Behavior of colloidal particles at an air/nematic liquid crystal interface

M.A. Gharbi, 1 M. Nobili, 1 M. In, 1 G. Prévot, 1 P. Galatola, 2 JB. Fournier, 2 and Ch. Blanc 1

1Laboratoire des Colloïdes, Verres et Nanomatériaux(LCVN), UMR5587 CNRS and Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier, France.
2Laboratoire Matière et Systèmes Complexes (MSC), UMR 7057 CNRS and Université Paris Diderot-Paris 7, CC 7056, 75205 Paris, France.

(Dated: July 6, 2010)

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 an hexagonal lattice and analyze the role of gravity for curved interfaces.

PACS numbers: 61.30.Jf,61.30.Hn,64.75.Xc

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. In bulk liquid crystals (LC), additional long-range interactions between particles are present because of the partial order and elasticity. 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 LC interfaces, complex ordered structures were also observed in several cases: glycerin droplets or solid beads at nematic/air interfaces or microparticles at 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 is 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 LC anchoring on the beads as well as of the flatness of interface would be suitable.

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 beads density, the interface curvature and the LC 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 LC elasticity and capillarity.

The studied systems are obtained by trapping solid spheres at the interface between air and a nematic LC at 21°C. Aggregates of dry silica beads (radius $R = 1.96 \mu m$ from Bangslabs) 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 LC layer (thickness in the range 10-100µm) 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-3aminopropyl 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. 19, which ensures a strong homeotropic surface anchoring on 5CB. They were then dried at $T = 110°C$ before use 20.

The colloids/LC 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 1024x768 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 [21, 22] thanks to a Mirau objective (x20) 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 x100 (NA 1.4) oil immersion objective, a 1064nm 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 [23]. Tracking procedures (St Andrews Tracker [24]) were used to determine accurately the beads position.

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 $\theta = \arccos (1 - h/R) = 31(\pm2)$°. The surrounding fluid is flat with 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 LC layer thickness. The planar case is summarized in Fig. 2. Between crossed polarizers, a point defect close to the bead is always observed in thin layers ($d < 30\mu m$). It is reminiscent of the hyperbolic defect that forms around beads of micrometer size in planar cells [13]. This defect disappears at large thickness, where the birefringence pattern looks more radial (Maltese Cross in top left). In thin layers, the 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 $40\mu m$. 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.mm$^{-2}$, crystalline hexagonal domains appear and form a single crystal in a few hours. If the density is higher (above 10000 colloids.mm$^{-2}$), an increasing number of amorphous 2D aggregates (top right picture) 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, the liquid structure at low density and the amorphous condensed state at large one are however 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 energy is $W \approx 10^{-2}J.m^{-2}$ [14]) whereas it is planar degenerated on glycerin. The detailed nematic texture still has to be deciphered but two suggestions are sketched in 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 [14].

As said above, the nature of the interactions between colloids trapped at a nematic interface is still debated.

FIG. 2: Patterns formed by 4μm diameter colloids trapped at the air/NLC interface when a strong planar anchoring is imposed by the lower substrate. In thin samples, chains form along the direction of alignment. They are not observed at large thicknesses ($d > 40\mu m$) where the patterns strongly depend on the colloids density, going from a liquid to a loose crystal and an amorphous condensed state. Sketches illustrate two main possible nematic textures around the beads.
The hexagonal lattices of glycerin droplets [10] or microparticles [13] have been explained by the existence of an equilibrium inter-beads distance. The latter results from the nematic elastic repulsion competing with a capillary attraction arising from the nematic pressure on each beads. In a recent paper, Oettel however [17] 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. [18]. In our case, the nematic elasticity is clearly a key ingredient, since the hexagonal patterns disappear through the nematic-isotropic phase transition. 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 3(a) a typical evolution of the separation distance \( r \). As long as \( r > 10.5 \pm 0.5 \mu m \), the beads move away from each other. They irreversibly aggregate for \( r_0 < r_a \) with a final separation of \( 1 \mu m \). Averaged over several trajectories, the interaction force \( f_p \) can be obtained from the Stokes law [27], and the pair potential energy \( E_p \) by its integration [26]. The latter is given in Fig 3(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 \( \mu m \)) and the pair orientation, indicating that the lower planar anchoring is screened by the homeotropic anchoring on air. Such a pair 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 distortion [17] around a bead (for textures with cylindrical symmetry). Dimensional analysis yields the following pair potential for the non-zero quadrupole moment [27]:

\[
E_p = \frac{36\pi K\beta^2 R^6}{r^5},
\]

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 \( f_d = -\gamma v = -\gamma r/2 \) and the driving force \( f_p = -\partial E_p/\partial r \):

\[
r(t) = \left(2520\pi K\beta^2 R^6 t/\gamma + r_o^7\right)^{1/7}.
\]

This expression correctly fits the trajectories (Fig. 3-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. [17] yields the same conclusion: an additional capillary attraction is unlikely 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 films [28] 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. [29] where such a reorganization clearly appears at short distances.

![Image](image-url)
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-beads 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 univocally 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 changes with area density. To probe if many-body effects can 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.

This work was supported in part by French ANR grant BLAN07-1_183526 “Surfoids”. The authors also thank M. Abkarian for fruitful discussions.

* Electronic address: nobili@cvn.univ-montp2.fr
† Electronic address: blanc@cvn.univ-montp2.fr

[1] U. Gasser et al., ChemPhysChem., 11, 963 (2010).
[2] B. P. Binks, Phys. Chem. Chem. Phys., 9, 6298 (2007).
[3] P. Pierensky, Phys. Rev. Lett., 45, 569 (1980).
[4] T. Terao and T. Nkayama, Phys. Rev. E, 60, 7157 (1999).
[5] A. D. Dinsmore et al., Science, 298, 1006 (2002).
[6] K. D. Danov, and P. A. Krchalovsky, J. Colloid Interf. Sci. 345, 505 (2010).
[7] B. J. Park et al., Langmuir, 24, 1686 (2008).
[8] E. Nouruzifar, and M. Oettel, Phys. Rev. E, 79, 051401 (2009).
[9] K. D. Danov, and P. A. Krchalovsky, Adv. Colloid Interfac. Sci. 154, 91 (2010).
[10] I. I. Smalyukh et al., Phys. Rev. Lett. 93, 117801 (2004).
[11] A. B. Nych et al., Phys. Rev. Lett. 98, 057801 (2008).
[12] I. H. Lin et al., J. Phys. Chem. B 112, 16552 (2008).
[13] G. M. Koeing et al., Proc. Natl. Acad. Sci. USA 107, 3998 (2010).
[14] P. Poulin and D. A. Weitz, Phys. Rev. E 57, 626 (1998).
[15] P. Poulin et al., Nature 275, 1770 (1997).
[16] T. Yamamoto, and M. Yoshida, Appl. Phys. Express 2, 101501 (2009).
[17] M. Oettel et al., Eur. Phys. J. E 28, 99 (2009).
[18] V. M. Pergamenschik, Phys. Rev. E 79, 011407 (2009).
[19] M. Škarabot et al., Phys. Rev. E 77, 031705 (2008).
[20] The anchoring was checked by dispersing some beads in a planar 5CB cell where colloidal chains and distinctive birefringence spontaneously form.
[21] P. J. Caber, Appl. Opt. 32, 3438 (1993).
[22] B. Bhushan, J. C. Wyant and C. Koliopoulos, Appl. Opt. 24, 1489 (1985).
[23] I. Muševic et al., Phys.Rev.Lett. 93, 187801 (2004).
[24] C. Lopez-Mariscal et al., Opt. Express 14, 4182 (2006).
[25] 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.
[26] M. Škarabot et al., Phys. Rev. E 76, 051406 (2007).
[27] T. C. Lubensky et al., Phys. Rev. E 57, 610 (1998).
[28] I. Muševic et al., Science 313, 954 (2006).
[29] D. Andrienko, M. Tasinkevych, and S. Dietrich, Europhys. Lett., 70, 95 (2005).