

Steric interaction of molecules and the flexoelectric effect in smectic-*C* liquid crystals

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It is shown that the steric interaction of asymmetric molecules, which, as is usually assumed, determines the flexoelectric effect in nematic liquid crystals, is unimportant in describing this effect in the smectic *C** phase, which produces a spontaneous polarization in the system.

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At present, the microscopic nature of the flexoelectric effect (FE) in nematic liquid crystals is usually associated with the steric interaction of asymmetric molecules.¹⁻⁴ Another microscopic interpretation of the FE, which is based on a direct relationship between the polarization of the liquid crystal and the gradient of the average quadrupole-moment density of the molecules, has been proposed.⁵ However, the microscopic mechanism discussed in Ref. 5 is obviously not the determining factor in the nematic phase, since it gives identical values for the two main, flexoelectric coefficients, which contradicts most experimental data.⁶ The FE also exists in the smectic phases, and it is especially important in describing the chiral, smectic *C* phase (the *C** phase). A spontaneous helicoidal twisting of the long axes of the molecules around the normal to the smectic layer occurs in the *C** phase; because of the FE, this results in an additional, spontaneous polarization in the plane of the layer.⁷ The role of the FE in the *C** phase has recently been discussed in the literature.^{8,9}

The spontaneous polarization resulting from the FE in the C^* phase is described by the following expression⁷:

$$\mathbf{P} = g \frac{\partial}{\partial z} (n_z \mathbf{n}_\perp) = g n_z \frac{\partial \mathbf{n}}{\partial z}, \quad \text{if } \partial n_z / \partial z = 0. \quad (1)$$

We note that in zeroth approximation of the inclination angle θ of the director n with respect to the normal e to the smectic layer $g = \text{const} \neq 0$ in Eq. (1). We show in this paper that the steric interaction of molecules does not contribute anything to the FE such as in Eq. (1) in zeroth approximation with respect to θ ; therefore, it is not essential in describing the ferroelectric state in the C^* phase in a broad region around the A- C^* transition point, where θ is small.

The FE-induced polarization of a liquid crystal in the case of an ideal orientational order can be written in the form⁴

$$\mathbf{P} = -N d_\perp \int \mathbf{b}_i \delta((\mathbf{b}_i \mathbf{n}_i)) \int (\mathbf{u}_{ij} \vec{\nabla}_j) U_s(\mathbf{n}_i, \mathbf{n}_j, \mathbf{r}_{ij}, \mathbf{b}_i, \mathbf{b}_j) \delta((\mathbf{b}_j \mathbf{n}_j)) \times d\mathbf{r}_{ij} d\mathbf{b}_i d\mathbf{b}_j. \quad (2)$$

Here $U(\dots)$ is the interaction energy of the molecules i and j , \mathbf{b}_i is the short axis of the molecule i , $(\mathbf{b}_i \mathbf{n}_i) = 0$, and $\mathbf{r}_{ij} = \mathbf{r}_{ij} \mathbf{u}_{ij}$ is the vector that joins the centers of gravity of the molecules i and j . Only the transverse component d_\perp of the dipole moment of a molecule is taken into account in Eq. (2), since the longitudinal component does not contribute to polarization of the form in Eq. (1), which is perpendicular to the director \mathbf{n} . The subscript s for the interaction energy U_s indicates that averaging over the direction of the unit vector \mathbf{u}_{ij} is performed in the smectic phase. According to Ref. 10, in the case of ideal smectic ordering

$$\int (\mathbf{u}_{ij} \vec{\nabla}_j) U_s(\dots) d\mathbf{r}_{ij} = \alpha \int (\mathbf{u}_{ij} \vec{\nabla}_j) U(\dots) \delta((\mathbf{u}_{ij} \mathbf{e})) d\mathbf{r}_{ij} + (1 - \alpha) \int U(\dots) \Big|_{\mathbf{u}_{ij} = \mathbf{e}} d\mathbf{r}_{ij}, \quad (3)$$

where α is the fraction of nearest neighbors located in one smectic layer with a given molecule. The first term in Eq. (3) does not contribute to the polarization such as in Eq. (1).

The arbitrary function $V(\mathbf{n}_i, \mathbf{n}_j, \mathbf{e}, \mathbf{b}_i) = \int \int U(\mathbf{n}_i, \mathbf{n}_j, \mathbf{e}, \mathbf{r}_{ij}, \mathbf{b}_i, \mathbf{b}_j) d\mathbf{r}_{ij} d\mathbf{b}_j$ can be expanded in spherical invariants,¹¹ which are scalar combinations of the vectors $\mathbf{n}_i, \mathbf{n}_j, \mathbf{e}$, and \mathbf{b}_j . We investigate nonchiral molecules, since the FE, generally speaking, is not related to the chirality. Thus, the expansion of the function $V(\dots)$ does not contain pseudoscalars, i.e., mixed products, and it reduces to an expansion in powers of the scalar products of these vectors. Let us examine the contribution to the polarization (2) of interest, which contains the derivative along the z axis [see Eq. (1)]:

$$P_1 = -Nd_{\perp}(1-\alpha) \int \mathbf{b}_i \delta((\mathbf{b}_i, \mathbf{n}_i)) \frac{\partial}{\partial z_j} V(\mathbf{n}_i, \mathbf{n}_j, \mathbf{e}_j, \mathbf{b}_i) d\mathbf{b}_i. \quad (4)$$

We differentiate each term of the expansion of the function V with respect to z_j , by retaining the first-order terms with respect to the derivative, which correspond to the FE, we can represent the integrand in Eq. (4) in the following form without loss of generality:

$$\begin{aligned} \frac{\partial}{\partial z_j} V(\mathbf{n}_i, \mathbf{n}_j, \mathbf{e}, \mathbf{b}_i) &= (\mathbf{b}_i, \mathbf{e}) \left(\mathbf{e} \frac{\partial \mathbf{n}}{\partial z} \right) V_1 \{ (\mathbf{b}_i, \mathbf{e})^2, (\mathbf{n}\mathbf{e}) \} \\ &+ (\mathbf{b}_i, \mathbf{e}) \left(\mathbf{b}_i \frac{\partial \mathbf{n}}{\partial z} \right) V_2 \{ (\mathbf{b}_i, \mathbf{e}), (\mathbf{n}\mathbf{e}) \} + \left(\mathbf{e} \frac{\partial \mathbf{n}}{\partial z} \right) V_3 \{ (\mathbf{n}\mathbf{e}) \} \\ &+ \left(\mathbf{b}_i \frac{\partial \mathbf{n}}{\partial z} \right) (\mathbf{n}\mathbf{e}) V_4 \{ (\mathbf{n}\mathbf{e})^2 \}. \end{aligned} \quad (5)$$

All the expansion terms in Eq. (5) that contain the scalar product $(\mathbf{b}_i, \mathbf{e})$ are grouped in the first two terms. The quantity $(\mathbf{b}_i, \mathbf{e})$ is $\sim \sin \theta$; therefore, the first two terms in Eq. (5) do not contribute to the polarization P_1 such as in (1) in zeroth approximation with respect to θ . Since the third term does not depend on \mathbf{b}_i , it does not contribute to the polarization P_1 . We shall examine the last term in Eq. (5). Thus far, we have not specified the interaction between the molecules. We assume that $U(\dots)$ is a steric interaction of two molecules, i.e., $U(\dots) = 1$ or 0 , depending on whether the molecular volumes intersect at their given location and orientation. Thus, if $\mathbf{n}_i \parallel \mathbf{n}_j \parallel \mathbf{e}$, then the function $V(\mathbf{n}_i, \mathbf{n}_j, \mathbf{e}, \mathbf{b}_i)$ is simply the distance between the centers of gravity of the molecules i and j , r_{ij} , which does not depend on the direction of the vector \mathbf{b}_i (see Fig. 1). The condition $\mathbf{n}_i \parallel \mathbf{n}_j \parallel \mathbf{e}$ corresponds to the condition $\theta = 0$. Consequently, Eq. (5) does not depend on \mathbf{b}_i when $\theta = 0$. Since $(\mathbf{b}_i, \mathbf{e}) = 0$ when $\theta = 0$, the last term in Eq. (5) must also vanish when $\theta = 0$. Taking into account $(\mathbf{n}\mathbf{e}) = \cos \theta$,

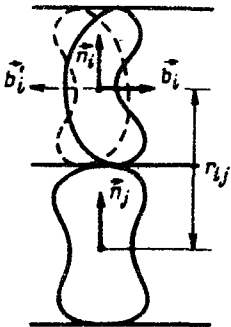


FIG. 1. Diagram of steric interaction of molecules i and j in adjacent smectic layers for different directions of the short \mathbf{b}_i axis. As a result of the interaction, the molecule j acquires essentially cylindrical shape because of the averaging in the \mathbf{b}_j direction in Eq. (2).

we obtain

$$\left(\mathbf{b}_i \frac{\partial \mathbf{n}}{\partial z} \right) \cos \theta V_4(\cos^2 \theta) = 0 \quad \text{for } \theta = 0. \quad (6)$$

We can see from Eq. (6) that $V_4(\cos^2 \theta) = 0$ for $\theta = 0$; consequently, $V_4(\cos^2 \theta) \sim \theta^2$. Thus, the last term in Eq. (5) in the case of a steric interaction of molecules does not contribute to the FE such as in (1) in the *C* phase in zeroth approximation with respect to θ .

As a result, we conclude that the steric interaction of molecules, which is considered the primary microscopic reason for the appearance of the FE in the nematic phase, cannot produce a large FE of the form (1) in the smectic *C* phase. A steric interaction gives corrections of the order of smallness of θ^2 and higher in the vicinity of the A-C transition point.¹ In view of this, the FE of the form (1), which is important in describing the ferroelectric state in the *C** phase, must be explained by the distribution of molecular quadrupole moments as in Ref. 5 or by electrostatic interaction. For example, in contrast to the steric interaction, the multipole interaction of molecules illustrated in Fig. 1 may depend on the direction of the short axis \mathbf{b}_i when $\mathbf{n}_i \parallel \mathbf{n}_j \parallel \mathbf{e}$; the last term in Eq. (5) in this case vanishes at $\theta = 0$. A separate paper will be devoted to a detailed analysis of this problem.

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¹Strictly speaking, the steric interaction in zeroth approximation in θ gives a small, fluctuational contribution to the FE of the form (1), which is proportional to the deviation from the ideal smectic order.

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