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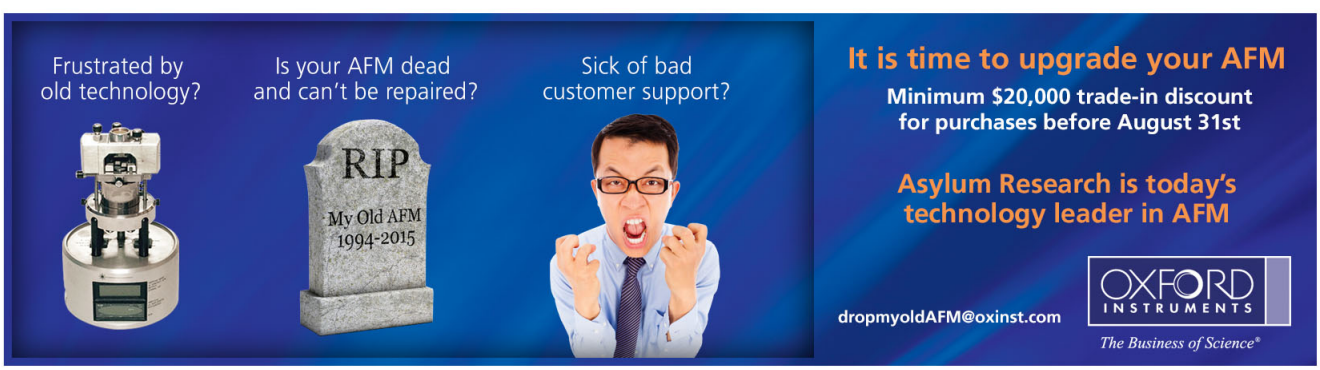

Temperature dependence of equilibrium separation and lattice parameters of nematic boojum-colloids

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We report experimental studies on the temperature dependence of equilibrium separation of a pair of nematic boojum colloids. The interparticle separation is linearly proportional to the elastic anisotropy and the orientation angle with respect to the rubbing direction. The latter result is in agreement with the recent prediction of computer simulations. We prepared two-dimensional colloidal crystals assisted by a laser tweezer and measured the temperature dependence of the lattice parameters. We observe a structural transition in boojum colloidal crystal across the N-SmA transition. The structural transition is mediated by the transformation of boojum defects into focal conic lines across the phase transition. The hexagonal close pack structure of the colloidal crystal in the SmA phase could be useful for designing photonic crystal. © *2015 AIP Publishing LLC*.
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Photonic crystals resemble solid crystals, where the atoms are replaced by larger dielectric particles with high refractive index and the electrons are replaced by photons.[1] Like solid crystals photonic crystals also have the band structure and band gap, consequently, the light with a range of wave vectors corresponding to the band gap cannot propagate. The photonic crystals with capability of varying band gap are known as tunable photonic crystals. One way of tuning the band gap is by changing the lattice spacing of the crystals. This can be done by several ways such as chemical tuning,[2,3] temperature tuning,[4,5] and field tuning.[6,7]

Colloidal particles dispersed in isotropic fluids show two or three dimensional aggregations due to the delicate balance of attractive dispersion forces (e.g., van der Waals) and the repulsive forces (e.g., Coulombic and Steric). In recent years, colloidal particles in liquid crystal (LC) have attracted a lot of scientific interest because of its possibility for the bottom up assembly of photonic crystal. When micron sized spherical colloidal particles are dispersed in anisotropic fluids, such as in nematic liquid crystals, stable defects are accompanied with each colloid.[8,9] It can give two stable defect configurations in the nematic phase when they are treated to promote vertical alignment of the molecules on its surface.[9–11] If the far field director (the average direction of molecular orientation) has the similarity to the field lines of electric dipole, in which a point-like hyperbolic hedgehog defect is associated with each colloidal particle, it is called a dipolar colloid. If the far field director has the similarity to the field lines of electric quadrupole, in which a ring of strength $-1/2$ defect is formed around the equatorial plane of the colloids, they are known as quadrupolar colloids.[11] When the colloids with planar anchoring of LC molecules are introduced, the particle creates a pair of surface defects called boojum, and the particle defect pairs are called as boojum colloids.[11–14] The interaction between two boojum colloids are similar to the quadrupolar interaction and the potential has r^{-5} dependence.[15,16] There are many reports on the theoretical and experimental studies on the associated defects and the colloidal interactions.[17–26] The long range structural elastic forces (typical binding energy of several 1000 k_BT per micron-sized particle) of the medium tends to bind the colloidal particles together. On the other hand, the accompanied point-like defects or loops give rise to a short-range repulsive force. The appropriate balance between these two forces can create diverse structures such as chains, two and three dimensional crystals.[8,9,27,28]

Most of the experimental reports are on the spherical particles dispersed either in nematic or in cholesteric liquid crystals. Very recently, we showed that the hyperbolic hedgehog defects of nematic colloids are strongly influenced by the elasticity and the onset of smectic-A (SmA) layering across the nematic to smectic-A (N-SmA) phase transition. We showed that the hyperbolic hedgehog defect is transformed into a focal conic line in the SmA phase. The phase transition of liquid crystal has a strong influence on the pairwise colloidal interaction.[29] In this letter, we report on the temperature dependence of equilibrium separation of a pair of isolated nematic boojum colloids. We show that the interparticle separation is linearly proportional to the orientation angle with respect to the rubbing direction and is the direct verification of the recent prediction of computer simulation. The hexagonal close pack crystal structure in the SmA phase could be used as a building block to make three-dimensional colloidal crystals.

We used silica microspheres of diameter $2R_0 = 5.2\ \mu$m and 2.34 μm obtained from Bangs Laboratory. Microspheres are coated with MAP (N-Methyl-3 aminopropyl trimethoxysilane, ABCR GmbH and Co-KG) to induce the planar anchoring of LC molecules on the particle's surface. These particles are dispersed in 8CB liquid crystal (4′-n-octyl-4cyano-biphenyl), which is obtained from Sigma Aldrich. The sample is filled in a cell made of thin glass plates sealed with optical adhesive. To induce planar alignment of liquid crystal molecules, glass plates are coated with a polyimide (AL-1254) and rubbed in antiparallel way after curing at 180 °C for 1 h. 8CB liquid crystal exhibits the following

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phase transitions: Cr 21.5 °C, SmA 33.5 °C, and N 40.5 °C I. A laser tweezer was built around an inverted microscope (Nikon eclipse Ti-U) using a CW diode pumped solid state laser operating at 1064 nm (Aresis: Tweez 250si). A computer interfaced acousto-optic deflector was used for the trap movement. The temperature of the sample was controlled by a heater and proportional-integral-derivative (PID) controller with an accuracy of ±0.1 °C. The trajectories of the particles were video recorded with a CCD camera at 20 frames per second. The center-to-center distance between the particles was measured by analysing the video using a particle tracking software with a resolution of ±10 nm.

Figure 1 shows the polarising optical microscope images of a boojum colloid and the transformation of boojum defect across the N-SmA phase transition. A video clip of the defect transformation is given in the supplementary material (video-1).[31] Just above the N-SmA transition, the area of distorted director field around the colloidal particle is extended along the rubbing direction (Fig. 1(b)). The extended regions are observed as a high contrast tails with dark straight lines on both poles of the microsphere. The reshaping of the boojum defect is somewhat similar to that observed in case of hyperbolic hedgehog defect in dipolar colloids across the N-SmA transition.[29] In the latter case, using Landau-de Gennes Q-tensor modeling (in the N phase), we showed that the increase of bend elastic constant (K_{33}) replaces the energetically costly bend distortion by more favorable splay distortion, concentrated in an elongated tail. However, one important difference is that, in case of dipolar colloid, the point defect moves toward the surface of the particle just before the transition, whereas in case of boojum defect similar movement is not observed. In the SmA phase, the brighter regions in the neighborhood of the microsphere indicate that the layers are strongly bent. To construct the molecular orientation around the microsphere, we observed images between crossed polarizers with an additional λ-plate (530 nm) inserted between the sample and the polariser. The red color corresponds to a horizontal orientation of the long axes of the molecules (Figs. 1(d)–1(f)), whereas the bluish and yellowish colors correspond to the clock-wise and anti-clockwise rotation of the director from the rubbing direction.[25] The schematic representations of LC director around the microspheres in the N phase (with boojum) and in the SmA phase (with focal conic lines) are shown in Figs. 1(g) and 1(h), respectively. The preexisting nematic distortion around the particle constrains the equal layer spacing requirement of SmA and hence the tails are transformed into focal conic lines with the cusp angle in the layer structure. These focal conic lines are parallel to the surrounding director, being less and less visible far from the microsphere. Our experimental observations of SmA focal lines around the microsphere are almost similar to the phenomena observed in case of spherical microdroplets of glycerin embedded in aligned SmA liquid crystal by Blanc and Kleman.[30] They calculated the curvature energy due to the spherical inclusion in aligned SmA liquid crystal and showed that the angular discontinuity of layers decreases continuously far from the interface.

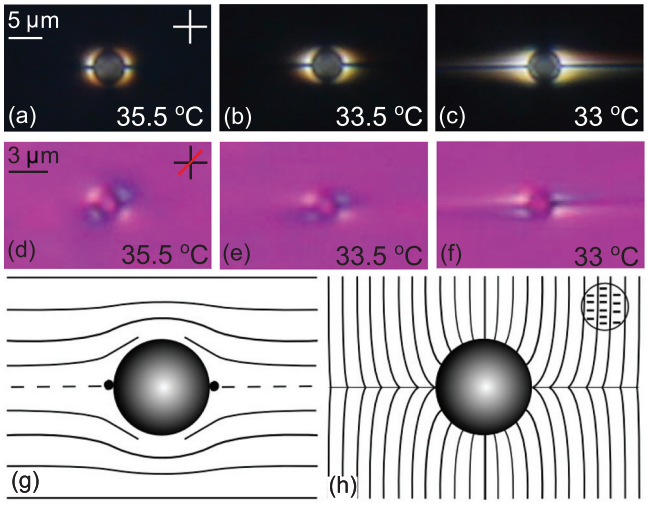

FIG. 1. Polarising optical micrographs of a boojum colloid in a planar cell (a) in the N phase, (b) at the N-SmA phase transition, and (c) in the SmA phase. (See supplementary material, video-1).[31] Photomicrographs of a boojum defect (diameter is 2.34 μm) with a λ plate between the analyser and the sample (d) in the N phase, (e) at the transition, and (f) in the SmA phase. Polarisers are marked with a cross and the λ-plate with a red line in Fig. 1(d). (g) Schematic diagram of the director orientation around the particle with boojum defect. The lines represent the LC director. (h) Schematic representation of SmA layers in the vicinity of the particle with focal conic line defects. A representative director orientation within SmA layers is also shown in a small circular area. Cell thicknesses for particles 5.2 μm and 2.34 μm are 8 μm and 4.5 μm, respectively.

In the nematic phase, boojum colloids are manipulated using a laser tweezer. Figure 2 shows the microscope images of a pair of boojum colloids in the N and SmA phases of 8CB liquid crystal. The focal conic line defects on both sides of the pair are observed in the SmA phase (Figs. 2(b) and 2(d)). The temperature of the sample was decreased at the rate of 0.3 °C per minute and the centre to centre separation (D) of two boojum colloids is measured as a function of temperature using an appropriate particle tracking program. Figure 3(a) shows the temperature dependence of separation across the N-SmA transition of two colloidal particles. The interparticle separation (D/R_0, where R_0 is the radius of the particle) decreases with decreasing temperature in the nematic phase. For example, above the N-SmA transition temperature ($T - T_{NA} \simeq 5$ °C), the equilibrium separation is 6.76 μm and it decreases to 6.2 μm in the SmA phase. A sharp discontinuity in the interparticle separation is

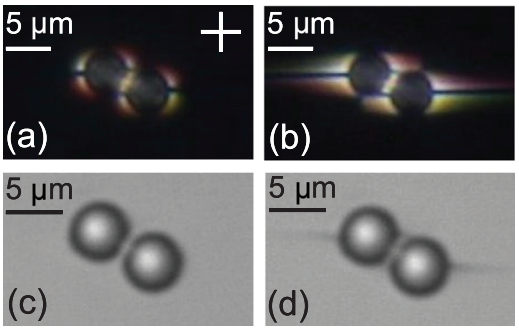

FIG. 2. Photomicrographs of a pair of colloidal particles before and after the N-SmA transition with and without polarisers. (a),(c) N phase (35.5 °C) (b),(d) SmA phase (33 °C). Particle diameter and cell thickness are 5.2 μm and 8 μm, respectively.

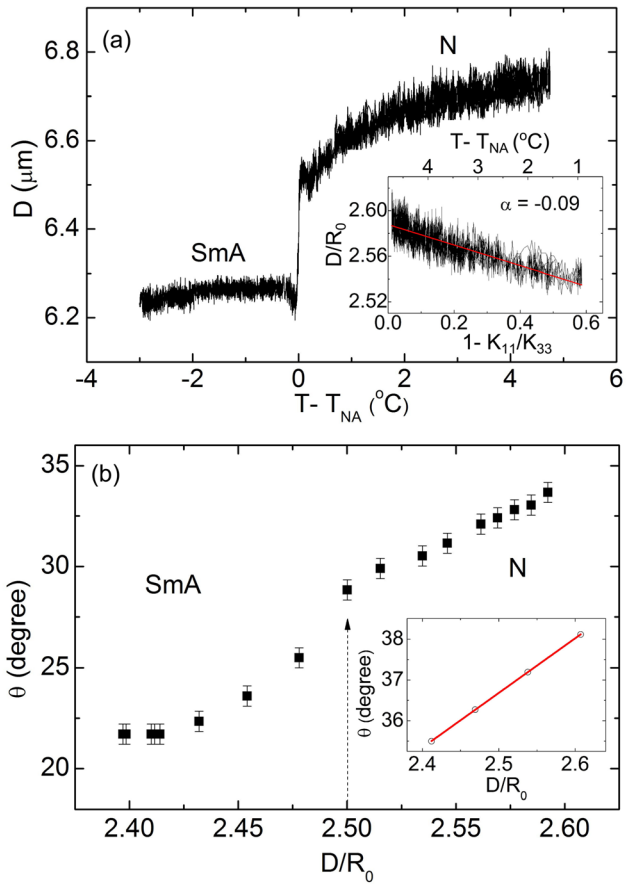

FIG. 3. (a) Variation of center to centre separation (D) between a pair of colloidal particles across N-SmA phase transition.[31] See supplementary material, video-2. (Inset) Variation of D/R_0 above the N-SmA phase transition as a function of the elastic constant anisotropy $(1-K_{11}/K_{33})$. The red line is the best fit with a slope $\alpha=-0.09$. The scale on the top shows the corresponding temperature range. Particle diameter and cell thickness are 5.2 μm and 8 μm, respectively. (b) Variation of θ with D/R_0 obtained from Video-2. The vertical arrow indicates a slope change at the N-SmA transition. (Inset) Computer simulated variation of θ with D/R_0. The simulated points are collected from Ref. 12.

observed, marking the discontinuity of the elastic constants and the onset of smectic layering. In case of dipolar colloids, the interparticle separation shows opposite behavior in the sense that it increases with decreasing temperature.[29] Recently, James and Fukuda[32] theoretically studied the effect of anchoring strength and elastic anisotropy on the separation of a pair of dipolar colloids in the N phase. They showed that in the strong anchoring regime ($K_{33}/WR_0 \leq 0.04$, where K_{33} being the bend elastic constant and W, the anchoring energy), the equilibrium separation increases linearly with the elastic anisotropy. Very recently, it was experimentally verified by us.[29] However, theoretically similar aspects of the boojum colloids have not been studied so far. In order to bring out the effect of elasticity, we collected temperature dependent splay and bend elastic constants (K_{11} and K_{33}) of 8CB liquid crystal from Ref. 33 and interpolated to obtain elastic constants for all temperatures. The inset of Fig. 3(a) shows the variation of D/R_0 as a function of elastic anisotropy $(1-K_{11}/K_{33})$. Interestingly, we observe that the equilibrium separation decreases linearly with increasing elastic anisotropy with a slope of -0.09. This is in contrast to the positive slope observed in dipolar colloids.[32] It would be interesting to supplement our experimental results either by computer simulation or by theory.

Above the N-SmA transition temperature ($T-T_{NA} \simeq 5\,^{\circ}$C), the line joining the centers of two colloidal particles makes an angle $\theta=33^{\circ}$ with respect to the rubbing direction, which is consistent with the previous reports.[16,26] When the temperature decreases, consequently the separation and also the angle decreases. Figure 3(b) shows the variation of angle (θ) with D/R_0 across the N-SmA transition. It decreases with decreasing temperature with a slope change at the transition. For example, in the nematic phase, $\theta=33^{\circ}\pm1^{\circ}$ and it decreases to 22° in the SmA phase. Recently, Mozaffari *et al.*, studied the interaction of nematic boojums and dependence of θ on the interparticle separation by computer simulations.[12] They showed that the particles attract each other at $\theta=60^{\circ}$ and $\theta=30^{\circ}$, with a strong attraction in the latter case. For smaller angles ($\theta\leq15^{\circ}$), the interparticle interaction exhibits a non-monotonous behavior as a function of interparticle separation. They also calculated the free energy of two nematic colloids at various values of D/R_0 and θ. From the global free energy minimum they found that θ decreases with D/R_0. In order to compare, we collected the simulated points from Ref. 12 that coincides with our experimental range of D/R_0 and are shown in the inset of Fig. 3(b). It is observed that the angle decreases linearly with D/R_0 in the nematic phase. Thus, our experimental results qualitatively verified the above prediction. Experimentally, θ decreases more rapidly than predicted in the simulation and this could be due to the specific choice of surface anchoring energy or one elastic constant approximation in the simulation.

Finally, we show the variation of lattice parameters across the N-SmA phase transition in 2D boojum colloidal crystal. We assembled 36 nematic boojum colloids using the laser tweezer and made a 2D crystal in the N phase (Fig. 4(a)). In the N phase, it forms a parallelogram unit cell with lattice parameters $a=b=6.7\pm0.05\,\mu$m and $\gamma=74^{\circ}\pm1^{\circ}$. When the temperature of the sample is reduced, there is a structural change in the crystal lattice (see the supplementary material, video-3).[31] Fig. 4(b) shows the image of 2D crystal in the SmA phase that is obtained by cooling the sample from N phase at the rate of 0.3 °C/min. Images in Figs. 4(c) and 4(d) are taken using a color camera by placing the sample in between crossed polarisers. In the SmA phase, it shows almost a hexagonal close pack unit cell. For example, in the SmA phase the lattice parameters $a=b=6.1\pm0.05\,\mu$m and $\gamma=60\pm1^{\circ}$ (Fig. 4(b)). We measured the temperature variation of all the lattice parameters across the N-SmA phase transition using the particle tracking program. Figure 4(e) shows the temperature variation of a and b in both the phases. It is observed that the lattice parameters a and b are almost equal and decrease with decreasing temperature with a sudden jump at the N-SmA phase transition. For example, both the lattice parameters decrease by about 9% in the SmA phase compared to the nematic phase. Figure 4(f) shows the temperature variation of the angle (γ) across the N-SmA transition. It is observed that in the nematic phase γ decreases almost linearly with a distinct slope change at the transition. For example, in the nematic phase $\gamma=74^{\circ}$ and it decreases to 60° in the SmA phase. In addition, the area of the 2D crystal also decreases from 1082 μm^2

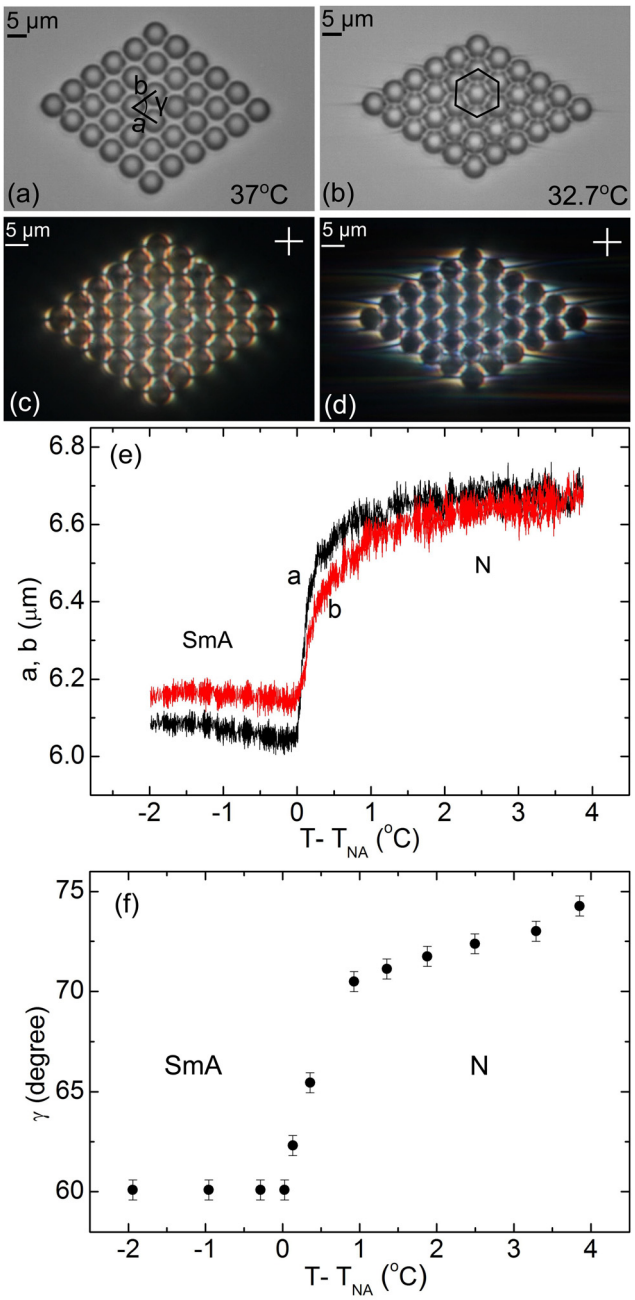

FIG. 4. Optical photomicrographs of a 2D boojum crystal in the (a),(c) N phase (37 °C) and (b),(d) SmA phase (32.7 °C) of 8CB liquid crystal. (a) and (b) without polarisers (c) and (d) with crossed polarizers.[31] See supplementary material, video-3. (e) Temperature variation of the lattice parameters a and b across N-SmA phase transition. (f) Temperature variation of γ across the N-SmA phase transition. Microsphere diameter and cell thickness are 5.2 μm and 8μm, respectively.

(N phase) to 910 μm^2 (SmA phase), which is about 16% reduction compared to the initial crystal area. Thus, the size of the crystal can also be tuned by changing the temperature.

In conclusion, we studied interparticle separation of nematic boojum colloids across the N to SmA phase transition. The dependence of angle of two assembled boojum colloids on the interparticle separation qualitatively agrees with the prediction of computer simulation. The point defects on the poles of the spherical particle in the N phase are transformed to focal conic lines in the SmA phase. The 2D boojum crystal with oblique lattice in the nematic (N) phase changes to a hexagonal close pack structure in the SmA phase showing a discontinuous change in the lattice parameters at the transition. The structural transition is driven by the transformation of topological defects. The tuning of lattice parameters by temperature could be useful for controlling photonic band gap. In addition, by measuring the interparticle separation and studying the topological defect transformation across the phase transition it could be possible to detect subtle phase transitions in various other liquid crystals.

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