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Evidence of dynamic long-range correlations in a nematic-liquid-crystal–aerogel system

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Dynamical behavior of a nematic liquid crystal in a silica aerogel host near the nematic-isotropic phase transition was studied by quasielastic light scattering. Just below the nematic-isotropic phase transition temperature two modes were observed. The faster mode does not depend on the scattering vector and is attributed to the intrapore orientational fluctuations. Close to the transition, its inverse relaxation time steeply increases due to the pretransitional order parameter fluctuations in smaller pores, where the phase transition to the isotropic phase occurs at lower temperatures. The second, slower mode has a quadratic dependence on the scattering vector, giving evidence of correlated interpore fluctuations. Their relaxation rate is slower than that of the bulk orientational fluctuations and approaches zero at the transition. This is not observed in the bulk. [S1063-651X(97)08501-2]

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I. INTRODUCTION

Recently many studies have been devoted to liquid crystals confined to porous glass matrices [1]. The voids of host matrices are in general interconnected in a random way and the mean void size is well below 1 μm. Liquid crystals immersed in such matrices exhibit many interesting physical phenomena such as the influence of finite size and surface effects on the statistical properties of the system. In addition, some kind of inherent [2,3] randomness is introduced into the system, which can strongly influence the behavior of the system.

Most of the recent studies are focused on the static properties of such systems across the nematic-isotropic (N-I) or nematic–smectic-A (N–Sm-A) phase transition. As porous matrices aerogels [4], sintered silica glasses [5], Vycor glass [6], or control porous glass [7] are commonly used. Studies show that the bulk characteristics of liquid crystals dramatically change when they are confined in such porous environment. In general, phase transition temperatures are shifted down a few degrees and in some cases the character of a transition changes [8]. Surface interactions can also initiate pretransitional ordering at the pores' surfaces [9].

Only a few studies have been devoted to dynamic properties of liquid crystals in porous glasses. Schwalb and Deeg [10] have studied dynamics of the liquid-crystal compound 4-pentyl-4′-cyanobiphenyl (5CB) confined to nanometer length scale pores of silica glasses above the I-N transition using time-resolved transient grating optical Kerr effect. They showed that the surface of the pores introduces into the system additional slow dynamics. Wu *et al.* [5] investigated liquid-crystal 4-octyl-4′-cyanobiphenyl (8CB) immersed into sintered silica gel using quasielastic light scattering. They found a logarithmic time dependence of the intensity autocorrelation function that samples order parameter fluctuations.

Bellini, Clark, and Schaefer [4] have investigated dynamic behavior of the 8CB liquid crystal confined to silica aerogel. They studied the temperature range from the isotropic to the smectic-A phase. Just below the isotropic-nematic phase transition temperature they observed bimodal behavior and a slow nonexponential relaxation, noticeable in the correlation function as a distinct tail. They suggested that the bimodal decay is due to the growth of the nematic ordering in large pores and suppression of nematic order in small pores. As the temperature is reduced the slow glasslike relaxation grows to dominate the long-time relaxation of the correlation function and they attribute this process to interpore coupling. Close to the bulk nematic–smectic-A phase transition temperature they observed a drastic slowing down connected with a local smectic ordering. In order to further elucidate the dynamics of this interesting disordered composite system we studied the dynamic light scattering in the 5CB liquid crystal immersed in the aerogel matrix very close to the nematic-isotropic phase transition.

II. EXPERIMENT

The silica aerogel used in our measurements has a density of 0.248 g/cm^3 and average pore size (the pore chord length) of 436 Å as was characterized by mercury porosimetry. The pore size is in agreement with the pore sizes determined by small-angle x-ray scattering in aerogels with similar densities [4]. The preparation of aerogels is described in Ref. [12]. Thin slices (below 1.5 mm) of the aerogel were cleaved from a larger block and filled with liquid-crystal 5CB using capillary action under vacuum. During the filling process the liquid crystal was in the nematic phase. The filled slices were fixed between flat glass plates with the UV cure glue with a refractive index that matched the refractive index of the isotropic 5CB. Only the samples with a good interface between the filled aerogel slices and glue, i.e., the samples completely transparent when the liquid crystal was in the isotropic phase, were used in our measurements to avoid the scattering on the interface.

We have studied the dynamical behavior of our samples using dynamic light scattering. The light source was a He-Ne laser with a wavelength of 632.8 nm. The collection optics was a standard two-pinhole scheme enabling selection of the detected intensity within one coherence area. The intensity correlation function was measured using an ALV5000 corr-

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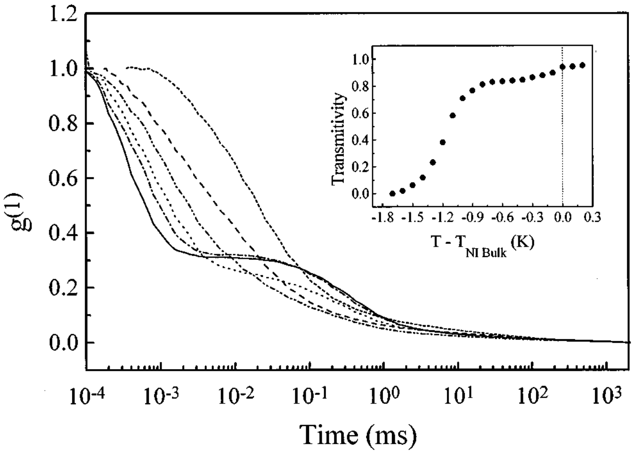

FIG. 1. Temperature dependence of the intensity autocorrelation function in the transition region. $T-T_{NI\ \mathrm{bulk}}=-1.0$ K (----), -0.9 K(– – –), -0.8 K (-·-·-·-), -0.7 K (····), -0.5 K (-·-·-), and -0.3 K (—). The scattering angle is 35°. Inset: temperature dependence of the transmittivity of the sample.

elator that enables measurements over a time range of 10^{-8}–10^{3} s. We have measured the normalized intensity correlation function $g^{(2)}(\tau)=\langle I(t)I(t+\tau)\rangle/\langle I(t)\rangle\langle I(t+\tau)\rangle$ of light exiting the sample as a function of the scattering angle and temperature for a scattering geometry with orthogonal polarizations of incident and scattered light.

The temperature behavior of the system can be divided in two regions. In the first the system is in the nematic phase and strongly scatters light. About 1.5 K below the bulk phase transition the transmitivity of the sample starts to increase and the system becomes transparent in the isotropic phase (inset of Fig. 1). A comparison of the turbidity measurements with the heat capacity measurements of the liquid-crystal 8CB in a silica aerogel [11] shows that this is the region where a broadened nematic-isotropic phase transition occurs. The bulk phase transition temperature can be determined by the small abrupt jump in turbidity that coincides with the bulk peak of the specific heat coming from a small amount of residual bulk liquid crystal in cracks or large pores, or on the surface of the sample, as was shown by Bellini *et al.* [11].

In contrast to the bulk, where the orientational fluctuation relaxations are exponential, the measured autocorrelation function, which samples the orientational fluctuation decay, in the nematic in the aerogel is nonexponential. Similar nonexponential behavior was also reported by other groups [4,5]. In addition to a fast, almost single exponent also a long tail was observed, which, in most cases, can be well fitted with a stretched exponential function (Fig. 1). The fast part of the correlation function is most probably due to the nematic intrapore orientational fluctuations [4] and it slightly differs from a single exponential function since an averaging over pore size as well as over different orientation of the director field must be considered [4]. The corresponding inverse relaxation time $1/\tau_1$ steeply increases when the nematic-isotropic phase transition temperature is approached (Fig. 2). A comparison of our results with the measurements of the relaxation time of the pretransitional order parameter fluctuations in a similar system in the region just above the bulk phase transition temperature [10] shows that we probably observed the same process.

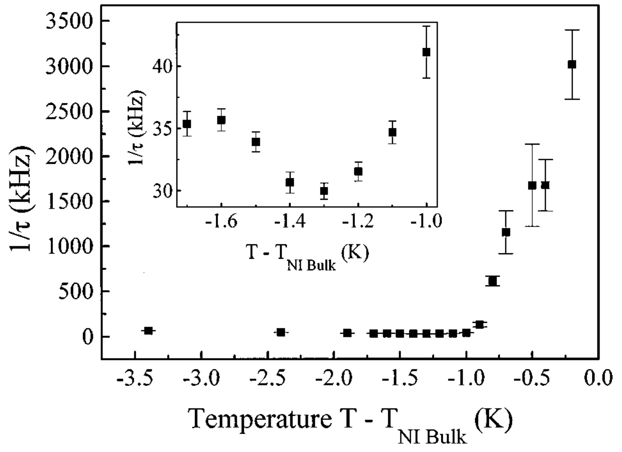

FIG. 2. Temperature dependence of the inverse relaxation time of the intrapore fluctuations at a scattering angle of 20°. The inset shows the slowing down at the onset of the phase transition to the isotropic phase.

Besides the intrapore fluctuations and the stretched exponential tail observed in the nematic phase, in the transition region another, slower mode appears. The amplitude of this mode is comparable to the intrapore fluctuation mode, suggesting that the scattered light comes from a comparable effective volume. A single exponential function and a stretched exponential function fit well the slower mode and the tail. Well in the nematic phase the correlation function does not depend on the scattering vector. In the transition region its fast part, i.e., the intrapore orientational fluctuation, remains independent of the scattering vector, while the slower mode shows a strong dependence (Fig. 3). At lower temperatures this dependence of the slower mode is not quadratic but becomes such closer to the phase transition temperature (Fig. 4). This is expected since the scattering of light in our system goes from a multiple-scattering regime in diffusive limit, where the scattered light does not depend on the scattering vector, to a nearly-single-scattering regime in the region close to the clearing point. Between both limits the dependence of the scattered light on the scattering vector becomes more and more pronounced. The pore size p limits the wave

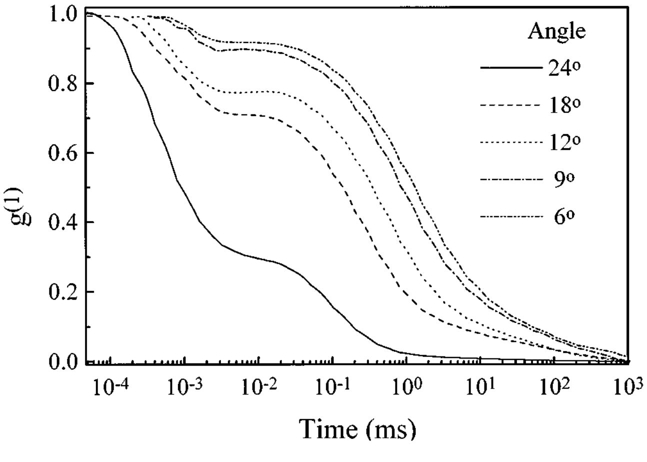

FIG. 3. Angular dependence of the intensity autocorrelation function in the transition region. $T-T_{NI}=-0.71$ K.

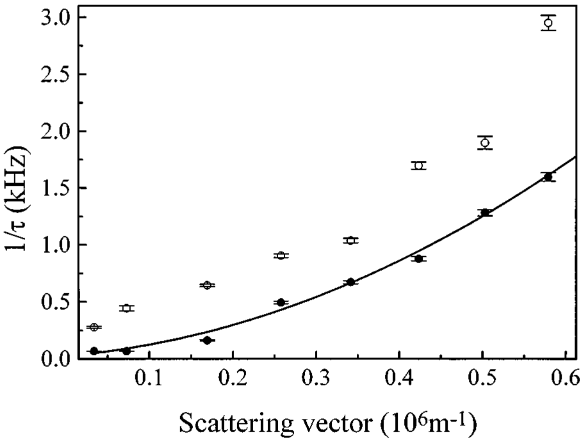

FIG. 4. Dependence of the interpore fluctuations on the scattering angle at two different temperatures: $T-T_{NI\ \mathrm{bulk}}=-0.52$ K (○) and -0.26 K (●). For higher-temperature data (●) a quadratic fitting function is also shown (—).

vector of the intrapore fluctuations to a minimal value of $\sim\pi/p$, which is much larger than the scattering vector. Therefore, even in the single-scattering regime we do not expect that the contribution of the uncorrelated intrapore fluctuations depends on the scattering vector. So our observations that the fast relaxation time close to the clearing point does not depend on the scattering vector (Fig. 3) confirms that it belongs to the uncorrelated intrapore fluctuations. On the other hand, the quadratic dependence of the slower mode shows that it has a correlation length of the order of the wavelength of light or more, that is, something like 100 average pore sizes. Therefore, we conclude that the pores in the aerogel are interconnected to allow such collective fluctuations of the order parameter.

The ratio between an effective orientational elastic constant and an effective viscosity was obtained by fitting the scattering vector dependence of the relaxation time of the slow mode with a quadratic function. These values can be compared to the relaxation rates of the bulk 5CB. As we are dealing with a system that is orientationally disordered, it is necessary to carry out an averaging of the bulk scattering correlation function over all possible orientations [13]. The values for bulk 5CB, obtained with the data of Ref. [14], and our measurements are shown in Fig. 5. The measured values are comparable with the values in bulk nematic 5CB at lower temperatures, but go towards zero when the bulk transition temperature is approached, while in the bulk this ratio remains almost constant in this temperature region (Fig. 5). So this mode cannot be attributed to the bulk nematic behavior in the largest pores of the aerogel.

III. DISCUSSION

Our measurements show that the independent pore model is not sufficient to understand the dynamical behavior of a nematic liquid crystal in an aerogel. It can explain the intrapore relaxation, but fails to give us understanding of the interpore dynamics. Since the estimated correlation length of the slower mode is of the order of 100 average pore sizes, it is obvious that interpore coupling plays important role in the dynamical behavior of the nematic liquid crystal.

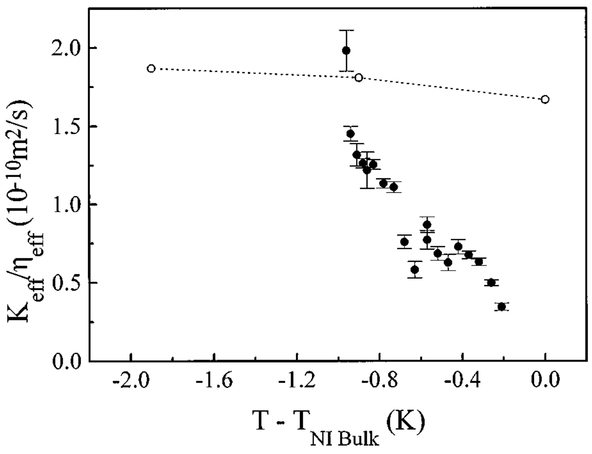

FIG. 5. Comparison of the temperature dependences of the orientational diffusivity of bulk 5CB [14] (○) and the measured diffusivity in the nematic in the silica aerogel (●).

The inverse relaxation time of the orientational fluctuations in the bulk nematic is proportional to the ratio between the effective elastic constant and the effective viscosity [15]

$$\frac{1}{\tau}=\frac{K(\mathbf{q})}{\eta(\mathbf{q})}\approx\frac{K_{\mathrm{eff}}}{\eta_{\mathrm{eff}}}|\mathbf{q}|^2.$$

Our measurements are performed at small wave vectors, i.e., in the long-wavelength limit $q\ll 1/d_0$, where d_0 is a typical distance in which the nematic order changes significantly or a typical distance between defects. This distance is comparable to the average pore size of the aerogel. So we certainly measure some kind of average of the elastic constant over the parts of nematic liquid crystal with different magnitude as well as the direction of the order parameter. The averaging of the correlation function over all possible orientations of the director but the same scalar order parameter gives almost a single exponential correlation function [13]. Let us neglect, for the moment, averaging over the orientation of the director and investigate only the influence of the spatial variation of the scalar order parameter that we believe is more important. Mean-field theory predicts that the elastic constants in the bulk are proportional to the square of the scalar order parameter $S(\mathbf{r})$ [15]; the same is true also for the bulk rotational viscosity that mainly contributes to the effective viscosity η_{eff} [15,16]. Therefore, in the bulk the ratio between the elastic constant and the viscosity remains almost constant, although the scalar order parameter changes (Fig. 5). Our measurements show that in the aerogel the situation is different. We believe that the local orientational elasticity is not altered significantly by the aerogel matrix, except through the decrease of the scalar order parameter, but the effective viscosity is influenced by the surface friction. Studies of the dynamics of surface anchoring breaking [17] in a nematic liquid crystal suggest that the effective viscosity is larger in the presence of the surface than in the bulk nematic liquid crystal with the same scalar order parameter. Since, in the aerogel, the nematic liquid crystal is in contact with a large surface, this effect could be significant and could explain the temperature behavior of the orientational diffusivity shown in Fig. 5.

The inverse relaxation time of the faster mode steeply increases when the bulk nematic phase transition temperature is approached, while in the bulk the relaxation time of the orientational fluctuations remains almost constant [14]. Since it does not depend on the scattering vector, it is due to the intrapore orientational fluctuations. Close to the phase transition this mode is also much faster than the orientational modes in the bulk nematic liquid crystal, so it could be attributed to the pretransitional order parameter fluctuations. The pretransitional order parameter fluctuations come from small clusters of the nematic phase that are formed in the isotropic phase just above the nematic-isotropic phase transition temperature [18]. Since the nematic-isotropic phase transition temperature is reduced in the smaller pores [8], the pretransitional order parameter fluctuations can be observed in those pores. The effect of a surface-induced increase of the effective viscosity must also affect the temperature behavior of the intrapore fluctuations and indeed the slowing down of the intrapore fluctuations can be observed before the phase transition to the isotropic phase occurs (the inset of Fig. 2).

IV. CONCLUSION

In conclusion, two modes are observed in the nematic-liquid-crystal–aerogel system just below the nematic-isotropic phase transition temperature. The faster mode is due to the intrapore orientational fluctuations and close to the clearing temperature its inverse relaxation time steeply increases. This increase can be attributed to the pretransitional order parameter fluctuations in smaller pores where the phase transition to the isotropic phase occurs at lower temperatures. The second, slower mode, which seems to have been observed but not investigated in 8CB in aerogels [4], depends on the scattering vector and is therefore due to the correlated interpore fluctuations in our system. Its temperature behavior is different from the bulk behavior even when considering the reduced scalar order parameter $S(\mathbf{r})$.

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