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Unusual Sequences of Tilted Smectic Phases in Liquid Crystals of Bent-Shape Molecules

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The first theoretical description of the experimentally often-observed isotropic-polar smectic phase transitions of symmetric and asymmetric bent-shape molecules is presented. The isotropic-tilted polar smectic phase transition requires a coupling among three types of ordering processes: polar packing, director tilt, and layer ordering. For explaining the unusual triclinic-monoclinic phase transition with the lower symmetry phase at higher temperature, observed in fluoro-containing compounds recently, a mechanism is proposed in which the layer ordering triggers the simultaneous onset of the tilt and polar order.

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Liquid crystals of bent-shape (“banana-shaped” or “bow-like”) molecules [1,2] represent the first example of bulk liquid crystals with chiral structures without chiral molecules [3,4]. Bent-shape molecules have no cylindrical symmetry, and two unit vectors \( \hat{l} \) and \( \hat{m} \) are needed for their description: \( \hat{m} \) is normal to the average molecular plane, and \( \hat{l} \) is along the average long axis (director), which is defined as the line connecting the two ends of the average molecules. Because of the most efficient packing of the molecules each layer becomes polar [4] described by the layer polarization \( \hat{P} \). For symmetric molecules with equal arms of achiral \( C_{2v} \) symmetry, the local average of the dipole moments \( \hat{P} \) is perpendicular to both \( \hat{m} \) and \( \hat{l} \). The average molecular orientation in a layer is represented by the axial vector \( \vec{\xi} = \hat{l} \times \hat{n} \), which measures the tilt \( (|\vec{\xi}| = \sin \theta) \) with respect to the layer normal \( \hat{n} \). All polar smectic phases of bent-shape molecules can be described by two angles: the tilt angle \( \theta \) and the angle \( \psi \) between \( \vec{\xi} \) and \( \hat{P} \). The structure of the most general double-tilted configuration of bent-shape molecules is shown in Fig. 1. \( \hat{P} \) and \( \vec{\xi} \) have distinct symmetries, and they are biquadratically coupled in contrast to the bilinear coupling valid for rod-shaped liquid crystal molecules possessing SmA-SmA transitions.

In bent-shape molecules the tilted smectic mesophases [5] often appear directly below the isotropic liquid without intermediate nematic and smectic \( A \) phases that are usual in calamitic liquid crystalline materials [6]. Another remarkable feature of the sequences of polar smectic “banana” phases has been observed recently in two fluoro-containing liquid crystals [7–9]. In these systems two types of tilted polar smectic phases appear below the isotropic phase, and the higher temperature smectic phase has a lower-triclinic symmetry than the lower temperature monoclinic smectic phase. In a symmetric material 1,3-phenylene-bis[4-(3-fluoro-4-decylxyloxyphenyliminomethyl)benzoate] (PFD) [10] the smectic phases are separated by a second-order transition, and both phases have antiferroelectric configurations. The low temperature phase of PFD has chiral \( C_{2} \) symmetry with the same tilt angles in the subsequent layers [Fig. 2(b)]. The high temperature phase of PFD has a double-tilted phase with \( C_{1} \) symmetry, where both the molecular plane and the director tilt are the same in the subsequent layers [8,9]. In 1,3-biphenylene-bis[4-(3-fluoro-4-octyloxyphenyliminomethyl)benzoate] (PFO), which is composed of asymmetric molecules [7], the low temperature phase has \( C_{2} \) symmetry with antiferroelectric polar order [Fig. 2(a)]. The high temperature phase is ferroelectric with \( C_{1} \) symmetry and with the same leaning and clinic directions in subsequent layers [Fig. 2(c)]. The transition between the two tilted smectic phases of PFO is weakly first order.

An increasing symmetry on cooling is very unusual in condensed matter. Although there are a few exceptions in some crystals, as in Rochelle salt [11] or in reentrant liquid crystal phases [12,13], to our best knowledge, the recent observations in the “banana smectics” are unique in the sense that the lowest symmetric phase occurs directly below the melt. Existing theories [14] assume

![Fig. 1. Layer structure of the most general double-tilted phase characterized by the angles \( \theta \) and \( \psi \).](image-url)
that the polar phase appears below a nonpolar SmA phase and that the molecules are symmetric. To describe the direct isotropic-polar smectic transitions for both symmetric and nonsymmetric [15] bent-shape molecules, a new theory is needed. This motivated us to investigate if a Landau-type theory can describe such phase sequences. Here we show that this unusual sequence of phase symmetries can be explained by a mechanism in which the mass density-wave instability triggers two other (tilt and polarization) instabilities involved in the formation of ferroelectric and antiferroelectric smectic banana phases.

We start our analysis considering the free-energy expansion of Roy et al. [14], assuming that the polar phase appears below a nonpolar SmA phase. In this case only the coupled $\hat{P}$ and $\vec{\xi}$ instabilities have to be considered and the covariant form of the homogeneous part of the free-energy density is given by

$$F_1(\xi, \vec{P}, \vec{I}, \vec{n}) = \frac{a}{2} \xi^2 + \frac{b}{4} \xi^4 + \frac{c}{6} \xi^6 + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 + \frac{\gamma}{6} P^6 + \delta_1 P^2 \xi^2 + C_1(\vec{\xi} \cdot \vec{P})^2 + \frac{1}{2\chi_0} (\vec{I} \cdot \vec{P})^2 + \frac{1}{2\chi_1} (\vec{n} \cdot \vec{P})^2$$

For symmetric molecules $\vec{I} \cdot \vec{P} = 0$ and $F_1$ reads

$$F_1(\vec{\xi}, \vec{P}, \psi) = \frac{a}{2} \xi^2 + \frac{b}{4} \xi^4 + \frac{c}{6} \xi^6 + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 + \frac{\gamma}{6} P^6 - \frac{\gamma_1}{2} \xi^2 P^2 \cos 2\psi + \delta \xi^2 P^2 + \text{H.O.T.}$$

where $\delta = \delta_1 + \frac{1}{2}(C_1 + \frac{1}{6\chi_1})$ and $\gamma_1 = \frac{1}{2}(\frac{1}{\chi_1} - C_1)$. The absolute minima of $F_1(\vec{\xi}, P, \psi)$ yield [14] a nonpolar phase with $C_{2h}$ symmetry corresponding to a normal SmC phase, and the following four polar layer configurations, which were also predicted by Brand et al. [16]

(a) A transversely polarized biaxial SmA phase with $C_{2h}$, achiral symmetry, where both $\vec{m}$ and $\vec{I}$ are perpendicular to the layer normal $\vec{n}$, i.e., $\xi = 0$ [see Fig. 3(a)]. In the literature this phase is referred to as either SmA$P$ or SmA$_B$ [4], or as SmC$_F$ [16], and was recently found below a nonpolar SmA phase [17].

(b) A transversely polarized SmC$^*$-type layer structure for $\psi = 0$, or $\pi$ with $\vec{P}$ normal to the tilt plane [Fig. 3(b)]. It has the standard monoclinic chiral symmetry $C_2$, and is referred to as $B_2$ [18] or SmC$^P$ ($P$ stands for “polar”) or SmC$_{B2}$ [16]. In banana systems this phase usually appears below the isotropic liquid. Note that in the preceding structures the polarization may alternate between layers and the twofold axis may become a twofold screw axis.

(c) An achiral layer structure with monoclinic $C_2$ symmetry for $\psi = \pm \pi$, in which the tilt plane ($\vec{I}, \vec{n}$) is a mirror plane containing the polarization $\vec{P}$, which has both transverse ($\vec{P}_t$) and longitudinal ($\vec{P}_l$) components [Fig. 3(c)]. It has been named as SmC$_{B1}$ [16] but experimentally it has not yet been observed.

(d) A general chiral configuration with triclinic symmetry $C_1$ [Fig. 3(d)]. It has both $\vec{P}_t$ and $\vec{P}_l$ components.

FIG. 2. Structures of the phases with $C_1$ and $C_2$ layer symmetry of fluoro-containing bent-shape molecules. (a) The lower temperature phase of both the symmetric and the asymmetric molecules; (b) the higher temperature phase of the symmetric molecules; (c) the higher temperature phase of the asymmetric molecules.

FIG. 3. Stable polar smectic phases of bent-shape molecules: (a) biaxial smectic A-type phase with $C_{2v}$ symmetry; (b) polar tilted phase with chiral $C_2$ symmetry; (c) polar tilted phase with achiral $C_2$ symmetry; and (d) double tilted polar smectic phase with chiral triclinic $C_1$ symmetry.
and it is obtained for an arbitrary angle \( \psi \) when considering at least eight-degree invariants (e.g., \( a\gamma \xi^4 P^4 \cos^2 2\psi \)). Experimental evidences of this phase were found recently both in freestanding films [19] and in bulk samples [20] below the isotropic phase.

In the following we will simply refer to the phases by their symmetry as \( C_2, C_{2h}, C_1 \), etc.

For asymmetric molecules with different arms and achiral \( C_\alpha \) symmetry \( \vec{P} \) is perpendicular to \( \vec{n} \) but not to \( \vec{l} \), and \( l \cdot \vec{P} = P \xi \sin \psi (1 + \cos \theta) \neq 0 \). The free-energy density becomes \( F_2(\xi, P, \psi, \theta) = F_1(\xi, P, \psi) + C(\psi)^2 \xi^2 \sin^2 \psi \), where \( C(\psi) = 1 + \cos \theta \left[ \frac{1}{2} + \frac{1}{2} \psi \cos \theta (\frac{\psi}{2} + d_1) \right] \). The constant \( C(\psi) \) additional invariant leads to a simple renormalization of the \( \delta \) and \( \gamma_1 \) coefficients in Eq. (2), which are replaced by \( \delta' = \delta + \frac{1}{2} C(\psi) \) and \( \gamma_1' = \gamma_1 + \frac{1}{2} C(\psi) \). Therefore, the molecular asymmetry does not modify the set of stable configurations, but induces only a \( \theta \) dependence of the orientation of the polarization vector \( \vec{P} \) with respect to the director \( \vec{l} \). Note that this configuration becomes noninvariant to the \( \vec{l} \rightarrow -\vec{l} \) symmetry.

The isotropic-tilted smectic phase transition requires a coupling between the polar orientational order described by \( \vec{P} \), the director tilt \( \vec{\xi} \), and the layer order represented by a scalar mass density wave \( \rho(z) = \rho e^{i\vec{K} \cdot \vec{z}} \). Here \( \rho \) and \( \vec{K} \) are the amplitude and phase of the mass density wave order parameter, and \( \vec{K} \) is the wave vector along the layer normal determining the layer spacing \( d = \frac{2\pi}{\vec{K}} \). Note that three order-parameters are implicitly involved for the SmC* phase of rodlike molecules, but there the phase usually appears below the SmA phase and the layer order can be neglected. In addition, in SmC* phase the polarization and the tilt order-parameters linearly couple, whereas in “banana smectics” the tilt and polarization order have distinct symmetries and are bi-quadratically coupled.

To obtain a full set of stable states associated with a given order-parameter symmetry [21] one has to cut the order-parameter expansion at not less than degree \( 2n \) \((n \) is the highest degree order-parameter invariant), and at the degree of \( 2n + 2 \), to describe a first order transition. In the present case \( n = 4 \), meaning that we need a 10th order expansion.

With these considerations one can write the free-energy density as

\[
F_3(\xi, P, \psi, \rho) = F_2(\xi, P, \psi) + \gamma_2 P^4 \xi^4 \cos^2 2\psi + \delta'_1 \xi^6 P^4 + \delta'_2 \xi^4 P^6 \\
+ \frac{C_1}{2} \rho^2 + \frac{C_2}{4} \rho^4 + (\mu_1 P^2 + \mu_2 \xi^2) \rho^2. \tag{3}
\]

In this equation both the mass density contribution and the coupling between \( \rho, P, \xi \) and \( \psi \) are taken into account, but only those invariants have been kept that ensure the stability for all phases. Based on the catastrophe theory of phase transitions [21] it can be shown that all other invariants have no influence on the structural stability of the phase diagrams, but only modify the shape of the transition lines or the width of the stability regions.

Using an expansion with two order-parameters, Holovkovsky demonstrated [22] that an order-parameter (taken up to the fourth degree) can directly trigger a nonzero order-parameter (expanded up to a higher degree), if there exists a biquadratic coupling between the two order-parameters. In our case the mass density-wave \( \rho \) (as triggering order-parameter) and the polarization \( P \) or tilt \( \xi \) (as triggered order-parameters) satisfy these conditions. When \( \mu_1 < 0, \mu_2 < 0, \beta - \frac{\mu_1^2}{C_2} < -4 \sqrt{\frac{\mu_2}{C_1}} \), and \( \beta - \frac{\mu_1^2}{C_1} < 4 \sqrt{\frac{\mu_2}{C_2}} < 0 \), only these phases appear below the isotropic liquid phase, which involve all three symmetry-breaking instabilities \((\rho, \xi, P)\). The latent phases corresponding to one or two instabilities (e.g., a SmA phase with \( P \neq 0, P = 0, \xi \neq 0 \) or the phases with \( C_{2h} \) and \( C_{2v} \) symmetry) become unstable.

Minimizing \( F_3 \) with respect to \( \rho \), and assuming that the conditions on the coefficients for the triggering mechanism are satisfied, the minimization with respect to \( \psi \) gives the equation of state as

\[
\frac{\partial F_3}{\partial \psi} = 2 \xi^2 P^2 \sin 2\psi (\xi_1 - \xi_2 P^2 \xi^2 \cos 2\psi) = 0. \tag{4}
\]

Assuming that the polar smectic phase is tilted \((P \neq 0 \text{ and } \xi \neq 0)\), this equation yields two classes of solutions: (i) \( \sin 2\psi = 0 \), and (ii) \( \cos 2\psi = \frac{\xi_1}{\xi_2 \rho^2} \). The solution (i) itself corresponds to two distinct states: when \( \psi = 0 \) or \( \pi \), one has SmC* type configurations with \( C_2 \) symmetry; when \( \psi = \pi/2 \), one obtains an achiral layer structure with \( C_s \) symmetry. The phase of \( C_2 \) symmetry is stable if \( \gamma_1 > \gamma_0 > 0 \), whereas the stability condition for phase with \( C_s \) symmetry is \( \gamma_1 < -\gamma_0 < 0 \). The solution (ii) describes a triclinic (double-tilted) phase, which is stable if \( -\gamma_0 < \gamma_1 < \gamma_0 \) with \( \gamma_0 = \delta - \frac{2\mu_1}{C_2} + \frac{aC_1 + C_1 \mu_2}{b\xi^2 - C_1^2 \mu_2} \).

Inserting the corresponding equilibrium values of \( \psi \) into \( F_3 \), one gets the effective forms of the free-energy \( F_3 \) in the \( C_1 \) and \( C_2 \) symmetry phases, denoted hereafter \( F_3(C_1) \) and \( F_3(C_2) \). One finds \( F_3(C_1) - F_3(C_2) = (\delta' - \gamma_1) + \gamma_2 P^2 \xi^2 \), where \( \delta' = \delta - \frac{2\mu_1}{C_1} \). The sign of this quantity determines which of the two phases is more stable below the isotropic liquid.

Successively minimizing the free energy with respect to \( P \) and \( \xi \), the temperature dependent equilibrium values and the phase sequences can be determined. Assuming the conditions \( \delta'_1 < 0 \) and \( \delta'_2 > (\beta - \frac{\mu_1^2}{C_1})(b - \frac{\mu_2}{C_2}) \), we obtained the phase diagram represented in Fig. 4. The preceding conditions mean that a large negative coupling is required between \( \vec{P} \) and \( \vec{\xi} \) for this specific phase diagram topology. The lines separating the phases are determined from the equation \( F_3(C_1) = F_3(C_2) \), whereas the triple points correspond to the condition \( F_3(C_1) = \ldots \)
F3(C2) = F3(P = 0, \xi = 0). It can be seen that the transition lines separating the phases with C1 and C2 symmetries can be either of first or of second order, the two regimes being separated by the tricritical points T1 and T2, which are defined by the condition that the jump of the corresponding order-parameters go to zero. It is possible to find specific thermodynamic routes in the phase diagram, which involve only the chiral phases with C2 and C1 symmetry, and where the lowest C1 symmetry phase appears at higher temperatures. The arrows of Fig. 4 denoted by 1 and 2 are the thermodynamic paths realized experimentally in PFO [7] and PFD [8,9], respectively. The above considerations mean that the onset of a triclinic phase below the melt and the further increase of symmetry on cooling is not a reentrance effect, which is connected to fluctuations, but is the result of a triggering mechanism, which allows the lower symmetric phase to appear directly below the isotropic liquid phase.

It remains to understand why the SmA phase, which generally appears directly above the tilted smectic phases of rod-shaped molecules, seems to play only a “triggering” role when bent-shape molecules are involved. One possible reason is that these molecules realize a natural strong coupling between the polar packing, the tilt order, and the layer stacking. This prevents the formation of an SmA phase, in which the two order-parameters would be decoupled.

[18] The B1, ..., B7 type nomenclature was adopted at the 1st Banana workshop, Berlin, 1997 [5].