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Experimental NMR spin-lattice relaxometry study in the liquid crystalline nematic phase of propylcyano-phenylcyclohexane

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The NMR spin-lattice proton relaxation dispersion $T_1(\nu_L)$ of the liquid crystal propylcyano-phenylcyclohexane is studied over several decades of Larmor frequencies and at different temperatures in the nematic mesophase. The results show that the order fluctuation of the local nematic director contribution to $T_1(\nu_L)$ undergoes a transition between two power regimes: from $T_1(\nu_L)\propto\nu_L^{1/2}$ to ν_L^{α} $(\alpha\sim 1/3)$ on going from low to high Larmor frequencies.

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I. INTRODUCTION

Liquid crystals have suscitated the interest of numerous studies due to their unique characteristic of behaving as an isotropic liquid or having collective motions on different time scales [1]. Field-cycling NMR relaxometry [2] has been widely used to probe reorientational molecular motions through the dispersion of the spin-lattice relaxation time $[T_1(\nu_L)]$. In thermotropic liquid crystals at Larmor frequencies higher than 10^6-10^7 Hz individual mechanisms of relaxation, such as molecular self-diffusion and rotations dominate the relaxation. 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. In addition, the interspin vector can rotate with the whole molecule. This process can be described by the step-by-step rotational diffusion model, widely used in frequency-dependent NMR studies [3].

For frequencies below 10^5-10^6 Hz collective molecular motions govern the relaxation. Thermally stimulated fluctuations of the local director produce orientational director fluctuations (ODF) [1] that can be represented by overdamped elastic modes propagating in a spherical way in the nematic mesophase. The overdamping is produced by dispersion of the elastic reorientation waves by defects. Since the first model proposed by Pincus [4] several improvements have been made to the theory including temperature dependence [5] and anisotropies in the elastic constants [6,7].

The discrimination of different NMR relaxation mechanisms is based on the identification of characteristic frequency dispersion laws of spin-lattice relaxation. The most known examples of ODFs are the square-root law $[T_1(\nu_L)\propto\nu_L^{1/2}]$ for the nematic mesophase [2] and the linear law $[T_1(\nu_L)\propto\nu_L]$ in smectics [6,8]. The identification of nematic domains in the smectic phase of thermotropic liquid crystals was possible due to the observation of a transition of power regimes from a linear dependence to a square root one [9].

In this work we measured $T_1(\nu_L)$ in propylcyano-phenylcyclohexane (3-PCH) in the nematic mesophase at several temperatures within the range of 10^3 Hz$<\nu_L<10^8$ Hz. In addition to the $T_1(\nu_L)\propto\nu_L^{1/2}$, the data behavior shows an anomalous dispersion law of $T_1\propto\nu_L^{\alpha}$ (with $\alpha\sim 1/3$) in the range of $2\times10^4-10^7$ Hz. We propose that the ν_L^{α} behavior should be produced by the proton spin pairs reorientational fluctuations which could in principle be represented by quasielastic modes with wavelengths in the short and medium range, as compared with ODFs and that the structure of the molecules could play an important role in its existence.

II. THEORETICAL BACKGROUND

Order director fluctuations give rise to spin-lattice relaxation by modulating the orientation of the internuclear vector with respect to an external magnetic field [10]. For a nuclear pair of two spin 1/2 nuclei, with a fixed separation distance r, the spectral density of the dipolar autocorrelation is given by

$$J_1(\nu_L)=S^2r^{-6}\int_{-\infty}^{\infty}\langle\delta\mathbf{n}(\mathbf{r},t),\delta\mathbf{n}(\mathbf{r},0)\rangle e^{i2\pi\nu_L}dt,$$

where $\delta\mathbf{n}(\mathbf{r},t)$ represents a fluctuation of the director $\mathbf{n}$, S denotes the order parameter, and ν_L is the Larmor frequency. Introducing Fourier components and carrying out the time integration the spectral density is expressed as a sum of contributions of normal modes representing different wave vectors $\mathbf{q}$:

$$J_1(\nu_L)=S^2r^{-6}\sum_{\alpha=1}^{2}\sum_{\mathbf{q}}\langle|\delta\mathbf{n}(\mathbf{q},0)|^2\rangle\frac{2\tau_\alpha(\mathbf{q})}{1+4\pi^2\nu_L^2\tau_\alpha^2(\mathbf{q})},$$

$\alpha=1,2$ rather than (x,y) denotes a proper diagonalization to minimize the free energy expressions [1]. The mean square amplitude for each mode can be obtained with the aid of the equipartition theorem and using the Landau-Kalatnikov equation. Replacing the summation by an integral from zero to the cutoff q_z and $q_\perp$ values the spectral density is

$$J_1(\nu_L)=\frac{9}{76\pi^2}k_BTS^2\sum_\alpha\ \eta_\alpha\int_0^{q_z}dq_z\times\int_0^{q_\perp}\frac{q_\perp dq_\perp}{(K_3q_z^2+K_\alpha q_\perp^2)^2+4\pi^2\eta_\alpha^2\nu_L^2},\quad\alpha=1,2, \tag{1}$$

where η_α is an appropriate viscosity, K_1, K_2, and K_3 are, respectively, the splay, twist, and bend elastic constants [1], $q_\perp^2=q_x^2+q_y^2$, k_B is Boltzman's constant, and T the absolute temperature. When anisotropies in the elastic constants are considered the integration in the wave space is done over different volumes. Blinc *et al.* [8,7] considered a cylindrical volume of integration and later Vold and Vold [6] considered an ellipsoidal one. The integration over different volumes gives rise to different expressions for the low frequency cutoff but the same dependence of the order fluctuation-induced spin-lattice relaxation time on the Larmor frequency which is the well-known square root law derived by Pincus [4].

The fitting model for ODFs is [11]

$$\frac{1}{T_{1\,\mathrm{ODF}}}=A\nu^{-1/2}\left(1-\frac{1}{\pi}\left\{\left[\tan^{-1}\left(\frac{\sqrt{2\nu/\nu_c}}{\nu/\nu_c-1}\right)+\tanh^{-1}\left(\frac{\sqrt{2\nu/\nu_c}}{\nu/\nu_c+1}\right)\right]-\Theta(\nu/\nu_c-1)\right\}\right)$$

with $A=\text{const}$, Θ the Heaviside function, and ν_c the low cutoff frequency.

Individual motions contribute to the relaxation in a lower time scale and can be described, for rotations as [12]

$$\frac{1}{T_{1\,\mathrm{rot}}}=B\tau_1\sum_{p=1}^{2}\frac{p^2}{1+(p\pi\nu\tau_1/3)^2}$$

with $B=\text{const}$ and τ_1 the time reorientation constant. The self-diffusion contribution to the relaxation process can be written as [13]

$$\frac{1}{T_{1\,\mathrm{dif}}}=C\tau_D\sum_{p=1}^{2}p^2\left[\frac{x}{2}-\frac{1}{x}+[F(x)+H(x)]e^{-x}\right]\frac{1}{x^4},$$

with

$$F(x)=\left(\frac{x}{2}-\frac{1}{x}\right)\sin x,$$

$$H(x)=\left(\frac{x}{2}+\frac{1}{x}+2\right)\cos x,$$

$x=\sqrt{12\pi p\nu_L\tau_D}$, $C=\text{const}$, and τ_D is the constant of translational molecular jump.

III. EXPERIMENT

Experimental T_1 profiles were recorded by means of a conventional (5×10^6 Hz$<\nu_L<10^8$ Hz) and a fast field cycling (10^3 Hz$<\nu_L<10^7$ Hz) 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 homemade [13]. The 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 [14]. Additional coils are used for shimming the detection magnetic field. The earth 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 quadrupolar dips [15] were found. 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.

Propylcyano-phenylcyclohexane ($C_{16}H_{21}N_1$) purchased from Merck Co. was first recrystallized and then purified by local fusion in the solid state, this is, melting a layer of the cylindrical sample scanning it slowly from the bottom to the top and vice versa. This process is repeated several times. Local fusion allows heavy and light residual impurities to migrate to the bottom and the top of the sample container, respectively. Afterwards the top and bottom of the sample, containing the impurities, are removed with the aid of a clean cutter. Glass sample containers of 10 mm diameter and 12 mm in length were filled with the purified sample and sealed under vacuum. Due to the hysteresis of 2 °C in the purified samples we applied the following treatment: the sample was heated to the isotropic state and then cooled to 26 °C in the nematic phase with the strongest static field present. Phase transitions of the purified compound were measured with a homemade DTA. The nematic-isotropic transition occurs at 46 °C and the crystal-nematic at 16 °C. This compound neither has a conjugated aromatic central system, nor, similar to cyanobiphenyls, a functional group in the central part. Nevertheless, it has very low bulk viscosity compared to cyanobiphenyls due to the weaker dispersion forces from the anisotropic molecules caused by the cyclohexyl ring [16]. Bulk viscosity is proportional to its flow viscosity coefficient η and to its elastic coefficients K.

Figure 1 shows $T_1(\nu_L)$ at two temperatures: 31 °C in the nematic phase and 66 °C in the isotropic phase. The isotropic data are fitted with a rotation of the long axis with a correlation time of $\tau_{RI}=3.3\times10^{-9}$ sec. In the nematic phase for frequencies higher than 6×10^6 Hz two rotations and self-diffusion are assumed. The $\nu_L^{1/2}$ behavior is present from $\nu_L\sim10^3$ through 10^4 Hz. A constant value is reached for frequencies below 5×10^3 Hz. A transition from $\nu_L^{1/2}$ to $\nu_L^{0.37}$ occurs at $\nu_t=4.8\times10^4$ Hz and extends to 6×10^6 Hz.

Figure 2 shows the experimental data of T_1 in the nematic phase at four different temperatures 26, 31, 36, and 41 °C. A typical nematiclike behavior is present at all temperatures, this is, the low frequency plateau and the $\nu_L^{1/2}$ dispersion law. The transition frequency from $\nu_L^{1/2}$ to ν_L^{α} is seen to decrease with temperature from 6×10^4 Hz to 2.3×10^4 Hz while the exponent $\alpha=0.37\pm0.02$ remains almost constant.

IV. DISCUSSION

In Fig. 1, a typical nematiclike behavior of $T_1(\nu_L)\propto\nu_L^{1/2}$ is seen between 10^2 Hz and 4.8×10^4 Hz for a temperature of

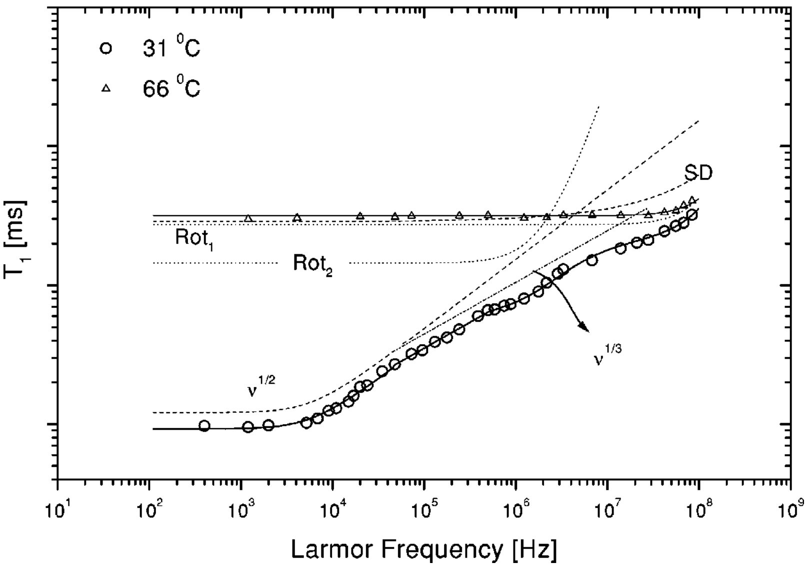

FIG. 1. Frequency dependence of the spin-lattice relaxation of 3-PCH in the isotropic mesophase ($T = 66\,°\mathrm{C}$) and in the nematic mesophase ($T = 31\,°\mathrm{C}$). Departure from the $T_1 \propto \nu_L^{1/2}$ to $\nu_L^{0.37}$ can be seen at $\nu_t = 30$ KHz.

31 °C. The plateau in $T_1(\nu_L)$ is reached for frequencies below $\nu_c = 5\times10^3$ Hz. This low-frequency cutoff is associated with a coherence length $\xi_c = \sqrt{2\pi K/(\eta\nu_c)}$, of 1.36×10^4 Å. The values for the effective viscosity η and elastic constants K_i measured by Schad *et al.* [17] were used in the calculation of ξ_c. A transition from the $\nu_L^{1/2}$ regime to a $\nu_L^{0.37}$ regime occurs at $\nu_t = 4.8\times10^4$ Hz and is present up to 6×10^6 Hz, where individual relaxation mechanisms dominate T_1. Two rotations influence T_1, one in the range $5\times10^5 - 5\times10^6$ Hz with $\tau_1 = 2.6\times10^{-7}$ sec and another for frequencies higher than 2×10^7 Hz with $\tau_2 = 4\times10^{-9}$ sec. Self-diffusion has a characteristic time of $\tau_D = 3.5\times10^{-10}$ sec. As it is well established for other nematic and smectic liquid crystals [18] τ_1 is assigned to rotations about the perpendicular axis and τ_2 about the axis of the molecule. Note that at 66 °C rotations about the long and short axis have τ_1 and τ_2 of the same order of magnitude as expected for an isotropic liquid.

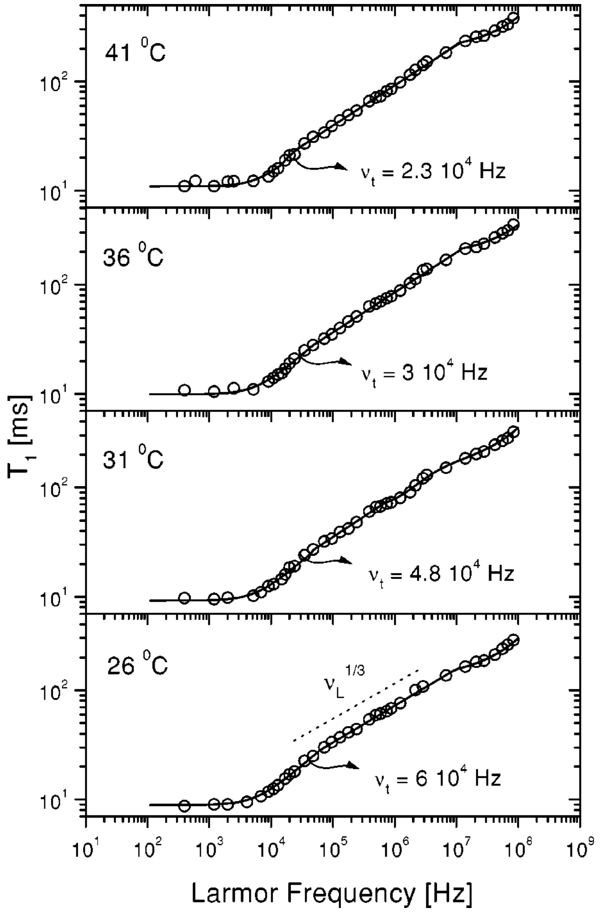

FIG. 2. Spin-lattice relaxation time in 3-PCH showing the decrease in the $T_1 \propto \nu_L^{1/2}$ regime with temperature.

Figure 2 shows the experimental data of T_1 in the nematic phase at four different temperatures. In Table I we observe two different behaviors: ν_c decreases with temperature while ν_t increases. The first behavior is consistent with a recent study carried out on 4-PCH [19] and means that the coherence length decreases as temperature approches the nematic-isotropic phase transition. For frequencies higher than ν_t the values of T_1 fall below the continuation of the $\nu_L^{1/2}$ curve, this indicates that there exists another mechanism contributing to the relaxation rate. As the frequency domain where this process takes place is larger than that of 3D-ODF, a smaller coherence length for it should be expected, this is, short range molecular interactions are expected. Bending of the molecules could generate different modes of collective fluctuation of the local director and might be favored in this compound because of its low viscosity. This is in agreement

TABLE I. Low cutoff frequency for the $T_1 \propto \nu^{1/2}$ regime, transition frequency to the $T_1 \propto \nu^{\alpha}$ and their correlation lenghts for different temperatures.

Temp. [°C]	ν_c [Hz]	ν_t [Hz]	$\alpha \pm 0.02$	ξ_c [Å]
26	5×10^3	6×10^4	0.34	1.35×10^4
31	5×10^3	4.8×10^4	0.37	1.36×10^4
36	5.2×10^3	3×10^4	0.37	1.31×10^4
41	5.5×10^3	2.3×10^4	0.37	1.24×10^4

with Fig. 2 which shows that with increasing temperature, this is, decreasing viscosity, the frequency range for this process is larger.

It was pointed out in Eq. (1) that anisotropies in the elastic constants give rise to different cutoff parameters and the square-root law for three-dimensional overdamped elastic waves [7,6]. On the other hand, the smectic phase is often referred to as a bidimensional liquid, so that this expression can be understood in the frame of ODF's as undulation waves, or waves that propagate in a bidimensional way. From Eq. (1) this can be seen to give a linear law for the dispersion profile by taking the limit $K_3 \ll K_1, K_2$ (or $K_3 \rightarrow 0$) [6]. Another example of how far the present theory can go is to think in terms of a very simplified one-dimensional model resembling a reptation, this is, waves propagating in the z direction. In this case $K_3 \gg K_1, K_2$ (or $K_1, K_2 \rightarrow 0$) gives a $T_1 \propto \nu_L^{3/2}$ law [10]. As a general rule the exponent of ν_L diminishes as the dimensionality of the director fluctuations propagation wave decreases. The fall in the exponent in the power law would then indicate a gain in dimensionality. If we consider that some mechanism, such as, for instance, molecular bending, is responsible for this new relaxation, it should be described by the addition of another term in the free energy expression. This would require adding another dimension to the integral of expression (1). An adequate theoretical frame explaining this process is material for future research.

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