Colloids in confined liquid crystals: a plot twist in the lock-and-key mechanism

Giuseppe Boniello,[a] Yimin Luo,[a] Daniel A. Beller,[b] Francesca Serra,[*c] Kathleen J. Stebe[*a]

[a] Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA, 19104, USA.

[b] Department of Physics, University of California, Merced, CA 95343, USA.

[c] Physics and Astronomy, Johns Hopkins University, Baltimore, MD, 21218, USA.

1. Numerical simulations of size-dependent interactions

In Fig. 8 and ESI Video S8 we show that docking mechanism in π-twisted configuration depends also on size-to-thickness ratio. Colloidal particles with dipolar defects and different sizes are observed in the same experimental cell. The large particle (2a=18 μm) finds an equilibrium site a few radii away from the wall. The small particle (2a=12 μm) docks in the dale. We attribute this size dependence to the effects of defect confinement. As stated in the main text, larger particles experience strong confinement that imposes antagonistic defect orientation with respect to the wall. This defect orientation inhibits docking. Smaller particles, on the contrary, can adjust their defect orientation to be compatible with the wall.

Here, we support this observation with simulated energy profiles for a similar system. As in experiments, we consider homeotropic spherical particles in π-twisted cholesteric liquid crystals. Molecular anchoring at the wall is perpendicular to the molecular anchoring at the glass slides. However, the kind of defects in experiments and simulations are different. In experiments, weak confinement resulting from the reduction in particle diameter does not allow stabilization of twisted loop defects around microscopic particles in all the range of sizes, and dipoles are observed. In simulations, computational constraints limit simulations to particle diameters for which the twisted loop defect is the stable state (see Section 2 of the main text). Regardless of the degree of confinement, only the twisted loop defect is obtained. For this reason, simulated energy profiles cannot fully explain the experimental data. However, they represent a useful complement to guide our thinking.

Simulation volumes are the same as reported in section 2: D_x = 600 nm (direction parallel to the wall), D_y = 400 nm (distance from the wall), $D_z = t$ = 400 nm (vertical direction, thickness of the cell). Simulated particles have different sizes (expressed in radius-to-thickness ratios, a/t), ranging from a = 30 nm to 130 nm. All the particles are centered above the dale, and the energy profiles are calculated with varying wall-particle distance d. The energy barrier is present for larger particles ($a/t \geq 0.20$), and disappears for smaller ones (Fig. S1).

Numerical simulations provide also an insight on defects behaviors under different confinement regimes. For a large particle, the defect line (blue line in Fig. S2) forms a twisted loop incompatible with docking conditions. Moreover, the small gaps between the particle and boundaries impose large distortions. All of these conditions are responsible for the energy barrier when approaching to the wall. For a small particle, given the reduced size and the weaker confinement, the simulated defect can re-adjust in a configuration similar to a pure Saturn ring (cf. Fig. 2b) and docks for splay-match interaction.

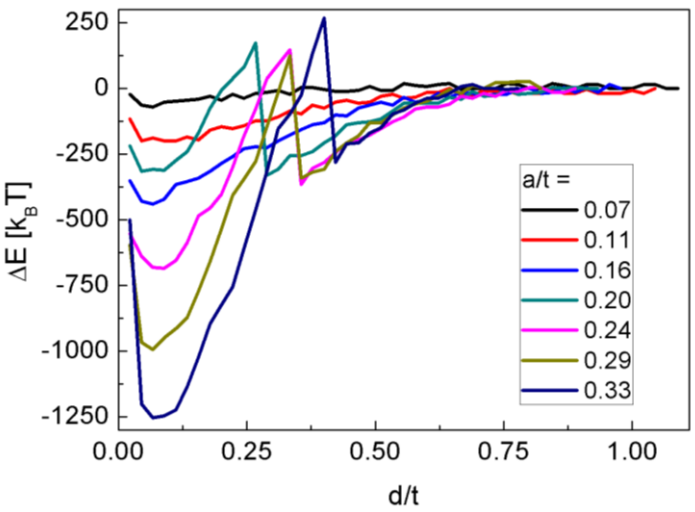

Fig. S1: Energy profiles of particles with twisted loop defects as a function of wall distance, for different particle sizes, expressed as ratios with respect to the cell thickness.

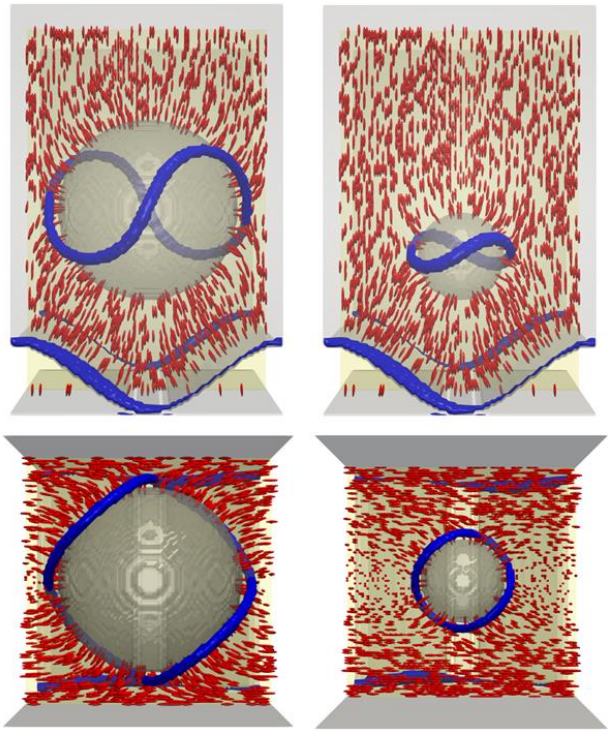

Fig. S2: Top view (top) and front view (bottom) of simulated particles with different sizes in π-twisted cholesteric LCs.

2. Supplementary videos

Images acquisition takes place at 1 frame/minute, given the slow dynamics of micrometric particles in viscous liquid crystal phases. Supplementary videos are sped up 180x (1 s in supplementary video corresponds to 3 min of acquisition) to ensure a better visualization.

2.1 ESI Video S1

A spherical particle with a dipolar defect oriented toward the wall in a 75°-twisted cell starts far from the wall. Tilting the cell by an angle α=0.04 rad introduces a gravitational driving force that moves the particle. The particle finds an equilibrium site determined by the balance of gravitational and elastic forces.

2.2 ESI Video S2

A spherical particle with a dipolar defect oriented toward the wall starts in proximity of the top of the hill in a 75°-twisted cell. The cell is planar, and there is no force to drive the particle motion. The purely repulsive potential pushes the particle away from the wall to a distance at which the repulsive force becomes negligible.

2.3 ESI Video S3

A spherical particle with a twisted loop defect is in a 75°-twisted cell. It is initially far from the wall and driven by an external driving force. The particle vertical motion stops at an equilibrium distance from the wall, by the balance of gravitational and elastic forces.

2.4 ESI Video S4

The same particle of ESI Video S3 is followed after vertical motion (perpendicular to the wall) is stopped. The particle is able to move because of diffusion and internal drift, showing that there is no pinning involved at the vessel boundaries. The distance between particle and wall remains constant, confirming the presence of an energy gradient.

2.5 ESI Video S5

A homeotropic particle is in π-twisted cholesteric liquid crystals. The molecular anchoring at the wall is parallel to the molecular anchoring at glass slides. The particle has a twisted loop defect at its equator. It tends to occupy the mid-cell plane, in the region of maximum mis-match between the wall anchoring and director twist (and so, maximum energy cost). Moving always in this horizontal plane, the particle docks in the dale.

2.6 ESI Video S6

A homeotropic particle is in π-twisted cholesteric liquid crystals. Molecular anchoring at the wall is perpendicular to molecular anchoring at glass slides. The particle has a twisted loop defect at its equator. In this configuration the maximum mis-match is achieved at the junctions between the boundaries, but these regions are inaccessible to the colloid for both elastic and steric repulsion. The particle is driven by an external driving force. Despite its action, the particle arrests at an equilibrium distance away from the wall.

2.7 ESI Video S7

A homeotropic particle is in a π-twisted cholesteric liquid crystals in the perpendicular configuration. The particle has a twisted loop defect at its equator. The initial position of the particle, when the liquid crystal is quenched from isotropic to cholesteric, is in proximity of the wall and beyond the energy barrier. The particle still docks in the dale, confirming the presence of an attractive potential well.

2.8 ESI Video S8

Two particles with different sizes (2a=18μm and 12μm) are observed at the same time. They are both in π-twisted cholesteric liquid crystals in perpendicular configuration, and have dipolar defects. The cell is tilted to ensure a gravitational driving force (right to left) moving the particles toward the wall. The larger particle stops at an equilibrium position away from the wall, determined by the balance of driving and elastic forces. The smallest one is able to re-orient the dipolar defect and adjust to a configuration compatible with the wall dale. It finally docks at the wall.