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

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

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

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

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

Simple Steps

a) $P_i = \frac{e^{-\beta E_i}}{Z}$

$$\frac{S}{k_B} = -\sum_i P_i \ln P_i$$

$$= -\sum_i \frac{e^{-\beta E_i}}{Z} \ln \frac{e^{-\beta E_i}}{Z}$$

$$= -\sum_i \frac{e^{-\beta E_i}}{Z}(-\beta E_i) + \sum_i \frac{e^{-\beta E_i}}{Z} \ln Z$$

$$= \sum_i -\frac{e^{-\beta E_i}}{Z}(-\beta E_i) + \ln Z \sum_i \frac{e^{-\beta E_i}}{Z}$$

$$\boxed{\frac{S}{k_B} = \beta \bar{E} + \ln Z}$$

So $\ln Z = \frac{S}{k_B} - \frac{\bar{E}}{k_B T} = -\frac{F}{k_B T}$

And

$$\boxed{Z = e^{-F/k_B T}}$$

b) $dU = TdS - pdV$

$$d(U - TS) = TdS - pdV - (TdS + SdT)$$

$F \equiv U - TS$ $\quad dF = -SdT - pdV$

$$d(F + pV) = -SdT - pdV + (pdV + Vdp)$$

$G = U - TS + pV$ $\quad \boxed{dG = -SdT + Vdp}$

c) So

$$-T^2 \left(\frac{\partial (F/T)}{\partial T}\right)_V = F - \left(T \frac{\partial F}{\partial T}\right)_V = F + TS$$

we used $dF = -SdT - pdV$. Then since $F = U - TS$, we have

i) $-T^2 \dfrac{\partial F/T}{\partial T} = U$ ✓

ii) $C_V = T\left(\dfrac{\partial S}{\partial T}\right)_V = -T \dfrac{\partial}{\partial T}\left(\dfrac{\partial F}{\partial T}\right)_V = -T\left(\dfrac{\partial^2 F}{\partial T^2}\right)_V$ ✓

iii)

$$-T^2 \left(\frac{\partial (G/T)}{\partial T}\right)_p = G - T\left(\frac{\partial G}{\partial T}\right)_p = G - T(-S) = G + TS$$

But $G = U - TS + pV$ and $H = U + pV$ and so

$$-T^2 \left(\frac{\partial (G/T)}{\partial T} \right)_p = H$$

So

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p = T \left(\frac{\partial}{\partial T} \right)_p \cdot \left(\frac{\partial G}{\partial T} \right)_p = T \left(\frac{\partial^2 G}{\partial T^2} \right)_p$$

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.

Ideal Gas:

2D

$$Z_1 = \int \frac{d^2r\, d^2p}{h^2} e^{-p^2/2mT}$$

$$\boxed{Z_1 = \frac{A}{\lambda_{th}^2}} \qquad \frac{1}{\lambda_{th}^2} \equiv \frac{2\pi m k_B T}{h^2}$$

1D

$$Z_1 = \int \frac{dr\, dp}{h} e^{-p^2/2mT}$$

$$\boxed{Z_1 = \frac{L}{\lambda_{th}}} \qquad \frac{1}{\lambda_{th}} \equiv \frac{\sqrt{2\pi m k_B T}}{h}$$

So $\quad Z_1 \equiv L^d / \lambda_{th}^d$

$$Z_{TOT} = \frac{1}{N!} Z_1^N \simeq \left(\frac{e Z_1}{N}\right)^N$$

So

$$F = -kT \ln Z_{TOT} = -kTN\left[\ln \frac{Z_1}{N} + 1\right]$$

$$= -kTN\left[-\ln(N/Z_1) + 1\right]$$

So

$$\boxed{F = -kTN\left[-\ln(n\lambda_{th}^{d}) + 1\right]}$$

where $d = 1, 2, 3$ for dimensions $1, 2, 3$

$$S = -\frac{\partial F}{\partial T}$$

Now $\lambda_{th} = \frac{h}{\sqrt{2\pi m k T}} = c\,T^{-1/2}$. Then

$$S = Nk\left[-\ln(n\lambda_{th}^{d}) + 1\right] + NkT\frac{\partial}{\partial T}(-\ln n\lambda_{th}^{d})$$

Now

$$\ln n\lambda_{th}^{d} = \ln(T^{-d/2}) + \text{const} \qquad \frac{\partial}{\partial T}\ln n\lambda_{th}^{d} = \frac{-d}{2T}$$

So

$$\boxed{S = Nk\left[-\ln(n\lambda_{th}^{d}) + 1\right] + \frac{NkT\,d}{2T}}$$

or

$$S = Nk\left[-\ln(n\lambda_{th}^{d}) + \frac{d+2}{2}\right] \quad \text{with } d = 1, 2, 3$$

The Energy

$$F = E - TS \qquad E = F + TS$$

So

$$E = -kTN\left[-\ln(n\lambda^d) + 1\right] + TNk\left[-\ln(n\lambda_{th}^d) + \frac{d+2}{2}\right]$$

$$\boxed{E = NkT\,\frac{d}{2}}$$

So finally we need the pressure

$$F = -kTN\left[-\ln\left(\frac{N}{V_d}\lambda_{th}^d\right) + 1\right]$$

Where $V_d = L, A, V = L^d$ in d-dimensions

$$p = -\left(\frac{\partial F}{\partial V_d}\right)_T = kTN\frac{\partial}{\partial V_d}\left(\ln V_d + \text{const}\right)$$

$$\boxed{p = \frac{kTN}{V_d}}$$

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.

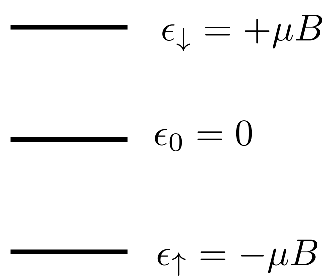

Figure 1: Energy level diagram for the three state paramagnet.

(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:

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

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:

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

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)), 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 $U/N\mu B$ versus $x = \beta\mu B$. Interpret 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:

$$\begin{aligned} f(x) =& \frac{d}{dx}\ln(1 + 2\cosh(x))\,, \qquad (18) \\ =& \frac{2\sinh(x)}{1 + 2\cosh(x)}\,. \qquad (19) \end{aligned}$$

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 functions $f(x)$ and $f'(x)$ are shown below.

The results below 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

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

(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 $m/N\mu$ versus $\beta\mu B$. Interpret physically the high and low temperature limits.

(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 in previous items.

(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? Check that these fractions add up to one. 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_*. Ans: $S = 7.95\,\mathrm{J/^\circ K}$.

(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 quantitatively using Eq. (23)

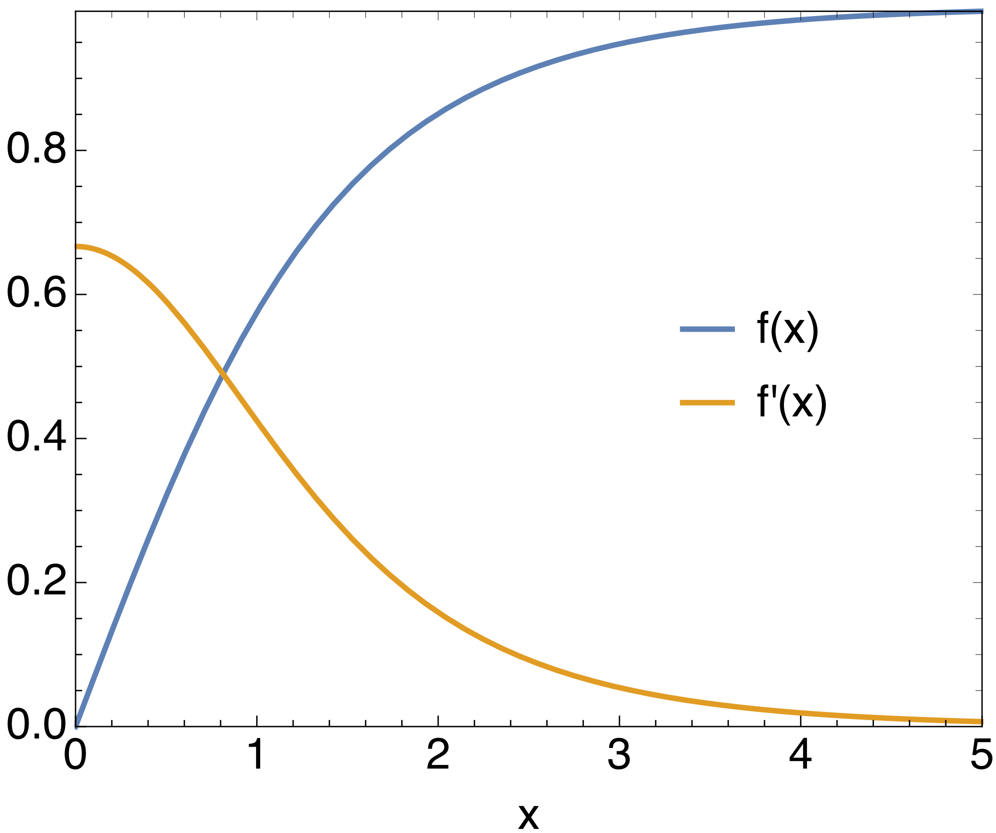

Figure 2: Some results for the three state paramagnet

Solution

(a) m is extensive. As the N grows the fraction $N_\uparrow/N$ remains fixed and likewise for $N_\downarrow/N$, so $m \propto N$. The mean energy is

$$U = (N_\uparrow \epsilon_\uparrow - N_\downarrow \epsilon_\downarrow) \tag{24}$$

Differentiating with respect to B just changes the energies, e.g. $\mathrm{d}\epsilon_\uparrow = -\mu \mathrm{d}B$. So

$$\mathrm{d}U = -(N_\uparrow - N_\downarrow)\mu \mathrm{d}B = -m\mathrm{d}B \tag{25}$$

(b) We have

$$\mathrm{d}U = T\mathrm{d}S - m\mathrm{d}B \tag{26}$$

Integrating by parts

$$\mathrm{d}(U - TS) = -S\mathrm{d}T - m\mathrm{d}B \tag{27}$$

So we have

$$\mathrm{d}F(T, B) = -S\mathrm{d}T - m\mathrm{d}B\,. \tag{28}$$

The partial derivatives can be read off from this differential

(c) The energy is a sum of indpenendent subsystems so $Z = Z_1^N$ with

$$Z_1 = e^{-\beta\epsilon_\uparrow} + e^{-\beta\epsilon_0} + e^{-\beta\epsilon_\downarrow} \tag{29}$$
$$= 1 + 2\cosh(\beta\mu B) \tag{30}$$

So the free energy energy

$$F = -kT \ln Z = -NkT \ln Z_1 = -kTN \ln(1 + 2\cosh(\beta\mu B)) \tag{31}$$

We also note that

$$-\beta F = \ln Z = N \ln(1 + 2\cosh(\beta\mu B)) \tag{32}$$

Then differentiating

$$U = -\frac{\partial \ln Z}{\partial \beta} = -2N\mu B \frac{\sinh(\beta\mu B)}{1 + 2\cosh(\beta\mu B)} \tag{33}$$

(d) Do the algebra and derivates for yourself

$$f'(x) = \left[\frac{2\cosh(x)}{(1 + 2\cosh(x))} - \frac{4\sinh^2(x)}{(1 + 2\cosh(x))^2}\right]. \tag{34}$$

(e) So we are to differentiate

$$U = -Nf(x)\mu B \tag{35}$$

with respect to B,

$$dU = -Nf'(x)\beta\mu B\mathrm{d}B - Nf(x)\mu\mathrm{d}B = N(xf'(x) - f)N\mathrm{d}B \tag{36}$$

(f) We should use

$$\frac{S}{k} = \ln Z + \beta U = N\left[\ln(1+2\cosh(x)) - xf(x)\right] \tag{37}$$

Dividing by N we find

$$\frac{S}{Nk} = \left[\ln(1+2\cosh(x)) - xf(x)\right] \tag{38}$$

This is graphed in Fig. 3. We note that as $x \to 0$, the second term in Eq. (38) vanishes and $2\cosh(x) \to 2$ so

$$\frac{S}{Nk} \to \ln(3) \tag{39}$$

The result is natural. In the high temperature limit all three states are equaly probable with probability $P_i = 1/3$. Thus the entropy per site is

$$\frac{S_1}{k} = -\sum_i P_i \ln(P_i) = \ln(3) \tag{40}$$

For N sites we have $\Omega = 3^N$ equally probably states and $S = Nk\ln(3)$.

(g) Then

$$\frac{1}{k}\mathrm{d}S = \frac{d}{dx}\left[\ln(1+2\cosh(x)) - xf(x)\right] N\beta\mu \mathrm{d}B \tag{41}$$

We find

$$\frac{1}{k}\mathrm{d}S = \left[f(x) - (f(x) + xf'(x))\right]\beta\mu\mathrm{d}B \tag{42}$$

Multiplying by k we find the expected result

$$\mathrm{d}S = -\frac{N\mu x f'(x)\mathrm{d}B}{T} \tag{43}$$

(h) From the differential we have

$$\mathrm{d}F = -S\mathrm{d}T - m\mathrm{d}B \tag{44}$$

So at fixed temperature

$$m = -\left(\frac{\partial F}{\partial B}\right)_T = NkT\frac{d}{dx}\ln(1+2\cosh(x))\beta\mu B \tag{45}$$

leading to

$$m = N\mu B f(x) \tag{46}$$

This is shown in figure Fig. 3(b)

(i) Since the differential is

$$\mathrm{d}F = -S\mathrm{d}T - m\mathrm{d}B\,. \tag{47}$$

We have the cross derivatives are equl

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B \tag{48}$$

We have already worked out that

$$\left(\frac{\partial S}{\partial B}\right)_T = -\frac{1}{T} N\mu x f'(x) \tag{49}$$

By differentiating m using the chain rule with $x = \mu B/T$

$$\left(\frac{\partial m}{\partial T}\right)_B = N\mu f'(x)\frac{\partial x}{\partial T} \tag{50}$$

$$= N\mu f'(x)\left(-\frac{\mu B}{T^2}\right) \tag{51}$$

$$= -\frac{1}{T} N\mu x f'(x) \tag{52}$$

Comparing these terms we see that the Maxwell relation Eq. (48) is satisfied

(j) We have $P = e^{-\beta\epsilon}/Z$ so

$$\frac{P_\downarrow}{P_\uparrow} = \frac{e^{-\beta\mu B}}{e^{\beta\mu B}} = e^{-2\beta\mu B} \tag{53}$$

We are looking when this is 1/4 so

$$e^{-2\beta\mu B} = \frac{1}{4}\,. \tag{54}$$

Solving we find

$$kT_* = 2\mu B/\ln(4) \tag{55}$$

We next note that

$$\frac{P_0}{P_\uparrow} = \frac{e^0}{e^{\beta\mu B}} = e^{-\beta\mu B} = \frac{1}{2} \tag{56}$$

So we have the following ratios

$$P_\downarrow : P_0 : P_\uparrow = \frac{1}{4} : \frac{1}{2} : 1 \tag{57}$$

Normalizing these probabilities we have

$$P_\uparrow = \frac{1}{1+\frac{1}{2}+\frac{1}{4}} = \frac{4}{7} \tag{58}$$

$$P_0 = \frac{1/2}{1+\frac{1}{2}+\frac{1}{4}} = \frac{2}{7} \tag{59}$$

$$P_\downarrow = \frac{1/4}{1+\frac{1}{2}+\frac{1}{4}} = \frac{1}{7} \tag{60}$$

(k) We have

$$\frac{S}{Nk} = -\sum_i P_i \ln(P_i) = \frac{1}{7}\ln(7) + \frac{2}{7}\ln(7/2) + \frac{4}{7}\ln(7/4) = 0.9557 \tag{61}$$

We also have the formula

$$\frac{S}{Nk} = \ln(1 + 2\cosh(x)) + x\frac{2\sinh(x)}{1 + 2\cosh(x)} \tag{62}$$

This should be evaluated when $x = \beta\mu B = \ln(4)/2$. Substituting we get

$$\frac{S}{Nk} = 0.9557 \tag{63}$$

as expected. Recognizing that $N_A k = R = 8.302\, J/^{\circ}\mathrm{K}$ we get $S = 7.93\, J/^{\circ}\mathrm{K}$

(l) We first collect results from all previous parts. The work is

$$đW = -m\mathrm{d}B = -N\mu f(x)\mathrm{d}B \tag{64}$$

The change in energy

$$\mathrm{d}U = -N\mu f(x)\mathrm{d}B - \mu N x f'(x)\mathrm{d}B \tag{65}$$

The change in free energy is

$$\mathrm{d}F = -NkTf(x)\beta\mu\mathrm{d}B = -N\mu f(x)\mathrm{d}B \tag{66}$$

and the change in S is

$$T\mathrm{d}S = -N\mu x f'(x)\mathrm{d}B \tag{67}$$

We see that the work done equals the change in free energy of the system. Since the process is is at finite temperature a heat $đQ = T\mathrm{d}S$ flows into the system. ($đQ$ is negative, so the heat flowing out is $đQ_{\mathrm{out}} = -T\mathrm{d}S$ is positive). So the work done is the change in internal energy plus the heat that flows out at constant temperature, i.e. the change in free energy $dU - TdS$ at constant temperature.

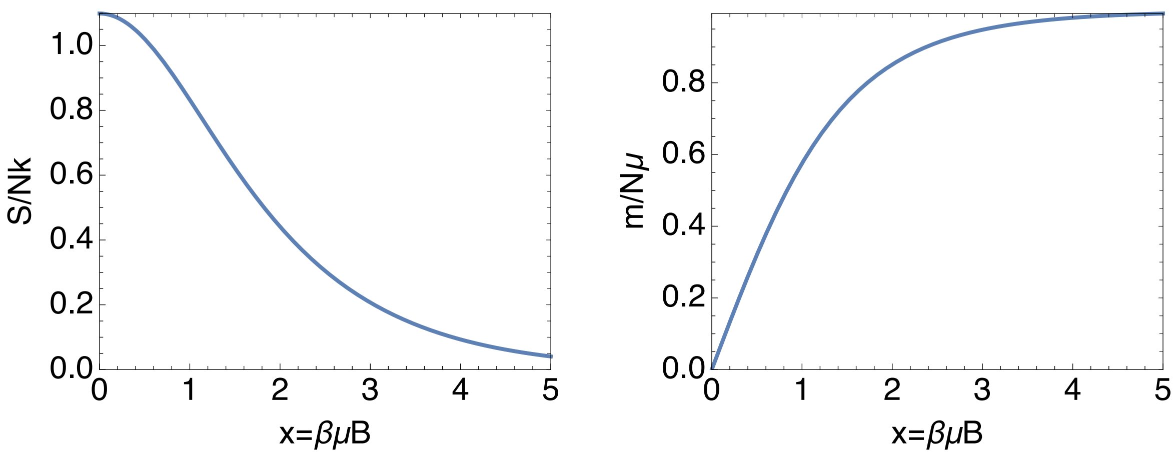

Figure 3: Entropy and magnetization versus temperature.