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## SYMMETRY CHANGES AND DIPOLE ORDERINGS IN THE SMECTIC A TO C PHASE TRANSITIONS OF SECOND ORDER (\*)

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**Résumé.** — L'existence de phases liquide-cristallines présentant un ordre de dipôles moléculaires est discutée. Un argument simple, reposant sur un calcul de champ moyen de l'énergie dipôle-dipôle, est d'abord présenté et permet d'avancer que seule la phase smectique C peut présenter un tel ordre. La théorie de Landau est ensuite utilisée pour étudier la transition du second ordre d'une phase smectique A à une phase smectique C. L'ordre moléculaire et sa symétrie en phase C sont alors déterminés en fonction de la symétrie de la phase A. Une transition du second ordre vers une phase smectique C ferroélectrique n'est possible que dans le cas d'une phase chirale.

**Abstract.** — We investigate the question as to whether there can exist some liquid crystal phases exhibiting dipole ordering. A simple argument based on a mean-field calculation of the dipole-dipole energy alone is presented first to advance the following hypothesis : only in smectic C phases can a certain dipole ordering appear. We then apply Landau theory to study the second-order phase transitions from the A to the C phase. For each symmetry of the A phase we find the allowed molecular orderings and corresponding symmetries in the C phase below  $T_c$ . We also find the dipole orderings allowed in each case considered. We show that a second-order transition to a bulk ferroelectric smectic C phase is not possible, but it is permitted to a smectic C phase with helicoidal arrangement of the dipoles.

**1. Introduction.** — The peculiarity of the liquid crystal phases is that the molecules have orientational order [1, 2], instead of positional order as in solids. In general, the theoretical approach in liquid crystals is based on microscopic models in which the role of different interactions like quadrupolar, Van der Waals, dipolar interaction is considered [3-8].

In the present work, we start from the observation that most of the molecules composing liquid crystals have one or more dipolar bonds. In the past, the

question of dipole ordering in liquid crystals has been often considered theoretically [4] or experimentally [9, 10], but without giving convincing evidence for ferroelectricity in the nematic phase. Recently the interest in this question was renewed by the first clear-cut evidence of dipole ordering in liquid crystals [11, 12]. Meyer *et al.* [11] have shown what the conditions are for the appearance of ferroelectricity in a smectic C phase. They also gave an experimental realization of this phenomenon, having synthesized appropriate materials with chiral molecules.

However, the question of dipole ordering in liquid crystals has not been studied from a general

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point of view, and we try in this paper to give an answer to the following question : what liquid crystal phases can exist with ordered dipoles (any kind of order) ? As we shall see below (section 2), using an argument based on free-energy stability, we find that only the smectic C phases can present dipolar ordering. The second question of interest is : what are the transitions to a smectic C phase which are allowed to be phase transitions of second order ? We deal with this question in section 3 (transition not involving dipole ordering) and in section 4 (transition going with dipole ordering).

## 2. Electrostatic energy due to the dipole-dipole interaction. — 2.1 LIQUID AND NEMATIC PHASES. —

Let us consider a liquid crystal molecule possessing a net dipole moment  $\mathbf{p}$  in its centre. In general the angle between  $\mathbf{p}$  and the long axis of the molecule will have a certain value  $\beta$ . We can calculate the electrostatic energy of the dipoles in various arrangements in the different phases, starting from the expression of the energy of two dipoles

$$E_{ij} = \frac{\mathbf{p}_i \cdot \mathbf{p}_j - 3 \left( \mathbf{p}_i \cdot \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|} \right) \left( \mathbf{p}_j \cdot \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|} \right)}{|\mathbf{r}_{ij}|^3}, \quad (1)$$

where  $\mathbf{r}_{ij}$  is the relative position vector of dipoles  $\mathbf{p}_i$  and  $\mathbf{p}_j$  of molecules  $i$  and  $j$ . The total energy is a sum over all pairs  $i$  and  $j$ . In the normal liquid the molecules wander randomly and the dipoles point in every direction. The total energy per molecule

$$E = \frac{1}{2N} \sum_{i,j} E_{ij}$$

( $N$  is the number of molecules) is obviously zero. In the normal nematic phase the direction of a dipole at each instant forms an angle  $\beta$  with the nematic direction (assuming perfect nematic alignment) and can rotate randomly around this direction ; the up and down directions of the dipoles are also equally probable. It follows that  $E$  is again zero. In a ferroelectric nematic phase with all the dipoles aligned in the  $z$  direction [14] (this is the case of maximum polarization), the energy per molecule can be written as follows (we choose, for the sake of simplicity, each dipole in the center of the molecule) :

$$E = \frac{2\pi}{V} \left[ \int_0^b dz \int_a^\infty E_{ij} \rho d\rho + \int_b^\infty dz \int_0^\infty E_{ij} \rho d\rho \right]. \quad (2)$$

From (1) we can write

$$E_{ij} = \rho^2(\rho^2 + z^2)^{-3/2} - 3 \rho^2 z^2(\rho^2 + z^2)^{-5/2}, \quad (3)$$

where

$$\rho = \sqrt{x^2 + y^2}, \quad (4)$$

$$p = |\mathbf{p}_i| = |\mathbf{p}_j|, \quad \mathbf{r}_{ij} = \sqrt{\rho^2 + z^2}, \quad (5)$$

and  $V$  is the volume per molecule in the sample. The parameters  $a$  and  $b$  are, respectively, the diameter and the length of a molecule, which we consider as a hard cylinder. After performing the integration on  $\rho$  in (2), the second term in square brackets contributes zero and we find :

$$E = \frac{2\pi p^2}{V} \int_0^b dz [(z^2 + a^2)^{-1/2} - z^2(z^2 + a^2)^{-3/2}]. \quad (6)$$

The integrand of (6) is positive for any finite  $z$ , therefore  $E > 0$  and the ferroelectric state has higher energy than the disordered state. Since the entropy of the disordered state is larger than that of the ordered state, we conclude that the ferroelectric nematic is unstable at any temperature with respect to the normal nematic. Our conclusions are not rigorous, because they are based on a mean field calculation, where any correlations between the molecules are neglected. Nevertheless we believe this calculation gives us the right qualitative picture. The evidence presented in references [9] and [10] disagrees with our conclusion. We suggest that a possible explanation of this disagreement is a long relaxation time from the polarized state aligned by the external electric field to the non-polarized nematic state, when the field is turned off. The existence of a ferroelectric nematic phase is not at all proved experimentally, and we feel that there is very little hope of ever finding one.

**2.2 SMECTIC A PHASE. —** We assume now a complete order in layers, and we calculate, as above, the electrostatic energy when all the dipoles are aligned along the direction perpendicular to the layers [15]. The calculation is repeated in the same way as in the previous case except that now the energy has two contributions :  $E_0$ , the electrostatic energy of interaction between molecules located in the same layer, and  $E^*$ , the energy of interaction between molecules located in different layers :

$$E_0 = \frac{\pi p^2}{S} \int_a^\infty \rho^{-2} d\rho, \quad (7)$$

$$E^* = \frac{2\pi p^2}{S} \sum_{n=1}^\infty \int_0^\infty \rho d\rho [(\rho^2 + n^2 b^2)^{-3/2} - 3(nb)^2 (\rho^2 + n^2 b^2)^{-5/2}]. \quad (8)$$

( $S$  is the total area per molecule in a layer,  $b$  is the distance between two successive layers, and  $n$  is the label number of the layer.) It is easy to see that  $E^*$

is zero, and this means that the dipole-dipole interaction between the layers does not contribute to the energy. This result can also be obtained if we calculate the field produced by one layer and acting on a molecule located in another layer. Since all the dipoles in one layer are parallel and the molecules are distributed uniformly, a smectic plane is an infinite dipole layer, outside which the field is zero.

$E_0$  in (7) is equal to  $\pi p^2/Sa$  and is again positive. The smectic A with disordered dipoles (along the long molecular axis) is again more stable than the polarized state. We disagree here with reference [8], where the authors find ferroelectricity in the smectic A phase, but we do not have an explanation for this disagreement.

**2.3 SMECTIC C PHASE.** — We now consider parallel dipoles at an angle  $\alpha$  to the normal to the smectic layers [16]. Choosing the direction of the dipoles in the  $yz$  plane, the components of the dipole  $\mathbf{p}$  are  $(0, p \sin \alpha, p \cos \alpha)$ , and those of the distance  $\mathbf{r}$  between two molecules are  $(\rho \cos \varphi, \rho \sin \varphi)$ , where  $\mathbf{\rho}$  is the projection of  $\mathbf{r}$  on the  $xy$  plane, and  $\varphi$  is the angle between  $\mathbf{\rho}$  and the  $x$  axis.

As above,  $b$  is the distance between the successive layers and  $n$  is the label number of the layer. The interaction energy (1) is

$$E_n = p^2(\rho^2 + n^2 b^2)^{-3/2} - 3p^2(\rho \sin \alpha \sin \varphi + nb \cos \alpha)^2 \times (\rho^2 + n^2 b^2)^{-5/2}. \quad (9)$$

The calculation is performed as in the smectic A phase and we have for the total energy per molecule :

$$E = (2S)^{-1} \left[ 2 \sum_{n=1}^{\infty} \int_0^{2\pi} d\varphi \int_0^{\infty} E_n \rho d\rho + \int_0^{2\pi} d\varphi \int_a^{\infty} E_0 \rho d\rho \right]. \quad (10)$$

The first integral is the interaction energy between molecules located in different layers. This energy is zero and the physical reason is the same as above. The second integral in (10), using (9), gives :

$$E = \frac{\pi p^2}{Sa} [1 - 3 \sin^2 \alpha]. \quad (11)$$

The electrostatic energy (11) has a minimum for  $\alpha = \pi/2$ , i.e. when the dipoles are parallel to the layer. From (11) one can see that  $E$  becomes negative if  $\sin^2 \alpha > 2/3$  or  $\alpha > 55.1^\circ$ . It follows from this that at low enough temperatures a tilted smectic phase with polarized layers can be more stable than a tilted smectic phase with complete disorder between dipoles. The tilt angle  $\alpha$  of the dipoles in the more stable phase must be greater than  $55.1^\circ$ . This ordering in polarized layers does not necessarily mean that the sample is polarized : in fact, since for every

$n \neq 0$  the first integral in (10) is zero, we conclude that the dipole-dipole interaction alone does not correlate different layers. If other interactions can align or correlate the polarizations of different layers, then we obtain the analogue of an *improper ferroelectric* in solids.

In nature one observes only C phases in which the tilt angle of the molecular axis reaches maximum values of about  $45-50^\circ$  [17]. Therefore, if  $\alpha = \theta$  (or  $\beta = 0$ ), one should not obtain a dipole-ordered phase as described above ; but if  $\beta \neq 0$  and freezing of the molecular rotation occurs, then one is likely to obtain such dipole-ordered phase [18].

### 3. Molecular orderings and symmetry changes in the A-C transition.

— The consideration of the possible types of dipole ordering in liquid crystal phases naturally involves the consideration of the possible symmetries of these phases. In particular, the study of dipole orderings that may arise in second-order phase transitions from the smectic A to the C phase necessarily involves the discussion of the molecular orderings and symmetry changes allowed in such transitions.

**3.1 CLASSIFICATION OF SMECTICS ACCORDING TO SYMMETRY.** — Let us first enumerate the possible symmetry groups of the A and C phases, with special attention to the possibility of dipole orderings compatible with these groups. Since a smectic A phase is uniaxial, the local symmetry belongs to one of the continuous groups :  $C_\infty$ ,  $C_{\infty v}$ ,  $C_{\infty h}$ ,  $D_\infty$  and  $D_{\infty h}$ , in Shonflies notation. The symmetry of the phase reflects to a certain extent the symmetry of the molecule itself. For example, the groups  $D_\infty$  and  $C_\infty$  do not contain reflection planes among their symmetry elements, and consequently the molecules are chiral. Among the five groups,  $C_\infty$  and  $C_{\infty v}$  are the only ones that can be ferroelectric, and from what we saw in the previous section we do not expect to observe them in nature. There can still be  $C_\infty$  and  $C_{\infty v}$  phases which are not ferroelectric, and we shall include all the cases in our classification, for the sake of completeness.

The space groups of the uniaxial smectic A phase are *symmorphic*, i.e. they contain the corresponding point groups ( $C_\infty$ ,  $C_{\infty v}$ ,  $C_{\infty h}$ ,  $D_\infty$ ,  $D_{\infty h}$ ) as their subgroups. Therefore, there always exists a point that belongs to the intersection of all point group elements (symmetry axes and planes) of the smectic A phase. For example, any point in a molecular layer (in the middle of its thickness) or in the middle of the distance between two adjacent layers, has such property. In the calculations to follow, we shall put the origin of our reference frame in such a point and direct the  $z$ -axis along the cylindrical axis of symmetry. Following de Gennes [2], one can group the smectic C phases in three classes according to the form of their biaxial tensor :  $C_M$ , C and  $C_G$ .

In the  $C_M$  phase the tilt angle (the angle between the long molecular axis and the  $z$ -axis perpendicular to the layer) is zero but the rotation around  $z$  is frozen. The possible groups of local symmetry [19] are  $C_{2v}$ ,  $C_s$ ,  $C_2$ ,  $C_1$ ; they can all be dipole-ordered in the sense described in the previous section, with the dipoles in the  $xy$ -plane (the layer plane).

In the  $C$  phase (non-zero tilt, long molecular axis in the  $yz$  plane) the groups  $C_{2h}$ ,  $C_s$ ,  $C_2$ ,  $C_1$  of local symmetry are possible. The first one cannot be dipole-ordered; the second can be dipole-ordered with the dipoles along the molecular axis if there is rotation or in the  $yz$ -plane if there is no rotation; the third can be dipole-ordered with the polarization in the  $x$  direction.

In the  $C_G$  phase one has the local symmetry group  $C_1$ .

**3.2 THE RULES OF THE LANDAU THEORY.** — The symmetry changes and molecular orderings occurring in second-order phase transitions must obey certain restrictions according to the Landau theory [13]. These restrictions are as follows :

1) Given the space group  $G_0$  of the higher-symmetry phase, the space group  $G$  of the lower-symmetry phase must be a subgroup of  $G_0$ .

2) The order parameter field describing the ordering in the lower-symmetry phase must transform under the elements of  $G_0$  according to a certain irreducible, or physically irreducible [20], representation  $\mathcal{D}$  of the group  $G_0$ .

3) The symmetric cube  $[\mathcal{D}]^3$  of  $\mathcal{D}$  should not contain the identity representation, i.e. there should be no cubic invariants (with respect to  $G_0$ ) formed from the order parameter.

In addition, there is another condition on  $\mathcal{D}$  which was first proposed in a very restrictive form by Lifshitz [13, 21], and further reinterpreted and reformulated in a weaker form by Dzyaloshinskii [22] and Haas [23]. This condition requires that the representation  $\mathcal{D}$  should correspond to a minimum of a certain function in  $\mathbf{k}$ -space, where  $\mathbf{k}$  is the wave-vector of the representation. (The meaning of this condition in the context of this paper will become clear below.) Another requirement [24] implicitly used in all applications of the Landau theory to particular phase transitions, is that the representation  $\mathcal{D}$  in question should correspond to a certain physical tensor field. In other words, the field of the order parameter must be an irreducible, or physically irreducible part of an appropriate physical tensor field involved in the phase transition.

To our knowledge there is no accepted formalism concerning the space groups and their representations for the liquid crystal phases. Therefore, if we want to avoid the task of building such a formalism it will be enough, for the purposes of the present work, to carry on our discussion on the basis of the appropriate expansion of the free energy and its stability

conditions. This discussion follows the Landau theory closely and will be based implicitly on the group theoretical considerations.

**3.3 FREE ENERGY EXPANSION.** — Since the question of molecular orderings and symmetry changes occurring in second-order transitions is of interest in itself, we will discuss them in the rest of this section, regardless of any dipole orderings which may occur. We postpone the discussion of dipole orderings to the next section.

The proper choice of the tensor field of which the order parameter is an irreducible part, is determined by the fact that the basic feature of the smectic A to C or  $C_G$  phase transition is the appearance of a tilt formed by the long axis of the molecule (more precisely by its direction averaged in time) with respect to the  $z$ -axis. The field of interest must therefore be associated with the *field* of orientations of the long molecular axes. Each direction is characterized by two angles,  $\theta$  and  $\varphi$ , where  $\theta$  is the tilt angle, and  $\varphi$  is the angle between the tilt plane and the  $xz$ -plane. However, the parameters  $\theta$ ,  $\varphi$  themselves do not possess tensor properties, since they do not transform linearly under the operations of the above point groups. One can choose, instead, the products

$$\begin{aligned} Q_{xz} &= n_x n_z = \frac{1}{2} \sin 2\theta \cos \varphi, \\ Q_{yz} &= n_y n_z = \frac{1}{2} \sin 2\theta \sin \varphi \end{aligned} \quad (12)$$

of the Cartesian components of the director  $\mathbf{n}$  [2]. The pair of variables  $Q_{xz}$ ,  $Q_{yz}$  does possess tensor properties and is in one-to-one correspondence with the set of all molecular orientations. Instead of  $Q_{xz}$ ,  $Q_{yz}$ , it is convenient to use the complex variables

$$Q_{\xi z} = Q_{xz} + iQ_{yz}, \quad Q_{\eta z} = Q_{\xi z}^*. \quad (13)$$

We note here that, since the angles  $\theta$  under consideration are small (we deal with second-order transitions),  $Q_{\xi z}$  coincides with de Gennes's order parameter [2]  $\theta e^{i\varphi}$ . However, for our purposes it is more convenient to use the order parameter in the tensorial form (12), (13).

Thus we shall consider the two-component field

$$Q_{\xi z}(x, y, n), \quad Q_{\eta z}(x, y, n), \quad (14)$$

where  $n$  is the number label of the successive molecular layers in the  $z$  direction. This field is continuous in the  $xy$  plane and discrete in the  $z$ -direction. The field of the order parameter of the smectic A to C phase transition is a certain irreducible (or physically irreducible) part of the field (14). Since the quantities  $Q_{\xi z}$  and  $Q_{\eta z}$  transform under an arbitrary rotation about the  $z$ -axis into  $Q_{\xi z} e^{i\psi}$ ,  $Q_{\eta z} e^{-i\psi}$ , respectively, where  $\psi$  is the angle of rotation, no cubic invariants

can be formed from the field (14). It follows that Landau's condition 3 is satisfied.

In the spirit of the Landau theory we must consider the free energy  $F$  at a given temperature  $T$  as a functional of the field (14) that can be expanded in terms of  $Q_{\xi z}$ ,  $Q_{\eta z}$ . Expanding  $F$  to second order in these variables, we can write (neglecting the constant zero-order term)

$$F = \sum_{nn'} \iiint dx dx' dy dy' \times \\ \times A(x, y, n; x' y' n') Q_{\xi z}(x, y, n) \\ \times Q_{\eta z}(x', y', n') + \dots \quad (15)$$

Due to the transformation properties of  $Q_{\xi z}$  and  $Q_{\eta z}$ , expression (15) can be interpreted physically as a quadrupole-quadrupole interaction: it can include Van der Waals forces as well [3, 5, 6]. The free energy must be invariant under the symmetry operations of the smectic A phase in question. Since this phase is homogeneous and isotropic in the  $xy$ -plane, and periodic in the  $z$ -direction, we must have

$$A(x, y, n; x', y', n') = A(\rho^2, n - n'), \quad (16)$$

where

$$\rho^2 = (x - x')^2 + (y - y')^2. \quad (17)$$

Further, since  $F$  is real,

$$A^*(\rho^2, n - n') = A(\rho^2, n' - n). \quad (18)$$

To diagonalize the quadratic functional (15), let us expand the field (14) in Fourier series (this is equivalent to expanding it in terms of irreducible representations of the space group of the smectic A phase):

$$Q_{\xi z}(x, y, n) = \sum_{\mathbf{k}} q(\mathbf{k}) e^{i(k_x x + k_y y)} e^{ik_z n b}, \quad (19)$$

and a similar expansion for  $Q_{\eta z}$ . Note that, because of the periodicity,  $k_z$  varies only in the interval  $[\pi/b, -\pi/b]$ . One can also expand  $A(\rho^2, n - n')$  according to

$$A(\rho^2, n - n') = \sum_{\mathbf{k}} a(\mathbf{k}) e^{i[k_x(x-x') + k_y(y-y') + k_z(n-n')b]}. \quad (20)$$

From (16) and (17) it follows that

$$a(\mathbf{k}) = a(k_0^2, k_z), \quad (21)$$

where

$$k_0^2 = k_x^2 + k_y^2, \quad (22)$$

and from (18) it follows that  $a(k_0^2, k_z)$  is real.

Substituting (19) and (20) into (15) we obtain

$$F = V \sum_{\mathbf{k}} a(k_0^2, k_z) |q_{\xi z}(\mathbf{k})|^2, \quad (23)$$

where  $V$  is the volume of the sample. The coefficients  $a(k_0^2, k_z)$  depend on  $T$  as a parameter.

**3.4 CLASSIFICATION OF THE SMECTIC A-C TRANSITIONS OF SECOND ORDER.** — In the smectic A phase, i.e. at  $T > T_c$ , the minimum of  $F$  must correspond to  $q_{\xi z}(\mathbf{k}) = 0$  for all  $\mathbf{k}$ . Accordingly, for  $T > T_c$ ,  $a(k_0^2, k_z) > 0$  for all  $k_0$  and  $k_z$ . A phase transition to the smectic C phase occurs when the smallest of the coefficients  $a(k_0^2, k_z)$  changes sign [22, 24]. Thus, at  $T = T_c$  the minimum of  $a(k_0^2, k_z)$  as a function of  $k_x, k_y, k_z$  must vanish. The values of  $k_x, k_y, k_z$  corresponding to this minimum are determined by the equations

$$\frac{\partial a}{\partial k_x} = 0, \quad \frac{\partial a}{\partial k_y} = 0, \quad \frac{\partial a}{\partial k_z} = 0. \quad (24)$$

The order parameter field at  $T$  slightly less than  $T_c$  is a superposition of the Fourier components corresponding to those values of  $k_x, k_y, k_z$  at which  $a(k_0^2, k_z)$  has a minimum (this minimum may in general be degenerate, i.e.  $a(k_0^2, k_z)$  may reach its minimum value at more than one point in  $\mathbf{k}$ -space). This is the meaning of the Dzyaloshinskii-Haas condition [22, 23] mentioned above.

Because of the symmetry, i.e. the dependence of  $a$  on  $k_x, k_y$  only in the combination (22), the first two equations in (24) are identically satisfied by

$$k_x = k_y = 0. \quad (25)$$

In principle, there may be other solutions, but only the solution (25) is due to symmetry; a solution with  $k_x, k_y \neq 0$  would also be unphysical since it would imply nonuniformity of the smectic layers along the  $x$  and  $y$  directions.

If the crystallographic class of the smectic A phase is  $C_\infty$  or  $D_\infty$ , the coefficients  $A(x, y, n; x', y', n')$  in (15) do not possess any symmetry properties in addition to (16) and (18). Then the coefficients  $a(\mathbf{k})$  in (20) do not possess any symmetry besides (21). In this case, substituting (25) into the third equation in (24), one obtains an equation which determines  $k_z$  as a function of  $T$ :  $k_z = K(T)$ . The corresponding order parameter is the two-component vector

$$\{q_{\xi z}(K\hat{z}), q_{\eta z}(-K\hat{z})\},$$

and the field of this order parameter is given by

$$Q_{\xi z}(x, y, n) = q_{\xi z}(K\hat{z}) e^{iKnb}. \quad (26)$$

The field (26) describes a helicoidal ordering of the molecules with a wave-vector  $\mathbf{k} = K\hat{z}$ . The dependence of  $K$  on  $T$  cannot be determined from general considerations within the framework of this theory. Thus, the smectic C phase arising at a second-order transition from a smectic A phase belonging to the crystallographic classes  $C_\infty$  or  $D_\infty$ , is helicoidal. This type of smectic C has already been observed [25].

In the cases where the crystallographic class of the smectic A phase is  $C_{\infty v}$ ,  $C_{\infty h}$ , or  $D_{\infty h}$ , the coeffi-

cients  $A(\rho^2, n - n')$  possess an additional symmetry property

$$A(\rho^2, n - n') = A(\rho^2, n' - n). \quad (27)$$

From (20) it follows that

$$a(k_0^2, k_z) = a(k_0^2, -k_z). \quad (28)$$

In view of (28) the third equation in (24) is satisfied identically by  $k_z = 0$  and  $k_z = \pi/b$  [ $a(k_0^2, k_z)$  may be regarded as a periodic function of  $k_z$  with a period  $2\pi/b$  and this fact, together with (27), yields the stationarity of  $a$  at  $k_z = \pi/b$ ].

In the case of  $k_z = 0$ , the field of the order parameter is (taking into account eq. (25))

$$Q_{xz}(x, y, n) = q_{xz}(0) = \text{const.} \quad (29)$$

By an appropriate choice of the direction of the  $y$ -axis in the  $xy$ -plane one can make  $Q_{yz} = 0$  and thus obtain a field

$$Q_{xz}(x, y, n) = \text{const.} \neq 0, \quad Q_{yz}(x, y, n) = 0. \quad (30)$$

This field is invariant under reflection in the  $xz$ -plane and under rotation about the  $y$ -axis. It follows that if the crystallographic class of the smectic A phase is  $C_{\infty v}$ , it decreases to the crystallographic class  $C_s$ . If the crystallographic class of the smectic A phase is  $C_{\infty h}$ , it decreases to  $C_1$ . This transition can be observed in materials with molecules which have only a mirror plane perpendicular to their long axis. Finally, if the initial crystallographic class is  $D_{\infty h}$ , it decreases to  $C_{2h}$ . It seems that a good example of such a second-order transition is given by TBBA.

In the case that the minimum of  $a(k_0^2, k_z)$  appears at  $k_x = k_y = 0$ ,  $k_z = \pi/b$ , we obtain, instead of (30) :

$$\begin{aligned} Q_{xz}(x, y, 2n) &= \text{const.} \neq 0, \\ Q_{xz}(x, y, 2n + 1) &= -Q_{xz}(x, y, 2n), \\ Q_{yz}(x, y, n) &= 0. \end{aligned} \quad (31)$$

In this case the transition to the smectic C phase is accompanied by a doubling of the period in the  $z$ -direction [26] and the  $z$ -axis becomes a screw axis of second order. Further, the field (31) is invariant under reflection in the plane parallel to the  $xy$ -plane and lying halfway between two adjacent layers, and under gliding reflection in the  $yz$ -plane, i.e. reflection combined with a translation in the  $z$ -direction by a half of the new period. Obviously, the field (31) also possesses the point symmetry elements of the field (30). It follows from here that if the smectic A phase belongs to the crystallographic class  $C_{\infty v}$ , it decreases to  $C_{2v}$ ; the corresponding space group has a screw axis and one gliding plane (in a certain sense this space group is analogous to the crystallographic  $C_{2v}^2$  group). The local symmetry is  $C_s$ . If the smectic A phase belongs to the crystallographic class  $C_{\infty h}$ , it decreases to  $C_{2h}$  and the corresponding space group

contains a screw axis (this group is analogous to the crystallographic  $C_{2h}^2$  group). The local symmetry becomes  $C_1$ . Finally, if the smectic A phase belongs to the crystallographic class  $D_{\infty h}$ , it reduces to  $D_{2h}$ ; the space group of the smectic C phase contains again a screw axis ( $z$ -axis) and a gliding plane ( $yz$ -plane). This space group is analogous to the crystallographic  $D_{2h}^5$  group. The local symmetry becomes  $C_{2h}$ . The molecular orderings for the cases  $k_z = 0$  and  $k_z = \pi/b$  are shown in figure 1.

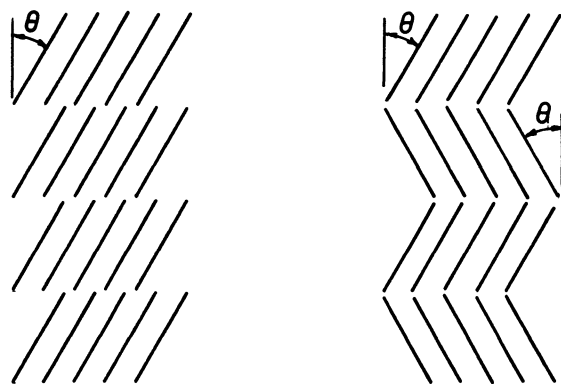


FIG. 1. — Molecular ordering in the smectic C phase : (a) in the case of  $k_z = 0$ ; (b) in the case of  $k_z = \pi/b$ .

Finally, besides minima at  $k_z = 0$  and  $k_z = \pm \pi/b$  due to symmetry, the function  $a(0, k_z)$  may have a minimum at some general  $k_z = K(T)$ . One can show that two possible types of molecular ordering may arise in this case in the smectic C phase : one of them is helicoidal, as discussed before ; the other is sinusoidal, with the tilt being in a single vertical plane and the tilt angle varying from layer to layer as  $\sin Knb$ . The latter type has never been observed in nature.

**4. Dipole ordering.** — We suppose now that the molecules possess a net dipole moment. As a result the molecular ordering occurring in a smectic A to smectic C phase transition may be accompanied by an ordering of the electric dipoles. The question is what kind of dipole ordering can accompany each of the second-order phase transitions mentioned above. Clearly, we need not investigate the transitions from the crystallographic classes  $C_{\infty}$  to  $C_1$ ,  $C_{\infty v}$  to  $C_s$ , and  $C_{\infty v}$  to  $C_{2v}$ , because the corresponding A phases are implied to be dipole-ordered : these are not likely to appear in nature, as we saw in section 2. To describe dipole ordering, let us introduce the field of electric polarization  $\mathbf{P}(x, y, n)$ . For this field to come into play in the phase transitions in question, it must be coupled to the field of molecular orientations (13). The coupling of lowest order is linear in  $Q$  and  $\mathbf{P}$ . It can be interpreted physically as a dipole-quadrupole interaction. Because of the axial symmetry of the smectic A phase, the polarization components that can be coupled to  $Q_{xz}$ ,

$Q_{yz}$  linearly in  $Q_{xz}$ ,  $Q_{yz}$  can be only  $P_x$  and  $P_y$ . Introducing the complex components

$$P_\xi = P_x + iP_y, \quad P_\eta = P_\xi^*, \quad (32)$$

we can now consider the free energy  $F$  as a functional of the fields and write the second-order term in the expansion of  $F$  in the form

$$F = \sum_{nn'} \iiint [A_{11}(\rho^2, n - n') Q_{\xi z}(x, y, n) Q_{\eta z}(x', y', n') + \\ + A_{12}(\rho^2, n - n') Q_{\xi z}(x, y, n) P_\eta(x', y', n') \\ + A_{21}(\rho^2, n - n') P_\xi(x, y, n) Q_{\eta z}(x', y', n') \\ + A_{22}(\rho^2, n - n') P_\xi(x, y, n) P_\eta(x', y', n')] dx dy dx' dy'. \quad (33)$$

The generalization of Eq. (18) is now

$$A_{ij}^*(\rho^2, n - n') = A_{ji}(\rho^2, n' - n). \quad (34)$$

Introducing, by analogy with (19) and (20), the Fourier components  $p_\xi(\mathbf{k})$ ,  $p_\eta(\mathbf{k})$  of  $P_\xi$  and  $P_\eta$ , respectively, and the Fourier components  $a_{ij}(\mathbf{k}) = a_{ij}(k_0^2, k_z)$  of  $A_{ij}$  ( $i, j = 1, 2$ ), we obtain from (33)

$$F = V \sum_{\mathbf{k}} [a_{11}(k_0^2, k_z) |q_{\xi z}(\mathbf{k})|^2 + a_{12}(k_0^2, k_z) q_{\xi z}(\mathbf{k}) p_\xi^*(\mathbf{k}) + \\ + a_{21}(k_0^2, k_z) p_\xi(\mathbf{k}) q_{\xi z}^*(\mathbf{k}) + a_{22}(k_0^2, k_z) |p_\xi(\mathbf{k})|^2] + \text{higher-order terms}; \quad (35)$$

here we have used the obvious relations

$$q_{\xi z}^*(\mathbf{k}) = q_{\eta z}(-\mathbf{k}), \\ p_\xi^*(\mathbf{k}) = p_\eta(-\mathbf{k}). \quad (36)$$

In view of (34), the coefficients  $a_{ij}(k_0^2, k_z)$  obey the hermiticity relations

$$a_{ij}^* = a_{ji}. \quad (37)$$

Hence the expression (35) can be diagonalized by an appropriate unitary transformation from the variables  $q_{\xi z}$ ,  $p_\xi$  to the new variables  $R_\xi$ ,  $T_\xi$  defined by

$$q_{\xi z}(\mathbf{k}) = \alpha_{11}(k_0^2, k_z) R_\xi(\mathbf{k}) + \alpha_{12}(k_0^2, k_z) T_\xi(\mathbf{k}) \\ p_\xi(\mathbf{k}) = \alpha_{21}(k_0^2, k_z) R_\xi(\mathbf{k}) + \alpha_{22}(k_0^2, k_z) T_\xi(\mathbf{k}); \quad (38)$$

$\alpha_{ij}$  are the coefficients of the unitary transformation. After diagonalization, (35) becomes :

$$F = V \sum_{\mathbf{k}} [a_1(k_0^2, k_z) |R_\xi(\mathbf{k})|^2 + \\ + a_2(k_0^2, k_z) |T_\xi(\mathbf{k})|^2] + \dots \quad (39)$$

The new coefficients,  $a_1(k_0^2, k_z)$  and  $a_2(k_0^2, k_z)$ , are the eigenvalues of the matrices  $a_{ij}(k_0^2, k_z)$  and are both positive above  $T_c$ . The phase transition occurs when the smaller of the minima of  $a_1(\mathbf{k})$  and  $a_2(\mathbf{k})$  as functions of  $k_x$ ,  $k_y$ ,  $k_z$ , changes sign from positive to negative at  $T = T_c$ . Without loss of generality, let us assume that the minimum of  $a_1$  is the smaller of the two. We obtain, analogously to eq. (24), the equations

$$\frac{\partial a_1}{\partial k_x} = 0, \quad \frac{\partial a_1}{\partial k_y} = 0, \quad \frac{\partial a_1}{\partial k_z} = 0. \quad (40)$$

Again a solution of the first two equations due to symmetry is  $k_x = k_y = 0$ . When the crystallographic class of the smectic A phase is  $C_\infty$  or  $D_\infty$ , Eq. (40) yield  $k_z = K(T)$ . Accordingly, the order parameter is now  $\{R_\xi(K\hat{z}), R_\xi^*(K\hat{z})\}$ . As for  $T_\xi(\mathbf{k})$ , it must be zero in thermodynamic equilibrium, because  $a_2(\mathbf{k})$  is positive in the vicinity of  $T_c$  ( $a_1 < a_2$ ). It follows from (39) that the smectic A to smectic C transition in question is accompanied by the appearance of two coupled helicoidal fields

$$Q_{\xi z}(x, y, n) = \alpha_{11}(0, K) R_\xi(K\hat{z}) e^{iKnb}, \\ P_\xi(x, y, n) = \alpha_{21}(0, K) R_\xi(K\hat{z}) e^{iKnb}. \quad (41)$$

In a mean field theory, the equilibrium value of  $R_\xi(K\hat{z})$  is proportional to  $(T_c - T)^{1/2}$  and so are the absolute values of both fields (41). The angle between the vector

$$\mathbf{P} = P_x \hat{x} + P_y \hat{y}$$

in a given layer and the tilt plane in this layer is determined by the complex phase of the ratio

$$\alpha_{21}(0, K)/\alpha_{11}(0, K).$$

It can easily be shown that

$$\frac{\alpha_{21}}{\alpha_{11}} = \frac{a_{21}}{a_1 - a_{22}}. \quad (42)$$

Since the denominator on the right-hand side of (42) is real, the angle in question is determined by the phase of  $a_{21}(0, K)$ .

If the crystallographic class of the smectic A phase is  $D_\infty$ , then the free energy  $F$  must be invariant under the rotation through  $\pi$  about the  $x$ -axis, which transforms  $P_\xi(x, y, n)$  into  $P_\eta(x, -y, -n)$  and  $Q_{\xi z}(x, y, n)$



into  $-Q_{\eta z}(x, -y, -n)$ . It follows from this invariance that

$$A_{12}(\rho^2, n - n') = -A_{21}(\rho^2, n - n'), \quad (43)$$

whence

$$a_{12}(k_0^2, k_z) = -a_{21}(k_0^2, k_z). \quad (44)$$

Eq. (44), together with (37), means that  $a_{21}(k_0^2, k_z)$  is purely imaginary, i.e. the phase of  $a_{21}(0, K)$  is  $\pi/2$  and this is also the angle between the layer polarization and the tilt plane. In this case then, the helicoidal smectic C phase has the property that the polarization of the layer is perpendicular to the tilt plane of this layer (and the local symmetry is  $C_2$ ). This seems to be the case for DOBAMBC and related materials studied by the French groups [11, 12, 27]. Meyer *et al.* have already presented a simple symmetry argument to predict the existence of the polarized layer in a smectic C phase (with non-zero tilt angle). However, we have shown that, in this case, a second-order transition is always from the smectic A to a helicoidal ordering. In particular, we rule out the possibility of a second-order transition to a uniformly polarized smectic C (see Table I).

Let us consider the cases where the crystallographic classes of the smectic A phase are  $C_{\infty h}$  and  $D_{\infty h}$ . They contain inversion, transforming  $P_{\xi}(x, y, n)$  into  $-P_{\xi}(-x, -y, -n)$  and  $Q_{\xi z}(x, y, n)$  into

$$Q_{\xi z}(-x, -y, -n).$$

From the invariance of  $F$  under this transformation it follows that

$$\begin{aligned} A_{ii}(\rho^2, n - n') &= A_{ii}(\rho^2, n' - n) \\ A_{ij}(\rho^2, n - n') &= -A_{ij}(\rho^2, n' - n), \quad i \neq j \end{aligned} \quad (45)$$

which is the generalization of eq. (27) for this case. It follows from (45) that

$$\begin{aligned} a_{ii}(k_0^2, k_z) &= a_{ii}(k_0^2, -k_z), \\ a_{ij}(k_0^2, k_z) &= -a_{ij}(k_0^2, -k_z), \quad (i \neq j), \end{aligned} \quad (46)$$

and from this we get

$$a_1(k_0^2, k_z) = a_1(k_0^2, -k_z) \quad (47)$$

with a similar equation for  $a_2$ . So the solutions of (40) due to symmetry are  $k_z = 0, k_z = \pi/b$ . Further,

$$a_{12}(0, 0) = -a_{12}(0, 0) = 0 \quad (48)$$

$$\text{and } a_{12}(0, \pi/b) = -a_{12}(0, \pi/b) = 0,$$

which means that the matrices  $a_{ij}(0, 0)$  and  $a_{ij}(0, \pi/b)$  are diagonal, so that

$$a_1(0, 0) = a_{11}(0, 0), \quad a_1(0, \pi/b) = a_{11}(0, \pi/b),$$

and similarly for  $a_2$ .

The order parameter is  $\{q_{\xi z}(0), q_{\eta z}(0)\}$  or

$$\{q_{\xi z}(\pi\hat{z}/b), q_{\eta z}(\pi\hat{z}/b)\},$$

depending on which of the coefficients  $a_1(0, 0), a_1(0, \pi\hat{z}/b)$  is the smaller one. The polarization components are decoupled from the order parameter; therefore the transition to the smectic C phase is not accompanied by a polarization effect or by dipole ordering. This result is evident in the case of the transitions  $D_{\infty h} \rightarrow C_{2h}$ ,  $D_{\infty h} \rightarrow D_{2h}$ , because in both cases the local symmetry of the smectic C phase is  $C_{2h}$  (see section 3), i.e. nonpolar; however, it is

TABLE I

*Summary of the results concerning the symmetry changes and dipole orderings in a smectic A-C phase transition of second order. The possible transitions are from one of the crystallographic classes in the leftmost column to one of the classes of the other columns, in the same line (and vice versa).*

Crystallographic class of the smectic A	Crystallographic class of the smectic $C_M(\theta = 0)$		Crystallographic class of the smectic C or $C_G(\theta \neq 0)$		Local symmetry of the helicoidal ordering
	$k_z = 0$	$k_z = \pm \pi/b$	$k_z = 0$	$k_z = \pm \pi/b$	
$C_{\infty v}$ (n.p.m.)			$C_s$	$C_{2v}$	
$C_{\infty h}$	$C_s$ (F)*	$C_{2h}$ (AF)	$C_1$ (n.d.o.)	$C_{2h}$	
$D_{\infty h}$	$C_{2v}$ (F)*	$D_{2h}$ (AF)	$C_{2h}$	$D_{2h}$	
$C_{\infty}$ (n.p.m.)					$C_1$
$D_{\infty}$					$C_2$ (dipole-ordered)

n.p.m. = non polar molecules

n.d.o. = no dipole ordering (even if the molecules have a net dipole moment)

F = ferroelectric (in the bulk)

AF = antiferroelectric

\* =  $\mathbf{P}$  in the  $xy$ -plane.

not obvious in the case of the transitions  $C_{\infty h} \rightarrow C_1$ ,  $C_{\infty h} \rightarrow C_{2h}$ , with local symmetry becoming  $C_1$ .

It may happen that the smaller eigenvalue is  $a_2(0, 0)$  or  $a_2(0, \pi/b)$  instead of  $a_1(0, 0)$  or  $a_1(0, \pi/b)$ . Then the order parameter of the phase transition is  $\{p_\xi(0), p_\eta(0)\}$  or  $\{p_\xi(\pi\hat{z}/b), p_\eta(\pi\hat{z}/b)\}$ , respectively. In both cases the C phase is of the type  $C_M$  (without tilt) and is ferroelectric or antiferroelectric, respectively [2, 4]. In the first case, if the crystallographic classes in the smectic A phase are  $C_{\infty h}$  or  $D_{\infty h}$ , then in the  $C_M$  phase they are respectively  $C_s$  (reflection in the  $xy$  plane) and  $C_{2v}$ . In the second case, the transition is from  $C_{\infty h}$  to  $C_{2h}$  and from  $D_{\infty h}$  to  $D_{2h}$ , with doubling of the periodicity along  $z$  (the  $z$  axis becomes a screw axis of second order).

Finally, dipole orderings may accompany transitions to helicoidal or sinusoidal smectic C phases from smectic A phases belonging to the crystallographic classes  $C_{\infty h}$ ,  $D_{\infty h}$ . We shall not discuss them here.

Within the smectic C phase additional second-order phase transitions may occur : from point group  $C_{2h}$  to  $C_s$ ,  $C_2$  or  $C_1$ ; from  $D_{2h}$  to  $C_{2v}$ ,  $C_{2h}$  or  $D_2$ , and from  $C_{2v}$  to  $C_2$  or  $C_s$ . The transitions  $C_{2h} \rightarrow C_s$ ,  $C_{2h} \rightarrow C_2$ ,  $D_{2h} \rightarrow C_{2v}$  can be accompanied by the appearance of bulk ferroelectricity.

To conclude with an example, consider the case of a polar molecule with the dipole component along the molecular axis. In the smectic A phase, the most favourable state is one with the dipoles of different molecules oriented in opposite directions at random, as we saw in section 2. The symmetry groups can be  $C_{\infty h}$  or  $D_{\infty h}$  (with a mirror plane perpendicular to the  $\infty$ -fold axis). Therefore the transition to a bulk ferroelectric can be only a first order transition.

**5. Conclusion.** — In the present paper we have discussed the possible symmetry of the smectic A and C phases of liquid crystals, and all the possible symmetry changes allowed at second-order transitions between them in the presence and in the absence of dipole ordering. We have also given a simple argument based on free energy considerations to find out in which phases one can expect dipole ordering of some sort.

The most interesting results can be summarized as follows :

From a mean-field calculation of the electrostatic energy of the molecular dipoles, it follows that one can expect alignment of the dipoles only in smectic C

phase and not in nematic or smectic A : this alignment is ferroelectric within the same smectic layer, but the sample can have bulk polarization only if other interactions are present.

The five crystallographic classes of the smectic A phase are discussed separately, by examining in each case the possible phase transitions of second order to the different C phases. The discussion is presented first in terms of molecular ordering regardless of dipole ordering, and then considering also the dipole ordering, on the basis of the Landau theory of second-order phase transitions. Table I summarizes the results of this discussion.

In particular :

1) When the A phase belongs to the class  $D_{\infty}$ , the C phase is tilted, with the long molecular axis precessing from layer to layer around the  $z$  direction. Furthermore, each layer is polarized and the polarization precesses also, always being perpendicular to the tilt plane. As mentioned above, this case of ordering has been already predicted by Meyer *et al.* [11] and observed experimentally [11, 12]. Our conclusion is in complete agreement with their results (second-order transition from the A phase to the C phase), since the chiral molecules of the ferroelectric compound DOBAMBC give effectively a smectic A phase belonging to the class  $D_{\infty}$ . We show here that it is the only possible realization of a smectic A-smectic C second-order transition in which a tilt and a polarization appear together in the layer. A more detailed theory will be published in a forthcoming paper [28].

2) When the A phase belongs to one of the classes  $C_{\infty h}$  or  $D_{\infty h}$ , the C phase below a second-order transition cannot be tilted and dipole-ordered at the same time. We do not rule out the possibility of a first-order transition leading to such a phase.

The model studied in detail by McMillan [4] corresponds to the transitions  $A \rightarrow C_{2v}(F) \rightarrow C_2(F)$  or  $A \rightarrow C_{2h} \rightarrow C_2(F)$ , with all the transitions being of second order. In agreement with our analysis the molecules of this model are compatible with a smectic A phase belonging to the class  $D_{\infty h}$ .

*Note.* — After this paper had been submitted, we learnt about the work of Indenbom *et al.* [29], who applied a more formal group-theoretical approach to determine the possible second-order phase transitions from the smectic A phase to phases with lower symmetry. Their results are similar to those we have obtained ; however, in contrast to their paper, we try to give a more physical picture.

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- [15] This is a smectic A phase only in the case analogous to i) and ii) of footnote 14, applied to smectics. If  $\beta \neq 0$ , and the rotation is frozen [case iii)], it is a smectic  $C_M$ .
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