Statistical Physics Section 12: Landau Theory of Phase Transitions

In the last section we saw that the ferromagnetic transition and the liquid-gas transition are related in the sense that the Ising model can describe them both. Here we will develop a deeper, model-independent theory of why the critical points of different systems share the same properties i.e. why we have *Universality*.

12. 1. Mean-Field Theory of Ising model revisited

First we redo the mean field theory of the Ising model by constructing an approximate free energy. In the mean-field approximation the mean Ising energy becomes

$$\overline{E} = -h \sum_{i=1}^{N} \langle S_i \rangle - J \sum_{\langle ij \rangle} \langle S_i S_j \rangle$$
$$\simeq -hNm - \frac{JzN}{2}m^2$$
(1)

where Nz/2 is the number of nearest neighbour pairs and m is the magnetisation. Further we can write

$$m = \langle S_i \rangle = c - (1 - c) \tag{2}$$

where c is the mean-field probability of a spin being up and we have

$$c = \frac{m+1}{2} \tag{3}$$

This gives the Gibbs entropy of an assembly of N spins as

$$S = -Nk \left[c \ln c + (1 - c) \ln(1 - c) \right]$$
(4)

The Helmholtz free energy as a function of m is then

$$F(m) = E(m) - TS(m)$$
⁽⁵⁾

and the free energy per spin is given by

$$f(m) = \frac{F(m)}{N} = -\frac{Jzm^2}{2} - hm + kT \left[c\ln c + (1-c)\ln(1-c)\right]$$
(6)

To find the equilibrium state we should minimise F or f with respect to m. You are invited to carry this out in the tutorial and the result is the familiar Weiss mean-field equation for the magnetisation

$$m = \tanh\beta(Jzm + h) \tag{7}$$

To summarise, the procedure is to approximate the free energy (in this case by using a non-interacting, mean-field energy) as a function of the order parameter, then minimise.

Remark: One can couch this approach as a formal variational problem (similar to what you will have met in quantum physics) and show that minimising the ersatz free energy with respect to m gives an upper bound for the true free energy (see Advanced Statistical Physics course)

12. 2. Spontaneous Symmetry Breaking

It is illuminating to plot the free energy as a function of m for different T. Let us take h = 0

$$\frac{f(m)}{kT} = -\frac{T_c}{T}\frac{m^2}{2} + \left[\left(\frac{1+m}{2}\right)\ln\left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right)\ln\left(\frac{1-m}{2}\right)\right]$$
(8)

Figure 1: Sketches of f(m) for $T > T_c$, $T = T_c$ and $T < T_c$

- Note that f(m) is symmetric in m i.e. f(m) = f(-m)
- For $T > T_c$ there is a single minimum at m = 0 which is the equilibrium state
- At the critical point

$$\left. \frac{\partial^2 f}{\partial m^2} \right|_{m=0} = 0 \quad \text{at} \quad T = T_c \tag{9}$$

- For $T < T_c$ two symmetric minima emerge and m = 0 becomes a maximum, thus is unstable.
- For $T < T_c$ the symmetry $m \to -m$ is spontaneously broken since the system must select one of the two minima for its equilibrium state.

The structure of f(m) is easier to see if take m small (i.e. assume that we are near the critical point) then expand in m.

With a bit of work (tutorial) one can show that (8) becomes

$$\frac{f(m)}{kT} = \frac{m^2}{2} \left(\frac{T - T_c}{T}\right) + \frac{m^4}{12} + O(m^6)$$
(10)

The first two non-zero terms are all that is required to give the characteristic structure of f(m) above and below T_c sketched in the figure. Indeed one sees clearly in (10) that at the critical point the coefficient of m^2 vanishes and the ferromagnetic phases emerge when the coefficient is negative $(T < T_c)$. Also note how there are no odd terms in m.

12. 3. Landau Free Energy

We now develop a theory where we write down an expression such as (10) directly, without going through detailed calculations. The idea is to forget the details of the microscopic model and consider just the symmetries.

- Identify the order parameter, m say, which should be zero in the high temperature, disordered phase
- We aim just to analyse the behaviour near to the critical point where m is small
- We define the free energy density as a power series in the order parameter m
- The series must only contain terms which respect the symmetry of the order parameter.
- The series is truncated as soon as the physics is captured

As an example we consider a magnetic system which has the symmetry $m \to -m$ (in zero applied field). The order parameter is just the magnetisation m and we write down the free energy as

$$f(m) = \text{constant} + am^2 + bm^4 + O(m^6) \tag{11}$$

Note that the symmetry $m \to -m$ excludes any odd powers of m. The constant is unimportant and we can set it to zero. As we shall see, we need only consider the m^2 and m^4 terms. The coefficients a, b are smooth functions of temperature

Minimising f wrt m

$$\frac{\partial f}{\partial m} = 0 \tag{12}$$

yields

$$2am + 4bm^3 = 0 \Rightarrow m = 0 \quad \text{or} \quad m^2 = -\frac{a}{2b} \tag{13}$$

The transition occurs when a changes sign. Therefore we identify the temperature dependence of a as

$$a(T) = (T - T_c) \times \text{constant} = t a_o \quad \text{where} \quad t = \frac{T - T_c}{T_c}$$
 (14)

In the presence of a small applied field h (which breaks the symmetry) we add a linear term

Figure 2: Sketch of Landau free energy $f(m) = am^2 + bm^4$ for a > 0 and a < 0.

in m to (11)

$$f(m) = -hm + am^2 + bm^4$$
(15)

We can then understand the discontinuous transition below T_c by sketching the form of f(m)when h passes through zero — the global minimum of f(m) changes discontinuously from |m| to -|m|. Figure 3: Sketch of Landau free energy $f(m) = -hm + am^2 + bm^4$ for a < 0, h > 0 and h < 0.

12. 4. Critical exponents

We can now recover very easily the mean-field critical exponents. We have straightaway from minimising f(m) (13) that in the low temperature, ordered phase

$$m = \left(\frac{a_0|t|}{2b}\right)^{1/2} \tag{16}$$

and we identify $\tilde{\beta} = 1/2$.

At T_c , t = 0 and we have

$$f(m) = -hm + bm^4 \tag{17}$$

Therefore minimising f yields

$$h = 4bm^3 \tag{18}$$

and we identify $\delta = 3$.

To work out the susceptibility χ near criticality we minimise (15)

$$0 = -h + 2am + 4bm^3 \tag{19}$$

then take the derivative wrt h to obtain

$$0 = -1 + 2a\chi + 12bm^2\chi$$
 (20)

Using the relevant expression for m (13) we find

$$\chi \simeq \begin{cases} \frac{1}{2at} & \text{for } t < 0 \quad (T > T_c) \\ \frac{1}{4a|t|} & \text{for } t > 0 \quad (T < T_c) \end{cases}$$
(21)

Thus $\gamma = 1$. The final heat capacity exponent $\alpha = 0$ is left to the tutorial. We now summarise the idea of *Universality*

- The Landau free energy is constructed on symmetry grounds so can hold for a variety of different systems where the order parameter has the same symmetry.
- Then critical exponents are implied by the form of the Landau free energy expansion

Universality: Critical exponents at a continuous phase transition depend

• only on the symmetry of the order parameter, the dimension of space and the range of interactions

Systems which are equivalent in this sense are said to be in the same *universality class*.

An example of two physically dissimilar transitions that lie in the same universality class is the ferromagnetic transition in the Ising model and the liquid-gas transition in a fluid. This is perhaps not surprising, since the lattice gas model maps onto the Ising Model so that clearly the two models have the same critical behaviour. But there is more to it than this, because the lattice gas model has a particle-hole symmetry $(c \rightarrow 1 - c)$ that is not apparently shared by real fluids. Despite this, the two do indeed lie in the same universality class as discussed in Section 12.6.

Unfortunately, the critical exponent values actually predicted from the Landau expansion are, in most cases, not correct!

For example, we can compare the Landau predictions for Ising magnets, which are the same in both two and three dimensions, with those of Onsager's exact solution (d = 2) and the best estimates in d = 3 from experiment and simulation:

Landau	$\beta = 1/2$	$\delta = 3$	$\alpha = 0$	$\gamma = 1$
Ising 2D	$\beta = 1/8$	$\delta = 15$	$\alpha = 0$	$\gamma = 7/4$
Ising 3D	$\beta = 0.31$	$\delta = 5.2$	$\alpha = 0.12$	$\gamma = 1.24$

The reason for the failure of Landau theory is the fact that it is a *mean-field* theory and thus neglects correlations and therefore *fluctuations* near the critical point.

Consider, for example, the heat capacity which in three dimensions behaves near the critical point like

$$C_h = \left. \frac{\partial E}{\partial T} \right|_{h=0} \sim |T - T_c|^{-0.12} \tag{22}$$

Referring back to our discussion in section 3 this means that even for a thermodynamically large system, the fluctuations in the energy $\langle \Delta E^2 \rangle = kT^2C_h$ becomes formally divergent at the critical point. (Note that for magnets we have C_h instead of C_V here.) Similar remarks hold for other thermodynamic quantities, all of whose fluctuations would normally be negligible in a large system. This includes the mean magnetisation m. So the idea of minimising the free energy density f(m) with respect to a *single*, well-defined value of m is questionable to say the least. Note that the fluctuations are cooperative: they involve many spins working in consort and cannot be viewed as the sum of many independent fluctuations of individual spins.

Important and elegant methods exist for dealing with the problem of cooperative phenomena near critical points; these are the subject of a separate P5 Advanced Statistical Physics course.

Let us note here that Landau theory can be extended to include the effect of space dimension and becomes 'Landau-Ginzburg' theory. Above an *upper critical dimension* (ucd), which is d = 4 for the Ising Universality Class, the fluctuations are not important and Landau exponents become exact.

We should also mention that in all of the above we assumed short range interactions.

12. 5. Other Landau Free Energies

One might have the impression from the discussion so far that Landau theory always leads to the same expansion for f(m). Let us illustrate that this is not the case with a quick look at some more complicated examples.

Vector order parameter Consider a vector magnetic moment \underline{m} . Where \underline{m} has components $\alpha = 1, 2...$ Since the free energy f is a scalar it involves scalar invariants of \underline{m} i.e. $|\underline{m}|^2$

$$f = at|\underline{m}|^2 + b|\underline{m}|^4 \tag{23}$$

In the figure we see for $\underline{m} = (m_1, m_2)$ that f has a 'Mexican hat' form and the ground

Figure 4: Sketch of Landau free energy in low T phase for $\underline{m} = (m_1, m_2)$

state has infinite degeneracy. Thus the system can be moved around the ground state 'manifold' with zero free energy cost. These are known as Goldstone excitations

Tensor order parameter An example of a tensorial order parameter occurs in the study of liquid crystals. These are rod-like molecules but with no head or tail. The orientation of a molecule is described by a 'head less' vector \underline{n} and the order parameter is given by the correlations between the \underline{n}

$$Q_{ij} = \langle n_i n_j \rangle - \frac{1}{3} \delta_{ij} \tag{24}$$

which is a tensor. If the orientations are random then since \underline{n} is normalised $(\sum_i n_i^2 = 1)$, $\langle n_i n_j \rangle = \frac{1}{3} \delta_{ij}$ and the order parameter vanishes in the high temperature 'isotropic phase'. However at low temperatures there are nematic phases where the molecules line up.

In the case of the tensor order parameter there is actually a cubic term $\text{Trace}[Q^3]$ which comes into play. This term is a scalar invariant and there is no symmetry to exclude it from the Landau expansion.

The interesting point is that a cubic term in the Landau expansion usually forces a discontinuous phase transition, and this indeed happens in liquid crystals. The presence of a cubic term and other topics in Landau/ Landau-Ginzburg theory are discussed for example in the book by Plischke and Bergersen.

12. 6. *Universality class of the liquid-gas transition

[This section was not covered in lectures and is nonexaminable.] Consider a fluid close to its gas liquid critical point. We work at fixed volume and choose as the order parameter $\rho = n - n_o$ where n = N/V is the number density; n_o is a reference value chosen below. In general there is no obvious symmetry in this system and an expansion of the free energy (per unit volume) f about an arbitrary density would contain both even and odd powers of ρ . For the grand potential $\phi = f - \mu n$ one therefore has

$$\phi = \phi_o - \mu\rho + f_1\rho + f_2\rho^2 + f_3\rho^3 + f_4\rho^4 + \dots$$
(25)

This is similar to the expansion for the Ising magnet, with $\mu - f_1$ playing the role of the field h, f_2 that of a ($\sim T - T_c$) and f_4 that of b. The equilibrium density (as a function of chemical potential and temperature) is found by minimizing this expression, just as before.

But what about f_3 ? This was absent for the magnet, and apparently spoils the correspondence. The important point, however, is that n_o is arbitrary. Hence we can choose n_o to make f_3 vanish. (If you doubt this, check the effect of adding a small shift to ρ in the above expression: you will find $f_3 \rightarrow f_3 + 4f_4\delta\rho$.) Having done this, we find an exact correspondence between the liquid-gas transition and the Ising transition, within the Landau theory. The symmetry breaking point occurs (when $\mu - f_1 = 0$ and a = 0) at $\rho = 0$, which enables us to identify n_o as the density of the fluid *at its critical point*.

The symmetry being broken is that between positive and negative density deviations (measured with respect to n_o). For the lattice gas (which has a symmetric phase diagram) this symmetry holds for arbitrarily large deviations. For a more realistic model, the symmetry is still there, but only for *small* deviations from the critical density. This is sufficient to ensure that the critical exponents are in the same universality class as the Ising model, and can be deduced from them by a suitable "translation table" of thermodynamic variables ($m \to \rho$ etc.).