NMR Investigation of Order Fluctuations, Self-Diffusion and Rotational Motions in the Nematic Liquid Crystal MBBA by T_1-Relaxation Spectroscopy

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We report on measurements of the proton spin T_1 relaxation dispersion at various temperatures in the nematic phase of the liquid crystal MBBA in the Larmor frequency range from 2 kHz to 270 MHz, which exceeds previous studies by more than 3 orders of magnitude. The new results cannot be interpreted in terms of either order fluctuations or self-diffusion as recently proposed by Doane et al.[1] and Blinc et al.[2], respectively. Instead, the dispersion and its temperature dependence indicate the significance of at least three relaxation mechanisms, namely order fluctuations (OF), self-diffusion (SD) and rotation of the molecular ellipsoids about the short axis (R). The combined OF-SD-R model presented in this work allows a quantitative analysis of the experimental findings! The correlation times and activation energies of the three molecular reorientations evaluated from the T_1 dispersion by means of a computer optimization procedure are in essential agreement with data provided by other spectroscopic methods [light scattering, tracer technique, dielectric relaxation], but differ from former NMR conclusions.

1. Introduction

Recent NMR investigations of the molecular dynamics of nematic liquid crystals have led to rather contradictory results: both *nematic order fluctuations*[1] (OF) and *self-diffusion*[2] (SD) were suggested to be the dominant mechanism for proton spin relaxation in nematics such as MBBA (p-methoxybenzylidene-p-butylaniline). In principle these processes should be easily distinguishable by their dependence of the longitudinal relaxation time T_1 on the Larmor frequency $\nu = \omega/2\pi$ of the relaxing nuclei, for the complete $T_1(\nu)$ dispersion relations for order fluctuations and self-diffusion are fundamentally different[3, 4]. Nevertheless, earlier T_1 measurements on MBBA as a function of ν did not lend themselves to a single interpretation because of the restricted frequency range accessible to conventional NMR spectrometers ($\nu \cong 4$ MHz to 100 MHz). Based on data in the Megahertz regime, Doane et al.[1] favoured the concept of relaxation by order fluctuations, whereas Blinc et al.[2] presented arguments for the alternative diffusion model.

The conflict arose primarily from the fact that the experimental data of both research groups were clearly not in satisfactory agreement with the original dispersion relations of either order fluctuation or self-diffusion controlled relaxation rates. Therefore, unfortunately, the basic theories did not allow a straight-forward interpretation of the relaxation dispersion for liquid crystalline MBBA, and the theoretical refinements discussed in the literature subsequently rendered the NMR analysis ambiguous. At first, Doane succeeded in eliminating the difficulties with the experimental $T_1(\nu)$ in the Megahertz regime by taking account of a frequency cut-off parameter (ν_c) in the order fluctuation model. Afterward Blinc's treatment of the diffusion model proved also capable to describe the available results by including a step-width parameter (α) in the theory, as well as an unspecified frequency independent contribution (B) to the relaxation rate. More recently, because the cut-off effect was argued to be not of major significance, the Doane group[5] reformulated the order fluctuation formalism in a more sophisticated manner, considering both collective order and local diffusive reorientations of proton spins. In the new approach, the decisive novel aspect originated from a cross-correlation term ($1/T_{1c}$) between the two types of motion that appeared to be important in the case of MBBA. Essentially by means of this improvement of the theory the authors again achieved a satisfactory curve fit to the T_1 dispersion data from the literature.

It will be shown in this paper that neither of the three viewpoints solves the problem of proton spin relaxation in nematic MBBA if additional measurements at very low frequencies, i. e. in the kilohertz range, are considered. Instead, a superposition of

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at least *three* processes is found necessary in order to explain the frequency and temperature dependences of the newly presented experimental results. Accordingly we propose and apply a relaxation model based on three fundamental molecular motions in nematics, namely

(a) orientational order fluctuations (OF) [1, 3];
(b) self-diffusion (SD) [2, 4];
(c) rotational reorientations (R) [6].

Due to the mixing of the respective T_1 contributions, the relaxation diagram of MBBA looks rather complicated and the characteristic features of order fluctuations or self-diffusion, believed to have been verified in several former NMR investigations, are not so easily revealed by the T_1 dispersion as generally supposed. In a previous, preliminary report [7] on the liquid crystal PAA (p-azoxyanisole) it was possible to analyse the experimental findings in terms of order fluctuations alone, but this should not initiate speculation on principle differences between both nematogens. The important low-frequency measurements were made only at one single temperature in the nematic phase and additional studies are necessary for a detailed comparison with MBBA. Recent high-frequency examinations of deuterated samples [8] clearly demonstrate the significance of different T_1 mechanisms in PAA.

This paper deals with the *nematic phase* of MBBA [9a]; results for the *isotropic phase* [9b] in the vicinity of the clearing point will be discussed in a forthcoming publication.

2. Experimental Techniques and Results

Proton relaxation times, T_1, for nematic MBBA were measured at 18, 27, 35 and 45 °C over the Larmor frequency range from about 2 kHz up to 270 MHz. The measurements below 100 MHz were made with a home-built pulsed NMR spectrometer described previously [7, 10], using field cycling techniques and standard NMR pulse programs [11] such as the $90^\circ - \tau - 90^\circ$ sequence. At 270 MHz we used a Bruker Fourier-Transform unit, which allowed T_1 experiments by observing the saturation of the proton resonance spectrum after a $90^\circ - \tau - 90^\circ$ pulse sequence [11]; it should be noted that different parts of the MBBA spectrum approximately led to identical time constants. When applying the field cycling technique the Larmor frequency of the relaxing nuclei cannot be determined directly with a counter. In this mode of our low-frequency apparatus ($\nu \leqq 7$ MHz) ν was derived from the associated magnetic field H by means of the Larmor condition ($\nu = \gamma \cdot H / 2\pi$; γ = proton magnetogyric ratio) and a calibrated Hall probe. The lowest value examined in the present work is due to the earth's magnetic field.

MBBA, obtained in the purest commercial grade from Riedel-de Haën and from Ega-Chemie, was filled in evacuated glass vials of appropriate dimensions without further purification. Although the clearing point ϑ_c of both materials differed markedly (Riedel: 46.3 °C; Ega: 43.9 °C), no significant differences could be observed between the respective T_1 data in the nematic or isotropic phase of the chemicals. The samples were found to be stable for many months if maintained below the clearing point. However, heating above this temperature led to a slight decrease of ϑ_c (about 0.5 °C), and this effect entailed a considerable change of T_1 in the vicinity of the nematic-isotropic phase transition. Therefore, such heating was strictly avoided with those samples, the T_1's of which are presented in this paper.

The results of our measurements on Riedel's MBBA in the nematic phase are illustrated in Fig. 1 in the form of T_1 versus Larmor frequency ν at four temperatures ϑ. For all frequencies and temperatures we observed a single exponential decay of the longitudinal spin magnetization, with relaxation times ranging from about 10^{-2} s in the kilohertz regime to nearly 1 s at the highest available fre-

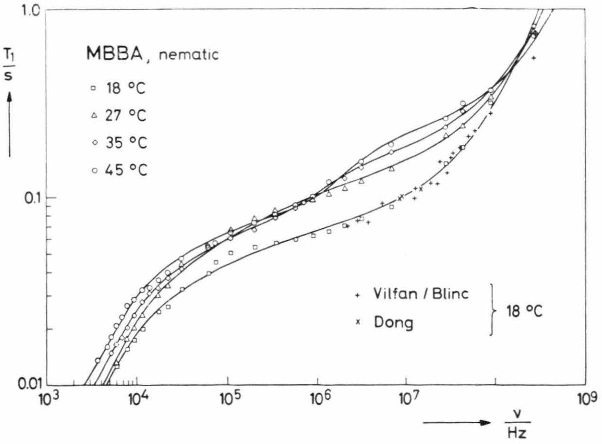

Fig. 1. T_1 proton spin relaxation dispersion in nematic MBBA at four temperatures. *Data points:* Experimental results of this work (□, △, ◇, ○) and data taken from Ref. [2] (+) and Ref. [12d] (×). *Curves:* Computer fit of the OF-SD-R model [Eqs. (1) – (5)] with parameters listed in Table II.

(*Note added in proof:* Recent measurements in fields below the earth's magnetic field show a more complicated low-frequency behaviour.)

quency. The individual experimental points were reproducible to better than ±7% (random error) on any one sample and proved to be independent on the considered section of the free induction decay. Some of the data reported previously in the literature by other research groups[2, 12] are included in the diagram to show the degree of agreement. A most interesting point of Fig. 1 is that a lowering of ν is followed by a continuous decrease of T_1 down to the smallest examined Larmor frequencies, even when the external magnetic field H becomes comparable with the local dipolar field H_L of nematic MBBA. Primarily due to the fact that the presented dispersion plots cover a frequency range of more than 5 decades it is possible to recognize several characteristics not observed previously:

(a) Frequency dependence. T_1 varies very slowly as a function of Larmor frequency, with maximum slopes in the low- and high-frequency regimes, where one finds $T_1 \sim \nu^{0.8}$ and $T_1 \sim \nu^{1.0}$, respectively. This observation answers two most interesting questions on the asymptotic behaviour of the $T_1(\nu)$ dependence. On the one hand it is clearly demonstrated that the relaxation dispersion extends to the lowest accessible magnetic fields, and on the other hand the exponent of ν becomes definitively greater than 1/2 for high values of ν.

(b) Temperature dependence. The shape of the dispersion is strongly dependent on the temperature ϑ of the sample. Whereas lowering ϑ within the nematic phase of MBBA steadily reduces T_1 at both low and high frequencies, the behaviour is completely different in the intermediate range. Near $\nu = 1$ MHz the various T_1 points, except for the supercooled nematic state (18 °C plot), show no temperature dependence at all!

(c) Number of dispersion regimes. The $T_1(\nu)$ increase at any temperature clearly splits into two steps, which indicate that at least two mechanisms contribute to the total relaxation rate. This coarse classification can be easily refined by considering $T_1(\vartheta)$: The unusual effect of temperature on the shape of the $T_1(\nu)$ curves for intermediate frequencies suggests that the relaxation diagram is composed of three regimes and, hence, reflects the significance of a low-, a medium- and a high-frequency relaxation process!

(d) Comparison with T_1, $T_{1\varrho}$ and T_d data from the literature. Except for the 270 MHz measurements, where we found at 18 °C a considerably longer relaxation time than a value reported by Blinc[2], our data essentially agree with less extensive previous T_1 results given in the literature[2, 12]. However, the now available low-frequency dispersion is rather different from the behaviour estimated from competitive low-field methods of relaxation spectroscopy, i. e. the $T_{1\varrho}$- and T_d-techniques[12]. In particular, neither of the experimentally observed regimes $T_{1\varrho} \sim \nu^0$ or $T_{1\varrho} \sim \nu^2$ (see Refs.[12a, 12b]) is verified in the case of T_1, and our low-field T_1 asymptote is not in accordance with the T_d plateau presented in Reference[12c].

3. Theory

3.1. General Remarks

At present, the generally accepted view is that the longitudinal proton spin relaxation in nematic MBBA originates from either *order fluctuations* or *self-diffusion*, and most recent NMR investigations center upon the question of which contribution prevails. However, it seems difficult to visualize why relaxation spectroscopy should reflect only one type of molecular reorientation instead of a superposition of both tumbling processes. It is even more surprising that no really comprehensive attempt appears to have been made to take into account the various *rotational motions* of the MBBA molecule in the nematic phase, which provide further potential relaxation mechanisms. As illustrated in Fig. 2, in our opinion a complete theory of T_1 should include, apart from the familiar contributions due to order fluctuations and self-diffusion, the effect of rotational reorientations, i. e. relaxation by diffusive jumps of the ellipsoid-like molecules about their long and short axis and, additionally, relaxation by the tumbling of the CH_2- and CH_3-groups within the ellipsoids! None of these contributions can be treated as negligible or prevalent without an ap-

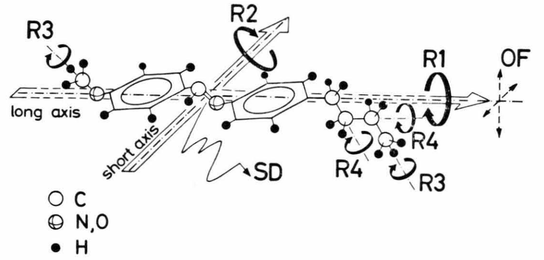

Fig. 2. Schematic structure of MBBA and reorientations of protons considered in this work. *OF:* Order fluctuations in the director ***n***. *SD:* Self-diffusion. *R_{1-4}:* Rotational tumbling of the molecular ellipsoids about the long axis (R_1); of the molecular ellipsoids about the short axis (R_2); of the CH_3-groups about the threefold axis (R_3); of the CH_2-segments about C—C bounds (R_4).

proximate knowledge of the pertinent magnetic correlation times, which, however, shall be determined by the experiment. For this reason we prefer to analyse our experimental findings quite generally in terms of the *three* afore-mentioned mobilities instead of a sophisticated theory with only *one* relaxation mechanism. Our approach differs from the one recently proposed by Ukleja et al.[5], although some of the basic ideas seem rather similar.

According to standard textbooks, the total longitudinal magnetic relaxation rate $(1/T_1)$ of a system of like nuclear moments (spin quantum number: I; magnetogyric ratio: γ) with various independent mobilities of the associated nuclei (jumping time: τ_j), and yet with a single exponential relaxation behaviour following changes of the applied magnetic field (H), is given by the weighted sum of the individual contributions $(1/T_{1j})$ originating from the different types (j) of motion. This is known as the 'fast exchange limit'[13]. Considering the relaxation rates of both the Zeeman energy and the dipolar energy $(1/T_z,\ 1/T_d)$ for spin pairs with purely dipolar interaction, $1/T_1$ is expressed by the basic equations[13, 14]

$$1/T_1 = \sum_j p_j/T_{1j}\,, \tag{1 a}$$

$$1/T_{1j} = [H^2/T_{zj} + H_L{}^2/T_{dj}]\,/\,[H^2 + H_L{}^2] \tag{1 b}$$

with

$$1/T_{zj} = (3/2)\,\gamma^4\,\hbar^2\,I(I+1)\,[J_j{}^{(1)}(\omega) + J_j{}^{(2)}(2\,\omega)]\,, \tag{2 a}$$

$$1/T_{dj} = R_j/T_{zj}\,. \tag{2 b}$$

In the present case, j refers to either order fluctuations (OF), self-diffusion (SD) or rotation (R) of the MBBA protons, and the p_j's are the fractions of the 21 protons per molecule concerned. H is the applied Zeeman field, $\omega \equiv 2\,\pi\,\nu = \gamma\,H$ the cor-

Table I. Intensity spectra of proton spin relaxation mechanisms in nematic MBBA used in this work [OF-SD-R model]. *OF-term.* S: order parameter; k_B: Boltzmann's constant; ϑ: absolute temperature; η: average viscosity; r_ring: distance of nearest benzene ring protons; K: average elastic constant; Γ: short range correlation time (Sung); Θ: angle between molecular long axis and director; γ: proton magnetogyric ratio; $2\,\pi\cdot\hbar$: Planck's constant. *SD-term.* N: number of proton spins per volume; d: distance of closest proton approach of neighbouring molecules; D: self-diffusion constant; τ_SD: translational jumping time; τ_M: magnetic correlation time; $B_{3/2}$: Bessel function of order 3/2; ϱ: variable of integration. *R-term.* k: index for protons of type k [ring, CH$_2$ or CH$_3$]; $p_{\mathrm{R,k}}$: relative abundance of type k protons; r_k: distance of nearest neighbours; A_k, B_k, C_k: relaxation amplitudes; l_k: direction cosine of internuclear vector of proton pairs [with respect to the molecular long axis]; τ_Ak, τ_Bk, τ_Ck: effective rotational correlation times of the Woessner formalism; τ_s, τ_L: jumping times of the molecular ellipsoids about the short and long axis; τ_Lk: additional intramolecular jumping times of type k protons about the long axis; $\varepsilon^{(1)}$, $\varepsilon^{(2)}$: anisotropy factors according to Eqs. (12), (13 a) and (13 b).

Relaxation mechanism j	Fourier intensity $J_j(\omega)$	Eq.	Weighting factor p_j	Parameters	References
Nematic order fluctuations (OF) with $\vec{n}$ nearly parallel $\vec{H}$	$J^{(1)}_\mathrm{OF}(\omega) = A'\,\omega^{-1/2} + B'$	(3 a)	8/21	A', B' (or $A = \frac{9}{8}\,\gamma^4\,\hbar^2\,A'$, $B = \frac{9}{8}\,\gamma^4\,\hbar^2\,B'$)	3a, 3b, 3c
	$A'(\vartheta) = \dfrac{\sqrt{2}}{\pi}\,\dfrac{S^2\,k_\mathrm{B}\,\vartheta\,\eta^{-1/2}}{r^6_\mathrm{ring}\,K^{3/2}}$	(3 b)			
	$B'(\vartheta) = 2\,\Gamma\,\dfrac{\langle \sin^2\Theta\,\cos^2\Theta\rangle}{r^6_\mathrm{ring}}$	(3 c)			
	$J^{(2)}_\mathrm{OF}(\omega) \cong 0$				
Isotropic self-diffusion (SD)	$J^{(1)}_\mathrm{SD}(\omega) = \dfrac{16\,N}{15\,d^3}\displaystyle\int_0^\infty \dfrac{[B_{3/2}(\varrho\,d)]^2}{\varrho}\,\dfrac{3\,\tau_\mathrm{SD}/(\varrho\,d)^2}{1 + [3\,\omega\,\tau_\mathrm{SD}/(\varrho\,d)^2]^2}\,\mathrm{d}\varrho$	(4 a)	1	d, τ_SD (or d, D)	4a, 4b, 4c
	$\tau_\mathrm{SD}(\vartheta) = d^2/6\,D = 5\,\tau_\mathrm{M}/6$	(4 b)			
	$J^{(2)}_\mathrm{SD}(\omega) = 4\,J^{(1)}_\mathrm{SD}(\omega)$	(4 c)			
Rotations of symmetrical ellipsoids (R)	$J^{(1)}_\mathrm{R,k}(\omega) = \varepsilon^{(1)}\,\dfrac{4}{15\,r^6_\mathrm{k}}$ $\cdot\left\{\dfrac{A_\mathrm{k}\,\tau_\mathrm{Ak}}{1+\omega^2\,\tau^2_\mathrm{Ak}} + \dfrac{B_\mathrm{k}\,\tau_\mathrm{Bk}}{1+\omega^2\,\tau^2_\mathrm{Bk}} + \dfrac{C_\mathrm{k}\,\tau_\mathrm{Ck}}{1+\omega^2\,\tau^2_\mathrm{Ck}}\right\}$	(5 a)	k = ring: 8/21 k = CH$_2$: 6/21 k = CH$_3$: 6/21	$\varepsilon^{(1)}$, τ_s	6a, 6b
	$A_\mathrm{k} = \frac{1}{4}(3\,l^2_\mathrm{k} - 1)$; $B_\mathrm{k} = 3\,l^2_\mathrm{k}(1 - l^2_\mathrm{k})$; $C_\mathrm{k} = \frac{3}{4}(l^2_\mathrm{k} - 1)^2$;	(5 b)			
	$\tau_\mathrm{Ak}(\vartheta) = \tau_\mathrm{s}$; $\tau^{-1}_\mathrm{Bk} \approx \tau^{-1}_\mathrm{Ck} \sim \tau^{-1}_\mathrm{L} + \tau^{-1}_\mathrm{Lk}$	(5 c)			
	$J^{(2)}_\mathrm{R,k}(\omega) = \varepsilon^{(2)}\,4\,J^{(1)}_\mathrm{R,k}(\omega)$	(5 d)		$\varepsilon^{(2)} \approx \varepsilon^{(1)}$	

responding angular Larmor frequency and H_L the local dipolar field within the sample. Most details of the three molecular reorientation processes are contained in the Fourier intensities $J_j^{(1)}(\omega)$ and $J_j^{(2)}(2\omega)$ of the dipolar interaction as well as in the characteristic ratios $R_j = T_{zj}/T_{dj}$; these quantities will be explained below (see Table I). T_{dj} will be taken into account only for the dominant low-frequency contribution, since according to Eq. (1 b) the influence of the dipolar relaxation rates becomes negligible in the regime $H \gg H_L$.

3.2. *A Model for Proton Spin Relaxation in Nematic MBBA*

Models for the separate intensities $J_{\mathrm{OF}}^{(1,2)}$, $J_{\mathrm{SD}}^{(1,2)}$ and $J_{\mathrm{R}}^{(1,2)}$ are well-known in the literature, particularly from the pioneering calculations of Pincus [3], Torrey [4] and Woessner [6], which by means of Eq. (1 a) allow to express the T_1 of the combined processes, at least in the high-frequency regime, provided that the three contributions are assumed to be independent. Since protons undergoing different motions do not exchange their positions within a MBBA molecule, the fast exchange limit implied in Eq. (1 a) is supposed to originate from rapid spin diffusion [14]. Both assumptions cannot be valid exactly, so they should be understood as the simplest way to extend previous treatments. Though the basic ideas of the various $J_j^{(1,2)}$ are excellently presented in the original papers, it is necessary to give some comments on the special situation encountered with MBBA. Table I lists the three types of Fourier intensities applied in the following relaxation analysis and summarizes the notation of the relevant parameters. For the sake of simplicity, only the elementary forms of the respective models, without more recently suggested refinements, are considered. This means that we use the Pincus theory without the cut-off and cross-correlation terms mentioned above; the Torrey formalism is discussed in the Abragam-Pfeifer limit, where the step width of diffusion is very small and isotropic, and Woessner's results are simplified to the special case of rotational tumbling of symmetrical molecular ellipsoids, with internal reorientations occurring only about the symmetry axis.

No similarly detailed calculations exist for the intensity spectra of dipolar relaxation, which according to Eq. (1 b) become important in the low-frequency regime of the T_1 dispersion. However, for the decisive low-frequency term in our analysis, i. e. the OF contribution, it seems adequate to follow the arguments of McElroy [3] and Goldman [14] predicting $T_{zj}/T_{dj} = 3$ for relaxation by correlated motions. This result, the approximations mentioned above and the available molecular data of MBBA allow to reduce the number of adjustable model parameters, otherwise unreasonably high, to six.

(a) Order fluctuations. As most clearly shown by Sung [3], the Zeeman relaxation time of spins induced by nematic order fluctuations, $T_{z\mathrm{OF}}$, is essentially expressed by two temperature dependent quantities $\mathrm{A}(\vartheta)$ and $\mathrm{B}(\vartheta)$, which are characteristic of the viscoeleatic properties of the liquid crystal [see Table I, Eq. (3)]. The B-term will be neglected in the following discussion because its contribution to the total relaxation rate can be calculated by Eq. (3) to be very small in the present case. Using the proton-proton distance $r_{\mathrm{ring}} = 2.44$ Å, the maximum molecular tilt angle $\Theta_{\max} \approx 30°$ and the short range correlation time $\Gamma \approx 10^{-10}$ s, Sung's formula yields $T_{z\mathrm{OF,B}} \approx 10$ s! Due to the high flexibility of the MBBA side chains, the remaining $T_{z\mathrm{OF,A}}$ mechanism is most probably restricted to nearest neighbours of the 8 benzene ring protons, whence we prefer to introduce the weight factor $p_{\mathrm{OF}} = 8/21$ instead of $p_{\mathrm{OF}} = 1$ often found in the literature. As a consequence, the A-term turns out to be less effective than generally supposed or, in other words, one needs a greater value of A to interpret a given experimental T_1.

Once $T_{z\mathrm{OF}}$ is known, the dipolar relaxation time $T_{d\mathrm{OF}}$ is obtained to the same approximation by means of the characteristic ratio $R_{\mathrm{OF}} = 3$ as pointed out before. Thus the evaluation of the total $T_{1\mathrm{OF}}$ dispersion relation according to Eq. (1 b) is straightforward, if the local dipolar field can be estimated. We decided to treat both H_L and A as adjustable parameters of the order fluctuation model.

(b) Self-diffusion. In the simplified Torrey theory [4] the Zeeman relaxation time of spins due to self-diffusion, $T_{z\mathrm{SD}}$, is described by the self-diffusion constant D [or the respective jumping time $\tau_{\mathrm{SD}} = d^2/6D$], the distance d of closest approach between spins of neighbouring molecules and the number N of spins per cm³ [see Table I, Eq. (4)]. From the molecular weight $M = 267.4$ g and the density [15] $\varrho \cong 1.05$ g cm^{-3} of MBBA, combined with the number of protons per molecule, one gets $N = 0.05$ Å^{-3}. The two other quantities must be determined from the experiment. Hence, assuming that

all molecules undergo translational diffusion, i. e. $p_{SD} = 1$, and neglecting the dipolar relaxation rate for reasons explained already, the considered diffusion model provides two adjustable parameters, namely D and d.

(c) Rotation. According to Woessner's molecular ellipsoid formalism[6] the Zeeman relaxation time of spins due to rotational motions, T_{zR}, essentially reflects the distances r_i, the direction cosines l_i and the reorientation times τ_i of rotating spin pairs [see Table I, Eq. (5)]. In the case of MBBA, at least three types of proton spin pairs with different mobilities must be distinguished and weighted corresponding to their relative abundances $p_{R,k}$: Protons of benzene rings (k = ring), of CH_2 segments (k = CH_2) and of CH_3 groups (k = CH_3). Restricting the calculation to nearest neighbours, the Woessner theory relates T_{zR} to three sets of well-known internuclear distances and direction cosines [$r_{\text{ring}} = 2.44$ Å, $l_{\text{ring}} \cong 1$; $r_{CH_2} = r_{CH_3} = 1.78$ Å, $l_{CH_2} \cong l_{CH_3} \cong 0$] and to four correlation times, the magnitudes of which are open to discussion [τ_L and τ_s for rotations of the whole ellipsoids about their long and short axis; τ_{CH_2} and τ_{CH_3} for rotations of the CH_2- and CH_3-groups about the long ellipsoid axis]. In our opinion *only one* of the various τ_i's, namely τ_s, should be of major significance with respect to T_{zR} for the following reason: As estimated from dielectric[16] and neutron scattering[17] experiments, the molecular ellipsoids in nematic MBBA rotate much faster about the long axis than about the short axis. Due to this retardation effect[18], the influence of the fast process on T_{zR} turns out to be completely negligible compared with the slow one, i. e. Woessner's formulae approximately reduce to the τ_s dependent terms. These contributions must be considered for the three types of proton pairs with relative weights $p_{R,\text{ring}} = 8/21$, $p_{R,CH_2} = 6/21$ and $p_{R,CH_3} = 6/21$, which, in principle, involves the correlation times τ_{CH_2} and τ_{CH_3} in addition to τ_s. However, as a consequence of the large τ_s/τ_L ratio it follows from Eq. (5) that the additional internal reorientations of CH_2 segments and CH_3 groups do not affect the relaxation rate within the scope of the simplified theory, because both mechanisms occur only in parallel with the fast rotation about the long axis of any molecule as a whole. If this were not the case, i.e. if $\tau_L \cong \infty$, τ_{CH_2} should considerably shorten T_{zR} due to its magnitude as estimated from ultrasonic measurements[19]; the CH_3 mechanism would remain negligible, since τ_{CH_3} is expected to be even shorter than τ_L[17].

A rather delicate problem arises with the anisotropy of the nematic liquid, because this aspect is not explicitly included in the original Woessner theory. We modified Woessner's intensity spectra by means of two weight factors $\varepsilon^{(1)}$ and $\varepsilon^{(2)}$ [for $J_R^{(1)}$ and $J_R^{(2)}$, respectively], which reflect the liquid crystalline order and considerably reduce the relaxation efficiency of the rotational mechanism as explained in Section 4. In the present case this approach approximately yields $\varepsilon^{(1)} \approx \varepsilon^{(2)} \approx \varepsilon$, so that our rotational model contains two adjustable parameters, namely ε and τ_s. No dipolar contribution, T_{dR}, was taken into account.

4. Discussion

4.1. Curve Fitting

To test the proposed model we fitted the six parameters of Eqs. (1) – (5), i. e. A, H_L, D, d, ε and τ_s, to the experimental T_1 data of Fig. 1 at the individual temperatures. This was achieved by a special computer procedure[20] which minimizes the sum of squares of deviations between the theoretical and experimental relaxation times and thereby determines the optimal values of the model parameters. In our opinion the usual technique to analyse the measurements by means of T_1^{-1} versus $\nu^{-1/2}$ plots is inadequate for unambiguous conclusions! As shown by the calculated curves in Figs. 1 and 3, our regression analysis of the T_1 dispersion produces a fit to within the experimental errors in each case. The adjusted values of the six quantities obtained by the computer optimization are summarized in Table II and will be discussed in Section 4.2.

In accordance with the qualitative arguments given above, it was not possible to interpret the observed relaxation dispersion by restricting the theory to order fluctuations and self-diffusion, i. e. to only two contributions, except for the lowest temperature. This finding is clearly demonstrated by Figs. 3 a and 3 b where the fitted contributions T_{1OF}, T_{1SD} and T_{1R} to the total relaxation rate are plotted separately as a function of the Larmor frequency at 18 °C and 45 °C. Obviously the significance of the rotational process strongly increases with increasing temperature, and near the nematic-isotropic phase transition the various relaxation rates become almost equal to each other at medium frequencies.

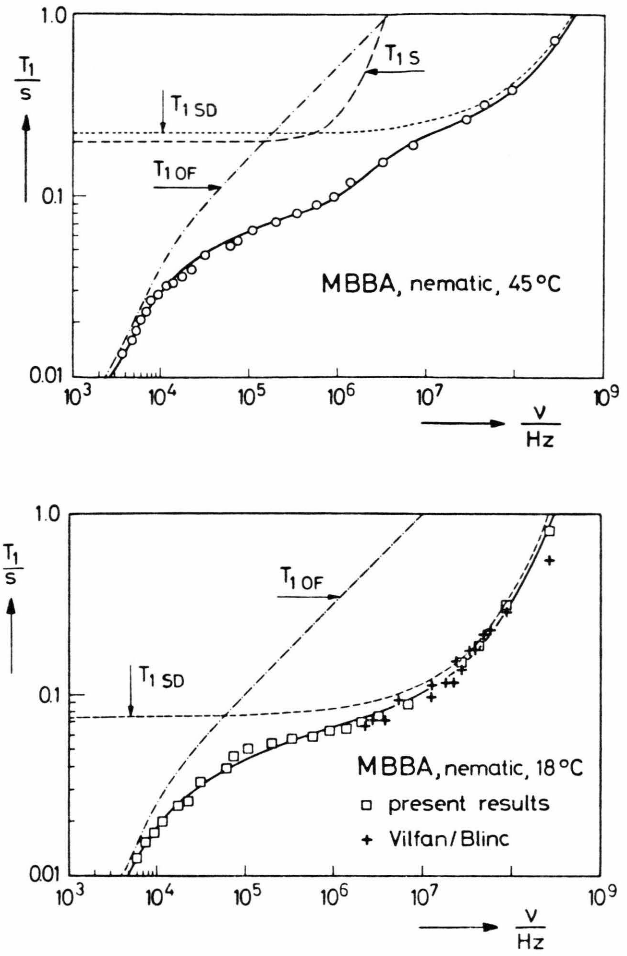

Fig. 3. T_1 proton spin relaxation dispersion in nematic MBBA at 45 °C (Fig. 3 a) and at 18 °C (Fig. 3 b). *Data points:* Experimental results taken from Figure 1. *Curves:* Computer fit of the OF-SD-R model [Eqs. (1) – (5)] with parameters listed in Table II and individual contributions T_{1OF}, T_{1SD} and $T_{1R} \equiv T_{1s}$ to the total relaxation time T_1.

A meaningful application of the aforementioned refinements[1, 4, 6] of the basic T_{1j} theories, which modify Eqs. (3) – (5), failed. (1) Attempts to include the *frequency cut-off* introduced by Doane et al.[1] in the order fluctuation model revealed no critical dependence on the additional parameter ν_c for values in the Megahertz regime. The reason for this negative result is evident: At high Larmor frequencies, where the cut-off effect is expected to reduce the relaxation rate $1/T_{1OF}$, this reduction is masked within the experimental error limits by the dominant diffusion term. (2) At present similar difficulties justify the simplified handling of Torrey's theory[4] of relaxation by self-diffusion. A more detailed analysis of this contribution which takes account of a *step-width parameter* α does not seem reasonable without further measurements at still higher frequencies where only the decisive transition from $T_{1SD} \sim \nu^{3/2}$ to $T_{1SD} \sim \nu^2$, associated with a finite value of α, can be proved or excluded. (3) The observed rotational contribution is too small to allow a more exact treatment of the *intramolecular reorientations* according to the complete Woessner formalism[6]; additional experimental data are necessary under conditions where T_{1R} becomes more important, i. e. in the immediate vicinity of the nematic-isotropic transition temperature or in appropriately deuterated samples.

We also compared our results with models used previously in the literature[1, 2a, 5, 12d] by other research groups. However, satisfactory curve fits could not be obtained in any case as expected. To illustrate this point, Fig. 4 shows the T_1 relaxation dispersion at 18 °C reproduced from the calculations and data of the papers of Doane et al.[1], Blinc et al.[2a], Ukleja et al.[5] and Dong et al.[12d], respectively, in comparison with our new approach. It is clearly seen that the former explanations must be rejected because of the large deviation between the theoretical and experimental relaxation times in the kilohertz regime! The main objections are the following: (1) Doane's cut-off model is not in agreement with the point of inflection of the relaxation dispersion plots. (2) Blinc's diffusion model completely fails at low Larmor frequencies. (3) Ukleja's calculations, based on a superposition of collective and local order fluctuations, cannot correctly describe the measurements primarily for two reasons. On the one hand a curve fitting of this model yields a negative activation energy for the local reorientation time τ_c, and on the other hand the predicted high-frequency limit, $T_1 \sim \nu^{1/2} \cdot \tau_c^0$, is not in accordance with the experimental findings. (4) Dong's recent treatment of the problem by combining the original order fluctuation term with an heuristic BPP term, suggested to come from the motions of side chains or from self-diffusion, leads to considerable discrepancies for medium and low frequencies, where the calculated T_1 values are much too low. This is not surprising in view of Figure 3.

4.2. Conclusions

From the computer optimization of the model parameters implied in Eqs. (1) – (5) a picture

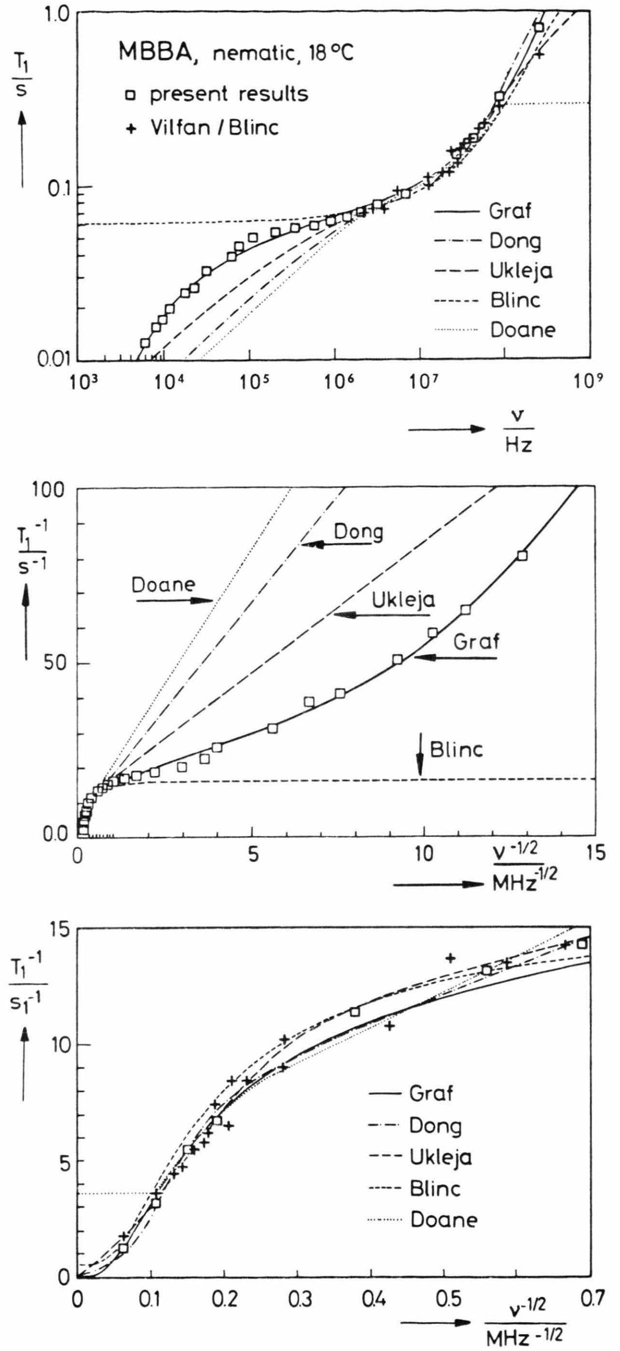

Fig. 4. Comparison of previous T_1 relaxation models for nematic MBBA with the new approach of the present work. *Upper diagram:* lg T_1 versus log ν plot. *Lower diagrams:* conventional T_1^{-1} versus $\nu^{-1/2}$ plot. The data points and the full curves are taken from the data of Fig. 1 at 18 °C. The broken curves are reproduced from the works of Doane [1], Blinc[2a], Ukleja [5] and Dong [12d] using the original parameters of the respective investigations.

develops of the underlying molecular reorientations in nematic MBBA which is reasonably consistent with data provided by other spectroscopic techniques. It should be emphasized that the good agreement is primarily due to the knowledge of the relaxation dispersion in the kilohertz range, since our new high-frequency measurements essentially reproduce the data available in the literature, and those data were believed to be at variance with optical and neutron studies! The significance of the three contributions $T_{1\mathrm{OF}}$, $T_{1\mathrm{SD}}$ and $T_{1\mathrm{R}}$ evaluated from the curve fit will now be considered in detail.

(a) Order fluctuations. The T_1 dispersion at low Larmor frequencies clearly reveals that order fluctuations are the dominant relaxation mechanism up to about 10^5 Hz. Unfortunately, the characteristic $\nu^{1/2}$ dependence is slightly masked at very low ν values by the transition from $T_{z\mathrm{OF}}$ to $T_{d\mathrm{OF}}$ controlled relaxation, which causes a somewhat stronger T_1 increase in the vicinity of $H \cong H_L$ or $\nu \cong \gamma H_L / 2\pi$. Nevertheless both the absolute value and the temperature dependence of the experimentally determined parameter A support the conclusion of relaxation by order fluctuations. The evaluation of the Pincus-Doane factor [1, 3]

$$A = \frac{9\sqrt{2}}{8\pi} \cdot \frac{\gamma^4 \hbar^2 S^2 k_{\mathrm{B}} \vartheta \eta^{1/2}}{r^6_{\mathrm{ring}} K^{3/2}} \tag{6 a}$$

from the distance of ring protons $r_{\mathrm{ring}} = 2.44$ Å [21], the order parameter S [15] and the well-known viscoelastic constants η and K [22] [one-constant approximation] gives a result not only of the correct order of magnitude, but in agreement with our experimental findings to better than 0.8%! [$\hbar$: Planck's constant divided by 2π; k_{B}: Boltzmann's constant; ϑ: absolute temperature.] E. g. using $S = 0.61$, $\eta \equiv (\eta_1 + \eta_2 + \eta_3)/3 = 0.19$ poise and $K \equiv (K_1 + K_2 + K_3)/3 = 5.8 \cdot 10^{-7}$ dyn near 295 K, Eq. (6 a) yields $A = 20100 \, \mathrm{s}^{-3/2}$ which compares well with the NMR result $A = 19940 \, \mathrm{s}^{-3/2}$ for 27 °C. We admit that in view of the numerous approximations implied in the theory and the rather large uncertainties of the averaged quantities η and K, the astonishingly good agreement seems a little fortuitous. However one should realize that estimations from the high-frequency T_1 dispersion discussed in the literature [5] are much smaller than our result.

Since the elastic modulus K is known to vary approximately proportional with S^2 and S is not very sensitive to temperature within the proper nematic phase, the temperature dependence of A according to Eq. (6 a) is mainly determined by the change of $\vartheta \cdot \eta^{1/2}$. Therefore, combining Eq. (6 a) with an Arrhenius-law for the average viscosity η gives

$$A(\vartheta) = \text{const} \cdot \vartheta \, [\eta_0 \exp(-E_\eta / R\,\vartheta)]^{1/2} \quad (6\,\text{b})$$

[η_0: preexponential factor; E_η: activation energy; R: gas constant], i. e. a relation which easily allows for the evaluation of the pertinent activation barrier of the viscous reorientation by plotting $\ln(A/\vartheta)$ versus $1/\vartheta$. From the data listed in Table II we find $E_\eta = 10.9$ kcal·mole^{-1}, which is in good agreement with mechanical and optical measurements of Meiboom et al.[23] and Gierke et al.[24]. Furthermore we note here that the analysis of the rotational relaxation term [see below] leads to almost the same result.

The adjustment of the local field parameter H_L was not very critical because the T_1 dispersion could not be extended to sufficiently low frequencies in the present work. We obtained $H_L \cong 1$ Oe, independent of the temperature. This value should be compared with the dipolar second moment M_2 of the NMR absorption line for MBBA according to the relation[14]

$$H_L = [\tfrac{5}{3} M_2]^{1/2}, \quad (7)$$

but to our knowledge no quantitative experimental or theoretical data are available till now.

(b) Self-diffusion. Due to the particular form of the relaxation dispersion for medium and high ν's we conclude that the high-frequency regime of the $T_1(\nu)$ diagram is mainly determined by the self-diffusion mechanism, i. e. by $T_{1\text{SD}}$. This finding essentially agrees with the previous interpretation of Blinc et al.[2] apart from Blinc's arguments concerning a finite step-width parameter of the random walk. As illustrated by Fig. 3, the significance of the $T_{1\text{SD}}$ contribution to the total relaxation rate increases considerably with decreasing temperature. However, even in the supercooled nematic state at 18 °C, it was not possible to substantiate the full dispersion characteristic of Eqs. (1), (2) and (4) up to the high-frequency asymptote $T_{1\text{SD}}(\nu) \sim \nu^{3/2}$ because self-diffusion is obviously too fast to realize the condition $2\pi\nu\tau_{\text{SD}} \gg 1$ with presently available magnets. Therefore, proton spin relaxation spectroscopy does not, as yet, seem the most adequate measure of the translational jumping time τ_{SD} in this case, and the adjusted parameters τ_{SD} and d listed in Table II as a function of temperature may not be very accurate. Nevertheless, they fit extremely well with data provided by various independent spectroscopic methods[25–28]. Making use of the identity

$$D = d^2/[6\,\tau_{\text{SD}}] \quad (8)$$

implied in the Torrey formalism, our curve fit yields diffusion constants ranging from $D = 0.98 \cdot 10^{-7}$ cm^2 s^{-1} at 18 °C to $D = 3.2 \cdot 10^{-7}$ cm^2 s^{-1} at 45 °C, which is in good agreement with studies by optical[25, 26] and tracer[27] techniques and also with recent NMR works[2, 28]. This is very remarkable, since it has been argued[26] that only mass transport experiments give reliable and consistent information on the self-diffusion process! Much higher D values than ours derived from neutron scattering[29] are now believed to be incorrect because of the overlooked effects of molecular rotations[30]. The origin of another, less pronounced inconsistency with multipulse NMR measurements[31] is not clear.

Figure 5 shows that the temperature dependence of D taken from Table II follows an Arrhenius-law

$$D(\vartheta) = D_0 \exp(-E_{\text{D}}/R\,\vartheta) \quad (9)$$

with the preexponential factor $D_0 = 0.34$ cm^2 s^{-1} and the activation energy $E_{\text{D}} = 8.7$ kcal·mole^{-1}. The numerical quantities reveal two interesting features: (1) E_{D} is only slightly smaller than E_η, which is surprising; a naive model of the nematic state rather requires $E_{\text{D}} \ll E_\eta$. (2) The magnitude of D_0 is extraordinarily small and does not lead to a

Table II. Parameters of the OF-SD-R relaxation model [Eqs. (1) – (5)] evaluated from the T_1 dispersion of nematic MBBA [Fig. 1] by computer optimization. δ denotes the average error of the model fit per point.

Temperature	Order fluctuation term		Self-diffusion term		Rotational term		Average error
[ϑ/°C]	[A/s$^{-3/2}$]	[H_L/Oe]	[τ_{SD}/s]	[d/Å]	[τ_s/s]	[ε]	[δ/%]
18	20840	1	$1.21 \cdot 10^{-9}$	2.67	$2.43 \cdot 10^{-7}$	$3.5 \cdot 10^{-4}$	5
27	19940	1	$0.65 \cdot 10^{-9}$	2.64	$1.45 \cdot 10^{-7}$	$9.5 \cdot 10^{-4}$	4.6
35	15980	1	$0.50 \cdot 10^{-9}$	2.61	$0.94 \cdot 10^{-7}$	$6.8 \cdot 10^{-3}$	2.1
45	12670	1	$0.30 \cdot 10^{-9}$	2.50	$0.57 \cdot 10^{-7}$	$1.6 \cdot 10^{-2}$	4.3

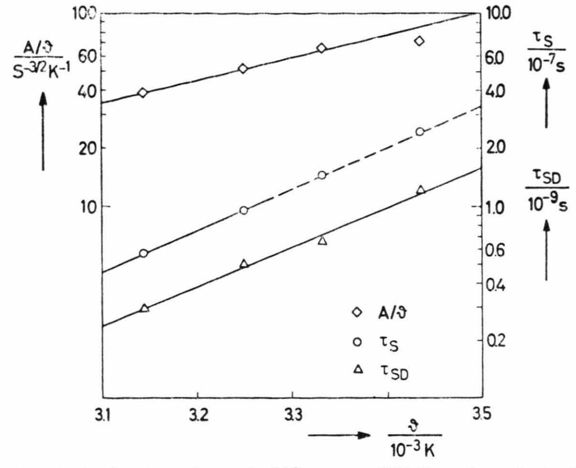

Fig. 5. Arrhenius plots of A/ϑ, $\tau_{\mathrm{SD}}=d^2/6\,D$ and τ_{s} derived from the T_1 model fit. For preexponential factors and activation energies see text [Eqs. (6 a), (9), (10)].

physically reasonable jumping time $\tau_{\mathrm{SD}_0}=d^2/[6\,D_0]$. Both aspects suggest some kind of cooperation of the diffusive motion[32] and hence, support speculation[26] that self-diffusion in nematics is not a *simple* mechanism.

(c) Rotation. The most complicated frequency range of relaxation dispersion is the transition regime between relaxation dominated by order fluctuations and relaxation dominated by self-diffusion, where the computer analysis indicates not only the two competing mechanisms dealt with so far, but still a third one. The effect of the additional process on the total T_1 is comparable to the $T_{1\mathrm{OF}}$ and $T_{1\mathrm{SD}}$ contributions only at temperatures near the nematic-isotropic phase transition, i. e. with decreasing temperature it becomes completely negligible within the experimental error limits of the present work. Both this unusual behaviour of $T_{1\mathrm{R}}$, which we attribute to the anisotropy factor $\varepsilon(\vartheta)$ [in normal isotropic liquids one usually finds $T_{1\mathrm{R}}\sim\vartheta$], and the absolute values of the rotational reorientation times $\tau_{\mathrm{s}}(\vartheta)$ obtained from the curve fitting, support the concept that the third relaxation term really reflects the rotation of the molecular ellipsoids about the short axis. *On the one hand* the observed range of $\tau_{\mathrm{s}}(\vartheta)$ from $2.4\cdot10^{-7}$ s at 18 °C to $5.7\cdot10^{-8}$ s at 45 °C compares well with dielectric studies[16, 18], which clearly demonstrate that in nematics the reorientation of the molecular long axis is compatible with the nematic ordering potential; the interpretation of our data in terms of an Arrhenius, law

$$\tau_{\mathrm{s}}(\vartheta)=\tau_{\mathrm{s}0}\exp(E_{\mathrm{s}}/R\,\vartheta) \tag{10}$$

yields $\tau_{\mathrm{s}0}=7.5\cdot10^{-15}$ s and $E_{\mathrm{s}}=10\,\mathrm{kcal}\cdot\mathrm{mole}^{-1}$ in fair agreement with the dielectric results. ['Fair' points out that the NMR analysis is not very critical for reasons given above and that the spread in the dielectric results of different research groups is very great!] *On the other hand* the values found for the anisotropy factor $\varepsilon(\vartheta)$ can be understood in terms of the considered rotation, if one includes the nematic order in the Woessner formalism. Unfortunately some difficulties arise from the quantitative discussion of the adjusted parameter.

In principle, any factor $\varepsilon\leqq1$ which reduces the effectiveness of the rotational relaxation as calculated by Woessner can be interpreted as a measure of the liquid crystalline anisotropy of the orientations of spin pairs. If one generalizes the theory, derived for isotropic liquids, by taking into account the nematic order via a simple distribution function of the molecular long axis[18]

$$f(\Theta)=f(0)\exp\{(q/k_{\mathrm{B}}\cdot\vartheta)\sin^2\Theta\} \tag{11}$$

[Θ: angle between the axis and the director $\vec{n}$; q: nematic order potential; k_{B}: Boltzmann's constant], it is possible to describe deviations from the original theory by a proper choice of $q(\vartheta)$. This is achieved by the replacement of the isotropically averaged Fourier intensities $J^{(1)}_{R,\mathrm{iso}}$ and $J^{(2)}_{R,\mathrm{iso}}$ by anisotropically weighted averages according to

$$J^{(\mathrm{h})}_{R}=\varepsilon^{(\mathrm{h})}\cdot J^{(\mathrm{h})}_{R,\mathrm{iso}}\cong\frac{(\varepsilon^{(1)}+\varepsilon^{(2)})}{2}\cdot J^{(\mathrm{h})}_{R,\mathrm{iso}}\equiv\varepsilon\cdot J^{(\mathrm{h})}_{R,\mathrm{iso}} \tag{12}$$

$$h=1,2$$

with

$$\varepsilon^{(1)}=\frac{\langle f(\Theta)\sin^2\Theta\cos^2\Theta\rangle}{\langle f(\Theta)\rangle\langle\sin^2\Theta\cos^2\Theta\rangle}=\frac{15}{8}\left\{1+\frac{1}{C}+\frac{1}{2\,C^2}-\frac{C-3/4}{2\,D\,(C^{1/2})\,C^{3/2}}\right\} \tag{13 a}$$

$$\varepsilon^{(2)}=\frac{\langle f(\Theta)\sin^4\Theta\rangle}{\langle f(\Theta)\rangle\langle\sin^4\Theta\rangle}=\frac{15}{8}\left\{\frac{3}{D\,(C^{1/2})\,C^{3/2}}-\frac{7}{C^2}\right\} \tag{13 b}$$

and $f(\Theta)$ from Eq. (11), where $\langle\ldots\rangle$ denotes volume averages, C stands for $q/k_{\mathrm{B}}\,\vartheta$ and $D\,(C^{1/2})$ is Dawson's integral[33]. Yet such a step does not solve the problem quantitatively, since it leads to values of q which are much greater than those estimated from the order parameter S using[18]

$$S\equiv\tfrac{1}{2}(3\,\overline{\cos^2\Theta}-1) \tag{14 a}$$

with

$$\overline{\cos^2 \Theta} = \frac{\langle f(\Theta) \cos^2 \Theta \rangle}{\langle f(\Theta) \rangle} = \frac{1}{2\, C^{1/2}\, D\, (C^{1/2})} - \frac{1}{2\, C}$$

$$\cong 1 - \frac{1}{2\, C} \text{ (for } C \gg 100) \, . \qquad (14\,\text{b})$$

E. g. from $\varepsilon = 1.64 \cdot 10^{-2}$ at 45 °C follows $q/k_{\text{B}}\, \vartheta = 300$ and $S = 0.98$, whereas direct measurements of the order parameter find $S \cong 0.50$. Discrepancies between S and q are well-known in the literature[18] and may be due to the neglection of short-range order effects as recently discussed by Ypma and Vertogen[34]. We hope to elucidate the anomaly by additional investigations in the immediate vicinity of the nematic-isotropic phase transition, where the rotational contribution to T_1 is large enough to allow a more exact evaluation of the motional parameters than possible with data available so far. Most probably the intramolecular rotations must be considered in a more detailed way than in the present work. The approximation $\varepsilon^{(1)} \cong \varepsilon^{(2)} = \varepsilon$ introduced to reduce the number of model parameters certainly is not responsible for the observed difficulties, since it is very good as easily checked by Eqs. (13 a) and (13 b)!

4.3. Comparison with PAA Results

The prevalent opinion in the literature[e.g. 35] that proton spin relaxation dispersion of nematic PAA and MBBA reflects different types of molecular motions, namely order fluctuations in the first case and self-diffusion in the second case, is not correct. By comparison of the present work with a preliminary report on PAA[7] one clearly sees that both nematogens behave qualitatively similarly with respect to T_1; in both liquid crystals there exists a low-frequency dispersion due to order fluctuations and a high-frequency regime essentially determined by self-diffusion. [In Table 1 of Ref.[7] the heading B' s^{-1} should be replaced by $B' \cdot \tau^{-1/2}\, \text{s}^{-3/2}$.] The well-known dissimilarities arise primarily from the different nematic temperature ranges of the nematogens, which shift *both* the $T_{1\text{OF}}$ *and* the $T_{1\text{SD}}$ contribution of PAA protons to considerably greater values than the respective terms of MBBA. This shift renders relaxation spectroscopy of low-temperature nematics like MBBA rather difficult! A more extensive study of PAA than the previous investigation, including measurements of the angular dependence of T_1 in the kilohertz regime, will be given in a forthcoming publication[36].

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