Determination of the effective splay-bend elastic constant of a lyotropic nematic liquid crystal

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The effective splay-bend elastic constant k_{13} is studied by means of an optical technique for a lyotropic nematic liquid crystal. The ratio between k_{13} and the usual Frank elastic constant found in this experiment is positive and of the order of 1. This result agrees with the one obtained recently for thermotropic liquid crystals.

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I. INTRODUCTION

The temperature-induced surface alignment transition in nematic liquid crystals (NLC's) is one of the most interesting subjects of research nowadays. Many theoretical [1,2] and experimental [3,4] works have been done to investigate the behavior of the surface anchoring energy of a liquid crystal limited by a solid substrate.

To describe the surface contribution to the elastic free energy, Nehring and Saupe [5] introduced the splay-bend elastic constant (k_{13}). In the usual experiments where the bulk contribution is dominant, the surface terms may be neglected and the continuum elastic theory with the three Frank elastic constants [6] works well. However, there are situations where the surface contribution is dominant, and the behavior of some physical parameters (such as the optical birefringence) gives access to the k_{13} elastic constant.

The temperature surface transition [7,8] is a kind of surface instability induced by the temperature in NLC's near to the nematic (N)–isotropic (I) phase transition. An elastic model has been recently proposed [1,3] to interpret the temperature surface transition. This model allows one to interpret the experiments concerning this kind of surface instability, in which the temperature dependence of the NLC average orientation is analyzed [4]. In [3,4] the ratio between the effective splay-bend elastic constant (k_{13}) and the usual Frank constant (k) has been measured by means of optical measurements. This ratio has been found positive and of the order of 1. From this result it is possible to conclude that the dispersion forces are not the most important for the usual thermotropic NLC's. To our knowledge, there are no experimental results of k_{13}/k for lyotropic NLC's available in the literature. Such results would be very interesting to compare with the thermotropic ones since in lyotropics the steric forces are expected to be very important.

In this paper we report on measurements of the optical birefringence for a lyotropic uniaxial NLC as a function of the temperature, near the N-I transition temperature. The results are analyzed on the basis of the elastic model described in [1,3] and extended in this paper.

The main points of the elastic model are stressed in Sec. II. An extension of the elastic model is given in Sec. III, where it is shown that a delocalized intrinsic anchoring energy may be responsible for subsurface deformations. The experimental setup is described in Sec. IV. Our results are reported in Sec. V and discussed in Sec. VI.

II. THEORY

In this section we briefly discuss the most relevant aspects of the model [1,3] used to describe the experimental results.

The uniaxial NLC is supposed to be semi-infinite, limited by the surface placed at $z = 0$ and occupying the $z > 0$ half space. The problem is supposed to be one-dimensional, i.e., all the physical quantities are only z dependent. The NLC director $\mathbf{n}$ lies in the (x, z) plane. The tilt angle made by $\mathbf{n}$ with the z axis is denoted by $\phi(z)$.

The total free energy per unit surface is given by [3]

$$F = \int_0^\infty \left(\frac{1}{2}k\phi'^2 + \frac{1}{2}k^*\phi''^2 \right) dz + \frac{1}{2}w\sin^2(\phi_0 - \phi_e) + \frac{1}{2}k_{13}\sin(2\phi_0)\phi_0'. \tag{1}$$

Here a prime means a derivative with respect to z, $\phi_0 = \phi(0)$, $\phi_0' = \phi'(0)$, w is the anchoring energy strength, k is the usual Frank elastic constant, k^* is the second order elastic constant [9,10], k_{13} is the splay-bend elastic constant [5], and ϕ_e is the easy direction characterizing the NLC-substrate interface [11].

The minimization of F with respect to $\phi(z)$ gives

$$\phi_b = \phi_0 - \frac{1}{2}K_{13}\sin(2\phi_0) \tag{2}$$

with

$$\frac{\sin[2(\phi_0 - \phi_e)]}{\sin(4\phi_0)} = \frac{L}{2b} K_{13}, \qquad (3)$$

where ϕ_b denotes the equilibrium bulk tilt angle, $b = (k^*/k)^{1/2}$ is a mesoscopic length, $L = k/w$ is the extrapolation length [11], and $K_{13} = k_{13}/k$ is the reduced splay-bend elastic constant.

In the limit of infinite anchoring energy ($L \ll b$), $\phi_0 = \phi_e$ and the temperature (T) dependence of ϕ_b is an effect of the variation of K_{13} with T. The splay-bend elastic constant k_{13} and the usual Frank elastic constant k can be expressed in terms of the scalar order parameter S [12,13]:

$$k_{13} = c_1 S + c_2 S^2 \quad \text{and} \quad k = k_2 S^2 \qquad (4)$$

where c_1, c_2, and k_2 are temperature-independent parameters [12,13]. The temperature dependence of the scalar order parameter is of the kind [6]

$$S(T) = \delta \left[1 - \frac{T}{T_c} \right]^{1/2}, \qquad (5)$$

where δ is a constant and T_c a temperature a little higher than the N-I transition temperature (T_{NI}). By means of Eqs. (4) and (5), Eq. (2) can be rewritten as [3]

$$\phi_b(T) = \phi_e - \frac{1}{2} \left[\frac{A}{\sqrt{T_c - T}} + B \right] \sin(2\phi_e), \qquad (6)$$

where $A = (\sqrt{T_c}/\delta)(c_1/k_2)$ and $B = c_2/k_2$. Finally, K_{13} can be calculated as

$$K_{13} = \frac{A}{\sqrt{T_c - T}} + B. \qquad (7)$$

According to the theory proposed in [1,3], the presence of the elastic term connected to the splay-bend elastic constant is responsible for a subsurface deformation $\phi_b - \phi_0 = -(K_{13}/2) \sin(2\phi_0)$, vanishing for $\phi_0 = 0$ and $\phi_0 = \pi/2$. This result is a consequence of an extended elastic theory. According to this theory, surface contributions depending on ϕ' are taken into account including also terms in ϕ''^2 in the bulk elastic energy density. Of course, if a finite deformation $\phi_0 - \phi_b$ takes place over a microscopic layer of thickness b, the elastic description may be questionable. In this case, in fact, the free energy density expressed in series of $\phi', \phi'^2, ..., \phi'', \phi''^2, ...$ could converge very slowly. Moreover, the meaning of the elastic constants is no longer very clear. A recent microscopic analysis [14,15] concerning the orientation of a NLC near an interface has completely confirmed the predictions of the extended elastic theory. In particular, it has been shown in [14,15] that intermolecular interactions depending on the orientation of the molecules with respect to their relative position give rise to subsurface deformation on a molecular scale.

III. EXTENSION OF THE ELASTIC MODEL

Equation (1) has been written considering the anisotropic surface energy $(1/2)w \sin^2(\phi_0 - \phi_e)$ as related to localized interactions between the NLC and the substrate. Of course, this is not always true, because the range of the interactions NLC-substrate may be of the same order as the NLC-NLC intermolecular interaction. This means that the anisotropic surface energy is obtained by integrating a bulk free energy density, which has an intrinsic and an extrinsic part [16]. Now we shall show that a delocalized anisotropic surface energy gives rise to terms renormalizing the effective k_{13} elastic constant. Hence, even in this case, the analysis reported above remains valid if the effective splay-bend elastic constant is properly defined and the anchoring energy can be considered strong.

With this aim, let $g(\mathbf{n}, \mathbf{n}'; \mathbf{r})$ be the intermolecular interaction energy responsible for the NLC phase, between the molecule at $\mathbf{R}$, whose orientation is $\mathbf{n} = \mathbf{n}(\mathbf{R})$, and the molecule at $\mathbf{R}' = \mathbf{R} + \mathbf{r}$, whose orientation is $\mathbf{n}' = \mathbf{n}(\mathbf{R}')$. As is well known [17], the elastic energy is obtained by expanding g in a power series of $\delta \mathbf{n} = \mathbf{n}' - \mathbf{n}$ in the following manner:

$$g(\mathbf{n}, \mathbf{n}'; \mathbf{r}) = g(\mathbf{n}, \mathbf{n}; \mathbf{r}) + \lambda_i \, \delta n_i + \frac{1}{2}\lambda_{ij}\delta n_i \delta n_j + O(\delta n^3). \qquad (8)$$

In Eq. (8), $g(\mathbf{n}, \mathbf{n}; \mathbf{r})$ is the uniform part of the interaction energy, and

$$\lambda_i = \left[\frac{\partial g}{\partial(\delta n_i)} \right]_{\delta n_i = 0}, \quad \lambda_{ij} = \left[\frac{\partial^2 g}{\partial(\delta n_i)\partial(\delta n_j)} \right]_{\delta n_i = 0}. \qquad (9)$$

Expansion (8) represents a good approximation for $g(\mathbf{n}, \mathbf{n}'; \mathbf{r})$ only if $|\delta n_i| \ll 1$. This means that the average NLC orientation has to change slowly over the range of the intermolecular forces responsible for the nematic phase.

In order to obtain the elastic energy density, it is necessary to expand δn_i in power series of x_i, the Cartesian components of $\mathbf{r}$:

$$\delta n_i = n_{i,j}x_j + \frac{1}{2}n_{i,jk}x_j x_k + O(x^3), \qquad (10)$$

where $n_{i,j} = \partial n_i/\partial X_j$ and $n_{i,jk} = \partial^2 n_i/\partial X_j \partial X_k$, in which X_i are the Cartesian components of $\mathbf{R}$. In the elastic limit $|n_{i,j}| \ll 1/\rho_0$, where ρ_0 is of the order of the range of the intermolecular forces giving rise to the NLC phase. In this case Eq. (10) represents well $\delta n_i(\mathbf{R}'; \mathbf{R}) = n_i(\mathbf{R}') - n_i(\mathbf{R})$. Introducing Eq. (10) into Eq. (8), simple calculations give

$$g(\mathbf{n}, \mathbf{n}'; \mathbf{r}) = g(\mathbf{n}, \mathbf{n}; \mathbf{r}) + L_{ij}n_{i,j}$$
$$+ \frac{1}{2}[L_{ijk}n_{i,jk} + L_{ijkl}n_{i,j}n_{k,l}], \qquad (11)$$

where

$$L_{ij} = \lambda_i x_j, \quad L_{ijk} = \lambda_i x_j x_k, \quad L_{ijkl} = \lambda_{ij} x_k x_l. \quad (12)$$

In the mean field approximation the free energy density is given by

$$f = \frac{1}{2} \int \int \int_{\tau_{int}} g(\mathbf{n}, \mathbf{n}'; \mathbf{r}) d\tau, \quad (13)$$

where the integration is performed over the interaction volume τ_{int}. By means of Eqs. (11) and (12), f can be rewritten in terms of the spatial derivatives of $\mathbf{n}$ as follows:

$$f = f_0 + K_{ij} n_{i,j} + \frac{1}{2}(K_{ijk} n_{i,jk} + K_{ijkl} n_{i,j} n_{k,l}). \quad (14)$$

In Eq. (14) f_0 is the uniform part of f and K_{ij}, K_{ijk}, and K_{ijkl} the elements of the elastic tensors. As follows from Eq. (13) they are defined by

$$f_0 = \frac{1}{2} \int \int \int_{\tau_{int}} g(\mathbf{n}, \mathbf{n}; \mathbf{r}) d\tau$$

and

$$K_{ij} = \frac{1}{2} \int \int \int_{\tau_{int}} L_{ij} d\tau, \quad K_{ijk} = \frac{1}{2} \int \int \int_{\tau_{int}} L_{ijk} d\tau,$$

$$K_{ijkl} = \frac{1}{2} \int \int \int_{\tau_{int}} L_{ijkl} d\tau.$$

The elastic tensors have to be decomposed in terms of the symmetry elements characterizing the phase under consideration [17,18]. In the bulk the symmetry elements of a NLC reduce to $\mathbf{n}$. In this case, f_0 is a constant independent of $\mathbf{n}$, K_{ij} are identically zero, and K_{ijk} and K_{ijkl} give rise to the usual elastic constants k_{11}, k_{22}, k_{33}, k_{24}, and k_{13}.

Close to a surface the symmetry elements of the interface NLC–isotropic solid substrate are $\mathbf{n}$ and the geometrical normal to the interface $\mathbf{k}$. In this situation [17–20] f_0 and the elastic tensors depend on the distance of the considered point from the solid substrate z and on the angle $\phi(z)$ between $\mathbf{n}$ and $\mathbf{k}$. As discussed elsewhere [21], to second order in $(\mathbf{n} \cdot \mathbf{k})^2$, f_0 may be expanded in the following way:

$$f_0 = \beta_0(z) + \beta_1(z)(\mathbf{n} \cdot \mathbf{k})^2 + \beta_2(z)(\mathbf{n} \cdot \mathbf{k})^4, \quad (15)$$

with the hypothesis that $\mathbf{n}$ is equivalent to $-\mathbf{n}$ even at the surface. Expansion (15) for f_0 follows from the symmetry of the NLC phase. The functions $\beta_i(z)$, $i = 1, 2, 3$, depend on the intermolecular interaction energy $g(\mathbf{n}, \mathbf{n}'; \mathbf{r})$ and on the interaction energy between the NLC and the isotropic solid substrate. $\beta_0(z)$ gives rise to the isotropic part of the surface tension, whereas β_1 and β_2 are connected with the anisotropic part of the surface tension. For the discussion reported above we have

$$\lim_{z \to \infty} \beta_1(z) = \lim_{z \to \infty} \beta_2(z) = 0, \text{ and } \lim_{z \to \infty} \beta_0 \neq 0, \quad (16)$$

because in the bulk f_0 has to be independent of the $\mathbf{n}$ orientation. This means that $\beta_1(z)$ and $\beta_2(z)$ are different from zero only in a surface layer whose thickness is of the order of the range of the intermolecular forces [19].

In the simple planar and one-dimensional case under consideration Eq. (14), by taking into account Eq. (15), can be written as [3]

$$f = f_0(z, \phi(z)) - \frac{1}{2}k_{13}\frac{d}{dz}[\sin(2\phi)\phi'] + \frac{1}{2}k\phi'^2, \quad (17)$$

where $f_0(z, \phi(z)) = \beta_0(z) + \beta_1(z)\cos^2\phi(z) + \beta_2(z)\cos^4\phi(z)$. In the case of strong anchoring, in which the surface tilt angle ϕ_0 is fixed by the surface treatment, the total free energy per unit surface of the NLC is obtained by integrating Eq. (17) over the thickness of the sample. If the NLC occupies the half space $z > 0$, the total free energy per unit surface is given by

$$F = \int_0^\infty f \, dz = \frac{1}{2}k_{13}\sin(2\phi_0)\phi_0'$$
$$+ \int_0^\infty \left[\frac{1}{2}k\phi'^2 + f_0(z, \phi(z))\right] dz. \quad (18)$$

Supposing that ϕ_b is not very different from ϕ_0, we have $\phi(z) = \phi_0 + \phi_0' z$ [22]. Consequently, the uniform term of the free energy density can be written as

$$f_0(z, \phi(z)) = f_0(z, \phi_0) + \left(\frac{df_0}{d\phi}\right)_{\phi(z)=\phi_0} \phi_0' z, \quad (19)$$

which is equivalent to

$$f_0(z, \phi(z)) = f_0(z, \phi_0) - [\beta_1(z) + 2\beta_2(z)\cos^2\phi_0] \times \sin(2\phi_0)\phi_0' z \quad (20)$$

if Eq. (15) is taken into account.

By introducing Eq. (19) into Eq. (18), after simple calculations one obtains

$$F = F_0 + \frac{1}{2}k_{13}^{\text{eff}}\sin(2\phi_0)\phi_0' + \int_0^\infty \frac{1}{2}k\phi'^2 dz, \quad (21)$$

where

$$F_0(\phi_0) = \int_0^\infty f_0(z, \phi_0) dz, \quad (22)$$

and

$$k_{13}^{\text{eff}} = k_{13} - \gamma(\phi_0), \quad (23)$$

with

$$\gamma(\phi_0) = \int_0^\infty z[\beta_1(z) + 2\beta_2(z)\cos^2\phi_0] dz. \quad (24)$$

Hence $\gamma(\phi_0)$, connected with the "uniform" part of f, renormalizes the effective splay-bend elastic constant.

Supposing that $\phi_0' = (\phi_b - \phi_0)/b$ and that $\phi'(z) \neq 0$ only for $0 \leq z \leq b$, we obtain from Eq. (21)

$$F = F_0(\phi_0) + \frac{1}{2}k_{13}^{\text{eff}} \sin(2\phi_0)\frac{\phi_b - \phi_0}{b} + \frac{1}{2}k\frac{(\phi_b - \phi_0)^2}{b}.$$

$$(25)$$

By minimizing (25) with respect to $\phi_b - \phi_0$, we obtain

$$\phi_b - \phi_0 = -\frac{k_{13}^{\text{eff}}}{2k}\sin(2\phi_0),$$

$$(26)$$

coincident with our fundamental Eq. (2). Equation (26) is valid when f_0 is given by Eq. (15). As stressed above, this follows from the symmetry of the NLC phase; it is not a consequence of simple mean-field operations. To discuss this point in more detail, we have just to remember that a NLC is described by a symmetric traceless tensor of rank 2. This tensor is defined by [6] $Q_{ij} = \frac{3}{2}S(n_i n_j - \frac{1}{3}\delta_{ij})$, where S is the scalar order parameter. According to the Landau theory, the uniform free energy density of the NLC is an analytical function of Q_{ij}. By expanding f_0 in power series of Q_{ij}, near the surface, at the second order in S [21], we obtain Eq. (15).

The result obtained above and summarized in Eq. (23) tells us simply that the sources of the subsurface deformation are the elastic terms connected to k_{13} and the uniform part of the delocalized anisotropic anchoring energy. Actually, this result is not surprising. In fact, it has been shown [17] that $g(\mathbf{n}, \mathbf{n}'; \mathbf{r})$ can be expanded in the form

$$g(\mathbf{n}, \mathbf{n}'; \mathbf{r}) = -\sum_{a,c,c'} J_{a,c,c'}(r)(\mathbf{n} \cdot \mathbf{n})^a(\mathbf{n} \cdot \mathbf{u})^c(\mathbf{n}' \cdot \mathbf{u})^{c'},$$

$$(27)$$

where $\mathbf{u} = \mathbf{r}/r$. According to the result reported in [17], the elastic constants of spontaneous splay, of splay-bend, and of the anisotropic contribution of the uniform part of the free energy density are different from zero only if the exponents c and c' are not identically zero. Hence the subsurface deformation depends on the functional dependence of g on $\mathbf{n} \cdot \mathbf{u}$ and $\mathbf{n}' \cdot \mathbf{u}$ and not only on the k_{13} elastic constant. This conclusion has also been confirmed by the microscopical calculation reported in [14,15].

IV. EXPERIMENT

The studied lyotropic mixture has the following concentration (in weight percent):

Decylammonium chloride (DaCl) 41.54%,

NH$_4$Cl 4.23%, H$_2$O 54.23%.

The phase sequence as a function of T (determined by x-ray diffraction and optical observation of the textures) is

$$L \underset{23\,^\circ\mathrm{C}}{\longleftrightarrow} N_D \underset{44.3\,^\circ\mathrm{C}}{\longleftrightarrow} I$$

where L and N_D are lamellar and discotic nematic, respectively.

A small quantity of a water base ferrofluid (Fe$_3$O$_4$ coated with oleic acid, Ferrofluid Inc.), 1 μl/cm^3, is added to the lyotropic mixture. The typical size of the magnetic grains is 100 Å, their concentration being about 10^{12} grains/cm^3. This concentration is larger than the minimum ferrofluid concentration required to produce a collective behavior of the NLC sample in the presence of small magnetic fields [23,24]. At this small concentration, we observed that the temperature transitions are not affected by the presence of ferrofluid doping. This result was already observed in x-ray and optical experiments with lyotropics [25]. In the N_D phase, as the anisotropy of the diamagnetic susceptibility is negative [26], $\mathbf{n}$ orients perpendicular to $\mathbf{H}$.

The sample is prepared with the lyotropic mixture placed in a glass microslide (4 mm×10 mm), 400μm thick. The filling process to obtain a homeotropic alignment is the following: initially the microslide's temperature is maintained at about 20 °C; the lyotropic mixture is heated to 30 °C (N_D phase) and is introduced in the microslide only to wet the inner glass surfaces; after that, the sample is introduced in the microslide by means of a strong flow and the ends are closed with Parafilm. The sample is left at rest for about 30 min at 30° C and a perfect homeotropic alignment is obtained. The microslide is then placed in a temperature controlled device allowing a magnetic field of 400 G (permanent magnets) to be applied, with the geometry sketched in Fig. 1.

The angles between $\mathbf{H}$ and the x axis were 10° and 30° in two independent experiments. The device is then placed in an INSTEC (HS1-i) hot stage which allows an accuracy in the temperature measurements of 2×10^{-2} °C. The measurements of the optical birefringence were made by means of a Leitz microscope with a Berek tilt compensator. Initially, without $\mathbf{H}$, the conoscopic figure observed in the microscope is the classical uniaxial cross with $\mathbf{n}$ parallel to the light propagation direction. After the application of $\mathbf{H}$ and when the steady state has been reached, hyperbolas appear and the optical path difference can be measured as a function of T.

To minimize the errors in the determination of the optical path difference, a series of five independent measurements were made at each temperature, and a mean value was calculated.
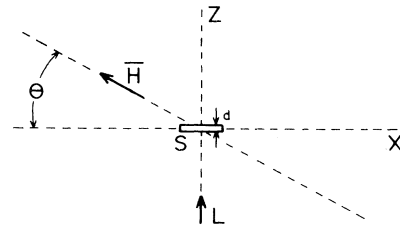

FIG. 1. Sketch of the experiment: S is the sample of thickness d, $\mathbf{H}$ is the magnetic field, L is the direction of the light propagation, and Θ is the angle between $\mathbf{H}$ and the x direction.

V. RESULTS AND DISCUSSION

It can be shown [27] that when the monochromatic light beam reaches a uniaxial NLC slab of thickness d with an angle ϕ between $\mathbf{n}$ and the light propagation direction, the optical path difference Δ, in the limit of small birefringence, is given by

$$\Delta = \frac{1}{2} d n_o \left(1 - \frac{n_o^2}{n_e^2} \right) \sin^2 \phi, \qquad (28)$$

where n_o and n_e are the ordinary and extraordinary refractive indices.

The tilt angle in the bulk $[\phi_b(T)]$ can be calculated using the measured $\Delta(T), n_o(T)$, and $n_e(T)$ by means of the equation

$$\phi_b(T) = \arcsin \sqrt{\frac{2\Delta}{d\nu n_o}}, \qquad (29)$$

where $\nu = 1 - (n_o/n_e)^2$. We measured $\Delta(T)$ using the setup described in the previous section and the values of $n_o(T)$ and $n_e(T)$ were taken from the literature [28].

Figure 2 shows the experimental results of ϕ_b calculated using Eq. (29), as a function of the temperature T. The error in ϕ_b is of the order of 5%. In this experiment, $\Theta = 30°$, as discussed in Sec. IV. As previously observed in thermotropic NLC's [3], ϕ_b increases as T approaches T_c.

To be sure that the ferrofluid doping does not alter the measurement of $\phi_b(T)$, we did the same experiment with a ferrofluid concentration two times greater. The values of $\phi_b(T)$ obtained exhibited the same behavior, and a variation smaller than 5% in the absolute values has been shown. The same Fig. 2 shows also a reasonable fit of Eq. (6) to the experimental values. In this fit we use $T_c = 45°C$ and $\phi_e = \Theta = 30°$. The parameters

FIG. 3. Temperature behavior of the ratio $K_{13} = k_{13}/k$, evaluated by means of the parameters of the best fit of Fig. 2 and using Eq. (7). $\Theta = 30°$.
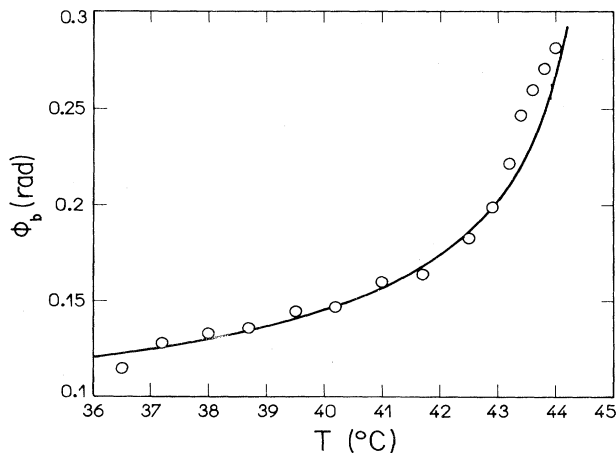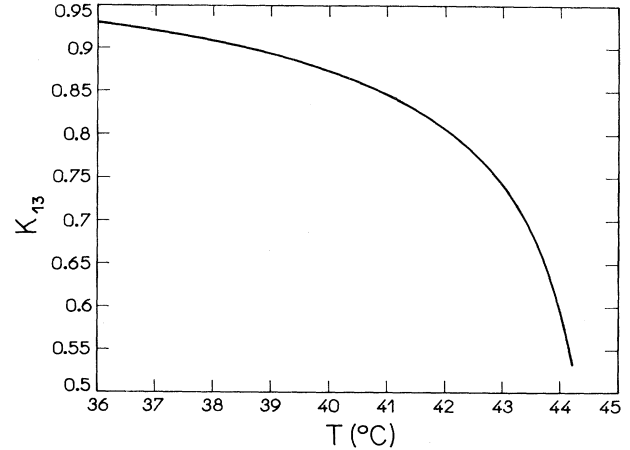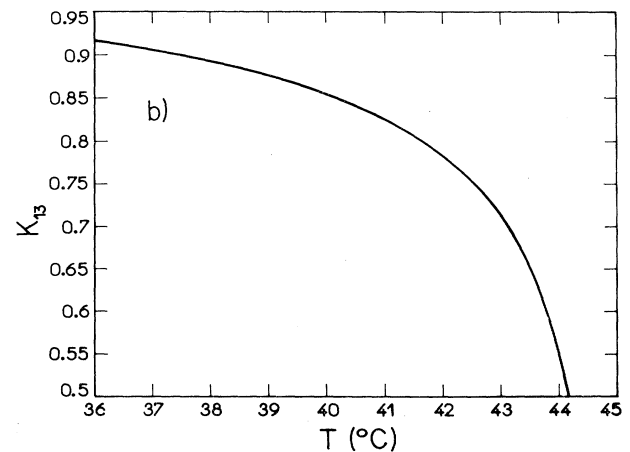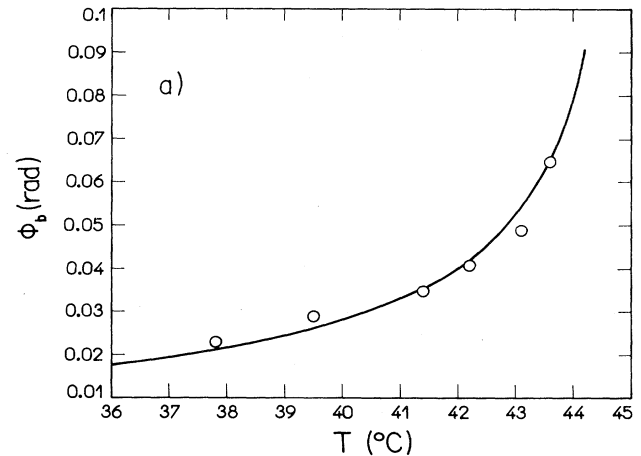

FIG. 2. Experimental results of ϕ_b as a function of temperature for a lyotropic NLC. The full line is the best fit obtained by means of Eq. (6).

FIG. 4. (a) ϕ_b as a function of T. $\Theta = 10°$. (b) K_{13} as a function of T. $\Theta = 10°$.

of the best fit were $c_1/k_2 = -6.5 \times 10^{-2}$ and $c_2/k_2 = 1.1$. Using these parameters $K_{13} = k_{13}/k$ is calculated through Eq. (7). The value of δ was obtained from the literature [28], evaluating S at $T = 296$ K, and we found $\delta = 0.858$

Figure 3 shows the values of K_{13} as a function of the temperature T. As observed in thermotropic NLC's [3], $c_1/k_2 < 0$, $c_2/k_2 \sim 1$, and $K_{13} \sim 1$ and positive.

The same experiment was done with $\Theta = 10°$. The corresponding results for ϕ_b and K_{13} versus T are shown in Fig. 4. The results for $\Theta = 10°$ and $\Theta = 30°$ are very similar, indicating that the experimental values of K_{13} are independent of Θ in the range from $10°$ to $30°$.

For a nearly homeotropic NLC sample, theoretical models [29,30] based on the induced dipole–induced dipole interaction predict $K_{13} = -1.2$. The lyotropic NLC is constituted by micelles, i.e., anisotropic aggregates of amphiphilic molecules. X-ray scattering experiments [31] performed with the lyotropic mixture of potassium laurate, decanol, and water showed that the distance between the micellar surfaces in the direction perpendicular to the amphiphilic bilayers is about 23 Å, the repeating distance is 48.8 Å, and the bilayer is about 26 Å thick. Due to the presence of ions and of a counterion layer at the micellar surfaces, water molecules may be attracted to this nonrigid structure. In this picture, we expect that the steric forces are very important to stabilize the NLC phase. This fact could be one of the reasons behind the difference between the experimental results of K_{13} and the theoretical prediction, based only on the dispersion forces. On the other hand, as lyotropic systems are very complex, it is not possible to conclude from this experiment that dispersion interactions are insignificant, compared to steric interactions. Experiments of the kind described above may give information only about the effective splay-bend elastic constant appearing in Eq. (26). Our technique does not allow us to separate $\gamma(\phi_0)$ from k_{13}. This is evident from the fact that by means of our optical method only ϕ_b can be detected, whereas ϕ_0 is known from the anchoring treatment. However, according to our point of view, it is not necessary to separate k_{13}^{eff} in $\gamma(\phi_0)$ and k_{13} for the following reasons. As has been shown in Sec. III, the uniform parts of f and of the k_{13} elastic term are responsible for the subsurface distortion. Such a distortion is localized over a surface layer whose thickness is of the order of ρ_0, and the range of the intermolecular forces responsible for the NLC phase. It follows that in this surface layer an elastic description is no longer valid. Consequently, from a phenomenological point of view, it is enough to characterize the distorting effect connected with the presence of the surface with a new parameter, which is k_{13}^{eff}. This is just the parameter determined in our experiment. We underline that to separate γ from k_{13} is meaningless, because this implies that an elastic description is valid also in the boundary layer. But we know that this is not the case, because in that region a finite deformation over a mesoscopic length occurs.

VI. CONCLUSION

We have extended the elastic model proposed to interpret the temperature surface transitions in NLC's. From the theoretical point of view, it has been shown that the uniform part of the anisotropic contribution to the free energy density introduces a subsurface "discontinuity." This can be interpreted as a renormalization of the effective splay-bend elastic constant. From the experimental point of view, the temperature dependence of the effective splay-bend elastic constant for a lyotropic NLC has been determined by means of optical methods. The order of magnitude and the sign of this ratio for the lyotropic NLC used in our investigation are in agreement with the ones found in some thermotropic NLC's.

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