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Molecular Models for the Ferroelectric Smectic C* Phase†

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The molecular-statistical theory of the ferroelectric smectic C* phase is summarized and generalized to the cases of the ferroelectric liquid crystals with large dipole in the chiral part of the molecule and to the mixtures of liquid crystals. The molecular model is proposed which is used to explain both ferroelectric and flexoelectric properties of the C* phase using a small number of molecular model parameters. In this model we consider the chiral intermolecular interaction, modulated by the banana-like shape of the molecules. The analysis of the model yields a simple chiral and polar interaction potential which is used in the statistical theory. The phenomenological constants of the smectic C* liquid crystals are expressed via the molecular model parameters.

In this report we consider also the microscopic interpretations of flexoelectricity in the smectic C phase. It is shown, that steric interaction of banana-like molecules results in the strong temperature dependence of flexoelectric coefficients. This result is used to explain the experimentally observed strong temperature variation of the helical pitch in the ferroelectric smectic C* phase.

I. INTRODUCTION

During the past decade extensive experimental studies have been carried out on the ferroelectric liquid crystals. After the first report by R. Meyer *et al.*[1] a number of various ferroelectric smectic C* liquid crystals, including the homologous series[4,5] have been synthesised and investigated.[2,3] Recently the ferroelectric properties have been discovered also in nonchiral smectic C doped with chiral molecules.[6,7]

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† Presented at the IX Int. Liquid Crystal Conference, Bangalore, 1982.

The ferroelectric ordering in the smectic C* phase was usually discussed in terms of the hindrande rotation of molecules around their long axis. However, the microscopic origin of this ordering (and hindrance) remained obscure. On the other hand the phenomenological theory[8] cannot account for some unusual properties of ferroelectric liquid crystals including the experimentally observed strong temperature variation of the pitch in the C* phase within 2 K from the transition temperature.[4,9,10] Therefore it was necessary to develop a molecular-statistical theory of ferroelectric liquid crystals which would clarify the microscopic origin of the dipolar ordering in the smectic C* phase and permit one to express the constants of the phenomenological theory via the molecular model parameters.

The molecular model of the ferroelectric smectic C* phase has been constructed in[11] by inclusion of the chiral and polar interaction energy into the Hamiltonian of the smectic C model proposed by Van der Meer and Vertogen.[13] The refined molecular theory is presented in section II of the present paper. Here we shall also describe the model for the interaction between chiral and polar molecules[12] which yields the same form of interaction potential as derived in ref. 11. This model is specified in sections II and III in order to describe ferroelectric ordering in liquid crystals with a dipole moment in the chiral part of the molecule. Such materials are important from the practical point of view since they exhibit the larger values of spontaneous polarization.[7,14] The theory of ferroelectric ordering can be generalized to the case of mixtures of liquid crystals.[12] The consistent consideration of different kinds of mixtures which exhibit ferroelectric properties will be presented in section III.

The statistical theory of flexoelectric effect in the smectic C phase has been developed in[14,15] by generalization of the Straley theory for the nematic phase. It has been shown in[15] that the steric interaction gives rise to the strong temperature dependence of flexocoefficients in the smectic C phase. This result enabled us to explain for the first time the strong temperature variation of the pitch in the ferroelectric C* phase. The results of the molecular-statistical theory of flexoelectricity in the smectic C phase are presented in section V.

Finally we want to emphasize that the main purpose of the present paper is the construction of the appropriate unified molecular model which can be used to explain the flexoelectric and ferroelectric properties of the C* phase using a small number of molecular model parameters: the average bend angle ϵ, length to breadth ratio L/D, transverse dipole moment $d_\perp$ and the parameter of molecular chirality Δ, which is described in section II.

II. INTERACTION ENERGY FOR CHIRAL AND BANANA-LIKE MOLECULES

The molecular shape is often considered to be the predominant factor in the formation of liquid crystalline phases (see, for example[19,20]). The molecular shape is often taken to be cylindrically symmetric due to the fast rotation of a molecule around its long axis. At the same time the effective banana-like molecular shape is taken into account in the microscopic theory of the flexoelectric effect.[16,21,22] In this paper we shall assume that the polar molecule of a smectic C* liquid crystal possesses the effective banana-like shape (see molecule *j* at Figure 1). It can also be stated that the molecular shape is characterized by a polar deviation from cylindrical symmetry, i.e. the molecule possesses the so called steric dipole.[23] The molecule *j* at Figure 1 can be

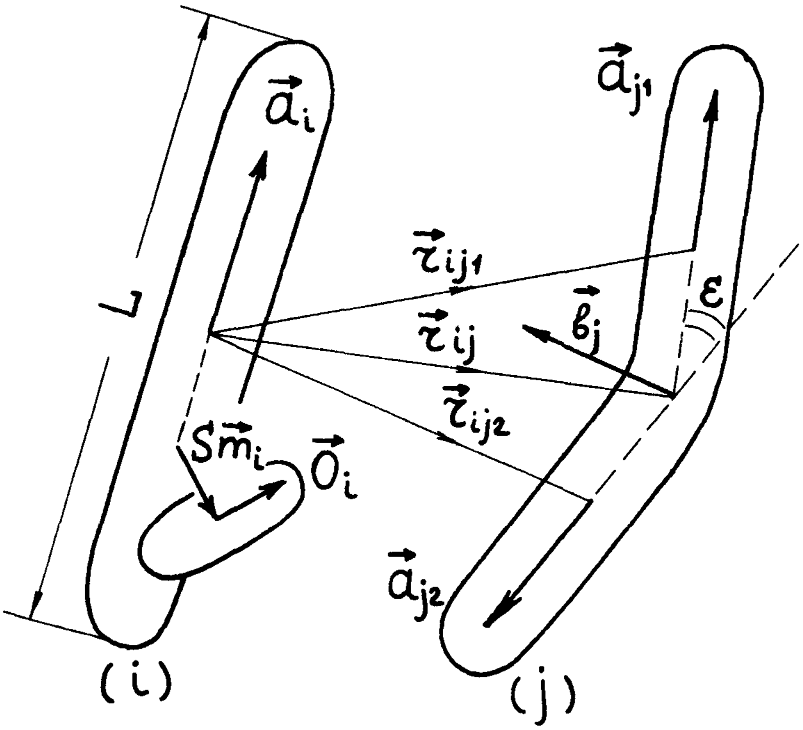

FIGURE 1 The schematic representation of the interaction between the chiral molecule *i* and the banana-like molecule *j*.

characterized by the average bend angle ϵ. When ϵ is small the orientation of such molecule can be conveniently specified by two vectors $\mathbf{a}_{j1}$ and $\mathbf{a}_{j2}$, $\mathbf{a}_{j1,2} = -\mathbf{a}_j + \epsilon\mathbf{b}_j$, $\epsilon \ll 1$. Therefore, at small ϵ, the banana-like molecule can be approximately considered to consist of two parts with the long axes $\mathbf{a}_{j1}$ and $\mathbf{a}_{j2}$.

Let us consider the interaction energy between the polar molecule j and the chiral molecule i. The first term of the general expansion of chiral intermolecular interaction energy between uniaxial molecules i and j is given by[8, 24]

$$V(i, j) = -J_{ij}(\mathbf{a}_i\mathbf{a}_j)([\mathbf{a}_i\mathbf{a}_j]\mathbf{u}_{ij}) \tag{1}$$

Now, to obtain the expressions for the interaction energy between the chiral molecule i and the banana-like molecule j one has to consider the potential[1] modulated by the asymmetric form of the molecule j.† In the case of small $\epsilon \ll 1$ the interaction potential between the chiral molecule i and banana-like molecule j can be approximately written in the form:[12]

$$\begin{aligned} V(i, j) = &-\tfrac{1}{2}J_{ij}(r_{ij1})(\mathbf{a}_i\mathbf{a}_{j1})([\mathbf{a}_i\mathbf{a}_{j1}]\mathbf{u}_{ij1}) \\ &-\tfrac{1}{2}J_{ij}(r_{ij2})(\mathbf{a}_i\mathbf{a}_{j2})([\mathbf{a}_i\mathbf{a}_{j2}]\mathbf{u}_{ij2}), \end{aligned} \tag{2}$$

where the intermolecular vectors $\mathbf{r}_{ij1,2}$ are shown at Figure 1 and $\mathbf{u}_{ij1,2} = \mathbf{r}_{ij1,2}/|\mathbf{r}_{ij1,2}|$. The expressions for the vectors $\mathbf{r}_{ij1,2}$ can be readily obtained with the help of Figure 1:

$$\mathbf{r}_{ij1,2} = \mathbf{r}_{ij} \pm \frac{L}{4}\mathbf{a}_j. \tag{3}$$

With the help of Eq. (3) the interaction potential (2) can be approximated by the following expression

$$\begin{aligned} V(i, j) \simeq &-J_{ij}(r_{ij})(\mathbf{a}_i\mathbf{a}_j)([\mathbf{a}_i\mathbf{a}_j]\mathbf{u}_{ij}) \\ &-v_{ij}(\mathbf{a}_i\mathbf{a}_j)(\mathbf{a}_j\mathbf{u}_{ij})([\mathbf{a}_i\mathbf{u}_{ij}]\mathbf{b}_j) + (\text{other terms}), \end{aligned} \tag{4}$$

$$v_{ij}(r_{ij}) = L\epsilon\left[\frac{dJ_{ij}}{dr_{ij}} - \frac{J(r_{ij})}{r_{ij}}\right], \tag{5}$$

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† This modulation can be interpreted in the spirit of Gelbart [19], i.e. as a modulation by the short range anisotropic repulsion.

where the terms, linear in ϵ, have been retained and the coupling constants $J_{ij}(r_{ij1,2})$ have been expanded in powers of $L/2r_{ij} < 1$, L being the molecular length. "Other terms" in (4) do not contribute to the ground state free energy of the smectic C* phase.

The second term in (4) is the chiral interaction potential which depends upon the direction of the short axis $\mathbf{b}_j$, i.e. it is sensitive to the dipolar ordering. The mathematical form of the potential (4) can be obtained on the general ground[11,12] without referring to the particular model. The model is important for the calculation of the coupling constant v_{ij} in Eq. (5). In order to detail the expression (5) one needs an additional expression for the coupling constant J_{ij} which is determined by chiral properties of the molecule i. Therefore the appropriate model of a chiral molecule can be useful here.

Ferroelectric chiral smectic liquid crystals can be obtained from nonchiral smectogens through the replacement of a hydrogen atom in the molecular chain by an appropriate group (CH_3, Cl, CN, etc.).[7,25,26] The model for such chiral molecule has been proposed recently by Van der Meer and Vertogen[27] (see molecule i at Figure 1) who used it in the description of non-sterol cholesterogens. In this model the coupling constant $J_{ij}(r_{ij})$ reads:

$$J_{ij} = -\frac{3}{2}s\frac{dJ_0}{dr_{ij}}(\mathbf{o}_i\mathbf{a}_i)([\mathbf{o}_i\mathbf{a}_i]\mathbf{m}_i) \tag{6}$$

where $\mathbf{o}_i$ is the long axis of the substitution group, $\mathbf{m}_i$ is a unit vector pointing from the substitution group to the long axis of the molecule, s is distance between the substitution group and the long axis, $J_o(r_{ij})$ is a coupling constant between the substitution group and the molecule j. The chirality of the molecule i at Figure 1 is determined by the orientation of the substitution group with respect to the long axis $\mathbf{a}_i$ and the vector $\mathbf{m}_i$. The molecule is chiral when these three vectors are not complanar, i.e. $([\mathbf{o}_i\mathbf{a}_i]\mathbf{m}_i) \neq 0$. In the Eq. (6) the molecular chirality is represented by the pseudoscalar $\Delta_i = (\mathbf{o}_i\mathbf{a}_i)([\mathbf{o}_i\mathbf{a}_i]\mathbf{m}_i)$ which changes sign under the inversion of molecular coordinate system.

Substitution of Eq. (6) into (5) yields the following expression for the coupling constant v_{ij}

$$v_{ij} = \frac{3}{2}L\epsilon s\left[\frac{d^2J_0}{dr_{ij}^2} - \frac{1}{r_{ij}}\frac{dJ_0}{dr_{ij}}\right](\mathbf{o}_i\mathbf{a}_i)([\mathbf{o}_i\mathbf{a}_i]\mathbf{m}_i). \tag{7}$$

The expression in brackets in Eq. (7) can be further simplified taking into account that the coupling constant $J_0(r_{ij})$ is determined by the short range interaction, i.e. $J_0(r_{ij}) \sim r_{ij}^{-k}$, where $4 \leq k \leq 10$. For the ordinary dipole-dipole dispersion interaction $k = 6$. In this case

$$v_{ij} \simeq 72 J_0 L \epsilon r_{ij}^{-2} s(\mathbf{o}_i \mathbf{a}_i)([\mathbf{o}_i \mathbf{a}_i]\mathbf{m}_i). \tag{8}$$

It is worth noting that all relevant parameters in Eqs. (7), (8) characterize the molecular shape. These parameters are: the average bend angle ϵ, the molecular length L and the parameters of the substitution group. We would like to underline that in the present model the chiral and polar intermolecular interaction originates from the interaction of chiral molecule substitution group with the neighbor asymmetric molecule.

As mentioned above, the largest values of spontaneous polarization have been observed in liquid crystals with a dipole moment located in the substitution group (chiral part) of the molecule.[7,14] This fact can be understood within the present model. Indeed, if the substitution group possesses a large dipole moment, it induces the dipole in the polarizable core of the neighbor molecule. Then it is necessary to take into account the dipole-dipole induction interaction which is a predominant one between the substitution group and the neighbor molecule due to the large value of the dipole. The corresponding dispersion interaction is much weaker because the polarizability of the substitution group is very small compared with that of the ring system.

The chiral part of the dipole-dipole induction interaction averaged over the rotations of the molecule j can be written in the form:

$$V^*_{ind}(i, j) = -J_1(i, j)\left[(\mathbf{a}_i\mathbf{a}_j) - 3(\mathbf{a}_i\mathbf{u}_{ij})(\mathbf{a}_j\mathbf{u}_{ij})\right]\left([\mathbf{a}_i\mathbf{a}_j]\mathbf{u}_{ij}\right), \tag{9}$$

$$J_1(i, j) = 3 s r_{ij}^{-7} \alpha_a (\mathbf{o}_i\mathbf{a}_i)([\mathbf{o}_i\mathbf{a}_i]\mathbf{m}_i)\, d_i^2, \tag{10}$$

where $\mathbf{d}_i = d_i \mathbf{o}_i$ is the dipole of the substitution group and α_a is the anisotropy of the molecular polarizability. Except for the second term in brackets the interaction potential (9) is the same as the chiral potential (1) which was used in the present section to derive the expressions (5), (6). Thus we can assume again that the interaction energy (9) is modulated by the effective banana-like shape of the molecule j and obtain the expression for the chiral and polar interaction potential repeating the derivation of the expressions (5), (6) from (1), (2). The result is:

$$V^*_{ind}(i, j) = -v_{ij}^{ind}(\mathbf{a}_i\mathbf{a}_j)(\mathbf{a}_j\mathbf{u}_{ij})\left([\mathbf{a}_i\mathbf{u}_{ij}]\mathbf{b}_j\right), \tag{11}$$

$$v_{ij}^{ind} = 72 s r_{ij}^{-8} L \epsilon d_i^2 \alpha_a (\mathbf{o}_i\mathbf{a}_i)([\mathbf{o}_i\mathbf{a}_i]\mathbf{m}_i), \tag{12}$$

It should be noted that the interaction energy (11), (12) can be considered as a particular case of the potential (4), (7) with the coupling constant $J_0(r_{ij}) = d_i^2 \alpha_a r_{ij}^{-6}$.

The induction interaction between uniaxial molecules has been considered recently by Van der Meer and Vertogen in their molecular theory for the Sm A–Sm C phase transition.[13] However, in[13] only the interaction between the dipole and the isotropic polarizability of the neighbor molecule has been taken into account whereas in the present model the interaction between the dipole and the anisotropic polarizability is considered. Secondly, the asymmetric position of the dipole $\mathbf{d}_i$ with respect to the long axis $\mathbf{a}_i$ is taken into account here in order to represent molecular chirality. Thus the potential (11), (12) corresponds to the chiral part of the total induction interaction energy between the molecule j and the dipole of the substitution group of the molecule i.

III. STATISTICAL THEORY OF FERROELECTRIC LIQUID CRYSTALS

In the smectic C phase the molecules are arranged in layers. Therefore it is possible to introduce the unit vector $\mathbf{e}$ which is normal to the smectic plane. (The vector $\mathbf{e}$ is supposed to be fixed in space.) Then $\mathbf{ne} = \cos\theta$, where θ is the tilt angle. Now the phenomenological expression for the free energy of the ferroelectric smectic C* phase can be written in the form:[12, 14, 28]

$$\begin{aligned} F = F_0 &- \lambda(\mathbf{ne})\left(\mathbf{n}\frac{\partial}{\partial z}[\mathbf{ne}](\mathbf{ne})\right) - \mu_1(\mathbf{ne})([\mathbf{ne}]\mathbf{P}_0) \\ &- g_0\left(\mathbf{P}_0\frac{\partial}{\partial z}\mathbf{n}(\mathbf{ne})\right) - g_\perp\left(\mathbf{P}_\perp\frac{\partial}{\partial z}\mathbf{n}(\mathbf{ne})\right) + \frac{1}{2}\left(P_0^2 + P_\perp^2\right) \\ &- \mathbf{P}_0\mathbf{E} - \mathbf{P}_\perp\mathbf{E}, \end{aligned} \qquad (13)$$

where only the gradients along the z axis ($\mathbf{z} \| \mathbf{e}$) are taken into account. In Eq. (13) $\mathbf{E}$ is the external electric field, $\mathbf{P}_0$ is the spontaneous polarization and $\mathbf{P}_\perp$ is the induced one, $(\mathbf{P}_0\mathbf{P}_\perp) = 0$. (See Figure 2) g_0 and $g_\perp$ are the flexocoefficients. If $\mathbf{E} = 0$, the induced polarization $\mathbf{P}_\perp = 0$ and $\mathbf{P}_0 = \chi\mu_1(\mathbf{ne})[\mathbf{ne}] - \chi g_0 \partial/\partial z \mathbf{n}(\mathbf{ne})$.

In the present section it will be shown that the interaction energy (4) contributes to the free energy of the smectic C* phase in accordance with the phenomenological theory and gives rise to the third term in Eq. (13). The transition from Eq. (4) to (13) can be qualitatively

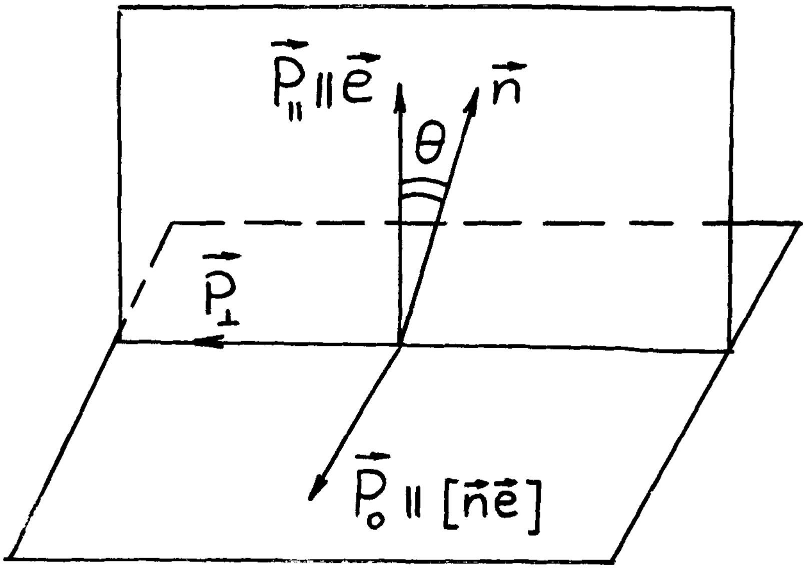

FIGURE 2 Three orthogonal vectors of the induced polarization in the smectic C phase.

understood in the following way. Indeed, after the statistical averaging of the interaction potential (4) over the orientations of the short axis $\mathbf{b}_j$ at perfect orientation $\mathbf{a}_i \simeq \mathbf{a}_j \simeq \mathbf{n}$ and $\mathbf{u}_{ij} = \mathbf{e}$ we arrive at the following expression $\langle V_{ij} \rangle \simeq -v_{ij}(\mathbf{ne})([\mathbf{ne}]\mathbf{P})$ which corresponds to the third term in (13). Here $\mathbf{P} = d_{\perp} \langle \mathbf{b}_j \rangle$ where the brackets denote the statistical averaging.

In the molecular field approximation the free energy density of the system with pair interaction potential $V_C(ij)$ reads

$$F(r) = \frac{1}{2}\rho^2 \int f(i) V_C(i, j) f(j) d(i) d(j)\, d\mathbf{r}_{ij} - \rho kT \int f(i) \ln f(i) d(i) \tag{14}$$

where $f(i)$ is the one-particle distribution function which depends upon the orientation and position of the molecule i, $f(i) = f(\mathbf{a}_i, \mathbf{b}_i, \mathbf{n}(\mathbf{r}_i), \mathbf{r}_i)$, $d(i) = \delta(\mathbf{a}_i \mathbf{b}_i)\, d\mathbf{a}_i d\mathbf{b}_i$. One can write $f(i) = f_0(i)(1 + \psi(i))$ where $f_0(i)$ is a distribution function for a freely rotating molecule i, $f_0(i) = f_0(\mathbf{a}_i, \mathbf{n}(\mathbf{r}_i), \mathbf{r}_i)$. The function ψ is small and depends upon the orientation of the short axis $\mathbf{b}_i$. In the model described in section II the intermolecular interaction energy $V_C(i, j)$ can be written in the form: $V_C(i, j) = U(i, j) + V^*(i, j) + V^*(j, i)$ where $U(i, j)$ represents the nonchiral interaction energy and $V^*(i, j)$ is given by Eq. (4). Then the expansion of the free energy (14) in powers of ψ yields the following expression for the free energy of the ferroelectric smectic C* phase

$$F = F_0 - \rho \int f_0(i) v_{ij}(r_{ij})(\mathbf{a}_i\mathbf{a}_j)(\mathbf{a}_j\mathbf{u}_{ij})([\mathbf{a}_i\mathbf{u}_{ij}]\mathbf{b}_j)\psi(j) f_0(j) \times \delta(\mathbf{a}_j\mathbf{b}_j)\, d\mathbf{a}_i\, d\mathbf{a}_j\, d\mathbf{b}_j\, d\mathbf{r}_{ij}, \tag{15}$$

where F_0 is the free energy of the nonchiral smectic C phase. The distribution function $f_0(i)$ is determined by the nonchiral interaction energy $U(i, j)$. The second term in Eq. (15) represents the average of the chiral and polar interaction potential (4). Note that the first term in eq. (4) contributes only to the gradient terms of the free energy.[16, 24]

In the smectic C phase the orientational order is rather high.[30] Therefore one can assume here that the orientational order is ideal and substitute the vectors $\mathbf{a}_i$ and $\mathbf{a}_j$ for the director $\mathbf{n}$ in Eq. (15). In Eq. (15) one has to calculate the average of the interaction potential over the directions of the intermolecular unit vector $\mathbf{u}_{ij}$. This averaging is difficult to perform in the general situation. Recently, however, Van der Meer and Vertogen have proposed the following interpolation procedure for this averaging in the smectic phase:[13]

$$\langle V_{ij}\rangle_{\mathbf{u}} = V_{ij}^N + \left[V_{ij}^S - V_{ij}^N\right]\langle\cos\phi\rangle^2. \tag{16}$$

Here $\langle\cos\phi\rangle$ is the smectic order parameter, V_{ij}^N is the interaction potential V_{ij} averaged over the orientation of $\mathbf{u}_{ij}$ in the nematic phase and V_{ij}^S is the potential V_{ij} averaged over the directions of $\mathbf{u}_{ij}$ in the case of ideal smectic order. In the latter case the molecular centers of mass are located in equidistant planes. Then if the molecules i and j are located in the same plane, $\mathbf{u}_{ij}\mathbf{e} = 0$. On the other hand, if the molecules are located in the adjacent planes, $\mathbf{u}_{ij} = \mathbf{e}$. Thus the averaged potential V_{ij}^S can be written as

$$V_{ij}^S = \int V_{ij}\left[(1-\alpha)\delta\left((\mathbf{u}_{ij}\mathbf{e})^2 - 1\right) + \alpha\delta(\mathbf{u}_{ij}\mathbf{e})\right] d\mathbf{u}_{ij} \tag{17}$$

where α is the fraction of nearest neighbors located in the same plane as the given molecule. Now we can substitute the Eq. (17) into Eq. (16) and obtain the following expression for the free energy difference between the ferroelectric and nonferroelectric smectic C* phases:

$$F = -\rho v_0(\mathbf{ne})([\mathbf{ne}]\mathbf{P})\langle\cos\phi\rangle^2\left(\tfrac{3}{2}\alpha - 1\right) d_\perp^{-1}, \tag{18}$$

$$v_0 = \int_{r_0}^{\infty} v_{ij}(r_{ij}) r_{ij}^2\, dr_{ij}, \tag{19}$$

where r_0 is the average diameter of the molecule, $r_0 \sim L$, $\mathbf{P} = d_\perp \langle \mathbf{b}_i \rangle$. The expression (18) corresponds to the third term of the Eq. (13) for the phenomenological free energy of the C* phase and one readily obtains the general expression for the phenomenological constant μ_1:

$$\mu_1 = -\rho v_0\left(\tfrac{3}{2}\alpha - 1\right)\langle\cos\phi\rangle^2 d_\perp^{-1}. \tag{20}$$

Here the particular form of the coupling constant v_{ij} can be obtained within an appropriate molecular model. In the model of steric interaction between chiral and banana-like molecules (see section II) the coupling constant v_{ij} is given by Eq. (5). Substitution of (5) into (19) yields

$$v_0 = L\epsilon \int_{r_0}^{\infty} \left[\frac{dJ_{ij}}{dr_{ij}} - \frac{1}{r_{ij}} J_{ij}\right] r_{ij}^2\, dr_{ij} \tag{21}$$

Here J_{ij} is the coupling constant of the chiral interaction between uniaxial molecules. This interaction is responsible for the helicoidal twisting in the smectic C* phase and hence determines the phenomenological constant λ in the free energy of the C* phase (13).[29] The statistical theory of the smectic C* phase has been developed by Van der Meer and Vertogen,[29] but the ferroelectric properties have been completely ignored in.[29] According to ref. [29] the constant λ reads

$$\lambda = -\frac{1}{2}\frac{dJ_0}{dR} Rs\left[1 - \langle\cos\phi\rangle^2 + 3(1-\alpha)\langle\cos\phi\rangle^2\right](\mathbf{o}_i\mathbf{a}_i)([\mathbf{o}_i\mathbf{a}_i]\mathbf{m}_i) \tag{22}$$

The comparison of Eqs. (20), (21) and the Eq. (22) enables one to obtain a simple approximate relation between the independent phenomenological constants μ_1 and λ:[12]

$$\frac{\mu_1}{\lambda} \sim (\rho\, d_\perp)^{-1} 10 \frac{\epsilon}{R}\left(\frac{L}{R}\right) \tag{23}$$

where R is the average intermolecular distance, $R^3 \sim \rho^{-1}$. The phenomenological constants μ_1 and λ have been estimated in[31] for the ferroelectric liquid crystal DOBAMBC (decyloxybenzylidene p'-amino 2 metilbutilcinnamate) $\mu_1 = 3\ 10^{-3}$ Cu/m^2, $\lambda = 10^{-4}$ J/m^2. Taking $R = 10^{-9}$ m, $L \simeq R$ and $d_\perp = 1, 5D$ we can estimate the average bend angle of the asymmetric molecule, $\epsilon \sim 10^{-2}$. This seems to be a realistic value.

It is possible to obtain the more detailed expression for the constant μ_1 using the Van der Meer and Vertogen model for a chiral molecule. In this case the coupling constant v_{ij} is given by Eqs. (7), (8) and one arrives at the following expression for the constant v_0 in (20)

$$v_0 = -3sL\epsilon\kappa J(r_0)r_0(\mathbf{a}_i\mathbf{o}_i)([\mathbf{a}_i\mathbf{o}_i]\mathbf{m}_i), \tag{24}$$

where it has been assumed that $J(r) \sim r^{-k}$, $6 \leq k \leq 10$, $\kappa = k(k-4)/(k-1) \simeq k-4$. The numerous coefficient in (24) should not be taken too seriously but we hope that the expressions (20) and (24) reveal the dependence upon the molecular parameters. Note that in the present model the constant μ_1 (and hence the spontaneous polarization) is determined by the parameters of the molecular shape. On the other hand, the absolute value of the constant μ_1 cannot be determined in this model since the initial coupling constant $J_0(r)$ is not specified.

The "traditional" ferroelectric liquid crystal DOBAMBC possesses a relatively low value of spontaneous polarization, $P \simeq 1, 5\ 10^{-9}$ C/sm^2.[1-3] The larger polarization is observed in liquid crystals with a dipole in the chiral part of the molecule.[7,5] According to reference[32] the spontaneous polarization strongly depends upon the value of this dipole, reaching the value of $2,2 \cdot 10^{-8}$ for a molecule with a strongly polar C≡N group in the chiral part. This strong dependence of the polarization upon the dipole moment cannot be explained with the help of Eqs. (20, 24). Nevertheless, this property can be accounted for if we detail the present model, i.e. specify the coupling constant $J_0(r_{ij})$ in (24). Indeed, in section II we have considered the dipole-dipole induction interaction between the substitution group of the chiral molecule and the polarizable core of the neighbor molecule. This interaction is predominant in the case of the strongly polar substitution group. In this case the coupling constant v_{ij} is given by Eq. (12). Substitution of the Eq. (12) into (19) and (20) yields the following expression for the phenomenological constant μ_1:

$$\mu_1 = -\tfrac{72}{5}\rho\left(\tfrac{3}{2}\alpha - 1\right)\langle\cos\phi\rangle^2 d_\perp s\epsilon L\alpha_a(\mathbf{o}_i\mathbf{a}_i)([\mathbf{o}_i\mathbf{a}_i]\mathbf{m}_i). \tag{25}$$

It is evident from Eq. (25) that in this model of the spontaneous polarization strongly depends upon the value of the transverse molecular dipole $d_\perp$, $P_0 \sim \chi\mu_1 \sim d_\perp^3$. Note that the initial dielectric susceptibility $\chi \sim d_\perp^2$ for molecules with constant dipoles. Thus the dipole-dipole induction interaction between the chiral molecule substitution group and the neighbor molecule is responsible for the rapid growth of the spontaneous polarization with the increasing dipole moment in the chiral part of the molecule.[32]

In conclusion we want to emphasize that the expression (25) corresponds to the most detailed version of the present model. On the contrary, in the most general version the constant μ_1 is given by the Eqs. (20), (21) which can be used for the description of the smectic C* phase composed of any chiral molecules including the ones which cannot be represented by Van der Meer and Vertogen model (cholesteril derivatives, for example). The general expressions can be also used in the case of mixtures.

IV. FERROELECTRICITY IN MIXTURES

The possibility of ferroelectric ordering in mixtures of different molecules in the smectic C* phase is evident from the general form of the chiral and polar interaction potential (4). According to section II the interaction energy V_{ij} depends upon the chirality of the molecule i and the asymmetry of the molecule j. Consequently the total interaction energy $U(i, j) = V_{ij} + V_{ji}$ is nonzero even if one of the interacting molecules is not chiral or not banana-like. Then the ferroelectric ordering is to be expected, for example, in nonchiral smectic C doped with chiral molecules. Recently this possibility has been proved experimentally.[6,7]

In the previous section the one-component ferroelectric liquid crystal has been considered, i.e. it was assumed that $v_{ij} = v_{ji}$ in (4). Now, let us consider a mixture of two compounds of concentrations x_1 and x_2, $x_1 + x_2 = 1$. We shall assume that this mixture can form the smectic C phase. Then the generalization of the molecular-statistical theory of section III is straightforward and the phenomenological constant μ_1 for this mixture reads

$$\mu_1 = \kappa_0\left[v_{11}x_1^2 + (v_{12} + v_{21})x_1x_2 + v_{22}x_2^2\right]$$

Here $$\kappa_0 = \rho(3\alpha/2 - 1/2)\langle\cos\phi\rangle^2 d_\perp^{-1}. \qquad (26)$$

In the Eq. (26) the constant $v_{\alpha\alpha}$, $\alpha = 1, 2$, is the coupling constant between the molecules of the same compound α. The constant $v_{\alpha\beta}$, $\alpha \neq \beta$, is the coupling constant between the molecules of different compounds α and β. Note that $v_{\alpha\beta}$ depends upon the chirality of the compound β and the asymmetry of the compound α and hence $v_{\alpha\beta} \neq v_{\beta\alpha}$. Thus the spontaneous polarization can appear in the mixture if $v_{\alpha\beta} \neq 0$ for any α, β. When the chiral molecule β has a dipole moment in the chiral part the coupling constant $v_{\alpha\beta}$ is given by

$$v_{\alpha\beta} = \tfrac{72}{5} L_{\alpha} \epsilon_{\alpha} \Delta_{\beta} d_{\beta}^{2} \alpha_{a\alpha} \tag{27}$$

where $\Delta_{\beta} = (\mathbf{o}_{\beta}\mathbf{a}_{\beta})([\mathbf{o}_{\beta}\mathbf{a}_{\beta}]\mathbf{m}_{\beta})$ represents the chirality of the compound β. In the rest of this section some particular cases will be considered.

1. The nonchiral smectic C liquid crystal doped with chiral molecules.

In such system the ferroelectric properties have been discovered experimentally.[6,7] The spontaneous polarization in this mixture is proportional to the concentration of chiral molecules. Now let us consider the general expression (26). In the present case $v_{11} = v_{21} = 0$ because the matrix molecules are not chiral. At small concentration $x_2 \ll 1$ the last term in (26) can be also neglected. On the other hand $v_{12} \neq 0$ and $P_0 \sim v_{12} x_1 x_2$ in accordance with the experiment. Thus the spontaneous polarization in this mixture is determined by the asymmetry of the matrix molecules and by the chiral properties of mixed organic materials. If the mixed chiral molecules have a strongly polar substitution group the spontaneous polarization can be written as

$$P_0 = \tfrac{1}{2}\chi\langle\cos\phi\rangle^2\left(\tfrac{3}{2}\alpha - 1\right) d_{\perp 2}\epsilon_1 L_1 \Delta_2 x_1 x_2 \sin 2\theta, \tag{28}$$

where $\chi \sim d_{\perp 1}^{2}$ and the subscripts 1 and 2 correspond to the molecules of the matrix and the mixed compound respectively.

2. The nonpolar chiral smectic C doped with nonchiral polar molecules.

There is no spontaneous polarization in the smectic C* phase composed of molecules without transvers dipoles. However, if such liquid crystal is doped with polar molecules, the constant $v_{21} \neq 0$ in Eq. (26) and the spontaneous polarization of the mixture is proportional to the chirality of matrix molecules and the dipole moment of the mixed material, i.e. $P_0 \sim \Delta_1 \epsilon_2 d_{\perp 2} x_1 x_2$. As far as we know, this system has not been studied experimentally.

3. The nonpolar and nonchiral smectic C liquid crystal doped with polar and chiral molecules.

In this case $v_{11} = v_{21} = v_{12} = 0$ but $v_{22} \neq 0$ and the spontaneous polarization is determined by the interaction of the mixed molecules contrary to the previous two cases. Then the spontaneous polarization is proportional to the square of the small concentration x_2, $P_0 \sim v_{22}x_2^2$ and hence we can predict that the polarization will be very small in such mixture.

4. Ferroelectric liquid crystals doped with nonchiral molecules.

In this case $P_0 = P_{00} - \Delta P$, where $\Delta P \sim v_{21}x_1x_2$, i.e. the spontaneous polarization of this mixture decreases linearly with the growing concentration x_2 of the mixed compound. This linear dependence has recently been observed in.[33]

5. The mixture of two ferroelectric liquid crystals.

The mixtures of ferroelectric liquid crystals have been investigated in.[5,34,35] In this case all coupling constants $v_{\alpha\beta} \neq 0$ and the spontaneous polarization is a nonlinear function of the concentrations x_1 and x_2.

V. MOLECULAR THEORY OF FLEXOELECTRICITY IN THE SMECTIC C PHASE

The flexoelectric effect in liquid crystals describes the coupling between the polarization and the orientational deformation of the medium. In the chiral smectic C phase the spontaneous twisting of the director around the smectic plane normal results in the flexoelectric contribution to the polarization of the smectic layer.[8] Thus the flexoelectric effect contributes to the spontaneous polarization and to the static dielectric constant in the ferroelectric C* phase.[8,28,11] According to the phenomenological theory[28,11] there exist three independent flexoelectric contributions to the free energy of the smectic C phase:

$$F = -g_0 n_z\left(\mathbf{P}_0\frac{\partial \mathbf{n}}{\partial z}\right) - g_\perp n_z\left(\mathbf{P}_\perp\frac{\partial \mathbf{n}}{\partial z}\right) - g_\parallel(\mathbf{P}_\parallel \mathbf{n})\left(\frac{\partial n_x}{\partial x} - \frac{\partial n_y}{\partial y}\right), \tag{29}$$

where three orthogonal polarizations $\mathbf{P}_0$, $\mathbf{P}_\perp$ and $\mathbf{P}_\parallel$ are shown at Figure 2. The flexoelectric effect is not associated with the molecular chirality and hence the expression (29) is valid also in the chiral smectic C phase. In the ferroelectric C* phase $\mathbf{P}_0$ is the spontaneous polarization $P_0 \sim \sin 2\theta \partial\phi/\partial z$, where ϕ is the asimuthal angle of the director $\mathbf{n}$. The polarizations $\mathbf{P}_\perp$ and $\mathbf{P}_\parallel$ are zero if the external field or stress is absent. In the general situation $P_\perp \sim \cos 2\theta \partial\theta/\partial z$.[28,11] The difference $g_0 - g_\perp \sim \theta^2$ contributes to the dielectric constant of the ferroelectric C* phase.[11,28]† The flexoelectric coefficient g_0 contributes also to the expression for the pitch in the ferroelectric C* phase:[8]

$$h = 2\pi \frac{K - \chi g_0^2}{\lambda + \chi \mu_1 g_0}, \tag{30}$$

where K is a bend elastic constant.

In recent years several authors have observed the strong temperature variation of the helical pitch in the number of ferroelectric liquid crystals.[3,9,10] It has been demonstrated that with decreasing temperature after the Sm A*–Sm C* phase transition the pitch increases steeply within 1–2 K, attains its maximum and then decreases gradually. Thus the temperature variation of the pitch in the ferroelectric C* phase is much stronger than that in the cholesteric phase. As shown in [15] this strong temperature variation of the pitch cannot be explained within the phenomenological theory. Consequently we need a molecular theory to account for this phenomena.

The statistical theory of flexoelectric effect in nematic liquid crystals has been developed by Straley.[16] Recently we have generalized the Straley theory to the case of smectic phases.[14,15] In the case of ideal translational and orientational order the induced polarization in the smectic C phase reads:[14]

$$P = \rho\beta \int (d_\perp \mathbf{b}_i + d_\parallel \mathbf{n}) \delta(\mathbf{b}_i \mathbf{n}_i) \Big[\alpha \int \mathbf{u}_{ij} \nabla_\perp V(\mathbf{n}, \mathbf{b}_i, \mathbf{u}_{ij})\, d\mathbf{u}_{ij} \\ + (1 - \alpha) \frac{\partial}{\partial z} V(\mathbf{n}, \mathbf{b}_i, \mathbf{e}) \Big]\, d\mathbf{b}_i, \tag{31}$$

where $V(\cdots)$ is the effective "interaction potential",

$$V(\mathbf{n}, \mathbf{b}_i, \mathbf{u}_{ij}) = \int [U(i, j) + kTB(i, j)]\, r_{ij}^3 \delta(\mathbf{b}_j \mathbf{n})\, d\mathbf{b}_j \tag{32}$$

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†Recently Martinot-Lagarde and Durand have concluded that the flexoelectric effect does not contribute at all to the static dielectric constant of the ferroelectric C* phase.[37] This conclusion is based, however, on the incomplete expression for the flexoelectric part of the free energy in the C* phase. Indeed in the Eq. (1) of ref. [37] the polarizations $\mathbf{P}_0$ and $\mathbf{P}_\perp$ are not distinguished and consequently the constants g_0 and $g_\perp$ are identified, i.e. $g_0 - g_\perp = 0$.

The expressions for the flexoelectric constants g_0, $g_\perp$, $g_\parallel$ can be obtained from Eq. (31) provided the potentials $U(i, j)$ and $B(i, j)$ are given. The effective potential $V(i, j)$ in (32) is determined by two parts: the attractive interaction energy $U(i, j)$ which includes the multipole and dispersion interaction potentials and the steric interaction potential $kTB(i, j) = kT\Omega(\xi_{ij} - r_{ij})$ which depends upon the parameters of the molecular shape. Here ξ_{ij} is the closest distance of approach for the molecules i and j and $\Omega(x)$ is a stepfunction. $\Omega(x) = 0$ if the molecules do not overlap and $\Omega(x) = -1$ otherwise. Therefore the flexoelectric constant g_α ($\alpha = 0, \perp, \parallel$) can be split into two parts:

$$g_\alpha = g_{\alpha 0} + g_{\alpha s}, \tag{33}$$

where g_0 is determined by the attractive interaction and g_s is determined by the steric one. The contributions from the dipole-quadrupole interaction and the ordering of molecular quadrupoles (which determine g_0) have been considered in.[14] It is important that the first term in (33) weakly depends on temperature in the smectic C* phase.

The steric contribution to the flexoelectric constant g_0 has been obtained in.[15] It has been shown that the constant g_0 strongly depends on temperature through the tilt angle θ. To write out the results one has to distinguish between the small tilt angles $\theta \ll D/L$ and the arbitrary ones. For small tilt angles $\theta \ll D/L$ the flexoelectric constant g_{0s} is given by the following expression [15]:

$$g_{0s} = \frac{1}{4\sqrt{2}} \rho^2 (1 - \alpha) d_\perp L^4 \left(\frac{L}{2R_0} \right) \epsilon \sqrt{1 + (\theta/\epsilon)^2} \tag{34}$$

where R_0 is the curvature radius at the top of the molecule. For example, for a spherocylinder $R_0 = D/2$. For the arbitrary tilt angle the constant g_0 depends upon the details of the molecular shape. In this case the approximate expression for $g_{0s}(\theta)$ can be obtained for the model of slightly bent ellipsoidal particles:[16]

$$g_{0s} \simeq \frac{1}{4\sqrt{2}} \rho^2 (1 - \alpha) L^4 \left(\frac{L}{D} \right)^2 d_\perp \epsilon \frac{\sqrt{1 + (\theta/\epsilon)^2}}{\left[1 + \theta^2 (L/D)^2\right]^{7/2}}. \tag{35}$$

The most important consequence of the Eqs. (34), (35) is the strong temperature dependence of the flexoelectric constant g_0 in the C phase. This unusual behaviour of g_0 is associated with the two small parameters of the molecule: the average bend angle ϵ and the breadth to length ratio D/L, $\epsilon \ll D/L$. The dependence of g_0 on θ is scaled by these small parameters, i.e. $g_0(\theta) = g_0(\theta/\epsilon, \theta/D/L)$. Therefore, when θ is small one cannot neglect the temperature dependence of g_0 since $\theta/\epsilon \sim 1$ or $\theta L/D \sim 1$ although $\theta \ll 1$. As follows from the Eq. (34) the value of the flexoelectric constant g_0 in the smectic C phase is larger than that in the nematic phase. Indeed, taking $d_\perp = 2D$, $L = 25$ Å, $\alpha = \frac{3}{4}$, $\rho = 10^{21}$ sm^{-3} one estimates $g_{0_s} \sim 5\ 10^{-3}\ \epsilon\sqrt{1 + (\theta/\epsilon)^2}$. The average bend angle has been estimated in section III for the ferroelectric liquid crystal DOBAMBC, $\epsilon \sim 10^{-2}$. Then, in the vicinity of the phase transition point (where $\theta \lesssim \epsilon$) one estimates $g_{0_s} \sim 5\ 10^{-3}$ $\epsilon \sim$ and 5 10^{-5}. With decreasing temperature, when $\theta > \epsilon$, one estimates $g_{0_s} \sim 5\ 10^{-3}\ \theta$. Therefore the maximum value of g_0 is in the 10^{-3} range.

It seems reasonable to explain the experimentally observed strong temperature dependence of the pitch in the ferroelectric C* phase by the strong temperature dependence of the flexoelectric constant g_0, given by Eqs. (34), (35). Note that the constant g_0 contributes to the expression (30) for the pitch. At small tilt angles $\theta \lesssim \epsilon$, $g_0 \sim [1 + \theta^2/2\epsilon^2] = [1 + a(T_c - T)/2\epsilon^2]$ according to (34). Substitution of this expression into (30) yields the following expression for the pitch:

$$h = h_0\left[1 + \sigma(T_c - T)\epsilon^{-1}\right], \qquad \theta < \epsilon, \tag{36}$$

where the constants h_0 and σ are composed of the parameters of Eqs. (30), (34). Thus, when the tilt angle is small, the pitch is growing linearly in the ferroelectric C* phase in accordance with the experiment.[4,9,10] Note that the large growth rate of the pitch within 1° from the transition temperature T_c is determined by the parameter $\epsilon^{-1} \gg 1$. When the temperature is decreased the growth rate of the flexoelectric constant g_0 (and hence the growth rate of the pitch) is reduced since $g_0 \sim \epsilon\sqrt{1 + (\theta/\epsilon)^2} \sim \theta \sim (T_c - T)^{1/2}$ when $\epsilon < \theta < D/L$. At lower temperatures $\theta \sim D/L$ and in this region one has to use the more complicated expression (35) because the dependence of g_0 upon $(\theta L/D)^2$ cannot be further neglected. The dependence of g_0 on $(\theta L/D)$ in Eq. (35) reduces the flexoelectric constant g_0 and it can be shown that the maximum pitch corresponds to the same tilt angle θ_0 as the maximum flexoelectric constant g_0. The value of θ_0 is determined by the small parameter D/L, i.e. $\theta_0 \sim D/L$. According to ref. [4] $\theta_0 \simeq 1/5$ for the liquid crystal DOBAMBC and hence $L \simeq 5D$.

In summary the present molecular-statistical theory permits to explain (qualitatively) for the first time the strong temperature variation of the pitch in the ferroelectric smectic C* phase. Recently the molecular-statistical theory of the chiral smectic C phase has been developed by Van der Meer and Vertogen[29] who have completely ignored ferroelectric and flexoelectric properties of the C* phase. Thus the following simplified expression for the pitch has been used in:[29] $h = 2\pi K/\lambda$. Here the elastic constant K is determined by the steric interaction and the constant λ is determined by steric and dispersion interactions. Therefore the temperature variation of the pitch in this model is associated with the packing entropy.[29] Such temperature variation corresponds to the gradual decrease of the pitch far from the transition temperature, which is observed in the experiment.[4,9,10]

It is worth noting that the flexoelectric constant g_0 contributes also to the expression for the critical magnetic field H_c which unwinds the helix in the ferroelectric C* phase. Minimization of the phenomenological free energy (13) yields

$$H_c = \frac{2(\lambda + \chi\mu_1 g_0)}{\sqrt{\chi_a\left(K - \chi g_0^2\right)}}, \tag{37}$$

where χ_a is the diamagnetic anisotropy. Thus one arrives at the conclusion that the strong temperature variation of H_c (similar to that of the pitch) should be observed in the ferroelectric C* phase. Very recently the corresponding temperature variation of the critical magnetic field H_c has been observed by Muševič *et al.*[39] in the ferroelectric liquid crystal DOBAMBC. It is interesting to note that in DOBAMBC the critical magnetic field H_c and the pitch h attain their extrema at the same temperature. This fact seems to be an independent argument in favour of the present theory.

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