Polarization modulation instability in liquid crystals with spontaneous chiral symmetry breaking

Nataša Vaupotič\textsuperscript{1,3} and Martin Čopič\textsuperscript{2,3}
\textsuperscript{1}Department of Physics, Faculty of Education, University of Maribor, Maribor, Slovenia
\textsuperscript{2}Department of Physics, Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia
\textsuperscript{3}Jozef Stefan Institute, Ljubljana, Slovenia

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 B2 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.

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 without possessing chirality on the molecular level \cite{1,2}. The polar order and the macroscopic chirality appear spontaneously as a result of broken orientational symmetries. The most widely studied phase formed by bow-shaped molecules is the B2 phase which is layered and the molecules inside the layer are tilted with respect to the layer normal. This tilt, together with polarization and the layer normal, breaks the chiral symmetry. The tilt in the neighboring layers can be either in the same (synclinic) or in the opposite (anticlinic) direction. Close packing of bow-shaped molecules results in polar order of each smectic layer. The neighboring layers can be either synpolar (ferroelectric) or antipolar (antiferroelectric). So, in all, four different structures are possible. The adopted nomenclature for these B2 phases is smectic C_{S,A}P_{F,A}, where the indices S and A behind the C stand for the synclinic or anticlinic tilt in the adjacent layers and F and A next to P stand for ferroelectric or antiferroelectric ordering of polarization in the adjacent layers.

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. Recent experimental findings that polar order can exist also without the tilt \cite{2} suggest that polar ordering is a fundamental property of liquid crystals formed by bow-shaped molecules while the tilt of the molecules with respect to the layer normal depends on the particular molecular structure.

Theoretical models of the bow-shaped molecular systems are scarce and 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 \cite{2}, and spontaneous polarization occurs due to the polar excluded volume effects \cite{2}. An exhaustive classification of the symmetry-allowed smectic phases was presented in \cite{2}, a phenomenological Landau model that produces many of the banana phases was introduced in \cite{3}. In \cite{2} it was shown that three order parameters (the first, the second and the third-rank tensor) are necessary to fully characterize the phases exhibited by bow-shaped molecules.

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 \textit{et al.} \cite{4} suggested that the structure of the B7 phase is identical to the Sm-Cg phase, which is lamellar with triclinic local layer symmetry. The Boulder group suggested a different structure of the B7 phase: it is a polarization splayed and layer modulated structure \cite{10} and their studies of the electric field induced transition between the polarization modulated and the ferroelectric smectic C_{S,F}P_{F} phase gave no evidence of the Sm-Cg ordering.

In this letter we present a theoretical model which shows the existence of an instability in the Sm-C_{S,F}P_{F} phase that leads to a spatially modulated phase with splayed polarization just as observed experimentally \cite{10}.

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_{S,F}P_{F} phase can be described by an extension of the model that was developed by the present authors to describe the structure in confined ferroelectric liquid crystals \cite{11,12}. Within this model the smectic structure is described in terms of the smectic order parameter \( \psi \), 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. \( \mathbf{11} \)) and the polar parameter \( \mathbf{p} \), which is the unit vector in the direction of the local polarization \( \mathbf{P} \). Due to the bow-shaped structure of the constituent molecules, the dipole moment of the molecule is always perpendicular to the
molecular long axis. Because of that we assume that the angle between the nematic director and the dipole moment of a cluster of molecules described by the nematic director is also fixed, and we set \( \mathbf{n} \cdot \mathbf{p} = 0 \).

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. This 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 \(i = 2\) has already been proposed [10]. 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 sample, such that the volume average \(\langle \nabla \cdot \mathbf{P} \rangle \neq 0\). So we write the free energy density in the following form:

\[
f = \frac{1}{2} \frac{\rho^2}{2 \varepsilon_0} p_x^2 + \tilde{K}_p (\nabla \cdot \mathbf{p}) |\mathbf{n} \times \nabla \psi|^2 + \frac{1}{2} K_p (\nabla \cdot \mathbf{p})^2 + K_{np} |\mathbf{p} \times (\mathbf{n} \times \nabla \psi)|^2.
\]

(1)

The first four terms are the terms that are used to describe the structure in ordinary, achiral, smectic liquid crystals. 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 \(\mathbf{n}\) with respect to the layer normal \(\nu\). The fifth term presents the energy due to the dipole-dipole self-interaction, when all the variables are function of the \(x\)-coordinate only. It is important in chiral smectics and bow-shaped systems with large value of the spontaneous polarization. \(P_0\) is the magnitude of the local polarization, \(\varepsilon\) is the dielectric constant and \(p_x\) is the \(x\)-component of the polar parameter.

The last three terms in Eq. (1) are new and describe the characteristics of the phases formed by bow-shaped molecules. The term with \(\tilde{K}_p\) 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, polarization modulated phase becomes stable with respect to the homogeneous (unmodulated) phase. The coupling term prefers negative splay if the parameter \(\tilde{K}_p\) is positive. 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 the direction of polarization being perpendicular to the plane defined by the layer normal and the director \(\mathbf{n}\) (in ordinary chiral SmC polarization is always perpendicular to this plane).

The smectic order parameter is expressed as \(\psi = \eta \exp\{iq_l(z + u(x))\}\), where \(q_l\) is the smectic layer periodicity along the \(z\)-axis, \(u(x)\) is the layer displacement from the bookshelf geometry of layers and \(\eta\) is the magnitude of the smectic order parameter and we assume that it is constant. The layer displacement is related to the tilt \(\Delta\) of the smectic layers as\(du(x)/dx = -\tan \Delta\). We express the free energy density (1) in terms of the angles \(\alpha, \varphi, \vartheta\) and \(\Delta\) (see Fig. II) 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 \(\delta V = \sum_q V_q \exp(irq)\) where \(V\) stands for any of the four variables \(\vartheta, \alpha, \varphi\) and \(\Delta\). The quadratic part of the variation in the free energy \(F\) is finally expressed as:

\[
\delta^2 F = \sum_{q \geq 0} \begin{pmatrix} \alpha - q \\ \varphi - q \\ \vartheta - q \\ \Delta - q \end{pmatrix} \mathbf{M}_q \begin{pmatrix} \alpha_q \\ \varphi_q \\ \vartheta_q \\ \Delta_q \end{pmatrix}.
\]

If the matrix \(\mathbf{M}_q\) 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. In general the relations are the following:

- The homogeneous structure becomes unstable if (all the rest of the parameters being fixed) the value of \(\tilde{K}_p\) is greater than the critical value \(\tilde{K}_p^{cr}\). In Fig. II we show analytically obtained results for the dependence of \(K_p^{cr}\) and \(q_{cr}\) (at \(K_p = \tilde{K}_p^{cr}\)) on \(K_p\) at different values of \(\vartheta_B\). The value of \(\tilde{K}_p^{cr}\) decreases if \(\vartheta_B\) increases or if \(K_p\) decreases.
- The eigenvector that corresponds to the critical value of \(q\) at the critical value of \(\tilde{K}_p\) has the components of deformations in \(\vartheta\) and \(\Delta\) much larger than the components of deformations in \(\varphi\) and \(\alpha\). As expected the magnitude of deformation in \(\alpha\) increases if \(K_{np}\) decreases. The deformation in \(\varphi\) is negligibly small.
• Modulated structure results due to the coupling between the polarization splay and the director tilt $\vartheta$. 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 polarization modulated structure.

At $K_p > K_p^c$ 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. 4). Two types of walls are expected, depending on whether the chirality switches across the wall or not.

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 we assume that it goes to zero. Spatial variation in 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 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

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

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 $\lambda_w$ is the characteristic width of the wall, and one finds

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

To estimate the characteristic widths the following set of parameters is used: $P_0 = 300 \text{ nC/cm}^2$, $\varv = 10$, $\vartheta_B = 40^\circ$, $|c_\perp|/c_\parallel = 0.1$ and $K_n = K_p \sim 10^{-11} \text{ N}$. We define the layer compressibility constant as $B = c_\parallel q_0^2 \eta^2 \sim 10^4 \text{ Jm}^{-3}$. The compressibility is rather low compared to the ordinary smectics \[\textbf{10}\]. The smectic penetration depth is then $\lambda_\parallel = \sqrt{K_n/B} \sim 30 \text{ nm}$. 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 ($\lambda_m$), i.e. the width of the stripe with the preferred polarization splay. In a very crude estimate we consider only the terms that contain spatial derivative of the $x$-component of the polarization vector and set $\vartheta$ to equal its bulk value. We find that the equilibrium value is $dp_x/dx \sim K_p q_0^2 \eta^2 \sin^2 \vartheta_B/K_p$. Setting $dp_x/dx = 1/\lambda_m$ and using the critical value of $K_p$ at $K_p/K_n = 1$ (see Fig. 2b) we obtain $\lambda_m \approx 80 \text{ nm}$. The modulation length can also be estimated from the critical value of $q$ at the critical value of $K_p$ (see Fig. 2b). One finds $\lambda_m = 2\pi/q_{cr} \approx 10 \text{ nm}$. Both values agree qualitatively with the experiment where the observed modulation lengths are of the order of 10 layer thicknesses.

To conclude we have presented a theoretical model which describes the phase transition from the smectic-$C_s\text{P}_F$ phase to the layer undulated and polarization modulated 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 the modulated phase.

FIG. 1: The local arrangement of the constituent molecules is described by the nematic director $\mathbf{n}$, by the polar parameter $\mathbf{p}$ and the smectic layer normal $\nu$. The orientation of these three vectors is described by the cone angle $\vartheta$ (the tilt of the director with respect to the smectic layer normal), the smectic layer tilt $\Delta$, the director position on the cone $\varphi$ and the angle $\alpha$ which describes the tilt of polarization from the direction perpendicular to the tilt plane (the plane determined by the director $\mathbf{n}$ and the smectic layer normal $\nu$).

FIG. 2: a) The dependence of $q_{cr}$ and b) the dependence of 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: $\vartheta_B = 20^\circ$; dotted line: $\vartheta_B = 30^\circ$; dashed line: $\vartheta_B = 40^\circ$. Parameter values: $|c_\perp|/c_\parallel = 0.1$, $B/(q_0^2K_n) = 7 \times 10^{-4}$, $P_0^2/(2\varepsilon_0B) = 5$, $K_{np}q_0^2\eta^2/B = 10$.


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. Figure presents the top view on the undulated layer, and at the wall (of width $\lambda_w$) there is the top of the hill or the bottom of the 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.
N. Vaupotic and M. Copic, PRL, Fig. 2
N. Vaupotic and M. Copic, PRL, Fig. 3