Example Sheet 1 Worked Solutions

Question 1

Question. Establish Stirling's Formula: $N \approx \sqrt{2\pi N} N^N e^{-N}$

Proof. We are first given $\int\limits_0^\infty e^{-x} x^N dx = \int\limits_0^\infty e^{-F(x)} dx$ and since the integrands are equal, we can equate:

$$\begin{aligned} e^{-x} x^N &= e^{-F(x)} \\ \Rightarrow F(x) &= x - N \ln x. \end{aligned} \tag{1}$$

We then differentiate twice in order to find the approximation $F(x) \approx F(x_0) + F''(x_0)(x - x_0)^2/2$ where x_0 is x value of the minimum of $F(x)$.

$$\begin{aligned} F'(x) &= 1 - \frac{N}{x} \\ F''(x) &= \frac{N}{x^2}. \end{aligned} \tag{2}$$

The minimum occurs when $F'(x) = 0$ which implies $x_0 = N$ (we assume this is a minimum as it is the only solution to $F'(x) = 0$ and the question asks us to find a minimum).

We know have all the information required to determine the approximation and can substitute into the 2nd integral given:

$$F(x) \approx -N + N \ln N - \frac{(x-N)^2}{2N} \tag{3}$$

$$\begin{aligned} N! &= \int\limits_0^\infty \exp\left(-N + N\ln N - \frac{(x-N)^2}{2N}\right) dx \\ &= e^{-N} N^N \int\limits_0^\infty \exp\left(-\frac{(x-N)^2}{2N}\right) dx. \end{aligned} \tag{4}$$

The time has come to apply the final approximation alluded to in the question. The term $x - N$ is effectively shifting the function to the right hand side of the y-axis. And since N is very large, the limits of the integral guarantee that we are integrating the entire curve as it tails to 0 at either end. *Note:* The factor of $1/2N$ does effectively nothing to affect this shifting.

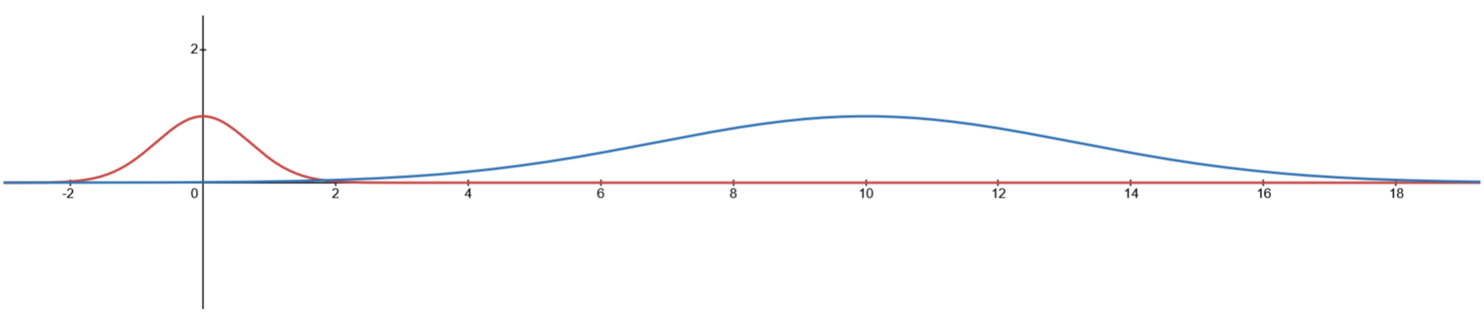

Figure 1: Graph of $\exp -x^2$ in red vs $\exp(-(x-10)^2/20)$ in blue

Thus, we make the approximation:

$$N! \approx e^{-N} N^N \int_{-\infty}^{+\infty} \exp\left(\frac{-x^2}{2N}\right) dx. \tag{5}$$

As this is the standard form of the Gaussian Integral:

$$\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}. \tag{6}$$

Thus, with $a = 1/2N$, we have:

$$N! \approx \sqrt{2\pi N} N^N e^{-N} \tag{7}$$

□

<u>Question 2i</u>

Question. For a two coupled system in the microcanonical ensemble, show that they maximise their entropy if the heat capacity, C, is positive.

Proof. Considering the system as a whole to have entropy S and equal temperature T, we have the equation:

$$\frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2 C} \tag{8}$$

If we want the system to have a maximum entropy, the equation on the right hand side must be negative and thus C must be positive.

□

<u>Question 2ii</u>

Question. Show that the energy fluctuations $\triangle E^2 = \langle E^2 \rangle - \langle E \rangle^2$ are proportional to C_V in the canonical ensemble.

Proof. The fluctuations in the canonical ensemble can be written as:

$$\triangle E^2 = -\frac{\partial \langle E \rangle}{\partial \beta} \tag{9}$$

The definition of the heat capacity C_V in this case is given as:

$$\begin{aligned} C_V &= \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V \\ \Rightarrow \partial \langle E \rangle &= C_V \cdot \partial T \\ \Rightarrow \triangle E^2 &= -C_V \cdot \frac{\partial T}{\partial \beta} \end{aligned} \tag{10}$$

where the subscript denotes that the volume is constant.

By definition:

$$\begin{aligned} \beta &= \frac{1}{k_B T}, T \neq 0 \\ \Rightarrow \frac{\partial \beta}{\partial T} &= -\frac{1}{k_B T^2} \\ \Rightarrow \frac{\partial T}{\partial \beta} &= -k_B T^2, T \neq 0 \\ \Rightarrow \triangle E^2 &= C_V k_B T^2, T \neq 0 \end{aligned} \tag{11}$$

$\square$

Question 2iii

Question. Show that the Gibbs entropy from the canonical ensemble can be written as

$$S = k_B \frac{\partial}{\partial T}(T \ln Z) \tag{12}$$

Proof. The entropy in the canonical system, derived using the standard definition of S and Stirlings formula is given as:

$$S = -k_B \sum_n p(n) \ln p(n). \tag{13}$$

The probability of the system being in a state $|n\rangle$ is given by the Boltzmann distribution:

$$p(n) = \frac{e^{-\beta E_n}}{Z} \tag{14}$$

Substituting into our form of S:

$$\begin{aligned} S &= -k_B \sum_n \frac{e^{-\beta E_n}}{Z} \ln\left(\frac{e^{-\beta E_n}}{Z}\right) \\ &= -k_B \sum_n \frac{e^{-\beta E_n}}{Z} \left[-\beta E_n - \ln Z\right] \\ &= k_B \sum_n \frac{\beta E_n e^{-\beta E_n}}{Z} + \frac{e^{-\beta E_n}}{Z} \ln Z \\ &= k_B \left[\sum_n \frac{\beta E_n}{Z} e^{-\beta E_n} + \ln Z\right], \end{aligned} \tag{15}$$

Where the last step is made as $\sum_n e^{-\beta E_n}/Z = \sum_n p(n) = 1$ as something must happen.

Now, we work backwards from the Gibbs entropy:

$$\begin{aligned} S &= k_b \frac{\partial}{\partial T}(T \ln Z) \\ &= k_B \left[T \cdot \frac{1}{Z} \cdot \frac{\partial Z}{\partial T} + \ln Z\right] \end{aligned} \tag{16}$$

Z is given as:

$$\begin{aligned} Z &= \sum_n e^{-\beta E_n} \\ &= \sum_n e^{-E_n/k_B T} \end{aligned} \tag{17}$$

Differentiating with respect to T:

$$\begin{aligned} \frac{\partial Z}{\partial T} &= \sum \frac{\partial}{\partial T}(e^{-E_n/k_B T}) \\ &= \sum_n \frac{\partial}{\partial T}\left(-\frac{E_n}{k_B T}\right) e^{-E_n/k_B T} \\ &= \sum_n \frac{E_n}{k_B T^2} e^{-E_n/k_B T} \\ &= \sum_n \frac{E_n}{k_B T^2} e^{-\beta E_n}. \end{aligned} \tag{18}$$

We can now substitute this into the Gibbs entropy equation:

$$\begin{aligned} S &= k_B \left[\frac{T}{Z} \sum_n \frac{E_n}{k_B T^2} e^{-\beta E_n} + \ln Z \right] \\ &= k_B \left[\sum_n \frac{\beta E_n}{Z} e^{-\beta E_n} + \ln Z \right] \\ &= k_B \frac{\partial}{\partial T} (T \ln Z) \end{aligned} \tag{19}$$

□

Question 3

Question. In a system of N spin 1/2 particles, each with energy of $\pm\mu B/2$ where μ is the magnetic moment, show that the partition function is

$$Z = 2^N \cosh^N \left(\frac{\beta \mu B}{2} \right), \tag{20}$$

Proof. A single particle in the system has two states $E_1 = -\mu B/2$ or $E_2 = +\mu B/2$, thus:

$$\begin{aligned} Z &= \sum_n e^{-\beta E_n} \\ &= e^{\beta \mu B/2} + e^{-\beta \mu B/2} \\ &= 2 \cosh \left(\frac{\beta \mu B}{2} \right). \end{aligned} \tag{21}$$

Since Z is multiplicative, i.e. $Z = Z_1 Z_2$ upon combining systems, we have:

$$Z = 2^N \cosh^N \left(\frac{\beta \mu B}{2} \right) \tag{22}$$

□

Question. Find the average energy $\langle E \rangle$ and entropy S. Show that the result makes sense when $T = 0$ and $T \to \infty$.

Solution. For the average energy:

$$\begin{aligned} \langle E \rangle &= -\frac{\partial}{\partial \beta} \ln Z \\ &= -\frac{\partial}{\partial \beta} \ln \left(2^N \cosh^N \left(\frac{\mu B}{2} \beta \right) \right) \\ &= -\frac{\partial}{\partial \beta} \left(\ln 2^N + N \ln \cosh \left(\frac{\mu B}{2} \beta \right) \right) \end{aligned} \tag{23}$$

Since 2^N is independent of β, its derivative evaluates to 0 and using the fact that:

$$\frac{d}{dx} \ln \cosh(ax) = a \tanh(ax), \tag{24}$$

we have:

$$\langle E \rangle = -\frac{N \mu B}{2} \tanh \left(\frac{\mu B}{2} \beta \right) \tag{25}$$

This is physically viable (thankfully) since when $T \to 0$, we have $\langle E \rangle \to -N\mu B/2$ which is the lowest possible energy of the system. And, when $T \to \infty$ we have $\langle E \rangle \to 0$ which is expected as when the system has infinite heat, none of the energy in the system remains accessible.

Now, for entropy:

$$\begin{aligned} S &= k_B \frac{\partial}{\partial T}(T \ln Z) \\ &= k_b \left[\frac{T}{Z} \frac{\partial Z}{\partial T} + \ln Z \right] \\ &= k_b \left[\frac{T}{Z} \frac{\partial}{\partial T} \left(2^N \cosh^N \left(\frac{\mu B}{2k_B T} \right) \right) + \ln 2^N \cosh^N \left(\frac{\mu B}{2k_B T} \right) \right] \\ &= k_b \left[\frac{T}{Z} \cdot 2^N \cdot N \cosh^{N-1} \left(\frac{\mu B}{2k_B T} \right) \cdot \left(-\frac{\mu B}{2k_B T^2} \right) \sinh \left(\frac{\mu B}{2k_B T} \right) + N \ln 2 \cosh \left(\frac{\mu B}{2k_B T} \right) \right] \end{aligned} \tag{26}$$

Luckily, the cosh and sinh terms cancel with the factor of $1/Z$ and turn to a single tanh term:

$$S = k_B \left[-\frac{N\mu B}{2k_B T} \tanh \left(\frac{\mu B}{2k_B T} \right) + \ln 2 \cosh \left(\frac{\mu B}{2k_B T} \right) \right]. \tag{27}$$

When $T \to 0$, $S \to 0$ which makes complete sense physically as when there is no heat, there is perfect order. When $T \to \infty$, $S \to N \ln 2$ which is also physically accurate as it is the maximum value of S (fact checked by true Desmos patriots).

Question. Compute the magnetisation $M = N_\uparrow - N_\downarrow$ and show that $\chi = \partial M / \partial B$ satisfies $\chi \sim 1/T$ at high temperatures (Curie's Law)

Proof. The energy of the system in total is given by:

$$E = \frac{\mu B}{2} N_\uparrow - \frac{\mu B}{2} N_\downarrow \tag{28}$$

And this total energy will be the average energy of the system as the fluctuations of energy tend to 0 as $N \to \infty$ which is the typical case for a classic system such as the Oxygen that Curie experimented with. Thus,

$$\begin{aligned} \frac{\mu B}{2} N_\uparrow - \frac{\mu B}{2} N_\downarrow &= -\frac{N\mu B}{2} \tanh \left(\frac{\mu B}{2} \beta \right) \\ \Rightarrow N_\uparrow - N_\downarrow &= -N \tanh \left(\frac{\mu B}{2} \beta \right) \\ &= M. \end{aligned} \tag{29}$$

Thus we now have a differentiable function of M:

$$\begin{aligned} M &= -N \tanh \left(\frac{\mu \beta}{2} B \right) \\ \Rightarrow \frac{\partial M}{\partial B} &= -\frac{N}{2} \cdot \frac{\mu \beta}{2} \operatorname{sech}^2 \left(\frac{\mu \beta}{2} B \right) \\ &= -\frac{N \beta \mu}{4} \operatorname{sech}^2 \left(\frac{\mu \beta}{2} B \right) \cdot \frac{1}{k_B T} \\ \Rightarrow \chi &= -\frac{N\mu}{4k_B} \operatorname{sech}^2 \left(\frac{\mu B}{2} \beta \right) \cdot \frac{1}{T}. \\ \Rightarrow \chi(T \to \infty) &= -\frac{N\mu}{4k_B} \cdot \frac{1}{T} \end{aligned} \tag{30}$$

At high temperatures, $\operatorname{sech}^2(\mu B \beta / 2) \to 1$ and thus, $\chi \sim 1/T$ as required. The negative demonstrates an anti-alignment with the magnetic field and the magnitudes of N and k_B are the same ($\approx 10^{23}$) and thus cancel. $\square$

Question 5

Question. Compute Z for a one dimensional quantum harmonic oscillator with frequency ω and:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{31}$$

Find the average energy and entropy as a function of T. Creating a system of N particles for a solid, show that at high temperatures

Solution.