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► To cite this version:

M.A. Osipov. The order parameter dependence of the flexoelectric coefficients in nematic liquid crystals. *Journal de Physique Lettres*, 1984, 45 (16), pp.823-826. 10.1051/jphyslet:019840045016082300 . jpa-00232417

HAL Id: jpa-00232417

<https://hal.science/jpa-00232417>

Submitted on 1 Jan 1984

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Classification
 Physics Abstracts
 61.30

The order parameter dependence of the flexoelectric coefficients in nematic liquid crystals

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(Reçu le 5 mars 1984, révisé le 25 mai, accepté le 19 juin 1984)

Résumé. — En utilisant la théorie générale de Landau-de Gennes pour les cristaux liquides, nous avons établi que la différence des coefficients flexoélectriques $e^* = e_1 - e_3$ se comportait comme S^2 , où S est le paramètre d'ordre nématique. Ce résultat, en accord avec celui des théories moléculaires, est néanmoins en contradiction avec des mesures récentes de e^* qui montrent un comportement linéaire en S . La contradiction peut être résolue si l'on prend en considération les degrés de liberté configurationnels dans la théorie moléculaire.

Abstract. — Within the general framework of Landau-de Gennes theory for nematic liquid crystals it is shown that the difference of flexoelectric coefficients $e^* = e_1 - e_3 \sim S^2$, where S is the nematic order parameter. This result agrees with the molecular theory but is in contradiction with recent measurements of the constant e^* which yield $e^* \sim S$. The contradiction can be resolved by the inclusion of conformational freedom into the molecular theory.

The flexoelectric effect in liquid crystals manifests itself in the appearance of induced polarization under the condition of a curvature strain. In the nematic phase there are two independent contributions to the induced polarization $\mathbf{P}$:

$$\mathbf{P} = e_1 \mathbf{n} \operatorname{div} \mathbf{n} + e_3 (\mathbf{n} \cdot \nabla) \cdot \mathbf{n}, \quad (1)$$

where $\mathbf{n}$ is the director and e_1, e_3 are the flexocoefficients. Two different microscopic interpretations of the flexoelectric effect have been suggested in the literature. The first one was proposed by Meyer [1] who assumed that macroscopic polarization is related to the orientation of asymmetric dipolar molecules in the distorted liquid crystal. The corresponding molecular theory has been developed in [2-5]. Prost and Marcerou [6] have taken into account the fact that macroscopic polarization can be caused by the gradient of the quadrupole density. According to Marcerou and Prost [7], the measurement of the temperature dependence of flexocoefficients can help to distinguish between these two interpretations. Indeed, the dipolar contribution is proportional to S^2 [1, 2] while the quadrupolar contribution is proportional to S [6], where S is the nematic order parameter. In a recent study [5], however, we have shown that a consistent molecular-statistical theory of the flexoelectric effect results in both S and S^2 dependence of flexocoefficients ⁽¹⁾. At

⁽¹⁾ This result was first obtained by J. P. Straley [4] for the gas of long rods.

the same time, all molecular theories of the flexoelectric effect [2-6] (both dipolar and quadrupolar) yield the S^2 dependence of the difference of flexocoefficients $e^* = e_1 - e_3$.

Recently Dozov, Martinot-Lagarde and Durand [8] have described the first direct measurement of the flexoelectric constant e^* and have concluded that e^* possesses the unexpected S -like temperature dependence in the nematic compound octyloxy cyanobiphenyl (8OCB). This result is in contradiction with the existing molecular theories [2-5]. However, the molecular theory is based on various simplifications and assumptions and thus it can yield the incorrect order parameter dependence of flexocoefficients if, for example, the inadequate molecular model is used in the calculations. According to [8], the S -like temperature dependence of the constant e^* is attributed to the conformational freedom of the long alkoxy chain of the 8OCB molecule. The molecular flexibility was not taken into account in the molecular theory [2-5].

In the present paper it will be shown that the relation $e^* \sim S^2$ is the general result of the phenomenological Landau-de Gennes theory for nematic liquid crystals and hence this result is not related to the shortcomings of molecular theory. Therefore we arrive at the more serious contradiction between the theory and the direct experiment. This contradiction indicates that the order parameter expansion of the free energy cannot be always used in the description of the nematic phase. In conclusion we discuss the relation between the molecular flexibility and the order parameter dependence of the flexoelectric constant.

In Meyer's continuum theory [1] the contribution to the free energy of the nematic phase, which describes the flexoelectric effect, can be written in the form

$$\delta F_{FE} = -e_1^0(\mathbf{P} \cdot \mathbf{n})(\nabla \cdot \mathbf{n}) - e_3^0 \mathbf{P} \cdot ((\nabla \times \mathbf{n}) \times \mathbf{n}) - \mathbf{P} \cdot \mathbf{E} - \frac{1}{2} \mathbf{P} \cdot \hat{\chi} \cdot \mathbf{P}, \quad (2)$$

where $\mathbf{E}$ is the external electric field, $\hat{\chi}$ is the dielectric susceptibility tensor, $\chi_{\alpha\beta} = \chi_{\perp} \delta_{\alpha\beta} + \Delta\chi n_{\alpha} n_{\beta}$. Minimizing the free energy (2) with respect to the polarization $\mathbf{P}$, one obtains expression (1) for $\mathbf{P}$ with $e_1 = e_1^0 \chi_{\parallel}$, and $e_3 = e_3^0 \chi_{\perp}$. Note that the constants e_1 and e_3 are temperature dependent.

On the other hand, the free energy of the nematic liquid crystal can be expanded in terms of the nematic order parameter $Q_{\alpha\beta}(\mathbf{r}) = S(\mathbf{n}_{\alpha}(\mathbf{r}) \mathbf{n}_{\beta}(\mathbf{r}) - (1/3) \delta_{\alpha\beta})$, $\alpha, \beta = x, y, z$. In this case the free energy δF_{FE} contains all first-order gradient terms which are linear in $\mathbf{P}$. Taking into account only the terms which are first and second-order in S , one obtains

$$\delta F_{FE} = -e P_{\alpha} \nabla_{\beta} Q_{\alpha\beta} - g_1 P_{\alpha} Q_{\alpha\beta} \nabla_{\gamma} Q_{\gamma\beta} - g_2 P_{\alpha} Q_{\beta\gamma} \nabla_{\gamma} Q_{\alpha\beta} - P_{\alpha} E_{\alpha} + \frac{1}{2} \chi_{\alpha\beta} P_{\alpha} P_{\beta} + \mathcal{O}(S^3). \quad (3)$$

Minimization of the free energy (3) with respect to $\mathbf{P}$ yields

$$\begin{aligned} \mathbf{P} = & Se\chi_{\parallel} \mathbf{n} \cdot (\nabla \cdot \mathbf{n}) + Se\chi_{\perp} (\mathbf{n} \cdot \nabla) \cdot \mathbf{n} + \frac{1}{3} S^2 (2g_1 - g_2) \chi_{\parallel} \mathbf{n} \cdot (\nabla \cdot \mathbf{n}) + \\ & + \frac{1}{3} S^2 (2g_2 - g_1) \chi_{\perp} (\mathbf{n} \cdot \nabla) \cdot \mathbf{n} + \mathcal{O}(S^3). \end{aligned} \quad (4)$$

Comparing expressions (1) and (4), one gets the following expressions for the flexocoefficients

$$e_1 = Se\chi_{\parallel} + \frac{1}{3} S^2 (2g_1 - g_2) \chi_{\parallel} + \mathcal{O}(S^3), \quad (5a)$$

$$e_3 = Se\chi_{\perp} + \frac{1}{3} S^2 (2g_2 - g_1) \chi_{\perp} + \mathcal{O}(S^3), \quad (5b)$$

and

$$e^* = e_1 - e_3 = S e (\chi_{\parallel} - \chi_{\perp}) + \frac{1}{3} S^2 [g_1 (2 \chi_{\parallel} + \chi_{\perp}) - g_2 (2 \chi_{\perp} + \chi_{\parallel})]. \quad (6)$$

It is well known that the anisotropy of the dielectric permittivity in the nematic phase is proportional to S (see, for example, [9]), i.e. $\Delta\chi = \chi_{\parallel} - \chi_{\perp} \sim S$. Therefore we arrive at the conclusion that $e^* \sim S^2$.

Thus the relation $e^* \sim S^2$ is the general result of the Landau-de Gennes theory for nematic liquid crystals and hence it is not related to the approximate character of the molecular theory. However, this result is in contradiction with the direct measurement of the constant e^* in the nematic compound 8OCB [8] which yields $e^* \sim S$. This contradiction can be resolved only if one assumes that, in certain cases, the temperature dependence of nematic parameters cannot be described by the order parameter expansion. This means that the expansion series cannot be truncated after the first terms. Dozov *et al.* [8] have assumed that the unusual S -like temperature dependence of the constant e^* is related to the flexibility of the long alkoxy chain of the 8OCB molecule. This suggestion seems to be attractive and it is interesting to find out how the inclusion of molecular flexibility can influence the results of the modern molecular theory of flexoelectricity [4, 5].

According to [5], the induced polarization in the distorted nematic liquid crystal can be written in the form

$$\mathbf{P} = \rho^2 (k_B T)^{-1} \int \mathbf{d}_i f_0(i) (\mathbf{J}_{ij} \cdot \nabla) f_0(j) d(i) d(j) \quad (7)$$

$$\mathbf{J}_{ij} = \int \mathbf{r}_{ij} U_{\text{eff}}(i, j) d^3 \mathbf{r}_{ij}, \quad (8)$$

where ρ is the number density, $\mathbf{d}_i$ is the molecular dipole, $f_0(i)$ is the one-particle distribution function, $U_{\text{eff}}(i, j)$ is the effective interaction potential for molecules i and j , and $\mathbf{r}_{ij}$ is the intermolecular vector. The potential U_{eff} represents the attraction interaction energy modulated by the asymmetric molecular shape. Consider now the model for a molecule with long flexible chain, represented in figure 1. For simplicity we have represented such a molecule by a hard core with a long axis $\mathbf{a}_i$ and a « tail » with a long axis $\mathbf{o}_i$. The angle ε between $\mathbf{a}_i$ and $\mathbf{o}_i$ is variable. On the other hand, $\varepsilon = \text{const.}$ for rigid molecules which are considered in the molecular theory of flexoelectricity [4, 5].

Fig. 1. — A model for a molecule with flexible alkoxy chain.

As shown in [5], the induced polarization $\mathbf{P}$ is determined by the asymmetric part of the potential U_{eff} and hence $|\mathbf{J}_{ij}| \sim \sin \varepsilon$. In the case of flexible molecules the expression (7) involves also the averaging over different angles ε . We shall assume for simplicity that $0 < \varepsilon < \varepsilon_0$. The distri-

bution function $f_0(i)$ can be written in the form [5]

$$f_0(i) = C \exp \left\{ -\beta \int [U_0(i, j) + U_1(i, j) \sin \varepsilon] f_0(j) d^3 \mathbf{r}_{ij} d(j) \right\}. \quad (9)$$

In the first approximation $\int U_1(i, j) f_0(j) d^3 \mathbf{r}_{ij} = V_1 S P_2(\mathbf{a}_i \cdot \mathbf{n})$, where $P_2(x)$ is the second Legendre polynomial. This expression corresponds to the model [10, 11] in which the alkoxy chain is subjected to the effective mean-field anisotropic potential, i.e. the chain is constrained by the ordered rigid cores of neighbouring molecules.

Then the average value $\langle \sin \varepsilon \rangle$ is given by

$$\langle \sin \varepsilon \rangle = \int_0^{\varepsilon_0} \sin \varepsilon f_1(\sin \varepsilon) d\varepsilon = C_1 \int_0^{\varepsilon_0} \sin \varepsilon \exp \{ -S a_{ij} \sin \varepsilon \} d\varepsilon \quad (10)$$

where $C_1^{-1} = \int_0^{\varepsilon_0} \exp \{ -S a_{ij} \sin \varepsilon \} d\varepsilon$, and $a_{ij} = V_1 \beta [P_2(\mathbf{a}_i \cdot \mathbf{n}) + P_2(\mathbf{a}_j \cdot \mathbf{n})]$. Taking that $\sin \varepsilon \approx \varepsilon$, when $\varepsilon < \varepsilon_0$, one readily obtains

$$\langle \sin \varepsilon \rangle = \varepsilon_0 [(\alpha S)^{-1} + (e^{\alpha S} - 1)^{-1}], \quad (11)$$

where $\alpha = a_{ij} \varepsilon_0$. Note that $\sin \varepsilon \approx \varepsilon_0/2$ when $\alpha S \ll 1$, i.e. S is small. On the other hand, the second term on the right hand side of equation (11) can be neglected when $\alpha S \gtrsim 2$. Therefore the relation $\sin \varepsilon = (\varepsilon_0/\alpha) S^{-1}$ can be approximately valid in the nematic phase (where $S > 0.3$) if $V_1 \gtrsim 3 k_B T$ (i.e. $\alpha \gtrsim 3$). At the same time $\sin \varepsilon = \text{const.}$ for a rigid banana-like molecule. Thus the averaging over the conformational degrees of freedom results in the additional S^{-1} -like temperature dependence of flexocoefficients. This result enables one to explain the relation $e^* \sim S$ which has been observed in the experiment. In conclusion it should be stressed that the present arguments are rather qualitative since the exact order parameter dependence of flexocoefficients can be determined only after a very complicated averaging over $\mathbf{a}_i$, $\mathbf{a}_j$ and $\mathbf{u}_{ij}$ in expressions (7) and (8). On the other hand, small deviations from the S -like temperature dependence of the constant e^* can hardly be determined experimentally since the variation of the order parameter S in the nematic phase of 8OCB is not large.

Acknowledgments.

The author is grateful to S. A. Pikin and E. M. Terentjev for valuable discussions.

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