Assignment 5: Statistical Physics, The Ideal Gas, and Simulations

Due Tuesday July 24 at 11:59PM under Fernando Rendon's door

Preface: In this assignment, we build and explore a model of molecule-receptor binding, derive some canonical results for the ideal gas model, and conclude by working through a soft-introduction to the use of simulations in computational science.

1 Challenge Problem

6. **Statistical physics of permutations**

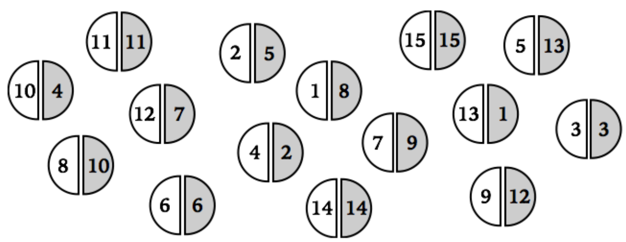

Figure 1: A particular microstate of a $N = 15$ system.

(a) The number of microstates in the system for N Bs and N Ws is the total number of ways to choose a collection of (B_k, W_ℓ) pairings. To find this number we can imagine arranging all the type-B objects along a line in order. Then, the number of collections of (B_k, W_ℓ) pairings is the number of ways we can order the type-W objects along the line of type-B objects. This number is simply the number of ways to order N distinct objects in a list. Therefore, the number of microstates in the system is

$$\boxed{N!} \tag{1}$$

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(b) We know that there is an energy contribution λ for each mismatched pair. Therefore, if there are j mismatched pairs in the system, then the energy is

$$\boxed{E = \lambda j.} \tag{2}$$

For the figure Fig. 1, there are 10 mismatched pairs, so the energy of this microstate is $\boxed{E = 10\lambda.}$

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(c) Whenever we are computing the partition function for a system, we can write the partition function as a summation over microstates or a summation over macrostates. If we write the partition function in terms of the latter, we need to include a degeneracy factor to account for the number of microstates associated with a particular macrostate. Schematically, a general partition function can be written as

$$Z = \sum_{\text{macrostate}} \big(\text{Degeneracy of macrostate}\big) e^{-\beta(\text{Energy of macrostate})}, \tag{3}$$

For example, the partition function of a set of N spins (each of which has magnetic moment μ) in a magnetic field H can be written as

$$Z_{\text{spins}} = \sum_{n_+=0}^{N} \binom{N}{n_+} e^{\beta\mu H(2n_+ - N)}. \tag{4}$$

In the summation, we define the macrostate by n_+, the number of up-spins, and $\binom{N}{n_+}$ represents the degeneracy factor (i.e., the number of microstates with n_+ up spins). The quantity $-\mu H(2n_+ - N)$ is the energy of the macrostate (or, equivalently, the energy of a microstate associated with that macrostate)

For our system of permutations, we can write the partition function as

$$Z_N(\beta\lambda) = \sum_{j=0}^{N} g_N(j) e^{-\beta\lambda j}, \tag{5}$$

where we define our macrostate by the number of mismatched pairs j, and the quantity $-\lambda j$ is the energy of at macrostate. Thus, by Eq.(3), $g_N(j)$ is the degeneracy of the macrostate. Specifically, it is the number of microstates associated with a particular value of j, and, given our definition of j, $g_N(j)$ is found by counting the number of ways we can have j mismatched pairs in a system with N Ws and N Bs.

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(d) In part (c), we surmised that $g_N(j)$ is the number of ways to have j mismatched pairs in the system. We can calculate this quantity by simple combinatorics. Let's say we begin with N matched pairs. To find the number of ways to have j mismatched pairs, we will count the number of ways to choose j of these N original pairs, and then count the number of ways to rearrange the objects in these pairs so that the j pairs are totally mismatched. $g_N(j)$ will then be the product of these two numbers.

First, the number of ways to choose j pairs out of N total pairs is $\binom{N}{j}$.

Next, the number of ways to completely rearrange (i.e., mismatch) the objects in a collection of j paired objects is simply the number of ways to completely rearrange j objects in a line. This quantity was computed in Assignment # 4 and denoted as the number of derangements of a list. For j elements in a list, the number of derangements is

$$d_j = \sum_{k=0}^{j} \binom{j}{k} (-1)^k (j-k)!. \tag{6}$$

Multiplying our two results (the number of ways to choose j pairs from N pairs and the number of ways to completely rearrange the objects in these pairs), we have

$$g_N(j) = \binom{N}{j} d_j. \tag{7}$$

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(e) It is possible to write the formula for derangements as an integral. If we have N items in a list, the number of possible derangements is

$$d_N = \sum_{k=0}^{N} \binom{N}{k} (-1)^k (N-k)!. \tag{8}$$

Using the integral definition of the factorial, we have

$$(N-k)! = \int_0^\infty dx\, e^{-x} x^{N-k}. \tag{9}$$

Inserting this result into Eq.(8) yields

$$\begin{aligned} d_N &= \sum_{k=0}^{N} \binom{N}{k} (-1)^k \int_0^\infty dx\, e^{-x} x^{N-k} \\ &= \int_0^\infty dx\, e^{-x} \sum_{k=0}^{N} \binom{N}{k} (-1)^k x^{N-k} \\ &= \int_0^\infty dx\, e^{-x} (-1+x)^N, \end{aligned} \tag{10}$$

where we used the binomial theorem in the final line. We thus have

$$\boxed{d_N = \int_0^\infty dx\, e^{-x} (x-1)^N.} \tag{11}$$

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(f) We now want to use Eq.(11) to compute an integral expression for the partition function. First, returning to Eq.(7) and using Eq.(11) to write the result as an integral, we have

$$g_N(j) = \binom{N}{j} \int_0^\infty dx\, e^{-x} (x-1)^j. \tag{12}$$

We can insert this result into Eq.(5) to obtain

$$\begin{aligned} Z_N(\beta\lambda) &= \sum_{j=0}^{N} g_N(j) e^{-\beta\lambda j} \\ &= \sum_{j=0}^{N} \binom{N}{j} \int_0^\infty dx\, e^{-x} (x-1)^j e^{-\beta\lambda j} \\ &= \int_0^\infty dx\, e^{-x} \sum_{j=0}^{N} \binom{N}{j} \left[(x-1)e^{-\beta\lambda}\right]^j. \end{aligned} \tag{13}$$

Using the Binomial theorem in the final line, we obtain

$$\boxed{Z_N(\beta\lambda) = \int_0^\infty dx\, e^{-x} \left[1 + (x-1)e^{-\beta\lambda}\right]^N.} \tag{14}$$

We note that if we set $\lambda = 0$, we find

$$\begin{aligned} Z_N(\beta\lambda)\Big|_{\lambda=0} &= \int_0^\infty dx\, e^{-x} \Big[1 + (x-1)\Big]^N \\ &= \int_0^\infty dx\, e^{-x} x^N = N!, \end{aligned} \tag{15}$$

which is the total number of microstates in the system. This is what we expect: When all the microstates have the same energy, the partition function reduces to the total number of microstates in the system.

$\blacksquare$

(g) We now seek to use Laplace's method to evaluate the integral in Eq.(14). First we write the partition function as

$$Z_N(\beta\lambda) = \int_0^\infty dx\, e^{-x}\Big[1+(x-1)e^{-\beta\lambda}\Big]^N = \int_0^\infty dx\, e^{-Nf(x,\beta\lambda)}, \tag{16}$$

where we defined

$$f(x,\beta\lambda) = \frac{x}{N} - \ln(1+(x-1)e^{-\beta\lambda}). \tag{17}$$

Then, by Laplace's method, we have

$$Z_N(\beta\lambda) \simeq \sqrt{\frac{2\pi}{Nf''(x_1,\beta\lambda)}}\exp\left[-Nf(x_1,\beta\lambda)\right], \tag{18}$$

where x_1 is the value of x at which $f(x,\beta\lambda)$ is at a local minimum. To find this value of x we calculate $f'(x,\beta\lambda)$ and set it to zero for when $x = x_1$. Doing so we have

$$\begin{aligned} 0 &= f'(x,\beta\lambda)|_{x=x_1} \\ &= \frac{1}{N} - \frac{e^{-\beta\lambda}}{1+(x_1-1)e^{-\beta\lambda}} \\ \frac{1}{N} &= \frac{e^{-\beta\lambda}}{1+(x_1-1)e^{-\beta\lambda}} \\ &= \frac{1}{e^{\beta\lambda}+x_1-1}. \end{aligned} \tag{19}$$

Calculating the inverse of the final line and adding $1-e^{\beta\lambda}$ to both sides gives us

$$x_1 = N - e^{\beta\lambda} + 1. \tag{20}$$

Eq.(20) gives us the value at which the first x derivative of Eq.(17) is zero. To apply Laplace's method, we need to ensure that Eq.(17) is at a local minimum at Eq.(20). Computing the second derivative of $f(x,\beta\lambda)$ at x_1, we have

$$\begin{aligned} f''(x,\beta\lambda)\Big|_{x=x_1} &= \frac{e^{-\beta\lambda}e^{-\beta\lambda}}{(1+(x_1-1)e^{-\beta\lambda})^2} \\ &= \left(\frac{e^{-\beta\lambda}}{1+(x_1-1)e^{-\beta\lambda}}\right) \\ &= \frac{1}{N^2}, \end{aligned} \tag{21}$$

where in the final line we used the equality above Eq.(19). We thus see that x_1 indeed defines a local minimum because $f''(x,\beta\lambda)$ is always positive at x_1. To complete our evaluation of Eq.(18), we need to compute $f(x,\beta\lambda)$ at x_1. Doing so, we have

$$\begin{aligned} f(x,\beta\lambda)|_{x=x_1} &= \frac{N-e^{\beta\lambda}+1}{N} - \ln(Ne^{\beta\lambda}) \\ &= \frac{N-e^{\beta\lambda}+1}{N} - \ln N - \beta\lambda. \end{aligned} \tag{22}$$

Finally, with Eq.(22) and Eq.(21), we find that Eq.(18) becomes

$$Z_N(\beta\lambda) \simeq \sqrt{\frac{2\pi}{N\frac{1}{N^2}}} \exp\left[-N\left(\frac{N - e^{\beta\lambda} + 1}{N} - \ln N - \beta\lambda\right)\right], \tag{23}$$

or, more simply,

$$\boxed{Z_N(\beta\lambda) \simeq \sqrt{2\pi N} \exp\Big[-\big(N - e^{\beta\lambda} + 1 - N\ln N - N\beta\lambda\big)\Big],} \tag{24}$$

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(h) We want to find an expression for $\langle j \rangle$, the average number of mismatched pairs, in terms of the partition function and its derivative. From the definition of the partition function as a finite sum, we have

$$Z_N(\beta\lambda) = \sum_{j=0}^{N} g_N(j) e^{-\beta\lambda j}. \tag{25}$$

From this expression, we can infer that $\langle j \rangle$ is

$$\begin{aligned} \langle j \rangle &= \frac{1}{Z_N(\beta\lambda)} \sum_{j=0}^{N} j\, g_N(j) e^{-\beta\lambda j} \\ &= -\frac{1}{Z_N(\beta\lambda)} \frac{\partial}{\partial(\beta\lambda)} Z_N(\beta\lambda). \end{aligned} \tag{26}$$

From the properties of chain rule, we then find

$$\boxed{\langle j \rangle = -\frac{\partial}{\partial(\beta\lambda)} \ln Z_N(\beta\lambda),} \tag{27}$$

which is the desired expression. ■

(i) Combining the results from (g) and (h), we can find an approximate expression for the average number of mismatched pairs as a function of temperature. We have

$$\begin{aligned} \langle j \rangle &= -\frac{\partial}{\partial(\beta\lambda)} \ln Z_N(\beta\lambda) \\ &\simeq -\frac{\partial}{\partial(\beta\lambda)} \left[\frac{1}{2}\ln(2\pi N) - \big(N - e^{\beta\lambda} + 1 - N\ln N - N\beta\lambda\big)\right] \\ &= -e^{\beta\lambda} + N, \end{aligned} \tag{28}$$

which yields the temperature dependent function

$$\boxed{\langle j \rangle \simeq N - e^{\lambda/k_B T}.} \tag{29}$$

Since $\langle j \rangle \geq 0$, we see that Eq.(29) is only valid for certain temperatures. Namely, solving for the temperature at which $\langle j \rangle \geq 0$, we find

$$\boxed{k_B T \geq \frac{\lambda}{\ln N}.} \tag{30}$$

Below this temperature, $\langle j \rangle$ assumes the value $\langle j \rangle = 0$.

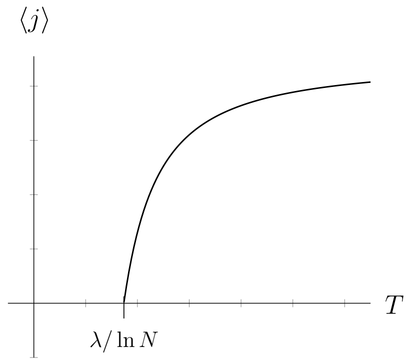

Figure 2: Plot of $\langle j \rangle$ as a function of T. Below the temperature $\lambda/\ln N$, the average number of mismatched pairs is zero.

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