The Mobilities of Micro- and Nano-Particles at Interfaces of Nematic Liquid Crystals

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Electronic Supplementary Information

Additional Experimental Considerations

1. Silica microparticles treated with dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (DMOAP) to cause homeotropic anchoring of the LC.

Briefly, 5 mg of particles were (i) rinsed twice by diluting in 5 mL of water, centrifuging, and removing the supernatant; (ii) dispersed in 3 mL of 2 M sulfuric acid and sonicated for 30 min; (iii) centrifuged and redispersed in 5 mL of water twice and 2 mL of water once; (iv) stirred (for 25 mins) vigorously while adding 20 µL of DMOAP (60% in methanol); (v) centrifuged and re-dispersed in water four times and finally centrifuged and allowed to dry under vacuum overnight.

2. Precautions required to obtain reliable measurements of diffusion coefficients.

Prior to reporting measurements of the mobilities of particles at the LC-aqueous interface, we comment that several precautions were found to be necessary in order to obtain reliable and reproducible measurements. First, we found it necessary to implement procedures that eliminated the effects of convection on the motion of the particles at the interface. In particular, we observed convection at the interface caused by the motion of the dipping objective. To avoid artefacts, following any motion of the objective, we found it necessary to wait several tens of minutes to allow the convection to dissipate. We also comment that LC interfaces can contain defects, and that defects can act as traps that arrest particle motion. Thus we measured the mobility of the particles in regions of the LC-aqueous interface that were observed optically to be free of defects. With this precaution, we did not observe particles to exhibit trajectories that were biased by interactions of the particles with defects on the interface (see below).

3. Possible role of interfacial viscosity in experimental measurements at 5CB-aqueous interface.

We considered the possibility that the higher apparent viscosity experienced by the nanoparticles (relative to microparticles) was due to an interfacial viscosity, the effects of which will increase with a decrease in particle size (as discussed in the Introduction). Specifically, if we use the drag coefficient calculated above ($f = 0.72$), and viscosities experienced by the nanoparticles in bulk 5CB (47.0 ± 10.4 mPa-s and 63.3 ± 13.2 mPa-s in the x-direction and y-direction, respectively), we calculate that an interfacial viscosity of 14.0 ± 2.8 mPa-s-µm can reproduce the experimental measurements of the mobility of the nanoparticles functionalized with the mixed monolayers. A similar analysis for nanoparticles with the single component monolayers (see below for details) leads to the prediction of an interfacial viscosity of 15.7 ± 2.4 mPa-s-µm, a value which is indistinguishable from that inferred from the behavior of nanoparticles functionalized with the mixed monolayers.

4. Calculation of the adsorption energy of particles at the 5CB-aqueous interface

The relation between adsorption energy and interfacial tension can be determined from the following equation (eq 8 from ref 35)

$$F' = -\frac{1}{4}(1-h'^2) + \frac{1}{2}\cos\theta(1-h') + \frac{1}{2}\tau\sqrt{1-h'^2}$$

where $F' = F/(\gamma_{12}A_p)$ is the reduced free energy. h'=h/R is the reduced position on the interface. A_p is the surface area of the particle, γ_{12} is the interfacial tension between the two liquid phases, R is the particle radius, θ is the three phase contact angle and τ is the line tension of the three-phase contact. The interfacial tension between 5CB and pure water has not been measured. Kim et al., however, (Kim, Langmuir (2004)) provide a lower bound from a pendent drop measurement (10 dyne/cm). There are no measurements of line tension for a 5CB-aqueous-silica system. Amirfazli et al. (Amirfazli, Advances in Colloid and Interface Science (2004)), however, present a review of line tensions for a variety of experimental conditions. They find that both experimental and theoretical measurements for the line tension range from 10^{-6}N to 10^{-10}N for a variety of oil-aqueous-particle systems with the majority of systems being closer to 10^{-10}N. In this range, the effects of line tension on the location of the particle at the interface are negligible. The particle location at the interface is found by minimizing the free energy. The location is dependent on the three-phase contact angle, h'=cos(θ). Based on an interfacial tension of 10 dyne/cm or greater, we calculate the free energy of adsorption to be at least ~10^7kT.

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