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Coexistence of Two Colloidal Crystals at the Nematic-Liquid-Crystal–Air Interface

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(Received 25 September 2006; published 1 February 2007)

Glycerol droplets at a nematic-liquid-crystal–air interface form two different lattices—hexagonal and dense quasi-hexagonal—which are separated by the energy barrier and can coexist. Director distortions around each droplet form an elastic dipole. The first order transition between the two lattices is driven by a reduction of the dipole-dipole repulsion through reorientation of these dipoles. The elastic-capillary attraction is essential for the both lattices. The effect has a many-body origin.

Introduction.—Colloidal structures are of a continuing interest for studying general ordering phenomena in condensed matter physics [1,2]. Recently, anisotropic colloidal systems, nematic-liquid-crystal (NLC) emulsions, have been added to the field [3,4]. In NLC emulsions, the particle interactions are mediated by the elastic distortions of the unit vector field, the director n. Because of the anisotropy of surface interactions at the nematic-particle interface, sufficiently large (typically >0.1 μm) colloidal particles induce director distortions in the nematic sensed by other particles [5–11]. This elastic interaction is of long range and in many respects similar to the electrostatic interactions between dipoles, quadrupoles, and so on [6–11]. Particle trapping techniques [12] have been used to test this analogy and to demonstrate experimentally the dipole–dipole [13,14] and quadrupole–quadrupole [15,16] pair interactions. The useful analogy with electrostatics has enabled one to predict theoretically the basic features of few-body systems with the dipole and quadrupole interactions, namely, formation of chain structures (for a review, see [4] and references therein).

The nematic colloids also demonstrate many-body ordered structures, namely, 2D ordering of hard spheres [17] and 2D crystalline hexagonal lattices (HLS) [18] formed by glycerol droplets trapped at the NCL-air interface and stabilized by elastic-capillary interactions [19]. A glycerol droplet trapped at the interface induces director distortions of the dipole type. The elastic dipole might be either perpendicular or tilted with respect to the interface, thus leading to HLS or chain structures, respectively [19]. Dipole reorientations allow the system to explore an additional degree of freedom in the search for equilibrium. In this work, we demonstrate that by reorienting the elastic dipoles when the area per droplet is reduced, the 2D crystalline HL of glycerol droplets at the NLC-air interface can undergo a phase transition into a dense lattice (DL) with a shorter period and different symmetry. The two crystalline structures can coexist. The reverse transition can be induced by an electric field reorienting the dipoles back to the normal state. We also demonstrate the importance of many-body effects in stabilization of the lattice: two droplets separated from the rest find themselves at distances larger than those in the DL.

Results.—The experimental setup was similar to that in [18,19]. A NLC layer (pentylcyanobiphenyl, 5CB, purchased from EM Industries) of thickness h = 30–100 μm is placed onto the free surface of glycerol. At the NLC-air interface, n is normal (homeotropic) while at the glycerol–NLC interface it is tangential, parallel to the interface. The sample is heated up to 50 °C to cause diffusion of glycerol into the LC layer. Cooling down to ~23 °C results in condensation and growth of glycerol droplets, some of which get trapped at the LC-air interface (the droplets might contain a significant amount of water absorbed from air) [19]. Their number and size can be changed by the temperature conditions (higher cooling rate produces smaller droplets). The procedure generally yields an HL [18,19], provided h is much larger than the droplet radius R (typically, 2–7 μm). In such a case the elastic dipoles induced by each droplet are practically normal to the interface despite the overall hybrid alignment of n in the NLC slab. The lattice vectors of HL are not related to the overall tilt of n and the center-to-center droplet separation D_HL measured along different directions is the same within about 7%. For example, within a monocristalline area with no dislocations, containing roughly 100 droplets with R = 2.5 μm, we found D_HL ≈ 10 ± 1 μm, without noticeable dependence on how the lattice vector was oriented with respect to the director tilt in the NLC slab; D_HL was determined by averaging the data in patterns video-recorded every 6 s for 10 min.

The HL undergoes a structural phase transition into a DL when the surface area of the structure is decreased in a cone-shaped Petri dish by changing the amount of glycerol through a syringe at the bottom of the dish, Fig. 1. In a typical experiment, the initial surface area ~400 mm² is reduced to 300 mm² with a rate of 10 mm² per hour. During this process, one observes nucleation of islands of
a new lattice, the DL, with a different symmetry and noticeably shorter period. For example, for $R = 2.5 \mu m$, the typical separations are $D \approx 6 \mu m$, much smaller than $D_{HL} \approx 10 \mu m$ in HL. The DL is not hexagonal, as droplets’ separation is different along the two principal directions $AB$ and $BB'$, Fig. 1(c) and 1(d), with the anisotropy parameter $\xi = (BB')/(AB) \approx 12/11 \approx 1.09$.

Both DL and HL are stable phases separated by the energy barrier; they (co)exist for many days. The HL-DL transition is irreversible: the DL areas remain stable when the total area is increased back by adding glycerol. The structures exist as islands disconnected from the sidewalls, i.e., under no wall pressure, see also [19]. The reverse, DL-HL transition, can be induced by an electric field perpendicular to the lattice, Fig. 2.

In the electric field experiment, we used glass substrates with indium tin oxide (ITO) electrodes coated first by a polymer (Elvamide 8061) film for planar alignment and then by a 50 $\mu m$ thick layer of 5CB. The glycerol droplets were formed by condensation on the plate kept upside down above the vessel with heated glycerol. The DLs appear if a sufficient number of droplets is condensed, Fig. 2(a). The second ITO electrode plate was placed near the free surface in air as to make a gap of 0.5 mm. 5CB is of a positive dielectric anisotropy and thus the field reorients $n$ parallel to itself. The electric voltage $\sim 250$ V, 1 kHz is applied across the gap. It sets the elastic dipoles normal to the interface: the texture of each droplet becomes clearly axially symmetric with four extinction brushes emerging from its center, Fig. 2(b). This dipole reorientation is accompanied by repulsion of the droplets within the DL, and the DL, Fig. 2(a), transforms into an HL with a much larger period, Fig. 2(b).

The electric field experiments also demonstrate that the many-body effects might be essential in the stability of lattices. The electric field applied along the NLC layer forces the droplets to approach each other at distances of the order of $AB$ or even smaller, Fig. 3. In this way, two droplets well separated from the others were brought together, but as soon as the field was switched off the droplets always moved away from each other and established their positions at distances noticeably larger than $D$ in the equilibrium DL. Thus, two droplets repel each other at distances $D$ whereas many droplets form stable lattices with the period $D$.

Discussion.—The director distortion around the droplet, Fig. 1(e) and 1(f), is of the elastic dipole type, with the axis $b$. The interaction energy of two parallel elastic dipoles is [4]

$$U \approx \alpha KR^4(1 - 3\cos^2\psi)/D^3,$$

where $K$ is the elastic constant, $\psi$ is the angle made by $b$ and the center-to-center vector $D$, Fig. 1(d), $D = |D|$, and the coefficient $\alpha$ [19] depends on the specific geometry of distortions. For normally anchored inclusions, Eq. (1) is confirmed experimentally [13,14].
cannot be larger than some gradients should increase sharply. Hence the dipole tilt must find itself in a very restricted volume bounded by the (where the maxima of elastic distortions are concentrated).

For \(m = 0.0024\), similar elementary rhombs \(AB\) can even alter the sign of the interface area occupied by the lattice. Finally, it is seen proportional to the anchoring strength \(AA\) coefficient for the 5CB-glycerol interface and \(0.0027\) of two droplets scales as \(\cos^2\) of the single rhomb can be written in the form

\[
\frac{F}{\alpha KR} = \frac{1}{(\xi r)^3} + \frac{2}{r^3} \left[1 - 3\sin^2\theta(1 - (\xi^2/4))\right] + \gamma_A WR \left(1 - \frac{\xi^2}{4}\sin^2\theta\right) + \gamma_C R \times \left[2\ln\left(\frac{r R}{\lambda}\right) + \ln\left(\frac{\xi r R}{\lambda}\right)\right].
\]

A finite tilt \(\theta\) does not change the dipole-dipole repulsion in the \(BB'\) direction [the first term in (2)], but does reduce that in the \(AB\) direction (the second term),

\(AB' = D\) and \(BB' = \xi D\). The elastic, anchoring, and capillary energy contained in the cell is the sum of four halves of the interaction energy between \(A\) and \(B\), the interaction energy between \(B\) and \(B'\), and the anchoring energy for the area of the NLC-air surface free of the droplets (interaction between \(A\) and \(A'\) screened by the droplets \(B\) and \(B'\) is neglected). Then, regarding for the anisotropy \(\xi\) and introducing the dimensionless distance \(r = D/R \geq 2\), the energy \(F\) of the single rhomb can be written in the form

\[
E_{\text{interaction}} = \int_0^L \frac{d\theta}{d\theta}\int_{-\pi/2}^{\pi/2} \frac{1}{r^3} \left[1 - 3\sin^2\theta(1 - (\xi^2/4))\right] + \gamma_A WR \left(1 - \frac{\xi^2}{4}\sin^2\theta\right) + \gamma_C R \times \left[2\ln\left(\frac{r R}{\lambda}\right) + \ln\left(\frac{\xi r R}{\lambda}\right)\right].
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\]
giving rise to the anisotropy in the tilted phase. The third term $\geq \gamma_A W r^2 \sin^2 \theta$ is that of anchoring at the nematic-air interface, written in Rapini-Papoular form, where the coefficient $\gamma_A \leq 1$ is accounted for that the actual orientation of $b$ is different from that of $n$. For large $r$ the surface anchoring is large if $\theta \neq 0$, and $F$ is minimum for $\theta = 0$ which is the case of HL. For small $r$, however, the capillary attraction and the tilt-induced reduction of repulsion can take over the anchoring energy loss. This picture is confirmed by our calculation. We minimized $F$ for $K = 7$ pN, $W = 10^{-5}$ J m$^{-2}$ [21], $\alpha = 0.1$, and $R = 3$ $\mu$m. The results can be described as following. If the upper bound of the tilt $\theta < \theta_c = 0.55$, then $F$ is minimized by $\theta = 0$ and $\xi = 1$. The curve $F(r, \theta = 0, \xi = 1)$ has a single minimum which takes the experimental value $r_{\text{HL}} = 5$ if $\gamma_C = 5.6 \times 10^{-8}$ J m$^{-2}$. Thus, if $\theta < \theta_c$, the only possible lattice is HL. If, however, $\theta > \theta_c$, then $F(r, \theta, \xi)$ shows two minima, corresponding to DL with $\theta > 0$ and HL with $\theta = 0$, separated by the energy barrier at $r_F \approx 3.9$. Below we describe the results for this case $\theta > \theta_c$. Fig. 4, setting $\gamma_A = 0.2$ for illustrative purposes (the results are similar in a wide range of $\gamma_A W$).

For any $r > r_B$, $F$ is minimum for $\theta = 0$ and no anisotropy, $\xi = 1$; $U$ (1) is maximum repulsive for all droplets, the anchoring term is zero. Here the curve $F(r, \theta = 0, \xi = 1)$ has a minimum at $r_{\text{DL}} \approx 5$ which corresponds to the HL reported in [18,19]. For $2 < r < r_B$, $F$ is minimum for the largest possible tilt $\theta = \theta_m$ and $\xi > 1$; the curve $F(r, \theta, \xi)$ shows two minima, corresponding to DL with $\theta > 0$ and HL with $\theta = 0$, separated by the energy barrier at $r_{\text{DL}} \approx 3.9$. Below we describe the results for this case $\theta > \theta_c$, Fig. 4, setting $\gamma_A = 0.2$ for illustrative purposes (the results are similar in a wide range of $\gamma_A W$).

Conclusions.—Nematic emulsions represent a unique colloidal system with rich ordering phenomena and diverse long range interactions. Using colloids of particular shape and varying their orientational properties in principle allows one to model different types of multipole interactions. We have demonstrated one more unique advantage of the nematic emulsions: they can be used to study a coexistence and mutual transformation of crystalline phases. The strength and symmetry of elastic distortions can be changed by changing the area per particle or by applying the electric field, thus allowing one to switch between the two lattices, HL and DL.

Authors thank Silvija Pirš for providing the Elamidine alignment material. The work was supported by NAS of Ukraine Grant No. #1.4.1B/109, CRDF No. #UK-P1-2617-KV-04, and NSF No. DMR 0504516. A.B.N. acknowledges support from INTAS No. YSF-05-109-5144.