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Accelerated dielectric relaxation in the isotropic phase of associating liquid crystals dispersed with aerosils

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The dielectric response of liquid crystals in their nematic phase shows an acceleration of the relaxation associated with the rotation around the short molecular axis when dispersed with aerosils. However, in the isotropic phase, this acceleration is only seen for certain liquid crystalline molecules. In this paper, an associating liquid crystal (5CB) and a shorter monotropic liquid crystalline member of the same homologous series (4CB), a liquid crystal that does not show association (5NCS) and a nonassociating liquid crystal ($\bar{5}$O5) have been studied by dielectric spectroscopy in the isotropic phase. Both 4CB and 5CB show a constant acceleration in the isotropic phase, observed over a broad temperature range. 5NCS and $\bar{5}$O5 do not show an acceleration in their isotropic phase. It seems that the disturbance of the dipole-dipole association process for the associating molecules is an important factor in the explanation of the acceleration of the relaxation in the isotropic phase.

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I. INTRODUCTION

Dispersions of liquid crystals with aerosil nanoparticles have been the subject of many studies since their introduction as a potential means for bistable liquid crystal displays [1]. However, it turned out that these aerosil dispersed liquid crystals (ADLCs) were also useful in the fundamental studies of disorder in liquid crystalline systems.

The aerosil particles form a hydrogen bonded network throughout the liquid crystal (LC). The interaction between the LC molecules and the aerosil particles leads to a number of changes in the properties of the liquid crystalline phases. We shortly mention some publications related to these changes. A number of the changes at the phase transitions are ascribed to quenched random disorder; they have been reviewed for 8CB [2]. Extensive calorimetric work is available, for example, [3–7]. Theoretical work predicts the disruption of long range order and a glasslike state [8,9]. The structure has been studied by x-ray and NMR [10–14]. Computer simulations and optical studies were used to investigate certain aspects of the disorder in ADLCs [15–17].

Apart from calorimetry, NMR, and other techniques, dielectric spectroscopy also has been applied to ADLCs. Since the initial work of Tschierske *et al.* [18], two main differences have been observed in the dielectric relaxation spectra of these systems as compared to bulk systems. The first one is a slow relaxation of LC molecules near the surface of the aerosil particles [19,20]. The second observation, an acceleration of the relaxation process related to the rotation around the short axis, was only recently discussed in two systems as the main subject of the study [21,22], although it was already reported by Tschierske *et al.* [18] and by others [23,24]. In our previous paper [21], we verified the existence of the acceleration mainly in the nematic phase of 5CB, and proposed a qualitative model to explain this acceleration. However, we also observed the existence of the acceleration in the isotropic phase, although less pronounced. In fact, the model of isotropization put forward in that paper, cannot explain the acceleration in the isotropic phase.

Isotropization, as presented in [21], states that the presence of the aerosil network divides the liquid crystalline phase in a number of domains. These domains, with local nematic order, are themselves randomly oriented. When looking at the systems at a mesoscopic scale, the long range nematic order is disrupted and the sample appears more isotropiclike to the observer. In such a case, one can expect that the dynamics of the liquid crystal molecules evolves toward that of the isotropic phase. Since the relaxation process in the isotropic phase is faster than the main one in the nematic phase, this results in the acceleration of the rotation around the short axis, as we have observed in 5CB.

However, this model fails to explain the (smaller) acceleration that we also observed in the isotropic phase of 5CB [21], since in the nematic phase it explicitly involves the presence of the nematic order. Therefore, in this paper, we want to explicitly address the behavior in the isotropic phase. Since the acceleration is only explicitly reported in 5CB, we want to extend the number of ADLCs in which the acceleration is seen, and more particularly by choosing different types of LCs in terms of their dipole moments. Therefore, measurements were performed on four molecules, namely, the associating molecules 5CB and 4CB, and the nonassociating molecules 5NCS and $\bar{5}$O5. Their associating or nonassociating nature will be discussed further in Sec. III. Section IV describes the results of the dielectric relaxation measurements, followed by a discussion in Sec. V.

II. EXPERIMENTS

4-*n*-pentyl-4′-cyanobiphenyl (5CB) was obtained from Merck and 4-*n*-butyl-4′-cyanobiphenyl (4CB) was obtained from British Drug Houses. 1-(4-*trans*-pentylcyclohexyl)-2-(4-isothiocyanatophenyl)ethane (5NCS) was obtained from the Military University of Warsaw. 4-*n*-pentylphenyl

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4′−*n*-pentyloxybenzoate ($\bar{5}$O5) was obtained from AWAT Co. Ltd., Poland. All were used without further purification. The phase sequences, in °C, are the following:

$$\text{4CB:}\quad \mathrm{I}\underset{48}{\leftarrow}\mathrm{K},$$

$$\text{5CB:}\quad \mathrm{I}\underset{35.3}{\leftarrow}\mathrm{N}\underset{22.5}{\leftarrow}\mathrm{K},$$

$$\text{5NCS:}\quad \mathrm{I}\underset{48.2}{\leftarrow}\mathrm{N}\underset{41.1}{\leftarrow}\mathrm{K},$$

$$\bar{5}\text{O5:}\quad \mathrm{I}\underset{54.4}{\leftarrow}\mathrm{N}\underset{40\pm2}{\leftarrow}\mathrm{K}.$$

For completeness it should be mentioned that 4CB has a monotropic nematic phase below 16.5 °C on supercooling [25,26]. The transition temperature values are those obtained in heating cycles. There is typically not much difference for the isotropic to nematic values (T_{NI}) between heating and cooling cycles, but substantial supercooling is observed for the transition to the crystalline phase.

The aerosils were obtained from Degussa. We used hydrophilic aerosils A300, with a typical diameter of 7 nm and a surface area of 300 m^2/g [27]. Samples were prepared according to the solvent evaporation method introduced by Haga and Garland [4], but with very pure acetone instead of ethanol. The aerosils were dried at 200 °C in a low vacuum for about 15 h. The required amounts of liquid crystal and aerosils were mixed in acetone and dispersed by ultrasound. Then the acetone was evaporated slowly from this mixture, while keeping the temperature above the isotropic to nematic transition temperature. The sample was then again dried under vacuum. Four samples were prepared: 5CB with 16.6% aerosils, 4CB with 14.5% aerosils, 5NCS with 16.9% aerosils, and $\bar{5}$O5 with 16.0% aerosils. 1% means that 0.01 g of aerosil particles was added to 1 cm^3 of liquid crystal.

Dielectric measurements were performed with a Hewlett-Packard HP4291B impedance analyzer, in the frequency range 1 MHz to 1 GHz. The sample was contained in a homemade parallel plate capacitor; temperature control was assured by a homemade oven, a cylindrical cavity where a temperature controlled fluid flows through the walls. The samples were measured under a permanent magnetic field of 0.4 T, such that the liquid crystalline compounds were aligned parallel to the probing electric field. This way, the rotation around the short axis is the dominant contribution to the dielectric spectrum in the liquid crystalline phase.

Analysis of the spectra was performed by fitting the imaginary part with one or two Havriliak-Negami functions. We have used the Havriliak-Negami function in the following form:

$$\epsilon^* = \sum_j \frac{\Delta\epsilon_j}{[1+(i\omega\tau_j)^{\alpha_j}]^{\beta_j}} + \epsilon_\infty, \tag{1}$$

where $\Delta\epsilon_j$ gives the strength of the relaxation process, τ_j is the relaxation time, and α_j and β_j describe, respectively, the symmetric and asymmetric broadening of the curve. The index j gives the number of terms included. ϵ_∞ is the high frequency limit of the real part of the permittivity. For 4CB, 5CB, and 5NCS, j was 1 for the isotropic phase and 2 for the liquid crystalline phase, however, in the LC phase β was fixed to 1. For $\bar{5}$O5 two relaxation terms with $\beta=1$ were used for both phases.

The relaxation times given further are those of the maximum of the peak. We chose the peak maximum because otherwise the relaxation times of spectra with asymmetric broadening cannot be compared. To calculate the relaxation time related to the maximum of the relaxation peak, the following formula was used [28]:

$$\tau_{\max} = \tau\left[\sin\frac{\alpha\pi}{2+2\beta}\right]^{-1/\alpha}\left[\sin\frac{\alpha\beta\pi}{2+2\beta}\right]^{1/\alpha}. \tag{2}$$

III. STATIC PROPERTIES OF THE LIQUID CRYSTALS

5CB is a well-studied LC. It consists of a biphenyl core, at one end terminated with a pentyl chain and at the other end by a cyano group. In this cyano end group a dipole moment of 5 D is located, oriented along the long molecular axis. 4CB is the same molecule as 5CB, except that its alkyl terminal chain is one carbon atom shorter. It forms a monotropic nematic phase on supercooling [25,26], however, our measurements for 4CB were made at least 20 °C above this transition.

Liquid crystals with a strong terminal dipole moment are known to exhibit antiparallel correlation of the dipole moment. Two molecules orient themselves antiparallel, and overlap each other partially. This results in a partial canceling of the dipole moments. The pair formation is a dynamical process: pairs are formed and broken continuously. The pair formation is particularly well studied in cyanobiphenyl liquid crystals. Among its consequences are the formation of the SmA_d phase, where the layer spacing of about 1.4 times the molecular length is interpreted as the length of the antiparallel correlated pairs [29]. For dielectric measurements, the measured static dielectric permittivity for associating molecules is lower than the calculated values from models in which they are considered molecules with noninteracting dipoles, because the effective dipole moment of such antiparallel pairs is much lower than the molecular dipole moment.

The pair formation is also the cause of a dielectric pretransitional effect at the isotropic to nematic ($I-N$) transition. On approaching the weakly first order $I-N$ transition, the pair formation is enhanced by the occurrence of growing nematic fluctuations: it is easier for two molecules to associate antiparallel in a nematic fluid than in an isotropic one. Away from the transition the number of pairs is not changing much and essentially only the not associated (on average) “free” (not paired) dipoles react to the probing field. As the fluctuations with nematic order increase, the formation of pairs becomes easier, their number increases, and the number of free dipoles that contribute to the static permittivity decreases. The result is a static permittivity that far from the transition behaves like the expected $1/T$, but on approaching the $I-N$ transition, it bends below this behavior, reaches a

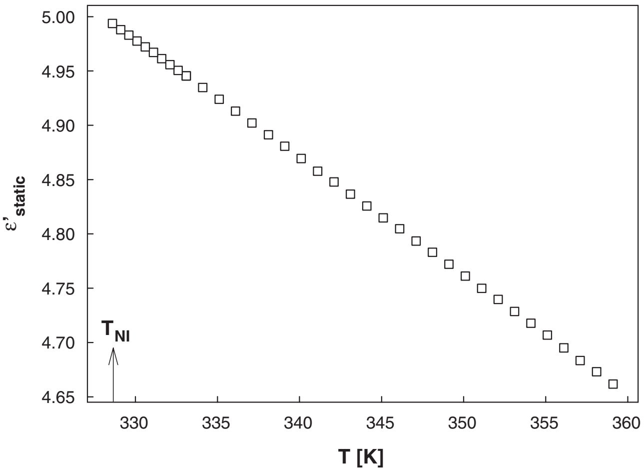

FIG. 1. Static dielectric permittivity of bulk $\bar{5}$O5 in its isotropic phase, measured at 12.6 kHz.

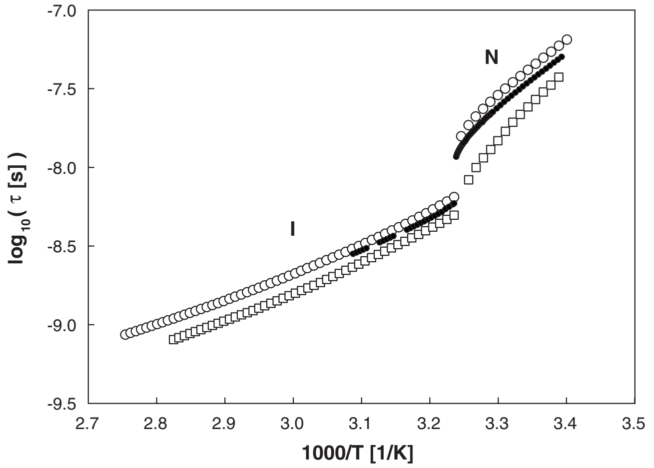

FIG. 2. Relaxation times of 5CB (○) and 5CB dispersed with 5% (●) and 16.6% aerosils (□). The $N-I$ transition temperatures have been shifted up toward the bulk value, by 0.59 K for 5% and 1.07 K for 16.6%.

maximum a few degrees above T_{IN}, and even decreases toward the transition. This behavior has been studied extensively in the past [25,26,30–36]. The dynamically antiparallel correlated pairs appear up to high temperatures in the isotropic phase.

5NCS has a core consisting of a cyclohexyl ring connected to a phenyl group by an ethyl group. The terminal group on the cyclohexyl is a pentyl chain; the phenyl group has a NCS group connected to it. The dipole moment is 2.5 D, located at the terminal NCS group, and is oriented mainly along the long molecular axis. Except for the weaker dipole moment, it resembles 5CB. The static dielectric properties of this LC have been determined earlier [37], showing that the static dielectric pretransitional effect is absent in this molecule. Although the dipole moment is located in a favorable part of the molecule to allow dipole correlation, this effect does not show. The cause for this may be the weaker dipole moment, however, the less linear shape of this molecule (because of the ethyl bridge) may be more important. The role of the dipole correlation in this LC can thus be neglected.

$\bar{5}$O5 consists of two phenyl groups connected by a COO group. One terminal chain is a pentyl group; the other is a pentoxy group. To our knowledge, dielectric measurements on $\bar{5}$O5 have not been performed before. However, we expect, based on the analogy with comparable molecules, that this LC is nonassociating. To support this claim, the static value of the dielectric permittivity has been measured. A Novocontrol Alpha analyzer has been used to measure a 50-μm-thick sample of $\bar{5}$O5 between messing electrodes in its isotropic phase. The result is shown in Fig. 1. The static value in the isotropic phase shows no indication of the bending associated with the presence of dipole correlation. Second, based on the static [26] and dynamic [38] properties of the somewhat analogous molecule 4$-n$-pentylphenyl-4$'-n$-pentylcyclohexylbenzoate (D55), we expect a dipole moment in the order of 1.6 D, but mainly oriented perpendicular to the long molecular axis. Analysis of the Kirkwood correlation factor shows that there is no correlation for D55 in the isotropic phase [26]. The properties of $\bar{5}$O5 will be quite like those of D55, however, with a stronger contribution of the short axis rotation in $\bar{5}$O5 because of the oxygen atom in its terminal chain. Another comparable molecule, which is considered nonassociating, is 4-methoxybenzylidene -4$-n$-butylaniline (MBBA); static [36] and dynamic [39,40] dielectric results are completely comparable to those of $\bar{5}$O5. These arguments make $\bar{5}$O5 a suitable LC for this work.

IV. RESULTS

A. Full temperature range

In Fig. 2 the relaxation times for 5CB and 5CB with 5% and 16.6% aerosils are plotted. The data for the 5% mixture are taken from data sets measured for Ref. [21]. The relaxation of aerosil dispersed 5CB is globally faster than that of bulk 5CB, as can be clearly seen from the figure. The relaxation for 16.6% aerosils is about 1.4 times faster in the isotropic phase, whereas it is about 1.15 times faster in the 5% dispersion. This smaller acceleration for the lower concentration is as expected, based on our earlier results in the nematic phase [21]: less aerosils means less influence. This also means that the regime change from soft (1%–10%) to stiff (>10%) gel (established by, e.g., [4,10,41]) has no profound influence on the molecular dynamics as it is probed by dielectric spectroscopy. Such conclusion can also be drawn from the dielectric results for the nematic phase presented in [21,22]. In the nematic phase, the difference in the relaxation times is less constant. The $I-N$ phase transition is clearly visible at about 3.25×10^{-3} K^{-1}. The step in the relaxation times is less pronounced in the aerosil dispersed systems. The bending of the relaxation time curve in the nematic phase toward the transition is more pronounced in the aerosils dispersion. This bending is related with the changes in the nematic order parameter (as observed earlier in 7CB and 8CB [42]).

In Fig. 3, the relaxation times for 4CB and 4CB with 14.5% aerosils are compared. Also, in this case the accelera-

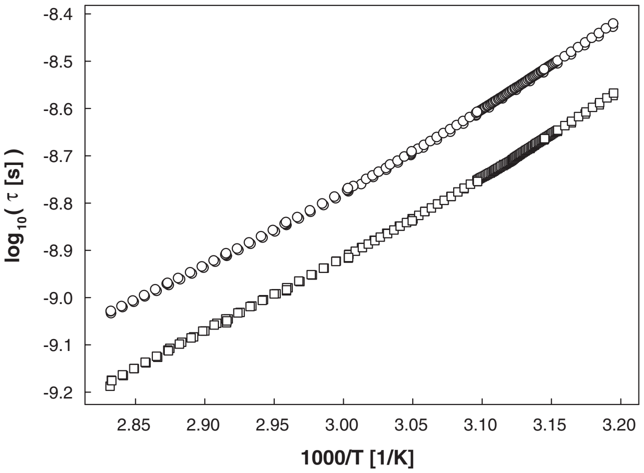

FIG. 3. Relaxation times of 4CB (○) and 4CB dispersed with 14.5% aerosils (□) in the isotropic phase.

tion for the aerosil dispersion is clear. The acceleration is of the order of a factor 1.4. According to literature, the sample should crystallize at about 3.11×10^{-3} K^{-1}, but as can be seen from the figure, this was not the case for several of the runs, although the sample temperature was varied very slowly near the crystallization temperature. We did not attempt to measure the samples toward the monotropic liquid crystalline phase, as in that case the relaxation processes slow down outside the range of the equipment that was used for this study.

The situation in 5NCS is different from that in the two cyanobiphenyl compounds (Fig. 4). In both samples the isotropic to nematic transition can be clearly seen at about 3.12×10^{-3} K^{-1}. In the isotropic phase, the relaxation times coincide, whereas in the nematic phase the aerosil dispersed 5NCS relaxes clearly faster than the bulk sample. So, in 5NCS there is an acceleration in the nematic phase, but no acceleration in the isotropic phase.

The final molecule is $\bar{5}$O5 (Fig. 5). Here the situation is the same as for 5NCS: a clear phase transition in both samples, separating the isotropic phase in which there is no acceleration, from the nematic phase where the short axis process is accelerated. The data on the long axis process were not included, as their accuracy is limited because of the high frequency characteristics of the measurement cell. However, they appear to confirm that the isotropization model also works for this faster process, as was suggested by us [43] and observed in 5CB [44]. The long axis process also appears not to be influenced in the isotropic phase.

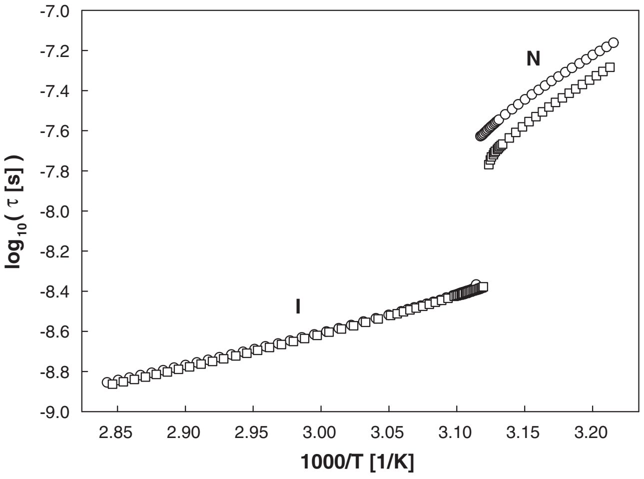

FIG. 4. Relaxation times of 5NCS (○) and 5NCS dispersed with 16.9% aerosils (□). In the isotropic phase the symbols overlap.

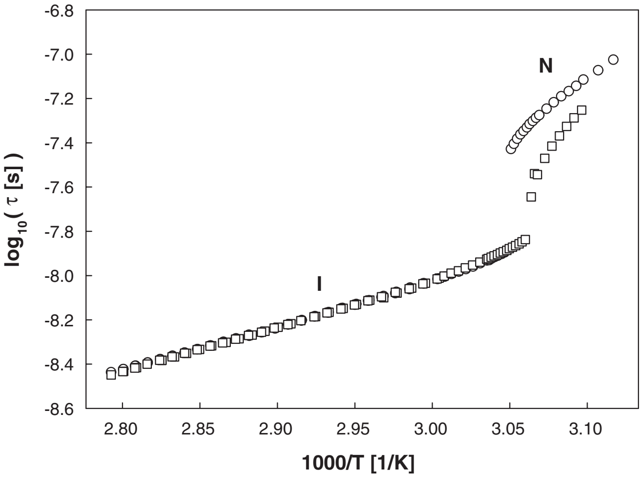

FIG. 5. Relaxation times of $\bar{5}$O5 (○) and $\bar{5}$O5 dispersed with 16.0% aerosils (□). In the isotropic phase the symbols overlap.

B. Detailed analysis near T_{NI}

It can be expected that the approach of the $N-I$ transition and the emerging pretransitional fluctuations not only influence the static dielectric permittivity as discussed in Sec. III, but also the dynamic dielectric properties. To verify that this is indeed the case, we performed a derivative analysis on the relaxation times, a procedure becoming increasingly popular in liquid crystal research in recent years [25,37,44–47]. The idea is based on the observation that a logarithmic derivative to $1/T$ of the Arrhenius relation for relaxation times, $\tau(T) = \tau_\infty \exp(E_A/k_B T)$, gives the activation energy per molecule E_A. Instead of considering this activation energy constant with temperature, it can also be regarded as temperature dependent. In such a case, one can write

$$k_B \frac{d \ln \tau}{d(1/T)} = E_A(T), \tag{3}$$

defining the temperature dependent activation energy $E_A(T)$. The Arrhenius equation describes the behavior for a process from one state to another separated by a potential barrier (such as, for example, a double well potential). The height of the barrier translates to the activation energy in the equation. This means that $E_A(T)$ describes how the barrier for rotational diffusion changes with temperature, or in other words, how the environment of the rotating molecule changes with temperature.

The result of this derivative analysis for 5CB, 5NCS, and $\bar{5}$O5, both in bulk and with aerosils, and some literature values [45–47] are presented in Fig. 6. First, we notice that all

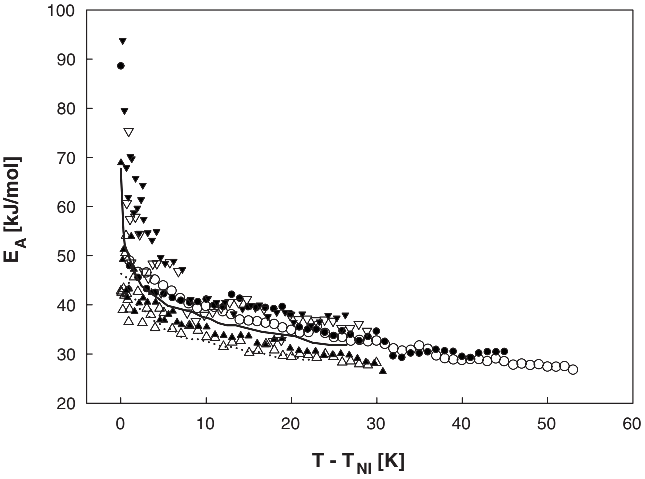

FIG. 6. Comparison of the temperature dependent activation energy $E_A(T)$ for a number of liquid crystalline compounds in the isotropic phase. The data have been shifted to T_{NI} for comparison. ○, 5CB; ●, 5CB with 16.6% aerosils; △, 5NCS; ▲, 5NCS with 16.9% aerosils; ▽, $\bar{5}$O5; ▼, $\bar{5}$O5 with 16.0% aerosils; (literature data) solid line, 7CB [45]; dotted line, 7CHBT [47].

the $E_A(T)$ curves have essentially a comparable form, with a slow increase of E_A far from T_{NI} going to a very steep increase close to T_{NI}. A second observation to make is the comparable value for all the liquid crystals. Third, the curves for the bulk samples and for the aerosil dispersion are coinciding. This observation has been made earlier for a larger number of 5CB aerosil dispersions [44].

The image that can be formed now is the following. Close to T_{NI}, the ordering in the prenematic fluctuations influences the rotational dynamics in the same way as in the nematic phase: the short axis rotation becomes hindered by the nematic potential and is retarded. The retardation can be seen as a consequence of a higher potential barrier between the rotational begin and end state, and thus a higher activation energy. This explains the increase of $E_A(T)$ on approaching T_{NI}.

The fact that the activation energy for the bulk samples and the aerosil dispersion is the same, suggests that the effect of the aerosil particles is only a global acceleration of the dynamics. They apparently do not interfere much with the pretransitional behavior of the relaxation times. However, the interaction at a molecular level between the aerosil particles and the reorienting dipoles that results in the observed global acceleration (over the entire measured isotropic range) is at present not clear to us.

V. DISCUSSION AND CONCLUSION

From the results in Secs. IV A and IV B, we can calculate an acceleration factor, the ratio of the bulk relaxation times, and the relaxation times in aerosils. From the analysis, it follows that this acceleration factor takes the same value over the entire isotropic phase, so we can quantify the acceleration with a single number. The rotation around the short axis is accelerated in the isotropic phase of the associating 4CB and 5CB molecules, with a nearly constant factor of about 1.4 for the high concentration, and a lower value of about 1.15 for the lower concentration 5CB dispersion. The two other, nonassociating LCs, 5NCS and $\bar{5}$O5, do not show an acceleration in their isotropic phase: their acceleration factor is 1 within the experimental uncertainty.

We think that the acceleration for 4CB and 5CB in the isotropic phase is a consequence of the associating character of the cyanobiphenyls. As discussed in Sec. III, two cyanobiphenyl molecules form a dynamically associating pair. We can imagine that the presence of the aerosils, and of the hydrogen bond interaction of these particles with the cyano group of the LCs as well as their disturbing influence, interferes with the normal dynamical pair formation and with the response to the probing ac field of the free dipoles. To verify the importance of the dipole moment association, one can compare the acceleration of an associating and a nonassociating liquid crystal, as in this work. The acceleration of the short axis rotation should then only be seen in the isotropic phase of associating liquid crystals. We do not wish to speculate on a molecular model for the disturbance of the pair formation and for the increased rotational mobility of the dipoles, because dielectric spectroscopy shows the properties averaged over the entire sample, whereas the structure on the level of individual molecules should be studied by, e.g., NMR or x-ray scattering.

In conclusion, we have measured the dielectric relaxation times for the relaxation around the short molecular axis for four liquid crystalline molecules, both in a bulk system and in a dispersion with aerosil particles. The results show that this relaxation in the nematic phase is faster in aerosil dispersions. This is a consequence of the disorder introduced by the aerosils. In the isotropic phase, however, the acceleration is only observed for molecules that show dipole association. Thus, the acceleration of the short axis relaxation times in both the nematic and isotropic phase is caused by the disordering effect of the aerosil particles. However, the exact mechanism differs in the isotropic phase (influencing the dipole-dipole interaction) and in the nematic phase (disturbing the long range nematic order in the sample).

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