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## Liquid Crystals

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**Probing director fluctuations in nematic solutions by N.M.R.  
The breakdown of the simple RD + DF model for tolan in nematic  
Phase V**

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Frequency dependent relaxation measurements have been carried out on the para deuterons of tolan- $d_{10}$  (diphenylethyne), dissolved in Merck Phase V. The results are compared with those of three smaller probe molecules, studied previously. The simple RD + DF model which works well for the smaller probes, cannot give a satisfactory explanation for the relaxation behaviour, in particular the strong relaxation dispersion, of the para deuterons of tolan. The simple RD + DF model does not account properly for the effects of director fluctuations if the degree of orientation of the probe molecule studied is too high; this appears to be the case for tolan.

### 1. Introduction

In recent years we have been studying molecular motion and hydrodynamic fluctuations in liquid crystals by means of nuclear spin relaxation measurements on rigid probe molecules. Nuclei of interest were  $^{14}\text{N}$  and  $^2\text{H}$ , whose relaxation is dominated by quadrupolar interactions. Our main objective has been to study the scope and the limitations of the RD + DF model by measuring the relaxation behaviour of a number of probe molecules of increasing size in a nematic solution. Previously, we have reported on results obtained for methylisocyanide [1] and toluene and *p*-xylene [2]. Here, we compare these results with those obtained recently from  $^2\text{H}$  relaxation measurements on diphenylethyne (tolan). A more detailed account of the tolan study will be published later. The choice of probe molecules was, apart from practical considerations, based on theoretical aspects of the RD + DF model; a discussion of this point is therefore deferred to the end of §2.

In the RD + DF model it is assumed that the molecular reorientational motion in a nematic liquid crystal is made up of two components: (i) slow cooperative motions; the director fluctuations (DF), and (ii) rapid rotational diffusion (RD), which is statistically dependent of the director fluctuations. The reorientational motion of a probe molecule is thus described as rotational diffusion, in an orienting potential that fluctuates on a hydrodynamic scale. In addition to the assumptions inherent in the model, we make two additional simplifications. First, we assume that all molecules studied may be regarded to orient as symmetric tops. This is, of course, not warranted for the aromatic molecules, although the relaxation of quadrupolar nuclei lying on the principal axis of these molecules may to a good approximation be described in terms of a single, effective, rotational diffusion constant  $\tau_{\perp}$ . Secondly, we assume for the moment that a treatment with a series expansion of the director fluctuations to first order, is satisfactory. Often, this assumption is taken implicitly in the RD + DF model, when applied to probe molecules.

At this stage we do not aim at testing the RD + DF model in its most extended form, but rather in a practically manageable form, which can be subjected to experimental verification. As will be shown in § 3, the results of the relaxation measurements for the para deuterons of tolan cannot be explained by the simple RD + DF model, which describes satisfactorily the results for the probe molecules studied previously. The next step would be, therefore, to remove the two additional simplifications mentioned above.

Several groups have contributed to the development of the RD + DF model [3–6]. Here, as in previous papers [1, 2] we have followed the formulation given by Freed [6]. In the next sections only those elements of Freed's approach will be summarized which are essential for our purpose. For details of the theory we refer to the original papers [6].

## 2. Theory

Consider an axially symmetric probe molecule with a quadrupolar nucleus with spin  $I = 1$ , lying on the principal axis. The relaxation of this nucleus is supposed to be dominated by its quadrupolar interaction. If the interaction is given in terms of Wigner rotation matrix elements, then the relevant spectral densities can be described by indices  $K$  and  $M$  which refer to the molecular and laboratory frames, respectively. To derive values of  $J_{01}(\omega)$  and  $J_{02}(2\omega)$ , it is sufficient to determine the Zeeman and quadrupolar relaxation rates  $R_1^Z$  and  $R_1^Q$ , since the equations

$$R_1^Z(\omega) = c\{J_{01}(\omega) + 4J_{02}(2\omega)\}, \quad (1)$$

$$R_1^Q(\omega) = 3cJ_{01}(\omega), \quad (2)$$

hold where

$$c = \frac{3\pi^2}{2} \left( \frac{e^2 q Q}{h} \right)^2,$$

with the quadrupolar coupling constant, equal to  $(e^2 q Q)/h$ . The index  $K$  is equal to zero, by virtue of the axial symmetry of the probe. In terms of the RD + DF model,  $J_{01}(\omega)$  and  $J_{02}(\omega)$  can be written as

$$\begin{aligned} J_{01} &= J_{01}^{\text{RD}}(\omega) + J_{01}^{\text{DF}}(\omega) + J_{01}^{\text{cross}}(\omega), \\ &\approx \kappa(0, 1)\tau_{\perp} + \frac{3}{2} \sqrt{\frac{\pi}{2}} (S_{z'z'}^0)^2 A \left\{ \frac{u(\omega/\omega_c)}{\sqrt{\omega}} - \frac{2}{\pi} \sqrt{(2\omega_c)\tau_{\perp}} \right\}, \end{aligned} \quad (3)$$

$$\begin{aligned} J_{02}(2\omega) &\approx J_{02}^{\text{RD}}(2\omega) \\ &\approx \kappa(0, 2)\tau_{\perp}. \end{aligned} \quad (4)$$

For the rotational diffusion components the extreme narrowing condition is assumed to apply, namely  $\omega^2 \tau_{\perp}^2 \ll 1$ . The coefficients  $\kappa(K, M)$ , the parameter  $A$ , the cut-off function  $u$ , and the cut-off frequency  $\omega_c$ , are defined by

$$\kappa(K, M) \approx \frac{1}{3} \{ 1 + a_1 S_{z'z'}^0 + a_2 (S_{z'z'}^0)^2 + a_3 (S_{z'z'}^0)^3 \}, \quad (5)$$

$$A = \frac{kT}{2\pi^{3/2} K} \left( \frac{K}{\eta} + D_{\text{tr}} \right)^{-1/2}, \quad (6)$$

$$\begin{aligned} u(\omega/\omega_c) &= 1 - \frac{1}{2\pi} \ln \left| \frac{1 + \sqrt{(2\omega/\omega_c) + \omega/\omega_c}}{1 - \sqrt{(2\omega/\omega_c) + \omega/\omega_c}} \right| - \frac{1}{\pi} \arctan(\sqrt{(2\omega/\omega_c) + 1}) \\ &\quad - \frac{1}{\pi} \arctan(\sqrt{(2\omega/\omega_c) - 1}), \end{aligned} \quad (7)$$

$$\omega_c = \left(\frac{2\pi}{L}\right)^2 \left(\frac{K}{\eta} + D_{tr}\right). \tag{8}$$

Coefficients  $a_1$ – $a_3$  in equation (5) are given in table VII of [7]. In equations (6)–(8),  $K$  is the elastic constant in the one-constant approximation [8],  $\eta$  is the effective viscosity [2, 5] and  $L$  is the wavelength at which the expansion of director fluctuations in decoupled hydrodynamic modes is cut off [4, 6]. The translation diffusion of the probe molecule is characterized, as an approximation, by a single diffusion constant  $D_{tr}$ . Finally,  $\tau_{\perp}$  is the correlation time characterizing the reorientational motions of the principal molecular axis of the probe molecule.

In agreement with a suggestion by Warner [9], the parameter  $S_{zz}^0$ , will be interpreted as a mean field order parameter [1], or, in mathematical form

$$S_{zz}^0 = \langle \mathcal{D}_{00}^2(\Omega) \rangle_{\Omega} \approx \int d\Omega P_{eq}(\Omega) \mathcal{D}_{00}^2(\Omega). \tag{9}$$

Here  $\Omega = \{\alpha, \beta, \gamma\}$  symbolizes the Euler angles, which characterize the transformation of the instantaneous molecular axis system to the space fixed axis system of the director at equilibrium.  $P_{eq}(\Omega)$  gives the equilibrium distribution of molecular orientations. The order parameter  $S_{zz}$  determining the average values of anisotropic spin-spin interactions, which give rise to additional line splittings in an anisotropic medium, can be written as

$$S_{zz} \approx \langle \mathcal{D}_{00}^2(\Omega) \rangle_{\Omega, \Psi} \approx \int d\Omega \int d\Psi f_{eq}(\Psi) P_{eq, \Psi}(\Omega) \mathcal{D}_{00}^2(\Omega). \tag{10}$$

Now  $\Psi = \{\theta, \phi\}$  represents the Euler angles carrying the axis system of the instantaneous director to the axis system of the director in its equilibrium orientation;  $f_{eq}(\Psi)$  is the equilibrium distribution function for the director fluctuations. In the lowest order approximation the relation between the so-called mean field order  $S_{zz}^0$  and the measurable order parameter  $S_{zz}$ , which is renormalized with respect to director fluctuations, is [2]

$$S_{zz} \approx S_{zz}^0 \left\{ 1 - \frac{3}{2} \langle \Theta^2 \rangle_{\Psi} \right\}, \tag{11}$$

where

$$\begin{aligned} \langle \Theta^2 \rangle_{\Psi} &\approx \frac{2kT}{\pi KL} \\ &= 2A \sqrt{\frac{\omega_c}{\pi}}. \end{aligned} \tag{12}$$

Because of the axial symmetry of the nematic phase and the supposed effective axial symmetry of the probe molecule, the director fluctuations, to first order, only contribute to  $K = 0$  and  $M = \pm 1$  terms of the spectral density. Carrying the series expansion of the director fluctuations to second order also gives contributions to  $K = 0; M = 0$ , and  $K = 0; M = \pm 2$  terms. These second order contributions may be neglected for low degrees of ordering ( $S_{zz}^0 \leq 0.15$ ) but become increasingly important at higher ordering [2], where, in addition, the simple relationship (11) is no longer

valid. It should be pointed out that the director fluctuations can only properly be taken into account by a series expansion, if first order terms dominate, and series expansion may be cut off after these terms. This is only warranted for low degrees of ordering; for higher ordering a series expansion of the director fluctuations is not tractable. The second order calculations in [2] can therefore only be used in a qualitative sense. A treatment which circumvents the series expansion of the director fluctuations is in preparation.

So far, we have only considered nuclei lying on the principal symmetry axis of an axially symmetric probe molecule. If the probe orients with its principal axis along the liquid crystal director, these nuclei will show the most pronounced relaxation dispersion due to director fluctuations, and thus are most suitable for determining parameters  $A$  and  $\omega_c$ . Off-axis nuclei are of interest for determining the anisotropy  $R = D_{\parallel}/D_{\perp}$  of the rotational diffusion. Studies of the relaxation behaviour of the ring deuterons in several aromatic probe molecules have shown that spectral densities  $J_M(\omega)$  [2], do not behave as predicted by the simple RD + DF model [10, 11]. The ortho- and meta deuteron measurements of toluene and xylene, even lead to ratios  $J_1(\omega)/J_2(2\omega)$  smaller than 1 [2]. These results are evidence of the incorrectness of the assumption of axial symmetry of the relevant probe molecules, which, of course, is not surprising. This stresses once more the importance of solving the diffusion problem for an asymmetric top in a non-axially symmetric orienting potential. An interesting and useful alternative of treating the problem of an asymmetric top (but not the non-axial symmetry of the orienting potential) has been given recently by Vold and Vold [11]. In the present study, however, we restrict ourselves to relaxation of on-axis quadrupolar nuclei.

The series of probe molecules of increasing size, which we used to study the effects of director fluctuations in nematic solutions, was chosen with the following considerations in mind.

- (a) Frequency-dependent relaxation measurements give information about the reorientational behaviour ( $\tau_{\perp}$ ) and the translational diffusion  $D_{tr}$  of the probes, and, furthermore, about the nematic environment ( $K$ ,  $L$ , and  $\eta$ : via  $\langle\theta^2\rangle$ ,  $A$ , and  $\omega_c$ ). As a working hypothesis we assumed that the hydrodynamic properties of the solutions are grossly independent of the molecular properties and size of the probe molecules, but depend mainly on their concentration. This assumption is justified by the experimental results, which give values of  $\langle\Theta^2\rangle$  that are approximately equal for the four solutions studied. This is a favourable condition for comparing the effects of director fluctuations on nuclear relaxation for probes of different size.
- (b) In the simple RD + DF model, applicable to low degrees of ordering, only  $J_{01}(\omega)$  is frequency dependent. The effect of director fluctuations depends not only on  $\langle\Theta^2\rangle$ , i.e. on the extent to which director fluctuations are excited (which, as we have just noticed, is approximately constant for the solutions studied), but also on the ordering. Indeed, for higher probe ordering  $S_{zz}^0$ , which can be achieved by increasing the probe size,  $J_{02}$  will also become frequency dependent [2] and the simple model will fail to give a satisfactory description of the experimental results. In this way the limitations of the simple RD + DF model can be defined more precisely.
- (c) A study of the relaxation behaviour of probe molecules in nematic solutions as a function of probe size, and consequently also of the magnitude of  $D_{tr}$ , may

reveal possible deviations from the hydrodynamic description of the director fluctuations [12].

### 3. Results and discussion

Tables 1–4 give a compilation of the results of spin-lattice relaxation measurements on  $^{14}\text{N}$  of methylisocyanide, para- and methyl deuterons of toluene- $\text{d}_8$ , methyl deuterons of *p*-xylene- $\text{d}_{10}$ , and para deuterons of tolan- $\text{d}_{10}$ ; all in a nematic solution in Merck Phase V, at a temperature of about  $31^\circ\text{C}$ . The parameters estimated by fitting the RD + DF model to the experimental relaxation rates are given in table 5. For details concerning sample preparation and other experimental and computational procedures, we refer to [1] and [2]. We only add that for the methyl groups in toluene and *p*-xylene, the internal rotation was assumed to be much faster than the end-over-end rotation of the molecules. Consequently,  $R = D_{\parallel}/D_{\perp}$  was taken to be infinite. The results in tables 1–5 lead to the following comments.

- (1) In view of the correspondence between the calculated (CALC) and experimental (EXP) relaxation rates and spectral densities, and also in view of the results of the F-test, the simple RD + DF model accounts well for the relaxation behaviour of  $^{14}\text{N}$  in  $\text{CH}_3\text{NC}$ , the para- and methyl deuterons in toluene, and the methyl deuterons of *p*-xylene. On the basis of the same criteria, the model provides no satisfactory picture of the para-deuteron relaxation of tolan. This is a direct consequence of the behaviour of  $J_{02}^{\text{EXP}}(2\omega)$ . For methylisocyanide, toluene and *p*-xylene this spectral-density component is not, or only weakly ( $\leq 10$  per cent) frequency dependent. This is in marked contrast to tolan, for which  $J_{02}^{\text{EXP}}(2\omega)$  is strongly frequency dependent, in fact even relatively stronger than is  $J_{01}^{\text{EXP}}(\omega)$ , though not in an absolute sense. This is due to the much stronger contribution of rotational diffusion to  $J_{01}(\omega)$  than to  $J_{02}(2\omega)$ :  $\kappa(0, 1)\tau_{\perp} \leq 100$  ps, and  $\kappa(0, 2)\tau_{\perp} \leq 37$  ps. The model cannot account for a frequency dependence of  $J_{02}(2\omega)$ . Consequently, the parameter estimation procedure only yields a sort of average value of  $J_{02}(2\omega)$ , thus underestimating  $R_1^Z$  for low frequencies and overestimating  $R_1^Z$  for high frequencies. If the model is only fitted to  $R_1^Q$ , the F-test can be satisfied, evidently because  $J_{02}(2\omega)$  does not appear in the expression for  $R_1^Q$  (equation (2)). It seems, therefore, justified to conclude that for tolan, an essential condition for applying the simple RD + DF model, namely sufficiently low ordering, is not fulfilled. We wish to emphasize that it is not the magnitude of the fluctuations which causes the failure of the model, but rather the fact that higher order contributions from director fluctuation are relatively heavily weighted by the

Table 1. Experimental and calculated values of  $^{14}\text{N}$  spin-lattice relaxation rates  $R_1$  and spectral densities  $J_{\text{KM}}$ , for 15 mole %  $\text{CH}_3\text{NC}$  in Phase V at  $30.4^\circ\text{C}$ ;  $e^2qQ/h = 220.9$  kHz. Superscripts Z and Q indicate relaxation of Zeeman and quadrupolar order, respectively.

$\nu_0/\text{MHz}$	$R_1^Z/\text{s}^{-1}$		$R_1^Q/\text{s}^{-1}$		$J_{01}(\omega)/\text{ps}$		$J_{01}^{\text{DF}}/\text{ps}$	$J_{02}(2\omega)/\text{ps}$	
	Exp	Calc	Exp	Calc	Exp	Calc	Calc	Exp	Calc
13.01	13.4	13.2	15.8	16.0	7.3	7.4	3.8	2.8	2.7
18.07	13.0	12.5	13.8	13.8	6.4	6.4	2.8	2.9	2.7
36.15	10.7	11.4	10.5	10.4	4.8	4.8	1.2	2.5	2.7

Table 2. Experimental and calculated values of deuterium spin-lattice relaxation rates  $R_1$  and spectral densities  $J_M(\omega)$ , for 13 mole % toluene- $d_8$  in Phase V at 31.7°C. For the para deuterium  $J_{KM}(\omega) = J_M(\omega)$  and for the methyl deuterons  $J_{KM}(\omega) = (0.105)^{-1} J_M(\omega)$ ; see [2].

$\nu_0/\text{MHz}$	$R_1^Z/s^{-1}$		$R_1^Q/s^{-1}$		$J_1/\text{ps}$		$J_{01}^{\text{DF}}/\text{ps}$	$J_2/\text{ps}$	
	Exp	Calc	Exp	Calc	Exp	Calc	Calc	Exp	Calc
Methyl deuterons; $e^2qQ/h = 159 \text{ kHz}$									
27.6	-	-	-	-	-	-	-	-	-
30.7	1.36	1.33†	1.60	1.63	1.43	1.45	5.7	0.55	0.53
		1.33†		1.57		1.40	5.2		0.54
38.4	1.29	1.28	1.50	1.47	1.34	1.31	4.4	0.53	0.53
		1.27		1.40		1.25	3.8		0.54
61.4	1.21	1.20	1.22	1.23	1.09	1.10	2.4	0.54	0.53
		1.20		1.17		1.04	1.8		0.54
76.8	1.13	1.17	1.16	1.15	1.03	1.03	1.7	0.50	0.53
		1.18		1.10		0.98	1.2		0.54
Para deuterons; $e^2qQ/h = 186 \text{ kHz}$									
27.6	-	-	21.6	21.7‡	14.1	14.1	5.8	-	-
30.7	-	-	20.7	20.4	13.5	13.3	5.0	-	-
38.4	17.0	16.6	17.8	18.2	11.6	11.8	3.5	5.40	5.14
61.4	15.9	15.6	15.5	15.2	10.1	9.9	1.6	5.24	5.14
76.8	14.7	15.3	14.2	14.4	9.2	9.4	1.1	4.87	5.13

† Upper entries in each row are calculated using methyl data only; lower entries are based on combined data from methyl- and para deuterons.

‡ Calculations based on para data only and on combined methyl- and para data give identical values.

Table 3. Experimental and calculated values of deuterium spin-lattice relaxation rates  $R_1$  and spectral densities  $J_M(\omega)$ , for 10 mole % xylene- $d_{10}$  in Phase V at 31.7°C. See also table 2.

$\nu_0/\text{MHz}$	$R_1^Z/s^{-1}$		$R_1^Q/s^{-1}$		$J_1/\text{ps}$		$J_{01}^{\text{DF}}/\text{ps}$	$J_2/\text{ps}$	
	Exp	Calc	Exp	Calc	Exp	Calc	Calc	Exp	Calc
Methyl deuterons; $e^2qQ/h = 159 \text{ kHz}$									
27.6	2.90	2.80	4.41	4.49	3.93	4.00	18.8	0.96	0.87
30.7	2.83	2.71	4.24	4.23	3.78	3.77	16.6	0.95	0.87
38.4	2.52	2.55	3.76	3.75	3.35	3.34	12.5	0.85	0.87
61.4	2.24	2.31	3.05	3.03	2.72	2.70	6.4	0.82	0.87
76.8	2.12	2.23	2.82	2.80	2.51	2.50	4.5	0.79	0.87

degree of static ordering [2]. If it were for the magnitude of the fluctuations, the RD + DF model would also fail for the other probe molecules, since  $\langle \Theta^2 \rangle$  has about the same value. The tolan results are probably the first clear-cut example of the breakdown of the simple RD + DF model for a nematic phase, which has no underlying smectic phase (compare [13]).

- (2) The data sets for all solutions give values for  $\omega_c$  in the range  $0.2 < \omega_c \times 10^{-8} < 6.8$ , when taking into account the confidence intervals of the T-test. These values, and those correspondingly found for  $\langle \Theta^2 \rangle$  emphasize the need for renormalizing the order parameters for director fluctuations, as proposed by Warner [9]. Another consequence of the range of values found for  $\omega_c$ ,

Table 4. Experimental and calculated values of deuterium spin-lattice relaxation rates  $R_1$  and spectral densities  $J_M(\omega)$ , for 10 mole % tolan-d<sub>10</sub> in Phase V at 31.3°C.

$\nu_0/\text{MHz}$	$R_1^Z/\text{s}^{-1}$		$R_1^Q/\text{s}^{-1}$		$J_1/\text{ps}$		$J_2/\text{ps}$	
	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc
	Para deuterons; $e^2 qQ/h = 186 \text{ kHz}$							
15.3	208	176	240	258	156	168	63	44
30.7	183	157	209	202	136	132	55	44
38.4	159	153	190	189	124	123	47	44
61.4	136	147	165	172	107	112	40	44
76.8	126	146	153	167	100	109	37	44

is that the cut-off wavelength is of molecular dimension:  $L \sim 2a$ , if  $a$  is the characteristic size of a liquid crystal molecule. For the calculation of  $L$  in table 5, use has been made of equation (12).  $K$  values were estimated on the basis of literature values for pure MBBA [14]. For each solution  $(T_{\text{NI}} - T)/T_{\text{NI}}$  was determined, where  $T_{\text{NI}}$  is the nematic-isotropic transition temperature. For each reduced temperature,  $K_1$ ,  $K_2$ , and  $K_3$ ; the splay, twist, and bend elastic constant, respectively, were determined using the empirical relations given by Haller [14]. The average value  $(K_1 + K_2 + K_3)/3$  was then used as an estimate of  $K$  [1, 2]. All data sets give comparable values for both  $\langle \Theta^2 \rangle$  and  $L$ , with the exception of the  $L$ -value from the tolan results. The latter is most likely to be a consequence of the relatively poor fit, although it cannot be excluded that the change in  $L$  is real, and is caused by the disturbing influence of the solute on the nematic structure.

- (3) Assuming all Phase V samples to have the same value of the viscosity, namely  $\eta = 0.06 \text{ Pa s}$  (which agrees with the rotational viscosity  $\gamma_1$  for MBBA, as found by Meiboom and Hewitt [15], see also [2]), values of the translational diffusion constant  $D_{\text{tr}}$  were calculated. Values of  $D_{\text{tr}}$  were also obtained from the Gierer-Wirtz model (see e.g. [16]), substituting the following effective hydrodynamic radii for methylisocyanide, toluene, *p*-xylene, tolan, and the Phase V molecules, respectively: 3.1; 6.0; 6.5; 12.8; and 25 Å, and again taking  $\eta = 0.06 \text{ Pa s}$ . It is conspicuous that both sets of values agree exceptionally well for methylisocyanide and the para deuteron results of toluene (and even for the results of tolan, but here the fit of model parameter is not satisfactory), whereas the agreement is poor for the methyl deuteron results of toluene and *p*-xylene (and for tolan if the model is fitted to  $R_1^Q$ s only; the confidence intervals of the estimated parameters are then, however, very large). The values found for  $\tau_{\perp}$ , which for the non-axially symmetric probes should be interpreted as effective correlation times, seem to be reasonable, considering the size of the probe molecules (see also [2] and [13 a]).

#### 4. Concluding remarks

The model parameters  $\tau_{\perp}$ ,  $A$  and  $\omega_c$ , as determined directly by the parameter estimation procedure, have values which are consistent with the relative size of the respective probe molecules. The values of  $A$  and  $\omega_c$  found from the methyl deuteron relaxation measurements, however, do not fall into this pattern. We have not yet found a satisfactory explanation of these deviating results.



Table 5. Experimental data and parameters estimated by fitting the RD + DF model to the relaxation rates in tables 1-4, for solutions of probe molecules in Merck Phase V. For all solutions  $\eta$  is taken 0.06 Pa s.  $T_{NI}$  is the nematic-isotropic transition temperature;  $T$  is the sample temperature.  $F_e$  is the F-value of the fit;  $F_\infty$  is taken from a table of F-values. Also given are values of  $K$ ,  $L$  and  $D_t$  that are consistent with the estimated model parameters.  $D_t$ (GW) refers to the Gierer-Wirtz model. For further explanation, see text.

Conc. (mole %) /Probe molecule	$T_{NI}/^\circ\text{C}$	$T/^\circ\text{C}$	$S_{zz}$	$S_{zz}^0$	$\langle \Theta \rangle^2$	$\tau_{\perp}/\text{ps}$	$A \times 10^6$ $/\text{s}^{1/2}$	$\omega_c \times 10^{-8}$ $/\text{rad s}^{-1}$	$K/\text{pN}$	$L/\text{nm}$	$D_t \times 10^{10}$ $/\text{m}^2 \text{s}^{-1}$	$D_t(\text{GW}) \times 10^{10}$ $/\text{m}^2 \text{s}^{-1}$	$F_e/F_\infty$
15/ $\text{CH}_3\text{NC}$	47	30.4	0.074	0.086	0.09	16.6	4.5	3.1	5.3	5.6	1.3	1.5	0.48/4.32
13/toluene- $d_8$	51	31.7	0.139	0.164	0.10	37.5	5.9	2.1	5.6	4.8	0.6	0.4	-
para			0.139	0.163	0.10	37.5	5.9	2.1	5.6	4.8	0.6	0.4	1.40/3.61
methyl			0.139	0.163	0.09	36.6	3.7	4.2	5.6	5.3	2.2	0.4	0.95/3.61
10/p-xylene- $d_{10}$	56.5	31.7											
methyl			0.262	0.302	0.08	88.8	3.6	3.6	6.2	5.4	1.5	0.3	0.71/3.07
10/tolan- $d_{10}$	51.5	31.3											
para; $R_1^z$ and $R_1^y$			0.281	0.340	0.12	524	6.7	2.5	5.7	4.0	0.04	0.03	3.80/3.61
$R_1^z$			0.281	0.33	0.11	501	5.6	3.2	5.7	4.2	0.5	0.03	3.63/9.16

As for the translation diffusion, the simplifying assumption was made that it may be represented by a single diffusion constant  $D_{tr}$ . To derive values of  $D_{tr}$ , use was made of literature values of  $K$  and  $\eta$ , which for the solutions studied may be somewhat speculative. Nevertheless, the values of  $D_{tr}$ , so found from the  $^{14}\text{N}$  results of methylisocyanide and the para-deuteron results of toluene and tolan, are in good agreement with estimations based on the Gierer–Wirtz model. For all Phase V solutions studied, which have comparable probe concentrations,  $\langle \Theta^2 \rangle$  is found to be about 0.1 (at a temperature of about 31°C). Using literature values of  $K$ , an approximately constant value of the cut-off wavelength  $L$  is found.

In order to test these tentative and somewhat speculative conclusions, we have started measuring the translation diffusion behaviour of the probes, by the pulsed field-gradient spin-echo method. Then no recourse need to be taken anymore to a comparison of the estimated  $D_{tr}$ -values with those from the rather crude Gierer–Wirtz model. Furthermore, knowledge of the translation diffusion behaviour may enable us to assess alternative descriptions of director fluctuations; e.g., that given by Zientara and Freed [12].

The simple RD + DF model is not applicable to the results for tolan, because the lowest order approximation of the director fluctuations, breaks down at the relatively high degree of ordering encountered here. In particular the contribution of director fluctuations to the spectral density  $J_{02}(2\omega)$  has to be evaluated for the case of higher ordering.

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*Note added in proof.*—Recently it has been shown (VAN DER ZWAN, G., and PLOMP, L., *Liq. Crystals* (submitted)) that the renormalization of the order parameter is severely overestimated when following Warner's approach, [9], as has been done in the present paper. In fact it turns out that the order parameter is hardly affected by the director fluctuations. This may lead to small changes in the calculated parameters, but it does not alter the conclusions.

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