Elastic interactions between colloidal microspheres and elongated convex and concave nanoprisms in nematic liquid crystals

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We study mutual alignment and interactions between colloidal particles of dissimilar shapes and dimensions when dispersed in a nematic host fluid. Convex pentagonal and concave starfruit-shaped nanoprisms and microspheres induce dipolar or quadrupolar director structures. The ensuing elastic pair interactions between microspheres and nanoprisms are highly dependent on the nanoparticle shape being omnidirectionally attractive for convex prisms but strongly anisotropic for concave prisms. Elastic deformations due to spherical particles cause well-defined alignment of complex-shaped nanoparticles at distances much larger than the microsphere size. We characterize distance and angular dependencies of elastic pair interaction forces, torques, and binding energies. The studied elasticity-mediated self-assembly of metal and dielectric nanoparticles with dissimilar shapes and sizes opens new possibilities for self-assembly based fabrication of structured mesoscopic composites with predesigned properties.

Introduction

Anisotropic interactions between colloidal particles in liquid crystals (LCs) attract a great deal of attention due to the possibility of their controlled orientated self-assembly into two- and three-dimensional structures useful for a broad range of applications.[1] These long-range colloidal interactions are mediated by particle-induced deformations of a LC director ***n*** (a unit vector representing the average orientation of mesogenic molecules) that typically propagate to large distances and can be partially "shared" by colloids to minimize elastic energy.[2] The ensuing nanoparticles as studied in ref. 36. CPN and CSN both have D_{5h} symmetry but pentagonal convex and star-like concave bases, respectively (insets of Fig. 1a and d). Silica spherical particles (SPs) of 3 μm diameter (Duke Scientific) were treated with a surfactant [3-(trimethoxysilyl)propyl]octadecyl-dimethylammonium chloride (DMOAP) to induce a strong homeotropic (normal to the surface) alignment[11] of LC molecules (Fig. 1g). To obtain isolated well-separated colloids in a nematic host, particles were added to LC at low concentrations (<0.05 vol%). First, SPs were dispersed in LC by direct mixing and a 15–30 min sonication to break apart pre-existing aggregates. Then gold nanoparticles were dispersed from ethanol to toluene and added to the mixture of LC and microspheres; this was followed by evaporation of toluene. The resulting colloidal dispersion was sonicated for 30–60 min while slowly changing the temperature from an isotropic to the LC phase. LC-colloid dispersions were filled in between two glass substrates spaced by glass microfibers of 10 μm in diameter (setting a cell thickness d) and treated to induce homeotropic or planar (tangential to the surface) far-field alignment $\boldsymbol{n}_0$ of LC. To set surface boundary conditions at confining substrates, we dip-coated them in an aqueous (1 wt%) solution of DMOAP for homeotropic alignment and used it while director bends around and follows the surface morphology of the nanoprism with the D_{5h} symmetry. The ensuing $\boldsymbol{n}(\boldsymbol{r})$ is of quadrupolar type,[10] with two surface point defects (called "boojums") at CSN ends (Fig. 1d). The grooved surface relief of the concave CSN with $\gtrsim 1$ (inset in Fig. 1d) forces $\boldsymbol{n}(\boldsymbol{r})$ to follow the surface morphology of CSN instead of satisfying antagonistic surface boundary conditions exerted by its concave facetted faces. More detailed studies of this $\boldsymbol{n}(\boldsymbol{r})$-structure are discussed in our previous work (ref. 36).

Elastic pair interactions between spheres and convex prisms

In a planar nematic cell, SP and CPN experience attraction from all studied initial positions (Fig. 2a and b) when placed by optical tweezers in a close vicinity of (4–6)R_{SP} to each other. This omnidirectional attraction is largely due to the fact that SP creates a highly distorted $\boldsymbol{n}(\boldsymbol{r})$ around it and displacing some of these distortions by a nanoparticle reduces the total elastic energy. The CPN seeks elastic energy-minimizing position and orientation. Fig. 2b shows trajectories of CPN approaching SP from different directions that we plot atop of the dipolar configuration of $\boldsymbol{n}(\boldsymbol{r})$ around SP (blue lines) calculated using an ansatz.[1 1]

During its motion (Fig. 2a), CPN is free to rotate around $\boldsymbol{n}_0$ as it is attracted to SP starting from different initial positions and orientations of a CPN–SP center-to-center separation vector $\boldsymbol{r}_{cc}$. By rotating around $\boldsymbol{n}_0$, the dipole and quadrupole moments induced by CPN also align with respect to the microsphere to further minimize the total elastic energy. In the SP vicinity with dipolar elastic distortions, $\boldsymbol{n}(\boldsymbol{r})$ around the CPN can be modified as compared to that in a uniformly aligned LC (Fig. 1a) or can even transition between two states with different alignments of $\boldsymbol{p}$ shown in the insets of Fig. 1a. However, the details of this behaviour cannot be probed by optical imaging due to spatial resolution limitations. After approaching SP from any direction, CPN slides along the sphere's surface (trajectories 1 and 4) to the equatorial plane (dashed black circles) where it elastically binds to SP (Fig. 2b) in the minimum-energy location and orientation. Equilibrium arrangement of CPN and SP is shown in Fig. 2a, b and e. The CPN resides in the equatorial plane (Fig. 2b and e) and can drift around SP unless restricted by the cell confinement. Fig. 2d and e show a schematic diagram of $\boldsymbol{n}(\boldsymbol{r})$ around these interacting colloids at the onset and in the end of their interaction. In the final elastically bound state, $\boldsymbol{n}(\boldsymbol{r})$ distortions due to CPN match distortions due to SP near its equator, which is reminiscent to dipole–quadrupole interactions between differently surface-treated colloidal microspheres. The total elastic energy is likely further minimized via alignment of the elastic dipole moment of CPN to -10.n,40.5(488ti-atiol8.966ellargel(discolloid))]TJ921of of the dipole moment is caused by the pentagonal shape of the CPN cross-section, a relatively small departure from the cylindrical shape for which only a quadrupole moment would be expected. The attractive elastic force measured at r_{cc} 2.5 μm is within the range of 0.5–1 pN; the strongest attraction is observed when the nanoparticle approaches from the directions (see trajectories 3–6 in Fig. 2b) opposite to the hedgehog. Elastic binding of CPN takes place within an experimentally determined belt surrounding SP along its equator (Fig. 2f). The character of elastic interactions between SP and CPN is dependent on the orientation of the elastic dipole moment of CPN with respect to the SP elastic dipole, yielding the strongest attraction when they are anti-parallel (Fig. 2e and f). The combination of the effects of the CPN-excluded volume of elastic distortions, dissimilar particle sizes, and CPN's rotation around ***n***(***r***) yields the unexpected omnidirectional CPN–SP attraction (Fig. 2b).

Elastic alignment and torque transfer to nanoprisms

Attractive interactions between CPNs and SPs in a homeotropic cell (Fig. 3 and 4) are accompanied by a long-range torque transfer mediated by nematic elasticity (Fig. 3). At $r_{cc} > 10R_{SP} \gg d$ (Fig. 3a), two particles drift randomly due to the Brownian motion and CPN freely rotates to arbitrary azimuthal angles (Fig. 3a and c) having no correlation with the angle describing azimuthal orientation of $\boldsymbol{r}_{cc}$ (Fig. 3a). However, at r_{cc} d, CPN aligns along $\boldsymbol{r}_{cc}$ so that = (Fig. 3a–c). Once this "communication" between CPN and SP via transfer of the elastic torque is established, it is possible to quite precisely (| − | < 5°) control the orientation of CPN by changing the position of SP using optical tweezers (Fig. 3a–c). The alignment can be understood as the elastic torque due to director deformations created by SP. Fig. 3d shows that ***n***(***r***) deformations caused by SP propagate to distances larger than d. The CPN introduces additional distortions into ***n***(***r***) due to the SP dipole. The elastic energy is at minimum when the CPN's long axis orients along $\boldsymbol{r}_{cc}$, giving rise to the elastic torque causing rotation of CPN if its orientation is different (Fig. 3). This elastic torque exerted on CPN is balanced by a hydrodynamic drag torque as $\Gamma_{el} = -c\, d(-)/dt$, where c 1.43 × 10^{-19} N m s is the rotational drag coefficient estimated from the rotational diffusion coefficient determined via tracking fluctuations of . The angular drift velocity d(−)/dt depends on r_{cc} and can be determined using the angular distribution shown in Fig. 3c. Γ_{el} decreases when r_{cc} increases being 0.06 pN μm rad^{-1} at r_{cc} 9 μm and 0.4 pN μm rad^{-1} at r_{cc} 3 μm (Fig. 4a and c). The observed effect of long-range elastic torque transfer can be used to control orientation of elongated nanoparticles. The attractive interactions between SPs and CPNs self-aligned along $\boldsymbol{r}_{cc}$ overcome the Brownian motion and become well pronounced at $r_{cc} < 8R_{SP}$ (Fig. 4a). The dipole–quadrupole term dominates in the attractive potential U_a and

(Fig. 5d). For this configuration, the equilibrium state corresponds to the angle 40° between r_{cc} and n_0 and an angle 0° between the CSN's long axis and n_0 (Fig. 5e and f); changes within $\sim$20° to 45° (Fig. 5e and o). The angle distribution in Fig. 5f shows that CSN changes its orientation up to $\sim\pm$20° with respect to n_0 while adjusting to the local deformations of $n(r)$ (Fig. 5b and c). The CSN quadrupole is also strongly attracted to the SP dipole when positioned at $r_{cc} \| n_0$ from the side of the SP hemisphere opposite to the location of the hedgehog (Fig. 5g and h). The CSN quadrupole and SP dipole repel when positioned at about 45° < | | < 135° (Fig. 5e and o) with the maximum repulsion at $r_{cc} \perp n_0$ (Fig. 5k–n).

Elastic attraction and repulsion between the CSN quadrupole and the SP dipole can be qualitatively understood considering $n(r)$ around both particles (Fig. 5b, i, l and n). When CSN approaches the SP along n_0, it matches the local $n(r)$ of the elastic dipole (Fig. 5b and i). When $r_{cc} \perp n_0$, antagonistic orientation of $n(r)$ at the surfaces of two particles, normal at SP and planar at CSN (Fig. 5l and n), causes repulsion (Fig. 5f). The angular zones of attraction are shown by a green colour in Fig. 5o and were determined using videomicroscopy observations (Fig. 5a, g, k and m). SP–CSN colloidal pairs can be moved and arranged into different structures. Fig. 5j shows the arrangement of two SP–CSN pairs into a chain due to the elastic dipole–dipole interactions between two SPs. For example, one can build the chain of unidirectionally aligned gold nanoprisms.

Conclusions

We have demonstrated that interactions between colloidal particles having dissimilar shapes, compositions, and dimensions can exhibit behaviour, such as omnidirectional attraction, not encountered for monodisperse colloids in LCs. Convex pentagonal nanoprisms align perpendicular to the far-field director and induce director distortions having both elastic dipole and quadrupole moments while concave nanoprisms align along the far-field director and induce elastic quadrupoles. Both nanoparticles elastically bind in well-defined positions and with well-defined orientations next to colloidal microspheres, with elastic binding energies on the order of hundreds of k_BT, allowing for the formation of well-defined colloidal pairs and other superstructures formed from them. Our findings pose new challenges for theoretical modelling of colloidal self-assembly in LCs and are of interest for applications in nanophotonics and nanoscale energy conversion.

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