Curie-Weiss theory of ferromagnetism

A ferromagnet can be seen as a crystal lattice where each site is occupied by a magnetic dipole, and magnetic dipoles want to be aligned with each other (actually real ferromagnetism is due to electrostatic interactions in a quantum mechanics formalism... but this is another story). $\longrightarrow$ Heisenberg in the '20s

The energy (Hamiltonian) of the system is

$$\boxed{H(\{S_i\}) = -J\sum_{\langle ij\rangle}\vec{S}_i\cdot\vec{S}_j - \vec{h}\sum_i\vec{S}_i}$$

where $\vec{S}_i$ is the magnetic dipole in i, the sum runs over nearest-neighbor pairs (dipole-dipole interactions decay quickly. The interaction J is assumed to be constant over the lattice and $\vec{h}$ is an external field trying to align the dipoles.

Computing the magnetization in a statistical mechanics framework means computing the average of $\sum_i \vec{S}_i$:

$$\vec{m} = \frac{1}{N}\langle\sum_i\vec{S}_i\rangle = \frac{1}{N}\sum_i\langle\vec{S}_i\rangle$$

N is the number of dipoles

Assuming the system is homogeneous : $\vec{m} = \langle\vec{S}_i\rangle \ \forall i$

The average is the thermodynamic average :

$$\langle \vec{S}_i \rangle = \sum_{\{\vec{S}_j\}} \vec{S}_i \, \frac{e^{-\beta H(\{\vec{S}_j\})}}{Z} \qquad \beta = \frac{1}{k_B T}$$

where the partition function is

$$Z = \sum_{\{\vec{S}_j\}} e^{-\beta H(\{\vec{S}_j\})}$$

and the sum runs over $\{\vec{S}_j\}$, which is the set of all possible configurations (directions) of all the dipoles.

We thus have

$$\langle \vec{S}_i \rangle = \sum_{\{S_j\}} \vec{S}_i \, \frac{e^{\beta J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + \beta \vec{h} \sum_i \vec{S}_i}}{Z}$$

Unfortunately, this expression cannot be computed exactly.

The Curie-Weiss theory consists in a clever approximation (Weiss' molecular field):

$$\vec{S}_i \cdot \vec{S}_j = \vec{S}_i \cdot \langle \vec{S}_j \rangle = \vec{m} \cdot \vec{S}_i$$

Essentially each dipole "sees" the average value of the others, not their instantaneous value.

The expression then becomes:

z is the coordination number of the lattice, that is, the number of nearest neighbors

$$\langle \vec{S}_i \rangle = \vec{m} = \sum_{\{\vec{S}_i\}} \vec{S}_i \frac{e^{\sum_i \beta\left(J \frac{z}{2} \vec{m} + \vec{h}\right)\cdot \vec{S}_i}}{Z}$$

$\longrightarrow$ of course, also Z will receive the same treatment

This is a self-consistent equation: $\vec{m}$ (l.h.s.) depends on $\vec{m}$ (r.h.s.)

We can further simplify our lives!

The dipole-dipole interaction term is invariant for a global rotation (scalar products: depend only on relative orientation). If they align, any direction is as good as any other. But the external field breaks the symmetry: we can expect then that the global alignment (if any) will be in the direction of $\vec{h}$: $\vec{m} \parallel \vec{h}$

We also assume for simplicity that dipoles have unitary length, $|\vec{S}_i| = 1 \quad \forall i$. Last but not least, we look at the component of $\vec{S}_i$ in the direction of $\vec{h}$:

$$\vec{S}_i \cdot \hat{h} = \cos\theta_i$$

At last we have

$$m = \langle \cos\theta_i \rangle = \sum_{\{\vec{S}_i\}} \cos\theta_i \frac{\prod_i e^{\beta\left(J\frac{z}{2} m + h\right)\cos\theta_i}}{Z}$$

But Z is $\quad Z = \sum_{\{\vec{S}_i\}} \cos\theta_i \prod_i e^{\beta\left(J\frac{z}{2}m + h\right)\cos\theta_i}$

We can now remember that actually $\vec{S}_i$ are continuos variables (point in any direction of space):

$$\sum_{\{\vec{S}_i\}} \longrightarrow \int_0^{2\pi} d\varphi_1 \int_0^{\pi} d\theta_1 \sin\theta_1 \dots \int_0^{2\pi} d\varphi_N \int_0^{\pi} d\theta_N \sin\theta_N$$

Thus we have (we use $i=1$, but irrelevant for generality)

$$m = \langle \cos\theta \rangle = \int_0^{2\pi} d\varphi_1 \int_0^{\pi} d\theta_1 \sin\theta_1 \dots \int_0^{2\pi} d\varphi_N \int_0^{\pi} d\theta_N \sin\theta_N \cos\theta_1 \prod_{i=1}^{N} e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta_i} \Big/ Z$$

$$\text{with} \quad Z = \int_0^{2\pi} d\varphi_1 \int_0^{\pi} d\theta_1 \sin\theta_1 \dots \int_0^{2\pi} d\varphi_N \int_0^{\pi} d\theta_N \sin\theta_N \prod_{i=1}^{N} e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta_i}$$

This can be factored as

$$m = \langle \cos\theta \rangle = \left[\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \, e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta}\right]^{N-1} \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta\cos\theta \, e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta} \Big/ Z$$

and

$$Z = \left[\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \, e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta}\right]^{N}$$

Putting these results together we have

$$m = \frac{\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta\cos\theta \, e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta}}{\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \, e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta}} =$$

$$= \frac{\cancel{2\pi} \int_0^{\pi} d\theta \sin\theta\cos\theta \, e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta}}{\cancel{2\pi} \int_0^{\pi} d\theta \sin\theta \, e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta}} =$$

If we call Z_1, for one site,

$$Z_1 = \int_0^\pi d\theta \, \sin\theta \; e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta}$$

we can write

$$m = \frac{1}{\beta Z}\frac{\partial}{\partial h} Z_1 = \frac{1}{\beta}\frac{\partial}{\partial h}\ln Z_1 = -\frac{\partial}{\partial h}\left(-k_B T \ln Z_1\right) = -\frac{\partial F_1}{\partial h}$$

We can now compute Z_1:

$$Z_1 = \int_0^\pi d\theta \, \sin\theta \; e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta} =$$

$$= \frac{-1}{\beta\left(J\frac{z}{2}m+h\right)} \int_0^\pi d\theta \, \frac{d}{d\theta} \, e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta} =$$

$$= \frac{-1}{\beta\left(J\frac{z}{2}m+h\right)} \left[e^{\beta\left(J\frac{z}{2}m+h\right)\cos\theta} \right]_0^\pi =$$

$$= \frac{2}{\beta\left(J\frac{z}{2}m+h\right)} \sinh\left(\beta\left(J\frac{z}{2}m+h\right)\right)$$

At last

$$m = \frac{1}{\beta Z_1}\frac{\partial Z_1}{\partial h} = \frac{1}{\cancel{\beta}} \frac{\cancel{\beta\left(J\frac{z}{2}m+h\right)}}{\cancel{2}} \sinh^{-1}\left(\beta\left(J\frac{z}{2}m+h\right)\right) \cdot$$

$$\cdot \left[-\frac{\cancel{2}}{\beta\left(J\frac{z}{2}m+h\right)^{\cancel{2}}} \cdot \sinh\left(\beta\left(J\frac{z}{2}m+h\right)\right) + \right.$$

$$\left. + \frac{\cancel{2}}{\cancel{\beta\left(J\frac{z}{2}m+h\right)}} \cdot \cancel{\beta} \cosh\left(\beta\left(J\frac{z}{2}m+h\right)\right) \right] =$$

$$= \coth\left(\beta\left(J\frac{z}{2}m+h\right)\right) - \frac{1}{\beta\left(J\frac{z}{2}m+h\right)} = \mathcal{L}\left(\beta\left(J\frac{z}{2}m+h\right)\right)$$

Langevin function

We have at last the self-consistent equation we were looking for:

$$\boxed{m = \mathcal{L}\left(\beta\left(J\frac{z}{2}m + h\right)\right)}$$

NOTE: What about the components of $\vec{S}_i$ perpendicular to $\vec{h}$? They are $\sin\theta\sin\varphi$ and $\sin\theta\cos\varphi$. Since the Boltzmann weigth does not depend on φ, their average is 0 because

$$\int_0^{2\pi} d\varphi \sin\varphi = \int_0^{2\pi} d\varphi \cos\varphi = 0$$

Let's study the Langevin function $\mathcal{L}(x)$:

$$\mathcal{L}(x) = \coth(x) - \frac{1}{x} = \frac{\cosh(x)}{\sinh(x)} - \frac{1}{x}$$

$x \to 0$:

$$\mathcal{L}(x) \simeq \frac{1+\frac{1}{2}x^2}{x+\frac{1}{6}x^3} - \frac{1}{x} = \frac{1+\frac{1}{2}x^2}{x\left(1+\frac{1}{6}x^2\right)} - \frac{1}{x} \simeq$$

$$\simeq \frac{1}{x}\left(1+\frac{1}{2}x^2\right)\left(1-\frac{1}{6}x^2\right) - \frac{1}{x} \simeq$$

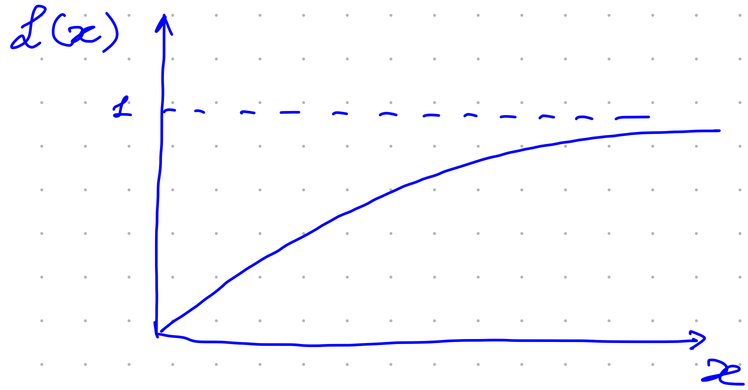
$$\simeq \frac{1}{x}\left(1+\frac{1}{3}x^2\right) - \frac{1}{x} = \frac{1}{3}x$$

$x \to \infty$:

$$\mathcal{L}(x) \simeq \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} = \frac{1+e^{-2x}}{1-e^{-2x}} - 1 =$$

$$\simeq \left(1+e^{-2x}\right)\left(1+e^{-2x}\right) - 1 = 1 - \frac{1}{x}$$

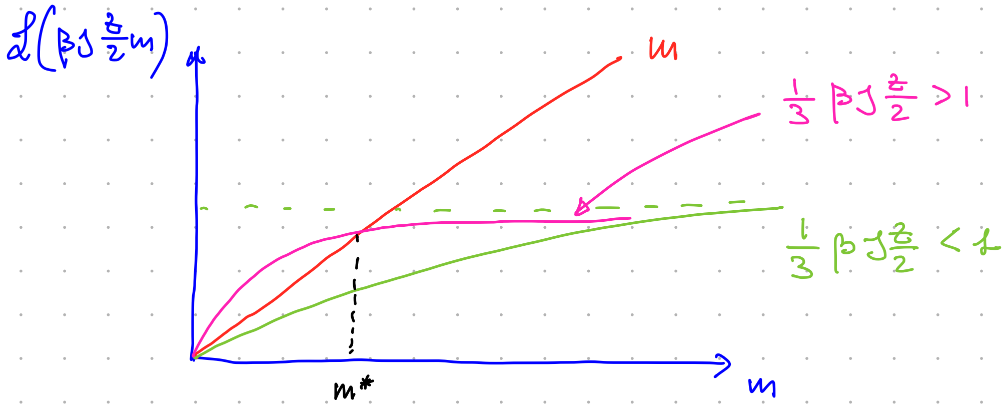
Thus



Back to the self-consistent equation:

$$m = \mathcal{L}\left(\beta\left(J\frac{z}{2}m + h\right)\right)$$

Let's start from $h=0$



Thus, if $\frac{1}{3}\beta J \frac{z}{2} < 1$, that is $T > \frac{Jz}{6k_B}$, $m=0$ is the only solution

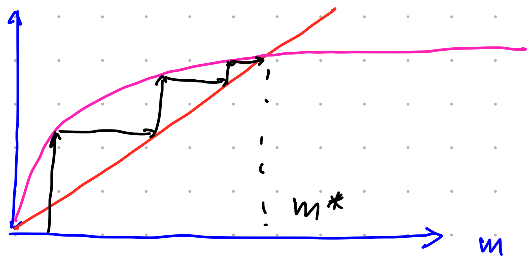
If $\frac{1}{3}\beta J \frac{z}{2} > 1$, then there are two solutions:

$m=0$ $\qquad$ $m=m^*$

Mathematically, $m=m^*$ is the stable solution:

iterative solution

m^* is stable



We will see that this corresponds to thermodynamic stability.

So we have $m(T) = \begin{cases} 0 & T > T_c = \frac{Jz}{6k_B} \\ \neq 0 & T < T_c \end{cases}$

Let's see what happens in proximity of T_c, when $m \simeq 0$, recalling that

$$\mathcal{L}(x) = \frac{\cosh(x)}{\sinh(x)} - \frac{1}{x} \simeq \frac{1 + \frac{1}{2}x^2 + \frac{1}{4!}x^4}{x + \frac{1}{3!}x^3 + \frac{1}{5!}x^5} - \frac{1}{x} =$$

$$= \frac{1}{x}\left(1 + \frac{1}{2}x^2 + \frac{1}{4!}x^4\right)\left(1 - \frac{1}{3!}x^2 - \frac{1}{5!}x^4 + \left(\frac{1}{3!}\right)^2 x^4\right) - \frac{1}{x} =$$

$$= \left(\frac{1}{2} - \frac{1}{3!}\right)x + \left(\frac{1}{4!} - \frac{1}{5!} + \left(\frac{1}{3!}\right)^2\right)x^3 =$$

$$= \frac{1}{3}x - \frac{1}{45}x^3$$

Then

$$m \simeq \frac{1}{3}\beta J \frac{z}{2} m - \frac{1}{45}\left(\beta J \frac{z}{2}\right)^3 m^3$$

Since we are looking for the $m \neq 0$ solution we divide by m

$$-\frac{1}{45} 27 \left(\beta J \frac{z}{2}\frac{1}{3}\right)^3 m^2 = 1 - \frac{Jz}{6k_B T}$$

recall that $T_c = \frac{Jz}{6k_B}$ then

$$\frac{3}{5}\left(\frac{T_c}{T}\right)^3 m^2 = \frac{T_c}{T} - 1$$

Then

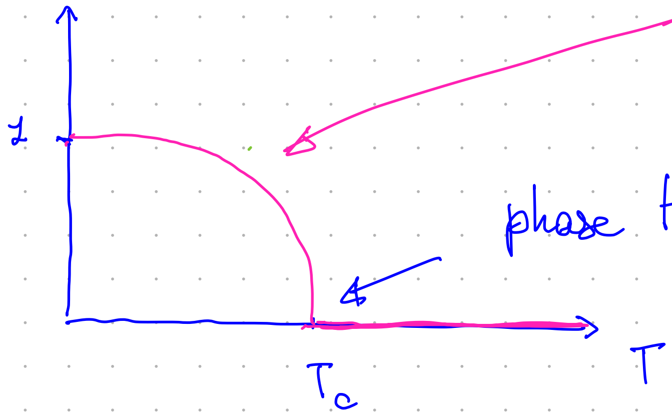
$$m^2 = \frac{5}{3} \left(\frac{T}{T_c}\right)^3 \frac{T_c - T}{T}$$

Let's choose $m>0$ (recall, $h=0$, no preferred direction)
and $T \simeq T_c$

$$m \simeq \sqrt{\frac{5}{3}} \left(\frac{T_c - T}{T_c}\right)^{1/2} = \sqrt{\frac{5}{3}}\, t^{1/2} \qquad t = \frac{T_c - T}{T_c}$$

! non analytic!

We can now plot $m(T)$



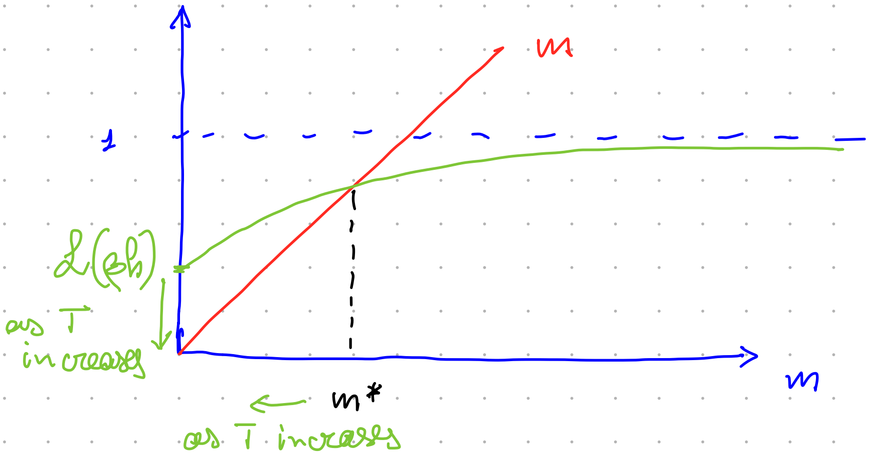
spontaneous (not induced by the field h, which is 0) magnetization

phase transition!!!

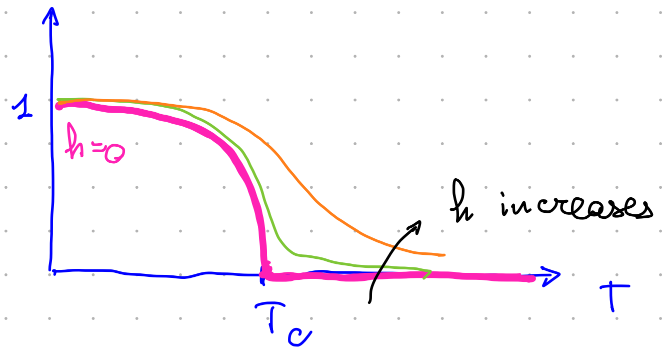
The magnetization is the first example of an order parameter, namely a quantity with a sharp change of behavior across the phase transition and which reports about a change of order in the system

Let's examine the $h \neq 0$ case

$$m = \mathcal{L}\left(\beta\left(J\frac{z}{2} m + h\right)\right)$$



as a consequence



Remarkably, the non-analyticity is lost

Let's see what happens when $h \to 0$ and $T = T_c = \frac{J z/2}{6 k_B}$.
We Taylor expand the self-consistent equation for $T = T_c$ and m small

$$m = \mathcal{L}\left(\beta_c\left(J \tfrac{z}{2} m + h\right)\right) = \mathcal{L}\left(\frac{J z/2}{\frac{J z/2}{6}} m + \frac{h}{k_B T_c}\right) = \mathcal{L}\left(3m + \frac{h}{k_B T_c}\right) \simeq$$

$$\simeq \frac{1}{3}\left(3m + \frac{h}{k_B T_c}\right) - \frac{1}{45}\left(3m + \frac{h}{k_B T_c}\right)^3 =$$

$$= m + \frac{h}{3 k_B T_c} - \frac{1}{5} m^3 - \frac{3}{5} m^2 \frac{h}{k_B T_c} - \frac{1}{5} m \frac{h^2}{(k_B T_c)^2} - \frac{1}{45} \frac{h^3}{(k_B T_c)^3}$$

m on both sides cancels and we are left with

$$\underbrace{\frac{1}{3}\frac{h}{k_B T_c} = \frac{1}{5} m^3}_{} + \frac{3}{5}\frac{h}{k_B T_c} m^2 + \frac{1}{5}\left(\frac{h}{k_B T_c}\right)^2 m + \frac{1}{45}\left(\frac{h}{k_B T_c}\right)^3$$

from here we get $m \sim h^{1/3}$

The next term then are

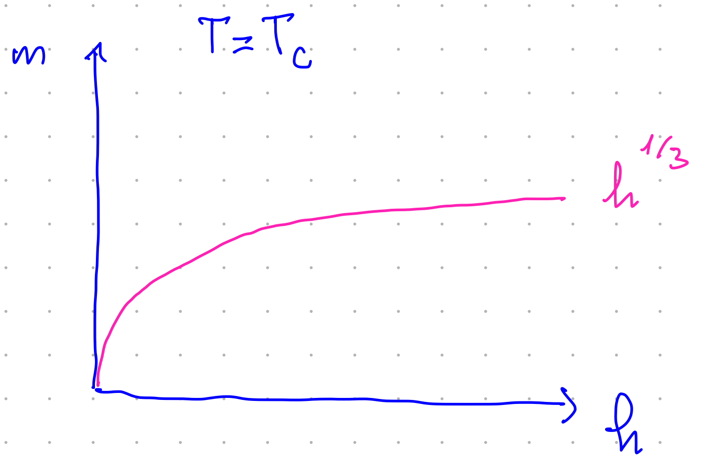
$m^2 h \sim h^{5/3} \longrightarrow 0$ faster than $h \to$ negligible

$m h^2 \sim h^{7/3} \longrightarrow 0$ " " " $\longrightarrow$ "

$h^3 \longrightarrow 0$ " " " $\longrightarrow$ "

then the correct scaling is $m \sim h^{1/3}$ $\Longleftarrow$ non-analytic behavior again!

word to remember



Summary

In this treatment of a magnetic system we have encountered several leit-motifs of the whole course:

1) Mean-field approximation (Weiss molecular field)

2) Phase transition for $h \to 0$

3) Non analytic behavior close to, or at, T_c:

$$m \sim t^{1/2} \qquad\qquad m \sim h^{1/3}$$

Unfortunately, the ferromagnet made by dipoles is not much useful.
We are going to revisit an apparently simpler model, the Ising model, that has played a crucial role in the development of statistical mechanics (and beyond) in the past 70 years and which continues to play, in itself and in its multiple variations.