Micellar shape anisotropy and elastic constants in discotic lyotropic liquid crystals

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The elastic constants of a discotic lyotropic nematic liquid crystal are calculated by means of a pseudomolecular approach as functions of the micellar shape anisotropy. By assuming that the temperature dependence of the ratio of the elastic constants comes from the temperature dependence of the micellar shape anisotropy, the theoretical predictions are connected with experimental measurements for the ratio K_{33}/K_{11}. This procedure permits one to determine, in a phenomenological way, the temperature dependence for the ratio of elastic constants and for the micellar shape anisotropy near the nematic-isotropic transition in agreement with the experimental data. [S1063-651X(99)15410-2]

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Lyotropic nematic liquid crystals (NLC) are formed by mixtures of amphiphilic molecules [1] and a solvent (usually water), under convenient temperature and concentration conditions. The basic units of these systems are anisotropic micelles [2]. Under concentration change, or temperature change, the system can exhibit two uniaxial phases and one biaxial phase [3]. In the temperature-concentration phase diagram, the biaxial phase appears to be an intermediate phase between the uniaxial ones. The uniaxial nematic phases are known as discotic (N_d), and calamitic (N_c), depending on their magnetic anisotropy [2]. For what concerns the elastic properties of a NLC, one of the fundamental aspects of the research is the determination of the Frank elastic constants. For a distorted NLC the spatial variations of the director are small over molecular dimensions and a continuum elastic theory can be applied. In the bulk of a NLC, in general, three basic types of distortions can occur: splay, twist, and bend. These distortions are associated with, respectively, the elastic constants K_{11}, K_{22}, and K_{33}. These elastic constants have been the object of extensive experimental and theoretical studies especially when dealing with thermotropic NLC. An important parameter in this study, in compounds with a rigid molecular structure, is related to the molecular length-to-width ratio [4].

Experimental results concerning lyotropic systems [5] show that the shape anisotropy of the micelles varies according to the composition and temperature. The micellar shape anisotropy (R) is defined as the ratio between the micellar diameter and the bilayer thickness. Its variation in a discotic nematic phase as a function of the temperature was determined in order to investigate a similar behavior of the orientational order parameter [6]. In this direction, it can be very instructive to investigate the dependence of the elastic constants on the anisotropy in the micellar shape of a lyotropic medium. In the literature [7], very few investigations have been reported on the elastic constants associated with the lyotropic systems. In particular, Haven, Armitage, and Saupe [8] have carried out precise measurements on the ratio of the elastic constants K_{33} and K_{11} as a function of the temperature for the discotic mixture of the decylammonium chloride (DACl), obtaining values comparable to those determined in nematic thermotropics.

From the theoretical point of view, a molecular approach to evaluating the micellar shape anisotropy dependence of the bulk elastic constants in a discotic nematic has recently been utilized by using the Maier-Saupe interaction law [9,10]. In that approach, the value for the ratio of the elastic constants K_{33}/K_{11} was determined as an increasing function of the parameter R. The tendency and the order of magnitude of the ratio of elastic constants was found to be in reasonable qualitative agreement with some available experimental results and with some calculations for thermotropics [11]. However, in that calculation, the value for this ratio was limited to a saturation value $K_{33}/K_{11}=2$, thus preventing a broad comparison with other experimental data.

In this paper we apply the molecular approach to calculate the elastic constants as a function of the micellar shape anisotropy keeping in mind a lyotropic nematic phase whose micelles are in the shape of a disk. We consider a special kind of interaction law which is a mixing between the Maier-Saupe and Nehring-Saupe interaction laws [12,13]. For this interaction law the ratios between the elastic constants are not limited to these relatively small values for lyotropic NLC. Furthermore, we use the experimental data of Ref. [8] to obtain a phenomenological dependence of the ratio of the elastic constants as a function of the temperature, by assuming that this dependence comes from the temperature dependence of the micellar shape anisotropy.

To determine the elastic constants of a discotic lyotropic we employ the pseudomolecular approach, which is an approximate technique used to determine the macroscopic properties of the system from the intermolecular interaction giving rise to the nematic phase [14–16]. In this approximated method the elastic energy density can be written as

$$f = f_0 + L_{ik} n_{i,k} + N_{ijk} n_{i,jk} + M_{ijkm} n_{i,k} n_{j,m}, \qquad (1)$$

where

$$L_{ik} = \frac{1}{2} \int_{v'} q_i u_k r \, dv', \qquad (2)$$

$$N_{ijk} = \frac{1}{4} \int_{v'} q_i u_j u_k r^2 \, dv', \qquad (3)$$

and

$$M_{ijkm}=\frac{1}{4}\int_{v'}q_{ij}u_ku_mr^2\,dv' \qquad (4)$$

are elastic tensors. In the above expressions,

$$q_i=\left(\frac{\partial g}{\partial n'_i}\right)_{\vec{n}'=\vec{n}} \quad \text{and} \quad q_{ij}=\left(\frac{\partial^2 g}{\partial n'_i\,\partial n'_j}\right)_{\vec{n}'=\vec{n}}. \qquad (5)$$

The derivatives of the interaction energy $g(\vec{n},\vec{n}',\vec{r})$ are evaluated on the reference state, and the summation convention is assumed. Furthermore, $\vec{u}=\vec{r}/r$, and hence $x_k=u_kr$.

The integrations are performed over the interaction volume. Since the micelles we are considering are disklike, we consider in the calculations an interaction volume in the shape of a disk. In assuming an interaction volume of this form we suppose that the interaction energy $g(\vec{n},\vec{n}',\vec{r})$ is different from zero in the region limited by two similar disks, whose inner part coincides with the micellar volume, and the outer part is defined by the long range part of the intermolecular interaction. For simplicity, the two disks are supposed to be similar, having the same shape anisotropy, $R=2a/d=2A/D$, where a and d refer to the inner (micellar) volume, whereas A and D refer to the outer volume. The bilayer thickness d is supposed to remain essentially independent of the temperature, according to the experimental results [6].

We will consider an intermolecular interaction in the mixed form [12,13]

$$g(\vec{n},\vec{n}',\vec{r})=-\frac{C}{r^6}[\vec{n}\cdot\vec{n}'-3\epsilon(\vec{n}\cdot\vec{u})(\vec{n}'\cdot\vec{u})]^2, \qquad (6)$$

where we have introduced a mixing parameter ϵ, such that for $\epsilon=0$ the interaction is reduced to the Maier-Saupe law [10]

$$g_{MS}=-\frac{C}{r^6}(\vec{n}\cdot\vec{n}')^2, \qquad (7)$$

whereas for $\epsilon=1$ it is reduced to the Nehring-Saupe law [14]

$$g_{NS}=-\frac{C}{r^6}[\vec{n}\cdot\vec{n}'-3(\vec{u}\cdot\vec{u}')(\vec{u}\cdot\vec{n})]^2. \qquad (8)$$

In the above expressions we have assumed perfect nematic order, i.e., we assume that the scalar order parameter $S=1$.

The details of the calculations of the elastic constants as functions of the eccentricity of the micellar (molecular) volume can be found in Ref. [13]. To obtain the elastic constants as a function of the micellar shape anisotropy one has to perform the integrations over an interaction volume of discotic shape, characterized by a shape anisotropy R. To perform the integrations in order to evaluate the elements of

the elastic tensors, we choose the z axis of the coordinate system along $\vec{n}$. In cylindrical coordinates $x=\rho\cos\theta$, $y=\rho\sin\theta$, and z, we have

$$u_1=\frac{x}{r}=\frac{\rho\cos\theta}{r}, \quad u_2=\frac{y}{r}=\frac{\rho\sin\theta}{r}, \quad u_3=\frac{z}{r}, \qquad (9)$$

and hence $N=\vec{n}\cdot\vec{u}=z/r$, where $r=\sqrt{\rho^2+z^2}$. In the calculations we need to evaluate integrals of the type [13]

$$I=\int_{v'}f(\rho,\theta,z)\rho\,d\rho\,d\theta\,dz, \qquad (10)$$

with $f(\rho,\theta,z)$ a continuous function of the variables. It is convenient to put the integrations in the form

$$\begin{aligned}
I&=\int_{v'}f(\rho,\theta,z)\rho\,d\rho\,dz\\
&=\int_0^{2\pi}d\theta\left\{\int_{-D/2}^{D/2}dz\int_0^A f(\rho,\theta,z)\rho\,d\rho\right.\\
&\quad\left.-\int_{-d/2}^{d/2}dz\int_0^a f(\rho,\theta,z)\rho\,d\rho\right\}, \qquad (11)
\end{aligned}$$

which is simply the integral over the outer volume minus the integral over the inner (micellar) volume of the same functions of Ref. [13], now in a cylindrical geometry. The integrations are easily performed and yield the following ratio for the elastic constants:

$$\frac{K_{33}}{K_{11}}=\frac{p_{31}}{q_{31}}, \qquad (12)$$

where

$$\begin{aligned}
p_{31}=4[&R(32(1+R^2)^2(1+2R^2)\\
&-48\epsilon(1+8R^2+11R^4+4R^6)\\
&+3\epsilon^2(3+136R^2+141R^4+48R^6))\\
&+(32-48\epsilon+9\epsilon^2)(1+R^2)^3\arctan(1/R)],
\end{aligned}$$

$$\begin{aligned}
q_{31}=[&R(64(1+R^2)^2(3+2R^2)-128\epsilon(3+8R^2+9R^4+4R^6)\\
&+9\epsilon^2(21+56R^2+123R^4+48R^6))\\
&+3(64-128\epsilon+63\epsilon^2)(1+R^2)^3\arctan(1/R)]. \qquad (13)
\end{aligned}$$

Let us consider first the case $\epsilon=0$, which corresponds to the Maier-Saupe interaction. In this limit we obtain

$$\frac{K_{33}}{K_{11}}=\frac{2(R+2R^3+(1+R^2)\arctan(1/R)}{R(3+2R^2)+3(1+R^2)\arctan(1/R)}. \qquad (14)$$

In the other limit, for $\epsilon=1$, which corresponds to the Nehring-Saupe interaction, we obtain

$$\frac{K_{33}}{K_{11}} = \frac{4(7R - 152R^3 - 55R^5 - 16R^7 + (7 + 21R^2 + 21R^4 + 7R^6)\arctan(1/R)}{3R + 8R^3 - 403R^5 - 48R^7 + (3 + 9R^2 + 9R^4 + 3R^6)\arctan(1/R)}. \tag{15}$$

These results indicate that the ratio of the elastic constants is an increasing function of the micellar shape anisotropy [9], but it tends to a saturation in both cases (see Fig. 1). In fact, when we consider $R \to \infty$, we obtain

$$\frac{K_{33}}{K_{11}} = \frac{4(2 - 3\epsilon)^2}{8 - 32\epsilon + 27\epsilon^2}, \tag{16}$$

and the saturation value obviously depends on the mixing parameter ϵ. For $\epsilon = 0$, $K_{33}/K_{11} = 2$, whereas for $\epsilon = 1, K_{33}/K_{11} = 4/3$. Of course, very high values for R make no physical sense. However, as we will discuss below, in order to account for the experimental values of the ratio K_{33}/K_{11} in a discotic phase, the saturation value obtained in the above calculation cannot be restricted to the interval $4/3 \leq K_{33}/K_{11} \leq 2$. To account for these experimental data we consider the results for the interaction law having a mixing parameter $\epsilon = 0.35$. For this value, the predicted saturation value for the ratio $K_{33}/K_{11} \approx 33.6$. It is important to stress again that the ''pure'' Maier-Saupe interaction and the ''pure'' Nehring-Saupe interaction cannot furnish a ratio of this magnitude since, as stressed before, they have saturation values which are small when compared with the ones experimentally found.

Our procedure to obtain the trend with temperature for the ratio K_{33}/K_{11} is the following. We assume that the dependence of this ratio with the micellar shape anisotropy is given by Eqs. (12) and (13). From the experimental data of Ref. [8] we obtain the micellar shape anisotropy R for the corresponding value of the reduced temperature T/T_{NI}, where T_{NI} is the nematic-isotropic transition temperature. This result in turn furnishes the trend of K_{33}/K_{11} versus the reduced temperature as predicted by the theoretical calculation we have performed.

In [8] the splay and bend elastic constants have been measured, as a function of the temperature, for the mixture DACl, NH_4Cl, and water, in a nematic discotic phase. From these experimental data it is possible to obtain the ratio K_{33}/K_{11}, studied by the authors, as a function of the temperature for two compositions: (mixture 1) DACl 7.00, NH_4Cl 2.53, and H_2O 90.40 mole %; this sample presents the following sequence of phases: neat soap, 35 °C, nematic, 55 °C, isotropic; (mixture 2) DACl 7.57, NH_4Cl 2.73, and H_2O 89.70 mole %; neat soap, 45.5 °C, nematic, 65.5 °C, isotropic. Their results show that in the vicinity of the neat soap phase the bend elastic constant diverges while the splay constant shows no critical behavior. Among the measured values for the ratio, the higher one is $K_{33}/K_{11} \approx 5.3$ for mixture 1 and $K_{33}/K_{11} \approx 19.3$ for mixture 2.

The ratio K_{33}/K_{11} versus the reduced temperature of the theoretical calculations (for a mixing parameter $\epsilon = 0.35$) and the experimental data for mixture 1 are shown in Fig. 2. The ratios, both experimental and theoretical, fall on the same curve. A similar behavior has been observed also for mixture 2. With this procedure we have obtained, in a phenomenological way, the dependence of the micellar shape anisotropy R on the reduced temperature for a nematic discotic phase. Furthermore, x-ray diffraction results [6], performed in a nematic discotic lyotropic mixture (potassium laurate, KL; 1-decanol-DeOH and D_2O, mixture 3) show that the temperature variations of the shape anisotropy and the orientational order parameter are similar within the experimental error. The bilayer thickness is found to remain independent of temperature and, in this lyotropic system, the nematic discotic exhibits a reentrant behavior. The connection between experimental and theoretical results for the ratios R versus reduced temperature are presented in Fig. 3. Note that, on coming from the nematic discotic to the isotropic phase, our results agree well with earlier measurements of the shape anisotropy on the mixture 3, particularly in the vicinity of the
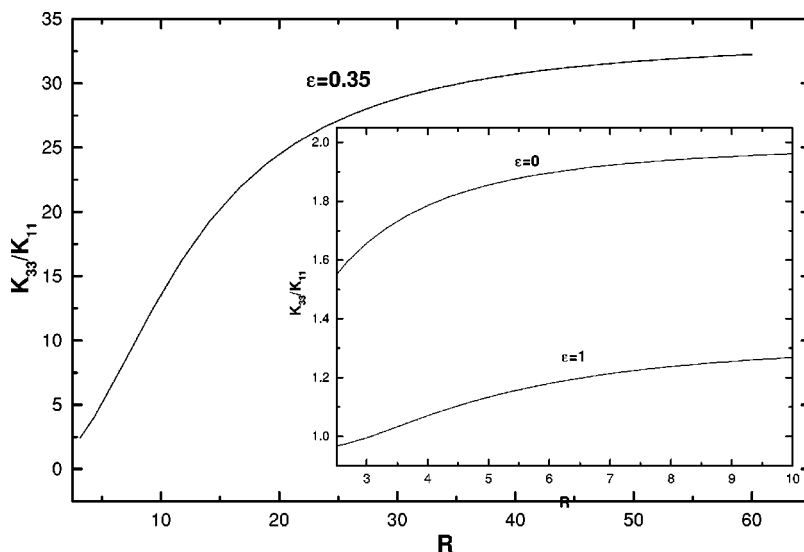

FIG. 1. Ratio of bend and splay elastic constant vs the micellar shape anisotropy R for distinct values of the mixing parameter ϵ [see Eq. (6)].
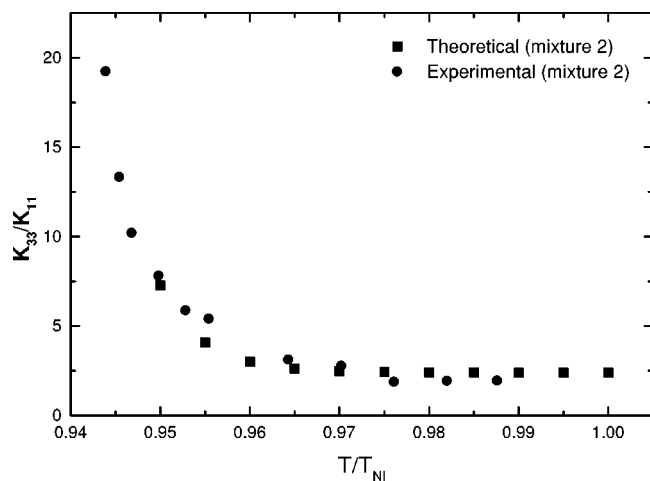
FIG. 2. Ratio of bend and splay elastic constant vs temperature for mixture 1 as predicted by this work. The experimental data comes from Ref. [8]. T_{NI} is the nematic-isotropic transition temperature.

FIG. 3. Trend of the micellar shape anisotropy R vs temperature. The curves for mixtures 1 ($\triangle$) and 2 ($\square$) come from our theoretical predicitions (best fits), whereas the curve for mixture 3 ($\diamond$) is based on the experimental result from Ref. [6].

nematic-isotropic phase transition. A more precise comparison between our theoretical calculations and the experimental data is difficult since there is little data available on the measurements of the shape anisotropy in lyotropic systems. The results show another interesting physical behavior since the temperature dependence of the ratio comes from the micellar shape anisotropy dependence on the temperature instead of the scalar order parameter dependence. In fact, the temperature dependence of the bulk elastic constants comes (approximated) from its quadratic dependence on the scalar order parameter. Therefore, this dependence is not decisive in the ratio of two bulk elastic constants of thermotropic NLC (it is particularly weak near the nematic-isotropic transition [17]). But the experimental data reported above for lyotropic NLC shows that 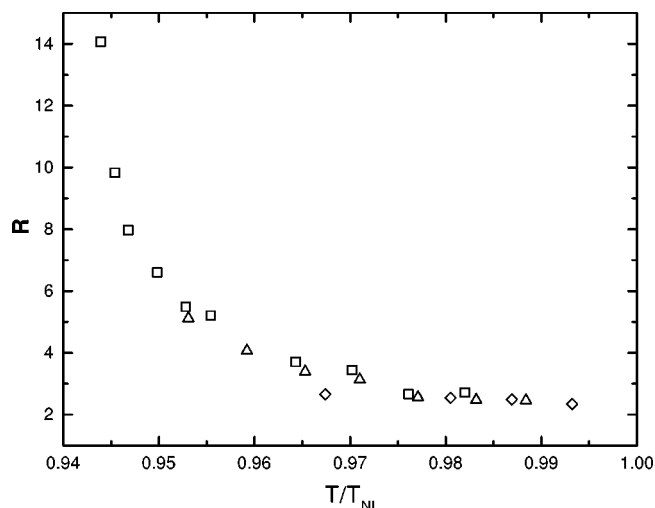this dependence exists and is also very strong. In this manner, it seems to be meaningful to consider that the temperature dependence for lyotropic NLC can be due mainly to the micellar shape anisotropy behavior with the temperature. Another important point to be considered here is the introduction of the mixing parameter ϵ on the intermolecular interaction law among micelles of the lyotropic medium, which seems to be the key of this study. The choice of $\epsilon = 0.35$ is just an indication that ''pure'' laws like the Maier-Saupe and Nehring-Saupe ones cannot account for the experimental results, and the mixed interaction has to be taken into account.

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