Title: Statistical Mechanics (PHYS 602) - Lecture 13

Date: Oct 15, 2009 10:30 AM

URL: http://pirsa.org/09100137

Abstract:

more is the same

one spin

statistical average: $<\sigma> = \tanh h$

many spins

focus on one spin

$$-H_{eff} / (kT) = \sigma_r\left[h_r + K\sum_s <\sigma_s>\right]$$

statistical average:

$$h_{eff} = [h + Kz <\sigma>]$$

z=number of nn

$$<\sigma> = \tanh(h_{eff})$$

or, if there is space variation, $h_{eff} = h_r + K\sum_{s\ nn\ to\ r} <\sigma_s>$
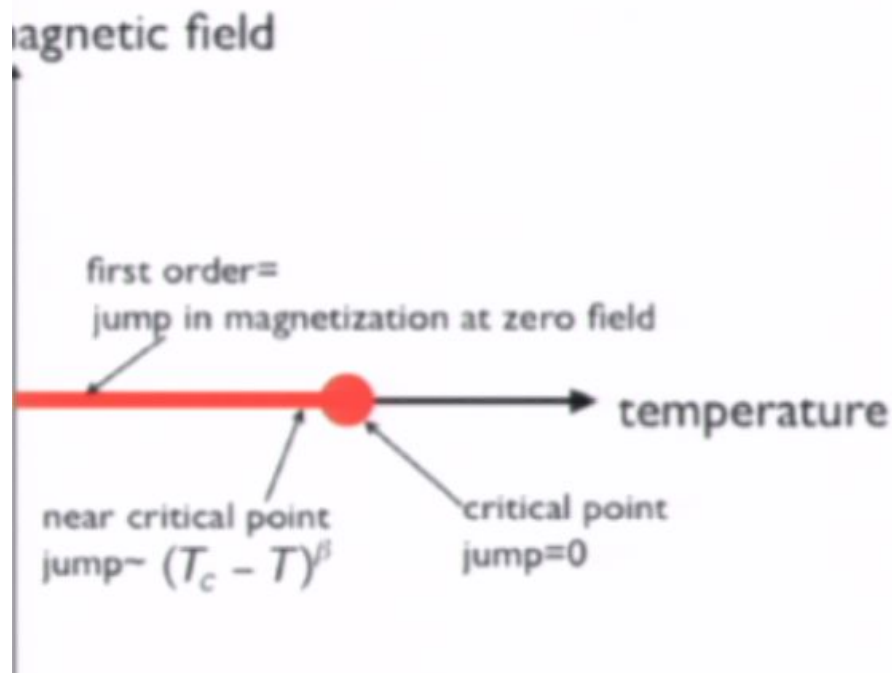
Mean Field Theory is Only Partially Right

Mean field theory says that spin moves in the average field produced by all other spins. But actual value is often larger in magnitude than mean value and fluctuates in sign. Net result is error, with unknown sign. The same ideas can be applied to lots of problems. (In particle physics mean field theory often goes with the words "one loop approximation" or "tadpole diagram".)

As we shall discuss in detail, mean field theory gives an interesting and instructive theory of phase transitions, but one which is only partially right. Near the critical point, for lower dimensional systems, including three dimensions, fluctuations dominate the system behavior and mean field theory gives the wrong answer, badly wrong. Very near first order phase transitions, fluctuations also count, but in a less obvious manner.

However in high dimensions, usually above four, mean field theory gives a good picture of phase transitions. It also has features which point the way toward the right theory. It is also simple to use

simplified phase diagram for ferromagnet

magnetic field

first order=
jump in magnetization at zero field

temperature

near critical point
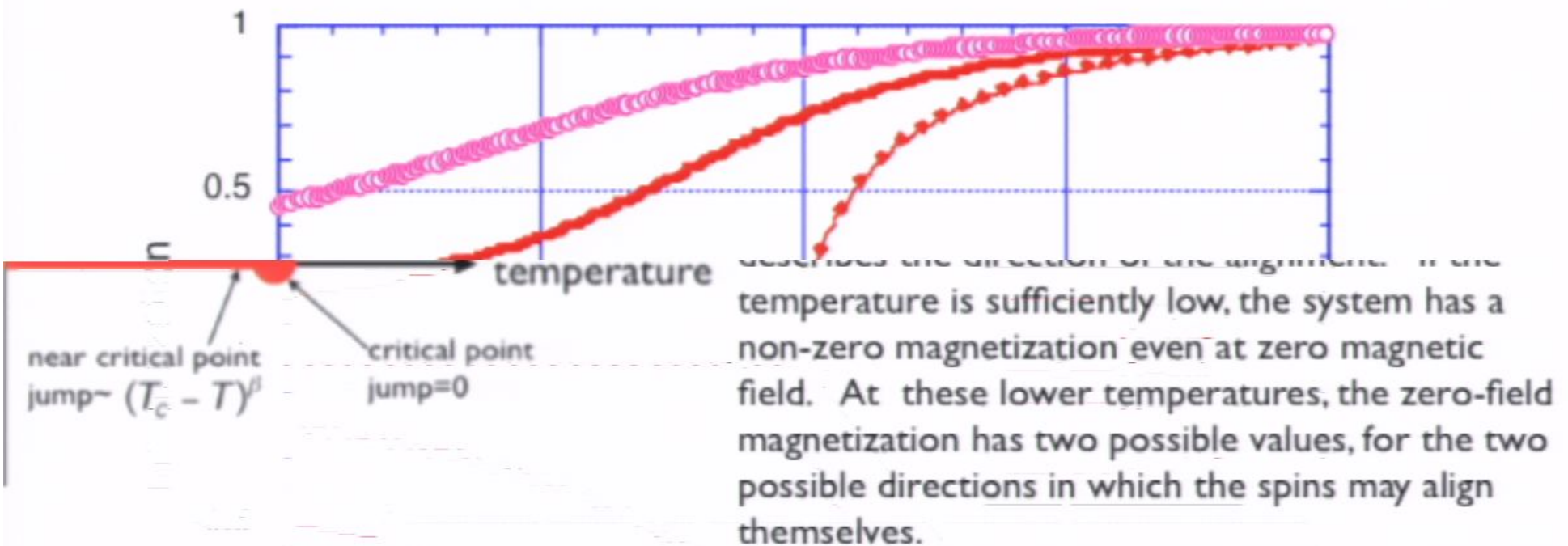jump~ $(T_c - T)^\beta$

critical point
jump=0

The basic variables defining the state of the system are the magnetic field and the temperature. We describe what is happening by looking at the magnetization. The magnitude of the magnetization measures the extent to which the spins in the system are lined up with each other. Its sign describes the direction of the alignment. If the temperature is sufficiently low, the system has a non-zero magnetization even at zero magnetic field. At these lower temperatures, the zero-field magnetization has two possible values, for the two possible directions in which the spins may align themselves.

The heavy line is the locus of points at which this spontaneous magnetization is non-zero. As one crosses this line, there is a discontinuous jump in the magnetization, which maintains its magnitude but reverses its direction. This jump is a first order phase transition. Typically, this jump decreases in size as the temperature gets higher until, at some critical point, the jump goes continuously to zero. This point is then the position of a continuous phase transition.
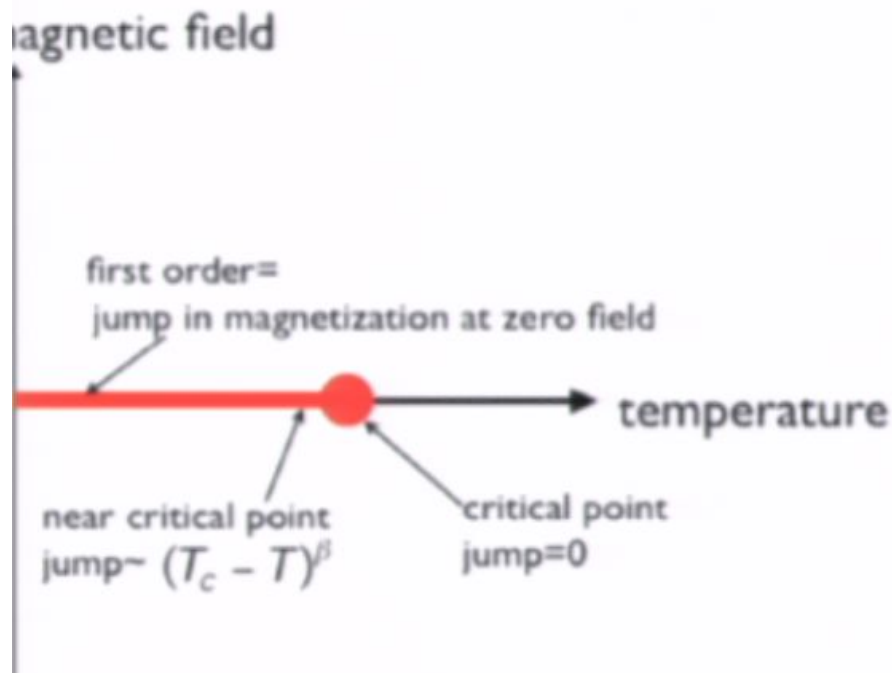
order parameter in mean field transition

legend "H" should be h

Graph axes: 1, 0.5 on vertical; temperature (horizontal)

near critical point
jump~ $(T_c - T)^\beta$

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describes the direction of the alignment. If the temperature is sufficiently low, the system has a non-zero magnetization even at zero magnetic field. At these lower temperatures, the zero-field magnetization has two possible values, for the two possible directions in which the spins may align themselves.

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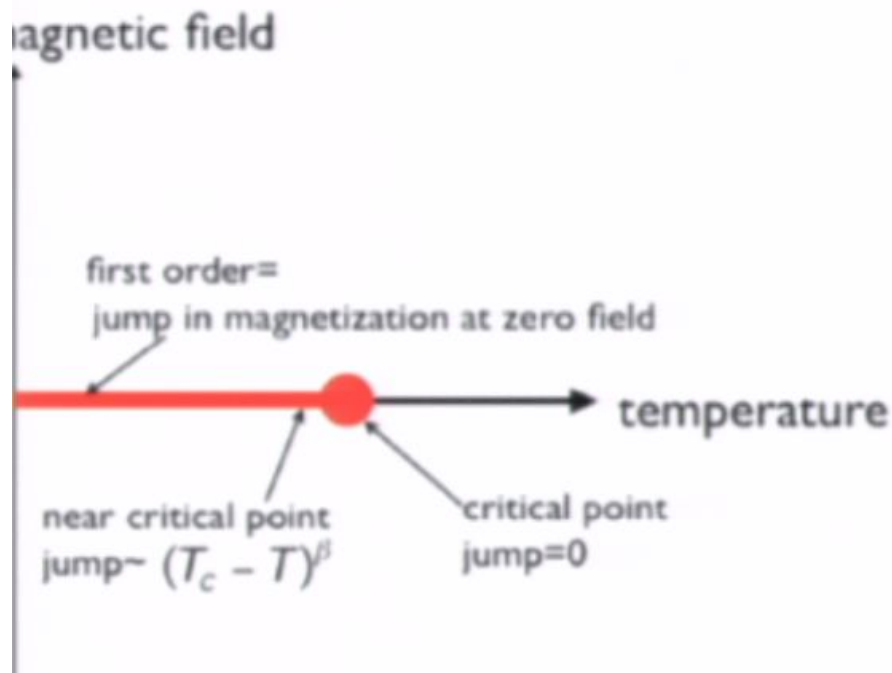
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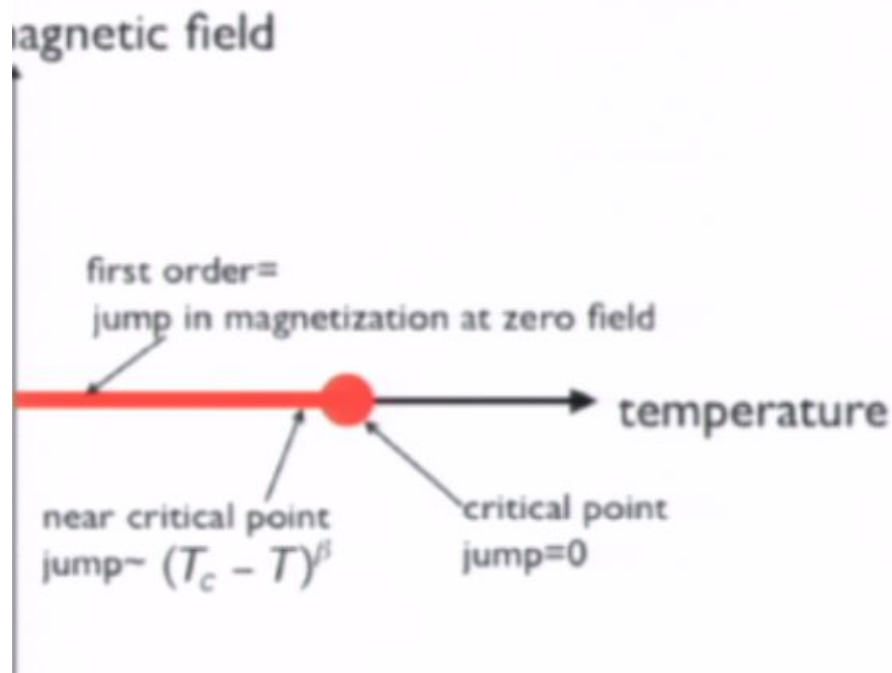
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$$K_z = \frac{T_-}{T_-}$$

simplified phase diagram for ferromagnet

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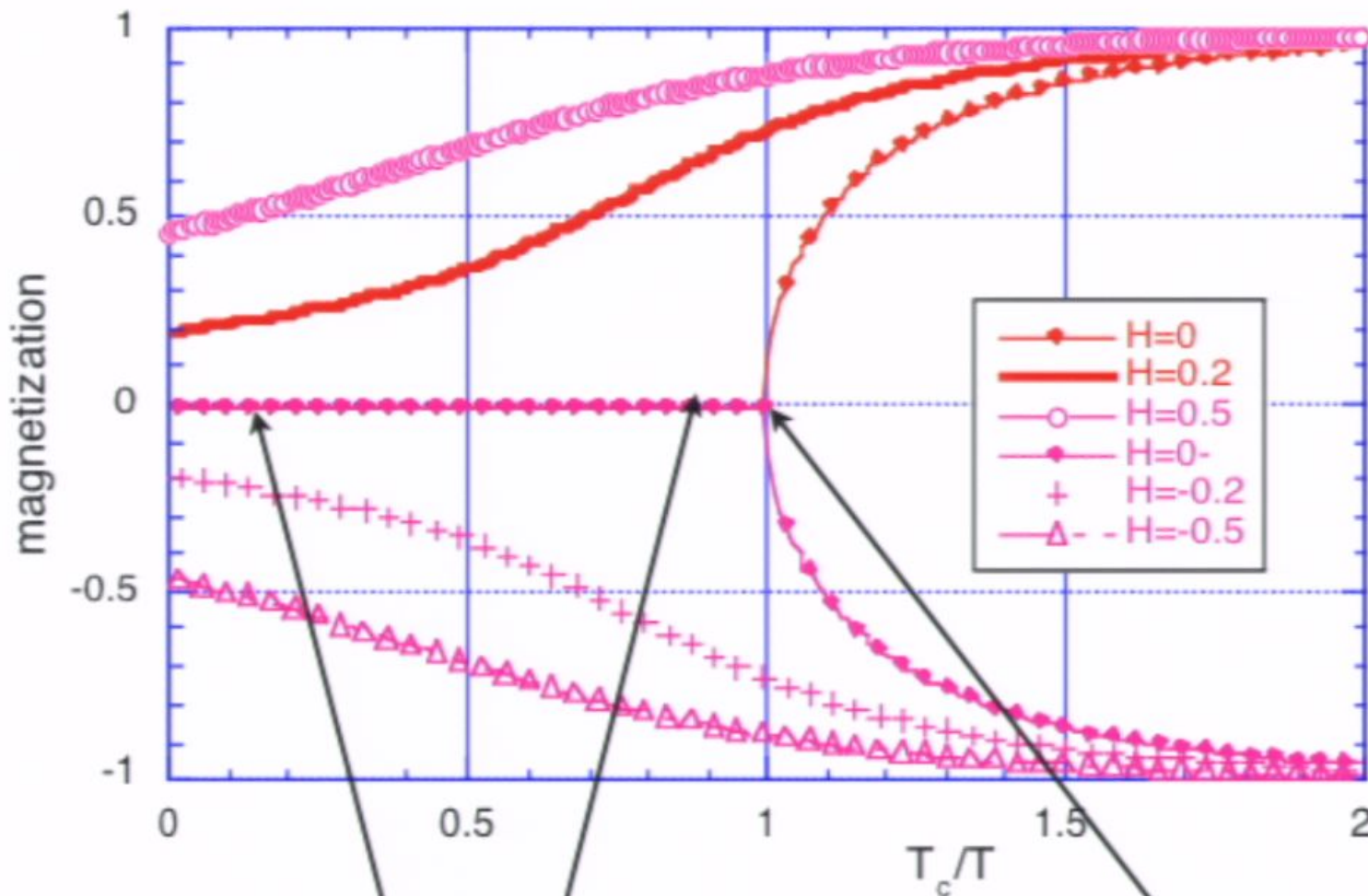jump~ $(T_c - T)^\beta$

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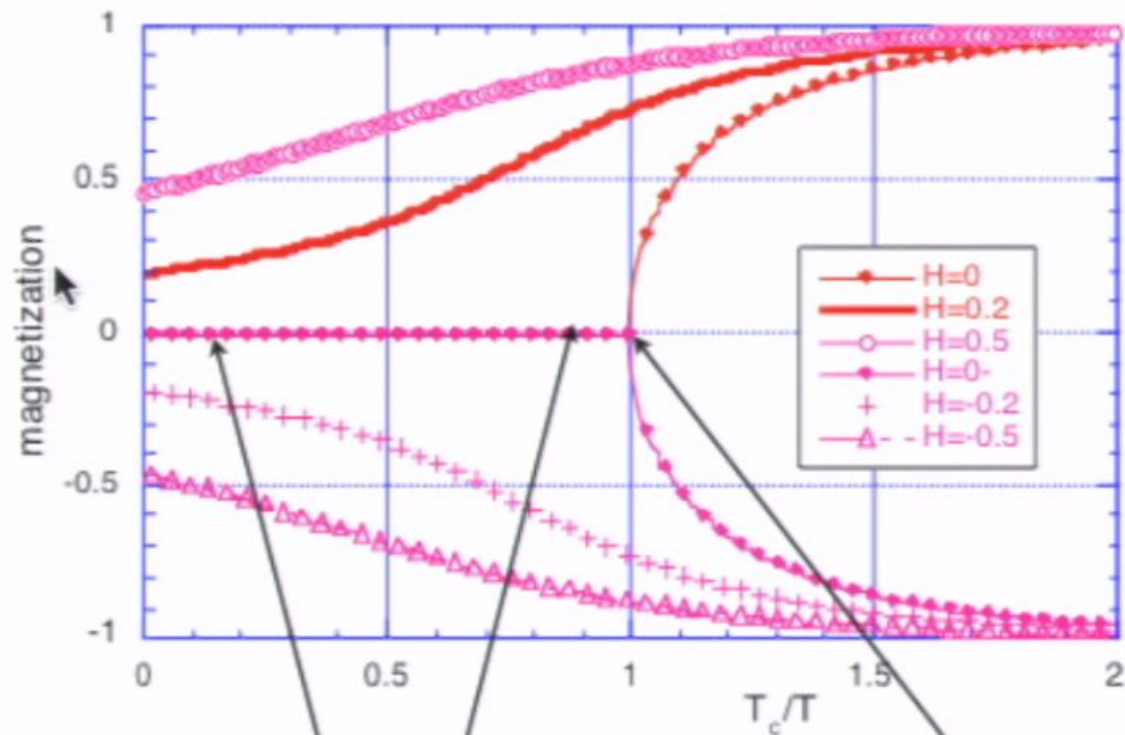# order parameter in mean field transition

legend "H" should be h

First order phase transition

critical point

Part 7 Mean Field Theory.key

New   Play   View   Themes   Masters   Text Box   Shapes   Table   Charts   Comment   Smart Builds   Mask   Alpha   Group   Ungroup

Master Slides

Title & Subtitle

My usual master

Master #14

Slides

field transition

In legend "H" should be h

critical point

First order phase tr

75%

exponents $K_z =$ $\dfrac{T_c}{T}$

$$\langle \sigma \rangle = \tanh\left[h + \dfrac{T_c}{T} \langle \sigma \rangle \right]$$

$\left[a_0 e^{-} - a_0 e^{t} \right]$

In legend "H" should be h

First order phase tr

critical point

$$K_z = \frac{T_c}{T}$$

$$\langle \sigma \rangle = \tanh\left[h + \frac{T_c}{T} \langle \sigma \rangle\right]$$

approx to

magnetic properties

of ferromagnets

Behavior in neighborhood of critical Point

The mean field equation is $\langle\sigma_r\rangle = \tanh h_{eff}$ with $h_{eff} = h_r + K\sum_{s\, nn\, to\, r}\langle\sigma_s\rangle$.
We assume that we are near the critical point both the field and the magnetization are small. Then we can expand the equation for $\langle\sigma_r\rangle$ in a power series in h_{eff} $\qquad \langle\sigma_r\rangle = \tanh h_{eff} \approx h_{eff} - h_{eff}^3/3$
We also assume slow variation in space and that the temperature is close to criticality. To lowest order $h_{eff} \approx Kz\langle\sigma_r\rangle \approx \langle\sigma_r\rangle$. The lowest order result is used in the cubic term and the rest is evaluated exactly as

$$\langle\sigma_r\rangle = h_r + \langle\sigma_r\rangle[1-t] + K\sum_{s\, nn\, to\, r}[\langle\sigma_s\rangle - \langle\sigma_r\rangle] - \langle\sigma_r\rangle^3/3$$

Here, t is the temperature deviation from criticality $t = 1-Tc/T$. Finally replace the remaining K by its critical value, $1/z$ and expand to second order in the difference **s-r** to obtain

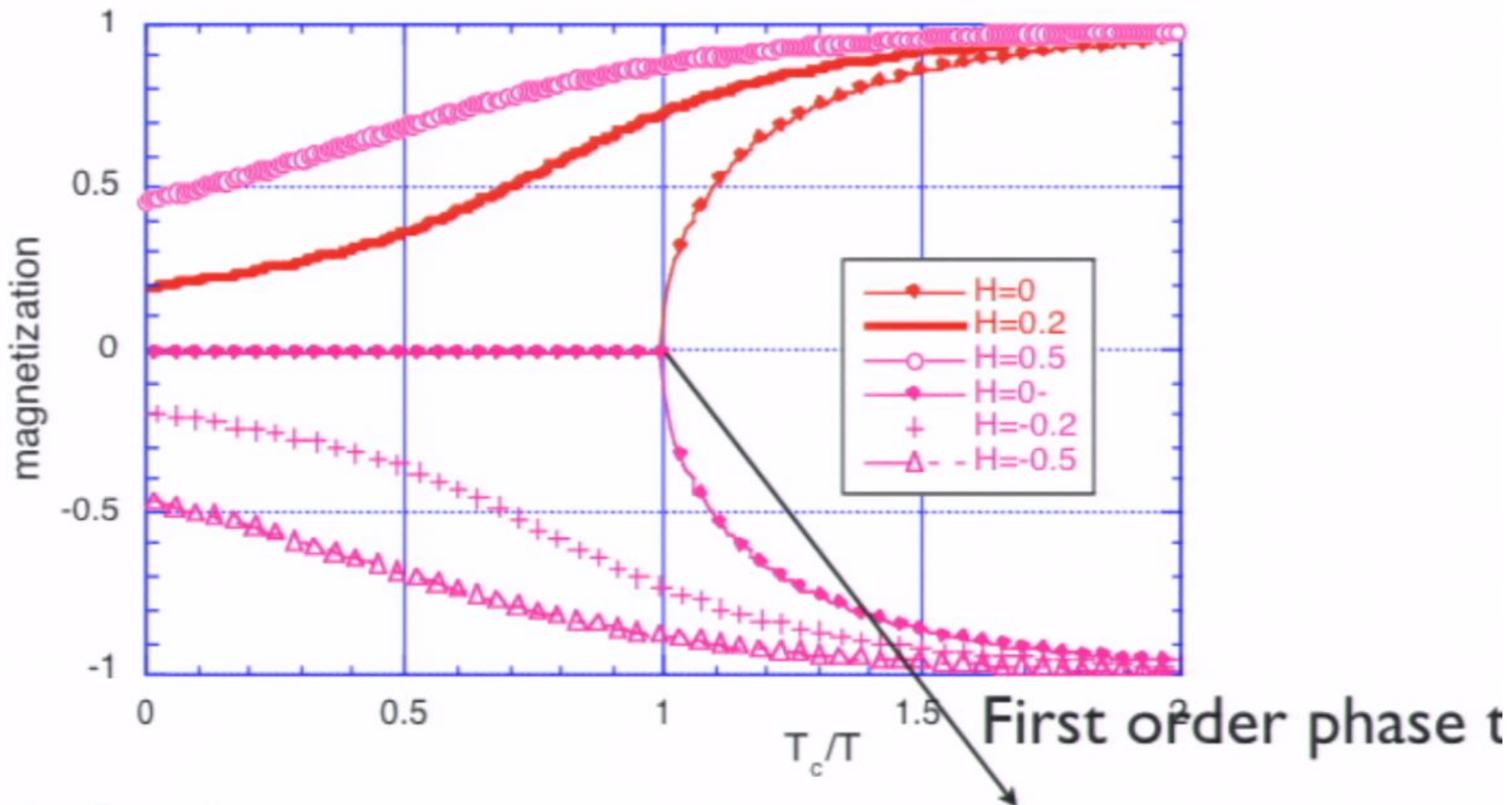$$0 = h_r - t\langle\sigma_r\rangle + a^2\nabla^2\langle\sigma_r\rangle/z - \langle\sigma_r\rangle^3/3$$

This is the near-critical mean field theory in the Weiss model of a ferromagnet. It is the continuum version. On the lattice

$$a^2\nabla^2\langle\sigma_r\rangle \longrightarrow \sum\nolimits_{s\, nn\, to\, r}[\langle\sigma_s\rangle - \langle\sigma_r\rangle]$$

order parameter in mean field transition

legend "H" should be h

First order phase t

critical point

$$\frac{T_c}{T} \gg 1 \text{ or } \gg K_z = \frac{T_c}{T}$$

$h = \text{small}$

$\langle \sigma \rangle = \tanh \left[h + \frac{T_c}{T} \langle \sigma \rangle \right]$

$\langle \sigma \rangle \approx$

approx for

magnetic pro

ferom

$$\langle \sigma \rangle = h + \frac{T_c}{T} \langle \sigma \rangle \qquad \frac{T_c}{T} \gg 1 \quad or \quad K_z = \frac{T_c}{T}$$

$$h\text{-small} \qquad \langle \sigma \rangle = \tanh\left[h + \frac{T_c}{T} \langle \sigma \rangle \right]$$

$$\langle \sigma \rangle_{11}$$

approx for
magnetic properties
of a ferromagnet

$$\langle \sigma \rangle = h + \frac{T_c}{T} \langle \sigma \rangle \qquad \frac{T_c}{T} \quad \text{near} \quad K_z = \frac{T_c}{T}$$

$$= \frac{1}{6}$$

h small

$\langle \sigma \rangle_{ii}$

$$\langle \sigma \rangle = \tanh\left[h + \frac{T_c}{T} \langle \sigma \rangle \right]$$

approx for
magnetic properties
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$$\langle \sigma \rangle = h + \frac{T_c}{T} \langle \sigma \rangle \frac{T_c}{T} \text{ near } | \quad K_z = \frac{T_c}{T}$$

$$-\frac{1}{6} \langle \sigma \rangle^3$$

$$\begin{array}{l} h\text{-small} \\ \langle \sigma \rangle_{||} \end{array} \quad \langle \sigma \rangle = \tanh \left[h + \frac{T_c}{T} \langle \sigma \rangle \right]$$

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From
Grains of
Pollen to
Evidence
for Atoms

How
Big Is A
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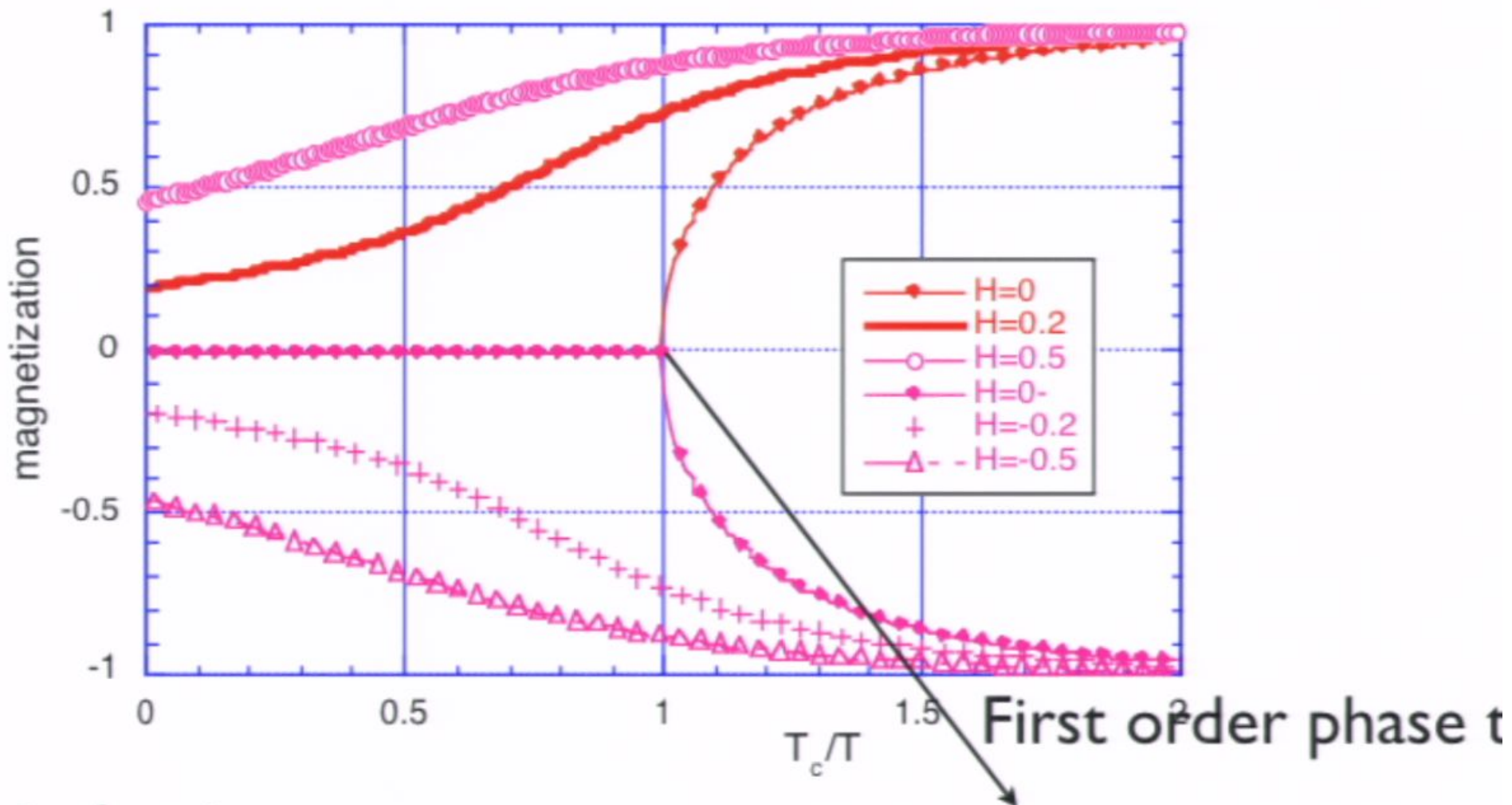
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$$a^2 \nabla^2 \langle \sigma_r \rangle \longrightarrow \sum [\langle \sigma_s \rangle - \langle \sigma_r \rangle]$$

order parameter in mean field transition

legend "H" should be h

First order phase t

critical point

$$\langle \sigma \rangle = h + \frac{T_c}{T} \langle \sigma \rangle \qquad \frac{T_c}{T} \quad \text{near } 1 \Rightarrow K_z = \frac{T_c}{T}$$

$$-\frac{1}{3} \langle \sigma \rangle^3$$

h-small

$$\langle \sigma \rangle_{11} \qquad \langle \sigma \rangle = \tanh\left[h + \frac{T_c}{T} \langle \sigma \rangle \right]$$

$$-\frac{\left[(1-t)\langle \sigma \rangle\right]^3}{3}$$

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Conclusions from Weiss Mean Field Theory

For example, go after magnetization when h=0, no variation in space

$$0 = t <\sigma> + <\sigma>^3/z$$

t is proportional to (T-Tc)

if t is positive there is but one real solution $<\sigma> = 0$.

if t is negative we have a possible solution $<\sigma> = 0$, and also the solutions

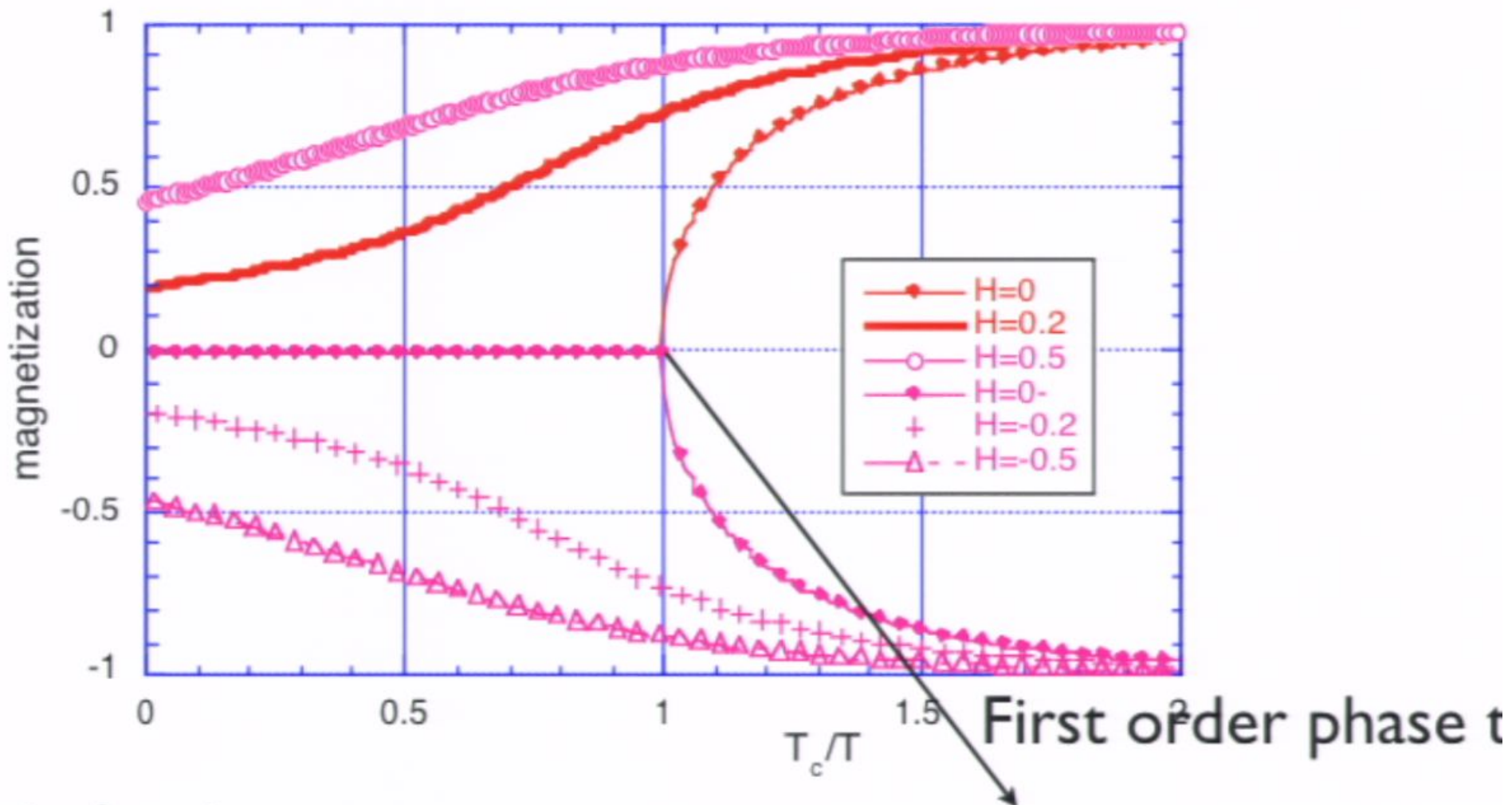$$<\sigma> = \pm (-tz)^{1/2}$$

One should choose the solution which actually minimizes the free energy. It turns out that this solution is the one which has the same sign as h. Therefore as h passes through zero for T less than Tc there is a jump in the magnetization proportional to the square root of -t.

order parameter in mean field transition

legend "H" should be h

- magnetization (y-axis)
- T_c/T (x-axis)

Legend:
- H=0
- H=0.2
- H=0.5
- H=0-
- H=-0.2
- H=-0.5

First order phase t

critical point

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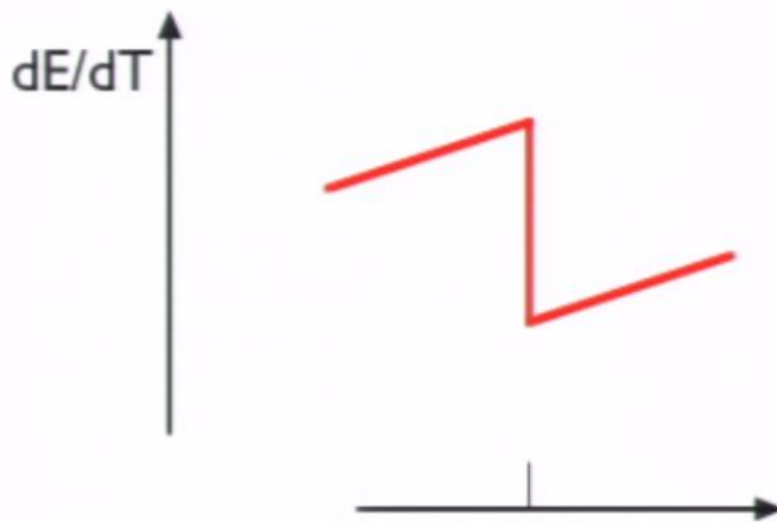
For example, go after $<H>$ when $h=0$, no variation in space

$$-H / kT = K \sum_{nn} \sigma_r \sigma_s + h \sum_r \sigma_r$$

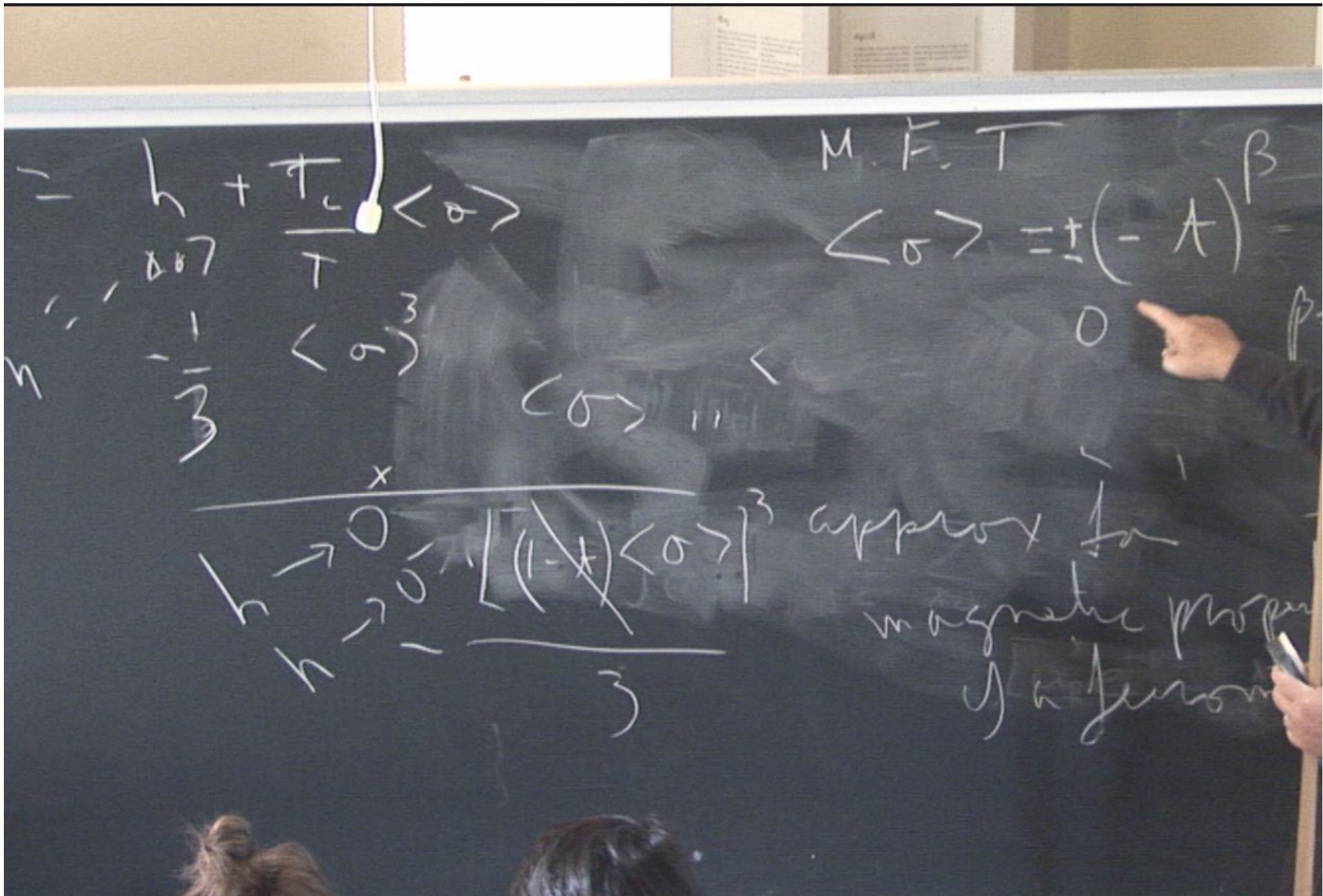We assume neighboring spins are uncorrelated

$-<H>/(kT) = Kz<\sigma><\sigma>$ + other effects

near T_c $<\sigma>^2 = 0$ above T_c $<\sigma>^2 = -tz$ below

Hence specific heat, $d <H>/dT$ has a jump at T_c. It looks like

$$= h + T_c \langle \sigma \rangle$$

$$\langle \sigma \rangle$$

$$\frac{\langle \sigma \rangle^3}{3}$$

M.F.T

$$\langle \sigma \rangle = \pm (-A)^{\beta}$$

$$\langle \sigma \rangle = $$

$$\frac{h \to 0^+}{h \to 0^-} \; \langle \sigma \rangle - \frac{[(1-t)\langle \sigma \rangle]^3}{3}$$

approx for

magnetic prop
of ferom

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$$= h + \frac{T_c}{T} \langle \sigma \rangle$$

$$-\frac{\langle \sigma \rangle^3}{3}$$

$$\langle \sigma \rangle \quad \text{''}$$

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M.F.T

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$$\beta$$

$$\left| \frac{dE}{dF} \right| \text{jump}$$

approx for

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Conclusions from Weiss Mean Field Theory

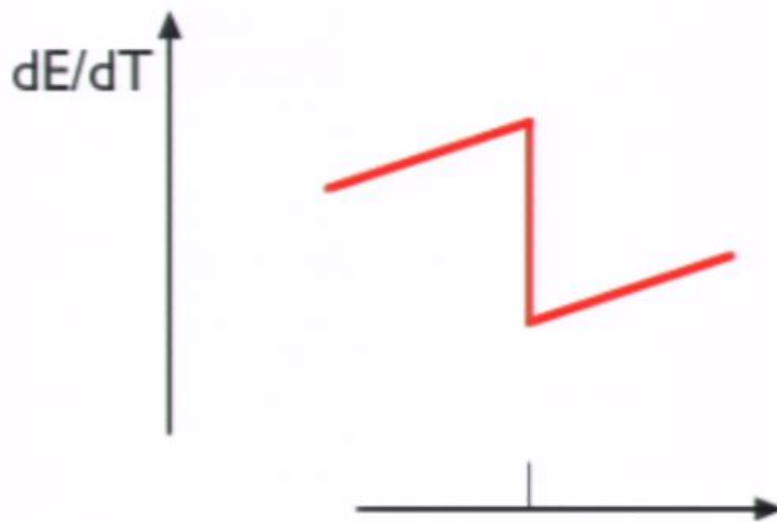For example, go after $<H>$ when $h=0$, no variation in space

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Critical Opalescence and Fluctuations

In the early 20th century experimenters observed what is called critical opalescence. As the critical point is approached, a fluid which is otherwise clear and transparent is seen to become milky and reflects light. This phenomenon was explained by Smoluchowski (1908) and Einstein (1910)

Einstein particularly showed that the scattering came from density fluctuations, and noted that these fluctuations diverged at the critical point. Soon thereafter, in 1916 and 1914, Ornstein and Zernike put together a theory which show that the fluctuations came from large regions of correlated fluctuations and derived a qualitatively correct mean field theory treatment of the phenomenon.

This development would prove to be particularly important because spatial and correlational structure would turn out to be the key to understanding phase transitions.

$$|\sigma\rangle = h + ?$$

on

$$\frac{1}{3}$$

$$h \to 0^+$$

$$h \to 0^- = \frac{[(1-t)\langle\sigma\rangle]^3}{3}$$

M.F.T

$$\langle\sigma\rangle = \pm(-A)^\beta$$

$$\beta = \frac{1}{2}$$

$$\left[\frac{dE}{dF} \quad jump\right]$$

$$0$$

approx for

magnetic properties

of a ferromagnet

Weiss Mean Field Theory for Correlations

For example, go after $<\sigma_r\sigma_s>$, when $h=0$, no variation in space, $T>Tc$

$$0 = h_r - t<\sigma_r> + \sum_{s \ nn \ to \ r} [<\sigma_s> - <\sigma_r>]/z - <\sigma_r>^3/3$$

neglect cubic term, differentiate equation with respect to h_u

$$0 = (d \ h_r /d \ h_u) - t (d<\sigma_r>/d \ h_u) + \sum_{s \ nn \ to \ r} [d<\sigma_s>/d \ h_u - d<\sigma_r>/d \ h_u]/z$$

$d<\sigma_r>/d \ h_u$ is correlation function $g(\mathbf{r-u}) = <[\sigma_r - <\sigma_r>] [\sigma_u - <\sigma_u>]>$, which then obeys

$$0 = \delta_{r,u} - t \ g(\mathbf{r-u}) + \sum_{s \ nn \ to \ r} [g(\mathbf{s-u}) - g(\mathbf{r-u})]/z$$

define $G(q) = \sum_r \exp[-i\mathbf{q}.(\mathbf{r-u})] \ g(\mathbf{r-u})$ so that

$$0 = 1 + \left[-t + 2\sum_{i=1,2...d} (\cos q_i - 1)/z \right] G(\mathbf{q})$$

Weiss Mean Field Theory for Correlations

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$$0 = 1 + \left[-t + 2\sum_{i=1,2...d} (\cos q_i - 1)/z \right] G(\mathbf{q})$$

Fourier transform of correlation function obeys

$$0 = 1 + \left\{ -t + 2 \sum_{i=1,2...d} [\cos(aq_i) - 1]/z \right\} G(\mathbf{q})$$

We can now solve for $G(\mathbf{q}) = 1/\{t + 2\sum_{i=1,2...d} [1 - \cos(aq_i)]/z\}$ and invert the Fourier transform to get

$$g(\mathbf{r}-\mathbf{s}) = \int dq \, \exp[i\mathbf{q}.(\mathbf{r}-\mathbf{s})]/(2\pi)^d \, 1/\{t + 2\sum_{i=1,2...d} [1 - \cos(aq_i)]/z\}$$

Here the integrals over each component of q extend from $-\pi/a$ to π/a. To get a result for large spatial separation expand to second order in q and extend the integrations to cover all q

One can perform the integral to find that

$$g(\mathbf{r}-\mathbf{s}) \sim \exp[-|\mathbf{r}-\mathbf{s}|/\xi]/|\mathbf{r}-\mathbf{s}|^{d-2}$$

when the exponent is of order one, and d >2. The correlation length, ξ, is given by $\xi = a/(zt)^{1/2}$

$$\frac{d \langle \sigma_r \rangle}{d h_s} = \langle [\sigma_r - \langle \sigma_r \rangle]$$

$$[\sigma_s - \langle \sigma_s \rangle]. \rangle$$

$$\frac{\partial \langle \sigma \rangle}{\partial h} = \int dr \, g(r)$$

$$\frac{}{\to 0^+}$$

$$h \to 0^+ \cdot \frac{[(1-t)\langle \sigma \rangle]^3}{3}$$

$$h \to 0^-$$

magnetic properties
of a ferromagnet

Correlation function looks like

The result is then of the form

$$g(r-s) \sim \exp[-|r-s|/\xi]/|r-s|^{d-2}$$

The correlation length, ξ, is given by $\xi = a/(zt)^{1/2}$

This result is important. It says that the correlations in space extend over longer distances as one gets closer to criticality.

So the fact that the phase transition will only occur in an infinite system partially shows up in mean field theory. The correlation extending to infinity is a crucial fact in phase transitions. However, mean field theory allows a phase transition in a periodic but finite system.

Also, mean field theory gets an answer which is somewhat incorrect in the neighborhood of the critical point. Near the critical point $\xi \sim a/(t)^{\nu}$ but $\nu = 1$ in $d=2$ and $\nu \approx 0.64$ in three dimensions.

$$\frac{d\langle\sigma_n\rangle}{dh_s} = \langle[\sigma_n - \langle\sigma_n\rangle]$$

$$\frac{}{} \xrightarrow{h\to 0^+} \sigma$$

$$\xrightarrow{h\to 0^-} \frac{[(1-t)\langle\sigma\rangle]^3}{3}$$

$$\xi = \frac{1}{h^{1/3}}$$

$$= \frac{1}{t^{1/2}} Q\left(\frac{t}{h^{1/3}}\right) t$$

$$\frac{\partial\langle\sigma\rangle}{\partial h} = \text{arg}$$

magnetic prop

$$\frac{d\langle\sigma_r\rangle}{dh_s} = \langle[\sigma_r - \langle\sigma_r\rangle]^2\rangle$$

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$$= \frac{1}{t^{1/2}} Q\left(\frac{t^{1/2}}{h^{1/3}}\right) t$$

$$\xrightarrow{h\to 0} \frac{[(1-t)\langle\sigma\rangle]^3}{3}$$

Widom

magnetic prop...

Conclusions from Weiss Mean Field Theory:

The magnetic susceptibility

The quantity $\partial <\sigma>/\partial h$, calculated at fixed T, is called the magnetic susceptibility. It is given by the Fourier transform of the spin correlation function as $\partial <\sigma>/\partial h = G(\mathbf{0})$. Thus. we know its value in mean field theory, which is

$\partial <\sigma>/\partial h \sim 1/t$.

So the infinite correlation length has as its direct consequence the infinity in this important thermodynamic derivative.

Mean Field Theory of Fluids

I did not describe the development of mean field theory in anything like historical order. Van der Waals derived the first mean field theory in the 1870s. He was interested in understanding the data of Andrews (1869) which showed a phase transition line separating a liquid and a vapor phase that then ends in a critical point in which the two become identically the same. Pierre Curie noticed that the behavior of a ferromagnet has a close analogy to that of a fluid in 1895. Later in 1907, Pierre Weiss worked this remark into a theory like the one mentioned here. Fluids no doubt came first because they were more familiar and because experiments existed.

T. Andrews, ``On the continuity of the gaseous and liquid states of matter," Phil. Trans. Roy. Soc. 159, 575-590(1869). Reprinted in: T. Andrews,, The Scientific Papers, Macmillan, London (1889).

J. D. van der Waals, thesis Leiden, 1873.

P. Curie, Ann. Chem. Phys. 5, 289 (1895).   P. Weiss, J. Phys. 6, 661 (1907).

van der Waals derivation

The starting point was the perfect gas law

$$P\Omega = NT \qquad \text{perfect gas law,}$$

which of course shows no phase transition. Van der Waals then introduced two corrections to describe what he had inferred about fluids and the atoms or molecules which formed them. First, he argued that the molecules could not approach each other too closely because of an inferred short-ranged repulsive interaction among the molecules. He probably based his understanding of this repulsion upon the fact that it is very hard to compress liquids like water. This repulsive effect should reduce the volume available to the molecules by an amount proportional to the number of molecules in the system. Thus, Ω in the perfect gas law should be replaced by the available or effective volume, $\Omega\text{-}Nb$, where b would be the excluded volume around each molecule.

van der waals' second effect

The second effect is more subtle. The pressure, P is a force per unit area produced by the molecules hitting the walls of the container. However, van der Waals inferred that there was an attractive interaction pulling each molecule towards its neighbors. This attraction is the fundamental reason why a drop of liquid can hold together and form an almost spherical shape. Again we see that familiar facts can be translated into theoretical understanding. As the molecules move toward the walls they are pulled back by the molecules they have left behind them, and their velocity is reduced. Because of this reduced velocity, their impacts impart less momentum to the walls   The equation of state contains the pressure as measured at the wall, P. This pressure is the one produced by molecular motion inside the liquid, $NT/(\Omega-Nb)$, minus the correction term coming from the interaction between the molecules near the walls. That correction term is proportional to the density of molecules squared. In symbols the correction is $a(N/\Omega)^2$ where a is proportional to the strength of the interaction between molecules. Van der Waals' corrected expression for the pressure is thus

$$P = NkT/(\Omega-Nb)-a(N/\Omega)^2$$

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Many Different Phase Transitions:

liquid -gas

paramagnetic to ferromagnetic

(un)mixing of solids and liquids

superconducting, ...

an der Waals: (1873) Different simple
quids-gas transitions have very similar
hermodynamic properties. Derives
ean field theory of liquid.

urie-Weiss (1907) mean field theory
f magnets.

ut, each different phase transition
alls for its own theory.

Johannes Diderik van der Waals ·

After van der Waals
Many Different Mean field theories

The theory of phase transitions involving the unmixing of fluids was developed by van der Waals himself, while such unmixing in solids was described by W. L. Bragg and E. J. Williams. Literally dozens of such theories were defined, culminating in the theory of superconductivity of Bardeen, Cooper and Schrieffer. These theories are all different in that they have different physical quantities playing the roles we have given to the magnetic field, or T-Tc, or serving as the order parameters. The order parameter is the quantity that can undergo a discontinuous jump in the first order transition, and describes the symmetry group of the physical situation. The magnetization is the order parameter of the ferromagnet, the density is the order parameter in the liquid-gas transition. Much effort and ingenuity has gone into the discovery and description of the order parameter in other phase transitions. In the anti-ferromagnetic transition the order parameter is a magnetization that points in opposite directions upon alternating lattice sites. In ferroelectrics, it is the electric field within the material. The superfluid and superconducting transition have as their order parameter the quantum wave function for a macroscopically occupied state. Liquid crystals have order parameters reflecting possible different kinds of orientation of the molecules within a liquid. The description of these different manifestations of the phase transition concept reflect more than a century of work in condensed matter physics, physical chemistry, etc.

Order Parameter, generalized

• Landau (~1937) suggested that phase transitions were manifestations of a broken symmetry, and used the order parameter to measure the extent of breaking of the symmetry.

• in ferromagnet, parameter = magnetization
• in fluid, parameter = density

L.D. Landau

Generalized Mean Field Schemes I

Many different mean-field schemes developed:. Each one has an order parameter, an average of a microscopic quantity. Landau generalized this by assuming an expansion of the free energy in an order parameter,

$$F = \int dr[a - hM + tM^2 + cM^4 + (\nabla M)^2]$$

expansion assumes a small order parameter (works near critical point) and small fluctuations (works far away?!)

h is magnetic field

t is proportional to $(T - T_c)$

minimize F in M: result General Solution $M(h, (T-T_c))$
singularity as t,h both go through zero!
singularity as h goes through zero for $T < T_c$

note: no cubic term This free energy applies to symmetry of Ising model

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This free energy applies to symmetry o Ising mode

$$= \mathcal{F}_n + \int d\mathbf{r} \left\{ \frac{1}{2m} |\nabla \Psi(\mathbf{r})|^2 + \alpha(T)|\Psi(\mathbf{r})|^2 + U(\mathbf{r})|\Psi(\mathbf{r})|^2 + \frac{b}{2}|\Psi(\mathbf{r})|^4 \right\}$$

Superfluid density near the critical temperature in the presence of random planar defects

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Department of Physics and Astronomy, McMaster University,
Hamilton, Ontario, Canada L8S 4M1
(Dated: November 14, 2008)

Why minimize?

Thermodynamics says that the free energy is extremized by the variation in any macroscopic parameter, e.g. any extensive variable. This is part of a general idea that the free energy is a probability, which arises from how the partition function is used. In statistical mechanics only the most probable things happen. This applies to all macroscopic phenomena, Now M(r) is not quite macroscopic, but Landau's idea was that at the long wavelength part of it it was "macroscopic enough" so that one could neglect its fluctuations. This point of view has turned out to be wildly successful.

Vary M(r) to vary F

$$F = \int dr [a - hM + tM^2 + cM^4 + (\nabla M)^2]$$

Integrate by parts in gradient term

$$\delta F = \int dr \, \delta M(r) \, [-h + 2tM(r) + 4cM(r)^3 - \nabla^2 M(r)]$$

to minimize F, coefficient of $\delta M(r)$ must vanish

$$0 = h + 2tM(r) + 4cM(r)^3 - \nabla^2 M(r)$$

Hence we have an equation for M! That is a general equation for the order parameter in mean field theory with the Z2 symmetry, i.e. symmetry under sign change of M.
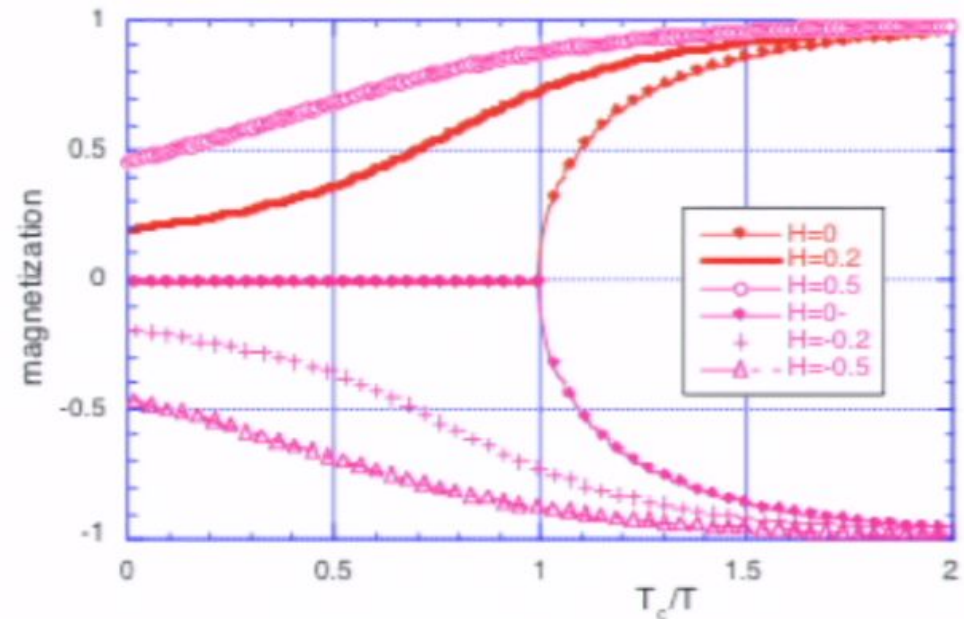
Generalized Mean Field Schemes II

Crucial part of the solution: for $T < T_c$, jump in order parameter goes as $M \sim (T_c - T)^\beta$ with $\beta = 1/2$

This square root ($\beta = 1/2$) appears to be a Universal result.

Mean Field Theory predicts all near-critical behavior

rder parameter, jump,

nd free energy were crucial concepts

order parameter in mean field transition

order parameter and free energy were crucial concepts

free energy could be expressed in terms on any descriptors of systems behavior. It is a minimized by the correct value of any one of them, We have thus come loose from the particular thermodynamic variables handed to us by our forefathers,

order parameter could be anything which might jump in the transition.

other variables could be anything at all.

In the meantime Schwinger was working on electromagnetic fields for World War II radar. He use variational methods and effective fields ("lumped variables") to build electromagnetic circuits.
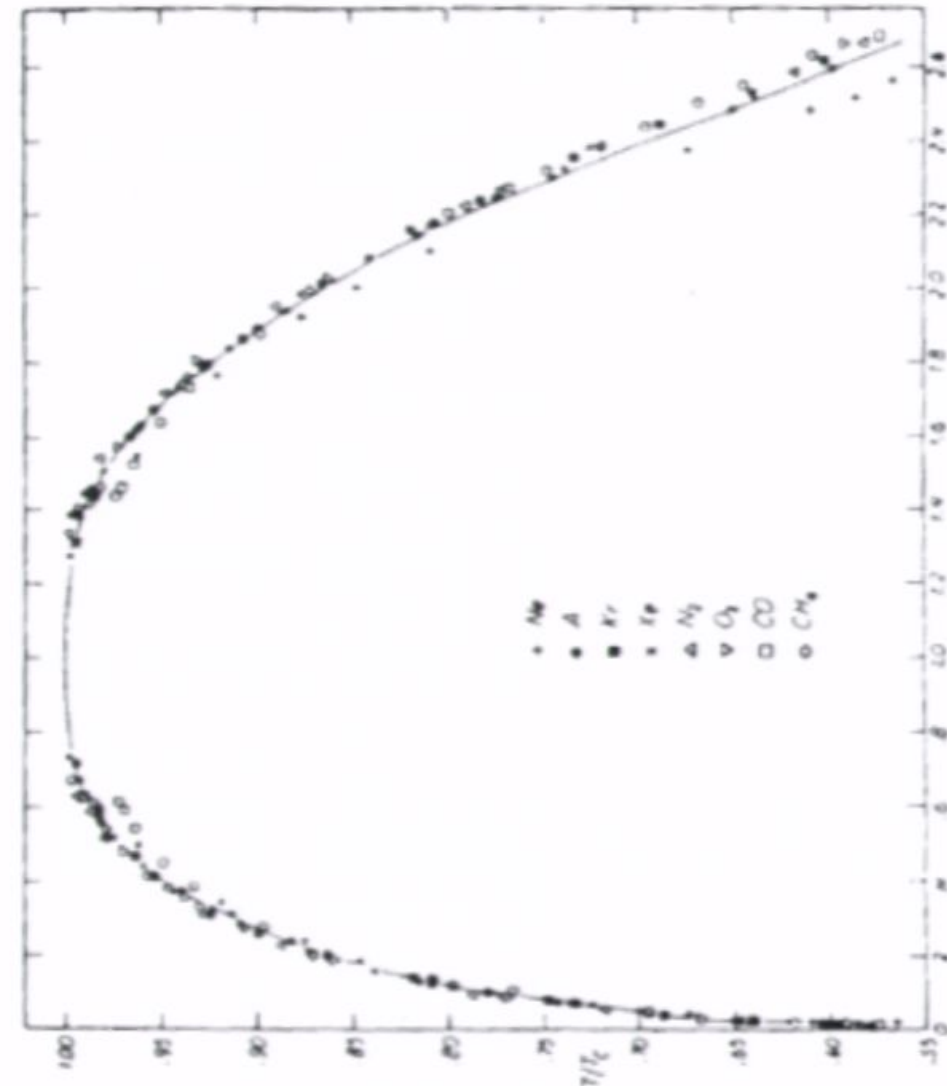
A worry?

Mean field theory gives

$$M \sim (T_c - T)^\beta$$

and $\beta = 1/2$
This power is, however, wrong. Experiments are closer to

$$M \sim (T_c - T)^{1/3} \quad \text{in 3-D}$$

1880-1960: No one worries much about discrepancies

order parameter: density versus Temperature in liquid gas phase transition. After E.A. Guggenheim J.

STOP Here