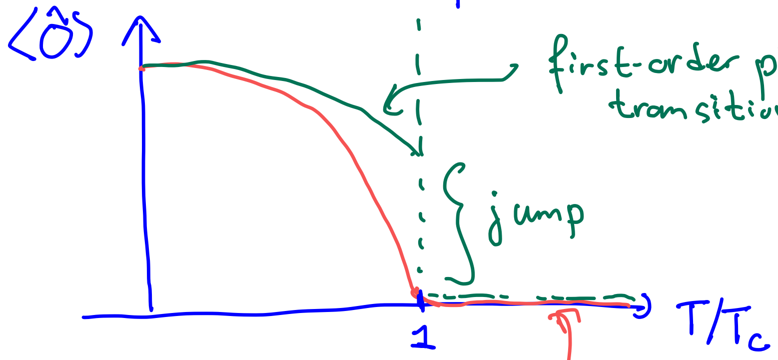
Lecture 9: Landau theory of phase transitions

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, $\rightsquigarrow$ a quantity that tells in which phase one resides.

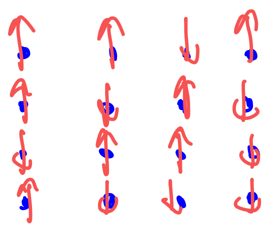
More general:



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

J_{ij}: coupling parameter

μ: magnetic moment of single spin.

B_i: local external magnetic field.

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

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

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

$\uparrow\ \uparrow\ \uparrow\ \uparrow$ $\qquad$ $\uparrow\ \downarrow\ \uparrow\ \downarrow$
$\uparrow\ \uparrow\ \uparrow\ \uparrow$ $\qquad$ $\downarrow\ \uparrow\ \downarrow\ \uparrow$
$\uparrow\ \uparrow\ \uparrow\ \uparrow$ $\qquad$ $\uparrow\ \downarrow\ \uparrow\ \downarrow$

ferromagnet $\qquad$ 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 in 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: $Z(N, \beta J, \beta \mu B) = \sum_{\{s_i\}} e^{-\beta E(\{s_i\})}$

$= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} e^{+\beta J \sum_{\langle i,j \rangle} s_i s_j + \beta \mu B \sum_i s_i}$ 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: $\langle \sum_{i=1}^{N} s_i \rangle = \sum_{\{s_i\}} \left(\sum_{j=1}^{N} s_j \right) e^{\beta J \sum_{\langle i,j \rangle} s_i s_j + \beta \mu B \sum_{i=1}^{N} s_i}$ 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:

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

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

Within mean-field approximation, we find:

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

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

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

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

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

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)

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

$T > T_c$: only one real solution.

$T < T_c$: three solutions.

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

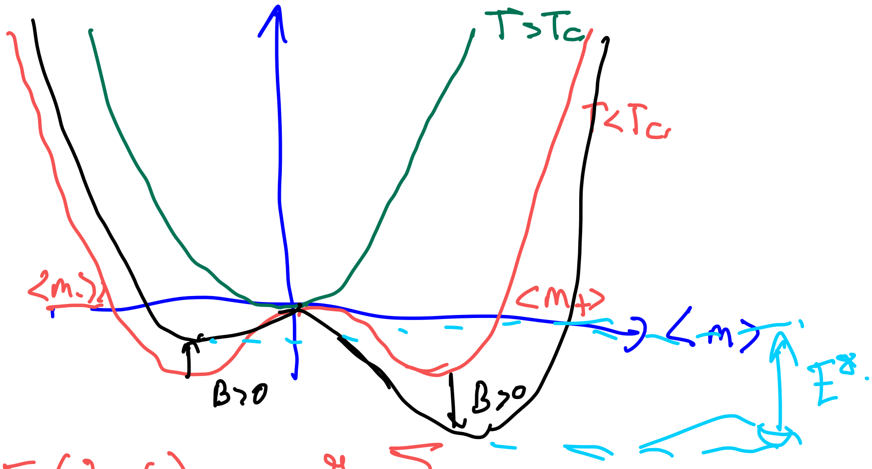
$$F = Nk_B(T-T_c)\langle m\rangle^2 + \frac{Nk_BT_c\langle m\rangle^4}{12} + \mathcal{O}(m^6) - Nk_BT\log 2.$$

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

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

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

Mental picture:



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

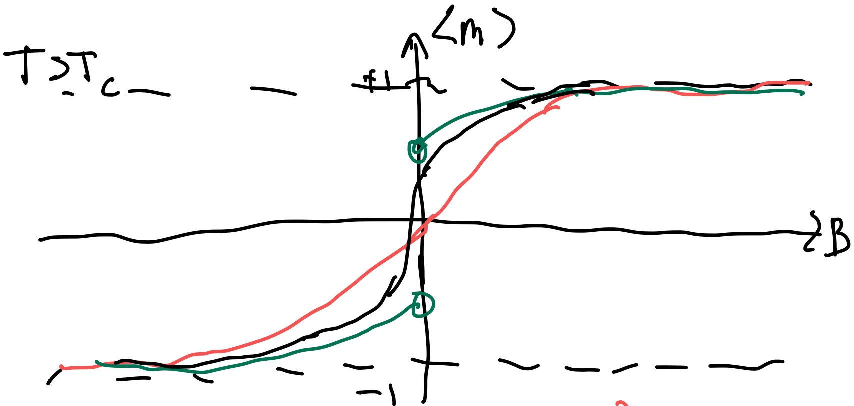
Symmetric under $\quad s_i \to -s_i \;\; \forall i$

This is an example of spontaneous symmetry breaking

$\rightsquigarrow$ 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

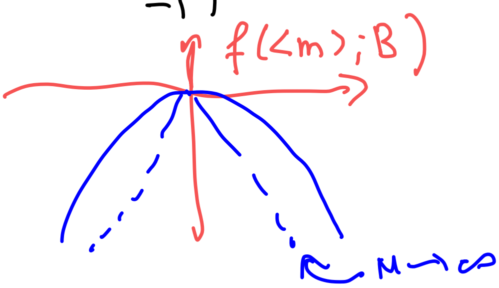


— $T < T_c$ but $N \to \infty$!

— $T > T_c$.

— $T < T_c$ but finite N

So:



How can this non-analytic behaviour occur?

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

Therefore,

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

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 approximation one neglect spin-spin correlations. How do we go beyond MF?

$$Z = \sum_{\{s_i\}} \exp\left(\beta J \sum_{\langle i,j \rangle} s_i s_j + \beta\mu \sum_i B_i s_i\right)$$

We introduce a fluctuating field m_i that on average is equal to $\langle s_i \rangle$ i.e. $\langle m_i \rangle = \langle s_i \rangle$.

Define $h_i = \beta\mu B_i$

and $K_{ij} = \beta J$ for i,j nearest neighbours and zero otherwise.

So we can write:

$$Z = \sum_{\{s_i\}} \exp\left[\frac{1}{2}\sum_{i,j} s_i K_{ij} s_j + \sum_i h_i s_i\right]$$

Using that: $$\exp\left[\frac{1}{2}\sum_{i,j} s_i K_{ij} s_j\right] \overset{C}{\propto} \int \prod_{i=1}^{N} dm_i \exp\left[-\frac{1}{2}\sum_{i,j} m_i K_{ij}^{-1} m_j + \sum_i s_i m_i\right]$$

The partition function becomes: Hubbard-Stratonovich transformation.

$$Z = C\int \prod_{i=1}^{N} dm_i \exp\left(-\frac{1}{2}\sum_{i,j} m_i K_{ij}^{-1} m_j\right) \sum_{\{s_i\}} \exp\left[\sum_i \underbrace{(m_i + h_i)}_{\text{each spin feels a fluctuating field } m_i + h_i} s_i\right]$$

Now we can perform the summation over spins:

Omitting irrelevant constants:

$$Z = \int \mathcal{D}m \exp\left(-\beta F_L[m]\right) \qquad \mathcal{D}m = \prod_{i=1}^{N} dm_i$$

in continuum limit $m_i \to m(\vec{r})$ then $\int \mathcal{D}m (\cdots)$ is called a functional integral.

With

$$\beta F_L[m] = \frac{1}{2}\sum_{i,j} m_i K_{ij}^{-1} m_j - \sum_i \ln\cosh(m_i + h_i)$$

Let's make a similarity transformation: $m_i = \sum_j K_{ij} \tilde{m}_j$

(This will only $\int \mathcal{D}m \to \tilde{C}\int \mathcal{D}\tilde{m}$), so

$$\Rightarrow \beta F_L[\tilde{m}] = \frac{1}{2}\sum_{ij} \tilde{m}_i K_{ij} \tilde{m}_j - \sum_i \ln\cosh\left(\sum_j K_{ij}\tilde{m}_j + h_i\right)$$

In continuum (i.e. long wavelength limit)

$$\sum_{ij} \tilde{m}_i K_{ij} \tilde{m}_j = \int \frac{d\vec{k}}{(2\pi)^3} \tilde{m}(\vec{k}) \tilde{K}(\vec{k}) \tilde{m}(\vec{k}) \qquad \tilde{m}(\vec{k}) = \tilde{m}(-\vec{k})$$

($\tilde{m}_i$ is real.)

with $\tilde{K}(\vec{k}) = K \sum_{\alpha=x,y,z} \cos(k_\alpha a) = \frac{1}{2} K\left[z - a^2 k^2 + \mathcal{O}(k^4)\right]$

So in continuum limit $a \to 0$ $N \to \infty$

and expanding the $\ln\cosh(\dots)$, we find:

$$\beta F_L[m] = \frac{1}{2}\int d\vec{r} \left\{ \gamma |\nabla m(\vec{r})|^2 + \alpha(T) m(\vec{r})^2 + \frac{\beta}{2} m(\vec{r})^4 + \dots - h(\vec{x}) m(\vec{x}) \right\}$$

$$Z = \int \mathcal{D}m \, e^{-\beta F_L[m]}.$$

Saddle-point approximation: integral is dominated where $-\beta F_L[m]$ is maximal:

$$Z \approx e^{-\beta F_L[\langle m\rangle]}.$$

with $\langle m \rangle$ given by $\left.\frac{\delta F_L[m]}{\delta m(\vec{r})}\right|_{m(\vec{r}) = \langle m\rangle} = 0$

$\Rightarrow$ Same result as the mean-field approximation!

We can generalise the result to the so called (classical) Heisenberg model:

$$H = -J \sum_{\langle ij\rangle} \vec{S}_i \cdot \vec{S}_j$$

This hamiltonian is invariant under $\vec{S}_i \to \underline{\underline{R}} \cdot \vec{S}_j$

$\underline{\underline{R}} \in SO(3)$ (rotation matrix)

Then we find.

$$Z = \int \mathcal{D}\vec{m} \, e^{-\beta F_L[\vec{m}]}$$

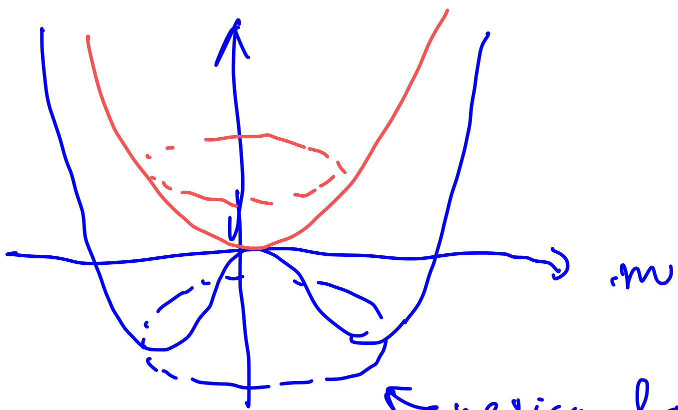
with Landau free energy:

$$\beta F_L[\vec{m}] = \frac{1}{2}\int d\vec{r}\,\left[\vec{m}(\vec{r})\cdot[\alpha(T)-\nabla^2]\vec{m}(\vec{r}) + \frac{1}{2}\beta(T)\vec{m}^4 + \dots\right]$$

ginzburg-Landau theory.

Notice now that this free energy is invariant under rotations of the order parameter $\vec{m}$.

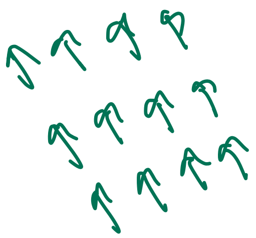
So now.



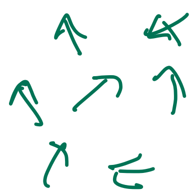
mexican hat potential.

So we have situation:

$T<T_c$. $\langle\vec{m}\rangle \neq 0$



$T>T_c$.



$\langle\vec{m}\rangle = 0$.

In contrast to Ising case where Hamiltonian (in absence of external magnetic field) is invariant under $\mathbb{Z}_2$ (discrete symmetry) we have no an "infinite amount" of ground states with equal energy.

If Hamiltonian is invariant under a continuous symmetry

$\Rightarrow$ there are excitations that cost no energy (Goldstone modes.)

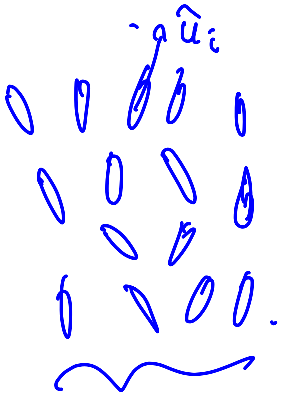
So for $T<T_c$ we can infinitesimally homogeneously rotate the system for $T<T_c$.

Local spin rotation result in a spin wave with dispersion relation

$$\hbar\omega_{\vec{k}} = \mathcal{J}k^2 \quad \text{(magnon)} \quad k \to 0 \text{ goldstone mode.}$$

Up until now we talked about magnets where Hamiltonian is invariant under global rotations.

But what about particles that look like:



collection of rods.

Now the orientation of each particle is not a good order parameter.

$\Rightarrow$ There is an up-down symmetry.

$\vec{n} \updownarrow$

disordered state: isotropic liquid !

$\Rightarrow$ Nematic liquid crystal: partially ordered system where translational symmetry is not broken, but rotational symmetry is broken with a "residual" up-down symmetry

$\Rightarrow$ Order parameter is a tensor $\underline{Q}$ $\Rightarrow$ automatically satisfies up-down symmetry

$$Q_{\alpha\beta} = \langle \hat{Q}_{\alpha\beta} \rangle = \left\langle \frac{3}{2N} \sum_{i=1}^{N} \left(\hat{u}_{i\alpha} \hat{u}_{i\beta} - \frac{1}{3}\delta_{\alpha\beta} \right) \right\rangle$$

↑ orientation of particle i.

because in eigen representation

unit vectors !

$$Q_{\alpha\beta} = \underbrace{\frac{3}{2} S \left(\hat{n}_\alpha \hat{n}_\beta - \frac{\delta_{\alpha\beta}}{3} \right)}_{\text{uniaxial order}} + \underbrace{\frac{P}{2} \left(e_\alpha^{(1)} e_\beta^{(1)} - e_\alpha^{(2)} e_\beta^{(2)} \right)}_{\text{"biaxial order"}}$$

$\alpha, \beta = x, y, z.$

$S = -\frac{1}{2}.$

↑ rod orders in a plane.

We can now write invariants:

$Q_{\alpha\beta} Q_{\beta\alpha}$; $Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha}$

$\mathrm{Tr}\, \underline{Q}^2$; $\mathrm{Tr}\, \underline{Q}^3$.

Based on symmetry principles (although in principle also derivable from field theory), we find the Landau-de Gennes free energy density

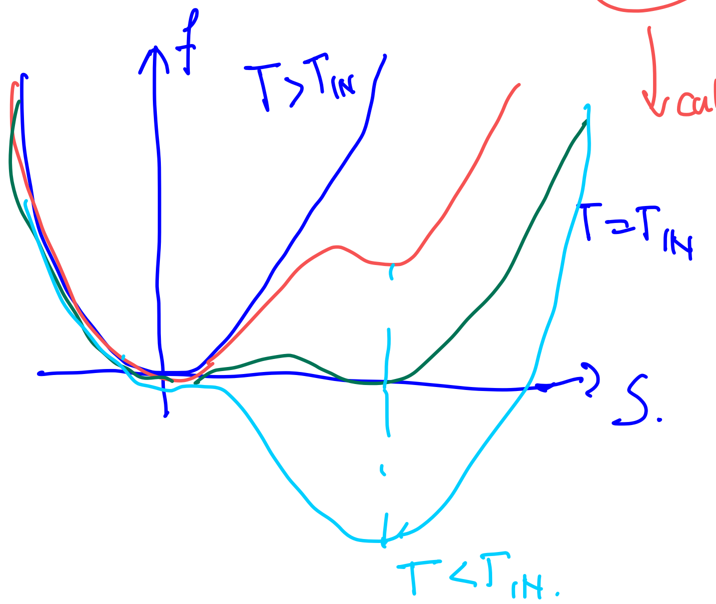
$$\frac{F(\underline{\underline{Q}})}{V} = \frac{a}{2}(T-T^*)\,\mathrm{Tr}\,\underline{\underline{Q}}^2 + \frac{B}{3}\,\mathrm{Tr}\,\underline{\underline{Q}}^3 + \frac{C}{4}\,\mathrm{Tr}(\underline{\underline{Q}}^2)^2 = f.$$

$(a, C > 0.)$
$(B<0)$

Assume uniaxial order $(P=0)$:

$$\Rightarrow f = \frac{3}{4}a(T-T^*)S^2 + \frac{B}{4}S^3 + \frac{9}{16}CS^4.$$

cubic term!



First order phase transition!