Statistical theory of the flexoelectric polarization for the uniaxial nematic phase

A. Kapanowski

Marian Smoluchowski Institute of Physics, Jagellonian University, ulica Reymonta 4, 30-059 Kraków, Poland
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A statistical theory for the dipole flexoelectric (FE) polarization in liquid crystals is derived in the thermodynamic limit at small distortions and a small density. General microscopic expressions for the FE coefficients are rederived in the case of the uniaxial nematic phase. The expressions involve the one-particle distribution function and the potential energy of two-body short-range interactions. It is shown that, for wedge-shaped polar molecules, the FE coefficients are proportional to the longitudinal component of the molecule dipole moment. The FE coefficients include a term linear in $\langle P_2 \rangle$ and a quadratic form in $\langle P_j \rangle$ (j-even). The theory is used to calculate the temperature dependence of the elastic constants and the FE coefficients for a system of rigid molecules similar to cones.

I. INTRODUCTION

Nematic liquid crystals are characterized by anisotropic positional short-range order and orientational long-range order [1]. In the case of the biaxial nematic phase (D_{2h} symmetry), the anisotropic molecules tend to be parallel to selected axes, labeled by the unit orthogonal vectors $\vec{L}$, $\vec{M}$, and $\vec{N}$. In the case of the uniaxial nematic phase ($D_{\infty h}$ symmetry), only the $\vec{N}$ axis is defined. The state of the molecule alignment can be described exactly by a distribution function but usually a set of numerical parameters—order parameters—is used.

In most practical circumstances there is some deformation of the alignment; the distribution function varies from point to point. The deformations usually are described by a continuum theory where it is assumed that the magnitude of the alignment anisotropy is unchanged; it is only the orientations of the axes $\vec{L}$, $\vec{M}$, and $\vec{N}$ that have been rotated. The free energy due to the distortion of the axes is expressed in terms of the vector derivatives and the elastic constants K_i. The distortion free-energy density of the uniaxial nematic phase has the form [2]

$$f_d = \frac{1}{2}K_1(\vec{\nabla} \cdot \vec{N})^2 + \frac{1}{2}K_2[\vec{N} \cdot (\vec{\nabla} \times \vec{N})]^2 + \frac{1}{2}K_3[\vec{N} \times (\vec{\nabla} \times \vec{N})]^2,$$
(1)

where K_1, K_2, and K_3 are the splay, twist, and bend elastic constants, respectively.

In a deformed uniaxial nematic liquid crystal, there should appear in many cases a spontaneous dielectric polarization described by Meyer [3]

$$\vec{P}_d = e_1\vec{N}(\vec{\nabla} \cdot \vec{N}) + e_3(\vec{N} \cdot \vec{\nabla})\vec{N} = e_1\vec{N}(\vec{\nabla} \cdot \vec{N}) - e_3\vec{N} \times (\vec{\nabla} \times \vec{N}),$$
(2)

where e_1 and e_3 are the splay and bend flexoelectric (FE) coefficients, respectively. The flexoelectric polarization leads to a separate contribution to the free energy

$$f_f = -\vec{P} \cdot \vec{E},$$
(3)

where $\vec{E}$ is an external electric field. The appearance of the spontaneous polarization in liquid crystals as a result of orientational deformations is referred to as the flexoelectric effect. It is the liquid crystal analogy to the piezoelectric effect in solids. The FE effect is also present in smectic phases [4].

Flexoelectric polarization can influence electro-optical properties, defect formation, and structural instability. Thus, different techniques have been suggested to observe possible mechanisms producing the FE effect. However, the accuracy of these measurements is influenced by a number of parameters such as dielectric and optical anisotropy, elastic constants, etc. Problems also arise with the determination of the sign of the observed effects. In principle, e_1 and e_3 could be obtained from two types of experiment [1].

(1) Measuring the polarization or the surface charges induced by an imposed distortion. In this case ultrapure materials are required because impurity conduction can screen out the charges.

(2) Using the inverse effect. When an electric field $\vec{E}$ is applied on a nematic single crystal, the alignment may become distorted, since a suitable distortion will imply a polarization $\vec{P}_d$ parallel to $\vec{E}$. This was observed by Schmidt *et al.* on N-(p-methoxybenzylidene)-p-butylaniline (MBBA) [5].

Madhusudana *et al.* [6] reported an instability in a flexoelectric nematic domain due to a linear coupling with an external dc electric field. A hybrid aligned nematic cell with two antiparallel flexopolarized domains was used and the field induced a twist instability in domains with the flexopolarization opposed to the field.

The flexoelectric polarization of 4–pentyl–4'–cyanobiphenyl (5CB) was measured in hybrid aligned nematic cells by means of a pyroelectric-effect-based technique [7,8]. The corresponding sum of the FE coefficients $e_1 + e_3$ was found negative and about -13 pC/m at room temperature (the molecular dipole moment was 4 D).

Recently Ewings *et al.* [9] demonstrated a technique inspired by the flexoelectic-optic effect [10] which used a twisted nematic cell with in-plane electric field. The chiral and achiral materials can be studied and the effects due to

ionic screening are taken into account. The sum of the FE coefficients $e_1 + e_3$ was $+9.3 \pm 0.3$ pC/m for E7 and $+3.5 \pm 0.2$ pC/m for a weakly chiral mixture of E70A with CB15.

A microscopic mechanism of the FE was proposed by Meyer [3], who showed that the flexoelectric polarization is a steric (packing) effect due to the asymmetry of the molecular shape. The distortion is coupled to the appearance of a nonzero polarization density. As has been emphasized by Prost and Marcerou [11] the polarization in a deformed liquid crystal is also produced as a result of a gradient in the average density of quadrupole molecule moments. Such a polarization does not need asymmetry in molecular shape.

A microscopic theory for the dipole contribution to the FE effect was developed in 1976 by Straley [12] by extending the Onsager theory of orientational ordering in hard-rod gases. In 1983 Osipov [13] considered also attractive forces between molecules. Other mean-field theories were given by Helfrich [14] and by Derzhanski and Petrov [15].

In 1989 Singh and Singh [16] used the density-functional formalism to derive expressions for the FE coefficients for both the dipole and quadrupole contributions. The dipole contribution was expressed in terms of direct correlation function of the isotropic liquid having a number density equal to that of the ordered medium. The quadrupole contribution was found to be independent of the direct correlation function and depends only on the anisotropic part of the molecular quadrupole tensor. The two contributions were found to be nearly equal in magnitude. The transverse component of the molecular dipole moment contributed significantly more than the longitudinal component.

The density-functional formalism was used also by Somoza and Tarazona [17] to derive the expressions for the elastic constants and the flexoelectric coefficients. The effect of the relaxation on the angular distribution function of the deformed nematic was included. Small corrections to the known results were obtained.

Zakharov and Dong [18] investigated theoretically FE coefficients by means of an integral equation approach, which took into account translational and orientational correlations as well as their coupling. The coefficients were evaluated from microscopic expressions derived on the basis of a density-functional method. Both e_i were negative when the data for 5CB were used.

Computer simulations offer a way to assert the molecular origins of flexoelectricity because they consider the short-range fluctuations in molecular alignment. In the Monte Carlo study by Stelzer et al. [19] the FE coefficients were evaluated for wedge-shaped molecules interacting via a generalized Gay-Berne potential. The molecules were modeled by a Gay-Berne ellipsoid with a Lennard-Jones sphere attached near one end. The FE coefficients were evaluated from microscopic expressions derived on the basis of a density-functional approach. The authors found for the elastic constants the strange relation $K_2 > K_1 > K_3 > 0$, whereas the typical relation for rodlike molecules is $K_3 > K_1 > K_2 > 0$. The FE coefficients were positive and small, e_3 was almost zero, and e_1 was increasing with decreasing temperature. In the extended study by Billeter and Pelcovits [20] the FE coefficients were measured using linear response theory

of Nemtsov and Osipov [21]. The isotropic and smectic phases were studied because the authors were not able to produce a stable nematic. The e_3 coefficients were found negligible for both phases. For the e_1 coefficient two different signs were found in the cases of more and less prominent wedges. We note that the results have sometimes a large computer error (from 10% to 100%).

The purpose of the present paper is to calculate the measurable macroscopic parameters—the elastic constants and the FE coefficients—from the microscopic molecular parameters in the case of the uniaxial nematic phase. Furthermore, we would like to prepare the background for further research on lower-symmetry systems. The organization of this paper is as follows: In Sec. II a statistical theory of uniaxial nematic phases with rigid wedge-shaped molecules is described and the expressions for the flexoelectric coefficients are rederived. In Sec. III the theory is applied to the system of molecules interacting via the selected potential. Section IV contains a summary.

II. EXPRESSIONS FOR FLEXOELECTRIC COEFFICIENTS

In the phenomenological approach we consider small deformations of the director $\vec{N}$ of the form

$$\vec{N}(\vec{r}) = [q_1 x + q_2 y - q_3 z, q_4 y - q_5 x - q_6 z, 1], \quad (4)$$

where the parameters $\{q_1, q_4\}$, $\{q_2, q_5\}$, and $\{q_3, q_6\}$ are connected with splay, twist, and bend, respectively ($1/q_i$ is a certain length much greater than the size of the sample). When we substitute the director $\vec{N}$ given by (4) to the total free-energy density (1) we get

$$f_d = \frac{1}{2} K_1 (q_1 + q_4)^2 + \frac{1}{2} K_2 (q_2 + q_5)^2 + \frac{1}{2} K_3 (q_3^2 + q_6^2), \quad (5)$$

where the positions of the parameters q_i point to the splay K_1, twist K_2, and bend K_3 elastic constants. The corresponding FE polarization has the form

$$\vec{P} = [-e_3 q_3, -e_3 q_6, e_1 (q_1 + q_4)]. \quad (6)$$

Note that the splay and bend parameters q_i only are present in Eq. (6). Now the microscopic expressions for the FE polarization should be provided in order to extract the FE coefficients.

Let us consider a set of N molecules contained in a volume V, at the temperature T. The molecules are rigid wedge-shaped blocks ($C_{\infty v}$ symmetry) with three translational and three rotational degrees of freedom. The state of a molecule is described by a vector of position $\vec{r}$ and the orientation $R = (\phi, \theta, \psi)$, where ϕ, θ, and ψ are the three Euler angles. Alternatively, the set of three orthonormal vectors $(\vec{l}, \vec{m}, \vec{n})$ can be used.

It is assumed that the molecules interact via two-body short-range forces that depend on the distance between the molecules $(\vec{u} = \vec{r}_2 - \vec{r}_1 = u\vec{\Delta})$ and their orientations; $\Phi_{12}(u, \vec{\Delta}, R_1, R_2)$ gives the potential energy of interactions. For uniaxial or wedge-shaped molecules the orientation is

completely described by the vector $\vec{n}$—the angle ψ is not determined in R_1, R_2.

The symmetries of the real potential energy Φ_{12} are as follows: (1) Translational invariance—Φ_{12} depends on $\vec{u}$ but not on $\vec{r}_1$ and $\vec{r}_2$; (2) rotational invariance—Φ_{12} do not depend on the reference frame choice; (3) invariance with respect to the permutation of identical molecules; (4) invariance with respect to the molecule symmetry $C_{\infty v}$, i.e., the molecules are achiral; (5) achirality of the interactions between molecules.

The free energy for the system can be derived in the thermodynamic limit ($N \to \infty$, $V \to \infty$, $N/V = $const) from the Born-Bogoliubov-Green-Kirkwood-Yvon hierarchy [22] or as the cluster expansion for uniaxial systems [23]. The total free energy F consists of the entropy term and the interaction term, namely,

$$F = F_{ent} + F_{int}, \qquad (7)$$

where

$$\beta F_{ent} = \int d\vec{r}\, dR\, G(\vec{r},R)\{\ln[G(\vec{r},R)\Lambda] - 1\}, \qquad (8)$$

$$\beta F_{int} = -\frac{1}{2} \int d\vec{r}_1 dR_1 d\vec{r}_2 dR_2 G(\vec{r}_1,R_1)G(\vec{r}_2,R_2)f_{12}. \qquad (9)$$

Here $f_{12} = \exp(-\beta\Phi_{12}) - 1$ is the Mayer function, $dR = d\phi\, d\theta \sin\theta\, d\psi$, $\beta = 1/(k_B T)$, and Λ is related to the ideal gas properties. The normalization of the one-particle distribution function G is

$$\int d\vec{r}\, dR\, G(\vec{r},R) = N. \qquad (10)$$

The equilibrium distribution G minimizing the free energy (7) satisfies the equation

$$\ln[G(\vec{r}_1,R_1)\Lambda] - \int d\vec{r}_2 dR_2 G(\vec{r}_2,R_2)f_{12} = \text{const.} \qquad (11)$$

In the case of the homogeneous uniaxial nematic phase composed of uniaxial or wedge-shaped molecules the distribution function depends on one argument

$$G(\vec{r},R) = G_0(R) = G_0(\vec{n} \cdot \vec{N}), \qquad (12)$$

where the unit orthogonal vector $\vec{N}$ describes the phase orientation. In order to derive expressions for the elastic constants it is enough to assume that, in the deformed phase, the phase orientation depends on the position but the magnitude of the alignment is constant,

$$G(\vec{r},R) = G_0(\vec{r},R) = G_0[\vec{n} \cdot \vec{N}(\vec{r})]. \qquad (13)$$

In order to derive expressions for the FE coefficients we have to take into account also the small change of the alignment

$$G(\vec{r},R) = G_0(\vec{r},R)[1 + g(\vec{r},R)], \qquad (14)$$

where g is expected to be small. The orientational polarization depends on the position and it is induced by the change of the alignment

$$\vec{P}(\vec{r}) = \int dR\, G(\vec{r},R)\vec{\mu}(R) = \int dR\, G_0(\vec{r},R)g(\vec{r},R)\vec{\mu}(R). \qquad (15)$$

The molecule electric dipole moment can have any orientation and it can be written as

$$\vec{\mu} = \mu_1 \vec{l} + \mu_2 \vec{m} + \mu_3 \vec{n}. \qquad (16)$$

According to Straley [12], the solution of our problem is a function g of the form

$$g(\vec{r},R_1) = \int d\vec{u}\, dR_2 f_{12}(\vec{u} \cdot \vec{\nabla})G_0(\vec{r},R_2). \qquad (17)$$

Let us calculate the derivatives under the assumption that the phase is deformed according to (4),

$$\begin{aligned}(\vec{u} \cdot \vec{\nabla})G_0(\vec{r},R) &= G_0'(R)(\vec{u} \cdot \vec{\nabla})[\vec{N}(\vec{r}) \cdot \vec{n}] \\ &= G_0'(R)(q_1 u_x n_x - q_5 u_x n_y + q_2 u_y n_x + q_4 u_y n_y \\ &\quad - q_3 u_z n_x - q_6 u_z n_y).\end{aligned} \qquad (18)$$

Finally, the components of the FE polarization (15) are

$$P_x = \mu_3 \int d\vec{u}\, dR_1 dR_2 f_{12} G_0(R_1)G_0'(R_2)(-q_3)u_z n_{1x} n_{2x}, \qquad (19)$$

$$P_y = \mu_3 \int d\vec{u}\, dR_1 dR_2 f_{12} G_0(R_1)G_0'(R_2)(-q_6)u_z n_{1y} n_{2y}, \qquad (20)$$

$$\begin{aligned}P_z = \mu_3 \int d\vec{u}\, dR_1 dR_2 f_{12} G_0(R_1)G_0'(R_2)(q_1 u_x n_{1z} n_{2x} \\ + q_4 u_y n_{1z} n_{2y}).\end{aligned} \qquad (21)$$

The FE coefficients e_1 (from q_1 or q_4) and e_3 (from q_3 or q_6) have the form

$$e_1 = \mu_3 \int d\vec{u}\, dR_1 dR_2 f_{12} G_0(R_1)G_0'(R_2)u_x n_{1z} n_{2x}, \qquad (22)$$

$$e_3 = \mu_3 \int d\vec{u}\, dR_1 dR_2 f_{12} G_0(R_1)G_0'(R_2)u_z n_{1x} n_{2x}. \qquad (23)$$

The elastic constants of the uniaxial nematic phase are [24]

$$\beta K_1 = \frac{1}{2} \int d\vec{u}\, dR_1 dR_2 f_{12} G_0'(R_1)G_0'(R_2)u_x^2 n_{1x} n_{2x}, \qquad (24)$$

$$\beta K_2 = \frac{1}{2} \int d\vec{u}\, dR_1 dR_2 f_{12} G_0'(R_1)G_0'(R_2)u_y^2 n_{1x} n_{2x}, \qquad (25)$$

$$\beta K_3 = \frac{1}{2} \int d\vec{u}\, dR_1 dR_2 f_{12} G_0'(R_1)G_0'(R_2)u_z^2 n_{1x} n_{2x}. \qquad (26)$$

III. EXEMPLARY CALCULATIONS

The aim of this section is to express the FE coefficients and the elastic constants by means of the order parameters for a relatively simple model with the interaction energy of the form $\Phi_{12}(u/\sigma)$, where u is the distance between molecules and σ depends on the molecule orientations R_1 and R_2, and on the vector $\vec{\Delta}$. For σ it is possible to write the general expansion proposed by Blum and Torruella [25] which is evidently invariant under rotations and translations. It involves the $3-j$ Wigner symbols and the standard rotation matrix elements. In the case of wedge-shaped achiral molecules the lowest order terms of the expansion are

$$\sigma = \sigma_0 + \sigma_1[(\vec{\Delta} \cdot \vec{n}_1)^2 + (\vec{\Delta} \cdot \vec{n}_2)^2] + \sigma_2(\vec{n}_1 \cdot \vec{n}_2)^2$$
$$+ \sigma_3(\vec{\Delta} \cdot \vec{n}_1 - \vec{\Delta} \cdot \vec{n}_2)(\vec{n}_1 \cdot \vec{n}_2) + \sigma_4(\vec{\Delta} \cdot \vec{n}_1)(\vec{\Delta} \cdot \vec{n}_2)$$
$$+ \sigma_5(\vec{\Delta} \cdot \vec{n}_1 - \vec{\Delta} \cdot \vec{n}_2) + \sigma_6(\vec{n}_1 \cdot \vec{n}_2). \quad (27)$$

The parameters σ_i are the molecular constants that determine the values of the FE coefficients and the elastic constants. The terms with σ_0, σ_1, and σ_2 describe uniaxial molecules with the symmetry $D_{\infty h}$. Note that in order to get nonzero FE coefficients it is necessary to have nonzero σ_3 or σ_5. As far as the functional dependence of the potential energy on u/σ is concerned, there are a number of possibilities and some of them were presented elsewhere [24]. We use the square-well potential energy of the form

$$\Phi_{12}(u/\sigma) = \begin{cases} +\infty & \text{for } (u/\sigma) < 1, \\ -\epsilon & \text{for } 1 < (u/\sigma) < R_{SW}, \\ 0 & \text{for } (u/\sigma) > R_{SW}. \end{cases} \quad (28)$$

The potential energy of the form $\Phi_{12}(u/\sigma)$ allows us to close the temperature dependence of many physical quantities inside the functions $B_s(T)$ defined as

$$B_s(T) = \int_0^\infty dx \, x^s f_{12}(x) = \int_0^\infty dx \, x^s \{\exp[-\beta \Phi_{12}(x)] - 1\}. \quad (29)$$

For the square-well potential energy we obtain

$$B_s(T) = \frac{1}{s+1}\{[\exp(\epsilon/k_BT) - 1](R_{SW}^{s+1} - 1) - 1\}. \quad (30)$$

It is convenient to use a dimensionless function $f(R) = G_0(R)V/N$ with the normalization

$$\int dR f(R) = 1. \quad (31)$$

The function f is the solution of the general equation (11) in the case of the homogeneous phase. For any function $A = A(R)$ we define the average value as

$$\langle A \rangle \equiv \int dR f(R)A(R). \quad (32)$$

We rewrite the general equation (11) for the distribution function in the case of a homogeneous phase. Let us define

$$K(R_1, R_2) = \int d\vec{\Delta}(\sigma/\sigma_0)^3, \quad (33)$$

$$\lambda = B_2(T)\sigma_0^3 N/V. \quad (34)$$

Note that for σ given by Eq. (27) it is possible to express the kernel K and the distribution function f as *finite* series,

$$K(R_1, R_2) = \sum_j K^{(j)}P_j(\vec{n}_1 \cdot \vec{n}_2), \quad (35)$$

$$\ln f(R) = \sum_j C_j P_j(R), \quad (36)$$

where $P_j(R) = P_j(\cos \theta)$ are the Legendre polynomials and the sums run from 0 to 6. The order parameters are defined as $\langle P_j \rangle$. We derive the coefficients C_j from the equations

$$C_j = \lambda K^{(j)}\langle P_j \rangle \quad \text{for } j > 0, \quad (37)$$

$$\langle P_0 \rangle = 1 \text{ (the normalization condition)}. \quad (38)$$

The distribution function f can be expanded in an infinite series with respect to polynomials P_j,

$$f(R) = \sum_j \langle P_j \rangle P_j(R)(2j+1)/(8\pi^2). \quad (39)$$

When we insert the series (39) into formulas for the FE coefficients and the elastic constants we get the finite sums

$$e_i = \zeta \sum_{jk} \langle P_j \rangle \langle P_k \rangle B_{(i)jk}, \quad (40)$$

$$K_i = \eta \sum_{jk} \langle P_j \rangle \langle P_k \rangle A_{(i)jk}, \quad (41)$$

where

$$\zeta = \mu_3 B_3(T)\sigma_0^4(N/V)^2, \quad (42)$$

$$\eta = k_B T B_4(T)\sigma_0^5(N/V)^2. \quad (43)$$

The coefficients $K^{(j)}$, $A_{(i)jk}$, and $B_{(i)jk}$ are polynomials in σ_i/σ_0 that can be calculated analytically. Note that σ_0 determines the length scale, whereas ϵ determines the energy scale. The FE coefficients can be expressed in units of μ_3/σ_0^2, the elastic constants in ϵ/σ_0, and the temperature in ϵ/k_B.

The mutually excluded volume V_e of two molecules with the fixed orientations R_1 ($\vec{n}_1$) and R_2 ($\vec{n}_2$) is approximated by

$$V_e(\vec{n}_1, \vec{n}_2) = \int d\vec{\Delta}\sigma^3/3 = K(\vec{n}_1, \vec{n}_2)\sigma_0^3/3. \quad (44)$$

We assume that the molecule volume is equal to

$$V_{mol} = V_e(\vec{e}_z, -\vec{e}_z)/8 = \sum_j K^{(j)}(-1)^j\sigma_0^3/24. \quad (45)$$

Note that for uniaxial molecules (the $D_{\infty h}$ symmetry) only $K^{(j)}$ with j even are nonzero and $V_e(\vec{e}_z, -\vec{e}_z) = V_e(\vec{e}_z, \vec{e}_z)$. We used the density $NV_{mol}/V = 0.1$ and $R_{SW} = 2$. We assumed that
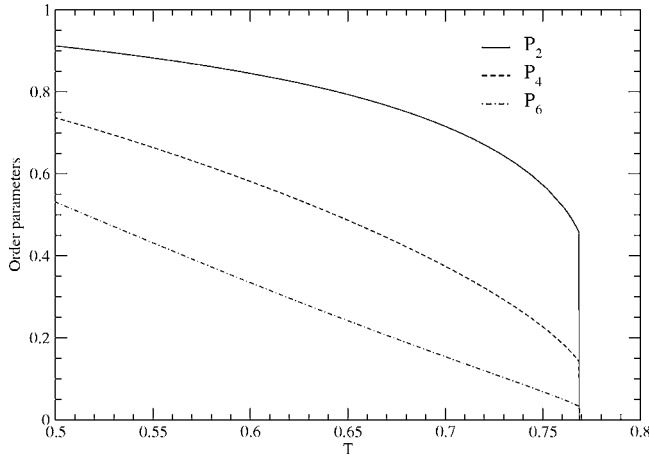
FIG. 1. Temperature dependence of the order parameters $\langle P_j \rangle$ (dimensionless). The temperature T is expressed in ϵ/k_B. The isotropic-nematic (I-N) transition is at $T_C = 0.7687$.

molecules are similar to cones with the height $4\sigma_0$ and the base diameter $2\sigma_0$. Then, by means of the excluded volume method [26], the parameters σ_i were calculated: $\sigma_1 = (13/8)\sigma_0$, $\sigma_2 = \sigma_6 = (1/2)\sigma_0$, $\sigma_3 = (-1/2)\sigma_4 = (5/8)\sigma_0$, and $\sigma_5 = (-1/8)\sigma_0$. The formula (45) yields $V_{mol} = 20.417\sigma_0^3$. In fact, the expansion (27) is too simple to reproduce exactly the molecule shape but higher-order terms do not change our results qualitatively.

In our system, on decreasing the temperature we meet the first-order transition from the isotropic to the uniaxial nematic phase at $T_C = 0.7687$. The temperature dependence of the order parameters $\langle P_j \rangle$ is presented in Fig. 1. The order parameters were used to calculate the temperature dependence of the elastic constants shown in Fig. 2 and the FE coefficients shown in Fig. 3.

In the nematic phase on decreasing the temperature the elastic constants become larger and the inequalities $K_3 > K_1 > K_2$ are satisfied. The same result was also found for uniaxial molecules in the past.

As far as the FE coefficients are concerned, negative values are obtained, $0 > e_3 > e_1$. On decreasing the temperature
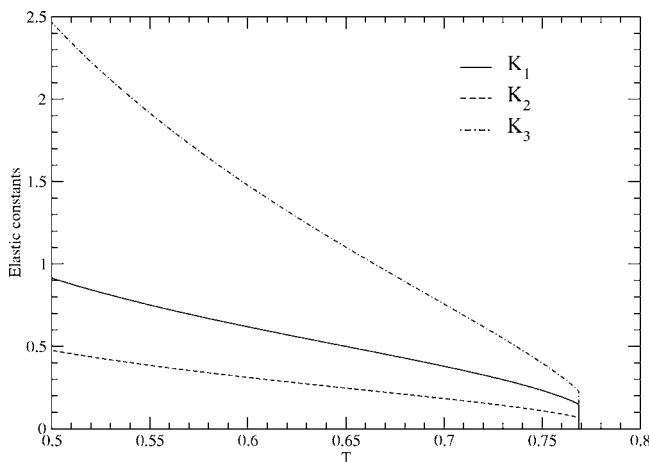

FIG. 2. Temperature dependence of the elastic constants K_i expressed in ϵ/σ_0. The temperature T is expressed in ϵ/k_B. The I-N transition is at $T_C = 0.7687$.
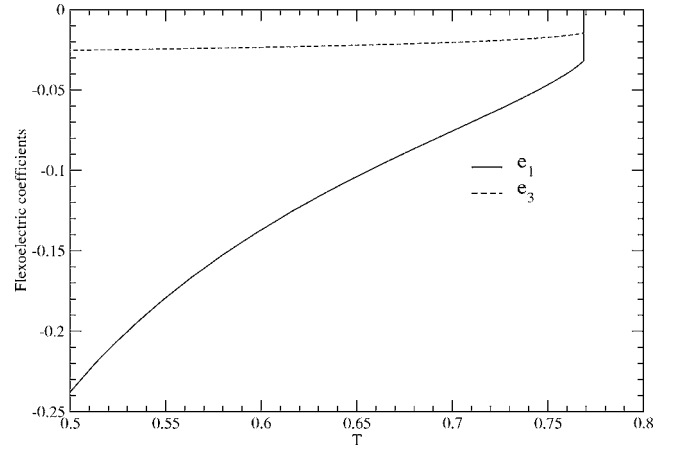

FIG. 3. Temperature dependence of the flexoelectric coefficients e_i expressed in μ_3/σ_0^2. The temperature T is expressed in ϵ/k_B. The I-N transition is at $T_C = 0.7687$.

the bend coefficient e_3 is almost constant while the splay coefficient e_1 goes deeper below zero. Let us explain the molecular picture under the assumption that the electric dipole moments are directed to the top of the cones (the molecules are similar to cones). In fact, the component of the dipole moment that is perpendicular to the molecule rotary symmetry axis does not produce the polarization.

The results for the splay and the discussion by Meyer are in agreement: there is an excess of cones pointing to the splay origin because they fit the splayed structure. Thus, the FE polarization points to the splay origin as shown in Fig. 4.

The results for the bend are not obvious because the molecules do not have a banana shape which fits the bend structure. It appears that the cones are slightly turned to the direction opposite to the bend center and this is the FE polarization direction as shown in Fig. 4.

IV. SUMMARY

In this paper we rederived the microscopic formulas for the FE coefficients of wedge-shaped molecules with the $C_{\infty v}$
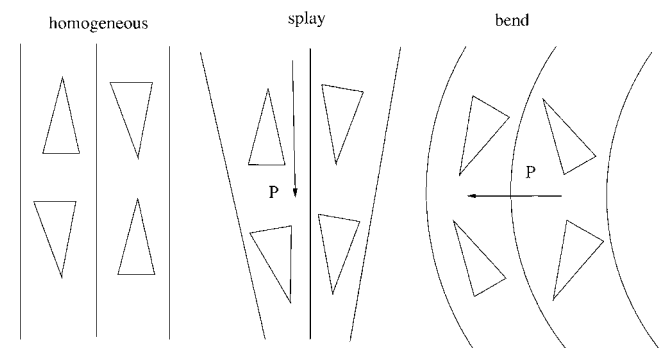

FIG. 4. The homogeneous, splay, and bend phases. The solid lines denote the local direction $\vec{N}$. The z axis is the symmetry axis of the homogeneous nematic phase. In the splay phase there is an excess of cones pointing down to the splay origin. In the bend phase there is an excess of cones pointing to the left whereas the bend center is on the right.

symmetry. The one-particle distribution function and the potential energy of molecular interactions are needed in order to calculate the FE coefficient values.

We showed that a potential energy of the form $\Phi_{12}(u/\sigma)$ allows us to express the FE coefficients and the elastic constants as a finite series of order parameters. The FE coefficients include a term linear in $\langle P_2 \rangle$ and a quadratic form in $\langle P_j \rangle$ (j even). We note that the analytical expressions for the macroscopic measurable parameters accelerate the calculations and simplify the design of systems with the selected characteristics.

The theory was applied to a system of molecules similar to cones. The temperature dependence of the FE coefficients and the elastic constants was obtained. Both FE coefficients were negative; the bend coefficient e_3 was almost constant whereas the splay coefficient e_1 was changing monotonically. The results are in the qualitative agreement with experiments on 5CB.

The theory in the present form is a starting point for further research. It is desirable to consider molecules with the C_{2v} symmetry in order to simulate banana-shaped molecules. Such molecules fit the bend deformation and we can expect different behavior of the FE coefficients. It is also possible to consider the FE effect in biaxial nematic phases; this is more complicated and the number of FE coefficients in this phase is, to our knowledge, unknown. Note that banana-shaped molecules could produce biaxial phases because C_{2v} is a subgroup of the D_{2h} (biaxial) symmetry group.

ACKNOWLEDGMENTS

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