Isign model: parmagnet, spin chain, and mean-field approximation

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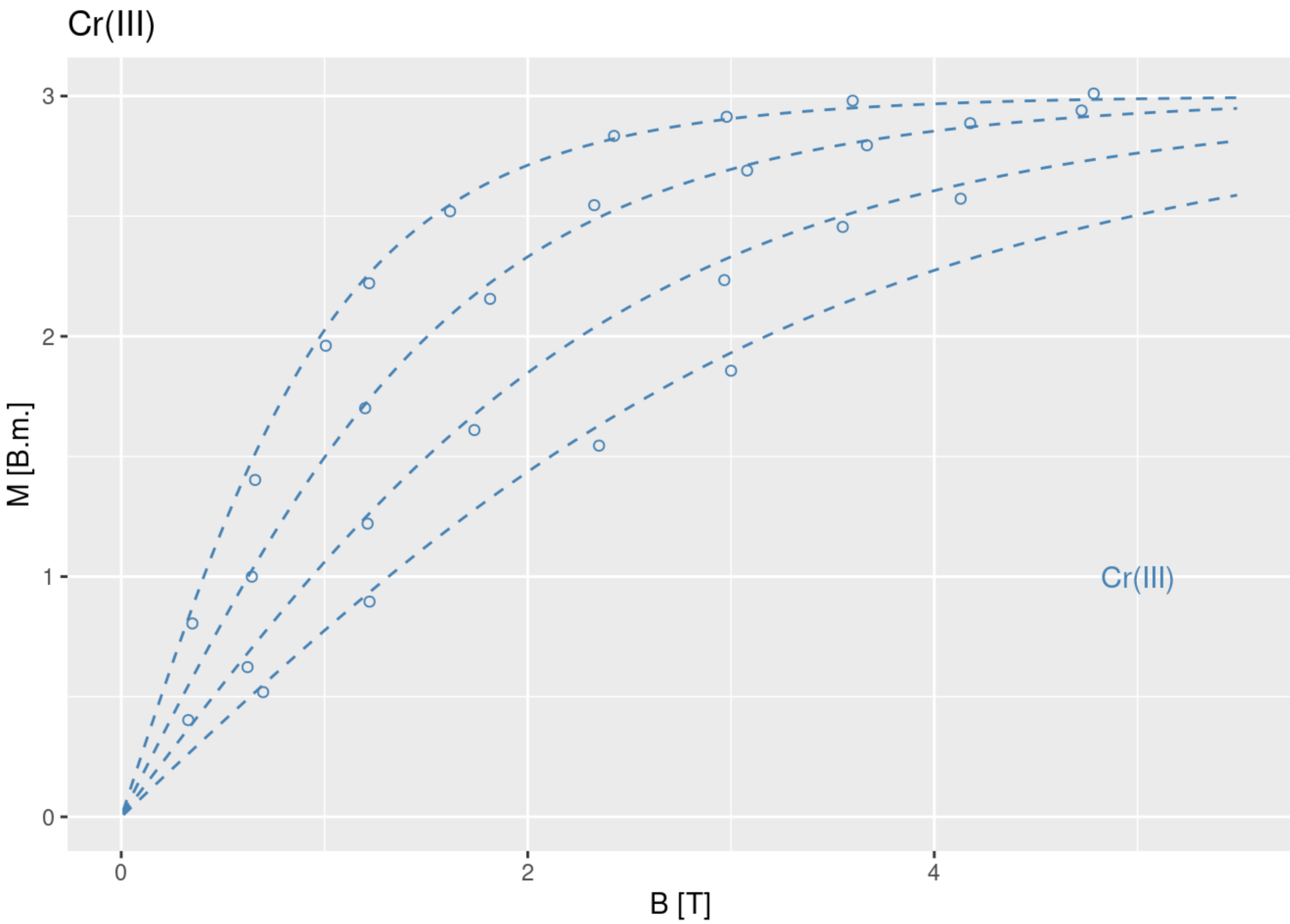
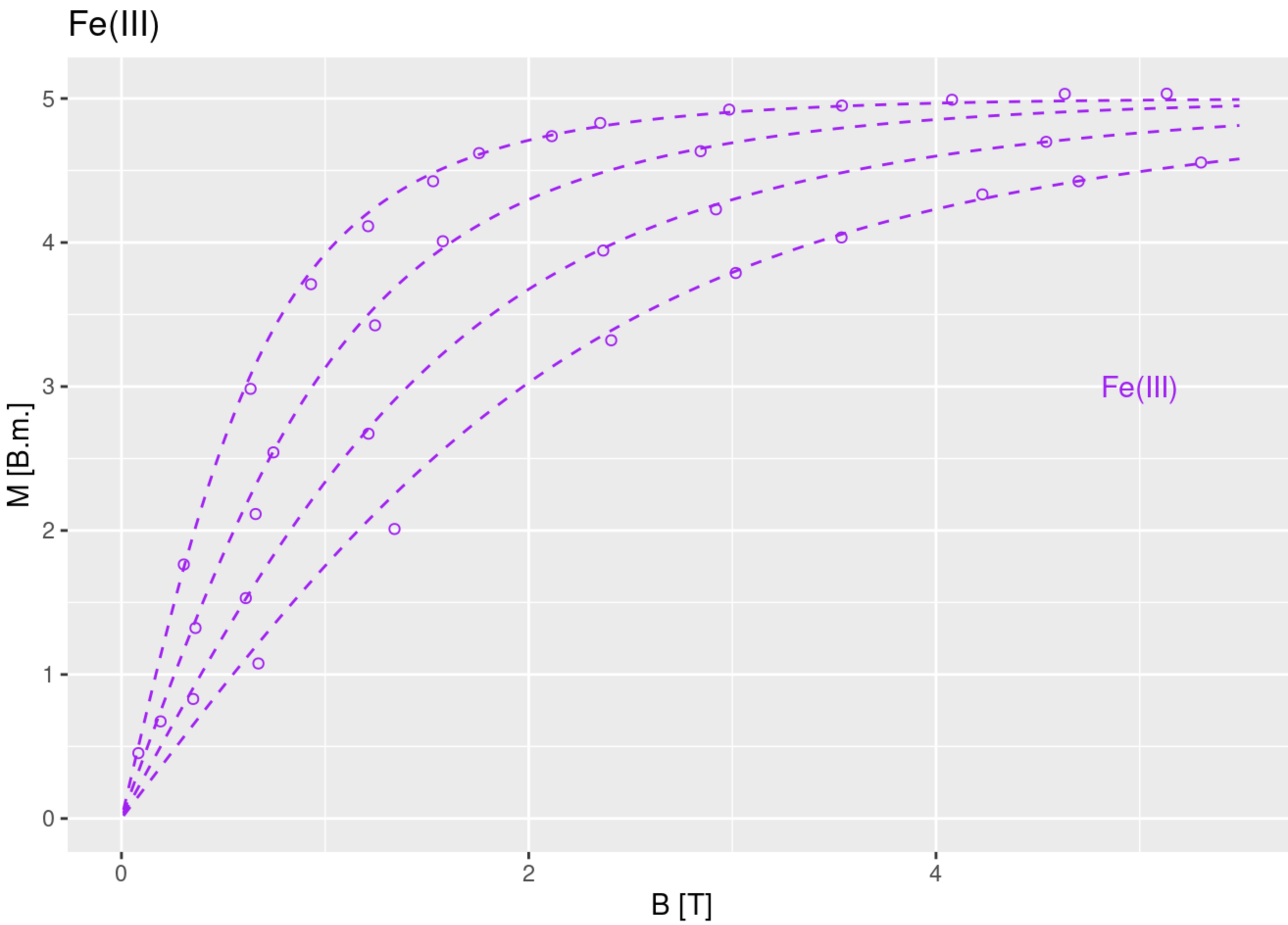
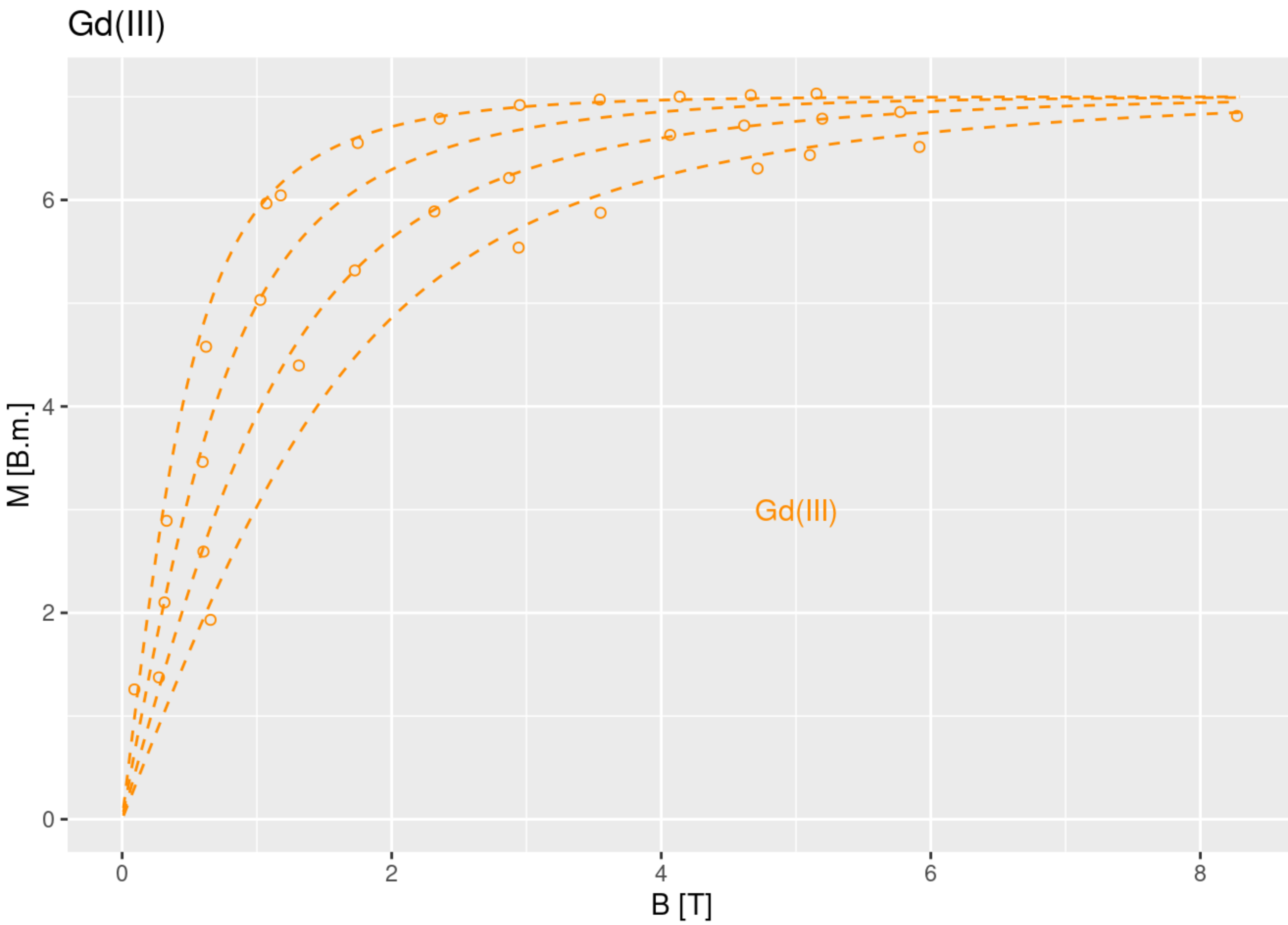
Fit data with the Brillouin function

The scripts in the following import data of the magnetization, in units of Bohr magnetons (B.m.), as a function of T and B for 3 different paramagnetic compounds in which the magnetic atoms are Fe^{3+}, Gd^{3+}, Cr^{3+}, respectively. Each set of data is plotted independently and the temperature of the measurement can be read directly from the relative csv files. It is possible to plot also the Brillouin function, passing the arguments S and the ratio B/T (see example).

For each data set identify the value of the total spin S for which the theoretical curves better fit the experimental data for the 3 different compounds (note that only integer or half-integer values are allowed). Based on what discussed in our previous lectures, justify the values of S that you find for the 3 cases: Fe^{3+}, Gd^{3+}, and Cr^{3+}.




Fe(III)
5
4
3
2
1
0
M [B.m.]
Fe(III)
0
2
4
B [T]

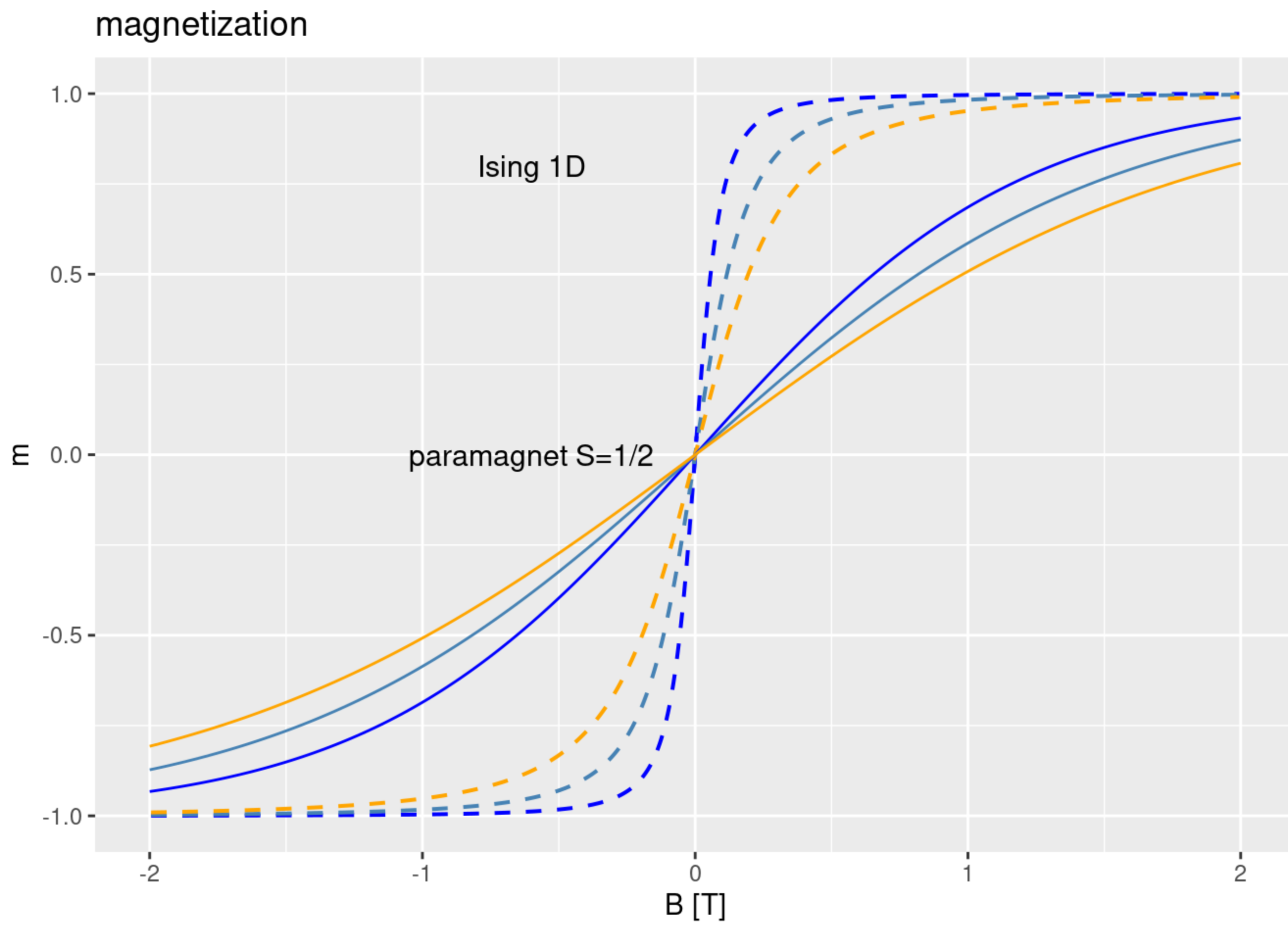


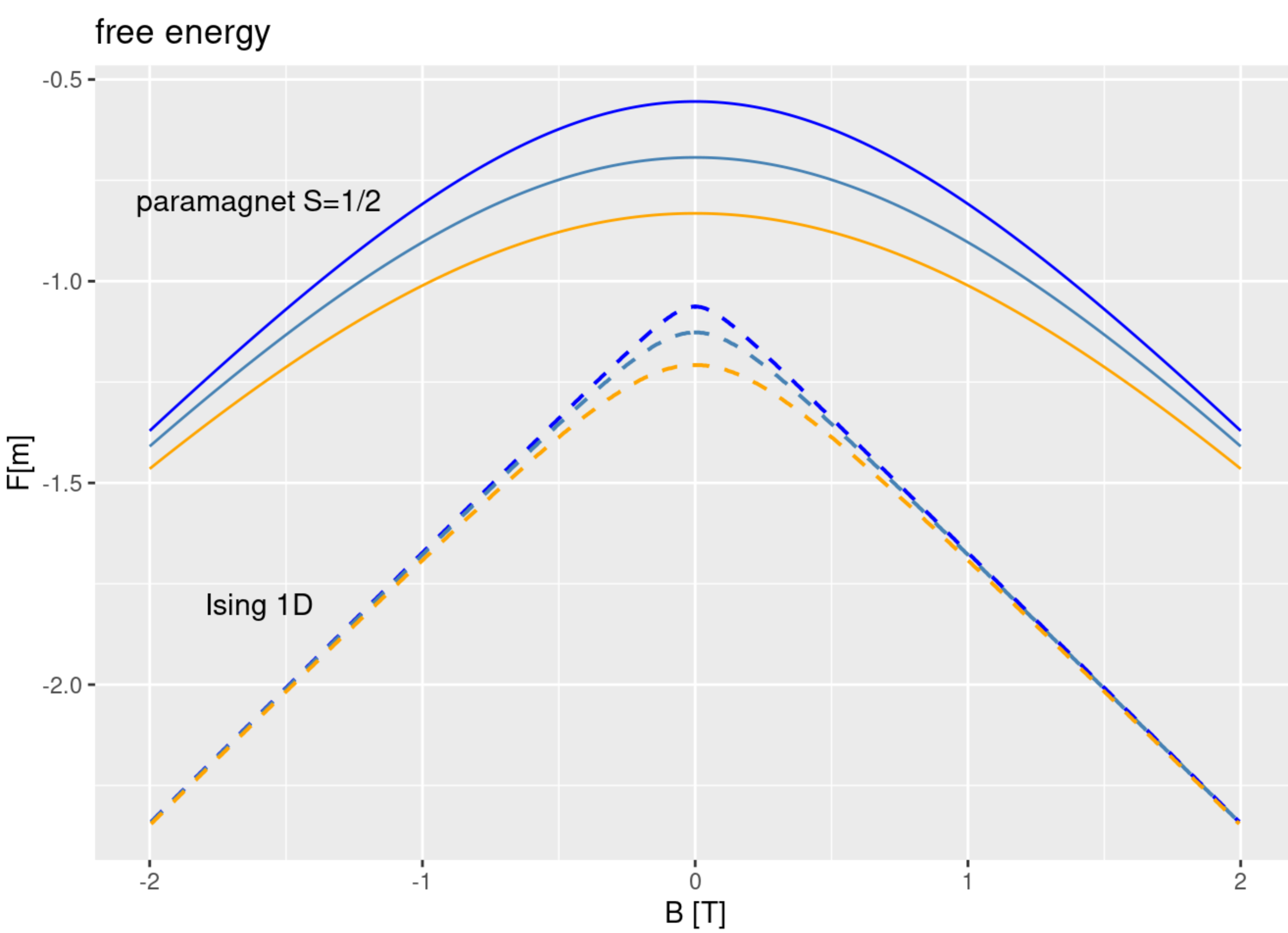
Answer

The values of the effective spin chosen for Fe^{3+} and Gd^{3+} can be also justified using the free-ion results, because both ions have $L = 0$ and, thus, there is no orbital contribution to their magnetic moment. For the case of Cr^{3+}, the value of $S = 3/2$ is justified only assuming total quenching of the angular momentum, which might be produced by a ligand field. For completeness, we note that the presence of a ligand field would not change the result (in HS configuration) for Fe^{3+} and Gd^{3+}.

Ising chain vs. paramagnet

In the underlying plots the magnetization curve and the free energy of an infinite Ising chain and of a paramagnet for S=1/2 are displayed for the temperatures $T = 0.8,\ 1,\ 1.2$ K, assuming $J = 1$ K.


magnetization
Ising 1D
paramagnet S=1/2
m
1.0
0.5
0.0
-0.5
-1.0
-2
-1
0
1
2
B [T]


free energy
paramagnet S=1/2
Ising 1D
F[m]
-0.5
-1.0
-1.5
-2.0
-2
-1
0
1
2
B [T]

Q1 In your opinion, what is the origin of the steeper increase of the magnetization of the spin chain as a function of B (w.r.t. the paramagnet) observed systematically around $B = 0$ for every temperature?
We have seen in the lecture that the susceptibility of a spin chain evaluated in $B = 0$ is

$$\chi = 2\,\frac{C}{k_{\mathrm{B}}T}\,\xi$$

where ξ is the correlation length. Note that when $\xi \simeq 1$ the Curie law is practically recovered, namely the susceptibility of the spin chains is comparable to that of a paramagnet with spin S=1/2. However, since

$$\xi \sim \exp(2\beta J)\,,$$

for the values of the ratio $J/(k_B T)$ used in this calculation, ξ is significantly larger than 1 and this is at the origin of the steeper increase of the magnetization of the spin chain as a function of B w.r.t. the same curve computed for the paramagnet.

Q2 Is the free energy as a function of B analytic or not for the Ising chain? what about the paramagnet? What is the role of the thermodynamic limit $N \to \infty$ which is taken in the Ising chain calculation?
$F(B)$ is analytic for both the paramagnet and the spin chain because no singularity appears in the plots.

Q3 If the free energy as a function of B was provided for the Ising model on an infinite 2D lattice, would its behavior resemble more the free energy of a paramagnets with $S = 1/2$, that of the Ising chain or the MF free energy (see below)?

*Qualitatively, the free energy of the 2D Ising model is more akin to the mean-field free energy than to that of the other two models. In fact, the 2D Ising model foresees a phase with **spontaneous magnetization** at low temperature which appears along with a singularity in the free energy. Yet, there are some quantitative differences because, e.g., the critical exponents predicted by the mean-field model differ from those predicted by the 2D (and 3D) Ising model.*

Ising model: mean-field approximation

For the Ising model, the mean-field (MF) approximation consists in assuming

$$S^z(\underline{n})S^z(\underline{n}') = -s_{\mathrm{av}}^2 + \left[S^z(\underline{n}) + S^z(\underline{n}')\right] s_{\mathrm{av}}$$

so that the Hamiltonian reads

$$\mathcal{H}_{\mathrm{MF}} = \frac{1}{2}J\bar{z}Ns_{\mathrm{av}}^2 + (g\mu_{\mathrm{B}}B - J\bar{z}s_{\mathrm{av}})\sum_{\underline{n}} S^z(\underline{n})\,,$$

where s_{av} is the average of $S^z(\underline{n})$ computed using the MF Hamiltonian itself, N is the number of spins in the lattice, and $\bar{z}$ the number of nearest neighbors of each spin.

Q1 Taking the trace over the variables $S^z(\underline{n})$ compute the partition function for the Hamiltonian $\mathcal{H}_{\rm MF}$ and derive an analytic expression for the MF free energy $F[s_{\rm av}]$ per particle.
The partition function Z is given by (note: $\beta := 1/(k_{\rm B}T)$)

$$Z = \mathrm{tr}\left(e^{-\beta\mathcal{H}_{\rm MF}}\right).$$

In our case, we get

$$\begin{aligned} Z &= e^{-\beta\frac{1}{2}J\bar{z}Ns_{\rm av}^2}\prod_{\underline{n}}\sum_{S^z(\underline{n})=\pm1} e^{-\beta\left(g\mu_{\rm B}B-J\bar{z}s_{\rm av}\right)S^z(\underline{n})} = \\ &= e^{-\beta\frac{1}{2}J\bar{z}Ns_{\rm av}^2}\prod_{\underline{n}}\left[e^{-\beta\left(g\mu_{\rm B}B-J\bar{z}s_{\rm av}\right)}+e^{\beta\left(g\mu_{\rm B}B-J\bar{z}s_{\rm av}\right)}\right] = \\ &= e^{-\beta\frac{1}{2}J\bar{z}Ns_{\rm av}^2}\left[2\cosh(\beta\left(g\mu_{\rm B}B-J\bar{z}s_{\rm av}\right))\right]^N. \end{aligned}$$

Therefore, the free energy per particle must be

$$F[s_{\rm av}] = -\frac{1}{N\beta}\log(Z) = \frac{1}{2}J\bar{z}s_{\rm av}^2 - \frac{1}{\beta}\log(2\cosh(\beta\left(g\mu_{\rm B}B-J\bar{z}s_{\rm av}\right)))$$

Q2 Show that the minimum of $F[s_{\rm av}]$ is found for

$$s_{\rm av} = \tanh\left(\frac{\bar{z}Js_{\rm av}-g\mu_{\rm B}B}{k_{\rm B}T}\right)$$

The minimum can be found with

$$\frac{\partial F[s_{\rm av}]}{\partial s_{\rm av}} = 0.$$

For the free energy density from above, we get

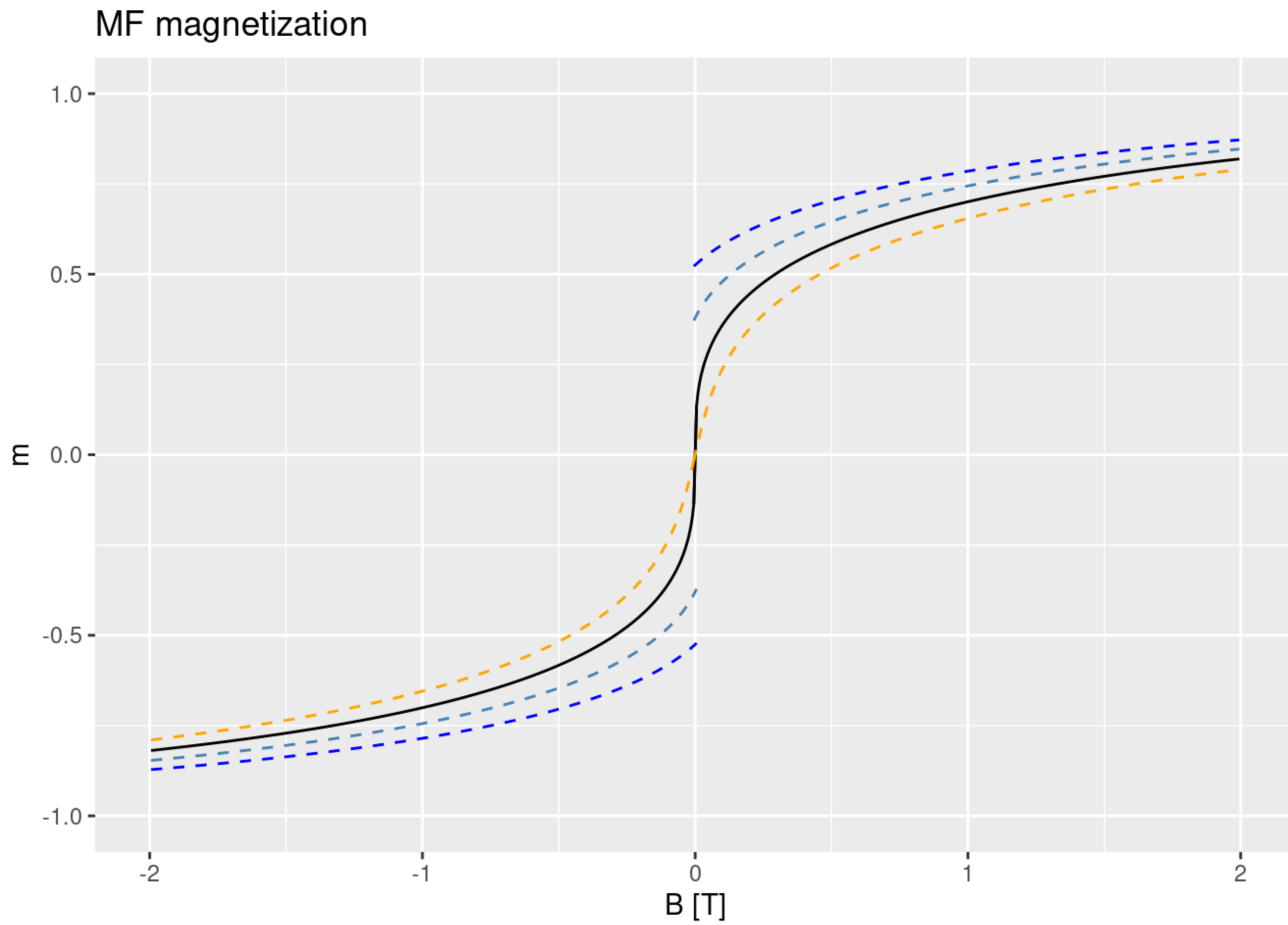
$$J\bar{z}s_{\rm av} + J\bar{z}\tanh(\beta\left(g\mu_{\rm B}B-J\bar{z}s_{\rm av}\right)) = 0.$$

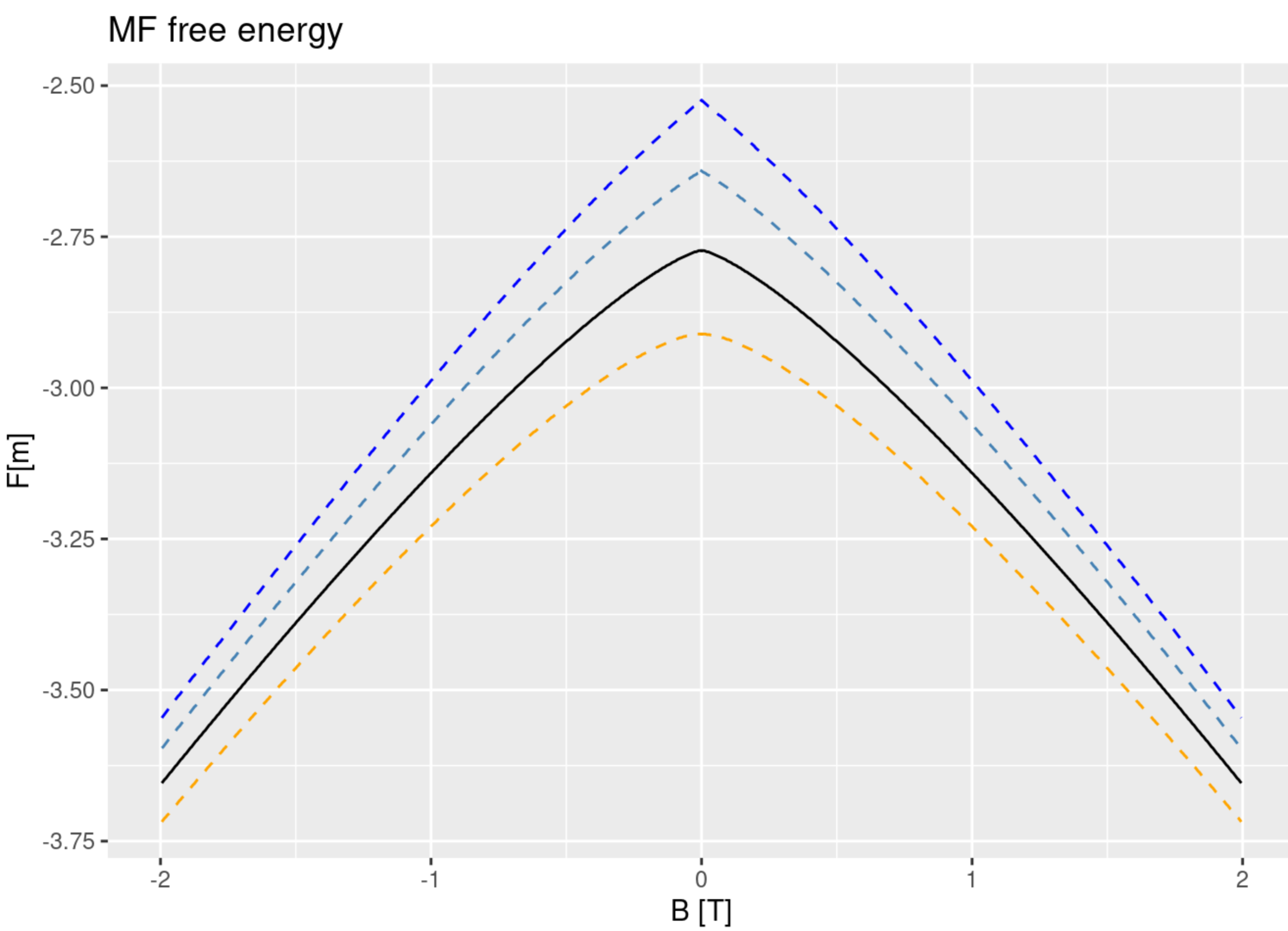
This leads to

$$s_{\rm av} = \tanh\left(\frac{\bar{z}Js_{\rm av}-g\mu_{\rm B}B}{k_{\rm B}T}\right)$$

Q3 How does the *self-consistent* equation given above for the optimal $s_{\rm av}$ relates to the Brillouin function for a spin S=1/2?
The r.h.s. of that equation has the same functional dependence as the Brillouin function for a spin 1/2, but in the present case the effective field at the numerator of the argument of $\tanh(\dots)$ consists of two contributions: the actual applied field B (external) and the Weiss field $B_{\rm W} = -\bar{z}Js_{\rm av}/(g\mu_{\rm B})$ (internal).

The plots below show the MF magnetization curve and the MF free energy, evaluated for the optimal $s_{\rm av}$, as a function of B for the temperatures $T = 3.6,\ 3.8,\ 4,\ 4.2$ K assuming $J = 1$ K and $\bar{z} = 4$ nearest neighbors for each spin.


MF magnetization
1.0
0.5
0.0
-0.5
-1.0
m
-2
-1
0
1
2
B [T]


MF free energy
-2.50
-2.75
-3.00
-3.25
-3.50
-3.75
F[m]
-2
-1
0
1
2
B [T]

Q4 What is the physical meaning of the black solid line, namely the separatrix between the two qualitatively different behaviors?

*It corresponds to the critical temperature T_c: below that temperature the **equilibrium** magnetization curve is discontinuous in $B = 0$, while for $T > T_\mathrm{c}$ the **equilibrium** magnetization curve is continuous and analytic.*