Behavior of colloidal particles at a nematic liquid crystal interface

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We examine the behavior of spherical silica particles trapped at an air–nematic liquid crystal interface. When a strong normal anchoring is imposed, the beads spontaneously form various structures depending on their area density and the nematic thickness. Using optical tweezers, we determine the pair potential and explain the formation of these patterns. The energy profile is discussed in terms of capillary and elastic interactions. Finally, we detail the mechanisms that control the formation of a hexagonal lattice and analyze the role of gravity for curved interfaces.

1. Introduction

Colloidal particles confined at liquid interfaces display rich two-dimensional (2D) phase properties. The spontaneous formation of ordered structures such as microcrystals has been mainly studied in simple fluids where the self-arrangement is controlled by direct colloidal interactions (electrostatic, magnetic) and possible capillary effects. The latter might come from the anisotropic shape or the roughness of the particles. It is only recently that an interest has developed in the behavior of particles trapped at an ordered fluid interface. For example, the ability of nematic liquid crystals (NLC) to spontaneously organize micron-size particles into regular patterns at interfaces was recently discussed in Ref. 12. Due to their high susceptibility to external fields in bulk or to surfactants at interfaces, such materials certainly provide new routes to control ordering transitions at liquid interfaces with the possibility of building complex artificial structures. Recent experiments have shown a set of rather exotic phenomena but a convincing explanation for this complex behavior is still being debated. In bulk NLC, additional long-range interactions between particles are present because of a competition between elasticity and NLC anchoring at their surfaces. Colloidal suspensions in a nematic matrix are thus qualitatively different from their isotropic analogues. They display rich self-ordering phenomena involving particles and topological defects. At NLC interfaces, complex ordered structures were also observed in several cases: glycerin droplets or solid beads at nematic/air interfaces or microparticles at a nematic/water interface. All these systems display 2D hexagonal crystals that were ascribed to the competition between a repulsion due to the bulk liquid crystal elasticity and a capillary attraction resulting from the interface distortions caused by the “nematic elastic pressure”. This new type of capillary interaction was however thoroughly discussed in two recent works and its role is not clearly established. To clarify the respective role of the elastic and capillary force a direct force measurement between trapped particles coupled with a careful control of the NLC anchoring on the beads is necessary. It would be also advantageous to study the problem in the simplest possible environment, avoiding the presence of chemicals at interfaces and accurately controlling the bead and the interface morphologies. We therefore chose to design and study a new experimental system with solid particles of fixed shape trapped at the interface between a liquid crystal and the air. The choice of air as the second medium also allowed us to measure accurately the interface morphology through interferometry techniques.

In this work, we present a simple technique for trapping colloids at the flat interface of an aligned thin layer of nematic liquid crystal. By controlling the bead density, the interface curvature and the NLC anchoring, we were then able to establish their respective role in the formation of the colloidal structures. A direct measurement of the pairwise interaction has been obtained with optical tweezers, which allowed us to discuss the respective roles played by NLC elasticity and capillarity.

2. Experimental section

The studied systems are obtained by trapping solid spheres at the interface between air and a nematic liquid crystal. Aggregates of dry silica beads (radius $R = 1.96 \mu m$ from Bangs) are “exploded” by an air pulse in a box. The individual spheres then gently settle on a liquid crystal slab (Fig. 1) which avoids the presence of colloids in bulk. The NLC layer (thickness in the range 10–100 $\mu m$) is obtained by spin coating 4-pentyl-4-cyanobiphenyl (5CB from Synthon) on a glass slide treated with polyimide (EHC Japan) that ensures a strong planar anchoring. The layer exhibits a hybrid texture due to the strong homeotropic...
anchoring at the air interface (Fig. 1 (b)). Homogeneous homeotropic layers have also been studied by using a silane treatment on glass with N,N-dimethyl-N-octadecyl-3-amino-propyl trimethoxysilyl chloride (DMOAP from Aldrich) but the poor wettability of 5CB on silanized surfaces requires using a surrounding glass wall as shown in Fig. 1 (c). Note finally that the beads—initially dispersed in water—were covered with a monolayer of DMOAP following Ref. 20, which ensures a strong homeotropic surface anchoring on 5CB. They were then dried at $T = 110$ °C before use.\textsuperscript{21}

The colloids/NLC systems were observed in transmission mode under a polarizing microscope (LEICA DM 2500 P) equipped with an INSTEC hot stage (temperature regulated at 0.1 °C) and a SONY $1024 \times 768$ digital camera. Birefringence measurements with a Berek compensator were used to determine the thickness of the thinnest hybrid films. The microscope also allows an accurate characterization of interfaces in reflection mode by Vertical Scanning and Phase Shift Interferometries\textsuperscript{22,23} thanks to a Mirau objective ($\times 20$) mounted on a Nano-F (MCL) nanopositioner focusing element. We also used optical tweezers based on a LEICA DMI 3000 B inverted microscope equipped with a $\times 100$ (NA 1.4) oil immersion objective, a 1064 nm laser (YLM 5W from IPG Photonics) and a piezoelectric XY stage (MCL). Silica beads cannot be directly trapped because of the inappropriate index contrast in 5CB but can nevertheless be manipulated with the ‘ghost’ effects due to the alignment.\textsuperscript{24}

Tracking procedures (St Andrews Tracker\textsuperscript{25}) were used to determine accurately the beads position.

3. Results

Observations

We first checked with vertical scanning interferometry that the beads were actually trapped at the interface. The top of a sphere is easily located with a Mirau objective and the height contrast $h$ (see Fig. 1) with the surrounding fluid additionally gives the contact angle of the beads at the air interface $\theta = \arccos\left(1 - h/R\right) = 31$ (±2)°. The surrounding fluid is flat without detectable localized deformation (with a typical vertical resolution of a few nanometers). After the sample preparation, beads begin to organize into larger clusters, depending on their area density, the anchoring conditions and the NLC layer thickness. The planar case is summarized in Fig. 2 and Fig. 3.

Between crossed polarizers, a point defect close to the bead is always observed (Fig. 2 (c)) in thin layers. It is reminiscent of the hyperbolic defect that forms around beads of micrometer size in planar cells.\textsuperscript{16} This defect disappears at large thickness, where the birefringence pattern looks more radial (Maltese cross in Fig. 2 (a)). The patterns formed by the beads correspondingly change as shown in Fig. 3. In thin layers, beads spontaneously form linear chains parallel to the easy axis. Individual colloids are then attracted by those chains which grow and finally collect all surrounding particles. When the thickness increases, the chains are much less defined and are no more observed typically above 40 μm. At larger thicknesses, the patterns are very sensitive to the area density of deposited colloids. This evolution is shown in the top pictures. At a low colloidal density, a stable liquid behaviour is observed. Increasing the density typically above 1000 colloids per mm$^2$, crystalline hexagonal domains appear and form a single crystal in a few hours. If the density is larger (above 10000

![Fig. 1](https://example.com/fig1.png)

Fig. 1 (a) Deposition of colloids at the air liquid crystal interface. The NLC texture is either hybrid due to the strong planar anchoring on polyamide and homeotropic at the air (b) or fully homeotropic on silanized glass (c).

![Fig. 2](https://example.com/fig2.png)

Fig. 2 Evolution of the birefringence pattern given by an isolated bead with the thickness of the nematic layer planarly anchored on the lower substrate. At large thicknesses ($d > 40$ μm), a Maltese cross is observed (a) between crossed polarizers. At smaller thicknesses ($d \approx 40$ μm), an asymmetric pattern (b) is observed and a point defect progressively appears in thin layers (c). The sketches illustrate the possible nematic textures around the beads.

![Fig. 3](https://example.com/fig3.png)

Fig. 3 Patterns formed by 4 μm diameter beads trapped at the air/NLC interface when a strong planar anchoring is imposed by the lower substrate. At large thicknesses ($d \approx 80$ μm) the patterns strongly depend on the colloids density, going from a liquid (a) to a crystal (b) and an amorphous condensed state (c). When the thickness decreases ($d \approx 40$ μm), loose chains are observed (d) and at thin layers, well-defined chains along the easy axis collect the beads (e).
colloids per mm²), an increasing number of amorphous 2D aggregates are observed in coexistence with the crystalline structure. When the anchoring on the lower substrate is homeotropic the same patterns and density thresholds are observed indicating that the colloids interactions are very similar in a homeotropic slab and in large hybrid layers. These observations are somewhat reminiscent of the hexagonal lattices formed by glycerin droplets at the air–liquid crystal interface.10,11 In that case however, the liquid structure at low density and the amorphous condensed state at high density are absent. Two main differences might explain these discrepancies. First the particles we used are solid silica spheres and are not deformed at the interface. Second, the anchoring on DMOAP is strongly homeotropic (the anchoring energy28 is $W \approx 10^{-2}$ J m⁻²) whereas it is planar degenerated on glycerin. The detailed nematic texture still has to be deciphered but two suggestions are sketched in the top of Fig. 2. They are based on observations of beads with homeotropic anchorings dispersed inside nematic planar cells which show the presence of either a hyperbolic hedgehog point defect or a Saturn ring.16

**Bead–bead interaction**

As said above, the nature of the interactions between colloids trapped at a nematic interface is still debated. First let us note that the patterns described in Fig. 3 are observed only below the nematic-to-isotropy phase transition temperature $T_{NI}$. They suddenly disappear above $T_{NI}$ in the isotropic phase where the beads move independently under Brownian motion except when they come into close contact. This observation shows that the nematic organization is at the origin, either directly or indirectly, of effective bead–bead interactions and rules out other direct bead interactions (screened Coulombic, van der Waals... interactions). The hexagonal lattices of glycerin droplets16 or microparticles13 have been explained by the existence of an equilibrium inter-bead distance. The latter results from the nematic elastic repulsion competing with a capillary attraction arising from the nematic pressure on each bead. In a recent paper however, Oettel et al.18 shows that the weak interface deformation cannot account for the observed effects. The possible role of many-body interactions in stabilizing the structures has also been discussed recently in Ref. 19. An equilibrium distance between two particles is, however, hardly compatible with the various observed structures and we focused on the bead–bead pair potential. With optical tweezers, two isolated beads are approached at an initial distance $r_0$ and are tracked after trap release. We show in Fig. 4 (a) a typical evolution of the separation distance $r$ at $T = 21$ °C. As long as $r_0$ is larger than $r_0 = 10.5 \pm 0.5 \mu m$, the beads move away from each other. They irreversibly aggregate for $r_0 < r_0$ with a final separation of 1 μm. Averaged over several trajectories, the interaction force $f_0$ can be obtained from the Stokes law,24 and the pair potential energy $E_0$ by its integration.27 The latter is given in Fig. 4 (b). For beads with homeotropic anchoring, our observations therefore prove that an unstable equilibrium distance $r_a$ separates a region of attraction at short distances, and of repulsion at larger ones. The value of $r_a$ is roughly constant with the thickness (above 40 μm) and the pair orientation, indicating that the lower planar anchoring is screened by the homeotropic anchoring on air. Such a pair

![Fig. 4](image-url)  
**Fig. 4** (a) Time dependence of the separation distance between two isolated particles released at $10.5 \mu m$ and at $11 \mu m$ (inset). (b) Corresponding pair potential (arbitrarily fixed at $k_BT$ at $r = 20 \mu m$) derived from several bead trajectories. Inset: zoom around the unstable equilibrium distance $r_a$.

energy profile differs from the one between two glycerin droplets expected in Ref. 10. We first checked if the repulsive part between two trapped beads was compatible with a “pure bulk” elastic interaction in a large-distance multipolar development. Whatever the exact nematic texture, the homeotropic anchoring at the air forbids a dipolar distortion14 around a bead (for textures with cylindrical symmetry). Phenomenological multipole expansion and symmetry arguments yield the following pair potential for the non-zero quadrupole moment:28

$$E_0 = \frac{36\pi K\beta^2 R^6}{r^3}, \quad (1)$$

where $K \approx 10^{11}$ N is the 5CB elastic modulus in the one constant approximation and $\beta$ a coefficient of order unity. The repulsive trajectory is then given by the competition between the drag force $f_v = -\gamma v = -\gamma dr/2$ and the potential energy $E_0$:26

$$r(t) = (2520\pi K\beta^2 R^6/\gamma + r_0^3)^{1/3}. \quad (2)$$

This expression correctly fits the trajectories (Fig. 4 (a)) with $\beta = 2.1 \pm 0.2$. To explain the short distance attraction, we first examined the simple approach of Ref. 10 that consists in adding a capillary attraction term. The corresponding logarithmic dependence is however overwhelmed by the algebraic elastic dependence at short distance. A more refined approach derived from Ref. 18 yields the same conclusion: an additional capillary attraction is unlikely to be responsible for the observed attraction. A strong reorganization of the director field could however explain it, as already observed in the short distances binding observed for homeotropically-treated beads in bulk nematic films29 and also supported by the similitude of the pair potential profile with the one theoretically computed for infinite parallel
cylinders located at the nematic/isotropic interface in Ref. 30 where such a reorganization clearly appears at short distances.

### Role of many-body effects into the formation of hexagonal lattices

The pairwise potential qualitatively explains the structures formed by the trapped beads. At low densities, the mean distance \( r_m \) between two beads is much larger than \( r_a \) and a liquid is observed. The hexagonal patterns spontaneously form for intermediate densities (where \( r_a < r_m \)) due to the strong inter-bead repulsion. The lattice period is however limited by \( r_a \) and for large enough densities (\( r_m < r_a \)) some particles spontaneously and irreversibly aggregate. Differently from the glycerin droplets case, the period is therefore not unequivocally defined but changes with area density. To probe if many-body effects strongly influence this scenario, a known additional interaction was applied on the crystals. We used slightly convex air–NLC interfaces resulting from a non-perpendicular contact angle on a cylindrical clean glass tube (see Fig. 1 (c)). After the deposition (at a weak density), the beads converge to the center. After a few days they form stable large crystals with a period depending on the distance \( x \) from the center. When more beads are added at the periphery the system reaches a new equilibrium with a decreasing distance \( r \) from the center. When more beads are added at the periphery the system reaches a new equilibrium with a decreasing distance \( r \) from the center. When more beads are added at the periphery the system reaches a new equilibrium with a decreasing distance \( r \) from the center. When more beads are added at the periphery the system reaches a new equilibrium with a decreasing distance \( r \) from the center.

\[
\Delta m \sin(a x) a(x) = -\frac{\partial \Pi(x)}{\partial x},
\]

(3)

where \( \Delta m \) is the effective mass of a buoyant trapped bead and \( a x \ll 1 \) the interface slope. Using eqn (1) as the pair potential, we obtain the form

\[
r = \left( A - B r^2 \right)^{-1/5},
\]

(4)

where \( A \) is an integration constant and \( B = \Delta mg a/756 \pi K \beta^2 R^6 \). This expression fits the data with \( B \approx 1.1 \times 10^2 \) m\(^{-3}\) (Fig. 5(c)) while we measured \( \alpha = 92.2 \) m\(^{-1}\). Although this result yields a slightly smaller value \( \beta = 1.4 \) when calculated for densities \( \rho_{\text{beads}} \approx 2 \) g cm\(^{-3}\) (provided by Bangslabs) and \( \rho_{\text{SCB}} \approx 1 \) g cm\(^{-3}\), we can conclude that the pairwise potential is enough to describe the observed hexagonal patterns at least in a first approximation. Let us however note that a simple pair-wise interaction at short distance would rather yield a condensed hexagonal crystal and not the amorphous condensed state that we observed in Fig. 5 (c) or in the center of convex interfaces. A further study remains to be fulfilled in this regime but we expect that the strong reorganization of the nematic director between beads closer than \( r_a \) necessitates us to take into account many-body effects.

### 4. Conclusions

In conclusion, we have exhaustively described the behavior of microparticles with a homoeotropic anchoring at a nematic/air interface and reported on the first direct measurements of the corresponding pairwise interaction. The latter is found attractive at short distances and repulsive at large ones. The long-range repulsive part is compatible with an elastic quadrupolar interaction. It satisfactorily accounts for the hexagonal crystals we observed under simple or gravitational confinement. This same repulsive interaction could also be at the origin of the recently observed crystals at the NLC/water interface.\(^{13}\) The origin of the attractive part is still an open question. The measured flatness of the interface and the expected spatial dependency of the capillary interaction suggest it also has an elastic origin. One possible mechanism of this all-elastic interaction from repulsion to attraction could be related to a defect transformation with consequent colloidal binding. We are confident that this work will stimulate further experimental and theoretical studies to elucidate these fascinating interfacial phenomena.

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### References and notes

The anchoring was checked by dispersing some beads in a planar 5CB cell where colloidal chains and distinctive birefringence patterns spontaneously form.\textsuperscript{16,20}

The Stokes's law $f = \gamma v$ acting at the velocity $v$ is determined from the diffusion coefficient $D = k_B T \gamma$ obtained from the mean squared displacement of an isolated bead.

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