Homework 4: Microcanonical and canonical review

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Due: October 27, 2021, 5PM NYC

1. **Entropy from a lattice gas**

   (a) Mixing of two distinguishable species Fig. 1 shows a lattice model for the mixing of two kinds of gas molecules, red and white. Before releasing a barrier, they are kept in separate containers that have a certain number of available sites N_{left} and N_{right}. Here $N_{red} = N_{left}$ and $N_{white} = N_{right}$. Compute the entropy of mixing for this process in the microcanonical ensemble by figuring out how many states of the system there are before and after the mixing process is complete. Hint: consider binomial coefficients.

   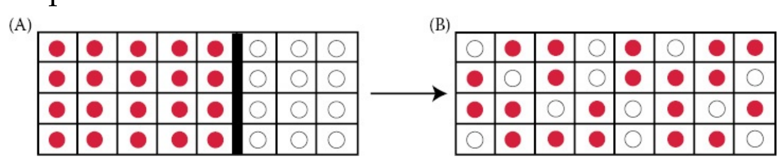

   Figure 1: Model for mixing of two gas species [From, Biomolecular Thermodynamics, Douglas Barrick].

   (b) A simple model for the properties of gas is the so called "lattice gas", where N gas molecules are spread over N_l lattice sites, with the rest being empty. We can represent "excluded volume" of the molecules (a non-ideal gas) by saying that two molecules cannot be on the same site. For this set up, compute the change of entropy during an expansion process where N_l goes from N_i to N_f (Fig. 2), and show that the classic formula for change in entropy appears, i.e. $\Delta S = k_B N \ln(V_f/V_i)$, where V_f and V_i are the volume of the box after and before expansion.

   To do this, make the following assumptions: (1) N_i, N_f and N are sufficiently large that you can apply Sterling's approximation. (2) After making Sterling's approximation and simplifying, find the result in the limit that $N_i >> N$ and $N_f >> N$ as would be true for a dilute gas.

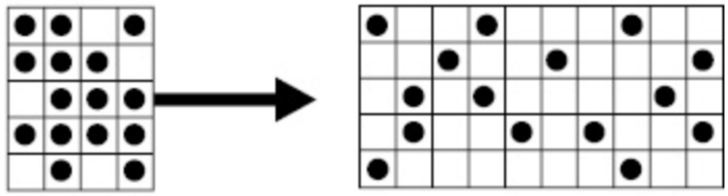

Figure 2: Model for expansion of one gas species [From, Biomolecular Thermodynamics, Douglas Barrick].

2. **Simple polymer attached to a weight**. A common model in statistical mechanics is that of a one-dimensional polymer attached to a weight (Fig. 3. This polymer is made of N links of length l, which can either point up or down. The total length of the polymer is related to the difference in number of up and down links, and the potential energy due to gravity is related to the total length. This problem is very illustrative because it can be 'solved' in either the canonical or microcanonical ensemble.

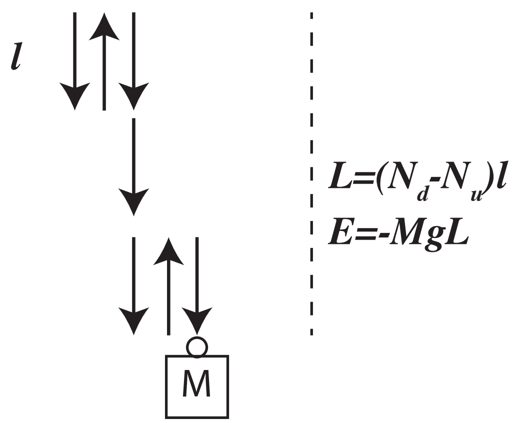

Figure 3: Simple one-dimensional polymer attached to a weight.

(a) *Microcanonical ensemble.* Remember that N and E are constants.

i. Rewrite the total length in two ways, one which depends only on N and N_u, and a second way which only depends on N and N_d.

ii. Plug the previous two results into the equation for energy. Rearrange these two equations to get equations for N_u and N_d in terms of N and E (plus M, g, l).

iii. Write Ω, the number of states of the system for a given fixed N, N_u, and N_d (hint: again consider binomial coefficients).

iv. Simplify an expression for the Boltzmann entropy in the large N, N_u and N_d limit using Sterling's approximation. Plug in your expressions for N_u and N_d to arrive at an expression for the entropy that depends on E instead.

v. Calculate the inverse temperature of the system from $1/T = \partial S/\partial E$.

vi. Solve for E, and then show that the length of the polymer at temperature T is given by $L = Nl \tanh(mgl/(k_B T))$ (given that L is a simple function of E).

vii. Sketch the length of the polymer as a function of temperature.

(b) *Canonical ensemble.* Here N and T are constants.

i. The canonical partition function for a discrete system with enumeratable states i can be written as $Z = \sum_i \Omega(E_i) e^{-\beta E_i}$, where Ω is the number of states at energy E, same as from the microcanonical ensemble. As you saw above, the energy of the system only depends on N_u or N_d. Rewrite Z as a sum over N_d from 0 to N.

ii. Simplify the formula for Z to something very simple. Hint: use the formula for a binomial sum, i.e. $(a+b)^N$.

iii. From Z, compute the average energy by taking a derivative as we learned in class.

iv. Using the fact that $L = -E/mg$, show that $L = Nl \tanh(\beta mgl)$, just as above.

v. Compute the variance of L at temperature T, by computing the variance of E using a formula we derived in class.

vi. Sketch the variance of L as a function of T.