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Elastic coupling of silica gel dynamics in a liquid-crystal–aerosil dispersion

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The dynamics of a thixotropic silica aerosil gel dispersed in an octylcyanobiphenyl liquid crystal were directly probed by x-ray intensity fluctuation spectroscopy. For all samples, the time-autocorrelation function of the gel was well described by a modified-exponential function over the q range studied. Compared to a pure gel sample, a dilute ($0.06\ \mathrm{g\,cm^{-3}}$) gel embedded within the liquid crystal displayed more complex and temperature dependent dynamics. Near the second-order smectic-A-to-nematic phase transition of the liquid crystal the gel relaxation became significantly more complex and slower ($\tau \simeq 2150$ s) compared to relaxations observed well within either phase. This clearly demonstrates coupling between the dynamics of the gel and the host liquid crystal, consistent with critical slowing down of smectic and director fluctuations. A random dampening field, elastically coupled to the liquid crystal, would explain the earlier observed crossover of this transition towards $3d$-XY behavior.

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Thixotropic aerosil (sil) gels embedded in organic liquid crystals (LC) appear to be good physical models of quenched random disorder effects for a variety of phase transitions and have attracted considerable theoretical [1] and experimental [2–4] attention. Such LC+sil systems are particularly attractive since random disorder can be introduced in a controlled manner. The aerosil particles can easily form long hydrogen-bonded chains in an organic medium [5,6], which can break under stress and reform quickly on time scales <1 s when the stress is removed. Without stress, the gel appears to be very stable. To date, there is little information, aside from the surface chemistry, of the physical properties of the unbroken gel.

Recently, the observation of a crossover behavior in a dispersion of silica aerosil in an octylcyanobiphenyl (8CB) liquid crystal system was reported for a silica density of $\rho \approx 0.1$ g(sil) cm^{-3}(total) [7]. The critical behavior at the smectic-A-to-nematic phase transition remains sharp and evolves towards $3d$-XY universality, i.e., the heat capacity critical exponent α approaches approximately zero with increasing ρ for $\rho < 0.1$ grams of silica per cm^3 of total sample volume [7–9]. Above this density, all phase transitions of 8CB become rounded and suppressed. Thus, there appears to be two distinct regimes of 8CB+sil dispersions, a *soft* regime below $0.1\ \mathrm{g\,cm^{-3}}$ where the phase transitions of 8CB remain thermodynamically sharp and a *stiff* regime above $0.1\ \mathrm{g\,cm^{-3}}$ where the transitions are all smeared [7].

To understand these results and the gel itself better, we studied a similar dispersion of silica aerosil in 8CB by x-ray intensity fluctuation spectroscopy (XIFS) in the various phases of the LC. Using the high coherent flux available at undulator sources of third generation synchrotrons XIFS can directly probe dynamics of disordered systems down to atomic length scales, on time scales down to milliseconds [10–21].

Pure 8CB ($291.44\ \mathrm{g\,mol^{-1}}$) exhibits crystal (Cr), smectic-A_d (SmA_d), nematic (N) and isotropic (I) phases with the following transition temperatures (in Kelvin) [22]: $\mathrm{Cr} \rightarrow \sim 295 \rightarrow \mathrm{Sm}A_d \rightarrow 306.95 \rightarrow N \rightarrow 313.95 \rightarrow I$. The molecule has an extended length of ~ 2 nm with a partial-bilayer smectic phase (SmA_d) of 3.2 nm layer spacing [23]. The aerosil was of type-300 from Degussa Corp. [5]. This aerosil consists of 7-nm-diameter SiO$_2$ spheres with a high density of hydroxyl groups covering their surfaces [24]. The smallest observed basic silica units, which have a size of ~ 20 nm, or 3 to 4 fused nodules, agglomerate by hydrogen bonding into mass-fractal structures up to ~ 400 nm in size or larger [7]. The 8CB and sil were used after thorough degassing. The 8CB+sil sample preparation, described elsewhere [7,8], yields a highly reproducible and stable dispersion.

For this study, we chose a sil density of $\rho = 0.06$ g(sil) cm^{-3}(total), well above the percolation threshold of pure aerosil of $\sim 0.017\ \mathrm{g\,cm^{-3}}$ [6] and below the crossover density to *stiff* behavior [7]. While the pure 8CB SmA_d-N phase transition temperature is $\mathrm{T}_{AN} \simeq 307.0$ K, this dispersion sample is expected to have a $\mathrm{T}_{AN} \sim 306.2$ K (extrapolated from Ref. [7]). For $\rho = 0.06\ \mathrm{g\,cm^{-3}}$, the mean distance between sil structures (mean void size) is $l_o \simeq 111$ nm and the fraction of LC molecules in direct contact with silica is $p \simeq 0.037$, or about 4% [7].

The XIFS experiments were conducted on the SRI-CAT 2-ID-B undulator beamline at the Advanced Photon Source [25] using a coherent x-ray beam, a transmission geometry, and a directly illuminated liquid nitrogen cooled charged-coupled device (CCD) detector. The x-ray energy was chosen to be 1.83 keV, just below the Si K-absorption edge in order to achieve good speckle contrast from the sil [26]. Measurements covered a momentum transfer (q) range from 0.017 to 0.097 nm^{-1}. Thin layers of sample material were supported in the x-ray beam by a silicon nitride membrane [27] fixed to a copper plate on a stage. The stage temperature was controlled by a recirculating chiller with an observed stability of ± 0.1 K. The absolute temperature was measured with a thermocouple to within 0.4 K.

A time series of CCD images of ~ 30 s exposure time with ~ 3 s between images were recorded over a period of 5900 s at each temperature. During the course of the measurements (~ 17 h), the 8CB+sil dispersion sample received an estimated radiation dose rate of 10^5 Gy s^{-1} without any apparent sign of damage.

The temporal intensity autocorrelation function $g_2(q,\tau)$ of the series,

$$g_2(q,\tau)=\frac{\langle I(q,t)\rangle_t\langle I(q,t+\tau)\rangle_t}{[\langle I(q,t)\rangle_t]^2}-1, \tag{1}$$

was evaluated using a software algorithm, including corrections for the storage ring current, similar to that used in Ref. [20]. These reduced data at each q were fit with a modified-exponential function $\phi(\tau)$,

$$\phi(\tau)=\Gamma_{\mathrm{fl}}\exp(-a_1\tau^{a_2})+a_3, \tag{2}$$

where Γ_{fl} describes the fluctuation contrast, a_1 is related to the relaxation time, a_2 gives a measure of the relaxation complexity, and a_3 reflects any static background. In all our data, $a_2\sim 1$ and $a_3\simeq 0$. For $0<a_2\leqslant 1$, Eq. (2) is called a Williams-Watts function (or a "stretched" exponential) and can be interpreted as the sum of single-exponential relaxations [28]. When $a_2=1$, Eq. (2) describes a single-exponential decay. For $a_2>1$, the relaxations have a more complex nature. In order to gauge the complexity of the observed relaxation processes, each $g_2(\tau)$ curve was fit twice with Eq. (2), once with $a_2=1$ and once with a_2 as a free parameter (modified exponential). Derived from these fits are (a) the fluctuation contrast Γ_{fl}, a measure for the relative strength of the fluctuations in the system, (b) the relaxation time $\tau_{0.5}$ defined as

$$\tau_{0.5}=\left[\frac{\ln(2)}{a_1}\right]^{1/a_2}, \tag{3}$$

in which the correlations decayed to half of their initial value, and (c) the parameter a_2.

The investigated q range corresponds to length scales, $d=2\pi/q$, from 65 to 370 nm in this system. These length scales are two orders of magnitude larger than the molecular or crystalline length scales of pure 8CB. As a test that the measured speckles of the 8CB+sil sample originated from the sil, a 50-μm-thick sample of pure 8CB was also studied. For pure 8CB, no speckles were detected in this q range despite the consistent observation of a broad diffraction ring at $q\cong 2$ nm^{-1} ($d=3.2$ nm) corresponding to the Sm*A* layer spacing that persists after numerous thermal cycles through the Sm*A*-*N* phase transition. The lack of any scattering from 8CB in the q range of 0.02 to 0.10 nm^{-1} demonstrates that the scattering cross section of the liquid crystal is much smaller than that of the sil. Thus, the data obtained with the 8CB+sil sample resulted almost exclusively from the scattering by the aerosil gel.

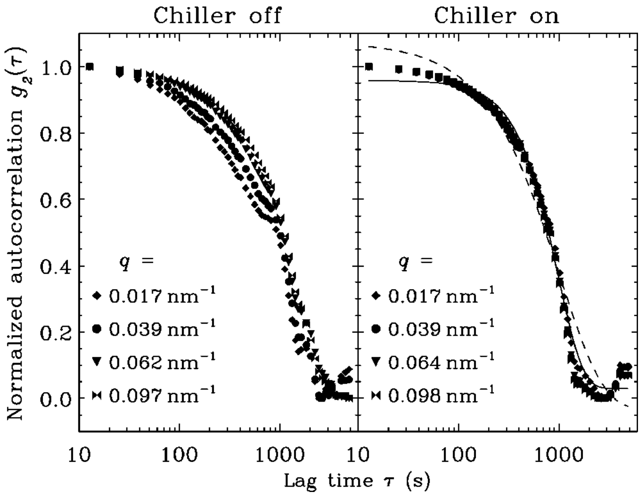

FIG. 1. Normalized time-autocorrelation curves $g_2(\tau)/g_2(0)$ for the pure aerosil gel without (left) and with (right) the chiller operating for four representative q values studied (see symbols). The feature at ~ 1000 s on the left is an artifact of the data reduction algorithm, exacerbated by the low fluctuation contrast and exaggerated by the normalization. The lines on the right represents typical fits using Eq. (2) with $a_2=1$ (dashed) and $a_2(\mathrm{free})=1.8$ (solid).

In addition to the pure 8CB sample, a pure aerosil gel sample was also studied. This was accomplished by sprinkling aerosil on a silicon nitride window and shaking off the excess (the rest was held in place by electrostatic forces). Although the coverage appeared uniform and approximately 100 μm thick, the density for this sample was not known. At room temperature (~ 294 K) without the chiller operating, clear q-dependent dynamics were observed, $\tau_{0.5}$ varied smoothly from 700 to 1200 s and $\Gamma_{\mathrm{fl}}=0.003$ to 0.012 with increasing q, while $a_2=1.2$ for all q. Given this value for a_2 and that χ^2_ν is only slightly larger for a fixed $a_2=1$, the gel relaxations are essentially described by a single exponential (see left panel of Fig. 1). At the same temperature but with the chiller operating, $\tau_{0.5}=770$ s and $a_2=1.8$, independent of q, were observed with the fit favoring $a_2\gtrsim 1$ (see right panel of Fig. 1 and Table I). However, for this case, Γ_{fl}

TABLE I. $g_2(\tau)$ fit results using Eq. (2), averaged over the q range studied for each sample and temperature studied. The reduced fit quality χ^2_ν for the case of a_2 being a fit parameter (modified exponential) and for the case of a fixed $a_2=1$ (single exponential) are also shown. The application of Eq. (1) generated standard deviations on the order of 20% for $g_2(\tau)$ leading to the anomalously small χ^2_ν [29].

Sample	T (K)	$\Gamma_{\mathrm{fl}}\times 10^2$	$\tau_{0.5}$ (s)	a_2	χ^2_{me}	χ^2_{se}
sil/OFF	294.0	0.6±0.2	928±147	1.2	0.12	0.13
sil/ON	294.0	3.1±0.6	769±20	1.8	0.07	0.31
8CB+sil	290.4	0.8±0.2	881±180	1.0	0.11	0.11
	294.6	0.4±0.1	625±172	1.1	0.42	0.38
	299.8	0.5±0.1	926±64	1.3	0.10	0.14
	305.2	2.8±0.3	2148±101	1.7	0.02	0.13
	308.2	0.8±0.2	1135±122	1.2	0.09	0.10
	311.8	2.0±0.3	624±144	0.9	0.04	0.05
	315.7	1.2±0.3	1056±94	1.4	0.03	0.13

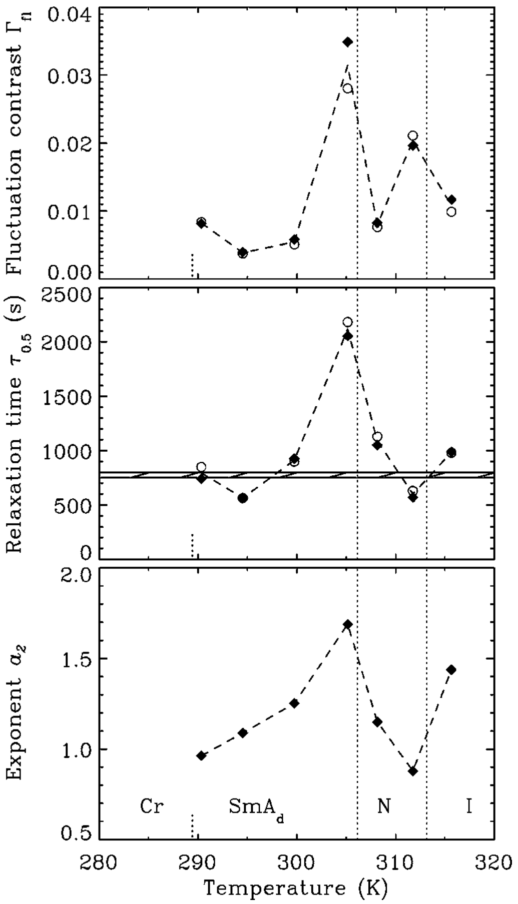

FIG. 2. Temperature dependence of the fitted fluctuation contrast (top), relaxation time (center), and exponent a_2 obtained from a fit with Eq. (2) (bottom). The open symbols represent the parameters derived from the fit with $a_2=1$, while the solid symbols are for a_2 free; the connecting dashed lines representing the average between the two fits. The dashed region in the center panel indicates the time scale affected by the operating chiller. Vertical dotted lines show the estimated transition temperatures.

increases from 0.017 to 0.044 with increasing q. Clearly, the gel has both intrinsic dynamics and a complex response ($a_2>1$ and a six times greater fluctuation contrast) to vibrations introduced by the chiller. Thus, for measurements on the 8CB+sil samples, observed relaxation times on the order of 770 s cannot be separated from relaxation processes induced by the chiller vibrations. Note that the very small Γ_{fl} observed without the chiller operating exposes an artifact of the data reduction algorithm, seen as a kink in the left panel of Fig. 1 [20].

An approximately 20-μm-thick dispersion sample of 8CB +sil with $\rho=0.06\ \mathrm{g\,cm^{-3}}$ exhibited different dynamic behavior depending on the phase of 8CB. Figure 2 shows the fluctuation contrast, relaxation times, and a_2 values obtained at different temperatures averaged over the q range studied. Most of the fits to the data with Eq. (2) did not show a large difference in the parameters Γ_{fl} and $\tau_{0.5}$ whether a_2 was fixed at 1 or was freely adjustable. However, for the measurements at 305.2 and 315.7 K, the fit with the modified-exponential function was of significantly better quality. This, together with the higher values of a_2 at these temperatures, indicates that the complexity of the relaxation processes increases near the SmA_d-N phase transition and in the isotropic phase. For all the other temperatures, the fit quality was very similar whether a_2 was freely adjustable or not, indicating a very shallow minimum in χ space and a single-exponential relaxation process (see Table I).

Near the second-order SmA_d-N phase transition, the dynamics in the gel grew stronger, slowed down, and became more complex. At 305.2 K (~ 1 K below T_{AN}), an increase in fluctuation contrast and a slowing down, both by about a factor of 3, were observed, consistent with the slowing down of relaxations that were too fast for detection in other phases of the LC. The q averaged relaxation times were about a value of 2148 s with $a_2=1.7$. A slight increase in the relaxation time over the chiller induced background to 1135 s and $a_2=1.2$ were also observed at 308.2 K (~ 2 K above T_{AN}). Both temperatures are well within the reduced temperature of $|t|\lesssim 10^{-2}$ where critical smectic fluctuations are expected to emerge.

The substantial slowing down of the fluctuations near the second-order SmA_d-N phase transition indicates that the gel mimics the expected critical behavior of the LC [30]. Pure SmA_d fluctuations mostly involve molecules sliding along the nematic director, causing variations in amplitude and phase of the smectic 1d-density wave, thus only weakly interacting with the gel. However, spatial and temporal fluctuations of the nematic director can lead to torques acting on the gel network. The prolonged relaxation times of the gel are likely driven by energy taken from the nematic director fluctuations, reducing their effect on the LC dynamics. The data suggest that the gel network provides a random-dampening field for the director fluctuations at this phase transition. The effect of this could be the observed crossover behavior of low-density 8CB+sil systems to the 3d-XY universality class of critical phenomena. In this class, order parameter and director fluctuations are suppressed.

In summary, this work has directly probed the behavior of an aerosil gel alone and when embedded within a liquid crystal, revealing evidence that (a) the pure gel is a dynamical system as opposed to the earlier view of a static, semiannealed, system [7], (b) the gel dynamics can be externally activated, and (c) the gel is dynamically coupled to the LC when embedded in it. The latter observation can be explained by the existence of a dynamic random field, elastically coupled to the liquid crystal. Essentially, the gel acts as a random "shock absorber" to the thermally driven director fluctuations in the LC. This mechanism would then account for the evolution of the SmA-N critical behavior with sil density [7–9].

To further understand the nature of the LC and sil interaction, investigations of dispersions with different aerosil density, particle size, and surface chemistry are planned. Theoretical modeling of this system as a random set of coupled mass springs to quantitatively estimate the coupling would be highly desirable. Finally, this work has revealed the feasibility of using XIFS on a system of a gel embedded in a low-viscosity isotropic solvent to study the possibility of a rigidity transition in the gel itself as a function of silica density. A rigidity transition may be responsible for the observed regimes of *soft* and *stiff* LC+sil behavior. Such a sil+solvent system would be particularly attractive as it would provide a physical model for the investigation of rigidity and connectivity percolation.

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