MITES 2010: Physics III
Survey of Modern Physics
Problem Set 3 Solutions

1. **Problem 1. Multiplicity function (Function for the Total number of states) for a 2-state system. Consider the chain of 2-state spins (i.e., chain of magnets) that we considered in class. At each site, a spin (magnet) can either point up (North) or down (South). There are a total of N spins (magnets) in the chain.**
(a.) Derive the multiplicity function for this system. This essentially boils down to finishing off the calculation that we did not have time to complete in lecture 7. You can reproduce the calculations by looking at lecture note 7.
(b.) What is the entropy $S(N, s)$ of this system? At what value of the spin excess s, is the entropy maximum? How does the entropy change as a function of N (i.e. does it double when you double N)?

Solution: (a) Our goal is to derive a form of the multiplicity function which reveals its Gaussian nature for large N. We believe that the multiplicity function has this form due to the **Central Limit Theorem** which asserts that any probability distribution with a sufficiently large sample will take the form of e^{-x^2} (a Gaussian) where x is one of the parameters of the distribution. We begin with our definition of the multiplicity function.

$$g(N, s) = \frac{N!}{N_\downarrow! N_\uparrow!}$$

We then invoke Stirling's Approximation[1]

$$N! \approx (2\pi N)^{1/2} N^N \exp[-N]$$

in order to remove the factorials from our definition. We then have

$$g(N, s) \approx \frac{(2\pi N)^{1/2} N^N \exp[-N]}{(2\pi N_\downarrow)^{1/2} N_\downarrow^{N_\downarrow} \exp[-N_\downarrow] (2\pi N_\uparrow)^{1/2} N_\uparrow^{N_\uparrow} \exp[-N_\uparrow]}$$

and using the definitions

$$\begin{aligned} N_\downarrow &= \frac{N}{2} - s \\ N_\uparrow &= \frac{N}{2} + s \\ N_\downarrow + N_\uparrow &= N \end{aligned}$$

[1] We removed the subsequent terms in the argument of the exponential because we are taking $N >> 0$.

we can simplify the partition function to become

$$\begin{aligned}
g(N,s) &\approx \frac{(2\pi N)^{1/2} N^N \exp[-N]}{(2\pi N_\downarrow)^{1/2} N_\downarrow^{N_\downarrow} \exp[-N_\downarrow] (2\pi N_\uparrow)^{1/2} N_\uparrow^{N_\uparrow} \exp[-N_\uparrow]} \\
&= \frac{1}{(2\pi)^{1/2}} \left(\frac{N}{N_\downarrow N_\uparrow}\right)^{1/2} \frac{N^N}{N_\downarrow^{N_\downarrow} N_\uparrow^{N_\uparrow}} \exp[-N + N_\uparrow + N_\downarrow] \\
&= \frac{1}{(2\pi)^{1/2}} \left(\frac{N}{N_\downarrow N_\uparrow}\right)^{1/2} \frac{N^N}{N_\downarrow^{N/2-s} N_\uparrow^{N/2+s}} \\
&= \frac{1}{(2\pi)^{1/2}} \left(\frac{N}{N_\downarrow N_\uparrow}\right)^{1/2} \left(\frac{N^{2N}}{N_\downarrow^{N-2s} N_\uparrow^{N+2s}}\right)^{1/2} \\
&= \frac{1}{(2\pi)^{1/2}} \left(\frac{N^{2N+1}}{N_\downarrow^{N+1-2s} N_\uparrow^{N+1+2s}}\right)^{1/2}
\end{aligned}$$

In order to obtain the necessary exponential function which reveals the Gaussian behavior of the distribution we will change the base of our exponent. This task is accomplished by writing

$$A^x = \exp[x \log A].$$

So, we must take the logarithm of the base our current exponent. Doing so yields

$$\begin{aligned}
\log\left(\frac{N^{2N+1}}{N_\downarrow^{N+1-2s} N_\uparrow^{N+1+2s}}\right) &= (2N+1)\log N - (N+1+2s)\log N_\uparrow - (N+1-2s)\log N_\downarrow \\
&= (2N+1)\log N - (N+1+2s)\log\left[\frac{N}{2}+s\right] - (N+1-2s)\log\left[\frac{N}{2}-s\right] \\
&= (2N+1)\log N - (N+1+2s)\log\left[\frac{N}{2}\left(1+\frac{2s}{N}\right)\right] \\
&\quad -(N+1-2s)\log\left[\frac{N}{2}\left(1-\frac{2s}{N}\right)\right] \\
&= (2N+1)\log N - (N+1+2s)\left[\log\frac{N}{2} + \log\left(1+\frac{2s}{N}\right)\right] \\
&\quad -(N+1-2s)\left[\log\frac{N}{2} + \log\left(1-\frac{2s}{N}\right)\right] \\
&= (2N+1)\log N - (N+1+2s+N+1-2s)\log\frac{N}{2} \\
&\quad -(N+1)\left[\log\left(1+\frac{2s}{N}\right) + \log\left(1-\frac{2s}{N}\right)\right] \\
&\quad -2s\left[\log\left(1+\frac{2s}{N}\right) - \log\left(1-\frac{2s}{N}\right)\right].
\end{aligned}$$

Now, employing the Taylor Approximation for the logarithm ($\log(1+x) \approx x - x^2/2$; for $|x| << 1$)

we obtain

$$
\begin{aligned}
\log\left(\frac{N^{2N+1}}{N_\downarrow^{N+1-2s}N_\uparrow^{N+1+2s}}\right) &= (2N+1)\log N - 2(N+1)\log\frac{N}{2} \\
&\quad -(N+1)\left[\frac{2s}{N}-\frac{2s^2}{N^2}-\frac{2s}{N}-\frac{2s^2}{N^2}\right] \\
&\quad -2s\left[\frac{2s}{N}-\frac{2s^2}{N^2}+\frac{2s}{N}+\frac{2s^2}{N^2}\right] \\
&= (2N+1)\log N - 2(N+1)[\log N - \log 2] \\
&\quad -(N+1)\left[-\frac{4s^2}{N^2}\right] - 2s\left[\frac{4s}{N}\right] \\
&= -\log N + (N+1)\log 4 + \frac{4s^2}{N} - \frac{8s^2}{N} + O\left(\frac{1}{N^2}\right) \\
&\approx \log\frac{4^{N+1}}{N} - \frac{4s^2}{N}.
\end{aligned}
$$

Plugging this result into our change of base formula for exponentials, we find

$$
\begin{aligned}
g(N,s) &\approx \frac{1}{(2\pi)^{1/2}}\left(\frac{N^{2N+1}}{N_\downarrow^{N+1-2s}N_\uparrow^{N+1+2s}}\right)^{1/2} \\
&= \frac{1}{(2\pi)^{1/2}}\exp\left[\frac{1}{2}\left(\frac{N^2N+1}{N_\downarrow^{N+1-2s}N_\uparrow^{N+1+2s}}\right)\right] \\
&\approx \frac{1}{(2\pi)^{1/2}}\exp\left[\frac{1}{2}\left(\log\frac{4^{N+1}}{N}-\frac{4s^2}{N}\right)\right] \\
&= \frac{1}{(2\pi)^{1/2}}\exp\left[\frac{1}{2}\log\frac{4^{N+1}}{N}\right]\exp\left[-\frac{2s^2}{N}\right] \\
&= \frac{1}{(2\pi)^{1/2}}\frac{2^{N+1}}{N^{1/2}}\exp\left[-\frac{2s^2}{N}\right] \\
&= \boxed{\left(\frac{2}{\pi N}\right)^{1/2} 2^N \exp\left[-\frac{2s^2}{N}\right]}.
\end{aligned}
$$

So, we see that if we take N to be very large the multiplicity function takes the form of a Gaussian distribution peaked at $s = 0$. This form of the Multiplicity function must also be properly normalized which means it must reproduces our standard summation result for the number of possible configurations of N spins i.e.

$$\sum_{s=-N/2}^{N/2} g(N,s) = \sum_{s=-N/2}^{N/2} \frac{N!}{N_\downarrow! N_\uparrow!} = 2^N$$

We can check that our Gaussian distribution adheres to this result by taking the **continuum limit** of our summation and using the standard formula for a Gaussian integral,

$$\int_{-\infty}^{+\infty} e^{-ax^2}\,dx = \left(\frac{\pi}{a}\right)^{1/2}.$$

So the total number of possible configurations is

$$\begin{aligned}
\text{Total Number of Configurations} &= \lim_{N\to\infty}\int_{-N/2}^{N/2}\left(\frac{2}{\pi N}\right)^{1/2}2^N\exp\left[-\frac{2s^2}{N}\right]ds \\
&= \left(\frac{2}{\pi N}\right)^{1/2}2^N\int_{-\infty}^{\infty}e^{-2s^2/N}\,ds \\
&= \left(\frac{2}{\pi N}\right)^{1/2}2^N\left(\frac{N\pi}{2}\right)^{1/2} \\
&= 2^N
\end{aligned}$$

which is the result we obtain in the discrete case and therefore our formula is properly normalized.

(b) We can find the entropy of our system by taking the logarithm of our multiplicity function

$$\begin{aligned}
S &= \log[g(N,s)] \\
&\approx \log\left[\left(\frac{2}{\pi N}\right)^{1/2}2^N\exp\left[-\frac{2s^2}{N}\right]\right] \\
&= \boxed{\log\left[\left(\frac{2}{\pi N}\right)^{1/2}2^N\right]-\frac{2s^2}{N}}
\end{aligned}$$

To find when entropy is maximized we employ the standard algorithm

$$\begin{aligned}
0 = \frac{d}{ds}S(N,s) &= -\frac{4s}{N} \\
\frac{d^2}{ds^2}S(N,s=0) &= -\frac{4}{N} < 0 \qquad \longrightarrow \qquad \boxed{S(N,s) \text{ is max when } s=0}
\end{aligned}$$

From our result for entropy it is clear that although entropy does not double when we double N it does increase monotonically as we increase N.

2. **Problem 2. Helmholtz free energy of a two state system.**
(a.) Find an expression for the Helmholtz free energy as a function of the temperature T of a system with two states, one at energy 0 and the other at energy ϵ.
(b.) From the Helmholtz free energy, find expressions for the energy and entropy of the system. Plot the entropy as a function of the ratio ϵ/k_BT. Show all the main features of this graph.

Solution: (a.) To find the Helmholtz Free Energy of the system we will use the definition in terms of the partition function

$$F = -\frac{1}{\beta}\log\mathcal{Z}$$

where we have denoted k_BT as $1/\beta$ for later convenience. We begin with the definition of the partition function

$$\mathcal{Z} = \sum_{i=i}^{N} e^{-\beta\epsilon_i}$$

where N denotes the number of configurations of the system and ϵ_i is the energy associated with a particular configuration i. In our case, there are two configurations because there are only two possible states. One state has $\epsilon_1 = 0$ and the other state has energy $\epsilon_2 = \epsilon$ so our partition function becomes

$$\begin{aligned}\mathcal{Z} &= e^{-\beta\cdot 0} + e^{-\beta\epsilon} \\ &= 1 + e^{-\beta\epsilon}\end{aligned}$$

which gives us a free energy of

$$\boxed{F = -\frac{1}{\beta}\log(1 + e^{-\beta\epsilon})}$$

(b.) To find the energy and entropy[2] of our system we will use the following definitions

$$\begin{aligned}\langle E\rangle &= -\frac{\partial \log \mathcal{Z}}{\partial \beta} \\ S &= -\frac{\partial F}{\partial (k_B T)} \\ &= -\frac{\partial F}{\partial (1/\beta)} \\ &= \beta^2 \frac{\partial F}{\partial \beta}\end{aligned}$$

Computing these quanties, we find for energy

$$\begin{aligned}\langle E\rangle &= -\frac{\partial \log \mathcal{Z}}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta}\log[1 + e^{-\beta\epsilon}] \\ &= \boxed{\frac{\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}}\end{aligned}$$

and for entropy

$$\begin{aligned}S &= \beta^2 \frac{\partial F}{\partial \beta} \\ &= \beta^2 \frac{\partial F}{\partial \beta}\left[-\frac{1}{\beta}\log(1 + e^{-\beta\epsilon})\right] \\ &= \beta^2\left[\frac{1}{\beta^2}\log(1 + e^{-\beta\epsilon}) + \frac{1}{\beta}\frac{\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}\right] \\ &= \boxed{\log(1 + e^{-\beta\epsilon}) + \frac{\beta\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}}\end{aligned}$$

Plotting this result is most easily accomplished with a graphing program. The transcribed result is on the attached document. From the graph we see that entropy is peaked at $\log 2$ and goes to 0 as $\epsilon \to \pm\infty$.

[2] Most common definitions of entropy do not include the factor of k_B in the following derivative, but we include it here in order to be consistent with our definition of entropy as a dimensionless quantity

3. **Problem 3. Zipper problem (Model for unzipping of DNA). A zipper has N links; each link has a state in which it is closed with energy 0 and a state in which it is open with energy ϵ. We require, however, that the zipper can only unzip from the left end, and that the link number s can only open if all links to the left $(1, 2, \ldots, s-1)$ are already open. (a.) Show that the partition function can be summed in the form**

$$\mathcal{Z} = \frac{1 - \mathbf{exp}\left[-\frac{(N+1)\epsilon}{k_B T}\right]}{1 - \mathbf{exp}\left[-\frac{\epsilon}{k_B T}\right]}$$

(b.) In the limit $\epsilon >> k_B T$, find the average number of open links. This model is a very simplified model of the unwinding of two-stranded DNA molecules.

Solution: (a)To obtain a feel for the problem we will begin by considering the case of $N = 2$. If we have two links connected successively, then there are three possible configurations: one with both links closed; one with the left link open and the right link closed; one with both links open. We do not have a state with the right link open and the left link closed because we require that the links open from the left. Considering the fact that each open link has an energy ϵ associated with it we know that the energy of the first configuration is 0, the energy of the second configuration is ϵ, and the energy of the last configuration is 2ϵ. This collection of configurations and associated energies generates a partition function of the form

$$\mathcal{Z} = e^{-\beta \cdot 0} + e^{-\beta\epsilon} + e^{-2\beta\epsilon}$$

We can easily generalize this example to our case of arbitrary N. We realize the partition function must then take on the form

$$\begin{aligned} \mathcal{Z} &= e^{-\beta \cdot 0} + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + \cdots + e^{-(N-1)\beta\epsilon} + e^{-N\beta\epsilon} \\ &= 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + \cdots + e^{-(N-1)\beta\epsilon} + e^{-N\beta\epsilon} \end{aligned}$$

which is a finite geometric series. We can sum the series using the formula

$$1 + r + r^2 + \cdots + r^{N-1} + r^N = \frac{1 - r^{N+1}}{1 - r^N}$$

with $r = e^{-\beta\epsilon}$. Therefore, we find that

$$\boxed{\mathcal{Z} = \frac{1 - e^{-\beta(N+1)\epsilon}}{1 - e^{-\beta\epsilon}}}$$

$$\mathcal{Z} = \sum_{i=0}^{N} e^{-\beta\epsilon_i}.$$

(b) To calculate the average number of open links, we will calculate the average energy of our various configurations and divide this result by ϵ, the energy of one open link. This procedure works because the only nonzero energy in our various configurations comes from the number of open links.

$$\langle n \rangle = \frac{\langle E \rangle}{\epsilon}$$

Computing the average energy, we find

$$\begin{aligned}
\langle E \rangle &= -\frac{\partial \log \mathcal{Z}}{\partial \beta} \\
&= -\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \beta} \\
&= -\frac{1}{\mathcal{Z}}\frac{\partial}{\partial \beta}\frac{1-e^{-\beta(N+1)\epsilon}}{1-e^{-\beta\epsilon}} \\
&= -\frac{1}{\mathcal{Z}}\left[\frac{\epsilon(N+1)e^{-(N+1)\beta\epsilon}(1-e^{-\beta\epsilon}) - \epsilon e^{-\beta\epsilon}(1-e^{-(N+1)\beta\epsilon})}{(1-e^{-\beta\epsilon})^2}\right] \\
&= -\frac{1-e^{-\beta\epsilon}}{1-e^{-\beta(N+1)\epsilon}}\left[\frac{\epsilon(N+1)e^{-(N+1)\beta\epsilon}(1-e^{-\beta\epsilon}) - \epsilon e^{-\beta\epsilon}(1-e^{-(N+1)\beta\epsilon})}{(1-e^{-\beta\epsilon})^2}\right] \\
&= -\frac{\epsilon(N+1)e^{-(N+1)\beta\epsilon}}{1-e^{-(N+1)\beta\epsilon}} + \frac{\epsilon e^{-\beta\epsilon}}{1-e^{-\beta\epsilon}}
\end{aligned}$$

Now, if we take $\beta\epsilon >> 1$, then we can take the following approximations

$$\begin{aligned}
1-e^{-\beta\epsilon} &\approx 1 \\
e^{-\beta\epsilon} &>> e^{-(N+1)\beta\epsilon}
\end{aligned}$$

So that our average energy becomes

$$\langle E \rangle \approx \epsilon e^{-\beta\epsilon}$$

and the average number of open links is $\boxed{\langle n \rangle = e^{-\beta\epsilon}}$.