Problem 1. Simple Steps

Each of these consists of small algebra and definitions.

(a) The probability of a system being in the ith microstate is

$$P_i = e^{-\beta E_i}/Z, \tag{1}$$

where E_i is the energy of the ith microstate and β and Z are constants. From the Gibbs expression for the entropy $S = -k_B \sum_m P_m \ln P_m$ show that the entropy is related to Z

$$\frac{S}{k_B} = \ln Z + \beta U \tag{2}$$

where $U = \sum P_i E_i$. Also show that

$$Z = e^{-\beta F} \qquad F = -kT \log Z \tag{3}$$

(b) Starting from the first Law $dE = TdS - pdV$ (i) derive the expression for dF in terms of its natural variables (T, V) and (ii) derive an expression for dG in terms of its natural variables (T, P)

(c) Show the following

$$U = -T^2 \left(\frac{\partial(F/T)}{\partial T}\right)_V \tag{4}$$

$$C_V = -T \left(\frac{\partial^2 F}{\partial T^2}\right)_V \tag{5}$$

$$H = -T^2 \left(\frac{\partial(G/T)}{\partial T}\right)_p \qquad \text{Optional} \tag{6}$$

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_p \qquad \text{Optional} \tag{7}$$

Problem 2. Ideal gas in one and two dimensions

- Use methods of partition functions to find the free energy, energy, pressure, and entropy in one and two dimensions. Compare your result to the 3D case. Express your result for the entropy in terms of the thermal debroglie wavelength.

Problem 3. A three state paramagnet

Consider a paramagnet at temperature T consisting of an Avogadro's number of atoms N 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

$$E_\uparrow = -B\mu, \quad E_0 = 0, \quad E_\downarrow = B\mu\,, \tag{8}$$

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

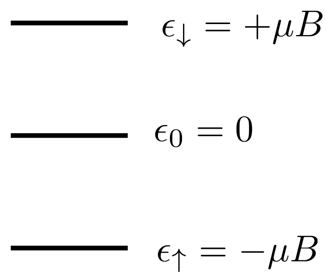

Figure 1: Energy level diagram for the three state paramagnet.

(a) The magnetization M of the magnet is defined as the difference between the number of up-spins and the number of down spins times an atom's magnetic moment:

$$M = (N_\uparrow - N_\downarrow)\mu\,. \tag{9}$$

(i) Is M an intensive or extensive variable? How about B? Explain.

(ii) If $N_\uparrow$, N_0, and $N_\downarrow$ are held fixed, but B is increased by dB, show that change in energy (or the work done by the magnetic field) is:

$$dU = dW = -MdB\,. \tag{10}$$

When $N_\uparrow$, N_0, $N_\downarrow$ are held fixed, it means that the entropy is fixed, i.e. there is no heat flowing into the system. This is because the entropy is determined by the fixed numbers $N_\uparrow$, N_0, and $N_\downarrow$:

$$S = k\ln\Omega = k\ln\left(\frac{N!}{N_\uparrow!N_\downarrow!N_0!}\right) \tag{11}$$

(b) In general, the first law of thermodynamics applied to magnets reads:

$$\begin{aligned} dU =& dQ + dW & (12)\\ =& TdS - MdB & (13) \end{aligned}$$

Define the free energy, find dF, and show that

$$\left(\frac{\partial F}{\partial T}\right)_B = -S \qquad \left(\frac{\partial F}{\partial B}\right)_T = -M \tag{14}$$

Thus, the free energy determines all relevant variables.

(c) Determine the partition function of the system. Find the free energy (as a function of temperature (T) and magnetic field (B) from the partition function, and find the mean energy $\langle U \rangle$ of the system. Express your result using hyperbolic functions as appropriate:

$$\cosh(x) = \frac{1}{2}\left(e^{x} + e^{-x}\right) \qquad \frac{\mathrm{d}\cosh(x)}{\mathrm{d}x} = \sinh(x) \tag{15}$$

$$\sinh(x) = \frac{1}{2}\left(e^{x} - e^{-x}\right) \qquad \frac{\mathrm{d}\sinh(x)}{\mathrm{d}x} = \cosh(x) \tag{16}$$

Graph the energy $U/\mu B$ versus $x = \beta\mu B$. Interpret the origin of the high and low temperature limits physically. You should find

$$\frac{U}{N} = -\frac{2\sinh(x)}{(1 + 2\cosh(x))}\mu B \tag{17}$$

where $x = \beta\mu B$ is a dimensionless variable.

(d) To simplify the algebra in what follows, define the function:

$$f(x) = \frac{d}{dx}\ln(1 + 2\cosh(x))\,, \tag{18}$$

$$= \frac{2\sinh(x)}{1 + 2\cosh(x)}\,. \tag{19}$$

Show that

$$f'(x) = \left[\frac{2\cosh(x)}{(1 + 2\cosh(x))} - \frac{4\sinh^2(x)}{(1 + 2\cosh(x))^2}\right] \tag{20}$$

The results here will simplify if you try to use $f(x)$ wherever you can, e.g. :

$$U = -Nf(x)\mu B \tag{21}$$

(e) By straightforward differentiation, show that if the magnetic field is increased by $\mathrm{d}B$, the change in energy of the system at fixed temperature is

$$dU = -N\mu\, f(x)\,\mathrm{d}B - \mu N\, x f'(x)\,\mathrm{d}B \tag{22}$$

(f) Determine the entropy of the system as a function of temperature. Graph the entropy S/Nk versus $\beta\mu B$. Explicitly interpret the limitting value of S in the high temperature limit.

(g) By straightforward differentiation, show that if B is increased at fixed temperature by dB that the change in entropy is

$$\mathrm{d}S = -\frac{N\mu}{T} x f'(x)\mathrm{d}B \tag{23}$$

(h) Determine the magnetization of the system as a function of temperature. What is the change in free energy when the magnetic field is increased by $\mathrm{d}B$ at fixed temperature? Graph M/μ versus $\beta\mu B$. Interpret physically the high and low temperature limits.

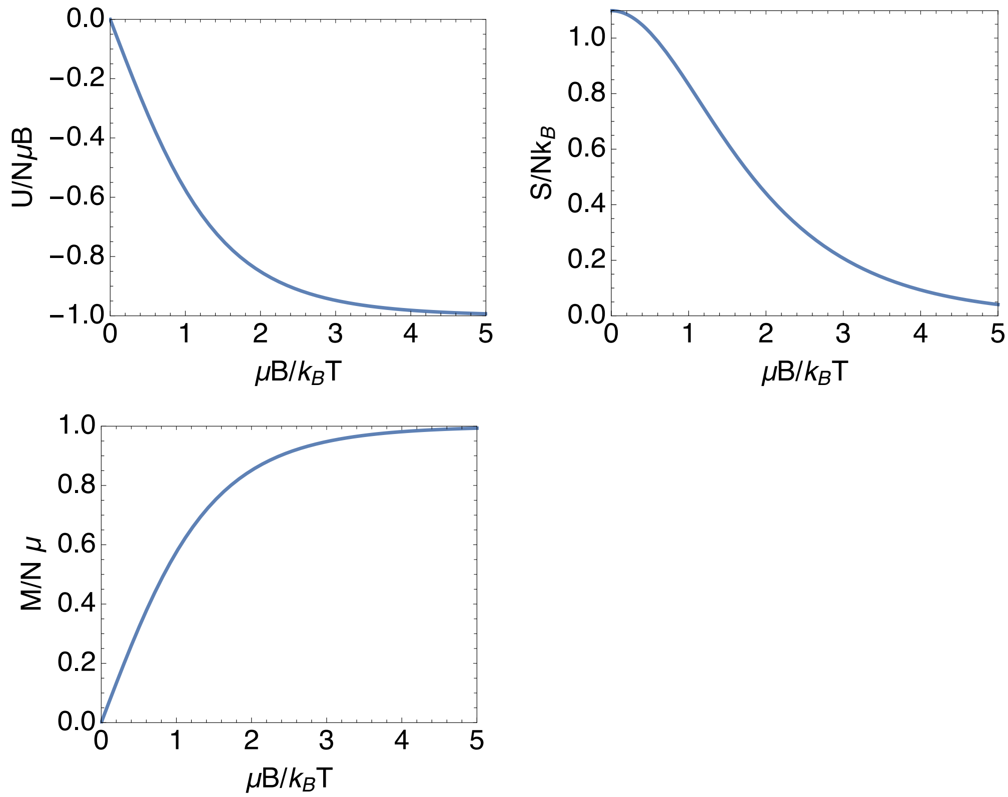

Figure 2: Some results for the three state paramagnet

(i) Determine a Maxwell relation relating $S(T, B)$ and $M(T, B)$ and verify that this is satisfied for the $S(T, B)$ and $M(T, B)$ found previously.

(j) 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? Ans: $kT_* = 2\mu B/\ln(4)$.

(k) At the temperature T_*, use the fractions of the previous item to determine the entropy. Check that your answer agrees with the previous result for $S(T, B)$ when you substitute T_*

(l) At fixed temperature T, the magnetic field increases by an amount dB. How much work is done and what is the change in energy and free energy of the system? How do you explain the difference between work done by the magnetic field and the change in energy of the system? Explain.