2D Interactions and Binary Crystals of Dipolar and Quadrupolar Nematic Colloids

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In this Letter, we demonstrate that the symmetry of the elastic interaction between the dipolar and quadrupolar colloidal particles in the nematic liquid crystal leads to a novel variety of 2D nematic "binary" colloidal crystals, which have not been observed in any colloidal system. The dipolar-quadrupolar interaction is highly anisotropic and shows a power-law dependence when the particles approach each other along the director field with a pair-binding energy of the order of several thousands of k_BT for 4 μm diameter colloids.

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Over the past ten years, studies of nematic liquid crystal (NLC) colloids have undergone tremendous development, transforming from little more than a collection of qualitative observations into a discipline with a solid theoretical and experimental foundation. It has not only boosted a set of novel concepts, which could provide an understanding of the many strange and interesting observations in NLC colloidal systems [1–11], but is also emerging as a field with great potential for materials with novel property combinations at different structural levels. An impressive example is colloidal crystals assembled from monodispersed microspheres, packed in ordered arrays in 3D, which represent a new class of advanced materials that have great potential for photonic applications [12,13].

It has recently been shown [14] that highly ordered and large-scale 2D colloidal crystals could be assembled by using the elastic colloidal forces, mediated by the thin layer of a nematic liquid crystal. These forces are fundamentally different from the forces of the electric origin, which bind water-based colloids. In NLCs, the forces between colloidal inclusions appear as a result of the perturbation of the orientational ordering of nematics. Each particle distorts the local orientation of the liquid crystal host, and the pair free energy depends on particle separation due to the overlapping of their regions of distortion. This generates forces between colloidal particles in NLCs, which are anisotropic and typically a thousand times stronger compared to water colloids. The nature of these interactions is determined by the director distribution around each inclusion and can be characterized either by localized defects associated with individual colloidal particles or by delocalized defects in the form of disclination lines entangling many colloidal particles [15]. The colloidal interaction, which is mediated by localized defects, is similar to the electrostatic interactions between electric multipoles [6,8] and is responsible for some fascinating self-assembled colloidal structures in liquid crystals, such as 1D chains of dipolar [2,16] and quadrupolar [14] particles, 2D arrangements of colloids at interfaces [17,18], highly ordered 2D colloidal crystals in thin layers of NLCs [14], regular arrays of defects [19], etc.

Despite significant research activities, the experiments have been mostly concentrated on either dipole-dipole or quadrupole-quadrupole nematic colloidal interactions only, and the "mixed" interaction between the inclusions of different symmetry of director distortions has not been studied yet. In this Letter, we report studies of the interaction in "binary mixtures" of the nematic colloids, i.e., the interaction between colloidal particles of "dipolar" and "quadrupolar" symmetry of the surrounding nematic fluid. We show that this mixed type of interactions results in a broad variety of assembled colloidal crystals in 2D, which cannot be realized in any known colloidal system.

The experiments were performed by using silica or acrylic resin composite microspheres (Licristar 40, Merck GmbH) of 4 μm diameter. The surfaces of the particles were covered with DMOAP [*Octadecyldimethyl(3-trimethoxysilylpropyl) ammonium chloride*, ABCR GmbH] to induce perpendicular surface anchoring of NLC molecules. The detailed description of the procedure can be found in Ref. [20]. Wedge-type cells with a thickness range from almost zero to 8 μm were assembled by using glass plates covered with rubbed polyimide PI-2555 (NISSAN chemicals) to ensure good planar alignment of NLC 5CB (4-*n*-pentyl-4-cyanobiphenyl, Merck). The cell is practically flat (0.03–0.04 μm thickness difference) across the 100 μm field of view, and the wedge effects can be neglected.

The experiments were performed at the critical cell thickness h_c, where the dipolar and quadrupolar colloids coexist. For our 4 μm particles, the critical thickness h_c is in the range 6–7 μm [20,21]. The microscope images of isolated dipolar and quadrupolar colloidal particles in the coexistence region are presented in Figs. 1(a) and 1(b). The observation that equal particles create different director

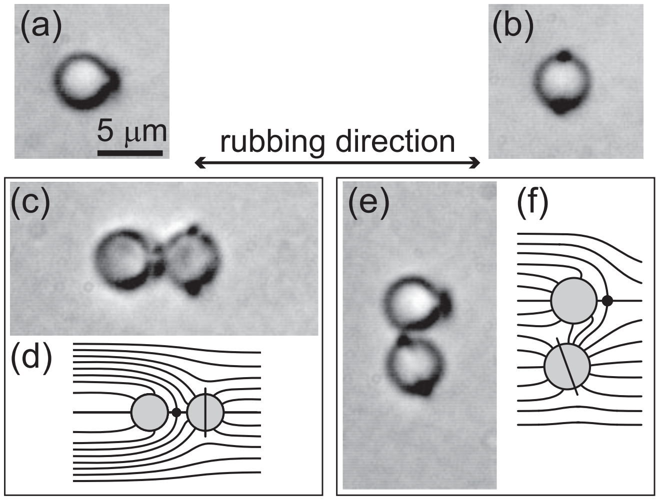

FIG. 1. Microscopic images of (a) dipolar and (b) quadrupolar 4 μm colloidal particles. Dipolar colloids are accompanied by a hyperbolic hedgehog defect (dark spot); quadrupolar colloids have the Saturn ring around them (two dark spots are projections of the ring) [2,5]. (c) A pair of dipole-quadrupole particles, attracted along the LC director and (d) schematics of the director field. (e) Dipole-quadrupole pair, attracted in a direction perpendicular to the bulk director and (f) the corresponding director.

configurations at apparently equal conditions can also be explained with variations of the DMOAP surface coverage [22]. In the experiments, the director field configuration did not switch between the Saturn and hedgehog configurations under the influence of laser light. We have used a laser tweezers setup described elsewhere [10], and the positions of the particles were calculated by using computerized videomicroscopy algorithms [23] with an accuracy of ±5 nm.

We have found that a single pair of dipolar and quadrupolar colloidal particles has three stable equilibrium arrangements, presented in Figs. 1(c) and 1(e). Figure 1(c) shows the first stable pair configuration, where the dipolar colloidal particle is attracted directly along the director to the quadrupolar colloidal particle. The pair is stabilized by the hyperbolic hedgehog point defect, which lies in between them, as shown schematically in Fig. 1(d). In the case where the defect is located on the other side of the particle, the interaction between the dipole and the quadrupole is strongly repulsive. There are two additional stable and symmetric pair configurations, where the particles are located sidewise, one of these being shown in Fig. 1(e), and the other is symmetric with respect to the rubbing direction. In these cases, the dipolar particle is attracted to the quadrupolar one at a certain angle with respect to the bulk director field. One can clearly see from Fig. 1(e) that, in the equilibrium, the orientation of the Saturn ring is tilted at an angle of 25° ± 5° with respect to the unperturbed orientation, and the ring seems to be distorted.

In order to measure the pair interaction energy, the particles were positioned by the laser tweezers at different separations from each other and at different angles with respect to the NLC director. The resulting trajectories of the dipolar particle approaching the quadrupolar one are presented in Fig. 2 (solid lines), along with the trajectories (dashed lines) calculated for the dipole-quadrupole interaction energy $E_{DQ} \propto \cos\theta(15\cos^2\theta - 9)/r^4$, derived by using the electrostatic ansatz [6]. For a given orientation of the dipole, the interaction is attractive for most of the

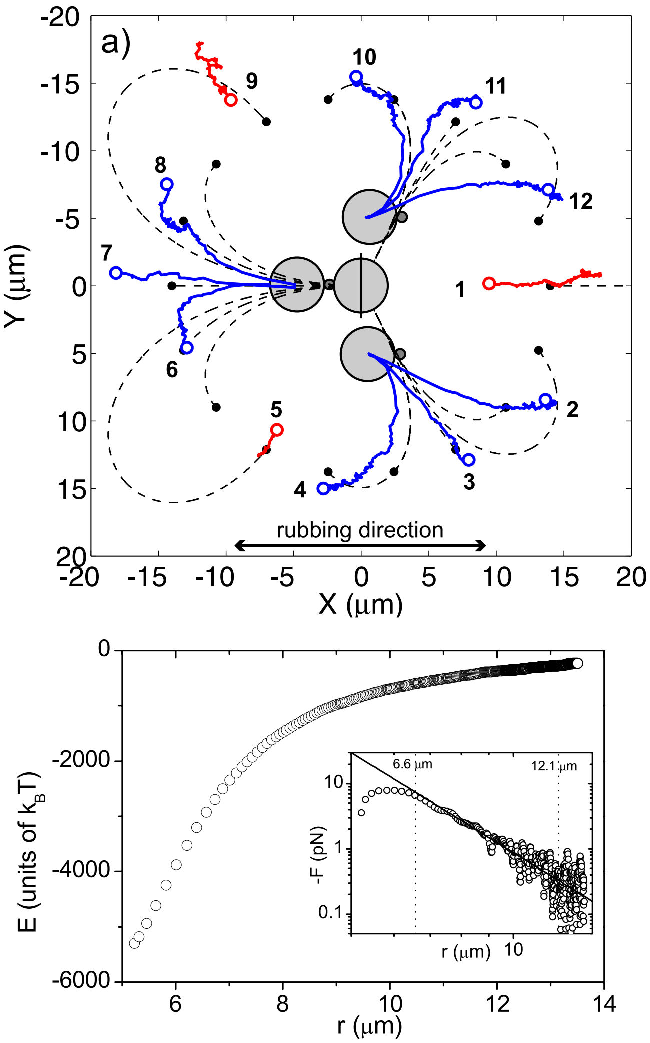

FIG. 2 (color online). (a) Trajectories of the dipolar colloidal particle after it was released from the optical trap near the quadrupolar colloidal particle, which is placed at the origin. Blue lines (2–4, 6–8, 10–12) show the attractive trajectories, red lines (1, 5, 9) show repulsive trajectories, and black dashed lines are calculated by using an electrostatic ansatz [6]. Open circles and black dots indicate the starting positions. The Saturn ring orientation corresponds to trajectories 5–9. It is tilted like in Fig. 1(f) for trajectories 10–12 and in the opposite direction for trajectories 2–4. The thickness of the cell is $h = 7$ μm. (b) The interaction potential as a function of separation between a pair of a dipolar and a quadrupolar colloidal particle for the starting position 7. Inset: log-log plot of the interaction force with the best fit to a power-law exponent of -5.1 ± 0.25. Vertical dashed lines indicate boundaries of the fitting region; their values are indicated at the top.

starting positions. Exceptions are here positions 1, 5, and 9, where the force on the dipole is clearly repulsive.

The trajectories of the dipolar particles, which approach the quadrupolar one along the NLC director, reflect the expected symmetry of the dipole-quadrupole interaction. We find a fairly good agreement with the calculated ones when the particles approach each other at a small angle with respect to the director field. The agreement is worse along the trajectories, which are tilted with respect to the NLC director. In this case, the agreement is qualitative at rather large separations, approximately $5R$ and farther. The above discrepancy may be explained by the rotation and distortion of the Saturn ring [Figs. 1(e) and 1(f)], which makes the experimental trajectories sufficiently different from those predicted in Ref. [6].

We have followed the procedure described in Ref. [24] to calculate the interaction potential. By observing the Brownian motion of isolated particles [25], we have determined the product of the effective radius and viscosity along the director field for both types of particles. At the cell thickness of $h \approx 7\ \mu\text{m}$, we have obtained $(R_{\text{eff}}\eta)_D = 1.629 \times 10^{-7}\ \text{kg/s}$ and $(R_{\text{eff}}\eta)_Q = 1.636 \times 10^{-7}\ \text{kg/s}$. By using the equation of motion for each particle $F = 6\pi(R_{\text{eff}}\eta)_i\dot{r}_i$ $(i = D, Q)$ and neglecting their acceleration, we have derived the interaction force as a function of their approach velocity $\dot{r} = \dot{r}_D + \dot{r}_Q$:

$$F = 6\pi\frac{(R_{\text{eff}}\eta)_D(R_{\text{eff}}\eta)_Q}{(R_{\text{eff}}\eta)_D + (R_{\text{eff}}\eta)_Q}\dot{r},$$

Finally, by integrating the force over the separation, the interaction energy $E_{DQ}(r)$ was calculated, which is shown in Fig. 2(b) for the starting position 7. The interparticle force shows for this case a power-law dependence over the center-to-center separation, which is shown in the log-log plot [26–28] in the inset in Fig. 2(b). Although the range of separations is less than one decade, one can still see that the observed dipolar-quadrupolar colloidal interaction follows $F(r) \propto r^{-5.10\pm0.25}$ power law, which is expected for the dipole-quadrupole interaction. Here one needs to note that the measured value of $(R_{\text{eff}}\eta)$ and thus $F(r)$ and $E_{DQ}(r)$ are affected by the cell thickness. Nevertheless, we have found that the power-law exponent does not depend significantly on the thickness of the cell, whereas the magnitude of the interaction energy is thickness-dependent.

Whereas the above experimental data demonstrate that a single pair of dipolar and quadrupolar colloidal particles can adopt three different equilibrium configurations for the selected dipole orientation, the question arises whether one could create 2D colloidal crystals by using this mixed type of interaction. Our experiments give a clear answer that there is indeed a very large variety of stable 2D colloidal crystalline structures, which were assembled by using the laser tweezers.

Figure 3 presents two selected examples (out of many more observed) of 2D binary colloidal crystals assembled from dipolar and quadrupolar particles. The colloidal structure in Figs. 3(a) and 3(b) is assembled from a pair of dipolar and quadrupolar chains, directed along the rubbing direction. This combination of chains repeats in a reverse orientation in the 3rd and 4th rows, resulting in the formation of a dense packed structure with a rectangular 2D unit cell, shown with solid lines. The unit cell consists of two quadrupolar and two dipolar colloidal particles, occupying an area of 93 μm^2 with the lattice vectors $a = 5.1\ \mu\text{m}$ and $b = 18.3\ \mu\text{m}$. The colloidal crystalline structure shown in Figs. 3(c) and 3(d) is of slightly lower surface density, and it is formed from alternating pairs of a single dipole and a single quadrupole. Here there are also two quadrupolar and two dipolar particles in the unit cell, occupying an area of 108 μm^2, with lattice vectors $a = 12.4\ \mu\text{m}$ and $b = 8.7\ \mu\text{m}$. A large variety of 2D structures with other symmetry were successfully assembled as well and will be presented elsewhere. Since colloidal particles are held together by intercolloidal bonds of different strength, the structures differ by their mechanical properties. The first structure in Fig. 3(a) is very stable and can be dragged by the laser trap as a whole. The less-dense structure in Fig. 3(c) has weaker intercolloidal bonds and can be split into separate parts along the double quadrupolar chain by pulling both parts apart by using two laser traps. However, when the separation be-

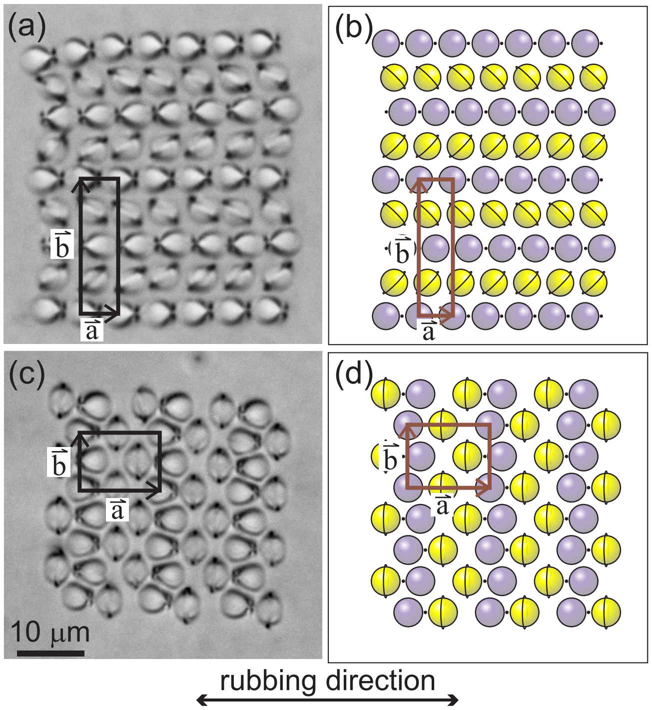

FIG. 3 (color online). (a),(c) Microscopic images of two different, mixed dipolar-quadrupolar 2D lattices of 4 μm particles in a 6.5 μm nematic liquid crystal cell, together with (b),(d) schematic presentations.

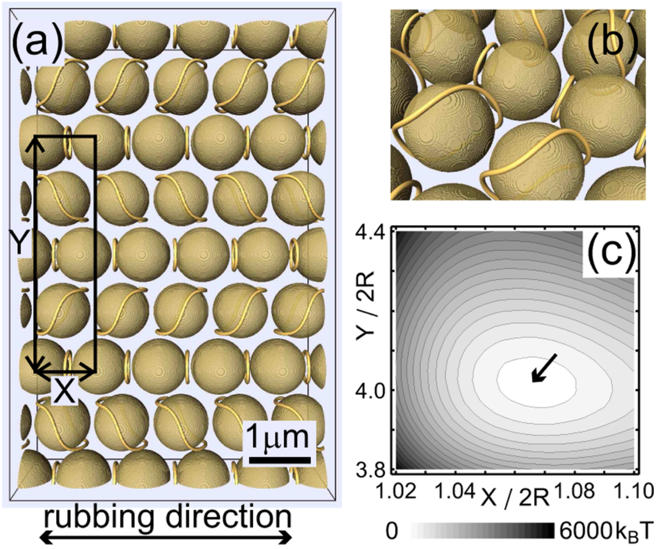

FIG. 4 (color online). Landau–de Gennes simulation of the stability of mixed dipolar-quadrupolar 2D colloidal crystals: (a) the most dense mixed 2D colloidal crystal, (b) close-up of the crystallite showing strongly deformed defect rings, and (c) binding potential of the 2D crystal as a function of the unit cell lattice constants X and Y. Particle radius is $R = 0.5\ \mu$m, the cell thickness is $h = 2\ \mu$m, and the Landau–de Gennes parameters are identical to those used in Refs. [20,29].

tween the two parts is of the order of the size of the colloidal particle, the structural forces bring the two parts together, and the lattice restores itself.

The stability of mixed colloidal crystals in 2D has been investigated by using a numerical Landau–de Gennes approach in its full tensorial form [15,20,29], with a strong Rapini-Papoular anchoring at the surface of the particles and rigid anchoring at the cell surface. The analysis focused on the most dense colloidal structure shown in Fig. 3(a). The results of the theoretical study (see Fig. 4) reveal that defect rings in such 2D binary colloidal configurations can be strongly deformed [see Figs. 4(a) and 4(b)] and typically do not only rotate but also bend to fit into the crystalline lattice. Bending of the defect rings is directly accompanied by the local increase of the elastic energy; however, it also consequently causes the size of the crystalline unit cell to decrease and thus also the total distorted volume of the nematic. The deformation of the disclination ring implies that, in order to describe these binary colloidal systems properly, one needs to use the full nematic order parameter tensor approach.

In conclusion, we have shown that the pair interaction between dipolar and quadrupolar colloidal microspheres in a 2D nematic host is highly anisotropic and in most cases strongly attractive. In the intermediate range, where the screening by surfaces is not relevant, the interaction force shows a power-law dependence $F(r) \propto r^{-5.10\pm0.25}$ along the NLC director, which is consistent with theoretical predictions [6]. We find that, in a binary mixture of dipolar and quadrupolar colloids, this interaction leads to a fascinating variety of 2D colloidal crystals, with structural properties which have not been observed previously. The mixed character of this interaction shows a great potential for assembling binary nematic colloidal crystals with interesting optical and material properties.

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