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Seminar for the course: Symmetries in Physics

# LANDAU THEORY OF PHASE TRANSITIONS

from group-theoretical perspective

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## Abstract

The core idea of this seminar is to present the Landau phenomenological theory of continuous phase transitions from the group-theoretical point of view. We begin by a brief review of second-order phase transitions and introduce several important physical concepts that are relevant for further discussion. In the second part of the seminar we begin from an entirely different setting, namely with the basis of an underlying symmetry group of a system. We restrict our discussion to symmetries in crystals. In the last part we present an example in order to support the theory from more practical perspective.

Nevertheless, our intention is not to provide a comprehensive formulation of the theory, but rather an illustration of the importance of symmetry restrictions in many physical processes. Therefore it is assumed the reader is well familiar with basic concepts of group theory, accompanied with some essentials of solid state physics.

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## 1 Classification of phase transitions

Broadly speaking we may divide phase transition processes into two classes<sup>1</sup>: (i) *first order* phase transitions are discontinuous in the sense that during the transition process system is found in a mixed phase, meaning that only a part of the system has completed the transition from one phase to another at certain temperature. Meanwhile the system is either absorbing or relaxing heat (thus process is associated with some latent heat). A familiar example of a first order phase transition is water-vapor phase transition<sup>2</sup>. (ii) *Second order* or *continuous* phase transitions where the state of the system changes in a continuous manner throughout the transition (i.e. each point in phase space represents a unique state of the system), but the symmetry changes discontinuously<sup>3</sup>. Examples of continuous phase transitions are ferromagnetic (ferroelectric) transitions, and transitions to superconductor or superfluid. As we will explicitly emphasize later on, these transitions involve phases of different symmetry. For the sake of simplicity, we are focusing our discussion only to symmetry transitions in crystals.

## 2 Continuous phase transitions (revisited)

This section offers a quick rehearsal of continuous phase transitions, purposively to refresh our knowledge of the Landau theory from undergraduate course of statistical physics.

It is clear that transition between phases possessing different symmetries (e.g. distinct crystal modifications) cannot occur in a continuous manner. Our system will always be found in a state that reflects either one symmetry properties or another. In crystals, a transition between two different modifications can always take place after sudden rearrangement of its constituents, which would result in a discontinuous change of the state. Nonetheless there exist another type of transition affecting only the symmetry

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<sup>1</sup>There are several known phase transitions that certainly do not belong to these two classes, e.g. phase transitions of *infinite order*, which are continuous, however not related to any symmetry-breaking mechanism.

<sup>2</sup>We know the water does not immediately turn into vapor. At a boiling point we are facing a mixture (coexistence) of both phases involved. Liquid phase does not vanish until we provide sufficient amount of energy (heat).

<sup>3</sup>Note that symmetry of the system can be affected by some infinitesimal transformations (distortion).

properties. Note that in such case there is no discontinuous change in the state of the system, i.e. positions of atoms are changing continuously, but there is a discontinuity in the symmetry at transition point <sup>4</sup>!

At *transition point* (also referred to as *critical point*) the state of two phases is the same, therefore symmetry elements of the system must be included in symmetry groups of both phases<sup>5</sup>. Moreover, as we will demonstrate later on, the symmetry of one of the phases has to be exactly the symmetry of the transition point itself. Since the symmetry of one phase is higher than that of the other, we will speak of *high-symmetry* and *low-symmetry* phases. In most cases the more symmetric phase corresponds to higher temperatures with respect to critical temperature ( $T \geq T_c$ ) and less symmetric to lower temperatures ( $T < T_c$ ), hence we will always assume this kind of situation.

At this point it is convenient to introduce a quantity called *order parameter* (abbrev. OP). In particular, we are interested in a quantity that takes a non-zero value below the critical point and **exactly** vanishes at the critical point, in the high-symmetry phase. Emphasizing once more, the symmetry is raised when order parameter becomes **identically** equal to zero – any finite (although small) value will reduce the symmetry of the high-symmetry phase to some lower symmetry.

As we have already mentioned, microstates of the system in question varies continuously through transition point. This implies that all thermodynamic functions of state will behave in such manner (e.g. energy, entropy, volume, etc.). Consequently, the process lacks any latent heat.

Let us now turn to the description of the equilibrium. The condition for thermodynamic equilibrium <sup>6</sup> is always associated with a minimization of a certain thermodynamic potential  $\Phi$ , e.g. Helmholtz free energy  $F = U - TS$  for systems at fixed temperature and volume. Without explicitly connecting order parameter to some physical quantity we may in general define our relevant potential as a function of pressure, temperature and order parameter  $\eta$ ,  $\Phi = \Phi(p, T, \eta)$ . First two arguments can be chosen arbitrary, while  $\eta$  is determined from the condition of equilibrium.

In the neighbourhood of transition point one can expand potential in powers of (some small) order parameter,

$$\Phi(p, T, \eta) = \Phi_0 + a_1\eta + a_2\eta^2 + a_3\eta^3 + a_4\eta^4 + \dots, \quad (1)$$

by omitting dependence of expansion coefficients on pressure and temperature,  $a_i = a_i(p, T)$ .  $\Phi_0$  will denote equilibrium value of thermodynamic potential taken at the critical temperature. Question arises whether we can say anything about above coefficients?

Including the first-order term  $a_1(p, T)\eta$  would imply a non-zero order parameter  $\eta \neq 0$  for an arbitrary temperature, which contradicts with the assumption (or better to say the definition) of order parameter to exactly vanish at  $T \geq T_c$ . Therefore,  $a_1 \equiv 0$ . Furthermore,  $a_2(p, T)$  is also easily seen to disappear at transition point,  $a_2(p, T_c) = 0$ . In the high-symmetry phase  $\eta = 0$  and hence only  $a_2 > 0$  provides us with a minimum of  $\Phi$ . On the other hand, for  $\eta \neq 0$  in low-symmetry phase we need to account  $a_2 < 0$ . These two arguments tell us  $a_2(p, T_c) = 0$  at the transition temperature  $T_c$ . As a consequence of the later statements we have to exclude third-order term as it would make critical point to become unstable,  $a_3(T_c) = 0$ . Finally, the fourth-order term is positive,  $a_4 > 0$ , in order to guarantee a proper global minimum. Clearly  $a_4 > 0$  also in vicinity of critical point, what about  $a_3$ ? One possibility is that  $a_3(p, T) \equiv 0$  due to the symmetry of a system under consideration. Transition point is then determined solely by the condition  $a_2(p, T) = 0$  which yields to a critical line  $T = T(p)$  in P-T phase diagram.

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<sup>4</sup>It should be stressed here that transition of the second kind is somewhat broader concept and thus does not necessary refer to a change in the lattice symmetry, as in our case. For example, ferromagnetic transition that occur at Curie points are associated with an emergence of spontaneous magnetization which breaks the so-called time-reversal symmetry (reversal of directions of electric currents).

<sup>5</sup>It is perhaps interesting to mention that in the case of first order phase transitions there is no such connection between the symmetries of the two phases.

<sup>6</sup>Essentially the system should display thermal equilibrium, as well as chemical and mechanical equilibriums. There should flow (on average) no currents at all!

On the contrary, provided  $a_3$  is not identically zero, we have transition *isolated points*, specified by the conditions  $a_2(p, T) = a_3(p, T) = 0$ .

Assuming  $a_3 \equiv 0$  and in addition that  $a_2(p, T)$  can be expanded to lowest order in transition parameter  $\Delta T = T - T_c$ ,  $a_2(p, T) = \tilde{a}(p)(T - T_c)$ , we may write

$$\Phi(p, T) = \Phi_0(p, T) + \tilde{a}(p)(\Delta T)\eta^2 + a_4(p)\eta^4. \quad (2)$$

By requiring  $\partial\Phi/\partial\eta = 0$  we obtain a non-trivial solution for  $a_2 < 0$ ,

$$\eta^2 = -a_2/(2a_4) = \tilde{a}(T_c - T)/(2a_4). \quad (3)$$

Let us check the consistency with the definition of continuous phase transition, namely, verifying if state variables which come from potential [Eq. (2)] are truly continuous functions of the critical parameter. For entropy, defined as  $S = -\partial\Phi/\partial T = S_0 - (\partial a_2(p, T)/\partial T)\eta^2$ , we get  $S = S_0 + (\tilde{a}^2/2a_4)(T - T_c)$  as we should. Higher-order derivatives of thermodynamic potential however display a discontinuity at transition point – specific heat,  $C_p = T(\partial S/\partial T)_p$ , takes value of  $C_p^0 \neq C_p^0(T)$  in high-symmetry phase ( $T \geq T_c$ ) and  $C_p = C_p^0 + (\tilde{a}^2/2a_4)T_c$  in low-symmetry phase. We thus obtain a positive contribution to specific heat at phase line crossing.

At last we briefly discuss the effect of an application of an external field. Generally speaking this would bring additional term of the form  $H_h = -\eta hV$  into Hamiltonian ( $h$  denotes field strength parameter that couples to our order parameter). Thermodynamic potential should now be equipped with extra degree of freedom, inducing a non-zero equilibrium value of order parameter  $\bar{\eta}$ , determined by  $V\bar{\eta} = -\partial\Phi(p, T, h)/\partial h$ . Accordingly we modify expanded potential [Eq. (2)] as

$$\Phi(p, T, \eta) = \Phi_0(p, T) + \tilde{a}[T - T_c(p)]\eta^2 + a_4\eta^4 - \eta hV. \quad (4)$$

It is not hard to realize that the presence of any (however weak) field forces the OP to become non-zero at any temperature and thus unconditionally breaks initial symmetry. There is no phase change in such case and previous discontinuity at transition point (in the absence of external field, of course) smooths out.

### 3 Group-theoretical approach

In the previous chapter we somehow postulated the existence of an order parameter and formulated an expansion of the thermodynamic potential resting on some symmetry properties of equilibrium state. Nevertheless, such approach is incapable of predicting whether phase transition can actually occur under given circumstances, and on the other hand the origin of order parameter remains a mystery as well. This motivates us to begin with more concise treatment.

We will limit our discussion to phase transitions related to the change of symmetry in the structure of the lattice. Positions of atoms will be described in terms of the *density function*  $\rho(x, y, z)$ , specifying their probability distribution. Symmetry of a crystal (precisely its space symmetry group) is defined by a set of operations under which  $\rho$  remains invariant. Let  $\mathbf{G}_0$  denote the full symmetry group of the crystal at the transition point. Density function  $\rho(x, y, z)$  can be always represented in terms of basis functions  $f_i$ , constituting an invariant space under operations of group  $\mathbf{G}_0$ <sup>7</sup>,

$$\rho = \sum_i \eta_i f_i. \quad (5)$$

In general the representation in [Eq. (5)] is reducible. By choosing an appropriate linear combinations of functions  $f_i$ , we can construct invariant spaces which are themselves irreducible. The density  $\rho$  is thus

<sup>7</sup>Total number of such functions strongly depends on symmetry of  $\rho$ . Beside that, their choice is not unique. For us it is only important that they sufficiently describe  $\rho$  and transform among themselves under the group  $\mathbf{G}_0$ .

expressed as a sum over all irreducible representations (abbrev. IR),

$$\rho = \sum_n \sum_i \eta_i^{(n)} \phi_i^{(n)}. \quad (6)$$

The reader might be unsatisfied by the choice of symbol  $\eta$  we were using in the previous chapter as a notation for order parameter. Our choice was done deliberately and is indeed completely adequate as will be justified afterwards.

It is important to point out that among basis functions  $\phi_i^{(n)}$  of  $n$ -th IR there is always one which is invariant under all transformations of the group  $\mathbf{G}_0$ , the one spanning an one-dimensional unit (irreducible) representation, since we have defined  $\mathbf{G}_0$  to be the total symmetry group of density function at transition point. We will denote it as  $\rho_0$  and decompose the total density as  $\rho = \rho_0 + \delta\rho$ . The remaining part (the deviation) of the density  $\delta\rho$ , can be viewed as a component of a lower symmetry. <sup>8</sup> Formally it can be written in exactly the same way as  $\rho$ ,

$$\delta\rho = \sum'_n \sum_i \eta_i^{(n)} \phi_i^{(n)}, \quad (7)$$

except that we are now summing over all IR excluding unit representation.

Once realizing that  $\rho_0$  is the part of  $\rho$  that is not relevant for the symmetry-breaking process since it is included in both phases, we subtract it from the density function of the crystal. We want to deal only with the quantity that contributes to the change of symmetry at the transition point, being the reason why it is appropriate to work with density increment  $\delta\rho$ . Beside that,  $\delta\rho$  can be considered as a small quantity and can thus serve as a variational object.

The reason for the splitting becomes quite obvious as we know that one of the phases (referred to as high-symmetry phase) possesses exactly the symmetry of the transition point. By subtracting the totally-symmetric part  $\rho_0$  we essentially ensure that the coefficients of IR  $\eta_i^{(n)}$  are all zero. The connection of the order parameter with coefficients of IR becomes thus more apparent.

It is worth giving a remark related to reducibility of the density function [Eq. (6)]. We must demand so called *physical reducibility* of the function  $\rho$ , meaning that the basis functions have to be real quantities along with the corresponding expansion coefficients <sup>9</sup>.

Upon varying external conditions, density  $\rho$  changes its form as coefficients depend on the temperature and the pressure,  $\eta_i^{(n)} = \eta_i^{(n)}(p, T)$ . Their values are conditioned by the thermodynamic equilibrium, i.e. by requesting that potential  $\Phi(p, T, \rho)$  reaches the minimum. This must hold on both sides of the transition point, thereby determines the symmetry of low-symmetry phase  $\mathbf{G}$  (the symmetry of part  $\delta\rho$ ). By construction, if system is to have the symmetry  $\mathbf{G}_0$  at the transition point, all the coefficients  $\eta_i^{(n)}$  in [Eq. (6)] are exactly zero there. Since the density function changes in a continuous manner, these coefficients must disappear continuously and thermodynamic potential  $\Phi(p, T, \rho)$  can be expanded in a Taylor series about critical point. In fact it suffices to expand only the density increment  $\delta\rho$ ; any transformation of coordinate system must leave functional  $\Phi(\rho_0 + \delta\rho)$  unchanged, therefore by choosing one of the elements of  $\mathbf{G}_0$  (under which  $\rho_0$  is invariant), we get  $\Phi(\rho_0 + \delta\rho) = \Phi(\rho_0 + \delta\rho')$ , which implies only variation with respect to the increment  $\delta\rho$  has to be considered for fixed  $\rho_0$ .

The next step is to determine the explicit form of the expansion. We will keep our basis functions fixed and rather transform associated coefficients (coordinates in function space). This is particularly convenient as magnitude factors and symmetry properties of functions are absorbed into the corresponding coefficients, thereby inducing a “small” symmetry-breaking increment  $\delta\rho$  which allows us to expand potential  $\Phi$  about the critical point.

<sup>8</sup>In comparison to component  $\rho_0$ , of course. However  $\delta\rho$  can still be found invariant under certain subgroup of  $\mathbf{G}_0$ . The symmetry group of  $\delta\rho$  will be denoted by  $\mathbf{G}$ .

<sup>9</sup>This is important since some representations can be reducible if we allow linear combinations with c-number coefficients – these are not of our interest as we demand physical, i.e. real-weighted, combinations.

### 3.1 Invariant polynomials

Function space  $\{\phi_i^{(n)}\}$  we are considering can be extended to a vector space of homogeneous polynomials of a degree  $p$ . All functions in such space can be represented by a linear combination of  $p$ -degree monomials. A polynomial of a degree  $p$  is always transformed into the polynomial of the same degree since group elements act linearly on coefficients  $\eta_j$ . The space of  $p$ -dimensional polynomials spans a representation of  $\mathbf{G}_0$  which is in general reducible. The reduction in principle contains several invariant subspaces, spanned by polynomials of degree  $p$ , one or several of them carrying the unit representation of  $\mathbf{G}_0$ . We call them *invariant polynomials* (with respect to the group  $\mathbf{G}_0$ ).

An example: Polynomial space spanned by functions  $\{x, y\}$  is irreducible under group of equilateral triangle  $C_3$ . Space of second-degree polynomials  $\{x^2, xy, y^2\}$  is on the contrary reducible –  $(x^2 + y^2)$  is the totally-symmetric function, i.e. function invariant under all symmetry operations of  $C_3$ .

### 3.2 Expansion of the thermodynamic potential about critical point

As we have stated above, we require from functional  $\Phi$  to be invariant under **all** transformations of group  $\mathbf{G}_0$ . Consequently the expansion can contain only invariant linear combinations of appropriate powers of scalar quantities  $\eta_i^{(n)}$ . Note that invariance must hold separately for each term in expansion, which is due to linearity of transformations on the space of OP components  $\eta_i^{(n)}$ . Accordingly, up to the leading term in  $\eta_i^{(n)}$ , expansion should be of the form

$$\Phi = \Phi_0 + \sum'_n A^{(n)}(p, T) \sum_i [\eta_i^{(n)}]^2 + \dots \quad (8)$$

There are no linear terms – clearly it is not possible to construct linear invariants from functions that transform according to non-unit physically IR of  $\mathbf{G}_0$ , otherwise it would contain also unit representation and become immediately reducible. Hence higher-order invariants have to be incorporated. The above included second-order invariant is unique, i.e. there is only one polynomial of second degree that is totally symmetric.

We continue with the treatment of functions (coefficients)  $A^{(n)}(p, T)$ .  $\Phi$  can have a minimum at critical point (when all  $\eta_i^{(n)}$  are zero) only if  $A^{(n)} \geq 0$ . However not all of them could be positive at the transition point – this would mean they would stay positive also beyond critical point and all  $\eta_i^{(n)}$  would have to be zero. Such situation contradicts with emergence of symmetry-breaking at the critical point, hence at least one of  $A^{(n)}$  must necessary vanish!<sup>10</sup> If we want the equilibrium to appear for some non-zero  $\eta_i^{(n)}$ , its function  $A^{(n)}$  must be negative [Fig. 1] in the low-symmetry phase (of corresponding symmetry  $\mathbf{G}$ ).

As we figured out, the symmetry of density increment in the low-symmetry phase is solely determined by basis functions of  $n$ -th IR,

$$\delta\rho = \sum_i \eta_i^{(n)} \phi_i^{(n)}. \quad (9)$$

Now index  $n$  can be omitted, and we can introduce new notation

$$\eta^2 = \sum_i [\eta_i^{(n)}]^2, \quad \eta_i = \eta \gamma_i, \quad (10)$$

where  $\gamma_i$  designates unit order-parameter (direction) vector and  $\eta$  its length.

Now we are ready to give a formal definition of **order parameter**: it is a set of scalar quantities  $\eta_i$ , marking an IR of the symmetry group  $\mathbf{G}_0$  at the transition point  $(p_c, T_c)$  associated with the coefficient

<sup>10</sup>Excluding phase transitions at singular points, exactly one  $A^{(n)}$  is allowed to vanish!

$A = A(p, T)$  ( $T \geq T_c$ ) for which  $A(p_c, T_c) = 0$  in a Taylor expansion of the thermodynamic potential about the transition point.

Third-order invariants do not appear! As we have already pointed out in the opening section, this terms in the potential for the value  $\eta = 0$  at the transition point do not represent a stable equilibrium, but a saddle point instead. Of course, we would like to exclude these terms also for the symmetry reasons. Their absence can be attributed to inability of finding unit representation inside the cube of a given representation of  $\mathbf{G}_0$  (referred to as *Landau condition*). If order parameter correspond to one-dimensional non-totally-symmetric IR, Landau condition is always satisfied. Other cases should be treated separately. In general third-order invariants can exist, but it can be argued this cannot lead to a non-singular continuous transition.

Just presented arguments are not applicable to fourth-order invariants. Instead of [Eq. (8)] we may rewrite potential by attaching higher-order powers of  $\gamma_i$ ,

$$\Phi(p, T) = \Phi_0(p, T) + \eta^2 A(p, T) + \eta^4 \sum_{\beta} B_{\beta}(p, T) h_{\beta}^{(4)}(\gamma_i) + \dots, \quad (11)$$

where functions  $h_{\beta}^{(4)}$  label  $\beta$ -th invariant of order 4. In order to ensure the minimum of potential, the sum  $\sum_{\beta} B_{\beta} h_{\beta}^{(4)}$  has to be positive at the critical point in every direction of the OP components  $\gamma_i$ . Second-order term does not depend on the OP direction, thus all values of  $B_{\beta}(p_c, T_c)$  can be simply obtained from the condition for a minimum of the fourth-order term (this yields an equilibrium value of the order parameter  $\gamma_i^0$ ).<sup>11</sup> If we simply set  $B \equiv \sum_{\beta} B_{\beta}(p_c, T_c) h_{\beta}^{(4)} > 0$  and assume  $B = const.$  in the vicinity of phase transition, and expanding  $A$  to lowest order in temperature difference, we arrive at the familiar form [Eq. (2)].

Undoubtedly, the core question at this stage is to explain the symmetry properties of low-symmetry phase with respect to high-symmetry phase. Can breaking lead to an arbitrary symmetry, or are there any constraints on that? But before continuing we are owing to present several crucial concepts.

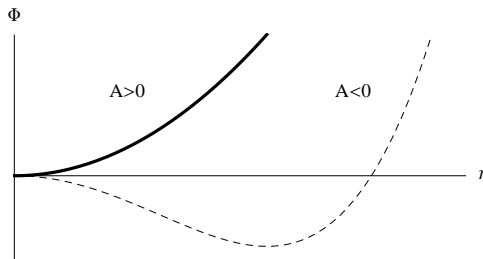


Figure 1: Schematic form of the thermodynamic potential  $\Phi[\rho(\eta)]$  as a function of second-order expansion coefficient  $A$  for the relevant IR. The value of order parameter for  $A > 0$  is identically zero, while for  $A < 0$  there is a minimum found at some non-zero value of  $\eta$ .

### 3.3 Irreducible representations of symmorphic groups

A cautious reader has probably noticed we have omitted one important physical property of crystals. Until now we have considered only point symmetries, but we are well aware that a particular crystal falls into one of numerous space groups which represent the actual symmetry of crystals, including translations. Therefore our basis functions of irreducible representations need to be equipped with

<sup>11</sup>A formalistic reader would probably object with such procedure, since it might happen the only fourth-order invariant is going to be  $\eta^4 = [\sum_i \eta_i^2]^2$ . This will unconditionally require higher (even) order terms.

another index  $\mathbf{k}$ , labeling IR of translation elements<sup>12</sup>. Due to the Bloch theorem, functions have to resemble the symmetry of a lattice and are thus of the form

$$\phi_{\alpha\mathbf{k}} = u_{\alpha\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (12)$$

Subscript  $\alpha$  is known as band index and distinguishes functions with the same wave vector  $\mathbf{k}$ . The latter is a continuous variable, but due to periodicity of Bravais lattice all wavevectors that differ by a reciprocal lattice vector are equivalent (hence only first Brillouin zone has to be considered). Bloch functions  $u_{\alpha\mathbf{k}}$  also reflect periodicity of the crystal lattice.

Under application of any *rotational element*  $R$ <sup>13</sup> Bloch wave  $\phi_{\alpha\mathbf{k}}$  transforms into linear combination of  $\phi_{\alpha\mathbf{k}'}$  ( $\mathbf{k}' = R\mathbf{k}$ ) with various  $\alpha$ . Here enters the notion of a *star* of the wave vector  $\mathbf{k}$  – the set of non-equivalent wave vectors  $\mathbf{k}$  that transform one into another under application of all ( $n$ ) rotational elements of the group [Fig. 2]. Star of an arbitrary  $\mathbf{k}$  in general case contains  $n$  vectors or *rays*, but for special values of  $\mathbf{k}$  there could be less than  $n$  rays<sup>14</sup>. Irreducible representations, spanned by basis functions  $\phi_{\alpha\mathbf{k}}$ , must include all rays of a star of a vector  $\mathbf{k}$ .

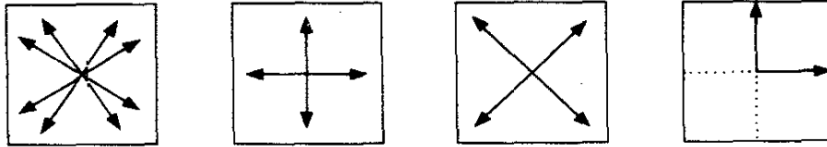


Figure 2: Some of representative stars of  $\mathbf{k}$  for a 2D square lattice with symmetry group  $C_{4v}$ , from left to right: general star, along  $x$ -axis, along square diagonal and Brillouin zone boundary at  $x$  (Image source: [3]).

Now, by forming a set of rotational elements within a given space group, which either do not affect wave vector  $\mathbf{k}$  either transform it into an equivalent wave vector, we define the *proper symmetry group* or *little group* of wave vector  $\mathbf{k}$ . This is a subgroup of the point symmetry group of  $\mathbf{k}$ , thus also one of the point symmetry groups. Furthermore, basis functions of IR can be slightly simplified if we restrict our discussion only to *symmorphic space groups* (i.e. groups without screw axes and glide planes), namely

$$\phi_{\alpha\mathbf{k}} = u_{\alpha}\psi_{\mathbf{k}}. \quad (13)$$

It is easy to understand why basis functions [Eq. (13)] factorize in such case. In non-symmorphic groups, rotational elements are connected with translational ones since, for example, a repeated application of a glide plane yields a translation for a lattice vector. For symmorphic space groups these elements are always separated, i.e. point operations represent a subgroup of a space group. Functions  $\psi_{\mathbf{k}}$  are here appropriate linear combinations of plane waves  $e^{i\mathbf{k}\cdot\mathbf{r}}$ , invariant under rotational elements of the little group of  $\mathbf{k}$ , and functions  $u_{\alpha}$  are  $\mathbf{k}$ -independent, hence translationally invariant functions. Wave vectors  $\mathbf{k}$  in [Eq. (13)] are thus taken from the star of  $\mathbf{k}$ . Translations for vector the  $\mathbf{a}$  bring into  $\phi_{\alpha\mathbf{k}}$  a factor of  $e^{i\mathbf{k}\cdot\mathbf{a}}$  (which are IR of the translational group) and leave  $u_{\alpha}$  unchanged, while point operations pertaining to the little group of  $\mathbf{k}$  leave  $\psi_{\mathbf{k}}$  unaffected and only transform  $u_{\alpha}$  among themselves ( $u_{\alpha}$  form irreducible representations of point groups, also referred to as *small representations*).<sup>15</sup> Of course, for a certain  $\mathbf{k}$  there exist in general also point operations that are not members of the little group of

<sup>12</sup>Plane waves  $e^{i\mathbf{k}\cdot\mathbf{r}}$  are one-dimensional IR of a translation operator.

<sup>13</sup>Under rotational elements we account rotations and reflections.

<sup>14</sup>This clearly happens if  $\mathbf{k}$  remains unaffected under application of symmetry transformation (e.g. if it coincides with a symmetry axis) or if it is transformed into an equivalent wave vector.

<sup>15</sup>Although this may not seem too important at first look, it severely simplifies further treatment, as we can construct IR of symmorphic groups by only classifying proper symmetry groups and already known IR of crystallographic point groups.



$\mathbf{k}$ . These will simply transform functions [Eq. (13)] with non-equivalent wave vectors into combinations of one another, forming a star having less than  $n$  rays. Eventually we can conclude the dimension of an IR of a given space group is the product of the number of rays in the star of  $\mathbf{k}$  and dimensionality of the small representation. For more detailed explanation see e.g. Ref. [3].

### 3.4 In search of properties of low-symmetry phase

The analysis is pretty straightforward if we can afford to neglect the translational symmetries. The symmetry of density increment is determined solely by the equilibrium value of OP, implying the low-symmetry phase comprises symmetries of the group  $\mathbf{G}$ ,

$$\delta\rho = \eta \sum_i \gamma_i \phi_i. \quad (14)$$

Unfortunately treatment of full space crystallographic groups raises some difficulties. Pure group-theoretical derivation of possible low-symmetry phases is out of scope of this seminar, therefore we will be satisfied with an explanation associated with the original derivation of Lifshitz, which is based on a free energy density for modulated order parameter that gives birth to so called *Lifshitz criterion*. Simply stated, Lifshitz criterion expresses the absence of linear terms in the  $\mathbf{q}$ -expansion of coefficients  $A(\mathbf{k}_0 + \mathbf{q})$  in the vicinity of  $\mathbf{k}_0$ . As we will see, Lifshitz criterion is only satisfied for specific wave vectors  $\mathbf{k}_0$ , precisely for those pertaining to certain high-symmetry points in Brillouin zone.

By accounting translational symmetries in the expression [Eq. (11)], the sum is actually replaced by the integral over all distinct star vectors  $\mathbf{k}^*$  over Brillouin zone, where the coefficients  $A^{(n)}$  now carry an explicit dependence on the wave vector  $\mathbf{k}$ . Phase transition point has still to be associated with some vanishing coefficient  $A^{(n)}(\mathbf{k}_0)$ ; this essentially means that the potential should have a minimum for  $\mathbf{k} = \mathbf{k}_0$  (and consequently for the star  $\mathbf{k}_0^*$ ). Clearly the expansion about  $\mathbf{k}_0$  should contain no linear term  $\mathbf{q} = (\mathbf{k} - \mathbf{k}_0)$ , as otherwise some of  $A^{(n)}(\mathbf{k})$  would vanish before  $A^{(n)}(\mathbf{k}_0)$  and thus the latter would not belong to the transition point [Fig. 3]. Wave vector  $\mathbf{k}_0$  defines the translational symmetry of functions  $\phi_i$  in [Eq. (14)] and determines the periodicity of the low-symmetry phase.

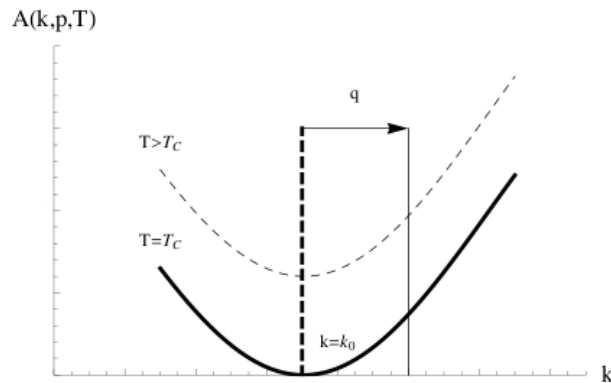


Figure 3: Vanishing of the second-order expansion coefficient  $A(\mathbf{k}_0; p, T)$  for a symmetry determined wave vector  $\mathbf{k}_0$ . According to the Lifshitz condition, there must be no linear term in  $\mathbf{q}$ -expansion around  $\mathbf{k}_0$  in order to have an extremum of the thermodynamic potential.

The crystal at  $\mathbf{k} = \mathbf{k}_0$  must obviously be a stable structure. Knowing this, let us take a look at what happens with the system for small deviations  $\Delta$  about the equilibrium value  $\mathbf{k}_0$ , namely for some  $\mathbf{k} = \mathbf{k}_0 + \Delta$ . Such perturbation can be understood as a slight modulation of a lattice periodicity (over

distances very large compared to cell size), i.e. we are facing the loss of a macroscopical homogeneity that can be attributed to a spatially non-homogeneous order parameter;  $\eta_i$ 's can be thus viewed as weakly varying functions of spatial coordinates. For this purpose, our thermodynamic potential (near the critical point) has to be expressed not only in terms of OP components  $\eta_i$ , but also of respective derivatives (or gradients)  $\nabla\eta_i$ . Note however, there should be no linear terms in gradients if we require the thermodynamic potential  $\Phi$  to have a minimum at the critical point for some constant OP components  $\eta_i$ .

Terms in the expansion of the the potential that contain only OP components will of course remain the same as before. The allowed spatial variation will thus contribute only (now we are dropping subscript index referring to a relevant IR)

$$\Phi_{\text{inhom}} = \sum_{ij} Q_{ij} \left( \frac{\partial\eta_i}{\partial x_j} \right) + \sum_{ijk} W_{ijk} \eta_i \left( \frac{\partial\eta_j}{\partial x_k} \right) + \sum_{ijkl} Y_{ijkl} \left( \frac{\partial\eta_i}{\partial x_j} \right) \left( \frac{\eta_k}{\partial x_l} \right), \quad (15)$$

considering an expansion up to the second-order in terms involving derivatives of order parameter. This is again justified by the fact that OP components are slowly varying quantities.

It is not too difficult to figure out that up to the second-order only antisymmetric terms of the form <sup>16</sup>

$$\eta_i \left( \frac{\partial\eta_j}{\partial x} \right) - \eta_j \left( \frac{\partial\eta_i}{\partial x} \right), \quad (16)$$

are present in the thermodynamic potential expansion. All the terms containing only the derivatives of  $\eta_i$  are irrelevant as they give a constant contribution to the potential (they are called surface terms). For the same reason the symmetric terms of the form  $\eta_i(\partial\eta_j/\partial x) + \eta_j(\partial\eta_i/\partial x) = \partial(\eta_i\eta_j)/\partial x$  can be dropped out as well. Remember that the potential should still contain only invariant (w.r.t. group  $\mathbf{G}_0$ ) combination of quantities [Eq. (16)]. Quadratic terms in OP derivatives are not important for the discussion as they are present for any OP symmetry.

The crucial observation is that if invariants of the form [Eq. (16)] do exist, the crystal is **stable** against spatial perturbation and  $\mathbf{k}_0$  would not be a stable point surrounded by unstable points as we have assumed. This imposes a criterion on  $\mathbf{k}_0$ 's for which phase transition can occur.

Essentially the discussion should be now turned into analysis of transformation properties of quantities [Eq. (16)]. Spatial coordinates transform as the components of a vector <sup>17</sup>. Note however that derivatives with respect to coordinates transform in the same way as corresponding basis vectors (for proof see e.g. Ref. [3], p. 81), thus the quantities  $(\partial\eta/\partial x)$  transform as the products of the relevant OP representation alpha and the representation of a vector component. Consequently, quantities [Eq. (16)] transform as the tensor product of antisymmetrized square representation of OP components  $\eta_i$  and vector representation (spanned by coordinates  $x_j$ ). If this product representation contains a totally-symmetric representation of  $\mathbf{G}_0$ , Lifshitz invariants will necessary exist. This in fact means that the reduction of antisymmetric product of OP representation should not contain any IR that transforming according to the representation of  $\mathbf{G}_0$  under which vectors transform.

This conclusion yields to the requirement that there should exist no combinations of antisymmetrized products of the form

$$\chi_{ij} = \phi_i(\mathbf{r})\phi_j(\mathbf{r}') - \phi_j(\mathbf{r})\phi_i(\mathbf{r}'), \quad (17)$$

that transform as the components of a vector, or explicitly in our case,

$$\chi_{\alpha\mathbf{k},\beta\mathbf{k}'} = \phi_{\alpha\mathbf{k}}(\mathbf{r})\phi_{\beta\mathbf{k}'}(\mathbf{r}') - \phi_{\alpha\mathbf{k}}(\mathbf{r}')\phi_{\beta\mathbf{k}}(\mathbf{r}), \quad (18)$$

where  $\mathbf{k}$  and  $\mathbf{k}'$  belong to the same star.

<sup>16</sup>For the sake of brevity we are explicitly stating only terms containing the derivatives in  $x$ -direction.

<sup>17</sup>Position vector  $\mathbf{r}$  lives in a 3D vector representation. As we know this representation is reducible under certain point groups, e.g.  $C_3$  symmetry where direction along coordinate  $z$  spans an IR subspace.

For some general wave vector  $\mathbf{k}$  (with no proper symmetry) we have  $n$  (that is the order of point group) rays in the corresponding star, which gives us  $n$  basis functions  $\phi_{\mathbf{k}}$ . Wave vectors of the star come in pairs  $\{\mathbf{k}, -\mathbf{k}\}$ . One can easily check that  $n$  functions (omitting label  $\alpha$  since there is only one)

$$\chi_{\mathbf{k}, -\mathbf{k}} = \phi_{\mathbf{k}}(\mathbf{r})\phi_{-\mathbf{k}}(\mathbf{r}') - \phi_{\mathbf{k}}(\mathbf{r}')\phi_{-\mathbf{k}}(\mathbf{r}) \quad (19)$$

are transformed among themselves under rotational symmetry elements and therefore constitute the representation of the corresponding point group of a crystal class (with the dimension of its order). They are in addition invariant under translations. This representation is known as *regular representation*<sup>18</sup> and consequently includes all IR of the point group, also those which transform as components of a vector – hence Lifshitz criterion is not fulfilled in this case<sup>19</sup>.

Essentially among an infinite number of IR of a group  $\mathbf{G}$  only those containing a **central point** of a vector  $\mathbf{k}$  are suitable for a phase transition of the second kind. Groups with central points contain axes that intersect one another or intersect symmetry planes. This of course puts a severe restriction on our little symmetry group of wave vector  $\mathbf{k}$ . Evidently, if group of wave vector includes inversion, which takes  $\mathbf{k}$  into an equivalent vector  $-\mathbf{k}$ , there is only one  $\phi_{\mathbf{k}}$  belonging to each  $\mathbf{k}$  of the star. Hence in such case no invariants  $\chi_{\mathbf{k}\mathbf{k}'}$  with respect to translations can be constructed. Lifshitz condition is thus satisfied!

Now is perhaps a good time to put forward the following theorem: a continuous phase transition **may** occur when there is a change in the structure of the system that halves the number of symmetry elements, either by doubling the size of the unit cell for a certain crystal class [Fig. 4] or changing the crystal symmetry by halving the number of rotational elements. However, as we shall see later, there are other possibilities as well.

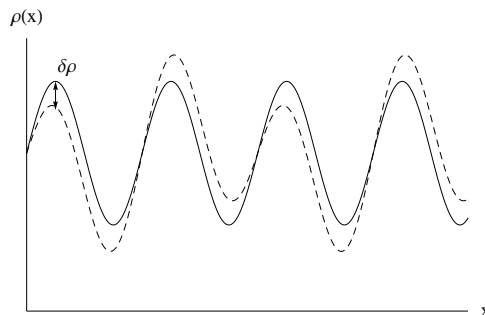


Figure 4: Change of periodicity of the lattice (e.g. period doubling) by adding a small density increment  $\delta\rho$ .

Finally we have to apologize to the reader who might be interested in the rigorous derivation. For more formal and concise derivation see Ref. [2]. Anyhow, we have tried to capture the idea of essential part of derivation in the appendix A.

## 4 Order-disorder phase transition

Our task will be to classify all possible *types of ordering* (called *superlattices*) in a lattice after occurrence of a phase transition of the second kind.

<sup>18</sup>This follows from the fact that every basis vector  $\chi_{\mathbf{k}, -\mathbf{k}}$  of the star transforms into another (single) basis vector.

<sup>19</sup>Similarly holds for  $\chi_{\alpha\mathbf{k}, \beta\mathbf{k}'}$ .

At this stage it should be emphasized that we are investigating so called *order-disorder* phase transitions. *Ordered crystals* correspond to the situation when the number of lattice sites that atoms of a given kind can occupy equals to the number of such atoms. At zero temperature every crystal is *completely ordered*, which means that the probability of finding an atom in the neighbourhood of a certain lattice point equals unity. As the temperature increases there is a finite probability of finding atoms also on *other* places. In many situations the *original* sites and the *other* sites are geometrically equivalent, and as soon as the probability of finding atoms of a given kind on other places becomes equal to the probability of finding them on original positions, the symmetry of ordered phase increases and crystal is said to be *disordered*. An illustrative example of such phase transition is a CuZn alloy [Fig. 5].

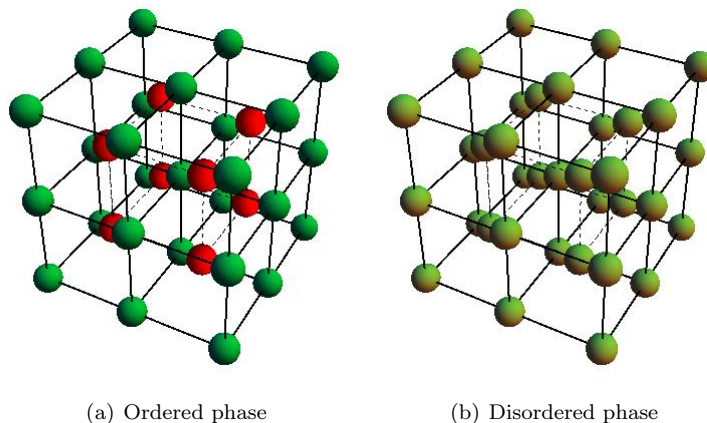


Figure 5: Order-disorder continuous phase transition in a CuZn alloy. In ordered phase Zn atoms (green) constitute simple cubic lattice with Cu atoms (red) in the middle. Disordered phase appears when the probability of finding either kind of atoms on original lattice sites becomes equal (atoms thus form body-centered cubic lattice).

At the phase transition point there is equal probability of finding either kind of atoms on body-centered cubic lattices sites. A suitable choice of order parameter would be given in terms of probabilities of finding atoms at the particular lattice point,

$$\eta = \frac{w_{\text{Cu}} - w_{\text{Zn}}}{w_{\text{Cu}} + w_{\text{Zn}}}. \quad (20)$$

#### 4.1 Practical example: superlattices of a BCC lattice

As an example we will take a (unit) body-centered cubic lattice. The corresponding reciprocal lattice is FCC (face-centered cubic) with edge length of  $4\pi$ , measured in the units of BCC edge length.

Let us write down all possible non-equivalent wave vectors  $\mathbf{k}$  (along with their star) with a central point and subsequently little symmetry groups they correspond to:

1.  $(0, 0, 0)$ , with symmetry of octahedron point group  $O_h$
2.  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , with symmetry of octahedron point group  $O_h$
3.  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  and  $(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$ , with symmetry of tetrahedron point group  $T_d$
4.  $(0, \frac{1}{4}, \frac{1}{4})$ ,  $(\frac{1}{4}, 0, \frac{1}{4})$ ,  $(\frac{1}{4}, \frac{1}{4}, 0)$ ,  $(0, \frac{1}{4}, -\frac{1}{4})$ ,  $(-\frac{1}{4}, 0, \frac{1}{4})$  and  $(\frac{1}{4}, -\frac{1}{4}, 0)$ , with symmetry of dihedral point group  $D_{2h}$

As we can see, these special points appear to be simple fractions of lattice vectors yielding the change of translational symmetry (Bravais lattice) in phase transition process. In most of the cases the crystal experiences a doubling of lattice vectors, but for some higher symmetric lattice one could in principle find also tripling or quadrupling of lattice vectors. Such modifications attribute to increase of the volume of unit cells for appropriate (small) integer factors.

Moreover, there will be another handy simplification concerning small representations. Not all of them need to be accounted since we are interested only in transition involving a formation of superlattices. Remember that the change of symmetry in crystal is not due to change in relative displacements (which in principle can also happen, but we are not treating such cases), but due to the change of ordering in crystal. Atoms thus remain on the existing sites, and since the number of atoms within a unit cell remains the same, the only possibility is that some lattice points become non-equivalent. Accordingly, the density increment  $\delta\rho$  has to stay invariant under group of wave vector  $\mathbf{k}$  and small representations formed by basis functions [Eq. (13)]  $u_\alpha$  can be simply substituted by totally-symmetric (unit) representation.

Let us now concentrate on all above enumerated cases. Function with  $\mathbf{k} = 0$  is totally translational invariant and therefore cannot contribute to the change of symmetry. Phase transition in this case is only possible if there is a change in a crystal class without affecting Bravais lattice.

For the wave vector  $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  we find the basis function

$$\phi_0 = \cos(2\pi x) \cos(2\pi y) \cos(2\pi z). \quad (21)$$

Here we have constructed an appropriate linear combination of  $\exp(2\pi i(x + y + z))$  and functions obtained from it under application of rotational symmetry operations, which are invariant under the group  $O_h$ . The corresponding density increment  $\delta\rho = \eta\phi_0$  is in addition invariant under translations along individual edges of a cubic lattice, however not under translation along half of diagonal  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . The resulting low-symmetry (ordered) phase is thus found to be a simple cubic Bravais lattice with a non-equivalent point, pertaining to a different atom, in the center of the cube (as in already mentioned CuZn alloy). Before continuing it is wise to remark that [Eq. (21)] does not represent an actual change of density function in a crystal but merely its symmetry property!

Functions belonging to wave vectors with the symmetry  $T_d$  are similarly found to be

$$\phi_1 = \cos(\pi x) \cos(\pi y) \cos(\pi z), \quad \phi_2 = \sin(\pi x) \sin(\pi y) \sin(\pi z). \quad (22)$$

These two can be combined into two different fourth-order invariants, namely  $(\phi_1^2 + \phi_2^2)^2$  and  $(\phi_1^4 + \phi_2^4)$ . Since the second-order invariant is unique, this yields to the thermodynamic potential of the following form:

$$\Phi = \Phi_0 + A\eta^2 + B_1\eta^4 + B_2\eta^4(\gamma_1^4 + \gamma_2^4), \quad \gamma_1^2 + \gamma_2^2 = 1. \quad (23)$$

For the time being let's assume  $B_2 < 0$ ; Minimum of  $\Phi$  is then located for  $(\gamma_1, \gamma_2) = (1, 0)$  (or equiv.  $(0, 1)$ ) and  $\delta\rho = \eta\phi_1$  displays symmetry  $O_h$  of a FCC lattice containing 16 atoms. Edge length of the new cubic lattice is twice the length of the original one (thus volume has been increased by a factor of 8). The new unit cell contains 4 atoms. By putting equal atoms on the equivalent sites we identify the superlattice as ternary alloy  $ABC_2$  (or  $AB_3$  if B and C are equal atoms). On the other hand, for  $B_2 > 0$  we find equilibrium value of  $\Phi$  at  $\gamma_1 = \gamma_2 = \frac{1}{2}$  which gives  $\delta\rho = \eta(\phi_1 \pm \phi_2)/\sqrt{2}$ . This density increment again belongs to the symmetry class  $O_h$  with a FCC Bravais lattice, but this time there are only two sets on non-equivalent points (binary alloy). Both configurations are shown on the figure [Fig. 6].

The last case (symmetry of  $D_{2h}$ ) corresponds to the following 6 basis functions,

$$\phi_{D1,D2} = \cos(\pi(x \pm y)), \quad \phi_{D3,D4} = \cos(\pi(x \pm z)), \quad \phi_{D5,D6} = \cos(\pi(y \pm z)). \quad (24)$$

Expansion of the thermodynamic potential  $\Phi$  to higher orders now become rather complicated. A careful analysis shows that there is one third-order invariant and four fourth-order invariants. Due to the presence of the former, a continuous phase transition cannot occur (except for the isolated points which have to be investigated separately). In the end of the day one can conclude there are three possible types of ordering that may appear from a BCC disordered phase.

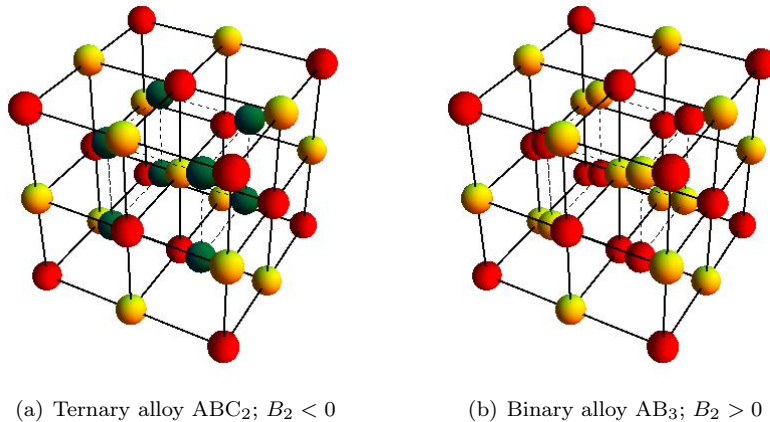


Figure 6: Two possible superlattices of a BCC lattice, corresponding to  $\mathbf{k}$  points with the tetrahedral symmetry. Edge length of an ordered phase is twice the length of an original (disordered) lattice.

## 5 Conclusions

In the present seminar we introduced the theory of continuous type phase transitions. In these transitions the order parameter changes continuously through the transition point when thermodynamic conditions are varied. When phase transition takes place, there is a (discontinuous) change in symmetry of the system. Our main goal was to explain the relation between symmetries of the high and the low temperature phases.

In the first part of the theoretical consideration we investigated the meaning of the order parameter in the sense of symmetry properties of the body and concluded that the components of the order parameter are essentially coefficients of an irreducible representation pertaining to the part of crystal density (referred to as density increment) which appears at phase transition point and lowers the symmetry of the crystal. Changes almost always correspond to single vanishing coefficient in the expansion of the relevant thermodynamic potential, e.g. free energy. Two different IR can vanish at the same temperature only by accident.

In the second part we presented the necessary condition for the stability of a homogeneous phase of crystals, pioneered by Lifshitz. This condition, which determines all possible orderings of a crystal after a transition of the second kind, is directly related to properties of IR of the underlying system. Since the symmetry of the crystal is one of the space groups, irreducible representations are labeled not only by a band index  $\alpha$  (belonging to IR of rotations and reflections) but also wave vector  $\mathbf{k}$ . A phase transition is always associated with an exact vanishing of a certain coefficient  $A^{(n)}(\mathbf{k}_0)$  in the second-order expansion of the thermodynamic potential. There must be no linear terms due to the definition of a minimum, however also particular terms involving linear terms of gradients must vanish, if we require a phase that is stable against losing macroscopical homogeneity. In turns that relevant invariants do not exist only when wave vector  $\mathbf{k}_0$  contains symmetry elements that intersect at single point (central point). This imposes a drastic restriction on possible orderings of a high-symmetry phase (as we demonstrated in our example in the last section on order-disordered transition of body-centered lattice). Translational symmetry (which is a subgroup of a translation group) of density increment is therefore determined by some high-symmetry point wave vector  $\mathbf{k}$ .

At last, let us mention that in reality it might happen  $A^{(n)}(\mathbf{k}_0)$  does not vanish by symmetry but equals zero for some other reasons. A transition of the second-order can still occur but the value of wave vector  $\mathbf{k}_0$  does not any more correspond to a special point in BZ. In such cases may result in

an incommensurate phase – a harmonic periodicity of the order parameter with a period not being a rational multiple of reciprocal lattice vectors.<sup>20</sup>

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## A Symmetry properties of second-order expansion term

Our aim here is to show how one can avoid resting on assumption of coordinate-dependent ordered parameter by investigating symmetry properties of a  $q$ -expansion of the coefficients in the second-order term of the thermodynamic potential expansion in amplitudes of OP (see Ref. [2], p. 112).

As a starting point we will take a relevant thermodynamic potential  $\Phi$ , which we may in general express a second-order expansion in density increment  $\delta\rho$  as follows:

$$\Phi = \Phi_0 + \int_{\text{BZ}} \left\{ \sum_i \left[ \alpha_i(\mathbf{k}, \rho_0(r), \phi_{j'\mathbf{k}'}(\mathbf{r})) \right] \left[ \sum_j \eta_j^2(\mathbf{k}, \tau_i) \right] \right\} d\mathbf{k} \quad (25)$$

There is a summation over all star vectors  $\mathbf{k}^*$  within the Brillouin zone and subsequent summation over small representations (index  $i$ ). One should always bear in mind an explicit dependence of functionals (coefficients)  $\alpha_i = \alpha_i(p, T)$  (standing in front of a quadratic polynomial OP invariant) on pressure and temperature, which we are omitting for the sake of simplicity. In the expression [Eq. (25)],  $\tau_i$  denotes  $i$ -th point operation of the little group of a wave vector  $\mathbf{k}$ ,  $\phi_{j,\mathbf{k}}(\mathbf{r})$  are functions carrying  $n$ -dimensional IR of the underlying space group  $\mathbf{G}_0$ . Stability against spatial perturbation is investigated in terms of the  $\mathbf{q}$ -expansion about a particular  $\alpha_i(\mathbf{k}_0)$ ,

$$\alpha_j(\mathbf{k}_0 + \mathbf{q}) = \alpha_j(\mathbf{k}_0) + \sum_m \left( \frac{\partial \alpha_j}{\partial \mathbf{q}_m} \right)_{\mathbf{q}=0} \cdot \mathbf{q}_m + \dots, \quad (26)$$

where we assume  $\mathbf{k}_0$  to be a wave vector associated with an irreducible representation of the order parameter, i.e. with a vanishing coefficient  $\alpha_j(\mathbf{k}_0)$  at the critical point. If one would like  $\alpha_j(\mathbf{k})$  as a function of  $\mathbf{k}$  to have a symmetry determined extremum at  $\mathbf{k}_0$ , linear terms in front of  $\mathbf{q}_m$  must all necessary vanish! Note that there could be in principle several branches joining at point  $\mathbf{k}_0$ , therefore the later condition must be satisfied for every branch  $j$  in [Eq. (26)].

Lifshitz condition, i.e. the requirement of the stability in a thermal equilibrium, is thus connected with a vanishing of above linear term due to the symmetry reasons (the symmetry of the order parameter has to be found incompatible with the existence of such terms). To this end we write a second-degree expansion of free energy as function of the density increment  $\delta\rho(\mathbf{r})$ ,

$$\Phi[\rho_0 + \delta\rho] = \Phi[\rho_0] + \int h(\mathbf{r}, \mathbf{r}') \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots, \quad (27)$$

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<sup>20</sup>Such transitions are for example known from magnetic crystals with a spiral configuration of spins.

where the linear terms are not present due to forementioned absence of linear invariants. We have essentially written the most general form of expansion [Eq. (27)], where  $h(\mathbf{r}, \mathbf{r}')$  is some unknown (symmetric) function of spatial coordinates. Now we expand  $\delta\rho$  for small  $\mathbf{q}$ ,

$$\delta\rho(\mathbf{r}) = \sum_{\mathbf{k} \in \mathbf{k}_0^*} \sum_i \int_{\mathbf{q}} \eta_i(\mathbf{k} + \mathbf{q}) \phi_{i(\mathbf{k} + \mathbf{q})}(\mathbf{r}) d\mathbf{q}, \quad (28)$$

which yields to (by keeping only translationally invariant terms)

$$\Phi_0 = \sum_{ijk} \int \eta_i(\mathbf{k} + \mathbf{q}) \eta_j(-\mathbf{k} - \mathbf{q}) \left\{ \int h(\mathbf{r}, \mathbf{r}') \phi_{i(\mathbf{k} + \mathbf{q})}(\mathbf{r}) \phi_{j(-\mathbf{k} - \mathbf{q})}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \right\} d\mathbf{q}. \quad (29)$$

This expression is a quadratic form in scalar OP components  $\eta_i(\mathbf{k})$ . In order to bring it into desired diagonal form [Eq. (25)], and extract expansion coefficients  $\alpha_i(\mathbf{k} + \mathbf{q})$ , one has to diagonalize the matrix

$$A_{ij}(\mathbf{k} + \mathbf{q}) \equiv \int h(\mathbf{r}, \mathbf{r}') \phi_{i(\mathbf{k} + \mathbf{q})}(\mathbf{r}) \phi_{j(-\mathbf{k} - \mathbf{q})}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (30)$$

Accounting  $\phi_{i(\mathbf{k} + \mathbf{q})}(\mathbf{r}) = e^{-i\mathbf{q} \cdot \mathbf{r}} \phi_{i\mathbf{k}}(\mathbf{r})$ , which follows from translational properties of basis functions spanning irreducible representations of the OP, and apply first-order  $\mathbf{q}$ -expansion, we may decompose [Eq. (30)] as

$$A_{ij}(\mathbf{k} + \mathbf{q}) = A_{ij}(\mathbf{k}) + \mathbf{q} \cdot \vec{B}_{ij}(\mathbf{k}), \quad (31)$$

$$A_{ij}(\mathbf{k}) \equiv \frac{1}{2} \int [\phi_{i\mathbf{k}}(\mathbf{r}) \phi_{j(-\mathbf{k})}(\mathbf{r}') + \phi_{j(-\mathbf{k})}(\mathbf{r}) \phi_{i\mathbf{k}}(\mathbf{r}')] h(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (32)$$

$$\vec{B}_{ij}(\mathbf{k}) \equiv i \int \mathbf{r} [\phi_{i\mathbf{k}}(\mathbf{r}) \phi_{j(-\mathbf{k})}(\mathbf{r}') - \phi_{j(-\mathbf{k})}(\mathbf{r}) \phi_{i\mathbf{k}}(\mathbf{r}')] h(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (33)$$

We exploited the symmetry  $h(\mathbf{r}, \mathbf{r}') = h(\mathbf{r}', \mathbf{r})$ . Since vector  $\vec{B}_{ij}(\mathbf{k})$  must vanish, provided  $\alpha_i(\mathbf{k})$  is non-zero away from the critical point, we are left with a requirement that each matrix element,

$$\mathbf{r} [\phi_{i\mathbf{k}}(\mathbf{r}) \phi_{j(-\mathbf{k})}(\mathbf{r}') - \phi_{j(-\mathbf{k})}(\mathbf{r}) \phi_{i\mathbf{k}}(\mathbf{r}')], \quad (34)$$

must vanish separately! Function of these type live in a tensor product space composed of vector space and antisymmetrized space of OP representation. Therefore, if there exist a vector representation subspace within the later, we will find combinations of quantities [Eq. (34)] in free energy expansion which are invariant under the action of the group  $\mathbf{G}_0$ . This would imply that the symmetry reasons could not prevent matrix elements of  $\vec{B}_{ij}(\mathbf{k})$  from being non-zero and system would be stable with respect from losing spatial homogeneity, since the thermodynamic potential in an inhomogeneous phase might have a lower value than that of the homogeneous phase.