Exercise 1 Statistical mechanics of magnetization

Consider a system of N distinguishable non-interacting spins in a magnetic field B. Each spin has a magnetic moment of size μ_B, pointing either parallel or anti-parallel to the field direction. Thus, the energy of a particular state is:

$$\mathcal{H} = \sum_{i=1}^{N} -s_i \mu_B B = -\mu_B B \sum_{i=1}^{N} s_i, \qquad s_i = \pm 1 \tag{1}$$

where $s_i \mu_B$ is the magnetic moment in the direction of the field.

(a) Show that the partition function of the system as a function of β, B, and N is given by

$$Q(\beta, B, N) = (2\cosh \beta \mu_B B)^N \tag{2}$$

(b) Determine the internal energy as a function of β, B, and N.

(c) Determine the entropy of this system as a function of β, B, and N.

(d) Determine the behavior of the energy and entropy for this system as $T \to 0$.

(e) Derive the average total magnetization,

$$\langle M \rangle = \langle \sum_{i=1}^{N} \mu_B s_i \rangle \tag{3}$$

as a function of β, B, and N.

(f) Given $\delta M = M - \langle M \rangle$, determine the average fluctuations $\langle (\delta M)^2 \rangle$ and compare it with the magnetic susceptibility,

$$\left(\frac{\partial \langle M \rangle}{\partial B} \right)_{\beta, N} \tag{4}$$

What is the relationship between the two quantities ?

(g) Derive the behaviour of $\langle M \rangle$ and $\langle (\delta M)^2 \rangle$ in the limit $T \to 0$.

Exercise 2 Ferromagnetic materials

In the previous exercise we learned to use statistical mechanics to understand properties of a paramagnetic material. You could note that you could simplify the partition function due to the non-interaction (or non-correlation) of spins, i.e. the flipping of any spin is independent with the rest of the spins in the systems.

In this exercise, we will apply principles of statistical mechanics to understand another class of magnetic material, ferromagnetic material. In a ferromagnetic material, there exist a finite interaction between spins given by J_{ij}. The *Hamiltonian* of the system of N spins is given by:

$$\hat{H} = -B\sum_{i}^{N} s_i - \frac{1}{2}\sum_{i\neq j} J_{ij} s_i s_j \tag{5}$$

where $s_i = 1$ or -1 and B is the magnetic field.

Because the interaction gives rise to $s_i s_j$ terms in the partition function, we cannot decouple the sum like in Exercise 1. Instead, we will make some useful approximation that can simplify the partition function while still reveals most important physics. This approximation is called "mean field theory" (MFT).

We assume that there is only neighbor interaction with the same strength J. Each spin in the system interacts with a z average neighbor spins whose value is given by:

$$\bar{s} = \langle \frac{1}{N}\sum_{i}^{N} s_i \rangle \tag{6}$$

(a) Write the expression of the partition function for a ferromagnetic material consisting of N spins and simplify it under the mean field theory approximation.

(b) Under what circumstances is this approximation valid?

(c) Derive an expression for the average (spontaneous) magnetization in the limit $B \to 0$. Examine it graphically and show that in a ferromagnetic material, there exists a phase transition temperature T_c.

(d) In the low temperature region near T_c (critical regime) in the limit $B \to 0$, what is the behavior of the average magnetization? What is the value of the critical exponent?

(e) Still in the limit $B \to 0$, determine the average magnetization in the low temperature region $T \to 0$.

(f) Now draw the dependence of average magnetization on temperature, and indicate T_c and phase regions.

(g) Determine the susceptibility at high temperature above T_c. The result is the so-called Curie-Weiss law.

(h) Draw susceptibility as a function of temperature.

(i) Describe the behavior of the specific heat at constant B, $C(B = 0)$ near T_c.

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Solution to Exercise 1

(a). A given microstate of the system is characterized by a configuration of up and down spins $(s_1, s_2, \ldots, s_N)$, where each spin can be $+1$ or -1, leading to a total of 2^N possible states. The probability of being in a state ν is given by

$$P(\nu) = P(s_1, s_2, \ldots, s_N) \propto e^{-\beta \mathcal{H}}, \tag{7}$$

with the energy given by $\mathcal{H} = -\mu_B B \sum_{i=1}^N s_i$. To normalize this into a proper probability, we need to compute the partition function at a given temperature T, number of particles N and applied field B as follows

$$\begin{aligned} Q(T, N, B) &= \sum_{\sigma_1=\pm1} \sum_{\sigma_2=\pm1} \cdots \sum_{\sigma_N=\pm1} \exp\left\{\beta \mu_B B \sum_i^N s_i\right\} \\ &= \sum_{s_1=\pm1} \sum_{s_2=\pm1} \ldots \sum_{s_N=\pm1} e^{\beta \mu_B B s_1} e^{\beta\ \mu_B B s_2} \ldots e^{\beta \mu_B B s_N} \\ &= \left(\sum_{s_1=\pm1} e^{\beta \mu_B B s_1}\right) \left(\sum_{s_2=\pm1} e^{\beta \mu_B B s_2}\right) \ldots \left(\sum_{s_N=\pm1} e^{\beta \mu_B B s_N}\right) \\ &= \left(e^{\beta \mu_B B} + e^{-\beta \mu_B B}\right)^N \\ &= (2 \cosh \beta \mu_B B)^N \end{aligned} \tag{8}$$

where we have used the fact that the spins are independent, which allowed us to factor the Hamiltonian into N independent terms only depending on one spin.

(b). The internal energy of the system can be computed by

$$U(T, N, B) = \langle E \rangle_{T,N,B} = -\frac{\partial}{\partial \beta} \ln Q(T, N, B) = -N \frac{\partial}{\partial \beta} \ln (2 \cosh \beta \mu_B B) = -N \mu_B B \tanh (\beta B \mu_B). \tag{9}$$

(c). Combining parts **(a)** and **(b)**, the entropy can be computed from the difference between the internal energy and the free energy: $A = U - TS \leftrightarrow S = \frac{1}{T}(U - A)$, and $A = -k_B T \log Q$, leading to

$$\begin{aligned} S(T, N, B) &= \frac{1}{T}(U - A) \\ &= \frac{1}{T} U + k_B \log Q \\ &= k_B N \left[\log (2 \cosh \beta \mu_B B) - \beta \mu_B B \tanh (\beta B \mu_B)\right]. \end{aligned} \tag{10}$$

(d). As $T \to 0$, for any $B > 0$ the expressiontanh $(\beta B \mu_B) \to 1$ and the internal energy reaches its minimum value, $U(T \to 0, N, B) \to -\beta \mu_B B N$ since all the spins are aligned in the direction of the applied field B. Thus the entropy reaches a minimum value

$$S(T, N, B) = k_B N \left[\beta B \mu_B - \beta B \mu_B\right] = 0. \tag{11}$$

(e). The total magnetization M is given by

$$M = \mu_B \sum_i^N s_i \tag{12}$$

In this particular case, it turns out that the Hamiltonian (or energy) is simply $\mathcal{H} = -BM$. Thus, we could simply take the average energy computed above and divide by $-B$. This method, however, does not work

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for more complicated systems like the Ising model. We will thus show the derivative trick, which also allows us to compute the magnetization for other systems.

$$\begin{aligned}
\langle M \rangle_{T,N,B} &= \sum_{\sigma_i} M \frac{1}{Q} e^{-\beta \mathcal{H}} && (13)\\
&= \sum_{\sigma_i} M \frac{1}{Q} e^{\beta B M} && (14)\\
&= \frac{\sum_{\sigma_i} M e^{\beta B M}}{\sum_{\sigma_i} e^{\beta B M}} && (15)\\
&= \frac{\frac{\partial}{\partial(\beta B)} \sum_{\sigma_i} e^{\beta B M}}{\sum_{\sigma_i} e^{\beta B M}} && (16)\\
&= \frac{\frac{\partial}{\partial(\beta B)} Q}{Q} && (17)\\
&= \frac{\partial}{\partial(\beta B)} \log Q && (18)
\end{aligned}$$

In our case, $\log Q = N \log(2\cosh \beta \mu_B B)$ and thus

$$\langle M \rangle_{T,N,B} = N\mu_B \tanh(\beta B \mu_B). \tag{19}$$

Note that this derivation also works if the Hamiltonian contains other terms that do not depend on the magnetic field. This includes the Ising Hamiltonian (in the presence of a magnetic field)

$$\hat{H} = -B \sum_{i}^{N} s_i - \frac{1}{2} \sum_{i \neq j} J_{ij} s_i s_j \tag{20}$$

since the derivative with respect to B is not affected by the extra term.

(f). The average fluctuations in magnetizations are given by $\langle (\delta M)^2 \rangle_{T,N,B} = \langle M^2 \rangle_{T,N,B} - \langle M \rangle^2_{T,N,B}$. The second moment of magnetization can be computed analogously to **(d)** as

$$\langle M^2 \rangle_{T,N,B} = \left\langle \left(\mu_B \sum_{i}^{N} s_i \right)^2 \right\rangle_{T,N,B} = \frac{1}{Q(T,N,B)} \frac{\partial^2}{\partial(\beta B)^2} Q(T,N,B) = N\mu_B^2 \left[(N-1) \tanh^2(\beta B \mu_B) + 1 \right], \tag{21}$$

while the square average is straightforward from the solution of **(d)**. Thus, we get:

$$\begin{aligned}
\langle (\delta M)^2 \rangle_{T,N,B} &= N\mu_B^2 \left[(N-1)\tanh^2(\beta B \mu_B) + 1 \right] - N^2 \mu_B^2 \tanh^2(\beta B \mu_B) = \\
&= N\mu_B^2 \left[1 - \tanh^2(\beta B \mu_B) \right] = N\mu_B \left(\frac{2}{e^{\beta B \mu_B} + e^{-\beta B \mu_B}} \right)^2 = N\mu_B^2 \operatorname{sech}^2(\beta B \mu_B).
\end{aligned} \tag{22}$$

An equivalent result can be obtained by differentiating the average magnetization with respect to the applied field:

$$\langle (\delta M)^2 \rangle = k_B T \frac{\partial \langle M \rangle}{\partial B} \tag{23}$$

(g). The average magnetization saturates to a maximum value of $\langle M \rangle \to N\mu_B$ as $T \to 0$, when all the spins are aligned along the field direction. On the other hand, this condition corresponds to an absence of fluctuations $\langle (\delta M)^2 \rangle \to 0$.

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Solution to Exercise 2

(a). We start by writing the Hamiltonian of the interaction as,

$$\hat{\mathcal{H}} = -B\sum_{i=1}^{N} s_i - \frac{1}{2}\sum_{\langle i,j\rangle} J s_i s_j \tag{24}$$

where instead of writing J_{ij}, we write $\sum_{\langle i,j\rangle}$ to be the sum over all pairs (i,j) that are neighbors of each other. Note that if atoms 3 and 5 are neighbors, the pairs $(i,j) = (3,5)$ and $(i,j) = (5,3)$ are both included in the sum. Thus, each pair is counted twice, which is compensated by the factor of 1/2 in front of the sum.

Let us focus on the interaction between two spins, terms of the form $s_i s_j$. By denoting by $\langle s\rangle$ the mean value of the spins, we can always write

$$s_i = \langle s\rangle + \delta s_i, \quad s_j = \langle s\rangle + \delta s_j. \tag{25}$$

by defining $\delta s_i = s_i - \langle s\rangle$. Then,

$$s_i s_j = (\langle s\rangle + \delta s_i)\cdot(\langle s\rangle + \delta s_j) \tag{26}$$
$$= \langle s\rangle^2 + \langle s\rangle(\delta s_i + \delta s_j) + \delta s_i \delta s_j \tag{27}$$

Here comes the key approximation step: We will neglect the last term, which is quadratic in the fluctuations. Naively, one could motivate this by saying that δs_i will be "small". More precisely, since we sum this over i,j, we are in fact neglecting the correlations between spins i and j.

Using this approximation, we get

$$s_i s_j \approx \langle s\rangle^2 + \langle s\rangle(\delta s_i + \delta s_j). \tag{28}$$

Computing the sum, we obtain

$$\frac{1}{2}\sum_{\langle i,j\rangle} J s_i s_j = \frac{J}{2}\sum_{\langle i,j\rangle}\Big[\langle s\rangle^2 + \langle s\rangle(\delta s_i + \delta s_j)\Big] \tag{29}$$
$$= \frac{J}{2}\sum_{\langle i,j\rangle}\langle s\rangle^2 + \frac{J}{2}\sum_{\langle i,j\rangle}\langle s\rangle\delta s_i + \frac{J}{2}\sum_{\langle i,j\rangle}\langle s\rangle\delta s_j. \tag{30}$$

Note that the sum over all neighboring pairs $\langle i,j\rangle$ contains $z\cdot N$ terms, where N is the number of "atoms" (or sites) and z is the number of neighbors per atom, also called the coordination number of the lattice. For example, $z = 4$ for a square lattice (in 2D), while $z = 6$ for a simple cubic lattice.

Coming back to the summation over all Ising interactions in eq. (30), we see that the first term does not depend on i,j anymore, and is just a constant shift in the energies, which does not affect the probabilities. Thus, we can just ignore it.

For the next two terms, note that we basically have the same summation, just with i replaced by j. Since the sum over all neighboring pairs $\langle i,j\rangle$ counts each pair like (i,j) and (j,i) separately, the two sums will be the same, so we obtain

$$\frac{J}{2}\sum_{\langle i,j\rangle}\langle s\rangle\delta s_i + \frac{J}{2}\sum_{\langle i,j\rangle}\langle s\rangle\delta s_j = J\sum_{\langle i,j\rangle}\langle s\rangle\delta s_i = zJ\sum_{i=1}^{N}\langle s\rangle\delta s_i \tag{31}$$

Ignoring constant terms, we therefore get

$$\frac{1}{2}\sum_{\langle i,j\rangle} J s_i s_j = zJ\sum_{i=1}^{N}\langle s\rangle\delta s_i + \text{const.} \tag{32}$$

Cont.

There is just one issue with this expression: we need to write the Hamiltonian in terms of the spin variables s_i rather than δs_i. For this, we can just rewrite

$$\langle s\rangle \delta s_i = \langle s\rangle(s_i - \langle s\rangle) = \langle s\rangle s_i - \langle s\rangle^2 \tag{33}$$

Thus, replacing back δs_i by s_i simply adds a constant term of $\langle s\rangle^2$, which again, does not affect the probabilities of being in a state. We therefore obtain

$$\frac{1}{2}\sum_{\langle i,j\rangle} J s_i s_j = zJ\sum_{i=1}^{N}\langle s\rangle s_i + \text{const.} \tag{34}$$

Thus, the total Hamiltonian that also contains a term corresponding to the magnetic field can be written as

$$\begin{aligned}\hat{\mathcal{H}} &= -B\sum_{i=1}^{N} s_i - \frac{1}{2}\sum_{\langle i,j\rangle} J s_i s_j &(35)\\ &\approx -B\sum_{i=1}^{N} s_i - zJ\sum_{i=1}^{N}\langle s\rangle s_i + \text{const.} &(36)\\ &= -\sum_{i=1}^{N}(B + zJ\langle s\rangle)s_i + \text{const.} &(37)\\ &= -\sum_{i=1}^{N} B_{\text{eff}} s_i + \text{const.} &(38)\end{aligned}$$

This is just the Hamiltonian of an ideal paramagnet, where the magnetic induction B has been replaced by $B_{\text{eff}} = B + zJ\langle s\rangle$. In other words, we have transformed a problem consisting of interacting spins (the Ising model) into a problem of independent spins in a modified magnetic field, which we already studied in the previous exercise.

To make this huge simplification possible, we had to use one approximation: the fact that we neglected the quadratic terms $\delta s_i \delta s_j$.

The partition function of this system will therefore just be

$$Q(T,N,B) = \left(e^{\beta B_{\text{eff}}} + e^{-\beta B_{\text{eff}}}\right)^N = (2\cosh(\beta B_{\text{eff}}))^N\,. \tag{39}$$

(b). Since the MF approximation essentially neglects the correlations between spins, it is supposed to hold whenever the mean interaction among spins dominates on the spin-spin correlations.

(c). The formal analogy with paramagnetic materials also implies that the MF average magnetization is written as

$$\bar{M} = N\tanh(\beta B_{\text{eff}}) = N\tanh[\beta(B + Jz\bar{s})], \tag{40}$$

which is a self-consistent equation in the average spin magnetization, because $\bar{M} = N\bar{s}$. This last relation allow us to continue the discussion in terms of the average spin $\bar{s}$. In the limit of an negligible applied field $B \to 0$, we get

$$\bar{s} = \tanh[\beta Jz\,\bar{s}], \tag{41}$$

which satisfies the limiting conditions $\bar{s} \to 1$ as $T \to 0$ (and therefore $\bar{M} \to \mu_B N$ as $T \to 0$) and $\bar{s} \to 0$ as $T \to \infty$ (and therefore $\bar{M} \to 0$ as $T \to \infty$). From this behaviour we find that the critical temperature of the system is given by $T_c = J\,z/k_B$, such that

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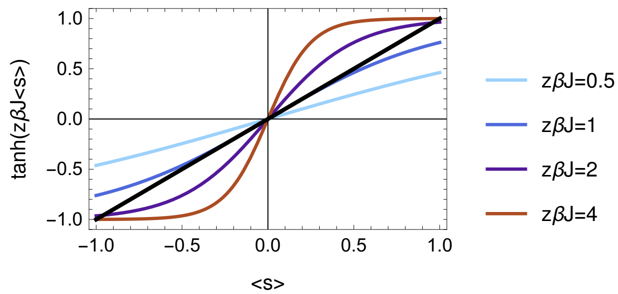
$$\bar{s} = \tanh\left[\frac{T_c}{T}\bar{s}\right]. \tag{42}$$

A graphical solution of the self-consistent equation is presented in the figure below.



Potential solutions of $\bar{s}$ are where the colored lines intersect the dotted line. For low temperatures, there are two (nonzero) solutions. As the temperature increases, the solid lines flatten out and will, at a certain point, fail to intersect the dotted line except at zero. The temperature at which this occurs is the critical temperature.

(d). For $T < T_c$ and near T_c, $\bar{s}$ is small and we can approximate the expression for the average spin (or the average magnetization) as

$$\bar{s} = \tanh\left[\frac{T_c}{T}\,\bar{s}\right] \approx \left[\frac{T_c}{T}\bar{s} - \frac{1}{3}\left(\frac{T_c}{T}\right)^3 \bar{s}^3\right], \tag{43}$$

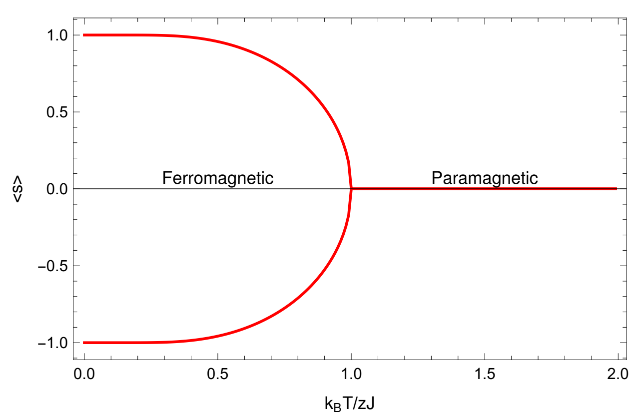
which implies $\bar{s} = \sqrt{3}\left(1 - \frac{T_c}{T}\right)^{1/2}$. The critical exponent is therefore 1/2.

(e). For $T \to 0$ and $B \to 0$ we get:

$$\bar{s} \approx \left[1 - 2\exp\left\{-2\frac{T_c}{T}\bar{s}\right\}\right]. \tag{44}$$

That is, $\bar{s} \approx 1$, and $\bar{M} \approx N$

(f). We know from **(c)**-**(e)** that the average magnetization approaches a constant as $T \to 0$ and that the average magnetization is zero for $T > T_c$. Based on **(d)**, we can also see that the derivative of $\bar{s}$ with respect to T is undefined at $T = T_c$. A sketch of the magnetization vs. temperature will then look something like the figure below.



(g). At $T > T_c$ we have:

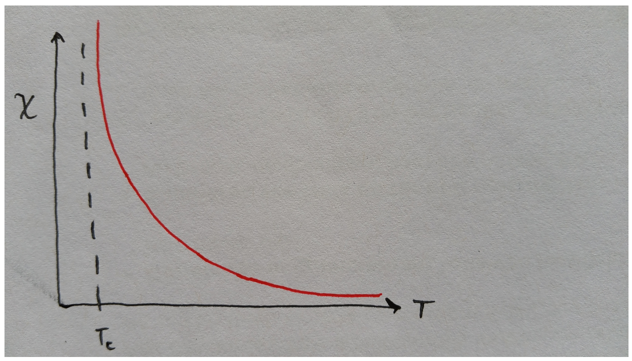
$$\bar{s} \approx \left[\beta B + \frac{T_c}{T}\bar{s}\right] \tag{45}$$

which implies:

$$\bar{s} = \frac{B}{k_B(T - T_c)} = \frac{C}{T - T_c} B = \chi\, B \tag{46}$$

with C the Curie-Weiss constant and χ the Curie-Weiss magnetic susceptibility.

(B). From **(g)**, we have $\chi = \frac{C}{T - T_c}$ for $T > T_c$. A sketch of the χ vs. T is given below, from which we can see that the magnetic susceptibility diverges as T approaches T_c.



(i). Using the definition of the average energy in the MF approximation and assuming T close to T_c we can write

$$\langle E \rangle \approx -N\bar{s}B \approx -N\sqrt{3}\left(1 - \frac{T}{T_c}\right)^{1/2} \times (B + \; J\, z\, \sqrt{3}\left(1 - \frac{T}{T_c}\right)^{1/2}), \tag{47}$$

which for $B \to 0$ implies

$$\langle E \rangle \approx -3N \left(1 - \frac{T}{T_c}\right) \; J\, z\, . \tag{48}$$

The heat capacity is therefore given by a finite value corresponding to

$$C = \frac{\partial \langle E \rangle}{\partial T} = 3NJ\, z \frac{1}{T_c}. \tag{49}$$

The End.