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Theoretical model for the discrete flexoelectric effect and a description for the sequence of intermediate smectic phases with increasing periodicity

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A general phenomenological description and a simple molecular model is proposed for the ''discrete'' flexoelectric effect in tilted smectic liquid crystal phases. This effect defines a polarization in a smectic layer induced by a difference of director orientations in the two smectic layers adjacent to it. It is shown that the ''discrete'' flexoelectric effect is determined by electrostatic dipole-quadrupole interaction between positionally correlated molecules located in adjacent smectic layers, while the corresponding dipole-dipole interaction is responsible for a coupling between polarization vectors in neighboring layers. It is shown that a simple phenomenological model of a ferrielectric smectic liquid crystal, which has recently been proposed in the literature, can be used to describe the whole sequence of intermediate chiral smectic C^* phases with increasing periods, and to determine the nonplanar structure of each phase without additional assumptions. In this sequence the phases with three- and four-layer periodicities have the same structure, as observed in the experiment. The theory predicts also the structure of intermediate phases with longer periods that have not been studied experimentally so far. The structures of intermediate phases with periodicities of up to nine layers are presented together with the phase diagrams, and a relationship between molecular chirality and the three-dimensional structure of intermediate phases is discussed. It is considered also how the coupling between the spontaneous polarization determined by molecular chirality and the induced polarization determined by the discrete flexoelectric effect stabilizes the nonplanar structure of intermediate phases.

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I. INTRODUCTION

Ferroelectric smectic liquid crystals are unique materials where the spontaneous polarization is determined by molecular chirality. In the chiral smectic C^* phase the polarization is induced by a tilt of the director with respect to the smectic layer normal. The direction of both tilt and polarization can be switched by an external electric field. About 14 yr ago it was shown experimentally [1] that similar materials may also exhibit the anticlinic antiferroelectric smectic C_A phase, where both polarization and direction of the tilt alternate in sign from layer to layer. The transition between synclinic and anticlinic smectic phases is of the first order, and according to the experimental data [2,3] the synclinic smectic C phase is always the higher temperature phase. The only exception is the anticlinic smectic I phase that also possesses the hexatic order [4–6]. It should be noted that the anticlinic structure itself is not related to molecular chirality because the anticlinic smectic C_A phase is observed in racemic mixtures [7–9] and even in some nonchiral compounds [10,11]. Chirality results in the appearance of the spontaneous polarization in each smectic layer in the direction perpendicular to the local tilt plane. In addition, the chiral smectic C_A^* phase is characterized by a helical structure with optical wavelength. One notes also that the energy barrier between the synclinic and the anticlinic phases is relatively low, and the corresponding phase transition can be induced by a moderate electric field. Recently a number of experimental studies have revealed that chiral smectic C^* liquid crystals exhibit a sequence of intermediate ferrielectric phases with modulation periods of more than two layers in a temperature interval between ferroelectric and antiferroelectric Sm-C^* phases. The most commonly observed intermediate phases are Sm-C_{FI1} and Sm-C_{FI2} phases that exhibit three- and four-layer superstructures, respectively, with a uniform tilt angle [12–15]. Very recently the detailed structure of these phases has been investigated with ellipsometry [16,17], the resonant x-ray scattering techniques [18,19], and optical rotatory power technique [15,20]. In contrast to the earlier qualitative models, the actual structure of Sm-C_{FI1} and Sm-C_{FI2} phases is not flat and, at the same time, it is different from the uniaxial ''clock'' model [21,22]. In fact, each intermediate phase is characterized by a unique set of azimuthal angles $\{\varphi_i\}$ that specify different azimuthal orientations of the director in each smectic layer inside the unit crystallographic cell. The structure of the unit cell appears to be chiral, and it is known that intermediate phases disappear in racemic mixtures. One thus concludes that their origin should be directly related to molecular chirality.

Transition between the ferroelectric Sm-C^* and the antiferroelectric Sm-C_A^* phases can theoretically be described by continuum theory [23,24] or by simple discrete phenomenological models that explicitly take into consideration coupling between director orientations in different layers [21,17]. Phases with more complex structure can be described phenomenologically using a number of additional order parameters [25] or by using more advanced discrete models which take into consideration various couplings be-

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tween nearest neighbor and next-nearest-neighbor smectic layers, as recently proposed by Cepic and co-workers [26,27]. In particular, Lorman [25] presented a possible four-layer phase that corresponds to that observed later in the experiment. Cepic *et al.* [27] have described the structure of intermediate phases with three- and four-layer periodicities using some approximation based on the experiment, and presented a phase diagram that includes also the smectic C_α^* phase. Another model of the three- and four-layer phases has recently been proposed by Huang and co-workers [28]. An important feature of the model proposed by Cepic and co-workers [26,27] is the new term essentially describing the effect that we propose here to call the ''discrete'' flexoelectric effect in order to distinguish it from the conventional flexoelectricity. The discrete flexoelectric effect results in the appearance of an induced polarization in a smectic layer, provided the two adjacent layers differ in their director orientation. This effect appears to be very important in the stabilization of the intermediate phases. In the general case this additional polarization is not parallel to the spontaneous polarization of the chiral layer, and thus a minimum of the total electrostatic energy may correspond to nonzero azimuthal angles between the directors in neighboring layers. One notes that in Refs. [26,27] no derivation of the corresponding formulas for the induced polarization has been given and an important difference with the conventional continuous flexoelectric effect has not been discussed. In this paper we present a general phenomenological description of the discrete flexoelectricity that manifests itself only in tilted smectic phases where the director undergoes finite rotations from layer to layer. We derive a more general expression for the induced polarization that is reduced to that considered by Cepic and co-workers [26,27] after some simplifications. A molecular model of the discrete flexoelectric effect based on electrostatic dipole-quadrupole interactions between molecules in adjacent smectic layers is also proposed. We then show that essentially the same free energy of a tilted smectic liquid crystal as that proposed by Cepic and co-workers [26,27] (but without direct coupling between next-nearest-neighbor layers) can be used to predict the whole sequence of distinct intermediate phases with different periods that may exist between the synclinic smectic C^* phase and the anticlinic smectic C_A^* phase, and to describe their structure using direct minimization of the free energy without qualitative assumptions based on actual experimental results. In this sequence the phases with three- and four-layer periodicities have qualitatively the same structure, as observed in the experiment (and the same as obtained in Ref. [27]). The theory predicts also the nonplanar structure of intermediate phases with longer periods, up to the period of nine smectic layers.

One notes that up to five different intermediate phases were observed about 10 yrs ago by Fukuda and co-workers [7,12]. During the past decade the structure of the two most stable subphases (Sm-C_{FI1}^* and Sm-C_{FI2}^*) has been extensively studied experimentally, as discussed above, and it has been confirmed that these phases are characterized by the periods of three and four layers, respectively. Other intermediate phases, observed in Ref. [12] have not been investigated in detail so far, but recently there has been a renewed interest in their structure [29]. It should be noted that in the present paper we consider only intermediate phases which may exist between the Sm-C^* and the Sm-C_A^* phase, i.e., sufficiently far from the Sm-C^*–Sm-A transition point. In this domain the tilt angle of the director is sufficiently large and weakly temperature dependent. For simplicity, it is assumed to be constant in the present theory. This means that the present approach cannot be used to describe the structure of the Sm-C_α^* phase which is observed directly below the Sm-A^* phase. In the Sm-C_α^* phase the tilt angle is small and depends strongly on the temperature.

The structure of particular intermediate phases in chiral smectic C^* is intimately related to the more general problem of the microscopic origin of the whole sequence of phases with increasing periodicity. In the early studies of antiferroelectric liquid crystals it has been assumed that the intermediate phases represent the so-called ''devil's staircase.'' It has been predicted theoretically for two types of Ising models [30–32]. The first one is a three-dimensional (3D) Ising model with competing nearest- and next-nearest-neighbor coupling [30]. This model, however, can hardly be applied to chiral smectics C^* because it contains no chiral interaction and will therefore predict the same phases for chiral and nonchiral liquid crystals, which strongly contradicts the experiment. It is also important that intermolecular interactions in liquid crystals cannot be adequately modeled by the Ising Hamiltonian having a different symmetry and different orientational dependence. The second, one-dimensional Ising model with long-range repulsive interaction [31,32], is much closer to the actual structure of smectic C liquid crystals. In the first approximation the direction of tilt in a smectic layer can be specified by an Ising-like variable that will now represent a collective property. Then the long-range interaction can be interpreted as a coupling between director orientations in distant smectic layers. This long-range interaction, specifying the existence of the ''devil's staircase,'' should be chiral in nature because intermediate phases must disappear in nonchiral smectic liquid crystals. In addition, the initial Ising model should be replaced by a more realistic planar rotator model to account for a continuous rotation of the director about the smectic layer normal. One notes, however, that the existence of a devil's staircase in such a model with continuous rotation has not been proved theoretically yet. In general terms the relevance of this simple model for ferroelectric and antiferroelectric smectic C^* liquid crystals is now reduced to the problem of finding an appropriate long-range coupling between smectic layers determined by molecular chirality. It has been shown that a long-range repulsion in ferroelectric smectics C^* may be determined by an interaction between thermally excited fluctuations of the spontaneous polarization [33]. The corresponding coupling constant is proportional to the square of equilibrium polarization, and therefore the interactions disappear in nonchiral systems. Direct estimates of the coupling constant, however, indicate that such an interaction should be much weaker than a typical coupling between neighboring layers, and therefore the intermediate phases should be stable only within a temperature interval that is much smaller than that observed in the experiment [16,18,19].

In this paper, we do not take into consideration any direct long-range interactions and even no direct interactions between nonadjacent smectic layers. At the same time, an effective long-range coupling between director orientations in different smectic layers emerges after averaging of the total free energy over polarizations in all layers. This effective coupling is determined by a combination of spontaneous polarization, discrete flexoelectric effect and an initial direct polarization coupling between adjacent layers, and stabilizes the intermediate phases with large periods.

This paper is arranged as follows. In Sec. II we discuss the concept of the discrete flexoelectric effect and the relevant symmetry aspects. We derive a general expression for the induced polarization and show how it is reduced to the one considered in Ref. [27]. In Sec. III we propose a simple molecular theory of the discrete flexoeffect based on the dipolar interactions between molecules in neighboring layers. In Sec. IV we show how the free energy proposed by Cepic and co-workers [26,27] can be minimized directly by combination of analytical and numerical methods to reveal the sequence of intermediate phases with increasing periodicity. Finally, in Sec. V we discuss the results and present several phase diagrams with detailed structure of six different intermediate phases.

II. DISCRETE FLEXOELECTRIC EFFECT IN SMECTIC C^* PHASES

At the beginning of this section we briefly discuss some well-known results of the existing phenomenological theory of the conventional flexoelectric effect in nematic and smectic liquid crystals in order to stress the difference from the discrete flexoelectric effect that is considered in detail below. In the general case the conventional flexoelectric effect in liquid crystals manifests itself in the appearance of polarization proportional to the gradients of the director. It is well known [34] that in the nematic phase it is possible to compose two independent polar vectors using the nematic ordering tensor $n_\alpha n_\beta - 1/3\,\delta_{\alpha\beta}$, where n is the nematic director, and the gradient vector $\boldsymbol{\nabla} \equiv \partial/\partial\,\mathbf{r}$. As a result the flexoelectric polarization is given by the following expression:

$$\mathbf{P}_f^{(N)} = e_s\,\mathbf{n}\,(\boldsymbol{\nabla}\cdot\mathbf{n}) - e_b\,(\mathbf{n}\cdot\boldsymbol{\nabla})\,\mathbf{n}, \tag{1}$$

which was originally given by Meyer [35]. From the symmetry point of view, Eq. (1) indicates that both splay and bend deformations of the director field reduce the point symmetry of the nematic phase creating a local polar direction, which can be associated with a local polarization. From the molecular point of view this means that steric molecular dipoles, associated with a polar molecular shape, will be ordered in the nematic phases subjected to splay or bend deformation [35]. If the molecules also possess electric dipoles, the polar ordering will result in a local induced polarization.

It is well known that flexoelectric effect also exists in tilted smectic liquid crystals. Conventional flexoelectricity in the Sm-C phase was first described theoretically by Pikin and co-workers [36–38]. One notes that in the general case the flexoelectricity in smectic liquid crystals appears to be a complex phenomenon because polarization may be induced both by gradients of the director and by appropriate layer deformations, or by a combination of both deformations. Thus, in the general case there are many contributions to the flexoelectric polarization that have been considered by Dahl and Lagerwall [39] and by De Gennes and Prost [34]. It is known, however, that in the smectic C phase there exists one ‘‘easy’’ deformation of the director that can readily be caused by a moderate electric field or by boundary conditions. This is a twist deformation that corresponds to a rotation of the director about the smectic layer normal. Thus, if the smectic layers are not deformed and the director is assumed to be homogeneous in the layer plane, the flexoelectric polarization in the Sm-C^* phase is described by a single term [36,37]. Using the notations of Ref. [40] such polarization can be expressed as

$$\mathbf{P}_f^{(C)} \sim -\mathrm{rot}\,\boldsymbol{\xi} = \boldsymbol{\xi}\frac{\partial\varphi}{\partial z}, \tag{2}$$

where the z axis is parallel to the layer normal $\mathbf{k}_0$, angle $\varphi(z)$ specifies the azimuthal orientation of the director and $\boldsymbol{\xi}$ is the pseudovector order parameter of the smectic C phase introduced by Pikin and co-workers [37,38]:

$$\boldsymbol{\xi}(z) \equiv (\mathbf{n}\cdot\mathbf{k}_0)\,[\mathbf{n}\times\mathbf{k}_0]. \tag{3}$$

The direction of the flexoelectric polarization $\mathbf{P}_f^{(C)}$ is determined by the vector order parameter $\boldsymbol{\xi}(z)$ that is parallel to the local C_2 symmetry axis, while the absolute value of the polarization is proportional to the gradient of the azimuthal angle $\partial\varphi/\partial z$.

It is also well known that in every layer of the chiral smectic C^* phase there exists a spontaneous polarization $\mathbf{P}_s$ that is also parallel to the local C_2 axis [37,38] i.e.,

$$\mathbf{P}_s = -\chi\, c_s\, \boldsymbol{\xi}, \tag{4}$$

where χ is the dielectric susceptibility and the coefficient c_s is a pseudoscalar determined by molecular chirality. In addition, the ferroelectric Sm-C^* phase possesses a macroscopic helical structure, i.e., there exists a spontaneous orientational deformation. This spontaneous deformation gives rise to the flexoelectric polarization according to Eq. (3) [37,38]. As a result, each smectic C^* layer in the bulk possesses a nonzero polarization that is a sum of the spontaneous polarization (4) and the flexoelectric one (2).

One notes that in the Sm-C^* phase the flexoelectric polarization is parallel to the spontaneous one, and therefore flexoelectricity does not effect the structure of the phase in a qualitative way. At the same time, the role of flexoelectricity may be completely different in intermediate smectic C^* phases where the director undergoes finite rotations from layer to layer within a period [16,18,19]. In such a structure the point symmetry of a layer will be dramatically reduced, and additional polarization appears in some direction within the smectic layer. Thus it is possible to generalize the concept of conventional flexoelectricity to take these effects into consideration. In the general case polarization may be induced not only by a gradual change of the director orienta-

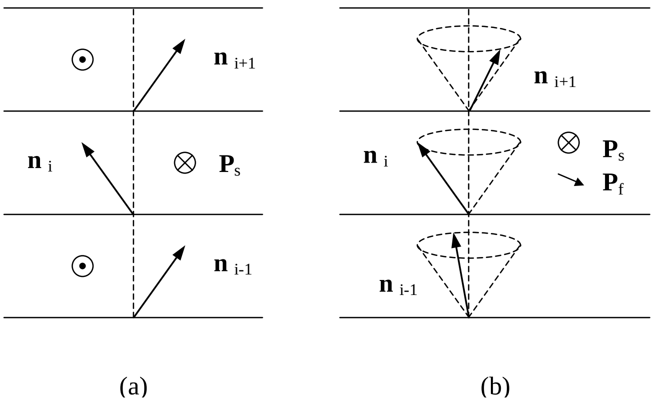

FIG. 1. Polarization in the anticlinic antiferroelectric smectic C_A^* phase (a) and in an intermediate phase (b).

tion (as in the nematic or conventional smectic C^* phase), but also by a discrete irregular change of director orientation from one smectic layer to another, as in intermediate smectic phases. Recently a simple term describing the onset of such a polarization was included in the free energy proposed by Cepic and co-workers [26,27]. We propose to call this type of flexoelectricity the "discrete flexoelectric effect" and consider both phenomenological and molecular theories of this effect in detail below.

Let us first consider the discrete flexoelectric effect from the general symmetry point of view using Fig. 1. The idealized structure of the anticlinic antiferroelectric smectic C_A^* phase is presented in Fig. 1(a). As first discussed by Brand and Cladis [41,42], in this phase there exists a C_2 symmetry axis in the middle of each layer in the direction perpendicular to the tilt plane. Thus, any polarization in the middle of the layer may only be parallel to the C_2 symmetry axis. This implies also the flexoelectric polarization determined by a weak z dependence of the orientation of the tilt plane. Now, let us assume that directors in the two adjacent layers rotate out of plane of the initial flat structure [see Fig. 1(b)]. If the director $\mathbf{n}_{i+1}$ in the layer $i+1$ is different from the director $\mathbf{n}_{i-1}$ in the layer $i-1$, the symmetry of the intermediate layer i becomes polar, and the resulting flexoelectric polarization may no longer be parallel to the spontaneous polarization of the layer $\mathbf{P}_s$ that is still determined by the vector $\boldsymbol{\xi}_i$ [see Fig. 1(b)]. This effect is related to the local breaking of symmetry between the directions represented by $\mathbf{k}$ and $-\mathbf{k}$ because it is now possible to distinguish between the two adjacent layers characterized by different director orientations. Thus, symmetry arguments indicate that if a tilted smectic layer is sandwiched between two other tilted layers with different director orientations, a flexoelectric polarization should appear in the intermediate layer. The direction of such a polarization is not specified by any symmetry elements because the symmetry of the layer is very low. It is interesting to note also that the discrete flexoelectric effect is a nonlocal effect and is determined by the space symmetry of the system. By contrast, the conventional flexoelectric effect is local, and thus the flexoelectric polarization is coupled to the gradients of the director at the same point. Taking this difference into account it is possible to compose the following invariants that contribute to the free energy of a smectic layer in an intermediate phase:

$$P_\alpha^{(i)}\{Q_{\alpha\beta}^{(i+1)}\,k_\beta^0-Q_{\alpha\beta}^{(i-1)}\,k_\beta^0\}, \tag{5}$$

$$P_\alpha^{(i)}\,Q_{\alpha\beta}^{(i)}\{Q_{\beta\gamma}^{(i+1)}\,k_\gamma^0-Q_{\beta\gamma}^{(i-1)}\,k_\gamma^0\}, \tag{6}$$

where we have taken into consideration only linear and quadratic terms in the tensor order parameter $Q_{\alpha\beta}^{(i)}$ of the layer i. In the first terms in brackets in Eqs. (5) and (6) the unit vector $\mathbf{k}_0$ is in the direction from the intermediate layer i to the "upper" layer $i+1$. The vector $\mathbf{k}_0$ is coupled with the tensor order parameter of the layer $i+1$. The second terms in Eqs. (5) and (6) stem from a coupling between the order parameter tensor of the "lower" layer $i-1$ with the unit vector $-\mathbf{k}_0$ in the direction from the layer i to the layer $i-1$. All flexoelectric invariants are nonzero if the tensor $Q_{\alpha\beta}^{(i+1)}$ in the layer $i+1$ is different from the tensor $Q_{\alpha\beta}^{(i-1)}$ in the layer $i-1$. Now the flexoelectric contribution to the total polarization of the smectic layer i can be obtained by minimization of the part of the free energy that is composed of invariants (5) and (6) and the standard dielectric term $1/2\,(\chi_i^{-1})_{\alpha\beta}P_\alpha^{(i)}P_\beta^{(i)}$, where $\chi_{\alpha\beta}^{(i)}$ is the local dielectric susceptibility tensor of the smectic layer i depending on the orientation of the local director:

$$\begin{aligned}\Delta F_f={}&\tfrac{1}{2}(\chi_i^{-1})_{\alpha\beta}P_\alpha^{(i)}\,P_\beta^{(i)}+c_f^{(1)}P_\alpha^{(i)}\{Q_{\alpha\beta}^{(i+1)}\,k_\beta^0-Q_{\alpha\beta}^{(i-1)}\,k_\beta^0\}\\&+c_f^{(2)}P_\alpha^{(i)}\,Q_{\alpha\beta}^{(i)}\{Q_{\beta\gamma}^{(i+1)}\,k_\gamma^0-Q_{\beta\gamma}^{(i-1)}\,k_\gamma^0\},\end{aligned} \tag{7}$$

where $c_f^{(1)}$ and $c_f^{(2)}$ are the flexoelectric coefficients. Minimization of Eq. (7) with respect to polarization yields the following expression for the induced discrete flexoelectric polarization in the layer i:

$$\begin{aligned}\mathbf{P}_f^{(i)}={}&-c_f^{(1)}\hat{\chi}_i\,\{\hat{Q}_{i+1}\,\mathbf{k}_0-\hat{Q}_{i-1}\,\mathbf{k}_0\}\\&-c_f^{(2)}\hat{\chi}_i\;\;\hat{Q}_i\,\{\hat{Q}_{i+1}\,\mathbf{k}_0-\hat{Q}_{i-1}\,\mathbf{k}_0\}.\end{aligned} \tag{8}$$

One notes that any tilted smectic layer is biaxial and therefore the tensors $\chi_{\alpha\beta}^{(i)}$ and $Q_{\alpha\beta}^{(i)}$ are also biaxial. They can be written in the following general form:

$$\begin{aligned}\chi_{\alpha\beta}^{(i)}={}&\overline{\chi}\,\delta_{\alpha\beta}+\Delta\chi\{n_\alpha^{(i)}n_\beta^{(i)}-\tfrac{1}{3}\,\delta_{\alpha\beta}\}\\&+\Delta\chi_\perp\{m_\alpha^{(i)}m_\beta^{(i)}-w_\alpha^{(i)}w_\beta^{(i)}\},\end{aligned} \tag{9}$$

$$Q_{\alpha\beta}^{(i)}=S\{n_\alpha^{(i)}n_\beta^{(i)}-\tfrac{1}{3}\,\delta_{\alpha\beta}\}+D\{m_\alpha^{(i)}m_\beta^{(i)}-w_\alpha^{(i)}w_\beta^{(i)}\}, \tag{10}$$

where we have assumed that the layers differ only in their director orientation. Here the unit vector $\mathbf{w}_i$ is parallel to the vector order parameter $\boldsymbol{\xi}_i$ and the unit vector $\mathbf{m}_i\perp\mathbf{w}_i$ and $\mathbf{m}_i\perp\mathbf{n}_i$. In Eq. (9) $\overline{\chi}$ is the average dielectric susceptibility, $\Delta\chi$ is the susceptibility anisotropy, and $\Delta\chi_\perp$ is the transverse anisotropy of the susceptibility. S is the scalar nematic order parameter and D is the corresponding biaxial order parameter.

The general expression for the induced flexoelectric polarization can be obtained by substitution of Eqs. (9) and (10) into Eq. (8). The resulting expression, however, can be simplified if one takes into account that biaxiality of a tilted smectic layer is generally weak. In this case $\Delta\chi_\perp \ll \Delta\chi$ and $D \ll S$, and thus all tensors can be expressed in terms of the local director $\mathbf{n}_i$. One then obtains the following expression for the flexoelectric polarization:

$$\mathbf{P}_f^{(i)} = -\tilde{c}_f^{(1)}\{(\mathbf{n}_{i+1}\,\mathbf{k}_0)\,\mathbf{n}_{i+1} - (\mathbf{n}_{i-1}\,\mathbf{k}_0)\,\mathbf{n}_{i-1}\} - \tilde{c}_f^{(2)}\,\mathbf{n}_i\{(\mathbf{n}_{i+1}\,\mathbf{k}_0)\,(\mathbf{n}_{i+1}\,\mathbf{n}_i) - (\mathbf{n}_{i-1}\,\mathbf{k}_0)\,(\mathbf{n}_{i-1}\,\mathbf{n}_i)\}, \tag{11}$$

where $\tilde{c}_f^{(1)} \equiv c_f^{(1)}\,\overline{\chi}$ and $\tilde{c}_f^{(2)} \equiv \Delta\chi\, c_f^{(1)} + c_f^{(2)}\,(\overline{\chi} + \Delta\chi)$. Equation (11) can be simplified further if one assumes that the tilt angle θ is approximately the same for all smectic layers in an intermediate phase. Then $(\mathbf{n}_i\,\mathbf{k}_0) = \cos\theta$ for all i, and Eq. (11) can be rewritten as

$$\mathbf{P}_f^{(i)} = -\tilde{c}_f^{(1)}\cos\theta\{\mathbf{n}_{i+1} - \mathbf{n}_{i-1}\} - \tilde{c}_f^{(2)}\cos\theta\,\mathbf{n}_i\{(\mathbf{n}_{i+1}\,\mathbf{n}_i) - (\mathbf{n}_{i-1}\,\mathbf{n}_i)\}, \tag{12}$$

where $\cos\theta = (\mathbf{n}_{i+1}\,\mathbf{k}_0) = (\mathbf{n}_i\,\mathbf{k}_0) = (\mathbf{n}_{i-1}\,\mathbf{k}_0)$. It should be noted that the approximation of the constant tilt angle may not be appropriate in the smectic C_α^* phase where the tilt angle is small and may depend on the azimuthal orientation of the director in each layer.

One notes also that the first term in Eq. (12) has the same form as the one used by Cepic and co-workers [26,27] without derivation. The theory presented in this section and in the following one reveals the origin of this term. The corresponding part of the flexoelectric polarization is always parallel to the smectic layer i because it is proportional to the difference $\Delta\mathbf{n}_{i\pm1} \equiv \mathbf{n}_{i+1} - \mathbf{n}_{i-1}$ between the director orientations in the two layers adjacent to the layer i. By contrast, the second term in Eq. (12) contains also a contribution to the flexoelectric polarization that is perpendicular to the smectic layer:

$$P_\parallel^{(i)} = -\tilde{c}_f^{(2)}\cos^2\theta\,(\Delta\mathbf{n}_{i\pm1}\,\mathbf{n}_i). \tag{13}$$

Thus one concludes that a unit cell of an intermediate phase may be polar in the direction of the layer normal provided the normal components of the polarization from different layers do not cancel each other.

If the director $\mathbf{n}$ weakly depends on z on a large scale (that corresponds to conventional Sm-C^* or Sm-C_A^* phase), the director in the layer $i \pm 1$ can approximately be expressed as

$$\mathbf{n}_{i\pm1} \approx \mathbf{n}_i \pm [\mathbf{k}_0 \times \mathbf{n}_i]\;\;\partial\varphi/\partial z, \tag{14}$$

and Eq. (12) is reduced to Eq. (2) that describes conventional flexoelectricity in the Sm-C^* phase.

One should also note another difference between the conventional and the discrete flexoelectric effect in smectic C^* liquid crystals. Equation (2) presents a unique expression for the conventional flexoelectric polarization that is linear in the gradient of the azimuthal angle φ. At the same time Eqs. (8)–(12) present only approximate expressions for the discrete flexoelectric polarization obtained taking into account only simple couplings between the vector $\mathbf{k}_0$ and the ordering tensors $Q_{\alpha\beta}^{(i+1)}$ and $Q_{\alpha\beta}^{(i-1)}$. It is possible to compose higher order contributions that will have the same symmetry as Eq. (5) and (6). This means that a theory of the discrete flexoeffect cannot be derived completely on the phenomenological ground. It is important to consider some molecular models that may provide one with a deeper insight into the effect. In the following section we consider such a simple molecular model that enables one to derive an expression for the flexoelectric polarization similar to Eq. (12).

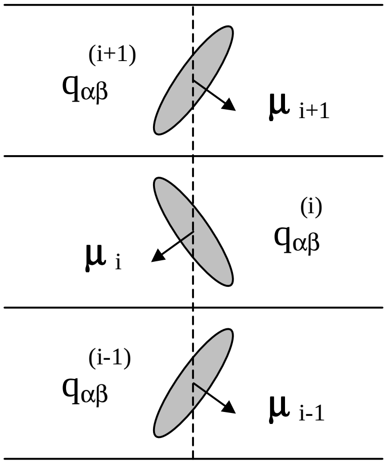

FIG. 2. Molecular model for the discrete flexoelectric effect in tilted smectics.

III. MOLECULAR MODEL FOR THE DISCRETE FLEXOELECTRIC EFFECT IN TILTED SMECTICS

Discrete flexoelectric effect should be determined by some polar interactions between molecules in neighboring layers. In this paper we take into consideration electrostatic dipole-dipole and dipole-quadrupole interactions. We consider a simple model of a smectic C liquid crystal composed of rigid molecules possessing permanent transverse dipoles and permanent quadrupoles (see Fig. 2). For simplicity we consider the case of perfect nematic and smectic order. In this simple case the long molecular axes are parallel to the local director $\mathbf{n}_i$ in the layer i, and the orientation of a short molecular axis, i.e., of the transverse dipole $\boldsymbol{\mu}_i$, is specified by the angle ψ. Then the average polarization in the layer i can be expressed as

$$\mathbf{P}_i = \rho \int \boldsymbol{\mu}(\mathbf{n}_i, \psi)\, f_i(\psi)\, d\psi, \tag{15}$$

where the orientational distribution function $f_i(\cos\psi)$ depends only on ψ. In the general case the orientational distribution function can be obtained by minimization of the total free energy of a smectic layer that includes the interaction with other layers. Using the generalized mean-field approximation [43] and taking into account dipole-dipole and dipole-quadrupole interactions between molecules one can write the following expression for the free energy of the nonchiral tilted smectic layer with perfect nematic order:

$$F_i = F_0^{(i)} + \Delta F_i , \tag{16}$$

where the free energy $F_0^{(i)}$ contains contributions from all interactions with molecules in the layer i that do not depend on the orientation of molecular transverse dipole $\boldsymbol{\mu}_i$ specified by the angle ψ. The additional free energy ΔF_i of the smectic layer i determined by polar intermolecular interactions is a functional of the orientational distribution function $f_i(\psi)$ that may be different in different layers. Taking into account only interactions between molecules within the same smectic layer and in adjacent layers, one can express the free energy ΔF_i in the following form:

$$\begin{aligned}
\Delta F_i = {} & \rho k_B T \int f_i(\psi) \ln f_i(\psi)\, d\psi + \frac{1}{2}\rho^2 \int f_i(\psi_1) f_i(\psi_2)\, g_{i,i}(\mathbf{r}_\perp) \{U_{dd}^{i,i}(\psi_1,\psi_2,\mathbf{r}) + U_{dq}^{i,i}(\psi_1,\psi_2,\mathbf{r})\}\, d^2\mathbf{r}_\perp\, d\psi_1\, d\psi_2 \\
& + \frac{1}{2}\rho^2 \int f_i(\psi_1) f_{i+1}(\psi_2)\, g_{i,i+1}(\mathbf{r}_\perp) \{U_{dd}^{i,i+1}(\psi_1,\psi_2,\mathbf{r}) + U_{dq}^{i,i+1}(\psi_1,\psi_2,\mathbf{r})\} d^2\mathbf{r}_\perp\, d\psi_1\, d\psi_2 \\
& + \frac{1}{2}\rho^2 \int f_i(\psi_1) f_{i-1}(\psi_2)\, g_{i,i-1}(\mathbf{r}_\perp) \{U_{dd}^{i,i-1}(\psi_1,\psi_2,\mathbf{r}) + U_{dq}^{i,i-1}(\psi_1,\psi_2,\mathbf{r})\} d^2\mathbf{r}_\perp\, d\psi_1\, d\psi_2 ,
\end{aligned} \tag{17}$$

where $\mathbf{r}$ is the intermolecular vector for molecule 1 located in layer i and molecule 2 located in layer $j=i$ or $i\pm1$. In the case of perfect smectic order $\mathbf{r} = \mathbf{k}_0 (j-i) z + \mathbf{r}_\perp$, where z is the thickness of a smectic layer and the vector $\mathbf{r}_\perp$ is a projection of the intermolecular vector $\mathbf{r}$ on the smectic layer plane. The dipole-dipole and dipole-quadrupole electrostatic interaction potentials in Eq. (17) are given by the following equations:

$$U_{dd}^{i,j}(\psi_1,\psi_2,\mathbf{r}) \equiv \mu_\alpha(\mathbf{n}_i,\psi_1)\, T_{\alpha\beta}(\mathbf{r})\, \mu_\beta(\mathbf{n}_j,\psi_2), \tag{18}$$

$$\begin{aligned}
U_{dq}^{i,j}(\psi_1,\psi_2,\mathbf{r}) \equiv {} & \mu_\alpha(\mathbf{n}_i,\psi_1) T_{\alpha\beta\gamma}(\mathbf{r}) q_{\beta\gamma}(\mathbf{n}_j) \\
& - \mu_\alpha(\mathbf{n}_j,\psi_2) T_{\alpha\beta\gamma}(\mathbf{r})\, q_{\beta\gamma}(\mathbf{n}_i).
\end{aligned} \tag{19}$$

Here $\boldsymbol{\mu}(\mathbf{n}_i,\psi)$ is the permanent dipole of a molecule in the layer i and $q_{\alpha\beta}(\mathbf{n}_i)$ is the permanent quadrupole tensor of a molecule in the layer i. For simplicity we assume that the molecular quadrupole is uniaxial and therefore it does not depend on the angle ψ. In this case the average quadrupole tensor $q_{\alpha\beta}(\mathbf{n}_i)$ may be expressed as follows:

$$q_{\alpha\beta}(\mathbf{n}_i) = Q_0 \{ n_\alpha^{(i)} n_\beta^{(i)} - \tfrac{1}{3}\delta_{\alpha\beta} \}, \tag{20}$$

where Q_0 is the molecular quadrupole moment. Finally, the coupling tensors $T_{\alpha\beta}(\mathbf{r})$ and $T_{\alpha\beta\gamma}(\mathbf{r})$ can be written as

$$T_{\alpha\beta}(\mathbf{r}) \equiv -\boldsymbol{\nabla}_\alpha \boldsymbol{\nabla}_\beta \frac{1}{r}, \tag{21}$$

$$T_{\alpha\beta\gamma}(\mathbf{r}) \equiv \boldsymbol{\nabla}_\alpha \boldsymbol{\nabla}_\beta \boldsymbol{\nabla}_\gamma \frac{1}{r}, \tag{22}$$

where $r \equiv |\mathbf{r}|$ is the distance between molecules 1 and 2. The first term in Eq. (17) is the orientational entropy of the smectic layer i that depends only on the orientational distribution function $f_i(\psi)$. The second term is a contribution from dipole-dipole and dipole-quadrupole interactions between molecules within layer i. Finally, the third and fourth terms in Eq. (17) present contributions from dipole-dipole and dipole-quadrupole interactions between molecules located in adjacent smectic layers i and $i\pm1$. The last three terms depend on the direct correlation functions $g_{i,i}(\mathbf{r})$ or $g_{i,i\pm1}(\mathbf{r})$ describing positional correlations between molecules within the same layer i or in adjacent layers i and $i\pm1$, respectively. Minimization of the free energy (17) yields the following expression for the orientational distribution function:

$$f_i(\psi) = \frac{1}{Z_i} \exp\{-\rho\beta\, U_{MF}^{(i)}(\psi)\}, \tag{23}$$

where $\beta \equiv 1/(k_B T)$,

$$Z_i = \int_0^{2\pi} \exp\{-\rho\beta\, U_{MF}^{(i)}(\psi)\}\, d\psi \tag{24}$$

and

$$\begin{aligned}
\rho\, U_{MF}^{(i)}(\psi) = {} & \mu_\alpha(\mathbf{n}_i,\psi)\, I_{\alpha\beta}^{i,i} P_\beta^{(i)} + \mu_\alpha(\mathbf{n}_i,\psi)\, \{ I_{\alpha\beta}^{i,i+1} P_\beta^{(i+1)} \\
& + I_{\alpha\beta}^{i,i-1} P_\beta^{(i-1)} \} + \mu_\alpha(\mathbf{n}_i,\psi)\, \{ I_{\alpha\beta\gamma}^{i,i+1} q_{\beta\gamma}(\mathbf{n}_{i+1}) \\
& + I_{\alpha\beta\gamma}^{i,i-1} q_{\beta\gamma}(\mathbf{n}_{i-1}) \}.
\end{aligned} \tag{25}$$

Here polarization $\mathbf{P}_i$ is determined by Eq. (15) and the tensors $I_{\alpha\beta}^{i,j}$ and $I_{\alpha\beta\gamma}^{i,j}$ are determined as follows:

$$I_{\alpha\beta}^{i,j} \equiv \int T_{\alpha\beta}(\mathbf{r})\, g_{i,j}(\mathbf{r}_\perp)\, d^2\mathbf{r}_\perp , \tag{26}$$

$$I_{\alpha\beta\gamma}^{i,j} \equiv \int T_{\alpha\beta\gamma}(\mathbf{r})\, g_{i,j}(\mathbf{r}_\perp)\, d^2\mathbf{r}_\perp , \tag{27}$$

where the tensors $T_{\alpha\beta}(\mathbf{r})$ and $T_{\alpha\beta\gamma}(\mathbf{r})$ are determined by Eqs. (21) and (22), respectively. In Eq. (25) it has been also taken into account that $I_{\alpha\beta\gamma}^{i,i} = 0$ since the function $g_{i,i}(\mathbf{r}_\perp)$ is even in $\mathbf{r}_\perp$. The resting quantities $I_{\alpha\beta}^{i,j}$ and $I_{\alpha\beta\gamma}^{i,j}$ in Eq. (25) characterize dipolar interactions and positional correlations between molecules in layers i and j. The direct correlation functions $g_{i,j}(\mathbf{r}_\perp)$ in Eqs. (26) and (27) are expected to decay rapidly with the increasing molecular separation. These functions have a strong peak at $r_\perp=0$. In this case the quantities $I^{i,i}_{\alpha\beta}$, $I^{i,i\pm1}_{\alpha\beta}$, and $I^{i,i\pm1}_{\alpha\beta\gamma}$ may be estimated in the saddle-point approximation:

$$I^{i,i}_{\alpha\beta}\approx-\frac{\langle g_{i,i}\rangle}{2\,d^3}T_{\alpha\beta}(\mathbf{k}_0), \tag{28}$$

$$I^{i,i\pm1}_{\alpha\beta}\approx\frac{\langle g_{i,i\pm1}\rangle}{z^3}T_{\alpha\beta}(\mathbf{k}_0), \tag{29}$$

$$I^{i,i\pm1}_{\alpha\beta\gamma}\approx\pm\frac{\langle g_{i,i\pm1}\rangle}{z^4}T_{\alpha\beta\gamma}(\mathbf{k}_0), \tag{30}$$

where in correspondence with Eqs. (21) and (22)

$$T_{\alpha\beta}(\mathbf{k}_0)=\delta_{\alpha\beta}-3\,k^0_\alpha\,k^0_\beta, \tag{31}$$

$$T_{\alpha\beta\gamma}(\mathbf{k}_0)=3\,\{k^0_\alpha\,\delta_{\beta\gamma}+k^0_\beta\,\delta_{\alpha\gamma}+k^0_\gamma\,\delta_{\alpha\beta}\}-15\,k^0_\alpha\,k^0_\beta\,k^0_\gamma. \tag{32}$$

In Eqs. (28)–(30) d is the breadth of a molecule, the thickness of a layer $z\equiv\ell\cos\theta$ is determined by the tilt angle θ and the length of a molecule ℓ, and the averages $\langle g_{i,i}\rangle$ and $\langle g_{i,i\pm1}\rangle$ are defined as follows:

$$\langle g_{i,j}\rangle\equiv\int g_{i,j}(\mathbf{r}_\perp)\,d^2\mathbf{r}_\perp\,. \tag{33}$$

The tilt angle θ is usually very small so that the correlation function $g_{i,i}(\mathbf{r}_\perp)$ and the minimal distance between molecules weakly depend on the orientation of the vector $\mathbf{r}_\perp$. In this case the minimal side-by-side distance is approximately equal to the diameter of a molecule d. This was also taken into account in Eq. (28). Finally, the mean-field potential $U^{(i)}_{MF}(\psi)$ can be written in the form

$$\rho\,U^{(i)}_{MF}(\psi)=-\frac{\langle g_{i,i}\rangle}{2\,d^3}\boldsymbol{\mu}_i\,\hat{\mathbf{T}}\,\mathbf{P}_i+\frac{\langle g_{i,i\pm1}\rangle}{z^3}\boldsymbol{\mu}_i\,\hat{\mathbf{T}}\,(\mathbf{P}_{i+1}+\mathbf{P}_{i-1}) +6\,Q_0\frac{\langle g_{i,i\pm1}\rangle}{z^4}\boldsymbol{\mu}_i\,\hat{\mathbf{R}}_i\,\mathbf{k}_0\,, \tag{34}$$

where $\hat{\mathbf{T}}$ and $\hat{\mathbf{R}}_i$ are the following second rank tensors:

$$T_{\alpha\beta}\equiv T_{\alpha\beta}(\mathbf{k}_0), \tag{35}$$

$$R^{(i)}_{\alpha\beta}\equiv n^{(i+1)}_\alpha\,n^{(i+1)}_\beta-n^{(i-1)}_\alpha\,n^{(i-1)}_\beta, \tag{36}$$

and where $\boldsymbol{\mu}_i\equiv\boldsymbol{\mu}(\mathbf{n}_i,\psi)$. Substituting Eq. (34) into Eqs. (23) and (24), and then into Eq. (15), and expanding the exponent in the expression for the distribution function in powers of polarization $\mathbf{P}_i$, one obtains the following set of equations:

$$\hat{\boldsymbol{\chi}}_i^{-1}\{\mathbf{P}_i+\hat{\mathbf{g}}_i(\mathbf{P}_{\mathbf{i+1}}+\mathbf{P}_{\mathbf{i-1}})\} +c_f\,(\mathbf{n}_i\,\mathbf{k}_0)\{\Delta\mathbf{n}_{i\pm1}-\mathbf{n}_i\,(\mathbf{n}_i\,\Delta\mathbf{n}_{i\pm1})\}=0, \tag{37}$$

where

$$\Delta\mathbf{n}_{i\pm1}\equiv\mathbf{n}_{i+1}-\mathbf{n}_{i-1}, \tag{38}$$

$$c_f\equiv3\,Q_0\frac{\rho\,\langle g_{i,i\pm1}\rangle\,\mu^2}{k_B\,T\,z^4}. \tag{39}$$

In Eq. (37) the inverse dielectric susceptibility tensor $\hat{\boldsymbol{\chi}}_i^{-1}$ and the dipolar coupling tensor $\hat{\mathbf{g}}_i$ are determined by the following expressions:

$$(\chi_i^{-1})_{\alpha\beta}\equiv\delta_{\alpha\beta}-\frac{\rho\,\langle g_{i,i}\rangle\,\mu^2}{4\,k_B\,T\,d^3}\varkappa^{(i)}_{\alpha\beta}, \tag{40}$$

$$g^{(i)}_{\alpha\beta}\equiv\hat{\chi}\frac{\rho\,\langle g_{i,i\pm1}\rangle\,\mu^2}{2\,k_B\,T\,z^3}\varkappa^{(i)}_{\alpha\beta}, \tag{41}$$

where

$$\varkappa^{(i)}_{\alpha\beta}\equiv\delta_{\alpha\beta}-3\,k^0_\alpha\,k^0_\beta-n^i_\alpha\,n^i_\beta+3\,(\mathbf{n}_i\,\mathbf{k}_0)\,n^i_\alpha\,k^0_\beta. \tag{42}$$

Equation (37) describes the discrete flexoelectric effect in the nonchiral tilted smectic, where dipolar interactions between molecules within the same layer and in adjacent layers are taken into account explicitly. This expression for the flexoelectric polarization has the same form as the phenomenological Eq. (12). In the present model, however, the flexoelectric coefficient c_{f2} is expressed in terms of c_{f1}, i.e., $c_{f2}=-c_{f1}=-c_f$ where c_f is given by Eq. (39).

From Eq. (37) it also follows that polarization in each layer is not parallel to the smectic layer plane. However, contribution to the polarization that is proportional to the first power of the small parameter $\sin\theta$ is parallel to the smectic layer plane. Neglecting the other terms in Eq. (37), which are proportional to higher powers of $\sin\theta$, one obtains the closed set of equations for the polarizations $\mathbf{P}_i$ that are parallel to the smectic layers:

$$\mathbf{P}_i+g(\mathbf{P}_{\mathbf{i+1}}+\mathbf{P}_{\mathbf{i-1}})+\chi\,c_f\cos\theta\,\Delta\mathbf{n}_{i\pm1}\approx\mathbf{0}, \tag{43}$$

where the inverse dielectric susceptibility χ^{-1} and the dipolar coupling coefficient g are determined by the following expressions:

$$\chi^{-1}\equiv1-\frac{\rho\,\langle g_{i,i}\rangle\,\mu^2}{4\,k_B\,T\,d^3}, \tag{44}$$

$$g\equiv\chi\frac{\rho\,\langle g_{i,i\pm1}\rangle\,\mu^2}{2\,k_B\,T\,z^3}, \tag{45}$$

and the flexoelectric coefficient c_f is given by Eq. (39). These three parameters depend on positional correlation functions $g_{i,i}$ and $g_{i,i\pm1}$, which are not calculated in this paper. In the rest of the paper they will be treated as phenomenological constants.

IV. THE SEQUENCE OF INTERMEDIATE PHASES WITH DIFFERENT PERIODS

A. Free energy of intermediate phases

In the framework of the discrete model [17,21] one can write the total free energy of an intermediate tilted smectic phase in the following general form:

$$F=\sum_{i=1}^{N}\{F_i^{(0)}+\Delta F_i\}, \tag{46}$$

where N is the total number of smectic layers and the free energy $F_0^{(i)}$ does not depend on the polarization. All polarization dependent terms are included in ΔF_i that can be written as

$$\begin{aligned}\Delta F_i=&\tfrac{1}{2}\,\mathbf{P}_i\cdot\hat{\boldsymbol{\chi}}_i^{-1}\cdot\mathbf{P}_i+\tfrac{1}{2}(\mathbf{P}_i\cdot\hat{\mathbf{G}}_i\cdot\mathbf{P}_{i+1}+\mathbf{P}_i\cdot\hat{\mathbf{G}}_i\cdot\mathbf{P}_{i-1})\\&+c_s\,(\mathbf{P}_i\cdot\boldsymbol{\xi}_i)+c_f^{(1)}\cos\theta\,(\mathbf{P}_i\cdot\Delta\mathbf{n}_{i\pm1})\\&+c_f^{(2)}\cos\theta\,(\mathbf{P}_i\cdot\mathbf{n}_i)(\Delta\mathbf{n}_{i\pm1}\cdot\mathbf{n}_i),\end{aligned} \tag{47}$$

where we have taken into account only quadratic terms in the polarization. The first two terms in Eq. (47) describe the dielectric energy of the smectic layer and the coupling between polarization vectors in neighboring layers. One notes that the anisotropy of the dielectric susceptibility tensor $\hat{\boldsymbol{\chi}}_i$ and the polarization coupling tensor $\hat{\mathbf{G}}\equiv\hat{\boldsymbol{\chi}}_i^{-1}\cdot\hat{\mathbf{g}}_i$ may be important if both components of the induced flexoelectric polarization (i.e., parallel and perpendicular to the smectic layer) are taken into consideration as discussed in Sec. II. The dimensionless parameter g, characterizing the relative strength of the coupling in the neighboring layers, is expected to be smaller than 1. The second term in Eq. (47) describes the coupling between the polarization $\mathbf{P}_i$ and the tilt $\boldsymbol{\xi}_i$ that is present only in chiral smectics [37,38], i.e., c_s is a pseudoscalar vanishing in racemic mixtures. It is well known that in the absence of any other effects this term gives rise to the spontaneous polarization of the layer $\mathbf{P}_s^{(i)}=-\chi\,c_s\,\boldsymbol{\xi}_i$ that is perpendicular to the tilt plane. In the general case, however, the direction of the total polarization of a smectic layer is not parallel to $\boldsymbol{\xi}_i$ because of the discrete flexoelectric effect described by the last two terms in Eq. (47). This effect has been considered in detail in the preceding section.

Now let us express the director $\mathbf{n}_i$ in terms of the tilt angle θ and the azimuthal angle φ_i:

$$\mathbf{n}_i=\{\sin\theta\cos\varphi_i\,,\sin\theta\sin\varphi_i\,,\cos\theta\}, \tag{48}$$

where we have assumed that the tilt angle is the same for all smectic layers. This assumption is supported by the experiment [3]. Now the free energy $F_i^{(0)}$ in Eq. (46), which depends on the relative orientation of the director $\mathbf{n}_i$, can be expressed in terms of the angles $\varphi_{i,i+1}\equiv\varphi_{i+1}-\varphi_i$ and $\varphi_{i-1,i}\equiv\varphi_i-\varphi_{i-1}$ between the tilt planes of the neighboring layers. In the first approximation [24]

$$\begin{aligned}F_i^{(0)}=&\tilde{F}_0(\theta)-\tilde{a}\frac{\Delta T}{T^*}\{\cos\varphi_{i-1,i}+\cos\varphi_{i,i+1}\}\\&-\tilde{B}\,\{\cos^2\varphi_{i-1,i}+\cos^2\varphi_{i,i+1}\},\end{aligned} \tag{49}$$

where $\Delta T\equiv T-T^*$, and T^* has the meaning of the transition temperature between the synclinic and anticlinic smectic C phases in the absence of any intermediate phases. The explicit expressions for the coefficients $\tilde{a}$ and $\tilde{B}$ have been obtained in Ref. [44] in the framework of a molecular model. One notes that $\tilde{a}\sim\sin^2\theta$ and $\tilde{B}\sim\sin^4\theta$ in the case of small θ. Finally, the free energy $\tilde{F}_0\,(\theta)$ is the same for all layers and depends on the homogeneous tilt angle θ.

One notes that the free energy (46)–(49) is very similar to that used by Cepic and co-workers [26,27] although in Eq. (47) the discrete flexoeffect is described by a more general expression. If one neglects the second flexoelectric term in Eq. (47), the total polarization of a smectic layer will always be parallel to the layer plane (see discussion in Sec. II). In this case the anisotropy of the tensors $\chi_{\alpha\beta}$ and $G_{\alpha\beta}$ can be neglected (because the dielectric anisotropy in the plane of the layers is expected to be small) and the total free energy of a tilted smectic phase can be rewritten essentially in the same form as proposed by Cepic and co-workers [26,27]:

$$\begin{aligned}F=\sum_{i=1}^{N}\Bigg\{&\tilde{F}_0\,(\theta)-\tilde{a}\frac{\Delta T}{T^*}(\cos\varphi_{i-1,i}+\cos\varphi_{i,i+1})\\&-\tilde{B}\,(\cos^2\varphi_{i-1,i}+\cos^2\varphi_{i,i+1})+\frac{1}{2\,\chi}[\mathbf{P}_i^2+g(\mathbf{P}_i\,\mathbf{P}_{i+1}\\&+\mathbf{P}_i\,\mathbf{P}_{i-1})]+c_s\,(\mathbf{P}_i\,\boldsymbol{\xi}_i)+c_f\cos\theta(\mathbf{P}_i\,\Delta\mathbf{n}_{i\pm1})\Bigg\},\end{aligned} \tag{50}$$

where χ is the average dielectric susceptibility in the plane of the layer and $c_f\equiv c_f^{(1)}$. In Eq. (50) we did not take into account any direct coupling between next-nearest-neighbor layers that play an important role in Ref. [27]. As discussed in more detail below, we do not need these additional terms to describe the structure of intermediate phases. We also believe that such direct coupling should be extremely small due to vanishing positional correlations between molecules in nonadjacent layers. One notes also that we do not take into consideration chiral interactions between different layers. Such interactions are very weak and are important only in the description of the macroscopic helical structure that is characteristic to all chiral tilted smectic phases. The existence of such a helicoidal structure with a macroscopic pith of the order of 1 μm results only in a very small change of all angles between adjacent layers (by a fraction of degree). In other words, the free energy associated with the macroscopic helicoidal structure is too small to make any qualitative effect on the structure of the unit cell of an intermediate phase with periodicity of few smectic layers. Thus the structure of the unit cell and the macroscopic helical structure can be described separately. It should be noted, however, that chiral interlayer interactions may be important in the description of the microscopic structure of the Sm-C_α^* phase where the tilt angle may be very small and the corresponding free energy is low. In this paper, however, we do not consider the Sm-C_α^* phase.

In Refs. [26,27] the free energy (50) (with few additional terms) has been used to describe the two intermediate phases with the periods of three and four layers, respectively, and the Sm-C_α^* phase. In that description the following major approximations have been made. First, the system of simultaneous equations for polarizations of all smectic layers, which appears after minimization of the free energy with respect to polarization, has been solved approximately leaving only the quadratic terms in dipolar coupling coefficient g. Second, the qualitative structure of the two intermediate phases is taken from actual experimental data thus leaving only one independent angle in each phase, which is then determined by minimization of the free energy. Finally, no attempt has been made to consider the stability of intermediate phases with larger periods. In this section we use a different method of the free energy minimization that enables one to go beyond the approximations made in Refs. [26,27] and to describe the whole sequence of intermediate phases with increasing periodicity that may exist between the synclinic Sm-C^* and the anticlinic Sm-C_A^* phases.

First, we present analytical solutions for the system of equations for polarizations of all layers, which is valid for any finite total number of layers. As shown below, the higher-order coefficients in these solutions are given by recurrence relations. An exact minimization of the free energy with respect to polarization results in an effective long-range coupling between different smectic layers with the coupling strength decreasing with the increasing distance between the layers. One notes that an approximation made in Ref. [26] results in a cutoff of this effective long-range coupling. At the same time, the long-range interlayer coupling is very important for the stability of the whole sequence of intermediate phases described in this paper. A sequence of similar phases with increasing periods, known as the devil's staircase, has been found in frustrated Ising systems with long-range interactions [31,32]. After minimization of the free energy with respect to polarization we consider an intermediate phase with a period of t smectic layers and determine its structure by direct numerical minimization of the free energy. The phase diagrams are obtained by comparing the free energies of all structures with different periods up to the period of nine layers. In this procedure we assume that angles between tilt planes of adjacent layers are relatively small, i.e., $\sin \varphi_{i,i+1} \approx \varphi_{i,i+1}$. This approximation works qualitatively well up to the angles $\varphi \sim \pi/4$, and for structures under consideration can only lead to some small quantitative mistakes. It should be noted that the minimization method used in this paper cannot be applied to describe incommensurate phases that are aperiodic. However, there is neither experimental nor theoretical evidence for the existence of any incommensurate phases in the corresponding temperature range, i.e., between Sm-C^* and Sm-C_A^* phases. The only incommensurate phase observed in chiral smectics C^* is the Sm-C_α^* phase that is stable in a different temperature range and is not considered here, as discussed above. As discussed in more detail by Musevich and Skarabot [17], the incommensurate structure of the Sm-C_α^* phase is determined by small values of the elasticity coefficient B that is proportional to θ at small θ. Far from the Sm-A phase the coefficient B is expected to be large and thus it is very unlikely that any incommensurate phase may be stable in that domain.

B. Minimization procedure

We are looking for intermediate phases with different periods that may be stable within a relatively narrow temperature interval between Sm-C^* and Sm-C_A^* phases. In this region the tilt angle θ is assumed to be constant and thus the total free energy should be minimized with respect to azimuthal angles φ_i and polarizations $\mathbf{P}_i$ of all layers. Minimizing the free energy (50) with respect to polarization $\mathbf{P}_i$, one obtains the following set of equations for $\mathbf{P}_i$:

$$\mathbf{P}_i + g\,(\mathbf{P}_{i-1}+\mathbf{P}_{i+1}) + \chi\,\mathbf{M}_i = 0, \tag{51}$$

where

$$\mathbf{M}_i \equiv c_s\,\boldsymbol{\xi}_i + c_f\,\cos\theta\,(\mathbf{n}_{i+1}-\mathbf{n}_{i-1}), \tag{52}$$

and where $\boldsymbol{\xi}_i \equiv \cos\theta[\mathbf{n}_i \times \mathbf{k}_0]$ is the order parameter [see Eq. (3)]. One can simplify Eq. (47) for the free energy ΔF_i using Eq. (51):

$$\Delta F_i = \tfrac{1}{2}\mathbf{P}_i\,\mathbf{M}_i\,. \tag{53}$$

Analytical solutions for the set of simultaneous equations (51) can be obtained for any finite number of smectic layers in the whole system and/or for any fixed number of layers in the unit cell of an infinite periodic intermediate phase. Thus, let us consider the intermediate phase with the period of t layers. For any odd number of layers $t=2n+1$ one obtains the following expression for polarization of an arbitrary layer i within the period:

$$\mathbf{P}_i^{(2n+1)} = -\frac{\chi}{r_{2n+1}}\Bigg[s_{2n+1}\mathbf{M}_i + \sum_{k=1}^{n}(-g)^k s_{2(n-k)+1} \times (\mathbf{M}_{i-k}+\mathbf{M}_{i+k})\Bigg], \tag{54}$$

where the coefficients r_k and s_k can be calculated analytically for any fixed value of k using the following relations:

$$\begin{aligned} r_1 &\equiv 1+2\,g,\\ r_3 &\equiv 1+g-2\,g^2,\\ r_5 &\equiv 1+g-3\,g^2-2\,g^3,\\ r_7 &\equiv 1+g-4\,g^2-3\,g^3+2\,g^4,\\ r_9 &\equiv 1+g-5\,g^2-4\,g^3+5\,g^4+2\,g^5,\\ &\ldots \end{aligned} \tag{55}$$

$$\begin{aligned} s_1 &\equiv 1,\\ s_3 &\equiv 1+g,\\ s_5 &\equiv 1+g-g^2,\\ s_7 &\equiv 1+g-2\,g^2-g^3,\\ s_9 &\equiv 1+g-3\,g^2-2\,g^3+g^4, \end{aligned} \tag{56}$$

Slightly different solutions can also be obtained for any even value $t=2n$:

$$\mathbf{P}_i^{(2n)} = -\frac{\chi}{r_{2n}}\left[s_{2n}\,\mathbf{M}_i + \sum_{k=1}^{n-1} (-g)^k s_{2(n-k)} (\mathbf{M}_{i-k}+\mathbf{M}_{i+k}) + \frac{1}{2}(-g)^n s_0\,(\mathbf{M}_{i-n}+\mathbf{M}_{i+n})\right], \tag{57}$$

where

$$\begin{aligned} r_2 = r_4 &\equiv 1-4\,g^2,\\ r_6 &\equiv 1-5\,g^2+4\,g^4,\\ r_8 &\equiv 1-6\,g^2+8\,g^4,\\ &\;\;\ldots \end{aligned} \tag{58}$$

$$\begin{aligned} s_0 &\equiv 2,\quad s_2 \equiv 1,\\ s_4 &\equiv 1-2\,g^2,\\ s_6 &\equiv 1-3\,g^2,\\ s_8 &\equiv 1-4\,g^2+2\,g^4, \end{aligned} \tag{59}$$

Substituting Eqs. (54) and (57) into Eq. (53), and then into Eq. (46), one obtains the following expression for the polarization contribution to free energy of the intermediate phase with the period of t layers:

$$F_t/N = \frac{1}{t}\sum_{i=0}^{t-1} F_i^{(0)} - \frac{\chi}{2\,t}\sum_{i=0}^{t-1}\sum_{k=0}^{t-1} f_k\,\mathbf{M}_i\,\mathbf{M}_{i+k}, \tag{60}$$

where

$$f_k \equiv \begin{cases} (-g)^k \dfrac{s_{t-2k}}{r_t} & \text{if } k=0\cdots[t/2],\\[2ex] (-g)^{t-k}\dfrac{s_{2k-t}}{r_t} & \text{if } k=([t/2]+1)\cdots(t-1), \end{cases} \tag{61}$$

and where the coefficients r_k and s_k are determined by Eqs. (55) and (56) for $t=2\,n+1$ or by Eqs. (58) and (59) for $t=2n$, respectively. In both cases $[t/2]=n$. Substituting Eq. (52) for $\mathbf{M}_i$ into Eq. (60) and adding the free energy $F_i^{(0)}$ given by Eq. (49), one obtains the following expression for the total free energy of the intermediate phase with the period of t layers:

$$\begin{aligned} \frac{F_t-\widetilde{F}_0(\theta)}{N\sin^2(2\,\theta)} = &-\frac{1}{2}\chi\{c_s^2 f_0 + c_f^2 f_0^{(2)}\}\\ &-\frac{\chi}{t}\sum_{i=0}^{t-1}\sum_{j=i+1}^{t-1}\{c_s^2 f_{j-i} + c_f^2 f_{j-i}^{(2)}\}\cos\varphi_{ij}\\ &+2\,c_s\,c_f\frac{\chi}{t}\sum_{i=0}^{t-1}\sum_{j=i+1}^{t-1} f_{j-i}^{(1)}\sin\varphi_{ij}\\ &-B\frac{1}{t}\sum_{i=0}^{t-1}\cos^2\varphi_{i,i+1} - a\frac{\Delta T}{T^*}\frac{1}{t}\sum_{i=0}^{t-1}\cos\varphi_{i,i+1}, \end{aligned} \tag{62}$$

where $a\equiv 2\tilde{a}/\sin^2(2\,\theta)$, $B\equiv 2\,\widetilde{B}/\sin^2(2\,\theta)$, the coefficients $f_k^{(1)}$ and $f_k^{(2)}$ are determined by expressions

$$\begin{aligned} f_k^{(1)} &\equiv f_{k-1}-f_{k+1},\\ f_k^{(2)} &\equiv 2f_k - f_{k-2} - f_{k+2}, \end{aligned} \tag{63}$$

and where the coefficients f_k $(k=0,1,\ldots,t-1)$ are determined by Eq. (61), $f_t\equiv f_0$, $f_{t+1}\equiv f_1$, $f_{-1}\equiv f_{t-1}$ and $f_{-2}\equiv f_{t-2}$. The angles φ_{ij} in Eq. (62) are defined as $\varphi_{ij}\equiv\varphi_j-\varphi_i$. Equation (62) describes the free energy of an intermediate tilted chiral phase with an arbitrary periodicity t. The last two terms in Eq. (62) describe direct coupling between director orientations in neighboring layers. The other terms in Eq. (62) appear after the minimization of the initial free energy with respect to polarizations of all smectic layers. One notes that in the present model only interactions between neighboring smectic layers are taken into account. At the same time, one can readily see from Eq. (62) that an effective coupling between any two layers within the period of the structure appears after a minimization of the free energy with respect to polarization. This effect is rather typical for systems with several interacting thermodynamic parameters. The strength of such effective coupling between distant layers i and j can be estimated to decay as $g^{|j-i|}$, where $g<1$ is the dimensionless dipolar coupling coefficient for neighboring layers. Thus, one concludes that there exists an effective long-range coupling between director orientations in different smectic layers determined by direct dipolar interaction between adjacent layers.

Finally it should be noted that only the last term in the free energy (62) is assumed to be temperature dependent. It vanishes at $T=T^*$. The system undergoes a transition from the synclinic to the anticlinic smectic C phase at the temperature $T=T^*$ if molecular chirality and the discrete flexoeffect are not taken into account. At the same time, in the presence of these two effects this simple temperature variation is sufficient to generate the whole sequence of nonplanar intermediate phases that are stable in the vicinity of $T=T^*$.

Now the free energy (62) should be minimized with respect to all angles φ_i that specify director orientations in smectic layers $i=0,1,\dots,t-1$ within the period t of the intermediate phase. It is more convenient to minimize the free energy (62) with respect to the differences φ_{ij} taking into account the constraints that directly follow from the fact that the given phase has a period of t layers:

$$\varphi_{nk}=\sum_{i=n}^{k-1}\varphi_{i,i+1}, \qquad \varphi_{t-1,t}=2\pi-\sum_{i=0}^{t-2}\varphi_{i,i+1}. \tag{64}$$

Then one obtains the following set of equations:

$$\begin{aligned} &B\sin(2\varphi_{i,i+1})+a\sin\varphi_{i,i+1}\\ &\quad+B\sin\left[2\sum_{j=0}^{t-2}\varphi_{j,j+1}\right]+a\sin\left[\sum_{j=0}^{t-2}\varphi_{j,j+1}\right]\\ &\quad+\chi\sum_{n=0}^{i}\sum_{k=i+1}^{t-1}\{c_s^2 f_{k-n}+c_f^2 f_{k-n}^{(2)}\}\sin\varphi_{nk}\\ &\quad+2c_s c_f\chi\sum_{n=0}^{i}\sum_{k=i+1}^{t-1}f_{k-n}^{(1)}\cos\varphi_{nk}=0, \end{aligned} \tag{65}$$

where $i=0,1,\dots,t-2$. In this paper we assume that intermediate phases may be non-planar, but the actual structure does not deviate strongly from the corresponding planar prototype. This assumption is in accordance with experimental data [16,18,19]. In this case the angles φ_{nk} may be split into two parts:

$$\varphi_{nk}=\sum_{i=n}^{k-1}\alpha_i^0+\sum_{i=n}^{k-1}\Delta\alpha_i, \tag{66}$$

where the angles $\alpha_i^0\equiv\varphi_{i,i+1}^0$ may be equal to 0 or π only (i.e., they specify the corresponding planar structure), while the angles $\Delta\alpha_i\equiv\Delta\varphi_{i,i+1}$ are assumed to be relatively small (i.e., $\sin\Delta\alpha_i\approx\Delta\alpha_i$). Then Eq. (65) may be linearized with respect to $\Delta\alpha_i$:

$$\sum_{j=0}^{t-2}c_{ij}\,\Delta\alpha_j=q_i \quad , \tag{67}$$

where

$$\begin{aligned} q_i&\equiv-2c_s c_f\sum_{n=0}^{i}\sum_{k=i+1}^{t-1}f_{k-n}^{(1)}\cos\varphi_{nk}^0,\\ c_{ij}&\equiv\sum_{n=0}^{j}\sum_{k=i+1}^{t-1}\{c_s^2 f_{k-n}+c_f^2 f_{k-n}^{(2)}\}\cos\varphi_{nk}^0+2B\\ &\quad+a\cos\alpha_{t-1}^0 \quad \text{if} \quad j=0,1,\dots,\ i-1;\\ c_{ij}&\equiv 4B+a(\cos\alpha_i^0+\cos\alpha_{t-1}^0) \quad \text{if} \quad j=i; \end{aligned} \tag{68}$$

$$\begin{aligned} c_{ij}&\equiv\sum_{n=0}^{i}\sum_{k=j+1}^{t-1}\{c_s^2 f_{k-n}+c_f^2 f_{k-n}^{(2)}\}\cos\varphi_{nk}^0+2B\\ &\quad+a\cos\alpha_{t-1}^0 \quad \text{if} \quad j=i+1,\dots,t-2. \end{aligned} \tag{69}$$

Equations (67) are solved for any particular sequence of α_i^0, and results are substituted back into the free energy (62). The latter is then minimized with respect to α_i^0 to determine the optimal structure. One notes that the solution is unique in this approximation, and therefore one finds a unique structure of the intermediate phase with fixed period of t layers. Finally, the free energies of phases with different periods are compared with each other to select the one that corresponds to a global minimum at a given temperature for a particular choice of the model parameters. We have performed the corresponding numerical calculations for all values of t up to $t=9$. The resulting structures of the intermediate phases and the phase diagrams are presented and discussed in the following section.

V. RESULTS AND DISCUSSION

The structures of the intermediate phases with the periods of 4, 3, 8, 5, 7, and 9 layers that have been obtained by minimization of the free energy (62) are presented in Fig. 3. One notes that the structures with three- and four-layer periodicities correspond to experimental findings [16,18,19] including the order of layers with different director orientations within the period, and to the theoretical results of Cepic *et al.* [27]. From the quantitative point of view the major discrepancy is in the three-layer phase where the angle $\Delta\varphi_{12}$ is smaller than the corresponding experimental value. It should be noted, however, that the angle in the three-layer phase has been determined experimentally for only one compound [16] by the ellipsometry method that is less precise than the resonant x-ray scattering method [18,19]. The resonant x-ray scattering method has only been used to specify the structure of the four-layer phase. On the other hand, new preliminary experimental data [29] indicate that the angle $\Delta\varphi_{12}$ in the three-layer phase may be significantly smaller than the value obtained in Ref. [16]. In any case more experimental data for different compounds are required to clarify this point. It is also desirable to investigate the structure of the three-layer phase by the resonant x-ray scattering method. As mentioned above, several other intermediate phases have been observed experimentally, but their structure has never been studied in detail. In this paper we predict the possible structures of new intermediate phases with the periods of 5 , 7, 8, and 9 smectic layers that are presented in Fig. 3. The structure with six-layer periodicity is not presented here because this phase appears to be unstable at least in the context of this simple model.

It is interesting to note that the structures of all intermediate phases presented in Fig. 3 possess a certain symmetry that is visible if the structures are viewed along the smectic layer normal. In fact, the tilt directions in different layers are antisymmetric with respect to the middle of the period. This property defines the chirality of these structures. It can be shown that the corresponding symmetry is contained already

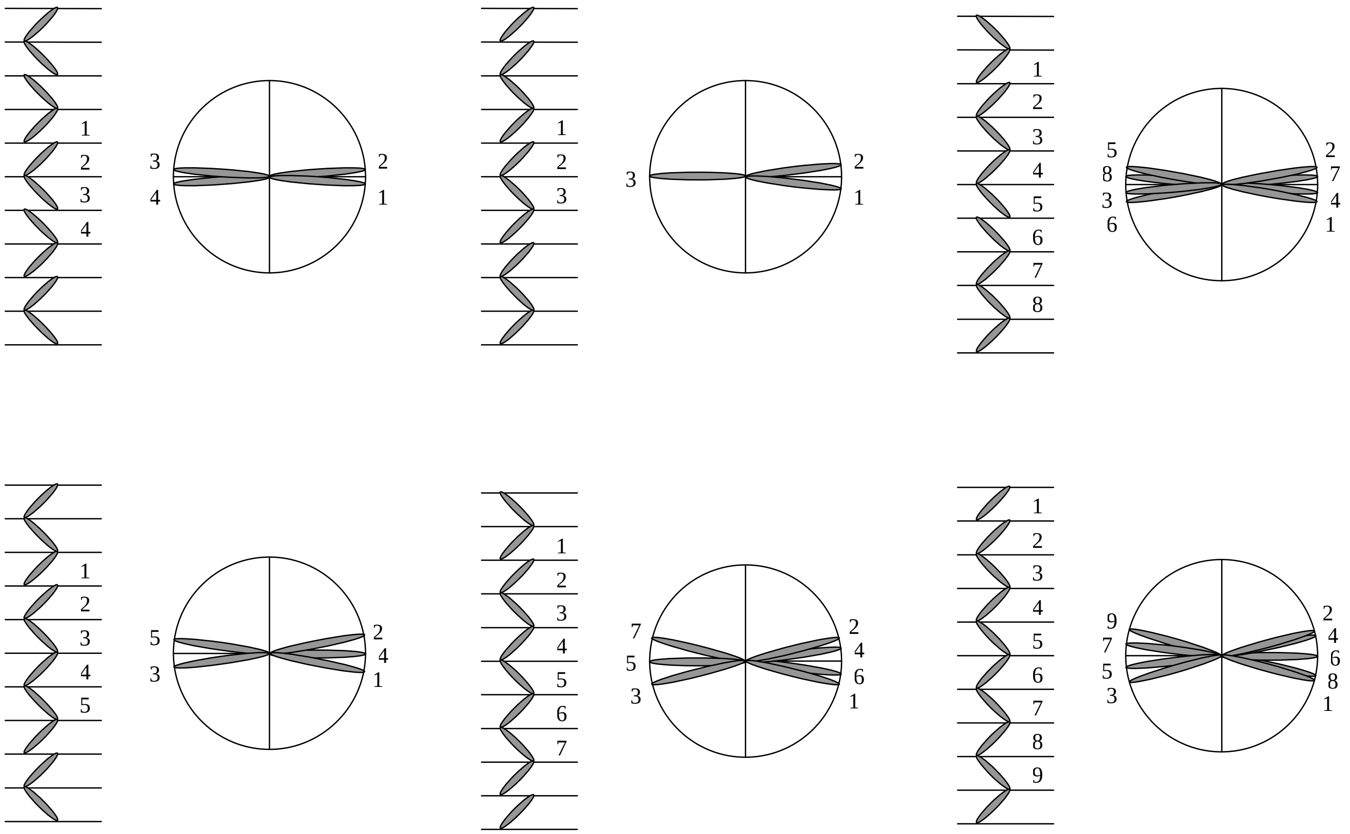

FIG. 3. Structure of the intermediate phases with the periods of 4, 3, 8, 5, 7, and 9 layers.

in the general Eq. (62) for the free energy of an intermediate phase with periodicity of t layers. For example, the free energy F_3 of the three-layer phase can be expressed as

$$\frac{F_3-\widetilde{F}_0(\theta)}{N\sin^2(2\theta)} = -\chi\left\{\frac{1}{2}c_s^2 f_0^{(3)} + c_f^2\left(f_0^{(3)}-f_1^{(3)}\right)\right\} - J_1^{(3)}(\cos\alpha_1+\cos\alpha_2+\cos\alpha_3) + J_2^{(3)}(\sin\alpha_1+\sin\alpha_2+\sin\alpha_3) - \tfrac{1}{3}B(\cos^2\alpha_1+\cos^2\alpha_2+\cos^2\alpha_3), \tag{70}$$

where only two angles are independent because $\alpha_1+\alpha_2+\alpha_3=2\pi$. The coefficients $J_1^{(3)}$ and $J_2^{(3)}$ in Eq. (70) are expressed as

$$J_1^{(3)} \equiv \frac{\chi}{3}\{c_s^2 f_1^{(3)} - c_f^2(f_0^{(3)}-f_1^{(3)})\} + \frac{a}{3}\frac{\Delta T}{T^*},$$
$$J_2^{(3)} \equiv \frac{2\chi}{3}c_s c_f(f_0^{(3)}-f_1^{(3)}), \tag{71}$$

where

$$f_0^{(3)} \equiv \frac{1+g}{1+g-2g^2}, \quad f_1^{(3)} \equiv -\frac{g}{1+g-2g^2}. \tag{72}$$

One can readily see that the free energy (70) is symmetric with respect to the interchange of any two angles from the set $\{\alpha_1, \alpha_2, \alpha_2\}$, i.e., it is invariant under the transformations $\alpha_1 \rightleftarrows \alpha_2$, $\alpha_2 \rightleftarrows \alpha_3$ and $\alpha_1 \rightleftarrows \alpha_3$. Thus, the free energy (70) should have three equivalent minima. The first one corresponds to $\alpha_1=\alpha_2$, the second one to $\alpha_2=\alpha_3$, and the third one to $\alpha_1=\alpha_3$. All these minima correspond to the same structure with different enumeration of layers. If, for example, $\alpha_2=\alpha_3$, the minimization of the free energy (70) results in the following expression for α_1:

$$\alpha_1^{(3)} \approx -\frac{4J_2^{(3)}}{2B+J_1^{(3)}}. \tag{73}$$

Likewise, the free energy F_4 of the four-layer phase can be expressed as

$$\frac{F_4-\widetilde{F}_0(\theta)}{N\sin^2(2\theta)} = -\chi\left\{\frac{1}{2}c_s^2 f_0^{(4)} + c_f^2\right\} - J_1^{(4)}(\cos\alpha_1+\cos\alpha_2+\cos\alpha_3+\cos\alpha_4) + J_2^{(4)}(\sin\alpha_1+\sin\alpha_2+\sin\alpha_3+\sin\alpha_4) - J_3^{(4)}\{\cos(\alpha_1+\alpha_2)+\cos(\alpha_3+\alpha_4)\} - \tfrac{1}{4}B(\cos^2\alpha_1+\cos^2\alpha_2+\cos^2\alpha_3+\cos^2\alpha_4), \tag{74}$$

where only three angles are independent because $\alpha_1+\alpha_2+\alpha_3+\alpha_4=2\pi$. The coefficients $J_1^{(4)}$, $J_2^{(4)}$, and $J_3^{(4)}$ in Eq. (74) are expressed as

$$J_1^{(4)}\equiv\frac{\chi}{4}c_s^2f_1^{(4)}+\frac{a}{4}\frac{\Delta T}{T^*},\quad J_2^{(4)}\equiv\frac{\chi}{2}c_s\,c_f,$$

$$J_3^{(4)}\equiv\frac{\chi}{4}\{c_s^2f_2^{(4)}-2\,c_f^2\},\tag{75}$$

where

$$f_0^{(4)}\equiv\frac{1-2\,g^2}{1-4\,g^2},\quad f_1^{(4)}\equiv-\frac{g}{1-4\,g^2},$$

$$f_2^{(4)}\equiv\frac{2\,g^2}{1-4\,g^2}.\tag{76}$$

One can see that the free energy (74) is invariant under the simultaneous transformations $\alpha_1\rightleftarrows\alpha_3$ and $\alpha_2\rightleftarrows\alpha_4$. Thus, the minimum of the free energy (74) should correspond to the case $\alpha_1=\alpha_3$ and $\alpha_2=\alpha_4=\pi-\alpha_1$. Then minimization of the free energy (74) results in the following expression for α_1:

$$\alpha_1^{(4)}\approx-2\frac{J_2^{(4)}}{B}=-\chi\frac{c_s\,c_f}{B}.\tag{77}$$

It follows from Eq. (77) that the azimuthal angle $\alpha_1^{(4)}$ specifying the direction of the tilt in the four-layer phase does not depend on the dipolar coupling coefficient g. This is determined by the special symmetry of the four-layer phase. By contrast, the azimuthal angles in other intermediate phases increase with the increasing parameter g [see, for example, Eq. (73) for the azimuthal angle in the three-layer phase]. Only one azimuthal angle appears to be independent in the phases with three- and four-layer structures.

In a similar way, the free energies of the other intermediate phases in Fig. 3 are symmetric with respect to the interchange of some azimuthal angles. As a result, only two azimuthal angles are independent in the phases with periods of eight and five layers, three angles are independent in the phase with period of seven layers, and four angles are independent in the phase with period of nine layers. The structures of all intermediate phases are essentially nonflat, i.e., tilt planes in different smectic layers are not parallel to each other. On the other hand, the deviation from the prototype flat structure is not too large and, as a result, the phases appear to be strongly biaxial. The biaxiality can be qualitatively characterized by the angles $\Delta\alpha_i$. If one neglects a deviation from the flat structure, each intermediate phase in Fig. 3 can be described as a sequence of synclinic and anticlinic pairs of neighboring layers. One notes that only one unique synclinic pair is present in the unit cell of each intermediate phase, and thus the phases with large periods resemble more and more the anticlinic smectic *C* phase. At the same time, the maximum deviation from the prototype flat structure $\Delta\alpha_1=\alpha_1$ increases with the increasing periodicity t (see Fig. 4). As already mentioned, the maximum angle α_1 in the four-layer phase is independent of the dipolar coupling g between neighboring layers. In other intermediate phases it grows with the increasing g (see Fig. 5).

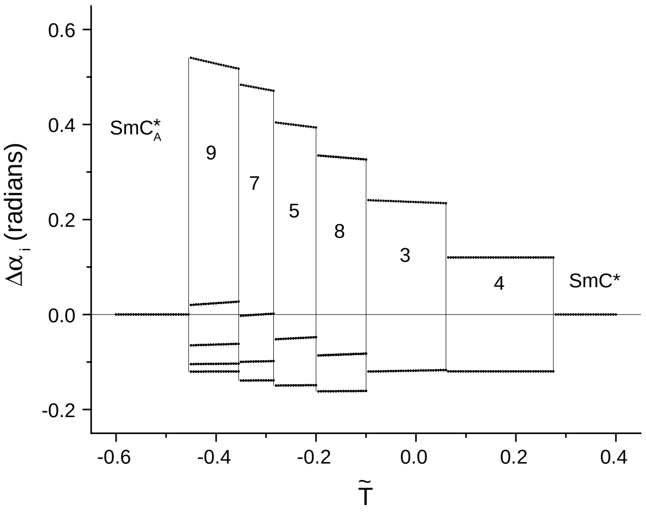

FIG. 4. Deviations of independent azimuthal angles in the intermediate phases from their values in the prototype flat structure in the case $\chi|c_s\,c_f|/B=0.12$, $|c_f/c_s|=1$ and $g=0.3$. Here $\tilde{T}\equiv a\,\Delta T/B\,T^*$ is the dimensionless temperature, and numbers indicate the periodicities of the intermediate phases.

There are only four independent dimensionless parameters $(a\,\Delta T/B\,T^*)$, $(\chi\,c_s\,c_f/B)$, c_f/c_s, and g in the free energy (62) that determine the phase diagram of the system. Only the parameter $(a\,\Delta T/B\,T^*)$ is temperature dependent. One can see from Eq. (77) that the parameter $(\chi\,c_s\,c_f/B)$, describing the relative strength of the polarization contribution, is related to the azimuthal angle in the four-layer phase,

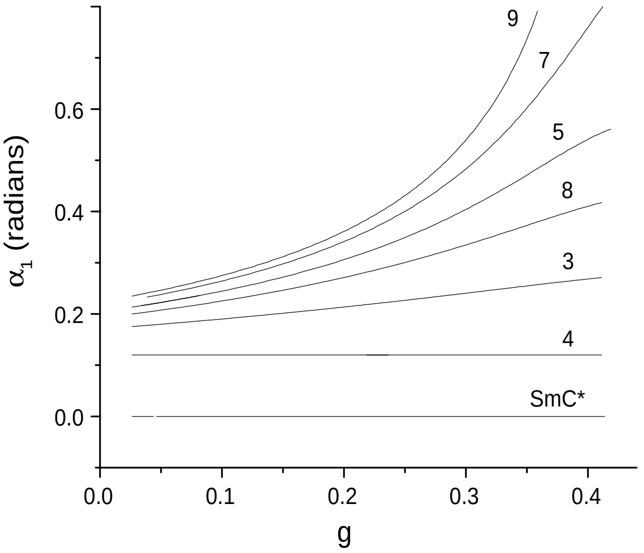

FIG. 5. Maximum azimuthal angles describing a deviation of the intermediate phases from the flat structure in the vicinity of the transition to the lower temperature phase in the case $\chi|c_s\,c_f|/B=0.12$ and $|c_f/c_s|=1$. Numbers indicate the periodicities of the intermediate phases.

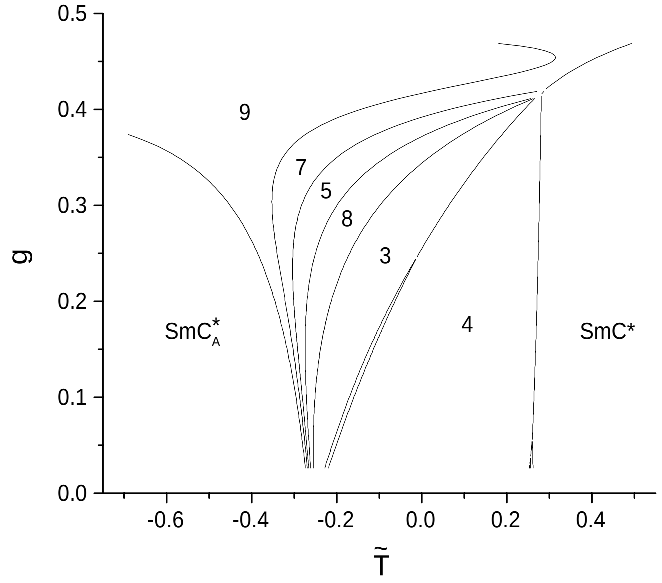

FIG. 6. Phase diagram in the case $\chi|c_s c_f|/B=0.12$ and $|c_f/c_s|=1$. Here $\tilde{T}\equiv a\,\Delta T/B\,T^*$ is the dimensionless temperature, and numbers indicate the periods of the intermediate phases.

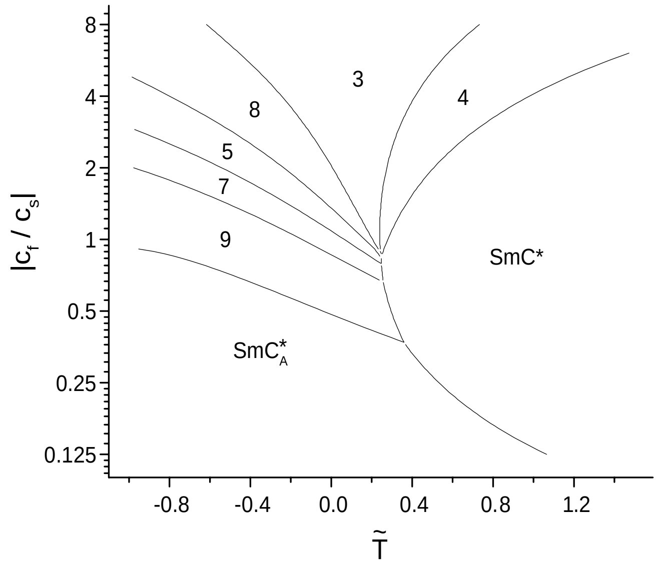

FIG. 7. Phase diagram in the case $\chi|c_s c_f|/B=0.12$ and $g=0.4$. Here $\tilde{T}\equiv a\,\Delta T/B\,T^*$ is the dimensionless temperature, and numbers indicate the periods of the intermediate phases in terms of layer thickness.

and therefore it cannot vary significantly. The parameter c_f/c_s describes the relation between flexoelectric and spontaneous polarizations. The $\{g,\tilde{T}\}$ phase diagram is presented in Fig. 6, where $\tilde{T}\equiv a\,\Delta T/B\,T^*$ is the dimensionless temperature. The coefficient g depends on the positional correlations between molecules in neighboring layers and is expected to be significantly smaller than 1. From Eqs. (61)–(63) it follows that in the case $g=0$ the only four-layer intermediate phase is possible. In the realistic range of $g\sim 0.1$–0.2 (see Fig. 6) the smectic C^* material exhibits a sequence of intermediate phases with the decreasing temperature intervals confined between the synclinic Sm-C^* and the anticlinic Sm-C_A^* phases. With the decreasing temperature the system undergoes a transition from the Sm-C^* phase to the intermediate phase with the period of four layers. The periodicity and the structure of this phase correspond to the experimentally determined structure of the so-called Sm-C_{FI2}^* phase. With the decreasing temperature the system undergoes a transition from the four-layer intermediate phase to the three-layer one. The structure of this phase corresponds to that of the so-called Sm-C_{FI1}^* phase. This sequence of phases is actually observed in the experiment [16,18,19]. At slightly lower temperatures the system exhibits the intermediate phases with periods of 8, 5, 7, and 9 layers. For small values of g the stability ranges of these phases are smaller than those of the three- and four-layer phases. It follows from the phase diagram (see Fig. 6) that intermediate phases with periods larger than four layers are becoming more stable with the increasing coefficient g. Thus, these phases are more likely to be observed in smectic materials with strong positional correlations between molecules in adjacent layers. Such correlations may be determined by some specific interactions between various groups in the molecular tails, and it may be interesting to synthesize new smectic materials with such properties. The phase diagram of smectic C^* materials with very large coefficient $g=0.4$ is presented in Fig. 7. In this case the stability range of some intermediate phases with large periods can be even larger than that of the three- and four-layer phases. One notes that these stable intermediate phases appear only if the flexoelectric coefficient c_f is sufficiently large, i.e. the flexoelectric polarization is of the same order or larger than the spontaneous polarization. It should be noted, however, that the difference in free energy between intermediate phases decreases with the increasing period, and it may be difficult to locate the corresponding transition points. In real systems such phases may also be suppressed by various factors including, in particular, surface effects. The structure of intermediate phases has been studied experimentally in thin free-standing smectic films [16,18,19] where the influence of boundaries is known to be very important [45,46]. Moreover, the detailed diagram of a thin film, in principle, may depend on the number of smectic layers in the film. If the total number of layers is sufficiently small and is not a multiple of the period of an intermediate phase, the remaining few layers may play a role of a strong surface defect, and the phase may be suppressed completely. This effect is expected to be more important for phases with large periods, and, thus, such phases should be more easily observed in thicker films.

In the framework of this model the particular structure of intermediate phases is determined by a coupling between the spontaneous polarization $\mathbf{P}_s$ and the flexoelectric polarization $\mathbf{P}_f$. In the general case these two components of the total polarization are not parallel. Then the coupling between $\mathbf{P}_s$ and $\mathbf{P}_f$ gives rise to an effective torque that results in a nonzero angle between tilt planes in adjacent layers. The corresponding contribution to the free energy is proportional to both parameters c_s and c_f. It is important to note that all intermediate phases disappear if $c_f=0$ (see Fig. 7), because in this case the effective free energy Eq. (62) contains only contributions proportional to $c_s^2 f_{j-i}$ and therefore alternate in sign from layer to layer. Such contributions may only stabilize the anticlinic structure. Thus, the existence of both flexoelectric polarization $\mathbf{P}_f$ and the spontaneous polarization $\mathbf{P}_s$ is essential for the stability and structure of intermediate phases. In real systems intermediate phases disappear in racemates [7]. Thus, the two enantiomers should exhibit the same intermediate phases with structures that are the mirror images of each other. This conclusion can be verified experimentally. In general, one concludes that the chiral structure of intermediate phases is directly determined by molecular chirality and is not a result of a chiral symmetry breaking.

Finally, one notes that according to the results of the theory of the discrete flexoelectric effect, presented in Secs. II and III, all intermediate phases should possess an additional polarization in the direction perpendicular to smectic layers. This polarization is expected to be small if $\theta \ll 1$, and thus it has not been taken into account in the calculation of the structure of intermediate phases. However, this polarization can always be taken into consideration as a secondary effect, and its role will be studied in detail in a forthcoming publication.

One concludes that a sequence of polar and tilted intermediate smectic phases with realistic structure can be described theoretically without taking into account any direct interactions between nonadjacent smectic layers. In the first approximation it is sufficient to take into consideration the discrete flexoelectric effect, discussed in Sec. II, the spontaneous polarization of each layer that is related to molecular chirality, and the coupling between polarizations of neighboring layers. As discussed above, the macroscopic helical structure of intermediate phases can be described separately taking also into account weak chiral interactions between adjacent layers that do not significantly affect the structure of a unit cell. At the same time, the approach used in this paper is limited to a temperature range far away from the Sm-C–Sm-A transition point where the tilt angle is small and cannot be approximated as a constant. Thus the present theory cannot be used to describe the Sm-C_α^* phase or any other incommensurate phases that, in principle, may exist in the domain of small tilt angles θ.

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