II) First-order transitions

Double-tangent construction (a.k.a bitangent) in a free energy profile

$\Leftrightarrow$ Maxwell plateau

Conditions for phase equilibria / Gibbs phase rule

Be able to read phase diagrams involving mixtures (eutectic points, azeotropic ...)

III) Critical phenomena : qualitative approaches

Message : a proper mean-field treatment should always be variational (could work if not variational, but severe pitfalls may ensue).

Key relation : Gibbs-Bogoliubov inequality

$$F \leqslant \underbrace{F_0 + \langle H - H_0 \rangle_0}$$

mean-field free energy, should be minimized wrt parameters entering H_0, while the stat mech treatment with H is impossible.

Among mean-field treatments, Landau approach plays a special role. It is motivated by the remark that close to T_c, the important degrees of freedom are long wavelength fluctuations, microscopic details no longer matter $\Rightarrow$ can we explain universality?

Fluctuations involve many particles/spins $\rightarrow$ coarse-grained approach may be appropriate for their description $\Rightarrow$ the goal is to construct such a statistical field theory

It is then convenient to frame the discussion in the langage of magnetic systems, where symmetries are more transparent.

Idea: change focus from original degrees of freedom (spins), to fields $\vec{m}(\vec{r})$, defined as the mean magnetization in a ball centered at $\vec{r}$, of size $\ell \gg a$, lattice spacing. Since $\ell \ll L$, macroscopic dimension, $\vec{m}(\vec{r})$ is a mesoscopic object

Transforming from original spins to $\vec{m}(\vec{r})$ is a non invertible change of variables. Knowing the microscopic, original, Hamiltonian $H(S_1, \dots S_N)$, we can compute the probability of a given profile $\vec{m}(\vec{r})$ by summing over all microscopic configurations leading to the chosen field. We have

$$Z = \sum_{S_1, \dots S_N} e^{-\beta H} = \underbrace{\int \mathcal{D}\vec{m}(\vec{r})}_{\text{integration over all allowed configurations, functional integral}} \, e^{-\beta \mathcal{R}[\vec{m}(\vec{r})]}$$

effective free energy
GINZBURG-LANDAU

Obtaining explicitly $\mathcal{R}[m(\vec{r})]$ is no easier than solving the full problem.
The goal is to capture its core features through a small number of phenomenological parameters (as when describing the energy of deforming a solid in terms of a few elastic ").
↳ approach first applied by Landau to describe onset of superfluidity in Helium.
We have:

$$e^{-\beta\mathcal{R}[\vec{m}(\vec{r})]} = \sum_{\mathcal{C},\ \text{all micro config giving } \vec{m}(\vec{r})} e^{-\beta\mathcal{H}(\mathcal{C})}$$

$$\frac{1}{Z} e^{-\beta\mathcal{R}[\vec{m}(\vec{r})]} \equiv P[\vec{m}(\vec{r})] \quad \text{proba to observe the profile } \vec{m}(\vec{r}).$$

The functional integral is obtained as limit of a discrete integral: the continuous position $\vec{r}$ ($\in \mathbb{R}^d$) is discretized into a lattice of $\mathcal{N}$ points, at distance a
(note that for a spin system on a lattice, no need to do this and reconstruct the original lattice!) and

$$\int \mathcal{D}\vec{m}(\vec{r}) = \lim_{\mathcal{N}\to\infty} \int \prod_{i=1}^{\mathcal{N}} d\vec{m}_i$$

Mathematically tricky object, due to large # of degrees of freedom at small distance.
↳ no pb here due to existence of underlying lattice.

→ Construction of $\mathcal{R}[\vec{m}(\vec{r})]$, the effective free energy.

(*) Locality. If the system is made of disconnected parts

$$\mathcal{R}[\vec{m}(\vec{r})] = \int d\vec{r}\ \ \phi[\vec{m}(\vec{r}), \cancel{\vec{r}}]$$

↳ uniformity (without an external field)

Yet, as a result of interactions, the different parts are coupled, and we seek for $\mathcal{R}$ as

$$\mathcal{R}[\vec{m}(\vec{r})] = \int d\vec{r}\ \ \phi[m(\vec{r}), \vec{\nabla}\vec{m}, \nabla^2\vec{m}, \ldots]$$

which is a local functional of $\vec{m}$ and its gradients. The reason for restricting to low order derivatives (and make a Taylor expansion in those), is that we are interested in large scale fluctuations, hence the gradients are expected small (keep in mind this requirement for checking self-consistency).
the locality assumption cannot be correct with long-range interactions. Take eg electrostatic energy functional $\displaystyle\int d\vec{r}\, d\vec{r}'\ \frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r}-\vec{r}'|}$, cannot be put as a local form

(*) Analyticity We next expand Φ in powers of $\vec{m}$ (to describe behavior close to $\vec{m}=\vec{0}$) and in powers of $\vec{\nabla}\vec{m}$. This amounts to searching for a generalized of the central limit theorem, that would give a term in $\vec{m}^2$ for non interacting degrees of freedom.

Going from micro to meso: washes possible non analyticity, in the averaging process and $R[\vec{m}]$ is analytic. ⚠ there are non analyticities associated to phase transitions, but these singularities involve an infinity (macroscopic #) of degrees of freedom. By focusing on mesoscopic scale, we avoid possible singularities both at short and large scales.

(*) Symmetry: survives the averaging process (Any underlying microscopic symmetry) For instance with XY model, take a global rotation R_n (applying to n-dimensional spins $\vec{S}\in\mathbb{R}^n$): $H(\vec{S}_1,\vec{S}_2,\dots \vec{S}_N) = H(R_n\vec{S}_1, R_n\vec{S}_2,\dots R_n \vec{S}_N)$

$$\Rightarrow R[\vec{m}(\vec{r})] = R[R_n\vec{m}(\vec{r})]$$

This selects terms like $\vec{m}^2$, $(\vec{m}^2)^2$, $\sum_{\alpha=1}^{n}(\vec{\nabla}m_\alpha)^2$, $\vec{m}\cdot\nabla^2\vec{m}$ See tutorial on liq Xtals

Take $n=1$ for simplicity (ie ferromagnetic transition for uniaxial magnets), we get

$$\beta R[m(\vec{r})] = \beta R_0 + \int d\vec{r}\left\{\frac{a_2}{2}m^2(\vec{r}) + \frac{a_4}{4}m^4(\vec{r}) + \dots + \frac{1}{2}b(\vec{\nabla}m)^2\right\}$$

↳ from $\int$ over short scales; analytic; ignored

We can also account for a magnetic field, which adds a term $-\int d\vec{r}\ B(\vec{r})m(\vec{r})$.

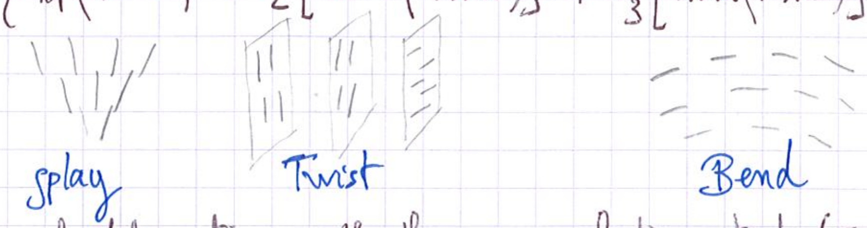
(*) Stability: our functional should not lead to any unphysical configuration, which sets a few constraints. Means above that $a_4>0$ and $b>0$.

NB1: a_2, a_4, b depend on microscopic parameters (coupling constant etc) but also on the external parameters, such as T or P. This is because the Ginzburg-Landau functional $R[m]$ is not a hamiltonian but an effective hamiltonian (ie a free-energy), where some degrees of freedom have already been integrated out. This is because we cannot perform exactly this integration that we had to postulate the form of $R[m(\vec{r})]$, relying on symmetry, analyticity, stability. The price to pay is that the phenomenological parameters ($a_2, a_4, b\dots$) have unknown dependence on microscopic details, and T, P.

NB2 : it is possible to obtain the above G.L. functional for Ising from variational mean-field treatment, or Bragg-Williams approximation (same thing)

NB3 : see tutorials for construction of $\mathcal{R}[\hat{n}(\vec{r})]$ for nematic liquid crystals, having nematic director field $\hat{n}(\vec{r})$, a unit vector

$$\mathcal{R}[\hat{n}(\vec{r})] = \frac{1}{2}\int \left\{ K_1 (\vec{\nabla}\cdot\hat{n})^2 + K_2 [\hat{n}\cdot(\vec{\nabla}\wedge\hat{n})]^2 + K_3 [\hat{n}\wedge(\vec{\nabla}\wedge\hat{n})]^2 \right\} d\vec{r}$$



↳ 3 independent types of deformation, with their own elastic constant (Franck cst)

In 2d, the K_2 term is absent. If furthermore, $K_1 = K_3$, then $\hat{n}$ can be parametrized by an angle θ : $\hat{n} \left| \begin{matrix} \cos\theta \\ \sin\theta \end{matrix} \right.$ and we find

$$\mathcal{R}[\hat{n}(\vec{r})] = \frac{1}{2} K_1 \int d\vec{r} \, (\vec{\nabla}\theta)^2$$; already met for | XY model / Heisenberg "

→ Saddle point approximation and mean-field theory

In spite of simplifications, it is still not possible in general to compute

$$Z = e^{-\beta F_0} \int \mathcal{D}m(\vec{r}) \, \exp\left[-\beta \mathcal{R}[m(\vec{r})] + \beta \int d\vec{r} \, m(\vec{r}) B(\vec{r}) \right]$$

First step: saddle-point approximation where integrand is replaced by its maximum value

↳ most probable configuration of the field $m(\vec{r})$

↳ m is then uniform, which opens for a simple discussion of thermodynamics

$$F_{s.p.} = F_0 + kT \, V \min_m \left[\frac{1}{2} a_2 m^2 + \frac{1}{4} a_4 m^4 - Bm \right]$$ s.p. ≡ saddle point ≡ mean-field

This captures the behavior of a phase transition: while $\mathcal{R}[m]$ is analytic (polynomial), taking the min to get F_{sp} is not an analytic procedure → introduces singularities.

The saddle pt is justified by thermodynamic limit where $V \to \infty$. Yet, we have to keep in mind that fluctuations beyond the saddle point have been neglected, and can play a key role.

$$F_{sp}(\cancel{m}) = \cancel{F_0} + kT \min_m \Big[\overbrace{\frac{a_2}{2} m^2 + \frac{a_4}{4} m^4 - mB}^{\Psi(m)} \Big]$$

The behavior depends strongly on the sign of a_2

and along the critical isotherm $(T=T_c)$: $a_4 (m^*)^3 = B \Rightarrow \boxed{\delta = 3}$

To get the last two missing critical exponents, we can compute the correlation function as well. To this end, we can remember a microscopic identity, in a system with hamiltonian $\mathcal{H} = \mathcal{H}_0(S_1, \dots S_N) - \sum_{i=1}^{N} B_i S_i$

$$\langle S_i \rangle = \left.\frac{\partial \ln Z}{\partial (\beta B_i)}\right|_T$$

exercise

$$\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle = \left.\frac{\partial^2 \ln Z}{\partial \beta B_i \partial \beta B_j}\right|_T = \left.\frac{\partial \langle S_i \rangle}{\partial \beta B_j}\right|_T \rightarrow \text{generalized susceptibility}$$

This transposes here to

$$G(\vec{r}, \vec{r}\,') \equiv \langle m(\vec{r}) m(\vec{r}\,') \rangle - \langle m(\vec{r}) \rangle \langle m(\vec{r}\,') \rangle = \frac{\delta\, m^*(\vec{r})}{\beta\, \delta B(\vec{r}\,')}$$

no $\langle\ \rangle$ since no fluctuations accounted for here

With the chosen function, we get the following equation of state for the most probable magnetization profile $m^*(\vec{r})$:

$$\beta R[m] = \int d\vec{r} \left[\frac{1}{2} a_2 m^2(\vec{r}) + \frac{1}{4} a_4 m^4(\vec{r}) + \frac{1}{2} b (\vec{\nabla} m)^2 - B(\vec{r}) m(\vec{r}) \right]$$

$- \int m B$

$$\Rightarrow \frac{\delta R[m(\vec{r})]}{\delta m(\vec{r})} = B(\vec{r}) = a_2 m^*(\vec{r}) + a_4 m^{*3}(\vec{r}) - b \nabla^2 m^*$$

(and it appears that it is simpler to compute $\frac{\delta B(\vec{r})}{\delta m^*(\vec{r})}$ rather than its inverse $\frac{\delta m^*(\vec{r})}{\delta B(\vec{r}\,')}$)

$$\left(\frac{\delta}{\delta B(\vec{r}\,')} \rightarrow kT \delta(\vec{r} - \vec{r}\,') = a_2 G^{-1}(\vec{r}, \vec{r}\,') + a_4 m^{*2} 3 G^{-1}(\vec{r}, \vec{r}\,') - b \nabla^2 G^{-1} \right)$$

$$\frac{\delta}{\delta m(\vec{r}\,')} \rightarrow kT\, G^{-1}(\vec{r}, \vec{r}\,') = (a_2 + 3 a_4 m^{*2} - b \nabla^2)\, \delta(\vec{r} - \vec{r}\,')$$

We finish the calculation in a homogeneous system where m^* does not depend on space, with $\vec{B} = \vec{0}$, by solving the differential equation:

$$G(\vec{r}, \vec{r}\,') = \int \frac{d\vec{q}}{(2\pi)^d} \frac{\exp(-i \vec{q} \cdot \vec{r})}{\underbrace{a_2 + 3a_4 m^{*2}}_{b\, \xi^{-2}} + b q^2} \underset{r \to \infty}{\propto} e^{-r/\xi}$$

$$\Rightarrow \xi \propto |T - T_c|^{-1/2} \quad \text{and at } T_c : G(r) \propto \frac{1}{r^{d-2}} \quad \text{(Coulomb pot)}$$

$$\Rightarrow \quad \nu = 1/2 \qquad\qquad \eta = 0$$

⚠ $G(r) \underset{r \to \infty}{\sim} \frac{1}{r^{d-2}} e^{-r/\xi}$ is WRONG $\rightarrow G \underset{\infty}{\sim} \frac{1}{r^{(d-1)/2}} e^{-r/\xi}$

Yet: $G(\vec{r}) = \frac{1}{r^{d-2}} \varphi(\kappa r)$, scaling form, is right.

and along the critical isotherm $(T=T_c)$: $a_4 (m^*)^3 = B \Rightarrow \boxed{\delta = 3}$

To get the last two missing critical exponents, we can compute the correlation function as well. To this end, we can remember a microscopic identity, in a system with hamiltonian $\mathcal{H} = \mathcal{H}_0 (S_1, \dots S_N) - \sum_{i=1}^{N} B_i S_i$

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$- \int m B$

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$$\frac{\delta}{\delta m(\vec{r}\,')} \rightarrow kT\, G^{-1}(\vec{r}, \vec{r}\,') = \left(a_2 + a_4\, m^{*2} - b \nabla^2 \right) \delta(\vec{r} - \vec{r}\,')$$

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$\longrightarrow$ Conclusion

We can notice that the validity of mean-field prediction improves when $d \nearrow$

	α	β	γ	δ	η	ν
Ising 2d	0-log	1/8	7/4	15	1/4	1
Ising 3d	0,11	0,33	1,24	5,2	0,03	0,63
Mean-field	0-dis	1/2	1	3	0	1/2

We will discuss what goes wrong with mean-field, but it is useful here to anticipate, with the following reformulation. In presence of a magnetic field, we introduced

$$Z[B(\vec{r})] = \int \mathcal{D}m(\vec{r})\; e^{-\beta \mathcal{R}[m(\vec{r})] + \beta \int B(\vec{r}) m(\vec{r}) d\vec{r}}$$

$$F[B(\vec{r})] = -kT \ln Z[B(\vec{r})] \quad ; \quad \frac{\delta F}{\delta B(\vec{r})} = -\langle m(\vec{r}) \rangle$$

Let us introduce the Legendre transform

$$\widetilde{F}[m(\vec{r})] = F[B(\vec{r})] + \int B(\vec{r}) m(\vec{r}) d\vec{r} \quad ; \quad \frac{\delta \widetilde{F}}{\delta m(\vec{r})} = B(\vec{r})$$

$\widetilde{F}$ is the free energy, fluctuations included, when $B(\vec{r})$ is such that the resulting magnetization is the chosen argument of the functional. $\widetilde{F} \neq \mathcal{R}$, since $\mathcal{R}$ does not include/account for fluctuations.

$\widetilde{F}[m(\vec{r})]$ is not analytic, includes fluctuations, and rules thermodynamics

$\mathcal{R}[m(\vec{r})]$ is analytic (as assumed by Landau), no fluctuations, does not rule ″