

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.

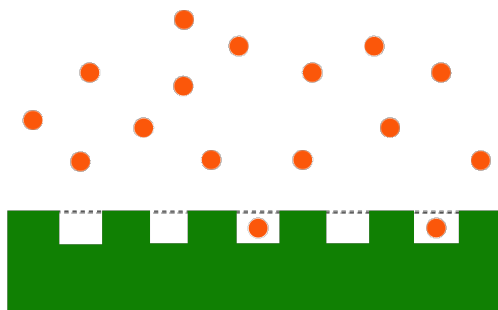


Figure 1: A particular microstate of a system with $M = 5$ receptor sites. There are two molecules bound to receptors so the energy of this microstate is $-2E_0$.

- Write down **three physics questions** we can ask about this system. Your questions should involve physics concepts and theories that we have discussed over the summer.
- Write solutions to **two** of the three questions you listed above.

2. Average Energy of an Ideal Gas

The partition function is defined as

$$Z = \sum_{\{i\}} e^{-\beta E_i}, \quad (1)$$

where i is a particular microstate of the system of interest, and $\sum_{\{i\}}$ defines the summation over all microstates in the system¹. From Eq.(1), we can show that the average energy satisfies

$$\langle E \rangle = \sum_{\{i\}} p_i E_i = -\frac{\partial}{\partial \beta} \ln Z, \quad (2)$$

where we used $p_i = e^{-\beta E_i} / Z$.

¹Eq.(1) presumes the microstates have a 1-1 correspondence with their energies so that we don't need a degeneracy factor.

- (a) Use Eq.(2) to compute the average total energy $\langle E \rangle$ of an ideal gas of N particles at a temperature T and in a volume V .
- (b) The standard deviation σ_E in the energy of gas particles can be computed from the variance

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = \sum_{\{i\}} p_i E_i^2 - \left(\sum_{\{i\}} p_i E_i \right)^2. \quad (3)$$

Show that

$$\frac{\partial^2}{\partial \beta^2} \ln Z = \sigma_E^2. \quad (4)$$

Hint: Begin on the left side of Eq.(4), use the chain rule, and show that it leads to Eq.(3).

- (c) Use Eq.(4) to compute the standard deviation σ_E of the total energy of an ideal gas of N particles at a temperature T .
- (d) From the **central limit theorem** one can infer that the probability distribution for the total energy of gas particles is a Gaussian with mean $\langle E \rangle$ and standard deviation σ_E . Given the results in (a) and (b), sketch a rough plot of the probability distribution of total energy and say what this plot implies about the total energy of N gas particles. Take $N \gg 1$ (e.g., $N \sim 10^{26}$). Your plot should be to scale with respect to how σ_E and $\langle E \rangle$ compare with each other.

3. Ideal Gas Law

We previously derived the partition function for the ideal gas. In this problem, we will derive the ideal gas law.

- (a) By conservation of energy, the change in the internal energy of a system ($dE_{\text{sys.}}$) is related to the work done on the system ($dW_{\text{on sys.}}$) and the heat entering the system ($dQ_{\text{ent.}}$) through the equation

$$dE_{\text{sys.}} = dW_{\text{on sys.}} + dQ_{\text{ent.}}. \quad (5)$$

For this situation, we can use Clausius's definition of the entropy change of the system to relate heat to entropy:

$$dS_{\text{sys.}} = \frac{dQ_{\text{ent.}}}{T}. \quad (6)$$

Using the definition of free energy in terms of energy and entropy, relate the free energy change of the system ($dF_{\text{sys.}}$) to the work done on the system ($dW_{\text{on sys.}}$). Assume that we are working at constant temperature T .

- (b) From classical mechanics, we know that an infinitesimal amount of work done on a system arises from an external force $f_{\text{on sys.}}$ applied to the system over a distance dx :

$$dW_{\text{on sys.}} = f_{\text{on sys.}} dx. \quad (7)$$

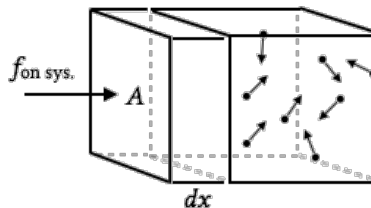


Figure 2: An external force $f_{\text{on sys.}}$ applied to a wall of area A on a volume V of gas. We can use this depiction to define a pressure exerted by the gas on the surroundings.

Consider the system shown in Fig. 2. The force $f_{\text{on sys.}}$ acts on a wall of area A and pushes it a distance dx . Because this force is acting on an area, we can define a pressure. In particular, we define the pressure exerted *by* a system on its surroundings as

$$P = \frac{f_{\text{by sys.}}}{A}, \quad (8)$$

where A is the area of the surface at which the pressure is exerted. By Newton's 3rd law, the force *on* a system is equal to the *negative* of the force *by* a system. Using this fact, along with Eq.(7), Eq.(8), and a reasonable definition of dV , show that the work done on the system is

$$dW_{\text{on sys.}} = -P dV. \quad (9)$$

- (c) For an ideal gas, the free energy is a function of T , V , and N . Therefore we can write $F_{\text{sys.}} = F(T, V, N)$. If there is some change in the free energy dF , then this change must be decomposable into changes in the free energy's various independent variables:

$$dF(T, V, N) = \left(\frac{\partial F}{\partial T}\right) dT + \left(\frac{\partial F}{\partial N}\right) dN + \left(\frac{\partial F}{\partial V}\right) dV. \quad (10)$$

Say we have a gaseous system that is changing volume but which has a fixed number of particles and a fixed temperature. Use Eq.(10), Eq.(9), and the equation derived in (a) to express the pressure of the gaseous system in terms of the free energy.

- (d) In Lecture notes 06 we derived the relationship between the partition function and the free energy of a system. Using this relationship, the partition function of the ideal gas from Lecture notes 08, and the result of (c) derive

$$PV = Nk_B T. \quad (11)$$

4. Laplace's Method and Stirling's Approximation

We previously showed that we can approximate exponential integrals over infinite domains² as

$$\int_{-\infty}^{\infty} dx e^{-Nf(x)} \simeq \sqrt{\frac{2\pi}{Nf''(x_1)}} e^{-Nf(x_1)}, \quad (12)$$

where x_1 is the value of x at which $f(x)$ has a local minimum, and the approximation gets better as $N \rightarrow \infty$.

- (a) Using the result above, derive an approximate formula for

$$\Gamma(N+1) = \int_0^{\infty} dx e^{-x} x^N. \quad (13)$$

- (b) Given the definition of the Gamma function, how can we approximate $N!$ for very large N ?
 (c) Choose a specific numerical value of N and use *WolframAlpha* to compute $N!$ exactly, and use the result of (b) to compute $N!$ approximately. What is the percent error of the approximation?
 "Percent error" is defined by

$$\% \text{ error} = \frac{|\text{approx. value} - \text{exact value}|}{\text{exact value}} \times 100. \quad (14)$$

Collaboration Note: Perform this calculation on your own. It would be highly suspicious if several people end up choosing the same specific value of N .

²This approximation sometimes gives reasonable values for finite domains as well.

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

$$P(N, k) = \frac{1}{2^N} \binom{N}{k}. \quad (15)$$

Using Stirling's approximation (proved in Problem 4 of this assignment), it is possible to show that for $N \gg 1$, the probability Eq.(15) can be approximated as the Gaussian

$$P(N, k) \simeq \sqrt{\frac{2}{\pi N}} \exp\left(-\frac{2}{N}(k - N/2)^2\right). \quad (16)$$

The relation between Eq.(15) and Eq.(16) 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.(15)? 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.

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. 3 depicts one such microstate for $N = 15$.

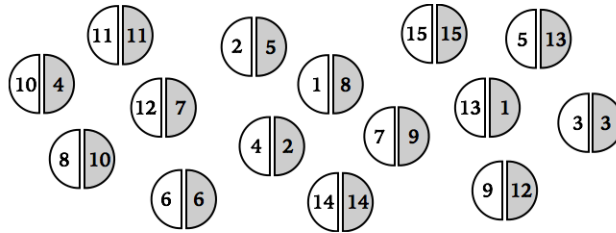


Figure 3: A particular microstate of a $N = 15$ system.

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

$$\mathcal{E}(B_k, W_\ell) = \begin{cases} 0 & \text{if } k = \ell, \\ \lambda & \text{if } k \neq \ell, \end{cases} \quad (17)$$

where $\lambda > 0$ is a parameter with units of energy. Namely, from Eq.(17), 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. 3?
- (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.(17)) can be written as

$$Z_N(\beta\lambda) = \sum_{j=0}^N g_N(j) e^{-\beta\lambda j}, \quad (18)$$

and explain what $g_N(j)$, λj , and the summation represent. (Hint: Eq.(18) is analogous to Eq.(6) from Assignment 4.)

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

$$g_N(j) = \binom{N}{j} d_j, \quad (19)$$

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

$$d_N = \sum_{j=0}^N (-1)^j \binom{N}{j} (N-j)!, \quad (20)$$

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

$$M! = \int_0^{\infty} dx e^{-x} x^M, \quad (21)$$

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.(18). 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

$$\langle j \rangle = \sum_{j=0}^N j p_j = \frac{\sum_{j=0}^N j g_N(j) e^{-\beta\lambda j}}{Z_N(\beta\lambda)}, \quad (22)$$

Using Eq.(18), 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.