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Bend and splay elastic constants at a reentrant isotropic–calamitic-nematic phase transition

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By measuring the ratio between the major and minor axes of closed elliptical loops created by a magnetic field, the ratio between the bend (K_{33}) and splay (K_{11}) elastic constants of a lyotropic mixture of potassium laurate, decanol, and water in the calamitic nematic phase is measured as a function of temperature. Since these systems present two nematic-isotropic phase transitions—the usual one, at high temperatures, and a reentrant one, at low temperatures—such measurements are used to compare the behavior of these elastic constants at the neighborhoods of these two distinct regions, which have in common the vanishing of the order parameter. The experimental data have revealed the existence of two elastic constant branches, characterizing a distinct low- and high-temperature behavior. To explain such asymmetry we support that, because of the lyotropic nature of the compound, the micellar variation, which is mainly responsible for the reentrant phase, plays a distinct role at these two phase transitions.

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I. INTRODUCTION

In the elastic continuum theory of nematic liquid crystals (LC), the elastic constants are phenomenological parameters introduced by taking into account the symmetry of the phase in order to describe its bulk properties [1,2]. In a pseudomolecular perspective, these elastic constants connect the energy necessary to produce macroscopic deformations on the director orientation with the microscopic cohesive forces responsible for molecular arrangement [3,4]. The elastic constants depend on material parameters and, since they vanish in the isotropic phase, they can characterize the thermodynamic behavior of the liquid crystalline state, being useful also to the study of the microscopic properties of nematic materials. The bulk elastic behavior of thermotropic systems is, at a large extent, a well-established subject [1,3,5]. The situation is less clear for what concerns lyotropic systems, whose elementary constituents are aggregates (micelles) and in which the mesogenic behavior is determined by the concentration. In these systems, a few investigations dealing with elastic constants have been reported. In particular, Haven *et al.* [6] have carried out experimental measurements of the bend (K_{33}) and splay (K_{11}) elastic constants as a function of the temperature for discotic nematic lyotropic mixtures, obtaining values that are comparable to those determined in a nematic thermotropic. Subsequently, these data have been used to obtain a phenomenological dependence of the ratio of elastic constants on the temperature, in the framework of a pseudomolecular model [7].

In this paper, a lyotropic mixture presenting two isotropic phases is used to study the influence of the proximity of the isotropic phase in the temperature behavior of the bend-to-splay elastic constant ratio. As is known [8], the lyotropic mixture of potassium laurate (KL) and decanol (DeOH)/H_2O presents a calamitic nematic phase bordered by two isotropic phases: a reentrant isotropic phase at low temperatures and a classical isotropic phase at high temperatures [1]. That is, besides the usual higher temperature transition to an isotropic phase, it has been observed that the reduction of the temperature of this mixture also induces a transition to an isotropic phase, in a temperature for which such transition is not expected to happen. Under normal conditions, it is expected that the nematic-isotropic phase transition (NIT) results from the random thermal fluctuations that, due to the increasing temperature, becomes large enough to destroy the orientational order of the micelles in the nematic phase, overcoming their global coherent alignment. However, such a mechanism cannot be responsible for the observed reentrant (NIT) [9]. Consequently, because of the connection between the elasticity and the cohesive forces that produce the nematic state, the study of elastic constants can shed some light on the complex mechanism that drives the order-disorder competition of the general (NIT). Namely, it is largely known [10], that although the reentrant phases mainly arises from the micellar shape variation, the high-temperature nematic-isotropic phase transition is mainly connected with the thermal angular fluctuations. Furthermore, it has been recently discovered that the reentrant transition presents a critical behavior visibly distinct from the one observed at the usual nematic-isotropic phase transition [9]. Consequently, we could expect that the nonequivalence of two phases could be detected on measurements of the elasticity of the system at the neighborhoods of the transition points and, furthermore, such measurements can be used to illuminate the nature of the distinction of these critical points. These are the main aims of this work.

II. FUNDAMENTALS

The usual method to measure the elastic constants deals with the determination of the Fréedericksz threshold [1]. Mainly because of the lack of an easy and secure method to control the anchoring of the oriented nematic material to the walls of the sample, this method is accompanied with unavoidable errors in the exact determination of the critical point [3]. After the work of Brochard [11], Leger [12] suggested that the geometry of the elliptical walls, usually observed in LC samples under the action of external magnetic fields, could be used to measure ratios between the elastic constants. This experimental procedure is employed in this work to determine the ratio between the bend and splay elastic constants. As the final results will reveal, any improvement in the precision of our data will not change our final conclusions. Therefore, let us begin by outlining the theoretical fundamentals of this method.

Consider a uniaxial nematic LC sample, whose bulk elastic energy is given by

$$F=\frac{1}{2}\int[K_{11}(\vec{\nabla}\cdot\vec{n})^2+K_{22}(\vec{n}\cdot(\vec{\nabla}\times\vec{n}))^2 + K_{33}(\vec{n}\times(\vec{\nabla}\times\vec{n}))^2]dV, \qquad (1)$$

where $\vec{n}$ is the director field and K_{11}, K_{22}, and K_{33} are, respectively, the splay, twist, and bend elastic constants. Suppose that the textures described by the above elastic energy are such that the director $\vec{n}$ stays in a planar configuration, as in the case of splay-bend deformation, for which

$$\vec{n}=\cos\theta\vec{e}_x+\sin\theta\vec{e}_y, \quad \theta\equiv\theta(x,y,z).$$

In terms of these variables, it is straightforward to show that the free energy F assumes the form

$$F=\frac{1}{2}\int\{(K_{11}\sin^2\theta+K_{33}\cos^2\theta)(\partial_x\theta)^2 + (K_{33}\sin^2\theta+K_{11}\cos^2\theta)(\partial_y\theta)^2+2(K_{11}-K_{33})\sin\theta \times\cos\theta(\partial_x\theta)(\partial_y\theta)+K_{22}(\partial_z\theta)^2\}dV. \qquad (2)$$

Since, on the plane (x,y), the quadratic expression in $(\partial_x\theta)$ and $(\partial_y\theta)$ presents a nonquadratic term, proportional to $(\partial_x\theta)(\partial_y\theta)$, a local coordinate transformation, $x=x(u,v)$ and $y=y(u,v)$, can be envisaged in such a way that on this plane F assumes a diagonalized quadratic expression. By setting

$$\partial_u\theta=\frac{\partial x}{\partial u}\partial_x\theta+\frac{\partial y}{\partial u}\partial_y\theta,$$

$$\partial_v\theta=\frac{\partial x}{\partial v}\partial_x\theta+\frac{\partial y}{\partial v}\partial_y\theta,$$

where

$$\frac{\partial x}{\partial u}=\sqrt{K_{33}}\cos\theta, \quad \frac{\partial x}{\partial v}=-\sqrt{K_{11}}\sin\theta,$$

$$\frac{\partial y}{\partial u}=\sqrt{K_{33}}\sin\theta, \quad \frac{\partial y}{\partial v}=\sqrt{K_{11}}\cos\theta,$$

one obtains

$$F=\frac{1}{2}\int\{(\partial_u\theta)^2+(\partial_v\theta)^2+K_{22}(\partial_z\theta)^2\}dV. \qquad (3)$$

Therefore, the variables u and v have diagonalized the free energy and incorporated the elastic constants. To interpret the meaning of this coordinate system let us study the directions $\vec{e}_u$ and $\vec{e}_v$. A straightforward calculation shows that

$$\vec{e}_u=\frac{\partial x}{\partial u}\vec{e}_x+\frac{\partial y}{\partial u}\vec{e}_y=\sqrt{K_{33}}(\cos\theta\vec{e}_x+\sin\theta\vec{e}_y)=\sqrt{K_{33}}\vec{n},$$

$$\vec{e}_v=\frac{\partial x}{\partial v}\vec{e}_x+\frac{\partial y}{\partial v}\vec{e}_y=\sqrt{K_{11}}(-\sin\theta\vec{e}_x+\cos\theta\vec{e}_y)=\sqrt{K_{11}}\vec{n}_\perp, \qquad (4)$$

where $\vec{n}_\perp$ gives the direction perpendicular to the director. Hence, although the direction $\vec{e}_u$ coincides with the director direction, but with lengths rescaled by the factor $\sqrt{K_{33}}$, the direction $\vec{e}_v$ gives the direction perpendicular to the director, with lengths rescaled by $\sqrt{K_{11}}$. That is, two points that are separated by the distance

$$\Delta\vec{r}=\Delta u\vec{e}_u+\Delta v\vec{e}_v,$$

in the (u,v) coordinate system, in laboratory coordinate system, (x,y) will be separated by the distance,

$$\Delta\vec{r}=\sqrt{K_{33}}\Delta u\vec{n}+\sqrt{K_{11}}\Delta v\vec{n}_\perp.$$

Hence, unitary dimensions in the (u,v) coordinate system will be expanded by $\sqrt{K_{33}}$ along the director direction and by $\sqrt{K_{11}}$ along the direction perpendicular to it. Therefore, a spherical texture at the (u,v) coordinate system would correspond, in the laboratory coordinate system, to an ellipse with one axis pointing along the director direction and another one pointing along the direction perpendicular to it. As the inverse of this reasoning is also true, the ratio of the semiaxis of an observed ellipsoidal texture would be given by $\sqrt{K_{33}}/\sqrt{K_{11}}$.

The lyotropic mixture investigated in this work was prepared with the following concentrations in weight percent: potassium laurate (KL:29.4), decanol (DeOH:6.6), and water (64.0). The phase sequence, I_{RE}-N_C (11.0 °C) and N_C-I (47.0 °C) was determined by optical microscopy and optical birefringence measurements. A calamitic nematic sample was encapsulated in flat glass microslides of 0.2 mm of thickness, placed in a Instec $(Hs1-i)$ hot-stage device. The sample temperature was controlled by a Heto circulating temperature bath, stable within of 0.01 °C. The laboratory frame axes are defined with the boundary surfaces parallel to the xy plane, and z is the axis normal to the biggest surface of the microslide. In order to obtain a well-oriented nematic sample, in a planar geometry, a magnetic field (**H**) of 12 kG is applied along the x axis of the sample. Afterward, the magnetic field along x is switched off. In second moment, a magnetic field of 8 kG is applied along the y axis. The periodic texture observed in a polarizing microscope shows a periodic distortion of director **n** with walls formed in the direction of **H** [8]. The relaxation is slow, and after about 20 h in the presence of the magnetic field, the calamitic nematic sample texture presents closed elliptical loops [12,13] as observed in Fig. 1. The ratio between the major a and minor b axes of the ellipse is given by $a/b=(K_{33}/K_{11})^{1/2}$, allowing a direct measurement of this ratio between the bend and splay elastic constants in the domain of N_C and near the N_C-I (I_{RE}) phase transitions, as a function of temperature.

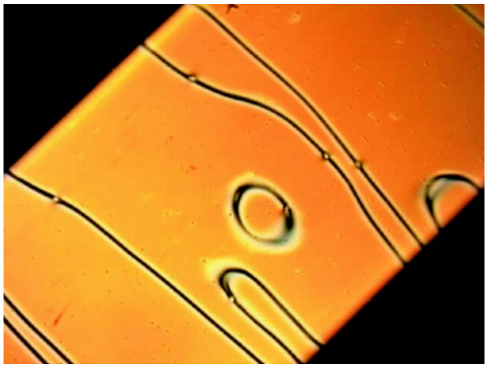

FIG. 1. (Color online) Closed elliptical loops observed at the polarizing microscope along the $\vec{e}_z$ axis between crossed polarizers, magnification ×50, in the presence of magnetic field $H=8kG$ applied along the $\vec{e}_y$ axis, after ~20 h. The calamitic nematic phase is 45 deg from the $\vec{e}_x$ axis.

III. RESULTS AND DISCUSSION

The experimental results of K_{33}/K_{11} as a function of the temperature in the N_C phase are plotted in Fig. 2. Note that near the N_C-I_{RE} phase transition K_{33}/K_{11} increases in magnitude and becomes maximum around 25.0 °C and, subsequently, decreases as the temperature increases near the N_C -I phase transition. When the experimental data shown in Fig. 2 are compared to similar results obtained from compounds that do not present the reentrant isotropic phase, the main lines of the behavior observed in that figure is also found [6,7]. In this sense, save from the fact that the lyotropic mixture that we are studying presents two distinct isotropic phases, the behavior depicted in Fig. 2 can be considered as an extension of the presently known results, with the evident difference that the curve obtained with the present experiment has two branches. This should suggest that one of them could be obtained by the reflection of the other with respect to a vertical line passing through the central peak position. Nevertheless, a careful observation shows that these curves are not symmetric; the elastic constants have different behaviors when the different isotropic phases are approached. This lack of symmetry in the two branches of the bend-to-splay ratio is the feature of the above data that will be detached here.

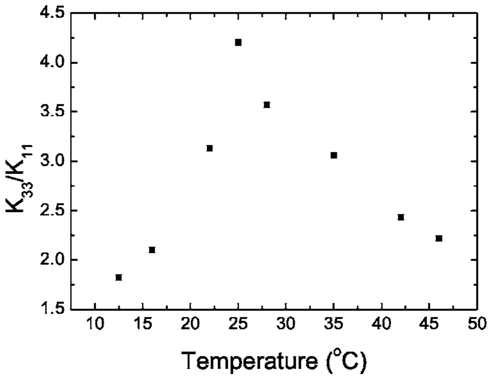

FIG. 2. Ratio between the bend and slay elastic constants K_{33}/K_{11} as function of the temperature. I_{RE}, N_C, and I are isotropic reentrant, calamitic nematic, and isotropic phases, respectively.

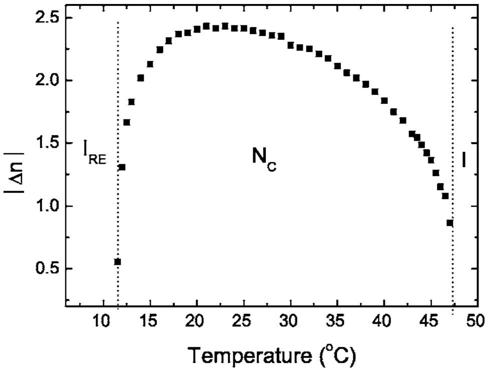

FIG. 3. Optical birefringence ($\Delta n \times 10^{-3}$) vs temperature obtained as described in Refs. [9,14]. Because the birefringence is a measure of the orientational anisotropy of the nematic sample, it must be proportional to the orientational order parameter [1]. Consequently, save for a multiplicative global parameter, these data are proportional to the order parameter [18].

To have rigorous information about the meaning of this asymmetry it would be better if we change the running variable from the temperature to the order parameter. Originally, the order parameter has been introduced to measure the ordering of a system that undergoes a phase transition. Consequently, as a phase is characterized by its symmetries, the order parameter has to contain the symmetries of the phase that it describes. Therefore, it is hoped that the thermodynamical variables could be expressed in terms of it. The main implicit hypothesis on the Landau assumption that the free energy can be expanded in terms of an order parameter is just this: the thermodynamic variables are univocal functions of the order parameter. In the LC phenomenology, the order parameter measures the degree of alignment of a nematic sample and all thermodynamical variables must be expressed as a function of it, in particular, the elastic constants. So, a correct analysis of the behavior of the elastic constants in the neighborhoods of phase-transition points will be done if we can express the elastic constants in terms of the order parameter of the nematic phase.

Optical birefringence (Δn) as a function of temperature, determined as described in the Refs. [9,14], is shown in Fig. 3. Except for a scale factor, the data shown in this figure are proportional to the order parameter. Thus, a parametric graph joining the results shown in Figs. 2 and 3, would give a graph of the bend-to-splay ratio as a function of the order parameter [9]. Furthermore, as the usual theory of the elastic constants assumes that they are univocally determined by the order parameter, both sides of the ratio have to lie on the same curve. However, Fig. 4 shows that this ratio is not an univocal function of the order parameter; there are two branches on the elastic constants ratios, one that characterizes the low-temperature reentrant NIT and another one characterizing the upper usual NIT.

The conclusion suggested by Eq. (4) is immediate: or the birefringence is not proportional to the order parameter or the order parameter, alone, is not the only thing responsible for the the physics of the elastic constants. In order to have an indication about what may be going on, let us remember a recent result comparing the physical nature of these two

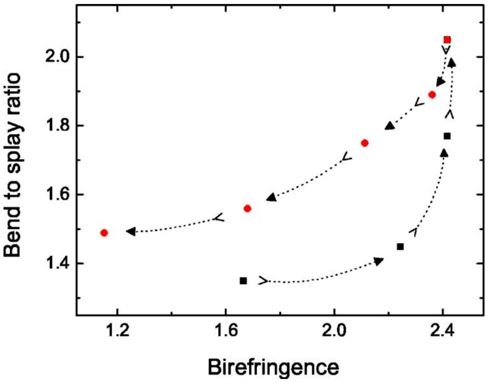

FIG. 4. (Color online) Parametric curve representing K_{33}/K_{11} vs optical birefringence. It reveals that the elastic constants are not univocally determined by the orientational order parameter showing, unambiguously, that another parameter must be introduced to fully describe the phenomenology of the lyotropic materials. Furthermore, it also confirms that the reentrant isotropic-calamitic nematic phase transition and the classical calamitic nematic-isotropic phase transition each have a different nature [9].

NITs. It has been shown that even both being nematic-isotropic phase transitions, these transitions present, from the thermodynamic point of view, some essential differences. Although the usual NIT is a first-order phase transition, there are some indications that the reentrant NIT could be a second-order phase transition [9]. Furthermore, their critical exponents do not agree, suggesting that they belong to distinct universality classes [9]. In essence, although both transitions connect orientated states to isotropic configurations, the results have shown that the mechanism driving those transitions is, at least from the critical phenomena point of view, distinct. The results that we have found here confirm this. It follows that some feature that distinguishes the neighborhoods of these two phase transitions is not being considered by the orientational order parameter.

To explain the behavior discussed above, we have to remember that it is characteristic of a lyotropic system, where the micellar shape is decisive. The nematic domains of these compounds are not formed by rigid molecules, but by assemblies of amphiphilic molecules that compose the micelles of the lyotropic material. It is well known that the resultant shape of this assembly of molecules is sensible to temperature [15,16]. In this manner, the low temperature isotropic phase can be explained by considering that, near the transition temperature, the molecular arrangement gives rise to a micellar geometry unable to sustain an average molecular orientation compatible with the nematic ordering. That is, at the reentrant NIT, the collective orientation of the micelles is frustrated, not by the thermal agitation, but by the geometrical conformation of the objects forming the phase. Therefore, one can argue that in this case the orientational order parameter alone is not enough to describe the microscopic dynamic driving the physical process. This conclusion is reinforced by pseudomolecular calculations, which are employed to determine the elastic constants. In fact, in Ref. [7], the ratio K_{33}/K_{11} was calculated for the Nehring-Saupe intermolecular interaction [4]. By considering discotic shape, both for the micelles and for the interaction volume, the ratio was shown to depend on the temperature by means of the micellar shape anisotropy. Furthermore, it was also shown that the ratio between the elastic constants also depends on a control parameter ϵ that can be shown to be dependent on the geometry of the objects forming the phase, which, in turn, is changing with temperature. The consequences of micellar geometry to the elastic constants seems evident. The nematic elasticity owes its origin to the interaction of anisotropic objects and, once this anisotropy is changed, this elasticity must change, correspondingly. The main concern here is that the elasticity resulting from this process is not directly related to the mean micellar orientation, as would happen in a classical NIT, but can have also contributions arising from the strong dependence that the micellar shape presents with the temperature.

In addition, this dependence of the shape anisotropy on the temperature can be investigated by means of a pseudomolecular model along the lines discussed in Refs. [7,17]. In principle, by considering an intermolecular interaction energy, it would be possible to establish closed analytical formulas connecting the ratio of the elastic constants with the eccentricity of the micellar volume or with some other suitable measure of the shape anisotropy. In this manner, from the experimental data of Fig. 2, it could be possible to obtain information about this dependence by performing a comparison to the theoretical predictions. However, this kind of investigation was not considered in the present analysis.

Finally, it is necessary to note that the present investigation refers to a sample in which the phase sequence is the well-established reentrant isotropic–calamitic-nematic-isotropic phases [8]. Furthermore, the concentration is not close to the biaxial or to the discotic nematic phase. The ratio K_{33}/K_{11} has a no univalent behavior with respect to the orientation order parameter, which is not found in a sample without the reentrant phase as the one considered in Ref. [7]. Therefore, the existence of a reentrant phase is responsible for the nonconventional behavior of the elastic constants in lyotropic samples, and this behavior is not connected with pretransitional effects.

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