Magnetic and optical holonomic manipulation of colloids, structures and topological defects in liquid crystals for characterization of mesoscale self-assembly and dynamics

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Magnetic and optical holonomic manipulation of colloids, structures and topological defects in liquid crystals for characterization of mesoscale self-assembly and dynamics

by

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B.S., Colorado State University, 1999
M.S., University of Colorado, 2007

A thesis submitted to the
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This thesis entitled:
Magnetic and optical holonomic manipulation of colloids, structures and topological defects in liquid crystals for characterization of mesoscale self-assembly and dynamics
written by Michael C. M. Varney
has been approved for the Department of Physics

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Ivan I. Smalyukh, Ph.D.

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John C. Price, Ph.D.

Date________________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Abstract

Varney, Michael C.M. (Ph.D., Physics)

Magnetic and optical holonomic control of colloids, structures and topological defects in liquid crystals for characterization of mesoscale self-assembly and dynamics

Thesis directed by Professor Ivan I. Smalyukh

Colloidal systems find important applications ranging from fabrication of photonic crystals to direct probing of phenomena encountered in atomic crystals and glasses; topics of great interest for physicists exploring a broad range of scientific, industrial and biomedical fields. The ability to accurately control particles of mesoscale size in various liquid host media is usually accomplished through optical trapping methods, which suffer limitations intrinsic to trap laser intensity and force generation. Other limitations are due to colloid properties, such as optical absorptivity, and host properties, such as viscosity, opacity and structure. Therefore, alternative and/or novel methods of colloidal manipulation are of utmost importance in order to advance the state of the art in technical applications and fundamental science.

In this thesis, I demonstrate a magnetic-optical holonomic control system to manipulate magnetic and optical colloids in liquid crystals and show that the elastic structure inherent to nematic and cholesteric liquid crystals may be used to assist in tweezing of particles in a manner impossible in other media. Furthermore, I demonstrate the utility of this manipulation in characterizing the structure and microrheology of liquid crystals, and elucidating the energetics and dynamics of colloids interacting with these structures. I also demonstrate the utility of liquid crystal systems as a table top model system to probe topological defects in a manner that may
lead to insights into topologically related phenomena in other fields, such as early universe cosmology, sub-atomic and high energy systems, or Skrymionic structures. I explore the interaction of colloid surface anchoring with the structure inherent in cholesteric liquid crystals, and how this affects the periodic dynamics and localization metastability of spherical colloids undergoing a “falling” motion within the sample. These so called “metastable states” cause colloidal dynamics to deviate from Stokes-like behavior at very low Reynolds numbers and is understood by accounting for periodic landscapes of elastic interaction potential between the particle and cholesteric host medium due to surface anchoring.

This work extends our understanding of how colloids interact with liquid crystals and topological defects, and introduces a powerful method of colloidal manipulation with many potential applications.
Dedication

This dissertation is dedicated my grandmother, Betty Jean Mason. As a dedicated teacher, many children would have been poorer without her caring instruction. She recognized the doors to opportunity an education would open, and not only helped open those doors for me, but gave me a good solid kick through them. Without her, I would have not have had the chance to pursue my dreams of an education, much less becoming a man of science.
Acknowledgements

I have been fortunate to have learned from and worked with a number of wonderful physicists (and human beings) throughout my graduate education. First and foremost I thank Ivan Smalyukh for welcoming me back to academia after my foray into industry. I owe much to his insight, kindness and boundless patience, and am grateful for his unwavering support in my research. Additionally I would like to thank John Price for teaching me how to be a physicist, not simply a student. I would also like to thank my thesis committee members, Noel Clark, David Walba and Kris Bertness for their support well as suggesting some very interesting physics to explore.

Scientific research in this age of cross disciplinary exploration almost dictates that one learn from and collaborate with a wide variety of scientists. It also requires having a cadre of colleagues to work with. I am very lucky to work with some fine people in the Smalyukh group, and would like to thank them all. In particular I would like to thank Julian Evans for our “walking discussions” on all aspects of my research, as well as on other far ranging subjects. I would like to thank Rahul Trivedi for showing me the ropes early on. I would also like to thank Bohdan Senyuk, Taewoo Lee, and Haridas Mundoor for their physical and technical insights.

Finally, I would like to thank my wife, Gemma May Varney, for her support and love during my research, and for not letting me give up on my educational goals.
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**Fig. 3.1.** Integrated holonomic magnetic and holographic optical manipulation system. (a) Electromagnetic iron or air-core solenoids arranged in a Cartesian aluminum frame mounted on an inverted microscope (not shown). The solenoids are driven by amplified power supplies via computer-controlled DAQ. The HOT is based on a fiber laser and trapping system’s optical elements: a polarizer (P), lenses (L1, L2, L3, and L4), a computer-controlled dynamically addressable liquid crystal based spatial light modulator (SLM), a 100 × oil immersion objective (OBJ), a half wave plate (HWP), a polarizer-rotator (PR), and a dichroic mirror (DM). The trapping beam is focused on the sample slide. (b) The magnetic and optical colloidal handles can be translated along the x, y, or z axes using the HOT and can be rotated in yaw, pitch, and roll using magnetic fields. This manipulation setup is integrated with an optical imaging system capable of both POM and 3PEF-PM imaging.

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**Fig. 3.3.** Manipulation of a dislocation defect line in a cholesteric liquid crystal by a single SPMB particle. (a) The SPMB is embedded into a cholesteric dislocation with a \( \lambda - \tau \) defect core. The location of the cross-sectional plane corresponding to the structure of the dislocation core shown in (d) is marked by a blue dashed line. (b) An ac magnetic field of \( \sim 40 \) Gs is rotated clockwise at a frequency of 8 Hz, which maximally rotates the SPMB to an angle \( \beta_{CW} \) and stretches the defect line. (c) At the same field amplitude and frequency, the SPMB is subsequently rotated counterclockwise to a maximum angle \( \beta_{CCW} \). (d) Director structure of the manipulated topological defect with the \( \lambda - \tau \) disclination core. (e) The defect structure’s asymmetry seen from (d) causes a marked asymmetry in the defect’s response to clockwise and counterclockwise bead rotation and in the difference between \( \beta_{CW} \) and \( \beta_{CCW} \). Regions \( R_1 \) and \( R_2 \) denote the time periods during which the SPMB is forced between its maximum angles of rotation in two opposite directions via magnetic-field rotation (\( R_1 \)) or is allowed to relax naturally (\( R_2 \)). (f)–(g) Rotation angle (in degrees) vs. time (in seconds) in the forcing regime and in the relaxing regime along with their exponential fit lines, respectively. (h)–(j) Optical POM micrographs showing a single dislocation with a \( \lambda - \tau \) disclination pair which exhibits transient undulations along its length when manipulated in the forcing regime as discussed in the text.

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**Fig. 4.1.** (a) Electromagnetic iron or air core solenoids arranged in a Cartesian aluminum frame mounted on an inverted microscope (not shown) optical imaging system capable of both POM and 3PEF-PM imaging. (b) Colloid COM position vs. rotation angle for multiple colloid species (SPMB and GaN nanowire) in various configurations. The inset is an SEM image of a SPMB showing surface roughness, indicating surface anchoring with “memory” of director orientation at the colloid surface. (c) Expected dynamics of SPMB in a CLC cell. Region I denotes a so called “wind-up/lift-off,” region II denotes a “fall” region, region III is the so called “sedimentation layer.”

**Fig. 4.2.** Metastable states evident in a 5 $\mu$m pitch CLC infused in a 30 $\mu$m thick, planar aligned cell. (Region I) A SPMB is “wound up” to the top cell surface using magnetic manipulation and then released. The inset plot shows a histogram of the number of counts per 3 degree bin over the range of Region II metastable states.
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Fig. 4.4. Metastable states evident in a 2.5 \( \mu m \) pitch CLC infused in a 60 \( \mu m \) thick, planar aligned cell. A SPMB is “wound up” to the top cell surface using magnetic manipulation and released, subsequently undergoing an elastically mediated “lift-off” from the cell surface followed by periodic dynamic metastability with an angular periodicity of \( 2\pi \) radians, or one cholesteric pitch. Unlike in the 5 \( \mu m \) pitch CLC, periodic dynamic metastability is apparent even in late Region I. Elastic interaction between the colloid and the top confining surface is highlighted by locating intercept points at each cholesteric pitch [red (gray) circles] and plotting them with respect to time (insert.) Data between \( 0 < \Delta \beta < 12\pi \) radians, or Region I, is fitted with an exponential function of time constant \( \tau = 2870 \text{ s} \). A linear fit with a slope of 0.005 rad/s (0.002 \( \mu m/s \)) is used for Region II, or \( \Delta \beta \geq 10\pi \) radians.

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Fig. 4.6. Colloid topography enhancement of metastable states in a 2.5 \( \mu m \) pitch CLC infused in a 60 \( \mu m \) thick, planar aligned cell. A SPMB with a spherical protrusion of diameter \( \sim 1/15^{th} \) that of the “mother bead” induced enhanced periodic dynamic metastable states. Metastable state transition within one cholesteric pitch as indicated by the sharp transition within the first 15 seconds (figure inset) shows where metastable effects dominate over elastic repulsion from the cell wall.

Fig. 4.7. Fall experiments with SPMB dimer. A SPMB dimer in 5 \( \mu m \) pitch CLC is allowed to fall in Region II in a 30 \( \mu m \) thick cell. The dimer tends to situate at an angle of (insert angle) with respect to the plane of the CLC lamella. This angle produces a distinct “double period” in the metastable states observed.

Fig. 4.8. Fall experiments with GaN nanowires, uncoated and coated respectively, in a 5 \( \mu m \) pitch CLC infused in a 60 micron thick cell which shows the effect of anchoring alignment on periodic dynamics and metastability. (a) Fall data from an uncoated GaN nanowire of nominal length of 10 \( \mu m \) and 350 nm diameter with planar anchoring. (b) Top image is an SEM of an uncoated GaN nanowire. Bottom image is an Al coated GaN nanowire highlighting so called “nanopyramid” structures on its surface. (c) Fall data from an Al coated GaN nanowire of nominal length of 10 \( \mu m \) and 350 nm diameter with homeotropic alignment dominant. Periodic
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List of Abbreviations

2PEFPM- 2-photon epi-fluorescence polarizing microscopy

3D- Three Dimensions

3PEFPM- 3-photon epi-fluorescence polarizing microscopy

5CB- pentylycyanobiphenyl

A- Analyzer

AFM- Atomic force microscopy

APS- Amplified Power Supply

BPF- Band Pass Filter

BTBP- n,n’-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenedicarboximide

CARS-PM- Coherent anti-Stokes Raman Scattering polarizing microscopy

CCD- Charge Coupled Device

CCW- Counter Clockwise

CF- Cholesteric Fingers

CLC- Cholesteric Liquid Crystal

CW- Clockwise

D- Diameter

D- diameter

d- often cell thickness

DAQ- Data Acquisition Card

DM- Dichroic Mirror
DMOAP- [3-(trimethoxysilyl)propyl]octadecyl-dimethylammonium chloride

FCPM- Fluorescence confocal polarizing microscopy

GaN- Gallium Nitride

H- Applied magnetic field (vector)

HOT- Holographic Optical Trapping

HWP- Half Wave Plate

IPA- Isopropyl alcohol

ITO- Indium Tin Oxide

L- length

LC- Liquid Crystal

LCE- Liquid Crystal Elastomer

m- induced magnetic moment (vector)

MO- Macroscopic Objective

MOCH- Magnetic and Optical Colloidal Handle(s)

n, N(r)- director

NA- numerical aperture

NLC- Nematic Liquid Crystal

NW- Nanowire

p- pitch

P- Polarizer

PI- Polyimide

PMT- Photomultiplier Tube
POM- Polarizing Optical Microscopy
PR- Polarization Rotator
PVA- Polyvinyl Alcohol
R-Retardation Plate
SEM- Scanning electron microscope
SLM- Spatial Light Modulator
SPMB- Superparamagnetic Bead
SPR- Surface Plasmon Resonance
TD- Topological Defect
TIC- Translationally Invariant Configuration
TPL-Two-photon luminescence
UV- Ultraviolet
χ- cholesteric helical axis
Chapter 1

Introduction

Colloidal particles, and methods of their manipulation, is a topic of great interest for physicists and engineers exploring a broad range of scientific, industrial and biomedical fields [1-5]. Wavelength selective scattering of sunlight off of gas molecules in the Rayleigh regime explains the age old question of why the sky is blue [6, 7]. Mie scattering in the large colloid diameter to wavelength regime allows scientists to characterize colloidal concentration in the atmosphere, such as smoke particulates [7]. Ordered arrays of colloids can be used to create metamaterials and photonic crystals with novel optical properties [8-10].

Liquid crystals can host interesting structures that interact with colloids. These interactions can produce templates that can guide the self-assembly of colloid structures, such as photonic crystals or patterned arrays [9-15]. Liquid crystals can also host fascinating topological structures that have analogs in cosmological fields, such as early universe cosmology, or sub-atomic and high energy systems, or Skrymionic structures [16-18]. Manipulation of such structures and defects, while impossible at the cosmological or sub-atomic scales, is relatively easy in soft condensed matter systems such as in liquid crystal hosts where one can directly manipulate topological defects, or use colloids as magnetic and optical “handles” as tools for defect manipulation. Therefore, alternative and/or novel methods of colloidal manipulation are of utmost importance in order to advance the state of the art in technical applications and fundamental science.

The ability to accurately position and manipulate particles of mesoscale size in various liquid host media is usually accomplished through optical trapping methods, which suffer
limitations intrinsic to trap laser intensity and force generation. Other limitations are due to colloid properties, such as index of refraction absorptivity, and host properties, such as viscosity, opacity and structure.

In this thesis, I demonstrate a magnetic-optical holonomic control system to manipulate magnetic and optical colloid handles in liquid crystal systems and furthermore show that the elastic structure inherent to nematic and cholesteric liquid crystals may be, reciprocally, optically and magnetically manipulated directly to assist in colloidal manipulation. This work extends our understanding of how colloids interact with liquid crystals and topological defects, and introduces a powerful method of colloidal manipulation with many potential applications in industry and in fundamental research, and explores the following topics and applications:

In chapter 2, a novel and robust method for unconventional structure-assisted optical manipulation of high-index nanowires in nematic and cholesteric liquid crystals is developed, where I use holographic optical traps to locally deform the liquid crystal director. Such induced distortions can be used to stably trap high index colloids, which would otherwise not be stably trapped by optical forces alone. I then apply this “elasto-optical” trapping method to manipulate GaN nanowires in three dimensions to explore the structure and micro-rheology of nematic and cholesteric liquid crystals, and to characterize topological defects that naturally occur in liquid crystals.

Chapter 3 introduces a magneto-optical manipulation system allowing geometrically unrestricted, full holonomic control of colloids, i.e. in all three Cartesian degrees of freedom, and rotation through all three Euler axes. Low gradient magnetic fields are used to apply very large torques on colloids, many orders of magnitude larger than can be achieved via optical methods. I use this holonomic control to create and manipulate topological defects such as Lehmann
clusters, twist disclinations and cholesteric fingers, thus laying the foundation for a tabletop laboratory to expand our understanding of the role defects play in fields ranging from subatomic particle physics to early-universe cosmology.

In chapter 4 I apply these magneto-optical manipulation methods to explore the dynamics of colloids falling under the force of gravity in liquid crystal systems which deviate from Stokes-like behavior at very low Reynolds numbers as observed in classical “fall experiments.” Not only are periodic dynamics and localization metastability observed within cholesteric liquid crystals, but elastic forces are measured between colloids and confining surfaces. Thus I am able to characterize metastable localization of colloids under the effects of elastic and surface anchoring periodic potential landscapes seen by the moving spheres forces, demonstrating the important roles played by anchoring memory and topological defect transformation in generating these periodic dynamics and metastable states.

Chapter 5 explores the use of surface anchoring periodic potential landscapes to help guide the three dimensional self-assembly of topologically and topographically complex colloids into stable, three dimensional structures. Furthermore, I use the topographical properties of the colloids to explore elastic structure of left and right handed cholesteric liquid crystals near confining surfaces, and orientational metastable states within the bulk.

In chapter 6 I explore stick-slip potential landscapes involving topological defects, particularly boojums, at the surface of a colloid. By rotating the colloid magnetically, we transfer energy to the local elastic field to a point where a surface point or handle-body boojum slips along the colloid surface to a lower energy configuration. The interaction of these boojums with
the near field elastic structure allows for complex motion of colloid monomers and dimers, creating motile engines that can “swim” through the bulk of the liquid crystal.

Chapter 7 explores dressing spherical colloids with torons, hopfions and other varieties of particle/soliton bound states, as well as exploring the motion and apparent asymmetry of colloid “orbital dynamics” within a torons’ double twist cylinder.

Chapter 8 explores the effect of colloid-structure interactions in cholesteric liquid crystals, particularly threshold undulation formation on the positioning and orientation of GaN nanowires and magnetic and optical colloidal handles. I show that such interactions lead to positional and orientational ordered arrays of colloids that self-assemble from the structural template imposed by the cholesteric liquid crystal under an AC electric field. Such ordering can be used to create templates for photonic crystals, or to create dynamic polarizers from liquid crystal colloid systems.

Chapter 9 presents concluding remarks, discussion of previous results, and paths of future exploration.

1.1. References


Chapter 2

Unconventional structure-assisted optical manipulation of high-index nanowires in liquid crystals

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Chapter Overview

Stable optical trapping and manipulation of high-index particles in low-index host media is often impossible due to the dominance of scattering forces over gradient forces. Here we explore optical manipulation in liquid crystalline structured hosts and show that robust optical manipulation of high-index particles, such as GaN nanowires, is enabled by laser-induced distortions in long-range molecular alignment, via coupling of translational and rotational motions due to helicoidal molecular arrangement, or due to elastic repulsive interactions with confining substrates. Anisotropy of the viscoelastic liquid crystal medium and particle shape give rise to a number of robust unconventional trapping capabilities, which we use to characterize defect structures and study rheological properties of various thermotropic liquid crystals.

2.1. Introduction

Optical trapping is a non-contact manipulation technique broadly used in science fields ranging from condensed matter physics to biology and biomedicine, as well as for various technological applications.

* In collaboration with D. Engström, M. Persson, R. P. Trivedi, K. A. Bertness, M. Goksör, and I. I. Smalyukh
applications [1–3]. Stable manipulation typically uses tightly focused laser beams that exert optical gradient forces and pull particles towards the maximum-intensity region of the focal plane and overcome scattering forces that tend to push the particle along the light-propagation direction [4]. This imposes restrictions on the refractive indices of the particles with respect to the fluid host media, specifically that the refractive index of particles has to be modestly higher than that of the medium. Particle shape is another factor that determines trapping stability, orientation, and possible rotation/motion of particles within the trap [1–9]. For example, colloidal cylinders with dimensions comparable to or smaller than the wavelength of the trapping laser spontaneously align along either the beam propagation or linear polarization directions [7, 8] while larger anisotropic microparticles can be trapped in desired orientations using multiple traps [10–12] or optical vortex beams [13]. Some of the remaining challenges include stable trapping of particles with a refractive index much larger than that of the surrounding host medium, manipulation of non-spherical particles while aligning them in desired orientations, as well as robust control of colloidal inclusions in anisotropic fluid hosts such as liquid crystals (LCs).

In our work, we explore optical manipulation of high-index GaN nanowires infused in nematic and cholesteric LCs in the regime when optical gradient forces are much weaker than scattering forces. We show that stable non-contact optical manipulation of these particles is still possible because of the structured LC self-organization and its response to laser beams. Laser manipulation properties are studied as a function of laser power, structure of long-range molecular alignment (described by the director field $N(r)$), and LC confinement conditions. This robust structure-assisted trapping allows us to characterize three-dimensional (3D) defect morphology and local rheological properties of LCs.
2.2. Optical setup

Our setup (Fig. 2.1) combines holographic optical tweezers (HOT) [14] with fluorescence confocal polarizing microscopy (FCPM) [15, 16] and allows for simultaneous optical 3D manipulation and imaging of a variety of systems.

Fig. 2.1. Integrated HOT and FCPM setup. The HOT part of the setup is composed of a laser (λ= 1064 nm), plano-convex lenses L1 (focal length 100 mm), L2 (250 mm), L3 (850 mm), and L4(400 mm) with anti-reflection coating, a Glan-Laser polarizer (P), a half-wave plate (HWP), a dichroic mirror (DM), a polarization rotator (PR), and a microscope objective (MO). The FCPM consists of an excitation laser, a dichroic filter (F), a beam-splitting cube (C), a pinhole, and a photomultiplier tube (PMT). The setup also allows for POM imaging.
The HOT is built around an electrically addressed liquid-crystal spatial light modulator (LC-SLM) with $512 \times 512$ pixels (BNS XY series P512-1064, with each pixel being $15 \, \mu m \times 15 \, \mu m$). Two telescopes, one before and another after the SLM, resize the beam to overfill the active area of the SLM and image the SLM on the back-aperture of the objective, respectively. While trapping is performed at 1064nm, the sample imaging in 3D is done via dye excitation at 488 nm and fluorescence detection in the range of 505–525 nm. Both the HOT and the FCPM use the same oil immersion objective. The used objectives with $60 \times$ and $100 \times$ magnification had numerical aperture of 1.42. In addition to laser manipulation and confocal microscopy, this setup allows us to perform conventional polarizing optical microscopy (POM) studies.

2.3. Sample and cell preparation

Figures 2.2(a), 2.2(b) shows representative GaN (lot C144 obtained from K.A. Bertness, NIST) nanowires grown via molecular beam epitaxy [17]. The method yields nanowires with a hexagonal cross-section of ~300 nm in width.

Fig. 2.2. Nanowires in NLCs. (a) and (b) SEM micrographs of (a) the side-view and (b) cross sections of GaN nanowires. (c) Schematic of $(N)(r)$ around a hexagonal faceted nanowire in an aligned NLC. (d) Micrograph and (e) schematic of $(N)(r)$ around a nanowire in an aligned NLC. (f) Micrograph and (g) schematic of $(N)(r)$ around a nanowire under the influence of a laser trap.
(light is propagating in the positive $z$-direction) centered at one of nanowire ends. The dotted lines in (e) and (g) indicates the image plane used to capture the micrographs shown in (d) and (f).

Ultrasonic removal of the nanowires from the growth substrate into a solvent (isopropanol) results in a fairly mono disperse solution with a typical nanowire length of ~10 $\mu$m. Our study utilized LC mixtures such as the nematic LC (NLC) E31, and a cholesteric LC (CLC) composed of an NLC host (e.g., E7, ZLI-3412, or ZLI-2806) mixed with a chiral agent (CB-15) [15, 18]. E31 is a mixture of cyanobiphenyl homologs, with elastic constants of bend, splay, and twist being $K_{33} = 25$ pN, $K_{11} = 17.5$ pN, and $K_{22} = 8.5$ pN, respectively [19]. For FCPM imaging, our samples were doped with a tiny amount (0.01 wt. %) of a fluorescent dye n,n’-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenedicarboximide (BTBP, Aldrich) that yields a strong fluorescence signal without affecting LC properties [20]. LC cells are fabricated with two glass substrates sandwiched together by the use of UV curable glue (Norland optical adhesive NOA-63). Silica spheres mixed with glue set a cell gap ranging from 10 $\mu$m to 60 $\mu$m. Spin-coated thin films of polyvinyl alcohol (PVA) are used as surface alignment layers; PVA coatings on the opposite inner surfaces of confining glass plates are rubbed in the antiparallel fashion before cell assembly to provide unidirectional planar surface anchoring. The nanowire solution is mixed into an LC sample via solvent exchange, after which the solvent is evaporated. This nanowire-LC dispersion is then infused into the cell in its nematic phase by means of capillary forces. Finally, the cell is sealed with fast curing epoxy.

2.4. Optical manipulation of nanowires in nematic liquid crystals
In a planar-aligned NLC, nanowires tend to align themselves parallel to the uniform far-field director \( N_0 \) to minimize elastic energy, Figs. 2.2(c)-2.2(e). Due to a director pre-tilt induced by anti-parallel surface rubbing of the PVA alignment layer, nanowires commonly tilt out of the \((x,y)\) plane at an angle < 8 degrees. POM images indicate that the nanowires weakly distort the director field, with areas of the strongest distortions occurring at their ends, Fig. 2.2(c). Heating of the surrounding LC during optical manipulation of nanowires is negligible because of their low absorption coefficient of \( \sim 80 \text{ cm}^{-1} \) at the laser wavelength of 1064 nm.

A laser beam of power < 25 mW initially attracts a nearby nanowire. However, once the nanowire overlaps with the focused laser beam, it is pushed along the light propagation direction, indicating that the high refractive index contrast between the nanowire (\( n_{\text{GaN}} = 2.4 \)) and the LC (\( n_{\text{LC}} \approx 1.5 \)) precludes stable 3D trapping. This is true regardless of trap position and beam polarization relative to the director or nanowire. This hypothesis is supported by numerical simulations, using the T-matrix method and a discrete-dipole approximation [21, 22], yielding a strong force of 30–80 pN in the positive \( z \)-direction. A trap positioned on one end of the nanowire rotates the nanowire out of the \((x,y)\)-plane to an angle at which the optical torque, due to scattering force acting on one of the nanowire’s ends, is balanced by the elastic torque tending to align the nanowire along \( N_0 \). Its initial orientation is restored when the beam is turned off.

Elastic distortions around the rotated nanowire are of monopole type and mediate repulsive elastic interactions of the colloid with the strong surface boundary conditions of the confining substrates. These interactions can be modeled using the method of images, analogous to that used in electrostatics [23]. Interactions between elastic monopoles induced by rotated nanowires with their image monopoles on the opposite sides of the LC substrate interfaces are repulsive [23] and are expected to slowly decay with distance \( d \) from the substrate as \( \propto 1/d^2 \). This assures that the
optical scattering force is balanced by the elastic force of nanowire’s repulsive interaction with the confining plates that tend to localize it in the cell midplane. Once the focused beam is removed, the elastic torque acting on the nanowire aligns the nanowire such that it returns to its initial orientation, again parallel to $N_0$, Figs. 2.2(d), 2.2(e).

Using an optical power of up to 20 mW, we have measured a maximum nanowire tilt angle of $\sim 10$ degrees from $N_0$, yielding an estimate of the axial optical force consistent with our numerical calculations below. Thus, an optically tilted nanowire can be stably localized in the LC cell close to its midplane, due to the balance of scattering and gradient forces augmented with elastic repulsive forces between a rotated nanowire and confining plates. On the other hand, when a trap is positioned in the middle of the nanowire rather than at one of its ends, there is no elastic torque, and the weak elastic distortions around the colloid remain quadrupolar (Fig. 2.2(e)). This results in much weaker nanowire-substrate elastic interactions (with the force decaying as $\propto 1/d^6$) and an apparent pushing of the nanowire to the opposite substrate of the cell by the optical force. Thus, this type of elasticity- and confinement assisted trapping has a number of limitations on cell thickness and trap position along a nanowire for which stable 3D trapping is achieved.

At optical powers of about 35 mW and higher, laser traps realign the local director $N(\mathbf{r})$ [16]. Thus, in addition to particle manipulation by optical forces, it is also possible to utilize the ensuing elastic forces to enable stable trapping of a GaN nanowire. Such trapping is accomplished when the trap polarization is orthogonal to $N_0$ and the trap is turned on after being centered on the nanowire. By the use of this type of trap activation, multiple traps can be used to manipulate the nanowire at any point along its length. On the other hand, traps activated in close vicinity of the nanowire do not result in a stable trapping as the particle is repelled from a trap.
These observations may be understood by considering the elastic energy cost of a laser-induced elastic distortion in the NLC, which is minimized when a trap is centered on the nanowire due to the volume of NLC with laser-induced distortions excluded by the presence of the nanowire. Due to tangential surface boundary conditions along the length of the rather long nanowire, it is typically repelled from the laser trap located nearby, again to minimize the elastic free energy. Clearly, this behavior at high laser powers is very different from that at low powers discussed above.

Figure 2.3(a) shows a nanowire manipulated by a single trap with laser power higher than the realignment threshold of 35 mW positioned at its left end. The trap, and consequently the end of the nanowire, is translated orthogonal to \(N_0\) at a constant rate of 0.5 μm/s, while elastic forces retain its alignment along \(N_0\).

![Figure 2.3(a)](image)

Fig. 2.3. Manipulation of a GaN nanowire in an NLC using high-power laser traps. (a) Nanowire manipulated by a single trap positioned at its left end: at elapsed time \(t_1 = 5.0\) s, the trap starts moving with a constant velocity. The inset shows this; \(N_0\) is along the \(x\)-axis. (b) Nanowire manipulated using two traps, one at each of its ends: at elapsed time \(t_1 = 2.1\) s, the left trap starts moving with a constant velocity while the right end trap is immobile. At elapsed time \(t_2 = 7.0\) s, the right end of the nanowire escapes its trap due to the elastic torque exerted by the NLC. Inset shows the nanowire at an elapsed time of 7.0 s; \(N_0\) is along the \(x\)-axis. In (a) and (b) graphs show nanowire’s left end position \(y_{nw}\) and rotation angle \(\beta_{nw}\) vs. time. The black solid line in (b) is obtained by the use of the model and parameters \(K = 13 \times 10^{-12}\) N, \(\eta = 0.45\) P, \(L_{nw} = 10\) μm, and \(R_{nw} = 150\) nm. The cell gap is 60 μm.
Figure 2.3(b) shows a similar experiment, where in addition to the moving trap, a stationary trap is positioned at the right end of the nanowire. As the left side trap is translated nearly orthogonal to \( \mathbf{N}_0 \), the two traps are strong enough to overcome elastic forces, resulting in an in-plane rotation \( \beta_{nw} \). At \( \beta_{nw} \sim 13 \) degrees, the right end of the nanowire escapes the trap and the nanowire rotates back to become parallel to \( \mathbf{N}_0 \) under the action of an elastic torque exerted by the NLC medium. The escape angle is experimentally observed to increase with increasing laser power, and is expected to depend on elastic and viscous properties of the NLC, and the angular velocity of trap motion, because both elastic and viscous torques oppose rotation of the nanowire away from the equilibrium alignment direction.

Relaxation of the nanowire toward \( \mathbf{N}_0 \) is determined by the balance of elastic restoring and viscous drag forces, while inertial effects are negligible. The angular motion of the nanowire with a viscous drag of Stokes-sphere-equivalent volume is [24, 25]

\[
\beta(t) = c_1 e^{-\gamma t} \tag{2.1}
\]

where \( c_1 \) is determined by the escape angle and \( \gamma \) is the relaxation time constant:

\[
\gamma = \frac{4}{3} \frac{K}{\eta L^2 \ln \left( \frac{2}{R} \right)} \left( \frac{L^2}{6R^2} \right)^{1/3} \tag{2.2}
\]

where \( K \) is the Frank elastic constant of the NLC in the “one-constant approximation”, \( L \) and \( R \) are the length and radius of a cylinder circumscribing the hexagonally-shaped nanowire, respectively, and \( \eta \) is an effective viscosity. Figure 2.3(b) shows the fit of this model to our data for known values for \( K \) and \( \eta \), and experimentally measured \( L \) and \( R \). The good agreement of our
experiment shown in Fig. 2.3(b) with this model for known material parameters [19] suggests that simple manipulation of optically trapped nanowires can allow for microrheological measurements of Frank elastic constants and viscosities. These measurements might be done locally in sample regions of interest, e.g. in NLC droplets and near or within defect lines [26–28].

2.5. **Optical manipulation of nanowires in cholesteric liquid crystals**

A cholesteric LC infused into a cell with parallel surface rubbing results in a helical director structure that induces a strong coupling between a nanowire’s $z$-position ($z_{nw}$) and its in-plane rotation angle ($\beta_{nw}$), Fig. 2.4(a). An optical beam focused on the center of a nanowire not only pushes the nanowire along the light-propagation direction but also forces it to rotate along the helical structure, as shown in Figs. 2.4(a)–2.4(f).
Manipulation of GaN nanowires in a CLC. (a) Schematic of an equilibrium director structure in a CLC cell with pitch $p$. (b)–(e) A single focused optical beam, initially positioned on the center of a nanowire, forces the nanowire to rotate away from the microscope objective. The optical beam is then blocked, refocused, and unblocked at elapsed times of unblocking 4.5 s and 35.0 s. (f) Nanowire in-plane angle $\beta_{nw}$ and $z$-position $z_{nw}$ vs. time. Frames shown in (b)–(e) correspond to elapsed times indicated with red circles in (f). (g) Measured nanowire position $z_{nw}$ as a function of the in-plane rotation angle $\beta_{nw}$. The cell gap is 60 μm. A laser beam power of 50 mW at the sample plane was used in these experiments.

The helical structure and CLC elasticity prevent the nanowire from tilting out of the $(x, y)$-plane, even when the trap is positioned at one of its ends. Since the $z$-component of the optical force (along the CLC helical axis) is balanced out by elastic forces preventing the nanowire tilt toward the helical axis, and since the rotations around and translations along the helical axis are mechanically coupled, optical manipulation of the ends of a nanowire allows for robust manipulation of the nanowire in 3D. For controlled displacement of a nanowire within the $(x, y)$-plane, at least two focused laser beams are moved while the orientation of their center-to-center separation vector is kept fixed. For movement along the $z$-direction, one or two traps are
positioned at each end of the nanowire and used to rotate the nanowire, resulting in a screw-like translation along the helical axis; it is somewhat easier to translate the nanowire along the direction of optical scattering force (away from the microscope objective) rather than opposed to it. This rotation-translation coupling allows for precise measurement of the local cholesteric pitch $p$, as shown in Fig. 2.4 (g). Best fit of the experimental data of vertical $z$-position vs. the in-plane orientation angle, measured using a previously described method [15, 16], yields cholesteric pitch of $p = 40.4 \pm 0.25 \mu m$ [15, 16], which is consistent with the equilibrium pitch of the CLC used in our study.

2.6. Trapping-assisted characterization of 3D defect morphology

There is a great interest in measuring and characterizing anisotropic properties and structure of LCs. Optical manipulation techniques demonstrated above give a simple and robust means for such measurements and also allow for mapping of complex director fields [15]. Figure 2.5 shows a nanowire manipulated in a CLC sample containing an “oily streak” defect at which cholesteric layers are discontinuous.
Fig. 2.5. GaN nanowire translated within and around an oily streak in a CLC. (a) FCPM vertical cross-section of the sample with an oily streak. (b) Schematic of the director structure around the defect with the nanowire translation trajectory (red line); the three rotated screws each indicate a 180° clock-wise rotation of the nanowire. (c) Shows the nanowire being moved from position #1 to #2 in (d), the dislocation prohibiting the nanowire from moving across one of the broken layers, position #5 in (d), and the nanowire being pushed between positions #8 to #9 in (d), respectively. (d) Layered structure obtained using FCPM images shown with co-located nanowire positions measured using either in-plane FCPM images (red circles) or video microscopy frames (blue squares).

By means of low-power manipulation, we have probed the CLC structure with a manipulated nanowire being used as a “compass” that always points along \( \mathbf{N}(\mathbf{r}) \). To demonstrate this, we have translated the nanowire above and below the oily streak defect along the \( x \)-direction, as shown in Fig. 2.5(d). The nanowire was also translated along a bent layer passing through the core of the oily streak, Fig. 2.5(c), revealing the director field in the vicinity and within this complex defect core. Similar non-contact manipulation reveals the layered structure...
of the cholesteric LC sample and presence of various nonsingular and singular disclinations within the oily streak defect core (Fig. 2.5).

### 2.7. Conclusions

We have presented new approaches for unconventional structure-assisted optical manipulation of high-index nanowires in nematic and cholesteric liquid crystals. Stable 3D manipulation in these approaches is enabled by augmenting the optical gradient and scattering forces with forces due to trap-induced elastic distortions or by coupling of translational and rotational motions due to intrinsic helicoidal structures, or by elastic repulsive interactions with confining substrates when traps rotate nanowires and induce elastic monopole-like low symmetry structures. Robust optical manipulation by above methods enables characterization of director structures, defect morphology, and local rheological properties of liquid crystals.

### 2.8. References


[18] Certain commercial materials are identified in this paper only to specify experimental procedures. Such identification implies neither recommendation nor endorsement by the National Institute of Standards and Technology, nor that materials identified are necessarily the best available for the purpose.


Chapter 3

Geometrically unrestricted, topologically constrained control of liquid crystal defects using simultaneous holonomic magnetic and holographic optical manipulation

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Chapter Overview

Despite the recent progress in physical control and manipulation of various condensed matter, atomic, and particle systems, including individual atoms and photons, our ability to control topological defects remains limited. Recently, controlled generation, spatial translation, and stretching of topological point and line defects have been achieved using laser tweezers and liquid crystals as model defect-hosting systems. However, many modes of manipulation remain hindered by limitations inherent to optical trapping. To overcome some of these limitations, we integrate holographic optical tweezers with a magnetic manipulation system, which enables fully holonomic manipulation of defects by means of optically and magnetically controllable colloids used as “handles” to transfer forces and torques to various liquid crystal defects. These colloidal handles are magnetically rotated around determined axes and are optically translated along three-dimensional pathways while mechanically attached to defects, which, combined with inducing spatially localized nematic-isotropic phase transitions, allow for geometrically unrestricted control of defects, including previously unrealized modes of noncontact manipulation, such as the twisting of disclination clusters. These manipulation capabilities may allow for probing topological constraints and the nature of defects in unprecedented ways, providing the

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foundation for a tabletop laboratory to expand our understanding of the role defects play in fields ranging from subatomic particle physics to early-universe cosmology.

3.1. Introduction

Topological defects play important roles in many branches of physics, ranging from early-universe cosmology [1, 2] and string theory [3, 4] to condensed matter physics [5]. Although theoretical studies of topological defects have progressed in many fields, their experimental exploration remains difficult in noncondensed matter systems, such as cosmology, where researchers deal with probing observable consequences of these defects on cosmic scales. For instance, analysis of NASA’s Cosmic Background Explorer satellite data provides insights into possible cosmic string imprints on the large scale structure of the Universe [6]. Tabletop physics, on the other hand, provides an opportunity to study phenomena of particle physics and cosmology [7] using various specially selected model systems in condensed matter, such as probing kinetics of cosmic string defects and the cosmological Kibble mechanism of their appearance using defects that occur at isotropic-nematic phase transition [8–14]. Recent advances in directly controlled generation, visualization, and manipulation of topological defects in condensed matter systems, such as liquid crystals (LCs) may provide a new means for experimental exploration of topological analogs to cosmic strings and Skyrmions and may probe topological aspects universal to these systems [15, 16].

The ability to manipulate colloidal particles via noncontact optical techniques, such as laser tweezers, has enabled great advances in many scientific and technological fields [17–19]. Optical tweezers, including holographic optical tweezers (HOT), allow one to exert well-
controlled forces (commonly within the range of 0.1–100 pN) and to reliably position and spatially translate individual particles or their arrays in three dimensions (3D) [17]. Although this enables noncontact manipulation of LC topological defects via the use of colloids as optically controllable “handles,” there remain many limitations in this control strategy due to accessible optical force ranges, manipulatable degrees of freedom, and potential heating and realignment effects at the high laser powers needed to generate strong forces and torques [20]. Rotational manipulation is typically limited to rotations around the optical axis of the trapping beam and requires the use of Laguerre-Gaussian modes or the use of shape and/or optically anisotropic particles manipulated by laser beams with well-controlled polarization states. Finally, optical trapping is ineffective in media that are optically opaque to a trapping beam, such as LCs formed by high concentrations of graphene flakes and, in general, where the use of a highly focused trapping beam is impractical. Magnetic manipulation of colloids can supplement the inherent strengths of HOT and can mitigate some of the aforementioned limitations despite having its own weaknesses, mainly in terms of spatial translation and localization or selectivity. Magnetic fields can exert large torques on ferromagnetic or superparamagnetic colloids [21–23] in a highly controllable manner with minimal or no heating of the host material. Likewise, the LC host may be designed or selected and the magnetic field used within a limited range so that magnetic manipulation fields do not affect the LC director structure. Finally, magnetic manipulation is realizable in LC hosts that are optically opaque, highly birefringent, or otherwise possessing properties that render optical trapping impractical.

In this paper, we describe a robust method for magnetic and optical manipulations of topological defects using magnetic and optical colloidal handles (MOCH) in various LC hosts. This method allows us to manipulate the MOCHs and topological LC defects attached to them in
a fully holonomic manner, i.e., in all three Cartesian degrees of freedom via HOT and in all three rotational degrees of freedom via magnetic control. Such combined magneto-optic manipulations allow us to probe the mechanical and structural properties of defects as well as to provide a powerful means for generating topologically and geometrically nontrivial defect configurations that would be difficult or impossible to achieve by optical or magnetic manipulation alone. We further supplement this magneto-optic manipulation technique by imaging with conventional polarizing optical microscopy (POM) and three-photon fluorescence excitation polarizing microscopy (3PEF-PM) applied in concert to simultaneously control and to probe topological line defects in nematic and cholesteric LCs.

3.2. Materials, methods, and techniques

3.2.1. Integrated holonomic magnetic and holographic optical manipulation system

Our integrated holonomic magnetic and holographic optical manipulation system is shown in Fig. 3.1. Magnetic manipulation is achieved using three iron-core electromagnets (Fisher Scientific International, Inc. S52051 air-core solenoids with custom machined cast iron cores) arranged in a Cartesian frame machined from aluminum and mounted directly on the microscope body.
Fig. 3.1. Integrated holonomic magnetic and holographic optical manipulation system. (a) Electromagnetic iron or air-core solenoids arranged in a Cartesian aluminum frame mounted on an inverted microscope (not shown). The solenoids are driven by amplified power supplies via computer-controlled DAQ. The HOT is based on a fiber laser and trapping system’s optical elements: a polarizer (P), lenses (L1, L2, L3, and L4), a computer-controlled dynamically addressable liquid crystal based spatial light modulator (SLM), a 100 × oil immersion objective (OBJ), a half wave plate (HWP), a polarizer-rotator (PR), and a dichroic mirror (DM). The trapping beam is focused on the sample slide. (b) The magnetic and optical colloidal handles can be translated along the x, y, or z axes using the HOT and can be rotated in yaw, pitch, and roll using magnetic fields. This manipulation setup is integrated with an optical imaging system capable of both POM and 3PEF-PM imaging.

The origin of the Cartesian frame is adjusted via shims. In some configurations, an ancillary Helmholtz coil is connected to a dc current source for high gradient magnetic-field pitch control, depth-resolved translation of defects, or to null magnetic-field gradients. A microscope slide holder is machined from aluminum and is positioned on the x-y plane using precision translation stages. Each electromagnet is independently driven via an amplified power supply (APS) BOP20-5M (obtained from Kepco). Each APS is voltage controlled using a computer-controlled data acquisition (DAQ) card (National Instruments USB-6259 BNC) and in-
house LABVIEW-based software (LABVIEW was purchased from National Instruments). The electromagnets are ambient-air cooled with the aluminum harness acting as a heat sink, and therefore, continuous operation over several hours does not thermally affect our samples. Each electromagnet can produce ac (up to 8 Hz) and/or dc magnetic fields up to 40 Gs as measured at the sample by a Gauss meter. This field affects all magnetic particles in the sample volume and, thus, is appropriate for manipulation of multiple particles in a similar way simultaneously rather than manipulation of single colloids on an individual basis. The use of low magnetic fields assures robust control of magnetically responsive ferromagnetic and superparamagnetic particles without significant direct coupling between the magnetic field and the LC director. Since most known LCs (including the ones used in this study) are diamagnetic materials, director realignment is typically a threshold like effect and requires fields of 1000 Gs and higher at our studied cell thickness values, and therefore, the influence of up to 40 Gs magnetic fields (used in all magnetic manipulations presented herein) on the LC director may be neglected in agreement with our experimental observations.

The magnetic colloids in our paper are superparamagnetic beads (SPMBs) (Dynabead M450, obtained from Invitrogen) with a nominal diameter of 4.5 ± 0.1 µm, which are fabricated using ferromagnetic nanoparticles (γ Fe₂O₃ and Fe₃O₄) approximately 8 nm in diameter and embedded into a highly cross-linked epoxy at a density of ~ 10⁵ nanoparticles per bead. Although the nanoparticles are ferromagnetic, their small size allows thermally activated flipping of their magnetic moments [24] that can be characterized by the Néel relaxation time,

\[ t = t_0 \exp \left( \frac{kV}{k_B T} \right) \]  \hspace{1cm} (3.1)
where $t_0$ is a material dependent preexponential attempt time on the order of 0.1–1 ns, $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, and the product $\kappa V$ is the energy barrier for net magnetic moment flipping determined by the nanoparticles magnetic anisotropy energy density $\kappa$ and volume $V$. Figure 3.2(a) shows a schematic of such a SPMB at no applied external field. The net magnetic moment of the SPMB is zero because its small volume sets the energy barrier product $\kappa V$ on the order of a few $k_B T$'s at room temperature. Random orientation of individual ferrite nanoparticles, coupled with this thermal moment flipping, creates a zero net magnetic moment in the SPMB. When an external magnetic field $\mathbf{H}$ is applied [Fig. 3.2(b)], the magnetic moment of a given $i$th ferrite nanoparticle ($\mathbf{m}_i$) is induced to favor one direction state along its easy axis, which may not necessarily align collinearly with $\mathbf{H}$.

Fig. 3.2. Superparamagnetic bead magnetic structure and surface anchoring. (a) A SPMB with a zero net magnetic moment is composed of ferrite nanoparticles fixed in an epoxy matrix. (b) An external magnetic field $\mathbf{H}$ is applied, inducing a transient net magnetic moment $\mathbf{m} = \sum \mathbf{m}_i$ at some angle with respect to $\mathbf{H}$. (c) The generated magnetic torque aligns the beads magnetic moment $\mathbf{m}$
coaxially along $\mathbf{H}$. Subsequent rotation of $\mathbf{H}$ rotates the SPMB. (d) SEM image of a SPMB showing surface roughness, indicating a strong surface anchoring which is tangential but with “memory” of director orientation at the surface. (e) The SPMB tends to distort the nematic director field, creating two surface point defects called “boojums,” which are seen under polarizing optical microscopy (f). Orientations of polarizers and the rubbing direction are marked by white double arrows. Note that the boojum’s coloring in (e) is a visual aid and is not meant to indicate charge or polarity.

It should be noted that, since the ferrite nanoparticle orientations are mechanically coupled to the epoxy of the SPMB microsphere, the magnetic interactions with the applied field prompt transient SPMB rotation and alignment of the net induced magnetic moment $\mathbf{m}$ (due to the vector sum $\sum \mathbf{m}_i$) to eventually point along $\mathbf{H}$. The ensuing torque on the epoxy matrix physically aligns the SPMB such that its net magnetic moment locks to be collinear with $\mathbf{H}$ and is given by \[ m = V_p \chi_p \mathbf{H} \] (3.2)

where $V_p$ is the colloid volume and $\chi_p$ is its effective magnetic susceptibility. Subsequent rotation of the magnetic field generates a torque on the SPMB as given by [21]

$$\tau = \mu \mathbf{m} \times \mathbf{H}$$ (3.3)

where $\mu$ is the colloid’s magnetic permeability. The superposition of magnetic fields from each solenoid allows us to set $\mathbf{H}$ in any direction and to rotate this field at a given frequency, allowing us to achieve the desired rotation of the MOCHs. Since our experiment deals with low Reynolds number flow ($\text{Re} \sim 10^{-7}$), we may neglect inertial effects and may roughly quantify the torque produced on our SPMB by balancing its rotational frequency with viscous drag in the LC host [26–28] as given by

$$\tau = \left( \frac{4\pi}{3} \right) \alpha R^3 \eta \Omega_c$$ (3.4)
where $R$ is the SPMB radius, $\eta$ is the effective viscosity coefficient of the LC host, $c$ is the critical decoupling frequency of the sphere rotation with respect to the external magnetic-field rotational frequency, and $\alpha$ is a numerical factor on the order of unity. We measured a magnetic torque of $\sim 5 \times 10^{-18}$ N m exerted on the particles in various LC systems.

In the presence of magnetic-field gradients, the force on a single colloid is proportional to the gradient of the magnetic field [29]. Although our manipulation system is designed to minimize this so-called “magnetic gradient force,” the finite radius of the solenoid core results in a residual in-plane field gradient that can yield residual forces of up to 0.07 pN as estimated via balancing this magnetic force with a known viscous drag force. These residual gradient forces are found to be comparable to the gravitational force acting on these particles while dispersed in the LC and can, therefore, be neglected when particles are cotrapped by laser tweezers or localized within defects that typically have line tension on the order of tens of piconewtons.

In addition to interacting with field gradients, SPMBs can also interact magnetically with each other. For a collection of $N$ colloids in an external field, the magnetic interaction force on a given colloid due to the other $(N - 1)$ colloids in the presence of an applied external field is [30]

$$
F_i = \frac{3\mu_0}{4\pi} \sum_{j=1,j\neq i}^{N} \frac{\hat{m}_i \cdot \hat{m}_j}{r_{ij}^4} \left[ (1 - 5(\hat{m}_i \cdot \hat{r}_{ij})^2) \hat{r}_{ij} + 2(\hat{m}_i \cdot \hat{r}_{ij})(\hat{m}_i) \right]
$$

(3.5)

where $r_{ij}$ is the distance between centers of the $i$th and $j$th colloids and $\hat{r}_{ij}$ is the corresponding unit vector. However, no magnetic interactions are present when the field is turned off. By appropriately positioning (e.g., using laser tweezers) superparamagnetic particles within the sample, one can exert well-controlled interparticle forces that can be utilized in probing LC defects and structures. On the other hand, these forces can also be avoided by assuring that only
single SPMBs or their clusters are present within the studied sample volume at distances within which these interaction forces are comparable to or stronger than thermal fluctuations.

Full holonomic control of a colloidal particle is achieved by combining mostly rotational magnetic manipulation with translational manipulation by HOT using a single integrated setup shown in Fig. 3.1 [31]. This allows us to define arbitrary positions and orientations of individual and multiple particles of interest. The HOT is built using a fiber laser operating at 1064 nm with output powers of up to 10 W (note that laser powers on the order of 1 mW per colloidal particle are typically sufficient for optical manipulation). The trapping beam passes through a polarizer (P) and two lenses (L1, L2) forming a telescope that is used to resize the beam diameter to slightly overfill the active area of a computer-controlled dynamically addressable LC-based spatial light modulator (SLM). The SLM generates a dynamic phase mask that creates and controls optical traps at a refresh rate of up to 20 Hz. After spatial modulation by the SLM, the trapping beam is linearly polarized in a desired orientation using a half wave plate and a polarizer and is subsequently directed via a second telescope (L3, L4) and reflection from a dichroic mirror to the back aperture of a 100 × oil immersion objective with a numerical aperture of NA = 1.42. Imaging is performed through a combination of POM and 3PEF-PM that are capable of operating in both epidetection and forward-detection (transmission) modes with the epi-detection mode being the primary configuration when implementing full three-axis holonomic manipulation.
3.2.2. Sample preparation

We use a commercial nematic mixture E-31 (from EM Chemicals) and a single-compound nematic LC pentylycyanobiphenyl (5CB, obtained from Frinton Laboratories). Cholesteric LC hosts are formed using one of these nematics doped with a small volume fraction of chiral agent (cholesteryl pelargonate obtained from Sigma-Aldrich Chemistry) to obtain chiral nematics with a cholesteric pitch in the range of 5–10 μm. In addition to the superparamagnetic beads discussed previously, we also use melamine resin spheres (obtained from Sigma-Aldrich Chemistry) 7 μm in diameter. All colloidal particles are dispersed in an LC host via either solvent exchange or sedimentation mixing with both methods yielding comparable dispersion efficiencies. Solvent exchange is performed by first vortex mixing the SPMB Dynabead carrier solution (de-ionized water with a density of 1 × 10^6 beads per μl) to disperse the beads evenly. Approximately 1 μl of this carrier is placed into a plastic vial and allowed to dry on a hot plate for 30 min after which 10 μl of isopropyl alcohol (IPA) is added and the mixture then sonicated at room temperature for 5 min to re-disperse the beads into the IPA. Some 100–200 μl of LC is subsequently added, and the mixture sonicated for an additional 10 min. The sample is placed in a water bath for 10 h at 95 °C to evaporate the solvent. Sedimentation mixing is accomplished by placing 1 μl of the Dynabead carrier on a well cleaned glass slide and evaporating on a hot plate at 100 °C for half an hour after which 1 to 2 μl of the LC host is added to the resulting sediment region on the slide, thoroughly mixed using a clean pipet tip, and dispersed into a larger volume of LC using vortex mixing for 30 s.

Cells are constructed from glass slide substrates cleaned in a water and detergent sonication bath at 60 °C, sequentially rinsed with acetone, methanol, and IPA, then dried, and plasma etched. Planar or homeotropic alignment of the cleaned substrates is set as determined by
intended experiments. For planar anchoring, we spin coat the substrates with either polyvinyl alcohol (PVA 1% weight-to-weight ratio) in deionized water at 8500 rpm or with polyimide PI-2555 at 7500 rpm after which they are baked for at least 1 h at 100 °C. They are subsequently rubbed with a velvet cloth, which forces the LC molecules to align along the rubbing direction and, thus, sets planar boundary conditions for \( n(r) \). For homeotropic alignment, the cleaned substrates are immersed into dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride (DMAOP obtained from Arcos Organics) for 1 min and then allowed to dry in ambient air. The substrates are assembled in various configurations as needed for desired boundary conditions: planar cells with a director pretilt angle of ~3°–6°, homeotropic cells, wedge cells, and twist cells. Cell thickness is typically set using spherical spacers dispersed in a UV curable epoxy (NOA-61, obtained from Norland Products) and varies from 10 to 120 \( \mu \)m, depending on the system under study. An LC host is infused into these cells via capillary forces and, subsequently, is sealed with fast setting epoxy.

The use of colloids as handles to manipulate director structures and defects depends greatly on the strength and nature of molecular interactions at the LC-colloid interface. POM studies [Fig. 3.2(f)] show that the particles induce tangential (planar) no degenerate surface anchoring for \( n(r) \) of the LC where the director tends to pin to colloid surfaces, a phenomenon often referred to as the “anchoring memory effect.” This behavior is consistent with the results of SEM imaging [Fig. 3.2(d)], which reveals nonuniform nanoscale surface morphology of a type that naturally allows for strong mechanical coupling between the superparamagnetic beads and various topological defects. Such coupling is an important aspect in our studies as discussed below.
3.3. Results

3.3.1. Magnetic and holographic optical manipulation of cholesteric line defects using superparamagnetic beads

Noncontact manipulation of topological defects in LCs was previously accomplished either through polarized optical trapping of defect structures directly via refractive index contrast or through the use of colloids as “optical handles” to enhance polarization-independent optical trapping capabilities [32, 33]. Our magnetic holonomic manipulation method employs superparamagnetic beads as “magnetic handles” and allows for robust, highly controllable three-axis rotation of colloids around their own center of mass, enabling modes of control of defects that would be impossible via the use of HOT methods alone. Furthermore, our magneto-optical holonomic manipulation system inherits all the noncontact control capabilities of HOT with the only peculiarity that the superparamagnetic particles tend to absorb substantial amounts of trapping light, imposing limitations on the laser powers that can be used (typically limited to about 3 mW at the sample plane). On the other hand, this optical absorption is, in some ways, beneficial as it enhances available modes of defect manipulation by allowing us to induce local melting within the LC when high laser powers are used and, thus, enables optically induced highly localized nematic-isotropic phase transitions within the bulk of the sample. We demonstrate the combined use of all of these noncontact control capabilities using examples of defect structures in various LC systems, starting with examples obtained for a cholesteric LC. Superparamagnetic particles are dispersed in a cholesteric LC (nematic host 5CB or E-31 doped with cholesteryl pelargonate at about 3.3 wt %) with pitch of about 5 μm as measured via direct 3PEF-PM imaging of sample cross sections. This dispersion is infused into planar cells with antiparallel rubbing and thicknesses between 30 and 60 μm. The samples are first studied with
POM and 3PEF-PM to locate defects and to determine their type and structure. Holographic optical trapping allows localizing particles next to a defect, whereas, the SPMB-assisted local melting with laser light at higher powers of about 10 mW allows the particles to be “inserted” into a defect line with the ends of an “interrupted” linear defect being pinned to the diametrically opposite sides of the colloidal sphere. Figure 3.3 shows magnetic and optical manipulations of a single dislocation of Burgers vector $|\mathbf{b}| = p/2$ with its core composed of a $\lambda$-$\tau$ disclination pair in a 5CB-based cholesteric LC (CLC).
Fig. 3.3. Manipulation of a dislocation defect line in a cholesteric liquid crystal by a single SPMB particle. (a) The SPMB is embedded into a cholesteric dislocation with a $\lambda$-$\tau$ defect core. The location of the cross-sectional plane corresponding to the structure of the dislocation core shown in (d) is marked by a blue dashed line. (b) An ac magnetic field of $\sim 40$ Gs is rotated clockwise at a frequency of 8 Hz, which maximally rotates the SPMB to an angle $\beta_{CW}$ and stretches the defect line. (c) At the same field amplitude and frequency, the SPMB is subsequently rotated counterclockwise to a maximum angle $\beta_{CCW}$. (d) Director structure of the manipulated topological defect with the $\lambda$-$\tau$ disclination core. (e) The defect structure’s
asymmetry seen from (d) causes a marked asymmetry in the defect’s response to clockwise and counterclockwise bead rotation and in the difference between $\beta_{\text{CW}}$ and $\beta_{\text{CCW}}$. Regions $R_1$ and $R_2$ denote the time periods during which the SPMB is forced between its maximum angles of rotation in two opposite directions via magnetic-field rotation ($R_1$) or is allowed to relax naturally ($R_2$). (f)–(g) Rotation angle (in degrees) vs. time (in seconds) in the forcing regime and in the relaxing regime along with their exponential fit lines, respectively. (h)–(j) Optical POM micrographs showing a single dislocation with a $\lambda$-$\tau$ disclination pair which exhibits transient undulations along its length when manipulated in the forcing regime as discussed in the text.

At equilibrium, the particle is resting within the straight defect line, effectively interrupting it by introducing an isotropic spherical region into the singularity. The particle can also be localized in a region of strong elastic distortion near the core of the dislocation so that the two disclinations in the dislocation core remain uninterrupted. A colloid thus embedded into or pinned to a defect can be manipulated by translating it in different directions and, thus, moving the defect line, unless this translation is performed along the defect line, a direction in which the defect structure is translationally invariant. These types of manipulation are similar to what was achieved in the past by HOT alone [32]. However, when a controlled ac magnetic field of 40 Gs is applied and its direction rotated at a constant amplitude and a fixed frequency, we can achieve types of rotational manipulation of the colloidal handle and defect that cannot be realized using HOT alone. In the case of an interrupted dislocation with the defect-particle pinning at diametrically opposite sides of the colloidal sphere, which is most effective for this type of manipulation, the dislocation can be stretched during the rotation of the particle in clockwise (CW) or counterclockwise (CCW) directions via continuously rotating the magnetic field in a clockwise or counterclockwise direction, respectively [Figs. 3.3(b) and 3.3(c)]. By varying the frequency of the field rotation, we are able to maximally rotate the colloid and hold it near a fixed angle with a slight oscillation about this angle due to the ac magnetic field temporarily losing phase lock with the SPMB rotation. Interestingly, this angle is different for clockwise and
counterclockwise rotations and is, for example, approximately $25^\circ$ and $-40^\circ$, respectively, at a field rotation frequency of 8 Hz. This result is natural due to the apparent asymmetry of the director structure on the two opposite sides of the defect line [Fig. 3.3(d)].

By reversing the rotation of the field, the SPMB can be rotated to a new angle in a rapid manner, forcing the colloidal particle rotation from one maximum angle to another in the so-called “forcing regime” [Fig. 3.3(e), regime $R1$]. Alternatively, by abruptly turning off the field, the colloidal particle is allowed to relax to its original orientation as the defect line straightens in order to minimize its corresponding free energy. This is the so-called “relaxation regime” $R2$ [Fig. 3.3(e)]. The relaxation rotational motion is characterized by a balance of viscous and elastic torques where the elastic torque arises due to a combination of elastic distortions around the particle and defect line’s tension. At small enough distortions from equilibrium, the colloid is expected to relax to its original orientation exponentially, $\beta(t) = \beta_0 e^{-t/\tau}$, where $\beta_0$ is the maximal SPMB rotation angle and $\tau$ is the relaxation time constant. Experimental colloidal particle rotation and relaxation data are shown in Fig. 3.3(e) along with exponential fits shown as differently colored lines. When forcefully rotating the SPMB between the maximal angles of $-35^\circ$ to $22^\circ$ and back again [Fig. 3.3(f)], we obtain time constants of $\tau = 0.24s$ [green line in $R1$ left] and $\tau = 0.27s$ [red line in $R1$ right], respectively. Video analysis of the SPMB in the relaxation regime [Fig. 3.3(g)] yields time constants of $\tau = 0.42s$ [blue line in $R2$ left] and $\tau = 0.34s$ [magenta line in $R2$ right], respectively. This is again consistent with the effects of the defect’s director field asymmetry on the embedded colloids rotational dynamics and the corresponding rotation of the twisted or stretched defect line, especially since the rotational motion of these particles in a cholesteric LC is coupled to its translation along the local orientation of the CLC helical axis.
An interesting effect occurs when a colloid is rapidly rotated from its maximal rotation angle to align again roughly along the defect line. Such manipulations induce undulations in the defect line due to the fact that the stretched disclination cannot contract fast enough (note that this contraction process is determined by the balance of elastic and viscous forces) to follow the fast rotation of the particle [Figs. 3.3(h)–3.3(j)]. The extra length of \( \sim 10 \, \mu m \) results in transient undulations in the defect line with peaks arising and disappearing simultaneously in the course of about 1 s. Coupling the cholesteric helical structure to the angular rotation of the SPMB [20] also induces a translation in the vertical direction perpendicular to the cell substrates (which is also along the helical axis direction far from the defect), bending the dislocation out of the \( x-y \) plane upward or downward, depending on the direction of particle rotation with respect to the handedness of the LC. This effectively allows us to manipulate the dislocation with a \( \lambda-\tau \) disclination core in different rotational and translational degrees of freedom.

Manipulation of defects provides an additional method for quantifying the torques that can be exerted by magnetically manipulated SPMBs. Since the defect line tension is known [27, 32], we can estimate the torque applied to the line at the maximal deflection angle to be \( \sim 2 \times 10^{-17} \, N \, m \) at an applied field of 40 Gs, comparable to that estimated using Eq. (3.4). SPMB chains allow for the application of even stronger torques, enabling considerable rapid distortions of defect lines as well as magnetic-field-assisted insertion and extraction of particles from defects. Figure 3.4 shows a pair of SPMB colloids manipulated by HOT while being colocated within a Lehmann cluster, which is achieved through localized melting of the LC surrounding the SPMBs. Relative motion of the SPMB pair within the defect can be controlled via a combination of dc magnetic dipole forces and linear confinement due to the defect core structure.
Fig. 3.4. Magnetic and optical manipulation of two SPMB colloidal particles in a Lehmann cluster. (a) The director structure of the Lehmann cluster is composed of two $\lambda^{+1/2}$ and two $\lambda^{-1/2}$ topological defect lines [marked by red (left and right) and blue (top and bottom) open circles, respectively]. (b) Optical manipulation of two SPMBs as they are embedded into the Lehmann cluster. The inset shows an intermediate step of incorporation of the SPMB particles into the defect line. (c) And (d) Bright field optical micrographs reveal magnetic manipulation of relative positions of two SPMBs trapped within the Lehmann cluster defect line, which is achieved through magnetic dipole-dipole interactions while controlling the magnetic dipole orientations via changing the external field direction. Aligning the applied magnetic-field vector [red arrow] orthogonal to the defect line causes dipole-dipole repulsion [blue arrows], whereas, aligning the magnetic-field vector parallel to the defect line leads to the dipole-dipole attraction. (e) and (f) Bright field optical micrographs depict magnetic torsion of a SPMB colloidal dimer while at two maximum particle-in-defect rotation angles; note that formation of a dimer allows for stronger magnetic torques and large rotation angles, providing modes of manipulation that cannot be achieved using a single SPMB.

As expected, aligning the applied dc magnetic field orthogonal to the defect line direction results in a repulsive dipole-dipole force that separates the SPMB pair, whereas, alignment with a field tangent to the defect line results in an attractive dipole-dipole force. It is possible to magnetically manipulate the pair in this manner as long as their surface-to-surface separation is larger than about 10% of the bead diameter, at which point, a colloidal dimer forms under the
effect of defect- and medium-mediated attractive forces. Separation of the two particles from each other, subsequently, can be achieved by combining magnetic manipulation with local melting of the LC. Rotation of the SPMB pair is accomplished by use of an ac magnetic field in a manner similar to single particle rotation. As compared to the case of single SPMBs, such rotational manipulations yield larger maximal bend angles of defect lines at a given magnetic-field strength and frequency.

3.3.2. Full holonomic control of magnetic colloids to manipulate twist disclinations in nematic liquid crystals

Nematic LCs with mixed boundary conditions are known to host a wide variety of defects in transient, metastable, and stable configurations [34, 35]. To demonstrate the power of our approach in noncontact manipulation of such defects, we introduce a nematic (5CB) MOCH particle dispersion into a twist/wedge cell formed by glass plates with rubbing directions aligned at 90° with respect to each other. The colloidal handles within the dispersion are composed of two species of particles, SPMBs and melamine resin microbeads. Due to the wedge geometry, the cell thickness ranges from 30 µm down to about 3µm. To satisfy the strong surface boundary conditions at each confining glass plate, the director forms a twisted configuration across the sample thickness. Domains with ±90° twist across the cell thickness occur with about equal probability and are separated by defect lines, which we identify as twist disclinations (note that wall defects could be observed for submicron sample thicknesses but they are not observed in our experiments performed using our relatively thick twisted nematic cells [36]). In addition to occurring spontaneously upon quenching from an isotropic state, domains of opposite handedness and twist disclination loops can also be induced “on demand” by SPMB-assisted
localized melting using in sample laser powers of approximately 10 mW or higher with resulting
disclinations of half-integer strengths [Fig. 3.5(a)].

Fig. 3.5. Full holonomic control of twist disclination loops in a $\pi/2$-twisted nematic cell. (a) Schematic of a twist disclination director structure and defect line (blue) in a $\pi/2$-twisted nematic cell; spatial variations in the director field are depicted using cylinders. (b) Schematic of the structure of the director field along the twist disclination loop; within a plane perpendicular to the twist disclination, the director circumscribes a Möbius strip. If the twist inside the loop is defined to be $+\pi/2$, or one quarter of a pitch, then the twist handedness outside the loop is $-\pi/2$. Colloids with tangential surface anchoring located in the cell midplane form surface point defects dubbed “boojums” that align at 45° to the two orthogonal rubbing directions set at the confining glass plates. Note that the molecule’s and boojum’s colorings in the schematics are visual aids and are not meant to indicate charge or polarity. Individual particles or particle chains, such as the trimer depicted in the schematic, can be colocated with the defect core. (c)–(f) An applied magnetic field of 40 Gs [with its in-plane and out-of-plane orientations indicated by red arrows and quantified by $(\theta, \phi)$, where $\theta$ is the in-plane angle referenced from the $x$ axis and $\phi$ is the azimuthal angle with respect to the $x$-$y$ plane] is rotated in three dimensions, allowing for robust three-dimensional manipulation and stretching of the defect line.

Once the director structure is determined, circumnavigation of the defect line reveals that the LC director around defect twists by $\pm \pi$ while circumscribing the surface of a Möbius strip in
a plane orthogonal to the disclination as shown in Fig. 3.5(b) with the interior cell region of the disclination loop possessing an oppositely handed twist to that of the exterior cell region. Optical manipulation at low laser powers (about 1mW) allows us to embed MOCHs into these defects. Figures 3.5(c) and 3.5(d) show a twist disclination with several such embedded colloids forming chains. A magnetic field segregates or aggregates particles into various chain configurations and realigns them through a combination of defect line tension, magnetic torque, and dipole-dipole interparticle forces, thus, distorting the defect line in three dimensions. Varying the direction and magnitude of the applied magnetic field allows us to induce complex deformations of the defect line, such as the ones depicted in Figs. 3.5(e) and 3.5(f), which is enabled by the fact that different segments of the defect line are pinned to particles and colloidal chains that respond to holonomic magnetic and HOT optical control.

Twist disclinations are topologically stable nematic defects and cannot simply terminate in or interrupt in the bulk of a nematic LC, unless accompanied with melting of the sample or introducing isotropic inclusions. However, they do tend to form disclination loops of a net topological hedgehog charge equal to zero that can disappear via shrinking [36]. Figure 3.6 shows such a half-integer twist disclination loop. This shrinking process results in minimization of the overall free energy due to the elimination of additional elastic distortions and defects in-between the domains of opposite handedness and is the only process expected to take place, eventually leading to larger domains or a single domain of the same handedness of twist. Using our manipulation system, we demonstrate that such twist disclination loops can be split into multiple loops of smaller sizes, both having topological hedgehog charges equal to zero. A melamine resin bead mediates restructuring of the local director field near the defect line such that the original defect loop can be split into two smaller loops (Fig.3.6).
Fig. 3.6. MOCH-mediated splitting of a twist disclination loop into two smaller loops. (a)–(c) Schematic showing reconnection or splitting progression of a twist disclination loop into two smaller disclination loops. The interior of the initial loop is defined with a twist of $+\pi/2$, whereas, the exterior is of twist $-\pi/2$. A melamine resin bead with planar surface anchoring induces two boojum defects that localize at the poles along the local director of the twisted structure in the cell midplane. During reconnection and defect loop splitting, the MOCH rotates by $\pi/2$ as can be seen by comparing parts (a) and (c). (d)–(g) Optical micrographs showing the time progression of a twist disclination loop splitting into two smaller loops, whereas, these defects are sliding on the surface of a 7 $\mu$m diameter melamine resin bead, eventually leading to two smaller defect loops, both being separated from the bead. Note the orientation of the boojums (indicated by small arrows) during reconnection. The double arrow in (f) marks orientations of the polarizer and analyzer, which were aligned parallel to each other.

In this process, two segments of the initial defect loop are first attracted to and then attached to a colloidal particle’s surface, consequently, locally merging and reconnecting into two smaller half-integer disclination loops. Both emerging loops of the twist disclinations have hedgehog charges equal to zero, and both are separating regions of opposite twist handedness with respect to their common exterior. Details of this reconnection are shown in experimental micrographs in Figs. 3.6(d)–3.6(g).
3.3.3. Patterning of cholesteric fingers in a frustrated cholesteric system

Cholesteric LCs confined in homeotropic cells are known to exhibit localized solitonic structures and defects, such as cholesteric fingers, torons, and other configurations that appear due to incompatibility of vertical surface boundary conditions and a uniform helicoidal structure. These solitonic structures can arise either spontaneously or when generated by electric fields or focused laser beams [34, 35]. In this section, we show that holonomic magnetic manipulation of colloids allows us to explore different aspects of this system that cannot be probed by other noncontact manipulation techniques.

SPMB colloids are dispersed into a CLC based on an AMLC-001 (from AlphaMicron, Inc.) nematic host and chiral additive CB-15 (from EM Chemicals) added at a percentage needed to yield an equilibrium pitch of \( p = 9 \, \mu m \). This dispersion is then infused into a wedge cell with homeotropic boundary conditions and thicknesses ranging from \( d = 7 \) to \( 10 \, \mu m \). Cholesteric fingers (Fig. 3.7) form in regions where the confinement parameter \( c = d/p = 0.75–1.0 \). There are at least four classes of cholesteric fingers [34, 35], the most common being the species of the first and second kinds denoted as CF-1 and CF-2, respectively.
Fig. 3.7. Manipulation of cholesteric fingers in a cholesteric LC cell with homeotropic boundary conditions. (a) Two CF-1 fingers are manipulated using two different SPMB dimers that are rotated via magnetic-field rotation. (b) Reversing rotation partly unwinds one of the two CF-1s, whereas, the SPMB dimer “escapes” from the second CF-1 finger. (c) A meander like configuration is formed from one of the two CF-1s, whereas, the other CF-1 relaxes to its natural linear state. (d)–(f) Repeated reversal of magnetic-field rotation allows us to create an arbitrary number of CF-1 meanders and spirals. (g) Director structure of the CF-1 finger composed of two $\lambda^{-1/2}$ and $\lambda^{+1/2}$ disclinations [marked by open (blue) and red (closed) circles, respectively].

Figures 3.7(a)–3.7(f) show CF-1s with SPMB dimers and trimers located in the defects and in the CLC bulk. An initial in-plane clockwise rotation of a 40 Gs magnetic field at 0.25 Hz produces a clockwise rotational motion of the dimers, which winds two CF-1s into spiral configurations [Fig. 3.7(a)]. It should be noted that, although CF-2 fingers were previously observed spontaneously forming spirals in an applied ac electric field, which was attributed to the inherent asymmetry in their structure [34, 35], CF-1 fingers are not known to form spirals spontaneously or in response to applied fields. This can be understood by considering the symmetry of their translationally invariant director structure with a cross section shown in Fig. 3.7(g). It is, therefore, interesting that, without spatial translation, magnetically rotated SPMBs,
which are mechanically coupled to the finger’s structure via elastic distortion sharing, can promote the formation of spiral configurations in CF-1 fingers. By subsequently reversing this magnetic-field rotation, we can partly reverse this winding, eventually forming a spiral of opposite handedness [Fig. 3.7(c)]. Figures 3.7(b)–3.7(f) also show that the elastic attachment of the SPMB to the finger is important for this manipulation because the bottom finger spiral, which detached from its dimer, has relaxed to its expected straight finger line configuration as the sequence progresses. By repeated reversals of the magnetic rotation, one can “draw” CF-1 meanders and spirals of significant complexity. One should mention here that the spiraling and meander like structures of the fingers shown here are still transient or metastable configurations that can eventually relax to straight finger lines. Although similar configurations of cholesteric fingers could be optically patterned by scanned laser beams as we have demonstrated previously [37], it is interesting that our magnetic manipulation method allows for accessing them through rotational manipulation alone.

3.3.4. Kink chain generation in Lehmann clusters

In the past, laser manipulation studies of defects, including disclinations, oily streaks, edge dislocations, and Lehmann clusters, have allowed exploration of defect properties, such as line tension and topological stability [33]. An interesting new manipulation capability enabled by our magnetic holonomic control of colloidal handles involves rotational torsion of defect lines as demonstrated above using several examples of defects in nematic and cholesteric LCs. This capability also allows us to produce so-called “kinks” [32] in topologically unstable Lehmann clusters of disclination defects that appear in layered cholesteric structures (Fig. 3.8). Lehmann clusters are composed of quadrupoles of nonsingular half-integer \( \lambda \) disclinations of opposite
signs and, thus, have a net winding number (strength) equal to zero. In terms of the cholesteric layered structure, these defects separate sample regions with the same number of cholesteric layers and, therefore, have a net Burgers vector also equal to zero. This makes them very different from topologically stable defect lines, such as the twist disclinations and edge dislocations discussed in previous sections because these defect clusters can terminate on the SPMB particles that we use for manipulation. Our combined magnetic and optical manipulations allow for controlled generation of Lehmann clusters via the optical translation of particles and the generation of various kinks within them via particle rotation. Figure 3.8 details how we generate multiple kinks in a Lehmann cluster via magnetic manipulation of SPMB colloids attached to its end.

Fig. 3.8. Generation of a series of kinks in a cholesteric Lehmann cluster. (a) A SPMB colloidal dimer is attached to a Lehmann cluster defect and is magnetically rotated clockwise [as shown by a red (curved) arrow] in the x-y plane. (b)–(d) Several kinks (marked by a black arrow) are generated by continuous rotation of the SPMBs. Note the defocusing of the SPMBs indicates a
translation of the defect along the vertical $z$-direction axis. (e) A kink and antikink pair generated by magnetic rotation in another Lehmann cluster attached to a colloidal aggregate. The antikink is seen closer to the aggregate and was generated by reversing the rotation direction as compared to that used to generate the kink in the same defect line. With time, the antikink eventually annihilates with the kink. (f) A well-defined series of equidistant kinks is formed in a Lehmann cluster due to repulsive interactions between the generated kinks. (g)–(i) Schematics of the director field in different cross-sectional planes, which represent the evolution of the director structure along the Lehmann cluster defect line with a kink. (g) A Lehmann cluster is shown with representative blue and red lines corresponding to $\lambda^{-1/2}$ and $\lambda^{+1/2}$, respectively. (h) Cross section of the kink tracing the path of the $\lambda^{-1/2}$ and $\lambda^{+1/2}$ defects. (i) The Lehmann cluster’s position across the cholesteric layers has been shifted in the vertical $z$ direction (along the direction of the cholesteric helix axis far from the defect).

We can adjust the number of kinks by selectively unwinding the Lehmann cluster or by generating antikinks with opposite winding of the defect cluster, which typically is followed by pair annihilation of the kink or antikink pair. The strong pinning of the Lehmann cluster’s end to a given particle [with the nanostructured surface morphology shown in Fig. 3.2(d)] is essential to our manipulation process. Figure 3.9 details an example of kink generation in a Lehmann cluster using SPMBs that are magnetically rotated clockwise.
Fig. 3.9. A schematic of generating kinks in a Lehmann cluster using magnetically controlled beads. (a) A colloidal dimer attached to a Lehmann cluster’s end is translating linearly due to minimizing line energy as shown by the orange arrow. (b) As the dimer is rotated clockwise by 180° [red arrow], it moves along the vertical z axis by 1/2 pitch [blue arrow], which is due to the need of preserving the low-energy nonsingular nature of the Lehmann cluster’s defect core and due to the coupling of rotation to translation along the helical axis of cholesteric LCs [30]. (c) And (d) Continuous colloidal dimer rotation generates a kink in the Lehmann cluster, which shifts the axial position of this defect in the cholesteric layered structure. The far-field helical axis of the CLC is aligned along the vertical z direction.

To preserve the nonsingular nature of the $\lambda$ disclinations within the cluster, this rotation locally translates the cluster in the vertical negative z direction while also lengthening and bending the cluster in the x-y plane. Continued rotation eventually pulls the colloid along z by one cholesteric pitch at which point the cluster is turned through 360° so that the kink is fully formed in the Lehmann cluster defect line. The resulting kink adopts the curvature of distortion of the Lehmann cluster and is approximately equal to one cholesteric pitch in diameter. By reversing the colloid rotation, we can either unwind the kink by reversing the generation stages depicted in Fig. 3.9 or, in some cases, generate an antikink of opposite winding that eventually
annihilates with the initial kink [Fig. 3.8(e)]. Interestingly, in cases when magnetic manipulation alone is used to generate a series of kinks, line tension tends to minimize the defect line length and, thus, limits the number of kinks that can be generated as this number is constrained by the number of layers in the cholesteric structure that the defect is crossing. By supplementing this magnetic noncontact control with linear optical manipulation and pinning of defects to particles and cell surfaces, we are able to rotate, stretch, and translate a defect line holonomically, allowing complex manipulations that may allow one to explore interesting topological configurations, potentially including free-standing knots and different types of linked defect loops.

3.4. Discussion

Our current study focused on examples of linear and rotational defect manipulations in nematic and cholesteric LCs, e.g., in mesomorphic phases with only orientational ordering. However, these studies can be extended to nematic point and wall defects in such mesophases as well as to a variety of different types of defects in LC phases with various degrees of partial long-range or quasi-long-range positional ordering. Defect structures that can be effectively probed by magnetic and optical holonomic controls may include focal domains in smectics, developable domains in columnar phases, and dispirations in smectics with antiferroelectric ordering. Although rotation of dielectric microspheres in smectic LCs was previously accomplished by applying dc or low-frequency ac fields [37], the particles could only be rotated around certain well defined axes predetermined by the geometries of electrodes and samples (unlike in our case of unrestricted holonomic rotational control), and its possible use in the
manipulation of defects has not been explored. The holonomic control of colloidal particles in various smectic and columnar phases may yield the means of generating new defect structures as well as controlling preexisting defects. Whereas, magnetic fields for particle manipulation in nematic and cholesteric phases need to be kept below 50 Gs to avoid significant effects of diamagnetic coupling directly to the LC director in these highly responsive mesophases, higher fields of up to ~ 500 Gs can be applied to manipulate particles in phases with partial positional ordering because magnetic realignment effects in these systems are typically hindered by the presence of this positional ordering. Although our study specifically avoided the use of strong magnetic-field gradients for spatial localization and translation of colloids, such capabilities can be added. Additional advantages and new possibilities in this case would arise from stronger particle localization induced by high magnetic-field gradients and the application of far stronger linear forces as compared to what can be achieved using optical tweezers. In addition to samples confined between parallel glass plates, manipulation of defects can also be performed in other confinement geometries, such as droplet geometries and free-standing films as well as in various mesomorphic phases with defects in the ground state (such as blue phases and twist grain boundary phases) in which studies of defects by laser tweezers are typically limited due to the fact that the use of immersion-oil high-numerical-aperture objectives is impractical.

By combining three-dimensional spatial translation of MOCHs mechanically coupled to defects with torsion of defects induced by their rotation and with various types of laser-induced local melting of the LC, one may be able to control twist and writhe [38–40] of defect lines forming loops, and thus, one may be able to generate defect loops with nonzero topological hedgehog charges. This potentially can be performed for individual or multiple defect loops that may or may not be linked with each other. Another interesting direction of extending the present
work may involve generation of topologically nontrivial configurations of defect lines in the forms of various free-standing knots, links, etc. Although our manipulation method is geometrically unrestricted in terms of the defect manipulation, such restrictions will be self-imposed naturally by topological constraints inherent in various LC systems, which, therefore, may allow one to explore the interplay of topologies of nematic director fields, defects, various loops, surfaces, etc. With careful calibration of magnetic forces and torques exerted on SPMBs, MOCHs may also allow for experimental exploration of mechanical properties of defect lines and wall defects, which remain poorly understood. By using nanoparticles instead of relatively large SPMB microbeads, one can potentially probe the core structure of defects and can explore variations in rheological properties within LC samples containing defects, etc.

3.5. Conclusion

We have developed an integrated magnetic and optical manipulation system for full holonomic control of topological defect lines in nematic and cholesteric liquid crystals. The rotational manipulation of colloidal chains and pinning of defects to colloidal particles allows us to form complex 3D patterns of defects not found naturally in liquid crystal systems, such as spirals in cholesteric fingers of the first kind. Furthermore, we have been able to integrate this magnetic rotational manipulation with linear holographic optical trapping in such a way as to enhance the strengths of each while ameliorating the inherent weaknesses in either method alone. Using specific examples, we demonstrated that our method provides powerful new tools for the study of topological defects as well as potentially allowing one to create fascinating topological defect configurations, such as free-standing knots and links of defects. Such exploration may be of interest not only from the standpoint of a general understanding of defects in condensed
matter, but also for their use in modeling topological defects in early universe cosmology, string theory, high energy physics, and other physical systems.

3.6. References


Chapter 4

Periodic dynamics, localization metastability, and elastic interaction of colloidal particles with confining surfaces and helicoidal structure of cholesteric liquid crystals

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Chapter Overview

Although nematic and cholesteric liquid crystals are three-dimensional fluids, they also possess long-range orientational ordering of constituent molecules, supporting both topological defects and chiral superstructures. However, the implications of this ordering remain unexplored even for such simple dynamic processes as found in so called “fall experiments”, or motion of a spherical inclusion under the effects of gravity. Here we show that elastic and surface anchoring interactions prompt periodic dynamics of colloidal microparticles in confined cholesterics when gravity acts along the helical axis. We explore elastic interactions between colloidal microparticles and confining surfaces as well as with an aligned ground-state helical structure of cholesterics for different sizes of spheres relative to the cholesteric pitch, demonstrating unexpected departures from the Stokes-like behavior at very low Reynolds numbers. We characterize metastable localization of the microspheres under the effects of elastic and surface anchoring periodic potential landscapes seen by the moving spheres, demonstrating the important roles played by anchoring memory, confinement, and topological defect transformation. These experimental findings are consistent with the results of numerical modeling that we perform through minimizing the total free energy due to colloidal inclusions at different locations along

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the helical axis and with respect to the confining substrates. Potential applications may include colloidal sorting based on particle shapes and sizes.

### 4.1. Introduction

Fall experiments, in which a body is allowed to fall under the effect of gravity, have a long and illustrious history in experimental physics. Early tests of the weak equivalence principle, i.e. tests of the equivalence of inertial and gravitational mass, were recorded as far back as the 6th century by Philoponus in experiments where he dropped balls of different masses [1]. These tests were refined in the 16th and 17th centuries by Steven and Galileo respectively [2, 3]. Modern fall experiments do not strictly require an unconstrained falling mass, and thus pendulum experiments can be considered as fall experiments, such as the famous Eötvös experiment [4, 5], and culminating in the present day with tests of equivalency, “big G” measurements, and tests of the gravitational inverse square law [6-9]. Fall experiments have been applied to explore aspects of physics other than tests of the weak equivalence principle, such as the study of the hydrodynamics of colloidal systems [10], and elementary particle charge and mass measurement [11-13]. Particularly in the case of colloids one is concerned with balancing the force of gravity with the buoyant and viscoelastic forces acting on the falling body. Such experiments have been of great importance in the field of soft condensed matter physics, specifically in studying rheological properties of colloidal particles in isotropic fluids and in liquids with orientational ordering, such as nematic and cholesteric liquid crystals (LCs) [14].

Fall experiments are relatively simple to perform in LC hosts as long as the colloid is located in the bulk of the LC system and far away from topological defects or confining surfaces.
in the system under study. The usual experimental procedure is to allow a colloid to settle to a location within the sample volume, then subsequently invert the sample cell and allow the colloid to fall under the influence of gravity. Optical manipulations, via optical tweezers, allows one to move a colloid to positions of interest within the cell, such as near topological defects and somewhat close to confining surfaces [15, 16]. However, optical manipulation has many drawbacks, such as being limited to optically transparent systems, and to systems where the elastic forces in regions of interest are less than the 10-100 pN forces typically generated by optical tweezers [15, 16]. Furthermore, optical manipulation can often affect the local director structure through local realignment of LC molecules near the colloid, and can modify the elastic properties near structures one wishes to explore, such as topological defects and confining surfaces. Recent progress in non-contact manipulation, such as magneto-optical holonomic control of colloids [15] have allowed robust and precise control of magnetic and optical handles (MOCH) used to directly probe the physical and rheological properties topological defects, and LC structure near confining surfaces.

In this paper, we use a magneto-optical manipulation system to perform fall experiments with magnetic colloids in cholesteric liquid crystal (CLC) systems. Such experiments allow us to not only explore the rheological and elastic structures inherent in these systems, but also allows us to manipulate colloids close to confining surfaces and within the bulk of the CLC in the Stokes flow regime. We find that, contrary to the previously seen (and expected) linear fall motion of a colloid balanced by viscous forces in a low Reynolds number system, particles in a CLC system with tangential surface anchoring at the colloid surface produces periodic dynamics and metastable states. These states are found to be enhanced by the so called “anchoring memory effect” [17-21] of orientational pinning at the colloidal surfaces, which in turn is enhanced by
topographical effects, such as surface defects and surface extrusions, and by topological defect transformation. We also explore elastic interactions of colloidal particles with confining surfaces of CLC cells, demonstrating elastic sedimentation of studied particles at a well-defined depth level above the bottom cell substrate.

4.2. Materials, methods, and techniques

4.2.1. Holonomic holographic optical and magnetic manipulation system

Our work uses an integrated magnetic and holographic optical manipulation system developed in-house, which allows us to manipulate MOCH in a fully holonomic manner, i.e. in all three Cartesian degrees of freedom via holographic optical tweezers (HOT), and in all three rotational degrees of freedom via magnetic control. Holographic optical tweezers allow us to exert well-controlled forces (commonly within the range of 0.1-100 pN) and to reliably position and spatially translate individual particles or their arrays in three dimensions. Magnetic fields can exert strong torques on ferromagnetic or super-paramagnetic colloids [22-24] in a highly controllable manner with little or no heating of the host material. Likewise the LC host may be designed or selected and the magnetic field used within a limited range so that magnetic manipulation fields do not affect the LC director structure through a direct coupling. This allows us to fully explore the elastic and structural landscape within a sample volume, including near to and within topological defects, and near confining surface and LC interfaces, such as glass cell walls.

Our integrated holonomic magnetic and holographic optical manipulation system is shown in (Fig. 4.1a). Magnetic manipulation is achieved using three iron-core electromagnets
(Fisher Scientific Company S52051 air core solenoids with custom machined cast iron cores) arranged on a Cartesian frame machined from aluminum and mounted directly to an inverted microscope. A microscope slide holder machined from aluminum is positioned in the x-y plane using precision translation stages. Each electromagnet is independently driven via an amplified power supply (APS) BOP20-5M (obtained from Kepco) and is voltage controlled using a computer controlled DAQ card (National Instruments USB-6259 BNC) and in-house LabView-based software (LabView was purchased from National Instruments). Each electromagnet can produce AC (up to 8 Hz) and/or DC magnetic fields up to about 40 Gs. The influence of up to 40 Gs magnetic fields (used in all magnetic manipulations presented herein) on the LC director \( \mathbf{n}(\mathbf{r}) \) may be neglected because director realignment is typically a threshold-like effect and requires fields of \( \sim 1000 \text{ Gs} \) at our studied cell thickness values, in agreement with our experimental observations.
Fig. 4.1. (a) Electromagnetic iron or air core solenoids arranged in a Cartesian aluminum frame mounted on an inverted microscope (not shown) optical imaging system capable of both POM and 3PEF-PM imaging. (b) Colloid COM position vs. rotation angle for multiple colloid species (SPMB and GaN nanowire) in various configurations. The inset is an SEM image of a SPMB showing surface roughness, indicating surface anchoring with “memory” of director orientation at the colloid surface. (c) Expected dynamics of SPMB in a CLC cell. Region I denotes a so called “wind-up/lift-off,” region II denotes a “fall” region, region III is the so called “sedimentation layer.”
The magnetic colloids in our work are superparamagnetic beads (SPMB) (Dynabead M450, obtained from Invitrogen) with a nominal diameter of 4.5 µm ± 0.1 µm and a density of ~1.9 g/cm³ which are fabricated using ferromagnetic nanoparticles (γ Fe₂O₃ and Fe₃O₄) approximately 8 nm in diameter which are embedded into a highly cross-linked epoxy at a density of ~ 10⁵ nanoparticles per bead. Random orientation of individual ferrite nanoparticles, coupled with thermal moment flipping, creates a zero net magnetic moment in the SPMB. When an external magnetic field \( \mathbf{H} \) is applied, a net magnetic moment \( \mathbf{m} \) is induced in the SPMB, as given by [24, 25]

\[
\mathbf{m} = V_p \chi_p \mathbf{H}
\]  

(4.1)

where \( V_p \) is the SPMB volume and \( \chi_p \) is its effective magnetic susceptibility. Subsequent rotation of the external magnetic field \( \mathbf{H} \) generates a torque on the SPMB given by [23]

\[
\tau = \mu \mathbf{m} \times \mathbf{H}
\]  

(4.2)

where \( \mu \) is the colloid’s magnetic permeability. The superposition of magnetic fields from each solenoid allows us to set \( \mathbf{H} \) in any direction and also to rotate this field at a given frequency, allowing us to achieve desired rotation of MOCHs. Since our experiment deals with low Reynolds number flow, on the order of \( \text{Re} \sim 10^7 \), we neglect inertial effects and roughly quantify the torque produced on our SPMB by balancing its rotational frequency with viscous drag in the LC host [26-28] as given by,

\[
\tau = \left( \frac{4\pi}{3} \right) \alpha R^3 \eta \Omega_c
\]  

(4.3)

where \( R \) is the SPMB radius, \( \eta \) is the effective viscosity coefficient of the LC host, \( \Omega_c \) is the critical decoupling frequency of the sphere rotation with respect to the external magnetic field rotational frequency, and \( \alpha \) is a numerical factor on the order of unity. Using this approach, we
measured a magnetic torque of ~$5 \times 10^{-18}$ N·m exerted on the particles in various LC systems [15]. The finite radius of the solenoid core results in a residual in-plane field gradient that can yield residual forces of up to 0.07 pN at 40 Gs, which is comparable to the gravitational force acting on these particles while dispersed in the CLC.

Full holonomic control of a colloidal particle is achieved by combining mostly rotational magnetic manipulation with translational manipulation by HOT using a single integrated setup shown in Fig. 4.1a. The HOT is built using a fiber laser operating at 1064 nm with output powers of up to 10 W. The trapping beam passes through a polarizer (P) and two lenses (L1, L2) forming a telescope that is used to re-size the beam diameter to slightly overfill the active area of a computer-controlled, dynamically addressable, LC-based Spatial Light Modulator (SLM). After spatial modulation by the SLM, the trapping beam is linearly polarized in a desired orientation using a half wave plate and a polarizer and subsequently directed via a second telescope (L3, L4) and reflection from a dichroic mirror to the back aperture of a 100x oil immersion objective with a numerical aperture of NA=1.42. Imaging is done through a combination of POM and 3PEF-PM that are capable of operating in both epi-detection and forward-detection (transmission) modes, with the epi-detection mode being the primary configuration when implementing full three-axis holonomic manipulation.

4.2.2. Sample preparation

We create a cholesteric LC host from a commercially obtained single-compound nematic LC pentylcyanobiphenyl (5CB, obtained from Frinton Labs) doped with small volume fraction of chiral agent cholesteryl pelargonate (purchased from Aldrich Chemistry) to obtain chiral
nematics with cholesteric pitch in the range of 2.5-10 µm. In addition to the superparamagnetic beads discussed previously, we also use GaN nanowires of two species, one coated with aluminum and the other uncoated (lots C004 and C144 respectively, obtained from K.A. Bertness at NIST). All colloidal particles are dispersed in a CLC host via either solvent exchange or sedimentation mixing [15], with both methods yielding comparable dispersion efficiencies for SPMB, and solvent exchange being required for GaN dispersion. Cells are constructed from clean glass slide substrates coated with polyimide and with planar anchoring to set boundary conditions for \( n(r) \). Cell thickness varies from 30 µm to 60 µm, depending on the system under study. Our CLC host is infused into these cells via capillary forces, and subsequently sealed with fast setting epoxy.

The use of colloids as handles to manipulate director structures and defects depends greatly on the strength and nature of molecular interactions at the LC-colloid interface. POM show that the particles induce tangential (planar) non-degenerate surface anchoring for \( n(r) \) of the LC, where the director tends to pin to colloid surfaces by a phenomenon often referred to as “anchoring memory effect.” This behavior is consistent with the results of SEM imaging (inset of Fig. 4.1 b), which reveals nonuniform, nanoscale surface morphology of a type that naturally allows for strong coupling between the superparamagnetic beads and the CLC director. Such coupling is important in locking the rotation of a colloid to its translation along the CLC helical axis. Experimentally (Fig. 4.1 b) we find that rotation of a colloid \( 2\pi \) radians around the CLC helical axis induces a translation of one cholesteric pitch along this axis, a relation that holds for a wide range of colloid species of different size, composition, and configurations including SPMB monomers and chains and GaN nanowires. This lock between rotation and translation is very strong, allowing us to manipulate SPMBs into contact with confining surfaces despite
strong elastic repulsion between the colloid and confining surface. Surface anchoring memory effects [17-21] are also key in understanding the origin of the so called “metastable states” observed in our work, as we will discuss below.

4.3. Results

4.3.1. Metastable states in CLCs of various pitch to colloid diameter ratios

Our initial studies of the interaction of CLC director structures with colloidal particles under gravitational forces at low Reynolds numbers were done with silicate or melamine resin spheres treated for either planar or homeotropic alignment. These studies noted a strong coupling (similar to that shown in Fig. 4.1b) between the translation of the colloid along the cholesteric helical axis, and its rotation about this axis. These studies could be performed by waiting for a colloidal dispersion in a CLC to “settle” under gravitational forces to a so called “sedimentation layer” where particle-substrate elastic repulsive and buoyant forces balance with gravitational forces. Once the colloids were in this sedimentation layer, the cell was inverted and the colloids allowed to fall under gravity in the Stokes flow regime. This allowed for characterization of the motion of these colloids along the helical axis, but the motion range is limited due to elastic repulsive forces near the cell surfaces, as it is impossible to gravitationally manipulate colloids below this sedimentation layer. Furthermore, fall times could be on the order of days for some small/light colloids and thus limits the ability to do repeated experiments on a single colloid. HOT manipulation allows one to reposition a given colloid within the cell volume, but (at relatively large laser powers) this could affect the LC structure or the colloid surface properties due to optical realignment of the local director, or thermal heating of the colloid surface [14].
Likewise, there are issues in optically manipulating colloids close to a cell surface, such as thermally induced heating and adhesion of the colloid to a given surface, and heating or quenching realignment of the anchoring memory effect on the colloid surface [18]. Magnetic manipulation allows us to position a magnetic colloid anywhere along the local helical axis in a CLC, including below sedimentation layers and even into contact with glass substrate walls without thermally affecting the LC structure or the colloid surface anchoring properties. Additionally we can rapidly move the colloidal particle, and repeatedly position it to a given location to study its dynamics [15].

Colloidal motion within the CLC cell is enriched by elastic forces, which appear in addition to buoyant, viscous drag and gravity forces that are also common for isotropic fluid hosts. These interactions can be highly complicated, especially elastic interactions between the CLC, the colloid and the confining cell surfaces. An approximation of the particle-substrate elastic force in very-large-pitch CLCs, where pitch $>>$ colloid diameter, and approaching the limit of a nematic LC, may be found by an “image charge” approach, similar to what was done previously for nematics [29]. However, as the pitch of the cholesteric LC approaches that of the diameter of the colloid, elastic interactions with the confining surfaces become complex and are best determined through a combination of experiments and numerical simulations [17, 30-32], as shown later in this paper.

Viscous drag force on a sphere in the Stokes flow regime is given by:

$$F_{\text{viscous}} = 6\pi \eta R v_{\text{cm}}$$  \hspace{1cm} (4.4)

where $v_{\text{cm}}$ is the center of mass speed of the colloid. Finally, the combination of gravity and buoyant force is given by:
\[ F_{\text{gravity\_reduced}} = \frac{4}{3} \pi R^3 g \left( \rho_{lc} - \rho_{spmb} \right) \]  \hspace{1cm} (4.5)

where \( g \) is Earth’s gravitational acceleration and \( \rho_{lc} \) and \( \rho_{spmb} \) are the LC and SPMB densities (1.38 g/cm\(^3\), 1.9 g/cm\(^3\) respectively.) By balancing the above forces, and numerically simulating the elastic forces near confining surfaces, an equation of motion may be obtained for the motion of a colloid. However, it is instructive to consider the equation of motion within particular regions of interest described below.

We can roughly define three regions of expected different dynamics in the fall experiment (Fig. 4.1 c): Region I is the so-called “wind-up and liftoff” regime, Region II is the “fall” regime, and region III is the “sedimentation” regime. In Region I, a “wind-up” consists of magnetically rotating a SPMB, thus translating it along the local helical axis until it almost comes in contact with either the top or bottom cell substrate. A “liftoff” occurs when the magnetic field is shut off and the SPMB is repelled from the substrate due to the elastic force of interaction between the SPMB and the substrate. In Region II, the SPMB would naïvely be expected to move as dictated by balancing its viscous drag force (Eq. 4) with its buoyant/gravitational force (Eq. 5):

\[ \dot{z}(t) = \frac{4gR^2 \left( \rho_{lc} - \rho_{spmb} \right)}{9h\eta} \]  \hspace{1cm} (4.6)

where \( z(t) = \frac{2}{h} \delta(t) \) with \( h \) being the cell thickness and \( \delta \) the distance from the cell midplane, and which has the expected linear solution characteristic of fall experiments in isotropic fluids in the Stokes flow regime. We note, however, that very thick cells would be required for elastic forces of repulsion from confining substrates to be smaller or negligible as compared to gravity.
forces, and even then the regime II can be realized only within the central part of the LC cell’s vertical cross-section. As the SPMB continued its “fall”, it would transition to Region III while repelling elastically from the bottom cell wall. The SPMB would be expected to slow down while approaching its sedimentation height.

4.3.2. Metastable states in CLCs

To quantify the expected dynamics of colloids, we introduce SPMBs into a 5CB-based CLC host with a pitch of 5 µm (as verified via 3PEF-PM imaging). This CLC colloidal dispersion is infused into a planar rubbed cell of thickness h = 30 µm. We let the cell relax for several hours to days, depending on cell thickness, so as to minimize the number of defects present in the sample, which can interact with and trap SPMBs within their defect cores, as well as distort the local helical axis. For our experiments, we selected SPMB spheres with visible surface features, such as a small defect or occlusion, in order to enhance video image tracking and analysis. Using our magnetic manipulation system alone, we rotated the SPMB at 0.25 Hz and 40 Gs in a clockwise direction as seen in the inverted microscope visual field, and translated the colloid along the CLC helical axis towards the top confining surface (due to the left handed chirality of the chiral dopant). We continued this rotation until the SPMB made a contact with the cell surface, at which point we switched off the magnetic field and observed the motion of the SPMB through the entire cross section of the cell.

The most striking observation are the periodic dynamics and metastable states present in Region II [Fig. 4.2.] In contrast to the predicted linear Stokes flow motion in this regime, we noted a periodic dynamics where the SPMB would rapidly rotate, then slow its rotation for a certain period of time before returning to its former rotation rate. This behavior repeated several times, each with a spatial period of one cholesteric pitch, and a somewhat constant temporal
period of approximately 1000 seconds. The SPMB subsequently transitioned to Region III where it settled at its sedimentation height of approximately 26 µm, or \( h_{\text{sed}} \approx 0.87 \ h \).

\[ \Delta \beta (\text{rad}) \]

\[ \text{Counts} \]

\[ \text{Distance (µm)} \]

\[ t (s) \]

Fig. 4.2. Metastable states evident in a 5 µm pitch CLC infused in a 30 µm thick, planar aligned cell. (Region I) A SPMB is “wound up” to the top cell surface using magnetic manipulation and then released. The inset plot shows a histogram of the number of counts per 3 degree bin over the range of Region II metastable states.

The origin of these metastable states lies in the tangential surface anchoring of molecules on the SPMB surface, and are greatly enhanced by the anchoring memory effect [19] wherein particles induce strong tangential (planar) non-degenerate surface boundary conditions for \( \mathbf{n}(\mathbf{r}) \) of the LC, causing the local director pinning to colloidal surfaces. As the SPMB particle falls
under gravity, this strong pinning hinders rotation of the bead, storing energy in the surrounding CLC elastic field and in deviations of the director at particle’s surface from the easy axis, as well as dilating/compressing the cholesteric pitch around the SPMB surface as the colloid falls. At some point, the free energy density becomes large enough that the pinned director “slips” along the colloid surface, partially relieving the distortion of the director field, and allowing the SPMB (and local cholesteric pitch) to rapidly relax to a new, lower energy position within the cell. This process is further enhanced by distortions of cholesteric layered structure around the sphere and repeats until elastic repulsion from the bottom cell wall balances all other forces (Region III), and the SPMB ceases its rotation.

4.3.3. Particle-wall elastic interactions

Analysis of Region I dynamics due to interaction of the SPMB with the cell substrates [Fig. 4.3] shows the center of mass motion due to a combination of the dominant elastic repulsion near the top and bottom confining surfaces, and the much weaker gravitational and buoyancy forces. For the top confining surface [Fig. 4.3 a], an exponential fit of the angular rotation vs. time yields a time constant $\tau = 21.27$ s (fitting is good, with a coefficient of determination $R^2 = 0.98$), indicating that the assumption of a Hookean elastic interaction between a colloid at small distances from a confining surface is well justified. The inset plot is the time derivative of this exponential fit and indicates that initial colloid speed is 0.18 $\mu$m/s, after which it exponentially decays.
Fig. 4.3. Elastic repulsion of SPMB from cell surfaces in a 5 μm pitch CLC infused in a 30 μm thick, planar aligned cell. (a) Analysis of the Region I top cell wall “lift-off” from Figure 4.2. An exponential fit indicates a time constant of $\tau = 21.27$ s. The inset is the time derivative of this fit. (b) Analysis of the Region I bottom cell wall “lift-off” from Figure 4.2. An exponential fit indicates a time constant of $\tau = 11.94$ s. The inset is the time derivative of this fit. The dotted line indicates the “sedimentation height” where the elastic repulsion between the SPMB and the cell wall balance buoyant and gravitational forces.
Colloidal particle motion near the bottom substrate surface is shown in Fig. 4.3 b, along with an exponential fit of experimental data yielding a time constant $\tau = 11.94 \text{ s}$ ($R^2 = 0.98$), with the inset again showing an initial “lift-off” speed of $\sim 0.18 \mu \text{m/s}$, but undergoing a faster exponential decay. The apparent asymmetry in dynamics and the difference in time constants at the top and bottom confining surfaces can be explained by gravity acting on the colloid. If there were no gravitational forces at work, and assuming the elastic repulsion of a colloid from the top and bottom confining surfaces were equal, we would expect the time constants for the top and bottom surfaces to be equal as well, with the colloid eventually coming to rest in an overdamped manner at half the cell thickness. However, elastic interactions with the bottom confining surface are balanced by the buoyant and gravitational forces acting on the SPMB, leading to sedimentation above the bottom confining surface. However near the top confining surface the directionality of the gravitational and elastic forces acting on the colloid coincide, and thus, the colloidal particle falling from the top surface is free to transition continuously from Region I to Region II.

### 4.3.4. Effects of particle size relative to cholesteric pitch

We further explored metastable states and periodic dynamics in cells composed of SPMB dispersed into a 5CB based CLC host with a pitch of 2.5 $\mu\text{m}$ (again verified via a direct 3PEF-PM imaging) infused into a planar rubbed cell of thickness $h = 60 \mu\text{m}$. We again obtained metastable states (Fig. 4.4). Interestingly, a larger number of metastable states were observed (which is due to the higher cell thickness to pitch ratio), and the elastic repulsion from a cell wall was observed over many more CLC layers as compared to that in a cell with $p=5.0 \mu\text{m}$. Additionally, in contrast to the behavior seen in Fig. 4.2, metastable states were apparent even in
Region I, as seen in Fig. 4.4. To emphasize this behavior, inset in Figure 4.4 was obtained by noting the points with the same phase of the SPMB rotational motion shown in Fig. 4.4. The angular rotations corresponding to these points vs. time are plotted in the inset of Fig. 4.4 and show a distinct exponential fit of time constant $\tau = 2390$ s over the first 6 pitches. A linear fit of the remaining pre-sedimentation data points indicated that at times $\sim$5000s and beyond elastic interaction with the surfaces were no longer dominant and the system was in Region II. This linear fit gives an average fall speed of approximately 0.002 $\mu$m/s. We note that elastic interaction with the bottom confining surface was likewise enhanced leading to a sedimentation at approximately 38 microns from the top confining surface, or $h_{sed} \sim 0.63$ h. This indicates a marked dependence of the particle-wall repulsive elastic force on the cholesteric pitch.
Fig. 4.4. Metastable states evident in a 2.5 μm pitch CLC infused in a 60 μm thick, planar aligned cell. A SPMB is “wound up” to the top cell surface using magnetic manipulation and released, subsequently undergoing an elastically mediated “lift-off” from the cell surface followed by periodic dynamic metastability with an angular periodicity of 2π radians, or one cholesteric pitch. Unlike in the 5 μm pitch CLC, periodic dynamic metastability is apparent even in late Region I. Elastic interaction between the colloid and the top confining surface is highlighted by locating intercept points at each cholesteric pitch [red (gray) circles] and plotting them with respect to time (insert.) Data between $0 < \Delta \beta < 12\pi$ radians, or Region I, is fitted with an exponential function of time constant $\tau = 2870$ s. A linear fit with a slope of 0.005 rad/s (0.002 μm/s) is used for Region II, or $\Delta \beta \geq 10\pi$ radians.

We finally explored formation of metastable states and periodic dynamics in large-pitch cholesterics by use of SPMB dispersion into an 5CB-based CLC with p=10 μm host infused into
a planar rubbed cell with thickness $h = 60 \, \mu m$. Figure 4.5 shows that metastable states are present, exhibiting a linear periodicity in both time and pitch. This may indicate that the elastic forces between the colloid and confining surface are somewhat lower for larger $p$ values, which is consistent with the observation of sedimentation at $39 \, \mu m$ from the top surface ($h_{\text{sed}} \sim 0.82$). These results indicate that metastable states are observed in CLCs in a wide range of CLC pitch and cell thickness values. We note, finally, that direct comparisons of sedimentation height and CLC pitch are appropriate only for the $p=2.5 \, \mu m$ and $p=10 \, \mu m$ CLCs as they are in cells of the same thickness (the $p=5 \, \mu m$ CLC is in a cell of $30 \, \mu m$ thickness, which alters the nature of elastic interactions with confining surfaces.
Fig. 4.5. Metastable states evident in a 10 μm pitch CLC infused in a 60 μm thick, planar aligned cell. A SPMB is “wound up” to the top cell surface using magnetic manipulation and released, undergoing an elastically mediated “lift-off” from the cell surface followed by “metastable states” with an angular periodicity of 2π radians, or one cholesteric pitch. Temporal periodicity appears linear, indicating that the elastic repulsion of the SPMB from the top surface extends less than one cholesteric pitch.

4.3.5. Effects of particle shape and topography

The above results show that metastable states and periodic particle dynamics in CLCs are influenced by the anchoring memory effects on SPMB surfaces. It is well known [18-21] that anchoring memory effect is determined by colloid material characteristics along with their
topography and topology. In order to explore the effect of topography on metastable state formation, we selected SPMBs with obvious differences in surface characteristics, including defects such as spherical extrusions from their surface or those with deliberately laser-induced surface damage. Such surface imperfections are expected to effectively increase the anchoring memory effect of the colloid and reduce the symmetry of the colloid, which in turn would likely enhance formation of metastable states. Figure 4.6 shows such a SPMB with a spherical extrusion located in our p=2.5 µm CLC infiltrated into a h = 60 µm cell. One can note the differences between metastable states observed for this colloid and the one sown in Fig. 4.4 within the same time span. The metastable states are much more apparent in Fig. 4.6.

The effects of topography of colloidal particles were also studied by performing fall experiments on SPMB dimers (an assembly of two SPMBs). Such a dimer located within the CLC sample was often tilted into the x-y plane by approximately 10-15 degrees, and could be magnetically manipulated within the sample volume. Upon undergoing a “fall”, the colloidal dimer exhibited a periodic dynamic and metastable states that had a distinct “double bump” signature, as seen in Fig. 4.7, which can be understood as a superposition of the metastable states of two separate spherical colloids mechanically coupled to each other. Such metastable states are expected to become more complex, but still periodic, as the topological and topographical complexity of the colloid is increased.
Fig. 4.6. Colloid topography enhancement of metastable states in a 2.5 μm pitch CLC infused in a 60 μm thick, planar aligned cell. A SPMB with a spherical protrusion of diameter ~ 1/15th that of the “mother bead” induced enhanced periodic dynamic metastable states. Metastable state transition within one cholesteric pitch as indicated by the sharp transition within the first 15 seconds (figure inset) shows where metastable effects dominate over elastic repulsion from the cell wall.
Fig. 4.7. Fall experiments with SPMB dimer. A SPMB dimer in 5 μm pitch CLC is allowed to fall in Region II in a 30 μm thick cell. The dimer tends to situate at an angle of (insert angle) with respect to the plane of the CLC lamella. This angle produces a distinct “double period” in the metastable states observed.

In order to further quantify topographical effects on the observed periodic dynamics, we performed fall experiments with uncoated and Al-coated GaN nanowires [Fig. 4.8]. An uncoated GaN nanowire [Fig. 4.8(b) top] imposes planar anchoring with the easy axis along the long axis of the wire [14]. Since our GaN wires are not magnetically responsive, we are unable to use our magnetic manipulation system to position a wire for a fall experiment, and thus are unable to explore colloid interactions very near confining surfaces as we were able to with SPMBs. However by judicious use of HOT to position a nanowire far from topological defects, and after allowing the GaN nanowires to sediment towards one surface, we inverted the cell and observed
the nanowire falling under gravity over a period of 12 hours. Weak periodic dynamics and metastable states were found [Fig. 4.8(a)] for the uncoated GaN wire.

Fig. 4.8. Fall experiments with GaN nanowires, uncoated and coated respectively, in a 5 μm pitch CLC infused in a 60 micron thick cell which shows the effect of anchoring alignment on periodic dynamics and metastability. (a) Fall data from an uncoated GaN nanowire of nominal length of 10 μm and 350 nm diameter with planar anchoring. (b) Top image is an SEM of an uncoated GaN nanowire. Bottom image is an Al coated GaN nanowire highlighting so called “nanopyramid” structures on its surface. (c) Fall data from an Al coated GaN nanowire of
nominal length of 10 µm and 350 nm diameter with homeotropic alignment dominant. Periodic dynamics and metastability are greatly suppressed. (d) Al coated GaN nanowire after three weeks where planar alignment is now dominant. Weak periodic dynamics and metastability are again apparent.

An Al-coated GaN nanowire [depicted in the bottom of Fig. 4.8(b)] is observed to initially have poorly defined or even homeotropic anchoring and alignment when first infused into our CLC host. This is evidenced by a nanowire initially aligning orthogonal to the far field director in a pure 5CB nematic host. A suppression of metastable states is observed in LC samples “freshly infused” with such Al-coated nanowires [Fig. 4.8(c)]. Interestingly, Al nanopyramids with a nominal base dimensions of 100 nm and a height of ~ 100 nm form at random locations on the faces of the GaN nanowire during coating, which also have a tendency to further randomize the local anchoring and, thus, suppress the metastable states. However, the initial (homeotropic) boundary conditions are transient. After several weeks, the boundary conditions become planar, so that the nanowires align along the far field director of its pure nematic host and the weak periodic dynamics in the fall experiment re-appears [Fig. 4.8(d)].

4.3.6. Numerical modeling of SPMBs in a cholesteric liquid crystal

To explore in more detail the energetics and symmetry breaking effects of various pitch CLC and colloid diameters on periodic dynamics and metastable states, we numerically minimize Landau-de Gennes free energy of a representative CLC around a spherical colloid in the bulk and close to a confining surface.

The Landau-de Gennes phenomenological description is based on a traceless, symmetric rank-3 tensorial order parameter $Q_{ij} (i,j = 1,\ldots,3)$, which has five independent components. In
the one elastic constant approximation, the Landau-de Gennes free energy of a representative chiral nematic may be written as [34]

\[
F_{LdG} = \int \left( aQ_{ij}^2 - bQ_{ij}Q_{jk}Q_{kl} + c(Q_{ij}^2)^2 + \frac{L}{2} \partial_k Q_{ij} \partial_k Q_{ij} + \frac{4\pi L}{P} \epsilon_{ijk} Q_{il} \partial_j Q_{kl} \right), \tag{6}
\]

where \(a, b, c, L, P\) are phenomenological material constants, the last defining the cholesteric pitch. \(\epsilon_{ijk}\) is the Levi-Civita symbol, and the Einstein convention for summation over repeated indexes is implied.

Fig. 4.9. Configurations obtained numerically. Colloidal particle is in the center of the cell and far from confining surfaces. \(L = 2.5P, H = 5P, R = 0.1\mu\). (a) \(P = R\). (b) \(P = 2R\). (c) \(P = 3R\). (d) \(P = 4R\). The color code represents \(n_x^2\), and the isosurfaces of the reduced scalar order parameter \(Q = 0.25\) are shown by green.
The constant $a$ is assumed to depend linearly on temperature $T$, and is usually written $a(T) = a_0(T - T^*)$, where $a_0$ is another material dependent constant, and $T^*$ is the supercoiling temperature of the isotropic phase. We describe planar degenerate anchoring of the director at colloidal interfaces by the following surface anchoring free energy [35]

$$F_s = W \int_{\partial \Gamma} \left( (\tilde{Q}_{li} - \tilde{Q}_{li}^\perp)^2 + \left( \tilde{Q}_{li}^\perp - \frac{3Q_s^2}{2} \right)^2 \right) ds,$$

where $W > 0$ is the anchoring strength favoring both tangential degenerate anchoring of the director, and $Q_s$ is the preferred surface scalar order parameter [1]; $\tilde{Q}_{li} = Q_{li} + Q_s \frac{\delta_{ij}}{2}$, $\tilde{Q}_{li}^\perp = (\delta_{li} - \nu_i \nu_l) \tilde{Q}_{lk} (\delta_{kj} - \nu_k \nu_j)$ with $\delta_{ij}$ being the Kronecker delta symbol, and $\nu$ is the unit outward normal vector to the confining surface. The total free energy $F = F_{ldg} + F_s$ is then minimized numerically by employing adaptive mesh finite elements method as described in more detail...
details in ref. [36]. We assume $V = \{0 \leq x, y \leq L, 0 \leq z \leq H\}$, and use uniaxial twisted nematic as the initial conditions $Q^0_{ij}$ for the minimization, i.e., $Q^0_{ij}(z) = \frac{q_0}{2}(3n^0_i n^0_j - \delta_{ij})$ with
\[
(n^0_x, n^0_y, n^0_z) = (\cos(q_0(H - z)), -\sin(q_0(H - z)), 0), \quad q_0 \equiv 4\pi/P. \]
The pitch axis is assumed in $z$-direction. At this point we would like to emphasize that in the cholesteric phase the order parameter $Q$ is necessarily biaxial [37]. We always set $H = n P$, where $n$ is an integer, and impose fixed boundary conditions on $Q$ with the values specified by the above expression on $Q^0_{ij}$ evaluated at the system boundaries $\partial V$. Following [37] we introduce the dimensionless temperature $\tau = 24a(T)c/b^2$ and the correlation length $\xi = \sqrt{12cL/b^2}$ at the nematic-isotropic $(q_0 = 0)$ transition. The cholesteric phase is stable for $\tau < \tau_{CI}$, where the cholesteric-isotropic coexistence temperature [37]
\[
\tau_{CI} = \left\{ \begin{array}{ll}
\frac{1}{2} \left(1 + (q_0\xi)^2 + \left(1 + \frac{1}{3}(q_0\xi)^2\right)^{\frac{3}{2}}\right), & q_0\xi \leq 3 \\
(q_0\xi)^2, & q_0\xi > 3.
\end{array} \right. \quad (8)
\]
We use following values of the bulk parameters $a_0 = 0.044 \times 10^6$ J/m$^3$, $b = 0.816 \times 10^6$ J/m$^3$, and $c = 0.45 \times 10^6$ J/m$^3$, $L = 6 \times 10^{-12}$ J/m, $T^* = 307$ K. The spatial extension of inhomogeneous regions and the cores of topological defects is of the order of $\xi \approx 7$nm. For simplicity we set both $Q^s$ and $Q^0$ equal to the value of the scalar order parameter in the bulk nematic phase $Q_N = b(1 + \sqrt{1 - \frac{8\tau}{9}})/8c$.

Figure 4.9 shows the cholesteric configurations as a function of the pitch. The surface director features four index 1/2 disclinations, two split-core boojums, connected by bulk half integer disclination lines. The length of the disclination line undergoes a rather sharp transition
(contrary to a smooth variation of the length with the pitch observed by Marenduzzo et al. [38].)
from an extended regime (Fig. 4.9a) for $P \leq P^* < 2R$ to a short one for larger values of the pitch
(Fig. 4.9b-d). Very long disclination lines are thermodynamically less stable, and occasionally
we observe splitting of such lines via creation of self-compensation $+1/2$, $-1/2$ pairs of surface
disclinations. Figure 4.10 summarizes the dependence of the free energy on the distance to the
wall. The general feature is an overall repulsion from the wall, plus an oscillatory with the period
equal $P$ behavior (see Fig. 4.10 e). Fig. 4.11 and 12 demonstrate the cholesteric configurations
around colloidal particle as a function of wall distance for two values of the pitch. It is worth to
emphasize how the surface director and the positions of the boojums, slide around the particles
surface as $d$ changes.

Fig. 4.11. Cholesteric structure obtained numerically as a function of the distance $d$ to the wall.
$R = 0.1 \mu m, P = R, L = 2.5P, H = 5P$. (a) $d = 1.3P$; (b) $d = 1.5P$; (c) $d = 1.8P$; (d) $P = 2.1P$. 

4.4. Discussion

One of the classic examples of non-trivial interaction of cholesteric ground-state structure with surfaces is the so-called “Bouligand arches,” a characteristic texture appearing when a surface in contact with a cholesteric material is at an oblique angle with respect to the helical axis [33]. It is not surprising that such “Bouligand arches” also appear on surfaces of spherical particles in some of the ranges of pitch to particle size ratios (see, for example, Fig. 4.5 b-d). Due to the fact the closed spherical particle’s surface is making continuously varying angles with respect to the helical axis, the pattern of the director on the surface is somewhat more complex, but it can be understood in a similar way as that of the Bouligand arches. Clearly, even when the anchoring on the particle surface is tangentially degenerate, so that only the polar component of the anchoring energy needs to be considered in the interaction of a spherical surface with the helicoidal configuration of the cholesteric host, this interaction is still highly dependent on particle’s center of mass position along the helical axis. Bulk elastic distortions of the uniform helicoidal structure are induced and the director at spherical particle’s surface deviates from the
easy plane in polar directions, resulting in both surface anchoring and bulk elastic free energy costs in a particle-medium interaction. Furthermore, the structure of topological defects (boojums and surface disclinations) varies as a function of particle location within the helicoidal structure of the LC. A combination of these effects, e.g. a superposition of periodic dependencies of surface anchoring, elastic, and defect core free energies, gives rise to potential energy landscape varying along the helical axis, as we observe in both experiments and in numerical modeling. In experiments, the dependence of free energy due to the colloidal inclusion on its position along the helical axis is further enhanced but anchoring memory effects which cause local transient pinning of easy axis of the LC director at certain orientations, so that the surface anchoring is non-degenerate. This pinning is promoted by rough non-uniform morphology of the particle’s surface profile seen in the inset of Fig. 4.1 b.

The distortions of the cholesteric ground state by an incorporated spherical inclusion can be decoupled into two different types: local perturbations of cholesteric LC order around the particle and long-range distortions of cholesteric layers far away from the particle. The first type of distortions is often accompanied by boojums with an extended core structure, often appearing in the forms of spiraling surface disclinations (Figs. 4.9, 11, and 12). The perturbations of the cholesteric structure can be observed as compressions of cholesteric layers immediately above and below the particle and other, boundary condition mediated distortions that allow one to match these perturbed parts of the layered structure with the equilibrium one in the rest of the sample. The strong elastic distortions and defects immediately around the particle contribute to the periodic potential energy landscape seen by the particle as it moves along the helical axis. On the other hand, long-range distortions of the layered cholesteric structure (mostly compressions of layers above and below the sphere, Figs. 4.11 and 12) mediate the observed
repulsive interactions with confining surfaces of the LC cell. The combination of the elastic forces due to these two types of distortions leads to highly nontrivial fall of particles under the effects of gravity. Firstly, unlike in isotropic fluids, the velocity is not constant and the particle periodically speeds up and slows down while traversing through the cholesteric LC medium due to its interaction with the periodic free energy landscape, which manifests itself somewhat differently, depending on the shape and the size of the colloidal inclusion relative to the cholesteric pitch (see experimental Figs. 4.2, 4.4-8 and theoretical Fig. 4.9). Secondly, the particles levitate at some height with respect to the bottom substrate, at which the gravity action is balanced by elastic repulsive forces due to the perturbation of the layered structure between the particle and the confining substrate (Fig. 4.2).

Magnetic and optical holonomic control allowed us to probe these effects in details, revealing how they are dependent on shape and size of particles as well as cell and material parameters of the system. Furthermore, the strong sensitivity of the lifetime of metastable states to particle shape and size of colloids may potentially be used for assembling these colloids into stable, three dimensional arrays within the CLC bulk.

4.5. Conclusion

We have demonstrated that complex interactions between the ground-state helicoidal structures of cholesteric liquid crystals and particles lead to one-dimensional periodic free energy landscape for colloidal inclusion’s position along the helical axis. This manifests itself in periodic dynamics due to particle motion under effects of gravity, and exhibits a spectacular departure from Stokes-like behavior known for such fall experiments in isotropic fluid hosts. It was suggested by J.C. Price that metastable states could be the product of stray magnetic fields
acting on our SPMB colloids. However, metastable states were observed for non-magnetically functionalized gourd-shaped colloids, melamine resin beads, and our GaN nanowires. This effectively rules out stray magnetic fields, although additional care was taken to null external stray fields. These experimental observations are consistent with the results of numerical modeling based on minimization of the Landau-de Gennes free energy, revealing the potential for their practical uses in sorting of colloidal particles of different shapes and sizes.

4.6. References


Chapter 5

Magnetically responsive gourd-shaped colloidal particles in cholesteric liquid crystals

Adapted from: Soft Matter (Submitted April 2014)*

Overview

Particle shape and medium chirality are two key features recently used to control anisotropic colloidal self-assembly and dynamics in liquid crystals. Here, we study magnetically responsive gourd-shaped colloidal particles dispersed in cholesteric liquid crystals with periodicity comparable or smaller than the particle’s dimensions. Using magnetic and optical tweezers, which allow one to position colloids near the confining walls, we measure the elastic repulsive interactions of these particles with confining surfaces and found that separation-dependent particle-wall interaction force is a non-monotonic function of separation and shows oscillatory behavior. We show that gourd-shaped particles in cholesterics reside not on a single sedimentation level, but on multiple long-lived metastable levels separated by a distance comparable to cholesteric periodicity. Finally, we demonstrate three-dimensional laser tweezers assisted assembly of gourd-shaped particles taking advantage of both orientational order and twist periodicity of cholesterics, allowing new forms of long-range orientationally and positionally ordered colloidal organization in these media.

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5.1. Introduction

Colloidal particles immersed in a liquid crystal (LC) medium show a wide variety of interesting properties and phenomena [1-47]. Elastic properties of LCs trigger anisotropic interactions between colloids [1-6], directing their self-assembly into macrostructures [7-14] useful, for example, in photonics applications [11-13]. During the last decades, experimental and theoretical studies covered different aspects of elastic interactions between spherical colloids mostly in nematic LCs [1-15]. Two- [7-11] and three-dimensional [14] crystals were designed in nematics using different elastic dipoles and quadrupoles, and singular defects were tailored using spherical [16] and topologically non-trivial [17] colloidal particles. Recent studies also showed the importance of size [18-24] and shape [24-31] in elastic interactions and ensuing assemblies of colloidal particles in nematics. On the other hand, colloidal dispersions in twisted nematic and cholesteric LCs (CLCs) have received less attention [32-44] due to the complexity of the problem caused by, for example, the screening of elastic interactions by periodic structure within cholesterics [44]. This complexity increases as the ratio between the particle’s size and cholesteric periodicity increases [32, 34, 39, 44]. Even though elastic pair interactions between colloids were thoroughly studied using optical tweezers [5, 39, 42-45], elastic interactions between particles and confining walls [46] have rarely been explored experimentally because of a limited number of means to systematically access the exact position of the particle across the experimental sample. Moreover, the combined effects of chirality and confinement in guiding colloidal self-assembly have not been considered.

In this article, we study complex-shape colloidal particles dispersed in CLCs. These particles are gourd-shaped with dimensions larger than a cholesteric pitch \( p \), and have been functionalized to respond to magnetic fields. We experimentally probe the elastic interactions
between these particles and confining walls using magnetic manipulation and elastic coupling between rotational and translational motion of these particles in CLCs. Particle-wall interactions are repulsive and generally decrease with increasing the separation between them. Intriguingly, a measured repulsive force is not monotonic with respect to increasing the separation, but exhibits an oscillatory behavior, which may be explained by screening of interactions due to the cholesteric periodicity. We show that gourd-shaped particles in CLCs reside not on a single sedimentation level, but on multiple long-lived metastable levels separated by distances comparable to the cholesteric periodicity along the helical axis. Finally, we demonstrate three-dimensional laser-tweezers-assisted assembly of gourd-shaped particles using both orientational order and the intrinsic periodicity of CLCs.

5.2. Materials and techniques

We used gourd-shaped polystyrene nonspherical colloidal particles with two lobes of dimensions $L_1 \approx 5 \mu m$ and $L_2 \approx 2 \mu m$ on average (Fig. 5.1a-d), which were synthesized using a modified seeded polymerization technique [48]. To make them responsive to magnetic fields, they were soaked in a toluene dispersion of synthesized CoFe$_2$O$_4$ ferromagnetic nanoparticles with a mean diameter of 10 nm [49] for ~ 48 hr.
Fig. 5.1. Colloidal gourd-shaped particles in CLCs: (a) shape of particles with two lobes $L_1 \approx 5 \mu m$ and $L_2 \approx 2 \mu m$; (b) bright and (c, d) polarizing microscopy textures of a gourd-shaped particle in a cholesteric cell; (e-g, h, i, k-n) three photon excitation fluorescence textures of gourd-shaped particles respectively in (e-g, k-n) thin ($d \approx 25 \mu m$) and (h, i) thick ($d \approx 60 \mu m$) cholesteric cells; (j) translational diffusion properties of particles in CLC; inset shows probability of rotational displacement of a gourd-shaped particle around a helical axis $\chi$. Displacement data were collected at a rate of 15 fps for about 10 min. Gourd-shaped particle in (m, n) is rotated using magnetic manipulation by $2\pi$ with respect to (k, l), which corresponds to a vertical displacement equal to a pitch $p$. A and P mark analyzer and polarizer, respectively. Red double arrow shows the direction of polarization of excitation.

Ferromagnetic nanoparticles were trapped in the surface layer of gourd-shaped particles due to partial swelling of polystyrene in toluene. A cholesteric LC with a pitch (distance at which LC molecules or a director $n$ twist by $2\pi$) of $p = 5 \mu m$ was prepared by mixing a nematic material ZLI-3412 and a chiral additive CB15 (both from EM Industries) in weight proportion of 96.8:3.2. The toluene was subsequently evaporated and the gourd-shaped particles then mixed into our CLC and sonicated for ~ 5 min to break apart pre-existing aggregates. This colloidal mixture was infused between two glass substrates spaced by glass microfibers setting the gap thickness $d = 25$ and $d = 60 \mu m$. To set planar surface boundary conditions at confining
substrates we used unidirectionally rubbed thin films of spin-coated and crosslinked polyimide PI2555 (HD MicroSystem). One of the substrates was 0.15 mm thick to minimize spherical aberrations in microscopy experiments involving high numerical aperture (NA) immersion oil objectives.

We used an experimental setup built around an inverted Olympus IX81 microscope to perform bright-field, polarizing, and three-photon excitation fluorescence polarizing microscopy (3PEF-PM) observations. A tunable (680–1080 nm) Ti:sapphire oscillator (140 fs, 80 MHz, Chameleon Ultra-II, Coherent) was used for the 3PEF-PM imaging [50, 51], which in our experiments was realized by the excitation at 870 nm of CB15 molecules, which are parallel to a local n and whose fluorescence signal was detected within a spectral range of 387–447 nm by a photomultiplier tube H5784-20 (Hamamatsu). Problems related to beam defocusing and the Mauguin effect in the 3PEF-PM imaging [51] were mitigated by using a nematic host with low birefringence (Δn = 0.078). A scanning unit (FV300, Olympus) was used to control an in-plane position of a focused excitation beam and its polarization was varied using a half-wave plate mounted immediately before a 100× (NA = 1.42) oil objective.

Translational and rotational motion of colloidal particles was recorded with a CCD camera (Flea, PointGrey) at a rate of 15 fps and the exact x-y position and orientation of gourd-shaped particles as a function of time was then determined from captured sequences of images using motion tracking plugins of ImageJ software. Optical manipulation and assisted assembly of gourd-shaped particles was realized with a holographic optical trapping system [50, 52] operating at a wavelength of λ = 1064 nm and integrated with our optical microscopy system. Rotational manipulation of magnetically functionalized gourd-shaped colloids was achieved using an in-house custom built holonomic magnetic manipulation system integrated within the
same experimental setup [53] which applied to the sample a magnetic field which was measured with a LakeShore 460 3-channel gauss meter.

5.3. Results and Discussion

5.3.1. Gourd-shaped particles and magnetic orientational trapping

In the absence of external forces, gourd-shaped particles are suspended within the LC bulk and undergo thermal motion only (Fig. 5.1b-d). Polarizing (Fig. 5.1b-d) and 3PEF-PM imaging (Fig. 5.1f, g) show that these polystyrene colloids tend to have tangential anchoring at their surface, which dominate even after surface functionalization with ferromagnetic nanoparticles. The orientation of anisotropic gourd-shaped particles in the CLC cell (Fig. 5.1b-d) is determined by the local director \( \mathbf{n}(\mathbf{r}) \) and depends on their vertical position in the cell along the helical axis \( \mathbf{z} \) (Fig. 5.1e-i). The vertical position of the particles in the cell is dictated by the balance between forces due to elastic interactions with walls of confining substrates and the gravitational force \( F_g \approx \pi(L_1^3 + L_2^3)\Delta \rho g/6 \approx 0.03 \) pN, where \( \Delta \rho \approx 43.5 \text{ kg/m}^3 \) is the difference between LC and polystyrene density, and \( g \approx 9.8 \text{ m/s}^2 \) is the gravitational acceleration. Colloids tend to reside at the equilibrium sedimentation height in the middle of comparably thin \( (d \approx 25 \text{ \mu m}) \) cells, equally separated from both walls (Fig. 5.1f,g); in the thick \( (d \approx 60 \text{ \mu m}) \) cells, they sink below the middle level closer to the bottom substrate (Fig. 5.1i). Elastic interactions with walls emerge due to significant deformations of cholesteric layers (Fig. 5.1f, g, i) by the gourd-shaped particles. A cholesteric layer of thickness \( p/2 \) [39, 54, 55] is represented in 3PEF-PM vertical cross-section textures (Fig. 5.1f) as a distance between two bright or dark consecutive stripes, where the polarization of the excitation beam is, respectively, parallel or perpendicular to local \( \mathbf{n} (\mathbf{n} \equiv -\mathbf{n}) \). Maximum displacement of the layers from their flat unperturbed state is near the particles, but decays with distance from the particle in all directions.
and is completely suppressed at walls with strong surface anchoring (Fig. 5.1f,g,i).

Freely floating gourd-shaped particles exhibit both translational and rotational diffusion. Figure 5.1j shows a distribution of translational displacements for an elapsed time of $\tau = 1/15$ s as measured from video tracking data collected in bright-field microscopy (Fig. 5.1b). Fitting the distribution by a Gaussian function \( P(\delta) = P_0(\delta)\exp[-\delta^2/(4D\tau)] \), where \( P(\delta) \) is the probability that over the time \( \tau \) a particle will displace by \( \delta \), \( P_0(\delta) \) is a normalization constant, and \( D \) is a diffusion coefficient, allows us to determine the diffusivity of gourd-shaped particles in the cholesteric material. Histograms of these displacements (Fig. 5.1j) readily yield almost the same translational diffusion coefficients \( D_x = 1.92 \times 10^{-3} \, \mu m^2/s \) and \( D_y = 2.28 \times 10^{-3} \, \mu m^2/s \) in the plane of the cell and a rotational diffusion coefficient \( D_\theta = 2.56 \times 10^{-4} \, \text{rad}^2/s \), which is coupled to the translational diffusion along the helical axis $\chi \parallel z$. An important feature of the system is this coupling between rotation of a gourd-shaped particle around its short axis parallel to $\chi$ and translational displacement along $\chi$, which we verified below using magnetic manipulation. This coupling allows determination of the vertical displacement of a particle along $z$-axis using the change of its orientation in the plane of the cell.

Application of a magnetic field $\mathbf{H}$ to the magnetically functionalized gourd-shaped particles results in an induced net magnetic dipole moment $\mathbf{m}$, which allows us to use magnetic manipulation techniques [53] to control the orientation of the gourd particles about all Euler angles (Fig. 5.2).
When magnetically trapped, the orientation of these particles fluctuates with respect to the direction of a maximum accessible applied magnetic field equal to 107 Gs by an angle \( \Delta \theta \approx \pm 0.86^\circ \) (Fig. 5.2a). The orientational trapping stiffness \( k_\theta \) associated with magnetic trapping can be determined similar to the approach in optical trapping \([57]\) using the equipartition theorem \( \langle \Delta \theta^2 \rangle = k_B T / k_\theta \), where \( \langle \Delta \theta^2 \rangle \) is a standard deviation in the orientation of a particle with respect to \( \mathbf{H} \), \( k_B \) is Boltzmann’s constant and \( T \) is temperature. Fitting the histogram of angular deviations (Fig. 5.2a) with a function \( f(\Delta \theta) = f_0 \exp[-\Delta \theta^2/(2\langle \Delta \theta^2 \rangle)] \), one finds \( \langle \Delta \theta^2 \rangle = 2.25 \times 10^{-4} \) rad\(^2\), which yields \( k_\theta = 18.39 \) pN·μm. The torque exerted by magnetic manipulation on a particle can be extracted from the time dependence of its reorientation \( \phi(t) \) upon changing the direction of a magnetic field of 107 Gs from \( \mathbf{H}_1 \) to \( \mathbf{H}_2 \) (Fig. 5.2b). The maximum angular speed of reorientation was found to be \( \Omega \approx 0.9 \) rad/s, so that rotational Reynolds number was small \( Re_r = \rho_{LC} R_{eff}^2 \Omega_0 / \eta \approx 10^{-8} \), where \( \rho_{LC} \approx 1000 \) kg/m\(^3\) is density of LC, \( R_{eff} = [(L_1^3 + L_2^3)/8]^{1/3} \approx 2.55 \) μm is the radius of an equivalent sphere having the volume...
equal to the volume of a gourd-shaped particle, and $\eta = 146 \text{ mPa}\cdot\text{s}$ is the viscosity of ZLI-3412, assuming non-turbulent flow and neglecting inertial effects. Thus, a magnetic field torque can be balanced with a viscous drag torque as $M = (k_B T / D^{\theta}) \Omega \zeta$, which yields a dependence of torque on an angle $\Delta \phi$ between the direction of $\mathbf{H}$ and $\mathbf{m}$ (Fig. 5.2c). At comparably small angles, torque increases linearly with deviation of particle from trapping direction, exhibiting Hookean behavior [6] $M = k_0 \Delta \phi$ (Fig. 5.2c). Using a linear fit in the Hookean regime of this dependence (Fig. 5.2c), one can again extract the trap stiffness $k_0 = 13.45 \text{ pN}\cdot\mu\text{m}$, which is in reasonable agreement with $k_0$ as determined above using the equipartition theorem.

The controlled rotation of gourd-shaped particle via magnetic manipulation and 3PEF-PM imaging allow for verification and determination of coupling between rotational and translational motion of gourd-shaped colloids in CLCs along $\chi||z$ (Fig. 5.1k-n). A particle with equilibrium orientation at $\mathbf{H} = 0$ (Fig. 5.1k,l) was rotated along $\chi$ counterclockwise by $2\pi$, which experimentally corresponded to a vertical displacement of the center of the particle’s large lobe upwards to the top substrate along $\chi$ by a distance equal to $p$ (Fig. 5.1m,n), which yields a relation between rotational $\Delta \theta$ and translational $\Delta z$ displacements as $\Delta z = \Delta \theta q^{-1}$, where $q = 2\pi/p$ is a cholesteric twist wavenumber [54] and $q > 0$ (a right-handed cholesteric) in the described experiments. One can then determine the relation between angular $\Omega_z$ and linear $V_z$ speeds as $V_z = \Omega_z q^{-1}$. The direction of translational displacement due to the sense of particle’s rotation depends on a handedness of the CLC. The right-hand rule can be applied to determine the direction of translational displacement depending on the rotation of the gourd: if one grips the twist axis $\chi$ so that fingers point in the direction of particle’s rotation, then, if the cholesteric helix twists with the same sense, the extended thumb points in the direction of translational displacement. Knowing the relation between rotational and translational displacements, one can
determine the probability of translational displacements $\delta z$ due to Brownian motion (Fig. 5.1j) not only in the plane of the cell but also out of the plane along $\chi \parallel z$ using experimentally measured data on rotational displacements $\delta \theta$ of the gourd-shaped particles (inset of Fig. 5.1j). Experimental plots (Fig. 5.1j) and determined $D_z = 1.67 \times 10^{-4} \, \mu m^2/s$ show that the translational diffusion of particles in the vertical direction along $\chi$ is an order of magnitude smaller than in the plane of the cell, which was verified to be the case in both thin (Fig. 5.1f) and thick (Fig. 5.1i) LC cells.

5.3.2. Particle-wall interaction

As an important benefit of the observed coupling between rotational and translational motion of particles in our system, and because of their orientational response to magnetic field, it is possible to move particles towards either the top or bottom substrates just by rotating them via magnetic manipulation (Fig. 5.3).
Fig. 5.3. Repulsive elastic interactions of gourd-shaped particles and confining walls in a thin \((d \approx 25 \, \mu m)\) planar cholesteric cells: multi-photon fluorescence (a, b, d, e) and bright field (f, g) microscopy textures of particles in a cholesteric cell; (c) time dependence of gourd-shaped particle motion from the wall after switching off the magnetic field \(H\) at \(t \approx 13\) s; repulsive elastic force from (h) bottom and (k) top walls vs. a wall-particle separation. Insets in (h) and (k) show time dependence of translational speed \(V_z\) of gourd-shaped particles.

Gourd-shaped particles forced with magnetic tweezers to the bottom (Fig. 5.3b) or top (Fig. 5.3a) substrates of the thin cell \((d = 25 \, \mu m)\) were repelled from the walls upon removal of the external field \(H\), and subsequently moved back to their initial position in the mid-plane of the cell (Fig. 5.3c-g). Bright field (Fig. 5.3f, g), 3PEF-PM (Fig. 5.3a, b, d, e) microscopy and the known coupling between \(\Omega z\) and \(V_z\) allow for probing a position (Fig. 5.3c) of particle during its motion along \(\chi||z\). Vertical displacement is not a monotonic function of time; one can clearly see a significant bump in the plot of a position of the center of a particle’s large lobe vs. time. Strong deformation of cholesteric layers near the confining walls (Fig. 5.3a, b) gives rise to a repulsive
elastic force $F_w$ which pushes particles away from the wall into the bulk. Comparably slow motion of gourd-shaped particles across the cholesteric layers (insets of Fig. 5.3h,k) is overdamped and inertial forces can be neglected since a translational Reynolds number

$$Re = \rho CRC_{eff}|V_z|/\eta \sim 10^{-8}$$

is small. Therefore, repulsive elastic force can be balanced by a viscous drag force against the translational vertical motion of the colloidal particle as

$$F_w = (k_BT/D_z)|V_z|.$$  

Effects related to hydrodynamic flow coupling to $n(r)$, which could be expected in cases of the very fast motion of a particle, can also be neglected since the Ericksen number $Er = \eta CRC_{eff}/K \approx 0.016$ is much smaller than 1 [54], where $K = 12.1 \times 10^{-12}$ N is an average Frank elastic constant of ZLI-3412. Thus, using time dependence of a particle’s motion from the walls (Fig. 5.3c) and estimated $D_z$ (Fig. 5.1j), one can plot the dependence of the repulsive force on a separation $r$ between the center of a gourd’s large lobe and the surface. It is maximum ($\sim 8-12$ pN) near the confining walls of the thin ($d = 25$ μm) cell and decreases to zero at the level where the particle reaches a sedimentation height in the middle of the cell at $z \approx 12.5$ μm (Fig. 5.3h,k). Integrating this force over the separation, one can determine an effective interaction potential at the onset of interactions as $\sim 10,000k_BT$. The repulsive force does not decrease with time $t$ monotonically; there is a clearly pronounced plateau of constant force of $\sim 1-2$ pN along $\sim 2$ μm long path (Fig. 5.3h, k). The slightly stronger $F_w$ from the bottom substrate can be explained by a stronger deformation of the near surface cholesteric layer (compare Figs. 5.1a and 5.1b). Downward motion of the gourd-shaped particle from the top wall coincides with the direction of a gravitational force, but opposes gravity when the particle is moving upward from the bottom substrate. However, as one can see from our estimated value of $F_g$, this gravitational force can be neglected in the case of relatively thin LC cells as it is one-to-three orders of magnitude smaller as compared to the maximum elastic force (Fig. 5.3h, k).
Magnetic manipulation is working against the repulsive force $F_w$ when moving the particle towards the wall. Thus, one can estimate an orientational trapping, or escape force, of $F_{\text{trap}} \approx 12$ pN exerted on the particle by a magnetic orientational trap as the maximum measured repulsive force at the minimum $r$ between the particle and wall (Fig. 5.3h).

### 5.3.3. Meta-stable periodic localization levels

The onset of repulsive interactions between gourd-shaped particles and confining walls in thick cells (Figs. 5.4, 5.5) is similar to that in thin cells. When released from the magnetic trap while close to substrates, colloidal particles repel quickly away from the walls (initial position 1), however, their separation increases non-monotonically (Figs. 5.4, 5.5).
Fig. 5.4. Repulsive elastic interaction of a gourd-shaped particle and the top confining wall in a thick ($d \approx 60 \, \mu m$) planar cholesteric cell: (a) time dependence of separation from the wall after switching off the magnetic field. Bright field microscopy image 1 shows the orientation of particle at time $t = 0$; 3PEF-PM cross-sectional textures of a gourd-shaped particle magnetically trapped near a top substrate (b) and moving down (d) after switching off the magnetic field; (c) repulsive elastic force vs. separation from the top wall. Shaded area shows a moment when laser tweezers were applied.
Fig. 5.5. Repulsive elastic interaction between a gourd-shaped particle and a bottom confining wall in a thick ($d \approx 60 \, \mu m$) planar cholesteric cell: (a) time dependence of separation from the bottom wall after switching off a magnetic field; Bright field microscopy images in the insets show the orientation of particle at different times indicated by arrows; 3PEF-PM cross-sectional textures of a gourd-shaped particle magnetically trapped near a bottom substrate (b) and moving up (d) after switching off the magnetic field; (c) repulsive elastic force vs. separation from the bottom wall. Shaded area in (a) shows the time interval when the laser tweezers were applied to perturb the particle in a metastable state.

Separation vs. time curves have a bump which is even more pronounced than in thin cells; this is seen in the plots as a long plateau in the dependence up to the distance $\sim 10-15 \, \mu m$. 

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away from the walls (level 2), at which particles eventually come to the rest (Figs. 5.4a and 5.5a). What is surprising and interesting is that this metastable level is far below the equilibrium sedimentation height for particles in the thick cells (Fig. 5.1i). Particles can reside at this metastable level without moving up or down (depending on the bottom or top substrates) due to a local potential energy minimum arising from the interplay between gravitational and elastic forces of repulsion from both substrates and particle’s interactions with the cholesteric’s periodic structure. However, we find from our microscopic observations that this level is only metastable. Using the low power (< 10 mW) optical trap, one can assist the particle to move slightly off this metastable level 2, so that it will start moving further towards the equilibrium sedimentation height (and never back to the substrate) by itself without further assistance of the laser tweezers, slowing down when reaching the new level 3 (Figs. 5.4a and 5.5a), which is still far away from the final equilibrium sedimentation height of ~25-30 μm. Metastable levels 2 and 3 are separated by a distance roughly equal to ~p. Plots show that the repulsive elastic force $F_w$ decreases non monotonically with increased separation from walls (Figs. 5.4c and 5.5c). A maximum repulsive force of ~6-7 pN was acting on the particle in its location closest to the wall (level 1), similar to the thin cells, and decreased to zero when approaching the level 2. However, there was also a sudden increase of the force to ~1 pN at the separation ~11 μm (from the top substrate) (Fig. 5.4c) and ~7.5 μm (from the bottom substrate) (Fig. 5.5c) that correspond to the small bumps in the time dependencies of separation (Figs. 5.4a and 5.5a) before reaching the level 2. The repulsive force increases again to ~0.5 pN during transition between levels 2 and 3 (Figs. 5.4c and 5.5c). Positions of particles on the intermediate meta-stable levels 2 and 3 correspond to the potential minima arising due to the particle’s interaction with the helicoidal director structure of CLC mediated by the surface anchoring on particle’s surface and supplemented by the
competition of $F_e$ and elastic forces of repulsion from both substrates.

We fit the separation dependence of the repulsive force on the onset of elastic interactions with a power-law equation $F_w(r) \sim r^{-a}$ and find $a \approx 3$ for the repulsion from both substrates in the thin cell (Fig. 5.3h, k) and from the top wall in the thick cell (Fig. 5.4c) and $a = 5.2 \pm 0.18$ for the repulsion from the bottom wall in the thick cell (Fig. 5.5c). This difference in the short-range interactions can be explained by qualitatively different structure of cholesteric deformations in the narrow region between the particle and wall (compare Figs. 5.3a, b, 5.4b, and 5.5b).

Figure 5.6 shows a time dependence of separation between a gourd-shaped particle and the bottom confining wall where the laser tweezers were used to assist displacing the particle away from the metastable levels until it approached the final equilibrium sedimentation level 5. There were four long-lived intermediate meta-stable levels, which were separated by a distance equal to $\sim \rho$, corresponding to $\sim 2\pi$ rotation of $\mathbf{n}$ (Fig. 5.6).
Fig. 5.6. Metastable levels of gourd-shaped colloids in a thick \((d \approx 60 \mu m)\) planar cholesteric cell. The inset shows separation vs. time at the onset of elastic interactions. Bright field images show the orientations of gourd-shaped particles at times indicated by arrows. Shaded areas show the moments when laser tweezers were applied to release the particles from the metastable states.

Recently, similar oscillatory behavior of elastic interactions in layered systems was experimentally observed between spherical colloids in the cholesterics [44] and theoretically predicted for smectics [47], although these interactions were of attractive type. A dimer formed from two single spheres when sedimenting in cholesterics also showed non-monotonic motion in other theoretical studies [38]. In principle, the observed periodic oscillations of repulsive elastic interactions between gourd-shaped particles and both confining walls in our system can be explained as arising due to the screening of elastic interactions by the periodic ground-state structure of CLC similar to [44].
One way to interpret the experimentally observed complex elastic interactions between a gourd-shaped particle and confining wall is by considering the deformations of a periodic cholesteric structure in the regions between the particle and confining walls as well as the local within-layer $n(r)$ deformations surrounding the particle. The cholesteric structure is significantly distorted by embedded gourd-shaped particles (Fig. 5.3b). Cholesteric layers are deformed from both sides of the particle and these deformations propagate towards confining walls, causing elastic interactions between the particle and both walls that tend to minimize the energetic cost of these distortions (Fig. 5.7).

![Diagram of a gourd-shaped particle embedded into a cholesteric cell. Two thick black lines show confining walls. Thin green lines depict local orientation of $n$ and are separated by $p/2$, corresponding to cholesteric layers. Cholesteric layers are deformed in regions 1 and 2 near a particle but remain unperturbed far from it in a region 3.](image)

Fig. 5.7. Schematic of a gourd-shaped particle embedded into a cholesteric cell. Two thick black lines show confining walls. Thin green lines depict local orientation of $n$ and are separated by $p/2$, corresponding to cholesteric layers. Cholesteric layers are deformed in regions 1 and 2 near a particle but remain unperturbed far from it in a region 3.

Repulsive forces acting on the particle from two walls have opposite directions.

Neglecting bend distortions in the regions 1 and 2, the elastic energy density due to the change of intrinsic twist wavenumber $q$ (as in an undistorted region 3) below and above the particle
depending on \( r \) can be expressed as 
\[
  f_1(r) = \left( K_2/2 \right) \left( q - q_1(r) \right)^2 
\]
and 
\[
  f_2(r) = \left( K_2/2 \right) \left( q - q_2(r) \right)^2,
\]
respectively, where \( K_2 \) is a twist elastic constant, \( q_1 \) and \( q_2 \) are twist wavenumbers in distorted regions 1 and 2 that exhibit noticeable layer compressions due to the embedded particle (Fig. 5.7). As the particle moves away from the cell wall into the LC bulk, \( q_1 \) and \( q_2 \) vary (\( q_2 \) increases when \( q_1 \) decreases) depending on \( r \). Strong elastic distortions and defects immediately surrounding the particle within a cholesteric layer also contribute to the periodic potential energy landscape seen by the particle as it moves along the helical axis. The combination of the elastic forces due to these two types of distortions leads to a highly nontrivial falling motion of particles under the effects of gravity. Unlike in isotropic fluids, the velocity \( V_z \) is not constant, and the particle periodically speeds up and slows down while traversing through the CLC medium due to its interaction with the periodic free energy landscape. Interestingly, the distance between metastable levels slightly decreases as the particle moves further away from the nearest confining wall, which can be seen from the orientation of the gourd-shaped particles on each such level (compare the orientation of particles in the insets 2, 3, and 4 in Fig. 5.6).

Elastic interactions between gourd-shaped particles and confining walls depend also on the orientation of particles with respect to \( \chi \parallel z \). For example, gourd-shaped particles with their long axes tilted in the vertical plane of the cell (Fig. 5.8c, d) did not repel from the wall into the bulk after being moved by the magnetic trap near confining walls and subsequently released as particles in Figs. 5.1-5.6. Instead, they remained near the wall, despite the fact that a direct contact between the particle and the wall was avoided (Fig. 5.8d).
Fig. 5.8. Elastic interactions of tilted gourd-shaped particles and confining walls in a planar cholesteric cells: (a, b) 3PEF-PM in-plane and (c, d) cross-sectional textures of tilted particles in a thick \((d \approx 60 \, \mu m)\) cell. (c) Moving a gourd-shaped particle down to the bottom substrate using magnetic manipulation. (d) Gourd-shaped particle staying in a metastable state near the bottom substrate after the magnetic field was switched off.
This particle’s indifference to being close to the wall can be explained by much smaller deformations of cholesteric layers, which vanish in the bulk faster before reaching the confining walls, as compared to the case when gourd-shaped particles are aligned in the plane of the cell (compare deformations of the cholesteric layers in experimental textures of Figs. 5.3a, d, 5.5b and 5.8d).

**5.3.4. Optically directed assembly of three-dimensional structures**

The observed periodicity of repulsive elastic interactions between gourd-shaped particles and confining walls and the existence of equally spaced, long-lived meta-stable states in CLC can be used for directed assembly of particles into complex three-dimensional colloidal structures. Advantage can be taken of not only orientationally dependent elastic interactions (present also between spherical colloids in nematics) [7-14], but also taken from the intrinsic translational periodicity of cholesteric hosts. In our work, to apply these general principles, we used thick cholesteric cells, which allow for multiple meta-stable states below the equilibrium sedimentation height (Fig. 5.6). Laser tweezers were used to collect particles residing on different meta-stable levels (Fig. 5.9a, d, g) and move them adjacent to each other (Fig. 5.9b, c).
Colloidal particles sitting on the same meta-stable level were oriented either in the same direction or antiparallel (Fig. 5.9b) showing orientational ordering defined by the orientation of $\mathbf{n}$ at the metastable level. When brought close to each other using laser tweezers, particles on different levels tended to attract to each other via elastic interactions and form colloidal structures (Fig. 5.9e-k) with centers of each particle’s large lobe separated from another by a distance of $\sim l$ (difference between levels pointed by yellow arrows 1 and 2), as determined by
the use of 3PEF-PM microscopy (Fig. 5.9 h, k). Strong bending of the cholesteric layers in the vertical plane (Fig. 5.9 h, k) prevents gourd-shaped particles from coming into direct contact with each other. Blocks of three (Fig. 5.9 e, h) and four (Fig. 5.9 c-k) gourd-shaped particles were assembled in the vertical plane of the cholesteric cell resulting in colloidal structures that were robust and which can be translated with laser tweezers or rotated via magnetic manipulation without breaking apart.

5.4. Conclusions

We have described the self-assembly and elastic interactions of magnetically responsive gourd-shaped colloidal particles dispersed in CLCs with a periodicity smaller than the particle’s dimensions. Particles magnetically manipulated to positions near the confining walls were subsequently repelled into the bulk with a maximum elastic force of ~10 pN. We demonstrated elastic interactions of these particles with confining walls using elastic coupling between rotational and translational motion of particles in CLCs using magnetic manipulation. Particle-wall repulsive interactions were dependent on their separation, and intriguingly this measured repulsive force behaved non-monotonically with increasing separation and exhibited an oscillatory force with periodicity comparable to the intrinsic cholesteric pitch, which we explained by considering local and long-range interactions of the incorporated particle with the cholesteric periodic structure. We showed that gourd-shaped particles in CLCs can reside on multiple long-lived metastable localization levels separated by a distance comparable to the intrinsic cholesteric periodicity. Finally, we have demonstrated three-dimensional laser tweezers assisted assembly of gourd-shaped particles using both the orientational order and translational periodicity of cholesterics, which enabled assembly of non-spherical particles in cholesteric media into low-symmetry colloidal structures with both positional and orientational ordering.
5.5. References


Chapter 6

Stick-slip motion of surface point defects due to magnetically controlled colloidal particle dynamics in nematic liquid crystals

Adapted from: Physical Review E (in draft) *

Chapter overview

We explore dynamics of topological point defects on the surface of magnetically responsive colloidal microspheres in a uniformly aligned nematic liquid crystal host. We show that pinning of the liquid crystal director to the particle surface with random nanostructured morphology results in an unexpected translational dynamics of both particles and topological point defects on their surfaces when the samples are subjected to rotating magnetic fields. We characterize and quantify the observed stick-slip motion of defects as a function of field rotation rates and temperature, demonstrating the roles played by the competition of elastic, surface anchoring and magnetic torques on the sphere as well as random-surface-mediated pinning of the easy axis of nematic director on colloidal microspheres. We analyze our findings using a simple analytical model and through their comparison to similar dynamic processes in other branches of science.

6.1. Introduction

Solid friction behavior, specifically stick-slip motions [1-8], describe a wide range of physical phenomena encountered in daily life. It describes the squeaking of chalk on a chalkboard and the squealing of sand compressed underfoot on a beach [2], as well as low

* In collaboration with Q. Zhang, R. Petschek and I. I. Smalyukh
frequency rumblings of a fault shift during earthquakes [3]. In acoustics it explains the stridulation (chirping) of crickets and the spiny lobster [4], and the beautiful sound of bowed instruments, such as the cello [5]. On the other hand, studies of defect motion span many branches of modern science and technology [9-22]. For example, dynamics of dislocations permits metals to be plastically deformable with ease, a circumstance upon which our modern technology is highly dependent [9, 10]. Dynamics of cosmic strings, topological defect lines that might have governed early universe development, could be modeled by considering nematic disclinations emerging during isotropic-nematic phase transition [11-14]. In various liquid crystal (LC) phases, defects often determine the scenario of numerous irreversible phenomena, when the liquid crystal reacts to an applied electric and magnetic fields, flow, or anchoring-transition-mediated changes of boundary conditions [15-19]. Controlling dynamics of the appearance and annihilation of defects in certain LC display modes is important to avoid degrading their performance [20]. In solid-state physics, glide and climb of dislocations are associated with a broad range of interesting fundamental phenomena, such as the Peierls-Nabarro friction [9, 10, 16]. In this case, as the dislocation glides across the periodic crystal lattice, the core structure changes accordingly, so that atomic reconstructions lead to periodic changes of the potential energy of the crystal. The applied stress needed to overcome the ensuing energy barriers is called the Peierls-Nabarro stress and is determined by the core structure of corresponding defects [9, 10]. Solid friction behavior, such as stick-slip motions, were previously described for several different types of line and wall defects in very different condensed matter systems, including domain walls in thin magnetic films [21], π-wall defects in LCs [22], and vortices in superconductors [23].
In this work, we design an experimental soft matter system to explore the stick-slip dynamics of surface point defects dubbed “boojums” [24-26]. Superparamagnetic microspheres with rough morphology and characteristic random surface features on the scales of 50-100nm are incorporated into a nematic LC (NLC) with an aligned far-field director \( \mathbf{n}_0 \) [27]. Complex interactions of the LC with these colloidal surfaces result in non-degenerate surface anchoring of the LC director \( \mathbf{n} \) and “memorized” \( \mathbf{n}(\mathbf{r}) \) field configuration with two boojums at the opposite particle’s poles along \( \mathbf{n}_0 \). When these colloidal superparamagnetic beads (SPMB) are rotated by in-plane ac magnetic fields, the induced magnetic torques on the colloid compete with surface anchoring and elastic torques resulting from non-degenerate tangential surface anchoring of \( \mathbf{n}(\mathbf{r}) \) on particle surfaces and ensuing particle-induced elastic distortions in the LC bulk. This results in unexpected complex motions of both colloidal particles and topological point defects (boojums) on their surfaces. We specifically identify and characterize this previously unreported boojum stick-slip motion.

6.2. Materials, methods, and techniques

6.2.1. Holonomic magnetic and holographic optical manipulation system

Magnetic and optical manipulation of magnetically responsive colloids is achieved by combining holographic optical trapping (HOT) with a three axis electromagnetic apparatus formed by air-core solenoids (Fisher Scientific International, Inc. S52051) with custom machined cast iron cores and arranged on an aluminum Cartesian frame mounted directly on the microscope body [27]. Each electromagnet (Fig. 6.1) is separately driven via an amplified power supply (APS) BOP20-5M (Kepco) which is controlled using a computer-driven data acquisition (DAQ) card (National Instruments USB-6259 BNC) via in-house LABVIEW-based software.
(National Instruments). Each electromagnet can produce ac and/or dc magnetic fields up to about 40 Gs at 8 Hz which manipulates all magnetically responsive colloids in a sample simultaneously rather than single colloids on an individual basis. These low magnetic fields are found to have little significant direct coupling with the nematic LC (NLC) director since most known LCs (including the ones used in this study) are diamagnetic materials, with director realignment typically a threshold like effect requiring fields of 1000 Gs and higher.

Fig. 6.1. Integrated holonomic magnetic and holographic optical manipulation system. (a) Electromagnetic iron or air core solenoids arranged in a Cartesian aluminum frame mounted on an inverted microscope (not shown) which driven by amplified power supplies via computer controlled DAQ. The HOT is based on a fiber laser and trapping system with the following optical elements: polarizer (P), lenses (L1, L2, L3, L4), computer controlled, dynamically addressable liquid crystal based spatial light modulator (SLM), a 100x oil immersion objective (OBJ), half wave plate (HWP), polarizer/rotator (PR) and a dichroic mirror (DM). The trapping beam focuses within the sample slide volume. This manipulation setup is integrated with an optical imaging system capable of both POM and 3PEF-PM imaging. (b) Solenoids in the x y plane with a net magnetic gradient force orientated along the arrow.
Although our solenoids are designed to minimize any magnetic gradient force at the sample volume, the solenoid cores have a finite radius and geometry which results in a residual in-plane fringe field gradient that can yield residual forces on our magnetically responsive colloids (Fig. 6.1 b) of up to 0.07 pN, directed along the y axis [26]. Although this gradient force is on the order of gravity at the scale of the colloidal suspension, over extended time periods this force can translate a colloid in the y direction a significant distance depending on colloid dynamics in the Stokes flow regime.

### 6.2.2. Sample preparation

We use a single-compound nematic LC (NLC) pentylcyanobiphenyl (5CB, Frinton Laboratories) in which we disperse magnetically responsive colloidal particles either via solvent exchange or sedimentation mixing [26]. Cells are constructed from glass slide substrates cleaned in a water and detergent sonication bath at 60 °C, sequentially rinsed with acetone, methanol, and IPA, then dried, and plasma etched. Planar alignment of the substrates are set in an anchoring layer comprised of polyvinyl alcohol (PVA 1% weight-to-weight ratio) in deionized water, spin coated at 8500 rpm then baked for at least 1 h at 100 °C. Rubbing this alignment layer with a velvet cloth forces the LC molecules to align along the rubbing direction and, thus, sets planar boundary conditions for \( \mathbf{n}(\mathbf{r}) \). The substrates are assembled as planar cells with a director pretilt angle of \( \sim 3° - 6° \) with cell thickness set using spherical silicon spacers dispersed in a UV curable epoxy (NOA-61, Norland Products) and which varies from 10 to 120 \( \mu \text{m} \). The NLC/colloid host is infused into these cells and sealed with fast setting epoxy.

The magnetically responsive colloids used in this work are superparamagnetic beads (SPMBs) (Dynabead M450, Invitrogen) which are fabricated using ferromagnetic nanoparticles
(γ Fe₂O₃ and Fe₃O₄) approximately 8 nm in diameter embedded into a highly cross-linked epoxy at a density of ~ 10⁵ nanoparticles per bead (Fig. 6.2).

Fig. 6.2. Superparamagnetic bead surface characteristics and “walking” motion. (a) SEM image of a SPMB showing surface roughness, indicating a strong surface anchoring of director orientation at the surface, which is tangential but with “memory” (non-degenerate). (b-c) A SPMB distorts the nematic director field, creating two surface point defects called “boojums” seen clearly under polarizing optical microscopy (b). Orientations of polarizer (P), rubbing direction (rub), analyzer (A) and the slow axis of a 530nm wave plate (W) are marked by double arrows. (d) Rotating the applied in-plane magnetic field $H$ [brown arrows on left] causes the SPMB to “barrel roll” out of the x-y plane [blue arrows shown at left] causing a “walking” motion of the SPMB along the x axis [green arrows on left], while a constant net magnetic gradient force pulls the SPMB in the y direction. The “barrel roll” motion is accompanied by a precession of one of the boojums around the boojum axis, while the other boojum circumscribes a smaller precessional arc.

Each bead has a nominal diameter of 4.5 ± 0.1 µm. The ferrite nanoparticle orientations are mechanically coupled to the epoxy of the SPMB microsphere and therefore alignment of the net induced magnetic moment $\mathbf{m}$ forces the SPMB to point along and lock with the applied magnetic field $\mathbf{H}$, as given by [26].
\[ \mathbf{m} = V_p \chi_p \mathbf{H} \quad (6.1) \]

with a resultant torque on the SPMB as given by
\[ \tau = \mu \mathbf{m} \times \mathbf{H} \quad (6.2) \]

where \( V_p \) is the colloid volume, \( \chi_p \) is its effective magnetic susceptibility and \( \mu \) is the colloid’s magnetic permeability. We can achieve magnetic torques of up to \( \sim 5 \times 10^{-18} \text{ N} \cdot \text{m} \) exerted on individual SPMB in various LC systems.

POM Imaging (Fig. 6.2.b) show that the particles induce tangential (planar) non-degenerate surface anchoring for \( \mathbf{n}(\mathbf{r}) \) of the LC where the director tends to pin to colloid surfaces, a phenomenon often referred to as the “anchoring memory effect.” This behavior is consistent with the results of SEM imaging (Fig. 6.2.a), which reveals nonuniform nanoscale surface morphology of a type that naturally allows for strong mechanical coupling between the superparamagnetic beads, \( \mathbf{n}(\mathbf{r}) \), and various topological defects. Such coupling is an important aspect in our studies as discussed below. This tangential anchoring induces distortion of the nematic director field, creating two surface point defects called “boojums” which are seen clearly under polarizing optical microscopy (Fig 6.2.b) and are schematically visualized in Figure 6.2.c.

When rotating the applied magnetic field \( \mathbf{H} \) in a counter-clockwise (CCW) direction, as indicated by the brown arrows on the top left of Figure 6.2.d, the SPMB tends to “barrel roll” out of the x-y plane as shown by the blue arrows. This barrel roll induces a “walking” motion of the SPMB along the x-axis which is accompanied by a precession of one of the boojums around the boojum-to-boojum colloid axis (2 in the inset of Fig. 6.2.d.), while the other boojum (1 in the inset of Fig. 6.2.d) usually circumscribes a smaller precessional arc. A constant net magnetic gradient force dominates SPMB motion in the y-direction, but motion along the x-direction originates from the complex barrel-roll motion of the particle with two boojums. Thus, by
rotational magnetic manipulation alone one can cause a SPMB to translate orthogonal to the far field director in an NLC.

6.3. Results

6.3.1 Dynamics of nematic based colloids in rotating magnetic fields

We assembled SPMBs into a “dimer” configuration in a 5CB NLC sample infused in a 60 μm thick, planar rubbed cell. Temperature of the sample was controlled via an objective heater between 25 °C and 33 °C, or “room temperature” and “high temperature” respectively. We applied a slowly rotating (0.01 Hz, to 0.05 Hz) ac magnetic field in the sample x-y plane, and imaged the resulting dimer rotation under polarizing optical microscopy (POM) at 60 to 500 fps. A detailed characterization of the ensuing motion is shown in Figure 6.3.
Fig. 6.3. SPMB and boojum angular motion with respect to the SPMB dimer center of mass at two different temperatures. A magnetic field is rotated at a constant rate of 0.05 Hz clockwise in the x-y plane thus rotating a SPMB dimer. (a) Colloid and boojum motion at a room temperature (26 °C). Inset shows a configuration of a SPMB dimer with each SPMB center of mass and each boojum designated as follows: Left SPMB (S1), right SPMB (S2) and each boojum assigned to its SPMB. For example S2B2 is the right SPMB, 2\textsuperscript{nd} boojum (lower right boojum). The second inset shows boojums aligned along the far-field director. The figure shows all colloid and boojum rotational motion with respect to time using the dimer center of mass as the reference frame and are labeled at the right of the plot. (b) Colloid and boojum motion at 33 °C.

We designated/marked the particles and associated boojums as seen in Figure 6.3.a (inset), with S1 and S2 being the left initial SPMB and the right initial SPMB, respectively. Each boojum was designated as B1 and B2 for the initial top and bottom boojums, respectively. The subsequent angular motions (with respect to the dimer center of mass) of these six points are plotted as a function of time at an $\textbf{H}$-field rotation frequency of 0.05 Hz at room temperature.
Interestingly, there is a periodic structure in the rotation of the SPMBs (S1, S2) that is caused by the competition between elastic and magnetic torques and related to a so-called “flip-flop” motion of the dimer. This motion is characterized in Figure 6.4 in terms of the dimer rotation with respect to the far-field director.

A dimer undergoing magnetic rotation “lags” the applied field $\mathbf{H}$ during certain critical points every $180^\circ$ of dimer/field rotation. These points correspond to regions of highest elastic free energy of distortion (and elastic torque) as the dimer is rotated far from its natural alignment with respect to the NLC far-field director. As the dimer is rotated in the CCW sense (Fig. 6.4. a-
g), we note that the pair starts to “flip” +180° through the x-y plane. This is prompted by the reduction of the elastic free energy as the dimer escapes the x-y plane and rotates on an imaginary cone to a lower-energy orientation state. This “flip” occurs during the first 180°, and is completely reversible via the so-called “flop” motion, a -180° through the x-y plane during the second 180° in plane rotation (Fig. 6.4 h). This “flip-flop” motion happens once during every 360° in-plane rotation of the field, with each flip and flop happening during the “lag” of the dimer rotation with the applied magnetic field. We note (Fig. 6.3.b) that this “lagging” is reduced at temperatures significantly above room temperature, and in fact disappears completely as the NLC transitions to isotropic at T_c. This is natural as the NLC elastic structure’s effect on colloid motion is removed when the LC transitions to an isotropic liquid.

6.3.2 Dynamics of boojums on rotating colloidal microspheres

Interestingly, rotation of the dimer pair leads to an unexpected “slipping” of boojums along the surface of each colloid. This presents itself as a series of jumps in the angular positions of the boojums (B1 and B2) with respect to the dimer center of mass. These so-called “boojum slips” are indicated in Fig 6.3.a-b but are not obvious due to scale. To quantify these fascinating dynamics, we measured the motion of boojums at two temperatures, 26 °C and 33 °C, and at three different rotational frequencies (0.01, 0.02 and 0.05 Hz), all in the counter-clockwise rotational direction. Representative motion at 0.02 Hz is shown in Figs. 6.5 and 6.6 (for data taken at 26 °C and 33 °C, respectively), with each SPMB and boojum designated as discussed above.
Fig. 6.5. SPMB and boojum angular motion with respect to the SPMB dimer center of mass at room temperature. A magnetic field is rotated at a constant rate of 0.02 Hz clockwise in the x-y plane, thus rotating the SPMB dimer. (a) Colloid and boojum motion at room temperature. Inset shows a configuration of the SPMB dimer with each SPMB center of mass and each boojum designated as follows: Left SPMB (S1), right SPMB (S2) and each boojum assigned to its SPMB. For example S2B1 is the right SPMB, 2nd boojum (lower right boojum). The figure shows all particle and boojum rotational motions with respect to time using the dimer center of mass as the reference frame and are labeled on the right-side of the plot. The boojum slipping is apparent. (b) Details of S1 boojum motion with respect to the SPMB center of mass reference frame. Top and bottom curves (black and red) correspond to the first and second boojums, respectively. Sharp jumps indicate “boojum slipping.” (c) Details of the S2 boojum motion with respect to the SPMB center of mass reference frame. Top and bottom curves (green and blue) correspond to the first and second boojums, respectively.
Within the used range of rotation rates and temperatures, the rotation at 0.02 Hz produces the clearest “stick-slip” motion of the boojum along the SPMB surface. At this rotation rate, slips are easily distinguished (Fig. 6.4.a). One can easily observe the slipping when the data are
presented using the given SPMB’s center of mass reference frame (Fig. 6.4.b-c). We note that temperature plays a crucial role in not only the frequency of slip occurrences, but also in the slip amplitude. At 26 °C the slips occur at a low and random frequency, with large amplitudes of approximately 5-20°. As seen in Figure 6.5.b-c, these slips tend to happen at ~ ± 120 °, which corresponds to a boojum deflection of ~ ± 30 ° from the far field director. This makes sense from the standpoint of elastic distortion of the local director field. As the dimer rotates, energy is “loaded” into the director structure due to the elastic deformation. The surface anchoring and easy axis pinning on the SPMB surface are able to withstand this elastic distortion to a point, at which the system must re-minimize its elastic and surface anchoring free energy. This can occur through several kinetic pathways, such as the so-called “flip-flop” motion described previously in Fig. 6.4 or through slipping of the pinned surface anchoring inherent with each boojum. This resistance to slipping can be thought of in terms of a potential barrier landscape, with molecular pinning and surface anchoring determining the potential barrier height to slip motion.

### 6.3.3 Effects of temperature

When the temperature of the sample is raised to 33 °C, we note that the frequency of slips is increased significantly (Fig 6.6. b-c), while the amplitude is commensurately reduced. High temperature slips tend to occur at angles of around ± 95°, which is ± 5° from the far-field director. Again, this makes sense from the standpoint of view of this potential barrier. Since the slipping process is determined by the strength of the surface pinning, a raise in temperature lowers the energy of the barrier. Additionally, the dimer does not have to first elastically distort the director field as much and subsequently “slip” the boojum. By plotting angular motion vs. time for all observed boojums at room temperature and at 33 °C as well as at frequencies ranging
from 0.01 to 0.05 Hz, we can comparatively characterize the key features of the boojum’s stick-slip motion at these different experimental conditions (Figs. 6.7 & 6.8).

Fig. 6.7. Boojum angular motion with respect to SPMB’s center of mass at room temperature. Inset image in (a-d) indicates the SPMBs boojum that is tracked, for a total of four plots. Each line indicates a different speed of dimer rotation; 0.01 Hz (black), 0.02 Hz (red), and 0.05 Hz (green). Note that boojum slipping period and amplitude is dependent on the rotation rate.
Fig. 6.8. Boojum angular motion with respect to its SPMB’s center of mass at a temperature of 33 °C. The inset image in (a-d) indicates the tracked boojums for a total of four plots. Each line indicates a different speed of dimer rotation; 0.01 Hz (black), 0.02 Hz (red), and 0.05 Hz (green). Boojum slipping period and amplitude are dependent on the rotation rate and temperature.

Interestingly, as the temperature of the NLC is raised closer to its nematic-isotropic transition temperature, the “flip-flop” motion of the dimer is greatly reduced to the point where each “flip” and “flop” turns the dimer over by much less than 180°. The dimer flip-flops happens due to this motion being the most efficient pathway to minimize the elastic and surface anchoring free energy of the local distorted director field as the particles are rotated. However, as the temperature of the NLC is increased, boojum slipping becomes more likely and frequent, and thus the observed re-arrangement of defects becomes a competing pathway to minimize the
elastic free energy of deformation under these conditions. A “boojum avoidance” scenario, prompted by the fact that topologically like-charged boojums should mutually repel, is shown (Fig. 6.9.), where two boojums situated on different SPMBs of the dimer are forced to approach each other during dimer rotation. In Fig.6.9 (b, c and d) we note that the boojums move to appear on opposite sides of the crossover. More study is needed to explore details of this process.

![Fig. 6.9. A model depicting boojum kinetics at high temperature associated with a reconfiguration of boojums. (a) A pair of boojums is designated, and a visual plane is designated. (b) As the dimer is rotated counterclockwise the marked boojums approach each other on the projection plane as well as physically. (b) At a room temperature, the primary way to reduce elastic free energy is for the dimer to “escape” by executing a “flip flop”, but no such motion is observed at a higher temperature of 33 °C. (c-d, bottom.)](image)

The dynamics of a boojum slip at a time scale of 60 fps is much too rapid to accurately quantify and as such we filmed a boojum slip event at a temperature of 33 °C using a high speed camera operating at 500 fps (Fig. 6.10.) We were able to obtain enough data points to observe a generally sigmoidal behavior of the slip (Fig. 6.10.a), which is given by
\[ \theta(t) = \theta_0 \frac{1}{1 + e^{-t/\tau}} \]  \hspace{1cm} (6.3)

where \( \tau \) is the time constant and \( \theta_0 \) is the initial angle prior to slip. A sigmoidal response is an identifying characteristic of stick-slip behavior in general [6-7]. By subtracting the steady state change in angle with respect to time from the sigmoidal response, we are able to better quantify the slip motion.
Fig. 6.10. Detailed analysis of one of the boojum “slips” using a high-speed camera video taken at 500 fps. (a) Slipping motion with respect to the dimer center of mass, with a sigmoidal fit (blue line) of time constant $\tau_s \sim 0.0036$ s (fitting with $R^2 = 0.995$) (b) Slipping motion with respect to dimer center of mass with constant change of angle with respect to time subtracted and exhibiting a sigmoidal (red line) fit of $\tau_s \sim 0.0034$ s (fitting with $R^2 = 0.987$) and exponential (green line) $\tau_e \sim 0.0012$ s (fitting with $R^2 = 0.946$).

The studied in details boojum slip occurs over a period of approximately 25-30 ms (Fig. 6.10.a) and has, in this instance, an amplitude of the jump-like motion of approximately 15° with respect to the far-field director and a sigmoidal fit (blue line), yielding the time constant $\tau_s \sim 0.0036$ s. By compensating for the background constant-rate change of angle with respect to time (Fig. 6.10.b), a sigmoidal (red line) fit yields $\tau_s \sim 0.0034$ s and the much worse exponential fit (green line) yields $\tau_e \sim 0.0012$ s. This indicates that the slip is sigmoidal and is a salient feature of a stick-slip motion.

6.4. Conclusions

We have observed surface point defect motion along colloid surfaces in uniformly aligned nematic liquid crystals. This motion is prompted by a competition of non-degenerate surface anchoring “with memory” and elastic and magnetic torques rotating superparamagnetic colloidal spheres. Analysis of this motion indicates a strongly sigmoidal response, indicative of true stick-slip behavior. We have also demonstrated related unusual translational dynamics of spherical superparamagnetic particles occurring as a result of their rotational motion and elastic coupling to the director field of the surrounding LC.

6.5. References


Chapter 7

Particle-stabilized twisted solitons in chiral nematics

Adapted from: Nature Physics (under draft)*

Chapter Overview

Metastable patterns formed by defects, inclusions, elastic deformations and topological solitons in liquid crystals, are a promising choice for building photonic crystals and metamaterials with a potential for new applications in the optical range. A moderately chiral nematic in a thin homeotropic cell can exist in a metastable state with homogeneous director field. By disturbing the director optically or by introducing colloidal inclusions, localized chiral solitons can be created in the sample. We induce the solitons by dispersing spherical particles with planar degenerate surface anchoring, and manipulate their state using focused optical beams. Two optically distinct metastable states with different topology are found and further investigated using Q tensor based numerical simulations to review the properties of the structures. We compare the reconstructed profiles with experimentally obtained images, and review the topological mechanism of the observed bistability.

7.1. Introduction

Among the principal advantages of soft matter over the solid state materials are their reconfigurability, possibility of self-assembly and self-healing, and strong response to external

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stimuli, which enables efficient control over their internal structure. While soft biological systems already excel in versatility and scalability, artificial soft matter is still in the phase of discovery of new applications, assembly and manipulation techniques, and viable materials. Liquid crystals and their composites are, due to their optical anisotropy and simplicity of manipulation, a common choice for creation of micro devices, photonic elements [5, 6] and sensors [1-4].

In nematic liquid crystals, molecules align along a local preferred direction called the director. The director $\mathbf{N}(r)$, which is a vector-like quantity without distinction between diametrically opposite directions (headless vector), forms point-like and line-like topologically stable defects, especially when boundary conditions disallow a defect free state [11, 12, 23]. In a cholesteric liquid crystal, the director field prefers to helically twist along a certain direction. Introduced in a cell with homeotropic anchoring at the boundaries, the helical structure is hindered by boundary conditions that prefer a homogeneous director field. When the cholesteric pitch is comparable to the cell thickness, we obtain a borderline frustrated environment where localized chiral excitations can be created and erased by manipulation with focused laser beams [13] and external electric field. This led to discovery of torons [8] and hopfions (Hopf fibrations in the director field) [14] which, once created, behave as quasi-particles that are stable under small perturbations. Unlike the point and line defects, standalone torons and hopfions owe their topological stability to entanglement of the entire nematic texture, not just the cross section in the vicinity of the singular regions. While having individual stable solitons is interesting both from theoretical as well as applied scientific standpoint, inclusion of particles fuses the topological versatility of solitons with the structural potential of colloidal lattices. This opens a great variety of particle/soliton bound states to explore.
In this work, we present the structure and manipulation of topological solitons in a homeotropic chiral nematic cell with the gap of $d = 10 \, \mu\text{m}$, anchored to dispersed microparticles. The particles are Melamine resin microspheres with diameter $D = 7 \, \mu\text{m}$ and tangential surface anchoring. Although these boundary conditions force the host molecules to align uniformly similar to NLCs, a complex director configuration is formed around the microparticles due to the host medium’s chirality (see Figure 7.1). In a certain range of thickness over equilibrium cholesteric pitch values (0:8 to 0:95), we observe that particles are “dressed” by well-defined twisted director configurations, which significantly alter interparticle interactions and response to stimulation with light.

Fig. 7.1. POM micrographs of microsphere-soliton hybrids in frustrated cholesteric LCs. (a-b) POM micrographs obtained for two different levels of the microscope’s focal plane (a), above and (b), below the cell midplane. The structures are (from left to right): A colloidal microsphere with boojums surrounded by minor distortions, a triple twist toron stabilized by the material’s chiral nature and two bulk point defects, a toron dressed microsphere and a hopfion dressed microsphere. (c) Two hopfion dressed microspheres at different levels of the sample. (d) A hopfion dressed microsphere that is in the midplane of the sample. (d) A toron in a 5CB-based CLC with a colloidal sphere having its center co-located with the looped axis of the double-twist cylinder of the toron.
From polarized light and bright field images (see Fig. 7.1a, g), we identify two types of bound states of solitons and particles. They differ in the streaks in the optical micrograph that twist clockwise and anticlockwise around the colloidal beads. We observe the director with the use of 3PEF-PM, which retrieves the angle of the local director relative to the light polarization. Combining the data at 4 different polarizations allows one to reconstruct the details of complex three dimensional director fields. We also used a circularly polarized excitation beam to further distinguish the structures according to where the director aligns predominantly in a horizontal direction (see Fig. 7.1b, h). Both the bright field images and the 3PEF-PM cross section resemble the looped double twist tubes seen in freestanding torons and hopfions [8, 14], which exist because frustration of a cholesteric in a homeotropic cell causes a lack of twist that strives to be at least locally released.

To confirm the validity of the reconstructed director, both states were reproduced with Landau deGennes numerical simulation. The study shows great agreement with the 3PEFPM data. We constructed a chiral nematic cell of dimensions $6 \, \mu\text{m} \times 6 \, \mu\text{m} \times 3 \, \mu\text{m}$ with a spherical particle inside, with diameter half of the cell thickness. Initial condition was constructed to resemble the experimental data. A double twist cylinder was imposed into torus shape to construct initial condition for toron structures [8]. Relaxation method was used to find global or local free energy minima at a certain particle position [16, 17]. The vertical position of the particle was adjusted to reach the true free energy minimum of the equilibrium state. Numerical and experimental results for both metastable structures were visualized by using the Pontryagin-Thom surface [14, 15] and iso-surfaces of the magnitude of director projection to two orthogonal horizontal directions (Fig. 7.1). Even considering a finite resolution and noise in the
experimental data, the structures show a qualitative agreement, confirming our reconstruction of the director.

A particle with planar degenerate anchoring by itself requires existence of surface defects, which manifest as boojums at the poles of the particle [23]. Both structures that we observed retain cylindrical symmetry and have two boojums at the poles, but break the chiral symmetry by having the director turn in plane on the particle surface instead of pointing along the meridians. The structure in Fig. 7.1 a-f has one small ring defect in bulk and resembles the toron structure with one of the defects replaced by a spherical particle. Following the surface from the bottom to the top pole, the director makes a $\pi$-turn in plane. In contrast, the structure in Fig. 7.1 g-l does not have any bulk defects and resembles the Hopf fibration (hopfion) soliton structure [14]. The director takes two opposite turns on the particle surface, amounting to a zero total turning angle, and is thus distorted, but topologically equivalent to the structure expected in achiral nematic.

The difference in the number of point defects in the bulk suggests the particle with its boojums carries a different charge in both structures, which deserves a quick digression into the topology of the textures. The director field on a sphere (or any surface, topologically equivalent to a sphere) with degenerate planar anchoring cannot exist without surface boojums. The degenerate planar alignment makes the director locally two-dimensional and the strength of the boojums is measured by their winding number. The sum of the winding numbers of all boojums equals 2 by the Poincare field theorem [18], which in our experiments and simulations is fulfilled by a pair of surface boojums with winding number 1.

The colloidal particle, together with both boojums, can be assigned a topological charge assuming that the director is consistently decorated with arrows to obtain a true vector field.
Following a similar procedure that was used to analyze the topology of spherical droplets in Ref. [18], we can cut the surface into two infinitesimally small circular patches around the boojums, and the rest of the surface, which contributes nothing to the topological charge. At the boojums, the director rapidly turns from parallel to perpendicular orientation relative to the surface. Each surface boojum contributes $\pm 1/2$ to the topological charge: the sign is positive if the director points outwards at the tip of the boojum and vice versa. This can be deduced from the fact that the director at the boojum covers exactly half of the unit sphere, as in [18]. The total topological charge of the particles and its surface boojums thus only depends on the director at the boojums facing inward or outward. Possible values are $q = 0$ and $q = \pm 1$, where the sign depends on director's arrow.

The only degree of freedom between the boojums is the in plane rotation of the director with changing polar angle (latitude), which can amount to any integer number of turns. Zero turns corresponds to the planar particle in an achiral nematic, which is known to have a zero topological charge, $q = 0$ (Fig. 7.2c). With increasing number of turns, the topological charge of these hypothetical structures alternates between $|q| = 1$ and $q = 0$ (Fig. 7.2d, e). The number of turns is easily determined by counting the latitudes where the director points in a horizontal (east-west) direction, taking into account the sense of director rotation. In the hopfion structure, the director is turning back and forth to accommodate the soliton around the particle, but amounts to zero total turns and thus has zero topological charge with no additional defects required (Fig. 7.2b). The toron structure (Fig. 7.2a) has one turn and therefore topological charge $q = \pm 1$, which explains the additional hyperbolic hedgehog in the bulk.

Unlike the achiral nematic, where the distortions tend to be localized around the particle, the deformation of the field extends more than a diameter away from the particle. From our
experiment, we can conclude that the presence of the particle with a planar anchoring binds and stabilizes the position of the soliton, but does not alter the integrity of its texture or its optical signature (Fig. 7.1). The switching between both structures with optical tweezers corresponds to switching between torons and hopfions [14], but with more control and reliability. Controlled creation and annihilation of an extra point defect is a bi-stable process, a desirable component in display and memory devices.

Fig. 7.2. Metastable twisted textures around colloidal particles with degenerate planar surface anchoring. (a, b, e, f) A structure, recognized as a toron, bound to a colloidal particle. (c, d, g, h) A hopfion, bound to a colloidal particle. Viewed between crossed polarizers (a, c), the structures swirl in opposite directions. A cross section with circularly polarized 3PEFPM (b, d) reveal existence of point defect only for the toron structure. (e, f, g, h) show the regions of maximum intensity of linearly polarized 3PEFPM signal for two perpendicular polarizations, extracted from numerical modeling and experiments. Notice that the toron structure has a detached defect (e, f), while the hopfion has just a surface boojum (g, h).

The particle-stabilized solitons extend the set of manipulable objects in frustrated cholesteric liquid crystal. Allowing multiple particles and quasi-particles to interact in the medium opens new possibilities for self-assembly and targeted assembly of superstructures with optical applications. The particles contribute their tendency to form lattices and act as a way of pinning the solitons, which contrasts to standalone solitons, which behave as unbound particles
and are free to move around the sample. Coexistence of both bound and free quasi-particles suggests composite materials and devices based on transport of the solitons in a custom built environment, possibly driven by flow. If the particle size and anchoring is varied as well, the properties can be fine-tuned to fit the design in mind.

7.2. Methods

The chiral nematic liquid crystal (CNLC) host is prepared by introducing chiral additive S811 to a commercial nematic LC, namely AMLC-0010. The LC host and the chiral dopant were provided by Alphamicron, Inc. and used as supplied. The value of the pitch \( p = 1/(h_{HTP} \times C_{\text{chiral}}) \) of the CNLC of interest is selected by choosing an appropriate concentration \( C_{\text{chiral}} \) of the chiral dopant in the nematic host for the known value of the so called “helical twisting power” \( h_{HTP} \). We use Melamine resin microparticles of diameter ~ 7 µm with tangential surface anchoring. The mixture of CNLCs and microparticles was sonicated for 10 h to get a uniform distribution of colloidal particles. LC cells are enclosed between glass plates. Strong vertical surface alignment on the inner surfaces of the confining glass plates is set by treating these substrates with N,N-dimethyl-n-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP) by means of dip-coating in a 1wt% aqueous solution. LC cells with the cell gap thickness \( d = 10 \) µm are produced by sandwiching glass substrates interspaced by glass fiber segments of corresponding diameter. CNLCs colloidal dispersions are then introduced into the cell of thickness less than the pitch of CNLCs by capillary forces at room temperature. We seal the cell with epoxy.

Optical manipulation and 3D imaging was performed with a setup composed of holographic optical tweezers (HOT) and three photon excitation fluorescence polarizing
microscopy (3PEF-PM) built around an inverted microscope IX 81 (Olympus). HOT utilized a reactive, phase-only spatial light modulator (SLM) obtained from Boulder Nonlinear Systems and an Ytterbium doped fiber laser (YLR-10-1064, IPG Photonics) operating at 1064 nm. The SLM controlled the phase of the laser beam on a pixel by pixel basis according to the computer generated holographic patterns at a refresh rate of 30 Hz. This phase modulated beam was imaged at the back aperture of the microscope objective while creating the spatial trap intensity pattern in a sample. For 3PEF-PM imaging, we have employed a tunable (680-1080 nm) Ti-Sapphire oscillator (Chameleon Ultra II, Coherent) emitting 140 fs pulses at a repetition rate of 80MHz. The laser wavelength was tuned to 870nm for the three photon excitation of 5CB molecules. The 3PEF-PM signal was collected in epidetection mode with a photomultiplier tube (H5784-20, Hamamatsu). An Olympus 100x oil immersion objective with high numerical aperture of 1:4 was used for both imaging and optical trapping.
Fig. 7.3. Topological analysis of director field textures. (a, b) Numerically obtained structures, visualized with the splay-bend parameter. Similarly to experiments, both structures are found to be (meta)stable: (a) toron structure with one point defect in bulk and one turn of the director on particle surface and (b) Hopf structure without bulk defects with two opposite turns on the particle surface. In-plane turns on the particle surfaces are counted by marking the horizontal (quarter turn) position with a red (clockwise) or green (anticlockwise) dashed line. (c, e) Theoretical evaluation reveals that only the boojums contribute to the topological charge $q$ of the whole, so the charge only depends on the arrow directions at the boojums. Compare (a) to (d). The structures can be roughly characterized by counting the number of latitudes with horizontal director field marked by red arrows. Note that (b) consists of two opposite turns and is thus topologically equal to the structure (c), not (e).
Computer simulations of CNLC medium use the extended Landau deGennes free energy [10]. In one elastic constant approximation, distortion free energy is expanded in powers of order parameter tensor $Q_{ij}$ and its first derivatives (See Ref. [16, 17]). As a model for the experiment degenerate planar anchoring on particle surface is ensured through construction by Fournier and Galatola. Surface of the particles is modelled as a shell of mesh points with the thickness of mesh resolution. The material constants are taken from [17], and strong degenerate planar anchoring of $W_d = 10^{-3} \text{ J m}^{-3}$ is used to model colloidal surfaces. Boundaries of homeotropic cell are fixed. Pitch was equal to cell thickness. Mesh resolution is 10 nm.

7.3. **Topologically neutral and charged nematic fields on colloidal spheres in contact with twisted solitons**

We identify solitonic nematic field configurations that are stabilized by the medium’s chirality and localized around colloidal microspheres. From polarizing optical microscopy (POM) textures, we demonstrate multistable optical switching and manipulation of these hybrid structures. Using optical manipulation of the LC director field and three dimensional (3D) imaging techniques, we gain insight into the confined hybrid system’s surface and bulk topology. Predictably, the 2D topology of the microsphere surface field is bound to the 3D field topology of the surrounding soliton. Multistable twisted solitons that arise due to the interplay of confinement and chirality can be optically controlled and manipulated.

In Figure 7.3 we show co-existence several structural states in a confined chiral nematic, comprised of different combinations of spherical particles, torons, hopfions, and bulk and surface point defects. POM micrographs for different depth location of the microscope’s focal plane (Fig.
7.3 a, b) demonstrate co-existence of, from left to right, (1) a bare microsphere inducing two boojums and weak distortions of the surrounding LC, (2) a toron [ref 8], (3) a toron-dressed microsphere with one bulk and two surface point defects and, (4) a hopfion-dressed microsphere with two boojums. The prominent swirls seen in POM textures arise due to broken symmetry about the cell mid-plane. The hybrid structure is identical for opposite swirls but flipped top for bottom (Fig. 7.3c). Hopfion dressed microspheres with “swirls” in Fig. 7.3c indicate that the microsphere is above or below the mid-plane of the cell and the amount of twisted LC above and below the microsphere is unequal. The toron-dressed microsphere is always observed with swirls due to its inherent asymmetry, however, the hopfion dressed microsphere can be both symmetric (Fig. 7.3d) and asymmetric (Fig. 7.3 a-c) with respect to cell mid-plane. A hopfion-dressed microsphere without “swirls” occurs when the microsphere is centered in the cell mid-plane. This experimentally less common hybrid structure forms in a thicker region of the cell ~11µm. When the particle size is reduced even further relative to the cell thickness and cholesteric pitch p (p/2 or smaller), one often also observes the microspheres localize on the axis of looped double twist cylinder (Fig. 7.3e). Using superparamagnetic particles rotated by rotating magnetic fields, we observed that the studied solitonic structures are all stable with respect to particle rotation, although this rotation in the case of the structure shown in Fig. 7.3e results in its orbital motion along the looped axis of the double twist cylinder (Fig. 7.5).

We demonstrate optical switching and manipulation of the microsphere-soliton hybrids. Focusing a laser beam in the cell mid-plane nearby the particle with different polarizations allows for inducing transformations (1) of the bare microsphere with boojums into a hopfion-dressed state (Fig. 7.5a-d), of the hopfion-dressed sphere back to the original state of the bare microsphere and again back to hopfion-dressed sphere (Fig. 7.5e-h), and so on. Although
boojums attached to microspheres could not be optically manipulated as individual objects, however, the bulk point defect of the toron-dressed microsphere could be manipulated individually (Fig. 7.5i-l).

Fig. 7.4. Optical switching and manipulation of microsphere-soliton hybrids. Images with a blue double-sided arrow approximately indicate where and when the laser was turned on or off and polarization orientation. Lower right numbers indicate the time corresponding to the elapsed time in supporting movies. (a-d) A laser induced hopfion surrounding a microsphere. (a) A bare microsphere surrounded by minor distortions (b) moments after the laser was introduced to the sample (c) the hopfion structure fully formed and (d) after the laser is removed and the structure is fully relaxed. (e-h) Optical switching of a hopfion-dressed microsphere. (e) The initial hopfion dressed microsphere switched to (f), a bare microsphere with a laser induced distortion that has opposing twist. (g) The hopfion induced again with the same laser position but with opposite twist. h, the final configuration after laser is removed. (i-l) A toron-dressed microsphere’s bulk point defect manipulated with a laser. (i) The initial toron dressed microsphere. (j) After pulling the hyperbolic hedgehog of the toron structure away from the microsphere. After removing the laser k, the bulk defect begins to return to the microsphere. (l) The final relaxed configuration.
7.4. Magnetically induced dynamics of colloids within torons

The colloids are superparamagnetic beads (SPMBs) (Dynabead M450, obtained from Invitrogen) with a nominal diameter of 4.5 ± 0.1 µm, which are fabricated using ferromagnetic nanoparticles (γ Fe₂O₃ and Fe₃O₄) approximately 8 nm in diameter and embedded into a highly cross-linked epoxy at a density of ~ 10⁵ nanoparticles per bead. The ferrite nanoparticle orientations are mechanically coupled to the epoxy of the SPMB microsphere, and magnetic interactions with the applied field prompt transient SPMB rotation and alignment of the net induced magnetic moment \( m \) to eventually point along an applied magnetic field \( \mathbf{H} \). The ensuing torque on the epoxy matrix physically aligns the SPMB such that its net magnetic moment locks to be collinear with \( \mathbf{H} \).

In addition to AMLC-0001, we use a commercial single-compound nematic LC pentylycyanobiphenyl (5CB, obtained from Frinton Laboratories). Cholesteric LC hosts are formed using one of these nematics doped with a small volume fraction of chiral agent (cholesteryl pelargonate obtained from Sigma-Aldrich Chemistry) to obtain chiral nematics with a cholesteric pitch in the range of 5–30 µm. All colloidal particles are dispersed in an LC host via either solvent exchange or sedimentation mixing with both methods yielding comparable dispersion efficiencies [S1]. Cells are constructed from glass slide substrates with homeotropic alignment using dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride (DMAOP obtained from Arcos Organics). The substrates are assembled in a wedge cell configuration with cell thickness typically set using spherical spacers dispersed in a UV curable epoxy (NOA-61, obtained from Norland Products) and varies from 5 to 30 µm, depending on the system under
study. An LC host is infused into these cells via capillary forces and, subsequently, is sealed with fast setting epoxy.

To rotationally manipulate the superparamagnetic beads described above we use a robust method for magnetic and optical “tweezing” in a fully holonomic manner, i.e., in all three Cartesian degrees of freedom via holographic optical tweezers and in all three rotational degrees of freedom via magnetic control. Magnetic manipulation is achieved using three iron-core electromagnets arranged in a Cartesian frame machined from aluminum and mounted directly on the microscope body. Each electromagnet is independently driven via an amplified power supply controlled using a computer-controlled data acquisition and in-house software. Each electromagnet can produce ac (up to 8 Hz) and/or dc magnetic fields up to 40 Gs as measured at the sample by a Gauss meter. This field affects all magnetic particles in the sample volume and, thus, is appropriate for manipulation of multiple particles in a similar way simultaneously rather than manipulation of single colloids on an individual basis.

Figure 7.5 shows a superparamagnetic colloidal particle with tangential surface anchoring embedded in a toron so that its center of mass roughly considers with the axis of a looped double twist cylinder.
Fig. 7.5. Superparamagnetic bead (SPMB) motion within a toron induced by rotational magnetic field. (a) A SPMB (highlighted with a green dot) embedded within the double twist cylinder of a toron (center of mass denoted by a red dot.) (b) Motional tracks of the SPMB and toron center of mass (green and red respectively) shows an orbital pattern around a colloid/toron barycenter. (c) Computer simulation of a SPMB with polar planar alignment and anchor memory effect situated within the double twist cylinder. (d) Motional analysis of the SPMB “orbiting” the toron center of mass reference frame. SPMB radius and angle with respect to time (black and green lines respectively) as referenced to the toron center of mass. The red line represents the angle of the magnetic field which rotates at 45 °/s. Average orbital radius is 5.1 μm for clockwise orbit, and 5.6 μm for a counterclockwise orbit. The magenta dotted line represents the equilibrium position of the SPMB when it is not being acted on by the rotating magnetic field. Periodic oscillations of this orbital radius is evident. The average angular velocity for CW₁ is -57 °/s, for CW₂; 45 °/s, and for CW₃ is -53 °/s. (e) Orbital polar angle vs. time indicating asymmetry in orbital angular velocity and period depending on field rotation direction. Note period and slope differences.

The SPMB was optically co-located within the double twist cylinder of a toron, which can be stable or metastable position of such a particle with respect to a toron or hopfion, depending on the relative size of the particle with respect to the size of the toron. When the particle is smaller than half of the size of troron, we find that the location of a particle within the double twist cylinder is at least metastable state, but often a ground state. A 40 Gs magnetic field rotating at 0.125 Hz was applied in the x-y plane to rotate the SPMB [S1], which when coupled via surface interactions with the local director induces a so called “orbital” motion around the toron/SPMB barycenter. The orbital motion is in the same sense as the rotating magnetic field.

Figure 7.6d shows this orbital motion with respect to the toron center of mass reference frame. SPMB radius and angle vary with time (black and green lines respectively) as referenced to the toron center of mass. The red line represents the angle of the magnetic field which rotates at ±45 °/s. Average orbital radius is 5.1 μm for clockwise orbit, and 5.6 μm for a counterclockwise orbit. The magenta dotted line represents the equilibrium position of the SPMB when it is not being acted on by the rotating magnetic field. Periodic oscillations of this orbital
radius is evident. The average angular velocity for CW\textsubscript{1} is -57 °/s, for CW\textsubscript{2}; 45 °/s, and for CW\textsubscript{3}
is -53 °/s. (e) Orbital polar angle vs. time indicating asymmetry in orbital angular velocity and
period depending on field rotation direction. Note period and slope differences. Rotating the
magnetic field in a CW/CCW manner allowed for stable orbital motion of the SPMB, while
rotation of the field in the opposite sense greatly increased the orbital radius, often to the extent
where the SPMB would escape the double twist cylinder of the toron. This is in line with the
observations seen in torons at a smaller pitch to SPMB diameter ratio.

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Chapter 8

Elastic interactions between colloidal particles and electrically driven periodic layer undulations in cholesteric liquid crystals

Adapted from: Physical Review E (under draft)*

Chapter overview

We study the interaction between colloidal particles and the Helfrich-Hurault undulation instability, in which a cholesteric liquid crystal confined between two parallel plates undergoes lamellar buckling under an electric field applied normal to the layers. We find that anchoring on the colloids surface prompts the nucleation of a periodic distortion lattice at electric fields below a threshold value seen in particle-free samples, and that the resulting lattice is constrained and aligned by the initial colloidal assemblies. Furthermore, subsequent magnetic rotation of superparamagnetic colloidal particles couples with the locally distorted spatially varying helical axis in a manner that allows for three-dimensional translation of the colloidal particle within the sample bulk. Shape-anisotropic colloidal GaN nanowires exhibit a preference for multi-stable azimuthal alignment defined by the undulation lattice. These findings lend insight to the physics of structure/colloid interaction, as well as reveal the potential of guided self-assembly of reconfigurable colloidal composites with applications in diffraction optics and photonics.

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8.1. Introduction

Liquid crystals (LCs) [1,2], including nematic, cholesteric, smectic and various more exotic thermodynamic phases, such as blue phases, recently became popular fluid host media for colloidal particle assembly and alignment [3-25]. As compared to isotropic fluid hosts, they bring many new possibilities in designing guided colloidal self-assembly arising from elasticity-mediated anisotropic interactions [3], nanoparticle localization by topological defects [19], and structural switching enabled by the LC’s facile response to external fields [10]. However, the main focus of these studies on LC colloidal dispersions was mostly on using ground-state phases or topological defect arrays to mediate self-assembly. Despite a large number of mesomorphic phases with different symmetries and combinations of partial positional and orientational ordering, the available means of using these structured media in positioning, aligning, and assembling nano- and micro-sized particles are still limited. In particular, one fundamental limitation is related to an inability to control periodic localization of particles in these media so that they can reversibly form periodic lattices in response to electric fields or other external stimuli.

In this work, we demonstrate the use of electrically driven cholesteric layer undulations [1, 26-29] to localize, align, and pattern colloidal particle assemblies within a cholesteric LC host medium. Since the helicoidal structure of these LCs is featured only in one direction, cholesterics possess layer periodicity equal to half of a cholesteric pitch \( p \) (distance along the helical axis along which the molecules, and the director \( \mathbf{n(r)} \) describing their local average orientation, twist by 360°) [1, 26, 30]. These media possess
many properties characteristic of lamellar phases [26, 30], since layers tend to preserve equidistance while easily bending in response to external stimuli and boundary conditions [1]. The morphology of layer configurations that satisfy these constraints is rich and includes dislocations [1, 2], disclinations [26], focal conic domains [1], undulations [26-29], etc. The latter is the most studied type of structural instability of equidistant layers that does not alter topology of the uniform ground state, also known as buckling of layers and the Helfrich-Hurault effect [26-29]. When an electric field is applied across and normal to the cholesteric layers of a material with a positive dielectric anisotropy, the layers tend to reorient parallel to the field [27-29], but completely free rotation is hindered by surface anchoring forces at confining surfaces. This results in periodic patterns of undulating layers, with the periodicity dependent on sample thickness and equilibrium pitch and the amplitude being tunable by the applied voltage above a certain well defined threshold [27-29].

Using laser tweezers, we manipulate colloidal inclusions in three dimensions (3D) and demonstrate that particles embedded into cholesteric layers can locally reduce this voltage threshold for forming periodically distorted layered patterns. We also show that colloidal particles also interact with the host LC and periodic distortions of the cholesteric layered structure through a combination of elastic and dielectrophoretic effects. These complex interactions result in the formation of periodic potential energy landscapes capable of localizing colloidal microspheres in well-defined locations of the undulation lattices. Moreover, anisotropic colloids, such as GaN nanowires, also exhibit controllable multi-stable alignment with respect to square-periodic undulation patterns. We show that the layer undulations also impinge on the dynamics of magnetically
controlled superparamagnetic microparticles in these media. These findings are discussed from the standpoint of view of designing reconfigurable colloidal composites with potential applications in diffraction optics [31, 32], nanophotonics [19], etc.

8.2. Materials, methods, and techniques

8.2.1. Sample preparation

Our work utilizes a cholesteric LC (CLC) composed of a single-compound nematic LC host (NLC) pentylicyanobiphenyl (5CB, Frinton Laboratories) mixed with a small volume fraction of chiral agent (cholesteryl pelargonate, Sigma-Aldrich Chemistry) to produce chiral nematics with a cholesteric pitch in the range of 5–30 μm. 5CB elastic constants of bend, splay, and twist are $K_{33} = 25$ pN, $K_{11} = 17.5$ pN, and $K_{22} = 8.5$ pN, respectively. Imaging is performed through a combination of polarizing optical microscopy (POM) and 3PEF-PM that is capable of operating in both epi-detection and forward-detection (transmission) modes with the epi-detection mode being the principle configuration when performing fully holonomic manipulation. For fluorescent confocal polarizing microscopy (FCPM) imaging, our samples are doped with a miniscule amount (0.01 wt. %) of a fluorescent dye n,n’-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenedicarboximide (BTBP, Aldrich) which produces a strong fluorescence signal, but does not otherwise affect LC properties.

Our magnetically controlled colloids are superparamagnetic beads (SPMBs, Dynabead M450, Invitrogen) with a nominal diameter of $4.5 \pm 0.1$ μm, which are fabricated using ferromagnetic nanoparticles ($\gamma$ Fe$_2$O$_3$ and Fe$_3$O$_4$) ~ 8 nm in diameter and
embedded into a strongly cross-linked epoxy at a density of ~ $10^5$ nanoparticles per bead. Random physical orientation of individual ferrite nanoparticles within the epoxy matrix, coupled with thermal moment flipping in each nanoparticle, creates a zero net magnetic moment in the SPMB. When an external magnetic field $\mathbf{H}$ is applied the magnetic moment of a given ferrite nanoparticle is induced to favor one direction state along its easy axis, which may not necessarily align collinearly with $\mathbf{H}$. It should be noted that, since the ferrite nanoparticle orientations are mechanically coupled to the epoxy of the SPMB microsphere, magnetic interactions with the applied field prompt transient SPMB rotation and alignment of its net induced magnetic moment $\mathbf{m}$ to eventually point along $\mathbf{H}$. The ensuing torque on the epoxy matrix mechanically aligns the SPMB such that its net magnetic moment locks collinear to $\mathbf{H}$ [33].

In addition to superparamagnetic beads, we also use melamine resin spheres (obtained from Sigma-Aldrich Chemistry) 7 $\mu$m in diameter as well as GaN nanowires nominally 10 $\mu$m in length and 300 nm in diameter. All colloidal particles are dispersed in a CLC host via either sedimentation mixing or solvent exchange, with both methods producing comparable dispersion quality.

Sample cells are fabricated from indium tin oxide (ITO) coated glass microscope slides cleaned in water and detergent, sonicated at 60 °C, and sequentially rinsed with acetone, methanol, and IPA. The slides are then dried and plasma-cleaned. Planar alignment of the cleaned substrates is set by spin coating the substrates with either polyvinyl alcohol (PVA 1% weight-to-weight ratio) in deionized water at 8500 rpm or with polyimide PI-2555 at 7500 rpm after which they are baked for a minimum of 1 h at 100 °C. This alignment layer is subsequently rubbed with a velvet cloth, which forces the
LC molecules to align along the rubbing direction and, thus, sets planar boundary conditions for $\mathbf{n}(\mathbf{r})$. These substrates are assembled in a planar cell configuration with a director pretilt angle of $\sim 3^\circ$–$6^\circ$ and are constructed with a thickness typically set using spherical spacers dispersed in a UV curable epoxy (NOA-61, Norland Products) and which varies between 10 to 120 $\mu$m, depending on the system under study. A CLC/colloid mixture is infused into these cells via capillary forces and sealed with a fast setting epoxy.

8.3. Results and discussion

8.3.1. Mutual patterning of undulations and colloidal arrays

The helicoidal ground state structure of CLCs have been extensively studied. A feature of these systems is an orientationally periodic helicoidal structure characteristic of lamellar phases but possessing no positional ordering of the constituent molecules [26, 30]. These cholesteric layers tend to preserve an equidistance (Fig. 8.1. a-b.) and periodicity equal to half of the cholesteric pitch $p$. This periodicity can be preserved while still allowing for bending of the layers in response to boundary conditions and external stimuli [1, 26, 30]. The resulting morphology of layer configurations that satisfy these constraints provides a rich experimental “hunting ground” that includes, for the purposes of this work, periodic distortions of the cholesteric lamellae, or so called “undulations” (Fig. 8.1. c-d) [26-29].
We first explore this rich landscape by manipulating colloids, via holographic optical trapping (HOT), into various configurations (Fig. 8.2.) before inducing Helfrich-Hurault lamellar buckling. Melamine resin beads of 7 μm nominal diameter are positioned via HOT into a given configuration (Fig. 8.2. a) which is arranged such that colloid-colloid interaction does not result in agglomeration of the particles under thermal motion. Subsequently, periodic distortions are induced by applying a sinusoidal ac electric field at a frequency of 1 kHz and an amplitude of 6.5 V normal to the lamellar plane. We find that these distortions start to nucleate around the configured colloids at a voltage ~0.5 V below the critical threshold voltage required without colloidal inclusions.

Fig. 8.1. Cholesteric lamellae and their periodic distortions above the critical electric field threshold. (a) A schematic of a liquid crystal cell with electrodes. (b) Cholesteric lamellae as probed by FCPM in the vertical cross-section and by PM in the horizontal x-y plane (left and right, respectively.) (c) Schematic representation of periodic distortions above the threshold field $> E_{\text{crit}}$. (d) Periodic cholesteric “undulations” imaged by the FCPM in the vertical cross-section, and by the PM in the horizontal x-y plane (left and right images, respectively.) “P” and “A” indicate the directions of linear light polarization for the polarizer and analyzer, respectively.
(Fig. 8.2. b.) Over a time period of approximately 30 s the lattice relaxes to a ground state configuration, which remains stable in both position, dimension and orientation unless disturbed by encroaching topological defect structures, such as so-called “oily streaks.” This lattice relaxation forces the colloidal assembly to re-order accordingly. If we then switch off the electric field, the colloids re-arrange into a new configuration (Fig. 8.2. c), which often significantly differs from their initial configuration defined by use of HOT.
Fig. 8.2. Colloidal interaction with periodic distortions above the critical electric field threshold $E_{\text{crit}}$. (a) Melamine resin beads of 7 $\mu$m nominal diameter manipulated via HOT into a given configuration. (b) Helfrich-Hurault lamellar buckling is induced. (c) Post buckling configuration. (d) SPMB of 4.5 $\mu$m nominal diameter manipulated via HOT into a given configuration. (e) Helfrich-Hurault lamellar buckling is induced. (f) Post buckling configuration. (h-l) Process performed in (d-f) is repeated.

By repeating the above experimental sequence for an ensemble of SPMB arranged in various configurations (Fig. 8.2. d-l), we note that the positioning of the SPMB array reproducibly dictates the orientation and (to some extent) the initial spacing of the nucleated undulation lattice, as demonstrated in Figures 8.2 (e) and (f),
respectively. This experimental procedure also allows us to induce edge dislocations of Burgers vector equal to the lattice period (Fig. 8.2. b.) We also note limited manipulation along the normal to cell substrates, as seen from defocusing of the colloids in Fig. 8.2.i.

Dynamic, non-contact manipulation of colloids in CLC systems have provided insight into LC structure, microrheology, and the production and control of topological effects in these systems [33]. Next, we also demonstrate the effect of the cholesteric structure with undulations on non-contact magnetic control of colloids that leads to spatially translating magnetically rotated colloidal particles as a result of their strong coupling to the local helical axis. For this experiment, the Helfrich-Hurault lamellar buckling is induced in a CLC infused electrocell 60 µm thick, and a SPMB is subsequently magnetically rotated by a 105 Gs ac magnetic field at 0.25 Hz (Fig. 8.3.)

Fig. 8.3. Magnetic rotation induced spatial manipulation of SPMB in undulations. (a) A POM image of an undulation lattice showing movement of the lattice points and motion of the SPMB in the x-y plane. (b) Open and closed circles represent the top and bottom confining surfaces corresponding to the undulation boundary conditions at these surfaces,
respectively. (c) SPMB motion between confining surfaces and within the x-y plane is highlighted. (d) A schematic of a SPMB moving under CCW rotation along the distorted local helical director [red (left) dotted line] from position 1 to 2. Subsequent CW rotation translates the colloid back to position 3 [purple (right) dotted line].

During colloid rotation, undulation lattice points are observed to shift with respect to time (Fig. 8.3. a.) and we posit that this motion is a result of a combination of the natural relaxation of the lattice after nucleation, and the elastic deformation induced by rotating the SPMB. We distinguish between the top and bottom confining surfaces as indicated by closed and open circles in Figure 8.3. b. A given SPMB initially located at the top confining surface at position 1 (Fig. 8.3 c.) when rotated in a counter-clockwise (CCW) direction, translates the SPMB along the local helical director towards the bottom confining surface as dictated by the left hand chirality of the CLC. This rotations ends at position 2 in the x-y plane. Subsequent clockwise (CW) rotation of the colloid translated the SPMB back to the top confining surface at position 3 (Fig. 8.3. d.). It should be noted that due to symmetries in the undulation lattice, one should expect that there are four possible paths between the top and bottom confining surfaces for each position in the lattice and that we should expect that each path is equally likely assuming no local variance in the periodic landscape. We have observed this to generally hold true, but a limited trial sample space precludes ruling out a “memory” of previous paths taken, and therefore further exploration should be undertaken.

8.3.2. Multi-stable alignment of anisotropic colloidal particles

Due to the spherical symmetry of the SPMB and melamine resin colloids, we are unable to study certain interactions with the CLC undulation structure that may be
apparent in shape-anisotropic colloids. To explore these interactions, we manipulated a high aspect GaN nanowire (Fig. 8.4 a) of length \( L = 10 \mu \text{m} \) and \( D = 300 \text{ nm} \) with planar surface anchoring to a specified location in the mid-plane of the cell using HOT and subsequently induced the buckling instability (Fig 8.4. b.) just above a critical voltage of \( V_c = 6.8 \text{V} \).

Fig. 8.4 Undulation lattice induced multi-stable alignment of GaN nanowires. (a) GaN nanowire false color SEM showing GaN nanowire growth on a substrate. (b) POM image showing GaN nanowire alignment after a periodic undulation lattice was formed. GaN
nanowires are indicated by arrows. (c) The GaN nanowire tends to randomly align along one of 8 different “multi-stable” directions.

As observed with spherical colloids, the GaN nanowires served as a nucleation centers for the undulation lattice. We also observed a reduction of the critical voltage needed to locally nucleate these undulations by approximately 0.2 V. We noticed a weak correlation between initial nanowire orientation and the spacing or orientation of the undulation lattice, as well as a tilting of the nanowire out of the plane during lattice nucleation ranging from 20 to 30 degrees, depending on the strength of the electric field, and lying roughly orthogonal to the local helical axis at the center point of the GaN nanowire. This indicates that an important role is played by the dielectrophoretic effect that results in coupling between the electric field and the GaN nanowire, as well as the elasticity-mediated interaction. Further study is needed to quantify the contribution of each of these two factors, but we posit that elastic realignment dominates as we note that at electric fields slightly below the threshold, this tilting is not as apparent.

Interestingly, a multi-stable alignment of the nanowire with respect to the lattice is observed to occur (Fig. 8.4. c) during each field-induced nucleation. After turning off the electric field, we either manipulated the GaN using HOT to a new location, or let thermal motion and gravity align the nanowire along a new direction. On nucleating a new lattice, the nanowire would align along a new direction out of the 8 multi-stable orientational states. Likewise observing an ensemble of nanowires within a given undulation showed a random distribution (Fig. 8.4.b) in their orientations out of 8 “allowed” orientations. Our findings could lead to orientational assembly of different reflective or refractive colloids. By dynamically reconfiguring these assemblies, one
could potentially design reconfigurable colloidal composites with expected applications in diffraction optics [31, 32] and nanophotonics [19].

8.4 Conclusions

We demonstrated that colloidal particles and their arrays locally reduce the critical threshold voltage needed to nucleate cholesteric undulations, which is natural because the particles perturb the uniform ground-state helicoidal structure, thus making it easier for the electric field to further enhance these distortions through the formation of undulations. In spherical colloidal systems, the resulting undulation lattice is orientationally constrained by the initial colloidal configuration, and subsequent magnetic rotation of these colloids couple with the locally distorted helical axis in a manner that allows for their three-dimensional translation within the cell. GaN nanowires in cholesterics with undulations exhibit multi-stable alignment along eight different well-defined lattice vectors. These interaction modes lend insight to the physics of structure/colloid interaction, as well as point the way towards guided self-assembly of reconfigurable colloidal composites with potential applications in diffraction optics and photonic crystals.

8.5. References


Chapter 9

Conclusion

Presented in this work are alternative and/or novel methods of colloidal manipulation which are of utmost importance in order to advance the state of the art in technical applications and fundamental science. These methods are developed to help understand the physics of colloidal interactions with liquid crystal structures, methods of colloid manipulation, and methods of creating and controlling fascinating topological structures that have analogs in cosmological fields, such as early universe cosmology, or sub-atomic and high energy systems, or Skrymionic structures. Beyond these fundamental physical understandings, applications of these robust manipulation methods are explored, including interactions that produce templates which can guide the self-assembly of colloid structures in a manner to create metamaterials and photonic crystals with novel optical properties.

I developed a magnetic-optical holonomic control system with the ability to accurately position and manipulate magnetic and optical colloidal handles of mesoscale size in various liquid host media, including liquid crystals (Ch. 2-3). Limitations intrinsic to trap laser intensity and force generation, as well as colloid properties, such as index of refraction, absorptivity; host properties, such as viscosity, opacity and structure are overcome, or at least greatly ameliorated, by the addition of magnetic and structure assisted manipulation techniques. Such techniques include using holographic optical traps to locally deform the liquid crystal director so as to stably trap high index colloids that normally cannot be stably trapped by optical forces alone. We can therefore explore the structure and micro-rheology of nematic and cholesteric liquid crystals, and to characterize topological defects that naturally occur in liquid crystals. Where structure assisted manipulation alone provides a powerful new method for controlling high index particles in liquid
crystals, we desired the ability to control all available degrees of freedom, including Cartesian degrees of freedom, and rotation through all three Euler axes. Magneto-optical manipulation allows for this type of geometrically unrestricted, full holonomic control of colloids through the use of low gradient magnetic fields to apply very large torques on colloids. These torques are many orders of magnitude larger than can be achieved via optical methods alone. In chapter 3, I discussed the use of this holonomic manipulation technique to create and control topological defects, including Lehmann clusters, cholesteric fingers and twist disclinations. This allowed me to use liquid crystals as a model host system as a “tabletop laboratory” to expand our understanding of the role defects play in fields ranging from subatomic particle physics to early-universe cosmology. Furthermore, the ability to spontaneously create certain topological structures, such as “kinks”, could find application in defect based optical connectors, such as light pipes to couple light to colloidal inclusions in liquid crystals. I explored dressing spherical colloids with torons, hopfions and other varieties of particle/soliton bound states, as well as exploring the motion and apparent asymmetry of colloid “orbital dynamics” within a torons’ double twist cylinder.

In classical fall experiments, a colloid is expect to fall linearly under the force of gravity in liquids observing Stokes-like behavior at very low Reynolds numbers. Interestingly, in cholesteric liquid crystals a departure from this expected behavior is observed in the form of periodic dynamics and localization metastability, and in the elastic forces measured between colloids and confining surfaces. Using our holonomic control technique I am able to characterize metastable localization of colloids under the effects of elastic and surface anchoring periodic potential landscapes as seen by the moving spheres forces, demonstrating the important roles played by anchoring memory and topological defect transformation. In chapter 5, I made use of
surface anchoring periodic potential landscapes to help guide the three dimensional self-assembly of topologically and topographically complex colloids into stable, three dimensional structures. Furthermore, I use the topographical properties of the colloids to explore elastic structure of left and right handed cholesteric liquid crystals near confining surfaces, and orientational metastable states within the bulk.

A reoccurring observation is that potential landscapes in structured systems, such as liquid crystals, often deviate significantly from those expected and observed in in isotropic systems. By magnetically rotating a colloid in a cholesteric liquid crystal host (Ch. 6.), we find that we can transfer energy to the local elastic field to a point where a surface point or handle-body boojum detaches from the colloid surface and slips to a lower energy position on the colloid surface. This is a novel observation, and somewhat unexpected from previous experimental studies and numerical simulations. This stick-slip potential landscape interacting with the near field elastic structure of the liquid crystal allows for the complex motion of colloid monomers and dimers. We note a dependence of this energetic potential landscape on temperature and colloid rotation speed. Such interactions allow us to create motile engines that can “swim” through the bulk of the liquid crystal, with possible applications in modeling motility modes in biological systems.

The Helfrich-Hurault undulation instability induced in a cholesteric liquid crystal under an ac electric field is a highly studied system, offering a rich “hunting ground” in studying colloid/structure interactions. For instance (Ch. 8.), the inclusion of certain colloid species reduced the critical voltage threshold of undulation formation significantly. I also noted that the tangential surface anchoring on the colloid’s surface energetically compel the nucleation of a periodic distortion lattice at this lowered threshold field. In spherical colloidal systems, such as
those using superparamagnetic beads, the resulting undulation lattice is constrained both dimensionally and orientationally by the initial configuration of the colloids with subsequent magnetic rotation of these colloids locally distorting the cholesteric liquid crystal helical axis in a manner that allows for three dimensional translation of colloids within the bulk. In physically anisotropic colloidal systems, such as those using high aspect GaN nanowires, a preference for multi-stable alignment offset along various undulation lattice vectors is noted. We notice the GaN colloidal inclusions weakly dictating lattice dimensions and orientation, and noticed a reduction of the critical transition field as well. Preliminary observations indicate that this multi-stable alignment is unbiased during formation, but further study may yield evidence of hysteresis in orientation.

The interaction modes explored in this work lend insight to the fundamental physics of structure/colloid interaction, topological defects in soft condensed matter systems as well as more esoteric cosmological fields, and points the way towards novel guided self-assembly of reconfigurable colloidal composites, with potential applications in diffraction optics and photonic crystals.
Chapter 10

References


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