1 Lecture 3. Symmetry change at a phase transition. Landau theory.

1.1 Order parameter. Symmetry classification

Landau theory of type II phase transitions can be viewed as a generalization of of the observations made in Lecture 2, when we discussed ordering transitions in a ferromagnet and binary alloy. This theory is using powerful argument based solely on the symmetry change in the transition. Suppose one has to describe a continuous phase transiton in which the symmetry group is reduced from G_0 to its subgroup $\mathsf{G} \in \mathsf{G}_0$, where G_0 and G are the symmetry groups of the disordered and ordered states, respectively.

The ordering is characterized by a function $\rho(\mathbf{x})$ that changes through the transition. In a structural transition $\rho(\mathbf{x})$ can be particle density, in a magnetic transition it is spin density, and so on. In a disordered state above T_c $\rho(\mathbf{x})$ is invariant under the symmetry group G_0. Below the transition, this quantity (we call it $\rho_1(\mathbf{x})$) is invariant only under the transformations from the subgroup G_1. Hence one can, following Landau, write the difference $\delta\rho = \rho_1 - \rho_0$ in terms of the basis functions $\phi_i^{(n)}$ of irreducible representations of the group G_0:

$$\delta\rho(\mathbf{x}) = \sum_n{}' \sum_i c_i^{(n)} \phi_i^{(n)}(\mathbf{x}) \,, \tag{1}$$

where n labels irreducible representations of G, and i labels the basis functions of each representation. The prime sign indicates that the unit representation is excluded from the sum, since it contributes equally to ρ_1 and ρ_0. At the transition $T = T_c$ all quantities $c_i^{(n)}$ vanish.

The coefficients $c_i^{(n)}$ characterize the system in thermodynamic equilibrium below the transition, and thus their values provide minimum for the thermodynamic potential Φ. In a type II transition just a bit below T_c the values $c_i^{(n)}$ can be arbitrarily small. Thus the potential can be expanded in powers of $c_i^{(n)}$. A number of general features of this expansion can be understood by noting that, since the function $\delta\rho$ is invariant under G, the coefficients $c_i^{(n)}$ transform the same way as the functions $\phi_i^{(n)}$. Since the potential is invariant under coordinate transformations and other symmetry operations from G, each order of the expansion is given by some invariant polynomials in $c_i^{(n)}$. Now, each irreducible representation has no linear invariants and just one quadratic invariant, $\sum_i (c_i^{(n)})^2$. Therefore the series expansion of Φ in $c_i^{(n)}$ begin with

$$\Phi = \Phi_0 + \sum_n{}' A^{(n)}(P,T) \left(\sum_i (c_i^{(n)})^2 \right) + O((c_i^{(n)})^3) \tag{2}$$

Thermodynamic stability requires $A^{(n)}(P,T) > 0$ for all n above T_c. In order to have broken symmetry, i.e. nonzero $c_i^{(n)}$, below T_c, one of the coefficients $A^{(n)}(P,T)$ has to change sign at $T = T_c$. (Simultaneous sign change of two ot more $A^{(n)}$ can take place only at isolated points of the (P, T) plane.)

Since only one of the representations of G corresponds to thermodynamic instability of a disordered state, we can discard all the terms in the expansion (2) except the one which changes sign at T_c. The quantities $c_i^{(n)}$ that become nonzero in the ordered state below T_c are called *the order parameter.*

Focussing on this representation, from now on we drop the index n, always assuming that the representation is the one that corresponds to the instability at T_c. It is useful to use the notations

$$c^2 = \sum_i c_i^2\,, \quad c_i = c\, x_i \tag{3}$$

with $\sum_i x_i^2 = 1$. Let us now consider the higher order terms in the expansion (2):

$$\Phi = \Phi_0(P,T) + c^2 A(P,T) + c^3 \sum_\alpha C_\alpha(P,T) f_\alpha^{(3)}(x_i) + c^4 \sum_\alpha B_\alpha(P,T) f_\alpha^{(4)}(x_i) + O(c^5) \tag{4}$$

Here the functions $f_\alpha^{(3)}$, $f_\alpha^{(4)}$, ..., are invariant polynomials of order 3, 4, etc. Each sum over α has as many terms as there are invariants of the required order. These terms determine the ordering just below the transition, and define the transition type.

To summarize, there are three main ingredients in this phenomenological theory: the symmetry groups G_0 and G above and below the transition, and the representation of G_0 that describes the order parameter properties. Usually, there is no ambiguity in G_0 and G, while some insight or additional experimental input is needed to choose the correct form of the order parameter (i.e. the relevant representation of G_0).

1.2 Transition type deduced from symmetry.

In a continuous phase transition (type II) the variables c_i found by minimizing Φ should become small near T_c (as in the prototype case of $\Phi(c) = A(T - T_c)c^2 + Bc^4$). One can ask when does the potential (4) has this propoperty. This mathematical question has a simple answer:[1] *If the transition in a system described by the potential (4) is of type II, no cubic invariants are allowed.* To prove this statement, one simply has to consider $\Phi(c)$ at $T = T_c$, when $A = 0$, and note that if $C \neq 0$ there exist other mimima $c = c^*$ with $\Phi(c^*) < \Phi(0)$.

This simple but very basic observation allows to predict which symmetry changes can take place as a type II transition, and which cannot. One has to look for cubic invariants of the order parameter representation that describes the transition and if they exist, the transition is guaranteed to be type I, whereas if there are no cubic invariants, the transition is most likely of type II. There are powerful goup theoretic methods for searching for cubic invariants. Mathematically speaking, this is a question of whether the tensor cube of the representation invloved in the transition, when split into irrreducible components, contains

[1] The absence of cubic invariants is a necessary condition. Another necessary condition is that the 4th order terms in (4) are positive and can stabilize the ordered phase at small c.

a unit representation. To find out, one can compute the sum $n_3 = \sum_{g\in\mathsf{G}} \chi^3(g)$, where $\chi(g)$ are representation characters. This sum gives the dimension of the invariant subspace in the tensor cube, and therefore, if it is zero, there no cubic invariants, while if it is nonzero, there are n_3 invariants.

Although this general methodology is quite helpful in analyzing some complex situations[2], in simple cases the absence or presence of cubic invariants can be figured out by a direct inspection. Two examples illustrating this approach are provided by ferromagnetic phase transition in a spin system and by crystallization of a liquid into a solid.

In a ferromagnetic transition, the order parametr is magnetization m, a scalar in the Ising model, or a vector in the Heisenberg model. The disordered state is time-reversal invariant: the transformation $m \to -m$ leaves Hamiltonian invariant, and thus it is part of the symmetry group G_0. Therefore, there are no cubic invariants and Landau free energy in this case has the form

$$\Phi(m) = A(P,T)m^2 + B(P,T)m^4\,, \quad A(P,T) = a(T-T_c) \text{ near } T_c \tag{5}$$

with $a > 0$, $B > 0$. Thus the ferromagnetic transition is second order.

In crystallization transition, ordering is described by the appearance of a density modulation $\delta\rho(\mathbf{x})$ in a uniform liquid state. Choosing the order parameter to be the amplitude $\delta\rho_k$ of density harmonics in the crystal phase, $\delta\rho(\mathbf{x}) = \sum_k \delta\rho_k e^{i\mathbf{k}\cdot\mathbf{x}}$ one can write the thermodynamic potential as

$$\Phi(\delta\rho) = \sum_k A(k)\delta\rho_k\delta\rho_{-k} + \sum_{k,k'} B(k,k')\delta\rho_k\delta\rho_{k'}\delta\rho_{-k-k'} + O(\delta\rho^4) \tag{6}$$

Here the cubic terms arize from the series expansion of Φ in density variations in a liquid. Note that they are not eliminated by any symmetry of the liquid phase hamiltonian. To see how the cubic terms affect the transition, we need to analyze the relations between different harmonics.

Let us first discuss quadratic terms. In a simple model, the function $A(k)$ is isotropic (due to rotational invariance of liquid state) and has a single minimum in $|\mathbf{k}| = k_0$. For example $A(k) = A_1 + A_2(|\mathbf{k}| - k_0)^2$. Suppose that, as a function of temperature, the minimal value of $A(k)$ becomes negative (i.e. $A_1 + A_2 < 0$). As soon as this happens, all harmonics with $|\mathbf{k}| \approx k_0$ become unstable. Which combination of harmonics gives the lower energy is decided by the 4th and higher order terms, but without going into this discussion, let us assume that there is *a star* of vectors $\mathbf{k}_i$ that defines the density harmonics in the ordered state. The symmetry of the set of vectors $\mathbf{k}_i$ reflects the symmetry of the crystal state

It is very often the case that some of the vectors from the star added together give another vector from the same star. Simple examples: ordering of a 2D liquid in a triangular crystal lattice, with the hexagonal star of harmonics $\mathbf{k}_i$, or face-centered cubic ordering

[2]The group theory is especially useful in solids, where there are 240 different space groups even before the magnetic ordering is taken into account. To understand how these symmetries can be broken at a phase transition, and which transition types are possible, often requires using heavy group-theretic tools.

in 3D (the star is defined by a tetrahedron, 6 vectors pointing along the edges plus their opposites). In fact, it has been shown by Landau that for any crystal symmetry, one can find triplets of harmonics that contribute to the cubic term. As a result, on very general symmetry grounds, crystrallization is a first order transition. This analysis shows that, despite symmetry being spontaneously broken in crystallization, the transition is of type I, i.e. discontinuous.

Another case, where on pure symmetry grounds one can reject type II transition, is formation of liquid crystals (see homework problem 5, PS#2)

1.3 Thermodynanmic quantities

Let briefly list the results derived for the type II transition with a scalar order parameter, such as the Ising model or a binary alloy. For concretenens, we discuss transition in a magnetic system with free energy of the form

$$\Phi = -a\tau m^2 + bm^4 + mh\,, \quad \tau = (T_c - T)/T_c \tag{7}$$

where h is the magnetic field. More generally, the field that couples linearly to the order parametr is called *ordering field.*

At $h = 0$, the order parameter equlibrium value is

$$m = \begin{cases} 0, & \text{at } \tau < 0 \\ (a\tau/2b)^{1/2} & \text{at } \tau > 0 \end{cases} \tag{8}$$

From that, the free energy is 0 at $\tau < 0$, and $F \propto -\tau^2$ at $\tau > 0$. The specific heat

$$C_M = -T(\partial^2 F/\partial T^2)_M \tag{9}$$

has a jump at the transition. The zero field susceptibility

$$\chi = (\partial M/\partial h)_T \propto \tau^{-1} \quad \text{at} \quad \tau < 0 \tag{10}$$

These results illustrate that thermodynamic quantities have singularities at the type II transition point. The specific form of temperature dependence at singularity can be modified by the effects of fluctuations, if those are strong.

1.4 Isomorphic phase transitions.

Another useful consequence of the symmetry approach is that it allows to identify *isomorphic phase transitions* in which the symmetry change is the same. Isomorphic transitions may take place in very different systems, and despite that, they have the same macroscopic charactersitics. Such transitions are saiud to belong to the same *universality class.*

One example, discussed already in Lecture 2, is the relation between the Ising phase transition, the liquid-gas critical point, and the binary alloy. In all three cases, the ordering is describes by a scalar order parameter. The symmetry is exact in the case of the Ising problem ($m \to -m$), and in the case of a binary alloy ($a \leftrightarrow b$), but only approximate near the liquid-gas critical point (however, it becomes exacvt asymptotically right at this point). For convenience, we list analogous quantities in a table:

System described by Ising model	Curie point of a ferromagnet	Liquid-gas critical point of a one component liquid	Critical point of a binary mixture
Density-like variable	Magnetization $M = -(\partial\Phi/\partial H)_T$	Density $\rho = -(\partial P/\partial\mu)_T$	Concentration $x = -(\partial\mu_1/\partial\mu^*)_T$
Field-like variable	Magnetic field $H = -(\partial F/\partial\mu_1)_T$	Chemical potential $\mu = F + PV = [\partial(\rho F)/\partial\rho]_T$	The difference of the chemical potentials of the components, $\mu^* = \mu_2 - \mu_1 = (\partial F/\partial x)_T$
Thermodynamic potential for the density variable	$F(T,M) = \Phi + Mh$, $dF = -SdT + hdM$	$\rho F(T,\rho) = -P + \rho\mu$, $d(\rho F) = -\rho SdT + \mu d\rho$	$F(T,x) = \mu_1 + \mu^* x$, $dF = -SdT + \mu^* dx$
Thermodynamic potential for the field variable	$\Phi(T,h) = F - Mh$, $d\Phi = -SdT - Mdh$	$-P(T,\rho)$, $-dP = \rho SdT - \rho d\mu$	$\mu_1(T,\mu^*) = F - \mu^* x$, $d\mu_1 = -SdT - xd\mu^*$
Order parameter ϕ	M	$(\rho - \rho_c)/\rho_c$	$x - x_c$
Ordering field h	h	$(\mu - \mu(\rho_c, T))/T_c$	$(\mu^* - \mu^*(\rho_c, T))/T_c$
Susceptibility $(\partial\phi/\partial h)_T$	$(\partial M/\partial h)_T$	$(T_c/\rho_c)(\partial\rho/\partial\mu)_T$	$T_c(\partial x/\partial\mu^*)_T$
Specific heat C_ϕ	$C_M = -T(\partial^2 F/\partial T^2)_M$	$\rho C_V = -T(\partial^2 \rho F/\partial T^2)_V$	$C_x = -T(\partial^2 \rho F/\partial T^2)_x$

1.5 Summarize

- **Symmetry change** determines many qualitative features of a phase transition, such as its type (I or II) and universality class.
- **Spontaneous symmetry breaking** occurs discontinuously, via a type I transition, when the free energy expansion in powers of order parametr contains cubic terms.
- **Fluctuations** are not accounted for in the Landau theory. Many conclusions, including the predicted temperature dependence of thermodynamic quantities, hold only when fluctuations are small.