

Aerosil Dispersed in a Liquid Crystal: Magnetic Order and Random Silica Disorder

Tao Jin and Daniele Finotello

Department of Physics, Kent State University, Kent, Ohio 44242-0001

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Dispersions of silica spheres (aerosil) in octylcyanobiphenyl (8CB) liquid crystal were investigated with deuteron NMR. For the lowest silica density dispersions, there is a field-induced liquid crystal alignment as the field anneals most elastic strains. Increasing the silica density, the molecular alignment is stabilized by the spheres and is retained after sample rotation in the field; in the process, a few silica strand links are broken by the field, which realigns some molecules. At higher densities, the aerosil dispersions are aerogel like and disordering effects are apparent.

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The behavior of liquid crystals (LC) in complex geometries formed by polymer or porous networks has received considerable attention [1] recently focusing on LC properties as affected by the dispersion in them of small silica spheres (aerosil) [2–4]. Depending on silica density, aerosil dispersions possess features ranging from similar to Millipore [5] to similar to aerogel [6,7]. With aerosil, random quenched disorder is introduced in a controlled fashion so such dispersions are suitable for testing existing theoretical models [8].

In this work we study quenched disorder effects on LC using hydrophilic aerosil particles (type 300): small silica spheres of 7 nm diameter and surface area $S = 300 \text{ m}^2 \text{ g}^{-1}$ with hydroxyl groups covering their surface. The spheres form a *gel* (network) if the density $\rho_S \sim 0.01 \text{ g/cm}^3$ exceeds the “gelation” (percolation) threshold. A network forms by diffusion limited aggregation and hydrogen bonding of the spheres. The hydroxyl groups on the surface and the polar nature of the LC likely yield a homeotropic LC alignment at the silica surfaces, while the director in the voids volume is parallel to the silica strands.

Dispersing aerosil spheres in a LC can be viewed as introducing a random field in it. In addition to introducing a random distribution of surfaces, the LC-surface interaction results in two primary effects altering the orientational order. First, there is surface-induced order that decays with distance from the surface and yields a local paranematic-like state. The magnitude of this “field” effect is fixed by the intrinsic properties of the surface and the LC; increasing the silica density only increases its extent. Second, there is elastic strain arising from competing surface interactions, whose magnitude, as it involves many surfaces, is likely to increase with silica density. Above a critical density, the latter presumably dominates.

Zero-field studies by Iannacchione *et al.* [2] for 8CB + aerosil dispersions revealed two distinct regimes depending on silica density. For $\rho_S = 0.022$ up to 0.1 g/cm^3 [9], the network is a “soft gel”: links among the spheres can easily break. In soft gels, the specific heat C_P at the smectic-A (SmA) to nematic (*N*) transition is sharp and characterized by a critical exponent α that decreases monotonically with increasing ρ_S . α changes from the

pure bulk “effective” value towards the bulk 3D-XY value [2,5]. At the *N* to isotropic (*I*) transition, there are two closely spaced and sharp specific heat features. For $\rho_S > 0.1 \text{ g/cm}^3$, the network is “stiff” and C_P at both transitions is a single rounded peak suggesting an elastic strain smearing of the transitions.

Mercuri *et al.* [3] reported on a photopyroelectric, near zero-field (in a weak aligning field) specific heat and thermal conductivity study for an 8CB dispersion, 0.005 g/cm^3 , below the gelation threshold. The thermal conductivity differed on cooling and heating: The magnitude measured on cooling was significantly smaller than that determined on heating. The effect was attributed to the presence of less orientational order in the system: In cooling, the onset of orientational order rearranges particles reducing the disorder. The elastic strain introduced by the silica particles is not fully annealed at the *N-I* transition. Cooling to the SmA phase and the onset of translational order complete the annealing process. On heating, a higher orientational order is retained, thus, a higher thermal conductivity.

We report on a systematic deuteron nuclear magnetic resonance (DNMR) study for several 8CB + aerosil dispersions. Dispersions studied the range from below the gelation threshold, to the soft-gel regime, to the stiff-gel regime with a silica density comparable to that in rigid aerogels. Spectra are obtained as a function of temperature, of sample orientation in the NMR magnetic field, and after zero-field cooling. These studies allow one to deduce the molecular alignment, assess the stiffness of the gel, and test for orientational order hysteresis.

Aerosil dispersions in 8CB- αd_2 , deuterated at the first carbon position along the hydrocarbon chain, were prepared as described in [10]: Silica powder is added to a dilute solution of 8CB in chemically pure acetone. The mixture is placed in an ultrasonic bath to achieve a good dispersion and then placed in a vacuum oven and pumped overnight at $\sim 330 \text{ K}$. The density $\rho_S = g$ of SiO_2 per cm^3 of LC of our samples is 0.003 (2.22), 0.005 (1.33), 0.012 (0.55), 0.030 (0.219), 0.062 (0.108), 0.094 (0.071), 0.347 (0.019), 0.698 (0.0096), and 0.825 (0.008). Values in parentheses refer to the mean void size l_0 (or the mean

distance between silica surfaces for no gel samples) in μm calculated from $l_0 = 2/\rho_S$ [2].

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 ^2H Larmor frequency $\nu_L = 30.8$ MHz. The DNMR 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 [11]:

$$\delta\nu = \delta\nu_0 Q \langle P_2 \rangle = \delta\nu_0 Q \left\langle \frac{1}{2} (3 \cos^2 \theta_B - 1) \right\rangle, \quad (1)$$

with $\delta\nu_0$ the maximum frequency splitting observable in a fully aligned bulk nematic sample, Q the scalar orientational order parameter, and θ_B the angle between the nematic director \hat{n} and the magnetic field \vec{B}_0 . For bulk, $\theta_B = 0^\circ$ due to the magnetic field-induced uniform alignment of \hat{n} along \vec{B}_0 . In confined LC, $\delta\nu$ has a positional dependence $\delta\nu = \delta\nu(\vec{r})$ through a director structure $\theta_B = \theta_B(\vec{r})$ and an order parameter structure $Q(\vec{r})$. Equation (1) becomes

$$\delta\nu(\vec{r}) = \frac{1}{2} \delta\nu_0 Q(\vec{r}) \langle [3 \cos^2 \theta_B(\vec{r}) - 1] \rangle. \quad (2)$$

For LC molecules parallel to \vec{B}_0 , $\theta_B = 0^\circ$ and $\delta\nu = \delta\nu_B = \delta\nu_0 Q$; if all molecules are perpendicular to \vec{B}_0 , $\delta\nu = \frac{1}{2} \delta\nu_B = \frac{1}{2} \delta\nu_0 Q$, since $\theta_B = 90^\circ$. The director structure induced by the surfaces is affected by \vec{B}_0 if the magnetic coherence length $\xi_M = \sqrt{\mu_0 K / B_0^2 \Delta\chi} \approx 1 \mu\text{m}$ 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 $\Delta\chi$ a measure of the anisotropy of the magnetic susceptibility [11].

The 0.003 and 0.005 dispersions (we drop g/cm^3 hereafter) are below the zero-field gelation threshold [9]. Their DNMR spectra at different temperatures are as for a pure LC: a single, centered, narrow absorption peak in the I phase, and a pair of peaks, the quadrupole splitting $\delta\nu$, in the N and SmA phases. Specifically, in the N or SmA phase of 0.003, Fig. 1(a), spectra are independent of sample orientation in the field. No gel forms and LC molecules are fully aligned by the NMR field. Near the N - I transition, an isotropic-like peak coexists with a weakly T -dependent splitting [12]. Cooling away from T_{NI} , the $\delta\nu$ T -dependence is bulk like with the usual enhancement of order in crossing to the SmA phase, Fig. 2. This effect is common to soft-gel samples (not seen in stiff gels) and is an empirical signature supporting the report of a prominent thermodynamic SmA- N transition [2,3]. The jump in order at T_{AN} (~ 5 kHz for bulk) quantifies the coupling between N and SmA order parameters [6]. It is 4.9 kHz for 0.003 decreasing to 4.2 kHz for the 0.094 sample. As in [2], dispersion's T_{NI} downshifts compared to bulk with a complex dependence on ρ_S , and, at the same $T < T_{NI}$, there is a small decrease in the magnitude of the splitting.

For 0.005, Fig. 1(b), there is no angular dependence in the N phase. Although no gel is expected and $l_0 > \xi_M$,

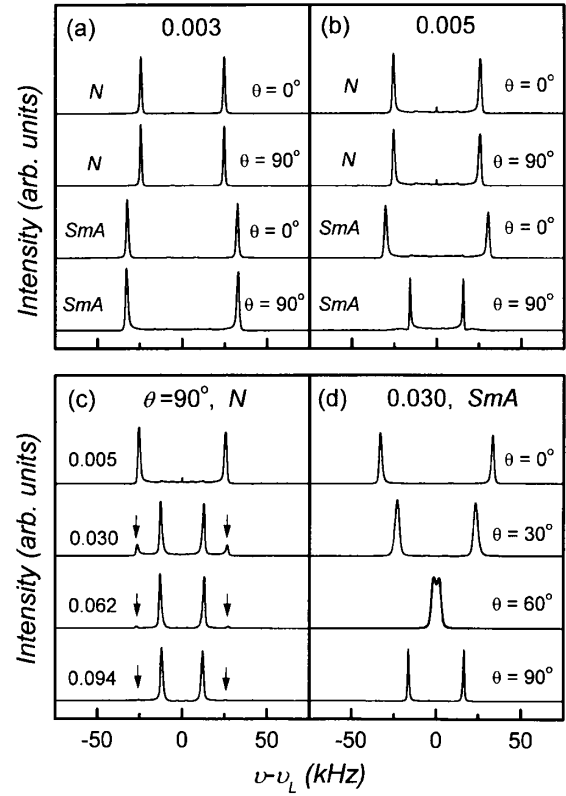


FIG. 1. (a) Spectra at 0° and 90° for 0.003. There is no angular dependence in N and SmA phases. (b) Spectra for 0.005. No angular dependence in the N phase, but there is one in the SmA phase: the splitting at 90° is $\frac{1}{2}$ of that at 0° . (c) 90° spectra for four samples showing the decrease in intensity of the outer singularities (arrows) with increasing density [13]. (d) Angular dependence typical P_2 behavior for 0.030 in the SmA phase.

there is angular dependence in the SmA phase: the splitting $\delta\nu$ at 0° orientation decreases to $\frac{1}{2} \delta\nu$ after a 90° rotation, bottom, Fig. 1(b). This dependence can be understood if (a) the viscosity of the dispersion increases and “locks-in” the director configuration; (b) the magnetic field enables an anisotropic diffusion field that removes elastic strains and aids the formation of a nearly complete network, fixing a remarkably uniform director configuration. (c) The field does not reorient smectic domains.

Further insight on the 0.005 dispersion can be obtained. Cooling from the I to the SmA phase ($T = 298$ K) outside the magnet and then placing it in the NMR field at the same temperature, Fig. 3(a), the spectrum is powder like indicating a random distribution of domains. The random pattern is fixed during the zero-field cooling process and is weakly affected by the field once in it: Shoulders expected at full splitting are replaced by two weakly intense peaks. This can be understood if the magnetic field breaks a few silica links freeing and fully reorienting some LC molecules. Alternatively, after zero-field cooling and due to a large viscosity in such dispersions, only molecules in domains larger than ξ_M are realigned.

Repeating the zero-field cooling study for 0.012 where $l_0 < \xi_M$, one finds an almost perfect powder pattern

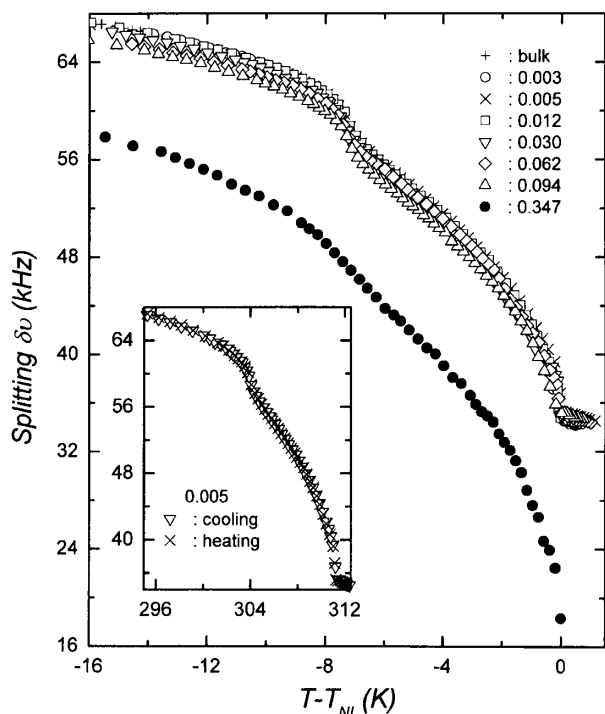


FIG. 2. Quadrupole splitting T dependence for bulk 8CB and aerosils; for 0.347, twice the inner splitting is plotted. Note the similarity in the $\delta\nu$ T -dependence of bulk and low density aerosils. The enhancement in orientational order at T_{AN} in bulk and low density samples is not seen in the 0.347 stiff gel. The jump in $\delta\nu$ at T_{NI} is smaller in 0.347 indicating that the NI transition is becoming continuous. Inset: Heating and cooling results for 0.005 showing no hysteresis.

[Fig. 3(b)]. Either no silica links are broken at any orientation or the viscosity is large and domains small that no reorientation occurs in the field. With increasing temperature, some LC molecules begin to reorient; at 302 K (still below T_{AN}) the pattern consists of four equally intense peaks. In such a temperature range, the dispersions' thermal conductivity changes slightly from its saturated value [3]. Thus, a combined mechanism of viscosity changes and links broken by the field may be responsible for the observations. Once in the N phase, the NMR patterns yield the same splitting earlier obtained in non-zero-field cooling.

The inset of Fig. 2 shows $\delta\nu$ vs T for 0.005 on cooling and heating: $\delta\nu$ overlap remarkably well in N and SmA phases (also for 0.003 not shown) except very near T_{NI} . No hysteresis is detected and the stable configuration retains the same amount of orientational order on heating or cooling. The absence of hysteresis raises the possibility of a field-aided gelation threshold density that depends on the LC phase and the strength of the field. Since no gel is formed in the N phase, the onset of SmA translational order plus the strong external field rearrange the silica strands to form an almost complete gel. Remnant elastic strains that are only annealed in near zero field once in the SmA phase [3] are fully annealed by the NMR field in the N phase.

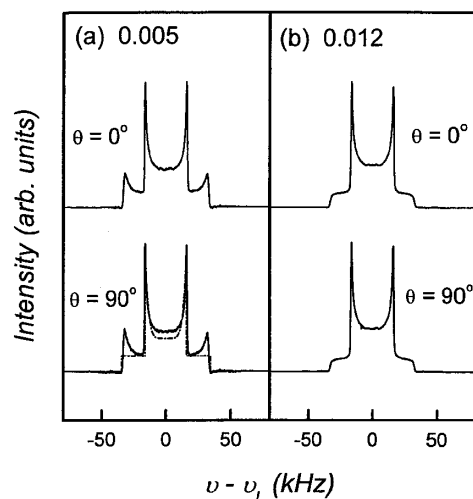


FIG. 3. SmA spectra for 0.005 and 0.012 are independent of sample orientation after zero-field cooling. (a) For 0.005, the powder pattern represents a random distribution of LC domains. Once in the field, the outer shoulders (dashed lines in the 90° spectra) turn into weak singularities. (b) In the 0.012 density, a powder pattern exists at all orientations in the SmA phase.

No elastic strains, the presence of a strong external field, and a large viscosity yield well-defined LC configurations.

DNMR spectra for soft-gel dispersions with silica densities of 0.030, 0.062, and 0.094, at 0° orientation, are like those of lower densities: a single I peak and a quadrupole splitting in the N phase. The $\delta\nu$ T -dependence of these dispersions, Fig. 2, is again bulk like. Rotating the sample by 90° , Fig. 1(c), reveals an angular dependence in N and SmA phases. In the N phase, the prominent $\delta\nu$ singularities at 0° (e.g., molecules parallel to the field), change at 90° into intense singularities at $\frac{1}{2}\delta\nu$ (molecules perpendicular to the field) and less intense ones at $\delta\nu$. At 90° , the intensity of the $\delta\nu$ singularities decreases with increasing density.

It thus appears that the molecular configuration established on cooling in the field is stabilized by silica strands likely growing along the field. Then, upon rotation, the NMR field breaks a few silica bonds and realigns a fraction of the molecules; fewer bonds break at higher silica density. The bonds breaking is quantified by calculating for the 90° spectra the fraction of molecules aligned along the field (area under full splitting peaks divided by area under all peaks) which decreases from 18% to 4% to 2% for the 0.030, 0.062, and 0.094 samples, respectively [13]. In the SmA phase of soft gels the silica stabilization of the LC configuration is substantial as there is the typical P_2 angular dependence predicted by Eq. (1), Fig. 1(d). An alternative scenario can be obtained by considering a high viscosity and a distribution in mean void size. Upon rotation, only molecules in voids larger than ξ_M are reoriented; with increasing density fewer voids satisfy such conditions.

For $\rho_S > 0.1$, a more rigid network with smaller void sizes forms, magnetic field ordering effects are weak, and silica-induced disordering effects dominate. This view is

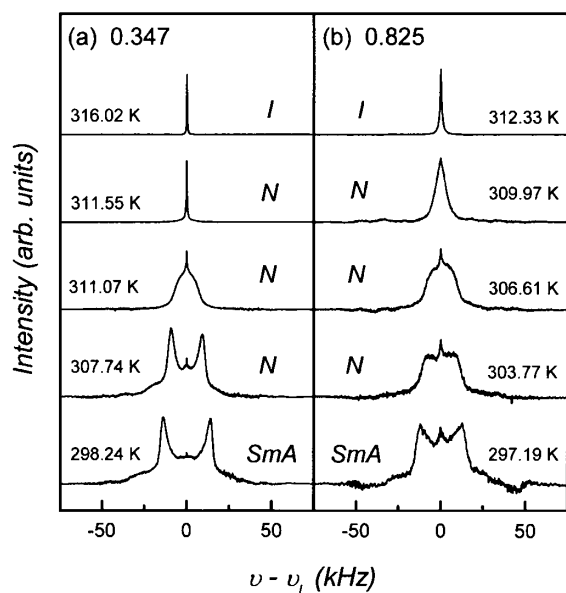


FIG. 4. T dependence of the spectra for (a) 0.347 and (b) 0.825. Note the powder pattern slowly appearing with decreasing temperature in (a), and the broadening of the peak indicating a continuous evolution of orientational order in (b). The different spectra of these two “stiff gels” are attributed to l_0 being larger (or smaller) than the nematic correlation length for 0.347 (or 0.825), respectively. LC phases are labeled by comparison to calorimetry results [2].

supported by the spectra in Fig. 4(a) for 0.347 evolving with decreasing temperature from an isotropic peak to a powder pattern. In this stiff-gel regime, there is no preferred orientation for the network growth; instead, there is a random distribution of nematic domains in the voids and no angular dependence. Cooling to the SmA phase of stiff gels further fixes the random distribution: limited-sized smectic layers form within the voids, and the powder-pattern shoulders are better defined, Fig. 4(a), bottom. Stiff gels are like rigid aerogel: disorder dominates, phase transitions are broad and suppressed [6,7], and there is no jump in order at T_{AN} , Fig. 2.

In the densest stiff gels, 0.698 and 0.825, the network has voids with $l_0 \leq 10$ nm, which are smaller than the thermal nematic correlation length at T_{NI} (~ 13 – 14 nm). Shown in Fig. 4(b) for 0.825, the spectra differ somewhat from the 0.347 ones, mostly consisting of a single and broad absorption peak. As in aerogel [6] or Vycor [14], in 0.825 (or 0.698) the full width at half maximum of the broad peak increases from 1 kHz (or 600 Hz) above T_{NI} to 30 kHz (or 20 kHz) at $T - T_{NI} = 13$ K. This is 2–3 times broader than in a 0.6 g/cm³, 12 nm voids aerogel. In the SmA phase, the peak evolves towards a powder pattern. In restrictive sizes, phase transitions are destroyed and there is only a continuous evolution of local orientational order [14].

In short, below the gelation threshold the orientational order is for the most part bulk like. No hysteresis is de-

tected suggesting that the NMR field completes the annealing of elastic strains introduced by the silica. Increasing density yields a network of silica strands that likely grow along the field and stabilize the LC alignment. Effects seen by reorienting the soft gels in the field can be understood by the field ability to break a few silica links together with a large viscosity and a distribution in void size. Soft gels are characterized by sharp transitions. In stiff gels, silica introduced random disorder increases and field-ordering effects weaken; with increasing density, random disorder dominates and a rigid and isotropic network of voids containing LC phases forms; phase transitions are broad. At the highest densities, the mean void size is highly restrictive and stiff gels are like rigid aerogel.

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- [1] *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks*, edited by G.P. Crawford and S. Zumer (Taylor & Francis, London, 1996).
 - [2] G.S. Iannacchione *et al.*, Phys. Rev. E **58**, 5966 (1998).
 - [3] F. Mercuri *et al.*, Phys. Rev. E **60**, R6309 (1999).
 - [4] T. Bellini *et al.*, Phys. Rev. E **57**, 2996 (1998); T. Bellini *et al.*, Phys. Rev. Lett. **85**, 1008 (2000).
 - [5] H. Zeng and D. Finotello, Phys. Rev. Lett. **81**, 2703 (1998); S. Qian *et al.*, Phys. Rev. E **53**, R4291 (1996).
 - [6] H. Zeng *et al.*, Phys. Rev. E **60**, 5607 (1999).
 - [7] T. Bellini *et al.*, Phys. Rev. Lett. **69**, 788 (1992); L. Wu *et al.*, Phys. Rev. E **51**, 2157 (1995).
 - [8] L. Radzihovsky and J. Toner, Phys. Rev. B **60**, 206 (1999); Phys. Rev. Lett. **79**, 4214 (1997); **78**, 4414 (1997).
 - [9] H. Sonntag and K. Streng, *Coagulation and Structure Formation* (Plenum, New York, 1987), pp. 134–145 and 172–177.
 - [10] H. Haga and C. W. Garland, Phys. Rev. E **56**, 3044 (1997).
 - [11] See M. Vilfan and N. Vrbancic-Kopac, *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks* (Ref. [1], Chap. 7).
 - [12] Apparently unique to aerosil, near T_{NI} , there is a coexistence of a nematiclike splitting and a isotropiclike peak; in this region $\delta\nu$ is weakly T dependent. Once the isotropic peak vanishes, $\delta\nu$ rapidly increases with decreasing temperature. The width of the plateau appears to depend on the strength of the NMR field, decreasing with increasing field. The plateau may be a NMR signature signaling the annealing of elastic strain, possibly related to the specific heat double peak seen in [2].
 - [13] This result at a single temperature in the N phase suggests a scaling with the square of the silica density; angular studies at other temperatures are needed.
 - [14] G.S. Iannacchione *et al.*, Phys. Rev. Lett. **71**, 2595 (1993).