

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. Model of Receptor Binding

On the cell membranes of cells, there are protein receptors to which extracellular molecules can bind and ultimately induce a signal in the cell. Let us consider a simple model of such receptor-molecule binding and analyze this model from the perspective of statistical physics.

Say we have many molecules each of which can either be free or bound to one of M distinct protein receptors (There are many more molecules than receptors). The molecules are identical to one another and each one has energy 0 when it is free and energy $-E_0$ when it is bound to a receptor. Our system exists at a temperature T . An example microstate is shown in Fig. 1.

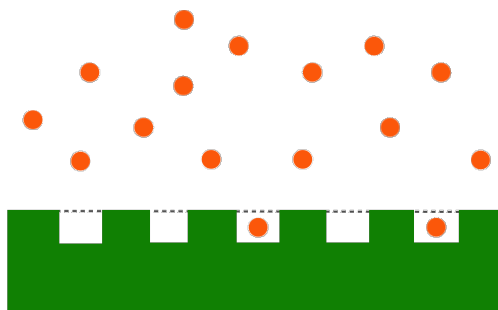


Figure 1: A particular microstate of a system with $M = 5$ receptor sites. There are two molecules bound to receptors so the energy of this microstate is $-2E_0$.

- (a) (6 points) There are a number of questions we can ask about the given physical system. You only needed to provide **three** questions; here are several possible ones
- What is the partition function of this system in terms of E_0 and T (or β)?
 - What is the average number of occupied receptor sites?
 - What is the average number of occupied receptor sites when $T \rightarrow 0$?
 - What is the probability that all M receptor sites are occupied?
 - What is the Gibbs entropy of this system?
 - As a function of k , the number of occupied receptor sites, what is the Boltzmann entropy of the system?
 - If we assumed the molecules not bound to the receptor behaved as particles in an ideal gas of volume V , what would the partition function be?

The important thing about these questions is that they be well-defined which means that we can answer them explicitly using the methods we have learned so far this summer. ■

- (b) (6 points) We will answer the first two questions listed above.

- **What is the partition function of this system in terms of E_0 and T (or β)?**

We have a system with many identical molecules, each of which has energy 0 when it is unbound and energy $-E_0$ when it is bound to a receptor site. There are M distinct receptor sites. Therefore, if $k \leq M$ molecules are bound to receptor sites, there is “ M choose k ” number of ways to arrange these identical molecules amongst the M sites, and such a microstate has energy $-E_0 k$. Therefore, the probability to have k occupied receptor sites is given by

$$p_k = \frac{1}{Z_M(\beta E_0)} \binom{M}{k} e^{\beta E_0 k}, \quad (1)$$

where Z is the partition function of the system. Given that k can run from 0 to M , we then find the partition function

$$Z_M(\beta E_0) = \sum_{k=0}^M \binom{M}{k} e^{\beta E_0 k} = (1 + e^{\beta E_0})^M, \quad (2)$$

where we used the binomial theorem in the final line.

- **What is the average number of occupied receptor sites?**

We can compute $\langle k \rangle$, the average number of occupied receptor sites, by using Eq.(1) in our probability based definition of average. We have

$$\langle k \rangle = \sum_{k=0}^M k p_k = \frac{1}{Z_M(\beta E_0)} \sum_{k=0}^M k \binom{M}{k} e^{\beta E_0 k}. \quad (3)$$

From Eq.(2), we can write Eq.(3) in terms of the partial derivative of the partition function. We then find

$$\begin{aligned} \langle k \rangle &= \frac{1}{Z_M(\beta E_0)} \frac{\partial}{\partial(\beta E_0)} \sum_{k=0}^M \binom{M}{k} e^{\beta E_0 k} \\ &= \frac{1}{Z_M(\beta E_0)} \frac{\partial}{\partial(\beta E_0)} Z_M(\beta E_0) \\ &= \frac{\partial}{\partial(\beta E_0)} \ln Z_M(\beta E_0). \end{aligned} \quad (4)$$

Using Eq.(2) to compute this quantity yields

$$\langle k \rangle = \frac{\partial}{\partial(\beta E_0)} \ln (1 + e^{\beta E_0})^M = \frac{M}{1 + e^{-\beta E_0}}. \quad (5)$$

Therefore, the Eq.(5) is bounded above by M (as we expect) and as $T \rightarrow 0$ (i.e., $\beta \rightarrow \infty$), $\langle k \rangle$ approaches M and all the receptor sites become fully occupied. Conversely, as $T \rightarrow \infty$, $\langle k \rangle$ approaches $M/2$ and half of the sites become occupied. Entropically, this makes sense because as $T \rightarrow 0$, entropy dominates the free energy and the system seeks the macrostate with the highest entropy. ■

2. Average Energy of an Ideal Gas

(a) In Lecture Notes 07, we showed that the partition function of the ideal gas is

$$Z_{\text{ideal gas}} = \frac{V^N}{N!} \left(\frac{\sqrt{2\pi m k_B T}}{h} \right)^{3N}. \quad (6)$$

Writing Eq.(6) in terms of $\beta = 1/k_B T$, we obtain

$$Z_{\text{ideal gas}} = \frac{V^N}{N!} \left(\frac{1}{h} \sqrt{\frac{2\pi m}{\beta}} \right)^{3N}. \quad (7)$$

Using Eq.(13) and Eq.(7), to compute the average energy of the ideal gas, we find

$$\begin{aligned} \langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z_{\text{ideal gas}} \\ &= -\frac{\partial}{\partial \beta} \ln \left[\frac{V^N}{N!} \left(\frac{1}{h} \sqrt{\frac{2\pi m}{\beta}} \right)^{3N} \right] \\ &= -\frac{\partial}{\partial \beta} \left[\ln \frac{V^N}{N!} + \ln \left(\frac{\sqrt{2\pi m}}{h} \right)^{3N} + \ln \frac{1}{\beta^{3N/2}} \right] \\ &= \frac{3N}{2} \frac{\partial}{\partial \beta} \ln \beta = \frac{3N}{2} \frac{1}{\beta}, \end{aligned} \quad (8)$$

where in the final line we dropped all terms that did not depend on β . With the definition of β in terms of temperature, we then find that

$$\boxed{\langle E \rangle = \frac{3}{2} N k_B T.} \quad (9)$$

Eq.(63) is an important result in statistical physics. Since $\langle E \rangle$ only comes from kinetic energy contributions to the ideal gas, the average kinetic energy per particle is

$$\text{Avg kinetic energy per particle} = \frac{\langle E \rangle}{N} = \frac{3}{2} k_B T. \quad (10)$$

or

$$T = \frac{2}{3k_B} (\text{Avg kinetic energy per particle}). \quad (11)$$

From Eq.(11) comes the interpretation of T as a proxy for the average kinetic energy of a gas particle in a gas.

- (b) We want to prove the relationship between the partial derivatives of $\ln Z$ and the variance σ_E^2 in the energy of an ideal gas. With Z defined as

$$Z = \sum_{\{i\}} e^{-\beta E_i}, \quad (12)$$

the average energy is given by

$$-\frac{\partial}{\partial \beta} \ln Z = \sum_{\{i\}} E_i \frac{e^{-\beta E_i}}{Z} = \langle E \rangle. \quad (13)$$

Computing the *negative* of the second derivative of Eq.(13), we obtain

$$\frac{\partial^2}{\partial \beta^2} \ln Z = -\frac{\partial}{\partial \beta} \sum_{\{i\}} E_i \frac{e^{-\beta E_i}}{Z}$$

$$\begin{aligned}
&= - \sum_{\{i\}} E_i e^{-\beta E_i} \left(\frac{\partial}{\partial \beta} \frac{1}{Z} \right) - \sum_{\{i\}} E_i \frac{1}{Z} \frac{\partial}{\partial \beta} e^{-\beta E_i} \\
&= - \sum_{\{i\}} E_i e^{-\beta E_i} \left(\frac{\partial}{\partial \beta} \frac{1}{Z} \right) + \sum_{\{i\}} E_i \frac{1}{Z} E_i e^{-\beta E_i} \\
&= \sum_{\{i\}} E_i e^{-\beta E_i} \frac{1}{Z^2} \left(\frac{\partial}{\partial \beta} Z \right) + \sum_{\{i\}} E_i^2 \frac{1}{Z} e^{-\beta E_i} \\
&= - \sum_{\{i\}} E_i e^{-\beta E_i} \frac{1}{Z^2} \left(\sum_{\{j\}} E_j e^{-\beta E_j} \right) + \sum_{\{i\}} E_i^2 \frac{1}{Z} e^{-\beta E_i}, \tag{14}
\end{aligned}$$

where we used

$$\sum_{\{j\}} E_j e^{-\beta E_j} = - \frac{\partial}{\partial \beta} \sum_{\{j\}} e^{-\beta E_j} = - \frac{\partial}{\partial \beta} Z, \tag{15}$$

in the final line. Given that the index defining the summation is unimportant, and scalar factors multiplying summations can be brought inside the integral symbol, we can write Eq.(14) as

$$\frac{\partial^2}{\partial \beta^2} \ln Z = - \left(\sum_{\{i\}} E_i \frac{e^{-\beta E_i}}{Z} \right) + \sum_{\{i\}} E_i^2 \frac{1}{Z} e^{-\beta E_i}. \tag{16}$$

Finally, with the definition of microstate probability as $p_j = e^{-\beta E_j} / Z$, we can write Eq.(16) as

$$\frac{\partial^2}{\partial \beta^2} \ln Z = - \left(\sum_{\{i\}} E_i p_i \right) + \sum_{\{i\}} E_i^2 p_i = - \langle E \rangle^2 + \langle E^2 \rangle = \sigma_E^2, \tag{17}$$

and the identity is therefore proved. ■

- (c) We want to find the standard deviation in the energy of an ideal gas, and in order to do this we must first compute the variance. Using Eq.(17), Eq.(7), and part of the result from (a), we find the variance

$$\begin{aligned}
\sigma_E^2 &= \frac{\partial^2}{\partial \beta^2} \ln Z_{\text{ideal gas}} \\
&= \frac{\partial^2}{\partial \beta^2} \left[\ln \frac{V^N}{N!} + \ln \left(\frac{\sqrt{2\pi m}}{h} \right)^{3N} + \ln \frac{1}{\beta^{3N/2}} \right] \tag{18}
\end{aligned}$$

$$= - \frac{\partial}{\partial \beta} \frac{3N}{2\beta} = \frac{3N}{2\beta^2}. \tag{19}$$

In terms of temperature, we therefore have the variance $\sigma_E^2 = \frac{3}{2} N (k_B T)^2$, and the standard deviation

$$\boxed{\sigma_E = k_B T \sqrt{\frac{3}{2} N}}. \tag{20}$$

- (d) If $\langle E \rangle$ and σ_E are the mean and standard deviation, respectively, of a Gaussian, then Eq.(63) and ■

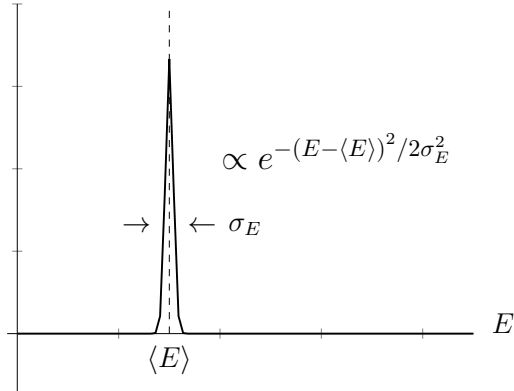


Figure 2: Plot of Gaussian distribution of ideal gas energies: The distribution of energies is sharply peaked about the mean. The width σ_E is much smaller (in scale) than $\langle E \rangle$. Given that there is a 99% chance that a random variable falls within 3 standard deviations away from the mean, this means that in real systems of gas molecules, the average energy of the system (the random variable in this situation) is essentially always very close to the theoretical mean $\langle E \rangle$.

Eq.(20) tell us that, for constant temperature,

$$\langle E \rangle \sim N, \quad \sigma_E \sim N^{1/2}. \quad (21)$$

For the Gaussian distribution, σ_E provides a rough scale for how wide the distribution is about the mean. What Eq.(21) tells us is that for $N \gg 1$ (like $N = 10^{26}$), **the mean of the distribution is many orders of magnitude larger than the standard deviation**. Therefore, for these very large values of N the distribution is highly peaked at $\langle E \rangle$ and has a very narrow distribution about this value.

A schematic of such a plot is shown in Fig. 2. ■

3. Ideal Gas Law

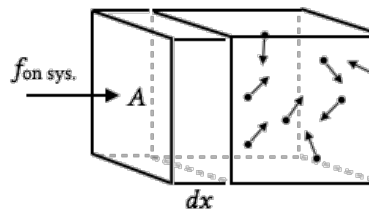


Figure 3: An external force $f_{\text{on sys.}}$ applied to a wall of area A on a volume V of gas. We can use this depiction to define a pressure exerted by the gas on the surroundings.

- (a) (4 points) We want to find a relationship between the change in free energy and the work done on a system. The free energy of a system is given by

$$F_{\text{sys.}} = E_{\text{sys.}} - TS_{\text{sys.}}. \quad (22)$$

For a constant temperature system, the change in free energy dF_{sys} can be related to the change in energy dE_{sys} and the change in entropy dS_{sys} through

$$dF_{\text{sys}} = d(E_{\text{sys}} - TS_{\text{sys}}) = dE_{\text{sys}} - TdS_{\text{sys}}, \quad (23)$$

where in the final equality we distributed the differential operator d across the terms in the parentheses and treated T as a constant. Now, by conservation of energy, we know that the change in the internal energy dE_{sys} of a system is given by

$$dE_{\text{sys}} = dW_{\text{on sys.}} + dQ_{\text{ent.}} \quad (24)$$

$dW_{\text{on sys.}}$ is the work done on the system, and $dQ_{\text{ent.}}$ is the heat entering the system. For the system of interest, we will take the entropy change of the system to be

$$dS_{\text{sys.}} = dQ_{\text{ent.}}/T, \quad (25)$$

which allows us to write Eq.(24) as

$$dE_{\text{sys.}} = dW_{\text{on sys.}} + TdS_{\text{sys.}} \quad (26)$$

Subtracting $TdS_{\text{sys.}}$ from both sides of Eq.(26), we have

$$dW_{\text{on sys.}} = dE_{\text{sys.}} - TdS_{\text{sys.}} \quad (27)$$

Finally, using Eq.(36) in , we obtain

$$\boxed{dW_{\text{on sys.}} = dF_{\text{sys.}}} \quad (28)$$

Namely, the work done on a system is equal to the change in the free energy of the system. ■

- (b) (4 points) Our objective is to prove a relationship between the work done on a system, the pressure of the system, and the change in the volume of the system. We begin with the equation for the incremental work $dW_{\text{on sys.}}$ done on a system given that an external force $f_{\text{on sys.}}$ is applied to the system over a distance dx :

$$dW_{\text{on sys.}} = f_{\text{on sys.}} dx. \quad (29)$$

By Newton's third law, the force that the surroundings exert on a system is equal in magnitude and opposite in direction to the corresponding force the system applies to its surroundings. Namely, if $f_{\text{by sys.}}$ is the force the system exerts on its surroundings, then we have

$$f_{\text{on sys.}} = -f_{\text{by sys.}} \quad (30)$$

Plugging Eq.(30) into Eq.(29), we have

$$dW_{\text{on sys.}} = -f_{\text{by sys.}} dx. \quad (31)$$

Say that our volume V consists of a rectangular prism of the kind in Eq.(??). For a volume V represented by a rectangular prism, if we translate a face of the prism with area A by changing a side length of the prism by a distance dx , then the volume change dV of the system is

$$dV = A dx. \quad (32)$$

This result, together with the definition of the pressure that a system exerts on its surroundings,

$$P = \frac{f_{\text{by sys.}}}{A}, \quad (33)$$

Eq.(31) becomes

$$dW_{\text{on sys.}} = -\frac{f_{\text{by sys.}}}{A} A dx = -PdV, \quad (34)$$

and the result is proved. ■

- (c) (4 points) We seek a relationship between the free energy of our ideal gas system and the pressure the ideal gas exerts on its surroundings. We write the free energy of our system explicitly in terms of its dependent variables T , V , and N as

$$F_{\text{sys.}} = F(T, V, N). \quad (35)$$

Any change in $F(T, V, N)$ can be written as a linear combination of the changes along its independent variables where the coefficients are defined by the appropriate partial derivative:

$$dF(T, V, N) = \left(\frac{\partial F}{\partial T}\right) dT + \left(\frac{\partial F}{\partial N}\right) dN + \left(\frac{\partial F}{\partial V}\right) dV. \quad (36)$$

For a system which is at constant temperature T and which does not change its number of particles N , the first and the last terms in Eq.(36) vanish and with Eq.(35) we are left with

$$dF_{\text{sys.}} = \left(\frac{\partial F}{\partial V}\right) dV.. \quad (37)$$

Now, from Eq.(28) and Eq.(34), Eq.(37) becomes

$$\left(\frac{\partial F}{\partial V}\right) dV = dF_{\text{sys.}} = dW_{\text{on sys.}} = -PdV. \quad (38)$$

Taking the coefficient of dV on the far left side of Eq.(38) to be equal to the coefficient of dV on the far right side of Eq.(38), we have

$$P = -\left(\frac{\partial F}{\partial V}\right), \quad (39)$$

which is the desired relationship between free energy and pressure. ■

- (d) (4 points) We will use the derived result Eq.(39) to derive the relationship between pressure P , volume V , temperature T , and number of particles N for the ideal gas. Given that the free energy F is related to the partition function Z through

$$F = -k_B T \ln Z, \quad (40)$$

we can use the ideal gas partition function Eq.(6), to find

$$P = -\left(\frac{\partial F}{\partial V}\right)$$

$$\begin{aligned}
&= k_B T \frac{\partial}{\partial V} \ln \left[\frac{V^N}{N!} \left(\frac{\sqrt{2\pi m k_B T}}{h} \right)^{3N} \right] \\
&= k_B T \frac{\partial}{\partial V} \left[\ln \frac{V^N}{N!} + \ln \left(\frac{\sqrt{2\pi m}}{h} \right)^{3N} + \ln \frac{1}{\beta^{3N/2}} \right] \\
&= N k_B T \frac{\partial}{\partial V} \ln V,
\end{aligned} \tag{41}$$

where in the last line we dropped all terms that were not functions of V . Differentiating the final line, we obtain

$$P = \frac{N k_B T}{V}, \tag{42}$$

or in its more standard form

$$PV = N k_B T. \tag{43}$$

We note that in form of the ideal gas law given in Eq.(43), N is the number of *particles* in the system, and $k_B = 1.3807 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ is Boltzmann's constant. The ideal gas law is sometimes written as

$$PV = nRT, \tag{44}$$

where n is the number of *moles* of particles in the system, and $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Eq.(43) and Eq.(44) are equivalent, given that $N/N_A = n$ and $N_A k_B = R$, where $N_A = 6.022 \times 10^{23}$ is Avogadro's number. ■

4. Laplace's Method and Stirling's Approximation

- (a) (4 points) We want to use Laplace's method to approximate the Gamma function. First we write the equation in a more suggestive form:

$$\Gamma(N+1) = \int_0^\infty dx e^{-x+N \ln x} \equiv \int_0^\infty dx e^{-Nf(x)}, \tag{45}$$

where we defined

$$f(x) = \frac{x}{N} - \ln x. \tag{46}$$

In standard derivation of the Laplace's method procedure, we did not assume the parameter N was part of the function $f(x)$, but it turns out the procedure still applies as long as there is a function proportional to N in the argument of the exponential. From the definition of the gamma function in Eq.(45), that function is $N \ln x$. Now, in order to compute the value of x at which Eq.(46) has a local minimum, we must first find the point at which $f'(x) = 0$. Labeling this point x_1 , we find it is constrained by

$$0 = f'(x = x_1) = \frac{1}{N} - \frac{1}{x_1}, \tag{47}$$

which implies

$$x_1 = N. \tag{48}$$

Now, computing the second derivative of Eq.(46) to ensure that $f(x)$ has a local minimum at the point, we have

$$f''(x = x_1) = \frac{d}{dx} \left(\frac{1}{N} - \frac{1}{x} \right) \Big|_{x=x_1} = \frac{1}{x_1^2} = \frac{1}{N^2}. \tag{49}$$

Since $N > 0$, we have $f''(x = x_1) > 0$ and therefore $x_1 = N$ defines a local minimum for this system. As the last step in the Laplace's method procedure, we need to compute $f(x)$ at the value $x = x_1$. We have

$$f(x = x_1) = \frac{x_1}{N} - \ln x_1 = 1 - \ln N. \quad (50)$$

Finally, with Eq.(49) and Eq.(50), we can apply the derived formula for Laplace's method. Doing so gives us

$$\begin{aligned} \Gamma(N + 1) &= \int_0^{\infty} dx e^{-x+N \ln x} \\ &= \int_0^{\infty} dx e^{-Nf(x)} \\ &\simeq \sqrt{\frac{2\pi}{N f''(x_1)}} e^{-Nf(x_1)} \\ &= \sqrt{\frac{2\pi}{N(1/N^2)}} e^{-N+N \ln N}. \end{aligned} \quad (51)$$

With $e^{-N+N \ln N} = (e^{-1} e^{\ln N})^N = (N/e)^N$, we then have the final result

$$\boxed{\Gamma(N + 1) \simeq \sqrt{2\pi N} \left(\frac{N}{e}\right)^N}. \quad (52)$$

- (b) (2 points) In Assignment #3, we derived that the Gamma function $\Gamma(N + 1)$ is equal to $N!$. Therefore, Eq.(86) indicates that we can approximate $N!$ as

$$N! \simeq \sqrt{2\pi N} \left(\frac{N}{e}\right)^N, \quad (53)$$

which is what we have been using as Stirling's approximation.

- (c) (4 points) We want to compute the percent error of the approximation Eq.(53). We will choose $N = 100$ as our value of N . Computing the result exactly using the definition $N! = N(N - 1) \cdots 2 \cdot 1$, we have

$$(N!)_{\text{exact}} = 9.332621 \times 10^{157}. \quad (54)$$

Now computing $N!$ approximately using Eq.(53), we find

$$(N!)_{\text{approx.}} = 9.324847 \times 10^{157}. \quad (55)$$

Finally, computing the percent error in the approximation, we have

$$\% \text{ error in approximation of } N! = \frac{|(N!)_{\text{approx.}} - (N!)_{\text{exact}}|}{(N!)_{\text{exact}}} \times 100 = 8.33 \times 10^{-2}. \quad (56)$$

Therefore when we apply Stirling's approximation to $N = 100$, we have a $\sim 0.1\%$ error in our result. As we increase N , this percent error gets even smaller and smaller such that when we are considering N on the order of Avogadro's number (10^{26}), the error is virtually non-existent.



5. Coin-Flip Simulation and the Gaussian Distribution

If we flip a fair coin N times, then the probability that we get k heads is

$$P(N, k) = \frac{1}{2^N} \binom{N}{k}. \quad (57)$$

Using Stirling's approximation (proved in Problem 1 of this assignment), it is possible to show that for $N \gg 1$, the probability Eq.(57) can be approximated as the Gaussian

$$P(N, k) \simeq \sqrt{\frac{2}{\pi N}} \exp\left(-\frac{2}{N}(k - N/2)^2\right). \quad (58)$$

The relation between Eq.(57) and Eq.(58) is another example of the **central limit theorem**, the theorem stating that some distributions reduce to the Gaussian distribution in the large N limit. In this problem, we will demonstrate this result computationally by simulating many different runs of coin flips. In science and engineering, simulations are used to understand theoretical models qualitatively in lieu of actual experiments, which may be difficult or time consuming to perform. For example, rather than flipping a coin 1000 times and counting the number of heads ourselves, we will run a simulation to do this coin-flipping and counting for us.

We will be using *Mathematica* to complete this problem, so we need to establish some code preliminaries.

- (i) Log in to your account in one of MIT's Athena Clusters, and go to the MITES 2018 –Physics III course website.
- (ii) Download the code `coin_flip_simulation.nb` from the course webpage and open it in *Mathematica*.
- (iii) Select a block of code and run it by pressing `Shift+Enter`.

Now we can begin the problem itself

- (a) What is the mean and what is the standard deviation of Eq.(57)? What are these values for $N = 1000$? *Hint: You already computed both of these quantities in Assignment #2 so you can just quote the answer.*
- (b) Run each line of the "Function Definitions" section of the code to determine what the associated function does.
- (c) Run each part of the "Simple Code Examples" section. For each line that has a `(*)`, explain the purpose of the line in the overall code (For example, "This line defines the function `v`" or "This line produces a random number between 0 and 1"). You can write your annotations between the asterisks of `(*)`.
- (d) In "Simulating Coin Flips", we have two code blocks. The first code block provides a single simulation of coin flips, like flipping a coin 100 times and counting the number of heads. A student wrote this block of code with the intention of making it depict flipping a **fair coin** (i.e., 50% chance of heads and 50% chance of tails) **1000 times** and **incrementing the tally of heads by 1** only if heads is obtained. However, he made some mistakes in his code. **Correct his code, annotate/explain each line with a `(*)`, and run it to produce the intended simulation.**
- (e) The second code block of "Simulating Coin Flips" provides *many* simulations of coin flips, like having 100 people *each* flip a coin 100 times and counting the distribution of heads across all people.

In the second code block of "Simulating Coin Flips", the student wanted to simulate **5000 people** flipping a **fair coin** (i.e., 50% chance of heads and 50% chance of tails) **1000 times** and he wanted to create a histogram of the number of heads obtained across all people. However, he made some mistakes in his code.

Correct his code, annotate/explain each line with a (* *), and run it to produce the intended simulation.

- (f) After you run (e), you should find the distribution, the mean, and standard deviation of number of heads for the 5000 simulations of 1000 coin flips.
- What probability distribution does the distribution of heads in the histogram remind you of?
 - How do the mean and standard deviation compare to the theoretical results computed in (a)?

Submitting: As your submission for this part of the assignment, you should first make sure you write your name at the top of the notebook. Then, you should print out the entire *Mathematica* notebook which should include your runs, corrections, and annotations from the various parts of the problem.

- (a) We want to determine the mean and the standard deviation for the distribution

$$P(N, k) = \frac{1}{2^N} \binom{N}{k}. \quad (59)$$

Eq.(59) is the binomial distribution with $p = 1 - p = 1/2$. In Assignment #2, we found that the mean and standard deviation of the binomial distribution for general p is

$$\langle k \rangle = Np, \quad \sigma_k = \sqrt{Np(1-p)}. \quad (60)$$

With our particular value of $p = 1/2$, we then have

$$\boxed{\langle k \rangle = \frac{N}{2}, \quad \sigma_k = \frac{\sqrt{N}}{2}.} \quad (61)$$

For $N = 1000$, Eq.(61) become

$$\boxed{\langle k \rangle = 500, \quad \sigma_k = 15.811.} \quad (62)$$

■

Solutions to parts (b)–(f) are given in the solutions notebook for this problem.

1 Challenge Problem

Rules of Play: The due date for this challenge problem is **Sunday July 29** at the start of our final exam review session. Students who complete parts of this problem receive awards. Here are how awards are meted out:

- (a) Any points obtained from solving the problem are added to your final exam score.
- (b) If **at least half** of the class completes up to and including **part (e)**, then Jason will bake something for the final exam.
- (c) In addition to (a), any student who solves the problem in full, will have **one fewer problem** on their final exam. (There will be 5-6 problems for the two hour final).

6. Statistical physics of permutations

We have $2N$ objects consisting of N objects of type- B denoted B_1, B_2, \dots, B_N and N objects of type- W denoted W_1, W_2, \dots, W_N . The objects can only exist in (B_k, W_ℓ) pairs, and the microstates of our system are defined by a particular collection of pairings between the B s and W s. Fig. 4 depicts one such microstate for $N = 15$.

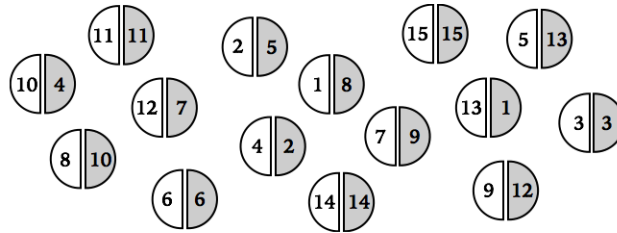


Figure 4: A particular microstate of a $N = 15$ system.

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

$$\mathcal{E}(B_k, W_\ell) = \begin{cases} 0 & \text{if } k = \ell, \\ \lambda & \text{if } k \neq \ell, \end{cases} \quad (63)$$

where $\lambda > 0$ is a parameter with units of energy. Namely, from Eq.(63), 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 B s and N W s?
- (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 Fig. 4?
- (c) Letting j be the number of mismatched pairs in a microstate, argue that the partition function for a system of N B s and N W s (governed by the energy Eq.(63)) can be written as

$$Z_N(\beta\lambda) = \sum_{j=0}^N g_N(j) e^{-\beta\lambda j}, \quad (64)$$

and explain what $g_N(j)$, λj , and the summation represent. (Hint: Eq.(64) is analogous to Eq.(6) from Assignment 4.)

(d) Explain why we can write $g_N(j)$ as

$$g_N(j) = \binom{N}{j} d_j, \quad (65)$$

where d_j is the number of derangements of j elements.

(e) You previously showed that the general formula for the number of derangements of N elements is

$$d_N = \sum_{j=0}^N (-1)^j \binom{N}{j} (N-j)!, \quad (66)$$

By using the integral expression for the factorial of a number,

$$M! = \int_0^\infty dx e^{-x} x^M, \quad (67)$$

and the Binomial theorem, derive an integral expression for d_N . Your expression should not have any unevaluated sums.

(f) Use your result from (e), the expression in (d), and the Binomial theorem to derive an integral expression for $Z_N(\beta\lambda)$ in Eq.(64). Your expression should not have any unevaluated sums, and should reduce to the result from (a) when $\lambda = 0$.

(g) Use Laplace's method to approximate the integral obtained in (f)

(h) The average number of mismatched pairs in the system can be defined as

$$\langle j \rangle = \sum_{j=0}^N j p_j = \frac{\sum_{j=0}^N j g_N(j) e^{-\beta\lambda j}}{Z_N(\beta\lambda)}, \quad (68)$$

Using Eq.(64), write $\langle j \rangle$ in terms of a partial derivative of a function of $Z_N(\beta\lambda)$.

(i) Use the result of (h) and the Laplace's method approximation of the partition function in (g) to find an approximate formula for $\langle j \rangle$ as a function of temperature T . Noting that $\langle j \rangle$ can only be greater than 0, at what value of T is the result of the approximation no longer valid? Plot $\langle j \rangle$ as a function of T making sure to show the point where $\langle j \rangle$ is zero.

(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

$$\boxed{N!} \quad (69)$$

■

(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

$$\boxed{E = \lambda j.} \quad (70)$$

For the figure Fig. 4, there are 10 mismatched pairs, so the energy of this microstate is $\boxed{E = 10\lambda.}$

■

(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

$$Z = \sum_{\text{macrostate}} (\text{Degeneracy of macrostate}) e^{-\beta(\text{Energy of macrostate})}, \quad (71)$$

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

$$Z_{\text{spins}} = \sum_{n_+=0}^N \binom{N}{n_+} e^{\beta\mu H(2n_+-N)}. \quad (72)$$

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

$$Z_N(\beta\lambda) = \sum_{j=0}^N g_N(j) e^{-\beta\lambda j}, \quad (73)$$

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.(71), $g_N(j)$ 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 W s and N B s. ■

- (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

$$d_j = \sum_{k=0}^j \binom{j}{k} (-1)^k (j-k)!. \quad (74)$$

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

$$g_N(j) = \binom{N}{j} d_j. \quad (75)$$
■

- (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

$$d_N = \sum_{k=0}^N \binom{N}{k} (-1)^k (N-k)! . \quad (76)$$

Using the integral definition of the factorial, we have

$$(N-k)! = \int_0^\infty dx e^{-x} x^{N-k} . \quad (77)$$

Inserting this result into Eq.(76) yields

$$\begin{aligned} d_N &= \sum_{k=0}^N \binom{N}{k} (-1)^k \int_0^\infty dx e^{-x} x^{N-k} \\ &= \int_0^\infty dx e^{-x} \sum_{k=0}^N \binom{N}{k} (-1)^k x^{N-k} \\ &= \int_0^\infty dx e^{-x} (-1+x)^N , \end{aligned} \quad (78)$$

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

$$\boxed{d_N = \int_0^\infty dx e^{-x} (x-1)^N .} \quad (79)$$

■

- (f) We now want to use Eq.(79) to compute an integral expression for the partition function. First, returning to Eq.(75) and using Eq.(79) to write the result as an integral, we have

$$g_N(j) = \binom{N}{j} \int_0^\infty dx e^{-x} (x-1)^j . \quad (80)$$

We can insert this result into Eq.(73) to obtain

$$\begin{aligned} Z_N(\beta\lambda) &= \sum_{j=0}^N g_N(j) e^{-\beta\lambda j} \\ &= \sum_{j=0}^N \binom{N}{j} \int_0^\infty dx e^{-x} (x-1)^j e^{-\beta\lambda j} \\ &= \int_0^\infty dx e^{-x} \sum_{j=0}^N \binom{N}{j} [(x-1)e^{-\beta\lambda}]^j . \end{aligned} \quad (81)$$

Using the Binomial theorem in the final line, we obtain

$$\boxed{Z_N(\beta\lambda) = \int_0^\infty dx e^{-x} [1 + (x-1)e^{-\beta\lambda}]^N .} \quad (82)$$

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

$$\begin{aligned} Z_N(\beta\lambda)\Big|_{\lambda=0} &= \int_0^\infty dx e^{-x} [1 + (x-1)]^N \\ &= \int_0^\infty dx e^{-x} x^N = N!, \end{aligned} \quad (83)$$

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. ■

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

$$Z_N(\beta\lambda) = \int_0^\infty dx e^{-x} [1 + (x-1)e^{-\beta\lambda}]^N = \int_0^\infty dx e^{-Nf(x,\beta\lambda)}, \quad (84)$$

where we defined

$$f(x, \beta\lambda) = \frac{x}{N} - \ln(1 + (x-1)e^{-\beta\lambda}). \quad (85)$$

Then, by Laplace's method, we have

$$Z_N(\beta\lambda) \simeq \sqrt{\frac{2\pi}{Nf''(x_1, \beta\lambda)}} \exp[-Nf(x_1, \beta\lambda)], \quad (86)$$

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

$$\begin{aligned} 0 &= f'(x, \beta\lambda)\Big|_{x=x_1} \\ &= \frac{1}{N} - \frac{e^{-\beta\lambda}}{1 + (x_1-1)e^{-\beta\lambda}} \\ \frac{1}{N} &= \frac{e^{-\beta\lambda}}{1 + (x_1-1)e^{-\beta\lambda}} \\ &= \frac{1}{e^{\beta\lambda} + x_1 - 1}. \end{aligned} \quad (87)$$

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

$$x_1 = N - e^{\beta\lambda} + 1. \quad (88)$$

Eq.(88) gives us the value at which the first x derivative of Eq.(85) is zero. To apply Laplace's method, we need to ensure that Eq.(85) is at a local minimum at Eq.(88). Computing the second derivative of $f(x, \beta\lambda)$ at x_1 , we have

$$\begin{aligned} f''(x, \beta\lambda)\Big|_{x=x_1} &= \frac{e^{-\beta\lambda}e^{-\beta\lambda}}{(1 + (x_1-1)e^{-\beta\lambda})^2} \\ &= \left(\frac{e^{-\beta\lambda}}{1 + (x_1-1)e^{-\beta\lambda}} \right)^2 \\ &= \frac{1}{N^2}, \end{aligned} \quad (89)$$

where in the final line we used the equality above Eq.(87). 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.(86), we need to compute $f(x, \beta\lambda)$ at x_1 . Doing so, we have

$$\begin{aligned} f(x, \beta\lambda)|_{x=x_1} &= \frac{N - e^{\beta\lambda} + 1}{N} - \ln(Ne^{\beta\lambda}) \\ &= \frac{N - e^{\beta\lambda} + 1}{N} - \ln N - \beta\lambda. \end{aligned} \quad (90)$$

Finally, with Eq.(90) and Eq.(89), we find that Eq.(86) becomes

$$Z_N(\beta\lambda) \simeq \sqrt{\frac{2\pi}{N\frac{1}{N^2}}} \exp \left[-N \left(\frac{N - e^{\beta\lambda} + 1}{N} - \ln N - \beta\lambda \right) \right], \quad (91)$$

or, more simply,

$$\boxed{Z_N(\beta\lambda) \simeq \sqrt{2\pi N} \exp \left[- (N - e^{\beta\lambda} + 1 - N \ln N - N\beta\lambda) \right]}, \quad (92)$$

■

- (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

$$Z_N(\beta\lambda) = \sum_{j=0}^N g_N(j) e^{-\beta\lambda}. \quad (93)$$

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

$$\begin{aligned} \langle j \rangle &= \frac{1}{Z_N(\beta\lambda)} \sum_{j=0}^N j g_N(j) e^{-\beta\lambda} \\ &= -\frac{1}{Z_N(\beta\lambda)} \frac{\partial}{\partial(\beta\lambda)} Z_N(\beta\lambda). \end{aligned} \quad (94)$$

From the properties of chain rule, we then find

$$\boxed{\langle j \rangle = -\frac{\partial}{\partial(\beta\lambda)} \ln Z_N(\beta\lambda)}, \quad (95)$$

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

$$\begin{aligned} \langle j \rangle &= -\frac{\partial}{\partial(\beta\lambda)} \ln Z_N(\beta\lambda) \\ &\simeq -\frac{\partial}{\partial(\beta\lambda)} \left[\frac{1}{2} \ln(2\pi N) - (N - e^{\beta\lambda} + 1 - N \ln N - N\beta\lambda) \right] \\ &= -e^{\beta\lambda} + N, \end{aligned} \quad (96)$$

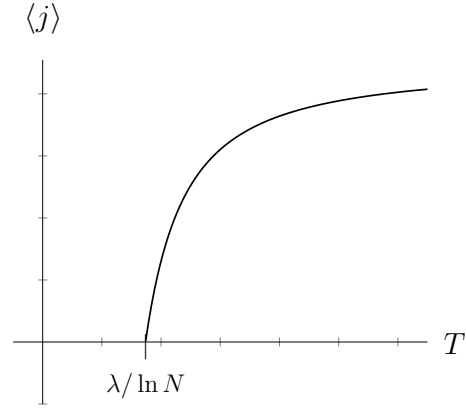


Figure 5: Plot of $\langle j \rangle$ as a function of T . Below the temperature $\lambda / \ln N$, the average number of mismatched pairs is zero.

which yields the temperature dependent function

$$\langle j \rangle \simeq N - e^{\lambda/k_B T}. \quad (97)$$

Since $\langle j \rangle \geq 0$, we see that Eq.(97) is only valid for certain temperatures. Namely, solving for the temperature at which $\langle j \rangle \geq 0$, we find

$$k_B T \geq \frac{\lambda}{\ln N}. \quad (98)$$

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