

## 3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

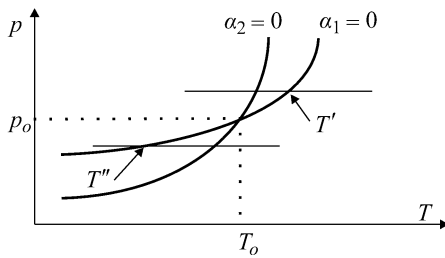


Fig. 3.1.2.3. Plots representative of the equations  $\alpha_1(p, T) = 0$  and  $\alpha_2(p, T) = 0$ . The simultaneous vanishing of these coefficients occurs for a single couple of temperature and pressure  $(p_0, T_0)$ .

$(T_0, p_0)$ . Let us consider, for instance, the situation depicted in Fig. 3.1.2.3. For  $p > p_0$ , on lowering the temperature,  $\alpha_1$  vanishes at  $T'$  and  $\alpha_2$  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  $\alpha_i$  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  $\alpha_i$  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,  $\alpha_1$ , 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

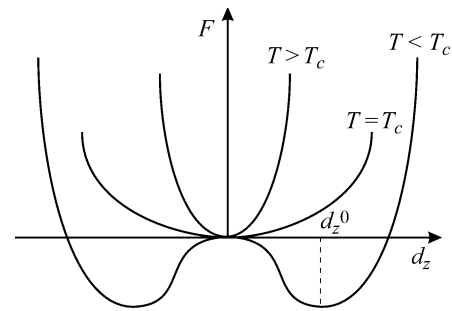


Fig. 3.1.2.4. Plots of the Landau free energy as a function of the order parameter, for values of the temperature above or below  $T_c$  or coincident with  $T_c$ . The shape of the plot changes qualitatively from a one-minimum plot to a two-minimum plot.

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  $\Delta S$  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  $\epsilon$ , which is thermodynamically conjugated to  $d_z$ , is therefore proportional to an electric field (the conjugation between quantities  $\eta$  and  $\zeta$  is expressed by the fact that infinitesimal work on the system has the form  $\zeta d\eta - cf$ .