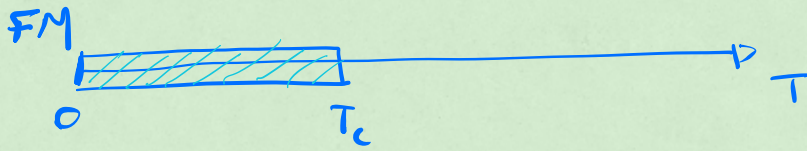


Lecture 21.11.2022

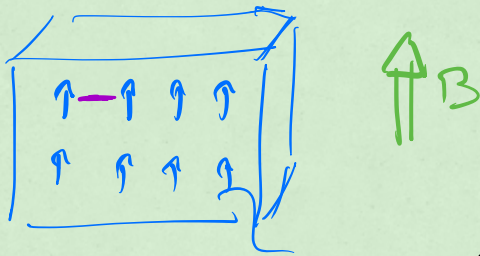
Goal: define what we understand theoretically for FerroMagn.



Solid

ideal gas

$J_{inter} = 0$ PARAMAGNET (single particle)



IDEAL GAS (single particle)



$$E_i = \frac{p_i^2}{2m}$$

$$H_{i,z} = \mu_B g_{eff} B \hat{S}_i^z$$

\hat{m}_{atom}

- RE $\hat{S}_i = \hat{J}$ & $g_{eff} = g_{J,L,S}$
 - TM $\hat{S}_i = \hat{S}_{eff}$ & $g_{eff} = g$ (even tensor)
- IN SOLIDS

Energy scales $\sim \frac{1}{(3d)^3}$

$$S^T = 1/2$$

$$\sim J_{intra} = 4 \cdot 10 \text{ eV} \sim 10^5 \text{ K}$$

$$S^T = 3/2$$

$$B = 0$$

$$B \neq 0$$

Complete

part. function

$$Z = \sum_{M=-S}^S e^{-\beta E_M}$$

$$E_M = \mu_B g B M$$

$$\sim 1 \text{ K} \lesssim k_B T$$

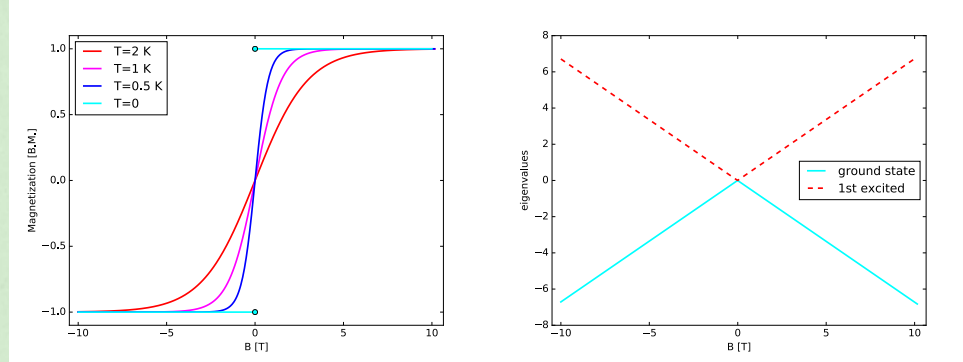


Figure 5.1: Left: Magnetization curve in Bohr magnetons given by the Brillouin function for $S = 1/2$, i.e. $\mathcal{B}_{1/2}(\alpha)$, as a function of the applied field B and different values of T indicated in the legend. Right: Energy levels of a Zeeman Hamiltonian corresponding to a $S = 1/2$ and $g = 2$ as functions of B .

Typically, the ground-state multiplet is separated from the first excited one by an energy gap of the order of the intra-atomic exchange interaction (\sim eV). The Zeeman energy is of the order of $0.1 \text{ meV} \sim 1 \text{ K}$ for one-Tesla applied field and, therefore, comparable to the thermal energy ($k_B T$). These two facts imply that only the ground-state multiplet shall be populated at realistic temperatures but the Zeeman splitting of its levels needs to be treated in the framework of statistical physics. Choosing as a quantization axis for the spin the direction along which the B field is applied, the Zeeman Hamiltonian reads

$$\mathcal{H}_Z = g \mu_B B \hat{S}^z, \quad (5.43)$$

where g is a generic Landé factor and $\hat{\mathbf{S}}$ the effective spin meant as explained above. The corresponding partition function is given by the relation

$$\mathcal{Z} = \sum_M e^{-\beta E_M} \quad (5.44)$$

where $\beta = 1/(k_B T)$ and $E_M = g \mu_B B M$ with $M = -S \dots S$. The partition function is related to the free energy

$$F = -k_B T \ln(\mathcal{Z}) \quad (5.45)$$

from which the average magnetic moment per atom can be computed to obtain

$$m = -\frac{\partial F}{\partial B} = -g \mu_B \langle \hat{S}^z \rangle = g \mu_B S \mathcal{B}_S \left[\frac{g \mu_B S B}{k_B T} \right], \quad (5.46)$$

with the Brillouin function

$$\mathcal{B}_S(\alpha) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S}\alpha\right) - \frac{1}{2S} \coth\left(\frac{\alpha}{2S}\right) \quad \text{and} \quad \alpha = \frac{g\mu_B S B}{k_B T}. \quad (5.47)$$

competition
order-
disorder

The derivation of the Brillouin function for a generic S can be found in the literature. We do not reproduce all the passages here because it is a relatively long calculation. Note that the Brillouin function equals the hyperbolic tangent for a spin $S = 1/2$. Moreover, $\mathcal{B}_S(\alpha)$ is only a function of the ratio B/T and not of these two external parameters independently. Expanded for small arguments α , Eq. (5.46) reduces to

$$m = \frac{(g\mu_B)^2 S(S+1)}{3k_B T} B. \quad (5.48)$$

The pre-factor of B on the right-hand side is the magnetic susceptibility of a paramagnet, defined with SI units as $\chi = \mu_0 \partial M / \partial B$ (computed in $B = 0$), and obeys the famous Curie law

$$\chi = \frac{\mu_0 C}{\alpha^3 T} \quad (5.49)$$

with Curie constant equal to

$$C = \frac{(g\mu_B)^2 S(S+1)}{3k_B}. \quad (5.50)$$

SI units

classically

$\frac{1}{3} S^2$

QM

$\frac{S(S+1)}{2}$

Note that, through g and S , the Curie constant contains information about the ground-state multiplet of individual magnetic ions in the paramagnetic phase. For this reason the Curie constant has played an important historical role in confirming the quantum-mechanical description of matter.

For the forthcoming discussion it is important to remark that in the derivation of the Brillouin function $\mathcal{B}_S(\alpha)$ we have implicitly used the knowledge of i) the eigenstates of the atom in the presence of an external, applied field E_M and ii) the way of performing *thermal averages* for a quantum system.

Appendix

Averages and thermodynamic potentials

Classical models

In the canonical ensemble, the partition function is given by

$$\mathcal{Z} = \frac{1}{N!} \int \frac{d^{3N}r d^{3N}p}{(2\pi\hbar)^{3N}} e^{-\beta\mathcal{H}(\{p_{\alpha,i}\},\{r_{\alpha,i}\})}, \quad (5.51)$$

\mathcal{H} being the Hamiltonian of the system and $\beta = 1/(k_B T)$. \mathcal{Z} is related to a thermodynamic potential, \mathcal{F} , via the general relation

$$\mathcal{F} = -\frac{1}{\beta} \ln \mathcal{Z}. \quad (5.52)$$

The average of any observable $\mathcal{O}(\{p_{\alpha,i}\},\{r_{\alpha,i}\})$ can be computed as

$$\langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}} \int \frac{d^{3N}r d^{3N}p}{(2\pi\hbar)^{3N}} \mathcal{O}(\{p_{\alpha,i}\},\{r_{\alpha,i}\}) e^{-\beta\mathcal{H}(\{p_{\alpha,i}\},\{r_{\alpha,i}\})}. \quad (5.53)$$

Classically, the trace operator is defined as

$$\mathcal{T}r = \int \dots \frac{d^{3N}r d^{3N}p}{(2\pi\hbar)^{3N}}, \quad (5.54)$$

which allows defining

$$\mathcal{Z} = \mathcal{T}r \{e^{-\beta\mathcal{H}(\{p_{\alpha,i}\},\{r_{\alpha,i}\})}\} \quad \text{and} \quad \langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}} \mathcal{T}r \{ \mathcal{O}(\{p_{\alpha,i}\},\{r_{\alpha,i}\}) e^{-\beta\mathcal{H}(\{p_{\alpha,i}\},\{r_{\alpha,i}\})} \}. \quad (5.55)$$

Quantum models

Assume that $|\psi_\alpha\rangle$ be a complete basis of the Hilbert space on which the Hamiltonian of the model is defined. Quantum-mechanically, the trace is then given by

$$\mathcal{T}r = \sum_{\alpha} \langle \psi_\alpha | \dots | \psi_\alpha \rangle. \quad (5.56)$$

By analogy with (5.55), the partition function and thermal averages are accordingly defined

$$\begin{aligned}\mathcal{Z} &= \mathcal{T}r \{ e^{-\beta\mathcal{H}} \} = \sum_{\alpha} \langle \psi_{\alpha} | e^{-\beta\mathcal{H}} | \psi_{\alpha} \rangle \\ \langle \mathcal{O} \rangle &= \frac{1}{\mathcal{Z}} \mathcal{T}r \{ \mathcal{O} e^{-\beta\mathcal{H}} \} = \frac{1}{\mathcal{Z}} \sum_{\alpha} \langle \psi_{\alpha} | \mathcal{O} e^{-\beta\mathcal{H}} | \psi_{\alpha} \rangle.\end{aligned}\quad (5.57)$$

In few advanced computations one stops at this level. Generally, the trace is evaluated on a complete basis of eigenstates of \mathcal{H} :

$$\mathcal{H}|\varphi^i\rangle = E^i|\varphi^i\rangle. \quad (5.58)$$

The computation of (5.57) is, consequently, simplified:

$$\begin{aligned}\mathcal{Z} &= \sum_i \langle \varphi^i | e^{-\beta\mathcal{H}} | \varphi^i \rangle = \sum_i e^{-\beta E^i} \\ \langle \mathcal{O} \rangle &= \frac{1}{\mathcal{Z}} \mathcal{T}r \{ \mathcal{O} e^{-\beta\mathcal{H}} \} = \frac{1}{\mathcal{Z}} \sum_i \langle \varphi^i | \mathcal{O} | \varphi^i \rangle e^{-\beta E^i}.\end{aligned}\quad (5.59)$$

Spin models

Limiting ourselves to a Hamiltonian of the type

$$\mathcal{H} = -\frac{1}{2}J \sum_{|\underline{n}-\underline{n}'|} = \hat{\mathbf{S}}(\underline{n}) \cdot \hat{\mathbf{S}}(\underline{n}') + g\mu_B B^{\text{ext}} \sum_{\underline{n}} \hat{S}^z(\underline{n}) \quad (5.60)$$

one possible choice for the basis of the Hilbert space is the following one: $|\psi_{\alpha}\rangle = |M_1, M_2, \dots, M_N\rangle = |M_1\rangle \otimes |M_2\rangle \cdots \otimes |M_N\rangle$ with $\hat{S}^z(n)|M_n\rangle = M_n|M_n\rangle$ and n label for the lattice site. Note that the Hamiltonian in Eq. (5.60) is not diagonal on this basis. After having diagonalized it, thermal averages can be computed according to Eqs. (5.59).

For many problems in magnetism, substituting the quantum-mechanical operators $\hat{\mathbf{S}}(\underline{n})$ by classical vectors is legitimate:

$$\hat{\mathbf{S}}(\underline{n}) \rightarrow \vec{S}(\underline{n}) \equiv S_0 (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta) \quad (5.61)$$

where $S_0^2 = S(S+1)$ (more often $S_0 = 1$). The partition function then reads

$$\mathcal{Z} = \int d\Omega_1 \int d\Omega_2 \cdots \int d\Omega_N e^{-\beta\mathcal{H}(\{\vec{S}(\underline{n})\})}, \quad (5.62)$$

with $d\Omega_{\underline{n}} = \sin \theta_{\underline{n}} d\theta_{\underline{n}} d\varphi_{\underline{n}}$ being the solid-angle element of the spin located at the site \underline{n} .

Chapter 6

Magnetic order at finite temperature

Lecture: 21.11.2022

Spin Hamiltonian as quantum N -body problem

While the intra-atomic exchange energy is of the order of $4 - 10 \text{ eV} \sim 10^5$ Kelvin, the inter-atomic exchange interaction is about $10 - 50 \text{ meV} \sim 100 - 500$ Kelvin. Thus, depending on the material and the temperature range of interest, a statistical-mechanic treatment is also required to study the cooperative effects arising from this type of coupling between different magnetic moments in a solid. The competition between this inter-atomic exchange interaction and thermal fluctuations is indeed responsible for the loss of ferromagnetism above a certain temperature, called Curie temperature T_c . Table 6.1 reports the values of that critical temperature for few selected magnetic materials.

Restricting ourselves to ferromagnetic inter-atomic exchange interactions, a system of coupled magnetic moments arranged in a lattice can be described

Typical transition temperatures of some ferromagnets

	Fe	Co	Ni	Fe ₃ O ₄	Nd ₂ Fe ₁₄ B	Gd	Dy	EuO	EuS
T_c [K]	1043	1388	627	858	593	292	88	69	16.5

Table 6.1: Some typical values of the Curie temperature T_c for few selected ferromagnets (more values can be found in [Wikipedia](#)).

by the Hamiltonian

$$\mathcal{H} = -\frac{1}{2}J \sum_{|\underline{n}-\underline{n}'|=1} \hat{\mathbf{S}}(\underline{n}) \cdot \hat{\mathbf{S}}(\underline{n}') + g\mu_{\text{B}}B \sum_{\underline{n}} \hat{S}^z(\underline{n}). \quad (6.1)$$

The dimension of the Hilbert space associated with this quantum many-body problem scales as $(2S + 1)^N$, N being the number of magnetic moments (spins) in the lattice. Due to such an **exponential** dependence on N , the exact treatment of a system of many coupled spins becomes intractable – even numerically – as far as the number of spins approaches that of realistic *extended* systems¹. In practice, one can try to circumvent this problem in several ways:

1. Reduce the many-body problem to a single-particle problem. This corresponds to the mean-field approximation (MFA).
2. Simplify the problem replacing the quantum-spin operators by classical vectors.
3. Take advantage of specific symmetries in the problem under investigation and use a Hamiltonian which can easily be diagonalized.
4. Consider only a selected family of excitations of the ground state, which can have either *local* (domain walls) or *non-local* (spin waves) character.

Non-analyticity in the magnetization curve

The goal of this chapter is to define the conditions for the persistence of ferromagnetism at finite temperatures in the framework of equilibrium thermodynamics. In other words, we will assume that the considered *ensembles* of interacting magnetic moments have had enough time to equilibrate, i.e., to populate different configurations according to the Boltzmann distribution. Before entering the details of specific models, it is useful to provide an operative definition of *ferromagnetism* itself. To this aim, we start from the paramagnetic response of a spin 1/2 given by the corresponding Brillouin function

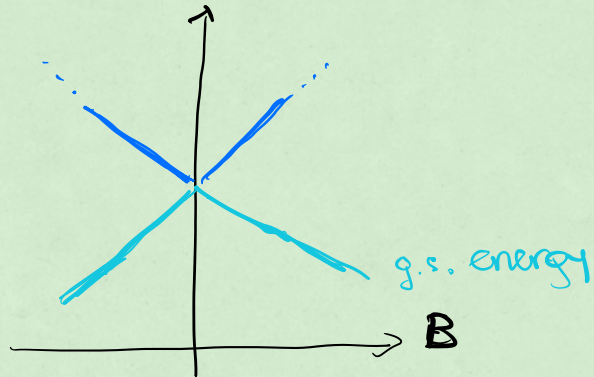
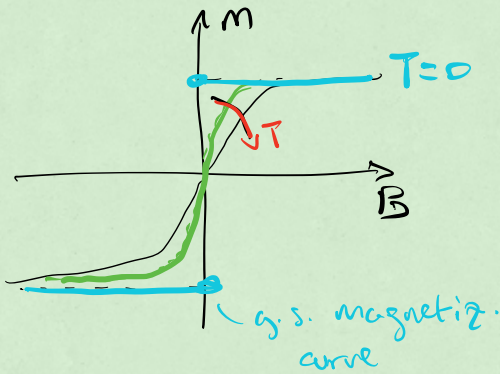
$$m = g\mu_{\text{B}} \frac{1}{2} \mathcal{B}_{1/2} \left[\frac{g\mu_{\text{B}} B}{2k_{\text{B}}T} \right] = g\mu_{\text{B}} \frac{1}{2} \tanh \left[\frac{g\mu_{\text{B}} B}{2k_{\text{B}}T} \right]. \quad (6.2)$$

¹Some effective zero-dimensional structures (magnetic clusters or nanoparticles) are also studied in the context of nanomagnetism. For some of these systems, exact diagonalization of the associated quantum problem is still feasible numerically and makes it possible to describe their magnetic behavior at any temperature.

Brillouin fct. for $s = 1/2$

$$\langle \mu \rangle_{th} = m = \frac{1}{2} g \mu_B \tanh\left(\frac{g \mu_B B}{2 k_B T}\right)$$

$$\Rightarrow E_m = \pm \frac{1}{2} g \mu_B B$$



we switch ON Jinter $\sim 500 - 1000$ K

$$H = - J \sum_{\substack{\langle n, n' \rangle \\ n, n'}} \hat{S}(n) \cdot \hat{S}(n') + g \mu_B \sum_n \hat{S}_z(n) B$$

$J > 0$
g.s.

$1 \uparrow \uparrow \uparrow \dots \uparrow$ α $1 \downarrow \downarrow \downarrow \dots \downarrow$
 $B < 0$ $B > 0$

@ $T = 0$

$$m = \begin{cases} N s g \mu_B & B > 0 \\ -N s g \mu_B & B < 0 \end{cases}$$

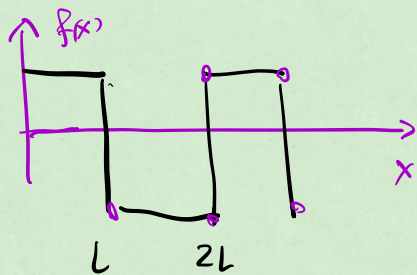
@ $T \neq 0$ SPONTANEOUS MAGNETIZ.

$$m = - \frac{1}{N} \lim_{B \rightarrow 0^+} \frac{\partial F}{\partial B} \neq 0$$

Def. of
Ferromagnetism

$$Z = \sum_n e^{-\beta E_n} \Rightarrow F = -k_B T \ln Z$$

Analogy square-wave



$$f(x) = \frac{4}{\pi} \sum_{n \text{ odd}} \frac{1}{n} \sin\left(\frac{n\pi x}{L}\right)$$

Definition of spontaneous magn.

- $N \rightarrow \infty$ th. dyn. limit
- Boltzmann Stat. : thermody. equilibrium.

Assume uniaxial anisotropy

$$H = -J \sum_{\langle nn' \rangle} \hat{S}_i^z \hat{S}_{i'}^z + \dots [\text{Zeeman}]$$

is diagonal on the basis

$$|\sigma_1 \sigma_2 \dots \sigma_N\rangle$$

$$\hat{S}_i^z |\sigma_i\rangle = \sigma_i \frac{1}{2} |\sigma_i\rangle$$

$$S_i = \frac{1}{2}$$

$$\sigma_i = \pm 1$$

$$E = -J \sum_{\langle nn' \rangle} \sigma(n) \sigma(n') + g \mu_B S B \sum_n \sigma(n)$$

energy is replaced by the free energy: A system is ferromagnetic if the *spontaneous magnetization*

$$\lim_{B \rightarrow 0^+} m(B, T) = -\frac{1}{N} \lim_{B \rightarrow 0^+} \frac{\partial F}{\partial B} \quad (6.6)$$

is different from zero (with the free energy F defined in Eq. (5.45)). We remark that one speaks of ferromagnetism when a sample remains magnetic in the absence of field, that is the reason why the limit for $B \rightarrow 0^\pm$ matters. The existence of atomic magnetic moments warrant only paramagnetism but – as we will see – not necessarily ferromagnetism at finite temperature. Based on the time-reversal symmetry of spin Hamiltonians in the absence of field ($B = 0$) it can be argued that the limit (6.6) can only be finite if the magnetization is discontinuous in $B = 0$, i.e., if the derivative $\partial m / \partial B$ is not analytic. Yet, in *equilibrium thermodynamics* the magnetization is expected to be an analytic function for any finite system. In fact, through Eq. (5.45), the magnetization is related to the first derivative of the partition function

$$\mathcal{Z} = \sum_n e^{-\beta E_n}, \quad (6.7)$$

n labeling the states of the system and E_n being the corresponding energies. Since for a finite system n is finite, \mathcal{Z} is a *finite* sum of analytic functions, which has to be analytic. This argument rules out the possibility of having *spontaneous* magnetization at finite temperature for *any* finite system². However, formally speaking, an infinite sum of analytic functions can be non-analytic. Think, for instance, of the Fourier series of a square or a saw-tooth wave. Therefore, the thermodynamic limit $N \rightarrow \infty$ practically underlines any theoretical description of ferromagnetism at finite temperature as an equilibrium phenomenon, namely as resulting from a thermodynamic phase transition. The concept of bistability is indeed broader than this definition of ferromagnetism because it includes the possibility of a sample being magnetic as a result of metastability, that is an out-of-equilibrium situation³.

²Note that this statement does not contradict what discussed previously for the ground-state magnetization because in the limit of $T \rightarrow 0$ the exponential functions appearing in Eq. (6.7) are not analytic either.

³Roughly speaking, when we use Boltzmann statistic we assume thermodynamic equilibrium, namely we assume that the system under investigation had enough time to visit all its statistically relevant states.

6.1 The Ising model

When consistent with the symmetry of the problem, two-value classical spins, $S^z = \pm 1$, can be assumed:

$$\mathcal{H} = -\frac{1}{2}J \sum_{|\underline{n}-\underline{n}'|=1} S^z(\underline{n}) S^z(\underline{n}') + g\mu_B B \sum_{\underline{n}} S^z(\underline{n}). \quad (6.8)$$

This approximation is obviously justified in the limit in which the anisotropy D is significantly larger than other energies at play ($J, k_B T$, etc.). Another instance is realized when the full degeneracy of the total angular momentum of unpaired electrons of a magnetic atom in the gas phase (spherically symmetric environment, Hund's rules) is reduced to the minimal two-fold degeneracy for $B = 0$ in the solid phase (Kramers doublet). In this case, magnetism can be described with an *effective spin* one-half. Beside its application to magnetism, the Ising Hamiltonian (6.8) is used in many different contexts, ranging from biophysics to social sciences.

Mean-field approximation

Assuming that the reader has encountered the mean-field approximation (MFA) in different courses, we refresh here only the aspects that are relevant to our discussion on ferromagnetism at finite T . The MFA is a simplified treatment of a many-body problem, which consists in replacing the original problem with its *best* single-particle counterpart. For magnetic systems, the reference single-particle problem is the paramagnet, which can be regarded as the equivalent of the "ideal gas" in the study of statistical thermodynamics. In formula, the MFA of Hamiltonian (6.8) reads

$$\mathcal{H} = -\frac{1}{2}J \sum_{|\underline{n}-\underline{n}'|=1} S^z(\underline{n}) S^z(\underline{n}') + g\mu_B B \sum_{\underline{n}} S^z(\underline{n}) \simeq g\mu_B B^{\text{eff}} \sum_{\underline{n}} S^z(\underline{n}) \quad (6.9)$$

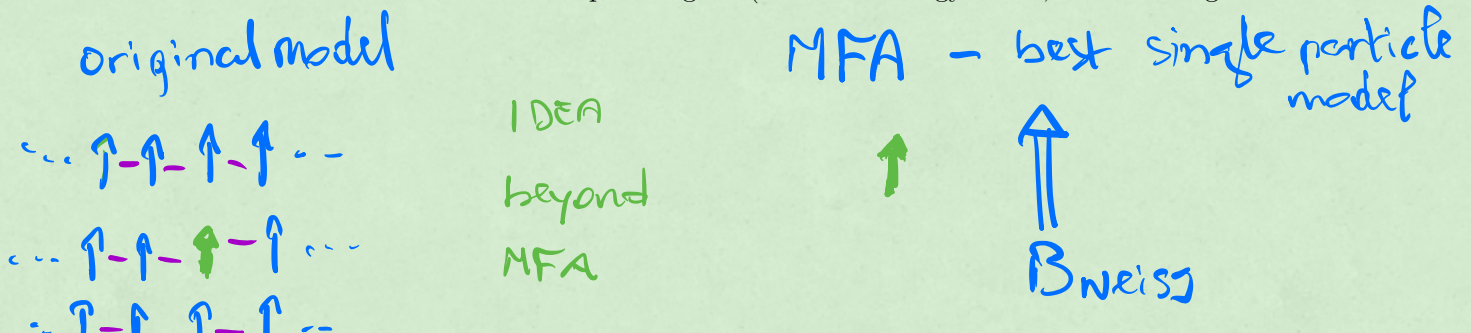
where the effective (Weiss) field B^{eff} depends parametrically on the single-particle averages of the z spin projection

$$s_{\text{av}} = \langle S^z(\underline{n}) \rangle. \quad (6.10)$$

Setting equal to zero terms like

$$[s_{\text{av}} - S^z(\underline{n})][s_{\text{av}} - S^z(\underline{n}')] = 0, \quad (6.11)$$

technically called *fluctuations*, makes it possible to rewrite Hamiltonian (6.8) as the Hamiltonian of a paramagnet (with two energy levels, for the Ising



model). In fact, in this way, the product of pairspins can be expressed in terms of the average s_{av} and single-particle contributions

$$S^z(\underline{n})S^z(\underline{n}') = -s_{\text{av}}^2 + [S^z(\underline{n}) + S^z(\underline{n}')] s_{\text{av}}. \quad (6.12)$$

Within the MFA the spontaneous magnetization behaves as follows

$$\begin{aligned} \lim_{B \rightarrow 0^+} m(B, T) &\neq 0 && \text{for } T < T_c \\ \lim_{B \rightarrow 0^+} m(B, T) &= 0 && \text{for } T > T_c \end{aligned} \quad (6.13)$$

where the critical temperature is defined as $k_B T_c = z_n J$, with z_n number of nearest neighbors of each spin. Below $T > T_c$, the spontaneous magnetization is predicted to behave critically

$$m(T, 0) \sim (T_c - T)^{\frac{1}{2}}. \quad (6.14)$$

critical exp.

In summary, the MFA predicts the occurrence of a phase with spontaneous magnetization at finite temperature, which is realized below a material-dependent T_c . In the following we will discuss some limitations of this approach that are mainly rooted in the crudeness of the approximation in Eq. (6.11).

1D Ising model

Probably one of the most striking failure of MFA is the prediction of a magnetically ordered phase below T_c for one-dimensional (1D) systems. In fact, the result in Eq. (6.13) is independent of the magnetic-lattice dimensionality. The latter corresponds to the number of directions along which the exchange coupling propagates indefinitely. In practice, this dimension may also be different from the actual dimensionality of the considered solid, like in molecular spin chains. A well-known result of Statistical Physics is that systems whose magnetic lattice has a dimensionality is smaller than 2D cannot sustain spontaneous magnetization at thermodynamic equilibrium⁴

Landau argument

Here we provide a heuristic argument presented in the Landau-Lifshitz series that applies to the 1D Ising model and more generally to spin chains with uniaxial anisotropy. We evaluate the variation of the free energy associated with the creation of a domain wall (DW) in a configuration with all the spins

Landau Argument.

with N spins

1D Ising model.

$$\sigma_i = \pm 1$$

① • $\uparrow \uparrow \uparrow \dots \uparrow \uparrow$ • $E_1, S_1 = 0$

② • $\downarrow \downarrow \downarrow \downarrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$ • E_2, S_2
 ΔW

$$F = E - TS$$

$$E_2 - E_1 = 2J'$$

$$S_2 - S_1 \approx k_B \ln(N-1) \approx k_B \ln(N)$$

$$\Delta F = F_2 - F_1 = 2J' - k_B T \ln(N)$$

$$\bar{N}: \Delta F = 0 \Rightarrow 2J' = k_B T \ln \bar{N}$$

$$\bar{N} = \exp\left(\frac{2J'}{k_B T}\right)$$

$$N < \bar{N}(T) \quad \Delta F > 0 \Rightarrow \text{it remains in the g.s.}$$

$$N > \bar{N}(T) \quad \Delta F < 0 \Rightarrow \text{it creates } \Delta W_1 \Rightarrow m \approx 0 \\ \Rightarrow \text{No spontaneous Magnetization}$$

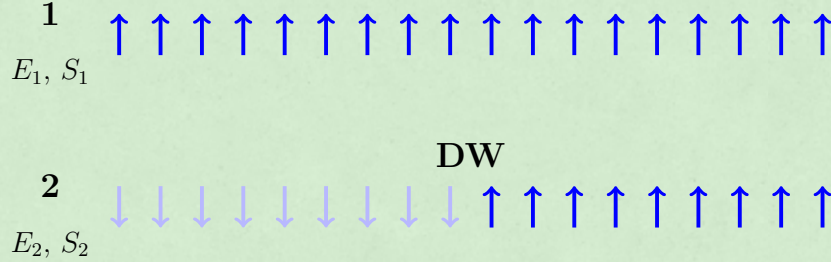


Figure 6.1: Sketch representing the configurations whose free-energy difference is evaluated in the text: 1) ferromagnetic ground state with all the spins parallel to each other (top) and 2) a configuration consisting of two domains with opposite spin alignment (bottom) and one domain wall (DW).

parallel to each other. Creating a DW in a spin chain where all the spins point along the same direction increases the energy by a factor $E_2 - E_1 = 2J$. This DW may occupy N different positions in the spin chain, so that this set of configurations has an entropy of the order of $S_2 \simeq k_B \ln(N)$. The entropy of the ground state vanishes if we assume that the two spins at the boundaries have been forced to point upward (otherwise one has $S_1 = k_B \ln(2)$). Therefore, the free-energy difference between the two configurations sketched in Fig. 6.1 is roughly given by

$$\Delta F \simeq 2J - k_B T \ln(N). \quad (6.15)$$

The qualitative behavior of ΔF is sketched in Fig. 6.2. A characteristic temperature-dependent threshold \bar{N} can be defined such that for $N > \bar{N}$ the free energy difference ΔF is negative and therefore DWs start forming *spontaneously* in the chain. The threshold \bar{N} is obtained by requiring $\Delta F = 0$, which gives

$$\bar{N} \simeq \exp(2\beta J). \quad (6.16)$$

Practically, when \bar{N} is larger than the number of spins⁵ in the chain N (low temperature), the ground-state configurations with all spins aligned are also minima of the free energy, since $\Delta F > 0$. In this case, as far as equilibrium properties are concerned, the behavior of the spin chain is reminiscent to that of a two-level paramagnet with magnetic moment $\mu = NgS\mu_B$. When

⁴The absence of a magnetically ordered phase at finite temperature is true in general for 1D systems provided that the coupling between spins is short-ranged enough.

⁵In molecular spin chains \bar{N} should be compared with the average number of sites separating two successive defects.

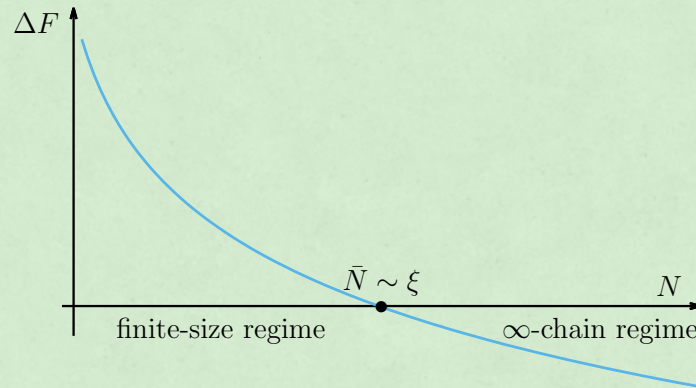


Figure 6.2: Qualitative behavior of the free energy $\Delta F = 2J - k_{\text{B}}T \ln(N/w)$ as a function of N (see the main text).

$\bar{N} < N$ (high temperature), instead, the ground-state configurations with all spins aligned do not minimize the free energy and DWs are always present in the system at equilibrium. In the limit of an infinite chain, the same argument can be repeated to justify the presence of an indefinite number of DWs. We refer to this condition – realized in spin chains at higher temperatures – as the *thermodynamic limit* in which the inverse of \bar{N} is proportional to the average density of DWs.

Correlation length

In 1D magnetic systems the averaged pair-spin correlation decays exponentially with the separation between spins. Focusing on the Ising model, in which only the spin component along z is defined, one has

$$\langle S_i^z S_{i+r}^z \rangle = e^{-r/\xi}. \quad (6.17)$$

The characteristic scale of this decay defines the correlation length ξ . It can be shown that ξ is related to the susceptibility measured along the easy axis in zero field by the general equation

$$\chi = 2 \frac{C}{k_{\text{B}}T} \xi, \quad (6.18)$$

where C is the Curie constant characterizing the magnetic centers coupled to form the chain. Apart from proportionality factors, \bar{N} defined above and

used for assignment in which
 $\chi = \frac{\partial M}{\partial B} \Big|_{B=0}$ (speedness magn.)
 curve

indicated with a dot in Fig. 6.2 can be identified with the correlation length ξ . Thus, similarly to \bar{N} , one expects a leading dependence of the Arrhenius type for the correlation length as well:

$$\xi \sim \exp(2\beta J) . \quad (6.19)$$

For a finite chain with $N < \bar{N}$ (see Fig. 6.2) the role of the correlation length in the susceptibility is – roughly speaking – replaced by the chain size N .