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Polarization modulation instability in liquid crystals with spontaneous chiral symmetry breaking

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We present a theoretical model which describes the polarization-modulated and layer-undulated structure of the $B7$ phase and gives the phase transition from the synclinic ferroelectric smectic-C_SP_F phase to the $B7$ phase as observed experimentally. The system is driven into the modulated phase due to the coupling between the polarization splay and the tilt of the molecules with respect to the smectic layer normal. The modulation wavelength and the width of the wall between two domains of opposite chirality are estimated.

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The discovery of the polar order and macroscopic chirality in smectic liquid crystals of bow-shaped (also called bent-core or banana-shaped) molecules is one of the most fascinating features found in liquid crystals in the last decade. These systems represent the first example of the formation of chiral structures that do not possess chirality on the molecular level [1,2]. The polar order and the macroscopic chirality appear spontaneously as a result of broken orientational and translational symmetries. The most widely studied polar chiral phases formed by bow-shaped molecules are the $B2$ phases. They are layered systems in which the molecules are tilted with respect to the layer normal. This tilt, together with polarization and the layer normal, breaks the chiral symmetry. The origin of the molecular tilt and the layer polarity is still not clear. The polar ordering is most probably directly driven by the strongly polar molecular shape [3], and spontaneous polarization occurs due to the polar excluded-volume effects [4]. Since the molecules are achiral the tilt of the molecules does not affect the polarization significantly and the latter is determined primarily by the magnitude of the dipole moment of the constituent molecules. The tilt in the neighboring layers can be either in the same (synclinic C_S) or in the opposite (anticlinic C_A) direction. Close packing of bow-shaped molecules results in polar order of each smectic layer. The neighboring layers can be either synpolar (ferroelectric P_F) or antipolar (antiferroelectric P_A). So, in all, four different structures are possible. The adopted nomenclature for these $B2$ phases is smectic-$C_{S,A}P_{F,A}$.

Recently, the $B7$ phase, which shows extremely rich and fascinating textures and has a more complicated structure than the $B2$ phase, received considerable attention. Jákli *et al.* [5] suggested that the structure of the $B7$ phase is identical to the smectic- (Sm-)Cg phase, which is lamellar with triclinic local layer symmetry. Coleman *et al.* [6] suggested a different structure of the $B7$ phase: it is a polarization-modulated and layer-undulated structure and studies of the electric-field-induced transition [7] between the polarization-modulated and the ferroelectric smectic-C_SP_F phases gave no evidence of the Sm-Cg ordering.

The structure of phases formed by bow-shaped molecules has been studied theoretically by several authors. An exhaustive classification of the symmetry-allowed smectic phases was presented in [8], and a phenomenological Landau model that produces many of the phases formed by bow-shaped molecules were introduced in [9,10]. In [11] it was shown that first-, second-, and third-rank tensor order parameters are necessary to fully characterize the phases exhibited by bow-shaped molecules.

In this paper we show that in a smectic phase with spontaneously broken chiral symmetry there is a symmetry-allowed coupling of the molecular tilt and divergence of polarization which can cause the $B2$ phase to become unstable and lead to the spatially modulated $B7$ phase with splayed polarization, as found experimentally [6,7].

Since the polarization-modulated structure has been observed only in ferroelectric systems where the tilt in the adjacent layers is synclinic and since the preferred local orientation of the polarization is perpendicular to the tilt plane, we propose that the $B7$ phase and the Sm-C_SP_F phase can be described by a model, based on our previous work [12], in which the smectic structure is described in terms of the smectic order parameter ψ, the nematic director $\mathbf{n}$, which describes the average local orientation of the axes that go through the top and the bottom of the molecules (see Fig. 1), and the polar parameter $\mathbf{p}$, which is the unit vector in the direction of the local polarization $\mathbf{P}$. Taking into account the $\mathbf{n}\to-\mathbf{n}$ symmetry we have a constraint $\mathbf{n}\cdot\mathbf{p}=0$.

Due to the vectorial symmetry of the polarization the local free energy contains terms of the form $(\nabla\cdot\mathbf{p})^i$, where i is an integer. These terms can stabilize a finite splay of polarization. Since the constituent molecules have thicker cores than tails, one type of splay (positive or negative) is privileged. The use of the terms with $i=1$ and 2 has already been proposed [6]. However, the linear term $\nabla\cdot\mathbf{p}$ is a surface term, and the quadratic term, even if its coefficient is negative, cannot stabilize the polarization modulation in bulk samples, such that the volume average $\langle\nabla\cdot\mathbf{p}\rangle\neq0$. The latter can be achieved if coupling between the polarization splay and the director tilt is included. So we write the free-energy density in the following form:

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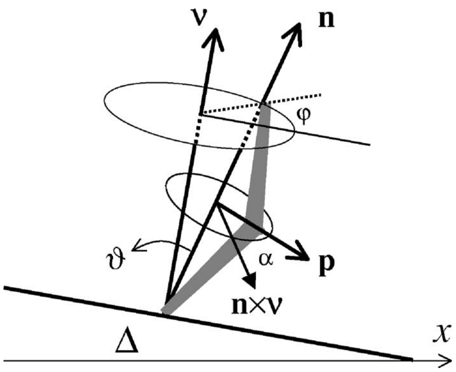

FIG. 1. The local arrangement of the constituent molecules is described by the nematic director **n**, by the polar parameter **p**, and by the smectic layer normal ν. The orientation of these three vectors is described by the cone angle ϑ (the tilt of the director with respect to the smectic layer normal), the smectic layer tilt Δ, the director position on the cone φ, and the angle α that describes the tilt of polarization from the direction perpendicular to the tilt plane (the plane determined by the director **n** and the smectic layer normal ν).

$$
\begin{aligned}
f = {} & \frac{1}{2}K_n[(\nabla\cdot\mathbf{n})^2+(\nabla\times\mathbf{n})^2]+c_{\parallel}|(\mathbf{n}\cdot\nabla - iq_0)\psi|^2 \\
& + c_{\perp}|\mathbf{n}\times\nabla\psi|^2 + D|(\mathbf{n}\times\nabla)^2\psi|^2+\frac{P_0^2}{2\varepsilon\varepsilon_0}p_x^2 \\
& + \widetilde{K}_p(\nabla\cdot\mathbf{p})|\mathbf{n}\times\nabla\psi|^2+\frac{1}{2}K_p(\nabla\cdot\mathbf{p})^2 \\
& + K_{np}|\mathbf{p}\times(\mathbf{n}\times\nabla\psi)|^2. \qquad (1)
\end{aligned}
$$

The first term gives the nematic elastic energy density. The second term describes the compressibility of the smectic layers and defines the smectic layer thickness. The parameter q_0 is defined as $q_0=2\pi/d_0$, where d_0 is the smectic layer thickness in the nontilted phase. In the tilted phases $c_{\perp}$ is negative and the D term stabilizes a finite tilt of **n** with respect to the layer normal ν. These four terms suffice to describe the structure in achiral smectic liquid crystals. The fifth term presents the energy due to the dipole-dipole self-interaction, when all the variables are functions of the x coordinate only. It is important in chiral smectics and bow-shaped systems with a large value of the spontaneous polarization. P_0 is the (constant) magnitude of the local polarization, ε is the dielectric constant, and p_x is the x component of the polar parameter.

The last three terms in Eq. (1) describe the characteristics of the phases formed by bow-shaped molecules. The term with $\widetilde{K}_p$ is the lowest-order coupling term between the splay of polarization and the tilt of the director with respect to the layer normal. If the coupling is large enough, the polarization-modulated phase becomes stable with respect to the homogeneous (unmodulated) phase. The term with K_p stabilizes a finite splay of polarization. The last term is the coupling term between the polar parameter, the layer normal, and the nematic director. This term prefers a direction of polarization perpendicular to the plane defined by the layer normal and the director **n** (in the ordinary chiral Sm-*C* phase polarization is always perpendicular to this plane).

The smectic order parameter is expressed as $\psi=\eta\exp[iq_t\,z+u(x))]$, where q_t is the smectic layer periodicity along the z axis, $u(x)$ is the layer displacement from the bookshelf geometry of layers, and η is the magnitude of the smectic order parameter; we assume that it is constant. The layer displacement is related to the tilt Δ of the smectic layers as $du(x)/dx=-\tan\Delta$. We express the free-energy density (1) in terms of the angles α, φ, ϑ, and Δ (see Fig. 1) and expand it around the homogeneous structure with bookshelf geometry of smectic layers ($\vartheta=\vartheta_B, \varphi=\Delta=\alpha=0$) up to the second-order terms in $\delta\vartheta$, $\delta\varphi$, $\delta\Delta$, and $\delta\alpha$. In order to check under which conditions the homogeneous structure becomes unstable we study the effect of the fluctuations with a wave vector q on the structure. The variables are expanded as $\delta V=\Sigma_q V_q\exp(iqx)$ where V stands for any of the four variables ϑ, α, φ, and Δ. Defining the layer compressibility constant as $B=c_{\parallel}q_0^2\eta^2$, the quadratic part of the variation in the free energy F is finally expressed in matrix form as

$$
\delta^2F=\sqrt{BK_n}\sum_{q>0}\begin{pmatrix}\alpha_{-q}\\ \varphi_{-q}\\ \vartheta_{-q}\\ \Delta_{-q}\end{pmatrix}\underline{M_2}\begin{pmatrix}\alpha_{q}\\ \varphi_{q}\\ \vartheta_{q}\\ \Delta_{q}\end{pmatrix},
$$

where the matrix elements m_{ij} of the Hermitian matrix $\underline{M}_2$ are

$$m_{11}=k_p\tilde{q}^2\cos^2\vartheta_B+2(k_\varepsilon\cos^2\vartheta_B+k_{np}\tan^2\vartheta_B),$$

$$m_{22}=2k_\varepsilon+(k_p+\sin^2\vartheta_B+r\tilde{q}_0^{-2}\cos^2\vartheta_B)\tilde{q}^2,$$

$$m_{33}=2(2r+\tan^2\vartheta_B)+(1+r\tilde{q}_0^{-2}\cos^2\vartheta_B\cot^2\vartheta_B)\tilde{q}^2,$$

$$m_{44}=-m_{34}=\tilde{q}^2,$$

$$m_{12}=2k_\varepsilon\cos\vartheta_B+k_p\tilde{q}^2\cos\vartheta_B,$$

$$m_{13}=m_{23}\cos\vartheta_B=2i\tilde{k}_p\tilde{q}\sin\vartheta_B,$$

$$m_{14}=m_{24}=0,$$

where $\tilde{q}=q\lambda_{\parallel}$ and $\lambda_{\parallel}=\sqrt{K_n/B}$ is the smectic penetration depth, $\tilde{q}_0=q_0\lambda_{\parallel}$, $k_p=K_p/K_n$, $\tilde{k}_p=\widetilde{K}_pq_0^2\eta^2/K_n$, $k_\varepsilon=P_0^2/(2\varepsilon\varepsilon_0B)$, $k_{np}=K_{np}q_0^2\eta^2/B$, $r=|c_{\perp}|/c_{\parallel}$, and $\tan^2\vartheta_B=|c_{\perp}|/(2Dq_0^2)$. If the matrix $\underline{M_2}$ has only positive eigenvalues the homogeneous structure is stable. Our main finding is that at some q_{cr} one of the eigenvalues becomes negative, so a modulated structure appears. The critical wave vector q_{cr} can be expressed analytically; however, it is a very complicated function that depends on all the parameters in the free-energy density. So we show the dependences graphically (Fig. 2). The homogeneous structure becomes unstable if (all the rest of the parameters being fixed) the value of $\widetilde{K}_p$ is greater than the critical value $\widetilde{K}_p^{cr}$. In Fig. 2 we show analytically obtained results for the dependence of $\widetilde{K}_p^{cr}$ and q_{cr} (at $\widetilde{K}_p=\widetilde{K}_p^{cr}$) on K_p at different values of ϑ_B. The value of $\widetilde{K}_p^{cr}$ decreases if ϑ_B increases or/and if K_p decreases.

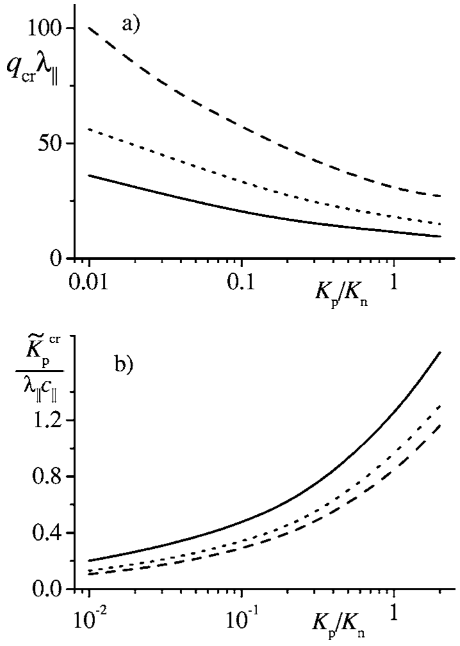

FIG. 2. The dependence of (a) q_{cr} and (b) the critical value of the coupling constant $\tilde{K}_p$ between the polarization splay and the director tilt on the ratio between the polar and nematic elastic constant. Solid line, $\vartheta_B=20°$; dotted line, $\vartheta_B=30°$; dashed line, $\vartheta_B=40°$. Parameter values: $|c_\perp|/c_\parallel=0.1$, $B/(q_0^2K_n)=7\times10^{-4}$, $P_0^2/(2\varepsilon\varepsilon_0B)=5$, $K_{np}q_0^2\eta^2/B=10$.

If $\tilde{K}_p=0$ the eigenvalues of the matrix $\underline{M}_2$ are always positive. So the modulated structure results due to the coupling between the polarization splay and the director tilt ϑ. There are other couplings possible (e.g., between the splay of polarization and the layer compressibility); however, they all give higher-order instabilities. The same is true for the term $(\nabla\cdot\mathbf{p})^3$. Therefore we conclude that the tilt is essential to obtain a polarization-modulated structure.

A possible mechanism for the coupling between the tilt and $\nabla\cdot\mathbf{p}$ is the following. In an environment with mirror symmetry, at any particular moment, the flexible parts of the molecules have with equal probability left- or right-handed conformation and the molecules are on average nonchiral. The collective molecular tilt breaks the mirror (chiral) symmetry so that left- and right-handed conformations are no longer equally probable. This reduces the disorder of the flexible tail parts of the molecule and increases their packing density. As the central parts, carrying the electric dipole, are rigid (and thicker than the tails), this induces the polarization splay.

At $\tilde{K}_p>\tilde{K}_p^{cr}$ the symmetry-required local preference for polarization is to be splayed. However, it is impossible to achieve splay of the preferred sign everywhere in space unless appropriate walls are introduced (Fig. 3). Two types of walls are expected, depending on whether the chirality switches across the wall or not.

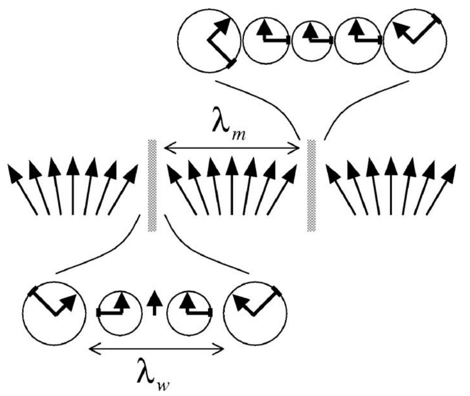

FIG. 3. In a ferroelectric domain stripes of the preferred polarization splay are divided by walls. The neighboring stripes can have the same or the opposite chirality. Below is shown the structure of the wall over which chirality switches and above the structure of the wall with no chirality switch is shown. The figure presents the top view of the undulated layer, and at the wall (of width λ_w) there is the top of a hill or the bottom of a valley. The radius of the circle is a measure for the cone angle, the arrows present the polar parameter, and the lines with bars present the director position on the cone.

Chirality switching occurs when the molecules rotate around the long axis. Due to the bow shape of the molecules this rotation is strongly hindered when the molecules are tilted. In order to rotate around the long axis the cone angle has to decrease significantly, and to estimate the wall width we assume that it goes to zero. Spatial variation in the magnitude of the cone angle is coupled to the layer deformation. The situation across the wall can, in the most simplified version, be described by no spatial variation of the director and the polarization director across the wall (see Fig. 3). Then the free-energy density has only three spatially dependent terms:

$$f=-|c_\perp|q_0^2\eta w^2+Dq_0^4\eta^2w^4+Dq_0^2\eta^2\left(\frac{dw}{dx}\right)^2,$$

where $w=du/dx$. The Euler-Lagrange equation that follows from the minimization of the free energy across the wall can be solved by the ansatz $w=w_0\tanh(x/\lambda_w)$, where λ_w is the characteristic width of the wall, and one finds

$$\lambda_w=\sqrt{\frac{2D}{|c_\perp|}}=\frac{1}{q_0\tan\vartheta_B}.$$

To estimate the characteristic widths the following set of parameters is used: $P_0=300\ \mathrm{nC/cm^2}$, $\varepsilon=10$, $\vartheta_B=40°$, $|c_\perp|/c_\parallel=0.1$, and $K_n=K_p\sim10^{-11}$ N. The compressibility is rather low compared to the ordinary smectics and we set $B\sim10^4\ \mathrm{J\,m^{-3}}$ [6]. The smectic penetration depth is then $\lambda_\parallel\sim30$ nm. With the chosen set of parameters the width of the wall over which chirality switches is $\lambda_w=0.2d_0$, i.e., only a few widths of the constituent molecules. The width of the wall over which chirality does not change is essentially of the same order of magnitude; however, the energy associated with the wall is lower since there is no need for the cone angle to reduce to zero (see Fig. 3).

Finally we estimate the modulation length (λ_m), i.e., the width of the stripe with the preferred polarization splay well below the instability. In a very crude estimate we consider only the terms that contain spatial derivatives of the x component of the polarization vector and set ϑ equal to its bulk value. We find that the equilibrium value of the polarization splay is $dp_x/dx \sim \tilde{K}_p q_0^2 \eta^2 \sin^2 \vartheta_B / K_p$. Setting $dp_x/dx = 1/\lambda_m$ and using the critical value of $\tilde{K}_p$ at $K_p/K_n = 1$ [see Fig. 2(b)] we obtain $\lambda_m \approx 80$ nm. The modulation length can also be estimated from the critical value of q at the critical value of $\tilde{K}_p$ [see Fig. 2(a)]. One finds $\lambda_m = 2\pi/q_{cr} \approx 10$ nm. Both values agree qualitatively with the experiment where the observed modulation lengths are of the order of ten layer thicknesses.

To conclude, we have presented a model that describes the phase transition from the smectic-$C_S P_F$ phase to the layer-undulated and polarization-modulated $B7$ phase. The system is driven into the modulated phase due to the coupling between the polarization splay and the tilt of the molecules. As the tilt is responsible for the breaking of chiral symmetry, the instability is due to the coupling between polarization and chirality. The transition from the homogeneous to the modulated phase occurs if the coupling term is strong enough. Since this coupling depends on the structure of the constituent molecules, we predict that a small change in the molecular structure, e.g., in the molecular tail, can lead to a significant change in the coupling and thus determine whether the system is in the homogeneous or in the modulated phase.

[1] T. Niori *et al.*, J. Mater. Chem. **6**, 1231 (1996).

[2] D. R. Link *et al.*, Science **278**, 1924 (1997).

[3] A. V. Emelyanenko and M. A. Osipov, Phys. Rev. E **70**, 021704 (2004).

[4] Y. Lansac, P. K. Maiti, N. A. Clark, and M. A. Glaser, Phys. Rev. E **67**, 011703 (2003).

[5] A. Jákli, D. Krüerke, H. Sawade, and G. Heppke, Phys. Rev. Lett. **86**, 5715 (2001).

[6] D. A. Coleman *et al.*, Science **301**, 1204 (2003).

[7] M. Nakata *et al.*, Phys. Rev. E **71**, 011705 (2005).

[8] H. R. Brand, P. E. Cladis, and H. Pleiner, Eur. Phys. J. B **6**, 347 (1998).

[9] M. Čepič, B. Žekš, and J. Mavri, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **328**, 47 (1999).

[10] A. Roy, N. V. Madhusudana, P. Toledano, and A. M. Figueiredo Neto, Phys. Rev. Lett. **82**, 1466 (1999).

[11] T. C. Lubensky and L. Radzihovsky, Phys. Rev. E **66**, 031704 (2002).

[12] N. Vaupotič and M. Čopič, Phys. Rev. E **68**, 061705 (2003).