Eur. Phys. J. B **10**, 509–513 (1999)

THE EUROPEAN PHYSICAL JOURNAL B
EDP Sciences

Memory of silica aggregates dispersed in smectic liquid crystals: Effect of the interface properties

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Received 31 July 1998 and Received in final form 17 December 1998

Abstract. Previous studies on nematic liquid crystals containing silica particles indicated memory effects that might be due to hydrogen bonds between the individual silica particles. We made smectic liquid crystal dispersions containing silica particles with various surface properties. Using a neutron scattering technique we studied the interfacial surface effects on the structure of the silica aggregates, and on the smectic layer alignment. Our observations indicate that the stability of the memory correlates to the number of OH groups on the silica surfaces. The observations imply that, with fine-tuning of the OH content of the silica surfaces, various types of memory devices can be designed. We considered three different effects that can memorise the alignment of the liquid crystal. Measurements on tilted SmC phases indicate that surface effects become important only after repeated heating-cooling cycles, as the average size of the aggregates decrease.

PACS. 61.30.-v Liquid crystals – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 61.12.Ha Neutron reflectometry

1 Introduction

During the last few years liquid crystal-composite systems have attracted significant interest, since they maybe useful for high information content flat panel displays [1,2]. In the majority of the composites liquid crystals are mixed with polymers. Liquid crystal composites containing silica particles are also promising for electro-optical applications. It was found that, in certain conditions, the electric field induced orientation remains stable after field removal [3]. This memory might be due to hydrogen bonds between the individual silica particles leading to stable clusters. The effect of the hydrogen bonds on the memory was studied further by Gluschenko *et al.* [4]. They observed the strongest memory when hydrophilic silica particles (the surface of the aerosil particles contain OH groups) were dispersed in liquid crystals containing cyano groups, which could also form hydrogen bonds. The role of the hydrogen bonds between the liquid crystal and the silica aggregates was assumed to enhance the anchoring energy.

Recently we observed that the structure of a smectic liquid crystal could also be memorised by hydrophobic silica dispersions. Cooling the material slowly ($\sim 1\,^{\circ}$C/min) in the presence of a magnetic field of $H = 1$ T from the isotropic to the smectic phase, the layer structure became aligned. Re-heating the material to the isotropic liquid phase, and then cooling back to the nematic and smectic A phases without magnetic field, the previous alignment of the liquid crystal recovered. The recovery ratio was found to be nearly proportional to the concentration. Small-angle-neutron-scattering measurements indicated that the silica particles form loosely connected porous aggregates that remain quite stable even at elevated temperatures [5]. Studies by triple axis spectrometer enabled us to measure the distribution of the smectic layer spacing, and the layer alignment simultaneously [6]. As the aerosil-liquid crystal interfaces increase, both the layer spacing and layer orientation become inhomogeneous.

All these studies indicate the importance of the interfacial surface effects. For this reason, we varied the surface properties of the dispersed particles and studied their effect on the structure of the silica aggregates, and on the smectic layer alignment.

2 Experimental results

We carried out small-angle-neutron-scattering measurements in Saclay (PAXE, Lab. Léon Brillouin) on different silica particles from Degussa AG. The properties of the silica particles are summarised in Table 1.

The OH contents were varied by a special silanization technique which substitutes the initial hydrophilic Si–OH groups on their surfaces by hydrophobic Si–O–CH_3 groups. Particles with small OH contents are hydrophobic, whereas those with large OH content (> 1 group/nm^2) are hydrophilic.

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Table 1.

name	Diameter (nm)	OH content (group/nm^2)
R 976[a]	7	0.5
R 812[b]	7	0.3
R 974	12	0.3
A 380	7	5
R 976/A380[c]	7	2.7

[a] It was studied previously by us in different concentrations [6], and it was found to be very useful in filled nematics [3], too.

[b] This silica was studied by Gluschenko *et al.* [4] and by Bellini *et al.* [7].

[c] 1% R 976 and 1% Aerosil 380 was dispersed together in the liquid crystal.

The silica particles were dispersed in 4-octyl-4'-cyanobiphenyl (8CB) with 2wt% concentrations. The phase sequence of 8CB is the following: Cr < 21 °C SmA 33 °C N 40.5 °C I. By adding the silica particles the phase transition temperatures did not change considerably (less than a few tenths of a degree). It indicates that the silica particles act as macroscopic entities and not as solvent.

For the Small Angle Neutron Scattering (SANS) studies 1.4 mm thick cells were used. First all the samples were heated up to 50 °C, then cooled slowly to room temperature (~ 0.5 °C/min) in a magnetic field of 0.85 T.

The Bragg reflection of the smectic layers (scattering at $q \sim 0.4$ Å^{-1} range) clearly indicated that all samples became aligned with the director parallel to the magnetic field. The scattering pattern of the 64 × 64-detector array is shown in Figure 1 for the dispersion with R 976. The line connecting the two major peaks is parallel to the magnetic field in which the sample has been cooled. Two other smaller peaks are also clearly visible by about 10 degrees away from the major ones. They are due to the remainder of a previous alignment, which was partially erased by keeping the sample at 50 °C for a few hours. The intensities of the Bragg peaks characterise the quality of the alignment. In Figure 2 we plotted the maximum intensities of the first Bragg peaks as measured at 27 °C after various temperature and mechanical treatments. It can be seen that the initial alignment is typically better for hydrophobic particles than for hydrophilic or mixed silicas. After heating to the nematic phase the alignments remained practically unchanged. After heating to 50 °C for 15 minutes the alignment almost disappeared for R 812 and decreased considerably also for R 974. However, the initial alignment still recovered for the other three materials (R 976, and the samples containing hydrophilic silica). After 1 hour of mechanical shaking in an ultrasound beaker at 50 °C the alignment practically disappeared for the 7 nm hydrophobic particles. The hydrophilic aerosils, however, still kept the alignment. We note, that in these materials the memory has not completely disappeared even after one day of ultrasound treatment (decreased to about 10%). Cooling the material in a magnetic field again, but in another direction, the new alignment coexisted together with the previous one.

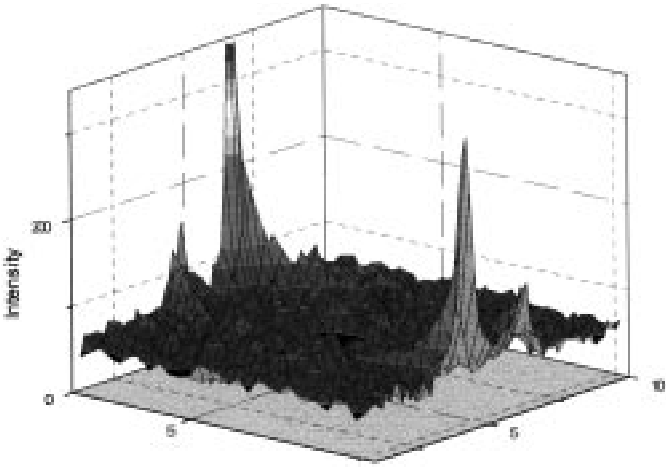

Fig. 1. Scattering pattern of the 64 × 64-detector array at large q range (0.4 Å^{-1}), due to the first Bragg reflection of the smectic layers. (8CB +2% R 976, T = 23 °C). The line connecting the two major peaks is parallel to the magnetic field (H = 0.85 T) in which the sample has been cooled. Two other smaller peaks are also clearly visible about 10 degrees away from the major ones. They are due to the remaining presence of a previous alignment, which was partially erased by keeping the sample at 50 °C for a few hours.

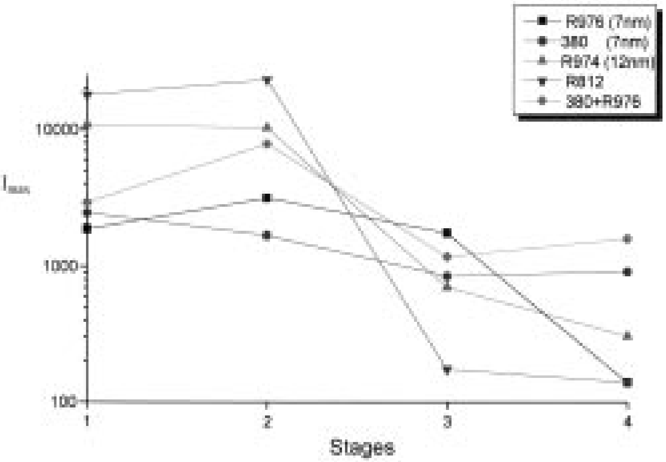

Fig. 2. Maximum intensities of the first Bragg peaks as measured at 27 °C after various temperature and mechanical treatments; (1) freshly aligned sample, (2) after heated to 38 °C for 20 minutes, (3) after heated to 50 °C for 15 minutes, (4) after 1 hour shaking in an ultrasound bath at 50 °C.

Measurements at small momentum transfer (0.007 Å^{-1} $< q <$ 0.1 Å^{-1}) showed the scattering from the silica aggregates. Within the experimental error ($\sim$ 3%) the scattering profiles are isotropic, although the previous observations clearly indicated that the silica aggregates are responsible for the memory effects. The scattering shows a power law behaviour ($I(q) \propto q^{-\alpha}$).

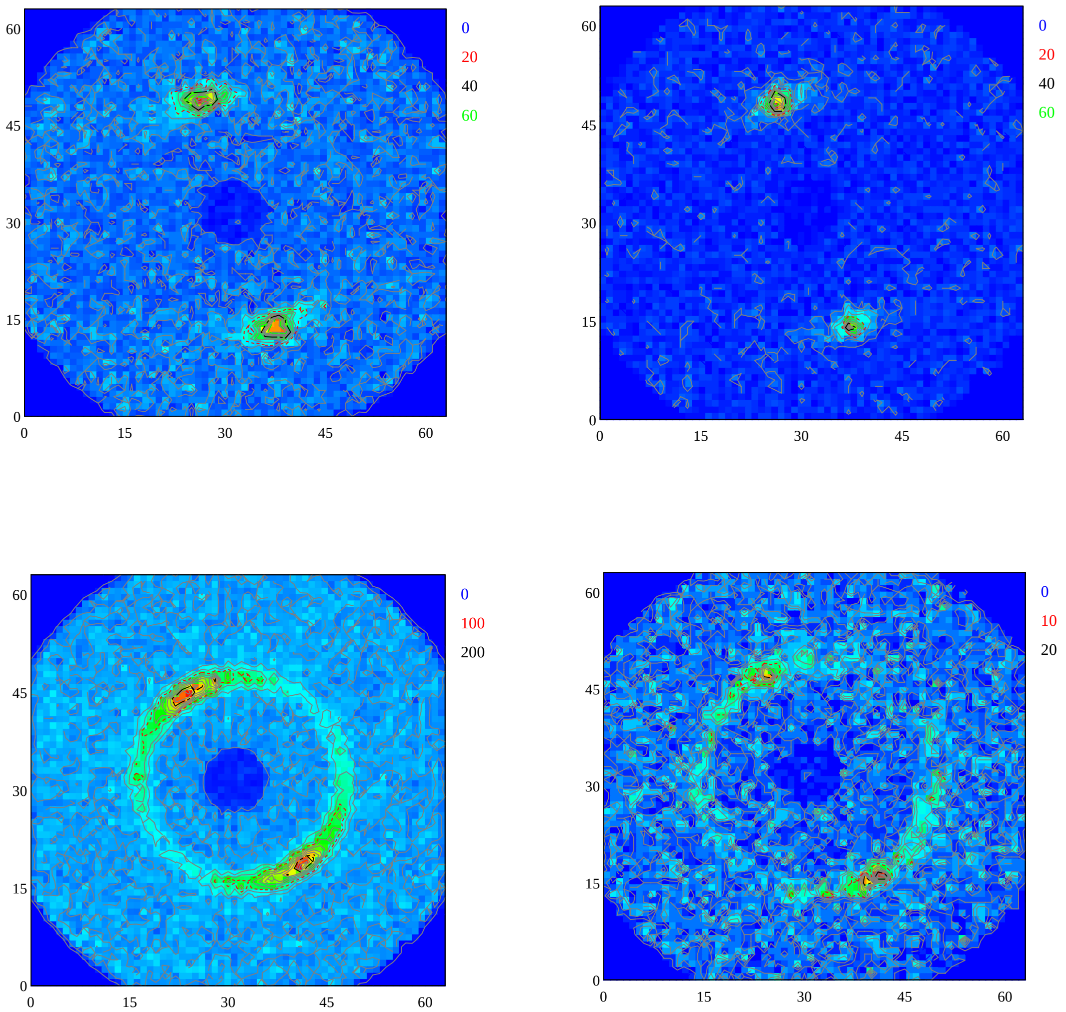

Fig. 3. Scattering pattern of the 64 × 64-detector array at large q range (0.4 Å^{-1}), due to the first Bragg reflection of the smectic layers (DOBHOP +2wt% of R 976). (a) SmA phase ($T = 80\,^\circ$C) after the material cooled from the isotropic phase in magnetic field of 1.2 T through the N-SmA phase transition; (b) $T = 72\,^\circ$C (SmC) after cooled without a magnetic field from the SmA phase; (c) $T = 80\,^\circ$C (SmA) after cooled from $T = 90\,^\circ$C (isotropic phase) without a magnetic field; (d) the same as (c) at $T = 72\,^\circ$C (SmC).

The exponent depends on the previous temperature and mechanical treatments. In the studied aligned samples $\alpha \sim 2.2{-}2.4$. These values agree well with the fractal dimension obtained by Bellini *et al.* [7] using a light scattering technique on 6CB-R 812 composites. After heat and mechanical treatments α did not change significantly, except for the sample that contains both hydrophobic and hydrophilic particles. There α almost reaches 3 after being heated to the isotropic phase, then drops to 2 after mechanical shaking. This indicates a considerable structural change of the aggregates; meanwhile the smectic layer structure remained stable.

The exact size distribution of the aggregates cannot be deduced from the measurements. It is very likely that the distribution is polydisperse (the largest aggregates can reach micrometer sizes, whereas the smallest is only a few tens of nanometer). The lower limit can be estimated assuming that the Porod-regime starts at $qR_{\mathrm{G}} \sim 5$. This gives that the minimum size is about 200 Å.

3 Discussion

Our observations show that there is memory for both hydrophilic and hydrophobic particles. The stability of the memory correlates to the number of OH groups on the silica surfaces. Even for hydrophobic surfaces with moderate OH concentration ($\sim$ 0.5 groups/nm^2) the memory is quite resistant against heat treatment, but disappears after mechanical shaking in an ultrasound bath. For hydrophilic particles the smectic layer alignment remains stable even after mechanical shaking. These observations suggest that various types of memory devices could be designed with fine-tuning of the OH content of the silica surfaces. It could be important that bulk samples can be aligned (remain optically transparent in the SmA phase) after cooling them in magnetic field. This may enable the construction of optically readable high information content memory devices.

The studies clearly show that the silica clusters are responsible for the observed effects. The necessary (but not satisfactory) condition to memorise the liquid crystal alignment is the stability of the silica aggregates that was observed already in nematics [3,4]. An interesting question is, how the silica dispersions impose the layer alignment.

One possibility is that the shape of the aggregates becomes anisotropic when the liquid crystal is aligned (*e.g.* when cooled in magnetic field). According to previous models [3,4] these aggregates exert anisotropic forces on the liquid crystal. The scattering profile at small momentum transfer indicates, however, that the anisotropy, if there is any, is less than 3%.

Another possibility for the dispersion-induced alignment is the so-called surface memory effect (SME), which is well-known in liquid crystal films [8]. To estimate whether it can have relevance, first we calculate the surface-volume ratio, λ. In the case of films with smooth surfaces $\lambda = d^{-1}$ (d is the film thickness). SMEs are observed in films, where $d \sim 10\,\mu\mathrm{m}$ and $\lambda \sim 10^5\,\mathrm{m}^{-1}$. In our experiments the silica particles form aggregates. Assuming k particles in each aggregate, the surface-volume ratio reads as $\lambda_k = 3ck^{-1/3}/r$, where c is the weight concentration of the dispersed particles of radius r. Taking $c = 2\%$, $r = 3.5$ nm and $k \sim 10^3$ we get $\lambda_k \sim 10^6\,\mathrm{m}^{-1}$. This is even larger than in films where surface memory has already been observed. The physical mechanism of SME is basically the following [9]. Initially the liquid crystal molecules at the interfaces are randomly distributed in local potential wells for rotation. Through molecule-molecule interactions the bulk liquid crystal molecules, aligned *e.g.* by external magnetic field, exert an effective torque on the surface liquid crystal molecules and reorient them along the bulk alignment. The alignment (and its relaxation when the bulk is isotropic) takes place *via* rotation diffusion of the surface liquid crystal molecules. The relaxation time of SME is typically in the range of hours [8], similar to our observations. Regarding the influence of surface composition on SME Clark [10] has found that hydrophilic surfaces exhibit no, or only very weak SME, while hydrophobic surfaces exhibit strong SME. In contrast to this, we observed memory effect even for hydrophilic materials. In dispersions SME is more complicated: the surfaces are not constant, but may disorient on heating or by mechanical shaking. As the hydrophilic particles form less stable clusters, the difference in SME of hydrophilic and hydrophobic particles becomes less pronounced. In spite of this we think that SME alone is not sufficient to explain the observed memory effects (especially for hydrophilic particles). Accordingly we have to suppose that the aggregates are slightly anisotropic and they have a role in the observed memory. While SME is purely surface mediated, the anisotropic aggregates interact with the liquid crystal *via* both surface and volume effects. The volume effect aligns the smectic layers by minimising the dislocations so that the layers become parallel to the longest axis of the aggregates, whereas the surface interacts with the director. The surface anchoring energy for nematic dispersions was estimated [11] as 10^{-4} J/m^2. It is very complicated, however, to express the anchoring energy due to SME, or due to the volume effect of the anisotropic surface. In order to compare the different effects we carried out further SANS experiments in the Budapest Neutron Centre. We examined what is happening with the layer alignment in a tilted smectic C phase. If the volume effect were dominating (*i.e.* the layers were aligned), no change in the Bragg-peaks should be observed during a SmA-SmC phase transition. Provided that the surface effects are much stronger the director remains constant in the SmC phase and the layers should tilt by $\pm\theta$ (θ is the director tilt angle). Accordingly, a splitting by 2θ is expected in the Bragg peak. To test this idea we dispersed 2wt% of R 976 in p-decyloxybenzoic acid-p'-(hexyloxy)-phenylester (DOBHOP). The phase sequence of DOBHOP is the following: Cr 60 °C (44 °C SmB) SmC 76 °C SmA 82 °C N 87 °C I. Our observations are represented in Figure 3. When the material is first cooled from the isotropic phase in a magnetic field of 1.2 T through the N-SmA phase transition the SmA layer alignment (Fig. 3a) remains practically unchanged (only a small widening is seen) in the SmC phase (Fig. 3b). This indicates that the surface interactions are relatively week, and the layers are aligned *via* the volume effect of the slightly elongated aggregates. This structure minimises the layer distortion energy, and hence keeps the layer alignment in SmC. After heating the sample to the isotropic phase and cooling back again, the layers became aligned in the SmA phase with a slightly decreased order (Fig. 3c). On further cooling to the SmC phase the preferred layer orientation stayed, but the profile widened considerably (Fig. 3d). This indicates that the surface effects became more pronounced. The reason for it could be that subsequent heating-cooling cycles lead to a decrease of the average size of the aggregates. Accordingly, the surface-volume ratio increases and the surface effects become more important.

As a conclusion we studied the interfacial surface effects on the structure of the silica aggregates, and on the smectic layer alignment. Our observations indicate that the stability of the memory correlates to the number of OH groups on the silica surfaces. We considered three different effects that can memorise the alignment of the liquid crystal. One is the surface memory effect (SME) which is expected to be relevant for hydrophilic surfaces. The second and third effects are due to surface and volume interactions between the liquid crystal and anisotropic aggregates. Measurements on tilted SmC phases indicate that the first two surface effects become more important after repeated heating-cooling cycles, as the average size of the aggregates decrease.

This work was supported partly by the grant PECO (CIPO CT-94-0080), the INCO COPERNICUS IC 15-CT 96-0744 and by the Hungarian National Science Fund (OTKA 016 943).

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