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Molecular theory of ferroelectric ordering in enantiomeric mixtures of smectic-C^* liquid crystals

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A molecular theory of ferroelectric ordering in smectic-C^* liquid crystals composed of left and right enantiomers is developed taking into account the effects of chiral discrimination. The recently observed nonlinear dependence of the spontaneous polarization on the enantiomeric excess is explained in the framework of a molecular model that takes into consideration the strong electrostatic interaction between effective atomic charges in the chiral centers of the two enantiomers. This nonlinear dependence is determined by a difference of interaction energies between the pairs of chiral molecules with equal and opposite handedness, respectively. A relation between the molecular structure of different ferroelectric smectics C^* and the dependence of the polarization on the enantiomeric excess is discussed in detail. [S1063-651X(99)10312-X]

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I. INTRODUCTION

Ferroelectricity in smectic-C^* liquid crystals is observed only if the material is chiral. In the case of mixed smectics C^*, however, only a part of the components need to be chiral. For example, a popular way to obtain new ferroelectric liquid crystals is to induce ferroelectricity using a small amount of chiral dopant added to a nonchiral smectic-C host phase [1,2]. Another interesting type of ferroelectric smectics C corresponds to enantiomeric mixtures composed of left- and right-handed chiral molecules. In enantiomeric mixtures the number density of left molecules ρ_L is generally different from the number density of right molecules ρ_R and thus the chirality of the mixture is characterized by the enantiomeric excess $\Delta x=(\rho_R-\rho_L)/\rho_0$, where $\rho_0=\rho_L-\rho_R$ is the total number density.

The importance of enantiomeric mixtures is related to the unique possibility to vary the chirality of the phase continuously by changing the value of the enantiomeric excess. The spontaneous polarization and other ferroelectric properties of the smectic-C^* phase strongly depend on the enantiomeric excess while the nonchiral parameters of the phase are only weakly affected by the nonzero Δx. For example, the smectic-C–smectic-A transition temperature does depend on the enantiomeric excess [3–5] but the maximum shift of the transition temperature ΔT_{AC} is typically within 5% of T_{AC}. Thus enantiomeric mixtures provide a possibility to change ferroelectric properties of the smectic-C^* phase practically without affecting other (nonchiral) parameters of the liquid-crystal material.

Experimental data indicate that usually the spontaneous polarization of an enantiomeric mixture is a linear function of enantiomeric excess [3–5]. This behavior has been observed in several ferroelectric smectics C^* with moderate and large spontaneous polarization. The linear dependence of the polarization on Δx seems to be reasonable and is confirmed by an elementary lattice theory [5]. Moreover, some authors claim that this linear dependence is a general feature that follows from some general physical arguments (see, for example, [6]). Recently, however, strongly nonlinear dependence of the spontaneous polarization on the enantiomeric excess has been observed in mixtures of right- and left-handed molecules with a sulfinate group as a unique chiral source [7]. These new chiral mesogenic molecules have been shown to exhibit rather large values of the spontaneous polarization [8]. The schematic structure of this chiral molecule is presented in Fig. 1 and the experimentally observed nonlinear dependence of the reduced polarization P_s/Θ on the enantiomeric excess Δx is presented in Fig. 2 for three different temperatures. One can readily see that the molecule in

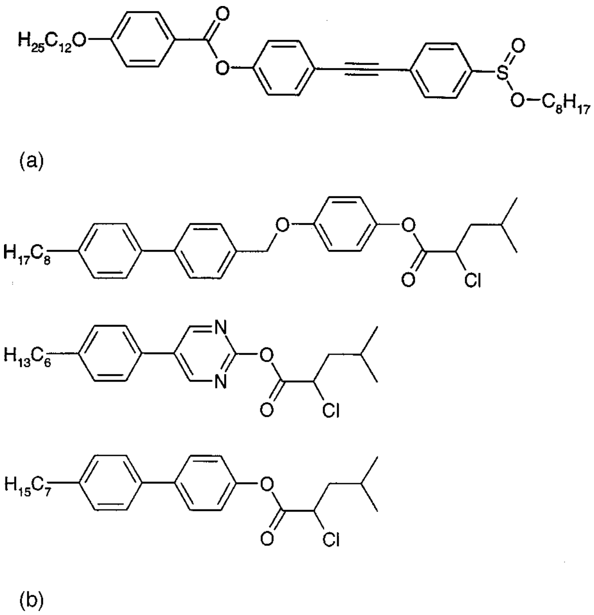

FIG. 1. Structure of chiral mesogenic molecules used in the study of the ferroelectric properties of enantiomeric mixtures [3–7]; (a) smectic liquid crystal material with the sulphinate group as a unique chiral source which yields a nonlinear dependence of polarization on the enantiomeric excess; (b) other chiral liquid crystal materials which yield a linear dependence of polarization on the enantiomeric excess.

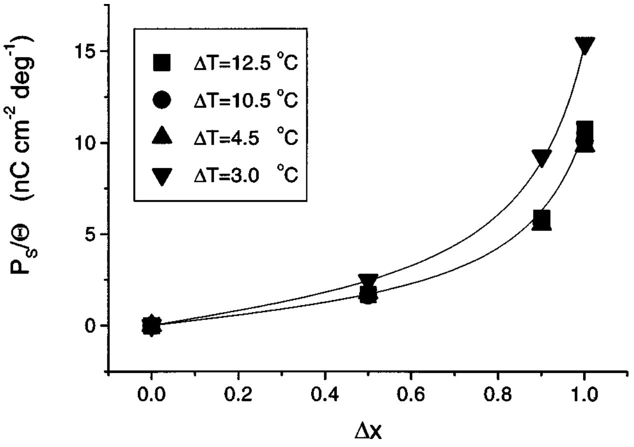

FIG. 2. Dependence of the reduced spontaneous polarization $P_0 = P_s/\Theta$ on the enantiomeric excess for the new liquid crystal material with the sulphinate group presented in Fig. 1(a). Solid curves represent the results of the present theory [see Eq. (15)] for $B = 0.74$ and $A = 0.38$ and 0.4.

Fig. 1(a) possesses a chiral center that differs significantly from the structure of chiral centers in molecules studied before [3–5] [see Fig. 1(b)]. This difference, related to the properties of the sulfinate group, is expected to be responsible for the anomalous behavior of the new material [7]. We note that recently a noninear dependence of the spontaneous polarization on the enantiomeric excess has also been observed in ferroelectric liquid-crystal mixtures of *S* enantiomer and its corresponding racemate, based on the leucine chiral group [9]. In our case, however, the nonlinear dependence is much more pronounced.

The purpose of this paper is to show that the possibility of a nonlinear dependence of the spontaneous polarization on the enantiomeric excess follows from the general statistical theory of ferroelectric ordering in mixed smectics C^*. Another purpose is to understand why in some cases the observed dependence is practically linear. The answer to this question is obviously related to the specific properties of the new chiral center with a sulfinate (or some other specific) group. However, before discussing this point in more detail, we consider the general qualitative arguments that are used to prove the universality of the linear dependence of the polarization on the enantiomeric excess.

According to the phenomenological theory of ferroelectric liquid crystals [10], the spontaneous polarization in the smectic-C^* phase is given by

$$P_s = \chi_\perp \mu_p \sin 2\Theta, \tag{1}$$

where Θ is the tilt angle, the pseudoscalar parameter μ_p is sensitive to molecular chirality, and $\chi_\perp$ is the transverse dielectric susceptibility of the smectic-C^* phase.

In the general case all coefficients in Eq. (1) depend on the enantiomeric exess. However, the experimental data correspond to the concentration dependence of the reduced polarization $P_0 = P_s/\Theta$ and therefore there is no need to consider the concentration dependence of the tilt angle (at least at small Θ). It is reasonable to assume (and the assumption is confirmed by the molecular theory of ferroelectric ordering in mixed smectics C^* [10–12]) that the coefficient μ_p is determined by some pairwise interactions between chiral and polar molecules. Then, in the first approximation, μ_p can be written as a quadratic form of the molar fractions $x_L = \rho_L/\rho_0$, $x_R = \rho_R/\rho_0$ of the two enantiomers:

$$\mu_p = \mu_{LL} x_L^2 + 2\mu_{LR} x_R x_R + \mu_{RR} x_R^2 + \mu_L x_L + \mu_R x_R, \tag{2}$$

where the coefficients $\mu_{\alpha\beta}$, $\alpha,\beta = L,R$ are determined by an interaction between the molecules of the components α and β and the coefficients μ_α describe an interaction with the rest of the media (i.e., the interaction that does not distinguish between left and right enantiomers [13]).

Using the relationship $x_L + x_R = 1$, the linear terms in Eq. (2) can be rewritten as $\mu_L x_L + \mu_R x_R = (\mu_L + \mu_R)/2 + \Delta\mu \Delta x$, where $\Delta x = x_L - x_R$ is the enantiomeric excess and $\Delta\mu = (\mu_L - \mu_R)/2$. Now it is possible to establish some relations between the coefficients of Eq. (2) using the symmetry properties of enantiomeric mixtures.

First, let us consider one-component smectics C^*, composed of pure left-handed or right-handed enantiomers, respectively. These two systems are completely equivalent in their properties and can be transformed into each other by a space inversion. The spontaneous polarization in these two systems must have the same absolute value and possess opposite signs,

$$P_s(x_L = 1) = -P_s(x_R = 1).$$

From Eqs. (1) and (2) we conclude that $\mu_p(x_L = 1,\ x_R = 0) = -\mu_p(x_L = 0,\ x_R = 1)$ and therefore

$$\mu_{LL} + \mu_L = -\mu_{RR} - \mu_R.$$

Now let us consider the racemic mixture of the same compounds. In this mixture the polarization must vanish, i.e., $P_s(x_L = x_R = 1/2) = 0$, and thus $\mu_p = 0$ for $x_L = x_R$. It follows then that

$$\mu_{LL} + \mu_{RR} + 2\mu_{LR} + 2(\mu_L + \mu_R) = 0.$$

Using these relationships and the condition $x_L + x_R = 1$, Eq. (2) can be rewritten as

$$\mu_p = (\mu_{LL} + \mu_L)\Delta x + \frac{1}{4}(\mu_L + \mu_R - 2\mu_{LR})(\Delta x)^2. \tag{3}$$

One notes that the spontaneous polarization of the enantiomeric mixture must be an odd function of the enantiomeric excess (because the states with $\Delta x = \Delta_0$ and $\Delta x = -\Delta_0$ can be considered as mirror images). Then the coefficient in the second term in Eq. (3) must vanish, i.e., $2\mu_{LR} = \mu_L + \mu_R$. Finally one ontains $\mu_{LL} = -\mu_{RR}$, $\mu_L = -\mu_R$, and $\mu_{LR} = 0$.

Thus we arrive at the conclusion that the reduced spontaneous polarization P_0 should simply be proportional to the enantiomeric exess Δx:

$$P_0 = \chi_\perp \mu_0 \Delta x, \tag{4}$$

where $\mu_0 = \mu_{LL} + \mu_L = -\mu_{RR} - \mu_R$. We note that the same qualitative result has been obtained by Ginzburg *et al.* [5] in the framework of a simple model.

The qualitative arguments presented above seem to be rather general. However, it is obvious that they are based on the following two main assumptions

(i) The coefficient μ_p is assumed to be determined by pair intermolecular correlations (by pair interactions in the mean-field theory). Thus many-body effects are neglected.

(ii) The dielectric susceptibility $\chi_\perp$ is assumed to be independent on the enantiomeric exess.

The assumption (i) seems to be reasonable. In the general case there can be some contribution from many-body correlations to the spontaneous polarization, but this contribution is not expected to be large enough to account for the strongly nonlinear concentration dependence of the reduced polarization observed in the experiment. At the same time the assumption (ii) is not justified because we cannot exclude a sufficiently strong dependence of the transverse dielectric susceptibility on the enantiomeric excess. We note that any dependence on the square of the enantiomeric excess $\chi_\perp = \chi_\perp[(\Delta x)^2]$ will not be in contradiction with the symmetry properties of enantiomeric mixtures. One can argue that usually nonchiral parameters of enantiomeric mixtures only weakly depend on the enantiomeric excess. At the same time it is possible to present simple contradicting examples. For example, the excluded volumes for the two left-handed (or right-handed) molecules can differ significantly from the excluded volume for a pair composed of one left-handed and one right-handed molecule if the molecular shape is strongly chiral.

In this paper we show that the strong dependence of $\chi_\perp$ on $(\Delta x)^2$ can be determined by a strong discrimination in interaction between the molecules of equal and opposite handedness, respectively. For new chiral molecules with a sulfinate group this discrimination mainly results from electrostatic forces between effective atomic charges. Numerical calculations show that the separation of charges in the vicinity of the chiral sulfur is much stronger than that in the chiral centers of common ferroelectric smectics C^* which have been investigated before.

This paper is arranged as follows. In Sec. II we present the general statistical theory of ferroelectric ordering in enantiomeric mixtures using the approach developed by one of the authors before [12] and derive a general expression for the spontaneous polarization as a function of the enantiomeric excess. In Sec. III we consider a chiral discrimination that is responsible for the nonlinear dependence of the polarization on the enantiomeric excess. In Sec. IV electrostatic interactions between chiral molecules in the smectic-C layer are considered in detail and the estimates are given for the parameter that is responsible for the nonlinear dependence of $\mathbf{P}_s$ on Δx. Finally, Sec. V contains discussion and conclusions. In Appendix A we consider the density-functional approach to the theory of ferroelectric liquid-crystal mixtures and derive some general expressions that are used in Sec. II.

II. THEORY OF FERROELECTRIC ORDERING IN A MIXTURE OF TWO ENANTIOMERS

Let us consider a mixture of two enantiomeric smectic-C^* liquid crystals with the molar fractions x_L and x_R (for left-handed and right-handed compounds, respectively). The spontaneous polarization of the mixture can be written in the general form

$$\mathbf{P} = \mathbf{P}_L + \mathbf{P}_R, \tag{5}$$

where $\mathbf{P}_L$ and $\mathbf{P}_R$ are the contributions from left-handed and right-handed molecules, respectively. These contributions are expressed as

$$\begin{aligned} \mathbf{P}_L &= \rho_0 x_L \langle \boldsymbol{\mu}_{L\perp} \rangle, \\ \mathbf{P}_R &= \rho_0 x_R \langle \boldsymbol{\mu}_{R\perp} \rangle, \end{aligned} \tag{6}$$

where $x_L + x_R = 1$, ρ_0 is the total number density of molecules in the smectic-C^* phase and $\boldsymbol{\mu}_\perp$ is the transverse molecular dipole. The brackets $\langle\ \rangle$ denote the statistical averaging.

The average molecular dipole can more explicitly be written as

$$\langle \boldsymbol{\mu}_{\perp\alpha} \rangle = \int \boldsymbol{\mu}_{\perp\alpha} f_{1\alpha}(\mathbf{x}) d\mathbf{x}, \tag{7}$$

where $\alpha = R,\ L$, and $f_{1\alpha}(\mathbf{x})$ is the orientational distribution function. The variable $\mathbf{x}$ specifies the molecular orientation.

General expression for the one-particle distribution function can be obtained using the density-functional approach [14]. For the case of mixtures of liquid crystals, this approach is described in Appendix A (see also [12]). As shown in Appendix A, the one-particle distribution function can be written in the form

$$\begin{aligned} f_{1L}(\mathbf{x}) &= Z_L^{-1} \exp[x_L C_{LL}(\mathbf{x}) + x_R C_{LR}(\mathbf{x})], \\ f_{1R}(\mathbf{x}) &= Z_R^{-1} \exp[x_L C_{LR}(\mathbf{x}) + x_R C_{RR}(\mathbf{x})], \end{aligned} \tag{8}$$

where the effective one-particle potentials are expressed as

$$C_{\alpha\beta}(\mathbf{x}_1) = \rho_0 \int \tilde{C}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2) f_{1\beta}(\mathbf{x}_2) d\mathbf{x}_2, \tag{9}$$

and where $\tilde{C}_{\alpha\beta}(\mathbf{x}_1, \mathbf{x}_2)$ is the direct pair correlation function for the molecules of the compounds α and β, averaged over the relative position of the two molecules in the smectic-C^* phase (see Appendix A).

At small tilt angles Θ the spontaneous polarization is also small and in this domain one can expand the effective potentials $C_{\alpha\beta}(\mathbf{b})$ in powers of the vector order parameter of the smectic-C^* phase $\mathbf{w}$ and the spontaneous polarization $\mathbf{P}$:

$$C_{\alpha\beta}(\mathbf{b}) = C_{\alpha\beta}^A + (\mathbf{S}_\alpha \cdot \mathbf{w}) + (\mathbf{G}_{\alpha\beta} \cdot \mathbf{P}_\beta) x_\beta^{-1} + \cdots, \tag{10}$$

where

$$\mathbf{w} = (\mathbf{n} \cdot \mathbf{e})[\mathbf{n} \times \mathbf{e}],$$

and where $C_{\alpha\beta}^A$ $(\alpha,\beta = L,R)$ are the effective one-particle potentials in the smectic-A phase, the unit vector $\mathbf{e}$ is in the direction of the smectic plane normal, and $\mathbf{n}$ is the director. In Eq. (10) we have taken into account only the first-order terms in Θ (we note that $w \propto \Theta$ and $P_\beta \propto \Theta$ at small Θ). The quantities $\mathbf{S}$ and $\mathbf{G}_{\alpha\beta}$ depend on the short axis $\mathbf{b}$ and are functions of the molecular parameters.

We note that the second term in Eq. (10) is sensitive to molecular chirality. The order parameter **w** is a pseudovector and therefore the quantity $\mathbf{S}_\alpha$ must also be a pseudovector because the potential itself is a true scalar. Thus the quantity $\mathbf{S}_\alpha$ represents somehow the chirality of the mixture.

Substituting Eq. (10) into Eqs. (7) and (8) and expanding the exponent in powers of small order parameter **w** and polarization **P**, we obtain the following equations for the two contributions to the total spontaneous polarization:

$$\begin{aligned}\mathbf{P}_L=&\tfrac{1}{2}\rho_0 x_L[x_L(\mathbf{S}_L\cdot\boldsymbol{\mu}_{\perp L})+x_R(\mathbf{S}_R\cdot\boldsymbol{\mu}_{\perp L})]\mathbf{w}\\&+\tfrac{1}{2}\rho_0 x_L[G_{LL}\mathbf{P}_L+G_{LR}\mathbf{P}_R],\\ \mathbf{P}_R=&\tfrac{1}{2}\rho_0 x_R[x_R(\mathbf{S}_R\cdot\boldsymbol{\mu}_{\perp R})+x_L(\mathbf{S}_L\cdot\boldsymbol{\mu}_{\perp R})]\mathbf{w}\\&+\tfrac{1}{2}\rho_0 x_R[G_{RR}\mathbf{P}_R+G_{RL}\mathbf{P}_L],\end{aligned}\tag{11}$$

where $G_{\alpha\beta}=(\mathbf{G}_{\alpha\beta}\cdot\boldsymbol{\mu}_{\perp\beta})$.

Now it is possible to establish some relations between the quantities S_L and S_R and G_{LL}, G_{LR}, and G_{RR}, respectively, using the general symmetry properties of the enantiomeric mixture. The symmetry arguments, that are used here, are similar to the ones discussed in the Introduction. First one notes that the systems with $x_L=1$ and $x_R=1$, respectively, can be considered as mirror images, and therefore $P_L(x_L=1)=-P_R(x_R=1)$. On the other hand, in a racemic mixture ($x_L=x_r=1/2$) the total polarization vanishes and therefore one again arrives at $\mathbf{P}_L=-\mathbf{P}_R$. These relations are compatible with Eqs. (11) only if

$$(\mathbf{S}_L\cdot\boldsymbol{\mu}_{\perp L})=-(\mathbf{S}_R\cdot\boldsymbol{\mu}_{\perp R});$$

$(\mathbf{S}_L\cdot\boldsymbol{\mu}_{\perp R})+(\mathbf{S}_R\cdot\boldsymbol{\mu}_{\perp L})$ and $G_{LL}-G_{LR}+G_{RL}-G_{RR}=0$.

We note that the parameters $G_{\alpha\beta}$ are true scalars and thus $G_{LL}=G_{RR}$ because the two enantiomers are completely equivalent. It follows then from Eqs. (11) that $G_{LR}=G_{RL}$.

Introducing the notations $C=(\mathbf{S}_L\cdot\boldsymbol{\mu}_{\perp L})=-(\mathbf{S}_R\cdot\boldsymbol{\mu}_{\perp R})$, $G=G_{LL}=G_{RR}$, $=G_1=G_{LR}=G_{RL}$, one can rewrite Eqs. (11) in the following simple way:

$$\begin{aligned}\mathbf{P}_L&=\tfrac{1}{2}\rho_0 x_L[C\mathbf{w}+G\mathbf{P}+\Delta G\Delta\mathbf{P}],\\ \mathbf{P}_R&=\tfrac{1}{2}\rho_0 x_R[-C\mathbf{w}+G\mathbf{P}-\Delta G\Delta\mathbf{P}],\end{aligned}\tag{12}$$

where $\Delta\mathbf{P}=\mathbf{P}_L-\mathbf{P}_R$, $G=(1/2)(G_0+G_1)$, $\Delta G=(1/2)(G_0-G_1)$.

The system of the two equations (12) can readily be solved to yield the expression for the total polarization:

$$\mathbf{P}=\tfrac{1}{2}\chi_0\rho_0 C\Delta x\mathbf{w},\tag{13}$$

where

$$\chi_0^{-1}=(1-\tfrac{1}{2}\rho_0 G)(1-\tfrac{1}{2}\rho_0\Delta G)-\tfrac{1}{4}\rho_0^2 G\Delta G(\Delta x)^2,\tag{14}$$

where $\Delta x=x_L-x_R$ is the enantiomeric excess.

One can readily see that the results of the statistical theory confirm the results of the phenomenological consideration and the assumptions discussed in the Introduction. Indeed, according to Eq. (13) the spontaneous polarization is proportional to the enantiomeric excess Δx. At the same time, the transverse dielectric permittivity χ_0 appears to be a quadratic function of Δx. As a result, the reduced polarization $P_0=P/\sin 2\Theta$ also appears to be a nonlinear function of the enantiomeric excess:

$$P_0=\frac{A\Delta x}{1-B(\Delta x)^2},\tag{15}$$

where

$$\begin{aligned}A&=\tfrac{1}{2}\rho_0 G/(1-\tfrac{1}{2}\rho_0 G)(1-\tfrac{1}{2}\rho_0\Delta G),\\ B&=\tfrac{1}{4}\rho_0^2 G\Delta G/(1-\tfrac{1}{2}\rho_0 G)(1-\tfrac{1}{2}\rho_0\Delta G).\end{aligned}\tag{16}$$

The dependence of the reduced polarization on the enantiomeric excess, given by Eq. (15), has qualitatively the same form as that observed in the experiment [7]. In Fig. 2 the experimental values of P_0 are presented as a function of the enantiomeric excess for four different temperatures not very far from the smectic-A^*–smectic-C^* transition point. The two solid curves in Fig. 2 represent the results of the present theory [Eq. (15)] for $B=0.74$ and $A=2.8;4$. One can readily see that Eq. (15) provides a reasonably good description of the experimental nonlinear dependence of P_0 on the enantiomeric excess for all temperatures used in the experiment. The experimental values of P_0 for $\Delta T=4.5\,°\mathrm{C}$, $\Delta T=10.5\,°\mathrm{C}$, and $\Delta T=12.5\,°\mathrm{C}$ have been fitted by Eq. (15) using the same values of parameters A and B. We note that for $\Delta T=3.0\,°\mathrm{C}$ (i.e., closer to the transition point) the dependence of P_0 on Δx can also be described by Eq. (15) (see the second solid curve in Fig. 2) but with a slightly higher value of the coefficient $A=4$. This indicates that there may be some additional dependence of the reduced polarization on the tilt angle Θ which is not accounted for in the present theory.

III. CHIRAL DISCRIMINATION IN RACEMIC MIXTURES OF SMECTICS *C*

The nonlinear dependence of the reduced polarization on the enantiomeric excess is determined by the parameter $\Delta G=(1/2)(G_{RR}-G_{LR})$ that characterizes the difference in interactions between the molecules of the same handedness (parameter G_{RR}) and the molecules of the opposite handedness (parameter G_{LR}). The parameter ΔG is nonzero in the general case but its absolute value strongly depends on the chiral molecular structure. In this section we obtain some estimates of ΔG in the mean-field approximation.

General expressions for the coefficients G_{RR} and G_{LR} in the case of perfect nematic and smectic ordering are derived in the Appendix [see Eq. (A10)]:

$$
\begin{aligned}
G_{RR}&=\frac{1}{2\pi^2\rho\mu_\perp^2}\int \tilde{C}_{RR}(\mathbf{b}_1,\mathbf{b}_2)(\boldsymbol{\mu}_{\perp 1}\cdot\boldsymbol{\mu}_{\perp 2})d\mathbf{b}_1 d\mathbf{b}_2,\\
G_{LR}&=\frac{1}{2\pi^2\rho\mu_\perp^2}\int \tilde{C}_{LR}(\mathbf{b}_1,\mathbf{b}_2)(\boldsymbol{\mu}_{\perp 1}\cdot\boldsymbol{\mu}_{\perp 2})d\mathbf{b}_1 d\mathbf{b}_2,
\end{aligned}
\tag{17}
$$

where $\tilde{C}_{RR}(\mathbf{b}_1,\mathbf{b}_2)$ and $\tilde{C}_{LR}(\mathbf{b}_1,\mathbf{b}_2)$ are the effective direct correlation functions for the R-R and L-R pairs, respectively, which depend on the orientation of the short axes $\mathbf{b}_1$ and $\mathbf{b}_2$ of the molecules ''1'' and ''2.'' These correlation functions have already been averaged over all relative positions of the neighboring molecules in the ideal smectic structure [see Eq. (A7) of the Appendix].

Simple estimates for the quantities G_{RR} and G_{LR} can be obtained in the mean-spherical approximation. In this approximation the direct correlation function is expressed in terms of the attraction intermolecular interaction energy $V_{\text{att}}(1,2)$ and the molecular shape:

$$
C_{\alpha\beta}=-\frac{1}{kT}V_{\text{att}}^{\alpha\beta}(1,2)\Theta(r_{12}-\xi_{12}^{\alpha\beta}). \tag{18}
$$

Here $\Theta(r_{12}-\xi_{12}^{\alpha\beta})$ is a step function which describes the so-called steric cutoff. The function $\Theta(r_{12}-\xi_{12}^{\alpha\beta})=0$ if the molecules penetrate each other (i.e., if $r_{12}<\xi_{12}^{\alpha\beta}$) and $\Theta(r_{12}-\xi_{12}^{\alpha\beta})=1$ otherwise. Here $\xi_{12}^{\alpha\beta}$ is the minimum distance of approach between the centers of the two molecules with fixed relative orientation. Thus the function $\xi_{12}^{\alpha\beta}$ depends on the relative orientation of the molecules.

We note that only intermolecular interactions of a particular symmetry contribute to the parameters $G_{\alpha\beta}$. One can readily see from Eqs. (17) that the integrals over $\mathbf{b}_1$ and $\mathbf{b}_2$ do not vanish only if the attraction potential $V_{\text{att}}^{\alpha\beta}(\mathbf{b}_1,\mathbf{b}_2)$ is odd both in $\mathbf{b}_1$ and in $\mathbf{b}_2$. Thus the interaction is supposed to be polar.

IV. ELECTROSTATIC INTERACTION BETWEEN CHIRAL CENTERS IN THE SMECTIC-*C* LAYER

The parameter $\Delta G=G_{LR}-G_{LL}$ that characterizes the chiral discrimination [see Eqs. (17)] can be sufficiently large only if the interaction between two equal chiral molecules differs significantly from the interaction between molecules of the opposite handedness. In this paper we assume that this discrimination is mainly determined by electrostatic forces between effective atomic charges in the vicinity of a chiral center. This assumption is confirmed by numerical MNDO calculations of the parameters of the molecular structure including effective charges. The effective atomic charges around the chiral center are shown in Fig. 3 for different molecules of ferroelectric smectics C^*. One can readily see from Fig. 3(a) that in the molecule of the new ferroelectric smectic C^* with the sulfinate group as a unique chiral source (that shows nonlinear dependence of P_s on the enantiomeric excess) there exists a strong separation of charges around the sulfur atom in the chiral center. In particular, the oxygen that goes out of the molecular plane possesses a large effective negative charge of about $-0.8e$. By contrast, in molecules of common ferroelectric smectics (that show a linear dependence of P_s on enantiomeric excess [3–5]) the separation of charges around the chiral center is much weaker. In fact, the charge separation along the $S^*=O$ bond in the chiral center of the molecule in Fig. 3(a) is about $1.6e$, while the separation along the C^*-Cl bond in the chiral center of the molecule in Fig. 3(b) is less than $0.2e$. This difference is becoming even more important if we take into account that electrostatic forces depend quadratically on charges.

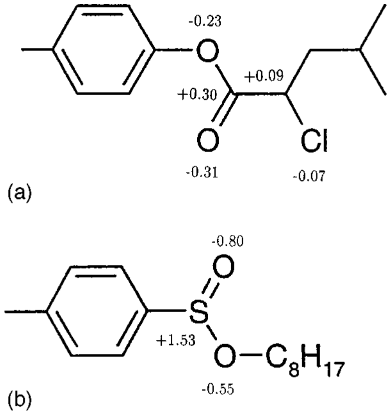

FIG. 3. Distribution of effective atomic charges around the chiral center in the molecule with the sulphinate group as a unique chiral source (a) and in a chiral molecule with an asymmetric carbon (b). Note that the charge separation in the chiral center is much stronger in the case (a).

The data presented in Fig. 3 enable one to understand in principle why some properties of ferroelectric smectics composed of molecules with a sulfinate group in the chiral center differ significantly from those of common ferroelectric liquid crystals with different structure of the chiral center. We now consider in more detail the contribution from electrostatic interaction between chiral centers to the discrimination parameter ΔG. For this purpose we estimate the quantities G_{LL} and G_{LR} taking into account the interaction between effective charges in the chiral centers of the two molecules. In these estimates we will use the simple molecular model presented in Fig. 4.

In this simple model the molecular chirality is determined

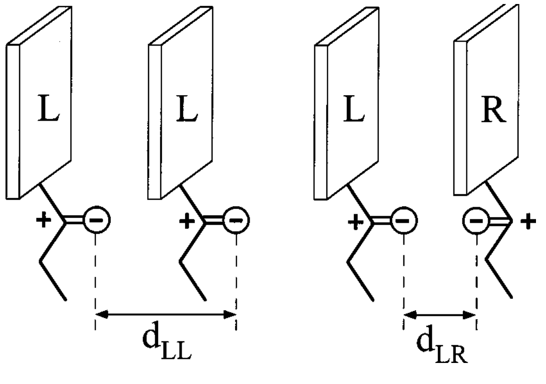

FIG. 4. Two pairs of neighboring chiral molecules in the smectic-*C* layer. In this model the molecular chirality is determined by the negative charge that goes out of the molecular plain. Note that in the first pair, which is composed of molecules of the same handedness, the distance between the negative charges is larger than in the second pair composed of molecules of the opposite handedness.

by the effective charge [associated with the oxygen atom in Fig. 3(a)] that goes out of the plane of the rings. Thus, in the estimate of the chiral discrimination it is sufficient to take into account the electrostatic interaction between these charges. Other charges in this molecular fragment are located in the plane and therefore they do not contribute to the discrimination of the interaction between L-L and L-R pairs.

The electrostatic interaction between the two charges of the neighbor molecules is written as

$$U_{\mathrm{el}}=\frac{q^2}{R_{12}},$$

where R_{12} is a complicated function of the relative orientation and position of the two molecules in the smectic layer.

To perform simple estimates we assume that the planes of the rings of the two neighbor molecules are parallel and the average distance between rings is equal to R_0. We also assume the perfect nematic ordering of the long molecular axes. In this case the distance between the charges R_{12} can be written as

$$\mathbf{R}_{12}^{\alpha\beta}=R_0\mathbf{u}_{12}+l_{\|}(\mathbf{a}_1-\mathbf{a}_2)+l_{\perp}(\mathbf{b}_1-\mathbf{b}_2)+h_\alpha\mathbf{c}_1-h_\beta\mathbf{c}_2, \tag{19}$$

where $\mathbf{u}_{12}$ is the unit vector pointing from the center of the ring system of the molecule ''1'' to that of the molecule ''2,'' the unit vector $\mathbf{a}$ is in the direction of the long molecular axis, and the unit vectors $\mathbf{b}$ and $\mathbf{c}$ are in the direction of the two short molecular axes, $(\mathbf{b}\cdot\mathbf{c})=\mathbf{0}$. The vector $\mathbf{b}$ is taken to be parallel to the molecular plane. In Eq. (19), the vector $\mathbf{a}_1 l_{\|}+\mathbf{b}_1 l_{\perp}$ points from the center of the ring system to the projection of the charge on the same plane and therefore $l_{\|}$ and $l_{\perp}$ are the corresponding coordinates of the projection point in the molecular frame. Finally, h_α is the distance from the charge to the plane. Here $\alpha,\beta=L,R$ and the parameters h_α, h_β possess opposite signs for left and right molecules. In the case of the perfect nematic ordering the long molecular axes are parallel to the director $\mathbf{n}$ and therefore $\mathbf{a}=\eta\mathbf{n}$, where $\eta=+1,-1$ is the discrete variable.

Now we substitute Eq. (19) into the expression for the electrostatic energy and then into the general Eq. (17). We then perform the averaging over the intermolecular vector $\mathbf{u}_{12}$ and over the orientations of the short axes of the two molecules. The averaging over the short axes $\mathbf{b}_1$ and $\mathbf{b}_2$ is simplified in the case when the molecular planes are always parallel. In this case $(\mathbf{b}_1\cdot\mathbf{b}_2)=1$ or $(\mathbf{b}_1\cdot\mathbf{b}_2)=-1$.

We note that the distance between the charges strongly depends on the orientation of the intermolecular unit vector $\mathbf{u}_{12}$. The integral over $\mathbf{u}_{12}$ can be estimated by using a linear interpolation between the orientations $\mathbf{u}_{12}=\mathbf{b}_1$ and $\mathbf{u}_{12}=\mathbf{c}_1$. In this case one can use the effective interaction energy

$$U_{\mathrm{el}}=\frac{1}{2}\frac{q^2}{R_{12}^{+}}+\frac{1}{2}\frac{q^2}{R_{12}^{-}}, \tag{20}$$

where the distances R_{12}^{+} and R_{12}^{-} are given by Eq. (19) with $\mathbf{u}_{12}=\mathbf{b}_1$ and $\mathbf{u}_{12}=\mathbf{c}_1$, respectively.

Finally the transverse molecular dipole $\boldsymbol{\mu}$ [that enters Eq. (17)] can be expressed as

$$\boldsymbol{\mu}=\mu_x\mathbf{b}+\mu_y\mathbf{c}. \tag{21}$$

Substituting Eqs. (20) and (21) into Eq. (17), assuming $\mu_y=0$, and averaging over the orientation of the short axes $\mathbf{b}_1$ and $\mathbf{b}_2$ we obtain the estimate

$$\begin{aligned}\rho_0 G_{LL}&\sim\frac{1}{6}\frac{\sigma q^2}{kT}\left(\frac{1}{R_0}-\frac{1}{R_0-2h+l_\perp}\right),\\ \rho_0 G_{LR}&\sim\frac{1}{4}\frac{\sigma q^2}{kT}\left(\frac{1}{R_0-2h}-\frac{1}{R_0+l_\perp}\right),\end{aligned} \tag{22}$$

where σ is the fraction of nearest neighbors which are located in the same smectic-C layer.

Assuming that $h\ll R_0$ and $l_\perp\ll R_0$, the parameter ΔG that characterizes the chiral discrimination can be estimated as

$$\rho_0\Delta G\sim\frac{\sigma q^2 h}{3R_0^2 kT}. \tag{23}$$

We note that the parameter ΔG is mainly determined by the value of the effective charge q and the distance h from this charge to the molecular plane. The distance h can be estimated as 1 Å while the average distance R_0 between molecules in the smectic layer is of the order of 10 Å. Thus the ratio h/R_0 in Eq. (23) is of the order of 10^{-1}. Now the value of ΔG is determined by the value of the dimensionless parameter q^2/kTR_0, which grows as a square of the effective charge q. In the molecule with a sulfinate group in the chiral center, the effective charge of the oxygen atom is rather large, $q\sim0.8$. In this case the parameter $q^2/kTR_0\sim40$ and the chirality discrimination parameter $\rho_0\Delta G\sim1$ for $\sigma=3/4$. By contrast, in the molecules of common ferroelectric smectics C^*, presented in Fig. 3, the effective charge q is much smaller and the parameter $q^2/kTR_0\sim0.6$. In this case $\rho_0\Delta G\sim10^{-2}$.

Equations (22) can also be used to obtain a crude estimate of the coefficient G. Taking $l_\perp=1$ Å, one obtains $\rho_0 G\sim0.5$. Now the coefficient B in Eq. (15) can be estimated using the estimates of the quantities $\rho_0\Delta G$ and $\rho_0 G$. Taking $\rho_0\Delta G=\rho_0 G=1$ we obtain $B=1$, which is rather close to the value 0.75 which has been obtained by fitting the experimental data. We note, however, that the estimates for $\rho_0 G$ and B are rather crude and should not be taken too seriously. The coefficient G is mainly determined by the average polar interaction between different molecular pairs in the enantiomeric mixture. This coefficient is a sum of various contributions, some of them being not sensitive to molecular chirality. In the context of the present simple model we can estimate only one particular contribution, which may not be the predominant one. The coefficient B strongly depends on G and, in addition, it is very sensitive to the particular numerical values of $\rho_0 G$ and $\rho_0\Delta G$ when both $\rho_0 G\sim1$ and $\rho_0\Delta G\sim1$. By contrast, the coefficient ΔG is determined by molecular chirality and is much more specific than G. We assume that in the present case ΔG is mainly determined by the electrostatic interaction between effective charges around the chiral centers of molecules presented in Fig. 1. Thus the value of the parameter ΔG seems to be a reasonable measure of the chiral discrimination in different ferroelectric smectics C^*.

We note that the nonlinear dependence of the spontaneous polarization on the enantiomeric excess can be sufficiently strong only if the parameter ΔG is of the order of 1. According to Eq. (23) this is achieved only if the effective charge q is sufficiently large. This explains why the nonlinear dependence of P_s on the enantiomeric excess has been observed in ferroelectric smectics composed of molecules with a sulfinate group that is characterized by a strong effective charge separation around the chiral sulfur.

V. DISCUSSION

In this paper we have considered in detail the dependence of the spontaneous polarization in the smectic-C^* phase on the enantiomeric excess. Both phenomenological arguments and the results of the molecular-statistical theory confirm that the polarization is always proportional to the enantiomeric excess Δx. The same result has been obtained before by Ginzburg *et al.* [5] using a simple lattice model. We note that this result is not related to any molecular model. Actually, it follows from the general fact that the spontaneous polarization must vanish in a racemic mixture and must possess opposite signs in the systems composed of pure left-handed and right-handed enantiomers, respectively. However, according to the molecular theory, presented in Sec. II, there exists an additional dependence of the polarization on the square of the enantiomeric excess. This additional nonlinear dependence is determined by the chiral discrimination, i.e., by a difference in interaction between the pairs of chiral molecules with equal and opposite handedness, respectively. Similar ideas have been used in the qualitative explanation of the nonlinear dependence $P_s(\Delta x)$ observed recently for molecules with a different structure of the chiral center [9]. In Ref. [9], however, the authors take into consideration a difference between host-host, host-dopant, and dopant-dopant interactions, where one enantiomer plays the role of a dopant and its racemate is treated as a nonchiral host. Thus this model is more suitable for a description of the dependence of polarization on the enantiomeric excess *in chiral dopant* added to a nonchiral smectic-C host [15].

We note that the difference in interaction energy between two enantiomers is nonzero for any chiral molecules. However, this discrimination will result in any noticeable nonlinear dependence on the enantiomeric excess only if the difference in intermolecular interaction energies is sufficiently large. We note that generally this difference is expected to be rather small and thus the effects of the chiral discrimination will be sufficiently important only if there exist some specific strong interactions between chiral molecules. In this paper we have concluded that the observed nonlinear dependence of the polarization on Δx can be related to the fact that in new chiral molecules with a sulfinate group one finds significant separation of the effective atomic charges. Then the chiral discrimination can be determined by the strong electrostatic interaction between the effective charges around the chiral center.

It is interesting to note also that the effects of chiral discrimination seem to be magnified in thin layers. In the smectic layer, chiral molecules possess less translational freedom and thus it is more difficult for them to avoid configurations with large energy that contribute to the chiral discrimination. By contrast, in three-dimensional systems the positional averaging is more complete and the contribution from these discriminating configurations is expected to be smaller. Thus we conclude that the dependence of various macroscopic parameters on the enantiomeric excess is expected to be stronger in quasi-two-dimensional systems such as smectic layers, Langmuir-Blodgett films, and surface structures. This conclusion is supported by the recent observation of the phase separation in the mixture of two enantiomers in a Langmuir monolayer [16]. We note that phase separation of left-handed and right-handed molecules is a very unusual chirality effect that requires a very strong chiral discrimination. As far as we know, such separation has not been observed in real three-dimensional systems without any additional phase transition that actually induces the separation (such as crystallization, for example).

Finally we discuss a different explanation of the nonlinear dependence of the spontaneous polarization on the enantiomeric excess proposed by Galerne [17]. According to Galerne, the nonlinear dependence of the polarization may result from long-range spatial fluctuations of the densities of left- and right-handed enantiomers in the smectic-C^* liquid crystal. These fluctuations can be taken into account if one considers the local polarization $P_s(\mathbf{r})$ which is related to the densities of left-handed and right-handed molecules by the same phenomenological relation (1),

$$P_s(\mathbf{r}) = \chi_\perp \mu_0 [x_R(\mathbf{r}) - x_L(\mathbf{r})],$$

where the local concentrations $x_R(\mathbf{r})$ and $x_L(\mathbf{r})$ are now the fluctuating quantities. The average spontaneous poalrization $\overline{P_s} = \chi_\perp \mu_0 \langle (x_R - x_L) \rangle$ will now be equal to the linear term $\chi_\perp \mu_0 \Delta x$ plus some fluctuation corrections that are nonlinear in the average enantiomeric excess Δx. We note, however, that these fluctuation corrections are expected to be sufficiently large only if the system is close to a local separation between left and right enantiomers. Such separation can take place only if the chiral discrimination is particularly strong even in comparison with the effects described in the present paper. In other words, this mechanism requires an even stronger influence of molecular chirality on the parameters of the system. In addition, this phenomenological explanation is incomplete because one still has to explain why in some cases the dependence is practically linear. To answer this question, one has to consider explicitly some specific interactions between chiral molecules in a similar way, as has been done in Sec. IV.

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APPENDIX A: DENSITY-FUNCTIONAL APPROACH TO THE THEORY OF FERROELECTRIC LIQUID-CRYSTAL MIXTURES

The general expression for the free energy of the smectic-C^* phase can be obtained using the density-functional approach to the theory of liquid crystals [13]. According to the density-functional approach, the free energy of the system can be represented as a functional of the one-particle density $\rho(\mathbf{x})=\rho_0 f_1(\mathbf{x})$. In the case of mixtures, the free-energy functional depends on the densities $\rho_\alpha(\mathbf{x})$ of all components α. This functional can be represented as a sum of two terms $F=\Phi+H$, where Φ is the free energy of the system without intermolecular interactions

$$\Phi=\Sigma_\alpha kT\rho_0 x_\alpha \int d\mathbf{x}\, f_\alpha(\mathbf{x})[\ln f_\alpha(\mathbf{x})+1],$$

where $f_\alpha(\mathbf{x})$ are the distribution functions of the molecules of the component α, and x_α are the corresponding molar fractions. In the case of enantiomeric mixtures, the indices α and β denote left and right molecules, $\alpha,\beta=L,R$. The functional derivatives of H are related to the direct correlation functions of the liquid crystal. For example,

$$\frac{\delta^2 H}{\delta f_\alpha(\mathbf{x}_1)\,\delta f_\beta(\mathbf{x})}=-kT\rho_0^2 C_{\alpha\beta}(\mathbf{x}_1,\mathbf{x}_2), \tag{A1}$$

where $C_{\alpha\beta}(\mathbf{x}_1,\mathbf{x}_2)$ is the direct correlation function between the molecules of the components α and β.

This relation enables one to expand the free energy of the ferroelectric smectic-C^* phase with respect to its value in the smectic-A phase, using the differences Δf_α as the expansion parameters. One can neglect the higher-order terms in the corresponding functional Taylor expansion of the free-energy functional because for small tilt angle Θ the differences Δf_α are also small.

Now the free energy of the induced smectic-C^* phase can be written as

$$\begin{aligned} F_C \approx{}& F_A+kT\rho_0 x_L\int d\mathbf{x}\, f_{CL}(\mathbf{x})\ln[f_{CL}(\mathbf{x})/f_{AL}(\mathbf{x})]\\ &+kT\rho_0 x_R\int d\mathbf{x}\, f_{CR}(\mathbf{x})\ln[f_{CR}(\mathbf{x})/f_{AR}(\mathbf{x})]\\ &-(kT/2)\rho_0^2\sum_{\alpha,\beta=L,R} x_\alpha x_\beta\\ &\times\int d\mathbf{x}_1 d\mathbf{x}_2 C_{\alpha\beta}(\mathbf{x}_1,\mathbf{x}_2)\Delta f_\alpha(\mathbf{x}_1)\Delta f_\beta(\mathbf{x}_2), \end{aligned} \tag{A2}$$

where $f_L(\mathbf{x})$ and $f_R(\mathbf{x})$ are the one-particle distribution functions of left-handed and right-handed molecules, respectively, while x_L and x_R are the corresponding molar fractions.

Minimization of the free energy (A2) yields the following expression for the distribution functions f_L and f_R:

$$\begin{aligned} f_\alpha(\mathbf{x})={}& f_\alpha^A\frac{1}{Z_\alpha}\exp\biggl(x_\beta\rho_0\int C_{\beta\alpha}(\mathbf{x}_1,\mathbf{x}_2)\Delta f_\beta(\mathbf{x}_2)d\mathbf{x}_2\\ &+x_\alpha\rho_0\int C_{\alpha\alpha}(\mathbf{x}_1,\mathbf{x}_2)\Delta f_\alpha(\mathbf{x}_2)d\mathbf{x}_2\biggr), \end{aligned} \tag{A3}$$

where $\alpha,\beta=L,R$.

One can readily see from Eq. (A3) that in the general case the distribution function of the left-handed molecule, for example, is determined both by the correlation function $C_{LR}(\mathbf{x}_1,\mathbf{x}_2)$ between the left-handed and right-handed molecules and the correlation function $C_{LL}(\mathbf{x}_1,\mathbf{x}_2)$ between the left-handed molecules.

In the case of the perfect nematic order, the distribution functions $f_L(\mathbf{x})$ and $f_R(\mathbf{x})$ depend only on the orientation of the short molecular axes $\mathbf{b}$ and $\mathbf{c}$. Then Eq. (A3) can be rewritten as

$$f_\alpha(\mathbf{b},\mathbf{c})=\frac{1}{Z_\alpha}\exp[C_\alpha(\mathbf{b},\mathbf{c})], \tag{A4}$$

where the effective one-particle potential $C_\alpha(\mathbf{b},\mathbf{c})$ can be represented as a sum of two terms:

$$C_\alpha(\mathbf{b},\mathbf{c})=x_\alpha C_{\alpha\beta}(\mathbf{b},\mathbf{c})+x_\beta C_{\alpha\beta}(\mathbf{b},\mathbf{c}), \tag{A5}$$

with

$$\begin{aligned} C_{\alpha\beta}(\mathbf{b},\mathbf{c})&=\rho_0\int \overline{C}_{\alpha\beta}(\mathbf{b},\mathbf{c},\mathbf{b}_2,\mathbf{c}_2)\Delta f_\beta(\mathbf{b}_2,\mathbf{c}_2)d\mathbf{b}_2,\\ C_{\alpha\alpha}(\mathbf{b},\mathbf{c})&=\rho_0\int \overline{C}_{\alpha\alpha}(\mathbf{b},\mathbf{c},\mathbf{b}_2,\mathbf{c}_2)\Delta f_\alpha(\mathbf{b}_2,\mathbf{c}_2)d\mathbf{b}_2, \end{aligned} \tag{A6}$$

and where $\overline{C}_{\alpha\beta}(\mathbf{b},\mathbf{c},\mathbf{b}_2,\mathbf{c}_2)$ and $\overline{C}_{\alpha\alpha}(\mathbf{b},\mathbf{c},\mathbf{b}_2,\mathbf{c}_2)$ are the effective direct correlation functions averaged over all positions of neighbor molecules in the ideal smectic structure:

$$\begin{aligned} &\overline{C}_{\alpha\beta}(\mathbf{b}_1,\mathbf{c}_1,\mathbf{b}_2,\mathbf{c}_2)\\ &\quad=\sigma\int C_{\alpha\beta}(\mathbf{b}_1,\mathbf{c}_1,\mathbf{b}_2,\mathbf{c}_2,\mathbf{r}_{12})\,\delta(\mathbf{r}_{12}\cdot\mathbf{e})d^3\mathbf{r}_{12}\\ &\qquad+(1-\sigma)\int C_{\alpha\beta}(\mathbf{b}_1,\mathbf{c}_1,\mathbf{b}_2,\mathbf{c}_2,\mathbf{e}r_{12})r_{12}^2 dr_{12}. \end{aligned} \tag{A7}$$

Here again $\alpha,\beta=L,R$ and σ is the fraction of the nearest neighbors which are in the same plane with the central molecule. The first term in Eq. (A7) is a contribution from the correlations between the central molecule and the nearest neighbor of the corresponding component, which are in the same smectic plane. For such molecules $\mathbf{r}_{12}\perp\mathbf{e}$. The second term is a contribution from the molecules which are in two neighbor planes. In this case $\mathbf{r}_{12}\|\mathbf{e}$.

Equations (A6) contain an averaging with the orientational distribution function of the smectic-C^* phase. The distribution function depends only on the direction of the short molecular axes **b** and in the vicinity of the Smectic-*A*–Smectic-*C* phase transition it can be expanded in powers of the spontaneous polarization $\mathbf{P}_s = \rho_0 \mu_\perp \langle \mathbf{b} \rangle$:

$$\Delta f_{C\alpha}(\mathbf{b}) = \frac{1}{2\pi}\left(1 + \frac{2}{\rho_0 \mu_\perp}\mathbf{b}\mathbf{P}_s + \cdots\right), \qquad \text{(A8)}$$

where μ is the transverse molecular dipole. Substituting Eq. (A8) into Eq. (A6) one obtains the following expression for the quantity $\mathbf{G}_{\alpha\beta}$ that enters Eq. (10):

$$\mathbf{G}_{\alpha\beta} = \frac{1}{\pi \rho_0 \mu_\perp^2}\int \tilde{C}_{\alpha\beta}(\mathbf{b}_1, \mathbf{b}_2)\boldsymbol{\mu}_2 d\mathbf{b}_2 . \qquad \text{(A9)}$$

Finally, the coefficients $G_{\alpha\beta}$ in Eq. (11) are given by

$$G_{\alpha\beta} = \frac{1}{2\pi}\int (\mathbf{G}_{\alpha\beta} \cdot \boldsymbol{\mu}_2) d\mathbf{b}_1 . \qquad \text{(A10)}$$

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[1] W. Kuczynski and H. Stegemeyer, Chem. Phys. Lett. **70**, 123 (1980).

[2] H. Stegemeyer, R. Meister, U. Hoffmann, A. Sprick, and A. Becker, J. Mater. Chem. **5**, 2183 (1995).

[3] C. Bahr, G. Heppke, and B. Sabaschus, Ferroelectrics **84**, 103 (1988).

[4] C. Bahr, G. Heppke, and B. Sabaschus, Liq. Cryst. **9**, 31 (1991).

[5] V. V. Ginzburg, R. Shao, N. A. Clark, and D. M. Walba, Proc. SPIE **2175**, 102 (1994).

[6] H. Stegemeyer, R. Meister, U. Hoffmann (unpublished).

[7] M. Z. Cherkaoui, J. F. Nicoud, Y. Galerne, and D. Guillon, Liq. Cryst. **26**, 1315 (1999).

[8] M. Z. Cherkaoui, J. F. Nicoud, and D. Guillon, Chem. Mater. **6**, 2026 (1994); M. Z. Cherkaoui, J. F. Nicoud, Y. Galerne, and D. Guillon, J. Chem. Phys. **106**, 7816 (1997).

[9] H.-R. Duball, C. Escher, and D. Ohlendorf, Ferroelectrics **84**, 143 (1988).

[10] S. A. Pikin and M. A. Osipov, in *Ferroelectric Liquid Crystals*, edited by G. Goodby (Gordon and Breach, New York, 1992).

[11] M. A. Osipov, Ferroelectrics **58**, 305 (1984); L. A. Beresnev, L. M. Blinov, M. A. Osipov, and S. A. Pikin, Mol. Cryst. Liq. Cryst., Special Topics XXIX **158A**, 1 (1988).

[12] M. A. Osipov, H. Stegemeyer, and A. Sprick, Phys. Rev. E **54**, 6387 (1996).

[13] The authors are grateful to Yves Galerne, who has pointed out the importance of these terms.

[14] T. J. Sluckin and P. J. Shukla, J. Phys. A **16**, 1539 (1983).

[15] M. Buividas, S. T. Lagerwall, F. Gouda, R. Dubal, and A. Takeichi, Ferroelectrics **212**, 55 (1998).

[16] P. Nassoy, M. Goldmann, O. Bouloussa, and F. Rondelez, Phys. Rev. Lett. **75**, 457 (1995).

[17] Y. Galerne (private communication).