

3.1. STRUCTURAL PHASE TRANSITIONS

3.1.2.2.2. Basic assumptions and strategy

Our aim is to determine the above displacement as a function of temperature. Landau's strategy is to determine \mathbf{d}_0 by a *variational method*. One considers an arbitrary displacement \mathbf{d} of the M^+ ion. For given temperature T and pressure p (or volume V), and specified values of the components of \mathbf{d} , there is, in principle, a definite value $F(T, p, d_x, d_y, d_z)$ for the free energy F of the system. This function is a *variational free energy* since it is calculated for an arbitrary displacement. The equilibrium displacement $\mathbf{d}_0(T, p)$ is defined as the displacement that minimizes the variational free energy F . The equilibrium free energy of the system is $F_{\text{eq}}(T, p) = F(T, p, \mathbf{d}_0)$. Note that, strictly speaking, in the case of a given pressure, one would have to consider a variational Gibbs function ($F + pV$) in order to determine the equilibrium of the system. We will respect the current use in the framework of Landau's theory of denoting this function F and call it a *free energy*, though this function might actually be a Gibbs potential.

The former strategy is not very useful as long as one does not know the form of the variational free energy as a function of the components of the displacement. The second step of Landau's theory is to show that, given general assumptions, one is able to determine simply the form of $F(T, p, \mathbf{d})$ in the required range of values of the functions' arguments.

The basic assumption is that of *continuity of the phase transition*. It is in fact a dual assumption. On the one hand, one assumes that the equilibrium displacement $\mathbf{d}_0(T, p)$ has components varying continuously across the transition at T_c . On the other hand, one assumes that F is a continuous and derivable function of (T, p, \mathbf{d}) , which can be expanded in the form of a *Taylor expansion* as function of these arguments.

Invoking the continuity leads to the observation that, on either side of T_c , $|\mathbf{d}_0|$ is small, and that, accordingly, one can restrict the determination of the functional form of $F(T, p, \mathbf{d})$ to small values of (d_x, d_y, d_z) and of $|T - T_c|$. F will then be equal to the sum of the first relevant terms of a Taylor series in the preceding variables.

3.1.2.2.3. Symmetry constraints and form of the free energy

The central property of the variational free energy which allows one to specify its form is a symmetry property. F is a function of (d_x, d_y, d_z) which is *invariant by the symmetry transformations of the high-temperature equilibrium structure*. In other terms, an arbitrary displacement \mathbf{d} and the displacement \mathbf{d}' obtained by applying to \mathbf{d} one of the latter symmetry transformations correspond to the same value of the free energy.

Indeed, both displacements determine an identical set of mutual distances between the positive and negative ions of the system and the free energy only depends on this 'internal' configuration of the ions.

Note that, in the case considered here (Fig. 3.1.2.1), the set of symmetry transformations comprises, aside from the lattice translations, fourfold rotations around the z axis, mirror symmetries into planes and the products of these transformations. The set of rotations and reflections forms a *group* G of order 16, which is the crystallographic point group $4/mmm$ (or D_{4h}).

Also note that this symmetry property of the free energy also holds for each degree of the Taylor expansion of F since the geometrical transformations of G act linearly on the components of \mathbf{d} . Hence, terms of different degrees belonging to the expansion of F will not 'mix', and must be separately invariant.

Let us implement these remarks in the case in Fig. 3.1.2.1. It is easy to check that by successive application to the components of \mathbf{d} of the mirror symmetries perpendicular to the three axes, no linear combination of these components is invariant by G : each of the three former symmetry transformations reverses one

component of \mathbf{d} and preserves the two others. *Linear terms are therefore absent from the expansion.*

As for second-degree terms, the same symmetry transformations preclude the existence of combinations of bilinear products of the type $d_x d_y$. Actually, one finds that the fourfold symmetry imposes that the most general form of the second-degree contribution to the variational free energy is a linear combination of d_z^2 and of $(d_x^2 + d_y^2)$. Hence the Taylor expansion of F , restricted to its lowest-degree terms, is

$$F = F_0(T, p) + \frac{\alpha_1(T, p)}{2} d_z^2 + \frac{\alpha_2(T, p)}{2} (d_x^2 + d_y^2). \quad (3.1.2.1)$$

3.1.2.2.4. Reduction of the number of relevant degrees of freedom: order parameter

Let us now derive the *key result of the theory*, namely, that either the component d_z or the pair of components (d_x, d_y) will take nonzero values below T_c (but not both). The meaning of this result will be clarified by symmetry considerations.

The derivation of this result relies on the fact that one, and one only, of the two coefficients α_i in equation (3.1.2.1) must vanish and change sign at T_c , and that the other coefficient must remain positive in the neighbourhood of T_c .

(a) Before establishing the latter property in (b) hereunder, let us show that its validity implies the stated key result of the theory. Indeed, if one α_i coefficient is strictly positive (e.g. $\alpha_1 > 0$), then the minimum of F with respect to the components of \mathbf{d} (e.g. d_z) multiplying this coefficient in (3.1.2.1) occurs for zero equilibrium values of these components (e.g. $d_z^0 = 0$) in the vicinity of T_c , *above and below this temperature*. Hence, depending on the coefficient α_i which remains positive, either d_z or the pair (d_x, d_y) can be omitted, in the first place, from the free-energy expansion. *The remaining set of components is called the order parameter of the transition*. At this stage, this fundamental quantity is defined as the set of degrees of freedom, the coefficient of which in the second-degree contribution to F vanishes and changes sign at T_c . The number of independent components of the order parameter (one in the case of d_z , two in the case of the pair d_x, d_y) is called the dimension of the order parameter.

Note that the preceding result means that the displacement of the M^+ ion below T_c cannot occur in an arbitrary direction of space. It is either directed along the z axis, or in the (x, y) plane.

(b) Let us now establish the property of the α_i postulated above.

At T_c , the equilibrium values of the components of \mathbf{d} are zero. Therefore, at this temperature, the variational free energy (3.1.2.1) is minimum for $d_x, d_y, d_z = 0$. Considering the form (3.1.2.1) of F , this property implies that we have (Fig. 3.1.2.2) $\alpha_i(T_c) \geq 0$ ($i = 1, 2$).

Note that these inequalities cannot be strict for both coefficients α_i , because their positiveness would hold on either side of T_c in the vicinity of this temperature. Consequently, the minimum of F would correspond to $\mathbf{d} = 0$ on either side of the transition while the situation assumed is only compatible with this result *above* T_c . Using the converse argument that the equilibrium values of the components of \mathbf{d} are not *all* equal to zero below T_c leads easily to the conclusion that one, at least, of the two coefficients α_i must vanish at T_c and become negative below this temperature.

Let us now show that the two coefficients α_i cannot vanish simultaneously at T_c . This result relies on the 'reasonable' assumption that the two coefficients α_i are *different* functions of temperature and pressure (or volume), no constraint in this respect being imposed by the symmetry of the system.

Fig. 3.1.2.3 shows, in the (T, p) plane, the two lines corresponding to the vanishing of the two functions α_i . The simultaneous vanishing of the two coefficients occurs at an isolated point

3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

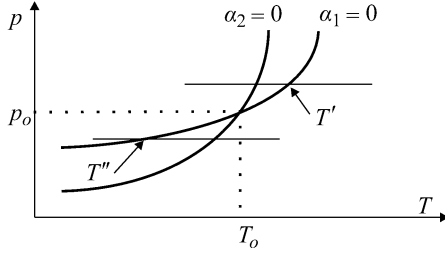


Fig. 3.1.2.3. Plots representative of the equations $\alpha_1(p, T) = 0$ and $\alpha_2(p, T) = 0$. The simultaneous vanishing of these coefficients occurs for a single couple of temperature and pressure (p_0, T_0) .

(T_0, p_0) . Let us consider, for instance, the situation depicted in Fig. 3.1.2.3. For $p > p_0$, on lowering the temperature, α_1 vanishes at T' and α_2 remains positive in the neighbourhood of T' . Hence, the equilibrium value of the set (d_x, d_y) remains equal to zero on either side of T' . A transition at this temperature will only concern a possible change in d_z^0 .

Likewise for p below p_0 , a transition at T'' will only concern a possible change of the set of components (d_x^0, d_y^0) , the third component d_z remaining equal to zero on either sides of T'' . Hence an infinitesimal change of the pressure (for instance a small fluctuation of the atmospheric pressure) from above p_0 to below p_0 will *modify qualitatively the nature of the phase transformation* with the direction of the displacement changing abruptly from z to the (x, y) plane. As will be seen below, the crystalline symmetries of the phases stable below T' and T'' are different. This is a singular situation, of *instability*, of the type of phase transition, not encountered in real systems. Rather, the standard situation corresponds to pressures away from p_0 , for which a slight change of the pressure does not modify significantly the direction of the displacement. In this case, one coefficient α_i only vanishes and changes sign at the transition temperature, as stated above.

3.1.2.2.5. Stable state below T_c and physical anomalies induced by the transition

We have seen that either d_z or the couple (d_x, d_y) of components of the displacement constitute the order parameter of the transition and that the free energy needs only to be expanded as a function of the components of the order parameter. Below the transition, the corresponding coefficient α_i is negative and, accordingly, the free energy, limited to its second-degree terms, has a maximum for $\mathbf{d} = 0$ and no minimum. Such a truncated expansion is not sufficient to determine the equilibrium state of the system. The stable state of the system must be determined by positive terms of higher degrees. Let us examine first the simplest case, for which the order parameter coincides with the d_z component.

The same symmetry argument used to establish the form (3.1.2.1) of the Landau free energy allows one straightforwardly to assert the absence of a third-degree term in the expansion of F as a function of the order parameter d_z , and to check the effective occurrence of a fourth-degree term. If we assume that this simplest form of expansion is sufficient to determine the equilibrium state of the system, the coefficient of the fourth-degree term must be positive in the neighbourhood of T_c . Up to the latter degree, the form of the relevant contributions to the free energy is therefore

$$F = F_0(T, p) + \frac{\alpha(T - T_c)}{2} d_z^2 + \frac{\beta}{4} d_z^4. \quad (3.1.2.2)$$

In this expression, α_1 , which is an odd function of $(T - T_c)$ since it vanishes and changes sign at T_c , has been expanded linearly. Likewise, the lowest-degree expansion of the function $\beta(T - T_c)$ is a *positive constant* in the vicinity of T_c . The function F_0 , which is the zeroth-degree term in the expansion, represents

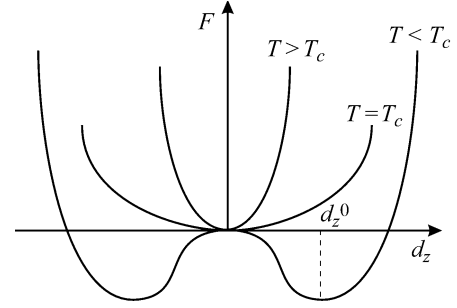


Fig. 3.1.2.4. Plots of the Landau free energy as a function of the order parameter, for values of the temperature above or below T_c or coincident with T_c . The shape of the plot changes qualitatively from a one-minimum plot to a two-minimum plot.

the normal ‘background’ part of the free energy. It behaves smoothly since it does not depend on the order parameter. A plot of $[F(d_z) - F_0]$ for three characteristic temperatures is shown in Fig. 3.1.2.4.

The minima of F , determined by the set of conditions

$$\frac{\partial F}{\partial d_z} = 0; \quad \frac{\partial^2 F}{\partial d_z^2} > 0, \quad (3.1.2.3)$$

occur above T_c for $d_z = 0$, as expected. For $T < T_c$ they occur for

$$d_z^0 = \pm \sqrt{\alpha \frac{(T_c - T)}{\beta}}. \quad (3.1.2.4)$$

This behaviour has a general validity: the order parameter of a transition is expected, in the framework of Landau’s theory, to possess a square-root dependence as a function of the deviation of the temperature from T_c .

Note that one finds two minima corresponding to the same value of the free energy and opposite values of d_z^0 . The corresponding upward and downward displacements of the M^+ ion (Fig. 3.1.2.1) are distinct states of the system possessing the same stability.

Other physical consequences of the form (3.1.2.2) of the free energy can be drawn: absence of latent heat associated with the crossing of the transition, anomalous behaviour of the specific heat, anomalous behaviour of the *dielectric susceptibility* related to the order parameter.

The *latent heat* is $L = T\Delta S$, where ΔS is the difference in entropy between the two phases at T_c . We can derive S in each phase from the equilibrium free energy $F(T, p, d_z^0(T, p))$ using the expression

$$S = -\frac{dF}{dT} \Big|_{d_z^0} = -\left[\frac{\partial F}{\partial T} \Big|_{d_z^0} + \frac{\partial F}{\partial d_z} \frac{d(d_z^0)}{dT} \Big|_{d_z^0} \right]. \quad (3.1.2.5)$$

However, since F is a minimum for $d_z = d_z^0$, the second contribution vanishes. Hence

$$S = -\frac{\alpha}{2} (d_z^0)^2 - \frac{\partial F_0}{\partial T}. \quad (3.1.2.6)$$

Since both d_z^0 and $(\partial F_0/\partial T)$ are continuous at T_c , there is no entropy jump $\Delta S = 0$, and *no latent heat at the transition*.

Several values of the specific heat can be considered for a system, depending on the quantity that is maintained constant. In the above example, the displacement \mathbf{d} of a positive ion determines the occurrence of an electric dipole (or of a macroscopic polarization \mathbf{P}). The quantity ϵ , which is thermodynamically conjugated to d_z , is therefore proportional to an electric field (the conjugation between quantities η and ζ is expressed by the fact that infinitesimal work on the system has the form $\zeta d\eta - cf$.