

Proton field-cycling nuclear magnetic resonance relaxometry in the smectic A mesophase of thermotropic cyanobiphenyls: Effects of sonication

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Proton field-cycling nuclear magnetic resonance relaxometry is used to study the spin-lattice relaxation dispersion of selected standard smectic A liquid crystals at different temperatures. Relaxation features at both, in the presence and absence of a monochromatic ultrasonic field are considered. We show that the laboratory-frame spin-lattice relaxation time is mainly governed by translational diffusion. Order director fluctuations (ODF) are less important while rotational diffusion seems to be only relevant near the clearing point. Our study suggests that sonication enhances the ODF contribution in the SmA mesophase. Within the framework of the approach we have outlined, different features associated with the ODF mechanism can be investigated. © 2004 American Institute of Physics. [DOI: 10.1063/1.1740751]

I. INTRODUCTION

The Larmor frequency ν dispersion of proton spin-lattice relaxation time T_1 in thermotropic liquid crystals may be analyzed through the superposition of different competing relaxation mechanisms. Among the most relevant we may consider collective molecular motions like order director fluctuations (ODF), and individual molecular motions such as translational and rotational self-diffusions. It should be emphasized that the smectic A (SmA) mesophase was scarcely studied with the field-cycling technique. Remarkably, some features related to the T_1 relaxometry of these systems are still left as an open question. A characteristic of these systems is the strong dispersion of the T_1 appearing in the low-frequency end of the available Larmor frequency window. Such strong dispersion was usually associated with the smectic ODF mechanism. However, it was recently shown that, at least for cyanobiphenyls, such dispersion is more connected with hardware setting and the presence of local fields.¹ Since we have lost the ideal scenario of a T_1 relaxation parameter measurable within the local field region, we decided to investigate again the SmA mesophase with the main spirit of disentangling ODF and diffusion contributions.

Two main theoretical models have been proposed up to now for the SmA mesophase. The former,² predicts a linear behavior of T_1 with Larmor frequency ν [$T_1(\nu) = \alpha\nu$]. However, this Larmor frequency dependence was estimated from the undulation layer mechanism in the limit where the correlation length ξ does not depend on the wave vector of the hydrodynamic modes \vec{q} . If a more realistic relationship $\xi \propto 1/q^2$ is assumed, a logarithmic dependence for $T_1(\nu)$ is obtained. A second relaxation model proposed by Vilfan *et al.*,³ foresees a behavior for $T_1(\nu)$ ranging approximately

from ν^0 at low frequencies (minor than 1 MHz) up to $\nu^{0.5}$ in the high frequency regime (in logarithmic scale). In a limiting case (when the SmA phase only involves splay deformations and compressions of the layers), the above mentioned logarithmic behavior is reobtained.

The characteristic leveling-off behavior predicted by this last model at low frequencies anticipates the difficulties that may arise in disentangling ODF from diffusion or other non-collective mechanisms. The situation can be partially circumvented by extending the relaxation dispersion study to higher frequencies, outside the technical limits of the field-cycling method (by measuring T_1 at fixed frequencies using standard pulse sequences). But a final word depends on how strong can be the dominance of individual molecular motions over the collective ones within that extended high frequency range. This last comment warrants a remarkable observation: There is no reason *a priori* to assume that collective motions are slow, since they may be effective up to frequencies corresponding to the high frequency cutoff (associated with molecular dimensions) within the high MHz regime. A completely different point is that ODF dominates, for example, the relaxation dispersion of nematogens in the kHz region.

The typical dispersion of the T_1 relaxation time experimentally observed in the SmA phase of cyanobiphenyls is characterized by a weak frequency dependence between 1 MHz and a frequency of about 20 kHz. At this frequency a noticeable steep dispersion appears until about 800 Hz, where a low frequency plateau manifests. The strong dispersion was usually explained through order director fluctuations, while the low frequency plateau was interpreted in terms of the low-frequency ODF cut-off mechanism.⁴⁻¹⁰ In most of these works, the simplified model that predicts a linear ODF dispersion was invoked. However, recent studies suggest that the observed steep dispersions are a conse-

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quence of improper hardware setting and data handling, in combination with the higher nonaveraged local fields owing to the smectic state.^{1,11}

Nematic (N) ODF may be enhanced with the application of an ultrasonic field.^{12,13} This behavior responds to the fact that the ultrasound couples with the director field, leading to changes in the relaxation dispersion. Such changes may be characterized by¹⁴

- (i) a variation on the dispersion exponent: A behavior that ranges from ν^α (for low frequencies) to $\nu^{1/2}$ is obtained for $T_1(\nu)$, being α bigger or smaller than 0.5 depending on the direction of the acoustic propagation;
- (ii) a uniform relaxation enhancement within the observed Larmor frequency window.

The coupling of ultrasound with noncollective motions was found to be negligible within experimental errors (at the working frequency employed in these experiments).

In this work we study the dependence of the T_1 relaxation dispersion in two different SmA cyanobiphenyls on the absence and presence of ultrasonic waves. Experiments were performed at different temperatures and restricted to those frequencies where the FC technique does not present limitations related to the presence of local fields. Our main goal at the outset is to investigate the observed changes in the dispersions in terms of the ultrasound—ODF coupling. To our knowledge, the present work constitutes the only case where information about smectic ODF mechanism is extracted from the proton field-cycling NMR T_1 relaxation dispersion in the SmA phase of cyanobiphenyls.

II. EXPERIMENT

Commercial samples of 4-octyl-4'-cyanobiphenyl (8CB) and 4-undecyl-4'-cyanobiphenyl (11CB) from Synthon and Merck Chemicals, respectively, were employed. 8CB presents three phase transition: Solid (K)—SmA at 294.5 K, SmA-N at 306.5 K and N—isotropic (I) at 313.5 K, while 11CB only displays two phase transitions: K—SmA and SmA—I at 326 and 330.5 K, respectively.

A Stellar FC2000 fast field cycling nuclear magnetic resonance (NMR) relaxometer was used to acquire all the proton relaxation dispersion curves. Standard pre-polarized (PP) and non-polarized (NP) sequences (0.25 and 0.23 T as polarization and detection fields, respectively) were used to obtain T_1 values.¹⁵ In all cases, sixteen points (four scan each) were used to determine T_1 . Relative errors were found to range between 2% and 8%.

The ultrasound was transmitted to the sample through a 3 mm diameter glass sonotrode coupled to a Hielsher UIP50 generator working at (29.8 ± 0.5) kHz. An efficient power transmission was obtained by directly placing the glass sonotrode into the sample volume. The temperature control was carried out by a Stellar VTC unit connected to a thermocouple located at about 30 mm from the bottom of the sample. The control unit was previously calibrated in order to display the real sample temperature. In order to ensure the temperature constancy during the whole experiment, the

sample temperature was measured before and after each T_1 dispersion acquisition with a thermocouple directly immersed into the sample. Direct temperature measurement during NMR acquisition might be grossly unfavorable from the standpoint of sensitivity. At our experimental conditions was not feasible due to the high noise introduced by the thermocouple. Absolute errors in temperature measurements were ± 0.2 K for 8CB and ± 0.5 K for 11CB (higher temperature gradients according to a major difference between sample and environment temperatures).

Two different ultrasound power levels were used in the experiments: 13.5 and 22.5 W/cm². Higher powers were not used to avoid cavitation and significant temperature gradients across the sample.

III. RELAXATION MODELS

As it was previously stated, three different relaxation mechanisms were used to explain the $T_1(\nu)$ behavior: One of collective nature (ODF) and two of individual nature (translational diffusion and molecular reorientations). By translational diffusion mechanism, or self diffusion, we mean the modulation of the dipole–dipole interaction between protons located on different molecules, as a consequence of the particle motion, usually thermally activated, from one site to another. Reorientations are intended to be the contributions to the spectral densities at the Larmor frequency caused by rotations around the long and short molecular axis, and rotations of the chain groups. Self diffusion was found to be the more important mechanism driving the T_1 relaxation in the SmA phase.⁴ This assertion was generally checked to be consistent with our results. Therefore, in the following we will refer to self diffusion as the only important individual relaxation mechanism.

Assuming different time scales for the different mechanisms and small cross terms between them at the correlation function level,¹³

$$\frac{1}{T_1} = \frac{a_1}{T_{1OF}} + \frac{a_2}{T_{1Tr}}, \quad (1)$$

where T_1^{-1} is the total proton spin relaxation rate; a_1 and a_2 are constants; and T_{1OF}^{-1} , T_{1Tr}^{-1} , are the relaxation rates produced by ODF and translational diffusion mechanisms, respectively, in the absence of the other mutually relaxation mechanisms.

At this point, it is important to remark that due to the low spectroscopic resolution of the field-cycling experiments, separate contributions from phenyl and chain protons, at least for these compounds, are not distinguishable. Rapid spin diffusion ensures a single average T_1 , as can be concluded from the mono-exponential evolution of the magnetization decay.

As described in the preceding section, there are essentially two proposed models that may be considered to explain the Larmor frequency dispersion due to the ODF relaxation mechanism in the SmA phase:

- The “nematic” approach.

Consider the nematic free energy:

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

where K_{11} , K_{22} , and K_{33} are splay, twist and bend elastic constants, respectively, and \vec{n} is the local director.

If the contribution of smectic undulation waves is taken into account while assuming that the correlation length in the direction perpendicular to the smectic layers does not rely on the mode's wave vector, we have²

$$T_{1OF}^{nem}(\nu) = C\nu, \quad (3)$$

where constant C depends on the Boltzmann and Planck constants, the gyromagnetic ratio, temperature T , splay elastic constant K_{11} , the interproton distance, order parameter S , and the coherence length in the direction perpendicular to the smectic layers. The previous supposition is mathematically (but not physically) equivalent to assume that the relation $K_{33} \ll K_{11}, K_{22}$ is satisfied in Eq. (2).¹⁶

• The “smectic” approach.

In this model the coupling of smectic order with director fluctuations is taken into account.³ Within this picture, smectic f_s and the nematic–smectic interaction f_I free energy terms are added to nematic–elastic free energy f_n to obtain total free energy f ,

$$f = f_n + f_s + f_I, \quad (4)$$

with,

$$f_s = \varepsilon(T) |\psi|^2 + \lambda(T) |\psi|^4 + \dots \quad (5)$$

$$f_I = (\nabla + iq_s \vec{\delta n}) \psi^* \frac{1}{2M} (\nabla - iq_s \vec{\delta n}) \psi. \quad (6)$$

In the last expressions, ε and λ are coefficients in the expansion of f_s in powers of ψ , M is a mass tensor with components M_{\parallel} and M_{\perp} , along the normal to the layers and perpendicular to them, respectively and $q_s = 2\pi/d$, d the distance between smectic layers and ψ , the smectic order parameter [$\psi = |\psi| \exp(i\phi)$].

Using the expression obtained in Refs. 17 and 18 for the amplitudes of the mean square fluctuations of the director for the q th mode ($\langle |n_{\alpha}(\vec{q})|^2 \rangle$; with $\alpha = 1, 2$) and their corresponding decay times [$\tau_{\alpha}(\vec{q})$], it is possible to arrive at

$$T_{1OF}^{sm}(\nu) = \beta \left[\frac{1}{\sqrt{\delta}} \eta_1 K_{11}^{-3/2} Y + \frac{1}{\sqrt{K_{33} \delta}} \eta_2 K_{22}^{-1} \frac{1}{\sqrt{1 + \sqrt{1 + \left(\frac{2\pi\nu}{\omega_{s2}} \right)^2}}} \right]^{-1}, \quad (7)$$

with

$$Y = \frac{B}{\delta} \int_0^1 \frac{dx}{x \left(\frac{B}{\delta} (1-x^2) + \frac{K_{33}}{K_{11}} x^2 \right)^{3/2} \sqrt{1 + \sqrt{1 + \left(\frac{2\pi\nu}{\omega_{s1}} \right)^2}}}, \quad (8)$$

where $B = \psi_0^2 q_s^2 / M_{\parallel}$ and $\delta = \psi_0^2 q_s^2 / M_{\perp}$ (ψ_0 is the equilibrium value of the smectic order), η_{α} are viscosities, $\omega_{s\alpha} = \delta / \eta_{\alpha}$ with $\alpha = 1, 2$, and β depends on the Planck constant, the gyromagnetic ratio, the interproton distance and molecular order parameter S .

Concerning T_{1Tr}^{-1} relaxation rate, Vilfan *et al.*¹⁹ extended to SmA phases the model previously proposed by Torrey²⁰ for the I phase. Although Vilfan *et al.*¹⁹ showed that for low frequencies the anisotropy of the molecules influences the relaxation rate, differences with Torrey's model in the dispersion behavior become important only when the Larmor frequency ν , varies from $0 < 2\pi\nu\tau_D < 0.3$, where τ_D is the diffusional correlation time. As in our experiments the factor $2\pi\nu\tau_D$ ranges from about 6×10^{-5} to 2×10^{-2} (only 7% of the range where both models differ significantly), in this frequency window we can approximate

$$T_{1i}(\nu) = \chi T_{1Sm}(\nu), \quad (9)$$

with an appropriate factor χ . In the last equation, $T_{1i}(\nu)$ is the expression obtained by Torrey for the I phase and $T_{1Sm}(\nu)$ is the expression obtained by Vilfan and Zumer for SmA phases.

Then, due to the exposed above and for the sake of simplicity, the following equation was used for T_{1Tr}^{-1} .²⁰

$$T_{1Tr}^{-1} = \frac{A_D}{\nu^2} [j(\alpha, x) + j(\alpha, \sqrt{2}x)], \quad (10)$$

where,

$$j(\alpha, x) = v \left(1 - \frac{1}{u^2 + v^2} \right) + \left(v \left(1 + \frac{1}{u^2 + v^2} \right) + 2 \right) e^{-2v} \times \cos(2u) + u \left(1 - \frac{1}{u^2 + v^2} \right) e^{-2v} \sin(2u), \quad (11)$$

$$\left(\frac{u}{v} \right) = \frac{1}{2} \left(\frac{q(1 \mp q)}{\alpha} \right)^{1/2},$$

$$q = \frac{\alpha x^2}{(1 + \alpha^2 x^4)^{1/2}}.$$

Here, $\alpha = \langle r^2 \rangle / 12b^2$, $x = \sqrt{2\pi\nu b^2 / D}$, and $\langle r^2 \rangle$ is the mean square jump distance, b is the distance of closest approach, $D = \langle r^2 \rangle / 6\tau_D$ is the isotropic self diffusion constant and A_D is a constant that depends on spin density n , D , α , and b .

As it was previously stated by Torrey, in the limit of small jump width ($\langle r^2 \rangle \ll b^2$) and low correlation times ($\omega\tau_D \ll 1$), a simplified version of the Torrey's model is obtained. In this limit, $u = v = x/2$, and

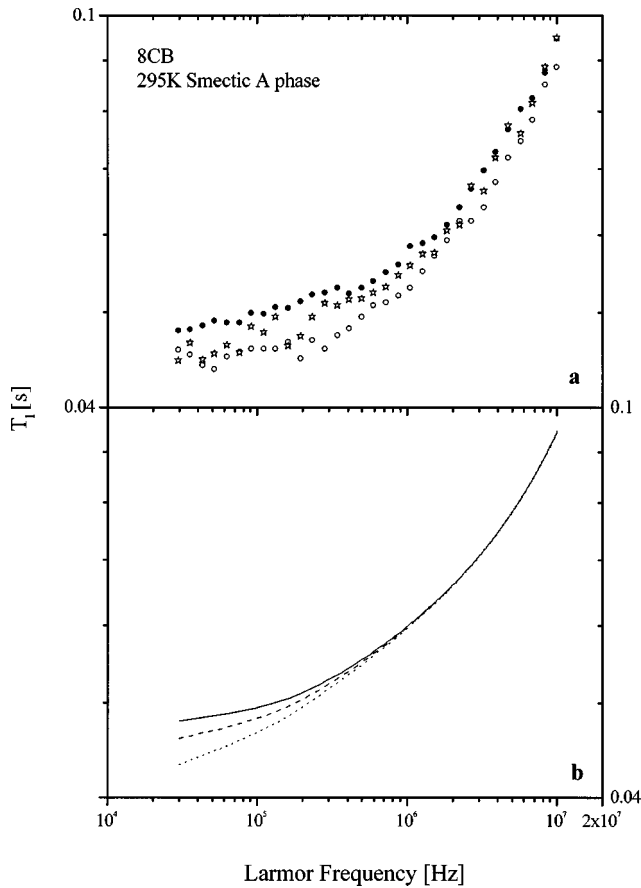


FIG. 1. Relaxation dispersions (a) and simulated curves (b) for 8CB liquid crystal at the SmA phase temperature of 295 K. The three data dispersions and their correlative simulated curves correspond to the three cases: Absence of sound (filled circles and solid line) and presence of it at two different powers (P' : Hollow stars and dashed line, and $P''=22.5 \text{ W/cm}^2$: Hollow circles and dotted line).

$$j(\alpha, x) = \frac{x}{2} - \frac{1}{x} + \frac{x}{2} e^{-x} \left(\left(1 - \frac{2}{x^2} \right) \sin(x) + \left(1 + \frac{4}{x} + \frac{2}{x^2} \right) \cos(x) \right). \quad (12)$$

As it can be observed, this result no longer depends on α .

Although hardly justified, this approximated model was broadly used in the analysis of field cycling dispersion curves in liquid crystals in the past.⁴⁻¹⁰ In the present work, the above simplified model was checked to be inappropriate because of the τ_D 's obtained by the corresponding fittings do not satisfy the hypothesis of low correlation times ($\omega\tau_D \ll 1$) assumed by the model in the whole ω spectrum.

A. Relaxation in the presence of ultrasound

Ultrasound couples with ODF causing changes in the whole spectrum of the relaxation dispersion curve.^{12,13} In this case, a new orienting term is added to the nematic free energy expression [Eq. (2)]. This term is given by^{12,21}

$$f_a = \frac{1}{2} a^2 (\hat{s} \cdot \hat{n}),$$

where a^2 depends on the acoustic intensity, the ultrasound velocity, the average of the sample density, the magnitude of

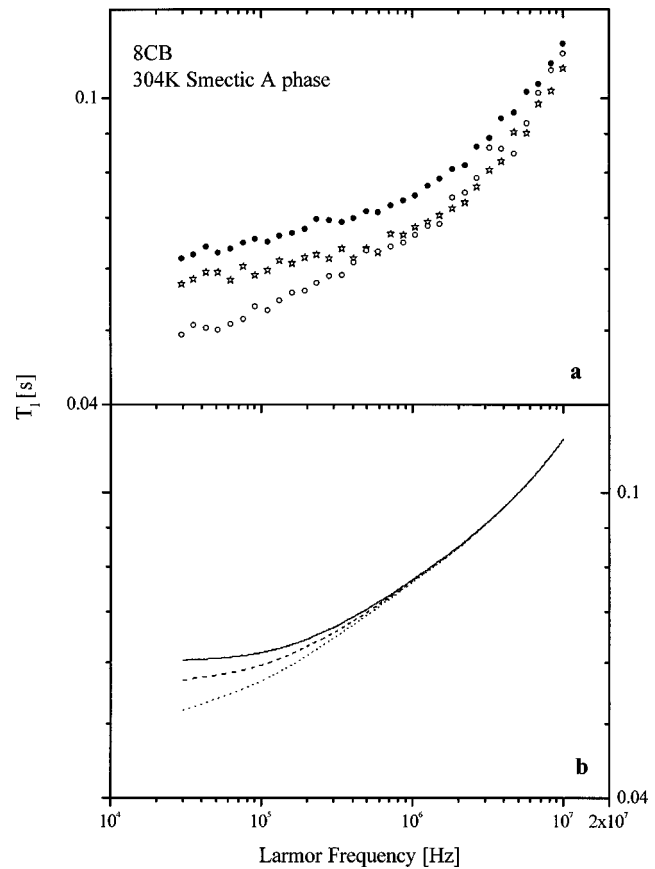


FIG. 2. Relaxation dispersions (a) and simulated curves (b) for 8CB liquid crystal at the SmA temperature of 304 K. The three data dispersions and their correlative simulated curves correspond to the absence of sound (filled circles and solid line) and presence of ultrasonic waves at two different powers: $P'=13.5 \text{ W/cm}^2$ (hollow stars and dashed line), and $P''=22.5 \text{ W/cm}^2$ (hollow circles and dotted line).

the ultrasound wave vector and the director-density coupling. In the last equation, \hat{s} is an unitary vector pointing along the ultrasonic wave vector, and \hat{n} is the director.

Starting from this new free energy expression, the following is obtained for both, nematic and smectic approaches, in the presence of ultrasonic waves parallel to the director [the detailed calculation is offered in Ref. 14]:

$$T_{1OF+S}^{nem}(\nu) = \left\{ \frac{3K_B T q_{zc}}{4\pi^2 \omega K_{11}} \frac{1}{\sqrt{1 + \frac{1}{(\omega\tau_0)^2}}} \times \left[2 \arctan \left(\frac{\frac{1}{\omega\tau_0}}{\sqrt{1 + \frac{1}{(\omega\tau_0)^2}}} \right) + \pi \right] \right\}^{-1}, \quad (13)$$

$$T_{1OF+S}^{sm}(\nu) = \beta \left[\frac{1}{\sqrt{D}} \eta_1 K_{11}^{-3/2} Y + j_{1,2}^{OF+S}(\omega) \right]^{-1}, \quad (14)$$

with

$$Y = \frac{B}{D} \int_0^1 \frac{dx}{\left(\frac{B}{D} (1-x^2) + \frac{K_{33}}{K_{11}} x^2 \right)^{3/2} \sqrt{x^2 - \frac{a^2}{D}} + \sqrt{\left(x^2 - \frac{a^2}{D} \right)^2 + \left(\frac{\omega}{\omega_{s1}} \right)^2}}, \quad (15)$$

$$j_{1,2}^{OF+S}(\omega) = \begin{cases} \frac{\eta_2}{K_{22}K_{33}^{1/2}\sqrt{|D-a^2|}} \frac{1}{\sqrt{\sqrt{1 + \left(\frac{\omega}{\omega_{s2}}\right)^2} - 1}} & \text{if } D \leq a^2 \\ \frac{\eta_2}{K_{22}K_{33}^{1/2}\sqrt{|D-a^2|}} \frac{1}{\sqrt{\sqrt{1 + \left(\frac{\omega}{\omega_{s2}}\right)^2} + 1}} & \text{if } D \geq a^2 \end{cases} \quad (16)$$

In Eqs. (13)–(16), $\tau_0 = \eta/a^2$, $\omega_{s2} = |D - a^2|/\eta_2$ and $\omega_{s1} = D/\eta_1$.

Based on experimental facts,^{12,13} it will be assumed that translational self-diffusion relaxation mechanism is not affected by the presence of ultrasonic waves.

IV. RESULTS

Figures 1 and 2 show the T_1 dispersion plots corresponding to a sample of 8CB at temperatures of 295 and 304 K within the SmA phase, respectively. Figures 1(a) and 2(a)

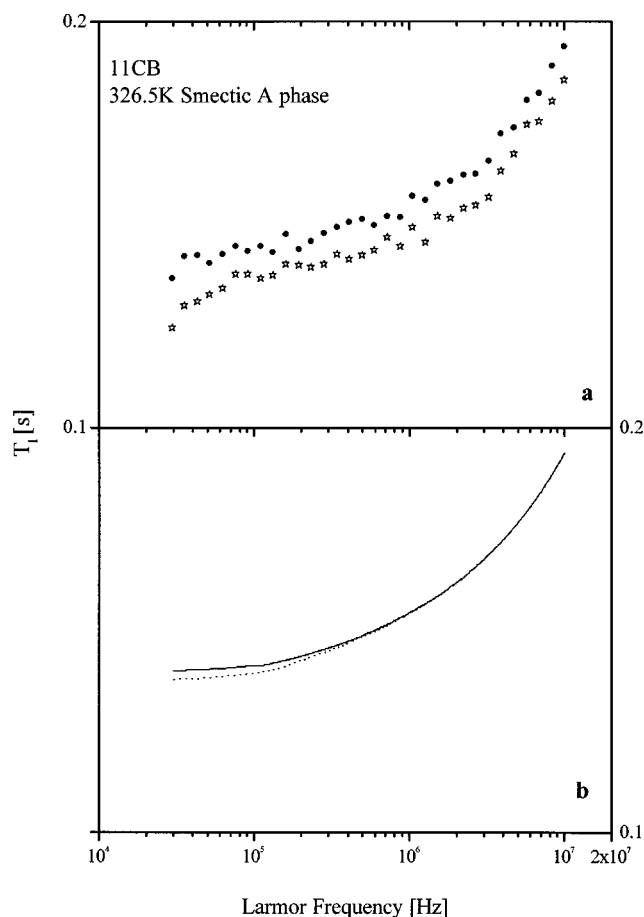


FIG. 3. Relaxation dispersions (a) and simulated curves (b) for 11CB liquid crystal at the SmA temperature of 326.5 K. A clear shift between both measured relaxation profiles (sonicated and nonsonicated) is observed. The two dispersion data and their simulated curves correspond to the absence of sound case (filled circles and solid line) and to the presence of it (at a power $P' = 13.5 \text{ W/cm}^2$: Hollow stars and dashed line).

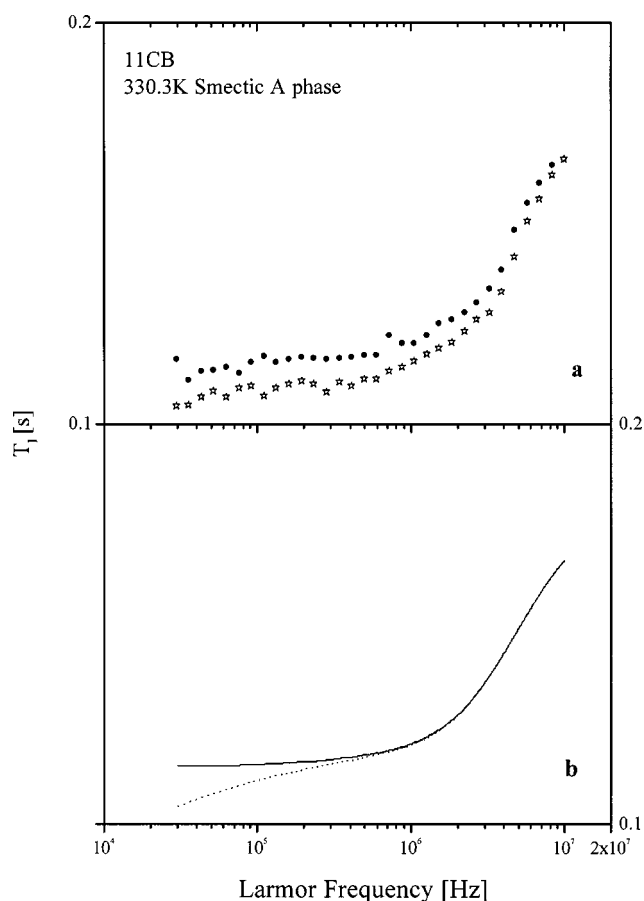


FIG. 4. Relaxation dispersions (a) and simulated curves (b) for 11CB liquid crystal at the SmA temperature of 330.3 K. As the temperature is near the SmA–I phase transition, rotational relaxation mechanism becomes important. The two data dispersions and their correlative simulated curves correspond to the two cases: Absence of sound (filled circles and solid line) and presence of it at a power of $P' = 13.5 \text{ W/cm}^2$ (hollow stars and dashed line).

TABLE I. Parameters used in the simulated curves. a' and a'' stand for the parameter a with ultrasonic powers $P' = 13.5 \text{ W cm}^{-2}$ and $P'' = 22.5 \text{ W cm}^{-2}$, respectively. For 11CB only one ultrasonic power (P'') was employed.

B [Nm^{-2}]	D [Nm^{-2}]	K_{11} [N]	K_{22} [N]	K_{33} [N]	η [Nsm^{-2}]	a'^2 [Nm^{-2}]	a''^2 [Nm^{-2}]
10^6	10^5	10^{-11}	0.7×10^{-11}	10^{-12}	0.1	2.5×10^4	5×10^4

show the data obtained in the absence of ultrasonic waves (filled circles) and in the presence of them: At a power of 13.5 W/cm^2 (hollow stars) and at a power of 22.5 W/cm^2 (hollow circles). Figures 1(b) and 2(b) show the corresponding simulated curves for the nonsonicated case (solid line) and in the presence of ultrasonic waves (dashed and dotted lines). Figures 3 and 4 show the corresponding data and simulated curves for 11CB at smectic temperatures of 326.3 and 330.3 K, respectively.

In the absence of sound, if the linear dispersion model (N approach) is assumed to be correct, fittings using Eqs. (1) and (3) indicates that the self-diffusion mechanism completely determines the $T_1(\nu)$ behavior in all curves, i.e., the presence of the ODF relaxation mechanism cannot be detected from the measured dispersion curves. This may be the case if the mechanism is masked by self-diffusion. But if this argument was correct, there would not be any difference between dispersion curves in the presence and absence of ultrasound, unless the ultrasonic field was able to pull-up the ODF contribution at considerable strength. In addition, the observed behavior in the presence of sonication cannot be explained through fittings using the nematic approach [Eq. (13) for the ODF contribution]. On the contrary, if the smectic character of the mesophase is added, the behavior obtained is qualitatively well described, as can be seen in Figs. 1–4.

Simulated curves (except for 11CB at 330.3 K) were obtained through Eq. (1), where (14) was used for T_{1OF} . Due to the high quantity of involved parameters and the complexity of the function, typical values of constants B , D , K_{11} , K_{22} , K_{33} , η , and a^2 were used to generate simulated curves instead of data fitting (see Table I).³ Also, α and τ_D values were fixed (curves without sound were fitted without ODF contribution in order to obtain these approximated values).³ Other parameters were fitted, and they can be appreciated in Table II.

In the particular case of 11CB at 330.3 K, it was found that individual motions were governed by rotations. Then, the simulated curves were obtained following the equation:

$$\frac{1}{T_1} = \frac{b_1}{T_{1OF}} + \frac{b_2}{T_{1Rot}} + C_D, \quad (17)$$

where²²

$$\frac{1}{T_{1Rot}} = A_R \left[\frac{\tau_R}{1 + (2\pi\nu\tau_R)^2} + \frac{4\tau_R}{1 + (4\pi\nu\tau_R)^2} \right]^{-1}, \quad (18)$$

being A_R a constant, τ_R the correlation time for rotations, and C_D a constant that represents the translational diffusion relaxation mechanism. This result is a consequence of the typical τ_D low values near the SmA–I phase transition ($\tau_D \sim 10^{-11}$ s, in most compounds). Then, $2\pi\nu\tau_D \ll 1$ in the whole Larmor frequency range of the measurements, giving a constant behavior for T_{1Tr}^{-1} .

Figures 5(a) and 5(b) show how this relaxation mechanism becomes important in the I phase of 8CB and 11CB samples, respectively (it is not possible to explain the relaxation in the I phase by using only self-diffusion). In these cases, a non-dispersive contribution for translational self-diffusion mechanism was found ($T_{1Tr}^{-1} = C_D$).

V. DISCUSSION

Considering we are comparing different compounds, it is important to note that τ_D and τ_R values obtained in the present work show a reasonable agreement with previous values obtained in the smectic phase of terephthal-bis-p-butylaniline (TBBA).⁵ Another important fact is that the α values obtained in the smectic phase for both compounds exhibit the same order of magnitude as the one obtained by Vilfan *et al.* in TBBA ($\langle r^2 \rangle / a^2 = 0.04$).¹⁹

T_1 relaxation dispersion data are consistent with a model where individual motions are the dominant relaxation mechanisms. It was found that ODF relaxation dispersion relative weight for 8CB ranges from 3% to 9% at higher

TABLE II. Parameters obtained for 8CB and 11CB. Relative errors on parameters α , τ_D , and τ_R are estimated to be of the order of 10%.

8CB							
T [K]	A_D [10^{15} s^{-1}]	A_R [10^6 s^{-1}]	β [$10^{14} \text{ s}^2 \text{ N}^{-1} \text{ m}^{-2}$]	C_D [s^{-1}]	α [10^{-2}]	τ_D [10^{-10} s]	τ_R [10^{-8} s]
295	4.3 ± 0.9	...	1.4 ± 0.2	...	1	2.4	...
298	5.5 ± 0.7	...	1.6 ± 0.8	...	1	2.0	...
301	7 ± 1	...	1.5 ± 0.2	...	1	1.6	...
304	6.5 ± 1	...	1.2 ± 0.2	...	1	1.6	...
326	...	5.0 ± 0.3	...	6.2 ± 0.4	1.6 ± 0.2
11CB							
326.5	6.5 ± 0.6	...	17 ± 3	...	2	2.5	...
330.3	...	2.2 ± 0.3	2.0 ± 0.4	5.8 ± 0.6	2.1
340.0	...	2.8 ± 0.2	...	6.2 ± 0.4	0.95 ± 0.09

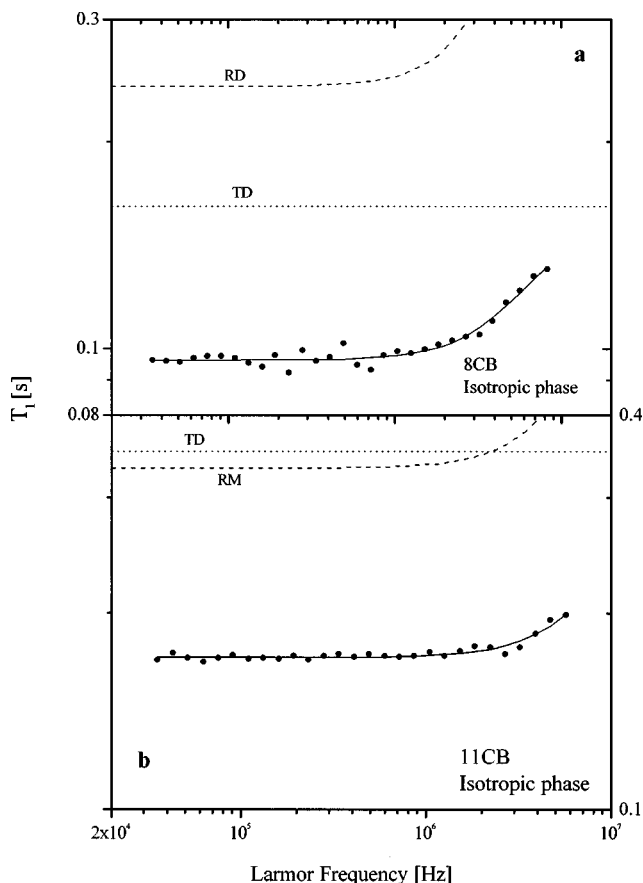


FIG. 5. Relaxation dispersion and fitting curves for 8CB (a) and 11CB (b) in the absence of sound at the I phase temperatures of 326 and 340 K, respectively. It is possible to observe the contribution of rotational diffusion (RD) and translational diffusion (TD) mechanisms in both $T_1(\nu)$ dispersions.

frequencies and from 15% to 25% at lower frequencies. For 11CB these values are significantly lower at 326.5 K (1.8% and 8% at higher and lower frequencies, respectively). This result is consistent with the relative ratio n_c/n_t (where n_c is the number of protons in the core and n_t is the number of protons in the tail).^{13,23} It was also found that this relative weight does not present a strong dependence with temperature.

Even though a qualitative agreement is clearly observed between results and the proposed model, there is an effect observable in the experimental data and not explained by the model: The ODF contribution to the relaxation dispersion under sonication is shifted to lower relaxation time values more noticeable in Fig. (3). As it was mentioned above, this effect was already observed in nematics,¹³ and can be attributed to a change in parameter β induced by the sound (assumed constant in the model). Physically, this change is related to a possible variation in macroscopic parameters (like viscosity or elastic constants, for example). It is important to mention that this effect was not taken into account in the generation of the simulated curves.

Rotational diffusion only contributes in the SmA phase of 11CB close to the SmA–I transition. In 8CB contribution from this mechanism is absent, even at temperatures close to

the SmA–N transition. This result can be explained by the presence of pre-translational disorder caused by the proximity to the SmA–I transition. This transition does not take place in 8CB.

The similitude of the frequency dependence presented by ODF and individual relaxation mechanisms at low frequencies does not allow us to determine the relative weight of each other from the dispersion curves in the absence of ultrasound. The change in the dispersion curve under sonication allow us to identify the presence and the relative weight of ODF in the dispersions.

VI. CONCLUSIONS

In this work we have shown that the $T_1(\nu)$ dispersion in the SmA phase of cyanobiphenyls is consistent with a model where translational diffusion is the dominant mechanism. We also have shown that rotational diffusion starts to be relevant close to the SmA–I phase transition, possibly being a consequence of that.

The measurement of relaxation dispersion with the sample subjected to ultrasonic irradiation allows detecting the presence of the ODF mechanism and quantifying its relative weight. Two previously proposed models were used to explain these data. It was found that a relaxation model including particular features of the smectic phase³ can be better used to describe the observed experimental data.

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- ¹E. Anoardo, F. Bonetto, and R. Kimmich, *Phys. Rev. E* **68**, 022701 (2003).
- ²R. Blinc, M. Luzar, M. Vilfan, and M. Burgar, *J. Chem. Phys.* **63**, 3445 (1975).
- ³M. Vilfan, M. Kogoj, and R. Blinc, *J. Chem. Phys.* **86**, 1055 (1987).
- ⁴T. Mugele, V. Graf, W. Wölfel, and F. Noack, *Z. Naturforsch. A* **35**, 924 (1980).
- ⁵F. Noack, M. Notter, and W. Weiss, *Liq. Cryst.* **3**, 907 (1988).
- ⁶D. Pusiol and F. Noack, *Liq. Cryst.* **5**, 377 (1989).
- ⁷D. Pusiol, R. Humpfer, and F. Noack, *Z. Naturforsch. A* **47**, 1105 (1992).
- ⁸R. H. Acosta, D. J. Pusiol, *Phys. Rev. E* **60**, 1808 (1999).
- ⁹R. H. Acosta and D. Pusiol, *Phys. Rev. E* **63**, 011707 (2000).
- ¹⁰A. Carvalho, P. J. Sebastião, A. C. Ribeiro, H. T. Nguyen, and M. Vilfan, *J. Chem. Phys.* **115**, 10484 (2001).
- ¹¹E. Anoardo and R. Kimmich, XXXII National Congress on Magnetic Resonance GIDRM, Pavia-Italy (2002).
- ¹²F. Bonetto, E. Anoardo, and R. Kimmich, *Chem. Phys. Lett.* **361**, 237 (2002).
- ¹³F. Bonetto, E. Anoardo, and R. Kimmich, *J. Chem. Phys.* **118**, 9037 (2003).
- ¹⁴F. Bonetto and E. Anoardo, *Phys. Rev. E* **68**, 021703 (2003).
- ¹⁵E. Anoardo, G. Galli, and G. Ferrante, *Appl. Magn. Reson.* **20**, 365 (2001).
- ¹⁶R. Y. Dong, *Nuclear Magnetic Resonance of Liquid Crystals* (Springer, New York, 1997), pp. 146–155.

- ¹⁷F. Brochard, *J. Phys. (Paris)* **34**, 411 (1973).
- ¹⁸R. Schaetzing and J. Litster, *Advances in Liquid Crystals* (Academic, New York, 1979), Vol. 4, p. 147.
- ¹⁹M. Vilfan and S. Zumer, *Phys. Rev. A* **21**, 672 (1980).
- ²⁰H. C. Torrey, *Phys. Rev.* **92**, 962 (1953).
- ²¹J. Selinger, M. Spector, V. Greanya, B. Weslowsky, D. Shenoy, and R. Shashidhar, *Phys. Rev. E* **66**, 051708 (2002).
- ²²A. Abragam, *Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961), pp. 298–300.
- ²³K. H. Schweikert and F. Noack, *Mol. Cryst. Liq. Cryst.* **212**, 33 (1992).