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Controlling disorder in liquid crystal aerosil dispersions

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The effect of disorder in the behavior of liquid crystal (LC) is assessed and controlled by dispersing known amounts of silica aerosil in the liquid crystal material. Using deuteron nuclear magnetic resonance, the director configuration and the orientational order was determined for hydrophilic aerosil dispersions in octylcyanobiphenyl. The confined liquid crystal exhibits a well-defined alignment as the silica spheres stabilize the molecular configuration. At low silica densities, a silica network is eventually established, forming a soft gel. When the sample orientation in the magnetic field is changed, a few silica strands links are broken and a fraction of the LC molecules is realigned. The field anneals the random disorder introduced by the aerosil up to a certain density beyond which, in the so-called stiff-gel regime, disordering effects completely dominate. At a fixed temperature in the isotropic phase, there is surface-induced order that is linearly proportional to the silica density.

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I. INTRODUCTION

Random disorder effects on physical systems are of fundamental interest in several areas of soft condensed matter physics. Examples of systems widely studied include superfluid helium in silica aerogels [1], doped magnetic systems [2], elastomers [3], and liquid crystals (LC's) imbedded in complex geometries [4]. LC-silica dispersions have been demonstrated to be particularly interesting systems to study through many distinct experimental and theoretical efforts [5–12]. LC-aerosil systems are of great importance as a way to access "soft" phases of continuous symmetry directly coupled to surfaces and external fields [11]. When nanosize random silica particles are imbedded in a LC, they destroy the long range orientational order yielding an exponentially decaying local nematic order with a correlation length depending on the disordering density [13,14].

As a function of silica density ρ_S of silica particles (spheres) dispersed in a LC, it is possible to probe different regimes of aerosil dispersions. At extremely low densities, the few aerosil particles added to the LC can be effectively treated and manifest their presence in the same manner as when a small amount of impurities are introduced in a LC. The quantity of silica particles is too small to form a network and they freely "float" in the material. If the density is increased, with ρ_S ranging from ~ 0.01 up to 0.1 $\mathrm{g/cm^3}$ [15], the silica spheres are able to bond and form a network. The network is known as a "soft gel" since links among the spheres are relatively weak, may break under shear, and rearrange on moderate time scales. At higher silica densities, the network is more rigid and the dispersion is known as a "stiff gel" and, as described below, is reminiscent of aerogel. Thus, aerosil introduces random disorder in the system. The disorder is controlled through the silica density allowing studies spanning from no-gel to soft-gel to the stiff-gel regime.

Aerosil gels are partly similar to another widely studied random disordering system: silica aerogel, a different type of fractal silica gel used to confine LC [11]. Aerogels are formed by a reaction-limited aggregation process in which the basic silica units are chemically fused together. Aerosil and aerogel are nearly identical in several aspects: fractal-like nature of the gel structure, surface composition and chemical properties, and density. The crucial difference between the two systems is their different response to elastic strains since aerogels possess much larger shear modulus than aerosil gels [15]. In LC-aerogel systems the silica network is fixed in space, and the elastic strains imposed by the random anchoring surfaces are fully quenched. The disorder introduced by even low density aerogels is so severe that phase transition features are dramatically smeared [11,16]. In contrast, in aerosil gels, a weaker, better controlled random disorder is introduced: elastic strains can be partially annealed thus reducing some of the disorder effects. In addition, the ability to grow a network directly within the LC permits the formation of structures of higher porosity [12]. Indeed, a tremendous advantage of aerosil systems is the ease of producing nearly arbitrary silica densities.

A significant difference between aerogel and aerosil was revealed by thermodynamic studies. For octylcyanobiphenyl (8CB) the specific heat anomaly at the second order smectic-*A* to nematic (*AN*) transition, extremely prominent in bulk, is either absent or greatly broadened when confined to aerogel, preventing the possibility of any critical behavior analysis [13]. In aerosil phase transitions are affected differently depending on the silica density. For 8CB dispersions in the soft gel regime, the specific heat at the *AN* transition is a sharp peak characterized by a critical exponent α that decreases monotonically with increasing ρ_S, changing from the pure bulk "effective" value towards the bulk 3D-*XY* value [7,17,18]. In addition, at the weakly first order nematic to isotropic (*NI*) transition, two closely spaced and sharp specific heat peaks were found; the mechanism yielding the second peak is not yet fully understood. At higher silica densities stiff-gel regime, the specific heat at both transitions consists of a single round peak suggesting an elastic strain smearing of the transitions. The random disorder introduced by the aerosil is fully quenched in this density regime. Quenched disorder refers to the fact that the disorder variables are frozen in space on the time scale of the experiments and thus do not anneal away. This is in contrast to the soft-gel regime, where the random silica network and the elastic strains are partially annealed by the confined LC molecules through the breaking and rearranging of the aerosil strands, and disorder is not fully quenched.

In this work we present a systematic deuteron nuclear magnetic resonance (DNMR) study of random disorder effects on a cyanobiphenyl liquid crystal 8CB by dispersing in it hydrophilic, type *A*300, aerosil particles [19–21]. The paper is organized as follows. Experimental details related to sample preparation and measuring technique are found in Sec. II. Results with 8CB dispersions divided according to density regime are found in Secs. III A to III D. A conclusions section ends this paper. Throughout the sections we introduce and compare with relevant results on aerosil dispersions obtained by other groups using different techniques. A considerably shorter version of this manuscript has already appeared [8].

II. EXPERIMENTAL DETAILS

A. Aerosil properties and sample preparation

The hydrophilic particles *A*300 are small silica spheres 7 nm in diameter, specific surface area $a = (300 \pm 30)\mathrm{m}^2/\mathrm{g}$, with hydroxyl groups covering their surface. The aerosil surface contains about 5 free OH $groups/\mathrm{nm}^2$ [20]. When dispersed in an organic media, the hydroxyl groups induce hydrogen bonding between particles forming aerosil strands. It is known [7] that aerosil particles form a thixotropic gel or network by diffusion-limited aggregation once the silica density ρ_S exceeds 0.01 $\mathrm{g/cm}^3$, the so-called "gelation" (percolation) threshold. In 8CB-aerosil dispersions, with ρ_S ranging from ~0.01 up to 0.1 $\mathrm{g/cm}^3$ [15], a network known as a "soft-gel" forms: links develop among the spheres but they are relatively weak, can easily break under shear and rearrange on moderate time scales. At higher silica densities, the network becomes more rigid and the dispersion is known as a "stiff-gel."

Our work investigated 8CB-aerosil dispersions ranging from below the gelation threshold, or no-gel regime, to the soft-gel regime to the stiff-gel regime, up to silica densities comparable to those in rigid aerogels. Table I lists the parameters that characterize the 8CB-aerosil systems [7,8,11]. There, ρ=g of SiO_2 per cm^3 of the total volume; ρ_S=g of SiO_2 per cm^3 of LC; $l_0 = 2/a\rho_S$ is the average void size in the aerosil network formed by 7 nm particles with $a = 300\ \mathrm{m}^2/\mathrm{g}$ for *A*300 hydrophilic aerosil; $\phi = \rho/\rho_S$ is the porosity or volume fraction of "pores;" $p = l_b a \rho_S$ is the percentage of 8CB molecules anchored by the SiO_2 surface assuming $l_b = 2$ nm for the thickness of an 8CB boundary layer.

TABLE I. Characteristics of 8CB-aerosil A300 dispersions.

ρ $(\mathrm{g/cm}^3)$	ρs $(\mathrm{g/cm}^3)$	l_0 (nm)	ϕ	p (%)
0.003	0.003	2219	0.999	0.18
0.005	0.005	1330	0.998	0.30
0.012	0.012	553	0.995	0.72
0.030	0.030	219	0.986	1.83
0.060	0.062	108	0.973	3.70
0.090	0.094	71	0.959	5.63
0.200	0.220	30	0.909	13.2
0.300	0.347	19	0.864	20.8
0.530	0.698	9.6	0.759	41.9
0.600	0.825	8	0.727	49.5

The 8CB-aerosil dispersions were prepared following procedures originally described in Ref. [6] where (1) the deuterated LC is heated 5 to 10 K above the clearing temperature (2) the proper dose of aerosil particles is introduced in the LC, (3) high purity acetone is added to the 8CB and aerosil mixture, (4) the solution is placed in a heated ultrasonic bath where it is kept agitating in excess of one day, (5) finally, the mixture is placed in a vacuum oven, slowly heated to about 350 K, where it is kept for a 3–4 h period to ensure complete evaporation of the solvent. If the solvent is not fully removed or if the solvent is not of the highest purity, the dispersion appears yellow and is discarded.

B. Networks

Dispersing aerosil spheres in a LC introduces a random field. Aside from introducing a random distribution of surfaces and distortions in the local LC directors, the additional LC-surface interaction translates in two primary effects that alter the orientational order (OO). First, the hydroxyl groups on the surface and the polar head of the LC likely yield a homeotropic LC alignment at the silica surfaces. Anchoring of LC molecules implies a surface-induced order, a local paranematic state whose order decays with the distance from the surface. The magnitude of this "field" effect is fixed by the intrinsic properties of the surface and specific LC; increasing the silica density increases its extent. This effect exists in both the isotropic phase and in the lower temperatures mesophases, and for instance, may shift the nematic to isotropic (*NI*) transition to higher temperatures since more thermal energy is necessary to destroy the additional surface-induced order. Second, in the mesophases, there are elastic strains (ES's) arising from competing surface interactions and the distortion of the local OO of the LC, leading to random disorder whose magnitude, as it involves many surfaces, likely increases with silica density. The surface-induced order and the random disorder compete; the latter is more important at higher silica density, presumably dominating above a critical density. The configuration of the aerosil gels can be thought of as random networks where the hosted LC molecules separate into many random domains (voids), as depicted in Fig. 1(a). The fractal-like structure is expected to have a wide distribution of void length scales where a mean void size l_0 characterizes the system [7].

In an anisotropic fluid such as a nematic or smectic LC that is fully aligned by a strong external field, the diffusion field is anisotropic leading to an anisotropic gel [aerosil network (AAN)], sketched in Fig. 1(b). In an anisotropic network, it is necessary to define two length scales $l_\parallel$ and $l_\perp$ to characterize the voids: $l_\parallel$ is the mean void length and $l_\perp$ is the mean void width, with $l_\parallel > l_0$ and $l_\perp < l_0$. The parameter σ

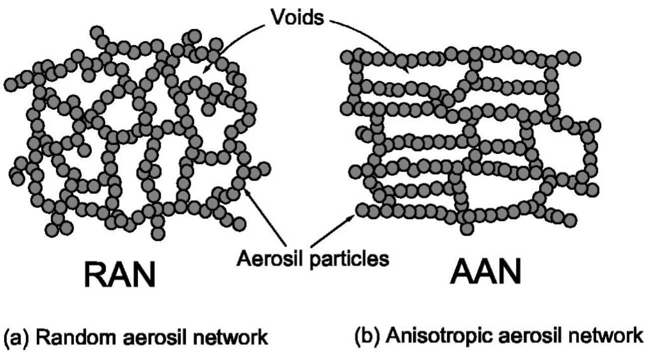

FIG. 1. Schematic representation of (a) a random aerosil network (RAN) and (b) an anisotropic aerosil network (AAN).

$\equiv l_{\parallel}/l_{\perp}$ is then used to quantify the extent of anisotropy of the network, with a larger σ indicating a more anisotropic network.

Another method to obtain an anisotropic gel is through the annealing of a random network by means of external fields, or, field-aided annealing. Assuming strong anchoring of the nematic director at the surfaces of aerosil particles forming the network, not only the surfaces act elastically on the director, but the director also acts on the surfaces and thus, on the network. Inside the NMR field, the confined LC molecules tend to align parallel to the field to minimize the free energy. This could lead to a rearrangement of the network through the breaking and relinking of aerosil strands. If the aerosil network is not too rigid or if the mean void size is not too small, a random aerosil network (RAN) anneals into an anisotropic one (AAN). Given a RAN, one expects that a stronger magnetic field would anneal it more easily, with the resulting AAN having a larger σ. With increasing aerosil density the RAN stiffens, the annealing is more difficult, and the anisotropy σ of the resulting annealed network decreases. As demonstrated below for our system, the field-aided annealing effect dominates in all soft gels, and also plays a role in the lower density stiff gels. While in the present study we focus on the magnetic field effects on aerosils, we note that the optical applications of anisotropic aerosil gels, memory effects, and electric field-aided annealing have been studied by several groups [22–24].

C. Deuteron nuclear magnetic resonance

DNMR spectra are obtained by a $\pi/2_x - \pi/2_y$ "solid echo" pulse sequence in a $B_0 = 4.7$ T magnet at the ^{2}H Larmor frequency $\nu_L = 30.8$ MHz. The spectrum from a domain of molecules with uniform director, namely, a nematic LC compound deuterated at a specific site, consists of two sharp absorption lines separated in frequency by [8,16,25]

$$\delta\nu = \frac{1}{2}\delta\nu_0 Q[3\cos^2\theta - 1] \tag{1}$$

with $\delta\nu_0$ the maximum frequency splitting observable in a fully aligned bulk nematic sample, Q the scalar orientational order parameter, and θ the angle between the nematic director and the magnetic field. In bulk, $\theta = 0°$ due to the magnetic field-induced uniform alignment of the director along the field. In a confined LC, the quadrupole frequency splitting has a positional dependence $\delta\nu = \delta\nu(\vec{r})$ through a director structure $\theta = \theta(\vec{r})$ and an order parameter structure $Q(\vec{r})$. Including the positional dependence Eq. (1) becomes

$$\delta\nu(\vec{r}) = \frac{1}{2}\delta\nu_0 Q(\vec{r})[3\cos^2\theta(\vec{r}) - 1]. \tag{2}$$

For LC molecules parallel to the direction of the field, $\theta(\vec{r}) = 0°$ and $\delta\nu(\vec{r}) = \delta\nu_0 Q$; if instead all molecules are perpendicular to the field then $\delta\nu(\vec{r}) = 1/2\,\delta\nu_0 Q$ since $\theta(\vec{r}) = 90°$. The director structure induced by the surfaces is affected the external magnetic field as long as the magnetic coherence length $\xi_M = \sqrt{\mu_0 K / B_0^2 \Delta\chi} \simeq 1\ \mu$m, is less than the mean void size ($\xi_M < l_0$). In this single elastic constant approximation, K is the average Frank elastic constant, and $\Delta\chi$ is a measure of the anisotropy of the magnetic susceptibility [25].

In confined LC systems, the DNMR spectra can be affected by translational diffusion motion. The diffusion length measuring the average distance a molecule migrates over the time scale of a NMR measurement is estimated from [16]

$$x_0 = \sqrt{\frac{D}{\delta\nu_B}} \tag{3}$$

with $\delta\nu_B$ the frequency splitting of the bulk liquid crystal and D the average translational diffusion constant. Using typical values for 8CB, $\delta\nu_B \simeq 40$ kHz and $D = 5\times 10^{-12}\,\mathrm{m}^2/\mathrm{s}$, one finds $x_0 \simeq 10$ nm in the nematic phase, while it is an order of magnitude larger in the isotropic phase, or $x_0 \simeq 150$ nm [16,26]. If the mean void size is much larger than x_0, the DNMR spectrum reflects the static director configuration and diffusion effects can be neglected. If the orientation order parameter and/or the local nematic director varies considerably over a length scale comparable to x_0, there is significant motional narrowing in the spectrum.

D. Length scale for the correlation of order in aerosil networks

In an anisotropic network, whether the magnetic field will have an effect is mostly determined by the smallest characteristic length of the voids: the mean void width $l_{\perp}$ and how it compares with the magnetic coherence length. In reality, in this interconnected system, the magnetic field affects the director configuration even when the mean void size is an order of magnitude smaller than ξ_M. This is to some extent a consequence of the wide distribution of void sizes, but more importantly, is due to the interconnected nature of the gel voids. LC domains inside each void are not isolated but rather correlated to their neighboring domains. An independent (single) pore model [5] would not be able to accurately represent the characteristics of the aerosil gels. More precisely, for the similar structure 8CB-aerogel systems, quasielastic light scattering results [27] clearly revealed that nematic correlations occur over length scales comparable to 100 average void sizes. This is not surprising as order correlated to length scales greatly exceeding the confining size has also been found at the helium superfluid transition in Vycor and aerogel glasses [1,28].

Light scattering results in the 6CB aerosil by Bellini and co-workers [29] clearly showed that the nematic director correlation length could be one order of magnitude larger than the mean void size l_0. X-ray results for 8CB aerosil [11] found that the smectic correlation length is comparable to l_0. These results suggest that when considering magnetic field ordering effects on aerosil dispersions, it is reasonable to assume that nematic domains effectively extend to length-scales comparable to $10l_0$ or longer, while in the smectic phase each smectic domain does not exceed the void size. In this scenario, the magnetic field will have a much weaker influence on the gel structure in the smectic phase. A weaker field effect in the smectic phase can be understood since ξ_M, which in the smectic phase cannot be obtained from the single elastic constant approximation, is expected to be longer than in the nematic phase due to the larger elastic constants and higher viscosity in the Sm*A* phase.

Finally, with regards to the type of networks that can be formed with aerosil, there is a significant difference between the random aerosil network (RAN) and the anisotropic aerosil network (AAN). For the same aerosil density, the orientational order (and if appropriate, the translational order) of LC's in the AAN is likely of longer range than in the RAN. In the AAN, the directors in neighboring domains are more alike than that in the RAN, therefore, its nematic and smectic correlation length should be longer. Combined with the fact that there are fewer elastic strains in the AAN, LC's in an anisotropic network are expected to have a greater orientational order parameter than in a random network.

III. EXPERIMENTAL RESULTS

A. 8CB-aerosil A300: No gel regime

When the aerosil density is below the gelation threshold $\rho_S \simeq 0.01$ g/cm^3, no thixotropic gel forms and the dispersions exhibit fluidity above the clearing point. No silica network forms, aerosil strands are isolated and float in the LC as impurities would. For the highest silica density dispersions within this regime, it may be possible that there are enough particles to almost have a complete network of relatively large mean void size ($l_0 \sim 1$ μm). The links among silica strands are too weak to elastically strain the hosted LC and thus no thixotropic gel forms. In this regime the random disorder introduced is small so the properties of these dispersions are not expected to differ much from those of the pure bulk LC. When 8CB dispersions are cooled from the isotropic to the nematic and smectic phases, most elastic strains (ES's) are annealed at the nematic to isotropic (*NI*) transition through the rearrangement of aerosil particles. The effect of random disorder on the orientational order and on the phase behavior is thus not substantial.

Marinelli's group [9,30] reported on simultaneous photopyroelectric measurements of the specific heat and the thermal conductivity for a low-density 8CB-aerosil dispersion, $\rho_S \simeq 0.005$ g/cm^3, considerably below the gelation threshold, in a near zero external field; in their apparatus there is a weak homeotropic aligning surface field. They found that the thermal conductivity *k* differed between the cooling and heating processes: in the nematic temperature range, the magnitude of *k* measured on the cooling process was considerably smaller than that determined on the heating process. This hysteretic behavior was attributed to the different annealing of elastic strains during the cooling and heating processes, leading to a difference in the amount of OO present in the system. Cooling from the isotropic to the nematic phase, the onset of OO in the presence of the weak surface alignment rearranges particles, partially annealing the disorder-induced elastic strain. Further cooling is required to complete the annealing: the appearance of smectic layering is needed as suggested by a large increase in thermal conductivity *k*, much larger than in bulk at the smectic-*A* to nematic (*AN*) transition. Heating from the Sm*A* to the nematic phase, the annealed structure can be retained to higher temperatures yielding a larger OO, and a correspondingly higher magnitude of the thermal conductivity than in cooling.

Given the previous results, to study the effects of a weak amount of randomness on the LC phase behavior, its manifestation in DNMR spectral patterns, and to test for possible orientational order hysteresis, two extremely low silica density dispersions in this no-gel regime were prepared. Except where noted, all measurements were obtained in cooling the dispersions from the isotropic phase within the NMR magnetic field. The temperature dependence of the spectral patterns for the $\rho_S = 0.003$ and 0.005 g/cm^3 dispersions (we drop the units hereafter), not shown, are almost indistinguishable from those of bulk 8CB: a single narrow absorption peak in the isotropic phase, and a full-splitting doublet (the frequency separation between absorption peaks) in the nematic and smectic-*A* phases. Basically, the effect of the random disorder on the spectral patterns and thus the LC director and the orientational order at these low densities is negligible. However, not everything is similar as evidenced by the angular dependence studies of the spectra for the two no-gel dispersions in the nematic and smectic phases seen in Fig. 2. For 0.003 in both mesophases, the spectra consist of a full-splitting doublet that is independent of sample orientation in the magnetic field: the LC molecules are all fully aligned by the magnetic field. For 0.005, the pattern is also independent of orientation in the nematic phase, however, surprisingly, there is a $P_2(\cos\theta)$ dependence in the smectic-*A* phase. The frequency splitting decreases with increasing angle, disappears at the so-called magic angle ($\cos^2\theta = 1/3$), and at the 90° orientation is a half-splitting doublet (exactly 1/2 of the full splitting measured at 0°), thus indicating that the LC director is now perpendicular to the field. This angular dependence is surprising since no gel is supposed to have formed at this density and from the results for the 0.003 dispersion it could be expected that the 4.7 T field is strong enough to align smectic domains. 0° is defined as the sample orientation during the initial cooling process.

The angular dependence in the Sm*A* phase for the 0.005 dispersion may be understood in terms of the following mechanisms. First, the viscosity of 8CB-aerosil dispersions increases with increasing aerosil density. This "locks in" the director configuration and the magnetic field is unable to realign the smectic domains. Second, it is possible that the

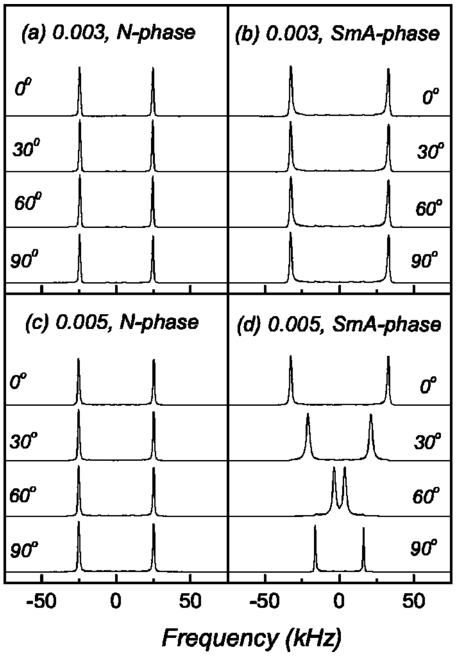

FIG. 2. No-gel regime: angular dependence of the DNMR spectra for the 0.003 and 0.005 8CB-aerosil A300 dispersions in the nematic ($T=307$ K) and smectic-A ($T=298$ K) phases. 0° is defined as the orientation in which the sample is first placed in the field.

magnetic field enables a strongly anisotropic diffusion field removing most of the elastic strains and aiding the formation of a complete field-induced anisotropic silica network with large σ. In this network all of the void widths are smaller than the corresponding magnetic coherence length in the smectic phase $l_{\perp}(0.005) < \xi_M(\mathrm{Sm}A)$, and consequently the field has no effect. The LC configuration in the dispersion is remarkably uniform.

More insight on the 0.005 dispersion behavior is obtained through what we refer to as a zero-field cooling study, namely, the dispersion is cooled from the isotropic phase to the Sm*A* phase but outside the magnetic field, and then placed into the NMR field at that same smectic temperature. Under such zero-field cooling conditions, the LC configuration is established in the absence of an aligning field. In fact, the angular dependent spectra for 0.005 after zero-field cooling [8] show an almost perfect powder pattern independent of the dispersion orientation in the field. It would be perfect if instead of the outer singularities, flat shoulders were present. The powder pattern indicates that a random distribution of smectic domains is established during the zero-field cooling process, and is only weakly affected by the magnetic field once the sample is placed in it: the shoulders expected at full splitting positions are replaced by two weakly intense singularities. Most smectic domains are still random and only a small fraction of LC molecules can be aligned by and follow the magnetic field. These zero-field results are different from the field-on results of Fig. 2(d), where the director configuration is fixed by the anisotropic silica network (resulting from cooling in the presence of the aligning field) and no LC molecules are aligned by the field. The zero-field cooling results are understood by noting that in the cooling process the diffusion field is random, the aerosil network is not fully complete, and only a few molecules are eventually aligned by the field. Alternatively, the RAN is complete but $l_0(0.005) < \xi_M(\mathrm{Sm}A)$ is not satisfied for all voids and LC molecules in the larger voids are aligned by the magnetic field once the sample is placed in the NMR apparatus.

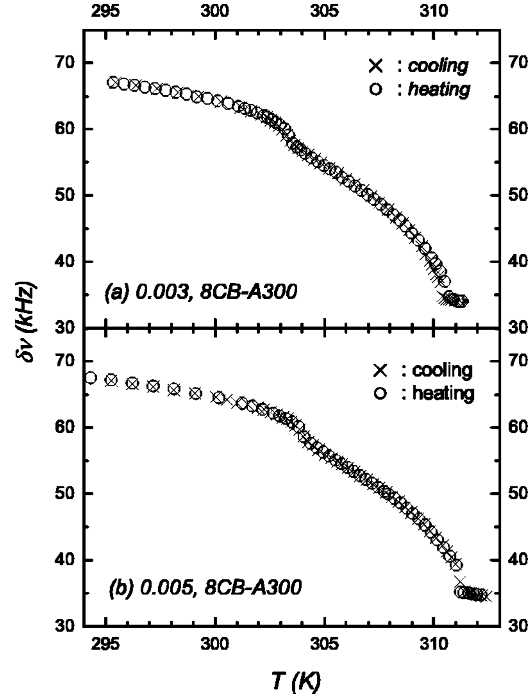

FIG. 3. Quadrupole frequency splitting temperature dependence for the two no-gel dispersions on heating and cooling.

The temperature dependence of the frequency splitting for the two no-gel dispersions on heating and cooling is illustrated in Fig. 3. For both samples, $\delta\nu$ is mostly bulklike with a remarkable overlap over the complete temperature range; there is only a small difference at temperatures very close to the *NI* transition. The stable configurations retain the same amount of OO on heating and cooling, and the hysteresis seen in the thermal conductivity studies is not reflected in $\delta\nu$. This difference is likely due to the fact that in the near zero-field thermal measurements [30] the aerosil-induced elastic strains are gradually annealed with decreasing temperature, the annealing being complete only once smectic layering order appears. The absence of hysteresis in these orientational order measurements in the presence of a strong field, is caused by the field-aided (stronger) annealing process in which the NMR field anneals most elastic strains at the *NI* transition with no further annealing occurring away from the transition.

In the vicinity of the *NI* transition there is a plateau in the orientational order that extends over a 1 K. In this region, the amount of order present in the system is very weakly dependent on temperature and the spectral pattern consists of an isotropicike peak coexisting with a nematiclike splitting. The orientational order begins to rapidly increase once the isotropiclike peak disappears. Although we do not have a clear understanding of this effect, we offer a possible explanation after the results discussed in the next section.

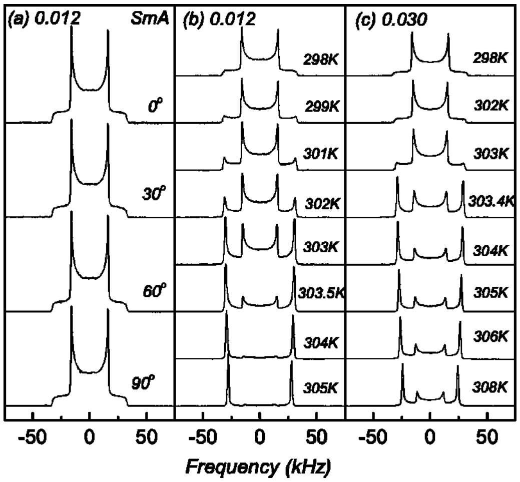

FIG. 4. The angular dependence study of the spectral pattern at room temperature, a nearly perfect powder pattern, after (a) zero-field cooling and (b) its temperature dependence on subsequent heating for the 0.012 dispersion. (c) Temperature dependence on heating for the 0.030 dispersion after an initial zero-field cooling that also yielded a powder pattern.

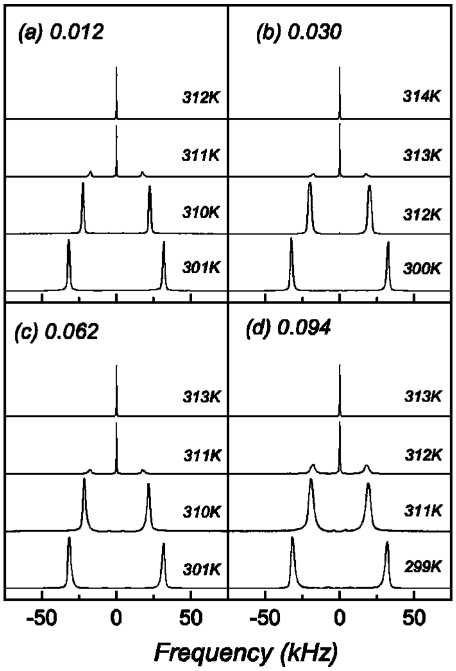

FIG. 5. Temperature dependence of the spectral patterns for soft-gel dispersions obtained while cooling from the isotropic phase in the NMR field.

B. Soft gel regime

In the soft-gel regime, the aerosil density is such that a complete network forms under zero-external field conditions. This is demonstrated here through the zero-field study for the 0.012 sample (slightly above the gelation threshold) seen in Fig. 4(a). Cooling from the isotropic phase outside the field, the room-temperature spectrum is now an almost perfect powder pattern with basically flat shoulders and no angular dependence. All smectic domains are random, the void average size is small, and there is no reorientation nor breaking of silica strands once the sample is placed in the magnetic field in the smectic-*A* phase. If the sample is now heated in the presence of the magnetic field, with increasing temperature LC molecules become aligned by the field, Fig. 4(b). Two weak singularities start replacing the flat shoulders above 300 K, and their intensity quickly grows (more molecules have the same alignment) with increasing temperature. The powder pattern spectrum eventually disappears giving rise to a full-splitting doublet at about 305 K, a temperature still in the smectic phase, indicating the random silica network has evolved into an anisotropic one. The change in network structure is presumably due to the breaking and rearrangement of the silica links along the direction of the external field. For densities just above the gelation threshold, silica links are not yet too strong and may break through the elastic coupling with the magnetic field. Also, as thermal fluctuations increase in the less viscous dispersions, weaker links break freeing LC molecules. The freed molecules and broken silica links are realigned by the magnetic field, yielding an anisotropic network.

The zero-field cooling study was also performed for a higher density soft-gel, 0.030, in which case the random silica network has stronger silica links and smaller mean void size. As expected, the spectrum is a perfect powder pattern at room temperature. With increasing temperature the director configuration remains at first random. Links start to break and rearrange only once the temperature approaches ~303 K, 3 K higher than in the 0.012 dispersion case: larger thermal fluctuations are needed to break the now stronger silica links, Fig. 4(c). The stronger silica links, in addition, prevent the random network to fully transform into an anisotropic one. The powder pattern component and the full-splitting doublet in fact coexist to temperatures close to the *NI* transition. At these densities, silica links are already strong enough (or the mean void size small enough) that not all random domains can be annealed by the magnetic field. The silica configuration is then a mixture of a random and an anisotropic network. Quantifying, at 308 K, the area of the powder pattern spectra (RAN part) is about 60 % of the total area under the spectral pattern.

Additional insight is gained from the temperature dependence obtained in field-cooling studies performed for four soft-gel dispersions 0.012, 0.030, 0.062, 0.094, that are shown in Fig. 5. For all of these samples, the spectrum is a single, centered, narrow peak in the isotropic phase, becoming a full splitting doublet in the nematic and smectic phases; this is similar to the no-gel or bulk 8CB cases. The random aerosil network in the 0.030 dispersion that was not fully annealed on heating after the zero-field cooling, now becomes fully annealed when cooling takes place in the field. As a function of temperature, the width [full width at half maximum (FWHM)] of the absorption peaks broadens while the frequency splitting $\delta\nu$ decreases, direct consequences of the increase in random disorder resulting from increasing ρ_S, Fig. 6. This density dependence, strikingly linear, is nicely exhibited in Fig. 7 where the FWHM and the and the orientational order parameter (calculated from its proportionality to $\delta\nu$) of these soft gels is plotted 10 K below T_{NI}.

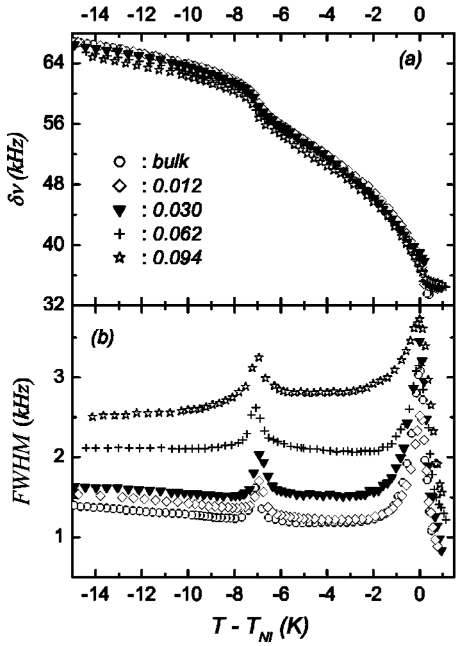

FIG. 6. Temperature dependence covering nematic and smectic-A phases for the frequency line splitting $\delta\nu$ (a), and the full width at half maximum FWHM (b), for dispersions in the soft-gel regime.

The decrease in OO as compared to bulk, with increasing ρ_S, is not substantial in this density regime. In fact, at the same reduced temperature in the smectic phase, the frequency splitting for 0.094 is only 6 % below bulk's. This reflects the essential role of the field-aided annealing that minimizes the effect of the silica induced random disorder on the OO. For all soft gels, there is a significant enhancement in the size of the frequency splitting (enhancement of OO) in crossing to the smectic phase (Fig. 6), an empirical DNMR signature signaling the onset of translational order and which results from the coupling between nematic and smectic-A order parameters. This observation is consistent with reports of a still prominent thermodynamic *AN* transition in soft gels [7,30]. The increase in OO at T_{AN} quantifying the coupling between nematic and smectic order parameters, is ~5 kHz for bulk 8CB, decreasing to ~4.3 kHz for the 0.094 dispersion. The dependence of the jump in OO on silica density for soft gels is shown in Fig. 7(c).

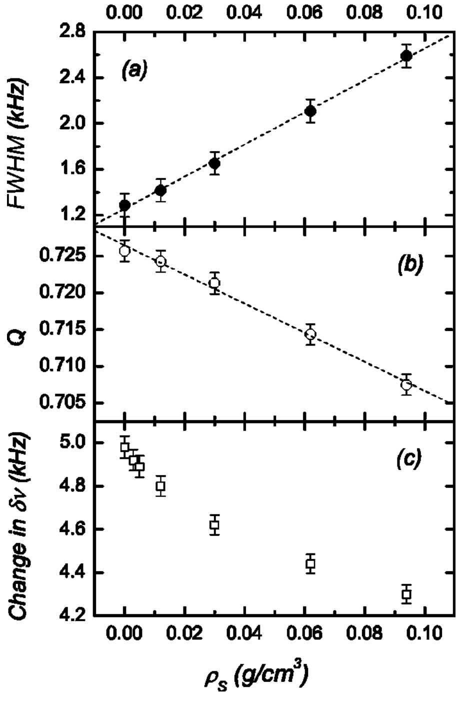

FIG. 7. The dependence on silica density of (a) the FWHM, (b) the orientational order parameter Q evaluated 10 K below T_{NI}, and (c) the enhancement of OO at T_{AN}.

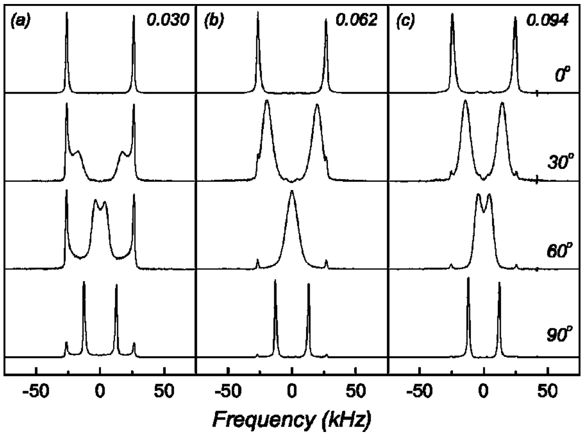

FIG. 8. Angular dependence in the nematic phase after cooling in the field from the isotropic phase for (a) 0.030, (b) 0.062, and (c) 0.094 soft-gel dispersions. Spectra were obtained at 307.7 K corresponding to 4.5, 3.8, and 3.5 K below the respective T_{NI}.

Also in soft gels, as before in the no-gel dispersions regime near T_{NI}, there is a ~1 K coexistence of the isotropic peak and the nematic doublet (Fig. 3) where there is a weakly temperature dependent line splitting [the plateau in Fig. 6(a)]. Once the isotropic peak disappears, the line splitting rapidly increases with decreasing temperature. While such a coexistence is also present in other systems [16], this is the only confined system that we have measured to date exhibiting such a plateau. The width of the plateau, almost independent of the aerosil density, appears to depend on the strength of the magnetic field. In fact, for a soft-gel studied in a stronger magnet (6.5 T), there is no evidence of a plateau. Conceivably, the plateau may represent the (DNMR) signature associated with the annealing of elastic strains. Recalling that in the near zero-field thermal conductivity work [9,30] the annealing took place over the full nematic range, for stronger fields and consequently shorter coherence length, the annealing occurs over a narrower temperature range.

Angular dependence studies in the nematic phase for three soft-gels after field cooling are presented in Fig. 8. At 0° orientation that we recall is defined as the orientation at which the sample is first placed in the magnet, the spectra consist of a full splitting doublet. This pattern is indicative of the anisotropic nature of the soft-gels with a LC director aligned by and parallel to the magnetic field. At other orientations, the spectra consist of the superposition of two components: a large intensity doublet that follows the $P_2(\cos\theta)$ dependence, and a weakly intense doublet fixed at the full-splitting frequency position at all orientations. With increasing silica density, the intensity of the small full-splitting doublet decreases, nearly disappearing for the 0.094 dispersion. Before placement in the field, the soft gels possess a random network. As they are cooled in the field, the nematic order appears, but more importantly, there is the aligning and annealing effect of the magnetic field that establishes an anisotropic silica network. As the soft gels are rotated in the field, weakly connected silica strands are broken and a fraction of the LC molecules is reoriented parallel to the field. With increasing ρ_S and thus a stronger network and bonds, fewer silica links are broken upon sample rotation. This effect is quantified by calculating the area under the absorption peaks at full splitting and dividing it by the area under the full spectral pattern obtained at the 90° orientation. This represents the fraction of molecules that are parallel and thus have been reoriented by the field. This ratio decreases from 18 to 4 to 2 for the 0.030, 0.062, and 0.094 samples, respectively, confirming that fewer links are broken as the silica density increase. However, as appealing as the previous scenario may be, an alternative explanation must be considered. Given that there is a distribution of void sizes in each anisotropic soft gel, upon rotation, LC molecules confined to domains of width $\sim 10 l_\perp > \xi_M$ are reoriented by the field. As the silica density increases, fewer domains satisfy such condition and thus fewer molecules are realigned. We are unable to distinguish which of the two mechanisms applies or if both are present simultaneously.

For soft gels in the smectic phase, the angular dependence of the spectra (not shown) are all $P_2(\cos\theta)$-like, thus, there is no reorientation of LC molecules. This is expected since such angular dependence was present even at lower densities, such as 0.005, in the no-gel regime. The lack of molecular reorientation is understood by noting that ξ_M in the smectic phase is longer than that in the nematic phase, while, at the same time, the domain size is about 10 times smaller than that in the nematic phase. Considering the higher smectic viscosity, smectic domains are in general considerably more difficult to reorient by a magnetic field of the size used here. In short, cooling in the field, the LC director configuration that is established entering the Sm*A* phase is locked-in and is unaffected by the field.

Finally, note that a "memory" effect has been found in anisotropic gels formed through the field-aided annealing process. If the samples are taken out of the magnet and stored at room temperature, their AAN is stable and the LC configuration retained for long periods of time. When the 0.030, 0.062, and 0.094 soft gels that had been stored at room temperature were remeasured one year after the original measurements, their DNMR spectral patterns still showed an anisotropic network. In contrast, in the lower density anisotropic gels, such as 0.012, possessing weaker silica links, the memory effect is relatively "weak." The AAN is easily transformed into a RAN through processes such as shaking the sample for a few minutes, or by heating it to isotropic phase, wait overnight, and cool it back down to room temperature again. For the low density stiff gels that will be discussed in the following section, the AAN is very stable and cannot be destroyed by any of the above methods, nor, can it be reannealed inside the field to yield a different AAN structure.

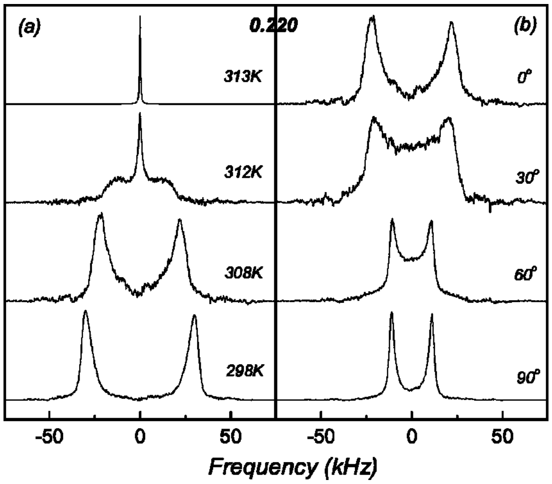

FIG. 9. Temperature (a) and angular dependence at 308 K (b) for the 0.220 stiff-gel dispersion.

C. Stiff gels

In the stiff-gel regime $\rho_S > 0.1$, an increasingly more rigid network with smaller void sizes forms. Magnetic field ordering effects are expected to become unimportant, thus, silica-induced disorder should dominate. For dispersions in this regime, specific heat results [7] suggest that elastic strains are fully quenched. Figure 9 illustrates the DNMR spectra for a 0.220 dispersion, a density that is about twice that of the lower limit for the stiff-gel regime. Cooling in the field [Fig. 9(a)] shows an evolution from the usual isotropic pattern to a nematiclike splitting formed by broad absorption peaks that become better defined once the smectic phase is entered. The angular study in the nematic phase [Fig. 9(b)] reveals the usual P_2 dependence. Curiously, this stiff-gel behavior is reminiscent of that found in the 0.094 soft gel, Fig. 8(c) and indicates the presence of a mostly anisotropic network. This can only be understood by considering that even at this high density some field-aided annealing still occurs. Although elastic strains in zero field are fully quenched, they may still anneal in the presence of a strong magnetic field.

A quantitative comparison between the 0.220 stiff-gel dispersion with the 0.094 soft gel indicates that the frequency linesplitting in the stift gel is narrower (a decrease in OO) by about 10 %, Fig. 10(a), while its linewidth has increased by more than twice. This reflects that the alignment is not perfect due to the increased randomness in the sample. Another difference is clear from the spectrum at 312 K, Fig. 9(a), where the coexistence of the isotropic peak with broad nematiclike peaks in the stiff gel are clearly seen. Combined with a lower frequency splitting in the vicinity of T_{NI}, namely, a lesser discontinuous jump in order from the isotropic to the nematic phase, it can be concluded that the *NI* transition is becoming less sharp. The plateau that was seen in the linesplitting near the transition, is not present in stiff gels, while the enhancement of order at the *AN* transition, now

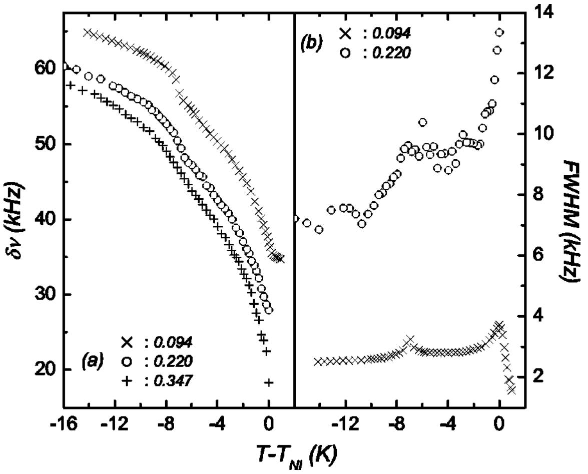

FIG. 10. (a) Quadrupole frequency splitting dependence on temperature for the 0.094 soft gel, and two stiff gels 0.220 and 0.347. For 0.347 what is plotted is twice the frequency splitting between the inner peaks of the powder pattern; (b) comparison of the FWHM between a soft and a stiff gel.

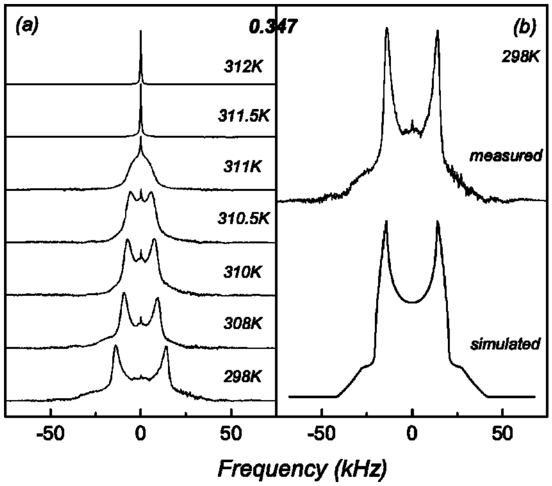

FIG. 11. (a) Temperature evolution of the DNMR pattern for the 0.347 stiff gel. (b) Lowest temperature experimental spectrum (top) compared with a sprectrum simulated from the superposition of powder patterns.

only ~3 kHz (a 40 % decrease from bulk), is more gradual. Yet, local smectic order still exists at this density. Further, Fig. 10(b), the FWHM shows well-defined phase transitions in the soft gel (0.094) but not in the stiff gel (0.220).

The results for the 0.220 dispersion are somewhat puzzling. The mean void size l_0 for this dispersion is estimated at only ~30 nm. Assuming that nematic domains are correlated to length scales an order of magnitude longer, i.e., $10l_0$, the mean void size would still be 3–4 times smaller than ξ_M. This analysis raises questions regarding the mechanism for the ordering magnetic field to still be able to anneal elastic strains yielding anisotropic networks in stiff-gel dispersions. To answer this question and in accordance with Refs. [7] and [31], we suggest the following scenario. As the silica concentration increases, some of the available surface area is lost due to multiple interconnections or aggregations of basic silica units. Effectively, the size of silica aggregates forming the network becomes larger as the aerosil density in the dispersion is increased. Then, a mean void size defined through l_0, and calculated assuming a constant 300 m^2/g aerosil surface area, may be applicable only to the dilute soft-gel regime [11]. In the soft-gel regime the addition of silica particles does not significantly change the specific surface area; this likely occurs only in stiff gels. It was in fact pointed out by Frunza *et al.* [31] that samples with high silica densities consist of aggregates and agglomerates covering a broad range of length scales. Assuming silica networks formed by 50 nm aggregates instead of 20 nm primary particles, they obtained a 2.5 times larger l_0. Under these conditions, order would be correlated to length scales becoming comparable to the magnetic coherence length, thus permitting a partial field-aided annealing.

The temperature dependence of the spectral patterns for a higher density 0.347 stiff-gel dispersion is seen in Fig. 11. With decreasing temperature the pattern evolves from an isotropic peak into a powder-pattern at 308 K. The random silica network is stronger and the void size small enough that at this density field effects are no longer possible: no annealing of elastic strains occurs nor rearrangement of silica links. There is a random distribution of LC domains in the voids that is stabilized, quenched, and no angular dependence is detected. Note from the 298 K spectrum, as emphasized by Fig. 11(b), that the powder-pattern shoulders are not flat, but unlike for soft-gels where this was attributed to the breaking of silica bonds, here, it is understood as a spectrum resulting from the superposition of many powder patterns possessing different orientational order parameter. This is possible since there is a distribution of random quenched LC domains of different sizes. Also, taking the frequency splitting between the inner peaks of the powder pattern (and doubling it) and plotting it as a function of temperature, Fig. 10, clearly shows that the OO is further suppressed as compared to the lesser dense dispersions. There is no enhancement in order at the *AN* transition, indicating the smearing and/or broadening of the transition. In this now very restrictive geometry, the smectic order is size-limited and unable to grow beyond the domains size. At these densities, aerosil dispersion are basically indistinguishable from aerogels: random quenched disorder dominates and phase transitions are broad and suppressed [13,16,32].

For the two densest stiff-gel dispersions studied in this work, 0.698 and 0.825, the mean void size $l_0 \leqslant 10$ nm (see Table I), is smaller than the nematic thermal coherence length at T_{NI}, which is estimated to be $\zeta \sim 14$ nm. For domain sizes below the thermal coherence length, it has been empirically established that phase transitions are completely destroyed and there is only a continuous evolution of local OO [33]. The temperature dependence of the spectral patterns for these high density dispersions is presented in Fig. 12, and it is partially different from that of the 0.347 dispersion. For most of the temperature range the spectrum is primarily a single, very broad absorption peak; this pattern persists for several degrees below the bulk T_{NI}. To understand such spectra, one must take into account translational diffusion effects. At these silica densities, LC molecules in the

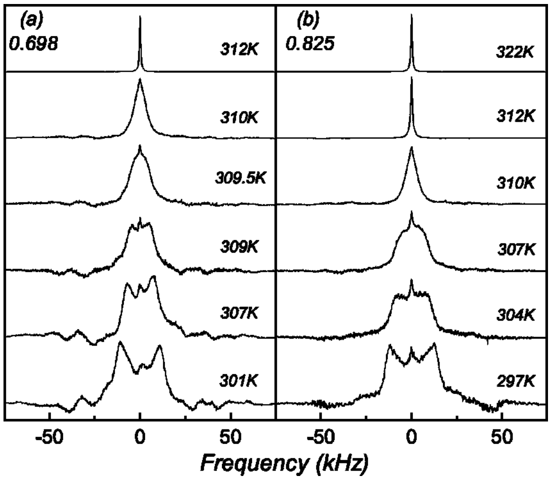

FIG. 12. Spectral patterns for the two densest stiff-gels studied: 0.698 (a) and 0.825 (b).

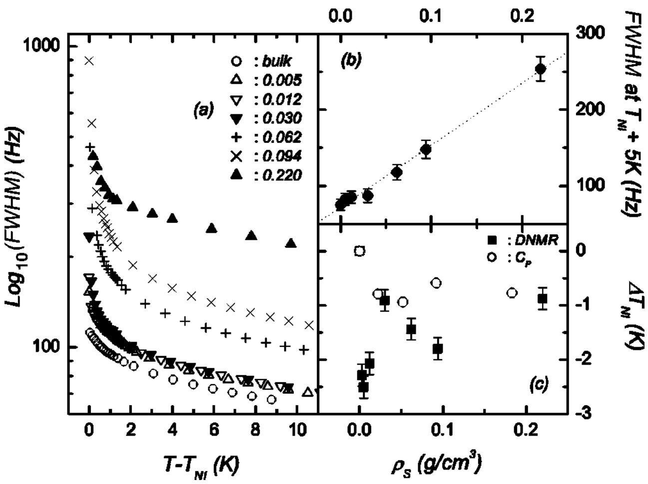

FIG. 13. (a) The FWHM of the isotropic peak as a function of reduced temperature for several dispersions. (b) Linear dependence on aerosil density of the FWHM determined at 5 K above T_{NI}. (c) T_{NI} shift from bulk as a function of aerosil density. Results from the specific heat (C_P) studies of Ref. [7] are also included.

center region of the voids will likely have a distinct orientational order parameter from the molecules that are near, or are anchored at, the aerosil surface. As demonstrated below, since the diffusion length $x_0 \approx 10$ nm is now comparable to the mean void size, translational diffusion greatly affects the measured spectra.

Following the analysis first employed in our earlier aerogel studies [16], the absorption spectra are affected if

$$\varepsilon \cong \frac{\delta \nu l_0^2}{6D} \leqslant 10. \tag{4}$$

Using typical LC values, we find $\varepsilon \approx 0.08(0.13)$ for the 0.825 (0.698) dispersion. The requirement stated by Eq. (4) is well satisfied even when taking into account effects from multiple connections and assuming for the mean void size a value up to 5 times larger than that quoted in Table I. Thus, the DNMR spectrum is strongly affected by motional narrowing resulting in the single broad peak. As in aerogel [16] and Vycor [33], in 0.825 (and in 0.698) aerosil gel, the linewidth of the broad single peak increases from 1 kHz (600 Hz) above bulk T_{NI} to 30 kHz (20 kHz) at $T-T_{NI}=13$ K. Cooling further to bulk-like smectic temperatures, the molecular diffusion slows down and a splitting is eventually resolved. The single broad peak evolves towards a powder-pattern-like spectrum that is the result of the superposition of random domains having a different local order. The central peak feature seen in the 297 K spectrum for the 0.825, can be attributed to defects with local order $Q \approx 0$. At a defect site, the director field undergoes drastic changes and due to local spatial averaging, this is manifest in a DNMR spectrum as a central peak [16,34].

D. Dispersions in the isotropic phase: Transition temperature shift

In LC mesophases, adding aerosil particles causes local distortions of the director thus introducing random disorder to the originally ordered states. In contrast, in the isotropic phase, and because there are surfaces, aerosil particles tend to produce an ordering effect through the anchoring of LC molecules to their surface. In the isotropic phase there is fast molecular diffusion through which the surface-induced order is completely motionally averaged. A nematiclike quadrupole splitting could only be observed if the surface is fairly uniform and the surface induced order is relatively large. In aerosil dispersions, the anchoring is totally random, the extent of the surface-induced order is expected to be proportional to the aerosil density, and the spectrum in the isotropic phase is a broader than bulk absorption peak.

Figure 13(a) shows the FWHM of the isotropic peak as a function of reduced temperature for several dispersions. The peak width increases with increasing density. From Table I, the percentage of 8CB molecules anchored by the surface increases linearly with ρ_S. This dependence is emphasized in the plot of the FWHM at a temperature 5 K above T_{NI}, Fig. 13(b), clearly showing its linear growth with increasing aerosil density.

Regarding the transition temperature in confined systems, T_{NI} can be shifted due to finite size effects, surface anchoring interactions, distortions, etc. In 8CB-aerogel systems, compared to bulk, there is a downward shift of magnitude linearly proportional to the aerogel density [16,32]. In aerosil dispersions the situation is more complicated. From DNMR results, T_{NI} is always downshifted compared to bulk, however, the magnitude of the shift has a complex dependence on the aerosil density, Fig. 13(c). This behavior is consistent with that determined by the specific heat measurements, a technique far more sensitive to transition temperatures [7]. This intricate behavior likely results from the complex nature of aerosil dispersions: aerosil networks are not fixed and (field-aided) annealing effects play an important role at the transition.

IV. CONCLUSIONS

When hydrophilic aerosil particles are dispersed in a LC material, they form a random interconnected network. The disordering effects, controlled through the amount of silica particles added to the LC, are manifest through the distortion of the local director and the suppression of the long range orientational and/or translational order of a LC phase. Depending on the aerosil silica density, the behavior in zero external field shows that there are different dispersions regimes: (1) no gel, where the amount of introduced disorder is minimal, (2) soft gel, in which the dispersions are in the presence of disorder that is not fully quenched, and (3) stiff gel where the disorder is large and fully quenched.

As a function of silica density up to low density stiff-gel dispersions, cooling the samples in the presence of a strong magnetic field leads to a rearrangement of silica links such that disorder-induced elastic strains are greatly annealed, and the random network converts into an anisotropic one. In no-gel dispersions at zero field, it was thermally determined that there is hysteresis in the orientational order with thermal cycling. The hysteresis is not present under a strong external field that is able to complete the annealing of elastic strains very close to the *NI* transition. In soft gels, the *NI* and *AN* transitions while somewhat broader than in bulk retain most of their sharpness. The amount of orientational order that exists in the dispersions decreases linearly with increasing silica density; the decrease is not substantial because of the field-aided annealing. Once disorder is fully quenched, as in the stiff-gel regime, phase transitions are first considerably smeared or very broad, and eventually completely suppressed. A continuously evolving and considerably reduced orientational order is all that remains.

The annealing of elastic strains occurs almost completely in the vicinity of the *NI* transition. In the smectic phase, field effects are not substantial due to the shorter domain-limited smectic correlation length, the longer magnetic coherence length, and the increased viscosity in this mesophase. In fact, beginning with some soft gels, cooling outside the field yields a perfectly disordered sample that the magnetic field is unable to affect until the temperature is increased above room temperature and nears the nematic phase. When the field-aided annealing effect is quantified, it is found to be inversely proportional to the aerosil density.

Finally, we also determined the existence of surface-induced order in the isotropic phase of these dispersions, evidenced through a broader than bulk isotropic peak. Through the anchoring of LC molecules to the aerosil particles, pretransitional order is induced. At a constant temperature, the width of the absorption peak is linearly proportional to the aerosil silica density.

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