Universal Nuclear Spin Relaxation and Long-Range Order in Nematics Strongly Confined in Mass Fractal Silica Gels

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We show how the low-frequency dependence of the proton spin-lattice relaxation time $T_1(\nu)$ of octylcyanobiphenyl liquid crystals confined in high-density silica gels evidences a long-range order nematic phase in spite of the strong confinement and random disorder of the gels. The universal value and frequency dependence observed, $T_1(\nu) \propto \nu^{2/3}$, is interpreted within a relaxation model due to director fluctuations in nematic liquid crystals confined to mass fractal porous media. The model provides a relation $T_1(\nu) \propto \nu^{2-d/2}$, giving a reliable value of the structural fractal dimension $d_f = 2.67$ for all the host silica gels.

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In recent years confined liquid crystals (LCs) have received considerable attention due to the apparent disappearance of the nematic phase when they are strongly confined [1–6]. A number of theoretical works have concluded that the inherent disorder of host porous media makes the long-range orientational order (LRO) characteristic of the nematic phase to be replaced by a "glassy" state [7–9]. But this seems to happen only under certain conditions [9–11]. To get direct evidence for the existence or not of the LRO nematic phase under strong confinement in disordered porous media, we probed a dynamic process which at large length scales is unique to the ordered phases of LCs: the orientational order director fluctuations (ODF).

Director fluctuations involve collective motions of a macroscopic number of molecules, and such motions have relatively long correlation times. The ODF are known to be the main cause of NMR relaxation at quite low frequencies, and the frequency dependence of the spin-lattice relaxation $T_1(\nu)$ in the range below about 1 MHz is used normally to get information on bulk ordered phases [12]. Pincus [13,14] proposed that in *bulk* LCs, $T_1(\nu) \propto \nu^{1/2}$, law that is supported by a large number of experimental results [12]. There is no indication of how Pincus law would be modified in an aerogel-LC system. Silica gel is of interest in the study of confined LC, due to its quenched disorder and mass fractal structure.

We report here on measurements of the proton-NMR spin-lattice relaxation frequency profiles between 0.01 to 10 MHz of the thermotropic 4-octyl-4'-cyanobiphenyl (8CB) liquid crystal both bulk and strongly confined in a series of silica gels of different densities. These measurements were performed over the temperature range of 25 to 50 °C, which spans the liquid crystalline and isotropic phases. We develop also a model for the NMR relaxation originated by the ODF in a nematic LC confined to a structurally fractal porous matrix. All silica gel samples were prepared by hydrolysis and polycondensation of tetraethoxysilane in ethanol under slightly acidic conditions of pH. Three kinds of gels were synthesized: a xerogel (X), a xeroaerogel (XA), and two xerogel composites (XC) [15]. The parameters characterizing each gel are given in Table I. In the case of xerogel composites some silica fumed particles (aerosil) were added during the hydrolysis step, namely 5% and 45% in wt.% for the 10 and 16 nm pore size samples, respectively. These composite samples have larger density and are more homogeneous. The silica surfaces have -OH and -OR groups in the xerogel and xeroaerogel and only -OH groups in the composites, due to a special thermal treatment. Dried gel samples were vacuum baked at 120 °C for more than 12 h. The filling process of 8CB was then performed by capillary action for more than 24 h at 60 °C, to ensure that 8CB was in the isotropic phase. Finally, the embedded gel samples were dried to eliminate any residual LC in the surface. Measurements of the T_1 frequency profiles were made using a fast-field-cycling NMR spectrometer from Stelar Company. The profiles were obtained from monoexponential time decays of longitudinal magnetizations, verifying that there were no fast components coming from cross relaxation with protons at the surface of the pores. The experimental error of the T_1 measurements was less than 5%, but increased slightly for short relaxation times of the order of the field switching time (1 ms). Figure 1 shows T_1 as a function of the Larmor frequency in the liquid crystalline and isotropic phases of bulk 8CB. All the expected behaviors are seen from this figure [12].

There is a crossover at $\nu_c = 1$ MHz from fast individual to slow collective molecular motions. In the high-temperature isotropic phase at 43 °C a leveling off of the T_1 dispersion curve is observed below ν_c, caused by the averaging of the fast isotropic reorientation of the 8CB molecules in the comparably long NMR time scale. The usual squared-root dispersion curve, appearing often below 0.1 MHz and characteristic of director fluctuations, is

TABLE I. The parameters of the xerogel (X), xeroaerogel (XA), and xerogel composites (XC) used in this work. The pore sizes were obtained by the nitrogen sorption-desorption method. Frequency dependences of T_1 obtained in bulk and confined samples in the smectic A (SmA), nematic (N), and isotropic (I) phases.

					N	I
Matrix	Pore size (nm)	Surface coverage	Density (g/cm^3)	SmA	$T_1(\nu)$	
X	2.5	-OH, -OR	0.63	$\cdots$	$\nu^{2/3}$	$1/\log\nu$
XC	10	-OH	0.77	$\cdots$	$\nu^{2/3}$	$1/\log\nu$
XA	15	-OH, -OR	0.33	$\cdots$	$\nu^{2/3}$	$1/\log\nu$
XC	16	-OH	0.75	ν	$\nu^{2/3}$	$1/\log\nu$
Bulk				Onset of ν	$\nu^{1/2}$	Plateau

seen in the nematic phase at 34 °C. We show in Fig. 2 the T_1 dispersion curves for 8CB confined to the xerogel composite sample with pore size of 16 nm at three different temperatures.

Similar behaviors were observed in the other samples studied. Clearly, there are significant differences with respect to the bulk LC. At low frequencies, the T_1 values are about an order of magnitude lower, a common effect observed in confined liquid and related to the enhancement by the confinement of the relaxation mechanism. The crossover from collective to individual molecular motions is shifted to a higher frequency at approximately 10 MHz, indicating an increase of collective molecular motions under confinement. In the high-temperature phase at 43 °C T_1 is no longer frequency independent, but follows $T_1 \propto 1/\log\nu$. Also at this temperature, T_1 is linearly proportional to the pore size of the samples at low-frequency and is pore-size independent at 10 MHz (behaviors not shown). These dependencies are characteristic of confined normal (isotropic) 2D liquids [16]. This rules out any chemical bonding or strong adsorption of these molecules to the polar groups present in the pore surface of our samples. The nonexistence of the chemical bonding is consistent with Raman spectra [17]. At the temperature of 34.5 °C, at which the nematic phase would be observed in bulk, one finds $T_1 \propto \nu^{2/3}$, unlike the common $\nu^{1/2}$ dependence found in bulk LCs. The data displayed in Fig. 3 indicate that the same behavior occurs for all the silica matrices studied. It is remarkable that this new frequency dependence is universal, i.e., independent of the pore size, surface chemistry, etc.

It is also surprising that the values of T_1 are in the same range for all the samples studied. On the other hand, in gels with similar high-density and small pore size as our silica gels the LRO nematic phase has been found to be replaced by a glassy phase [1–5]. The power-law frequency dependence obtained here suggests, however, the existence of a long-range ordered phase, whose collective motions are affected by the host porous solid. Power-law dependencies have been observed often in confined isotropic liquids, but as indicated above in the present case $T_1 \propto 1/\log\nu$ in this type of liquids. We thus conclude that any glasslike or random-type phase should not yield a power-law behavior of T_1 in this system.

We believe we are in the presence of a truly nematic phase under quite strong confinement and disorder. Thus, we now propose a theoretical model for NMR relaxation

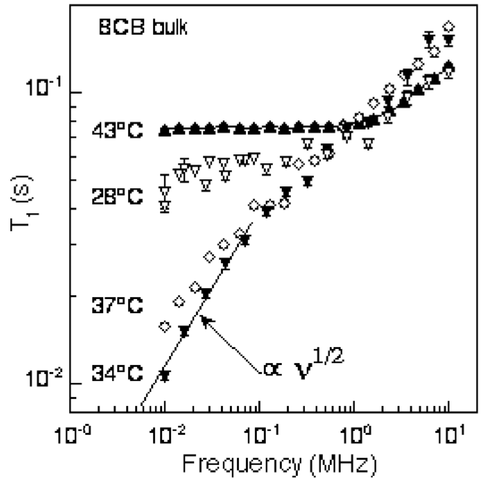

FIG. 1. T_1 as a function of the Larmor frequency in bulk 8CB in the SmA (open triangle down), N (full triangle down and open diamond), and I (full triangle up) phases. The continuous line is the best fit obtained with Eq. (4) with $d = 3$.

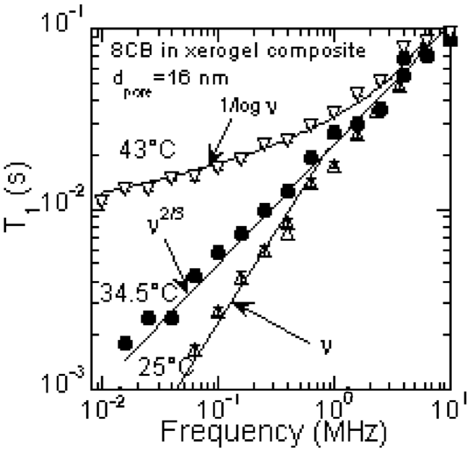

FIG. 2. T_1 as a function of the Larmor frequency in 8CB confined to the xerogel composite of pore size 16 nm in the SmA (open triangle up), N (full circle), and I (open triangle down) phases.

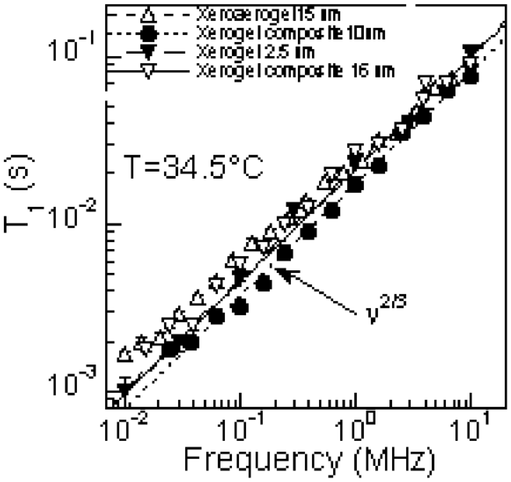

FIG. 3. T_1 as a function of the Larmor frequency in 8CB confined to the studied gel samples. The continuous lines are the best fits obtained using Eq. (4) with $d = 2.67$.

due to director fluctuations in nematic LCs confined to mass fractal porous media. A successful theory of proton nuclear relaxation of a bulk liquid crystal either in a smectic or nematic phase is already known [12,13]. It considers that the ODF come from dynamic distortions in a continuous medium characterized by an elastic constant K. Such a theory is valid when the characteristic distances L involved are large compared to molecular dimensions. It is known [4] that for small pore sizes and strong confinements, like those of our gel samples, slow cooperative fluctuations span over length scales significantly exceeding the confining length. Thus, such a condition is fulfilled in the present case. One could then describe the deformational fluctuations in the confined LC by a field director $\mathbf{n}(\mathbf{r})$ and an average director $\mathbf{n}_0 = \langle \mathbf{n}(\mathbf{r}) \rangle$. For uniaxial phases and small angular amplitudes of the director fluctuations relative to the average direction $\mathbf{n}_0(\mathbf{r})$, it was shown [13,14] that the proton spin-lattice relaxation T_1 follows

$$\frac{1}{T_1} = \frac{9}{4} \frac{\pi}{\sqrt{2}} \omega_{\text{dip}}^2 S^2 J(\omega_0). \tag{1}$$

Here the dipolar interaction $\omega_{\text{dip}} = \gamma_H^2 \hbar / R^3$, where γ_H is the proton gyromagnetic ratio and R is the minimal proton pair distance ($\sim$1.6 Å). S is the usual order parameter and $J(\omega_0)$ is the spectral density, which is the time exponential Fourier transform of the correlation function $G(\tau) = \langle \mathbf{n}_+(t) \mathbf{n}_-(t+\tau) \rangle$ for the transverse director $\mathbf{n}_+(t)$. $G(\tau)$ can be expanded as a superposition of exponential time decays in the reciprocal q space [13]:

$$G(\tau) = \frac{2}{V} \sum_{\mathbf{q}} \langle |n_x(\mathbf{q})|^2 \rangle \exp\left[-\frac{\tau}{\tau(\mathbf{q})} \right], \tag{2}$$

where V is the sample volume. Assuming the one-constant approximation with unique elastic constant K and viscosity η, $\langle |n_x(\mathbf{q})|^2 \rangle = k_B T / 2Kq^2$ and the correlation time is $\tau(\mathbf{q}) = \eta / Kq^2$. k_B is the Boltzmann constant. Then, converting the discrete summation into an integral in a d-dimensional fractal space, one has

$$J(\omega_0) = \frac{k_B T}{K} \text{Re}\left[\int_0^\infty d\tau \exp(-i\omega_0 \tau) \int_0^{q_c} d^3 q \rho(q) \frac{1}{q^2} \times \exp\left(-\frac{Kq^2}{\eta} \tau \right) \right]. \tag{3}$$

Here $q_c = 2\pi / \lambda_c$ is a high-frequency cutoff with λ_c being of the order of the molecular size, and $\rho(q)$ is the dimensionless density of modes per unit volume for a fractal medium. The number of modes between q and $q + dq$ is computed using an analytical expansion to the case of a fractal space of the well known result related to a hypersphere surface in a d-dimensional space. Then, we compute the equivalent $3D$ density of modes giving the same number of modes between q and $q + dq$. This yields $\rho(q) = C(d)(q\lambda_c)^{d-3}$, where $C(d) = (2\pi)^2 (4\pi)^{-d/2} r_{\max}^{d-3} / \Gamma(d/2)$ is a dimensional-dependent constant with the Γ function. Here $r_{\max} = L/\lambda_c \gg 1$ is a scaling parameter, where L is the size of the fractal domain where dynamical correlations occur. When $d = 3$, $C(3) = 1$ and $\rho(q) = 1$ in accordance with the uniform density of modes. Then, Eq. (1) becomes at low frequency

$$\frac{1}{T_1} = A(d) \omega_{\text{dip}}^2 \tau_c S^2 \frac{k_B T}{K \lambda_c} \frac{1}{(\omega_0 \tau_c)^{2-(d/2)}}. \tag{4}$$

$A(d) = [9/(8\sqrt{2})] \pi^{(d/2-1)} r_{\max}^{d-3} / \Gamma(d/2)$ is a dimensional-dependent constant. For $d = 3$, this equation tends to the Warner's results [14]. $\tau_c = \eta / K q_c^2$ is the shortest correlation time. The various parameters of Eq. (4) can be estimated. $\omega_{\text{dip}} = 2\pi * 29$ kHz for $R = 1.6$ Å, $T = 34.5\,^\circ\text{C}$, $K = 10^{-11} N$ [12,13], $\lambda_c = 10$ Å (molecular size). $k_B T / K \lambda_c = 0.4$ is a measure of the magnitude of the director fluctuation. We take $S = 0.5$ for the nematic order. A comparison of the experimental data of Fig. 3 with the theoretical prediction of Eq. (4) yields $d = 2.67$ for all samples. There remains only the shortest correlation time τ_c and $r_{\max}$. To get these parameters, we fit the bulk data of Fig. 1 in the temperature range of nematic order and obtained a value $\tau_c = 17$ ps with Eq. (4) with $d = 3$. Then, we use Eq. (4) with $d = 2.67$ and fit the data of confined nematics LC with the same bulk τ_c value but vary the single parameter $r_{\max}$. We present in Fig. 3 the best fits obtained for all 8CB confined LC in various pore sizes, surface, and materials and find $r_{\max} = 1500$. This shows that fast LC motions are not influenced by the confinement, surface chemistry and density. This is consistent with the idea that all the low-frequency relaxation features are due to slow collective motions. Such a model gives an estimation of the distance $L \geq 1.5$ μm over which such LRO occurs. The fractional dimension $d = 2.67$ implies that the space sensed by the liquid crystal molecules is fractal. It is known that xerogels and xeroaerogels have no fractal pore sizes, but have mass fractal structures. Because of the high density, the structure in our gels fills almost entirely the pore space, forcing all available space to be close to the surfaces. This space is fractal with the same dimension of the mass structure. That the LC resides in the space near the surfaces is consistent with the result of the confined isotropic phase discussed above. We argue now that $d = 2.67$ is, indeed, quite close to the mass fractal dimension of high-density silica gels. Our samples can be classified into two classes: gels and composite gels. Gel structures have been studied extensively, and their formation are well described by the cluster-cluster aggregation process [18–20]. The mass fractal dimension of silica gels depends strongly on the synthesis conditions, i.e., on the pH and mass concentration of the gelifying solution [21,22]. By doing a short extrapolation of the results produced by numerical simulations employing the diffusion-limited cluster aggregation process [22], we estimate that for a gel density around 0.6 g/cm^3 the short-range fractal dimension $d_f = 2.6$. For acid-catalyzed polymeric gels, like our samples, this dimension is expected to be slightly larger. In similar systems, alumina aerogels grown in acid conditions the mass fractal dimension $d_f = 2.6$–2.8 [23]. On the contrary, composite gels have been hardly studied. Their structures can be thought of as the sum of a polymeric gel and a network formed by the aerosil particles. For aerosil content below about 40% the short-range fractal structure of the composite is that of the polymeric gel [24]. This explains why we get the same fractional dimension for all our gel and composite gel samples. Moreover, for acid-catalyzed composite gel samples the mass fractal dimension of the polymeric gel ranges between 2.3 and 2.7 [24]. Thus, the fractal dimension 2.67 favorably fits the range of typical experimental and theoretical data. The backbone fractal dimension can then be determined from the low-frequency T_1 dispersion obtained by field-cycling NMR relaxometry. This is particularly relevant for high-density gels, for which Lach-hab *et al.* [25] showed that d_f systematically larger than the true value is obtained by scattering techniques.

To summarize, we have studied the behavior of the 8CB liquid crystal confined to randomly disordered and high-density silica gels. We found that the LRO nematic phase does not disappear under these conditions, and that in this phase T_1 has a universal value and frequency dependence $T_1(\nu) \propto \nu^{2/3}$. Based on the fractal nature of our gel structures, we proposed a model that accounts for all the new features observed in $T_1(\nu)$ and with which we estimated that the mass fractal dimension of gel samples was 2.67.

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