Structure and Dynamics of Exotic Nematic Liquid Crystals by

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Structure and Dynamics of Exotic Nematic Liquid Crystals

Thesis directed by Prof. Noel A. Clark

Exfoliated monolayer zirconium phosphate sheets (1 μ m diameter \times 2.78 nm thick) in water form colloidal suspensions exhibiting liquid crystal (LC) ordering above a critical concentration. Studies of the phase behavior and phenomenology of such suspensions show that the LC is nematic, in agreement with theory, but that the predicted lamellar smectic phase does not appear. At high concentration lamellar correlations grow in the nematic but are limited in range, either by the finite size of the sheets or by defects in the sheets. Coexistence of the nematic with an isotropic phase is observed at all concentrations, indicating a long range attraction between the sheets. At high concentration the coexisting LC forms lens-shaped nematic tactoids, analysis of which enables estimates of the nematic elasticity and surface tension. Transmission electron microscopy reveals the bispherical internal structure of the nematic director field in the tactoids. Nematic cells with initial homeotropic orientation exhibit a periodic instability in the director field, which is unstable against the formation of a bend undulation of the sheets. This phenomenon, which is also observed in lyotropic colloidal suspensions of graphene oxide sheets, may be attributed to flexopolydispersity, the slow internal rearrangement of sheets of different size to optimize their spacing and thereby maximize entropy.

Azobenzene-based molecules which form a self-assembled monolayer (SAM) tethered to a glass surface are highly photo-sensitive and dynamically orient liquid crystals in contact with them when illuminated with polarized actinic light. We probe the coupling of such monolayers to the nematic liquid crystal in a hybrid cell by studying the dynamics of liquid crystal reorientation in response to local orientational changes of the monolayer by a focused actinic laser with a rotating polarization. This locally reorients the nematic, winding up a set of nested rings of splay-bend nematic director reorientation until the required torque exceeds that of the surface coupling, after which the nematic director starts to slip. Quantitative analysis of the dynamics enables measurement of the coupling between the azo-SAM and the nematic liquid crystal.

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CHAPTER 1

Introduction to Liquid Crystals

1.1 Liquid Crystals

Liquid crystal (LC) phases have the intermediate properties between solid crystalline phase and liquid isotropic phase, therefore they are also called mesophases. The liquid crystal materials exhibit some degree of fluidity like liquid, but their molecules are oriented in a certain way like a solid crystal showing anisotropic properties.

In general, liquid crystals can be divided into two categories: thermotropic and lyotropic phases. Thermotropic liquid crystals are the materials which go through one or more mesophases from isotropic liquid phase to crystalline solid as decreasing temperature. Lyotropic liquid crystals are mixtures of solute, for example, amphiphilic molecules, block copolymers or colloidal particles, in solvent, and their properties are related to the solute concentration in addition, which is usually more important.

The essential feature of the liquid crystal materials is their anisometric shape of the molecules or compounds, for example, rod-shape and disk-shape. Therefore, when they are packing together, they have the tendency to orient in a certain way that shows anisotropic phases. The direction of the preferred orientation of the molecules is called director, denoted as a unit vector \boldsymbol{n} . There are many different liquid crystal phases based on its molecule orders, for example, nematic phase, smectic phase, cholesteric phase, and so on. I will briefly introduce some of the phases related to my projects later on.

Because of the anisotropic property, when LC materials are observed under crossed polarizers, birefringent textures are observed. Different LC phase with different orderings show different and characteristic textures. The depolarized optical microscopy is one of the essential tools to explore LC phases. It composites an optical microscope with crossed polarizers: polarizer (P) and analyzer (A). When observed under crossed polarizers, birefriengent LC material shows the transmission light intensity

$$I = I_0 \sin^2(2\theta) \sin^2(\pi \Delta n d/\lambda), \qquad (1.1)$$

where θ is the angle between molecule director \mathbf{n} and polarizer P, Δn is the birefringence and d is the thickness. When the director is aligned parallel to the polarizer P or analyzer A, i.e., $\theta = 0$ or $\pi/2$, no light can transmit through and the texture appears dark, and when $\theta = \pi/4$, the texture is the brightest.

1.2 Liquid Crystal Alignment and Anchoring

For most of the applications of LCs, the alignment of LCs is essential. Mauguin reported that the rubbed glass surfaces could provide the LC alignment in 1911 [1], which promotes the most commonly used mechanical rubbing methods for LC alignment. Since that, various substrate treatment techniques giving different LC alignments have been developed, such as rubbed polyimide (PI) layers [2,3], ion-beam-processed polyimide films [4], lithographically micro-patterned polymers [5], obliquely evaporated SiO_x [6,7], Langmuir-Blodgett films [8], nanopatterned surfaces using an ion-beam etching surfaces [9], photo-aligned light sensitive polymers [10], etc. There are some general types of LC alignment, which are shown in Figure 1.1 as an example for rod-shape molecules. An orientation with the director oriented in the plane of the substrate and pointing in the same direction is called homeogeous. And the one with the director oriented perpendicular to the substrate plane is called homeotropic. For disk-shape molecules, the director n is perpendicular to the disk plane, so the disk planes are oriented perpendicular to the rods correspondingly for the alignment types in Figure 1.1.



Figure 1.1: Illustration of different alignments for the rod-shape LC molecules, cited from [11].

The preferred direction at the alignment surface is called "easy axis". If the director at the surface deviates from the easy axis, it costs energy. The surface anchoring energy was given by Rapini and Papoular [12]:

$$f_{s} = \frac{1}{2} W_{\theta} \sin^{2}(\theta - \theta_{0}) + \frac{1}{2} W_{\phi} \sin^{2}(\phi - \phi_{0})$$
(1.2)

where W_{θ} and W_{ϕ} are the polar and azimuthal anchoring coefficients with the dimension of energy per unit area; θ_0 and ϕ_0 are the easy axis of polar and azimuthal orientations. The surface anchoring is considered to be strong in the range ~ 10^{-4} J/m² and week in the range ~ 10^{-6} J/m².

1.3 The Nematic Phase

When the LC material is in nematic phase, its molecules only have long-range orientational order and no long-range translational order. For the rod-shape molecules, the director n is the average long axis orientation of the molecules, and for the disk-shape molecules, n is the average director normal to the disk plans (Figure 1.2). Order parameter S is used to describe the average molecular orientation along n [13]:

$$S = \frac{1}{2} < 3\cos^2\theta - 1 >$$
(1.3)



Figure 1.2: Schematic illustration of nematic phase of rod-shape (a) and disk-shape molecules (b). n denotes the director.

The typical texture of nematic phase is shown in Figure 1.3, called Schlieren texture. The curved dark brushes are observed because the directors are along either P or A. They end at the singularities, which are the topological defects. The strength of the defect is indicated by parameter *s*, which is defined as the director turns on a closed curve around the center over 2π .



Figure 1.3: Schlieren texture of nematic phase, cited from [14].

1.4 Smectic Phase

The smectic phase has well defined layers and the molecules are liquid-like and free to flow within the layers. Therefore, it has one dimensional positional order in addition to the orientational order of nematic phase. Within the layer, the molecules orient in certain ways in different smectic phases. The most common smectic phases are Smectic A (SmA) and Smectic C (SmC) phases. In the SmA phase, the molecules are oriented along the layer normal, while in the SmC phase, the molecules are tilted from the layer normal, as shown in Figure 1.4.

The most commonly observed texture of SmA is the fan-shaped or focal conics textures (Figure 1.5). They consist of focal domains topologically, and the smectic layers are arranged in the so-called Dupin cyclides (Figure 1.6). The fan-shaped and focal conics textures are different views of the focal domains. If the molecules are homeotropically anchored to the substrates, it appears dark between crossed polarizers.



Figure 1.4: Schematic illustration of molecule orientations of Smectic A and Smectic C phase. The molecules are oriented along the layer normal in the SmA phase (a), and tilted from the layer normal in the SmC phase (b).



Figure 1.5: Typical focal conic texture of SmA phase, cited from [11,14]: (a) fan-shaped texture, (b) focal conics texture.



Figure 1.6: Schematic illustration of the smectic layers arranged in Dupin cyclides, cited from [14]. The ellipse and hyperbolic are in the confocal position.

1.5 Cholesteric Phase

The LC phases introduced above are formed by achiral molecules. If there is a chiral center in a molecule, the molecule will lose mirror symmetry, and chiral LC phase will show up. The chiral nematic phase (N*, where * denotes the chirality) is also called cholesteric phase. Similarly, the molecules only have long-range orientational order and no long-range translational order. Because of the chirality, a spontaneous helical structure forms with the twist axis perpendicular to the local director (Figure 1.7). The helical twist can be right- or left-handed depending on the chirality of the molecule. *p* denotes the cholesteric pitch over which the director continuously rotates through 2π measured along the twist axis. The periodicity length is actually half of this distance (*p*/2) since *n* = -*n*, like a pseudo-layers.

Typical textures of cholesteric phase are shown in Figure 1.8, depending on the surface alignment. Oily streaks textures are usually observed with planar alignment on the substrate. The pitch of the cholesterics is usually of the order of several hundred nanometers, comparable to the

wavelength of visible light, thus responsible for the characteristic colors of selective reflection. The oily streaks are due to dislocation lines. Fingerprint textures are observed with the homeotropic anchoring where the helical axes are in the plane of the substrate with the periodicity corresponds to p/2. If the pitch is comparable to the cell thickness, the deformation of the helical structure by elastic interactions with the bounding substrates makes this measurement inaccurate. Further increase the cholesteric pitch results in cholesteric fingers (bright lines) in a homeotropic area (black). Since virtual layers with thickness p/2 in cholesteric phase can be interpreted as pseudo-layers, fan-shaped focal conic textures are also observed, usually in strongly twisted material. If the pitch is long, the superstructure can be resolved in the fans by optical microscopy. Polygonal texture is also observed with the cholesteric pseudo-layers inclined with respect to the substrates.



Figure 1.7: Schematic illustration of the helical structure formed in cholesteric phase, where p denotes the helical pitch. The stars denote the chirality of the molecules.



Figure 1.8: Cholesteric textures: (a) Oily streaks texture, (b) fingerprint texture, (c) cholesteric fingers, (d) smooth fan-shaped focal conics texture, (e) fan-shaped focal conics texture with superstructure distinguishable, (f) polygonal texture. The pictures are cited from [11,14,15].

1.6 Liquid Crystal Deformation and Energy

Because of the liquid properties of liquid crystals, it can be easily deformed and the deformation costs elastic energy, which can be calculated by the Oseen-Frank free energy density. In achiral nematics, there are three types of deformation: splay $(\nabla \cdot n \neq 0)$, twist $(n \cdot \nabla \times n \neq 0)$ and bend $(n \times \nabla \times n \neq 0)$ (Figure 1.9). The Oseen-Frank free energy density related to the bulk distortions can be calculated as [13]

$$f_e = \frac{1}{2}K_{11}(\nabla \cdot \boldsymbol{n})^2 + \frac{1}{2}K_{22}(\boldsymbol{n} \cdot \nabla \times \boldsymbol{n})^2 + \frac{1}{2}K_{33}(\boldsymbol{n} \times \nabla \times \boldsymbol{n})^2, \qquad (1.4)$$

where K_{ii} is the elastic constants for splay (K_{11}), twist (K_{22}) and bend (K_{33}) respectively. The dimension of the free energy f_e is energy/volume, and K_{ii} is energy/length.



Figure 1.9: The three types of deformation of rod-shaped nematic liquid crystal: splay, twist and bend, cited from [11].

For chiral nematic liquid crystals, the free energy is modified to be:

$$f_e = \frac{1}{2}K_{11}(\nabla \cdot \boldsymbol{n})^2 + \frac{1}{2}K_{22}(\boldsymbol{n} \cdot \nabla \times \boldsymbol{n} + q)^2 + \frac{1}{2}K_{33}(\boldsymbol{n} \times \nabla \times \boldsymbol{n})^2, \quad (1.5)$$

where $2\pi/q$ is the cholesteric pitch *p*.

There are terms that are divergences in the bulk and may be manifest only at the boundaries of the liquid crystal phase and contribute to the surface free energy density

$$f_e = \frac{1}{2} K_{11} (\nabla \cdot \boldsymbol{n})^2 + \frac{1}{2} K_{22} (\boldsymbol{n} \cdot \nabla \times \boldsymbol{n} + q_0)^2 + \frac{1}{2} K_{33} (\boldsymbol{n} \times \nabla \times \boldsymbol{n})^2$$
$$-K_{24} \nabla \cdot [\boldsymbol{n} (\nabla \cdot \boldsymbol{n}) + \boldsymbol{n} \times \nabla \times \boldsymbol{n}] + K_{13} \nabla \cdot [\boldsymbol{n} (\nabla \cdot \boldsymbol{n})], \qquad (1.6)$$

where K_{24} and K_{13} are the saddle-splay elastic constant and splay-bend elastic constant respectively, and are also called "surface-like elastic constants", which are usually neglected when only consider the bulk.

In nematic, usually the elastic constants for splay, twist and bend are roughly equal, and people use the one constant assumption in calculation. However, bend and twist are prohibited in the achiral smectic phase due to the layer structure. K_{22} and K_{33} become divergence as approaching the N-Sm transition, especially K_{33} (bend), because of the extent of the pretransitional smectic-like ordering in the nematic phase. Figure 1.10 is an example of the temperature dependence of K_{ii} in the nematic phase of 8CB near the N-SmA phase transition. K_{22} and K_{33} are divergent according to the scaling relation

$$K_{ii} \sim (T - T_{NS})^{-\nu}, \tag{1.7}$$

where for 8CB, v = 0.7 for K_{33} , and v = 0.35 for K_{22} [16].



Figure 1.10: Elastic constants of 8CB in the nematic phase, cited from [17]. K_{22} and K_{33} are divergent near the N-SmA phase transition. 1 dyn=10⁻⁵ N.

CHAPTER 2

Lyotropic Colloidal Suspensions of Graphene Oxide Nanosheets

In lyotropic liquid crystals, highly anisometric particles in suspensions are ordered to form liquid crystalline phase, which is basically expected by Onsager's theory [18] due to the competition between the orientational entropy of the isotropic state and the packing entropy of anisotropic excluded volume pair interactions. I will focus on the lyotropic liquid crystals formed by the inorganic platelets colloidal dispersions.

Inorganic platelets such as gibbsite [19], niobate [20,21], layered double hydroxide [22,23], solid acids of the HnMnZ2O3n+5 species [24], graphene [25] have been found to form nematic, columnar, or smectic (lamellar) phase. Unlike other discotic liquid crystals, the phases of the colloidal inorganic platelets are determined by particle concentration and polydispersity, rather than temperature. The nematic phase is commonly observed with only long-range orientational order. As concentration goes higher, colloidal platelet dispersion with lower polydispersity shows the columnar phase [19], where the platelets stack into liquid-like columns, and the columns order into a two-dimensional hexagonal lattice. The lamellar phase is more favorable for the high-polydispersed platelet suspensions with high-aspect-ratio [23,24]. The platelets not only possess orientational order, but also assemble into a one-dimensional periodic array of layers (Figure 2.1).

The lyotropic suspension of GO nanosheets has been also been reported [26] to have nematic phase. I will study the similar GO suspension in detail.

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Figure 2.1: Structure of the liquid crystal phases formed by plate-shaped particles: (a) nematic phase, (b) columnar phase, and (c) smectic (lamellar) phase. [19]

2.1 Graphene Oxide Exfoliation

The graphene oxide (GO) is obtained by oxidizing graphite by interrupting the contiguous aromatic lattice into, for example, epoxide, hydroxyl, ketone carbonyls and carboxylic groups [27]. The thickness of the graphene oxide nanosheet increases from 3.7 Å (graphene) to about 1 nm [28] by oxidation. The polar groups on the GO nanosheet make it to be hydrophilic and can be exfoliated into monolayer in water.

The graphene oxide we used is commercial available from Graphene Supermarket company, synthesized through modified Hummers' method [29]. Dried GO flakes were dissolved in deionized water by stirring at 60°C for 1 hour and followed by sonication for 30 minutes and repeat twice to form uniformly dispersed 2 mg/ml suspensions (at least 2 month) (Figure 2.2 (a)). The hydrophilicity of GO platelet allows it to be deposited onto a substrate homeotropically while water evaporating, enables the image of a single plate. A TEM image of a dried drop of GO solution (Figure 2.2 (b)) shows micron-sized GO platelets with high polydispersity.



Figure 2.2: (a) 2 mg/ml GO aqueous suspension in a glass vial. (b) TEM image of polydisperse graphene oxide platelets.

2.2 Dynamic Light Scattering

To explore the size and polydispersity of GO nanosheets, dynamic light scattering (DLS) apparatus was built (Figure 2.3). A He-Ne laser with a wavelength of $\lambda = 632.8$ nm (power = 1 mW) is focused onto a glass vial. The laser is polarized perpendicular to the scattering plane. The detecting fiber is mounted on a free-rotating arm with a focusing lens and a pinhole. The scattered light is collected at certain scattering angle Θ . Vectors k_o and k_s represent the incident and scattered wave vectors, and q is the scattering vector defined as the difference of the incident and scattered wave vectors, whose magnitude is

$$q = \left| \vec{k}_0 - \vec{k}_s \right| = \frac{4\pi}{\lambda/n} \sin(\Theta/2).$$
(2.1)



Figure 2.3: Dynamic light scattering apparatus. The normalized scattered intensity time autocorrelation is recorded.

The phase of the field scattered by each particle relative to that of the other particles changes in time as the particles move, and thus the scattered light intensity fluctuates, reflecting Brownian motion of the particles [30]. The scattered light was sent into a photomultiplier tube (PMT) by the fiber at certain angle, and then processed by a correlator to get the normalized intensity time autocorrelation signal:

$$C(\tau) \equiv \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)I(t)\rangle} = 1 + \gamma [g^{(1)}(\tau)]^2, \qquad (2.2)$$

where $g^{(1)}(\tau)$ is the normalized first order time autocorrelation function of scattered electric field.

For a monodispersed spherical particle system, $g^{(1)}(\tau)$ shows a single exponential decay $g^{(1)}(\tau) = \exp(-\Gamma \tau)$, where $\Gamma = Dq^2$. D is translational self-diffusion coefficient of the particles, which is related to their hydrodynamic size. For a polydispersed system, $g^{(1)}(\tau)$ is a

sum of exponentials over all distributions. Cumulants method [31], where $\exp(-\Gamma\tau)$ is expanded around $\exp(-\overline{\Gamma}\tau)$, expands the intensity time autocorrelation as

$$C(\tau) = 1 + \gamma \exp(-2\overline{\Gamma}\tau)(1 + \frac{\mu_2}{2!}\tau^2 - \frac{\mu_3}{3!}\tau^3 \cdots)^2, \qquad (2.3)$$

where $\overline{\Gamma}$ is the size weighted average value of Γ_i , and μ_2 is the variance. $\mu_2 / \overline{\Gamma}^2$ is a measure of polydisersity, which is also called polydisersity index (PI). Truncating this polynomial at the second order term, Eqn. (2.3) can be approximated by:

$$C(\tau) = 1 + \gamma \exp(-2\overline{\Gamma}\tau)(1 + \mu_2 \tau^2). \qquad (2.4)$$

For sphere particles, the diffusion constant is related to the particle size (radius b) based on the Stokes-Einstein relation:

$$D = \frac{kT}{6\pi\eta b} \,. \tag{2.5}$$

For ellipsoid particles, Perrin's theory [32] can be used to calculate the translational and rotational diffusion constant [33]. For GO nanosheets, the aspect ratio is so big ($a \ll b$) (see the cartoon for GO platelets in Figure 2.6 (c)), that we can obtain the expressions for translational diffusion constant of the nanosheets to be

$$D_T = \frac{kT}{12\eta b}, \qquad (2.6)$$

and the rotational diffusion constant

$$D_R = \frac{3kT}{32\eta b^3},\tag{2.7}$$

where k is Boltzmann's constant, T is the temperature, η is the solvent viscosity, and b is the hydrodynamic radius of the GO nanosheets.

Figure 2.4 shows typical intensity autocorrelation data from dynamic light scattering of GO nanosheet suspension (2 mg/ml). Eqn. (2.4), which takes polydispersity in to account, gives better fitting than monodispersed fitting. From the fitting, we get the translational diffusion constant $D_T = 4.7 \times 10^{-13} m^2 / s$, which gives the mean hydrodynamic radius of the GO platelets as about 0.8 µm, and a polydispersity of about 0.8.



Figure 2.4: Intensity autocorrelation data from dynamic light scattering of a 2 mg/ml GO suspension (black dots) at 20 degree. The blue solid line is the fitting regardless of polydispersity. The red solid line is a fit to Eqn. (2.3), which considers the polydispersity and shows better fitting to the data. The fitting gives the translational diffusion constant $D_T = 4.7 \times 10^{-13} m^2 / s$, and polydisersity ~ 0.8.

2.3 Lyotropic Liquid Crystal Phase of Graphene Oxide

We start our experiment with the capillary filled with the 2 mg/ml GO suspension, which doesn't show any liquid crystal phases. To increase the concentration of GO, the suspension was centrifuged in a glass capillary. The resulting high concentration sediment showed birefringence under crossed polarizers, giving liquid crystal phase (Figure 2.5 (c)). The concentration of GO as a function of position in the flat capillary (rectangular-shaped cross section with 0.2 mm thickness) was calculated by comparing the transmission spectra with that of the 2 mg/ml suspension before centrifugation using the Beer-Lambert Law $T = 10^{-\varepsilon LC}$, where T is the transmission and C is the suspension concentration. A few days after centrifugation, the originally sharp sediment boundary diffused to give a visible concentration gradient. The blue and yellow lines in Figure 2.5 (a) are measured near the boundary of LC and isotropic phase, giving the critical concentration for the isotropic to LC phase transition at about 10 mg/ml. The birefringence has also been measured and marked in Figure 2.5. The critical concentration in the deionized GO suspension is somewhat lower, around 6.4 mg/ml. The values are comparable to the calculated transition concentration of 7.78 mg/ml based on the polydispersed hard disk model [34, 35]

$$n_l \langle D^3 \rangle = 3.68 - 2.43\sigma^2 \tag{2.8}$$

$$n_N \langle D^3 \rangle = 3.98 + 15.82\sigma^2, \tag{2.9}$$

where *n* is the number density of the colloidal platelets, σ is the normalized standard deviation, and σ^2 is the polydisperisty of the platelets. The dimensionless density can be converted to the volume fraction ϕ and weight concentration $\phi_w = \rho \phi$, where the mass density of graphene oxide ρ ~ 1.8 g/mL [26],

$$n\langle D^3 \rangle = \frac{\pi}{4} \phi \frac{\langle D^3 \rangle}{\langle D^2 \rangle t} = \frac{\pi}{4} \phi \frac{(1+3\sigma^2)\langle D \rangle^3}{(1+\sigma^2)\langle D \rangle^2 t} = \frac{\pi}{4} \phi \frac{(1+3\sigma^2)\langle D \rangle}{(1+\sigma^2)t}.$$
 (2.10)



Figure 2.5. (a) The absorption spectrums of GO before and after centrifugation within visible light region. All data are measured in a rectangular capillary $(0.2 \times 2 \text{ mm})$. Concentrations are determined by the absorption spectrum based on the 2 mg/ml GO suspension before centrifugation. It gives the critical value of the isotropic and LC phase transition is about 10 mg/ml. All calculations are made at wavelength 600 nm. (b) Full absorption spectrum of GO suspension. (c) Concentrated graphene oxide platelets concentrated at the bottom of a flat capillary after it has been centrifuged at 4320 g for 2.5 hours (top). The concentrated sediment shows birefringence between crossed polarizers (bottom).

A glass cell was filled by capillarity with the high concentration GO sediment. A typical nematic LC texture was observed between crossed polarizers (Figure 2.6). The black areas enclosed by the red ellipses are birefringent, appearing black in both figures, implying that the slow axes of the GO platelets are parallel to either the polarizer or the analyzer in both images, and that the platelets are, on average, oriented perpendicular (edge on) to the glass, i.e., have

homogenous orientation. The GO platelets are dichroic: when the illuminating light is polarized along the plane of the GO platelets (Figure 2.6 (c)), the platelets absorb more light than when the polarization is normal to the plates (Figure 2.6 (d)), allowing us to determine their absolute orientation in the cell. Using a compensator, we have determined that the normal of the



Figure 2.6: Nematic ordering in a graphene oxide suspension. (a) Nematic texture with crossed polarizers in a 25 μ m glass cell. (b) Same region rotated by 90 degrees. The area marked with a red ellipse is black at both orientations, but appears bright at other angles, indicating the platelets oriented homogeneously and parallel to either polarizer or analyzer. (c-d) Same regions with only one polarizer. The dichroism indicates that the graphene oxide platelets orient on average parallel to the polarizer in (c), as indicated schematically by short lines, which represent the side view of disks.

GO platelets is the fast axis (lower refractive index), i.e., the GO platelets have negative refractive index $(n_{II} > n_{\perp})$.

Freeze-fracture images give an intuitive picture of how the GO platelets pack in the nematic LC phase (Figure 2.7): the platelets are relatively flat and are orientationally ordered in the suspension.



Figure 2.7: Freeze-fracture images of the nematic phase formed by GO suspension with the fracture plane: (a) approximately parallel to and (b) making an angle with the platelet plane. They show the GO platelets packing in the LC phase, and also the micron size GO platelets are distinguishable.

As expected for lyotropic LC phases, the magnitude of its birefringence increases as the concentration of the GO suspension gets higher, the measured refractive index anisotropy Δn ranging from -3×10^{-5} to -0.04 with increasing concentration (Figure 2.8). For example, the birefringence of the middle area in the sediment in Figure 2.5 (c) was measured to be -2.4×10^{-4} , and the birefringence of the sample in Figure 2.6 was measured to be -3.3×10^{-3} .


Figure 2.8: Birefringence measurements of GO suspension in a glass cell as concentration increases by water evaporation. After filling a glass cell (25 μ m), it shows grey color texture with low birefringence $\Delta n \sim -0.0033$ initially.

2.4 Stripe Pattern Formed by Graphene Oxide Suspension

An interesting periodic texture of alternating bright and dark bands is observed between crossed polarizers in the high concentration GO suspension cell during slow evaporation of the solvent (Figure 2.9). When the stripes form at the interfaces of a GO suspension and air, they are always aligned parallel to the interface. The bright bands are birefringent (whether they are bright or dark depends on their orientation relative to the polarizer and analyzer), while the dark bands are extinguishing independent of their orientation. The dichroism of the birefringent bands indicates that the platelets are aligned along the stripes, i.e., the director is normal to the stripes. Tilting the cell seems not to affect the appearance of the dark bands. The stripes are not pinned to the boundaries, with the patterns moving as a whole when the cell is squeezed. The stripe patterns remain up to the boiling temperature of water.



Figure 2.9: Stripe patterns formed by GO suspension in a 13 μ m glass cell observed in transmission between crossed polarizers. In the birefringent LC bands, the GO platelets are aligned homogeneously with long axis along the bands.

The stripe periodicity when they first form was measured showing linear dependence on the cell thickness. The stripe periodicities vs. cell thicknesses are listed in Table 2.1, and plotted in Figure 2.10.

Cell thickness d (µm)	Average stripe periodicity p (µm)
40	13
25	5.6
20	5.2
14	2.9
13	2.5

Table 2.1: Stripe periodicity observed in different cell thicknesses.



Figure 2.10: Stripe periodicity as a function of cell thickness.

By adjusting the focal plane of the microscope, we see that there are actually two interdigitated sets of dark bands with alternating depths (Figure 2.11). Defocusing above and below the mid-plane of the cell shows that the texture corresponds to two distinct sets of dark bands that have alternating depths close to the top and bottom substrates respectively.



Figure 2.11: Stripe pattern of graphene oxide formed in a 30 μ m glass cell show different depths. (b) Image in the mid-plane of the cell. Defocusing above (a) and below (c) the mid-plane of the cell. The scale bar is 20 μ m.

There is no obvious difference while tilting the cell, which indicates that the dark lines may be in isotropic phase. To determine whether the dark bands are really isotropic fluid domains, we add polystyrene fluorescent microspheres (53nm in diameter, catalog code: DG06M from Bangs Laboratories, Inc.) to the GO sample (Figure 2.12). Stronger fluorescence is observed at the position of the original dark bands, indicating that the microspheres tend to gather here rather than in the birefringent bands. This suggests strongly that the black bands are indeed isotropic and the birefringent bands liquid crystalline. As the GO concentration in the cell increased due to evaporation of water, the stripes became narrower and the black bands became thinner until they could no longer be resolved. Polyethylene glycol (PEG), an isotropic polymer used as a depletant, was mixed in to the GO suspensions to see whether this would promote stripe pattern formation. It is hard to have the stripe texture consistently in the GO suspension, but with the help of PEG, the stripe patterns are easier to form. However, the stripe periodicity with PEG shows no significant change to that without PEG, following the same linear dependence of the cell thickness in Figure 2.10, neglecting the molar weight of PEG (M_n ranges from 400 to 20,000 were tested). We conclude, on the basis of all of these observations, that the stripe patterns formed in GO suspensions are due to the phase separation of liquid crystalline and isotropic regions.

As the water evaporates from the cell, the stripe pattern gets narrower and the dark bands become thinner until they could no longer be resolved (Figure 2.13), indicating the existence of water play a role in the stripe pattern formation.

Black dots are seen in the stripe texture, especially at the places where the black lines terminate. When the sample is rotated between crossed polarizers, the black dots show non-uniform extinction (Figure 2.14). Therefore, the black dots are different from the dark bands.

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They are formed because the director field is non-uniform at the places where the dark lines terminate.



Figure 2.12: Stripe pattern formed in a graphene oxide suspension doped with 53 nm polystyrene fluorescent microspheres. (a) Stripe pattern observed between crossed polarizers. (b) Corresponding fluorescence image taken with exciting light at 480 nm and emission at 520 nm. Bright regions are where the microspheres tend to gather. Comparison of the two images indicates that the microspheres are concentrated in the dark bands of the images at left and expelled by the bright birefringent LC regions.



Figure 2.13: Time evolution of the stripe pattern as water evaporates. The pattern gets narrower and the dark bands becomes thinner until they could no longer be resolved. The cell thickness is $25.44 \mu m$.



Figure 2.14: Black dots in the stripe pattern change brightness while rotating. (a) and (b) are the same area with 53° rotation relative to each other. The red ellipses are marked at the same areas. The black dots can disappear while rotating, which indicates it is due to the orientation deformation of the directors.

2.5 Summary

We have proven that graphene oxide nanosheets, with ultra-high aspect ratio and polydispersity, can form nematic liquid crystal phase in water suspension at sufficiently high concentration. Dynamic light scattering is used to measure the size and polydispersity of the nanosheets. The phase transition concentration of the suspension from isotropic to nematic phase is determined by their optical transmission spectrum, giving a reasonable value compared to the value calculated by the polydispersed hard disk model.

An interesting stripe pattern of alternating bright and dark bands has been observed between crossed polarizers during slow evaporation of the solvent. As water evaporating, the stripe pattern gets narrower and the dark bands become thinner until they could no longer be resolved. This pattern is formed probably due to phase separation of liquid crystal phase and isotropic phase, suggested by the fluorescent images of the doped suspension with polystyrene fluorescent microspheres.

However, the structure and mechanism of the stripe pattern formation is not clear, and the stripe pattern is unfortunately very hard to form in GO nanosheet suspension. In addition, the small-angle X-ray scattering (SAXS) (beamlines X10A or X20A at Synchrotron Brookhaven National Laboratory, Upton, NY) cannot detect any signal from the GO suspension. At the time of trying to understand the stripe pattern, another platelet suspension of Zirconium Phosphate came into our sight which can form the same stripe pattern in the aqueous suspension. Therefore, we turn to the new material and hopefully can understand the interesting stripe pattern.

CHAPTER 3

High Resolution Small Angle X-Ray Scattering Study of Lyotropic Colloidal Suspension of Monolayer α-Zirconium Phosphate Nanosheets

Small angle X-ray scattering has been used to study the ordering of the lyotropic platelet suspensions [19-25,36]. Another clay material called zirconium phosphate (ZrP) was studied recently, and the aqueous suspensions of monolayer ZrP nanosheets were reported to form liquid crystal phases [36]. We are using the high resolution small angle X-ray scattering (SAXS) to study the order of lyotropic monolayer ZrP platelet suspensions in detail.

3.1 Introduction to α-Zirconium Phosphate Suspension

 α -zirconium phosphate crystals (α -Zr(HPO4)₂·H₂O, abbreviated as α -ZrP) were synthesized by Min Shuai and Prof. Zhengdong Cheng from McFerrin Department of Chemical Engineering, Texas A&M University using the hydrothermal method [37,38]. To make aqueous suspensions of monolayer ZrP nanosheets (ZrP-NS), first a dried powder of α -ZrP disks was uniformly suspended in water via Vortex shaking for a few minutes. Then the same molar amount of n-tetrabutylammonium hydroxide (TBA⁺OH⁻) solution was added to the suspension and followed by Vortex shaking for about 2 minutes and bath sonication for 30 min. The TBA⁺ ions intercalate from the edges of the α -ZrP disks, and diffuse inward to fully exfoliate the disks into monolayer ZrP nanosheets [39] (Figure 3.1 (a) (c)). The thickness of the exfoliated monolayer is known to be 26.8 Å [40], as shown in Figure 3.1 (d), and the density of the ZrP monolayer is calculated to be 1.6 g/mL. This aqueous suspension was then diluted for further experiments with volume fraction ϕ_{mix} , ranging from 0.3% to 24% as listed in Table 3.1. The ZrP-NS suspensions of increasing concentrations under white light and cross-polarized light are shown in Figure 3.2. Except for the most dilute sample, all of the other ZrP-NS suspensions had permanent birefringence ($\phi_{mix} \ge 0.6\%$), indicative of liquid crystalline order. Their average diameter (D = 1.06 µm) and polydispersity ($\sigma = 14\%$) were determined by dynamic light scattering. The phase transition concentration calculated based on Eqn (2.9) and (2.10) give the critical volume concentration to be $\phi_{LN} \sim 1\%$.



Figure 3.1: (a) Structure of crystalline α -ZrP, and an illustration of the intercalation and exfoliation process of α -ZrP layers using TBA⁺OH⁻. (b) Structure of exfoliator TBA⁺OH⁻. (c) The exfoliation process from left to right: A SEM image of the α -ZrP crystal disks, a TEM image of a partially exfoliated α -ZrP disk and a fully exfoliated ZrP nanosheet, cited from [41].

Sample name	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14
Volume fraction	0.003	0.006	0.009	0.012	0.015	0.018	0.021	0.024	0.027	0.030	0.045	0.09	0.18	0.24
$\phi_{ m mix}$														

Table 3.1: Monolayer ZrP aqueous suspensions of increasing concentration.



Figure 3.2: Aqueous suspensions of monolayer ZrP-NS with concentration increasing from left to right (A1- A14), viewed in 6.5mm thick vials between cross-polarizers (top) and without polarizers (bottom). The volume fractions of the samples are shown in Table 3.1. All of the samples except A1 show birefringence. Samples A11-A14 do not show birefringence colors here because of light scattering.

3.2 High Resolution Synchrotron X-ray Study of ZrP-NS Suspensions

To study the liquid crystal ordering of the monolayer ZrP-NS suspensions, SAXS experiments were performed by Yongqiang Shen on beamlines X10A or X20A at Brookhaven National Laboratory, Upton, NY. Suspensions were loaded and sealed into glass capillaries and subjected to the X-ray measurement.



Figure 3.3: SAXS data of ZrP-NS suspensions of different concentrations (scatter points). Peaks of the highest concentration suspension ($\phi_{mix} = 24\%$) is fitted with Lorentzians (black line). The sharp peak at $q = 0.31 \text{ Å}^{-1}$ shows the resolution of the synchrotron. The intensities of the scattering are rescaled for better display.

All the materials of different concentrations were measured (Figure 3.3). A4 (ϕ_{mix} =

1.2%) is the lowest concentration suspension for which Bragg peaks can be barely discerned. As

the concentration increases, the peaks get stronger and sharper, and up to three or four harmonic peaks are visible. However, the Bragg peak of A14, which is the highest concentration we have, is still much broader than the resolution peak of the synchrotron. Therefore, all the ZrP suspensions have short range order. According to the theory reported by Martínez-Ratón and Velasco [42], all the ZrP suspensions in our study should have only nematic phase, align with the short correlations of the nanosheets from the SAXS results.



Figure 3.4: SAXD data of A5-A11 in a log-log scale. The insert shows the first peak of A8 fitted with a Lorentz function and a local power-law background.

To fit the SAXS data, the background should be taken into account to extract the correct peak informations. Basically, all the backgrounds of the X-ray scattering of ZrP suspensions show power-law decay, which are obvious when plotted in a log-log scale (Figure 3.4), as

expected for the platelet suspension [24]. The backgrounds of the suspension of A5-A11 do not overlap each other. Therefore, each scattering peak is fitted with a Lorentz function with a local power-law background, as shown as an example of A8 in the insert of Figure 3.4. However, the scatterings of A12-A14 have the same background (Figure 3.5). In this case, the background can be obtained by spline connecting all the data without peaks, which is called smoothed background. Then the peaks can be fitted by Lorentz functions with the smoothed background. A fitting example is given for A14 ($\phi_{mix} = 24\%$) in Figure 3.3: the scan gave the main peak and its 2^{nd} harmonic peak, both of which can be fitted with Lorentzian peaks with background.



Figure 3.5: SAXS data of A12-A14 with smoothed background.

Based on the fitting method mentioned above, we can get the inter-plate spacings (which will be discussed in the next section) and also the correlations of the ZrP nanosheets in the

suspensions. The full width at half maximum (FWHM) of the harmonic peaks is plotted in Figure 3.6, indicating an almost linear dependence on the harmonic order. It corresponds to a linear change of sheet orientations within a finite-sized domain, i.e., splay (bend) deformation of the nanosheets (director). To compare, a perfect layering order within a finite domain yields a constant width of the harmonic peaks, while for the case that each sheet vibrates around its equilibrium position, the width of the harmonic peaks gives quadratic dependence. Therefore, the short correlation length and the linear dependence behavior of the peak width with the harmonic order suggest a nematic ordering within the ZrP-NS suspension.



Figure 3.6: The width (FWHM) of different harmonic peaks of the monolayer ZrP suspensions as a function of harmonic order.

3.3 Swelling Behavior of the ZrP-NS Suspensions

The inter-plate spacing *d* can be obtained through main peak positions q_0 ($d = 2\pi/q_0$) of SAXS, and plotted as a function of $1/\phi_{mix}$ (black squares in Figure 3.7), which shows a linear swelling behavior. The black line in Figure 3.7 is the asymptote corresponding to uniform swelling $\phi_d = t/d$, where *t* is the thickness of the monolayer ZrP nanosheet, i.e., 26.8 Å. The observed inter-plate spacing is, however, much smaller than that of a uniformly swelled system. The similar observation also reported by Gabriel, et al. in solid acids of the H_nM_nZ₂O_{3n+5} species [24], and Yamaguchi, et al. in niobate system [43,44].



Figure 3.7: Swelling behavior of the monolayer ZrP-NS suspension. Black squares are the interplate spacing of the original suspensions with volume fraction ϕ_{mix} . The black line corresponds to homogeneous swelling with $\phi_d = t/d$. Dash line is at $\phi = 1$.

Since the measured inter-plate spacing is much smaller than a uniform swelled system, we propose that the ZrP nanosheets are not uniformly dispersed in water, and phase separation exists in the suspension. Similar phase separation idea was proposed by Gabriel [24], saying that "Once the maximum swelling is reached, water molecules can no longer be inserted into the interlamellar space and excess water is expelled, leading to phase separation". Assuming the liquid crystal domain exists in the suspension, which is in nematic phase, its volume fraction can be calculated using $\phi_N = t/d$, determined by the measured interlayer spacing *d*, and plotted as a function of the concentration of the entire suspension ϕ_{mix} in Figure 3.8. As concentration of the ZrP-NS suspension increases, nematic domains occupy more space in the suspensions. The ZrP-



Figure 3.8: Volume fraction of the proposed nematic phase ϕ_N as a function of the nanosheet concentration, where $\phi_N = t/d$. There is no experimental data on the dash line, which is drawn roughly connecting the most concentrated data with the limit of $\phi_{mix} = 1$.

NS suspensions, after aging under gravity for a certain time, stratified into clear upper isotropic phase and denser lower liquid crystal phases [36,41], which we propose also to be a result of the phase separation.

3.4 Centrifugation of the ZrP-NS Suspensions

To confirm the phase separation proposal, we centrifuged the material and repeated the SAXS experiments. The original suspensions were loaded into glass capillaries and flame-sealed. Then the glass capillaries went into a Swing Bucket Centrifuge (Lourdes Clinical Centrifuge CHT). We did "weak centrifugation" with relative centrifugal force (RCF) about 7K g for between a few minutes to 1 hour. After centrifugation, there was denser sediment at the bottom of the capillary and clear supernatant on top (Figure 3.9). The volume fraction of the sediment, indicated as ϕ_{sed} , was calculated based on the volume (length) fraction of the sediment compared with the entire suspension: $\phi_{sed} = \phi_{mix} \cdot (V_{mix}/V_{sed})$. After centrifuging, the capillary was immediately loaded into the X-ray diffractometer. The clear supernatant did not show any scattering peak, while the scattering from the sediment shows little change of either the peak position or the correlation length, when compared with the original suspension (Figure 3.10). The inter-plate spacing after weak centrifugation is plotted as open circles in Figure 3.12. These results suggest that the monolayer ZrP suspensions have some empty spaces inside, and phase separation is proposed. Weak centrifugation mostly squeezes the empty spaces out, but not strong and long enough to squeeze the inter-plate spacing.

When the centrifugation is strong and long enough, the inter-plate spacing can be squeezed and therefore shrinks. "Hard centrifugation" was done using a swing bucket centrifuge

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Figure 3.9: (Left) Original suspension of A12 in a flame-sealed glass capillary before centrifugation. (Right) Centrifugation leaves denser sediment at bottom and a clear supernatant on top. Sediment volume fraction is calculated and indicated as ϕ_{sed} .



Figure 3.10: Centrifugation and SAXS result of the main peak of A10. There is no change of either the peak position or the FWHM. The only change is the peak intensity, which is related to the concentration of the sediment and its alignment.

(Sorvall Instruments RC70) with RCF about 108K g (centrifugation speed is 25000 rpm). The original ZrP-NS suspension was loaded into glass capillary and flame-sealed as before, and the hard centrifugation at 108K g lasted for 4 hours. The duration was chosen based on the experiment that after step by step centrifugation at 25000 rpm for 4 hours, the length of sediment didn't change any more. Therefore, it is considered to reach equilibrium at this centrifugation strength. The centrifugation-to-equilibrium process will be referred as "hard centrifugation" throughout this thesis. After centrifugation, the supernatant was carefully removed and the sediment was sealed for further synchrotron SAXS measurements. Figure 3.11 is an example of suspension A11 before and after hard centrifugation. Obviously, compared to original suspension, hard centrifugation squeezes the inter-plate spacing of the ZrP nanosheets. All of the ZrP-NS suspensions in Table 3.1 are centrifuged hard and the resulting inter-spacing are plotted



Figure 3.11: Main peak of A11 before/after hard centrifugation at 108Kg. The inter-plate spacing shrinks after hard centrifugation. In addition, the peak becomes nonsymmetrical. Blue lines are the Lorentz function fittings with power-law background.

in Figure 3.12. After hard centrifugation, the inter-plate spacing shrinks and approaches to the homogeneous swelling line.



Figure 3.12: The swelling behavior of ZrP-NS suspensions after centrifugation based on SAXS experiments. Solid black dots are the original suspensions. Open circle is the spacing after soft centrifugation for a short time (7K g). Blue dot is after hard centrifugation (108K g). Red stars are the results of the ZrP suspensions with different molar ratio of TBA⁺OH⁻. Lines between data points are used to connect the same original suspension.

Hard centrifugation was also done for the ZrP-NS suspensions (A2, A6, A10 and A12) with different concentration RCF: 4.32K g, 8.47K g, 17.28K g, 38.89K g and 69.12K g. The experimental procedure is the same as described above for the centrifugation of 108K g. The equilibrium time lengthens as the centrifugation speed (RCF) decreases. The 4.32K g, 8.47K g, 17.28K g, 38.89K g and 69.12K g centrifugations take 16 hours, 14.5 hours, 12.5 hours, 9.5 hours, and 6 hours respectively. The inter-plate spacing shrinks more and approaches closer to

the homogeneous swelling line with higher centrifugation RCF (Figure 3.13). Figure 3.14 gives the width of the main X-ray scattering peak after hard centrifugation. Except for the very dilute one (A2), which doesn't show any signal from SAXS experiment in the original suspension without centrifugation, the scattering peak width after centrifugation shows small increase with increasing centrifugation strength. Therefore the correlation of the ZrP nanosheets at the LC phase decreases after hard centrifugation, but not much.



Figure 3.13: The swelling behavior of ZrP-NS suspensions after hard centrifugation at different g: 4.32K g, 8.47K g, 17.28K g, 38.89K g and 69.12K g.

To better understand the SAXS results of the ZrP-NS suspension before and after hard centrifugation, FFTEM is used to compare their structure in detail (Figure 3.15). The original

suspension without any centrifugation shows very smooth platelets, while the one after hard centrifugation shows crinkled platelets. If the micro-phase separation exists in the suspension, the centrifugation expels the water domains, the LC domains overlap and the empty spaces are squeezed out in between. Under this assumption, the correlation between the platelets before and after hard centrifugation shouldn't have obvious change. In addition, due to hard centrifugation, the overlapped nanosheet-rich LC domains deform to get compact packing with each other, resulting in the crinkled platelets in FFTEM image, aligns with the SAXS results (Figure 3.14).



Figure 3.14: The main peak width (FWHM) of ZrP-NS suspensions after hard centrifugation at different g: 4.32K g, 8.47K g, 17.28K g, 38.89K g and 69.12K g.



Figure 3.15: Freeze-fracture TEM images of the ZrP-NS suspension before and after hard centrifugation. (a) A6 after hard centrifugation (108K g). (b) Original A12 suspension.

3.5 Ionic Effect on ZrP-NS Suspension Swelling

In the centrifugation-SAXS experiments, removing the supernatant after centrifugation won't disturb the inter-plate spacing of the sediment. However, if the same amount of DI water is added to replace the supernatant, after mixing well with the sediment, the inter-plate spacing increases (Figure 3.16). This is consistent with the phenomena that the ZrP nanosheet swells when it was made into lower concentration by adding DI water. Since there are no ZrP platelet left in the supernatant after centrifugation, the only thing that matters should be the ions. The ions should distribute equilibriumly in both the sediment and the supernatant, so that removing the supernatant won't disturb the inter-plate spacing of the sediment. Since the suspension was made with DI water, α -ZrP crystal and TBA⁺OH⁻, and the ZrP-NS suspensions was measured to have the similar pH ~ 8 for the 1:1 ZrP:TBA ratio, the TBA⁺ ions are proposed to control the inter-plate spacing.



Figure 3.16: SAXS data of A11 after hard centrifugation with the supernatant replaced by the same amount of DI water. The inter-plate spacing increases compared to both the sediment after hard centrifugation and the original suspension.

To explore the ionic effect, the ZrP-NS suspensions were made by varying TBA⁺OH⁻ concentration to reach different ZrP:TBA ratio in the exfoliation process. The suspensions were made with the same ZrP platelet concentration, which is the same as A12 ($\phi_{mix} = 0.09$), called D3 in this situation, changing the ZrP:TBA ratio from 1:1 to 1:0.8 (D1), 1:0.9 (D2), 1:1.1(D4) and 1:1.2 (D5). These ratios were chosen to make sure the ZrP plates can be fully exfoliated and cannot be corroded [39]. We can see that as the concentration of TBA⁺OH⁻ increases, the layer spacing gets smaller and the peak gets sharper (Figure 3.17), which is similar to the effect of higher concentration of the ZrP-NS suspension with 1:1 ZrP:TBA ratio. The suspensions of D1 and D5 were also hard centrifuged with RCF of 108K g, and the data are shown as red starts in Figure 3.12, showing that the inter-plate spacing is squeezed in the same way as the suspension with 1:1 ZrP:TBA ratio.



Figure 3.17: SAXS result of the ZrP-NS suspensions with different ZrP:TBA ratios (1:0.8 – 1:1.2). As the concentration of TBA⁺OH⁻ increases, the inter-plate spacing gets smaller and the peak gets sharper.

Therefore, the TBA⁺ ion concentration probably contributes to the layer spacing of the ZrP-NS suspension. When α -ZrP crystal is intercalated and exfoliated by the same molar amount of TBA⁺OH⁻, the ZrP-NS should consist of half H⁺ ions being exchanged with a monolayer of alternative TBA⁺ ions on either side of each ZrP nanosheet ideally [40]. Since the TBA⁺ cation has a lower charge/area ratio than the nanosheet charge density, it is unable to neutralize all the

negative charges on the ZrP nanosheet. When the ZrP nanosheets are suspended in water, partial TBA⁺ may re-dissolve into water, reaching equilibrium concentration of the TBA⁺ in water and on the ZrP nanosheets. This may be determined by the entire concentration of ZrP nanosheet and TBA⁺ ion of the system. If more water is added into the suspension, the equilibrium breaks, more TBA⁺ cations release into water, and less TBA⁺ leave on the nanosheet, therefore, more unscreened ionized phosphate groups are exposed and cause stronger repulsive interaction between ZrP nanosheets, which leads to larger inter-plate spacing. This model is consistent with the experimental result of the suspensions with different ZrP:TBA ratio. If more TBA⁺OH⁻ are added, the equilibrium will be broken, resulting in more TBA⁺ in the water and also more on the ZrP nanosheets, therefore less unscreened ionized phosphate groups and less repulsive interaction, giving smaller inter-plate spacing.

3.6 Summary

Monolayer ZrP-NS suspensions were made by exfoliating the α -ZrP crystals by adding TBA⁺OH⁻ in water, and then diluting to different concentrations. Monolayer ZrP-NS suspensions have been known to form liquid crystal phases above certain concentration. We study the ZrP-NS suspensions using high-resolution small-angle X-rays scattering. As the nanosheet concentration increases, the inter-plate spacing decreases with increasing correlation. The interplate spacing shows linear swelling behavior, but at a rate slower than expected for a uniformly swelled system. Soft centrifugation of the suspension over a short time at low speed results in little change of the inter-plate spacing. Therefore, micro-phase separation is proposed and requires further demonstration.

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There is no change of the inter-plate spacing after removing the supernatant after centrifugation. However, the spacing increases if the supernatant is replaced by the same amount of DI water. ZrP-NS suspensions with the same ZrP concentration but different ZrP:TBA ratios were also made and measured by SAXS. The result indicates that when more TBA⁺OH⁻ is added the inter-plate spacing decreases with increasing correlation. Therefore, the swelling of the monolayer ZrP-NS suspension is controlled by both the concentration of ZrP and the TBA⁺ ions.

Hard centrifugation of ZrP-NS suspensions at different concentrations was also performed at different speeds until reaching equilibrium, and then followed by SAXS experiments. The inter-plate spacing can be reduced by hard centrifugation, and the harder the centrifuging the smaller the spacing becomes. Together with the experimental results of the next chapter, an explanation is in demand.

CHAPTER 4

Micro-Phase Separation in Lyotropic Colloidal Suspensions of Platelets

4.1 Confocal Observation of Micro-Phase Separation in ZrP-NS suspensions

From the SAXS and centrifugation-SAXS experiments, we know that the layer spacing of ZrP-NS suspensions is much smaller than a uniform swelled system, and soft centrifugation doesn't change the peak position or the FWHM of the suspension. We propose that the micro-phase separation exists in the ZrP-NS suspensions. The ZrP nanosheets are not uniformly suspended in water: the suspension has water-rich domain and ZrP-rich domain. When doing soft centrifugation, the main effect is to expel the water-rich domains out of ZrP-NS rich domains. The inter-plate properties only change when the centrifugation is hard enough to squeeze the nanosheets within the ZrP-rich domain.

Confocal fluorescence microscopy (Nikon A1R) and a water-soluble dye (fluorescein) are used to reveal the detailed structure of the suspensions. Confocal microscopy is achieved by placing a spatial pinhole at the back focal plane before the detector so that out-of-focus light from the sample is eliminated to increase optical resolution and contrast in z direction for 3D imaging. We use Nikon A1R Confocal microscope from the BioFrontiers Advancing Imaging Resource of University of Colorado-Boulder. Fluorescein is a water-soluble dye, so that if there is phase separation, water-rich domains are expected to fluoresce more strongly than the ZrP-rich domains. The intensity of fluorescence of fluorescein can be affected by pH value of the suspension [45]. The ZrP-NS suspension has a pH around 8, where the fluorescein shows very strong fluorescence intensity.

The monolayer ZrP-NS suspensions were mixed with fluorescein powder by Vortex shaking (Thermolyne Type 16700 Mixer). The mixtures were then filled into a glass cell and sealed with mineral oil to prevent evaporation of the water. A 488 nm laser was used to excite fluorescence. Examples of A10 and A11 under confocal fluorescence microscope are shown in Figure 4.1, where individual platelet of 1 μ m diameter is distinguishable. All of the ZrP-NS suspensions we studied were observed to be phase separated into ZrP-rich and water-rich domains. Lower concentration ones had bigger domain size with lower contrast between the two domains.

After the ZrP-NS suspensions aged under gravity for a certain time, they stratified into clear upper isotropic phase and denser lower liquid crystal phases [36,41], proposed to be a result of the separation of the ZrP-rich and water-rich domains. We propose the similar situation may occur in other clay suspensions which deviate from the normal swelling behavior [24,43,44]. For the low concentration suspensions ($\phi_{mix} \leq 9.0\%$), the stratified suspensions can be mixed up by Vortex shaking showing the same phase separation just like the freshly made ones, but the process of the high concentration suspensions seems irreversible, which will be discussed in the following section.



Figure 4.1: Micro-phase separation in ZrP-NS suspensions revealed by confocal fluorescence microscopy and fluorescein. (a) Well-mixed A10 and fluorescein. (b) Well-mixed A11 and fluorescein. Larger water-rich and ZrP-rich domains with lower contrast are observed in lower concentration suspensions. The observation is with a 100x oil immersion objective (NA 1.45).

4.2 Origin of Micro-phase Separation of the ZrP-NS Suspensions

The observed micro-phase separation together with the smaller inter-plate spacing of the ZrP-NS suspensions suggests the existence of a long-range attraction force, resulting in a secondary minimum in the potential energy, which is similar to the void structure [46,47,48,49], gas-liquid condensation [50,51], gas-solid [52,53] and reentrant solid-liquid transition [54,55] phenomena observed in other charged colloidal suspensions.

The DLVO theory, named after B. Derjaguin, L. Landau, E. Verwey and J. Overbeek [56,57], is a classical theory describing the interactions between charged colloidal particles through a liquid medium. The interaction between two particles involves the repulsive screened coulomb interaction (Yukawa potential [58]) and attractive the van der Waals force. If the

repulsion interaction dominates, the suspension is stable, and if it is small, the suspension is unstable and flocculation may occur. In theory, the van der Waals attraction could introduces a secondary minimum with increasing electrolyte concentration. However, the secondary minimum is too shallow and primary minimum has an infinite depth, which suggests the probability of colloid escape from the infinitely deep primary minimum is zero [51]. The DLVO theory has been challenged by the highly charged colloids at low ionic strength in the solvent with the observations mentioned above [46-55]. In addition, the observed inter-particle spacing was inversely proportional to the square root of the electrolyte concentration [59], whereas the DLVO theory predicted a much more rapid variation. In the DLVO theory, the repulsive coulomb interaction decays exponentially as a function of κ , which is called the Debye-Hückel reciprocal length and κ^2 is proportional to the electrolyte concentration, and the van der Waals force is essentially independent of it.

Sogami-Ise theory [60,61] considers the macroion (colloidal particle) charge and their interaction with the counter-ions in the suspension. It proposes that the "Gibbs pair potential leads to repulsion at small inter-particle separations and attraction at large distances, creating a secondary minimum, without taking refuge in a van der Waals attraction" instead of considering Helmholtz free energy as in the DLVO theory. The long-range attraction is a result of coulomb interaction, and thus named as coulombic attraction. Smalley adapts the Sogami-Ise theory on the electrostatic interaction in spherical macroionic solutions to plate particles and successfully explains the swelling behavior of n-butylammonium vermiculite system [62,63].

The long-range coulombic attraction probably also accounts for the phase-separation observed in the ZrP-NS suspensions. It requires further works, for example, measurements of the pair correlation function related to the effective pair potential, or the surface charge density of

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the platelets and free ions in the suspension, and on the other side it requires the corresponding calculations.

4.3 Lens-Shaped Tactoids Formed in High-Concentration ZrP-NS Suspensions

The phase separation is more obvious in high concentration of ZrP-NS suspensions (A13 and A14), to the extent that it is even visible under the optical microscope. The suspension coarsens over days after the suspension was freshly made and the platelets self-assemble into tactoids (Figure 4.2). The stratification of the high concentration suspensions could not be reversed by Vortex shaking or sonication. Actually, shaking or sonication could promote and speeded up the stratification and self-assembling process. Longer aging time gave more pronounced stratification and more regular-shaped structures, which developed into lens-shaped tactoids (Figure 4.3).

Lens-shaped tactoids were observed after about 1 year in high concentration ZrP-NS suspensions (Figure 4.3). Under crossed polarizers, the lens-shaped tactoids show strong birefringence when they are standing up, and are almost black when they are lying down. A quartz wedge compensator was inserted at 45° to the polarizers as shown in Figure 4.3 (c). It is obvious that the lying-down tactoids barely change the birefringence color, while the standing-up or the tilted ones either increase or decrease the birefringence color depending on their orientations: when the long axis of the lens-shaped tactoid is along the slow axis γ , the birefringence increases, and when the long axis is perpendicular to γ , the birefringence decreases. Based on confocal microscopy observation and using an optical compensator, we have determined the plates have negative refractive index, i.e., the slow axis is in the plane of the

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plates. Therefore, the ZrP platelets are oriented in the lens plane. The standing-up lens-shaped tactoids show nonuniform extinction between crossed-polarizers, which indicates the platelets have a non-uniform director field, which will be further confirmed by following experiments.



Figure 4.2: Microstructure evolution of a high-concentration ZrP-NS suspension with time. The suspension with $\phi_{\text{mix}} = 18\%$ observed in transmission with optical microscope with crossed polarizers (top), with only one polarizer (middle), and observed with confocal fluorescence microscope (bottom). Each column indicates the samples with the same aging time (0, 3, 10, and 17 days).



Figure 4.3: Lens-shaped tactoids formed in a high concentration ZrP-NS suspension after about one year ($\phi_{mix} = 18\%$). (a) Optical microscope image of lens-shaped tactoids between crossed polarizers. (b) Corresponding image with only with one polarizer. (c) A wedge compensator is inserted with birefringence increasing from bottom-right to top-left, with a yellow arrow indicating its slow axis γ . The scale is the same for (a-c).

Confocal fluorescence microscopy is also used to show the lens-shaped tactoids in the suspension. Fluorescein was used to mix with the high concentration ZrP-NS suspensions as described before. Figure 4.4 shows a frame of the confocal fluorescence image of the mixture of A13 and fluorescein. A stronger fluorescent background with dark tactoids was observed, as expected. The lens-shaped tactoid is constructed from spherical caps, where the boundary of a cross-section of the tactoid can be fitted with circular arcs. A14 suspension which also forms lens-shaped tactoids are also explored using optical and confocal fluorescence microscopy, and similar lens-shaped tactoids are observed.

The same polystyrene fluorescent microspheres used in the graphene oxide experiments were chosen to add to the ZrP-NS suspensions. The fluorescent nanoparticles don't aggregate by themselves, which was demonstrated by the confocal fluorescence microscopy imaging of the nanoparticles only, showing a uniform fluorescence all over the cell. Based on the SAXS results, the inter-plate spacing of ZrP-NS suspensions varies from 33 Å to 270 Å, which is much smaller

than the diameter of the microspheres. Therefore, the microspheres can only go into the waterrich domain, and shouldn't go into the ZrP-NS rich domains.



Figure 4.4: Confocal fluorescence image of the tactoids. The boundary of the cross-section of a tactoid is fitted with circular arcs (white dash lines).

To do the experiments, A13 suspension with lens-shaped tactoids was mixed at volume ratio of 3:1 with the nanoparticles, which is a water suspension with 1% solid. The mixture was subjected to mix by Vortex shaking for 5 min and followed by water bath sonication for another 5 min, and repeat twice for better mixing. The mixture resulted in a volume fraction of ZrP-NS at about 13.5%, whose inter-plate spacing is still much smaller than the size of the fluorescent nanoparticles. A 50 µm cell was made and the mixture was loaded into the cell and sealed by Fluorinert oil FC-70 (3M) to prevent water evaporation. The cell was loaded into the confocal fluorescence microscope immediately after the cell was made. Figure 4.5 shows a three-

dimensional confocal fluorescence image of the mixture, from which we can see that some fluorescent nanoparticles aggregate into clusters in the suspension, and the fluorescent lensshaped tactoids are observed, in contrast to our expectation, giving us an intuitive and nice view of the lens-shaped tactoids.



Figure 4.5: A three-dimensional confocal fluorescence image of the mixture of A13 and fluorescent microspheres (53 nm in diameter). The scale of x and y direction are both 127.28 µm.

The reason of the discrepancy may due to the weakly adsorbed Dragon Green dye on the fluorescent microspheres, which is a small hydrophobic dye molecule. According to Bangs Laboratories, Inc., the microspheres were internally loaded via a solvent swelling/dye entrapment method with Dragon Green, that most of the dye should be entrapped within the polymer bead matrix; however, it is possible that a very small amount of dye is absorbed to the bead surface.
Organic solvent can cause bead swelling and dye leaching. The TBA⁺ ((C_4H_9)₄N⁺) ion has four 4-carbon-alkyl chains, which is favorable to hydrophobic dye molecules. Therefore, the fluorescent lens-shaped tactoids observed in Figure 4.5 may be actually marked by the hydrophobic Dragon Green dye instead of the nanoparticles.

If necessary, it may be possible to swell the beads in an organic solvent and release the dye to give better fluorescent images in further work. The protocol is proved as:

1. Add 4.9 mL acetone to a 0.1 mL volume of dyed microsphere suspension (10% solids), and mix by Vortex shaking for 2 minutes.

2. Allow the mixture to sit for 2 hours, with periodic shaking or Vortex shaking, while the acetone swells the microspheres and extracts the dye.

3. Pellet the microspheres using a high speed (Eppendorf) centrifuge at ~20,000 rpm for 5 minutes. Decant the supernatant for usage. If necessary, it may require centrifugation at a higher speed or for a longer period of time to remedy the presence of microspheres.

4.4 Freeze-Fracture TEM Study of the Lens-Shaped Tactoids

The platelet orientation within the lens-shaped tactoids was observed directly using FFTEM, as shown in

Figure 4.6. The ZrP platelets were relative flat and oriented with the director **n** along the surface normal of the lenses. These tactoids have a non-uniform director field with homeotropic anchoring. The local plate orientations show clearly that there is bend deformation especially near the tip, suggesting nematic-like ordering inside the tactoids. In addition, the micron-sized thickness of the lens-shaped tactoid (2*r*) gives ~ 3000 platelets with average inter-plate spacing 38.79 Å, which is much larger than the N ~ 32 platelets from the SAXS correlation length

assuming perfect layering stacking. This result is qualitatively consistent with the non-uniform platelet director field observed in the tactoids.

A more detail analysis of the platelet ordering is done based on the FFTEM images (Figure 4.7). The standing-up tactoids boundary is fitted with a circle, and the long axis of the tactoid is a straight line connecting the two tips in Figure 4.7 (a). The visible platelet orientations are measured relative to the long axis of the tactoid along different lines perpendicular to the long axis, which are plotted as scatter points in Figure 4.7 (c). The lines in Figure 4.7 (c) are the calculations based on the circles intersecting at the same points where the boundary circle and the long axis intersect. The measurements and the calculations are relative close. Therefore, the lens-shaped tactoid has the nematic bispherical internal structure.



Figure 4.6: Freeze-fracture TEM images of lens-shaped tactoids in the high-concentration ZrP-NS suspension A13. (a) Tactoids at low magnification. (b) A tilted tactoid with higher magnification. The boundary between its cross-section and outer surface is outlined. (c) The cross-section of a tactoid at higher magnification. The boundary is outlined to show the escape of deformation near the tip.



Figure 4.7: Orientation analysis of the platelets within a lens-shaped tactoid based on the freezefracture TEM images. (a) Tactoids at low magnification. The lower boundary of a tactoid is fitted by a circular arc and the long axis of the tactoid is a straight line connecting the two tips (pink), which are also indicated in (b). (b) The cross-section of the boundary-fitted tactoid at higher magnification, which is also the same tactoid as

Figure 4.6 (c). The visible platelets are highlighted with short cyan lines. (c) Plate orientation vs. distance from the long axis of the tactoid. The measurements of the plate orientations are along different lines (1-5) perpendicular to the long axis. The scatter points are the measurements from (b), and the lines are the calculations based on the circles which have the same intersection with the outer boundary and the long axis.

4.5 Shape Analysis of Lens-Shaped Tactoids

Nematic tactoids formed in suspensions of rod-like colloidal particles have been studied extensively in a variety of systems since Zocher [64] from 1920s, ranging from suspensions of vanadium pentoxide [64,65], aluminum hydroxide [66], tobacco mosaic virus [67], fd virus [68], and F-actin [69] to carbon nanotubes [70]. Tactoids formed by colloidal plates, in contrast, have only recently been observed by Verhoeff, Lekkerkerker, et al. in gibbsite suspensions [71,72, 73]. In plate-like colloidal systems, the observed shapes depend on their sizes, with large size one tending to form spheres with a radial director field, while smaller tactoids are lens or oblateshaped with a uniform or asymmetric director field [71].

The tactoid shape is determined by a competition between surface energy and bulk elastic free energy. The surface energy is $\sigma = \gamma + w \sin^2 \theta$, where γ is the bare surface tension, w is the anchoring strength coefficient, and θ is the angle between the surface normal and the director field at the surface. Plate-like particles for entropy reasons prefer homeotropic anchoring, implying w > 0.

The aspect ratio of the tactoids of A13 ($\phi_{mix} = 18\%$) measured from the optical microscope images is plotted as a function of tactoid diameter in Figure 4.8. The expectation of the non-uniform director field should have a decreasing aspect ratio with increasing size [71]. The tactoids in this sample have a relative uniform aspect ratio with a slow decreasing slope. The observed spread in aspect ratio is probably due to the fact that the image is a 2D projection of an anisotropic 3D objects. Although the measurement were collected from the standing-up lenses, it is hard to guarantee their orientations. The aspect ratio of lens-shaped tactoids with a uniform director field should be larger than the largest aspect ratio found for that with a nonuniform

director field. So the aspect ratio of uniform lens-shaped tactoids should be larger than 4, giving a lower bound for the dimensionless anchoring strength $\omega = w/\gamma > 1.414$, where $R/r = 2\sqrt{\omega}$ for lens-shaped tactoids with a uniform director field, aligns with the expectation of a flat tactoid with a sharp rim $\omega > 1$, according to the Wulff construction [74].



Figure 4.8: Size measurements of the lens-shaped tactoids. (a) Aspect ratio R/r as a function of diameter (2*R*) of lens-shaped tactoids in a cell of the ZrP-NS suspension with $\phi_{\text{mix}} = 18\%$ (one year old sample). The red line is a least-squares fit: R/r = 3.62-0.044R. (b) Histogram of tactoid diameters (2*R*).

Since the platelets are oriented parallel to the tactoid surface at the boundary with perfect anchoring, only bare surface tension counts. The surface energy of a drop of radius *R* scales as γR^2 , and the bulk elastic free energy scales as *KR*, the crossover from a spherical drop to an elongated drop happens when $R < K/\gamma$, when the bulk elastic free energy dominates. The largest lens-shaped tactoid observed in our experiment is $R = 21.1 \,\mu\text{m}$, giving a lower bound for $K/\gamma \sim 13.5 \,\mu\text{m}$, which is larger than the reported value in gibbsite system [71,72]. Furthermore, when looking at the FFTEM images near the tip of the lens-shaped tactoid in

Figure 4.6 (c), an escape of the bend deformation is observed: instead of forming a perfect lens-shaped rim with strong splay deformation, the plates reorient to form a cusped edge, lowering the bulk elastic free energy, at the expense of increasing the surface energy. Therefore, the lower bound of K/γ should be even higher than our previous estimate.

4.6 Stripe Patterns Formed by ZrP-NS Suspensions

As mentioned in Chapter 2, stripe patterns are formed in graphene oxide nanosheet suspensions in a glass cell. The same stripe patterns are also observed in monolayer ZrP-NS suspensions. A12 with volume fraction of 9% is the one that can form stripe patterns very easily. Lower concentration suspensions can also form stripe patterns but take longer. The stripe patterns of ZrP-NS suspension mentioned below are all formed by A12 in glass cells.

After a cell filled with A12, it appears dark between crossed polarizers but becomes bright when the cell is tilted, indicating homeotropic alignment of the nanosheets. The cell stays black if the cell is sealed well and left undisturbed. In cells that are not sealed perfectly, stripe patterns of alternating bright and dark bands develop as water evaporates slowly from the sample, usually along the interface of the ZrP-NS suspension and air (Figure 4.9). The bright bands are birefringent while the dark bands are extinguishing independent of their orientation as the stripes of graphene oxide.

With the help of a wedge compensator, we determine the ZrP platelets aligned along the stripes in the birefringent bands. The birefringence of wedge compensator increases from bottom-right to top-left in Figure 4.10. Figure (a) and (b) are the same stripes oriented parallel or perpendicularly to the slow axis of the compensator. It is clear that when the stripes are along γ ,

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birefringence increases, and when the stripes are perpendicular to γ , birefringence decreases. We have determined the plates have negative refractive index, i.e., the slow axis is in the plane of the plates. Therefore, the ZrP platelets are oriented with their long axes along the stripes.



Figure 4.9: Stripe pattern development as water evaporates slowly from a 40 μ m glass cell viewed between crossed polarizers (a-c). The stripe pattern develops along the interface of the ZrP suspension and air (black region on the right). The black bands become narrower as the sample continue to dry. (d) Stripe pattern at higher magnification. The scale bar is 100 μ m.



Figure 4.10: Stripe pattern with crossed polarizers and a wedge compensator. The slow axis is indicated as γ with an arrow, and the birefringence of the compensator increases from bottom-right to top-left. (a) When the stripes are perpendicular to γ , the birefringence decreases. (b) When the stripes are along γ , the birefringence increases.

Stripe patterns can also be induced in the originally homeotropic areas by squeezing the cell (Figure 4.11). The induced stripes are oriented along the flow direction, which is further confirmed by squeezing the same area with different flow directions (Figure 4.12). Pumping the suspension in a flat capillary with a syringe also induces stripes along the flow direction (Figure 4.13).



Figure 4.11: Stripes induced by squeezing the cell. (a) A 40 μ m glass cell filled with a ZrP-NS suspension before squeezing. The black areas are due to the homeotropic alignment of the platelets. (b) The same area after squeezing the cell.



Figure 4.12: Squeezing the cell to induce the flow in different directions (red arrow) in the same cell as in Figure 4.11. Stripes are induced along the flow direction.



Figure 4.13: Stripes induced in a 100 μ m thick, flat capillary by pumping the suspension along the capillary. Red arrows indicate the flow direction.

The stripe pattern formed by ZrP-NS suspensions show exactly the same phenomena as that formed by GO suspensions. Besides the ones described above, the stripes also show no pinning effect to the boundaries, with the patterns moving as a whole when the cell is squeezed. The stripe periodicity when they first form depends linearly on the cell thickness. The dark bands also have two interdigitated sets with alternating depths. Therefore, we conclude that the stripe patterns formed in both the GO suspensions and the ZrP-NS suspensions are the same phenomena and have the same physical origin.

4.7 Phase Separation and Stripe Pattern Formation

Fortunately, the ZrP-NS suspensions can be easily explored by confocal fluorescence microscopy with the help of the water-soluble dye fluorescein. The stripe patterns were also explored in this way. A glass cell was filled with a ZrP-NS suspension A12 mixed with

fluorescein powder. After allowing the water to evaporate for a few hours, the cell with stripe patterns was observed with transmission depolarized microscope (Figure 4.14 (d)). Then the cell was explored by a confocal fluorescence microscope (Figure 4.14 (a-c)). Water-rich domains with stronger fluorescence are observed, corresponding to the black bands in the stripe pattern. The birefringent bands observed with white light correspond to ZrP-rich domains where dim fluorescence with predominantly homogenous alignment of the platelets is observed. The confocal fluorescence microscopy thus confirms that the stripe pattern is a result of phase separation of the lyotropic colloidal platelet dispersions. Careful inspection of the confocal fluorescence scan gives a detail structure of the stripes (Figure 4.14 (a)). Phase separation is observed from the top substrate with alternating ZrP-rich bands and water-rich bands. As going deeper into the cell, the water-rich bands get narrower. Another set of water-rich bands appears at the middle of the cell, interdigitating with the set starting from the top substrate. As approaching the bottom, the set of water-rich domain which starts from the top substrate terminates and the other set gets broader and reaches the bottom substrate finally. A cartoon illustrating the newly formed stripe pattern is shown in Figure 4.14 (e).



Figure 4.14: A newly formed stripe pattern of ZrP-NS suspension explored with confocal fluorescence microscopy. (a-c) Confocal fluorescence microscopy scans from the top surface into the cell of newly formed stripes in a 20 μ m thick glass cell; imaged 0 μ m, 9.75 μ m, and 14.95 μ m from the top surface of the cell. (d) Stripe patterns of the same cell between crossed polarizers. (e) A cartoon illustrating the newly formed stripe pattern. The black regions indicate the water-rich domain, and the short lines represent the side view of the platelets.

Another cell filled with the ZrP-NS suspension A12 mixed with fluorescein powder was also inspected in the same way. Expect evaporating for a few hours to form a "fresh" stripe pattern, this cell evaporated for a day to allow the stripes drying for a while. The "drying" stripes were then scanned by confocal fluorescence microscopy (Figure 4.15). Phase separation is observed from the top surface (Figure 4.15 (a)), but each water-rich band splits into two quickly and gets connected as going away from the substrate (Figure 4.15 (b)). As going deeper into the cell, another set of the water-rich bands appears, interdigitating with the set starting from the top surface (Figure 4.15 (c)). The two sets overlap for a longer distance until the first one terminates. The one approaching the bottom substrate splits into two and gets connected again near the substrate. The structure is symmetric across the cell, like the "fresh" stripes. A cartoon illustrating the corresponding "drying" stripe pattern is shown in Figure 4.15 (e).



Figure 4.15: A "drying" stripe pattern of ZrP-NS suspension explored with confocal fluorescence microscopy. (a-c) Confocal fluorescence microscopy scans of a 40 μ m thick striped cell after stripes formed and are allowed to dry for about one day; imaged 0 μ m, 7.70 μ m, and 18.15 μ m from the top surface of the cell. (d) Stripe pattern of the same cell between crossed polarizers. (e) A cartoon illustrating the corresponding drying stripe pattern. The black regions indicate the water-rich domain, and the short lines represent the side view of the platelets.

In conclusion, the stripe structure evolves over time: in a newly formed stripe pattern,

two separate sets of individual water domains were observed, while two continuous water

domains were observed after the stripes evolved and dried for a day. Two sets of the water

domains are interdigitated with alternating depths, consistent with the observation under transmission depolarized microscope.

4.8 Undulation Instability and Stripe Pattern Formation

The formation of the stripe is proposed to be triggered by an undulation instability [75,76]. The cell-dilation and layer-compression strain due to evaporation of the water is relaxed by the nanosheet undulations and promoted by the presence of water-rich domains, which rearrange to intercalate between the undulations and constrained by anchoring of the interface. Similar periodic stripe patterns are observed in the meniscus of smectic membranes due to undulations of the smectic-air interface [77]. As the water evaporates, the water-rich domains get narrower and become connected, and eventually shrink until they disappear. The stripes induced by squeezing are also the result of undulation instability, responding to dilation of the cell. The flow rearranges the undulations so that the two domains are along the flow direction, to reduce the energy cost by deforming the undulations and the inter-platelets spacing by the non-uniform flow velocity in the cell. The similar mechanism is also responsible for the stripes formed by pumping in the capillary, where the undulations are thought to be caused by roughness in the capillary walls.

The stripe patterns are also observed in graphene oxide aqueous suspension, which is discussed in Chapter 2, showing exactly the same properties as those observed in ZrP-NS suspension. The stripe patterns formed in both suspensions probably have the same physical origins, i.e., phase separation and undulation instabilities. However, the GO suspensions are hard to be detected using the same fluorescent method. The inter-plate spacing of GO suspensions

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was measured by SAXS according the work by Z. Xu and C. Gao [78]. The inter-plate spacing is smaller than expected for a uniformly swelled system with the fitting thickness of the GO nanosheet to be 0.46 nm instead of 1 nm. Therefore, the similar phase separated probably exists in the GO suspension and contributes to the stripe pattern formation. Compared for the phase separation in ZrP-NS suspension, where the phase separation is more obvious with larger deviation from the normal swelling (4.2 Å /26.8 Å), the phase separation of GO suspension is less obvious (0.46 nm/1 nm), which may be the reason why it is harder to observe the stripe pattern in the GO suspension. With the depletant PEG, the tripe pattern becomes easier to form as a result of increased isotropic domains. In addition, the stripe periodicity with PEG shows no significant change to that without PEG, following the same linear dependence of the cell thickness, neglecting the molar weight of PEG (M_n ranges from 400 to 20,000 were tested). It indicates the significant role of the phase separation to the stripe pattern formation.

The stripe pattern formation may need enough correlations between the nanosheets, which require the concentration of the nanosheet-rich domains to be above certain value. In the ZrP-NS suspensions, low concentration ones can only form the stripe pattern if the cell is left long enough time for more water evaporation, compared to A12 which can form the stripes very quickly. For GO suspension, adding PEG as depletant will not dilute the liquid crystalline nanosheet domains (or may further increase the concentration in the LC domains by grabbing more water), but increasing the volume of the isotropic domains, promoting the stripe pattern formation.

4.9 Flexopolydispersity

The undulations of the nanosheets may contribute to flexopolydispersity, a new concept that is first proposed here indicating the slow internal rearrangement of sheets of different size to optimize their spacing and thereby maximize entropy. Polydispersity exists in both graphene oxide and ZrP nanosheets, the strain of n(r) due to the undulations causes a size flux J(r), where

$$J(r) = f \nabla (\nabla \cdot \boldsymbol{n}). \tag{4.1}$$

Since $J(r) = -D\nabla \delta m$, where m(r) is the size distribution of the nanosheets, it gives

$$\delta m(r) = -f/D(\nabla \cdot \boldsymbol{n})$$

Therefore, the strain of n(r) squeezes out larger particles and promotes depletion interaction. The depletion stabilizes defect cores with the phase separation.



Figure 4. 16: Schematic illustration of flexopolydispersity: the strain of n(r) squeezes out larger particles and promotes depletion interaction.

4.10 Summary

Micro-phase separation in lyotropic colloidal suspensions of platelets is further explored in this chapter. With the help of the water-soluble dye fluorescein, the water-rich isotropic domains and ZrP-rich liquid crystal domains in the ZrP-NS suspensions are distinguishable under a confocal fluorescence microscope. Lower concentration suspensions have bigger domain size with lower contrast between the two domains. The two domains distribute uniformly inside the suspensions. After aging, the low concentration ZrP-NS suspensions (at the concentration of A12 or below) stratify into isotropic phase on top and LC phase at the bottom, but the suspensions can come back to the state of uniformly distributed two domains after Vortex shaking, just like the freshly made ones. The observed micro-phase separation together with the smaller inter-plate spacing of the ZrP-NS suspension suggests the existence of a long range attraction force, resulting in a secondary minimum in the potential energy, which may be explained by Sogami-Ise theory where the long-range attraction is a result of coulombic attraction.

The stratification process of the high concentration ZrP-NS suspensions (A13 and A14) is irreversible. The high concentration ZrP-NS suspensions coarsen over days after the suspensions are freshly made and the platelets self-assemble into tactoids. Lens-shaped nematic tactoids with the director field normal to the nematic-isotropic interface are observed after long aging time. Quantitative analysis of the shape of tactoids gives estimated ratios of the bulk elastic constant and bare surface tension to the anchoring strength.

Slow water evaporation and squeezing-dilating of the inter-plate spacing of the ZrP-NS suspension result in periodic stripe patterns appearing as alternating bright and dark bands

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between crossed polarizers in a cell or capillary. Confocal fluorescence microscopy reveals that the two alternating bands are actually ZrP-rich liquid crystal domains and the interdigitating water-rich isotropic domains. The formation of the stripe pattern is proposed to be triggered by undulation instability. The stripe patterns are also observed in graphene oxide aqueous suspension, which show exactly the same properties as those observed in ZrP-NS suspension. Therefore, the stripe patterns formed in both suspensions are proposed to have the same physical origins, i.e., phase separation and undulation instabilities.

CHAPTER 5

Dynamic Localized Reorientation of Liquid Crystals by a Photo-Spun Spot on an Azobenzene-based Self-Assembled Monolayer

Liquid crystals show a facile response to applied fields and interfacial forces, a combination enabling the development of a variety of useful electro-optic devices, such as displays. In this context, the control of liquid crystal (LC) alignment by surfaces is of key importance and has been studied extensively. The alignment of liquid crystals in devices is typically achieved by making the cell substrates anisotropic, as introduced in Chapter 1. In particular, photoaligment mechanisms based on the trans-cis-trans photoisomerization cycle of azobenzene and its derivatives have been widely investigated and applied, with the realignment of LCs over large areas achieved by azo-doping of the surfaces [79,80,81,82] or of the liquid crystal itself [83]. Here we investigate the dynamics of photo-reorientation of liquid crystals in a surface-induced process controlled by changing the polarization direction of an actinic laser beam focused to a small spot on a high-sensitivity azobenzene-based self-assembled monolayer (azo-SAM).

5.1 Introduction to Azobenzene-based Self-Assembled Monolayers for Liquid Crystal Alignment

Azobenzene group undergoes a reversible transformation between *trans* and *cis* isomers (Figure 5.1), which is called photoisomerization [84]. The *trans* isomer is more stable and

optically anisotropic, while the *cis* isomer is the excited state and optically isotropic. Under the illumination of linearly polarized light (LPL) of proper wavelength, the *trans* isomer which is parallel to the polarization of the light absorbs more light and is excited to the *cis* form. Then the *cis* isomer relaxes back to the *trans* form with random oritentation. As a result of the *trans-cis* photoisomerization circle, a preferred orientation can be induced perpendicularly to the polarization of the illumination light, which is called the angular hole burning effect [85]. On the other hand, the aligned azobenzene groups can be randomized either by illuminating with circularly polarized light (CPL) or by thermal relaxation [86].



Figure 5.1: *Trans* and *cis* isomers of azobenzene group.

One of the robust and high effective methods to incorporate the azobenzene group to liquid crystal alignment is by using an azo-SAM [82,88-90], which is obtained by covalent bound the molecules onto glass substrate surfaces and through silicon-oxygen bond formation and a crosslinking polysiloxane network (Figure 5.2) [87]. A derivatized methyl red azo-dye dMR, i.e., 2-(4-Dimethylamino-phenylazo)-N-(3-triethoxysilane-propyl)-benzamide, was designed and synthesized by Prof. D. M. Walba's group in the Department of Chemistry at the University of Colorado, and has been studied extensively [88-92]. This molecule was designed to include an aminoazobenzene group, a short alkyl chain, and a triethoxysilane group. The

triethoxysilane group forms a SAM on the glass substrate and the azobenzene group is tilted from the surface normal and aligns rod-shaped LC molecules in contact with the chromophores by surface anchoring, giving an excellent planar alignment layer [81,88,89,90]. The alkane connection is sufficiently flexible to allow photoisomerization-induced anisotropy. When irradiated with linearly polarized light of wavelength $\lambda \leq 600$ nm, azobenzenes undergo photoisomerization [81] with the resulting long axis perpendicular to the incident polarization.



Figure 5.2: Silane-based self-assembled monolayer formation process. The ethoxysilane groups are hydrolyzed into silanol groups and then covalently bonds to the hydrolyzed glass substrate and adjacent molecules by the condensation of water. [91]

Nematic LC in contact with dMR azo-SAM shows planar alignment, with the nematic director **n**, the local average orientation of the LC molecular axes, parallel to the mean molecular long axis of the dMR [81]. The dMR azo-SAM system has record high photosensitivity for dynamic LC realignment, with a 90° photo-driven reorientation of *n* achieved for a fluence F as small as $F \sim 6 \text{ mJ/cm}^2$, corresponding to only ~ 1.3 photons of 450 nm linearly polarized light

absorbed per dMR molecule [89]. Comparison of the orientational photoresponse of bare dMR azo-SAMs, made using high precision birefringence measurements, with the induced reorientation of nematic LC in contact with the SAM, shows that the SAM-LC coupling is visco-elastic, with the LC response lagging when there are sudden changes in polarization direction of the incident light [90].



Figure 5.3: Chemical structure of 2-(4-Dimethylamino-phenylazo)-N-(3-triethoxysilane-propyl)benzamide molecule (dMR), the azobenzene precursor to form azobenzene-based self-assembled monolayer (Azo-SAM).

5.2 Preparation of DMR Azo-SAM

The preparation of dMR Azo-SAMs is given as follows, which was provided by Dr. Y.

W. Yi, and also be described in detail in Dr. G. Fang's Thesis [92]:

1. Dissolve 272 mg dMR in 70 ml toluene (8.2 mM). Then add 0.25 ml n-butyl amine as

a catalyst. Heat the solution to 45°C in a water bath.

2. Clean the glass slides: Clean the slides with soap water, and then immerse and sonicate the slides in acetone, isopropanol alcohol, and DI water one by one for 5 min each. Blow-dry the cleaned glass slides with pure nitrogen gas.

3. Make piranha solution by add sulfuric acid to hydrogen peroxide at the volume ratio of 3:1. Immerse the dried clean glass slides in the piranha solution for 30min at 90°C. This is to further remove any organic contamination and hydrolyze the glass surface to form covalent bonds with the triethoxysilane group in dMR.

4. Rinse the piranha-treated glass slides with DI water and blow-dry with pure nitrogen gas, then immerse them in the dMR solution at $45 \,^{\circ}$ C for 90 min.

5. Take the slides out and rinse with toluene until the toluene does not absorb color (dMR) from the glass substrate to remove the physically attached dMR on the slides. Then blow-dry the glass slides with pure nitrogen gas.

6. Anneal the glass slides in an oven in air at 115°C for two hours.

DMR solution can be used several times over a year by adding few drops of n-butyl amine into the solution eachtime. It has been demonstrated by AFM that a smooth and uniform monolayer is formed on the slides using this method [89]. The dMR-SAM on glass slide can be tested using UV/Vis, which should give an absorption peak position ~ 446 nm with the peak height ~0.014. It can also be tested using the water contact angle measurement, which gives 60° - 66° [91]. For further reference, the contact angle for OTE-SAM should be above 90°, and for GLYMO-SAM should be around 54°.

5.3 Experimental Apparatus

The purpose of this project is to investigate the dynamic localized photo-reorientation of LC by dMR azo-SAM. The experiments employ cells with the room temperature nematic LC E31 [93] in a gap of thickness $d = 2.53 \mu m$ between two glass plates, one of which is coated by a dMR-SAM and the other by an octadecyl-triethoxysilane (OTE) SAM. The OTE-SAM gives homeotropic orientation of the LC (*n* normal to the surface) [87], while the dMR-SAM gives planar orientation (*n* parallel to the surface), stabilizing the so-called hybrid alignment characterized by splay-bend distortion of *n* in the plane containing *n* and *z* as indicated in Figure 5.4 (b). The local principal optic axis of the cell is along the intersection of the surface. The SAM plates were assembled into cells, and filled with the LC by capillarity at temperature T ~ 80 °C, well in the isotropic phase. Upon cooling into the nematic phase, cells not yet exposed to actinic light exhibited a Schlieren texture, indicating random planar orientation of *n* on the SAM surface, with local but not global in-plane alignment.

In order to study the local photo-reorientation of the nematic, an actinic laser ($\lambda = 532$ nm) is focused to a small spot (4.3 µm in diameter) in a region of the LC cell with nearly uniform director field. The actinic laser beam is initially circularly polarized through a quarter-wave plate, and then passed through a linear polarizer whose orientation can be rotated at a controlled rate using a motor. The cell is illuminated with red-filtered white light ($\lambda > 600$ nm, which does not induce any additional isomerization) and observed using depolarized transmission optical microscopy, as sketched in Figure 5.4. This enables visualization of the azimuthal distribution of the hybrid splay-bend plane of the nematic LC and thus of *n* at the SAM surface. To analyze these reorientation dynamics, we note that the laser focal spot and the length scales of the ring

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patterns are large compared to the $d = 2.53 \,\mu\text{m}$ sample thickness. We therefore assume that the hybrid LC structure is locally maintained throughout the experiment and that we may describe the local LC orientation using the single azimuthal variable $\phi(r,t)$.



Figure 5.4: (a) Schematic diagram of the experimental setup. (a) The actinic beam is a green laser ($\lambda = 532$ nm), focused to a small spot ($a = 2.15 \mu m$ in radius) by an objective lens on the dMR -SAM. The polarization p is rotated using a polarizer mounted on a motor. Red light is used to visualize the nematic director field in the cell. (b) Cell structure: Nematic liquid crystal is sandwiched in the $d = 2.53 \mu m$ gap between the dMR-SAM and the OTE-SAM, forming a cell with hybrid alignment.

5.4 Measurements of Nematic LC Orientation Dynamics on Azo-SAM

A typical reorientation sequence is shown in Figure 5.5, induced by a 115.4 μ W actinic beam incident on the SAM (green spot). The LC texture is viewed between crossed polarizer P and analyzer A, with ψ the orientation of the actinic polarization (measured from P), and ϕ the

director orientation at the focal spot (measured from A), which we take to be at r = 0. The initial director orientation on the as-synthesized dMR SAM is quite uniform (Figure 5.5 (a)), with nnearly parallel to A, at an angle $\phi \sim -\pi/10$. The laser is switched on and **p** rotated from $\psi = 0$ to $\psi = \pi/4$, giving the bright red region surrounding the green spot in Figure 5.5 (b) with an intensity corresponding to the maximum probe light transmission $T(\phi)$ observed, implying, since $T(\phi) \propto \sin^2 2\phi$, an orientation of *n* at the origin of $\phi(r=0,t) = \pi/4$. The bright region is bounded by a dark ring at $r_1 \sim 18.07 \ \mu m$ with $\phi(r) = 0$. Continuous rotation of the actinic polarization is then commenced, with $\phi(r = 0)$ increasing at a constant rate (in this case, with an angular frequency, $\omega = 4.2 \text{ sec}^{-1}$). Figure 5.5 (c) shows the evolution of the LC orientation as the polarization is rotated through $\pi/2$ up to $\psi(t) = 3\pi/4$, during which n(r = 0) also reorients through 90°, generating a second dark ring in which $\phi(r) = \pi/2$, expanding in radius to $r_2 \sim 13.38 \,\mu\text{m}$ when $\psi(t)$ has reached $3\pi/2$. The continuous reorientation near the beam center thus generates a radial pattern of reorientation in the form of concentric, approximately ring-shaped dark bands. Four dark bands appear for each complete rotation of the polarization, with the *j*th dark band first appearing at r = 0 at time $t_i = j(T/4)$, where $T = 2\pi/\omega$. The generation and expansion of successive dark rings, corresponding to director orientations $\phi_i(r,t) = (j-1)\pi/2$, is shown in Figure 5.5 (b). The radius of the *j*th dark band $r_i(t)$, measured from the origin along the radial yellow line indicated in Figure 5.5, is plotted in Figure 5.6.

The first dark band (j = 1) appears at r = 0 for $\psi = 0$ (red open circle in Fig. 3) and then expands monotonically in radius with increasing ψ (red solid circles), out to $R_1 \sim 18.07 \mu$ m, after which this ring expands more slowly, with oscillations in the radius. The j = 2 ring appears when $\psi = \pi/2$ and expands in similar fashion but to a smaller saturation radius, and with an oscillation in radius that is 180° out-of-phase with that of the j = 1 ring. The appearance and growth of the next four rings are similar, with successive rings saturating at smaller radii, and each oscillating out of phase with its neighbors. For j < 6, the rings expand smoothly from the origin. The j = 6ring, on the other hand, emerges and expands from the origin at $\psi = 5\pi/2$, but when the radius reaches $r \sim 5.43 \mu m$, crosses the orientation of maximum torque relative to ψ and therefore slips, shrinking back to r = 0. The ring reappears half a cycle later, after which the saturation radius has increased such that the j = 6 ring can follow the behavior of the earlier rings and continue to grow without slipping. The j = 7 ring appears and slips for eight cycles before expanding,



Figure 5.5: Concentric rings appear in the cell as the nematic director field is wound up in response to the azimuthal reorientation of the dMR-SAM by the actinic laser. The polarization of the actinic laser \mathbf{p} ($\lambda = 532$ nm at 115.4 µW), indicated by a green arrow, is rotated clockwise at $\omega = 4.2 \text{ sec}^{-1}$. The white arrows indicate the director orientation of the LC within the beam focus. (a) The actinic laser is shone on the cell and (b) the polarization rotated clockwise, resulting in the generation of concentric ring pattern. A new dark ring appears whenever the polarization is rotated through another 90° (bottom row). (c) Rotating the polarizer continuously through 90° generates a second dark ring (top row). (d) Sketches of the corresponding LC director field for selected frames. (e) Schematic illustration of the orientation of the actinic laser polarization \mathbf{p} and the LC director orientation with respect to the polarizer P and analyzer A used for visualizing the texture.

preventing the growth of the j = 8 ring. The j = 8 ring appears transiently during this time but can form only once the j = 7 ring has stopped slipping. Once it appears, the j = 8 ring continues to slip, and is the last ring that light of this intensity can generate.

5.5 Dynamics Modeling of Liquid Crystals Localized Reorientation by Azo-SAM

We begin the analysis of the ring pattern by assuming that ring growth is driven principally by photo-induced reorientation of the part of the SAM closest to the center of the laser, in the absence of slipping presenting the boundary condition $\phi(a, t) = \psi(t) = \omega t$. The radial variation of the orientation as a function of time outside this central region (r > a) is then given by the orientational diffusion equation $D\nabla^2 \phi(r,t) - \partial \phi/\partial t = 0$ in cylindrical coordinates, where $D = K/\gamma$ is the reorientational diffusion constant of the liquid crystal, *K* is the Frank elastic constant in the one elastic constant approximation, and γ is the orientational viscosity. We first consider a case with a uniform initial LC director orientation of $\phi(r,0) = 0$ everywhere in the cell except for $r \le a$, where the orientation is fixed at ϕ_a . The orientation at r > a evolves as [94]

$$\phi_0(r,t) = \Phi_0 + \frac{2\Phi_0}{\pi} \int_0^\infty \frac{e^{-Du^2t}}{u} \frac{J_0(ur)Y_0(ua) - Y_0(ur)J_0(ua)}{J_0^2(ua) + Y_0^2(ua)} du.$$
(5.1)

We may use the asymptotic expansions of the Bessel functions, and only consider the first term, obtaining

$$\phi_0^c(r,t) = \phi_a \sqrt{\frac{a}{r}} \operatorname{erfc}(\frac{r-a}{2\sqrt{Dt}}), \qquad (5.2)$$

Now we allow the orientation at the inner boundary to increase linearly in time, as $\phi_a = \psi(a, t) = \omega t$. The response of the director field at radius *r* is found by integrating Eqn. (5.2), yielding for the case where the rings are expanding freely at early times

$$\phi_o(r,t) = \omega \int_0^t \sqrt{\frac{a}{r}} \operatorname{erfc}\left(\frac{r-a}{2\sqrt{D(t-s)}}\right) ds, \qquad (5.3)$$

giving,

$$\phi_0(r,t) = \omega_1 \sqrt{\frac{a}{r}} \left[t + \frac{(a-r)^2}{2D} + \frac{e^{-\frac{(a-r)^2}{4Dt}}(a-r)t}{\sqrt{\pi Dt}} + \frac{(a^2 - 2ar + r^2 + 2Dt)\operatorname{erf}(\frac{a-r}{2\sqrt{Dt}})}{2D} \right].$$
(5.4)

This solution is plotted as a magenta curve in Figure 5.6 for each ring.

The asymptotic dependence of $\phi(r,t)$ at large *t* is described well by the static orientation field $\phi_s(r)$ of a nematic confined between two concentric cylinders (black curves, Figure 5.6). In the steady state, the LC orientation can be calculated by minimizing the free energy density [13]: $\nabla^2 \phi_s(r) = 0$. With the cylindrical boundary conditions $\phi_s = \phi_{inner}$ at $r = R_{inner}$ and $\phi_s = \phi_{outer}$ at r= R_{outer} , we obtain the static solution

$$\phi_s(r) = \phi_{outer} + \Delta \phi_s \frac{\ln(r/R_{outer})}{\ln(R_{inner}/R_{outer})}$$
(5.5)

where $\Delta \phi_s = \phi_{inner} - \phi_{outer}$. The inset in

Figure 5.8 shows a fit of $\phi_s(r)$ to the experimental saturation radii with the director azimuth $\phi_{outer} = 0$ at $R_{outer} \sim R_I$, the outermost ring, and $\phi_{inner} = 7\pi/2$ at $R_{inner} \sim R_7$, showing that this model describes the overall final structure of the concentric ring pattern well.

After the initial regime where the rings are expanding freely, the ring growth is given by a combination of $\phi_0(r, t)$ of Eqn. (5.4) and $\phi_s(r)$ of Eqn. (5.5), yielding

$$\phi(r,t) = \omega \left[\int_{t-\tau_c}^t \phi_0(r,t-s) \,\mathrm{d}s + \int_{\tau_c}^t \phi_s(r) \,\mathrm{d}s \right],\tag{5.6}$$

where we set $R_{outer} = R_j$ of each ring to be the saturation radius in Eqn. (5.5) and τ_c marks the crossover from the initial free expansion of the rings to slower growth and eventually saturation. At times $t > \tau_c$, the azimuthal angle of the LC is the cumulative result of two processes: the first



Figure 5.6: Ring radius *r* vs. polarization azimuth of the actinic beam ψ during ring winding shown in Figure 5.5. The plot shows the appearance and subsequent expansion of eight different dark rings. The 8th ring appears only sporadically, indicating that the torque from the azo-SAM driven by the actinic laser is not sufficient to sustain this ring. The radial oscillations of the rings are evidence of SAM reorientation by off-center light. The solid curves are theoretical fits. The predictions for ring-growth at early times based on Eqn. (5.4), are shown in magenta. The fits at later time, based on Eqn. (5.6), are shown in black. The fits yield an orientational diffusion constant of the liquid crystal E310f D = 5×10^{-10} m²/s.

is the initial reorientation, from time t- τ_c to t, during which the rings expand freely, and the second is the orientation generated earlier from time 0 to t- τ_c expanding slower and eventually saturation. Fits based on Eqn. (5.6) are shown as black lines in Figure 5.6.

5.6 Surface Anchoring and Torques

As more and more rings are generated near the middle, the torque from the elastic distortions increases until it becomes comparable to the torque that can be sustained by the surface anchoring provided by the SAM at the center. The maximum number of rings has been achieved saturates when the newest ring in the center slips (for example, the j = 8 ring in Figure 5.6). Assuming the director reorientation distribution along **z** is linear, the hybrid LC cell with cell gap *d* can be treated approximately as a cell with gap d/2 that has uniform planar alignment. The elastic torque due to the radial distortion of the LC director field can be expressed as

$$\Gamma_e = K \frac{\partial \phi_s(r)}{\partial r} \cdot S = K \frac{d}{2} 2\pi r \frac{\partial \phi_s(r)}{\partial r} = \frac{\pi dK \Delta \phi}{\ln(R_{inner}/R_{outer})}.$$
(5.7)

The surface anchoring torque of the SAM is given by

$$\Gamma_s = \int \frac{\partial W(\phi)}{\partial \phi} dS = \int_0^a \frac{1}{2} W_\phi \sin[2(\phi(r) - \psi)] \cdot 2\pi r \, \mathrm{d}r, \tag{5.8}$$

where W_{ϕ} is the surface anchoring coefficient, ψ is the orientation preferred by the dMR-SAM molecules exposed to the actinic light, and $\phi(r)$ is the LC azimuthal orientation induced across the focused laser spot.

The surface anchoring strength at the focus of the beam can be calculated by equating the elastic and anchoring torques, giving an estimate of the average surface anchoring between dMR-SAM and E31 [95], within the focus under the illumination dose of 591.8 J/cm² per π rotation of the actinic laser $W_{\phi} \sim 4.2 \times 10^{-4}$ J/m². For comparison, the anchoring energy of a

weakly-illuminated dMR-SAM (about 10 mJ/cm² dose illumination (450 nm) with fixed polarization) was found previously from twist angle measurements on uniformly twisted cells of 5CB to be on the order of $W_{\phi} \sim 10^{-6}$ J/m² [89]. The anchoring strength of rubbed nylon is on the order of 10^{-5} J/m².

The experiments were repeated with varying laser intensity, at fixed rotation frequency $(\omega = 4.2 \text{ sec}^{-1})$. The surface anchoring coefficient shows a logarithmic dependence on illumination dose, as shown in Figure 5.7. According to Sonin [96], the surface anchoring coefficient W_{ϕ} depends linearly on the surface order parameter. Birefringence measurements on bare dMR-SAMs also show that above the saturation illumination dose, the order parameter of



Figure 5.7: Surface anchoring strength W_{ϕ} vs. illumination dose J_D of the actinic laser for the "steady ring patterns". The polarization rotation frequency is $\omega = 4.2 \text{ sec}^{-1}$. The surface anchoring depends logarithmically on the illumination dose. The red line is a least-squares fit of the form $W_{\phi} = 9.1 \times 10^{-5} \cdot \log J_D - 8.3 \times 10^{-5}$.

the monolayer depends logarithmically on the actinic laser dose [86], behavior which is consistent with our observation.

In the picture presented so far, the LC molecules within the central, illuminated region rotate in response to photo-induced reorientation of the chromophores of the SAM. LC molecules outside this region are elastically coupled to those in the laser beam, but the degree to which they reorient is limited by the molecules even further away that tend to retain their original orientation. The balance between the anchoring torque from the dynamically changing azo-SAM in the center and the elastic torque associated with distorting the nematic director field ultimately limits the spatial extent of the photo-induced reorientation, generating a radial pattern of reorientation of finite extent in the form of concentric rings (Figure 5.5).

While assuming that the actinic light is confined to a circular spot on the SAM is convenient and leads to a reasonable description of the overall behavior, this simplification ignores the fact that the laser has a Gaussian profile, convoluted with the diffraction from the objective aperture, which truncates the incident actinic laser before focusing it onto the sample. In principle, we therefore photo-induce reorientation effects at larger radii. The SAM reorientation at larger radii is the main reason that the ring growth is finite. For example, once the polarization is rotated to $\pi/2$, the 1st ring, which has an orientation of $\phi = 0$, is not favored and stops growing; when the polarization is rotated beyond $\pi/2$, for example, $\pi/2+\delta$, the LC molecules in the first ring experience a negative torque and the ring shrinks instead of growing further. However, the intensity away from the central spot is small, and not strong enough to overcome the continual reorientation near the beam center, so that the ring will not shrink and disappear. The fluence is sufficient, however, to reorient the azo-SAM enough to perturb the ring structure, causing oscillation in the ring radius. When the optical polarization favors the LC orientation halfway between two adjacent rings, say j and j+1, the distance between these two rings increases. At the same time the orientation in the gap between neighboring pairs, j-1/j, and j+1/j+2, is not preferred, so the distance between these pairs decreases. In other words, alternating gaps expand while the other ones shrink. The surface anchoring in the vicinity of the *j*th ring can be estimated based on the amplitude of the undulations, as follows.

The director orientation in the region containing the jth ring varies approximately as

$$\phi_{Aj} = \phi_s(a) \frac{\ln(r/R_1)}{\ln(a/R_1)} + A_j \cos[\pi \frac{r-R_j}{L_j}],$$
(5.9)

where $\phi_s(a) \frac{\ln(r/R_1)}{\ln(a/R_1)}$ is the static orientation within this region given by Eqn. (4) between $\phi_j - \pi/4$ and $\phi_j + \pi/4$, where ϕ_j is the orientation of the director field in the *j*th ring, L_j is the distance between the $\phi_j - \pi/4$ and $\phi_j + \pi/4$ contours, and A is the oscillation amplitude. The elastic free energy density is

$$f_e = \frac{\kappa}{2} \left(\frac{\partial \phi_{Aj}}{\partial r}\right)^2 = \frac{\kappa}{2} \left\{\frac{\phi_s(a)}{\ln(a/R_1)} \frac{1}{r} - A_j \frac{\pi}{L_j} \sin[\frac{\pi}{L_j}(r - R_j)]\right\}^2,$$
(5.10)

and the total elastic free energy of this annulus is

$$F_e = \frac{\pi dK}{2} \int_{R_j - L_j}^{R_j + L_j} \{ \frac{\phi_s(a)}{\ln(a/R_1)} \frac{1}{r} - A_j \frac{\pi}{L_j} \sin[\frac{\pi}{L_j} (r - R_j)] \}^2 r \, dr.$$
(5.11)

The surface anchoring energy density is

$$f_{w} = \frac{W_{j}}{2} \sin^{2}(\phi_{Aj} - \frac{(2j-1)\pi}{4}) = \frac{W_{j}}{2} \sin^{2}[\phi_{s}(a)\frac{\ln(r/R_{1})}{\ln(a/R_{1})} + A_{j}\cos\left[\pi\frac{(r-R_{j})}{L_{j}}\right] - \frac{(2j-1)\pi}{4}], \quad (5.12)$$

and the total surface anchoring energy in this annulus is

$$F_{w} = \int_{R_{j}-L_{j}/2}^{R_{j}+L_{j}/2} f_{w} \, 2\pi r \, dr.$$
(5.13)

This integral can be evaluated from $R_j - L_j/2$ to R_j and then from R_j to $R_j + L_j/2$ using the small-angle approximation.

The total energy $F = F_e + F_w$ may be minimized with respect to the oscillation amplitude A_i as

$$\frac{\partial F}{\partial A_j} = \frac{\partial F_e}{\partial A_j} + \frac{\partial F_w}{\partial A_j} = 0$$
(5.14)

Analysis of the oscillation amplitude of the rings shown in Figure 5.6 yields $W_2 = 3.5 \times 10^{-6} \text{ J/m}^2$ at $R_2 = 15.714 \text{ }\mu\text{m}$, $W_3 = 4.9 \times 10^{-6} \text{ J/m}^2$ at $R_3 = 12.222 \text{ }\mu\text{m}$, $W_4 = 1.12 \times 10^{-5} \text{ J/m}^2$ at $R_4 = 10.282 \text{ }\mu\text{m}$, $W_5 = 1.8 \times 10^{-5} \text{ J/m}^2$ at $R_5 = 7.566 \text{ }\mu\text{m}$, $W_6 = 3.7 \times 10^{-5} \text{ J/m}^2$ at $R_6 = 6.79 \text{ }\mu\text{m}$, $W_7 = 1.0 \times 10^{-4} \text{ J/m}^2$ at $R_7 = 3.298 \text{ }\mu\text{m}$.

The experimental azimuthal profile at selected time derived from intensity variation of the corresponding ring patterns are plotted in

Figure 5.8. The azimuthal distributions ϕ vs. radius *r* based on the model of Eqn. (5.4) when $\psi = (j-1)\pi/2$ are also shown. The experimental $\phi(r)$ profiles are almost flat near the center, achieving $\phi(r) \sim \psi(a)$ for r > a with much less curvature than the model predicts. This discrepancy is confirmation that the optically-induced surface torque is being applied not only at $r \le a$ but over a much larger region surrounding the central spot. Thus the model of Eqn. (5.4) describes the director reorientation well only for $r \approx a$, i.e., where $\phi(a,t) \approx \psi(t)$. The orientational diffusion constant of $D = 5 \times 10^{-10} \text{ m}^2/\text{s}$ derived from Figure 5.6 is about one order of magnitude larger than the expected value [95,97], a discrepancy that may be due to synchronous, off-center reorientational by the photo-buffed SAM.



Figure 5.8: LC azimuth distribution vs. radius at different times during ring winding. The experimental data are shown as dots. For example, the green dots show the orientation at t_2 when $\psi = \pi/2$ and the 2nd ring starts to appear; the yellow dots show the director azimuth at t_3 when $\psi = \pi$ and the 3rd ring starts to appear. The solid magenta lines are calculations of $\phi(r,t_j)$ vs. r based on Eqn. (5.4). The black solid curves is a fit of the steady state using Eqn. (5.5) at the time when $\psi = 3\pi$. The vertical dashed lines indicate the average radii of the rings. Inset: The steady state solution ϕ_s as a function of *r* for the ring pattern. The symbols correspond to the measured radii of the first 7 rings shown in Figure 5.6. Each data point represents the average radius in the final steady state around $\psi = 14\pi$, with the oscillation amplitude represented as an error bar. The red line is a fit to the final state based on Eqn. (5.5).

5.7 Long-term Collective Interactions

The concentric ring patterns can be maintained by keeping the actinic laser turned on with fixed polarization direction after the patterns are formed, or can be unwound by reversing the rotation direction of the polarization. If instead the laser is turned off, most of the ring pattern remains unchanged, but the very innermost rings, which were slipping during the winding up process, may disappear. The remaining rings do not disappear even after many weeks at room temperature, in strong contrast with the behavior of bare dMR-SAMs, where the azimuthal orientation of the molecules is randomized by thermal diffusion within just a few minutes or hours after the photo-buffing laser is turned off [90]. The orientational stability of the azo-SAM in contact with LC has been reported previously [89,90] and is ascribed to the long-term collective interactions between the orientationally ordered SAM and the director field of the LC, which prevents the SAM molecules from relaxing because of the local ordering of the LC molecules. Concentric ring patterns have been observed and studied in freely-suspended smectic-C films, driven by an in-plane rotating electric field [98] or mechanically, using a rod inserted through the middle of the film to provide an anchoring torque at the center [99]. Similar phase winding and slipping phenomena are observed, but in films there is no substrate to provide orientational memory once the driving torque is removed.

In addition to forming concentric ring patterns, when adjacent rings are close enough together they may break during the winding process, leading to the formation of a disclination



Figure 5.9: Disclination pairs are formed after rings break with rotating actinic light and maintained after the laser off.
pair (s = \pm 1), an effect prevoisly observed in freely-suspended films [99]. Such defects usually annihilate if the actinic laser is left on, even if the polarization direction is fixed, by traveling in opposite directions around the pattern center. If the laser is turned off, the disclination pair is frozen in space (Figure 5.9), similar to the stable ring pattern with actinic light off, and does not annihilate.

5.8 Nematic LC Reorientation by Azo-SAM Near the N-I Phase Transition

Besides the reorientation experiments of nematic LC on azo-SAM discussed above, more reorientation experiments were carried out using the same setup (Figure 5.4) to learn the reorientation ability of the dMR azo-SAM. The nematic LC near phase transition of nematic to isotropic and near nematic to smectic were studied. The reorientation of smectic phase will be reported in the following sections. 5CB and 8CB were used for this purpose. The phase diagram of 5CB is Iso (35.3 °C) N (4.1 °C) Cr, and 8CB is Iso (40 °C) N (33.5 °C) SmA (21.1 °C) Cr [100]. 2 µm dMR-OTE cells were used for these experiments. With the boundary confinement, the phase transition temperature is different.

Above 34 °C in a 5CB-dMR-OTE cell (checked 34 °C and 34.7 °C) near the nematic to isotropic phase transition, two rings can be wound up with rotation. However, as the second ring approaches the first ring, the two rings annihilate when they touch each other. In an 8CB-dMR-OTE cell, when the temperature is close to N-Iso phase transition, fewer rings can be wound up and the rings are thicker and less stable: the rings will disappear after blocking the actinic laser. At high temperature near the N-Iso transition, the elastic constants are small and thus the elastic free energy is small, but the thermo fluctuation is large and the Brownian motion becomes

stronger at high temperature, which can overcome the elastic energy distortion. Therefore, if the actinic laser is blocked and doesn't contribute to hold the pattern, the wound-up rings could be erased by thermo energy. As lowering the temperature in the ring winding experiments, more and thinner rings will be wound up, and the rings are more stable at lower temperature (Figure 5.10).



Figure 5.10: Ring winding in an 8CB-dMR-OTE cell at (a) 37 °C (b) 35 °C (c) 32 °C at the areas nearby to each other. As temperature decreases from isotropic phase, more and thinner rings can be wound up, and the rings are more stable.

5.9 LC Reorientation by Azo-SAM in Smectic Phase and Near N-Sm Phase Transition

Smectic phase between a homeotropic surface and a random homogenous surface forms focal-conic texture under crossed polarizers. I tested the focal-conic textures of smectic phase with the same reorientation setup (Figure 5.4). An 8CB-dMR-OTE cell at room temperature is put on the sample holder, which is in the SmA phase, and the green actinic laser is focused on with rotating polarization. No reorientation effect was observed even with highest laser power. Therefore, the anchoring of dMR is not strong enough to deform smectic layers.

However, what happens if approaching the N-Sm phase transition temperature? An 8CBdMR-OTE cell at different temperatures is tested. When 8CB is in the N phase, it can be reoriented and wind up rings as expected. As approaching the SmA phase, the liquid crystal is frustrated by adopting stripes. The liquid crystal can still be reoriented in the stripe pattern, but not anymore after cooling to the SmA phase with focal-conic texture. Figure 5.11 shows the changes of the ring pattern with the actinic laser on and rotating while decreasing temperature from N to SmA phase. As approaching the N-SmA phase transition temperature, the rings become asymmetric, i.e., the adjacent rings approach each other alternatively at opposite position, and stripes start to show up. The liquid crystal can still be reoriented in the stripe pattern. Finally 8CB goes into SmA phase with focal-conic texture, and cannot be reoriented by



Figure 5.11: Wind up rings using the rotating actinic laser in an 8CB-dMR-OTE cell near the N-SmA phase transition with decreasing temperature. (a) Wind up rings in nematic phase at 29.7°C. (b) As approaching the phase transition temperature, the rings become asymmetric. (c-e) As further cooling down, the rings adapt to the stripe pattern, and still have the ability of reorientation. (f) After cooling down to SmA phase (29.4 °C), where the focal conic textures show up, the LC molecules cannot be reoriented any more. All of the pictures are the snapshots from the videos recorded.

the dMR azo-SAM any more.

Keep the 8CB-dMR-OTE cell at 29.6 °C, when the stripes form near the N-SmA phase transition, shine the actinic laser on the dMR-SAM coated substrate and rotate the polarization clockwise to watch the reorientation. The LC molecules can be reoriented and rings are wound up, but asymmetric (Figure 5.12). Stripy texture is still distinguishable in the reorientation area (Figure 5.12 (a1) (b1) (c1)), compared to the normal nematic orientation shown in Figure 5.5.



Figure 5.12: Asymmetric concentric rings are wound up in the stripes in a 8CB-dMR-OTE cell near the N-SmA phase transition temperature $(29.6 \,^{\circ}\text{C})$ in response to the rotating azimuthal orientation of the dMR-SAM driven by actinic laser. Starting from (a), shine the actinic laser on the cell and rotate the polarization clockwise, successively every 90°, until to (g) when the rings break. The subsequence frames in between are shown in the consequent frames of (a1), (b1) and (c1). (h) is a frame of the rings as the actinic laser keep rotating after rings break.

The stripe pattern with hybrid boundary conditions near the N-SmA transition was first

observed by Cladis and Torza [101]. The explanation of these stripes was given by Allender,

Hornreich and Johnson [102,103]. The hybrid anchoring conditions impose a bend deformation of the director field, which is forbidden in the smectic phase. As approaching to the smectic phase, twist and bend elastic constants are divergent near the N-SmA phase transition, with the bend elastic constant divergent at a much larger speed, as introduced in Chapter 1. Therefore, the energy cost for the hybridity is so large that the system becomes unstable and tries to escape it by adapting a periodic modulation at the expense of producing the periodic splay and twist deformations. However, the nematic can still be reoriented in our experiments in this situation. After the transition to the smectic phase, a focal-conic texture develops, and cannot be reoriented by dMR azo-SAM anymore.



Figure 5.13: The follow-up experiment of the same ring pattern in Figure 5.11 which goes into SmA phase with increasing temperature: After the N-SmA phase transition, and stay in the SmA phase (28.8 °C) for 8 min, increase the tempreture to N phase (34.7 °C). The ring pattern recovers.

After the wound-up-rings go into the SmA phase (28.8 °C) and stay for 8 min, increase the temperature to nematic phase again, rings can be recovered (Figure 5.13). Therefore, the long-term collective interactions and memory effect between the orientationally ordered azo-SAM and the director field of the LC still exists even when the LC is in smectic phase.

5.10 Cholesteric LC Reorientation by Azo-SAM

From the results of previous sections, the nematic director can be wound up in response to the rotating azimuthal orientation of the dMR azo-SAM driven by actinic laser, but the smectic layer structure is too strong to be reoriented. How about cholesteric (chiral nematic) phase N*, which doesn't have real layer structure, but have the chirality pitch?

First, a room temperature cholesteric material *p*-Ethoxybenzal-*p*-(β -methylbutyl) aniline (EBMBA for short) was tested. The phase diagram of the active form of EBMBA was given as iso (60 °C) N* (15 °C) Cr, and the pitch was measured to be 0.223 µm [104]. A 2 µm EBMBA-dMR-OTE cell was made and tested with the rotation setup (Figure 5.4). The cell was observed to show fan-shaped focal conic texture in N* phase in the hybrid cell. No reorientation effect was observed in the EBMBA material for all N* temperature range with the highest laser power.

Sample name	C1	C2	C3	C4	C5	C6	C7	C8
CB15 concentration (wt%)	1.49	3.1	3.98	6.35	8.7	9.71	12.97	19.99
Pitch (µm)	8.72	4.19	3.27	2.05	1.50	1.34	1.00	0.65

Table 5.1: Mixtures of 5CB and chiral dopant CB15 with different concentrations

To study whether the reorientation is related to the pitch of the N* phase, mixtures of 5CB with different concentrations of chiral dopant CB15 were made, which are listed in Table 5.1. The pitches are calculated using $p = 1/(\text{HTP}\cdot\text{C}_{\text{chiral}})$, where HTP is the helical twisting power of the chiral dopant (1/13 μ m⁻¹ for CB15), and C_{chiral} is its weight concentration [13].

In a thin hybrid cell, the N* twist can be frustrated in the confined geometry, depending on the dimensionless confinement ratio C = d/p where *d* is the cell thickness and *p* is the natural N* pitch. The experiments are performed on the same rotation setup, and the hybrid cells are constructed using the similar dMR-OTE cells with the N* materials listed in Table 5.1.

In a 2 μ m dMR-OTE hybrid cell, sample C1 ($p = 8.72 \mu$ m) and C2 ($p = 4.19 \mu$ m) show Schlieren texture, where the confined geometry completed unwinds the N* pitch. Applying the actinic laser with rotating polarization, rings were wound up, as expected similar to that in nematic experiments. No obvious difference was observed with different rotating directions (clock-wise or counter-clock-wise).

Sample C4 with $p = 2.05 \mu m$, in a 2 μm dMR-OTE hybrid cell, is deformed between the planar and homeotropic substrate but the pitch is not completely unwound. The cell shows



Figure 5.14: Nested ring patterns are wound up in a 2 μ m N*-dMR-OTE cell filled with mixture C4 ($p = 2.05 \mu$ m). The actinic laser polarization is rotated CCW.

frustrated chiral nematic texture with bluish color and some fingerprint texture. Applying the actinic laser with rotating polarization, the material can be easily reoriented, and nested ring pattern which was formed probably by "cholesteric finger" were wound up (Figure 5.14). Figure 5.14 was taken with counter-clock-wise (CCW) rotation of the laser polarization.

Clock-wise rotation (CW) was also tested, which didn't show any ring pattern. It causes moving fingers and uniformly reoriented background around with a short rotating time. More detailed study is required, including the detailed winding process, and also the comparison of different rotation directions at longer time.

Sample C5 ($p = 1.50 \mu m$), C6 ($p = 1.34 \mu m$) and C7 ($p = 1.00 \mu m$) were also tested using the same method. Fan-shaped focal-conic textures were observed in these materials in the dMR-OTE cells. For sample C6 and C7, the fan-shaped focal conic is stable and easy to form in the 2 μm dMR-OTE cell. However, the sample C5 in a 2 μm dMR-OTE cell form frustrated chiral nematic texture with bluish color with some fingerprints (see background of Figure 5.15 (c)), while focal conics tend to form with slowly cooling from isotropic phase. The superstructure of the twist is distinguishable in sample C5 and C6 with visible fingerprints in the fans (Figure 5.15 (d)), while C7 only showing smooth fan-shaped focal conic texture. Applying the actinic laser with rotating polarization, the cholesteric material can be reoriented. A focal conic structure with the center located at the laser spot were wound up with CCW rotation of the laser polarization (Figure 5.15 (a) and Figure 5.16 (a)). CW rotation ends up with a fan-shaped focal-conic texture around the laser spot (Figure 5.15 (b) and Figure 5.16 (b)). As expected, the superstructure of fingerprints is distinguishable in the wound-up pattern in C5 with periodicity around 1.5 µm, but not in C7. A thicker C5-dMR-OTE cell (5.5 μ m) is also tested which shows similar phenomena, with the fingerprint periodicity around 2 μ m to 2.5 μ m.

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The mixture C8 with the shortest pitch ($p = 0.65 \mu m$) shows smooth fan-shaped texture in the hybrid cell. It cannot be reoriented by dMR azo-SAM, same as the results of EBMBA, which has an even tighter pitch.



Figure 5.15: Different focal-conic patterns with fingerprints are wound up in a N*-dMR-OTE cell filled with C5 ($p = 1.50 \mu$ m) by different rotating directions: (a) CCW (b) CW. The periodicity of the wound-up fingerprint texture is measured to be 1.57 μ m. (c) The same area imaged using a depolarized optical microscopy with white light illumination after rotation. The pattern on the right corresponds to (a), and the one on the left corresponds to (b). (d) Fingerprint focal conic texture at the same area of (c) after heating to isotropic and then slowly cooling down to room temperature with 0.2 °C/min cooling rate.



Figure 5.16: Different focal-conic patterns are wound up in a N*-dMR-OTE cell filled with C7 ($p = 1.00 \mu m$) by different rotating directions: (a) CCW (b) CW.

In conclusion, dMR azo-SAM is capable to reorient the cholesteric material with long pitch. Short pitch one has too strong twisting power to be reoriented. The reorientation may also relate to the dimensionless confinement ratio, which needs further experiments with varying cell thickness and helical pitch. The CW and CCW reorientations result in different patterns, which may depend on the chirality of the chiral material. Experiments with different chirality materials may be interesting. Further analysis of the wound-up pattern is also needed.

5.11 Summary

Liquid crystal materials in a hybrid cell constructed by dMR azo-SAM and OTE-SAM on two glass substrates were studied by a focused actinic laser with a rotating polarization inside a small circular area on the dMR Azo-SAM. Putting the highly photo-sensitive dMR azo-SAM with such a photo-spun spot in contact with a nematic liquid crystal results in winding up a set of nest rings of splay-bend nematic director field. The azimuthal reorientation of the ring-growth process can be calculated using Laplace transformation to solve the diffusion equation. The ring pattern stops to grow and the nematic director starts to slip finally with certain illumination dose, where the director distribution of the concentric ring pattern can be calculated as a steady state.

The ring pattern stops to grow until the required elastic torque exceeds that of the surface coupling. The surface anchoring coupling at the laser focus spot can be calculated from the torque balance. And the experiments and calculations are repeated with different laser powers, giving a logarithm dependence of the anchoring coefficient with the actinic laser dose as expected.

The off-focus light exists due to the Gaussian profile of the laser and diffraction due to the objective aperture in the setup, causing oscillating rings at all radii, because the off-center beam intensity is weak and cannot produce strong enough torque to drive the orientation of the LCs rotating continuously. Quantitative analysis of the oscillations enables measurement of the off-focus coupling between the azo-SAM and nematic LC. Another reorientation effect of the off-focus light is the almost uniform LC orientation distribution near the center during the winding process.

Smectic liquid crystals cannot be reoriented by dMR azo-SAM, where the layer structure is too strong to be deformed by the coupling between the azo-SAM and LC at the surface. The liquid crystal material near the nematic to isotropic and the nematic to smectic phase transitions are also tested. Near the I-N transition temperature, the elastic deformation tends to be overcome by thermal fluctuation. Near the N-SmA transition temperature, the wound-up rings become asymmetry and adapt to the stripe patterns in a hybrid cell. The LC molecules can still be reoriented in the stripe pattern near the phase transition temperature. Cholesteric LC materials with different pitches are also studied with some preliminary results. The reorientation of cholesteric LC depends on its pitch, with long pitch ones reorientable but short pitch ones not. Different rotating directions end up with different patterns, which may depend on both the chirality of the material and the rotating direction.

Bibliography

- [1] C. Mauguin, Bull. Soc. Fr. Miner. **34**, 71 (1911).
- [2] J. Cognard, *Alignment of Nematic Liquid Crystals and Their Mixtures*, Mol. Cryst. Liq. Cryst. Suppl. (1982).
- [3] M. Geary, J. W. Goodby, A. R. Kmetz, and J. S. Patel, J. Appl. Phys. 62, 4100(1987).
- [4] S.-C. A. Lien, P. Chaudhari, J. A. Lacey, R. A. John, and J. L. Speidell, IBM Journal of Research and Development 42, 537 (1998).
- [5] A. J. Pidduck, S. D. Haslam, G. P. Bryan-Broan, R. Bannister, and I. D. Kitely. Appl. Phys. Lett. **71**, 2907–2909 (1997).
- [6] J. L. Janning, Appl. Phys. Lett. 21, 173 (1972).
- [7] M. B. Feller, W. Chen, and Y. R. Shen, Phys. Rev. A 43, 6778 (1991).
- [8] R. Sun, J. Guo, X. Huang, and K. Ma, Appl. Phys. Lett. 66, 1753 (1995).
- [9] P. Chaudhari, J. Lacey, J. Doyle, E. Galigan, S.-C. A. Lien, A. Callegari, G. Hougham, N. D. Lang, P. S. Andry, R. John, K.-H. Yang, M. Lu, C. Cai, J. Speidell, S. Purushothaman, J. Ritsko, M. Samant, J. Stöhr, Y. Nakagawa, Y. Katoh, Y. Saitoh, K. Sakai, H. Satoh, S. Odahara, H. Nakano, J. Nakagaki, and Y. Shiota, Nature **411**, 56 (2001).
- [10] S. C. Jain and H.-S. Kitzerow. Appl. Phys. Lett. 64, 2946 (1994).
- [11] I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH (2003). D. Demus and L. Richter, *Textures of Liquid Crystals*, Weinheim (1978).
- [12] A. Rapini and M. Papoular, J. Phys (France), 30 Coll. C4, 54 (1969).
- [13] P. G. De Gennes, J. Prost, *The Physics of Liquid Crystals*(2nd ed.), Oxford Univ. Press, NewYork (1993)
- [14] D. Demus and L. Richter, *Textures of Liquid Crystals*, Weinheim (1978).
- [15] P. Oswald and P. Pieranski, *Nematic and Cholesteric Liquid Crystals*, Taylor & Francis (2005).
- [16] D. W. Allender, R. M. Hornreich, and D. L. Johnson, Phys. Rev. Lett. **59**, 2654 (1987).
- [17] H. Hakemi, Liq. Crys. 5, 327 (1989).
- [18] L. Onsager, Ann. N. Y. Acad. Sci. **51**, 627 (1949).

- [19] F. M. Van der Kooij, K. Kassapidou, and H. N. W. Lekkerkerker, Nature **406**, 868 (2000).
- [20] N. Miyamoto and T. Nakato, Adv. Mater. 14, 1267 (2002).
- [21] N. Miyamoto and T. Nakato, J. Phys. Chem. B. **108**, 6152 (2004).
- [22] S. Liu, J. Zhang, N. Wang, W. Liu, C. Zhang, and D. Sun, Chem. Mater. 15, 3240 (2003).
- [23] M. C. D. Mourad, E. J. Devid, M. M. van Schooneveld, C. Vonk, and H. N. W. Lekkerkerker, J. Phys. Chem. B 112, 10142 (2008).
- [24] J. C. P. Gabriel, F.Camerel, B. J. Lemaire, H. Desvaux, P. Davidson, and P. Batail, Nature (London) **413**, 504 (2001).
- [25] N. Behabtu, J. R. Lomeda, M. J. Green, A. L. Higginbotham, A. Sinitskii, D. V. Kosynkin, D. Tsentalovich, A. N. G. Parra-Vasquez, J. Schmidt, E. Kesselman, Y. Cohen, Y. Talmon, J. M. Tour, and M. Pasquali, Nat. Nanotechnol. 5, 406 (2010).
- [26] J. E. Kim, T. H. Han, S. H. Lee, J. Y. Kim, C. W. Ahn, J. M. Yoon, and S. O. Kim, Angew. Chem. Int. Ed. **50**, 3043 (2011).
- [27] H. He, J. Klinowski, M. Forster, and A. Lerf, Chem. Phys. Lett. 287, 53, (1998).
- [28] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z.Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, and J. M. Tour, ACS Nano. 4, 4806 (2010).
- [29] W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc. 80, 1339 (1958).
- [30] N. A. Clark, J. H. Lunacek, and G. B. Benedek, Am. J. Phys. 38, 575 (1970).
- [31] D. Koppel, J. Chem. Phys. 57, 4814 (1972).
- [32] F. Perrin, J. Phys. Radium 5, 497 (1934).
- [33] S. B. Dubin, N. A. Clark, and G. B. Benedek, J. Chem. Phys. 54, 5158 (1971).
- [34] F. M. van der Kooij and H. N. W. Lekkerkerker, J. Phys Chem. B 102, 7829, (1998).
- [35] M. A. Bates and D. Frenkel, J. Chem. Phys. **110**, 6553 (1999).
- [36] D. Sun, H.-J. Sue, Z. Cheng, Y. Martinez-Raton, and E. Velasco, Phys. Rev. E. 80, 041704 (2009).
- [37] M. Shuai, A. F. Mejia, Y.-W. Chang, and Z. Cheng, CrystEngComm. 15, 1970 (2013).
- [38] L. Y. Sun, W. J. Boo, H.-J. Sue, and A. Clearfield, New J. Chem. 31, 39 (2007).
- [39] D. M. Kaschak, S. A. Johnson, D. E. Hooks, H. -N. Kim, M. D. Ward, and T. E. Mallouk, J Am. Chem. Soc. **120**, 10887 (1998).

- [40] H.-N. Kim, S. W. Keller, T. E. Mallouk, J. Schmitt, and G. Decher, Chem. Mater. 9, 1414 (1997).
- [41] M. Shuai, *Synthesis and Liquid Crystal Phase Transitions of Zirconium Phosphate Disks*, Ph. D. Thesis, Texas A&M University (2013).
- [42] Y. Martínez-Ratón and E. Velasco, J Chem. Phys. **134**, 124904 (2011).
- [43] D. Yamaguchi, N. Miyamoto, S. Koizumi, T. Nakato, and T. Hashimoto, J. Appl. Cryst. 40, S101 (2007).
- [44] D. Yamaguchi, N. Miyamoto, T. Fujita, T. Nakato, S. Koizumi, N. Ohta, N. Yagi, and T. Hashimoto, Phys. Rev. E **85**, 011403 (2012).
- [45] R. Sjöback, J. Nygren, and M. Kubista, Spectrochim. Acta, Part A **51**, L7 (1995)
- [46] A. Kose, M. Ozaki, K. Takano, K. Kobayashi, and S. Hachisu, J. Colloid Interface Sci. 44, 330 (1973).
- [47] R. Kesavamoorthy, M. Rajalakshmi, and C. B. Rao, J. Phys. Cons. Matter 1, 7149 (1989).
- [48] N. Ise, *Ordering and Organization in Ionic Solutions*, edited by N. Ise and I. S. Sogami World Scientific, Singapore (1988).
- [49] K. Ito, H. Yoshida, and N. Ise, Science **263**, 66 (1994).
- [50] B. V. R. Tata, M. Rajalakshmi, and A. K. Arora, Phys. Rev. Lett. 69, 3778 (1992).
- [51] A. K. Arora and B. V. R. Tata, *Ordering Phase Transitions in Charged Colloids*, VCH Publishers, New York, (1996).
- [52] B. V. R. Tata, E. Yamahara, P. V. Rajamani, and N. Ise, Phys. Rev. Lett. 78, 2660 (1997).
- [53] P. S. Mohanty, B. V. R. Tata, A. Toyatoma, and T. Sawada, Langmuir **21**, 11678 (2005).
- [54] J. Yamanaka, H. Yoshida, T. Koga, N. Ise, and T. Hashimoto, Phys. Rev. Lett. 80, 5806 (1998).
- [55] A. Toyotama, T. Sawada, J. Yamanaka, and K. Kitamura, Langmuir **19**, 3236 (2003).
- [56] B. V. Derjaguin and L. Landau, Acta Physicochimica 14, 633 (1941).
- [57] E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam (1948).
- [58] H. Yukawa, Proc. Phys. Math. Soc. Japan 17, 48 (1935).
- [59] G. F. Walker, Nature **187**, 312 (1960).
- [60] I. Sogami and N. Ise, J. Chem. Phys. **81**, 6320 (1984).

- [61] N. Ise and I. Sogami, *Structure Formation in Solution: Ionic Polymers and Colloidal Particles*, Springer, Germany (2005).
- [62] M. V. Smalley, Mol. Phys. **71**, 1251, (1990).
- [63] M. V. Smalley, *Clay swelling and colloid stability*, Taylor & Francis (2006).
- [64] H. Zocher, Anorg. Chem. **147**, 91 (1925).
- [65] A. V. Kaznacheev, M. M. Bogdanov, and S. A. Taraskin, J. Exp. Theor. Phys. **95**, 57 (2002).
- [66] H. Zocher and C. Török, Kolloid-Zeitschrift **170**, 140 (1960).
- [67] J. D. Bernal and I. Fankuchen, J. Gen. Physiology 25, 111 (1941).
- [68] Z. Dogic and S. Fraden, Phil. Trans. R. Soc. A **359**, 997 (2001).
- [69] P. W. Oakes, J. Viamontes, and J. X. Tang, Phys. Rev. E 75, 061902 (2007).
- [70] N. Puech, E. Grelet, P. Poulin, C. Blanc, and P. Van der Schoot, Phys. Rev. E 82, 020702 (2010).
- [71] A. A. Verhoeff, I. A. Bakelaar, R. H. J. Otten, and P. van der Schoot, H. N. W. Lekkerkerker, Langmuir **27**, 116 (2011).
- [72] A. A. Verhoeff, R. H. J. Otten, P. van der Schoot, and H. N. W. Lekkerkerker, J. Chem. Phys. **134**, 044904 (2011).
- [73] A. A. Verhoeff and H. N. W. Lekkerkerker, Soft Matter 8, 4865 (2012).
- [74] G. Wulff, Z. Kristallogr. **34**, 449 (1901).
- [75] N. A. Clark and R. B. Meyer, Appl. Phys. Lett. 22, 493 (1973).
- [76] R. Ribotta, G. Durand, and J. D. Litster, Solid State Commun. 12, 27 (1973);
 M. Delaye, R. Ribotta, and G. Durand, Phys. Lett. 44A, 139 (1973).
- [77] J. C. Loudet, P. V. Dolganov, P. Patrício, H. Saadaoui, and P. Cluzeau, Phys. Rev. Lett. 106, 117802 (2011).
- [78] Z. Xu and C. Gao, Nature Communications 2, 571 (2011).
- [79] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki, and K. Aoki, Langmuir 4, 1214 (1988).
- [80] W. M. Gibbons, P. J. Shannon, S.-T. Sun, and B. J. Swetlin, Nature 351, 49 (1991).
- [81] Y. W. Yi, T. E. Furtak, M. J. Farrow, and D. M. Walba, J. Vac. Sci. Technol., A 21, 1770 (2003).

- [82] K. Aoki, T. Seki, Y. Suzuki, T. Tamaki, A.Hosoki, and K. Ichimura, Langmuir 8, 1007 (1992).
- [83] I. Jánossy and T. Kósa, Opt. Lett. 17, 1183 (1992).
- [84] Z. Sekkat and W. Knoll, *Photoreactive Organic Thin Films*, Academic Press (2000).
- [85] T. G. Pedersen and P. M. Johansen, Phys. Rev. Lett. **79**, 2470 (1997)
- [86] G. Fang, J. E. Maclennan, Y.W. Yi, M. A. Glaser, M. Farrow, E. Korblova, D. M. Walba, T. E. Furtak, and N. A. Clark, Nature Communications 4, 1521 (2013).
- [87] D. M. Walba, C. A. Liberko, E. Korblova, and M. J. Farrow, Liquid Crystal **31**, 481 (2004).
- [88] Y.W. Yi and T. E. Furtak, Appl. Phys. Lett. 85, 4287 (2004).
- [89] Y.W. Yi, M. J. Farrow, E. Korblova, D. M. Walba, and T. E. Furtak, Langmuir 25, 997 (2009).
- [90] G. Fang, Y. Shi, J. E. Maclennan, and N. A. Clark, Langmuir 26, 17482 (2010).
- [91] Y. W. Yi, *High Sensitivity Azobenzene-Modified Monolayers for Optical Switching of Liquid Crystal Alignment*, Ph. D. Thesis, School of Mines (2004).
- [92] G. Fang, *Orientation Dynamics of Azobenzene-Based Self-Assembled Monolayers*, Ph. D. Thesis, University of Colorado-Boulder (2007).
- [93] E31 is a mixture of cyanobiphenyl homologs, primarily 5-8CB, having the phase transition sequence S-9°C-N-61.6 °C-Iso.
- [94] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford (1959).
- [95] K_{33} , K_{11} , and K_{22} are ~ 25, 17.5, and 8.5 pN respectively [13]. We assumed K ~ 20 pN in the one constant approximation.
- [96] A. A. Sonin, *The Surface Physics of Liquid Crystals*, Gordon and Breach Publishers (1995).
- [97] R. P. Pan, S. M. Chen, and T. C. Hsieh, Mol. Cryst. Liq. Cryst. 198, 99 (1991).
- [98] D. R. Link, L. Radzihovsky, G. Natale, J. E. Maclennan, N. A. Clark, M. Walsh, S. S. Keast, and M. E. Neubert, Phys. Rev. Lett. **84**, 5772 (2000).
- [99] P. E. Cladis, P. L. Finn, and H. R. Brand, Phys. Rev. Lett. 75, 1518 (1995).

- [100] A. J. Leadbetter, J. L. A. Durrant, and M. Rugman, Mol. Cryst. Liq. Cryst. 34, 231 (1976).
- [101] P. E. Cladis and S. Torza, J. Appl. Phys. 46, 584 (1975).
- [102] D.W. Allender, R.M. Hornreich, and D.L. Johnson, Phys. Rev. Lett., 59, 2654 (1987).
- [103] P. Oswald and P. Pieranski, *Smectic and Columnar Liquid Crystals*, Taylor & Francis (2006).
- [104] D. Dolphin, Z. Muljiani, J. Cheng, and R. B. Meyer, J. Chem. Phys. 58, 413 (1973).