

# Statistical Mechanics: Lecture A2

## Landau Theory of Phase Transitions

Landau's approach to phase transitions involves making a series of assumptions regarding the free energy of the system. The essential steps involved in Landau's recipe are the following:

1. Identify an order parameter  $\psi$ : Order parameter is a quantity which characterizes the phase transition. It is zero in the phase which is called "disordered" in some kinds of phase-transitions, and is non-zero in the "ordered" phase. In a ferromagnet, the order parameter is macroscopic magnetization. It is zero in the paramagnetic phase, and non-zero in the ferromagnetic phase. In a liquid-solid transition, it could be the density - density in the liquid phase. Or it could be the amplitude of Fourier modes in a crystal. It could be the degree of orientation in a nematic liquid crystal. It could be the density of superconducting electrons in a superconductor.
2. Assume a free energy *functional*: Assume that the free energy is a functional of the order parameter, and can be written in the form:

$$F = F_0(T) + F_L(T, \psi) \quad (1)$$

where  $F_0$  is a smooth analytic function temperature, but does not depend on the order parameter  $\psi$ .  $F_L$  contains all the information about dependence of free energy on the order parameter.

3. Construction of  $F_L(\psi)$ : The Landau free energy functional is assumed to be an analytic function of  $\psi$ , so that it can be expanded in series in  $\psi$ . The expansion should be such that it respects all possible symmetries associated with the order parameter. This will typically include translational and rotational invariance.
4. Temperature Dependence of  $F_L$ : It is assumed that all the nontrivial temperature dependence lies in the lowest order term in the expansion of  $F_L(\psi)$ .
5. Minimization of free energy: Of all the possible forms that  $\psi$  can take, the one which described equilibrium is the one which minimizes the free energy. So, the free energy functional has to be minimized with respect to the order parameter.

Let us now carry out in detail, Landau's recipe for studying phase transitions. We first write a free energy functional, as a power series in  $\psi$

$$F = F_0(T) + \frac{1}{2}g_2(T)\psi^2 + \frac{1}{4}g_4(T)\psi^4 + \frac{1}{6}g_6(T)\psi^6 + \dots \quad (2)$$

Odd powers are left out keeping in mind the fact that the sign of the order parameter is irrelevant. For example, a ferromagnetic system is equally likely to have magnetization in any direction. Ignoring the  $\psi^6$  and higher order terms in the series, if we minimize the free energy with respect to  $\psi$ , we will obtain

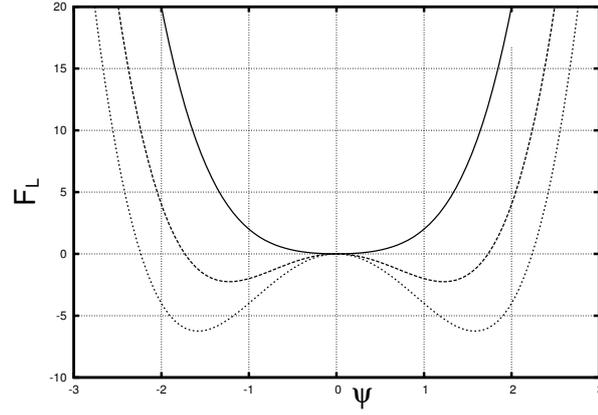
$$\frac{\partial F}{\partial \psi} = g_2(T)\psi + g_4(T)\psi^3 = 0 \quad (3)$$

which in turn implies that

$$\psi = 0, \quad \psi^2 = -g_2/g_4 \quad (4)$$

The physics of phase transitions tells us that at  $T = T_c$ , the order parameter should become zero, if one is going from the ordered to the disordered phase. If we assume, for simplicity, that all the interesting temperature dependence of the Landau free energy is in  $g_2(T)$  and  $g_4(T)$  is temperature independent, it implies that

$$g_2(T_c) = 0, \quad (5)$$



if  $\psi^2$  is to be zero at  $T = T_c$ . Let us expand  $g_2(T)$  in a Taylor series in  $T$ , around  $T = T_c$ ,

$$\begin{aligned} g_2(T) &\approx g_2(T_c) + (T - T_c) \frac{\partial g_2(T)}{\partial T} \Big|_{T=T_c} \\ &= (T - T_c)a \end{aligned} \quad (6)$$

where  $a$  is a constant given by  $a = \frac{\partial g_2(T)}{\partial T} \Big|_{T=T_c}$ . Since  $g_4(T)$  is assumed to be temperature independent, we equate it to a constant,  $g_4(T) = b$ . The free energy functional can now be written, up to 4th order in  $\psi$ , as

$$F = F_0(T) + \frac{1}{2}a(T - T_c)\psi^2 + \frac{1}{4}b\psi^4 \quad (7)$$

We initially assume both  $a$  and  $b$  to be non-negative, and will explore the consequences later. We look for the extrema of the free energy:

$$\frac{\partial F}{\partial \psi} = a(T - T_c)\psi + b\psi^3 = 0 \quad (8)$$

$$\psi(a(T - T_c) + b\psi^2) = 0 \quad (9)$$

$$\psi = 0, \quad \psi = \pm \sqrt{\frac{a(T_c - T)}{b}} \quad (10)$$

At  $\psi = 0$ ,  $\frac{\partial^2 F}{\partial \psi^2} = a(T - T_c)$ . Thus, for  $T > T_c$ ,  $\psi = 0$  is a minimum of the free energy,

while for  $T < T_c$ , it is a maximum. So, for  $T < T_c$ ,  $\psi = \pm \sqrt{\frac{a(T_c - T)}{b}}$  are the minima of the free energy, and hence describe the equilibrium. So, we see that while above  $T_c$  the order parameter is zero, there is a phase transition which makes the order parameter non-zero below  $T_c$ . Putting the expressions for  $\psi$  in the free energy, we obtain

$$F = \begin{cases} F_0(T) & T > T_c \\ F_0(T) - \frac{1}{4} \frac{a|T_c - T|^2}{b} & T < T_c \end{cases} \quad (11)$$

Notice that  $\frac{\partial F}{\partial T} = \frac{\partial F_0}{\partial T}$  at  $T = T_c$  whether you approach  $T_c$  from above or below - first derivative of free energy is continuous. However, the second derivative is given by

$$\frac{\partial^2 F}{\partial T^2} = \begin{cases} \partial^2 F_0 / \partial T^2 \Big|_{T=T_c} & T \rightarrow_+ T_c \\ \partial^2 F_0 / \partial T^2 \Big|_{T=T_c} - \frac{a}{2b} & T \rightarrow_- T_c \end{cases} \quad (12)$$

This shows that the second derivative of the free energy is discontinuous at  $T = T_c$ . Hence this is a **second-order phase transition**

## First order phase transition

Let us now explore a situation where  $b$  comes with a minus sign. In such a situation, (7) indicates that the free energy would keep decreasing with increasing  $\psi$ , and unphysical scenario. Here we need to take into account the next higher order term in  $\psi$ . Doing that, the free energy assumes the form

$$F = F_0(T) + \frac{1}{2}a(T - T_0)\psi^2 - \frac{1}{4}b\psi^4 + \frac{1}{6}c\psi^6 \quad (13)$$

Here we have replaced  $T_c$  by  $T_0$  because, as we shall see later, this temperature  $T_0$  is not the transition temperature. In order to find the minima of the free energy, we differentiate (13) with respect to  $\psi$  and equate it to zero:

$$\frac{\partial F}{\partial \psi} = a(T - T_0)\psi - b\psi^3 + c\psi^5 = 0 \quad (14)$$

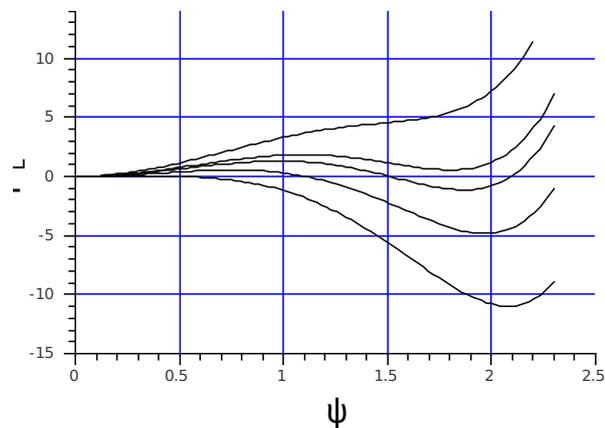
The solutions are  $\psi = 0$  and

$$\psi^2 = \frac{b \pm \sqrt{b^2 - 4ca(T - T_0)}}{2c} \quad (15)$$

Here, if  $\psi = 0$  is a minimum, then  $\psi^2 = \frac{b - \sqrt{b^2 - 4ca(T - T_0)}}{2c}$  should be a maximum, and

$\psi^2 = \frac{b + \sqrt{b^2 - 4ca(T - T_0)}}{2c}$  another minimum.

If one plots the Landau free energy in (13) (i.e., the free energy without the  $F_0$  term), it typically looks like as shown in the figure. The graphs from top to bottom are in the decreasing order of temperature. In the topmost curve, there is only one minimum, at  $\psi = 0$ , which indicates that at this temperature, the equilibrium value of the order parameter will be zero. This is the so-called disordered phase. As one lowers the temperature, another minimum of free energy forms, although it is higher than the one at  $\psi = 0$ . As one lowers the temperature further, this new minimum becomes lower, and at a temperature  $T = T_c$  it has the same value of free energy as the one at  $\psi = 0$ . Below this temperature, the new minimum is lower than the one at  $\psi = 0$ . This new minimum corresponds to the ordered phase.



One would notice from the curves that even at  $T = T_c$ , the value of  $\psi$  at the new minimum is finite, sufficiently away from zero. So, the order parameter takes a discontinuous jump from  $\psi = 0$  to a finite value, at  $T = T_c$ . Contrastingly, in the second order phase transition discussed earlier, the order-parameter starts from zero at  $T = T_c$ , and becomes finite gradually. So, one can say in general that second order phase transition is a continuous phase transition, and the first order phase transition is a discontinuous one. As an example, the density of a liquid changes discontinuously, as it freezes into a solid.

At sufficiently low temperature (lower than  $T_c$ ), the  $\psi = 0$  is no longer a minimum, rather it becomes a maximum. We explore all this in more detail in the following discussion. Let us now find out the temperature at which the new minimum of free energy becomes equal to the one at  $\psi = 0$ . From (13) we see that at  $\psi = 0$ , the Landau free energy  $F_L(\psi)$  is zero. We take the expression for the Landau free energy, and put it equal to zero, because that is the value of Landau free energy at  $\psi = 0$ :

$$\begin{aligned} \frac{a(T - T_0)}{2}\psi^2 - \frac{b}{4}\psi^4 + \frac{c}{6}\psi^6 &= 0 \\ a(T - T_0) - \frac{b}{2}\psi^2 + \frac{c}{3}\psi^4 &= 0 \end{aligned} \quad (16)$$

The second equation in the above, does not include the solution  $\psi = 0$ . Next we take the expression of  $\psi$  at the new minimum,  $\psi^2 = \frac{b + \sqrt{b^2 - 4ca(T - T_0)}}{2c}$ , plug it into the equation above, and thus obtain the temperature at which the new minimum becomes equal to the one at  $\psi = 0$ :

$$a(T_c - T_0) - \frac{b}{2} \left( \frac{b + \sqrt{b^2 - 4ca(T_c - T_0)}}{2c} \right) + \frac{c}{3} \left( \frac{b + \sqrt{b^2 - 4ca(T_c - T_0)}}{2c} \right)^2 = 0 \quad (17)$$

After some algebra, one obtains

$$T_c = T_0 + \frac{3b^2}{16ac} \quad (18)$$

This is the temperature at which the phase transition takes place. Below  $T_c$  the system is in an "ordered" phase, and above it, in a "disordered" phase.

$\psi^2 = \frac{b - \sqrt{b^2 - 4ca(T - T_0)}}{2c}$  is the point at which the free energy has a hump. Notice that at  $T = T_0$ , this point shifts to  $\psi = 0$ . At this temperature,  $\psi = 0$  is no longer a local minimum, but a local maximum of free energy. Below  $T = T_0$ , there is only one local minimum of free energy.

For  $T_c > T > T_0$ , the ordered phase has a lower free energy, but the disordered phase, characterized by  $\psi = 0$  is a local minimum, and hence a stable state. This means that the ordered phase is the most stable one, but the system may also be trapped in a disordered phase. This is called the *supercooled-liquid* state, in which the system is at temperatures below  $T_c$ , but continues to remain in the disordered phase as one lowers the temperature. At such temperatures the system should normally be in the ordered state. So,  $T_0$  is the temperature below which the supercooled-liquid state is not possible.

For  $T > T_c$  the disordered phase  $\psi = 0$  has a lower free energy, and hence, is the most stable state. But the ordered state, characterized by  $\psi^2 = \frac{b + \sqrt{b^2 - 4ca(T - T_0)}}{2c}$  is also a local minimum of the free energy, and hence, a stable state. This is the so-called *superheated-solid* state. In this state, the system is above its melting point, but the system is still trapped in a solid state. At  $T = T_0 + \frac{b^2}{4ac} = T_c + \frac{b^2}{16ac}$ , the hump merges with the second minimum of the free-energy, to form a shoulder on the curve. At this temperature, and above it, the free energy has only one minimum, which is at  $\psi = 0$ . Above this temperature, the superheated-solid state is not possible.

Let us now examine the derivative of free energy with respect to temperature. Firstly, the derivatives of free energy with temperature characterize the phase transition as first

order or second order. Secondly, the derivatives of free energy are related to various thermodynamics quantities. From (7), we see that

$$\frac{\partial F}{\partial T} = \frac{\partial F_0}{\partial T} + \frac{1}{2}a\psi^2 \quad (19)$$

If we approach  $T = T_c$  from  $T > T_c$ ,  $\psi = 0$ , which gives us

$$\left. \frac{\partial F}{\partial T} \right|_{T_c} = \left. \frac{\partial F_0}{\partial T} \right|_{T_c} \quad (20)$$

If we approach  $T = T_c$  from  $T < T_c$ , the order parameter has the value  $\psi^2 = \frac{b + \sqrt{b^2 - 4ca(T_c - T_0)}}{2c} = 3b/4c$ . So the derivative of free energy has the value

$$\left. \frac{\partial F}{\partial T} \right|_{T_c} = \left. \frac{\partial F_0}{\partial T} \right|_{T_c} + \frac{3b}{4c} \quad (21)$$

So we see that the first derivative of free energy is discontinuous at  $T = T_c$ . This indicates that the transition is of first order. The first derivative of free energy being discontinuous, reflects in the second derivative of free energy becoming infinite at  $T = T_c$ .

Now the entropy of a system is related to the free energy by the relation  $S = -\partial F/\partial T$ . If the first derivative of free energy is discontinuous across the phase transition, it will result in a latent heat of the transition given by  $\Delta Q = T\Delta S$ .

Landau's approach to phase transitions is thus able to explain the broad features of the first order and second order phase transitions.

