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Apparent low-field spin-lattice dispersion in the smectic-*A* mesophase of thermotropic cyanobiphenyls

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Proton field-cycling spin-lattice relaxometry T_1 of the smectic-*A* mesophase in cyanobiphenyls revealed the presence of steep dispersions in the low-frequency regime. We clearly show that the strong dispersion characteristic of smectic organizations cannot be attributed to the collective molecular dynamics (order director fluctuations), as it is usually interpreted. We present two independent experimental evidences: the dependence of the dispersion with the slew rate of the magnetic field cycle and the dependence of the dispersion with the presence and power of an ultrasonic field.

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Field-cycling nuclear magnetic resonance (NMR) relaxometry allows one to scan spin-lattice relaxation parameters within a typical frequency range from about 100 Hz to 10 MHz [1–3]. The spin-lattice relaxation time T_1 dispersion has been widely used for the study of the molecular dynamics in thermotropic liquid crystals.

The Larmor frequency ν dispersion due to the order director fluctuations (ODF) in the smectic-*A* (Sm-*A*) phase may present a characteristic frequency dependence of the type ν^1 [4]. This behavior corresponds to the limiting situation where the relaxation is driven by smectic undulation waves, assuming that the coherence length in the direction along the local director is independent of the in-plane wave vector, and for Larmor frequencies much lower than the high-frequency cutoff. Otherwise, the frequency dependence may take a logarithmic law. A nematiclike contribution also exists in the Sm-*A* phase, but strongly reduced due to the large increase of the twist and bend elastic constants [4,5]. However, on the ground of the Landau–de Gennes elastic theory, the spectral densities were calculated including both smectic order parameter fluctuations and nematiclike deformations, resulting in a dispersion law that may range from ν^0 to $\nu^{0.5}$ [5].

The field-cycling technique was hardly applied for the study of thermotropic smectic phases [6–12]. Only a few of these last references correspond to cyanobiphenyls in the Sm-*A* mesophase [8,10]. The typical NMR relaxation dispersion in the Sm-*A* phase looks nearly flat until a minimum frequency of about 20 kHz, where a noticeable steep down dispersion appears up to a low-frequency plateau [see Fig. 1(a)]. The steep dispersion was currently attributed to ODF through a ν^1 dispersion law, while the low-frequency plateau, usually between 300–800 Hz, interpreted in terms of the cutoff of the ODF modes. In this Brief Communication, we experimentally show that the steep dispersion usually observed in the spin-lattice dispersion of thermotropic smectics has no connection with the ODF dynamics. It has been recently proposed that these "false dispersions" are due to the presence of local fields [13].

At Larmor frequencies higher than the starting point of the steep decay (30 kHz–10 MHz), where the T_1 frequency dependence is minor, the observed dispersion was usually explained in terms of individual motions with a dominant role of the translational diffusion. From the present results, this traditional interpretation deserves a careful revision.

Seemingly, the ODF contribution is masked by individual molecular motions in the higher-frequency range. In addition, they are difficult to observe at low frequencies due to the prominent residual local fields surviving in the smectic order, thus limiting the applicability of the field-cycling technique for this particular case. It was recently observed that in

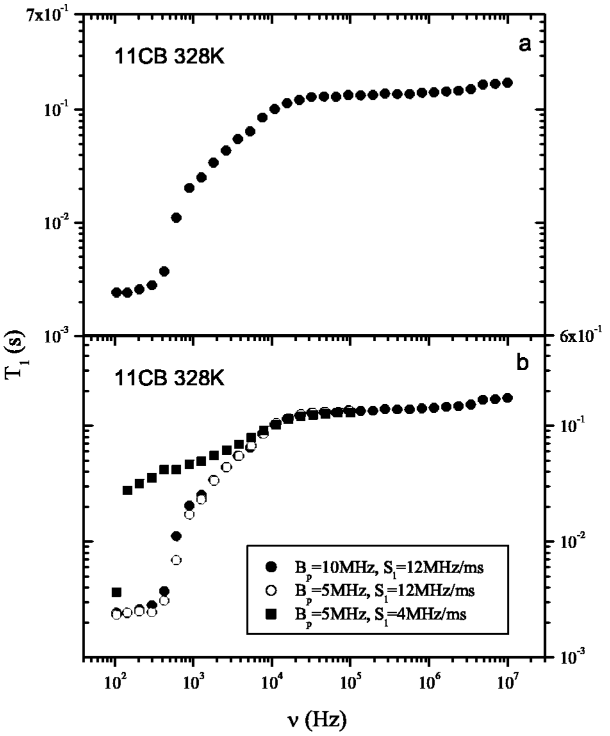

FIG. 1. (a) Typical smectic dispersion for 11CB at 328 K for standard values of slew rate and polarization field (see text). (b) Relaxation dispersions measured for different slew rates and polarization fields.

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the Sm-*A* phase formed by larger molecules such as organosiloxanes, the linear frequency dispersion law manifest at higher Larmor frequencies [14]. Even for small molecules, such as cyanobiphenyls, the dipolar spin-lattice relaxation time T_{1D} shown to be much more sensitive to the ν^1 frequency dependence at least, in the MHz frequency range [15]. These results should be considered in favor of the ν^1 picture, clearly hidden for cyanobiphenyls in the high-frequency regime of T_1. According to these evidences, it seems to be that the diffusion plays an important role, masking the ODF contribution for small molecules where the smectic layers are more liquidlike. On the contrary, for larger molecules diffusion is less efficient thus allowing the ODF mechanism to be manifested in the resulting dispersion. This picture, however, must be revised with care. Herein, we only limit in presenting clear experimental evidences against the currently wrong interpretation of the relaxation dispersion in the Sm-*A* phase of molecular systems conformed by small molecules such as cyanobiphenyls.

Commercial samples of 8CB and 11CB from Synthon and Merck Chemicals were used in the experiments. In 8CB (octyl-cyanobiphenyl), phase transition from the solid to the Sm-*A* occurs at 294.5 K, and from the Sm-*A* to the nematic at 306.5 K, while 11CB (undecyl-cyanobiphenyl) shows a solid-Sm-*A* and Sm-*A*-isotropic phase transitions at 326 K and 330.5 K, respectively. Relaxation dispersion curves were acquired using a Stelar FC2000 fast field cycling NMR relaxometer. T_1 values were measured using standard compensated prepolarized and nonpolarized sequences [3]. A 0.25 T polarization field and a 0.23 T detection field (10 MHz and 9.3 MHz in Larmor proton frequency units, respectively) were used as standard values. Sixteen points (four scans each with four quadrant phase cycling scheme) were used to determine T_1. In all cases, relative errors in T_1 measurements are between 2% and 8%. The magnetic field was compensated from external contributions with the aid of two orthogonal coil sets and an offset current in the magnet. The system was calibrated with the help of a commercial Hall probe and tested with known samples.

Temperature control was carried out by a Stelar VTC unit connected to a thermocouple located at about 30 mm below the sample. The control unit was previously calibrated to display the sample temperature. In addition, sample temperature was determined before and after each T_1 dispersion experiment. An embedded thermocouple was used for this purpose in order to check the sample temperature constancy, specially in the sonicated experiments. Direct temperature measurement during NMR experiments was not possible due to the high noise introduced by the thermocouple. Absolute errors in temperature measurements were ± 0.2 K in all experiments.

The slew rate of the magnetic field was directly controlled from the Stelar software menu. The ultrasonic field was transmitted to the sample through a 3-mm (diameter) glass sonotrode coupled to a Hielsher UIP50 generator working at (30 ± 1) kHz. The temperature increment due to sonication was compensated by an appropriate setting of the temperature control system. The sonotrode was placed within the sample at a position corresponding to the top of the radio-frequency coil.

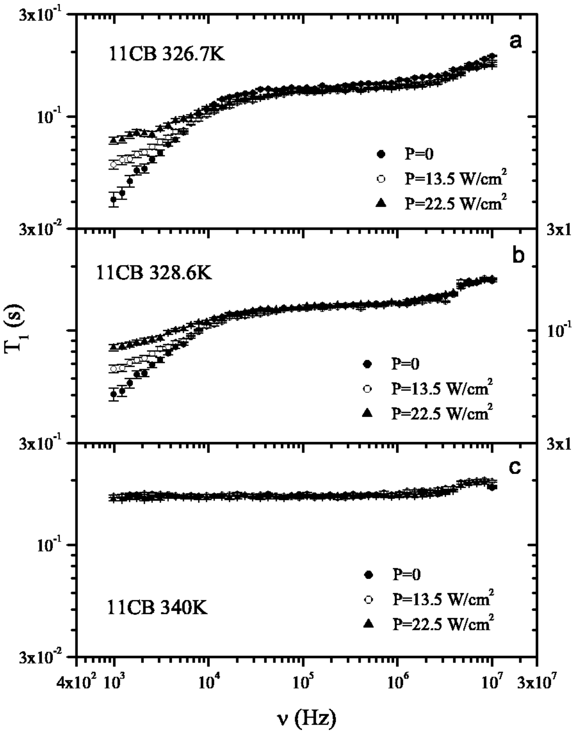

FIG. 2. Relaxation dispersion of 11CB at different temperatures and ultrasonic power levels *P*. (a) Sm-*A* at 326.7 K. (b) Sm-*A* at 328.6 K. (c) Isotropic phase at 340 K.

Figure 1(a) shows the typical T_1 dispersion of the Sm-*A* mesophase of 11CB at 328 K. The displayed curve corresponds to a slew rate of 12 MHz/ms. It can be observed that the obtained dispersion strongly agrees in the low frequency range with previous data in the literature [8]. Figure 1(b) depicts the dependence of the low-frequency dispersion on the slew rate S_l and the strength of the polarization field B_{pol}. In the plot, we can distinguish three curves: a complete dispersion measured from 10 MHz to 100 Hz using standard values of $S_l = 12$ MHz/ms and $B_{pol} = 10$ MHz (we express this quantity in terms of the equivalent proton Larmor frequency), and two dispersions measured from 100 kHz down with different values for S_l and B_{pol}. A drastic reduction in the switching velocity strongly affects the dispersion in the lower-frequency range (from about 6 kHz down). From these curves, it can also be observed that the strength of the polarizing field is not as important as the slew rate during the magnetic field transitions.

Figure 2 shows the T_1 dispersion of the same smectic compound at a fixed slew rate $S_l = 5$ MHz/ms, in the presence and absence of sonication, and different temperatures. Figures 2(a) and 2(b) corresponds to the Sm-*A* phase while Fig. 2(c) to the isotropic state. In each case, the dispersion was measured without sonication and for two different powers of the ultrasonic field (13.5 W/cm^2 and 22.5 W/cm^2). Figure 3 includes equivalent results for the Sm-*A* and isotropic phases of 8CB. In both cases, at frequencies higher than 20 kHz, the corresponding dispersions are nearly coincident.

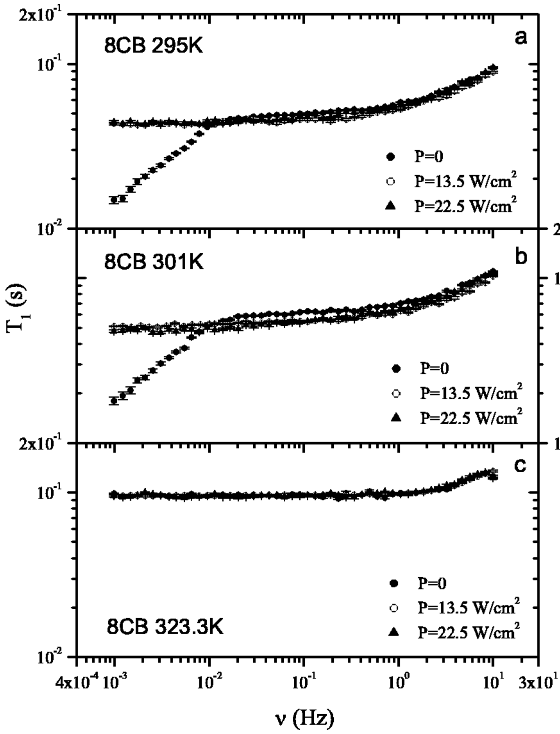

FIG. 3. Relaxation dispersion of 8CB at different temperatures and ultrasonic power levels *P*. (a) Sm-*A* at 295 K. (b) Sm-*A* at 301 K. (c) Isotropic phase at 323.3 K.

This fact comes to support the statement that all temperatures are the same within experimental errors. At lower frequencies, the slope of the dispersion clearly depends on the presence and power of the sonication. No effect is produced by the sonication in the isotropic phase.

The strong Sm-*A* dispersion usually appears under a frequency threshold where local fields are relevant, i.e., in a frequency range where the switching properties of the magnetic field become crucial. Local fields for smectic order in cyanobiphenyls may be of the order of 10 kHz or even higher [16]. Therefore, the conditions for an adiabatic switching become critical within this frequency interval. The normal components of the local fields play a significant role in connection with the shape and velocity of the magnetic field switching [14].

The time dependence of the magnetization during the relaxation process is essentially determined by the characteristics of the magnetic field cycle during the switch down process. Unless the cycle is fully adiabatic, the magnetization will evolve according to a combined effect of relaxation and decay of coherences. At frequencies higher than a critical value, the longitudinal relaxation prevails. For lower frequencies, the zero-field condition dominates [17]. This behavior has also been observed in terms of zero-field NMR [18]. When this change in the magnetization evolution regime is inadverted by the operator, a false value of the associated relaxation time constant is obtained, which in turn becomes meaningless. In some cases this fact is experimentally manifested as a departure from a pure exponential magnetization decay as the relaxation field is lowered. The problem is, however, very tricky in smectic phases and lamellar organizations, where a macroscopic superposition of induced coherences with different frequencies are observed, resulting in an exponential-like evolution that may be easily confounded with a pure relaxation decay.

During the switching down of the magnetic field, there is a critical moment where a transition from a pure adiabatic regime to a partial adiabatic condition takes place. It is possible to calculate the corresponding critical Larmor frequency in terms of the time dependence of the magnetic field variation and the nature of the local fields [19]. The estimation of this critical frequency allows one to prevent the use of the field-cycling relaxometry technique within a conflictive region. Alternatively, when the critical frequency is clearly recognized from the experimental conditions, the physical background can be used to inquire about the nature of the local fields.

It was recently verified that NMR relaxometry is sensitive to the coupling between ultrasonic waves and the collective molecular dynamics in the nematic phase [20,21]. A similar result was observed in the Sm-*A* phase, even when the contribution of ODF may be masked by diffusion [22]. However, the experiments here discussed clearly show that the steep dispersion in the low-frequency range is not associated with a pure ODF mechanism. In this low-frequency range, the main effect of the ultrasonic field seems to be adding new molecular motions that are efficient in averaging the local fields (thus, turning the switching conditions more favorable). In the case of 11CB, the averaging process is partial and depends on the applied power (Fig. 2), while for 8CB, even the minimum power is enough to completely average the local field components responsible for the nonadiabatic conditions (Fig. 3). We can see in Figs. 3(a) and 3(b) that the sonicated dispersions are completely flat for both ultrasonic powers.

In summary, we have presented two independent experiments based on different grounds. Both suggest that the strong dispersions usually observed in the Sm-*A* mesophase of cyanobiphenyls in the low-frequency regime cannot be explained in terms of the ODF mechanism. The problem is now centered in disentangling ODF and diffusion contributions. On the other hand, the real behavior of the Sm-*A* ODF in cyanobiphenyls remains as an open question.

Similar false dispersions were found in lamellar systems such as lipid bilayers, where the switching times had to be prolonged in order to keep the adiabatic condition of the magnetic field cycle [23]. In the particular case of the thermotropic Sm-*A* phase, it may happen that the switching times needed to preserve the adiabaticity of the cycle should be of the order of the spin-lattice relaxation time constant. Such a situation represents a limit for the application of the field-cycling technique. In cases where relaxation time constants are longer, the problem can be circumvented by setting an adequate switching rate for the magnetic field. The mentioned limitations may also be present in other physical systems such as confined thermotropics, lyotropics, and membranes.

The results here presented provide evidences towards a correct interpretation of the relaxation dispersion in the Sm-

A mesophase of cyanobiphenyls. It should be emphasized that the mentioned limitations of the technique are strongly connected with the nature of the residual local fields. In systems where the molecular dynamics is effective in averaging the dipolar fields (such as polymers, gels, elastomers, etc.) the problem is absent or extended to much lower frequencies. It is the case, for instance, of the nematic phase, where the mentioned problem is much weaker.

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