

Investigation of Molecular Motion in Smectic Phases of the Liquid Crystal TBBA by NMR Relaxation Dispersion

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Z. Naturforsch. **35a**, 924–929 (1980); received July 7, 1980

The proton spin T_1 relaxation dispersion in the smectic A and C phase of TBBA, and for comparison also in the nematic phase, have been studied using time dependent fast field-cycling techniques in the Larmor frequency range from $\nu_p = 100$ Hz to 44 MHz. Our measurements considerably extend recent ones by Blinc et al., performed with other NMR methods for frequencies ≥ 140 kHz. The new experimental data are consistent with the reported ones for Sm C but not for Sm A, the difference being that the essential T_1 dispersion observed with our technique occurs at much lower frequencies, namely below about 100 kHz. As a consequence, the relaxation dispersion for both smectic phases looks very similar. It can be described quantitatively in terms of relaxation by “nematic-like” order fluctuations, self-diffusion, and by a third molecular mechanism with (for simplicity) Debye-like power spectrum, which is possibly a second type of order fluctuation or a molecular rotation about the short axis. The analysis reveals surprisingly far going parallels between the spin relaxation of simple smectics and that of high-temperature nematics like PAA.

1. The Problem

Up to date, the nuclear spin relaxation mechanisms in *smectic liquid crystals* is far less understood than those in *nematics*. Only very few systematic papers on the subject have been published [1–3], and none of the recent reviews on nuclear relaxation in liquid crystals [4] includes a detailed treatment of smectic phases. Since 1975 the pioneering works in the field have been performed by Blinc et al. [1], who transferred the basic ideas of the well-established relaxation models for nematics to smectics and who applied this theory to experimental data obtained for the various mesophases of TBBA (terephthal-bis-p-butylaniline) with emphasis on smectic A (Sm A) and smectic C (Sm C). From measurements of the longitudinal proton spin relaxation time T_1 in the Larmor frequency range between $\nu_p \equiv \omega_p/2\pi = 140$ kHz and 90 MHz it was concluded for these two high-temperature smectic phases, which alone will be considered in the following, that order fluctuations (OF), self-diffusion (SD), and rotational motions (R) contribute to the total relaxation rate with different strength. Like in nematics, the OF mechanism was found dominant at low frequencies, whereas the SD mechanism took over in the high-frequency regime. Surprisingly, the

T_1 dispersion for Sm A and Sm C proved to be rather different, and as a consequence, the rotational contribution was only detected in the latter case. The principal observations of T_1 spectroscopy could be confirmed in subsequent NMR works by investigations of the dipolar relaxation time T_{1d} and the self-diffusion constant D [2, 3]. However, none of the presented analysis was very critical, on the one hand because of the numerous theoretical parameters involved, and on the other hand because of the rather restricted Larmor frequency range in which the experiments were performed.

In order to make the discussion more quantitative, we extended Blinc's work to considerably lower proton resonance frequencies (100 Hz), hoping to penetrate into the regime where T_1 should be totally governed by order fluctuations. Our main objective was to test the theory under this severe condition, and to find out if the OF power spectrum obtained in this way allows to make the interpretation of the high-frequency regime consistent with known self-diffusion constants and rotational jumping times of TBBA. Some of our results were presented recently at the Liquid Crystal Congress in Garmisch-Partenkirchen [5].

2. Experimental Techniques and Results

The proton spin relaxation dispersion, $T_1(\nu_p)$, was measured for the smectic A and C phase of

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TBBA using techniques described previously [6], i. e. time dependent field-cycling for $\nu_p < 7$ MHz and conventional pulsed methods for $\nu_p \geq 7$ MHz. We have chosen similar sample temperatures as in Blinc's work (Sm C: $\vartheta = 156^\circ\text{C}$; Sm A: $\vartheta = 181^\circ\text{C}$) to make the comparison straightforward. The new results, illustrated in Figs. 1 and 2, are only in accordance with the literature for Sm C, whereas strong discrepancies exist for Sm A, the origin of which is not clear. In particular, the reported cross-over of the Sm A and Sm C relaxation rates at medium frequencies ($10^6 - 10^7$ Hz) could not be confirmed by us.

Since we observed T_1 to depend somewhat on the procedure by which the mesophases were oriented in the magnetic relaxation field, we took care to prepare the samples before the measurements in the same way. Heating the liquid crystal slightly above the nematic-isotropic transition point ($\vartheta_c = 236^\circ\text{C}$) in a sufficiently strong magnetic field ($H_0 = 0.16 \dots 1.6$ T) always produced the same form of the free induction decay at a given temperature, i. e. obviously led to a well-defined smectic order within the spin system [7]. From the root mean square deviation of individual T_1 measurements the random error limits of the data were estimated to be smaller than $\pm 5\%$ for high and about $\pm 10\%$ for low frequencies. The error is somewhat larger than in our previous studies of nematics [6] due to the elevated temperature range.

As already observed by Blinc, the T_1 relaxation dispersions for Sm A and Sm C look different. However, the new low-frequency results demonstrate that the differences are smaller than expected from the extrapolation of Blinc's data to low values of ν_p . Our measurements show that T_1 for Sm A is always longer than for Sm C, with the ratio $T_1(\text{Sm A})/T_1(\text{Sm C})$ slightly dependent on the frequency. At the highest available resonance fields the ratio tends towards unity. In both smectic phases the dispersion essentially occurs between 10^3 and 10^5 Hz, i. e. at frequencies not studied by Blinc. Below this range the relaxation rates become completely frequency independent, above this range the relaxation rates do not change substantially, but probably indicate the beginning of a second strong dispersion regime for very high ν_p 's. Qualitatively, the $T_1(\nu_p)$ profiles seem not very distinct from the behaviour previously found for high-temperature nematogens like PAA [6], but a comparison with

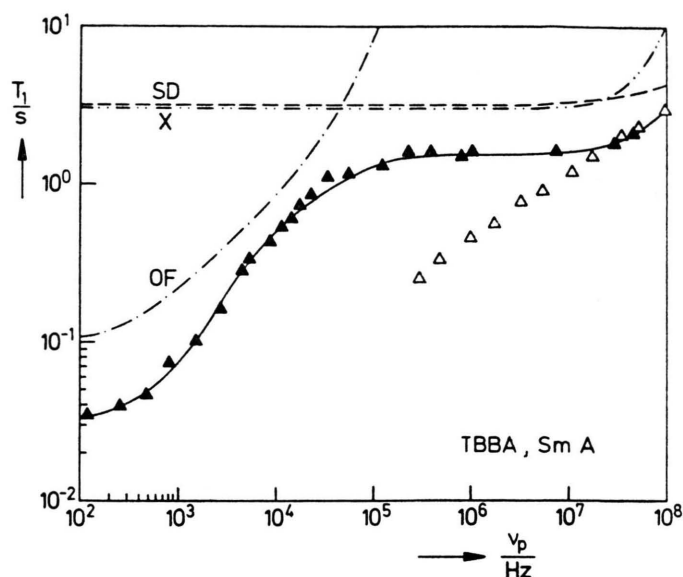


Fig. 1. Proton spin relaxation dispersion, $T_1(\nu_p)$, for Sm A TBBA at 181°C . Data points: Experimental results of this work ($\blacktriangle$) and from the literature [1] ($\triangle$). Curves: Fit of the OF-SD-X model, Eq. (2), with parameters listed in Table 1, and individual contributions $T_{1\text{OF}}$, $T_{1\text{SD}}$, and $T_{1\text{X}}$. Note that Blinc's data below $\nu_p = 1.5 \cdot 10^7$ Hz are not included in the fit.

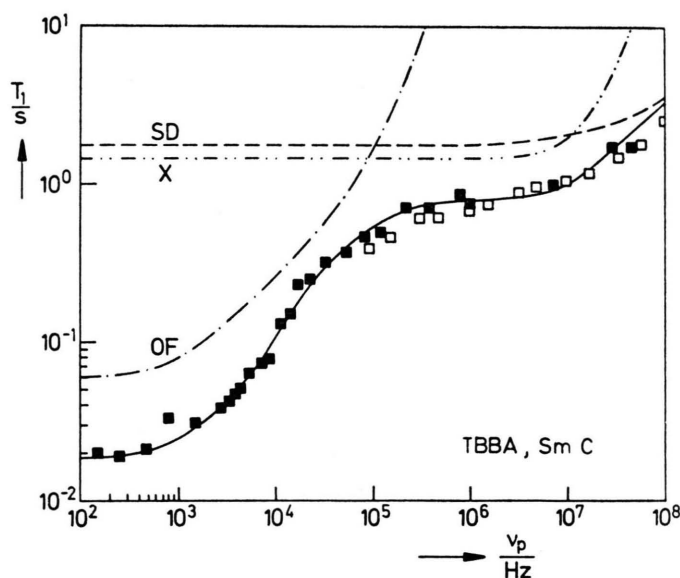


Fig. 2. Proton spin relaxation dispersion, $T_1(\nu_p)$, for Sm C TBBA at 156°C . Data points: Experimental results of this work ($\blacksquare$) and from the literature [1] ($\square$). Curves: Same notation as in Figure 1. In this case all of Blinc's data are taken into account.

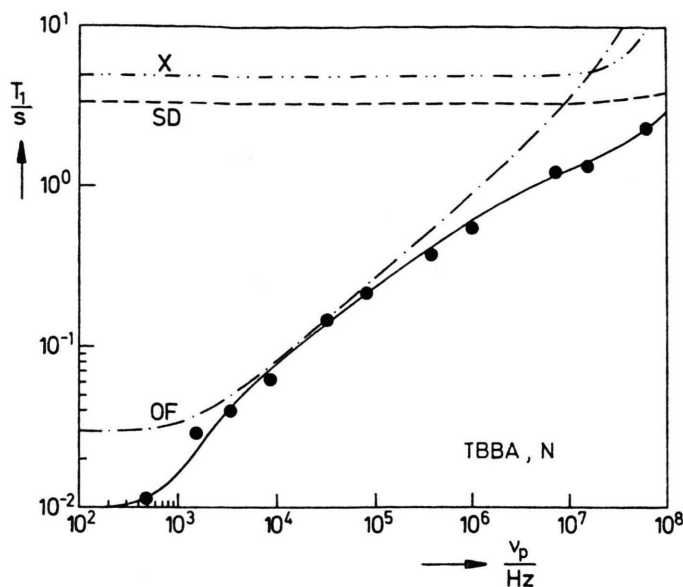


Fig. 3. Proton spin relaxation dispersion, $T_1(\nu_p)$, for N TBBA at 205°C. Data points: Experimental results of this work (●) Curves: Same notation as in Figure 1.

supplementary measurements on nematic (N) TBBA reveals clear dissimilarities (Figure 3). These dissimilarities are also demonstrated by the temperature dependence of T_1 at several frequencies as shown in Fig. 4, where particularly in the kHz regime the three studied mesophases (Sm A, Sm C, N) are separated by dramatic T_1 changes, with the Sm C-Sm A transition rather different from the Sm A-N transition. In view of Fig. 4, it should be noted that the widths of the various T_1 jumps are surprisingly large (nearly half the range of the mesophases) and hence exceed the experimentally nonavoidable temperature gradients by far.

3. Discussion and Conclusions

From the shape of the T_1 relaxation dispersion in both Sm A and Sm C TBBA it is not easily seen how many and what kind of mechanisms contribute to the total relaxation time T_1 . None of the criteria typical for specific molecular reorientations, at Larmor frequencies that are large compared with the reorientation times (OF: $T_1 \sim \nu_p^{-1/2}$; SD: $T_1 \sim \nu_p^{-3/2}$; R: $T_1 \sim \nu_p^{-2}$), is verified explicitly. Nevertheless, considering the similarity with results for nematics like PAA [6] and following the arguments of Blinc [1], the $T_1(\nu_p)$ profiles at low and high Larmor frequencies suggest that below $\nu_p \cong 10^5$ Hz the

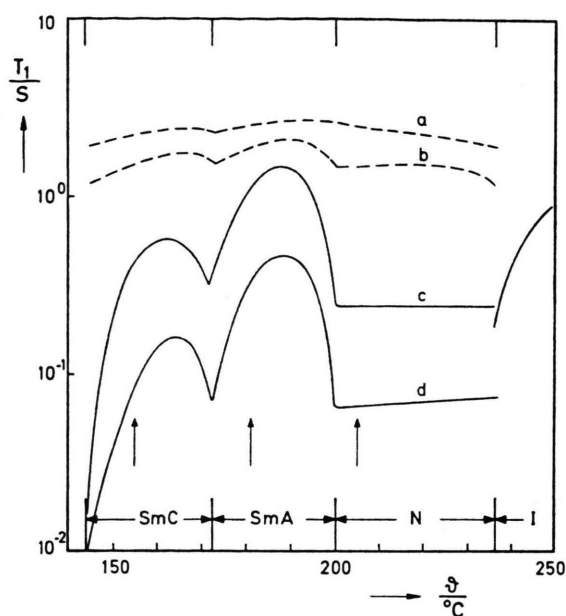


Fig. 4. Experimental temperature profiles, $T_1(\theta)$, for Sm C, Sm A, and N TBBA at 4 Larmor frequencies ν_p . (a) 60 MHz, data from [1]; (b) 15 MHz, data from [2]; (c) 80 kHz, this work; (d) 8.5 kHz, this work. The arrows show the temperatures where the $T_1(\nu_p)$ plots of the preceding figures have been registered. Due to temperature gradients in the samples, the error limits strongly increase near the phase transition points.

relaxation process is governed by OF's of the nematic director $\mathbf{n}$ and/or tilt angle φ (OFn, OF φ or shorter: OF), whereas above $\nu_p \cong 10^6$ Hz SD becomes dominant. Surprisingly it turned out to be possible to describe the relaxation dispersion for both smectic phases (including Blinc's data for $\nu_p \geq 1.5 \cdot 10^7$ Hz) quantitatively by means of the well-known theoretical T_{10F} model (parameters: amplitude factor A_{0F} ; low-frequency and high-frequency cut-offs of the OF spectrum, $\nu_{\min}$, $\nu_{\max}$, or related correlation times $\tau_{0F} \equiv 1/2\pi\nu_{\min}$, $\tau'_{0F} \equiv 1/2\pi\nu_{\max}$; dipolar local magnetic field B_{loc} or related dipolar frequency $\nu_{loc} \equiv \gamma_p B_{loc}/2\pi$; γ_p = proton magnetogyric ratio; for details of notation see Ref. [6 d]) in combination with the most simple SD contribution, T_{1SD} (parameters; average molecular jumping time τ_{SD} ; distance of closest intermolecular spin approach d ; diffusion constant $D = d^2/(6\tau_{SD})$; for details of notation see Ref. [6 d]), i.e. by *only two* contributions acting independently:

$$T_1^{-1} = T_{10F}^{-1}(A_{0F}, \nu_{\min}, \nu_{\max}, \nu_{loc}) + T_{1SD}^{-1}(\tau_{SD}, d). \quad (1)$$

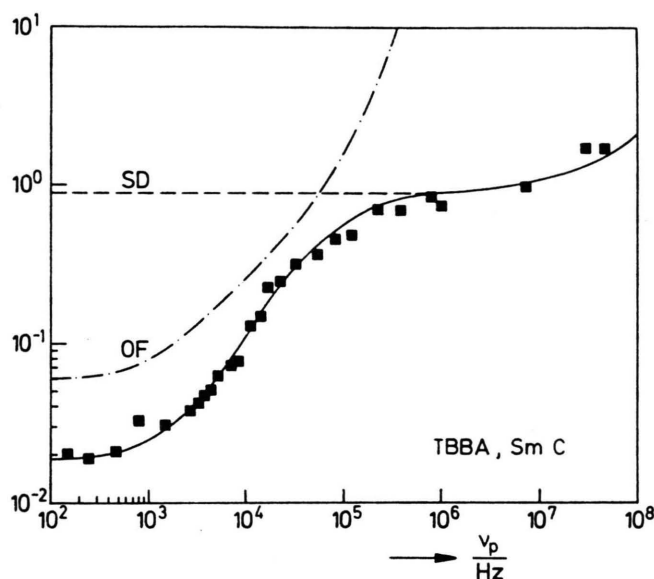


Fig. 5. Illustration of the quality of the OF-SD model, Eq. (1), for Sm C TBBA. The experimental points are the same as in Fig. 2, whereas the fitted model parameters ($A_{OF} = 1200 \text{ s}^{-3/2}$, $\nu_{\min} = 600 \text{ Hz}$, $\nu_{\max} = 2 \cdot 10^5 \text{ Hz}$, $\nu_{loc} = 8 \cdot 10^3 \text{ Hz}$; $\tau_{SD} = 5 \cdot 10^{-10} \text{ s}$, $d = 4.5 \cdot 10^{-8} \text{ cm}$) slightly differ from the results obtained with the OF-SD-X model. In particular, the diffusion constant D is too large by a factor 2.5.

Figure 5 illustrates the best results obtained for the Sm C phase by computer assisted eyeball fittings of (1) to the available experimental data (computer simulation). At first sight the model used seems quite satisfactory; however, the analysis has to be rejected because it fails certainly to yield diffusion constants in accordance with more direct measure-

ments of D [8], and therefore necessitates the use of a more sophisticated theory. Similar difficulties are well-known from works on nematics [6]. Another reason for the necessity to consider additional relaxation mechanisms follows from the strong temperature dependence of T_1 in the vicinity of the Sm C-Sm A or Sm A-N phase transition (Fig. 4), since such a behaviour cannot be reasonably interpreted in terms of the parameters specified in (1). The sign of the $T_1(\vartheta)$ slope near 170°C and 190°C excludes T_{1SD} , and the magnitude of the $T_1(\vartheta)$ change in the range $\nu_{\min} < \nu_p < \nu_{\max}$ excludes the T_{10F} contribution as a cause of the observed effect.

To overcome the problem with the incorrect value of D , we extended (1) by a third term, T_{1X}^{-1} , which for simplicity was assumed to possess a Debye-like power spectrum (parameters: amplitude factor A_x ; correlation time τ_x) as a first approximation to any type of molecular reorientation open to discussion, e.g. rotational motions or other order fluctuation mechanisms that are not included in (1). As seen from the curve fits in Figs. 1 and 2 obtained by computer simulations as in Fig. 5, the refined model

$$T_1^{-1} = T_{10F}^{-1} + T_{1SD}^{-1} + T_{1X}^{-1} \quad (2a)$$

with

$$T_{1X}^{-1} = A_x \frac{\tau_x}{1 + (2\pi\nu_p\tau_x)^2} + \frac{2\tau_x}{1 + (4\pi\nu_p\tau_x)^2} \quad (2b)$$

allows an excellent description of the relaxation dispersion in full agreement with D values from the

Table 1. Parameters of the OF-SD-X relaxation model evaluated by curve fits of Eq. (2) to the experimental data shown in Figures 1–3. To illustrate the similarity between smectics and nematics, results on PAA [6c, 6f] are also listed. The notation is as usual, for details see e.g. [6d].

	Order Fluctuations (OF)	Self-Diffusion (SD)	Third Mechanism (X)
	nematic-like $A_{OF}[\text{s}^{3/2}]$ $\nu_{\min}[\text{Hz}]$ $\nu_{\max}[\text{Hz}]$ $\nu_{loc}[\text{Hz}]$	isotropic $\tau_{SD}[\text{s}]$ $d[\text{cm}]$ $D[\text{cm}^2/\text{s}]$	Debye-like $\tau_x[\text{s}]$ $A_x[\text{s}^2]$
TBBA, SmC (156 °C)	$1.2 \cdot 10^3$ $5 \cdot 10^2$ $2 \cdot 10^5$ $8 \cdot 10^3$	$2.5 \cdot 10^{-10}$ $5 \cdot 10^{-8}$ $1.2 \cdot 10^{-6}$	$5.5 \cdot 10^{-9}$ $1.4 \cdot 10^8$
SmA (181 °C)	$4 \cdot 10^2$ $3 \cdot 10^2$ 10^5 $2 \cdot 10^3$	$1.0 \cdot 10^{-10}$ $4 \cdot 10^{-8}$ $2.7 \cdot 10^{-6}$	$1.6 \cdot 10^{-9}$ $1.9 \cdot 10^8$
N (205 °C)	$2.7 \cdot 10^3$ 10^3 10^8 10^3	$4.0 \cdot 10^{-11}$ $3 \cdot 10^{-8}$ $5.4 \cdot 10^{-6}$	$1.5 \cdot 10^{-9}$ $1.1 \cdot 10^8$ ($A_x \tau_x = 1.6 \cdot 10^1$)
PAA, N (125 °C)	$1.54 \cdot 10^3$ $5 \cdot 10^3$ $8.1 \cdot 10^9$ $1 \cdot 10^4$	$9.9 \cdot 10^{-11}$ $3.0 \cdot 10^{-8}$ $1.5 \cdot 10^{-6}$	$< 5 \cdot 10^{-10}$ $> 10^8$ ($A_x \tau_x = 5 \cdot 10^2$)

literature. Table 1 summarizes the adjusted model parameters. Note that despite of the rather different $T_1(\nu_p)$ profile for the nematic phase, the concept of three contributions is supported by the analysis of nematic TBBA, where just as in the smectic states the fitted diffusion constant comes out somewhat too small if T_{1X} is neglected. Obviously and in accordance with the $T_1(\vartheta)$ behaviour shown in Fig. 4 one finds $T_{1X}(N) > T_{1X}(Sm)$.

Now, what can be learnt from our study? (I) In our opinion the most important finding is that Blinc's calculations on T_{10F} , which under certain conditions point out parallels between nematic and smectic order fluctuations, make a quantitative interpretation of the T_1 relaxation dispersion for Sm A, Sm C, and N TBBA possible, if the well-known refinements of the T_{10F} theory (hydrodynamic cut-off frequencies, local field effects) are taken into account and if T_{10F} is properly combined with two additional contributions (T_{1SD} , T_{1X}). The new results eliminate the unexpected strong deviations between Sm A and Sm C observed by Blinc, i. e. they show that in both phases T_1 is determined by (at least) three mechanisms, what implies that the square root dependence $T_1 \sim \nu_p^{1/2}$, characteristic for pure OFn or OF φ , cannot be seen directly. The OF relaxation rates in the smectic mesophases were found of similar magnitude as but somewhat smaller than T_{10F}^{-1} for high-temperature nematics like PAA, with the changes of the parameter A_{0F} in going from Sm C to Sm A and N being qualitatively predicted by the theoretical relation $A_{0F} \sim \bar{\eta}^{1/2} \cdot \bar{K}^{-3/2}$ ($\bar{\eta}$: average viscosity; $\bar{K}$: average elastic constant). For in smectics $\bar{K}$ is known to be much greater than $\bar{K}$ for nematics, and the available estimates on $\bar{\eta}$ yield $\bar{\eta}(Sm C) > \bar{\eta}(Sm A)$ [9]. Similarly, the evaluated temperature dependencies of the OF parameters ν_{min} and ν_{loc} are not unreasonable within the error limits in view of the fact that both the order parameter S and the coherence length ξ are known or expected to become smaller with increasing ϑ ($\nu_{min} \sim 1/\xi^2$; $\nu_{loc} \sim S$ [1, 6]). The only surprising result comes from ν_{max} , which unexpectedly varies by a factor 10^3 at the Sm A-N transition. Obviously the effective OF power spectrum for the smectic phases is considerably shifted towards lower frequencies as compared with the nematic state. (II) The second point worth to note is that the model fitting can be achieved with the diffusional contribution T_{1SD} based on the "correct" diffusion constants and more realistic

values of the approach parameter d ($3 \dots 5 \cdot 10^{-10}$ m) than used in Blinc's paper ($7 \cdot 10^{-10}$ m). For a long time, with nematics such a consistent interpretation was a great problem that has only recently been solved [6]. Surprisingly, d reveals a rather strong temperature dependence, the origin of which is not quite clear, since it exceeds the variation expected from changes of the density by far. Very probably the effect must be attributed to insufficient experimental data in the high-frequency range, but possibly it also indicates the limits of the isotropic diffusion model, which up to now has been successfully applied to liquid crystals. Theoretical refinements have been proposed recently [10]. (III) The appearance of a third relaxation contribution T_{1x} for both smectic phases as a consequence of the constraints on the diffusion constants parallels results available for nematics [6], and suggests that T_{1X} may reflect similar (slow!) processes in all mesophases, although its magnitude differs considerably. Hence we believe that x most likely refers to either the highly hindered molecular rotation about the short axis (Rs) or to another type of order fluctuations not included in the T_{10F} term, namely fluctuations of the order parameter S (OFS).

Both mechanisms yield a strongly temperature dependent relaxation rate in the vicinity of the phase transition points, i. e. just the feature of Fig. 4 that is not covered by T_{10F} or T_{1SD} . In the present case preference is given to $x = \text{OFS}$ because of the rather small evaluated τ_x -values, which seem not in accordance with the considered type of rotation [11], and because of the diminishing temperature dependence of T_1 with increasing Larmor frequency, which is typical for OFS terms [6]. However, our conclusion is not definitive since a quantitative description of the complex temperature profiles requires A_x to be a function of ν_p for low frequencies, a property we are not familiar with from both the Rs or OFS theory. This problem cannot be eliminated by using the exact form of both models instead of the Debye-approximation, because the refinements do not change the vanishing dispersion of the power spectrum in the critical regime. The difficulties with the amplitude factor make it seem probable that T_{1X} really is composed of two mechanisms with different correlation times and thus indicate another similarity to nematics; but more detailed studies of $T_{1X}(\vartheta)$ are necessary to find out its origin unambiguously.

Obviously all given arguments point out surprisingly far going parallels between the proton spin relaxation of nematics and smectics. As a consequence eventual reorientations specific for smectics, like undulations or layer sliding, are severely concealed and hard to detect.

Acknowledgements

We are indebted to Dr. Drauz for the synthesis of TBBA and to Dr. K. F. Reinhart for helpful discussions. Thanks are also due to Mrs. G. Seeliger for reading the English text. The work was supported by the Deutsche Forschungsgemeinschaft.

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