Homework for week 1 (PDF)

1. Energy, Entropy, and Probabilities

The goal of this problem is to show that once we have maximized the entropy and found the microstate probabilities in terms of a Lagrange multiplier $\beta$, we can prove that $\beta = \frac{1}{kT}$ based on the statistical definitions of energy and entropy and the thermodynamic definition of temperature embodied in the thermodynamic identity.

The internal energy and entropy are each defined as a weighted average over microstates:

$$U = \sum_i E_i P_i \quad S = -k_B \sum_i P_i \ln P_i \quad (1)$$

We saw in class that the probability of each microstate can be given in terms of a Lagrange multiplier $\beta$ as

$$P_i = \frac{e^{-\beta E_i}}{Z} \quad Z = \sum_i e^{-\beta E_i} \quad (2)$$

Put these probabilities into the above weighted averages in order to relate $U$ and $S$ to $\beta$. Then make use of the thermodynamic identity

$$dU = TdS - pdV \quad (3)$$

to show that $\beta = \frac{1}{kT}$.

2. Gibbs entropy is extensive

Consider two non-interacting systems $A$ and $B$. We can either treat these systems as separate, or as a single combined system $AB$. We can enumerate all states of the combined by enumerating all states of each separate system. The probability of the combined state $(i_A, j_B)$ is given by $P_{ij}^{AB} = P_i^A P_j^B$. In other words, the probabilities combine in the same way as two dice rolls would, or the probabilities of any other uncorrelated events.

a) Show that the entropy of the combined system $S_{AB}$ is the sum of entropies of the two separate systems considered individually, i.e. $S_{AB} = S_A + S_B$. This means that entropy is extensive. Use the Gibbs entropy for this computation. You need make no approximation in solving this problem.

b) Show that if you have $N$ identical non-interacting systems, their total entropy is $NS_1$ where $S_1$ is the entropy of a single system.

Note: In real materials, we treat properties as being extensive even when there are interactions in the system. In this case, extensivity is a property of large systems, in which surface effects may be neglected.

3. Boltzmann probabilities

Consider the three-state system with energies $(-\epsilon, 0, \epsilon)$ that we discussed in class.

a) At infinite temperature, what are the probabilities of the three states being occupied?

b) At very low temperature, what are the three probabilities?

c) What happens to the probabilities if you allow the temperature to be negative?