

Broadband dielectric spectroscopy study of molecular dynamics in the glass-forming liquid crystal isopentylcyanobiphenyl dispersed with aerosils

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The glass-forming liquid crystal isopentylcyanobiphenyl (CB15) filled with different concentrations of hydrophilic and hydrophobic aerosils has been investigated by broadband dielectric spectroscopy in the frequency range from 10^{-2} Hz to 10^7 Hz over a temperature range of 173 K–300 K. CB15 that consists of chiral molecules has a monotropic system of phases nematic (N^*) and smectic-A upon supercooling and forms a glass further on. In the isotropic phase a single Davidson-Cole process exists in the substance, which is due to the rotation of the molecules around their short axes. In the supercooled N^* phase a Cole-Cole process that is an order of magnitude faster is additionally present and is due to the rotation in a cone around the local director. The relaxation times of the process due to rotation around short axes obey the empirical Vogel-Fulcher-Tamman behavior typical for glass-forming systems. Filling of the liquid crystal (LC) with different concentrations of hydrophilic aerosils leads to the emergence of a slow relaxation process that grows with the increasing concentration of the aerosils. The aerosil particles, which form a three-dimensional network dividing the LC phase into domains, have little effect on the relaxation times of the bulk processes. As a consequence the glass transition temperature is merely affected. On the other hand, in LCs dispersed with hydrophobic aerosils the slow process is quite weak. The slow process is attributed to the relaxation of the molecules that are homeotropically attached at the surfaces of the aerosil particles. The LC-aerosil surface interaction leads to a considerable slowing down of the molecular rotation around their short axis. The process has an Arrhenius-like temperature dependence of the relaxation times with an activated type of dynamics, which can be explained by considering a nonincreasing rearranging region of cooperativity in surface layers.

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I. INTRODUCTION

The influence of confinement on the bulk properties of liquid crystals (LCs) has been a topic of great interest in recent years as can be seen from the surge in myriad forms of investigational activities [1–10]. Such confined systems have been very useful in exploring the fundamental physics of condensed matter as a variety of novel effects could be expected in these systems primarily based upon the restricting size of confinement, the presence of large interfacial area, and the types of confining geometry [11–20]. The issue of the structure, phase and glass transitions, as well as the dynamics of molecular motion of isotropic liquids and liquid crystals in confining geometries have been the point of focus in these studies [21–28]. Recently, filling of LCs by introducing inclusions into the phase have been used for studying confinement effects and surface interactions between the inclusions and the LC molecules. The standard has been to use mainly hydrophilic aerosil particles in these experiments. These aerosils have several hydroxyl groups on their surfaces giving them a hydrophilic character [29]. Hydrophobic aerosils have also been used for such investigations. The aerosils can attach to each other by hydrogen bonding in the presence of a medium like LCs. These particles can form hydrogen-bonded three-dimensional network above a gelation threshold $\rho_s \sim 0.01$ g/cm³, where ρ_s is the weight of silica per cm³ of LC [28,30]. Such systems are similar to aerogels except that in aerogels the silica particles attach to each other by covalent bonds. In the case of LCs dispersed with aerosils

the network can break and regroup itself in time and hence can be termed as weakly connected gels [28,31]. For a given silica density in the hydrogen-bonded aerosil gels, the interaction between the surfaces of the gel and liquid crystal molecules are less than the rigid aerogels. The added advantage of the aerosil filled LC system over the other confined LCs is the flexibility in varying the size of confinement. Several studies such as dielectric [32–39], calorimetric [39–44], light scattering [34,35], deuteron nuclear magnetic resonance [45], x-ray intensity fluctuation spectroscopy [46], acoustic [47], and small angle x-ray scattering [31,48] on filled LCs have been reported.

In one of the studies of the influence of hydrophilic aerosils on the phase transitions of LC by adiabatic scanning calorimetry and ac calorimetry, surface-induced ordering was observed where the experimental results could not be explained by either pinned-boundary-layer or random field (RF) models [42,43]. In a similar work, using a photopyroelectric technique to study the specific heat and thermal conductivity of these samples below the gelation threshold, similar conclusions were drawn [49]. Dielectric measurements that probe the dipole moment time autocorrelation function can be very informative for the examination of relaxation processes near the LC-substrate interface. In the case of polar LCs filled with aerosils, the polar ordered layer at the interface can lead to changes of molecular mobility due to molecule-surface interactions, resulting in a slower dynamics of molecules at the interface. In a dielectric study performed on heptylcyanobiphenyl filled with hydrophilic aerosils at high concentrations, an additional process was observed that

was attributed to the hindered rotation of the molecules located in the surface layers formed at the aerosil surface [32]. In an electron spin resonance study that probes the dynamics at the molecular level [50] surface-induced dynamics, similar in case to the dielectric study, was also observed. In this study it was observed that increasing the hydrophobic aerosil concentration did not show a strong difference on the rotational dynamics of the bulklike modes that one might expect on the basis of the macroscopic viscosity of the system.

In this paper we study the influence of both hydrophilic and hydrophobic aerosils on the dielectric behavior of the glass-forming chiral nematic isopentylcyanobiphenyl (CB15). The measurements have been performed on four different concentrations of hydrophilic aerosils above the gelation threshold. For comparison, measurements have also been done on bulk as well as on LCs filled with a high concentration of hydrophobic aerosils. The main aim of our investigation was to study the dynamics in such systems for which dielectric spectroscopy is an ideal method. CB15 can be easily supercooled and has cholesteric phases from 243 K to 219 K and Smectic-A phase below 219 K [51]. It eventually forms a glass below 214 K. In the bulk state, CB15 has been extensively investigated by dielectric spectroscopy [52,53] and calorimetry [54,55]. Nonlinear effects in such systems have also been studied by Rzoska and co-workers [56–58]. Our interest was to investigate the dynamics of the CB15 aerosil filled CB15 in the supercooled phases as well the changes observed upon approaching the glass transition.

The investigation of effects of confinement on physical properties of glass-forming liquids have provided additional information on the dynamics of glass transition [16,17,21,26,59–65]. According to the plausible concept of cooperativity, the molecules rearrange themselves cooperatively within a volume characterized by a size called the “cooperativity length” (sphere of radius ξ). On approaching the calorimetric glass transition temperature T_g' the cooperative length tends to diverge with the cooperative region finally comprising the whole system. Thus confinement of liquids could be of interest in cases where the pore radius is comparable to the length of cooperativity of the material.

Based on different experiments it was concluded that all fluids in pores separate into two distinct liquid phases: one corresponding to molecules physisorbed at the surface which exhibits a dramatic frustration of their mobility and another one of relatively “free” molecules in the inner pore space [17,26,61,62]. The interfacial properties depend on the polarity, adsorption energies, and surface coverage leading to attractive or repulsive surface forces. The behavior of the phase in the inner pore depends upon the intermolecular interactions (e.g., van der Waals or hydrogen bonding), size, mass, and shape of molecules. In an alternative interpretation of the influence of confinement on the dynamics of supercooled liquids based on solvation dynamics results, it was conjectured that in the geometrically restricted liquid the relaxation function decays initially like the bulk until a transition at certain time τ' leads to nonergodic behavior on the relaxation time scale of the bulk material [61,66]. To the authors' knowledge studies about confinement on glass-forming liquid crystals is scarce. The most important work

was performed to study the relaxation behavior in a thin film of a glass-forming LC on a silica plate. The study involved second-harmonic generation and offered a direct evidence that the collective character of molecular motion is responsible for the slowing down of mobility in glasses [21].

The paper has been organized as follows. In Sec. II we describe our samples and the experimental setup. The dielectric properties of bulk CB15 are described in the following section. In Sec. IV the dielectric spectra of CB15 dispersed with aerosils are presented. In this section a slow dielectric relaxation that has similar origin to the one observed in Ref. [32] is shown. The temperature dependence of the relaxation times of the bulklike processes, which follow a Vogel-Fulcher-Tamman (VFT) type of behavior typical for glasses, are presented in Sec. V. The main finding of our experiment is the Arrhenius-like temperature dependence of the relaxation times of the slow process, which is also presented in this section. Here we also explore the origin and properties of the slow process. In the final section we present the conclusions of our finding.

II. EXPERIMENT

We have studied filled CB15, both with hydrophilic and hydrophobic aerosils. CB15 was obtained from MERCK and was used without further purification. The material can exist for indefinite periods as isotropic liquid at room temperature and has an isotropic to crystal transition at 277 K. CB15 can be easily supercooled that has a monotropic cholesteric phase from 243 K to 219 K and a Smectic-A phase below 219 K [51]. Below 214 K the relaxation process moves out of the accessible frequency range of our measurement setup. However, the substance has a tendency to crystallize in between 277 and 243 K. The glass transition obtained by Mayer *et al.* using heat capacity measurements was around 210.5 ± 0.3 K, which was independent of the rate of cooling [54]. CB15 is, however, more stable on annealing to a temperature below the I-Ch transition and can stay in the cholesteric phase for at least a few days. For filling of the liquid crystal with inclusions, hydrophilic and hydrophobic aerosils, obtained from Degussa Corp. were used. The hydrophilic aerosils of type 300 with diameters around 70 Å and surface area 300 ± 30 m²/g and hydrophobic aerosils of type R812 with diameter around 70 Å and surface area 260 ± 30 m²/g were used for our experiment. On the surface of hydrophilic aerosil, there is one silanol group ($\equiv\text{Si-OH}$) per 0.28–0.33 nm². Hence the aerosils we used have about 9.7×10^{20} silanol groups per gm. The silanol groups are chemically reacted with dimethyldichlorosilane in a continuous process to obtain the hydrophobic aerosils [29].

The filled LCs were prepared in the following way. CB15-acetone mixture was prepared such that there was around 0.02 g of LC per cm³ of acetone. The required amount of aerosils, both hydrophilic and hydrophobic, dried under vacuum at 200 °C for around 15 h were then added to the CB15-acetone mixture. The whole mixture was then sonicated for 1 h to obtain a good dispersion of the aerosils in the medium. Acetone was then allowed to evaporate slowly while keeping the temperature of the mixture above 40 °C.

The mixture took about 20 h to dry out. The remaining sample was then kept overnight in vacuum, to ensure complete evaporation of acetone with the vacuum jar placed in an oven at 50 °C. Four different concentrations of hydrophilic aerosils were prepared with ρ_s equal to 0.050, 0.099, 0.153, and 0.199 g cm⁻³, where

$$\rho_s = \frac{m_s}{m_{LC}} \rho_{LC} \approx \frac{m_s}{m_{LC}} (1 \text{ g cm}^{-3}). \quad (1)$$

m_s and m_{LC} are the masses of the aerosils and LCs used in the mixture preparation. One concentration of hydrophobic aerosils with ρ_s as 0.205 g cm⁻³ was also prepared for comparison.

Measurements of the real (ϵ') and the imaginary (ϵ'') parts of the complex dielectric permittivity in the frequency range 10⁻² Hz–10 MHz were performed using the NOVOCONTROL broadband dielectric spectrometer which consists of a high resolution Dielectric/Impedance Analyzer ALPHA and an active sample cell. The active sample cell works exclusively with the ALPHA system where the sample capacitor is not directly connected to the analyzer by BNC cables but through an active impedance converter mounted on the cell head. The connection from the converter to the sample is done by rigid air insulated RF lines that avoid cable effects. The sample was placed in a liquid sample cell where the electrodes were separated by circular teflon rings of thickness around 1 mm. The liquid cell was then sandwiched between the capacitor plates of the active sample cell. For the temperature control of the sample cell the NOVOCONTROL four circuit Quatro system was used. The samples were measured in the temperature range from 173 K to 300 K with 0.1 K stability.

We were able to easily supercool the substance into the glassy state so the measurements were carried out in the following way. A required temperature was set whereupon we waited for stabilization for about 5 min. A frequency scan was performed and then we moved on to the next temperature. Due to the fast settling time of the NOVOCONTROL Quatro system the data were easily measured in the cooling regime for the above mentioned range of temperatures. Software packages WINDETA and WINFIT provided by NOVOCONTROL were used for the measurements and data analysis, respectively. For the quantitative analysis of the dielectric spectra we used the Havriliak-Negami function [67] which is incorporated in the WINFIT software. For the case of more than one relaxation process, taking into account the contribution of the dc conductivity to the imaginary part of dielectric permittivity, the Havriliak-Negami function in the frequency domain is given as

$$\epsilon^* = \epsilon_\infty + \sum_j \frac{\Delta\epsilon_j}{[1 + (i2\pi f\tau_j)^{1-\alpha_j}]^{\beta_j}} - i \frac{\sigma}{2\pi\epsilon_0 f^n}, \quad (2)$$

where ϵ_∞ is the high-frequency limit of the permittivity, $\Delta\epsilon_j$ the dielectric strength, τ_j the mean relaxation time, and j the number of the relaxation process. The exponents α_j and β_j describe the symmetric and asymmetric distribution of relax-

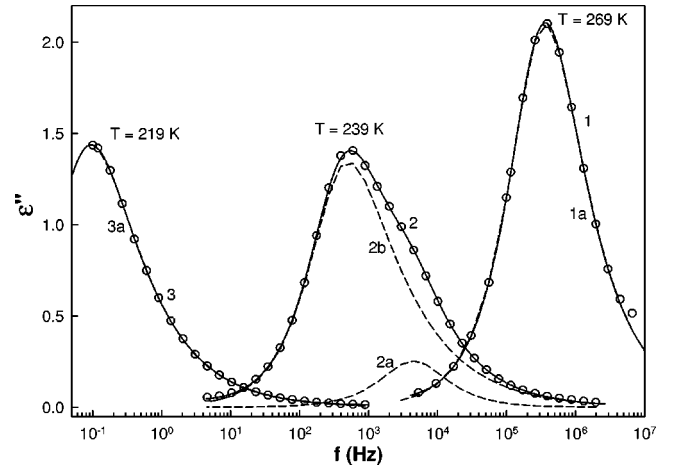


FIG. 1. ϵ'' vs frequency for bulk CB15 at $T=269$ K, 239 K, and 219 K (circles). Solid lines (1, 2, and 3) show fitting according to Eq. (2); dashed lines (1a, 2a, 2b, and 3a) represent deconvolution into elementary contributions.

ation times. The term $i\sigma/2\pi\epsilon_0 f^n$ accounts for the contribution of conductivity σ , with n as fitting parameter.

III. DIELECTRIC SPECTRA OF BULK CB15

Figure 1 represents a typical dielectric relaxation behavior for CB15. The data have been presented in the range where the d.c. conductivity has almost no contribution. In the isotropic and supercooled isotropic phase CB15 has one relaxation process, as has been observed before [52–54], and is of Davidson-Cole type (see data for $T=269$ K). It means that α in Eq. (2) is equal to zero whereas β is <1 . In the case of Debye behavior α should be equal to 0 and $\beta=1$. In the figure the solid lines represent fitting to Eq. (2). Upon further cooling, the sample enters a cholesteric phase whereupon we can observe two relaxation processes (curve 2, $T=239$ K). The secondary process, however, disappears below 219 K. The dashed lines (1a, 2a, 2b, and 3a) represent deconvolution into elementary contributions, and coincide with the solid line in the case of lines 1a and 3a. The main process (1a, 2a, and 3a) is due to the rotation of the molecules around their short axis [52–54]. The secondary process could probably be due to the precession of the elongated CB15 molecules around a local director [54]. The value of the static (average) dielectric permittivity was found to increase slightly upon cooling. The parameter β is around 0.75 for the main process in the supercooled isotropic phase whereas it is around 0.55 in the cholesteric phase. α is close to zero for the whole temperature range. The values of β were found to be comparable to the values of a typical glass-forming material [66]. The additional second process could easily be fitted to a Debye-type process. The dielectric strength of the secondary process gradually decreases and the process disappears below $T=219$ K. This dependence additionally suggests that the process is of precessional motion because with the decrease in temperature the order parameter is increasing and hence the angle of the precession is reduced. Below $T \approx 214$ K the relaxation processes moved out of the acces-

TABLE I. Fitting parameters for bulk CB15 and CB15 filled with aerosils.

$T(K)$	$\Delta\epsilon_a$	τ_a (s)	α_a	β_a	$\Delta\epsilon_b$	τ_b (s)	α_b	β_b	$\Delta\epsilon_c$	τ_c (s)	α_c	β_c
Bulk CB15												
269.0	4.9	5.4×10^{-7}	0	0.78								
239.0	0.51	3.5×10^{-5}	0	1	3.6	5.0×10^{-4}	0	0.56				
219.0	3.8	2.4	0	0.66								
CB15 filled with hydrophilic aerosils at $\rho_s = 0.050 \text{ g cm}^{-3}$												
268.0	8.4	6.7×10^{-7}	0.02	0.78	0.26	1.8×10^{-4}	0.56	1				
238.0	0.94	5.8×10^{-5}	0	1	7.0	8.8×10^{-4}	0	0.56	0.19	0.1	0.42	1
218.0	7.6	5.97	0	0.61								
at $\rho_s = 0.099 \text{ g cm}^{-3}$												
281.0	8.3	1.3×10^{-7}	0.01	0.70	0.5	5.7×10^{-6}	0.48	1	2.9	0.4	0.32	1
235.0	0.7	1.1×10^{-4}	0	1	6.9	1.9×10^{-3}	0.03	0.55	0.7	0.8	0.47	1
at $\rho_s = 0.153 \text{ g cm}^{-3}$												
269.0	6.8	7.0×10^{-7}	0	0.64	0.9	5.7×10^{-5}	0.59	1				
254.0	6.9	6.2×10^{-6}	0.06	0.79	0.8	3.7×10^{-3}	0.59	1				
at $\rho_s = 0.199 \text{ g cm}^{-3}$												
256.0	5.5	4.4×10^{-6}	0.07	0.79	0.9	1.3×10^{-3}	0.57	1				
238.0	0.59	4.9×10^{-5}	0.02	1	4.4	7.1×10^{-4}	0.03	0.56	1.2	0.2	0.67	1
at $\rho_s = 0.205 \text{ g cm}^{-3}$												
256.0	7.4	4.1×10^{-6}	0.08	0.79	0.1	4.2×10^{-4}	0	1				
239.0	1.1	3.8×10^{-5}	0.11	1	5.9	4.6×10^{-4}	0.05	0.63	0.2	3.0×10^{-2}	0	1

sible frequency range. The above described behavior was found to be almost independent of the rate of cooling of the sample. The fitting parameters obtained for the curves in Fig. 1 are given in Table I. The data presented in the paper are taken from the cooling run only. Similar behavior was observed in the heating run. The data obtained in the heating run had a tendency to crystallize in between 243 K and 277 K, making the measurements more difficult and hence were not considered in the analysis.

The temperature dependence of relaxation times of the main process obeyed the VFT law [66]

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right), \quad (3)$$

typical for a glass-forming liquid, where B is the fragility index, τ_0 is the limiting high temperature relaxation time, and T_0 is the Vogel temperature. In Fig. 2 we represent the plot of $\ln \tau$ vs $1/(T - T_0)$ where the value used for T_0 was chosen such that we obtained the best linear fit for $\ln \tau$ vs $1/(T - T_0)$. The fitting parameters obtained are given in Table II. In addition to the VFT temperature dependence the dielectric function is a stretched exponent, as obtained by Fourier transforming the non-Debye spectrum into dipole moment time autocorrelation function, clearly supporting the fact that CB15 is a glass former [66]. If we use the definition of T_g as the temperature at which the relaxation time is 100 s then $T_g = 214.0$ K.

IV. DIELECTRIC SPECTRA OF CB15 DISPERSED WITH AEROSILS

The dielectric spectra were measured at various temperatures in the cooling run for different concentrations of CB15 filled with hydrophilic aerosils. The values of the dielectric permittivity are not absolute as it was difficult to obtain a precise value of the thickness of the sample, at least for the high concentration samples. The data in the paper have been presented such that we can see an increasing influence of

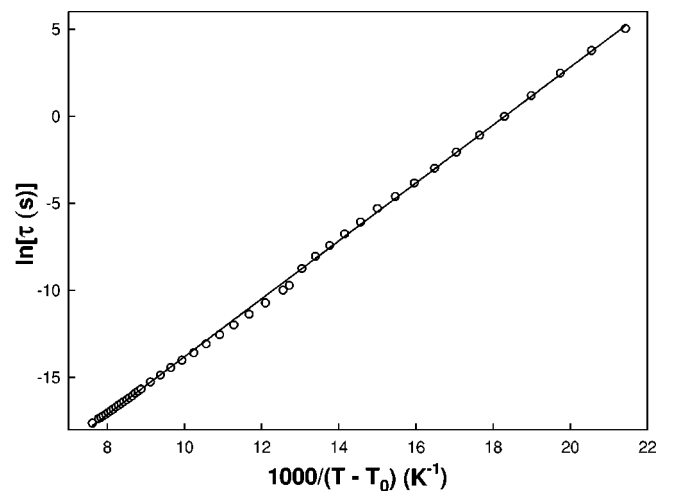


FIG. 2. Plot of $\ln \tau$ vs $1/(T - T_0)$ (circles) for the main relaxation process in CB15 obtained in cooling run. The line is a fit with a straight line.

TABLE II. Fitting parameters for Eq. (3) for bulk CB15 and CB15 filled with aerosils.

ρ_s (g cm ⁻³)	ℓ_0 (Å)	$\ln\{\tau_0$ (s) $\}$	B (K)	T_0 (K)	T_g (K)
Bulk CB15					
0	∞	-29.7	1512.8	169.9	214.0
CB15 filled with hydrophilic aerosils					
0.050	1330	-29.6	1517.2	169.8	214.2
0.099	675	-29.4	1502.6	169.7	213.9
0.153	440	-29.1	1446.7	171.1	214.1
0.199	335	-28.1	1290.3	174.9	214.4
CB15 filled with hydrophobic aerosils					
0.205		-28.8	1407.8	171.5	213.7

confinement with increasing aerosil concentration. In Fig. 3 we show the dielectric behavior for CB15 filled with 0.05 g cm⁻³ of hydrophilic aerosils. The solid lines represent fit according to Eq. (2) by taking the dc conductivity into account also. The dashed lines represent the separated relaxation processes. The bulklike relaxation for CB15 filled with 0.05 g cm⁻³ of hydrophilic aerosils were similar to that observed for bulk CB15. Additionally the dc conductivity

[curve 1c in Fig. 3(a)] is also similar to the bulk behavior (not shown in the figures). The fitting parameters corresponding to curve 1c are $\sigma=2.1 \times 10^{-10}$ S m⁻¹ and $n=0.98$. The process due to the rotation of molecules around short axis is of Davidson-Cole type similar to that observed in bulk. In addition to the bulklike process we see evidence of a slower process that is more obvious when seen on log-log scale [Fig. 3(a)]. The characteristic frequency of the slow process is about two decades lower in magnitude than the main process. This process could be fitted with a Cole-Cole process with α around 0.55, which means the process has a wide distribution of relaxation times. In fact the process can also be fitted with Havriliak-Negami distribution function, but such a method can complicate the fitting analysis as we have to take into account an extra fitting parameter. The dielectric strength of this process is more or less constant as a function of temperature and is roughly 2% of the main relaxational process. The process exists at all temperatures but could not be measured for very low temperatures as it shifted to very low frequencies. At temperatures corresponding to the cholesteric phase a secondary process similar to the one observed in bulk CB15 was also observed. This process was also not influenced by the presence of the aerosil particles. The fitting parameters of the spectra shown in Fig. 3 are given in Table I. We believe that the slow relaxation process is due to the rotation of molecules around their short axis for molecules that are close to the surface of the aerosils. This process is slower than the bulk rotation around the short axis because the viscosity in the surface layers is greater than the bulk viscosity. The cause of the higher viscosity could be due to the preference of the dipole moment that is at the edge of the molecule to hydrogen bond with the silanol group present at the surface of the aerosils. This kind of bonding is also responsible for the homeotropic alignment at the surface of the particles [43]. Additionally a preferential polar ordering can also exist at the surface with the polar cyano group pointing towards the aerosil surface [68]. The bonding could be breaking and mending with time leading to a considerable slowing of the rotation of the molecules. The behavior is typical of all concentrations where the surface process becomes more prominent at higher concentrations of hydrophilic aerosils.

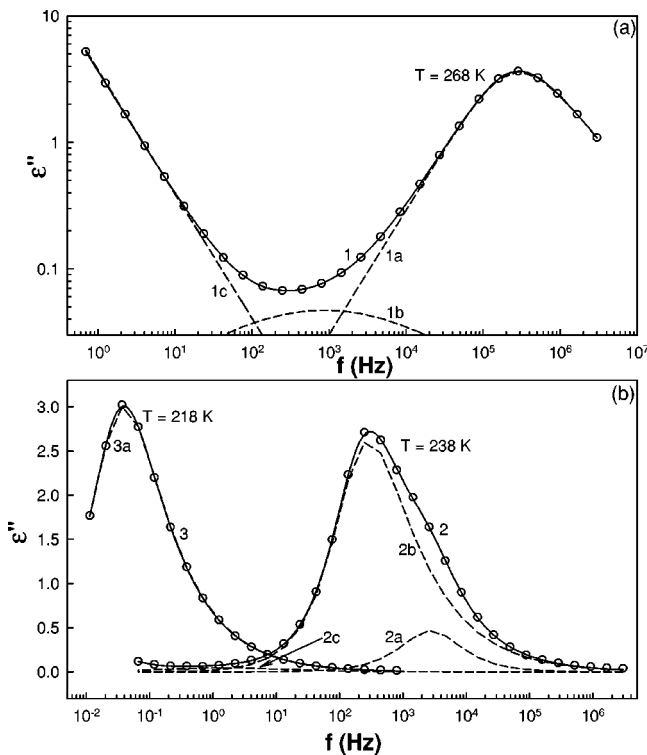


FIG. 3. (a) Log-log plot of ϵ'' vs frequency for CB15 filled with 0.05 g cm⁻³ hydrophilic aerosils at $T=268$ K (circles). Solid line 1 shows fitting according to Eq. (2); dashed lines (1a, 1b) represent the separated relaxation processes whereas 1c is the dc conductivity. (b) Semilog plot of ϵ'' vs frequency of CB15 filled with 0.05 g cm⁻³ hydrophilic aerosils at $T=238$ K and 218 K. Solid lines (2 and 3) show fitting according to Eq. (2); dashed lines (2a, 2b, 2c, and 3a) represent the separated relaxation processes. See Table I for fitting parameters.

In Fig. 4 we show the dielectric behavior for CB15 filled

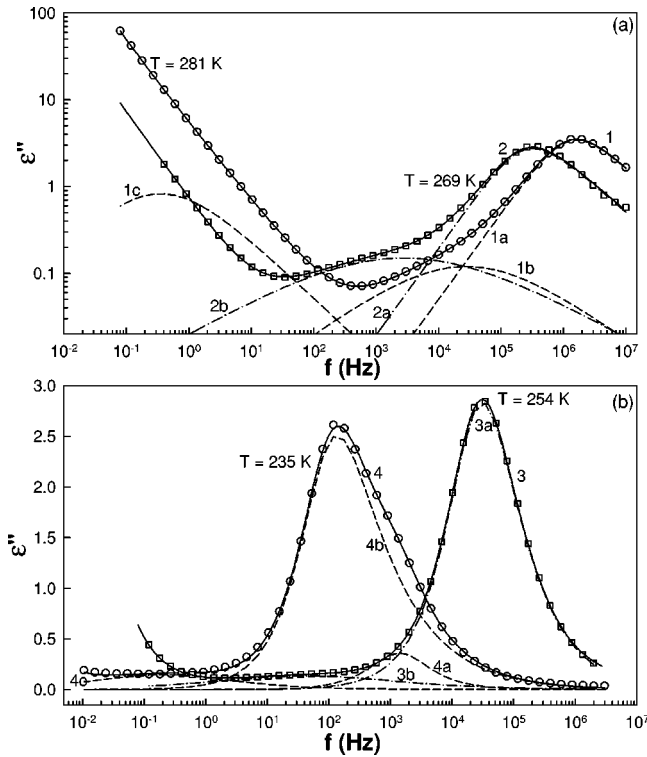


FIG. 4. (a) Log-log plot of ϵ'' vs frequency for CB15 filled with 0.099 and 0.153 g cm^{-3} hydrophilic aerosils at $T=281$ K (circles) and $T=269$ K (squares), respectively. Solid lines (1 and 2) are fitting lines; dashed lines (1a, 1b, and 1c) represent the separated relaxation processes for 0.099 g cm^{-3} ; and dash-dotted lines (2a and 2b) represent the separated relaxation processes for 0.153 g cm^{-3} . (b) Semilog plot of ϵ'' vs frequency of CB15 filled with 0.153 g cm^{-3} hydrophilic aerosils at $T=254$ K (squares) and 0.099 g cm^{-3} hydrophilic aerosils at $T=235$ K (circles). Solid lines (3 and 4) are fitting lines; dash-dotted lines (3a and 3b) represent the separated relaxation processes for 0.153 g cm^{-3} ; and dashed lines (4a, 4b, and 4c) represent the separated relaxation processes for 0.099 g cm^{-3} .

with 0.099 and 0.153 g cm^{-3} hydrophilic aerosils. In Fig. 4(a) we show the spectra on log-log scale whereas the spectra are shown on a semilog scale in Fig. 4(b). In the case of filled LCs with concentrations of aerosils, 0.099 g cm^{-3} hydrophilic aerosils or higher, we could see a very slow relaxation process with the maximum around 1 Hz. In Fig. 4(a) we show one such typical process represented by a dashed curve 1c that was obtained for 0.099 g cm^{-3} at $T=281$ K. We want to specify that the whole spectrum below 100 Hz could also be fitted without considering the extra process but taking only conductivity into account. However, in such case the value of the fitting parameter n was around 0.8 whereas this parameter in the bulk and at 0.050 g cm^{-3} was above 0.95 . On including a slow relaxation process such as the one shown as curve 1c in the figure the value of n was greater than 0.95 . The relaxation time of the process is similar to that observed for 5CB filled with 2.3% volume percent of hydrophilic and hydrophobic aerosils in Ref. [34]. The origin of this process could be due to relaxation of the interfacial polarization arising at the aerosil particle-liquid crystal inter-

face as described in Ref. [34]. However, our main aim is not to investigate this unclear process; hence, we will not consider it any further. The bulklike processes observed for 0.099 g cm^{-3} and 0.153 g cm^{-3} samples are also not influenced by the presence of aerosil particles. The skewness fitting parameter β is similar to those observed in bulk samples with α remaining close to zero. The secondary process (curve 4a) is also present in the temperature range from 243 K down to 219 K for each of the concentrations and is also not influenced by the presence of the external particles. However the processes shown as curves (1b— $T=281$ K; 4c— $T=235$ K) at 0.099 g cm^{-3} and (2b— $T=269$ K; 3b— $T=254$ K) at 0.153 g cm^{-3} in the figure, which form our main consideration, are strongly influenced by the amount of the aerosils present in the sample. This process is quite weak for the 0.05 g cm^{-3} sample, but becomes more significant for 0.099 g cm^{-3} and higher concentrations. The dielectric strength of this process is now 8% of the main bulklike process for 0.099 g cm^{-3} . The distribution of the relaxation time parameter α however remains similar to that observed for the bulk sample. Similar values were also obtained for 0.153 g cm^{-3} samples except for the fact that the dielectric strength of the process increased even further to around 11% of the main relaxation process. This process has similar origin as described for 0.05 g cm^{-3} and was also observed for a nonglass-forming LC 7CB at a high concentration of hydrophilic aerosils [32].

For the highest aerosil concentration sample the surface process was even more prominent. In order to relate the origin of this process to the relaxation in surface layers, the high concentration sample was compared with CB15 filled with hydrophobic aerosils with more or less similar concentration. The hydrophobic aerosils R812 are prepared from the hydrophilic 300 particles and hence their size and surface area are close to each other. In Fig. 5 we show the comparison for the data obtained for hydrophilic and hydrophobic aerosils at similar concentrations. Not much influence is observed for the bulklike processes in either hydrophilic or hydrophobic case even at this high concentrations. The fitting parameters are similar to those observed for other concentrations. A major difference is observed only for the surface process for hydrophilic samples at 0.199 g cm^{-3} where the dielectric strength is around 16% of the main process. The α parameter representing the distribution of relaxation times is similar to the values obtained for lower concentrations. In the case of CB15 filled with hydrophobic aerosils this process was very weakly present as would be the case if the surface interaction between the aerosil surface and the LC molecules were weaker. The dielectric strength is around 2% of the main process. For the hydrophobic aerosils not all the silanol groups are covered with the methyl groups, in fact only 75% of them chemically react [29], hence there could be some CB15 molecules, much less in number as compared to the hydrophilic samples, that have the tendency to form hydrogen bond with the unreacted silanol groups. In such case the surface process observed for hydrophobic sample at 0.205 g cm^{-3} could be comparable to 0.05 g cm^{-3} sample with hydrophilic aerosils. In summary, we can safely conclude that the slow process observed for high concentration

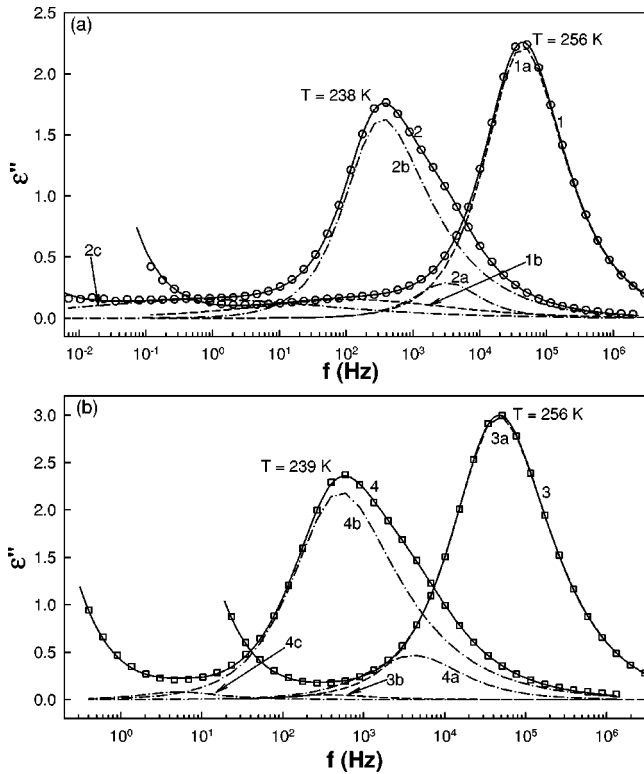


FIG. 5. (a) Semilog plot of ϵ'' vs frequency for CB15 filled with 0.199 g cm^{-3} hydrophilic aerosils at $T=256 \text{ K}$ and 238 K (circles). Solid lines (1 and 2) are fitting lines; dashed lines (1a and 1b— $T=256 \text{ K}$); and dash-dotted lines (2a, 2b, and 2c— $T=238 \text{ K}$) represent the separated relaxation processes. (b) Semilog plot of ϵ'' vs frequency for CB15 filled with 0.205 g cm^{-3} hydrophobic aerosils at $T=256 \text{ K}$ and 239 K (squares). Solid lines (3 and 4) are fitting lines; dashed lines (3a and 3b— $T=256 \text{ K}$); and dash-dotted lines (4a, 4b, and 4c— $T=239 \text{ K}$) represent the separated relaxation processes.

of hydrophilic aerosils is due to obstructed dynamics of the molecules that are in the vicinity of the aerosil surfaces. With the increasing concentration of aerosils, the total surface area of the aerosils per unit volume of the sample is increasing, causing an increase in the number of molecules close to the surface and hence a larger contribution to the dielectric strength of the surface process.

V. TEMPERATURE DEPENDENCE OF RELAXATION TIMES

The temperature dependence of the relaxation times corresponding to the rotation around the short axis for bulk CB15 and CB15 filled with aerosils at different concentrations are presented in Fig. 6. The relaxation times for the secondary process observed in the cholesteric phase have been also shown. As we can see from the figure the presence of either hydrophilic or hydrophobic aerosils has no influence on the relaxation times of the bulklike processes. This could be due to the fact that the confining regions are not small enough to have an influence over the bulk processes. The relaxation times obtained for bulk CB15 (circles) has also been plotted for comparison. If we use the method of

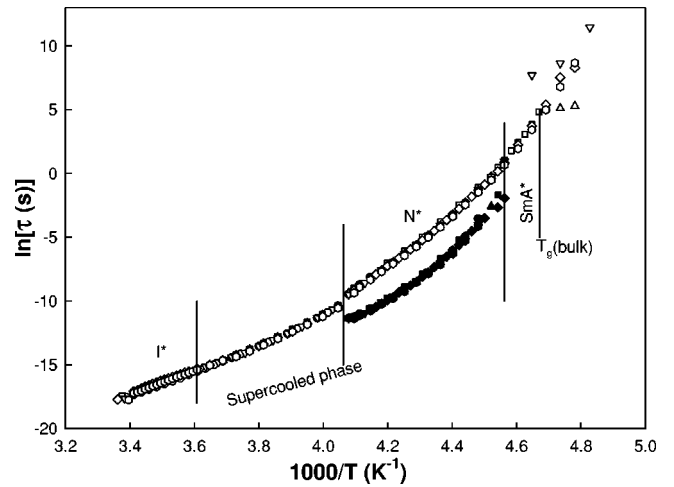


FIG. 6. Temperature dependence of relaxation times for bulklike processes for bulk CB15 (circle) and various other concentrations (hydrophilic aerosils: square— 0.050 , triangle up— 0.099 , triangle down— 0.153 , and diamond— 0.199 ; and hydrophobic aerosils: hexagon— 0.205 g cm^{-3}). Open symbols—rotation around short axis, closed symbols—rotation in a cone around the local director. All symbols may not be visible as they lie on top of each other representing no influence of the presence of aerosils on the bulklike modes.

calculating the size of the confinement from Ref. [43] then the size of the domains of LCs would be given by $\ell_0 = 2/a\rho_s$, where ℓ_0 is the length scale, a is the surface area of the aerosils ($\sim 300 \text{ m}^2 \text{ g}^{-1}$), and ρ_s is $(m_s/m_{LC})\rho_{LC}$. On using such relation we obtain the aerosil void sizes where the LC molecules reside as 1330 \AA for 0.05 , 675 \AA for 0.099 , 440 \AA for 0.153 , and 335 \AA for 0.199 g cm^{-3} of hydrophilic aerosils, respectively. Such a size could be an underestimate as it has been found that at least three to four of the particles usually lump together in the final mixture [43]. Hence the actual size maybe greater than our estimate. The length scales of this size of confinement may not have a significant influence on the bulk modes. From Fig. 6 we can additionally see that all the concentrations have similar VFT-like temperature dependence of relaxation times as observed for bulk CB15 (Fig. 2). In Table II we represent the fitting according to Eq. (3) for the data represented in the figure, where an estimate of the glass transition obtained by using the definition as described before has been given. We observe that with our size of confinement there is little influence on the glass transition temperature. In the case of the highest concentration (0.199 g cm^{-3}) there is an indication of a slight decrease in the glass transition.

Figure 7 represents the temperature dependence of the relaxation times for the surface process. The figure shows the extracted relaxation times for various concentrations. First of all, the values of relaxation times are similar for all the concentrations, although it is more noisy in the case of the low concentration sample with $\rho_s = 0.050 \text{ g cm}^{-3}$. The data for all cases follow a straight line on a plot of $\log_e \tau$ vs $1/T$. We can thus say that the surface process follows an activated type of dynamics whereas the bulk processes follow a glasslike behavior. The glasslike behavior in bulk is observed due

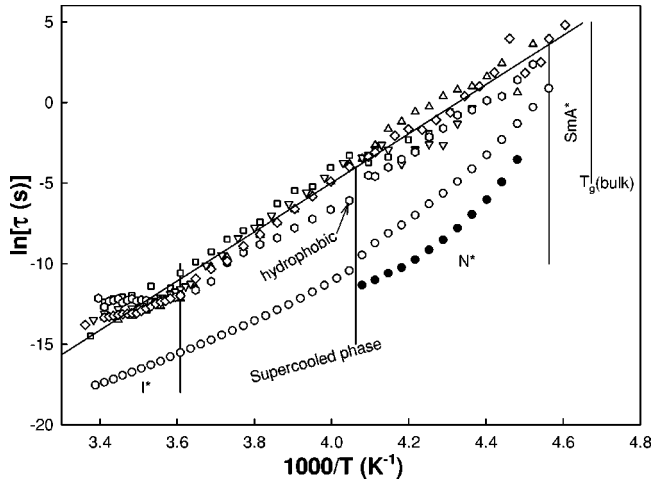


FIG. 7. Temperature dependence of relaxation times for surface processes for CB15 at different concentrations (hydrophilic aerosils: square—0.050, triangle up—0.099, triangle down—0.153, and diamond—0.199; and hydrophobic aerosils: hexagon—0.205 g cm⁻³). Line represents fitting to a straight line. For comparison the processes observed for bulk CB15 have also been shown where open circles represent rotation around short axis and closed circles represent rotation in a cone around the local director.

to the exponential growth of the rearranging region of cooperativity of the relaxing molecules as we lower the temperature [69]. Within a region of cooperativity after a molecule undergoes rotation, the rest of the molecules rearrange themselves in pursuit. However, in the case of the surface process the region of cooperativity is limited to the molecules close to the surface, which does not grow. The fixed number of the molecules in the surface layer can be inferred from the constant value of the dielectric strength of the surface process as a function of temperature. In Fig. 8 we show the dielectric strengths for the surface processes at different concentrations of the aerosils. To make a proper comparison of $\Delta\epsilon_{surf}$ among different samples, where systematic errors due to unequal capacitor and sample geometries could exist, the mag-

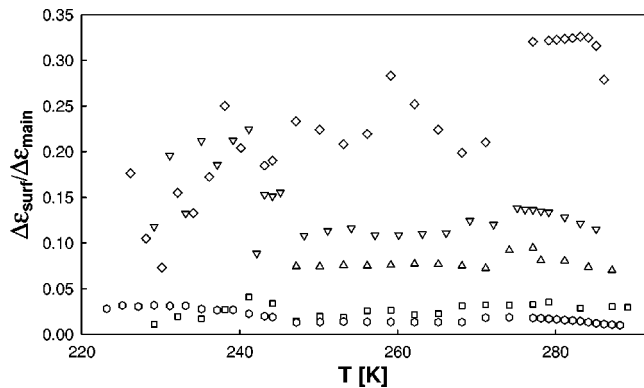


FIG. 8. Temperature dependence of dielectric strength of the surface process normalized with the values of the main process for CB15 filled with different concentrations of hydrophilic and hydrophobic aerosils. Hydrophilic aerosils: square—0.050, triangle up—0.099, triangle down—0.153, and diamond—0.199; and hydrophobic aerosils: hexagon—0.205 g cm⁻³.

nitudes normalized to $\Delta\epsilon_{bulk}$ have been presented. The dielectric strength of the surface process is seen to be increasing with the increase in the number of molecules close to the surfaces; however, the values are almost static with changes in temperature. The scatter in the data at low temperatures is because the surface process is getting out of measurement range. The rise in the dielectric strength for this process at temperatures above 269 K for $\rho_s = 0.199$ g cm⁻³ may be unrealistic and could be due to an influence from the main process in fitting analysis. In the study of the dynamics of glass-forming LC in thin layers [21], it was shown that the relaxation time of the interfacial molecules depended on the film thickness of the LCs, i.e., on the number of molecules present in the region of cooperativity. In the investigation a direct evidence that the molecular motion in glass-forming liquids is collective was also shown. If we follow the above conclusion then in our case the thickness of the surface layer should not be changing as the relaxation times are more or less the same for all concentrations at a given temperature. The thickness of the surface layer at all temperatures seems to be considerably thin because in a film of thickness less than the length of cooperativity the mobility of the molecules would be different from that of a film with thickness greater than the size of the cooperating region. Thus for a film of glass-forming material the temperature dependence of the relaxation times should have different dependencies for temperatures where the thickness of the film is below the size of cooperativity than at temperatures where the size is greater.

Let us consider the following estimate. For the 0.199 samples, the amount of aerosils in 1 cm³ of the sample can be calculated to be around 0.182 g using a value of 2.2 g cm⁻³ as the density of silica. The amount of LCs would be around 0.917 g per cm⁻³ of the sample. Thus the surface area of the aerosils would be 54.6 m² per cm⁻³ of the sample. Using the value of the molecular weight of CB15 (=249.40 g mol⁻¹) the number of LC molecules in each cm³ of the sample would be 2.21×10^{21} . Following the Kirkwood-Frölich approach the relation:

$$\Delta\epsilon \propto \frac{\mu_{eff}^2 N}{kTV} \quad (4)$$

holds, where k is the Boltzmann constant, T is the temperature, and N/V is the number of molecules per unit volume of the sample [70,71]. μ_{eff} is the effective dipole moment given by the following expression:

$$\mu_{eff}^2 = g\mu^2, \quad (5)$$

where g is the Kirkwood correlation factor. In the case of nearest neighbor interaction

$$g = 1 + z\langle \cos \theta_{ij} \rangle, \quad (6)$$

where z is the number of nearest neighbors and $\cos \theta_{ij}$ is the angle between the dipole moments of molecule i and the nearest neighboring molecules. If we assume for the moment that there is no polar ordering at the surface then the value of g should be around 0.5 as for bulk [70]. In that case 14% of the molecules should be contributing to the surface relax-

ation, which in number of molecules corresponds to be 3.09×10^{20} in the surface layers. Taking the number of LC molecules attaching directly at the surface as $3 \times 10^{18} \text{ m}^{-2}$ gives the number of particles right on the surface. On dividing the number of particles in surface layers by this number we would get the number of layers. Using similar calculations for other concentrations we got the number of layers as 1.1, 2.0, 1.7, and 1.9 for 0.05, 0.099, 0.153, and 0.199 g of aerosil cm^{-3} of LC samples, respectively. In the case when three to four particles lump together, the surface available should be smaller. In such a case the depth of the surface layer should be greater by a few more lengths of the LC molecules. However, in the case of preferential polar ordering near the surface, the correlation factor is greater than the bulk value. In general, $g \geq 1$ for a parallel orientation. Hence in our case, where there is a preferential orientation at the surface and possibly at the next layer, g could be greater or close to one. Thus the effective dipole moment should be greater than the bulk value. In such a situation the number of layers should be less than the estimated value obtained by considering no polar ordering. The above estimate is a very rough estimate which may be off by 100%. A proper estimate is quite difficult as the information about the dipole-dipole correlation in the surface layers are unavailable.

From the data for hydrophilic samples we can obtain an activation energy for the surface process, which is around 126 kJ/mol, by taking the slope of the combined data. This value is much greater than the value for 5CB in the nematic phase. The value reflects the rather large potential barrier the molecule has to overcome in order to rotate in the surface layers. The potential barrier also entails the additional potential due to the interaction of the aerosil surface and the LC molecules. In the case of the hydrophobic aerosils the slope is slightly smaller than in the case of hydrophilic aerosils. The relaxation time in a rearranging region of cooperativity can be obtained by the following relation [69]:

$$\tau(T) = \tau_0 \exp \frac{n\Delta\mu}{kT}, \quad (7)$$

where τ is the relaxation time, τ_0 is the limiting high temperature relaxation time, $\Delta\mu$ is the potential barrier hindering the cooperative rearrangement per molecule, k is the Boltzmann constant, and n is the number of molecules in the rearranging region. On comparing the value of the tangent at 295 K for the Arrhenius plot of the relaxation times vs temperature, where the region of cooperativity is close to the molecular size, with the value of the activation energy obtained from the surface process, we can obtain the surface interaction energy. The value obtained by using such a procedure was 40.2 kJ mol^{-1} . This value is comparable to the strength of hydrogen bonds of 40 kJ mol^{-1} found for some systems [72].

VI. CONCLUSION

Using broadband dielectric spectroscopy, glass-forming liquid crystal CB15 filled with different concentrations of hydrophilic and hydrophobic aerosils has been investigated over a temperature range of 173 K–300 K. Three relaxation processes are observed, where two of the processes are very similar to that observed in bulk. The other slow process is related to the relaxation of molecules in the surface layers and is two orders of magnitudes slower than the main bulk process. The bulklike processes show a Vogel-Fulcher-Tamman-like temperature dependence whereas in the surface layers an activated type of dynamics is observed. The Arrhenius-like temperature dependence of relaxation times for the slow process can be explained by considering that the region of cooperativity is limited to a thin size corresponding to the thickness of the thin surface layers.

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