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Use of topological defects as templates to direct assembly of colloidal particles at nematic interfaces

Mohamed Amine Gharbi [a,b,*], Maurizio Nobili [a], Christophe Blanc [a,*]

[a] Laboratoire Charles Coulomb (L2C), UMR5221 CNRS and Université Montpellier 2, Place Eugène Bataillon, 34095 Montpellier, France
[b] Department of Physics and Astronomy, University of Pennsylvania, 209 S. 33rd Street, Philadelphia, PA 19104, USA

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ABSTRACT

In this work, we experimentally investigate the ability of topological defects to guide interfacial assembly of spherical particles with homeotropic anchoring confined to nematic interfaces. We propose two different systems: In the first one, particles are trapped at an air/nematic interface where they spontaneously form various 2D patterns. We demonstrate that the phase transition between these patterns can be controlled by defects formed in the nematic bulk. In the second system, we explore the behavior of particles at the surface of bipolar nematic drops. We found that particles assemble into linear chains and interact with surface defects at the North and South poles of the drop, giving rise to the formation of *star structures* in a self-assembly process. We detail the mechanism that guides the behavior of particles and discuss the role of defects in the formation of the observed patterns.

1. Introduction

During the past 30 years, there has been an increasing interest in investigating particles trapped at interfaces between two immiscible liquids [1–4]. It is known that the interfacial environment between isotropic phases causes a range of interparticle forces that guide the assembly of particles and arrange them into two-dimensional systems with rich phase properties [5–8].

Recently, it has become evident that the trapping of particles at complex fluid interfaces, nematic (N) liquid crystal (LC) interfaces for example, provides additional mechanisms to control 2D ordering transitions, with the ability of building complex artificial structures [9–16]. Let us recall that in a nematic liquid crystal, molecules are locally oriented on average in the same direction, the so-called director n. The presence of the director field strongly modifies the physics of nematic/isotropic liquid interfaces. First, the interfacial energy density $\gamma(n \cdot k)$ now depends on the direction of n with respect to the interface normal k. It usually shows a minimum energy when the director is either parallel (planar anchoring) or perpendicular (homeotropic anchoring) to the interface, which tends to distort the director in the preferred direction. Second, a bulk free energy density is attached to the space variations of the director field n [17] and the distortions due to the anchoring might be energetically costly. Even if generalized Young–Laplace equations (see for example [18]) can be found in the literature, the simplest capillary/elastic problems (such as finding the shape and director field of a nematic droplet) are technically cumbersome. However, fluids (such as air or water) having large interfacial energies (larger than 10^{-3} J m^2) with common thermotropic liquid crystals are much simpler to describe since interface energy dominates nematic elastic energy and therefore controls alone the interface geometry. The director field is then constrained by the boundary conditions and arranges itself to minimize the elastic free energy (classic limit of strong anchoring conditions [19]). The same effects are responsible for the appearance of long-range elastic forces between trapped particles at the interfaces. Due to the nematic anchoring at their surface, particles modify the director in their vicinity. New structures emerge due to the interplay between elastic forces and other lateral interparticles forces that act parallel to the interface. For example we have recently shown that colloidal particles with homeotropic anchoring trapped at flat air/nematic interface form various structures ranging from 1D chains to 2D patterns (stable liquid, hexagonal crystal and amorphous aggregates), depending on the anchoring conditions and the density of trapped particles [20]. In this first set of experiments, the liquid crystal was initially homogeneous and the patterns were not spatially controlled. Moreover transitions between the patterns could not be spontaneously obtained, due to the negligible capillary forces, which were dominated by the strong elastic repulsions at NLC interfaces [21,22]. The present work was stimulated by studies [23,24] which have shown that colloidal particles dispersed in bulk NLC could also interact with fixed defects (disclinations) via

* Corresponding authors. Address: Department of Physics and Astronomy, University of Pennsylvania, 209 S. 33rd Street, Philadelphia, PA 19104, USA (M.A. Gharbi).
E-mail addresses: mgharbi@sas.upenn.edu (M.A. Gharbi), christophe.blanc02@univ-montp2.fr (C. Blanc).

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elastic interactions. In bulk, particles are finally trapped at the core of the defects which provides an original template mechanism but we could expect that the simultaneous trapping by the interface could provide additional flexible strategies.

In this work, we therefore present an experimental study where we use defects, created in bulk or at nematic surface, to guide interfacial assembly of homeotropic silica beads. We offer two systems obtained by different methods. In the first one, we describe the behavior of particles at an air/nematic interface in the presence of defect lines in bulk. We then detail the role of those defects in confining particles at the interface and controlling their phase diagram. In the second system, we investigate the behavior of particles confined at complex nematic interfaces: at the surface of bipolar droplets. We thus discuss the role of surface defects (boojums) in the creation of new patterns with star-like symmetry.

2. Materials and methods

2.1. Experimental systems

The first system was obtained by trapping dry silica particles of diameter $2R = 3.92$ μm (from Bangslabs) at flat air/nematic interface following reference [20]. The nematic film (thickness range between 10 and 120 μm) was prepared by spin coating 4-pentyl-4-cyanobiphenyl (5CB from Synthon) on a glass slide treated with polyvinyl alcohol (PVA from Sigma–Aldrich) and rubbed along one direction, to ensure oriented planar anchoring. The texture of the nematic is hybrid as shown in Fig. 1, due to the strong perpendicular anchoring of 5CB in contact with air (planar in contact with the base and perpendicular in contact with air).

The second system was obtained by trapping silica particles at the surface of bipolar 5CB droplets dispersed in aqueous solution that contains 1 wt% of PVA, generated in microfluidic glass capillary device following reference [25] (see Fig. 2). The PVA stabilizes 5CB droplets and ensures strong planar anchoring at the 5CB/water interface. Used silica particles were covered with a monolayer of N,N-dimethyl-N-octadecyl-3-aminopropyl trimethoxysilyl chloride (DMOAP purchased from Aldrich) to impose perpendicular anchoring of the nematic at their surfaces. All experiments were performed at room temperature $T = 23$ °C.

2.2. Materials characterization

We used a polarising microscope (LEICA DM 2500P) to observe studied systems equipped with an INSTEC hot stage, a SONY 1024 × 768 digital camera and a Nikon color camera. The shape of the air/nematic interface was characterized using home built interferometric techniques: Vertical Scanning Interferometry (VSI) and Phase Shift Interferometry (PSI). Optical tweezers based on a LEICA DMI 3000 B inverted microscope equipped with a 100× (NA 1.4) oil immersion objective, a 1064 nm laser (YLM 5W from IPG Photonics) and a piezoelectric XY stage (MCL), were also used to manipulate individual particles.

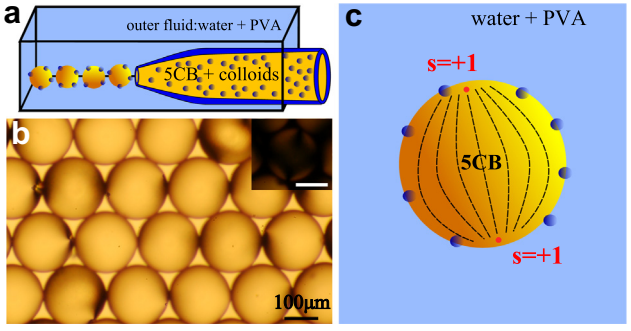

Fig. 2. (a and c) Experimental set-up used to generate monodisperse nematic droplets (b). Inset of (b): POM image of the bipolar configuration of the 5CB drop (bar scale is 10 μm). Silica particles are initially dispersed in the nematic liquid crystal. During the process of droplet formation, they are captured by the water/nematic interface.

3. Results and discussions

3.1. Silica particles at an air/nematic interface

We prepared hybrid nematic films of controlled thickness by imposing unidirectional planar anchoring of the 5CB in contact with the lower substrate. This configuration causes distorted alignment of the director that could involve topological defects, disclinations, separating two domains of different orientations as shown in Fig. 1(a) and (c). The nature of these disclinations evolves along a loop (Fig. 1(b)), from a disclination splay–bend of winding number $m = +1/2$ (Fig. 1(a)) to a disclination of winding number $m = -1/2$ (Fig. 1(c)), as illustrated in the sketch of Fig. 1(d) [26]). Experientially, these $\pm 1/2$ disclinations can be created by heating the nematic to the isotropic phase then cooling the system below the nematic-to-isotrope phase transition temperature T_{NI}. Typically, the loops spontaneously shrink after formation and decrease

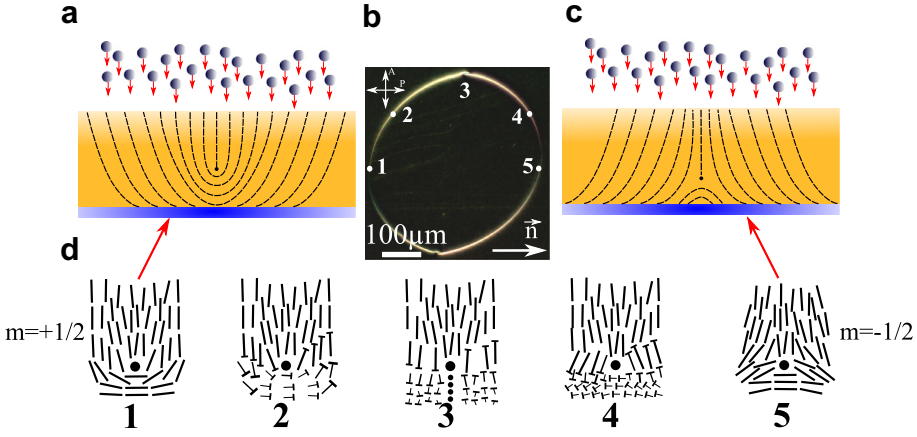

Fig. 1. Silica particles trapped at an air/nematic interface in presence of disclinations in bulk. Schematics of a disclination of winding number $m = +1/2$ (a) and a disclination of winding number $m = -1/2$ (c). (b) Polarized optical microscopy (POM) image of a loop separating two domains of different orientations. (d) Schematics of the continuous transformation along the loop from a disclination $m = +1/2$ to a disclination $m = -1/2$.