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$$\xi = \sqrt{\frac{Kh}{\alpha_0 d U}}.$$  

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DEDICATION

To my parents.

献给我的父母
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CHAPTER 1

Introduction

1.1 Lyotropic Chromonic Liquid Crystals

Lyotropic liquid crystals (LCs) represent an extended family of dispersed systems that possesses a long-range orientational order (the prefix lyo- means “to loosen, dissolve” in Greek) [1,2]. The basic building units of such systems are usually supramolecular assemblies of high aspect ratio dispersed in solvent (usually water). Examples include: amphiphiles that form wormlike micelles, double-strand DNA (ds-DNA) molecules, tobacco mosaic viruses (TMV) representing rigid protein polymer rods, and cylindrical stacks of disk-like molecules in water solution. Molecules in the last category are usually drugs or dyes molecules that have a polyaromatic center and ionizable groups at the periphery. The liquid crystal phases formed by such molecules in water solution are called lyotropic chromonic liquid crystals, or LCLCs [3-7]. Classical examples include antiasthma drug disodium cromoglycate (DSCG), food and textile dyes Sunset Yellow (SSY), Allura red, Tartrazine, Blue 27, Violet 20, Fig 1.1, and many more. An extended family of chromonics also includes ds-DNA assemblies [4,8], that share many structural features with the classical LCLCs such as SSY and DSCG, including: repeating distance of molecules along the aggregate’s axis being 0.34nm, diameter of aggregates being 1-2nm, persistence length being on the order of tens of nanometers, and so on.
Figure 1.1: Molecular structures of some lyotropic chromonic liquid crystal materials.

In lyotropic LC, the underlying mechanism for a dispersion of elongated objects to achieve an orientationally ordered state is very different from that of thermotropic LCs. In thermotropic LCs, the basic building units are molecules of covalently fixed shape. The ordered phases (nematic, smectic, etc.) occur at a lower temperature when the molecular interactions favoring parallel arrangement of neighboring molecules win over entropy. In lyotropic LCs, the orientational order occurs when the building units sacrifice
orientational freedom and align with neighbors to gain translational entropy. For example, in an Onsager-type system [9] composed of identical rigid rods, the isotropic-to-nematic phase transition occurs only if the volume fraction of the rods in the system is larger than a threshold value, \( \phi > \phi_{\text{nem}} = 4.5D/L \), where \( L \) and \( D \) are the length and diameter of the rods, respectively. Temperature does not play a role here, leaving the volume fraction \( \phi \), or equivalently, the mass concentration \( c \), being the only tuning parameter. In comparison, the phase behavior of lyotropic chromonic liquid crystals can be controlled by both concentration and temperature, due to the very different underlying mechanism of how the basic building units of the LCLCs, the cylindrical aggregates, are formed. When LCLC molecules are dissolved in water, the hydrophobic aromatic centers stack on top of each other. At the same time, positive ions at the periphery of the molecules are disassociated, leaving behind negative charged aggregates, with a maximum charge density \( \tau^\text{max} = 6e/\text{nm} \), Fig 1.2. The effective interaction, counting both the attraction of the aromatic centers \( (E_0) \) and electrostatic repulsions of the periphery \( (E_e) \) is characterized by the so-called scission energy \( E = E_0 - E_e \approx 10k_B T \), an energy needed to break one aggregate into two. The equilibrium average length of chromonic aggregates, as described more in detail later in this thesis, is determined by \( E \),

\[
\bar{L} \propto \exp\left(\frac{E}{2k_B T}\right) \tag{3.4,10,11}.
\]

At lower temperature, the length of the aggregates increases [12], thus an ordered phase is preferred over isotropic phase. Moreover, keeping \( c \) and \( T \) the same, but increasing the ionic concentration in the system screens the repulsion...
between molecules in the aggregates, decreases $E_e$, thus increases $\bar{L}$, promoting a more ordered phase. On the contrary, adding NaOH enhances the disassociation of sodium ions, increases $E_e$, thus decreases $\bar{L}$, destabilizes the ordered phase. Phase dependence of LCLCs on $c$, $T$, $c_{ion}$, pH value, presence of crowding agents, etc. are experimentally studied in Ref [12,13], and also in Chapter 2-4 in this thesis.

Figure 1.2: Molecular structure and schematic of a SSY-water LCLC. (a) Molecular structure and schematic of disassociation of sodium ions from a single molecule in water. (b) Schematic of SSY assembly in water (represented by the blue background) to form nematic LCLC; aromatic centers stack on top of each other while the sodium ions are disassociated, leaving the aggregates negatively charged.

Another important difference between LCLCs and the Onsager-type lyotropic LCs composed of rigid rods (such as water suspension of TMV [14]) is that LCLC
aggregates are flexible. The flexibility of LCLC aggregates is characterized by the persistence length $\lambda_p$, a length over which unit vectors tangential to the aggregates lose correlation. Since $E$ is on the order of $10k_BT$, the aggregates may be bent easily by thermal fluctuations. In a similar system composed of ds-DNA molecules face-to-face assembled with a scission energy $E \approx (4-8)k_BT$, the persistence length is estimated to be 50nm [8]. The flexibility of the aggregates can be influenced by ion concentration which controls the Debye screening length $\lambda_D$. Since the bend deformation brings negative surface charges closer and causes stronger electrostatic repulsion, a decreased $\lambda_D$ at higher ionic concentration relieves the repulsion, and makes the aggregates more flexible. Similar effects of ionic contents on flexibility of biomolecules are of prime importance in biological processes such as DNA wrapping around nucleosomes, packing inside bacteriophage capsids, binding to proteins and so on [15,16].

Despite the growing interests of the LCLCs, very little is known about their elastic and viscous properties. Knowledge of viscoelastic constants, such as the Frank elastic moduli in the nematic phase, the viscosities associated with different flow geometries, is of essential importance to understand both static and dynamic phenomena such as template assisted alignments [17-20], behavior of LCLCs in samples with various thickness [21-23], LCLC-guided orientation of nanoparticles [24], shape of LCLC tactoids [25,26], effect of spontaneously broken chiral symmetry [27,28], and flow behavior of LCLC [29]. LCLCs also provide a model system to study how these
macroscopic viscoelastic properties are connected with microscopic features such as the contour length $L$ and the persistence length $\lambda_p$, which can help our understanding of the biological systems such as DNA assemblies, where very often direct measurements of microscopic properties are not easily available.

1.2 Active Colloids and Collective Behavior

If liquid crystals can be described as “passive”, there is another kind of systems, known as “active matter”, composed of self-driven individuals that use stored or locally harvested energy to drive systematic movement [30]. A distinctive feature of active matter, as compared to non-equilibrium state of a passive system (e.g. LC director reorientation driven by external field), is that the energy input that drives the system out of equilibrium is local, often at the level of each particles, rather than at the boundaries of the system. A particular interesting subset of active matter is active colloids. Colloids are suspensions of particles whose sizes range from 10nm to 100μm, usually in fluid or gas. They are prevalent in our daily life (e.g., milk, ink, blood) and play critical roles in many industries (e.g., food, printing, medicine, nanotechnology) [31]. Interactions between colloids are governed by various forces, such as steric repulsion, electrostatic and magnetic forces, van der Waals forces, entropic forces, hydrodynamic forces, etc.[32]. Colloidal science has been a traditionally important field of research. A large body of work has been dedicated to the equilibrium self-assembled colloidal structures [33,34], which have important potential in applications such as photonic band gap (PBG)
structures [35-37]. Bringing activity into colloidal particles gives rises to new fascinating phenomena, including: activity induced crystallization at low density [38], self-organization of microtubules driven by molecular motor [39], spontaneous and constant creation, annihilation and self-propulsion of topological defects [40,41], reduction of viscosity in active particle suspension [42,43] and so on. Self-assembled active colloids also open new doors to produces materials with functions not available in equilibrium conditions, such as self-healing [44,45], self-propulsion [46-48], formation of unusual shapes (reconfigurable snakes, asters, etc.) and transport of cargo [48,49].

The simplest way to create an active colloid is to suspend microorganisms in water; examples include bacteria [50] such as Escherichia coli (E-coli) [51] and Bacillus subtilis, green algae such as Chlamydomonas reinhardtii [52] and sperm cells [53]. These self-motile microorganisms are also called microswimmers. Depending on the direction of flow field along the axis of swimming, they are classified as “puller” or “pusher” types [30,54]. For example, bacteria such as E-coli and Bacillus subtilis are pushers, since they pump fluid away from them along the direction of propulsion, by rotating helicoidal flagella, Fig 1.3a. Chlamydomonas reinhardtii is a puller, as it pulls fluid towards its body along the direction of motion, by stoking two arm-like flagella, Fig 1.3b. The pair of forces that drive the fluid motion are pointing inward (puller) or outward (pusher), corresponding to a positive or negative force dipole on the swimmer body, respectively [30]. Since the self-motile swimmers are not driven by an external field (electric,
magnetic, flow field, etc.), the net force is zero. Inspired by the biological microswimmers, researchers developed synthetic microswimmers in a variety of forms [55-57], including bimetallic rods that use chemical reaction with hydrogen peroxide [58], water droplets that use Marangoni effect to drive themselves in oil [59], metallic-dielectric Janus spherical particles propelled by an electric field [60], high-speed bilayer microtubes [61], magnetic field [48,49] or light driven [38] microspheres, silicon dioxide swimmers with nanostructured helical shape [62], and so on.

Figure 1.3: “Pusher” vs “puller” swimmers. (a) shows a pusher swimmer, best represented by rod-shaped bacteria such as *E-coli* or *Bacillus subtilis* [51]. The forces (showing with red arrows) that drive the flow are pointing outwards along the swimming direction $\mathbf{v}$. (b) shows a puller swimmer, best represented by green algae
Chlamydomonas reinhardtii [52]. Black arrows on bacteria bodies show direction of motion of bacteria parts. Grey curved arrows show schematic flow field.

In this thesis, we deal with a typical “pusher” microswimmer, bacteria Bacillus subtilis. Bacillus subtilis is a rod-shaped bacterium 5-7μm long and 0.7μm in diameters. It has about 20 pieces of helicoidal 10-μm long flagella filaments attached to the bacterial body. In isotropic media, the bacteria swim in the so called “run-and-tumble” fashion [63,64]. During an approximately 1 second “run” phase, the flagella form a bundle at one end of the bacterial body and rotate counter-clock wise (ccw, viewing behind an swimming-away bacterium along the body axis), thus powering unidirectional “head-forward” motion. In the following tumble phase of about 0.1s, one or a few of the flagella reverse their rotation to clock wise (cw) and leave the bundle, causing bacterium to “tumble” and change its orientation randomly. Then flagella rotate ccw again, forming the bundle and power the forward motion in a new direction. The motility of this aerobic bacterium can be controlled by the amount of dissolved oxygen.

One spectacular phenomenon observed in an isotropic Bacillus subtilis suspension is the spontaneous collective motion [54,64-66]: at high enough concentration (~2% by volume), bacteria swarm together with their velocity field correlated over ~10times body length and with a up to 4 fold increase in speed as compared to individual bacterium at dilute concentration [67,68]. In fact, collective motion can be found in many active
matter systems [69-72] of different sizes, ranging from microscopic organisms such as bacteria swarms, to macroscopic creatures such as fish schools, birds flocks and herds of mammals, Fig 1.4. In the collective motion mode, bacteria suspension exhibit unusual properties such as greatly reduced viscosity [42,52] and increased diffusivity [73,74]. A very interesting phenomenon is the unidirectional rotation of asymmetric millimeter size gears [75,76] driven by the chaotic motion of swimming bacteria, Fig. 1.4a. By contrast, in an equilibrium system of suspension of passive particles, this rotation cannot be observed since it is against the second law of thermodynamics. However, in condensed bacterial suspension, even though the motion of individual particles is still random and looks very much like Brownian motion of passive particles, one can still harvest energy, a signature that the system is not in the equilibrium states.
Figure 1.4: Collective motion at different scales and in different media. (a) High density suspension of *Bacillus subtilis* powers the unidirectional rotation of asymmetric gears (schematic redrawing of Fig. 2A,E of ref. [75]). (b) School of fish. (http://www.coralreefphotos.com/big-school-of-fish-schooling-fish-school-of-bogas/) (c) Flock of birds. (http://www.howitworksdaily.com/why-do-birds-flock-together/) (d) Herd of migration animals in South Sudan, Africa. (http://www.reuters.com/article/us-sudan-wildlife-idUSN1225815120070612)

Collective motion in active matter systems results in ordered states with polar [77,78] or nematic [79-82] symmetry. For example, in a system composed of microtubules, crowding agents and molecular motors, Dogic and his collaborators [40,41]
demonstrate that at high enough concentration, microtubules absorbed on flat oil-water interface undergo a transition to the nematic phase. When the activity is turned on with adenosine triphosphate (ATP) supply, one observes constant creation and annihilation of topological defects of charge 1/2 and -1/2, distinctive from the uniform alignment of director observed in the equilibrium nematic phase. However, in this system, the nematic order and activity are both tightly connected to the parallel aligned microtubules. As a result, one sees only one steady state, i.e., active nematic with topological defects. In this thesis, we take advantage of non-toxic lyotropic chromonic liquid crystal disodium cromoglycate [83] and mix in active particles, the bacteria \textit{Bacillus subtilis}. By varying the bacterial concentration and oxygen supply, we independently (and continuously) change the activity of the system from zero to high values. As a result, our system exhibits three major steady states: (i) equilibrium uniform nematic embedding small amount of active particles in their inactive form (non-swimming), (ii) active nematic with uniform bend modulation, and (iii) active nematic with topological defects. We also demonstrate that LCLCs have the ability to control the motion of active particles through the spatially varying director field, and to visualize the fluid motion induced by 24nm thick bacterial flagella. The studies of this system that we call a living liquid crystal are presented in Chapter 5.
1.3 Scope and Objectives of the Dissertation

The scope of this dissertation is two-fold. First, we aim to understand the elastic and viscous properties of LCLCs, and how factors such as temperature, concentration and ionic contents influence them. Second, we study the interaction between self-propelled particles (bacteria *Bacillus subtilis*) and the long-range nematic order provided by DSCG LCLC. The studies involve various experimental techniques, such as magnetic field induced Frederiks transition, dynamic light scattering (DLS), polarizing optical microscopy, LC-PolScope and video-microscopy.

The objectives of the dissertation are to study experimentally: (i) the temperature and concentration dependence of Frank elastic moduli of Sunset Yellow LCLC, using magnetic Frederiks transition technique; (ii) the ionic-content dependences of elastic moduli and rotation viscosity of Sunset Yellow LCLC, using the same technique; (iii) elasticity, viscosity and orientational fluctuation of DSCG LCLC using dynamic light scattering technique; (iv) the interaction between active self-propelling bacteria and the nematic order in the living liquid crystal.

The dissertation is organized as follows.

Chapter 2 describes the experimental study of Frank elastic constants of SSY LCLC, probed by Frederiks transition in a magnetic field. In this study, we observed unusual anisotropy of elastic properties. Namely, the splay $K_1$ and bend $K_3$ constants are found to be 10 times larger than the twist constant $K_2$. $K_1$ has the strongest temperature dependence among all three. We explain our findings through the idea of semiflexible
aggregates, whose length dramatically increases as temperature decreases or concentration increases.

Chapter 3 is an extension of the study in Chapter 2 in two aspects: 1) we aim to understand how ionic content in the system influences the properties of LCLC; 2) we measure rotation viscosity $\gamma_1$ by the relaxation of twist deformation in a magnetic field, in addition to the Frank elastic moduli. Here we fix the concentration of SSY but vary the type and concentration of ionic components and temperature. Using the same magnetic Frederiks transition technique, we find that the ionic content influences the elastic constants in dramatic and versatile ways. For example, the monovalent salt NaCl decreases $K_3$ and $K_2$, but increases $\gamma_1$, while pH agent NaOH decreases all of them.

Chapter 4 deals with LCLC material DSCG. DSCG is not only the earliest and most studied LCLC material, but also a bio-compatible one [83] with optical transparency in visible wavelength, an advantage for optical study and applications [84]. DLS technique allows one to extract both elastic moduli and viscosity coefficients at the same time. The results obtained are rather astonishing. In addition to anisotropy of elastic constants, $K_1 \approx K_3 \approx 10K_2$, similar to SSY LCLC, the viscosity of bend deformation $\eta_{\text{bend}} \approx \eta_{\text{scb}}^{\text{CB}}$ can be up to 4 orders of magnitude smaller than $\eta_{\text{play}}$ and $\eta_{\text{twist}}$. The temperature dependences of $K_1$, $\eta_{\text{play}}$ and $\eta_{\text{twist}}$ are exponential. Again, we explain our findings through the idea of semi-flexible aggregates whose lengths strongly depend on
T. We also find an additional mode in the DLS experiments, which we attribute to the diffusion of stacking faults of the aggregates.

In Chapter 5, we combine two fundamentally different systems, the nematic DSCG LCLC and bacteria *Bacillus subtilis*, in order to create the living liquid crystal in which the activity and orientational order can be tuned independently. The coupling between the active particles and long-range nematic order results in intriguing dynamic phenomena, including (i) nonlinear trajectories of bacterial motion guided by a non-uniform director, (ii) local melting of the liquid crystal caused by the bacteria-produced shear flows, (iii) activity-triggered transition from a non-flowing equilibrium uniform state into a flowing out-of-equilibrium one-dimensional periodic pattern and its evolution into a turbulent array of topological defects, and (iv) birefringence enabled visualization of micro-flow generated by the nanometers thick bacterial flagella.

Chapter 6 summarizes the results in this dissertation.

The following publications cover the topics discussed in the dissertation:

[2]: Shuang Zhou, Adam J. Cervenka, and Oleg D. Lavrentovich, “Ionic-content dependence of viscoelasticity of the lyotropic chromonic liquid crystal sunset yellow” 


The research also results in the following publication:


and two more publications that are currently being prepared for submission:

[6]: Shuang Zhou, A. Sokolov, Igor Aranson, Oleg D. Lavrentovich, “Control of dynamic behavior of bacteria by lyotropic chromonic liquid crystals with homeotropic orientation of director”, in preparation
CHAPTER 2
ELASTICITY OF LYOTROPIC CHROMONIC LIQUID CRYSTALS PROBED
BY DIRECTOR REORIENTATION IN MAGNETIC FIELD

2.1 Introduction

Soft non-covalent attraction of organic molecules in solutions often results in elongated aggregates [4,8,10,85]. Examples include “living polymers”, wormlike micelles of amphiphiles, stacks of disk-like dye and drug molecules [4,10], and nucleic acids [8]. In a broad range of concentrations and temperatures, the self-assembled polydisperse aggregates of relatively rigid flat organic molecules form nematic and columnar liquid crystal (LC) phases, generally classified as lyotropic chromonic LCs (LCLCs) [4,10]. Since the aggregates are bound by weak van der Waals forces, their length varies strongly with concentration, temperature, ionic content, making the LCLCs very different from thermotropic LCs with molecules of covalently fixed shape and from lyotropic LCs formed by objects such as tobacco mosaic viruses [14] or polymers of fixed molecular weight [86]. An intriguing question is how this fundamental structural feature of LCLCs reflects on their elastic properties.

Despite the growing interest in LCLCs, very little is known about their elasticity. Theory and numerical simulations have reached the level at which one can describe phase diagrams of LCLCs [87,88], but not their elastic moduli. The main challenge is in
accounting for length distribution and flexibility of aggregates. The average length of aggregates $\bar{L}$ in the nematic LCLC can be estimated (see 2.5.1), following the work of van der Schoot and Cates [89] on wormlike surfactant micelles, as a function of stacking energy $E$, volume fraction $\phi$ of the chromonic molecules, persistence length $\lambda_p$ of the LCLC aggregates of diameter $D$, and absolute temperature $T$:

$$
\bar{L} = L_0\phi^{2/3}\left(\frac{\lambda_p}{D}\right)^{1/3}\exp\left(\frac{E + \kappa\phi}{2k_B T}\right)
$$

(2.1)

where $L_0 = 2\pi^{2/3}\sqrt{a_c D}$ is a length characterizing the size of a monomer, $a_c$ is the period of molecular stacking along the aggregate, $\kappa$ is a constant describing the enhancement of aggregation by the excluded volume effects; in the second virial approximation, $\kappa \approx 4k_B T$ [89]. Experimental characterization of elastic parameters is also challenging as it requires two types of uniformly aligned samples, with the director $\hat{n}$ (average orientation of aggregates) being in plane of the cell (planar alignment) and perpendicular to it (homeotropic alignment). The elastic properties can then be determined by applying a magnetic field $B$ to realign $\hat{n}$ (Frederiks effect). Only planar cells were used so far. In these cells, $B$ causes twist or mixed twist-bend of $\hat{n}$, depending on the rate of field increase [90,91]. Golovanov et al. [92,93] used this effect to extract the twist constant $K_2 = 0.36pN$ and the bend-twist ratio $K_3/K_2 = 12.2$ for disulphoidantrone-water LCLC.
In this letter, we take advantage of the new techniques to align LCLC in both planar and homeotropic fashion, and determine all three bulk elastic constants, in geometries where the field-induced director gradients are small and correspond to equilibrium states. We study aqueous solutions of disodium salt of 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonic acid, also known as Sunset Yellow (SSY). In this LCLC, the disk-like molecules reversibly aggregate face-to-face and form elongated stacks with one molecule per cross section [12,94,95]. We find that dependences of $K_1$, $K_2$, $K_3$ on concentration $c$ and temperature ($t$, in °C) are highly unusual as compared to other classes of LCs and explain the results by the varying contour length and persistence length of self-assembled flexible polydisperse aggregates.

2.2 Samples and Experimental Set-up

SSY was purchased from Sigma Aldrich and purified as described in Ref.[94]. The study is performed for the nematic phase at $c = 29.0, 30.0, \text{ and } 31.5 \text{ wt\% (} \phi = 0.18, 0.19 \text{ and } 0.20, \text{ respectively, see 2.5.3). The diamagnetic susceptibility measured parallel to } \hat{n} \text{ is smaller than its orthogonal counterpart, } \Delta \chi = \chi_{||} - \chi_{\perp} < 0. \text{ We used a magnetometer with a superconducting quantum interference device and determined } \Delta \chi \text{ following Ref. [96] as } \Delta \chi = 3(\chi_{av} - \chi_{\perp}), \text{ where } \chi_{av} = \frac{1}{3}(\chi_{||} + 2\chi_{\perp}) \text{ is the average volumetric magnetic susceptibility. The LC sample, flame-sealed in a glass tube and placed in the superconducting solenoid, was heated well above the nematic-to-isotropic
transition and slowly cooled down to 25°C in presence of a 5T field. $\chi_{av}(t)$ was measured in the isotropic phase and linearly extrapolated to the nematic phase region, following Ref [96]. At 25°C, the magnetization was monitored for over 10 hours until its value saturated, indicating an equilibrium homogeneous nematic state with $\hat{n} \perp \mathbf{B}$, which allowed to determine $\chi_{\perp}$. An independent measurement of $\chi_{\perp}$ at 1T shows little ($\sim 1\%$) difference from the 5T data, indicating that the field-induced order is negligible, which is consistent with the data on Cotton-Mouton constant [97]. Mass densities were measured with a densitometer DE45 (Mettler Toledo). At 25°C and $c=29.0\%$, we find $\Delta \chi = (-7.2 \pm 0.7) \times 10^{-7}$.

To determine the elastic parameters, we used flat glass cells of thickness $d = 20 - 25 \mu m$. A relatively large $d$ and the smallness of director gradients in the Frederiks effect help us to avoid possible changes of scalar order parameters in a strongly distorted LCLC [23]. For planar alignment, the substrates were rubbed with a superfine abrasive paper (001K Crystal Bay™ Crocus Cloth, 3M), washed, dried, and treated with UV ozone for 5 min to improve wettability. Homeotropic alignment of SSY was achieved with unrubbed polyimide SE-7511L (Nissan).

The cell is placed in the magnetic field and probed with two orthogonal polarized laser beams. One beam is parallel to $\mathbf{B}$. The normal to the cell $\hat{z}$ makes an angle $\alpha$ with $\mathbf{B}$, $\hat{y}$ is the axis of rotation, and the $\hat{x}$ axis is parallel to $\hat{n}$ in the planar cell (Fig. 2.1). The angle $\alpha$ is controlled with a precision better than 0.1°.
Figure 2.1: Schematic of experiment setup. Sample is held in a hot stage for temperature control (not shown here). Both laser 1 and 2 are He-Ne lasers ($\lambda = 633\text{nm}$).

2.3 Results

2.3.1 Homeotropic cells, bend constant $K_3$

$K_3$ is determined by setting $\alpha = 0$ and detecting the optical phase retardation for the laser beam 1, transmitted through the cell and two pairs of crossed circular polarizers (each comprising a linear polarizer and a $\lambda/4$ plate). Light transmission increases at the threshold

$$B_3 = \frac{\pi}{d} \sqrt{\frac{\mu_i K_3}{-\Delta \chi}}$$

(2.2)
at which \( \hat{n} \) starts to tilt from the \( z \) axis (\( \mu_0 \) is the magnetic permeability constant). The circular polarizers allowed us to detect the tilt regardless of its direction. To avoid the possible effect of umbilics [98], we used beams of the expanded cross section (\( \approx 2 \text{ mm}^2 \)); moving the sample in the \( xy \) plane did not change the values of \( B_3 \).

In principle, Eq. (2.2) might need a correction, \( d \to d + l \), where \( l \) is the so-called surface anchoring extrapolation length [2]. We verified the validity of Eq. (2.2) by measuring \( B_3 = 3.5T \) in ultrathin cells (\( d \approx 4 \mu m \)), using a 31 T solenoid at the National High Magnetic Field Laboratory (Tallahassee, FL). The result leads to \( l = 0.15 \mu m \), much smaller than \( d \) in the measurements of \( K_3 \), which validates Eq. (2.2).

We extracted \( B_3 \) from the hysteresis-free field dependences of transmitted light intensity obtained for a very low rate of field increments, 0.002 T/min (see 2.5.4). Repeating measurements at different points of the cell and on different cells, we established that the results were reproducible within 5%. The temperature and concentration dependences of \( K_3 / (-\Delta \chi) \) determined from the threshold field \( B_3 \) are plotted in FIG 2.2 (a).
Figure 2.2: Temperature and concentration dependences of (a) $K_{1,3}/(-\Delta \chi)$ and (b) $K_2/(-\Delta \chi)$. The vertical dash lines mark the nematic-biphasic transition temperature upon heating (same for other plots).

2.3.2 Planar cells, splay constant $K_1$

The splay Frederiks transition for $\Delta \chi < 0$ requires a planar cell placed at $\alpha = 90^\circ$, i.e., $\mathbf{B} \parallel \mathbf{\hat{n}}$, FIG. 2.1. However, as $K_2$ is about an order of magnitude smaller than $K_1$, FIG. 2.2, twist will develop before splay. To impose splay, we aligned the cell at $\alpha = 25^\circ$. As $\mathbf{B}$ increases from 0 to 0.33T, the director experiences threshold-less mixed splay-bend deformation. We measured the field dependence of optical retardation of the
cell $R(B)$ by Senarmont technique [99]. The theoretical dependence $R(B)$ was determined by numerically calculating the profile of director tilt $\theta(z)$ (with respect to the $z$-axis) from the bulk equilibrium equation (see 2.5.5)

$$f = \frac{1}{2} \left( K_1 \sin^2 \theta + K_3 \cos^2 \theta \right) \theta'^2 - \frac{1}{2} \frac{\Delta \chi}{\mu_0} B^2 \cos^2 (\alpha - \theta)$$

(2.3)

Since $\frac{K_3}{-\Delta \chi}$ is already known, we fit the experimental $R(B)$ to extract $\frac{K_1}{-\Delta \chi}$ as the only fitting parameter, Figure 2.2(a).

### 2.3.3 Planar cells, twist constant $K_2$

The magnetic field applied parallel to $\hat{n}$ in the geometry $\alpha = 90^\circ$ often leads to periodic distortions instead of a uniform twist [90-92]. To avoid this regime, we use $\alpha = 75^\circ$. The increasing field first sets up a uniform splay, followed by a uniform twist above the threshold (see 2.5.6):

$$B_2 \approx \frac{\pi}{d \sin \alpha} \sqrt{\frac{\mu_0 K_2}{-\Delta \chi}}$$

(2.4)

We used the laser beam 2 polarized parallel to $\mathbf{B}$, Fig. 2.1. In the absence of twist, the propagating mode is purely extraordinary and is extinguished by the analyzer. When the field reaches $B_2$, the transmittance increases. Measuring $B_2$, we determine $\frac{K_2}{-\Delta \chi}$, Fig. 2.2(b). The azimuthal anchoring length was small $l_{az} \approx 0.15 \mu m$, as determined by
measuring $B_2$ in thin cells with $d \approx 7 \mu m$. The optical response was hysteresis-free for the rate $0.002 T/min$ of field change.

To determine the absolute values $K_{1,2,3}$ we used $\Delta \chi$ presented above for $t = 25$ C, and found $K_1 = (4.3 \pm 0.4) pN$, $K_2 = (0.7 \pm 0.07) pN$, $K_3 = (6.1 \pm 0.6) pN$ for $c = 29.0\%$. Comparing these to 4-n-pentyl-4'-cyanobiphenyl (5CB) values [2], $K_1 = 6.6 pN$, $K_2 = 3 pN$, $K_3 = 10 pN$, one sees that $K_1$ and $K_3$ are of the same order but $K_2$ is much smaller than that in 5CB. The SSY data are close to those for a lyotropic polymer LC (LPLC) formed by monodisperse poly-$\gamma$-benzylglutamate (PBG) in organic solvents, with $\phi = 0.20$ and length-to-diameter ratio $L/D = 32$ [86]: $K_1 = 10 pN$, $K_2 = 0.6 pN$, $K_3 = 10 pN$.

### 2.4 Discussion and Conclusion

The most dramatic and unusual (as compared to other types of LCs, either thermotropic or lyotropic, see, e.g., review by Singh [100]) trend observed in LCLC SSY is that the splay constant and its ratios such as $\frac{K_1}{K_3}$ and $\frac{K_1}{K_2}$ increase when $c$ increases and $t$ decreases, Fig. 2.3(b,c,d). As already indicated, the detailed theoretical interpretation tools to describe the elasticity of LCLCs are yet to come. We first compare the observed trends to the predictions of the phenomenological Landau-de Gennes (LdG) model [1] and models developed for LPLCs [101-104].
Figure 2.3 Temperature and concentration dependences of (a) $\frac{K_2}{-\Delta \chi S}$, (b) $\frac{K_{1,3}}{-\Delta \chi S}$, (c) $\frac{K_{1,3}}{K_2}$, and (d) $\frac{K_1}{K_3}$.

Within the LdG model, the temperature dependences of $K_{1,2,3}$, $\Delta \chi$, and $\Delta n$ are determined by that of the scalar order parameter $S$, namely, $K_{1,2,3} \propto S^2$, $\Delta \chi$, and $\Delta n$. 

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\[ \Delta n \propto S \Delta \chi \] [1]. We measured \( \Delta n(t) \) and \( S(t) \), using the technique described in [25], Fig. 2.4. As seen from Fig. 2.3(a), only \( K_2 \) follows the LdG behavior, with \( \frac{K_2}{-\Delta \chi S} \) being practically independent of \( t \). In contrast, \( \frac{K_1}{-\Delta \chi S} \), \( \frac{K_1}{K_2} \), and \( \frac{K_1}{K_3} \) decrease strongly when \( t \) increases, Fig. 2.3(b,c,d). Such a behavior is at odds not only with the LdG model, but also with the experiments for thermotropic LCs, which typically show \( \frac{K_1}{K_3} \) and \( \frac{K_1}{K_2} \) increasing with \( t \) [100].

In the models of LPLCs [101-104], the molecules of covalently fixed length \( L = \text{const} \) and diameter \( D \ll L \) are considered either as rigid or semiflexible. If the rods are rigid, the excluded volume theory [101] predicts \( K_1 \propto \phi \left( \frac{L}{D} \right) \), \( K_1 / K_3 = 3 \), and \( K_3 \propto \phi^3 \left( \frac{L}{D} \right)^3 \), so that \( \frac{K_1}{K_3} \propto \phi^2 \left( \frac{D}{L} \right)^2 \) will be much smaller than 1 and decreasing at high \( \phi \). The behavior of SSY is very different, with \( K_1 / K_2 \approx 6-11 \) and \( K_1 \approx K_3 \); importantly, \( K_1 / K_3 \) increases with \( \phi \propto c \), Fig. 2.3(d). The disagreement remains when one considers a bidisperse system [101] or takes into account electrostatic effects [103]. The SSY aggregates are charged, as the ionizable groups at periphery dissociate in water. For the typical volume fractions of SSY in the nematic phase, \( \phi \approx 0.2 \), the Debye length \( \lambda_d \) is about 0.3 nm [12]. The electrostatic interactions lead to a “twisting effect”, as two similarly charged aggregates tend to align perpendicularly to each other. The effect
decreases $K_2$ by a small factor $\approx (1 - 0.1h)$ [103], where $h = \lambda_d / (D + 2\lambda_d)$ is only about 0.2 for the nematic phase of SSY [12]. In LPLCs, the electrostatic effect might also increase $K_3$ [103] (thus making $K_1 / K_3$ even smaller than in the model of non-charged rods), since the mutual repulsion of similar charges along the polymer makes it stiffer. We conclude that the elasticity of SSY cannot be described by the model of rigid rods of fixed length, whether charged or not, and turn to the models of semiflexible LPLCs [101-104].

The SSY aggregates should be flexible, as the attraction between monomers is weak, with the scission energy $E$ in the range $(7 - 11)k_BT$ [12,94,105]. In the theory of semiflexible LPLCs, $K_2$ and $K_3$ are determined by the persistence length $\lambda_p$ of the polymers rather than by $L$ [101,102,104]:

$$K_2 = \frac{k_BT}{D} \phi^{1/3} \left( \frac{\lambda_p}{D} \right)^{1/3} [101];
K_3 = \frac{4}{\pi} \frac{k_BT}{D} \phi \frac{\lambda_p}{D}$$

(we use the standard definition [106] $\lambda_p = B / k_BT$ through the bend modulus $B$, which makes $K_3$ twice as large as in Ref. [104]). The last formula, with the experimental $K_3 = 6pN$ at $\phi = 0.18$, $t = 25^\circ C$ and $D = 1.1nm$ [12,94], yields $\lambda_p \approx 10$ nm. We are not aware of any other estimates of $\lambda_p$ for LCLC, but the result appears reasonable when compared to $\lambda_p \approx 50$nm for DNA duplex [106], as the latter is about twice wider than the SSY aggregate and we expect $\lambda_p$ to increase with $D$. 

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Temperature and concentration dependences of $\Delta n$ (at 633 nm) and scalar order parameter $S$.

The splay modulus $K_1$ still grows with the contour length $L$ (as opposed to the persistence length $\lambda_p$) in flexible LPLCs: as explained by Meyer [85], splay deformations, under the condition of constant density, limit the freedom of molecular ends, which increases the entropy. A larger $L$ implies a smaller number of molecular ends available to accommodate for splay and thus a higher $K_1 : K_1 = \frac{4 \beta T}{\pi} \frac{L}{D}$ [104].

The model of semiflexible LCLC aggregates, supplemented by the idea that their average length $\bar{L}$ in LCLCs is not fixed [4,10,85,89], Eq. (2.1), explains the observed $T$ and $\phi$ dependences of elastic ratios, expressed as
\[
\frac{K_1}{K_3} = \frac{\bar{L}}{\lambda_p}, \quad \frac{K_1}{K_2} = \frac{4}{\pi} \phi^{2/3} \frac{\bar{L}}{\lambda_p^{1/3} D^{2/3}}, \quad \frac{K_3}{K_2} = \frac{4}{\pi} \phi^{2/3} \left( \frac{\lambda_p}{D} \right)^{2/3}.
\]

The dramatic decrease of \( \bar{L}(\phi,t) \propto \exp\left( E / 2k_B T \right) \) at elevated temperatures is expected to cause the strongest \( T \)-dependence of the splay constant \( K_1 \). The persistent length is determined mainly by \( E \) and should be only a weak function of \( T \) and \( \phi \).

Numerical simulations [87] show that \( \lambda_p \propto 5 + 2.14 E / k_B T \) for chromonic aggregates. Using this empirical result and Eq. (2.1), we estimate the trends as:

\[
\frac{K_1}{K_3} \propto \phi^{5/6} \exp\left[ \left( E + \kappa \phi \right) / 2k_B T \right] \left( E / k_B T \right)^{2/3},
\]

\[
\frac{K_1}{K_2} \propto \phi^{3/2} \exp\left[ \left( E + \kappa \phi \right) / 2k_B T \right],
\]

and

\[
\frac{K_3}{K_2} \propto \phi^{2/3} \left( E / k_B T \right)^{2/3}.
\]

All three ratios increase when \( T \) decreases and \( \phi \) increases, as in the experiment, Fig. 2.3 (c, d). The ratio \( K_1 / K_2 \) is the most sensitive to \( \phi \) and \( T \), in a good agreement with Fig.2.3(c). The strong increase of \( K_1 / K_2 \) explains the effect of spontaneous chiral symmetry breaking in osmotically condensed LCLC tactoids [27]. The estimate \( K_1 / K_3 = \bar{L} / \lambda_p \) combined with the experimental fact that \( K_1 / K_3 = 1.1 - 0.7 \), Fig. 2.3(d), implies that \( \bar{L} \) and \( \lambda_p \) are of the same order and that \( \bar{L} / \lambda_p \) decreases at high temperatures, where the aggregates shorten while SSY approaches the isotropic phase.
From the tilt of temperature dependencies, \[ \frac{K_1}{K_i} \frac{d\left(K_1 / K_3\right)}{dT} \quad \text{and} \quad \frac{K_2}{K_i} \frac{d\left(K_1 / K_2\right)}{dT} , \] we deduce \( E \approx 10k_BT \) and \( 13k_BT \), respectively (for \( \kappa = 4k_BT \) [89]).

To conclude, we measured the temperature and concentration dependences of Frank moduli of the self-assembled nematic LCLC. \( K_1 \) and \( K_3 \) are found to be comparable to each other and to the corresponding values in thermotropic LCs, while \( K_2 \) is one order of magnitude smaller. The splay constant \( K_1 \) and the elastic ratios \( \frac{K_1}{K_3}, \frac{K_1}{K_2} \) increase significantly when the concentration of SSY increases or the temperature decreases. This unusual behavior is explained within a model of semiflexible SSY aggregates, the average length of which increases with concentration and decreases with temperature, a feature that is absent in conventional thermotropic and lyotropic LCs formed by units of fixed length.

2.5 Supplemental Information

2.5.1 Estimation of average aggregation length

Van der Schoot and Cates [89] described the isotropic-to-nematic transition in the solution of semiflexible polydisperse micelles of spherocylindrical shape formed by surfactant molecules. The polar heads of the rod-like surfactant molecules are located at the interface with water while the hydrophobic hydrocarbon tails are hidden in the
interior of the micelles. The theory [89] operated with the volume fraction of surfactant molecules $\phi$ (related to the numerical density of surfactant molecules $n$ as $\phi = \pi v D^3 / 6m$), where $D$ is the micelle diameter and $m$ is the minimum aggregation number equal the number of surfactant molecules that reside in the semispherical caps at the two ends of the cylindrical body of the micelles), scission energy $E$ (required to create two new ends of the micelle), persistence length $\lambda_p$, numerical constant $\kappa$ close to $4k_B T$ and the growth parameter $\bar{a}$ found to be $\bar{a}^{3/2} = \frac{8\lambda_p}{\sqrt{\pi D}} \phi$. In these notations, the aggregation number is

$$\bar{n} = \frac{\sqrt{\bar{a} v}}{2} D^{3/2} \exp \frac{E + \kappa \phi}{2k_B T}$$

(2.5)

One can apply this expression to describe the average length $L$ of the LCLC aggregates, by noticing that in the latter case, $L = \bar{n} a_z$, where $a_z$ is a repeat distance of stacking along the aggregate axis (the “thickness” of the chromonic molecule, typically equal 0.34 nm) and that $vD^3 = \frac{4\phi D}{\pi a_z}$ rather than $vD^3 = 6\phi m / \pi$ as in Ref. [89]. The result is

$$\bar{L} = \frac{2}{\pi^{2/3}} \sqrt{D a_z \phi} \frac{\lambda_p^{5/6}}{D^{1/3}} \exp \frac{E + \kappa \phi}{2k_B T}$$

(2.6)

which is rewritten as Eq.(2.1) in the beginning of this chapter.
2.5.2 Measurement of $\Delta \chi$

We used a superconducting quantum interference device to determine the mass diamagnetic susceptibility of the sample as described in Ref [107]. The LC sample, flame-sealed in a glass NMR tube (2cm length, 5mm outer diameter), was placed in the center of a superconducting solenoid soaked in a liquid He bath. The solenoid provided a uniform magnetic field up to 5T. The magnetization was determined by moving the sample up and down by a step motor and measuring the magnetization signal as a function of $z$ coordinate using three sets of coils. The temperature of the sample space was controlled by heating wires on the outside shield and by a cooling stream of He gas with a low pressure of 800Pa taken from the liquid He bath.

In the sample space, the glass tube with SSY was heated to 67°C (well above nematic-isotropic transition for $c=29\%$) and slowly cooled down to the nematic phase at 25°C with 5T field applied. At 25°C, a strong field aligns $\hat{n} \perp \mathbf{B}$, thus we measured $\chi_\perp$ after monitoring the magnetization for over 10 hours until its value saturated, indicating an equilibrium state of a homogeneous nematic phase. At high temperatures in the isotropic phase, the measurements of magnetization yield $\chi_{iso}(t)$ as a function of temperature, in the range (67-47)°C for 29%. Following Stefanov and Saupe [96], we extrapolate the measured $\chi_{iso}(t)$ to $t = 25$°C to find $\chi_{av} = (\chi_\parallel + 2\chi_\perp)/3$. Using the measured $\chi_\perp$ and extrapolated $\chi_{av}$, we calculated $\Delta \chi = 3(\chi_{av} - \chi_\perp)$ [96]. An independent measurement of $\Delta \chi$ done under 1T field gave only a small difference of 1%, indicating
that the magnetic field induced changes in the degree of orientational order are negligible, in agreement with the Luoma’s data on the Cotton-Mouton constant [97].

The measurement errors are caused by several factors. First of all, the system was designed for samples of sub-millimeter size, much smaller than the motor scan range (4-6) cm. Our samples are longer, representing a 1 cm long SSY volume confined in a glass NMR tube. Second, the sample motion noise caused by the step motor limits the accuracy of sample positioning [107]. To estimate the possible errors introduced by these factors and the validity of the Stefanov-Saupe method, we measured the diamagnetic anisotropy of a standard thermotropic nematic material 4-n-pentyl-4'-cyanobiphenyl (5CB) (by extrapolating $\chi_{iso}$ to obtain $\chi_{av}$ and measuring directly $\chi_{||}$) and found it to be about 10% lower than the value reported previously [107]. We thus estimate the accuracy of our measurements as ±10%. Since the Frederiks technique measurements yield a much better accuracy $K_i/\Delta \chi$ (< ±4%), we use the data on diamagnetic anisotropy $\Delta \chi$ only to estimate the absolute values of the elastic constants at one temperature 25°C (that is certainly corresponding to a homogeneous nematic phase) and discuss the temperature and concentration dependencies in terms of elastic ratios rather than their absolute values.

2.5.3 Volume fraction measurements

In previous studies [12,94], volume fraction of SSY was calculated by taking the SSY mass density $\rho_{SSY} = 1.4 \times 10^3$ kg m$^{-3}$ from Ref [94] and assuming both volume and
mass are additive quantities, as if water is a continuous medium and $\rho_{SSY}$ is the mass density of individual aggregates. However, these assumptions are not needed if one knows the density of SSY solutions. We used a densitometer DE45 (Mettler Toledo) to measure the density of SSY solutions directly (Fig. 2.5) and with the obtained data determined volume fraction $\phi$. As water molecules (typically 0.15nm) are much smaller than SSY aggregates ($\sim$ 1.1nm diameter, $\sim$ 7nm length [12,94]), we approximate water as a continuous medium. Given the weight concentration of SSY $c$, one can calculate the volume fraction of water $\phi_w$:

$$\phi_w = \frac{(1-c)/\rho_w}{1/\rho_{sol}} = (1-c)\frac{\rho_{sol}}{\rho_w}$$

(2.7)

where $\rho_w$ and $\rho_{sol}$ are the densities of water and solution, respectively. $\phi_{SSY} = 1 - \phi_w$ is shown in Fig. 2.5.

We can also calculate the effective mass density of SSY in the solution by:

$$\rho_{SSY} = \frac{c}{1 - \phi_{SSY}}$$

(2.8)

which yields $\rho_{SSY} = (1.82 \pm 0.02) \times 10^3$kgm$^{-3}$, significantly different from the value of $\rho_{SSY} = 1.4 \times 10^3$kgm$^{-3}$ presented in Ref [97]. If one takes the typical parameters of SSY aggregates, the outer diameter $D = 1.1$nm, repeating distance $a = 0.34$nm, and molar mass $M_{SSY} = 0.452$kgmol$^{-1}$, one estimates the mass density for individual aggregates as
\[ \rho_{SSY} = \frac{4M_{SSY}}{\pi D^2 a_z} = 2.32 \times 10^3 \text{kgm}^{-3} \] (\(N_A\) is the Avogadro’s number), different from \(\rho_{SSY} = (1.82 \pm 0.02) \times 10^3 \text{kgm}^{-3}\) calculated from Eq. (2.8). This difference might result from an inaccurate estimation of the aggregates size (e.g., \(\rho_{SSY} \propto D^{-2}\) and \(D\) varies from 1.1nm to 1.4nm in literatures [12,94,97]), and from the assumption that water is a continuous medium.

**Figure 2.5:** Mass density measurements and calculated volume fraction.
2.5.4 Optical response of bend distortion

To determine \( K_3 \), we measure the intensity of light passing through the homeotropic cell and two circular polarizers; this intensity depends on optical phase retardation \( R(B) \) associated with the field-induced director distortions:

\[
I = I_0 \sin^2 \frac{R}{2}
\]  \hspace{1cm} (2.9)

where \( I_0 \) is the intensity of the incident light. When the field was changed at a very slow rate (0.002 T/min, or 200 s pauses between 0.0065 T increments), the \( I(B) \) curve shows no hysteresis, Fig. 2.6. Higher rates might cause hysteresis; as an example, we show a hysteresis observed for 0.013 T/min (30 s pauses between 0.0065 T increments), Fig 2.6. From the linear part of the \( I(B) \) curve, we found the critical field intensity \( B_3 \).
Figure 2.6: Intensity vs. $B$ for bend deformation. Inset equation is the fitting from linear part of the curve.

2.5.5 Optical simulation to determine splay constant $K_1$

When the LC is distorted by the magnetic field $B$, the free energy density in the general form writes [1]:

$$f = \frac{1}{2} K_1 (\nabla \hat{n})^2 + \frac{1}{2} K_2 (\hat{n} \cdot \nabla \times \hat{n})^2 + \frac{1}{2} K_3 (\hat{n} \times \nabla \times \hat{n})^2 - \frac{1}{2} \frac{\Delta \chi}{\mu_0} (\hat{n} \cdot \mathbf{B})^2 \quad (2.10)$$

In our cases, the deformation is always uniform in the $xy$ plane parallel to the cell, thus we express the director $\hat{n}$ as a function of the normal $z$ coordinate only:

$$\hat{n}(z) = (n_x, n_y, n_z) = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta),$$

where $\theta(z)$ is the polar angle with respect to $\hat{z}$, and $\varphi(z)$ the azimuthal angle with respect to $\hat{x}$ (the easy axis of the planar cell). For $\mathbf{B} = B (\sin \alpha, 0, \cos \alpha)$, as shown in Fig. 2.1 in 2.2, Eq. (2.10) becomes:

$$f = \frac{1}{2} \left( K_1 \sin^2 \theta + K_3 \cos^2 \theta \right) \left( \frac{d\theta}{dz} \right)^2 + \frac{1}{2} \left( K_2 \sin^2 \theta + K_3 \cos^2 \theta \right) \sin^2 \theta \left( \frac{d\varphi}{dz} \right)^2$$

$$- \frac{1}{2} \frac{\Delta \chi}{\mu_0} B^2 \left( \cos \alpha \cos \theta + \sin \alpha \sin \theta \cos \varphi \right)^2 \quad (2.11)$$

In $K_1$ experiment, the boundary conditions at the two surfaces are $\theta(0) = \theta(d) = 90^\circ$. A relatively small 0.3T field applied at $\alpha = 25^\circ$ induces a weak deformation in the bulk. In the midplane, for 0.3 T field, director orientation changes
from $\theta(\pi/2) = 90^\circ$ to $\theta(\pi/2) = 80^\circ$, but $\varphi(z)$ remains 0, as follows from the numerical minimization of the energy. Eq. (2.11) for $\varphi(z) = 0$ simplifies to:

$$f = \frac{1}{2} \left( K_1 \sin^2 \theta + K_3 \cos^2 \theta \right) \left( \frac{d\theta}{dz} \right)^2 - \frac{1}{2} \frac{\Delta \chi}{\mu_0} B^2 \cos^2(\alpha - \theta) \quad (2.12)$$

As $\cos^2 80^\circ \approx 0.03$, the main contribution to the elastic energy is from the splay term. Solving the Euler- Lagrange equation,

$$\frac{\partial f}{\partial \theta} - \frac{d}{dz} \left( \frac{\partial f}{\partial \theta'} \right) = 0 \quad (2.13)$$

where $\theta' = \frac{d\theta}{dz}$, we find the $\theta(z)$ profile as a function of $B$ and can calculate the optical retardation and light transmission, as explained below.

With $\theta(z,B)$ obtained from Eq. (2.13), one can calculate the effective extraordinary refractive index $n_{\text{eff}}(z,B)$ in the cell:

$$n_{\text{eff}}(z,B) = \frac{n_e n_o}{\sqrt{n_e^2 \cos^2(\beta - \theta(z,B)) + n_o^2 \sin^2(\beta - \theta(z,B))}} \quad (1.14)$$

where $n_e$ and $n_o$ are the extraordinary and ordinary refractive indices, respectively; we also take into account that the light propagation direction $\hat{k}$ within the LC, characterized by the polar angle $\beta$ measured with respect to $\hat{z}$, is different from $\mathbf{B}$ direction (polar angle $\alpha$), because of refraction at interfaces. Since the birefringence of the LCLC is low, we use an average refractive index $n_{av} = 1.4$ to calculate $\beta = \sin^{-1} \left( \frac{\sin \alpha}{n_{av}} \right)$. 

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Integration over the cell thickness gives the total phase retardation of the splayed director field [99]:

$$R(B) = \frac{2\pi}{\lambda \cos \beta} \int_0^d (n_{\text{eff}}(z, B) - n_o) dz$$  \hspace{1cm} (1.15)

Using this equation to fit the experimental data of $R(B)$ with an independently measured $\frac{K_i}{\Delta \chi}$, we obtain $\frac{K_i}{\Delta \chi}$, as shown in Fig 2.7.

**Figure 2.7:** Experimental measurement and numerical simulation of $R(B)$ which result in $\frac{K_i}{-\Delta \chi} = 13.2 \mu N$ for a cell of 31.5% SSY with $\Delta n = -0.0768$ for $\lambda = 633$nm at 25°C.
2.5.6 Planar cells, twist constant $K_2$

Transient periodic patterns in twist geometry of Frederiks transition have been observed since 1980’s [90], including the case of LCLCs [91]. We observed the same phenomenon in SSY. When $B$ is applied at $\alpha = 90^\circ$ direction, it causes “bamboo” patterns, Fig 2.8, similar to that presented in Ref [91]. As pointed in Ref [91], the periodic patterns does not appear when $B$ is tilted away from $\hat{n}_0$ direction. In our experiments, we used a 15° tilt away from $\hat{n}_0$ to avoid non-uniform twist, $\alpha = 75^\circ$.

Figure 2.8: Periodic pattern in a planar SSY cell induced after abruptly applying a magnetic field of 0.4T at $\alpha = 90^\circ$. 

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When $B$ is applied at $\alpha = 75^\circ$, the numerical simulations of the director field show that first a weak splay develops, with a small ($< 3^\circ$) deviation from the original orientation. Above some threshold $B_2$, a uniform twist develops, Fig 2.9. Experimentally, $B_2$ can be determined from the $I(B)$ curves, similar to the $K_3$ case described above. The value can also be determined theoretically; analysis below shows that the threshold is determined mainly by the tilt angle $\alpha$ and by the constant $\frac{K_2}{\Delta \chi}$, and that the correction caused by splay is small ($\approx 1\%$).

As the splay is weak, we present the polar angle as a sinusoidal function of $z$, i.e. $\theta(z) = \frac{\pi}{2} + \delta \sin \left( \frac{\pi}{d} z \right)$, where $\delta$ is the maximum polar angle change that occurs in the middle plane of the cell. For fixed boundary condition (strong anchoring), $\theta(0) = \theta(d) = \pi / 2$. For the twisted state near the threshold, we write

\[ \varphi(z) = 0 + \gamma(z) = \varphi_m \sin \left( \frac{\pi}{d} z \right), \quad (\varphi(0) = \varphi(d) = 0 \text{ fixed at two boundaries}). \]

If the twisted state is preferred as compared to pure splay, then the following integral should be negative:

\[ J = \int_0^d \left( \frac{\partial f}{\partial \varphi} \gamma + \frac{\partial f}{\partial \varphi'} \gamma' \right) dz < 0 \quad (1.16) \]

where $\varphi' = \frac{d \varphi}{dz}$, $\gamma' = \frac{d \gamma}{dz}$. Using Eq. (2.11) and $\theta(z)$, $\varphi(z)$ specified above, we find (up to the first order in $\delta$):
Thus,

\[ B_2 = \frac{\pi}{d \sin \alpha} \sqrt{\frac{\mu_0 K_2}{-\Delta \chi \left(1 - \frac{8}{3\pi} \delta \cot \alpha\right)}} \]  

(1.18)

With \( \delta = 3^\circ \), one finds \( \frac{8}{3\pi} \delta \cot \alpha \approx 0.01 \), thus we conclude that the spay correction to the \( B_2 \) value is negligible, and use the simplified equation,

\[ B_2 = \frac{\pi}{d \sin \alpha} \sqrt{\frac{\mu_0 K_2}{-\Delta \chi}} \]  

(1.19)

to determine \( \frac{K_2}{\Delta \chi} \), as indicated in Chapter 2.3.3.
**Figure 2.9:** Numerically simulated dependencies $\theta(d/2)$ and $\varphi(d/2)$ vs $B$ representing maximum deformations in the midplane of cell, for a cell with $d = 23.8\mu m$,

$$
\frac{K_2}{-\Delta \chi} = 1.22 \mu N, \quad \frac{K_1}{-\Delta \chi} = \frac{K_3}{-\Delta \chi} = 9.8 \mu N.
$$
CHAPTER 3
IONIC-CONTENT DEPENDENCE OF VISCOELASTICITY OF THE
LYOTROPIC CHROMONIC LIQUID CRYSTAL SUNSET YELLOW

3.1 Introduction

Self-assembly of organic molecules in water is central to functioning of biological systems and to a broadening range of modern technologies utilizing soft matter. The mechanisms driving a diverse spectrum of self-organized structures are complex and involve a delicate balance of dispersive, hydrophobic/hydrophilic, depletion, and electrostatic forces. To understand these mechanisms, it is important to design model systems in which the structural and mechanical features can be experimentally measured in a reliable way and connected to the underlying composition. In this work, we explore the lyotropic chromonic liquid crystals (LCLCs) as such a system that allows one to deduce the effect of ionic content on viscoelastic properties of orientationally ordered assemblies of organic molecules in aqueous solutions.

Presence of ionizable groups at the surface of chromonic aggregates makes the LCLCs very sensitive to the ionic environment in the solution, evidenced by the shifts in phase diagrams [12,13,108,109], Fig. 3.1C. Similar effects of ionic content on biomolecules are of prime importance in biological processes such as DNA wrapping around nucleosomes, packing inside bacteriophage capsids, and binding to proteins and
so on [15,16]. In this work, we quantify the effect of ionic content on the anisotropic elastic and viscous properties of the nematic LCLCs. The advantage of using the nematic LCLC in exploring the role of electrostatics is that the anisotropic viscoelastic parameters are well defined and can be accurately measured through the macroscopic deformations caused by the realigning action of an applied magnetic field (the so-called Frederiks effect) [110] Using this technique, we measure the elastic constants of splay, bend and twist and rotational viscosity. These viscoelastic parameters have different and often very pronounced responses to the added monovalent and divalent salts and to pH changing agents. The observed dependencies of the viscoelastic parameters are discussed in terms of changes of the chromonic aggregates, namely, their contour and persistence lengths.

3.2 Material and Methods

The aqueous solution of SSY is probably the simplest LCLC in terms of aggregate organization [4,10]. The molecules, Fig. 3.1A, have two ionizable sulfonate groups at the periphery. When in water, they stack on top of each other, forming aggregates with only one molecule in its cross-section [10,94], Fig. 3.1B. The diameter of aggregates is $D \approx 1.1$nm, while the typical molecular separation along the axis is $a_z \approx 0.34$nm [12,94]. The maximum linear charge density along the aggregates is $	au_{\text{max}} e \approx 6e$/nm, similar to double-strand DNA (ds-DNA) molecules, where $\tau_{\text{max}}$ is the maximum degree of ionization of the surface groups. Unlike ds-DNA, the length of SSY aggregates is not covalently fixed, a feature that makes the effect of ionic content on the length of chromonic aggregates very profound.
To vary the ionic content of the dispersions, we use a monovalent salt NaCl, divalent salt MgSO₄, and the pH-increasing agent NaOH. The volume fraction of SSY in all solutions remains constant, $\phi \approx 0.2$ [110] (see Appendix B). The phase diagrams of the SSY dispersion with different additives is shown in Fig. 3.1C. The elastic constants of splay ($K_1$), twist ($K_2$) and bend ($K_3$) as well as the rotation viscosity $\gamma_1$ were measured as a function of temperature and additive concentration using the magnetic field realignment technique, as described in Ref. [110] and in Appendix C.

**Figure 3.1:** Molecular structure (A), schematic of nematic LCLC phase (B), and phase diagram (C) of SSY aqueous solution with ionic additives. (A) The prevailing NH Hydroazoine tautomer form is shown. (B) Red dots on aggregates surface represent
sulfonate groups, while isolated circles represent disassociated Na\(^+\) ions. (C) Dash line marks the nematic to nematic-isotropic phase transition temperature \(T_{N\rightarrow N+I} = 316.5\) K of the original SSY LCLC.

### 3.2.1 LCLC SSY with ionic additives

The disodium salt of 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonic acid, a widely used food dye generally known as sunset yellow (SSY) was purchased from Sigma-Aldrich (90% purity) and purified twice following previously established procedures[12,94,97]. Deionized water (resistivity > 18.1 M\(\Omega\)·cm) was used to make the original \(c_{SSY} = 0.98\text{mol/kg}\) solution. The mixing was done on a vortex mixer at 2000rpm in isotropic phase for several minutes, then room temperature overnight. The SSY mixture was then split into smaller portions to add salts NaCl (99.5%, Sigma-Aldrich) or MgSO\(_4\) (Reagent, Sigma-Aldrich). The new mixtures were mixed again on vortex overnight at 2000rpm. Comparing to the previously reported procedure [12], in which SSY was added into pre-mixed salt solution, current procedure minimizes the error of \(c_{SSY}\) and its influence on the viscoelastic measurements.

The \(c_{SSY} = 0.98\text{mol/kg} + \text{NaOH}\) solutions were made following previously reported procedure [12] by adding SSY into NaOH (Reagent, Acros) solutions of 0.01 and 0.02mol/kg and then mixing in vortex for 3hrs. Plastic vials and pipets were used to avoid reaction between NaOH and glass that reduces pH and affects LCLC properties.
3.2.2 Viscoelastic constants measurement

We follow the customized magnetic Frederiks transition technique for LCLCs, using cells of two distinct surface alignments, planar and homeotropic anchoring, to measure $\frac{K_1}{\Delta \chi}$, $\frac{K_2}{\Delta \chi}$ and $\frac{K_3}{\Delta \chi}$ [110]; $\Delta \chi$ is the diamagnetic anisotropy. In the twist measurement setup, we measure the dynamics of optical response to abruptly changed magnetic field and obtain the rotation viscosity coefficient $\gamma_1$ [1] (see Appendix C). $\Delta \chi$ is measured using a superconducting quantum interference device (SQUID) following Ref [107,110] (results will be reported elsewhere).

3.3 Results

3.3.1 Splay constant $K_1$

Splay constant $K_1$ is on the order of 10 pN and decreases as $T$ increases, Fig. 3.2A. $K_1$ shows a dramatic response to the addition of divalent salt MgSO$_4$, by increasing its value by a factor of about 3. Similarly strong but opposite effect of decreasing $K_1$ is observed upon addition of small amount (~0.01mol/kg) of NaOH. The monovalent salt NaCl shows little, if any, effect.

Following the earlier models of Onsager [9], Odijk [101] and Meyer [85], $K_1$ is expected to grow linearly with the length of aggregates $\bar{L}$, since splay deformation require one to fill splay-induced vacancies by the free ends of aggregates, as discussed by Meyer [85]:
The LCLC aggregates are polydisperse, so that the length \( L \) is some average measure of the balance of the attractive forces of stacking, characterized by the so-called scission energy \( E \) and entropy. The scission energy, estimated to be roughly of the order of \( 10k_BT \) \([12,88,94,97]\), measures the work one needs to perform to separate a single aggregate into two. In both isotropic and nematic phases \([89,110]\), the dependency of \( L \) on \( E \) is expected to be exponentially strong, \( L \propto \exp \left( \frac{E}{2k_BT} \right) \), where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. The scission energy can be approximated as \( E = E_0 - E_e \) to reflect the fact that it depends on the strength (\( E_0 \)) of \( \pi-\pi \) attractions of aromatic cores and electrostatic repulsion (\( E_e \)) of ionized sulfonate groups at the periphery of SSY molecules. The strength of \( E_e \) should depend quadratically on linear charge density \( \tau \) on aggregates, \( E_e \propto \tau^2 \). According to Manning \([111-113]\), condensation of counterions reduces linear charge density from \( \tau_{\text{max}} e \approx 6e/\text{nm} \) to an effective one, \( \tau e = \frac{1}{Zl_B} e \), where \( Z \) is the valence of counter ions, and \( l_B = e^2/(4\pi\varepsilon\varepsilon_0k_BT) \approx 0.7\text{nm} \) is the Bjerrum length in water at 300K. \( E_e \) should further decrease as Debye screening is enhanced by addition of ions. Following MacKintosh et al \([114]\), we estimate (see Appendix A) that \( E_e \) scales as:

\[
K_1 = \frac{4}{\pi} \frac{k_BT}{D} \phi \frac{L}{D}
\]

(3.1)
\[ E_e \propto \tau^2 \lambda_D \]  

where \( \lambda_D = \sqrt{\frac{\varepsilon e_i k_B T}{\varepsilon^2 \sum n_i q_i^2}} \) is the Debye screening length, \( n_i, q_i \) are the number density and strength of the \( i \)-th ions in solution, respectively. According to Eq. (3.2), one expect the proportions of the electrostatic parts \( E_e \) of the scission energy for the salt-free SSY, SSY with added \( c_{NaCl} = 0.9 \text{mol/kg} \) of NaCl and SSY with \( c_{MgSO_4} = 1.2 \text{mol/kg} \) of MaSO_4 to be as following: \( E_e^{NaCl} : E_e^{NaCl} : E_e^{MgSO_4} = 1:0.72:0.10 \). This estimate suggests that Mg\(^{2+}\) has a stronger effect than Na\(^{+}\) in the increase of \( E \) and thus \( K_1 \), since \( K_1 \propto \tilde{L} \propto \exp \left( \frac{E}{2k_B T} \right) \), in qualitative agreement with the experimental data. Interestingly, end-to-end attraction of short DNA strands has been observed in presence of divalent ion Mg\(^{2+}\) but not in presence of Na\(^{+}\) [115]. Ionic additives are also known to change the aggregation length in self-assembled polyelectrolytes such as worm-like micelles [114,116,117].

The effect of NaOH is opposite to that of the addition of salts since high pH increases the degree of ionization \( \tau \) of the sulfonate groups [12,118], thus enhancing electrostatic repulsions of the molecules, shortening the aggregates and making the splay constant \( K_1 \) smaller.
Figure 3.2: Temperature and ionic content dependence of (A) splay constant $K_1$, (B) bend constant $K_3$ and (C) twist constant $K_2$ of SSY LCLC, $c_{SSY}=0.98\,\text{mol/kg}$ with ionic
additives. Insets illustrate the corresponding director deformation, where (A) splay creates vacancies that require free ends to fill in, (B) bend can be accommodated by bending the aggregates and (C) twist can be realized by stacking “pseudolayers” of uniformly aligned aggregates within the layers; director rotates only when moving across layers.

### 3.3.2 Bend constant $K_3$

Bend constant $K_3$ is on the order of 10 pN and decreases as $T$ increases, Fig. 3.2B. When salts are added, at a given temperature, the effect of NaCl and MgSO₄ is different, namely, NaCl leads to a smaller $K_3$ and MgSO₄ makes $K_3$ larger. In presence of even small amount of NaOH (0.01mol/kg), $K_3$ decreases. The bend constant is determined first of all by the flexibility of the aggregates that can be described by the persistence length $\lambda_p$, defined as the length over which unit vectors tangential to the aggregates lose correlation. The expected trend is [85,101,110]:

$$K_3 = \frac{4 k_B T \phi \lambda_p}{\pi D}$$  \hspace{1cm} (3.3)

Flexibility of SSY aggregates should depend on the electrostatic repulsions of surface charges since bend brings these like-charges closer together. As discussed above, addition of NaCl does not change the scission energy $E$ and the transition temperatures $T_{N\to N+1}$ much. However, when the bend deformation are imposed, the NaCl-induced
screening of the like charges might become stronger at shorter distances, thus reduces $K_3$, Fig. 3.3. Interestingly, $K_3$ shows a linear dependence on $\lambda_D^2$ that decreases as $c_{NaCl}$ increases, Fig. 3.3B. A similar mechanism of increased flexibility upon addition of salts such as NaCl is considered for isolated molecules of ds-DNA [119-121]. In the Odijk-Skolnick-Fixman (OSF) model [122,123], the expected decrease of persistence length is on the order of 10% and only if the concentration of salt is below 0.05 M. In Manning’s approach [111-113], the decrease of persistence length is larger, about 45% when NaCl concentration increases from 0.1 to 1 M. Our experimental data fall in between the two limits. Both models [112] predict $\lambda_p \propto \lambda_D^2$, consistent with our experimental $K_3$ and Eq. (3.3), Fig. 3.3B.

The effect of MgSO$_4$ on $K_3$ is harder to describe as the divalent salt noticeably enhances the temperature range of the nematic phase, increasing the scission energy and the transition point $T_{N\rightarrow N+I}$ (by up to 17K). If the data are compared at the same temperature, $K_3$ is increased in the presence of MgSO$_4$, Fig. 3.2B. However, if one plots $K_3$ versus a relative temperature, $\Delta T = T - T_{N\rightarrow N+I}$, Fig. 3.3A, then the effect of added MgSO$_4$ is in reduction of $K_3$, in agreement with the idea of salt-induced screening of the surface charges that make the aggregates more flexible.
3.3.3 Twist constant $K_2$

Twist constant $K_2$ is on the order of 1 pN, about 10 times smaller than $K_1$ and $K_3$, Fig. 3.2C. Similarly to the case of $K_3$, addition of NaCl decreases $K_2$, while divalent salt MgSO$_4$ increases $K_2$; small amounts (~0.01mol/kg) of NaOH decrease $K_2$.

As compared to other modes of deformation, twist is the easiest one in LCLCs, since it does not require finding free ends or deforming the aggregates. In an ideal arrangement, aggregates lie in consecutive “pseudolayers”, with the director $\hat{n}$ rotating by a small angle only when moving between the pseudolayers, Fig. 3.2C inset. The aggregates may be displaced across the layers by thermal fluctuation and interfere with aggregates of a different orientation. This interference can be relieved by bending the aggregates to follow local orientational order. Thus $K_2$ is expected to be independent of $\bar{L}$ and weakly dependent on $\lambda_p$ (as compared to $K_3$); as suggested by Odijk [101]

$$K_2 = \frac{k_B T}{D} \phi^{1/3} \left( \frac{\lambda_p}{D} \right)^{1/3}$$ (3.4)

From Eq. (3.4), we expect twist constant $K_2$ to change in a similar way as $K_3$ does in response to the ionic additives, since both of them depend on $\lambda_p$. Experimental results, Fig. 3.2C, do show a qualitative agreement with this prediction.
Figure 3.3: (A) $K_3$ as a function of $\Delta T = T - T_{N \to N+1}$ for different ionic contents; insets show schematically that enhanced Debye screening increases the flexibility of aggregates. (B) For values measured at different $\Delta T$, $K_3$ show linear relations with $\lambda_D^2$, which decreases as $c_{NaCl}$ increases.
3.3.4 Rotation viscosity $\gamma_1$

Rotation viscosity $\gamma_1$ covers a range of (0.2-7) kgm$^{-1}$s$^{-1}$, several orders of magnitudes higher than $\gamma_1 \sim 0.01$ kgm$^{-1}$s$^{-1}$ of a standard thermotropic LC 5CB (4'-n-pentyl-4-cyanobiphenyl) [124]. $\gamma_1$ decreases exponentially as $T$ increases, Fig. 3.4. Addition of NaCl increase $\gamma_1$ by a small factor, while MgSO$_4$ increases $\gamma_1$ dramatically; addition of NaOH decreases $\gamma_1$. Analysis of the experimental data shows that $\gamma_1 \propto K_T^2$ in all cases, Fig 3.4. insets.
Figure 3.4: Temperature and ionic contend dependence of rotation viscosity $\gamma_1$ of SSY LCLC, $c_{SSY} = 0.98\text{mol/kg}$ with ionic additives. Insets show the linear relation, $\gamma_1 \propto K_i^2$ for all measurements.

Director rotation in the nematic LCs composed of long slender particles ($L/D >> 1$) induces mass displacement, and is thus coupled with macroscopic flows. According to Meyer’s geometry argument [85,86,125,126], a twist deformation that induces shear flow $\frac{\partial v}{\partial z} = \text{constant}$ causes power dissipation per monomer along the aggregates as $P = \mu z^2 \left( \frac{\partial v}{\partial z} \right)^2$, where $\mu$ is a friction coefficient and $z$ is the distance of the monomer to the rotation center. The mean power dissipation

$$\bar{P} = \frac{1}{L} \int_{-L/2}^{L/2} Pdz = \mu \frac{E}{12} \left( \frac{\partial v}{\partial z} \right)^2;$$

thus the rotation viscosity $\gamma_1$ scales as:

$$\gamma_1 \propto \bar{L}^2$$  \hspace{1cm} (3.5)

According to previous analysis of $\bar{L} \propto \exp \left( \frac{E}{2k_BT} \right)$ and Eq. (3.5), the exponential dependence $\gamma_1 \propto \bar{L}^2 \propto \exp \left( \frac{E}{k_BT} \right)$ makes $\gamma_1$ sensitive to $T$ and $E$, and implies that $\gamma_1 \propto K_i^2$, Eq. (3.1). The experimental findings for $\gamma_1$, Fig. 3.4, such as exponential dependence on $T$, effect of MgSO$_4$ and NaOH, and the scaling $\gamma_1 \propto K_i^2$, all agree with
these expectations and are consistent with the previous analysis of the $K_1$ behavior. The only discrepancy is that the addition of NaCl increases $\gamma_1$ while shows little influence on $K_1$. Of course, these trends are discussed only qualitatively and in the simplest terms possible, avoiding other important factors, such as possible structural defects in formation of SSY aggregates [12,127,128], collective and dynamic effects, etc.

3.4 Conclusion

We measured the temperature and ionic content dependences of anisotropic elastic moduli and rotation viscosity of the self-assembled orientationally ordered system formed by the polydisperse self-assembled aggregates of dye SSY bound by weak non-covalent forces. We observe dramatic and versatile changes of the viscoelastic properties induced by the ionic additives that alter the electrostatic interactions caused by charged groups at the surface of aggregates. We connect these macroscopic properties to the microscopic structural and mechanical features of the aggregates, such as the average contour length $\bar{L}$ and persistence length $\lambda_p$, and explain our findings through the idea that both $\bar{L}$ and $\lambda_p$ are controlled by the ionic content. This type of sensitivity of the building units of an orientationally ordered system to the ionic properties of the medium are absent in the conventional thermotropic and lyotropic LCs (such as polymer melts) featuring the building units with the shape that is fixed by the strong covalent bonds. Further understanding of the link between the viscoelastic anisotropy and composition of the chromonic system require a substantial advance in theoretical description at the level
of individual aggregates and their collective behavior. The presented experimental data might be of importance in verifying the validity of various models.

3.5 Supplemental Information

3.5.1 Estimation of $E_c$

Disassociation of Na\textsuperscript{+} into water makes SSY aggregates charged, with a maximum possible charge density $\tau^{\max} \approx 6e/\text{nm}$, corresponding to Manning’s reduced charge density $\tilde{\zeta} = l_B \tau \approx 4.2$, where $l_B = e^2 / (4\pi\varepsilon_0 k_B T) \approx 0.7\text{nm}$ is the Bjerrum length in water at 300K. Counterion condensation happens at the aggregate surfaces\cite{88,111} and renormalizes $\zeta > \frac{1}{Z}$ to $\zeta = \frac{1}{Z}$, thus reduces $\tau$ to $\frac{1}{Zl_B}$, where $Z$ is the valence of the counter ions. The repulsive interaction is further reduced by counterion screening. MacKintosh et al\cite{114} estimates $E_c$ in the form of:

$$E_c = \frac{l_B D \tau^2 k_B T}{2\phi^{3/2}}$$

(3.6)

where $\phi = \phi + (D / \lambda_D)^2$ considers screening effect from both increases volume fraction $\phi$ (ions are pushed closer to aggregates) and enhanced screening by addition of ions. In all studied SSY, $\lambda_D \leq 0.31\text{nm}$, $(D / \phi)^2 \gg 1$, thus we approximate $\phi \approx (D / \lambda_D)^2$ to simplify $E_c$.
3.5.2 Measurement of volume fraction $\phi$

We approximate the solvent of SSY (pure water, or water solution of ionic additives) as continuum media and measure the density of both the solvents $\rho_{\text{solvent}}$, and nematic SSY LCLC, $\rho_{\text{SSY}}$, with a densitometer DE45 (Mettler Toledo). From the molality of SSY and ionic additives, we calculate the weight percentage ($w$) of SSY in the final LCLC.

$$w = \frac{c_{\text{SSY}}M_{\text{SSY}}}{c_{\text{SSY}}M_{\text{SSY}} + c_{\text{ion}}M_{\text{ion}} + 1}$$  \hspace{1cm} (3.8)

where molality of SSY $c_{\text{SSY}} = 0.98\text{mol/kg}$ is fixed in all experiments, $M_{\text{SSY}} = 0.452\text{kg/mol}$ is the molecular weight of SSY, $c_{\text{ion}}$ and $M_{\text{ion}}$ are the molality and molecular weight of ionic additives. We then calculate the volume fraction $\phi$ of SSY:

$$\phi = 1 - \phi_{\text{solvent}} = 1 - \frac{\rho_{\text{solvent}}}{1} = 1 - (1 - w)\frac{\rho_{\text{SSY}}}{\rho_{\text{solvent}}}$$  \hspace{1cm} (3.9)

The result of $\phi$ is shown in Fig 3.5. The change of $\phi$ is insignificant, with a maximum increase of about 0.004, thus we can treat $\phi$ as constant in calculations. Notice that NaCl barely changes $\phi$, while MgSO$_4$ slightly increases $\phi$ as $c_{\text{MgSO}_4}$ increases. This is consistent with the analysis of the elongation of aggregates and enhanced nematic
order reflected on phase diagram, Fig 3.1. NaOH doped SSY solutions are not measured due to the corrosive nature of NaOH to SiO$_2$, which can damage the equipment and affect accuracy.

![Figure 3.5](image)

**Figure 3.5:** Temperature and ionic content dependences of volume fraction $\phi$ of SSY.

### 3.5.3 Measurement of rotation viscosity $\gamma_i$

In the twist geometry, as the magnetic field increases, the director experiences first a small splay deformation, then a uniform twist across the cell. Since change of the polar angle $\theta$ is less than $5^\circ$, we approximate $\theta=90^\circ$, and describe the director field with a pure twist deformation with a director field $\hat{n}=(\cos \varphi, \sin \varphi, 0)$, where $\varphi(z)$ is the azimuthal angle of local director at height $z$. The magnetic field $\mathbf{B} = B(\sin \theta_B, 0, \cos \theta_B)$
is applied with $\theta_b = 75^\circ$, and planar surface alignment provides the initial director direction $n_0 = (1,0,0)$. The Frank-Oseen elastic energy density is:

$$f = \frac{1}{2} K_z \left( \frac{\partial \varphi}{\partial z} \right)^2 - \frac{1}{2} \frac{\Delta \chi}{\mu_0} B^2 \sin^2 \theta_b \cos^2 \varphi$$

(3.10)

We define a frictional coefficient $\gamma$ to describe the energy dissipation when the total free energy changes:

$$A \int_0^d \gamma \left( \frac{dn}{dt} \right)^2 = - \frac{d}{dt} A \int_0^d f dz$$

(3.11)

Plug in $\dot{n}$ and $f$, the differential form of Eq. (3.11) reads:

$$\gamma \frac{\partial \varphi}{\partial t} = K_z \frac{\partial^2 \varphi}{\partial z^2} - \frac{\Delta \chi}{\mu_0} B^2 \sin^2 \theta_b \sin \varphi \cos \varphi$$

(3.12)

At small $\varphi$, we linearize the above equation with approximations $\cos \varphi \approx 1$ and $\sin \varphi \approx \varphi$, and assume that $\varphi$ follows a simple form of $\varphi = \varphi_0 \exp \left( \frac{t}{\tau} \right) \sin(qz)$, where $\varphi_0$ is the azimuthal angle at center of the cell, $\tau$ is a characteristic time describing the decay ($\tau < 0$) or growth ($\tau > 0$) of $\varphi$, $q = \frac{\pi}{d}$. The linearized Eq. (3.12) then turns into a linear relation between $\frac{1}{\tau}$ and $B^2$:

$$\frac{1}{\tau} = -\frac{1}{\gamma} \frac{\Delta \chi}{\mu_0} B^2 \sin^2 \theta_b - \frac{1}{\gamma} K_z q^2$$

(3.13)
Experimentally, we can obtain relaxation rate $\frac{1}{\tau}$ from the dynamics of light intensity $I(t)$.

In the twist geometry, we expect:

$$ I \propto \sin^2 \frac{\Gamma}{2} $$

(3.14)

where $\Gamma$ is the total retardation caused by the azimuthal rotation of the director field, experienced by the oblique incident light. An analytical calculation of $\Gamma$ is difficult, but in general one can assume:

$$ \Gamma = \int_0^d \phi_i \sin qz \cdot g(z) dz \propto \phi_i $$

(3.15)

where $\phi_i = \phi_0 \exp \left( \frac{t}{\tau} \right)$ is the time dependence of azimuthal angle, and $g(z)$ describes the detail of phase retardation calculation. At small $\Gamma$, we linearize Eq. (3.14):

$$ I \propto \left[ \phi_0 \exp \left( \frac{t}{\tau} \right) \right]^2 $$

(3.16)

Numerical simulation supports our expectation of Eq. (3.16), Fig. 3.6C. Up to $\phi_0 \approx 12^\circ$, $I \propto \phi_0^2$ is satisfied. In the experiments, we measure $I(t)$ up to $10^{-2} I_{\text{max}}$ (to satisfy small $\Gamma$ condition) and fit it with exponential function to obtain $1/\tau$ at various $B$ values, Fig. 3.6AB. Then we fit $1/\tau$ vs. $B^2$ to obtain $\gamma$, Fig. 3.6D. A calculation strictly following nematodynamics [1] shows that $\gamma$ is equivalent to the generally defined rotation viscosity $\gamma_1$. 

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Figure 3.6: Measurement of rotational viscosity $\gamma_1$ from the relaxation of magnetic field induced twist. (A) Intensity increase in response to suddenly applied magnetic fields $B > B_{th}$; $B_{th}$ is the threshold field of twist Frederiks transition. (B) Intensity decay in response to suddenly reduced magnetic field. (C) Numerical simulation shows that intensity increases quadratically with the mid-plane twisting angle $\varphi_0$. (D) Linear fit of $1/\tau$ vs $B^2$, where the rotation viscosity $\gamma_1$ can be extracted from the slope.
CHAPTER 4:
ELASTICITY, VISCOSITY, AND ORIENTATIONAL FLUCTUATIONS OF A
LYOTROPIC CHROMONIC NEMATIC LIQUID CRYSTAL DISODIUM
CROMOGLYCATE

4.1 Introduction

There are two primary experimental techniques to determine the viscoelastic properties of nematic liquid crystals (LCs)[129]: (1) the Frederiks transition, i.e., reorientation of the axis of nematic order (director) by an applied field, and (2) light scattering on thermal fluctuations of the director. The magnetic Frederiks transition has been applied to explore the elastic properties of two LCLCs, disulphoindantrone[92,93] and sunset yellow (SSY) [110], as discussed in Chapter 2-3. The Frederiks approach requires the LC director to be uniformly aligned in two different fashions, planar and homeotropic, with the director parallel to the bounding substrates of the sample cell and perpendicular to them, respectively. Such a requirement is difficult to satisfy for lyotropic systems. In particular, homeotropic anchoring of LCLCs has been reported only for a few cases [23,110,130]. One of the most studied LCLCs, representing water dispersions of disodium cromoglycate (DSCG), shows only transient homeotropic alignment (although there is a recent report on the homeotropic alignment at a grapheme substrate [130]), thus making it difficult to determine the viscoelastic properties of this material. On the other
hand, knowledge of viscoelastic properties of DSCG is of particular importance for further understanding of LCLCs, since DSCG is optically transparent and has been used as a biocompatible component in real-time biological sensors[131] and in formulations of LCLC-bacterial dispersions[132-134].

In this chapter, in order to characterize the material parameters of the nematic phase of water solutions of DSCG, we use the dynamic light scattering (DLS) that requires only one type (planar) of surface anchoring. The approach is similar to the one used previously by Meyer et al to characterize polymer solutions exhibiting the nematic phase[85,86,104,125,126,129], and allows one to extract both the elastic moduli and the viscosity coefficients. By calibrating the set-up with the measurement of DLS spectrum for the well-studied nematic 4'-n-pentyl-4-cyanobiphenyl (5CB), we extract the absolute values of the elastic constants and viscosities for DSCG. The approach allows us to trace both the concentration and temperature dependences of these viscoelastic parameters. A small portion of these results (one concentration only) were made available in 2008 in electronic-Liquid Crystal Communications[135] and arXiv[136].

In these measurements, we observe that the splay elastic constant $K_1$, splay and twist viscosities $\eta_{splay}$ and $\eta_{twist}$ all increase dramatically as the temperature is reduced. The DLS spectrum not only shows the modes that correspond to the standard viscoelastic response (director modes), but also reveals an additional fluctuation mode weakly coupled to the director. We suggest that this mode is associated with structural defects in packing of chromonic aggregates such as stacking faults. The observed peculiarities of
viscoelastic properties of LCLCs, absent in other LCs, originate from the fact that the chromonic molecules in the aggregates are bound by weak non-covalent interactions. As a result, the length of aggregates and the viscoelastic parameters that depend on it are extremely sensitive to both concentration and temperature.

4.2 Experimental Details

4.2.1 Materials

Disodium Cromoglycate (DSCG), Fig. 4.1(A), was purchased from Spectrum Chemicals (98% purity) and subsequently dissolved in deionized water (resistivity 18 MΩ cm) at concentrations of $c=12.5$, 14.0, 16.0 and 18.0 wt%. Following Ref [5], the corresponding volume fractions are: $\phi=0.089$, 0.100, 0.115, and 0.129. The transition temperatures of the nematic to nematic-isotropic biphasic region are $T_{ni}=297.0\pm0.2K$, 299.6±0.4K, 303.5±0.3K and 306.2±0.2K, respectively, according to the established phase diagram[137] and our independent microscopy analysis. The DLS measurements were performed in the homogeneous nematic phase over the temperature range from 294.5K to within 1K of $T_{ni}$. The nematic director was aligned in a planar fashion by glass substrates coated with buffed layers of polyimide SE-7511 (Nissan Chemical Inc.)[25]. Optical cells of thickness 19 μm were sealed with epoxy to prevent water evaporation from the samples. The value of $T_{ni}$ of each sample was checked before and after the measurement, showing changes of less than 1K in all cases. For light scattering
measurements, the samples were housed in a hot stage with optical access and temperature control with an accuracy of 0.1 K and stability of 0.01 K over 1 hr.

The thermotropic nematic liquid crystal 4'-n-pentyl-4-cyanobiphenyl (5CB), used for reference measurements, was purchased from Sigma-Aldrich (98% purity). Planar alignment of the director in a 13.7 μm thick sample is produced by buffed polyimide PI2555 layers (HD MicroSystems) applied to surfaces of the flat glass substrates.

**Figure 4.1:** (A) Structure of the DSCG molecule and generic representation of LCLC aggregates formed in aqueous solution. (Each disk in the aggregate stack may represent single or paired DSCG molecules.) (B)(C) Schematic of experimental light scattering
geometries used in our measurements: (B) “1&2”, splay+twist (pure splay shown) geometry and (C) “3” bend-twist (pure bend shown) geometry.

4.2.2 Experimental set-up

In the two studied light scattering geometries, the director \( \hat{n} \) is either perpendicular (geometry “1&2”, Fig 4.1(B)) or parallel (geometry “3”, Fig 4.1(C)) to the scattering plane. The polarization (\( \hat{i} \)) of the normally incident \( \lambda =532 \) nm laser light is vertical; depolarized scattering was collected through a horizontal analyzer (\( \hat{s} \)). The laser power was kept below 3 mW to avoid parasite effects of light absorption. Homodyne cross-correlation functions of the scattered light intensity (evenly split between two independent detectors) were recorded as a function of time on a nanosecond digital correlator. The angular-dependent average light intensity \( I_{1\&2}(\theta) \) (divided by the incident light intensity \( I_0 \) in the sample) measured in geometry “1&2” may be expressed as[1]:

\[
I_{1\&2} = I_1(\theta) + I_2(\theta) = (\Delta \varepsilon)^2 (\pi \lambda^{-2}) \Omega d A k_B T \left[ \frac{G_1(\theta)}{K_1q_\parallel^2(\theta)} + \frac{G_2(\theta)}{K_2q_\perp^2(\theta)} \right]
\]

(4.1)

where \( \theta \) is the laboratory scattering angle, \( \Omega \) is the collection solid angle, \( A \) is the cross-sectional area and \( d \) the thickness of the illuminated sample volume, \( \Delta \varepsilon = \varepsilon_\parallel - \varepsilon_\perp = n_\parallel^2 - n_\perp^2 \) is the dielectric anisotropy at optical frequency, \( n_\parallel \) and \( n_\perp \) are the refractive indices for light polarized parallel and perpendicular to the director, respectively, and \( q_\parallel(\theta) \) and \( q_\perp(\theta) \) are the two components of scattering vector \( \mathbf{q} = \mathbf{k}_s - \mathbf{k}_i \).
along and perpendicular to \( \hat{n} \) respectively. The geometrical scattering factors \( G_1(\theta) \) and \( G_2(\theta) \) are:

\[
G_1(\theta) = \frac{\cos^2 \frac{\theta}{2} (1 + p)^2}{1 + p + s^2}, \quad G_2(\theta) = \frac{\left( \sin \frac{\theta}{2} - s \cos \frac{\theta}{2} \right)^2}{1 + p + s^2}
\] (4.2)

where \( s = \frac{\Delta n}{2 n_\perp \sin \frac{\theta}{2}} \), \( p = \frac{\Delta n}{n_\perp} \), and \( \Delta n = n_\parallel - n_\perp \) is the optical birefringence of the LCLC sample. The separation of \( I_1(\theta) \) and \( I_2(\theta) \) is done by fitting the time correlation function of the scattered intensity \( I_{1\&2}(\theta) \) to two overdamped decay processes with different relaxation rates \( \Gamma_1 \) and \( \Gamma_2 \) (as discussed below).

The expression for the scattered intensity in geometry “3” is:

\[
I_3(\theta) = (\Delta \varepsilon)^2 (\pi \lambda^{-2})^2 \Omega d A k_B T \frac{G_3(\theta)}{K_2 q_{\parallel}^2(\theta) + K_2 q_{\perp}^2(\theta)}
\] (4.3)

where \( G_3(\theta) = \cos^2 \theta \). In DSCG LCLC, as we will confirm below, \( K_2 \ll K_3 \). Over the range of angles \( \theta = (5 - 35)^\circ \) studied, we estimate \( \left( \frac{K_2 q_{\parallel}^2}{K_3 q_{\parallel}^2} \right)_{\text{max}} \approx 0.01 \). Thus we neglect \( K_2 q_{\perp}^2 \) in Eq. (4.3), leading to:

\[
I_3(\theta) = (\Delta \varepsilon)^2 (\pi \lambda^{-2})^2 \Omega d A k_B T \frac{G_3(\theta)}{K_3 q_{\parallel}^2(\theta)}
\] (4.4)

The cell gap (sample thickness) \( d \) was measured by interferometry in empty cells.
The measured intensities \( I_{1,2,3} \) are functions of material parameters such as \( \Delta \varepsilon \) and \( K \)'s, and experimental conditions such as \( d \) and \( T \). To obtain absolute values of \( K_3 \), we calibrated the scattered intensity \( (I_3(\theta)) \) measured on DSCG LCLC against measurements made in the identical geometry “3” set-up on a reference 5CB sample, whose values of \( \Delta \varepsilon \), \( K_2 \) and \( K_3 \) are well known[124,138,139]. We can then deduce the absolute values of the DSCG elastic constant \( K_3 \) from the ratio

\[
\frac{[I_3(\theta)]_{\text{DSCG}}}{[I_3(\theta)]_{\text{SCB}}} = \frac{[K q_3^2 + K_2 q_2^2]_{\text{SCB}} [G_3(\theta)(\Delta \varepsilon)^2 Td]_{\text{DSCG}}}{[K q_3^2]_{\text{DSCG}} [G_3(\theta)(\Delta \varepsilon)^2 Td]_{\text{SCB}}} \tag{4.5}
\]

and the values of \( K_1 \) and \( K_2 \) from similar ratios for \( I_1(\theta) \) and \( I_2(\theta) \).

From measurements of the homodyne intensity correlation function in time (\( \tau \)), we obtain the angular dependent relaxation rates \( \Gamma_\alpha(\theta) \) for the director fluctuations by fitting the experimental data in Fig. 4.2 to the standard expression for overdamped modes:

\[
\langle I(0,\theta)I(\tau,\theta) \rangle = \bar{I}^2(\theta) + g^2 \left[ \sum_\alpha \bar{I}_\alpha(\theta) \exp(-\Gamma_\alpha \tau) \right]^2 \tag{4.6}
\]

Here \( g \) is the optical coherence factor [140]. For geometry “1&2”, \( \alpha = 1,2 \), the splay and twist modes contribute separately to the total intensity; for geometry “3”, \( \alpha = 3 \), from Eq. (4.4) only the bend mode should contribute to the total intensity. From \( \Gamma_\alpha(\theta) \), we
obtain the corresponding orientational viscosities as: 
\[ \eta_{\text{splay}} = K_1 q_{\perp}^2(\theta) / \Gamma_1(\theta) \]
\[ \eta_{\text{twist}} = K_2 q_{\perp}^2(\theta) / \Gamma_2(\theta) \] and 
\[ \eta_{\text{bend}} = K_3 q_{||}^2(\theta) / \Gamma_3(\theta) \].

**Figure 4.2:** Correlation functions (open circles) collected at T = 294 K for \( q_{||} = 1.64 \times 10^6 \text{ m}^{-1} \) in a bend (left) and for \( q_{\perp} = 1.00 \times 10^7 \text{ m}^{-1} \) in splay + twist geometries (right) for the nematic LCLC formed by 14 wt % DSCG in water. Solid lines represent fits of the correlation functions (double exponential in the splay + twist geometry, stretched double exponential in bend geometry) to obtain relative normalized amplitudes \( I_\alpha \) and relaxation rates \( \Gamma_\alpha \) (\( \alpha = 1 - 3 \)), of the fluctuation modes. In the bend geometry, the
analysis reveals an additional, weak mode $\Gamma_4$. In this case, the best single-exponential fit (the dashed line) clearly misses the data in the $(10^{-4} - 10^{-3})$ s region (left insert). The right inset shows the relaxation time spectrum obtained by the regularization method [141] for the bend geometry correlation function; the small secondary peak confirms the presence of the additional mode.

4.3 Results

4.3.1 Elastic constants

The temperature and concentration dependences of the elastic moduli $K_1$, $K_2$ and $K_3$ of the nematic phase of DSCG are shown in Fig. 4.3. The splay constant $K_1$ and bend constant $K_3$ are comparable to each other, being on the order of 10 pN, while the twist constant $K_2$ is about 10 times smaller (confirming the estimate leading to Eq. (4.4)). Similar values and large anisotropy were recently reported for another LCLC, Sunset Yellow[110]. All three elastic moduli increase as the temperature $T$ decreases, but $K_1$ shows a much steeper dependence than that of $K_2$ and $K_3$. For example, for $c=18$ wt%, $K_1$ increases by a factor of 9 within a $\sim 10$K temperature decrease, while $K_2$ increases only 3 fold and $K_3$ less than 2 fold. The temperature dependence of $K_1$ follows a universal exponential law for all concentrations
\[ K_1(T) \propto \exp(-\beta_K T) \]  \hspace{1cm} (4.7)

where \( \beta_K = 0.20 \pm 0.01 \) K\(^{-1}\) is independent of concentration, Fig. 4.3(A).

The anisotropy of the elastic moduli is further illustrated in Fig. 4.4 where the ratios of elastic constants are plotted as a function of \( T \) for different concentrations. When \( T \) decreases, both \( K_1/K_3 \) and \( K_1/K_2 \) increase. \( K_3/K_2 \) remains practically constant \((35\pm 5)\) over a wide temperature range for \( c = 12.5, 14, 16 \) wt\%, whereas for \( c = 18 \) wt\%, the value slightly decreases to about 25 at \( T \approx 294 \)K.
Figure 4.3: Temperature and concentration dependences of elastic constants of (A)splay $K_1$, (B)bend $K_3$ and (C)twist $K_2$ in nematic phase. Dashed vertical lines on the horizontal axes indicate the transition temperature from nematic to nematic-isotropic
coexistence phase. The insert shows $K_1$ has an exponential dependence of temperature $T$. $K_3$ and $K_2$ fit well with linear functions of temperature $T$.

4.3.2 Viscosities

The concentration and temperature dependences of viscosities $\eta_{\text{splay}}$, $\eta_{\text{twist}}$ and $\eta_{\text{bend}}$ are shown in Fig 4.5. The viscosities $\eta_{\text{splay}}$ and $\eta_{\text{twist}}$ are comparable to each other and are in the range of $(1 - 500) \text{ kgm}^{-1}\text{s}^{-1}$, several orders of magnitude larger than $\eta_{\text{bend}} = (0.007 - 0.03) \text{ kgm}^{-1}\text{s}^{-1}$. $\eta_{\text{splay}}$ and $\eta_{\text{twist}}$ show very strong temperature dependences, changing by over two orders of magnitudes when the temperature changes by only about 10K, Fig 4.5(A)(B). For the same temperature range, $\eta_{\text{bend}}$ changes by a factor of 3 only, Fig 4.5(C). The temperature dependence of $\eta_{\text{splay}}$ and $\eta_{\text{twist}}$ are described by the exponential laws

$$
\eta_{\text{splay}}(T) \propto \exp(-\beta_s T), \quad \eta_{\text{twist}}(T) \propto \exp(-\beta_t T)
$$

where the concentration independent coefficients are $\beta_s = 0.41 \pm 0.02 \text{ K}^{-1}$, $\beta_t = 0.37 \pm 0.01 \text{ K}^{-1}$. Note that $\beta_s$ and $\beta_t$ are roughly twice as large as $\beta_K$.

The ratio $\eta_{\text{splay}} / \eta_{\text{twist}}$ slowly increases with $T$, Fig 4.5(D). In the vicinity of nematic to nematic-isotropic biphasic transition (low concentrations or small $\Delta T$), $\eta_{\text{splay}} / \eta_{\text{twist}}$ remains close to 1 within the accuracy of experiments. Deeper into the
nematic phase (and specifically for the highest concentration $c = 18$ wt\% and for $\Delta T \approx 12$K), $\eta_{splay}/\eta_{nematic}$ increases to about 2.

Figure 4.4: Temperature and concentration dependences of the ratios between elastic constants. (A) $K_1/K_3$, (B) $K_1/K_2$ both increase as $T$ decreases or $\phi$ increases; (C) $K_3/K_2$ remains practically constant for a wide range of $T$, but decreases at $T \approx 294$K for 18 wt\%.
**Figure 4.5:** Temperature and concentration dependences of viscosities and their ratios:

(A) $\eta_{\text{splay}}$, (B) $\eta_{\text{twist}}$, (C) $\eta_{\text{bend}}$ and (D) $\eta_{\text{splay}}/\eta_{\text{twist}}$ over the nematic range. Dashed lines in the horizontal axis indicate $T_n$.

### 4.3.3 An additional mode in bend geometry

As indicated by Eqs (4.1) and (4.6), two modes, namely pure splay and pure twist, contribute separately to the total intensity in the “1&2” scattering geometry. The corresponding correlation function should reveal two relaxation processes

$$
\Gamma_1(\theta) = \frac{K_1 q^2(\theta)}{\eta_{\text{splay}}} , \quad \Gamma_2(\theta) = \frac{K_2 q^2(\theta)}{\eta_{\text{twist}}} .
$$

This is indeed what we obtain by fitting experimental data, as indicated in Fig. 4.2. On the other hand, Eqs. (4.4) and (4.6) predict that bend fluctuations contribute to the intensity in geometry “3”, and thus the correlation function should show a single relaxation process with

$$
\Gamma_3(\theta) = \frac{K_3 q^2(\theta)}{\eta_{\text{bend}}} .
$$

However, fitting the experimental data with a single exponential decay fails to match the data, Fig 4.2. A minimum of two relaxation modes, with a stretching exponent $b = 0.9$, are needed to fit the correlation data:

$$
\langle I(0,\theta)I(\tau,\theta) \rangle = \bar{I}^2(\theta) + g^2 \left[ I_3(\theta) \exp\left(-\frac{K_3 q^2}{\eta_{\text{bend}}} \tau\right)^b + I_4(\theta) \exp(-\Gamma_4 \tau)^b \right]^2
$$

(4.9)
Fits of the data in geometry “3” to Eq. (4.9) indicate $\Gamma_4 \propto q_{ij}^2$, thus the additional mode is hydrodynamic. The fact that $b$ is close to 1 implies that the relaxation rates do not have single values but show narrow dispersion[142]. Since $I_4 / I_3 \approx 0.1$, the presence of the additional mode does not increase the uncertainty in the values deduced for $K_3$ and $\eta_{\text{bend}}$ by more than 10%; the other viscoelastic parameters (measured in geometry “1&2”) are unaffected.

4.4 Discussion

The LCLC DSCG shows some unique features as compared to conventional thermotropic nematics such as 5CB and to other nematic lyotropic LC systems, including the LCLC SSY and nematic polymeric LCs such as poly($\gamma$-benzyl glutamate)(PBG), Table 1, Fig 4.2-4.5. First, the anisotropy of the elastic constants of DSCG is the largest among all the representative nematics shown in Table 1. The twist constant ($K_2$) is more than 10 times smaller than the splay ($K_1$) and bend ($K_3$) constants, while the latter two are comparable to each other, Fig. 4.4(A). Second, $K_1$ has a much stronger (exponential) temperature dependence as compared to the linear dependences of $K_2$ and $K_3$. Third, the DSCG viscosities associated with splay and twist deformation, $\eta_{\text{splay}}$ and $\eta_{\text{twist}}$, are both anomalously large, 3-5 orders of magnitude larger than the bend viscosity $\eta_{\text{bend}}$ of DSCG and the viscosities measured in thermotropic LCs such as 5CB (which are on the order of 0.01kgm$^{-1}$s$^{-1}$). Fourth, the temperature dependence of the parameters $K_1$, $\eta_{\text{splay}}$ and
\( \eta_{\text{twist}} \) can be described by concentration–independent exponential laws, Eq. (4.7) and (4.8) with the exponents \( \beta_K =0.2, \beta_s =0.41 \) and \( \beta_t =0.37 \), respectively.

We now proceed to discuss our results in terms of relevant theoretical models for viscoelastic properties of lyotropic nematics.

<table>
<thead>
<tr>
<th>LCs</th>
<th>( K_1 ) (pN)</th>
<th>( K_2 ) (pN)</th>
<th>( K_3 ) (pN)</th>
<th>( \eta_{\text{spay}} ) (kgm(^{-1})s(^{-1}))</th>
<th>( \eta_{\text{twist}} ) (kgm(^{-1})s(^{-1}))</th>
<th>( \eta_{\text{bend}} ) (kgm(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSCG</td>
<td>10.2</td>
<td>0.7</td>
<td>24.9</td>
<td>11.7</td>
<td>10.5</td>
<td>0.009</td>
</tr>
<tr>
<td>SSY</td>
<td>4.3</td>
<td>0.7</td>
<td>6.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PBG</td>
<td>7.5</td>
<td>0.6</td>
<td>6</td>
<td>2.5</td>
<td>2.5</td>
<td>0.025</td>
</tr>
<tr>
<td>5CB</td>
<td>4.5</td>
<td>3</td>
<td>5.5</td>
<td>0.088</td>
<td>0.094</td>
<td>0.015</td>
</tr>
</tbody>
</table>

**Table 4.1**: Viscoelastic parameters of different liquid crystals. LCLC DSCG: 16 wt\%, \( \phi = 0.115 \), \( \Delta T = 4.3K \); LCLC SSY: 29 wt\%, \( \phi = 0.20 \), \( \Delta T = 2K \); lyotropic polymeric LC PBG: \( L/D = 32 \), \( \phi = 0.16 \); thermotropic LC 5CB: \( \Delta T = 4 K \).

**4.4.1 Elastic constants**

The viscoelasticity of lyotropic systems is usually described by the Onsager type models [101-104] based on the idea of excluded volume. In the simplest version, the building units are considered as long slender rods with the length-to-diameter ration \( L/D \) being fixed and much larger than 1. The nematic ordering is caused by the increase of concentration; the rods sacrifice orientational freedom to maintain the ability to translate. The model is athermal as the behaviour is controlled exclusively by entropy.
The excluded volume theory predicts the elastic constants in a system of rigid long rods[101] as follows: 

\[ K_1 = \frac{7}{8\pi} \frac{k_BT}{D} \phi \frac{L}{D}, \quad K_2 = K_1 / 3 \quad \text{and} \quad K_3 = \frac{4}{3\pi^2} \frac{k_BT}{D^3} \left( \frac{L}{D} \right)^3. \]

Clearly, this model does not describe our experimental findings for the LCLC system well. For example, the measured \( K_1 / K_2 \) can be as high as \(-30\) (\( c=18\) wt\%, \( T \approx 294K \)), Fig. 4.4(B), much larger than the expected constant value of 3. Furthermore, to form a nematic phase, the system of rigid rods should be of a volume fraction that exceeds a critical value \( \phi_c = 4.5D/L \) [1]. If that is the case, then one would expect 

\[ \frac{K_1}{K_i} \approx \frac{1}{2} \phi^2 \left( \frac{L}{D} \right)^2 > 10, \]

while our experiment yields a much lower value \( \frac{K_1}{K_i} \sim (1-3) \) in nematic DSCG, Fig. 4.4(A).

To explain the smallness of \( K_2 \), one may consider effects such as the electrostatic interaction of charged rods [103], since the dissociation of ionic groups into water from the periphery of the DSCG aggregates makes them charged. However this correction turns out to be negligible. Coulomb repulsion of similarly charged cylinders tends to arrange them perpendicularly to each other. This “twisting effect” thus modifies \( K_2 \) by a factor \( \approx (1-0.1h) \), where \( h = \lambda_D / (D + 2\lambda_D) \), \( D \approx 1.6 \) nm is the “bare” diameter of DSCG aggregates[137] and \( \lambda_D \) is the Debye screening length. For the DSCG solutions used in this work, \( \lambda_D \approx 0.5 \) nm[109]. Therefore, the twisting effect might lead to a decrease of \( K_2 \) by only a few percent, and is most likely not the main reason for the
observed smallness of $K_2$. The situation is very similar to the one recently discussed for LCLC Sunset Yellow [110].

The next level of theoretical modelling is to take into account that the aggregates comprising the LCLC are not absolutely rigid but possess some flexibility[101,102,126], characterized by a finite persistence length $\lambda_p$, that should directly affect $K_3$. The persistence length is a measure of the length scale over which the unit vectors tangential to the flexible elongated object lose their correlations. Flexibility of LCLC aggregates is evident in recent numerical simulations [87,88] and suggested by recent nuclear magnetic resonance measurements, where column undulation within the molecular stack involving 4-8 molecules was observed [143].

When the aggregates are flexible, the bend deformation is no longer inhibited by their length; each aggregate can bend to follow the director pattern, Fig. 4.6(A). According to the well-known result of the elastic theory [144,145], the bending energy of an elastic rod is $F_b = \frac{1}{2} \kappa L \rho^2$, where $\kappa$ is the bending stiffness and $\rho$ is the curvature of the bent rod. The volumetric elastic energy density for a dispersion of elastic rods is then[104] $f_3 = F_3\phi \left( \frac{\pi}{4} D^2 L \right)^{-1}$. Using the relationships between the persistence length $\lambda_p$ and bending stiffness[144], $\lambda_p = \kappa / k_B T$, and between the energy density of bend and $K_3$, $f_3 = \frac{1}{2} K_3 \rho^2$, one arrives at
The last result is twice as large as the expression derived by Taratuta et al.[104], who defined \( \lambda_p \) as \( \frac{2\kappa}{k_BT} \). Equation (4.10) with the typical experimental values \( K_3=10 \) pN, \( \phi = 0.1 \) and \( D = 1.6 \) nm [137] yields an estimate \( \lambda_p = 50 \) nm. This value is close to the persistence length of double-stranded DNA (dsDNA)[8], which has structural parameters similar to the aggregate of DSCG (diameter \( \sim 2 \) nm and 6 ionizable groups per 1 nm of length).

The value of \( K_3 \) for DSCG at \( \phi \approx 0.1 \) is several times larger than the value \( K_3 = 6.1 \) pN reported for SSY[110] with \( \phi \approx 0.20 \), Table 1. To discuss the difference, it is convenient to represent the bending stiffness of the chromonic aggregate through the Young’s modulus \( Y \) of a homogeneous elastic cylinder[144]: \( \kappa = \pi Y D^4 / 64 \). Therefore,

\[
K_3 = \frac{\phi Y D^2}{16} \tag{4.11}
\]

The aggregates in the DSCG LCLC have a larger cross section[10] (\( D^2 \sim 2.4 \) nm\(^2\)) than those for SSY[10] (\( D^2 \sim 1.2 \) nm\(^2\)), so that the product \( \phi D^2 \) in Eq. (4.11) is essentially the same for the two LCLCs. Hence, the difference in the values of \( K_3 \) can be attributed to the difference in the Young modulus \( Y \), which is worthy of further investigation. When \( K_3 = 10 \) pN, Eq. (4.11) leads to \( Y = 6.7 \times 10^8 \) N/m\(^2\), which is the

\[
K_3 = \frac{4 k_BT \phi \lambda_p}{\pi D^2} \tag{4.10}
\]
same order of magnitude as the sequence dependent Young’s modulus for dsDNA [146] (for example, \( Y \approx 3 \times 10^8 \text{ N/m}^2 \) for the \( \lambda \)-phage dsDNA [147]).

The flexibility of aggregates does not affect the splay constant \( K_1 \) much. As explained by Meyer [85], splay deformations, under the condition of constant density, limit the freedom of molecular ends, which decreases the entropy, Fig. 4.6(B). A larger contour length \( L \) implies a smaller number of molecular ends available to accommodate for splay and thus a higher \( K_1 \)[104]:

\[
K_1 = \frac{4 k_B T}{\pi D} \frac{\bar{L}}{\phi} \frac{1}{D}
\]

Here we introduced a new notation \( \bar{L} \) for the characteristic (average) length of aggregates. Using this expression and the values of \( K_1 = 5 \text{ pN}, \phi=0.1, D =1.6 \text{ nm} \) for \( c =14\text{wt}\% \text{ DSCG at } T = 297\text{K} \) (3K below \( T_{ni} \)), we find \( \bar{L} \approx 25\text{nm} \), which compares well with a previous estimate[148] \( \bar{L} =18\text{nm} \) for the isotropic phase of the same concentration at 305K (5K above \( T_{ni} \)).

The twist elastic constant in the model of flexible rods is predicted to be[47]

\[
K_2 = \frac{k_B T}{D} \phi^{1/3} \left( \frac{\lambda_p}{D} \right)^{1/3}
\]

implying a rather weak dependency on \( \lambda_p \) and \( \phi \). The smallness of \( K_2 \) and its independence of the contour length \( \bar{L} \) in LCLCs can be explained as follows[85], Fig. 4.6(C). Consider an ideal arrangement of the aggregates in layers to accommodate a
twisted director field. Within each layer, the aggregates are straight and closely packed; the direction of director is changed by a small angle only when moving between consecutive layers. Successive layers of aggregates simply stack on top of each other to form a twisted nematic distortion with \( n \perp \) helical axis. However, in reality, the aggregates cannot perfectly remain in the layers; for example, thermal fluctuations will displace the aggregates across layers and thus cause them to interfere with aggregates that have a different orientation. This interference can be relieved by bending the aggregates to conform to the local orientational order in the layer, instead of being aggravated by the extended aggregate length. Thus \( K_2 \) is independent of \( L \) and weakly dependent on \( \lambda_p \) (as compared to the bend elasticity \( K_3 \)). From Eqs. (4.10) and (4.13), for typical values \( \phi = 0.1, \lambda_p = 50 \text{ nm}, D = 1.6 \text{ nm} \), we deduce \[
\frac{K_2}{K_3} = \frac{\pi}{4} \left( \frac{\lambda_p}{D} \right)^{-2/3} \approx 0.37,
\]
which qualitatively agrees with our argument that \( K_2 \) has weak dependence on \( \lambda_p \), but still does not quantitatively explain the smallness of the observed ratio (\( K_2 / K_3 \) in the range of 0.025-0.04 for all concentrations and temperatures). Clearly, an improved theory is needed.

Similarly to our previous study of SSY [27], and the ratio in DSCG decreases as the temperature increases, Fig. 4.4. As follows from Eqs (4.10) and (4.12) for the model of flexible aggregates, the ratio is:

\[
\frac{K_1}{K_3} = \frac{L}{\lambda_p} \quad (4.14)
\]
The observed temperature dependence of $K_1/K_3$ cannot be explained by the Onsager-type models either for rigid rods or for flexible rods, if the mean aggregate length $\overline{L}$ remains constant. Instead, as we now argue, different temperature dependences of the aggregate contour length $\overline{L}$ and persistence length $\lambda_p$ are responsible, a possibility which is absent in LCs with a fixed, temperature-independent shape of building units.

Consider $\overline{L}$ first. Theoretical works suggest that $\overline{L}$ depends on volume fraction $\phi$, temperature $T$ and scission energy $E_a$ [4,10,85,110,149]. Compared to the expression for $\overline{L}$ in a dilute ($\phi \ll 1$) isotropic phase, $\overline{L} = L_0 \sqrt{\phi} \exp\left(\frac{E_a}{2k_BT}\right)$, the form of $\overline{L}$ in the nematic state exhibits a stronger dependence on $\phi$ due to the orientational order [110]:

$$\overline{L} = L_0 \phi^{3/6} \left(\frac{\lambda_p}{D}\right)^{1/3} \exp\left(\frac{E_a + \sigma \phi}{2k_BT}\right)$$  (4.15)

Here $L_0 = 2\pi^{-2/3} \sqrt{a_z D}$ is a length characterizing the size of a monomer, $a_z$ the period of molecular stacking along the aggregate, and $\sigma$ a constant describing the enhancement of aggregation by the excluded volume effects. (In the second virial approximation[89], $\sigma \approx 4k_BT$.) For DSCG, $D = 1.6\text{nm}$, $a_z = 0.34\text{nm}$[12], $L_0 = 0.7\text{nm}$. Using Eq. (4.12) for $K_1$, we estimate that $\overline{L}$ is in the range of (20-270) nm, and $E_a(\phi,T) \approx (8-14)k_BT$, close to the estimates for SSY LCLC by Collings et al[94], $E_a \approx 7k_BT$, and by Day et al[105],
\( E_a \approx 11 k_B T \), and for DNA oligomers [8] by Clark et al, \( E_a \approx (4-8) k_B T \). To make contact with the empirical expression above for \( K_1 \) in Eq. (4.7), we expand \( \frac{E_a(\phi, T)}{k_B T} \) near \( T_m \approx 300 \text{ K} \) as follows:

\[
\frac{E_a(\phi, T)}{k_B T} = \frac{E_a(\phi, T_m)}{k_B T_m} - \frac{E_a}{k_B T_m} \left( \frac{\partial E_a}{k_B T_m} \right)_T \frac{1}{T_m} (T - T_m) + O(T - T_m)^2
\]

(4.16)

This gives (to lowest order in \( T - T_m \)):

\[
L \propto \exp \left[ - \left( \frac{E_a}{k_B T_m} - \frac{\partial E_a}{k_B T_m} \right)_T \frac{T}{2T_m} \right]
\]

(4.17)

Inserting this result into Eq. (4.12) and comparing to Eq. (4.7), we identify \( \beta_K = \frac{1}{2T_m} \left( E_a - \frac{\partial E_a}{k_B T_m} \right)_T \). Then using the experimental value of \( \beta_K = 0.2 \pm 0.01 \text{ K}^{-1} \) and the above estimates for \( E_a(\phi, T) / k_B T \sim 10 \), we find:

\[
\frac{\partial E_a}{k_B T_m} \bigg|_{T_m} = \frac{E_a}{k_B T_m} - 2\beta_K T_m < 0
\]

(4.18)

and therefore conclude that \( E_a(\phi, T) \) decreases with increasing \( T \).

As shown by numerical simulations[87], the persistence length \( \lambda_p \) scales with \( \phi \) and \( T \) as

\[
\frac{\lambda_p}{L_0} \approx \frac{E_a(\phi, T)}{k_B T}, \quad \text{and thus has a much weaker dependence on } \phi \text{ (mainly through}
\]

90
ionic effects) and $T$ than does $L$ for chromonic aggregates formed by cylindrical monomers. From Eqs. (4.10), (4.12), and (4.15), we can deduce

$$\frac{K_1}{K_3} \propto \phi^{5/6} \exp \left( \frac{E_a + \kappa \phi}{2k_B T} \left( \frac{E_a}{k_B T} \right)^{2/3} \right)$$  \hspace{1cm} (4.19)$$

This equation implies that $\frac{K_1}{K_3}$ decreases when $T$ increases or $\phi$ decreases, consistent with our measurements, Fig 4.4(A). Our experimental values of $\frac{K_1}{K_3}$ suggest that $\frac{L}{\lambda_p}$ is in the range of (0.25-1.2), depending on $T$ and $\phi$. Interestingly, the numerical results of Kuriabova et al[87], $L / \lambda_p \approx 1$, fall in this range.

The exponential dependence of $K_1$ on $\frac{E_a}{k_B T}$ and the weak dependence of $K_2$ on $\lambda_p$, Eq. (4.13), predict that $\frac{K_1}{K_2} \propto \phi^{3/2} \exp \left( \frac{E_a + 2\kappa \phi}{k_B T} \right)$ increases when $T$ decreases or $\phi$ decreases, again consistent with our measurements, Fig. 4.4(B). Regarding $\frac{K_3}{K_2}$, Eqs. (4.10) and (4.13) indicate $\frac{K_3}{K_2} \propto \phi^{2/3} \left( \frac{\lambda_p}{D} \right)^{2/3} \propto \phi^{2/3} \left( \frac{E_a}{k_B T} \right)^{2/3}$. As temperature $T$ decreases ($\Delta T$ increases), $\lambda_p$ and $\frac{E_a}{k_B T}$ increase, thus $\frac{K_3}{K_2}$ should increase. However, experiments show that $\frac{K_3}{K_2}$ remains practically constant over a wide range of temperature for all
studied $\phi$, and that in fact it decreases at $T \approx 294$K for the highest volume fraction $\phi = 0.129$ (c=18 wt%), Fig 4.4(C). Apparently, some additional factor must account for this behaviour. One possibility is the following. For the c =18 wt% sample at $T \approx 291$K (3K below our experimental range), the system transforms into a columnar phase[137]. In this phase, twist deformations are severely inhibited by the hexagonal packing of the long aggregates, and consequently $K_2 \to \infty$ is expected. A pretransitional increase of $K_2$ would explain the decrease in $\frac{K_3}{K_2}$ seen at low temperatures in Fig 4.4(C).
Figure 4.6: Mechanism of viscoelastic processes in LCLC, following Meyer et al.[85].

(A) Flexible rods accommodate bend deformation by deforming the rods. (B) Splay deformation tends to create vacancies that require free ends (marked by dashed lines) to fill in. (C) Twist deformation causes minimum inter-aggregates interference by arranging aggregates in layers. (D) Shear flow associated with twist deformation.

4.4.2 Viscosities

The large values of the splay and twist viscosities measured in the DSCG LCLC, and the relatively small value of the bend viscosity, can be understood following the arguments put forward by de Gennes [150] and Meyer [85,86,125,126] for nematic LC polymers in the “infinite” chain limit, $\bar{L}/D \to \infty$. In this limit, twisting the director field is associated with mass displacement of single chains, which produces flows perpendicular to the director with a gradient along the director. If the chains are not allowed to break, twist deformation, even though conceptually possible as a static state as we argued earlier, is forbidden as a dynamic process since it induces flows that tend to cut the chains; as a result $\eta_{\text{twist}} = \gamma_1 \to \infty$, where $\gamma_1$ is the rotation viscosity of the director field[1]. In a practical system with a finite (but still large) $\bar{L}/D \gg 1$, $\eta_{\text{twist}}$ must increase as $\bar{L}$ increases. A simple geometric argument due to Meyer [85,86] shows that $\eta_{\text{twist}} = \gamma_1 \propto \bar{L}$, Fig. 4.6(D). Consider a twist deformation that induces shear flow $\frac{\partial v}{\partial z} = \text{const}$. The power dissipated per monomer along the aggregates
is \( P = \mu \delta^2 \left( \frac{\partial v}{\partial z} \right)^2 \), where \( \mu \) is a friction coefficient and \( \delta \) is the distance of the monomer to the rotation centre. The mean power dissipation \( \bar{P} = \frac{1}{L} \int_{-L/2}^{L/2} Pdz = \mu \frac{L}{12} \left( \frac{\partial v}{\partial z} \right)^2 \); thus the effective viscosity for the twist process is \( \eta_{\text{twist}} \propto \bar{L}^2 \). A similar analysis applies to splay deformation, giving \( \eta_{\text{splay}} \propto \bar{L}^2 \). These predictions are consistent with our experimental results for the \( \eta \)’s and with the linear dependence \( K \propto \bar{L} \). Namely, as indicated in Fig. 3(A) and Fig. 4.5(A)(B): \( K \propto \exp(-\beta_K T) \) with \( \beta_K = 0.20 \pm 0.01 \) K\(^{-1}\); \( \eta_{\text{twist}} \propto \exp(-\beta_t T) \) with \( \beta_t = 0.37 \pm 0.01 \) K\(^{-1}\); and \( \eta_{\text{splay}} \propto \exp(-\beta_s T) \) with \( \beta_s = 0.41 \pm 0.02 \) K\(^{-1}\). The result \( \beta_t \approx \beta_s \approx 2 \beta_K \) agrees with the theoretical scaling relations, \( K, \eta_{\text{splay}}, \eta_{\text{twist}} \propto \bar{L} \), and the temperature dependence of the viscoelastic parameters predicted by Eq. (4.17) in the vicinity of \( T_m \) is also confirmed.

The viscosity associated with bend deformation, \( \eta_{\text{bend}} \), is comparable to values for thermotropic LCs, Table 1, and is several orders of magnitude smaller than \( \eta_{\text{splay}} \) and \( \eta_{\text{twist}} \). This is explained by the fact that bend deformation is associated with “sliding” the aggregates parallel to each other [85,86,104,125], which is not inhibited even if \( \bar{L} / D \) becomes very large.

An important difference in the hydrodynamic properties of LCLCs relative to those of low-molecular LCs is illustrated in Fig. 4.5(D), which shows the temperature
dependence of $\eta_{\text{splay}} / \eta_{\text{twist}}$. In DSCG, this ratio is close to but still somewhat larger than 1. The result is unusual from the point of view of the Ericksen-Leslie model[1], in which the twist viscosity $\eta_{\text{twist}} = \gamma_1$ is always larger than splay viscosity $\eta_{\text{splay}} = \gamma_1 - \frac{\alpha_3^2}{\eta_b}$. (Here $\alpha_3$ is one of the Ericksen-Leslie coefficients[1], and $\eta_b > 0$ is one of the Miezowicz viscosities[1].) Our experimental results, Fig 4.5(D), however, show that $\eta_{\text{splay}} / \eta_{\text{twist}} \approx 1$ holds only in the vicinity of the transition to the isotropic phase. When $\Delta T$ increases and the system moves deeper into nematic phase, $\eta_{\text{splay}} / \eta_{\text{twist}}$ can be as larger as 2. This finding suggests that the explanation of the anomalous behaviour seen in Fig. 4.5(D) is again rooted in the strong temperature and concentration dependencies of the mean aggregate length $\bar{L}$.

4.4.3 Origin of the additional fluctuation mode in the bend geometry

Finally, we discuss the origin of the additional fluctuation mode ($\bar{T}_4$, $\bar{\Gamma}_4$) detected in the bend scattering geometry. The key features of this mode are: (1) it is hydrodynamic ($\bar{\Gamma}_4 \propto q^2$); (2) it couples weakly to light ($\bar{T}_4$ is about 10 times smaller than $\bar{T}_3$ for the director bend mode); and (3) it is $\sim 10$ times slower than the bend fluctuations but $\sim 10^2 - 10^3$ times faster than splay or twist.

We propose that the additional mode is associated with the thermal diffusion of structural defects in the chromonic aggregates. To establish this conjecture, we point out the following. The plank-like chromonic molecules tend to aggregate face-to-face, to
shield the exposure of extended aromatic cores to water. The scission energy $E_a$ of this non-covalent association is about $10k_BT$ as shown in our analysis above and references [8,94,105]. The molecular association might therefore form metastable configurations that do not correspond to the absolute minimum of the interaction potential. For example, the association might happen with a lateral shift or rotation of the molecular planes. Some of these defects or their combinations alter the aggregate structure so significantly that they impose deformations on the surrounding director field. As illustrated in Fig. 4.7, a pair of lateral shifts, which we call a “C” defect, tends to impose a bend deformation ($\hat{n}\times\text{curl}\hat{n}$) on the director $\hat{n}$. A sequence of such “C” defects can be pictured as a crankshaft. On the other hand, a junction of three aggregates, with the symmetry of the letter “Y”, creates a different type of defect that imposes a splay distortion ($\hat{n}\text{div}\hat{n}$) on the director field, Fig. 4.7. The presence of both defect types has already been suggested to explain a discrepancy between the length of chromonic aggregates expected from the point of view of the Onsager model of lyotropic mesomorphism and the length inferred from X-ray scattering data [12]. Interestingly, recent structural studies of sunset yellow support the existence of stacking features in the form of lateral shifts [128].
The stacking defects illustrated in Fig. 4.7 are polar. To incorporate their thermal diffusion into a description of the orientational fluctuation modes, we let the j-th type of polar defect be described by the vector density $v_j(r)$. For example, $j = 1$ for “C” type, and $j = 2$ for “Y” type, Fig. 4.7. The effect of the defect dynamics on the light scattering is caused by their interaction with director distortions. This interaction, which may be termed flexopolarity, results in additional symmetry-allowed cross terms in the Frank elastic free energy. These terms couple the distortion vector $G(r) = g_s \hat{n} \text{div} \hat{n} + g_b (\hat{n} \times \text{curl} \hat{n})$, where $g_s$ and $g_b$ are splay and bend flexopolar coefficients, respectively, to the vector density $v_j$. Additionally, in the free energy we
must consider an interaction between defects that penalizes fluctuations in their concentration. Generally, this may be expressed by a tensor coupling of the form \( v \cdot h \cdot v \), where the tensor core \( h_{jk}(r-r') \) defines the energy penalty for the polar defect densities and also ensures positivity of the free energy. To simplify the analysis, we neglect the interaction between different defect types and thus take \( h_{jk}(r-r') = h_{j}(r-r')\delta_{jk} \). Based on these considerations, the free energy becomes:

\[
F = \int \left[ f_{FO} + \sum_j v_j(\mathbf{r}) \cdot \mathbf{G}(\mathbf{r}) \right] d\mathbf{r} + \frac{1}{2} \int \left[ \sum_j \mathbf{v}_j(\mathbf{r}) \cdot \mathbf{h}_j(\mathbf{r}-\mathbf{r}') \cdot \mathbf{v}_j(\mathbf{r}') \right] d\mathbf{r} d\mathbf{r}'
\]  

(4.20)

where \( f_{FO} = \frac{1}{2} \left[ K_1(\text{div}\hat{\mathbf{n}})^2 + K_2(\hat{\mathbf{n}} \cdot \text{curl}\hat{\mathbf{n}})^2 + K_3(\hat{\mathbf{n}} \times \text{curl}\hat{\mathbf{n}})^2 \right] \) is the standard Frank-Oseen bulk elastic energy[1].

Using the Fourier transform \( \mathbf{v}_j(\mathbf{r}) = V^{-1} \sum_q \mathbf{v}_j(q) \exp(i\mathbf{q} \cdot \mathbf{r}) \) and the standard quadratic representation for director fluctuation modes around the equilibrium director \( \hat{\mathbf{n}}_0, \hat{\mathbf{n}}(\mathbf{r}) = \hat{\mathbf{n}}_0 + V^{-1} \sum_q \sum_{\alpha=1,2} n_{\alpha}(q) \hat{\mathbf{e}}_{\alpha} \exp(i\mathbf{q} \cdot \mathbf{r}) \) in the frame \( \{\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{n}}_0\} \), where \( \mathbf{q} = q_\perp \hat{\mathbf{e}}_1 + q_\parallel \hat{\mathbf{n}}_0 \), we obtain:

\[
F = \frac{1}{2V} \sum_q \left\{ \left( K_2 q_\perp^2 + K_3 q_\parallel^2 \right) \left| n_{\alpha}(q) \right|^2 + 2i g_{j} q_\parallel v_{j\parallel}(q) n_{\alpha}(q) - 2i g_{j} q_\parallel v_{j\parallel}(q) n_{\alpha}(q) + h_{j}(q) \right| v_{j\parallel}(q) \right|^2 + h_{j}(q) \right| v_{j\parallel}(q) \right|^2 \}
\]  

(4.21)

where \( v_j(q) = v_{j\parallel} \hat{\mathbf{e}}_1 + v_{j\parallel} \hat{\mathbf{e}}_2 + v_{j\parallel} \hat{\mathbf{n}}_0 \), summation is performed in Eq. (4.21) over indices \( j \), and \( \alpha = 1, 2 \) in the terms where they appear. Due to uniaxial anisotropy with respect
to \( \hat{n}_0 \), the tensors 
\[ h_j(q) = \int h_j(\mathbf{r} = r - r') \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \]
are diagonal with components 
\( h^i_j(q) \) and \( h^j_i(q) \) being parallel and perpendicular to \( \hat{n}_0 \), respectively. We consider the polar defect mode \((j\beta), \beta = 1, 2, 1, 2, \beta \) as a 'fast' or 'slow' mode, depending on the magnitude of its relaxation rate \( \Gamma_{j\beta} \) compared to the relaxation rate \( \Gamma^n_a \) of the director distortions \( n^a(q) \).

**Fast defect regime** \((\Gamma_{j\beta} \gg \Gamma^n_a)\): When the director fluctuations are slow compared to the defect modes, their effect on the defect densities \( n^a(q) \) results in quasi-equilibrium values, 
\[ \tilde{v}^s_{ja}(q) = ig_b q n^a(q) / h^s_j(q) \] and \[ \tilde{v}^s_{ji}(q) = ig_s q n^1(q) / h^s_j(q) \], determined by the minimization of \( F \), Eq. (4.21), over \( v^s_{ja}(q) \) and \( v^s_{ji}(q) \). This "instantaneous" response effectively renormalizes the elastic constants for 'spontaneous' director fluctuations

\[ K^1 \rightarrow K^1 - \sum_j g^2 / h^s_j(q), K^3 \rightarrow K^3 - \sum_j g^2 / h^s_j(q) \] (4.22)
where the summation is over the fast defect modes. Except for this effect on the elastic moduli, "fast" defect modes are almost invisible in the DLS experiment probing director fluctuations. This fact is consistent with the lack of evidence for an additional, defect mode in the splay+twist scattering geometry, where the observed director fluctuations are much slower than either of the modes detected in the bend geometry.
*Slow defect regime* \((\Gamma_{j\beta} \ll \Gamma_{n}^{a})\): Here the defect diffusion modes serve as a slowly changing random force field, that creates the quasi-equilibrium, defect-induced director distortions, obtained by minimizing \(F\), Eq. (4.21), over \(n_{a}(\mathbf{q})\):

\[
\bar{n}_{a}(\mathbf{q}) = \sum_{j} \bar{n}_{a}^{(j)}(\mathbf{q}) = i \sum_{j} \frac{g_{b}q_{\parallel}v_{j\alpha}(\mathbf{q}) - g_{b}q_{\perp}v_{j\parallel}(\mathbf{q})}{K_{\alpha}q_{\parallel}^{2} + K_{\alpha}q_{\perp}^{2}}
\]

(4.23)

where the summation is over slow defect modes.

The bend scattering geometry, where the director mode is relatively fast, is the most favourable situation for directly observing fluctuations of \(v_{j\beta}\), and is indeed the case where we do detect an extra mode. With \(\alpha = 2\) (corresponding to the twist-bend director mode) and \(q_{\parallel} \gg q_{\perp}\) (corresponding to nearly pure bend), we see from Eq. (4.23) that the diffusive modes \(v_{j2}\) couple to the director mode with coupling strength controlled by the parameter \(g_{b}\). Even if \(v_{j2}\) fluctuations are slower than the bend fluctuations, their contribution to scattering can be weak, provided \(g_{b}\) is small, and thus agree with the behaviour observed experimentally for the additional mode \((\bar{T}_{d}, \Gamma_{d})\).

In principle, both translational and rotational diffusion of the polar defects could explicitly contribute to temporal variations of the defect density \(\partial v_{j2} / \partial t\). However, when \(q_{\perp} = 0\), the directions \(\mathbf{\hat{e}}_{1}\) and \(\mathbf{\hat{e}}_{2}\) in the plane perpendicular to \(\mathbf{\hat{n}}_{0}\) are equivalent, \(v_{j2}\) and \(v_{ji}\) are degenerate, and rotational diffusion does not directly change the defect density that couples to the director mode. However, translational diffusion along \(\mathbf{\hat{n}}_{0}\) can
modulate $v_{j2}$ (or $v_{j1}$) in regions of high or low bend distortion of the director. For $q = q_{||}$ (as is essentially the case in the bend scattering geometry studied), we therefore expect a hydrodynamic mode with $\Gamma_{j2} \propto q_{||}^2$, consistent with the experimental $q$ dependence of $\Gamma_4$.

The fact that the stretching parameter $b$ used in stretched exponential fits of the correlation functions in the bend geometry (Eq.(4.0)) is ~0.9 rather than 1 (pure exponential) indicates that both bend deformation and thermal diffusion of the configuration defects are associated with slightly dispersed instead of single valued relaxation rates $\Gamma_3$ and $\Gamma_4$. This could result from a geometric dispersion of stacking defects. Since the stacking of the DSCG molecules into aggregates is isodesmic [4,94], there is no obvious preference for certain geometrical parameters, such as the length of the arms of the “C” or “Y” defects, to prevail over others. As a result of dispersed geometric parameters of the stacking defects, we would expect some dispersion in relaxation rates $\Gamma_{j\beta}$ and $\Gamma_{\alpha}$ (Eq. (4.9) and Fig. 4.2).

### 4.5 Conclusions

We have measured the temperature and concentration dependences of the orientational elastic moduli and corresponding viscosities for the lyotropic nematic phase of a self-assembled LCLC system. Over the (3-10) K nematic temperature range of $c = (12.5 - 18)$ wt% DSCG LCLCs, $K_3 \approx K_1 \approx 10$ pN, $K_2 \approx 1$ pN, $\eta_{\text{twist}} \approx \eta_{\text{splay}} \approx (1 - 500)$ kg m$^{-1}$ s$^{-1}$ and $\eta_{\text{bend}} \approx 0.01$ kg m$^{-1}$ s$^{-1}$. Of the three elastic constants, the splay constant ($K_1$)
has the strongest temperature dependence, which is described by an exponential function of $T$. The twist and splay viscosities, $\eta_{\text{twist}}$ and $\eta_{\text{splay}}$, show similar exponential temperature dependences. We qualitatively explained these results by using the viscoelastic theory developed for LC systems formed by semi-flexible long chain particles with aspect ratio $L/D \gg 1$ and by specifically confirming the predicted scaling of parameters, $K_1, \sqrt{\eta_{\text{splay}}}, \sqrt{\eta_{\text{twist}}} \propto L$, with the strongly temperature-dependent average contour length $\bar{L}$. Our results demonstrating weak temperature dependence of the other parameters ($K_2, K_3$, and $\eta_{\text{bend}}$) also agree with theory. We detect an additional fluctuation mode in the bend geometry, which we attributed to the thermal diffusion of structural defects of the chromonic aggregates. These features, absent in conventional thermotropic LCs and lyotropic polymer LCs, highlight the fact that in LCLC system, the building units are non-covalently bound aggregates rather than molecules of fixed size.
CHAPTER 5: 
LIVING LIQUID CRYSTALS 

5.1 Introduction

Active matter has recently emerged as an important physical model of living systems that can be described by the methods of non-equilibrium statistical mechanics and hydrodynamics [30,70,72]. The active matter is driven by the internal sources of energy, associated with the self-propelled particles such as bacteria or synthetic swimmers. The interaction of these active particles among themselves and with the medium produces a rich variety of dynamic effects and patterns. Most of the studies deal with active particles embedded into a Newtonian isotropic fluid. In this case the interactions among particles are caused by long-range hydrodynamic and short-range excluded volume effects [38,40,68,77,151-156]. In our work, we conceive a new general class of active fluids, termed living liquid crystals (LLCs). The suspending medium is a non-toxic liquid crystal that supports the activity of self-propelled particles, namely, bacteria. At the very same time, the medium imposes long-range anisotropic interactions onto bacteria, thanks to the intrinsic orientational order that persists even when the bacteria are not active. The importance of the new system is two-fold. Firstly, the bacterial activity modifies the orientational order of the system, by producing well-defined and reproducible patterns with or without topological defects. Secondly, the
orientational order of the suspending medium reveals new facets of bacterial behavior, allowing one to control trajectories of individual bacteria and to visualize rotation of flagella through birefringence of the host. The LLCs represent a new example of a biomechanical system, capable of controlled transduction of stored energy into a systematic movement, which is of critical importance in a variety of application, from bio-inspired micromachines to self-assembled microrobots [49,75]. The study of bacterial motion in LCs and non-Newtonian fluids takes us a step closer to realizing in vitro environments that more closely resemble conditions in vivo [83,157].

5.2 Materials and Methods

5.2.1 Bacteria

Experiments were conducted with the strain 1085 of *Bacillus subtilis*, rod-shaped bacterium 5 \( \mu \text{m} \) long and 0.7 \( \mu \text{m} \) in diameter. The bacteria were initially grown on LB agar plates, then transferred to a Terrific Broth liquid medium (Sigma T5574) and grown in shaking incubator at temperature 35°C for 10-12 hours. To increase resistance to oxygen starvation the bacteria are grown in sealed vials under micro-aerobic conditions [68]. We monitored the concentration of bacteria by the measurement of the optical scattering of the growth media. The bacteria at the end of their exponential growth stage were extracted and washed. The growth medium was separated from the bacteria and removed as completely as possible by centrifugation.
5.2.2 LLC preparation

Chromonic lyotropic LC material disodium cromoglycate (DSCG) purchased from Spectrum Chemicals, 98% purity, was dissolved in Terrific Broth at 16 wt%. This solution was added to the concentrated bacteria obtained as described above. The resulting LLC was mixed by stirring with a clean toothpick and then in a vortex mixer at 3000 rpm. The LLC mixture was injected (by pressure gradient) into a flat cell made from two square glass plates (10×10 mm) separated by spacers. Two interior surfaces were pretreated with polyimide SE7511 and rubbed with velvet cloth to provide a uniform planar alignment of the LLC. The cell was sealed with high vacuum grease (Dow Corning) to prevent water evaporation. The temperature shift of the LC phase diagrams during several hours of the experiments is less than 1˚C and thus does not affect the data presented. The observations were started immediately after the sealed cells were placed in a heating stage (Linkam PE94) at 25˚C. For the used lyotropic LC, the average value of the splay and bend elastic constants is $K = 10^{-12} \text{pN}[110]$; the average viscosity $\eta \approx 10 \text{kgm}^{-1}\text{s}^{-1}$ as determined in an experiment with director relaxation in cells with magnetically induced director distortions (Frederiks effect) [2,110].

5.2.3 Videomicroscopy

An inverted microscope Olympus IX71 with a motorized stage, mounted on a piezoelectric insolation platform Herzan TS-150 and Prosilica GX 1660 camera (resolution of 1600x1200) were used to record motion of individual bacteria in thin cells. Images were acquired with the frame rate up to 100 frames/sec, at 60x magnification, oil-
immersion objective, in cross-polarized light. Color camera with the resolution 1280x1024 and the frame rate 10 frames/second and 2x-20x magnifications were used to acquire large-scale patterns of collective motion. The acquired images were processed in Matlab.

5.2.4 PolScope microscopy

The LLC textures were examined by a polarizing microscope (Nikon E600) equipped with Cambridge Research Incorporation (CRI) Abrio LC-PolScope package. The LC PolScope uses a monochromatic illumination at 546 nm and maps optical retardance \( \Gamma(x,y) \) in the range (0-273) nm and orientation of the slow axis \([158]\). For tangentially anchored LLC, \( \Gamma = |n_e - n_o| \hat{n} h \), where \( n_e \) and \( n_o \) are the extraordinary and ordinary refractive indices, \( h \) is the cell thickness. For DSCG, optical birefringence is negative, \( n_e - n_o \approx -0.02 \) \([5]\). The slow axis is thus perpendicular to the optic axis and to \( \hat{n} \). The PolScope was set up to map the local orientation \( \hat{n}(x,y) \), Fig. 5.5b.

5.3 Results

The concept of LLC is enabled by the recent progress in water-soluble non-toxic chromonic LCs \([5,83,157]\) and growing expertise in control and manipulation of bacterial suspensions in confined geometries \([68,75,154-156]\). Our studies have shown that living bacteria can be transferred to the LC media, and yield highly nontrivial interactions with the molecular ordering of the LC. The experiments are conducted with common swimming bacteria (Bacillus subtilis) in lyotropic chromonic, see Materials
and Methods. We examined the simplest nematic phase of the LLC. In the absence of activity, the LLC is a standard nematic characterized by the long-range orientational order described by a unit director \( \hat{n} \) with the property \( \hat{n} = -\hat{n} \). Its ground state is a uniform director field, \( \hat{n} = \text{const.} \). When activity is turned on, the LLC exhibits the onset of large-scale undulations of a nematic director with a characteristic length \( \lambda \) (see below) determined by the balance between bacteria activity and anisotropic viscoelasticity of the lyotropic chromonic. The nematic phase of the LLC depends on both the concentration of the mesogenic material and temperature; at low concentrations and/or high temperatures, the material melts into an isotropic fluid. The bacterial-free chromonic LC and the LLC show approximately the same phase diagram in the concentration-temperature coordinates. In an experimental cell, the direction of \( \hat{n} \) is preselected by surface anchoring, namely, by a rubbed layer of polyimide coated onto the glass substrates [25], see Materials and Methods; this direction is along the \( x \)-axis, so that the unperturbed director is \( \hat{n}_0 = (1, 0, 0) \).
Figure 5.1: Distortion of the nematic director detected by optical microscopy. (A) Snapshot of swimming bacteria observed under a microscope with slightly de-crossed polarizer (P) and analyzer (A). The bacterium shown in green box swims from the right to left. (B) Optical retardance pattern around a swimming bacterium, see also Fig 5.4-
5.6. (C) Time evolution of the director waves created by rotating flagella in the co-moving reference frame. (D) Space-time diagram for director waves extracted for the bacterium shown in panel (C). A total of 240 cross-sections were extracted from 2.4 sec video. Dashed green line depicts phase velocity of the flagella wave. Dots mark an immobilized dust particle. (E) The trajectory of a single bacterium around a tactoid. (F) Trace of isotropic tactoids left by a bacterium at temperature about 0.5 °C below the nematic-biphase transition point. Observations are made under a microscope with slightly de-crossed polarizer (P) and analyzer (A). Scale bar 5 μm (A,B), 2 μm (C), 10 μm (E), 20 μm (F).

5.3.1 Single bacteria motion

A typical bacterium has a cylindrical body of length 5-7 μm and diameter 0.7 μm. There are also about 20 helicoidal 10 μm long flagella filaments attached to the bacterial body. In an active (motile) bacterium, the filaments bundle on one end of the bacterium and rotate, thus powering unidirectional “head-forward” motion. The motility of aerobic bacteria (such as *Bacillus subtilis*) is controlled by the amount of dissolved oxygen [159]. When placed in the uniformly aligned LC, the bacteria show a number of intriguing dynamic phenomena that can be attributed to the coupling of the LC structure to an individual bacterium and to the collective effects. Since the individual behavior is pertinent for the understanding of emerging collective motion, we first discuss the
dynamics of individual bacteria in relatively thin (of thickness $h = 5 \, \mu m$) LLC flat glass cells, Fig 5.1.

Because of the rod-like shape of the bacterium, and because of the strong orienting effect of the surface anchoring in a thin LC cell, individual bacteria tend to swim along director $\hat{n}_0$, in agreement with earlier observations [157,160]. The most striking feature observed in our experiments is that the bacterial flagella, having a diameter of only about 24 nm, produces director perturbations on a scales of micrometers, Fig. 5.1A,B,C. Birefringence of the LLC makes these perturbations clearly seen under the polarizing microscope, Fig. 5.1A. The texture in Fig. 5.1A observed with de-crossed polarizers, reveals periodic dark and bright elongated spots tilted with respect to $\hat{n}_0$ and caused by the broken chiral symmetry of the director distortions (see 5.5). The map of optical retardance in Fig. 5.1B, obtained with a PolScope (see Materials and Methods) [158], demonstrates that the effective birefringence near the bacterium is reduced as compared to the uniform director surrounding.

The pattern of alternating bright and dark spots in the bacterium wake propagates with a wavelength about $d = 2 \, \mu m$. At a fixed distance from the body of bacterium, the bright and dark regions alternate with the frequency of about 16 Hz, Fig. 5.1C. The wavelength is determined by the pitch of helical flagella, and the frequency by the flagella rotation rate. We constructed a space-time diagram by stacking a total of 240 consecutive cross-sections along the bacterium’s axis in a co-moving reference frame from each image, Fig. 5.1D. From the space-time diagram we clearly see propagation of
the flagella wave (parallel white lines between 0 and 15 μm) and counter-rotation of the bacterial body (dark regions at -5 μm) with a rate of 2.5 Hz. The ratio of flagella rotation to the counter-rotation of the body is about 7:1, similar to that known for *Bacillus subtilis* under normal conditions (160 Hz flagella rotation and 20 Hz body counter-rotation [161]).

Individual behavior of bacteria and its coupling to the orientational order becomes especially interesting as the temperature is increased and the LLC approaches a biphasic region, in which the isotropic and nematic phases coexist. The isotropic regions appear as characteristic “negative tactoids” elongated along the overall director of the surrounding nematic [2,26]. The isotropic tactoids, seen as dark islands in Fig. 5.1E, distort the director around them and change the trajectories of the bacteria. As shown in Fig. 5.1E, far away from the tactoid, a bacterium is swimming along a straight line set by the uniform director. In the vicinity of tactoid, the trajectory deviates from the straight line and follows the local distorted director. After a collision with the isotropic-nematic interface, the bacterium follows the curved interface, and finally escapes at the cusp of the tactoid.

Even more strikingly, the bacteria themselves can create isotropic tactoids in their wake if the LLC temperature is close to the biphasic region, Fig. 5.1F. The LLC acts as miniature “Wilson chamber” in which the isotropic droplets decorate the path of swimming bacteria. The feature underscores the complexity of interplay between velocity fields and the state of orientational order that can involve a number of different
mechanisms, such as existence of a nucleation barrier, non-uniform distribution of components between the nematic and isotropic phase, etc. Nucleation of the isotropic phase in Fig. 5.1F implies that the bacterial flows reduce the local degree of orientational order, most probably through disintegration of the chromonic aggregates [5]. The fact that bacteria can follow the nematic-isotropic interface and the overall director in the LLC offers numerous design concepts of reconfigurable microfluidic devices for the control and manipulation of bacteria. The desired trajectories of bacterial transport can be engineered by patterned surface anchoring and by local dynamic heating (for example, with focused laser beams).

5.3.2 Collective behavior

Now we discuss collective behavior of LLC emerging at higher concentrations of bacteria. We discovered that a long-range nematic alignment of the LLC is affected by the flow created by the swimming bacteria. The coupling of the orientational order and hydrodynamic flow yields nontrivial dynamic patterns of the director and bacterial orientations, see Figs. 5.2 and 5.3.
**Figure 5.2:** Emergence of a characteristic length scale in LLCs. (A,B) LLC with inactive bacteria is at its equilibrium state with the director and bacteria (highlighted by ellipses) aligned uniformly along the rubbing direction; (C,D) active bacteria produce periodically distorted director. (E) Proliferation of stripe pattern in the sample of thickness \( h = 20 \, \mu m \)
and for low concentration of bacteria, \( c \approx 0.9 \times 10^9 \) cells/cm\(^3\). Oxygen permeates from the left hand side. (F) LLC patterns in thicker sample \((h=50 \, \mu m)\) and for higher concentration of bacteria, \( c \approx 1.6 \times 10^9 \) cells/cm\(^3\). White arrow points toward a higher concentration of oxygen. (G) Zoomed area in panel (F) shows nucleating disclinations of strength \( +1/2 \) (semi-circles) and \(-1/2\) (triangles). Bright dashes visualize bacterial orientation. (H) Dependence of characteristic period \( \xi \) on \( c \) and \( h \); dashed lines depict fit to theoretical prediction \( \xi = \frac{K h}{\sqrt{\alpha_\phi c U_0}} \). Inset illustrates collapse of the data into a universal behavior that follows from the theoretical model. (I) Director realignment (shown as a rod) caused by the bacterium-generated flow (shown by dashed lines with arrows). Scale bar 50 \( \mu m \) (A-D), 100 \( \mu m \) (E-G). Error bars are \( \pm 10\% \) SEM (standard error of the mean), except for \( \pm 30\% \) SEM at \( c/c_0 = 5.05 \).

The first example, Fig. 5.2, demonstrates the existence of a characteristic spatial length scale \( \xi \) in LLCs that sets this non-equilibrium system apart from standard equilibrium LCs. The LLC is confined between two glass plates that fix \( \hat{n}_0 = (1,0,0) \) along the rubbing direction. In the samples with inactive bacteria the steady state is uniform, \( \hat{n} = \hat{n}_0 = \text{const} \), and the immobilized bacteria are aligned along the same direction, Fig. 5.2A,B. In chambers with active bacteria, supported by the influx of oxygen through the air-LLC interface (on the left hand side in Fig. 5.2E), the uniform state becomes unstable and develops a stripe pattern with periodic bend-like deviations of \( \hat{n} \) from \( \hat{n}_0 \), Fig. 5.2C-E. The swimming bacteria are aligned along the local director \( \hat{n} \),
Fig. 5.2D. Since the oxygen permeates the LLC from the open side of the channel, its concentration is highest at the air-LC interface; accordingly, the stripes appear first near the air-LLC interface. The period $\xi$ of stripes increases with the increase of the distance from the air-LLC interface as the amount of oxygen and the bacterial activity decrease. Figure 5.2H shows that $\xi$ increases when the concentration $c$ of bacteria and the chamber height $h$ decrease. The data in Fig. 5.2H are collected for different samples in which the velocity of bacteria was similar ($8 \pm 3 \, \mu m/s$), as established by a particle-tracking velocimetry; the concentration is normalized by the concentration $c_0 \approx 8 \times 10^8 \, \text{cells/cm}^3$ of the stationary growth phase.

As time evolves, in the regions with the highest bacterial activity, near the open edge, the stripe pattern becomes unstable against nucleation of pairs of $\pm \frac{1}{2}$ disclinations, Fig. 5.2F, G. Remarkably, the pattern-forming instabilities occurring here have no direct analog for bacterial suspensions in Newtonian fluids or for bacteria-free pure LCs. The concentration of bacteria in our experiments (close to 0.2% of volume fraction) is about 1/10 of that needed for the onset of collective swimming in Newtonian liquids (about $10^{10} \, \text{cells/cm}^3$ [68]).
Figure 5.3: LLC in sessile drop. (A) Texture with multiple disclination pairs, green rectangle indicates the region shown in (B,C,D). Bacteria are aligned along the local nematic director, as revealed by the fine stripes. Scale bar 30 μm. No polarizers. (B,C,D) LLC texture with -1/2 and 1/2 disclinations and the pattern of local flow velocity (blue arrows) determined by particle-image velocimetry. The flow typically encircles the close pair of defects.

Figure 5.3 illustrates the profound effect of bacterial activity on spatio-temporal patterns in a sessile drop of LCCs [68,162] in which there is no preferred director orientation in the plane of film. Bacterial activity generates persistently rearranging bacterial and director patterns with $\pm \frac{1}{2}$ disclinations that nucleate and annihilate in pairs, similarly to the recent experiments on active microtubule bundles [40], Fig. 5.3A. The
characteristic spatial scale of the pattern, determined as an average distance between the
disclination cores, is in the range of 150-200 μm, of the same order of magnitude as ξ in
the stripe pattern in strongly anchored sample. The fluid flow typically encircles
disclination pairs, Figs. 5.3B-D.

5.4 Discussion and conclusion

Emergence of a characteristic length scale ξ in LCCs, either as a period of the
stripe pattern in Fig. 5.2 or as a characteristic separation of disclinations in Fig. 5.3, is
caused by the balance of director-mediated elasticity and bacteria-generated flows, Fig.
5.2I. Since no net force is applied to a self-propelled object, a swimming bacterium
represents a moving negative hydrodynamic force dipole of the strength $U_0$ ("pusher"), as
it produces two outward fluid streams coaxial with the bacterial body [163]. The strength
of the dipole (of a dimension of torque or energy) is of the order 1 pN μm [164]. In the
approximation of nearly parallel orientation of the bacterium and the local director $\hat{n}$,
the bacteria-induced streams, Fig. 5.2I, impose a reorienting torque $\sim \alpha(h)cU_0\theta$, where
$\alpha(h)$ is a dimensionless factor that describes the flow strength and depends on the cell
thickness $h$; $c$ is the concentration of bacteria, and $\theta$ is the angle between local
orientation of bacteria and $\hat{n}$. Similar torques caused by shear flow are well known in
the physics of liquid crystals [2], see section 5.5 and Fig. 5.6. Mass conservation yields
an estimate $\alpha=\alpha_0l/h$, where constant $\alpha_0\approx O(1)$, and $l$ is the length of a bacterium. It
implies that the channel’s thickness reduction increases the flow because the bacteria
pump the same amount of liquid. The local bacterium-induced reorienting hydrodynamic torque is opposed by the restoring elastic torque \( \sim K \frac{\partial^2 \theta}{\partial x^2} \); \( K \) is an average Frank elastic constant of the LC. In the case of a very thin layer confined between two plates with strong surface anchoring, the strongest elastic torque \( K_2 \frac{\partial^2 \theta}{\partial z^2} \) will be associated with the twist deformation along the vertical \( z \)-axis. However, since the elastic constant for twist is an order of magnitude smaller than the splay and bend constants [110], the restoring torque in relatively thick (20 and 50\( \mu m \)) samples is caused mainly by in-plane distortions. By balancing the elastic and bacterial torques, \( \frac{\partial^2 \theta}{\partial x^2} = \theta / \xi \), one defines a “bacterial coherence length” \( \xi = \sqrt{\frac{Kh}{\alpha_0 lc U_0}} \) (somewhat similar arguments for the characteristic length of bending instability in active nematics were suggested in [72]). This expression fits the experimental data on the periodicity of stripe patterns for different concentrations of bacteria \( c \) and thicknesses \( h \) remarkably well with a choice of \( \alpha_0 \approx 1 \), see Fig. 5.2H.

The experiments in Fig. 5.2 and 5.3 clarifies the rich sequence of instabilities by which the activity of bacteria transforms the initial non-flowing homogeneous uniform steady state in Fig. 5.2A,B into the state of self-sustained active fluid turbulence, Fig. 5.3. The first step is through appearance of the periodic director bend with a characteristic length scale \( \xi \), Fig. 5.2C-E. The period becomes shorter as the activity increases, Fig. 5.2H. Further escalation of the activity causes a qualitative transformation, namely,
nucleation of defect pairs, Fig. 5.2F,G. Note that the axis connecting the cores of $1/2$ and $-1/2$ disclinations in the pair and the local director $\hat{n}$ along this axis are perpendicular to the original director $\hat{n}_0$, Fig. 5.2G. Once the system can overcome the stabilizing action of surface anchoring, as in Fig. 5.3, the dynamic array of moving defects forms a globally isotropic state in which the local director $\hat{n}$ is defined only locally (somewhat similar dynamic behavior was observed in simulations of “active nematic” in Refs. [165,166]). The final state, Fig. 5.3, is an example of “active fluid” turbulence at vanishing Reynolds number [68,162], which is in our case on the order of $10^{-5}$.

In conclusion, LLC demonstrates a wealth of new phenomena not observed for either suspension of bacteria in a Newtonian fluid or in passive ordered fluid. The concept of a characteristic length $\xi$, contrasting the elastic response of orientationally ordered medium and the activity of microswimmers, may also be useful for understanding hierarchy of spatial scales in other active matter systems [38,68,77,152-154]. Our studies were focused on the simplest nematic LLC. However, more complex LLCs can be explored as well, for example, smectics and cholesteric LCs with controlled chirality. Exploration of LLCs may have intriguing applications in various fields. Our biomechanical system may provide the basis for devices with new functionalities, including specific responses to chemical agents, toxins, or photons. Swimming bacteria can also serve as autonomous “microprobes” for the properties of LCs. Unlike passive microprobes [167], swimming bacteria introduce local perturbations of the LC molecular order both in terms of the director and the degree of order, and thus provide unique
information on the mesostructure of the material. In turn, LC medium provides valuable optically accessible information on the intricate submicrometer structure of bacteria-generated microflow that deserves further investigation.

5.5 Supplemental information

5.5.1 Optics of director patterns in the wake of a moving bacterium

We numerically simulated the optical patterns observed under the polarizing microscope, using standard Berreman 4x4 matrix method [168]. We model the director field distorted by the flagella as following:

\[
\begin{align*}
n_x(x, y, z) &= \sin \varphi_0 \sin(-kx) (1 - \beta |z - z_0|) \exp \left(-\frac{|y - y_0|}{\lambda} \right), \\
n_y(x, y, z) &= -\sin \varphi_0 \cos(-kx) (1 - \beta |z - z_0|) \exp \left(-\frac{|y - y_0|}{\lambda} \right), \\
n_z(x, y, z) &= \sqrt{1 - n_y^2 - n_z^2} \\
\end{align*}
\]

where \((x, y_0, z_0) = (x, r_0 \cos(-kx), r_0 \sin(-kx))\) defines the position of left handed helical flagella along \(x\)-axis and centered at \((0,0)\) of \(y\)-\(z\) plane. By its rotation, director \(\hat{n}\) deviates from \(\hat{n}_0 = (1,0,0)\) by the angle \(\varphi_0 = 10^\circ\) at the flagella and linearly decay in \(z\) direction with the rates \(\beta = \left(\frac{z_0 + \frac{h}{2}}{2} \right)^{-1} \) (for \(z < z_0\)) and \(\left(\frac{h}{2} - z_0 \right)^{-1} \) (for \(z \geq z_0\)), and exponentially decay in the \(y\) direction with a characteristic decay length \(\lambda = 1 \mu m; r_0 = 0.5 \mu m\) is the rotation radius of flagella; \(k = 2\pi P^{-1}, P = 2 \mu m\) is the helical pitch of
the flagella. By using this model, we display in Fig. 5.4 the textures for different analyzer orientations in the area corresponding to four periods of the director pattern along the $x$ direction and to $3\lambda$ along the $y$ direction.

**Figure 5.4:** Light intensity pattern for a linearly polarized light passing through the twisted director configuration as described in the section 5.5.1. (a,b) polarizing microscopy textures of oblique black and white regions in the wake area of swimming bacteria. (c,d,e) Optical simulation of director textures deformed by the helicoidal flagella viewed between two linear polarizers making a different angle $\delta_{AP} = 80^\circ$ (c), $90^\circ$ (d) and $100^\circ$ (e). Scale bar 5μm.
5.5.2 Optics of director patterns distorted by flows produced by individual bacterium

Fig 5.1a shows that the regions under and above a moving bacterium have a different optical density. Fig. 5.5 shows a clear manifestation of this effect, for a bacterium that is pinned or does not swim (but otherwise active and has rotating flagella), apparently because it is close to the stage of division into two bacteria and has two sets of flagella. For this bacterium, the optical density pattern resembles a butterfly, Fig. 5.5a, in which the director distortions propagate over tens of micrometers. PolScope image of the director field indicates that the director forms a tilted pattern in the shape of the letter “X”, Fig. 5.5b. The effect can be explained by the flow-induced reorientation of the director, schematically shown in Fig. 5.5c (see also Fig. 5.3i). Optical simulations based on the Berreman matrices show that these director distortions results in the butterfly pattern when the sample is observed between two polarizers, Fig. 5.5d,e,f. Analytical calculation with Jones matrix method shows that the field of light passing through a polarizer, a sample with retardance $\Gamma$ oriented at $\varphi$, and a analyzer at $\varphi_{AP}$ follows

$$
\begin{bmatrix}
E_a \\
0
\end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix}
1 & 0 \\
0 & 0
\end{bmatrix}
\begin{bmatrix}
\cos \varphi_{AP} & \sin \varphi_{AP} \\
-\sin \varphi_{AP} & \cos \varphi_{AP}
\end{bmatrix}
\begin{bmatrix}
\cos \varphi & -\sin \varphi \\
\sin \varphi & \cos \varphi
\end{bmatrix}
\begin{bmatrix}
e^{-i\Omega T/2} & 0 \\
0 & e^{i\Omega T/2}
\end{bmatrix}
\begin{bmatrix}
\cos \varphi & \sin \varphi \\
-\sin \varphi & \cos \varphi
\end{bmatrix}
\begin{bmatrix}
1
\end{bmatrix}
$$

(5.2)

thus intensity at the analyzer

$$
I_a = \frac{1}{2} \cos^2(\varphi_{AP} - \varphi) \cos^2 \varphi + \sin^2(\varphi_{AP} - \varphi) \sin^2 \varphi - \frac{1}{4} \sin 2(\varphi_{AP} - \varphi) \sin 2\varphi \cos \Gamma
$$

(5.3)
For $\Gamma = -1.15$ (\( h = 5\mu m \), $\Delta n = -0.02 \), wavelength of the light 546nm) as in our samples, $I_a$ has minimum values at $\varphi_{\varphi} \approx 90^\circ + \frac{1}{2} \varphi$ when $\varphi < 25^\circ$. This confirms the experimental and optical simulation texture of “butterfly” shaped director field, Fig. 5.5a,d,e,f For a moving bacterium, the effect is qualitatively similar, with the difference that the propulsion enhances the front two “wings” of the butterfly and weakens the rear two wings; as a result, the regions below and above the bacterium’s head have different brightness, Fig. 5.1a,c.
Figure 5.5: Director distortions around an immobile bacterium. (a) Optical polarizing microscopy texture with de-crossed polarizers shows a “butterfly” pattern. (b) PolScope texture maps director pattern (yellow lines) resembling an “X” letter; color scale is proportional to the angle that the local director makes with the long axis of the image. (c) A schematic representation showing how the director (red bar) deviates from \( \mathbf{n}_0 = (1, 0, 0) \) (blue dashed lines) due to the flow (blue arcs with arrows) induced by non-
swimming two-tail bacterium. (d,e,f) Optical simulation of the director pattern in part (b) shows the butterfly pattern in the intensity map when the two polarizers are crossed at different angles (a,b). Scale bar 5 μm (a), 10 μm(b).

Besides the two coaxial streams, the bacterium also creates velocity fields associated with rotations of its body and its flagella (in opposite directions, Fig. 5.6a,b). These rotations cause director reorientations that lack the mirror symmetry with respect to the plane passing through the long axis of the bacterium, Fig. 5.6c; these deformations would further complicate the director pattern in the close vicinity of a moving bacterium; these effects will be explored in details in the future.

The director distortions would be created by a moving bacterium when the viscous torque overcomes the elastic one, which is equivalent to the requirement that the Ericksen number of the problem is larger than 1. For a rotating bacterium in a cell of thickness $h$, the Ericksen number \( [2] \) is $Er = ωfrh / K$, where $ω$ is an effective viscosity, $f$ is the frequency of bacterium head rotation, $r$ is the bacterium radius. For typical values of parameters in our problem, $K = 10$ pN, $ω = 10$ kg/(m·s), $f = 2$ Hz, $r = 0.4$ μm, $h = 20$ μm, this requirement is easily satisfied, as $Er = 16$. As already discussed in the main text, the shear flows produced by the bacteria can also cause a decrease in the degree of orientational order, which corresponds to Deborah numbers close to 1 or larger.
Figure 5.6: Chiral symmetry breaking of the LLC director pattern caused by a rotating bacterium. (a,b). Schematics of the flows generated by the rotating bacterium. (c) Scheme of the director twist along the vertical z-xis.
Lyotropic chromonic liquid crystals (LCLCs) represent a novel type of liquid crystals formed by self-assembly of disk-shape molecules in aqueous environment. The underlying physics that governs the anisotropic elastic and viscous properties of such materials is fundamentally different from that of thermotropic LCs, lyotropic LCs formed by rigid rods, and lyotropic polymer LCs (LPLCs) formed by semi-flexible chains with fixed size. In the LCLCs, the aggregates are formed by weak van der Waals force, thus their length and flexibility strongly depend on temperature, concentration, ionic contents, pH of the system and so on. As a result, the macroscopic viscoelastic properties show dramatic dependence when temperature, concentration, ionic content of the solution, or pH changes. LCLCs also provide biocompatible environment so that bacteria remain motile in them. The interaction between self-propelled rod-shape bacteria Bacillus subtilis and long-range nematic order of LCLCs gives rise to intriguing phenomena and new design concepts of manipulating active colloids. The results are summarized as follows.

1. We determined experimentally the viscoelastic parameters of LCLCs. In the first experiment, we measured the Frank elastic moduli of Sunset Yellow LCLC by studying the director reorientation in magnetic field. We find that the splay constant $K_1$ and bend constant $K_3$ are on the order of 10pN, comparable to each other and to those of
the thermotropic LC 5CB. The twist constant $K_2 \approx 1pN$ is about 10 times smaller. The
splay constant $K_1$ and the elastic ratios $\frac{K_1}{K_3}$, $\frac{K_1}{K_2}$ increase significantly as the
concentration of SSY increases or temperature decreases. We explain our findings within
a model of semi-flexible SSY aggregates, the length of which changes dramatically when
the concentration increases or temperature decreases. $K_1$, determined by the contour
length of aggregates $L$, thus has the strongest temperature dependence among all three.
$K_4$ is determined by the persistence length $\lambda_p$. $K_2$ is the smallest among all three since
twist deformation can happen at imaginary “pseudo-layers” without disturbing the
orientation of aggregates on each layer. We also estimated the scission energy
$E = (7 - 13) k_B T$ and persistence length $\lambda_p$ on the order of tens of nm, in agreement with
estimations obtained by other researchers using different methods. The strong increase of
$K_1$ at increased concentration or decreased temperature matches well with the fact that in
the neighboring columnar phase, $K_1$ diverges.

2. In the next set of experiments, we study the effect of ionic additives on the
viscoelastic properties of LCLC. We use the same material, Sunset Yellow and fix its
concentration with respect to water, while adding different ionic additives (monovalent
salt NaCl, divalent salt MgSO$_4$, pH agent NaOH) into the system at different
concentrations. Using the same Frederiks transition technique, we measure the Frank
elastic constants of each solution as a function of temperature. We also measure the
rotation viscosity $\gamma_1$ by director relaxation in the magnetic field. We observe dramatic and versatile changes of the viscoelastic properties induced by the ionic additives. For example, adding monovalent salt NaCl decreases $K_3$ and $K_2$, shows little influence on $K_1$, and increases $\gamma_1$, while adding divalent salt MgSO$_4$ increases $K_1$, $K_2$ and $\gamma_1$ but decreases $K_3$. Increasing pH by adding NaOH decreases all $K$’s and $\gamma_1$. These changes of viscoelastic properties induced by ionic additives are explained through the idea that ion concentration in the solution modulates the interaction between aggregates in different ways, changing two characteristic lengths, namely, the contour and persistence length. For example, a stronger Debye screening at higher salt concentration makes the aggregates longer (because of the increased scission energy) but at the same time more flexible. On the other hand, adding NaOH enhances disassociation of sodium ions, elevating the charge density on SSY aggregates. A stronger electrostatic repulsion of molecules within the aggregate decreases the average aggregation length.

3. Another important LCLC material is disodium cromoglycate, due to its optical transparency at visible wavelengths and biocompatibility. We extend our study of LCLC viscoelasticity to this material using a different technique: dynamic light scattering. We determined all three elastic constants of splay, twist, and bend, and also measured the viscosity coefficients associated with these deformations. Similar to the SSY case, DSCG exhibits significant anisotropy of the elastic constants ($K_1 \approx K_3 \approx 10K_2$) and strong temperature and concentration dependence of $K_1$. We also find that the anisotropy of
viscosity coefficients is even larger: $\eta_{\text{bend}}$ of DSCG is comparable to that of 5CB, but can be up to 4 orders of magnitudes smaller than $\eta_{\text{play}} \approx \eta_{\text{twist}}$, $K_1$, $\eta_{\text{play}}$ and $\eta_{\text{twist}}$ grow exponentially as temperature decreases or concentration increases. We explain our findings of temperature dependence of viscoelasticity with a model of semi-flexible aggregates whose length and flexibility are functions of $T$ and $c$. The experimental study of DSCG shows that $\eta_{\text{play}} \approx \eta_{\text{twist}} \propto L^2$ which correlates well with the model of semi-flexible chains and is consistent with the relationship $K_1 \propto L$. Weak temperature dependence found for other parameters ($K_2, K_3$ and $\eta_{\text{bend}}$) also agree with the theory. In addition, we detect unexpected mode in the dynamic light scattering and we attribute it to the stacking fault of DSCG aggregates.

4. Taking advantage of its biocompatibility, we combined DSCG with motile bacteria *Bacillus subtilis*, and created a new active nematic system, the living liquid crystals. In this system, independent of the nematic order, we continuously changed the activity from zero to high values by changing bacterial concentration and oxygen availability. The interaction between bacteria induced flow and the long-range nematic order of DSCG give rise to a wealth of fascinating phenomena not observed in bacterial suspensions in isotropic fluids. (i) At the very low bacteria concentration, individual bacterium swims along the local director. Motion of 24nm thick flagella disturbs the local nematic order and is thus visible under polarizing optical microscope. On the hand, bacteria flow changes the nematic order by triggering nematic-isotropic transition at high
enough temperature. (ii) At higher bacteria concentration, bacterial motion collectively creates bend deformation with a characteristic coherent length \( \xi = \sqrt{\frac{K_h}{\alpha_0/c U_0}} \), determined by the balance between the activity of bacteria and elastic energy of the distorted nematic director. (iii) At very high bacteria concentration (~0.2% by volume), bend deformation becomes unstable; instead, topological defects are constantly created and annihilated. Note that 0.2% is only about 1/10 of the concentration for collective motion in isotropic media. Our work provides a platform where one can further explore the interaction of activity and ordered system, as well as provides design concepts to control and manipulate the dynamic behavior of soft active matter for potential biosensor and biomedical applications.
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