Problem 1. Paramagnets from the Microcanonial Ensemble

In a model of a paramagnet there are N independent atoms. Each atom can be in one of two spin states: “up” or “down” (see below). We use $N_\uparrow$ to notate the number of up spins and $N_\downarrow$ for down spins. There’s a magnetic field, B, pointing in the z direction, and the spins tend to align with this field. The magnetization of the magnet is proportional to the difference in up versus down spins, $M \equiv \mu(N_\uparrow - N_\downarrow)$, where μ is the magnetic dipole moment of an individual atom.

The energy of an up spin is $\epsilon_\uparrow = -\mu B$, where μ is the atom’s magnetic moment. On the other hand, the energy of a down spin is $\epsilon_\downarrow = +\mu B$. The reason up spins have lower energy than down spins is that up spins are aligned with the magnetic field, while the down spins are aligned opposite to the field. The energy difference between these levels is $\Delta = \epsilon_\downarrow - \epsilon_\uparrow = 2\mu B$.

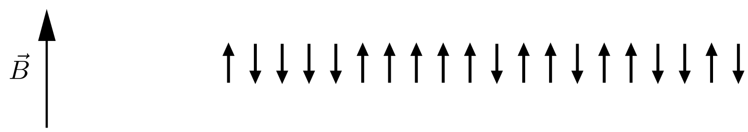


Figure 3.6. A two-state paramagnet, consisting of N microscopic magnetic dipoles, each of which is either “up” or “down” at any moment. The dipoles respond only to the influence of the external magnetic field B; they do not interact with their neighbors (except to exchange energy). Copyright ©2000, Addison-Wesley.

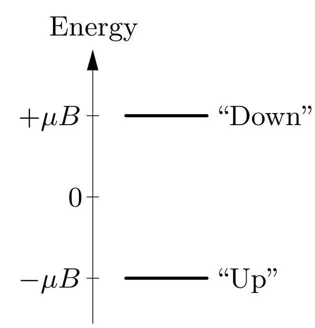


Figure 3.7. The energy levels of a single dipole in an ideal two-state paramagnet are $-\mu B$ (for the “up” state) and $+\mu B$ (for the “down” state). Copyright ©2000, Addison-Wesley.

Figure 1: (a) A visualization of the paramagnet (Schroeder). (b) The energy levels of a paramagnet (Schroeder).

The number of excited atoms (spin down) per site is $n = N_\downarrow/N$. The total energy of the atoms is $E = -\mu B(N_\uparrow - N_\downarrow) = -MB$.

(a) Determine the state of lowest possible energy (the ground state), and show that the energy of this state is $-\mu BN$. Define the *excitation* energy $\mathcal{E} = E - (-N\mu B)$, i.e. the energy *above* the ground state energy. Show that

$$\frac{\mathcal{E}}{N} = n\Delta \tag{1}$$

where $n = N_\downarrow/N$ is the number of excited atoms.

(b) By directly counting the states $\Omega(N_\downarrow, N_\uparrow)$ show that the entropy as a function of energy is

$$S(\mathcal{E}) = Nk_B\left[-(1-n)\log(1-n) - n\log n\right] \tag{2}$$

(c) Using Eq. (2) show that the temperature of the system with a given $\mathcal{E}$ is related to the fraction of atoms that are excited (down arrows)

$$\frac{\Delta}{kT} = \ln\left(\frac{1-n}{n}\right) . \tag{3}$$

Show that

$$n = \frac{e^{-\Delta/kT}}{1+e^{-\Delta/kT}} , \tag{4}$$

as can be found with the canonical approach.

(d) The hyperbolic cosine, sine, and tangent are defined by

$$\cosh(x) \equiv (e^x + e^{-x})/2 \tag{5}$$
$$\sinh(x) \equiv (e^x - e^{-x})/2 \tag{6}$$
$$\tanh(x) \equiv \frac{\sinh(x)}{\cosh(x)} = \frac{1-e^{-2x}}{1+e^{-2x}} \tag{7}$$

and arise frequently in stat mech and quantum mechanics. Sketch these functions and show that the Taylor series expansion of $\tanh(x)$ is $\tanh(x) \simeq x$.

(e) Show that the magnetization can be written

$$M = N\mu \tanh(\mu B/kT) . \tag{8}$$

Using the Taylor expansion of the previous part show that at small magnetic fields the magnetization is proportional to the applied magnetic field

$$M \simeq \chi(T)B \quad \text{with a proportionality constant} \quad \chi(T) \equiv \frac{N\mu^2}{kT} \propto \frac{1}{T} . \tag{9}$$

The proportionality constant $\chi(T)$ is known as the magnetic susceptibility. The fact that magnetization is inversely proportional to the temperature is known as the Curie Law. A comparison of the Curie Law and the $\tanh(x)$ form to experimental data on the magnetization of paramagnets is shown below. Answer the following:

(i) Qualitatively why would one expect the magnetization to disappear at high temperatures?

(ii) When is the Curie Law and the Taylor series expansion valid, i.e. what conditions should be satisfied by the magnetic field and temperature for its validity? Do you see deviations from the Curie Law in comparison with experiment in the right place? Explain.

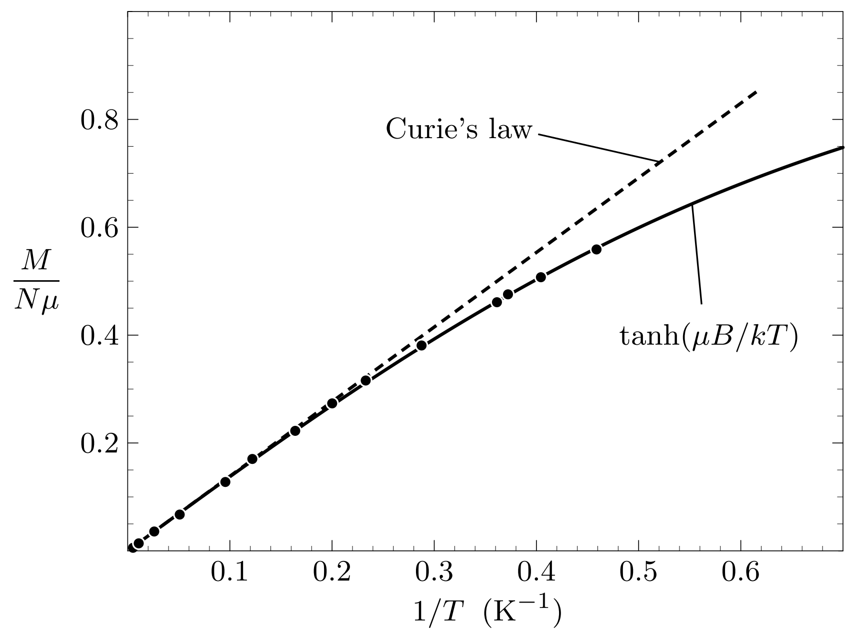


Figure 3.12. Experimental measurements of the magnetization of the organic free radical "DPPH" (in a 1:1 complex with benzene), taken at $B = 2.06$ T and temperatures ranging from 300 K down to 2.2 K. The solid curve is the prediction of equation 3.32 (with $\mu = \mu_B$), while the dashed line is the prediction of Curie's law for the high-temperature limit. (Because the effective number of elementary dipoles in this experiment was uncertain by a few percent, the vertical scale of the theoretical graphs has been adjusted to obtain the best fit.) Adapted from P. Grobet, L. Van Gerven, and A. Van den Bosch, *Journal of Chemical Physics* **68**, 5225 (1978). Copyright ©2000, Addison-Wesley.

Solution

(a) The state of lowest energy is with all atoms spin up. This is energy $E_0 = -N\mu B$, i.e. N times the energy of one atom spin up. Then if I have $N_\uparrow$ atoms up and $N_\downarrow$ atoms down, the energy is:

$$E = N_\uparrow \mu B - N_\downarrow \mu_B = N_\uparrow \mu B - (N - N_\uparrow \mu B = N_\uparrow \mu B - N\mu B \tag{10}$$

So the excitation energy is :

$$\mathcal{E} = E - E_0 = E + N\mu B = N_\uparrow \mu B = Nn\Delta \tag{11}$$

where we identified $n = N_\uparrow/N$. The answer follows after dividing by N

(b) The entropy is the number of configurations with specified excitation energy (meaning $N_\uparrow$ and $N_\downarrow$ are fixed)

$$\frac{S}{k} = \ln \Omega = \ln \frac{N!}{N_\uparrow! N_\downarrow!} \simeq -N_\uparrow \ln(N_\uparrow/N) - N_\downarrow \ln(N_\downarrow/N) \tag{12}$$

Then

$$N_\uparrow = nN \qquad N_\downarrow = (1-n)N \tag{13}$$

So

$$\frac{S}{k} = N\left[-n\ln(n) - (1-n)\ln(1-n)\right] \tag{14}$$

The dependence on $\mathcal{E}$ is hidden in $n = \frac{\mathcal{E}}{N\Delta}$. Below we will work with the entropy per particle in units of k, i.e.

$$\frac{S}{Nk} = \left[-n\ln(n) - (1-n)\ln(1-n)\right] \tag{15}$$

(c) We differentiate

$$\frac{1}{kT} = \frac{1}{k}\left(\frac{\partial S}{\partial E}\right) = \frac{1}{k}\frac{\partial S}{\partial \mathcal{E}} = \frac{1}{kN\Delta}\frac{\partial S}{\partial n} = \frac{1}{\Delta}\frac{\partial (S/Nk)}{\partial n} \tag{16}$$

Differentiating we find

$$\frac{\partial (S/Nk)}{\partial n} = \frac{\partial}{\partial n}\left[-n\ln(n) - (1-n)\ln(1-n)\right] = \left[-\ln(n) - \frac{n}{n} + \ln(1-n) + \frac{(1-n}{(1-n)}\right] \tag{17}$$

$$= \ln(\frac{1-n}{n}) \tag{18}$$

So we find as claimed

$$\frac{1}{kT} = \frac{1}{\Delta}\ln((1-n)/n) \tag{19}$$

Now straight forward algebra give

$$e^{\Delta/kT} = \frac{1}{n} - 1 \tag{20}$$

So

$$n = \frac{1}{e^{\Delta/kT} + 1} \tag{21}$$

(d) The Taylor series is

$$\tanh(x) \simeq \frac{1-(1-2x)}{1+(1+2x)} \simeq \frac{2x}{2+2x} \simeq x \tag{22}$$

In the last step we recognized that we worked only to order x inclusive, and dropped $\mathcal{O}(x^2)$. Thus, we do not need to expand out the denominator, which (since the numerator is already of order x) can be truncated at its leading (constant) term, i.e. 2 in this case. More precisely we are saying the following – we found to $\mathcal{O}(x^2)$:

$$\tanh(x) \simeq \frac{2x}{2+2x} + \mathcal{O}(x^2) \simeq x(1-x+\ldots) + \mathcal{O}(x^2) \simeq x - x^2 + \mathcal{O}(x^2) \simeq x \tag{23}$$

But, there is no need to keep the $-x^2$ (and higher) terms, since terms of order $\mathcal{O}(x^2)$ have already been dropped. In fact the corrections to $\tanh(x) \simeq x$ must be $\mathcal{O}(x^3)$, since the $\tanh(x)$ is an odd function of x. You should see this from your graph of $\tanh(x)$.

(e) We have

$$M = (N_\uparrow - N_\downarrow)\mu = N\mu(n-(1-n)) = N\mu(2n-1) \tag{24}$$

Putting in the what we found for n and noting $\Delta = 2\mu B$ we find

$$M = N\mu(2n-1) = N\mu\left(\frac{2}{e^{2\mu B/kT}+1} - 1\right) \tag{25}$$

Rearranging we find

$$M = N\mu\left(\frac{e^{2\mu B/kT}+1}{e^{2\mu B/kT}+1}\right) \tag{26}$$

We finally note

$$\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{e^{2x}-1}{e^{2x}-1} \tag{27}$$

So

$$M = N\mu\tanh(\mu B/kT) \tag{28}$$

For small $x = \mu B/kT$ we have $\tanh(x) \simeq x$ leading to

$$M = \frac{N\mu^2}{kT}B + \mathcal{O}(x^3) \tag{29}$$

(i) At high temperature the directions of the spins are essentially random. Then the magnetization, which is proportional to the difference in up and down spins, approaches zero.

(ii) For the the Taylor series to be valid we need

$$x = \frac{\mu B}{kT} \ll 1 \tag{30}$$

so that $\tanh(x) \simeq x$. Looking at the graph we see that at low temperatures (or high $1/T$) the Curie Law is violated meaning that x is no longer small $x \sim 1$. In this regime the full form of the $\tanh(x)$ is needed.

Problem 2. Manipulating Taylor Series

You are expected to know the following Taylor series in addition to $\sin(x)$ and $\cos(x)$:

$$e^x = 1 + x + \frac{1}{2!}x^2 + \mathcal{O}(x^3) \tag{31}$$

$$\log(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \mathcal{O}(x^4) \tag{32}$$

$$(1+x)^\alpha = 1 + \alpha x + \frac{\alpha(\alpha-1)}{2!}x^2 + \frac{\alpha(\alpha-1)(\alpha-2)}{3!}x^3 + \mathcal{O}(x^4) \tag{33}$$

$$\frac{1}{1+x} = 1 - x + x^2 + \mathcal{O}(x^3) \tag{34}$$

These get me through life. Here x is considered to be a small, dimensionless, number. The $\mathcal{O}(x^3)$ etc shows an estimate for the size of the terms that have been dropped. Some Taylor expansions will be needed in the next problem and throughout the course. These are to be found by combining the Taylor series above. The function we will study in detail is wildly important:

$$\frac{1}{e^x - 1}\,. \tag{35}$$

It determines the average number of vibrational quanta in a quantum harmonic oscillator at temperature T.

(a) (Optional) Show that Eq. (32) follows from Eq. (34) by integration.

(b) (Optional) Show that the Taylor series $(1+x)^\alpha$ gives the exact result for $\alpha = 2$.

(c) Consider large x, i.e. $x \gg 1$. Then e^{-x} is very small, i.e. $e^{-x} \ll 1$. Show that

$$\frac{1}{e^x - 1} \simeq e^{-x}\left(1 + e^{-x} + e^{-2x} + \mathcal{O}(e^{-3x})\right) \tag{36}$$

The first two terms are compared to the full function in Fig. 2

(d) By combining the expansion of $1/(1+x)$ and e^x derive the following expansion for $x \ll 1$:

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} - \frac{1}{2} + \frac{1}{12}x + \mathcal{O}(x^2) \tag{37}$$

The first two terms are compared to the full function in Fig. 2

Hint: First expand e^x to second order inclusive (i.e. the error is $O(x^3)$). Substitute this in Eq. (37) and pull out a factor of $\frac{1}{x}$. You should find that the resulting expression takes

$$\frac{1}{e^x - 1} \simeq \frac{1}{x}\left(\frac{1}{1+u}\right) \tag{38}$$

where $u \simeq \frac{1}{2}x + \frac{1}{6}x^2$. Then expand further:

$$\frac{1}{1+u} \simeq 1 - u + u^2 + \mathcal{O}(u^3) \tag{39}$$

When evaluating u^2 to an accuracy of $\mathcal{O}(x^3)$ you can (and should!) keep only the first term of $u(x) \simeq \frac{1}{2}x$:

$$u^2 + \mathcal{O}(x^3) = \left(\tfrac{1}{2}x + \tfrac{1}{6}x^2\right)^2 + \mathcal{O}(x^3) \simeq \left(\tfrac{1}{2}x\right)^2 + \mathcal{O}(x^3) \tag{40}$$

This is better (and less work) than evaluating the "exact" result:

$$u^2 + O(x^3) = \left(\tfrac{1}{2}x + \tfrac{1}{6}x^2\right)^2 + \mathcal{O}(x^3) = \tfrac{1}{4}x^2 + \tfrac{1}{6}x^3 + \tfrac{1}{36}x^4 + \mathcal{O}(x^3)\,, \tag{41}$$

which is mathematically inconsistent, since other terms of order $O(x^3)$ have already been discarded. Indeed, there is no reason to keep the terms $\frac{1}{6}x^3$ and $\frac{1}{36}x^4$ after other terms of order $O(x^3)$ and $O(x^4)$ have been discarded.

(e) Following the methodology of (c), determine an approximate series for

$$\frac{1}{e^{-x}+1} \tag{42}$$

for $x \gg 1$. This is useful in describing the thermodynamics of metals.

(f) Following the methodology of part (d), combine Taylor series to show that

$$\log(1 - e^{-x}) \simeq \log(x) - \frac{1}{2}x + \frac{x^2}{24} + \mathcal{O}(x^3) \tag{43}$$

for $x \ll 1$. This is useful in entropy of ideal gas of photons.

(g) (Optional) A clever student will notice that Eq. (43) follows from Eq. (37) via integration as in part(a). Give the details of this clever thought process.

Manipulating Taylos Series

a) $$\frac{1}{1+x} = 1 - x + x^2 - x^3 + \ldots$$

This follows from the geometric series $1/(1-u) = 1 + u + u^2 + \ldots$ with $u = -x$

Integrating

$$\int_0^x \frac{dx'}{(1+x')} = \log(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} \ldots$$

b)

c) For x large we have $e^{-x} \ll 1$

$$\frac{1}{e^x - 1} = \frac{e^{-x}}{1 - e^{-x}}$$

call $u = e^{-x} \ll 1$

$$\frac{1}{e^x - 1} = \frac{u}{(1-u)} = u\,(1 + u + u^2 + \ldots)$$

$$\boxed{\frac{1}{e^x - 1} = e^{-x}\left(1 + e^{-x} + e^{-2x} + O(e^{-3x})\right)}$$

d) $\dfrac{1}{e^x - 1}$

we expand $e^x = 1 + x + \dfrac{x^2}{2} + \dfrac{x^3}{6}$

$$\frac{1}{e^x-1} \simeq \frac{1}{x + x^2/2 + x^3/6} = \frac{1}{x} \frac{1}{(1 + x/2 + x^2/6 + O(x^3))}$$

calling, $u = x/2 + x^2/6$, we lave

$$\frac{1}{e^x-1} \simeq \frac{1}{x}\left(\frac{1}{1+u} + O(x^3)\right)$$

$$\simeq \frac{1}{x}(1 - u + u^2 + O(x^3))$$

$$\simeq \frac{1}{x}\left(1 - \left(\frac{x}{2} + \frac{x^2}{6}\right) + \left(\frac{x^2}{4}\right) + O(x^3)\right)$$

$$\boxed{\frac{1}{e^x-1} \simeq \frac{1}{x}\left(1 - \frac{x}{2} + \frac{x^2}{12}\right) + O(x^2)}$$

e) $\dfrac{1}{e^{-x}+1} \simeq 1 - e^{-x} + e^{-2x}$ set $u = e^{-x}$

f) $\log(1-e^{-x}) \simeq \log\left(1 - \left(1 - x + \dfrac{x^2}{2} - \dfrac{x^3}{6}\right)\right)$

$$\simeq \log x\left(1 - \frac{x}{2} + \frac{x^2}{6}\right) = \log x + \log\left(1 - \frac{x}{2} + \frac{x^2}{6}\right)$$

So

$$\log(1-e^{-x}) = \log(x) + \log(1 \underbrace{- \frac{x}{2} + \frac{x^2}{6}}^{\text{Call it } u}) + O(x^3)$$

Settinu $u = -\frac{x}{2} + \frac{x^2}{6}$ we have

$$\log(1+u) = u - \frac{u^2}{2} + O(u^3)$$ with x of order u

So

$$\log(1-e^{-x}) \simeq \log(x) + \left(-\frac{x}{2} + \frac{x^2}{6}\right) - \frac{1}{2}\left(-\frac{x}{2}\right)^2 + O(x^3)$$

$$\boxed{\log(1-e^{-x}) \simeq \log x - \frac{x}{2} + \frac{x^2}{24} + O(x^3)}$$

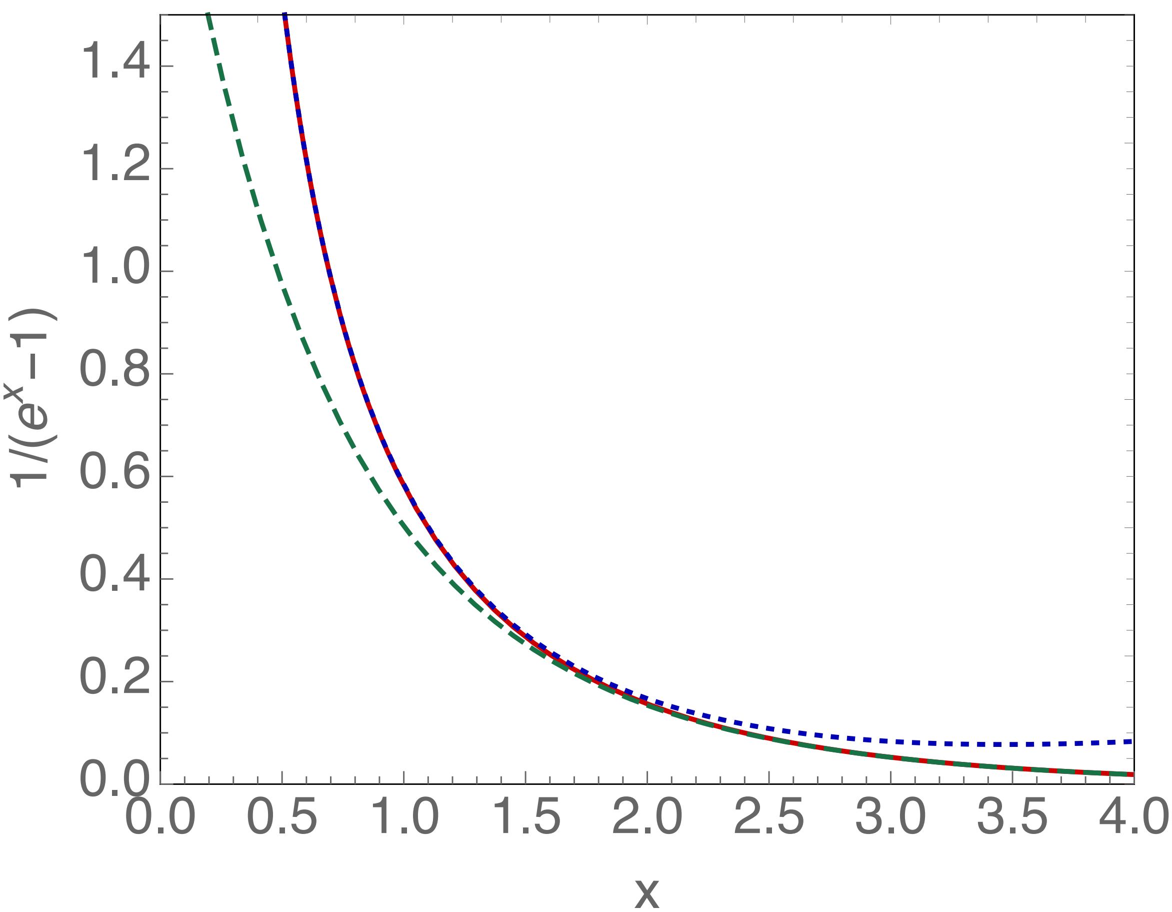


Figure 2: The function $1/(e^x - 1)$ (red) and our approximations to it. At small x the function is well approximated by $\frac{1}{x} - \frac{1}{2}$ (blue dotted line). At large x the function is well approximated by $e^{-x} + e^{-2x}$, green dashed line.

Problem 3. Energy of the quantum harmonic oscillator

Recall from previous homework that the mean energy of a single classical harmonic oscillator interacting with the thermal environment is

$$\langle \epsilon \rangle = kT \tag{44}$$

Now we will compare this classical result to the quantum version of the harmonic oscillator. This builds on the previous which worked out the partition function.

Recall that the energy levels of the oscillator are $\epsilon_n = n\hbar\omega_0$, where we have shifted what we call zero energy to be ground state energy $n = 0$, while higher vibrational states have $n = 1, 2, \ldots$.

(a) Determine the average energy $\langle \epsilon \rangle$ of the quantum harmonic oscillator at temperature T or $\beta = 1/kT$, using the partition function from a previous homework. Express your result using β and $\hbar\omega_0$. You can check your result using the next item.

(b) How is the mean vibrational quantum number $\langle n \rangle$ related to $\langle \epsilon \rangle$? Plot the mean number of vibrational quanta $\langle n \rangle$ versus $kT/\hbar\omega_0$ for $kT/\hbar\omega_0 = 0 \ldots 4$. Determine (from your graph) the temperature in units of $\hbar\omega_0$ where $\langle n \rangle = 1$. I find $T = 1.4427\,\hbar\omega_0/k_B$. Compare your exact number 1.4427 to your graphical estimate from the estimate previous homework.

(c) Plot

$$\frac{\langle \epsilon \rangle}{kT} \tag{45}$$

versus $kT/\hbar\omega_0$ for $kT/\hbar\omega_0 = 0 \ldots 4$.

(d) You will now use the Taylor expansions of the previous problem. Show that at low temperatures $T \ll \hbar\omega_0$ we have

$$\langle \epsilon \rangle \simeq \hbar\omega_0 e^{-\hbar\omega_0/kT} \tag{46}$$

or more generally

$$\langle \epsilon \rangle \simeq \hbar\omega_0 e^{-\beta\hbar\omega_0} \left(1 + e^{-\beta\hbar\omega_0} + \ldots\right) \tag{47}$$

Show that at high temperatures $T \gg \hbar\omega_0$ we have

$$\langle \epsilon \rangle \simeq kT \tag{48}$$

or more generally

$$\langle \epsilon \rangle \simeq kT \left(1 - \frac{\hbar\omega_0}{2kT} + \ldots\right) \tag{49}$$

A plot of the two approximations to the full function is shown in Fig. 3.

(e) Consider a *classical* harmonic oscillator. Determine the mean energy $\langle \epsilon \rangle$ in the classical case, using any method you like from previous homework. Now reexamine the *quantum* result and notice that in the high temperature limit $T \gg \hbar\omega_0$ is

$$\lim_{T\to\infty} \langle \epsilon \rangle \simeq kT \tag{50}$$

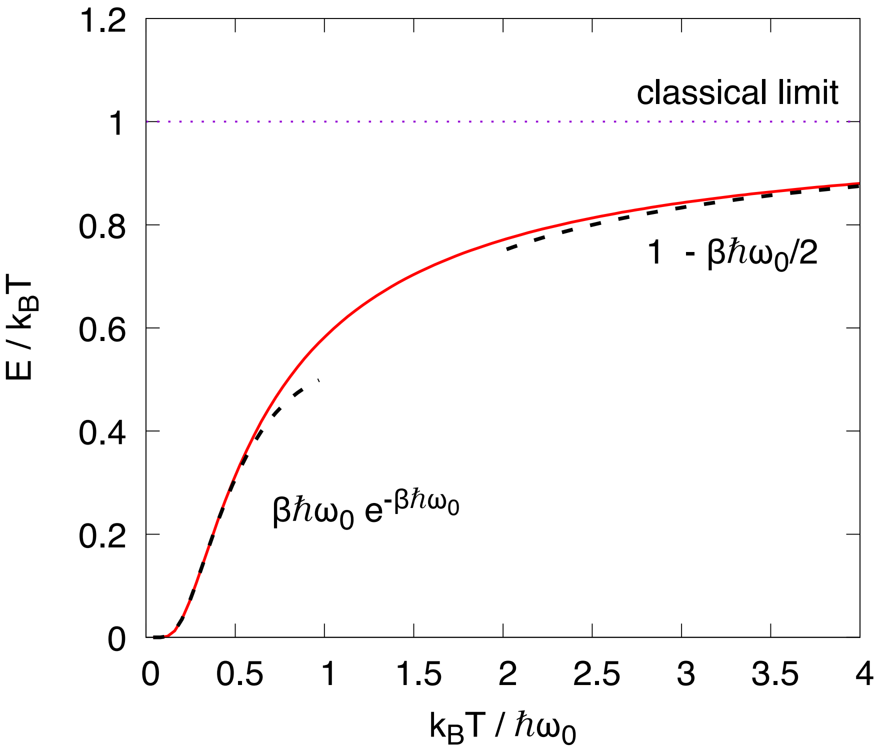


Figure 3: The energy $\langle\epsilon\rangle/kT$. Together with the expansions developed at large and small temperatures

(i) What is the percent change in energy for a quantum harmonic oscillator which transitions from the energy level with $n = 1$ to the energy level with $n = 2$? What about from $n = 1000000$ to $n = 1000001$?

(ii) Explain why at high temperatures the $\langle \epsilon \rangle$ of the quantum oscillator agrees with the classical one by discussing the significance of the graph in part (b).

Hint: When as a function of temperature is discrete nature of the energy levels truly important?

(f) Consider a diatomic ideal gas. Recall that the mean energy of each molecule consists of a classical contribution from translational degrees of freedom $\frac{3}{2}kT$, plus a classical contribution from the rotational degrees of freedom $\frac{2}{2}kT$. Now, a quantum mechanical contribution from the vibrations can added. The energy computed in part (a) is the contribution of the vibrational motion, and was computed quantum mechanically. As discussed in class, the total energy for an ideal gas takes the form

$$U = Ne_0(T) \tag{51}$$

and is independent of the volume.

(i) What is $e_0(T)$? (Hint: just read the question!)

(ii) What are C_V and C_p? You should find that the specific heat C_p is

$$C_p = Nk_B \left[\frac{7}{2} + \frac{(\beta\hbar\omega_0)^2 e^{-\beta\hbar\omega_0}}{(1 - e^{-\beta\hbar\omega_0})^2} \right] \tag{52}$$

and that the specific heat per mole

$$C_p^{1\text{ml}} = R \left[\frac{7}{2} + \frac{(\beta\hbar\omega_0)^2 e^{-\beta\hbar\omega_0}}{(1 - e^{-\beta\hbar\omega_0})^2} \right] \tag{53}$$

(iii) Recall that for diatomic hydrogen the first vibrational frequency is $\hbar\omega_0 \simeq 0.54\,\text{eV}$. Using this number together with $k_B = 0.025\,\text{eV}/300\,^\circ\text{K}$, I made a graph of Eq. (53) that is shown below. Compare the result to the experimental data. What qualitatively does the (simple-minded) calculation get right and wrong? Explain.

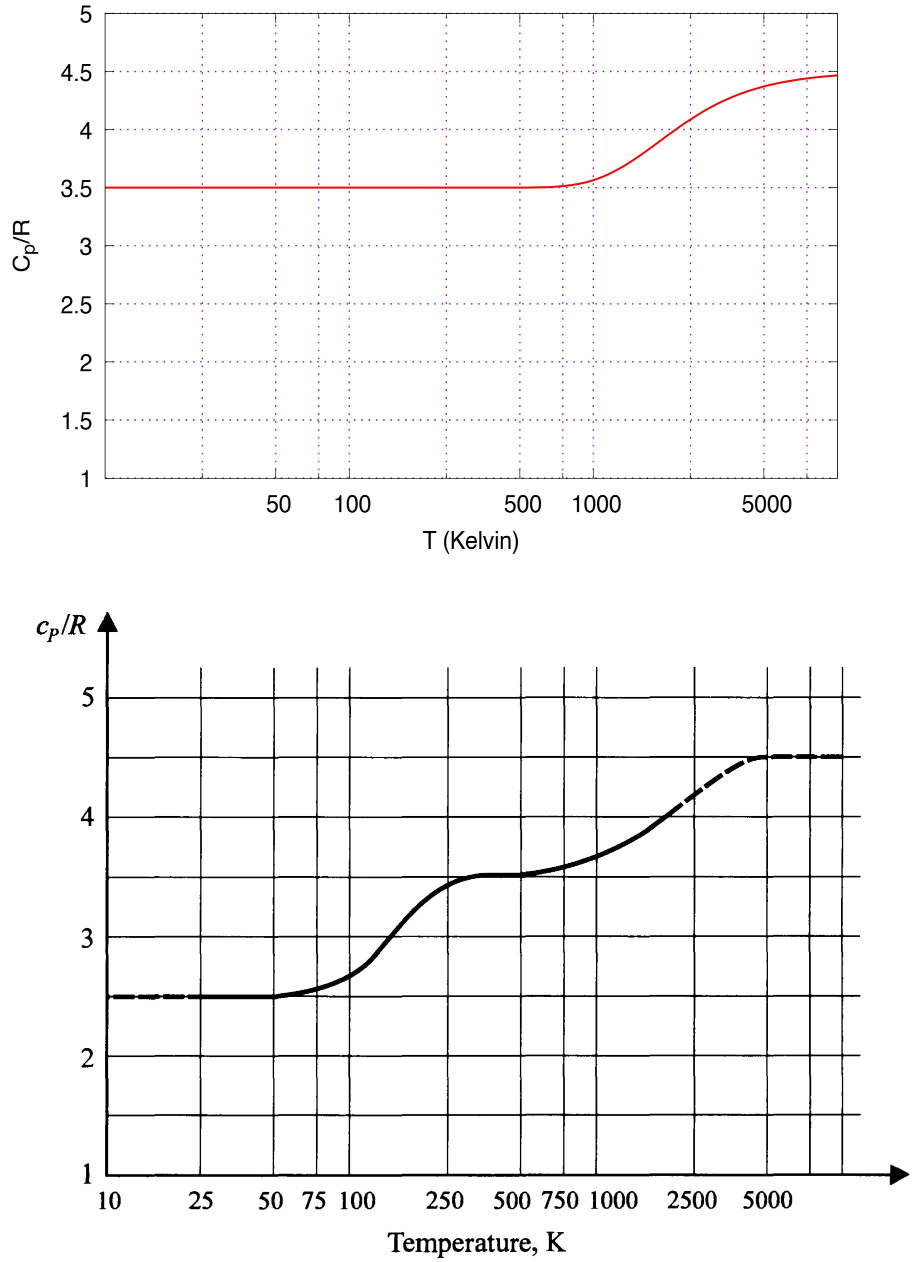


Figure 4: Top: a calculation of the specific heat per mole of diatomic hydrogen in units of R. Bottom: experimental data on C_p per mole in units of R

Energy of SHO

a) We have

$$Z = \frac{1}{1 - e^{-\beta \hbar \omega_0}}$$

Then

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z = +\frac{\partial}{\partial \beta} \log\left(1 - e^{-\beta \hbar \omega_0}\right)$$

$$= \frac{1}{1 - e^{-\beta \hbar \omega_0}} e^{-\beta \hbar \omega_0} \hbar \omega_0$$

$$\boxed{\langle E \rangle = \frac{\hbar \omega_0}{e^{\beta \hbar \omega_0} - 1}}$$

b) Then

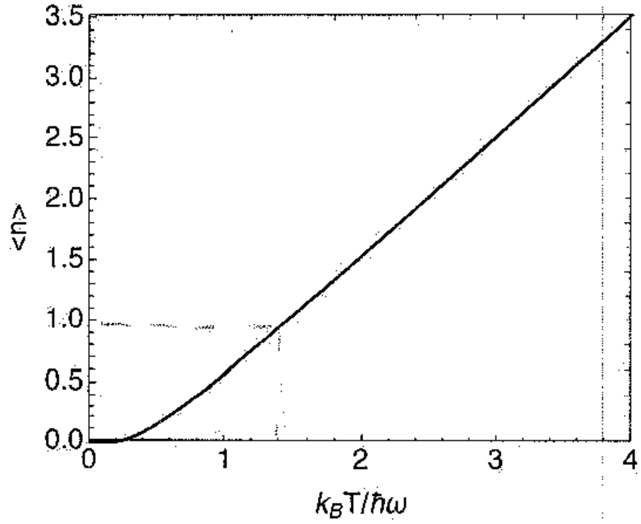
$$\frac{\langle E \rangle}{\hbar \omega_0} = \frac{1}{e^{\hbar \omega / kT} - 1} = \langle n \rangle$$

Then

Then from graph

$\langle n \rangle = 1$ when

$k_B T / \hbar \omega_0 = 1.45$



3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
<n>
0
1
2
3
4
k_B T/ħω

or

$$\boxed{k_B T = 1.45\,\hbar\omega_0}$$

c) Then a nice plot of $\langle E \rangle$ is given in the problem statement.

d) Using the series of problem 1

with $x \equiv \hbar\omega/kT$

at low temperature $kT \ll \hbar\omega_0$ then $x \gg 1$, and

$$\frac{1}{e^x - 1} = \frac{e^{-x}}{1 - e^{-x}} \simeq e^{-x}(1 + e^{-x} + \ldots)$$

And

$$\boxed{\langle E \rangle = \hbar\omega_0\, e^{-\beta\hbar\omega_0}(1 + e^{-\beta\hbar\omega_0} + \ldots)}$$

At high temperature $x \ll 1$

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} - \frac{1}{2}$$

$$\langle E \rangle = \hbar\omega_0\left(\frac{k_B T}{\hbar\omega_0} - \frac{1}{2}\right) \simeq k_B T\left(1 - \frac{\hbar\omega_0}{2kT}\right)$$

e) At high temperature the number of quanta $\langle n \rangle$ is very large. In this regime $\langle n \rangle \gg 1$, quantum mechanics becomes continuous, $\frac{\Delta E}{E} \ll 1$, and it approaches classical mechanics

This is the Bohr correspondence principle

f) We have

i) $$\boxed{U = N\left[\frac{5}{2}kT + \underbrace{\frac{\hbar\omega_0}{e^{\beta\hbar\omega_0}-1}}_{\text{this is } f_0(T)}\right]}$$

Then

ii) $$C_V = \left(\frac{dU}{dT}\right)_V = N\left[\frac{5}{2}k + \frac{-\hbar\omega_0 e^{\beta\hbar\omega_0}}{(e^{\beta\hbar\omega_0}-1)^2}\hbar\omega_0 \frac{\partial}{\partial T}\frac{1}{kT}\right]$$

$$= N\left[\frac{5k}{2} + \frac{(\beta\hbar\omega_0)^2 e^{\beta\hbar\omega_0}}{(e^{\beta\hbar\omega_0}-1)}k\right]$$

$$C_V = Nk\left[\frac{5}{2} + \frac{(\beta\hbar\omega_0)^2 e^{\beta\hbar\omega_0}}{(e^{+\beta\hbar\omega_0}-1)^2}\right]$$

So

$$C_p = C_v + Nk_B$$

$$\boxed{C_p = Nk_B \left[\frac{7}{2} + \frac{(\beta\hbar\omega_0)^2}{(e^{\beta\hbar\omega_0} - 1)^2} \right]}$$

iiv) So we see that the model nicely captures the transition from $C_p = \frac{7}{2} = 3.5$ to $\frac{9}{2} = 4.5$

but misses the transition to $\frac{5}{2}$ at low temperatures

Problem 4. Distribution of energies

The speed distribution is

$$\mathrm{d}\mathscr{P} = P(v)\,\mathrm{d}v \tag{54}$$

where $P(v) = (m/2\pi kT)^{3/2}\, e^{-mv^2/2kT} 4\pi v^2$.

(a) Show that the probability distribution of energies $\epsilon = \frac{1}{2}mv^2$ is

$$\mathrm{d}\mathscr{P} = P(\epsilon)\, d\epsilon \tag{55}$$

where

$$P(\epsilon) = \frac{2}{\sqrt{\pi}}\beta^{3/2} e^{-\beta\epsilon}\, \epsilon^{1/2} \tag{56}$$

Note: that the distribution of energies is independent of the mass, and recall $\beta = 1/kT$.

(b) Compute the variance in energy using $P(\epsilon)$. Express all integrals in terms $\Gamma(x)$ (as given in the previous homework) – it is helpful to change to a dimensionless energy $u = \beta\epsilon$. You should find (after evaluating these Γ functions as in the previous homework) that

$$\left\langle (\delta\epsilon)^2 \right\rangle = \frac{3}{2}(k_B T)^2 \tag{57}$$

Energies

- $$P(v)\, dv = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, 4\pi v^2\, dv$$

$$v = \left(\frac{2E}{m}\right)^{1/2} \qquad dv = \frac{1}{2\left(\frac{2E}{m}\right)^{1/2}} \frac{2E}{m} = \frac{dE}{(2mE)^{1/2}}$$

- So

$$P(\varepsilon)\, d\varepsilon = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\varepsilon/kT}\, \frac{2\varepsilon}{m}\, \frac{d\varepsilon}{\sqrt{2m}\, \varepsilon^{1/2}}$$

$$= 2\pi\, \frac{2^{3/2}}{2^{3/2}}\, \frac{m^{3/2}}{m^{3/2}}\, \frac{\varepsilon^{1/2} d\varepsilon}{(k_B T)^{3/2}}\, \frac{1}{\pi^{3/2}}\, e^{-\varepsilon/kT}$$

$$\boxed{P(\varepsilon)\, d\varepsilon = \frac{2}{\sqrt{\pi}}\, \beta^{3/2}\, e^{-\beta\varepsilon}\, \varepsilon^{1/2}\, d\varepsilon}$$

So

- $$\langle \varepsilon \rangle = \int_0^\infty \varepsilon\, P(\varepsilon)\, d\varepsilon$$

$$= \int_0^\infty \frac{2}{\sqrt{\pi}}\, \beta^{3/2}\, e^{-\beta\varepsilon}\, \varepsilon^{1/2}\, d\varepsilon \times \varepsilon$$

- Change vars $u = \beta \varepsilon$

$$\langle \varepsilon \rangle = \frac{1}{\beta} \int_0^\infty \frac{2}{\sqrt{\pi}} e^{-u} u^{3/2} \, du$$

$$\boxed{\langle \varepsilon \rangle} = \frac{1}{\beta} \frac{2}{\sqrt{\pi}} \Gamma(5/2) = \frac{1}{\beta} \frac{2}{\sqrt{\pi}} \frac{3}{2} \Gamma\left(\frac{3}{2}\right)$$

Similarly

$$= 1/\beta \cdot 2 \cdot \frac{3}{2} \cdot \frac{1}{2} = \boxed{\frac{3}{2} k_B T}$$

$$\langle \varepsilon^2 \rangle = \frac{1}{\beta^2} \int_0^\infty \frac{2}{\sqrt{\pi}} e^{-u} u^{5/2} \, du$$

$$\langle \varepsilon^2 \rangle = \frac{1}{\beta^2} \frac{2}{\sqrt{\pi}} \Gamma(7/2)$$

So

$$\boxed{\langle \varepsilon^2 \rangle} = \frac{1}{\beta^2} \cdot \frac{2}{\sqrt{\pi}} \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} \Gamma(1/2)$$

$$= \frac{1}{\beta^2} 2 \cdot \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} = \boxed{\frac{1}{\beta^2} \frac{15}{4}}$$

So

$$\boxed{\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = \frac{1}{\beta^2} \left(\frac{15}{4} - \frac{9}{4} \right) = \frac{3}{2} (k_B T)^2}$$

Problem 5. Three state paramagnet

Consider a paramagnet at temperature T consisting of an Avogadro's number of atoms N_A in a constant magnetic field B pointing in the z direction. The atoms in the paramagnet have a magnetic moment μ and can be in one of three spin states: spin up ($\uparrow$), spin down ($\downarrow$), and neutral (0) as shown below.

$$\uparrow\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow\ 0\,0\,0\,0\ \uparrow\ 0\,0\ \downarrow\uparrow\uparrow\uparrow\uparrow\uparrow\ 0\ \uparrow\ 0\ \uparrow\uparrow\uparrow\uparrow\ 0\ \uparrow\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow\uparrow\ 0\ \uparrow\ 0\ \uparrow\uparrow\uparrow$$

The energy of these three states is given by

$$E_\uparrow = -B\mu, \quad E_0 = 0, \quad E_\downarrow = B\mu\,, \tag{58}$$

as shown below. *Note:* The spin-down states ($\downarrow$) have higher energy than the spin-up states.

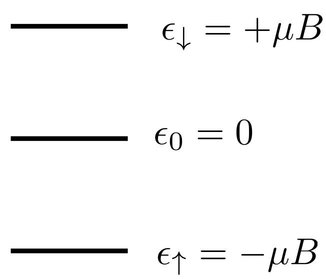


Figure 5: Energy level diagram for the three state paramagnet.

(a) (4 + 6) Determine the partition function and mean energy $\langle U \rangle$ of the system. Express your result using hyperbolic functions as appropriate:

$$\cosh(x) = \frac{1}{2}\left(e^x + e^{-x}\right) \qquad \frac{\mathrm{d}\cosh(x)}{\mathrm{d}x} = \sinh(x) \tag{59}$$

$$\sinh(x) = \frac{1}{2}\left(e^x - e^{-x}\right) \qquad \frac{\mathrm{d}\sinh(x)}{\mathrm{d}x} = \cosh(x) \tag{60}$$

(b) (6 points) Find the leading (non-zero) term in a Taylor series expansion for $\langle U \rangle$ when the magnetic field is very weak, $\mu B \ll kT$. Use the result to find the specific heat C_V when the magnetic field is weak.

These questions are independent of (a) and (b) :

(c) (8 points) Determine a specific temperature T_* when the number of atoms in the spin-down state is one quarter of those in the spin-up state? At this temperature, what fraction of the atoms are in the up, neutral, and down states, respectively?

(d) (8 points) At the temperature T_*, what is the entropy of the system?
Hint: Consider the Shannon entropy of the system based on (c).

(e) (4 points) If the probability (or fraction) of each atomic state is held fixed to their values in part (c), how does the mean energy depend on the magnetic field? In other words, determine:

$$\left(\frac{\partial U}{\partial B}\right)_{\text{fixed-prob}} \tag{61}$$

This does *not* correspond to a fixed temperature!

Hint: The result does not require a lot of algebra, so if your result becomes too lengthy, return to basics.

Solution:

(a) We have for a single spin

$$Z = e^{\beta\mu B} + 1 + e^{-\mu B} = 1 + 2\cosh(\beta\mu B) \tag{62}$$

Then

$$\langle\epsilon\rangle = \frac{1}{Z}\frac{-\partial Z}{\partial\beta} = \frac{-2\sinh(\beta\mu B)\mu B}{1 + 2\cosh(\beta\mu B} \tag{63}$$

The energy of the whole system is

$$U = N\langle\epsilon\rangle = -\,2N\left(\frac{\sinh(\beta\mu B)\mu B}{1 + 2\cosh(\beta\mu B}\right) \tag{64}$$

(b) For small magnetic field we expand the $\sinh(x) \simeq x$ and $\cosh(x) \simeq 1$ leading to

$$U \simeq -\frac{2N}{3}\beta(\mu B)^2 \tag{65}$$

Note for $T \to \infty$, the energy is zero, as all three states become equally likely. So the specific heat is $C_V = \frac{dU}{dT}$. Using

$$\frac{\partial\beta}{\partial T} = -k\beta^2 \tag{66}$$

we find

$$C_V \simeq \frac{2Nk}{3}(\beta\mu B)^2 \tag{67}$$

(c) We have

$$\frac{P_\downarrow}{P_\uparrow} = e^{-\beta(\epsilon_\downarrow - \epsilon_\uparrow)} = e^{-\beta\Delta} = \frac{1}{4} \tag{68}$$

So we find

$$\beta\Delta = \ln(4) \qquad T = \frac{\Delta}{k\ln(4)} \tag{69}$$

We also have

$$\frac{P_0}{P_\uparrow} = e^{-\beta(\epsilon_0 - \epsilon_\uparrow)} = e^{-\beta\Delta/2} = \sqrt{\frac{1}{4}} = \frac{1}{2} \tag{70}$$

Then the overall probability is normalized to unity

$$P_\uparrow + P_0 + P_\downarrow = 1 \tag{71}$$

So

$$P_\uparrow\left(1 + \frac{1}{2} + \frac{1}{4}\right) = P_\uparrow\frac{7}{4} = 1 \tag{72}$$

So we have finally

$$P_\uparrow = \frac{4}{7} \qquad P_0 = \frac{2}{7} \qquad P_\downarrow = \frac{1}{7} \tag{73}$$

(d) The Shannon Entropy is

$$S = N\left[-P_{\uparrow}\ln P_{\uparrow} - P_0 \ln P_0 - P_{\downarrow}\ln P_{\downarrow}\right] \tag{74}$$

and so with the fractions given in Eq. (73) we find:

$$S = N \cdot 0.9557 \tag{75}$$

(e) We have

$$U = N\left[P_{\uparrow}\cdot(-\mu B) + P_0 \cdot 0 + P_{\downarrow}\cdot(\mu B)\right] \tag{76}$$

Differentiating, while leaving the probabilities fixed gives

$$\left(\frac{\partial U}{\partial B}\right)_{fixedprob} = N\left[P_{\uparrow}(-\mu) + P_{\downarrow}\cdot \mu\right] \tag{77}$$

We find

$$\left(\frac{\partial U}{\partial B}\right)_{fixedprob} = -N\mu\left[\frac{4}{7} - \frac{1}{7}\right] = -N\mu\frac{3}{7} \tag{78}$$

We note that the result is negative. As the magnetic field is increased more of the spins are pointing up making the magnetic field increasingly negative

Since the probabilities determine the entropy $S_1 = \sum_i -P_i \ln P_i$, we will later in the course discuss that this derivative is the derivative of U with respect to B at fixed entropy:

$$\left(\frac{\partial U}{\partial B}\right)_{fixedprob} = \left(\frac{\partial U}{\partial B}\right)_S \tag{79}$$