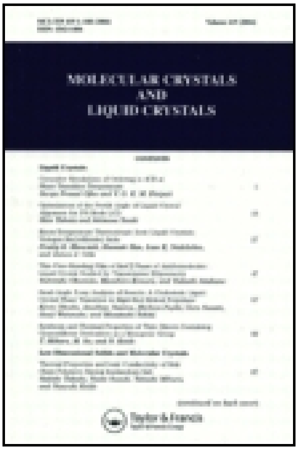

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Translational Self-Diffusion Measurements and Analysis of a Calamitic Smectogen

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Translational Self-Diffusion Measurements and Analysis of a Calamitic Smectogen

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Translational self-diffusion measurements have been performed in the mesophases of the p-hexyloxybenzylidene-p'-fluoroaniline (FAB.OC6) liquid crystal, by means of a static fringe field gradient approach. The method provides an accurate enough data set of the diffusion tensor as a function of temperature in the nematic and smectic A phase to be used for accurate analysis exploiting well established self-diffusion models. Also measurements in the smectic B phase have been carried out and the results obtained seem to be consistent with a picture where the out of plane diffusion is strongly inhibited ($< 10^{-15} m^2/s$) *and only a slow in plane diffusion* ($\sim 10^{-13} m^2/s$) *is present.*

Keywords: fringe field diffusometry; liquid crystals; self-diffusion

INTRODUCTION

It is well known that translation self-diffusion behaviour can provide valuable information on the molecular assemblage in liquid crystals phases [1–3]. Being self-diffusion strictly connected to the phase anisotropy and the molecular order, collection of accurate data set of self-diffusion tensors can be a valuable means to confirm (or confute) diffusional models [4], as well as to determine valuable properties such as molecular ordering. In this context, pulsed-field-gradient (PFG) nuclear magnetic resonance (NMR) proved to be a unique tool as it allows direct determination of self-diffusion

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coefficients without the use of probes and tracers or isotopic labelling [5–6]. In particular recent experimental protocols have been proposed for this aim by Dvinskikh and Furó [3–4] and the author [7] and the results obtained have been used to critically evaluate diffusional models.

In the present work we used the approach proposed in references [7,8] to investigate the translational self-diffusion of the mesogen p-hexyloxybenzylidene-p’-fluoroaniline, from here on referred to as FAB.O6. The interest in this system lies in its variety of phases, where also the strongly positional ordered smectic B crystal phase is present and the necessity to enrich the number of data sets present in literature in order to encourage further theoretical investigations.

The communication proceeds as follows: firstly the methodology is briefly surveyed, then the experimental results are presented and discussed. Finally a detailed analysis of the diffusion data, in terms of theoretical models is reported.

THE METHODOLOGY

Translational self diffusion has been measured in the FAB.O6 phase using a ^{1}H static fringe field gradient approach, following the protocol already described in references [7,8].

The method, that exploits the high static gradient (typically of strength 25–80 T/m) present in the fringe field of commercial superconducting magnet has been used by Kimmich *et al.* to measure diffusion in polymer melts [9]; by Feweier *et al.* in super-cooled fluids [10] and Karakatsanis and Bayerl in phospholipids bilayers [11]. In liquid crystals, it has been used by Vilfan and co-workers to measure self diffusion of the nematic phase of 4-n-pentyl-4′-cyanobiphenyl (5CB) both in the bulk and confined in controlled porous glasses [12], and by the author to measure diffusion in the nematic and smectic A phase of 4-n-octyloxy -4’-cyanobiphenyl (8OCB) [7] and 4-4′-di-n-octyloxy-azoxybenzene (OAB) [8].

In the isotropic phase, where only spin relaxation and diffusion contribution to the echo decay should be addressed, a single shot Stimulated Echo relaxation compensated experiment could be used:

$$\left(\frac{\pi}{2}\right)_x - \left(\frac{\tau+\delta}{2}\right) - \pi_y - \left(\frac{\tau-\delta}{2}\right) - \left(\frac{\pi}{2}\right)_y - (\Delta-\tau) - \left(\frac{\pi}{2}\right)_y - \left(\frac{\tau-\delta}{2}\right) - \pi_y - \left(\frac{\tau+\delta}{2}\right) - \left(\frac{\pi}{2}\right)_y - echo \qquad (1)$$

and the echo intensity can be written as

$$A_{5p}^{STE}(\delta) = \exp\left\{-\frac{1}{6}\gamma^2 G^2 D(\tau^3 - 3\tau^2\delta + 3(\tau + 2(\Delta - \tau))\delta^2 + 3\delta^3)\right\}$$
$$\exp\left\{-\frac{(\Delta-\tau)}{T_1}\right\}\exp\left\{-\frac{2\tau}{T_2}\right\} \tag{2}$$

In case the echo is collected as a function of δ, keeping constant τ and Δ, only diffusion affects the echo decay, as the spin relaxation terms remain constant, and the diffusion coefficient can be determined fitting the experimental echo decay with equation (2) as all the parameters are known, expect the diffusion coefficient.

When diffusion is measured in the nematic, smectic A and smectic B phases, on the other hand, two other complications should be considered, namely:

(i) Dipolar Correlation Effects (DCE), due to non zero average of the dipolar interactions
(ii) Sample Orientation in the magnetic field.

I discuss briefly these two points, already deeply surveyed in reference [7–8]. Point (i) can be tackled recurring to a double experiment approach, consisting of two Stimulated Echoes tailored as follows [7,8]:

$$\left(\frac{\pi}{2}\right)_x - \tau - \left(\frac{\pi}{2}\right)_x - (\Delta - \tau) - \left(\frac{\pi}{2}\right)_x - \tau - echo \tag{3}$$

$$\left(\frac{\pi}{2}\right)_x - \left(\frac{\tau+\delta}{2}\right) - \pi_y - \left(\frac{\tau-\delta}{2}\right) - \left(\frac{\pi}{2}\right)_y - (\Delta-\tau) - \left(\frac{\pi}{2}\right)_y - \left(\frac{\tau-\delta}{2}\right)$$
$$- \pi_y - \left(\frac{\tau+\delta}{2}\right) - \left(\frac{\pi}{2}\right)_y - echo \tag{3a}$$

As already diffusely discussed in reference [7], the two echoes intensities for the same time delays differ only for the diffusional contribution to the echo decay and the ratio:

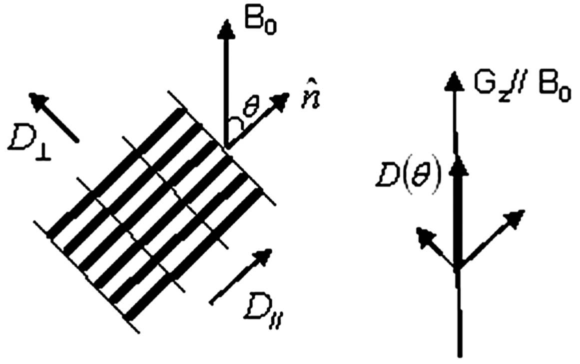
$$\frac{A^{STE}}{A_{5p}^{STE}} = \exp\left\{-(\gamma G)^2 D\Delta\left(\tau^2 - \delta^2\right)\right\} \tag{4}$$

can be used to determine the diffusion coefficient D along the gradient G direction, as all the other parameters are known.

Regarding point (ii), it is well known that thermotropic nematic phases usually orient uniformly in the static magnetic field in a direction dependent on the diamagnetic susceptibility of the molecules. For instance, the nematic phase of $\Delta\chi > 0$ mesogens homogeneously aligns with the phase director parallel to the static magnetic field B_0 [13]. In this configuration, the second rank diffusion tensor for a uniaxial phase is expressed as:

$$\widetilde{\mathbf{D}} = \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix} = \begin{pmatrix} D_{\perp} & 0 & 0 \\ 0 & D_{\perp} & 0 \\ 0 & 0 & D_{//} \end{pmatrix} \tag{5}$$

where D_{xx}, D_{yy}, D_{zz} are the diffusion coefficients expressed in the principal axis frame for a $\Delta\chi > 0$ mesogen aligned in the static field $(\hat{n}//B_0//\hat{z})$ and $D_{\perp}$ and $D_{//}$ represent the diffusion components of a uniaxial phase $(D_{xx} = D_{yy} = D_{\perp})$, such as nematic and smectic A. In the case of fringe field diffusometry, the gradient direction is normally fixed by the magnet geometry to $G \ // \ B_0$ and direct measurement of $D_{//}$ only is allowed for $\Delta\chi > 0$ mesogens. However, this limitation can be practically overcome in case of a viscous enough smectic A phase where sample reorientation through director rotation in the magnetic field is possible. In this case, if the smectic A phase is formed cooling an homogeneously oriented nematic phase, the determination of the complete diffusion tensor can be obtained measuring the diffusion coefficient as a function of the angle θ between the phase director and the field gradient direction as shown in Figure 1, as already shown, for example, in reference [8].



$$D(\theta) = \cos^2\theta \cdot D_{//} + \sin^2\theta \cdot D_{\perp}$$

FIGURE 1 Schematic representation of a smectic A phase with the phase director n tilted of a $\boldsymbol{\theta}$ angle in respect with the static field B_0 and gradient G_z direction. In this case the diffusion coefficient D($\boldsymbol{\theta}$) is expressed by in equation (6), as a combination of diffusion parallel and perpendicular to the phase director.

In particular, the diffusion coefficients measured at different θ angles should follow the equation:

$$D(\theta) = D_{//}\cos^2\theta + D_{\perp}\sin^2\theta \tag{6}$$

Consequently, the determination of $D_{\perp}$ and $D_{//}$ can be obtained fitting the $D(\theta)$ behaviour as a function of θ, with Equation (6), being the two diffusion components the best fitting parameters, as already reported in reference [8] for the 4-4'-di-n-octyl-azoxybenzene (OAB) smectogen.

SELF-DIFFUSION MEASUREMENTS

Each of the standard stimulated echo decays collected can be well fitted to a single exponential decay:

$$A^{STE} = A_0\exp(-c\Delta) \tag{7}$$

where A_0 is a normalization factor determined for $\Delta \to 0$ and c is the decay constant. This observation leads us to conclude that, since the diffusion and relaxation attenuation are exponential, then so too is the dipolar correlation attenuation. That is

$$c = (\gamma G\tau)^2 D(\theta) + \frac{1}{T_1} + c^{DCE} \tag{8}$$

where c^{DCE} represents the contribution due to dipolar correlations.

Also the echo decay amplitudes from the STE_{5p} experiments can be fit to single exponential decays, according to:

$$A_{5p}^{STE} = A_0^{5p}\exp(-c_{5p}\Delta) \tag{9}$$

where A_0^{5p} and c_{5p} are again a normalization factor and decay constant respectively. The latter is given by

$$c_{5p} = (\gamma G\delta)^2 D(\theta) + \frac{1}{T_1} + c^{DCE} \tag{10}$$

It is found that $c_{5p} < c$, at all the temperature and orientations investigated. From the two decay constants $D(\theta)$ can be obtained as:

$$D(\theta) = \frac{(c - c_{5p})}{(\gamma G)^2(\tau^2 - \delta^2)} \tag{11}$$

The diffusion coefficients $D_{\perp}$ and $D_{//}$ measured and determined exploiting Equation (6) in the different phases of FAB.O6 are reported in Figure 2.

Now, it's convenient to discuss the results obtained for each phase separately.

i) *Isotropic phase*: In the isotropic phase the diffusion coefficient is a simple scalar quantity (no orientation dependence). A single diffusion coefficient as been hence measured at each temperature investigated.

ii) *Nematic phase*: In this case the diffusion is indeed expressed as a second rank tensor (see Equation (6)). However, only the D for $\theta = 0^\circ$ could be measured, corresponding to $D_{//}$, as the nematic phase reorients in the magnetic field if the sample is rotated.

iii) *Smectic A and B phases*: $D(\theta)$ at different angle can be measured, starting from a macroscopically oriented phase with the director oriented at $\theta = 0^\circ$ cooling from the nematic phase. In these phases, full information on the diffusion tensor could be obtained, performing measurements of the translational diffusion

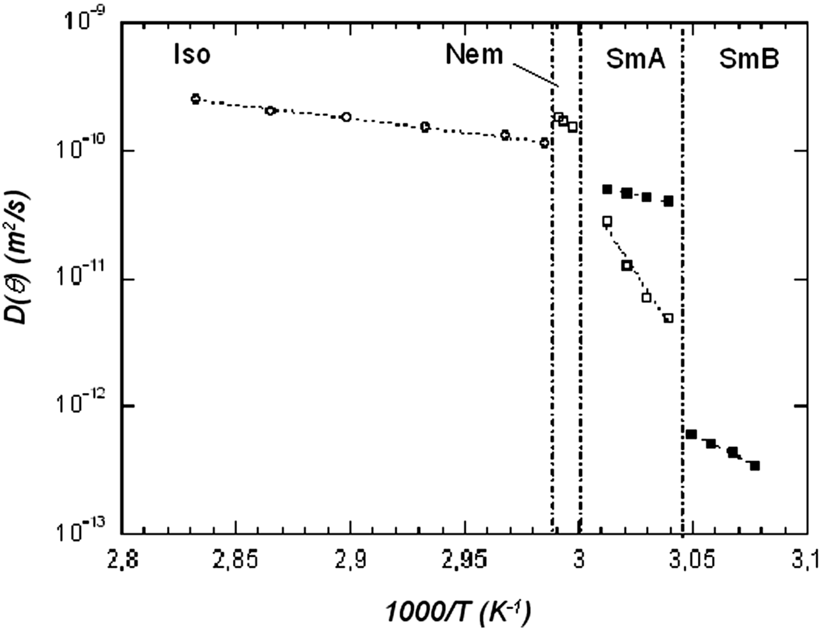


FIGURE 2 Experimentally determined self-diffusion coefficients of FAB.OC6 mesogen as a function of the reduced temperature, in the isotropic phase (empty circles), in the nematic and smectic A phases, along the phase director (empty squares) and perpendicular to the phase director in the smectic A and smectic B phases.

coefficient as a function of the angle θ, fitting the $D(\theta)$'s data set with Equation (7), where $D_\perp$ and $D_{//}$ figure as best fitting parameters. A graphical representation of two of these fittings is reported in Figure 3, for the diffusion evaluation at T = 331 K in the smectic A phase and and T = 327 K in the smectic B phase.

Figure 3 indeed deserves some comments. First of all, the reader surely notices that no direct measurements have been performed in the smectic A phase for angles $\theta < 30°$, while in the smectic B phase the explored θ range was further reduced to $50° < \theta < 72°$. These limitations are due to the fact that, pragmatically, we wanted to limit our measurements to orientations where the echo decays followed a single exponential decay where equations (7) and (9) hold. For this particular sample, measurements outside the range reported as example in Figure 3, presented relevant deviations from the expected behaviour that could be ascribed to longitudinal cross relaxation [16]. Notwithstanding, the fitting reported in the picture show that determination of the two relevant diffusion components $D_\perp$ and $D_{//}$ was possible within a few percent accuracy. In particular we must notice that in the smectic B phase the extrapolated $D(\theta)$ at $\theta = 0°$ is consistent with $D_{//} \approx 0$, that more realistically should be considered as a $D_{//} < 10^{-15} m^2/s$ that is the detection limit for the experiments

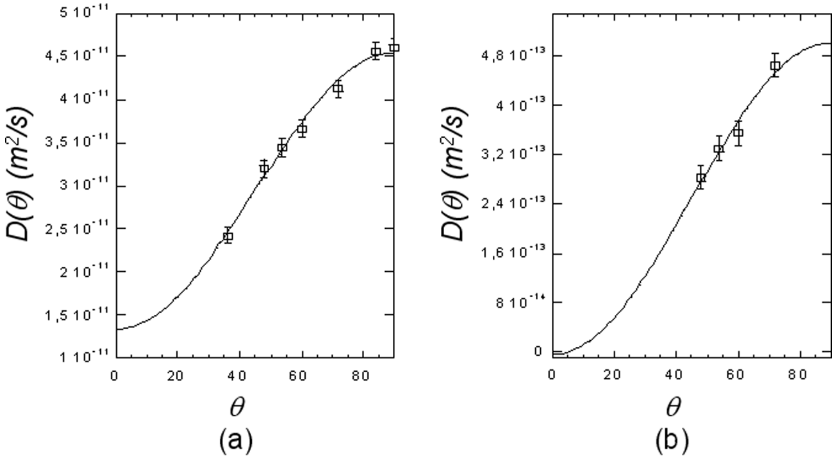


FIGURE 3 Self-diffusion coefficients D(θ) measured as a function of angle θ in the smectic A (T = 331 K) and smectic B phase (T = 327 K). The self diffusion coefficients at $\theta = 0°$ and $\theta = 90°$ correspond to $D_{//}$and $D_\perp$, respectively, as discussed in the text.

performed. In other words, with the time delays τ and Δ used to cope with the limitations imposed by relaxation times T_1 and T_2 ($\tau < T_2$, $\Delta < T_1$), it's reasonable to consider negligible diffusion contributions smaller than $10^{-15} m^2/s$ in Eq. (6).

SELF DIFFUSION DATA DISCUSSION AND ANALYSIS

From Figure 2, the phase transitions can be easily identified by sudden changes in the diffusion coefficients and each phase can be framed in its temperature range.

In particular, the Isotropic to Nematic phase is characterized by a sudden increase of the diffusion coefficient moving from the isotropic coefficient D to the $D_{//}$, describing the diffusion process along the phase director. This is of course the expected result for a nematic phase formed by calamitic molecules that uniformly orients its director along the field gradient direction [1,4,7].

The Nematic to Smectic A phase transition is accompanied by a strong failure of $D_{//}$, denoting a first order transition. This behaviour is in agreement with the McMillan theory for the nematic to smectic A phase transition, which predicts a stronger first transition the larger is the ratio between the transition temperatures $T_{Iso-Nem}/\ T_{Nem-SmA}$ [17]. In the smectic A phase also $D_{\perp}$ could be measured, and the ratio $D_{//}/D_{\perp} < 1$ holds in all the range measured and decreases as the temperature decreases. A look to the temperature behaviour of the two diffusion processes modelled with the typical Arrhenius equation shows, as expected, $E_a^{//} > E_a^{\perp}$. However, the values determined $E_a^{//} = 510 KJ/mol$, $E_a^{\perp} = 72 KJ/mol$ appear significantly higher than the values normally obtained in other smectic A phases. In particular $E_a^{//}$ is about 5–7 times higher than the one determined in cyanobiphenyls [4,7] and azoxy-benzenes [8].

In the smectic B phase, only the in plane component $D_{\perp}$ of the self diffusion is reported, as, the out of plane diffusion coefficient was indirectly estimated $D_{//} \approx 0$, as previously discussed. This result is somewhat in disagreement with previous data reported for the smectic B phase [1]. In particular, a reduction of the diffusion anisotropy $D_{//}/D_{\perp}$ was found in previous measurements [1], passing from the Smectic A to the Smectic B phase and this was qualitatively explained considering the incoming a certain order in the smectic layers [1]. In the present case, however, the data measured in the smectic B phase of FAB.CO6, seem to be more consistent with a phase where some translational diffusion freedom is still present within the smectic layer, while translation across the layer is so strongly inhibited to be not detectable by our experimental setup. In this picture, the anisotropy $D_{//}/D_{\perp}$ further decreases in respect to one in the smectic A phase. Moreover, the in plain diffusion coefficient here measured is about one order of magnitude smaller than the ones previously reported [1]. Of course, other measurements should be carried out in similar systems in order to investigate this behaviour in more details. In particular we think that it would be fruitful to perform measurements in those systems presenting also the intermediate Smectic B hexatic phase [18]. This will be material for further work.

Self-Diffusion Data Analysis Exploiting Theoretical Models

As previously reported good quality data sets can be used to determine the activation energy of the different diffusion process, the diffusion anisotropy and test theoretical models for the nematic and smectic A phases [4,7,8]. In this context, we report a detailed analysis of the present data set, in the isotropic, nematic and smectic A phases.

Isotropic Phase

The translational self-diffusion in the isotropic phase follows Arrhenius behaviour

$$D_{iso}(T) = D^{*}e^{-\frac{E_a}{RT}} \tag{12}$$

The fitting is reported in Figure 4. The best fitting parameters obtained are $D^{*} = 2.9\text{e-}04\,\mathrm{m}^2/\mathrm{s}$ and $E_a = 41\,\mathrm{KJ/mol}$. The activation energy is in qualitative agreement with other mesogens already investigated [4,5,8].

Nematic Phase

Several models have been proposed for the nematic phase [19,20,21]. Recently, the model proposed by Allen *et al.* [21], based on the modified affine transformation (MAT) theory, has been successfully tested on the nematic phases of three mesogens [4], proving to be the most reliable. This model derives the expressions for $D_{//}$ and $D_{\perp}$ considering the affine transformation from the isotropic diffusion of hard spheres to the space of aligned uniaxial ellipsoids. That is, for molecules with a axial ratio $Q = l/d$ (l is the long axe of the ellipsoid and d is the diameter) $D_{//}$ and $D_{\perp}$ are expressed as:

$$D_{//} = \widetilde{D}\alpha\left\{Q^{\frac{4}{3}} - \frac{2}{3}Q^{\frac{-2}{3}}(Q^2 - 1)(1 - S)\right\} \tag{13}$$

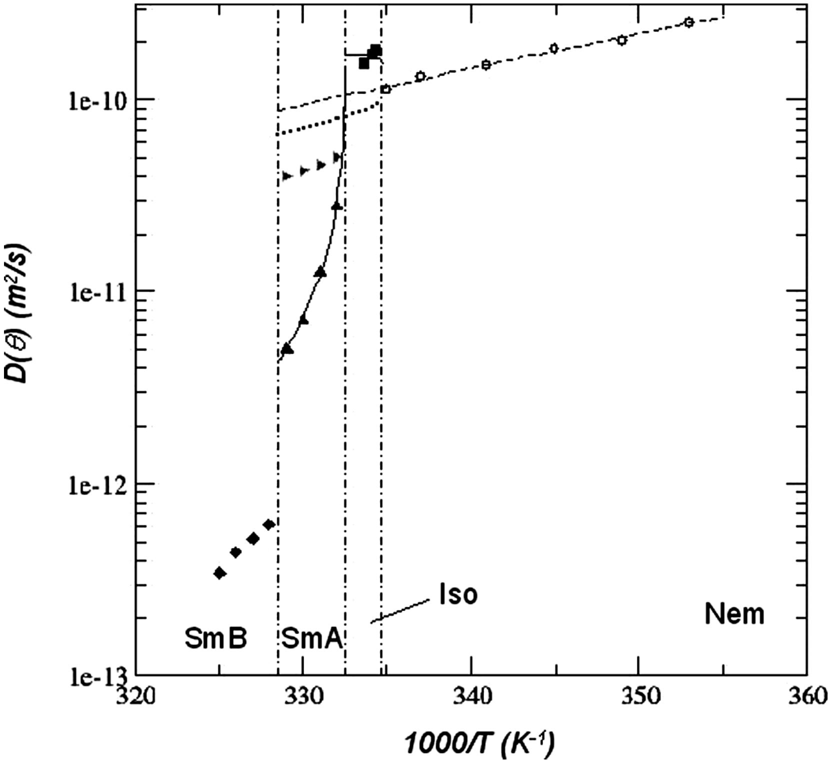


FIGURE 4 Results of the experimental data analysis exploiting the theoretical models for the nematic and smectic A phase, as discussed in the text. The curves represent the best fitting of the experimental data in the different phases analyzed; the broken line reproduces the isotropic behaviour while the full line is the best fit for the experimental $D_{//}$'s in the nematic and smectic A phases. Also the behaviour of $D_{\perp}$ in the nematic and smectic A phase (dotted line), calculated using the MAT model is reported, denoting a discrepancy between the calculated and experimental behaviour in the smectic A phase.

$$D_{\perp} = \widetilde{D}\alpha\left\{Q^{\frac{-2}{3}} - \frac{1}{3}Q^{\frac{-2}{3}}(Q^2-1)(1-S)\right\} \tag{14}$$

where

$$\alpha = \left[1+\frac{2}{3}(Q^2-1)(1-S)\right]^{-\frac{1}{3}}\left[1+\frac{1}{3}(Q^{-2}-1)(1-S)\right]^{-\frac{2}{3}} \tag{15}$$

S being the nematic order parameter. Practically the order parameter scales down the results obtained in a perfectly ordered ($S = 1$) nematic cluster of prolate ellipsoids.

In particular it has been shown that the geometric average:

$$\widetilde{D} = \left(D_{//}D_{\perp}^2\right)^{\frac{1}{3}} \tag{16}$$

well reproduces the extrapolated isotropic behaviour in the nematic phase [4], that is:

$$\widetilde{D} = (D_{//}D_{\perp}^2)^{\frac{1}{3}} = D_{iso}^{Ext} = D^* e^{-\frac{E_{iso}}{RT}} \tag{17}$$

where D^* and E_{iso} are the best fitting parameters obtained from the Arrhenius fitting in the isotropic phase, while T is within the nematic range.

This finding gives the opportunity to determine $D_\perp$, from our data set, exploiting the experimental determined $D_{//}$ and the extrapolated D_{iso} in the nematic phase.

$$D_\perp = \sqrt{\frac{\widetilde{D}}{D_{//}}} = \sqrt{\frac{D_{iso}^{Ext}}{D_{//}}} = \sqrt{\frac{D^* e^{-\frac{E_{iso}}{RT}}}{D_{//}}} \tag{18}$$

The so determined $D_\perp$ data set is also reported in Figure 4 (dotted line).

Now, in order to fully exploit Equations (13) and (14) for modelling diffusion data in the nematic phase, we notice that both depend on the geometric average $\widetilde{D}$, the orientational order parameter S and the axial ratio Q. Of these three parameters, the geometrical average $\widetilde{D}$ can be calculated recurring to Eq. (18) using the Arrhenius parameters determined in the isotropic phase, while the S temperature behaviour can be modelled fitting literature data, obtained by means of deuterium NMR [14], with the phenomenological Haller expression [22]:

$$S = \left(1 - \frac{T}{T^\circ}\right)^{\nu} \tag{19}$$

where T° is a temperature near the isotropic-nematic phase transition and ν an exponent. The fitting produces the following parameters: $T^\circ = 334.5\,\mathrm{K}$ and $\nu = 0.179$.

It follows that the fitting procedure reduces to the optimization of the Q parameters only that turns out to be $Q = 2.66$, after the fitting optimization. The best fit curve is reported in Figure 4 with experimental $D_{//}$ data.

Actually, it must be noticed that the fitting is not as good as for other previously investigated mesogens [4]. This could be ascribed to the short range of the nematic phase making difficult to frame the fitting in a "good" minimum, but also to the presence of a bi-phasic region in which the nematic and smectic A phase coexist [14]. As in the present measurements it hasn't been possible to evaluate separately the two contributions to self diffusion the best fitting parameters obtained have been considered just as a reasonable starting point for smectic A data analysis that follows in the next section.

Smectic A Phase

The effect of the layered structure on the self-diffusion behaviour of FAB.O6 can be considered in detail following the model proposed by Volino and Dianoux [23]. In the model out of plane diffusion in a smectic A phase is reconsidered assuming a periodic temperature independent potential along the nematic director:

$$V = (V_1/2)\cos(2\pi z/d) \tag{20}$$

d being the layer spacing.

This leaves unaffected the in-layer diffusion (that should hence remain nematic-like) but creates a potential barrier for the cross-layer component $D_{//}$. Consequently, the two diffusion coefficients are rewritten as:

$$D_{//}^{smectic} = D_{//}^{nematic}[I_0(V_1/2RT)]^{-2} \tag{21}$$

$$D_{\perp}^{smectic} = D_{\perp}^{nematic} \tag{22}$$

where I_0 is the modified Bessel function of the first kind and zero order [23]. From Eqs. (21) and (22) is clear that only changes in the diffusion along the phase director should be expected while the in plane diffusion remains nematic-like. The same theoretical result has also been obtained by Moro *et al.* [24] by considering the diffusion equation in presence of a periodic potential.

Recently the model has been slightly modified, taking into account a temperature dependent potential [4] is analogous to that describing translational order parameter behaviour modelled by McMillan for the smectic A phase [17].

$$V_1(T) = V_0(1 - T/T_0)^p \tag{23}$$

with V_0, T_0 and p phenomenological parameters.

This modification was necessary to fit experimental data in the case of 8CB [4] and 8OCB [7], otherwise not reproducible in the case of the original temperature independent potential and also confirmed by simulations of the diffusional behaviour in the nematic and smectic A phases of a Gay-Berne mesogen by Bates and Luckhurst [25].

Within this picture, the equations describing the diffusion coefficients in the smectic A phase have to be rewritten as:

$$D_{//}^{smectic} = D_{//}^{nematic}[I_0(V_0(1 - T/T_0)^p/2RT)]^{-2} \tag{24}$$

$$D_{\perp}^{smectic} = D_{\perp}^{nematic} \tag{25}$$

Equation (24) can be confidently used to fit the diffusion data set collected in the smectic A phase, with the nematic parameters fixed from the previous fitting and V_0, T^* and p allowed to float [4,8].

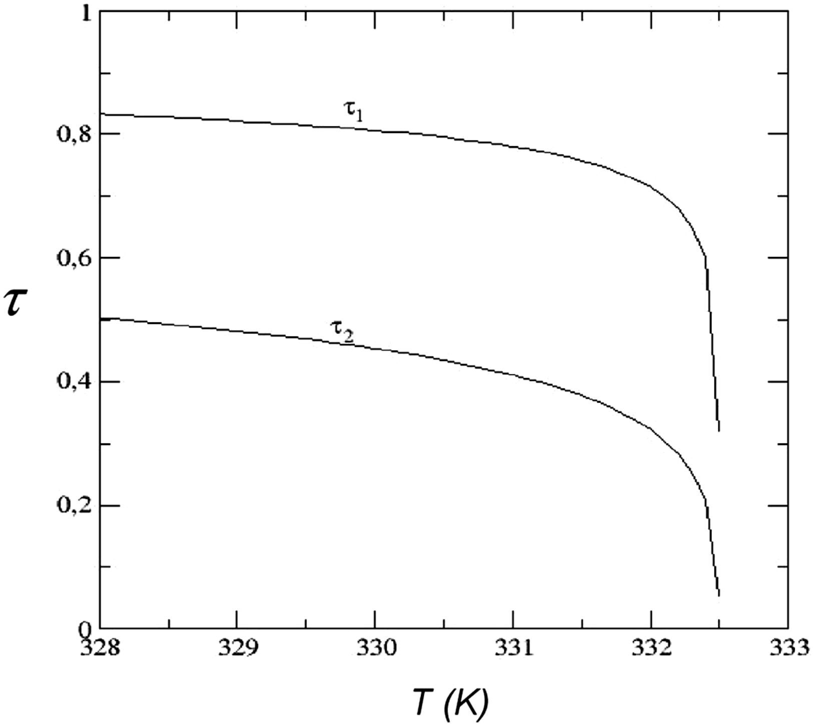


FIGURE 5 First and second order positional order parameters calculated from Equation (27) using the barrier potential V_1, evaluated as described in the text. It can be noticed that the τ_1 behaviour is in agreement with a first order nematic-smectic A phase transition with a sudden consolidation of a positional order (~ 0.3), that increases as the temperature decreases.

The best fit is reporter in Figure 4, obtained optimizing the parameters to $V_0 = 44.4 KJ/mol$, $T^* = 332.5 K$ and $p = 0.206$. The high V_0 potential is indeed in agreement with the McMillan theory for the nematic to smectic A phase transition, which predicts a stronger first transition the larger is the ratio between the transition temperatures $T_{Iso-Nem}/T_{Nem-SmA}$ [17], with a smectic order the sudden consolidates to a reasonably high value at the phase transition and then increases as the temperature decreases (see Fig. 5).

Concerning diffusion perpendicular to the phase director, it appears clear that the extrapolated values in the nematic phase and the measured values in the smectic A phase (see Fig. 4) do not deviate from the assumption of Equation (25). It seems actually that a strong first order nematic to smectic A transition also affects $D_\perp$ going from the nematic to the smectic A phase, as already noticed in the case of the nematic-smectic A transition of the mesogen 4-4′-di-n-octyl-azoxybenzene. This will be also a subject for further investigation.

CONCLUSIONS

^{1}H Fringe field NMR diffusometry has been used to measure diffusion coefficients in the isotropic, nematic and smectic phases of the fluorinated mesogen FAB.OC6. The good quality of the data set allowed a detailed investigation of the diffusional behaviour in terms of well established models for the nematic and smectic A phases.

In particular, it emerges that the model accepted for the smectic A phase provides a good description of the in out of plains diffusion coefficient but it seems to fail for the in plain one, where the assumption of Equation (22) $D_\perp^{smectic} = D_\perp^{nematic}$ does not work properly if we consider that the nematic phase of the FAB.O6 follows a typical nematic behaviour. This suggest that maybe the model should be reconsidered at least for the $D_\perp$ component. In this context it would be useful to perform direct measurements of $D_\perp^{nematic}$ in samples that (of course) present a nematic-smectic A phase transition with different ratio of $T_{Iso-Nem}/T_{Nem-SmA}$, in order to provide reliable experimental data sets. With this in mind, we're preparing an experimental setup that exploits an electric field as orientation means of the liquid crystal that will allow the determination of $D(\theta)$ at different θ angles in the nematic phase also. A similar approach has been already used by Holstein *et al.*, to orient the 5CB nematic phase at the magic angle in respect to the static magnetic field [26]. In that case however the work was limited to determine the $D(54.7^\circ)$ coefficient in the nematic phase at one temperature.

Finally, we notice that the determination of the smectic potential $V_1(T)$ may also provide a way to obtain information on smectic A positional order parameters of Nth order:

$$\tau_N = \left\langle \cos\left(2\pi N \frac{\mathbf{r}\cdot\hat{n}}{d}\right)\right\rangle \tag{26}$$

where $\mathbf{r}$ is the molecule position, $\hat{n}$ is the director direction and d the layer spacing. In fact, these parameters can be expressed, within the Volino and Dianoux model as [23]:

$$\tau_N = \frac{I_N(V_1/2RT_1)}{I_0(V_1/2RT_1)} \tag{27}$$

and hence determining V_1 should lead to a determination of smectic order parameters τ_N from Eq. (27).

As a matter of example, the τ_1 and τ_2 evaluation for the present case are reported in Figure 5, but the procedure has been recently tested by means of simulations and applied to the experimentally determined diffusion tensors data of two azoxy-mesogens and reported in one other work [27].

EXPERIMENTAL

All the experiments were performed in the fringe field gradient of a 9.4 T Varian Infinity plus Spectrometer. The exact position corresponded to a proton resonance frequency of 161.86 MHz, (located 280 mm below the iso-centre), where the nominal field gradient strength in the vertical ($z//B_0$) direction of the magnet has been evaluated 63 T/m.

A wide line multi-frequency probe has been used with a pw90 pulse of 1 μs for the proton at the work frequency. The probe is also equipped with a goniometer that allowed sample rotation in the smectic phases, uniformly aligned along the magnetic field from the nematic phase.

Diffusion was measured in a sample of magnetic field oriented *p*-hexyloxybenzylidene-p′-fluoroaniline liquid crystal (FAB.OC6). This liquid crystal presents nematic smectic A and smectic B phases. The sample was obtained by Dr. C. Gandolfo and used without further purification. It showed a isotropic to nematic phase transition at 334.4 K, a nematic to smectic A phase transition at 330.7 K and a smectic A to smectic B phase transition at 328 K, in good agreement with other results reported in literature [14]. As in previous cases [7] the static fringe field NMR did not allow to directly verify the degree of orientation of the nematic phase director with respect to the static magnetic field. However, to our knowledge, magnetic fields less than 3.78 T, as the one here used, homogeneously align the nematic phase of similar mesogens [15]. We then considered that this also happened in the present case.

The echo decays were collected using the two pulse sequences previously discussed as a function of the diffusion time Δ. The interval τ (fixed for each experiment) ranged from 30 to 70 μs as the temperature decreased while δ was fixed to 6 μs. The echoes appear very narrow in the time domain due to the high field gradient. The echoes were sampled at intervals of 1 μs and the echo maximum amplitude extracted. Between 32 and 160 echoes were acquired and averaged for each experiment with a repetition time of 5 seconds to ensure full longitudinal spin relaxation.

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