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GROUP THEORETICAL ARGUMENTS ON THE LANDAU THEORY OF SECOND-ORDER PHASE TRANSITIONS APPLIED TO THE PHASE TRANSITIONS IN SOME LIQUID CRYSTALS*

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The phase transitions between liquids and several of the simplest liquid crystalline phases (nematic, cholesteric, and the simplest types of smectic A and smectic C) were studied from the point of view of the group-theoretical arguments of Landau theory. It was shown that the only possible candidates for second-order phase transitions are those between nematic and smectic A, between centrosymmetric nematic and smectic C and between centrosymmetric smectic A and smectic C. Simple types of density functions for liquid crystalline phases are proposed.

1. Introduction

It is well established that ordinary liquids composed of complicated molecules frequently form liquid crystaline phases when cooled. There are many types and subtypes of liquid crystals among which the simplest, or the most common, are nematics, cholesterics, smectics A and C. Here we consider only the simplest phases of smectics, i.e., de Vries smectic A_2 and smectic C_2 [1, 2]. Phase transitions between liquid and liquid crystalline phases or between two liquid crystalline phases are associated with a change of symmetry introduced by directional or positional ordering of molecules. The first attempt to apply group theoretical arguments of the Landau theory to predict the order of the phase transitions mentioned above was that by Goshen et al. [3]. In a very brief report they showed that a phase transition from an ordinary liquid to a liquid crystalline phase should be of the first order. Their proof, except for some small details, is basically correct. Then, there

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followed two other papers [4, 5] which dealt with similar problems (smectic A to smectic C transitions).

One purpose of this paper is to extens the results of papers [3–5] to study phase transitions between different liquid crystalline phases. A second purpose is to present the older results more explicitly.

Our starting point will be a short summary of group-theoretical aspects of the Landau theory [6–12]. Before doing this it is necessary to stress that the group-theoretical arguments are not equivalent to the minimalization of the termodynamic potential and therefore are not conclusive [10]. All the group-theoretical rules are simply the necessary conditions for a second-order phase transition to occur. If they are violated we can conclude that the phase transition must be of the first order. If, however, they are fulfilled we can only say that there is a possibility that a given phase transition may be of the second order. The final answer can be given only after the investigation of the thermodynamic potential.

In this paper we will not investigate the problem of finding the minima of the potential as the problem would be at least very lenghty and laborious [4, 24, 28]. We will simply apply the rules (given below) to the known symmetries of high and low temperature phases of liquid crystals and we will find which phase transition must occur as the first order transition.

The group theoretical rules are as follows: Suppose that a space symmetry group of a certain phase is G_0. As a result of a phase transition we obtain a new phase with a symmetry group G_1. The necessary conditions for the phase transition to be continuous. (Second order pase transition is another very common but not very precise term). These are as follows: *R. 1.* $G_0 \supset G_1$ i.e. G_1 is subgroup of G_0.

R. 2. The density function of the phase with symmetry group G_0 is ϱ_0 and the density function of the phase with the symmetry group G_1 is $\varrho_0+\delta\varrho$. The function $\delta\varrho$ is a linear combination of the basis functions of a single irreducible (or physically irreducible) representation $D^{kn}(G_0)$ of the group G_0. k and n are star and the index of the representation.

R. 2'. The rule R. 2 can be relaxed somewhat. $\delta\varrho$ may consist of a linear combination of the basis functions belonging to $D^{kn}(G_0)$ and to another different representation, $D^{k'n'}(G_0)$ [29–31]. The point is, however, that whereas the scalar value $\tilde{\eta}$ of the order parameter associated with the representation $D^{kn}(G_0)$ is very small near the phase transition point, the scalar value of the order parameter associated with $D^{k'n'}(G_0)$ is of the order $\tilde{\eta}^2$ i.e., it is practically negligible in comparison with $\tilde{\eta}$. For details see Appendix B and Appendix C. We will call the order parameter associated with the representation $D^{kn}(G_0)$ — a primary order parameter and the second one associated with $D^{k'n'}(G_0)$ — a secondary order parameter.

Instead of one additional $D^{k'n'}(G_0)$ there can be a few such representations. Here for simplicity we consider the case of only one $D^{k'n'}(G_0)$. The general case does not involve any qualitative differences.

R. 3. The symmetrized cube, $\{D^{kn}(G_0)\}^3$, must not contain $D^0(G_0)$ — totally symmetrical representation of G_0.

R. 4. $D^{kn}(G_0) \downarrow G_1$, which is a representation obtained when the representation $D^{kn}(G_0)$ of G_0 is restricted to G_1, must contain the totally symmetric representation of G_1.

R. 4'. If $D^{kn}(G_0)$ is one dimensional or if $D^{kn}(G_0)$ "subduces" only multiple of totally symmetric representation of G_1, then G_1 is normal in G_0 [9].
R. 4''. Chain subduction criterion[1].

If $G_0 \supset G_1 \supset G_1'$ and $D^{kn}(G_0) \downarrow G_1$ contains the totally symmetrical representation of G_1 c times and $D^{kn}(G_0) \downarrow G_1'$ contains the totally symmetrical representation of G_1' also c times, then the continuous transition $G_0 \to G_1'$ is not possible.
R. 5. $D^{kn}(G_0)$ corresponds to a physical tensor field [8, 9].
R. 6. Weak Lifshitz condition [12]:

$$([D^{kn}(G_0)]^2 | D^{v}(G_0)) = m,$$

where $[D^{kn}(G_0)]^2$ is the antisymmetrical square of $D^{kn}(G_0)$, $D^{v}(G_0)$ is the vector representation of G_0, $(D \mid D')$ denotes the scalar product of the characters of the two representations D, D' and m is a number of degrees of freedom of the representation $D^{kn}(G_0)$ i.e.,

(a) if k point is in a general position, then $m = 3$,

(b) if k point is in a general position on certain symmetry plains, then $m = 2$,

(c) if k point is in a general position on certain symmetry axes, then $m = 1$,

(d) if, however, the star k belongs to a physically irreducible representation then m from the point (c) is equal to zero,

(e) if k point is in a special position, for example $k = 0$ then $m = 0$; in this case we have the original Lifshitz condition [6, 7].

R. 7. If besides $D^{kn}(G_0)$ there is also the second representation, $D^{k'n'}(G_0)$, responsible for a phase transition (see the point R. 2') then:

(a) the representation $D^{kn}(G_0)$ must fulfill the conditions of R. 1–R. 4',

(b) the representation $D^{kn}(G_0)$ does not need to fulfill the condition R. 4'',

(c) the representation $D^{k'n'}(G_0)$ must fulfill the conditions of R. 4 and R. 4',

(d) the reducible representation $D = D^{kn}(G_0) + D^{k'n'}(G_0)$, must fulfill the weak Lifshitz condition which in the "spirit" of paper [12] we formulate as follows: the representation $[D]^2 \otimes D^{v}(G_0)$ contains the identity representation, $D^{0}(G_0)$, exactly as many times as is a number of degrees of freedom of the representation D [12]. To clarify this point we use a very simple example. If $D = D^{kn}(G_0) + D^{k'n'}(G_0)$ and if $k \neq 0$, $k' = 0$ then exactly as in R. 6 we have:

$$([D^{kn}(G_0)]^2 | D^{v}(G_0)) = m,$$

where m is a number of degrees of freedom of the representation D^{kn}. There is also the second condition:

$$(D^{k'n'}(G_0) \,|D^{v}(G_0)) = 0$$

and finally the third condition

$$(D^{kn}(G_0) \otimes D^{k'n'}(G_0) \,|D^{v}(G_0)) = 0$$

which, however, is satisfied authomatically ($k + k' \neq 0$).

(e) The modified chain subduction criterion[1].

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[1] Just recently, it has been shown that the chain subduction criterion is not exactly equivalent to the necessary condition based on the original Landau theory [33]. Fortunately, in the following, we will not encounter any case where it would be absolutely necessary to apply this criterion.

In the spirit of papers [8, 11] we can formulate this for the reducible representation D exactly as we did for the single representation $D^{kn}(G_0)$ in the point R. 4′. The other equivalent formulation is as follows. If each of the representations $D^{kn}(G_0)$ and $D^{k'n'}(G_0)$ fulfilles the normal chain subduction criterion in R. 4′ then the second order phase transition $G_0 \to G'_1$ is eliminated.

If one of the conditions in R. 1–R. 7 is not fulfilled then the phase transition associated with the symmetry change $G_0 \to G_1$ cannot be of the second order and therefore must be of the first order.

In the following sections we will determine whether the Landau conditions in R. 1–R. 7 are fulfilled for all phase transitions which can occur within the group such as normal liquids, nematics, cholesterics, smectics A and C.

2. *The irreducible representations of the symmetry group of a normal liquid*

The symmetry group, G_{Is}, of the isotropic noncentrosymmetric liquid is $R_3 \wedge T_3$. R_3 is the three dimensional rotation group and T_3 is the three dimensional translation group, $\wedge$ denotes semi-direct product and $(R_3 \otimes I) \wedge T_3$ is for a centrosymmetric liquid while I is an inversion group. A liquid which is composed of equal mixtures of left and right handed molecules can be treated as centrosymmetric.

The irreducible representations of G_{Is} are well known [14–16]. Here we will, however, introduce them somewhat differently than in [14–16]. Our approach will be analogous to the classical approach for space groups (Koster [13]).

2.1. The irreducible representations of $R_3 \wedge T_3$

We will construct them in the space of continuous and bounded functions $f(\boldsymbol{r}, \tilde{\boldsymbol{r}})$[2] where $\boldsymbol{r}$ is the centre of the mass position vector of a certain object such as a molecule or a cluster of molecules and $\tilde{\boldsymbol{r}}$ is unit vector which gives an orientation of the object. In the case when one unit vector is not enough to describe the orientation of the object we can consider the space of $f(\boldsymbol{r}, \omega)$ functions, where ω are Euler angles [17–19] describing the object's orientation with respect to a fixed laboratory frame.

The left regular representation of $R_3 \wedge T_3$ is defined by:

$$\{\omega|\boldsymbol{t}\}f(\boldsymbol{r}, \tilde{\boldsymbol{r}}) = f(\omega^{-1}(\boldsymbol{r}-\boldsymbol{t}), \omega^{-1}\tilde{\boldsymbol{r}}) \tag{2.1}$$

where $\{\omega \mid \boldsymbol{t}\}$ is an operator of coordinate transformation; $\boldsymbol{\omega}$ is an operator corresponding to the rotational part of the coordinate transformation and $\boldsymbol{t}$ is a translation vector.

The regular representation can be decomposed into the sum of all "unitary" irreducible representations of G_{Is}.

According to [6, 13] to construct an irreducible representation of G_{Is} we must choose one particular vector, $\boldsymbol{k}$, in the reciprocal space, form the star of $\boldsymbol{k}$ (i.e., the set of all vectors

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[2] We omit the rigorous mathematical discussion. It is enough to know that the orthogonal basis in the space is $f_{\boldsymbol{k},l,m}(\boldsymbol{r}, \tilde{\boldsymbol{r}}) = \exp(i\,\boldsymbol{k} \cdot \boldsymbol{r}) Y^{l}_{m}(\tilde{\theta}, \tilde{\varphi})$. The orthogonality relations are:

$$\int f_{\boldsymbol{k},l,m}(\boldsymbol{r}, \tilde{\boldsymbol{r}}) f_{\boldsymbol{k}',l'\,m'}(\boldsymbol{r}, \tilde{\boldsymbol{r}}) d^3r d(\cos\tilde{\theta})\, d\tilde{\varphi} = \delta(\boldsymbol{k}, \boldsymbol{k}')\delta_{l,l'}\delta_{m,m'}.$$

$\omega\boldsymbol{k}$ which in our case is the surface of the sphere of the radius $k = |\boldsymbol{k}|$) and choose one of irreducible representations of group $\mathscr{K}$ of the $\boldsymbol{k}$ vector. $\mathscr{K}$ is the subgroup of operation of G_0 which do not change $\boldsymbol{k}$ or add to $\boldsymbol{k}$ a vector of reciprocal lattice. In the case of G_{Is}, $\mathscr{K}$ is the subgroup of operations which do not change $\boldsymbol{k}$ at all. The rotational part of $\mathscr{K}$ contains all rotations around the axis of the $\boldsymbol{k}$ vector.

Any irreducible representation $D^{km}(\mathrm{Is})$ of G_{Is} has two important parameters: k — that of the star, and m — that of the chosen irreducible representation of $\mathscr{K}$.

One particular basis function is enough to generate all the others. It is easy to find the form of such a function for $D^{km}(\mathrm{Is})$. It is

$$\exp(i\boldsymbol{k}_z \cdot \boldsymbol{r})Y^l_m(\tilde{\boldsymbol{r}}) = \exp(i\boldsymbol{k}_z \cdot \boldsymbol{r})Y^l_m(\tilde{\theta}, \tilde{\varphi}), \tag{2.2}$$

where $\boldsymbol{k}_z = (0, 0, k)$, Y^l_m is an ordinary spherical harmonics. The index m is the relevant one, and l can take any value — for fixed m and different l we always obtain the same irreducible representation $D^{km}(\mathrm{Is})$.

All the representations $D^{km}(\mathrm{Is})$ are irreducible. Only $D^{00}(\mathrm{Is})$ is reducible and can be decomposed into the sum of the well known irreducible representations, D^l, of the group R_3 [17–20].

2.2. The irreducible representations of $(R_3 \otimes I) \wedge T_3$

In the present case $\mathscr{K}$ — the symmetry group of the vector $\boldsymbol{k}$ contains not only all the rotations around $\boldsymbol{k}$ but reflections as well. This means that if we omit the translational group for simplicity, we pass from the C_∞ group to $C_{\infty v}$. The notation is that of Schoenflis. In the former case of C_∞ (for $R_3 \wedge T_3$) the functions $\exp(im\tilde{\varphi})$ and $\exp(-im\tilde{\varphi})$ (or Y^l_m and Y^l_{-m}) belong to the different irreducible representations of $\mathscr{K}$, and now for $C_{\infty v}$, the pair, $\exp(im\tilde{\varphi})$, $\exp(-im\tilde{\varphi})$, belongs to the same irreducible representation. Keeping this in mind it is clear that for $\boldsymbol{k} \neq 0$ the irreducible representations of $(R_3 \otimes I) \wedge T_3$ are: $D^{km}(\mathrm{Is/c})$ with a representative pair of basis functions $\exp(i\boldsymbol{k}_z\boldsymbol{r})Y^l_{\pm m}$, $D^{k0+}(\mathrm{Is/c})$ with basis function $\exp(i\boldsymbol{k}_z\boldsymbol{r})$ or $\exp(i\boldsymbol{k}_z\boldsymbol{r})Y^{2l}_0$ (the basis functions are invariant under inversion), $D^{k0-}(\mathrm{Is/c})$ with the basis function $\exp(i\boldsymbol{k}_z\boldsymbol{r})Y^{2l+1}_0$ (the basis function changes its sign under inversion). Subscript "/c" stands for "centrosymmetric".

For $\boldsymbol{k} = 0$ the irreducible representations of $G_{\mathrm{Is/c}}$ coincide with those of $R_3 \otimes I$, i.e., with the representations D^{l+}, D^{l-} [17, 19]. Superscripts + and − distinguish representations for which basis functions are invariant under inversion or change sign under inversion, respectively.

3. *The phase transitions from isotropic liquids to liquid crystalline phases*

3.1. The symmetry groups of liquid crystalline phases

As we already mentioned we will study the simplest nematic, cholesteric and de Vries A_2 and C_2 smectic liquid crystals [23, 25]. For simplicity we only consider in this section noncentrosymmetric liquids.

(a) The symmetry group of a nematic liquid crystal consists of the semidirect product of the D_∞ point group and T_3 is the three dimensional translation group.

(b) The symmetry of cholesteric liquid crystal can be described by the following construction: we take a plane, π_0, and on it we have normal nematic symmetry, that is the nematic director is parallel to the plane. Then there is a screw axis perpendicular to this plane. The arrangement of the molecules on any other plane, π, which is perpendicular to the screw axis, is almost the same as the arrangement on π_0. The only difference is that the nematic director on the plane π is rotated with respect to the nematic director on the plane π_0. The angle of the rotation is proportional to the distance between π and π_0.

(c) The symmetry group of smectic A_2 liquid crystal is similar to that for the nematic liquid crystal with the exception that the allowed translations parallel to the nematic director (or with the axis C_∞) form a one dimensional crystal lattice having a period which is called "the interlayer distance".

(d) Finally smectic C_2 symmetry can be obtained from smectic A_2 symmetry by uniformly tilting all the directors on the smectic planes.

The optical modeling of the above liquid crystals is schematically sketched in Fig. 1.

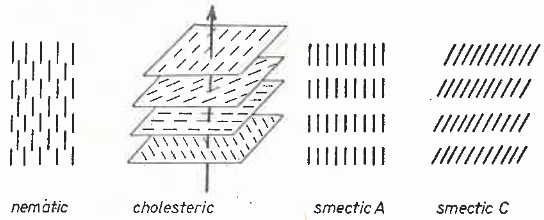

Fig. 1. The optical modeling of liquid crystals [1, 2, 25, 28]

3.2. The phase transition: isotropic to nematic

We write $G_{\mathrm{Is}} \to G_{\mathrm{N}}$ or $G_{\mathrm{Is/c}} \to G_{\mathrm{N/c}}$ where G_{N} denotes the symmetry group of the nematic. The meaning of "c" is the same as above.

The infinitesimal change $\delta\varrho$ of ϱ_0 — isotropic liquid density function, which leads to the symmetry change $G_{\mathrm{Is}} \to G_{\mathrm{N}}$ should be

$$\delta\varrho = \eta Y_0^2(\tilde{\theta}, \tilde{\varphi}) + \mathrm{const}\, \eta^2 Y_0^4(\tilde{\theta}, \tilde{\varphi}) + \dots \tag{3.1}$$

η is a small parameter connected with the primary nematic order parameter. The representation D^2 for $R_3 \wedge T_3$ or D^{2+} for $(R_3 \otimes I) \wedge T_3$ are the active representations. Checking the conditions of R. 1–R. 7 we immediately find that condition R. 3 is not fulfilled [3]. Indeed D^2 contains an invariant. It is

$$\sum_m \begin{pmatrix} 2 & 2 & 2 \\ m_1 & m_2 & m_3 \end{pmatrix} \cdot Y_{m1}^2 Y_{m2}^2 Y_{m3}^2, \tag{3.2}$$

where $\begin{pmatrix} 2 & 2 & 2 \\ m_1 & m_2 & m_3 \end{pmatrix}$ denotes the $3j$ symbol [21, 22]. Similarly, D^4 contains an invariant, etc.

The phase transition: isotropic to nematic in both centrosymmetric and noncentrosymmetric liquids must be of the first order.

3.3. The phase transition: isotropic to smectic A

We write $G_{\mathrm{Is}} \to G_{\mathrm{SA}}$ or for centrosymmetric liquids $G_{\mathrm{Is/c}} \to G_{\mathrm{SA/c}}$. The only allowed form which possibly could lead to second order phase transition according to reference [3] is:

$$\delta\varrho = \eta \operatorname{Re}(\exp(i\boldsymbol{k}_z \cdot \boldsymbol{r}) Y_0^2(\tilde{\theta}, \tilde{\varphi})), \tag{3.3}$$

where Re(z) is the real part of a complex z. We will discuss the form (3.3) but we will also show that the choice (3.3) is not a proper choice for a $G_{\mathrm{Is}} \to G_{\mathrm{SA}}$ second-order phase transition.

In the case of $G_{\mathrm{Is}} \to G_{\mathrm{SA}}$, $\delta\varrho$ belongs to D^{k0}(Is) and when $G_{\mathrm{Is/c}} \to G_{\mathrm{SA/c}}$, $\delta\varrho$ belongs to D^{k0+}(Is/c). What the authors of reference [3] did not consider in detail is the model of SA induced by $\delta\varrho$ of the form (3.3) i.e.,

$$\delta\varrho = \eta \cos(kz) Y_0^2(\tilde{\theta}, \tilde{\varphi}). \tag{3.4}$$

The model should be like this: in the smectic layers when $\cos(kz) > 0$ there is a nematic order, the probability for the molecules to be parallel with the z axis is higher than for the other directions. In the interlayers, however, when $\cos(kz) < 0$ the molecules are instead perpendicular to the z axis.

In addition, for such a model, the angle independent density function does not depend on $\boldsymbol{r}$ because:

$$\int \delta\varrho d(\cos\tilde{\theta}) d\tilde{\varphi} = 0. \tag{3.5}$$

Such a model of SA certainly does not belong to the class of models of liquid crystals that people generally accept (compare this to Fig. 1). To end the discussion of form (3.3) we note that for the representations $\{D^{k0}(\mathrm{Is})\}^3$ and $\{D^{k0+}(\mathrm{Is/c})\}^3$ invariants do exist. As an example we can take [3]:

$$\exp\{i(\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3)\boldsymbol{r}\} = 1, \tag{3.6}$$

where $\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3 = 0$ and $\boldsymbol{k}_1$, $\boldsymbol{k}_2$, $\boldsymbol{k}_3$ all belong to the same star. This is why the authors of reference [3] concluded that the $G_{\mathrm{Is}} \to G_{\mathrm{SA}}$ phase transition must be of the first order.

Now we will show which is the proper choice for $\delta\varrho$. The form of $\delta\varrho$ which is possible, is simply:

$$\delta\varrho = \eta \cos(kz) + \mathrm{const}\, \eta^2 Y_0^2(\tilde{\theta}, \tilde{\varphi}) \tag{3.7}$$

or

$$\delta\varrho = \eta Y_0^2(\tilde{\theta}, \tilde{\varphi}) + \mathrm{const}\, \eta^2 \cdot \cos(kz) \tag{3.7'}$$

with the two dependent order parameters [29]: the primary one, which is of the order η and the secondary one of the order η^2.

Studying the terms of the order η we see that in both cases the third order invariants in the symmetrized cubes of the appropriate representations do exist and consequently the phase transition must be of the first order.

3.4. The phase transition: isotropic to cholesteric ($G_{\mathrm{Is}} \rightarrow G_{\mathrm{Ch}}$)

We consider only noncentrosymmetric liquids because only for such is a cholesteric phase possible [26].

The authors of reference [3] consider the representation $D^{k2}(\mathrm{Is})$ as the only candidate which possibly could lead to a second-order phase transition. The form of $\delta\varrho$ consistent with $D^{k2}(\mathrm{Is})$ would be

$$\delta\varrho = \eta\,\mathrm{Re}\,\{\exp(i\boldsymbol{k}_z \cdot \boldsymbol{r}) Y_2^2(\tilde{\theta}, \tilde{\varphi})\} = \eta \sin^2(\tilde{\theta}) \cos(kz + 2\tilde{\varphi}). \tag{3.8}$$

Such a form, however, in spite of sinusoidal modulation of the desity function, ϱ_0, would lead to an unacceptable model of a cholesteric phase. In fact, such a phase would not be cholesteric at all because when $\cos(kz+2\tilde{\varphi}) > 0$ the molecules tend to be perpendicular to the z axis but when $\cos(kz+2\tilde{\varphi}) < 0$ they tend to be parallel instead. Even allowing that such a peculiar non-cholesteric liquid crystalline phase is possible we still find that the phase transition under consideration must be of the first order (see Appendix A).

In reality to study the second-order phase transition from isotropic to cholesteric it is necessary to consider different $\delta\varrho$, i.e., having the form:

$$\delta\varrho = \eta \sin^2\tilde{\theta} \cdot \cos^2(kz + \tilde{\varphi}). \tag{3.8$'$}$$

Such a $\delta\varrho$ has all the desired characteristics necessary to describe the cholesteric phase (Fig. 1). However, one can easilly check that $\delta\varrho$ is a combination of basis functions of the physically irreducible representation $D^{2k,2}(\mathrm{Is})$ and of the representation D^2. The appropriate order parameters are of the same order — rule R. 2 (and R. 2′) is violated. Consequently, the phase transition must be of the first order.

3.5. The phase transition: isotropic to smectic C ($G_{\mathrm{Is}} \rightarrow G_{\mathrm{SC}}$ or $G_{\mathrm{Is/c}} \rightarrow G_{\mathrm{SC/c}}$)

We consider only "normal SC" (de Vries C_2 [23, 24]). This phase transition was not studied by the authors of [3].

Looking at Fig. 1 it is easy to see that the acceptable form of $\delta\varrho$ is:

$$\delta\varrho = \eta\,\mathrm{Re}\,\{\exp(i\boldsymbol{k}_z \cdot \boldsymbol{r})\} + \mathrm{const}\,\{\sum_n D^2_{n0}(0, \eta^2, 0) Y^2_n(\tilde{\theta}, \tilde{\varphi}) - Y^2_0(\tilde{\theta}, \tilde{\varphi})\} \tag{3.9}$$

or

$$\delta\varrho = \{\sum_n D^2_{n0}(0, \eta, 0) Y^2_n - Y^2_0\} + \eta^2\,\mathrm{const}\,\mathrm{Re}\,\{\exp(i\boldsymbol{k}_z \cdot \boldsymbol{r})\}, \tag{3,9$'$}$$

where the first term in (3.9) (and the second in (3.9′)) describes a density modulation from one smectic layer to another and the second term describes the development of a uniform tilt of all the molecules. Functions D^l_{mn} are well known Wigner spherical rotator functions [17–20]. Their arguments are three Euler angles. The second term of (3.9) has a maximum which can be obtained from the nematic maximum (at $\tilde{\theta} = 0$ i.e., the nematic director is parallel to the z axis) by rotation around the y axis by an angle η^2, which is called the tilt angle. $\delta\varrho$ having the form (3.9) and (3.9′) are composed of basis functions of the irreducible representation $D^{k0}(\mathrm{Is})$ and of the irreducible representation D^2 (for noncentrosymmetric liquids). Both forms are such that they do agree with the conditions of R. 2′.

As in the part 2.4 we find that the third order symmetric invariants for the representations associated with the primary order parameters (the terms of order η) do exist and therefore the phase transition must be of the first order.

4. The density functions for nematics, cholesterics, and smectics A and C

Using a similar way of reasoning as in part 3 we obtain the density functions for nematic, cholesteric and smectic A and C phases in the form of expansions in basis functions of the irreducible representations of $R_3 \wedge T_3$. In the following we will treat only noncentrosymmetric liquids — the modifications for centrosymmetric liquids are trivial.

For nematic liquids:

$$\varrho_{\mathrm{N}} = \sum_l c_{2l} Y_0^{2l}(\tilde{\theta}, \tilde{\varphi}), \tag{4.1}$$

where the letters "c" denote the expansion coefficients.

For smectics A (de Vries A_2):

$$\varrho_{\mathrm{SA}} = \{\sum_n c_n \cos(k_0 zn)\} \{\sum_l \tilde{c}_{2l} Y_0^{2l}(\tilde{\theta}, \tilde{\varphi})\}. \tag{4.2}$$

The terms of the type $\sin(k_0 zn)$ are absent because ϱ_{SA} must be invariant under a two-fold rotation: $x \to -x,\ y \to y,\ z \to -z$.

For smectics C (de Vries C_2):

$$\varrho_{\mathrm{SC}} = \{\sum_n c_n \cos(k_0 zn)\} \{\sum_{lm} c_{2l} D_{m0}^{2l}(0, \beta, 0) Y_m^{2l}(\tilde{\theta}, \tilde{\varphi})\}. \tag{4.3}$$

For cholesteric liquid crystals the explicit expansion in basis functions is difficult to obtain The simplest model for ϱ_{Ch} as we already know is:

$$\varrho_{\mathrm{Ch}} = \mathrm{const} + \eta\, \mathrm{const}' \cdot \sin^2(\tilde{\theta}) \cdot \cos^2(k_0 z + \tilde{\varphi}) \tag{4.4}$$

(the representations $D^{2k,2}(\mathrm{Is})$, D^2 and D^0).

The more realistic model for ϱ_{Ch} would be:

$$\varrho_{\mathrm{Ch}} = \sum_{lm} c_l D_{m0}^{2l}(0, k_0 y, 0) Y_m^{2l}(\tilde{\theta}, \tilde{\varphi}). \tag{4.5}$$

Unfortunately, a single term in (4.5) is not a single basis function. Nevertheless, it is easy to understand the way of constructing (4.5). We start from ϱ_{N} in the form (4.1) and then rotate ϱ_{N} around the y axis. For a fixed y and for arbitrary x, z (on the plane $y = \mathrm{const}$) we obtain a nematic order. The orientation of the nematic director depends on y and changes from plane to plane. The cholesteric pitch is equal to $2\pi/k_0$.

5. The irreducible representations of the symmetry group of the nematic phase

The symmetry group G_N of the nematic phase is $D_\infty \wedge T_3$ for noncentrosymmetric liquids or $(D_\infty \otimes I) \wedge T_3$ for centrosymmetric liquids.

5.1. The irreducible representations of $D_\infty \wedge T_3$.

We will not repeat all the considerations of Section 2 here. The final results are as follows:

For the star with points in a general position (the rotational part of $\mathscr{K}$ is identity) we have the representation $D^k(\mathrm{N})$ with a representative basis function

$$\exp(i\boldsymbol{k}_1 \cdot \boldsymbol{r}), \tag{5.1}$$

where $\boldsymbol{k}_1$ is one of the $\boldsymbol{k}$ vectors which belong to the star. The star is now composed of all $\boldsymbol{k}$ vectors which fulfill equations: $k_z = \pm|k_{1z}|$, $k_x^2+k_y^2 = k_{1x}^2+k_{1y}^2$ i.e., the ends of the $\boldsymbol{k}$ vectors form two circles.

For the star with $\boldsymbol{k}$ perpendicular to the C_∞ rotation axis (to denote that $\boldsymbol{k}$ is perpendicular to C_∞ we will write $\boldsymbol{k}_\perp$) the rotational part of $\mathscr{K}$ is C_2 group with two irreducible representations. Therefore we now have two types of irreducible representations of G_N: $D^{k\perp+}(\mathrm{N})$ and $D^{k\perp-}(\mathrm{N})$. Two representative basis functions are:

$$\exp(i\boldsymbol{k}_y \cdot \boldsymbol{r}) Y_0^l(\tilde{\theta}, \tilde{\varphi}). \tag{5.2}$$

The vector $\boldsymbol{k}_y \perp C_\infty$ and $k_x = 0$, l is even for $D^{k\perp+}(\mathrm{N})$ and l is odd for $D^{k\perp-}(\mathrm{N})$. (Indeed we can easily check that by rotating Y_0^l around the y axis by angle π we obtain $(-1)\, Y_0^l$.)

For k parallel with the C_∞ axis (we will write $\boldsymbol{k}_\parallel$) the star consists of only two vectors and k is invariant under the whole C_∞ group. The basis functions of one dimensional representations of C_∞ are $\exp(im\tilde{\varphi})$ or $Y_m^l(\tilde{\theta}, \tilde{\varphi})$ for $C_\infty || z$. Therefore, we obtain the irreducible representations, $D^{k\parallel m}(\mathrm{N})$ of $D_\infty \wedge T_3$, with the basis functions

$$\exp(i\boldsymbol{k}_z \cdot \boldsymbol{r}) Y_m^l(\tilde{\theta}, \tilde{\varphi}). \tag{5.3}$$

One has to remember that the index l is an irrelevant one.

For the star with $\boldsymbol{k} = 0$ the irreducible representations of $D_\infty \wedge T_3$ coincide with those of the D_∞ group (A_1, A_2 are one dimensional representations and E_1, E_2, etc. are two dimensional representations [27] of the D_∞ group).

5.2. The irreducible representations of $(D_\infty \otimes I) \wedge T_3$

For k in a general position we have the representations $D^{k+}(\mathrm{N/c})$ and $D^{k-}(\mathrm{N/c})$. Signs + and − represent basis functions that are even and odd under reflexion which is contained in the $\mathscr{K}$ subgroup.

For $\boldsymbol{k}_\perp$ we have representations, $D^{k\perp+}(\mathrm{N/c})$, $D^{k\perp b1}(\mathrm{N/c})$, $D^{k\perp b2}(\mathrm{N/c})$, and $D^{k\perp b3}(\mathrm{N/c})$ because the rotational part of $\mathscr{K}$ coincides with the C_{2v} point group with 4 irreducible representations: the identity one (+), and three other, one dimensional representations ($b1$, $b2$, $b3$).

For $\boldsymbol{k}_{\|}$ the rotational part of $\mathscr{K}$ is identical to the $C_{\infty v}$ point group. $C_{\infty v}$ has two one dimensional representations: the identity representation and the representation which upon reflexion changes the sign of basis function (for superscripts we will use + and −). There is also an infinite number of two dimensional representations with pairs of basis functions $\exp(\pm im\tilde{\varphi})$ where $\tilde{\varphi}$ is an angle of rotation around C_∞. Therefore, we obtain three new types of the representations of the $G_{\mathrm{N/c}}$ group: $D^{k_{\|}+}(\mathrm{N/c})$, $D^{k_{\|}-}(\mathrm{N/c})$ and $D^{k_{\|}|m|}(\mathrm{N/c})$.

For $\boldsymbol{k} = 0$ we obtain the irreducible representations which coincide with the representations of the $D_\infty \otimes I$ point group (A_1^+, A_1^-, A_2^+, A_2^-, E_1^+, E_1^-, E_2^+, E_2^-, etc. [27]).

The basis functions for the irreducible representations of $G_{\mathrm{N/c}}$ also can be found easily in the same way as before.

6. The phase transitions from nematic liquid to other liquid crystalline phases

6.1. The phase transition: nematic to smectic A

We write $G_{\mathrm{N}} \to G_{\mathrm{SA}}$ or $G_{\mathrm{N/c}} \to G_{\mathrm{SA/c}}$. For $G_{\mathrm{N}} \to G_{\mathrm{SA}}$ we can expect that the simplest $\delta\varrho$ will be:

$$\delta\varrho = \eta \operatorname{Re}\{\exp(i\boldsymbol{k}_z\boldsymbol{r})\} + \eta^2 \operatorname{const} \operatorname{Re}\{\exp(i2\boldsymbol{k}_z\boldsymbol{r})\} + \ldots \tag{6.1}$$

$\delta\varrho$ is composed of the basis functions of the irreducible representations $D^{nk_{\|},0}(\mathrm{N})$ where $n = 1, 2, 3$, etc.

It is relatively easy to study $D^{k_{\|}0}(\mathrm{N})$. First, it is obvious that the invariants of the third order do not exist. To show this it is enough to multiply any three basis functions of the form (5.3). The product is not invariant under a two fold rotation around the y axis. Now let us find whether the weak Lifshitz condition for $D^{k_{\|}0}(\mathrm{N})$ alone is fulfilled. As $\boldsymbol{k}_{\|} || C_\infty$ we have only one degree of freedom for the star. Now let us form $[D^{k_{\|}0}(\mathrm{N})]^2$. We have only two basis functions: $f_1 = \exp(i\boldsymbol{k}_z\boldsymbol{r})$ and $f_2 = f_1^* = \exp(-i\boldsymbol{k}_z\boldsymbol{r})$. There exists only one antisymmetric combination of the second order:

$$f_{\mathrm{an}} = f_1 f_2' - f_1' f_2 = 2 \operatorname{Re}\{\exp[i\boldsymbol{k}_z(\boldsymbol{r}-\boldsymbol{r}')]\}. \tag{6.2}$$

Under translations and C_∞ rotations f_{an} is invariant. However, any two fold rotation perpendicular to the C_∞ axis changes the sign of f_{an}. It follows that f_{an} must belong to the A_2 representation of the D_∞ point group. Finally we notice that the vector representation of G_{N} can be decomposed into:

$$D^{\mathrm{v}}(\mathrm{N}) = A_2 + E_1.$$

Writing down the condition in (R. 6) we find that:

$$(D^{\mathrm{v}}(\mathrm{N}) \mid [D^{k_{\|}0}(\mathrm{N})]^2) = 1. \tag{6.3}$$

Therefore, the weak Lifshitz condition for $D^{k_{\|}0}(\mathrm{N})$ is fulfilled. Going now to the secondary order parameters and the representations $D^{2k_{\|}0}(\mathrm{N})$, ... we see that each of the representations $D^{2k_{\|}0}(\mathrm{N})$, ... fulfills (6.3) and all together fulfill the condition in R. 7. All the other conditions are very easy to check and we find that the second order phase transition from noncentrosymmetric nematic to smectic A is possible in agreement with experimental and earlier theoretical results [23–25, 28].

For centrosymmetric nematics the way of reasoning, all the calculations and the final results are nearly the same.

The only difference is that instead of $D^{k_\parallel 0}(\mathrm{N})$ we have $D^{k_\parallel +}(\mathrm{N/c})$, instead of the D_∞ point group with $A_1, A_2, E_1, \dots$ representations we deal with $D_\infty \otimes I$ with the representations $A_1^+, A_1^-, A_2^+, A_2^-, E_1^+, \dots$. The vector representation, $D^{\mathrm{v}}(\mathrm{N/c})$, can be decomposed into $A_2^- + E_1^-$ and $[D^{k_\parallel +}(\mathrm{N/c})]^2 = A_2^+$. Therefore, each of the representations $D^{nk_\parallel +}(\mathrm{N/c})$ itself fulfills the *original* Lifshitz condition.

The second order phase transition $G_{\mathrm{N/c}} \to G_{\mathrm{SA/c}}$ is therefore possible.

6.2. The phase transition: nematic to smectic C

We write $G_{\mathrm{N}} \to G_{\mathrm{SC}}$ or $G_{\mathrm{N/c}} \to G_{\mathrm{SC/c}}$. Let us start with centrosymmetric nematics. The realistic form for $\delta\varrho$ should be

$$\delta\varrho = \eta \operatorname{Re}\{\exp(ik_z r)\} + \mathrm{const} \sum_l c_{2l} \{\sum_m D^{2l}_{m0}(0, \eta^2, 0) Y^{2l}_m(\tilde{\theta}, \tilde{\varphi}) - Y^{2l}_0(\tilde{\theta}, \tilde{\varphi})\}. \tag{6.4}$$

We find that a second order phase transition is possible.
The proof:
The representation $D^{k_\parallel +}(\mathrm{N/c})$ connected with the primary order parameter as we know from the previous section is the active representation. It fulfills all the necessary conditions of the Landau theory.

Going now to the terms of the order η^2 (secondary order parameters) we see that we must consider the representations $E_1^+, E_2^+, \dots$ (for $m = 1, 2, \dots$) of $D_\infty \otimes I$. The most important thing is to check whether the Lifshitz condition in R. 7d is fulfilled. This is because $D^{\mathrm{v}}(\mathrm{N/c}) = A_2^- + E_1^-$ and $((A_2^- + E_1^-) | [E_1^+]^2) = 0$. The other conditions are also very easy to check and consequently the second-order phase transition $G_{\mathrm{N/c}} \to G_{\mathrm{SC/c}}$ is possible.

For noncentrosymmetric liquids the situation is different:

$$(D^{\mathrm{v}}(\mathrm{N}) \,|\, [E_1]^2) = ((A_2 + E_1) \,|\, A_2) = 1.$$

In such a case the Lifshitz condition in R. 7d is not fulfilled and the second order phase transition $G_{\mathrm{N}} \to G_{\mathrm{SC}}$ is not possible.

Finally, let us notice that all the above results concerning the order of the phase transition remain valid if in formula (6.4) we change the order of the terms as follows:

$$\delta\varrho = \{\sum_m D^2_{m0}(0, \eta, 0) Y^2_m - Y^2_0\} + \eta^2 \,\mathrm{const} \operatorname{Re}\{\exp(ik_z r)\}, \tag{6.4'}$$

6.3. The phase transition: nematic to cholesteric

Experimentally such a phase transition is not observed [2]. Therefore, we will not discuss the possibility of a second order phase transition $G_{\mathrm{N}} \to G_{\mathrm{Ch}}$. However, one can easily check that such a hypothetical phase transition could not be a continuous transition.

There are some thermodynamical arguments which suggest that the $G_N \rightarrow G_{Ch}$ phase transition is not possible.

7. The symmetry group of cholesteric liquid crystal

The cholestric liquid crystals can be formed only in noncentrosymmetric liquids [26].

Here we will not look for irreducible representations of G_{Ch} as we did in the previous section. To study the order of any possible phase transition from cholesterics to other liquid crystals this is simply not necessary.

We will immediately find that any such phase transition must be a first order transition.

7.1. The phase transition $G_{Ch} \rightarrow G_{SA}$

The continuous phase transition $G_{Ch} \rightarrow G_{SA}$ or $G_{SA} \rightarrow G_{Ch}$ is not possible because rule R. 1 is not fulfilled:

(a) $G_{Ch} \not\supset G_{SA}$ — one of the elements G_{SA} is a rotation around the z axis. It is, however, not present in G_{Ch}, but there is a screw axis instead.

(b) $G_{SA} \not\supset G_{Ch}$ — one of the elements of G_{Ch} is a screw rotation for such a small angle that translation along the screw axis associated with the rotation is much shorter than the smectic interlayer distance.

7.2. The phase transition $G_{Ch} \rightarrow G_{SC}$

The continuous phase transition is not possible because: $G_{Ch} \not\supset G_{SC}$, $G_{SC} \not\supset G_{Ch}$.

8. The irreducible representations of G_{SA} and $G_{SA/c}$

These are almost the same as the representations of G_N. The only single difference is that instead of $D_\infty \wedge T_3$ we have

$$G_{SA} = D_\infty \wedge (T_\perp \otimes T_\parallel^0), \tag{8.1}$$

where $T_\perp$ is the translation group in two dimensions (planes perpendicular to C_∞) and $T_\parallel^0$ is the group of discrete translations in one dimension (one dimensional lattice parallel to the C_∞ axis).

All we must do is to use the irreducible representations of G_N keeping in mind that k_z of any star can have only certain discrete values.

The same that held for $G_{N/c}$ is valid also for $G_{SA/c}$.

9. The phase transition: smectic A to smectic C

With the phase transition $G_{SA} \rightarrow G_{SC}$ we associate $\delta\varrho$ of the form:

$$\delta\varrho = \sum_l c_{2l}\{\sum_n D_{n0}^{2l}(0, \eta, 0) Y_n^{2l}(\tilde{\theta}, \tilde{\varphi}) - Y_0^{2l}(\tilde{\theta}, \tilde{\varphi})\}, \tag{9.1}$$

where

$$\sum_l c_{2l} Y_0^{2l} = \lim_{V\rightarrow\infty} V^{-1} \int_V \varrho_{SA}(r, \tilde{r}) d^3 r \tag{9.2}$$

is the orientational part of the density function for SA. V is a volume of a sample. The way of constructing a form of the type (9.1) with a tilt angle, η, was already discussed in the former parts of this paper.

The function $\delta\varrho$ is a combination of basis functions belonging to $E_1, E_2, \ldots$ representations of D_∞. The primary order parameter is associated with the representation E_1. Let us now examine the representation E_1.

First, $\{E_1\}^3$ does not contain an identity representation:

$$\{E_1\}^3 = E_3+3E_1. \tag{9.3}$$

Next we check the Lifshitz condition. As in section 6.1 we have:

$$D^{\mathrm{v}}(\mathrm{SA}) = E_1+A_2 \quad \text{and} \quad [E_1]^2 = A_2. \tag{9.4}$$

Therefore,

$$(D^{\mathrm{v}}(\mathrm{SA}) \mid [E_1]^2) = 1 \tag{9.5}$$

and the Lifshitz condition in R. 7d cannot be fulfilled. The phase transition $G_{\mathrm{SA}} \rightarrow G_{\mathrm{SC}}$ must be of the first order.

For centrosymmetric liquids the results are different:

$$D^{\mathrm{v}}(\mathrm{SA/c}) = E_1^- + A_2^-, \quad [E_1^+]^2 = A_2^+, \quad (D^{\mathrm{v}}(\mathrm{SA/c}) \mid [E_1^+]^2) = 0. \tag{9.6}$$

The Lifshitz condition is therefore fulfilled for E_1^+. The same is true for $E_2^+, \ldots$ and, consequently, the condition in R. 7d is fulfilled. After checking the remaining conditions we conclude that the $G_{\mathrm{SA/c}} \rightarrow G_{\mathrm{SC/c}}$ phase transition can be of a second order.

10. Conclusion

The results for isotropic liquids, nematics, cholesterics and smectics A_2 and C_2 are as follows:
From the group theory point of view only N → SA, N/c → SA/c, SA/c → SC/c and N/c → SC/c phase transitions can occur as the second order phase transition. All the other phase transitions which can occur within the group mentioned above must be of the first order.

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APPENDIX A

To prove that there is an invariant in the representation $\{D^{k2}(\mathrm{Is})\}^3$ let us write one basis function which belongs to $D^{k2}(\mathrm{Is})$:

$$f_0 = \exp(i\boldsymbol{k}_z \cdot \boldsymbol{r})Y_2^2(\tilde{\vartheta}, \tilde{\varphi}). \tag{A.1}$$

The other functions which also transform according to $D^{k2}(\mathrm{Is})$ are:

$$f_\omega = \exp\left(i(\boldsymbol{\omega}\boldsymbol{k}_z)\cdot\boldsymbol{r}\right)\cdot\sum_n D^2_{n2}(\omega)Y^2_n(\tilde{\theta},\tilde{\varphi}), \tag{A.2}$$

where ω denotes Euler angles of some rotation and $\boldsymbol{\omega}$ is the operator of this rotation. Now let us form the product

$$f_0 f_{\omega_1} f_{\omega_2} = \sum_{n,m} D^2_{n2}(\omega_1)D^2_{m2}(\omega_2)\exp\left\{i(\boldsymbol{k}_z+\boldsymbol{\omega}_1\boldsymbol{k}_z+\boldsymbol{\omega}_2\boldsymbol{k}_z)\boldsymbol{r}\right\}Y^2_2Y^2_nY^2_m \tag{A.3}$$

and in the same way the products $f_{\omega_1}f_0f_{\omega_2}$, $f_{\omega_2}f_{\omega_1}f_0$, ... We select ω_1 and ω_2 in such a way that:

$$\exp\left\{i(\boldsymbol{k}_z+\boldsymbol{\omega}_1\boldsymbol{k}_z+\boldsymbol{\omega}_2\boldsymbol{k}_z)\boldsymbol{r}\right\} = 1,$$

for example $\omega_1 = (\alpha, 2\pi/3, 0)$ and $\omega_2 = (\alpha+\pi, 2\pi/3, 0)$.

In short, we write:

$$f_0 f_{\omega_1} f_{\omega_2} = \sum_{n,m} c_{n,m}Y^2_2Y^2_nY^2_m, \tag{A.4}$$

where $c_{n,m}$ are appropriate constants.

Let us look for invariants in the sum (A.4). The necessary condition for an invariant is $n+m = -2$. If we write the explicit form of $c_{0,-2}$ ($c_{0,-2} = c_{-2,0} \neq 0$, check for example in [17]) we notice at once that as α is arbitrary we can choose α in such a way that invariants, if any, standing with $c_{-2,0}$ and with $c_{-1,-1}$ cannot cancel, i.e., they are linearly independent.

Therefore, the only thing one has to check is whether the product $Y^2_{-2}Y^2_2Y^2_0$ indeed contains an invariant. It does because:

$$\int Y^2_{-2}Y^2_2Y^2_0\,d(\cos\tilde{\theta})d\tilde{\varphi} \sim \begin{pmatrix}2 & 2 & 2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}2 & 2 & 2\\ -2 & 2 & 0\end{pmatrix} \neq 0, \tag{A.5}$$

where (:::) denote $3j$ symbols [22].

Now the problem remains whether it is possible to form a *symmetric* combination of the type (A.5) which contains an invariant.

It is easy to find that one such combination is:

$$\sum_{r,s,t}\begin{pmatrix}2 & 2 & 2\\ r & s & t\end{pmatrix}Y^2_rY^2_sY^2_t, \tag{A.6}$$

where r, s, t — any permutation of $2, -2, 0$. The combination (A.6) is symmetric because $\begin{pmatrix}2 & 2 & 2\\ r & s & t\end{pmatrix}$ is invariant under the exchange of any two columns.

APPENDIX B

The fact that $\delta\varrho$ can consist of a linear combination of the basis functions belonging to two different irreducible representations and that there are two order parameters i.e., the primary and the secondary one — was already known long ago [29–31]. However, the occurence of such a situation was thought to be "exotic" and was consequently almost forgotten. Therefore, to recall some of the results of papers [29–31] seems reasonable. We will do this in a much simpler way than was done in paper [29].

We know that a modulation, $\delta\varrho$, of the density function, which is responsible for the lowering of the symmetry of the high symmetry phase, is:

$$\delta\varrho = \sum_i c_{kn,i} f_{kn,i} = \eta \sum_i d_{kn,i} f_{kn,i}, \tag{B.1}$$

where η is a small parameter and c, d are coefficients. If the group of symmetry of the high symmetry phase is G_0 then $f_{kn,i}\,(i = 1, 2, \ldots)$ are basis functions of one irreducible or physically irreducible representation $D^{kn}(G_0)$, which is called the active representation [6–11].

There is, however, one slight modification which is possible [29–31]. Let us assume that $\delta\varrho$ has the form:

$$\delta\varrho = \sum_i c_{kn,i} f_{kn,i} + \sum_i c_{k'n',i} f_{k'n',i} + \ldots, \tag{B.2}$$

$f_{k'n',i}$ are basis functions belonging to other different irreducible representation, $D^{k'n'}(G_0)$

Let us expand the density of the Gibbs functional G:

$$G(p, T, \varrho) = G_0(p, T, \varrho_0) + G_2(p, T, \varrho_0, \delta\varrho) + G_3(p, T, \varrho_0, \delta\varrho) + \ldots, \tag{B.3}$$

where

$$G_2(p, T, \varrho_0, \delta\varrho) = \sum_{ij\mu\nu} c_{\mu i} c_{\nu j} G_2(p, T, \varrho_0, f_{\mu i}, f_{\nu j}),$$
$$G_3(p, T, \varrho_0, \delta\varrho) = \sum_{ijr\mu\nu\tau} c_{\mu i} c_{\nu j} c_{\tau r} G_3(p, T, \varrho_0, f_{\mu i}, f_{\nu j}, f_{\tau r}), \tag{B.4}$$

and where $\mu, \gamma, \tau = (kn), (k'n'), (k''n''), \ldots$.

If we assume that:

$$\left.\begin{aligned} c_{kn,i} = \eta d_{kn,i}, \quad c_{k'n',i} &= \mathrm{const}_{k'n'} \cdot \eta^{2+s} d_{k'n',i} \quad \text{for} \quad j \neq 0,\ s = 0 \text{ or } 1, 2, 3 \ldots \\ \sum_i |d_{\nu i}|^2 &= 1 \quad \text{for} \quad \nu = (kn), (k'n'), \ldots, \end{aligned}\right\} \tag{B.5}$$

where $\mathrm{const}_{k'n'}$ are arbitrary constants, we again have the normal Landau theory without any significant changes. To understand the physical meaning of the assumption in B.5 see Appendix C.

Let us check if this is indeed so. For G_2 we find that

$$G_2(p, T, \varrho_0, \delta\varrho) = \eta^2 \sum_{ij} G_2(p, T, \varrho_0, f_{kn,i}, f_{kn,j}) d_{kn,i} d_{kn,j}$$
$$+ \eta^4 \cdot \mathrm{const}_{k'n'} \sum_{ij} G_2(p, T, \varrho_0, f_{k'n',i}, f_{k'n',j}) d_{k'n',i} d_{k'n',j} + \ldots . \tag{B.6}$$

The term with η^3 is not present as the products $D^{kn} \cdot D^{k'n'}$ do not contain a totally symmetric representation of G_0.

This part of (B.6) which is proportional to η^2 changes its sign at the phase transition point. There is, however, no such need for the second part, which is proportional to η^4. Subsequently, there is no danger that the new equation (the second one) of the type:

$$\sum_{i,j} G_2(p_c, T_c, \varrho_0, f_{k'n',i}, f_{k'n',j}) d_{k'n',i} d_{k'n',j} = 0$$

will appear. Such an equation could change the line of phase transitition points $p_c = p_c(T_c)$ into one isolated point (p_c, T_c) on the phase diagram [6, 7].

For G_3 we find that:

$$G_3(p, T, \varrho_0, \delta\varrho) = \eta^3 \sum_{ijr} G_3(\ldots, f_{kn,i}, f_{kn,j}, f_{kn,r}) d_{kn,i} d_{kn,j} d_{kn,r}$$
$$+\eta^4 \operatorname{const}_{k'n'} \sum_{ijr} G_3(\ldots, f_{kn,i}, f_{kn,j}, f_{k'n',r}) d_{kn,i} d_{kn,j} d_{k'n',r} + \ldots . \tag{B.7}$$

The first term of (B.7) must vanish, exactly as in the original Landau theory, and the second term do not jeopardize the theory because the power of η is too high.

In conclusion we see that no new conditions were introduced into the original theory and as a matter of fact no serious modifications. For $D^{k'n'}$ there exist only trivial conditions which were already listed in the Introduction.

As a concluding remark let us note that as in the original Landau theory we obtain:

$$G = G_0 + \eta^2 A + \eta^4 B, \tag{B.8}$$

where B is positive and A changes its sign at the phase transition point. Of course, the terms of the order η^2, η^3 in $\delta\varrho$ will change the value of B, which should be smaller than B corresponding to the theory with only one active representation. If there is no possibility to lower the value of B, it follows that the terms of the order η^2, η^3 in $\delta\varrho$ cannot exist and we end with the old original Landau theory with only one active representation and one order parameter.

APPENDIX C

For the sake of simplicity we consider equation (B.2) with only two different representations. If we look for the minima of G with respect to $\{c_{kn,i}\}$ and $\{c_{k'n',i}\}$ we must consider two independent scalar values of order parameters, η_1, η_2:

$$\eta_1 = \sqrt{\sum_i |c_{kn,i}|^2}, \quad \eta_2 = \sqrt{\sum_i |c_{k'n',i}|^2} \tag{C.1}$$

or

$$c_{kn,i} = \eta_1 d_{kn,i}, \quad c_{k'n',i} = \eta_2 d_{k'n',i}, \tag{C.2}$$

where

$$\sum_i |d_{kn,i}|^2 = \sum_i |d_{k'n',i}|^2 = 1. \tag{C.3}$$

The Gibbs potential, G, as the function of η_1, η_2 can be written in the form:

$$G = (A_1\eta_1^2 + A_2\eta_2^2) + (B_2\eta_1^2\eta_2 + B_3\eta_1\eta_2^2 + B_4\eta_2^3) + (C_1\eta_1^4 + \ldots) + \ldots, \tag{C.4}$$

where $A_1, A_2, B_2, \dots$ are some functions of temperature and pressure. We assume that the term $B_1\eta_1^3$ is not present in order to rule out a first order transition. If $A_1 > 0$ and $A_2 > 0$, then the minimum of G is realised for $\eta_1 = \eta_2 = 0$. However, if A_1 changes from positive to negative and A_2 is still greater than zero, then there is a phase transition. At the point where $A_1 = 0$ there is an instability in the potential G [32]. To study this instability we follow Haken [32]: let $G = G(\eta_1, \eta_2^0+\tilde\eta_2)$, where η_2^0 is chosen so that G has its minimum for $\eta_2^0 = 0$, or in other words, that

$$\left.\frac{\partial G}{\partial \tilde\eta_2}\right|_{\tilde\eta_2=0} = 0$$

holds. This may be considered as an equation for η_2^0. For any given η_1 we may thus determine η_2^0 so that $\eta_2^0 = \eta_2^0(\eta_1)$. Let us now calculate η_2^0:

$$\left.\frac{\partial G}{\partial \tilde\eta_2}\right|_{\tilde\eta_2=0} = 2A_2\eta_2^0+B_2\eta_1^2+2B_3\eta_1\eta_2^0+3B_4(\eta_2^0)^2+C_2\eta_1^3+\dots = 0, \tag{C.5}$$

$$\eta_2^0 \approx \frac{-B_2\eta_1^2}{2A_2+2B_3\eta_1} \approx \text{const}\,\eta_1^2. \tag{C.6}$$

The above equation, (C.6), is valid only for very small η_1. For $\tilde\eta_2 \neq 0$ but small, we may use the expansion:

$$G = \tilde G(\eta_1)+(\tilde\eta_2)^2\tilde A_2+\text{higher terms}, \tag{C.7}$$

where $\tilde A_2 > 0$ and where $\tilde G(\eta_1)$ depends only on η_1. We will not specify the explicit form of $\tilde A_2$ and $\tilde G$. In the neighbourhood of $\eta_1 = 0$ the potential G retains its stability in $\tilde\eta_2$ and it is unstable only in η_1. Therefore, the minimum of G will be for some value of η_1 and for $\tilde\eta_2 = 0$. In other words:

$$\eta_2|_{\text{at minimum}} = \eta_2^0 \approx \text{const}\,\eta_1^2, \tag{C.8}$$

which finally explains equation (B.5).

In conclusion: close to the phase transition point the order parameter η_2 associated with the secondary representation $D^{k'n'}$ is not independent of the first order parameter. To a good approximation η_2 changes as a square of the primary order parameter η_1; therefore it follows that

$$\lim_{\eta_1\to 0} \eta_2/\eta_1 = 0. \tag{C.9}$$

Finally let us note that in equation (C.6) we assumed $B_2 \neq 0$. This in the language of representations can be expressed as: $((D^{kn})^2|D^{k'n'}) \neq 0$. If $B_2 = 0$ and $C_2 \neq 0$ the similar condition should be $((D^{kn})^3|D^{k'n'}) \neq 0$.

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