



Active Shape-Morphing Elastomeric Colloids in Short-Pitch Cholesteric Liquid Crystals

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(Received 21 October 2012; published 30 April 2013)

Active elastomeric liquid crystal particles with initial cylindrical shapes are obtained by means of soft lithography and polymerization in a strong magnetic field. Gold nanocrystals infiltrated into these particles mediate energy transfer from laser light to heat, so that the inherent coupling between the temperature-dependent order and shape allows for dynamic morphing of these particles and well-controlled stable shapes. Continuous changes of particle shapes are followed by their spontaneous realignment and transformations of director structures in the surrounding cholesteric host, as well as locomotion in the case of a nonreciprocal shape morphing. These findings bridge the fields of liquid crystal solids and active colloids, may enable shape-controlled self-assembly of adaptive composites and light-driven micromachines, and can be understood by employing simple symmetry considerations along with electrostatic analogies.

DOI: [10.1103/PhysRevLett.110.187802](https://doi.org/10.1103/PhysRevLett.110.187802)

PACS numbers: 61.30.Jf, 64.75.Yz, 82.70.Dd

Dispersions of particles in liquid crystals (LCs) attract a constantly growing interest and exhibit many fascinating phenomena, ranging from particle-induced topological defects to novel types of elastic interactions [1–3]. Structures of LC molecular alignment around particles, typically described by a director $\mathbf{n}$ pointing along the local average molecular orientation, give rise to elasticity mediated colloidal self-assembly not encountered in isotropic fluid hosts. Within a far-field approximation, even spherical particles with strong boundary conditions induce dipolar or quadrupolar $\mathbf{n}(\mathbf{r})$ distortions arising due to the anisotropic nature of the host medium and particle-induced satellite defects, such as point defects and disclination loops [1,2]. Although many methods for self-assembly of anisotropic particles in isotropic solvents have been introduced [4], LC hosts bring a number of unique capabilities, such as the well-defined long-range alignment of anisotropic particles with respect to $\mathbf{n}$ controlled by external fields [3,5–10]. The shape of the particles dictates colloidal self-assembly [3,7–15] and may enable practical utility of these fascinating LC-colloidal systems. Although complex-shaped particles can be fabricated using photolithography [3,6], two-photon polymerization [10], nanocrystal growth [8], and wet chemical synthesis [7,9], these approaches provide nematic dispersions of nonresponsive particles with no means for altering their shape, alignment, locomotion, and self-assembly [3,5–8].

In this Letter, we describe an optically reconfigurable double-LC colloidal system that allows for an unprecedented optical control of particle shapes and motion while being dispersed in a LC host. These active particles are made from a nematic LC elastomer (LCE) [16–18] doped with gold nanocrystals to enable photothermal energy transfer and are morphed into low-symmetry configurations via laser-directed bending and aspect ratio control. We explore director structures in the LC host induced by these active colloids and describe them using electrostatic analogies. Finally, we discuss potential applications in reconfigurable self-assembly and controlled dynamics of active colloids in structured fluid hosts.

Cylindrical particles were obtained using replica molding and polymerization in a strong magnetic field of about 1 T that aligns $\mathbf{n}$ of the LCE along the cylinder axis [16,17,19]. Particles with diameter $\times$ length dimensions of 2×4 , 17×70 , and $20 \times 100 \mu\text{m}$ were then passively infiltrated with 2 nm gold nanocrystals (obtained using wet synthesis described in Ref. [20]) by letting them soak in the dispersion of nanocrystals in toluene for 24 h [16]. LCE microparticles with embedded gold nanocrystals were then redispersed in an aqueous cholesteric LC (CLC) solution of hydroxypropylcellulose (HPC, at 55 wt %) [21,22]. The sample was sheared to a partially unwound state which then relaxed to a ground-state CLC configuration with a uniform helical axis perpendicular to the shear direction, as

also observed in other studies of HPC-based LCs [21–25]. The equilibrium pitch $p \approx 350$ nm [21–25] and “layer” periodicity [26] $p/2 \approx 175$ nm allow for optical exploration of elastic distortions due to colloidal particles much larger than $p/2$. The LC cells were constructed from $170 \mu\text{m}$ thick glass plates optimized for high-resolution imaging and laser manipulation when using microscope objectives with high numerical aperture. After shearing, the glass plates were sealed together using epoxy to form cells of thickness ranging from $100 \mu\text{m}$ to 2 mm.

To control particle shapes, we used laser tweezers [27–29] consisting of a two-axis scanning-mirror head (XLRB2, Nutfield Technology) and a continuous wave Ytterbium-doped fiber laser (wavelength $\lambda = 1064$ nm, IPG Photonics). The tweezers setup was integrated with an optical microscope BX-51 (Olympus). LCE particles in the LC were manipulated via steering a focused beam and monitored by polarizing optical microscopy (POM) using microscope objectives with magnifications $10\times$, $50\times$, and $100\times$ and numerical aperture within 0.25 – 1.4 .

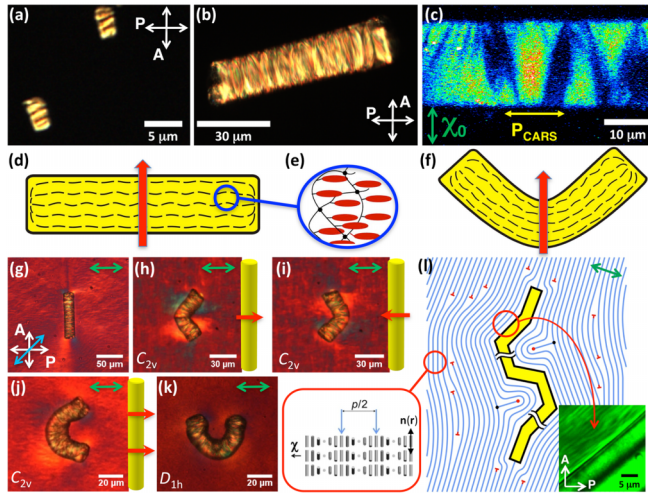


FIG. 1 (color online). LCE particles in isotropic and LC hosts. (a),(b) POM images of LCE particles in water. (c) CARS-PM image of an LCE cylinder in a lyotropic LC obtained for a linear laser polarization marked by a yellow double filled arrow. (d), (e), (f) $\mathbf{n}(\mathbf{r})$ in LCE particles (d) before and (f) after the scanning along direction marked by red arrows. (g) LCE cylinder in a CLC. (h),(i) Bent cylinders obtained by laser scanning along directions shown by red arrows in the insets. (j),(k) LCE particles shaped into letters (j) C and (k) U by means of laser scanning along red arrows shown in (j). Crossed polarizer P and analyzer A are marked by white crossed double arrows while the “slow” axis of a 530 nm retardation plate is shown by a blue tilted double arrow in (g) and correlates with the darker blue color in the texture, visualizing regions where CLC layers are roughly along the blue tilted double arrow; green double opened arrows mark χ_0 . (l) Schematic of an optically shaped LCE colloid distorting CLC and introducing edge dislocations (red nails); cylinders in the inset represent $\mathbf{n}(\mathbf{r})$. POM image in the inset of (l) shows that CLC layers are parallel to the particle’s surface.

Linear polarization of the laser beam was controlled by rotating a $\lambda/2$ wave plate. LCE particles were also studied using broadband coherent anti-Stokes Raman scattering polarizing microscopy (CARS-PM) [30,31] via probing the polarized CARS-PM signals from the aromatic $\text{C}=\text{C}$ stretching within 1400 – 1600 cm^{-1} . Broadband Stokes (obtained by means of a photonic crystal fiber) and 780 nm pump-probe femtosecond pulses were used for excitation. The CARS-PM signal at around 694 nm was detected using a band pass filter with center wavelength at 700 nm and 13 nm bandwidth [31]. POM and CARS-PM [Figs. 1(a)–1(c)] revealed weakly undulating $\mathbf{n}(\mathbf{r})$ of LCE with an average orientation along the cylinder [Figs. 1(d) and 1(e)] [16].

Unlike LCE particles, the LC host was designed to be insensitive to laser beams: (a) optical Fréedericksz transition in this system does not occur up to powers of 1 W (much higher than powers <200 mW used in experiments); (b) polymer solutions of HPC are practically insensitive to photothermal effects, as long as solvent evaporation is avoided; (c) gold nanocrystals uniformly distribute within the LCE but are immiscible with the aqueous solution of HPC, so that they do not diffuse into the surrounding host; (d) having entropic origin, tangentially degenerate surface anchoring of the HPC-based LC is insensitive to the scanned beams. This allows for morphing particle shapes without direct coupling between $\mathbf{n}(\mathbf{r})$ of the HPC-based host and laser light [Figs. 1(d)–1(l)] as well as POM imaging of the ensuing structural changes. Since the lamellar periodicity $p/2 \approx 175$ nm [21–25] of the HPC

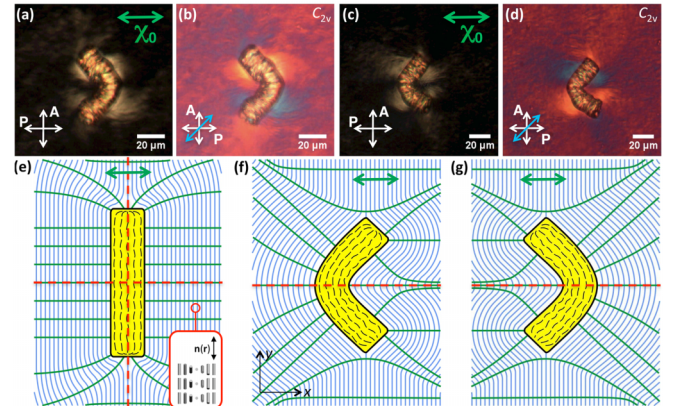


FIG. 2 (color online). Control of $\chi(\mathbf{r})$ - symmetry and layered structures in a CLC via optical control of LCE colloidal shapes. (a)–(d) POM images of LCE particles obtained (a),(c) without and (b),(d) with a 530 nm retardation plate. (e) $\mathbf{n}(\mathbf{r})$ within the cylindrical LCE particle (black dashed lines), and the layer structures (blue thin lines) and $\chi(\mathbf{r})$ (green thick lines) around it have mirror symmetry planes marked by dashed red lines as well as coinciding with the plane of the schematic. Cylinders in the inset represent $\mathbf{n}(\mathbf{r})$ twisting by π within each cholesteric layer. (f),(g) Layer structures and $\chi(\mathbf{r})$ induced via bending of LCE particles.

cholesteric in the ground state is smaller than the resolution of an optical microscope (≈ 300 nm or worse, depending on the objective), acetic acid is used as a solvent instead of water to increase p up to $3\ \mu\text{m}$ and directly observe cholesteric layers in POM, as shown in the inset of Fig. 1(l). POM textures obtained without and with a λ -retardation plate also reveal the spatial variations of the helical axis $\chi(\mathbf{r})$ structures.

Unidirectional laser scanning controls the particle shape via photothermal heating mediated by LCE-entrapped gold nanocrystals uniformly distributed within the particle bulk (Fig. 1) [32–35]. LCE microcylinders bend toward the beam scanning direction typically chosen to be orthogonal or tilted with respect to the cylinder axis [Figs. 1(d)–1(l), 2, and 3] [16], giving rise to a number of low-symmetry LCE particles. Bidirectional scanning of a laser beam along the cylinder axis allows for both reversible and irreversible modification of the diameter-length ratio, depending on whether the power of the scanning beam is reduced

gradually or switched off abruptly (Fig. 4). POM imaging with and without a λ plate reveals layered structures and $\chi(\mathbf{r})$ of the surrounding LC that follow laser-guided changes of colloidal shapes (Figs. 2–4), which is due to the surface anchoring of $\chi(\mathbf{r})$ at the LC-LCE interface [inset of Fig. 1(l)]. In addition to smooth deformations of layers at relatively weak bending of pillars, POM textures also provide evidence for the presence of dislocations [Fig. 1(l)] that appear to assist in preserving layer equidistance while accommodating boundary conditions on optically controlled LCE particles.

Particle-induced perturbations of a homogeneous ground-state director $\mathbf{n}_0$ in nematic LCs have the form of a transverse two-component vector $\delta\mathbf{n}$ [36]. Along with symmetry considerations, this brings about an expansion into multipole series and electrostatic analogies between long-distance colloidal interactions and that of multipoles in electrostatics [1–11,36]. The ground state in a CLC is strongly twisted and a direct parallel with the

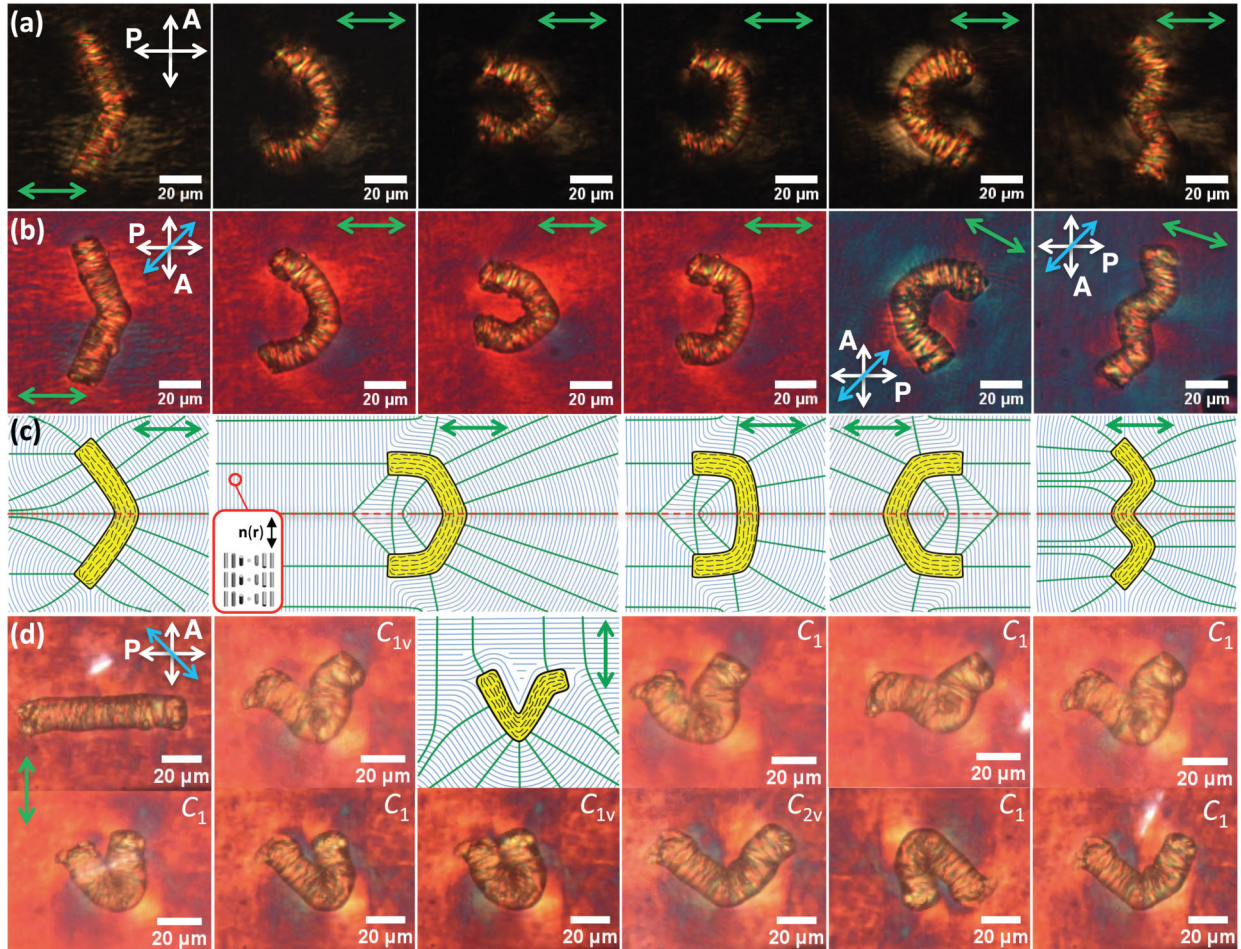


FIG. 3 (color online). Low-symmetry $\chi(\mathbf{r})$ structures induced by continuous optical morphing of LCE colloids. (a),(b) POM images of LCE particles and $\chi(\mathbf{r})$ in the surrounding LC host obtained (a) without and (b) with a 530 nm retardation plate. (c) Schematics of cholesteric layers and $\chi(\mathbf{r})$ around LCE particles corresponding to POM images shown in (a),(b). (d) POM images obtained with a retardation plate showing examples of shapes and $\chi(\mathbf{r})$ configurations obtained by morphing LCE particles in a CLC. The last two images on the right side of (b) were taken when the sample was rotated with respect to crossed polarizers.

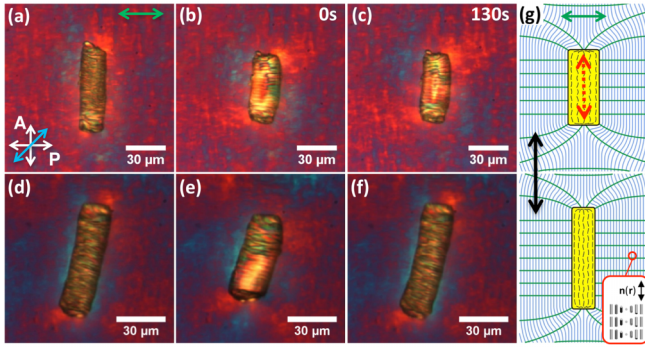


FIG. 4 (color online). Reversible and irreversible control of aspect ratios of LCE cylinders in a CLC. (a) LCE cylinder in a sheared CLC. (b),(c) Length shrinking and diameter increase induced by bidirectional laser scanning along the cylinder axis that retains $\chi(\mathbf{r})$ symmetry and persists with time (marked in top right corners of POM images) after scanning is discontinued abruptly. (d) LCE particle in a non-sheared CLC. (e), (f) Reversible shape modification induced by similar bidirectional scanning but terminated via a continuous decrease of laser power within ~ 2 min and accompanied by reversible change of $\chi(\mathbf{r})$ in the CLC. (g) A schematic showing changes in $\chi(\mathbf{r})$ and layer structures that follow laser-induced modification of the particle shape; the dashed red double arrow depicts bidirectional scanning of the beam. The modified shape of particle is long-term stable if scanning is discontinued via turning laser off, but relaxes back to the original one when intensity of the beam decreases gradually.

homogeneous nematic ground state is impossible because homogeneity of the ground state is a prerequisite of the symmetry-based considerations [11]. However, a similar approach for cholesterics is prompted by the de Gennes–Lubensky model [36], which describes a short-pitch CLC in terms of the director χ normal to cholesteric layers. The model assumes that distortions occur over length scales much larger than p , which is the case of distortions due to our particles of size $\gg p$. The ground state χ_0 of the χ director is homogeneous and has the same symmetry $D_{\infty h}$ as that of $\mathbf{n}_0$, and its small distortion is a two-component transverse vector similar to $\delta \mathbf{n}$. Hence allowed symmetries of χ in CLCs are similar to those of $\mathbf{n}$ in nematics and this approach can be used at distances much larger than the particle size. At the same time, we note that the short-distance $\chi(\mathbf{r})$ and $\mathbf{n}(\mathbf{r})$ distortions around particles and the ensuing colloidal assemblies can be fully described only numerically [37].

LCE particle's surface induces a normal alignment of χ and tangential alignment of the CLC layers [inset of Fig. 1(l)]. The unperturbed axis of a LCE microcylinder is normal to χ_0 and parallel to both the CLC layers and cell substrates. $\chi(\mathbf{r})$ around the cylinder is of the quadrupolar type [Figs. 1(g) and 2(e)] with three mirror symmetry planes: the two planes passing through the cylinder axis, one along χ_0 and the other normal to χ_0 , and the plane normal to the cylinder axis. Optical morphing removes

some or all of these symmetry planes, thus creating different types of elastic multipoles (Figs. 1–3). One can also vary the strength of distortions without altering the symmetry of ensuing elastic configurations by changing the aspect ratio of particles (Fig. 4) or their fragments [Fig. 1(l)]. Using laser scanning, we can tune the strength and geometrical distribution of elastic multipoles by controlling angles between the bent fragments of the LCE pillar, their diameters, and lengths (Figs. 3 and 4).

Experimental dipolar V- and U-shaped particles with apex along χ_0 shown in Figs. 1(h)–1(j), 2(a)–2(d), and 3(a)–3(c) and zigzag-shaped particles in the right-side parts of Figs. 3(a) and 3(b) induce same-symmetry $\chi(\mathbf{r})$ shown in Figs. 2(f) and 2(g) and Fig. 3(c). Allowed symmetry elements of these $\chi(\mathbf{r})$ structures are those of the group C_{2v} : a rotation by an angle π about the vertical axis passing through the apex of the V, and a vertical mirror plane lying in the plane of the particle's V and passing through the vertical axis, as further illustrated by sketches of $\chi(\mathbf{r})$ in the vertical and horizontal planes in the supplemental Fig. S1a [38]. The particle shown in Fig. 1(k) has apex of V pointing along layers and normal to χ_0 . The symmetry elements of $\chi(\mathbf{r})$ are those of the group D_{1h} and include a vertical mirror plane lying in the particle's plane, a horizontal mirror plane normal to it and passing through the apex of the V, and a π rotation about the horizontal axis passing through the apex, as illustrated in the supplemental Fig. S2a [38]. Thus, these dipolar colloids in a CLC are described by point groups C_{2v} or D_{1h} , depending on the angle the apex direction makes with χ_0 . By continuous morphing particle shape, we can further lower the symmetry of $\chi(\mathbf{r})$ around LCE particles by, for example, removing symmetry elements of C_{2v} . Figure 3(d) shows several examples of particles with just one vertical mirror plane coinciding with the plane of the image (symmetry group C_{1v}) and asymmetric particles with no mirror planes (trivial group C_1), as revealed by birefringent textures and defocusing of different parts of the particle. An interesting interplay between symmetries of distortions in $\mathbf{n}(\mathbf{r})$ and $\chi(\mathbf{r})$ can be noticed when comparing like-shaped particles introduced into nematic and cholesteric LCs, respectively, as we discuss in the Supplemental Material [38]. Furthermore, since four types of pure and many hybrid elastic dipoles in nematic LCs can be identified using a tensorial description based on different symmetries of elastic distortions [11], we extend this description to CLCs and then further classify elastic dipoles obtained in our experiments in the Supplemental Material [38,39]. In both nematic and cholesteric LCs, LCE colloids rotate to minimize elastic energy of the surrounding $\mathbf{n}(\mathbf{r})$ or $\chi(\mathbf{r})$ in response to changes of particle shape (video 1 in [38]) and even the simplest non-reciprocal dynamic morphing of the shape results in a directional locomotion (video 2 in [38]).

To conclude, we have introduced a new class of active LCE particles with light-controlled rigidly connected

fragments of cylinders in fluid LCs that can be described by employing analogies with charge distributions in electrostatics. These elastomeric colloids will allow one to explore light-driven rotational and translational motion in low-viscosity nematic and cholesteric LCs of varying pitch and will bridge the fields of LC solids and active colloids. Furthermore, our double-LC colloidal system may allow one to explore the role of geometric shape in determining the complex dipolar structures, light-controlled self-assembly, reconfigurable knotting of defects, and formations of LC gels [37,39–41]. Potential applications include laser-guided assembly of reconfigurable materials for photonic and electro-optic applications and light-driven micromachines.

We acknowledge the support of NSF Grant No. DMR-0847782, Grant No. P200A030179 of the U.S. Department of Education, and ANR Grant No. ANR-2010-INTB-904-01, as well as technical assistance of P. Ackerman, Z. Qi, and R. Trivedi.

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