Periodic structures in a biaxial nematic phase

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In this work experimental and theoretical results will be used to show that under convenient conditions; appropriated geometry, well chosen boundary conditions, and suitable external fields, the elastic and dynamic behavior of a sample of a biaxial nematic liquid crystal can become similar to the one observed on usual uniaxial nematic liquid crystals. It is shown that this result can be used to determine the values of some combinations of the rheologic parameters of the biaxial phase.

In this work it is shown that when a sample of a biaxial nematic liquid crystal (BNLC) [1] is submitted to appropriate conditions, to be described below, it can present the dynamic and static behaviors characteristic of uniaxial nematic liquid crystals (UNLC) [2]. That is, it will be shown that it is possible to prepare a biaxial material in such a way that its rheological parameters, elastic constants, and viscosity coefficients, become mixed in such a way that the macroscopic behavior determined by these quantities can be mapped in the corresponding ones of an UNLC. To present an experimental evidence of this property, we have submitted a prepared biaxial material to a magnetic field perpendicular to the direction of one of the directors, which was previously homogeneously aligned. Under these conditions we have observed the arising of magnetic walls with characteristics similar to the ones observed in a common uniaxial material [3]. We believe that this property would be important to measure combinations of rheological parameters of a BNLC sample. Up to our knowledge this is the first observation of these structures in a biaxial material. Ahead, theoretical and experimental justifications of these results will be presented.

The biaxial nematic phase is characterized by three orthogonal axes of symmetry, $\vec{l}$, $\vec{m}$, and $\vec{n}$, fixed in the micelle [4,5]. Nevertheless, these three axes are not independent, it is enough to fix two of them and the third one will be automatically determined. That is, they are connected by the orthonormal relation,

$$l_i l_j + m_i m_j + n_i n_j = \delta_{ij}. \tag{1}$$

With the use of this relation the biaxial order parameter [6] $Q_{ij}^b = -\frac{1}{3}(S-T)l_i l_j - \frac{1}{3}(S+T)m_i m_j + \frac{2}{3}S n_i n_j$, that depends on $\vec{l}$, $\vec{m}$, and $\vec{n}$, may be reduced to $Q_{ij}^b = 1/3(S-T)(3n_i n_j - \delta_{ij}) - 2/3T(m_i m_j - n_i n_j)$, where the dependence on $\vec{l}$ was eliminated. Now, suppose that through the use of some physical process one can be sure that the direction of one of these three axes, $\vec{l}$ by example, is homogeneously fixed in the entire sample in such a way that the rotations of all molecules becomes limited to the plane given by the axes $\vec{m}$ and $\vec{n}$. As a result of this additional restriction no more two directors, $\vec{m}$ and $\vec{n}$, are necessary to describe the planar rotation of the molecules; only one is enough. Consequently, Eq. (1) can be rewritten as

$$m_i m_j + n_i n_j = \frac{2}{3}\delta_{ij}, \tag{2}$$

and the director $\vec{n}$, for example, becomes sufficient to describe the order parameter of such configuration. Using this relation an immediate computation shows that

$$Q_{ij}^b = \frac{1}{9}(3S+T)(3n_i n_j - \delta_{ij}). \tag{3}$$

So, when $\vec{l}$ is homogeneously fixed in the entire sample the order parameter of a planar BNLC becomes reduced to the form of an order parameter of a uniaxial material. Now on, a biaxial configuration in which one of the directors is maintained fixed will be named as biaxial planar configuration (BPC). An important aspect of this equivalence is that under these conditions all physical properties of a biaxial material, which are uniquely determined by the order parameter given by Eq. (3), would present a behavior similar to an uniaxial material. Consequently, in a BPC, the elastic and dynamic behavior of a biaxial material would be analogous to the ones given by the usual uniaxial theories [7,8]. For instance, the free energy of any nematic liquid crystal would be given by the sum of the spatial derivatives of the order parameter [9],

$$F_e = L_{\alpha\beta\gamma}(\vec{r})\partial_\alpha Q_{\beta\gamma} + L_{\alpha\beta\gamma\mu\nu\rho}(\vec{r})[\partial_\alpha Q_{\beta\gamma}\partial_\mu Q_{\nu\rho}]$$
$$+ L_{\alpha\beta\gamma\mu}(\vec{r})\partial_\alpha\partial_\beta Q_{\gamma\mu}, \tag{4}$$

hence, as in a BPC the order parameter assumes a uniaxial form, the elastic properties resulting from the minimization of this free energy must be indistinguishable from the ones resulting from an uniaxial problem. That is, the simple observation of the elastic properties of a sample in a BPC would not give any indication of its biaxial nature.

Let us give an explicit example of how the expressions for elastic free energy of UNLC and BNLC can becomes elastically similar. The bulk elastic properties of a UNLC are described by the uniaxial Frank elastic free energy density [2]

$$F_u = \frac{1}{2}\{K_{u1}(\vec{\nabla}\cdot\vec{n})^2 + K_{u2}(\vec{n}\cdot\vec{\nabla}\times\vec{n})^2 + K_{u3}(\vec{n}\times\vec{\nabla}\times\vec{n})^2\},$$
(5)

where K_{u1}, K_{u2}, and K_{u3} are the uniaxial elastic constants of splay, twist, and bend. The subscript u was introduced to remember that these coefficients describes uniaxial elastic constants. Otherwise, the corresponding biaxial elastic free energy is given by [9]

$$F_b = \frac{1}{2}\{K_{b1}(\vec{\nabla}\cdot\vec{n})^2 + K_{b2}(\vec{\nabla}\cdot\vec{m})^2 + K_{b3}(\vec{n}\cdot\vec{\nabla}\times\vec{n})^2$$

$$+ K_{b4}(\vec{m}\cdot\vec{\nabla}\times\vec{m})^2 + K_{b5}(\vec{n}\times\vec{\nabla}\times\vec{n})^2 + K_{b6}(\vec{m}\times\vec{\nabla}\times\vec{m})^2$$

$$+ K_{b7}[\vec{n}\cdot(\vec{m}\times\vec{\nabla}\times\vec{m})]^2 + K_{b8}[\vec{m}\cdot(\vec{n}\times\vec{\nabla}\times\vec{n})]^2$$

$$+ K_{b9}[\vec{m}\cdot\{\vec{\nabla}\times(\vec{n}\times\vec{m})\}]^2 + K_{b10}[\vec{n}\cdot\{\vec{\nabla}\times(\vec{m}\times\vec{n})\}]^2$$

$$+ K_{b11}[\vec{\nabla}\times(\vec{m}\times\vec{n})]^2 + K_{b12}[\vec{\nabla}\cdot(\vec{m}\times\vec{n})]^2\},$$
(6)

where $K_{bi}\{i=1,\ldots,12\}$ are twelve biaxial elastic constants. To show that in a BPC these two expressions become equivalent, we consider a uniaxial nematic phase in planar configuration described by the director components,

$$\vec{n} = (\cos\theta, \sin\theta, 0).$$
(7)

Substitute these components in the uniaxial elastic energy, given, by Eq. (5), and take into account the magnetic field coupling term, getting

$$F_u = \frac{1}{2}K_{u2}(\partial_z\theta)^2 + \frac{1}{2}(\partial_x\theta)^2\{K_{u1}\sin^2\theta + K_{u3}\cos^2\theta\}$$

$$+ \frac{1}{2}(\partial_y\theta)^2\{K_{u1}\cos^2\theta + K_{u3}\sin^2\theta\} + (K_{u3} - K_{u1})$$

$$\times \partial_x\theta\,\partial_y\theta\cos\theta\sin\theta - \frac{1}{2}\chi_a H^2\sin^2\theta.$$
(8)

Now, consider that in the BNLC the director $\vec{l}$ is fixed in the entire sample pointing to the $\vec{e}_z$ direction. Under such condition $\vec{n}$ and $\vec{m}$ would be given by

$$\vec{n} = (\cos\theta, \sin\theta, 0),$$

$$\vec{m} = (-\sin\theta, \cos\theta, 0).$$
(9)

Substituting this in Eq. (6) and including the magnetic field coupling term, one arrives at

$$F_b = \frac{1}{2}(K_{b3} + K_{b4})(\partial_z\theta)^2 + \frac{1}{2}(\partial_x\theta)^2\{(K_{b1} + K_{b6}$$

$$+ K_{b7})\sin^2\theta + (K_{b2} + K_{b5} + K_{b8})\cos^2\theta\}$$

$$+ \frac{1}{2}(\partial_y\theta)^2\{(K_{b1} + K_{b6} + K_{b7})\cos^2\theta + (K_{b2} + K_{b5}$$

$$+ K_{b8})\sin^2\theta\} + [K_{b2} + K_{b5} + K_{b8} - (K_{b1} + K_{b6}$$

$$+ K_{b7})]\partial_x\theta\,\partial_y\theta\cos\theta\sin\theta - \frac{1}{2}\chi_a^b H^2\sin^2\theta.$$
(10)

With the changes in the elastic constants

$$K_{b2} + K_{b5} + K_{b8} \leftrightarrow K_{u1},$$

$$K_{b3} + K_{b4} \leftrightarrow K_{u2},$$

$$K_{b1} + K_{b6} + K_{b7} \leftrightarrow K_{u3},$$
(11)

one observes that Eq. (8) and Eq. (10) become identical. So, this transformation realizes the equivalence announced in Eq. (5) and, additionally, shows how the elastic constants of the biaxial nematic is mapped on a uniaxial nematic.

Once established the correspondence of the static structures that would appear in the BPC with the structures of a UNLC, we must remember that the hydrodynamic behavior of a BPC would also be equivalent to the one expected from some UNLC. This demonstration is simple. In the hydrodynamic equations the parameter describing the anisotropy of the material is the viscosity stress tensor σ_{ij}. According to Govers and Vertogen [6], this parameter can be computed through a derivative of Rayleigh's dissipation function, $\sigma_{ij} = \partial D / \partial(\partial_i v_j)$, where D consist of all independent invariants that can be constructed from $\partial_i v_j$, δ_{ij}, Q_{ij}, and $\partial_t Q_{ij}$. Consequently, as in this equation the unique parameter distinguishing the BNLC from the UNLC is the order parameter Q_{ij}, and as in this case they have a formal identity, all the hydrodynamics of the BPC would also be equivalent to the one of some UNLC.

In order to give an empiric support to this equivalence a lyotropic mixture of potassium laurate, in a BPC, was submitted to elastic and dynamic experiments, in such a way that results could be compared with the known results of uniaxial materials. The mixture [1,10] was prepared with the following concentrations in weight percent: potassium laurate (KL:25.30), decanol (DeOH:6.24), and (D$_2$O:68.46). The nematic phases were determined by optical microscopy and optical birefringence measurements performed through a Berek compensator [5], which presents the following sequence: $I_{RE} - N_D(13.8\,°C)$, $N_D - N_B(18.6\,°C)$, $N_B - N_C(21.2\,°C)$, and $N_C - I(40.3\,°C)$. The optical birefringence Δn as a function of temperature, near the $N_D - N_B - N_C - I$ phase transitions, is presented in Fig. 1. As one can see from Fig. 1, the temperature range of the biaxial nematic phase is around 2.6 °C. This result is in agreement with the phase diagrams reported in the literature [1,10], and it is also
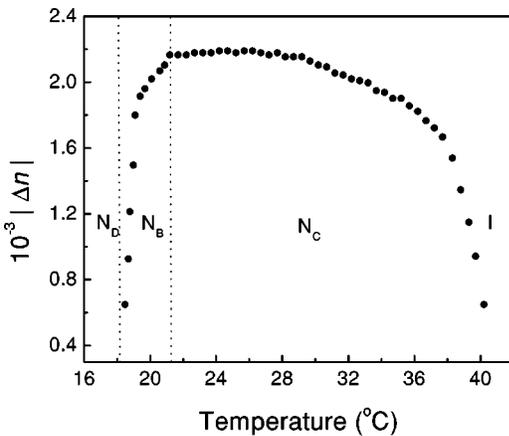
FIG. 1. Birefringence Δn as a function of the temperature of the KL-DeOH-D_2O system. N_D, N_B, N_C, and I are discotic nematic, biaxial nematic, calamitic nematic, and isotropic phases, respectively.

(a)

(b)

(c)

FIG. 2. Structures observed at the polarizing microscope along the $\vec{e}_z$ axis between crossed polarizers, magnification $\times 50$, in the presence of magnetic field ~ 4.0 kG along the $\vec{e}_y$ axis. The biaxial nematic sample at $T = 19.5$ °C is 45° from the x axis: (a) after a time of exposure Δt_e to the magnetic field of 20 min; (b) the magnetic walls begin to lose their regularity at $\Delta t_e \sim 2$ h; (c) the walls begin the process of formation of closed elliptical loops after $\Delta t_e \sim 7$ h.

consistent with optical birefringence measurements performed on the similar lyotropic mixtures [5,11]. The sample was encapsulated in flat glass microslides of 0.2 mm thickness, width is 2.5 mm, and length is 2 cm and placed in a hot stage (MK200) device. The temperature was controlled by a Heto circulating temperature bath, stable within 0.01 K. The laboratory frame axes are defined with the boundary surfaces parallel to the xy plane and $\vec{e}_z$ is the axis normal to the biggest surface of the microslide [11]. To obtain the geometry of the BPC the sample was submitted, during some hours, to a magnetic field (~ 10 kG) that completely align one direction of the director, $\vec{n}$ by assumption, along the $\vec{e}_x$ direction. This procedure is justified by the result of Saupe [1], which discovered that the principal diamagnetic susceptibilities satisfies the relations $\chi_1 > \chi_2 > \chi_3$. Consequently, the strong magnetic field aligns the director along the direction of χ_1, which is assumed as the direction of the director $\vec{n}$. Furthermore, to obtain the alignment along the other direction a very thin sample has been used, in such a way that along the $\vec{e}_z$ direction the alignment is induced by the boundary conditions, and the director $\vec{l}$ becomes parallel to the surface direction. Additionally, birefringence measurements have been made to give further assurance that at the temperature, concentration, and geometry utilized, the system is actually in a biaxial phase. When a good alignment is achieved, the magnetic field along $\vec{e}_x$ axis is switched off and a fixed strength controlled magnetic field is apllied along the $\vec{e}_y$ axis. Some of the patterns observed after the application of such magnetic field are shown in Figs. 2(a)–2(c). The structure of these biaxial patterns, shape and sequence, is similar with the structures observed in the UNLC [12]. The relaxation time of these configurations happens in a slow process [13], and after about 7 h in the presence of the magnetic field, the walls begin the process of formation of the closed elliptical loops [14] observed in the Fig. 2(c).

An important aspect of this experiment is that to be in accord with the theoretical considerations described above,

we need be sure that during all the experiment the director $\vec{l}$ is aligned with the $\vec{e}_z$ direction. The major evidence of this alignment is in fact indirect, but it is given by the proper existence of these structures (magnetic walls) in a biaxial material. To understand the reason of this affirmation the physical origin of the magnetic walls must be considered.

These patterns are very well known in uniaxial nematic liquid crystals and, as it was demonstrated by Lomberg *et al.* [3], they are consequence of the simultaneous action of the elastic and hydrodynamic physics of uniaxial nematics. Namely, in uniaxial NLC they are result of the application of a magnetic field that, breaking the symmetry of the initially uniformly aligned director, simultaneously provokes a rotation of the director and fluid flow of the nematic material. It is important to observe that such director rotation is entirely contained in the plane determined by the initial orientation of the director (direction $\vec{e}_x$) and the direction of the magnetic field used to break the initial symmetry (direction $\vec{e}_y$). Consequently, rotations changing the planar configuration are not allowed. If these same considerations are applied to a biaxial material, prepared as described above, the fact that the observed patterns are in correspondence with those observed in a uniaxial material (with the same spatial and temporal order) lead us to conclude that they have suffered from the same physical process occurred in the uniaxial sample and, as a immediate consequence, the molecular rotation only occurred in the plane formed by the directions of the magnetic field and the initial director alignment. Consequently, only the direction of the directors $\vec{m}$ and $\vec{n}$ have changed, leaving the director $\vec{l}$ fixed. This is exactly the condition for the application of our theoretical arguments. Consequently, the observation of some these structures in a biaxial sample, gives a strong evidence that under the conditions of the experiment the biaxial system is presenting a static and dynamic behavior typical of a uniaxial system.

So, using the equivalence stated in Eq. (11) it is easy to demonstrate that the ratio between the major a and minor b axes of the ellipse is given by $a/b = [(K_{b1} + K_{b7} + K_{b6})/(K_{b2} + K_{b8} + K_{b5})]^{1/2}$, allowing a direct measurement of this ratio between the elastic constants of the biaxial material. Our experimental results point up for the ratio $a/b \sim 1.3$. New experiments, with another experimental technique, are required to investigate these elastic constants. Concluding, we have proposed that it is possible to arrange a biaxial sample of a lyotropic nematic liquid crystal in such a way that its elastic and dynamical properties can be mapped in the behavior of a uniaxial sample. A sample of a biaxial material has been used to experiment this property and, with the use such mapping, the ratio between some elastic constants of the biaxial material has been evaluated.

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