PHYSICAL REVIEW E VOLUME 54, NUMBER 4 OCTOBER 1996

Quadrupolar interaction in nematic liquid crystals

G. Barbero, L. R. Evangelista,* and S. Ponti
Dipartimento di Fisica del Politecnico di Torino and Istituto Nazionale di Fisica della Materia, Corso Duca degli Abruzzi 24,
10129 Torino, Italy

(Received 24 January 1996)

In this paper we show that the screened quadrupolar interaction among liquid crystal molecules cannot give rise to the nematic phase. This result follows from the fact that the associated splay and bend elastic constants appearing in the elastic energy density are negative. The elastic energy density is evaluated by supposing that the interaction volume has spherical shape, whose inner excluded part coincides with the molecular volume. A generalization of our model to interaction volume of ellipsoidal shape is also discussed. In both cases the total elastic energy for splay-bend deformations is negative, indicating that the molecules have no tendency to align along a common direction, as required by a nematic phase. [S1063-651X(96)05209-9]

PACS number(s): 61.30.Gd, 61.30.Cz

Nematic liquid crystals (NLCs) are ferroelectric quadrupolar materials [1]. This means that they possess an electrical quadrupolar moment, even in the absence of an external electric field. The electrostatic description of these media has been recently discussed [2]. In this paper we evaluate the elastic constants for a NLC [3] by assuming that the quadrupolar interaction is the only one existing among the molecules. We shall show that this kind of intermolecular interaction does not favor the NLC phase. This conclusion holds in the hypothesis that the interaction volume has a spherical or ellipsoidal shape, whose inner excluded volume coincides with that of the molecule [4–6].

Let us consider a NLC material whose molecules possess an electrical quadrupole moment of elements D_{ij}. As is well known [1], the electric quadrupolar moment is proportional to the tensorial order parameter, of elements [7] $Q_{ij}=(3/2)S[n_i n_j-(1/3)\delta_{ij}]$, where S is the scalar order parameter and $\vec{n}$ is the NLC director. $\vec{n}$ is the statistical average of the major axis of molecules $\vec{a}$, whereas S is defined by $S=(3/2)\langle(\vec{n}.\vec{a})^2-(1/3)\rangle$, where $\langle\cdots\rangle$ means statistical average. The scalar order parameter S is connected with the fluctuations of $\vec{a}$ around $\vec{n}$. In the following we suppose a perfect nematic order, hence $\vec{n}=\vec{a}$. Consequently we shall assume that the particle-particle distribution function is not altered by the quadrupolar interaction under consideration.

Let us focus our attention on the case in which a molecule of quadrupolar moment $\mathbf{D}$ is located in $\vec{R}$ and another one with quadrupolar moment $\mathbf{D}'$ is in $\vec{R'}=\vec{R}+\vec{r}$, where $\vec{r}$ is the relative position of $\mathbf{D}'$ with respect to $\mathbf{D}$. The electric quadrupolar moment $\mathbf{D}$ creates in $\vec{R'}$ the electric potential [8]

$$V(\vec{r})=D_{ij}\frac{x_i x_j}{2r^5}e^{-r/\lambda}, \tag{1}$$

where x_i are the Cartesian components of $\vec{r}$, and λ a screening length introduced to take into account the short-range intermolecular forces responsible for the elastic properties of the NLC. Note that for $\lambda\to\infty$ the quadrupolar potential is long-ranged. As is well known [9], an elastic theory may be formulated only for intermolecular forces of short interaction range. In this context, short means very small with respect to the scale over which the spatial variation of the macroscopic order takes place. Hence, the case of $\lambda\to\infty$ is expected to give unusual results, as stressed a few years ago [4]. For this reason we shall consider in the following λ to be of the order of a few molecular sizes, in order to evaluate the elastic constants of a material whose intermolecular energy has a quadrupolar symmetry. In Eq. (1) and henceforth, Einstein's summation convention is assumed. The electrostatic energy of $\mathbf{D}'$ in the external field due to $\mathbf{D}$ is [8]

$$g(\mathbf{D},\mathbf{D}';\vec{r})=D'_{\alpha\beta}\frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}. \tag{2}$$

If $\mathbf{D}'=\mathbf{D}+\Delta\mathbf{D}$, where ΔD_{ij} are small quantities with respect to D_{ij}, Eq. (2) can be expanded to second order in ΔD_{ij} as follows [10]:

$$g(\mathbf{D},\mathbf{D}';\vec{r})=g_0+L_{ij}\Delta D_{ij}+\frac{1}{2}K_{ijkl}\Delta D_{ij}\Delta D_{kl}, \tag{3}$$

where the interaction energy for the undeformed state is given by $g_0=g(D_{ij},D_{ij};\vec{r})$, and the tensors $\mathbf{L}$ and $\mathbf{K}$ are defined by

$$L_{ij}=\left(\frac{\partial g}{\partial D'_{ij}}\right)_{\mathbf{D}=\mathbf{D}'}=\frac{\partial^2 V}{\partial x_i \partial x_j}$$

and

$$K_{ijkl}=\left(\frac{\partial^2 g}{\partial D'_{ij}\partial D'_{kl}}\right)_{\mathbf{D}'=\mathbf{D}}=0\,. \tag{4}$$

Consequently, to the second order in ΔD_{ij}, the interaction energy is found to be

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*Permanent address: Departamento de Fisica, Universidade Estadual de Maringá, Avenida Colombo 3690, 87020-900 Maringá, Paraná, Brazil.

$$g=g_0+\frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}\Delta D_{\alpha\beta}. \tag{5}$$

By supposing that **D** changes slowly over the range of the quadrupolar interaction λ, it is possible to expand $\Delta\mathbf{D}$ in power series of x_i in the usual way,

$$\Delta D_{\alpha\beta}=\left(\frac{\partial D_{\alpha\beta}}{\partial x_\mu}\right)_{\vec{R}} x_\mu+\frac{1}{2}\left(\frac{\partial^2 D_{\alpha\beta}}{\partial x_\mu \partial x_\nu}\right)_{\vec{R}} x_\mu x_\nu. \tag{6}$$

It follows that the interaction energy between **D** and **D**′, in the limit of small distortion, is

$$g=g_0+\left[\left(\frac{\partial D_{\alpha\beta}}{\partial x_\mu}\right)_{\vec{R}} x_\mu+\frac{1}{2}\left(\frac{\partial^2 D_{\alpha\beta}}{\partial x_\mu \partial x_\nu}\right)_{\vec{R}} x_\mu x_\nu\right]\frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}. \tag{7}$$

The elastic energy density, in the mean field approximation, is obtained by integrating $(1/2)(g-g_0)$ over the interaction volume τ_N of the intermolecular forces [10]. Hence

$$F=\frac{1}{2}\int_{\tau_N}(g-g_0)d\tau=M_{\alpha\beta\mu}\frac{\partial D_{\alpha\beta}}{\partial x_\mu}+\frac{1}{2}N_{\alpha\beta\mu\nu}\frac{\partial^2 D_{\alpha\beta}}{\partial x_\mu \partial x_\nu}, \tag{8}$$

where

$$M_{\alpha\beta\mu}=\frac{1}{2}\int_{\tau_N} x_\mu \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}d\tau$$

and

$$N_{\alpha\beta\mu\nu}=\frac{1}{2}\int_{\tau_N} x_\mu x_\nu \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}d\tau. \tag{9}$$

The tensors **M** and **N**, whose symmetries are apparent, play the role of elastic tensors. Simple calculations give

$$M_{\alpha\beta\mu}=\frac{1}{2}\int_\Sigma\left(x_\mu\frac{\partial V}{\partial x_\alpha}N_\beta-\delta_{\beta\mu}VN_\alpha\right)d\Sigma \tag{10}$$

and

$$N_{\alpha\beta\mu\nu}=\frac{1}{2}\int_\Sigma\left[x_\mu x_\nu\frac{\partial V}{\partial x_\alpha}N_\beta-V(\delta_{\beta\mu}x_\nu+\delta_{\nu\beta}x_\mu)N_\alpha\right]d\Sigma+\frac{1}{2}(\delta_{\beta\mu}\delta_{\alpha\nu}+\delta_{\nu\beta}\delta_{\mu\alpha})\int_{\tau_N}Vd\tau, \tag{11}$$

where $\Sigma=\Sigma_i+\Sigma_o$, and Σ_i and Σ_o are the inner and outer surfaces limiting the interaction volume τ_N. In Eqs. (10) and (11) $\vec{N}$ is the geometrical normal to Σ, directed outwards. The surfaces Σ_i and Σ_o are similar and hence for corresponding points $\vec{N}^i=-\vec{N}^o$.

A simple analysis shows that for quadrupolar symmetry $\mathbf{M}\equiv\mathbf{0}$. In fact, in the bulk $M_{\alpha\beta\mu}$ has to be decomposed in terms of $D_{\alpha\beta}$ and of $\delta_{\alpha\beta}$, according to general rules [11]. But this decomposition is impossible for a tensor of third order.

Let us analyze now the elastic tensor of elements $N_{\alpha\beta\mu\nu}$ given by Eq. (11). By substituting Eq. (1) into Eq. (11), after simple calculations we obtain

$$N_{\alpha\beta\mu\nu}=\frac{1}{4}\left\{D_{ij}[\Delta(\delta_{i\alpha}I_{\mu\nu\beta j}+\delta_{j\alpha}I_{\mu\nu\beta i}-\delta_{\beta\mu}I_{\alpha ij\nu}-\delta_{\nu\beta}I_{\alpha ij\mu})-(5\Delta+\Delta^*)J_{\mu\nu\beta ij\alpha}]+2(\delta_{\beta\mu}\delta_{\nu\alpha}+\delta_{\nu\beta}\delta_{\mu\alpha})\int_{\tau_N}Vd\tau\right\}, \tag{12}$$

where

$$\Delta=e^{-R_o/\lambda}-e^{-R_i/\lambda}$$

and

$$\Delta^*=(R_o/\lambda)e^{-R_o/\lambda}-(R_i/\lambda)e^{-R_i/\lambda} \tag{13}$$

depend on the screening length λ, and the tensors **I** and **J** are defined by

$$I_{ijlm}=\int_{4\pi}u_i u_j u_l u_m d\Omega$$

and

$$J_{ijlmno}=\int_{4\pi}u_i u_j u_l u_m u_n u_o d\Omega, \tag{14}$$

where $\vec{u}=\vec{r}/r$ and $d\Omega=\sin\theta d\theta d\phi$ is the element of a solid angle in a Cartesian reference frame in which $\vec{n}$ is coincident with the polar angle. Evidently, the tensors **I** and **J** are by definition symmetric with respect to all the indices. Note that for $\lambda\rightarrow\infty$, corresponding to the nonscreened potential, Δ and Δ^* tend to zero. This limit, however, is not interesting in the present context. For finite λ values it is possible to perform the limit $R_o\rightarrow\infty$. In this case, Δ and Δ^* are two negative quantities given by

$$\Delta=-e^{-R_i/\lambda}\quad\text{and}\quad\Delta^*=-(R_i/\lambda)e^{-R_i/\lambda}. \tag{15}$$

A simple analysis shows that the contribution to the elastic tensor **N** of the integral over τ_N of Eq. (12) is identically zero when V has quadrupolar symmetry. In fact, taking into account the expression (1) for V, one gets

$$\int_{\tau_N}Vd\tau=\frac{2\pi}{3}E(R_i,R_o)D_{mn}\delta_{mn}=0, \tag{16}$$

where $E(R_i,R_o)$ is the exponential integral defined by

$$E(R_i,R_o)=\int_{R_i}^{R_o}e^{-r/\lambda}\frac{dr}{r}. \tag{17}$$

In the limit $\lambda\rightarrow\infty$, $E(R_i,R_o)\rightarrow\ln(R_o/R_i)$, but this logarithmic divergence can be neglected in our analysis, because when $\lambda\rightarrow\infty$ long-ranged forces arise, as previously stated. In this situation it is impossible to write down an elastic energy density of the type of Eq. (8), having a local character. However, it should be stressed that the bulk term given by Eq. (16) does not contribute to the tensor **N** for reasons of symmetry.

The tensors **I** and **J** can be decomposed in terms of the unit tensor of elements δ_{ij}. Simple calculations give

$$I_{ijlm}=\frac{4}{15}\pi(\delta_{ij}\delta_{lm}+\delta_{il}\delta_{jm}+\delta_{im}\delta_{jl}) \tag{18}$$

and

$$\begin{aligned}J_{ijlmno}=\frac{4}{105}\pi[&\delta_{ij}(\delta_{lm}\delta_{no}+\delta_{\mathrm{ln}}\delta_{mo}+\delta_{lo}\delta_{mn})+\delta_{il}(\delta_{jm}\delta_{no}\\&+\delta_{jn}\delta_{mo}+\delta_{jo}\delta_{mn})+\delta_{im}(\delta_{jl}\delta_{no}+\delta_{jo}\delta_{\mathrm{ln}}+\delta_{jn}\delta_{lo})\\&+\delta_{in}(\delta_{jl}\delta_{mo}+\delta_{jm}\delta_{lo}+\delta_{jo}\delta_{lm})+\delta_{io}(\delta_{jl}\delta_{mn}\\&+\delta_{jm}\delta_{\mathrm{ln}}+\delta_{jn}\delta_{lm})].\end{aligned} \tag{19}$$

By substituting Eqs. (16), (18), and Eq. (19) into Eq. (12) we obtain the elastic tensor **N** expressed in terms of the elements of symmetry of the NLC, D_{ij}, and of the unit tensor, of elements δ_{ij}. Inserting this expression for **N** into Eq. (8), and taking into account the quadrupolar symmetry $\mathbf{M}\equiv 0$, one obtains, after some calculations,

$$\begin{aligned}F=-\frac{\pi}{105}\Bigg\{&(2\Delta-\Delta^*)\frac{\partial D_{\alpha\beta}}{\partial x_\mu}\frac{\partial D_{\alpha\beta}}{\partial x_\mu}-4(5\Delta+\Delta^*)\\&\times\left[\frac{\partial D_{\alpha\beta}}{\partial x_\alpha}\frac{\partial D_{\beta\mu}}{\partial x_\mu}-\frac{\partial}{\partial x_\mu}\left(D_{\beta\mu}\frac{\partial D_{\alpha\beta}}{\partial x_\alpha}\right)\right]\Bigg\},\end{aligned} \tag{20}$$

where the first term on the right-hand side of Eq. (20) is related to the tensor **I**, whereas the second and the third contributions are related to the tensor **J** [see Eq. (12)]. In order to obtain Eq. (20) we have taken into account the following equations, deriving from the condition $D_{\alpha\beta}D_{\alpha\beta}=\text{const}$:

$$D_{\alpha\beta}\frac{\partial D_{\alpha\beta}}{\partial x_\mu}=0 \quad \text{and} \quad D_{\alpha\beta}\frac{\partial^2 D_{\alpha\beta}}{\partial x_\mu \partial x_\nu}=-\frac{\partial D_{\alpha\beta}}{\partial x_\nu}\frac{\partial D_{\alpha\beta}}{\partial x_\mu}. \tag{21}$$

In order to write Eq. (20) in a form containing the NLC director only [12,13], one has to remember that **D** has the symmetry of **Q**, the NLC tensor order parameter. Hence, $D_{ij}=D[n_in_j-(1/3)\delta_{ij}]$, where D is a scalar quantity, positive for cigarlike molecules and negative for disklike molecules, and $\vec{n}$ is the NLC director ($n_in_i=1$). By substituting this expression for D_{ij} into Eq. (20), one gets

$$\begin{aligned}F=&\frac{1}{2}[k_{11}(\mathrm{div}\vec{n})^2+k_{22}(\vec{n}\cdot\mathrm{rot}\vec{n})^2+k_{33}(\vec{n}\times\mathrm{rot}\vec{n})^2]\\&+k_{13}\mathrm{div}(\vec{n}\mathrm{div}\vec{n})+(k_{22}+k_{24})\mathrm{div}(\vec{n}\mathrm{div}\vec{n}+\vec{n}\times\mathrm{rot}\vec{n}).\end{aligned} \tag{22}$$

The elastic constants in Eq. (22) are given by

$$k_{11}=k_{33}=\frac{4}{105}\pi D^2(8\Delta+3\Delta^*),$$

$$k_{22}=-\frac{4}{105}\pi D^2(2\Delta-\Delta^*),$$

$$k_{13}=\frac{4}{105}\pi D^2\frac{5\Delta+\Delta^*}{3},$$

$$(k_{22}+k_{24})=-\frac{2}{105}\pi D^2\frac{4\Delta+13\Delta^*}{3}. \tag{23}$$

Equations (23) show that in the limit $\lambda\rightarrow\infty$, corresponding to the nonscreened quadrupolar potential, all the elastic constants vanish [10], but this case is out of our analysis. When λ is a finite quantity, the limit $R_o\rightarrow\infty$ may be performed. In this situation $k_{11}(=k_{33})$ is a negative quantity. This means that the ground state of the phase is not the undistorted state, but the distorted one. In other words, the molecules interacting via a screened quadrupolar potential do not tend to be parallel to a common direction. These results have beeen obtained by assuming an interaction volume limited by two spherical surfaces of radii R_o ($\gg R_i$) and R_i for the outer and the inner surface, respectively. This is equivalent to assuming the excluded volume of spherical shape, and the electrical quadrupole responsible for the interaction localized in the center. This approximation is widely used in the molecular models proposed to evaluate the NLC elastic constants [4,11–13]. For $\lambda\rightarrow\infty$, it is possible to show that all the elastic constants are zero also under the hypothesis that the interaction volume is limited by two similar surfaces of ellipsoidal shape, a quite reasonable assumption. However, this case is not physically relevant because in an elastic theory only intermolecular forces of negligible interaction range can be considered. For finite λ and an ellipsoidal shape of the interaction volume the calculations are more complex. In this case, the tensors **I** and **J** appearing in Eq. (12) have to be decomposed in terms of the unit tensor and of **D**. It follows that these tensors are no longer simply given by Eqs. (18) and (19), because now also terms of the type $D_{ij}D_{lm}$ and of the type $D_{ij}\delta_{lm}$ have to be considered. However, the main results do not change, as shown by a numerical analysis [14].

In this paper we have considered molecules interacting via a quadrupolar force, either in the presence or in the absence of screening effects. Expressions for the elastic energy density and for the elastic constants connected to this intermolecular interaction have been obtained in the continuum approximation. In the case of nonscreened quadrupolar potential, all the elastic constants have been shown to be identically zero, whereas for finite λ the splay and bend elastic constants are found to be negative. In both cases the molecules do not tend to be oriented along a common direction, as required by the nematic phase. As a consequence, even if the NLC can be considered as quadrupolar ferroelectric materials, the quadrupole-quadrupole interaction does not favor the nematic phase. These results have been obtained by supposing the interaction volume to be limited by two spherical surfaces of inner radius R_i and outer radius R_o ($\geqslant R_i$). However, the present conclusions hold also in the case of an interaction volume having ellipsoidal shape.

Many thanks are due to S. Faetti (Pisa), G. Durand (Orsay), P. Galatola, and P. Allia (Torino) for useful discussions. One of us (L.R.E) acknowledges the financial support of INFM (Italy) and CNPq (Brazil).

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