

Supporting Information

Koenig et al. 10.1073/pnas.09109311107

SI Text

Previous Study of Microparticles at Liquid Crystal–Water Interfaces.

We comment that our current study differs in concept and experimental methodology relative to our previous publication (1). In brief, the key concept that is revealed in our current paper is that it is possible to manipulate (reversibly) the topological defects formed about particles at liquid crystal–aqueous interfaces so as to drive (reversibly) ordering transitions in assemblies formed by the microparticles at these interfaces. Furthermore, the changes in symmetry of the assemblies are related to the changes in symmetry of the topological defects in the liquid crystal. In contrast, in our previous paper, changes in the ordering of the liquid crystal did not lead to ordering transitions in the particle assemblies—indeed, the particles in our previous publication were irreversibly aggregated. Furthermore, heating of the liquid crystal through the nematic-to-isotropic transition did not disperse the aggregates of particles in our previous study—that is, the aggregates observed in our previous study were not held together by liquid crystal-mediated forces. The above-described advance that is detailed in our current paper was made possible by changing important elements of the experimental design: (i) We used a different methodology to deliver microparticles to the interface of the liquid crystal; (ii) we used different methods to control the surface properties of the particles—in the current study, the particles have surfaces that are modified by monolayers of organic molecules that are covalently attached to the particles. In contrast, in our previous study, the particles were covered by monolayers that were physically adsorbed. We suspect the monolayers desorbed in our previous experiments to cause the above-noted irreversible aggregates; (iii) we used smaller particles in the current study in order to weaken the interparticle interactions and thus promote reversible interactions mediated by the liquid crystal (LC).

Observations Supporting the Presence of the Microparticles at the 4-pentyl-4'-cyanobiphenyl (5CB)–Aqueous Interface. Several observations support our conclusion that the microparticles used in this study did not sediment through the 5CB–aqueous interface but, rather, were located at the interface. First, we observed the 5CB–aqueous interface and the microparticles to be located at a common focal plane when using a high-magnification (50×) objective. Second, careful inspection of colors generated by the interference of white light transmitted through the 5CB (Fig. 1*B*, *D*, and *F*) reveals that the 5CB–aqueous interface was curved near each of the microparticles. These conclusions regarding the interfacial location of the microparticles are also consistent with an order-of-magnitude calculation of the energy of adsorption of micrometer-sized particles at the 5CB–aqueous interface. The energy E to remove a microparticle from a liquid–liquid interface is given by $E = \pi a^2 \lambda (1 + \cos(\alpha))^2$, where a is the microparticle radius ($\sim 10^{-6}$ m), λ is the surface tension (~ 0.03 N/m), and α is the contact angle ($\sim 40^\circ$, measured). For our microparticles at the 5CB–aqueous interface, this energy is $\sim 10^7 k_B T$, which means the microparticles leaving the 5CB–aqueous interface would be energetically very costly.

Classification of Defects as Boojums. The term “boojum” is used in various branches of condensed matter physics to refer to a point defect that forms near a surface or interface. An account of the origins of the term boojum can be found in ref. 2. The defect shown in Fig. 2*C* (and illustrated schematically in Fig. 2*D* and *E*) is close to the interface formed between the LC and water,

and thus the defect can be viewed as an example of a boojum formed near a planar interface.

Irreversible Microparticle Aggregates at the 5CB–Aqueous Interface.

We note that not only do the irreversible aggregates influence the ability of individual microparticles to form more well-ordered assemblies of microparticles, but the aggregates remain unchanged during the reversible adsorption and desorption of SDS to the 5CB–aqueous interface. However, during SDS adsorption and desorption, additional aggregates are not formed: Aggregates are formed only during the initial sedimentation process. More irreversible aggregates were formed when the 5CB was heated above the nematic-to-isotropic transition (Fig. S3*C* and *D*) and subsequently cooled back into the nematic phase (Fig. S3*E* and *F*). The aggregate formation was likely because of the nematic-isotropic front at the interface driving the microparticles into irreversible aggregates, similar to solid particles driven into aggregates by nematic-isotropic fronts in thin films of LC as reported in ref. 3.

Experimental Details of the Reversible Assembly of Microparticles at the 5CB–Aqueous Interface.

We comment on the time scale of the reversible ordering of the assemblies of microparticles reported above. Adding concentrated SDS to an SDS-free aqueous phase to achieve a final concentration of 1,300 μ M will result in the interface transitioning from planar to perpendicular, typically over ~ 3.5 min. However, in the micrographs shown in Fig. 3 and Fig. S1, concentrated SDS was added to the aqueous phase over 10 separate sequential intervals. Each SDS addition took 15 min, and assemblies of microparticles were observed to be stable after < 10 min. In addition, when SDS was removed from the 5CB–aqueous interface, the aqueous phase was diluted with SDS-free solution over 10 separate stages with 15 min for each dilution stage. Both the procedures for increasing and decreasing the concentration of SDS in the aqueous phase were done to ensure that images taken were of microparticle assemblies that were in equilibrium and not of transient structures that might result as the SDS reaches the appropriate concentration at the 5CB–aqueous interface. We also note that the chains formed in Fig. S1*C* and *D* and Fig. S1*G* and *H* are not exactly the same in length or direction, indicating that the system does not retain memory of its previous states. This lack of memory in the system was also present for the location of the void regions for the images seen in Fig. S1*A* and *B* compared to Fig. S1*E* and *F* and Fig. S1*I* and *J*.

Patterning Underlying Substrates to Control 5CB Azimuthal Ordering and Direction of Chaining at the 5CB–Aqueous Interface.

To control the azimuthal orientation of the 5CB, we supported the 5CB on a chemically patterned surface formed by patterning self-assembled monolayers (SAMs) on obliquely deposited films of gold. We used 20-nm-thick films of gold obliquely deposited onto glass microscope slides at an angle of 45° (measured from the normal). Past studies (4) have shown that gold films deposited under these conditions, when functionalized with either SAMs of hexadecanethiol (C16) or pentadecanethiol (C15), will orient 5CB parallel or perpendicular to the direction of gold deposition, respectively. We patterned the azimuthal orientation of the 5CB at the gold substrate by microcontact printing the alkanethiol monolayers with polydimethylsiloxane stamps.

Fig. S6*A* is a polarized light micrograph of chains of microparticles observed at the 5CB–aqueous interface when the LC was supported on a surface patterned as described above. Fig. S6*B* is a

cartoon of the azimuthal ordering provided by the underlying regions of C15 (lower right region) and C16 (top left region). Inspection of Fig. S64 reveals that the microparticle chains as-

sumed orientations that were consistent with the patterned orientation of the 5CB. For Fig. 6 in the main text, only a C15 SAM was used.

1. Lin IH, Koenig GM, de Pablo JJ, Abbott NL (2008) Ordering of solid microparticles at liquid crystal-water interfaces. *J Phys Chem B* 112:16552–16558.
2. Mermin ND (1981) E Pluribus Boojum: The physicist as neologist. *Phys Today* 34:46–53.

3. Meeker SP, Poon WCK, Crain J, Terentjev EM (2000) Colloid-liquid-crystal composites: An unusual soft solid. *Phys Rev E* 61:R6083.
4. Gupta VK, Abbott NL (1997) Design of surfaces for patterned alignment of liquid crystals on planar and curved substrates. *Science* 276:1533–1536.

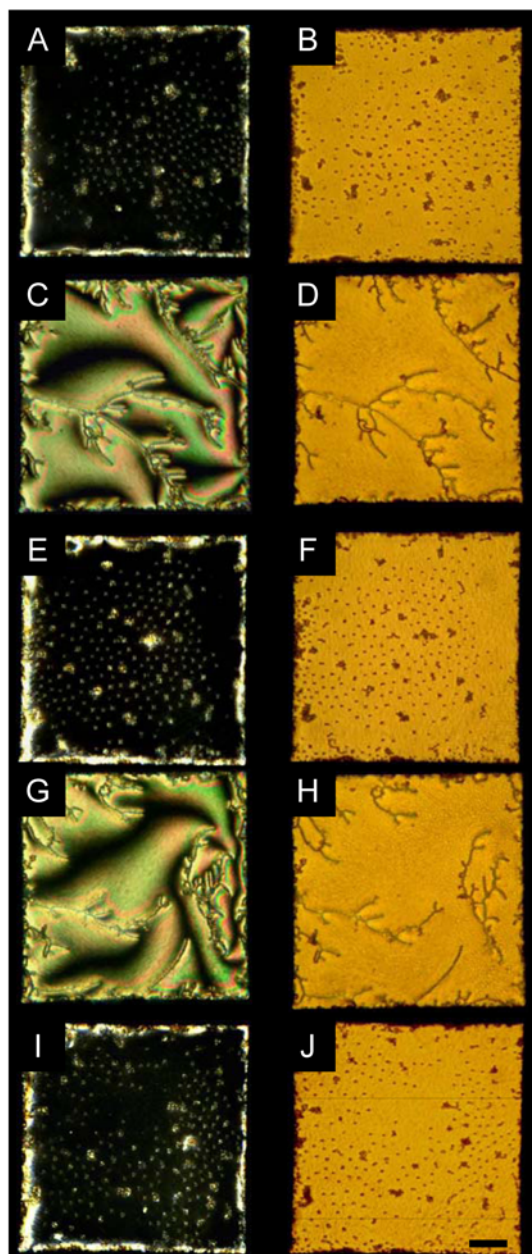


Fig. S1. Optical micrographs demonstrating the reversibility of the restructuring of microparticle assemblies at a nematic 5CB–aqueous interface upon the adsorption and desorption of the surfactant SDS. The concentration of SDS in the aqueous phase was <5 (C, D, G, and H) and $1,300 \mu\text{M}$ (A, B, E, F, I, and J). Images on the left were taken with crossed polars, and the corresponding images on the right were taken in bright field. (Scale bar: $50 \mu\text{m}$.)

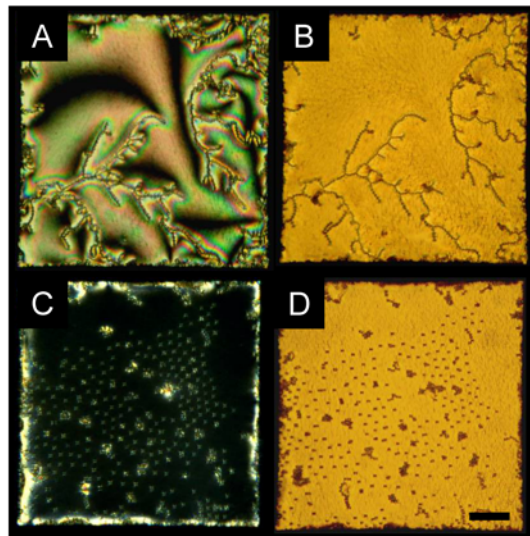


Fig. S2. Optical micrographs of the restructuring of microparticle assemblies at the nematic 5CB–aqueous interface upon the addition of the surfactant SDS. The concentrations of SDS in the aqueous phase were 400 (A and B) and 1,100 μM (C and D). Images in the left column were taken with crossed polars, and images in the right column were taken in bright field. These images are supplementary to Fig. 3 in the main text. (Scale bar: 50 μm .)

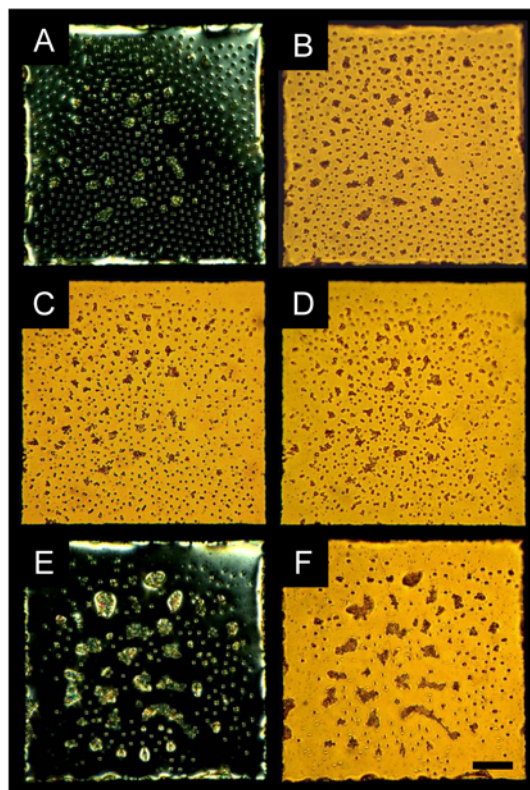


Fig. S3. (A) Polarized and the corresponding (B) bright-field optical micrographs of assemblies of microparticles at an SDS-laden 5CB–aqueous interface with a concentration of SDS in the aqueous phase of 1,300 μM . The sample was heated to 40 °C (above the nematic-to-isotropic transition temperature of 5CB), and bright-field optical micrographs were taken after (C) 2 min and (D) 8 min. (E) Polarized and corresponding (F) bright-field optical micrographs of the same sample after recoiling into the nematic phase for 10 min. (Scale bar: 50 μm .)

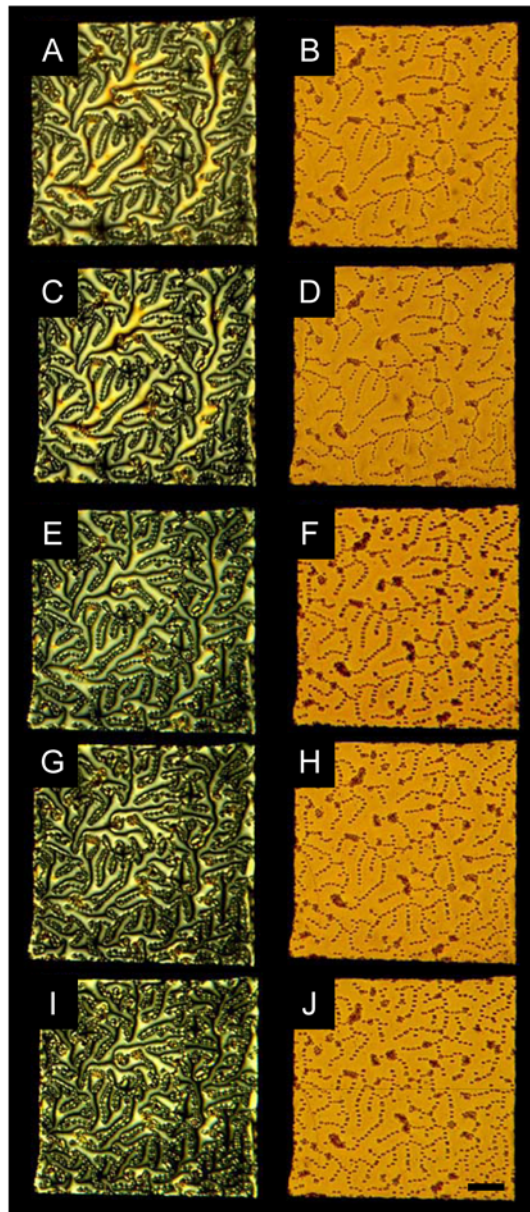


Fig. 54. Optical micrographs showing the stability of the microparticle assemblies at the nematic 5CB–aqueous interface when the SDS concentration in the aqueous phase was kept constant at 700 μM . Images on the left were taken with crossed polars, and images on the right were taken in bright field. (Scale bar: 50 μm .)

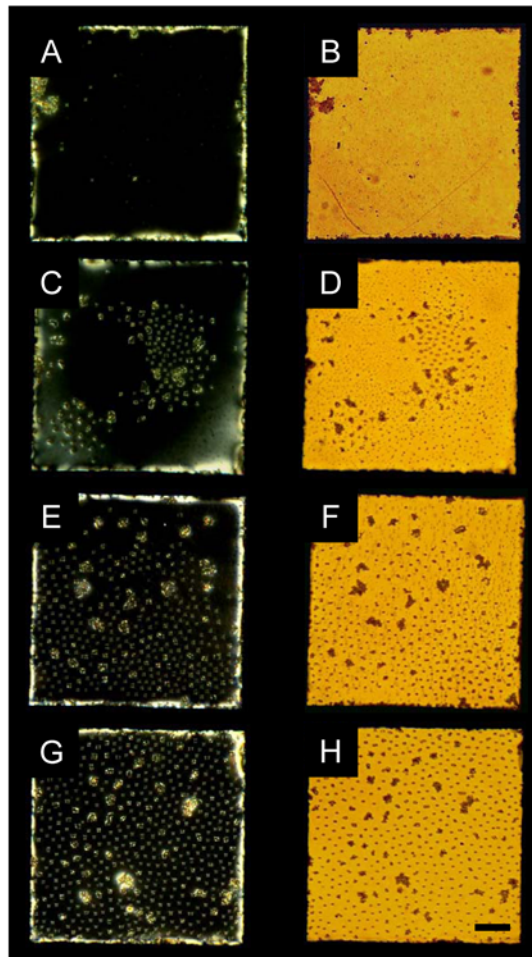


Fig. S5. Optical micrographs of assemblies of microparticles of increasing surface density at an SDS-laden nematic 5CB–aqueous interface. The SDS concentration was $1,300 \mu\text{M}$. The density of microparticles at the 5CB–aqueous interface was (A and B) 100, (C and D) 1,100, (E and F) 3,300, and (G and H) 5,200 microparticles/ mm^2 . Images on the left were taken with crossed polars, and images on the right were taken in bright field. (Scale bar: $50 \mu\text{m}$.)

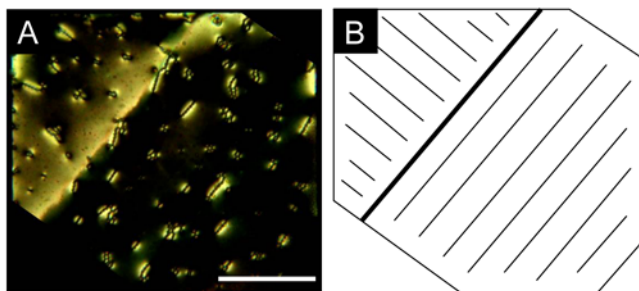


Fig. S6. (A) Polarized optical micrograph of microparticle assemblies at the nematic 5CB–aqueous interface when the azimuthal ordering of the 5CB at the interface was controlled by patterning the underlying substrate. (B) Cartoon depicting the director alignment in LC regions. (Scale bar: $100 \mu\text{m}$.)