Three-dimensional complex-shaped photopolymerized microparticles at liquid crystal interfaces

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Microparticles of arbitrary shapes immersed in the bulk of nematic fluids are known to produce dipolar or quadrupolar elastic distortions that can mediate long-range colloidal interactions. We use two-photon photopolymerization to obtain complex-shaped surface-bound microparticles that are then embedded into a nematic liquid crystal host with a uniform far-field director. By means of three-dimensional imaging with multi-photon excitation fluorescence polarizing microscopy, we demonstrate low-symmetry, long-range elastic distortions induced by the particles in the liquid crystal director field. These director distortions may provide a means for controlling elastic interactions in liquid crystals between custom-designed photopolymerized microparticles attached to confining solid substrates and nematic fluid-borne colloids, thus enabling elasticity-mediated templated self-assembly.

A beautiful analogy between the distortion of a nematic liquid crystal (NLC) around colloidal inclusions and the electric field

patterning bulk alignment of NLCs and the design of novel long-range interactions between the NLC fluid-borne and surface-attached particles for their structured elasticity-mediated self-assembly.

A schematic diagram of a two-photon photopolymerization and 3PEF-PM setup is shown in Fig. 1a. A tunable (680–1080 nm) femtosecond Ti:sapphire laser (140 fs, 80 MHz, Chameleon Ultra-II, Coherent) is used as an excitation light source for both photopolymerization and 3PEF-PM (which is an imaging modality of nonlinear optical polarizing microscopy described in detail in references 24 and 25). For the two-photon photopolymerization, a femtosecond laser beam tuned to a wavelength of 780 nm is introduced into an inverted micro-

the epoxy-spacer mix is cured, binding the glass plates together, we filled the cell with a room-temperature NLC, pentylcyano-biphenyl (5CB, obtained from Frinton Labs), and then sealed the edges with epoxy.

To study elastic interactions between colloids and the surface-bound photopolymerized particles, we have prepared an NLC colloidal dispersion of 2 μm spheres with vertical surface boundary conditions for $\mathbf{n(r)}$. We obtained these boundary conditions at the surface of particles by first dispersing the silica spheres in 5 wt% aqueous solution of the surfactant [3-(trime-thoxysilyl)propyl]octadecyl-dimethylammonium chloride (DMOAP, purchased from Aldrich) and then sonicating for 30 minutes. The particles were then rinsed via sequential centri-fugation at 3000 rotations per minute, replacement of the solvent with deionized water, and sonication for about 30 seconds. The rinsing process was repeated five times and the remaining water was then evaporated on a hot stage at about 120 °C for 10 hours. Once the particles were added to the NLC, the obtained dispersion was again sonicated for three hours to break colloidal aggregates and then used to fill in the cells immediately after the sonication.

3D imaging of the NLC was performed using 3PEF-PM. A femtosecond laser beam at the wavelength of 870 nm is intro-duced into the laser-scanning unit (FV-300, Olympus) and is focused into a sample using an oil-immersion objective (100×, NA = 1.4) of the inverted IX-81 microscope (Fig. 1a). A galvano-mirror pair in the scanning unit steers the position of a focused laser beam laterally within the focal plane of the objective while the motion of the objective along the microscope's optical axis is implemented by the use of a stepper motor. The 3PEF-PM signals are collected either by the same objective and detected in epi-detection mode with a photomultiplier tube (PMT2) or by another oil-immersion objective (60×, NA =

director n_0, the substrate-bound particle is orientated so that all of its side faces are misaligned and at different angles with respect to n_0. This, along with the shape of the top part of the particle, imposes strong elastic distortions of $n(r)$ around the particle. We observe a twisted director structure propagating from the top surface of the particle toward the opposite dMR-coated glass substrate. Although the surface boundary conditions for $n(r)$ at the NLC–particle interface are tangentially degenerate, the shape of the particle and the side faces lift this degeneracy so that $n(r)$ in the central part of the top particle–NLC interface aligns roughly along a diagonal of the L-shaped top interface, as schematically shown in Fig. 3e. The twist distortion of $n(r)$ then matches this average alignment of the director at the particle–NLC interface to the boundary conditions at the top substrate set by the optically controlled dMR monolayer (Fig. 3). Consistent with the results of 3PEF-PM imaging, the region above the particle appears bright in POM under crossed polarizers (Fig. 2a). Individual particles and their arrays (such as the 2×2 array shown in Fig. 2a) exhibit a similar behaviour and all induce twist of the same handedness, which is pre-determined by the symmetry and orientation of the used complex-shaped surface-bound particles (Fig. 2 and 3). Since the ensuing 3D structures of $n(r)$ have all mirror symmetry planes broken and induce net twist with the helical axis along the normal to the substrates of the cell, this implies that the surface-bound photopolymerized particles in this geometry exert a torque on the NLC director. Experimental images indicate that $n(r)$ at the NLC interface with the top dMR-coated substrate above the photopolymerized particle might slightly deviate (not shown in the schematic in Fig. 3e) from the easy axis set by polarized illumination, due to the fact that the surface anchoring at the dMR–NLC interface is finite (soft boundary conditions) and this deviation partially relieves the twist distortion in the NLC bulk above the particle (Fig. 3).

We have explored interactions of NLC-borne colloidal inclusions with the complex-shaped photopolymerized particles attached to the substrates. Despite the screening caused by the confinement, these elasticity-mediated interactions are long-range and strongly anisotropic. Fig. 4a shows an example of a trajectory of particle motion due to the elastic interaction between the floating colloid and a surface-bound particle. Both particles generate elastic distortions of $n(r)$ in the NLC. The floating silica microsphere induces a hyperbolic point defect of charge N $= -1$, which compensates for the vertical boundary conditions, and the ensuing radial director structure around the particle surface (the radial director field is equivalent to a point defect of charge N $= 1$), as shown in Fig. 4d. These elastic distortions around the microsphere have a dipolar symmetry of $n(r)$ while the distortions around the photopolymerized particle are monopole-like (since this surface-bound particle was intentionally fabricated to be oriented differently from what would be its equilibrium orientation in the NLC bulk). When the mobile particle is attracted toward the stationary one, the two particles share some of the induced elastic distortions and thus minimize the elastic energy cost due to the overall $n(r)$ distortions in the cell. Although the elastic interactions are strongly screened by the proximity of confining substrates (especially the one to which the photopolymerized particle is bound) from which the floating dipolar colloidal particle repels,[26] the elastic binding energy of the mobile colloid to the stationary particle exceeds 1000 k_BT (Fig. 4c) and is comparable to the elastic binding energies between floating microparticles in the NLC bulk.[9] Furthermore, despite having physical underpinnings of elastic interactions similar to those studied for colloids in the NLC bulk, they may enable a qualitatively different type of medium-mediated templated self-assembly of particles using specially designed structured surfaces.

Elastic inter-particle interaction forces are characterized by the use of their balance with viscous forces, which are measured by video-tracking particle motion. We track the particle positions vs.

surrounding "corona" of $n(r)$ distortions. η_{eff} depends on the motion direction of the particle with respect to n_0 and also on the $n(r)$ structure around the colloid. We use $\eta_{\text{eff}} = 86.4$ cP, as previously determined for a particle with dipolar $n(r)$ in 5CB for a similar geometry.[27] We find that the maximum attractive elastic force is about 2.3 pN (Fig. 4b). This is an external force needed to separate the mobile colloid from the elastic trap produced by the surface-attached particle and, in analogy to the case of optical trapping, can be called "elastic trap escape force." Since the elastic force increases linearly (for small distances) as a function of the separation distance between the particle and its equilibrium location in the elastic trap, one can also determine the stiffness of this elastic trap, which is $\sim$4.6 pN μm^{-1}. The elastic force decays rather weakly with distance to the final equilibrium location of the mobile dipolar colloid at the edge of the photo-polymerized surface-bound particle (Fig. 4b). This might be due to the fact that the low-symmetry $n(r)$ around the photo-polymerized particle is monopole-like. In a bulk of an NLC, the interaction force between an elastic monopole (obtained, for example, by means of exerting an external torque on a non-spherical colloid) and an elastic dipole is expected to scale with center-to-center separation r_{cc} as r_{cc}^{-3}. Indeed, the log–log plot in the inset of Fig. 4b shows that the elastic force between the NLC-borne and surface bound particles decays with distance weaker than what is expected for bulk dipole–dipole interactions (r_{cc}^{-4}), although the slope changes from about -2 to about