Pseudonematic order fluctuations of the director in the smectic phase of thermotropic liquid crystals

R. H. Acosta and D. J. Pusiol

Faculdad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

The NMR spin-lattice proton relaxation dispersion in the smectic mesophase of two liquid crystals, 4cyano-4'-8-alkylbiphenyl and 4,4'-bis-heptyloxyazoxybenzene, are studied over several decades of Larmor frequencies. The results show that the order fluctuation of the local smectic director contribution to $T_1(\nu_L)$ undergoes a transition between two power regimes: from $T_1(\nu_L) \propto \nu_L^1$ to $\nu_L^{1/2}$ on going from low to high Larmor frequencies. We explain this behavior by assuming, in the smectic mesophases, short coherence length nematiclike cooperative molecular reorientations. [S1063-651X(99)01508-1]

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I. INTRODUCTION

Liquid crystals are compounds that simultaneously show characteristics common to both isotropic liquids and solid crystals. In nematic mesophases molecules maintain its long axis locally oriented, resembling a tridimensional oriented liquid. Smectic structures, however, include a higher ordering degree; i.e., molecules are arranged in layers, roughly speaking, as in a bidimensional oriented liquid. Within each mesophase the local—or domain—director suffers thermally stimulated orientational order fluctuation called order fluctuations of the director (OFD) [1]. This OFD are represented by elastic overdamped hydrodynamical modes, expanding in three dimensions in the case of nematic mesostructures or in two-dimensional layers (or undulation modes) in smectic mesophases. In this paper we report a detailed NMR proton spin-lattice relaxometry study in two representative smectic liquid crystals, showing that undulation modes are present in smectic thermotropic liquid crystals just at short wavelengths, while short **k**-vector fluctuations in the same mesophase are three-dimensional nematiclike.

NMR spin lattice relaxation time T_1 is due to the fluctuations producing modulation in the orientation of the internuclear vector of two protons with respect to the external magnetic field [2]. It is well known that in NMR studies of thermotropic liquid crystalline mesophases the protons spin-lattice relaxation Larmor frequency dispersion $T_1(\nu_L)$ (or T_1) relaxometry [3] is essentially determined by the superposition of several competing relaxation mechanisms: (i) individual molecular motions, such as self-diffusion $(T_1)_{SD}$ and molecular rotations $(T_1)_{Rot}$, and (ii) collective molecular motions or order fluctuations of the local director $(T_1)_{OFD}$ [4].

Self-diffusion modulates the intramolecular dipolar interactions by reorientations of individual molecules with respect to the external Zeeman magnetic field while they are translationally diffusing through the liquid crystalline locally oriented domains. The inter spin-pair vector can, in addition, rotate together with the whole molecule or with a tail. The step by step rotational diffusion model has been widely used since the first frequency dependent NMR studies [4]. Both translational and rotational diffusions in liquid crystals present very short correlation times (typically in the range 10^{-10}–10^{-11} s) contributing significantly to $T_1(\nu_L)$ at Larmor frequencies in the range of conventional spectrometers; i.e., $\nu_L > 10$ MHz. OFDs has been proved to be the relaxation mechanism dominating $T_1(\nu_L)$ in the frequency range below the MHz's [4].

II. THEORETICAL BACKGROUND

A. Nematic phase

The spin-lattice relaxation time for two spin $I = \frac{1}{2}$ nuclei with a constant internuclear distance may be expressed as [2]

$$T_1^{-1}(\nu) = \frac{9}{8} \gamma^4 \hbar^2 r^{-6} [J_1(\nu) + J_2(2\nu)], \qquad (1)$$

where γ is the nuclear gyromagnetic ratio, r is the internuclear separation, and $J_s(s\nu)$ are the spectral densities of motion at a frequency ν. It has been shown that $J_2(2\nu)$ is negligible in almost every case [2].

The theoretical model for the contribution of the OFD's to T_1 in the nematic phase was first developed by Pincus [5]. The local director $\mathbf{n}(\mathbf{r},t)$ and consequently the molecules were considered to thermally fluctuate, making deviations from a fixed orientation $\mathbf{n_o}$ established by the magnetic field direction. Thus, the expression

$$\mathbf{n}(\mathbf{r},t) = \mathbf{n_o} + \delta\mathbf{n}(\mathbf{r},t) \qquad (2)$$

describes the orientational order fluctuation at a time t at the position $\mathbf{r}$ in the nematic liquid crystal. $\delta\mathbf{n}(\mathbf{r},t)$ represents, thus, a fluctuation in the director describing the local orientation of the molecules.

The integration of the Fourier transform of the orientation correlation functions summed over all possible states, that is, over a sphere in wave-vector space and assuming isotropic elastic constants and viscosities, gives a square root law $[(T_1)_{OFD} \propto \nu_L^{1/2}]$. This model was later improved by Doane *et al.* [6] and by Blinc *et al.* [7,8]. When anisotropies in the elastic constants are considered, the integration in the wavespace is done over a cylinder including ''cut-off'' terms, $q_\perp \sim \pi/a$ and $q_z \sim \pi/l$, where a and l are the two extreme limits for the OFDs coherence length.

The spectral density is thus

$$J_1(\nu) = \frac{9}{76\pi^2} kTS^2 \sum_\alpha \eta_\alpha \int_0^{q_z} dq_z$$

$$\times \int_0^{q_\perp} dq_\perp \frac{q_\perp dq_\perp}{(K_3 q_z^2 + K_\alpha q_\perp^2)^2 + \eta_\alpha^2 \nu^2} \quad \alpha = 1,2, \quad (3)$$

where S is the nematic order parameter, K_1, K_2 and K_3 are respectively the splay, twist, and bend elastic constants, and the viscosities η_1 and η_2 are related to the twist viscosity γ_1 [1]. $\mathbf{q}$ is a wave vector and $q_\perp^2 = q_x^2 + q_y^2$ is used to appropiately diagonalize the free energy expressions [1]. Later, Vold and Vold [9] replaced the cylindrical volume of integration by a rotational ellipsoid, obtaining similar results but with the advantage that this model, on the contrary of Blinc's, reduces to the usual 3D isotropic case [5,6]. Examples of both behaviors have been found in Ref. [10] $T_1(\nu_L) \propto \nu_L^{0.5}$ are reported, while in a polymeric liquid crystal Zeuner et $al.$ [11] has measured an exponent equal to 0.65.

B. Smectic phase

The nature of local order in the smectic (Sm) mesophases is a problem that has been studied extensively for the last twenty years, and yet it is not fully understood. While in the nematic phase OFD are assumed to propagate in a spherical way, it was first pointed out by Blinc et $al.$ [7] and later by Vold and Vold [9] that in smectic phases the propagation of the order fluctuation is restricted to the plane of the layer, i.e., to two dimensions. Taking the limit $K_1, K_2 \gg K_3$ (or $K_3 \to 0$) in Eq. (3) leaves out the integration over q_z, that is, integration is performed over a disk in the $\mathbf{k}$ space, where it is assumed that neighboring layers do not interact. This way, the spectral density becomes

$$J_1(\nu) = S^2 \frac{kT}{4K_1 \xi_s} \nu^{-1}. \quad (4)$$

where ξ_s is the coherence length in the direction perpendicular to the smectic planes, giving a linear frequency dependence $[(T_1)_{OFD} \propto \nu_L^1]$ [10,12, 13]. In addition, Vilfan et $al.$ [14] pointed out that close to the smectic-A–nematic transition, where fluctuations in the smectic layer thickness occur, a nematiclike behavior ($\nu_L^{1/2}$) should be present, although until now no experimental confirmation had been provided.

C. Quadrupolar dips

Measurements of $T_1(\nu_L)$ in a large enough Larmor frequency window (meaning at least four orders of magnitude) need to be implemented using the fast field cycling technique. T_1 profiles in smectic phases show the presence of broad quadrupole dips (QDs) [3], originated by the relaxation of ^1H through quadrupolar nuclei (^{14}N) [13] . It was recently pointed out [15] that previous $T_1(\nu_L)$ measurements could be strongly affected by artificial narrowing of QDs. The width of QDs in $T_1(\nu_L)$ profiles can be at least one order of magnitude diminished by a proper control of the Zeeman magnetic field during the relaxation period [16]. It is
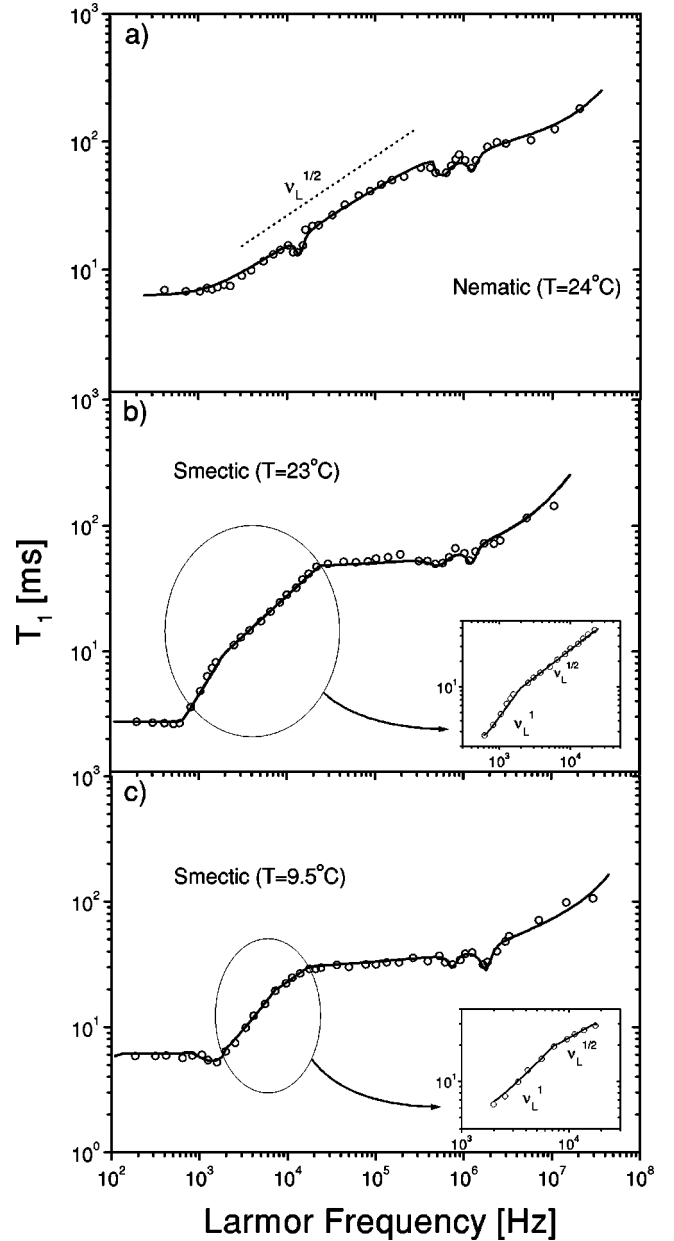

FIG. 1. Proton T_1 relaxation dispersion of 8-CB, showing the different behaviors of the order fluctuation. (a) In the nematic phase the square-root law ($T_1 \propto \nu_L^{1/2}$) is shown. (b) In the smectic phase, at a temperature close to the phase transition a nematiclike contribution is present in the smectic order. (c) The nematiclike contribution can be seen in a smaller frequency range at higher frequency.

now possible to reduce the effect of QDs to a very reduced Larmor frequency band, practically not affecting the general OFD behavior.

III. EXPERIMENT

Experimental T_1 profiles are recorded by means of a conventional ($5 \times 10^6 < \nu_L < 10^8$) and a fast field cycling ($10^3 < \nu_L < 10^7$) NMR spectrometer. With both instruments the random error of the individual T_1 points is less than 10% after appropriate signal averaging, and the sample temperature has been controlled with an accuracy of at least 0.2 °C. The FFC experimental setup is home made [16], the
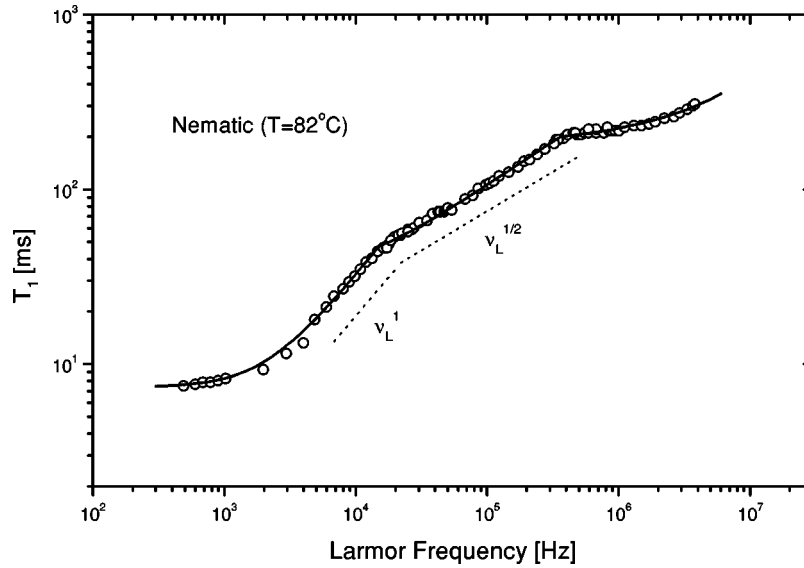
FIG. 2. Proton T_1 relaxation dispersion in the smectic C mesophase of a nonpolar compound: HpAB. The nematiclike contribution in the smectic order relaxation profile is present in the Larmor frequency range of 10^3 to 10^4 Hz.

design is based on a electronically switched FFC-NMR spectrometer which uses a special air core magnet design and a MOSFETs magnet control and power switching [17]. Additional coils are used for shimming the detection magnetic field. The earths field is compensated by an external pair of dc driven Helmholtz coils. The relaxation field B_r was measured by means of a double resonance experiment in a sample of water where no QDs take place. During the relaxation period, water protons are irradiated with a second pulse of frequency ν_r. Absorption of the second frequency is produced just as the relation $\gamma B_r = \nu_r$ is met. The quantity $\gamma \Delta \nu_r$, which is extracted from the convenient scan of the rf absorption at ν_r, gives us a measure of the B_r dispersion. In the frequency range of our interest we have, for instance, a dispersion in B_r of approximately 0.5 and 0.1 % at respectively $\nu_L = 400$ Hz and 2 MHz. Very fine improvements on the electronics of our FFC spectrometer were necessary before reaching the final performances.

4,4'-bis-heptyloxyazoxybenzene (HpAB) and 4cyano-4'-8-alkylbiphenyl (8-CB) samples are commercial from Merck and BDH, respectively. Samples were first purified by several recrystallizations. Glass sample holders were filled under vacuum and sealed. To obtain reproducible T_1 results at a selected temperature, in view of the strong hysteresis of the phase transitions in the purified samples, the temperature adjustments had to be preceded by suitable thermal treatment of the samples. We applied the following procedure: before starting the T_1 measurements the sample was heated to the isotropic state, then cooled to the lowest temperature in the smectic phase in the maximum field (0.5 T) of our field-cycling spectrometer.

Figure 1 shows T_1 profiles of 8-CB at three temperatures: (a) $T = 24$ °C, in the nematic phase and (b) in the Sm-A at $T = 23$ °C, and (c) in the Sm-A at $T = 9.5$ °C. In Fig. 1(a) the $\nu_L^{1/2}$ behavior is present over two decades of $\nu_L \approx 10^3$ through 10^5 Hz. A constant value is reached for frequencies below 2×10^3 Hz. This low-frequency cut off, $2 \pi \nu_{c,l} = K q_l^2 / \eta$ is determined by the fact that the wave length of the order fluctuation cannot be longer than the nematic order correlation length ($2 \pi / \lambda_{max} = q_l$). Three small QD's can be observed at $\nu_L = 2 \times 10^4$, 6×10^5, and 1.6×10^6 Hz, respectively. At Larmor frequencies higher than 3×10^6 Hz the SD mechanism is dominant. In the smectic-A phase, two slopes can be observed in Fig. 1(b). A transition from ν_L^1 to $\nu_L^{1/2}$ regimes takes place at 1.9×10^3 Hz, for frequencies higher than 2.6×10^4 Hz the usual SD mechanism takes place. In Fig. 1(c), 12 °C below the $N-$Sm-A phase transition, the change in the $T_1(\nu_L)$ slope takes place at a higher frequency, $\nu_L = 8 \times 10^3$ Hz. At 1.7×10^4 Hz the SD dominates the relaxation.

Figure 2 shows the experimental data [18] of T_1 in the smectic-C phase of HpAB at $T = 82$ °C. The transition temperatures for this compound are 95.4 °C for the N–Sm-C and 74.5 °C for the Sm-C–crystalline solid. These results show a change in the $T_1(\nu_L)$ slope at 2×10^4 Hz from ν_L^1 to $\nu_L^{1/2}$. Above 4×10^5 Hz the SD behavior is observed.

IV. DISCUSSION

Figures 1(b), 1(c), and 2 show that the $T_1 \propto \nu_L^1$ behavior predicted by Eq. (4) is not valid for the whole frequency range. This suggests that integrating the spectral density over a layer does not give an accurate description in a broad time scale of the order fluctuations in the smectic phase. Although the $\nu_L^{1/2}$ regime had been predicted by Vilfan et al., their treatment is valid only within the critical temperature range of the N–Sm-A transition and cannot be applied in the present case due to the broad temperature range involved in the experiments in 8-CB. If we consider that a small region confined to the layer of integration looks like a sphere of radius of the order of few molecular lengths, this can give rise to a nematiclike behavior for an interval of frequencies. Moreover, the interaction between neighboring layers can also produce short length nematic domains. The maximum coherence size of these *pseudo-Nematic* OFDs can be estimated from $\xi = \sqrt{2 \pi K / \eta \nu}$, when the one-constant approximation is used ($K_1 = K_2 = K_3$; $\eta_1 = \eta_2$) and ν is the regime

transition frequency. In the case of 8-CB at 23 °C, ξ can be calculated to be approximately 7000 Å, and the smectic cut-off coherence length $\xi_c \sim 18\,800$ Å. At 9.5 °C ξ diminishes to 3400 Å, and the smectic cutoff to $\xi_c \sim 11\,100$ Å. This reduction in the pseudo-N coherence length is attributed to the fact that at lower temperatures the inter-smectic layer interaction diminishes far away from the N-Sm first order phase transition. There, undulation modes are more plausible to dominate the OFD. Pseudo-N OFDs propagate in a volume which is one order of magnitude smaller than pure undulation Sm OFD modes.

We conclude that in both SmA and SmC mesophases, a nematiclike behavior in the OFDs is present. The inter-smectic-layer interactions that produce the pseudonematic OFDs are not a property of the molecular electric polarity, because it takes place in both polar 8-CB and nonpolar HpAB compounds. The phenomena could be a consequence of two effects: (1) one related to a loss of local order in the layered Sm structure due to the proximity of the Sm-N transition, and (2) the presence of pseudonematic domains in the smectic phase. Both could be present together, but nevertheless the second one drives the T_1 profile in the middle of both the HpAB Sm-C and the 8-CB Sm-A mesophases.

Nematic and smectic mesophases are always distinguishable through different experimental methods. This experiment shows that in a determined time scale both mesophases are indistinguishable from its slow dynamics. From our results at frequencies below 10^3–10^4 Hz pseudonematic OFDs in the smectic mesostructures is not expected to be detectable. This should explain why by means of ''static'' techniques, like optical or x-ray scattering, N and Sm mesophases are clearly distinguishable.

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