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Anisotropic self-diffusion in nematic, smectic-A, and reentrant nematic phases

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The nature of the reentrant nematic phase has been actively investigated both experimentally and theoretically during the past few decades. Most studies concluded that, as concerning molecular dynamics, a reentrant nematic phase is essentially analogous to a conventional nematic one. Recent computer simulations [Mazza *et al.*, Phys. Rev. Lett. **105**, 227802 (2010)], however, predicted molecular translational self-diffusion along the phase director that was dominated by a collective transport mode and was, relative to that observed in a conventional nematic phase, enhanced by an order of magnitude. In the present work, the principal components of the diffusion tensor in a reentrant nematic phase are determined experimentally and compared to those in conventional nematic and smectic-A phases. We find that the temperature dependence of the translational diffusion in the two nematic phases, within experimental error, follows a uniform trend and can be adequately described in terms of available diffusion models in nematics. Hence, we find no evidence for enhanced diffusion but confirm instead the similarity of conventional and reentrant nematic phases with respect to molecular translational dynamics.

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I. INTRODUCTION

Recently, there has been renewed interest in molecular dynamics in reentrant nematic phases of thermotropic liquid crystals (LCs) [1,2]. Conventionally, thermotropic LCs exhibit the phase sequence isotropic-nematic-smectic (I-N-Sm) as the temperature decreases [3]. In the 1970s, it was discovered that in some mixed mesogenic compounds a second nematic phase, called reentrant nematic (RN), is present below the smectic-A phase (SmA) [4]. The SmA-to-RN phase transition implies that the two-dimensional layer structure present in SmA melts on *lowering* the temperature. The nature of this intriguing phenomenon has been actively investigated both experimentally and theoretically during the past few decades [5–7]. Most studies concluded that molecular dynamics in a reentrant nematic is essentially analogous to that in a conventional nematic phase. In contrast to an invariant *local* molecular dynamics, recent computer simulations of the reentrant phase predicted molecular translational self-diffusion along the director that is substantially enhanced [1]. An increase by up to an order of magnitude compared to diffusion in the corresponding conventional nematic phase has been linked to the stringlike arrangement of perfectly aligned and translationally synchronized molecules [2]. Reentrant nematic phases obtained by rising pressure [1] or under isobaric cooling [8] exhibited essentially similar diffusion enhancement effects. While the simulations were performed in a confined mesophase, it was argued that bulk reentrant nematics exhibit similar features [7,8].

Yet, no direct experimental studies of translational diffusion have been reported in an RN phase. Estimates based on NMR relaxation rates are rather speculative as relaxation by translational diffusion cannot be reliably separated from other, often dominating, relaxation mechanisms [9,10]. While pulsed-field-gradient spin-echo-type NMR [11] is nowadays a routine method for diffusion studies in isotropic liquids, it is not directly applicable in a mesophase due to the fast decay of spin coherences in an anisotropic environment [12,13]. In fact, it has only been recently that reliable NMR methods for studies of diffusion in mesophases have been developed which, when applied with insight, provide accurately the diffusion tensor components [12,14,15]. These approaches have been demonstrated in a number of lyotropic and thermotropic systems [16–18]. In the present work, the principal diffusion coefficients in a reentrant nematic phase are measured. The results obtained in a wide temperature range permit us to compare the diffusion behavior to that in both SmA and conventional nematic phases of the same compound as well as in nematic and SmA phases of the LCs without reentrant phases.

II. EXPERIMENT

Mesogens 6OCB and 8OCB were obtained from Sigma-Aldrich. Samples of pure components and their mixture containing 27.2 wt% of 6OCB were prepared in 5 mm NMR tubes. The transition temperatures of the mixture as determined by direct visual inspections of the sample (the sample is turbid in both nematic phases but turns transparent in the isotropic and smectic-A regions) were $T_{IN} = 351$ K, $T_{N\text{-Sm}A} = 316$ K, and $T_{\text{Sm}A\text{-RN}} = 304$ K in agreement with the reported phase diagram [19,20].

All ^{1}H pulsed-field-gradient spin-echo-type NMR measurements were performed on a Bruker Avance III 500 MHz spectrometer equipped with a Micro5 microimaging probe with gradient strength up to 290 G/m in three orthogonal directions. An NMR diffusion experiment in isotropic liquids typically proceeds by recording the decay of the NMR signal intensity with increasing gradient strength, as given by the expression [11]

$$A(g,\delta,\Delta) \propto \exp[-(\gamma g\delta)^2(\Delta - \delta/3)D], \qquad (1)$$

where D is the self-diffusion coefficient, γ is the magnetogyric ratio, g is the strength of the magnetic field gradient, δ is the length of the gradient pulse, and Δ denotes the diffusion delay. To achieve sufficient attenuation of the NMR signal,

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gradient pulse length δ in the millisecond range is typically required [11]. In isotropic liquids, the transverse relaxation time T_2 sets the upper limit for the length of δ. Hence, routine diffusion experiments are only possible in samples with sufficiently long relaxation $T_2 > 1$ ms. In mesophases and in other anisotropic materials, the decay of spin coherences is, in addition to transverse relaxation, affected by static dipolar (or quadrupolar) broadening which limits the lifetime of spin coherences to 100 μs or lower. Fortunately, this lifetime can be prolonged by using spin decoupling [21]. Suitable combinations of pulse field gradient and spin decoupling have been developed by us some years ago and have been used for studies of diffusion processes in a number of lyotropic and thermotropic samples [12]. In the present work, we combine pulsed-field-gradient stimulated echo (STE) with magic-echo decoupling. Detailed experimental protocol is given elsewhere [12,14]. In the isotropic phase a conventional STE sequence was applied [11].

III. RESULTS AND DISCUSSION

All measurements were performed in samples with their directors aligned homogeneously parallel to the magnetic field of the NMR magnet. Diffusion coefficients along and normal to the director, $D_\parallel$ and $D_\perp$, were obtained in separate experiments with the gradients applied either parallel or perpendicular to the main magnetic field direction.

In Fig. 1 the experimental echo decays obtained in the nematic phase of the 6OCB/8OCB mixture for two orthogonal gradient directions are displayed and also compared to the decay in the isotropic phase. Single-component decay of signal intensity by up to two orders of magnitude reflects free (unrestricted) diffusion. It is also obvious that diffusion in the nematic phase is anisotropic and $D_\parallel > D_\perp$ [cf. Eq. (1)]. Similar features were observed in SmA and RN phases. The diffusion coefficient in the isotopic phase D_{iso} was, as expected, independent of the gradient direction.

The diffusion data for the whole temperature range of mesophase existence of the 6OCB/8OCB sample are displayed as an Arrhenius plot in Fig. 2(a). The following features are observed: (i) the diffusion is anisotropic and the relationship $D_\parallel > D_\perp$ holds in the whole mesophase range; (ii) the diffusion coefficients decrease monotonously with the temperature; (iii) no significant discontinuities are observed at the N-SmA and SmA-RN phase transitions; (iv) in a wide temperature range covering the RN, SmA, and most of the N phases the temperature dependence of the diffusion coefficients can be approximated by Arrhenius behavior with corresponding activation energies $E_\parallel \leqslant E_\perp$; and (v) $D_\parallel$ and $D_\perp$ bend toward D_{iso} in the immediate vicinity of the clearing temperature T_{IN}.

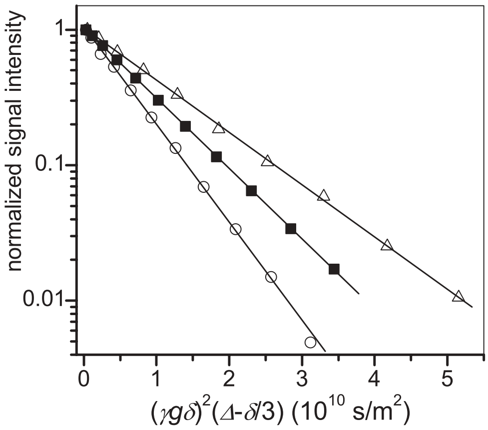

FIG. 1. NMR diffusional signal decays recorded in the isotropic phase at 80 °C (squares) and in the nematic phase at 77 °C of the 6OCB/8OCB mixture along and normal to the director (circles and triangles, respectively).

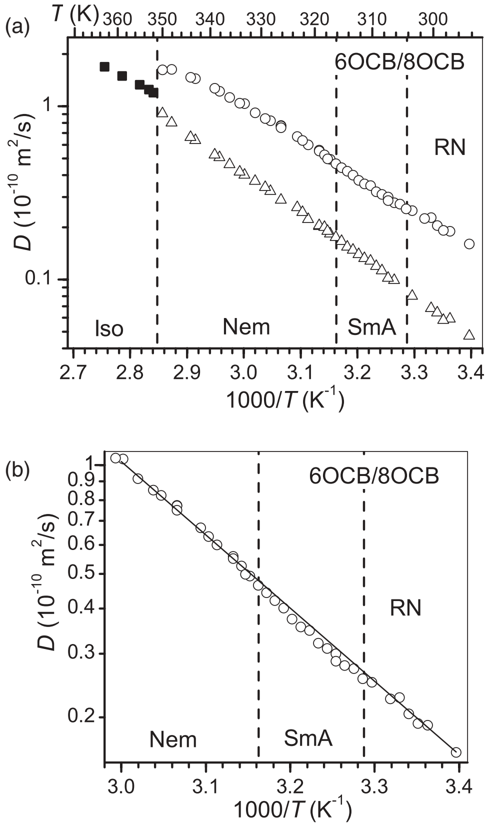

FIG. 2. (a) The temperature dependence of the diffusion coefficients D_{iso}, $D_\parallel$, and $D_\perp$ (squares, circles, and triangles, respectively) in 6OCB/8OCB (27 wt% 6OCB) mixture. (b) Expansion showing the comparison of $D_\parallel$ in nematic, smectic-A, and reentrant nematic phases.

Our main finding is that no dramatic changes of diffusion can be observed while passing from the nematic to the reentrant nematic phase. In fact, the diffusion coefficients in both nematic phases can be fit by a single Arrhenius-type temperature dependence with activation energy of $E_\parallel = 39$ kJ/mol. In contrast, a slight decrease of $D_\parallel$ in the SmA phase is observed, when compared to the trends in the N and RN phases [Fig. 2(b)]. Such a decrease is expected due to the layered SmA structure and has previously been observed in other smectic-A liquid crystals [17,22]. It is striking that upon entering the RN phase, the diffusion trend observed at higher temperatures in the nematic phase is restored. Transition to the smectic phase has no influence on the behavior of $D_\perp$. Activation energy $E_\perp$ is estimated to 45 kJ/mol. Considering that molecular displacements monitored in an NMR diffusion experiment

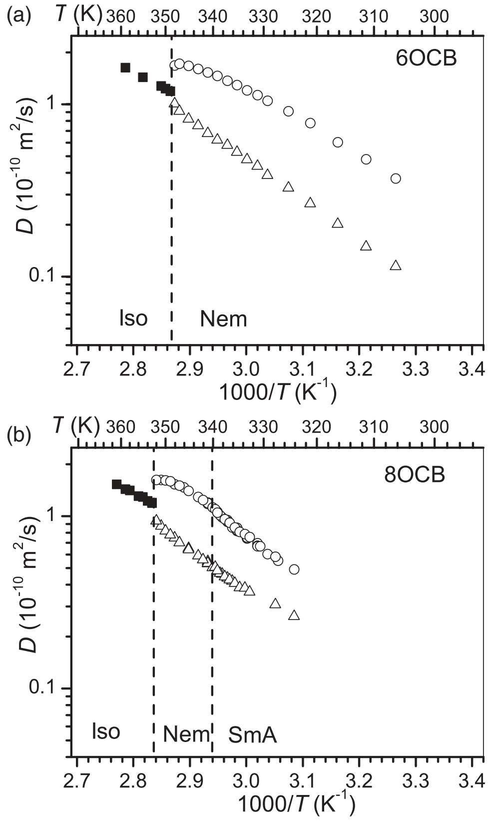

FIG. 3. The temperature dependence of the diffusion coefficients $D_{\text{iso}}, D_{\|}$, and $D_{\perp}$ (squares, circles, and triangles, respectively) in (a) 6OCB and (b) 8OCB.

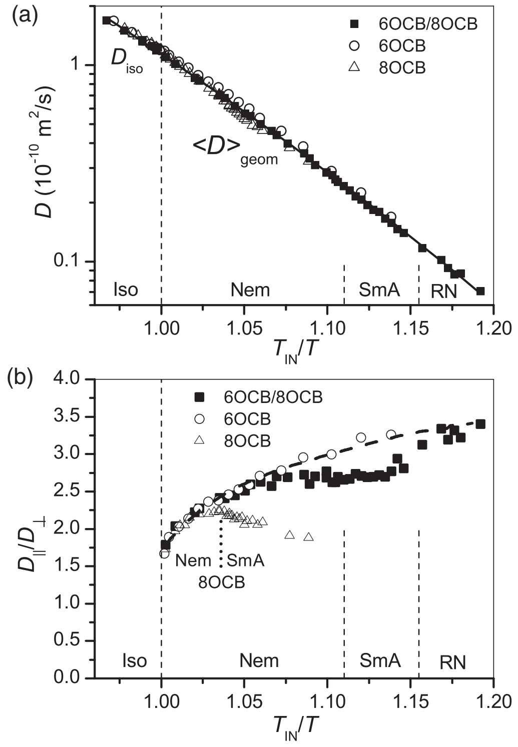

FIG. 4. Comparison of (a) the geometric average diffusion coefficient $\langle D\rangle_{\text{geom}} = D_{\|}^{1/3} D_{\perp}^{2/3}$ and (b) the anisotropy ratio $D_{\|}/D_{\perp}$ in 6OCB/8OCB, 6OCB, and 8OCB samples. The line in (a) represents a Vogel-Fulcher-Tamman fit [Eq. (2)] to the $\langle D\rangle_{\text{geom}}$ data in 6OCB/8OCB with $D_0 = 6.56 \times 10^{-7}$ m^2/s, $B = 2000$ K, and $T_0 = 120$ K. Line in (b) is a guide for the eyes. Phase boundaries *N*-*Sm*A and *Sm*A-RN for the 6OCB/8OCB mixture are shown by dashed lines, and phase boundary *N*-*Sm*A for 8OCB is shown by dotted line.

are in the order of micrometers, our results confirm that two nematic phases are identical as concerning translational dynamics on this scale.

To get further insight into the translational dynamics in the 6OCB/8OCB mixture, we performed diffusion studies in the pure components 6OCB and 8OCB (Fig. 3). 6OCB exhibits only a nematic phase, while in 8OCB a nematic and a Sm*A* phase are present. The diffusion behavior in pure components is in agreement with previous observations in other nematic and smectic compounds and can be described by established models [15,17,22]. In particular, the geometric average of the principal diffusion coefficients in the nematic phase, $\langle D\rangle_{\text{geom}} = D_{\|}^{1/3} D_{\perp}^{2/3}$, fits accurately to the temperature dependence extrapolated from the isotropic phase [Fig. 4(a)] as predicted by the affine transformation model [23]. In the SmA phase, the decrease of $D_{\|}$ with respect to that in the nematic phase at higher temperatures [Fig. 3(b)] is described by a suitably modified model of Volino *et al.* [17,24].

In Fig. 4 we compare pure 6OCB, 8OCB, and the 6OCB/8OCB mixture in terms of geometric average coefficient $\langle D\rangle_{\text{geom}}$ and diffusion anisotropy $D_{\|}/D_{\perp}$ plotted against reciprocal temperature normalized to the clearing temperature T_{IN}. A continuous change of $\langle D\rangle_{\text{geom}}$ at the phase transitions including isotropic-nematic is evident [Fig. 4(a)] and the data for the three samples virtually coincide. A slight deviation from the Arrhenius behavior [note the larger temperature range as compared to Fig. 2(b)] is observed which is common in liquids if a sufficiently large temperature range is considered [25] and is often well represented by the Vogel-Fulcher-Tamman equation

$$D = D_0 \exp[-B/(T - T_0)]. \tag{2}$$

The anisotropy ratios in 6OCB/8OCB, 6OCB, and 8OCB samples coincide in the nematic range. The trend extrapolated to the RN phase compares well with the experimental anisotropy values obtained there. As expected [17], the anisotropy ratio is lower in the Sm*A* phase and also in the nematic phase in the pretransitional region adjacent to Sm*A*.

In the theoretical models of the nematic phase the diffusion coefficients are typically expressed in terms of the molecular order parameter *S* and the geometry of the mesogenic units, either molecules or molecular aggregates [23,26]. The order parameter *S* of the 6OCB/8OCB system obtained by different experimental techniques has been reported [27,28]. While often in disagreement as concerning the absolute value of *S*, the consistent conclusion from the data is that the molecular order parameter is very similar in the *N* and RN phases (if the conventional temperature effect is accounted for). Molecular geometry is typically accounted for in terms of axial ratio $Q = L/d$, where L and d are the molecular length and diameter, respectively. When molecular aggregates are present, for example, in the form of dimers [20,29,30], as is typical for molecules with a terminal cyano group, the axial ratio of the whole aggregate is relevant. Some models of reentrant nematic behavior point to molecular association as an important factor for RN phase formation [30–33]. However, if the shape of the mesogenic unit were significantly different in the *N* and RN phases, that should be reflected in the diffusion anisotropy ratio. Instead, we can conclude from the similar anisotropy observed in the *N* and RN phases that, if aggregates are present, they are of similar appearance and prevalence in the two phases.

IV. CONCLUSION

We have presented here the experimental values of the principal components of the translational diffusion tensor in a thermotropic liquid crystal exhibiting nematic, smectic-*A*, and reentrant nematic phases. The results in the nematic and smectic phases are in agreement with behavior in similar systems and can be described in the terms of established theoretical models. The diffusion tensor was measured in a reentrant nematic phase. In contrast to the predictions of computer simulations [1] we find no sign of any significant acceleration of molecular self-diffusion in the RN phase when compared to conventional nematics. Instead, translational dynamics of the molecules in those two phases is very similar and any difference can be accounted for by conventional Arrhenius-type thermal activation. Changes in the diffusion coefficients upon transitions to smectic *A* both from normal and reentrant nematic phases are minor, confirming subtle molecular rearrangement in the transverse plane upon the nematic-smectic transition [19]. In addition, we find that the similar value of the diffusion anisotropy points to similar shapes of the mesogenic units, single molecules or molecular aggregates, in the nematic and reentrant nematic phases.

The studied sample with a reentrant phase is a mixture of two thermotropic components and in our experiments the diffusion of two constituents was not observed separately. It is, though, possible to independently measure the diffusion of the different molecules in the mixture, e.g., by using deuterated components. However, considering the very similar molecular shapes and the close values of the diffusion coefficients in the pure samples, as well as the single-exponential diffusional decay observed in the reentrant phase, it seems unlikely that the two constituents exhibit significantly different diffusion behavior. Studies of other samples exhibiting reentrant phases may show how general the present findings are. Particularly, reentrant phases formed in single-component LCs are of interest even though they may turn out to be somewhat more difficult to measure at the typically high temperatures where such mesophases exist [7,33].

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[1] M. G. Mazza, M. Greschek, R. Valiullin, J. Karger, and M. Schoen, Phys. Rev. Lett. **105**, 227802 (2010).

[2] M. G. Mazza, M. Greschek, R. Valiullin, and M. Schoen, Phys. Rev. E **83**, 051704 (2011).

[3] D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill, *Handbook of Liquid Crystals* (Wiley-VCH, Weinheim, 1998).

[4] P. E. Cladis, Phys. Rev. Lett. **35**, 48 (1975).

[5] T. Narayanan and A. Kumar, Phys. Rep. **249**, 135 (1994).

[6] S. Singh, Phase Transit. **72**, 183 (2000).

[7] M. G. Mazza and M. Schoen, Int. J. Mol. Sci. **12**, 5352 (2011).

[8] T. Stieger, M. G. Mazza, and M. Schoen, Int. J. Mol. Sci. **13**, 7854 (2012).

[9] S. Miyajima, K. Akaba, and T. Chiba, Solid State Commun. **49**, 675 (1984).

[10] P. J. Sebastiao, A. C. Ribeiro, H. T. Nguyen, and F. Noack, J. Phys. II **5**, 1707 (1995).

[11] P. T. Callaghan, *Translational Dynamics and Magnetic Resonance* (Oxford University Press, Oxford, 2011).

[12] S. V. Dvinskikh and I. Furó, Russ. Chem. Rev. **75**, 497 (2006).

[13] I. Furó and S. V. Dvinskikh, in *Modern Magnetic Resonance*, edited by G. A. Webb, Vol. 1 (Springer, Dordrecht, 2006), p. 113.

[14] S. V. Dvinskikh, I. Furó, D. Sandström, A. Maliniak, and H. Zimmermann, J. Magn. Reson. **153**, 83 (2001).

[15] S. V. Dvinskikh and I. Furó, J. Chem. Phys. **115**, 1946 (2001).

[16] M. Kadi, S. V. Dvinskikh, I. Furó, and M. Almgren, Langmuir **18**, 5015 (2002).

[17] S. V. Dvinskikh, I. Furó, H. Zimmermann, and A. Maliniak, Phys. Rev. E **65**, 061701 (2002).

[18] M. Cifelli, V. Domenici, S. V. Dvinskikh, M. Glogarova, and C. A. Veracini, Soft Matter **6**, 5999 (2010).

[19] A. R. Kortan, H. V. Kanel, R. J. Birgeneau, and J. D. Litster, Phys. Rev. Lett. **47**, 1206 (1981).

[20] P. E. Cladis, Liq. Cryst. **24**, 15 (1998).

[21] M. J. Duer, *Introduction to Solid-State NMR Spectroscopy* (Blackwell, Oxford, 2005).

[22] M. Cifelli, P. J. McDonald, and C. A. Veracini, Phys. Chem. Chem. Phys. **6**, 4701 (2004).

[23] S. Hess, D. Frenkel, and M. P. Allen, Mol. Phys. **74**, 765 (1991).

[24] F. Volino, A. J. Dianoux, and A. Heidemann, J. Phys. Lett. (Paris) **40**, L583 (1979).

[25] W. S. Price, H. Ide, and Y. Arata, J. Phys. Chem. A **103**, 448 (1999).

[26] K.-S. Chu and D. S. Moroi, J. Phys. Colloque (Paris) **36**, C1 99 (1975).

[27] M. K. Das and R. Paul, Mol. Cryst. Liq. Cryst. **239**, 107 (1994).

[28] R. Y. Dong and M. Cheng, J. Chem. Phys. **113**, 3466 (2000).

[29] P. E. Cladis, Mol. Cryst. Liq. Cryst. **165**, 85 (1988).

[30] A. Prasad and M. K. Das, Phase Transit. **82**, 780 (2009).

[31] A. Ferrarini, G. R. Luckhurst, P. L. Nordio, and E. Spolaore, Mol. Phys. **89**, 1087 (1996).

[32] P. E. Cladis, R. K. Bogardus, and D. Aadsen, Phys. Rev. A **18**, 2292 (1978).

[33] G. Sigaud, N. H. Tinh, F. Hardouin, and H. Gasparoux, Mol. Cryst. Liq. Cryst. **69**, 81 (1981).