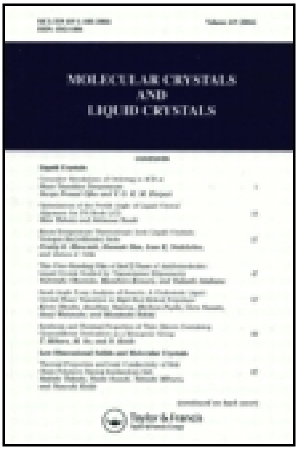

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Glass-like Behavior at Molecular Level Induced in a Nematic by a Dispersion of Aerosil Nanoparticles

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Glass-like Behavior at Molecular Level Induced in a Nematic by a Dispersion of Aerosil Nanoparticles

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Random disorder effects of an hydrophobic aerosil on the order and dynamics of the 3β-DOXYL-5α-cholestane spin probe in the liquid crystal 4-n-pentyl-4′-cyanobiphenyl (5CB) were studied using the ESR technique. Increasing the aerosil concentration up to 10 wt% does not change the nematic–isotropic transition temperature but decreases the probe order parameter. The dynamics in the isotropic phase is of Arrhenius type and essentially independent of the concentration. Deviations from this behavior are clearly observed in the nematic phase even at 1 wt% of aerosil and are well represented by a Vogel-Fulcher-Tammann type law, suggesting that a glass-like behavior can be induced by a very small amount of random disorder.

PACS numbers: 61.30.Gd, 76.30.-v, 82.70.Gg

Keywords: ESR spin probe; filled nematics; hydrophobic aerosil; non Arrhenius dynamics; random disorder

I. INTRODUCTION

Aerosil nanoparticles dispersed in a liquid crystal (LC) matrix (Filled Nematics) have been attracting an increasing interest related to their promising applications in the field of high-information-content flat displays [1]. These materials, in fact, can exhibit a “memory effect” where the electric field-induced orientation of the LC remains stable after field removal. This effect was explained assuming that the LC reorientation causes a reorganization of the initial random structure of the

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Address correspondence to Claudio Zannoni, E-mail: claudio.zannoni@cineca.it aerosil network which then stabilizes the oriented state [2]. The memory effect can be considered as a manifestation of the macroscopic glass-like state of the system. It might be argued that the glassy behavior could be observed also at molecular level or, alternatively, that it is a reflection, on a larger scale, of the slowing down of the dynamics originating directly at molecular level.

In order to understand the origin of the memory effect and of the glassy behavior of filled nematics, during the last years, dynamic studies aiming at understanding the relationships between the macroscopic and the molecular level have received a growing attention. Collective dynamics, associated with director fluctuations, appears to be strongly influenced by the aerosil concentration and by the chemistry of its surface [3] whereas, at molecular level, the local dynamics remains essentially bulk-like [4] even if the macroscopic viscosity of the dispersion increases by several order of magnitude from that of a liquid to that of a gel [5]. Interestingly, this locally fluid dynamics can have a temperature dependence typical of a fragile glass forming system [5,6].

In the present paper we focus the attention on the dynamic behavior of R812 hydrophobic aerosil dispersions in 4-n-pentyl-4$'$-cyanobiphenyl (5CB) LC. Using ESR spin probe technique, we analyze the effects induced by the aerosil on the LC host across the gelation threshold ($0.01\,\mathrm{g/cm^3}$) and in the soft-gel regime (up to $0.1\,\mathrm{g/cm^3}$).

II. EXPERIMENTAL

The liquid crystal 5CB was obtained from Merck KGaA (Darmstadt, Germany). This compound exhibits, on heating, the nominal phase sequence: Crystal – N (295.7 K), N –I (308.5 K), as reported by the manufacturer, and was used without further purification. The nitroxide spin probe was the N-oxyl-4,4-dimethylspiro(oxazolidine-2,3$'$-5α-cholestane) (3β-DOXYL-5α-cholestane, hereafter referred to as CSL), free radical which has been used in a number of studies (see e.g. [7] and refs. therein). It was obtained from Aldrich and was chosen because of its rigidity which results in a strong orientation by the liquid crystal host. The CSL structure is shown in Figure 1 together with the chosen ordering (xyz, solid line) and magnetic (x$'$y$'$z$'$, dashed line) molecular frames and the principal components $D_\perp$ (reorientation of the molecular long axis) and $D_\parallel$ (rotation around the molecular long axis) of the rotational diffusion tensor. The convention adopted for the ordering and magnetic frames has been discussed in detail [7]. In particular, we observe that the magnetic frame is tilted relative to the ordering frame and that the Euler angles taking the ordering into

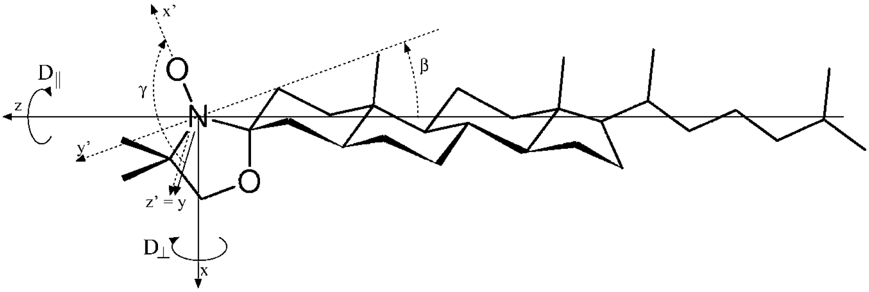

FIGURE 1 Structure of the CSL spin probe together with the chosen ordering and magnetic molecular frames (see text for details).

the magnetic frame are: $\alpha = 0°$, $\beta \sim 15°$ and $\gamma = 90°$ [7]. The second Euler angle β was included as a variable parameter in the data analysis (see Results and discussion section) which yielded a best fit value of $14.8 \pm 2.4°$.

For this compound, dissolved in the 5CB liquid crystal, the principal g factors and hyperfine splitting tensor components used were $g_{x'x'} = 2.0088$, $g_{y'y'} = 2.0061$, $g_{z'z'} = 2.0027$, corresponding to the standard literature values [7] and $A_{x'x'} = A_{y'y'} = 5.98\,\mathrm{G}$ and $A_{z'z'} = 31.74\,\mathrm{G}$ ($1\,\mathrm{G} = 10^{-4}\,\mathrm{T}$), which correspond to the literature values [7] corrected for the polarity of the environment so as to recover the scalar hyperfine constant $a = 14.565\,\mathrm{G}$ observed experimentally.

The aerosil (pyrogenic silicon dioxide) employed was the Degussa [8] type R812, an hydrophobic aerosil where about 90% of the surface SiOH is protected by methyl groups with a density of only 0.29 free OH groups/nm^2 [9]. The aerosil primary particles have a size of the order of 7 nm and do not exist in isolation but form aggregates and agglomerates with a very large specific surface area ($\sim$260 m^2/g) which is almost entirely external and is not derived from any porosity [10].

Sample preparation and measurements were done according to the procedures and instrumentation previously described [5,6]. To minimize thermal history and "aging" effects on the samples and ensure the best reproducibility, all data presented here were obtained using fresh samples which were thoroughly thermalized at the highest field available in our instrument (see also the Results and discussion section for further details on the individual samples).

III. RESULTS AND DISCUSSION

By using the solvent method, we prepared one sample without aerosil and three samples filled with 1, 3 and 10 wt% R812 (1 wt% aerosil

$\sim$0.01 g/cm^3, since 5CB density $\sim$1.0 g/cm^3 in the temperature range considered). The ESR measurements were done both in the nematic (N) and the isotropic (I) phase. For each sample, ESR spectra were recorded at 26 different temperatures on heating and then at the same temperatures on cooling during a continuous run at the rate of one spectra every 5–10 min, depending upon the time required to reach the equilibrium at each new temperature.

Before a typical run, each sample was placed in the cavity under the action of a magnetic field of 6300 G, which is the highest field available in our instrument, and was subjected to the same programmed temperature cycle taking it from 298.2 K (N phase) to 343.2 K (I phase) and then cooling it down slowly to 298.2 K at an average rate of $\sim 1-2$ K/min which was reduced to $\sim 0.1-0.2$ K/min across the phase transition. This "field cooling" (FC) procedure was able to fully anneal the liquid crystal to form a monodomain in the pure and in the 1 and 3 wt% samples, as monitored from a typical ESR line shape. For the 10 wt% sample, despite the stronger field and the longer thermalization than the one used in a previous study [5], the FC procedure was able to align only partially the initial isotropic, three dimensional distribution of local liquid crystalline domains (isotropic, poly-domain state).

The analyses of ESR spectra were performed using a software package which combines an implementation of a modified Gauss-Newton-Marquardt non-linear least-squares fitting [11], developed in our group [12], with the slow tumbling theory FORTRAN codes for the simulation of the ESR line shapes, developed and implemented by Freed and collaborators [13–15] which was summarized in a previous work [5]. Typical experimental spectra and fits are shown in Figure 2 for samples at the various concentrations of aerosil in the N and I phase.

In the preliminary fits, the principal components $D_\perp$ and $D_\parallel$ of the rotational diffusion tensor were considered as independent variables, but the results exhibited a certain correlation between the parameters and relatively large errors. To minimize this correlation the following globalization scheme was adopted in the fits presented here. For each sample, the experimental data corresponding to different temperatures within the same stage of a measurement run (heating or cooling) and within the same phase (N or I), were fitted simultaneously in a global analysis. The diffusion coefficient ratio $D_r = D_\parallel / D_\perp$ was introduced as a variable global parameter. In the I phase, it was considered independent of the temperature, while, in the N phase, it was assumed to have a temperature dependence of Haller-type [16] (an empirical equation which is often used to describe the temperature dependence

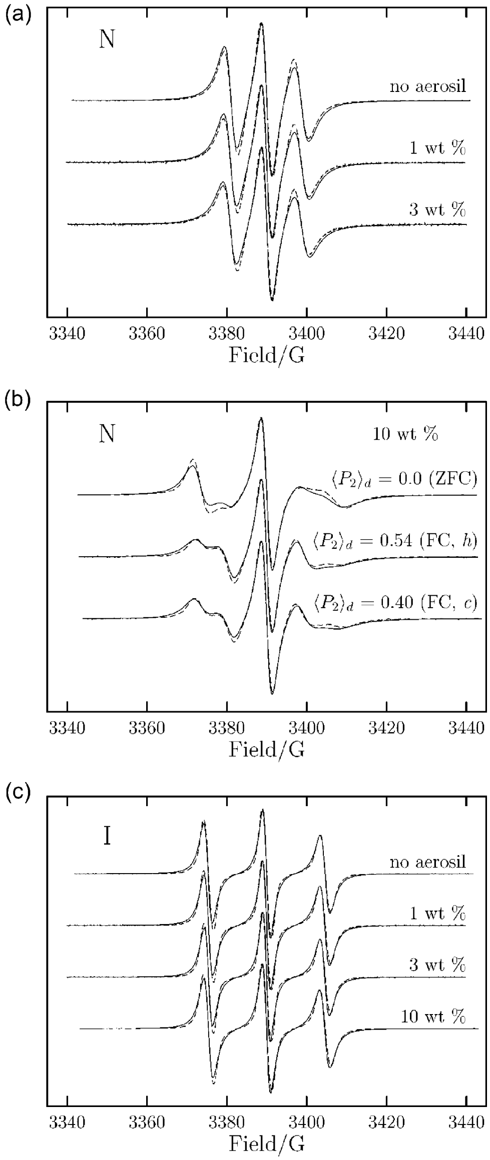

FIGURE 2 Typical experimental spectra (dashed lines) and fits (solid lines) of the samples in the nematic (a, b: T = 298.2 K) and isotropic (c: T = 343.2 K) phase at various aerosil concentrations; (a) Monodomain spectra obtained for the pure ("no aerosil") and for the 1 and 3 wt% samples, after the "field cooling" (FC) procedure, (b) The 10 wt% sample in the nematic phase was only partially aligned and remained in a poly-domain state: zero field cooled sample (ZFC), field cooled sample at the beginning of the heating stage (FC, *h*) and FC sample after cooling from the I phase (FC, *c*; see also text for details).

of the order parameter $\langle P_2 \rangle$ of a mesophase):

$$D_r(T) = D_r^0(1 - T/T_c)^{\nu} + D_r^I, \tag{1}$$

where T_c is the temperature at which the local $\langle P_2 \rangle$ drops to zero according to the ESR spectra, D_r^I was kept fixed to the value of the diffusion coefficient ratio found in the I phase whereas ν and D_r^0, the limiting deviation of D_r from the isotropic value at zero temperature, are adjustable parameters. Finally, the diffusion coefficient $D_\perp$ was considered as an independent fit parameter for each temperature. This globalization improved significantly the analysis of the monodomain spectra reducing the correlation and the errors on the recovered parameters.

In a typical fit of a monodomain spectrum, the variable parameters were thus: the *local* order parameter $\langle P_2 \rangle$, the perpendicular component of the rotational diffusion tensor $D_\perp$, the ratio D_r between the principal components of this tensor, the Euler angle β which takes the ordering into the magnetic molecular frame of CSL (see Experimental section) and the inhomogeneous line width T_2^{*-1}. The fit of a poly-domain spectrum required an extra parameter, $\langle P_2 \rangle_d$, to describe the orientational distribution of the domains.

In Figure 3 we present the temperature dependence of the local orientational order parameter $\langle P_2 \rangle$ of the spin probe at various concentrations of aerosil. The spectra obtained at corresponding temperatures in the heating (h) and in the cooling (c) stage for the pure 5CB ("no aerosil") and for the 1 and 3 wt% samples were essentially identical. On cooling, the system was fully annealed to a monodomain and no significant hysteresis of the $\langle P_2 \rangle$ values was observed. In particular, the values of $\langle P_2 \rangle$ in the cooling stage of the pure system were identical to the heating stage and are not shown. In the 1 and 3 wt% samples, the differences were very small, except for a few temperatures very close to the N–I transition.

The poly-domain spectra (N phase) obtained at the same temperatures on heating and on cooling for the 10 wt% sample exhibited, instead, small but clear differences (compare, e.g., the FC spectra h and c for the 10 wt% sample in Fig. 2b). This was assumed to be due to a different distribution of the nematic domain directors, which depends on the magnetic field intensity and which is likely to be broader after cooling from the I phase, with respect to the initial distribution achieved with the FC procedure. The initial FC was done, in fact, with a magnetic field of 6300 G (see above), whereas, during the measurements, the field sweep was set between 3340 and 3440 G. The degree of order *within* each nematic domain, instead, can be assumed to be only dependent on the temperature and on the

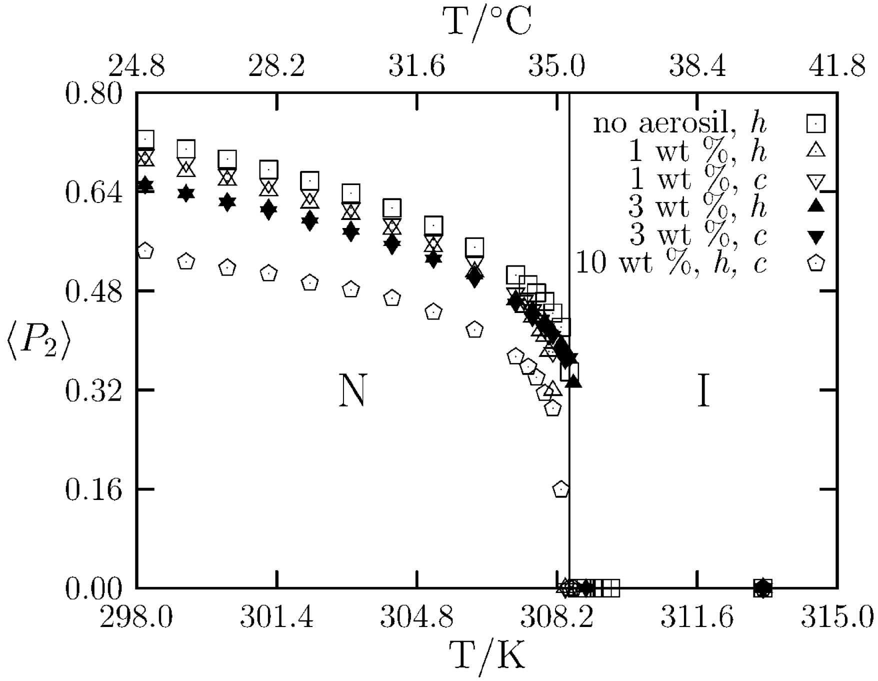

FIGURE 3 Temperature dependence of the orientational order parameter $\langle P_2 \rangle$ of the spin probe at various aerosil concentrations on heating (h) and on cooling (c).

aerosil concentration and it should be the same for corresponding temperatures on heating and on cooling. The fits of these poly-domain spectra presented a certain correlation between the local order parameter $\langle P_2 \rangle$ and the parameter $\langle P_2 \rangle_d$ which describes the distribution of the local domain directors. To improve the analysis, according to the above assumptions, the previous globalization scheme was modified considering that the spectra obtained at corresponding temperatures, on heating and on cooling, have the same value of the local domain order parameter $\langle P_2 \rangle$ but different values of the $\langle P_2 \rangle_d$. In practice, one $\langle P_2 \rangle_d$ was used for the spectra of the heating stage and a different one for the spectra of the cooling stage. Best fit values of $\langle P_2 \rangle_d$ in the heating (h) and in the cooling (c) stage are reported in Figure 2b.

According to the previous globalization, we retained the Haller-type dependence for the diffusion coefficient ratio D_r and $D_\perp$ was considered, as before, independent for each temperature. A very good fit was obtained for all the spectra. The temperature dependence of

$\langle P_2 \rangle$ for the 10 wt% R812 sample is shown in Figure 3. The recovered value of $\langle P_2 \rangle_d$ on cooling was 0.40 which is, as expected, lower than the initial one of 0.54 (see Fig. 2b).

The N–I transition temperature, observed for the pure sample, is in agreement with the value declared by the manufacturer of 308.5 K and it remains essentially unchanged in the presence of the aerosil at the concentrations studied. This fact is an indication that the aerosil suspension does not act simply as a dissolved impurity, but it forms an extensive surface (the aerosil network) which changes the shape and the complexity of the container rather than the composition of the system.

The $\langle P_2 \rangle$ values of the pure sample ("no aerosil") are in good agreement with previous values for 5CB reported in the literature (see [17] and refs. therein). In a previous work [5], using the 5-doxyl stearic acid spin probe in 8CB, we noticed that the $\langle P_2 \rangle$ values of the pure sample were smaller than those calculated from NMR quadrupole splitting data of bulk 8CB, deuterated on the first carbon position along the hydrocarbon chain, obtained by Jin and Finotello [18] (see Table 1 in [5]). This difference was explained by assuming that the flexible stearic aliphatic chain, where the nitroxide group is located, was interacting mainly with regions along the flexible hydrocarbon chain of 8CB so that the nitroxide group was experiencing a reduced local ordering. Our present results, instead, indicate, as expected, that the rigid CSL spin probe is monitoring the order of the more rigid portion of

TABLE 1 Best Fit Values of the Activation Energy E (Arrhenius Model) and of the Parameters B and T_0 (Vogel-Fulcher-Tammann model) Obtained from the Analysis of the Temperature Dependence of the Tumbling Diffusion Coefficient $D_\perp$ (see text for details). All the Analyses were done Separately for the Nematic (N) or Isotropic (I) phase. Upper Section: "No Aerosil" Sample; Lower Section: R812 Samples

Phase		E/(kJ/mol)	B/(10^3 K)	T_0/K
N	no aerosil	55.1 ± 1.6		
I	no aerosil	40.5 ± 2.1		
Phase	**R812 conc. (wt%)**	**E/(kJ/mol)**	**B/(10^3 K)**	**T_0/K**
N	1		6.3 ± 0.2	16 ± 4
N	3		5.9 ± 0.1	37 ± 4
N	10		4.3 ± 0.3	115 ± 14
I	1	39 ± 3		
I	3	39 ± 3		
I	10	39 ± 3		

the 5CB host. The decrease of the orientational order parameter with increasing aerosil concentration appears to be roughly linear in the range studied so that, qualitatively, the behavior of the R812 samples is similar to that observed in a previous study [5].

The temperature dependence of the tumbling diffusion coefficient $D_\perp$ of the spin probe at various concentrations of the R812 aerosil is shown in Figure 4a. At all the aerosil concentrations, the values of $D_\perp$ in the cooling stage (not shown) were identical to those in the heating stage and are consistent with the values of $D_\perp$ obtained for CSL in similar liquid crystal systems [7,19]. As in our previous work [5] we observe that the local rotational dynamics is only slightly affected by the presence of the aerosil even at a concentration of 10 wt%, where the macroscopic viscosity of the sample becomes very large (even at the highest temperature studied, the 10 wt% sample does not flow).

The data in the I phase were fitted to both an Arrhenius-type equation, $D_\perp = D_\perp^0 \exp[-E/(RT)]$, and to the Vogel-Fulcher-Tammann (VFT) equation, $D_\perp = D_\perp^0 \exp[-B/(T - T_0)]$, where B is a temperature corresponding to an activation energy RB in the limiting case of an Arrhenius behavior ($T_0 = 0\,\mathrm{K}$) and T_0 is the temperature of apparent divergence of viscosity. The quantity T_0/B can be used as a material-specific parameter to quantify the kinetic fragility [20]. We found the Arrhenius model always appropriate to describe the temperature dependence of $D_\perp$ in the I phase (Fig. 4a, solid lines). In all the cases the VFT model, which has an extra adjustable parameter, did not improve the Arrhenius fit and was therefore rejected. Best fit values of the activation energy E are shown in Table 1.

A comparison between the Arrhenius and the VFT model in the N phase is presented in Figure 4b. We found that the data for the pure ("no aerosil") sample obey the Arrhenius model (solid line) and the VFT model did not improve the fit. Interestingly, at increasing aerosil concentrations, the data consistently deviate from the Arrhenius model (solid lines) and are better described by the VFT model (dashed lines). This deviation is very small for the 1 and 3 wt% sample but becomes clear at 10 wt% of aerosil. Best fit values of the activation energy E are shown in Table 1 together with the VFT fit parameters, B and T_0.

The values of E for the I phase, reported in Table 1, are essentially concentration-independent and are smaller than the value observed in the N phase for the pure ("no aerosil") sample. In the N phase, the deviation from an Arrhenius-type behavior of the samples containing aerosil is well described by the VFT parameters B and T_0. In particular, we observe an increase of the VFT temperature T_0, indicating the onset of a glass-like behavior at molecular level. In our previous

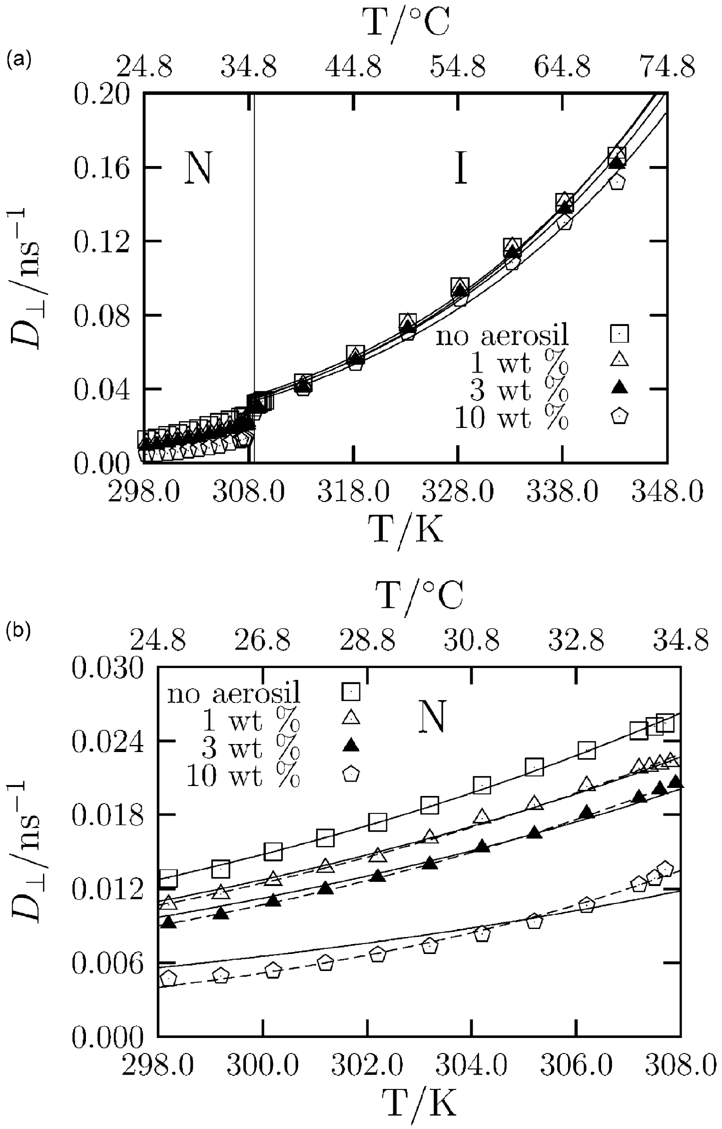

FIGURE 4 (a) Temperature dependence of the tumbling diffusion coefficient $D_\perp$ of the spin probe at various concentrations of the hydrophobic aerosil. Data in the isotropic phase obey a simple Arrhenius-type equation (solid lines), (b) Detail of the nematic region shown above. Experimental data points in the vicinity of T_{NI} (above $\mathrm{T} = 308.0\,\mathrm{K}$) have been removed. Solid lines: fit to the Arrhenius equation; dashed lines: fit to the Vogel-Fulcher-Tammann (VFT) equation (see text for details). Best fit values of the activation energy E (Arrhenius fit) or for the B and T_0 parameters (VFT fit) are shown in Table 1.

work on 8CB LC [5], this onset was observed at a concentration of R812 aerosil of 3 wt%, whereas here it is clearly visible already at 1 wt%.

The value of the diffusion coefficient ratio D_r for all the samples in the I phase was found to be 7.4 ± 2.4 which is in reasonable agreement with the value of 4.7 expected in the Stokes-Einstein limit [7]. The temperature dependence of D_r in the N phase is shown in Figure 5a. The ratio is always larger than in the I phase and it increases with the aerosil concentration. The temperature dependence of $D_{\|}$, obtained as the product of $D_{\perp}$ and D_r, is presented in Figure 5b. Despite the quite large uncertainties, it appears evident that all the behaviors are very similar, indicating that the rotation around the main molecular axis remains almost unaffected, while the presence of the aerosil has mainly the effect of decreasing the tumbling motion of the spin probe (and hence of the liquid crystal host). Such behavior could be explained by the formation of hydrogen-bonds between the liquid crystal cyano group and the residual hydroxyl groups on the aerosil surface.

IV. CONCLUSIONS

We have found that, by increasing the aerosil concentration up to 10 wt%, the order parameter $\langle P_2 \rangle$ of the spin probe in the filled nematic systems is depressed. When the system is no longer able to form a monodomain (e.g. at an aerosil concentration of ~10 wt%), the dependence of the degree of alignment of the local nematic domains on the annealing conditions (field intensity, aerosil type, thermal history of the sample and aging) can be observed providing information on the reorganization of the aerosil network which is considered to be crucial in the memory effect.

The small influence of the aerosil concentration on the molecular dynamics is surprising, considering that the macroscopic viscosity of the system changes considerably, with increasing aerosil concentration, from that of a fluid, for the pure 5CB, to that of a gel at 10 wt% R812. A simple explanation for these results is that, at the concentrations used in this work, only a small fraction of the liquid crystal molecules is in direct contact with the aerosil surface and that the effects are quickly lost as we move away from the surface. Therefore, on the average, the spin probe will sample the bulk of large "pools" of liquid crystal where the surface effects are relatively weak. In particular, we observed that only the molecular tumbling motion is affected by increasing aerosil concentration whereas the rotation around the main molecular axis is essentially independent of the concentration.

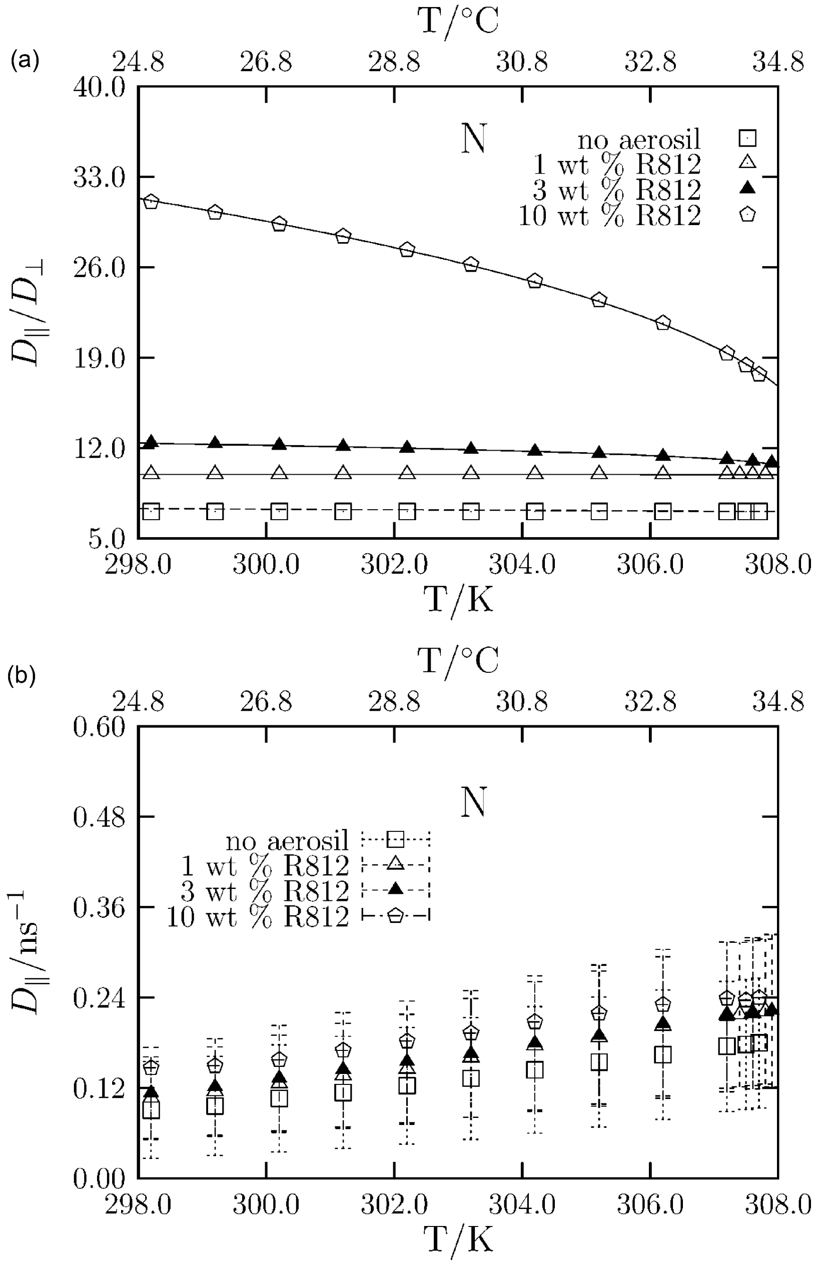

FIGURE 5 Temperature dependence of (a) the spin probe diffusion coefficient ratio $D_r = D_\parallel/D_\perp$ obtained via the globalization scheme described in the text and (b) the spin probe diffusion coefficient $D_\parallel$, for all the nematic samples studied.

Despite this, we were able to detect a fundamental difference between the pure liquid crystal and the aerosil dispersions in the N phase. This is represented by a deviation from the Arrhenius behavior of the temperature dependence of the rotational diffusion coefficient $D_{\perp}$. The deviation is well represented in all cases by a Vogel-Fulcher-Tammann type law. This non-Arrhenius behavior can be appreciated even at 1 wt% of aerosil, suggesting that a glass-like state can be induced in a nematic by a very small amount of random disorder.

This result raises a question about the presence of an aerosil concentration threshold between a liquid-like and a glass-like behavior at molecular level as opposed to the possibility of obtaining a glassy state with an arbitrarily small amount of random disorder. Our findings suggest that, if present, this threshold should be lower than 1 wt%.

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