Assignment 4: Free Energy and Partition Functions

Due Tuesday July 17 at 11:59PM under Fernando Rendon's door

Preface: In this assignment, we apply our understanding of free energy to compute how the average spin of a spin system is affected by an external magnetic field. We then compute partition functions for various systems. In the penultimate problem, we derive the formula for the number of derangements of a list, and thus establish the mathematical groundwork for the final problem: the statistical physics of permutations.

1. **Spins in a Magnetic Field: Macrostates**

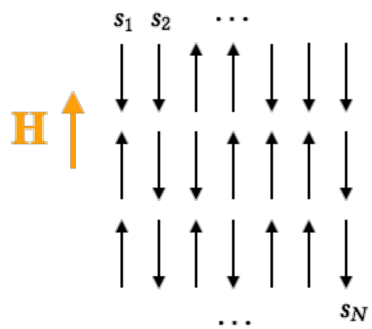


Figure 1: N spins in an external magnetic field H. If a spin s_i is pointing in the same direction as the magnetic field, then its energy is $-\mu H$, and if the spin is pointing in the opposite direction as the field, then its energy is $+\mu H$.

We have N spins in a magnetic field H. The spins are denoted $s_1, s_2, \ldots, s_N$ each of which can take on the value $s_i = \pm 1$, and the system has an energy given by

$$E = -\mu H \sum_{i=1}^{N} s_i. \tag{1}$$

We define the average magnetization of the system as

$$m = \frac{1}{N} \sum_{i=1}^{N} s_i. \tag{2}$$

The system is in thermal equilibrium at a temperature T.

(a) Write the free energy $F_N(m, T)$ of the system as a function of the order parameter m. Use Stirling's approximations and some algebra to simplify the entropic term as much as possible. (*You can quote the relevant entropy result from the notes*).

(b) Compute the value of m for which the free energy in (a) is at a local minimum. Denote this quantity as $\overline{m}$. *(You should find $\overline{m}$ as a function of the parameters of the problem.)*

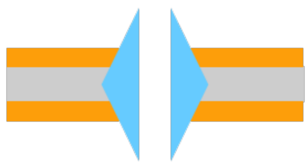
(c) Plot $\overline{m}$ as a function of H for **three** different values of temperature. *(Hand drawn plots are fine.)*.

(d) As $T \to 0$, what happens to $\overline{m}$? What happens to the entropy of the system? *(Demonstrate both results analytically)*

*Hint: For part (a), I **strongly** recommend you do a close reading of the last sections of Lecture Notes 05 "Free Energy and Order Parameters" so you don't spend time re-inventing the wheel.*

2. **Open and Closed Ion Channel**

   An ion channel can be in either an open or a closed microstate (shown in Fig. **??**). When the channel is open, the system has energy $\varepsilon_{\text{open}}$, and when the channel is closed, the system has energy $\varepsilon_{\text{closed}}$.



(a) Ion channel in open microstate

(b) Ion channel in closed microstate

Figure 3

   (a) Our system exists in thermal equilibrium at temperature T. Compute the partition function for this system.

   (b) Define $\Delta\varepsilon \equiv \varepsilon_{\text{closed}} - \varepsilon_{\text{open}}$. What is the probability to be in the open state as a function of T and $\Delta\varepsilon$? Plot a schematic of this probability as a function of T. (A hand-drawn plot is fine.)

   (c) Using the Gibbs definition, compute the entropy of this system as a function of T and $\Delta\varepsilon$. Calculate the value of this entropy when $T \to 0$.

3. **Lattice Model of a Single Dimer**

   At thermal equilibrium defined by a temperature T, say we have two identical particles and L lattice sites arranged along a line. Each of these lattice sites can be occupied by at most one particle at a time. When the particles are on adjacent lattice sites, the system has an energy $-E_0$ and we say the system exists as a dimer. When the particles are separated by at least one lattice site, the system has an energy 0.

Figure 4: A possible microstate in a $L = 10$ system. This microstate has energy $E = 0$.

   (a) What is the partition function of this system? *Hint: You will have to determine the microstates and the energy of each microstate.*

   (b) What is the probability to be in the dimerized state?

   (c) Below what temperature is there a higher likelihood to be in the dimerized state?

4. **Spins in a Magnetic Field: Microstates**

   If we have N spins (labeled $s_1, \ldots s_N$) in a magnetic field H, the energy of a particular microstate is given by

$$E\left(\{s_i\}\right) = -\mu H \sum_{i=1}^{N} s_i, \tag{3}$$

where μ is a magnetic dipole moment. By summing over each value of s_i, weighted by the appropriate Boltzmann factor, we find the partition function

$$Z_N(\beta\mu H) = \sum_{\{s_j=\pm 1\}} \exp\left(\beta\mu H \sum_{i=1}^{N} s_i\right) = 2^N \cosh^N(\beta\mu H), \tag{4}$$

where $\cosh(x)$ is the **hyperbolic cosine** defined as

$$\cosh(x) = \frac{e^x + e^{-x}}{2}. \tag{5}$$

However, we can compute this partition function in a different way.

(a) Letting $n_\uparrow$ be the number of spins with the value $+1$ and $n_\downarrow$ be the number of spins with the value -1, argue that the partition function for this system can be written as

$$Z_N(\beta\mu H) = \sum_{n_\uparrow=0}^{N} \binom{N}{n_\uparrow} e^{\beta\mu H(n_\uparrow - n_\downarrow)}. \tag{6}$$

We term the factor $\binom{N}{n_\uparrow}$ the **degeneracy factor** of the state characterized by $n_\uparrow$ $+1$ spins. The degeneracy factor defines the number of individual microstates associated with the macrostate defined by $n_\uparrow$.

Aside: In general, when computing the partition function of a system in terms of the *macrostate* (instead of the microstate), we compute the product between the Boltzmann factor and the degeneracy factor of a macrostate and then we sum over all macrostates of the system. In the standard formula for the partition function, we sum over microstates which are uniquely specified and thus have a degeneracy factor of 1.

(b) Using the Binomial theorem and the fact that $n_\downarrow = N - n_\uparrow$, show that Eq.(6) reproduces the final equality in Eq.(4).

5. **Number of Derangements**

Say we have an original list of items. A **derangement** of this list is a permutation in which no element in the list is in its original position. In this problem we determine the general formula for the number of derangements of an N item list.

If we have a list of three elements $(1, 2, 3)$ we know there are $3! = 6$ ways we can order the elements. But how many ways can we order these elements such that 1 is *not* the first element, 2 is *not* the second element, and 3 is *not* the third element? That is, for this list of three elements, how many possible derangements are there? We will answer this question in two ways: One by brute force and the other through a derivation which can be generalized.

(a) *Brute Force:* List all the permutations of the three elements $1, 2, 3$. How many permutations have neither 1, 2, nor 3 in the first, second, or third positions, respectively?

(b) *Generalizable derivation:* We can represent the number of permutations of the elements $1, 2, 3$ as a three circle Venn diagram where each circle contains permutations for which the associated number is in its original position:

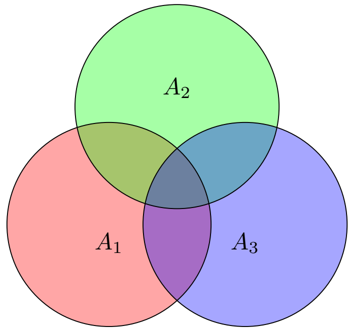


Figure 5: The circle A_k represents all the orderings such that k *is* in the kth position. To find the number of derangements, we will count the number of unique elements in the above diagram and subtract the result from the total number of permutations of three elements.

i. We use $\cap$ to define overlaps between areas in the diagram and $|\,|$ to denote the total number of orderings associated with an area. For example, $|A_k|$ is the total number of orderings such that k is in the kth position, $|A_k \cap A_\ell|$ is the total number of orderings such that k and ℓ are in the kth and ℓth positions respectively, and so on.

   Express the total number of unique orderings in the entire Venn diagram using this $||$ and $\cap$ notation. Simplify the result as much as possible.

   (Hint: There should be seven terms. If we only had two *overlapping circles the answer would be* $|A_1| + |A_2| - |A_1 \cap A_2|$*.)*

ii. Express each of the terms in i. as a factorial (*Note:* $0! = 1$.), and rewrite the result of i. in terms of these factorials. The final expression should have three terms.

iii. The result calculated above is the number of ways to order the numbers $1, 2, 3$ such that *at least one* element is in its original position. How can we compute the number of ways such that *no* element is in the original position?

   We call this quantity d_3 (as in "derangements for a list of three elements"). Write d_3 as an expression with four terms (again keep the factorial symbols).

iv. Express d_3 in summation notation. Namely find an expression

$$d_3 = \sum_{j=0}^{3} (\text{something}), \tag{7}$$

   where "something" is a function of j. *(Hint: for* $j = 0, 1, 2, 3$, $\binom{3}{j} = 1, 3, 3, 1$.*)*

v. Say we have N numbers $1, 2, \ldots, N$. Generalizing the formula above, find an expression for d_N, the number of derangements of a list of N elements.

(c) Use the formula for d_N in (b) v. to fill in the following table:

Number of Elements in List	Number of Derangements
1	–
2	–
3	–
4	–

6. **(Moved to Problem Set 5 as a Challenge Problem)**
Statistical physics of permutations, I

We have $2N$ objects consisting of N objects of type-B denoted $B_1, B_2, \ldots, B_N$ and N objects of type-W denoted $W_1, W_2, \ldots, W_N$. The objects can only exist in (B_k, W_ℓ) pairs, and the mircostates of our system are defined by a particular collection of pairings between the Bs and Ws. Fig. 6 depicts one such microstate for $N = 15$.

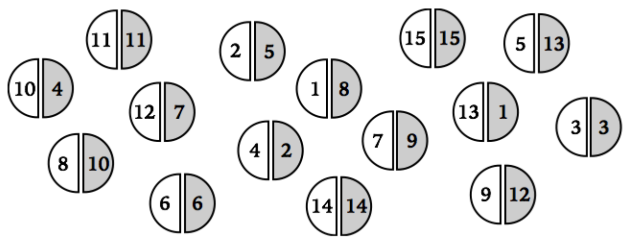


Figure 6: A particular microstate of a $N = 15$ system.

The energy of a microstate is the sum of the energies of all the pairs. The energy of a particular pair (consisting of (B_k, W_ℓ)) is

$$\mathcal{E}(B_k, W_\ell) = \begin{cases} 0 & \text{if } k = \ell, \\ \lambda & \text{if } k \neq \ell, \end{cases} \tag{8}$$

where $\lambda > 0$ is a parameter with units of energy. Namely, from Eq.(8), if a pair consists of (B_k, W_k), for any k, then the energy of the pair is zero, and if a pair consists of (B_ℓ, W_k), for $\ell \neq k$, then the energy of the pair is λ. We call the former a ”matched pair” and the latter a ”mismatched pair”.

(a) How many possible microstates are there for a system with N Bs and N Ws?

(b) Let j be the number of mismatched pairs in a microstate. What is the energy of a microstate written in terms of j? What is the energy for the microstate shown in Eq.(8)?

(c) Let j be the number of mismatched pairs. Argue that the partition function for a system of N Bs and N Ws (governed by the energy Eq.(8)) can be written as

$$Z_N(\beta\lambda) = \sum_{j=0}^{N} g_N(j) e^{-\beta\lambda j}, \tag{9}$$

and explain what $g_N(j)$, λj, and the summation $g_N(j)$ represent. *(Hint: Consider Eq.*(6) *as the analogous expression for a spin system in a magnetic field.)*

(d) We can write $g_N(j)$ as

$$g_N(j) = \binom{N}{j} d_j, \tag{10}$$

where d_j is the number of derangements of j elements. Using the formula for d_j derived in problem 4 of this assignment, the Binomial theorem, and the integral expression for $M!$

$$M! = \int_0^\infty dx\, e^{-x} x^M, \tag{11}$$

derive an integral expression for $Z_N(\beta\lambda)$. *The final expression should not have any un-evaluated sums. Hint: You should first use Eq.*(11) *to express* d_j *as an integral and then use the result in Eq.*(10) *and Eq.*(9).