

Flexoelectric effect and helicoidal twisting in chiral smectic C liquid crystals

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The steric interaction between asymmetric banana-shaped molecules in smectic C liquid crystals, which is one of the microscopic causes of the flexoelectric effect in the smectic C phase, is considered in detail. In contrast to other mechanisms of the flexoelectric effect, the steric interaction of the molecules leads to a strong temperature dependence of the flexoelectric coefficients in the smectic C phases, and this explains the unusual temperature dependence of the pitch of the helix in the ferroelectric C* phase.

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1. The flexoelectric effect (FE) in the smectic C phase manifests itself in the appearance, in the liquid crystal, of a polarization that is proportional to the orientational deformation of the field of the director \mathbf{n} . At small inclination angles θ there exist in the C phase three independent FE coefficients¹: g_0 , g_1 , and g_{11} , corresponding to three mutually perpendicular polarization directions \mathbf{P}_0 , \mathbf{P}_1 , and \mathbf{P}_{11} . The polarization \mathbf{P}_0 lies in the plane of the smectic layer and is parallel to the 2 axis, \mathbf{P}_{11} is directed along the crystal axis z perpendicular to the planes of the smectic layers, and \mathbf{P}_1 also lies and the plane of the smectic layer, with $\mathbf{P}_0 \perp \mathbf{P}_1$.¹⁾

In the chiral smectic C phase (C* phase), the flexoelectric coefficient g_0 contributes to the expression for the pitch h of the helicoid³:

$$h = 2\pi \frac{K - \chi g_0^2}{\lambda + \chi \mu_1 g_0} \quad (1)$$

where K is the elastic constant, λ and μ_1 are phenomenological constants that characterize the chirality of the molecules,³ and χ is the dielectric susceptibility. It is seen from (1) that the strong temperature dependence of the flexoelectric coefficient g_0 should influence the $h(T)$ dependence. In experiment one observes a strong temperature dependence of the helix pitch in the C* phase.^{4,5} The helix pitch h increases rapidly as the temperature decreases from the phase-transition point T_c , and then the growth rate of the pitch decreases sharply and the amplitude h reaches its maximum. Thus, e.g., the pitch of the helix in the liquid crystal DOBAMBC increases by several times when the temperature is changed by 1°C (see Fig. 1 of Ref. 4). The pitch of the helix decreases with further decrease of the temperature.

Such a strong temperature dependence of the helix pitch in the C* phase has found no explanation to this day. The phenomenological theory leads to a constant value of the pitch if the corresponding constants in (1) are temperature-independent. In the general case one can write the phenomenological expansion $h = h_0 (1 + a\theta^2 + b\theta^4 + \dots)$. In order to describe the steep linear growth of the pitch h at small angles θ , however, it must be assumed that $a \sim 10^2$ (for the smectic $d-n$ -

decyloxybenzilidene- n' -amino-2-methylbutyl-cinnamate-DOBAMBC, Ref. 4). In addition, the fact that $h(T)$ has a maximum⁴ at $\theta_0 \sim 10^{-1}$ leads to the condition $b \sim a^2 \sim 10^4$. Thus, all the terms in the expansion of h in powers of θ^2 are of the same order and the expansion itself becomes inapplicable. We show in the present paper that the temperature dependence of the helix pitch h in the C* phase can be explained by starting from the strong temperature dependence of the flexoelectric coefficient g_0 , calculated on the basis of the molecular-statistical theory.

The microscopic nature of the FE in the C* phase was considered by us in Ref. 2, where it was shown that there exist three principal contributions to the flexoelectric coefficients. These contributions are connected with the ordering of the molecular quadrupoles, with the dipole-quadrupole interaction, and with the steric interaction of the molecules. The quadrupole and dipole-quadrupole contributions are discussed in detail in Ref. 2, where it is shown that they depend little on the temperature and can be represented in the form of an expansion in powers of $\theta^2 = a'(T_c - T)$. At the same time, one of us has concluded that the steric interaction plays an insignificant role in the description of the flexoelectric effect in the vicinity of the transition point.⁶ This conclusion, however is valid only in the limit as $\theta \rightarrow 0$,

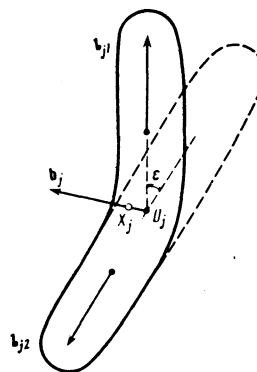


FIG. 1. Banana-shaped molecule j . The dashed outline is that of a cylindrically symmetrical molecule obtained in the limit as $\epsilon \rightarrow 0$.

so that the question of the influence of the steric interaction on the temperature dependence of the FE coefficients in the C^* phase remains open.

We show in the present paper that the steric interaction of the asymmetric molecules leads to a strong temperature dependence of the FE coefficients even at $\theta^2 \ll 1$. Therefore, in a certain sense, the steric interaction can be regarded as the main cause of the FE in the C^* phase. The strong temperature dependence of the coefficient g_0 can be explained in the following manner. The FE can result from a deviation of the molecule shape from cylindrical,⁷ and in this case an important role is the effective "banana-like" shape of the molecule, which can be characterized by two small parameters: the average inflection angle of the molecule $\varepsilon \ll 1$, and the ratio of the width of the molecule to its length $D/L \ll 1$. It is the presence of these two small parameters which leads to a strong temperature dependence of the FE coefficients, since the quantities g_0 and g_1 depend in the general case on the combinations θ/ε and $\theta L/D$, which are not small at inclination angles $\theta \sim \varepsilon$ or $\theta \sim D/L$. In this case the expansion of the coefficients g_0 and g_1 in powers of θ^2 is itself inapplicable. In fact, the expression $[1 + (\theta/\varepsilon)^2]^{1/2}$, e.g., cannot be approximated by the first several terms of the expansion in powers of θ^2 if $\theta \gtrsim \varepsilon$. In Sec. 4 of the present paper we shall show that expressions of this type appear when the contributions made to the coefficients g_0 and g_1 by the steric interaction of the molecules are calculated. It follows from the foregoing that it is necessary to review the conclusion of Ref. 6 that the steric interaction plays a negligible role, and the description of the FE in the C^* phase, for when account is taken of the small parameter ε the proof presented in Ref. 6 can be valid only at $\theta \ll \varepsilon$.

2. We examine now in greater detail the flexoelectric coefficients g_0 and g_1 , which connect the polarization with the derivatives of the director along the z axis.¹ The director direction \mathbf{n} in the C phase is described by the polar inclination angle θ and by the azimuthal angle φ :

$$n_x = \sin \theta \cos \varphi, \quad n_y = \sin \theta \sin \varphi, \quad n_z = \cos \theta. \quad (2)$$

In this case the polarizations are given by $P_0 \sim \partial \varphi / \partial z$ and $P_1 \sim \partial \theta / \partial z$ (Ref. 2). Thus, to determine the flexoelectric coefficients g_0 we need take into account only the dependence of φ on z . In this case

$$P_0 = -g_0 n_z \partial n / \partial z \quad \text{at} \quad \partial \theta / \partial z = 0. \quad (3)$$

In the case of steric interaction of the molecules, the statistical thermodynamics of the liquid crystal is completely determined in the molecular-field approximation by the function ξ_{ij} , which depends on the shape of the molecule and is the shortest possible distance between the mass centers of the molecules i and j at a given mutual orientation of these molecules.^{2,8} The orientations of the molecule i can be characterized by the unit vectors \mathbf{a}_i and \mathbf{b}_i of the long and short axes, respectively, $\mathbf{a}_i \perp \mathbf{b}_i$. Then

$$\xi_{ij} = \xi_{ij}(\mathbf{a}_i, \mathbf{b}_i, \mathbf{a}_j, \mathbf{b}_j, \mathbf{u}_{ij}).$$

Here $\mathbf{u}_{ij} = \mathbf{r}_{ij} / |\mathbf{r}_{ij}|$, where \mathbf{r}_{ij} is the vector joining the

mass centers of the molecules i and j . With the aid of the function ξ_{ij} , the following expression was obtained in Ref. 2 for the polarization P that appears, on account of the flexoelectric effect, in the result of the steric interaction of the molecules:

$$P = \rho^2 (1 - \alpha) d_{\perp} \iint \mathbf{b}_i \xi_{ij}^3 \frac{\partial \xi_{ij}}{\partial z_j} \delta(\mathbf{b}_i, \mathbf{n}_i) \delta(\mathbf{b}_j, \mathbf{n}_j) d\mathbf{b}_i d\mathbf{b}_j, \quad (4)$$

where $\xi_{ij} = \xi_{ij}(\mathbf{n}_i, \mathbf{n}_j, \mathbf{b}_i, \mathbf{b}_j, \mathbf{e})$ and $\delta(x)$ is the delta function. Expression (4) was obtained in the approximation of ideal nematic and smectic orders, therefore the vectors \mathbf{a}_i and \mathbf{a}_j were replaced by the local values \mathbf{n}_i and \mathbf{n}_j of the director at points \mathbf{r}_i and \mathbf{r}_j . In Eq. (4), \mathbf{e} is a unit vector fixed in space and perpendicular to the plane of the smectic layer, and α is the fraction of the molecules nearest neighbors located in the same smectic layer as the molecule. It is seen from (4) that the FE in the C^* phase, just as in the nematic phase,⁸ can result from the asymmetry of the shape of the molecule, inasmuch as for cylindrically symmetrical molecules the value of ξ_{ij} does not depend on the directions of the short axis \mathbf{b}_i and \mathbf{b}_j , and the integral in (4) vanishes.

We assume a model in which the molecules of the liquid crystals have the effective banana shape (Fig. 1) considered in the description of the FE in the nematic phase.⁷ It is convenient to describe the banana-like molecule by an average bending angle $\varepsilon \ll 1$, shown in Fig. 1. At small deviations from cylindrical symmetry, the value of ξ_{ij} depends little on the directions of the short axes \mathbf{b}_i and \mathbf{b}_j , and it can be represented approximately in the form

$$\xi_{ij} \approx \xi_{ij}^0 + \frac{\partial \xi_{ij}}{\partial \cos \omega_i} \mathbf{b}_i \mathbf{n}_j + \frac{\partial \xi_{ij}}{\partial \cos \omega_j} \mathbf{b}_j \mathbf{n}_i + \frac{\partial \xi_{ij}}{\partial \cos \kappa_i} \mathbf{b}_i \mathbf{e} + \frac{\partial \xi_{ij}}{\partial \cos \kappa_j} \mathbf{b}_j \mathbf{e}; \quad (5)$$

$$\cos \omega_i = \mathbf{b}_i \mathbf{n}_j, \quad \cos \omega_j = \mathbf{b}_j \mathbf{n}_i, \quad (6)$$

$$\cos \kappa_i = \mathbf{b}_i \mathbf{e}, \quad \cos \kappa_j = \mathbf{b}_j \mathbf{e},$$

where ξ_{ij}^0 does not depend on the \mathbf{b}_i direction. All the derivatives in (5) are taken at the points $\cos \omega = 0$, $\cos \kappa = 0$. We note that

$$|\xi_{ij} - \xi_{ij}^0| \sim \varepsilon \xi_{ij}^0.$$

We substitute now (5) in (4) and differentiate with respect to z_j , putting $\mathbf{n}_j = \mathbf{n}_i = \mathbf{n}$ after the differentiation, inasmuch as to describe the FE it is necessary to take into account only the terms that are linear in the gradients. Contributions to the polarization P_0 are made only by the gradients of the angle φ , so that to determine the flexoelectric coefficient g_0 it is necessary to differentiate only the quantity $\mathbf{b}_i \cdot \mathbf{n}_j$, since all the remaining coefficients in (5) depend only on the scalar product $\mathbf{n} \cdot \mathbf{e} = \cos \theta$. As a result we obtain the following expression for the polarization P_0 :

$$P_0 = \frac{1}{2} \rho^2 (1 - \alpha) d_{\perp} (\xi_{ij}^0)^2 \frac{\partial \xi_{ij}}{\partial \cos \omega_i} \frac{\partial \mathbf{n}}{\partial z}, \quad \frac{\partial \theta}{\partial z} = 0, \quad (7)$$

from which follows an expression for the flexoelectric coefficient g_0 :

$$g_0 = \frac{1}{2 \cos \theta} \rho^2 (1 - \alpha) d_{\perp} (\xi_{ij}^0)^2 \frac{\partial \xi_{ij}}{\partial \cos \omega_i}, \quad (8)$$

where the derivative is taken at the point $\cos \omega_i = 0$. Thus, the quantity g_0 is a function of only the inclination angle θ . At small inclination angles, ξ_{ij}^0 depends little on θ , and $\xi_{ij}^0 \approx L$, where L is the length of the molecule. Therefore at small inclination angles $\theta \ll D/L$ the temperature dependence of the flexoelectric coefficient g_0 is determined by the quantity $\partial \xi_{ij} / \partial \cos \omega_i$, which will be considered in Secs. 3 and 4.

3. To calculate the flexoelectric coefficient g_0 it is necessary to derive an expression for the quantity $\partial \xi_{ij} / \partial \cos \omega_i$, which is determined by the shortest distance ξ_{ij} between the mass centers. A general analytic expression for ξ_{ij} cannot be obtained even in the simplest cases. The quantity ξ_{ij} cannot be formally expanded in powers of ε (this situation is discussed in Sec. 1), i.e., the terms of higher order in the expansion of ξ_{ij} can be discarded, provided they do not contain combinations of the form $(\theta/\varepsilon)^2$. At small ε , however, the function ξ_{ij} can nevertheless be approximately expressed in terms of the simpler function Δ_{ij} , the form of which is determined only by the shape of the cylindrically symmetrical molecules, (i.e., as $\varepsilon \rightarrow 0$). To determine the form of the function Δ_{ij} we make the following change of variables that characterize the orientation of an asymmetrical molecule.

We consider again the banana-shaped molecule j in Fig. 1. At small bending angle ε such a molecule can be characterized by two vectors l_{j1} and l_{j2} (see Fig. 1), i.e., such a molecule can be approximately regarded as consisting of two cylindrically symmetrical parts with long axes l_{j1} and l_{j2} . Let now the point X_j in Fig. 1 be the mass center of the molecule j , and let the point O_j lie on the intersection of the axes l_{j1} and l_{j2} . The point O_j can also be defined as the limiting position of the mass center of the molecule as $\varepsilon \rightarrow 0$. The distance $X_j O_j \sim \varepsilon L$. We define also the vector k_{ij} joining the points O_i and O_j of the molecules i and j . Then, in analogy with ξ_{ij} , we can define Δ_{ij} as $\min |k_{ij}|$ at a given orientation of both molecules. The quantity Δ_{ij} has here the meaning of the shortest distance between the mass centers of the cylindrically symmetrical molecules with axes of length l_{j1} and l_{j2} . This cylindrically symmetrical molecule is shown dashed in Fig. 1.

We can now fix the orientation of the two touching banana-like molecules located in neighboring smectic layers in two stages (Fig. 2):

- 1) we fix the positions of the long axes l_{i2} and l_{j1} of the two touching parts of the molecules i and j ;
- 2) we fix the positions of the short axes of the molecules b_i and b_j by rotating them around the axes l_{i2} and l_{j1} .

We note that Δ_{ij} is not changed by the rotation of the corresponding molecules around the axes l_{i2} and l_{j2} , i.e.,

$$\Delta_{ij} = \Delta_{ij}(\cos \alpha, \cos \beta, \cos \gamma),$$

where

$$\cos \beta = l_{i2} v_{ij}, \quad \cos \alpha = l_{j1} v_{ij}, \quad \cos \gamma = l_{i2} l_{j1}, \quad v_{ij} = k_{ij} / |k_{ij}|.$$

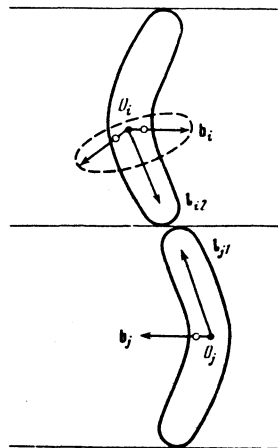


FIG. 2. Relative orientation of two touching banana-shaped molecules located in a neighboring smectic layers.

When the two molecules touch, the quantities Δ_{ij} and ξ_{ij} are connected by the following exact relations (see Fig. 2):

$$\Delta_{ij} v_{ij} = \xi_{ij} u_{ij} + \frac{1}{2} \varepsilon L_1 (b_i + b_j), \quad (9)$$

where εL_1 is the distance between the points X_i and O_j . At $\varepsilon \ll 1$ we have $L_1 \approx L$. It follows from (9) that $|u_{ij} - v_{ij}| \sim \varepsilon$, and expression (9) can be approximately rewritten in the form

$$\xi_{ij} \approx \Delta_{ij} - \frac{1}{2} \varepsilon L_1 (b_i u_{ij} + b_j u_{ij}). \quad (10)$$

We note that in this expression the quantity ξ_{ij} is a function of the scalar products of the vectors a_i , a_j , b_i , b_j , and u_{ij} , while Δ_{ij} is a function of the scalar products of the new vectors l_i , l_j , and v_{ij} introduced in the present section.

We can now express the derivative $\partial \xi_{ij} / \partial \cos \omega_i$ in terms of the quantity Δ_{ij} . In fact, it follows from (10) that

$$\frac{\partial \xi_{ij}}{\partial \cos \omega_i} = \frac{\partial \Delta_{ij}}{\partial \cos \omega_i}, \quad \cos \omega_i = b_i \cdot n_i. \quad (11)$$

The quantity Δ_{ij} depends on the scalar product $b_i \cdot n_j$ via quantities $l_i \cdot l_j$, $l_i \cdot v_{ij}$, and $l_j \cdot v_{ij}$. To determine the derivative in (11), and consequently to determine the flexoelectric coefficient g_0 , we must express the scalar products of the vectors l_i , l_j , and v_{ij} introduced by us in terms of the scalar products of the initial vectors a_i , a_j , b_i , b_j , u_{ij} ; $l_i = l_{i2}$, $l_j = l_{j1}$.

In the ideal nematic order, $a_i = n_i$ and the vectors n_i and l_i are connected by the relation (see Fig. 1)

$$n_i \cos \varepsilon = l_i + \sin \varepsilon b_i. \quad (12)$$

With the aid of (9) and (10) we can also express the vector v_{ij} in terms of the vectors u_{ij} , b_i , and b_j :

$$v_{ij} \approx u_{ij} + \varepsilon \frac{L_1}{\Delta_{ij}} [b_i + b_j - u_{ij} (b_i u_{ij}) - u_{ij} (b_j u_{ij})]. \quad (13)$$

Equations (12) and (13) allow us to express the scalar products of the vectors l_i , l_j , and v_{ij} introduced by us in terms of the scalar products of the vectors a_i , a_j , b_i , b_j , and u_{ij} . The derivative of interest to us in the right-hand side of Eq. (11) can then be written as the

derivative of a complicated function. As a result we arrive at the following expression:

$$\frac{\partial \Delta_{ij}}{\partial \cos \omega_i} \approx \frac{\partial \Delta_{ij}}{\partial \cos \beta} \frac{\epsilon L_i}{\Delta_{ij}} - \frac{\partial \Delta_{ij}}{\partial \cos \gamma} \epsilon. \quad (14)$$

Thus, the determination of the flexoelectric coefficient g_0 was reduced to a determination of the shortest distance Δ_{ij} between the mass centers of two cylindrically symmetrical molecules as a function of their relative orientation. The form of the function Δ_{ij} is determined by the simpler form of the cylindrical molecules ($\epsilon = 0$), while the nontrivial dependence on the asymmetry of the shape of the molecule is contained in the dependences of the new variables on the old ones [see (12) and (13)]. An expression for Δ_{ij} will be obtained in the next section.

4. The function Δ_{ij} can likewise not be expressed analytically even for bodies of simple shape. Nevertheless, when smectic C crystals are considered, additional simplifications arise, since the corresponding molecules are sufficiently elongated and are stacked on the average smectic layers. Therefore the main contribution to the steric interaction in (7) is made by molecules that touch end to end. Under these conditions we actually do not need to know the form of the function Δ_{ij} at all the values of the variables, so that the reliable approximate expressions can be obtained for Δ_{ij} in the case of bodies of simple shape.

We note above all that at $D/L \ll 1$ the limits of the variation of one of the angles α , β , and γ , which characterize the mutual orientation of the molecules in contact, depend strongly on the values of the two other angles, so that it is possible to express one of the angles approximately in terms of the two others. In fact, we consider the plane π (Fig. 3) that is parallel to the long axis of two touching molecules i and j and passes through the mass center of the molecule j . We consider also the projection v'_{ij} of the vector v_{ij} on the π plane. It is then obvious that $|x| \leq D/L$, where $x = v'_{ij} - v_{ij}$. At small inclination angles θ in the C phase, the ends of the molecules of the neighboring smectic layers are in contact, and $k_{ij} \sim L$. In this case we obtain the following relations:

$$\cos \alpha = l_i v_{ij} = l_i v'_{ij} + o(D/L), \quad (15a)$$

$$\cos \beta = l_j v_{ij} = l_j v'_{ij} + o(D/L). \quad (15b)$$

The three vectors l_i , l_j , and v'_{ij} lie in the same plane π and consequently

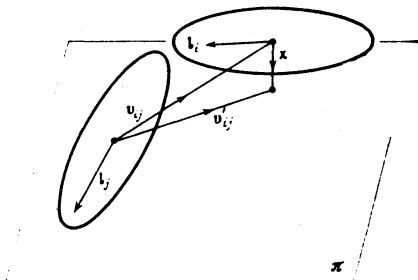


FIG. 3. Position of touching molecules i and j relative to the plane π parallel to the long axis of the molecules l_i and l_j and passing through the mass center of the molecule j .

$$\cos \alpha \approx \cos(\gamma - \beta), \quad (16)$$

$$\Delta_{ij} = \Delta_{ij}[\cos(\gamma - \beta), \cos \beta, \cos \gamma] + o(D/L),$$

assuming that $0 \leq \alpha, \beta, \gamma \leq \pi/2$.

Thus, for strongly elongated molecules Δ_{ij} depends effectively only on two angles, β and γ or respectively α and γ . In the case when the vectors l_i , l_j , and v_{ij} lie approximately in one plane, Δ_{ij} can be expressed in explicit form at small angles $\gamma < \beta < D/L$ for arbitrary convex cylindrically symmetrical molecules

$$\Delta_{ij} \approx L \cos \beta + \frac{L^2}{8R} \sin 2\beta \sin \gamma. \quad (17)$$

We have taken into account here the fact that the ends of the molecules are in contact, and that the shapes of the ends can be approximated by sections of a sphere of radius R , where R is the curvature radius of the surface of the molecule at the point of intersection with the long axis.

We can now use (17) to express in explicit form the derivatives contained in (14):

$$\frac{\partial \Delta_{ij}}{\partial \cos \beta} \approx L - \frac{L^2}{4R} \frac{\sin \gamma}{\sin \beta}, \quad (18a)$$

$$\frac{\partial \Delta_{ij}}{\partial \cos \gamma} \approx -\frac{L^2}{4R} \frac{\sin \beta}{\sin \gamma}, \quad \gamma < \beta \ll \frac{D}{L}. \quad (18b)$$

To obtain the final expressions, we must again change to the initial variables $n_i \cdot n_j$, $n_i \cdot u_{ij}$, and $n_j \cdot u_{ij}$. The vectors n_i , n_j , and u_{ij} are connected with the vectors l_i , l_j , and v_{ij} by relations (12) and (13), in which we must put $n_j = n_i = n$ and $u_{ij} = e$, in accordance with the range of definition of expressions (7) and (8). Under these conditions the angles β and γ in (18) are defined by

$$\cos \gamma = \cos^2 \epsilon, \quad \cos \beta = \cos \theta \cos \epsilon, \quad (19)$$

from which it follows that

$$\sin \beta / \sin \gamma \approx [1 + (0/\epsilon)^2]^{1/2}. \quad (20)$$

Thus, the condition of smallness of the angle $\gamma \ll D/L$ in (18) is always satisfied, since $\epsilon \ll D/L$, and the condition of the smallness of the angle β is satisfied at small inclination angles $\theta \ll D/L$ in the C* phase.

We have now obtained all the expressions needed to determine the flexoelectric coefficient g_0 at small inclination angles. In the general case the flexoelectric coefficient g_0 can be represented in the form

$$g_0 = g_{00} + g_{0s}, \quad (21)$$

where g_{00} depends little on the temperature and is the sum of the contributions due to the ordering of the molecular quadrupoles, the dipole-quadrupole interaction, and others,² while g_{0s} is determined by the steric interaction and depends strongly on the temperature:

$$g_{0s} \approx \frac{1}{4\sqrt{2}} \rho^2 (1 - \alpha) d_{\perp} L^4 \left(\frac{L}{2R} \right) \epsilon \left[1 + \left(\frac{\theta}{\epsilon} \right)^2 \right]^{1/2}. \quad (22)$$

In the derivation of this expression we have substituted (20) in (18), and next in (11) and in the initial expression (8), recognizing that $\xi_{ij}^0 \approx L$ in (8) at $\theta \ll D/L$. We have neglected here the contribution from (18a), since it decreases rapidly with increasing angle θ .

Expression (22) for the flexoelectric coefficient g_{0s} is valid at small inclination angles θ in the C^* phase. At the same time, when the temperature is lowered, the angle θ increases rapidly in the C^* phase and saturates at $\theta_{\max} \sim 1/2$ (Ref. 4). At $\theta \sim D/L$ we can no longer use the approximate expression (17) for Δ_{ij} , and it is necessary in this case to have an expression for the quantity $\Delta_{ij} = \Delta_{ij}(\beta, \gamma)$ at all β , i. e., at all angles θ . The form of the function Δ_{ij} should depend in this case on the actual shape of the molecule.

By way of specific model examples of the molecule shape, we have considered simple bodies: an ellipsoid of revolution with axes L and D , and a spherocylinder, constituting a cylinder of length L and diameter D , terminated on both ends by hemispheres of diameter D . For the ellipsoids of revolution obtained for Δ_{ij} , an expression that is asymptotically exact as $\gamma \rightarrow 0$ and is valid for all angles β :

$$\Delta_{ij} = \frac{1}{2} L \left[\cos^2 \beta + \left(\frac{L}{D} \right)^2 \sin^2 \beta \right]^{-1/2} + \frac{1}{2} L \left[\cos^2(\beta - \gamma) + \left(\frac{L}{D} \right)^2 \sin^2(\beta - \gamma) \right]^{-1/2}. \quad (23)$$

In this case a general expression valid at all angles $\theta < 1$ can be obtained for the flexoelectric coefficient g_{0s}

$$g_{0s} = \frac{1}{4\sqrt{2}} \rho^2 (1 - \alpha) d_{-L} \left(\frac{L}{D} \right)^2 \epsilon \frac{[1 + (\theta/\epsilon)^2]^{1/2}}{[1 + \theta^2 (L/D)^2]^{1/2}}, \quad (24)$$

with allowance for the fact that $\xi_{ij}^0 = \Delta_{ij}$ at $\beta = \theta$ and $\gamma = 0$ [see Eq. (6)]. We note that at $\gamma < \beta \ll D/L$ expression (24) actually goes over into Eq. (22) at $R = R_{el} = (D/2)(D/L)$, where R_{el} is the curvature radius of the ellipsoid of revolution at the point of intersection with the long axis. It follows from (24) that the flexoelectric coefficient g_{0s} increases rapidly at $\theta \ll D/L$, reaches a maximum, and at sufficiently large angles $\theta > D/L$ it begins to decrease slowly. At $\theta \ll D/L$ expression (24) goes over into expression (22). One can state, however, that expression (24) overestimates the flexoelectric coefficient g_{0s} at $\theta \ll D/L$, since $R_{el} \ll D/2$. This circumstance does not make it possible to use the ellipsoidal molecules for quantitative calculations of the flexoelectric coefficient g_{0s} , since the ellipsoids have ends that are too sharp, (at $D/L \ll 1$) with a small curvature radius $R_{el} \ll D/2$, and this influence strongly the steric interaction of the molecules at small angles θ . It is natural to assume that a real molecule has $R \approx D/2$, and consequently a real molecules is closer to a spherocylinder than to an ellipsoid.

The steric interaction of two spherocylinders in contact was considered in Ref. 12 and the value of Δ_{ij} is given in this case by the following exact expression, which can be easily obtained with the aid of Fig. 1 of Ref. 12 at $\beta > D/L$:

$$\Delta_{ij} = \frac{L \sin \gamma}{2 \sin \beta} + \frac{D}{\sin \beta} \left(\frac{D}{L} < \beta, \gamma < \frac{D}{L} \right). \quad (25)$$

Expression (25) also decreases with increasing angle θ [just as Δ_{ij} (24) for ellipsoids], i. e., the shape of the molecule does not affect the qualitative behavior of the flexoelectric coefficient g_{0s} as a function of the angle θ .

We have thus shown that steric interaction of asymmetric molecules leads to a complicated temperature dependence of the flexoelectric coefficient g_{0s} , of the form (24), and that this dependence is determined by the relation between the inclination angle θ in the C phase and the small parameters ϵ and D/L , $\epsilon < D/L$, which characterize the geometric shape of the molecules.²⁾

5. We proceed now to a discussion of the results. We note first that the flexoelectric coefficient g_{0s} is large enough compared with the characteristic values of the flexoelectric coefficients in the nematic phase. Indeed, substituting in (22) the constants typical of molecules that make up the smectic C phase, namely $d_1 = 1$ D, $L = 40$ Å, and $D = 5$ Å, and also $\alpha = 3/4$, $\rho = 10^{21}$ cm⁻³, we obtain the estimate $g_{0s} \sim 10^{-2} \epsilon [1 + (\theta/\epsilon)^2]^{1/2}$ cgs. The effective bending angle ϵ for long smectic molecules is apparently much smaller than for the short ones that make up the nematic phase (the molecules of the PAA liquid crystal, e. g., have $\epsilon = 5 \times 10^{-1}$, Ref. 9). It can be assumed that $10^{-2} \leq \epsilon \leq 10^{-1}$ for molecules that make up the C phase. Then the flexoelectric coefficient is $g_{0s} \sim 10^{-2} \theta > 10^{-3}$ at $(\theta/\epsilon)^2 \gg 1$, higher than the characteristic values of the flexoelectric coefficients in the nematic phase, which are of the order of $g \sim 10^{-4}$ cgs. As $\theta \rightarrow 0$ the value of g_{0s} decreases considerably and becomes negligible compared with the coefficient g_{00} in (21). Large values of the flexoelectric coefficient g_{0s} , compared with the characteristic values of the flexoelectric coefficients in the nematic phase (despite the smaller ϵ), are due mainly to the following factors:

- The coefficients g_{0s} is determined by the steric interaction of molecules lying in neighboring smectic layers, therefore we always have here $\xi_{ij}^0 \approx L$ in (8). At the same time, in the nematic phase the molecule mass centers are randomly distributed and the distances ξ_{ij}^0 between them take on values from L to D , i. e., in the nematic phase the averaged value is $\langle (\xi_{ij}^0)^3 \rangle \ll L^3$.
- Smectic molecules are longer than nematic, and $g_{0s} \sim L^4$.
- A factor $L/D \gg 1$ appears in expression (22) for the coefficient g_{0s} .

We consider now the influence of the FE on the temperature dependence of the pitch h of the helix in the ferroelectric C^* phase. The experimental $h(T)$ dependence is given in Ref. 4 and was discussed in Sec. 1 of the present paper together with the phenomenological theory. As already noted, the phenomenological theory does not explain the strong temperature dependence of the helix pitch $h(T)$ in the C^* phase. An expression for the helix pitch h in the C^* phase was obtained in Ref. 11 without allowance for the ferroelectric effect. In Ref. 11, accordingly, $h = 2\pi K/\lambda$ [see (1)], where the elastic constant K is determined by the steric interaction of the molecules: $K = K_0(1 + T/T_p)$ (T_p is a parameter that characterizes the shape of the molecule¹¹⁾ and the constant λ characterizes the chirality of the molecules and is determined both by the steric and the dispersion interactions of the molecules: $\lambda = \lambda_p + \lambda_s(1 + T/T_p)$. This temperature dependence of the constants K and λ leads to a smooth decrease of the helix pitch h with decreasing

temperature, and such a decrease is indeed observed in the C^* phase at large inclination angles θ . At the same time, at small angles $\theta \ll D/L$, corresponding to $T_c - T \sim 0-3^\circ\text{C}$, the temperature dependence of $h(T)$ considered in Ref. 11 can be neglected, whereas it is precisely in this region that experiment reveals a strong temperature dependence of the helix pitch.

The strong temperature dependence of the flexoelectric coefficient g_{0s} as a function of the angle θ explains all the main features of the temperature dependence of the helix pitch, since $\theta^2 = a'(T_c - T)$. It follows from (22) that at $\theta \leq \varepsilon$ we have

$$g_{0s} \sim [1 + (\frac{1}{2}) (\theta/\varepsilon)^2], \quad h \approx h_0 [1 + \sigma (\theta/\varepsilon)^2], \quad (26)$$

where the constants h_0 and σ are expressed in terms of the constants of Eqs. (1), (8), and (22). Thus, the linear growth of the helix pitch at $T_c - T \sim 1^\circ\text{C}$ is connected with the parameter $\varepsilon^{-2} \gg 1$. With further decrease of the temperature the growth rate of h decreases and the dependence of g_{0s} on $\theta L/D$ becomes simultaneously substantial [see (24)], leading to the appearance of a maximum in the function $h(\theta)$. It can be shown that at typical values of the constants the maximum of the helix pitch (which is observed in experiment^{1,5}) is reached at the point of the maximum of the function g_{0s} when $\theta = \theta_0$ ($\theta_0 = D/6L$ for ellipsoids). The value of θ_0 is determined from experiment, and for DOBAMBC we obtain the reasonable value $L/D \approx 6$. With further lowering of the temperature and with increasing angle θ , the g_{0s} ($\theta L/D$) becomes predominant and the helix pitch decreases. At still lower temperatures, the inclination angle saturates and in this region there is already necessary to take into account the temperature dependence of the constants K and λ in accordance with Ref. 11, which leads to further slow decrease of the pitch h . Thus, the flexoelectric effect plays an essential role in the smectic C^* phase, since the steric interaction of the molecules leads to large values of the flexoelec-

tric coefficient g_0 in the C^* phase, which depends strongly on the temperature and determines the temperature dependence of the helix pitch.

- ¹) It is known that the flexoelectric effect is not connected with the chirality of the molecules,^{1,2} therefore the phenomenological theory of the FE and all the expressions for the flexoelectric coefficients, obtained in the present paper, are valid for both the chiral and the nonchiral C phases.
- ²) We note that the steric interaction of the molecules determines also the stability of the C phase itself.¹⁰ In this case, however, steric forces of different symmetry act, since the C phase is formed in the model of cylindrical molecules,¹⁰ whereas the FE is determined by the deviation from cylindrical symmetry, which is characterized by the parameter ε .

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