Apr. 27

# Magnetism

We have now completed our discussion of the basic principles of statistical mechanics and the general formalism for calculating thermodynamic functions from the underlying classical or quantum mechanical equations of motion. Up to this point, though, we have only discussed models that are relatively straightforward to analyze. In all cases (except for the case of the ideal Bose gas), the complete solution for the qualitative behavior was smooth in the underlying parameters and involved simple trade-offs between energy and entropy.

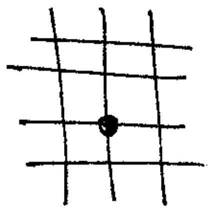
Many systems, though, have behavior that is intrinsically more complex. In many systems, atoms can interact *cooperatively* with one another. A strong correlation between two atoms can enhance their interaction with neighboring atoms. The resulting strong correlations may cause the system to have different macroscopic behaviors that are qualitatively distinct from one another. These are called *thermodynamic phases.* The transition points between phases may be marked by *discontinuous* changes in the thermodynamic functions.

Cooperativity, thermodynamic phases, and phase transitions are the most fascinating aspects of statistical mechanics. I will devote most of the rest of the course to these topics.

To introduce this subject, I will study a simple model problem that is a part of the theory of magnetism. Magnetism is a famous example of cooperativity. In certain materials—iron, cobalt, and alloys that include these metals—spins carried by $f$ orbitals in individual atoms interact with one another in a way that favors spin alignment. It turns out that these orienting forces collectively enhance one another, resulting in macroscopic spin alignment, that is, *magnetization* of the block of material. The magnetized and unmagnetized states constitute two distinct thermodynamic phases. The transition between these phases not only is not smooth, but also it is characterized by weird non-analytic behavior of the thermodynamic functions. In this lecture and the next, I will study a simple statistical mechanics model of these phenomena.

In setting up this model, I will concentrate on the statistical and cooperative aspects. I will assume that individual atoms carrying spins have an interaction that favors spin alignment. (You should have learned in your quantum mechanics class that, for transition-metal atoms, this follows from *Hund's rule.*) I will then put that information into a statistical mechanics description of a crystal of atoms and ask what the macroscopic properties of this system are.

Consider, then, a model built on a cubic lattice of atoms. At each lattice point, I will put a spin variable



$$\vec{S}_n$$

I will assume that these spins interact through the model Hamiltonian

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \vec{s}_i \cdot \vec{s}_j - \mu \vec{h} \cdot \sum_i \vec{S}_i$$

where $i$ is a lattice site and $\langle ij \rangle$ represents a set of two sites that are nearest neighbors on the lattice. An interaction favoring alignment of spins corresponds to $J > 0$. Finally $\vec{h}$ represents the external magnetic field, with $\mu$ the magnetic moment of the atom. I will assume that $\mu > 0$. This model is called the *Heisenberg model.*

Heisenberg could not solve the Heisenberg model, even for a 1-dimensional chain of spins. So he gave his graduate student Ising an easier problem to work on. This is the *Ising model*, in which the spin variables take only the two values

$$s_i = \pm 1$$

Then the Hamiltonian is

$$\mathcal{H} = -J \sum_{\langle ij \rangle}' s_i s_j - \mu h \sum_i s_i$$

In this lecture and the next, I wlll study the statistical mechanics of this model. The Ising model turns out to accurately describe the magnetization transition for magnets with an *easy axis* of magnetization. I will argue in a later lecture that it also gives a qualitative description of many other systems with phase transitions.

I will study this model in the following way: First, I will solve the model using an approximation method called *mean field theory.* This is a powerful method that gives a consistent picture of all of the thermodynamic phases of the model. After this, I will give an exact solution of the Ising model in one dimension. This analysis is intended to shake your faith in mean field theory. Then, I will present some exact results for the Ising model in higher dimensions that are intended to restore some part of your faith in mean field theory. In all, the discussion of the Ising model from several points of view will provide some relevant materials for the general understanding of phase transitions that we will develop in the second half of this course.

I will begin with the mean field theory analysis. The thermal properties of the Ising model follow from the partition function

$$Z = \sum_{s_i = \pm 1} \exp\Big[\beta J \sum_{\langle ij \rangle} s_i s_j + \beta \mu h \sum_i s_i\Big]$$

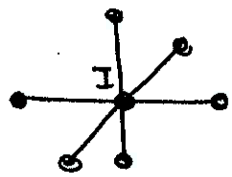
Let the total number of lattice sites be $N$. I will study this problem first for $h = 0$. It is not so easy to compute $Z$ exactly, because there are $N$ sums over the spin values, and these sums are all coupled to one another. The analysis would be trivial if we could decouple the sums. This is done approximately by *mean field theory.* To sum over the spin $s_i$, I will assume that all of the neighboring spins are fixed at the thermal average value $\langle s \rangle$ given by

$$\langle s \rangle = \frac{\sum_s s_I \, e^{\beta J \sum s_i s_j}}{\sum_s e^{\beta J \sum s_i s_j}}$$

I will evaluate this expression by applying the same approximation to the sums that appear here. Then the terms in the exponent that involve the spin $s_I$ become

$$\beta J \, s_I \cdot \sum_{\text{neighbors}} \langle s_j \rangle = 6 \beta J \langle s \rangle \cdot s_I$$

where the factor 6 comes from the fact that a site of a cubic lattice has 6 nearest neighbors. (This number is $2d$ in $d$ dimensions.)




The thermal average value of $s_I$ is then

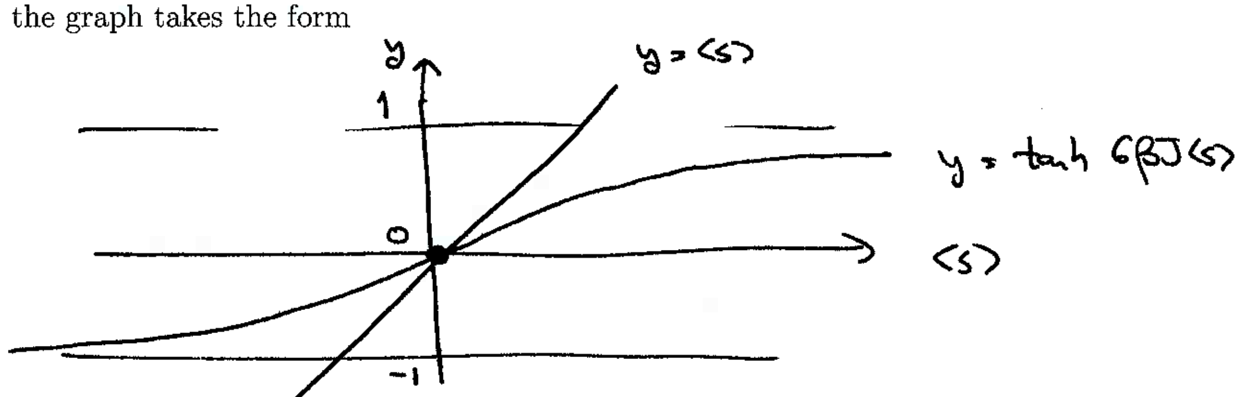
$$\langle s_I \rangle = \frac{e^{6\beta J\langle s\rangle}\cdot(+1) + e^{-6\beta J\langle s\rangle}\cdot(-1)}{e^{6\beta J\langle s\rangle} + e^{-6\beta J\langle s\rangle}}$$

$$= \tanh\left(6\beta J\langle s\rangle\right)$$

Setting this equal to $\langle s\rangle$, we obtain a self-consistency equation that we can solve for $\langle s\rangle$,

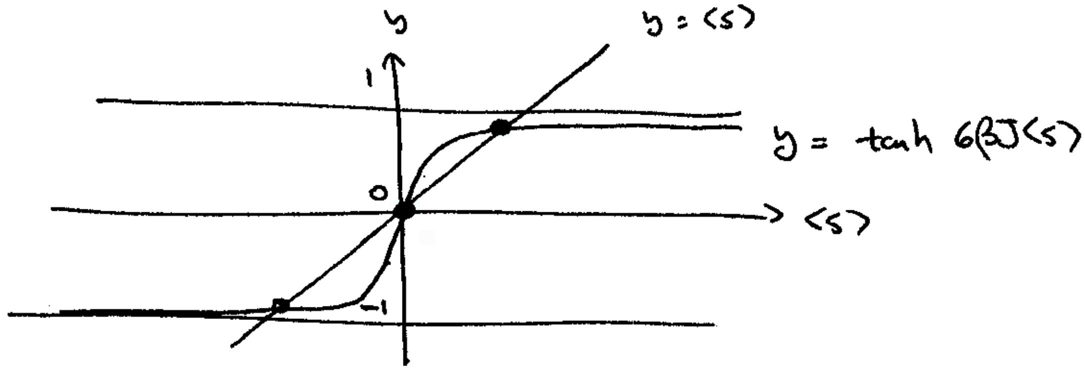
$$\langle s\rangle = \tanh 6\beta J\langle s\rangle$$

We can solve this equation graphically by plotting the left- and right-hand sides of the equation versus $\langle s\rangle$. For the left-hand side, $y = \langle s\rangle$; the slope of this line is 1. If high temperature and small $\beta$, the right-hand side has a shallow slope near $\langle s\rangle = 0$, so the graph takes the form




There is one solution at $\langle s\rangle = 0$.

However for large $\beta$ or low temperature, the function $\tanh(6\beta J\langle s\rangle)$ has a steep slope near $\langle s\rangle = 0$. Then the picture changes to




Now the equation for $\langle s \rangle$ has three solutions, the one at $\langle s \rangle = 0$ and two new solutions at

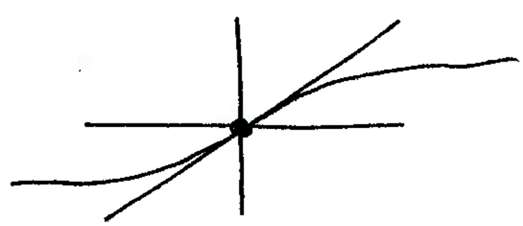
$$\langle s \rangle = \pm s_0$$

The solutions with $\langle s \rangle \neq 0$ turn out to have a higher statistical weight than the solution at $\langle s \rangle = 0$, so these solutions are preferred. I will demonstrate in a later lecture that one can assign values to the free energy for the three cases, and that the two nontrivial solutions have a lower free energy than the solution at $\langle s \rangle = 0$. The two nontrivial solutions have *the same* free energy. This is obvious, because they are related by a *symmetry* of the model,

$$s_i \longrightarrow -s_i$$

These are *distinct* but *equivalent* thermodynamic states.

The boundary between the two behaviors occurs when the functions $y = \langle s \rangle$ and $y = \tanh(6\beta J \langle s \rangle)$ are *tangent* at $\langle s \rangle = 0$.



To locate this point, expand the equation about $\langle s \rangle = 0$. Since

$$\tanh x = x - \frac{x^3}{3} + \cdots$$

the self-consistency equation becomes

$$\langle s \rangle = 6\beta J \langle s \rangle - \frac{1}{3}\left(6\beta J \langle s \rangle\right)^3 + \cdots$$

Tangency occurs when

$$6\beta J = 1$$

This defines the *critical temperature* $\beta_c$ or $T_c = 1/\beta_c$. Explicitly,

$$6\beta_c J = 1 \quad \text{or} \quad T_c = 6J$$

In a general dimensionality,

$$T_c = 2dJ$$

For $T > T_c$, the only solution is $\langle s \rangle = 0$. For $T < T_c$ but $T$ close to $T_c$, we can solve for $s_0$ in a power series expansion in $(T_c - T)$;

$$\langle s \rangle = 6\beta J \langle s \rangle - 72(\beta J)^3 \langle s \rangle + \cdots$$

$$(6\beta J - 1)\langle s\rangle = 72(\beta J)^3 \langle s\rangle^3$$

$$\left(1 - \beta_c/\beta\right) = 12(\beta J)^2 \langle s\rangle^2$$

so that

$$\approx \tfrac{1}{3}\langle s\rangle^2 = \tfrac{1}{3} s_0^2 \quad \text{near } T = T_c$$

$$s_0 \cong \left[3\left(1 - T/T_c\right)\right]^{\frac{1}{2}} \quad \text{for } T \lesssim T_c$$

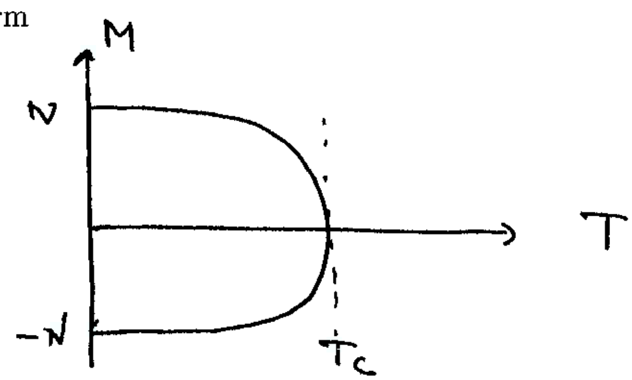
The macroscopic magnetization of the magnet is given by

$$M = \sum_i \langle s_i\rangle = N\langle s\rangle$$

Then

$$M = \begin{cases} 0 & T > T_c \\ \pm\left[\frac{3}{T_c}(T_c - T)\right]^{\frac{1}{2}} & T < T_c \end{cases}$$

This is an explicitly non-analytic behavior in the vicinity of $T_c$. As a function of $T$, $M(T)$ has the form



We can readily repeat this calculation for a nonzero value of the magnetic field. The statistical weight for a single spin in mean field theory is now

$$e^{6\beta J \langle s \rangle s_I + \beta \mu h s_I}$$

The expectation value of $s_I$ then becomes

$$\langle s \rangle = \frac{e^{6\beta J\langle s \rangle + \beta\mu h} \cdot (+1) + e^{-6\beta J\langle s \rangle - \beta\mu h} (-1)}{e^{6\beta J\langle s \rangle + \beta\mu h} + e^{-6\beta J\langle s \rangle - \beta\mu h}}$$

$$= \tanh\left(6\beta J\langle s \rangle + \beta\mu h\right)$$

Analyze this first for $J = 0$, the limit of large $h$ or of small coupling between the spins. The self-consistency equation is

$$\langle s \rangle = \tanh \beta\mu h$$

and is exact in this case. The external field drives a finite magnetization at any temperature,

$$M = N \tanh \beta\mu h$$

Define the *magnetic susceptibility* as

$$\chi = \frac{\partial M}{\partial h}$$

The magnetic susceptibility at $h = 0$ is

$$\chi(h=0) = \left.\frac{\partial M}{\partial h}\right|_{h=0} = N\beta\mu$$

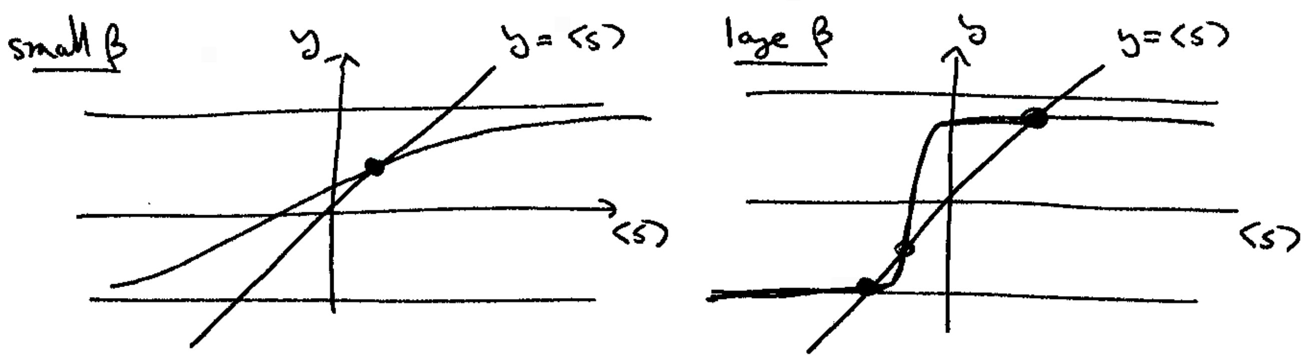
This behavior is characteristic of solids with free atomic spins. It is called the *Curie-Weiss law*,

$$\left.\chi\right|_{h=0} \sim \frac{1}{T}$$

Now restore $J$ and analyze the consequences in mean field theory. The self-consistency equation is

$$\langle s\rangle = \tanh\left(6\beta J\langle s\rangle + \beta\mu h\right)$$

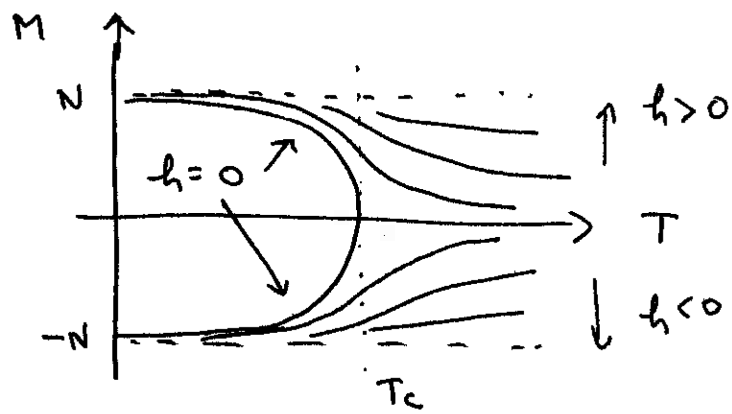
We can again solve this equation graphically. The tanh curve shifts to the left relative to the figures above. The graphical solution then looks like



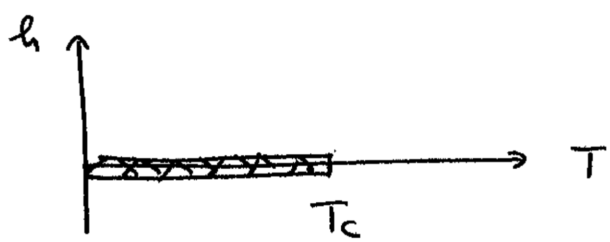

For small $\beta$ there is one solution that agrees qualitatively with the idea that $\langle s\rangle = 0$ solution in the previous case is forced to a nonzero value by the magnetic field. For large $\beta$, there can be 3 solutions. For $h > 0$, the solution with the lowest free energy and thus the highest statistical weight is the one furthest to the right. This solution evolves continuously from the solution with $\langle s\rangle = +s_0$ as $h$ is increased from zero. If

$h < 0$, there is a mirror-image solution with the same free energy at a negative value of $\langle s \rangle$.

The solution for $h \neq 0$ and small $\beta$ evolves smoothly into the favored solution for $h \neq 0$ and large $\beta$ as $\beta$ is increased. The plot of $M$ versus $T$ for $h \neq 0$ then has the form




All of the $M$ versus $T$ contours are smooth except for the contour at $h = 0$. Note the presence of an *excluded region* in the $(M, T)$ plane that does not correspond to any thermodynamic state. The plane of $h$ versus $T$ appears as




For $T > T_c$, $M$ is zero on the line $h = 0$ and changes continuously as $h$ is varied from negative to position values. However, for $T < T_c$, $M$ takes different values on opposite sides of the line $h = 0$. As $h$ is increased from negative to positive values, $M$ changes *discontinuously* across this line. The special point $T = T_c$, $h = 0$ where the essential nonanalytic behavior occurs is called the *critical point.*

It is interesting to compute the magnetic susceptibility at zero field for $T > T_c$. Return to the self-consistency equation

$$\langle s \rangle = \tanh\left(6\beta J \langle s \rangle + \beta \mu h\right)$$

and expand as before for small $\langle s \rangle$ and for small $h$.

$$\langle s\rangle = 6\beta J\langle s\rangle + \beta\mu h - \frac{1}{3}\left(6\beta J\langle s\rangle + \beta\mu h\right)^3 + \cdots$$

The term linear in $\langle s\rangle$ and $h$ is

$$(1 - 6\beta J)\langle s\rangle = \beta\mu h$$

Then

$$M = N\langle s\rangle = \frac{N\beta\mu h}{1-6\beta J} = \frac{N\mu h/T}{1-T_c/T}$$

and therefore

$$\chi(h=0) = \left.\frac{\partial M}{\partial h}\right|_{h=0} = \frac{N\mu}{T-T_c}$$

We see that the Curie-Weiss law is modified in a way that makes $\chi$ *singular* at $T = T_c$. It can also be shown that

$$\chi(h=0) \sim \frac{A}{T_c - T}$$

as $T$ approaches $T_c$ from below.

The same analysis gives the magnetization as a function $h$ at $T = T_c$. Keeping the leading terms for small $\langle s\rangle$ and $h$ at $T = T_c$,

$$\cancel{\langle s\rangle} = \cancel{6\beta_c J\langle s\rangle} + \beta_c\mu h - \frac{1}{3}\left(6\beta_c J\langle s\rangle + \cdots\right)^3 + \cdots$$

Then

$$h = \frac{1}{3\beta_c \mu} \langle s \rangle^3$$

$$\langle s \rangle = (3\beta_c \mu h)^{\frac{1}{3}}$$

so that, finally,

$$M = N \cdot (3\beta_c \mu h)^{\frac{1}{3}}$$

We have now shown that, when we use mean field theory to solve for the behavior of the Ising model, we find a variety of remarkable behaviors:

- a spontaneous magnetization at $h = 0$ that appears for $T < T_c$. There are two possible values of this magnetization,

$$M = \pm N s_0(T)$$

- a line of discontinuities in the $(h, T)$ plane, or an excluded region in the $(M, T)$ plane.
- singular behaviors in many thermodynamic functions in the vicinity of the critical point $T = T_c$, $h = 0$:

$$M \sim (T_c - T)^{\frac{1}{2}} \qquad T \leq T_c, \; h = 0$$

$$\chi \sim |T - T_c|^{-1}$$

$$M \sim h^{\frac{1}{3}} \quad \text{at } T = T_c$$

We would now like to know whether these behaviors are true properties of the Ising model that survive when we analyze this model using more exact methods. I will address that question in the next lecture.