

3. General properties of phase transitions and the Landau theory

In this Section we review the general properties and the terminology used to characterise phase transitions, which you will have already seen to some extent in the Statistical Physics course. We also review the Landau approach, and use it to compute four critical exponents in the Ising model – these are used to identify how the order parameter or other thermodynamic quantities behave close to the transition. Quite generally, these quantities will behave as power laws: later on in the course we will see that there is quite a deep reason as to why this is so.

3.1. Classification and general features of phase transitions

Phase transitions are drastic changes in the thermodynamic behaviour of a physical system. A familiar example of a phase transition is the liquid-gas transition, or the crystallisation of a liquid. Very relevant to our course is the Ising model which we have been discussing in Section 2 (although in order to get an ordered phase at finite temperature we will need $d \geq 2$).

Phase transitions often break symmetries (this is the case of the Ising model). In these cases, the high temperature (low coupling) phase has typically the symmetry of the Hamiltonian $\mathcal{H}$, whereas the low temperature (high coupling) phase shows a lower symmetry (and an enhanced order). Physically, this is because not all the states of $\mathcal{H}$ are “accessible” anymore by fluctuations – energy wins over entropy in other words. The phenomenon that the system chooses one state during the phase transition is called spontaneous symmetry breaking. For example the Hamiltonian of the Ising model has a spin-flip symmetry, while the ferromagnetic state is either spin-up or spin-down. This symmetry is spontaneously broken during the phase transition as the system selects one of the two possible states as the ground state.

The thermodynamic behaviour in each of the phases can be characterized by an order parameter, let us call it m (for magnetisation in the Ising model), and restrict to a scalar order parameter for simplicity (this is fine when discussing most order-disorder phase transitions). The order parameter m changes in a non-analytical way at the phase transition point. The order parameter is usually constructed in that way that $m = 0$ in the disordered state and $m = 1$ in a perfectly ordered state.

At *first order phase transitions*, the order parameter jumps discontinuously at the transition temperature, typically T_c , from 0 to a finite value. This involves a latent heat $\Delta Q = T_c \Delta S$: while T remains constant at the critical value T_c during the transition, the entropy S changes. As the energy in terms of the latent heat cannot be instantaneously redistributed, a mix of phases occurs during the transition (e.g. liquid water and ice at the melting point).

At *second order phase transitions*, instead, the order parameter increases slowly and continuously from 0 to a finite value at T_c . There is a discontinuity in the specific heat at T_c , while the correlation length and the susceptibility diverge at T_c .

We know that the order parameter can be obtained as a derivative of the partition function. As the order parameter is non-analytic (either it is discontinuous, or so is one of its derivatives), the partition function also needs to be non-analytic. However, at finite N for instance a spin system only has a finite number of microstates hence the partition function is a finite sum of exponentials (with the appropriate Boltzmann factors). This of course *is* analytic. How can there be any phase transitions at all then? The resolution of this apparent paradox is that Z_N and its logarithm, which is related to the free energy, can become non-analytic in the $N \rightarrow \infty$ limit, which is the thermodynamic limit – of central importance to statistical physics. This is then the limit we are interested in when discussing phase transitions.

3.2. Landau Theory

The Landau theory offers a useful phenomenological route to a free energy functional, $\mathcal{F}$. Without caring too much about the microscopic details of the system, the Landau approach starts by just considering the symmetries of the order parameter. The free energy $\mathcal{F}$ has to be invariant under all transformations which leave the disordered high temperature phase invariant. The order parameter, m , has to be a small quantity in the vicinity of the critical point, which is the case in for a second order transition. Therefore the idea is to expand the free energy functional $\mathcal{F}$ in a power series of m .

We then write up the free energy as an integral over space of a free energy density f ,

$$\mathcal{F} = \int d^d \mathbf{x} f(\mathbf{x}). \quad (1)$$

A popular choice for the free energy density is

$$f(m, \nabla m) = -hm + Am^2 + Bm^3 + Cm^4 + \dots + K [\nabla(m(\mathbf{x}))]^2 \quad (2)$$

where h is an external field (promoting positive values of m if $h > 0$), and A , B , C , D and K are phenomenological coefficients - while their exact value depends on the detail of the microscopic model, whether they are non-zero, zero, positive or negative can often be determined simply on the basis of some symmetries of the system under investigation, and of other simple physical arguments.

The main idea underlying Landau theory is that one can find a reasonable approximation for the free energy density of the system by minimising $f(m, \nabla m)$. This is because in the partition function it is $\exp(-\beta\mathcal{F})$ which contributes, and due to the exponential and to the fact that $\mathcal{F}$ is an extensive quantity (it is proportional to V , the volume of the system) it is reasonable to assume that only the values of m maximising $\exp(-\beta\mathcal{F})$, hence minimising $f(m)$, “count” for the partition integral. If you are familiar with saddle point methods, you may note that this argument is equivalent to estimating the partition function of the system via a saddle point approximation.

Classical mean field Landau theory further assumes $\nabla(m(\mathbf{x})) = 0$, i.e. a spatially homogeneous magnetisation. We will adopt this approximation for the

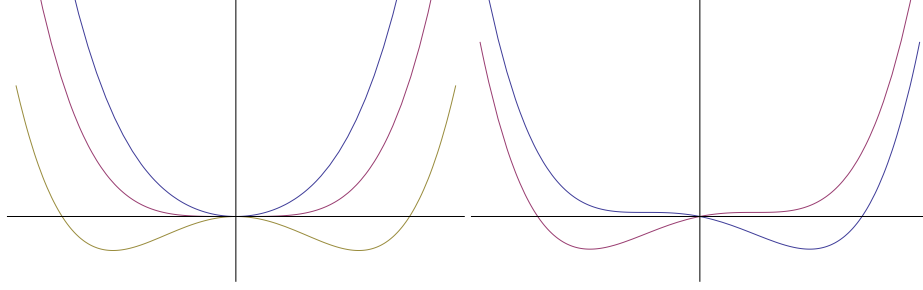


Figure 1: Free energy in the Ising model: left picture: $\frac{1}{2}rm^2 + um^4$ for $r > 0$, $r = 0$ and $r < 0$; right picture: $\frac{1}{2}rm^2 + um^4 - hm$ for $r < 0$, $h < 0$ and $h > 0$. The external field breaks the symmetry.

time being (we will consider the spatially varying case later on and in Section 6). The free energy density in the first term is usually expanded up to the relevant order to capture the right physics.

3.3. Mean field theory of the Ising model

The order parameter for the Ising model is defined as the average magnetization of a spin, which is 0 in the disordered phase.

$$\langle \sigma_i \rangle = m. \quad (3)$$

The Hamiltonian $\mathcal{H}$ is symmetric under the *global* transformation $\sigma_i \rightarrow -\sigma_i$ for all $i = 1, \dots, N$. This symmetry is spontaneously broken in the ordered phase. The free energy density must therefore show the same symmetry and cannot depend on odd powers of m ,

$$f(m) = \frac{1}{2}rm^2 + um^4. \quad (4)$$

The dependence of f on the temperature is introduced as

$$r = a(T - T_c) = aT_c\epsilon. \quad (5)$$

In the presence of an external field h the free energy density becomes

$$f(m) = -hm + \frac{1}{2}rm^2 + um^4. \quad (6)$$

The local minima of f are given by

$$\frac{\partial f}{\partial m} = -h + rm + 4um^3 = 0. \quad (7)$$

For $r > 0$, $h = 0$, $T > T_c$ respectively there is only one solution $m = 0$. Below T_c two further minima exist.

The temperature dependence of the order parameter reads (for $h = 0$)

$$m = \begin{cases} 0 & ; T > T_c \\ \pm \sqrt{-\frac{r}{4u}} & ; T < T_c \end{cases} \quad (8)$$

In the ordered phase the order parameter depends via a power law on the “distance” from T_c .

$$m \propto \left(\frac{T - T_c}{T_c} \right)^\beta = \epsilon^\beta, \quad (9)$$

therefore within the Landau theory $\beta = \frac{1}{2}$.

The dependence of the order parameter on the external field at $r = 0$, so just at criticality, also follows a power law. The minima of the free energy under this condition are given by:

$$h - 4um^3 = 0, \quad (10)$$

so that

$$m \propto h^{1/\delta}, \delta = 3. \quad (11)$$

The susceptibility $\chi = \frac{\partial m}{\partial h}$ is calculated by deriving Eq. (7) with respect to h . This yields

$$-1 + r\chi + 12um^2\chi. \quad (12)$$

Now let us consider $r \rightarrow 0^+$, so T slightly larger than T_c , and $h \rightarrow 0$. In this case $m \rightarrow 0$, and the m^2 term may be neglected – so that χ diverges for $T \rightarrow T_c$ as

$$\chi \propto \epsilon^{-\gamma}, \gamma = 1. \quad (13)$$

The same exponent $\gamma = 1$ can be found for the divergence of χ for $t \rightarrow T_c^-$, or $\epsilon \rightarrow 0^-$ (see tutorial).

In order to determine the specific heat we first need to know the temperature dependence of the free energy density, which is

$$f = \begin{cases} 0 & ; T > T_c \\ -\frac{r^2}{16u} & ; T < T_c \end{cases} \quad (14)$$

Therefore

$$c_V = -T \frac{\partial^2 f}{\partial T^2} = \begin{cases} 0 & ; T > T_c \\ T \frac{r^2}{8u} & ; T < T_c \end{cases} \quad (15)$$

and

$$c_V \propto \begin{cases} \epsilon^\alpha & ; T > T_c \\ \epsilon^{-\alpha} & ; T < T_c \end{cases}, \alpha = 0, \quad (16)$$

which shows a discontinuity, rather than a divergence, at the critical point.

3.4. Critical exponents and universality

The exponents $\alpha, \beta, \gamma, \delta$ in the above power laws for the temperature dependence of the different quantities are called *critical exponents*.

Two or more systems can have the same exponents although they might differ quite considerably in their details. If this is the case we say the systems belong to the same *universality class*. For example, the critical exponents at the liquid/gas transition do not depend on the chemical details of the fluid and are the same of those for the ferromagnetic transition.

On the other hand, critical exponents typically depend on

- the dimension of space
- the symmetry of the order parameter
- the range of the interactions

Their values generally deviate from the mean field values when fluctuations, which were neglected here, become more important. We will focus later during this course on how exact values can be gained.

3.5. Isotropic-nematic transition in liquid crystals

The Landau free energy functional can also be used to model first-order phase transitions if the order parameter is sufficiently small. One example is the transition in liquid crystals from an isotropic liquid to an ordered, nematic state, in which the elongated molecules show no spatial but rather orientational order.

In the nematic state the centres of mass of the molecules are still randomly distributed just like in a normal liquid. The symmetry axis of the molecules is oriented on the average along a particular direction, which is characterized by a unit-vector field $\vec{n}$. However, a vector order parameter describes the order in a liquid crystal only insufficiently as it assumes a dipolar structure. The molecules in liquid crystals behave rather like quadrupoles i.e. like arrows without head or tail. An order parameter is more appropriately defined as a traceless, symmetric tensor of the form

$$Q_{ij} = S(n_i n_j - \frac{1}{3}\delta_{ij}) \quad (17)$$

whereas the scalar S is called the scalar order parameter, which is 0 in the isotropic phase.

The free energy density contains a third order term which allows to model the first-order isotropic-nematic phase transition

$$\begin{aligned} f &= \frac{1}{2}r \left(\frac{3}{2}Tr(Q^2) \right) - w \left(\frac{9}{2}Tr(Q^3) \right) + u \left(\frac{3}{2}Tr(Q^2) \right)^2 \\ f &= \frac{1}{2}rS^2 - wS^3 + uS^4, \end{aligned} \quad (18)$$

where $w, u > 0$, and r may change sign as before. It is clear that $S = 0$ is always a local minimum, with $f(S = 0) = 0$. If r approaches $r_c = \frac{w^2}{2u}$ from

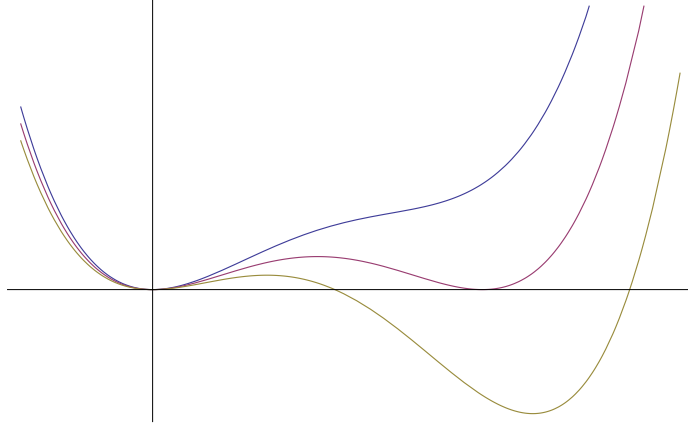


Figure 2: Free energy density: $\frac{1}{2}rS^2 - wS^3 + uS^4$ for $r > r_c = \frac{w^2}{2u}$, $r = r_c$ and $r < r_c$.

above, the free energy develops a second local minimum. This can be seen from the following equations,

$$f = \left(\frac{1}{2}r - wS + uS^2\right)S^2 = 0 \quad (19)$$

$$\frac{\partial f}{\partial S} = (r - 3wS + 4uS^2) = 0 \quad (20)$$

For $r < r_c$ the second minimum becomes the absolute minimum. The critical value of the scalar order parameter is

$$S_c = \frac{w}{2u}. \quad (21)$$