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DEVELOPMENT AND CHARACTERIZATION OF MIXED ANCHORING ELASTIC MULTIPOLES IN LIQUID CRYSTAL COLLOIDS

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Reviewed and approved* by the following:

Iam-Choon Khoo William E. Leonhard Chair Professor of Electrical Engineering Thesis Supervisor

Ivan I. Smalyukh Professor of Physics, University of Colorado Boulder Research Supervisor

> Richard W. Robinett Professor of Physics Honors Adviser

*Signatures are on file in the Schreyer Honors College.

Abstract

Colloidal science has long been intrigued by the prospect of self-assembly of materials. The orientational order of the rod-shaped molecules within nematic liquid crystals (LCs) gives them particularly strong potential as colloidal hosts due to the interactions between the LC and colloidal particles at surfaces between the two. Depending on the boundary conditions (BCs) at these surfaces, a variety of topological defects can arise, creating particles which affect a uniform LC field similarly to how electrostatic multipoles affect a uniform electric field. However, although elastic dipoles, quadrupoles, and hexadecapoles have all been previously reported, no such examples of octupoles have been created thus far. Here we show that glycerol droplets doped with specific concentrations of certain surfactants can be dispersed within both 4-Cyano-4'-pentylbiphenyl (5CB) and ZLI-2806 nematic liquid crystals to reliably produce elastic octupoles containing one "boojum" and one "Saturn ring" topological defect. The resulting elastic multipole has mixed BCs and is an intermediate state in the transition from completely planar BCs in the elastic quadrupole with boojums and the completely homeotropic BCs in the elastic dipole with a hedgehog defect. The results from this work provide an additional building block in colloidal self-assembly.

Table of Contents

List of Figures								
Li	List of Tables							
Ac	know	ledgements	v					
1	Intr	oduction	1					
	1.1	Overview of Liquid Crystals	1					
	1.2	Liquid Crystal-Colloidal Surface Interactions	3					
	1.3	Analogies to Electric Multipoles and Chemical Orbitals	4					
	1.4	Overview of Brownian Motion	6					
	1.5	Motivation	8					
2	Exp	erimental Methods	9					
	2.1	Colloidal Dispersion Materials	9					
	2.2	Liquid Crystal Cell Creation	10					
	2.3	Microscopy and Data Analysis	12					
3	Resu	ilts and Discussion	15					
	3.1	Mixed Anchoring Elastic Hexadecapoles	17					
	3.2	Elastic Octupole	20					
	3.3	Discussion	24					
Bi	bliogı	raphy	26					

List of Figures

1.1	Example of a Liquid Crystal Colloid
1.2	Boundary Conditions for Spherical Colloids
1.3	Representations of Multipoles
2.1	Liquid Crystal Cell
2.2	Schematic of the Polarizing Optical Microscope
3.1	Multipole Transition
3.2	Transition Mechanism
3.3	Mixed Anchoring Hexadecapole Images and Diagrams
3.4	Interaction of Two Hexadecapoles
3.5	Graphs for Hexadecapole Interaction
3.6	Octupole Images and Diagrams
3.7	Histogram of Octupole Displacements
3.8	Interaction of Two Octupoles
3.9	Graphs for Octupole Ineraction

List of Tables

2.1 Surfactant Concentrations and Liquid Crystal Combinations	10
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Chapter 1

Introduction

Liquid crystal colloids takes two types of soft matter systems, liquid crystals (LCs) and colloids, and combine them into a new type of system which can exploit the individual properties of each. They are constructed by taking colloidal particles, which can either be solid or liquid depending on the material of interest, and dispersing them within a liquid crystal medium. The colloidal aspect of these materials is of interest because of the possibility of new materials to be built using colloidal particles as building blocks, and the liquid crystals are an intriguing host due to their addition of anisotropy in interactions [1]. In this work, we detail the development and characterization of two types of colloidal atoms, the mixed anchoring hexadecapole and the octupole, which could act as additional options for building blocks in future materials.

1.1 Overview of Liquid Crystals

Liquid crystals, which will be used as the fluid host of our samples, are a state of matter which has properties of both a solid and a traditional, isotropic liquid. They have positional disorder, so they can flow just as any other liquid can, but maintain some level of orientational order. The molecules which make up a liquid crystal are usually either rod-like or disk-like in shape, although more complicated shapes are possible [2]. In any case, however, a direction of the molecule can always be determined, and this direction of the particles tends to align, just as in a solid. The director **n** defines the average orientation of the particles in a region, as shown in Figure 1.1 [1, 3].



Figure 1.1: Schematic showing the basic construction of a liquid crystal colloid. Colloidal particles, which in our case are always spherical, are submerged in the liquid crystal host. The colloidal particle will be one to several orders of magnitude larger than the LC molecules. The average direction for the rod-like LC molecules is given by the director \mathbf{n} . [1]

The existence of orientational order leads to several interesting properties in liquid crystals. They are birefringent, which means that light polarized along the director **n** will travel at a different speed than light polarized orthogonal to the director. The level of birefringence Δn in the materials can be determined by comparing the indices of refraction for these two directions:

$$\Delta n = n_e - n_o \tag{1.1}$$

where n_e is the index of refraction for light whose electric field component is aligned with the director and n_o is the index of refraction for light whose electric field component is orthogonal to the director [2].

There are several different classifications of LCs, including cholesteric or smectic, although all the liquids crystals in this work are nematic liquid crystals. In nematic liquid crystals, there is only a single director which is preferable for molecules to align to even over a large volume, and the director has no polarity associated with it (i.e. $+\mathbf{n} = -\mathbf{n} = \mathbf{n}$)[2, 4]. However, it is important to

note that even though one director is preferred for the entire material (referred to as the far-field director \mathbf{n}_0), deformations can occur in the orientation which causes local directors to vary from the far-field director. This is exactly the case at the surface between the liquid crystal and colloidal particles, as will be explained in section 1.2.

Just as with other states of matter, the liquid crystal phase is temperature dependent and phase transitions can occur if the temperature is raised or lowered. A solid can melt into a liquid crystal at some melting temperature T_m , and a liquid crystal can transform into an isotropic liquid at some higher clearing temperature T_c (both such transitions can also occur in the opposite directions) [2]. These respective temperatures will vary based on the specific liquid crystal being observed.

1.2 Liquid Crystal-Colloidal Surface Interactions

Colloids are a type of mixture commonly interacted with throughout day-to-day life, with examples including milk, gelatin, and smoke from a fire. They are systems where particles from one material are dispersed within another, but rather than dissolving into the host material or settling to the bottom of the mixture, they stay suspended throughout it. In an LC colloid, the host of choice is a liquid crystal, which leads to interesting interactions at the interface between the two materials. As noted in section 1.1, nematic liquid crystals have one far-field director \mathbf{n}_0 with which it is energetically favorable for the LC molecules to stay aligned. However, surfaces of colloidal particles can also have certain directions to which it is preferable for the local LC molecules to align, depending on the chemistry of the particle and the shape of the surface [1]. These are referred to as the boundary conditions of the colloidal particle, and the three main categories of boundary conditions are shown in Figure 1.2. When placed within a nematic liquid crystal, colloidal particles will alter the orientation of nearby LC molecules, causing the director field to transition from the uniform far-field director to the direction set by the nearby boundary conditions and being aligned with the far-field director, with different terms being dominant depending on a LC molecules'

proximity to the colloidal particle. It is these manipulations of the director field which cause the unique interactions between the particles in a liquid crystal colloid, thereby leading to their interest and potential as building blocks of new and interesting materials [1].



Figure 1.2: The three types of boundary conditions which can arise when spherical colloidal particles are placed in nematic liquid crystal. Boundary conditions force the director field near the colloidal particle into specific configurations which depend on the interaction between the colloidal particle and the liquid crystal molecules. [1]

1.3 Analogies to Electric Multipoles and Chemical Orbitals

Since colloidal particles are known to alter the uniform director fields in nematic liquid crystals, a methodology is needed to describe these distortions. This is done both to classify different types of colloidal particles and to understand how these different types of particles will interact. Thankfully, these field alterations closely resemble effects studied in other fields, so analogies to previously developed systems can be made, specifically electric multipoles and chemical orbitals.

Multipole expansion is a topic studied in undergraduate electricity and magnetism courses which details how electric fields can be expressed as a weighted sum of contributions from specific charge configurations, similar to how a Taylor expansion can express a functions as a weighted sum of polynomials. The charge configurations used as the basis for the expansion are the multipoles: a monopole being a single charge, a dipole being a pair of opposite charges close together, a quadrupole being two pairs of opposite charges arranged in a square with like charges set in opposite corners, etc. Each of these charge configurations has a specific electric field associated with it, and so by adding together these these fields with different weighting coefficients, a general electric field can be obtained. This weighting is referred to as the moment of the multipole.



Figure 1.3: Examples of different types of elastic multipoles formed by spherical colloidal particles in liquid crystal. The order of the pole is given by 2^l , and m is used to classify the direction and amount of tilt, with the restriction that $-l \leq m \leq l$. For each type of multipole, a microscope image under crossed polarizers is shown at the top, followed by a schematic showing how the director field lines are affected by the multipole. For each of these, a uniform, vertical far-field director has been used, as indicated by \mathbf{n}_0 . The next schematics show the atomic orbitals which correspond to the type of multipole. Finally, we show how the directors are tilted by the multipole at its surface. (a) Elastic dipole with perpendicular, or homeotropic, BCs. The topological defect is called a "hedgehog", and is a bulk point defect in the LC. (b) Elastic quadrupole with homeotropic BCs and a "Saturn ring" topological defect. (c) Elastic quadrupole with tangential, or planar, BCs. The two topological defects at the poles are called "boojums" [6, 7] and occur on the surface of the colloidal particle. (d) Elastic hexadecapole with tilted, conically degenerate BCs. A Saturn ring as well as two boojums occur as topological defects. [8]

We can apply the same terminology to LC colloids, since the distortions of the director field caused by the main types of boundary conditions shown in Figure 1.2 correspond to the electric fields from several low order electric multipoles. These are referred to as elastic multipoles, since it is an elastic, restorative force which wants to align with the far-field director that stores energy for LC colloids. Images and schematics of four different types of elastic multipoles are shown in Figure 1.3. For many years only dipoles (via homeotropic alignment only) or quadrupoles (via homeotropic or planar alignment) could be created [1, 4]. Recently, hexadecapoles were also discovered using the tilted, conically degenerate alignment [9].

Since we seek to use colloidal particles as building blocks for new types of materials, we can also make analogies to the atomic orbitals taught in VSEPR theory in introductory undergraduate chemistry courses. This is rooted in the mathematical description of spherical harmonics for certain electron orbitals of atoms [8]. However, we can compare this to the tilts of the LC molecules at the surface of colloidal particles, as shown in Figure 1.3. This is particularly useful as the interactions of different types of orbitals has been well studied in the atomic theory of molecules, so we can apply this knowledge to predict how different types of elastic multipoles should interact.

1.4 Overview of Brownian Motion

One key property for both measuring the forces acting on the colloidal particles and for ensuring that they were free to move in the bulk of a LC cell (as opposed to trapped along one of the glass slides) was Brownian motion. First observed by Robert Brown in 1827 [10] and explained by Albert Einstein in 1905 [11], Brownian motion is the small, random changes in the position of a particle submerged in a fluid caused by collisions with the surrounding fluid molecules. These collisions are due to thermal fluctuations in atoms, and therefore can be described through connections to temperature and the mean kinetic energy of particles. We can usually take a particle undergoing Brownian motion to be under two forces: one due to the collisions with the fluid molecules and one due to the frictional drag of the fluid which opposes motion. Because the submerged particles is being bombarded on all sides by the fluid molecules, but occasionally on some sides more than other, the force due to collisions is random in direction but causes an average displacement of zero when measured over very long time scales. We can, however, describe the total motion by looking at the probability density functions for the one-dimensional displacements of the particle, which are described by:

$$\frac{\partial f(x,t)}{\partial t} = D \frac{\partial^2 f(x,t)}{\partial x^2} \tag{1.2}$$

where D is the diffusion coefficient [12]. By talking the initial position to be at the origin, this partial differential equation has a solution of:

$$f(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$$
(1.3)

This is the normalized formula for a Gaussian distribution with a variance of 2Dt. Because of its random nature, the Brownian motions along various axes can be taken to be independent of one another. Thus, this description can be applied to higher dimensions by calculating the components of the motion in the various directions.

One important note when applying these formulae to higher dimensions is that the standard assumption is isotropic interactions between the submerged particle and the fluid molecules, which usually holds for most Brownian motion systems. This implies that a single diffusion coefficient can completely define the motion. However, because of the nature of liquid crystal colloids, the frictional drag force mentioned above has different magnitudes in the parallel and perpendicular directions of the director \mathbf{n}_0 . Thus, when plotting histograms of the displacements, these two directions must be graphed separately, as they will each lead to their own diffusion coefficients, D_{\parallel} and D_{\perp} [13]. Nevertheless, we can still take data for two dimensional motion and create data sets for these two directions and assume them to be independent of one another.

1.5 Motivation

The motivation behind this research is two-fold. First, as shown in Figure 1.3, examples of elastic dipoles, quadrupoles, and hexadecapoles have been previously discovered and thoroughly characterized, leaving a clear gap for the elastic octupole. Thus, discovering a colloidal particle which displays the characteristics of an octupole is of interest for completeness of the model. Additionally, having an octupole is important should a director field structure with a strong octupolar moment be desired, similar to how certain types of functions would not be able to be represented by a Taylor expansion if the x^3 term could not be included.

The second main motivation behind the work is rooted in self-assembly [14]. Colloidal particles have shown the possibility of automatically aligning themselves into specific configurations, ranging from straight lines to larger three-dimensional structures, based on the types of multipoles available in a system [15]. Thus, by discovering new types of multipoles, we provide additional building blocks from which new types of larger configurations could be created. It is this fundamental research which is crucial to support the eventual hope of utilizing colloidal particles as atoms in new types of materials.

Chapter 2

Experimental Methods

2.1 Colloidal Dispersion Materials

The main variable explored in the experiment was the various combinations of liquid crystal host and colloidal droplets used to make the liquid crystal colloids. Two different types of liquid crystal were used: 4-Cyano-4'-pentylbiphenyl (5CB) and ZLI-2806. All colloidal droplets were primarily made of glycerol, with small amounts of surfactants being added to affect the interactions at the surface between the droplets and the liquid crystal. The surfactants were sodium dodecyl sulfate (SDS) and octadecyldimethyl(3-trimethoxysilylpropyl) ammonium chloride (DMOAP), and the various concentrations and combinations used are shown in Table 2.1. To create a glycerol and surfactant mixture, we added known amounts of the two materials to a glass vial and then evenly dispersed the surfactant by stirring with a glass pipette and using a vortex mixer. The mixtures were always allowed to sit for at least 4 hours before any experiments were performed. It should be noted that lower concentration mixtures were also sometimes created by taking some amount of a previous mixture and diluting it with a set amount of pure glycerol, once again repeating the stirring and mixing processes.

Surfactant	Concentration Range	Concentration Type	Liquid Crystal(s) Used
SDS	0.071% - 2.14%	By mass	5CB, ZLI-2806
DMOAP	0.01% - 0.20 %	By volume	5CB

Table 2.1: Combinations of surfactants and liquid crystal used when searching for the new types of elastic multipoles. The concentration of surfactant was determined either by mass or by volume, in comparison to the glycerol to which the surfactant would be added.

2.2 Liquid Crystal Cell Creation

In order to observe the interactions between the liquid crystal molecules and the colloidal particles, we first had to construct liquid crystal cells in which to store our samples, an example of which is shown in Figure 2.1. Regardless of the type of liquid crystal or colloid being studied, the procedure for constructing these cells kept constant throughout all experiments. Glass microscope slides and 22x22 mm glass coverslips (hereafter referred to as slides) were sonicated for one hour at 55°C in a mixture of deionized water and Alconox powder detergent. The water was then allowed to cool to room temperature, and the slides were rinsed with, in order: deionized water, acetone, methanol, and isopropyl alcohol. The slides were then spin coated with PI2555 polyimide and baked for two hours at 285°C. This coating was completed to induce planar boundary conditions for the liquid crystal in the cell. The direction of these planar BCs was set by rubbing the slides in only one direction with a velvet cloth. These slides were then stored in an airtight container to minimize any accumulation of dust, since slides could be prepared in bulk with the cells made directly before for each experiment.



Figure 2.1: Example of a LC cell which would be used to store and view samples. The central square is the glass coverslip, which would be kept a roughly constant distance from the glass microscope slide using either $16 \,\mu\text{m}$ or $30 \,\mu\text{m}$ spacers. Once the LC colloid had been dispersed between the glass, epoxy glue was used to seal the sample, which can be seen on either side of the coverslip.

To create a liquid crystal cell, we first prepared the glue mixture which would seal the microscope slides and the coverslips together. Norland Optical Adhesive 63 and a small amount of spherical spacers were combined in a glass vial and stirred thoroughly. $30 \,\mu\text{m}$ spacers were used for the vast majority of experiments, although 16 μm spacers were used occasionally at the start of the project. Dots of this glue mixture were placed on the coverslip, which was then pressed to the microscope slide. The glue was set by directly applying ultraviolet light for 30 seconds. Finally, epoxy glue sealed two opposite sides of the coverslip to the microscope slide, with the other two sides left open. To create the liquid crystal colloid, we filled $0.5 \,\text{mL}$ microcentrifuge tubes with about $100 \,\mu\text{L}$ of liquid crystal and a small drop of the glycerol surfactant mixture. The tube was sonicated for 8-10 seconds and flicked approximately 40 times from various directions to disperse the glycerol and to create tiny droplets within the liquid crystal host. The cell was then filled with liquid crystal colloid by capillary forces, where small droplets of the mixture would be placed at one of the two open ends of the cell and then drawn through towards the other open end. Once the entire cell had been filled and no air remained between the coverslip and the microscope slide, we used epoxy glue to seal the final two edges of the coverslip. Once this was done, the liquid crystal cell was complete and ready to be used in experiment.

2.3 Microscopy and Data Analysis

All data was taken by polarizing optical microscopy (POM) on an Olympus IX81 inverted microscope with a camera attached, using either a 60x or 100x oil-immersion objective (depending on the size of the droplet). A schematic of the POM setup is shown in Figure 2.2. The key thing that differentiates POM from standard optical microscopy methods is the addition of the analyzer and the polarizing, which are two linear polarizing filters. By varying the directions of the polarizer and analyzer with respect to the director field, different characteristics of the liquid crystal colloid would be displayed. In the setup through which most of our data was taken, the polarizer was set parallel to the far-field director and the analyzer was set perpendicular to them. This orthogonal relationship is displayed in Figure 2.2. Since the polarizer and analyzer are orthogonal to one another, when no sample is present all light from the source is blocked before reaching the eyepiece. This is also true when viewing liquid crystal molecules by themselves, since the far-field director is parallel to the polarizer. Thus, the polarization of the light will not be changed by the liquid crystal molecules. However, when viewing the colloidal molecules, light is allowed to pass through because the colloidal particle distorts the liquid crystal field, making it misaligned from the far-field director. These liquid crystal molecules will affect the light that passes through, causing it to change polarization direction and become in-line with the liquid crystal field. Since this new polarization is no longer perpendicular to the analyzer, the light becomes able to pass through to the eyepiece. In addition, we could also add a birefringent waveplate which would

change the speed of light based on its polarization. This would add or subtract some amount of phase retartdation, which allowed for color to be used to differentiate between different directions of polarization, thereby providing further insight into the local liquid crystal field.



Figure 2.2: Schematic of the Olympus IX81 inverted microscope, with crossed polarizers active. Unfiltered light enters the system, is polarized in one direction by the polarizer, passes through the sample and the objective lens (usually set to either 60x or 100x magnification), and then goes to the analyzer, which is set orthogonal to the direction of the polarizer. Thus, the only light that goes to the eyepiece is light which had its polarization altered through interaction with the liquid crystal sample.

When viewing colloidal particles under the microscope, we first watched for the existence of Brownian motion, since this ensured that the particles were moving freely within the liquid crystal bulk. This was important since colloidal droplets could get stuck to the microscope slide or coverslip while distorting light in ways similar to an elastic multipole. These stuck droplets would still look spherical under the two-dimensional slice that the microscope displays, but would actually be roughly hemispherical in shape with the flat side attached to the glass. Such stuck particles could not be used to study the surface interactions between colloid and liquid crystal, since they have an ill-defined topological charge. Once colloidal droplets in the bulk had been identified, we would first take images under a variety of polarizer and analyzer combinations to identify the type of elastic multipole being viewed. By taking videos of droplets and tracking their positions over time, we could determine the diffusion coefficients in the parallel and perpendicular directions, with respect to the far-field director. We also took data of interactions between nearby multipoles, since this would display the attractive and repulsive forces for different angles between them. However, colloidal droplets of the correct type and size were rarely close enough to directly interact, so we would manually control their positions 1064 nm holographic optical tweezer (HOT).

All data was processed using ImageJ software, with the wrMTrck plug-in used for automated particle tracking. A micrometer slide was first used to determine that the relationship between physical distances and pixels, which was found to be 13.6 pixels per micrometer. The ImageJ smoothing process and automated contrast adjustment was applied to improve the particle tracking. Excel was used for data manipulation, and OriginPro was used for all plotting.

Chapter 3

Results and Discussion

In this work, all of the colloidal particles are droplets of isotropic liquid glycerol which are dispersed throughout the liquid crystal. These droplets keep their shape when mixed with the LC because of the high surface tension and viscosity of glycerol. When pure glycerol is used as a colloidal particle, it naturally sets planar BCs for the LC molecules near the surface. However, by mixing a surfactant in with the glycerol before dispersing into LC, we can alter these boundary conditions and create colloidal particles with homeotropic BCs. Whenever such glycerol and surfactant mixtures are dispersed into liquid crystal, the particles initially appear as boojum [6, 7] quadrupoles with fully planar BCs. However, as time passes, the droplets will begin to transition, with the boojums breaking and forming defect loops on the surface of the droplet. As more time passes, these loops move down towards the equator of the droplet, combining to form one Saturn ring defect and transitioning the particle to a quadrupole with fully homeotropic BCs. This one loop may then move up towards one of the poles, shrinking as it moves and eventually forming a hedgehog defect in the bulk near the particle. Diagrams and experimental images of the various stages of this transition are shown in Figure 3.1.



Figure 3.1: Diagrams and images of different stages in the transition of a colloidal particle. (a) Elastic quadrupole with two boojum defects. (b) Particle once the two boojums have broken into defects, but before they meet at the equator. (c) Elastic quadrupole with a Saturn ring defect. (d) Elastic dipole with a hedgehog defect.

The mechanism for this transition is the movement of the surfactant molecules within the colloidal particle, as shown in Figure 3.2. Initially the surfactant molecules are dispersed throughout the bulk of the isotropic fluid, which in this case is always glycerol. Thus, the droplet will maintain its original planar BCs, because not enough surfactant molecules are near the surface of the droplet to affect the interaction with LC molecules. As time passes, the surfactant molecules (which cause homeotropic BCs) will move towards the surface of the droplet, beginning at the poles of the droplet. This is because homeotropic alignment of liquid crystal molecules at the poles will have the same orientation as the nearby far field director \mathbf{n}_0 , so it is a lower energy state than planar alignment. As time passes, surfactant molecules will continue to move towards the surface with a higher density at the poles, because homeotropic BCs at the equator force an orientation which is normal to the far field director and have a much higher energy cost. Eventually, enough surfactant will be at the surface to create an entirely homeotropic colloidal particle. However, by controlling the amount of surfactant present in the glycerol droplet, we can cause this transition to begin but not be able to finish. If there is not enough surfactant to create a fully homeotropic droplet, the transition will stop in a mixed state: parts of the surface will obtain homeotropic BCs while other parts will stay as planar. It is through this mixed anchoring state that we obtain our new types of elastic multipoles.



Figure 3.2: Visualization of the surfactant molecules within a glycerol droplet through the multipole transition shown in Figure 3.1, beginning with full planar BCs and going to full homeotropic BCs.

3.1 Mixed Anchoring Elastic Hexadecapoles

As mentioned above, elastic hexadecapoles were first discovered using a colloidal particle with tilted, conically degenerate BCs over the entire surface, which caused two boojums and a Saturn ring as topological defects [9]. However, by limiting the colloidal particle's ability to fully transition between planar and homeotropic BCs, we have created a new type of elastic hexadecapole (Figure 3.3). It has two topological defects in the form of loops which stop moving somewhere between the pole and the equator of the particle (Figure 3.3 d). Between the loops the particle maintains planar BCs, and in the regions between a loop and a pole it has homeotropic BCs (Figure 3.3 b,e). The switching of colors between blue and orange/yellow (Figure 3.3 c,f) eight times when

travelling around the droplet indicates the same effect on the director field $\mathbf{n}(\mathbf{r})$ as was reported for the tilted, conically degenerate BC hexadecapole.



Figure 3.3: (a-d) POM images showing a colloidal glycerol droplet in the mixed anchoring elastic hexadecapole state. (e) Schematic of mixed anchoring elastic hexadecapole, displaying two defect loop topological defects, as well as the combination of planar BCs and homeotropic BCs. (f) Visualization of the change to the director field for a sphere surrounding the mixed anchoring elastic hexadecapole slightly off of the surface. Yellow and blue colors indicate clockwise and counterclockwise changes to a vertical far field director $\mathbf{n}(\mathbf{r})$, respectively.

Besides the director field configuration, the large distinction between the two types of hexadecapoles comes in the interactions between two such particles. Just like other types of elastic multipoles, the interaction depends on the angle between the particles with respect to the director. However, the regions of attraction between the two types differ in the presented configuration (Fig. 4). Whereas the tilted hexadecapole has attractive regions centered around $\theta \approx 25^{\circ}$ and $\theta \approx 70^{\circ}$ [9, 16], the mixed anchoring hexadecapole has attractive regions centered around $\theta \approx 15^{\circ}$ and $\theta \approx 30^{\circ}$ (Figure 3.4). It should be noted that these angles are only approximate, and can vary depending on the level of tilt in the tilted hexadecapole or the position of the defect loops on the mixed anchoring hexadecapole.

From the video of the interaction of the particles, frames from which are shown in Figure 3.4, we can determine both the force of attraction and the interaction potential. We assume that the interaction force is of equal magnitude to the Stokes drag force $F_{stokes} = c_f v$, where c_f is the drag coefficient determined from Brownian motion (the process for which is described in section 3.2) and v is the velocity of one particle with respect to the other. This vecocity is determined by plotting their separations as a function of time (Figure 3.5 a). We then calculate the interaction potential by integrating the force of interaction along this separation path, $U_{int} = \int F_{int} ds$. We arrive at a maximum attractive force of approximately 0.5 pN (Figure 3.5 b) and an interaction potential near contact of approximately 1000 k_BT.



Figure 3.4: Images of the interaction between two mixed anchoring elastic hexadecapoles. This pair attracted in the $\theta \approx 70^{\circ}$ region of separation.



Figure 3.5: (a) Separation of the two particles as a function of time, with a polynomial fit applied. (b) Force of attraction between the particles as a function of their separation.

3.2 Elastic Octupole

We arrive at an elastic octupole through a similar process as the mixed anchoring elastic hexadecapole (Figure 3.6). It once again requires enough surfactant for a boojum to split into a defect loop but not enough for the loop to travel all the way to the equator. However, in this case we require that one of the boojums sticks to a pole while the other boojum splits into a loop (Figure 3.6 d,e). This results in planar BCs for the majority of the particle, with homeotropic BCs only in the region between the single defect loop and its nearest pole. The elastic octupole also has six alternating regions of clockwise and counterclockwise tilting of the director for a sphere surrounding the particle in agreement with theoretical predictions (Figure 3.6 f).



Figure 3.6: (a-d) POM images showing an elastic octupole. (e) Schematic of elastic octupole, displaying the boojum and defect loop topological defects, as well as the combination of planar BCs and homeotropic BCs. (f) Visualization of the change to the director field for a sphere surrounding the elastic octupole slightly off of the surface. Yellow and Blue colors indicate clockwise and counterclockwise changes to a vertical far field director \mathbf{n}_0 , respectively.

From videos of the Brownian motion of the particles, we obtain distributions of particle movement from which we can calculate the friction coefficient for the elastic octupole (Figure 3.7). We know that for a given distribution of frame-by-frame displacements, the count for a given displacement Δx should be proportional to $e^{-\frac{\Delta x^2}{4D\tau}}$, where τ is the time in between frames and D is the diffusion coefficient, as shown in section 1.4. We then convert D into the friction coefficient c_f using the equation $c_f = \frac{k_B T}{D}$ and arrive at 1.35×10^{-6} kg/s for the parallel direction and 1.35×10^{-6} kg/s for the perpendicular direction, with respect to the far field director \mathbf{n}_0 .



Figure 3.7: Histograms of the frame-by-frame displacements of an elastic octupole due to Brownian motion, both in the parallel (dy) and perpendicular (dx) directions with respect to the far field director \mathbf{n}_0

Interaction potential between general elastic multipoles is governed by the equation:

$$U_{int} = 4\pi K \sum_{l,l'=1}^{N} a_l a'_{l'} (-1)^{l'} \frac{(l+l')!}{R^{l+l'+1}} P_{l+l'}(\cos\theta)$$
(3.1)

where $a_l = b_l r_0^{l+1}$ is the elastic multipole moment of the *l*th order (the 2^{*l*}-th pole, θ is the angle between the particles with respect to the far field director, *R* is the distance between the interacting multipoles, and $P_{l+l'}(\cos \theta)$ are the Legendre polynomials [16]. For example, in elastic quadrupoles, the b_2 term will dominate this interaction potential. In the case of the pure octupole, we have b_3 as the only non-zero coefficient and arrive at:

$$U_{int} = 4\pi r_0 K b_3^2 6! \frac{P_6(\cos\theta)}{R^7}$$
(3.2)

These equations can be used to make theoretical predictions of the interactions between two octupoles, which suggest six alternating regions of attracting and repelling forces as the elastic octupole is circled. Using holographic optical tweezers, we brought together two elastic octupoles with angle $\theta \approx 3^{\circ}$ and allowed them to interact (Figure 3.8). They attracted, and ultimately ended in an alignment with $\theta \approx 19^{\circ}$. From this data, we calculate the magnitude of attractive force and interaction potential (Figure 3.9 b,c) using the same processes as in section 3.1 and arrive at a maximum force of approximately 0.1 pN and an attractive potential at contact of approximately 250 kBT.



Figure 3.8: Time lapsed images of the interaction between two elastic octupoles, ending with an angle of 19° with respect to the director.



Figure 3.9: (a) Separation of the two particles as a function of time, with a polynomial fit applied. (b) Force of attraction and (c) interaction potential between the particles as a function of their separation.

3.3 Discussion

We have demonstrated that two new types of elastic multipoles can be consistently fabricated using a colloidal droplet with a combination of homeotropic BCs and planar BCs. This is done through careful tuning of the concentration of surfactant within the colloidal droplet, which determines the level of multipole transformation which occurs. The mixed anchoring hexadecapole has the same eight pairs of clockwise and counterclockwise director tilt when compared to the tilted hexadecapole, but the angles of attraction for the two types are dramatically different. Initial investigations into the interactions between octupoles shows agreement with theoretical predictions about the angular dependence of the interactions. Future work based off of this project would include further characterization as well as modelling of these new multipoles and their interactions.

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Academic Vita Kevin Crust

Education

The Pennsylvania State University

Eberly College of Science, Schreyer Honors College Majors: Physics and Mathematics

Employment

Research with Ivan Smalyukh in CU Boulder REU	Boulder, CO			
Undergraduate Researcher in Soft Materials Physics Laboratory	May 2019 – Aug 2019			
• Created new types of colloidal molecules which were introduced to	o liquid crystals cells			
• Analyzed samples through Polarizing Optical Microscopy and object tracking software to to				
how the elastic forces were altered for different types of colloidal n	nolecules			
Research with Mauricio Terrones on 2D TMD Material Growth	University Park, PA			
Undergraduate Researcher in Condensed Matter Physics Laboratory	Sept 2017 –Dec 2019			
Grew 2D Transition Metal Dichalcogenides (TMDs) using chemic	al vapor deposition techniques			
• Characterized samples through a variety of techniques, including F	Raman spectroscopy, AMD,			
fluorescence microscopy, and photoluminescence mappings				
• Tuned parameters for growth of W _{1-x} Mo _x S ₂ hybrids to increase flal	ke size and material coverage			
Research with Eric Hudson in Penn State Physics REU	University Park, PA			
Undergraduate Researcher in Condensed Matter Physics Laboratory	May 2018 – Aug 2018			

Undergraduate Researcher in Condensed Matter Physics Laboratory

- Applied deep learning data science techniques to Scanning Tunneling Microscopy (STM), working towards the goal of a 'self-driving STM'
- Developed deep learning code in TensorFlow for automatic classification of STM images
- Collaborated with experimentalists and data scientists to improve the development process

Research with Doug Cowen on IceCube Neutrino Observatory

Undergraduate Researcher in Neutrino Particle Physics Laboratory

- Explored potential for neutron detection in the South Pole ice cap using FLUKA simulations •
- Contributed to development of new neutrino event reconstruction software •
- Worked in large collaboration setting as a part of IceCube via international conference calls

Leadership, Teaching, and Volunteering

Learning Assistant, Theoretical Mechanics

- Assisted during in-class activities by monitoring the classroom to observe students' progress and helping with questions as they arose
- Held weekly office hours where students could receive assistance on homework problems or improve their understanding of course materials to prepare for weekly quizzes
- Provided feedback from students to the instructor, thereby acting as a bridge between the two

Science Lionpride, Treasurer

- Provided tours for prospective students of the Eberly College of Science
- Engaged with alumni for networking and development of skills to prepare for a career in science
- Handled funds to ensure that the club remained in strong financial standing
- Led the club by making decisions about future events and issues present in the group as a member of the executive board

Penn State IFC/Panhellenic Dance Marathon Committee Member

Graduation: May 2020

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Aug 2019 – Dec 2019

Aug 2017 – *Apr* 2020

Oct 2017 – *Feb* 2019

University Park, PA

May 2017 – Apr 2018

- Volunteered in the THON store, providing friendly and welcoming service to customers and restocking the store when necessary
- Coordinated assembly-line system during heavy distribution days, increasing efficiency
- Prepared online orders for shipping, helping to contribute to THON donation total, supporting families affected by pediatric cancer and helping to fund cancer research

Publications

Zhang, T., Fujisawa, K., Zhang, F., [et al, including Crust, K.] (2019) "Universal In-Situ Substitutional Doping of Transition Metal Dichalcogenides by Liquid Precursor-Based Chemical Vapor Deposition." Manuscript submitted to ACS Nano for publication.

Presentations

Penn State Undergraduate Exhibition. (2019). "Halide-Assisted Growth and Optical Properties of Two-Dimensional TMD Alloys."

- Penn State Office of Science Engagement Fall Undergraduate Poster Exhibition. (2019). "Halide-Assisted Growth and Optical Properties of Two-Dimensional TMD Alloys."
- University of Colorado Boulder Soft Materials Research Center REU Student Presentation Session. (2019). "Mixed Anchoring Elastic Multipoles in LC Colloids."
- Penn State Interdisciplinary Materials and Materials Physics REU Student Poster Session. (2018). "Automatically Classifying STM Images Using Deep Learning."
- Penn State Undergraduate Exhibition. (2018). "Hypothesis Generation for Event Reconstruction in IceCube."

Honors and Awards

- Schreyer Honors College Academic Excellence Scholarship (2016, 2017, 2018, 2019)
- John and Elizabeth Holmes Teas Scholarship (2019)
- Bert Elsbach Honors Scholarship (2018)
- Penn State Office of Science Engagement Research Grant (2017, 2018)
- Evan Pugh Scholar Senior Award (2019)
- The President Sparks Award (2018)
- The President's Freshman Award (2017)
- Seven Time Dean's List (2016, 2017, 2017, 2018, 2018, 2019, 2019)
- Sigma Pi Sigma Honors Society (2019)