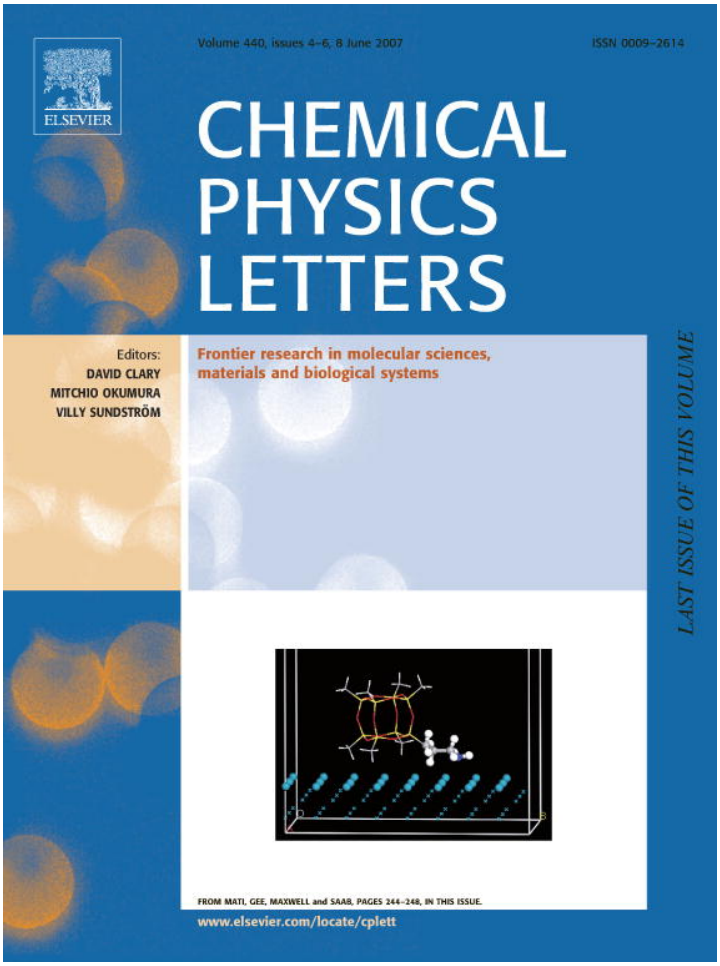

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Field-cycling NMR detection of magnetoacoustically manipulated nematic ordered states: Memory effects

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Abstract

The proton spin–lattice relaxation time (T_1) dispersion was studied under simultaneous sonication in the nematic phase of 5CB. It appears that metastable ordered states subject to a memory effect can be induced by the combined action of an amplitude-modulated ultrasonication and a pulsed magnetic field. We argue that the acoustic amplitude modulation adds instability to the nematic phase through director order fluctuation enhancement. Different manipulated states of the director were unambiguously identified by the Larmor frequency dispersion of T_1. The field-cycling NMR technique was used for T_1 measurements.

1. Introduction

The proton Larmor frequency (ν_0) dispersion of the nuclear spin–lattice relaxation time (T_1) is sensitive to the molecular dynamics and order in bulk and confined mesomorphic materials [1,2].

Sound tends to align the nematic director [3]. The nature of the sound - mesophase director interaction was investigated by using nuclear magnetic resonance (NMR) relaxometry in bulk samples [4], and optical experiments in thin cells [5]. Sound-induced changes in the nematic collective dynamics were identified by the frequency dispersion of T_1 [4,6].

For a sonicated nematic immersed in a magnetic field, the mean square amplitude of the hydrodynamic modes as derived from the equipartition theorem can be expressed as:

$$\langle |n_\alpha(\vec{q})|^2 \rangle = \frac{K_B T V}{f(\vec{q}) - \beta I}, \tag{1}$$

where $n_\alpha(\vec{q})$ represents a pair of uncoupled hydrodynamic modes [7], T is the temperature, K_B the Boltzmann constant, q is the magnitude of the hydrodynamic wave vector $\vec{q} = (q_x, q_y, q_z)$, V the volume, and I the sound intensity. $\beta = 2\xi\rho_0 k^2/v^3$ where ξ is the strength of the director and sound-induced density gradient coupling, ρ_0 the average density, k the magnitude of the acoustic wave vector and v the sound velocity. $f(\vec{q}) = K(\vec{q})^2 + (\Delta\chi/\mu_0)B^2 = f(q)$ with B the magnetic flux density, K the average elastic constant, $\Delta\chi$ the anisotropy in the magnetic susceptibility and μ_0 the vacuum magnetic permeability.

Ignoring the wave vector dependence of the viscosities ($\eta_\alpha(\vec{q})$), the viscoelastic relaxation time for the modes can be expressed as:

$$\tau_\alpha(q) = \frac{\eta_\alpha}{f(q) - \beta I}. \tag{2}$$

The last equations suggest that the acoustic field intensity can be tuned to compensate the elastic and magnetic energies for a given wave vector magnitude. We refer here to those modes satisfying $I = f(q)/\beta$ as excited modes. In this limit, the corresponding mode amplitude and viscoelastic relaxation time diverge. That is, only for those modes (the q-mode set), the acoustic energy compensates the magnetic and elastic energies. The fact that a given excited q_1-mode set will present long relaxation times, sug-

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gests that a second q_2-mode set can be simultaneously excited by changing the sound intensity I. This process can be repeated by increasing or decreasing the sound intensity at a given rate, thus successively exciting q_n-mode sets. If during the time needed for the q_1-mode set to relax the process is suddenly restarted, several hydrodynamic modes can be held in the excited state. In practice, this can be implemented by a suitable amplitude modulation of the acoustic field. The consequence should be an increase of the nematic phase instability.

A question addressed in our study concerns the possibility of inducing order-disorder or order–order transitions in a bulk sample by using the time dependence of the acoustic field intensity as a control parameter. A second question focuses on the detection of such states in studies of the $T_1(\nu_0)$ dispersion. Excited modes exhibiting large viscoelastic relaxation times will not contribute to the frequency dispersion of T_1.

If the orienting action of the acoustic field becomes dominant, the director tends to be aligned orthogonal to the acoustic wave vector. In this case the $T_1(\nu_0)$ dispersion should correspond to the case where director and magnetic fields are perpendicular. In such a case the whole dispersion is expected to be shifted to lower T_1 values [8]. As a third possibility, the sound induced instability may provoke a transition to a new state with a different molecular order, possibly showing a completely different T_1 dispersion.

2. Experimental and results

To examine these possibilities, we ran new experiments including acoustic field amplitude modulation as a new feature. The ultrasonic generator was the same used in previous experiments [4,6], a Hielscher UIP50 unit operating at 30 kHz and modified by ourselves to allow for amplitude modulation (AM). T_1 relaxation dispersion was measured using a Stelar FFC2000 NMR relaxometer. The experimental setup was as described in Ref. [6]. In order to deal with pure nematics, pentylcyanobiphenyl (5CB) was used in all experiments. This compound has a nematic phase between 297 K and 308.3 K. A 25 Hz – 75% saw tooth waveform AM was used (see the inset in Fig. 1). The monitoring signal was picked-up from a piezoelectric device already included in the generator for feedback purposes.

2.1. Experiment I

Dispersions measured at 303 K and an acoustic power of (3.0 ± 0.2) W/cm^2 with no modulation reproduced previous findings [4,6]: under sonication the dispersion tends to be flatter. A crucial point with these experiments was in what sequence the experiments were carried out. After isotropization (cooling back from a temperature four to six degrees above the clearing point), unsonicated sample was exposed to several magnetic field pulses (0.25 T at an average effective duty cycle of 50%). The mesophase director became ordered with the magnetic field. We refer then

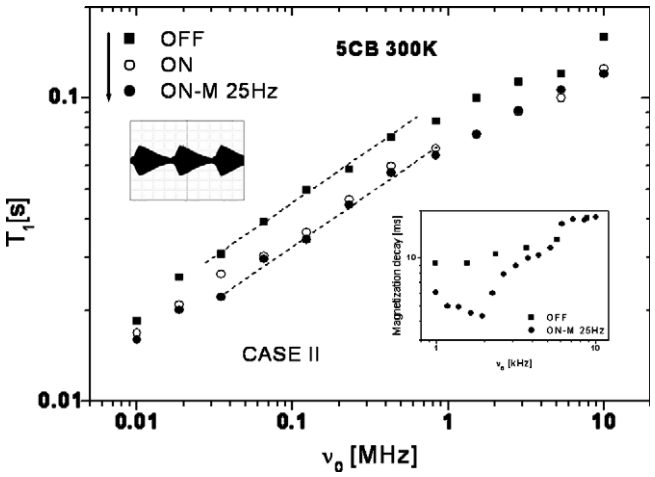

Fig. 1. $T_1(\nu_0)$ dispersions at 300 K in unsonicated (OFF), sonicated with no modulation (ON) and sonicated with modulation (ON-M 25 Hz). The insets show the modulated ultrasonic waveform and the local minimum centered at 2 kHz as discussed in Ref. [8]. The arrow indicates the sequence of measurements.

to a 'magnetically ordered state' (case I). Here, the previously described theory applies [7]. For this case, dispersions measured under sonication showed to be insensitive to AM modulation.

2.2. Experiment II

A different experiment was done at a lower temperature and an acoustic power deposition of (3.3 ± 0.2) W/cm^2 (Fig. 1). The arrow in the upper-left corner of the figure indicates the measurement sequence: the unsonicated sample (OFF) was first studied after isotropization. However, before measuring T_1 in the sonicated sample, the system was heated-up to the isotropic phase in order to erase any memory to the magnetically ordered state. It was then cooled down to 300 K under continuous sonication. In this way, an 'acoustically ordered state' corresponding to the director perpendicular to the magnet axis was obtained. The corresponding dispersions were parallel to the unsonicated case, but shifted to lower T_1 values (case II). This effect can also be observed when switching the magnetic field by an angle of 90° during the relaxation delay of the magnetic cycle, with the sample magnetically oriented along the polarizing field [8]. The minimum centered at about 2 kHz (as observed in the angular dependent field-cycling experiment) was verified (see inset in Fig. 1). This last result is important since it unambiguously confirms that an acoustically ordered state can be created within the NMR sensitive volume, and shows that it can be preserved even against the magnetic field pulses applied during the NMR relaxation experiment.

2.3. Experiment III

Fig. 2 shows a new experiment starting from an acoustically ordered state at a temperature of 303 K and a power

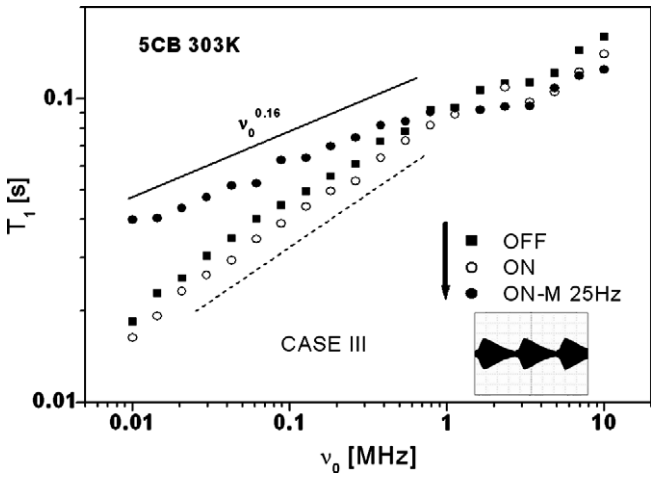

Fig. 2. $T_1(\nu_0)$ dispersions at the different experimental conditions measured at 303 K. After modulating the amplitude of the ultrasonic intensity, the dispersion changes abruptly following a characteristic $\nu_0^{0.16}$ law.

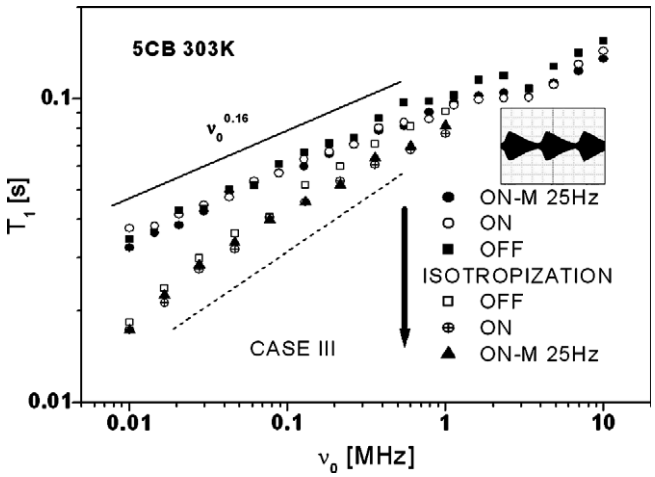

Fig. 3. Repetition of the experiment (described in Fig. 2, see text) in a different sequence. The new dispersion law is preserved after several hours in the absence of ultrasound and magnetic field. This indicates a transition to a metastable state showing memory capacity. The order is erased after isotropization and the typical nematic behavior is recovered.

of (3.0 ± 0.2) W/cm^2. The first dispersion was measured without sonication. Under steady sonication (unmodulated), the T_1 dispersion data are shifted to slightly lower values. The result resembles the previous case, with a dispersion slightly shifted to lower T_1 values. That is, the system was able to preserve memory to its previous acoustically ordered state, in spite of the fact that a whole dispersion was measured without sound (several magnetic pulses in between). This last result clearly suggests that a pure magnetically ordered state can only be recovered after passing through an erasing isotropization. Within the kHz Larmor frequency range, the observed dispersions show the typical nematic behavior. A new and surprising result was obtained after a new measurement was performed by including AM: the dispersion changed abruptly to a new ν_0^x law with $x = (0.16 \pm 0.05)$ within the sub-megahertz Larmor frequency range (case III).

In view of this apparently conflicting result, a new experiment was done but starting from an acoustically ordered state after isotropization and subjecting the sample to overnight sonication at 303 K with continuous modulation. A first dispersion was then measured holding the sonication status (Fig. 3). The obtained dispersion followed again the $(\nu_0^{0.16})$ law, which was preserved after repeating the measurement without modulation. In a subsequent step, the ultrasound was switched-off and the sample temperature compensated to repeat the experiment without sonication. After a stabilization period of about four hours without ultrasound nor magnetic field, the resulting dispersion was preserved. We can be certain, therefore, that the new dispersion law corresponds to a metastable ordered state showing memory capacity. Prior to a new unsonicated experiment, the sample was heated up to the isotropic phase in order to erase the metastable state. The dispersion was then measured at 303 K showing again the typical nematic law (measurements only up to a Larmor frequency of 1 MHz). Consistent with a magnetically ordered state, it appears that the subsequent sonication experiments show the corresponding flattening of the dispersion as described for case I.

3. Discussion

Results are summarized in Table 1. Two main questions originate from these results. A first question is how can an acoustically ordered state survive when the relaxometry experiment implies subjecting the sample to relatively strong magnetic field pulses (0.25 T) of 0.8–1 s length, even during continuous sonication? The second question concerns the transition induced by the modulation: what are the conditions met in case III that are not given in case II? To analyze the problem we need to consider the torque balance between acoustic, magnetic and viscous contributions:

$$\gamma_1 \frac{\mathrm{d}\theta}{\mathrm{d}t} = \beta I \sin[2(\phi - \theta)] - \frac{\Delta\chi}{2\mu_0} B^2 \sin(2\theta), \tag{3}$$

where θ is the angle between director and magnetic fields, ϕ is the angle between the acoustic wave vector $\vec{k}$ and the magnetic field and γ_1 is the Leslie–Ericksen rotational viscosity coefficient.

The solution of the differential equation has the form:

$$\tan[\theta(t) - \theta_{\mathrm{eq}}] = \tan(\theta_0 - \theta_{\mathrm{eq}}) \exp(t/t_{\mathrm{r}})$$

Table 1
Summary of results according to the type of initial ordered state: M, magnetic; A, acoustic

Case	$T \pm 1$ (K)	Initial order	Dispersion under sonication	Effect of modulation
I	303	M	Modified	NO
II	299–300	A	Shifted nematic	NO
III	303	A	Shifted nematic	Switch to $\nu_0^{0.16}$

where θ_0 and θ_{eq} are the initial and equilibrium values of θ respectively, and t_r the director reorientational relaxation time:

$$t_r = \gamma_1 \left[\sqrt{\left(\frac{\Delta\chi}{\mu_0} B^2\right)^2 + (\beta I)^2 + 2\frac{\Delta\chi}{2\mu_0} B^2 \beta I \cos(2\phi)} \right]^{-1}. \quad (4)$$

If $I = 0$ and $\theta \neq 0$, the magnetic field will order the director field with a characteristic time given by:

$$t_r^M = \frac{\mu_0 \gamma_1}{\Delta\chi B^2}.$$

For $I \neq 0$ we confront $(\Delta\chi/\mu_0)B^2 \approx 0.05\ \mathrm{N/m^2}$ with $\beta I \approx 2.10^4\ \mathrm{N/m^2}$. It becomes clear that the acoustic interaction prevails. Here we used $\mu_0 = 4\pi \times 10^{-7}\ \mathrm{N/A^2}$, $\Delta\chi \approx 10^{-6}$, $B = 0.25$ T, $K \approx 10^{-11}$ N and a typical diffusion constant $D \approx 10^{-11}\ \mathrm{m^2/s}$. βI was evaluated from previous fittings [6], and corrected for the difference in the effective power.

Then, the acoustic reorientation time can be approximated to:

$$t_r^a = \frac{\gamma_1}{\beta I}.$$

With a typical value of $\gamma_1 \approx 0.1$ Pa s, we obtain $t_r^M \approx 2$ s and $t_r^a \approx 5$ μs, i.e., $t_r^a \ll t_r^M$.

It can be assumed that the NMR sensitive volume is divided in three different regions: a main region of acoustic domain, a fringe region where the magnetic field torque prevails and, a transition interface in between where magnetic and acoustic torques are comparable in magnitude. Once an acoustically ordered state is established, as far as the acoustic field will be active, the acoustic order will persist. Since the magnetic field polarizing pulses are half as long as the magnetic reorientational time, magnetic ordering effects will be weak within the interface and even within the magnetic domain region. If a T_1 dispersion is measured without sonication but starting from an acoustically ordered state, during the first magnetic field pulses (usually performed before measurement at the parameter adjusting step) the system will tend to a magnetically ordered state. However, clusters surviving within the acoustic domain, not oriented with the magnetic field (for instance, at the surface of the sonotrode), will act as memory kernels that will reestablish the acoustic order at a new presence of sound. On such clusters the acoustic torque will be huge with extremely short reorientational time. On the contrary, if the system is initially prepared in a magnetically ordered state (case I), since $\theta = 0$ and $\phi = 0$, the average acoustic torque will be weak and the magnetic order will prevail even against a rear presence of the acoustic field.

By considering the temperature dependence of γ_1 [9] and $\Delta\chi$ [10], we observe that at higher temperatures (303–305 K), t_r^M becomes comparable to the length of the magnetic field pulses. This means that within the magnetic domain region the director partially orders with the magnetic field. In addition, the thermal energy is higher and a crucial additional instability is gained through the AM modulation. The interface region then becomes a kernel where the needed conditions for a transition to a metastable state occurs: phase instability and coexisting torques.

4. Conclusions

In summary, we have experimentally shown that an acoustic ordered state can be created in the bulk, and that this state can unambiguously be identified through NMR relaxometry. We show that metastable states subjected to memory effects can be created in the bulk by the combined action of an acoustic field with AM-modulation and a pulsed magnetic field. Our experiments show that the initial ordered state is crucial for the manipulation of the final order.

Processes like those taking place in Fréedericksz transitions of surface-oriented nematics under the action of a magnetic field, may lead to the formation of spatially periodic structures or 'inversion walls' as a consequence of spontaneous symmetry breaking [11,12]. Wrinkled nematic states of this sort may also be created by electric fields due to electric conduction [13], or through the combined action of electric and magnetic fields [14]. As a common feature, these states have a metastable character (memory capacity) [11,15]. Since a key feature for the creation of such states is the combined action of competing orthogonal torques, the new observed state may be a 3D version of this sort. Alternatively, a network of topological defects may be induced under the conditions of our experiment [16]. In both cases, the corresponding hydrodynamics (3D inversion walls or topological defects) would be responsible of the modified relaxation dispersion law.

Understanding the conditions for the occurrence of these phenomena, a more detailed physical description of such metastable states and the corresponding model for the observed relaxation dispersion law will spur more experimental and theoretical effort. Work is in progress.

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