Recapitulation

S(E)=ln(number of configurations with energy E.

- $1/(k_B T) = \frac{\partial S(E\quad)}{\partial E}$.
- .

The Boltzman canonical distribution :

$$P' = e^{-E_S/k_B T}$$

- The average of a physical quantity Q ,
- $< Q > = \int dx Q(x) P'(x) \,/\, \int dx P'(x)$;
- *Angular bracket means an average.*

Thermodynamics studies average properties.
An average thermodynamics quantity: Free energy F

- We define a free energy F which measures the number of configurations of the system and its environment. *F need to be extremized for equilibrium at fixed temperature to maximize* the number of configurations
- $e^{-F/kT} = \int d\{x\} e^{-\frac{E}{k_B T}}$
- $We\ define\ a\ partition\ function\ Z$ *which is useful for calculations by*
- $Z = \int d\{x\} e^{-\frac{E}{k_B T}}$
- $\mathrm{F} = -\mathrm{k\,T\,ln}[\,Z].$

The Boltzman canonical distribution

P=$e^{-\beta E}$ $/\mathbf{Z}$, $\beta = 1/kT$

Z $= \int d\{x\} e^{-\beta E}$ is the normalization so that

$\int dx P(x)$=1

- The average of a physical quantity Q is
- $< Q > = \int dx Q(x) P(x)$,
- For example, $< E > = \int dx E(x) P(x)$
- $\partial \ln Z / \partial\beta = - \prec E > = \partial(\beta F)/\partial\beta$

Another thermodynamic quantity:
Entropy S=-k <ln P>,

- $P = e^{-\beta E} / \boldsymbol{Z}$ (1)
- S is an average measure of the number of configurations of the environment
- Entropy S = -k <ln P>, (We take a log so that S is extensive. *Angular bracket means an average.)*
- From (1) S=$<E> / T + k \ln Z$
- $S = <E> / T - F / T$
- $F = U - TS, \quad U = <E>,$

Usually the calculation using the Boltzmann distribution cannot be carried out exactly. A very useful approximation is to replace some of the variables by a constant, their average value, and to determine them later self-consistently. This is called the mean field approximation

Recapitulation: Energy of spins in a magnetic field

Atoms in magnets are charged particles with angular momenta **S** called spins that, in some units, are interger or half integer.

Their magnetic moments **M** = $g\mu_B$**S** where $g\mu_B$ is some constant.

In a magnetic field **B**, the energy is -**B.M** = -$g\mu_B B$**.S**.

Including heat change, we get the total energy change of a magnetic system is

dE=TdS+other terms-**B.**d**M**

One can define a quantity F'=F+BM so that dF'=-SdT+MdB+other terms

For processes under a constant magnetic field and at fixed temperature, F' is minimized.

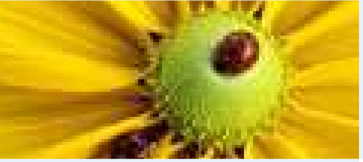
Energy of magnetic systems and mean field approximation

- Atoms in magnets have magnetic moments proportional to their angular momenta **S**, we call the angular momenta spins.
- For a ferromagnet (antiferromagnet) the interaction energy between two spins is lowest when they are parallel (antiparallel).
- We write this energy as $\mathrm{H} = -J\sum_{i<j}\overrightarrow{\boldsymbol{S}_i}\cdot\overrightarrow{\boldsymbol{S}_j}$ where J is called the exchange energy. It is positive (negative) for a ferromagnet (antiferromagnet).
- It is not ususally possible to do analytic calculations summing over all configurations for all orientations of the spins.
- The mean field approximation replace one of them by an average with fixed orientation and magnitude:
- $\mathrm{H} \cong -J\sum_{i<j}\overrightarrow{<\boldsymbol{S}_i>}\cdot\overrightarrow{\boldsymbol{S}_j}$

Ising model

- We shall look at a special case where the spin only has a z component of value $\sigma = \pm 1$

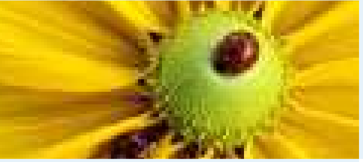
An example: **Interacting spins and the mean-field approximation**



Thermodynamics

- The partition function for the Ising model is

$$\begin{aligned} Z_C &= \sum_{\sigma} \exp(-\beta E_\sigma) \\ &= \sum_{\sigma} \exp\left(\beta J \sum_{\langle ij \rangle} \sigma_i \sigma_j + \beta h \sum_i \sigma_i \right). \end{aligned}$$



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\end{aligned}
$$

- Before we try to calculate Z_C, note that our key thermodynamic identities remain valid for interacting spins:

$$
\begin{aligned}
\tilde{A} &\equiv U - TS - MB = -k_{\mathrm{B}} T \log Z_C, \\
\langle E \rangle &= \left(\frac{\partial(\beta \tilde{A})}{\partial \beta}\right)_B = \tilde{U} = U - MB, \\
M &\equiv \left\langle \sum_i \mu_i \right\rangle = -\left(\frac{\partial \tilde{A}}{\partial B}\right)_T,
\end{aligned}
$$

with

$$
M = -\frac{g\mu_{\mathrm{B}}}{2} N \langle \sigma \rangle, \qquad \langle \sigma \rangle = \frac{1}{N\beta} \frac{\partial}{\partial h} \log Z_C.
$$

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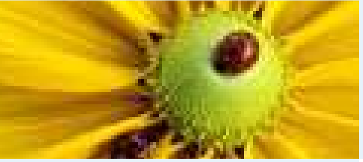
Partition function

- Now reconsider the partition function

$$Z_C = \sum_\sigma \exp\left(\beta J \sum_{\langle ij\rangle} \sigma_i\sigma_j + \beta h \sum_i \sigma_i\right).$$

- Is there any way to simplify this calculation for arbitrary dimensions?



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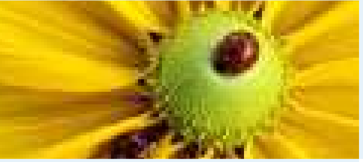
- We can always write σ_i as

$$\sigma_i = \langle \sigma_i \rangle + \Delta\sigma_i, \qquad \Delta\sigma_i \equiv \sigma_i - \langle \sigma_i \rangle,$$

where $\langle \sigma_i \rangle$ is the (as yet unknown) mean value of σ_i.



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- The product $\sigma_i \sigma_j$ is then

$$\sigma_i \sigma_j = \langle \sigma_i \rangle \langle \sigma_j \rangle + \Delta\sigma_i \langle \sigma_j \rangle + \Delta\sigma_j \langle \sigma_i \rangle + \Delta\sigma_i \, \Delta\sigma_j .$$

Partition function

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$$Z_C = \sum_{\sigma} \exp\left(\beta J \sum_{\langle ij \rangle} \sigma_i \sigma_j + \beta h \sum_i \sigma_i \right).$$

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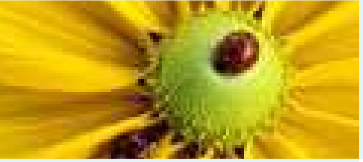
- If we assume that the fluctuations $\Delta\sigma_i$ can be regarded as small, then to first order in small quantities we have approximately

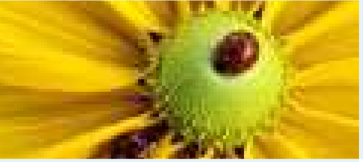
$$\begin{aligned} \sigma_i \sigma_j &\approx \langle \sigma_i \rangle \langle \sigma_j \rangle + \Delta\sigma_i \langle \sigma_j \rangle + \Delta\sigma_j \langle \sigma_i \rangle \\ &= \sigma_i \langle \sigma_j \rangle + \sigma_j \langle \sigma_i \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle . \end{aligned}$$



Mean field

- Let us further assume that $\langle \sigma_i \rangle$ is independent of i:

$$\langle \sigma_i \rangle = \langle \sigma \rangle \equiv \frac{1}{N} \left\langle \sum_{i=1}^{N} \sigma_i \right\rangle .$$



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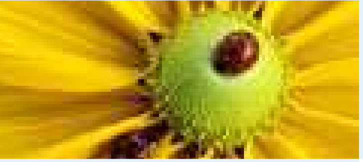
$$\langle \sigma_i \rangle = \langle \sigma \rangle \equiv \frac{1}{N} \left\langle \sum_{i=1}^{N} \sigma_i \right\rangle .$$

- In this case, the partition function reduces simply to

$$Z_C = \exp\left(-\frac{\beta J q N}{2} \langle \sigma \rangle^2 \right) \sum_{\sigma} \exp\left[\beta \big(h + J q \langle \sigma \rangle \big) \sum_i \sigma_i \right],$$

where q is the number of nearest neighbors of each spin,[2] and $qN/2$ is the total number of distinct nearest-neighbor pairs.



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- Apart from the constant factor in front, this expression for Z_C is just what we had for a system of non-interacting spins, with the replacement

$$h \rightarrow h + Jq\langle \sigma \rangle .$$

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- Apart from the constant factor in front, this expression for Z_C is just what we had for a system of non-interacting spins, with the replacement

$$h \rightarrow h + Jq\langle\sigma\rangle.$$

- The term $Jq\langle\sigma\rangle$ is called the “mean field”, because we have replaced the fluctuating term $J\sigma_j$ in the product $J\sigma_i\sigma_j$ with an effective constant magnetic field.

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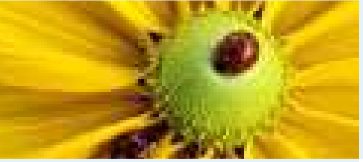
[2] Also known as the coordination number.



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- In the non-interacting case we found $Z_C = (2\cosh\beta h)^N$, so the mean-field partition function is

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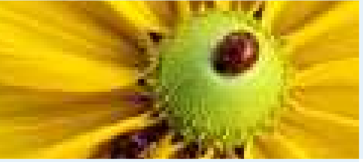

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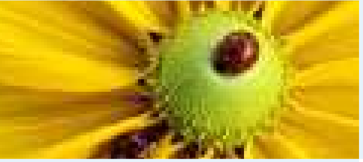
$$Z_C = \exp\left(-\frac{\beta J q N}{2}\langle\sigma\rangle^2\right)[2\cosh\beta(h + Jq\langle\sigma\rangle)]^N.$$

- Likewise, for non-interacting spins we had $\langle\sigma\rangle = \tanh\beta h$, so in the mean-field approximation

$$\langle\sigma\rangle = \tanh\beta(h + Jq\langle\sigma\rangle).$$

- This self-consistency condition determines the allowed values of $\langle\sigma\rangle$.
- Once $\langle\sigma\rangle$ is known, we can use Z_C to calculate any other thermodynamic quantity of interest in the mean-field approximation.



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- Let us now examine the special case $h = 0$:

$$\langle\sigma\rangle = \tanh(\beta J q \langle\sigma\rangle).$$

- This equation is always satisfied when $\langle\sigma\rangle = 0$.
- Are there any nontrivial solutions with $\langle\sigma\rangle \neq 0$?

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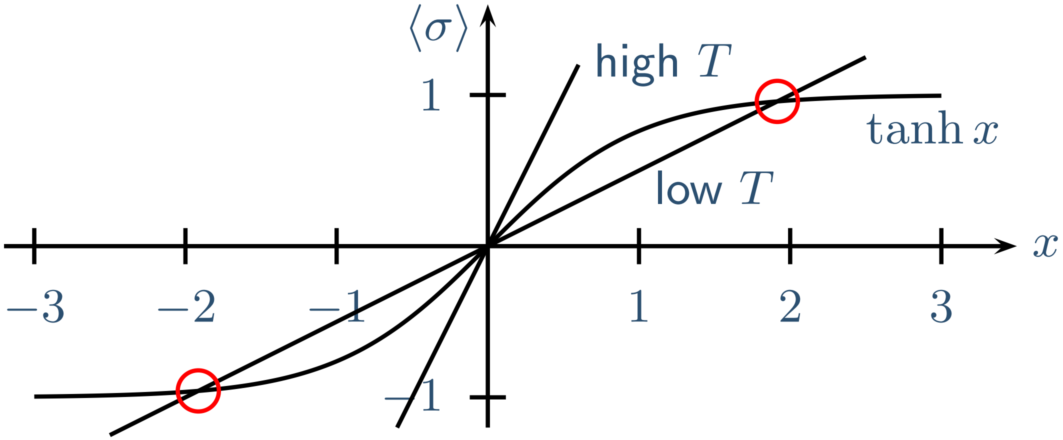
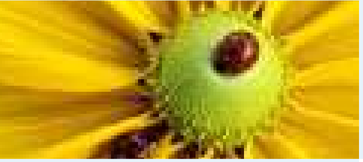
- We can write the consistency condition as

$$\left(\frac{k_\mathrm{B} T}{qJ}\right) x = \tanh x, \qquad x \equiv \beta J q \langle\sigma\rangle,$$

which can then be solved graphically:





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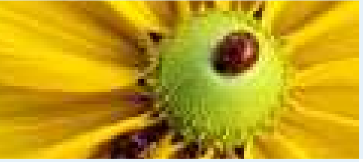
- We find a nontrivial solution ($\langle\sigma\rangle \neq 0$) provided that $T < T_c$, where

$$T_c = \frac{qJ}{k_{\mathrm{B}}}.$$



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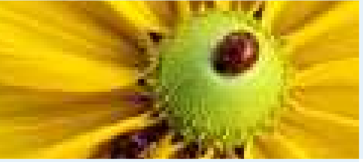
$$M = -\frac{g\mu_\mathrm{B}}{2} N \langle \sigma \rangle.$$



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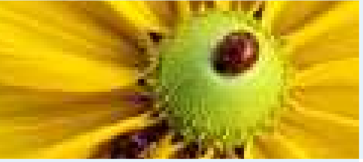
- Hence, our mean-field calculation predicts that when $T < T_c$, the system can exhibit a spontaneous magnetic order.



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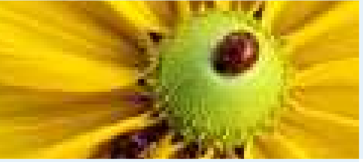
- Physically, if $T < T_c$, the thermal disordering is insufficient to overcome the ordering influences of the spin-spin interactions.



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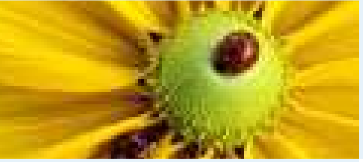

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- This tells us to expect a phase transition at $T = T_c$, going from a disordered state for $T > T_c$ to an ordered state for $T < T_c$.
- We call $\langle\sigma\rangle$ the order parameter, and to emphasize the physical relationship with magnetization we often denote it as

$$m \equiv \langle\sigma\rangle.$$

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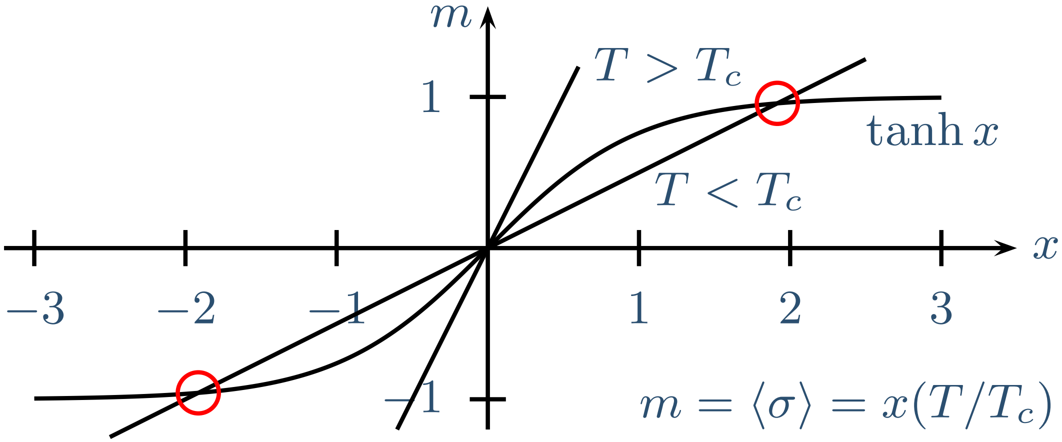
- Notice that when $T < T_c$, m can be either positive or negative:



Symmetry breaking

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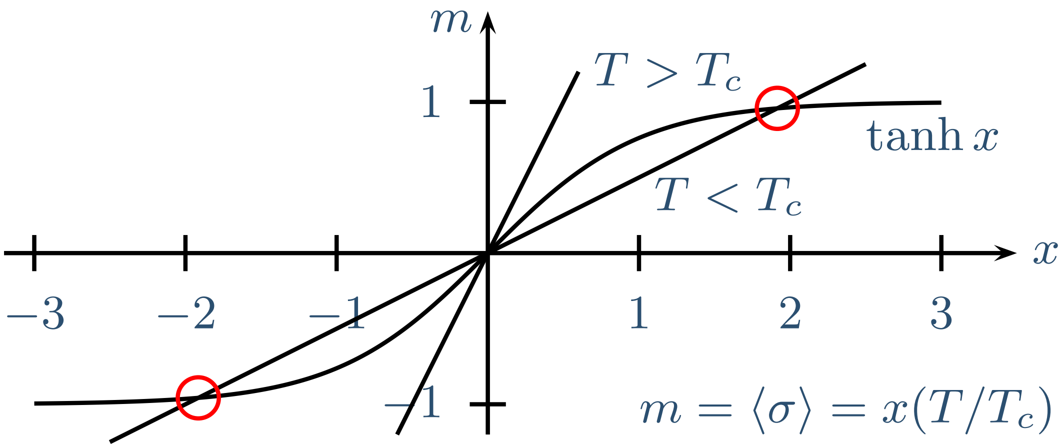
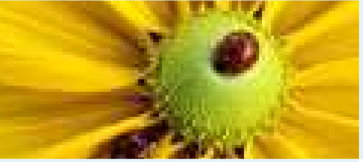


- However, for $h = 0$, the Ising Hamiltonian

$$H_{\text{Ising}} = -J_0 \sum_{\langle ij\rangle} S_{zi} S_{zj}$$

is symmetric under a "spin flip" operation that changes the sign of all spins.



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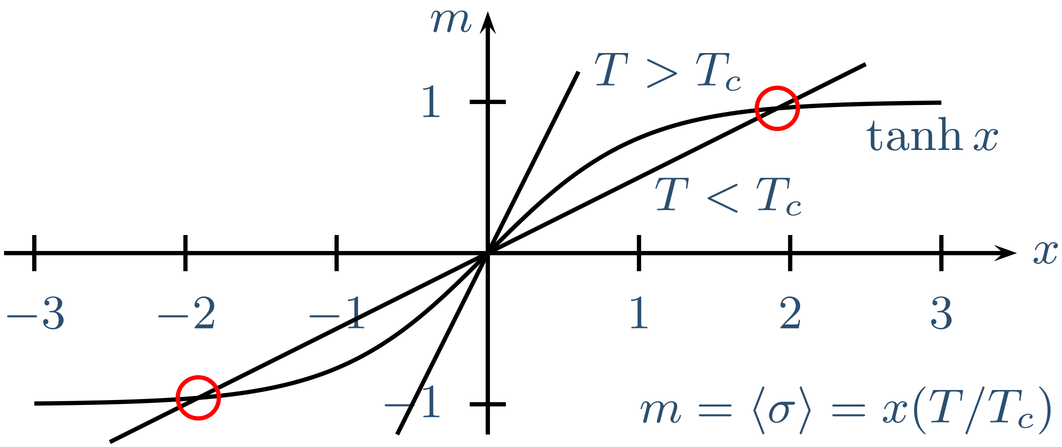

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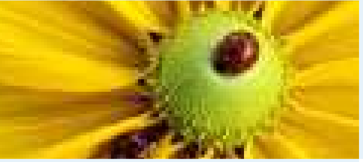
  is symmetric under a "spin flip" operation that changes the sign of all spins.
- The ordered state with $m \neq 0$ therefore breaks the symmetry of the Hamiltonian.
- This is known as "spontaneous symmetry breaking."



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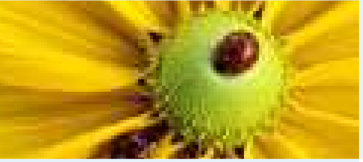
- What is the temperature dependence of the order parameter m in the broken-symmetry state?



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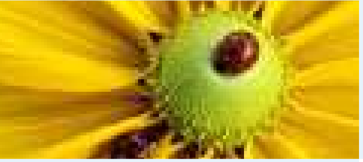

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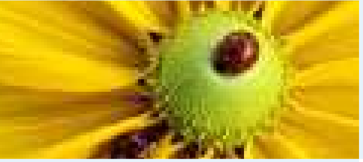

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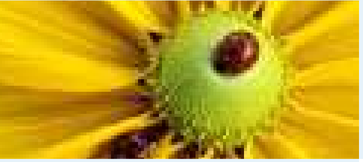

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- Under these conditions, the order parameter $m = x(T/T_c)$ is approximately

$$\begin{aligned} m &\approx \pm\sqrt{3}(T/T_c)(1 - T/T_c)^{1/2} \\ &= \pm\sqrt{3}(T/T_c)^{3/2}(T_c/T - 1)^{1/2}. \end{aligned}$$

Low temperature

- At very low temperatures ($T \ll T_c$), we cannot use this approximation, so let us reconsider the consistency equation

$$m = \tanh(mT_c/T).$$

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- The low-temperature solution with $m > 0$ is therefore given by

$$m \approx 1 - 2\exp(-2mT_c/T) \approx 1 - 2\exp(-2T_c/T).$$

- Including also the solution with $m < 0$, our final result at low temperature is

$$m \approx \pm[1 - 2\exp(-2T_c/T)].$$

Numerical solution $(h = 0)$

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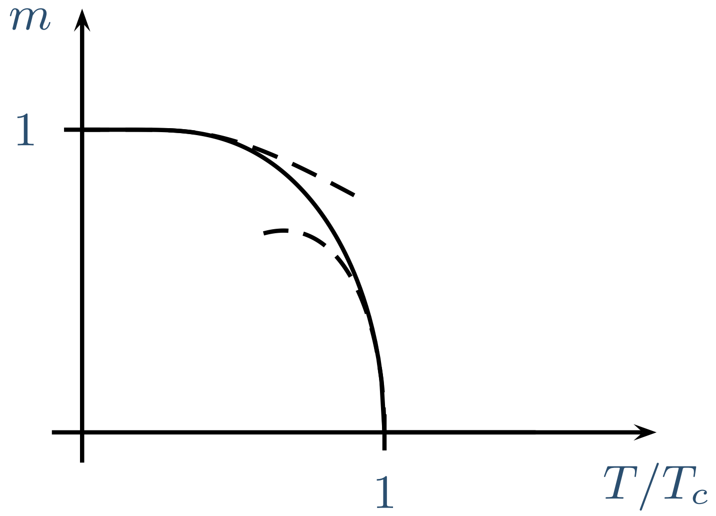
- A numerical solution for $m(T)$ is shown below, together with our two approximate solutions (shown as dashed lines):



- The value of $m(T)$ is continuous at $T = T_c$, but its slope is discontinuous.

Numerical solution ($h = 0$)

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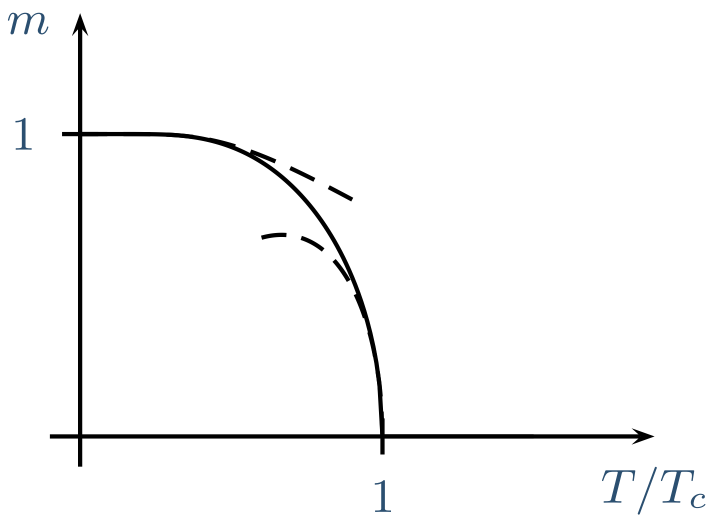
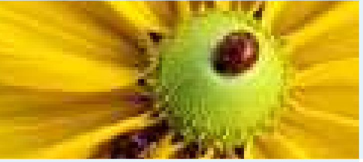


- The value of $m(T)$ is continuous at $T = T_c$, but its slope is discontinuous.
- A phase transition with a continuous order parameter is called a continuous (or second-order) phase transition.[3]

---

[3] In a first-order phase transition, the order parameter $m(T)$ is discontinuous. In an nth-order phase transition, $\mathrm{d}^n m/\mathrm{d}T^n$ is singular but $\mathrm{d}^{n-1} m/\mathrm{d}T^{n-1}$ is finite.



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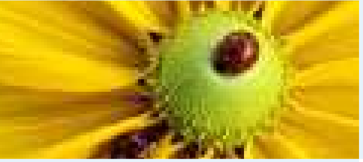
- A key prediction of the mean-field theory is the behavior

$$m(T) \propto \left(\frac{T_c}{T} - 1\right)^{1/2}$$

just below the critical point $T = T_c$.



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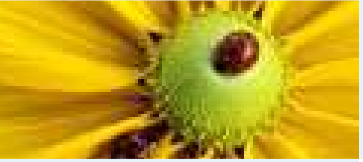
- For ferromagnets (i.e., $J > 0$) in 3D, the true critical behavior is indeed of the form

$$m(T) \propto \left(\frac{T_c}{T} - 1 \right)^{\beta},$$

but the critical exponent β is closer to 1/3 than 1/2 (experimentally, $\beta \approx 0.334$).[4]



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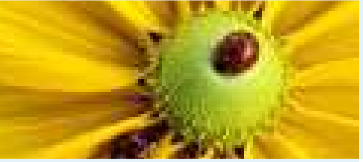

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- Although T_c varies from one material to another (Fe, Ni, etc.), the value of β is independent of the material.
- Hence, there exist both universal properties (e.g., β) and non-universal properties (e.g., T_c) associated with phase transitions.

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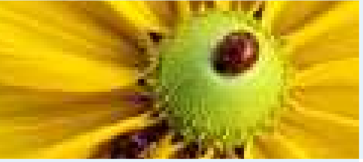
[4] The distinction between the inverse temperature $\beta = 1/k_{\mathrm{B}}T$ and the critical exponent β will always be clear from the context.



Nonzero magnetic field

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- To find $m(T)$ when $h \neq 0$, we must return to the original consistency equation
$$m = \tanh[\beta(h + Jqm)].$$

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- A graphical solution can be found by substituting $x = \beta(h + Jqm)$, which yields
$$\tanh x = \frac{T}{T_c}x - \frac{h}{k_{\mathrm{B}}T_c}.$$

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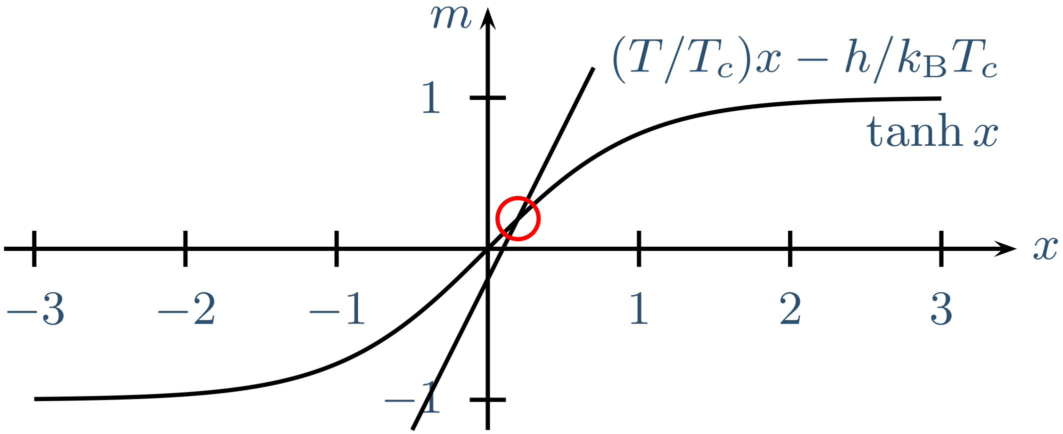
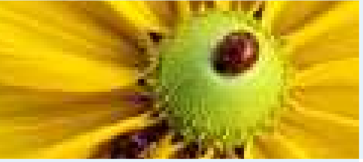
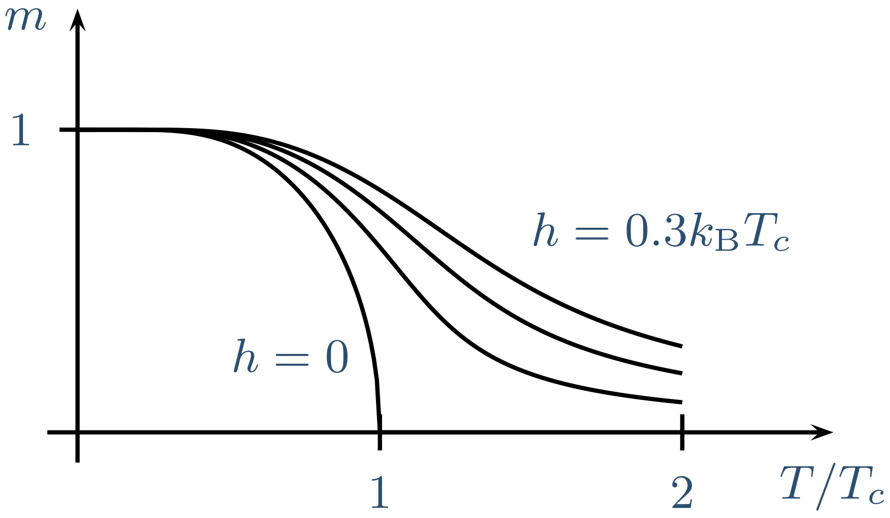
- Hence, a solution with $m \neq 0$ always exists when $h \neq 0$:





Order parameter ($h \neq 0$)

- Numerical solutions for $m(T)$ are shown below, for magnetic fields with $h/k_\mathrm{B}T_c$ between 0 and 0.3:



- Notice that the discontinuity in $\mathrm{d}m/\mathrm{d}T$ for $h = 0$ is no longer present when $h \neq 0$.