Celal Bayar University Journal of Science
Volume 17, Issue 2, 2021, p 115-120
Doi: 10.18466/cbayarfbe.835483

Celal Bayar University Journal of Science

Positioning of Cubic Shaped Particles with Different Edge Structures in Nematic Medium

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Received: 9 November 2020
Accepted: 24 May 2021
DOI: 10.18466/cbayarfbe.835483

Abstract

Liquid crystals (LC) are phases of matter that possess long range orientational order while maintaining fluidic properties. LCs have been shown to provide a medium that result in self-assembly of the colloidal particles through elastic interactions. One parameter that affects the positioning of the particles in LC medium is the edge sharpness of the particles. Simulation studies in the literature suggests that the edge sharpness of the particles directly affect the LC director profile at the vicinity of the particles, and playing a critical role in the formation and the shapes of the topological defects. This article presents a systematic study to show the effects of the edge sharpness on the orientation and the defect structure around the cubic shaped particles. The particles were shown to orient with their diagonal preferably parallel to the direction of the far field nematic director when the particles mediate planar anchoring. Whereas the particles with homeotropic anchoring did not exhibit strong preference in their orientation. We also showed defect structures to form around the particles with homeotropic surface anchoring. The defect structure around the particles with round edges were ring shaped, whereas the defects with S-shapes were formed around sharp-edged or truncated particles. The findings herein were found to be consistent with the simulations present in literature. The findings would find use in next generation materials for optics, photonics and responsive systems.

Keywords: *Alignment, Colloids, Defects, Liquid Crystals*.

1. Introduction

Liquid crystals (LCs) are the phases of matter that exhibit both fluidic properties and molecular ordering which are currently being developed for emerging applications.[1–3] In the nematic phases, the molecules exhibit orientational order along a unique direction called the director.[1] When colloidal particles are dispersed in a LC medium, the director profile is affected due to the interfacial interactions, which leads to useful observations that are unique to LCs.[4, 5, 14–16, 6–13] These interfacial phenomena can be described using three generalized concepts, which can be classified as surface anchoring, elasticity and the formation of the defects.[2] When a LC medium is in contact with a surface, the interaction of the mesogenic molecules at the interface results in a preferred orientation of the LCs, called the easy axis, which is the outcome of the maintained minimum energy state. This orientation can then be shifted due to the external fields, which is penalized with a surface anchoring energy. The long-range orientation of the LCs underlies the existence of the elastic properties of the LCs. When the natural orientation of the LC medium is affected by a geometric constraint, for example the presence of the colloids or surfaces, the director is strained that results in an energetic penalty. When LCs cannot satisfy the present surface anchoring in its medium via just elastic deformations, topological defects occur, which are defined as the local regions of low orientational ordering, or singularity. These three concepts were used in the current literature to define the positioning of the colloidal species dispersed in LC medium.

Studies in the literature showed that the surface anchoring and the director field around a particle is critically important in their positioning, and their interaction with the colloidal particles in a LC media.[4, 7, 11] For example, Poulin and Weitz demonstrated that the chaining of the spherical particles, which mediate planar anchoring of LCs on their surfaces, in a direction that is around an angle of 30° from the far-field director.[7] Musevic and collaborators showed that spherical particles with homeotropic surface alignment which causes the formation of a satellite point or a Saturn ring to maintain straight chain or as kinked chains, respectively.[17] These different symmetries of the aggregates can be explained by the minimization of the elastic energy free energy.

The effect of particle shape on particle organization in LCs has not yet fully been studied in the literature.[5, 8, 9, 11, 18, 19] Recently, the experimental studies of Lapointe and his collaborators and the simulation studies of Hung and Bale demonstrated that the interaction of the particles that have different shapes (cube, triangle and pentagonal prism) is strongly related to the orientation of these particles towards each other.[9, 20] This effect varies depending on the orientation of the particles with respect to the far field director and the strain of the LC ordering at the vicinity of the particles. As a result, the organization of the particle in LC media is strongly affected. Lapointe and his collaborators also showed that these particles can form assemblies as the multiple (double and triple) organizations, with their shapes to critically effect the symmetry of the interactions. Thus, the studies presented in the literature highlights the critical importance of the particle shapes on their individual orientation and their interaction symmetry. Although the studies showed the importance of the particle shapes on their positioning, the experimental studies are currently limited to the particles with planar surface anchoring.[9] A recent simulation study by Beller et al. showed that the colloidal particles with homeotropic anchoring to mediate defect structures that are critically dependent on the shapes and sharpness of the particles.[21] For example, the cubic shaped particles maintain minimum energy state with their surface normal orientation of 45° with respect to the far field nematic director. In addition, the particles with curved edges maintain a ring-shaped defect, where increasing the sharpness of the edges resulted in the formation of the S-shaped defects that follow the sharp edges of the particles. The studies followed in this article would also be considered as an experimental that mimics a similar system to these simulation studies.

In this study, we experimentally investigated the positioning of the cubic shaped particles in nematic LC medium. We determined the effect of surface anchoring and the edge sharpness of the particles on their alignment in LC medium. In addition, we characterized the shapes of the defects formed around the colloidal particles dispersed in nematic medium. The study highlights the importance of the details of the particle geometry on their positioning in LC medium and suggests routes for the design of the self-assembled colloidal particles in LCs.

2. Materials and Methods

2.1. Materials

A room temperature nematic liquid crystal 4-cyano-4′-pentylbiphenyl (5CB) was purchased from HCCH Jiangsu Hecheng Chemical Materials Co., Ltd. (Nanjing, China). Dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride (DMOAP), polyvinyl alcohol (PVA), and anhydrous ethanol were obtained from Sigma-Aldrich Co. Ltd. (St. Louis, USA) and used without further purification. Glass slides were obtained from Marienfeld GmbH (Lauda-Königshofen, Germany). The cubic shaped zeolite A particles were obtained from Prof. Halil Kalıpçılar and Prof. Berna Topuz.

2.2. Methods

2.2.1. DMOAP Functionalization of the Particles

Approximately 2% wt particle (zeolite 4A) in 1 mL deionized water was prepared and placed into ultrasonic bath for 10 minutes to disperse the particles. Then, 100 µl of DMOAP was added and the solution was kept in ultrasonic bath for another 10 minutes. The particles were then rinsed three times with deionized water and water was substituted with ethanol.

2.2.2. Functionalization of the Glass Surfaces

PVA coated surfaces were used for planar anchoring. Glass surfaces were coated with 5% wt PVA in water using a spincoater (5000 rpm for 2 minutes) and then rubbed with a velvet cloth to maintain unidirectional surface anchoring of LCs. DMOAP functionalization was used for the homeotropic anchoring. Before functionalization of the glass surfaces, O_2 plasma etching was applied to the glass slides using a Diener Electronics, Zepto Plasma Unit. Then, DMOAP was deposited on the glass surfaces from 10 minutes incubation in its 1% wt aqueous solution. The glass slides were finally rinsed with water and dried with nitrogen stream.

2.2.3. Preparation of the Liquid Crystal-Microparticle Suspensions

The particles (about 1 g/L) were dispersed in 5CB using a vortex mixer. 5CB, the particles and anhydrous ethanol was mixed in the isotropic phase until homogenous suspension is maintained. Then, ethanol was evaporated under vacuum to obtain a nematic suspension at room temperature. The suspension is then filled between two glass slides in the nematic phase and equilibrated for about an hour before the imaging.

2.2.4. Optical Microscopy

Optical characterizations of the films were performed using Olympus BX50 and BX53 microscopes (Olympus

Inc., Japan) equipped with a polarizer and an analyzer filter. Three independent samples were prepared to determine angle distribution of the particles. An average of around 100 images were collected from each sample. The images were analyzed using angle analysis of Fiji imagej, an open source image processing software.

2.2.5. Scanning Electron Microscopy

Quanta 400F Field Emission series scanning electron microscope was used to characterize the shapes of the particles at higher resolution.

3. Results and Discussion

We used cubic shaped particles to study the effect of the edge sharpness on the alignment and the LC director profiles around the particles. For the systematic studies, we obtained cubic shaped zeolite 4A particles with round, truncated and sharp edges as shown in the scanning electron micrographs in Figure 1. As shown, the sizes of the particles were in the range of 1 µm to 6 µm. This range is important and useful when considering the range 1 µm to 10 µm, where the interplay of the elasticity and the surface anchoring usually occur.[2] Although the sizes of the particles are within a range of interest in the field, the particles used in this study is not common in studying such interactions. Thus, we first performed studies to understand the surface anchoring of LCs on bare and functionalized particles in the first section below. Then, the next two sections are dedicated to the alignment and positioning of the particles in LCs and the investigation of the defect structures around the particles, respectively.

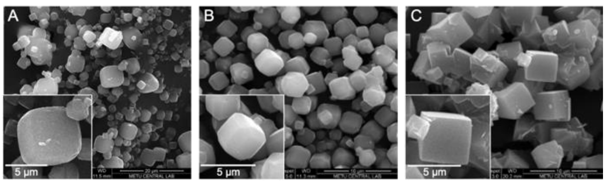

Figure 1. Scanning electron micrographs of zeolite 4A with (A) rounded edge, (B) truncated edge, (C) sharp edges. Insets showing the magnified images of the representative particles.

3.1. Determination of Surface Anchoring of LCs on the Surfaces of the Microparticles

The anchoring condition on the surface of the particles is one of the important parameters affecting the alignment of the particles in liquid crystalline media. Thus, we first analyzed the anchoring of the LCs on the surfaces of these particles since the anchoring of 5CB on the surfaces of the zeolite particles was not readily available in the literature. For this purpose, we dispersed zeolite 4A into 5CB in its nematic phase and collected images of the particles within the range of 2-6 µm using a polarized microscope equipped with crossed polarizers and a first order retardation plate (FOP). As seen in Figure 2A, the far field director of the nematic 5CB was in the direction of one of the polarizers (shown as *R*, far from the particles), thus, dark appearance was observed under polarized light. However, the distortion of the nematic director around the particles due to the anchoring condition at the surface of the particle resulted in a bright transmitted light as shown by white arrows in the polarized micrographs of Figure 2A-*ii*. Also, when FOP was inserted into the light path, red and blue colors were observed (shown by blue and red arrows in Figure 2A-*iii*).[22] This coloring was consistent with the planar alignment of LCs at the sides of the particles. Using this characterization, the LC anchoring on particle surface was determined as planar and a sketch of the ordering profile of the LCs at the vicinity of the particles was shown in the right panel of Figure 2A-*iv*. Here we note that we observed ~80% of the zeolite 4A particles exhibited planar anchoring of the LCs on their surfaces.

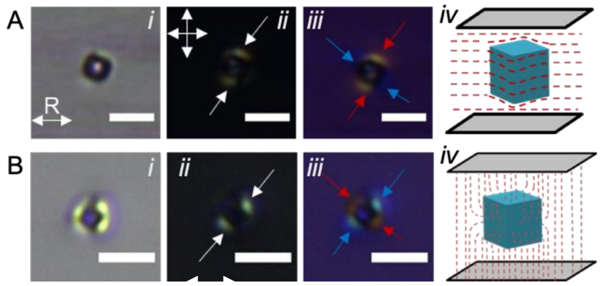

Figure 2. Optical characterizations of the (A) bare and (B) DMOAP functionalized zeolite particles. Brightfield (*i*), polarized light (*ii*) and polarized with first order retardation plate (*iii*) micrographs of single particles dispersed in nematic 5CB). The sketch in the right panel shows the schematic representation of the LC director profile around the particles determined from the micrographs. Double headed arrow indicates the rubbing direction of the two glass slides, R indicates the far field nematic director. Scale bars: 5 µm.

We then modified the LC surface anchoring of the particles with dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride (DMOAP) for the expectation of a homeotropic surface anchoring. After functionalization, we checked the anchoring from polarized light micrographs as shown in Figure 2B. The far field director in the images shown in Figure 2B-*ii* is perpendicular to the imaging plane (in-plane), so dark appearance was observed under polarized light. However, the distortion of the nematic director around the particles due to the anchoring condition at the surface of the particle resulted in a bright appearance as indicated by white arrows in the polarized micrographs of Figure 2B-*ii*. Also, when FOP was inserted, red and blue colors were observed (Figure 2B-*iii*), which is with a different symmetry compared with that of the planar

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Volume 17, Issue 2, 2021, p 115-120
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particles. When we compared the FOP micrographs of DMOAP coated particles and bare particles, it was seen that the red and blue colors around the particles were located at different sides that pointed out the difference in the anchoring conditions on the surface of the particles. This coloring suggested a homeotropic anchoring of LCs at the surfaces of particles, which would appear dark if particle surface mediated planar anchoring. Using this characterization, the LC anchoring on particle surface was determined as homeotropic and a sketch of the ordering profile of the LCs at the vicinity of the particles was shown in the right panel of Figure 2B-*iv*. We note that we observed ~90% of the zeolite 4A particles exhibited homeotropic anchoring of the LCs on their surfaces.

3.2. Particle Alignment in Nematic Liquid Crystals

After characterizing the surface anchoring of LCs on the surfaces of bare and DMOAP functionalized zeolite 4A particles, we next characterized the orientation of particles in nematic 5CB. For the analysis, orientations of the single zeolite 4A particles were examined by measuring the angles that the particles maintain in 5CB. When we analyzed bare zeolite 4A particles with sharp edges in planar and homeotropic cells, we evidenced the particles to maintain a position with an angle of 0° in planar medium whereas there was no significant tendency in the case of particles in homeotropic cells as shown in Figure 3.

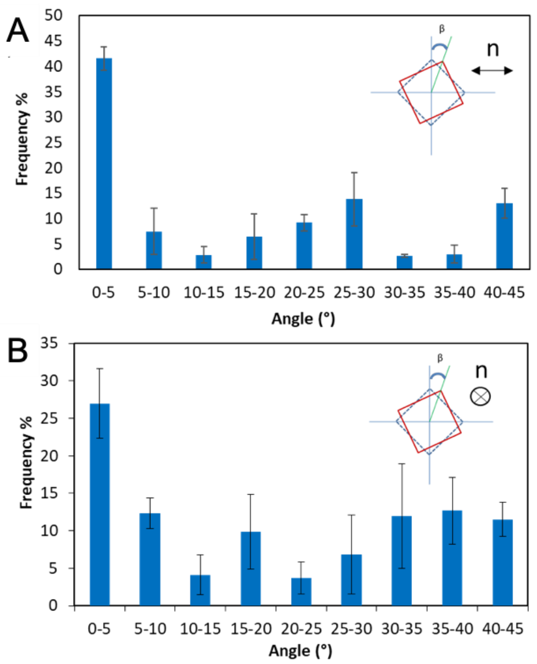

Figure 3. Angle distribution of the bare single zeolite 4A particles with sharp edges in a) planar cell b) homeotropic cell and schematic representation of orientations of the particles. β indicates the angle that the particle oriented in LC media.

As shown in Figure 3, the particles exhibited a preferred orientation along the nematic director, which was expected due to the elastic effects of the LC medium. However, that elastic anisotropy is missing in the direction orthogonal to the nematic director due to the lack of the elastic force anisotropy. Consistent with this, we also observed the same trend in the relative orientation of the DMOAP coated particles with respect to the far field nematic director.

In order to investigate the effect of the edge sharpness of the particles on their orientation in nematic medium, zeolite 4A with rounded and truncated edges were also used. When we analyzed the orientation of the single bare zeolite 4A with truncated edges (Figure 4, red data) and round edges (Figure 4, green data), we observed that the single particles dispersed in planar medium to generally maintain an orientation with an angle around 0° with respect to the far field nematic director, consistent with the observations described above for the particles with sharp edges. However, when compared among the three types of the particles, the frequency of the round-edged particles to maintain an angle of 0° is significantly lower than that of the other two particle shapes. This is expected when considering the loss of the shape anisotropy with the rounding of the edges of a cubic particle.

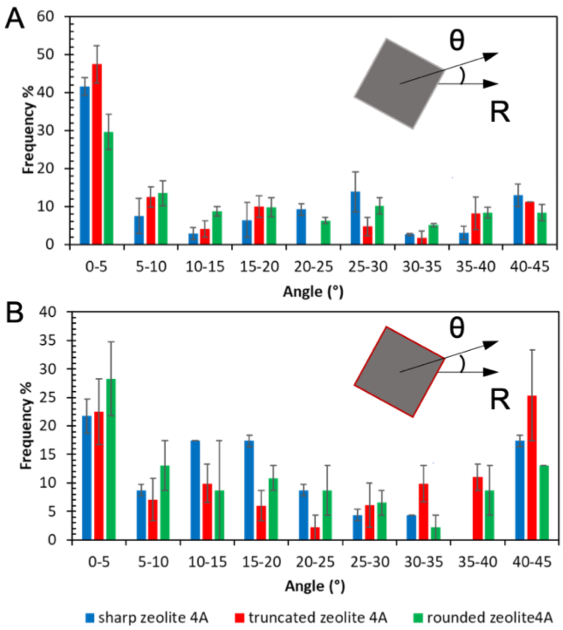

Figure 4. Angle distribution of (A) the bare and (B) the DMOAP coated single zeolite 4A particles with sharp, truncated and rounded edges in planar LC medium. The schematic representation of orientations of the particles are shown as insets where β indicates the angle that the particle oriented in LC media.

When the orientation of the DMOAP functionalized particles were quantified in nematic 5CB, we did not observe a significantly pronounced orientation of the particles with respect to the far field nematic director, independent of the particle shapes. As shown in Figure 4B, the particles maintaining an average orientation of 0 to 5° with respect to the nematic director were almost half of those observed in particles with planar surface anchoring. We reasoned that this significant difference in the distribution of the orientation of the particles would be due to the formation of defects around the particles with surfaces mediating homeotropic orientation, which we detailed below.

3.3. Defect Structures Around Cubic Particles Suspended in Nematic Medium

The literature suggested a range of defect shapes that could form around the cubic shaped particles.[21] Interestingly, simulation studies suggested that at the vicinity of the cubic particles mediating homeotropic orientations, defect loops form that wraps the particles.[21] When the sharpness of the particles at their edges are increased, they have found that the ring shapes of the defects were deformed and maintained shapes that follows the edges of the particles. Herein, we collected images of the three types of the DMOAP coated particles under the microscope to provide evidence of whether or not there are defects present, and whether or not their shapes are affected by the sharpness of the cubic particles.

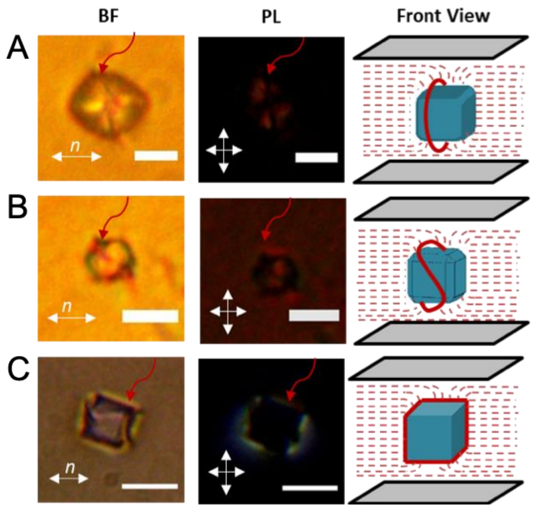

Figure 5. Brightfield (BF) and polarized light (PL) micrographs of DMOAP-coated zeolite 4A particles with (A) rounded, (B) truncated and (C) sharp edges and the corresponding schematic illustrations of the nematic director field and the shapes of the defects around the particles in nematic planar cell. Red arrows in micrographs indicate the defects around the particles. Dashed and solid red lines in schematic illustrations represent the director field and defects, respectively. Scale bars: 5 µm

Figure 5A-B demonstrates the representative micrographs of the particles with round, truncated and sharp edges, respectively. Evidently, defect structures around DMOAP coated particles with rounded edges were in the shape of a ring (Figure 5A). Defects with S-shapes were formed around DMOAP coated, truncated particles (Figure 5B). As the sharpness of the particles is high (Figure 5C), the shapes of the disclinations (indicated with solid red lines) are deformed and maintained a shape that wrapped the edges of the particles. These observations of the sharpness-dependent shapes of the defects formed around the cubic particles provides the first experimental evidence to the findings of the simulations.[21]

After finding the evidence of the formation of the defects around particles mediating homeotropic surface anchoring, we revisited the alignment of the particles in nematic medium shown in Figure 4. When we compared the distributions of the alignments of the DMOAP coated particles, we did not observe a significant difference in their alignment with respect to the defect structures. However, when the alignment of the particles mediating homeotropic orientation were compared with that of the particles mediating planar anchoring, we found that the particles with homeotropic anchoring not to exhibit a strong preference in the alignment with respect to the far field nematic director. There exists a slight preference of the angles close to 0° and 45°, which is consistent with the literature.[21] However, it does not appear to be strong when compared with the planar particles.

4. Conclusion

We have investigated the positioning of the cubic shaped microparticles with different edge sharpness in nematic liquid crystals. Our results of this study are two-folds. First, we found a relationship between the edge sharpness and the alignment of the particles with respect to the far field director. Specifically, the planar particles with sharp edges to preferentially align with their diagonal parallel to the far field nematic director, which was lowered with the rounding of the particle edges. Second, from the imaging of the particles with homeotropic surface anchoring in the nematic LCs, we found that the defect structure around the particles to be affected by the edge sharpness of the particles. The defect structures observed around the rounded particles were close to a ring shapes, whereas the defects around the cubic particles with sharp edges to maintain a deformed ring with line defects following the proximity of the edges. The observations reached in this study is consistent with the simulations performed on similar systems in literature. The findings would find use in next generation materials for optics, photonics and responsive systems.

Acknowledgement

The authors thank the financial support provided by Scientific and Technological Research Council of Turkey (TÜBİTAK) under award number 116C093.

Author's Contributions

Aslı Karausta: Performed the experiment and result analysis.
Emre Bukusoglu: Assisted in analytical analysis on the structure, supervised the experiment's progress, result interpretation and helped in manuscript preparation.

Ethics

There are no ethical issues after the publication of this manuscript.

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