Sept. 28

Physics 212 – Statistical Mechanics

Magnetism

Now that we have reviewed the basic principles of Statistical Mechanics, I would like to go into more detail on the systems that will be the main subject of this course. In the first lecture, I referred to these systems as having *phase transitions*. Now I would like to refine that concept into a more specific one, that of *order-disorder transitions*. Our typical example will be an idealized model of a magnet. However, the concept will extend to a wide variety of other systems, including superconductors and superfluids, liquid crystals, structural and composition transitions in solids, and to the liquid-gas transition.

To begin, I will say a few words about the relation between the magnets in this course and real magnets. Real magnets are complex physical systems. Among all metals and solid-state compounds, magnetism is limited to a small region of the periodic table, mainly to the 1st row transition metals Mn through Cu. In these atoms there are d orbitals containing unpaired electrons. The electrons in these orbitals interact in such a way as to promote parallel or antiparallel spin orientations

(1)

Naively, you might think that this is a consequence of spin-spin magnetic dipole interactions, but actually these give only a minor contribution. The main force driving magnetism comes from the quantum chemistry of the electronic states. In fact, the long-ranged dipole interactions are a complication; they cause a uniform magnetized state to break up into randomly oriented magnetic domains. In the idealized magnets that I will study, I will ignore the dipole interactions and treat the quantum chemistry interactions phenomenologically. This will give us a nice setting to investigate the fundamental issues of Statistical Mechanics.

Let me back up and add a little background. Consider first a collection of spin 0 atoms with all electrons paired. Such a system exhibits *diamagnetism*, that is, a magnetic moment induced in the direction opposite to an external magnetic field,

$$\chi = \left.\frac{\partial M}{\partial H}\right|_T < 0 \ . \tag{2}$$

The ground state does not interact directly with the external field, so the dominant effect comes from transitions to excited states that appear in second order perturbation theory.

A collection of atoms with unpaired electron spins exhibits *paramagnetism*, that is, a magnetic moment induced parallel to an applied field,

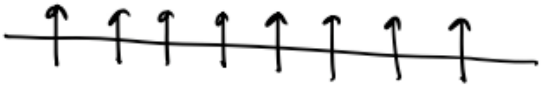
$$\chi > 0 \ , \tag{3}$$

with, typically, a much larger magnitude of χ. In this case, the free spins can rotate to orient themselves with the applied field. This leads to a characteristic behavior of the magnetic susceptibility at high temperatures

$$\chi \sim \frac{1}{T} \ , \tag{4}$$

which called the *Curie law*, after Pierre Curie.

Unpaired electrons within a single atom or a cluster of atoms can interaction with one another through the form of their wavefunctions. For a single atom, the form of the ground state is represented by *Hund's rules.* Simply stated, these imply that the spin of the atom prefers to be as large as possible. This preference follows from the electons' Coulomb repulsion. Because of the Pauli exclusion principle, the wavefuntions of electrons with parallel spins are naturally further apart and, consequently, they have lower energy. The same logic applies to electrons in clusters of atoms. But sometimes second-order effects dominate and cause this interaction to favor antiparallel spins. In the first case, the ground state of the materials displays *ferromagnetism*



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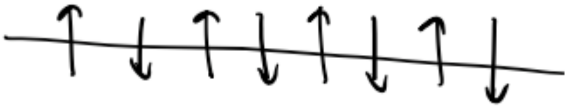
in the second case, the ground state displays *antiferromagnetism*,



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A typical behavior of these systems is that, at high temperature, they are paramagnetic, with magnetic ordering setting in at a critical temperature T_c. Some values of T_c for real materials are

ferromagnets:	T_c (°K)	antiferromagnets	T_c (°K)
Fe	1043	MnO	122
Co	1388	CoO	291
Ni	627	NiO	600

(7)

In the case of ferromagnetism, T_c is also called the *Curie temperature*; in antiferromagnets, it is called the *Néel temperature*, after Louis Néel. If you would like to read more about magnetism in real-world materials, I recommend the chapters on magnetism in Ashcroft and Mermin, *Solid State Physics*.

For the purpose of this course, I will adopt an idealized model of these systems. I will define a magnet to be described by a lattice of points with a spin at each lattice site, with the spins interacting through simple phenomenological Hamiltonian terms. These can be of ferromagnetic or antiferromagnetic sign. Spins are of course 3-dimensional vectors, but often the symmetry of the problem is broken by effects of the crystal structure. Real materials might have magnetic orientation along a prefered axis or parallel to a prefered plane. In my idealization, I will treat spins as classical vectors with a fixed number n of components. (For some examples, I will consider quantum spins.) I will most often consider the model Hamiltonians

$$\mathcal{H} = -\sum_{i\nu} J\vec{S}_i \cdot \vec{S}_{i+\nu} - \sum_i \vec{H} \cdot \mu\vec{S}_i \tag{8}$$

Here, i is a lattice point and ν is a unit lattice vector (so that i and $i+\nu$ are nearest neighbors), $\vec{S}_i$ is a unit vector with n components, H is the external magnetic field, J is a positive constant representing the spin-spin interaction, and μ is the effective electron magnetic moment. I will write N for the total number of lattice sites. For definiteness, consider a square (simple cubic, etc.) lattice of dimension d; then there are d independent unit vectors ν. In these lectures, I will set $\mu = 1$; that is, I absorb μ into the normalization of H.

A standard nomenclature for these Hamiltonians is to name them according to the value of n or the symmetry of the model. The most important cases are

model	N (components of S_i)	symmetry of $\mathcal{H}$
Ising model	1	Z_2
XY model	2	$SO(2) = U(1)$
Heisenberg model	3	$SO(3)$

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Note the column giving the symmetry group of the Hamiltonian. Z_2 is the discrete group consisting of elements

$$\{1, -1\} \tag{10}$$

$SO(2)$ is the rotation group in 2 dimensions, or, equivalently, the group $U(1)$ of phase rotations

$$\phi \to e^{i\alpha}\,\phi \tag{11}$$

$SO(3)$ is the full rotation group in 3 dimensions. This model can also be used to describe a large number of other physical systems. In particular, cases with $n > 3$ can be realized in real, 3-dimensional systems.

The introduction of a symmetry group allows us to characterize the phenomenon of magnetization more precisely. The magnetic state is an *ordered* state in the following sense: The underlying Hamiltonian has a symmetry,but the thermodynamic state described by this Hamiltonian does not respect that symmetry. Instead, it chooses an orientation within the symmetry group. This important situation is called "spontaneously broken symmetry". The transition from a symmetric state at temperatures $T > T_c$ to a broken-symmetry state at $T < T_c$ is called an "order-disorder transition".

It is useful to have a thermodynamic observable that characterizes the phenomenon of spontaneous symmetry breaking. To find one, choose a macroscopic thermodynamic observable Q that transforms nontrivially under the symmetry group. Then, by symmetry,

$$\langle Q \rangle = 0 \tag{12}$$

in the symmetric, high temperature phase. In an ordered, low-temperature state, we will have

$$\langle Q \rangle \neq 0 \ . \tag{13}$$

Then Q is called the *order parameter*. Usually, Q will be an integral over a local measure of order. For the idealized magnet above, we can use as the magnetization M as the order parameter. Here,

$$M = \sum_i S_i \qquad \text{or} \qquad M = \int d^3x \ m(x) \tag{14}$$

where S_i or $m(x)$ measures the local magnetic order.

It is totally nontrivial that there exists a thermodynamic state for which $\langle Q \rangle \neq 0$. I will discuss this point in a moment, but, first, I would like to explore the phase diagram of our idealized magnet. For concreteness, I will consider the Ising case, $n = 1$.

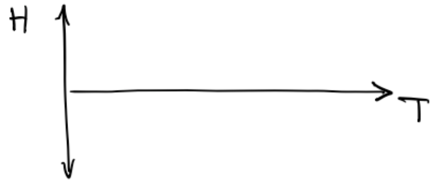
Let's pause for a word about Ising. Ernst Ising ws a student of Wilhem Lenz in Hamburg. He computed the free energy of the 1-dimensional Ising model in his Ph.D. thesis (1924). We will study this solution in a future lecture. Being Jewish, he had to flee Nazi Germany. After a string of non-academic occupations and difficult escapes, he came to the US in 1947 and eventually became a professor of physics at Bradley University in Peoria, Illinois. He was surprised to learn that, in his years outside of physics, his model had become a touchstone of Statistical Mechanics.

The Ising partition function is

$$Z = \sum_{\{S_i = \pm 1\}} \exp\Big[-\beta J \sum_{i\nu} S_i S_{i+\nu} - \beta H \sum_i S_i \Big] \tag{15}$$

The spins are summed individually over the values ±1. With J fixed, there are two parameters, T and H, so the various phases of the model are contained in the (T, H)

plane,



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For $T \gg J$, $\beta J \to 0$, and the interaction term proportional to βJ can be ignored. The partition function then becomes a product of uncoupled spins interacting with the external field. This describes a paramagnetic phase. It is not difficult to compute the response of the magnetization to an external field. The partition function becomes

$$\begin{aligned} Z &= \sum_{\{S_i=\pm 1\}} \prod_j e^{\beta H S_j} \\ &= \prod_j 2\cosh\beta H = \Big(2\cosh\beta H\Big)^N \end{aligned} \tag{17}$$

so that

$$F = -\frac{N}{\beta}\log(2\cosh\beta H). \tag{18}$$

Again, N is the total number of lattice sites. Then

$$M = -\left.\frac{\partial F}{\partial H}\right|_T = \frac{N}{\beta}\frac{\beta\sinh\beta H}{\cosh\beta H}\ , \tag{19}$$

or

$$M = N\tanh\beta H \tag{20}$$

In this regime

$$\chi = \left.\frac{\partial M}{\partial H}\right|_T = N\beta\frac{1}{\cosh^2\beta H}\ . \tag{21}$$

For for small H/T

$$\chi \sim N\cdot\frac{1}{T}\ , \tag{22}$$

following the Curie Law.

Next, consider the behavior as $T \to 0$. Here we must maximize $e^{-\beta\mathcal{H}}$ or minimize $\mathcal{H}$. The minimum energy is obtained when all of the spins are aligned. There are two possible cases:

$$\begin{aligned} &\text{all } S_i = +1 \qquad E = N(-dJ - H) \\ &\text{all } S_i = -1 \qquad E = N(-dJ + H) \end{aligned} \tag{23}$$

Which one wins depends on the sign of H. For $H > 0$,

$$Z = \Big[e^{\beta(dJ+H)}\Big]^N\ , \tag{24}$$

so that

$$F = -N(dJ + H) \tag{25}$$

and

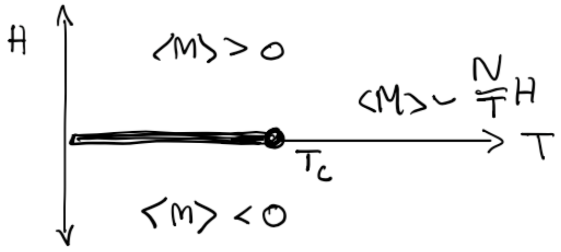
$$M = N \tag{26}$$

so M is a constant. The spins are stuck at their maximum value. Similary, for $H < 0$,

$$F = -N(dJ - H) \qquad M = -N \tag{27}$$

These results imply that M is discontinuous as a function of H at $T = 0$.

Assuming that the limits are reached continuously, we can fill in the phase diagram



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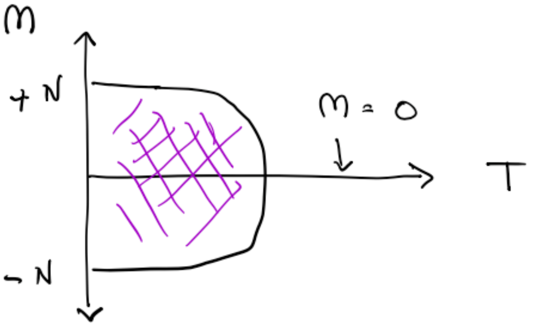
Along the line $H = 0$, M is zero at high temperator but must become discontinous above and below the line at some finite temperature. The values of M along this line will have the form



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The point where M becomes nonzero along the line $H = 0$ is the critical temperature $T = T_c$. In the next lecture, I will show you an approximate computation of the partition function that realizes the details of this picture.

In the 1920's and 1930's, it was controversial whether the Ising partition function actually predicted a discontinuous behavior. In 1936, Rudolf Peierls finally gave a mathematical proof that the 2-dimensional Ising model has an ordered state at low temperatures.

Actually, using our axiom that the macroscopic properties of a state of thermal equibrium are given by an average over the energy surface, it is easy to show that it is impossible to have a thermodynamic state at $H = 0$ with $\langle M \rangle \neq 0$. Consider

$$\langle M \rangle = \frac{\sum_{\{S_i\}} e^{-\beta \mathcal{H}[S]} (\sum_i S_i)}{\sum_{\{S_i\}} e^{-\beta \mathcal{H}[S]}} \ . \tag{30}$$

At $H = 0$, for every spin configuration $\{S_i\}$, there is a corresponding configuration $\{-S_i\}$ that has the same energy and the opposite value of M. Adding these terms in pairs in the numerator, we find

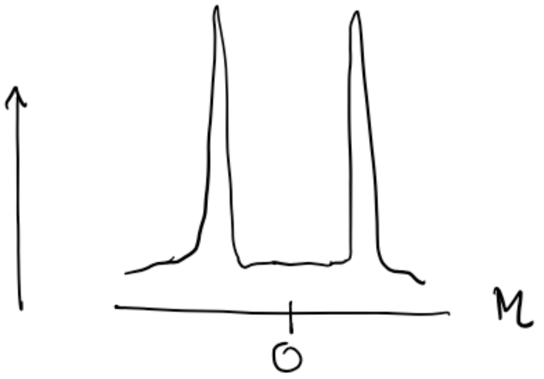
$$\langle M \rangle = 0 \tag{31}$$

This is a direct consequence of the Z_2 symmetry.

The actual picture must be more subtle. To analyze it, think about writing the partition function as an integral over the variable M

$$Z = \int dM \ \ \sum_{\{S_i\}} e^{-\beta \mathcal{H}[S]} \delta(M - \sum_i S_i) \tag{32}$$

From the description of the minima of $\mathcal{H}$ at $T = 0$, we might have intuition that the integrand of the dM integral has the form



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The peak on the left has most of the spins down, $S_i = -1$. The peak on the right has most of the spins up, $S_i = +1$. The integrand is left-right symmetric, reflecting the Z_2 symmetry of the problem. In a finite system, the peaks are a finite distance apart and of finite height, and the only correct prescription would be to integrate over both of them. This gives $\langle M \rangle = 0$.

However, in a macroscopic system, a different treatment might be appropriate. If N is very large, moving from the left-hand to the right-hand peak requires flipping a number of spins of order N. As the temperature is decreased, the spins become more correlated, and so even the most easily realized path requires flipping spins together in larger and larger groups. At some point, there is no practical way to move between the two peaks. Then the partition function splits into a sum over two distinct spaces of configurations that do not communicate with one another. Call these $\mathcal{S}_-$, containing the left-hand peak, and $\mathcal{S}_+$, containing the right-hand peak. Our original partition function can then be written

$$Z = \int e^{-\beta\mathcal{H}} = \int_{\mathcal{S}_+} e^{-\beta\mathcal{H}} + \int_{\mathcal{S}_-} e^{-\beta\mathcal{H}} \ . \tag{34}$$

However, if we prepare the system in a configuration in $\mathcal{S}_+$, this system will stay in $\mathcal{S}_+$ forever, or for all practical purposes. Then the correct way to compute thermal expectation values in the state of equilibrium would be to integrate only over states in $\mathcal{S}_+$,

$$Z_+ = \int e^{-\beta\mathcal{H}} = \int_{\mathcal{S}_+} e^{-\beta\mathcal{H}} \ . \tag{35}$$

A similar situation would hold if the system were prepared with a configuration in $\mathcal{S}_-$. This would lead to a description with a partition function Z_-, integrating over $\mathcal{S}_-$ only. These two partition functions represent the two possible states of spontaneously broken symmetry. In Z_+,

$$\langle M \rangle = \frac{\sum_{\mathcal{S}_+} e^{-\beta\mathcal{H}[S]} (\sum_i S_i)}{\sum_{\mathcal{S}_+} e^{-\beta\mathcal{H}[S]}} \ > 0 \ , \tag{36}$$

and in Z_- the expectation value of M is negative and (by symmetry) equal in magnitude to that in Z_+. The sets of states $\mathcal{S}_+$ and $\mathcal{S}_-$ are called *superselection sectors.* In practice, we can prepare the thermodynamic state $\mathcal{S}_+$ by starting with $H > 0$ and then sending $H \to 0$ at fixed T. To prepare the state $\mathcal{S}_-$, we would start from $H < 0$.

In the next few lectures, I will do some calculations that will test and challenge this intuition and hopefully make the picture more precise.