Assignment #3

PHYS-410
Fall 2013
Mr. Scofield

Announcements

1. Your solutions to this HW assignment are due on Friday, September 27.

Reading

The heart of *Statistical Mechanics* is found by turning away from isolated systems and focusing, instead, on a system in thermal equilibrium with at heat bath at temperature T. This leads to what is called the *Canonical Ensemble*. So long as the particles in our system are distinguishable or we work at sufficiently high temperatures that few particles are found in the ground state, we end up with Boltzmann statistics.

Read Chapter 6 of Schroeder. We will spend roughly two weeks on this important chapter.

Key ideas include:

> the Boltzmann factor $e^{-\varepsilon/kT}$, the partition function Z(T,V,N), paramagnetism (an important 2-level system), the equipartition theorem, the Maxwell speed distribution, and Free energy (F=U-TS). Here we finally treat the ideal gas with some rigor. The density of states is a useful idea here.

I will introduce the idea of a *Density of States* to aid our discussion of the ideal gas. You may find it useful to read pp. 279-281 in your textbook on this topic. I will also put some notes on the web page on this topic.

Schroeder's derivation of the equipartition theorem uses *Classical Statistical Mechanics* – I will skip this for now and come back to it later in the course.

An isolated system (microcanonical ensemble) will adjust its internal parameters so as to <u>maximize</u> its entropy. In contrast, a system in equilibrium with a heat reservoir will adjust its internal parameters so as to <u>minimize</u> its (the system's) *Free Energy*.

Homework Problems (from Schroeder, unless otherwise specified)

Your solutions to the problems below are due at the beginning of class, Friday, Sept. 28.

<u>3.01</u> Problem 2.22 (hint: use expression derived for Schroeder Problem 2.18)
<u>3.02</u> Problem 2.28
<u>3.03</u> Problem 2.29
<u>3.04</u> Problem 2.30
<u>3.05</u> Problem 6.1
<u>3.06</u> Problem 6.2
<u>3.07</u> Problem 6.3
<u>3.08</u> Problem 6.6

Problem 2.22. This problem gives an alternative approach to estimating the width of the peak of the multiplicity function for a system of two large Einstein solids.

(a) Consider two identical Einstein solids, each with N oscillators, in thermal contact with each other. Suppose that the total number of energy units in the combined system is exactly $2N$. How many different macrostates (that is, possible values for the total energy in the first solid) are there for this combined system?

(b) Use the result of Problem 2.18 to find an approximate expression for the total number of microstates for the combined system. (Hint: Treat the combined system as a single Einstein solid. Do *not* throw away factors of "large" numbers, since you will eventually be dividing two "very large" numbers that are nearly equal. *Answer*: $2^{4N}/\sqrt{8\pi N}$.)

(c) The most likely macrostate for this system is (of course) the one in which the energy is shared equally between the two solids. Use the result of Problem 2.18 to find an approximate expression for the multiplicity of this macrostate. (*Answer*: $2^{4N}/(4\pi N)$.)

(d) You can get a rough idea of the "sharpness" of the multiplicity function by comparing your answers to parts (b) and (c). Part (c) tells you the height of the peak, while part (b) tells you the total area under the entire graph. As a very crude approximation, pretend that the peak's shape is rectangular. In this case, how wide would it be? Out of all the macrostates, what fraction have reasonably large probabilities? Evaluate this fraction numerically for the case $N = 10^{23}$.

Problem 2.28. How many possible arrangements are there for a deck of 52 playing cards? (For simplicity, consider only the order of the cards, not whether they are turned upside-down, etc.) Suppose you start with a sorted deck and shuffle it repeatedly, so that all arrangements become "accessible." How much entropy do you create in the process? Express your answer both as a pure number (neglecting the factor of k) and in SI units. Is this entropy significant compared to the entropy associated with arranging thermal energy among the molecules in the cards?

Problem 2.29. Consider a system of two Einstein solids, with $N_A = 300$, $N_B = 200$, and $q_{\text{total}} = 100$ (as discussed in Section 2.3). Compute the entropy of the most likely macrostate and of the least likely macrostate. Also compute the entropy over long time scales, assuming that *all* microstates are accessible. (Neglect the factor of Boltzmann's constant in the definition of entropy; for systems this small it is best to think of entropy as a pure number.)

Problem 2.30. Consider again the system of two large, identical Einstein solids treated in Problem 2.22.

(a) For the case $N = 10^{23}$, compute the entropy of this system (in terms of Boltzmann's constant), assuming that *all* of the microstates are allowed. (This is the system's entropy over long time scales.)

(b) Compute the entropy again, assuming that the system is in its most likely macrostate. (This is the system's entropy over short time scales, except when there is a large and unlikely fluctuation away from the most likely macrostate.)

(c) Is the issue of time scales really relevant to the entropy of this system?

(d) Suppose that, at a moment when the system is near its most likely macrostate, you suddenly insert a partition between the solids so that they can no longer exchange energy. Now, even over long time scales, the entropy is given by your answer to part (b). Since this number is less than your answer to part (a), you have, in a sense, caused a violation of the second law of thermodynamics. Is this violation significant? Should we lose any sleep over it?

Problem 6.1. Consider a system of two Einstein solids, where the first "solid" contains just a single oscillator, while the second solid contains 100 oscillators. The total number of energy units in the combined system is fixed at 500. Use a computer to make a table of the multiplicity of the combined system, for each possible value of the energy of the first solid from 0 units to 20. Make a graph of the total multiplicity vs. the energy of the first solid, and discuss, in some detail, whether the shape of the graph is what you would expect. Also plot the logarithm of the total multiplicity, and discuss the shape of this graph.

Problem 6.2. Prove that the probability of finding an atom in any particular energy *level* is $\mathcal{P}(E) = (1/Z)e^{-F/kT}$, where $F = E - TS$ and the "entropy" of a level is k times the logarithm of the number of degenerate states for that level.

Problem 6.3. Consider a hypothetical atom that has just two states: a ground state with energy zero and an excited state with energy 2 eV. Draw a graph of the partition function for this system as a function of temperature, and evaluate the partition function numerically at $T = 300$ K, 3000 K, 30,000 K, and 300,000 K.

Problem 6.6. Estimate the probability that a hydrogen atom at room temperature is in one of its first excited states (relative to the probability of being in the ground state). Don't forget to take degeneracy into account. Then repeat the calculation for a hydrogen atom in the atmosphere of the star γ UMa, whose surface temperature is approximately 9500 K.