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Ferroelectric ordering in chiral smectic-C^* liquid crystals determined by nonchiral intermolecular interactions

M. A. Osipov[1] and M. V. Gorkunov[1,2]
[1]*Department of Mathematics, University of Strathclyde, Glasgow G1 1XH, United Kingdom*
[2]*Institute of Crystallography, Russian Academy of Sciences, 119333 Moscow, Russia*

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General microscopic mechanism of ferroelectric ordering in chiral smectic-C^* liquid crystals is considered. It is shown that if the mesogenic molecules have a sufficiently low symmetry, the spontaneous polarization is proportional to one of the biaxial vector order parameters of the smectic-C phase. This order parameter may be determined by intermolecular interactions which are not sensitive to molecular chirality. At the same time, the polarization is also proportional to a pseudoscalar parameter which vanishes if the molecules are nonchiral. The general statistical theory of ferroelectric ordering is illustrated by two particular models. The first model is based on electrostatic quadrupole-quadrupole interactions, and it enables one to obtain explicit analytical expressions for the spontaneous polarization. In the second model, the molecular chirality and polarity are determined by a pair of off-center nonparallel dipoles. For this case, the spontaneous polarization is calculated numerically as a function of temperature. The theory provides a more general interpretation of the previous approaches including the classical Boulder model.

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I. INTRODUCTION

Ferroelectric smectic liquid crystals are unique systems where the spontaneous polarization is determined by molecular chirality. Ferroelectric ordering in the chiral smectic-C^* phase has been predicted theoretically about three decades ago [1], and both ferro- and antiferroelectric phases continue to attract a significant attention because of their unusual structure and properties, and because of their applications in electro-optical devices [2]. Ferroelectricity is observed only in tilted smectic phases. In these systems the spontaneous polarization is induced by the tilt and does not appear self-consistently like in proper solid ferroelectric materials. Using the terminology widely used in the theory of solid ferroelectrics, the ferroelectric ordering in the smectic-C^* phase may be called improper because the polarization is not the primary order parameter. It is well known that the primary order parameter of the Sm$A-$SmC transition is the tilt pseudovector which possesses a different symmetry compared with the polarization which is a polar vector. The polarization is then induced by the tilt pseudovector in a chiral medium. In solid crystals, a similar improper ferroelectric state occurs, for example, in ferroelastics [3] where the polarization is induced by spontaneous deformation.

In every tilted layer of a chiral smectic phase, the polarization appears in the direction of the polar C_2 symmetry axis which is perpendicular to the tilt plane. In the bulk tilted phase, molecular chirality also results in the formation of the macroscopic helical structure. In this structure, the direction of the tilt rotates while moving along the z axis which is perpendicular to the smectic layers. As a result, chiral tiled smectics are characterized by the helical distribution of the spontaneous polarizations and thus may also be called "helielectric." Ferroelectric ordering is observed also in more complex smectic-F^* and I^* tilted phases which possess a partial translational or hexatic order (see, e.g., [4,5]). One notes that recently ferro- and antiferroelectric ordering has also been found in smectic liquid crystal phases formed by achiral bent-core molecules. In those phases the spontaneous polarization is not induced by the tilt and thus appears also in orthogonal smectic phases [6].

In the synclinic smectic-C^* phase, the direction of the tilt in adjacent layers is practically the same and thus the spontaneous polarization only slowly varies from layer to layer. In contrast, in the anticlinic smectic-C_A^* phase the direction of the tilt alternates from layer to layer together with the polarization creating the structure with an antiferroelectric type ordering. In addition, many chiral smectic materials exhibit a sequence of the so-called intermediate phases in a narrow temperature interval between the synclinic ferroelectric smectic-C^* and the anticlinic antiferroelectric smectic-C_A^* phase. Intermediate smectic phases are characterized by a 3D chiral distribution of the spontaneous polarization within the unit cell of three or four smectic layers [2]. Recently, the remarkably wide intermediate phases have also been discovered in mixtures of synclinic and anticlinic smectics where they can exist in a broad temperature range of up to 50° [7,8].

In spite of all diversity of tilted smectic phases with ferro-, antiferro-, and ferrielectric ordering, the underlying mechanism is always related to the induction of the polarization by the tilt in individual chiral smectic layers. Complex structures with a polarization distribution along the direction perpendicular to the layers appear due to interactions between the molecules in different layers (see, for example [9,10]) which are generally weaker than intermolecular interactions within the same layer.

The detailed microscopic mechanism of ferroelectric ordering in tilted smectics which is responsible for the induction of the polarization by the collective molecular tilt has been the issue of debate during the past two decades. In particular, the role of molecular chirality has not been completely clarified. On the one hand, there is a general agreement that the spontaneous polarization in tilted smectics can-

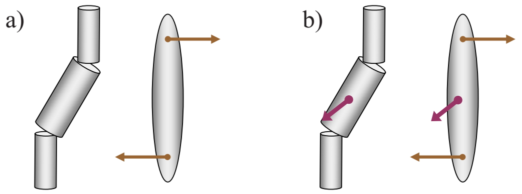

FIG. 1. (Color online) (a) Simple models for nonchiral molecules of the C_{2h} symmetry used by Wulf [32] and Goossens [24,25]. (b) Corresponding models for chiral molecules where chirality is determined by the additional dipole perpendicular to the molecular plane.

not exist without molecular chirality, i.e., at least a fraction of molecules must be chiral. On the other hand, the role of chiral intermolecular interactions remains unclear. Some molecular models of the ferroelectric smectic-C^* phase are based on the assumption that the spontaneous polarization is directly determined by appropriate interactions between chiral molecules including, for example, interactions with a molecular chiral center [11–15]. These models have been developed using an analogy with cholesteric liquid crystals where the helical twisting power is determined by chiral (albeit nonpolar) intermolecular interactions [16–18]. Other models are based on a different microscopic mechanism [19–26] which also requires molecular chirality, but, at the same time, takes into consideration only nonchiral intermolecular interactions. Some of these models are rather qualitative, but the underlying microscopic mechanism is essentially the same.

The first extended description of this mechanism has been given by Goossens [24,25] who considered the electrostatic interaction between model molecular quadrupoles composed of two antiparallel dipoles which are perpendicular to the long molecular axis (see Fig. 1). Goossens has shown that the polarization in the smectic-C^* phase may be induced by the nonchiral quadrupole-quadrupole electrostatic interaction provided the molecules possess the additional dipole in the direction perpendicular to the molecular plane. The latter dipole is responsible for the molecular chirality in this simple model, and the spontaneous polarization is proportional to the magnitude of the dipole and to the novel order parameter of the smectic-C phase [24], which is related to the low symmetry of the molecule presented in Fig. 1. One notes, however, that the papers of Goossens are focused into one particular model, and do not contain any general theory of ferroelectric ordering or general expressions for the spontaneous polarization.

A more general and a very successful model has been proposed by the Boulder group [19–21]. In the Boulder model, the molecules of the zig-zag shape (see Fig. 2) are ordering in the so-called binding cites which have the same point symmetry as the smectic-C phase itself. Then transverse molecular dipoles are ordered in the particular direction perpendicular to the tilt plane simply because the zig-zag molecule fits into the binding cite of the same shape only for a particular direction of the transverse dipole. The Boulder model has been successfully used to describe and predict the value and sign of the spontaneous polarization for a significant number of chiral smectic materials. This indicates that the corresponding mechanism of the ferroelectric ordering may be predominant at least for conventional smectics-C^*. One notes also that the symmetry of a zig-zag molecule is exactly the same as that of the molecule with two equal antiparallel dipoles considered by Goossens. The interaction between the molecule and the binding cite, which is responsible for the polar order, is also nonchiral in nature because the binding cite itself is nonchiral. Boulder model emphasizes the steric mechanisms of the ordering, but the idea behind the model is much more universal. In the recent paper [21] the ordering of a molecule in the binding cite has been interpreted as an ordering in the effective mean-field potential. In the present paper we develop this idea and show that indeed in the context of a rather general molecular-statistical theory the concept of the "binding cite" corresponds to the particular form of an average one-particle mean-field potential which is created by all other molecules of the medium, and which reflects the symmetry of the nonchiral smectic-C phase and its orientational distribution function.

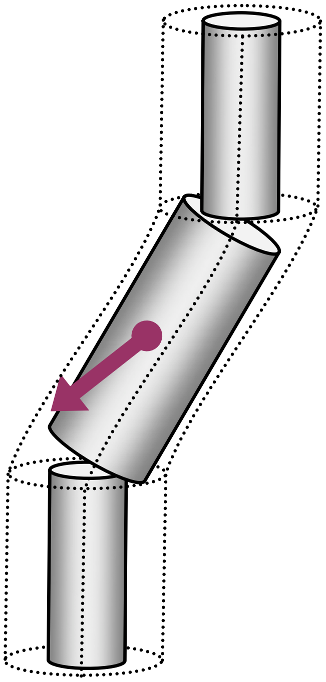

FIG. 2. (Color online) Schematic of biaxial molecule in the curved binding site as assumed in the Boulder model.

Terzis *et al.* have developed a similar model [22,23]. This detailed model is based on a mean-field-like one-particle orientational potential for each molecular segment and, similar to the Boulder model, involves a summation over the molecular conformations. Using this model Terzis *et al.* have obtained good quantitative results for the spontaneous polarization of a number of ferroelectric smectics-C^* [23].

Existing microscopic models for ferroelectric smectics C^* have played an important role in the development of the theory of such materials. At the same time, from the point of view of theoretical physics, these models are too detailed in terms of a molecular structure and a particular choice of a coupling with the macroscopic environment. As a result, the models only indirectly address some of the more general physical problems related to the origin of ferroelectricity in tilted smectic phases including, for example, the description of the symmetry properties of relevant model interaction potentials and an interplay between the spontaneous polarization and the order parameters of the smectic-C^* phase.

In this paper we develop a general mean-field molecular-statistical theory of ferroelectric ordering in the smectic-C^* phase based on the mechanism described above, i.e., we consider the ferroelectric ordering in chiral smectics caused by *nonchiral* intermolecular interactions. We obtain a simple expression for the model interaction potential which may be responsible for ferroelectric ordering in tilted smectics, and interpret the general microscopic mechanism of the ordering mathematically using the concept of the pseudovector order parameter. The results of the theory will be used to obtain explicit expressions for the spontaneous polarization in the smectic-C^* phase composed of biaxial molecules with quadrupole-quadrupole interaction potential. The spontaneous polarization together with other order parameters of the smectic-C^* phase will also be calculated numerically for another two interaction model. Finally, we will consider in detail the molecular origin of the ferroelectric ordering in novel smectic materials which have recently been investigated by Lemieux *et al.* [27–30]. These materials, which are used as chiral dopants in a nonchiral smectic-C host, possess a molecular structure rather different from that of conventional ferroelectric smectics. In particular, the molecular chirality is mainly determined by the chiral distribution of permanent dipoles within the molecular structure. It is shown that despite a different nature of intermolecular interactions, the spontaneous polarization in smectics C doped with such molecules is still determined by the same general mechanism.

II. SPONTANEOUS POLARIZATION AND ORDER PARAMETERS OF THE SMECTIC-C^* PHASE

A. Coupling between polarization, tilt, and chirality

It is well known since the work by Meyer [31] that from the purely macroscopic point of view the ferroelectric ordering in tilted smectics is determined by the linear coupling between the polarization and the tilt in a chiral medium. In terms of the Landau–de Gennes expansion, the free energy of the ferroelectric smectic-C^* phase can be expressed as (see, for example, [15]):

$$F_C = F_A + F(\Theta) + \frac{1}{\chi_\perp} P_s^2 + c_p(\mathbf{P}_s \cdot \mathbf{w}), \tag{1}$$

where F_A is the free energy of the smectic-A phase, $F(\Theta)$ is the expansion of the excess free energy of the smectic-C phase in powers of the tilt angle Θ and the last two terms describe the contribution which depends on the spontaneous polarization $\mathbf{P}_s$. Here $\mathbf{w}=(\mathbf{n}\cdot\mathbf{k})(\mathbf{k}\times\mathbf{n})$ is the so-called pseudovector tilt order parameter of the SmC phase where $\mathbf{n}$ is the director and $\mathbf{k}$ is the smectic layer normal as shown in Fig. 3. Minimization of the free energy (1) yields the well known result

$$\mathbf{P}_s = c_p\mathbf{w} = c_p(\mathbf{n}\cdot\mathbf{k})(\mathbf{k}\times\mathbf{n}), \tag{2}$$

which indicates that the spontaneous polarization is proportional to the pseudovector tilt order parameter and the coupling constant c_p.

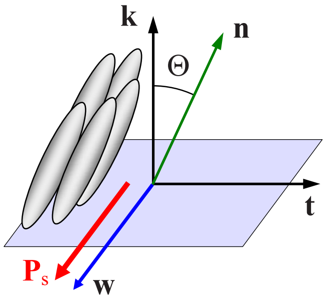

FIG. 3. (Color online) Spontaneous polarization P_s and the pseudovector tilt order parameter w in the Sm C^* phase.

One notes that the polarization is a polar vector while the tilt order parameter $\mathbf{w}$ is a pseudovector with different transformation properties (i.e, in contrast to the polar vector $\mathbf{P}_s$ it *does not* change sign under space inversion). Thus the linear relationship (2) between polarization and the tilt is only possible if the coupling constant c_p is a pseudoscalar (which also changes sign under space inversion). Then the product of the pseudoscalar c_p and the pseudovector $\mathbf{w}$ makes the polar vector like polarization. Pseudoscalar quantities are nonzero only in a chiral medium. They are proportional to molecular chirality and change sign when all chiral molecules reverse their handedness. Thus one arrives at a well established conclusion that the spontaneous polarization in tilted smectic phases occurs only if at least a fraction of molecules are chiral.

At the same time, the pseudovector order parameter $\mathbf{w}$ is nonzero also in the nonchiral smectic-C phase. Indeed, $\mathbf{w}$ is invariant under all symmetry transformations of the smectic-C phase including the reflection with respect to the tilt plane, which is a symmetry plane. This is related to the transformation properties of a pseudovector different from those of a polar vector. In this case, $\mathbf{w}$ is invariant under a reflection with respect to the tilt plane because both vectors $\mathbf{n}$ and $\mathbf{k}$ are in the tilt plane and thus are not effected by the reflection. In contrast, the spontaneous polarization $\mathbf{P}_s$, of course, changes sign under a reflection with respect to the tilt plane. One notes that this does not violate the linear relationship (2) because the pseudoscalar parameter c_p also changes sign under the reflection. In a nonchiral smectic-C phase the coupling constant c_p vanishes identically and the spontaneous polarization does not appear.

B. Microscopic interpretation

The purpose of any molecular theory of ferroelectric ordering in tilted smectics is to establish a relationship between the general macroscopic description presented in the previous subsection and the molecular ordering on the microscopic level. An intuitive interpretation of the ferroelectric ordering in the chiral smectic-C^* phase [20,22,26] can be illustrated using Fig. 4.

For illustration only, let us consider a simple model of a chiral biaxial molecule represented as a rigid rod with two “lateral groups” and a permanent dipole perpendicular to the molecular plane as shown in Fig. 4(a). Note that the lateral groups make the molecule biaxial while the chirality is de-

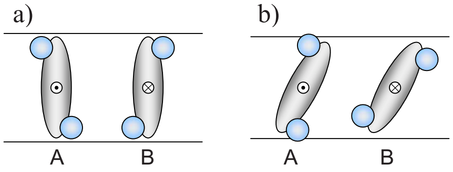

FIG. 4. (Color online) (a) Molecular orientation *A* and *B*, which correspond to the opposite directions of the molecular transverse dipole, are equivalent in the Sm*A* phase. (b) In the Sm C^* phase molecular orientation *A* is more energetically favorable than the orientation *B*.

termined by the transverse dipole. Without this dipole, the molecule possesses a mirror plane and thus is nonchiral. Now let us assume that the lateral groups have a tendency to point in the direction of the region between two adjacent smectic layers. One can readily see that in the smectic-*A* phase (i.e., without any tilt) the two orientations of such a molecule, which correspond to opposite directions of the transverse dipole $\boldsymbol{\mu}$, are energetically equivalent. Thus the macroscopic polarization in the untilted smectic phase should vanish. In contrast, in the tilted phase the balance between two opposite directions of the transverse molecular dipole is violated because the molecular orientation A is more favorable than the orientation B [see Fig. 2(b)]. As a result, the average molecular dipole does not vanish, and a macroscopic polarization appears in the direction perpendicular to the tilt plane. One notes that this simple argument is directly valid for rigid chiral molecules of sufficiently low symmetry. Nonchiral flexible molecules may also posses chiral conformations which will order in the smectic-*C* phase according to the simple mechanism discussed above. In this case, however, the macroscopic polarization does not occur (as it should be in a nonchiral Sm*C* phase) because the ordered dipoles of, say, left-handed conformers will exactly be canceled by those of the right-handed conformers, which point in the opposite direction. Now one has to clarify how this type of ordering corresponds to the general macroscopic description presented above.

First one notes that this simple argument is valid for molecules which are characterized by the C_{2h} symmetry when the transverse dipole is removed. Simple examples of molecules of the C_{2h} symmetry, presented in Fig. 1, include a molecule with two in-plane antiparallel dipoles (a model considered by Goossens [24]) and a molecule of the "zigzag" shape (considered by Wulf [32] and others) which very roughly characterize the actual shape of typical mesogenic molecules. Orientation of any rigid biaxial molecule can be specified by the unit vectors $\mathbf{a}$ and $\mathbf{b}$ in the direction of short and long molecular axis, respectively. In practice, the orientation of a nonpolar molecule is usually characterized by second rank tensors composed of the components of the vectors $\mathbf{a}$ and $\mathbf{b}$. For example, uniaxial molecules are characterized by the molecular tensor $Q^M_{\alpha\beta}=a_\alpha a_\beta-(1/3)\delta_{\alpha\beta}$. The statistical average of $\mathbf{Q}^M$ is the nematic tensor order parameter $\mathbf{Q}$. Biaxial molecules of high symmetry, which possess two mutually perpendicular symmetry planes, are also characterized by the second molecular tensor $B^M_{\alpha\beta}=b_\alpha b_\beta-c_\alpha c_\beta$ where the unit vector $\mathbf{c}\perp\mathbf{b}$ is the second molecular short axis. In addition, the molecules of the C_{2h} or lower symmetry are characterized by the third molecular tensor $a_\alpha b_\beta$ which is invariant under all symmetry operations which leave the molecule intact. Indeed, one can readily see that the molecules presented in Figs. 1 and 4 are not invariant under the sign inversion of the axes $\mathbf{a}$ or $\mathbf{b}$ individually. At the same time, the molecules are invariant under simultaneous inversion of both axis $\mathbf{a}$ and $\mathbf{b}$. This symmetry enables one to introduce the transverse molecular pseudovector $(\mathbf{a}\times\mathbf{b})$ which is related to the skew part of $a_\alpha b_\beta$. One notes that the existence of this transverse pseudovector does not violate the mirror symmetry of the molecule because the pseudovector $(\mathbf{a}\times\mathbf{b})$ is invariant under a reflection with respect to the molecular mirror plane which is parallel to $\mathbf{a}$ and $\mathbf{b}$.

Now it can readily be shown that the average $\langle\mathbf{a}\times\mathbf{b}\rangle$ is nonzero only in a tilted smectic phase and is proportional to $\mathbf{w}=(\mathbf{n}\cdot\mathbf{k})(\mathbf{k}\times\mathbf{n})$. Thus the expression

$$\mathbf{w}_{ab}=\langle\mathbf{a}\times\mathbf{b}\rangle \tag{3}$$

is a microscopic definition of a pseudovector tilt order parameter of the smectic-*C* phase. One notes that in the smectic-*C* phase composed of biaxial molecules there exist several tilt order parameters. However, only the parameter (3) is directly related to the spontaneous polarization.

Indeed, one notes that the molecular orientations *A* and *B* in Fig. 4 are characterized by the opposite directions of molecular pseudovector $(\mathbf{a}\times\mathbf{b})$ (because the short axis $\mathbf{b}$ points in the opposite directions while the long axis $\mathbf{a}$ is the same). Thus one concludes that the average pseudovector $\langle\mathbf{a}\times\mathbf{b}\rangle\neq 0$ in the smectic-*C* phase where the orientation *A* is more energetically favorable than the orientation *B*. Moreover, it follows from the general symmetry arguments that $\langle\mathbf{a}\times\mathbf{b}\rangle\propto\mathbf{w}=(\mathbf{n}\cdot\mathbf{k})(\mathbf{k}\times\mathbf{n})$ because $\mathbf{w}$ is the only pseudovector allowed by the symmetry of the smectic-C^* phase. Indeed, any macroscopic vector or pseudovector must be parallel to the C_2 symmetry axis of the smectic-C^* layer which is normal to the tilt plane. This is exactly the direction of $\mathbf{w}$. A different derivation of this result is presented in Sec. III.

Finally it can be shown that the spontaneous polarization $\mathbf{P}_s$ is proportional to the average $\langle\mathbf{a}\times\mathbf{b}\rangle\propto\mathbf{w}$. We assume for simplicity that the transverse molecular dipole is parallel to the short molecular axis $\mathbf{c}\perp\mathbf{b}\perp\mathbf{a}$, i.e, $\boldsymbol{\mu}=\mu_\perp\mathbf{c}$. Then the macroscopic polarization in the smectic-C^* phase equals

$$\mathbf{P}_s=\rho\langle\boldsymbol{\mu}\rangle=\rho\mu_\perp\langle\mathbf{c}\rangle, \tag{4}$$

where ρ is the molecular number density.

The unit vector $\mathbf{c}$ can be expressed in terms of the unit vectors $\mathbf{a}$ and $\mathbf{b}$ in the following way:

$$\mathbf{c}=\Delta(\mathbf{a}\times\mathbf{b}), \tag{5}$$

where $\Delta=[(\mathbf{a}\times\mathbf{b})\cdot\mathbf{c}]$ is the molecular unit pseudoscalar which specifies the handedness of the molecular coordinate system. Note that in Eq. (5) $\mathbf{c}$ is the conventional polar vector which is expressed as a product of the pseudovector $(\mathbf{a}\times\mathbf{b})$ and the pseudoscalar Δ.

Now the spontaneous polarization (4) can be rewritten as

$$\mathbf{P}_s = \rho\mu_\perp \langle \mathbf{c} \rangle = \rho\mu_\perp \Delta \langle \mathbf{a} \times \mathbf{b} \rangle = \rho\Delta_\mu \langle \mathbf{a} \times \mathbf{b} \rangle, \tag{6}$$

where $\Delta_\mu = [\boldsymbol{\mu} \cdot (\mathbf{a} \times \mathbf{b})]$. Here we have taken into account that the parameter Δ is independent of the molecular orientation.

According to Eq. (6), the spontaneous polarization $\mathbf{P}_s$ is proportional to the tilt order parameter $\langle \mathbf{a} \times \mathbf{b} \rangle \propto \mathbf{w} = (\mathbf{n} \cdot \mathbf{k}) \times (\mathbf{k} \times \mathbf{n})$. Thus the simple microscopic interpretation of the appearance of the spontaneous polarization in the smectic-C^* phase, presented in this subsection, is fully consistent with the general phenomenological theory outlined in Sec. II A.

In summary, one concludes that if the smectic-C^* phase is composed of molecules of the C_{2h} symmetry or lower with an additional transverse dipole in the direction perpendicular to the molecular plane, the spontaneous polarization is proportional to the order parameter (3) and the pseudoscalar quantity $\Delta_\mu = [\boldsymbol{\mu} \cdot (\mathbf{a} \times \mathbf{b})]$ which characterizes the molecular chirality determined by the transverse dipole $\boldsymbol{\mu}$. A consistent statistical theory of the ferroelectric ordering in the smectic-C^* phase is presented in the following section.

III. MOLECULAR STATISTICAL THEORY OF FERROELECTRIC ORDERING IN THE SMECTIC-C* PHASE

A. General results

As discussed in the previous section, the orientation of a biaxial molecule can be specified by the unit vectors **a** and **b** in the direction of the long and short molecular axis, respectively. The second molecular short axis **c** is then given by Eq. (5). The spontaneous polarization can be expressed in the following general form:

$$\mathbf{P}_s = \rho \langle \boldsymbol{\mu}_\perp \rangle = \rho \int \boldsymbol{\mu}_\perp f_1(\mathbf{a},\mathbf{b}) d\mathbf{a}\, d\mathbf{b}, \tag{7}$$

where $f_1(\mathbf{a},\mathbf{b})$ is the orientational distribution function of the smectic-C^* phase, and the transverse molecular dipole $\boldsymbol{\mu}_\perp = \mu_\perp \mathbf{c}$. The orientational distribution function can always be expressed in terms of the effective one-particle potential $U_1(\mathbf{a},\mathbf{b})$:

$$f_1(\mathbf{a},\mathbf{b}) = \frac{1}{Z} \exp\left[-\frac{U_1(\mathbf{a},\mathbf{b})}{k_B T} \right], \tag{8}$$

where

$$Z = \int \exp\left[-\frac{U_1(\mathbf{a},\mathbf{b})}{k_B T} \right] d\mathbf{a}\, d\mathbf{b}. \tag{9}$$

For molecules which are polar in the direction of the **c** axis, in the quadrupolar approximation the effective one-particle potential depends on the unit vector **c** and the second rank molecular tensors $a_\alpha a_\beta, b_\alpha b_\beta$, and $a_\alpha b_\beta$ which are invariant under all symmetry operations of a molecule. Here **c** is expressed in terms of **a** and **b** by Eq. (5). As discussed in Sec. II B, the invariant $a_\alpha b_\beta$ exists only for biaxial molecules of sufficiently low symmetry. Thus in the quadrupolar approximation the potential $U_1(\mathbf{a},\mathbf{b})$ reads

$$U_1(\mathbf{a},\mathbf{b}) = a_\alpha a_\beta A_{\alpha\beta} + b_\alpha b_\beta B_{\alpha\beta} + (a_\alpha b_\beta + b_\alpha a_\beta) C_{\alpha\beta} + (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{w}, \tag{10}$$

where **W** and $A_{\alpha\beta}, B_{\alpha\beta}, C_{\alpha\beta}$ are the material pseudovector and tensors correspondingly, which depend on the symmetry of the chiral smectic-C^* phase. This symmetry, in turn, is determined by the two tensors $n_\alpha n_\beta$ and $k_\alpha k_\beta$ which specify the macroscopic structure of the phase. One notes that the last term in Eq. (10) contains a pseudovector $(\mathbf{a} \times \mathbf{b})$, which means that **W** has also to be a pseudovector in order to insure that $U_1(\mathbf{a},\mathbf{b})$ is a scalar. We conclude that this last term is determined by chiral interactions in the system, i.e., the interactions depending on the handedness of the interacting molecules. Indeed, let us consider the case when Eq. (10) describes an effective one-particle potential of a chiral dopant in the chiral smectic-C^* host. Inversion of the host chirality results in sign inversion of the pseudovector **W** while all material tensors $A_{\alpha\beta}, B_{\alpha\beta}$, and $C_{\alpha\beta}$ remain the same. As a result, the last term in Eq. (10) changes sign. Thus the last term describes the so-called chiral discrimination energy, i.e., the difference of energy of interaction between the same chiral molecule and the two enantiomeric forms of the chiral host. In many cases such a discrimination is small and then this term may be neglected.

Taking into account that all macroscopic quantities in the smectic-C phase must be quadratic both in **n** and **k**, the pseudovector **W** can be expressed in the following general form:

$$\mathbf{W} = \omega \mathbf{P}_s + \kappa \mathbf{w}, \tag{11}$$

where ω is a pseudoscalar and κ is a scalar. The symmetric tensors **A**, **B**, and **C** are expressed as

$$A_{\alpha\beta} = A_1 n_\alpha n_\beta + A_2 k_\alpha k_\beta + A_3 (\mathbf{n} \cdot \mathbf{k})(n_\alpha k_\beta + k_\alpha n_\beta),$$

$$B_{\alpha\beta} = B_1 n_\alpha n_\beta + B_2 k_\alpha k_\beta + B_3 (\mathbf{n} \cdot \mathbf{k})(n_\alpha k_\beta + k_\alpha n_\beta),$$

$$C_{\alpha\beta} = C_1 n_\alpha n_\beta + C_2 k_\alpha k_\beta + C_3 (\mathbf{n} \cdot \mathbf{k})(n_\alpha k_\beta + k_\alpha n_\beta), \tag{12}$$

where we have neglected the terms quadratic in $\mathbf{P}_s$ and **w** because these terms are of the order of Θ^2 at small tilt angle $\Theta \ll 1$ while all other terms in Eq. (12) are of the order of 1.

The effective one particle potential $U_1(\mathbf{a},\mathbf{b})$ is determined by intermolecular interactions in the smectic-C^* phase which may, or may not be sensitive to molecular chirality. For example, the electrostatic interaction between permanent dipoles and quadrupoles is not sensitive to molecular chirality while the interactions involving molecular octupoles are different for the pairs of molecules of equal and opposite handedness, respectively. In particular, the pseudovector quantity **W** in Eq. (11) must vanish if the molecules are nonchiral. This parameter is determined by some chiral intermolecular interactions which exist only between chiral molecules. All other material parameters in Eqs. (10)–(12) are scalars, and therefore they are generally nonzero in the corresponding nonchiral smectic-C phase. The difference between scalar and pseudoscalar material parameters in the effective one-particle potential enables one to distinguish between two different microscopic mechanisms of ferroelectric ordering in the smectic-C^* phase.

Taking into account that the spontaneous polarization $\mathbf{P}_s$ and the pseudovector $\mathbf{w}$ are small at small tilt angles Θ, the orientational distribution function (8) can be expanded in powers of $\mathbf{P}_s$ and $\mathbf{w}$ keeping the linear terms, and substituted into the general expression for the spontaneous polarization (7). As a result, the spontaneous polarization in the smectic-C^* phase can be expressed as

$$\boldsymbol{\xi} \cdot \mathbf{P}_s = \rho \Delta \kappa \boldsymbol{\lambda} \cdot \mathbf{w} + \rho \int \boldsymbol{\mu}_\perp \frac{1}{Z_0} \exp\left[- \frac{U_1^{(0)}(\mathbf{a},\mathbf{b})}{k_B T} \right] d\mathbf{a}\, d\mathbf{b}, \tag{13}$$

where the inverse polarizability tensor $\xi_{\alpha\beta} = \delta_{\alpha\beta} + (\rho/k_B T) \times \langle \omega \mu_{\perp\alpha} c_\beta \rangle_0$, the tensor $\lambda_{\alpha\beta} = -(\rho/k_B T)\langle \mu_{\perp\alpha} c_\beta \rangle_0$, the averaging $\langle \cdots \rangle_0$ is performed with the orientational distribution function $f_0 = (1/Z_0)\exp(-U_1^{(0)}(\mathbf{a},\mathbf{b})/k_B T)$ and $U_1^{(0)}(\mathbf{a},\mathbf{b})$ is given by Eqs. (10)–(12) with $\mathbf{W}=0$.

According to Eq. (13) there exist two qualitatively different contributions to the spontaneous polarization of the smectic-C^* phase which correspond to the two terms in the right-hand side of Eq. (13). The first term comes from the last term in the one-particle potential (10), which is determined by chiral intermolecular interactions. This contribution corresponds to the microscopic mechanism of ferroelectric ordering determined by chiral interactions which has been considered in Refs. [11,13–15]. In contrast, the second term describes the ferroelectric ordering of chiral molecules determined by nonchiral intermolecular interactions. Indeed, this contribution describes the ordering of a transverse molecular dipole in a nonchiral effective one-particle potential $U_1^{(0)}(\mathbf{a},\mathbf{b})$. This potential does not depend on any pseudoscalar parameters, and thus, in the first approximation, it is exactly the same as in the corresponding nonchiral smectic-C phase. Molecular chirality in this case is determined by the orientation of the molecular transverse dipole and manifests itself during the averaging process as described below. Now let us consider this contribution in more detail.

In the general case the effective one-particle potential $U_1^{(0)}(\mathbf{a},\mathbf{b})$ can be expressed as a sum of the following two terms:

$$U_1^{(0)}(\mathbf{a},\mathbf{b}) = U_a(\mathbf{a}) + U_b(\mathbf{a},\mathbf{b}), \tag{14}$$

where $U_a(\mathbf{a}) = a_\alpha a_\beta A_{\alpha\beta}$ and $U_b(\mathbf{a},\mathbf{b}) = b_\alpha b_\beta B_{\alpha\beta} + (a_\alpha b_\beta + b_\alpha a_\beta) C_{\alpha\beta}$. In Eq. (14) the first term depends only on the orientation of the long molecular axis $\mathbf{a}$ while the second term depends also on the orientation of the short axis $\mathbf{b}$. Smectic liquid crystals are composed of strongly anisotropic molecules, and in this case one may assume that the intermolecular interaction energy associated with a change of orientation of the long axes is much larger than the change of the energy associated with the rotation of short molecular axes. Then the second term in Eq. (14) is expected to be much smaller than the first one, i.e., $U_b \ll U_a$. One notes that the first term in Eq. (14) determines the orientational (nematic) ordering of long molecular axis, while the second term is responsible for a weaker ordering of short molecular axes. Now the orientational distribution function $f_0(\mathbf{a},\mathbf{b})$ can be expanded in powers of U_b keeping the linear term:

$$\frac{1}{Z_0} \exp\left[- \frac{U_1^{(0)}(\mathbf{a},\mathbf{b})}{k_B T} \right] \approx f_a(\mathbf{a}) \left[1 - \frac{U_b(\mathbf{a},\mathbf{b})}{k_B T} \right], \tag{15}$$

where the uniaxial orientational distribution function $f_a(\mathbf{a})$ depends only on the orientation of the long axis $\mathbf{a}$:

$$f_a(\mathbf{a}) = \frac{1}{Z_a} \exp\left[- \frac{U_a(\mathbf{a})}{k_B T} \right]. \tag{16}$$

Substituting Eq. (15) into the second term in Eq. (13) one obtains the following expression for the spontaneous polarization:

$$\mathbf{P}_s \approx -\Delta \frac{\rho \mu_\perp}{k_B T} \int (\mathbf{a} \times \mathbf{b}) U_b(\mathbf{a},\mathbf{b}) f_a(\mathbf{a}) d\mathbf{a}\, d\mathbf{b}. \tag{17}$$

Now Eqs. (14) and (16) can be substituted into Eq. (17) where the averaging is performed over $\mathbf{b}$ and $\mathbf{a}$ taking into account that the function $f_a(\mathbf{a})$ is independent of $\mathbf{b}$. Neglecting biaxiality of the smectic-C phase one may use the following simple formulas:

$$\frac{1}{2\pi} \int b_\alpha b_\beta d\mathbf{b} = \frac{1}{2}(\delta_{\alpha\beta} - a_\alpha a_\beta) \tag{18}$$

and

$$\frac{1}{4\pi} \int f_a(\mathbf{a}) \left(a_\alpha a_\beta - \frac{1}{3}\delta_{\alpha\beta} \right) d\mathbf{a} = S \left(n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta} \right), \tag{19}$$

and obtain the final expression for the spontaneous polarization:

$$\mathbf{P}_s = \frac{\rho \Delta_\mu C_3 S}{2 k_B T} [\mathbf{n} \times \mathbf{k}](\mathbf{n} \cdot \mathbf{k}), \tag{20}$$

where S is the nematic order parameter.

Equation (19), which has been obtained without using any particular model, presents a general expression for the spontaneous polarization of the chiral smectic-C^* phase determined by nonchiral intermolecular interactions. The spontaneous polarization is proportional to the pseudoscalar parameter $\Delta_\mu = [\boldsymbol{\mu}_\perp (\mathbf{a} \times \mathbf{b})]$ which specifies molecular chirality determined by the orientation of the transverse dipole, and the parameter C_3 which is determined by nonchiral interactions. One notes that the general microscopic mechanism of ferroelectric ordering described by the present theory is qualitatively the same as the one considered in the Boulder model [19,20]. In the framework of the Boulder model the restrictions imposed by the binding cite on the orientation of a given molecule are equivalent to the specific form of the effective one-particle potential $U_1^{(0)}(\mathbf{a},\mathbf{b})$. From the qualitative point of view, both the binding cite and the effective one-particle potential possess the same symmetry as the nonchiral smectic-C phase (i.e., the C_2 symmetry axis and the mirror plane) and are not sensitive to molecular chirality. On the other hand, the present theory also covers the model of Goossens [25] based on the electrostatic interaction between molecules with pairs of antiparallel dipoles. Detailed numerical results obtained using a version of this model are presented in Sec. IV. Explicit expressions for effective one-particle potential and the spontaneous polarization in the quadrupole-quadrupole interaction model are derived in the following section using the mean-field approximation.

B. Quadrupole-quadrupole interaction model

In this section we obtain explicit analytical results for the spontaneous polarization in the smectic-C^* phase using the simple model of a rigid molecule with essentially uniaxial quadrupole tensor slightly tilted with respect to the primary molecular axis (which is determined by the shape or molecular inertia tensor and orders along the director). Such a molecule is biaxial, and the molecular biaxiality is determined by the angle between the axis of the quadrupole tensor and the primary molecular axis. Assuming that this angle is small, one obtains approximate expressions for the polarization using the generalized mean-field theory.

Let us consider the system of rigid molecules with primary axes $\mathbf{a}_i$. The molecules are characterized by the permanent quadrupole tensor $q_{\alpha\beta}$ which depends on the distribution of effective charges within a molecule. It should be noted that for molecules of the C_{2h} symmetry, considered here, one primary axis of any molecular tensor (including the quadrupole one) must be parallel to the twofold symmetry axis of the molecule $\mathbf{c}$. At the same time, the orientation of the two remaining primary axes, which lie in the symmetry plane of the molecule, is not specified by the molecular symmetry. As a result, the orientation of these axes should generally be different for different molecular tensors characterizing different molecular properties. In particular, the primary axes of the quadrupole tensor $q_{\alpha\beta}$ are not expected to coincide with those of the molecular inertia tensor, $\mathbf{a}$ and $\mathbf{b}$. Thus in the general case the traceless symmetric quadrupole tensor can be expressed in terms of molecular axes $\mathbf{a}\perp\mathbf{b}\perp\mathbf{c}$ in the following way:

$$q_{\alpha\beta} = q_1(a_\alpha a_\beta - \delta_{\alpha\beta}/3) + q_2(b_\alpha b_\beta - c_\alpha c_\beta) + q_3(a_\alpha b_\beta + b_\alpha a_\beta). \tag{21}$$

It will be shown below that the spontaneous polarization is proportional to the off-diagonal element q_3, which characterizes the difference in the orientation of the molecular inertia and quadrupole tensors.

The electrostatic interaction between permanent quadrupoles of the molecules i and j can be written in the form:

$$U_{qq}(i,j) = q^i_{\alpha\beta} D_{\alpha\beta\gamma\delta} q^j_{\gamma\delta}, \tag{22}$$

where the quadrupole-quadrupole coupling tensor $\mathbf{D}$ is given by

$$\begin{aligned} D_{\alpha\beta\gamma\delta} = \frac{3}{4R^5}(&\delta_{\alpha\delta}\delta_{\beta\gamma} + \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} - 5\delta_{\alpha\beta}u_\gamma u_\delta \\ &- 5\delta_{\alpha\gamma}u_\beta u_\delta - 5\delta_{\alpha\delta}u_\gamma u_\beta - 5\delta_{\beta\gamma}u_\delta u_\alpha - 5\delta_{\delta\beta}u_\gamma u_\alpha \\ &- 5\delta_{\gamma\delta}u_\alpha u_\beta + 35u_\alpha u_\beta u_\gamma u_\delta), \end{aligned} \tag{23}$$

where $\mathbf{R}=\mathbf{R}_{ij}$ is the intermolecular vector and the unit vector $\mathbf{u}=\mathbf{R}/|\mathbf{R}|$.

Now the quadrupole-quadrupole interaction can be taken into account in the generalized mean-field approximation of the smectic-C^* phase. In this approximation (see, for example, [33–35]) the free energy of the system without positional order can be expressed as

$$\begin{aligned} F/V = {}& \frac{1}{2}\rho^2 \int f_1(\Omega_1)U(1,2)f_1(\Omega_2)d^2\mathbf{R}\, d\Omega_1 d\Omega_2 \\ &+ \rho k_B T \int f_1(\Omega_1)\ln f_1(\Omega_1)d\Omega_1, \end{aligned} \tag{24}$$

where $f_1(\Omega)$ is the one-particle orientational distribution function, the variable $\Omega_i=[\mathbf{a}_i,\mathbf{b}_i]$ specifies the orientation of the molecule i, $U(1,2)$ is the effective pair interaction potential which takes into account the steric cutoff, and ρ is the number density of molecules per unit area of the smectic layer.

Minimization of the free energy (24) yields the one-particle distribution function in the form (8) and (9) with the one-particle potential U_1 being equal to the mean-field potential

$$U_{\mathrm{MF}}(\mathbf{a},\mathbf{b}) = \rho \int U(1,2)f_1(\mathbf{a}_2,\mathbf{b}_2)d^2\mathbf{R}\, d\mathbf{b}_2\, d\mathbf{a}_2. \tag{25}$$

The total effective pair interaction potential $U(1,2)$ can be expressed as

$$U(1,2) = U_0(1,2) + U_{qq}(1,2), \tag{26}$$

where $U_0(1,2)$ is the effective interaction potential for molecules without permanent quadrupole moments, and $U_{qq}(1,2)$ is the quadrupole-quadrupole interaction energy given by Eq. (22). We assume for simplicity that the potential $U_0(1,2)$ is even in $\mathbf{a}_1,\mathbf{a}_2,\mathbf{b}_1,\mathbf{b}_2$, and thus it cannot be responsible for the ferroelectric ordering in the smectic-C^* phase.

Substituting Eqs. (22) and (23) for the quadrupole-quadrupole interaction potential into Eq. (26) and then into Eq. (25) one obtains the following expression for the total mean-field potential after averaging over $\mathbf{a}_2,\mathbf{b}_2$ and integrating over $\mathbf{R}$:

$$U_{\mathrm{MF}}(\mathbf{a},\mathbf{b}) = U^{(0)}_{\mathrm{MF}}(\mathbf{a},\mathbf{b}) + U^{qq}_{\mathrm{MF}}(\mathbf{a},\mathbf{b}), \tag{27}$$

where $U^{(0)}_{\mathrm{MF}}(\mathbf{a},\mathbf{b})$ is even in $\mathbf{a}$ and $\mathbf{b}$, and where

$$U^{qq}_{\mathrm{MF}}(\mathbf{a},\mathbf{b}) = \frac{\pi}{4}\rho R_0^2 q^{(1)}_{\alpha\beta} D_{\alpha\beta\gamma\delta}(\mathbf{k})\langle q_{\gamma\delta}\rangle. \tag{28}$$

Here $q^{(1)}_{\alpha\beta}$ is the quadrupole tensor of the molecule 1 given by Eq. (21), R_0 is the distance of minimum approach between the neighboring molecules in the layer, and the tensor $\mathbf{D}$ is given by Eq. (23) with $R=R_0$ and $\mathbf{u}=\mathbf{k}$.

At this point we can neglect the weak biaxiality of the molecular distribution and use the average of the quadrupole tensor (21) in the simple form

$$\langle q_{\alpha\beta}\rangle = q_1 S(n_\alpha n_\beta - \delta_{\alpha\beta}/3). \tag{29}$$

After some algebra the corresponding expression for $D_{\alpha\gamma\delta\beta}(\mathbf{k})\langle q_{\gamma\delta}\rangle$ can be written as

$$\begin{aligned} M_{\alpha\beta} &= D_{\alpha\beta\gamma\delta}(\mathbf{k})\langle q_{\gamma\delta}\rangle \\ &= \frac{3}{4R_0^5} q_1 S[\delta_{\alpha\beta}(1-5\cos^2\Theta) + 2n_\alpha n_\beta \\ &\quad - 5(1-7\cos^2\Theta)k_\alpha k_\beta - 10(\mathbf{k}\cdot\mathbf{n})(n_\alpha k_\beta + n_\beta k_\alpha)]. \end{aligned} \tag{30}$$

Assuming that the off-diagonal element q_3 of the molecular quadrupole tensor is small one may expand the exponent in Eqs. (8) and (9) in powers of q_3 keeping the linear terms. This yields the following approximate expression for the orientational distribution function:

$$f_1(\mathbf{a},\mathbf{b}) = f_0(\mathbf{a},\mathbf{b}) + \Delta f(\mathbf{a},\mathbf{b}), \tag{31}$$

where

$$f_0(\mathbf{a},\mathbf{b}) = \frac{1}{Z_0}\exp\left[-\frac{U_{\mathrm{MF}}^{(0)}(\mathbf{a},\mathbf{b})}{k_BT} + \frac{\pi\rho R_0^2 q^0_{\alpha\beta} M_{\alpha\beta}}{4k_BT}\right] \tag{32}$$

and

$$\Delta f(\mathbf{a},\mathbf{b}) = \frac{\pi\rho}{4k_BT} R_0^2 q_3 (a_\alpha b_\beta + a_\beta b_\alpha) M_{\alpha\beta} f_0(\mathbf{a},\mathbf{b}), \tag{33}$$

and where $q^0_{\alpha\beta}$ is the molecular quadrupole tensor given by Eq. (21) without the off-diagonal term.

Only the term containing Δf makes a contribution to the spontaneous polarization given by the general equations (6) and (7). Substituting Eqs. (31)–(33) and assuming that the biaxial ordering in the system is weak [i.e., using Eqs. (18) and (19) for the averaging] one obtains the following expression for the spontaneous polarization of the smectic-C^* phase:

$$\mathbf{P}_s = \rho\Delta_\mu c_p^0[\mathbf{n}\times\mathbf{k}](\mathbf{n}\cdot\mathbf{k}), \tag{34}$$

with

$$c_p^0 = \frac{15\pi\rho}{16k_BTR_0^3} q_1 q_3 S^2 (4 - 7\sin^2\Theta). \tag{35}$$

This explicit analytical expression for the spontaneous polarization was obtained in the context of the model of the quadrupole-quadrupole intermolecular interactions and confirms all results of the previous section which have been obtained using general theory arguments. In particular, the spontaneous polarization is proportional to the pseudoscalar parameter $\Delta_\mu = (\boldsymbol{\mu}\cdot[\mathbf{a}\times\mathbf{b}])$ which specifies molecular chirality. At the same time, the remaining factor c_p^0 is completely independent of the molecular chirality, and is obtained using the orientational distribution function of the nonchiral smectic-C phase. In this simple model, the factor c_p^0 depends only on the diagonal components of the molecular quadrupole moment, the orientational order parameters of the smectic-C phase and the distance of minimum approach R_0.

In the following section we consider a more realistic model based on electrostatic interactions between localized molecular dipoles.

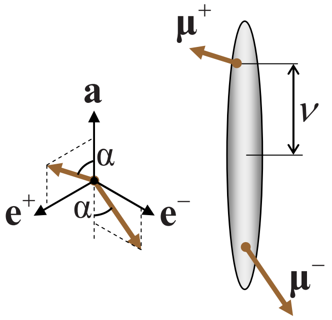

FIG. 5. (Color online) Schematic of molecular axes and dipoles.

IV. INTERACTION BETWEEN CHIRAL PAIRS OF MOLECULAR DIPOLES

In a recent series of papers by Lemieux *et al.* [27–30] a number of different compounds with unconventional structure have been used as chiral dopants to induce the large spontaneous polarization in the smectic-C phase. One notes that the chirality of these molecules is not determined by any chiral centers, but is a consequence of a chiral distribution of permanent molecular dipoles. Disregarding other elements of the actual molecular structure, one can use the minimum model shown in Fig. 5. In this model, the molecule is presented by a rigid rod (with some dispersion interactions between rods) and a pair of off-center dipoles with large transverse components lying in orthogonal planes. Introducing the orthogonal transverse unit vectors $\mathbf{e}^\pm$ we write

$$\boldsymbol{\mu}^\pm = \mu(\mathbf{e}^\pm \sin\alpha \pm \mathbf{a}\cos\alpha). \tag{36}$$

One can readily see that the molecule presented in Fig. 5 is chiral because it does not have any symmetry planes. The total dipole moment of the molecule is transverse $\boldsymbol{\mu}_\perp = (\boldsymbol{\mu}^+ + \boldsymbol{\mu}^-)$ and directed along the unit vector $\mathbf{c} = (\mathbf{e}^+ + \mathbf{e}^-)/\sqrt{2}$. Accordingly, another short molecular axis is to be defined as $\mathbf{b} = (\mathbf{e}^+ - \mathbf{e}^-)/\sqrt{2}$. The spontaneous polarization in such a system is given by the general equations (4) and (6) where the pseudoscalar parameter is expressed as

$$\Delta_\mu = \frac{\sqrt{2}}{\mu\sin\alpha}\mathbf{a}\cdot[\boldsymbol{\mu}^+ \times \boldsymbol{\mu}^-] = \sqrt{2}\Delta\mu\sin\alpha, \tag{37}$$

This parameter quantitatively determines the molecular chirality in the context of the present model.

An interaction potential for a pair of such molecules is expressed as a sum of effective interaction potentials between rigid uniaxial cores and the sum of all electrostatic dipole-dipole interactions:

$$U(1,2) = U^{\mathrm{aa}}(\mathbf{a}_1,\mathbf{R},\mathbf{a}_2) + U_\mu(1,2), \tag{38}$$

with U_μ depending also on the orientation of short molecular axes:

$$\begin{aligned} U_\mu(1,2) &= \boldsymbol{\mu}_1^+\cdot\mathbf{D}_{\uparrow\uparrow}\cdot\boldsymbol{\mu}_2^+ + \boldsymbol{\mu}_1^-\cdot\mathbf{D}_{\uparrow\uparrow}\cdot\boldsymbol{\mu}_2^- + \boldsymbol{\mu}_1^+\cdot\mathbf{D}_{\uparrow\downarrow}\cdot\boldsymbol{\mu}_2^- \\ &\quad + \boldsymbol{\mu}_1^-\cdot\mathbf{D}_{\uparrow\downarrow}\cdot\boldsymbol{\mu}_2^+, \end{aligned} \tag{39}$$

where both tensors $\mathbf{D}$ involved have the form

$$D_{ij}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{R}) = \frac{1}{r^5}(r^2\delta_{ij} - 3r_ir_j), \tag{40}$$

with the distance between the interacting dipoles $\mathbf{r}$ being the function of molecular orientation and intermolecular distance: $\mathbf{r}=\mathbf{r}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{R})$. For $\mathbf{D}_{\uparrow\uparrow}$ it reads $\mathbf{r}=\mathbf{R}+\nu\mathbf{a}_2-\nu\mathbf{a}_1$, while for $\mathbf{D}_{\uparrow\downarrow}$ it is $\mathbf{r}=\mathbf{R}+\nu\mathbf{a}_2+\nu\mathbf{a}_1$.

We assume that the tilting of the director in the smectic-C phase is due to the long-axes potential $U^{\text{aa}}(1,2)$. We then employ the following model expression for the uniaxial potential which has been extensively used in the general theory of Sm A–Sm C transition [36,37]:

$$\begin{aligned}U^{\text{aa}}(\mathbf{a}_1,\mathbf{R},\mathbf{a}_2) \approx{}& v_1(R)[(\mathbf{a}_1\cdot\mathbf{u})^2+(\mathbf{a}_2\cdot\mathbf{u})^2]+v_2(R)(\mathbf{a}_1\cdot\mathbf{a}_2)^2\\ &+v_3(R)(\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_1\cdot\mathbf{u})(\mathbf{a}_2\cdot\mathbf{u})\\ &+v_4(R)(\mathbf{a}_1\cdot\mathbf{u})^2(\mathbf{a}_2\cdot\mathbf{u})^2,\end{aligned} \tag{41}$$

As discussed in detail in [36,37] the corresponding mean-field potential

$$\begin{aligned}U^{\text{aa}}_{\text{MF}}(\mathbf{a}) ={}& w_1P_2(\cos\gamma)+w_2S_kP_2(\cos\gamma)+w_3P_k\sin^2\gamma\cos 2\phi\\ &+w_4V\sin 2\gamma\cos\phi,\end{aligned} \tag{42}$$

depends on three order parameters

$$S_k=\langle P_2(\cos\gamma)\rangle,\quad P_k=\langle\sin^2\gamma\cos 2\varphi\rangle, \tag{43}$$

$$V=\langle\sin 2\gamma\cos\varphi\rangle, \tag{44}$$

where γ and φ are the polar and azimuthal angles of the unit vector $\mathbf{a}$, respectively.

If these order parameters are known, conventional order parameters such as nematic order parameter S, nematic tensor biaxiality P, and the tilt angle Θ can be easily calculated as

$$\tan 2\Theta = \frac{V}{S_k-0.5P_k}, \tag{45}$$

$$S=\frac{1}{4}S_k+\frac{3}{8}P_k+\frac{3V}{4\sin 2\Theta}, \tag{46}$$

$$P=\frac{1}{2}S_k+\frac{3}{4}P_k-\frac{V}{2\sin 2\Theta}. \tag{47}$$

The potential (42) promotes the tilt if the nematic order parameter exceeds the critical value

$$S_{\text{AC}}=\frac{3w_1}{4w_4-3w_2}, \tag{48}$$

which means that the growth of the nematic order is the driving force of the tilting transition. Thus in this model the molecular dipoles are not responsible for the tilt of the director, but the interaction between such pairs of dipoles gives rise to the spontaneous polarization as shown below.

One notes that the actual form of the interaction potential for off-center dipoles is too complicated to be used directly in the statistical theory [37]. In particular, substituting the actual potential (39) into Eq. (25) one cannot obtain the mean-field potential as an explicit function of the orientational order parameters. As a result, the free energy cannot be minimized to determine the transition point and the temperature variation of the parameters. However, we can expand the actual dipole-dipole potential in spherical invariants neglecting the higher order terms. One notes that the statistical averages of higher order terms are expressed in terms of higher order orientational order parameters which are normally not important from the qualitative point of view [35]. The details of the expansion procedure are presented in the Appendix.

As shown in the Appendix, the actual interaction potential between the pairs of off-center dipoles can be approximated by the relatively simple expression:

$$\begin{aligned}U^{\Gamma}_{\text{MF}}={}&w_5[\cot\alpha V(\mathbf{a}\cdot\mathbf{k})(\mathbf{b}\cdot\mathbf{t})+\cot\alpha\Gamma\sin 2\gamma\cos\varphi\\ &+\sqrt{2}\Gamma(\mathbf{a}\cdot\mathbf{k})(\mathbf{b}\cdot\mathbf{t})],\end{aligned} \tag{49}$$

which involves the biaxial order parameter $\Gamma=\langle(\mathbf{a}\cdot\mathbf{k})(\mathbf{b}\cdot\mathbf{t})\rangle$. Combining this with the uniaxial mean-field potential (42) we can write the total mean-filed approximation of the LC free energy (24).

Now the orientational order parameters can be evaluated by numerical minimization of the free energy at a given temperature, and the spontaneous polarization can be calculated using the general Eq. (7) for the orientational distribution function (8) and the sum of Eqs. (42) and (49) as the total mean-field potential. Typical results of these calculations are presented in Fig. 6.

Thus the present general theory enables one to calculate the spontaneous polarization explicitly as a function of temperature using the model of rodlike molecules with chiral distribution of dipoles. In this case the ferroelectric ordering also occurs according to the general mechanism described in the previous sections. Indeed, one can readily see from Fig. 6 that the spontaneous polarization is approximately proportional to the order parameter Γ which is mainly determined by the nonchiral part $U_0(1,2)$ of the total interaction potential. At the same time, the spontaneous polarization is proportional to the pseudoscalar parameter $\Delta_\mu \propto (\mathbf{a}\cdot[\boldsymbol{\mu}^+\times\boldsymbol{\mu}^-])$, which, of course, vanishes if the molecules are nonchiral, for example, if both dipoles and the long axis of the molecule presented in Fig. 5 are in the same plane.

V. CONCLUSIONS

In this paper we have used the general statistical theory and two particular molecular models to demonstrate how the ferroelectric ordering of polar and chiral molecules in the smectic-C^* phase may be determined by *nonchiral* intermolecular interactions. It has been shown that if the molecules are characterized by C_{2h} symmetry or lower, the spontaneous polarization is given by the general expression $\mathbf{P}_s=\rho\Delta_\mu\langle\mathbf{a}\times\mathbf{b}\rangle$ [see Eq. (6)], which is an exact result derived without any approximations. Here the parameter $\Delta_\mu=[\boldsymbol{\mu}_\perp\cdot(\mathbf{a}\times\mathbf{b})]$ characterizes the molecular chirality determined by the relative orientation of the transverse molecular dipole and the molecular plane containing the long and short molecular axes, $\mathbf{a}$ and $\mathbf{b}$, respectively. For rigid molecules of C_{2h} symmetry (see Fig. 1), the spontaneous polarization is always

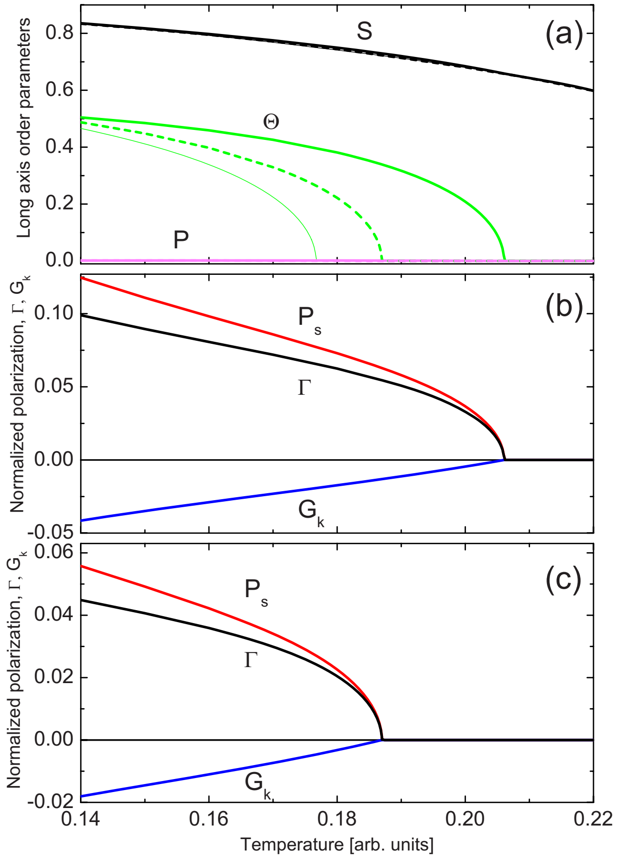

FIG. 6. (Color online) (a) Sm A-Sm C phase transition obtained using the parameters $w_1=-0.05$, $w_2=-1$, $w_3=-0.9$, $w_4=-0.8$, $w_5=0$ (thin lines), $w_5=-0.05$ (dashed), $w_5=-0.1$ (solid), and $\alpha=30°$. Biaxial order parameters Γ and G_k together with the normalized polarization $P_s/\rho\Delta_\mu$ are shown in (b) for the case $w_5=-0.05$ and in (c) for $w_5=-0.1$.

proportional to the pseudovector order parameter $\langle \mathbf{a}\times\mathbf{b}\rangle$ which is nonzero also in the nonchiral smectic-C phase. Thus, if specific chiral and polar intermolecular interactions are not important, the spontaneous polarization is essentially determined by the molecular chirality coefficient Δ_μ and the order parameter $\langle \mathbf{a}\times\mathbf{b}\rangle$ emerging due to nonchiral molecular interactions in the corresponding nonchiral smectic-C phase.

One notes that this general mechanism of ferroelectric ordering corresponds to the one considered in the Boulder model [19,20]. In the Boulder model, a single molecule of sufficiently low symmetry is ordered in the binding cite which plays the role of the effective one-particle (mean-field) potential considered in the present statistical theory. Similar to the effective mean-field potential, the binding site itself has exactly the same symmetry as the nonchiral smectic-C phase (see Fig. 2), i.e., possesses the mirror plane and the twofold symmetry axis and thus is nonchiral. One notes also that, in the first approximation, the ordering of a molecule of the zig-zag shape in the binding site is not determined by its possible chirality. The corresponding nonchiral molecule with a similar overall shape will also order in the same binding site, although no polarization will be created in this case, of course. The ordering of such a nonchiral molecule in the binding site is described by the same nonchiral pseudovector order parameter $\mathbf{w}$ which is considered in this paper. The same general mechanism corresponds also to the one considered in [22–24] for some particular cases. At the same time, the Boulder model as well as the models considered in [22,23] enable one to account for a selection of molecular conformations which fit the site or minimize some interaction potential. This effect is not taken into consideration in the present paper which deals with rigid molecules.

In this paper, the general mechanism of ferroelectric ordering has been illustrated using two particular molecular models. The first model is based on the electrostatic interaction between anisotropic molecular quadrupoles. Here the molecular quadrupole tensor is assumed to be nondiagonal in the molecular frame determined by the molecular axes $\mathbf{a},\mathbf{b}$, and $\mathbf{c}$ (i.e., one of the primary axes of the molecular quadrupole is tilted with respect to the long axis $\mathbf{a}$). The existence of the nonzero off-diagonal element q_3 [see Eq. (21)] determines the C_{2h} symmetry of the molecule. If this off-diagonal element is small, it is possible to expand the orientational distribution function in powers of q_3 and obtain the explicit analytical expression for the spontaneous polarization proportional to q_3. This models shows that the electrostatic quadrupole-quadrupole interaction, which is not sensitive to molecular chirality, may be responsible for the ferroelectric ordering of chiral molecules in the smectic-C^* phase.

Finally, we have considered a more realistic molecular model related to the materials recently synthesized by Lemieux *et al.* [27–30], in which the molecular chirality is mainly determined by the distribution of permanent dipoles. We consider a simple model of a uniaxial rod with two nonparallel off-center dipoles which make approximately an angle of 90°. In this simple case, the pair of permanent dipoles is responsible for both molecular chirality, polarity and biaxiality. The model interaction potential for such molecules is composed of the uniaxial interaction responsible for the tilt in the smectic-C phase, and the electrostatic interaction between all dipoles. We obtain that here the ferroelectric ordering also follows the general mechanism described above, and the spontaneous polarization is proportional to the pseudovector order parameter $\mathbf{w}$. The polarization is also proportional to the pseudoscalar parameter Δ_μ which vanishes if we set the molecule to be nonchiral by placing the two dipoles and the long molecular axis $\mathbf{a}$ within the same plane. One notes that for real materials of the type reported in [27–30], the direct interaction between pairs of dipoles may not be the only cause of spontaneous polarization. Such molecules may also possess a zig-zag shape or have conformational states of the corresponding symmetry. Then the molecule would order in the binding site according to the Boulder model just due to steric interactions, and this will make an additional contribution to the spontaneous polarization. Which contribution is predominant for particular materials can be determined by experiments involving systematic variation of the molecular structure.

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APPENDIX: APPROXIMATION FOR THE ELECTROSTATIC INTERACTION BETWEEN PAIRS OF DIPOLES

Let us consider the electrostatic dipole-dipole interaction (39) between two molecules described in Sec. IV. In order to calculate the corresponding part of the mean-field potential (25), one has first to integrate Eq. (39) over the intermolecular distances. This involves the integrals

$$\bar{\mathbf{D}}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{k}) = \int_{\mathbf{R}\notin\Pi(\mathbf{a}_1,\mathbf{a}_2)} \mathbf{D}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{R})d^2\mathbf{R} \tag{A1}$$

taken over the distances $\mathbf{R}$ within the smectic plane and accounting for the steric cut off between the rigid cores of the molecules with long axes $\mathbf{a}_1$ and $\mathbf{a}_2$.

The tensors (A1) have important properties: They are invariant under the following transformations

$$\mathbf{a}_1 \leftrightarrow \mathbf{a}_2 \quad \text{and } \mathbf{a}_1,\mathbf{a}_2 \leftrightarrow -\mathbf{a}_1,-\mathbf{a}_2, \tag{A2}$$

and are traceless and symmetric:

$$\delta_{ij}\bar{D}_{ij} = 0, \quad \bar{D}_{ij} = \bar{D}_{ji}. \tag{A3}$$

Furthermore, the substitutions

$$\mathbf{a}_1,\mathbf{a}_2 \leftrightarrow -\mathbf{a}_1,\mathbf{a}_2 \quad \text{and } \mathbf{a}_1,\mathbf{a}_2 \leftrightarrow \mathbf{a}_1,-\mathbf{a}_2 \tag{A4}$$

transform $\bar{\mathbf{D}}_{\uparrow\uparrow}$ into $\bar{\mathbf{D}}_{\uparrow\downarrow}$ and vice versa.

We are interested in the orientational interaction containing the lowest possible (i.e., first) power of $\mathbf{a}_{1,2}$. There are four tensorial expressions obeying the above requirements, and thus one can approximately present the tensor $\mathbf{D}$ in the following form:

$$\begin{aligned} r_0\bar{D}_{ij}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{k}) = {} & D_1[a_{1i}a_{2j} + a_{2i}a_{1j} - 2(\mathbf{a}_1\cdot\mathbf{a}_2)\delta_{ij}/3] + (k_ik_j \\ & - \delta_{ij}/3)[D_2(\mathbf{a}_1\cdot\mathbf{a}_2) + D_3(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{a}_2\cdot\mathbf{k})] \\ & + D_4[(\mathbf{a}_1\cdot\mathbf{k})(a_{2i}k_j + a_{2j}k_i) + (\mathbf{a}_2\cdot\mathbf{k})(a_{1i}k_j \\ & + a_{1j}k_i) - 4\delta_{ij}(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{a}_2\cdot\mathbf{k})/3]. \end{aligned} \tag{A5}$$

Note that we have introduced a characteristic scale parameter, molecular breadth r_0, which is used to make the constants D_{1-4} dimensionless.

In order to evaluate the constants D_{1-4} it is convenient to convolute the tensor (A5) with another second rank tensor. There are several possible second-rank tensors which can be constructed from the vectors $\mathbf{a}_1,\mathbf{a}_2$, and $\mathbf{k}$. We use the simple tensor $a_{1i}a_{2j}-\delta_{ij}$, which is orthogonal to the long axes of both molecules in the case of ideal nematic order. It results in a convenient form of the convolution product:

$$\begin{aligned} \tilde{D}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{k}) &= r_0\bar{\mathbf{D}}:(\mathbf{a}_1\ \mathbf{a}_2 - \mathbf{I}) \\ &= D_1 + D_4[(\mathbf{a}_1\cdot\mathbf{k})^2 + (\mathbf{a}_2\cdot\mathbf{k})^2] \\ &\quad + (\mathbf{a}_1\cdot\mathbf{a}_2)^2[D_1/3 - D_2/3] + (\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_1\cdot\mathbf{k}) \\ &\quad \times(\mathbf{a}_2\cdot\mathbf{k})[D_2 - D_3/3 + 2D_4/3] \\ &\quad + D_3(\mathbf{a}_1\cdot\mathbf{k})^2(\mathbf{a}_2\cdot\mathbf{k})^2. \end{aligned} \tag{A6}$$

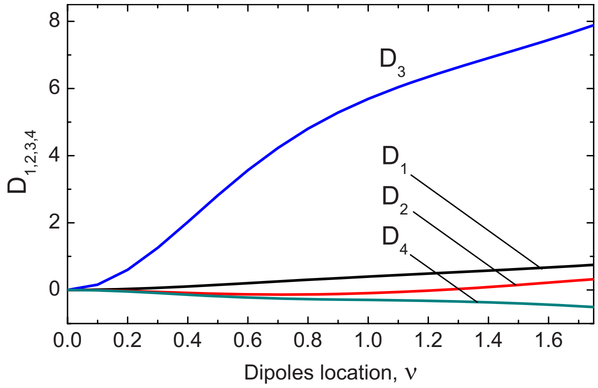

FIG. 7. (Color online) Coefficients D_{1-4} for the tensor $\mathbf{D}_{\uparrow\uparrow}$ as functions of the dipole location on the molecular long axis. The molecular axial ratio is set to be equal to 4.

Equation (A6) can be expressed as a function of the molecular tilting angles $\gamma_{1,2}$ and the difference of molecular azimuthal angles $\phi=\varphi_2-\varphi_1$:

$$\begin{aligned} \tilde{D}(\gamma_1,\gamma_2,\phi) = {} & d_0 + d_1[P_2(\cos\gamma_1) + P_2(\cos\gamma_2)] \\ & + d_2P_2(\cos\gamma_1)P_2(\cos\gamma_2) \\ & + d_3\sin^2\gamma_1\sin^2\gamma_2\cos2\phi \\ & + d_4\sin2\gamma_1\sin2\gamma_2\cos\phi, \end{aligned} \tag{A7}$$

where the coefficients are

$$d_0 = 10D_1/9 - 2D_2/27 + 20D_4/27, \tag{A8}$$

$$d_1 = 2D_2/9 + 4D_3/27 + 22D_4/27, \tag{A9}$$

$$d_2 = 2D_1/9 + 2D_2/9 + 8D_3/27 + 8D_4/27, \tag{A10}$$

$$d_3 = D_1/6 - D_2/6, \tag{A11}$$

$$d_4 = D_1/6 + D_2/12 - D_3/12 + D_4/6. \tag{A12}$$

It is possible to determine the coefficients d_{1-4} by calculating numerically the coefficients of the spherical harmonic representation of $\tilde{D}$ (see, e.g., [36] for details). Then the coefficients D_{1-4} can be expressed as

$$D_1 = -d_1 + 5d_2/4 + 5d_3/3 + 8d_4/3, \tag{A13}$$

$$D_2 = -d_1 + 5d_2/4 - 13d_3/3 + 8d_4/3, \tag{A14}$$

$$D_3 = 9d_2/4 + d_3 - 4d_4, \tag{A15}$$

$$D_4 = 3d_1/2 - 3d_2/4 + d_3. \tag{A16}$$

In Fig. 7 the coefficients D_{1-4} for $\mathbf{D}_{\uparrow\uparrow}$ are presented. They have been calculated for the molecules with ellipsoidal core. One can readily see that the coefficient D_3 clearly dominates in $\mathbf{D}$, and thus one may neglect other coefficients and write

$$\bar{D}_{\uparrow\uparrow ij} \approx r_0^{-1}D_3(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{a}_2\cdot\mathbf{k})(k_ik_j - \delta_{ij}/3). \tag{A17}$$

Obviously, the approximate form (A5) changes sign under the transformations (A4), which means that $\bar{\mathbf{D}}_{\uparrow\downarrow} = -\bar{\mathbf{D}}_{\uparrow\uparrow}$. As a result one can write the integrated interaction energy as

$$\bar{U}_\mu(1,2)=\int U_\mu(1,2)d^2\mathbf{R}=(\boldsymbol{\mu}_1^+-\boldsymbol{\mu}_1^-)\cdot\bar{\mathbf{D}}_{\uparrow\uparrow}\cdot(\boldsymbol{\mu}_2^+-\boldsymbol{\mu}_2^-). \tag{A18}$$

Substituting the dipole moments (36) one arrives at the potential which depends on both long and short molecular axes. The uniaxial part, which depends only on the long axes, provides a small correction to initial uniaxial interaction potential, and we omit it here. Secondly, there is a part which depends on a coupling of the short axes of the two molecules:

$$\bar{U}^{\mathrm{bb}}(1,2)=\frac{2\mu^2}{r_0}D_3\sin^2\alpha(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{a}_2\cdot\mathbf{k})\times\left[(\mathbf{b}_1\cdot\mathbf{k})(\mathbf{b}_2\cdot\mathbf{k})-\frac{1}{3}(\mathbf{b}_1\cdot\mathbf{b}_2)\right]. \tag{A19}$$

Finally, there exists the most important contribution which contains terms describing the coupling of the short axis of one molecule with the long axis of the other. This part is responsible for the induction of biaxial ordering by the tilt of long axes, which is of primary importance for the description of ferroelectricity in the smectic-C^* phase. This part of the potential can be written in the form

$$\bar{U}^{\mathrm{ab}}(1,2)=\frac{\sqrt{2}\mu^2}{r_0}D_3\sin 2\alpha(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{a}_2\cdot\mathbf{k})\left[(\mathbf{b}_1\cdot\mathbf{k})(\mathbf{a}_2\cdot\mathbf{k})+(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{b}_2\cdot\mathbf{k})-\frac{1}{3}(\mathbf{b}_1\cdot\mathbf{a}_2)-\frac{1}{3}(\mathbf{a}_1\cdot\mathbf{b}_2)\right], \tag{A20}$$

The corresponding contribution to the mean-field potential is obtained after averaging of Eqs. (A19) and (A20) over all orientations of the molecule "2," $U_{\mathrm{MF}}(1)=\rho\langle\bar{U}(1,2)\rangle_2$, which yields

$$U_{\mathrm{MF}}^{\mathrm{bb}}(1)=\frac{2\mu^2}{r_0}\rho D_3\sin^2\alpha\times\left[\frac{2}{3}G_k(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{b}_1\cdot\mathbf{k})-\frac{1}{3}\Gamma(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{b}_1\cdot\mathbf{t})\right] \tag{A21}$$

and

$$U_{\mathrm{MF}}^{\mathrm{ab}}(1)=\frac{2\sqrt{2}\mu^2}{9r_0}\rho D_3\sin 2\alpha\Bigg((2S+1)(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{b}_1\cdot\mathbf{k})+G_k[2P_2(\cos\gamma)+1]-\frac{3}{4}V(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{b}_1\cdot\mathbf{t})-\frac{3}{4}\Gamma\sin 2\gamma\cos\varphi\Bigg), \tag{A22}$$

where the order parameters $G_k=\langle(\mathbf{a}\cdot\mathbf{k})(\mathbf{b}\cdot\mathbf{k})\rangle$ and $\Gamma=\langle(\mathbf{a}\cdot\mathbf{k})(\mathbf{b}\cdot\mathbf{t})\rangle$ have been introduced. Apparently, the terms containing $V(\mathbf{a}_1\cdot\mathbf{k})(\mathbf{b}_1\cdot\mathbf{t})$ and $\Gamma\sin 2\gamma\cos\varphi$ induce the biaxial order parameter Γ below the tilting transition.

The order parameter G_k is of minor importance, since it is nonzero already in the Sm A phase. We have found that it is normally of the order of 0.1 and does not affect the transition significantly. The biaxial potential is significantly simplified if one neglects all terms containing G_k and $(\mathbf{a}\cdot\mathbf{k})(\mathbf{b}\cdot\mathbf{k})$. The corresponding simplified mean-field potential can then be written as

$$U_{\mathrm{MF}}^{\Gamma}=w_5[\cot\alpha V(\mathbf{a}\cdot\mathbf{k})(\mathbf{b}\cdot\mathbf{t})+\cot\alpha\Gamma\sin 2\gamma\cos\varphi+\sqrt{2}\Gamma(\mathbf{a}\cdot\mathbf{k})(\mathbf{b}\cdot\mathbf{t})], \tag{A23}$$

where the parameter $w_5=-\sqrt{2}/3\,\rho\mu^2r_0^{-1}D_3\sin^2\alpha$ is negative and can be easily estimated for given values of molecular breadth r_0, 2D molecular number density ρ, dipole strength μ, and dipole orientation angle α. The reasonable values of the constant D_3 are between 4 and 8 (see Fig. 7).

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