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T. Othman[a]; M. Gharbia[a]; A. Gharbi[a]; C. Destrade[b]; G. Durand[c]
[a] Laboratoire de Physique Moléculaire, Faculté des Sciences de Tunis, Tunis, Tunisie [b] Centre de Recherche Paul Pascal, Domaine Universitaire, Talence, France [c] Laboratoire de Physique des Solides, Btiment 510 Centre Universitaire, Orsay Cedex, France

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Orientational diffusivities measurement by light-beating spectroscopy for a disk-like thermotropic nematic phase (N_D)

by T. OTHMAN*, M. GHARBIA, A. GHARBI, C. DESTRADE† and G. DURAND‡

Laboratoire de Physique Moléculaire, Faculté des Sciences de Tunis, 1060 Belvédère, Tunis, Tunisie

† Centre de Recherche Paul Pascal, Domaine Universitaire, 33405 Talence, France

‡ Laboratoire de Physique des Solides, Bâtiment 510 Centre Universitaire, 91405 Orsay Cedex, France

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Using a light-beating technique and for an appropriate scattering geometry, we have measured separately the orientational diffusivities D_{splay} and D_{twist} for an 'hexa-*n*-alcanoyloxytruxene' (HATX $C_{12}H_{25}$) sample which exhibits a disk-like thermotropic nematic phase (N_D) between 57°C and 84°C. D_{splay} and D_{twist} are about 100 times weaker than those corresponding to rod-like thermotropic nematics. The deviation can be attributed to higher viscosities η_{splay} and η_{twist}.

1. Introduction

In a nematic liquid crystal, the long range orientational order undergoes thermal fluctuations about an equilibrium position. These fluctuations produce an intense Rayleigh scattering of light [1–3]. In many works to get information on the dynamical behaviour of these fluctuations, the light-beating technique was used to measure the intensity and the spectrum of the scattered light. For example, in [4] this technique was used to measure the critical angular fluctuation in the smectic A phase close to a S_A–S_C second-order transition. The same technique was used [5], to measure the time corresponding to the thermally excited undulations of layers in a smectic A phase.

In this work, we use the same technique to measure the orientational diffusivities D_{splay} and D_{twist} for a disk-like thermotropic nematic phase. The material used here is the hexa-*n*-alkanoyloxytruxene (HATX $C_{12}H_{25}$) which exhibits a disk-like thermotropic nematic phase between 57°C and 84°C [6]. The disk-like molecule does not have exactly the same rod-like molecule's shape: one would then expect the diffusivity orientational constants to be different. In a rod-like nematic phase, D_{splay} and D_{twist} are of the same order of magnitude, while D_{twist} and D_{bend} present a large ratio, $D_{bend}/D_{twist} \sim 10$ [7]. Hence the discotic molecular shape leads us to expect an exchange between splay and bend deformations, and a divergence between D_{twist} and D_{splay} will be expected. This behaviour was observed for a disk-like lyotropic phase and was attributed to the backflow [7]. We want therefore, to verify this behaviour for a disk-like thermotropic nematic phase.

Let us first recall, for a nematic liquid crystal, some theoretical predictions [2, 3, 8]. We choose a coordinate system (o, x, y, z) in which the mean direction $\mathbf{n}_o$ lying along the $\mathbf{z}$ axis, $\mathbf{e}_1$ and $\mathbf{e}_2$ are two unit vectors lying respectively along $\mathbf{x}$ and $\mathbf{y}$ axis (see figure 1). The wavevector $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$ is in the (x, z) plane ($\mathbf{k}_i$ and $\mathbf{k}_s$ are, respectively, the incident and scattered wavevectors).

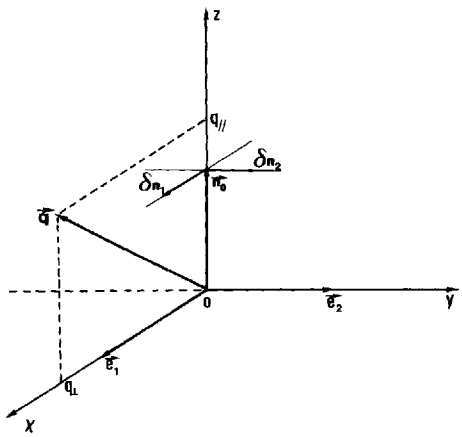

Figure 1. Fluctuation modes: The δn_1 mode which is in the $(\mathbf{q}, \mathbf{n}_o)$ plane is the combination of bend and splay deformation. The δn_2 mode which is perpendicular to the $(\mathbf{q}, \mathbf{n}_o)$ plane is the combination of bend and twist deformation. $\mathbf{n}_o$ is the equilibrium direction.

* Author for correspondence.

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At a point **r**, the local director **n**(**r**) can be expressed as

$$\mathbf{n}(r) = \mathbf{n}_o + \delta n_1 \mathbf{e}_1 + \delta n_2 \mathbf{e}_2$$

The mode δn_1 is a combination of bending and splay, while the mode δn_2 is a combination of twist and bending.

For both modes, with a fixed direction for **q**, the relaxation frequencies Γ_i are proportional to q^2 and can be given by the following expression:

$$\Gamma_i = \frac{1}{\eta_i(\mathbf{q})} [K_{ii} q_\perp^2 + K_{33} q_{//}^2]. \quad (1)$$

Where $i = 1$ or 2 denotes the mode of fluctuations δn parallel (normal) to the ($\mathbf{q}$, $\mathbf{n}_o$) plane. K_{11}, K_{22} and K_{33} are the curvature Frank elastic constants characterizing splay, twist and bend deformations, $\eta_1(\mathbf{q})$ and $\eta_2(\mathbf{q})$ are the viscosities associated to mode 1 and mode 2, $q_{//}$ and $q_\perp$ denote, respectively, the parallel and perpendicular components of the wavevector **q** with respect to $\mathbf{n}_o$.

From (1) and for an appropriate choice of scattered geometry, one can measure separately $D_{\text{splay}} = K_{11}/\eta_1$ and $D_{\text{twist}} = K_{22}/\eta_2$ which are, respectively, the splay and twist orientational diffusivities.

2. Experimental

The material was introduced by capillary action between two parallel glass plates. The thickness of the sample was adjusted with a mica spacer to 60 μm. To obtain an homeotropic orientation (director $\mathbf{n}_o$ perpendicular to the plates), the plates were treated by an organic agent: poly-vinyl-alcohol (PVA) and rubbed, and the sample then heated at 65°C. We obtained a good homeotropic orientation which was checked by a conoscopy. A 10 mw He–Ne laser ($\lambda = 6328$ Å) was used to illuminate the sample. To change the vertical polarization to a circular one, the laser beam was passed through a $\lambda/4$ plate. We selected the incident polarization by a rotating linear polarizer. The sample was placed on a goniometer which allowed variation of the air angle θ between $\mathbf{k}_i$ and $\mathbf{k}_s$ from 0° to 29°. A cooled S_{20} photomultiplier is placed on a rotatable arm which could turn around the vertical goniometer axis. It allowed us to collect the light along the scattered direction $\mathbf{k}_s$. The scattered light passed through an horizontal linear analyser. A pin-hole of radius 50 μm placed in front of the photomultiplier allowed us to collect the scattered light over less than one coherence area. The photocurrent $i(t)$ was sent to a 64 channel digital correlator to be analysed. A computer related to the correlator gave the photocurrent autocorrelation function $C_i(t)$. In absence of multiple scattering, $C_i(t)$ can be given by the following expression [9]:

$$C_i(t) = (i_s + i_o)^2 + i_s^2 \exp(-2t/\tau) + 2 i_o i_s \exp(-t/\tau).$$

Where i_s is the intensity of the signal coming from the fluctuations of the nematic director **n**, i_o is the 'local oscillator' intensity when it exists and τ is the damping time. In a purely heterodyne regime ($i_s \ll i_o$), the autocorrelation function $C_i(t)$ is reduced to a single exponential decay with a characteristic time $\tau_c = \tau$. If the regime is purely homodyne ($i_o \approx 0$), $C_i(t)$ is also reduced to a single exponential but with a characteristic time $\tau_c = \tau/2$. By fitting the experimental autocorrelation function with two exponential functions, $A \exp(-2t/\tau) + B \exp(-t/\tau) + C$, we obtain the damping time τ. The constants A, B and τ are deduced from a fit to the experimental $C_i(t)$ while C is fixed to the measured value. The relative difference between fitted C and the measured value is smaller than 5 per cent for all the spectrum. To measure, separately this time, corresponding, respectively, to purely twist and splay fluctuations in the (N_D) phase, we chose an appropriate geometry in which the wavevector **q** is closely perpendicular to the mean direction $\mathbf{n}_o$.

For the pure twist deformation, the incident polarization is ordinary, while the scattered one is extraordinary (o, e). We chose incident and scattering angles to be equal in air and the wavevectors $\mathbf{k}_i$ and $\mathbf{k}_s$ to also be symmetric normal to the glass plates (see figure 2 (*b*)). In this case, the geometrical factor $(i_2 f_z + i_z f_2)^2$, which defines the selection rules [8] is equal to $\sin^2(\theta/2)$. Inside the sample, $\mathbf{k}_i$ and $\mathbf{k}_s$ are not symmetric normal to the glass, so $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$ has two components $q_{//}$ and $q_\perp$. In our experiment for all angles θ ($0° < \theta \leq 29°$), we have calculated $(q_{//}/q_\perp)^2$ which lies in the interval (2×10^{-6}, 5×10^{-5}). From [10], the ratio between K_{22} and K_{33} for disk-like molecules in a nematic phase is $K_{22}/K_{33} \sim 5$. The quantity $K_{33} q_{//}^2$ can then be neglected with respect to $K_{22} q_\perp^2$. We can say therefore that in this geometry, we measure a damping time of purely twist deformation (δn_2).

For the pure splay deformation, the two polarizations (incident and scattered) must be extraordinary–extraordinary (e, e), (see figure (2 *a*)). We chose, in air $\mathbf{k}_i$ and $\mathbf{k}_s$ to

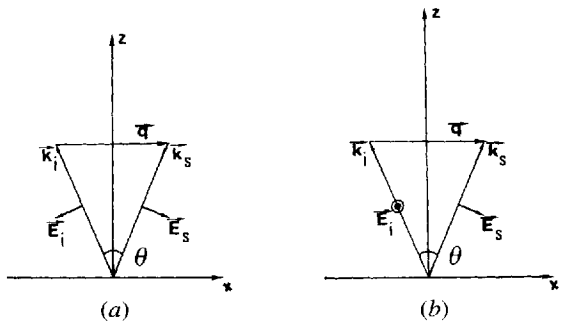

Figure 2. Scattering geometry in air: $\mathbf{k}_i$ = incoming wavevector; $\mathbf{k}_s$ = scattering wavevector; $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$. (*a*) Polarized scattering associated to splay deformations (mode 1), and (*b*) depolarized scattering associated to twist deformations (mode 2).

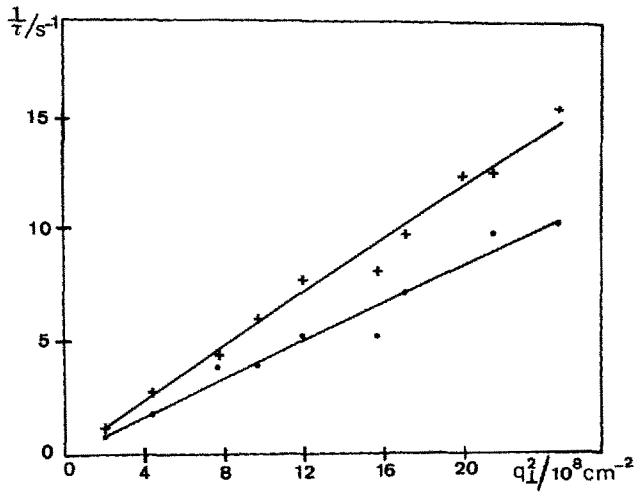

Figure 3. Relaxation rates $1/\tau$ versus the square of the wavevector $q_\perp^2$: (+) polarized scattering associated to mode 1. (•) Depolarized scattering associated to mode 2.

be symmetric normal to the glass plates. This symmetry exists even inside the sample. In this case the geometrical factor $(i_1 f_z + i_z f_1)^2 = 0$ [8] and there is no light scattered by splay deformation. In our experiment and in the (e, e) configuration, we have observed a scattered signal albeit weak. This can be explained by a weak misalignment of the director $\mathbf{n}_0$ normal to the glass plates, or by the uncertainty of the incident and scattering angles. The misalignment and uncertainty effect can be estimated as $\alpha \sim 4 \times 10^{-2}$ rad. In this situation the geometrical factor $(i_1 f_z + i_z f_1)^2$ is equal to $\sin^2 \alpha$ and the parallel component $q_{//}$ which is of α^2 order can be neglected compared to $q_\perp^2$. Now we consider the case when incident (**i**) and scattered (**f**) polarization are not in the scattering plane, but has a component along the y axis. In this situation, the scattering signal contains weak contributions from both the splay–bend and twist–bend modes. The geometrical factor $(i_2 f_z + i_z f_2)^2$ corresponding to the δn_2 mode (twist-bend mode) is approximately equal to $\alpha^2(\beta + \gamma)^2$, where β and γ denote, respectively, the inclination of **i** and **f** with respect to the scattering plane. An upper estimate for β and γ is about 2×10^{-2} rad. The geometrical factor $(i_1 f_z + i_z f_1)^2$ is always equal to $\sin^2 \alpha \approx \alpha^2$. Thus the ratio between $(i_1 f_z + i_z f_1)^2$ and $(i_2 f_z + i_z f_2)^2$ is equal to $(\beta + \gamma)^2 \approx 10^{-3}$. Therefore, the twist–bend mode contribution can be neglected compared to the splay–bend mode, and a measure of damping time of purely splay deformation (δn_1) is reached.

3. Results and discussion

For each scattering angle and keeping **q** normal to $\mathbf{n}_o$, we measure the twist damping time τ_2 corresponding to the depolarized configuration (o, e) and the splay damping time τ_1, corresponding to the polarized configuration (e, e).

Orientational diffusivity coefficients for thermotropic disk-phase nematic (N_D) of truxene HATX ($C_{12}H_{25}$) obtained by the light-beating technique. For comparison, typical values for a thermotropic nematic phase and for a lyotropic disk-phase are shown.

Sample	$D_{splay}/m^2 s^{-1}$	$D_{twist}/m^2 s^{-1}$	D_{splay}/D_{twist}
Truxene (HATX)$C_{12}H_{25}$ disk-thermotropic phase (N_D) $T = 65$°C	0.59×10^{-12}	0.42×10^{-12}	1.4
Disk-lyotropic phase (N_D) [7]	1.15×10^{-11}	0.16×10^{-11}	7.2
MBBA $T = 25$°C [8]	$\approx 0.56 \times 10^{-10}$	$\approx 0.43 \times 10^{-10}$	1.3

We plot in figure 3 the inverse of these two damping times τ versus $q_\perp^2$. Data are well fitted by two straight lines. The corresponding slopes give the orientational diffusivities. We report in the table our measurement at 65°C and other typical results obtained from a disk-like lyotropic nematic phase (N_D) [7] and a rod-like thermotropic nematic phase (N_B) [8]. We note that for the truxene sample (HATX $C_{12}H_{25}$) in a discotic nematic phase (N_D), the orientational diffusivity constants D_{splay} and D_{twist} are of the same order of magnitude. In our case and from [10], which estimates $K_{22}/K_{11} \sim 2$ for a disk-like nematic phase, we expect that the two viscosities η_{splay} and η_{twist} will have the same order of magnitude. This behaviour was observed in the rod-like thermotropic nematic phase as in *N*-(*p*-metoxybenzylidene)-*p*-butylaniline (MBBA) [8]. But it is not the case in a disk-like lyotropic nematic phase; there is a divergence between the constants D_{splay} and D_{twist} with a ratio equal to 7.2 [7]. This divergence was attributed to the anisotropy of viscosities η_{splay} and η_{twist}.

We remark also that the two constants D_{splay} and D_{twist}, corresponding to the truxene sample (HATX $C_{12}H_{25}$) in a thermotropic nematic phase (N_D), are about 100 times weaker than those measured in a rod-like thermotropic nematic phase. From the K_{33} measurement obtained by a Freedericks transition method, $K_{33} \sim 0.22 \times 10^{-11}$ N [11] and the ratios $K_{22}/K_{33} \sim 5$; $K_{11}/K_{33} \sim 2$ [10], for a disk-like nematic phase, we deduce that the factor 100 can be attributed to the viscosity coefficients. It appears to be very high compared to those in a thermotropic phase (MBBA).

4. Conclusion

We have measured the orientational diffusivity constants D_{splay} and D_{twist} in a disk-like thermotropic nematic phase (N_D) corresponding to truxene HATX ($C_{12}H_{25}$) in a homeotropic geometry. Using the light-beating technique and for an appropriate choice of geometry, we have

measured separately the damping time associated with the splay and twist deformation modes; the two constants, D_{splay} and D_{twist}, have a magnitude 100 times weaker than those found in a rod-like thermotropic nematic phase, for example, MBBA. This can be due in greater part to the viscosity coefficient which is expected to be higher than in a rod-like nematic phase. In this way, measurements of this viscosity coefficient are interesting to determine the curvature Frank elastic constant. From another viewpoint the high ratio between D_{splay} and D_{twist} in disk-like lyotropic phase was attributed to the backflow effect [7] which reduces the splay viscosity (η_{splay}). In our case for the disk-like thermotropic phase we found $D_{splay}/D_{twist} \approx 1$, which means that the backflow effect is negligible. Most probably this effect has an important contribution in bend deformation as in a rod-like thermotropic phase. This interpretation could be supported by the measurement of D_{bend}.

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