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Temperature dependence of the molecular reorientational dynamics in nematic and isotropic EBBA and 5CB by fluorescent probe depolarization spectroscopy

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Information on molecular reorientational dynamics in nematic and isotropic phases has been obtained by a simple combination of time resolved and steady state fluorescence measurements on the dyes DMANS and DPH dissolved in homeotropically aligned samples of EBBA (4-ethoxybenzylidene-4′-*n*-butylaniline) and 5CB (4-*n*-pentyl-4′-cyanobiphenyl) respectively. In particular, two reorientational correlation times τ_0^r and τ_2^r have been identified. Their evolution with temperature, both in the nematic and well within the isotropic phase, has been studied and evaluated using stochastic models for the molecular reorientational dynamics.

1. Introduction

For several years now the polarization of fluorescence emitted by suitable dyes has been used as a probe of molecular ordering and reorientational dynamics in anisotropic media, such as liquid crystals [1–14] and membranes [15–18], in which the dyes were dissolved. In particular valuable information may be obtained on static orientational order parameters such as $\langle P_2 \rangle$ and $\langle P_4 \rangle$ and the reorientational diffusion coefficients D_r or relaxation times τ_r. Using the fundamental assumption that the dye molecule is rigidly bound to the host molecule, such static and dynamic parameters are presumed to refer to the host medium itself.

In principle, time resolved fluorescence spectroscopy on the subnanosecond time scale could yield complete information on all the relevant parameters. However to our knowledge only one such a study has been attempted [12], and the relaxation time τ_r directly measured. Ordinary time-resolved luminescence of *a-fortiori* steady state luminescence are less complete, and in most cases have been used to determine only the static order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ [2–11].

Here we wish to show that a simple combination of time resolved measurements (to determine precisely the radiative fluorescence lifetime τ_f) and steady state measurements (which yield τ_r/τ_f with good accuracy) can yield useful information on the reorientational dynamics of probe molecules dissolved in a liquid-crystalline medium. The basic theory is summarized in § 1 while the experimental details and results are presented in § 2. Finally, the temperature dependence of the reorientational relaxation time and of the corresponding diffusion coefficients are discussed in the final section.

2. Theoretical background

We consider here only the case of elongated fluorecent molecules, similar in shape to the mesomorphic ones. The absorption (μ_a) and emission (μ_e) dipole moments are assumed to be parallel to the long molecular axes. Although this is not the most general situation, it is the most useful one at least from the dynamical point of view. In any case, on the time scale of the fluorescence experiments which we shall discuss, the contribution of the components of μ_a and μ_e, perpendicular to the long molecular axes, is averaged due to the fast spinning motion ($\tau_r^{\parallel} \simeq 10\,\mathrm{ps}$) [19].

Let us suppose that the dye molecule is excited by an infinitely short light pulse at time $t = 0$. The fluorescence intensity $I_{ik}(t)$ ($i, k = x, y, z$ where x, y refer to the polarization of the exciting and emitted light respectively and z is parallel to the nematic director) at time t is given by [20]

$$I_{ik}(t) = C_{ik}F(t)i_{ik}(t), \qquad (1)$$

where $F(t)$ is the fluorescence decay function and

$$\begin{aligned}
i_{xx}(t) &= 1 - 2\langle P_2\rangle + \Phi^2_{00}(t) + 3\Phi^2_{20}(t),\\
i_{xy}(t) &= 1 - 2\langle P_2\rangle + \Phi^2_{00}(t) - 3\Phi^2_{20}(t),\\
i_{xz}(t) &= 1 + \langle P_2\rangle - 2\Phi^2_{00}(t),\\
i_{zz}(t) &= 1 + 4\langle P_2\rangle + 4\phi^2_{00}(t);
\end{aligned}$$

$\Phi^l_{mn}(t)$ are the correlation functions of the Wigner matrices $D^l_{mn}(\Omega)$ [20]. The coefficients C_{ik} depend on the experimental conditions, concentration of the dye, sample thickness, etc., and more importantly also include all the depolarization factors due to the optical anisotropy of the medium and the instrumentation. Through these factors, C_{ik} depends on the polarization and on the order parameters but not on the reorientational processes. Explicit expressions for C_{ik} have been presented elsewhere [10, 11]; furthermore we assume that the intensity $I_{ik}(t)$ has already been corrected and so in what follows we shall omit the coefficients C_{ik} from the equations.

From equation (1) it is easy to obtain

$$\left.\begin{aligned}
F(t) &= \tfrac{1}{9}[I_{zz}(t) + 4I_{xz}(t) + 2I_{xx}(t) + 2I_{xy}(t)],\\
\langle P_2\rangle &= \frac{1}{9}\frac{[I_{zz}(t) + I_{xz}(t) - I_{xx}(t) - I_{xy}(t)]}{F(t)},\\
\Phi^2_{00}(t) &= \frac{1}{9}\frac{[I_{zz}(t) - 2I_{xz}(t) + \frac{1}{2}I_{xx}(t) + \frac{1}{2}I_{xy}(t)]}{F(t)},\\
\Phi^2_{20}(t) &= \frac{1}{6}\frac{[I_{xx}(t) - I_{xy}(t)]}{F(t)}.
\end{aligned}\right\} \qquad (2)$$

The intensities $I_{ik}(t)$ on the right-hand side of equation (2) can be measured using two sample configurations [9], homeotropic and homogeneous (or only one of them in the case of angle resolved experiments [15–18]). Thus in principle all of the relevant static and dynamic characteristics can be calculated from equation (2). However, this is true only in the limit of an exciting pulse duration which is short compared to the characteristic relaxation times of $F(t)$ and the correlation functions. This condition is hardly satisfied in our case and therefore we need a more detailed analysis.

2.1. *Steady state experiment*

In a steady state experiment only the integral intensities

$$\bar{I}_{ik} = \int_0^\infty I_{ik}(t)\,dt$$

are measured and we have [22]

$$\left.\begin{aligned}\langle P_2\rangle &= \frac{[\bar{I}_{zz}+\bar{I}_{zx}-\bar{I}_{xx}-\bar{I}_{xy}]}{[\bar{I}_{zz}+4\bar{I}_{zx}+2\bar{I}_{xx}+2\bar{I}_{xy}]},\\ \bar{\Phi}^2_{00} &= \frac{[\bar{I}_{zz}-2\bar{I}_{zx}+\frac{1}{2}\bar{I}_{xx}+\frac{1}{2}\bar{I}_{xy}]}{[\bar{I}_{zz}+4\bar{I}_{zx}+2\bar{I}_{xx}+2\bar{I}_{xy}]},\\ \bar{\Phi}^2_{20} &= \frac{3}{2}\frac{[\bar{I}_{xx}-\bar{I}_{xy}]}{[\bar{I}_{zz}+4\bar{I}_{zx}+2\bar{I}_{xx}+2\bar{I}_{xy}]},\end{aligned}\right\} \tag{3}$$

where

$$\bar{\Phi}^2_{m0} = \int_0^\infty \Phi^2_{m0}(t)F(t)\,dt \quad \text{for} \quad m = 0;\ 2.$$

These equations (and similar ones) have been used extensively to measure the order parameters and in some cases the ratio τ_r/τ_f [9–11, 14–18]. For this purpose two assumptions have been made:

(1) The fluorescence decay function $F(t)$ is a single exponential [9, 15, 16]

$$F(t) = \frac{1}{\tau_f}\exp\left(-\frac{t}{\tau_f}\right). \tag{4}$$

This has been confirmed in some time-resolved measurements [3, 12–14].

(2) In order to reduce the number of independent dynamical parameters specific models for the reorientation [21] are assumed, usually small step rotational diffusion [9] or strong collision [16] models

When the reorientation time is small compared to τ_f (as in our case) some difficulties arise in the calculation of the dynamical parameters from equation (3). We have already mentioned that the intensities $\bar{I}_{ik}$ should be renormalized for the depolarizing factors related to the optical anisotropy of the liquid crystal. These factors are numerous and the error accumulated in the right-hand side of equation (3) can be rather large compared to the small values of $\bar{\Phi}^2_{20}$ and $\bar{\Phi}^2_{00} - \langle P_2\rangle^2$ (the component of $\bar{\Phi}^2_{00}$ which depends on the dynamics). Moreover, one of the most important corrections is related to the local field anisotropy [10, 11]. This correction might be as large as 10–20 per cent since the optical anisotropy of the mesomorphic materials is rather high. So far many models have been proposed for the calculation of the local field tensor in liquid crystals [23–25], but in our opinion the existing experimental data are too scarce and indirect to establish firmly or to reject unambiguously any of these models.

To avoid these difficulties in the determination of τ_r/τ_f here we shall use the polarization ratio

$$\bar{r}^h = \frac{\bar{I}_{xx}-\bar{I}_{xy}}{\bar{I}_{xx}+2\bar{I}_{xy}} \tag{5}$$

measured in the *homeotropic* configuration along the optical axis z. In this case we do not need to correct for the optical anisotropy of the sample and we obtain

$$\bar{r}^h = \frac{2\bar{\Phi}^2_{20}}{[1 - 2\langle P_2\rangle + \bar{\Phi}^2_{00} - \bar{\Phi}^2_{20}]}. \tag{6}$$

Furthermore we suppose that equation (4) is valid and so

$$\Phi^2_{m0}(t) = \Phi^2_{m0}(\infty) + [\Phi^2_{m0}(0) - \Phi^2_{m0}(\infty)]\exp\left(-\frac{t}{\tau^m_r}\right) \tag{7}$$

where τ^m_r ($m = 0; 2$) are the reorientational correlation times. In the strong collision model this is related to an exact result [21], while in the framework of the small step rotational diffusion model it is a good approximation [9, 26]. In both cases the model independent initial and equilibrium values of the correlation functions are

$$\left.\begin{aligned}\Phi^2_{00}(0) &= \tfrac{1}{35}(7 + 10\langle P_2\rangle + 18\langle P_4\rangle),\\ \Phi^2_{00}(\infty) &= \langle P_2\rangle^2,\\ \Phi^2_{20}(0) &= \tfrac{1}{35}(7 - 10\langle P_2\rangle + 3\langle P_4\rangle),\\ \Phi^2_{20}(\infty) &= 0,\end{aligned}\right\} \tag{8}$$

Using the preceding equations we obtain

$$\bar{r}^h = \frac{2}{5}\frac{\tau^r_2}{\tau^r_2 + \tau_f}\left[1 - \Delta + (1 + \Delta)\frac{\tau^r_0}{\tau^r_0 + \tau_f} - \frac{\tau^r_2}{\tau^r_2 + \tau_f}\right]^{-1}, \tag{9}$$

where

$$\Delta = \frac{4\langle P_2\rangle + 3\langle P_4\rangle - 7\langle P_2\rangle^2}{7 - 10\langle P_2\rangle + 3\langle P_4\rangle}. \tag{10}$$

Equation (9) is very useful in the case $\tau^r_m \ll \tau_f$ ($m = 0; 2$) where we obtain to the first order in τ^r_2/τ_f,

$$\tau^r_2 \simeq \tfrac{5}{2}\bar{r}^h(1 - \Delta)\tau_f. \tag{11}$$

This result, although approximate, is essentially model independent. When $\tau_f \approx \tau_r$ a good approximation for τ^r_2/τ_f can be obtained in the framework of the small step rotational diffusion model [9] from which we have

$$\left.\begin{aligned}\tau^r_0 &= \frac{1}{6D^r_\perp}\frac{7 + 10\langle P_2\rangle + 18\langle P_4\rangle - 35\langle P_2\rangle^2}{7 + 5\langle P_2\rangle - 12\langle P_4\rangle},\\ \tau^r_2 &= \frac{1}{6D_\perp}\frac{7 - 10\langle P_2\rangle + 3\langle P_4\rangle}{7 - 5\langle P_2\rangle - 2\langle P_4\rangle},\end{aligned}\right\} \tag{12}$$

where $D^r_\perp$ is the rotational diffusion coefficient around the short axis. As we shall see in the next section, equations (11) and (12) are not very sensitive to the order parameters and a reasonable approximation for the reorientational correlation times can be obtained even with very crude approximations for the values of $\langle P_2\rangle$ and $\langle P_4\rangle$. Thus the coupled steady state and time-resolved (on the ns scale) experiments can yield information about the rotational molecular dynamics in a way which is simpler and more accurate than the direct time-resolved determination of τ^r_m when $\tau^r_m \ll \tau_f$.

2.2. *Time-resolved fluorescence experiments*

In the case of time-resolved experiments the measured intensities are the convolution of the fluorescence decay and the reorientational correlation functions with the excitation pulse function $L(t)$

$$I_{ik}^{\mathrm{TR}}(t) = \int_0^{\infty} F(t')i_{ik}(t')L(t-t')dt'. \tag{13}$$

Usually the characteristic time of the lamp τ_{L} ($\sim$ 1 ns) is longer than the typical reorientational time τ_{r} of the dye molecule dissolved in the nematic liquid crystal and is comparable to the fluorescence life-time (a few nanoseconds). In this case equation (2) leads to the accumulation of significant errors due to the deconvolution procedures and to the corrections for the optical anisotropy of the sample. Another drawback is caused by the necessity of measuring two different pulses $I_{ik}(t)$ (each pulse shape requiring many hours of data accumulation) for two different samples. In order to avoid this difficulty many authors have measured only the polarization ratio in planar samples [3, 13] where

$$\begin{aligned} r^{\mathrm{p}}(t) &= \frac{I_{zz}^{\mathrm{TR}}(t) - I_{zx}^{\mathrm{TR}}(t)}{I_{zz}^{\mathrm{TR}}(t) + 2I_{zx}^{\mathrm{TR}}(t)} \\ &= \frac{\int_0^t[\langle P_2\rangle + 2\Phi_{00}^2(t')]F(t')L(t-t')dt'}{\int_0^t[1 + 2\langle P_2\rangle]F(t')L(t-t')dt'}. \end{aligned} \tag{14}$$

In this approach, however, the error due to the deconvolution procedures and to the optical anisotropy could also be significant in the case when τ_0^{r} is smaller than τ_{f} and/or τ_{L}. Some improvements can be obtained by using

$$\begin{aligned} r^{h}(t) &= \frac{I_{xx}^{\mathrm{TR}}(t) - I_{xy}^{\mathrm{TR}}(t)}{I_{xx}^{\mathrm{TR}}(t) + 2I_{xy}^{\mathrm{TR}}(t)} \\ &= \frac{\int_0^t \Phi_{20}^2(t')F(t')L(t-t')dt'}{\int_0^t[1 - 2\langle P_2\rangle + \Phi_{00}^2(t') - \Phi_{20}^2(t')]F(t')L(t-t')dt'}, \end{aligned} \tag{15}$$

in order to avoid at least the optical anisotropy corrections. However, in the homeotropic configuration the signal is smaller than in the planar one because of the strong absorption dichroism of a well aligned sample: for perfectly aligned molecules and perfectly coaxial transition dipole moments, no signal would be observed. This is a major drawback for the homeotropic configuration.

In conclusion, it seems difficult to obtain accurate information about the molecular reorientational dynamics if τ_{r} is smaller than τ_{L} and/or τ_{f} using all the approaches reported here. All of the useful information about the reorientation of the guest molecule is in this case in the rising portion of the measured pulses. In consequence, the signal-to-noise ratio is rather bad and the results for τ_0^{r} or τ_2^{r} are rather indirect and with large errors. Thus for typical thermotropic liquid crystals the time-resolved technique alone is not sufficient to yield the required information (unless of course we go to the picosecond range).

3. Experimental part

We have investigated the nematic and isotropic phases of two different guest-host systems. The first is a solution of the fluorescent dye 4-dimethylamino-4 nitrostilbene (DMANS) in 4-ethoxybenzylidene-4′-*n*-butylaniline (EBBA) with concentration

5×10^{-4} (by weight). This system has a wide nematic range, from ~ 35 to 77·8°C and has been used extensively in steady state fluorescent experiments in order to obtain the orientational order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ of the dye [1, 2, 7–11]. The guest molecule is nematic-like, very well oriented in the nematic solvent and with both absorption and emission dipole moments approximately parallel to the long molecular axis [1, 2, 27]. The fluorescence was excited at $\lambda_e \approx 436$ nm and emission was recorded at $\lambda_f \approx 630$ nm. In both these regions the absorption of the nematic solvent is reasonably small.

The other sample was a solution of the fluorescent dye 1,6-diphenyl-1,3,5-hexatriene (DPH) in 4-*n*-pentyl-4′-cyanobiphenyl (5CB) with a concentration $1{\cdot}2 \times 10^{-3}$ (by weight). This system is nematic in the temperature range ~ 20–35·2°C. This fluorescent dye has been used widely in fluorescence experiments and is usually supposed to satisfy reasonably well our assumptions [3, 4, 14, 15, 17]. The excitation and emission wavelengths are 365 nm and 430 nm respectively.

For both dyes we have obtained a steady state polarization ratio $\bar{r} = 0{\cdot}37$ using a viscous isotropic solvent (an epoxy resin). This value is close to the theoretical one (0·4) for dyes with parallel transition dipole moments in the absence of rotational dynamics and indicates that our assumptions are well founded.

The excitation source in the steady state measurements was a 500 W Hg lamp provided with a polarizer and suitable filters. The emitted fluorescence was recorded with single photon counting in a near forward scattering geometry after passing through an analyser, a filter, a polarization scrambler and a SPEX double monocromator. The measurement was also performed by interposing a 0·25 m grating monochromator in the excitation path, in order to check the effects of eventual spurious excitation light on the measured degree of polarization of the luminescence. We found essentially no difference in the results within the error limits of our measurement.

The luminescence decay pulseshape was measured by a single photon time correlated method in a system consisting of an Edinburgh thyratron gated H_2 flash lamp (model 199F) operated at a repetition frequency of 20 kHz, input and output polarizer with appropriate filters, cooled EMI 9816 QB photomultiplier and an ORTEC electronic system based on a fast time-to-voltage converter whose output was fed to a SILENA multichannel analyser.

Planar and homeotropic alignment of the nematic director was achieved using suitable surfactants and the orientation was controlled by observing conoscopic figures on a polarizing microscope.

The measurements were performed in the temperature range 20–100°C using an RC6 (MGW LAUDA) temperature controller.

4. Results and discussion

The typical time dependence of the lamp function and the isotropic part of the fluorescence

$$\tfrac{1}{3}[I_{zz}^{\mathrm{TR}}(t) + 2I_{zx}^{\mathrm{TR}}(t)] = (1 + 2\langle P_2\rangle)\int_0^t F(t')L(t - t')dt' \tag{16}$$

is presented in figure 1 for DMANS in EBBA. After deconvolution we found that the fluorescent decay is a single exponential with time constant $\tau_f = 2{\cdot}0 \pm 0{\cdot}2$ ns in both phases. Within our experimental error, τ_f was temperature independent.

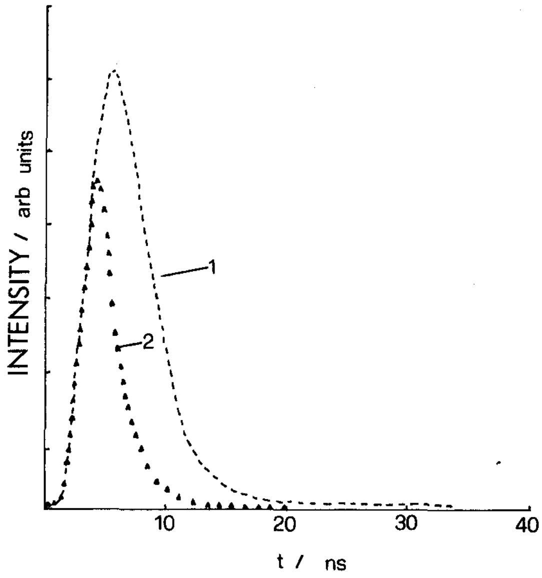

Figure 1. Typical time shape of an isotropic luminescence pulse (1) and the lamp pulse (2).

In the region 2–10 ns where our signal-to-noise ratio is reasonable we do not see any significant difference between the behaviour of $I_{zz}(t)$ and $I_{zx}(t)$ which could be attributed to the rotational dynamics of the dye molecule. This is due to the fact that τ_0^r and τ_2^r are small for our system (less than 0·5 ns as we shall demonstrate later) and all useful information about the molecular reorientation is concentrated in the first few time channels for most temperatures. In that region, however, the signal-to-noise ratio is very low and the error introduced by the deconvolution procedure is large. So, with a nanosecond pulse lamp technique it is practically impossible to obtain direct and reliable information on the reorientational times in our type of system.

In the steady state part of our experiment we have selected the homeotropic geometry in order to avoid the complications related to the corrections for the optical anisotropy of the sample. The temperature dependence of the polarization ratio $\bar{r}^h$ for the system DMANS-EBBA is presented in figure 2. The values of $\bar{r}^h$ throughout the nematic phase are small and equation (11) can be applied as a useful approximation (in the isotropic phase this equation is exact). The temperature dependence of τ_2^r obtained from equation (11) is presented as circles in figure 3 (here we use the value of τ_f obtained for the DMANS-EBBA system from our time-resolved experiments). This result for τ_2 is approximate but model-independent and demonstrates that in the nematic phase the temperature dependence of the reorientational time is not trivial.

In order to obtain quantitative results we have used equation (9) and equation (12) for the data interpretation, based on the small step rotational diffusion model. In this case we need the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ which cannot be obtained from our experiments. In figure 3 we present τ_0^r(▲) and τ_2^r(★) calculated using the values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ from the Maier–Saupe theory [28, 29]. For comparison we have calculated τ_0^r and τ_2^r with three sets of values for the order parameters from [11], obtained for the same guest-host system from the steady state fluorescence experiment with a correction for the optical anisotropy and assuming three different models for

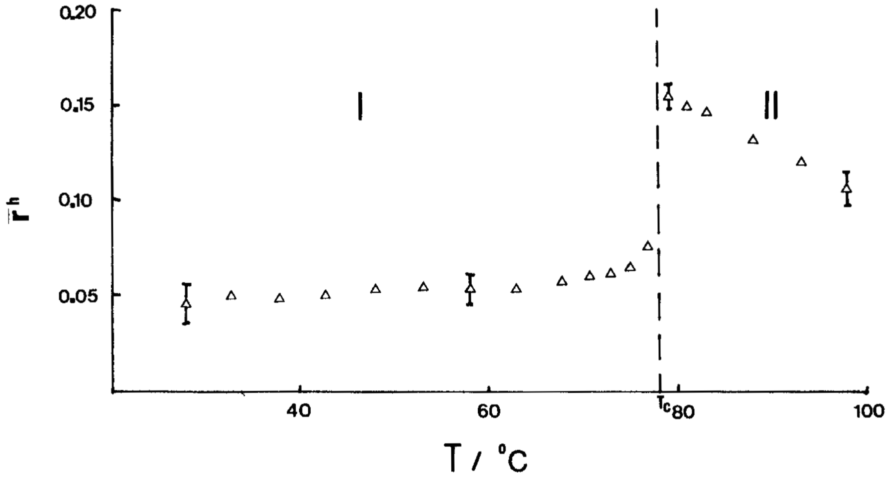

Figure 2. Temperature dependence of the polarization ratio $\bar{r}^h$ in both nematic and isotropic phases of DMANS-EBBA.

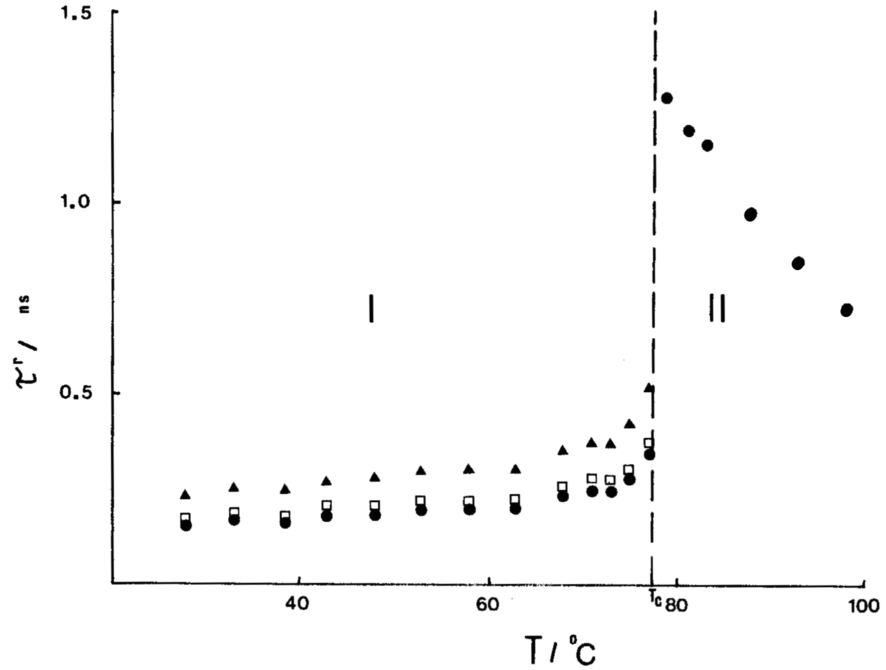

Figure 3. Temperature dependence of the reorientational relaxation times: τ_2^r (●); τ_0^r (▲); τ_2^r (★). The first τ_2^r was obtained using equation (11) (see text). The second τ_2^r and τ_0^r were obtained using the Maier–Saupe values for $\langle P_2 \rangle$ and $\langle P_4 \rangle$ (DMANS-EBBA).

the local field. The results are close to those presented in figure 3, showing that the error introduced with the order parameters values is not relevant.

The values of τ_2^r obtained from equation (9) and equation (11) are slightly different but with a similar temperature dependence. In the isotropic phase the reorientation time decreases, as expected, with increasing temperature. In the nematic phase,

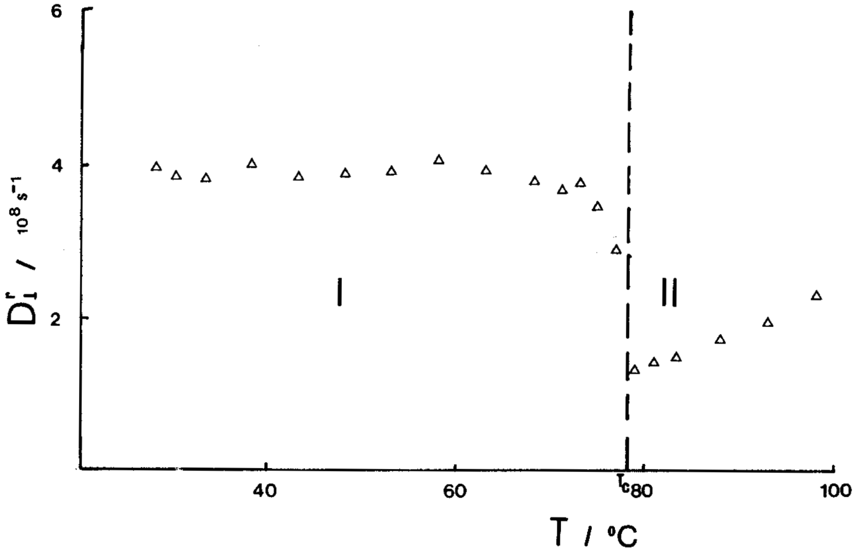

Figure 4. Temperature dependence of the perpendicular diffusion coefficient $D_\perp^r$ in the nematic and isotropic phases of DMANS-EBBA.

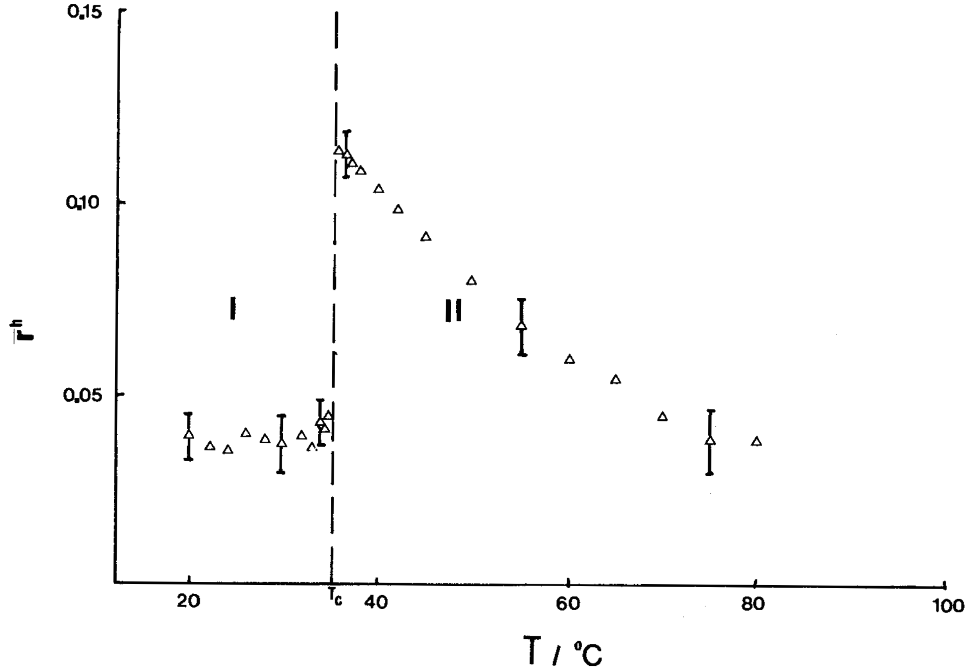

Figure 5. Temperature dependence of the polarization ratio $\bar{r}^h$ in DPH-5CB.

however, τ_0^r and τ_2^r have the opposite temperature dependence, increasing drastically close to the transition to the isotropic liquid. The reorientational correlation times depend on $\langle P_2 \rangle$ and $\langle P_4 \rangle$ and it is useful to consider also the temperature dependence of the rotational diffusion coefficient $D_\perp^r$, which is supposed to be order independent. Figure 4 demonstrates that the temperature dependence

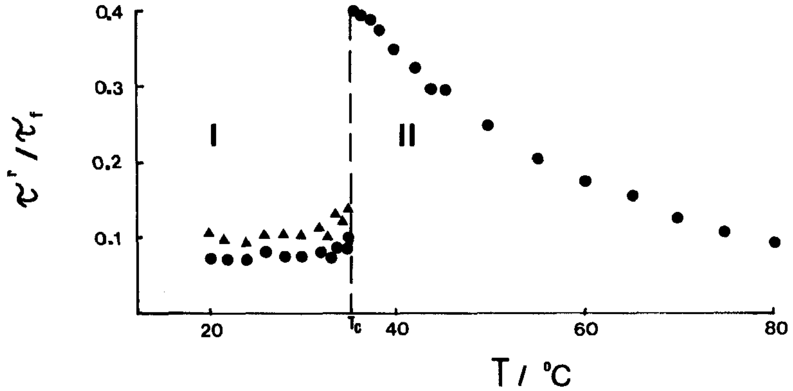

Figure 6. Temperature dependence of τ_2^r/τ_f (▲) and τ_0^r/τ_f (●) in the nematic and isotropic phases of DPH-5CB.

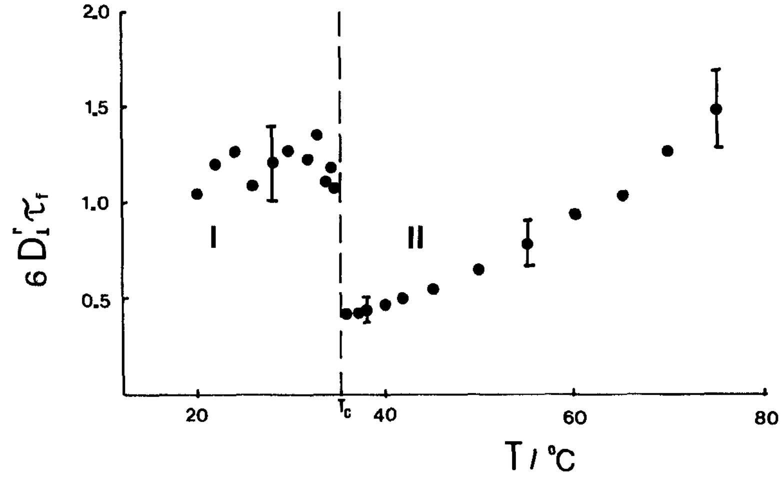

Figure 7. Temperature dependence of the coefficient $6D_\perp^r\tau_f$ as obtained using equation (9) (see text) in DPH-5CB.

of $D_\perp^r$ in the nematic phase deviates consistently from the expected Arrhenius behaviour.

Similar results have been obtained from the steady state fluorescence measurements of DPH in 5CB. In figure 5 we present the polarization ratio $\bar{r}^h$ in the nematic and isotropic phases. Figure 6 shows the temperature dependences of τ_2^r/τ_f(▲) and τ_0^r/τ_f(●). $6D_\perp^r\tau_f$ (●), obtained from equation (9) are reported in figure 7. For this system we have no data for τ_f but we expect its temperature dependence not to be very strong as confirmed by the time-resolved study of the same fluorescent dye in another nematic [13]). This leads us to the conclusion that the same unusual behaviour of the rotational correlation times in the nematic phase will also exist in the system DPH-5CB [30].

5. Comments and conclusions

A good basis to comment our results are the recently reported time resolved measurements [13] of the fluorescence of DPH in the nematic trans,trans4′-alkylbicylohexyl-4-carbonitriles (ZLI-1167). The order of magnitude of τ_0^r and $D_\perp^r$, the

Arrhenius behaviour of $D_\perp^r$ in the isotropic phase and the jump in $D_\perp^r$ at the nematic-isotropic transition observed by us are similar to those reported in [13]. On the other hand, an Arrhenius behaviour of $D_\perp^r$ in the nematic phase was reported in [13], while we obtain a constant or even slightly decreasing $D_\perp^r$ with increasing temperature in the nematic phase, in both the systems investigated. This disagreement can be due to the different systems and different approaches used in the two experiments. In particular, in [13] the dynamical parameters are calculated from equation (14), assuming the small-step rotational diffusion model and applying the global target analysis of the data; the data corresponding to all temperatures in the same phase are treated together and fitted to an *assumed* Arrhenius behaviour for $D_\perp^r$. This approach may therefore conceal the real temperature dependence of $D_\perp^r$. In comparison, our approach does not depend on the optical anisotropy corrections and deconvolution procedures as discussed before and, at least for τ_2^r, it should give a model-independent true temperature dependence.

The reorientational correlation times τ_0^r and τ_2^r obtained by us are of the same order of magnitude ($\sim$ 1 ns) as those obtained by other fluorescence measurements [12, 13] and E.S.R. experiments [31] in nematic phases. On the other hand, in experiments which are sensitive to the picosecond time scale, as for example. I.R. and Raman bandshape analysis [32] and neutron scattering [33], the reorientational times around the short molecular axes have been reported to be about more than one order of magnitude faster, i.e. less than 100 ps. This discrepancy, together with the temperature behaviour of τ_0^r, τ_2^r and $D_\perp^r$ in the nematic phase and at the nematic-isotropic transition, is difficult to explain in the framework of both the strong collision and the small-step rotational diffusion models. In our opinion, this clearly demonstrates the fact that the rotational dynamics of the mesomorphic molecules and of the mesomorphic-like probe molecules is much more complex than usually assumed. Some features of the molecular reorientational processes could be better understood in the framework of the slowly relaxing local structure model suggested by Freed *et al.* [34, 35]. In the spirit of that model two different regimes of reorientation may be identified:

(1) On the picosecond time scale the reorientation around the short molecular axis is hindered not only by the mean molecular field (as in the small-step rotational diffusion model) but also by the steric and attractive intermolecular interactions with its close neighbours. This hindrance seems so effective that on this time scale the molecule librates with small amplitude around its equilibrium orientation.

(2) At longer times the collective motion of the surrounding molecules changes the potential well where the central molecule reorientates, leading to a new equilibrium orientation for the molecule itself.

In the framework of this model at least two different reorientational times can be measured, depending on the frequency window of the experiment. Moreover, the order (and temperature) dependence of both these relaxation times is different to that expected from the simpler stochastic models. In particular, τ_0^r and τ_2^r measured in our experiment refer to regime (2) and their unusual temperature dependence may be due to the fact that the collective motion of the close neighbours of the probe molecule becomes faster as the orientational order becomes higher. Thus there would be a competition of the ordinary Arrhenius behaviour and this latter effect in determining the actual temperature dependence of molecular reorientations about the short axis. A further complication may result from an active role of the probe molecule in determining the local ordering, both in regimes (1) and (2). This of course may also have the effect influencing somewhat the intrinsic reorientational dynamics of the nematic phase. Our results in any case imply that reorientational dynamics in these complex molecular systems is by no means trivial, and more careful experimental work is needed.

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