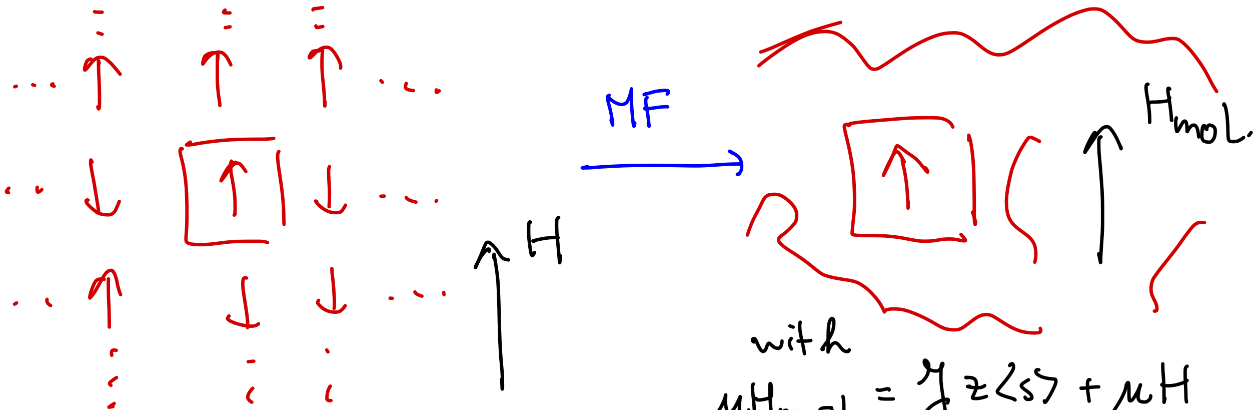
Lecture 3: Breakdown of mean-field theory

Phase transitions $\Leftrightarrow$ Thermodynamic instability $\Leftrightarrow$ Non-analyticities in free energy.

To highlight how phase transitions can occur microscopically, we considered the Ising model:
$$E(\{s_i\}) = -J\sum_{\langle i,j\rangle} s_i s_j - \mu H \sum_{i=1}^{N} s_i. \qquad s_i = \pm 1, \quad i = 1,\dots,N.$$

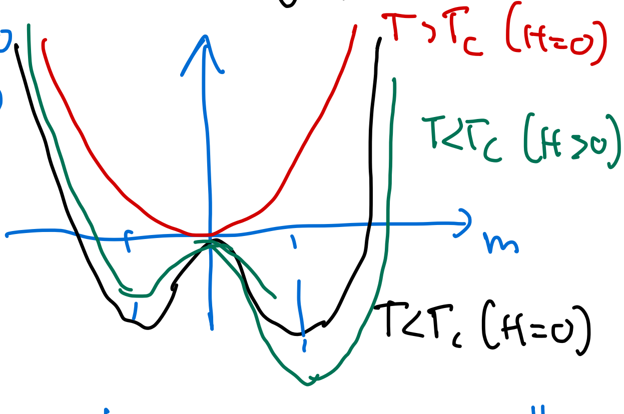
We determined the partition function in the mean-field (MF) approximation, which amounts to:



with
$$\mu H_{mol} = \underbrace{Jz\langle s\rangle}_{\text{field generated by surrounding spins.}} + \mu H$$

and we found: $(H=0)$
$$Z = e^{-\beta N f(\langle m\rangle)} \quad \text{with} \quad \left.\frac{\partial f}{\partial m}\right|_{\langle m\rangle} = 0, \quad \left.\frac{\partial^2 f}{\partial m^2}\right|_{\langle m\rangle} > 0$$

where $f(\langle m\rangle)$ has qualitative behaviour:

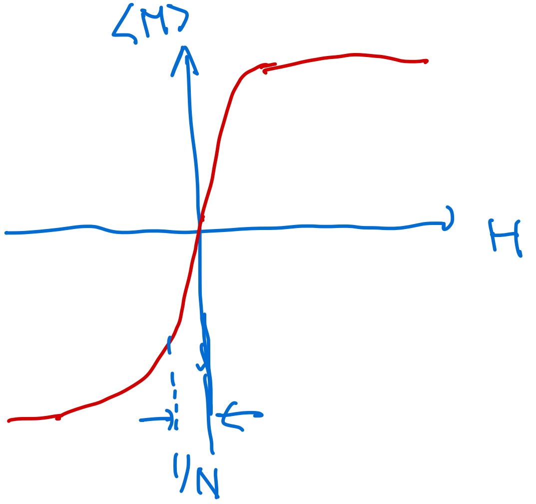


So for $T<T_c$: degenerate minima

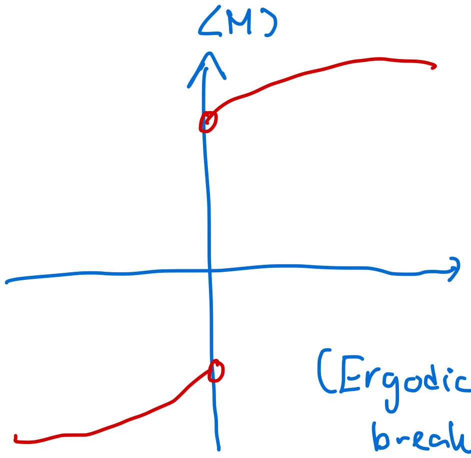
but there is an energy barrier that separates the two minima. This energy barrier becomes macroscopically large in the thermodynamic limit.

So which minimum will be chosen by the system? We apply an external field

We find:
$$\langle m\rangle(H=0) = \begin{cases} 0 & (T>T_c) \\ \lim\limits_{H\to 0^\pm} \lim\limits_{N\to\infty} \langle m\rangle(H) \neq 0 \\ \lim\limits_{N\to\infty} \lim\limits_{H\to 0} \langle m\rangle(H) = 0 \end{cases}$$



Thermo. $\longrightarrow$ limit.



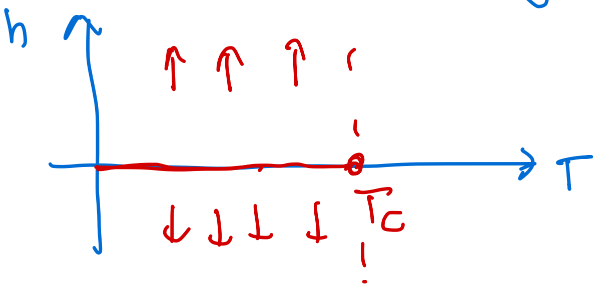
(Ergodicity breaking)

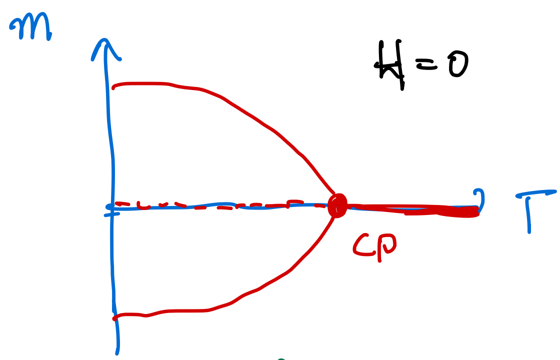
Close to the Curie temperature, we can expand $f(\langle m \rangle)$ and find:

$$f_L(m) = \frac{1}{2} a(T)\, m^2 + \frac{1}{4} b(T)\, m^4 + \dots \qquad (a, b \text{ are intensive})$$

and $f_L(\langle m \rangle) = -\dfrac{a(T_c)^2}{2b(T_c)}$ So in MF, activation barrier scales with N!

We can draw the phase diagram





Q: where is the spinodal?

How good is MF theory?

We found $T_c = \dfrac{zJ}{k_B}$ For (hyper) cubic lattices $z = 2D$ ← spatial dimensionality

and we found $\langle m \rangle \sim \sqrt{-3t} \sim (-t)^{\beta}$ (for $t \uparrow 0$)

$t = \dfrac{T - T_c}{T_c}$ (β here is critical exponent).

So we find for:

$\dfrac{k_B T_c}{J}$:

	MFT	exact
D=1	2	0
D=2	4	2.27
D=3	6	4.0

β:

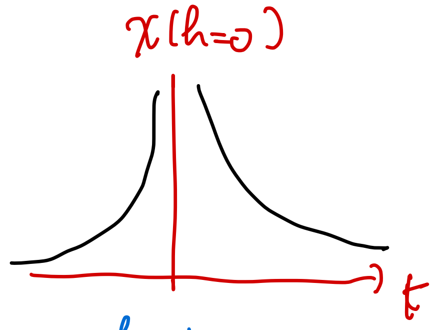
	MFT	Exact
D=1	1/2	not defined (no PT)
D=2	1/2	1/8
D=3	1/2	1/3

What about other thermodynamic properties stemming from non-analyticities?

$\langle m\rangle (t=0) \sim \left(\frac{h}{b}\right)^{1/3} \sim h^{1/\delta} \qquad \delta = 3.$

So we find:

	MFT	exact
D=1	3	exp
D=2	3	15
D=3	3	4.85



Magnetic susceptibility $\qquad \chi_T = \lim_{H\to 0}\left(\frac{\partial M}{\partial H}\right)_T.$

We find: $\beta \chi_T^{-1} = \frac{\partial h}{\partial \langle m\rangle}\Big|_{h=0} \sim t + 3\langle m\rangle^2 = \begin{cases} t & \text{for } t>0 \\ -2t & \text{for } t<0. \end{cases}$

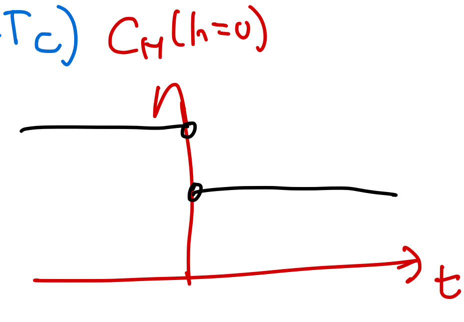
We define γ as $\chi_T \sim |t|^{-\gamma}$. So:

	MFT	Exact
D=1	1	exp
D=2	1	7/4
D=3	1	1.24

Heat capacity

$C_H = \left(\frac{\partial \langle E\rangle}{\partial T}\right)_{N,H} \qquad$ with $\langle E\rangle = \left(\frac{\partial \beta F}{\partial \beta}\right)_{N,H}$

We find $\qquad C_H(H=0) = \begin{cases} C_0 & (T>T_c) \\ \frac{3}{2}N k_B + C_0 & (T<T_c) \end{cases}$



$C_H = |t|^{-\alpha}$:

	MFT	Exact
D=1	0	exp
D=2	0	log.
D=3	0	0.11

$\alpha, \beta, \gamma, \delta$ are called critical exponents $\Rightarrow$ they characterize the behaviour of the system close to the critical point $\Leftrightarrow$ universality

MFT becomes progressively worse with decreasing dimensionality.

We noted in the previous lecture that the MF approximation is equivalent to setting $\langle s_i s_j\rangle \simeq \langle s_i\rangle\langle s_j\rangle$ in the Ising model. (for the internal energy)

$\langle m \rangle = \mu \langle s \rangle$.

Let's go back to Ising model:

Recall $$Z = \sum_{\{s_i\}} e^{\beta J \sum_{\langle ij \rangle} s_i s_j + \mu H \sum_i s_i} \quad \text{and} \quad s = \frac{1}{N} \sum_{i=1}^{N} s_i$$

Then $$\langle s \rangle = \frac{1}{N} \frac{1}{Z} \left(\frac{\partial Z}{\partial \beta \mu H} \right)_{N, \beta J} \quad \text{and} \quad \langle s^2 \rangle = \frac{1}{N^2 Z} \left(\frac{\partial^2 Z}{\partial (\beta \mu H)^2} \right)_{N, \beta J}.$$

So: $$\langle s^2 \rangle - \langle s \rangle^2 = \frac{1}{N^2} \left(\frac{\partial^2 \ln Z}{\partial (\beta \mu H)^2} \right)_{\beta J, N} = \frac{1}{N} \left(\frac{\partial \langle s \rangle}{\partial \beta H \mu} \right)_{\beta J, N}$$

$$\propto \frac{1}{N} \chi_T$$ Magnetic susceptibility is related to magnetic (spin) fluctuations.

$$\chi_T = N \left(\langle s^2 \rangle - \langle s \rangle^2 \right) = \frac{1}{N} \sum_{i=1}^{N} \left[\sum_{j=1}^{N} \left(\langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle \right) \right].$$

$$=: \frac{1}{N} \sum_{i=1}^{N} \left[\sum_{j=1}^{N} C_{ij} \right].$$

C_{ij} is the spin-spin correlation function $\Leftrightarrow$ Quantifies range of which spins are correlated.

Note that $\chi_T \to \infty$ at CP.

So @ CP we have long-ranged correlations (although interactions are shortranged !)

Note that this relation goes beyond that of lattice models.

Generally speaking: $$\chi_T = \frac{1}{k_B T} \left(\langle M^2 \rangle - \langle M \rangle^2 \right).$$

Suppose $M = \int d\vec{r}\, m(\vec{r})$. $\Rightarrow$ $$k_B T \chi_T = \int d\vec{r} \int d\vec{r}\,' \left[\langle m(\vec{r}) m(\vec{r}\,') \rangle - \langle m(\vec{r}) \rangle \langle m(\vec{r}\,') \rangle \right]$$

Suppose system is homogeneous: $m(\vec{r}) = m \equiv \text{cst}$.

and we define: $$G(\vec{r} - \vec{r}\,') = \langle m(\vec{r}) m(\vec{r}\,') \rangle.$$

Then: $\chi_T = \beta V \int d\vec{r}\, [\overbrace{G(\vec{r}) - m^2}^{:= G_c(\vec{r})}]$

bulk response function.

correlations of microscopic degrees of freedom.

This is our first example of a fluctuation-dissipation relation,

Typically, we have that: $G_c(\vec{r}) \sim e^{-r/\xi}$ for $r > \xi$

with ξ the so-called correlation length. $\Leftrightarrow$ length scale of

If fluctuations become macroscopic in size, they can scatter light when $\xi \sim \lambda$
↑ wavelength of light.

This is called critical opalescense (Video).

At CP $\chi_T \to \infty \Leftrightarrow \xi \to \infty$ defines new critical exponent ν:

$$\xi(T, h=0) \propto |t|^{-\nu}$$

Macroscopic correlation is what drives the formation of ordered phases!

Why does MF approximation breakdown?

The 1D Ising model does not exhibit a phase transition at finite temperature and short-ranged interactions. However the MFT predicts a finite T phase transition. What is going on?

Suppose we have a T=0 ground state for N spins:

$$\ldots \uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow \ldots \qquad E = -NJ k_B T$$

↓ flip M spins

$$\ldots \uparrow\uparrow \underbrace{\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow}_{M} \uparrow\uparrow \ldots \qquad E = (-NJ + 4) k_B T.$$

$\beta \Delta E = 4J$.

The energy cost of flipping a block of M spins is independent of M!

So flipping a block of 1, 2, 5, 2000... spins have all same Boltzmann weight. Such fluctuations will occur at finite T and destroy long-ranged order! This is called the Peierls argument.

Creating domain walls is in 1D an "easy" source of entropy.

What about 2D? The energetic cost of flipping a block of M spins now scale with $M^{1/2}$. So $\Delta E \propto J M^{1/2}$.

Large fluctuations are more "expensive" and occur statistically speaking less. Suppression of large-scale fluctuations leads to finite T phase transition! In 3D: $\Delta E \propto J M^{2/3}$ $\Rightarrow$ larger suppression of large fluctuations.

$\Rightarrow$ Explains why MFT becomes better for increasing D!

It turns out: $D \geq 4$ MFT becomes exact.

This is called the upper critical dimension.

When is MFT accurate? Far from the CP. Qualitative behaviour is accurately captured by MFT. So mean-field theory is still worthwhile to study if the spatial dimension is large enough!

How good is the Ising model?

The true microscopic picture of a ferromagnet is of course more complex than what is inside the Ising model. This is the essence of modelling: finding out which features of the system are relevant to describe the phenomenon we are interested in. Close to CP are the long-wavelength spin excitations. So we want to have a systematic way of deriving physics on the mesoscopic scale.

Goal: microscopic degrees of freedom $\rightarrow$ mesoscopic (fluctuating) order parameter field.

E.g. spins $\Leftrightarrow$ $\vec{m}(\vec{r})$. $\vec{r}$ is continuous, but no variations on scales smaller than the lattice spacing a.

I.e. FT of $\vec{m}(\vec{r})$ does not include wavevectors $|\vec{k}| < 1/a$.

Let us denote a general order parameter field by $\vec{\phi}(\vec{r})$

So what we want: $Z = \mathrm{Tr}[e^{-\beta H_{mic}}] = \int \mathcal{D}\vec{\phi}\; e^{-\beta F_L[\vec{\phi}]}$

Integration over all possible field configurations $\vec{\phi}(\vec{r})$

Should be viewed as a reparametrization of Z in terms of a fluctuating order parameter $\vec{\phi}(\vec{r})$

Behaviour of $F_L[\vec{\phi}]$ can be captured by few phenomenological parameters (Landau).

$\vec{r} \in \mathbb{R}^d$ (space) ; $\vec{\phi} \in \mathbb{R}^n$ (vectorial order parameter).

Examples:

$n=1$: gas-liquid phase transition, binary mixtures, Ising magnets (uniaxial)

$n=2$: Superfluidity, superconductivity, planar magnets.

$n=3$: Magnets.

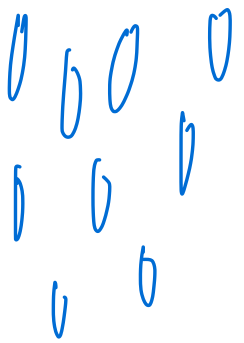
$d=1$: wires

$d=2$: surfaces / interfaces.

$d=3$: our world.

$d=4$: relativistic field theory.

Sometimes the order parameter is tensorial; e.g. in liquid crystals.



Example of a partially ordered phase.

$$\underline{\underline{Q}} = \left\langle \frac{3}{2N} \sum_{i=1}^{N} \left(\hat{u}_i \hat{u}_i - \frac{1}{3}\mathbb{I} \right) \right\rangle.$$

$$= \underbrace{\frac{3}{2} S \left(\hat{n}\hat{n} - \frac{1}{3}\mathbb{I} \right)}_{\text{uniaxial order}} + \underbrace{\frac{P}{2} \left(\hat{e}^{(1)}\hat{e}^{(1)} - \hat{e}^{(2)}\hat{e}^{(2)} \right)}_{\text{biaxial order.}}$$

Symmetry-based approach to $F_L[\vec{\phi}]$.

We write: $$F_L[\vec{\phi}] = \int d^d\vec{r}\, f_L\Big(\vec{\phi}(\vec{r}), \underbrace{\nabla\vec{\phi}(\vec{r}), \nabla^2\vec{\phi}(\vec{r}), \dots}_{\text{non-local interactions.}} \Big)$$

(short-range interactions)

For now: no explicit $\vec{r}$ dependence (bulk system: i.e. no external potential or localised impurity).

$f_L(\vec{\phi}(\vec{r}))$ is then written as an expansion in terms of powers of $\vec{\phi}$ and its gradients. Allowed since singular behaviour only occurs at the macroscopic scale (thermodynamic limit).

$f_L(\vec{\phi}(\vec{r}))$ must respect the symmetries of the microscopic Hamiltonian.

E.g. Heisenberg model (classical): $$-J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j$$

is invariant under rotations of spin degrees of freedom.

if we set $\langle \vec{\phi}(\vec{r}) \rangle \propto \left\langle \frac{1}{N} \sum_{i=1}^{N} \vec{S}_i \right\rangle$ then it amounts to:

$$F_L[\underset{\text{rotation in order parameter space.}}{R}\, \vec{\phi}(\vec{r})] = F_L[\vec{\phi}(\vec{r})].$$

This means only allowed terms are $\left(\vec{\phi}(\vec{r}) \cdot \vec{\phi}(\vec{r})\right)^n$.

If the underlying space is isotropic. $\Rightarrow$ only derivatives that are invariant under spatial rotations.

e.g.: $|\nabla\vec{\phi}|^2$.

or $(\nabla^2\vec{\phi})^2$ or $|\vec{\phi}(\vec{r})|^2\,|\nabla\vec{\phi}(\vec{r})|^2$ etc.

So for magnetic system we find: $(\vec{\phi}=\vec{m})$

$$\beta F_L[\vec{m}] = \text{const} + \int d^d\vec{r}\left[\frac{a}{2}m(\vec{r})^2 + \frac{b}{4}m(\vec{r})^4 + \frac{K}{2}|\nabla\vec{m}|^2 + \dots - \vec{h}\cdot\vec{m}(\vec{r})\right]. \quad (*)$$

short scales + non magnetic dofs.

Stability f_L should be bounded from below. (else probability would diverge!)

In other words, for e.g. $(*)$ $\Rightarrow$ $b>0$.

Remark $a, b, K, \dots$ depend on microscopic interactions and thermodynamic state variables.

They are <u>not</u> universal.

They also typically depend on temperature.

$F_L[\vec{\phi}]$ follows from coarse graining: integrating (summing) over microscopic degrees of freedom while constraining their average to $\vec{\phi}(\vec{r})$.

Finally, note that in MF approximation:

$$Z = \int D\vec{\phi}\, e^{-\beta F_L[\vec{\phi}]} \approx e^{-\beta \min_{\vec{\phi}} F_L[\vec{\phi}]}. \quad \text{(saddle point approximation)}$$

Although $F_L[\phi]$ is analytic, it does not mean that $\min_{\vec{\phi}} F_L[\vec{\phi}]$ is analytic!