

Changing the Surface-Liquid Crystal Interaction through the Adsorption of Silica Nanoparticles

Daniele Finotello and Tao Jin

Department of Physics, Kent State University, Kent, OH 44242, USA, dfinotel@kent.edu

Abstract

We studied a low density 8CB liquid crystal-hydrophobic aerosil dispersions imbedded in submicron-size cylindrical pores. The nanosize spherical aerosil particles are adsorbed at the pore wall and hinder the planar anchoring. The adsorption is temperature dependent, and an axial to radial molecular configuration transition occurs within the cylindrical pores.

1. Introduction

A technologically important feature of liquid crystal (LC) materials is that they can be oriented and ordered by an interface. The induced order is retained over macroscopic scales. In addition, at a fundamental level, and depending on the interaction with a surface, liquid crystals exhibit different structural configurations when the interface are solid walls that completely surround the LC, or when small particles are dispersed in the LC, or when the LC is confined to a polymer network.¹

Using deuteron nuclear magnetic resonance (DNMR) to study the orientational order of elongated LC molecules in porous media has contributed substantially to our understanding of the surface-liquid crystal interaction and the determination of director fields and molecular configurations.

For the cyanobiphenyl liquid crystal 8CB confined to, and completely filling the submicron size cylindrical pores of Anopore membranes, the director configuration is uniform axial, namely, the LC molecules are oriented by the surface parallel to the cylindrical pore axis.²⁻⁴ The surface induced configuration is stable and retained independent of the sample thermal history.

When low density hydrophobic aerosil – liquid crystal dispersions are formed, the spherical particles form agglomerates, effectively behaving like impurities. However, they also introduce strains which are not completely annealed at the transition from the isotropic phase. The small amount of aerosil induced disorder, however, does not prevent the sample from being oriented by an external field, but some hysteresis is present in the presence of weak fields that are unable to anneal the stresses. The hysteresis is not present in strong fields⁴.

2. Experimental Technique

The deuteron nuclear magnetic resonance technique (DNMR) is a powerful tool to determine the liquid crystal configuration in confined systems. DNMR is sensitive to the local degree of orientational order, $S(r)$, and the molecular ordering direction (or director field), $n(r)$, through the quadrupole frequency splitting $\delta\nu(r) = \delta\nu_0 S(r)[3\cos^2\theta(r) - 1]/2$, where $\delta\nu_0$ is the quadrupole splitting of a perfectly orientationally ordered phase (saturating typically at $\delta\nu_0 \sim 90$ kHz for nCB's) and $\theta(r)$ is the angle between the local director and the magnetic field B .⁶

In DNMR, a uniform axial alignment is indicated by spectral patterns exhibiting a quadrupole frequency splitting (frequency separation between absorption peaks) nearly equal to that of a perfectly aligned bulk sample. In the case of a homeotropic alignment, the quadrupole splitting is reduced to only one-half that of a fully aligned bulk sample. Sample rotation in the magnetic field allows orienting the cylindrical pore axis from parallel to perpendicular to the external B . Since the magnetic coherence length is larger than the Anopore membrane' pore diameter, there is no influence of the DNMR field on the local director and the director field (LC configuration) that is determined in the pores is surface-induced.

3. Materials

Hydrophobic aerosil type R812 spherical nanoparticles⁴ have a 7nm diameter and a specific surface area $a = 260 \pm 30$ m²/g. LC-aerosil dispersions were prepared by dosing aerosil powder in a diluted solution of 8CB and chemically pure acetone. The dispersions were kept in a heated ultrasonic bath for 12 hours to ensure proper mixing and complete solvent evaporation. The aerosil silica density prepared was $\rho_s = 0.01$ g/cm³ (we drop the units hereafter). The dispersions were again heated to temperatures well above the corresponding LC clearing points.

Alumina Anopore membranes, with cylindrical pore radius $R \approx 100$ nm, were cut into 4x25mm strips and dipped in the dispersions for 24 hours. The prepared hydrophobic aerosil dispersions correspond to densities below the gel threshold: no network forms, they exhibit fluidity above the clearing point, and thus can easily enter the robust pores. Since unconfined hydrophobic dispersions show some level of sedimentation after a few days, samples were measured immediately after preparation.

Deuterated 8CB liquid crystal has a bulk isotropic to nematic (I-N) transition temperature at 40.5°C and a lower temperature nematic to smectic-A (N-A) transition at 33.5°C.

4. Results

When the LC-aerosil dispersions are imbedded in the pores, liquid crystal molecules effectively "see" two surfaces: the "flat" ordering pore wall promoting a planar or axial ordering aligning direction, and the aerosil spherical particles surfaces introducing local elastic distortions disordering the liquid crystal director. Consequently, in Anopore confined dispersions, the overall director configuration will result from the competition between the Anopore pore surface ordering field wall and the random field due to the spherical nanoparticles.

In the nematic or in the smectic-A phase of pure 8CB confined to Anopore membranes, the director configuration is induced by the molecular anchoring at the pore wall. This results in a

parallel axial (PA) structure. A PA structure is manifest in a DNMR spectrum as two adsorption peaks (frequency doublet) with a full-splitting when the cylindrical pore axis is parallel to the external magnetic field B ($\theta=0^\circ$). This is evident from Figure 1a showing the evolution with decreasing temperature from the isotropic phase (a single, centered and narrow peak), to a nearly identical to a bulk-aligned 8CB sample frequency splitting.

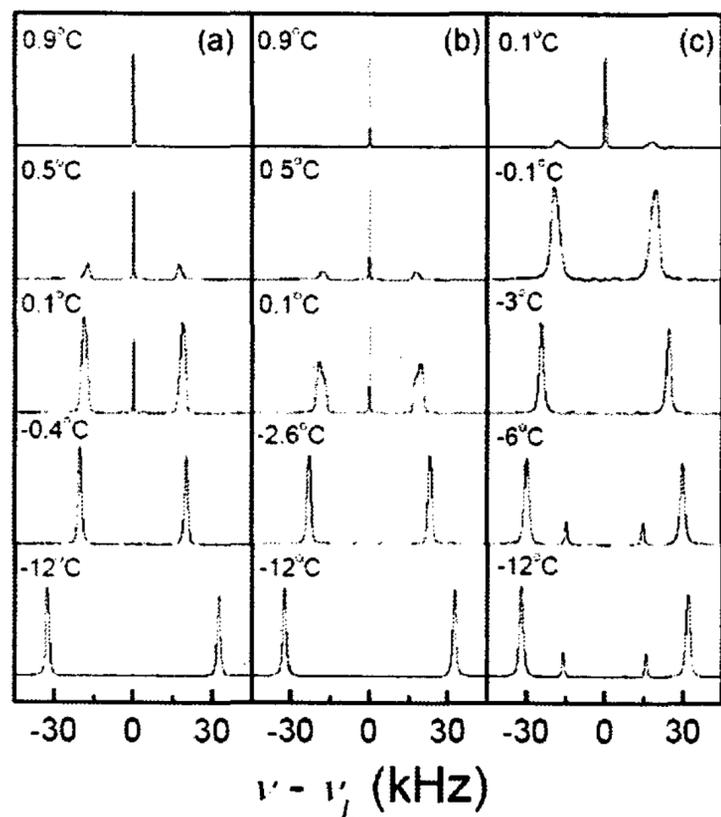


Figure 1. Temperature dependence of the DNMR spectral patterns for pure 8CB in Anopore (a), for the unconfined 0.01 hydrophobic 8CB dispersion (b), and, for the Anopore confined 0.01 8CB dispersion (c). Temperatures are quoted as compared to the respective nematic to isotropic transition temperature.

The spectra for the unconfined hydrophobic dispersion are shown in Figure 1(b). As expected, these spectra are consistent with those for a sample that is aligned by the DNMR field, except that the largest measured frequency splitting is slightly reduced from that of the bulk-aligned sample at the same temperature. At this low aerosil density, the aerosil effectively behaves like if a small dose of impurities are present in a bulk sample.

If the hydrophobic dispersion is now confined to the small Anopore pores, the measured spectral patterns exhibit more complex characteristics. As the temperature is decreased, in addition to a frequency splitting comparable in magnitude with that of the unconfined dispersion, a less intense inner splitting begins to emerge.

With decreasing temperature, the spectrum for the confined dispersion, Figure 1(c), is a mixture of a full-splitting and a half-splitting doublets, unlike for Anopore confined pure 8CB or for

the unconfined dispersion where only a full-splitting is present. A half-splitting doublet indicates that some LC molecules have become radially aligned, namely, perpendicular to the field (equivalently, perpendicular to the pore axes). The intensity of the inner frequency splitting increases with decreasing temperature.

Since the area under the DNMR absorption peaks is proportional to the number of liquid crystal molecules that exhibit a specific orientation, the axial (outer frequency splitting) to radial (inner frequency splitting), occurs gradually. Comparing the areas under the inner to outer splitting, the number of radially aligned molecules increases from 1% at 37.5°C (-3°C in Figure 1(c)) to 13% at 28.0°C (-12°C in Figure 1(c)).

The results can be understood in terms of an "adsorption-induced" anchoring transition: the aerosil spherical particles effectively modify the liquid crystal surface anchoring properties through their adsorption to the pore wall. Hydrophobic silica aerosil individual particles or aggregates adsorb to the cavity wall; since the spheres have CH_3 groups covering their surface, typical of methyl groups, a homeotropic anchoring that is typical of a CH_3 surface is promoted. This scenario is supported by a more complete study that includes higher silica aerosil densities and other members of the nCB liquid crystal family⁷.

5. Conclusions

With this work, we have shown that silica aerosil nanoparticles adsorb to the alumina Anopore pore walls and promote a temperature dependent anchoring transition where the confined liquid crystal configuration changes from planar to radial.

6. Acknowledgements

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7. References

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