing." - attributed to Duncan Haldane

Reading: Read chaps. 1, 2 and 6 of Dill and Bromberg and the article by Jaynes on the course website.

1. A Feeling for the Numbers: Avogadro's Number and Beyond.

Though I am a big fan of nice, general formulae for illustrating how quantities scale in abstract terms, it is also necessary to have an intuition for the numerical magnitudes that attend our physical reasoning as well. To that end, in this problem, you will have a chance to estimate some of the key scales that arise in reasoning about thermodynamic systems.

(a) As will become more evident in coming days, thermodynamic systems are often characterized by their energy E, their volume V and the number of particles they contain, N. In this problem, we get a sense for the types of numbers that arise. First, let's examine the meaning of Avogadro's number from a few different angles. i) How many molecules are there in a cm^3 of water? How many moles is this? ii) As a simple model of an *E. coli* cell, consider a cylinder of length $1\mu m$ and of radius $0.5\mu m$, then imagine that the top and bottom of the cylinder are capped off with hemispheres, also of radius $0.5\mu m$. If the cell were filled with just water, how many molecules (and how many moles) of water molecules would fill this cell? iii) In fact, as you well know, much of the interior of a typical cell is filled with stuff other than water. Indeed, roughly 25 percent by weight of the cell is filled with proteins. Assuming each protein molecule is a sphere of diameter $30\mathring{A}$ and further, assuming that the density of the proteins and water are equal (not right, fix this assumption if you want), estimate how many protein molecules are found within such a cell. Report in both number of molecules and number of moles. Also, just to amuse us, compute the mean spacing of these proteins. iv) In

Professor Roukes' group, very small cantilever beams are being constructed to detect biological molecules. Consider a cantilever of length $5 \mu m$ and of width and height $1000 \mathring{A}$. Estimate the number of atoms in such a device. v) In a crystal growth process, consider the deposition of one monolayer of atoms per second over an area of 1 μm^2, how many molecules (how many moles) are deposited per second? vi) pH is a measure of concentration of H^+ ions. For the *E. coli* cell that we considered above, make a plot of the number of H^+ ions in the cell as a function of the pH. Also, make a plot of the mean spacing of such ions as a function of pH. vii) Finally, estimate the number of molecules in a liter of air at sea level and on top of Mt. Everest.

(b) As the next step in trying to assess the scales of interest in contemplating thermodynamic systems, we examine the energetics of such systems. i) The energy of an ideal gas is given by $E = \frac{3}{2} N k_B T$, where N is the number of molecules. Consider a liter of air and assume that it is an ideal gas (also, forget about the fact that there is both oxygen and nitrogen in air). Compute the internal energy of this gas at room temperature and report your results in eV, joules and kcal/mole. ii) Consider a liter of water that is boiling. The heat of sublimation for water is 40.66 kJ/mol (check me on this, but I think it is right). How much energy is spent in boiling this liter of water and turning it completely into gas? iii) $k_B T$ sets the energy scale for kinetic processes such as diffusion and chemical reactions. Compute $k_B T$ in units of eV, Joules, kcal/mole and pN nm. vi) $e^{-E/k_B T}$ determines the rates of the kinetic processes described above. For room temperature, plot the value of this quantity as a function of E for E ranging from 0 to 100 $k_B T$ (note that my energy units here are $k_B T$) and comment on what this means about the barrier heights for typical kinetic processes.

2. A Feeling for the Numbers Part 2: Engines and the Atmosphere.

In a fascinating book entitled **An Introduction to Thermal-Fluid Engineering: The Engine and the Atmosphere**, Z. Warhaft makes a number of compelling arguments concerning the linkage of thermodynamics and fluid mechanics in understanding two important phenomena - the behavior of internal combustion engines and the atmosphere. Please refrain from looking at Warhaft's book until *after* you have done this problem. We are going to use the engine and the atmosphere as a vehicle to continue the numerical estimates commenced in problem 1 above.

Let's assume that gasoline is really octane, C_8H_{18} and that combustion goes according to the equation

$$C_8H_{18} + 25O \rightarrow 8CO_2 + 9H_2O + 48 \times 10^6 \text{J/kg fuel}, \tag{1}$$

which Warhaft prefers to write as

$$C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2 + 48 \times 10^6 \text{J/kg fuel}, \tag{2}$$

where the strange factor of 3.76 is meant to reveal the relative proportion of nitrogen and oxygen in the atmosphere. Note that the nitrogen in this equation does not participate in the reaction.

a) We note that for every molecule of octane (our surrogate for gasoline) that is burnt, it produces 8 molecules of CO_2. You see where we are going with this. Your job is to figure out how many kilograms (and how many molecules) of CO_2 are produced for every gallon (and every liter - need to be familiar with both units) of gasoline burnt. Next, assume that there are 500 million cars in the world and make a reasonable estimate of the number of gallons of fuel consumed per year by all of these cars and finally, use this to compute how many kilograms of CO_2 are emitted by cars each year.

b) In this part of the problem, your job is to compute the mass of the atmosphere in kilograms and then to work out the ratio of CO_2 emitted each year to total atmospheric mass. The simplest way to estimate the mass of the atmosphere is

$$M_{atm} g = p A_{surface}, \tag{3}$$

where M_{atm} is the mass of the atmosphere, g is the acceleration due to gravity on the earth, p is the pressure of the atmosphere at sea level and $A_{surface}$ is the surface area of the earth. Explain why this is a reasonable scheme for computing the mass of the atmosphere and then use this (or some other) scheme to get the mass in kilograms. Next, how many parts per million of CO_2 are cars putting into the atmosphere? Take a look at *http://www.co2science.org/subject/other/co2con_twohundred.htm* as one example of the type of data that is out there on this subject.

3. The Dice Problem Revisited.

In class I described the use of inference to make a best guess for the probability distribution describing a dishonest die. In this problem I want you to repeat my derivations and work the problem out all the way to the end for three different cases: $\langle i \rangle = 2.5$, $\langle i \rangle = 3.5$ and $\langle i \rangle = 4.5$. Make a plot (a bar plot) of the probability distribution for all three of these cases. Make sure you explain your use of Lagrange multipliers when you do the derivations, describe the meaning of your results, etc. Further, obviously, you are going to have to solve for the relevant Lagrange multiplier numerically - make sure you explain in detail how you solved the problem numerically. In addition, work out the entropy for the two distributions that we "guessed" in class - a) the one in which 4 and 5 had probability 1/2 and b) the linear distribution. Note that for the linear distribution you will need to make sure you compute a distribution that is properly normalized AND satisfies the constraint on the average value.