1. (a) Return now to problem #2 in Assignment 5, where only three energy levels of a particle in a one-dimensional box are accessible to a particle: \( \epsilon = \{0, 1, 4\} \epsilon_1 \), where \( \epsilon_1 = \frac{\hbar^2 \pi^2}{2mL^2} \). The partition function is

\[
Z = 1 + e^{-\beta \epsilon_1} + e^{-4\beta \epsilon_1}.
\]

The probabilities of being in the energy states are therefore \( p_0 = \frac{1}{Z}, p_1 = \frac{e^{-\beta \epsilon_1}}{Z}, \) and \( p_4 = \frac{e^{-4\beta \epsilon_1}}{Z} \). In the microcanonical ensemble, we found that the maximum entropy condition required the following relationship among the probabilities:

\[
\frac{p_2 p_3^3}{p_1^4} = 1.
\]

Clearly, our definition of the probabilities is consistent with this:

\[
\frac{p_4 p_3^3}{p_1^4} = \frac{e^{-4\beta \epsilon_1}}{e^{-4\beta \epsilon_1}} = 1.
\]

We also automatically satisfy that the sum of probabilities is unity. The last equation is \( \frac{p_1 + 4p_4}{N} = U/N \), which is also satisfied. So these probabilities must be identical to those found in the microcanonical ensemble. This means that all quantities involving those probabilities must be the same, and the numerical results in the attached Mathematica notebook bear this out.

The mean energy per particle can be found directly using the definition of the mean:

\[
\frac{U}{N} = p_1 \epsilon_1 + p_4 4 \epsilon_4 = \frac{e^{-\beta \epsilon_1} + 4e^{-4\beta \epsilon_1}}{1 + e^{-\beta \epsilon_1} + e^{-4\beta \epsilon_1}} \epsilon_1.
\]

It is useful to check that this expression is consistent with the formal one tied to the partition function:

\[
\frac{U}{N} = -\frac{\partial}{\partial \beta} \ln(Z) = -\frac{e^{-\beta \epsilon_1} - \epsilon_1 e^{-4\beta \epsilon_1}}{1 + e^{-\beta \epsilon_1} + e^{-4\beta \epsilon_1}},
\]

which is exactly the same. The entropy per particle is therefore

\[
\frac{S}{N} = k_B \ln(Z) + \frac{U}{NT} = k_B \ln(1 + e^{-\beta \epsilon_1} + e^{-4\beta \epsilon_1}) + k_B(\beta \epsilon_1) \frac{e^{-\beta \epsilon_1} + 4e^{-4\beta \epsilon_1}}{1 + e^{-\beta \epsilon_1} + e^{-4\beta \epsilon_1}}.
\]

The remainder of this question is done on the attached Mathematica notebook.

(b) This is also done on the attached Mathematica notebook.

2. (a) Recall that for a particle in a box, the energy levels depend entirely on the volume. This means that changes in volume actually change the energy levels (rather than the distribution of particles in the energy levels); this does work in the form of \( dW = -PdV \). Likewise, in a magnetic system, the energy levels depend only on the external magnetic field \( B \); changing the magnetic field therefore does work on the spin direction, and this will change the magnetization. The work for a magnetic system is therefore \( dW = -MdB \). Thus, volume and pressure for an ideal gas become magnetic field and magnetization, respectively. One simply needs to recopy the formulas in Chapter 5, replacing all instances of \( V \) with \( B \) and \( P \) with \( M \).

Consider first the total energy. \( dU = Q + W = TdS - MdB \). Clearly then \( U \) is a simultaneous function of the two parameters \( S \) and \( B \), i.e. \( U = U(S, B) \). So we can write:

\[
dU = \left( \frac{\partial U}{\partial S} \right)_B dS + \left( \frac{\partial U}{\partial B} \right)_S dB = TdS - MdB,
\]
which immediately yields the following two equations

\[ T = \left( \frac{\partial U}{\partial S} \right)_B, \quad M = -\left( \frac{\partial U}{\partial B} \right)_S. \]

The second of these equations unfortunately isn’t very handy, because it is difficult to keep entropy fixed in practise.

The fact that \(dU\) is an exact differential of the quantity \(U\) allows us to derive another useful relation. If we took a second derivative of \(U\), the result can’t depend on the order, i.e.

\[
\left( \frac{\partial}{\partial B} \right)_S \left( \frac{\partial U}{\partial S} \right)_B \equiv \left( \frac{\partial}{\partial S} \right)_B \left( \frac{\partial U}{\partial B} \right)_S
\]

\[ \Rightarrow \left( \frac{\partial T}{\partial B} \right)_S = -\left( \frac{\partial M}{\partial S} \right)_B. \]

For the Helmholtz free energy \(U - TS\), instead consider the quantity \(TS\), for which we have \(d(TS) = TdS + SdT\). Then

\[ dU = TdS - MdB = d(TS) - SdT - MdB \quad \Rightarrow \quad d(U - TS) \equiv dF = -SdT - MdB. \]

Now, \(F = F(T, B)\) so that

\[ dF = \left( \frac{\partial F}{\partial T} \right)_B dT + \left( \frac{\partial F}{\partial B} \right)_T dB \equiv -SdT - MdB, \]

which immediately yields the following two equations

\[ S = -\left( \frac{\partial F}{\partial T} \right)_B, \quad M = -\left( \frac{\partial F}{\partial B} \right)_T. \]

These are very useful equations! Now either the magnetic field or the temperature have to be kept constant, which is much easier to do. And again, using the second-derivative trick above, one finds:

\[ \left( \frac{\partial S}{\partial B} \right)_T = \left( \frac{\partial M}{\partial T} \right)_B. \]

Thus, knowing how the magnetization varies with temperature (at constant external magnetic field) is enough to tell you how the entropy varies with magnetic field (at constant temperature)! This is very handy.

(b) Next let’s see if these equations apply to the Pauli paramagnet, the ‘canonical’ example of a magnetic system (pun intended). Let’s keep things simple, and assume that we have spin-1/2 particles. The two energy levels are \(\epsilon\) and \(-\epsilon\), where \(\epsilon = g\mu_B B/2 \equiv \alpha B\). The partition function is then

\[ Z = e^{\beta \epsilon} + e^{-\beta \epsilon} = 2 \cosh(\beta \epsilon) = 2 \cosh(\beta \alpha B). \]

The mean energy is

\[ U = -N \frac{\partial}{\partial \beta} \ln(Z) = -N \alpha B \tanh(\beta \alpha B), \]

and the entropy is

\[ S = Nk_B \ln(Z) + \frac{U}{T} = Nk_B \ln[2 \cosh(\beta \alpha B)] - \frac{N \alpha B}{T} \tanh(\beta \alpha B) \]

\[ = Nk_B \left\{ \ln[2 \cosh(\beta \alpha B)] - \beta \alpha B \tanh(\beta \alpha B) \right\}. \]

The (Helmholtz) free energy is therefore

\[ F = U - TS = -Nk_B T \ln(Z) = -Nk_B T \ln[2 \cosh(\beta \alpha B)] \].
The easiest equations to check are those associated with the free energy, so let’s do those first:

\[
S = -\left(\frac{\partial F}{\partial T}\right)_B = Nk_B \frac{\partial}{\partial T} \left[ T \ln \left( 2 \cosh \left( \frac{\alpha B}{k_B T} \right) \right) \right] \\
= Nk_B \ln \left( 2 \cosh \left( \frac{\alpha B}{k_B T} \right) \right) - \frac{Nk_B \alpha B}{k_B T} \tanh \left( \frac{\alpha B}{k_B T} \right),
\]

which is exactly the expression above. Now for the magnetization:

\[
M = -\left(\frac{\partial F}{\partial B}\right)_T = Nk_B T \frac{\partial}{\partial B} \left\{ \ln \left( 2 \cosh \left( \frac{\alpha B}{k_B T} \right) \right) \right\} = \frac{Nk_B \alpha}{k_B} \tanh \left( \frac{\alpha B}{k_B T} \right),
\]

which is just the expression in the notes for the magnetization. Last let’s check the Maxwell relation: Using Mathematica (see the attached notebook) I obtain

\[
\left(\frac{\partial S}{\partial B}\right)_T = -\frac{N \alpha B}{k_B T} \frac{1}{\cosh^2 \left( \frac{\alpha B}{k_B T} \right)} = \left(\frac{\partial M}{\partial T}\right)_B.
\]

So it all hangs together!

In order to use the expressions involving the mean energy, we would need to figure out how to express the mean energy as a function of \(S\) and \(B\) only. The problem is that the expression for the entropy above is very complicated! We would need to invert the equation for entropy to solve for \(\beta\), and then plug it into the expression for the energy. I don’t think that there is any way to do this! So I will give up on the idea.

3. The variance of the energy about the mean is \((\Delta U)^2 = \overline{u^2} - \overline{u}^2\). Consider the mean energy per particle; in the canonical ensemble, these are:

\[
\overline{u} = \sum_i p_i \epsilon_i = \sum_i \epsilon_i e^{-\beta \epsilon_i} - \frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{1}{Z} \frac{\partial \ln(Z)}{\partial \beta},
\]

where \(Z = \sum_i e^{-\beta \epsilon_i}\). Let’s work out \(\overline{u^2}\):

\[
\overline{u^2} = \sum_i p_i \epsilon_i^2 = \sum_i \frac{\epsilon_i^2 e^{-\beta \epsilon_i}}{Z}.
\]

We know that

\[
\frac{\partial^2 Z}{\partial \beta^2} = \sum_i \epsilon_i^2 e^{-\beta \epsilon_i},
\]

so that

\[
\overline{u^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}.
\]

The variance is therefore

\[
(\Delta u)^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2.
\]

Notice that this expression is consistent with:

\[
(\Delta u)^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = \frac{\partial^2}{\partial \beta^2} \ln(Z).
\]

But \(\partial \ln(Z)/\partial \beta = -u = -U/N\), which means that

\[
(\Delta u)^2 = -\frac{1}{N} \frac{\partial U}{\partial \beta}.
\]

(b) For the particle in the 3D box, the partition function was found to be (at high temperatures) \(Z = V/\lambda_B^3 = V(mk_B T/2\pi \hbar^2)^{3/2} = \alpha/\beta^{3/2}\), where \(\alpha\) includes all of the constants. Using Mathematica, I obtain gives \((\Delta u)^2 = \)
\( (3/2)(k_B T)^2 \). This is consistent with the famous ‘fluctuation-dissipation theorem’ \( N(\Delta u)^2 = k_B T^2 C_V \). Thus, the standard deviation \( \Delta u \sim N^{-1/2} \), just as we saw at the beginning of the term when talking about random walks.

For the 3D harmonic oscillator, the full partition function is more complicated (though the high-temperature version is also simple):

\[
Z = \frac{1}{(1 - e^{-\beta \hbar \omega})^3}.
\]

The variance comes out to be

\[
(\Delta u)^2 = \frac{3}{4} \left( \hbar \omega \text{csch} \left( \frac{\beta \hbar \omega}{2} \right) \right)^2.
\]

This isn’t very informative. At high temperatures, the mean energy and the variance become \( \bar{u} = u = 3k_B T \) and \( 3(k_B T)^2 \), respectively. These results are again consistent with the fluctuation-dissipation theorem.
Assignment 7 Solutions

(2) Here is the definition of the partition function, where $\alpha = \epsilon_1/k_B$:

$$Z = 1 + \exp[-\alpha/T] + \exp[-4\alpha/T]$$

$$1 + e^{-\frac{3\alpha}{T}} + e^{-\frac{4\alpha}{T}}$$

Here is the definition of the mean energy per particle, noting that $kB = \epsilon_1/\alpha$:

$$u = \text{FullSimplify}[\epsilon_1/\alpha * T^2 * D[Log[Z], T]]$$

$$\frac{4 + e^\frac{3\alpha}{T}}{1 + e^\frac{3\alpha}{T} + e^\frac{4\alpha}{T}}$$

Let's express the total energy per particle in units of the energy scale $\epsilon_1$, i.e. $u_p = U/N\epsilon_1$:

$$u_p = \frac{\left(4 + e^\frac{3\alpha}{T}\right)}{1 + e^\frac{3\alpha}{T} + e^\frac{4\alpha}{T}}$$

$$s = \text{FullSimplify}[kB * Log[Z] + u/T]$$

$$\frac{4 + e^\frac{3\alpha}{T}}{1 + e^\frac{3\alpha}{T} + e^\frac{4\alpha}{T}} + kB \log \left[1 + e^\frac{4\alpha}{T} + e^\frac{\alpha}{T}\right]$$

noting that $\epsilon_1 = kB^{*}\alpha$, we can rewrite this as $sp$, where $sp = S/NkB$

$$sp = \frac{\left(4 + e^\frac{3\alpha}{T}\right) \alpha}{\left(1 + e^\frac{3\alpha}{T} + e^\frac{4\alpha}{T}\right) T}$$

$$\frac{4 + e^\frac{3\alpha}{T}}{1 + e^\frac{3\alpha}{T} + e^\frac{4\alpha}{T}} + \log \left[1 + e^\frac{4\alpha}{T} + e^\frac{\alpha}{T}\right]$$

Here are the probabilities:
\( p_0 = \frac{1}{Z} \)
\( p_1 = \exp\left(-\frac{\alpha}{T}\right)/Z \)
\( p_4 = \exp\left(-4\times\frac{\alpha}{T}\right)/Z \)

Now plot the probabilities as a function of the total energy, as was done in Assignment 5:

\( \alpha = 1; \) Show[{ParametricPlot[{up, p0}, \{T, 0.01, 100\}, PlotRange \rightarrow \{\{0, 5/3\}, \{0, 1\}\}, PlotStyle \rightarrow \text{Red}], ParametricPlot[{up, p1}, \{T, 0.01, 100\}, PlotRange \rightarrow \{\{0, 5/3\}, \{0, 1\}\}, PlotStyle \rightarrow \text{Blue}], ParametricPlot[{up, p4}, \{T, 0.01, 100\}, PlotRange \rightarrow \{\{0, 5/3\}, \{0, 1\}\}, PlotStyle \rightarrow \text{Green}]}

Unsurprisingly, these curves are identical to those found in Assignment 5 for the range of validity. Now for the energy as a function of temperature:

\( \text{Plot[up, \{T, 0.01, 50\}, PlotRange \rightarrow \{\{0, 50\}, \{0, 5/3\}\]]} \)

It is clear that at low temperature the mean energy goes to zero, while at high temperatures it asymptotes as 5/3, as expected.
It is clear that at low temperature the mean energy goes to zero, while at high temperatures it asymptotes as $5/3$, as expected. Now for the entropy:

$$\text{Plot}\left[ sp, \left\{ T, 0.01, 5 \right\}, \text{PlotRange} \rightarrow \left\{ \left\{ 0, 5 \right\}, \left\{ 0, \text{Log}[3] \right\} \right\} \right]$$

The entropy also saturates (to Log[3]), but much more quickly than the energy.

(b) Now imagine that there are four energy levels. Let’s repeat the calculations above:

$$\text{Clear} \left[ \alpha \right]; \quad Z = 1 + \text{Exp}[-\alpha / T] + \text{Exp}[-4 \alpha / T] + \text{Exp}[-9 \alpha / T]$$

$$u = \text{FullSimplify} \left[ e_1 / \alpha * T^2 * D[\text{Log}[Z], T] \right]$$

$$u = \frac{\left( 9 + 4 e^{T / 10} + e^{T / 9} \right) e^{T / 10}}{1 + e^{T / 10} + e^{T / 9} + e^{T / 8}}$$

$$u = \frac{\left( 9 + 4 e^{T / 10} + e^{T / 9} \right) e^{T / 10}}{1 + e^{T / 10} + e^{T / 9} + e^{T / 8}}$$

$$\text{FullSimplify} \left[ \frac{kB \times \text{Log}[Z] + u / T} \right]$$

$$s = \text{FullSimplify} \left[ \frac{\left( 9 + 4 e^{T / 10} + e^{T / 9} \right) e^{T / 10}}{1 + e^{T / 10} + e^{T / 9} + e^{T / 8}} \right] + kB \text{Log} \left[ 1 + e^{T / 10} + e^{T / 9} + e^{T / 8} \right]$$

$$s = \frac{\left( 9 + 4 e^{T / 10} + e^{T / 9} \right) e^{T / 10}}{1 + e^{T / 10} + e^{T / 9} + e^{T / 8}} + kB \text{Log} \left[ 1 + e^{T / 10} + e^{T / 9} + e^{T / 8} \right]$$

$$s = \frac{\left( 9 + 4 e^{T / 10} + e^{T / 9} \right) e^{T / 10}}{1 + e^{T / 10} + e^{T / 9} + e^{T / 8}} + kB \text{Log} \left[ 1 + e^{T / 10} + e^{T / 9} + e^{T / 8} \right]$$
\[ P_0 = 1 / Z \]
\[ P_1 = \exp[-\alpha / T] / Z \]
\[ P_4 = \exp[-4 \alpha / T] / Z \]
\[ P_9 = \exp[-9 \alpha / T] / Z \]
\[ \frac{1}{1 + e^{-\frac{\alpha}{T}} + e^{-\frac{4 \alpha}{T}} + e^{-\frac{9 \alpha}{T}}} \]
\[ \frac{1}{1 + e^{-\frac{\alpha}{T}} + e^{-\frac{4 \alpha}{T}} + e^{-\frac{9 \alpha}{T}}} \]
\[ \frac{1}{1 + e^{-\frac{\alpha}{T}} + e^{-\frac{4 \alpha}{T}} + e^{-\frac{9 \alpha}{T}}} \]
\[ \frac{1}{1 + e^{-\frac{\alpha}{T}} + e^{-\frac{4 \alpha}{T}} + e^{-\frac{9 \alpha}{T}}} \]

The highest energy corresponds to all probabilities equal to 1/4, which gives

\[ u_{\text{max}} = 1 \times 1 / 4 + 4 \times 1 / 4 + 9 \times 1 / 4 \]
\[ 7 \]
\[ 2 \]

\[ \alpha = 1; \text{Show}[[\text{ParametricPlot}[[\text{up}, P_0], \{T, 0.01, 100\}, \text{PlotRange} \to \{(0, 7/2), (0, 1)\}, \text{PlotStyle} \to \text{Red}], \text{ParametricPlot}[[\text{up}, P_1], \{T, 0.01, 100\}, \text{PlotRange} \to \{(0, 7/2), (0, 1)\}, \text{PlotStyle} \to \text{Blue}], \text{ParametricPlot}[[\text{up}, P_4], \{T, 0.01, 100\}, \text{PlotRange} \to \{(0, 7/2), (0, 1)\}, \text{PlotStyle} \to \text{Green}], \text{ParametricPlot}[[\text{up}, P_9], \{T, 0.01, 100\}, \text{PlotRange} \to \{(0, 7/2), (0, 1)\}, \text{PlotStyle} \to \text{Orange}]]] \]

Not much to say about these, they look much like the case with three levels! They all meet at the same place at the right energy.
This seems to approach the upper limit only later, at higher temperatures.

The entropy saturates (to Log[4]), but now only does so at higher temperatures. The inference is that as the number of accessible states increases, one will need much higher temperatures to guarantee that all of the probabilities will become close to equal.

(3) First let’s define the Helmholtz free energy (well, its negative actually):

\[
\text{Clear}[\alpha]; \quad \text{func} = \text{Num} \cdot k \cdot T \cdot \text{Log}[2 \cdot \text{Cosh}[\alpha \cdot B / k \cdot T]]
\]

\[
k \cdot \text{Num} \cdot T \cdot \text{Log}
\left[2 \cdot \text{Cosh}\left[\frac{B \cdot \alpha}{k \cdot T}\right]\right]
\]

The entropy is therefore:

\[
S = \text{FullSimplify}[\text{D}[\text{func}, T]]
\]

\[
k \cdot \text{Num} \cdot \text{Log}
\left[2 \cdot \text{Cosh}\left[\frac{B \cdot \alpha}{k \cdot T}\right]\right] - \frac{B \cdot \text{Num} \cdot \alpha \cdot \text{Tanh}\left[\frac{B \cdot \alpha}{k \cdot T}\right]}{T}
\]
\text{FullSimplify}[D[S, B]] \\
B \text{ Num } \alpha^2 \text{ Sech}\left[\frac{B \alpha}{kT}\right]^2 \\
-\frac{k T^2}{k T} \\

Likewise, the magnetization is: \\
M = \text{FullSimplify}[D[\text{func}, B]] \\
\text{Num } \alpha \text{ Tanh}\left[\frac{B \alpha}{kT}\right] \\

\text{FullSimplify}[D[M, T]] \\
B \text{ Num } \alpha^2 \text{ Sech}\left[\frac{B \alpha}{kT}\right]^2 \\
-\frac{k T^2}{k T} \\

Notice that the derivative of the entropy with respect to the magnetic field indeed coincides with the derivative of the magnetization with respect to the temperature, as predicted by the Maxwell relation. 

(4) Let’s plug in the variance formula for the 3D box first:

\( Z = \alpha / \beta^{(3/2)}; \)
\( \text{mean} = -D[Z, \beta] / Z \)
\( \text{variance} = D[Z, \{\beta, 2\}] / Z - (D[Z, \beta] / Z)^2 \)

Next let’s do the 3D harmonic oscillator:

\( Z = 1 / (1 - \text{Exp}[-\beta * \hbar * \omega])^3 \)
\( \text{mean} = \text{FullSimplify}[-D[Z, \beta] / Z] \)
\( \text{variance} = \text{FullSimplify}[D[Z, \{\beta, 2\}] / Z - (D[Z, \beta] / Z)^2] \)

\( \frac{1}{(1 - e^{-\hbar \beta \omega})^3} \)
\( \frac{3 \hbar \omega}{-1 + e^{\hbar \beta \omega}} \)
\( \frac{3}{4} \hbar^2 \omega^2 \text{Csch}\left[\frac{\hbar \beta \omega}{2}\right]^2 \)

At high temperatures one obtains:
\[ \text{Series}[\text{mean}, \{\beta, 0, 1\}] \]
\[ \text{Series}[\text{variance}, \{\beta, 0, 1\}] \]
\[ \frac{3}{\beta} - \frac{3}{2} \left( \frac{\hbar \omega}{\beta} \right) + \frac{1}{4} \hbar \omega^2 \beta + O[\beta]^2 \]
\[ \frac{3}{\beta^2} - \frac{\hbar^2 \omega^2}{4} + O[\beta]^2 \]