

3.1. STRUCTURAL PHASE TRANSITIONS

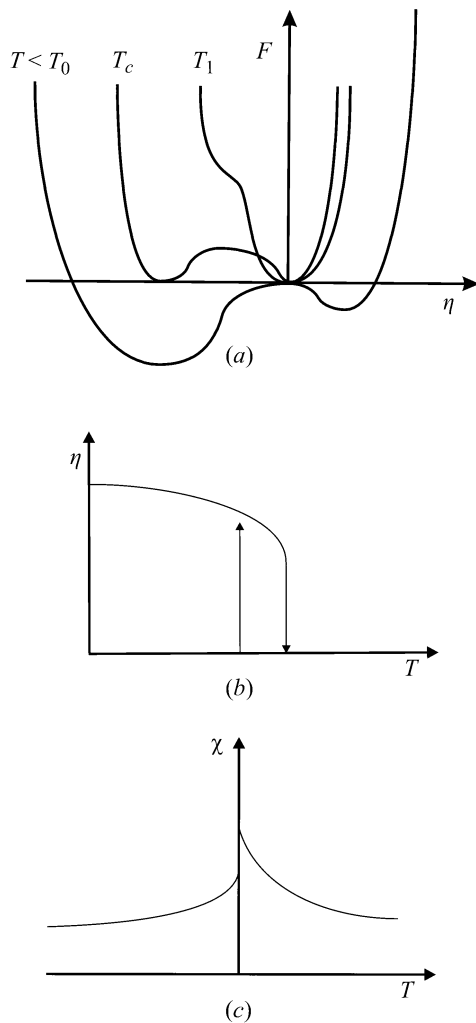


Fig. 3.1.2.6. (a) Plots of the free energy as a function of the order parameter for various temperature values in the framework of the model of a discontinuous transition associated with equation (3.1.2.13). (b) Temperature dependence of the equilibrium value of the order parameter, as determined by the model of a discontinuous transition. (c) Temperature dependence of the susceptibility in this model.

ered as valid. Indeed, the total free energy of the system depends on the distance between atoms, because this distance controls the strength of the interaction energy within the system. Hence, the transition only changes in a minor way the value of the system's free energy.

On the other hand, one has to check that there are systems of physical interest for which the crystallographic symmetry allows free-energy forms of the type (3.1.2.13), (3.1.2.16). Indeed, the crystallographic symmetry relative to the example in Section 3.1.2.2 was such that the presence of a third-degree term in the Landau free energy was excluded.

Such verification is not necessary for the free energy of type (3.1.2.16). This free energy is only characterized by a *specific sign* of the coefficient of the fourth-degree term, a circumstance that is not defined by symmetry considerations.

By contrast, an actual crystallographic model of a transition described by (3.1.2.13), which involves a term of degree three, is required to support the relevance of the corresponding model. Such a model is provided, for instance, by a crystal the high-temperature phase of which has a rhombohedral symmetry (e.g. $R3m$), and which undergoes a transition corresponding to an atomic displacement \mathbf{d} perpendicular to the ternary axis (Fig. 3.1.2.8).

If we refer the components to a rectangular frame of coordinates, the matrices representing the mode of transformation of the components (d_x, d_y) under application of the generating

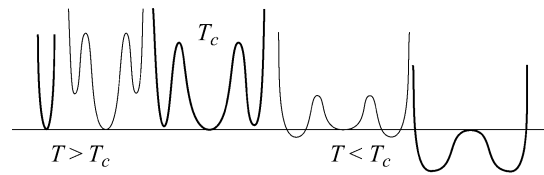


Fig. 3.1.2.7. Plots of the free energy as a function of the order parameter for various temperatures in the framework of the model of a discontinuous transition associated with equation (3.1.2.16). The temperature decreases from right to left, the transition being reached for the temperature corresponding to the third plot.

elements of the group $R3m$ have a form reproduced in existing tables. It is easy to check that the form of the Landau free energy resulting from a search of invariant polynomials of successive degrees is

$$F = F_0 + \frac{\alpha(T - T_0)}{2}(d_x^2 + d_y^2) + \frac{\delta}{3}(d_x^2 - 3d_y^2) + \frac{\beta}{4}(d_x^2 + d_y^2)^2. \quad (3.1.2.17)$$

We note that the form of the free energy of this system, determined by its symmetry, involves a third-degree term. Let us show that the thermodynamic properties corresponding to this form are qualitatively identical to the ones derived from the canonical free energy (3.1.2.13). In this view, let us put $d_x = \eta \cos \theta$ and $d_y = \eta \sin \theta$. The free energy takes the form

$$F = F_0 + \frac{\alpha(T - T_0)}{2}\eta^2 + \frac{\delta}{3}\eta^3 \cos \theta (\cos^2 \theta - 3 \sin^2 \theta) + \frac{\beta}{4}\eta^4. \quad (3.1.2.18)$$

For such a free energy, it is remarkable that for $\eta \neq 0$ the directions θ of the extrema, which are determined by $\partial F / \partial \theta = 0$, are independent of the value of η . These directions form two sets which we denote A ($\theta = 0, 2\pi/3, 4\pi/3$) and B ($\pi/3, \pi, -\pi/3$). If we replace in equation (3.1.2.18) η by one of these values, we obtain

$$F = F_0 + \frac{\alpha(T - T_0)}{2}\eta^2 \pm \frac{\delta}{3}\eta^3 + \frac{\beta}{4}\eta^4, \quad (3.1.2.19)$$

the sign in front of the δ coefficient being $+$ for the A set of θ angles and $-$ for the B set. We are therefore brought back to a form close to the canonical one [equation (3.1.2.13)]. Note that for $\delta > 0$, the stable second minimum of the free energy [equation (3.1.2.15)] corresponded to $\eta < 0$, i.e. to $\delta\eta < 0$. Hence in (3.1.2.19), η being a positive modulus, the second stable minimum will correspond to a negative coefficient for η^3 . Depending on the sign of δ , the direction θ of this minimum will either be the set A or the set B of θ values.

3.1.2.4. Generalization of the approach

Let us summarize the results obtained in the study of the specific models described in the preceding sections. We have shown that an order parameter (e.g. d_z or d_x, d_y) is a set of scalar degrees of freedom that allows the description of the symmetry and physical changes accompanying the phase transition in a system. The equilibrium values of the n components of the order parameter are zero for $T \geq T_c$ and *not all zero* for $T < T_c$. The n components define a vector space that is an irreducible invariant

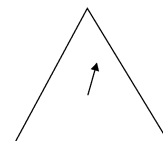


Fig. 3.1.2.8. Schematic representation of the displacement associated with the order parameter in a crystal having trigonal (rhombohedral) symmetry.

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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

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the α_γ coefficient that vanishes at T_c . The set $\eta_{\gamma,j}$ ($j = 1, 2, \dots, m$) constitutes the m -dimensional order parameter of the transition considered. As this set comprises all the degrees of freedom contributing to a single second-degree term in the free energy, it necessarily constitutes a basis for an irreducible vector space with respect to G , according to the group-theoretical rules recalled above.

3.1.2.4.3. Stable states and symmetry in the vicinity of T_c

Above T_c , due to the positivity of α (we can drop the γ index), the equilibrium values of the η_j are zero and the symmetry is G , identical to the symmetry at T_c . Below T_c , α is negative and the minimum of F occurs away from the origin in the $\{\eta_j\}$ space. The symmetry of the system is defined by all the transformations leaving invariant the density:

$$\rho^{\text{eq}} = \rho_0 + \sum \eta_j^0 \varphi_j(\mathbf{r}). \quad (3.1.2.25)$$

Since the η_j^0 contribution to the second member is small, these transformations have to be selected among those belonging to the invariance group of ρ_0 . The space $\{\eta_j\}$ defines a *non-trivial representation* of the latter group since the linear combination of the order-parameter components present in ρ^{eq} cannot be invariant by all the transformations of G . The symmetry group of the system below T_c is therefore a subgroup F of G .

As pointed out in Section 3.1.2.2, in order to determine the minimum of F below T_c , it is necessary to expand the free energy to degrees higher than two. The relevant expression of the free energy is then

$$F = F_0(T, \rho_0) + \frac{1}{2}\alpha(T - T_c)(\sum \eta_j^2) + f_3(\eta_j) + f_4(\eta_j) + \dots, \quad (3.1.2.26)$$

where we have developed the coefficient α , which is an odd function of $(T - T_c)$ to the lowest degree in $(T - T_c)$. It can be shown that the existence of a third-degree term $f_3(\eta_j)$ depends exclusively on the nature of the representation τ_γ associated with the order parameter. If the symmetry of the order parameter is such that a third-degree term is not symmetry forbidden, the transition will be of the type analysed in Section 3.1.2.3: it will be discontinuous.

For any symmetry of the order parameter, fourth-degree terms $f_4(\eta_j)$ will always be present in the free-energy expansion (there will be at least one such term that is the square of the second-degree term). No further general statement can be made. Depending on the form and coefficients of this term, a continuous or discontinuous transition will be possible towards one or several distinct low-symmetry phases. The form of the $f_4(\eta_j)$ term can be determined by searching the most general fourth-degree polynomial that is invariant by the set of transformations belonging to G .

In summary, in the light of the preceding considerations, the study of a phase transition according to the Landau scheme can be developed along the following lines:

(a) Search, as a starting information on the system, the symmetry group G of the more symmetric phase surrounding the transition and the nature of the irreducible representation τ_γ associated with the order parameter. Both can be obtained from a crystallographic investigation as illustrated by the example in the next section.

(b) Check the possibility of a third-degree invariant on symmetry grounds.

(c) Construct the free energy by determining the form of the invariant polynomials of the required degrees.

(d) Determine, as a function of the coefficients of the free-energy expansion, the absolute minimum of F .

(e) For each minimum, determine the invariance group of the density ρ^{eq} , *i.e.* the ‘low-symmetry’ group of the system.

(f) Derive the temperature dependence of the quantities related to the order parameter component η_j .

(g) Consider (as discussed in the next section) the coupling of the order parameter to other relevant ‘secondary’ degrees of freedom, and derive the temperature dependence of these quantities.

3.1.2.5. Application to the structural transformation in a real system

Let us examine the particular ingredients needed to apply Landau’s theory to an example of *structural* transitions, *i.e.* a transition between crystalline phases.

3.1.2.5.1. Nature of the groups and of their irreducible representations

The phases considered being crystalline, their invariance groups, G or F , coincide with *crystallographic space groups*. Let us only recall here that each of these groups of infinite order is constituted by elements of the form $\{R|\mathbf{t}\}$ where R is a point-symmetry operation and \mathbf{t} a translation. The symmetry operations R generate the point group of the crystal. On the other hand, among the translations \mathbf{t} there is a subset forming an infinite group of ‘primitive’ translations \mathbf{T} generating the three-dimensional Bravais lattice of the crystal.

For a space group G , there is an infinite set of unequivalent irreducible representations. An introduction to their properties can be found in Chapter 1.2 as well as in a number of textbooks. They cannot be tabulated in a synthetic manner as the better-known representations of finite groups. They have to be constructed starting from simpler representations. Namely, each representation is labelled by a double index.

(i) The first index is a \mathbf{k} vector in reciprocal space, belonging to the first Brillouin zone of this space. The former vector defines a subgroup $G(\mathbf{k})$ of G . This group is the set of elements $\{R|\mathbf{t}\}$ of G whose component R leaves \mathbf{k} unmoved, or transforms it into an ‘equivalent’ vector (*i.e.* differing from \mathbf{k} by a reciprocal-lattice vector). The group $G(\mathbf{k})$ has irreducible representations labelled $\tau_m(\mathbf{k})$ of dimension n_m which are defined in available tables.

(ii) A representation of G can be denoted $\Gamma_{\mathbf{k},m}$. It can be constructed according to systematic rules on the basis of the knowledge of $\tau_m(\mathbf{k})$. Its dimension is $n_m r$ where r is the number of vectors in the ‘star’ of \mathbf{k} . This star is the set of vectors, unequivalent to \mathbf{k} , having the same modulus as \mathbf{k} and obtained from \mathbf{k} by application of all the point-symmetry elements R of G .

3.1.2.5.2. The example of gadolinium molybdate, $Gd_2(MoO_4)_3$

Gadolinium molybdate (GMO) is a substance showing one complication with respect to the example in Section 3.1.2.2. Like the prototype example already studied, it possesses below its phase transition an electric dipole (and a spontaneous polarization) resulting from the displacement of ions. However, one does not observe the expected divergence of the associated susceptibility (Fig. 3.1.2.5).

3.1.2.5.2.1. Experimental identification of the order-parameter symmetry

The high-temperature space group G is known for GMO from X-ray diffraction experiments. It is the tetragonal space group $P4_21m$. The corresponding point group 4_2m has eight elements, represented in Fig. 3.1.2.9.

The \mathbf{k} vector labelling the irreducible representation associated with the order parameter can be directly deduced from a comparison of the diffraction spectra above and below T_c . We have seen that the difference of the two stable structures surrounding the transition is specified by the equilibrium density:

$$\rho(T, \mathbf{r}) - \rho(T_c, \mathbf{r}) = \sum \eta_{\mathbf{k},m} \varphi_{\mathbf{k},m}(\mathbf{r}). \quad (3.1.2.27)$$