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NMR Study of the Local Molecular Dynamics in the Isotropic Phase of a Thermotropic Liquid Crystal

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Nuclear Magnetic Resonance proton spin-lattice measurements in phenylcyano-phenylcyclohexane liquid crystal at the Larmor frequencies 1.235 MHz and 48 kHz in a temperature range above the nematic-isotropic phase transition are reported.

The Landau-De Gennes theory for nematic-isotropic phase transition is used to analyze the temperature dependence of the spin-lattice correlation functions. We conclude that the low frequency approximation can be applied only when the experiment is carried out at Larmor frequencies in the kHz range.

Keywords: Liquid crystals; Molecular dynamics; NMR

I. INTRODUCTION

Several experimental studies show clearly that the nematic-isotropic (N-I) phase transition in thermotropic liquid crystals is a weak first order transition [1]. In the isotropic phase, there is no long range positional or orientational order, but a short range order in the molecular orientation persists, corresponding to a few molecular distances. A measure of this local order is given by the orientational coherence length, ξ .

The effect of the isotropic phase short range ordering in the NMR spin-lattice relaxation time, T_1 , was first suggested by Blinc *et al.* [2]. They measured respectively T_1 in the laboratory frame (T_1) and in

the rotating frame ($T_1\rho$) in *p*-azoxyanisole (PAA) and *p*-azoxyphenetole (PAP). Later, Dong *et al.* [3] measured the temperature dependence of ^{14}N linewidth in the isotropic phase of *p*-n-butylaniline (MBBA) liquid crystal at 3 MHz Larmor frequency. Their results were explained in terms of the Landau-De Gennes (L-DG) theory [4], using the *low frequency approximation*, it means $\omega\tau \ll 1$ ($\omega = 2\pi\nu_L$), where τ is the correlation time for this process and ν_L is the Larmor frequency.

Extensive experimental and theoretical studies of nuclear magnetic relaxation in the nematic phase indicate that, in the proton spin relaxation dispersion, $T_1(\nu_L)$, orientational director fluctuations (ODF) contribute significantly at frequencies below 1 MHz, meanwhile above a few MHz, ODF are masked by much larger contributions from individual molecular motions like rotations and translational self-diffusion [5].

Following the L-DG theory, in the isotropic phase, two relaxation regimes can be distinguished, too. Whereas at "low frequencies", when ν_L is smaller than the frequency of the local order fluctuations (OF), T_1 is only temperature dependent (low frequency approximation), the relaxation times are independent of ν_L , meanwhile the opposite behaviour is observed at high frequencies. In all previous works the low frequency approximation is not clear, because the temperature dependence of T_1 has never been studied for Larmor frequencies in the kHz range, where the low-frequency approximation is highly expected to be valid.

In order to check the L-DG theory and the low frequency approximation, we extend the measurement of the temperature dependence of T_1 in the isotropic phase to the kHz range. In the present work we measured phenylcyano-phenylcyclohexane (5-PCH) liquid crystal at 1.235 MHz and 48 kHz Larmor frequencies. On the other hand, we analyze the different relaxation mechanisms present in this Larmor frequencies scales.

II. EXPERIMENTAL SECTION AND RESULTS

Phenylcyano-phenylcyclohexane liquid crystal was purchased to Merck Co., recrystallized and purified by local fusion in the solid state. Glass sample holders were filled under vacuum and sealed.

The measurements of the longitudinal proton relaxation dispersion at different frequencies were performed by means of a home-

built fast field-cycling [6] NMR spectrometer. 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 0.2 °C.

Figures 1 and 2 show the proton T_1 at $\nu_L = 1.235$ MHz and 48 kHz measured as a function of temperature in the isotropic phase of 5-PCH. For this compound $T_c \sim 326$ K [7], respectively.

The data presents a similar temperature dependence at 12 K above T_c , however, T_1 presents a different dependence on temperature as well at 1.235 MHz as at 48 kHz in the vicinity of T_c .

III. DISCUSSION

Since even in the nematic phase many aspect of molecular dynamics are close to those of an isotropic liquid, it is expected that the experimental T_1 should not be solely due to critical fluctuations, but rather should have two contributions in general. We can write

$$\frac{1}{T_1} = \frac{1}{T_{1OF}} + \frac{1}{T_{1IM}} \quad (1)$$

where the subscripts OF and IM denote, respectively, contributions to the experimental T_1^{-1} from order fluctuations and other sources expected to be presented, such rotations about the molecular axis and random traslational motions.

Following the Landau-De Gennes theory for thermotropic liquid crystals, above the isotropic - nematic transition temperature, T_c , the contribution to T_1 due OF is [4,8]:

$$\frac{1}{T_{1OF}} = AT\sqrt{\eta} \left[\frac{\tau_1}{1 + \sqrt{1 + \omega^2 \tau_1^2}} \right]^{1/2} \quad (2)$$

where A is a temperature independent constant, $\omega = 2\pi\nu_L$, $\tau_1 = \frac{\eta\xi^2}{L}$, η is the effective viscosity, ξ is the correlation length that measures the distance over which the local nematic order persists in the isotropic

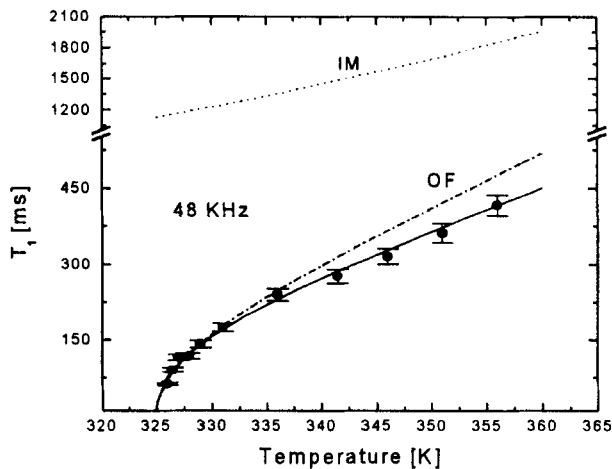


FIGURE 1: Temperature dependence of the T_1 in the isotropic phase at $\nu_L = 48$ kHz for 5-PCH. Individual relaxation contributions are obtained from the curve fit of eq. (1).

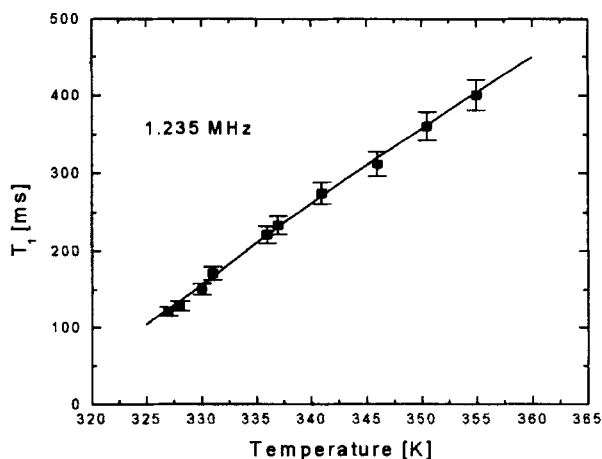


FIGURE 2: Temperature dependence of the spin lattice relaxation above the clearing point at $\nu_L = 1.235$ MHz for 5-PCH with the fitting curve following eq. (1).

phase, $\xi = \sqrt{\frac{L}{a(T-T_c^*)}}$, ($a > 0$ is temperature independent), T_c^* is the critical temperature slightly below T_c ($T_c - T_c^* \sim 1$ K) and L is related to the elastics constants.

We assume Arrhenius-like behavior for the viscosity $\eta = \eta_0 \exp\left(\frac{E_{OF}}{RT}\right)$, whit η_0 a constant and E_{OF} is the activation energy for this process [9].

If the condition $\omega\tau \ll 1$ is fulfilled, it means the low frequency approximation, the contribution to T_1 due the OF is

$$\frac{1}{T_{1OF}} = A' \frac{T \exp\left(\frac{E_{OF}}{RT}\right)}{(T - T_c^*)^{1/2}} \quad (3)$$

Then T_{1OF} is strongly temperature dependent and independent of the frequency.

On the other hand, the T_{1IM} term is assumed to be [10]:

$$\frac{1}{T_1} = B \exp\left(\frac{E_{IM}}{RT}\right) \quad (4)$$

with B a constant and E_{IM} is the activation energy for this process. Such a relation follows from the BPP theory when the relaxation process is governed by diffusion effects, as a simple liquid.

To test the model described above we fitted the experimental $T_1(T)$ and treated E_{OF} , E_{IM} , T_c^* , A , A' , B , as adjustable parameters. The obtained values are $T_c^* = 325$ K, $E_{OF} = 9.8$ kJ/mol and $E_{IM} = 24.9$ kJ/mol.

Figure 1 illustrates the fitting of the experimental data at 48 kHz, using eq. (1) and the contribution of each relaxation mechanism. The OF dominate the relaxometry profiles and the experimental data are fitted using the low frequency approximation (eq. (3)) with a small contribution of individual motions given by eq. (4). As it can be observed in this figure the OF dominate in the temperature range close to T_c . This result is plausible due to the L-DG theory is expected to be valid at T close to T_c .

At 1.235 MHz (fig. 2) the relaxation profiles show a contribution only of OF and data were fitted using eq. (2). In this cases the low frequency approximation is not applicable.

From the fittings it can be seen that for 48 kHz the approximation $\omega\tau \ll 1$ is fulfilled for the whole temperature range. On the other hand, the activation energies present the same order in magnitude than those

corresponding to others compounds, such as MBBA, EBBA [11] and PAA [12].

From this results we can say that, like in the nematic phase [13], in the isotropic phase, OF is the most important dominant relaxation processes in the kHz range.

We conclude that the critical order fluctuations in the isotropic phase of 5-PCH liquid crystal can be studied by means of proton spin relaxation measurements, and the Landau-De Gennes theory is appropriate to describe it, if the scale frequency used is in the range where the OF are the more effective relaxation mechanism.

IV. ACKNOWLEDGMENTS

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