Particle size effects on nanocolloidal interactions in nematic liquid crystals

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(Received 13 November 2012; revised manuscript received 16 January 2013; published 4 March 2013)

We study the interactions of submicrometer diameter silica particles, surface functionalized with DMOAP (N,N-dimethyl-n-octadecyl-3-aminopropyl-trimethoxysilyl chloride), in the nematic liquid crystal 5CB (pentylcyanobiphenil). Using the methods of video-tracking dark-field microscopy, we have measured the pair-binding energy of 35- to 450-nm-diameter silica particles, which is in the range between 100 and 1000 k_BT . It is therefore high enough for the formation of thermally stable nanocolloidal pairs of 35 nm diameter. We find that smaller colloids with the diameter around 22 nm do not form thermally stable pairs, which seems to be currently the lower limit for nanocolloidal assembly in the nematic liquid crystals. We also study the particle interactions with point and Saturn-ring defects and discuss the possibility of hierarchical structures generated by particles of different sizes assembled by topological defects.

DOI: 10.1103/PhysRevE.87.032501

PACS number(s): 61.30.Jf, 47.57.J-, 64.75.Yz

I. INTRODUCTION

The development of modern technology has a clear tendency toward further miniaturization of optical and electronic devices. This has led to a significant increase of scientific interest in the search for nanometer scale systems that could controllably self-assemble in space. The aim is the formation of precisely arranged and predetermined spatial aggregates, such as three-dimensional (3D) photonic crystals [1], metamaterials [2], and biological tissues [3], with unusual and controllable electric, optical, chemical, and other properties.

Self-organization is possible when the interacting objects are mobile (that is, in a carrier fluid) and the interactions between these objects (such as nanoparticles, macromolecules, and the like) are strong enough to surmount the thermal fluctuations. The particles therefore organize themselves into spatially organized patterns, which remain stable for a long period of time. The controllable assembling of well-defined hierarchical structures of different sizes and shapes and on many length scales remains a demanding task and requires a complete understanding of the processes and forces responsible for that. Nowadays, several techniques are used for the arrangement of entities on different scales, such as template patterning [4,5], solvent evaporation [6,7], molecular crosslinking [8-11], and laser or optoelectronic tweezers trapping and manipulation [12–19]. The interparticle forces, such as the electrostatic, magnetic, van der Waals [20], and elastic forces mediated by a liquid crystal ordering field [21-25] provide different interactions exhibiting diverse architectures of the assembled structures. In many cases, the lattices are formed from particles with controlled chemical properties of their surface. For example, in liquid crystals, the colloids have to be surface functionalized with different and well-defined surfactants that determine the symmetry and topology of the long-range interactions arising from particle surface-induced elastic distortions in the liquid crystal. Here, the topological defects provide a new and powerful tool for precise micro- and nanoparticles assembly. The colloidal interactions mediated by topological defects generate 2D microlattices and micrometersized split ring resonators [26], and could potentially be utilized in a new field called "soft matter photonics" [27]. Selforganized subunits of hypothetical optical integrated circuits, such as optical microresonators [28] and microlasers [29], semiconductor quantum dots, molecules, nanowires, and metal nanoparticles [30,31], can be implemented for light generation, guiding, and switching in future photonic devices.

The mechanism of microcolloid self-organization in a nematic liquid crystal is well understood and reported in a number of papers [21–25,29,32–35]. Elastic distortion of the nematic liquid crystal (NLC), arising around the colloidal inclusion suspended in the NLC, is energetically costly for a system. When two or more colloidal particles are localized in close vicinity, the regions of their distortions start overlapping and the particles move either towards each other, coalescing in an organized pattern, or repel from each other. Colloidal attraction or repulsion in the NLC is extremely strong and of long range and depends on the detailed nature of the overlapping regions.

In spite of our good understanding of pair interactions in nematic colloids, the nature and strength of nanocolloidal interactions (that is, less than ~ 100 nm) and their self-assembly in the NLCs are still under discussion. The interactions between nanocolloidal particles in the NLC have remained rather unexplored because of their smallness and difficulties associated with observing and tracking their motion. That is, the interparticle forces in the NLCs are measured by following and tracking the trajectories of the particles during their interaction [36,37].

The strength of the colloidal interaction depends directly on the surface anchoring strength of the NLC molecules at the particles' surfaces. The interaction should vanish when the diameter 2*R* of nanocolloids is equal to the surface extrapolation length $\lambda = K/W$, which is of the order of 10–100 nm. Here, *K* is the elastic constant of the NLC and *W* is the surface anchoring strength [38]. It was predicted for 5CB nematic liquid crystal [26] that colloidal pair interaction is comparable to the thermal energy of the particles below the diameter of 50 nm, when the surface anchoring strength is of the order of $W \approx 1 \text{ mJ/m}^2$. It is known that DMOAP-treated silica surfaces induce very strong homeotropic anchoring of cyano-biphenyl liquid crystals, with a typical surface anchoring strength of $W \approx 0.1 \text{ mJ/m}^2$ [39]. This corresponds to the surface extrapolation length of $K/W \sim 50-70$ nm for cyano-biphenyl LCs on DMOAP surfaces, which should be the cutoff limit of nanocolloidal interaction. Recent numerical analysis of size-dependent nanocolloidal interactions [40] has demonstrated that the interaction between nanoparticles suspended in a liquid crystal can be tuned over a wide range of magnitudes (from several to hundreds k_BT) through the control of interfacial chemistry and size. However, these interactions are significant only when the colloids are very close to each other, i.e., separated by ~100 nm, and have the Saturn-ring defect configuration. The analysis predicts that colloidal interaction should vanish at colloidal diameter $2R \sim$ 50 nm for surface anchoring strength of $W \approx 0.1 \text{ mJ/m}^2$.

The size of the particle also dictates the topology of the surrounding nematic liquid crystal, which can be either of a dipolar or quadrupolar symmetry. Early theoretical work [21,35] predicts that the Saturn ring (i.e., quadrupolar symmetry) is an absolutely stable configuration for colloids below \sim 700 nm, and the dipolar configuration is here metastable. Koenig et al. [41] demonstrated that a pair of 169-nm-diameter golden (Au) nanocolloids, surface functionalized by the selfassembled monolayer (SAM) of decanethiol or a mixture of decanethiols and hexadecanethiols, associated and dissociated reversibly at room temperature. The pair-binding energy was found to be very small, i.e., of the order of $\sim 5 k_B T$ and therefore susceptible to thermal fluctuations. Skarabot and Musevic [32] recently reported that DMOAP-treated silica colloids with a diameter as small as 125 nm form colloidal chains in 5CB. This is clear evidence that the colloidal particles induce dipolar symmetry of the surrounding NLC. They measured the binding energy of the 125 nm dipolar colloidal pair and found that it is very high, i.e., of the order of $\sim 700 \ k_B T$. The apparent discrepancies between different experiments on different nanocolloids can be explained by different anchoring strengths and differences in particles' surfaces. Obviously, both the particle size and the surface anchoring strength [42] play an important role in nanocolloids self-assembly in NLCs.

The other open question is related to the interaction between a nanoparticle and different topological defects that are induced by a bigger colloidal particle [26,32] or are generated from walls confining the LC [43]. The trapping of plasmonic nanoparticles of different shapes in topological defects around micrometer-sized colloidal particles was discussed recently in Refs. [44,45]. Nanoparticles of different shapes, covered with acrylate or polystyrene, were observed in the NLC using dark-field and two-photon luminescence. It was found that topological defects possess significant trapping potential of the order of 10 k_BT , which depends on the shape and size of a trapped nanocolloid.

The aim of this work is to study systematically the nanocolloidal pair interaction energy as a function of particle diameter only. All other parameters are kept constant in the experiments, which means that all experiments have been performed on a series of nanocolloidal particles of a single producer, with the same chemical composition and the same surface treatment, but the particles' diameter varied from 450 nm down to 22 nm. The surfaces of the particles were in all cases functionalized with a silane monolayer, giving an excellent homeotropic alignment. The paper is organized as

follows. We first present experimental details and methods in Secs. II and III. Section IV first describes the self-diffusion properties of nanocolloids in 5CB. Then, the pair interactions of nanocolloids of different diameters are described, as well as the interaction of nanocolloids with point hedgehog defects and -1/2 Saturn-ring defects. The main results are presented at the end of Sec. IV, where the colloidal pair-binding energy is shown as a function of colloidal diameter down to 22 nm. We show that silica colloids as small as 35 nm in diameter form stable colloidal pairs if their surface is functionalized with DMOAP.

II. METHODS

We have used four different methods to observe and track the time-dependent position of nanocolloids in 5CB nematic liquid crystal: bright-field (BF) microscopy, crossed-polarized (CP) microscopy, fluorescence microscopy (FM), and darkfield (DF) microscopy. Each of the methods has advantages and disadvantages and they have to be used simultaneously for good characterization of nanocolloidal interactions.

Bright-light microscopy is the simplest imaging technique and can be implemented for the imaging of nanocolloids because of the distortion of the liquid crystal around the nanoparticle. Although this distortion represents an optical inhomogeneity that additionally scatters light and increases the effective particle size, this technique provides a low-contrast and low optical resolution. Crossed-polarized light microscopy is a contrast-enhancing method because the birefringent material generates optical interferences that result in high contrast of the light intensity captured by a photodetector. As most of the light is blocked between crossed polarizers, there are special requirements to the photodetector's sensitivity. Fluorescence microscopy has long been used for the visualization of low-contrast objects or small particles, with fluorescent dyes attached to the surface or incorporated inside the particle. This detection method has no limitation in particle size and enables the visualization of colloids well below the Rayleigh resolution limit (\sim 200 nm). The main disadvantage of this imaging technique is low light emission from dyes, which is caused by several factors. First, the brightness of the colloids is proportional to the amount of dye attached or incorporated into the particle, and it decreases with the particle's size reduction. Second, the brightness and photostability (quenching) of the fluorophores depend on the surrounding liquid and particle capping. In our experience, cyanobiphenyl liquid crystals and DMOAP-monolayer enhance the dye quenching. Third, 5CB liquid crystal and the polyimide alignment layers are by themselves weakly fluorescent in the visible range. This generates additional light background and lowers the image contrast. In our experience, it turns out that the best possible solution is dark-field microscopy. This imaging technique is based on the light scattering at the particle's interfaces and allows for the observation of the particles well below the optical resolution limit. The smaller the particle, the brighter the illumination source and more sensitive the light detecting system are required. The reflectivity of the particle-liquid crystal interface is also an important factor, and gold particles have much higher reflectivity than the silica particles, which have the refractive index only slightly different than the

average refractive index of the liquid crystal. However, as will be shown, this approach has been used successfully in visualizing and tracking the dynamics of silica nanoparticles in 5CB that are as small as 22 nm in diameter.

III. EXPERIMENT

A. Preparation of nanocolloidal dispersion in 5CB

The experiments have been carried out with fluorescently labeled silica nanoparticles with diameter from 22 to 450 nm (Micromod). The particles contain a high amount of covalently bound rhodamine B ($\lambda_{ex} = 569$ nm, $\lambda_{em} = 585$ nm) and are extremely stable in organic solvents and buffers. The scanning electron microscope (SEM) images of particles are presented in Fig. 1, with histograms of the particles' sizes showing a standard deviation of $\pm 10\%$. In another set of experiments, we studied the interaction of nanocolloids with topological defects generated by bigger colloids. Colloids of 5 μ m (silica; Bangs Laboratories) and 10 μ m diameter (borosilicate; Duke Scientific) were used. Strong homeotropic surface anchoring of the nematic LC molecules was ensured by functionalizing the particles with N,N-dimethyl-n-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP). The particles were dispersed in a 2% DMOAP-water solution and mixed for five minutes. DMOAP chemically bonded to the particles surfaces forming a well-defined monolayer. After mixing and stirring, the particles were washed with distilled water several times in order to remove excess DMOAP, and dried for one hour at



FIG. 1. (Color online) SEM images of silica nanocolloids and histograms of colloidal size distribution. (a) 500-, (b) 300-, (c) 100-, (g) 70-, (h) 50-, and (i) 30-nm-sized particles functionalized with DMOAP. (d)–(f) and (j)–(l) show histograms of colloidal size distribution, derived from analysis of SEM images. The calculated mean values of colloidal diameters are (d) 450, (e) 270, (f) 90, (j) 60, (k) 35, and (l) 22 nm. The scale bars are 200 nm in all panels.

120 °C. The particles were then dispersed in 5CB liquid crystal (4-pentyl-4-cyanobiphenyl) at a concentration around 100 ppm. After dispersing, we found that the nanoparticles formed aggregates in 5CB, which most likely formed during the drying procedure. Breaking these aggregates proved to be a very complicated task, which was accomplished by thoroughly mixing and sonificating the dispersion in an ultrasound bath (Elma). The sonification time had to be increased with the decrease of particle diameter and was as long as five hours for 22 nm colloids. As prepared, the dispersions were stable for 24 hours.

Pair interactions of nanocolloids were studied in planar aligned glass cells (Brewer Science; polyimide PI 5291) with a variable gap between 0.7 and 3.4 μ m that were filled with the 5CB-colloidal dispersion. The interactions between nanocolloids and topological defects were investigated in 5.7 μ m planar cells, filled with 5CB dispersion of 5 μ m colloids. For hierarchical assemblies of small and bigger colloids, special cells were made. The upper 0.7-mm-thick glass slide was replaced by 0.13 mm glass to enable the use of high magnification objectives with short working distance. The cell thickness was 16 μ m and was measured in empty cells using the standard white-light interference technique.

B. Bright-field, dark-field, and crossed-polarized light microscopies

Bright-field, dark-field, and crossed-polarized light microscopies were used for the imaging and tracking of nanocolloidal pair interaction on the polarizing microscope (Nikon Eclipse, TI-U) with a water immersion objective (Nikon, NIP Apo 60/1.0 W). For the determination of the hierarchical assembly of big and small colloids, an oil immersion objective (Nikon, 100/1.4 Oil) was used. In order to enhance the illumination system of the microscope, the standard 100 W bulb was replaced by a 250 W halogen lamp with extra cooling. The microscope was equipped with a special oil immersion dark-field condenser (Nikon, NA 1.43-1.20) for high-contrast dark-field imaging. This condenser permits operation with immersion and high magnification objectives and was crucial for the imaging and tracking of nanocolloids. The rays of light travel in a hollow cone formed by the condenser, pass through the objective, and generate a dark region at its focus. In this case, images of even the smallest nanocolloids (i.e., 22 nm) possess high optical contrast. To determine the forces acting on nanoparticles, their motion was recorded by a high speed ultra sensitive camera (Neo CMOS; Andor Inc.). The small pixel size of 6.5 μ m of this camera assisted in the achievement of a very good spatial resolution. The single-particle position as a function of time was determined from the sequence of recorded images using particle tracking software with an accuracy of ± 3 nm. To manipulate a single nanocolloid and assemble hierarchical structures, the laser tweezers setup, based on acousto-optic deflectors, controlled by the computer system and the IR laser, was used (Aresis, Tweez; $\lambda = 1064$ nm).

C. Fluorescent microscopy

For the fluorescent microscopy, a Nikon polarized microscope (Nikon Eclipse, TI-U) was modified. To illuminate the sample, the cw laser light (B&W Tek; $\lambda = 532$ nm, output

power 3 mW) was guided into an air microscope objective (Nikon, Plan Fluor 20/0.5), positioned instead of a bright-field condenser (Nikon, LWD 0.52) above the sample. Its optical axis coincided with the optical axis of the inverted immersion microscope objective. The focus and position of the objective were controlled by 3D microstages. The fluorescent signal was filtered from the green background by a long-pass red filter ($\lambda \ge 560$ nm) located between the inverted objective and the camera. The images were captured by a sensitive Neo CMOS camera (exposure time is around 1 s). The upgraded setup enabled us to apply simultaneously bright-field, crossed-polarized, and fluorescent microscopies, which greatly simplified particle detection and allowed for single colloid manipulation with laser tweezers.

IV. RESULTS AND DISCUSSION

A. Diffusion coefficients

Nematic liquid crystal is a complex anisotropic fluid that possesses a long-range orientational order. NLC rodlike molecules are spontaneously aligned in a preferable direction, which is called the director and described by the unit vector **n**. Inclusions introduced into the NLC cause its local distortion because of the alignment of NLC molecules at the surface of inclusions. As a result of this surface alignment, the topological defects appear. In the case of homeotropic orientation of the LC molecules on the colloidal surface, two configurations of topological defects are possible: Saturn-ring defect (also known as the line defect or disclination) and the point defect (also called hyperbolic hedgehog). The line defect of strength -1/2 encircles the colloid at the "equator." The strength indicates a respective rotation of the director by $-360^{\circ}/2$ [46] and is also called the winding number. The distribution of the director field around a particle established by the Saturn-ring defect has quadrupolar symmetry. In a crossed-polarized microscope, it is presented as a bright distorted birefringent cloud around a particle featured with a dark cross. The point hedgehog defect accompanies a particle and positions along the **n** in the NLC bulk. The director field around the particle has a dipolar symmetry and, between crossed polarizers, appears as two bright hemispheres.

The topological defects determine the nature of interparticle interactions. Elastic dipoles attract to each other, building up chains along the NLC director orientation. Elastic quadrupoles interact and form chains perpendicular to n. The interparticle interaction is measured by tracking the time-dependent positions of two interacting particles, as described by Grier et al. [36]. To this aim, one needs to determine the viscosity coefficient of the interacting particles via observation of the Brownian motion of that particle. To study the Brownian motion, the video microscopies and single-particle tracking techniques were utilized. For each experiment, 18 000 trajectory steps of a colloidal particle were acquired. The recording time depended on the visibility of particles and varied from 3 minutes (100 frames per second) to 15 minutes (20 frames per second). Typical particle trajectories of 18 000 snapshots each are presented in Figs. 2(a)-2(f). To record the motion of 450 nm and 270 nm colloids, the bright-field method was used, as it allows one to use crossed polarizers and particles



FIG. 2. (Color online) Brownian trajectories of silanized silica nanocolloids in a nematic liquid crystal 5CB. The particle mean diameter is (a) 450, (b) 270, (c) 90, (d) 60, (e) 35, and (f) 22 nm. The time between steps is 5, 3.51, 20, 20, 20, and 20 ms, respectively. Videos (a) and (b) are acquired with bright-field microscopy; (c)–(f) are taken with dark-field microscopy. 18 000 trajectory steps are recorded in each experiment. (g) Dependence of particles' diffusion coefficients on the inverse colloidal diameter. Diffusion coefficients of quadrupolar and dipolar colloids along D_{\parallel} (**■**) and perpendicular D_{\perp} (**●**) to the LC director are shown.

could be separated by their defect type. Unfortunately, the particles below 90 nm are not observable by bright-field and crossed-polarized light microscopies. In the former case, they appear as very faded objects on a bright background. In the latter case, the LC distortion around the colloidal particle is very small and merges with the NLC fluctuations. However, videos of silica particles smaller than 90 nm were successfully recorded using dark-field microscopy.

The analysis of a random walk of the particle enables one to estimate the diffusivity along (D||) and perpendicular (D \perp) to the NLC director [37]. From particle tracking data, one can calculate the displacement $\delta_{x,y} = |\mathbf{r}(x, y, t + \tau) - \mathbf{r}(x, y, t)|$ of colloids along the $x(||\mathbf{n})$ and $y(\perp \mathbf{n})$ axes and determine the probability *P* that the particle will diffuse at a certain distance within the time *t*. Recently, it has been demonstrated that in some soft-matter systems, the Brownian motion is not an ergodic process and the displacement distributions cannot be fitted by a Gaussian function [47]. The analysis

Colloidal diameter	Dipolar defect $D_{\parallel} (\text{m}^2/\text{s})$	Dipolar defect D_{\perp} (m ² /s)	D_\parallel/D_\perp	Quadrupolar defect D_{\parallel} (m ² /s)	Quadrupolar defect $D_{\perp} (m^2/s)$	D_{\parallel}/D_{\perp}
450 nm	1.23×10^{-14}	0.85×10^{-14}	1.48	1.5×10^{-14}	1×10^{-14}	1.5
270 nm	1.41×10^{-14}	0.96×10^{-14}	1.47	1.72×10^{-14}	1.2×10^{-14}	1.43
90 nm	2.2×10^{-14}	1.5×10^{-14}	1.47	2.87×10^{-14}	1.94×10^{-14}	1.48
60 nm	2.8×10^{-14}	1.87×10^{-14}	1.5	3.72×10^{-14}	2.46×10^{-14}	1.51
35 nm	4×10^{-14}	2.7×10^{-14}	1.48	5.6×10^{-14}	3.67×10^{-14}	1.53
22 nm	5.8×10^{-14}	3.9×10^{-14}	1.49	8.1×10^{-14}	5.4×10^{-14}	1.5

TABLE I. Diffusion coefficients of dipolar and quadrupolar colloids and anisotropic ratios derived from the experiments.

of our experimental data at different time intervals (up to 2 s) and directions (\parallel and \perp) to **n** has shown that displacement probability distributions can be ideally approximated by a Gaussian function:

$$P(\delta_{\parallel,\perp},\tau) = P_{0,\parallel,\perp}(\tau) \exp[-\delta_{\parallel,\perp}^2/\Delta_{\parallel,\perp}^2(\tau)].$$
(1)

Here, $P_{0,\parallel,\perp}$ is the normalization constant, $\Delta_{\parallel,\perp}^2(\tau)$ is the width of the distribution, and $\delta_{\parallel,\perp}$ is the displacement of the particle along the chosen direction. The width of the Gaussian distribution is directly related to the diffusivity by $\Delta_{\parallel,\perp}^2 = 4D_{\parallel,\perp}/\tau$ [37].

The dependence of the self-diffusion coefficients on the inverse colloidal diameter (d^{-1}) is presented in Fig. 2(g). Each point on the graph corresponds to the average value over ten experiments. As can be seen from the plot, the $D_{\parallel,\parallel}$ depends on the defect type. Bigger colloids (450 and 270 nm) were imaged by bright-field and crossed-polarized light microscopies, and it turns out that bigger quadrupoles have slightly higher self-diffusion coefficients than dipoles. The colloidal defect type for smaller nanocolloids (d < 100 nm) was determined from the analysis of their diffusivity deviations. A typical error in the calculation of D_{\parallel} and D_{\perp} is around $\pm 10\%$, while the experimental data scattering of the $D\parallel$ and $D\perp$ reached more than 30%, which was assigned to different symmetry of the elastic distortion. The obtained data for smaller colloids was therefore separated in two groups corresponding to either dipolar or quadrupolar symmetry. The mean values of D were estimated and plotted in Fig. 2(g).

One can clearly see from this figure that the colloidal diffusivity $D_{\parallel,\perp}$ is linearly proportional to the inverse diameter of the particle d^{-1} . This is quite different from the results obtained in Ref. [32], where the self-diffusion coefficients for silica colloids were nearly constant in the range 125 < d < 500 nm. The discrepancy can be explained by different surface anchoring of the nanoparticles. In this work, we are using fluorescently labeled silica colloids with incorporated rhodamine B. This means that the surfaces of rhodamine-doped particles are not chemically homogeneous and provide less surface active sites for chemical binding of DMOAP molecules. Surface coverage of rhodamine-doped silica colloids with DMOAP molecules is therefore expected to be lower, meaning the surface anchoring energy is lower and the distortion region around a particle is smaller, therefore increasing its diffusivity. By fitting the experimental data in Fig. 2 using a linear function, one can estimate the average D_{\parallel}, D_{\perp} as well as the anisotropy ratio D_{\parallel}/D_{\perp} (Table I).

It is known that colloidal dipolar chains can only form if the elastic dipoles are stable. Stark has predicted [35] that the dipolar colloidal configuration might not be stable for colloidal diameters below 100 nm. However, we found in this work that dipolar colloids are stable down to 22 nm diameter. It is only the relative number of dipolar colloids compared to quadrupolar colloids that strongly decreases with decreasing diameter of the nanocolloid. For instance, we found that nearly 95% of colloids with 450 nm diameter are of dipolar symmetry. However, for 60 nm particles, the number of observed elastic dipoles and quadrupoles is approximately equal. And about only 10-20% of 22-nm-diameter rhodamine-doped silica particles were dipoles. For a colloidal particle in the NLC, the diffusion coefficients D_{\parallel} and D_{\perp} correspond to a colloidal diameter that is larger than the real diameter of the particle. This is because the elastic distorted region around the particle, induced by the surface anchoring, is moving together with the particle, thus effectively increasing its size. The effective size of the colloidal particle is therefore a sum of the real colloidal diameter (d) and the thickness of the NLC distorted region around the particle (d_{rodist}) . From the Stokes-Einstein relation $D = k_B T / (3\pi \eta d)$, where η is the viscosity of 5CB, one can estimate the effective particle diameter $d^* = k_B T / (3\pi \eta D)$. Here the viscosity η of 5CB is taken from Ref. [32], $\eta_{\parallel} = 0.052 \text{ kg/ms}, \eta_{\perp} = 0.075$ kg/ms, T = 298 K, and diffusion coefficients D are taken from the Table I. Figure 3 presents the effective particles sizes as a function of real particle diameter. As one can see, d^*



FIG. 3. (Color online) Dependence of the effective particle size on the colloid diameter. (\blacksquare) for colloids with point defect; (\bullet) for colloids with Saturn-ring defect. The effective colloid diameter is calculated from corresponding diffusion coefficients (Table I).

decreases with particle size and equals approximately 150 nm for 22 nm colloids. That is still about seven times larger than the real diameter of the particle.

B. Nanocolloid pair interactions

Long-range orientational distortions created by the alignment of NLC molecules along curved surfaces of inclusions are responsible for the appearance of forces between colloids. The total free energy of a colloidal pair is different than the energy of individual particles, therefore the particles attempt to minimize it by assembling in different aggregations [48]. This self-assembly mechanism leads to the formation of complex colloidal structures in liquid crystals.

Surprisingly, thermally stable and spontaneously formed nanoassemblies of colloids smaller than 100 nm were observed in our experiments and are presented in Fig. 4. This figure shows micrographs of colloidal dipolar chains assembled from DMOAP-functionalized silica colloids of 450, 270, 90, 60, 35, and 22 nm. Images were acquired with bright-field [first image in Figs. 4(a)-4(f)], crossed-polarized [second image in Figs. 4(a)-4(f)], and dark-field [Figs. 4(a)-4(f)] microscopies. Bright-light images clearly show elongated colloidal associations in the direction parallel to the director **n** [Figs. 4(a)-4(d)]. The bright birefringent parallel lines on the crossed-polarized micrographs are evidence of a single colloidal chain formation, which is characteristic of elastic dipoles. For more complex aggregations, the intensity distribution would have had a more complex structure. One can also clearly see the dipolar chains on images obtained with dark-field microscopy [Figs. 4(a)-4(d)]. Furthermore, this method also enables one to resolve

individual colloids in the assembly all the way down to the Rayleigh resolution limit [Figs. 4(a) and 4(b)] and we could estimate the distance between colloidal centers (L). For 450 and 270 nm particles, the distances between colloidal centers are $L_{450} = (790 \pm 90)$ nm and $L_{270} = (690 \pm 80)$ nm. Obviously, L > d and colloids do not touch each other. The separation s between the particles' surfaces depends on the size of the colloid and corresponds to 2(R - d), where R is the distance from the center of the particle to the point hedgehog singularity [35] and $R \approx 1.3d$ [24]. Hence, s = 0.6d and the distance between the centers of two colloids is L = 1.6d. For 450 nm and 270 nm colloids, we expect from theory $L_{450} \approx$ 720 nm and $L_{270} \approx 430$ nm, respectively. The experimental results for d = 450 nm are close to predicted, but there is 40% discrepancy between theoretical and experimental data for d = 270 nm particles. The possible explanation could be that the theoretical model based on Landau-de Gennes theory does not describe completely the behavior of nanometer-sized colloids and/or additional interaction mechanisms could be involved.

In Figs. 4(e) and 4(f), dark-field micrographs (right panels) show bright spots that are aggregates of nanocolloids. However, there is a lack of evidence from these images of the formation of long dipolar chains for d < 60 nm.

One of the most important parameters describing nanocolloidal assembly is the binding energy (W_o) between a pair of colloids [40]. Binding energy of $1000 k_B T$ is considered strong enough and assures thermally stable associations. To measure nanocolloidal interactions, a pair of colloids were collinearly positioned (i.e., along the director) and released. The time sequences of snapshots of interacting dipolar particles are



FIG. 4. Spontaneously formed structures of silica nanocolloids functionalized with DMOAP in 5CB. The images were acquired with bright-field (left column), crossed-polarized light (central column), and dark-field (right column) microscopies. Mean diameters of colloids: (a) 450, (b) 270, (c) 90, (d) 60, (e) 35, and (f) 22 nm. Images size is $8.7 \times 8.7 \mu$ m.



FIG. 5. (Color online) Series of snapshots of two nanocolloids attracted into a dipolar pair. Mean diameter of colloids: (a) 450, (b) 270, (c) 90, (d) 60, (e) 35, and (f) 22 nm. Images (a) and (b) are acquired with bright-light microscopy; images (c)–(f) are taken with dark-field microscopy. Image size is $11 \times 11 \mu$ m. (g) Dependence of dipolar colloidal pair-binding energy on particle diameter: Squares indicate pair-binding energy of parallel dipolar particles; circles indicate pair-binding energy of antiparallel dipolar particles. The measured binding energy of the dipolar pair is decreasing by reducing the colloid size. (h) Dependence of dipolar pair colloids interaction potential on the separation between colloids: $450 (-\Box-)$; $270 (-\circ-)$; $90 (-\Delta-)$; $60 (-\nabla-)$; 35 (-⊲-); and 22 (-⊳-) nm colloids.

shown in Figs. 5(a)-5(f) for different particle diameters. One can see that dipolar particles always attract each other in the direction $\parallel \mathbf{n}$, regardless of their initial position. For example, in Fig. 5(c), the particles were positioned perpendicular to \mathbf{n} or experienced intermediate Brownian motion such as is shown in Fig. 5(e), but, at the end, they always attracted along the director. This behavior is a clear indication that, surprisingly,

even the smallest particles with diameters 35 < d < 100 nm form dipolar pairs. If these were quadrupoles, they would attract in the direction perpendicular to **n**. The difference between different sizes is that the time interval required for a pair binding increases with the particle size reduction. For 450 nm particles, it takes only 8.24 s to bind, and for 35 nm colloids, the required time drastically increases to ~50 s. In

Fig. 5(f), the 22 nm particles were initially separated by 5 μ m. The fifth micrograph in Fig. 5(f) was obtained after 10.25 s and shows a "dimer" state, where the particles are temporarily bound. The nanoparticles remain in this bound state for the following 50–60 s [sixth to ninth images in Fig. 5(f)]. However, the two particles suddenly dissociate after ≈ 60 s [tenth image in Fig. 5(f)]. A similar dynamics with transient colloidal binding was observed in Ref. [41], where 169-nm-diameter gold particles were used.

The pair interaction potential of nanocolloids was measured using the standard technique. Video microscopy and particle tracking software were used to measure positions of the particles as a function of time. For the recorded trajectories, we could then determine instantaneous velocities of the particles. As Reynolds number $\text{Re} = \rho vr \eta^{-1}$ (~10⁻⁸) of particles is much smaller than one, $\text{Re} \ll 1$, the inertia effects are negligible, $ma \approx 0$. Knowing the diffusivities of colloids, one can calculate the interacting force between the two particles through the force balance equation [32]:

$$\mathbf{F}_{\text{int}} = \mathbf{F}_1 - \mathbf{F}_2. \tag{2}$$

Here, \mathbf{F}_{int} is the interaction force, and \mathbf{F}_1 and \mathbf{F}_2 are the driving forces of the first and second colloid. $\mathbf{F}_{1,2}$ can be found from the balance with the Stokes drag force: $\mathbf{F}_{1,2} = 3\pi \eta d\mathbf{v}_{1,2}$. Hence,

$$\mathbf{F}_{\rm int} = 3\pi \eta d(\mathbf{v}_1 - \mathbf{v}_2),\tag{3}$$

where $v_{1,2} = \Delta r_{1,2}/\Delta t$. As the NLC is an anisotropic material, the diffusion coefficients for motion along and perpendicular to the director are different, and

$$\mathbf{F}_{\text{int},x} = k_B T (v_{x1} - v_{x2}) / D_x, \tag{4}$$

$$\mathbf{F}_{\text{int},y} = k_B T (v_{y1} - v_{y2}) / D_y.$$
(5)

After integrating the measured interaction force along the trajectory, one obtains the pair interaction potential $P_o =$ $\int \mathbf{F}_{int} dr = \int \mathbf{F}_{int,x} dx + \int \mathbf{F}_{int,y} dy$. The minimum of the interaction potential indicates the binding energy W_o of the colloidal pair. Since the region of elastic distortion around nanocolloids did not exceed 0.8 μ m, it was not possible to detect the point defect orientation. However, that orientation was obtained from the analysis of the particle interaction behavior. A large number of videos were recorded and analyzed. According to observations, parallel dipoles strongly attract to each other by moving along the director [Fig. 5(a)]. The attraction between two antiparallel dipoles is weaker and the particles interact at some small angle with respect to the **n** [Fig. 5(b)]. Quadrupoles interact weakly with each other in the direction perpendicular to the n. After identification, they were not taken into consideration.

Figure 5(g) shows the dependence of the binding energy (W_o) of a dipolar colloidal pair on the particle diameter. The initial separation between the particles was, in all cases, set to 5 μ m. In Fig. 5, the antiparallel dipoles are marked as circles (\circ) and the parallel dipoles are marked as squares (\Box). One can see that W_o drastically reduces with decreasing particle size. For the smallest 22 nm nanocolloids, the pairbinding energy is of the order of $W_o \approx 20-50 k_BT$ and is therefore very weak. In a recent work [41], the estimated binding energy of 169 nm colloidal dimers was $\sim 5 k_BT$.

The discrepancy in results can be explained by stronger surface anchoring of DMOAP-functionalized silica particles and much bigger elastic distortions (\sim 150 nm) around these particles.

Using experimental data, one can estimate the interaction force between a 22 nm particle pair, $\mathbf{F}_{int} \approx 0.22$ pN. The Brownian force can be estimated as $\mathbf{F}_{Br} = 2 k_B T v/D =$ $2 k_B T v/\sqrt{D_{\parallel}^2 + D_{\perp}^2}$. For 22 nm particles, $\mathbf{F}_{Br} \approx 0.2$ pN $(k_B = 1.38 \times 10^{-23} \text{ J/K}, T = 298 \text{ K}, v \approx 1.2 \times 10^{-6} \text{ m/s};$ $D_{\parallel} = 5.8 \times 10^{-14} \text{ m}^2/\text{s}, D_{\perp} = 3.9 \times 10^{-14} \text{ m}^2/\text{s})$. We see that the Brownian force is practically equal to the elastic interaction force. This explains why a colloidal dimer is not a very stable colloidal assembly.

Very low binding energy between particles (\sim 20 nm) and thermal fluctuations perform a possibility of obtaining longterm stable dispersions of nonaggregating nanocolloids. This is of particular interest for concentrated dispersions, where many-body interactions are involved. For instance, concentrated golden nanorod composites can exhibit new properties presented neither in isotropic nanodispersions nor in pure LCs, such as polarization-sensitive surface plasmon resonance (SPR), large absorption anisotropy, and enhanced optical birefringence with sign reversal at the longitudinal SPR peak [49].

C. Nanoparticle interactions with topological defects

The segregation of nanocolloids in topological singularities attracted a lot of attention in recent years because it could provide assembly of a new "artificial" type of matter with novel physical properties, such as metamaterials. Topological defects are easily achieved in NLCs by introducing inclusions [25] or by laser realignment [50]. It has been shown theoretically that the aggregation of 50 nm conductive nanoparticles in a -1/2 defect loop around 5 μ m colloids in LC may lead to the formation of split ring resonators (SRR) with resonant frequency of the order of 15 THz [26]. Experimentally, such a ringlike hierarchical superstructure was constructed of 2.3 μ m and 10 μ m microparticles only. Of particular interest is therefore the generation or self-assembly of the superstructures of nanocolloids with sizes close to the nanolevel.

The nature of particle aggregation in topological defects is well understood now. The colloids are driven by an anisotropic interaction force that results from the minimization of the free elastic energy. Nanocolloids migrate from an energetically costly region of distorted NLC to the nearly isotropic region (with reduced order parameter $S \sim 0$) of the defect core [24,45,46]. Here we present a study of the interaction of 90-nm-diameter silica colloids with Saturn rings and hedgehog defects around 5 μ m silica microspheres.

We have used the laser tweezers to position individual 90-nm-diameter nanoparticles of dipolar or quadrupolar topological configurations at a distance of 5 μ m from the hedgehog point defect [Figs. 6(a) and 6(d)] and Saturn-ring defect [Figs. 6(c) and 6(d)]. These defects were generated by 5 μ m silica microspheres. The series of micrographs presented in Fig. 6 illustrate the dynamics of 90 nm colloids in the vicinity of such singularities. The images were acquired with bright-field microscopy. The defect configuration of each nanocolloid was determined with crossed-polarized light microscopy.



FIG. 6. (Color online) Series of snapshots of nanocolloids attracted into microparticle-induced topological defects. The distorted region around nanocolloids exhibits a (a),(c) dipolar and (b),(d) Saturn-ring (quadrupolar) configuration. Nanocolloidal size is 90 nm. Micrograph size is 13 micro m \times 13 μ m. (e) Dependence of nanocolloid binding energy with microparticle-induced point and Saturn-ring defects in 5CB. (f) Dependence of the interaction potential between microparticle-induced singularities and nanocolloids in 5CB. In both panels (e) and (f), squares (\Box) depict dipole nanocolloid–Saturn-ring interaction, circles (\circ) show antiparallel dipoles interaction, triangles (Δ) show quadrupolar nanocolloid point defect interaction. Nanocolloidal size is 90 nm.

The snapshots in Fig. 6(a) depict the attraction of dipolar nanoparticles to the point defect. One can see that the nanocolloid does not move towards the centrally symmetric part of the defect. It is trapped by "side" distortions of the defect core [Fig. 6(a)]. This particle dynamics demonstrates the interaction between two antiparallel dipoles. For quadrupolar nanocolloids, the interaction dynamics with a point defect is different. Figure 6(b) shows that the nanoparticle is attracted to the defect core along the director **n**.

In Figs. 6(c) and 6(d), one can see the attraction of dipolar and quadrupolar nanoparticles by a disclination line encircling the microparticle. As soon as the particle overcomes the energy barrier, it moves towards the disclination line at an angle of $\sim 45^{\circ}$. Similar trajectories were observed in a previous work [43] and explained by the symmetry properties of -1/2 defect lines. We could not find any observable differences in the dynamics of dipolar and quadrupolar nanocolloids; however, a significant discrepancy is associated with their interaction time. For dipolar colloids, the interaction time is 15 s, and for quadrupolar ones, it is much higher, i.e., 70 s.

The binding energies (W_o) of nanocolloids into singularities were determined by the same method described in the previous section. The results are plotted in Fig. 6(g). The experiments were carried out for 450, 270, and 90 nm colloids. The detection of nanocolloids smaller than 90 nm is very problematic. Single colloids are not observable with bright-light microscopy. The dark-field technique is not applicable due to overillumination of the camera's detector by the scattered light from a much bigger micrometer colloid. A reduction of illumination intensity results in a loss of the nanoparticle signal. The fluorescence of an individual nanoparticle is very weak and requires long exposure times to collect a sufficient



FIG. 7. Small 270 nm colloids are attracted into a Saturn ring of 10 μ m colloid. Images are acquired with (a), (b) bright-field and (c), (d) fluorescent microscopies at distances (a), (c) 5 μ m and (b), (d) 0 μ m with respect to colloid waist. 270 nm and 10 μ m colloids are functionalized with DMOAP and suspended in a 5CB liquid crystal cell. Image size is 26 × 26 μ m.

number of photons and detect the particle position. Additionally, 5CB and polymide alignment layers are fluorescing in the wavelength range of the nanoparticle's fluorescent emission. These facts have severely obstructed the direct observation of nanoparticle-singularity interactions.

The experimental results in Fig. 6(g) were fitted by the exponential decay function. For a 90 nm particle, the highest binding energy is achieved for dipolar-line defect interaction $W_o \approx 700 \ k_B T$, while the lowest $W_o \approx 350 \ k_B T$ is for the quadrupolar–Saturn-ring interaction. One can clearly see from Fig. 6(h) that the interaction potential decreases with decreasing particle size and, for 22 nm colloids, the binding energy is of the order of $W_o \approx 100-250 \ k_B T$. It is clear that the binding energy between nanocolloids and defects is much higher than the energy between a pair of nanocolloids, $W_o \approx 20-50 \ k_B T$. Moveover, for such low energies, it is not possible to form thermally stable assemblies of nanocolloids only (Fig. 4) because small nanocolloids (~20 nm) will preferentially migrate towards singularities.

Finally, we discuss a laser-tweezers-guided assembly of 270 nm silica particles towards the line defect of $10 \,\mu$ m colloid. The particles were attracted to the defect core and segregated inside the core, building up a chain.

Figure 7 shows bright [Fig. 7(a) and 7(b)] and fluorescent [Fig. 7(c) and 7(d)] images of a 10 μ m colloid, decorated with 270 nm colloids. Figures 7(a) and 7(c) illustrate the upper of a colloid at a distance $z = 5 \ \mu$ m from the particle waist. Figures 7(b) and 7(d) show the plane at distance $z = 0 \ \mu$ m. Technically, it was possible to fill with colloids a semiring only. Further chain growth inside the ring was obstructed by two factors. First, due to the high interparticle binding

energies (~1200 k_BT), agglomerations grow uncontrollably in all directions inside the ring. Second, the Saturn ring is deformed in the place where the particle approaches the glass surface due to sedimentation. Colloids prefer to remain in the melted core of the ring rather than migrate towards the energetically costly distorted ring region.

Nevertheless, self-decoration of the Saturn-ring defect with small nanocolloids seems to be realistic due to the very low interparticle interactions and much stronger attraction to the massive topological defects. However, the nanoparticle detection (d < 100 nm) within the defect line remains problematic. First, confocal microscopy resolution is limited to ≈ 200 nm. Second, due to very low light emission and a high number of optical elements, the fluorescent signal intensity is strongly reduced. In order to access this region, one should apply another nanoparticles detection technique, for instance, stimulated emission depletion microscopy [51–53].

V. CONCLUSION

Our study of the dynamics and assembly of silica nanoparticles in a nematic liquid crystal compares the advantages and disadvantages of bright-field, crossed-polarized, dark-field, and fluorescent microscopies. We found without a doubt that dark-field microscopy is the superior technique for this purpose and enables one to resolve the dynamics of nanocolloids down to the particle size of \sim 22 nm on a time scale of 50 ms.

Using combinations of different optical microscopies, we have clearly demonstrated the thermally stable formation of nanocolloidal structures with sizes below d < 100 nm. Surprisingly, we conclude from our experiments that even the 35-nm-diameter silica colloids form thermally stable colloidal dimers. This is because of very strong orientational anchoring of 5CB molecules on the surfaces of silica nanoparticles, which is also reflected in the very large elastic distortions of the director field around the nanoparticles. We observe that this region of director distortion is from two to eight times bigger than the original size of the particle.

We have demonstrated that by following the Brownian motion and by analyzing the diffusion coefficients, we could distinguish dipolar and quadrupolar topological configurations for colloids as small as 22 nm < d < 450 nm. We measured the binding energies of dipolar colloidal pairs and we found that for 22 nm colloids, it is quite small, 20–50 k_BT , and the pair formation is thermally unstable. The colloids bigger than 35 nm can form thermally stable structures with binding energies $\approx 100-1000 k_BT$.

The existence of a dipolar defect configuration in colloidal particles with tens of nanometer in diameter (<100 nm) and their rather strong interaction are somewhat surprising. However, by considering typical values of the surface anchoring strength of DMOAP on borosilicate glass surfaces, $W \approx 0.1 \text{ mJ/m}^2$ [39], and the average value of the elastic constant of 5CB at room temperature, $K \approx 7 \text{ pN}$ [54], the surface extrapolation of 5CB at DMOAP silanized silica surface is $K/W \sim 70 \text{ nm}$. It is therefore expected that the surface anchoring is too low to resist the increasing elastic distortion forces due to the curved colloidal interface for a colloidal diameter of the order of 140 nm, where the elastic distortion should vanish and also the interactions. This is in contradiction with the clear observation of dipolar colloidal elastic pair interaction for 35-nm-diameter nanocolloids. It is possible that the liquid crystal anchoring on the surfaces of colloidal particles, used in the experiments, is somewhat larger than that used in the experiments on silanized borosilicate glass [39]. On the other hand, the surface extrapolation length [38] is only an approximate measure for the strength of the orientational anchoring on flat surfaces. This means that the elastic deformation could be large enough and result in significant colloidal interaction even if the colloidal radius is a fraction of the surface extrapolation length. Moreover, it is not straightforward whether we can apply this measure, developed for flat surfaces, to highly curved interfaces also.

We have observed that the colloidal particles used in our experiments are rather highly charged in 5CB, and these results will be provided in a forthcoming paper. A similar effect was observed in colloidal experiments by Tatarkova et al. [55]. This raises the question of the contribution of the surface electric field, arising from the charged colloidal surface, to the strength of orientational anchoring and colloidal pair interaction. Considering that the surface electric field is screened by ionic impurities, the Debye screening length becomes important for the colloidal interaction. This length has been measured before using electrostatic-sensitive atomic force microscope [56] and it is of the order of 60-100 nm at DMOAP silanized glass-8CB interfaces. For bigger colloidal particles, i.e., $R \gg 1 \ \mu m$, the electric field will be efficiently screened over the Debye length and we do not expect electrostatic repulsion. However, when the diameter

of particles is comparable to the Debye length, the repulsion due to equally charged colloidal surfaces will become more and more important.

We studied also the interaction between individual colloids and topological singularities and we found that the interaction between the Saturn-ring defect and the dipolar nanocolloid is the strongest. It is as high as 100–700 k_BT for the inclusion of a 90 nm colloidal particle into the Saturn ring of 5 μ m colloid. We demonstrate the "decoration" of the Saturn ring of a 10 μ m colloid with 270 nm nanoparticles. It is shown that particles easily attract and segregate within the defect line, forming a semiring. Completion of the full ring is technically problematic due to the nanoparticles interactions within the singularity. The strong interparticle interactions result in hierarchical uncontrollable structures. This obstructs the nice single-colloid chain formation inside the line defect. However, self-decoration of the line defect with colloids below 100 nm seems to be realistic due to the low interparticle interactions and significantly high attraction to the topological singularities.

ACKNOWLEDGMENTS

This work was supported by the European Commission Marie Curie project HIERARCHY, Grant No. PITN-GA-2008-215851 (A.V.R.), and the Slovenian Research Agency (ARRS) Contracts No. P1-0099 and No. J1-3612. The authors thank Polona Umek for providing SEM images. A.V.R. acknowledges Miha Skarabot for fruitful discussions.

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A. V. RYZHKOVA AND I. MUŠEVIČ

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