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# Interactions of single nanoparticles in nematic liquid crystal

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## ABSTRACT

We studied interactions of single silica nanoparticles with homeotropic surface anchoring in a confined planar nematic liquid crystal cell. Nanoparticles form stable pairs down to a size of 35 nm with the pair binding energy proportional to the size of the particle. 22 nm particles do not form stable pairs, only metastable states were observed due to strong thermal motion and electrostatic repulsion. These nanoparticles strongly interact with the confining surfaces and the larger clusters, which prevents the formation of stable homogenous dispersions. In addition we have shown that nanoparticles are strongly attracted by topological defects induced by the microparticles. The origin of the attractive forces in nanoparticle dispersions is the minimization of free energy. These forces strongly depend on the strength and type of the liquid crystal anchoring at the surface of the nanoparticles. © 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Nematic liquid crystals (LC) are unique materials with extraordinary optical properties which are widely used in LC display technology. It has been shown that the electrooptical properties of LCDs could be improved and tuned by adding nanoparticles to the LCs [1]. Addition of nanoparticles improves display properties, for example decreases the threshold voltages and reduces the switching times. One of the pioneering researchers in this field was Prof. Reznikov, whose group first doped LCs with ferroelectric nanoparticles to decrease the switching time of displays [2]. He was also a member of the group which studied the effects of the strong electric field induced by the ferroelectric particles on the nematic orientational coupling, clearing temperature, birefringence and dielectric anisotropy [3]. The group of Prof. Reznikov also studied dispersion of carbon nanotubes filled with ferrite in a nematic liquid crystal, where they have observed the reorientation of the LC molecules by an external magnetic field due to the coupling between nanotubes and the LC molecules [4]. This reorientation was observed only close to the aggregated nanotubes and was not homogenous over the whole sample, but a few years later a group from Ljubljana had prepared truly ferromagnetic liquid crystalline material as a dispersion of thin magnetic platelets in a nematic liquid crystal [5]. Another interesting phenomenon is segregation of nanoparticles in topological singularities, which could be used in different applications. It has been shown that dispersion of nanoparticles can stabilize blue and twist grain boundary (TGB) phases [6-8]. In this case nanoparticles are trapped and segregated in the disclination lines of the blue and TGB phases, which decreases the overall free energy and makes the system more stable. Lines are stabilized, because they lose the molten core and the temperature range of these phases is therefore expanded. The group of Prof. Reznikov used this phenomenon to assemble nanoparticles in arrays of disclination lines, created in chiral liquid crystals. Using homogenous LED illumination they were able to manipulate disclination lines and arrays of nanoparticles [9]. Another interesting application of the nanoparticle LC dispersions is metal dispersions which can act as plasmonic materials and metamaterials in photonics. There are several studies of assembling plasmonic nanoparticles in nematic LCs and their optical properties [10–14].

The size of nanoparticles in all display applications should be much smaller than the wavelength of visible light that particles will not reduce the image quality. The main problem of these materials is the preparation of homogenous and stable dispersions [15–17]. There are quite strong interactions between nanoparticles and interactions of nanoparticles with surfaces and defects, which could lead to agglomeration and segregation of nanoparticles and would result in non-functional dispersions. This means that we have to understand the nature of the interparticle forces in nematic LCs in order to understand the stability and the homogeneity of dispersions.

In this contribution we shall review a series of experiments with dispersed silica particles in a nematic LC, ranging in diameters from 1  $\mu$  down to 22 nm [18–20]. We are interested in the interaction between nanoparticles and in the interactions of single nanoparticles with topological defects, surfaces and aggregates. We also explore which methods could be used for nanoparticle observation, tracking and manipulation.

#### 2. Materials and experimental methods

In the experiments we use two types of nanoparticles: fluorescently labelled silica nanoparticles with diameters from 22 to 450 nm





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(Micromod) and silica nanoparticles with diameters from 125 to 310 nm (Bangs Laboratories). In the experiments, where the interaction of nanoparticles with topological defects was studied, particles with 5 µm diameter (Bangs Laboratories) were also used. All particles were treated with the same type of surfactant to ensure stable surface anchoring and reproducible experiments. Strong homeotropic surface anchoring of the nematic LC molecules was ensured by functionalizing the particles with N,N-dimethyl-n-octadecyl-3-aminopropyl-trimethoxysilyl chloride (DMOAP, ABCR). The particles were dispersed in a 2% water solution of DMOAP and a well-defined monolayer of DMOAP was formed at the surface. After mixing and stirring, the particles were washed with distilled water several times in order to remove excess DMOAP, and dried for 1 h at 120 °C. The particles were then dispersed in 5CB liquid crystal at a concentration of around 0.1 wt%. The dispersion was afterwards sonicated with a powerful ultrasonic homogenizer (Up200St, Hielscher) and ultrasonic bath (Elma) to break the aggregates of nanoparticles, which can form spontaneously in dispersions. The sonication time was around 1 h for the smallest particles. Colloidal dispersions were injected into the glass cells with planar alignment, which is achieved by rubbed polyimide layer (PI 51291, Brewer Science). The thickness of the cell was between 1 and 3 µm for the pair interaction measurements and around 10 µm for the measurements of the nanoparticle interaction with the micro-particle induced topological defects.

Bright-, dark-field and crossed polarized light microscopies were used for imaging and tracking of nanoparticles. A polarizing microscope (Nikon Eclipse, TI-U) with water immersion objective (Nikon, NIP Apo 60/1.0 W) was used for observation of nanoparticle interactions. For determination of the assembly of nanoparticles in topological defects around bigger colloidal particles an oil immersion objective (Nikon, 100/1.4 Oil) was used. To increase the illumination intensity, the standard 100 W bulb was replaced by 250 W halogen lamp with extra cooling. Oil immersion dark-field condenser (Nikon, NA 1.43-1.20) was used for dark-field microscopy, which enabled the high contrast observation of very small nanoparticles in a LC, such as the 22 nm nanoparticles. The motion of nanoparticles was recorded by a high speed camera (Neo sCMOS, Andor Inc.). The single particle position was determined as a function of time from the sequence of recorded images using the particle tracking software with an accuracy of app. 40 nm. To manipulate single nanoparticle and to assemble them into topological defects, a laser tweezers set-up based on computer-controlled acousto-optic deflectors and an IR laser was used (Aresis, Tweez,  $\lambda = 1064$  nm). The



**Fig. 2.** Sub-micrometer colloids with diameter from 60 to 310 nm and with strong homeotropic LC surface orientation in a planar nematic cell. The self-assembled chains are parallel to the rubbing direction and typically have dipolar symmetry, which can be observed using polarizing microscope (b–e).

manipulation is achieved by the migration of nanoparticles due to the thermally induced gradient of the order parameter, obtained by focused IR laser in the nematic LC [21].

## 3. Results and discussion

#### 3.1. Observation and self-diffusion of single nanoparticles in nematic LC

It is well known that there are strong interactions between microparticles in nematic LCs due to the distortion of otherwise homogenous nematic field around the particles [22]. This distortion is induced by the



rubbing direction

**Fig. 1.** (a–d) Micrographs of 125 nm silica particle in the 3 µm thick layer of a planar nematic 5CB. Image of a quadrupolar nanoparticle with only a polarizer inserted (a) and between crossed polarizers where the quadrupolar distortion is visible (b). Image of a dipolar nanoparticle with only polarizer inserted (c) and between crossed polarizers with the dipolar distortion (d). (e) Dark-field image of a 22 nm silica particle.

mismatch between the orientation induced by the closed surface of the particle and the far-field homogenous director induced by the flat surfaces of the LC cell. In this contribution we are going to discuss only particles with perpendicular orientation of LC molecules at the surface of particles in a nematic cell with planar anchoring. In this case the director field around the particles can exhibit two different types of the distortion patterns: (i) with dipolar symmetry and the topological point defect or (ii) with the quadrupolar symmetry and the Saturn-ring defect, depending on the surface anchoring strength and the size of the particle. The dipolar configuration is stable for large particles and the strong surface anchoring and the quadrupolar configuration is stable for smaller particles and the weak surface anchoring. In our case the DMOAP coated silica surface has strong anchoring (W  $\sim 10^{-4}$  J/m<sup>2</sup>) [23] and the dipolar configuration is observed for silica microspheres larger than hundreds of nanometers. However, for particles with a diameter of 125 nm both dipolar and quadrupolar configurations can be observed (Fig. 1). When a quadrupolar particle is observed with inserted polarizer, only a dark spot is visible due to the scattering of light at the particle (Fig. 1a), while the Saturn ring cannot be resolved as in the case of larger micro-particles. A crossed-polarizer image of the same particle has a quadrupolar configuration of the distorted nematic with a typical four-fold symmetry (Fig. 1b). On the other hand, for a dipolar particle there are two black spots on the image, one is due to the particle and the other one is due to the point defect which also scatters and depolarizes the light (Fig. 1c). In Fig. 1(b) and (d) one can clearly see the differences between quadrupolar and dipolar configurations obtained between crossed polarizers.

When the size of the particle is decreased, also the distorted region of the nematic liquid crystal is decreased and the single particles cannot be clearly observed with bright-field and polarizing microscopy. In this case dark field microscopy gives much better contrast and even particles with 22 nm diameter can be clearly observed (Fig. 1e). In a dark-field setup the special condenser is used and the particle is illuminated by a hollow cone of light, which illuminates particle only at high incident angles. Because of this only scattered light is collected and the particle appears bright on a dark background. The nanoparticle is clearly observed but one cannot distinguish between the dipolar and the quadrupolar orientations of the director because the particle is much smaller than the diffraction limit of the microscope. Another possibility for observing nanoparticles is through their fluorescence, where the emitted light of fluorescent nanoparticles is observed, but there is a problem with the very low level of the emitted fluorescent light.

When the concentration of nanoparticles is increased, spontaneously self-assembled aggregates and clusters can be observed. The main origin of the aggregation is the decrease of elastic energy and the emergence of attractive forces between particles. Two individual nanoparticles induce larger elastic distortion than a bound pair of nanoparticles. In the case of spherical particles with strong homeotropic anchoring and size above 100 nm, the majority of them behave as dipolar particles and after aggregation they form dipolar chains along the rubbing direction (Fig. 2). Dipolar chains can be observed with polarizing microscopy also in the case of smaller particles down to 50 nm.

By reducing the size of the particles, the induced distortion around them transforms to the quadrupolar one, but this transition is not



Fig. 3. Series of snapshots of two nanoparticles attracted into a dipolar pair. Size of particles: 270 nm (a), 60 nm (b) and 35 nm (c). Images are taken with bright- (a) and the dark-field microscopy (b, c). The separation dependence of the measured potential between two nanoparticles (d).

sharp, because the surface anchoring is different for different particles. The critical size, where the number of dipoles and quadrupoles is approximately equal, is around 70 nm. Using the microscopy we cannot resolve the type of the distortion around the smallest nanoparticles (d = 22 nm). We can only observe their thermal motion and we have measured the different diffusion coefficient for particles of the same sample. It is clear that the particle of the same size with dipolar distortion induces bigger distorted region in comparison to the quadrupolar one and the effective size of the dipolar nanoparticle is bigger. Hence, in the monodisperse sample one can distinguish between different types of particles by monitoring their Brownian motion. However, the coverage with the surfactant may not be quite homogenous and in the case of smallest nanoparticles this could result in the different type of the nematic distortion, which is neither dipolar nor quadrupolar.

To characterize and quantify inter-particle interactions we have performed several experiments with a pair of colloids to observe and measure the pair interaction. The separation dependence and the strength of the pair interaction are determined in several steps. Firstly, two particles are brought to a separation of several microns using the laser tweezers and released. Their motion is video recorded and time dependence of their positions is determined in off-line analysis. Second, the Stokes drag force on both particles is calculated for each position, using the measured velocities and the effective drag coefficient, which is determined in a separate experiment, where the thermal motion in the absence of other particles is observed. The Stokes drag force on the particle is equal to the attractive force, since the acceleration of the particle is negligible. Finally, the attractive force is integrated over the path of the attraction and the minimum value of the inter-particle potential defines the pair-binding energy for the different colloidal sizes. We should note here that the Brownian motion is very strong in the case of smaller nanoparticles and the separation between nanoparticles does not decrease monotonically. Averaging and smoothing procedures of attracting trajectories were used to minimize the effect of Brownian motion.

Fig. 3 shows series of snapshots of two nanoparticles attracted into a dipolar pair for three different sizes of particles. It is clear that nanoparticles can form stable pairs with a binding energy of the order of  $100 k_{\rm B}T$ even for the smallest 35 nm particles. However, not all pairs of the colloids with size below 100 nm form stable pairs. An analysis of a larger number of experiments with 22-90 nm pairs showed that other forms are present as well. We have roughly divided them into three categories: stable pairs, metastable pairs, and pairs without measurable attractive interaction (no pairs). Fig. 4 presents these three different behaviors of colloidal pairs, which resulted in the formation of a stable pair (a,b), a metastable pair (c,d), or no-pair (e,f). We have not observed any permanent binding of two 22 nm particles, so we present a formation of a stable pair with two 35 nm particles. In the case of 22 nm particles, we have observed that two particles can form a temporarily bound pair, which is however unstable and the pair can dissociate after a certain time and then associate again. This process of binding and unbinding can repeat for several times. It clearly indicates the formation of a meta-stable pair of 22 nm particles, with a binding energy close to the thermal energy. Fig. 4d shows corresponding time evolution of the distance of both particles from their starting point (red and blue curves) and the separation between the particles (black curve). One can resolve the random movement of a weakly interacting pair, which migrates away from its starting point. This meta-stable state exists only for a certain time and after several minutes dissociates into two



Fig. 4. The snapshots of pair interaction and the separations of two nanoparticles, initially positioned at a separation of 2–3  $\mu$ m. Blue and red lines show the distance of each particle from its starting position and the black line shows the separation between them. (a) The pair of 35 nm particles forms a stable pair. Two 22 nm particles can form metastable pair (c, d), or they do not show any attraction (e, f).



Fig. 5. Dark-field images of a 22 nm particle, being trapped by a surface defect (a) and the corresponding distance between the particle and the defect (b). Dark-field images of a 22 nm particle, being trapped by an aggregate (c). Red and blue lines show the distance of the particle and the aggregate from their origin, and the black line shows the distance between them (d).

individual particles due to the strong thermal motion. The third possibility is that the particles do not show any measurable attraction and the distance between them increases with time. In the case of 22 nm particles around half of the experiments exhibit metastable state and the other half do not show any attraction. By increasing the size of particles the number of no-pairs and metastable pairs is decreased, while



**Fig. 6.** A series of snapshots of a 90 nm nanoparticle attraction into two types of the topological defects induced by a 5 µm silica particle. The nanoparticle is trapped by the point defect (a) or the Saturn-ring defect (b). The separation dependency of the measured trapping potential of both defects (c).

the number of stable pairs is increased and above 100 nm almost all pairs are stable after they are formed.

There are two main reasons why nanoparticles do not form stable pairs. First, the elastic distortion around small particles is smaller due to the small surface of particles. Moreover, the coverage of the particle's surface with the DMOAP, which induces perpendicular anchoring may not be quite homogenous and therefore the elastic distortion can be reduced substantially. The second reason is the electrostatic repulsion between nanoparticles, since they are charged in the liquid crystal. We have measured the surface charge of particles by measuring the velocities of particles in the external electric field. The estimated value of the total charge of a 22 nm particle is around 35 electron charges, which means that the electrostatic repulsion can prevent the association of nanoparticles. DMOAP is an ionic liquid and can contribute to the surface charge of nanoparticles. Our observations show that prepared dispersions of 22 nm particles are stable within few days in a bulk sample, but we have not observed any free 22 nm particles in a glass cells with a thickness of few micrometers after 10 h. This leads to the conjecture that the majority of the particles have migrated to the surface of the cell, where they accumulate permanently. Fig. 5(a,b) shows snapshots of a nanoparticle, approaching a surface defect. It is clear that the nanoparticle is permanently attached to the surface defect, which also scatters light like a nanoparticle. In the case of bigger particles the mismatch between homeotropic anchoring at the surface of a particle and the planar anchoring at the surface of the substrate prevents segregation at surfaces and apparently this repulsion is not strong enough in the case of smallest nanoparticles. Another process which destabilizes homogenous dispersions is the attraction of single colloids to the already formed agglomerates of nanoparticles as shown in Fig. 5(c, d). Such aggregates can remain in the dispersion even after sonication.

Finally, we present the interaction of a single nanoparticle with a topological defect induced by a micro-particle. Segregation of nanoparticles in topological defects is interesting for different applications, like stabilization of the LC phases or as configurable arrays which can be used in nanoscale photonics and plasmonics [13]. Fig. 6 shows the trapping of a 90 nm nanoparticle by the point defect and the Saturn ring defect induced by a 5 µm particle in a nematic liquid crystal. The trapping is very efficient with a binding energy approximately twice larger than in the case of a pair of nanoparticles. One can see that there is almost no difference between the trapping by the point defect or by the Saturn ring. The principle of trapping is simple. The defect presents a region with high elastic energy, where the liquid crystal is elastically deformed with decreased order parameter. The elastic distortion induced by the nanoparticle is lower inside the defect than outside in the oriented nematic. In addition, the trapped nanoparticle replaces the energetically unfavorable distorted or even molten nematic. It means, that also small nanoparticles with negligible induced distortion are trapped.

## 4. Conclusion

The main message of this article is that we are able to see nanoparticles in nematic liquid crystals by dark-field microscopy. We are able to monitor their positions and determine the forces, which are acting on the nanoparticles directly. We have shown experimentally strong pair interactions between nanoparticles with homeotropic anchoring in confined nematic LC down to the size of approximately 35 nm with binding pair energy roughly proportional to the size of particles. Below this size not all particles form stable pairs, 22 nm particles form only metastable pairs or they show no interaction. This is the consequence of electrostatic repulsion of their charges and the inhomogeneous surface anchoring. However, the nematic dispersion of 22 nm particles in a confined geometry is not stable, because of nanoparticle interactions mainly with surfaces and also with clusters of particles. The homeotropic surface anchoring energy of small nanoparticles is not strong enough to prevent adhesion of nanoparticles to the planaroriented substrates, and consequently the elastic repulsion between the homeotropic particle and the planar flat surface is not strong enough. The stability of the nematic dispersions of nanoparticles could be improved by using charged surfaces or chemical repulsion of surfaces. We have also shown that nanoparticles are also strongly attracted to topological defects induced by microparticles. Consequently different arrays of topological defects can be used for self-assembling of nanoparticles.

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