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Two-stage model for molecular orientational relaxation in liquid crystals

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The molecular reorientation in anisotropic fluids is considered as two-stage process—fast single molecule rotation in the volume restricted by close neighbours and slow collective relaxation of the local surrounding. The theoretical results are applied to explain the discrepancy between the rotational diffusion coefficients $D^r_\perp$ obtained by infrared bandshape analysis and polarized fluorescence techniques.

1. Introduction

During the past 20 years molecular orientational dynamics in anisotropic media (such as liquid crystals and membranes) has been studied extensively using a wide variety of experimental techniques, these include dielectric relaxation [1], electron paramagnetic resonance [2-4], quasielastic neutron scattering [5, 6], infrared absorption and Raman bandshape analysis [7-9] and steady state or time-resolved fluorescence spectroscopy [10-12]. Two simple reorientational models are usually employed to interpret the data, namely the small step rotational diffusion model [1-4, 7-12] and the strong collision model [2, 13].

Although the number of the studies of the molecular reorientation in anisotropic systems is rather impressive, usually it is not possible to compare the results obtained by various techniques reported in the literature. The reasons for this are both the wide variety of theoretical approaches to the data interpretation and the sensitivity of the different experimental techniques to different dynamical processes. For example, electronic paramagnetic resonance (EPR) and fluorescence spectroscopy investigate the reorientation of specific probe molecules dissolved in the mesogenic media, quasielastic neutron scattering is sensitive mainly to rotation around the long molecular axis, and dielectric relaxation depends on the collective motion of few near neighbours. So far, to our knowledge, only the results of bandshape analysis in infrared absorption and Raman scattering could be directly compared, i.e. the same compound could be used in both techniques and the theoretical approach for data interpretation is usually the same (based on the small step rotational diffusion model). Both techniques have been applied to determine the tumbling rotational diffusion coefficient $D^r_\perp$ in some nematic liquid crystals [7-9] and the results agree quite well. Typically $D^r_\perp$ increases within the range of the nematic phase from $5 \times 10^9\,s^{-1}$ to $20 \times 10^9\,s^{-1}$.

It has been demonstrated that the value of $D^r_\perp$ can be easily obtained with polarized fluorescence spectroscopy by combining time-resolved measurements of the fluorescence lifetime, τ^f, and steady-state measurement of $\tau^f D^r_\perp$ [11]. Evidently, the fluorescence technique gives $D^r_\perp$ of a suitable fluorescence dye, dissolved in the liquid-crystalline media and not of the host molecules. Fortunately, many dyes with molecular structure and dimensions very close to those of the mesogens are available. Most of them orient quite well in the liquid crystal matrix and so it should be expected that $D^r_\perp$ of the guest molecules will be close to $D^r_\perp$ of the mesomorphic host. However, surprisingly, the first measurements of rotational relaxational dynamics, carried out with three suitable dyes, have given values of $D^r_\perp$ more than an order of magnitude lower than those obtained by vibrational spectroscopy [10–12]. Moreover, the temperature behaviour of $D^r_\perp$ is also completely different; in the nematic phase $D^r_\perp$ decreases slightly with temperature and at the clearing point it decreases by more than a factor of 2. In the isotropic phase $D^r_\perp$ has the usual Arrhenius behaviour. In figure 1 we compare the rotational diffusion coefficients obtained by infrared band-shape analysis and by steady-state fluorescence measurements of the liquid crystal 4-*n*-octyloxy-4′-cyano-biphenyl (8OCB). Such a large discrepancy cannot be explained by the approximations adopted for the data interpretation in the different techniques. A possible explanation of these experimental data, taking into account the different time windows of both techniques, has been proposed [11, 12] where the reorientation of the long molecular axis is assumed to be a two-stage process, namely fast rotation of the molecule in the volume restricted by its close neighbours and slow reorientation of that volume.

A similar physical picture has been proposed by Doi in a series of papers [14–16]. He has considered the rotational dynamics of rod-like molecules in viscous solutions (isotropic or mesomorphic polymers). The basic idea of Doi is that the fast reorientation of the long molecular axis is restricted in a narrow tube by entanglement with the near neighbours. At long times the molecules can escape from the tube, e.g. by longitudinal translation, and large angle reorientation (due to a different orientation of the tube in a new location). This approach gives a satisfactory qualitative explanation of the rheological properties of isotropic or nematic polymers. Another approach has been proposed by Freed *et al.* [22, 23] in order to explain the relaxation times obtained by ESR experiments. In their slowly relaxing local structure model Freed and his co-workers have assumed that the almost spherical probe molecule reorients in the aligning field of the highly anisotropic local surroundings. Two different relaxation processes are involved in this case: (i) fast, large amplitude reorientation of the probe molecule in the frozen local neighbourhood and (ii) slow small amplitude reorientation of the local director.

In the present paper we develop a simple quantitative model, based on a physical picture similar to that presented by Doi [14–16]. Some of our notations and equations are similar to those in slowly relaxing local structure model [22, 23]. We introduce, however, an additional feature (transferring the character of the slow collective motions) and we explore a more suitable mathematical formalism for the interpretation of data obtained by infrared absorption and fluorescence depolarization in thermotropic mesophases. The main difference between our model and other approaches is that we consider the high anisotropy of the probe molecule (in the depolarized fluorescence technique) and of the mesogenic molecule itself (in the infrared measurements). The basic equations of the model are given in §2. In §3 adopting the small step rotational diffusion model we propose equations for the interpretation of the data derived from infrared and fluorescence spectroscopy. The discussion is presented in §4.

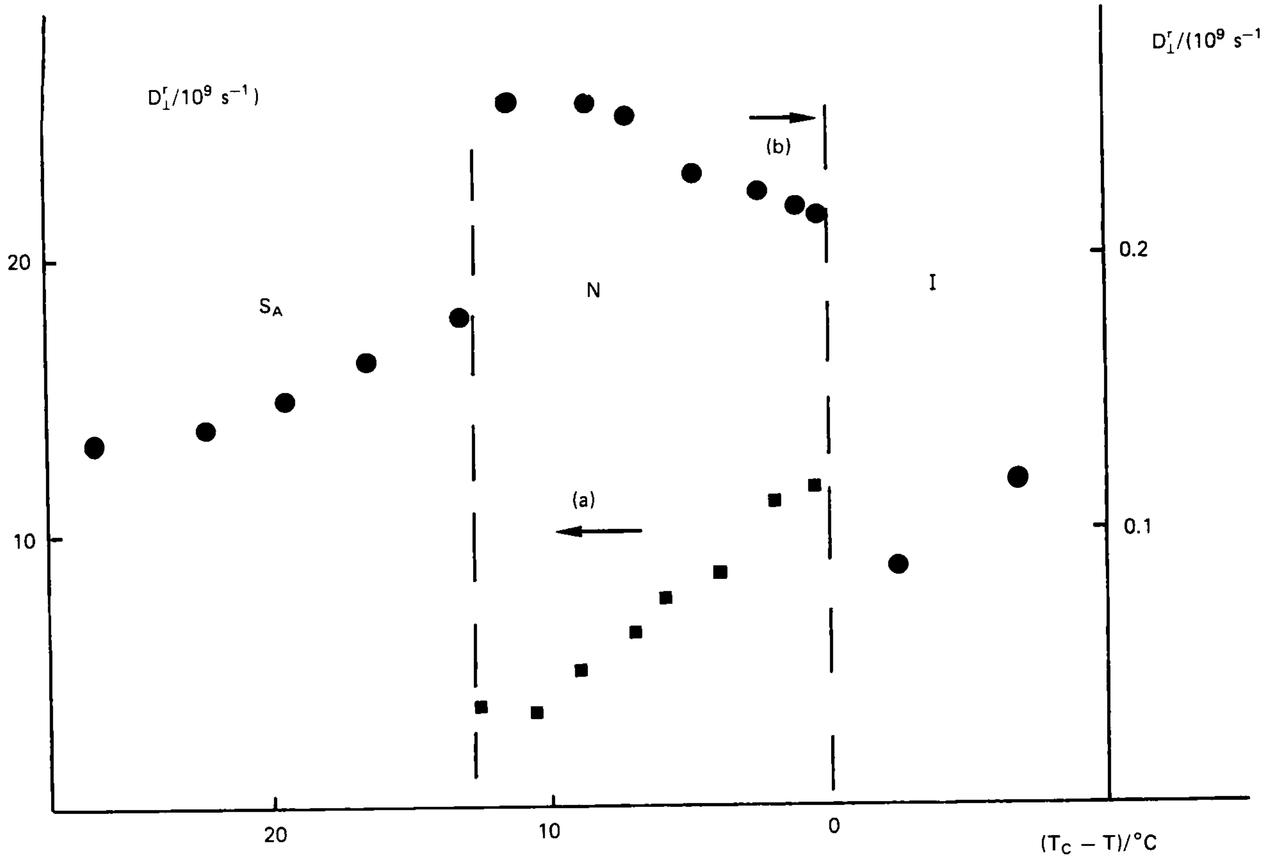

Figure 1. The rotational diffusion coefficient $D^{\mathrm{r}}_{\perp}$ obtained for 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) by (*a*) infrared bandshape analysis and (*b*) polarized fluorescence of the dye 4-dimethylamino-4′-nitrostilbene dissolved in 8OCB.

2. Theoretical model

Rotational dynamics even in isotropic liquids is a very complicated process which should be treated thoroughly only approximately [17, 18]. In liquid crystals, where the molecules and the medium are highly anisotropic, the dynamic processes become extremely difficult to investigate and interpret. That is why reorientational processes are usually considered analogous to the simplest (Ivanov–Valiev [19]) model where the orientation is approximated as a Markov stochastic variable and one of the two obvious limiting cases is adopted [20], namely lack of any correlation between the orientation before and after the jump (the strong-collision model) or very strong correlation (the small step rotational diffusion model). At least for the long axis reorientation, in which we are interested here, the second model seems to have a more sound physical basis. In fact, for fast rotation through large angles, the long mesogenic (or probe) molecule has to disturb the orientation of tens other heavy molecules, which requires a large energy ($E \gg kT$). This is why we present our model in terms of the rotational diffusion approach, although in this section our formulae are quite general and might be applied to any orientational relaxation process with arbitrary correlations.

Let $\Omega(t)\{\equiv(\alpha(t), \beta(t), \mu(t))\}$ be the set of Euler angles describing the time dependent orientation of the molecule in the reference laboratory frame. At any time the molecule undergoes an orienting action by the molecular field of all the other molecules, represented by the potential of mean torque $U(\Omega)$. Assuming that both the molecules and the phase are cylindrically symmetric (e.g. a nematic or a smectic A phase) we obtain $U(\Omega) = U(\beta)$. The equilibrium orientational distribution function is

$$F(\Omega) = F(\beta) = \frac{1}{4\pi^2} \frac{\exp(-U(\beta)/kT)}{\int \exp(-U(\beta)/kT) d\cos\beta} \tag{1}$$

and

$$F(\Omega) = \sum_{s-\text{even}} \frac{2s+1}{8\pi^2} \langle P_s \rangle D^s_{00}(\Omega), \tag{2}$$

where

$$\langle P_s \rangle = \langle D^s_{00} \rangle = \int F(\Omega) D^s_{00}(\Omega)\, d\Omega \tag{3}$$

are the usual orientational order parameters of rank s [21].

Apart from the orienting action of $U(\Omega)$ the molecule during its reorientation also undergoes steric hindrance from the surrounding molecules. Let us suppose that the molecule reorients itself from $\Omega_0(t)$ to $\Omega(t + \delta t)$ where δt is small. In Ω-space there is some small volume $V_{\Omega_0(t)}$ into which the molecule can rotate easily, colliding with no more than one or two neighbours. On the other hand, the probability of molecular reorientation with $\Omega(t + \delta t)$ outside $V_{\Omega_0(t)}$ is low since the energy required for displacement of several other molecules is too high. The main feature of our model is that the relaxation time of Ω (τ_Ω) is much shorter than the relaxation time for the reorientation of V_Ω (τ_V). In fact, τ_Ω characterizes the relaxational dynamics of individual mesogenic or probe molecules, while τ_V describes the collective motion of a large number of near neighbours. On the other hand, the shape of V_Ω fluctuates on a time scale even faster than τ_Ω—a rotation or translation of any neighbour changes slightly the geometry of V_Ω. Therefore, we presume that the Ω-relaxation takes place in some volume $\bar{V}_\Omega$, already averaged over the small fluctuations of V_Ω. In the real space some mean cavity (or restricted volume) into which the molecule can reorient corresponds to $\bar{V}_\Omega$. We expect that the average cavity has cylindrical and a plane of symmetry (like the molecule) with the long axis defined in the laboratory frame by the set of Euler angles $\Sigma(t)$. Moreover, we assume for simplicity that the geometry of the cavity does not depend either on Σ or on Ω.

As we have already mentioned the relaxation time for the reorientation of Ω (at fixed Σ) is much shorter than that of Σ. Therefore we proceed further in the adiabatic approximation. In fact, we suppose that prior to any appreciable change of the orienting direction $\Sigma(t)$ of the local neighbourhood, $\Omega(t)$ has already relaxed to its equilibrium orientational distribution function in the frame of reference Σ. Thus

$$\tilde{f}(\Delta) = \sum_{s-\text{even}} \frac{2s+1}{8\pi^2} \langle \tilde{p}_s \rangle D^s_{00}(\Delta), \tag{4}$$

where $\Delta = \Omega - \Sigma$ in the sense of a sum of rotations. The corresponding equilibrium distribution of Σ-directions in the laboratory frame is

$$f(\Sigma) = \sum_{s-\text{even}} \frac{2s+1}{8\pi^2} \langle p_s \rangle D^s_{00}(\Sigma). \tag{5}$$

All of the information about the reorientation of the molecule and its local neighbourhood contains in the conditional probability $P(\Omega_0, \Sigma_0 | \Omega, \Sigma, t)$ with the initial condition

$$P(\Omega_0, \Sigma_0 | \Omega, \Sigma, t = 0) = \delta(\Omega - \Omega_0)\delta(\Sigma - \Sigma_0) \tag{6}$$

(we assume that the reorientation is a many-dimensional Markov process). The introduction of the transferring reference frame $\Sigma(t)$ leads immediately to the factorization of the conditional probability

$$P(\Omega_0, \Sigma_0 | \Omega, \Sigma, t) = p(\Sigma_0 | \Sigma, t)\tilde{p}(\Delta_0 | \Delta, t). \tag{7}$$

From the physical point of view the separation of the Σ and Δ processes is equivalent to disregarding the back reaction of the Δ relaxation on the local neighbourhood.

At $t \to \infty$ the conditional probability tends to the equilibrium distribution function and from equation (7) we have

$$F(\Omega, \Sigma) = f(\Sigma)\tilde{f}(\Omega - \Sigma). \tag{8}$$

Integrating over all Σ values we obtain the usual singlet orientational distribution function

$$F(\Omega) = \int d\Sigma F(\Omega, \Sigma) = \int d\Sigma f(\Sigma)\tilde{f}(\Omega - \Sigma) \tag{9}$$

and from equations (2), (4) and (5) we have

$$\langle P_s \rangle = \langle p_s \rangle \langle \tilde{p}_s \rangle. \tag{10}$$

The joint probability $P(\Omega_0, \Omega, t)$ for the molecule to be with orientations Ω_0 and Ω at time $t = 0$ and t respectively, is obtained from equation (7) as

$$\begin{aligned} P(\Omega_0, \Omega, t) &= F(\Omega_0)P(\Omega_0 | \Omega t), \\ &= \int d\Sigma_0 \int d\Sigma F(\Omega_0, \Sigma_0) P(\Omega_0, \Sigma_0 | \Omega, \Sigma, t), \\ &= \int d\Sigma_0 \int d\Sigma f(\Sigma_0) p(\Sigma_0 | \Sigma t) \tilde{f}(\Delta_0) \tilde{p}(\Delta_0 | \Delta t). \end{aligned} \tag{11}$$

Defining the orientational correlation functions for the two-stage Ω process in the usual way [1]

$$G^{l\ \ l'}_{mn\ m'n'}(t) = \int d\Omega \int d\Omega_0 F(\Omega_0) P(\Omega_0 \,|\, \Omega t) D^{l}_{mn}(\Omega_0) D^{l'*}_{m'n'}(\Omega) \tag{12}$$

and taking into account equation (11) and the properties of the Wigner matrices we obtain

$$G^{l\ \ l'}_{mn\ m'n'}(t) = \sum_{m''} \sum_{n''} g^{l\ \ l'}_{mm''\ m'n''}(t) \tilde{g}^{l\ \ l'}_{m''n\ n''n'}(t), \tag{13}$$

where

$$\left.\begin{aligned} g^{l\ \ l'}_{mm''\ m'n''}(t) &= \int d\Sigma_0 \int d\Sigma f(\Sigma_0) p(\Sigma_0 \,|\, \Sigma t) D^{l}_{mm''}(\Sigma_0) D^{l'*}_{m'n''}(\Sigma), \\ \tilde{g}^{l\ \ l'}_{m''n\ n''n'}(t) &= \int d\Delta_0 \int d\Delta \tilde{f}(\Delta_0) \tilde{p}(\Delta_0 \,|\, \Delta t) D^{l}_{m''n}(\Delta_0) D^{l'*}_{n''n'}(\Delta), \end{aligned}\right\} \tag{14}$$

are the orientational correlation functions for Σ and Δ processes respectively.

Assuming axial symmetry of both the molecule and the mesophase we obtain the usual selection rules [20]

$$G^{l\ \ l'}_{mn\ m'n'}(t) = G^{l\ \ l'}_{mn\ mn}(t) \delta_{mm'} \delta_{nn'} = \delta_{mm'} \delta_{nn'} G^{ll'}_{mn}(t) \tag{15}$$

and taking also into account the cylindrical symmetry of the cavity we have

$$\begin{aligned} G^{ll'}_{mn}(t) &= \sum_{m''} \sum_{n''} \delta_{m''n''} g^{ll'}_{mm''mn''}(t) \tilde{g}^{ll'}_{m''nn''n}(t) \\ &= \sum_{m''} g^{ll'}_{mm''}(t) \tilde{g}^{ll'}_{m''n}(t) \end{aligned} \tag{16}$$

i.e. the correlation function for Ω is easily expressed in terms of the correlation functions for the Σ and Δ processes. At this point it would be useful to compare our model with the slowly relaxing local structure approach, proposed by Freed *et al.* [22, 23]. Although some of our basic physical assumptions, notation and equations are similar to those of Freed and his co-workers [22, 23], there are also drastic differences between both models. In fact, the local structure approach treats the case of an almost spherical probe molecule (with $|\langle P_2 \rangle| \lesssim 0{\cdot}1$) which reorients in a highly anisotropic local surrounding. The only influence of the neighbours on the probe molecule is the slow change of the orientation Σ of the local director and the angular distribution $\tilde{f}(\Delta)$ is much broader than $f(\Sigma)$. Therefore, the composite correlation function can be expanded as a power series in Σ (see [22]). In our model this approach is obviously impossible—we are interested in a highly anisotropic probe (or mesogenic) molecule which orients quite well in the cavity. Then $F(\Omega)$ and therefore $f(\Sigma)$ is much broader than $\tilde{f}(\Delta)$ and we assume statistical independence between Σ and $\Delta = \Omega - \Sigma$ (as is clear from our choice of the transferring frame Σ). Naturally, the different physical bases of both approaches leads to different final results.

It is obvious that our model and that of slowly relaxing local structure are complementary to each other. The approach of Freed *et al.* [22, 23] is convenient only for an almost isotropic probe molecule (with low order in the mesogenic matrix)—otherwise the Σ expansion does not converge fast enough. In contrast, our model is convenient for the description of the dynamics of the mesogenic molecule itself (or a highly anisotropic probe molecule) but not for a nearly spherical probe, since in this case our assumption that Σ frame is transferring fails.

3. Data interpretation

In order to calculate the correlation functions in equation (16) we need to adopt suitable mechanisms for Σ and Δ relaxations. Here we treat both of these processes within the framework of the small step rotational diffusion model in an anisotropic medium [1–4]. For the Σ relaxation this is an evident choice since the collective character of the Σ process excludes the possibility of large orientational jumps. For the Δ relaxation, however, there is no clear physical evidence for the reorientational mechanism; in the restricted volume $\tilde{V}_\Omega$ we might have diffusion, uncorrelated jumps, inertial motion with collisions on the cavity walls, etc. Therefore, our choice of the diffusion model is mainly imposed by computational reasons; this model is well developed and simple analytical expressions for the correlation functions are available to a good approximation [7, 8, 24]. *A posteriori*, the applicability of the diffusion model is confirmed by the good agreement between the rotational diffusion coefficient $D^{\mathrm{r}}_{\perp}$ obtained by infrared and Raman methods [9]. Let the diffusion coefficients for Σ and Δ processes be $D^{\mathrm{r}}_{\perp} = D$ and $\tilde{D}^{\mathrm{r}}_{\perp} = \tilde{D}$, respectively. In the spirit of our model $\tilde{D} \gg D$ and $D^{\mathrm{r}}_{\parallel} = 0$ for the Σ process since the cavity is assumed to be axially symmetric and its rotation around the symmetry axis has no physical meaning. The equilibrium distribution function for the fast process $\tilde{f}(\Delta)$ has a large anisotropy, i.e. the first order parameters $\langle \tilde{p}_s \rangle$ are close to unity. This corresponds to a large anisotropy of the cavity. Obviously, we have no information about the functional form of $\tilde{f}(\Delta)$. It might be, for example, a uniform distribution within some part of the angular space and zero in the remainder. In that case the fast Δ relaxation can be treated as a diffusion-in-a-cone process [26, 27]. We prefer, however, to assume the usual Maier–Saupe form for $\tilde{f}(\Delta)$ [28] and to treat both Σ and Δ diffusions in the same way. We note that at the limit of high Δ order $(1 - \langle \tilde{p}_2 \rangle \ll 1)$, which we consider in this paper; our approach gives approximately the same results as the diffusion-in-a-cone model [29].

3.1. *Infrared bandshape analysis*

We consider an infrared absorption band with transition dipole moment parallel to the long molecular axis (in order to avoid the influence of the much larger spinning diffusion coefficient $\tilde{D}^{\mathrm{r}}_{\parallel}$). Let $a_i(t)$ be the Fourier transform of the band taken with polarization parallel $(i = z)$ or perpendicular $(i = x)$ to the liquid crystal director, By considering the ratio $a_z(t)/a_x(t)$ we avoid the contribution of vibrational relaxation in the bandshape;

$$\frac{a_z(t)}{a_x(t)} = \frac{G^{11}_{00}(t)}{G^{11}_{00}(0)} \frac{G^{11}_{10}(0)}{G^{11}_{10}(t)}. \tag{17}$$

The Fourier transforms $a_i(t)$ can be obtained with good accuracy only for times no longer than a few picoseconds. In this time domain $tD \ll t\tilde{D} \ll 1$ and the correlation functions in equation (16) can be replaced by Taylor's expansions around $t = 0$; they have been already reported in [7, 12] and give

$$\frac{a_z(t)}{a_x(t)} \approx 1 - t\,\frac{9\langle p_2 \rangle \langle \tilde{p}_2 \rangle (D + \tilde{D}) - D\langle p_2 \rangle (1 - \langle \tilde{p}_2 \rangle)(1 + 2\langle \tilde{p}_2 \rangle)}{(1 + 2\langle p_2 \rangle \langle \tilde{p}_2 \rangle)(1 - \langle p_2 \rangle \langle \tilde{p}_2 \rangle)} \tag{18}$$

Taking into account that $D \ll \tilde{D}$, $1 - \langle p_2 \rangle \ll 1$, and neglecting the second term, we obtain

$$\frac{a_z(t)}{a_x(t)} = 1 - t\,\frac{9\langle P_2 \rangle (D + \tilde{D})}{(1 + 2\langle P_2 \rangle)(1 - \langle P_2 \rangle)}. \tag{19}$$

Comparison of this result with equation (3) from [25] shows that the influence of the relaxation of the local neighbourhood on the infrared data is via the renormalization of the diffusion constant ($D^{\mathrm{r}}_{\perp} = D + \tilde{D} \approx \tilde{D}$).

3.2. *Steady-state polarized fluorescence measurements*

We now consider a fluorescent dye with both absorption and emission dipole moments parallel to the long molecular axis. It has been demonstrated [11] that in such a case valuable dynamical information can be extracted from the polarization ratio measured in a homeotropically aligned sample. Here

$$r^{\mathrm{h}} = \frac{I_{xx} - I_{xy}}{I_{xx} + 2I_{xy}} = \frac{2\overline{G^{22}_{20}}}{1 - 2\langle P_2\rangle + \overline{G^{22}_{00}} - \overline{G^{22}_{20}}}, \tag{20}$$

where I_{ik} are the steady state intensities measured with polarization of the exciting and emitted light, respectively i and k and

$$\overline{G^{22}_{m0}} = \int F(t) G^{22}_{m0}(t)\, dt, \quad m = 0; 2, \tag{21}$$

where

$$F(t) = (1/\tau^{\mathrm{f}}) \exp(-t/\tau^{\mathrm{f}}) \tag{22}$$

is the fluorescence decay function.

Here, in contrast to the infrared case, we are interested in the long time behaviour of $G^{22}_{m0}(t)$ because $\tilde{D}\tau^{\mathrm{f}} \gg D\tau^{\mathrm{f}} \gg 1$. In this limit a good approximation for the correlation functions is [24]

$$g^{22}_{mn}(t) = g^{22}_{mn}(\infty) + (g^{22}_{mn}(0) - g^{22}_{mn}(\infty)) \exp\left(t \frac{\dot{g}^{22}_{mn}(0)}{g^{22}_{mn}(0) - g^{22}_{mn}(\infty)} \right), \tag{23}$$

where $g^{22}_{mn}(\infty) = \delta_{m0}\delta_{n0}\langle p_2\rangle$ is the value of the correlation function as $t \to \infty$ and $g^{22}_{mn}(0)$ and $g^{22}_{mn}(\infty)$ are well-known model independent functions of the order parameters. In addition

$$\dot{g}^{22}_{mn}(0) = \lim_{t \to 0} \frac{d}{dt} g^{22}_{mn}(t) \tag{24}$$

are easily obtained in the diffusion model as a function of the order parameters and the rotational diffusion coefficients [8, 24]. Substituting equations (16) and (23) in equation (21) we have

$$\begin{aligned} \overline{G^{22}_{m0}} = {} & \langle p_2\rangle^2 \langle \tilde{p}_2\rangle^2 \delta_{m0} + \frac{\langle p_2\rangle^2 \tilde{b}_{m0}}{1 + \tau^{\mathrm{f}} \tilde{a}_{m0}/\tilde{b}_{m0}} \delta_{m0} + \frac{\langle \tilde{p}_2\rangle^2 b_{m0}}{1 + \tau^{\mathrm{f}} a_{m0}/b_{m0}} \\ & + \frac{b_{m0}\tilde{b}_{00}}{1 + \tau^{\mathrm{f}}(a_{m0}/b_{m0} + \tilde{a}_{00}/\tilde{b}_{00})} + \frac{2b_{m1}\tilde{b}_{10}}{1 + \tau^{\mathrm{f}}(a_{m1}/b_{m1} + \tilde{a}_{10}/\tilde{b}_{10})} \\ & + \frac{2b_{m2}\tilde{b}_{20}}{1 + \tau^{\mathrm{f}}(a_{m2}/b_{m2} + \tilde{a}_{20}/\tilde{b}_{20})}. \end{aligned} \tag{25}$$

Here the following notation has been introduced:

$$\left. \begin{aligned} b_{mn} &= g^{22}_{mn}(0) - g^{22}_{mn}(\infty), \\ a_{mn} &= -\dot{g}^{22}_{mn}(0) \end{aligned} \right\} \tag{26}$$

and similarly for $\tilde{b}_{mn}$ and $\tilde{a}_{mn}$. The explicit expressions for the coefficients in this equation as functions of the order parameters and diffusion coefficients are given in [24].

Many terms in equation (25) are small and can be neglected within the framework of our assumptions. Then we obtain

$$\left.\begin{aligned}\overline{G^{22}_{00}} &= \left[\langle p_2\rangle^2\langle \tilde{p}_2\rangle^2 + \frac{\langle \tilde{p}_2\rangle^2}{35}\,\frac{7 + 10\langle p_2\rangle + 18\langle p_4\rangle - 35\langle p_2\rangle^2}{1 + 6D\tau^{\mathrm{f}}\,\dfrac{7 + 5\langle p_2\rangle - 12\langle p_4\rangle}{7 + 10\langle p_2\rangle + 18\langle p_4\rangle - 35\langle p_2\rangle^2}}\right](1 + O_0),\\ \overline{G^{22}_{20}} &= \frac{\langle \tilde{p}_2\rangle^2}{35}\,\frac{7 - 10\langle p_2\rangle + 3\langle p_4\rangle}{1 + 6D\tau^{\mathrm{f}}\,\dfrac{7 - 5\langle p_2\rangle - 2\langle p_4\rangle}{7 - 10\langle p_2\rangle + 3\langle p_4\rangle}}(1 + O_2).\end{aligned}\right\} \tag{27}$$

Here the terms O_0 and O_2 are of the order of $D(1 - \langle \tilde{p}_2\rangle)/\tilde{D}$ and with our assumptions are small and can be neglected. As $\langle \tilde{p}_2\rangle \rightarrow 1$ equations (27) reduce to the corresponding equations for a simple one-stage diffusion process [11]. When $0 < (1 - \langle p_2\rangle) \ll 1$ equations (27) differ only slightly from the expressions for simple diffusion process, but D in the spirit of our model is the diffusion coefficient for the orientational relaxation of the local neighbourhood and it is much smaller than the molecular rotational diffusion coefficient $\tilde{D}$.

In order to recalculate the fluorescence data from figure 1 we need the (unknown) value of $\langle \tilde{p}_2\rangle$. In fact, the experiment gives directly $\overline{G^2_{00}}$, $\overline{G^2_{20}}$ and $\langle P_2\rangle$ [11]. At given $\langle \tilde{p}_2\rangle$ from equation (10) we obtain $\langle p_2\rangle$ and solve the equations (27) in order to find D. In figure 2 we present the rotational diffusion coefficient D for 4-dimethylamino-4′-nitrostilbene (DMANS) in 8OCB calculated in this way for $\langle \tilde{p}_2\rangle = 1$ (as in figure 1) as well as for $\langle \tilde{p}_2\rangle = 0{\cdot}9$ and $0{\cdot}8$. The values of D decrease with decreasing $\langle \tilde{p}_2\rangle$ and are about two orders lower than the corresponding data obtained by infrared bandshape analysis (see figure 1).

4. Discussion

The large discrepancy in the rotational diffusion coefficients obtaifned by the infrared and fluorescent techniques is easily understood within the framework of our two-stage rotational relaxation model. In fact, these experiments are sensitive to different dynamic processes. The infrared bandshape analysis gives us the molecular rotational mobility $\tilde{D}$, while the near neighbours collective rotational diffusion data D is provided by fluorescence spectroscopy.

The discussion of the temperature dependences of D and $\tilde{D}$ is much more complicated. Our fluorescence experiments could not give us the temperature dependence of D since we have no data for the temperature behaviour of $\langle \tilde{p}_2\rangle$. The curves at figure 2 are calculated at constant $\langle \tilde{p}_2\rangle$ but in reality it is quite possible that it could vary appreciably with the temperature and change at phase transitions. Obviously it will lead to some serious corrections to the temperature dependence of D in figure 2. It should be noted here that in the spirit of our model D is not a molecular characteristic but is a collective feature and depends on the collective rotational and translational

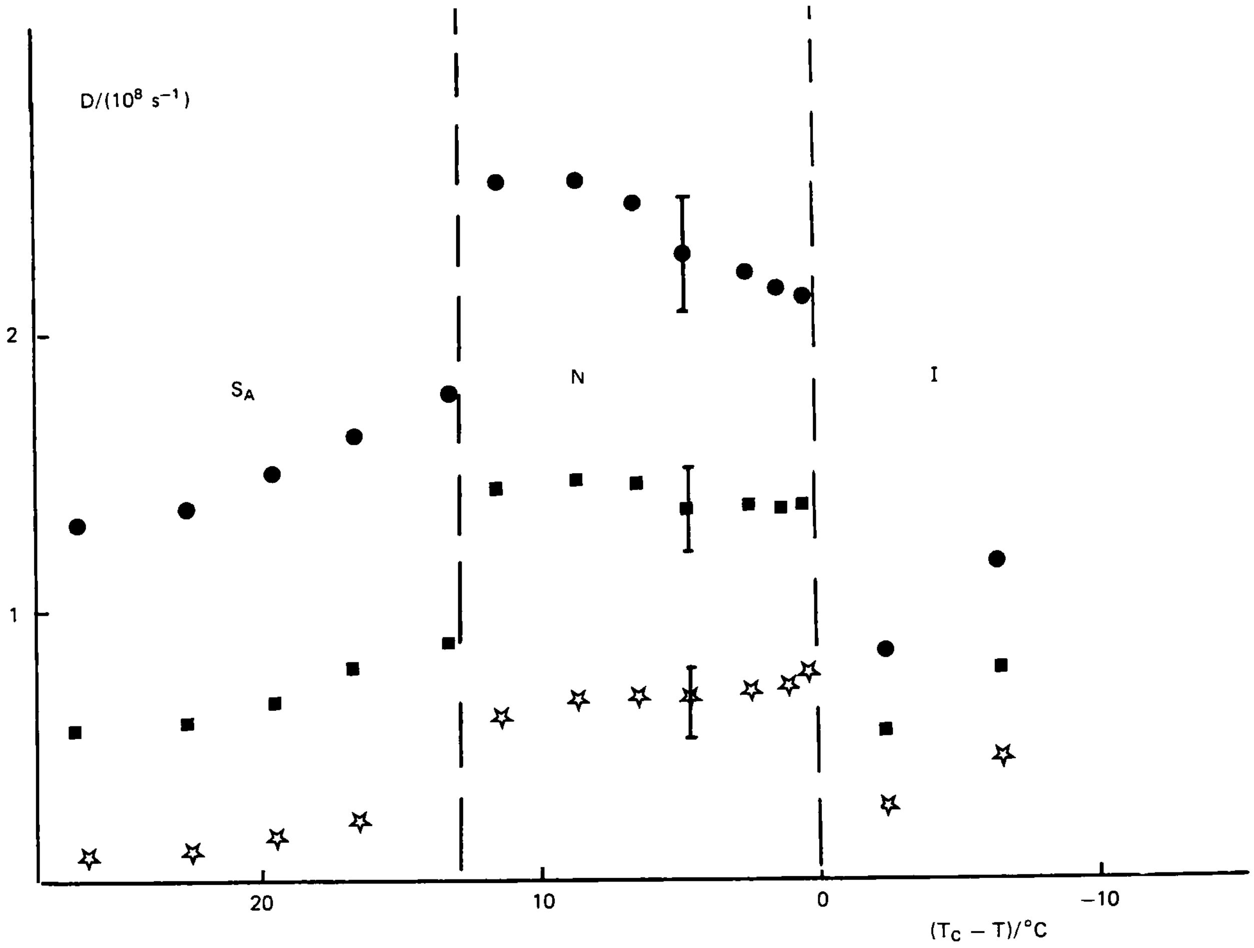

Figure 2. The rotational diffusion coefficient D measured by polarized fluorescence of dimethylamino-4′-nitrostilbene dissolved in 4-n-octyloxy-4′-cyanobiphenyl: ●, $\langle \tilde{p}_2 \rangle = 1$; ■, $\langle \tilde{p}_2 \rangle = 0{\cdot}9$; ☆, $\langle \tilde{p}_2 \rangle = 0{\cdot}8$.

mobility of the mesogenic molecules and, probably on the orientational and translational order in the phase. This can explain the non-Arrhenius behaviour of D and the large variation at the phase transitions.

Investigating the mesomorphic state, in order to simplify the problem one should make many approximations in the models and in the data interpretation. In the isotropic phase of the highly anisotropic mesogenic molecules the main physical features of our two-stage orientational relaxation model are the same, while some of the approximations are not necessary any more, since the order parameters $\langle P_s \rangle$ and $\langle p_s \rangle$ vanish. From this point of view the isotropic phase is a better test of our model than the liquid-crystalline state. The Raman bandshape analysis gives for the isotropic phase of 4-*n*-pentyl-4′-methoxytolane (PMT) $D^{\mathrm{r}}_{\perp} = 16 \times 10^9\,\mathrm{s}^{-1}$ [8], i.e. two orders of magnitude larger than our fluorescent data for DMANS dissolved in 8OCB. This discrepancy cannot be explained by the slightly different viscosity and molecular structure of the two mesogens employed and therefore supports our two-stage relaxation model.

In conclusion, the two-stage relaxation model explains the discrepancy between the values of the rotational diffusion coefficients $D^{\mathrm{r}}_{\perp}$ obtained by different techniques. There is no obvious disagreement between the suggested model and the experimental temperature behaviour of $D^{\mathrm{r}}_{\perp}$. However, in order to prove directly the validity of our model we need some experiments with a large time window (e.g. 5–500 ps), sensitive to both molecular reorientation and the orientational relaxation of the neighbourhood. A good candidate for such measurements might be picosecond time resolved fluorescence spectroscopy, which can provide directly the time behaviour of the orientational correlation functions. Such an investigation is already under way.

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[29] The distribution function $\tilde{f}(\Delta)$ has two large peaks corresponding to the molecule oriented parallel or antiparallel to the cavity axis. In the diffusion-in-a-cone model the potential barrier between the peaks is infinitely high and π-jumps of the molecule are prohibited. For the Maier–Saupe expression for $\tilde{f}(\Delta)$ π-jumps become possible but at high $\langle \tilde{p}_2 \rangle$ their probability is extremely low (at least for the times $t \lesssim 1$ ns considered in this paper). In this limit the substantial difference between our approach and the diffusion-in-a-cone model disappears.