

Physics 112

Magnetic Phase Transitions, and Free Energies in a Magnetic Field

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I. INTRODUCTION

There is considerable interest in the effects of magnetic fields on the properties of materials, and also in magnetic phase transitions. This handout gives a brief discussion of these topics, which, unfortunately, are largely omitted from the book by Kittel and Kroemer.

As discussed in class, the thermodynamic identity becomes, in the presence of a magnetic field,

$$dF = -S dT - M dB, \quad (1)$$

where F is the free energy, B is the external magnetic field and M is the total magnetic moment of the system, i.e. the integral of the magnetization over the sample. In what follows we will always assume that the volume and number of particles is constant. From Eq. (1) we see that the free energy should be expressed as a function of the external magnetic field and temperature so that the derivative with respect to B (at constant T) gives the magnetization,

$$M = - \left(\frac{\partial F}{\partial B} \right)_T. \quad (2)$$

It is possible to define several different free energies for a system in a magnetic field, just as for non-magnetic systems¹. Some of these are discussed in Sec. VI at the end of this handout.

You will recall from E&M classes that the magnetic field inside a magnetic material can differ from the externally applied field B_{ext} and from an auxiliary field H which is often introduced. In particular the relation between B , H , and M is

$$B = \mu_0(H + M),$$

where μ_0 is a constant. In this course we shall only consider “weakly magnetic” materials where $M \ll H \simeq B/\mu_0$, and so the difference between B , B_{ext} and $\mu_0 H$ will be negligible. From now on, we will just label the field in Eqs. (1) and (2) by B and ignore any fine distinctions.

II. A SINGLE SPIN

As a simple example, consider an “Ising” spin S which takes value ± 1 . The magnetic moment is given by $\mu = \gamma S$, where γ is the magnitude of the magnetic moment¹. We can think of this as being a simple model for the magnetic moment of the atom, in which the environment of the atom has anisotropy which causes the spin to only be aligned in the $+z$ or $-z$ directions.

As is well known from E&M, the energy of a magnetic dipole in a field is $-\mu B$, i.e.

$$E = -\gamma B S. \quad (3)$$

There are two states,

$$\begin{aligned} \text{“}\uparrow\text{”}, & \quad S = 1, & \quad E = -\gamma B, \\ \text{“}\downarrow\text{”}, & \quad S = -1, & \quad E = \gamma B. \end{aligned}$$

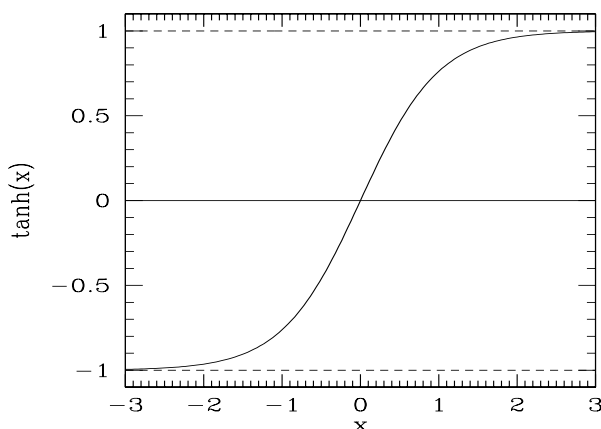
The probabilities of these states are

$$P_{\uparrow} = \frac{e^{\beta\gamma B}}{e^{\beta\gamma B} + e^{-\beta\gamma B}}, \quad \text{and} \quad P_{\downarrow} = \frac{e^{-\beta\gamma B}}{e^{\beta\gamma B} + e^{-\beta\gamma B}}.$$

Hence the expectation of the magnetic moment, which we call m , is given by

$$m \equiv \langle \mu \rangle = \gamma (1 \cdot P_{\uparrow} + (-1) \cdot P_{\downarrow}) = \gamma \left(\frac{e^{\beta\gamma B} - e^{-\beta\gamma B}}{e^{\beta\gamma B} + e^{-\beta\gamma B}} \right) = \boxed{\gamma \tanh \left(\frac{\gamma B}{k_B T} \right)}. \quad (4)$$

The tanh function is sketched below.



¹ In atomic physics, the magnetic moment of an atom, μ , is related to the total angular momentum \mathbf{J} by $\mu = g\mu_B\mathbf{J}$, where g is the Landé g-factor, and $\mu_B \equiv e\hbar/(2mc)$ is the Bohr magneton.

It has the following properties, which you should be familiar with or at least be able to derive:

$$\tanh(-x) = -\tanh(x), \quad \text{i.e. } \tanh \text{ is an odd function,} \quad (5)$$

$$\tanh(x) = x - \frac{x^3}{3} + \dots \quad \text{small } x, \quad (6)$$

$$\tanh(x) = 1 - 2e^{-2x} + \dots \quad \text{large } x. \quad (7)$$

From Eq. (4) we deduce that for $\gamma B/k_B T \gg 1$ (i.e. large fields) we have $m \rightarrow \gamma$ so all the spins are aligned along the direction of the field as expected. For small fields, $\gamma B/k_B T \ll 1$, we have

$$m = \frac{\gamma^2}{k_B T} B.$$

Hence the magnetization is proportional to B for small B . This is reasonable since for $B = 0$ we expect $m = 0$ on symmetry grounds, because there is no reason for the spin to point up more than down on average. The constant of proportionality is called the magnetic *susceptibility* χ . We see that

$$\chi = \frac{C}{T},$$

where $C = \gamma^2/k_B$ is a constant. This $1/T$ dependence is called **Curie's Law**, and is observed in many materials with a *dilute* concentration of magnetic atoms.

Things get more complicated with a high concentration of magnetic atoms since they interact when they are neighbors. We shall discuss the effects of interactions in a certain approximation (mean field approximation) in the next section. In a homework problem you will use the mean field approximation to determine the behavior of the susceptibility. You will see that, in the presence of interactions, the susceptibility diverges not at $T = 0$ but at a finite transition temperature T_c . (The mean field approximation works better in high space dimensions, and, in the opposite extreme of $d = 1$, the finite temperature transition predicted by mean field theory does not, in fact, occur.)

We can also compute the free energy of the spin Hamiltonian in Eq. (3). Since the energies are $\pm\gamma B$ we have

$$F = -k_B T \ln Z = -k_B T \ln \left(e^{\beta\gamma B} + e^{-\beta\gamma B} \right) = -k_B T \ln [2 \cosh(\beta\gamma B)].$$

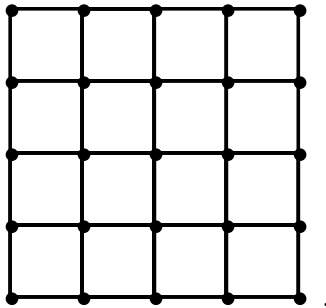
The magnetization can be obtained by differentiating with respect to B according to Eq. (2), which gives

$$m = \gamma \tanh(\beta\gamma B),$$

in agreement with Eq. (4).

III. SPIN-SPIN INTERACTIONS, PHASE TRANSITION AND MEAN FIELD THEORY

Next we include interactions between the spins, and describe the resulting phase transition at a certain level of approximation (called mean field theory). We still consider Ising spins, for simplicity, and assume that they lie at the sites of a regular lattice. In two dimensions, we could consider a square lattice where the spins lie at the corners of a regular square grid shown below:

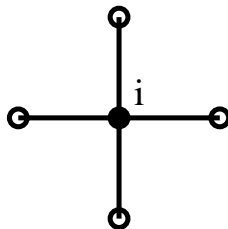


In three dimensions, we could take a “simple cubic” lattice in which the spins lie at the corners of a regular cubic grid (the natural generalization of the square lattice to three dimensions).

We assume that nearest-neighbor spins have a lower energy if they are oriented parallel to each other than if they are anti-parallel. Such systems are called **ferromagnets**. There are also materials in which neighboring spins align in opposite directions; these are called **antiferromagnets**. For the ferromagnetic case considered here the energy can be written as

$$E = -J \sum_{\langle i,j \rangle} S_i S_j - B \sum_i S_i, \quad (8)$$

where J is the strength of the interaction, $S_i = \pm 1$ is the spin on lattice site i , and the sum $\langle i,j \rangle$ indicates that each nearest-neighbor pair of spins is included *once*. We have set $\gamma = 1$ for convenience, If i denotes a particular site, then, on the square lattice, S_i is coupled to four neighbors, which are in the $+x, -x, +y$ and $-y$ directions as shown below.



The Ising model with interactions described by Eq. (8) can not be solved exactly in general. There *is* an exact solution for a *one-dimensional* chain, but one-dimension turns out to be special and, in contrast to higher dimensions, there is no finite-temperature transition. For the *two dimensional* case in zero field a solution for certain quantities was found by Onsager in a mathematical

tour-de-force. In three dimensions there is no exact solution. Hence, we will consider an *approximate* treatment, restricting ourselves to the simplest, but very useful, approximation, known as mean field theory.

Let us consider all terms in the energy which involve a particular site i . These are

$$-S_i \left(J \sum_j S_j + B \right), \quad (9)$$

where the sum is over the neighbors of i . In the mean field approximation we replace the value of the spin on a neighbor by its expectation value $\langle S_j \rangle$, which is m since the expectation value of a spin is the same on all sites for a ferromagnet. In other words we write Eq. (9) approximately as

$$-H_{MF} S_i, \quad (10)$$

where

$$H_{MF} = zJ\langle S \rangle + B = zJm + B = J_0m + B, \quad (11)$$

in which z is the number of neighbors (4 for the square lattice shown) and

$$J_0 = zJ.$$

More generally, if we have interactions of different strengths J_{ij} for different distances, then J_0 is given by

$$J_0 = \sum_j J_{ij}.$$

We call H_{MF} the “mean field”. (Historically it was often called the “molecular field”.) It includes the *average* effect of the neighbors but neglects *correlations* between the spin and its neighbors.

In Eq. (4) in Sec. II we determined the magnetization of a spin in a field B . We can apply this result here, replacing B by H_{MF} in Eq. (11) (and setting $\gamma = 1$ for convenience from now on), i.e.

$$\langle S_i \rangle \equiv m = \tanh \left(\frac{H_{MF}}{k_B T} \right)$$

or, in other words,

$$\boxed{m = \tanh \left(\frac{J_0 m + B}{k_B T} \right)}, \quad (12)$$

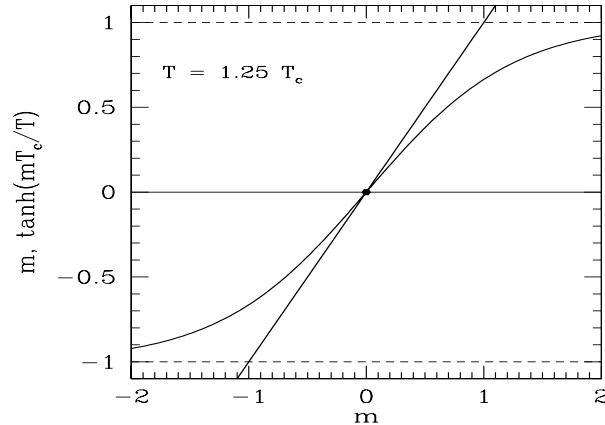
which is a “self-consistent” equation for m . (Self-consistent means that m appears on both sides of the equation, and the equation can *not* be rearranged to give an *explicit* expression of the form: $m =$ “some function of T and B ”.)

Now we will determine the form of the solutions of this equation in the absence of an external magnetic field ($B = 0$), i.e.

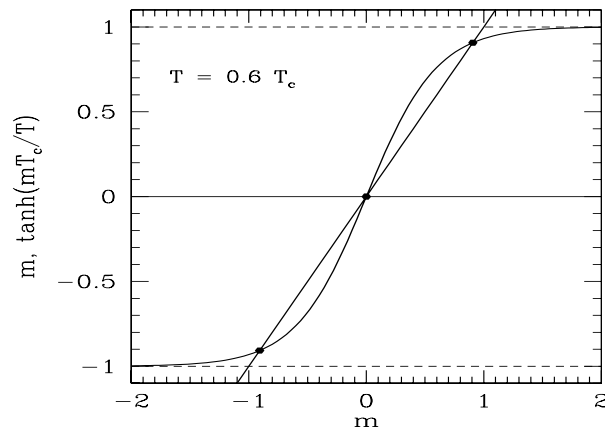
$$m = \tanh\left(\frac{J_0 m}{k_B T}\right). \quad (13)$$

We obtain solutions graphically by looking for the intersection of the curve $y = m$ with the curve $y = \tanh(J_0 m/k_B T)$.

- The slope of the tanh function at small m is $J_0/k_B T$, see Eq. (6). For $k_B T > J_0$ this is less than 1, and hence the only point where the curve $y = \tanh(J_0 m/k_B T)$ meets the curve $y = m$ is at $m = 0$, see the figure below, which is for $k_B T = 1.25 J_0$. The equilibrium value of the magnetization is therefore zero.



- However, for $k_B T < J_0$ the slope is greater than 1 so, in addition to the solution at $m = 0$ there are also solutions at a positive value of m and the negative of this, see the figure below which is for $k_B T = 0.6 J_0$.



The solution with $m > 0$ corresponds to spins aligned up, and that with $m < 0$ to spins aligned down. Since we have no magnetic field these states are equivalent. We shall see in the next section that they have lower free energy than the $m = 0$ solution, and so one or either of them describes the equilibrium state. Hence there is a transition at $T = T_c$ where

$$\boxed{k_B T_c = J_0,} \quad (14)$$

between a state with $m = 0$ (paramagnetic state) for $T > T_c$, and a state with $m \neq 0$ (ferromagnetic state) for $T < T_c$. We shall see below that m drops *continuously* to zero as $T \rightarrow T_c^-$, so this is a continuous (often called *second order*) transition.

Which state, you might ask, is selected, the one with positive m or the one with negative m ? In the absence of any small perturbation to bias the spins up or down, such as a magnetic field, the system will select one of these *at random* as it is slowly cooled through T_c . This is an example of *spontaneous symmetry breaking* in which the energy of the system is invariant under some transformation (in this case flipping all the spins) but the state of the system has a lower symmetry (because *either* the “up” spin *or* the “down” spin state has been selected). Once one of the two states has been chosen at random, the system will stay in that state as long for as the temperature stays below T_c . It would take an astronomical time for the system to fluctuate to the other state, since, to do this, it would have to go through intermediate states with a much higher energy.

To see how m varies just below T_c we expand the tanh in Eq. (13) up to third order using Eq. (6). (This is valid since m will turn out to be small in this region.) We get

$$m = m \left(\frac{T_c}{T} \right) - \frac{m^3}{3} \left(\frac{T_c}{T} \right)^3,$$

or

$$3m \left(\frac{T_c - T}{T} \right) = m^3 \left(\frac{T_c}{T} \right)^3.$$

The factor of $(T_c/T)^3$ on the RHS is very close to 1 for T close T_c and so we replace it by 1. We can also replace T in the denominator of the LHS by T_c with negligible error in this limit. Hence either $m = 0$ (which is *not* the physical solution as stated above) or

$$\boxed{m^2 = 3 \left(\frac{T_c - T}{T_c} \right), \quad (T \rightarrow T_c^-).} \quad (15)$$

We see that m has a square root variation near T_c . It is common to write this as

$$m \sim (-t)^\beta, \quad (16)$$

where

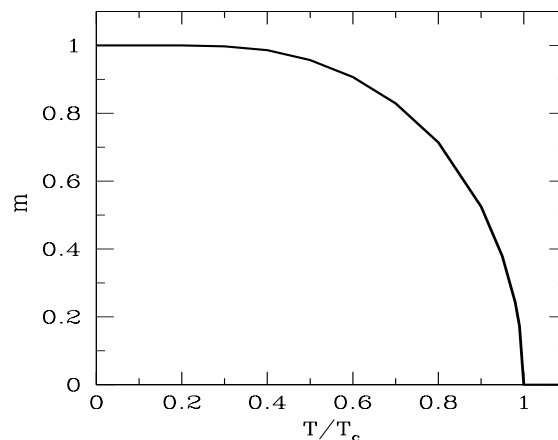
$$t = \left(\frac{T - T_c}{T_c} \right)$$

is called the *reduced temperature*, and the power

$$\beta = 1/2$$

is called a *critical exponent*. Many quantities are found to vary with a power of reduced temperature near T_c , with the result that there is a “zoo” of critical exponents, generally denoted by Greek letters,

A plot of the positive solution for m against T/T_c is shown below.



IV. MEAN FIELD FREE ENERGY

In this section we will derive the mean field equation, Eq. (13), another way, which will also give us the free energy. We will then be able to confirm that the $m \neq 0$ solutions have a lower free energy than the $m = 0$ solutions for $T < T_c$.

We compute the free energy from $F = U - TS$. To determine U in the mean field approximation, we take the average of Eq. (8), replacing $\langle S_i S_j \rangle$ by $\langle S_i \rangle \langle S_j \rangle = m^2$ since the difference $\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle$ is the correlation between S_i and S_j , which is neglected in mean field theory. Hence we obtain

$$U = -N \left[\frac{zJ}{2} m^2 + Bm \right] = -N \left[\frac{J_0}{2} m^2 + Bm \right], \quad (17)$$

where the factor of 1/2 in the first term is present otherwise we would count each of the two-spin terms in Eq. (8) twice rather than once.

Next we consider the entropy S . In mean field theory we neglect correlations and so the total entropy will just be the sum of the entropies of each spin considered separately. Each spin is up with probability P_\uparrow and down with probability P_\downarrow where

$$P_\uparrow = \left(\frac{1+m}{2}\right), \quad P_\downarrow = \left(\frac{1-m}{2}\right),$$

which correctly gives $P_\uparrow + P_\downarrow = 1$, $P_\uparrow - P_\downarrow = m$. Using the Boltzmann definition of entropy discussed in class, $s = -k_B \sum_l P_l \ln P_l$, we have

$$S = Ns = -Nk_B \left[\left(\frac{1+m}{2}\right) \ln \left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right) \ln \left(\frac{1-m}{2}\right) \right]. \quad (18)$$

Combining Eqs. (17) and (18), we obtain the free energy

$$\boxed{\frac{\tilde{F}(m, B)}{N} = -\frac{J_0}{2}m^2 - Bm + \frac{k_B T}{2} [(1+m) \ln(1+m) + (1-m) \ln(1-m)] - k_B T \ln 2.} \quad (19)$$

This free energy is a function of both m and B , and the “tilde” indicates that it is a “generalized” free energy in which m need not necessarily take its equilibrium value. Kittel calls \tilde{F} the “Landau function” since Landau used it in his important theory of phase transitions which we discuss briefly in the next section. In Sec. VI we discuss various other free energies that can be defined for magnetic materials. Note that m is defined here to be the expectation value of *a single spin*.

In class, we showed in handout [2] that the (generalized) free energy is a minimum when the system is in thermal contact with a heatbath. Furthermore, at the minimum, \tilde{F} is equal to the actual free energy F . The same is true here, as we will discuss more in the Sec. VI. We therefore have to minimize \tilde{F} in Eq. (19) with respect to m (keeping the external field B constant) which gives

$$J_0 m + B = k_B T \frac{1}{2} \ln \left(\frac{1+m}{1-m} \right). \quad (20)$$

Now

$$\frac{1}{2} \ln \left(\frac{1+m}{1-m} \right) = \tanh^{-1} m,$$

as can easily be determined from the definition of $\tanh x$ since

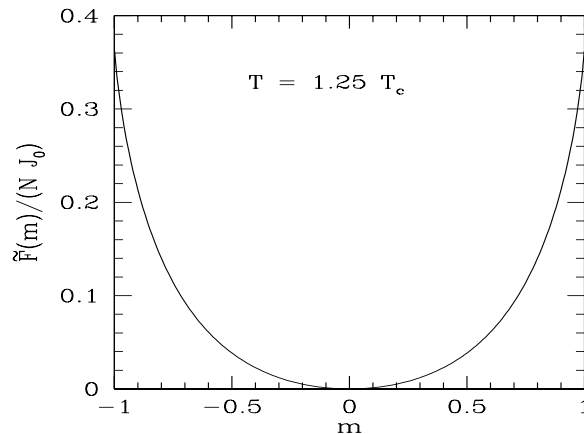
$$m = \tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{e^{2x} - 1}{e^{2x} + 1} \quad \text{implies } e^{2x} = \frac{1+m}{1-m}, \quad \text{so } x = \frac{1}{2} \ln \left(\frac{1+m}{1-m} \right). \quad (21)$$

Hence Eq. (20) is equivalent to Eq. (12).

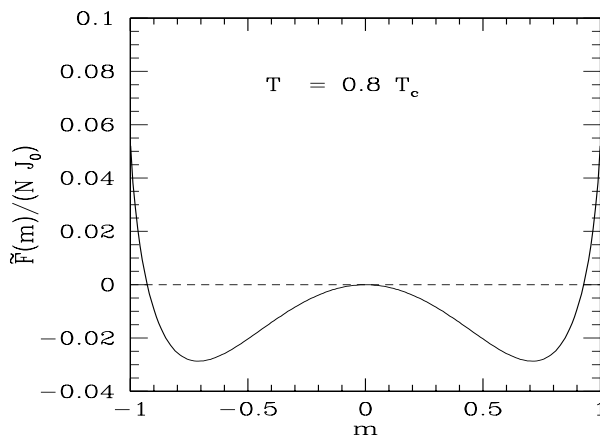
It is instructive to see how \tilde{F} varies for small m . Expanding out the logs in Eq. (19), and ignoring the factor of $-k_B T \ln 2$ which is independent of m (and comes from the entropy of N free spins), gives

$$\frac{\tilde{F}(m, B)}{N} = -Bm + \frac{1}{2}(k_B T - J_0)m^2 + \frac{k_B T}{12}m^4 \dots \quad (22)$$

We consider $B = 0$ in the rest of this section. For $T > T_c = J_0/k_B$, see Eq. (14), the coefficient of m^2 is positive (as is the coefficient of m^4) and so \tilde{F} has a single minimum at $m = 0$, which must be the equilibrium solution, see the figure below.



However, for $T < T_c$ the coefficient of m^2 is negative so there is a *maximum* of \tilde{F} at $m = 0$, not a minimum, and two minima appear at non-zero values of m , one the negative of the other, as shown in the figure below.



It is these minima with non-zero m which describe the two (equivalent) possible equilibrium states of the system below T_c .

The temperature dependence of the value of m at the positive minimum is shown in the figure at the end of the last section. Note that minimizing Eq. (22) gives

$$m^2 = 3 \left(\frac{T_c - T}{T} \right) \simeq 3 \left(\frac{T_c - T}{T_c} \right),$$

where, in the last expression, we replaced the factor of T in the denominator by T_c , which is OK to lowest order in $(T_c - T)$. Hence we recover Eq. (15).

V. LANDAU THEORY

In this section we prefer to write expressions in terms of the magnetization per unit volume, M , rather than per spin, m , where $M = mN/V$. In this case, \tilde{F} is the generalized free energy per unit volume.

In the previous section we saw that the mean field generalized free energy (Landau function) can be expanded in powers of M and the coefficients are smooth functions of T . A transition occurs for $B = 0$ when the coefficient of m^2 (or equivalently M^2) in Eq. (22) vanishes. We shall see that the transition occurs quite generally when the coefficient of M^2 is zero for a continuous (2nd order) transition but there is a different condition if the transition is discontinuous (1st order).

Now we ask what happens if we go beyond the mean field approximation. In his famous theory of continuous (second order) phase transitions Landau assumed that the structure of \tilde{F} is the *same* as in mean field theory. In particular Landau assumed that \tilde{F} can be expanded in powers of M , and that the coefficients are smooth functions of T . The difference from mean field theory is that the coefficient of the quadratic term vanishes at the *exact* transition temperature rather than the mean field approximation to it, and the other coefficients in the expansion also have non mean field values. Hence the Landau free energy is

$$\boxed{\tilde{F}(M, B) = -MB + \frac{a(T)}{2} M^2 + \frac{c}{4} M^4 + \dots}, \quad (23)$$

where

$$\boxed{a(T) = \alpha(T - T_c)}, \quad (24)$$

in which T_c is the exact transition temperature, and α and c are parameters. If the transition is continuous then M is small near T_c so it is justified to terminate the expansion as shown.

The temperature dependence of c will be small and unimportant and so can be neglected. This assumes that c does not also vanish at same temperature as a . This rare occurrence gives rise what is called a “tricritical point” which is beyond the scope of the course. Minimizing Eq. (23) with respect to M gives

$$B = a(T) M + c M^3.$$

For $B = 0$, the shape of \tilde{F} varies from a single minimum for $T > T_c$ to a double minimum for $T < T_c$, as shown in the figures in the previous section. Minimizing Eq. (23) gives either $M = 0$ or

$$M^2 = -\frac{a(T)}{c} = \frac{\alpha}{c}(T_c - T).$$

Hence $M \sim (T_c - T)^\beta$ with $\beta = 1/2$, as in mean field theory. Since the structure of Landau theory is the same as the structure of mean field theory, *all* critical exponents in Landau theory have mean field values.

We have presented Landau theory for the simplest case of an Ising model. More generally, the quantity that becomes non-zero for $T < T_c$ is called an “order parameter” and Landau emphasizes that one should put all terms consistent with the symmetry of the order parameter into the generalized free energy. For example, suppose the spin is a vector and the energy is invariant under rotating all the spins by the same amount, i.e. the energy is given by

$$E = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - \mathbf{B} \cdot \sum_i \mathbf{S}_i.$$

This is called the Heisenberg model. The free energy must then also be invariant under a rotation of the order parameter vector \mathbf{M} , so its expansion has the form

$$\tilde{F}(\mathbf{M}, \mathbf{B}) = -\mathbf{M} \cdot \mathbf{B} + \frac{a(T)}{2} \mathbf{M} \cdot \mathbf{M} + \frac{c}{4} (\mathbf{M} \cdot \mathbf{M})^2 + \dots.$$

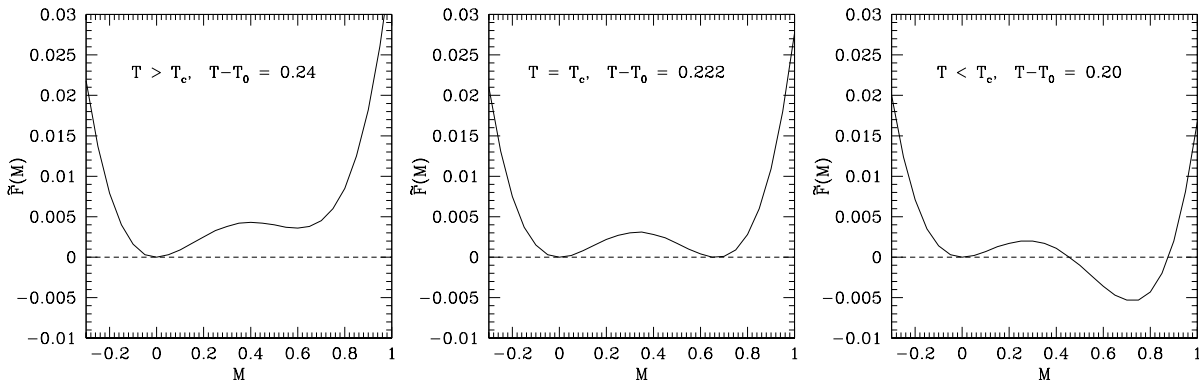
As another example, let us assume that symmetry allows a term third order in the free energy, so we have (in zero external field)

$$\tilde{F}(M) = \frac{a(T)}{2} M^2 + \frac{b}{3} M^3 + \frac{c}{4} M^4 + \dots,$$

with

$$a(T) = \alpha(T - T_0).$$

The figure below plots $\tilde{F}(M)$ for three different temperatures for $\alpha = c = 1, b = -1$.



The equilibrium value of M is that which minimizes \tilde{F} . In the figures we see that a second minimum starts to appear even above T_0 (the temperature at which $a = 0$), and, furthermore, at a temperature T_c which is still greater than T_0 , this second minimum has the same free energy as the minimum at $M = 0$. Let us call the location of this second minimum M_0 . Clearly T_c is the transition temperature, since, as soon as T is less than T_c , the minimum near M_0 is the lowest. Hence the equilibrium value of M jumps from 0 to M_0 at $T = T_c (> T_0)$. This is an example of a discontinuous (often called *first order*) transition. At the critical point, $T = T_c$, we have $\tilde{F}(M_0) = \tilde{F}(0)$, and $\tilde{F}'(M_0) = 0$. Eliminating the solution with $M_0 = 0$ these conditions can be written as:

$$\frac{\alpha(T_c - T_0)}{2} + \frac{b}{3}M_0 + \frac{c}{4}M_0^2 = 0, \quad (25)$$

$$\alpha(T_c - T_0) + bM_0 + cM_0^2 = 0. \quad (26)$$

Multiplying Eq. (25) by 2 and subtracting it from Eq. (26) yields

$$M_0 \left(b + cM_0 - \frac{2}{3}b - \frac{c}{2}M_0 \right) = 0, \quad (27)$$

which gives

$$M_0 = -\frac{2}{3} \frac{b}{c}. \quad (28)$$

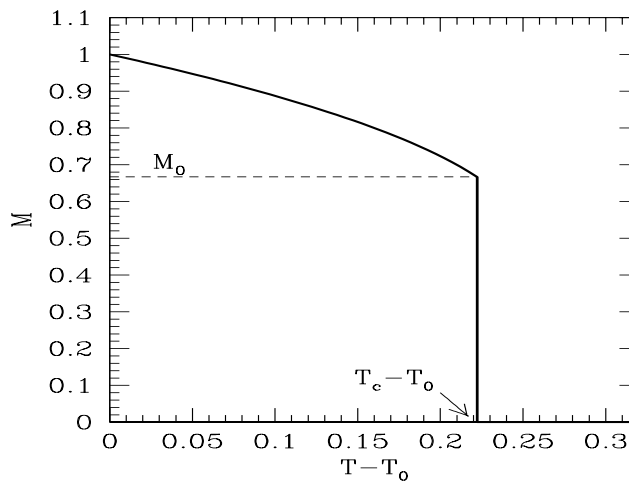
Substituting this value for M_0 into Eq. (26) gives

$$T_c - T_0 = \frac{2}{9} \frac{b^2}{\alpha c}. \quad (29)$$

With the parameters used in the above plots, $\alpha = c = 1, b = -1$, we have

$$T_c - T_0 = \frac{2}{9} = 0.222 \dots, \quad M_0 = \frac{2}{3}.$$

The jump in the value of M at T_c is clearly shown in the figure below.



Contrast this figure, which shows the behavior of the order parameter at a first order (i.e. discontinuous) transition, with the figure at the end of Sec. III which is for a second order (i.e. continuous) transition. We should mention, though, that the assumption made in Landau theory that one can expand the (generalized) free energy in powers of M is not strictly valid at a first order transition, because M is not necessarily small just below T_c .

Just below T_c , the $M = 0$ state is a “local minimum” of the free energy, as shown in the right hand of the triplet of figures above. Such a state is known as a “metastable state” and can be quite long lived before it eventually decays into the state which is the “global minimum” of the free energy. A discussion of how a metastable state decays is given in Kittel and Kroemer Ch. 10, p. 294-5.

You will show in a homework problem that one can also have a first order transition, even in the absence of a third-order term, if the quartic term is negative at T_c .

The assumptions made in Landau’s theory of continuous phase transitions are not actually correct, though it turns out that they would be correct in space dimension greater than four. As a result, critical exponents such as β in Eq. (16) are not given by their mean field values. In recent decades there has been a major industry trying to go beyond Landau theory to understand “critical phenomena”, the behavior of systems near their critical point (second order phase transition). There is particular interest in determining accurate values for the exponents because these are predicted to be “universal”, which means they only depend on a few broad features of the model such as the dimension of space and the symmetry of the order parameter, but not on microscopic details. Most textbooks on statistical mechanics, with the notable exception of Kittel and Kroemer, have a discussion of critical phenomena and universality. Although Landau theory is, in the end, not correct it is still important for two reasons:

1. it emphasizes the important role played by the symmetry of the order parameter, and
2. it provides a starting point for better theories.

VI. DIFFERENT FREE ENERGIES FOR MAGNETIC SYSTEMS

As discussed in an earlier handout², the free energy

$$F = -k_B T \ln Z = -k_B T \ln \left(\sum_n e^{-\beta E_n} \right), \quad (30)$$

can be decomposed into a partial sum of states with a fixed value of some parameter, energy U in that case, and a sum over different values of that parameter. Here we will use the same approach

but consider different values of the magnetization M . We therefore write

$$F = -k_B T \ln \left(\sum_M \sum'_\alpha e^{-\beta E_\alpha} \right), \quad (31)$$

where α labels a state with a particular value of M and second sum (with the prime) is only over these states. Now $\sum_\alpha e^{-\beta E_\alpha}$ is the partition function for those states with magnetization M , and so is just $e^{-\beta \tilde{F}(M, B)}$, where \tilde{F} is the generalized free energy in Eqs. (19) or (23). Hence we have

$$F = -k_B T \ln \left(\sum_M e^{-\beta \tilde{F}(M, B)} \right). \quad (32)$$

As discussed several times in the course, e.g. handout [2], the sum is completely dominated by the value of M which maximizes the exponent, i.e. minimizes $\tilde{F}(M, B)$, because \tilde{F} is extensive (i.e. proportional to N). Denoting this value of M by M^* then we also showed that, to an excellent approximation, $F = \tilde{F}(M^*, B)$, i.e. the equilibrium free energy is equal to the generalized free energy evaluated at the minimum.

Sometimes, one sees other definitions of the free energy of a magnetic system from that in Eq. (32). To clarify this, in the first edition of the book, Kittel uses the term $F_A(B, T)$ for the free energy we call F here, and adopts a different notation, F_B , for another free energy which one often sees in the literature, which is defined by

$$\boxed{F_B = F + MB.} \quad (33)$$

From the thermodynamic identity, Eq. (1), we have

$$dF_B = -M dB - S dT + M dB + B dM = B dM - S dT. \quad (34)$$

Hence $F_B(M, T)$ should be expressed in terms of M and T (as opposed to F which should be expressed in terms of B and T). According to Eq. (34), the field B which would give the prescribed value of M is given by

$$B = \left(\frac{\partial F_B}{\partial M} \right)_T. \quad (35)$$

The difference between F_B and F is rather like that between the Helmholtz and Gibbs free energies, and some authors use that terminology. However, I prefer to use the terms ‘‘Helmholtz’’ and ‘‘Gibbs’’ just for free energies which differ by a factor of PV .

From Eqs. (19) or (23) we see that there is a factor of $-MB$ in \tilde{F} , which is just the interaction energy of the magnetic dipoles in the external magnetic field. Separating this out we can write

$$\boxed{\tilde{F}(M, B) = -MB + \tilde{F}_B(M),} \quad (36)$$

where $\tilde{F}_B(M)$ represents all the other terms in Eqs. (19) or (23), which can be thought of as the “internal” free energy. Since $\tilde{F} = F$ at equilibrium, we see from Eqs. (33) and (36) that

$$\tilde{F}_B(M) = F_B(M), \quad (37)$$

so the “tilde” on F_B in Eq. (36) is not necessary.

To summarize, we have discussed the following quantities:

- The *equilibrium* free energy F , defined by

$$F = -k_B T \ln Z, \quad (38)$$

(called F_A in Kittel 1st edition) which is a function of the external field B . The equilibrium magnetization is obtained from

$$M = -\frac{\partial F}{\partial B}. \quad (39)$$

- The *equilibrium* free energy F_B defined by

$$F_B = F + M B, \quad (40)$$

which is a function of the magnetization M . The field that would produce this magnetization is given by

$$B = \frac{\partial F_B}{\partial M}. \quad (41)$$

- The *generalized* free energy (Landau function) $\tilde{F}(M, B)$ which is a function of *both* M and B . It is defined by

$$\tilde{F}(M, B) = -k_B T \ln \left(\sum_{\alpha} e^{-\beta E_{\alpha}} \right), \quad (42)$$

where the sum is over all states with the specified value of M .

The equilibrium magnetization M^* is obtained by minimizing \tilde{F} at constant B , i.e.

$$\left(\frac{\partial \tilde{F}}{\partial M} \right)_{M=M^*} = 0. \quad (43)$$

In value of \tilde{F} at the equilibrium magnetization is just, the equilibrium free energy, i.e.

$$\tilde{F}(M^*, B) = F. \quad (44)$$

It is often convenient to separate the interaction energy of the magnetic dipoles with the external field from the “internal energy” as follows:

$$\tilde{F}(M, B) = F_B(M) - M B, \quad (45)$$

so Eq. (43) is equivalent to Eqs. (41).

I emphasize that the generalized free energy is applicable in *non-equilibrium* as well as equilibrium situations.

In addition to F ($\equiv F_A$) and F_B one also sometimes sees other definitions of the the free energy of magnetic materials, and the situation is rather confusing. Consequently, my colleague Onuttom Narayan and I wrote an article³ for the American Journal of Physics (a journal for physics teachers) discussing the relationships between all of them. An on-line version is available on the archive at <http://arxiv.org/abs/cond-mat/0408259> and the published version at <http://ajp.aapt.org/resource/1/ajpias/v73/i4/p293.s1>

¹ Physics 112 handout: *Various “Free Energies”*, <http://physics.ucsc.edu/~peter/112/thermofun.pdf>.

² Physics 112 handout: *The (generalized) free energy is a minimum in equilibrium*, <http://physics.ucsc.edu/~peter/112/fmin.pdf>.

³ *Free energies in the presence of electric and magnetic fields*, O. Narayan and A. P. Young, Am. J. Phys. **73**, 293 (2005)