

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:

$$m = (N_{\uparrow} - N_{\downarrow})\mu. \quad (5)$$

- (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:

$$dU = dW = -mdB. \quad (6)$$

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} :

$$S = k \ln \Omega = k \ln \left(\frac{N!}{N_{\uparrow}! N_{\downarrow}! N_0!} \right) \quad (7)$$

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

$$dU = dQ + dW \quad (8)$$

$$= TdS - mdB \quad (9)$$

Define the free energy, find dF , and show that

$$\left(\frac{\partial F}{\partial T} \right)_B = -S \quad \left(\frac{\partial F}{\partial B} \right)_T = -m \quad (10)$$

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:

$$\cosh(x) = \frac{1}{2} (e^x + e^{-x}) \quad \frac{d \cosh(x)}{dx} = \sinh(x) \quad (11)$$

$$\sinh(x) = \frac{1}{2} (e^x - e^{-x}) \quad \frac{d \sinh(x)}{dx} = \cosh(x) \quad (12)$$

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

$$\frac{U}{N} = -\frac{2 \sinh(x)}{(1 + 2 \cosh(x))} \mu B, \quad (13)$$

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

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

$$f(x) = \frac{d}{dx} \ln(1 + 2 \cosh(x)), \quad (14)$$

$$= \frac{2 \sinh(x)}{1 + 2 \cosh(x)}. \quad (15)$$

Show that

$$f'(x) = \left[\frac{2 \cosh(x)}{(1 + 2 \cosh(x))} - \frac{4 \sinh^2(x)}{(1 + 2 \cosh(x))^2} \right]. \quad (16)$$

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. :

$$U = -Nf(x)\mu B \quad (17)$$

(e) By straightforward differentiation, show that if the magnetic field is increased by dB , the change in energy of the system at fixed temperature is

$$dU = -N\mu f(x) dB - \mu N x f'(x) dB \quad (18)$$

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

$$dS = -\frac{N\mu}{T} x f'(x) dB \quad (19)$$

(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 dB 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.

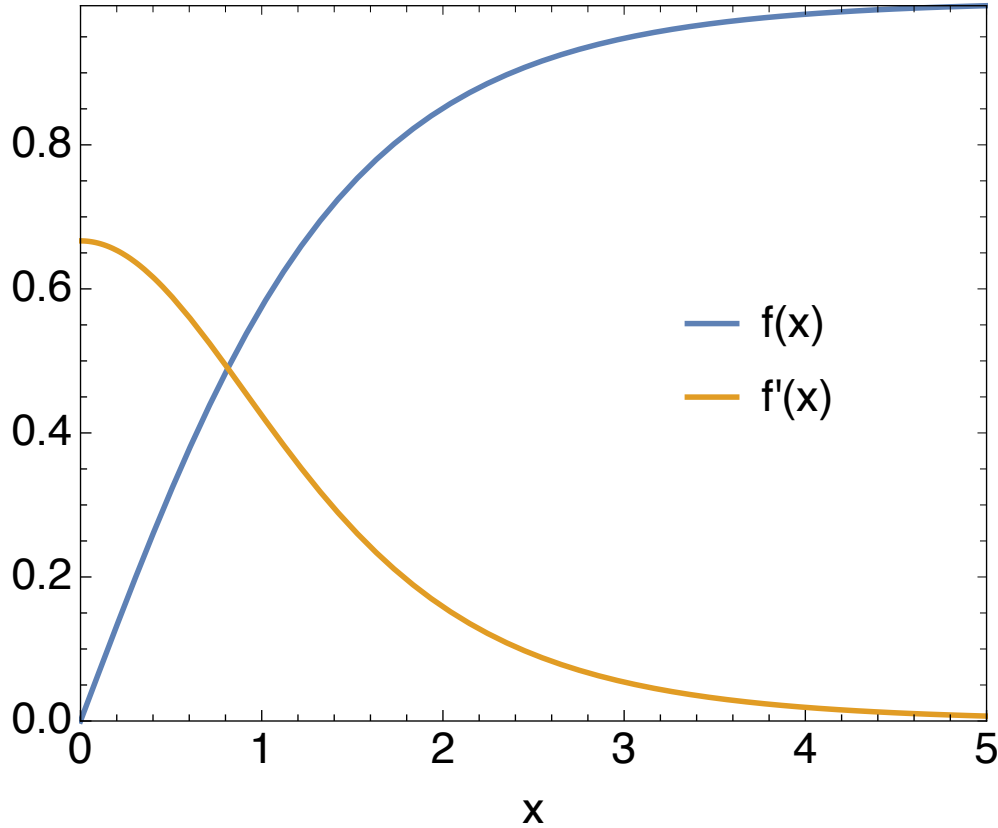


Figure 2: Some results for the three state paramagnet

- (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: $S = 7.95 \text{ J/}^\circ\text{K}$.
- (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. (19)

Problem 4. Rotational Partition Functions

(a) **This week's homework:** Consider HCl gas, which is composed of Hydrogen of mass m_H and chlorine Cl

- (i) Give a typical distance between the Hydrogen and the Chlorine atoms, r_0 (in meters). We will assume this distance is fixed.
- (ii) Use classical considerations, to find the center of mass of the two atoms, and compute the moment of inertia of the two atoms around the center of mass exactly. Assume that the HCl is rotating in the xy plane. Show that

$$I = m_H r_0^2 \left(1 - \left(\frac{m_H}{m_{Cl}} \right) + \dots \right) \quad (20)$$

up to terms further suppressed by terms of order $(m_H/m_{Cl})^2$. We will keep the leading term only $m_H r_0^2$ in what follows.

- (iii) The rotational energy levels are

$$\epsilon_{\text{rot}} = \left\langle \frac{L^2}{2I} \right\rangle = \frac{\ell(\ell+1)\hbar^2}{2I} = \ell(\ell+1)\Delta \quad (21)$$

where $\Delta = \hbar^2/2I$. Estimate Δ in eV and in GHz (i.e. $f = \Delta/h$). Estimate Δ/kT at room temperature, you should find that kT/Δ is around 12.

(b) **(Next weeks homework)**

- (i) (Show that for any system that C_V is directly determined by the variance in the energy

$$C_V = k_B \beta^2 (\langle E^2 \rangle - \langle E \rangle^2) \quad (22)$$

- (ii) Recall that the partition function of N molecules of H HCl consists of a translational partition function, and a rotational one:

$$Z_{\text{tot}} \simeq \left(\frac{e Z_{\text{trans}}}{N} \right)^N Z_{\text{rot}}^N \quad (23)$$

(Where does the factor $(e/N)^N$ come from?). Show that

$$C_V = \frac{3}{2} N k_B + N k_B \beta^2 [\langle \epsilon_{\text{rot}}^2 \rangle - \langle \epsilon_{\text{rot}} \rangle^2] \quad (24)$$

where

$$\beta^2 \langle \epsilon_{\text{rot}}^2 \rangle = \frac{1}{Z_{\text{rot}}(\beta\Delta)} \sum_{\ell=0}^{\infty} (2\ell+1) (\ell(\ell+1)\beta\Delta)^2 e^{-\ell(\ell+1)\beta\Delta} \quad (25)$$

$$\beta \langle \epsilon_{\text{rot}} \rangle = \frac{1}{Z_{\text{rot}}(\beta\Delta)} \sum_{\ell=0}^{\infty} (2\ell+1) (\ell(\ell+1)\beta\Delta) e^{-\ell(\ell+1)\beta\Delta} \quad (26)$$

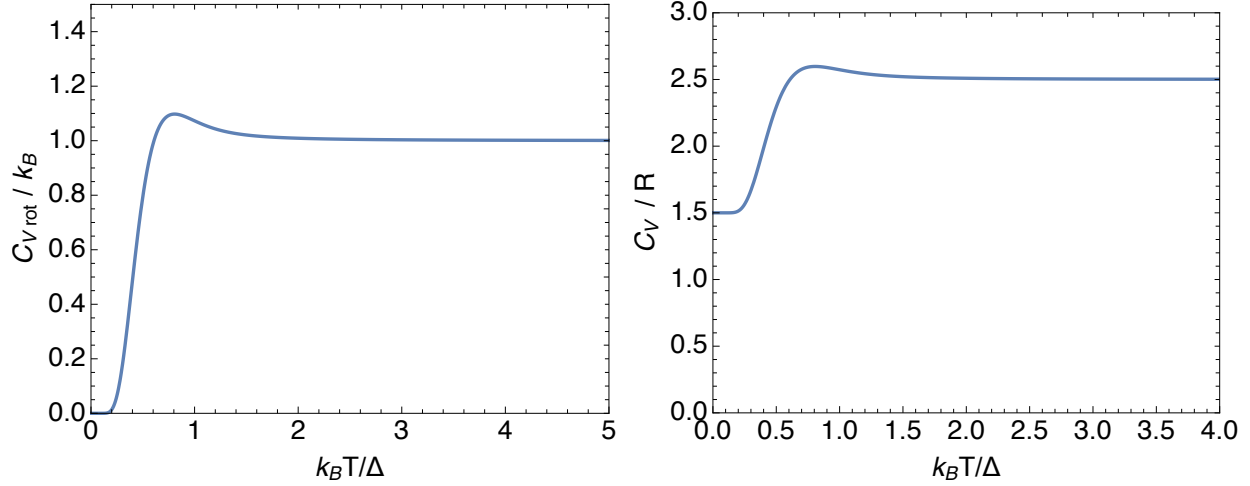


Figure 3: Left: the rotational contribution to the partition function (per particle), i.e. $\beta^2(\langle \epsilon_{\text{rot}}^2 \rangle - \langle \epsilon_{\text{rot}} \rangle^2)$. Right: the full partition function for one mole.

- (c) Write a program to sum from $\ell = 0$ up to 20 and to compute

$$\beta^2 \langle \epsilon_{\text{rot}}^2 \rangle, \quad \beta^2 \langle \epsilon_{\text{rot}} \rangle^2, \quad C_V / k_B \quad (27)$$

Make a graph of C_v / R vs. kT / Δ for one mole of substance. You should find something analogous to Figure. 3.

- (d) For HCl, use your graph estimate the temperature (in Kelvin) where the classical approximation for the rotational partition function works at the 20% level. What would be the corresponding temperature for diatomic hydrogen H_2 .