

Physics 127b: Statistical Mechanics

Landau Theory of Second Order Phase Transitions

Order Parameter

Second order phase transitions occur when a new state of *reduced symmetry* develops continuously from the disordered (high temperature) phase. The ordered phase has a *lower symmetry* than the Hamiltonian—the phenomenon of *spontaneously broken symmetry*. There will therefore be a number (sometimes infinite) of equivalent (e.g. equal free energy) symmetry related states. These are macroscopically different, and so thermal fluctuations will not connect one to another in the thermodynamic limit. To describe the ordered state we introduce a macroscopic *order parameter* that describes the *character* and *strength* of the broken symmetry.

Examples

1. Ising ferromagnet: the Hamiltonian is invariant under all $s_i \rightarrow -s_i$, whereas the low temperature phase has a spontaneous magnetization, and so is not. A convenient order parameter is the total average spin $S = \sum_i \langle s_i \rangle$ or the magnetization $M = \mu S$. This reflects the nature of the ordering (under the transformation $s_i \rightarrow -s_i$ we have $S \rightarrow -S$) and goes to zero continuously at T_c .
2. Ising antiferromagnet on a simple cubic lattice: the ordering is the staggered magnetization $N = \sum_n (-1)^n \langle s_n \rangle$ where alternate sites are labelled even or odd.
3. Heisenberg ferromagnet: now the Hamiltonian is invariant under any rotation of all the spins together. The ordering is characterized by a *vector* order parameter. A convenient choice is again the total spin $\vec{S} = \sum_i \langle \vec{s}_i \rangle$ or magnetization.
4. Heisenberg antiferromagnet on a simple cubic lattice: the staggered magnetization is now a vector $\vec{N} = \sum_n (-1)^n \langle \vec{s}_n \rangle$.
5. Superfluid: the broken symmetry is the invariance of the (quantum) Hamiltonian under a phase change of the wave function. Since for a charge system a gauge transformation also changes the quantum phase, this is also known as broken gauge symmetry. The order parameter can be thought of as the one particle wave function into which the particle Bose condense, multiplied by the number of condensed atoms. This picture is good for a non- or weakly interacting system. For a strongly interacting system a better definition is the “expectation value of the particle annihilation operator” $\langle \psi(\vec{r}) \rangle$.
6. Solid: has broken translational and rotational symmetry, and a convenient order parameter is the amplitude of the density wave. In three dimensions the liquid-solid transition is always first order, but in two dimensions may be second order.
7. Nematic liquid crystal: consists of long molecules which align parallel to one another at low temperatures, although the position of the molecules remains disorder as in a liquid. The liquid becomes anisotropic, and a second rank tensor characterizes the strength of the anisotropy and can be used as the order parameter.

Free energy expansion

Since the order parameter grows continuously from zero at the transition temperature, Landau suggested that an expansion of the free energy in a Taylor expansion in the order parameter would tell us about the behavior near the transition. The free energy must be invariant under all symmetry operations of the Hamiltonian, and the terms in the expansion are restricted by symmetry considerations.

The order parameter may conceivably take on different values (“point in different directions”) in different parts of the system (for example due to thermal fluctuations), and so we first write

$$A = \int d^3x f(\psi, T) \quad (1)$$

introducing the Helmholtz free energy density f which is a function of the local order parameter $\psi(\vec{r})$ and temperature, and is then expanded in small ψ .

To be explicit, let's consider the Ising ferromagnet, and $\psi = m(\vec{r})$, with $m(\vec{r})$ the magnetization per unit volume or the magnetization per spin averaged over some reasonably macroscopic volume. Since the free energy is invariant under spin inversion, the Taylor expansion must contain only even powers of m . Hence

$$f(m, T) = f_o(T) + \alpha(T)m^2 + \frac{1}{2}\beta(T)m^4 + \gamma(T)\vec{\nabla}m \cdot \vec{\nabla}m. \quad (2)$$

The last term in the expansion gives a free energy cost for a nonuniform $m(\vec{r})$, again using the idea of a Taylor expansion, now in spatial derivatives as well. A positive γ ensures that the spatially uniform state gives the lowest value of the free energy A . Sixth and higher order terms in m could be retained, but are not usually necessary for the important behavior near T_c . Note that we keep the fourth order term, because at T_c the coefficient of the second order term $\alpha(T)$ becomes zero. Only quadratic derivative terms are usually needed, since $\gamma(T_c)$ remains nonzero.

Minimum free energy

We expect the state that minimizes the free energy to be the physically realized state. This is true so long as the fluctuations around this most probably value are small compared to this value. We will find that this is not always the case, and Landau's theory then corresponds to a mean field theory that ignores these fluctuations.

For the Ising ferromagnet the minimum of A is given by a uniform $m(\vec{r}) = \bar{m}$ satisfying

$$\alpha\bar{m} + \beta\bar{m}^3 = 0. \quad (3)$$

The solutions corresponding to a minimum are

$$\bar{m} = \pm\sqrt{-\alpha/\beta} \quad \text{for } \alpha < 0, \quad (4a)$$

$$= 0 \quad \text{for } \alpha > 0. \quad (4b)$$

We identify $\alpha = 0$ as where the temperature passes through T_c , and expand near here

$$\alpha(T) \simeq a(T - T_c) + \dots \quad (5a)$$

$$\beta(T) \simeq b + \dots \quad (5b)$$

$$\gamma(T) \simeq \gamma + \dots \quad (5c)$$

so that

$$f \simeq f_o(T) + a(T - T_c)m^2 + \frac{1}{2}bm^4 + \gamma(\vec{\nabla}m)^2 \quad (6)$$

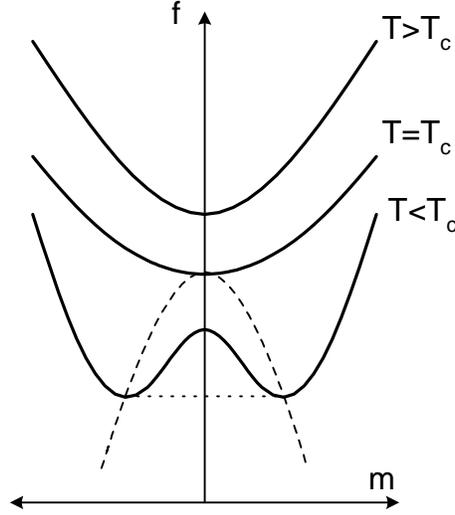


Figure 1: Free energy density f as a function of (uniform) m . Below T_c new minima at nonzero $\pm\bar{m}$ develop (the dashed curve denotes $\bar{m}(T)$). If the magnetization of the system is varied (rather than the field) the dotted line is the tie line giving the variation of the free energy as a function of the total magnetization density $m = M/V$.

and

$$\bar{m} \simeq \left(\frac{a}{b}\right)^{1/2} (T_c - T)^{1/2} \quad \text{for } T < T_c. \quad (7)$$

Evaluating f at \bar{m} gives

$$\bar{f} = f_0 - \frac{a^2(T - T_c)^2}{2b} \quad (8)$$

showing the lowering of the free energy by the ordering. Note that $\bar{f}(T)$ deviates from f_0 quadratically, as we found for the mean field theory of the Ising ferromagnet. This will yield a jump discontinuity in the specific heat

$$c = \begin{cases} c_0 & T \geq T_c \\ c_0 + \frac{a}{b}T & T < T_c \end{cases}, \quad (9)$$

with c_0 the smooth contribution coming from $f_0(T)$.

We can gain useful insight into the transition by plotting $f(m)$ for a uniform m for various temperatures, as in Fig. 1. For $T > T_c$ the free energy has a single minimum at $m = 0$. Below T_c two new minima at $\pm\bar{m}$ develop. Right at T_c the curve is very flat at the minimum (varying as m): we might expect fluctuations to be particularly important here.

It is easy to add the coupling to a magnetic field

$$f(m, T, B) = f_0(T) + a(T - T_c)m^2 + \frac{1}{2}bm^4 + \gamma(\vec{\nabla}m)^2 - mB. \quad (10)$$

The magnetic field couples directly to the order parameter and is a *symmetry breaking* field: with the magnetic field the full Hamiltonian is not invariant under spin inversion. Now the free energy is minimized by a non zero m . Minimizing f again with respect to m , we find above T_c the diverging susceptibility

$$\chi = \left. \frac{\bar{m}}{B} \right|_{B=0} = \frac{1}{2a}(T - T_c)^{-1}, \quad (11)$$

and at $T = T_c$ for small B

$$m = \left(\frac{1}{2b}\right)^{1/3} B^{1/3}. \quad (12)$$

Note that the exponents (power laws) are the same as we found in the direct mean field theory calculation.

Other Symmetries

The Landau approach is readily generalized to other symmetries. For example for the Heisenberg ferromagnet the order parameter is a vector \vec{m} . The free energy is expanded as a Taylor expansion in the components m_x, m_y, m_z and each term must be invariant under rotations of \vec{m} , and also the derivative term must be invariant under rotations of the space axes separately from \vec{m} . The component terms can be combined to give the simple expression in vector notation

$$f(\vec{m}, T, \vec{B}) = f_0(T) + a(T - T_c)\vec{m} \cdot \vec{m} + \frac{1}{2}b(\vec{m} \cdot \vec{m})^2 + \gamma\left(\sum_{i\alpha} \nabla_i m_\alpha \nabla_i m_\alpha\right)^2 - \vec{m} \cdot \vec{B}.$$

Notice the “dot product form” of the gradient term separately in the gradient and \vec{m} components: this guarantees the invariance under separate rotations of spin and space coordinates. We might schematically write this term as $(\vec{\nabla}\vec{m})^2$, but the double summation is what is meant!

Similarly for a complex order parameter ψ , we do a Taylor expansion in $\text{Re } \psi$ and $\text{Im } \psi$, and demand the invariance of each term under a change of the phase. This leads to the form

$$f(\psi, T) = f_0(T) + a(T - T_c)|\psi|^2 + \frac{1}{2}b|\psi|^4 + \gamma\vec{\nabla}\psi \cdot \vec{\nabla}\psi^*.$$

Note that it is nicest to write the expression in terms of $|\psi|$, but the correct approach—and the best way to avoid confusion—is to establish the expansion in $\text{Re } \psi$ and $\text{Im } \psi$ and then simplify. For example a term $|\psi|^3$ is not allowed, since even though it is invariant under changing the phase, it does not correspond to a term in the Taylor expansion in $\text{Re } \psi, \text{Im } \psi$.

First order transitions

We can also encounter first order broken-symmetry transitions. For example the liquid solid transition is described by the strength of density waves $\rho e^{i\vec{q}\cdot\vec{r}}$. In three dimensions we need three density waves with wave vectors that prescribe the reciprocal lattice; we will suppose all three components have the same magnitude ρ . Since the density perturbation is added to the uniform density of the liquid, there is no symmetry under changing sign of the density wave, and so the free energy expansion now may have a cubic term

$$f - f_0 = a(T - T_c)\rho^2 + c\rho^3 + \frac{1}{2}b\rho^4 \quad (13)$$

(we suppose uniform ρ for simplicity).

Now the behavior of $f(\rho, T)$ is rather different, as in Fig. 2a. At high temperatures there is a single minimum at $\rho = 0$ corresponding to the liquid phase. As the temperature is lowered a second minimum develops, but at a free energy that remains higher than the liquid. Only at T_m does the new free energy become lower, and this is the melting temperature where the liquid and solid have the same free energy. Below T_m the solid is the lower free energy. Note the jump in ρ at T_m , rather than a continuous variation as at a second order transition. The temperature T_c at which the minimum in the free energy at $\rho = 0$ disappears (i.e. the liquid state no longer exists) is not of great physical significance.

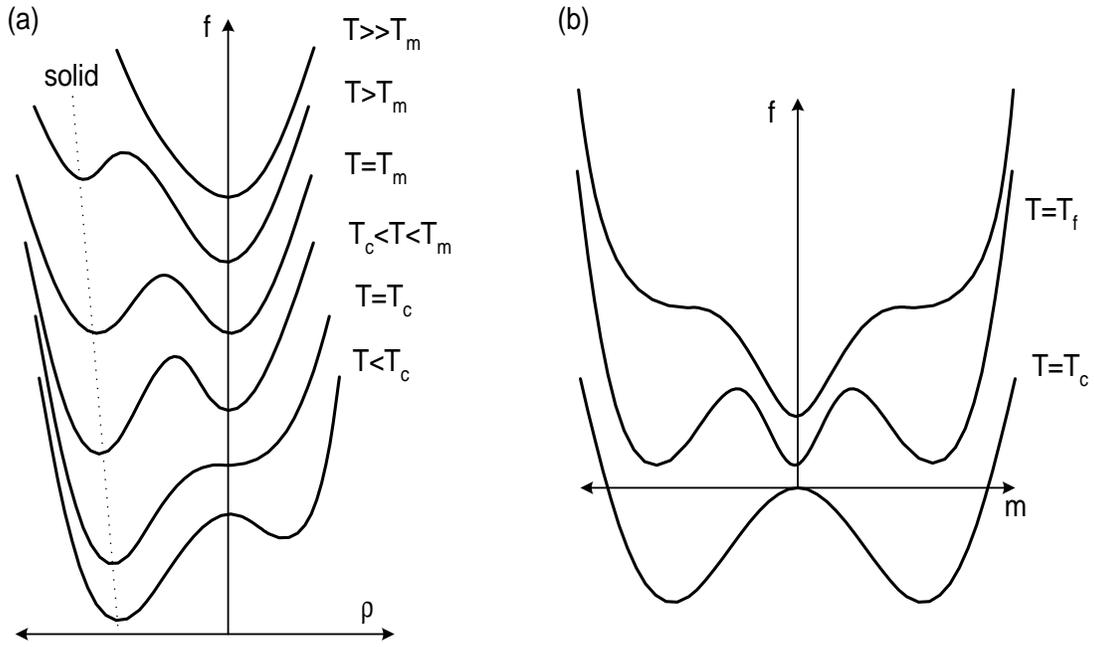


Figure 2: (a) Free energy plots for a free energy with cubic invariants; (b) Free energy plots in the case where the coefficient of the quatic term is *negative*.

The Landau expansion technique may not be accurate at a first order transition: since there is a jump in ρ at the transition, there is no guarantee that the truncated expansion in ρ is a reasonable approximation here. Indeed the liquid-solid transition is usually strongly first order, so that the power series expansion in the order parameter is not useful, and can give misleading conclusions.

Another way a first order transition can occur, even in the absence of cubic terms in the free energy, is if the coefficient of the quatic term turns out to be *negative*. Then we must extend the expansion to *sixth* order to get finite results (otherwise the free energy is unbounded below). Again assuming uniform m for simplicity:

$$f - f_0 = a(T - T_c)m^2 - \frac{1}{2}|b|m^4 + \frac{1}{3}cm^6. \quad (14)$$

Now, see Fig. 2b two symmetric secondary minima develop for $T > T_c$, and become the lowest minima at temperature $T = T_f > T_c$ which we identify as the first order transition temperature. Again, at T_c the minimum at $m = 0$ corresponding to the disordered phase disappears, but this is not often relevant to the physics.