What went wrong with mean field solution?

We said that need $N \to \infty$ degrees of freedom to have a phase transition — but mean field theory is essentially a theory with only <u>one</u> degree of freedom — the order parameter. The singular behavior in the mean field theory comes when we "fix" the mean field solution using the Maxwell construction. But there is no true consideration of the many degrees of freedom which give <u>fluctuations</u> around the average value of the order parameter m

For Ising model, $\chi = \frac{dm}{dh} \to \infty$ at T_c

Now $\quad m = -\frac{\partial g}{\partial h} \Rightarrow \chi = -\frac{\partial^2 g}{\partial h^2} = \frac{1}{N} k_B T \frac{\partial^2 \ln Z}{\partial h^2}$

$$\chi = \frac{k_B T}{N}\left\{\frac{1}{Z}\frac{\partial^2 Z}{\partial h^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial h}\right)^2\right\}$$

$$Z = \int_{\{s_i\}} e^{-\beta H + \beta h M} \qquad \frac{\partial Z}{\partial h} = \int e^{-\beta H + \beta h M} (\beta M)$$

$$\frac{\partial^2 Z}{\partial h^2} = \int e^{-\beta H + \beta h M} (\beta M)^2$$

$$\chi = \frac{k_B T}{N}\beta^2 \left\{\langle M^2 \rangle - \langle M \rangle^2\right\} \qquad M = Nm$$

$$\chi = \frac{1}{k_B T}\,\frac{\langle M^2 \rangle - \langle M \rangle^2}{N}$$

fluctuation in total magnetization M

$m = M/N$ magnetization density

$$\chi = \frac{N}{k_B T} \left\{ \langle m^2 \rangle - \langle m \rangle^2 \right\}$$

For $T \neq T_c$, χ is finite as $N \to \infty$ in the thermodynamic limit

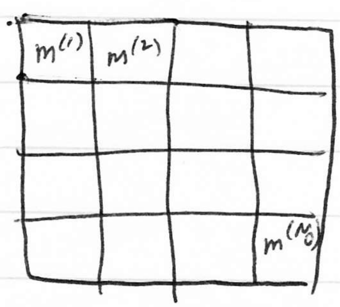
$$\Rightarrow \langle m^2 \rangle - \langle m \rangle^2 \sim \frac{1}{N}$$

or fluctuations in magnetization density

$$\sqrt{\langle m^2 \rangle - \langle m \rangle^2} \sim \frac{1}{\sqrt{N}} \to 0 \quad \text{as} \quad N \to \infty$$

We can understand the $1/\sqrt{N}$ dependence as follows.

Imagine we subdivide our total system into N_0 subsystems. If each subsystem is sufficiently large we can expect the subsystems will be behaving independently of one another. $\Rightarrow$ the



measured magnetization densities $m^{(i)}$ in each subsystem (i) would be a set of N_0 independent and identically distributed random variables. ~~the~~ If the total system average is the average of these $m^{(i)}$, $m = \frac{1}{N_0} \sum_i m^{(i)}$, then the variance of m is the variance of $m^{(i)}$ divided by N_0. So the standard deviation of m, $\sqrt{\langle m^2 \rangle - \langle m \rangle^2} \propto \frac{1}{\sqrt{N_0}}$.

Now as long as the influence of the subsystem at position $\vec{r}$ is no longer felt at a finite distance ξ away, one can choose the size of each subsystem to be ξ^d (d = dimensionality) and $N_0 = \frac{N}{\xi^d}$ so $\sqrt{\langle m^2 \rangle - \langle m \rangle^2} \propto \sqrt{\frac{\xi^d}{N}}$

$$\propto \frac{1}{\sqrt{N}}$$

For $\underline{T = T_c}$ however, $\chi \to \infty$ as $N \to \infty$

$\Rightarrow$ $\sqrt{\langle m^2 \rangle - \langle m \rangle^2}$ <u>does not</u> vanish as quickly as $1/\sqrt{N}$ as $N \to \infty$.

$\Rightarrow$ above arguement about considering independent subsystems cannot apply.

$\Rightarrow$ the length scale ξ that describes how far the system is correlated in space must <u>diverge</u> as $T \to T_c$!

<u>At $T \neq T_c$</u>, the state of the system $m(\vec{r})$ at position $\vec{r}$ has no effect on the state of the system at $\vec{r} + \vec{r}_0$ if $\vec{r}_0$ is sufficiently large, $|\vec{r}_0| \gg \xi$. <u>At $T = T_c$</u> the state of the system at $\vec{r}$ influences the state of the system throughout its entire volume, $\xi \to \infty$!

Landau Theory of Phase transitions

We saw that all the singular behavior near T_c in the mean-field solution to the Ising model follows from assuming the following simple form for the Helmholtz free energy density

$$f(m,T) = a\,m^2 + b\,m^4$$

with b a constant and $a = a_0(T - T_c)$

so $a < 0$ for $T < T_c$, and $a > 0$ for $T > T_c$

We call m the "order parameter" of the transition at $h=0$. In the high temperature phase – the disordered phase – $m = 0$. In the low temperature phase – the ordered phase – $m \neq 0$.

For the Ising model, the order parameter is just the equilibrium magnetization $m_0(T)$. As another example, for the liquid-gas transition, the jump in particle density $\Delta n(T)$ as one crosses the 1st order liquid to gas transition line could be taken as the order parameter.

Since the order parameter $m(T)$ should vanish continuously as $T \to T_c$ from below, Landau said that one should just assume that $f(m,T)$ can be expanded as a power series in m, keeping only terms that have the desired symmetry. Since we expect $f(m,T) = f(-m,T)$ for the Ising model, we then get

$$f(m,T) = a\,m^2 + b\,m^4 + \text{constant}$$

as the leading terms.

odd powers of m vanish by symmetry

The Gibbs free energy density is then given by

$$g(h, T) = \min_m \left[f(m,T) - hm \right]$$

where h is the "ordering field" conjugate to the order parameter m.

When one assumes that the coefficients a, b have temperature dependence $b \simeq \text{const}$, $a \simeq a_0(T-T_c)$ near T_c, then one recovers all the results of mean-field theory for behavior near T_c.

We can use this approach to treat other problems. For n-component spin with $\vec{m} = \frac{1}{N}\sum_i \vec{S}_i$ we would have $f(\vec{m}, t) = f_0 + a|\vec{m}|^2 + b|\vec{m}|^4$ to lowest order provided we assume the system has rotational symmetry and so depends only on $|\vec{m}|$ and not the orientation of $\vec{m}$
$\Rightarrow$ behavior comes out the same as for the Ising model!

But we can get interesting behaviors by doing other things. Suppose we assumed

$$f(m,T) = f_0 + am^2 - bm^4 + cm^6 \qquad \text{with } b > 0.$$

quartic term negative $\Rightarrow$ need m^6 term to give stability so that minimizing value of m is finite

This turns out to describe a tricritical point where a line of 1st order phase transitions becomes a line of 2nd order phase transitions. This behavior is observed in an Ising antiferromagnet in an external magnetic field.

Now we want to go beyond the Landau approach to try and include the effects of fluctuations in m away from the mean-field value. This gives the <u>Landau - Ginzburg</u> approach.

We assume that the configurations we should consider can be written in terms of small, spatially varying fluctuations away from the mean field m_0

$$m(\vec{r}) = m_0 + \delta m(\vec{r})$$

We then construct a free energy functional $F[m(\vec{r})]$ that tells us the weight of the config $m(\vec{r})$ in the statistical ensemble

$$F[m(\vec{r})] = \int d^d r \left\{ a m^2 + b m^4 + c |\vec{\nabla} m|^2 \right\}$$

integration in d-dimensional space

new term that gives cost in energy for a spatially varying $m(\vec{r})$

The goal is then to construct the partition function

$$Z = \int_{\delta m(\vec{r})} e^{-\beta F[m(\vec{r})]}$$

by integrating over all possible small fluctuation $\delta m(\vec{r})$. In this way we can explore the effects that small fluctuations have on the mean field solution.

Landau-Ginzburg approach

Order parameter may vary slowly in space to represent a fluctuation from a perfectly ordered system.

free energy functional — general d-dimensional space

$$F[m(\vec{r})] = \int d^d r \left\{ a m^2 + b m^4 + c |\vec{\nabla} m|^2 \right\}$$

where $a = a_0 (T - T_c)$ vanishes at T_c as before

b = constant

c = constant — measures stiffness to spatial variations in $m(\vec{r})$.

Consider small fluctuations away from the mean field solution m_0. $m_0 = 0$ for $T > T_c$, $m_0 = \sqrt{\dfrac{a_0 (T_c - T)}{2b}}$ for $T < T_c$

$m(\vec{r}) = m_0 + \delta m(\vec{r})$ expand F to $o(\delta m^2)$

$$F[m(\vec{r})] = \int d^d r \{ a m_0^2 + 2 a m_0 \delta m + a \delta m^2 + b m_0^4 + 4b m_0^3 \delta m + 6b m_0^2 \delta m^2 + c |\vec{\nabla} \delta m|^2 \}$$

the constant terms $a m_0^2 + b m_0^4$ give the mean field free energy.

the linear terms $(2 a m_0 + 4 b m_0^3) \delta m$ vanish because m_0 minimizes F. use $m_0^2 = -\dfrac{2a}{b}$

The remaining quadratic terms are

$$\delta F = \int d^d r \left\{ [a + 6bm_0^2] \delta m^2 + c |\vec{\nabla} \delta m|^2 \right\}$$

integral is over vol L^d let $a' \equiv a + 6bm_0^2$

Fourier transforms

$$\delta m(\vec{r}) = \frac{1}{L^{d/2}} \sum_q e^{i\vec{q}\cdot\vec{r}} \delta m_q$$

sum over all q s.t. $q_\mu = \frac{2\pi n_\mu}{L}$, n_μ integer

$$\delta m_q = \frac{1}{L^{d/2}} \int d^d r \, e^{-i\vec{q}\cdot\vec{r}} \delta m(\vec{r})$$

Then

$$\delta F = \frac{1}{L^{d/2}} \frac{1}{L^{d/2}} \sum_q \sum_{q'} [a' - c\vec{q}\cdot\vec{q}'] \delta m_q \delta m_{q'} \times \underbrace{\int d^d r \, e^{i(\vec{q}+\vec{q}')\cdot\vec{r}}}_{L^d \delta(\vec{q}+\vec{q}')}$$

$$\boxed{\delta F = \sum_q [a' + cq^2] \delta m_q \delta m_{-q}}$$

<u>Correlation function</u>

To average over fluctuations we should compute the partition function averaged over $\delta m(\vec{r})$

$$Z = \int_{\{m(\vec{r})\}} e^{-\beta F[m(\vec{r})]}$$

and Gibbs free energy at $h=0$ $G(h=0,T) = -k_B T \ln Z$

$$Z = \prod_r \int_{-\infty}^{\infty} d\delta m(\vec r)\, e^{-\beta \delta F[\delta m(\vec r)]}$$

↑ integrate over all values of $\delta m(\vec r)$ at all positions $\vec r$

Now lets transform variables of integration from

$$\{\delta m(\vec r)\} \to \{\delta m_q\}$$

Our Fourier transforms were defined so that the Jacobian of this transformation is unity.

$$Z = \prod_q \int d\delta m_q\, e^{-\beta \delta F[\delta m_q]}$$

Note however that δm_q is complex $\Rightarrow$ $\delta m_q = \underset{\text{real part}}{\delta m_{1q}} + i\,\underset{\text{complex part}}{\delta m_{2q}}$

Since $\delta m(\vec r)$ is real $\Rightarrow$ $\delta m_q^* = \delta m_{-q}$, so δm_q and δm_{-q} are <u>not</u> independent. When we integrate over δm_q we should therefore integrate over real values δm_{1q} and δm_{2q} but restrict $\vec q$ to $q_z > 0$ so as not to double count δm_q and δm_{-q}.

$$Z = \left(\prod_{\substack{q \\ \text{st } q_z > 0}} \int_{-\infty}^{\infty} d\delta m_{1q} \int_{-\infty}^{\infty} d\delta m_{2q}\right) e^{-\beta \delta F[\delta m_{1q} + i\delta m_{2q}]}$$

Use

$$\delta F = \sum_{\vec q} (a' + cq^2)\, \delta m_q \delta m_{-q}$$

$$= \sum_{\vec q} (a' + cq^2)\left(\delta m_{1q}^2 + \delta m_{2q}^2\right)$$

$$= 2 \sum_{\substack{\vec q \\ \text{st } q_z > 0}} (a' + cq^2)\left(\delta m_{1q}^2 + \delta m_{2q}^2\right)$$

since we restricted sum to $q_z > 0$ we multiply by 2 to include $q_z < 0$ terms now use exponential of sum = product of exponentials

$$\Rightarrow \quad Z = \prod_{\substack{q \\ \text{st } q_z > 0}} \left[\int_{-\infty}^{\infty} d\delta m_{1q} \int_{-\infty}^{\infty} d\delta m_{2q} \, e^{-2\beta(a' + cq^2)(\delta m_{1q}^2 + \delta m_{2q}^2)} \right]$$

$\Rightarrow$ Correlation function – how big is fluctuation δm_q on average?

$$\langle \delta m_q \delta m_{-q} \rangle = \langle \delta m_{1q}^2 + \delta m_{2q}^2 \rangle$$

$$= \frac{\int_{-\infty}^{\infty} d\delta m_{1q} \int_{-\infty}^{\infty} d\delta m_{2q} \, e^{-2\beta(a'+cq^2)(\delta m_{1q}^2 + \delta m_{2q}^2)} (\delta m_{1q}^2 + \delta m_{2q}^2)}{\int_{-\infty}^{\infty} d\delta m_{1q} \int_{-\infty}^{\infty} d\delta m_{2q} \, e^{-2\beta(a'+cq^2)(\delta m_{1q}^2 + \delta m_{2q}^2)}}$$

$$= \underbrace{\frac{1}{4\beta(a'+cq^2)}}_{\langle \delta m_{1q}^2 \rangle} + \underbrace{\frac{1}{4\beta(a'+cq^2)}}_{\langle \delta m_{2q}^2 \rangle} = \frac{1}{2} \frac{k_B T}{(a'+cq^2)}$$

<u>Real space correlation function</u> is then

$$\langle \delta m(\vec{r}) \delta m(0) \rangle = \frac{1}{L^{d/2}} \frac{1}{L^{d/2}} \sum_q \sum_{q'} e^{i\vec{q}\cdot\vec{r}} \langle \delta m_q \delta m_{q'} \rangle$$

Because δF involves only $\delta m_q \delta m_{-q} = \delta m_{1q}^2 + \delta m_{2q}^2$,
$\langle \delta m_q \delta m_{q'} \rangle = 0$ unless $q' = -q$

$$\langle \delta m(\vec{r}) \delta m(0) \rangle = \frac{1}{L^d} \sum_q e^{i\vec{q}\cdot\vec{r}} \langle \delta m_q \delta m_{-q} \rangle$$

$$= \frac{1}{L^d} \sum_q e^{i\vec{q}\cdot\vec{r}} \frac{1}{2} \frac{k_B T}{a'+cq^2}$$

continuum limit $L \to \infty$

$$= \int \frac{d^d q}{(2\pi)^d} e^{i\vec{q}\cdot\vec{r}} \frac{1}{2} \frac{k_B T}{a'+cq^2}$$

$$\sim \frac{e^{-r/\xi}}{r^{d-2}}$$ Ornstein - Zernicke form

where $\xi = \sqrt{\frac{c}{a'}}$ is the "correlation length"

ξ gives the length scale over which fluctuations $\delta m(\vec{r})$ decay

This result for ξ comes from the integral having its poles at $|\vec{q}| = \pm i \sqrt{a'/c}$

For $T > T_c$, $a' = a = a_0(T - T_c)$ since $m_0 = 0$

$$\xi \sim \frac{1}{\sqrt{a'}} \sim \frac{1}{\sqrt{T - T_c}} \sim \frac{1}{|t|^{\nu}} \quad \text{with } \nu = 1/2$$

ν is called the correlation length exponent

For $T < T_c$,
$$\begin{aligned} a' &= a + 6b m_0^2 \\ &= a - 6b\left(\frac{a}{2b}\right) = -2a \\ &= 2a_0(T_c - T) \end{aligned}$$

$$\xi \sim \frac{1}{\sqrt{a'}} \sim \frac{1}{\sqrt{T_c - T}} \sim \frac{1}{|t|^{\nu}} \quad \text{with } \nu = 1/2$$

As $T \to T_c$ the correlation length diverges.
Since fluctuations propagate out a distance $\xi \to \infty$ one can never divide the system up into independent boxes on any finite length scales.
This is why $\sqrt{\langle m^2 \rangle - \langle m \rangle^2}$ does not vanish as $\frac{1}{\sqrt{N}}$ at T_c. $\Rightarrow$ fluctuations can be important at the critical point

Contribution of fluctuations to the total free energy

$$\delta F = \sum_{\vec{q}} (a' + cq^2)\, \delta m_q\, \delta m_{-q}$$

$$= 2 \sum_{\substack{\vec{q} \\ \text{st } q_z > 0}} (a' + cq^2)(\delta m_{1q}^2 + \delta m_{2q}^2)$$

$$Z = \prod_{\substack{\vec{q} \\ \text{st } q_z > 0}} \left[\int_{-\infty}^{\infty} d\,\delta m_{1q} \int_{-\infty}^{\infty} d\,\delta m_{2q}\, e^{-2\beta (a' + cq^2)(\delta m_{1q}^2 + \delta m_{2q}^2)} \right]$$

$$= \prod_{\substack{\vec{q} \\ \text{st } q_z > 0}} \underbrace{\left[\frac{2\pi}{4\beta (a' + cq^2)} \right]^{1/2}}_{\text{from } \delta m_{1q}} \underbrace{\left[\frac{2\pi}{4\beta (a' + cq^2)} \right]^{1/2}}_{\text{from } \delta m_{2q}}$$

$$= \prod_{\substack{\vec{q} \\ \text{st } q_z > 0}} \left[\frac{\pi}{2} \frac{k_B T}{a' + cq^2} \right]$$

Gibbs free energy due to fluctuations

$$\delta G = -k_B T \ln Z = -k_B T \sum_{\substack{\vec{q} \\ \text{st } q_z > 0}} \ln\left(\frac{\pi}{2} \frac{k_B T}{a' + cq^2} \right)$$

$$= -\frac{k_B T}{2} \sum_{\vec{q}} \ln\left(\frac{\pi}{2} \frac{k_B T}{a' + cq^2} \right)$$

now sum over all $\vec{q}$, so multiply by $\frac{1}{2}$

$$= -\frac{k_B T}{2} L^d \int \frac{d^d q}{(2\pi)^d} \ln\left(\frac{\pi}{2} \frac{k_B T}{a' + cq^2} \right)$$

Contribution to specific heat per volume δc

$$\delta c = -\frac{T}{L^d}\frac{\partial^2 \delta G}{\partial T^2}$$

Consider $T > T_c$ so $a' = a_0(T - T_c)$

(result will be similar for $T < T_c$ where $a' = 2a_0(T_c - T)$)

$$\frac{1}{L^d}\frac{\partial \delta G}{\partial T} = -\frac{k_B}{2}\int\frac{d^dq}{(2\pi)^d}\ln\left(\frac{\pi}{2}\frac{k_B T}{a' + cq^2}\right)$$

$$-\frac{k_B T}{2}\int\frac{d^dq}{(2\pi)^d}\left\{\frac{1}{T} - \frac{a_0}{a' + cq^2}\right\}$$

comes from T dependence of $a' = a_0(T - T_c)$

$$\frac{1}{L^d}\frac{\partial^2 \delta G}{\partial T^2} = -\frac{k_B}{2}\int\frac{d^dq}{(2\pi)^d}\left\{\frac{1}{T} - \frac{a_0}{a' + cq^2}\right\}$$

$$+\frac{k_B}{2}\int\frac{d^dq}{(2\pi)^d}\frac{a_0}{a' + cq^2}$$

$$-\frac{k_B T}{2}\int\frac{d^dq}{(2\pi)^d}\frac{a_0^2}{(a' + cq^2)^2}$$

$$\delta c = \frac{k_B}{2}\int\frac{d^dq}{(2\pi)^d}\left\{1 - \frac{2Ta_0}{a' + cq^2} + \frac{T^2 a_0^2}{(a' + cq^2)^2}\right\}$$

this gives classical $\frac{1}{2}k_B$ per degree of freedom

corrections due to T-dependence of $a(T)$ in δF

To see how the integrals behave as $T \to T_c$

$$I_1 = \int d^d q \, \frac{a_0}{a_0 t + c q^2} \quad \text{where } t = T - T_c$$

let $q^2 = t q'^2$

$$I_1 = t^{d/2} \int d^d q' \, \frac{a_0}{a_0 t + c t q'^2} = t^{\frac{d}{2}-1} \underbrace{\int d^d q' \, \frac{a_0}{a_0 + c q'^2}}_{\text{just some number}}$$

$$I_1 \sim t^{\frac{d}{2}-1} = t^{\frac{d-2}{2}} \propto \xi^{2-d}$$

$$(\text{since } \xi \sim t^{-1/2})$$

Similarly

$$I_2 = \int d^d q \, \frac{a_0^2}{(a_0 t + c q^2)^2} \propto t^{\frac{d}{2}-2} = t^{\frac{d-4}{2}} \propto \xi^{4-d}$$

The second integral is the more singular one

For mean field theory to be valid as $T \to T_c$, we want the correction δC to be small compared to C_{MF} the mean field value.

In mean field theory, $C_{MF} \sim$ finite at T_c

$$\delta C \sim t^{\frac{d-4}{2}}$$

δC will diverge whenever $d < 4$

$\Rightarrow$ $d > 4 \Rightarrow$ fluctuations negligible
mean field theory gives correct critical exponents

$d < 4 \rightarrow$ fluctuations give singular corrections
mean field theory breaks down
$\Rightarrow$ Renormalization Group approach.

$d_c = 4$ is called the upper critical dimension
the value of d_c can vary with the symmetry of $F[m(r)]$.
$d_c = 4$ for spherically symmetric
n component spin models
mean field theory is OK only when $d > d_c$

Also a lower critical dimension - depends on n
For $d <$ lower critical dimension, there is no phase transition at finite temperature