Microscopic nature of the flexoelectric effect in smectic-*C* liquid crystals

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Zh. Eksp. Teor. Fiz. **80**, 2380–2391 (June 1981)

The connection is considered between the microscopic and phenomenological description of the flexoelectric effect in the smectic-*C* phase. The role of the known microscopic mechanisms of the flexoelectric effect, namely the steric interaction of asymmetric molecules and the ordering of the molecular quadrupoles, is discussed. The flexoelectric effect, which is essential for the description of the ferroelectric state in the chiral smectic-*C* phase, is discussed in detail, and it is shown that the steric interaction of the molecules is of no importance for the description of this effect in the vicinity of the transition point from the *C* phase to the *A* phase. A new microscopic mechanism of the flexoelectric effect (dipole-quadrupole interaction of molecules), which manifests itself only in the smectic-*C* phase, is proposed.

PACS numbers: 77.80. – e

1. The flexoelectric effect (FE) in nematic liquid crystals is usually attributed to the steric interaction of asymmetric molecules having dipole moments. Under the influence of curvature strains in the liquid crystal, this interaction produces polarization in the crystal. This explanation was first proposed by Meyer[1] and was subsequently developed by Derzhanski and Petrov[2] and Helfrich[3], where expressions were obtained for the principal flexoelectric coefficients in the nematic phase. In Refs. 2 and 3 they used a semiphenomenological methods of calculation, and a general microscopic approach to the description of the FE in nematics was developed by Straley.[4]

Prost and Marcerou[5] have proposed a new microscopic mechanism of the FE, based on the fact that the gradient of the average density of the molecular quadrupole moment in an anisotropic medium corresponds to the appearance of macroscopic polarization. Despite its being general, the mechanism considered in Ref. 5 has a major shortcoming, since it leads to identical (or to very close) values for the two flexoelectric coefficients in the nematic phase, in contradiction to many experimental data.[6] At the same time, it is possible in principle to separate the dipole and quadrupole contributions to the flexoelectric coefficients, since the dipole contribution[2,3] is proportional to S^2, where S is the nematic-order parameter, whereas the quadrupole contribution is proportional to S.[5]

In a recent study, Marcerou and Prost[7] investigated the temperature dependence of the flexoelectric coefficients and found that as a rule they are proportional to S, with the exception of substances with large dipole moments. A strong FE was observed[7] in a liquid crystal consisting of symmetrical molecules that have no dipole moments. Thus, on the whole the question of the basic microscopic cause of the FE remains unclear, and a complete solution of this problem will apparently require new experiments.

The flexoelectric effect is present also in smectic phases. In the smetic-*A* and -*C* phases the polarization can result from strains in the smectic layers.[8] At the same time, in the smectic-*C* phase, in analogy with the nematic phase, the polarization can be linearly connected with the curvature of the director field. The FE in the smectic-*C* phase has recently been extensively discussed in the literature in connection with the description of the ferroelectric state in the chiral smectic-*C* phase (C^* phase).[9-11] In the C^* phase, owing to the chirality of the molecules, spontaneous helicoidal twisting of the long axes of the molecules takes place around the normal to the smectic layers. This leads, owing to the FE, to the appearance of additional spontaneous polarization in the smectic-layer plane. Thus, the construction of the complete microscopic picture of the ferroelectric state in the C^* phase is impossible without clarification of the microscopic nature of the FE in this phase.[1)]

It is usually assumed that the FE in the *C*-phase is similar to the FE in nematics.[11] One of us, however, has shown[13] that the steric interaction of the molecules makes no contribution to the FE along the z axis in the vicinity of the point of transition from the *C* phase to the *A* phase. In the present paper this question is discussed in detail in Sec. 4. In addition, we consider a new microscopic mechanism of the FE, which manifests itself only in the smectic phase, namely dipole-quadrupole interaction of molecules.

In Sec. 2 we present the results of a phenomenological theory of the FE in the C^* phase.[2)] In Sec. 3 is developed a general microscopic approach to the description of the FE in the smectic C^* phase. In Sec. 4 we discuss the role of the steric and dipole-dipole interaction of the molecules. In Sec. 5, finally, we calculate the flexoelectric coefficients on the basis of the dipole-quadrupole interaction and discuss possible methods of experimentally verifying the results of the present paper.

2. We consider now a phenomenological approach to the description of the FE in the C^* phase. In weak electric fields $E \ll E_c$, where E_c is the orientational-helix untwisting field, the induced polarization P in the C^* phase does not necessarily coincide with the axis 2 (the $\mathbf{n}'$ axis in Fig. 1), and generally speaking, contains three independent contributions:

$$\mathbf{P}=\mathbf{P}_0+\mathbf{P}_\perp+\mathbf{P}_\parallel.$$

The vector $\mathbf{P}_0$ is oriented here along the axis 2, i.e., along the direction of the spontaneous polarization in

0038-5646/81/061245-06$02.40

the smectic layer, the vector $\mathbf{P}_{\parallel}$ is oriented along the crystal axis z, and the vector $\mathbf{P}_{\perp}$ is perpendicular to the vectors $\mathbf{P}_0$ and $\mathbf{P}_{\parallel}$.

We note that $\mathbf{P}_0 \neq 0$ also in the absence of an external electric field, owing to the spontaneous twisting of the orientational structure; this spontaneous FE corresponds to the presence of the following invariant in the free energy of the system[9]:

$$-g_0\left(P_{0x}\frac{\partial(n_z n_x)}{\partial z}+P_{0y}\frac{\partial(n_z n_y)}{\partial z}\right)=\frac{1}{2}g_0\sin 2\theta\frac{\partial\varphi}{\partial z}P_0, \tag{1}$$

where g_0 is the flexoelectric coefficient, θ and φ are the polar and azimuthal angles in the distribution

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

The spontaneous polarization $\mathbf{P}_0$ resulting from the FE is described by the expression[9]

$$\mathbf{P}_0=-g_0\frac{\partial}{\partial z}n_z\mathbf{n}_{\perp}=-g_0 n_z\frac{\partial\mathbf{n}}{\partial z}\quad\text{at}\quad\frac{\partial n_z}{\partial z}=0,$$
$$g_0=\text{const}\neq 0\ \text{at}\ \theta=0. \tag{2}$$

In the presence of a homogeneous external field $\mathbf{E}$, the initial distributions $\theta=\theta_0=\text{const}$ and $\theta=\theta_0=q_0 z$ are subjected to inhomogeneous perturbations $\varphi(z)-\varphi_0(z)$ and $\theta(z)-\theta_0$; in a weak field these perturbations are small and independent of each other. Accordingly, we can write for the C^* phase the additional flexoelectric contributions to the free energy in the form

$$-g_{\perp}\left(P_{\perp x}\frac{\partial(n_z n_x)}{\partial z}+P_{\perp y}\frac{\partial(n_z n_y)}{\partial z}\right)=-g_{\perp}\cos 2\theta\frac{\partial\theta}{\partial z}P_{\perp}, \tag{3a}$$

$$-g_{\parallel}P_{\parallel}\left(\frac{\partial(n_z n_x)}{\partial x}+\frac{\partial(n_z n_y)}{\partial y}\right), \tag{3b}$$

where $g_{\perp}$ and $g_{\parallel}$ are the flexoelectric moduli. Thus, the coefficients $g_{\perp}$ and $g_{\parallel}$ connect respectively the quantities $\mathbf{P}_{\perp}$ with $\partial\theta/\partial z$ and $\mathbf{P}_{\parallel}$ with the derivatives of the angles θ and φ with respect to the coordinates x and y. The indicated invariants contain the lowest powers of the small polar angle θ. On going to the A-phase, the angle θ_0 vanishes, and the directions $\mathbf{P}_0$ and $\mathbf{P}_{\perp}$ become equivalent, i.e., the coefficients g_0 and $g_{\perp}$ should differ by an amount proportional to θ_0^2 if $\theta_0^2 \ll 1$:

$$g_0-g_{\perp}\sim\theta^2.$$

3. We proceed now to the microscopic description of the FE in the C^* phase. In the nematic phase, a consistent microscopic approach was developed by Straley[4] and we shall apply it with slight modifications and generalizations to the smectic phase. The free energy of the liquid crystal per molecule, in the molecular-field approximation, can be written in the form

$$F=\rho\int f(\mathbf{v}_i,\mathbf{r}_i)U(\mathbf{v}_i,\mathbf{v}_j,\mathbf{r}_i-\mathbf{r}_j)f(\mathbf{v}_j,\mathbf{r}_j)\,d\mathbf{v}_i\,d\mathbf{v}_j\,d\mathbf{r}_i\,d\mathbf{r}_j$$
$$-kT\int f(\mathbf{v},\mathbf{r})\ln f(\mathbf{v},\mathbf{r})\,d\mathbf{v}\,d\mathbf{r}. \tag{4}$$

Here $U(\boldsymbol{\nu}_i,\boldsymbol{\nu}_j,\mathbf{r}_i-\mathbf{r}_j)$ is the potential of the interaction of the molecules i and j, located at the points $\mathbf{r}_i$ and $\mathbf{r}_j$; $\boldsymbol{\nu}_i$ is the set of angles that specify the orientation of the molecule; ρ is the number of molecules per unit volume.

We represent the distribution function f in the form

$$f(\mathbf{v},\mathbf{r})=f_0(\mathbf{v},\mathbf{r})+\psi(\mathbf{v},\mathbf{r}),$$

where f_0 is the single-particle distribution function for a liquid crystal without strains. This representation is justified because in the description of the FE it suffices to consider only terms linear in the gradients.

Minimizing expression (4) with respect to f we obtain the following expression for $f(\nu,\mathbf{r})$, which is similar to Eq. (9) of Ref. 4:

$$f(\mathbf{v}_i,\mathbf{r}_i)=f_0(\mathbf{v}_i,\mathbf{r}_i)+\beta\rho\int\mathbf{r}_{ij}f_0(\mathbf{v}_i,\mathbf{r}_j+\mathbf{r}_{ij})U(\mathbf{v}_i,\mathbf{v}_j,\mathbf{r}_{ij})\nabla_j f_0(\mathbf{r}_j)\,d\mathbf{r}_{ij}\,d\mathbf{v}_j,$$
$$\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j. \tag{5}$$

Unlike in the nematic phase considered in Ref. 4, in the smectic phase the single-particle distribution function depends on the coordinates not only via the director $\mathbf{n}=\mathbf{n}(r)$, but also indirectly, a fact reflected in (5), since the distribution functions $f_0(\nu,\mathbf{r})$ have not been taken outside the integral with respect to $\mathbf{r}_{ij}$. We are interested here in the linear connection between the polarization and the derivatives of the director. Therefore in the differentiation with respect to $\mathbf{r}_j$ this additional dependence on the coordinates is not taken into account, since it leads to the FE connected with the bending of the layers.

Expressions (4) and (5) include the averaging of the molecule interaction potential over various directions of the intermolecular vector $\mathbf{r}_{ij}$. In the nematic phase, the gravity centers of the molecules are randomly disposed, and the averaging over $\mathbf{r}_{ij}$ is simply integration with respect to all the $\mathbf{r}_{ij}$. In smectic phases, the gravity centers of the molecules are on the average located in the planes of the smectic layers, and different directions become nonequivalent. In the general case, the averaging over $\mathbf{r}_{ij}$ can be carried out with the aid of the following interpolation proposed in Ref. 14:

$$\int f_0(\mathbf{v}_i,\mathbf{r}_j+\mathbf{r}_{ij})U(\mathbf{v}_i,\mathbf{v}_j,\mathbf{r}_{ij})\mathbf{r}_{ij}\,d\mathbf{r}_{ij}=[1-\langle\cos\varkappa\rangle^2]f_0(\mathbf{v}_i)\int\mathbf{r}_{ij}U(\mathbf{v}_i,\mathbf{v}_j,\mathbf{r}_{ij})\,d\mathbf{r}_{ij}$$
$$+\alpha\langle\cos\varkappa\rangle^2 f_0(\mathbf{v}_i)\int\mathbf{r}_{ij}U(\mathbf{v}_i,\mathbf{v}_j,\mathbf{r}_{ij})\delta(\mathbf{r}_{ij}\mathbf{e})\,d\mathbf{r}_{ij} \tag{6}$$
$$+(1-\alpha)\langle\cos\varkappa\rangle^2 f_0(\mathbf{v}_i)\mathbf{e}\int r_{ij}^3\,U(\mathbf{v}_i,\mathbf{v}_j,r_{ij}\mathbf{e})\,dr_{ij}.$$

Here $\langle\cos\varkappa\rangle$ is the smectic-order parameter, $\mathbf{e}$ is the normal to the smectic layer, and α is the fraction of the nearest neighbors of the given molecule located in the same smectic layer with it. The second and third terms in (6) are respectively the contributions from the interactions of the nearest neighbors within the limits of one smectic layer and between neighboring layers. Expression (6) is exact in the limiting cases $\langle\cos\varkappa\rangle=0$ (nematic phase) and $\langle\cos\varkappa\rangle=1$ (ideal smectic order).

We shall find it convenient to characterize the orientation of a given molecule i by the unit vectors a_i and b_i of the long and short axis of the molecule, respectively. Recognizing that $\mathbf{a}_i\cdot\mathbf{b}_i=0$, we have

$$f(\mathbf{v}_i)\,d\mathbf{v}_i=f(\mathbf{a}_i,\mathbf{b}_i)\delta(\mathbf{a}_i\mathbf{b}_i)\,d\mathbf{a}_i d\mathbf{b}_i.$$

The polarization produced in the liquid crystal under the influence of the curvature strains can then be written, after averaging with the aid of the function $f=f_0+\psi$, in the form

$$\mathbf{P}=\rho d_{\perp}\langle\mathbf{b}_i\rangle+\rho d_{\parallel}\langle\mathbf{a}_i\rangle=\rho\int(d_{\perp}\mathbf{b}_i+d_{\parallel}\mathbf{a}_i)\psi(\mathbf{b}_i,\mathbf{a}_i)\delta(\mathbf{b}_i\mathbf{a}_i)\,d\mathbf{b}_i\,d\mathbf{a}_i, \tag{7}$$

where $d_{\perp}$ and $d_{\parallel}$ are the components of the dipole moment of the molecules. No account was taken in (7) of the contribution made to the polarization by the gradient of the average quadrupole moment in accordance with Ref. 5. This will be considered separately in Sec. 5.

Substituting (5) in (7), we can obtain with the aid of (6) a general expression for the polarization P in both the nematic and the smectic phases. When describing the smectic-C phase we can approximately assume the translational and orientational orders to be ideal, since the order parameters S and $\langle\cos\varkappa\rangle$ are close to unity. We therefore put $\mathbf{a}_i=\mathbf{n}_i$, i.e.,

$$f_0(\mathbf{a}_i,\mathbf{n}_i)=\delta((\mathbf{a}_i\mathbf{n}_i)^2-1),$$

and neglect also the first term of (6). Taking the foregoing into account, we obtain the following expression for the polarization produced in the smectic-C^* phase on account of the FE:

$$\begin{gathered}\mathbf{P}=\rho^2\langle\cos\varkappa\rangle^2\beta\int(d_\perp\mathbf{b}_i+d_\parallel\mathbf{n}_i)\,\delta(\mathbf{b}_i\mathbf{n}_i)\\ \times\left[\alpha\int\mathbf{u}_{ij}\nabla_jV(\mathbf{n}_i,\mathbf{n}_j,\mathbf{b}_i,\mathbf{u}_{ij})\,\delta(\mathbf{u}_{ij}\mathbf{e})\,d\mathbf{u}_{ij}+\mathbf{e}\nabla_j(1-\alpha)\,V(\mathbf{n}_i,\mathbf{n}_j,\mathbf{b}_i,\mathbf{e})\right]d\mathbf{b}_i,\\ \mathbf{r}_{ij}=r_{ij}\mathbf{u}_{ij},\quad|\mathbf{u}_{ij}|=1.\end{gathered}\tag{8}$$

We have introduced here the function

$$V(\mathbf{n}_i,\mathbf{n}_j,\mathbf{b}_i,\mathbf{u}_{ij})=\int U(\mathbf{n}_i,\mathbf{n}_j,\mathbf{b}_i,\mathbf{b}_j,r_{ij}\mathbf{u}_{ij})\,\delta(\mathbf{b}_j\mathbf{n}_j)\,r_{ij}^3\,dr_{ij}\,d\mathbf{b}_j,\tag{9}$$

which represents the averaged effective interaction for molecules i and j. It is this interaction which is decisive in the microscopic description of the FE.

To obtain the flexoelectric coefficients, it is now sufficient to substitute the actual molecule interaction potential in the general formulas (6) and (9) and carry out the corresponding integrations. However, we shall consider first in general form the FE component of the type (2), which is essential for the description of the ferroelectric state in the C^* phase, as noted in Sec. 1. The general expression for the FE of the type (2) can be obtained from (8) and (9) by considering the gradient only along the z axis which is parallel to the normal to the smectic layers:

$$\mathbf{P}_0+\mathbf{P}_\perp=\rho^2\beta\langle\cos\varkappa\rangle^2(1-\alpha)\,d_\perp\int\mathbf{b}_i\frac{\partial}{\partial z_j}V(\mathbf{n}_i,\mathbf{n}_j,\mathbf{b}_i,\mathbf{e})\,\delta(\mathbf{b}_i\mathbf{n}_i)\,d\mathbf{b}_i.\tag{10}$$

In (10) we took into account only the perpendicular component of the dipole moment of the molecule $d_\perp$, since the longitudinal component makes no contribution to the polarization perpendicular to the director $\mathbf{n}$.

The arbitrary function $V(\mathbf{n}_i,\mathbf{n}_j,\mathbf{b}_i,\mathbf{e})$ can be expanded in accordance with Ref. 15 in eigenfunctions, the so-called spherical invariants, which are polynomials of different degress of various scalar combinations of the vectors $\mathbf{n}_i$, $\mathbf{n}_j$, $\mathbf{b}_i$, and $\mathbf{e}$. We shall consider for simplicity the interaction of nonchiral molecules, since the FE, generally speaking, is not connected with chirality. In this case the function $V(\ldots)$ can be represented in the form of an expansion in all possible powers of only scalar products of the indicated vectors. We now differentiate each term of such an expansion with respect to z_j and put after the differentiation $\mathbf{n}_i=\mathbf{n}_j=\mathbf{n}$, since we are considering terms linear in the gradients. Then, after differentiation, the considered expansion will contain only scalar products

$$\mathbf{b}_i\mathbf{e},\ \mathbf{n}\mathbf{e},\quad \mathbf{e}\frac{\partial\mathbf{n}}{\partial z},\quad \mathbf{b}_i\frac{\partial\mathbf{n}}{\partial z},$$

since

$$\mathbf{n}\frac{\partial\mathbf{n}}{\partial z}=0\ \text{and}\ \mathbf{b}_i\mathbf{n}=0.$$

Thus, after differentiation, the quantity $(\partial/\partial z_j)V(\ldots)$ can be represented in the form of a series (or of a finite sum), each term of which is a product of the indicated scalar products raised to different powers. Each term of the series can contain only one scalar product that includes $\partial n/\partial z$. In addition, the averaged interaction potential $V(\ldots)$, and consequently, also its derivative $(\partial/\partial z_j)\,V(\ldots)$, must be even in $\mathbf{n}$ because the states with $\mathbf{n}$ and $-\mathbf{n}$ are indistinguishable. In the quantities $(\partial/\partial z_j)V(\ldots)$ it suffices to take into account only the contributions odd in $\mathbf{b}_i$, which do not cause the integrand of (8) to vanish identically.

Taking the foregoing into account, we can represent the quantity $(\partial/\partial z_j)V(\ldots)$ after differentiation in the form

$$\begin{aligned}\frac{\partial}{\partial z_j}V(\mathbf{n}_i,\mathbf{n}_j,\mathbf{e},\mathbf{b}_i)={}&\left(\mathbf{e}\frac{\partial\mathbf{n}}{\partial z}\right)(\mathbf{b}_i\mathbf{e})\sum_{l,k}L_{lk}(\mathbf{n}\mathbf{e})^{2l+1}(\mathbf{b}_i\mathbf{e})^{2k}\\ &+\left(\mathbf{b}_i\frac{\partial\mathbf{n}}{\partial z}\right)(\mathbf{b}_i\mathbf{e})^2\sum_{l,k}M_{lk}(\mathbf{n}\mathbf{e})^{2l+1}(\mathbf{b}_i\mathbf{e})^{2k}\\ &+\left(\mathbf{b}_i\frac{\partial\mathbf{n}}{\partial z}\right)\sum_{l}M_l(\mathbf{n}\mathbf{e})^{2l+1},\end{aligned}\tag{11}$$

where M and L are numerical coefficients.

In (11) we have specially separated in the last term all the expansion terms that do not contain the product $\mathbf{b}_i\cdot\mathbf{e}$, since it can be shown that to describe an FE of the type (2) only this last term of (11) is of significance. Indeed when describing the ferroelectric state, one uses for the FE expression (1) in which the flexoelectric coefficient g_0, generally speaking, does not vanish at $\theta=0$, i.e., at $\mathbf{n}\cdot\mathbf{e}=1$.[9] At the same time, the quantity $\mathbf{b}_i\cdot\mathbf{e}\sim\sin\theta$, since $\mathbf{b}_i=\mathbf{k}\sin\gamma+\mathbf{n}'\cos\gamma$, where $\mathbf{k}$ and $\mathbf{n}'$ are unit vectors lying in a plane perpendicular to the long axis of the molecule $\mathbf{a}_i$, $\mathbf{n}'\cdot\mathbf{e}=0$ (see Fig. 1), γ is the azimuthal angle of rotation of the molecule around the long axis, and $\mathbf{b}_i\cdot\mathbf{e}=\mathbf{k}\cdot\mathbf{e}\sin\gamma=\sin\theta\sin\gamma$.

Therefore the first two terms in (11) yield only small corrections to the flexoelectric coefficient g_0 in the vicinity of the A–C^* transition, where θ is small.

4. All the expressions and results obtained in the preceding section are valid for any interaction potential. We consider now steric interaction of the molecules and show that it makes no contribution to the ferroelectric coefficient g_0 in (2) in the zeroth approximation in

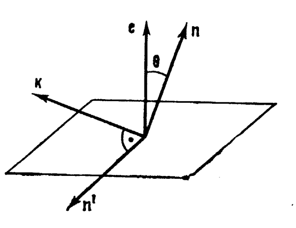

FIG. 1. Positions of the orthogonal vectors $\mathbf{n}'$, $\mathbf{k}$, and $\mathbf{n}$ relative to the crystallographic axis $\mathbf{e}$ in the smectic C phase.

θ. When account is taken of the steric interaction, the quantity $U(\dots)$ must be rewritten in the form[4]

$$\beta U(\mathbf{a}_i, \mathbf{a}_j, \mathbf{b}_i, \mathbf{b}_j, \mathbf{r}_{ij}) = \Omega(\xi_{ij} - r_{ij}),$$

where $\Omega(\dots)$ is the step function, ξ_{ij} is the closest approach distance of the molecules i and j with their orientations specified. We have $\Omega(\xi_{ij} - r_{ij}) = 1$ if the volumes of the molecules overlap, and $\Omega(\xi_{ij} - r_{ij}) = 0$ in the opposite case. For steric interaction, the function $V(\dots)$ then acquires the form

$$V(\mathbf{n}_i, \mathbf{n}_j, \mathbf{b}_i, \mathbf{u}_{ij}) = kT \int \Omega(\xi_{ij} - r_{ij}) r_{ij}^3 \delta(\mathbf{b}_j \mathbf{n}_j)\, dr_{ij}\, d\mathbf{b}_j = {}^1/_4\, kT \int \xi_{ij}^4 \delta(\mathbf{b}_j \mathbf{n}_j)\, d\mathbf{b}_j. \tag{12}$$

Thus, the effective potential of the steric interaction is proportional to the fourth power of the molecule closest-approach distance and is averaged over the rotations of the molecule j around the long axis. We note that the definition (9) of the effective interaction potential $V(\dots)$ does not contain averaging over $\mathbf{u}_{ij}$. We consider now the steric interaction of the molecules at $\theta = 0$, i.e., at $\mathbf{n}_i \parallel \mathbf{n}_j \parallel \mathbf{e}$. This molecule configuration is shown in the figure of Ref. 13. As seen from this figure, the closest-approach distance ξ_{ij} is equal to the length of the molecule and does not depend on the direction $\mathbf{b}_i$ of the short axis of the molecule i. We arrive therefore at the conclusion that under these conditions the averaged potential of the steric interaction $V(\cdots)$ does not depend on the direction $\mathbf{b}_i$ of the short axis at $\theta = 0$. But then expression (9) should likewise be independent of $\mathbf{b}_i$ at $\theta = 0$ in the case of steric interaction. The result can be explained as follows. At $\theta = 0$, the C^* phase goes over into the A phase, in which all the directions perpendicular to the crystal axis z become equivalent. Therefore the direction of the short axis of the molecule does not influence in this case the steric interaction of the molecules along the z axis, since this interaction is determined by the projection of the form of the molecule on this axis.

As already noted, the first two terms in (11) vanish at $\theta = 0$ for any potential $V(\dots)$. At the same time, the third term in (11) depends on $\mathbf{b}_i$. Therefore, from the condition that the expression (11) be independent of the direction $\mathbf{b}_i$ at $\theta = 0$ it follows that the third term in (9) should also vanish at $\theta = 0$. Recognizing that $\mathbf{n} \cdot \mathbf{e} = \cos\theta$, we obtain the relation

$$\sum_l M_l (\cos\theta)^{2l+1} = 0 \quad \text{at} \quad \theta = 0. \tag{13}$$

It follows from (11) that

$$\sum_l M_l (\cos\theta)^{2l+1} = \theta^2 \Phi(\theta), \tag{14}$$

where the function $\Phi(\theta)$ is bounded at zero.

We have thus shown that in the case of steric interaction of the molecules all the terms in (11) tend to zero as $\theta \to 0$, and consequently the steric interaction leads only to small corrections to the principal value of the flexoelectric coefficient g_0 in (2) in a vicinity of the A–C^* transition point, where θ is small. The result means that the FE of the type (2) can be determined mainly by the ordering of the quadrupole moments of the molecules in accordance with Ref. 5, or by some other (non-steric) interaction of the molecules. A quadrupole FE undoubtedly exists in the C^* phase and will be discussed in the next section.

We propose to consider a new microscopic FE mechanism in the smectic-C phase, namely dipole-quadrupole interaction of the molecules. Indeed, from the foregoing analysis it follows that the steric interaction was of no importance for the description of the FE of type (2) in the vicinity of the A–C transition point, since it does not depend on the direction $\mathbf{b}_i$ of the short axis at the molecule arrangement shown in the figure of Ref. 13. At the same time it is obvious that the multipole interaction of the molecules under the same conditions depends generally speaking on the direction $\mathbf{b}_i$ (e.g., if the dipole of the molecule i is directed along $\mathbf{b}_i$). At the same time, the dipole-dipole and quadrupole-quadrupole interactions, as well as the corresponding induction and dispersion interactions, make no contribution to the FE, since the potentials of these interactions are even in $\mathbf{u}_{ij}$, and the integrals with respect to $\mathbf{u}_{ij}$ in (5) and (6) should vanish. It remains to consider the dipole-quadrupole interaction of the molecules, which has all the necessary properties. In this case the interactions of the higher multipoles make apparently a small contribution.

We assume for simplicity that the axes $\mathbf{a}_j$ and $\mathbf{b}_j$ coincide with the principal axes of the quadrupole-moment tensor of the molecule j, and the dipole of the molecule i lies in the $\mathbf{a}_i \mathbf{b}_i$ plane. Then the dipole-quadrupole interaction of the molecules i and j can be written in the form[3)]

$$\begin{gathered} U_{d-q}(i,j) = r_{ij}^{-4} (U_{d-q}^{ij} + U_{d-q}^{ji}), \\ U_{d-q}^{ij} = \frac{3}{2} \left(\sum_l q_{lli} \right) [d_\perp \mathbf{b}_j \mathbf{u}_{ij} + d_\parallel \mathbf{a}_j \mathbf{u}_{ij}] \\ + 3 \sum_l q_{lli} (\mathbf{l}_i \mathbf{u}_{ij}) [d_\perp \mathbf{l}_i \mathbf{b}_j + d_\parallel \mathbf{l}_i \mathbf{a}_j] - \frac{15}{2} [d_\perp \mathbf{b}_j \mathbf{u}_{ij} + d_\parallel \mathbf{a}_j \mathbf{u}_{ij}] \sum_l q_{lli} (\mathbf{l}_i, \mathbf{u}_{ij})^2. \end{gathered} \tag{15}$$

Here $l = x, y, z$, $\mathbf{l}_i = \mathbf{a}_i$, $\mathbf{b}_i$, $\mathbf{c}_i$, the unit vectors $\mathbf{a}_i$, $\mathbf{b}_i$, and $\mathbf{c}_i$ are directed along the axes z, x, y, and q_{ll} are the diagonal matrix elements of the quadrupole moment of the molecule.

Substituting the interaction potential (15) in (10) and averaging over $\mathbf{b}_j$ and r_{ij}, we obtain an expression for the effective potential $V(\dots)$ in the form

$$\begin{gathered} V(\mathbf{a}_i, \mathbf{a}_j, \mathbf{b}_i, \mathbf{u}_{ij}) = {}^9/_4 (q_{xx} + q_{yy}) [d_\perp \mathbf{b}_i \mathbf{u}_{ij} + d_\parallel \mathbf{a}_i \mathbf{u}_{ij}] \\ + 3Q [d_\perp \mathbf{a}_j \mathbf{b}_i + d_\parallel \mathbf{a}_i \mathbf{a}_j] (\mathbf{a}_j \mathbf{u}_{ij}) [1 - {}^5/_2 (\mathbf{a}_j \mathbf{u}_{ij})^2], \end{gathered} \tag{16}$$

where Q is the asymmetrical part of the quadrupole of the molecule, $Q = q_{zz} - (q_{xx} + q_{yy})/2$.

Substituting in (16) $\mathbf{u}_{ij} = \mathbf{e}$, $\mathbf{a}_i = \mathbf{n}_i$, and $\mathbf{a}_j = \mathbf{n}_j$, and comparing with the general expansion (11), we verify that the averaged potential of the dipole-quadrupole interaction, in contrast to the steric interaction, contains terms that depend on the $\mathbf{b}_i$ direction and do not vanish at $\theta = 0$. Therefore the dipole-quadrupole interaction contributes to the FE of type (2) in the zeroth approximation in θ. The expressions for the corresponding flexoelectric coefficients will be presented in the next section.

5. We note that the dipole-quadrupole interaction leads to the appearance of the FE only in the smectic-C

phase. It can be shown that in the nematic phase the corresponding contribution to the polarization vanishes identically on account of the higher symmetry of this phase. Indeed, putting in (6) $\langle\cos\varkappa\rangle=0$, we can easily obtain with the aid of (5)–(7) an expression for the polarization produced in the nematic phase on account of the FE:

$$\mathbf{P}=\rho^2\beta\int(d_\perp\mathbf{b}_i+d_\parallel\mathbf{a}_i)\int f_0(\mathbf{a}_i,\mathbf{n}_i)\tilde{V}(\mathbf{a}_i,\mathbf{a}_j,\mathbf{b}_i)\nabla_j f_0(\mathbf{a}_j,\mathbf{n}_j)\times\delta(\mathbf{b}_i\mathbf{a}_i)\,d\mathbf{b}_i\,d\mathbf{a}_i\,d\mathbf{a}_j, \tag{17a}$$

$$\tilde{V}(\mathbf{a}_i,\mathbf{a}_j,\mathbf{b}_i)=\int\mathbf{u}_{ij}V(\mathbf{a}_i,\mathbf{a}_j,\mathbf{b}_i,\mathbf{u}_{ij})\,d\mathbf{u}_{ij}. \tag{17b}$$

Integrating (17b) with respect to $\mathbf{u}_{ij}$, we obtain the simple result

$$\tilde{\mathbf{V}}_{d-q}(\mathbf{a}_i,\ \mathbf{b}_i,\ \mathbf{a}_j)={}^1/_2(q_{xx}+q_{yy}+q_{zz})(d_\perp\mathbf{b}_i+d_\parallel\mathbf{a}_i). \tag{18}$$

Expression (17a) can now be rewritten in the form

$$\mathbf{P}=\lambda\int(d_\perp\mathbf{b}_i+d_\parallel\mathbf{a}_i)^2 f_0(\mathbf{a}_i,\mathbf{n}_i)\delta(\mathbf{b}_i\mathbf{a}_i)\,d\mathbf{b}_i\,d\mathbf{a}_i\int\nabla_j f_0(\mathbf{a}_j,\mathbf{n}_j)\,d\mathbf{a}_j=0, \tag{19}$$

since

$$\int\nabla_j f_0(\mathbf{a}_j,\mathbf{n}_j)\,d\mathbf{a}_j=\nabla_j\int f_0(\mathbf{a}_j,\mathbf{n}_j)\,d\mathbf{a}_j=0,$$

by virtue of the normalization condition

$$\int f_0(\mathbf{a}_j,\mathbf{n}_j)\,d\mathbf{a}_j=1,$$

where

$$\lambda=\rho^2\beta(q_{xx}+q_{yy}+q_{zz})/2.$$

We proceed now to calculate the different contributions to the FE on account of the dipole-quadrupole interaction in the smectic-C^* phase. We calculate first the liquid-crystal polarization component proportional to the gradient along the z axis. To this end we substitute expression (16) for the function $V_{d-q}(\ldots)$ in the last term of (8), differentiate with respect to z_j, and integrate over the direction of the $\mathbf{b}_i$ axis. As a result we obtain

$$\mathbf{P}=-\frac{1}{2}\rho^2\beta(1-\alpha)Q\left[d_\perp^2\left(3n_z\frac{\partial\mathbf{n}}{\partial z}-15\mathbf{k}(\mathbf{ke})n_z\frac{\partial n_z}{\partial z}\right)+d_\parallel^2\mathbf{n}(2-5n_z^2)\frac{\partial n_z}{\partial z}\right]. \tag{20}$$

Here $n_z=\mathbf{n}\cdot\mathbf{e}$; the unit vector $\mathbf{k}$ is shown in the figure, $\mathbf{k}\cdot\mathbf{e}=\sin\theta$. The first term in (20) coincides in form with the phenomenological expression (2), and it is possible to write down immediately an expression for the flexoelectric coefficient g_0 determined by the dipole-quadrupole interaction

$$g_0=-{}^3/_2\rho^2\beta(1-\alpha)Qd_\perp^2=-{}^3/_2(1-\alpha)\beta\rho d_\perp^2 g_q; \tag{21}$$

here $g_q\approx\rho Q$ is the quadrupole flexoelectric coefficient at $S=1$.[5]

In accord with (21), the ratio of the dipole-quadrupole and pure quadrupole contributions to the flexoelectric coefficient is determined, in order of magnitude, by the dimensionless coefficient $\beta\rho d_\perp^2$. Assuming $\rho=10^{21}$ cm^{-3} and $T=300$ K, we obtain the estimate $\beta\rho d_\perp^2\sim3\times10^{-2}\times|d_\perp|^2$, where $|d_\perp|$ is in decibels. Thus, for molecules with small dipole moments $d_\perp\lesssim1$ dB, the contribution from the dipole-quadrupole interaction is small compared with the pure quadrupole contribution. At the same time, to obtain the ferroelectric state in the chiral smectic-C phase one usually employs substances with large dipole moments, especially 2-chloropropylcyannamate and TDOBAMBCC,[14] where $d_\perp\gtrsim3$ dB. Therefore, when describing the ferroelectric state, the dipole-quadrupole and quadrupole FE turns out to be commensurate. The dipole-quadrupole interaction leads to essentially different values of the various flexoelectric coefficients [see (20)], in contrast to the quadrupole FE.

In view of the importance of this difference, let us examine in greater detail the quadrupole FE in the smectic-C phase. In accordance with Ref. 5, the contribution to the polarization of a nematic liquid crystal is proportional to the average gradient of the quadrupole moment of the molecules

$$P_l=\rho QSs_{lm}\frac{\partial}{\partial x_k}\left(n_m n_k-\frac{1}{3}\delta_{mk}\right), \tag{22}$$

where $s_{lm}\sim\delta_{lm}$ is a tensor connected with the Lorentz correction. In the first approximation, the presence of translational ordering in the smetic phase does not influence the quadrupole FE, since it is determined in practice by the sum of the signal-particle independent contributions from the individual molecules. Translational ordering can influence only the anisotropic part of the Lorentz correction in the tensor s_{lm}, but according to the estimates of Marcerou and Prost[7] this correction is small. Therefore the quadrupole FE in the smectic-C phase is completely analogous to this FE in nematics. The corresponding contribution to the polarization, which is proportional to the gradient along the z axis, takes in this case the form

$$\mathbf{P}=g_q\mathbf{n}\frac{\partial n_z}{\partial z}+g_q n_z\frac{\partial\mathbf{n}}{\partial z}. \tag{23}$$

Comparing (20) and (23), we easily note that the two orthogonal polarization directions parallel to the vectors $\mathbf{n}$ and $\partial\mathbf{n}/\partial z$ correspond to identical flexoelectric coefficients in the case of the pure quadrupole flexoelectric effect, and to different coefficients when account is taken of the dipole-quadrupole interaction. Therefore, at substantially different values of $d_\perp$ and $d_\parallel$ it is possible in principle to separate experimentally the dipole-quadrupole contribution against the background of the quadrupole contribution.

We have considered polarization proportional to the gradients along the z axis. The remainder of the polarization, proportional to the gradients in the plane of the smectic layer, can be similarly calculated by substitutiting the averaged potential (16) in the second term of the general formula (8), and by carrying out the appropriate integrations. As a result we obtain the following expression:

$$\mathbf{P}_\parallel={}^3/_8\sigma d_\perp^2\{{}^5/_2 n_z\nabla_\perp n_z-{}^5/_2\mathbf{n}n_z(\mathbf{n}_\perp\nabla_\perp)n_z-3(\mathbf{n}_\perp\nabla_\perp)\mathbf{n}+{}^5/_2\mathbf{k}(\mathbf{ke})[n_z(\nabla_\perp\mathbf{n}_\perp)+(\mathbf{n}_\perp\nabla_\perp)n_z]\}+{}^3/_8\sigma d_\parallel^2(5n_z^2-1)\bar{\mathbf{n}}(\nabla_\perp\mathbf{n}_\perp); \tag{24}$$

$$\nabla_\perp=\left\{\frac{\partial}{\partial x},\frac{\partial}{\partial y},0\right\},\quad\sigma=\rho^2\beta\alpha Q.$$

Despite the complicated structure of (24), as $\theta\to0$ an important role is played in it only by the last term, since the remaining terms of (24) are proportional to

$\sin\theta$ raised to various powers. If we disregard the quantities proportional to $\sin\theta$, then expression (24) can be approximately represented in the form

$$\mathbf{P}_\parallel \approx {}^3/_8\,\sigma d_\parallel^2(5n_z^2-1)\mathbf{n}(\nabla_\perp\mathbf{n}_\perp) \approx {}^3/_8\,\sigma d_\parallel^2\,\mathbf{e}(5n_z^2-1) \times\left[\frac{\partial}{\partial x}(n_z n_x)+\frac{\partial}{\partial y}(n_z n_y)\right]. \tag{25}$$

Expression (25) corresponds exactly to the phenomenological expansion (3b), and we obtain a formula for the contribution made to the phenomenological coefficient by the dipole-quadrupole interaction:

$$g_\parallel=3(5n_z^2-1)\beta\rho^2 d_\parallel^2\alpha Q/8. \tag{26}$$

A contribution to the flexoelectric coefficient of the type (24) may turn out to be particularly important for liquid crystals whose molecules contain the strongly polar nitryl group $C\equiv N$, when $d_\parallel \sim 5$ dB.[16] These molecules have a tendency to combine into pairs with antiparallel dipoles, and this should decrease considerably the flexoelectric coefficient connected with the steric interaction of the molecules, since it is proportional to the dipole moment raised to the first power. At the same time, the dipole-quadrupole contribution is proportional to $d^2_\parallel$ and remains practically unchanged when the pairs are produced.

Taking (20) and (21) into account, we can also obtain the difference of the FE coefficients

$$g_0-g_\perp\approx-15\rho^2\beta d_\perp^2(1-\alpha)Q\theta^2/2, \tag{27}$$

which corresponds to a phenomenological expansion in powers of θ (see Sec. 2).[4)] For a pure quadrupole FE this difference is equal to zero.

The described FE introduces a definite correction to the linear response of the C phase to an external field $\mathbf{E}$ ($\mathbf{E}$ is perpendicular to the z axis). In fact, action of such a field gives rise to the modulations $\theta(z)-\theta_0$ and $\varphi(z)-\varphi_0$, which introduce a correction $\delta\chi$ to the dielectric susceptibility

$$\mathscr{P}=\langle\mathbf{P}\rangle=(\chi_0+\delta\chi)\mathbf{E},$$

$$\delta\chi_C=\frac{1}{2}\left[\frac{\mu^2}{Kq_0^2}+\frac{(\mu-(g_0-g_\perp)q_0)^2}{Gq_0^2+a}\right],$$

where K and G are the elastic constants, $a\sim\theta^2\sim(T_c-T)$, μ is the piezoelectric coefficient, and q_0 is the wave vector of the helicoid.

We note that in this case a contribution to $\delta\chi_c$ is made not only by the piezoelectric effect, but also by the flexoelectric effect, and, just as in nematic liquid crystals,[17] this contribution is determined by the combination of the coefficients $g_0-g_\perp$. Experiment[10] shows that g_0 and $g_\perp$ have values comparable with μ/q_0. Since the moduli μ and $(g_0, g_\perp, g_\parallel)$ have a different microscopic nature, one can expect in experiment situations in which the inequalitities $\mu \lesssim g_0 q_0\theta_0^2$ and $Gq_0^2 < a$ are satisfied below the phase-transition point T_c, and this should manifest itself in the temperature dependence of $\delta\chi_C(T)$.

[1)] In our preceding paper[12] the molecular model of the ferroelectric state in the C^* phase was constructed without allowance for the FE.

[2)] The FE by itself if not connected with the chirality of the molecules, and the expressions for the FE coefficients obtained in the present paper are valid both in chiral and in non-chiral C phases. For the sake of argument we refer throughout to the chiral C^* phase.

[3)] In liquid crystals, the average intermolecular distances are comparable with the dimensions of the molecules, therefore the coefficients in (15) are approximate and expression (15) is the first nonvanishing approximation. This approach is usually used in the microscopic description of liquid crystals.

[4)] We note that the steric interaction of the molecules also contributes to expression (27), since the flexoelectric coefficients corresponding to it are of order θ^2.

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Translated by J. G. Adashko