Photo-Tunable Compression and Realization of Colloidal Spin Ice in Skyrmion Arrays in Chiral Nematic Liquid Crystals

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Photo-Tunable Compression and Realization of Colloidal Spin Ice in Skyrmion Arrays in Chiral Nematic Liquid Crystals

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Department of Physics Undergraduate Honors Thesis
Defense Date: April 5, 2019

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Abstract

Topological solitons are field configurations that are important to theorists in particle physics and cosmology, but recently have been studied in condensed matter systems with reconfigurable fields, like chiral magnets and liquid crystals. In these communities, there is a strong interest in studying and understanding the dynamic behavior of these solitons, many examples of which I will present in this thesis. This includes exploring the dynamic motion and patterning behavior of large number-densities of two-dimensional topological structures called skyrmions with external stimulation by light. With these techniques we can realize for the first time a colloidal spin ice system in a chiral nematic liquid crystal. These experiments simulate the theoretical state of spin ice by using patterned “light-traps” in photo-sensitive azobenzene-based chiral nematic.

Acknowledgements

I would like to thank professor Smalyukh for providing me with the opportunity to work on this project and for guiding me in my experimental endeavours. I would also like to thank Hayley R. O. Sohn, who cooperated with me on this project and provided me with so much help every step of the way. Furthermore, I would like to thank everyone in the Smalyukh research group for their assistance with the lab equipment and for granting me time to conduct my research in the lab.
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I. Introduction

1.1 Liquid Crystals

There are four common states of matter: plasma, gas, liquid, liquid crystal, and solid. Therefore, for crystalline materials, liquid crystal (LCs) is the state of the materials that is intermediate between state of crystalline solid and state of liquid [1]. The liquid crystalline phase can be reached by heating the crystalline material in a particular range of temperature above the melting point and below the nematic-isotropic liquid transition. LCs usually are composed of organic molecules that are thermotropic liquid crystal (another one is lyotropic LCs) and usually has two types anisotropic shape: rod-like molecules and disk-like molecules [2]. Using a visualization of the nematic phase with rod-like molecules (Figure 1), it is clear that the LC phase demonstrates orientational order (with all the rods more or less pointing in the same direction), but not positional order, as would be the case with a solid crystal (Figure 1).

**Figure 1:** Common phases of matter with increasing temperature, where the order of matter decreases from solid phase to liquid phase, through the liquid crystalline phase.
Within the regime of the liquid crystalline state of matter, there are three common phases: nematic, cholesteric, and smectic. As previously mentioned, the nematic phase consists of rod-shaped molecules that demonstrate orientational order (Figure 2a) [2]. The directional orientation field is defined as the director, \( \mathbf{n}(\mathbf{r}) \), made up of unit vectors that point along the long-axis of the rodlike molecules. In the smectic phase, the rodlike molecules also demonstrate orientational order and are also arranged in layers (Figure 2c) [1]. I will be presenting results from liquid crystals in the chiral phase, in which there is helicoidal twist within a nematic liquid crystal phase (Figure 2b). [3] The twist is characterized by the helical pitch, \( p \), which represents the distance over which the director field rotates around the helical axis by \( 2\pi \) [18].

**Figure 2:** Schematics of (a) nematic phase (b) cholesteric phase and (c) smectic phase with their averaged director \( \mathbf{n}(\mathbf{r}) \) displayed in gray and cholesteric pitch, \( p \), marked in (b).
1.2 Topological Solitons in Liquid Crystals

In fields ranging from fluid dynamics to optics, the dynamic behavior of self-reinforcing solitary wave packets called “solitons” has attracted a great deal of interest among physicists and mathematicians for nearly two centuries [5,6]. These solitons maintain their spatially-localized shape while propagating and typically emerge from a delicate balance of nonlinear and dispersive effects in the physical host medium [5]. Solitons of a very different type, often called “topological solitons”, initially drew the interest of theorists in high energy physics and cosmology, but nowadays we study them extensively in condensed matter systems such as magnets and liquid crystals (LCs) [7-17]. Topological solitons are topologically-nontrivial, spatially-localized nonsingular field configurations that, unlike the solitary wave solitons mentioned above, are rarely associated with out-of-equilibrium dynamics, and instead are studied as static field configurations embedded in a uniform background [21]. In this report, I will present an experimental mechanism we have developed for driving dynamic behavior of topological solitons in confined chiral nematic liquid crystals by selective light patterning and manipulation of the elastic free energy landscape within the material to induce motion.

Although both three-dimensional (3D) and two-dimensional (2D) analogs of Skyrme solitons have been realized in confined chiral nematics, [6,14] here I will focus on the two-dimensional case, often called the “baby skyrmion.” These structures can be classified by a Skyrmion number, defined as the integer number of times the field configuration can be mapped onto the order parameter sphere, $S^2$, which encompasses all possible directional unit vectors.
The simplest type of baby skyrmion exhibits $\pi$-twist from the center to the periphery in all radial directions and, in mapping the field configuration onto the $S^2$ sphere, covers it completely precisely once and its Skyrmion number is therefore one. We realize baby skyrmions in chiral nematic liquid crystals (Figure 1), where the ground state has a helicoidal structure that is quantified by the cholesteric pitch, $p_0$, the distance over which $\mathbf{n}(\mathbf{r})$ twists by $2\pi$. If we confine such a material between substrates with a cell-gap separation approximately equal to $p_0$ and perpendicular surface boundary conditions, the boundary conditions are incompatible with the helicoidal structure and the energetic frustration can lead to spontaneous formation of a twisted structure called a “toron”, which terminates close to the substrates with two hyperbolic point defects (Figure 3b) [20]. The LC toron has been analyzed extensively, including comparison of numerical simulations to experimental imaging, both with and without application of electric fields, to confirm a complex understanding of the structure of such field configurations [19]. In the x-y mid-plane of the toron’s vectorized $\mathbf{n}(\mathbf{r})$ structure, it is a baby skyrmion with Skyrmion number equal to one (Figure 3a).

**Figure 3:** The vectorized structure of a chiral liquid crystal skyrmion (toron), displayed with arrows, where $S^2$ is the unit sphere that includes all possible directional unit vectors. (a) Top view of the structure and (b) side view of the structure.
II. Experimental Methods

2.1 Sample and Experiment Setup

The sample used for the presented experiments was composed of the mixture of the nematic host liquid crystal E7 and the photo-tunable chiral dopant QL76. The material E7 consisted of four rod-like nematics: 5CB (51%), 7CB (25%), 8OCB (16%) and 5CT (8%) [28]. The structure of each molecule is shown in Figure 7 (a). 5CB is the main component so the E7 has similar properties as 5CB. QL76, an axially chiral bis(azo) molecule (see Figure 4 (b)), can be tuned via a trans-cis isomerization by using UV-light excitation. The $h_{HTP}$ (helical twisting power) of QL76 mixed with E7 decreases from a ground-state value of 60 $\mu m^{-1}$ in the trans/trans state to 27 $\mu m^{-1}$ in the cis/cis state upon UV-light excitation [18, 21, 29]. Since the value of $h_{HTP}$ can be reduced by UV-light excitation, the pitch $p_0 = \frac{1}{h_{HTP}c}$ increases (where $c$ is the concentration of chiral dopant, so it is a constant in this case). Therefore, the ratio $d/p_0$ decreases with the light excitation.
To prepare the sample cell, we used two glass substrates. In order to impose strong homogeneous vertical surface boundary conditions, the glass substrates with transparent indium tin oxide (ITO) electrodes that were treated with polyimide SE-1211. Then put the glass substrates with SE-1211 to the ITO electrodes through spin coating at 2700 rpm, after 30s baked them on baker 90 °C for 5 minutes and 190 °C for 1 hour. We used glass fiber segments that distributed in ultraviolet-curable glue as “spacers” that can separate the glass substrates with gap, \( d = 12.5 \, \mu m \). Then added small drops of the glue between the substrates with ITO electrodes and alignment layers facing inward and put substrates in the OmniCure UV lamp exposure for 60 s. Filled the mixture of E7 and QL76 into the confinement cells by using capillary forces then using 5-min fast-setting epoxy to seal the edges of cell. Finally, soldered leads to the ITO electrodes in order to provide electrical connection through the cells, which we do to erase the torons [26, 29].

In order to generate torons, we use a computer-controlled laser tweezers system that consists of a 1064 nm wavelength ytterbium-doped fiber laser with a collimated output beam diameter of 5 mm, a pair of scanning mirrors, two-lens telescope with no magnification, dichroic mirror (DM), the objective of the BX51microscope and a homemade Labview-based software (Figure 5) [22]. Voltage-controlled two-dimensional beam deflection and computer-programmed steering of the focused beam within the sample can be enabled by the scanning mirrors [22]. The torons can be generated via a process that the director couples in LC to the optical-frequency electric field of the laser beam and realigns away from the far-field background \( \mathbf{n}(r) \) [21, 22, 26].

**Figure 4:** (a) The composition of E7 and the structure of each molecule [26] (b) the chemical structure of QL76 chiral dopant [27]
The range of the output power in order to “print” toron is 17mW to 28nW, that varies with different sample cells.

**Figure 5:** A schematic of the computer-controlled laser tweezers system [22]

The blue light patterning system will be discussed in the Results section and is coupled to an Olympus BX-51 optic upright microscope with 4x, 10x and 20x objective. Polarizing optical microscopy (POM) images and videos were obtained with a CCD (charge-coupled device) camera (PointGrey) [18].

### III. Results

#### 3.1 Drawing Arrays of Torons with CNLCs

In order explore large-scale dynamics of skyrmions in LCs, a reliable technique of drawing large amount arrays of torons is first required. For drawing arrays, we utilized the computer-controlled laser tweezers and the homemade Labview-based software with 4x or 10x objective of
the BX-51 system that I stated above. The output power for the sample cell is 18mW to 28mW, which relies on different area in the cell. For example, printing the edge of large amount of skyrmions usually requires a larger number of power than printing arrays in the middle, which happened because convex lens of the objective. What’s more, it is very significant to adjust the focus, especially using the 4x objective. After finished all set up of Labview-based software, POM images were captured with the CCD camera.

The more precise value of the output power for drawing arrays is 27.4mW to 28.0 mW. If we use a power less than 27.4mW, torons will disappear within 5s. On the other hand, if the power is larger than 28.0 mW, double-torons will be frequently generated [7]. If the power very large, the laser beam could melt the LCs to the isotropic phase (it could produce a spot that cannot be erased by applied voltage. The focus should be slightly out of focus (clockwise rotate fine focus knob) that can avoid producing “pinned” torons, because of the focus of camera (Flea) is slightly different with eyepiece on the BX-51 microscope. There are four different arrays: square arrays, hexagonal arrays, diamond arrays and quasi-hexagonal arrays (Figure 6). The process of drawing the arrays should be as quick as possible before the experiment is done on the large array, because the torons that are unpinned to the surface always move slowly apart due to repulsive interactions.
Figure 6: Variety of arrays of torons drawn in a chiral nematic LC using LabView software.
3.2 Compression of Arrays

We can control the dynamics of skyrmions in LCs by means of optical manipulation using patterned light. Various azo-chiral liquid crystalline materials have been synthesized and studied extensively by chemists [30] and it is well-understood that an azobenzene-based chiral dopant can be tuned via a trans-cis isomerization upon UV-light excitation, leading to a decrease in the helical twisting power of the chiral molecule [30-32]. For these experiments, we use an azobenzene-based chiral dopant, QL-76 (see Methods) [36, 37].

According the Frank-Oseen expression for elastic free energy (Eqn. 1), the helicoidal pitch contributes to the twist-free-energy of a cholesteric LC.

Figure 7: Frank elastic: $K_{11}$, $K_{22}$, $K_{33}$ (Reproduced from Dr. Smalyukh’s lecture note, used with permission)
\[ W = \int \left\{ \frac{K_{11}}{2} (\nabla \cdot \mathbf{n})^2 + \frac{K_{22}}{2} \mathbf{n} \cdot (\nabla \times \mathbf{n}) + q_0 \right\}^2 + \frac{K_{33}}{2} \left[ \mathbf{n} \times (\nabla \times \mathbf{n}) \right]^2 - \frac{\varepsilon_0 \Delta \varepsilon}{2} (\mathbf{E} \cdot \mathbf{n})^2 \right\} dV \quad \text{Eqn. 1} \]

where \( K_{11}, K_{22}, K_{33} \) are Frank elastic and they represent the elastic costs for splay, twist, and band deformation of \( \mathbf{n}(r) \) [15, 20]. \( q_0 \) is the chiral wavenumber of the ground-state chiral nematic mixture and it has the mathematic relation \( q_0 = \frac{2\pi}{p_0} \). \( \varepsilon_0 \) is the permittivity of vacuum and \( \Delta \varepsilon \) is the dielectric anisotropy. The number values for the material parameters are reported in the Refs. 15 & 20.

And so, by selectively increasing the pitch via blue-light illumination, the free-energy landscape within the exposed regions of the sample changes from the ground state equilibrium free energy. Because topological solitons, by definition, represent local minima in the ground-state equilibrium free energy, they, too are sensitive to light. Figure 7 demonstrates how the skyrmions change their size to adapt to the changing pitch with blue-light illumination.
Figure 8: Skyrmion structure with changing pitch. (A, B) Numerically-simulated skyrmions in a chiral nematic liquid crystal shown at (A) $d/p = 0.925$ and (B) $d/p = 1.25$, where the vectorized $\mathbf{n}$ is colored according to orientation on the $S^2$ sphere (inset). (C) Numerically-measured skyrmion diameter measured within the $d/p$ stability range, where $d$ is fixed at 10 $\mu$m and corresponding diameters from (A) and (B) marked in red. (D, E) Experimentally-measured skyrmion diameter upon 5s of blue-light exposure, with corresponding polarizing optical images (inset) shown for (D) Sample A ($d/p = 1$) and (E) Sample B ($d/p = 1.25$). Crossed polarizer orientation is marked with white double arrows. Numerical simulations are based on material parameters of nematic host E7 and left-handed chiral additive QL-76, with thickness = 10 $\mu$m. (Used with permission from manuscript in preparation.)

In order to have a broad stability range in our samples, we use a cell with a starting stability ratio of $d/p = 1.25$ (Sample B in Figure 8). By projecting patterns of blue light, we selectively create an energy and pitch gradient over the illuminated area that the solitonic
structures can feel and adjust by moving towards a dark region with lower energy and lower pitch to maintain their energetic stability (Figure 9).

**Figure 9:** Photo-sensitive cholesteric experimental background. (a) Molecular structure of QL-76 chiral additive [34] (b) Schematic of blue-light patterning projection and red imaging light. Polarizer (P), analyzer (A), dichroic mirror (DM 505LP), and charge-coupled device camera (PointFrey, FlyCap) positions are labeled. 4x, 10x, and 20x Olympus dry-objectives were used. Inset graph shows pitch dependence on chiral additive concentration and UV-excitation, where the red line represents equilibrium ground-state pitch and the blue line represents maximum pitch upon exposure. For the reported E-7 sample with QL-76, the black dashed lines mark the minimum and maximum possible pitch values. (c) Numerical demonstration of
Upon UV-light excitation, the QL-76 additive exhibits a maximum decrease from a ground-state value of 60 µm$^{-1}$ to 27 µm$^{-1}$ upon excitation. [41] We use low-intensity (~ 1nW) [35] patterned blue light projection in the 425-480nm range (Figure 9b) to tune the pitch of an E7 – QL-76 mixture, in this case in the range from ~10 to $\leq$ 22 µm (inset).

To prepare the large size of the arrays, I drew on the knowledge I presented above. I chose the camera called Spot for a large view and selected a suitable area with the stable ratio $d/p_0 \approx 1.25$ in the cell and used the same method in section 2.2.1 to draw large square arrays. After finished drawing the array, I switched the camera from Spot to PointGrey, connected a laptop with the projector and project the pattern from PowerPoint slides using the system presented in Figure 9. I adjusted the focus of the projector until the pattern from the projector on the cell had a sharper edge in another empty area far away from the array. I exposed the cell with the pattern for 5s and recorded the video by using the CCD of for 5000 s.

We utilize this setup to demonstrate dramatic reconfigurable control over arrays of solitons and study various interesting materials-science inspired puzzles and demonstrations. In the case of a region where we have selectively drawn a grain boundary between two triangular lattices of solitons (Figure 10a), exposing the outer boundaries pushes the solitons together into a healed lattice without a grain boundary. Time-coded colored trajectories show how the solitons move smoothly towards each other (Figure 10b). We can also demonstrate precisely tuned control of...
solitonic motion that allows for creation and healing of a small crack in a close-packed triangular lattice (Figure 11a). The time-coded colored trajectories displayed in Figure 11b once again show that we have extremely precise and tunable control over selected dynamics on the order 10 \( \mu \)m, while the diameter of the solitons is only 15 \( \mu \)m.

**Figure 10:** Photo-induced healing of a grain boundary in an array of skyrmions. (a) POM images of a grain boundary in a skyrmion lattice and subsequent lattice healing upon blue light illumination at the boundaries of the frame. White dashed lines mark the grain boundary in the initial frame. Polarizer orientation is marked with white double arrows and elapsed time is noted in the bottom left corner of images. (b) Time-coded trajectories of smooth skyrmion motion following illumination. The material is E7 with QL-76. *(Used with permission from manuscript in preparation.)*
Figure 11: Photo-induced crack formation and healing in a lattice of skyrmions. (a) POM images of a close-packed triangular lattice of skyrmions reacting to blue light illumination pattern, shown as an overlay in the first frame, and subsequent lattice healing with time. Polarizer orientation is marked with white double arrows and elapsed time is noted in the bottom right corner of images. (b) Time-coded trajectories of precise skyrmion manipulation to create a crack in the lattice. The material is E7 with QL-76. (Used with permission from manuscript in preparation.)

Figure 12 shows the compression of a square lattice into a triangular/hexagonally-packed lattice. After 5s of exposure, the torons outside of the black square (on the blue area) shrinked and moved inward, and the torons inside the black began to compact together. After 5000 s the torons are more densely packed, which is the expected result.
**Figure 12:** Compression of square arrays to hexagonal in 5000s. *(Used with permission from manuscript in preparation.)*

I also demonstrate compression of an array that is slightly different to start, as it has an extra row of torons inserted (Figure 13 (b)). The defect array is “compressed” with blue light to form a triangular/hexagonally-packed array without an insertion.

**Figure 13:** (a) The square projection pattern and (b) the insertion row in the square lattice highlighted in white region.
Figure 14 shows that, upon tracking the shape of the insertion row with compression, the insertion buckles and gives way to a defect-free array.

Figure 14: Compression of the defect lattice into a quasi-hexagonal lattice (a-b) over 2000 s and (g) the corresponding buckling in the insertion layer.

3.3 Spin Ice

“Spin ice” is a state of magnetic spins that was found from the research of geometric frustration in the ferromagnetic pyrochlore $H_{02}T_{12}O_{7}$. It is a theoretical state of a geometrically-frustrated ferromagnetic system [23]. Two spin “in” and two spin “out” is the “ice rule” for tetrahedron of ferromagnetic pyrochlore shown in Figure 15 (a) [24]. The theories of spin ice have been used in artificial spin ice system. For example, in colloidal spin ice system that consists of a group of interacting colloidal particle that are confined to lattices of gravitational traps [25]. There
are two types of the colloidal spin ice system: square colloidal spin ice and Kagome (or quasi-hexagonal) spin ice (see Figure 15 (b) and (c)) [25].

**Figure 15:** (a) Two spin “in” and two spin “out” in a single tetrahedron structure in ferromagnetic pyrochlore. (b) Kagome (or quasi-hexagonal) spin ice (c) Square colloidal spin ice [24]

In this experiment, we utilized the photo-tunable patterning and array drawing techniques to create an analog of colloidal spin ice in an LC system, with “photo traps” instead of gravitational traps. [25] After preparation of the projector, we draw several different sizes of diamond arrays until found the suitable size then redrew new arrays with the correct value to fit the projected pattern. In various experiments, I exposed it for 5s, 10s, 15s, 30s, and 60s with the pattern that is the “light traps” that limits the motion of torons, for example, in the square lattice spin ice the torons only can move left or right, or move up and down (shown in Figure 16). I waited for 30 mins after exposure and the process were recorded by the CCD.
Figure 16: A schematic plan for colloidal spin ice. (a,b) Colloidal spin ice [25] (c,d) Skyrmion array templates for (c) quasi-hexagonal “Kagome” colloidal spin ice and (d) square colloidal spin ice. (e,f) Photopatterning masks for (e) Kagome and (f) square templates, with a sample skyrmion position and two possible directions of motion marked with a red dot and yellow arrows in (e).

Figure 17: Preliminary experimental results for a square-lattice analog of colloidal spin ice, with the photo mask shown in the middle panel and the movement of the torons shown with white arrows on the right.
As we know, the objective consists of convex lens, thus the light from the projector refract by objective that is why the edge of the pattern are distorted. Thus, we chose middle area of the array that the pattern that did not distort as the experimental subject. We found that there were some torons that showed a same behavior with colloidal spin ice. Figure 17 shows the “two in two out” phenomenon. The distance of motion of torons for 1 min exposure is less than that of the 5s exposure, which happened because of the overexposure. However, the results are only preliminary, and this project is ongoing.

VI. Conclusion, Discussion and Future Plan

All in all, there are four types of arrays, square arrays, hexagonal arrays, diamond arrays and quasi-hexagonal arrays, that we could print in the cell with computer-controlled laser tweezers system. The correct output power and focus are most important condition to make prefect arrays.

I realized that the photo-tunable patterning control technique can shrink the array, heal the grain boundary arrays, heal a lattice that has a crack, and change the shape of lattices. I have also demonstrated photo-tunable patterning control of these large arrays of skyrmions, which can be applied to a soft-matter analog of a hard-condensed matter phenomenon in magnets. Although we have found there were several torons that have similar behavior with colloidal spin ice, in the future, we plan to refine the pattern of spin ice and explore the best exposure time in order to improve the experiment.
Significant progress has been made in understanding and utilizing these large-scale arrays of skyrmions to understand larger lessons in collective behavior.
V. References


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