

Molecular theory of flexoelectric effect in nematic liquid crystals

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Stanley's theory of the flexoelectric effect (FE) in an ordered solution of solid rods is generalized to the case of a thermotropic liquid crystal with allowance made for both short-range repelling forces and attracting forces between the molecules. General equations are obtained for the flexocoefficients and it is shown that the main contribution is made by the isotropic attraction between the molecules, modulated by their anisotropic form. After a number of simplifications, approximate expressions for the flexocoefficients are obtained and depend explicitly on the characteristic parameters of the molecules. The ratio of the dipole and quadrupole FE is discussed and it is shown that the dipole FE is significant only for molecules with large transverse dipoles and determines the difference between the flexocoefficients.

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1. The flexoelectric effect (FE) in liquid crystals constitutes the appearance of spontaneous polarization as a result of orientational deformation of the medium. In the nematic phase there exist two independent flexocoefficients, e_{\perp} and e_{\parallel} , which determine the values of the two contributions to the induced polarization^{1,2}:

$$\mathbf{P} = e_{\parallel} \mathbf{n} (\nabla \mathbf{n}) + e_{\perp} (\mathbf{n} \nabla) \mathbf{n}, \quad (1)$$

where \mathbf{n} is the director. A microscopic mechanism of the FE effects was first proposed by Meyer,¹ who pointed out that under conditions of orientational deformation of a liquid crystal the banana-shaped or conical molecules (see the figure) should be so oriented that their constant dipoles are ordered and macroscopic polarization sets in. Petrov, Derzhanskii,³ and Helfrich⁴ obtained expressions for the flexocoefficients on the basis of the Meyer model, but used qualitative semiphenomenological arguments, for which it is difficult to trace a connection with the existing molecular-statistics theories of liquid-crystal order. This question will be discussed in greater detail below.

A consistent statistical theory of the FE in the nematic phase was developed by Straley⁵ for the case of a weak solution of rods. He therefore took into account only short-range collisions of the molecules. At the same time, Straley actually developed for the calculation of the flexocoefficients a general method that can be used in a number of particular cases.¹⁾

Prost and Marcerou⁶ proposed recently a new microscopic interpretation of the FE, which requires neither asymmetry of the molecule shape nor a constant dipole moment. Polarization is produced in a deformed liquid crystal as a result of the appearance of a gradient of the average density of the quadrupole moment of the molecules. This quadrupole mechanism is in principle more general and is significant not for liquid crystals only, but the question of the ratio of the dipole and quadrupole FE in real liquid crystals nevertheless still remains open. A sufficiently detailed discussion of this question can be found in Refs. 2 and 9. We note also that according to estimates by Marcerou and Prost¹⁰ the Straley theory leads to flexocoefficient values

smaller by two orders than the experimental ones. On the basis of this fact it is concluded in Ref. 9 that the theories of Petrov, Derzhanskii, Helfrich^{3,4} and of Straley⁵ consider different macroscopic mechanisms of the dipole FE, the contribution of the Straley mechanism being negligibly small.

We shall show in this paper that this conclusion is not justified, inasmuch as in thermotropic liquid crystals it does not suffice to take into account only the steric interaction of the molecules (as was done in Ref. 5 for the case of a lyotropic liquid crystal). Actually, as shown by Gelbart,⁹ the strongest orientational interaction in the nematic phase is isotropic attraction of the molecules, modulated by their anisotropic shape. It is important here that such an interaction also makes a predominant contribution to the flexocoefficient, as will be shown below.

In Sec. 2 of this paper general expressions are obtained for the flexocoefficients in nematic liquid crystals with account taken of both the short-range repulsion and of the attraction of the molecules. We use the general method developed by Straley.⁵ In Sec. 3 we attempt to estimate the contributions made to the flexocoefficients by various types of interaction, and discuss the influence of the characteristic molecule parameters on the values of e_{\perp} and e_{\parallel} . We consider the ratio of the dipole and quadrupole contributions to the

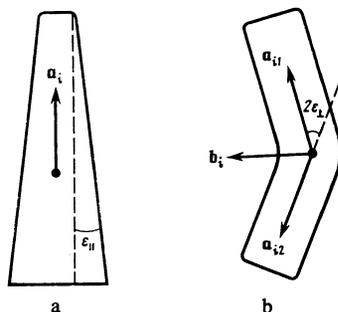


FIG. 1. Models of asymmetric molecules in the form of a truncated cone (a) and a bent rod (b), corresponding to longitudinal and transverse steric dipoles.

flexocoefficients. Also discussed is the connection between the molecular theory developed in the present paper and the semiphenomenological theory of Petrov, Derzhanskii, and Helfrich.^{3,4}

2. In the molecular-field approximation with allowance for the short-range repulsion of the molecules, the free energy of a liquid crystal can be written in the form^{9,11}

$$F = \frac{1}{2} \rho^2 \int f_1(i) V(i, j) \theta(r_{ij} - \xi_{ij}) f_1(j) d\mathbf{r}_{ij} d(i) d(j) + \frac{1}{2} kT \rho^2 \int f_1(i) \theta(\xi_{ij} - r_{ij}) f_1(j) d\mathbf{r}_{ij} d(i) d(j) + kT \rho \int f_1(i) \ln f_1(i) d(i), \quad (2)$$

where $f_1(i)$ is the single-particle distribution function; $V(i, j)$ is the energy of the interaction of molecules i and j ; r_{ij} is a vector joining the mass centers of molecules i and j ; $\theta(x)$ is a step function: $\theta(x) = 0$ at $x < 0$ and $\theta(x) = +1$ at $x \leq 0$. The function ξ_{ij} is the minimum possible distance between the mass centers of molecules i and j at a given relative orientation. The integration with respect to r_{ij} in (2) is thus restricted to values $r_{ij} < \xi_{ij}$, i.e., it is recognized that the molecules cannot penetrate into one another. It is convenient to define the orientation of an arbitrary elongated molecule i by the unit vectors of \mathbf{a}_i and \mathbf{b}_i of the long and short axes, with $\mathbf{a}_i \cdot \mathbf{b}_i = 0$. Then $d(i) = \delta(\mathbf{a}_i \cdot \mathbf{b}_i) d\mathbf{a}_i d\mathbf{b}_i$.

The first term in (2) is the internal energy of the system. We note that the interaction energy $V(i, j)$ itself need not necessarily depend on the orientation of the molecules i and j , since it is modulated by the step function $\theta(r_{ij} - \xi_{ij})$, which depends on the molecule orientation via the function $\xi_{ij} = \xi_{ij}(\mathbf{a}_i, \mathbf{a}_j, \mathbf{b}_i, \mathbf{b}_j, \mathbf{u}_{ij})$, where $\mathbf{u}_{ij} = \mathbf{r}_{ij} / |\mathbf{r}_{ij}|^{-1}$. The second term in (2) is the so-called packing entropy,^{11,12} which is determined only by the steric interaction of the molecules. Straley⁵ takes into account only the last two terms in expression (2) for the free energy. If, however, we introduce the effective interaction energy

$$U_{eff}(i, j) = [V(i, j) - kT] \theta(r_{ij} - \xi_{ij}), \quad (3)$$

the first two terms in (2) can be combined into one, so that the mathematical form of (2) will coincide with the mathematical form of the free energy which was considered by Straley [see Eq. (1) of Ref. 5]:

$$F = \frac{1}{2} \rho^2 \int f_1(i) U_{eff}(i, j) f_1(j) d\mathbf{r}_{ij} d(i) d(j) + kT \int f_1(i) \ln f_1(i) d(i). \quad (4)$$

In a deformed nematic liquid crystal the single-particle distribution function $f_1(j)$ depends on the coordinate \mathbf{r}_j , but at relatively small deformations this dependence is determined only by the spatial inhomogeneity of the director $\mathbf{n}(\mathbf{r})$. In this case we can write⁵

$$f_1(j) = f_0(j) [1 + g(j)],$$

where $f_0(j)$ is the single-particle distribution function of the undeformed liquid crystal, i.e., $f_0(j) = f_0(\mathbf{a}_j, \mathbf{n}_j(\mathbf{r}_j))$, and the function $g(j)$ is assumed small. Expanding the first term in (4) in powers of ∇f_1 and retaining the first terms (since we are considering the linear FE), and then minimizing the free energy (4) with respect to f_1 , we can obtain the following expression for the function $g(i)$ ⁵:

$$g(i) = \rho \beta \int (\mathbf{J}(i, j) \nabla) f_0(j) d(j), \quad (5)$$

$$\mathbf{J}(i, j) = \int \mathbf{r}_{ij} U_{eff}(i, j) d\mathbf{r}_{ij}, \quad \beta = 1/kT. \quad (6)$$

It can be seen from (5) that the difference between the distribution functions of the deformed and undeformed liquid crystals $g(i)$ is proportional to the gradient of the distribution function $f_0(j)$, i.e., to the derivatives of the director $\mathbf{n}(\mathbf{r})$.

The polarization induced in a deformed liquid crystal by ordering of the molecular dipoles is determined by the expression

$$\mathbf{P} = \rho d_{\perp} \langle \mathbf{b}_i \rangle + \rho d_{\parallel} \langle \mathbf{a}_i \rangle, \quad (7)$$

where d_{\parallel} and d_{\perp} are the longitudinal and transverse components of the dipole moment of the molecules, and the angle brackets denote averaging over the ensemble. In the case considered by us we have

$$\mathbf{P} = \rho \int (d_{\perp} \mathbf{b}_i + d_{\parallel} \mathbf{a}_i) f_0(i) g(i) d(i), \quad (8)$$

since the function $f_0(i)$ is even in \mathbf{b}_i and \mathbf{a}_i . The FE is thus determined by that part of the total interaction energy $U_{eff}(i, j)$ which is odd in \mathbf{u}_{ij} , \mathbf{a}_i and \mathbf{u}_{ij} , \mathbf{b}_i . Such a dependence of the interaction energy $U_{eff}(i, j)$ on the direction of the axes \mathbf{b}_i and \mathbf{a}_i can appear, for example, if account is taken of the polar asymmetry of the molecule shape^{1,5} (see the figure).

Recognizing that

$$\nabla f_0(i) = \nabla f_0((\mathbf{a}_i, \mathbf{n}_i(\mathbf{r}_i))^2) = f_0' \nabla (\mathbf{a}_i, \mathbf{n}_i)^2,$$

we can rewrite expressions (5), (6), and (8) in the form

$$P_{\alpha} = e_{\alpha\beta\gamma\delta} \nabla_{\beta} n_{\delta} n_{\gamma}, \quad (9)$$

where $\alpha, \beta, \gamma, \delta = x, y, z$ and

$$e_{\alpha\beta\gamma\delta} = \rho^2 \beta \int (d_{\perp} b_{i\alpha} + d_{\parallel} a_{i\alpha}) f_0(i) f_0'(j) J_{\beta}(i, j) a_{j\gamma} a_{j\delta} d(i) d(j), \quad (10)$$

$e_{\alpha\beta\gamma\delta}$ is a uniaxial tensor of fourth rank, symmetric in the two indices γ and δ . Such a tensor can be written in the form of a sum of six invariants:

$$e_{\alpha\beta\gamma\delta} = e_1 \delta_{\alpha\beta} \delta_{\gamma\delta} + e_2 (\delta_{\beta\gamma} \delta_{\alpha\delta} + \delta_{\beta\delta} \delta_{\alpha\gamma}) + e_3 \delta_{\alpha\beta} n_{\gamma} n_{\delta} + e_4 (\delta_{\alpha\delta} n_{\gamma} n_{\beta} + \delta_{\alpha\beta} n_{\gamma} n_{\delta}) + e_5 (\delta_{\beta\delta} n_{\alpha} n_{\gamma} + \delta_{\beta\gamma} n_{\alpha} n_{\delta}) + e_6 n_{\alpha} n_{\beta} n_{\gamma} n_{\delta}. \quad (11)$$

Substituting (11) in (9) and comparing with (1) we get

$$e_{\perp} = 2(e_2 + e_4), \quad e_{\parallel} = 2(e_2 + e_5). \quad (12)$$

Recognizing that $e_2 + e_4 = e_{xxxx}$ and $e_2 + e_5 = e_{zzzz}$, we obtain now the final general equations for the flexocoefficients:

$$e_{\perp} = 2\rho^2 \beta \int (d_{\perp} b_{iz} + d_{\parallel} a_{iz}) f_0(i) f_0'(j) J_x(i, j) a_{jz} a_{jz} d(i) d(j), \quad (13)$$

$$e_{\parallel} = 2\rho^2 \beta \int (d_{\perp} b_{iz} + d_{\parallel} a_{iz}) f_0(i) f_0'(j) J_z(i, j) a_{jz} a_{jz} d(i) d(j). \quad (14)$$

The flexocoefficients e_{\perp} and e_{\parallel} are thus determined by the quantity $\mathbf{J}(i, j)$, which depends on the attraction energy $V(i, j)$ and on the shapes of the interacting molecules.

The polar asymmetry of the molecule shape can be described by the values of the steric dipole¹² in the directions of the long and short axes. For molecules in the form of a bent rod and a truncated cone, shown in the figure, the steric dipole is proportional to the angles ε_{\perp} and ε_{\parallel} , respectively. At small angles $\varepsilon \ll 1$ the function ξ_{ij} can be expanded in powers of ε :

$$\xi_{ij} = \xi_{ij}^0 + \varepsilon_{\perp} \xi_{\perp}(i, j) + \varepsilon_{\parallel} \xi_{\parallel}(i, j) + \dots, \quad (15)$$

where ξ_{ij}^0 is the minimum distance between the mass centers of the cylindrically symmetric molecules i and j (i.e., as $\varepsilon_{\perp} = \varepsilon_{\parallel} \Rightarrow 0$). The interaction energy $U_{\text{eff}}(i, j)$ can then be approximately represented in the form

$$U_{\text{eff}}(i, j) \approx \theta(r_{ij} - \xi_{ij}^0) [V(i, j) - kT] + \delta(r_{ij} - \xi_{ij}^0) \times [\varepsilon_{\perp} \xi_{\perp}(i, j) + \varepsilon_{\parallel} \xi_{\parallel}(i, j)] [V(i, j) - kT]. \quad (16)$$

We note that the expansion (16) is meaningful only after the integration with respect to r_{ij} with a certain function $V(r_{ij})$. In the present paper we consider only the FE connected with the symmetry of the molecule shape, and we therefore assume² that the attraction energy $V(i, j)$ is even in \mathbf{a}_i , \mathbf{a}_j , \mathbf{b}_i , and \mathbf{b}_j . In this case the first term of (16) makes no contribution to ε_{\perp} and ε_{\parallel} . Substituting now the second term of (16) in (6), we obtain a final expression for $\mathbf{J}(i, j)$:

$$\mathbf{J}(i, j) = \int (\xi_{ij}^0)^3 [\varepsilon_{\perp} \xi_{\perp}(i, j) + \varepsilon_{\parallel} \xi_{\parallel}(i, j)] [V(\xi_{ij}^0) - kT] \mathbf{u}_{ij} d\mathbf{u}_{ij}. \quad (17)$$

We note that the main contribution to the flexocoefficients is made by the molecule attraction energy $V(i, j)$, and particularly by its isotropic part, since generally speaking, $V(\xi_{ij}^0) \gg kT$ at $\xi_{ij}^0 \sim R$, where R is the average distance between the molecules of the liquid crystal (this question will be discussed in greater detail in Sec. 3). This statement agrees with the conclusion of Gelbrat and of others^{9,11} that the predominant role in the formation of the orientational order in liquid crystals is played by the isotropic attraction modulated by the anisotropic molecule shape. In this case the purely steric molecule interaction considered by Straley⁵ makes in the case of thermotropic liquid crystals a negligible contribution that can be separated by putting $V(i, j) = 0$ in (17).

3. The general expressions (13), (14), and (17) for the flexocoefficients depend on ξ_{ij} , which is a complicated function of the relative orientation of the molecules i and j and cannot be written in analytic form even for uniaxial molecules of simple shape.⁹ The calculation of the function $\mathbf{J}(i, j)$ in (17) entails therefore very great difficulties, taking into account also that the explicit form of the attraction energy $V(\xi_{ij}^0)$ is also unknown. Let us attempt, however, to estimate the flexocoefficients ε_{\perp} and ε_{\parallel} by simplifying (17). Indeed, we take outside the integral sign in (17) the average attraction energy

$$\bar{V}(i, j) = \frac{1}{4\pi} \int V(\xi_{ij}^0) d\mathbf{u}_{ij}.$$

This can be done if the isotropic part of the interaction energy $V(i, j)$ is much larger than the anisotropic part that depends on the molecule orientation. The averaged interaction energy $\bar{V}(i, j)$ depends only on the product $\mathbf{a}_i \cdot \mathbf{a}_j$ and can be expanded in Legendre polynomials of even index:

$$\bar{V}(i, j) = A + BP_2(\mathbf{a}_i \mathbf{a}_j) + \dots \quad (18)$$

It is easy to show that the accuracy of this approximation is determined by the parameter B/A . The quantity B is the characteristic energy of the orientational interaction of the molecules, therefore $B \sim kT$. At the same time, the quantity A is the isotropic part of the attraction energy $V(i, j)$, and one

can expect that $A \gg kT$. The interaction energies of typical mesogenic molecules were calculated directly in Refs. 13 and 14. Using these results, we obtain the estimate $A \approx 5 kT$ (Ref. 13) or $A \approx 10 kT$ (Ref. 14). We note that the foregoing approximation allows us to disregard the actual form of the energy $V(i, j)$ and to use only the two parameters A and B that can be easily calculated if the form of $V(i, j)$ is known.

Expression (17) can therefore be very approximately rewritten in the form

$$\mathbf{J}(i, j) \approx [A + BP_2(\mathbf{a}_i \mathbf{a}_j) + kT] \left(\varepsilon_{\perp} \frac{d}{d\varepsilon_{\perp}} + \varepsilon_{\parallel} \frac{d}{d\varepsilon_{\parallel}} \right) \int \xi_{ij}^4 \mathbf{u}_{ij} d\mathbf{u}_{ij}, \quad (19)$$

where we have used also expression (15). As already noted, the function ξ_{ij} cannot be determined in explicit form even for molecules of simple shape, although the integral

$$\mathbf{C}(i, j) = \int \xi_{ij}^4 \mathbf{u}_{ij} d\mathbf{u}_{ij} = \int \mathbf{r}_{ij} \theta(r_{ij} - \xi_{ij}) d\mathbf{r}_{ij} \quad (20)$$

in (19) can be calculated for molecules having the shape of a bent rod and a truncated cone (see the figure). The result is given in Straley's paper.⁵ For truncated cones

$$C_1(i, j) = {}^1/6 \varepsilon_{\parallel} D L^3 (\mathbf{a}_i - \mathbf{a}_j) | [\mathbf{a}_i \mathbf{a}_j] |, \quad (21)$$

where D and L is the diameter and length of the molecule. For bent rods

$$C_2(i, j) = {}^1/6 \varepsilon_{\parallel} D L^3 \{ (\mathbf{a}_i - \mathbf{a}_j) (| [\mathbf{a}_{i1} \times \mathbf{a}_{j1}] | - | [\mathbf{a}_{i2} \times \mathbf{a}_{j2}] |) + (\mathbf{a}_i + \mathbf{a}_j) (| [\mathbf{a}_{i1} \times \mathbf{a}_{j2}] | - | [\mathbf{a}_{i2} \times \mathbf{a}_{j1}] |) \}, \quad (22)$$

where $\mathbf{a}_{i1,2} = \varepsilon_{\perp} \mathbf{b}_i \pm \mathbf{a}_i$, $\mathbf{a}_{j1,2} = \varepsilon_{\perp} \mathbf{b}_j \pm \mathbf{a}_j$,

$$\varepsilon_{\perp} \frac{d}{d\varepsilon_{\perp}} C_2(i, j) |_{\varepsilon_{\perp}=0} = -\frac{1}{4} \varepsilon_{\perp} D L^3 \mathbf{a}_i (\mathbf{a}_i \mathbf{a}_j) (\mathbf{b}_i \mathbf{a}_j) | [\mathbf{a}_i \mathbf{a}_j] |^{-1}. \quad (23)$$

Expanding the quantities $|\mathbf{a}_i \times \mathbf{a}_j|$ and $|\mathbf{a}_i \times \mathbf{a}_j|^{-1}$ in (21) and (23) in Legendre polynomials and substituting the expression

$$\left(\varepsilon_{\perp} \frac{d}{d\varepsilon_{\perp}} + \varepsilon_{\parallel} \frac{d}{d\varepsilon_{\parallel}} \right) \Big|_{\varepsilon=0} \mathbf{C}(i, j) = \varepsilon_{\perp} \frac{dC_2(i, j)}{d\varepsilon_{\perp}} \Big|_{\varepsilon_{\perp}=0} + \varepsilon_{\parallel} \frac{dC_1(i, j)}{d\varepsilon_{\parallel}} \Big|_{\varepsilon_{\parallel}=0} \quad (24)$$

in (19), and then (19) in (13) and (14), we obtain the estimates

$$\varepsilon_{\perp} \approx \rho^2 \beta D L^3 S [(d_{\parallel} \varepsilon_{\parallel} \lambda_1 + d_{\perp} \varepsilon_{\perp} \lambda_1) S + d_{\parallel} \varepsilon_{\parallel} \lambda_2 + d_{\perp} \varepsilon_{\perp} \lambda_2], \quad (25)$$

$$\varepsilon_{\parallel} \approx \rho^2 \beta D L^3 S [(d_{\parallel} \varepsilon_{\parallel} \lambda_1 - d_{\perp} \varepsilon_{\perp} \lambda_3) S + d_{\parallel} \varepsilon_{\parallel} \lambda_2 + d_{\perp} \varepsilon_{\perp} \lambda_2], \quad (26)$$

where S is the nematic-order parameter,

$$\lambda_1 = [{}^3/2 B + {}^1/2 (A - kT)] \cdot 10^{-2}, \quad \lambda_2 = [2B + A - kT] \cdot 10^{-2}, \\ \lambda_3 = [2(A - kT) + B] \cdot 10^{-1}, \quad \lambda_2 = [A - kT + {}^1/2 B] \cdot 10^{-1}, \quad (27) \\ \lambda_3 = [A - kT + B] \cdot 10^{-1}.$$

We have taken it into account in (24)–(26) that the molecule can have both a longitudinal and a transverse steric dipole.

It must be noted that the approximation made in the present section does not make it possible to construct in the general case a quantitative theory of the dipole FE. At the same time it permits a transition from the general integral expressions (13), (14), and (6), which contain unknown functions, to the rather simple formulas (25) and (26), which depend explicitly on the characteristic parameters of the mole-

cules. This approximation is accurate in the a model in which the liquid crystal consists of asymmetric molecules that interact via forces of isotropic attraction modulated by short-range repulsion. As already noted, this interaction predominates in nematic liquid crystals⁹ and the corresponding model is actively used in contemporary molecular theory.^{9,11}

In the case of the dipole FE, expressions for the flexocoefficients e_{\perp} and e_{\parallel} were obtained also by Petrov and Derzhanskii³ and Helfrich.⁴ An opinion was adopted in the literature (see, e.g., Ref. 10) that the flexocoefficients calculated by Straley⁵ and in Refs. 3 and 4 correspond to two different mechanisms of the dipole FE, and that the mechanism considered by Straley leads to neglect of small values of e_{\parallel} and e_{\perp} (Ref. 10). It follows from our present results that this general conclusion is unfounded. Indeed, (25)–(27) lead to an estimate for the flexocoefficients

$$e \sim 10^{-1} \beta (A+B-kT) \rho^2 DL^3 S d \epsilon.$$

Putting $\rho = 10^{21} \text{ cm}^{-3}$, $D = 5 \cdot 10^{-8} \text{ cm}$, $L = 3 \cdot 10^{-7} \text{ cm}$, $S = 1/2$, and $d = 1 \text{ dB}$, we obtain $e \sim 5 \cdot 10^{-6} \beta (A+B+kT)$ cgs. Since $A \gg kT$, the flexocoefficients turn out to be close to the experimental values $e \sim 10^{-4}$ cgs,² albeit somewhat undervalued. Actually, the estimate at $A \sim 10 \text{ kT}$ corresponds to the estimate given in Ref. 6 for the dipole contribution to the flexocoefficients, $e \sim 7 \times 10^{-5}$ cgs, based on an analysis of the FE mechanism considered by Petrov, Derzhanskii, and Helfrich. The purely steric interaction considered by Straley⁵ actually yields a small contribution, $e \sim 5 \times 10^{-6}$ cgs.

The substantial difference between the microscopic approach proposed by Straley and elaborated upon in the present paper, and the approach of Petrov, Derzhanskii, and Helfrich^{3,4} is that the latter consider the energy of an asymmetric molecule in a field of macroscopic elastic forces. The flexocoefficients are therefore expressed in Refs. 3 and 4 in terms of elastic constants. This approach is quite approximate, for actually a molecule of microscopic size is acted upon by microscopic "elastic" forces that are connected with the derivatives of the direction $\mathbf{n}(\mathbf{r})$ via the gradient of the distribution function [see Eqs. (5) and (6)]. Thus, our microscopic theory actually considers the same FE mechanism as in the semiphenomenological theory of Petrov *et al.*^{3,4}

We examine now expressions (25) and (27) in greater detail. It must be noted first of all that the flexocoefficients e_{\perp} and e_{\parallel} contain terms proportional both to S and S^2 . In Refs. 6 and 10 was proposed a method of separating the dipole and quadrupole contributions to the flexoelectric coefficients on the premise that the quadrupole contribution is proportional to S (Ref. 6) and the dipole contribution to S^2 (Refs. 3 and 4). From our results, however it can be concluded that the relation $e \propto S^2$ is the result of shortcomings of the semiphenomenological approach.^{3,4} The results cast doubt on the quantitative estimate of the ratio of the dipole and quadrupole contributions as obtained from the ratio of e_1 and e_2 in the expression $e = e_1 S + e_2 S^2$ (Ref. 10). At the same time, the absence of a term $\Delta e \propto S^2$ in the experimental $e(S)$ dependences of a number of substances^{6,10} points as before to

a predominant role of the quadrupole mechanism of the FE in these cases.

It is natural to assume that typical molecules of liquid crystals have $\epsilon_{\perp} \sim \epsilon_{\parallel}$. It follows then from (25)–(27) that the molecule longitudinal dipole d_{\parallel} makes a considerably smaller contribution to the coefficients e_{\perp} and e_{\parallel} than the transverse dipole d_{\perp} , since $\lambda/\kappa \sim 10^{-1}$. Thus, the dipole FE should be substantial only for molecules with large transverse dipoles. We note that a significant dipole contribution to the flexocoefficients was actually observed in Ref. 10 for liquid crystals whose molecules have large transverse dipoles. At the same time, in the case of cyanobiphenyl, which has a large longitudinal dipole, Marcerou and Prost¹⁰ did not observe a dipole FE; this can be attributed not only to a tendency to formation of pairs with antiparallel dipoles, but also to a small value of the dipole contributions themselves to the flexocoefficients. It would therefore be of interest to investigate experimentally the intermediate case, when $d_{\perp} = 0$ and d_{\parallel} differs from zero but is insufficient for pair formation.

Of greatest interest, however, is apparently the flexocoefficient difference $e_{\perp} - e_{\parallel}$. In the case of the quadrupole FE this difference is connected with the anisotropy of the Lorentz tensor, and $e_{\perp} - e_{\parallel} \propto S^2$, while $e_{\perp} - e_{\parallel}$ is small because the relation $e \propto S$ is well satisfied for liquid crystals consisting of nonpolar molecules.¹⁰ At the same time the difference $e_{\perp} - e_{\parallel}$ is generally speaking not small. Actually $e_{\perp} - e_{\parallel} \approx 1.7 \cdot 10^{-4}$ cgs in the liquid crystal BMAOB (*n*-butyl-*n'*-methoxyazoxybenzene),^{15,16} and $e_{\perp} - e_{\parallel} \approx 1.0 \cdot 10^{-4}$ cgs in MBBA (*n*-methoxybenzylidene-*n*-butylaniline).¹⁷ The observed flexocoefficient difference $e_{\perp} - e_{\parallel}$ should therefore be explained by the dipole mechanism of the FE. It follows from (25)–(27) that

$$e_{\perp} - e_{\parallel} \approx \rho^2 \beta DL^3 S^2 d_{\perp} \epsilon_{\perp} (\kappa_1 + \kappa_3). \quad (28)$$

Thus,³⁾ $e_{\perp} - e_{\parallel} \sim e_{\perp} + e_{\parallel}$. It must be noted here that the difference $e_{\perp} - e_{\parallel}$ is determined only by the transverse dipole and by the transverse asymmetry (by the steric dipole) of the molecule. For molecules with $d_{\perp} = 0$ the difference of the flexocoefficients should be small, as can be verified in experiment. Unfortunately, the available experimental data are too scanty for a comparison with (28). The sign of the difference $e_{\perp} - e_{\parallel}$ is determined in (28) by the sign of the steric dipole e_{\perp} . Indeed, the direction of the polarization of the medium corresponds to the direction of the average dipole moment, therefore d_{\perp} is considered everywhere to be positive. At the same time, the sign of ϵ_{\perp} is determined by the direction of the transverse steric dipole relative to the transverse electric dipole.

We examine, finally, the dependence of the flexocoefficients on the molecule length. The density of the liquid crystal should correspond in order of magnitude to close packing of the molecules, therefore $\rho D^2 L \sim 1$, whence it follows that $e \propto L$. The linear dependence of the flexocoefficients on the length of the molecule might be verified experimentally for a suitable homologous sequence. Then, however, we must confine ourselves to relatively short tail chains, whose flexibility can be disregarded.

In conclusion, the author thanks S. A. Pikin for numerous opinions and discussions.

¹The Straley theory is generalized to include smectic-C liquid crystals in Refs. 7 and 8.

²In the general case the quantity $V(i, j)$ includes, naturally, polar terms that are odd in $\mathbf{a}_i, \mathbf{a}_j, \mathbf{b}_i, \mathbf{b}_j$, and contribute to the flexocoefficients e_{\perp} and e_{\parallel} . It can be shown, however, that the corresponding contribution (determined by the asymmetric part of the dispersion and multipole interaction) is a small correction to the values of e_{\perp} and e_{\parallel} and depend on the asymmetry of the molecule shape.

³We note that the relation $e_{\perp} - e_{\parallel} \propto S^2$ is obtained in all the existing FE theories, including the present paper.

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