

Origin of spontaneous polarization, tilt, and chiral structure of smectic liquid-crystal phases composed of bent-core molecules: A molecular model

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A simple molecular model is proposed for novel bent-core smectic phases that enables one to explain the origin of the experimentally observed chiral structure of the $B2$ phase composed of nonchiral banana-shaped molecules. It is shown that in the perfectly ordered smectic phase the distributed dispersion interaction between banana-shaped molecules stabilizes the spontaneous polarization and may be responsible for the tilt of the director. The orientation of the spontaneous polarization with respect to the tilt plane is determined by the balance between the dispersion and electrostatic dipole-dipole intermolecular interactions. In particular, sufficiently strong dipole-dipole interaction promotes the $B2$ phase where the polarization is normal to the tilt plane. The actual chiral structure of each smectic layer in the $B2$ phase appears as a result of the symmetry breaking. In the case of small molecular dipoles the nonchiral polar smectic phase is formed where the spontaneous polarization is parallel to the tilt plane. The role of the opening angle and of the axial ratio of banana-shaped molecules is also considered and a phase diagram is presented.

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I. INTRODUCTION

Ferroelectric and antiferroelectric ordering in liquid crystals is an interesting phenomenon that continues to attract significant attention due to its fundamental importance and due to various applications in display devices and telecommunication systems. In conventional ferroelectric liquid crystal phases, such as the smectic- C^* phase, the spontaneous polarization is determined by molecular chirality [1–3]. The polarization does not appear in a self-consistent way, but is induced by the tilt of the director \mathbf{n} (that specifies the preferred orientation of long molecular axes) with respect to the layer normal \mathbf{k} . The tilt of the director can be characterized by the pseudoscalar $\mathbf{w} \equiv (\mathbf{n} \cdot \mathbf{k})[\mathbf{n} \times \mathbf{k}]$ which is parallel to the C_2 symmetry axis perpendicular to the tilt plane. It is well known since the original work of Meyer [1] that the spontaneous polarization \mathbf{P}_s may be proportional to the tilt \mathbf{w} only if the coupling coefficient is a pseudoscalar, i.e., if it is determined by molecular chirality. Recently, however, a new class of smectic liquid crystals has been discovered [4,5] that is characterized by spontaneously polar and chiral layers formed by nonchiral bent-core molecules which have “banana” or more exactly “bow” shaped cores. These new materials exhibit a number of smectic phases [6], but the most investigated one is the so-called $B2$ phase having the same point symmetry as the conventional ferroelectric Sm- C^* phase [5]. One notes that the $B2$ phase in the ferroelectric state is characterized by very large second-order nonlinear optical coefficients [7–9], and thus these materials are promising for future applications in nonlinear optical devices.

The local structural chirality of the $B2$ phase can be characterized by the pseudoscalar quantity $\Delta \equiv (\mathbf{w} \cdot \mathbf{P}_s)$. In the

Sm- C^* phase the sign of Δ is determined by the handedness of chiral molecules while in the $B2$ phase the sign of Δ is random. As a result, one finds domains of opposite chirality or a “racemic” $B2$ phase, where chirality alternates from layer to layer [5]. The origin of the spontaneously polar and chiral structure of the $B2$ phase is still unclear. Experimental data and general theoretical studies [10] indicate that there may be some relationship between polar and chiral symmetry breaking in bent-core liquid crystals. On the other hand, one cannot expect the spontaneous polarization simply to be proportional to the tilt as in the Sm- C^* phase. Recently an untilted polar smectic Sm- AP_A phase has been reported, which means that spontaneous polarization may appear without a tilt. Moreover, in binary mixtures of bent-core and rod-like molecules the tilt angle in the $B2$ phase decreases with the increasing concentrations of rods, while the polarization remains practically constant [11]. All these experimental results suggest that polar ordering is a fundamental property of bent-core smectic liquid crystals, while tilt may or may not occur depending on particular molecular structure. This conclusion is supported by the results of recent computer simulations of Lansac *et al.* [12], who have investigated the phase diagram of hard spherocylinder dimers with different opening angles. Lansac *et al.* have found a transition from the nonpolar smectic- A phase to the polar orthogonal Sm- AP_A phase with increasing opening angle. At the same time no tilted phase has been found. Thus, the polar ordering in bent-core phases may be directly determined by strongly polar molecular shape. Spontaneous polarization may occur due to polar excluded volume effects as in the model of Lansac *et al.* [12], or/and it may be determined by a combination of repulsion and attraction between banana molecules as discussed below. At the same time, the experimentally observed chiral structure of the $B2$ phase should be stabilized by some additional intermolecular interactions. In this paper we consider a simple model of a bent molecule

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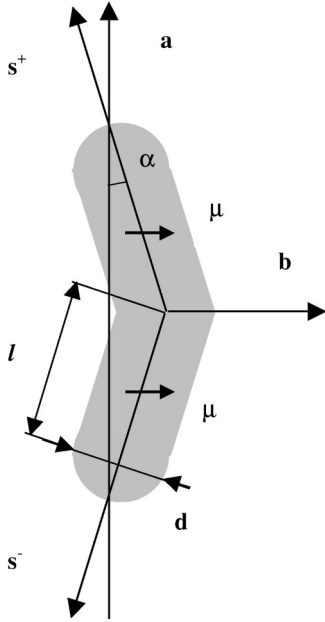


FIG. 1. Simple model of a bent-core molecule.

composed of two rigid rods with permanent dipoles. In this model total interaction between such molecules includes short-range steric repulsion, interaction between permanent dipoles and the dispersion interaction with interacting centers distributed continuously along the molecule. We show that in the limiting case of perfect orientational and translational order a combination of these interactions stabilizes the tilted, polar and chiral structure which corresponds to the $B2$ phase. In the case of small molecular dipole a nonchiral smectic phase is stabilized which corresponds to one of the structures suggested by Brandt, Cladis, and Pleiner [13].

II. MOLECULAR MODEL

In the present model the banana molecule is represented by a rigid dimer composed of two equal rods (“arms”) with the opening angle $\pi - 2\alpha$ (see Fig. 1). The orientation of an arbitrary molecule i can be specified by the unit vector \mathbf{a}_i in the direction of the long axis which points from one end of the molecule to the other, and by the unit vector \mathbf{b}_i in the direction of the short molecular axis which is parallel to the symmetry axis of the dimer. The orientations of the two “arms” of banana molecule i are given by the vectors \mathbf{s}_i^+ and \mathbf{s}_i^- determined by

$$\mathbf{s}_i^\pm \equiv \pm \mathbf{a}_i \cos \alpha + \mathbf{b}_i \sin \alpha. \quad (1)$$

The “arms” cannot penetrate into each other, and there is also a dispersion interaction between such molecules with the interaction centers distributed continuously and homogeneously along the axes of “arms.” Let the variables t_1 and t_2 specify the positions of the interaction centers along the “arms” of random banana molecules 1 and 2, respectively. The dispersion interaction between any two points t_1 and t_2 of molecules 1 and 2 decays as $\rho^{-6}(t_1, t_2)$, where $\rho(t_1, t_2)$ is the distance between these points. In addition every molecule

i possesses a pair of permanent parallel dipoles located at the centers of both “arms” (see Fig. 1). These dipoles are parallel to the symmetry axis \mathbf{b}_i of the molecule.

As shown by Lansac *et al.* [12], rigid banana molecules of the type presented in Fig. 1 can form polar smectic phases simply due to packing effects. Thus, we assume that the smectic phase exists and consider a simple case of the perfect orientational and translational order. In this case the molecular centers are located in the same plane within one smectic layer and the long axes are parallel to the local director. For simplicity one may neglect the interaction between the opposite “arms” of molecules (i.e., the “arms” located in different half-spaces with respect to the layer mid-plane), since both dispersion and dipole-dipole interactions strongly decrease with the increasing distance between the interaction centers. Then the total interaction potential between molecules 1 and 2 can be expressed as a following sum:

$$U_{12} \approx U_{12}^+ + U_{12}^-, \quad (2)$$

where U_{12}^\pm are the sums of dispersion and dipole-dipole interactions between the corresponding “arms” of molecules 1 and 2 (i.e., the “arms” located in the same half-space with respect to the layer mid-plane):

$$U_{12}^\pm = - \int_{-\ell/2}^{\ell/2} dt_1 \int_{-\ell/2}^{\ell/2} dt_2 \frac{J_0 d^4}{\rho_\pm^6(t_1, t_2)} + \frac{\mu^2}{r_{12}^3} [(\mathbf{b}_1 \cdot \mathbf{b}_2) - 3(\mathbf{u} \cdot \mathbf{b}_1) \times (\mathbf{u} \cdot \mathbf{b}_2)], \quad (3)$$

where μ is one of the molecular dipole moments, \mathbf{r}_{12} is the intermolecular vector that joins the midpoints of both corresponding “arms” of molecules 1 and 2, the unit vector \mathbf{u} is defined as \mathbf{r}_{12}/r_{12} , parameter ℓ is the length of the banana “arm” (i.e., the length of one rod in the dimer presented in Fig. 1), both parameters t_1 and t_2 are equal to zero in the midpoints of the corresponding “arms,” and the constant J_0 characterizes the strength of the dispersion attraction interaction. The dimensional factor d^4 has been introduced for convenience, where d is the diameter of the rod.

The first term in Eq. (3) describes the dispersion interaction between the corresponding “arms” of molecules 1 and 2. The vector $\rho_\pm(t_1, t_2)$ connecting point t_1 of the first molecule and point t_2 of the second molecule may be expressed as

$$\rho_\pm(t_1, t_2) = \mathbf{r}_{12} + t_2 \mathbf{s}_2^\pm - t_1 \mathbf{s}_1^\pm. \quad (4)$$

Here the vectors \mathbf{s}_1^\pm and \mathbf{s}_2^\pm are given by Eq. (1), where the long molecular axes \mathbf{a}_1 and \mathbf{a}_2 are assumed to be parallel to the nematic director \mathbf{n} . The second term in Eq. (3) represents the electrostatic interaction between the dipoles located in the corresponding “arms” of molecules 1 and 2.

In Ref. [12] it was shown that steric repulsion of bent molecules may also lead to the polar ordering of molecular short axes \mathbf{b}_1 and \mathbf{b}_2 . Here we show that dispersion interaction distributed along the axes of such molecules will act in the same direction increasing the polar order. This can be seen from the dependence of the averaged dispersion interaction potential on the angle ψ between the short axes \mathbf{b}_1 and \mathbf{b}_2 . In the case of perfect orientational and translational order the dispersion interaction energy $U_{disp}(1,2)$ [i.e., the first term in Eq. (3)] should be averaged over all relative positions

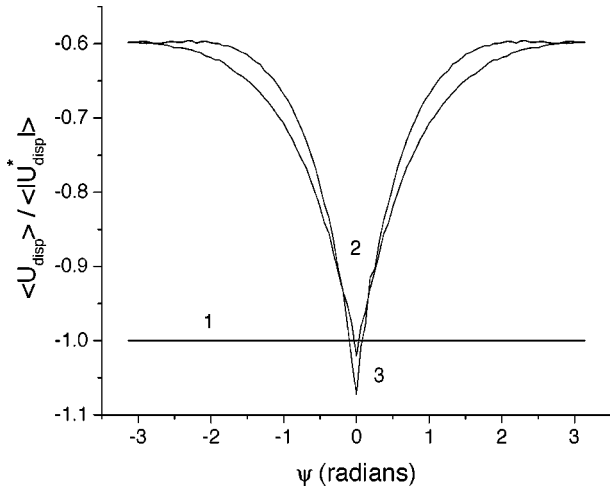


FIG. 2. Average dispersion interaction energy between untilted molecules located in the same smectic layer as a function of the angle between the short molecular axes \mathbf{b}_1 and \mathbf{b}_2 in the case $(\ell \cos \alpha)/d = 1.5$: (1) $\alpha = 0$; (2) $\alpha = \pi/10$; (3) $\alpha = \pi/7$. The energy is normalized by that for two corresponding rod-like molecules $\langle U_{disp}^* \rangle$.

of the two molecules in the smectic layer plane specified by the intermolecular vector \mathbf{r}_{12} also taking into account the excluded volume effects at close contact. Then the average dispersion interaction between the corresponding “arms” of two banana molecules can be written as

$$\langle U_{disp}^\pm \rangle = - \int_0^{2\pi} d\varphi \int_{\xi_{12}}^{\infty} r_{12} dr_{12} \int_{-\ell/2}^{\ell/2} dt_1 \int_{-\ell/2}^{\ell/2} dt_2 \frac{J_0 d^4}{\rho_\pm^6(t_1, t_2)}, \quad (5)$$

where the angle φ specifies the orientation of the unit vector \mathbf{u} , ξ_{12} is the minimum distance between molecules 1 and 2 with parallel long axes, and the vector $\rho_\pm(t_1, t_2)$ is determined by Eq. (4).

In the general case it is difficult to find the minimum of the averaged dispersion interaction between molecules 1 and 2 (that is a sum of $\langle U_{disp}^+ \rangle$ and $\langle U_{disp}^- \rangle$) with respect to the angle ψ . However, taking into account that the tilt angle is usually small, one may estimate the average dispersion interaction in the untilted smectic phase. In this case $\rho_\pm^2(t_1, t_2)$ may be expressed as

$$\begin{aligned} \rho_\pm^2(t_1, t_2) = & \{r_{12} \mp [t_2 \cos(\varphi + \psi/2) - t_1 \cos(\varphi - \psi/2)] \sin \alpha\}^2 \\ & + [t_2 \sin(\varphi - \psi/2) - t_1 \sin(\varphi + \psi/2)]^2 \sin^2 \alpha \\ & + (t_2 - t_1)^2 \cos^2 \alpha. \end{aligned} \quad (6)$$

One notes, however, that the integral (5) cannot be taken analytically even when the distance $\rho_\pm^2(t_1, t_2)$ is determined by Eq. (6). The minimum distance ξ_{12} also depends on the angles φ and ψ , and, as a result, only the integral with respect to the intermolecular separation r_{12} can be calculated analytically. Taking this integral and calculating the other three integrals in Eq. (5) numerically, one obtains the average dispersion interaction energy as a function of the angle ψ between the short molecular axes that is presented in Fig. 2.

One can see from Fig. 2 that the average dispersion interaction between banana molecules has a deep minimum at $\psi = 0$. The minimum becomes deeper for larger angles α . One notes that the cusp at $\psi = 0$ is related to the fact that the interaction energy is averaged with the steric cut-off function which is discontinuous. As a result, the average energy has a discontinuous first derivative at the point of minimum.

Packing of bent rods simulated in [12] and the behavior of the average dispersion interaction presented in Fig. 2 give a strong indication that the short axes of banana molecules with sufficiently large angles α should be ordered in the smectic phase. In the rest of this paper we assume for simplicity that the ordering of transverse dipoles of such molecules is also perfect. In this case a number of important results can be obtained analytically. It should be noted that perfect ordering of short molecular axes implies that the spontaneous polarization is nearly temperature independent. For real bent-core mesogens this is not always the case. In fact, temperature variation of the spontaneous polarization depends on the molecular structure. For example, a significant temperature dependence of the polarization has been found by Jakli *et al.* (see Fig. 5 in Ref. [14]) within 5° – 10° below the transition point in the $B2$ phase. At the same time, on a bent-core material with a wider $B2$ phase a very weak temperature variation of the polarization has been found more than 5° below the transition temperature [15]. A weak temperature variation of the polarization has also been reported by Schroder *et al.* [11] for a pure chlorine-substituted bent-core mesogen. On the other hand, the binary mixture of the same bent-core and a calamitic mesogen is characterized by a temperature-dependent spontaneous polarization (see Fig. 8 in [11]). As far as we know, temperature variation of the tilt angle in the $B2$ phase is generally weaker than that of the polarization. Variation of the tilt angle can qualitatively be characterized by the variation of the layer spacing. Experimentally the layer spacing is nearly constant, for example, for the pure bent-core mesogen studied in [11], and for one of the mesogens investigated by Wirth *et al.* [16]. Thus one concludes that the approximation of perfect orientational order is rather crude, in particular with respect to the ordering of short molecular axes. Some consequences of such an approximation are discussed in the last section. From the thermodynamical point of view this approximation means that thermal fluctuations are not expected to be very important. In this case the free energy is dominated by the internal energy and in the mean-field approximation it can be written as $F/V \approx \rho^2 \langle U_{12} \rangle / 2$, where the angular brackets denote the integration over the intermolecular vector \mathbf{r}_{12} taking into account the steric cut-off. Here ρ is the number density of molecules.

One notes that in the present simple model there is still a significant amount of freedom. The spontaneous polarization, in principal, may point in any direction and the director may or may not be tilted. It is shown in Sec. III that the actual chiral structure of the $B2$ phase determined by the unique relative orientation of the director, spontaneous polarization and the smectic layer normal, may be obtained by minimization of the sum of the average dispersion and dipole-dipole interaction energies. In addition it is shown that in the case of small molecular dipoles the most stable tilted structure is the

nonchiral one with the polarization parallel to the tilt plane. Such a phase has been suggested by Brandt *et al.* [13] on phenomenological grounds.

III. STRUCTURE OF THE TWO BENT-CORE TILTED PHASES

The structure of an ideal smectic phase composed of banana molecules is determined by the minimum of the average interaction energy that includes the dispersion and the dipole-dipole parts. In the case of perfect orientational order (i.e., $a_{1\alpha}a_{2\beta}=n_\alpha n_\beta$ and $\mathbf{b}_1=\mathbf{b}_2=\mathbf{m}$) the interaction between the corresponding ‘‘arms’’ (that are parallel to each other) of the two neighboring banana molecules is determined by the following expression [see Eq. (3)]:

$$U_{12}^\pm = -J_0 d^4 \int_{-l}^l d(\Delta t) \frac{\ell - |\Delta t|}{\rho_\pm^6(\Delta t)} + \frac{\mu^2}{r_{12}^3} [1 - 3(\mathbf{u} \cdot \mathbf{m})^2], \quad (7)$$

where $\Delta t \equiv t_2 - t_1$ and where the distance $\rho_\pm(\Delta t)$ [see Eq. (4)] is given by

$$\rho_\pm^2(\Delta t) = r_\pm^2 + (\Delta t + \Delta r_\pm)^2. \quad (8)$$

Here $\Delta r_\pm \equiv r_{12}(\mathbf{u} \cdot \mathbf{s}_\pm)$, $r_\pm^2 \equiv r_{12}^2 - \Delta r_\pm^2$, and the unit vectors $\mathbf{s}_\pm \equiv \pm \mathbf{n} \cos \alpha + \mathbf{m} \sin \alpha$. The total dipole-dipole and dispersion interaction between molecules 1 and 2 (that is equal to the sum of U_{12}^+ and U_{12}^-) should be averaged over all orientations of the intermolecular vector $\mathbf{r}_{12} \equiv r_{12}\mathbf{u}$ within the smectic layer.

The minimum distance ξ_{12} between banana molecules 1 and 2 is equal to $\max[\xi_+, \xi_-]$, where ξ_+ and ξ_- are the minimum distances between the ‘‘upper’’ and ‘‘lower’’ ‘‘arms’’ of a pair of banana molecules, respectively. These distances can be expressed in the following way. For example, ξ_+ is the minimum distance of approach between the centers of two equal rods which are both parallel to \mathbf{s}_+ . In contact the vector \mathbf{r}_{12} connecting the centers of such rods is given by $\mathbf{r}_{12} = \xi_+ \mathbf{u}$, and the minimum distance between the axes of the rods is equal to the rod diameter d . On the other hand, the same distance is given by the projection of the vector \mathbf{r}_{12} on the plane perpendicular to \mathbf{s}^+ . Taking this into account one obtains

$$d/\xi_\pm = \cos \gamma_\pm = \sqrt{1 - (\mathbf{u} \cdot \mathbf{s}_\pm)^2}, \quad (9)$$

where $\sin \gamma_\pm = (\mathbf{u} \cdot \mathbf{s}_\pm)$. It follows from Eq. (9) that $\xi_+ > \xi_-$ if

$$(\mathbf{n} \cdot \mathbf{u})(\mathbf{m} \cdot \mathbf{u}) > 0, \quad (10)$$

and $\xi_- > \xi_+$ otherwise.

Now let us define the unit vector \mathbf{w} in the layer plane perpendicular to both vectors \mathbf{n} and \mathbf{k} . One notes that the direction of any of the three vectors \mathbf{k} , \mathbf{n} , and \mathbf{w} does not have any physical meaning because only the corresponding second rank tensors $n_\alpha n_\beta$, $k_\alpha k_\beta$, and $w_\alpha w_\beta$ are fixed by the symmetry of the phase. In addition we define the unit vectors \mathbf{c} and \mathbf{l} in the tilt plane, which are normal to \mathbf{k} and \mathbf{n} , respectively, i.e., $(\mathbf{c} \cdot \mathbf{k}) = (\mathbf{l} \cdot \mathbf{n}) = 0$. Now the unit vectors \mathbf{c} and \mathbf{w} form an orthogonal basis in the layer plane, the vectors \mathbf{c} and \mathbf{k} form the basis in the tilt plane and the vectors \mathbf{w} and \mathbf{l} form

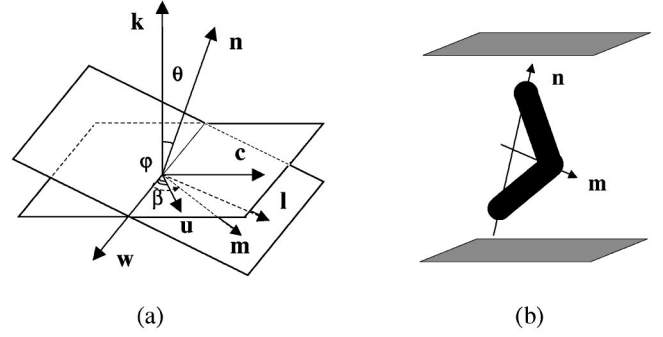


FIG. 3. The coordinate system (a) and orientation of the bent-core molecule in the tilted amectic layer (b).

the basis in the plane perpendicular to the director \mathbf{n} . Choosing these vectors as shown in Fig. 3 one obtains the following expressions for the vectors \mathbf{u} and \mathbf{m} :

$$\mathbf{u} = \mathbf{w} \cos \varphi + \mathbf{c} \sin \varphi, \quad (11)$$

$$\mathbf{m} = \mathbf{w} \cos \beta + \mathbf{l} \sin \beta, \quad (12)$$

where the vector φ specifies the orientation of the intermolecular vector in the layer plane and the vector β specifies the orientation of the spontaneous polarization which is always perpendicular to the director in the present simple model. Then the scalar products $(\mathbf{n} \cdot \mathbf{u})$ and $(\mathbf{m} \cdot \mathbf{u})$ may be expressed as:

$$(\mathbf{u} \cdot \mathbf{n}) = \sin \varphi \sin \theta, \quad (13)$$

$$(\mathbf{u} \cdot \mathbf{m}) = \cos \varphi \cos \beta + \sin \varphi \sin \beta \cos \theta, \quad (14)$$

where θ is the tilt angle. In the cases $\{-\pi/2 < \theta \leq \pi/2, -\pi/2 < \beta \leq \pi/2\}$ and $\{\pi/2 < \theta \leq 3\pi/2, \pi/2 < \beta \leq 3\pi/2\}$ one obtains from Eqs. (10), (13), and (14):

$$\xi_+ > \xi_- \text{ if } 0 < \varphi \leq \frac{\pi}{2} + \Delta\varphi, \quad (15)$$

$$\xi_- > \xi_+ \text{ if } \frac{\pi}{2} + \Delta\varphi < \varphi \leq \pi,$$

where

$$\Delta\varphi \equiv \arctan(\cos \theta \tan \beta). \quad (16)$$

In the opposite cases $\{-\pi/2 < \theta \leq \pi/2, \pi/2 < \beta \leq 3\pi/2\}$ and $\{\pi/2 < \theta \leq 3\pi/2, -\pi/2 < \beta \leq \pi/2\}$ one obtains:

$$\xi_- > \xi_+ \text{ if } 0 < \varphi \leq \frac{\pi}{2} + \Delta\varphi, \quad (17)$$

$$\xi_+ > \xi_- \text{ if } \frac{\pi}{2} + \Delta\varphi < \varphi \leq \pi.$$

Equations (15)–(17) together with Eq. (9) completely define the minimum distance between two banana molecules for different values of the parameters θ and β .

A. Analytical results for the dispersion interaction

Taking into account that in Eq. (8) $\Delta r_{\pm} \ll \ell$ and that the distance ρ_{\pm} strongly decreases with the increasing parameter Δt , one may extend the limits of integration in Eq. (7) to the infinity:

$$U_{disp}^{\pm} \approx -J_0 d^4 \int_{-\infty}^{\infty} d(\Delta t) \frac{\ell - |\Delta t|}{\rho_{\pm}^6(\Delta t)}. \quad (18)$$

Substituting Eq. (8) into Eq. (18) one obtains:

$$U_{disp}^{\pm} \approx J_0 d^4 \left\{ -\frac{3\pi}{8} \frac{\ell}{r_{\pm}^5} + \frac{1}{2(r_{\pm}^2 + \Delta r_{\pm}^2)^2} + \frac{\Delta r_{\pm}^2}{4r_{\pm}^4} \frac{5r_{\pm}^2 + 3\Delta r_{\pm}^2}{(r_{\pm}^2 + \Delta r_{\pm}^2)^2} + \frac{3\Delta r_{\pm}}{4r_{\pm}^5} \arctan \frac{\Delta r_{\pm}}{r_{\pm}} \right\}. \quad (19)$$

Taking into account that $r_{\pm}^2 + \Delta r_{\pm}^2 = r_{12}^2$ and $\Delta r_{\pm} \equiv r_{12}(\mathbf{u} \cdot \mathbf{s}_{\pm})$, one obtains $|\Delta r_{\pm}|/r_{\pm} = \tan \gamma_{\pm}$ and $r_{\pm}/r_{12} = \cos \gamma_{\pm}$ where $\sin \gamma_{\pm} = |\Delta r_{\pm}|/r_{12} = |(\mathbf{u} \cdot \mathbf{s}_{\pm})|$. Then Eq. (19) can be rewritten as

$$U_{disp}^{\pm} \approx -\frac{3\pi}{8} J_0 \frac{\ell}{d} \left(\frac{d}{r_{12}} \right)^5 \frac{1}{[1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2]^{5/2}} + \frac{1}{4} J_0 \left(\frac{d}{r_{12}} \right)^4 \left\{ \frac{2 + (\mathbf{u} \cdot \mathbf{s}_{\pm})^2}{[1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2]^2} + \frac{3(\mathbf{u} \cdot \mathbf{s}_{\pm}) \arcsin(\mathbf{u} \cdot \mathbf{s}_{\pm})}{[1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2]^3} \right\}. \quad (20)$$

Now the total dispersion interaction between molecules 1 and 2, that is equal to the sum of U_{disp}^+ and U_{disp}^- , should be averaged over all orientations of the intermolecular vector $\mathbf{r}_{12} \equiv r_{12} \mathbf{u}$ in the layer plane. The result strongly depends on the minimum distance ξ_{12} between the two molecules. One notes [see Eqs. (15)–(17)] that the minimum distance is equal to ξ_+ or ξ_- depending on the relative values of the angles θ and β . Let us assume for simplicity that $-\pi/2 < \theta \leq \pi/2$ and $-\pi/2 < \beta \leq \pi/2$. In this case the minimum distance is equal to ξ_+ if $0 < \varphi \leq \pi/2 + \Delta\varphi$, and is equal to ξ_- if $\pi/2 + \Delta\varphi < \varphi \leq \pi$. From Eqs. (13) and (14) one obtains

$$(\mathbf{u} \cdot \mathbf{s}_{\pm}) = \pm(\mathbf{u} \cdot \mathbf{n}) \cos \alpha + (\mathbf{u} \cdot \mathbf{m}) \sin \alpha = \pm \sin \varphi \sin \theta \cos \alpha + [\cos \varphi \cos \beta + \sin \varphi \sin \beta \cos \theta] \sin \alpha. \quad (21)$$

Taking into account Eq. (21), one notes that the functions U_{disp}^{\pm} [see Eq. (20)] and ξ_{\pm} [see Eq. (9)] are periodic with respect to the angle φ with the period π . Thus, the integral over φ from $\pi/2$ to $3\pi/2$ is the same as the one from $-\pi/2$ to $\pi/2$. As a result, the average dispersion interaction potential may be written as

$$\langle U_{disp} \rangle = 2d^{-2} \int_0^{\pi/2 + \Delta\varphi} d\varphi \int_{\xi_+}^{\infty} U_{disp} r_{12} dr_{12} + 2d^{-2} \int_{\pi/2 + \Delta\varphi}^{\pi} d\varphi \int_{\xi_-}^{\infty} U_{disp} r_{12} dr_{12}, \quad (22)$$

where the parameter $\Delta\varphi$ is determined by Eq. (16). The integral over the intermolecular distance r_{12} in Eq. (22) can be taken analytically. For example, in the case $\xi_{12} = \xi_+$ one obtains

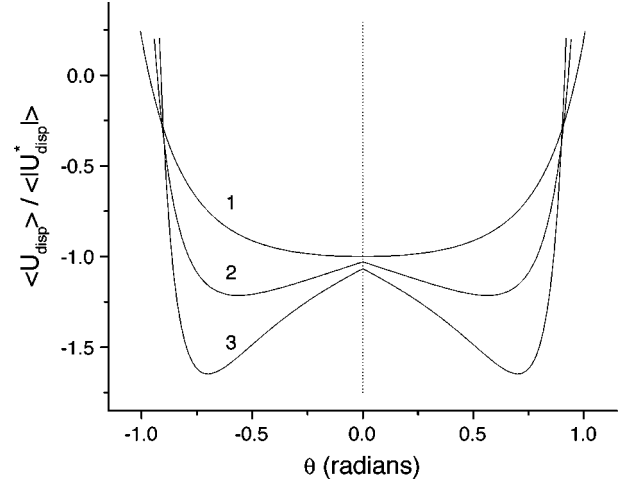


FIG. 4. Average dispersion interaction energy between parallel banana molecules located in the same smectic layer as a function of the tilt angle for $(\ell \cos \alpha)/d = 1.5$: (1) $\alpha = 0$; (2) $\alpha = \pi/15$; (3) $\alpha = \pi/10$. The energy is normalized by that for the pair of corresponding rod-like molecules $\langle U_{disp}^* \rangle$.

$$d^{-2} \int_{\xi_+}^{\infty} U_{disp}^{\pm} r dr = \frac{1}{8} J_0 \frac{2 - \pi \ell/d + (\mathbf{u} \cdot \mathbf{s}_{\pm})^2}{1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2} + \frac{3}{8} J_0 \frac{(\mathbf{u} \cdot \mathbf{s}_{\pm}) \arcsin(\mathbf{u} \cdot \mathbf{s}_{\pm})}{[1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2]^{3/2}} + \frac{1}{8} J_0 \frac{[1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2][2 + (\mathbf{u} \cdot \mathbf{s}_{\pm})^2]}{[1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2]^2} + \frac{1}{8} J_0 \frac{3[1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2](\mathbf{u} \cdot \mathbf{s}_{\pm}) \arcsin(\mathbf{u} \cdot \mathbf{s}_{\pm})}{[1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2]^{5/2}} - \frac{1}{8} \pi J_0 \frac{\ell [1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2]^{3/2}}{d [1 - (\mathbf{u} \cdot \mathbf{s}_{\pm})^2]^{5/2}}. \quad (23)$$

In the opposite case $\xi_{12} = \xi_-$ the signs “+” and “−” are interchanged on the right-hand side of Eq. (23). Substituting Eqs. (21) and (23) into Eq. (22) and integrating the result numerically with respect to the angle φ , one obtains the average dispersion potential $\langle U_{disp} \rangle$. The dependence of the average dispersion interaction on the tilt angle θ is presented in Fig. 4 for different angles α . One can readily see that for sufficiently large angles $\alpha \neq 0$ the minimum of the average dispersion interaction potential corresponds to a nonzero tilt. Moreover, in the tilted phase the minimum of the averaged dispersion interaction corresponds to $\beta = \pm \pi/2$ and thus the spontaneous polarization is parallel to the tilt plane.

B. Analytical results for the dipole-dipole interaction

The dipole interaction between the neighboring parts of the two banana molecules can be written as

$$U_{dd} = 2 \frac{\mu^2}{r_{12}^3} [1 - 3(\mathbf{u} \cdot \mathbf{m})^2], \quad (24)$$

where r_{12} is the distance between the dipoles. By analogy with Eq. (22) the average dipole-dipole interaction may be written in the form:

$$\begin{aligned} \langle U_{dd} \rangle = & 2d^{-2} \int_0^{\pi/2+\Delta\varphi} d\varphi \int_{\xi_+}^{\infty} U_{dd} r_{12} dr_{12} \\ & + 2d^{-2} \int_{\pi/2+\Delta\varphi}^{\pi} d\varphi \int_{\xi_-}^{\infty} U_{dd} r_{12} dr_{12}. \end{aligned} \quad (25)$$

In the case $\xi_{12}=\xi_+$ the integration over r_{12} results in

$$\begin{aligned} d^{-2} \int_{\xi_+}^{\infty} U_{dd} r dr &= 2 \frac{\mu^2}{d^3} \frac{d}{\xi_+} [1 - 3(\mathbf{u} \cdot \mathbf{m})^2] \\ &= 2 \frac{\mu^2}{d^3} \sqrt{1 - (\mathbf{u} \cdot \mathbf{s}_+)^2} [1 - 3(\mathbf{u} \cdot \mathbf{m})^2]. \end{aligned} \quad (26)$$

In the opposite case $\xi_{12}=\xi_-$ the corresponding integral over r_{12} is equal to

$$\begin{aligned} d^{-2} \int_{\xi_-}^{\infty} U_{dd} r dr &= 2 \frac{\mu^2}{d^3} \frac{d}{\xi_-} [1 - 3(\mathbf{u} \cdot \mathbf{m})^2] \\ &= 2 \frac{\mu^2}{d^3} \sqrt{1 - (\mathbf{u} \cdot \mathbf{s}_-)^2} [1 - 3(\mathbf{u} \cdot \mathbf{m})^2]. \end{aligned} \quad (27)$$

Substituting Eqs. (14), (21), (26), and (27) into Eq. (25) and integrating the result numerically over the angle φ , one obtains the average dipole-dipole potential $\langle U_{dd} \rangle$.

By contrast to the dispersion interaction, the minimum of the average dipole-dipole interaction corresponds to $\beta = 0 \pm \pi n$, i.e., the dipole-dipole interaction promotes the perpendicular orientation of the spontaneous polarization with respect to the tilt plane.

C. Phase diagram

If both the dipole-dipole and the dispersion interactions are taken into account, the total averaged interaction energy may have its minimum either at $\beta = \pm\pi/2 \pm \pi n$ or at $\beta = 0 \pm \pi n$ depending on the relative strength of these two interactions that can be measured by the dimensionless parameter $\mu^2/(d^3 J_0)$. The corresponding $\{\alpha, \mu\}$ phase diagrams are presented in Fig. 5 for different values of the axial ratio ℓ/d of the rod in the banana dimer. It follows from the phase diagram that the tilted phase with the spontaneous polarization perpendicular to the tilt plane is more stable for large dipoles and small angles α . In this phase corresponding to the commonly observed *B2* phase the spontaneous polarization breaks the mirror symmetry, and, as a result, every smectic layer appears to be chiral. By contrast, the nonchiral banana phase, where the polarization is parallel to the tilt plane, is more stable for small molecular dipoles and large angles α .

The dependence of the equilibrium tilt angle θ on the reduced square dipole is presented in Fig. 6 for different values of the angle α . One can readily see that the tilt angle increases with the increasing angle α . The discontinuity in the tilt angle corresponds to the first-order phase transition between the *B2* phase which is more stable for large dipole moments, and the nonchiral phase where the polarization is parallel to the tilt plane. The dependence of the equilibrium tilt angle θ on the angle α is presented in Fig. 7 for different

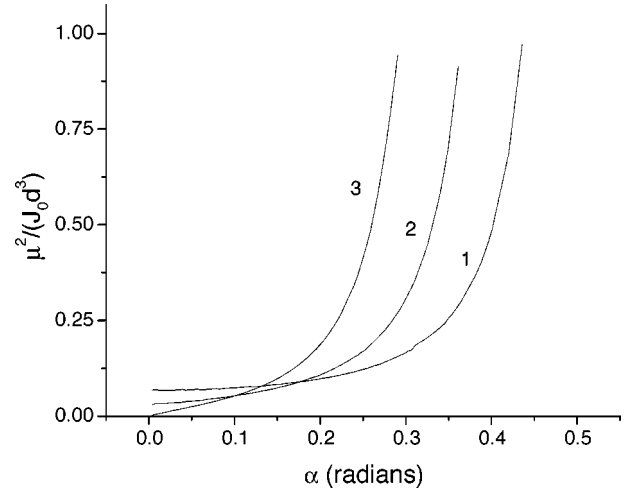


FIG. 5. Phase diagram for the system of perfectly ordered banana molecules. Solid lines corresponding to different axial ratios (1) $\ell/d=1.5$; (2) $\ell/d=1.7$; (3) $\ell/d=2$ separate the *B2* phase, where the polarization is perpendicular to the tilt plane, from the nonchiral phase, where the polarization is parallel to the tilt plane. The *B2* phase is more stable for large dipoles and small angles α .

values of the dimensionless parameter $\mu^2/(d^3 J_0)$. It follows from Fig. 7 that the tilt angle increases with the increasing molecular dipole. Similar to Fig. 6, the discontinuity in the tilt angle corresponds to the first-order transition between the two banana phases with different orientations of the polarization with respect to the tilt plane. The *B2* phase is more stable for larger values of the opening angle $\pi-2\alpha$.

IV. CONCLUSIONS

It has been shown that in the smectic phase formed by perfectly aligned bent-core molecules the tilt of the director

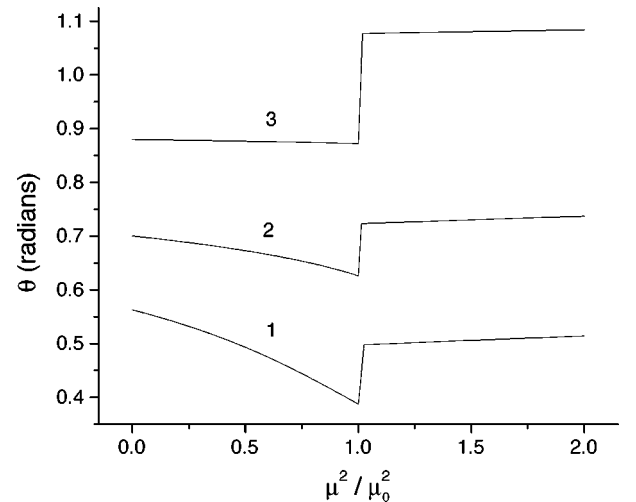


FIG. 6. Equilibrium tilt angle in a banana smectic phase as a function of the reduced square dipole for $(\ell \cos \alpha)/d=1.5$ and for different values of α : (1) $\alpha=\pi/15$; (2) $\alpha=\pi/10$; (3) $\alpha=\pi/7$. For each curve the dipole moment is normalized separately by the critical value $\mu_0=\mu_0(\alpha)$ that is the value of the dipole at the transition point for a given α .

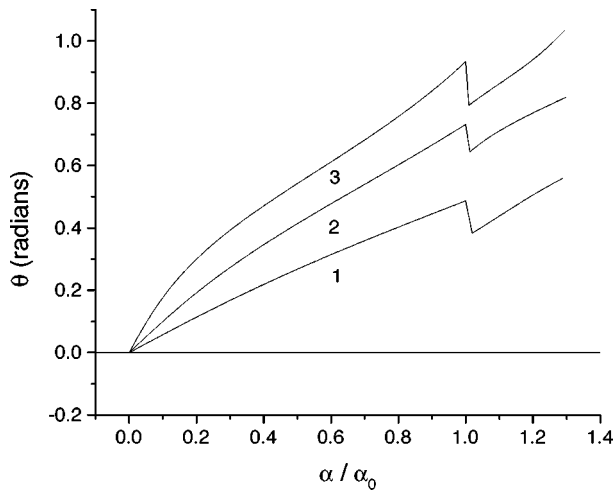


FIG. 7. Equilibrium tilt angle as a function of the reduced angle α for $(\ell \cos \alpha)/d=1.5$ and for different values of the dimensionless dipole: (1) $\mu^2/(d^3J_0)=0.1$; (2) $\mu^2/(d^3J_0)=0.2$; (3) $\mu^2/(d^3J_0)=0.5$. For each curve the angle α is normalized separately by the critical value $\alpha_0=\alpha_0(\mu)$ that is the angle corresponding to the transition point for a given μ .

may be determined by the dispersion interaction between the interaction centers distributed along the molecules. The bent shape appears to be very important as the tilt is stabilized only for banana molecules with sufficiently small opening angles. In the context of the present model the tilt of the director is further stabilized by the electrostatic interaction between permanent dipoles located at the centers of two “arms” of different banana molecules, and also by the increasing molecular axial ratio. It should be noted that the magnitude of the tilt angle obtained from the present model is significantly larger than typical experimental data. Typical experimental values of the tilt angle are in the domain between $14\text{--}25^\circ$ [6,14,15] and $30\text{--}40^\circ$ [6,11,22,24]. This discrepancy can partly be explained by the geometry of the molecular model used in this paper. Here the molecule is represented by two rigid rods joined at a certain fixed opening angle. In real bent-core materials the opening angle characterizes the bent of the rigid core, while the molecule typically possesses also two alkyl tails. As a result the average effective bent angle α of such a molecule may be significantly smaller than that of the core, and the corresponding experimental values of the tilt angle may be closer to theoretical results for smaller α (see Fig. 6 and Fig. 7). On the other hand, the low values of the tilt angle obtained in the present model may partly be related to the approximation of perfect orientational order. Thermal fluctuations are known to decrease the corresponding order parameters including the average tilt of long molecular axes in smectic phases.

In the tilted and polar smectic phase the equilibrium direction of the spontaneous polarization is determined by a balance between the dispersion and dipole-dipole interactions. As shown on the phase diagram (see Fig. 5), in the context of the present simple model there exist two tilted polar phases which differ by the orientation of the spontaneous polarization with respect to the tilt plane. For sufficiently large dipole moments and/or sufficiently large opening

angles the most stable tilted phase is the one with the polarization perpendicular to the tilt plane. This structure corresponds to the most common $B2$ phase observed in many bent-core molecular systems [6]. In particular, the $B2$ phase is stabilized by the electrostatic dipole-dipole interaction between banana molecules if the dipoles are located within the bent-core structure. The stability range of the $B2$ phase decreases with the increasing axial ratio of the molecule. It is well known that the $B2$ phase is chiral, and the chirality of a smectic layer can be specified by the pseudoscalar parameter $(\mathbf{P}_s \cdot [\mathbf{n} \times \mathbf{k}])(\mathbf{n} \cdot \mathbf{k})$ that changes sign under polarization reversal. In the present model the chirality appears as a result of the spontaneous symmetry breaking, and the two directions of the spontaneous polarization are completely equivalent from the energy point of view. In this case domains of opposite chirality, which have been observed experimentally [5], should always be present in a sufficiently large system. One notes that the point symmetry of the $B2$ banana phase is the same as that of the conventional ferroelectric smectic- C^* phase. However, the microscopic origin of the chiral structure in the $B2$ phase is completely different from that of the Sm- C^* phase. In the conventional Sm- C^* phase spontaneous polarization appears only if the molecules are chiral, and the direction of the polarization is specified by the molecular chirality. In other words, the opposite directions of the spontaneous polarization are not energetically equivalent, and the actual direction is stabilized by some specific interactions between chiral molecules [17,18]. By contrast, in the $B2$ phase the molecules are nonchiral (at least on average), and the spontaneous polarization appears in a self-consistent way, mainly due to excluded volume effects [12,19,20]. Thus, this is an example of the *proper* ferroelectricity similar to the one observed in solid crystals. The actual chiral structure of the $B2$ phase is then determined by a spontaneous chiral symmetry breaking. In the simple model considered in this paper the equilibrium polarization is either parallel or perpendicular to the tilt plane. In principle the polarization can make an arbitrary angle with the tilt plane, as proposed by de Gennes [21]. There are experimental indications that such a chiral smectic phase which is characterised by the C_1 symmetry, indeed exists [22–25]. The present model does not describe this phase because it does not correspond to the minimum of the simple model interaction potential. However, if the approximation of the perfect orientational order is not used, one has to take into consideration an entropy term which generally possesses a more complex orientational dependence. Then the low symmetry bent-core phase may correspond to one of the minima of the corresponding free energy under favorable conditions. This problem deserves a separate investigation.

It should be noted that chirality effects in real banana liquid crystal materials may be more complicated. For example, under application of suitable electric fields the chirality of the bent-core phase may be interchanged between homochiral and racemic [16]. Moreover, chiral domains appear even in the untilted $B4$ phase as clearly indicated by observations of circular dichroism and microscopic textures [26,27]. The chirality is also preserved during the transition between the $B2$ and $B4$ phases [28]. These effects may be determined by a spontaneous deracemization in the system

of chiral conformers. The existence of two chiral conformations of a typical bent-core molecule is strongly suggested by NMR data [29]. The role of chiral conformations in the banana phases will be considered in the future publication.

The analysis of the present molecular model indicates that if the molecular dipoles are small and/or the opening angle of the bent-core molecule is small, the most stable tilted smectic phase possesses a nonchiral structure with the spontaneous polarization being parallel to the tilt plane. Such a phase corresponds to one of the structures suggested in Ref. [13]. One notes, however, that this combination of molecular parameters is not typical for real bent-core materials. In the case of small opening angles the shape of a bent-core molecule is becoming too biaxial and the smectic layered structure may lose its stability. Instead, such systems may exhibit a columnar phase [6]. This enables one to understand why this nonchiral tilted phase should be far less common than the B_2 phase. Recently a similar phase has been observed in banana-shaped 4-cyanoresorcinol derivatives [30] although it is difficult to distinguish it from the orthogonal Sm-A type

polar biaxial phase. Finally it should be noted that the present results have been obtained using a molecular model with homogeneous distribution of interaction centers along the molecule. The dispersion interaction between real banana molecules is mainly determined by the interaction between bent cores located in the central part of the molecule. Thus it may be interesting to consider the influence of the distribution of interaction centers on the phase diagram. This problem is currently under study.

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