

Flexoelectric polarization in the biaxial nematic phase

A. Kapanowski

Marian Smoluchowski Institute of Physics, Jagellonian University, ulica Reymonta 4, 30-059 Kraków, Poland

(Received 5 February 2007; revised manuscript received 2 May 2008; published 28 May 2008)

The dipole flexoelectric (FE) polarization in liquid crystals is derived in the thermodynamic limit at small distortions and small density. General microscopic expressions for the FE coefficients are obtained in the case of the uniaxial and biaxial nematic phases composed of C_{2v} molecules. The expressions involve the one-particle distribution function and the potential energy of two-body short-range interactions. In the case of the biaxial nematic phase, six basic deformations produce FE polarization but there are only five independent FE coefficients.

DOI: [10.1103/PhysRevE.77.052702](https://doi.org/10.1103/PhysRevE.77.052702)

PACS number(s): 61.30.Cz, 77.84.Nh

Biaxial nematic liquid crystals are characterized by anisotropic positional short-range order and orientational long-range order [1]. 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 uniaxial nematic phase only the \vec{N} axis is defined. Stable biaxial phases were observed in 1980 in lyotropic systems by Yu and Saupe [2] but their existence in thermotropic systems was not certain for many years [3]. Recently, Madsen *et al.* [4] synthesized banana-shaped mesogens and evidence for biaxiality was achieved using NMR spectroscopy. Acharya *et al.* [5] revealed biaxiality of bent-core mesogens by means of low-angle x-ray diffraction. Merkel *et al.* [6] carried out infrared absorbance measurements on two liquid crystalline organosiloxane tetrapodes and showed the existence of a biaxial nematic phase.

Theoretical predictions of biaxial nematic phases started in 1970 with the paper by Freiser [7]. Then they were studied using a number of theoretical methods, e.g., mean-field theory [8,9], counting methods [10,11], Landau–de Gennes theory [12,13], bifurcation analysis [14], and density-functional theory [15]. All the theories mentioned above predict that the system will exhibit four phases as the molecular biaxiality varies: a positive and a negative uniaxial phase, respectively, formed by prolate and oblate molecules, a biaxial, and an isotropic phase. The nematic-isotropic phase transition is expected to be first order and to weaken as the biaxiality increases until it becomes continuous at the point (Landau bicritical point) of maximum molecular biaxiality. At this point the system should go directly from a biaxial to an isotropic phase. The uniaxial-biaxial transition is expected to be second order.

A microscopic mean-field theory [16,17] predicts the possibility of lines of second-order and first-order uniaxial-biaxial transitions joined at a tricritical point. The experimental results by Merkel *et al.* [6] were successfully interpreted in terms of this theory. A weakly first-order uniaxial-biaxial transition was also revealed by dynamic light scattering from orientational order fluctuations in a liquid crystalline tetrapode [18]. Recently, two-particle cluster theory was applied to study the biaxial molecules in the Sonnet model [16] and qualitative agreement with the mean-field theory was obtained [19]. A Monte Carlo study of biaxial nematic phases composed of V-shaped molecules was done by Bates and Luckhurst [20].

In most practical circumstances the liquid crystal phase alignment is deformed. The deformations usually are described by a continuum theory where the free energy is expanded to the second order around the free energy of the undeformed state in ascending powers of a parameter that measures the deformation. The free energy due to the distortion of the axes is expressed in terms of the vector spatial derivatives and the elastic constants.

In a deformed uniaxial nematic liquid crystal, there should appear in many cases a spontaneous dielectric polarization described by Meyer [21]:

$$\vec{P} = e_1 \vec{N} (\vec{\nabla} \cdot \vec{N}) + e_3 (\vec{N} \cdot \vec{\nabla}) \vec{N} = e_1 \vec{N} (\vec{\nabla} \cdot \vec{N}) - e_3 \vec{N} \times (\vec{\nabla} \times \vec{N}), \quad (1)$$

where e_1 and e_3 are the splay and the bend flexoelectric (FE) coefficients, respectively. The appearance of spontaneous polarization in liquid crystals as a result of orientational deformations is referred to as the flexoelectric effect.

A microscopic mechanism of the FE effect was proposed by Meyer [21], who pointed out that, under the condition of orientation deformation of a liquid crystal, banana-shaped or conical molecules should be so oriented that their constant dipoles are ordered and macroscopic polarization sets in. On the other hand, Prost and Marcerou [22] showed that polarization in a deformed liquid crystal is also produced as a result of a gradient in the average density of the molecule quadrupole moments. Such a polarization does not need asymmetry in molecular shape of the banana or cone kind. Later, the FE coefficients for the uniaxial nematic phase were calculated by means of a statistical-mechanical theory [23], mean-field theories [24,25], the density-functional formalism [26,27], an integral equation approach [28], and computer simulations [29,30]. The expressions connecting the molecular asymmetry, the elasticity of the liquid crystal, and the FE coefficients were obtained by Derzhanski and co-workers [31]. It was also shown [32] that the FE coefficients can have nontrivial dependence on the details of the molecule's chemical structure (an isomerization, a charge distribution).

The 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 [33]. The FE coefficients can be obtained experimentally from measuring the

polarizations or the surface charges induced by an imposed distortion or using the inverse effect, because when an electric field is applied on a nematic, the alignment may become distorted and this will imply a polarization [34]. The flexoelectric polarization of 5CB (4-pentyl-4'-cyanobiphenyl) was measured by means of a pyroelectric-effect-based technique [35,36] and recently a technique inspired by the flexoelectric-optic effect was demonstrated [37].

Below, we would like to investigate the FE effect in biaxial nematic phases. In the case of the uniaxial nematic phase there are three independent phase deformations: splay, twist, and bend. The symmetry considerations of Rudquist and Lagerwall [38] prove that in uniaxial nematic liquid crystals the FE effect can be induced by splay or bend. The polarization connected with bend has to be perpendicular to the director \vec{N} , whereas in the splay deformation, a polarization along the director is admitted. The twist is not connected with a local polarization of the medium because there is always a twofold symmetry axis perpendicular to the helix axis.

It was shown [39] that in the case of the biaxial nematic phase there are 12 independent phase deformations and six of them are connected with splays and bends of the vectors \vec{L} , \vec{M} , and \vec{N} . Thus, we can expect that there are six FE coefficients for the biaxial nematic phase.

Let us assume that the FE polarization, which is a vector quantity, depends on the spatial derivatives of the vectors \vec{L} , \vec{M} , and \vec{N} ,

$$P_\alpha = s_{ij}R_{i\alpha}\partial_\beta R_{j\beta} + b_{ij}R_{i\beta}\partial_\beta R_{j\alpha}, \quad (2)$$

where we denoted

$$L_\alpha = R_{1\alpha}, \quad M_\alpha = R_{2\alpha}, \quad N_\alpha = R_{3\alpha}. \quad (3)$$

The matrix elements $R_{i\alpha}$ ($i=1,2,3$ and $\alpha=x,y,z$) satisfy the conditions

$$\sum_\alpha R_{i\alpha}R_{j\alpha} = \delta_{ij}, \quad \sum_i R_{i\alpha}R_{i\beta} = \delta_{\alpha\beta}. \quad (4)$$

The above relations express the orthogonality and the completeness of the local frame. It is also possible to derive the identity (to be used later)

$$\sum_i (R_{i\alpha}\partial_\beta R_{i\beta} + R_{i\beta}\partial_\beta R_{i\alpha}) = 0. \quad (5)$$

The number of independent FE coefficients will be determined with the help of symmetry requirements. The local frame can be transformed into the new one

$$R'_{i\alpha} = T_{ij}R_{j\alpha}, \quad (6)$$

where T_{ij} ($i,j=1,2,3$) are the elements of the orthogonal transformation. The polarization may be expressed in terms of new variables with new (primed) FE coefficients. As the FE coefficients do not change under symmetry operations, we can identify the independent FE coefficients. As a result we get six FE coefficients s_{ii} and b_{ii} . But from the identity (5) we conclude that the coefficients s_{ii} and b_{ii} are not unique. The same polarization P can be obtained by means of the transformed coefficients

$$s'_{ii} = s_{ii} + c, \quad b'_{ii} = b_{ii} + c, \quad (7)$$

where c is any constant. Thus, only five coefficients are independent. Note that the differences $s_{ii}-s_{jj}$, $b_{ii}-b_{jj}$, or $s_{ii}-b_{jj}$ do not depend on the constant c .

Now we consider six small deformations of the directors ($\vec{L}, \vec{M}, \vec{N}$) of the form [39]

$$\begin{aligned} \vec{L}(\vec{r}) &= [1, q_7y - q_5x, q_9z - q_4x], \\ \vec{M}(\vec{r}) &= [q_5x - q_7y, 1, q_8z - q_6y], \\ \vec{N}(\vec{r}) &= [q_4x - q_9z, q_6y - q_8z, 1], \end{aligned} \quad (8)$$

where the parameters q_i ($i=4, \dots, 9$) describe the deformations ($1/q_i$ is a certain length much greater than the size of the sample). The corresponding FE polarization has the form

$$\begin{aligned} P_x &= q_7(s_{11} - b_{22}) + q_9(s_{11} - b_{33}) = q_7a_7 + q_9a_9, \\ P_y &= q_5(s_{22} - b_{11}) + q_8(s_{22} - b_{33}) = q_5a_5 + q_8a_8, \\ P_z &= q_4(s_{33} - b_{11}) + q_6(s_{33} - b_{22}) = q_4a_4 + q_6a_6, \end{aligned} \quad (9)$$

where we introduced six physical FE coefficients a_i which satisfy the identity

$$a_4 - a_5 - a_6 + a_7 + a_8 - a_9 = 0. \quad (10)$$

Equations (9) are phenomenological expressions and we should provide alternative microscopic expressions in order to obtain microscopic expressions for the FE coefficients.

Let us consider a system of N rigid molecules with the C_{2v} symmetry. Such molecules can form uniaxial ($D_{\infty h}$) and biaxial (D_{2h}) nematic phases. The free energy for the system can be derived in the thermodynamic limit ($N \rightarrow \infty$, $V \rightarrow \infty$, $N/V = \text{const}$) from the Born-Bogoliubov-Green-Kirkwood-Yvon hierarchy [40] or as a cluster expansion [41]. The total free energy F consists of the entropy term and the interaction term

$$F = F_{\text{ent}} + F_{\text{int}}, \quad (11)$$

where

$$\beta F_{\text{ent}} = \int d\vec{r} dR G(\vec{r}, R) \{\ln[G(\vec{r}, R)\Lambda] - 1\}, \quad (12)$$

$$\beta F_{\text{int}} = -\frac{1}{2} \int d\vec{r}_1 dR_1 d\vec{r}_2 dR_2 G(\vec{r}_1, R_1) G(\vec{r}_2, R_2) f_{12}. \quad (13)$$

We define $dR = d\phi d\theta \sin\theta d\psi$, $f_{12} = \exp(-\beta\Phi_{12}) - 1$ (the Mayer function), $\beta = 1/(k_B T)$, $\vec{u} = \vec{r}_2 - \vec{r}_1 = u\vec{\Delta}$; and Λ is related to the ideal gas properties. The normalization of the one-particle distribution function G is

$$\int d\vec{r} dR G(\vec{r}, R) = N. \quad (14)$$

The equilibrium distribution G minimizing the free energy (11) satisfies the equation

$$\ln[G(\vec{r}_1, R_1)\Lambda] - \int d\vec{r}_2 dR_2 G(\vec{r}_2, R_2) f_{12} = \text{const.} \quad (15)$$

In the homogeneous biaxial nematic phase composed of C_{2v} or D_{2h} molecules the distribution function has the form [39]

$$G_0(R) = G_0(\vec{l} \cdot \vec{L}, \vec{l} \cdot \vec{N}, \vec{n} \cdot \vec{L}, \vec{n} \cdot \vec{N}), \quad (16)$$

where the unit orthogonal vectors $(\vec{l}, \vec{m}, \vec{n})$ describe the molecule's orientation. For the C_{2v} molecules, the molecule symmetry axis is determined by the vector \vec{n} . Note that this is the *long* axis of wedge-shaped molecules and the *short* axis of banana-shaped molecules. 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,

$$G_0(\vec{r}, R) = G_0[\vec{l} \cdot \vec{L}(\vec{r}), \vec{l} \cdot \vec{N}(\vec{r}), \vec{n} \cdot \vec{L}(\vec{r}), \vec{n} \cdot \vec{N}(\vec{r})]. \quad (17)$$

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

$$G(\vec{r}, R) = G_0(\vec{r}, R)[1 + g(\vec{r}, R)], \quad (18)$$

where g is expected to be small. The microscopic polarization depends on the position inside the phase via the distribution function

$$\vec{P}(\vec{r}) = \int dR G(\vec{r}, R) \vec{\mu}(R). \quad (19)$$

The molecule electric dipole moment can be defined in the molecular frame as

$$\mu_\alpha(R) = \mu_1 l_\alpha + \mu_2 m_\alpha + \mu_3 n_\alpha, \quad \alpha = x, y, z. \quad (20)$$

According to Straley [23], the function g can be obtained from the expression

$$g(\vec{r}, R_1) = \int d\vec{u} dR_2 f_{12}(\vec{u} \cdot \vec{\nabla}) G_0(\vec{r}, R_2). \quad (21)$$

Finally, from Eqs. (19), (21), and (8), we get the components of the microscopic FE polarization,

$$\begin{aligned} P_x &= \int d\vec{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_x(R_1) [(U_{2z} - W_{2x}) q_9 u_z \\ &\quad + U_{2y} q_7 u_y], \\ P_y &= \int d\vec{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_y(R_1) [W_{2y} (-q_8 u_z) \\ &\quad + U_{2y} (-q_5 u_x)], \\ P_z &= \int d\vec{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_z(R_1) [(U_{2z} - W_{2x}) (-q_4 u_x) \\ &\quad + W_{2y} q_6 u_y], \end{aligned} \quad (22)$$

where we denoted

$$U_\alpha = \partial_1 G_0 l_\alpha + \partial_3 G_0 n_\alpha,$$

$$W_\alpha = \partial_2 G_0 l_\alpha + \partial_4 G_0 n_\alpha. \quad (23)$$

When we compare Eqs. (9) and (22), we obtain the equations for the FE coefficients:

$$\begin{aligned} a_4 &= \int d\vec{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_z(R_1) (-u_x) (U_{2z} - W_{2x}), \\ a_5 &= \int d\vec{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_y(R_1) (-u_x) U_{2y}, \\ a_6 &= \int d\vec{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_z(R_1) u_y W_{2y}, \\ a_7 &= \int d\vec{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_x(R_1) u_y U_{2y}, \\ a_8 &= \int d\vec{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_y(R_1) (-u_z) W_{2y}, \\ a_9 &= \int d\vec{u} dR_1 dR_2 f_{12} G_0(R_1) \mu_x(R_1) u_z (U_{2z} - W_{2x}). \end{aligned} \quad (24)$$

Let us consider the uniaxial nematic phase composed of wedge-shaped molecules. The long molecule axes \vec{n} are almost parallel to the \vec{N} axis, and we get

$$U_\alpha = 0, \quad a_5 = a_7 = 0. \quad (25)$$

We recover the Meyer expression (1) with two FE coefficients,

$$e_1 = a_4 = a_6, \quad e_3 = -a_8 = -a_9. \quad (26)$$

Finally we consider the uniaxial nematic phase composed of banana-shaped molecules. The long molecule axes \vec{l} are almost parallel to the \vec{L} axis, and we get

$$W_\alpha = 0, \quad a_6 = a_8 = 0. \quad (27)$$

We obtain the Meyer expression (1) where \vec{N} is replaced with \vec{L} . The FE coefficients are

$$e_1 = a_7 = a_9, \quad e_3 = -a_4 = -a_5. \quad (28)$$

Note that Eqs. (26) and (28) describe C_{2v} molecules, whereas very often simpler expressions for $C_{\infty v}$ molecules are present in the literature.

In conclusion, we derived microscopic formulas for the six FE coefficients in the case of the biaxial nematic phase of C_{2v} molecules. It appears that only five FE coefficients are independent. In order to calculate the values of the FE coefficients one needs the one-particle distribution function and the potential energy of molecular interactions. The Meyer expressions [21] are recovered in the case of the wedge-shaped and banana-shaped molecules in the uniaxial nematic phase. Generally, the splitting of the two Meyer FE coefficients and the appearance of new small FE coefficients are expected at the uniaxial-biaxial nematic transition. In order to describe real substances, the presented results should be

generalized beyond the low-density limit, where the Mayer function f_{12} is replaced with a better approximation of the direct correlation function c_2 . On the other hand, other sources of dielectric polarization should be taken into account: the quadrupole contribution or the ordoelectric polarization. But even then a qualitative comparison between theory and experiment may be difficult, because the experi-

mental data on FE coefficients are still scarce and sometimes contradictory [33].

This work was supported by the Faculty of Physics, Astronomy and Applied Computer Science, Jagellonian University (WRBW Grant No. 45/06). The author is also grateful to J. Spałek for his support.

-
- [1] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).
- [2] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).
- [3] R. Berardi and C. Zannoni, J. Chem. Phys. **113**, 5971 (2000).
- [4] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Phys. Rev. Lett. **92**, 145505 (2004).
- [5] B. R. Acharya, A. Primak, and S. Kumar, Phys. Rev. Lett. **92**, 145506 (2004).
- [6] K. Merkel, A. Kocot, J. K. Vij, R. Korlacki, G. H. Mehl, and T. Meyer, Phys. Rev. Lett. **93**, 237801 (2004).
- [7] M. J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).
- [8] J. P. Straley, Phys. Rev. A **10**, 1881 (1974).
- [9] B. M. Mulder and Th. W. Ruijgrok, Physica A **113**, 145 (1982).
- [10] C.-S. Shih and R. Alben, J. Chem. Phys. **57**, 3055 (1972).
- [11] W. Li and K. F. Freed, J. Chem. Phys. **101**, 519 (1994).
- [12] R. Alben, Phys. Rev. Lett. **30**, 778 (1973).
- [13] E. F. Gramsbergen, L. Longa, and W. H. de Jeu, Phys. Rep. **135**, 195 (1986).
- [14] B. Mulder, Phys. Rev. A **39**, 360 (1989).
- [15] R. Holyst and A. Poniewierski, Mol. Phys. **69**, 193 (1990).
- [16] A. M. Sonnet, E. G. Virga, and G. E. Durand, Phys. Rev. E **67**, 061701 (2003).
- [17] F. Bisi, E. G. Virga, E. C. Gartland, Jr., G. De Matteis, A. M. Sonnet, and G. E. Durand, Phys. Rev. E **73**, 051709 (2006).
- [18] K. Neupane, S. W. Kang, S. Sharma, D. Carney, T. Meyer, G. H. Mehl, D. W. Allender, S. Kumar, and S. Sprunt, Phys. Rev. Lett. **97**, 207802 (2006).
- [19] Zhi-Dong Zhang, Yan-Jun Zhang, and Zong-Li Sun, Chin. Phys. Lett. **23**, 3025 (2006).
- [20] M. A. Bates and G. R. Luckhurst, Phys. Rev. E **72**, 051702 (2005).
- [21] R. B. Meyer, Phys. Rev. Lett. **22**, 918 (1969).
- [22] J. Prost and J. P. Marcerou, J. Phys. (Paris) **38**, 315 (1977).
- [23] J. P. Straley, Phys. Rev. A **14**, 1835 (1976).
- [24] W. Helfrich, Z. Naturforsch. A **26**, 833 (1971).
- [25] A. Derzhanski and A. G. Petrov, Phys. Lett. **34A**, 483 (1971).
- [26] Y. Singh and U. P. Singh, Phys. Rev. A **39**, 4254 (1989).
- [27] A. M. Somoza and P. Tarazona, Mol. Phys. **72**, 911 (1991).
- [28] A. V. Zakharov and R. Y. Dong, Eur. Phys. J. E **6**, 3 (2001).
- [29] J. Stelzer, R. Berardini, and C. Zannoni, Chem. Phys. Lett. **299**, 9 (1999).
- [30] J. L. Billeter and R. A. Pelcovits, Liq. Cryst. **27**, 1151 (2000).
- [31] A. Derzhanski, A. G. Petrov, and I. Bivas, in *Advances in Liquid Crystals Research and Applications*, edited by L. Bata (Pergamon Press/Akademiai Kiado, Budapest, 1981), Vol. 1.
- [32] A. Ferrarini, Phys. Rev. E **64**, 021710 (2001).
- [33] A. G. Petrov, in *Physical Properties of Liquid Crystals*, edited by D. A. Dunmur, A. Fukuda, and G. L. Luckhurst, EMIS Datareview Series Vol. 25 (IEE, London, 2001).
- [34] D. Schmidt, M. Schadt, and W. Helfrich, Z. Naturforsch. A **27**, 277 (1972).
- [35] L. M. Blinov, M. I. Barnik, M. Ozaki, N. M. Shtykov, and K. Yoshino, Phys. Rev. E **62**, 8091 (2000).
- [36] L. M. Blinov, M. I. Barnik, H. Ohoka, M. Ozaki, N. M. Shtykov, and K. Yoshino, Eur. Phys. J. E **4**, 183 (2001).
- [37] R. A. Ewings, C. Kischka, L. A. Parry-Jones, and S. J. Elston, Phys. Rev. E **73**, 011713 (2006).
- [38] P. Rudquist and S. T. Lagerwall, Liq. Cryst. **23**, 503 (1997).
- [39] A. Kapanowski, Phys. Rev. E **55**, 7090 (1997).
- [40] L. E. Reichl, *A Modern Course in Statistical Physics* (Edward Arnold Publishers, London, 1980).
- [41] J. Stecki and A. Kloczkowski, J. Phys. (Paris) Colloq. **40**, C3-360 (1979).