Dynamic response of a nematic liquid crystal in silica aerogel in an external electric field

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The change in optical transmittivity of the nematic-aerogel system in an alternating external electric field was investigated near the nematic-isotropic phase transition. We observed a slow, glasslike dynamical reorientation process that is probably correlated over many pores. The magnitude of the change in the transmittivity can be explained by the model of Bellini *et al.*
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I. INTRODUCTION

Liquid crystals confined to disordered matrices are very convenient systems to study the structural, thermodynamical, and dynamical effects of randomness. They are experimentally very accessible and can be easily incorporated into structures with various degrees of randomness [1]. Their properties are especially interesting near phase transitions. Liquid crystals in general exhibit a number of phase transitions that have been extensively studied in the bulk. Confinement to random network strongly influences the nature of the transitions. The transition regions become remarkably broadened and usually shifted with respect to the bulk transition temperatures. Phase sequences, phase stability, and orientational dynamics of liquid crystals have been studied in several porous matrices such as aerogels [2–6], Vycor glass [7], sintered silica glasses [8], and control porous glasses [9,10].

In this paper we report on the investigation of the orientational dynamics of the liquid crystal confined to silica aerogel near the nematic-isotropic phase transition. The response of the material to an alternating external electric field was measured. Our measurements are complementary to the dynamic light scattering experiments (DLS) as they allow us to concentrate on the low frequency dynamics of the system. The DLS experiments that have been performed up to now have shown rather complicated behavior of the orientational dynamics. In particular, in addition to the main relaxation processes in the microsecond range originating from intrapore orientational fluctuations, a much slower relaxation mode with a broad distribution of the relaxation times appears [2,5]. Its temporal dependence can be represented with a stretched exponential function with the value of the exponent decreasing with decreasing temperature, a behavior that is expected of a system exhibiting a glasslike transition. This slow component of the orientational dynamics is attributed to the interpore director coupling.

In order to gain some additional insight into the slow frequency part of the orientational dynamics, we measured changes in turbidity of the system as a function of a frequency of an external electric field. The measurements were performed at several temperatures near the phase transition. The turbidity of the nematic-aerogel system strongly depends on the temperature [4]. The system goes from a transparent state when a nematogen material is in the isotropic phase to a strongly scattering translucent state a few degrees in the nematic phase. The strong scattering is a result of large variations of refractive index due to the random orientation of the nematic director within the porous matrix. An external electric field induces some partial ordering of the director and so effectively decreases the variations of the refractive index. Consequently the turbidity of the system also decreases.

II. EXPERIMENT

The silica aerogel used in our measurements has a density of 0.248 g/cm^3 and an average pore size (the pore chord length) ζ of 43.6 nm as was characterized by mercury porosimetry. The pore size is in agreement with the pore sizes determined by small angle x-ray scattering in the aerogels with similar densities [5]. The preparation of aerogels is described in Ref. [11]. Thin slices (below 1.5 mm) of the aerogel were cleaved from a larger block and filled with liquid crystal 4-pentyl-4'-cyanobiphenyl (5CB) using capillary action under vacuum. The 5CB was used as purchased from Merck Ltd. During the filling process the liquid crystal was in the nematic phase. The bulk 5CB exhibits the isotropic-nematic transition at $t_{NI\ \mathrm{bulk}}=35\ ^\circ\mathrm{C}$ and the nematic-solid transition at 22.5 °C. The filled slices were fixed between flat ITO coated glass plates with the UV cure glue with a refractive index that matched the refractive index of the isotropic 5CB.

An unpolarized beam from a He-Ne laser with a wavelength of 632.8 nm passed the focusing lens and entered the sample in the direction normal to the glass plates. The transmitted light was collected with an objective $f3.5/100$ and detected by a photodiode. The output of the photodiode was connected to the lock-in amplifier referenced to a sinusoidal driving voltage $U(\omega)$ that was applied to the sample. The maximum amplitude of the electric field in the sample was around 200 kV/m. The photodiode signal at the doubled frequency 2ω was measured. This signal was proportional to the field induced variation of the sample transmittivity $\delta T(2\omega)$, that is to the quadratic electro-optic response of the system. A possible explanation of the transmittivity changes and the underlying reorientational mechanism is given in the discussion. The dependence of the $\delta T(2\omega)$ on the field amplitude E_0 is shown in Fig. 1. The dependence is almost

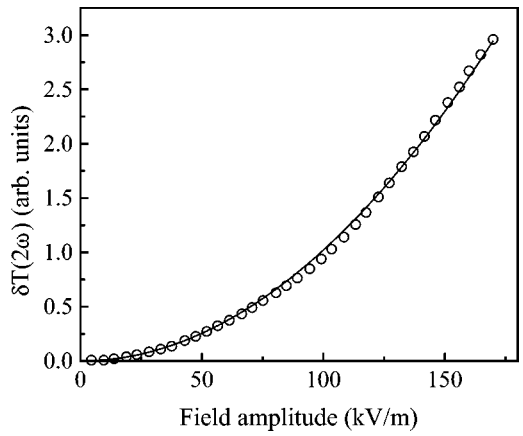

FIG. 1. Variation of transmittivity as a function of the external electric field amplitude at frequency 270 Hz. The solid line is the fit to quadratic dependence.

perfectly quadratic in the whole probed interval from $E_0 = 0$ to $E_0 = 170$ kV/m. Synchronously with the transmittivity variation $\delta T(2\omega)$ also the average transmittivity $\langle T \rangle$ of the sample was monitored.

The temperature dependence of the average transmittivity $\langle T \rangle$ of the nematic-aerogel system in alternating electric field is shown in Fig. 2(a). It exhibits a behavior very similar to the behavior without the external field [5]. When the sample is slowly cooled from the isotropic to the nematic phase the abrupt decrease in $\langle T \rangle$ appears, which is followed by a gradual decrease. At about 1 K below the first jump $\langle T \rangle$ starts to decrease more rapidly again until it finally saturates at a very low value. Comparison of this characteristic behavior to the heat capacity data suggests that the first jump in the transmittivity coincides with the sharp but low peak of the specific heat coming from the small amount of the residual

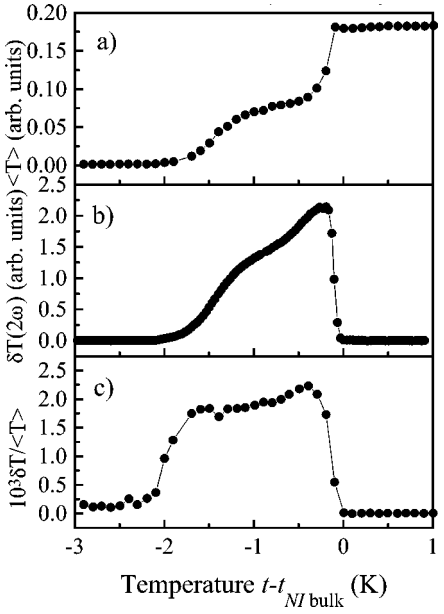

FIG. 2. Average transmittivity (a), change in transmittivity (b), and the ratio of change in transmittivity to average transmittivity (c) as a function of the relative temperature with respect to the bulk nematic-isotropic transition. The data were obtained at the field frequency of 270 Hz.

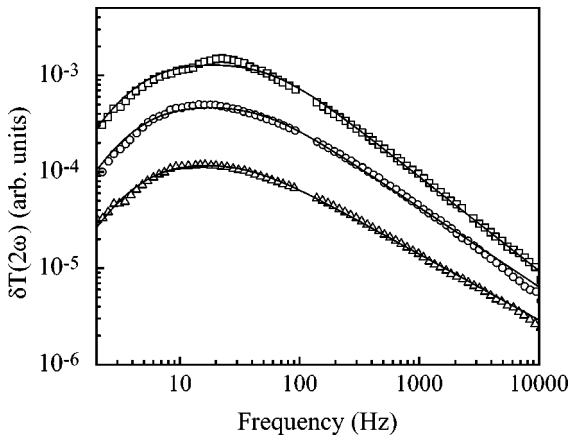

FIG. 3. Magnitude of the change in transmittivity as a function of frequency of the external electric field at various temperatures: $t - t_{NI\ \mathrm{bulk}} = -0.1$ K (squares), $t - t_{NI\ \mathrm{bulk}} = -1.2$ K (circles), and $t - t_{NI\ \mathrm{bulk}} = -1.8$ K (triangles). Full lines are fits to Eq. (1).

bulk liquid crystal in the cracks or at the surface of the sample [4]. The intermediate region where the transmittivity slowly decreases coincides with the prominently broadened peak of the nematic-isotropic transition within the aerogel network, while the second more rapid decrease very probably starts when the nematic correlation length l_c reaches the average pore size ζ of the aerogel. The coherent signal disappears when the diffusive scattering regime is reached [4,12].

The temperature dependence of a quadratic electrooptic response $\delta T(2\omega)$ of the sample is shown in Fig. 2(b). During cooling $\delta T(2\omega)$ starts to increase steeply at the point where the bulk phase transition takes place. In the region of the gradual phase transition the $\delta T(2\omega)$ decreases slowly with the temperature approximately following the behavior of the average transmittivity $\langle T \rangle$. Figure 2(c) shows the temperature dependence of the normalized electro-optic response of the sample, that is the ratio between the variation of the transmittivity $\delta T(2\omega)$ and the average transmittivity $\langle T \rangle$. The normalized electro-optic response is nearly constant in the region of the gradual phase transition and sharply decreases outside this interval. Such behavior was observed for various frequencies of the driving voltage and in various samples, some of them prepared also without using the index matching glue.

The dependence of the quadratic electro-optic response $\delta T(2\omega)$ on the frequency ω of the external field was measured in the interval from 2 Hz to 10 kHz, the upper frequency being limited by the bandwidth of our high voltage amplifier. Compared to DLS experiments, which generally cover the frequency region from mHz to MHz this frequency interval is very narrow, but it coincides well with the characteristic time scale associated with the interpore director reorientation. The results obtained at three different temperatures are shown in Fig. 3. For frequencies lower than 10 Hz $\delta T(2\omega)$ decreases with the decreasing frequency. We relate this decrease to the ionic conduction of the sample. At higher frequencies the motion of the ions, which screen the external field, is hindered by the viscosity of the system. A maximum in the electro-optic signal $\delta T(2\omega)$ appears at about 20 Hz.

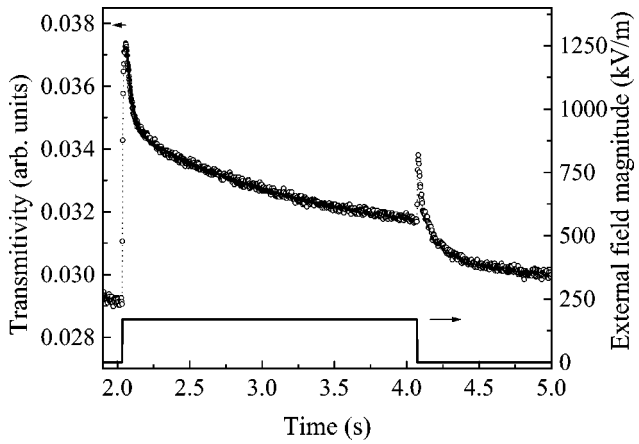

FIG. 4. Response of the transmittivity to a step increase and to a step decrease of the external electric field. The solid line plotted on top of the transmittivity data corresponds to the fit to second order exponential decay.

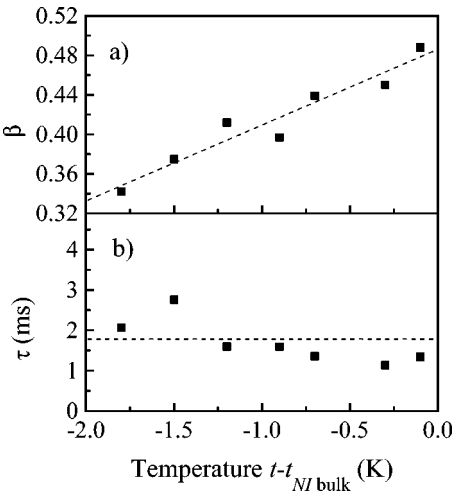

FIG. 5. Temperature dependence of parameters β and τ.

Above this frequency $\delta T(2\omega)$ decreases monotonically with increasing frequency.

The low-frequency behavior of $\delta T(2\omega)$ is more clearly observed when measurements are performed in the time domain. Figure 4 shows the time response of the sample transmittivity to a step increase (switching on) and to a step decrease (switching off) of the external electric field E. When the field is switched on the transmittivity first rapidly increases. The increase takes place in an initial time interval of about 10 ms. After this a two step decreasing process occurs, which can be well fitted to two exponentials. The value of the faster relaxation time is always close to 40 ms, while the value of the slower relaxation time is more variable and is on the time scale of 10 s. When the external field is switched off the transmittivity does not fall to the initial value, but it rapidly increases again and shows a very similar temporal behavior as in the case of switching on the field. This phenomenon can be explained by a remaining screening field of the ions and other charged impurities. When the external field vanishes the ions cause an increase of the effective internal field E_{eff} acting on the nematic molecules and correspondingly also the transmittivity increases. The remaining ionic field has an opposite direction with respect to the external field E, but as the nematic director is coupled to the E_{eff}^2, the effect is similar in both cases. The two step nature of the screening process is very probably related to the intrapore and to the interpore motion of the ions. In the case of the alternating external fields of the frequencies above 2 Hz which were used in our $\delta T(2\omega)$ measurements only the screening due to the intrapore ionic motion is important.

The observed frequency dependence of the $\delta T(2\omega)$ (Fig. 3) was fitted by a modified Debye relaxation function

$$\delta T(2\omega) = E_{\mathrm{eff}}^2(\omega)\frac{A}{[1+(2\omega\tau)^2]^{\beta}}, \tag{1}$$

where $E_{\mathrm{eff}}^2(\omega) = E_0^2\{(\omega\tau_i)^2[1+(\omega\tau_i)^2]^{-1}\}$ describes the effect of the intrapore ionic screening and the parameter of the ionic relaxation time τ_i had a fixed value of 40 ms as obtained from the step field measurements (Fig. 4). The corresponding fitting curves are shown as solid lines in Fig. 3. The results of the fit are shown in Fig. 5. For a pure Debye relaxation dynamics the exponent β has a value of 0.5, whereas in our system it decreases with the decreasing temperature from $\beta \approx 0.5$ at the bulk nematic-isotropic transition temperature down to $\beta \approx 0.35$ at about 2.5 K below [Fig. 5(a)]. The orientational relaxation time τ on the other hand remains more or less independent of the temperature and has a value of about 2 ms [Fig. 5(b)].

III. DISCUSSION

Our measurements show the existence of the slow nematic director reorientations in the aerogel host. Due to the superposition of the reorientational dynamics and the dynamics of the ionic motion the determined value of $\tau \sim 2$ ms is a bit uncertain, but it is obviously much larger than the characteristic relaxation time of the intrapore orientational fluctuations that appear in the microsecond range [8,5,6]. Taking into account the ratio of effective elastic constant K_{eff} to effective viscosity η_{eff} for the bulk 5CB [13], we can deduce an interpore dynamic correlation length $l_d = 2\pi(\tau K_{\mathrm{eff}}/\eta_{\mathrm{eff}})^{1/2} \approx 2\times 10^{-6}$ m. This value of the $l_d \gg \zeta$ is a strong evidence of a dynamically correlated orientational process extending through tens of the aerogel pores. Such a correlated dynamics was also observed by our recent DLS experiments, where in addition it was shown that close to the nematic-isotropic transition the orientational fluctuations have a well defined quadratic dependence of $1/\tau$ on the scattering wave vector [6]. This is only possible if the fluctuations are correlated over distances comparable to the wavelength of light.

Another similarity between the DLS experiments and our $\delta T(2\omega)$ measurements is also the temperature dependence of the characteristic dynamic exponent of the slow mode. This dependence was studied in the DLS measurements of Bellini *et al.* [1,5]. There it was observed that the correlation function of the intensity of the scattered light has a stretched exponential form $g^{(2)}(\tau) \propto e^{-(t/\tau)^s}$ with the parameter s decreasing with the decreasing temperature. In the frequency domain this implies that the spectrum at $\omega \gg \tau^{-1}$ has the form $(\omega\tau)^{-1-s}$. So the lowest determined value of the parameter $\beta = 0.35$ in the electro-optic response corresponds to

$s \cong 0.4$ in the DLS measurements. This is just the value of s that Bellini *et al.* obtained [5] at the point where the intrapore dynamic correlation length becomes equal to the pore size. Also, the slope in temperature dependence of β [Fig. 5(a)] is very similar to the slope of temperature dependence of s in Ref. [5].

To explain the magnitude of $\delta T(2\omega)$ we have extended the model of Bellini *et al.* [2] to calculate the change in turbidity due to the external electric field. In this model the nematic in the aerogel is assumed to consist of single uniaxial domains with a form of domain size distribution being equivalent to the form of the pore size distribution of the aerogel but with a temperature dependent mean domain size. Each domain is assumed to be immersed in an optically isotropic surrounding medium. The scattering of light from a single domain is due to the mismatch of its index of refraction with respect to an average of all other domains. The scattering from a large ensemble of the domains is an incoherent sum of the single scattering events.

For the case of randomly oriented domains of a uniform size the total scattered power in this model is [2,14]

$$P_{\mathrm{tot}} = \frac{I_0 V^2 \varepsilon_a^2 k^4}{27\pi \bar{\varepsilon}}, \tag{2}$$

where I_0 is the intensity of the incident beam, V the volume of the domain, k the wave vector of light, ε_a the optical dielectric anisotropy, and $\bar{\varepsilon}$ the average dielectric constant of the medium. When an external electric field is applied to the system the domains tend to align along the direction of the field and the distribution of the domain orientation changes. It becomes anisotropic and since the anisotropy is small it can be calculated as a perturbation of the initial isotropic distribution. Let θ, with possible values in the interval $0 < \theta < \pi/2$, be the angle between the orientation of the domain and the direction of the external field. As the initial distribution of the domain orientation is isotropic, i.e., $f_0(\theta) = 1/2\pi$, the number of domains found within the cone angle of $0 < \theta < \psi$ is given by

$$N(\psi) = 2\pi N_0 \int_0^{\psi} f_0(\theta) \sin\,\theta d\theta = N_0(1 - \cos\,\psi), \tag{3}$$

where N_0 is the total number of domains. The magnitude of the field-induced change in the orientation $\delta\psi$ can be obtained by comparing the competing elastic and electric field torques. Assuming strong anchoring of the director at the domain surface this comparison results in

$$\delta\psi = -\frac{2\varepsilon_a^{(0)} \varepsilon_0 E_{\mathrm{eff}}^2 R^2}{K_{\mathrm{eff}}} \sin\,\psi\,\cos\,\psi = C\,\sin\,\psi\,\cos\,\psi, \tag{4}$$

where $\varepsilon_a^{(0)}$ is the dielectric anisotropy at low frequencies and R the radius of the domains. The related increased number of domains within the cone $0 < \theta < \psi$ is therefore

$$N'(\psi) = N(\psi + \delta\psi) = N_0[(1 - \cos\,\psi) + C\,\sin^2\psi\,\cos\,\psi)] \tag{5}$$

and the corresponding perturbed distribution of the domain orientation is then

$$f'(\theta) = -\frac{1}{N_0}\frac{dN'(\theta)}{2\pi d(\cos\,\theta)} = \frac{1}{2\pi}[1 + C(3\,\cos^2\theta - 1)]$$
$$= f_0(\theta) + \delta f(\theta). \tag{6}$$

The perturbed orientational distribution (6) results in a decrease of the total scattered power that is given by

$$\frac{\delta P_{\mathrm{tot}}}{P_{\mathrm{tot}}} = -\frac{\int_0^{\pi/2} P(\theta)\,\delta f(\theta) \sin\,\theta d\theta}{\int_0^{\pi/2} P(\theta) f_0(\theta) \sin\,\theta d\theta} = -\frac{2}{5}\frac{\varepsilon_a^{(0)} \varepsilon_0 E_{\mathrm{eff}}^2 R^2}{K_{\mathrm{eff}}}, \tag{7}$$

where

$$P(\theta) = \frac{I_0 V^2 \varepsilon_a^2 k^4}{81\pi \bar{\varepsilon}}\left(\frac{7}{3} - \cos\,2\theta\right) \tag{8}$$

is the scattered power from a single domain with a definite orientation θ of the director, i.e., the optical axis averaged over all possible incoming polarizations [14].

In order to describe the variation of the turbidity of the nematic-aerogel system relation (7) has to be averaged also over the domain size distribution. This distribution is assumed to have the form $p(R) = R^{-2}\zeta^{-2}e^{-R/\zeta}$ [1]. The relative increase of the transmittivity due to the external field, which is in our situation proportional to the relative decrease of the turbidity, then yields

$$\frac{\delta T}{T} = -\frac{\langle \delta P_{\mathrm{tot}} \rangle}{\langle P_{\mathrm{tot}} \rangle} = \frac{144}{5}\frac{\varepsilon_a^{(0)} \varepsilon_0 E_{\mathrm{eff}}^2 \zeta^2}{K_{\mathrm{eff}}}. \tag{9}$$

Taking into account the data for bulk 5CB [13,15]: $\varepsilon_a^{(0)} \sim 10$, $K_{\mathrm{eff}} \sim 10^{-11}$ N, $E_{\mathrm{eff}} \sim 10^5$ V/m, and $\zeta \sim 5 \times 10^{-8}$ m, the ratio $\delta T/T$ is estimated to be of the order of 10^{-3}. This result is in good agreement with our measurements.

Expression (9) is valid when the nematic correlation length l_c is equal to the average pore size ζ. In the intermediate temperature region where $l_c < \zeta$ the director in most pores is not pinned to the walls so that the reorientation of each domain is larger than estimated by Eq. (4) and accordingly also the variation of the transmittivity increases. And indeed in our experiments in the temperature interval where the nematic correlation length is supposed to be smaller than the pore size [2], that is in the temperature interval from the bulk transition temperature down to about 1.2 K below the bulk transition, the change of the transmittivity in the external electric field is larger [Fig. 2(c)] than predicted by Eq. (9) and slightly decreases with the decreasing temperature. The point where the nematic correlation length l_c reaches the pore size ζ can be observed as a knee in Fig. 2(c). The knee is usually smooth since the pore sizes are distributed over a wide range.

In summary, our measurements support the idea of the existence of an extensive interpore dynamic orientational coupling of nematic liquid crystal in silica aerogel which has been established previously on the basis of the DLS experiments [5,1,6]. They present a set of complementary measurements that demonstrate a glasslike behavior of the interpore reorientational processes. The glasslike nature of this process becomes more pronounced with decreasing temperature.

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