

3. PHASE TRANSITIONS, TWINNING AND DOMAIN STRUCTURES

space by the group G , which is the crystallographic symmetry group of the high-temperature phase. A variational free energy F associated with the transition, and termed the Landau free energy, can be expanded as a function of the components of the order parameter. The second-degree term of this expansion has a coefficient that vanishes and changes sign at the transition temperature. The form of F is determined by the symmetry properties of the order parameter, *i.e.* by the mode of transformation of the components of the order parameter into each other when the operations of G are applied to them. The specific form of F determines the symmetries of the potentially stable phases below T_c , the degeneracy of these phases, the temperature dependencies of relevant physical quantities and, in certain cases, the thermodynamic order of the phase transition.

In this section, let us briefly outline the arguments used in order to formulate the theory in a general framework.

These arguments rely in part on the properties of the irreducible representations of a group. The reader can refer to Chapter 1.2 for a comprehensive presentation of irreducible representations. We will consider here representations of a group G carried by a set of degrees of freedom $(\eta_1, \eta_2, \eta_3, \dots)$, and use essentially the following properties.

(a) If the set is irreducible and non-totally symmetric (trivial), there is no linear combination $f_1(\eta_i) = \alpha_1\eta_1 + \alpha_2\eta_2 + \dots$ of the η_i that is invariant by all the elements of G .

(b) If the set is irreducible, there is a single homogeneous polynomial of degree two that is invariant by the group G . Its form is $f_2 = \sum \eta_i^2$.

(c) If $g(\mathbf{r})$ is an arbitrary function of the space coordinates $[\mathbf{r} = (x, y, z)]$, one can always write

$$g(\mathbf{r}) = \sum_{\gamma} \sum_j \varphi_{\gamma,j}(\mathbf{r}), \quad (3.1.2.20)$$

where each set of functions $\varphi_{\gamma,j}$ ($j = 1, 2, \dots, p$) defines a space generated by the p functions which is invariant and irreducible by the group G and corresponds to the irreducible representation labelled τ_{γ} of G .

3.1.2.4.1. Description of the phase transition

In order to generalize the considerations developed in the preceding sections, we have to define, independently from any specific structure, the basic ingredients of the theory: definition of a variational set of degrees of freedom; construction of a free energy; determination of the stable states on either side of a transition temperature.

In a first step, we describe an arbitrary atomic configuration of a system by the set of densities $\rho_i(\mathbf{r})$ of the particles of type (i) . This set constitutes variational degrees of freedom, which can be used to construct the variational free energy of the system $F[T, \rho_i(\mathbf{r})]$. The equilibrium of the system is defined by the set of functions $\rho_i^{\text{eq}}(T, \mathbf{r})$ that minimize the free energy.

The symmetry of the system at a given temperature is defined as the set of geometrical transformations that leave invariant all the ρ_i^{eq} . This set forms a group.

We are then in a position to define a *continuous transition* at T_c by two conditions:

(i) The $\rho_i^{\text{eq}}(T, \mathbf{r})$ are functions whose forms change continuously across T_c .

(ii) The symmetry group of the system just above T_c is different to the symmetry just below T_c .

Hence the phase transition, though associated with a *continuous* change of the spatial configuration of the atoms, is associated with a *sudden* change of the symmetry.

3.1.2.4.2. Order parameter

As compared with the set (d_x, d_y, d_z) used in the example of Section 3.1.2.2, the variational functions $\rho_i(\mathbf{r})$ have the drawback

of not being *small and scalar* quantities, thus making an expansion of the free energy more complicated.

Without loss of generality, let us restrict ourselves to a single type of (i) particles. In order to remove the difficulty mentioned above we put

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \sum_{\gamma} \sum_j \eta_{\gamma,j} \varphi_{\gamma,j}(\mathbf{r}), \quad (3.1.2.21)$$

where $\rho_0 = \rho^{\text{eq}}(T_c, \mathbf{r})$ is the equilibrium density at T_c . Let us denote by G the symmetry group of this equilibrium density. The sum in the second part of (3.1.2.21) is a small increment since the transition is continuous. This increment has been expanded, as in (3.1.2.20), as a function of irreducible functions with respect to the group G . Moreover, each function has been expressed as the product of a normalized function $\varphi_{\gamma,j}$ and of small scalar parameters $\eta_{\gamma,j}$. It is easy to convince oneself that it is possible to consider that under the action of G either the $\varphi_{\gamma,j}$ transform into each other, the $\eta_{\gamma,j}$ being fixed coefficients, or the $\eta_{\gamma,j}$ transform into each other, the functions $\varphi_{\gamma,j}$ being fixed. *We shall adopt the second convention.* The variational free energy can then be written in the form

$$F = F[T, \eta_{\gamma,j}, \varphi_{\gamma,j}(\mathbf{r})]. \quad (3.1.2.22)$$

At each temperature, the characteristics of the system are specified by the following conditions:

(i) The equilibrium corresponds to the values $\eta_{\gamma,j}$ that make the free energy a minimum. These values define through (3.1.2.21) the equilibrium density of particles in the system.

(ii) The symmetry of the system is defined as the group of invariance of the determined equilibrium density.

Note that, in $(\rho - \rho_0)$, the contribution of the degrees of freedom $\eta_{\gamma,j}$ spanning a *totally symmetric representation* can be ignored in the first place. One can show that such a contribution would have the same symmetry on either side of the transition. Therefore it is not crucially associated with the symmetry change defining the phase transition.

Following the ideas introduced in Section 3.1.2.2, the free-energy form is obtained as a Taylor expansion as a function of the small parameters $\eta_{\gamma,j}$. Besides, each polynomial term of a given degree of this expansion is invariant by G . Indeed, F , being a scalar, is unchanged by any rotation or reflection. Among the transformations, those belonging to G have the additional property of leaving invariant the density ρ_0 which is, besides T and the $\eta_{\gamma,j}$, an argument of the function F .

It is easy to check that the group-theoretical rules recalled at the beginning of this section determine the absence of an invariant linear term in the expansion. Moreover, these rules specify the form of the second-degree contribution. We have

$$F = F_0(T) + \sum_{\gamma} \alpha_{\gamma} (\sum_j \eta_{\gamma,j}^2). \quad (3.1.2.23)$$

On the other hand, the equilibrium density is

$$\rho^{\text{eq}} - \rho_0 = \sum_{\gamma} \sum_j \eta_{\gamma,j}^0 \varphi_{\gamma,j}(\mathbf{r}). \quad (3.1.2.24)$$

Let us first consider the system at T_c . The equilibrium values of all the $\eta_{\gamma,j}$ are zero. Hence, on the basis of (3.1.2.23), we conclude that all the α_{γ} satisfy the condition $\alpha_{\gamma} > 0$ (since the second-degree expansion must be minimum at the origin). Note that this condition *cannot be strict for all γ* . Otherwise, these coefficients would also be positive in the vicinity of T_c , on either side of this temperature. As a consequence, the equilibrium values $\eta_{\gamma,j}^0$ would all be zero and the symmetry would be unchanged. *Hence, one at least of the α_{γ} has to vanish and to change sign at T_c .* An argument already invoked in Section 3.1.2.2 allows one to assert that one α_{γ} coefficient only has this property. The $\eta_{\gamma,j}$ corresponding to the other indices γ keep zero equilibrium values in the vicinity of T_c and can be ignored in the first place. We can therefore drop in (3.1.2.23) all degrees of freedom except the ones associated with