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Two-Dimensional Order in Liquid Crystals: a Phenomenological Approach

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The two-dimensional ordering reported for a number of smectic and discotic phases is discussed in the framework of the Landau theory. It is shown that, within a phenomenological approach, distinction should be made between the long-range bond-orientational order, the in-plane positional order, and the orientational (tilting) ordering of the molecules. Accordingly, the configuration of the smectic liquid crystal phases B_H , C , F , and smectic crystal phases I , J , G , H , K , E are shown to be related to irreducible degrees of freedom of definite parent smectic phases. Along the same line, discotic phases are shown to be induced by specific irreducible representations of the nematic phase.

§1. Introduction

The smectic A (S_A) phase has a discrete one-dimensional translational order along the direction perpendicular to the layers, and no long-range positional order within the layers, i.e. the in-plane correlations are liquid like. In the hexatic smectic B_H (S_{B_H}), the packing of the molecules possesses a sixfold symmetry which denotes a long-range bond-orientational order,¹⁾ the in-plane positional correlation length being shortrange (e.g., of about a few hundred Ångströms). The smectic C (S_C) and F (S_F) phases are the tilted analogues of the S_A and S_{B_H} phases respectively.²⁾

A much longer range of correlation appears for the in-plane translational order in another hexatic phase, namely the smectic I (S_I) phase.³⁾ This phase, which is most commonly observed between the S_C and S_F phases, exhibits within each layer both long-range (or quasi-long-range⁴⁾) bond-orientational and positional orders. Such a dual type of two-dimensional long-range ordering is also found within the layers of the other main types of already identified smectic phases, labelled B_C , J , G , E , H , and K .⁵⁾ These three-dimensional systems can be differentiated: 1) by the packing of the molecules in the layers which are respectively hexagonal or pseudo-hexagonal (S_{B_C} , S_J , and S_G), orthorhombic (S_E), and monoclinic (S_H , S_K); 2) by the molecular orientation which can be orthogonal to the layers (S_{B_C} , S_E), tilted to apex (S_I) or side (S_G) of the hexagon, to a corner or to the side of the monoclinic net (S_H , S_K).

Another example of two-dimensional ordering is realized with the so-called columnar discotic phases.^{6,7)} Here, the molecules are packed to form one-dimensional columns with an irregular distribution of their center of gravity along the axis, the columns themselves forming a regular two-dimensional hexagonal lattice, whose plane is parallel to the plane of the molecules.

Three essentially different types of symmetry breaking mechanisms can be distinguished among the preceding transitions: 1) At the S_A – S_{B_H} or S_C – S_F transitions, a two-dimensional bond orientational order takes place. 2) A two-dimensional long-range in-plane positional order arises at the S_C – S_I , S_F – S_I , S_F – S_G , S_{B_H} – S_{B_C} , S_C – S_H or nematic-discotic transitions. 3) At the S_A – S_C or S_{B_C} – S_H modifications the breaking of symmetry consists only in molecular reorientation ("tilting"

symmetry breaking).

The present paper deals with the phenomenological approach of the preceding categories of transitions in the framework of the Landau theory. The group-theoretical considerations which are necessary for this approach are examined in §2. In §3 some illustrative examples are briefly discussed.

§2. Symmetry groups and irreducible degrees of freedom

The space-group of a liquid crystal phase can be written:^{8,9)}

$$S = T \wedge G \quad (1)$$

i.e., as the semi-direct product of a group of translation T by the group of symmetry operations G which leave invariant the molecular subunit (i.e. the molecules and their packing). As we deal with elongated molecules, G is necessarily a continuous or discrete subgroup of $\infty.m$: m ($D_{\infty h}$ in the Schönflies notation), at least if we do not consider the isotropic phase. T can be composed of continuous and discrete translations. For example, for the one-dimensional smectics (S_A , S_C , S_I , S_{B_H}), $T = R^2 \otimes (d)$, where \otimes denotes the direct product of the two-dimensional group R^2 of continuous in-layer translations, by the group (d) of discrete translations in one dimension (d symbolizes the interlayer distance). In Table I columns (f) and (g) provide respectively, for each liquid-crystal phase under consideration, the group G currently admitted,^{2,10,11)} and the corresponding translation group T .

From Table I, one can see that some important features of the various smectic phases, such as the orientation and packing of the molecules, are not always distinguished by the associated group G . Thus, smectic phases displaying different molecular packings, such as the S_C and S_F phases, or the S_J and S_I phases, are associated with the same monoclinic C_{2h} group. Such a confusion is due to the fact that G is currently assumed to account for the overall macroscopic point symmetry of the molecular arrangement *including the tilting of the molecules* (which lowers a $D_{\infty h}$ symmetry to monoclinic). This shortcoming can be corrected by considering that the G group *expresses exclusively the packing of the center of gravity of the molecular clusters*, an eventual tilting of the molecules being taken into account by an additional degree of freedom.

Table I. Symmetry properties of the main smectic phases (from ref. 5) and discotic phase. In column (f) the highest possible G group is given.

(a) Phase	(b) Bond-orient. ordering	(c) In-plane position. ordering	(d) Molecular orientation	(e) Molecular packing	(f) G	(g) T	(h) Parent phase
S_A S_C S_{BH} S_F	Short Range	Short Range	Ortho	Random	$D_{\infty h}$	$R^2 \otimes (d)$	N
			Tilted	Random	C_{2h}		S_A
			Ortho		D_{6h}		S_A
			Tilted (side)		C_{2h}		S_C
S_I	Long Range	Long Range	Tilted (apex)	Hexag.	C_{2h}	$Z^2 \otimes (d)$	S_C, S_F
S_{BC}			Ortho		D_{6h}		S_C, S_{BH}
S_J			Tilted (apex)		C_{2h}		S_C, S_F
S_G			Tilted (side)	Orthorh. Monocl. Monocl. Hexag.	C_{2h}		S_C, S_F
S_E			Ortho		D_{2h}		S_A, S_{BC}
S_H			Tilted		C_{2h}		S_C, S_{BC}
S_K			Tilted		C_{2h}		S_C
Disc.			Ortho		D_{6h}	$Z^2 \otimes R$	N

For a phenomenological approach of phase transitions between liquid crystal phases, one needs to identify: 1) *the high temperature parent phase*. Due to the complexity of the phase diagrams in liquid crystal systems, the choice of the relevant parent phase is not always obvious and is not necessarily, as for crystalline transitions, the more symmetric phase observed in a given sequence of phases. In column (h) of Table I the more natural parent phase, on the basis of symmetry, is given for each low-temperature phase listed in column (a). 2) *The irreducible representation (IR) of the parent phase inducing the observed symmetry modification*. Such an IR can be denoted $\Gamma_m(k^*)$ where k^* is the star of the wave-vector k lying in the first Brillouin-zone (BZ) associated with the parent phase.¹²⁾ In the examples discussed in §3, it is suggested that one should refer to a one, two or three dimensional BZ depending on the maximal dimensionality of the considered high and low symmetry phases. In the notation of the IR the index m is indicative of the chosen IR of the group of the k -vector G_k ,¹²⁾ which is spanned by the basis functions:¹³⁾

$$\exp(i\mathbf{k} \cdot \mathbf{r}) \cdot Y_{\pm m}^l(\theta, \varphi) \quad (2)$$

where \mathbf{r} locates the average position of the molecular subunit, while the angles (θ, φ) characterize the molecular orientation (the tilting angle) with respect to a fixed frame of reference. The spherical harmonics $Y_m^l(\theta, \varphi)$ are such that for fixed m and different l , the same IR is obtained.

§3. Illustrative examples

Let us first consider the transitions which may take place directly from a S_A phase with $G = \infty: 2$ (D_∞) (the cases of a S_A phase with $G = \infty \cdot m$: m and $G = \infty \cdot m$ have been already discussed in refs. 14 and 15). We can initially examine the simplest situation where the transitions lead to a smectic phase with no tilting of the molecules, and a one-dimensional translational order. Accordingly, the corresponding IR's are associated with a one dimensional BZ, i.e. with values of k comprised between $-(\pi/d)$

Table II. Low-symmetry groups (column (c)) induced by the IR's of a smectic S_A phase with $G = \infty: 2$ and $T = R^2 \otimes (d)$. (a): different classes of IR's; (b) characters of the IR's. The notation are the same as in ref. 14.

(a) $S = T \infty: 2$	(b) $(C(\phi) t)$	(c) Low-symmetry group
$K=0$		
A_1	1	$\infty: 2(d)$
A_2	1	$\infty(d)$
E_{n1}	$2 \cos n\phi$	$n: 2(d)$
$K=K_0/2$		
A_3	-1	$\infty: 2(2d)$
A_4	-1	$\infty: 2(2d)$
E_{n2}	$-2 \cos n\phi$	$(2n)_n: 2(2d)$
$K=K_0/n_0$		
E_k	$2 \cos kd$	$\infty: 2(n_0d), \infty(n_0d)$
G_{nk}	$4 \cos n\phi \cos kd$	$\begin{cases} (n_0n)_n(n_0d) \\ (n_0n)_n: 2(n_0d) \end{cases}$

d) and (π/d) , where d is the interlayer distance in the high-temperature phase. As can be seen in Table II, three different classes of IR's are found depending if k is located at the center ($k=2\pi/d \equiv 0$), the surface ($k=\pm\pi/d$), or inside the first BZ. At the utmost the star k^* possesses two arms $\pm k$ and IR's are four-dimensional.

The results of Table II can be summarized as follows:

1) The one-dimensional IR's A_1, A_2 ($k=0$), A_3, A_4 ($k=\pm\pi/d$), and the two-dimensional IR E_k ($k<\pi/d$), are associated to S_A-S_A transitions, with respectively the same G -symmetry (A_1), a lowering of the continuous $\infty: 2$ symmetry, a doubling of the translation along the C axis (A_3, A_4), and a multilayer ordering (E_k). Such IR's are not of interest in the present study.

2) The two-dimensional IR's E_{n1}, E_{n2} , and the four-dimensional IR's G_{nk} lead to a breaking of the continuous S_A symmetry, with the onset of n -fold axes symmetry groups. *This can be interpreted as the induction of a two-dimensional bond-orientational ordering within the smectic layers*. Thus, E_{11} give rise to a monoclinic packing of the molecules. Similarly $E_{21}, E_{31}, E_{41}, E_{51} \dots$ are respectively associated with molecular packing

having respectively an orthorhombic, trigonal, tetragonal, pentagonal... symmetry. E_{61} induces a S_{B_H} phase with $G=622$, an hexatic phase being also related to E_{62} and G_{6k} , with respectively a bilayer and multilayer ordering.

The generalisation of the preceding approach to the case where a long-range positional order takes place within the layers, possibly accompanied by a modification in the packing of the molecules, but with no tilting of the molecules, as in the S_A-S_E or $S_{B_H}-S_C$ transitions, requires use of a three-dimensional BZ. More precisely, in addition to the one-dimensional BZ corresponding in real space to the stacking of the layers, one has to consider a virtual two-dimensional BZ reflecting the existence of pretransitional effects that will lead to the breaking of the continuous translational symmetry within the smectic layers (e.g. at the $S_A-S_{B_C}$ transition). Except the selection of the active stars k^* , the practical procedure for treating such situations is similar to the one used for crystalline transitions and will not be illustrated here.

The case of transitions involving a molecular tilting, such as the S_A-S_C or S_F-S_I transitions, is more cumbersome as one has to make use of the general form for the basis function (2). For example, at the S_A-S_C transition, the suitable basis functions corresponding to the tilting symmetry breaking (the in-plane packing remaining isotropic) are:¹³⁾

$$D_{n0}^{21}(0, \eta, 0) Y_n^{21}(\theta, \varphi) - Y_0^{21}(\theta, \varphi) \quad (3)$$

where η is the tilting angle. The functions D_{mn}^l are the Wigner spherical rotator functions, the argument of which are three Euler angles,¹⁶⁾ which account for the orientational degrees of freedom of the molecules.

The remaining transitions listed in Table I, involving smectic phases, can be treated by using part or combinations of the preceding mechanisms. Thus, at the S_C-S_F transition, the tilting angle remains fixed, and a sole bond-orientational ordering takes place. The transitions from the S_C phase to the S_I, S_J, S_G, S_H or S_K phases involve simultaneously a change of the tilting angle, and of the bond-orientational and in-plane translational orders.

Finally we briefly discuss the symmetry approach to the nematic-discotic transition, considering again a $\infty:2$ symmetry group for the molecular subunits in the nematic phase. The onset of a two-dimensional translational order below the transition, requires to assume a two-dimensional virtual BZ with, let say, the two basic reciprocal space vectors $2\pi/a, 2\pi/b$. The symmetry assumed for the BZ will determine the type of transla-

Table III. Two-dimensional symmetry groups induced by the IR's of a nematic phase with $G=\infty:2$ and $T=Z^2 \otimes R$, at a two-arms star k^* located inside the virtual BZ ($2\pi/a, 2\pi/b$). Same notation as in ref. 14.

(a) $S=T\infty:2$	(b) $(C(\phi) \alpha)$	(c) $(U_2(\phi) \phi)$	Low-symmetry group
$\begin{cases} k \neq 0 E_k \\ k \in Z^2 G_{nk} \end{cases}$	$\begin{cases} 2 \cos kd \\ 4 \cos n\phi \cos kd \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} \infty:2(Z^2) \\ \begin{cases} n(Z^2) \\ n:2(Z^2) \end{cases} \end{cases}$

tional symmetry i.e. the Bravais lattice associated with the discotic state. In Table III the IR's corresponding to a two-arms star k^* ($\pm k$) have been considered. Thus, two classes of transitions are obtained. A first class is connected with the two-dimensional IR's E_k and do not involve any breaking of the molecular symmetry i.e. one gets a two-dimensional lattice of molecules which retain the $\infty:2$ local symmetry. Accordingly, one cannot speak of a true two-dimensional order but only of a quasi long-range two-dimensional positional order. The transitions induced by the four-dimensional IR's G_{nk} lead by contrast, to molecular packings displaying a discrete symmetry. Actually two possible configurations are found to be stable, having respectively the symmetry groups $G=n$ and $G=n:2$. Only this latter situation can be interpreted as a genuine discotic order with a true long-range positional order in the planes perpendicular to the molecular columns.

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