Lecture 2: Phase transitions

microscopic world (classical mechanics, quantum mechanics) $\xleftrightarrow[\text{mechanics}]{\text{statistical}}$ macroscopic world (thermodynamics)

In introductory courses: ideal systems (effectively one-body systems)

If we add interactions: new collective properties such as emergence of phases (e.g. solids, liquid crystals, magnets, superconductor ...)

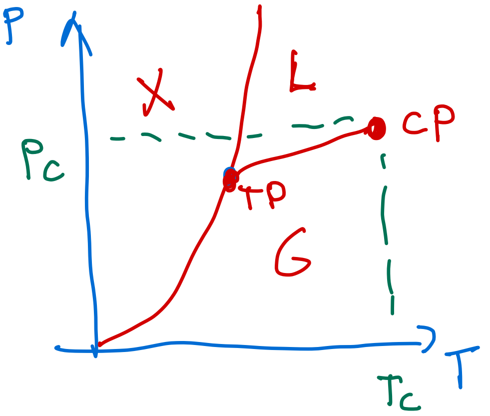
in the thermodynamic limit.

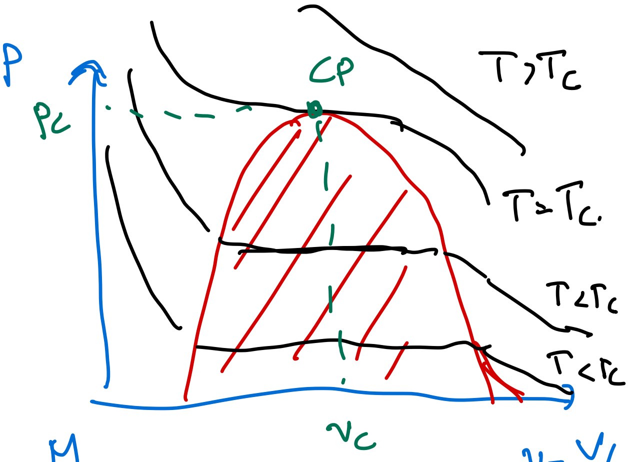
The occurrence of thermodynamic phases is captured in phase diagrams.

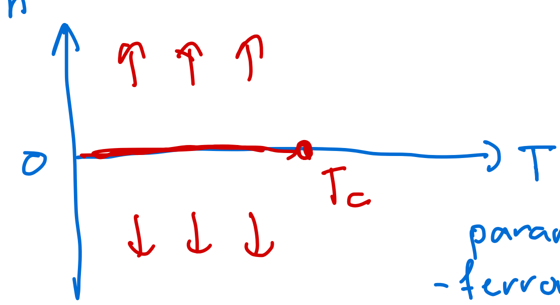
Since there are typically many thermodynamic variables, we can draw various projections.

Examples:

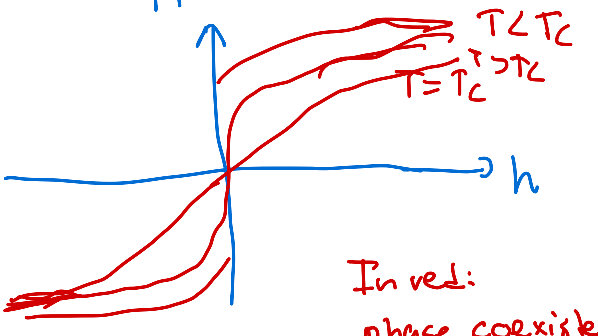
Gas-liquid phase transition





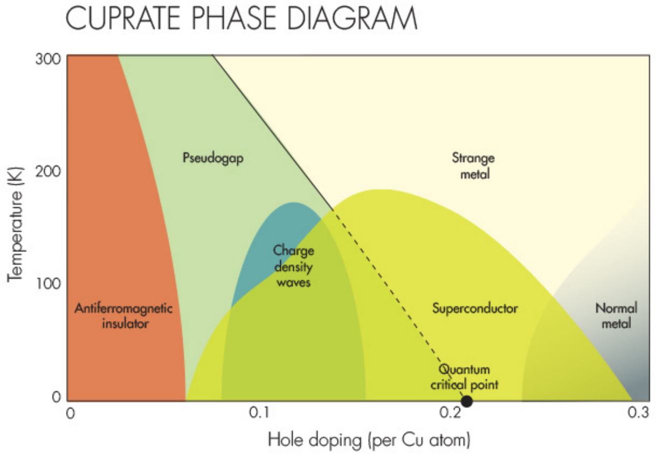


paramagnet-ferromagnet transition.



In red: phase coexistence lines: all intensive thermodynamic variables are constant!

High-temperature superconductors



Today: first two examples

Phase transitions are accompanied by thermodynamic instabilities

As an example, we take the vdW gas:

$$\beta f(\rho) = \rho\left[\log\left(\frac{\rho\Lambda^3}{1-b\rho}\right)-1\right]-\beta a\rho^2$$

$f=\frac{F}{V}$ free energy density

$$\Rightarrow p = -f+\rho\left(\frac{\partial f}{\partial\rho}\right)_T = \frac{\rho k_B T}{1-\rho b}-a\rho^2$$

⇝ Derived by VdW without knowing the existence of atoms and molecules.

Recall thermodynamic stability criteria:

$$\left(\frac{\partial I_i}{\partial X_i}\right)_{X_1,\dots,X_{i-1},X_{i+1},\dots X_r,I_{r+1},\dots I_n} \geq 0$$

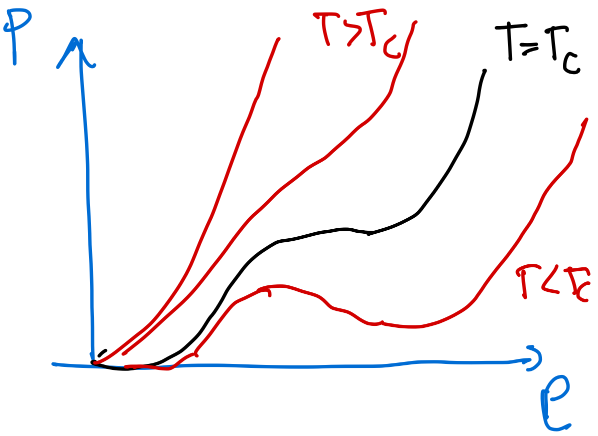
with I_i and X_i conjugate (see tutorials!).

Here: I_i : intensive variables, X_i : extensive variables.

One such thermodynamic stability criterion is $-\left(\frac{\partial p}{\partial V}\right)_{N,T}\geq 0$ (positive isothermal compressibility).

In other words $\left(\frac{\partial p}{\partial\rho}\right)_T\geq 0$

However, for vdW gas we have a parameter regime for which $\left(\frac{\partial p}{\partial\rho}\right)_T<0$



At $T=T_c$ we have an inflection point in the pressure, i.e.:

$$\left(\frac{\partial p}{\partial\rho}\right)_T=0\ ;\quad \left(\frac{\partial^2 p}{\partial\rho^2}\right)_T=0 \quad \text{at } (\rho_c,T_c).$$

Example for vdW model: $\rho_c b=\frac{1}{3}$; $k_B T_c=\frac{8a}{27b}$

More generally, the thermodynamic stability criterion says:

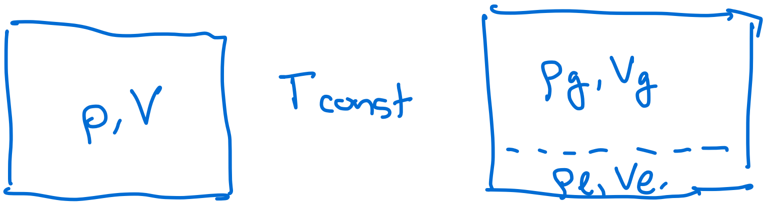
$$\left(\frac{\partial p}{\partial\rho}\right)_T>0 \quad \underset{p=-f+\rho\left(\frac{\partial f}{\partial\rho}\right)_T}{\Longrightarrow} \quad \left(\frac{\partial^2 f}{\partial\rho^2}\right)_T>0$$

free energy density isotherms should be a convex function of ρ.

Locus of all points $\rho(T)$ for which $\left(\frac{\partial^2 f}{\partial \rho^2}\right)_T = 0$ defines the spinodal

The spinodal denotes the limit of stability. Within spinodal, system is absolutely unstable (free energy density is concave).

We will now show that for $T<T_c$ the system can lower its total free energy by phase separation.



Neglecting surface effects: $F_{PS} = V f_{PS} = V_l f(\rho_l) + V_g f(\rho_g)$.

In canonical ensemble N, V are fixed. $V = V_l + V_g$

$\rho V = \rho_g V_g + \rho_l V_l$.

Using these constraints

$$f_{PS} = \frac{V_l}{V} f(\rho_l) + \underbrace{\frac{V_g}{V}}_{\frac{V-V_l}{V}} f(\rho_g) = f(\rho_g) + \frac{V_l}{V}\left[f(\rho_l) - f(\rho_g)\right]$$

$$\begin{aligned} \rho V &= \rho_g (V - V_l) + \rho_l V_l \\ &= \rho_g V + (\rho_l - \rho_g) V_l \end{aligned} \iff \frac{V_l}{V} = \frac{\rho - \rho_g}{\rho_l - \rho_g}$$

$\Rightarrow$

We conclude:

$$f_{PS}(\rho,T) = f(\rho_g,T) + \frac{\rho-\rho_g}{\rho_l-\rho_g}\left[f(\rho_l,T) - f(\rho_g,T)\right]$$

$\rho_g \le \rho \le \rho_l$

$T<T_c$.

$f_{PS}(\rho) < f(\rho)$ for suitable choices of ρ_l and ρ_g! !

(cannot occur when $T>T_c$ i.e f convex)

(ρ_g, ρ_ℓ) are determined by minimisation of free energy.

Geometrically:
$$\left(\frac{\partial f}{\partial \rho}\right)\Big|_{\rho=\rho_g} \overset{(*)}{=} \left(\frac{\partial f}{\partial \rho}\right)_{\rho=\rho_\ell} \overset{(**)}{=} \frac{f(\rho_\ell)-f(\rho_g)}{\rho_\ell-\rho_g},$$

Note that:

$(*) \Leftrightarrow \mu(\rho_\ell, T) = \mu(\rho_g, T)$ (use that $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = V\left(\frac{\partial f}{\partial \rho}\frac{\partial \rho}{\partial N}\right)_{V,T} = \left(\frac{\partial f}{\partial \rho}\right)_T$)

$(**) \Leftrightarrow p(\rho_\ell, T) = p(\rho_g, T)$

Why? Define $\mu_{co}(T) \equiv \mu(\rho_\ell, T) = \mu(\rho_g, T)$

$$\mu_{co}(T) = \frac{f(\rho_\ell)-f(\rho_g)}{\rho_\ell-\rho_g} \underset{\substack{\uparrow \\ \rho_\ell \neq \rho_g}}{\Longrightarrow} -f(\rho_\ell, T) + \rho_\ell\, \mu(\rho_\ell, T) = -f(\rho_g, T) + \rho_g\, \mu(\rho_g, T)$$

which is just equal pressure condition.

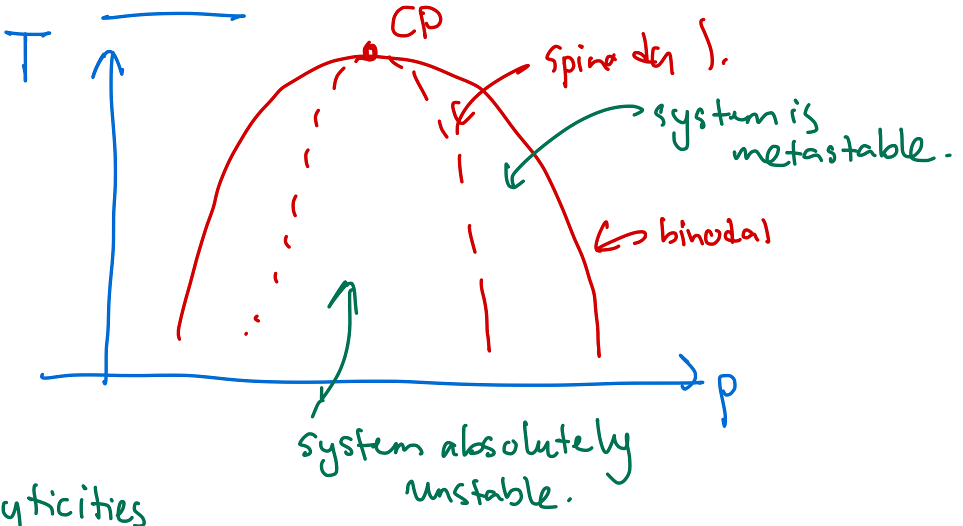
Common tangent construction $\Leftrightarrow$ $\left.\begin{array}{l}\text{equal chemical potential}\\ \text{equal pressure}\end{array}\right\}$ both phases

(Generally, it should hold for all intensive variables).

$\rho_g(T)$ is called gas branch and $\rho_\ell(T)$ the liquid branch.

Together they are called the binodal

Typical phase diagram:



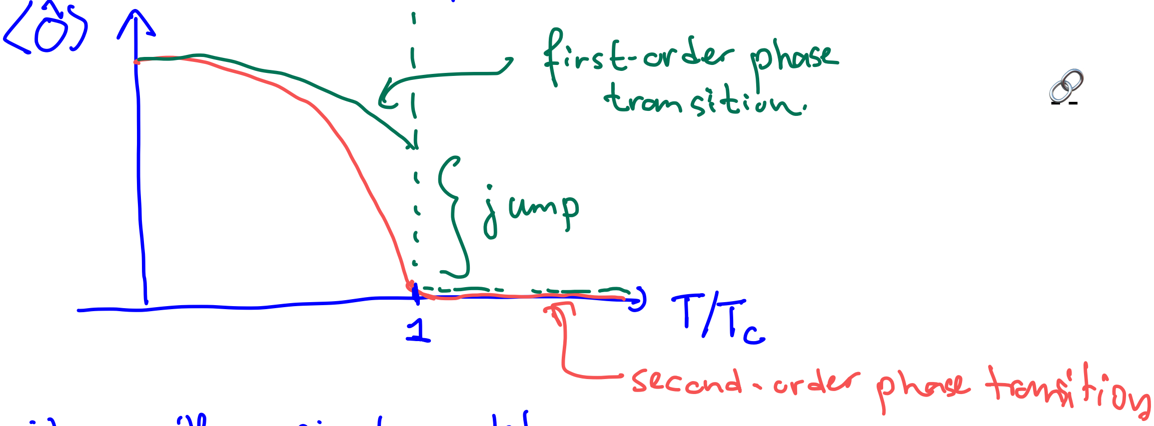
VdW model highlights subtle point: phase transitions are accompanied by non-analyticities in the free energy! How does non-analytic behaviour occur from the partition function?

Let's illustrate this with a model with a simple microscopic picture.

How can a phase transition occur from a microscopic picture?

Up until now we focused only on gas-liquid phase transitions. Here, a sample prepared with overall density ρ can phase separate into a dilute gas with density ρ_g and a dense liquid with density ρ_ℓ. The density here plays the role of an order parameter, ⇝ a quantity that tells in which phase one resides.

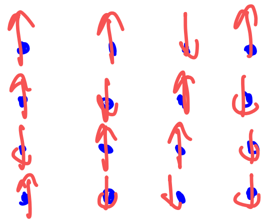
More general:



Let's illustrate this idea with a simple model.

Take a lattice with on each lattice site a "spin" with value $s_i = \pm 1$

E.g.



N lattice sites.

Energy of a spin configuration:

$$E(\{s_i\}) = -\sum_{i<j} J_{ij} s_i s_j \mp \mu \sum_{i=1}^{N} B_i s_i$$

(Ising model)

Wilhelm Lenz, 1920

coupling parameter

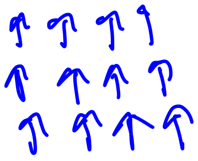
magnetic moment of single spin.

local external magnetic field.

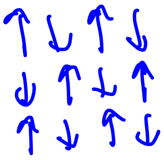
When coupling parameter $J_{ij} < 0 \Rightarrow$ antiferromagnetic order.

$J_{ij} > 0 \Rightarrow$ promotes ferromagnetic order.

So the ground state $(T=0)$:



ferromagnet



antiferromagnet.

When we "turn on" temperature this ordered state is destroyed

$\Rightarrow T \to \infty$ most stable state is a "random" spin state.

Paramagnet: acquire magnetization same direction as external magnetic field.

Diamagnet: Acquires magnetization opposite to the external magnetic field.

Here, we focus on the transition from paramagnet to ferromagnet.

So let's consider the Ising model with just nearest neighbour interactions:

$E(\{s_i\}) = -J\sum_{\langle i,j\rangle} s_i s_j$ (no external magnetic field).

Canonical partition function: $Z(N,\beta J,\beta\mu B) = \sum_{\{s_i\}} e^{-\beta E(\{s_i\})}$

$= \sum_{s_1=\pm 1}\cdots\sum_{s_N=\pm 1} e^{+\beta J\sum_{\langle i,j\rangle} s_i s_j + \beta\mu B\underset{\rightsquigarrow}{\sum_i s_i}}$ solvable in 1D (transfer matrix method)

solvable in 2D (Onsager)

No analytical solution in 3D !

However, we can gain some insights by introducing the magnetization:

per site: $m = \frac{\mu}{N}\sum_{i=1}^{N} s_i \equiv \mu S$. ≡ spatially averaged spin.

constant magn. field

Note that: $\left\langle \sum_{i=1}^{N} s_i \right\rangle = \sum_{\{s_i\}}\left(\sum_{j=1}^{N} s_j\right) e^{\beta J\sum_{\langle i,j\rangle} s_i s_j + \beta\mu B\sum_{i=1}^{N} s_i}$ Z^{-1}

$= \sum_{\{s_i\}}\frac{\partial}{\partial(\mu B\beta)} e^{\beta J\sum_{\langle i,j\rangle} s_i s_j + \beta\mu B\sum_i s_i} = Z^{-1}\frac{\partial}{\partial(\beta\mu B)}\sum_{\{s_i\}} e^{\beta J\sum_{\langle i,j\rangle} s_i s_j + \beta\mu B\sum_{i=1}^{N} s_i}$

$= \frac{1}{Z}\frac{\partial Z}{\partial(\beta\mu B)}$ Hence $\langle m(B)\rangle = \frac{\mu}{N}\frac{\partial \ln Z(N,\beta J,\beta\mu B)}{\partial(\beta\mu B)}$

$= -\left(\frac{\partial f}{\partial B}\right)_{N,T}.$ f: free energy per site.

Since, we cannot compute Z analytically, we need to resort to approximations

Write $s_i = \langle s\rangle + \delta s_i$ and keep only contributions up to quadratic order in δs_i. (fluctuation expansion) coordination number

Within this approximation: $\sum_{\langle i,j\rangle} s_i s_j = \frac{1}{2}\sum_{i=1}^{N}\sum_{j(i)=1}^{z} s_i s_{j(i)}$

$$= \frac{1}{2}\sum_{i=1}^{N}\sum_{j(i)=1}^{z}\left(\langle s\rangle^2 + \langle s\rangle \delta s_i + \langle s\rangle \delta s_j + \mathcal{O}(\delta s_i^2)\right)$$

So we find:

$$E(\{s_i\}) = \frac{1}{2} J N z \langle s\rangle^2 - \underbrace{\left(J z \langle s\rangle + \mu B\right)}_{\mu B_{mol}} \sum_{i=1}^{N} s_i$$

Each spin feels an external magnetic field but also the average field caused by surrounding spins.

Within mean-field approximation, we find:

$$Z = \left\{2\cosh\left(\beta J z \langle s\rangle + \beta \mu B\right) \exp\left(-\frac{zJ}{2}\beta \langle s\rangle^2\right)\right\}^N$$

So we find: $\langle s\rangle = \tanh\left(\beta J z\langle s\rangle + \beta\mu B\right)$ (*) (self consistency condition)

Same is found if we compute free energy $F(\langle s\rangle)$

$\Rightarrow \quad \frac{\partial F}{\partial \langle s\rangle} = 0 \quad !$

Now, let's consider $B = 0$ and set units: $\mu = 1 \Rightarrow \boxed{s = m}$

Taylor expansion of (*) $\Rightarrow \langle m\rangle = \beta J z \langle m\rangle - \frac{1}{3}(\beta J z \langle m\rangle)^3 + \mathcal{O}(\langle m\rangle^5)$

Three solutions

$m_0 = 0$ (paramagnetic solution)

$m_\pm = \pm\sqrt{-3\tau}$; $\tau = \frac{T - T_c}{T_c}$; $T_c = zJ/k_B$.

$T > T_c$: only one real solution.

$T < T_c$: three solutions.

Free energy can be expanded for small $\langle m\rangle$:

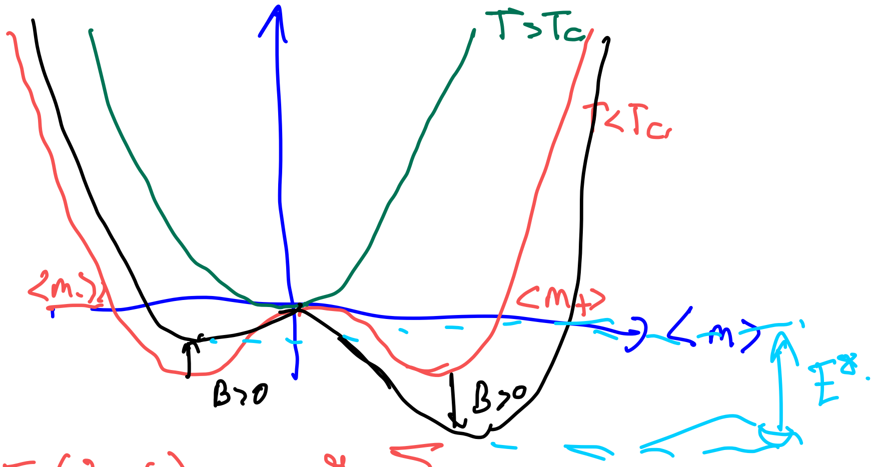
$$F = N k_B (T - T_c)\langle m\rangle^2 + \frac{N k_B T_c \langle m\rangle^4}{12} + \mathcal{O}(m^6) - N k_B T \log 2.$$

$\Rightarrow F_L(\langle m\rangle) = \text{constant} + \frac{1}{2}\alpha(T)\langle m\rangle^2 + \frac{\beta(T)}{4}\langle m\rangle^4 + \ldots$

When $\alpha(T), \beta(T) > 0$ $\langle m\rangle = 0$ global minimum.

when $\alpha(T) < 0 \Rightarrow \langle m\rangle = \sqrt{-3\tau}$ global minimum!

Mental picture:



Note the following: $E(\{s_i\}) = -J\sum_{\langle i,j\rangle} s_i s_j$

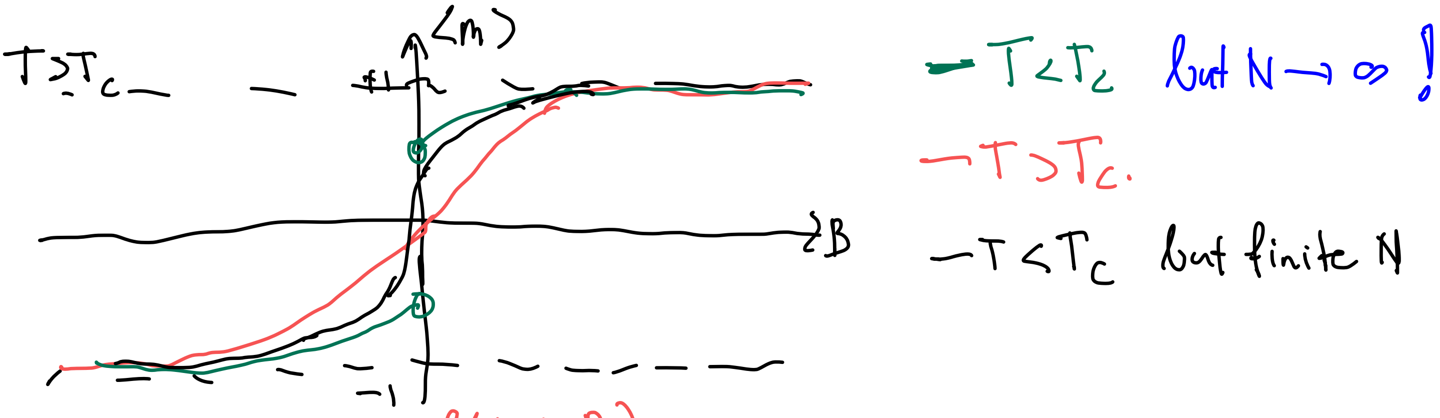
Symmetric under $s_i \to -s_i \ \forall i$

This is an example of spontaneous symmetry breaking

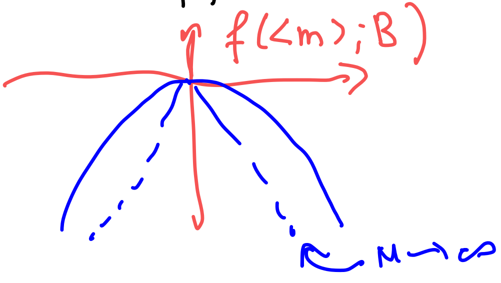
⤳ Ground state has different symmetry from the symmetry of the underlying Hamiltonian.

But wouldn't we expect that $\langle m\rangle = 0$?

So in presence of external magnetic field: (say $B > 0$) $\Rightarrow \langle m_+\rangle$ global minimum below T_c



So:



How can this non-analytic behaviour occur?

$Z^{(B)} = \sum_\nu e^{-\beta E_\nu}$. can only be non-analytic if $N \to \infty$

$\star$

Therefore,

$$\langle m\rangle(B=0) = \begin{cases} 0 & T > T_c \\ \lim\limits_{B\to 0}\lim\limits_{N\to\infty} \langle m\rangle(B) \neq 0 & \\ \lim\limits_{N\to\infty}\lim\limits_{B\to 0} \langle m\rangle(B) = 0 & \end{cases}$$

non analytic!

$\Downarrow$

phase transition.

Symmetry-broken state is stabilized by surface tension $\Rightarrow E^* \to \infty$ in therm limit.

We call $F_L(m) = \frac{1}{2}\alpha(T) m^2 + \frac{1}{4}\beta(T) m^4 + \dots$

the Landau free energy $\Rightarrow$ minimum gives the most stable phase.

Can be set up phenomenologically $s_i \to -s_i$ symmetry translates that $m = \frac{1}{N}\sum_i s_i$ should inherit this symmetry.

$$F_L(m) = F_L(-m).$$

Note that in MF approximation one can show that amounts to

$\langle s_i s_j\rangle = \langle s_i\rangle\langle s_j\rangle$ Because: $U = \frac{\partial \beta F}{\partial \beta}$

but also $U = \left\langle -J \sum_{\langle i,j\rangle} s_i s_j \right\rangle$

$\Rightarrow$ check!

In MF approximations one neglect spin-spin correlations

How valid is this?