Role of Molecular Shape on Bent-Core Liquid-Crystal Structures

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We show how frustrations in molecular packing generated by molecular substitutions and electrostatic potentials necessitate a local $C_1$ symmetry and lead to spontaneous polarization splay and layer bending in bent-core liquid crystals. By estimation of the entropic changes due to curvature, we calculated the elastic constants that drive the spontaneous layer bend and polarization splay and obtained length scales of these deformations. Finally, we propose a structural phase diagram which describes how the experimentally observed helical superstructures, layer undulation, polarization splay, and spontaneous fiber formation depend on the direction and magnitude of the spontaneous polarization.


The introduction of kinks in the shape of liquid-crystal mesogens [1] led to an exciting new field in soft matter physics [2–4] with a number of new theoretical predictions [5] and experimentally observed nematic [6], smectic, and columnar phases [7–12]. In spite of a decade of intensive research, the structures of a number of these phases are still not completely clear and most of the phases are usually denoted as $B_1, \ldots, B_7$ according to the chronological order of their discovery. The most active debate concerns the $B_7$ structures [13], which are most notable for the formation of freestanding fluid fibers [14], banana leaf-shaped domains [15], and helical superstructures [16–19] including helical filaments [20].

Although many materials with $B_7$ type textures have been reported in the literature [21–23], it remains unclear whether all of these textures have the same phase structure or not. Based on some characteristic differences between their behavior [24–28] we may speak about two different types of $B_7$ materials. Some of the mesogens, for example, the first $B_7$ materials [16], have distinct sharp peaks in the low angle X-ray range [2], which is characteristic to columnar-type structures. Other $B_7$ materials, which we denote $B_7^\gamma$, have strong commensurate reflections indicating a layered structure, and small incommensurate satellite peaks which are very close to each other and hard to resolve with normal X-ray techniques [29]. These satellite peaks were associated with a one-dimensional undulation of the smectic layers with a relatively long wavelength, between 10–100 nm [29], and the undulation was attributed to a frustrated in-layer polarization structure in the form of polarization splay domains. Such modulated structures have been the subject of a number of studies [24–26,29,30] and various names, such as SmCP-mod and polarization modulated-layer undulated, were used for them. The $B_7$ materials do not switch electro-optically or show polarization switching for applied electric fields below 40 V $\mu$m$^{-1}$, whereas the $B_7^\gamma$ materials possess ferroelectric or antiferroelectric [22] polarization peaks above a threshold of $E > 10$ V $\mu$m$^{-1}$ that decreases on cooling [22,31], unlike the single titled smectic SmCP or SmC$^*$ phases. Based on these observations and on field-induced polar shifts of transition temperature [32] it has been suggested that the $B_7$ materials have $C_1$ symmetry with a double tilted (SmCP$_C$) [5] structure, where the polarization has components in and out of the smectic layers. In this Letter we will show that not only $B_7^\gamma$ but the $B_7$ type materials also have the same $C_1$ local symmetry, and differences exist only in the direction and magnitude of their layer polarizations.

The arguments we present below were based on simulations of the equilibrium molecular structures and electrostatic potentials of virtually all published mesogens [2,6,16,18–21,33,34]. From these simulations, we found that only the molecules of the SmCP phase with $C_2$ symmetry can be modeled as a bent series of spheres [35] [Fig. 1(a)]. However, all the $B_7$ mesogens have a single or multiple large steric units attached to the center or outer benzene rings, such as a nitro group [33], which would appear as “bumps” on their model structures [Fig. 1(c)]. Although the $B_7^\gamma$ mesogens may have only small units, such as chlorines or fluorines attached to their outer benzene rings, or have no steric inclusions at all [34], one also sees “bumps” in their complex electrostatic potentials generated by the distribution of charges within the chemical structures [Fig. 1(b)]. Based on these observations, we modeled the molecules as simple triangles. The effect of the end tails and the reality that the bumps do not completely fill these triangles are taken into account only by assuming that they favor polar packing with respect to antipolar. To determine the effects of frustrated packing, we calculated the excluded volumes and then predicted the strength of these interactions by calculating the resulting changes in translational entropy.

The important geometrical parameters, along with the resulting spontaneous distortions, can be seen in Fig. 2, where we have divided the packing interactions along two orthogonal planes, one perpendicular to the layer normal $\hat{k}$ (splay plane) and the other within the plane generated by $\hat{k}$

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and \( \hat{n} \) (bend plane). For a given radius of curvature \( r \) describing polar bend, the excluded volume \( V_b \) of a single model molecule in the (\( \hat{n}, \hat{p} \)) plane can be given as

\[
V_b(\hat{n}, \hat{p}) = \frac{1}{2} \phi[(r + L)^2 - r^2] - \frac{1}{4} L^2(\tan \beta) b - \frac{1}{2} L^2(\tan \beta) b \left[ \phi + \frac{2r}{L} - \frac{1}{2} \tan \beta \right].
\] (1)

Here \( b \) is the width of the molecular plane, \( L \) is the molecular length, \( \beta \) is the kink angle, and \( \phi = \tan^{-1}\left(\frac{\tan \beta}{1+\frac{r}{L}}\right) \) is the curvature angle [see Figs. 2(b) and 2(c)].

The excluded volume in the bend plane becomes \( V_b(\hat{k}, \hat{x}) = V_b(\hat{n}, \hat{p}) \sin^2 \alpha \), which correctly accounts for the projection of the molecule onto the bend plane [see Fig. 2(a)]. For the splay case, for radius of curvatures \( \rho \gg L \), the excluded volume \( V_s \) in the (\( \hat{p}, \hat{m} \)) plane is

\[
V_s(\hat{p}, \hat{m}) = L \alpha^2 \left[ \tan \left(\frac{\delta}{2}\right) - \tan \left(\frac{\gamma}{2}\right) \right].
\] (2)

where \( \delta \) is the wedge angle [see Fig. 2(b)] and \( \gamma \approx \frac{h}{\rho} \) is the curvature angle [see Fig. 2(c)]. From Fig. 2(a), one can see that the correct excluded volume within the smectic layers is the projection of (2) determined by \( V_s(\hat{x}, \hat{y}) = V_s(\hat{p}, \hat{m}) \cos^2 \alpha + \cos^2 \theta \sin^2 \alpha \).

It is useful to analyze \( V_b(\hat{k}, \hat{x}) \) and \( V_s(\hat{x}, \hat{y}) \) by comparing the undeformed (\( \phi, \gamma \to 0 \)) with the deformed (\( \phi, \gamma \neq 0 \)) states. For flat layers, (\( \phi \to 0 \)), \( V_b(\hat{k}, \hat{x}) = \frac{1}{2} L^2 b \tan \beta \sin^2 \alpha \), which has a minimum when \( \alpha = 0 \) (SmCP). However taking the difference of the excluded volumes of bent and flat layers we find that it is always

![FIG. 1](color online). Examples of typical bent-core mesogenic materials with their phase sequences and chemical, steric, and electrostatic structures for the \( B_2 \) [15] (a), the \( B_{7r} \) [34] (b), and the \( B_7 \) [33] (c) phases, as obtained by the ChemOffice® software package. The extra circles in their model structures represent the unit that frustrates close packing, and the dashed triangles show the effective regions that cannot be occupied by other molecules.

![FIG. 2](color online). The geometries of the frustrated packing model. (a) The molecular orientation: \( \hat{n} \) is the director along the long axis, \( \hat{p} \) is the layer polarization axis, and \( \hat{k} \) is the layer normal; \( \hat{n} \) tilts in (\( \hat{x}, \hat{k} \)) plane by angle \( \theta \), and the molecular plane makes an angle \( \alpha \) with respect to the \( \hat{y} \) axis. (b) The model molecular dimensions in the (\( \hat{n}, \hat{p} \)) and (\( \hat{p}, \hat{m} \)) planes. (c) Illustration of the excluded volumes (gray areas) for bend and splay deformations. (d) The model [29] of the in-layer polarization splay. (e) The model [14] of the fibers made of \( B_7 \) and \( B_{7r} \) materials illustrating the effects of layer bending.

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negative; i.e., the bent layers have smaller excluded volumes for any $\alpha \neq 0$. It is readily seen for the tightly bent case, which gives $\Delta V_b = V_b(\phi = \beta) - V_b(\phi \to 0) = \frac{1}{2} L^2 h(\beta - \tan \beta) \sin^2 \alpha$, which for $\alpha \neq 0$ is always negative because $\tan \beta > \beta$. Accordingly, once $\alpha$ is not zero, a bent layer structure provides closer packing of the molecules. Because $\Delta V_b$ has a maximum at $\alpha = 0$, a flat system becomes unstable for any small perturbation of $\alpha$, thus driving a bend of the layers, which in turn stabilizes $\alpha \neq 0$.

Considering the difference between the excluded volumes of the splay deformed and uniform states $V_s(\gamma > 0) - V_s(\gamma \to 0) = -\frac{1}{2} L a^2 \frac{b}{\rho} \sqrt{\cos^2 \alpha + \cos^2 \theta \sin^2 \alpha}$, we see that it is also always negative, but now with a minimum at $\alpha = 0$ if $\theta > 0$. This means that the effects of layer bend and polarization splay on the polarization angle are competing. A layer bend favors $\alpha = 90^\circ$ (SmLP), whereas a polarization splay favors $\alpha = 0$ (SmCP). A combination of these two effects therefore sets $0 < \alpha < 90^\circ$ (SmC$\beta$).

In order to estimate the natural length scales of the bend and splay deformations we need to calculate the energy gain $U_{h,s} = -TS_{h,s}$ of these deformations arising from increasing the entropy $S_{h,s}$, which can be written as

$$S_{h,s} = -k_B \ln(1 - n \Delta V_{h,s}) = k_B (n \Delta V_{h,s}).$$

(3)

Here $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann’s constant. $\Delta V_{h,s}$ are the differences between the excluded volumes between the bend or splay deformed and uniform states, and $n$ is the number density of the material. This approximation is valid if $n V_{h,s} \ll 1$, which is true in our situation for curvatures in the continuum limit. The bend or splay energy densities $f_{h,s}$ then can be calculated by multiplying $U_{h,s}$ by the number density $n$, thus giving $f_{h,s}(r) = n^2 k_B T [V_b(r > 0) - V_b(r = \infty)]$ and $f_{s}(\rho) = n^2 k_B T [V_s(\rho > 0) - V_s(\rho = \infty)]$. In the continuum limit, i.e., when $r, \rho \gg \frac{L}{\rho}$, we expand $\Delta V_{h,s}$, up to first order in $r^{-2}$ and $\rho^{-1}$, obtaining

$$f_{h}(r) = -\frac{1}{2} n^2 k_B T \left( \frac{1}{12} L^4 \tan^2 \beta \right) \left( \frac{\cos^2 \theta \sin^2 \alpha}{r^2} \right)$$
$$= \frac{1}{2} k_B \left( \vec{\nabla}_\perp \times \hat{p} \right)^2$$

(4)

$$f_{s}(\rho) = -n^2 k_B T \left( \frac{1}{8} L^2 \tan^2 \beta \right) \left( \frac{\sqrt{\cos^2 \theta + \sin^2 \theta \sin^2 \alpha}}{\rho} \right)$$
$$= C(\vec{\nabla}_\parallel \cdot \hat{p}).$$

(5)

The extra factor of $\cos^2 \theta$ in (4) is due to the fact that $r$ must be rescaled by a factor of $\frac{1}{\cos \alpha}$ to correctly account for the molecular tilt within the layer. In (5) we have written $a = \frac{1}{2} L \tan \beta$. As we show, the energy density can be written in terms of vector operations of the in-layer director $\hat{c}$, the in-layer divergence ($\vec{\nabla}_\parallel \cdot \hat{p}$), and the out-of-layer curl ($\vec{\nabla}_\perp \times \hat{p}$) of the polarization direction. By using typical values of the molecular and physical parameters $n = 7.5 \times 10^{26}$ m$^{-3}$, $T = 425$ K, $L = 5$ nm, $b = 1$ nm, and $\beta = \frac{\pi}{6}$, we calculate that $C = -0.034$ N/m and $K_p = -6.6 \times 10^{-11}$ N. We note that $K_p$ is slightly larger than typical Frank elastic constants, and $C$ is greater than the measured surface tension $\sigma$, which is $-0.025$ N/m in air [14,36] and $<0.02$ N/m in an isotropic melt. These spontaneous deformations lead to the spatial changes of the polarization angle $\alpha$, which in turn lead to layer compressions with a modulus $B_{eff} = \frac{P_s + \Delta \sigma \cos \theta}{\sigma \varepsilon_{0}} + B_{c}$, which was derived in our earlier publication discussing fiber stability [37]. The first term of $B_{eff}$ is due to electric self-interactions of the spontaneous layer polarization $P_s$ and the biaxial layer compression $B_c$ arises from the rotations of the polar direction about a fixed director. To estimate a typical value of $B_{eff}$ we use reasonable physical parameters, $P_0 = 200$ nC/cm$^2$, $\theta = \frac{\pi}{6}$, $\varepsilon_0 = 9 \times 10^{-11}$ C$^2$/J$m^2$, and $B_c = 5 \times 10^4$ N/m$^2$ (see Ref. [37]), which gives $B_{eff} = 1.6 \times 10^4$ N/m$^2$. $B_{eff}$ and the surface tension $\sigma$ oppose the effects desired by $K_p$ and $C$, from which we can construct two natural length scales, $\lambda = \sqrt{\frac{k_p}{B_{eff}}} \sim 60$ nm and $R = (|C| - \sigma)/B_{eff} \sim 2$ $\mu$m. These two length scales are in excellent agreement with the experimentally observed periodicity (10 nm $< \lambda < 100$ nm) of splay domains [29] [see Fig. 2(d)], the observed radii of the fibers standing in air [32], and helical filaments formed in isotropic melt [20] [see Fig. 2(e)].

The amount of splay in a domain can be estimated from our model, which gives $\Delta \phi = [(\delta - \gamma) / \lambda] / b$. Here $\delta - \gamma$ is the angle between the sides of two neighbor molecules. According to Coleman et al.’s model [29] [see in Fig. 2(d)], the amount of splay in one domain is twice the tilt angle. The model by Vaupotic et al. finds that it is even smaller, about 10°. Our model gives twice the tilt angle with $\delta - \gamma > 1^\circ$, and agrees with Vaupotic et al.’s model with $\delta - \gamma < 0.2^\circ$ indicating a tighter packed structure.

As shown above, the steric or electrostatic inclusions not only lead to spontaneous layer bending and polarization splay modulations but also drive a symmetry reduction from $C_{2v}$ of the SmCP phase to $C_1$ of the SmC$\beta$ phase, characterized with $0 > \alpha > 90^\circ$. This means that the splay of an out-of-plane polarization component necessarily induces an additional layer bend modulation, which has been indeed observed experimentally [29]. This coupling results in a wide variety of local molecular and layer configurations that all have the same local symmetry, but their properties depend both on the magnitude and the direction of the spontaneous polarizations.

A suggested structural phase diagram of the $B_z$ and $B_{y}$ materials as a function of the spontaneous layer polarization $P_o$ (x axis) and the polarization angle $\alpha$ (y axis) is shown in Fig. 3. The strength of $B_{eff}$ increases with $P_o$, which decreases toward higher temperatures. The fiber stability is enhanced with increasing $P_o$ and $\alpha$ (which increases with temperature) [37]. At small $\alpha$ bilayer structures may arise to cancel out the out-of-layer polar-
showed that frustrated molecular structures necessitate a layers become stiff and break into ribbons, representing and the spontaneous polarization splay and layer bending. perpendicular to the tilt plane leading to a coupling between increasing B_{eff}, temperature, and fiber stability are also included. 

izations and appear as SmCP, as experimentally observed by Bedel et al. [15] in a B_{T} material. For intermediate \alpha and P_{o}, the effects of the negative C and \kappa_{b} begin to overcome the effect of B_{eff}, leading to small layer bending and a macroscopically observable out-of-layer polarization [34]. At large \alpha pronounced layer undulations occur if P_{o} is small, since there B_{eff} is small. For larger P_{o} the layers become stiff and break into ribbons, representing columnar-type structure.

To summarize, by excluded volume calculations we showed that frustrated molecular structures necessitate a local C_{1} symmetry where the molecular plane is not perpendicular to the tilt plane leading to a coupling between the spontaneous polarization splay and layer bending.

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