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Effect of silica aerosil dispersions on the dielectric properties of a nematic liquid crystal

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The static and dynamic aspects of (4-*n*-heptyl-4′-cyanobiphenyl) (7CB) perturbed by the dispersion of 70-Å-diameter hydrophilic silica aerosil spheres have been investigated using dielectric spectroscopy. Results on five mixtures of 7CB plus silica aerosil are presented in order to probe systematically the disorder introduced by the silica aerosil network on the 7CB molecules. Measurements on homeotropically aligned samples have been made from 75 kHz to 30 MHz in the temperature range 30−60 °C. It was found for the mixtures that the nematic-isotropic transition temperature is lower than that of the bulk 7CB. Bulklike relaxation processes due to the rotation of the molecules around the short axis have been analyzed, and were found to follow Arrhenius-type behavior in the nematic phase except in the vicinity of the nematic-isotropic transition temperature. These processes are slightly faster in the mixture than in the free phase. A dielectric process in the low frequency range, absent in the bulk, has been observed in samples with higher silica concentration. All the observed relaxation processes in the mixtures are of non-Debye type.

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I. INTRODUCTION

In the past few years, a lot of research has been devoted to the effect of confinement of liquid crystals (LC's) in restricted geometries [1]. Understanding the influence of confining geometry on the physical properties of LC's is of considerable academic and technical interest [1–4]. The interaction of a liquid crystalline compound with a solid surface depends on the nature of both the surface and the liquid crystalline material. Nematic liquid crystals in a confining geometry represent simple examples of complex systems where orientational ordering and surface interaction can be studied in detail [5].

The intricate mechanisms which govern the physical properties of LC's confined to well defined geometries, as well as to more complex and random ones, have revealed various properties and effects not observed in the same substances when they are in the bulk. For example, structure and ordering, phase transitions, order parameter fluctuations, the dynamics of molecular motion, and the dynamics of collective modes are affected, and have received considerable attention in trying to understand the effect of confinement on the interfacial properties of confined LC's [6–8]. For well characterized confining geometries, studies have clearly shown the existence of ordered surface layers above the phase transition temperature [9], and a continuous development of nematic ordering instead of the weakly first order nematic-isotropic transition [10,11]. Various studies of the phase behavior of open structures of high-porosity silica aerogels containing liquid crystals have been made [12–16]. Structural aspects of the influence of confinement of 8CB in an aerogel matrix were studied [13]. Some features of nematic ordering in the aerogel porous matrix were qualitatively explained in terms of the random-field Ising model. Using high-resolution ac calorimetric studies [12], it was also shown in such random system that the phase transition regions became broadened and usually shifted with respect to the bulk transition temperatures as a function of aerogel density. Recently, dispersions of silica particles with diameters of approximately 7 nm covered with hydroxyl groups (aerosil), were also studied intensively [17–20]. These particles can hydrogen bond in a network, and allow the introduction of disorder in LC's. Using calorimetric and x-ray scattering studies [18], important questions investigated in the different systems were related to finite-size effects, random field effects and the role of quenched or (partially) annealed elastic strain disorder. Aerosil systems seem to be particularly attractive since one hopes that random disorder could be introduced in a controlled manner.

In this paper, we report on a comprehensive study of the dielectric properties of the liquid crystal (heptylcyanobiphenyl) (7CB) perturbed by the dispersion of 70-(Å)-diameter hydrophilic silica spheres (aerosil). Results on five mixtures of 7CB plus silica aerosil are presented in order to probe the systematic effect of the silica network buildup on the static and dynamic properties of the 7CB molecules. To our knowledge, earlier investigations on the dielectric properties of silica aerosil dispersions in LC's involved only one mixture [21,22]. Among the main findings of this work is that the nematic-isotropic phase transition temperature T_{NI} decreases with increasing silica concentration ρ_s. This decrease follows a complicated behavior as a function of ρ_s, comparable to the one previously obtained for 8CB plus silica aerosil from calorimetric studies [18]. This behavior was interpreted [18] following two ρ_s-dependent regimes where, for $\rho_s < 0.1\ \mathrm{g/cm^3}$, there is a rapid downshift of T_{NI}; however, for ρ_s above 0.1 g/cm^3, the shift is comparable to that seen in aerogel [15] and randomly interconnected media [23]. Imposing homeotropic alignement on our samples, the

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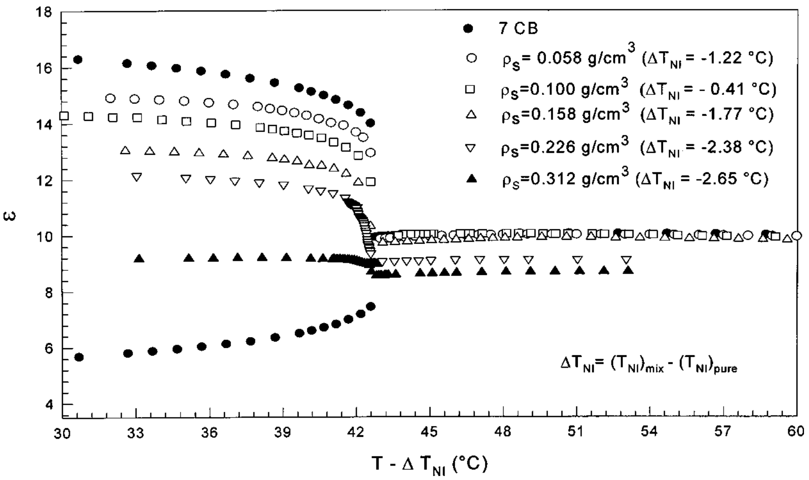

FIG. 1. Temperature dependence of the static dielectric constant of 7CB and silica aerosil dispersions in the isotropic phase and nematic phases. The data for the dispersions have been shifted by $\Delta T_{NI} = (T_{NI})_{\text{mix}} - (T_{NI})_{\text{pure}}$ in order to make the isotropic to nematic transition temperatures coincide. The ΔT_{NI} value for each mixture is shown accordingly.

dynamical behavior of the longitudinal complex dielectric permittivity ($\varepsilon_{\parallel}^{*}$), connected with the LC molecular flips around the short axis, has been investigated. A dielectric process (about two decades slower than the molecular dynamics in the free phase) absent for pure 7CB is observed in mixtures with higher silica concentrations.

II. EXPERIMENT

The present experiment consists of measuring the real (ε') and imaginary (ε'') parts of the complex dielectric permittivity (ε^{*}) of the liquid crystal 7CB and five dispersions of silica spheres (aerosil) in 7CB. In the frequency range 75 kHz to 30 MHz, the complex permittivity is measured using a Hewlett-Packard four terminal *LCR* meter model HP 4285A. The precision on the measurements is about 0.1%. The sample cell is a 316-type stainless steel parallel plate capacitor with a guard ring, in order to eliminate the stray capacitance caused by the edge effect. The electrode spacing is about 200 μm, and can be adjusted using Teflon or Mylar spacers. The sample cell is properly centered inside an automatically temperature controlled cylindrical cavity oven. This cavity is connected to the ground potential to be used as a shield against any noise pickup. Temperature control and measurement, respectively, are achieved via a heating coil (surrounding the cylindrical cavity) and a calibrated thermistor in contact with the oven. The accuracy on the temperature control and measurements is better than 0.01 °C.

In order to orient the director and hence measure either $(\varepsilon^{*})_{\parallel}$ or $(\varepsilon^{*})_{\perp}$ for pure 7CB, the dielectric sample cell inside the temperature controlled cavity is inserted between the poles of two powerful permanent magnets. As the case may be, the permanent magnets are positioned such that the static magnetic field is either parallel or perpendicular to the applied electric field. The magnetic field at the position of the liquid crystal is measured to be around 0.5 T. However, this magnetic field strength was insufficient to orient the 7CB plus silica aerosil systems. Therefore, an ac electric field (at 500 Hz), with a maximum magnitude of 35 000 V/cm, was applied to the sample between the electrodes. The procedure for applying the electric field is as follows: first we fill the dielectric cell with a 7CB plus silica aerosil mixture of known silica aerosil concentration. Then the temperature of the system is raised to the isotropic phase where the voltage is applied gradually to the sample. After the maximum voltage has been reached, the sample is cooled slowly to the lowest desired temperature in the nematic phase. Thereafter, the voltage is switched off, and the dielectric cell is connected to the LCR meter for subsequent measurements of the dielectric permittivity $(\varepsilon^{*})_{\parallel}$. At this stage, the homeotropic alignment is retained after the field is switched off.

The 7CB plus aerosil systems were prepared following the solvent preparation method described in Ref. [18]. After drying the aerosil powder under vacuum at 200 °C overnight, it is added to the liquid crystal (LC), which is dissolved in pure acetone (0.02-g LC per cm^3 of solvent). Then the mixture is sonicated for 1 h in order to achieve good dispersion. Afterward, the solvent is evaporated off slowly (15 h) above 43 °C before the sample is placed in a vacuum system at 10^{-3} Torr, and pumped on for one day at 50 °C. The resulting density ρ_s denotes the grams of silica aerosil per cm^3 of liquid crystal.

For the present experiment, a hydrophilic aerosil (type 300) was used, as obtained from Degussa Corp. [24]. This sil consists of 70-Å-diameter SiO$_2$ spheres with hydroxyl groups covering the surface, and with a specific surface area of $a = 300$ m^2/g determined from a Brunauer-Emmet-Teller adsorption isotherm [24]. The liquid crystal 7CB is obtained from the Merck BDH Corp, and used without further purification.

III. RESULTS AND DISCUSSION

Figure 1 shows a general survey of the temperature variation of the static permittivity obtained for 7CB, and five silica aerosil dispersions in 7CB. These measurements were made at 100 kHz, in a temperature range from 30 to 60 °C. Our static values of the 7CB campound are in excellent agreement with several previously reported values in the literature [25,26]. For 7CB, the nematic-to-isotropic transition temperature (T_{NI}) is around 42.7 °C. The permittivities $\varepsilon_{\parallel}$ ($\varepsilon_{\perp}$), shown for the nematic phase, refer to those measured with the nematic director aligned parallel (perpendicular) to the measuring field. In the nematic phase, the increase

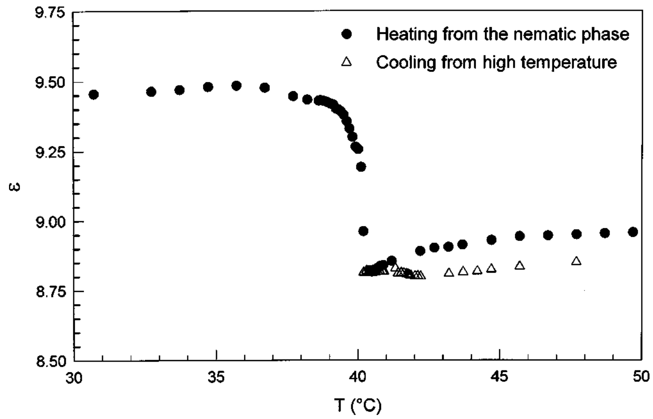

FIG. 2. Temperature dependence of the static dielectric data for $\rho_s = 0.312\ \mathrm{g/cm^3}$. Black dots represent the data set on heating the homeotropically aligned sample from the nematic phase, while the triangles correspond to the data set obtained on cooling in the isotropic phase before alignment with a strong ac electric field.

of $\Delta\boldsymbol{\varepsilon} = (\boldsymbol{\varepsilon}_\parallel - \boldsymbol{\varepsilon}_\perp)$, with decreasing temperature, reflects the increasing nematic order. At the nematic-isotropic transition, there is a discontinuity in $\varepsilon_\parallel$ and $\varepsilon_\perp$ behaviors which is consistent with the first order nature of the transition. Figure 1 also displays the temperature behavior of the static permittivities of silica aerosil dispersions in 7CB in the isotropic phase, and that of $\varepsilon_\parallel$ in the nematic phase. These values were obtained on heating from the lowest temperature in the nematic phase subsequently after cooling the sample from the isotropic phase under the action of an external low frequency ac electric field (≈35 000 V/cm at 500 Hz).

At a given temperature in the isotropic phase, the static permittivity is shown to decrease with increasing silica concentration. This decrease is more pronounced for higher silica densities. Our measurements were performed on heating from the nematic phase to the isotropic one; however, it is believed that the decrease in ε with increasing ρ_s at fixed T in the isotropic phase, is partially offset by a contribution due to the appearance of remanent order above T_{NI}. To further check this point, Fig. 2 shows two data sets obtained for $\rho_s = 0.312\ \mathrm{g/cm^3}$ on heating and on cooling. The permittivity values obtained in the isotropic phase on cooling are systematically smaller than the ones obtained on heating a homeotropically oriented sample from the nematic phase.

At a fixed temperature in the nematic phase, Fig. 1 shows $\varepsilon_\parallel$, which undergoes a gradual decrease with increasing silica network. Consequently, the discontinuity of ε at the nematic-isotropic (N-I) transition becomes less defined. This is essentially due to the silica aerosil network, which induces disorder and defects that degrade the orientational order.

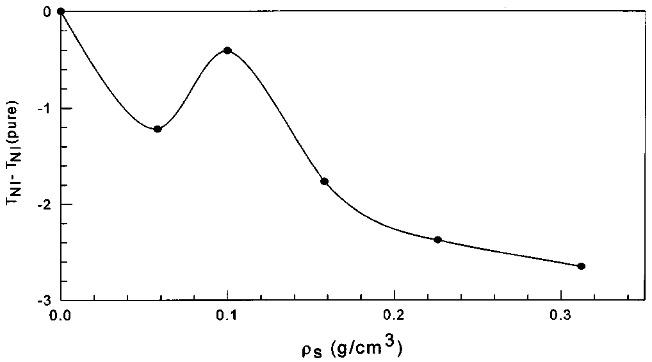

FIG. 3. Comparison of the nematic-isotropic transition temperature shift $\Delta T_{\rm NI} = (T_{\rm NI})_{\rm mix} - (T_{\rm NI})_{\rm pure}$ for the silica aerosil dispersions investigated.

Figure 3 shows the N-I transition temperature shifts $\Delta T_{NI} = T_{NI} - T_{NI}$ (pure) versus ρ_s. For low ρ_s below 0.1 g/cm^3, there is a rapid shift of T_{NI} to lower temperature, while for larger ρ_s values the behavior is comparable to that seen for the 8CB plus aerogel systems [15]. These temperature shifts follow the same trend as the one obtained for 8CB plus aerosil, from calorimetric studies by Iannachione and Garland *et al.* [18]. These authors interpreted these trends following two distinct regimes of ρ_s-dependent behavior, with a crossover between them at $\rho_s \cong 0.1\ \mathrm{g/cm^3}$. In the low-$\rho_s$ regime, the gel is labeled as ‘‘soft,’’ meaning that the bonds among the aerosil particles can easily break, allowing a rearrangement of the particles to form a network in which the elastic energy; therefore, the elastic strain in the liquid crystal are minimized. In this regime, the rapid T_{NI} shift to lower temperature is believed to be better described by a purely random field Ising model. In the high-ρ_s regime, the gel is ‘‘stiff’’ or rigid, having similarities with the aerogel system which is dominated by quenched elastic-strain smearing effects that destroy long range order, and where randomness only introduces a distribution of strain.

In order to characterize the influence of disorder and randomness introduced by the silica particles on the different aspects of the dynamical behavior of 7CB, Fig. 4 shows the real and imaginary parts spectrums of ($\varepsilon^*_\parallel$) of the bulk 7CB along with that of five dispersions of silica aerosil in 7CB at $T = 30.680\,^\circ\mathrm{C}$. As mentioned above, these measurements were taken in the frequency range from 75 kHz to 30 MHz. It can be seen from Fig. 4(b) that the maximum in the loss curve becomes less defined and decreases in magnitude with increasing silica concentration. A broadening of the loss curve is usually associated with the broadening of the spectrum of relaxation times associated with the dispersions. In the present study, we have investigated the influence of the silica particles on the molecular process associated with the rotation of the 7CB molecules around their short molecular axis.

For the quantitative analysis of the dielectric spectra, the Cole-Cole function [27] has been used:

$$\begin{aligned}\boldsymbol{\varepsilon}^*_\parallel(\omega) &= \boldsymbol{\varepsilon}'_\parallel(\omega) - \mathbf{i}\boldsymbol{\varepsilon}''_\parallel(\omega)\\ &= \boldsymbol{\varepsilon}_\infty + \sum_j \frac{\Delta\mathbf{k}_j}{1+(\mathbf{i}\boldsymbol{\omega}\boldsymbol{\tau}_j)^{1-\alpha_j}}. \qquad (1)\end{aligned}$$

Here $\boldsymbol{\varepsilon}_\infty$ is the high frequency limit of the permittivity, $\Delta\mathbf{k}_j$ the dielectric strength, $\boldsymbol{\tau}_j$ the mean relaxation time, and j the number of the relaxation process. The exponent $\boldsymbol{\alpha}_\mathbf{j}$ $(0 \leqslant \boldsymbol{\alpha}_\mathbf{j} < 1)$ represents the distribution of the relaxation times, and goes to zero when a single relaxation time is effective. Both the real and imaginary parts of the dielectric permittivity

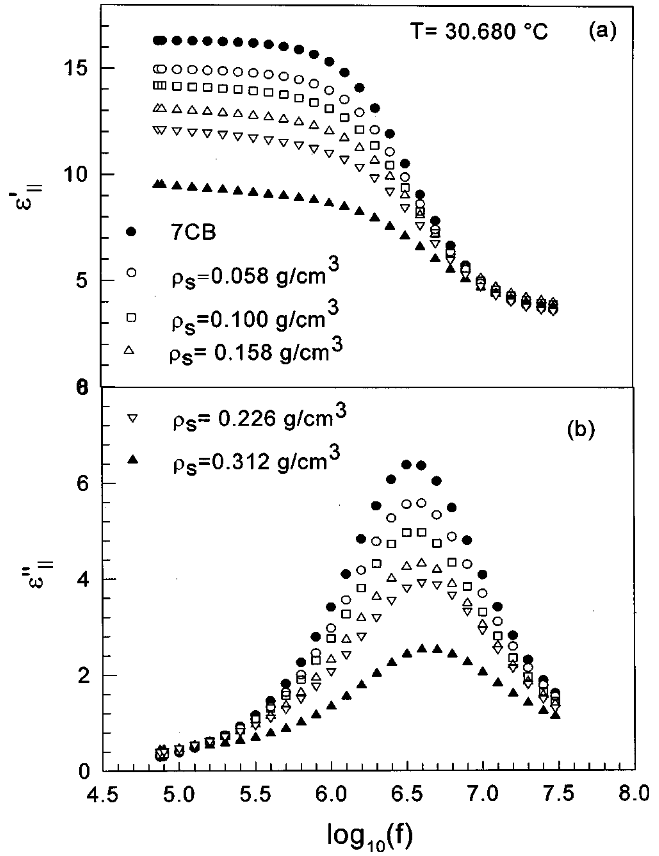

FIG. 4. Frequency dependence of the real and imaginary parts of the parallel component of the complex permittivity.

have been analyzed. The fitting of the Cole-Cole function to the experimental spectrum has been performed using a least square fitting procedure. Cole-Cole plots for the bulk 7CB and five 7CB plus silica aerosil samples are shown in Fig. 5. Here it can be seen that for 7CB in the absence of silica network, a semi circle is obtained. This agrees well with earlier observations [25,26], and shows that the dielectric process can be described with a well-defined single relaxation time. As the silica aerosil concentration increases, the Cole-Cole arcs deviate from being semicircular, and tend to become flattened semicircular arcs indicative of a broadening of the distribution of relaxation times associated with the rotation of the 7CB molecules about their short axis. The influence of the silica aerosil concentration on the dielectric behavior of 7CB molecules is quite apparent in Fig. 5. As shown, a dielectric process can be identified in the low frequency region below the MHz range. Barely seen in the mixtures up to $\rho_s = 0.226\,\mathrm{g/cm^3}$, this nonbulklike process is observed in the low frequency range for $\rho_s = 0.312\,\mathrm{g/cm^3}$ (see Fig. 5). To identify properly the dispersion region associated with this process, we have extended the dielectric measurements for this mixture to the low frequency range starting from 1 kHz using the HP *LCR* meter 4284*A*.

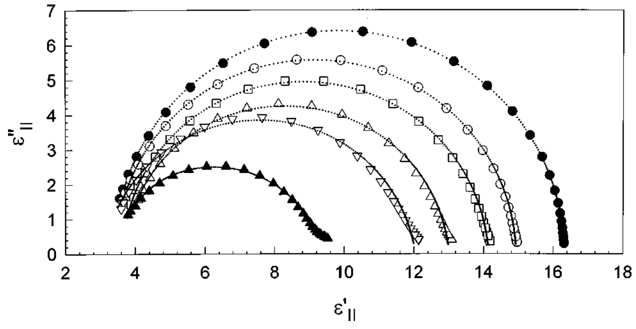

FIG. 5. Cole-Cole plots for 7CB and the five silica aerosil dispersions at $T = 30.680\,^\circ\mathrm{C}$. The different symbols representing the data correspond to the same samples as in Fig. 4. The dotted lines represent the fit to the experimental data as given by Eq. (1) for one broadened relaxation mechanism for 7CB and all the mixtures except for $\rho_s = 0.312\,\mathrm{g/cm^3}$ where two mechanisms were applied.

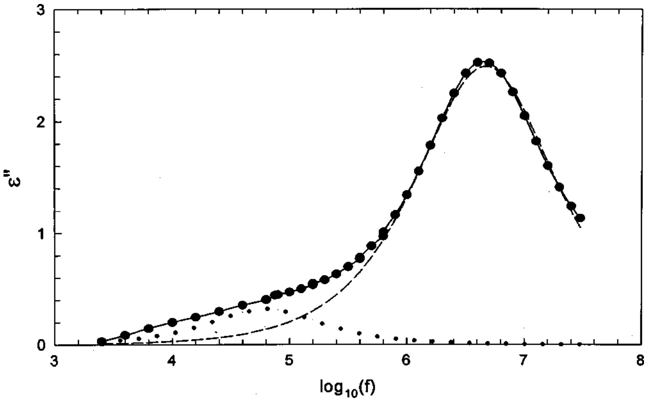

FIG. 6. The large black dots represent the frequency dependence of the imaginary part of the dielectric permittivity for $\rho_s = 0.312\,\mathrm{g/cm^3}$ at $T = 30.680\,^\circ\mathrm{C}$. The solid line correspond to the fit obtained for two relaxations processes according to Eq. (1). The small dotted line and the dashed lines correspond to the contribution of the nonbulklike and bulklike processes, respectively.

A quantitative evaluation has been performed by fitting the dielectric data for $\rho_s = 0.312$ g/cm^3 to a superposition of two processes as given by the Cole-Cole function [Eq. (1)]. Figure 6 shows the frequency dependence of the imaginary part of the dielectric permittivity for this sample. The dashed and dotted lines indicate the contribution of the two individual processes to the solid line from the fit with function (1). Figure 7 shows the corresponding Cole-Cole plots of these processes.

For 7CB and 7CB plus aerosil mixtures up to $\rho_s = 0.226\,\mathrm{g/cm^3}$, the Cole-Cole function for a single relaxation process fits better the measured dielectric data in the frequency range from 75 kHz. To 30 MHz. The parameter α, which empirically represents the spectrum of the relaxation times, varies from 0.03 at $T = 30.680\,^\circ\mathrm{C}$ for $\rho_s = 0.058\,\mathrm{g/cm^3}$, to a value of 0.13 for $\rho_s = 0.226\,\mathrm{g/cm^3}$ at the highest temperature in the nematic phase. For $\rho_s = 0.312\,\mathrm{g/cm^3}$, the Cole-Cole distribution parameter for the bulklike process varies between 0.12 at $T = 30.680\,^\circ\mathrm{C}$ to 0.15 at the highest temperature in the nematic phase. For the bulk 7CB, the Cole-Cole parameter is zero in the nematic phase, indicating a Debye-type process, as shown by the semi-circle in the Cole-Cole diagram plotted in Fig. 5.

Figure 8 presents the temperature dependence plots of the relaxation times. The high frequency process labeled ‘‘pro-

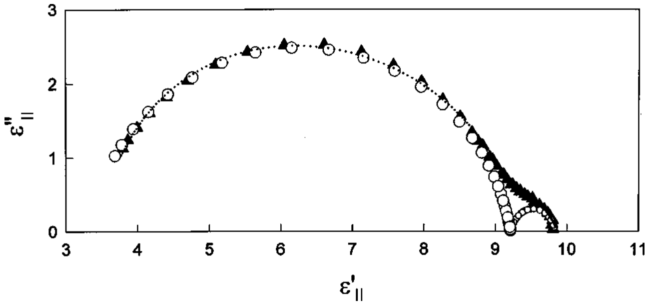

FIG. 7. Cole-Cole plot for the complete experimental data (see text) for $\rho_s = 0.312\,\mathrm{g/cm}^3$ at $T = 30.680\,°\mathrm{C}$ (black triangles). The white circles represent the elementary contributions to the investigated dielectric spectra, namely, the low frequency process (right) and the bulklike process. The dotted line represent the best fit as given by Eq. (1) with two relaxation processes.

cess I'' is bulklike, with $\tau \sim 10^{-8}$ s, and corresponds to the rotation of the molecules around the short axis. This high frequency process for the mixtures almost coincides with that of the pure 7CB at the lowest temperatures investigated. If one considers the silica aerosil plus 7CB samples as a collection of nematic domains or agglomerates created by the presence of silica particles aggragates [4], one might assume that process I originates from unbound molecules in the aggregate volumes.

Process II represents the nonbulklike relaxation observed at $\rho_s = 0.312\,\mathrm{g/cm}^3$. The existence of a second dynamic process with $\tau \sim 10^{-6}$ s absent in the bulk, and observable only in mixtures with high silica aerosil concentrations, suggest the occurrence of a surface layer (formed at the silica network–LC interface) with hindered rotational dynamics. It should also be noted that there is no appreciable difference for this process, as it is the case for process I, between the nematic and isotropic phases. Retarded by almost two decades and following the same temperature dependence as the bulklike process in the nematic phase, this low frequency relaxation mechanism is not described by the Debye-type relaxation function, and there is a spectrum of relaxation times. The Cole-Cole distribution parameter varies between 0.212 at 30.680 °C, to a value of 0.221 at the highest temperature in the nematic phase. In his pioneering dielectric work on confined liquid crystals in random porous media, Aliev and co-workers [6,28] observed a similar relaxation process in 8CB confined in 100-Å pores. They suggested that this process is due to the rotation of the molecules, located in the surface layer formed at pore walls. This process is slower than the process due to the rotation of molecules in bulk, because the viscosity in surface layers is expected to be greater than the bulk viscosity [28].

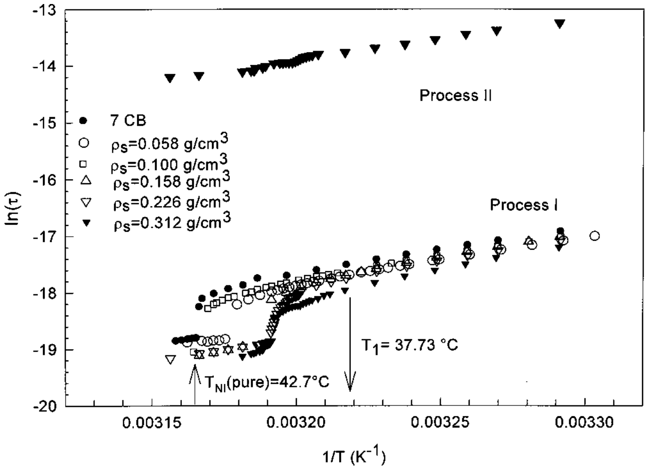

FIG. 8. Temperature dependence of the relaxation times of the bulklike (process I) and the nonbulklike (process II) processes.

Both processes exhibit Arrhenius-like behavior in the nematic phase except in the vicinity of T_{NI}. While approaching T_{NI}, the relaxation times are slightly faster in the mixtures as compared to the bulk 7CB, but the difference are probably not significant and might be attributed to a slightly changed order parameter. For 7CB, an Arrhenius plot far below T_{NI}, i.e., $T < T_1$ for example (see Fig. 8), yields the activation energy $U_{\mathrm{bulk}} = 67.5$ kJ/mol. To show the impact of the silica network on the activation energy, we calculated $U_{\rho s} = 84.6$ kJ/mol for $\rho_s = 0.312\,\mathrm{g/cm}^3$ in the temperature range below T_1 in Fig. 8. The increase of the activation energy with increasing silica concentration can easily be seen from the increase of the slope of ln (τ) versus $1/T$ in Fig. 8 with increasing silica density. The supplemental activation energy $U_S = U_{\rho s} - U_{\mathrm{bulk}}$ can be attributed to an additional potential due to the influence of the silica network-liquid crystal molecules interaction. The behavior of the relaxation times in the vicinity of the phase transition temperature T_{NI} is quite similar to that of the static permittivity versus temperature (Fig. 1). A clear difference in the behavior of the effective relaxation times of the mixtures, from that of the bulklike times of 7CB, becomes evident in the nematic phase near the nematic to the isotropic phase temperature (see Fig. 8), where for higher concentrations the relaxation times decrease continuously to the isotropic phase.

IV. CONCLUSION

We have investigated the systematic effect of silica aerosil dispersion on liquid crystal 7CB molecules by means of dielectric spectroscopy. The mixture transition temperature T_{NI} is lowered with respect to the free bulk phase, and is shown to follow a behavior as a function of the silica density consistent with that found for the aerosil plus 8CB systems [18]. The dominant relaxation process, which pertains to the rotation of the molecules around the short axis, is shown to follow an Arrhenius-like behavior in the nematic phase away from the T_{NI} transition temperature. In the vicinity of T_{NI}, the effective relaxation times decreases more gradually with increasing silica concentration, toward the isotropic phase value. A slower dielectric process was observed in mixtures with higher silica concentrations. This process is absent in the bulk 7CB, and is not of Debye type. It is suggested that this process is due to the hindered rotation of the molecules located in the surface layers formed by the 7CB molecules at the silica aerosil surface.

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