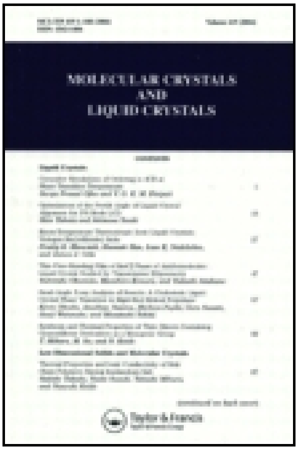

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SYNCLINIC AND ANTICLINIC ORDERING IN FRUSTRATED SMECTICS

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Molecular origin of synclinic and anticlinic ordering in the smectic-C and smectic-C_A phases is considered in detail. The model potential for the anticlinic phase is proposed and possible contributions between various intermolecular interactions are discussed. It is concluded that conventional dispersion and steric interactions between mesogenic molecules generally do not promote the Sm-C_A phase. A particular model of the anticlinic phase is proposed which is based on interlayer orientational correlations between transverse molecular dipoles located in the flexible chains. Such correlations are not sensitive to molecular chirality and thus the theory accounts for the formation of the anticlinic phase in racemic mixtures. Finally the microscopic origin of ferrielectric and antiferroelectric subphases is discussed and the concept of the 'discrete' flexoelectric effect is introduced which can in principle be used to explain the particular structure of subphases.

Keywords: liquid crystal; phase transition; Casimir force; anticlinic ordering; frustrated smectics; subphase

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1. INTRODUCTION

Before the discovery of the antiferroelectric SmC_A* structure [1] it has been believed that the packing entropy effect as well as the Maier-Saupe type intermolecular interaction causes the tilting of molecules in the same direction and sense except for a slight precession from layer to layer due to chirality [2,3]. At that time the chiral ferroelectric smectic C phase (SmC*) and the achiral smectic C phase (SmC) were the only known tilted smectic phases with fluid layers. After the antiferroelectric SmC_A* structure was established, it has become clear that titled smectic phases can be either synclinic or anticlinic, and the problem related to the microscopic origin of

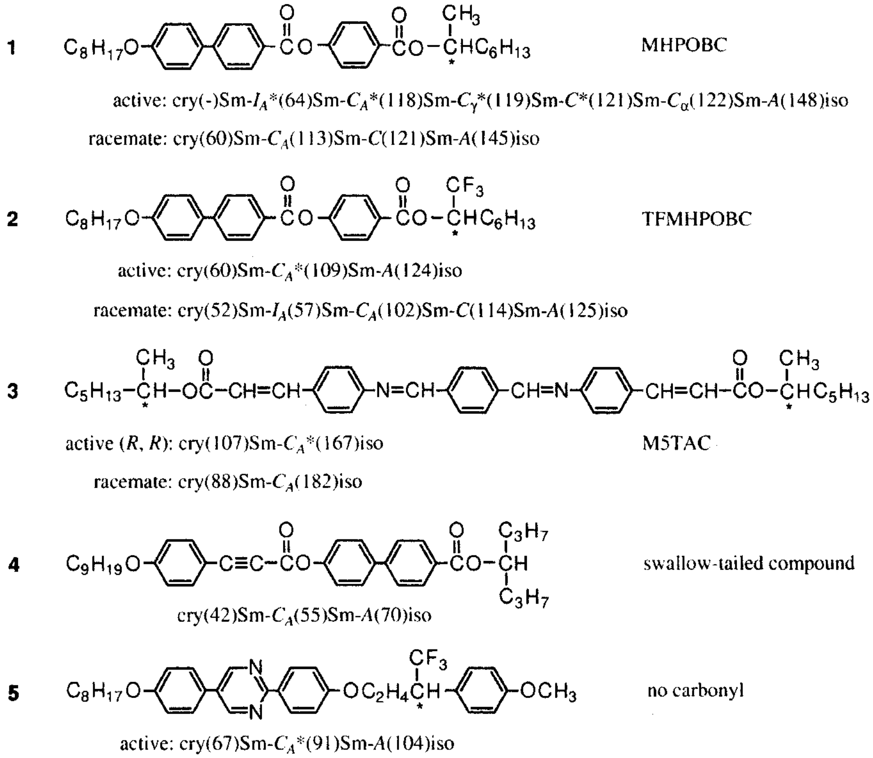

FIGURE 1 Some examples of compounds showing SmC_A* or SmC_A. Compounds **1** and **2** are prototype antiferroelectric liquid crystals. Compound **3** was used to confirm on the molecular scale the anticlinic and/or antiferroelectric phase, which was originally designated as SmO* and SmO. A swallow-tailed compound **4** is achiral but shows the SmC_A phase.

these phases has become very important. The anticlinic structure was first speculated by Beresnev *et al.* [4] in a study of pyroelectricity for a liquid-crystalline mixture. Chandani *et al.* [1] have confirmed the anticlinic SmC$_{\mathrm{A}}$* structure in compound **1** (see Fig. 1) by observing the disappearance of the so-called full-pitch reflection band that clearly emerges in SmC*. Furthermore, they have shown that an external electric field can induce the phase transition from SmC$_{\mathrm{A}}$* to ferroelectric SmC* and produces an electric current peak during the transition, confirming the existence of antiferroelectricity in the SmC$_{\mathrm{A}}$* phase. On the molecular scale, the anticlinic structure has first been confirmed by Galerne and Liebert [5] and then by Bahr and Fliegner [6]. Quite recently Mach *et al.* [7] have directly observed the double-layer periodicity by means of the resonant X-ray scattering technique. In this way, it has been firmly established that SmC$_A$ and the SmC$_{\mathrm{A}}$* have the anticlinic herringbone structure.

One notes that similar to synclinic, ferroelectric SmC*, the tilt of the director induces the spontaneous polarization in each layer of anticlinic, antiferroelectric SmC$_{\mathrm{A}}$*. The spontaneous polarisation of a smectic layer is perpendicular to the tilt plane and its sense is uniquely determined by the tilt sign. At the same time, in the anticlinic SmC$_{\mathrm{A}}$* phase there exists the additional ***in-plane*** spontaneous polarisation, which is parallel to the tilt plane and is located at a smectic layer boundary. It is well known that chirality plays a crucial role for the emergence of the polarisation in the direction of the tilt plane normal [8–10]. On the other hand, the emergence of the anticlinic structure itself is not related to molecular chirality because it has been shown experimentally that swallow-tailed compounds with two terminal chains of equal length [11,12] (see Fig. 1) as well as racemate mixtures [13–15] may also exhibit the SmC$_A$ phase.

The transition between synclinic SmC* and anticlinic SmC$_{\mathrm{A}}$* is of the first order and in many materials the sequence of interesting phases is found in a narrow temperature interval between the ferro- and antiferroelectric smecticC* phases. In this domain the system is characterised by a frustration between synclinic and anticlinic ordering [16], and the frustration causes the temperature induced sequence of phase transitions to resemble the Devil's staircase [13,17,18]. These polar smectic phases, which are often called 'subphases' are characterised by periods of more than two molecular layers. Very recently the detailed structure of some of these subphases has been determined experimentally [7, 19–21] but so far no realistic molecular models for those phases have been proposed. One notes that the frustration is also related to the thresholdless, hysteresis-free, V-shaped switching, induced by an external field [17,22,23] which is very promising for a new generation of liquid crystal displays [17,24–26].

Several experimental groups have been able to determine a detailed structure of smectic subphases with three and four layer periodicity using a number of high resolution techniques [7,19–21]. Before that, only the periods of these subphases were known and two conflicting models were proposed. The first model was based on an assumption that the tilt planes of all smectic layers are parallel to each other [27]. In this case the spontaneous polarisation only changes sign from layer to layer. The second model (the so called clock model [28,29]) is based on a simple phenomenological theory which takes into account orientational interactions between nearest neighbour and next to nearest neighbour smectic layers. The minimum of that free energy corresponds to a uniform rotation of the tilt plane about the layer normal. In this case the angle between tilt planes in neighbouring smectic layers equals $2\pi/n$ where n is the periodicity of the structure. Recent experimental data [7,19–21], however, do not support either of these models. The structure of three- and four-layer subphases is not flat but, at the same time, it is substantially different from the clock model. In addition, a consistent molecular model should enable one to explain why the subphases with periodicity larger than two are observed only in chiral materials. This point has not been addressed at all neither in the Ising nor in the clock model. One notes that the understanding of the role of molecular chirality is intimately related to the more general problem of the microscopic origin of subphases with large periodicity in smectic liquid crystals. So far, no consistent solution of this problem has been proposed in the literature.

In this paper we consider some answers to the following general questions:

i) Why the synclinic phase is far more common than the anticlinic one?
ii) Why the synclinic phase is generally the higher temperature one?
iii) What is the origin of subphases between SmC* and $\mathrm{SmC_A}$*?
iv) Why the structure of the subphases is not flat and why it is also different from the 'clock' model?
v) What is the role of chirality?

At present it is only possible to give reasonable answers to the first two questions. The remaining three questions are still open and we will be able to discuss only some speculations. This paper is arranged as follows. In Section 2 we discuss the molecular origin of tilt in smectic phases and consider the model potential which promotes the tilt. In Section 3 we propose a model potential for the anticlinic SmC_A phase which distinguishes between different directions of the tilt and discuss various intermolecular interactions which may or may not stabilise the anticlinic structure. We also estimate typical energies associated with synclinic and anticlinic ordering. In Section 4 we consider a particular model of the anticlinic SmC_A phase based on orientational correlations between transverse molecular dipoles in neighbouring smectic layers. In Section 5 we discuss an origin of the subphases and introduce the concept of the 'discrete' flexoelectric effect which may be responsible for the particular structure of the subphases with three and four layer periodicity.

2. MOLECULAR ORIGIN OF THE TILT IN SMECTIC PHASES

It is interesting to note that tilted smectic phases do not appear naturally in model systems composed of rod-like molecules with simple intermolecular interactions. Computer simulations of fluids composed of rigid rods without attraction or uniaxial particles interacting via the Gay-Berne potential reveal only orthogonal smectic phases A and B. This is understandable because tilt of molecules within a smectic layer is unfavourable from the packing entropy point of view [30]. Thus one needs some additional interaction which promotes the tilt. Various molecular models for the synclinic SmC phase have already been proposed many years ago [30–34]. These models reveal different factors which, in principle, may be responsible for the tilt. For example, the model of McMillan takes into consideration the electrostatic interaction between pairs of antiparallel molecular dipoles [31]. In a similar way, the model of Benguigui is based on the interaction between pairs of antiparallel transverse molecular dipoles [32]. On the other hand, Wulf has taken into consideration steric interaction between 'zig-zag' molecules [33] and Van der Meer and Vertogen have proposed a rather realistic model based on the induction interaction between of-centre molecular dipole and polarizability of a neighbour molecule [30]. In spite of a difference between particular interactions taken into account in these models, the corresponding model interaction potentials appear to be quite similar from the mathematical point of view. In fact, they all have the symmetry of the quadrupole-quadrupole interaction. Indeed, the models of McMillan and Benguigui operate with pairs of antiparallel dipoles which are equivalent to permanent molecular quadrupoles. On the otherhand, in the Wulf's model a 'zig-zag' molecule can be presented as a pair of antiparallel transverse steric dipoles, and this is again equivalent to a steric quadrupole. Even the averaged induction interaction considered by Van der Meer and Vertogen is mathematically similar to the interaction between permanent quadrupoles. One notes that the model of the SmC phase directly based on the interaction between molecular quadrupoles has also been proposed in the literature [34].

The analysis of these models enables one to single out the simple model potential which promotes the tilt in smectic phases. This potential may have different physical origins, but mathematically it can be written in the following simple form:

$$V_C(1,2) = J_C(r_{12})((\mathbf{a}_1 \cdot \mathbf{u}_{12})^2 + (\mathbf{a}_2 \cdot \mathbf{u}_{12})^2), \tag{1}$$

where the unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are in the direction of the long axes of the molecules '1' and '2', respectively, and the unit vector $\mathbf{u}_{12}$ is along the intermolecular vector $\mathbf{r}_{12}$. One notes that the potential (1) depends on an angle between the long molecular axis and the direction to neighbouring molecule. In this sense the potential (1) is very different from the familiar Maier-Saupe potential which depends on the coupling between two long molecular axes. The potential (1) manifests itself in smectic phases, while in the nematic phase it reduces to a constant after averaging over all orientations of the intermolecular vector. One can readily see that this model potential can be responsible for the tilt of the director in the SmC phase. Indeed, for two neighbouring molecules in the same smectic layer, the unit intermolecular vector is perpendicular to the layer normal, $\mathbf{e}$, $\mathbf{u}_{12} = \mathbf{u}_{12}^{\perp} \perp \mathbf{e}$. Therefore, the potential (1) can be written as

$$J_C(\sin^2 \omega_1 + \sin^2 \omega_2), \tag{2}$$

where ω_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 coupling constant J_C is negative. This means that the potential (1) can be considered as a model potential for SmC. The contribution of the potential (1) to the free energy of the SmC phase can be established by taking a simplified statistical average of (1) in one smectic layer in the limiting case of the perfect orientational ordering. In this case the long axes $\mathbf{a}_1$ and $\mathbf{a}_2$ in Eq. (1) can be replaced by the director $\mathbf{n}$, and then the potential (1) can be written as $2J_C(\mathbf{n} \cdot \mathbf{u}_{12})^2$. Averaging this expression over all orientations of the unit intermolecular vector within one smectic layer (*i.e.* over all $\mathbf{u}_{12} \perp \mathbf{e}$) one obtains

$$< V_C(1,2) >= J_C(1 - (\mathbf{n} \cdot \mathbf{e})^2) = J_C \sin^2 \Theta, \tag{3}$$

where Θ is the tilt angle of the director. One can readily see that the minimum of the averaged potential (1) corresponds to largest possible values of the tilt angle if the coupling constant J_C is negative.

It should be noted, however, that the interaction potential (1) does not distinguish between the synclinic SmC phase and the anticlinic SmC$_A$ phase because it is not sensitive to the relative orientation of the neighbouring molecules in adjacent layers, and thus it is not sensitive to relative directions of the tilt in different layers. This potential just promotes tilt in a smectic layer regardless of its direction.

3. MODEL POTENTIAL FOR THE ANTICLINIC SMECTIC-C_A PHASE

3.1. Model Interaction Potential

The interaction potential that stabilises the anticlinic configuration can be determined by taking into consideration the difference between the free energies of the SmC and SmC$_A$ phases [35]. For this purpose it is interesting to consider a general expansion of the pair interaction potential between two uniaxial rigid molecules, for simplicity. This potential can be written as [30,35]

$$\begin{aligned} & \upsilon_0 + \upsilon_1 P_2(\mathbf{a}_1 \cdot \mathbf{a}_2) + \upsilon_2\{(\mathbf{a}_1 \cdot \mathbf{u}_{12})^2 + (\mathbf{a}_2 \cdot \mathbf{u}_{12})^2\} \\ & \quad + \upsilon_3(\mathbf{a}_1 \cdot \mathbf{a}_2)(\mathbf{a}_1 \cdot \mathbf{u}_{12})(\mathbf{a}_2 \cdot \mathbf{u}_{12}) + \upsilon_4(\mathbf{a}_1 \cdot \mathbf{u}_{12})^2(\mathbf{a}_2 \cdot \mathbf{u}_{12})^2, \end{aligned} \tag{4}$$

where we have taken into account only the lowest order nonpolar terms which are quadratic in $\mathbf{a}_1$ and $\mathbf{a}_2$. The second term in Eq. (4) represents the Maier-Saupe type of interaction that promotes the parallel alignment of neighbouring molecules, and the third term represents the model potential of the synclinic SmC phase discussed in the previous section. Finally, the fourth term in Eq. (4) is sensitive to the orientation of the two long axes of the interacting molecules *and* the intermolecular unit vector $\mathbf{u}_{12}$. This term determines the lowest order contribution to the free energy difference between SmC and SmC$_A$ [35] and, therefore, can be considered as a simple model potential of the anticlinic ordering.

The role of the fourth term in the expansion (4) can be clarified by statistical averaging of this part of the interaction potential in the case of perfect nematic and smectic order. Let us first consider the interaction between neighbouring molecules within the same smectic layer described by the potential

$$J_{CA}(\mathbf{a}_1 \cdot \mathbf{a}_2)(\mathbf{a}_1 \cdot \mathbf{u}_{12})(\mathbf{a}_2 \cdot \mathbf{u}_{12}), \tag{5}$$

which corresponds to the fourth term in Eq. (4). In the case of perfect nematic order $\mathbf{a}_1 = \mathbf{a}_2 = \mathbf{n}$ and the potential (5) can be rewritten as

$$J_{CA}(\mathbf{n} \cdot \mathbf{u}_{12})^2.$$

This is exactly the same expression as the one given by Eq. (2). Thus one concludes that within one smectic layer the fourth term in the interaction potential (4) plays qualitatively the same role as the smecticC model potential (1) which simply promotes the tilt in any direction. On the other hand, a contribution from the fourth term in Eq. (4) has a very different form if one considers the interaction between neighbouring molecules in adjacent smectic layers. In this case the intermolecular vector is approximately parallel to the smectic layer normal $\mathbf{e}$, *i.e.* $\mathbf{u}_{12} \approx \mathbf{e}$. Now the potential (5) can be rewritten as

$$J_{CA}(\mathbf{n}_1 \cdot \mathbf{n}_2)(\mathbf{n}_1 \cdot \mathbf{e})(\mathbf{n}_2 \cdot \mathbf{e}), \tag{6}$$

where $\mathbf{n}_1$ and $\mathbf{n}_2$ are the directors in the two neighbouring smectic layers. Assuming that the absolute value of the tilt angle is the same in all layers, one can substitute $(\mathbf{n}_1 \cdot \mathbf{e}) = (\mathbf{n}_2 \cdot \mathbf{e}) = \cos\Theta$ and $(\mathbf{n}_1 \cdot \mathbf{n}_2) = \cos^2\Theta + \sin^2\Theta\cos(\phi_1 - \phi_2)$ into Eq. (6), where ϕ_1 and ϕ_2 are the azimuthal angles of the directors $\mathbf{n}_1$ and $\mathbf{n}_2$, respectively. Finally one obtains the following expression for the averaged potential (5)

$$< V_{CA} > = J_{CA}\cos^2\Theta(\cos^2\Theta + \sin^2\Theta\,\cos(\phi_1 - \phi_2)). \tag{7}$$

One can readily see that the minimum of the potential (7) corresponds to $\phi_1 - \phi_2 = \pi$ if the coupling constant J_{CA} is positive. This means that anticlinic structure can be stabilised by a sufficiently strong ***repulsive*** interaction potential (5).

Now the model potential of the SmC$_A$ phase is given by a sum of the potential (1), which promotes the tilt irrespective to its sense, and the potential (5), which distinguishes between the synclinic and anticlinic configurations:

$$\begin{aligned} U_{CA}(1,2) = & J_C((\mathbf{a}_1 \cdot \mathbf{u}_{12})^2 + (\mathbf{a}_2 \cdot \mathbf{u}_{12})^2) \\ & + J_{CA}(\mathbf{a}_1 \cdot \mathbf{a}_2)(\mathbf{a}_1 \cdot \mathbf{u}_{12})(\mathbf{a}_2 \cdot \mathbf{u}_{12}). \end{aligned} \tag{8}$$

3.2. Molecular Origin of the Anticlinic Ordering

It is important to identify the intermolecular interactions that can stabilise the anticlinic structure. As a first step one can look for such interactions among standard interaction potentials used to describe liquid crystalline ordering. According to Van der Meer and Vertogen [30] and Gelbart [36], the predominant orientational interaction in thermotropic liquid crystals, which determines the orientational order, is the isotropic (dispersion) attraction modulated by anisotropic molecular shape. The expansion of the corresponding interaction potential does contain the required term of the form (5) but the corresponding coupling constant appears to be negative [30], *i.e.* the potential is of an attractive type. Consequently, it destabilises the anticlinic configuration. By contrast, the *anisotropic* dipole-dipole dispersion interaction contains the required repulsive contribution of the form (5) which stabilises the SmC$_A$ phase. This can be shown in the following way. For two uniaxial molecules the anisotropic dispersion interaction potential can be written as

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

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’ [3].

One notes that the coupling constant J_2 in Eq. (9) is approximately proportional to the square of the anisotropy of the molecular polarizability $(\Delta\alpha)^2$ [37]. The isotropic dispersion interaction, modulated by the anisotropic molecular shape, which is discussed above, is proportional to the square of the average molecular polarizability $(\bar{\alpha})^2$ and therefore is expected to be stronger. The ratio of these two contributions can be roughly estimated as $(\bar{\alpha}/\Delta\alpha)^2$, *i.e.* the former contribution is predominant. Taking into account that the first term in Eq. (9) also destabilises the SmC$_A$ phase, we arrive at the conclusion that the conventional dispersion interaction between typical mesogenic molecules does not stabilise the anticlinic SmC$_A$ phase. This conclusion seems to be reasonable because otherwise SmC$_A$ 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 SmC$_A$ has been observed only in one type of achiral (one component) smectic liquid crystals [11,12]. We note also that the corresponding compound is a swallow tailed one, *i.e.* it is quite similar to the structure of the chiral compounds that show SmC$_{\rm A}$*. Qualitative arguments presented above indicate that SmC$_A$ is stabilised, apparently, by some specific intermolecular interactions. In practice, the anticlinic configuration is usually observed in chiral smectics with large spontaneous polarisation. It is very unlikely that chirality is of any importance here. Chiral interactions are generally weak and, in addition, achiral anticlinic SmC$_A$ has been observed in racemic mixtures [13–15]. On the other hand, such chiral compounds also contain relatively large dipoles in the vicinity of the chiral centre in the flexible chain. It can be shown [35] that interlayer orientational correlations between such transverse molecular dipoles can be responsible for the stabilisation of SmC$_A$ phase.

One notes also that the interaction potential (5) should be much weaker than the SmC model potential (1). Indeed, the potential (1) which promotes the tilt of the director is determined mainly by interactions with neighbouring molecules in the same smectic layer [3,30,35,38]. At the same time, the potential (5) which selects between different directions of the tilt in adjacent layers is determined by much weaker interactions between molecules located in different layers. This enables one to understand why the free energy difference between the synclinic and the anticlinic smecticC phases is so small. The free energies associated with the synclinic and anticlinic structure in the smecticC phase can be estimated in the following way.

Let us first consider the synclinic SmC phase. The free energy of this phase can be estimated by using the familiar Landau- de Gennes expansion in powers of the tilt angle Θ,

$$F_C = F_A + \frac{1}{2}\alpha(T - T^*)\sin^2\Theta + \frac{1}{4}B\sin^4\Theta + \dots, \tag{10}$$

where F_A is the free energy of the SmA phase and T^* is the second-order SmA–SmC transition temperature. The free energy difference between SmA and SmC phases is mainly determined by the second term in Eq. (10) if the tilt angle is small. In this term the material parameter α has been measured experimentally for a number of compounds. According to Giesselmann [39], for typical ferroelectric SmC*, the parameter α is in the range between $5 \cdot 10^4$ and $2 \cdot 10^5\, JK^{-1}m^{-3}$. Substituting these numbers into Eq. (10) one concludes that the free energy difference $\Delta F = F_C - F_A$ associated with the tilt of the director in the SmC phase can be estimated as

$$\Delta F \sim 10^6\Theta^2\, Jm^{-3} \tag{11}$$

when $T^* - T \approx 10^\circ C$.

The free energy difference between the synclinic SmC phase and the anticlinic SmC$_A$ phase can be estimated using the averaged potential (7) which depends on the azimuthal angle $\Delta\phi_{12} = \phi_1 - \phi_2$ between the two directors in neighbouring layers. A strongly simplified version of this potential has been used by Qian and Taylor [40] who have assumed that the corresponding free energy difference $\Delta F \approx U\cos\Delta\phi_{12}$. Using the experimental data which describe the response of the anticlinic phase to the external electric field, the coefficient U has been estimated as $U \sim 10^3\, Jm^{-3}$. Thus the free energy difference can be estimated as

$$F_C - F_{CA} \sim 10^3\, Jm^{-3}. \tag{12}$$

Comparing the estimates (11) and (12) one arrives at the conclusion that the free energy difference between synclinic and anticlinic phases is always much smaller than the free energy associated with the tilt in the SmC phase, except for a narrow interval around the SmA–SmC transition temperature where $\Theta^2 \ll 1$. In fact, the free energy difference between synclinic and anticlinic configurations appears to be so small that the corresponding phase transition can easily be induced by moderate electric fields $E \sim 10^5 Vm^{-1}$. This means that the anticlinic structure can also be strongly affected by other macroscopic factors including boundary conditions in this films. By contrast, the SmA–SmC phase transition can be induced by moderate electric fields only in the vicinity of the transition point where the tilt angle is very small (the electroclinic effect in chiral smectics).

4. MOLECULAR MODEL FOR THE ANTICLINIC SMECTICC$_A$ PHASE

At present there are more than 1,000 compounds which exhibit SmC$_A^*$ [41]. All these molecules are quite similar in their chemical structures and possess significantly large transverse permanent dipole moments in the vicinity of the chiral centres. It is interesting to note that antiferroelectric, anticlinic SmC$_A$* has been discovered during the experimental studies of *chiral* ferroelectric, synclinic SmC* with large spontaneous polarisation. We may conclude that the anticlinic configuration should be determined by some details of the molecular structure which are typical for ferroelectric SmC* with large spontaneous polarisation. One obvious structural element of this kind is the transverse dipole that is often located near the joint of the flexible chiral alkyl chain (See Fig. 2). On the other hand, the direct interaction between such dipoles vanishes after the orientational averaging. It can be shown that SmC$_A$ 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 centre.

The direct dipole-dipole interaction between molecules in adjacent layers cannot be responsible for the anticlinic configuration because the average dipole-dipole interaction between two parallel polar planes vanishes. This has already been shown by Prost and Bruinsma [42] and by Bruinsma and Prost [43]. However, the instant (*i.e.* non-averaged) interaction between the dipoles of two neighbouring molecules can be rather large. This means that there exist strong dipole-dipole correlations which may be important. Such correlations are taken into account in the frame work of the thermodynamic perturbation theory. Taking into account that the average dipole-dipole interaction potential vanishes, *i.e.* $< V_{dd} >= 0$,

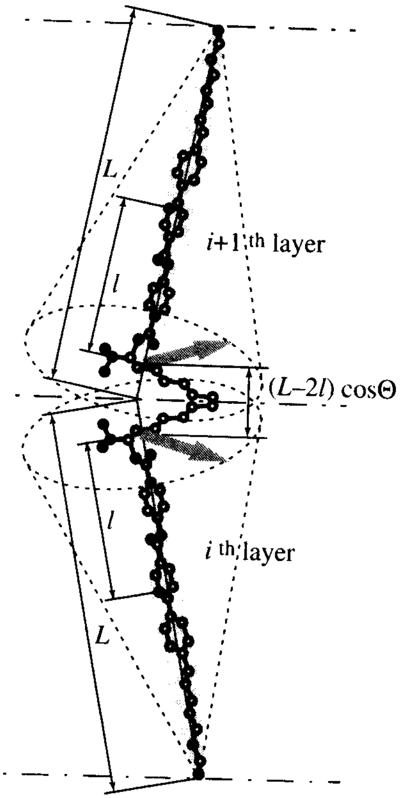

FIGURE 2 Schematic illustration of interlayer orientational correlations between transverse molecular dipoles. The dipole is assumed to be located at the joint of the flexible chain, which is projecting obliquely from the core part. Here l is the distance between the dipole and the molecular center of mass.

the free energy of the tilted smectic phase is written as

$$\frac{F}{N} \approx \frac{F_0}{N} - \frac{1}{2kT} < V_{dd}^2 >, \tag{13}$$

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

$$V_{dd}(1,2) = \frac{d_\perp^2}{r_{12}^3} \{(\mathbf{b}_1 \cdot \mathbf{b}_2) - 3(\mathbf{b}_1 \cdot \mathbf{u}_{12})(\mathbf{b}_2 \cdot \mathbf{u}_{12})\}, \tag{14}$$

where the short molecular axis $\mathbf{b}$ is taken to be parallel to the transverse molecular dipole $\mathbf{d}_\perp$. Now one can average the square of the interaction potential (14) 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, neglecting any biaxial ordering of short molecular axes in the first approximation because the biaxial order parameter is not expected to be large. Then the averaging of $V_{dd}^2(1,2)$ over all orientations of short molecular axes results in the following expression,

$$\begin{aligned}
&-\frac{1}{2k_BT} < V_{dd}^2(1,2) >_{\mathbf{b}_1,\mathbf{b}_2} \\
&= \frac{d_\perp^4}{8k_BTr_{12}^6}\{-4-(\mathbf{a}_1\cdot\mathbf{a}_2)^2+3(\mathbf{a}_1\cdot\mathbf{u}_{12})^2+3(\mathbf{a}_2\cdot\mathbf{u}_{12})^2-9(\mathbf{a}_1\cdot\mathbf{u}_{12})^2(\mathbf{a}_2\cdot\mathbf{u}_{12})^2 \\
&+6(\mathbf{a}_1\cdot\mathbf{u}_{12})(\mathbf{a}_2\cdot\mathbf{u}_{12})(\mathbf{a}_1\cdot\mathbf{a}_2)\}. \qquad (15)
\end{aligned}$$

We note that Eq. (15) presents a kind of the effective uniaxial interaction potential. The last term in Eq. (15) has the form of the SmC_A model potential with a positive coupling constant and therefore it promotes the anticlinic ordering.

Now the contribution of the dipole-dipole fluctuations to the free energy difference between synclinic SmC and anticlinic SmC$_A$ (at the same value of the tilt angle Θ) can be written in the following explicit form,

$$\begin{aligned}
&-\frac{1}{2kT}(< V_{dd}^2 >_{CA} - < V_{dd}^2 >_C) \\
&= \gamma(1-\sigma)\frac{d_\perp^4}{8kT(R_{12}^{\|})^6}\{1-6(\mathbf{n}\cdot\mathbf{e})^2 \\
&\quad -(\mathbf{n}_1\cdot\mathbf{n}_2)^2+6(\mathbf{n}_1\cdot\mathbf{e})(\mathbf{n}_2\cdot\mathbf{e})(\mathbf{n}_1\cdot\mathbf{n}_2)\} \\
&= -\gamma(1-\sigma)\frac{d_\perp^4}{4kT\{(L-2l)\cos\Theta\}^6}\sin^2 2\Theta < 0, \qquad (16)
\end{aligned}$$

where the $R_{12}^{\|} \approx (L-2l)\cos\Theta$ is the distance between the transverse dipoles of neighbouring molecules in adjacent smectic layers as shown in Figure 2. Here L is the molecular length and l is the distance between the dipole moment in the alkyl chain and the molecular centre of mass. Thus we arrive at the conclusion that orientational correlations between transverse molecular dipoles can stabilise SmC$_\text{A}$ with respect to SmC. We note that this contribution rapidly grows with increasing the tilt angle Θ. 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 near the joint of the flexible chiral chain obliquely projecting from the core part. In this case the average distance between such dipoles, which belong to neighbouring molecules in adjacent layers, can be significantly smaller than the molecular length [44].

Finally the free energy difference between the synclinic and the anticlinic phase can approximately be written as

$$\frac{F_{CA} - F_C}{N} = V^{\|} \sin^2 2\Theta - \frac{d_\perp^4 \sin^2 2\Theta}{4kT\{(L-2l)\cos\Theta\}^6}, \qquad (17)$$

where the constant $V^{\|}$ represents a contribution from all other relevant interactions between neighbouring layers which distinguish between the synclinic and the anticlinic configurations. We assume that those interactions generally stabilise the synclinic phase and thus $V^{\|} > 0$. Now the transition temperature between SmC and SmC$_\text{A}$ phases is determined by a balance between the two terms in the r.h.s. of Eq. (17): the contribution from the interlayer dipole-dipole correlations promoting the anticlinic configuration and the first term which is mainly determined by excluded volume effects and which promotes SmC. The correlation contribution grows rapidly with the increasing molecular transverse dipole moment $d_\perp$

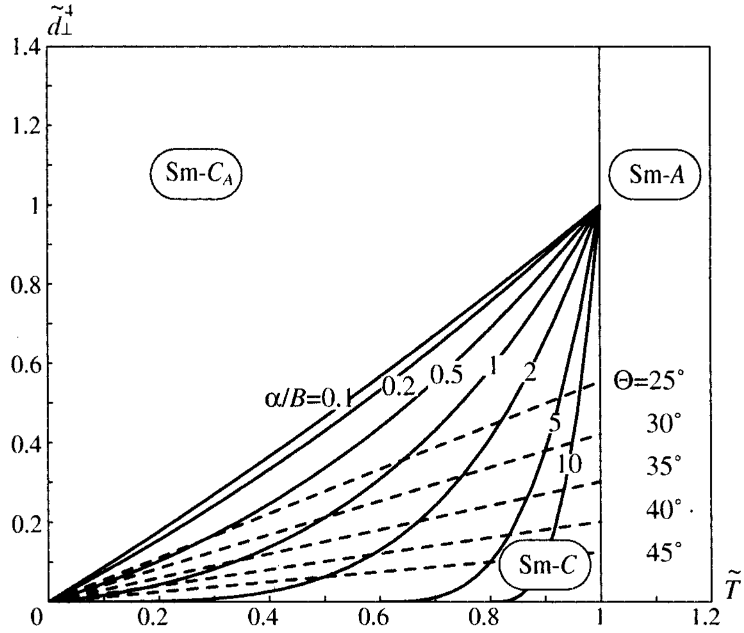

FIGURE 3 A simple phase diagram of the perfectly ordered smectic liquid crystal which contains SmA, SmC, and SmC$_\text{A}$. The abscissa is the normalized temperature $\tilde{T}$ and the ordinate is the ratio $\tilde{d}_\perp^4/\tilde{V}^{\|}$ (See text below Eq. (17)). The boundary between SmC$_A$ and SmC depends on the tilt angle Θ; solid and dotted lines are obtained by using Eq. (10) and by assuming Θ = *const.*, respectively.

and with the increasing separation between the dipole and the molecular center of mass. The corresponding phase diagram, which includes SmA, sinclinic SmC, and anticlinic $\mathrm{SmC_A}$, is presented in Figure 3 where the abscissa is the normalised temperature, $\tilde{T} = T/T^*$, and the ordinate is the 4 th power of the dimensionless dipole, $\tilde{d}_\perp = d_\perp/\{(2k_\delta T^*)^{1/2}(L-2l)^{3/2}\}$, divided by $\tilde{V}^{\|} = V^{\|}/k_\delta T^*$. We note that in Figure 3 the boundary between SmA and SmC (or $\mathrm{SmC_A}$) is a vertical line. This is a result of an approximation which is valid if the relevant interactions between molecules in neighbouring smectic layers are much weaker than the interactions within one layer. In this case the transition temperature into the SmA phase is not affected by the weak interlayer interactions which determine the difference between SmC and $\mathrm{SmC_A}$. One can readily see that 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 Θ. Consequently, SmC is always a higher temperature phase than SmC_A when both emerge. In the hexatic smectic phases, however, $\mathrm{SmI_A}$* may appear just below $\mathrm{SmC_A}$* and then a phase transition to SmI* may occur [45]. At present there is no explanation of this fact.

The molecular model of $\mathrm{SmC_A}$ presented in this paper takes into consideration only one particular microscope mechanism of the anticlinic ordering, based on orientational interlayer dipole-dipole correlations. This model is not in contradiction with the existing experimental data, but we cannot exclude that in some cases $\mathrm{SmC_A}$ may be stabilised by some other specific interactions or correlation effects. One may assume that steric interaction between swallow-tail chains can give rise to some peculiar packing effects, as pointed out by Nishiyama and Goodby [11,12]. Note, however, that the swallow-tail molecule possesses rather large transverse electric dipole moments near the joint of the flexible chiral chain to the core part and that the swallow tails are considered to be bent with respect to the molecular long axis thus producing transverse steric dipoles. The anticlinic phase can also be stabilised by some specific packing entropy effects which have been considered by Glaser [46] and by Walba [47]. In the general case, however, any intermolecular interaction that may stabilise $\mathrm{SmC_A}$ should be characterised by the effective interaction potential of the form (5), at least in the first approximation.

5. MICROSCOPIC ORIGIN OF THE SUBPHASES

5.1. Ising Models and the Devil's Staircase

In many smectic materials a sequence of polar subphases with increasing periodicities is formed between ferroelectric SmC* and antiferroelectric

SmC_A*. In this domain, synclinic and anticlinic structures have nearly the same energy and thus the subphases should be stabilised by some relatively weak additional factors. All existing models of subphases are based on some interactions between different smectic layers. In phenomenological models [28,29] one takes into account competing orientational interactions between nearest neighbour and next to nearest neighbour smectic layers. Then the minimum of the free energy corresponds to a uniform rotation of the tilt plane about the layer normal, and the angle between tilt planes in neighbouring smectic layers appears to be equal to $2\pi/n$ where n is the periodicity of the structure. In this way one can explain qualitatively the formation of subphases with three and four layer periodicity, but it is difficult to explain the existence of the whole sequence of phases with increasing periods. In addition, the structure of the subphases is not described correctly and it remains to be unclear why the subphases are observed only in chiral materials. Another approach to the description of subphases is based on microscopic Ising models with competing repulsive and attractive interactions between nearest neighbours and next to nearest neighbours [48]. It is known that in such a model one indeed can obtain a sequence of subphases which resemble the Devil's staircase [49–51]. However, the Ising-like Hamiltonian itself can hardly be directly applied to smectic liquid crystals. In Ising models actual continuous orientation of the long molecular axis is replaced by two states, one of which is parallel to the director and the other is parallel to the opposite direction of the tilt. In real smectics, however, the orientational order parameter is always rather high and long molecular axes are predominantly oriented along the local director. Similar to the clock model, the Ising model does not take into account molecular chirality and cannot explain the particular structure of the subphases which have been determined in recent experiments. Prost and Bruinsma [42] and Bruinsma and Prost [43] proposed a more consistent model by taking into account long range polarisation fluctuations and tried to explain the formation of the sequence of subphases. This mechanism seems to be very promising and it should be taken into consideration in a more general theory. However, this mechanism alone cannot explain the experimentally determined structure of the subphases, either.

Thus one arrives at the conclusion that none of the existing approaches can explain rather complex non-planar structures of the ferrielectric and antiferroelectric subphases which has been determined experimentally [20,21] and that it is necessary to account for the role of chirality in the origin of subphases. This means that an essential factor is missing. We believe that these problems can be resolved by taking into account the effect of the additional polarisation determined by the 'discrete' flexoelectric effect which is discussed in the following subsection.

5.2. 'Discrete' Flexoelectric Effect

The conventional flexoelectric effect describes the polarisation which is proportional to gradients of the director in a liquid crystal phase [52,53]. For example, in ferroelectric SmC* the flexoelectric polarisation is determined by a slow rotation of the tilt plane which describes a helix. By contrast, in anticlinic SmC$_A$ the director orientation changes discontinuously from layer to layer. This alternation of tilt sense results in another symmetry-determined polarisation which is parallel to the tilt plane. The existence of such polarisation also follows from general symmetry arguments [35,54,55] and it has been observed experimentally [56,57]. One notes that this polarisation can approximately be written as a gradient of the smectic-C order parameter if the actual discontinuous variation of the direction along the z-axis is replaced by a cosine wave with the double periodicity. Then the in-plane polarisation can be written as [35]

$$\mathbf{P}_\perp = -\mu_f \chi_\perp \mathrm{curl}\mathbf{w}(\mathrm{r}), \tag{18}$$

where $\mathbf{w} = [\mathbf{n} \times \mathbf{e}](\mathbf{n} \cdot \mathbf{e})$ is the vector order parameter of the SmC$_A$ phase which depends on z as $\cos(qz/2)$ where $q = 2\pi/d$ is the wave vector of the density wave in the SmC phase. Here μ_f is the corresponding flexocoefficient and $\chi_\perp$ the susceptibility tensor.

By contrast to the SmC$_A$ phase, the three and four-layer subphases are not planar and the orientation of the tilt plane changes discontinuously from layer to layer in a rather asymmetric way within a period [20,21]. In this case the point symmetry of a smectic layer appears to be very low, and there should be an additional polarisation in each layer determined by the difference between director orientations in two neighbouring layers. Such polarisation is similar to the in-plane polarisation in the anticlinic phase, but due to the lower symmetry of each smectic layer the polarisation is no longer parallel to the tilt plane. In the first approximation the additional 'flexoelectric' polarisation in the smectic layer 'i' can be written in the form

$$\mathbf{P}_i = \frac{\mu_f \chi_\perp}{d} [\mathbf{e} \times (\mathbf{w}_{i+1} - \mathbf{w}_{i-1})], \tag{19}$$

where $\mathbf{w}_{i+1}$ and $\mathbf{w}_{i-1}$ are the order parameters of the neighbouring layers 'i+1' and '$i-1$', respectively, d is the thickness of the smectic layer, and μ_f is a 'flexoelectric coefficient'. One notes that such polarisation has qualitatively the same general origin as the in-plane polarisation in the SmC$_A$ phase and even as in the conventional flexoelectric effect. However, the corresponding 'discrete' flexoelectric effect has never been considered before although a molecular theory of such a flexoelectric effect can be developed employing the primary ideas of the existing theory of flexoelectricity in nematics [58–60].

5.3. Casimir Force Due to Ordinary and Discrete Fleoelectric Polarizations

Finary, let us consider whether the above frame work can explain the emergence of experimentally observed subphases, in particular, three-layered and four-layered ones. We begin with the Ising model. The Hamiltonian is given by

$$\begin{aligned} H &= (1-q_T)F_{CA} + q_T F_C + J\sum_i\sum_j \frac{S_iS_j}{|i-j|^2} \\ &= F_{CA} + q_T(F_C - F_{CA}) + J\sum_i\sum_j \frac{S_iS_j}{|i-j|^2}. \end{aligned} \tag{20}$$

Here $S_i = 0 \pm 1$ and q_T is a fraction of the synclinic ferroelectric ordering in the subphase under consideration; $q_T = 1/3$ and 1/2 represent the three- and four-layered structures, respectively. The subphase structure has frequently been characterized by the wave number q, and there exists a simple relation between q_T and q, $q_T = 1-2q$. The free energy difference between SmC and SmC$_\mathrm{A}$ is given by Eq. (17). By normalizing the free energy by kT^* (T^* is the transition temperature from SmA to a tilted fluid smectic phase) and by using dimensionless parameters defined in Section 4 together with $\tilde{J} = J/k_BT^*$, Eq. (20) now becomes

$$\begin{aligned} \tilde{H} &= const + q_T\left\{-\tilde{V}^{\|} + \frac{\tilde{d}_\perp^4}{\tilde{T}\cos^6\Theta}\right\}\sin^2 2\Theta \\ &\quad + \tilde{J}\sum_i\sum_j \frac{S_iS_j}{|i-j|^2}. \end{aligned} \tag{21}$$

Note that, in this frame work, the existence of spontaneous polarization is necessary for the appearance of subphases between SmC$_\mathrm{A}$* and SmC*. This is in accordance with our experience that racemization always destroys the subphases. Moreover, it is also consistent with the fact that the several subphases observed in (*R*)-MHPBC quickly disappear by mixing (*S*)-TFMHPBC with the opposite polarity while they remain stable by mixing (*R*)-TFMHPBC with the same polarity [13].

In the discrete Ising model, the last term summation in Eq. (21) can easily be calculated numerically, giving −1.64 for $q_T = 0, -0.612$ for $q_T = 1/3, -0.411$ for $q_T = 1/2$, and 3.29 for $q_T = 1$. Let us first assume that the tilt angle does not change with temperature, $\Theta = const = 30^\circ$ and that $\tilde{d}_\perp^4/|\tilde{V}^{\|}| = 0.4$. Then we obtain Figures 4(a) and (b). Without taking into account the Casimir force given by the last term of Eq. (21), that is, when $\tilde{J} = 0$, only SmC$_\mathrm{A}$($q_T = 0$) and SmC($q_T = 1$) exist stably as shown in

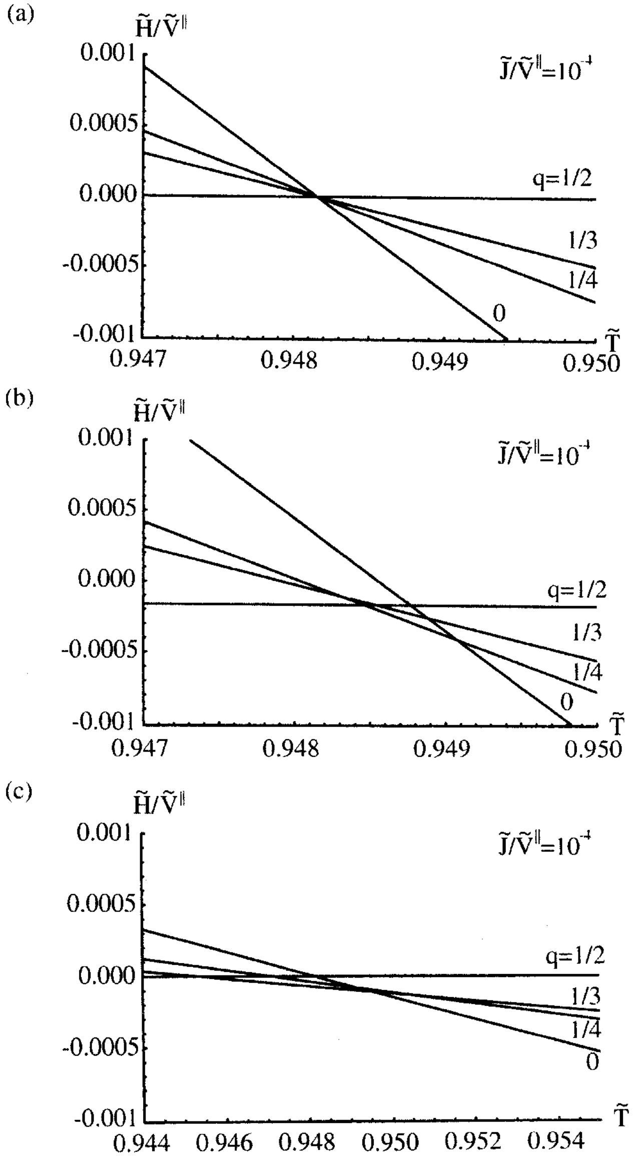

FIGURE 4 Three energies responsible for the stability of subphases obtained by using Eq. (21) with $\Theta = 30°$ and $\tilde{d}_{\perp}^{4}/\tilde{V}^{\|} = 0.4$, (a) no Casimir force, (b) the Casimir force due to ordinary polarization, and (c) the Casimir force due to discrete flexoelectric polarization are taken into account.

Figure 4(a). The Casimir force stabilizes the $q_T = 1/2$ subphase but not the $q_T = 1/3$ one, as is clear in Figure 4(b). Here we assumed $\tilde{J} = 1.0\times 10^{-4}$ and obtained the subphase temperature range $\Delta\tilde{T} \approx 0.0125$, which realistically corresponds $\Delta\tilde{T} \approx 5\,K$ since $T^* = 400\,K$ and the temperature range of the tilted fluid smectics is considered to be $100\,K$. The calculated stability does not critically depends on $\tilde{J}$. We could not stabilize the $q_T = 1/3$ subphase even when the temperature dependence of tilt angle Θ is appropriately taken into account. Experimentally, the $q_T = 1/3$ subphase is stabler than the $q_T = 1/2$ one.

The flexoelectric polarization of the smectic layer is given by Eq. (19), which is perpendicular to $\mathbf{w}_{i+1} - \mathbf{w}_{i-1}$. Hence, in the Ising model, the flexoelectric polarization is in the tilt plane. Now the Casimir force is quite different from the one due to the ordinary polarization perpendicular to the tilt plane. The last term summation in Eq. (21) can easily be calculated numerically, giving 0 for $q_T = 0, -0.731$ for $q_T = 1/3, -0.411$ for $q_T = 1/2$, and 0 for $q_T = 1$. Figure 4(c) shows the calculated result. The Casimir force due to the flexoelectric spontaneous polarization stabilizes the $q_T = 1/3$ subphase but not the $q_T = 1/2$ one. The result is not sensitive to the parameter value of $\tilde{J}$. The situation was just opposite in the case of the Casimir force due to the ordinary spontaneous polarization. The stabilization of $q_T = 1/3$ mainly results from the fact that, in the $q_T = 0$ and $q_T = 1$ subphases, no spontaneous polarizations are produced by the discrete flexoelectric effect and hence the Casimir force does not contribute to the free energy.

By appropriately taken into account of both the spontaneous polarizations, we may be able to stabilize not only $q_T = 1/3$ and $q_T = 1/2$ but also all the other $\mathrm{SmC_A}^*$ $(0 < q_T < 1)$ subphases experimentally observed. An open question is how to combine both the spontaneous polarizations that are not parallel. We believe that an interplay between the 'discrete' flexoeffect and the spontaneous polarisation determined by molecular chirality can explain the particular non-planar structures of three- and four-layer smectic phases. The corresponding research is currently in progress.

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