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# Molecular model for the anticlinic smectic-$C_A$ phase

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Both phenomenological and molecular-statistical theories of the anticlinic smectic-$C_A$ phase (Sm-$C_A$) are considered in detail. The anticlinic structure produces antiferroelectricity in the chiral smectic-$C_A$ phase (Sm-$C_A$*). The molecular theory is based on a simple model potential which stabilizes Sm-$C_A$ with respect to the synclinic smectic-$C$ phase (Sm-$C$). Conventional dispersion and steric interactions between mesogenic molecules generally do not promote Sm-$C_A$. It may be stabilized by interlayer orientational correlations between transverse molecular dipoles located in the flexible chains. Such correlations are not sensitive to molecular handedness (chirality), and thus the theory accounts for the formation of the anticlinic phase in racemic mixtures. The model is also confirmed by other experimental data. Finally a simple phase diagram of the perfectly ordered smectic liquid crystal is presented which contains Sm-$A$, Sm-$C$, and Sm-$C_A$.

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## I. INTRODUCTION

The discovery of the chiral antiferroelectric smectic-$C_A$ phase (Sm-$C_A$*) in a liquid crystal compound has shown that the antiferroelectric ordering can be stabilized in a mesophase without true long-range positional order [1]. This was a surprising and fundamental condensed matter finding, and prompted intensive research into the structure and properties of Sm-$C_A$* [2]. Before the discovery of the antiferroelectric Sm-$C_A$* structure it was believed that the packing entropy effect as well as the Maier-Saupe-type intermolecular interaction causes a tilting in the same direction and sense except for a slight precession from layer to layer due to chirality [3,4]. At that time the chiral, possibly ferroelectric, smectic-$C$ phase (Sm-$C$*) and the achiral smectic-$C$ phase (Sm-$C$) were the only known tilted smectic phases with fluid layers. After the antiferroelectric Sm-$C_A$* structure was established, it became clear that tilted smectic phases can be either synclinic or anticlinic. Similar to synclinic, ferroelectric Sm-$C$*, the tilt of the director induces the spontaneous polarization in each layer of anticlinic, antiferroelectric Sm-$C_A$*; the spontaneous polarization is perpendicular to the tilt plane, and its sense is uniquely determined by the tilt sign. At the same time, an additional *in-plane* spontaneous polarization, which is parallel to the tilt plane, emerges at each smectic layer boundary in Sm-$C_A$*. Chirality plays a crucial role for the emergence of the polarization in the direction of the tilt plane normal [5–7], but not for the emergence of the polarization in the tilt plane [8–11]. We note that the anticlinic structure is the primary feature of Sm-$C_A$* and Sm-$C_A$, and that the emergence of the anticlinic structure is independent of chirality. In this paper we make an attempt to develop a molecular theory of achiral anticlinic Sm-$C_A$.

The molecular theory helps one to understand the most interesting properties found in the vicinity of the phase transition between Sm-$C$* and Sm-$C_A$*. The transition is of first order, and in this domain the system is characterized by a frustration between synclinic and anticlinic ordering [12,13]. The frustration is not only fundamentally interesting but also very attractive from an application point of view, causing the temperature induced sequence of phase transitions to resemble the Devil's staircase [13,14]. The frustration is also related to the thresholdless, hysteresis-free, V-shaped switching induced by an applied electric field [13,15,16]. The V-shaped switching is very promising for a new generation of liquid crystal displays [13,17,18]. To understand the frustration and to develop new liquid crystal materials, it is important to elucidate the intermolecular interactions that stabilize Sm-$C_A$* and to propose a realistic molecular model.

We begin with a summary of the experimental findings that are useful for the theoretical considerations presented below. The anticlinic structure was first speculated by Beresnev *et al.* [19] in a study of pyroelectricity for a liquid-crystalline mixture. Chandani *et al.* [1] confirmed the anticlinic Sm-$C_A$* structure in compound 1 (see Fig. 1) by observing the disappearance of the so-called full-pitch reflection band that clearly emerges in Sm-$C$*. Furthermore, they showed that an external electric field can induce a phase transition from Sm-$C_A$* to ferroelectric Sm-$C$*, and produces an electric current peak during the transition, confirming the existence of antiferroelectricity in Sm-$C_A$*. On the molecular scale, the anticlinic, antiferroelectric structure was first confirmed in compound 3 by Galerne and Liebert [20] and then in compound 1 by Bahr and Fliegner [21]. Both groups used very thin films either floating at the free surface of an isotropic droplet or freely suspended in a frame. We note that because of the liquidlike order in smectic layers, it is very difficult to establish the existence of an anticlinic structure by using x-ray diffraction. Quite recently, however, Mach *et al.* [2] were successful in directly observing double-layer periodicity by means of the resonant x-ray scattering technique. It was confirmed that the tilting planes in adjacent layers are exactly parallel in Sm-$C_A$, and almost exactly parallel in Sm-$C_A$*. In the latter case a small splitting of half-order diffracted peaks due to the helicoidal structure induced by the chirality was detected. In this way, it was firmly established that Sm-$C_A$ and Sm-$C_A$* have the anticlinic herringbone structure.

At present there are more than 1000 compounds which

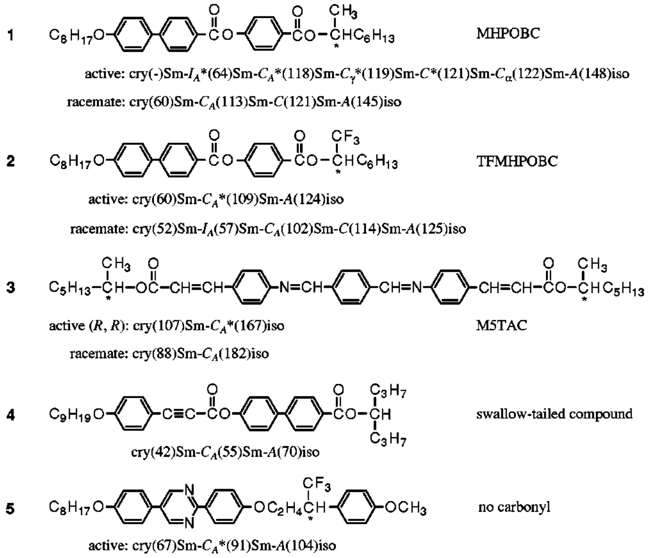

FIG. 1. Some examples of compounds showing Sm-$C_A$* or Sm-$C_A$. Compounds 1 and 2 are the prototype antiferroelectric liquid crystals [1]. Compound 3 was used to confirm the anticlinic, antiferroelectric phase, on a molecular scale, which was originally designated as Sm-$O$* and Sm-$O$ [20]. A swallow-tailed compound 4 is achiral but shows Sm-$C_A$ [31,32]. All these compounds 1–4 have large transverse dipole moments near the joint of the chiral or swallow-tail chain, which projects obliquely from the core part [23–29]. Compound 5 does not have any carbonyl groups [38]; still we believe that the chiral chain is bent significantly in Sm-$A$ and Sm-$C_A$*.

exhibit Sm-$C_A$* [22]. All these molecules are quite similar in their chemical structures, and possess significantly large transverse permanent dipole moments in the vicinity of the chiral centers, as illustrated in Fig. 1. It has been shown that the chiral chain is bent even in the smectic-$A$ phase (Sm-$A$) for compound 1, which is a prototype antiferroelectric liquid crystal, and for some other compounds [23–29]. In this case the large dipole moments are located in such a way that they can interact strongly when the two neighboring molecules belong to adjacent layers. One of the intermolecular interactions, which may stabilize Sm-$C_A$* against Sm-$C$*, was considered as the pairing of large transverse dipole moments in adjacent layers [30]. However, it was shown experimentally that swallow-tailed compounds with two terminal chains of equal length [31,32] as well as racemate mixtures [33–35] (see Fig. 1) may also exhibit Sm-$C_A$. These results can hardly be explained in the context of the pairing model without additional *ad hoc* assumptions that the pairing occurs between enantiomers of the same handedness [33].

Miyachi and co-workers [10,22] proposed another stabilization mechanism for Sm-$C_A$*, which was based on the following experimental fact revealed using polarized IR spectroscopy. In Sm-$C_A$* the carbonyl group near the chiral center has a tendency to lie in the tilt plane, while in Sm-$C$* it assumes a fairly upright orientation. We note that the in-plane spontaneous polarization perpendicular to the tilt plane normal, $P_x$, is independent of chirality and exists even in racemates and achiral swallow-tailed compounds. As will be discussed in Sec. II below, the existence of the in-plane alternating perpendicular polarization in achiral Sm-$C_A$ is supported by general symmetry arguments [8,9]. Thus the $P_x$ model does not seem to be in contradiction with any experimental data. However, it remains unclear how the in-plane polarization is able to stabilize the anticlinic phase. As shown by Prost and Bruinsma [36,37], the direct electrostatic interaction between polar planes vanishes in any smectic phase, and thus the in-plane polarization can manifest itself only via coupling with the tilt order parameter. We will show in Sec. II [see Eq. (9)] that this coupling does contribute to the stability of Sm-$C_A$, but the effect is not strong enough to be responsible for the formation of the anticlinic configuration.

It is interesting to note that antiferroelectric, anticlinic Sm-$C_A$* has been discovered during the experimental studies of *chiral* ferroelectric, synclinic Sm-$C$* with large spontaneous polarization. We may conclude that the anticlinic configuration should be determined by some molecular structural features that are typical of ferroelectric Sm-$C$* with large spontaneous polarization. One obvious structural element of this kind is the transverse dipole that is often located in the alkyl chain close to the molecular end. On the other hand, the direct interaction between such dipoles vanishes after the orientational averaging. It is shown in this paper that Sm-$C_A$ may be established by strong orientational correlations between such transverse molecular dipoles when they are located in adjacent smectic layers. These correlations are not sensitive to chirality, and are weakly affected by any polar ordering. At the same time they can be sufficiently strong if the transverse dipoles are large and are located far from the molecular center.

This paper is arranged as follows. In Sec. II we discuss the symmetry and phenomenological theory of Sm-$C_A$, and consider the origin of the in-plane perpendicular spontaneous polarization in the achiral anticlinic phase. In Sec. III we give the free energy of the tilted smectic phase composed of rigid biaxial molecules. In this simple theory both quadrupole and dipole order parameters of the short molecular axes are neglected. Then, in Sec. IV, we determine the mathematical form of the interaction potential that promotes the anticlinic Sm-$C_A$ structure and discuss common intermolecular interactions in smectic liquid crystals. It is shown that conventional dispersion and steric intermolecular interactions generally do not stabilize Sm-$C_A$. In Sec. V the orientational correlations between transverse molecular dipoles are considered, and it is concluded that such correlations may be responsible for the stability of Sm-$C_A$. Finally, the simplified phase diagram of a smectic liquid crystal material is presented in Sec. VI, and concluding remarks are given in Sec. VII.

## II. PHENOMENOLOGICAL THEORY OF THE SMECTIC-$C_A$ PHASE

### A. Symmetry elements of the anticlinic Sm-$C_A$ phase

The main difference in symmetry between anticlinic Sm-$C_A$ and common Sm-$A$ and Sm-$C$ is the coupling between the translation and the director orientation. By contrast to Sm-$A$ and Sm-$C$, Sm-$C_A$ is not invariant with respect to an elementary translation $z' \rightarrow z+d$ along the smectic layer normal, where $d$ is the smectic period. Instead, there is a gliding plane which is parallel to the $z$ axis and perpendicular to the tilt plane. This plane corresponds to the translational-

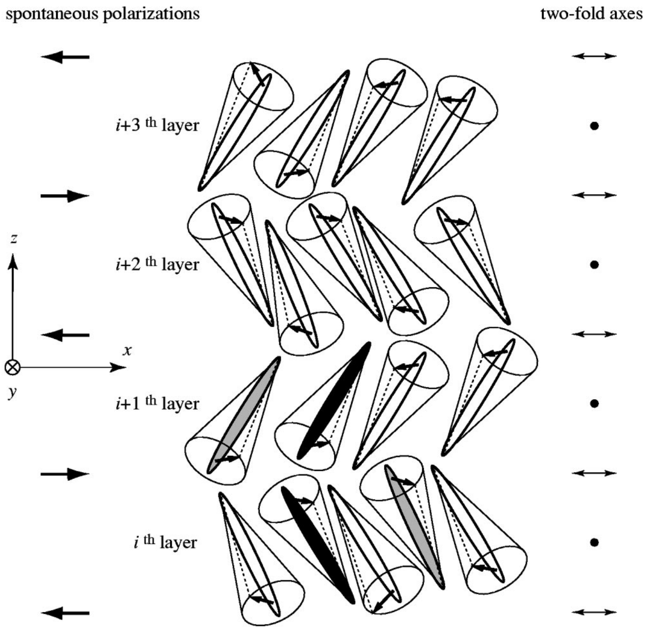

FIG. 2. Schematic illustration of the Sm-$C_A$ anticlinic herringbone structure, which is stabilized by the orientational correlations of transverse dipoles in adjacent layers. The right handed Cartesian coordinates, $x$, $y$, and $z$ are so defined that the $y$ and $z$ axes are parallel to the tilt plane normal and the smectic layer normal, respectively. Two types of $C_2$ symmetry axes are located as indicated on the right side. In-plane spontaneous polarizations emerge at smectic layer boundaries as shown on the left side.

inversion symmetry element of Sm-$C_A$ which is invariant under an elementary translation along the $z$ axis, plus the inversion with respect to the $yz$ plane where the $y$ axis is perpendicular to the tilt plane (see Fig. 2). Thus in Sm-$C_A$ we have to take into consideration the space symmetry group, unlike Sm-$C$, where only the point symmetry group needs to be considered. In practical terms this means that it is important to consider the *location* of the symmetry axes within the Sm-$C_A$ structure.

Similar to simple Sm-$C$, there exists a twofold symmetry axis which is parallel to the tilt plane normal (the $y$ axis) and is located in the middle of a layer. At the same time there exists another twofold axis which is parallel to the $x$ axis in the tilt plane, and is located at the layer boundary (see Fig. 2). Brand *et al.* were perhaps the first who insisted on the importance of this axis [8,9]. In addition, in achiral Sm-$C_A$ (which has been observed in racemates), the tilt plane is also a mirror plane, similar to achiral Sm-$C$. Therefore, in achiral Sm-$C_A$ there is no spontaneous polarization in the direction parallel to the tilt plane normal (even within a single layer). On the other hand, the $C_2$ axis at the layer boundary is not perpendicular to any mirror plane. Thus, according to the Curie principle, in the general case there must be a spontaneous polarization in the tilt plane along this axis. This spontaneous polarization is located at the layer boundary, and its sign is reversed under the elementary translation along the $z$ axis.

The existence of the perpendicular spontaneous polarization along the $x$ axis was confirmed experimentally [10,11]. In chiral antiferroelectric Sm-$C_A$* we find also an independent spontaneous polarization parallel to the tilt plane normal. This parallel spontaneous polarization is related to molecular chirality, and alternates its sign from layer to layer. Thus the ordering of molecular dipoles in real antiferroelectric liquid crystals can be rather complicated. For example, the molecular dipoles located near the chiral center can simultaneously take part in two different kinds of antiferroelectric ordering determined by different (chiral and achiral, respectively) intermolecular interactions.

### B. Order parameter and the free energy expansion

The phenomenological theory of antiferroelectric Sm-$C_A$* and ferroelectric Sm-$C$* was developed by several authors [5,6,13,39–44]. All these existing theories operate with the free energy that depends on the Sm-$C$ order parameters for individual layers. In this paper we use a more traditional phenomenological approach similar to the one used by Pikin and Osipov in their theory of ferroelectric Sm-$C$* [45]. We will limit ourselves to achiral Sm-$C_A$, because in the context of this approach the description of every new phase requires an introduction of the corresponding new order parameter. The primary goal of our investigation is the analyses of the stability of the anticlinic ordering.

Taking into account the spatial periodicity of Sm-$C$ the smectic order parameter can be written as

$$\vec{\xi}_C(z)=\vec{\xi}_0\exp(iqz), \tag{1}$$

where $q=2\pi/d$, and the amplitude $\vec{\xi}_0$ is expressed in terms of the smectic layer normal $\mathbf{e}$ and the director $\mathbf{n}$. Thus

$$\vec{\xi}_0=(\mathbf{e}\cdot\mathbf{n})[\mathbf{e}\times\mathbf{n}]. \tag{2}$$

In ordinary Sm-$C$ the spatial periodicity of the order parameter is insignificant because all quantities have the same periodicity with no phase shift. By contrast, in anticlinic Sm-$C_A$ the situation is different. For example, the ''primitive cell'' of Sm-$C_A$ has the dimension of $2d$, while the density is oscillating with the period $d$ along the $z$ axis. The order parameter of Sm-$C_A$ can also be written in the form of Eq. (1) with $q=2\pi/d$ substituted for the $(1/2)q=2\pi/2d$,

$$\vec{\xi}_{CA}(z)=\vec{\xi}_0\exp\left(\frac{iqz}{2}\right), \tag{3}$$

where the vector $\vec{\xi}_0$ is given by Eq. (2). We can readily see from Eq. (3) that the actual direction of the tilt has opposite signs in adjacent layers due to the factor $\exp(iqz/2)$.

Using the vector order parameter (3), we can expand the free energy of Sm-$C_A$ as

$$\begin{aligned}F_{CA}={}&F_A+a\xi_{CA}^2+b\xi_{CA}^4+\frac{1}{2}\mathbf{P}_\perp\cdot\chi_\perp^{-1}\cdot\mathbf{P}_\perp\\&+\mu_f\mathbf{P}_\perp\cdot\operatorname{curl}\ \vec{\xi}_{CA}+g(\operatorname{curl}\vec{\xi}_{CA})^2,\end{aligned} \tag{4}$$

where the polarization $\mathbf{P}_\perp$ is parallel to the tilt plane, and $\chi_\perp$ is the corresponding susceptibility tensor. Minimization of the free energy with respect to the polarization yields

$$\mathbf{P}_\perp=-\mu_f\chi_\perp\operatorname{curl}\ \vec{\xi}_{CA}=-\frac{iq}{2}\mu_f\chi_\perp[\mathbf{e}\times\vec{\xi}_{CA}]. \tag{5}$$

Then the real part of the polarization $\mathbf{P}_\perp$ can be written as

$$\mathbf{P}_\perp = \frac{q}{2}\mu_f \chi_\perp [\mathbf{e}\times\vec{\xi}_0]\sin\left(\frac{qz}{2}\right). \tag{6}$$

At the same time the real part of Sm-$C_A$ order parameter reads

$$\vec{\xi}_0 \cos\left(\frac{qz}{2}\right), \tag{7}$$

where the vector $\vec{\xi}_0$ is given by Eq. (2).

Thus we see that Sm-$C_A$ possesses the oscillating spontaneous polarization that is perpendicular to the tilt plane normal and to the smectic layer normal. The polarization is located at the layer boundary, as can be seen from the $\pi/2$ phase shift between the polarization in Eq. (6) and the order parameter in Eq. (7). This polarization changes sign from one layer boundary to another. The macroscopic in-plane alternating spontaneous polarization $\mathbf{P}_\perp$ appears due to a flexoelectric effect, because $\mathbf{P}_\perp$ is determined by the rotation of the order parameter according to Eq. (5). Thus the microscopic origin of such polarization may be related to steric interaction between molecules of polar shape. Substituting the equilibrium value of the polarization back into the free energy, we obtain the expression for the free energy as a function of the order parameter,

$$F_{CA} = F_A + \tilde{a}\xi_{CA}^2 + b\xi_{CA}^4, \tag{8}$$

where the coefficient $a$ in Eq. (4) is now renormalized:

$$\tilde{a} = a + \frac{q^2}{4}g - \frac{q^2}{8}(\mu_f)^2\chi_\perp = \alpha(T - T_c) + \frac{q^2}{4}g - \frac{q^2}{8}(\mu_f)^2\chi_\perp . \tag{9}$$

The last term in Eq. (9) is determined by the coupling between the polarization and the order parameter in Sm-$C_A$. Thus the coupling between the order parameter and the polarization $\mathbf{P}_\perp$ increases the stability of Sm-$C_A$, and increases the transition temperature to Sm-$A$. However, the in-plane perpendicular polarization does not seem to be sufficiently strong to induce a direct transition into Sm-$C_A$.

## III. STATISTICAL THEORY

Let us consider the free energy of a smectic phase composed of rigid biaxial molecules. From the statistical point of view the smectic phase is characterized by the one-particle distribution function that determines the probability to find a given molecule at the point $\mathbf{r}$ and with the orientation $\omega$, $f_1(1) = f_1(\mathbf{r},\omega)$. The orientation of an arbitrary rigid biaxial molecule can be specified by the unit vectors $\mathbf{a}$ and $\mathbf{b}$ in the direction of the long and short molecular axes, respectively. Thus $f_1(\mathbf{r},\omega) = f_1(\mathbf{r},\mathbf{a},\mathbf{b})$. Now the free energy of the smectic phase can be written in the generalized mean-field approximation as

$$\begin{aligned} F = {} & \rho kT \int f_1(\mathbf{r},\omega)\log f_1(\mathbf{r},\omega)\, d\mathbf{r}\, d\omega \\ & + \frac{1}{2}\rho^2 \int \Omega(r_{12} - \xi_{12}) V_{att}(\mathbf{r}_{12},\omega_1,\omega_2) f_1(\mathbf{r}_1,\omega_1) \\ & \times f_1(\mathbf{r}_2,\omega_2)\, d\mathbf{r}_1 d\mathbf{r}_2 d\omega_1 d\omega_2 \\ & + \frac{1}{2}\rho^2 kT \int \{\Omega(r_{12} - \xi_{12}) - 1\} f_1(\mathbf{r}_1,\omega_1) \\ & \times f_1(\mathbf{r}_2,\omega_2)\, d\mathbf{r}_1 d\mathbf{r}_2 d\omega_1 d\omega_2, \end{aligned} \tag{10}$$

where $V_{att}(\cdots)$ is the interaction energy between molecules 1 and 2, and $\Omega(r_{12} - \xi_{12})$ is a step function. Here the function $\xi_{12}$ is the closest distance of approach for the molecules 1 and 2 with fixed mutual orientation. The function $\Omega(r_{12} - \xi_{12}) = 0$ if $r_{12} < \xi_{12}$, i.e., if the molecules penetrate each other, and $\Omega(r_{12} - \xi_{12}) = 1$ otherwise. Thus the function $\Omega(r_{12} - \xi_{12})$ describes the so called steric cutoff. The first term in Eq. (10) is the orientational entropy, the second term is the internal energy, and the third term is the packing entropy.

We will consider possible phase transitions from Sm-$A$ to Sm-$C$ or to Sm-$C_A$ that are located far from the nematic or isotropic phases. Thus we will use the simple approximation of the perfect orientational and translational order. In this approximation the long molecular axes $\mathbf{a}$ are assumed to be parallel to the local director $\mathbf{n}(\mathbf{r})$, i.e., $a_\alpha a_\beta = n_\alpha n_\beta$, and the molecular centers of mass are assumed to be located in smectic planes. We will also consider only short-range intermolecular interactions. (The long-range dipole-dipole interactions will be discussed in Sec. V.) A molecule is supposed to interact only with its nearest neighbors that are located in the same smectic layer and in adjacent layers. If the two nearest neighbors are located in the same layer, the intermolecular vector $\mathbf{r}_{12}$ is perpendicular to the smectic layer normal (i.e., the wave vector of the smectic structure) $\mathbf{e}$. By contrast, for the two nearest neighbors in adjacent layers the vector $\mathbf{r}_{12}$ is approximately parallel to $\mathbf{e}$.

Then the free energy [Eq. (10)] can be rewritten as

$$\frac{F}{N} = kT \int f_1(\mathbf{b})\log f_1(\mathbf{b})\, d\mathbf{b} + \gamma\sigma U_{eff}^{\perp} + \gamma(1-\sigma)U_{eff}^{\parallel}, \tag{11}$$

where $\gamma$ is the total number of nearest neighbors, and $\sigma$ is the fraction of nearest neighbors located in the same smectic layer. Here $U_{eff}^{\perp}$ and $U_{eff}^{\parallel}$ are the averaged interaction energies between two neighboring molecules in the same layer and in adjacent layers, respectively. These averaged energies are expressed as

$$U_{eff}^{\perp} = \int V_{eff}(\mathbf{b}_1,\mathbf{b}_2,\mathbf{R}_{12}^{\perp},\mathbf{n}) f_1(\mathbf{b}_1) f_1(\mathbf{b}_2)\, d\mathbf{u}_{12}^{\perp} d\mathbf{b}_1 d\mathbf{b}_2 \tag{12}$$

and

$$U_{eff}^{\parallel}=\int V_{eff}(\mathbf{b}_1,\mathbf{b}_2,\mathbf{R}_{12}^{\parallel},\mathbf{n}_1,\mathbf{n}_2)f_1(\mathbf{b}_1)f_1(\mathbf{b}_2)d\mathbf{b}_1 d\mathbf{b}_2. \tag{13}$$

Here

$$V_{eff}(\mathbf{b}_1,\mathbf{b}_2,\mathbf{r}_{12})=\Omega(r_{12}-\xi_{12})V_{att}(\mathbf{b}_1,\mathbf{b}_2,\mathbf{r}_{12}) + kT\{\Omega(r_{12}-\xi_{12})-1\} \tag{14}$$

is the effective pair interaction potential. The distance between the centers of the two parallel neighboring molecules located in the same smectic layer is approximately equal to the molecular diameter $D$. Thus the corresponding interaction energy in Eq. (12) depends on the intermolecular vector $\mathbf{r}_{12}=\mathbf{R}_{12}^{\perp}=D\mathbf{u}_{12}^{\perp}$, where $\mathbf{u}_{12}^{\perp}$ is the unit intermolecular vector perpendicular to the smectic layer normal. In Eq. (13) the interaction energy between two neighboring molecules in adjacent layers depends on the intermolecular vector $\mathbf{r}_{12}=\mathbf{R}_{12}^{\parallel}$ which is approximately parallel to the smectic layer normal $\mathbf{e}$. The absolute value of $\mathbf{R}_{12}^{\parallel}$ is approximately equal to the layer thickness $d$. Thus $\mathbf{R}_{12}^{\parallel}\approx\mathbf{e}d=\mathbf{e}L\cos\Theta$, where $L$ is the molecular length and $\Theta$ is the tilt angle of the director. The unit vectors $\mathbf{n}_1$ and $\mathbf{n}_2$ are the directors in adjacent smectic layers. In Sm-$C_A$ the angle between $\mathbf{n}_1$ and $\mathbf{n}_2$ is equal to $2\Theta$, i.e., $(\mathbf{n}_1\cdot\mathbf{n}_2)^2=(\cos 2\Theta)^2$, while in synclinic Sm-$C$ $\mathbf{n}_1=\mathbf{n}_2$.

In Sm-$C$ and Sm-$C_A$ the director is tilted with respect to the smectic layer normal, and therefore these phases are locally biaxial. There should be some degree of the quadrupole order of short molecular axes $\mathbf{b}$. This means that $\langle\cos 2\psi\rangle\neq 0$, where the angle $\psi$ specifies the orientation of the short axis $\mathbf{b}$ around the long axis $\mathbf{a}=\mathbf{n}$. Moreover, as discussed in Sec. II, there exists a spontaneous polarization in Sm-$C_A$, perpendicular to the tilt plane normal and the smectic layer normal, which is located between the layers and alternates in sign from boundary to boundary. Thus in this phase the polar order parameter $\mathbf{p}_{\perp}=\langle\mathbf{b}\rangle$ is also nonzero. Since both quadrupole and dipole order parameters of the short molecular axes are not supposed to be large, however, we will neglect them in the present consideration. It will be shown in Sec. V that the stability of Sm-$C_A$ can be explained without taking biaxiality into account. Then the averaged interaction energies $U_{eff}^{\perp}$ and $U_{eff}^{\parallel}$ can be expressed as simple averages of the effective pair interaction potential $V_{eff}(1,2)$ over all orientations of the short molecular axes:

$$U_{eff}^{\perp}(\mathbf{n},\mathbf{e})=\int V_{eff}(\mathbf{b}_1,\mathbf{b}_2,\mathbf{R}_{12}^{\perp},\mathbf{n})d\mathbf{u}_{12}^{\perp}d\mathbf{b}_1 d\mathbf{b}_2, \tag{15}$$

$$U_{eff}^{\parallel}(\mathbf{n}_1,\mathbf{n}_2,\mathbf{e})=\int V_{eff}(\mathbf{b}_1,\mathbf{b}_2,\mathbf{R}_{12}^{\parallel},\mathbf{n}_1,\mathbf{n}_2)d\mathbf{b}_1 d\mathbf{b}_2. \tag{16}$$

In this approximation the free energy can be written in a simple form:

$$\frac{F}{N}=\text{const}+\gamma\sigma U_{eff}^{\perp}(\mathbf{n},\mathbf{e})+\gamma(1-\sigma)U_{eff}^{\parallel}(\mathbf{n}_1,\mathbf{n}_2,\mathbf{e}). \tag{17}$$

Equation (17) can be used to describe the free energy of both Sm-$C$ and Sm-$C_A$. We note that the difference in the free energies between Sm-$C$ and Sm-$C_A$ is determined only by the last term of Eq. (17), that represents a contribution from the interaction of neighboring molecules located in adjacent smectic layers given in Eq. (16). This contribution is much smaller than the total free energy [Eq. (17)], because it is determined by the interaction between molecules in adjacent smectic layers. The averaged interaction energy in Eq. (16) is determined by the value of the effective pair potential taken at $r_{12}\approx L\cos\Theta$, while the interaction between neighboring molecules in the same smectic layer given in Eq. (15) is determined by $V_{eff}(1,2)$ taken at $r_{12}\approx D$. For any short-range potential the interaction between the nearest neighbors in the same layer is much stronger than that between the nearest neighbors in different layers. In addition the number of the nearest neighbors within the same layer is rather large $(\gamma\sigma\approx 6)$ as compared with that in adjacent layers $[\gamma(1-\sigma)\approx 2]$. Thus the difference between the free energies of Sm-$C$ and Sm-$C_A$ is expected to be orders of magnitude smaller than the total free energy associated with the tilt.

This enables one to understand why the energy barrier between Sm-$C$ and Sm-$C_A$ appears to be so small experimentally. It is well known that antiferroelectric Sm-$C_A$* can be switched into ferroelectric Sm-$C$* by applying a moderate electric field. The difference between the free energies of the two phases should be of the order of the interaction energy between the external electric field and the smectic liquid crystal material. The latter energy per molecule is always much less than $kT$. This also explains why the free energies of synclinic Sm-$C$ and anticlinic Sm-$C_A$ have been found to be nearly the same in the simple two-dimensional steric model recently considered by Vanakara *et al.* [46]. The transition from Sm-$A$ to Sm-$C$ or Sm-$C_A$ can be second order. In this case the free energy of the tilted phase can be expanded in powers of the tilt angle $\Theta$,

$$\frac{F}{N}=\alpha(T-T_c)\Theta^2+b\Theta^4+\cdots, \tag{18}$$

where $T_c$ is the corresponding transition temperature. We note that the values of the parameters $\alpha,b$ and $T_c$ in expansion (18) are different for Sm-$C$ and Sm-$C_A$, respectively. This difference is, however, also determined by the interlayer interaction, and thus is expected to be very small. If the transition is second order, the actual phase that is stable directly below Sm-$A$ is the one that corresponds to the higher transition temperature $T_c$ in the free energy expansion (18).

## IV. MODEL POTENTIALS FOR THE SYNCLINIC SMECTIC-*C* PHASE AND THE ANTICLINIC SMECTIC-$C_A$ PHASE

In this section we determine the mathematical form of the interaction potential that promotes the anticlinic Sm-$C_A$ structure. For this purpose let us use the general expansion of the averaged interaction potential $U_{eff}(\mathbf{a}_1,\mathbf{r}_{12},\mathbf{a}_2)$ (i.e., the effective pair interaction potential averaged over all orientations of the molecular short axes) in spherical invariants [47]:

$$U_{eff}(\mathbf{a}_1,\mathbf{r}_{12},\mathbf{a}_2)=\sum_{l,\lambda,L} J_{l,\lambda,L}(r_{12})T^{l,\lambda,L}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2). \tag{19}$$

The spherical invariants $T^{l,\lambda,L}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2)$ can be expressed in terms of the spherical harmonics [47], and form a complete orthogonal set of functions. The function $T^{l,\lambda,L}(\mathbf{a}_1,\mathbf{u}_{12},\mathbf{a}_2)$ contains the unit vectors $\mathbf{a}_1,\mathbf{u}_{12}$, and $\mathbf{a}_2$ up to the power $l,\lambda$, and $L$, respectively, where $\mathbf{u}_{12}$ is the unit vector along $\mathbf{r}_{12},\mathbf{u}_{12}=\mathbf{r}_{12}/r_{12}$. Explicit expressions for the low order spherical invariants are given, for example, in Ref. [48]. Taking into account only the lowest order nonpolar terms (i.e., the terms which are quadratic in $\mathbf{a}_1$ and $\mathbf{a}_2$), we obtain the following approximate representation of the averaged interaction potential:

$$v_0+v_1P_2(\mathbf{a}_1\cdot\mathbf{a}_2)+v_2\{(\mathbf{a}_1\cdot\mathbf{u}_{12})^2+(\mathbf{a}_2\cdot\mathbf{u}_{12})^2\} +v_3(\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_1\cdot\mathbf{u}_{12})(\mathbf{a}_2\cdot\mathbf{u}_{12})+v_4(\mathbf{a}_1\cdot\mathbf{u}_{12})^2(\mathbf{a}_2\cdot\mathbf{u}_{12})^2. \tag{20}$$

The second term in Eq. (20) represents a Maier-Saupe type of interaction that promotes the parallel alignment of neighboring molecules. The third term can be responsible for the tilt of the director in Sm-*C*. For two neighboring molecules in the same smectic layer the unit intermolecular vector is perpendicular to the layer normal, $\mathbf{u}_{12}=\mathbf{u}_{12}^{\perp}\perp\mathbf{e}$, and therefore the potential

$$v_2\{(\mathbf{a}_1\cdot\mathbf{u}_{12})^2+(\mathbf{a}_2\cdot\mathbf{u}_{12})^2\} \tag{21}$$

can be written

$$v_2(\sin^2\omega_1+\sin^2\omega_2),$$

where $\omega_i$ is the tilt angle of the molecule *i* with respect to the smectic layer normal. Thus this potential promotes the molecular tilt in the smectic phase provided that the constant $v_2$ is negative. This means that potential (21) can be considered as a model potential for Sm-*C*. From the physical point of view, potential (21) can be determined, for example, by the induction interaction between an off-center transverse dipole and the polarizability of the neighboring molecule, as described in the model of Van der Meer and Vertogen for Sm-*C* [49]. The same interaction potential with the negative coupling constant also appears as a part of the general quadrupole-quadrupole interaction [4]. We note that this kind of potential can also be obtained by taking into account steric repulsion between molecules of specific shape (zigzag shape, for example). However, interaction potential (21) does not distinguish between Sm-*C* and Sm-$C_A$ because it is not sensitive to the angle between the long axes of the neighboring molecules in adjacent layers. This potential promotes tilt in any tilted smectic phase.

The interaction potential that stabilizes the anticlinic configuration can be determined by taking into consideration the difference between the free energies of Sm-*C* and Sm $C_A$. As discussed in Sec. III, the average interaction between molecules inside one smectic layer is the same in both phases (provided they have the same tilt angle). Taking into account Eq. (17), the difference between the free energies of the two tilted phases can be written as

$$\frac{\Delta F_{CA-C}}{N}=\frac{F_{CA}-F_C}{N} =\gamma(1-\sigma)\{U_{eff}^{\parallel}(\mathbf{n}_1,\mathbf{n}_2,\mathbf{e})-U_{eff}^{\parallel}(\mathbf{n},\mathbf{e})\}, \tag{22}$$

where $(\mathbf{n}_1\cdot\mathbf{n}_2)^2=\cos^2 2\Theta$. Using expansion (20) of the effective uniaxial interaction energy in Eq. (22), we obtain

$$\frac{\Delta F_{CA-C}}{N}\approx-\gamma(1-\sigma)\left(\frac{3}{2}v_1+\frac{1}{2}v_3\right)\sin^2 2\Theta. \tag{23}$$

We note that the coefficient $v_1$ is expected to be negative because the corresponding Maier-Saupe type interaction potential [the second term in Eq. (20)] stabilizes the parallel orientation of neighboring molecules. Thus the free energy of Sm-$C_A$ will be lower than that of Sm-*C* only if the coefficient $v_3$ is larger than $3|v_1|$. This means that anticlinic Sm-$C_A$ can be stabilized by a sufficiently strong repulsive type interaction potential of the symmetry

$$v_3(\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_1\cdot\mathbf{u}_{12})(\mathbf{a}_2\cdot\mathbf{u}_{12}), \tag{24}$$

where $v_3>3|v_1|$.

Now the model potential of Sm-$C_A$ is given by a sum of potential (21), which promotes the tilt irrespective to its sense, and potential (24), which distinguishes between the synclinic and anticlinic configurations:

$$U_{CA}(1,2)=v_2\{(\mathbf{a}_1\cdot\mathbf{u}_{12})^2+(\mathbf{a}_2\cdot\mathbf{u}_{12})^2\} +v_3(\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_1\cdot\mathbf{u}_{12})(\mathbf{a}_2\cdot\mathbf{u}_{12}). \tag{25}$$

An important aim of the present study is to identify the intermolecular interactions that can stabilize Sm-$C_A$. In the search for such interactions we first consider standard interaction potentials used to describe liquid crystalline ordering. According to Van der Meer and Vertogen [49] and Gelbart [50], the predominant orientational interaction in thermotropic liquid crystals, which determines the orientational order, is the isotropic (dispersion) attraction modulated by anisotropic molecular shape. The corresponding effective interaction potential can be expanded in spherical invariants according to Eq. (20). This expansion does contain the required potential [Eq. (24)] but the corresponding coupling constant $v_3$ appears to be negative [49], i.e., the potential is of an attractive type. Consequently, it destabilizes the anticlinic configuration. On the other hand, the *anisotropic* dipole-dipole dispersion interaction contains a contribution of the form of Eq. (24), which stabilizes Sm-$C_A$. For two uniaxial molecules this dispersion interaction potential can be written as

$$U_{dd}^{disp}(1,2)=-\frac{1}{r_{12}^6}[J_2\{(\mathbf{a}_1\cdot\mathbf{a}_2)^2-6(\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_1\cdot\mathbf{u}_{12})(\mathbf{a}_2\cdot\mathbf{u}_{12}) +9(\mathbf{a}_1\cdot\mathbf{u}_{12})^2(\mathbf{a}_2\cdot\mathbf{u}_{12})^2\}-J_{12}P_2(\mathbf{a}_1\cdot\mathbf{u}_{12}) -J_{21}P_2(\mathbf{a}_2\cdot\mathbf{u}_{12})], \tag{26}$$

where the coupling constants $J_2,J_{12}$, and $J_{21}$ are expressed in terms of the dipole matrix elements and the excitation energies of the excited states of the molecules 1 and 2 [4]. If molecules 1 and 2 are of the same kind, the constants $J_2, J_{12}$, and $J_{21}$ are given by [47]

$$J_2 = 9 \sum_{n_1,n_2} \frac{\delta_{on1}\delta_{on2}}{E_{n_1,n_2} - E_{o_1,o_2}} \tag{27}$$

and

$$J_{12} = J_{21} = 9 \sum_{n_1,n_2} \frac{\delta_{on1}(f_{on1} - \delta_{on2})}{E_{n_1,n_2} - E_{o_1,o_2}}, \tag{28}$$

with

$$f_{oni} = \frac{1}{3}(|p_{zi}^{on}|^2 + |p_{xi}^{on}|^2 + |p_{yi}^{on}|^2) \tag{29}$$

and

$$\delta_{oni} = \frac{1}{3}\left(|p_{zi}^{on}|^2 - \frac{1}{2}|p_{xi}^{on}|^2 - \frac{1}{2}|p_{yi}^{on}|^2\right). \tag{30}$$

Here $n_1$ and $n_2$ denote the excited states of the molecules 1 and 2, $E_{n_1,n_2} - E_{o_1,o_2}$ is the excitation energy, and the quantities $p_{\alpha i}^{on}$ $(\alpha = x,y,z; i = 1,2)$ denote electric dipole matrix elements. We note that the familiar Maier-Saupe interaction potential $-JP_2(\mathbf{a}_1 \cdot \mathbf{a}_2)/r_{12}^6$ is obtained from potential (26) after averaging over all orientations of the intermolecular unit vector $\mathbf{u}_{12}$.

The coupling constant $J_2$ in Eq. (26) is approximately proportional to the square of the anisotropy of the molecular polarizability $(\Delta\alpha)^2$. The isotropic dispersion interaction, modulated by the anisotropic molecular shape, which is discussed above, is proportional to the square of the average molecular polarizability $(\overline{\alpha})^2$, and therefore is expected to be stronger. The ratio of these two contributions can be roughly estimated as $(\overline{\alpha}/\Delta\alpha)^2$, i.e., the former contribution is predominant. Taking into account that the first term in Eq. (23) also destabilizes Sm-$C_A$, we arrive at the conclusion that the conventional dispersion interaction between typical mesogenic molecules does not stabilize Sm-$C_A$. This conclusion seems to be reasonable because otherwise Sm-$C_A$ would be observed much more frequently. In particular, many achiral Sm-$C$ liquid crystals would exhibit the anticlinic phase. We know, however, that this is not the case. As far as we are aware, anticlinic Sm-$C_A$ has been observed only in one type of achiral (one component) smectic liquid crystals [31,32]. We note also that the corresponding compounds are swallow-tailed ones, i.e., the structure is quite similar to the one of the chiral compounds that show Sm-$C_A$*. Qualitative arguments presented above indicate that Sm-$C_A$ is stabilized, apparently, by some specific intermolecular interactions. In practice, the anticlinic configuration is usually observed in chiral smectics with large spontaneous polarization. It is very unlikely that chirality is of any importance here. Chiral interactions are generally weak and, in addition, achiral anticlinic Sm-$C_A$ has been observed in racemic mixtures [33–35]. On the other hand, such chiral compounds also contain relatively large dipoles in the vicinity of the chiral center in the flexible chain. It is shown in Sec. V that interlayer orientational correlations between such transverse molecular dipoles can be responsible for the stabilization of Sm-$C_A$.

## V. DIPOLE-DIPOLE CORRELATIONS IN THE ANTICLINIC SMECTIC-$C_A$ PHASE

In Sec. IV we considered only short-range interactions between molecules in Sm-$C_A$. As discussed in Sec. II, the anticlinic phase possesses an alternating spontaneous polarization (in the tilt plane) even if the molecules and/or the system are achiral. Thus the long-range dipole-dipole interactions may be important. We note, however, that the average dipole-dipole interaction between two parallel polar planes vanishes. This was already shown by Prost and Bruinsma [36] and Bruinsma and Prost [37], and the same result can be obtained in the following simple way. Let us consider Sm-$C_A$ with the average dipole density $\mathbf{d}(\mathbf{r})$. Then the average dipole-dipole interaction energy of the sample can be written as

$$\begin{aligned}\langle V_{dd}\rangle &= \int\int \frac{1}{r_{12}^3}[\mathbf{d}(\mathbf{r}_1)\cdot\mathbf{d}(\mathbf{r}_2) - 3\{\mathbf{d}(\mathbf{r}_1)\cdot\mathbf{u}_{12}\} \\ &\quad \times \{\mathbf{d}(\mathbf{r}_2)\cdot\mathbf{u}_{12}\}]d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{V}\sum_{\mathbf{k}} \frac{1}{k^2}(\mathbf{d}_{\mathbf{k}}\cdot\mathbf{k})(\mathbf{d}_{\mathbf{k}}\cdot\mathbf{k}),\end{aligned} \tag{31}$$

where $\mathbf{d}_{\mathbf{k}}$ is the Fourier transform of the dipole density. In ideal Sm-$C_A$ the spontaneous polarization varies only along the $\mathbf{z}$ axis, which is perpendicular to the smectic layers. Thus the summation in Eq. (31) is restricted to the wave vectors $\mathbf{k}\|\mathbf{z}$. Since the spontaneous polarization itself is perpendicular to the axis $\mathbf{z}$, we obtain $(\mathbf{d}_{\mathbf{k}}\cdot\mathbf{k}) = 0$. As a result the average dipole-dipole interaction [Eq. (31)] vanishes.

The direct dipole-dipole interaction between molecules in adjacent layers cannot be responsible for the anticlinic configuration. However, the instant (i.e., nonaveraged) interaction between the dipoles of two neighboring molecules can be rather large. This means that there exist strong dipole-dipole correlations which may be important. Such correlations can be taken into account in the framework of the thermodynamic perturbation theory. Taking into account that $\langle V_{dd}\rangle = 0$, the free energy of the tilted smectic phase can be written as

$$\frac{F}{N} \approx \frac{F_0}{N} - \frac{1}{2kT}\langle V_{dd}^2\rangle, \tag{32}$$

where $F_0/N$ is the free energy of the smectic phase without dipole-dipole interaction. Approximate expressions for this free energy were obtained in Sec. IV. We assume that molecules possess only transverse dipoles $\mathbf{d}_\perp$. In this case the dipole-dipole interaction potential reads

$$V_{dd}(1,2) = \frac{d_\perp^2}{r_{12}^3}\{(\mathbf{b}_1\cdot\mathbf{b}_2) - 3(\mathbf{b}_1\cdot\mathbf{u}_{12})(\mathbf{b}_2\cdot\mathbf{u}_{12})\}, \tag{33}$$

where the short molecular axis $\mathbf{b}$ is taken to be parallel to the transverse molecular dipole $\mathbf{d}_\perp$. Now we have to average the square of the interaction potential (33) [see Eq. (32)] over all orientations of the short molecular axes $\mathbf{b}_1$ and $\mathbf{b}_2$ about the corresponding long molecular axes $\mathbf{a}_1$ and $\mathbf{a}_2$, respectively. As assumed in Sec. III, we neglect any biaxial ordering of short molecular axes (in each layer). This biaxiality order parameter is not expected to be large. Then the averaging of $V_{dd}^2(1,2)$ over the short molecular axes results in the expression

$$\begin{aligned}-\frac{1}{2kT}\langle V_{dd}^2(1,2)\rangle_{\mathbf{b}_1,\mathbf{b}_2}=\frac{d_\perp^4}{8kTr_{12}^6}\{&-4-(\mathbf{a}_1\cdot\mathbf{a}_2)^2\\ &+3(\mathbf{a}_1\cdot\mathbf{u}_{12})^2+3(\mathbf{a}_2\cdot\mathbf{u}_{12})^2\\ &-9(\mathbf{a}_1\cdot\mathbf{u}_{12})^2(\mathbf{a}_2\cdot\mathbf{u}_{12})^2\\ &+6(\mathbf{a}_1\cdot\mathbf{u}_{12})(\mathbf{a}_2\cdot\mathbf{u}_{12})(\mathbf{a}_1\cdot\mathbf{a}_2)\}.\end{aligned} \tag{34}$$

We note that from the mathematical point of view Eq. (34) presents a kind of effective uniaxial interaction potential. The last term in Eq. (34) has the form of the Sm-$C_A$ model potential with a positive coupling constant, and therefore it promotes the anticlinic ordering.

Using the same approximations as in Sec. III, the contribution of the dipole-dipole fluctuations to the free energy difference between synclinic Sm-$C$ and anticlinic Sm-$C_A$ (at the same value of the tilt angle $\Theta$) can be written in the explicit form

$$\begin{aligned}\frac{(F_{CA}-F_C)}{N}&=-\frac{1}{2kT}(\langle V_{dd}^2\rangle_{CA}-\langle V_{dd}^2\rangle_C)\\ &=\gamma(1-\sigma)\frac{1}{8kT(R_{12}^{\parallel})^6}\{1-6(\mathbf{n}\cdot\mathbf{e})^2-(\mathbf{n}_1\cdot\mathbf{n}_2)^2\\ &\quad+6(\mathbf{n}_1\cdot\mathbf{e})(\mathbf{n}_2\cdot\mathbf{e})(\mathbf{n}_1\cdot\mathbf{n}_2)\}\\ &=-\gamma(1-\sigma)\frac{1}{4kT\{(L-2l)\cos\Theta\}^6}\sin^2 2\Theta<0,\end{aligned} \tag{35}$$

where $R_{12}^{\parallel}\approx(L-2l)\cos\Theta$ is the distance between the transverse dipoles of neighboring molecules in adjacent smectic layers as shown in Fig. 3. Here $L$ is the molecular length, and $l$ is the distance between the dipole moment in the alkyl chain and the molecular center of mass. Thus we arrive at the conclusion that orientational correlations between transverse molecular dipoles can stabilize Sm-$C_A$ with respect to Sm-$C$. We note that this contribution rapidly grows as the tilt angle $\Theta$ is increased. This growth is mainly determined by the factor $\{(L-2l)\cos\Theta\}^{-6}$. In particular, the effect of dipole-dipole orientational correlations becomes important when the dipole is located in the flexible chain closer to the molecular end. In this case the average distance between such dipoles, which belong to neighboring molecules in adjacent layers, can be significantly smaller than the molecular length.

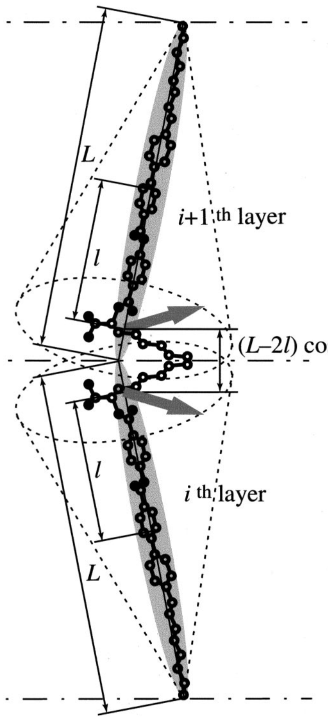

FIG. 3. Schematic illustration of interlayer orientational correlations between transverse molecular dipoles. The dipole is assumed to be located at the joint of the flexible chain, which projects obliquely from the core part. Here $l$ is the distance between the dipole and the molecular center of mass, and $\Theta$ is the tilt angle. The smectic layer spacing is considered to be equal to the molecular length $L$.

## VI. PHASE DIAGRAM

According to Eqs. (17) and (32), the free energy of a smectic phase with fluid layers in the approximation of the perfect nematic and smectic order can be written as

$$\begin{aligned}\frac{F}{N}=&\gamma\sigma U_{eff}^{\perp}(\mathbf{n},\mathbf{e})+\gamma(1-\sigma)U_{eff}^{\parallel}(\mathbf{n}_1,\mathbf{n}_2,\mathbf{e})\\ &-\frac{\gamma(1-\sigma)}{2kT}\langle V_{dd}^2\rangle_{\mathbf{b}_1,\mathbf{b}_2}.\end{aligned} \tag{36}$$

Here the first term is an intermolecular interaction within one smectic layer, and thus it depends only on the orientation of the director $\mathbf{n}$ with respect to the layer normal $\mathbf{e}$. This contribution is proportional to $\sigma$, the fraction of the nearest neighbors that are located in the same layer. The second term is determined by an interaction between the nearest neighbor molecules located in adjacent layers. It depends on the relative orientation of the two directors $\mathbf{n}_1$ and $\mathbf{n}_2$, which correspond to layers 1 and 2, respectively, and the smectic layer normal. We have $\mathbf{n}_1=\mathbf{n}_2$ in Sm-$C$, and $\mathbf{n}_1\neq\mathbf{n}_2$ in Sm-$C_A$. Finally, the third term in Eq. (36) is a contribution from the orientational dipole-dipole correlations between neighboring molecules in adjacent layers averaged over all orientations of the molecular short axes.

As discussed in Sec. IV, the effective potentials $U_{eff}^{\perp}(\mathbf{n},\mathbf{e})$ and $U_{eff}^{\parallel}(\mathbf{n}_1,\mathbf{n}_2,\mathbf{e})$ can be expanded in spherical invariants preserving the first few terms:

$$U^{\perp}_{eff}=\text{const}+(2v^{\perp}_2+v^{\perp}_3)\{1-(\mathbf{n}\cdot\mathbf{e})^2\}+v^{\perp}_4\{1-(\mathbf{n}\cdot\mathbf{e})^2\}^2, \tag{37}$$

and

$$\begin{aligned}U^{\parallel}_{eff}=&\text{const}+v^{\parallel}_1 P_2(\mathbf{n}_1\cdot\mathbf{n}_2)+v^{\parallel}_2\{(\mathbf{n}_1\cdot\mathbf{e})^2+(\mathbf{n}_2\cdot\mathbf{e})^2\}\\&+v^{\parallel}_3(\mathbf{n}_1\cdot\mathbf{n}_2)(\mathbf{n}_1\cdot\mathbf{e})(\mathbf{n}_2\cdot\mathbf{e})+v^{\parallel}_4(\mathbf{n}_1\cdot\mathbf{e})^2(\mathbf{n}_2\cdot\mathbf{e})^2.\end{aligned} \tag{38}$$

The contribution from the orientational dipole-dipole correlations can be written as [see Eq. (34)]

$$\begin{aligned}-\frac{1}{2kT}\langle V^2_{dd}(1,2)\rangle_{\mathbf{b}_1,\mathbf{b}_2}=&\frac{d^4_{\perp}}{8kT(R^{\parallel}_{12})^6}\{-4-(\mathbf{n}_1\cdot\mathbf{n}_2)^2\\&+3(\mathbf{n}_1\cdot\mathbf{e})^2+3(\mathbf{n}_2\cdot\mathbf{e})^2\\&-9(\mathbf{n}_1\cdot\mathbf{e})^2(\mathbf{n}_2\cdot\mathbf{e})^2\\&+6(\mathbf{n}_1\cdot\mathbf{e})(\mathbf{n}_2\cdot\mathbf{e})(\mathbf{n}_1\cdot\mathbf{n}_2)\}.\end{aligned} \tag{39}$$

We note that Eq. (36) presents an expression for the free energy of the bilayer smectic phase with arbitrary orientation of the two directors $\mathbf{n}_1$ and $\mathbf{n}_2$ in adjacent smectic layers. In the general case $(\mathbf{n}_1\cdot\mathbf{e})=\cos\Theta_1$, $(\mathbf{n}_2\cdot\mathbf{e})=\cos\Theta_2$, and $(\mathbf{n}_1\cdot\mathbf{n}_2)=\cos\Theta_1\cos\Theta_2+\sin\Theta_1\sin\Theta_2\cos(\phi_1-\phi_2)$ where $\Theta_1$ and $\Theta_2$ are the tilt angles in the neighboring layers, and $\phi_1$ and $\phi_2$ are the corresponding azimuthal angles that specify the orientation of the tilt planes. In Sm-*C*, $\Theta_1=\Theta_2=\Theta$ and $\phi_1=\phi_2$, and therefore $(\mathbf{n}_1\cdot\mathbf{n}_2)=1$ and $(\mathbf{n}_1\cdot\mathbf{e})=(\mathbf{n}_2\cdot\mathbf{e})=\cos\Theta$. In Sm-$C_A$, on the other hand, we find that $\Theta_1=\Theta_2=\Theta$ and $\phi_1-\phi_2=\pi$; hence $(\mathbf{n}_1\cdot\mathbf{n}_2)=\cos 2\Theta$ and $(\mathbf{n}_1\cdot\mathbf{e})=(\mathbf{n}_2\cdot\mathbf{e})=\cos\Theta$. In the smectic phase each molecule is interacting with approximately eight nearest neighbors. Six of them are located in the same smectic layer, and two nearest neighbors are located in adjacent layers. Thus we can put $\gamma=8$ and $\sigma=3/4$ in Eq. (36).

Finally the free energies can be written in Sm-*C* as

$$\begin{aligned}\frac{F_C(\Theta)}{N}=&F_{\perp}(\Theta)+2v^{\parallel}_1+2(2v^{\parallel}_2+v^{\parallel}_3)\cos^2\Theta+2v^{\parallel}_4\cos^4\Theta\\&+\frac{d^4_{\perp}}{8kT(R^{\parallel}_{12})^6}(-5+12\cos^2\Theta-9\cos^4\Theta)+\text{const},\end{aligned} \tag{40}$$

and in Sm-$C_A$ as

$$\begin{aligned}\frac{F_{CA}(\Theta)}{N}=&F_{\perp}(\Theta)-v^{\parallel}_1(1-3\cos^2 2\Theta)\\&+2(2v^{\parallel}_2+v^{\parallel}_3\cos 2\Theta)\cos^2\Theta+2v^{\parallel}_4\cos^4\Theta\\&+\frac{d^4_{\perp}}{8kT(R^{\parallel}_{12})^6}(-5+4\cos^2\Theta-\cos^4\Theta)+\text{const}.\end{aligned} \tag{41}$$

Here

$$F_{\perp}(\Theta)=A\cos^2\Theta-B\cos^4\Theta, \tag{42}$$

and $A=6(2v^{\perp}_2+v^{\perp}_3)$, $B=6v^{\perp}_4$, and $R^{\parallel}_{12}=(L-2l)\cos\Theta$.

The transition temperature to Sm-*A* and the absolute value of the tilt angle $\Theta$ are mainly determined by the term $F_{\perp}(\Theta)$, which stems from intermolecular interactions within one smectic layer. As shown by Van der Meer and Vertogen [48] (also see Ref. [4]), excluded volume intermolecular interactions make a contribution to the coefficient *A* destabilizing the tilted smectic phase. On the other hand, there exist some specific intermolecular interactions, and, in particular, the induced dipole-dipole interaction between the off-center dipole and the polarizable core of the neighbor molecule [48], which make a contribution to the coefficient *A* promoting the tilt of the director. In the general case the coefficient *A* can be written in the form $A=\alpha(T^*-T)/T^*$, where $T^*$ is approximately equal to the Sm-*A*–Sm-*C* phase transition temperature and $\alpha>0$. As discussed in Sec. IV, the interlayer intermolecular interactions and correlations make a relatively small contribution to the total free energy of the tilted smectic phase. Thus the corresponding terms in Eqs. (40) and (41) can only weakly affect the transition temperature. At the same time these terms determine the difference between the free energies of Sm-*C* and Sm-$C_A$. The temperature of the first order phase transition between Sm-*C* and Sm-$C_A$ can be found by equating the free energies given by Eqs. (40) and (41):

$$\frac{F_{CA}-F_C}{N\sin^2 2\Theta}=-(3v^{\parallel}_1+v^{\parallel}_3)-\frac{d^4_{\perp}}{4kT\{(L-2l)\cos\Theta\}^6}=0. \tag{43}$$

We can readily see from Eq. (43) that the Sm-*C*–Sm-$C_A$ transition temperature is determined by a balance between the contribution from the interlayer dipole-dipole correlations promoting the anticlinic configuration and the first term in the right hand side of Eq. (43), which is mainly determined by excluded volume effects and which promotes Sm-*C*. The correlation contribution grows rapidly with the increasing molecular transverse dipole moment $d_{\perp}$, and with the increasing separation between the dipole and the molecular center of mass. The corresponding phase diagram, which includes Sm-*A*, sinclinic Sm-*C*, and anticlinic Sm-$C_A$, is presented in Fig. 4 where the abscissa is the normalized temperature, $T/T^*$, and the ordinate is the dimensionless dipole, $d_{dim}=d_{\perp}/\{(2kT^*)^{1/2}(L-2l)^{3/2}\}$. The phase boundary between Sm-*C* and Sm-$C_A$ has been calculated for $(3v^{\parallel}_1+v^{\parallel}_3)/kT^*=0.1$ and $\alpha/B=2$. The value of the parameter $\alpha/B=2$ has been chosen to describe the typical temperature variation of the tilt angle; the value of the parameter $(3v^{\parallel}_1+v^{\parallel}_3)/kT^*$ has been taken into account for the realistic values of the transverse molecular dipole in the chiral bent chain ($d_{\perp}\sim 3$ D), the average distance between the two such dipoles in the neighboring smectic layers ($L-2l\sim 1$ nm), and the typical temperature interval of the Sm-*C* ($\Delta T_C\sim 10\,^{\circ}\mathrm{C}$) as observed in racemates (see Fig. 1). We note that in Fig. 4 the boundary between Sm-*A* and Sm-*C* (or Sm-$C_A$) is a vertical line. This is the result of an approximation, because we have assumed that the relevant interaction between molecules in neighboring smectic layers is much smaller than the interaction within one layer. In this case the

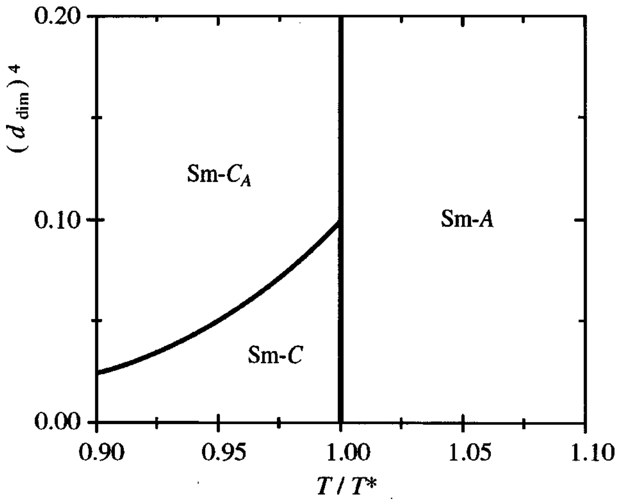

FIG. 4. A simple phase diagram of the perfectly ordered smectic liquid crystal which contains Sm-*A*, Sm-*C*, and Sm-$C_A$. The abscissa is the normalized temperature $T/T^*$ and the ordinate is the dipole in a dimensionless unit $d_{dim}$. See text for details.

transition temperature into Sm-*A* is not affected by the weak interactions which determine the difference between Sm-*C* and Sm-$C_A$.

## VII. CONCLUDING REMARKS

In this paper we have presented a model interaction potential that stabilizes the anticlinic Sm-$C_A$ phase, and proposed a particular molecular model based on interlayer orientational correlations between off-center transverse molecular dipoles. It has been shown that conventional dispersion and steric intermolecular interactions generally promote the synclinic Sm-*C* phase. This explains why Sm-*C* is observed much more frequently than Sm-$C_A$, in particular, in achiral smectic liquid crystals. At the same time the transition into the antiferroelectric, anticlinic Sm-$C_A^*$ phase is often found in chiral smectics, which possess a large spontaneous polarization in the ferroelectric, synclinic Sm-$C^*$ phase. Such materials are composed of molecules with large transverse dipoles located in the vicinity of the chiral center in the flexible chain. In the context of the present model, Sm-$C_A$ is stabilized by orientational correlations between such transverse dipoles located in adjacent smectic layers. These correlations make a contribution to the total free energy, which in this case possesses a minimum for the anticlinic director orientation in adjacent layers. By contrast, the steric intermolecular interactions (the packing entropy) promote Sm-*C* .

We note that all these interlayer interactions appear to be relatively weak, and this enables us to explain why Sm-$C_A$* can be switched to Sm-*C** by applying a moderate electric field. It should also be noted that although transverse dipoles in the flexible bent chain are typical for the chiral molecules, the corresponding dipole-dipole interactions are achiral (i.e., they are not sensitive to molecular handedness), and therefore must yield the same effect in racemic mixtures. We also note that recently *ab initio* studies by Glaser *et al.* confirmed the bent conformation of the chiral chain of the compound 1 in Fig. 1 [51]. They showed that the anticlinic structure can be induced by using mesogenic molecules which possess the same bent chain as compound 1. At the same time the structure of the rigid core may be different. Moreover, the anticlinic phase is observed even when the core part is a hydrogen-bonded dimer [52]. These new results support the general conclusion that the anticlinic structure is mainly determined by an interaction between bent dipolar end chains, while an interaction between hard cores seems to be of secondary importance.

The contribution from the orientational dipole-dipole correlations strongly depends on the average distance between the transverse dipoles located in adjacent layers. As a result it increases with the increasing tilt angle $\Theta$. Consequently, Sm-*C* is always a higher temperature phase than Sm-$C_A$ when both emerge. In the hexatic smectic phases, however, Sm-$I_A$* may appear just below Sm-$C_A$*, and then a phase transition to Sm-*I** may occur [53–55]. At present there is no explanation for this fact. When the system undergoes a direct transition from Sm-*A* to Sm-$C_A$, it is quite common that the transition is of first order and a rather large value of $\Theta$ suddenly appears.

The mechanism of Sm-$C_A$ stabilization due to interlayer correlations between transverse molecular dipoles may also be relevant to the understanding of the variety of recently discovered new smectic phases formed by nonchiral banana-shaped (or bow-shaped) molecules [56–59]. Such molecules possess strong transverse dipoles in the bent core [56], and form not only synclinic ferroelectric and anticlinic antiferroelectric phases but also anticlinic ferroelectric and synclinic antiferroelectric phases [57]. In particular, dipole-dipole correlations between molecules in adjacent smectic layers may be important in the so-called $B_2$ phase [59], which is characterized by the anticlinic antiferroelectric structure in the homochiral ground state [57] and is switchable by an electric field. One notes, however, that the present molecular mechanism does not seem to be predominant in the case of banana-shaped molecules. First, the average distance between transverse dipoles in neighboring layers is several times larger than that in the conventional Sm-$C_A$. The corresponding decrease in the strength of the dipole-dipole correlations is not fully compensated for by a larger value of the molecular dipole. On the other hand, the stability of the anticlinic configuration in the $B_2$ phase may be determined by the specific packing of banana-shaped molecules. Indeed, the neighboring chains of the two banana-shaped molecules in the anticlinic configuration are approximately parallel, and thus this configuration may be stabilized by various interactions which are normally responsible for the formation of Sm-*C* composed of rodlike molecules. This effect is related to the strong biaxiality of banana-shaped molecules, and is expected to be particularly strong in $B_1$ and $B_6$ phases [59], where the terminal molecular chains seem to penetrate deeply into adjacent layers.

The molecular model of Sm-$C_A$ presented in this paper takes into consideration only one particular microscopic mechanism of the anticlinic ordering, based on orientational interlayer dipole-dipole correlations. This model is not in contradiction with existing experimental data, but we cannot exclude that in some cases Sm-$C_A$ may be stabilized by some other specific interactions or correlations. We may assume that steric interaction between swallow-tail chains can give rise to some peculiar packing effects, as pointed out by Nishiyama and Goodby [31] (also see Ref. [32]). Note, however, that the swallow-tail molecule possesses rather large transverse electric dipole moments in the joint of the end chain to the core part, and that the swallow tails are considered to be bent with respect to the molecular long axis. In the general case, any intermolecular interaction that may stabilize Sm-$C_A$ should be characterized by the effective interaction potential of the form of Eq. (24), at least in the first approximation.

Finally we note that the Sm-$C$–Sm-$C_A$ phase transition is generally of the first order, and in the vicinity of the transition point the synclinic and anticlinic configurations corresponds to the same free energy. In this narrow temperature interval the system is frustrated, and some relatively weak additional effects may become very important. In particular, weak correlations between distant smectic layers (starting from second and third nearest neighbors) may promote the formation of subphases with periodicities larger than the double smectic layer thickness.

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