**Liquid Crystals**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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M. B. Lacerda Santos[a]; W. B. Ferreira[a]; M. A. Amato[a]
[a] Departamento de Física, Universidade de Brasília, Brasilia, DF, Brazil

**To cite this Article** Santos, M. B. Lacerda , Ferreira, W. B. and Amato, M. A.(1994) 'Micellar fluctuations in a calamitic nematic phase of a lyotropic liquid crystal studied by photon correlation', Liquid Crystals, 16: 2, 287 — 298
**To link to this Article: DOI:** 10.1080/02678299408029153
**URL:** http://dx.doi.org/10.1080/02678299408029153

LIQUID CRYSTALS, 1994, VOL. 16, NO. 2, 287–298

# Micellar fluctuations in a calamitic nematic phase of a lyotropic liquid crystal studied by photon correlation

by M. B. LACERDA SANTOS*, W. B. FERREIRA and M. A. AMATO
Departamento de Física, Universidade de Brasília,
70910 Brasília DF, Brazil

(*Received 12 July 1993; accepted 2 August 1993*)

Using a Rayleigh scattering light beating technique, we have made new measurements on the slow polarized fluctuations, previously identified as being of micellar origin, for a lyotropic system consisting of K-laurate, decanol, $D_2O$ and presenting only the uniaxial calamitic nematic ($N_C$) phase (from among the three known nematic types: uniaxial disk-like ($N_D$), calamitic ($N_C$) and biaxial ($N_B$) phases). An elaborated analysis of these data is made in order to clarify the relationship between the light scattering signals coming from the micellar fluctuations and those from (classical) orientational fluctuations. The main conclusions of this analysis are that the micellar mode is independent of the temperature and wave-vector, and that its relaxation frequency is substantially lower than that found previously for the same lyotropic components, but presenting the biaxial nematic phase. Finally, some considerations are made of the possible relationships between the micellar fluctuations and the structural properties of lyotropic nematics.

## 1. Introduction

Since the pioneering work of the Orsay Group [1], the occurrence of strong light scattering in nematic liquid crystals has become commonly associated with thermal fluctuations of the nematic director **n**. These long wavelength fluctuations are described in terms of two overdamped normal modes [2], with relaxation rates given by

$$\Gamma_i(q)=\frac{1}{\eta_i(\mathbf{q})}(K_i q_\perp^2+K_3 q_\parallel^2), \tag{1}$$

where $i=1$, (2) denotes the fluctuation mode with $\delta\mathbf{n}$ parallel (normal) to the plane defined by **n** and the scattering wavevector **q**. $K_1$, $K_2$ and $K_3$ are the Frank elastic constants characterizing the splay, twist and bend deformations, respectively. $\eta_1(\mathbf{q})$ and $\eta_2(\mathbf{q})$ are the effective viscosities associated with the modes 1 and 2, and the wave-vector components $q_\perp$ and $q_\parallel$ are defined with respect to **n**.

Besides these vector-type fluctuations, scalar fluctuations may also become important, as in the classical case of pretransitional effects in the isotropic phase [3], near to the isotropic–nematic transition.

The picture summarized above is very satisfactory for thermotropic nematics, but the situation is more complex for lyotropic nematics. These systems are constituted by micelles, which are surfactant aggregates dispersed in water. Three types of nematic phase occur with lyotropic systems: the uniaxial $N_C$ (calamitic), $N_D$ (disk-like) [4] and $N_B$ (biaxial) [5] phases.

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* Author for correspondence.

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Indeed, lyotropic nematics present a far richer variety of thermal fluctuation phenomena causing light scattering than thermotropic nematics. One aspect of these new phenomena appears when the $N_B$ phase is present in the system under study [6, 7]. Another aspect, that concerns us here, comes in connection with the slow branch of fluctuations with a lifetime of 0·1 s or more, that were found some years ago [7] for the lyotropic system K-laurate, decanol, $D_2O$. These fluctuations give rise to a strong polarized light scattering signal, and have been assigned to a micellar origin [7].

The measurements from [7] refer to all kinds of fluctuation modes, ranging through large intervals both in frequency (time) and temperature. In such an exploratory survey, the micellar mode appears merged with the scalar and orientational fluctuations. These two types of collective or order–disorder fluctuations could be shown to be consistent with the predictions from a Landau–de Gennes model extended by the authors [7]. Although such a comparative study of the different modes could appear to be important for identification of the new mode, the measurements of [7] have shown that micellar fluctuations have a number of characteristic signatures that made such a process unnecessary. The strategy of the present work was to study the micellar fluctuations by isolating this effect as far as possible from other dynamical effects in lyotropic nematics.

By taking this approach one hopes to begin to understand a number of questions raised about micellar fluctuations in early work, such as: How do they behave with temperature and wavevector? What is the role of the biaxial nematic phase? By addressing such questions, we expect to contribute to an understanding of the fundamental problems concerning the formation and stability of lyotropic phases.

We therefore present in this paper new photon correlation measurements on the calamitic nematic ($N_C$) phase of the lyotropic system K-laurate, decanol, $D_2O$. In contrast with earlier work [7], the $N_B$ phase is absent in the system under study here. The measurements have been carried out in a specially designed microcomputer-based photon correlator [8]. This system, though not too fast, allows study of the slow branch of fluctuations, since it uses highly multibit storage channels in calculating the autocorrelation function. Furthermore, wavevector dependencies of the slow branch are presented for different temperatures through the $N_C$ range of the lyotropic sample.

The results obtained for the relaxation rates of the micellar fluctuations show no temperature dependence across the $N_C$ phase, agreeing with the previous referenced results. On the other hand, two new aspects will be discussed. First, the absence of the $N_B$ phase appears to make the slow micellar fluctuations still slower. Second, in our analysis for the wavevector dependence, or conclusion is at variance with earlier experiment [7], in which a weak $q$-dependence has been found. In fact, we show that this apparent dependence is caused by an artifact that is almost unavoidable in the experiment.

## 2. Experimental

The lyotropic phase was prepared by mixing potassium laurate (purified by recrystallization), 1-decanol (> 99 per cent, from Fluka) and $D_2O$ (Sigma) in the weight proportions 25·80 per cent, 6·20 per cent and 68·00 per cent, respectively. The mixture was sealed in a pyrex tube, homogenized by vigorous shaking combined with centrifugations and then left at rest for several weeks.

Before filling a light scattering cell, the lyotropic mixture was submitted to further centrifugation for one hour at 4000 rpm to sediment dust. Care was then taken to pipette the lyotropic phase from the upper part of the tube into the cell. This was a

Hellma cell made of two glass plates separated by a 1 mm thick glass spacer, the whole being assembled using a specially designed mounting system allowing high compression of the plates. This system practically eliminated water loss problems experienced before [7, 9]. All glass surfaces were previously thoroughly cleaned (with strong detergent) and rinsed in hot deionized distilled water.

The sample cell was placed with its plates horizontal in an oven in thermal contact with a circulating, controlled heat bath. The long term thermal stability (1 h) was 0·1°C and the sample temperature was measured with a chromel–constantan thermocouple.

This lyotropic mixture exhibits the calamitic (or cylindrical-like) nematic ($N_C$) phase in the temperature range 6·3°C to 48·5°C. At higher temperatures, the system exhibits a fluid milky phase, sometimes referred to as 'polyphasic' [10]. The low temperature phase is a viscous birefringent phase. We do not know its exact nature. Both high and low temperature phase transitions can be reversed in order to recover the $N_C$ phase.

A 6 in. magnet (Newport) was then moved into the sample oven and a horizontal magnetic field ($B$) (5 kG) applied for several hours. The $N_C$ phase has a positive diamagnetic anisotropy and the magnetic field parallel to the glass plates, combined with wall effects, results in a homogeneous alignment of the sample director $\mathbf{n}$ parallel to $\mathbf{B}$ (figure 1). The photon correlation measurements were made with the magnet moved out from the sample emplacement, but refreshment of the alignment procedure (reapplication of $\mathbf{B}$ during 2–3 h) was carried out each time the temperature was changed or alternatively no longer than 6 h after the last application of $\mathbf{B}$. The quality of the alignment, controlled by observation of the sample between crossed polarizers, was generally quite good, but surface defects remain at the level of the glass plates.

Figure 1 shows the scattering geometry. A He–Ne 35 mW laser (Spectra-Physics, mod. 127) beam directed along $\mathbf{k}_i$ crosses the sample cell making an (internal) angle of $\theta/2$ with respect to the glass plate normal, i.e. the $z$ axis. The direction of the scattered wavevector $\mathbf{k}_f$ is selected by an optical alignment procedure [9] that uses the reflected beam from the cell, resulting in a well-defined scattering plane ($y, z$). The direction of $\mathbf{n}$ is

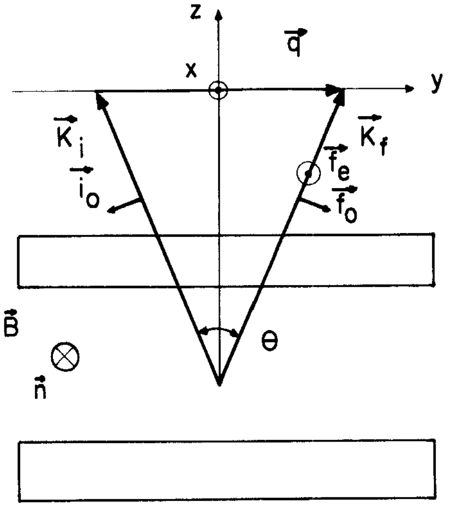


Figure 1. Scattering geometry: the nematic director $\mathbf{n}$ is normal to the scattering plane. $\mathbf{i}_o$: polarization vector of the incident laser beam. $\mathbf{f}_o$ ($\mathbf{f}_e$): polarization vector of the scattered beam in the polarized (depolarized) configurations.

perpendicular to the scattering plane. In fact **n** follows the direction of **B**, so it is parallel to the $x$ axis within an error of $\sim 2°$. As $|\mathbf{k}_i| \approx |\mathbf{k}_f|$, due to the low birefringence of lyotropic nematics ($\Delta n \sim 10^{-3}$), this results in **q** parallel to the $y$ axis. To calculate $|\mathbf{q}|$ one needs the (mean) refractive index. We used the value $n = 1{\cdot}38$, determined for a lyotropic mixture with similar concentrations [11]. The four values of $q$ used in the experiment were, in units of $10^6\,\mathrm{m}^{-1}$: $q_1 = 1{\cdot}00$, $q_2 = 2{\cdot}08$, $q_3 = 3{\cdot}49$ and $q_4 = 4{\cdot}44$.

The incident polarization vector $\mathbf{i}_o$ was made parallel to the scattering plane by a Nicol prism regulated to better than 0·5°. A polarizer sheet was used to define the polarization of the scattered beam parallel or perpendicular to the scattering plane for the ordinary ($\mathbf{f}_o$) and extraordinary ($\mathbf{f}_e$) polarizations, respectively according to a well-known selection rule [2], the ($\mathbf{i}_o$, $\mathbf{f}_o$), or simply the (o, o) configuration is the only one forbidden for orientational fluctuations, and thus it is used to detect other eventual contributions to the 'polarized' scattering (meaning the one in which input and output beams have the same polarizations), like micellar fluctuations. For the 'depolarized' configurations (only (o, e) has been used here); the geometry of figure 1, with $\mathbf{q}\perp\mathbf{n}$, provides optical coupling with mode 2 giving pure twist deformations. Thus, equation (1) turns out to be simply,

$$\Gamma_2 = \frac{K_2 q^2}{\gamma_1}, \tag{2}$$

where $\gamma_1$ ($\equiv \eta_{\mathrm{twist}}$) is the rotational viscosity coefficient [2].

The selected scattered light beam was collected through a pin-hole with opening area $A \ll A_c$, where $A_c$ is the coherence area [12], and then focused on to the photocathode of the photomultiplier tube (ITT, mod. FW-130). The whole optical set-up was assembled on a heavy bench floating on pneumatics to eliminate mechanical vibrations. Detailed information about our light beating spectrometer has been given elsewhere [13].

At the low angles used here ($\theta < 20°$), we always obtain a pure heterodyne signal, the 'local oscillator' probably being provided by the defects [7]. For the fundamental concepts of light beating spectroscopy we make reference to Berne and Pecora [12].

The output pulses of the photomultiplier are square-shaped by a pre-amplifier-discriminator (PAR-1182) and then sent to the photon correlator. A detailed description of our software correlator has been published [8]. It uses 14 bit registers, which turn out to be more suitable for handling with slow signals (< 10 Hz) than conventional 4-bit correlators. Indeed, such large registers prevent attenuation of the optical signal during long time-scales, allowing more rapid accumulation of the data.

Finally, the accumulated autocorrelation function was then fitted, according to the case, to a single or double exponential function [12] with a free baseline, i.e., the functions

$$y_1 = A_1 \exp(-t/T_1) + B,$$

with three adjustable parameters ($A_1$, $T_1$ and $B$), or

$$y_2 = A_1 \exp(-t/T_1) + A_2 \exp(-t/T_2) + B$$

with five adjustable parameters ($A_1$, $A_2$, $T_1$, $T_2$ and $B$). For the fits, we developed an adaptation for PC computers of a high performance 1- and 2-exponential program, originally conceived by Galerne [14] for the HP-9825 desk calculator. The quality of the fit was checked by comparing the data and the adjusted curve graphically in each case.

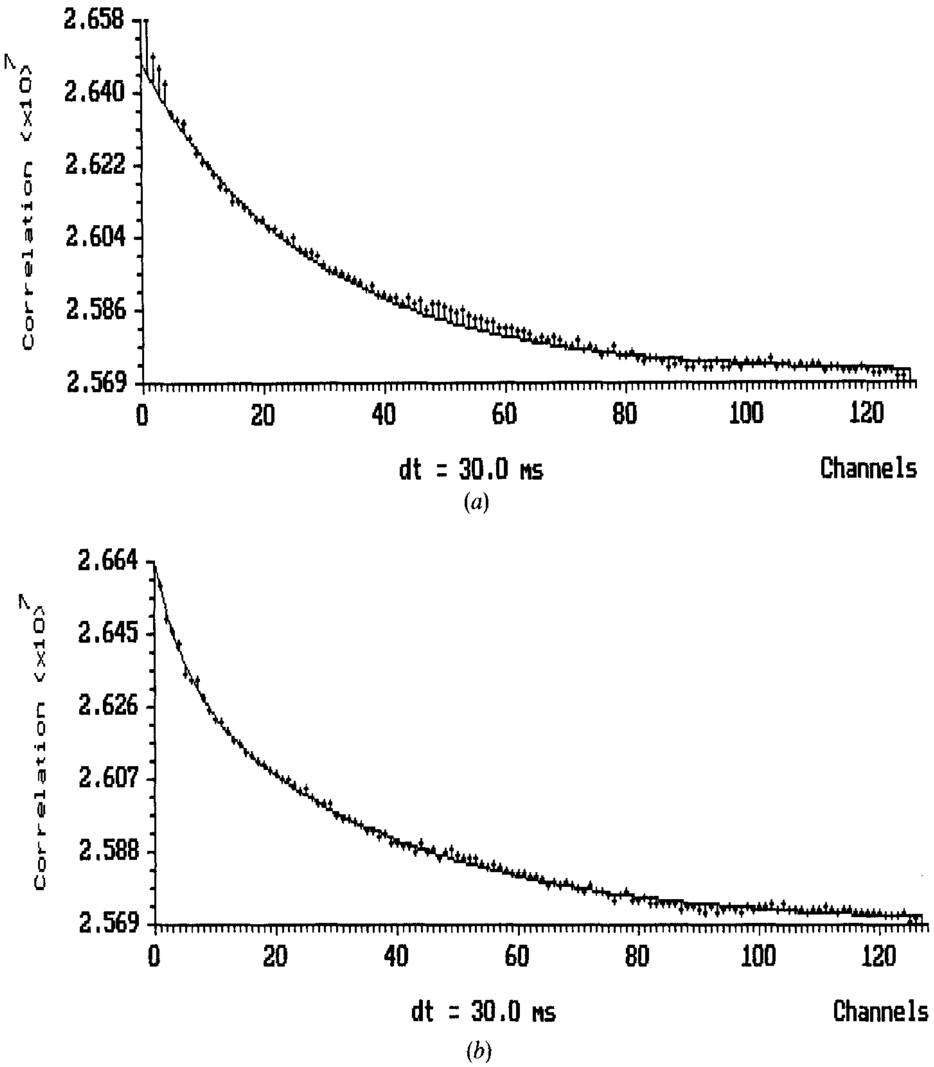
Now we discuss briefly the main experimental difficulties, i.e. those which tend to limit the precision of the measurements. (i) *Sample alignment*: Even though the bulk alignment is good, there remain the surface defects mentioned above. We recall that this problem comes about due to the absence of the $N_D$ (and $N_B$) phase, in which sample alignment is easier [7]. However, this source of error seems not to be very important. (ii) *Convective instabilities*: The tendency of these lyotropic nematic systems to become unstable is remarkable and has been detected in earlier Rayleigh scattering experiments [9]. We shall return to this question when analysing the data, in § 3. Some precautions were taken to minimize such effects: maintaining the horizontal positioning of the sample cell; avoiding excessive laser power and mechanical perturbations of the sample; waiting a long time for stabilization after any thermal perturbation; keeping the thermal isolation of the sample as good as possible. This last point was limited in our light scattering experiment in which one desires to have optical access to the sample at several angles. Although more involved experimental solutions could be tried (windows, etc.), the complete elimination of these instability effects seems to be difficult. From an estimate made in [9], one can deduce that small temperature gradients, about $\sim 10^{-2}$ °C across the 1 mm of the cell thickness can be responsible for onset of the instability under the most favourable case, that is, the one in which the cell is positioned horizontally, as explained above. (iii) *Chemical Stability*: By its very nature, accumulation of the photon correlation signals in the slow branch consumes much time. On the other hand, in spite of the elimination of the water loss, this lyotropic system is known [15] to have limited chemical stability; this causes small changes in the sample composition, affecting its physical properties (for example, $T_c$ drifts). Hence, the measurements presented in this paper (all using a single sample), comprising both wavevector and temperature runs, were confined to a period of three days.

## 3. Methodology of analysis and results

Figure 2 shows one autocorrelation function signal obtained from the experiment in the (o, o) configuration. This example illustrates a recurrent feature of the experiment, namely, the presence of a weak short time component superimposed on the intense slow decaying signal. This feature becomes clear when one compares the 1- and 2-exponential fits for this signal (figures 2 (*a*) and (*b*), respectively). What is the meaning of two relaxation times in the (o, o) signal? Before answering this question, remember that the (o, o) configuration is a forbidden selection rule for orientational (or vector-type) fluctuations [2]. For lyotropic nematics, [7] explains the appearance of a strong (o, o) signal in terms of slow micellar fluctuations. However, a second (o, o) signal would appear to be rather troubling.

A plot of the relaxation rates $\Gamma$ (inverse of the characteristic times) versus the square of the scattering wave-vectors ($q^2$) helps us to understand the situation. Figure 3 illustrates this plot for a fixed temperature (43·4°C). The open squares (□) come from the short time components and the (×)s from the long time components of the (o, o) data. The solid squares (■) are the relaxation rates from depolarized (o, e) data corresponding here, as explained in § 2, to the twist fluctuations. The straight lines passing through the origin are the best fits for the (o, e) data (solid line) and the short time component of the (o, o) data (dashed line) according to equation (2).

The identification of both results is reasonable, within experimental error. So, we conclude that the short time component is simply a leakage signal in the (o, o) configuration from the strong depolarized signal of the twist fluctuations. The reasons for this are in part due to errors in polarization and also in sample alignment, errors



(*a*)

(*b*)

Figure 2. Typical photon correlation signal adjusted with (*a*) one exponential, $A1 = 7{\cdot}598 \times 10^5$, $T1 = 8{\cdot}4\| \times 10^{-1}$ s and $B = 2{\cdot}571 \times 10^7$; (*b*) two exponentials, $A1 = 2{\cdot}707 \times 10^5$, $T1 = 1{\cdot}364 \times 10^{-1}$ s, $A2 = 6{\cdot}2802 \times 10^5$, $T2 = 1{\cdot}02 \times 10^{0}$ s and $B = 2{\cdot}569 \times 10^7$.

which can either be simply statical or originate from coupling between the nematic director and (spurious) velocity gradients in the sample, caused by the instabilities discussed in § 2. We shall return to this point later.

Thus, we can use these secondary results arising from our data to extract from the two straight lines of figure 3 an average value for the twist diffusivity coefficient for the $N_C$ phase of our lyotropic system:

$$D_{\text{twist}} = K_2/\gamma_1 \approx (0{\cdot}67 \pm 0{\cdot}04) \times 10^{-12}\,\mathrm{m^2\,s^{-1}},$$

for the temperature $T_3 = 43{\cdot}4$°C. Although this value can change with temperature for the same sample, it is interesting to check its order of magnitude. To our knowledge, no previous determination of $D_{\text{twist}}$ for the $N_C$ phase has been made. However, $D_{\text{twist}}$ was

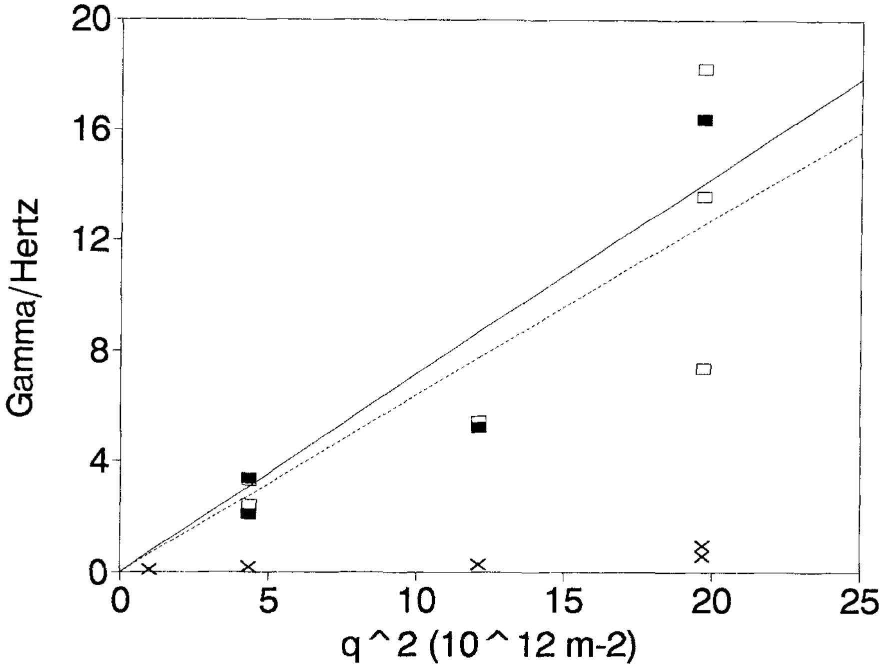


Figure 3. All data for $T=43{\cdot}4°C$: comparison between the relaxation rates (inverse of characteristic times) coming from the short time component of the polarized signal (□) and those from the depolarized signal (■), due to twist fluctuations. The long time components of the polarized signals ( × ) are also shown for comparison. Curves: best fits with straight lines constrained to pass through the origin for (■) (solid line) and for (□) (dashed line).

determined [11] for the $N_D$ phase, at room temperature, as $1{\cdot}6\times10^{-12}\,m^2\,s^{-1}$. The comparison is pertinent as $D_{twist}$ is expected to have similar dynamical behaviour (lack of backflow effects [11]) for both $N_C$ and $N_D$ phases. Copic *et al.* [16], have done light scattering measurements with a different lyotropic system. For the $N_D$ phase, they obtained $D_{twist}$ values ranging from $0{\cdot}4\times10^{-12}\,m^2\,s^{-1}$ to $1{\cdot}0\times10^{-12}\,m^2\,s^{-1}$, according to the temperature. Therefore change of composition appears not to cause any drastic change in the behaviour of orientational fluctuations of a given character. On the other hand, the last two quoted references [11, 16] show dramatic effects when one compares $D_{twist}$, $D_{splay}$ and $D_{bend}$ for the same sample.

To conclude the discussion of figure 3, the remaining low frequency components constitute therefore the micellar mode which we seek; these components, represented by the ( × )s, are not on an appropriate scale and are simply for comparison.

Let us now concentrate on the discussion of the micellar mode. After making the same considerations of figure 3 for other temperatures, we made a separate plot (see figure 4) for the micellar relaxation rates at the four different temperatures, namely, $T_1=24{\cdot}4°C$, $T_2=33{\cdot}2°C$, $T_3=43{\cdot}4°C$ and $T_4=48{\cdot}7°C$. Notice first that if one ignores the three ‘anomalous’ higher frequency points, the others show, within experimental error, no dependence either on temperature or in wavevector. This means that the micellar fluctuations for this lyotropic system have the relaxation rate,

$$\Gamma_{micellar}\approx(0{\cdot}2\pm0{\cdot}1)\,Hz.$$

Before justifying the abandonment of these three points, it appears important to point out that the poor precision of the two plots in figures 3 and 4 are not caused by bad correlation signals. On the contrary, most of the data presented here comes from autocorrelation functions of a quality comparable to that shown in figure 2.

Two relevant reasons for the dispersion of the slow branch photo-correlation data are: (1) the presence of instabilities; (2) the signal leakage already explained, which yields the two component signals.

The origin of problem (1) has already been commented upon in § 2. The existence of a propagative mode, due for instance to a convective instability, leads to a cosinus photon correlation function. In spite of the efforts reported in § 2 to minimize such effects, propagative components appear, to a greater or lesser degree, superimposed on virtually all autocorrelation functions obtained in the experiment. As an illustration of that, a small cosinus-like component may just be seen on the data of figure 2 (inspection at a low or glancing angle helps to visualize the oscillations), with a period ($T$) corresponding to 50–60 channels, i.e. $T = 1{\cdot}7 \pm 0{\cdot}1$ s. In order to make an estimate, let us recall that, by the theory of Laser Doppler Anemometry [12], this period is related to the characteristic velocity $v$ of the flow by

$$2\pi/T = \mathbf{v} \cdot \mathbf{q}. \tag{3}$$

In a study [9] that made use of the $N_D$ phase in the same lyotropic system, the convective instability has been dramatically reinforced by simply standing the sample cell with its glass plates parallel to the vertical. Then, by varying the magnitude of the

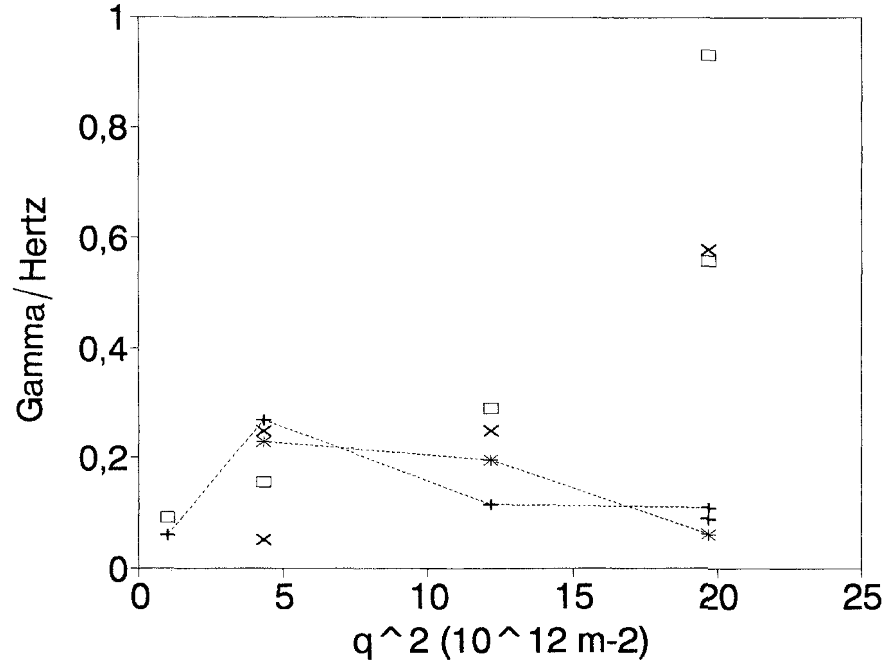


Figure 4. Micellar mode, detected by polarized scattering, at temperatures: $T_1 = 24{\cdot}4°C$ (+), $T_2 = 33{\cdot}2°C$ (*), $T_3 = 43{\cdot}4°C$ (□), and $T_4 = 48{\cdot}7°C$ (×). The data corresponding to the higher wavevector and temperature values are 'attracted' to the high frequencies by the leakage from the strong depolarized signal of the twist fluctuations (see text). The lines are only guides for the eyes.

scattering wavevector **q**, and keeping the geometry with **q** parallel to the plates, the relation (3) could be verified, giving flow velocities ranging from $0{\cdot}1\,\mu\mathrm{s}^{-1}$ to $0{\cdot}5\,\mu\mathrm{s}^{-1}$.

In the case of the autocorrelation function of figure 2, the scattering geometry of figure 1 allows us to suppose that coupling is made within some segment of the convective cell giving flow along the $\pm y$ direction. Using the corresponding $q_4$ value, one obtains $v \approx 0{\cdot}8\,\mu\mathrm{s}^{-1}$, a value compatible with the ones quoted above.

At this point one may answer the following question: Why should these small, spurious instabilities be responsible for such important errors? The presence of propagative components generates two kinds of error: first, some distortion on the curve data; in many cases, as for the data of figure 2, the deviation from the expected one or two exponential functions is negligible. Second, and worst, is the misalignment of the sample, caused by the coupling between the nematic director and the velocity field gradients. Let us estimate the magnitude of this misalignment by equating [2] the viscous torque associated with the flow and the elastic torque associated with the softer distortion in the system. Taking $v \approx 0{\cdot}8\,\mu\mathrm{s}^{-1}$ and the cell thickness $e = 1\,\mathrm{mm}$, the viscous torque per unit volume is $\eta \nabla v \sim 0{\cdot}8 \times 10^{-4}\,\mathrm{ergs\,cm}^{-3}$, where we used $\eta \sim 0{\cdot}1$ poise. The elastic torque associated with the mode with $q = \pi/e \approx 30\,\mathrm{cm}^{-1}$ amounts to $Kq^2\,\delta\theta \sim 2 \times 10^{-4}\,\delta\theta\,\mathrm{erg\,cm}^{-3}$, for $K \sim 2 \times 10^{-7}$ dyne. By equating the two torques one gets $\delta\theta \sim 0{\cdot}4\,\mathrm{rad} \approx 23°$. Such a large deviation might be considered rather as an upper limit [17]. Nevertheless, the estimate is useful in clarifying why such good signals, in the sense of signal to noise ratio, give such disperse data on the plots.

Finally, let us consider the labelled reason (2) for the dispersion of the data, namely, the influence of the leakage signal. This is important in justifying the abandonment of the three anomalously high frequency points of figure 4, as they are in fact biased by the superposition with the twist relaxation rates, which assume high values at large wavevectors.

However, the following objection could be made: Why have only the high temperature (o, o) data been 'attracted' to the high frequencies? This follows as a consequence of the temperature dependence of the leaked depolarized signal due to twist fluctuations. Although the detailed measurement of this orientational mode is outside the scope of the present work, we have taken some punctual data, for the sample used here; these indicate that the $D_{\mathrm{twist}} = 0{\cdot}67 \times 10^{-12}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ value obtained from figure 3 for $T_3 = 43{\cdot}4°\mathrm{C}$, falls to as low as $0{\cdot}2 \times 10^{-12}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ for $T_1 = 24{\cdot}4°\mathrm{C}$. This important variation can be qualitatively understood recalling that

$$D_{\mathrm{twist}} = K_2/\gamma_1,$$

and that both $K_2$ and $\gamma_1$ are temperature dependent: $\gamma_1$ tends to increase with lowering $T$, while $K_2$, according to mean-field theories [18], varies as $S^2$, where $S$ stands for the nematic degree of order. In the present case, the dynamical measurements seem to indicate that $S(T_1) < S(T_3)$, but knowledge of the order parameter behaviour would require independent measurements (for example, birefringence versus $T$) on the same sample, and this has not been done.

This last consideration completes the argument for abandoning the three higher frequency points of figure 4 as artifacts, intrinsic to the experiment, and so difficult to eliminate.

As a final remark on the micellar fluctuation data, note that the temperature $T_4 = 48{\cdot}7°\mathrm{C}$ lies on the side of the so-called 'polyphasic' phase. However, apart from the presence of multiple scattering, no difference in the dynamical behaviour with respect to the $N_C$ phase (including that for twist fluctuations) has been noticed from the autocorrelation data. Probably this is a coexistence phase, and in close proximity to $T_c$, the $N_C$ phase is still dominant at $T_4$.

## 4. Discussion

Let us compare the three main features found here for the micellar mode, with those found in [7].

(1) *Lack of temperature dependence*: This feature is very remarkable from the data of [7], as the micellar relaxation rates assume a constant value, within experimental error, across the whole temperature interval comprising the three nematic phases $N_D$, $N_B$, and $N_C$. The only exception to this overall behaviour occurs very close to the $N_C$–isotropic phase transition (within ~ 2°C over the investigated temperature interval of 35°C) when some temperature effect occurs. This phase transition, however, is absent in the present system, as seen in § 2.

(2) *Lack of q dependence*: As noted, this result emerged only after the analysis that recognized the influence of the leakage signal from twist fluctuations (see § 3). A similar artifact, due to bend fluctuations (according to the scattering geometry with $\mathbf{q}\|\mathbf{n}$), might have influenced the data of [7] and probably caused the weak wavevector dependence obtained. Note that the absence of a diffusive component for the Rayleigh linewidth is more consistent with the high concentration of micelles in the scattering volume [12].

(3) *Low value of* $\Gamma_{\mathrm{micellar}}$: The approximately constant value of 0·2 Hz for the relaxation rate of the micellar fluctuations obtained here is about 15 times lower than the slower rate obtained in [7]. One can hardly explain such a large discrepancy based only on the small differences between the sample composition of [7] and that of the present work. In fact, as we have seen in § 3, the behaviour of $D_{\mathrm{twist}}$ suggests that the sample composition does not have dramatic effects on the dynamical properties. Therefore, we are led to raise the question as to whether this very low relaxation frequency of the micellar fluctuations is caused by the absence of the $N_B$ phase in the system. Below, we give an argument for that.

Let us consider the mechanisms that can originate slow micellar fluctuations. The possibility of association–dissociation of the micelles, discussed in [7], was useful in providing a simple model to explain the observed properties of the slow branch signal, namely, its polarization, bad optical coupling in the isotropic phase, and lack of temperature dependence. It is important to note, however, that other mechanisms could equally fulfil these requirements, as, for example, size and form fluctuations. Of course, questions concerning the microstructure can hardly be answered by Rayleigh scattering techniques—even the dynamical ones. More local probes, as provided by resonance [19] or fluorescence [20] techniques, should be used to tackle this interesting problem.

Even though we bear in mind the limitations of our technique for structural investigations, the existence of micellar fluctuations raises questions about their possible relationships with the microstructure and the phase transitions. One crucial question relates to whether the micellar aggregates differ in size and shape in the three nematic phases or are essentially the same, but arranged with different degrees of orientational order. The first structural studies [4] considered that the $N_C$ phase is formed by prolate micelles and the $N_D$ phases by oblate micelles. Recent studies [21] on the system K-laurate, decanol, $D_2O$, conduct the analysis of high resolution synchrotron X-ray data on the basis of an intrinsically biaxial micellar model. On the other hand, light scattering and magnetic birefringence studies on the same [22] and also a related system [23] present evidence that change in micellar shape drives the transitions from $N_D$ and $N_C$ to the isotropic (normal and re-entrant) phase.

All this apparently contradictory phenomenology, if confirmed, must be explained by any future model for lyotropic nematic systems. At this point one may however speculate about whether micellar fluctuations play a role in these structural problems. We recall that when the $N_B$ phase is present, biaxiality fluctuations [6, 7] appear in the neighbouring $N_D$ and $N_C$ phases. As the uniaxial–biaxial transition is approached, these fluctuations undergo a critical slowing down [6] towards some limiting relaxation frequency, say $\Gamma_0$, at $T_c$. For $q \rightarrow 0$ and for polarized scattering, the measured $\Gamma_0$ becomes unresolved from the micellar frequency, that is, the lowest frequency of the system. This value is 4 Hz from [6] and 3 Hz from [7], both results obtained for systems having the $N_B$ phase. Here, without the $N_B$ phase, this lowest frequency falls to 0·2 Hz. As we have seen for the orientational fluctuations, such a disparity can hardly be attributed to the slight differences in chemical composition involved.

Instead, recalling the above discussion about the mechanisms, one may think that higher frequency micellar fluctuations could be associated with small relative changes in the aggregation number of the micelle; this is consistent with the picture [21] of uniaxial–biaxial transitions without significant changes at the micellar level. Conversely, lower frequency micellar fluctuations would mean large fluctuations in the aggregation number, and eventually complete association–dissociation of the micelle. This could act as a precursor for transitions where micellar size intervenes (for example, N–I transitions [22, 23]). It might be interesting to test this hypothesis by returning to a system possessing the $N_B$ and isotropic phases (but keeping a similar methodology) and looking for some cross-over between the two regimes for the micellar fluctuations.

## 5. Conclusions

To summarize, we have performed dynamical Rayleigh scattering measurements, as a function of temperature ($T$) and wavevector magnitude ($q$), on the calamitic nematic ($N_C$) phase of a lyotropic mixture of K-laurate, decanol, $D_2O$ which does not produce the biaxial nematic phase ($N_B$). After an involved analysis to circumvent the problem of parasitic signals, we can stress the following conclusions concerning the relaxation rate ($\Gamma_{\text{micellar}}$) for the micellar fluctuations: $\Gamma_{\text{micellar}}$ is independent of $T$ and $q$, $\Gamma_{\text{micellar}} \approx 0{\cdot}2$ Hz, a result 15–20 times lower than those for the same lyotropic system possessing the $N_B$ phase [6, 7].

In addition, a subsidiary result concerning orientational fluctuations has been obtained, namely that the diffusivity coefficient $D_{\text{twist}}$ for the $N_C$ phase:

$$D_{\text{twist}} = 0{\cdot}67 \times 10^{-12}\,\text{m}^2\,\text{s}^{-1}.$$

In the discussion section we have considered the possible implications of the results on the micellar fluctuations for the structure of lyotropic nematic phases.

As a final comment concerning the experiment, we feel that the data presented in this paper allow us to make some progress in describing the slow micellar mode, in comparison with the original measurements of [7]. However, further improvements in the experimental techniques are necessary in order to achieve the same degree of precision as obtained, for example, for light scattering data from thermotropic nematics. An important challenge to overcome in order to accomplish this goal is to have a better control over the instabilities, which are easily demonstrated for the sample in these slow spectral ranges.

It is a pleasure to thank Professor M. M. Ventura and co-workers from the Biophysics Laboratory, Universidade de Brasilia, for their kind assistance with sample preparations. We are also grateful to Professor H. Gallardo from Santa Catarina University for providing us with purified K-laurate. W. B. F. thanks CNPq for a Junior (IC) scholarship.

## References

[1] Orsay Group on Liquid Crystals, 1969, *Phys. Rev. Lett.*, **22,** 1361; 1969, *J. chem. Phys.*, **51,** 816.
[2] For a comprehensive discussion, see de Gennes, P. G., 1974, *The Physics of Liquid Crystals* (Oxford), Chap. 5.
[3] Stinson, T. W., Litster, J. D., and Clark, N. A., 1972, *J. Phys., Paris, Colloq.*, **33,** C1-69.
[4] Radley, K., Reeves, L. W., and Tracey, A. S., 1976, *J. phys. Chem.*, **80,** 174. Charvolin, J., Levelut, A. M., and Samulski, E. T., 1979, *J. Phys. Lett., Paris*, **40,** L-587.
[5] Yu, L. J., and Saupe, A., 1980, *Phys. Rev. Lett.*, **45,** 1000.
[6] Lacerda Santos, M. B., Galerne, Y., and Durand, G., 1984, *Phys. Rev. Lett.*, **53,** 787.
[7] Lacerda Santos, M. B., and Durand, G., 1986, *J. Phys., Paris*, **47,** 529.
[8] Jota, F. G., Braga, A. R., and Santos, M. B. L., 1992, *Meas. Sci. Technol.*, **3,** 643.
[9] Lacerda Santos, M. B., 1985, Thèse d'État, Orsay.
[10] Figueiredo Neto, A. M., Liébert, L., and Galerne, Y., 1985, *J. Phys. Chem.*, **89,** 3737.
[11] Lacerda Santos, M. B., Galerne, Y., and Durand, G., 1985, *J. Phys., Paris*, **46,** 933.
[12] Berne, B. J., and Pecora, R., 1976, *Dynamic Light Scattering* (Wiley).
[13] Santos, Marcus, B. L., 1992, *Rev. Fis. appl. Instrum. (Br.)*, **7,** 1 (in Portuguese).
[14] Galerne, Y. (private communications).
[15] Oliveira, E. A., Liébert, L., and Figueiredo Neto, A. M., 1989, *Liq. Crystals*, **5,** 1669.
[16] Copic, M., Ovsenik, T., and Zgonik, M., 1987, *Liq. Crystals*, **2,** 643.
[17] Stephen, M. J., and Straley, J. P., 1974, *Rev. mod. Phys.*, **46,** 597.
[18] Notice that in the geometry considered, both $\mathbf{v}$ and $\nabla\mathbf{v}$ are perpendicular to $\mathbf{n}$, which makes the viscous torque less effective (Miesowicz coefficient$^2$ $\eta_a$).
[19] Halle, B., Quist, P.-O., and Furó, I., 1992, *Phys. Rev.* A, **45,** 3763.
[20] Arcioni, A., Bertinelli, F., Tarroni, R., and Zannoni, C., 1987, *Molec. Phys.*, **61,** 1161. Johansson, L. B.-Å., and Lindblom, G., 1986, *Liq. Crystals*, **1,** 53.
[21] Figueiredo Neto, A. M., Galerne, Y., Levelut, A. M., and Liébert, L., 1985, *J. Phys. Lett., Paris*, **46,** L-499. Figueiredo Neto, A. M. Galerne, Y., and Liébert, L., 1991, *Liq. Crystals*, **10,** 751. Figueiredo Neto, A. M., 1992, *Braz. J. Phys.*, **22,** 85.
[22] McClymer, J. P., Oxborrow, C. A., and Keyes, P. H., 1990, *Phys. Rev.* A, **42,** 3449.
[23] Rosenblatt, C., 1986, *Molec. Crystals liq. Crystals*, **141,** 107.