

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 [1–4]. Examples include “living polymers”, wormlike micelles of amphiphiles, stacks of disk-like dye and drug molecules [1, 2], and nucleic acids [4]. 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) [1, 2]. Since the aggregates are bound by weak van der Waals forces, their length varies strongly with concentration, temperature or 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 [5] or polymers of fixed molecular weight [6]. 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 [7, 8], but not their elastic moduli. The main challenge is in accounting for the length distribution and flexibility of aggregates. The average length of aggregates $\bar{L}$ in the nematic LCLC can be estimated (see Sect. 2.5.1), following the work of van der Schoot and Cates [9] on wormlike surfactant micelles, as a function of stacking energy E , volume fraction ϕ of the chromonic molecules, persistence length λ_p of the LCLC aggregates of diameter D , and absolute temperature T :

$$\bar{L} = L_0 \phi^{5/6} \left(\frac{\lambda_p}{D} \right)^{1/3} \exp \frac{E + \kappa \phi}{2k_B T} \quad (2.1)$$

where $L_0 = 2\pi^{-2/3}\sqrt{a_z D}$ is a length characterizing the size of a monomer, a_z is the period of molecular stacking along the aggregate, κ is a constant describing the enhancement of aggregation by the excluded volume effects; in the second virial approximation, $\kappa \approx 4k_B T$ [9]. Experimental characterization of elastic parameters is also challenging as it requires two types of uniformly aligned samples, with the director $\hat{\mathbf{n}}$ (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 $\mathbf{B}$ to realign $\hat{\mathbf{n}}$ (Frederiks effect). Only planar cells were used so far. In these cells, $\mathbf{B}$ causes twist or mixed twist-bend of $\hat{\mathbf{n}}$, depending on the rate of field increase [10, 11]. Golovanov et al. [12, 13] used this effect to extract the twist constant $K_2 = 0.36$ pN and the bend-twist ratio $K_3/K_2 = 12.2$ for disulphoindantrone-water LCLC.

In this chapter, 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 [14–16]. We find that the 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. [14]. The study is performed for the nematic phase at $c = 29.0$, 30.0 , and 31.5 wt% ($\phi = 0.18$, 0.19 and 0.20 , respectively, see Sect. 2.5.3). The diamagnetic susceptibility measured parallel to $\hat{\mathbf{n}}$ is smaller than its orthogonal counterpart, $\Delta\chi = \chi_{\parallel} - \chi_{\perp} < 0$. We used a magnetometer with a superconducting quantum interference device and determined $\Delta\chi$ following Ref. [17] as $\Delta\chi = 3(\chi_{av} - \chi_{\perp})$, where $\chi_{av} = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp})$ 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. [17]. At 25 °C, the magnetization was monitored for over 10 h until its value saturated, indicating an equilibrium homogeneous nematic state with $\hat{\mathbf{n}} \perp \mathbf{B}$, which allowed us

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 [18]. Mass densities were measured with a densitometer DE45 (Mettler Toledo). Concentration and temperature dependences of $\Delta\chi$ are presented in Sect. 2.5.2.

To determine the elastic parameters, we used flat glass cells of thickness $d = 20 - 25 \mu\text{m}$. 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 [19]. For planar alignment, the substrates were rubbed with a superfine abrasive paper (001 K Crystal BayTM Crocus Cloth, 3 M), 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 $\hat{\mathbf{z}}$ makes an angle α with $\mathbf{B}$, $\hat{\mathbf{y}}$ is the axis of rotation, and the $\hat{\mathbf{x}}$ axis is parallel to $\hat{\mathbf{n}}$ in the planar cell (Fig. 2.1). The angle α is controlled with a precision better than 0.1° .

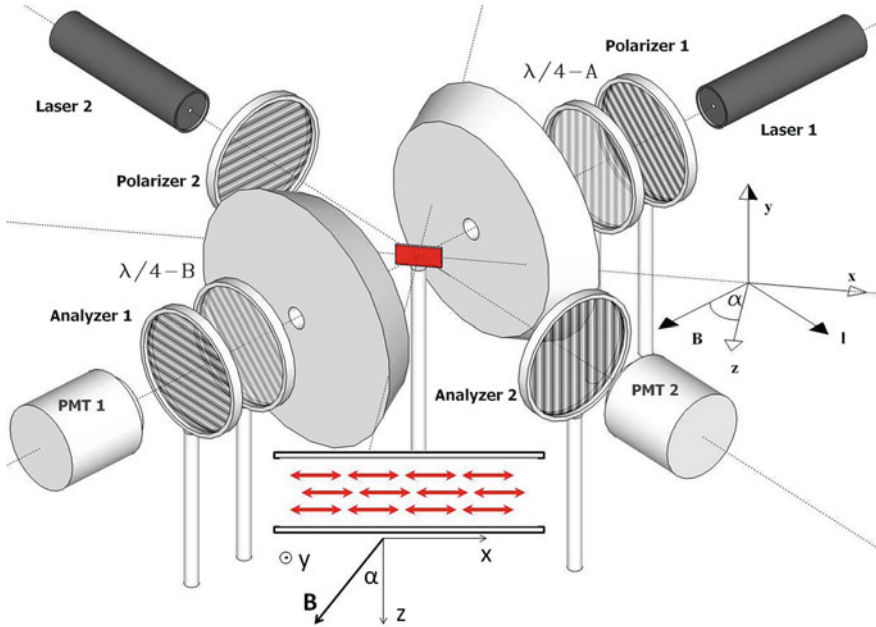


Fig. 2.1 Schematic of experiment setup. Sample is held in a hot stage for temperature control (not shown here). Both laser 1 and 2 are He-Ne lasers ($\lambda = 633 \text{ nm}$)

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

$$B_3 = \frac{\pi}{d} \sqrt{\frac{\mu_0 K_3}{-\Delta\chi}} \quad (2.2)$$

at which $\hat{\mathbf{n}}$ starts to tilt from the z axis (μ_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 umbilicus [20], 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, $d \rightarrow d + l$, where l is the so-called surface anchoring extrapolation length [21]. We verified the validity of Eq. (2.2) by measuring $B_3 = 3.5 \text{ T}$ in ultrathin cells ($d \approx 4 \mu\text{m}$), using a 31 T solenoid at the National High Magnetic Field Laboratory (Tallahassee, FL). The result leads to $l = 0.15 \mu\text{m}$, 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 Sect. 2.5.4). Repeating measurements at different points of the cell and on different cells, we established that the results were reproducible within 5%. Combining the corresponding measurement of $\Delta\chi$, we determine the temperature and concentration dependences of K_3 , Fig. 2.2a.

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., $\mathbf{B} \parallel \hat{\mathbf{n}}$, 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 0.33 T, 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 [22]. 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 Sect. 2.5.5)

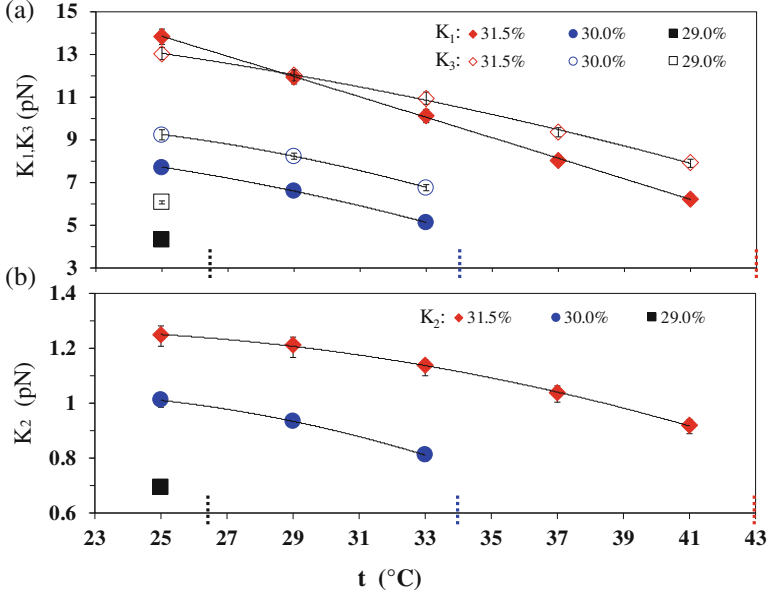


Fig. 2.2 Temperature and concentration dependences of **a** K_1 , K_3 and **b** K_2 . The vertical dash lines mark the nematic-biphasic transition temperature ($T_{N \rightarrow N+I}$) upon heating (same for other plots) for each concentration: 26.6 ± 0.6 °C, 34.4 ± 0.4 °C, 44.1 ± 0.5 °C for $c = 29, 30$ and 31.5% respectively

$$f = \frac{1}{2} (K_1 \sin^2 \theta + K_3 \cos^2 \theta) \left(\frac{d\theta}{dz} \right)^2 - \frac{1}{2} \frac{\Delta\chi}{\mu_0} B^2 \cos^2(\alpha - \theta) \quad (2.3)$$

Since K_3 is already known, we fit the experimental $R(B)$ to extract K_1 as the only fitting parameter, Fig. 2.2a.

2.3.3 Planar Cells, Twist Constant K_2

The magnetic field applied parallel to $\hat{\mathbf{n}}$ in the geometry $\alpha = 90^\circ$ often leads to periodic distortions instead of a uniform twist [10–12]. 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 Sect. 2.5.6):

$$B_2 \approx \frac{\pi}{d \sin \alpha} \sqrt{\frac{\mu_0 K_2}{-\Delta\chi}} \quad (2.4)$$

We used the laser beam 2 polarized parallel to **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 K_2 , Fig. 2.2b. The azimuthal anchoring length was small $l_{az} \approx 0.15 \mu\text{m}$, as determined by measuring B_2 in thin cells with $d \approx 7 \mu\text{m}$. The optical response was hysteresis-free for the rate 0.002 T/min of field change.

For SSY concentration $c = 29.0\%$ at $t = 25^\circ\text{C}$, we found $K_1 = (4.3 \pm 0.4) \text{ pN}$, $K_2 = (0.7 \pm 0.07) \text{ pN}$, $K_3 = (6.1 \pm 0.6) \text{ pN}$. Comparing these to 4-n-pentyl-4'-cyanobiphenyl (5CB) values [21], $K_1 = 6.6 \text{ pN}$, $K_2 = 3 \text{ pN}$, $K_3 = 10 \text{ pN}$, 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- γ -benzylglutamate (PBG) in organic solvents, with $\phi = 0.20$ and length-to-diameter ratio $L/D = 32$ [6]: $K_1 = 10 \text{ pN}$, $K_2 = 0.6 \text{ pN}$, $K_3 = 10 \text{ pN}$.

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 [23]) 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, Figs. 2.2a and 2.3c, 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 [24] and models developed for LPLCs [25–28].

Within the LdG model, the temperature dependences of $K_{1,2,3}$, $\Delta\chi$, and Δn are determined by that of the scalar order parameter S , namely, $K_{1,2,3} \propto S^2$, $\Delta\chi \propto S$, $\Delta n \propto S$ [24]. We measured $\Delta n(t)$ and $S(t)$, using the technique described in [29], Fig. 2.4. As seen from Fig. 2.3a, 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. 2.3b–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 [23].

In the models of LPLCs [25–28], 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 [25] predicts $K_1 \propto \phi \frac{L}{D}$, $K_1/K_3 = 3$, and $K_3 \propto \phi^3 (\frac{L}{D})^3$, so that $\frac{K_1}{K_3} \propto \phi^{-2} (\frac{D}{L})^2$ will be much smaller than 1 and decreasing at high ϕ . 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. 2.3d. The disagreement remains when one considers a bidisperse system [25] or takes into account electrostatic effects [27]. 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 λ_d is about 0.3 nm [16]. The electrostatic interactions

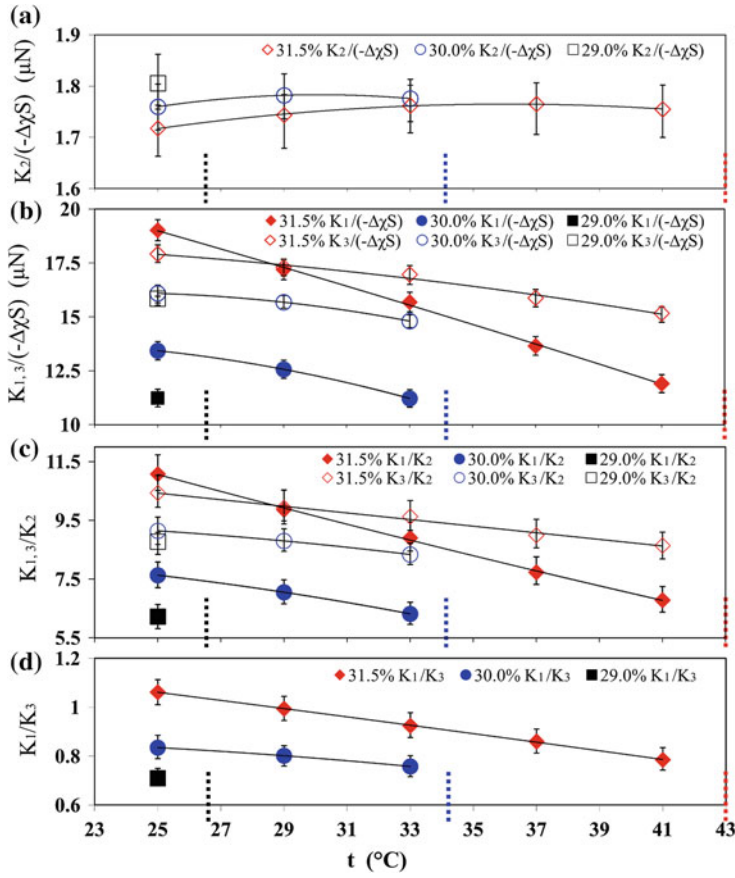


Fig. 2.3 Temperature and concentration dependences of **a** $\frac{K_2}{-\Delta\chi S}$, **b** $\frac{K_{1,3}}{-\Delta\chi S}$, **c** $\frac{K_{1,3}}{K_2}$, and **d** $\frac{K_1}{K_3}$

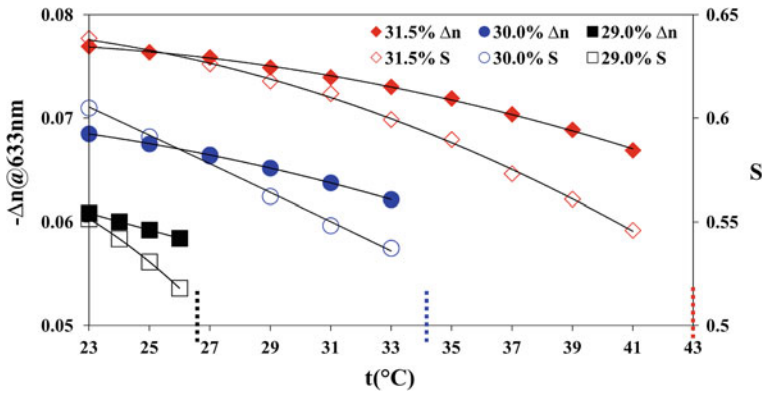


Fig. 2.4 Temperature and concentration dependences of Δn (at 633 nm) and scalar order parameter S

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 $\approx (1 - 0.1h)$ [27], where $h = \lambda_d/(D + 2\lambda_d)$ is only about 0.2 for the nematic phase of SSY [16]. In LPLCs, the electrostatic effect might also increase K_3 [27] (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 [25–28].

The SSY aggregates should be flexible, as the attraction between monomers is weak, with the scission energy E in the range $(7 - 11)k_B T$ [14, 16, 30]. In the theory of semiflexible LPLCs, K_2 and K_3 are determined by the persistence length λ_p of the polymers rather than by L [25, 26, 28]: $K_2 = \frac{k_B T}{D} \phi^{1/3} \left(\frac{\lambda_p}{D}\right)^{1/3}$ [25]; $K_3 = \frac{4}{\pi} \frac{k_B T}{D} \phi \frac{\lambda_p}{D}$ (we use the standard definition [31] $\lambda_p = B/k_B T$ through the bend modulus B , which makes K_3 twice as large as in Ref. [28]). The last formula, with the experimental $K_3 = 6 \text{ pN}$ at $\phi = 0.18$, $t = 25^\circ \text{C}$ and $D = 1.1 \text{ nm}$ [14, 16], yields $\lambda_p \approx 10 \text{ nm}$. We are not aware of any other estimates of λ_p for LCLC, but the result appears reasonable when compared to $\lambda_p \approx 50 \text{ nm}$ for DNA duplex [31], as the latter is about twice wider than the SSY aggregate and we expect λ_p to increase with D .

The splay modulus K_1 still grows with the contour length L (as opposed to the persistence length λ_p) in flexible LPLCs: as explained by Meyer [3], 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 : $K_1 = \frac{4}{\pi} \frac{k_B T}{D} \phi \frac{L}{D}$ [28].

The model of semiflexible LCLC aggregates, supplemented by the idea that their *average* length $\bar{L}$ in LCLCs is not fixed [1–3, 9], Eq. (2.1), explains the observed T and ϕ 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 $\bar{L}(\phi, t) \propto \exp(E/2k_B T)$ 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 ϕ . Numerical simulations [7] show that $\lambda_p \propto 5 + 2.14E/k_B T$ for chromonic aggregates. Using this empirical result and Eq. (2.1), we estimate the trends as:

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

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

and

$$\frac{K_3}{K_2} \propto \phi^{2/3} (E/k_B T)^{2/3}.$$

All three ratios increase when T decreases and ϕ increases, as in the experiment, Fig. 2.3c, d. The ratio K_1/K_2 is the most sensitive to ϕ and T , in a good agreement with Fig. 2.3c. The strong increase of K_1/K_2 explains the effect of spontaneous chiral symmetry breaking in osmotically condensed LCLC tactoids [32]. 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. 2.3d, implies that $\bar{L}$ and λ_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, $\frac{K_3}{K_1} \frac{d(K_1/K_3)}{dT}$ and $\frac{K_2}{K_1} \frac{d(K_1/K_2)}{dT}$, we deduce $E \approx 10k_B T$ and $13k_B T$, respectively (for $\kappa = 4k_B T$ [9]).

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 [9] 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 [9] operated with the volume fraction of surfactant molecules ϕ (related to the numerical density of surfactant molecules ν as $\phi = \pi\nu D^3/6m$, 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 λ_p , numerical constant κ close to $4k_B T$ and the growth parameter $\bar{\alpha}$ found to be $\bar{\alpha}^{3/2} = \frac{8\lambda_p}{\sqrt{\pi D}} \phi$. In these notations, the aggregation number is

$$\bar{n} = \frac{\sqrt{\bar{\alpha}v}}{2} D^{3/2} \exp \frac{E + \kappa \phi}{2k_B T} \quad (2.5)$$

One can apply this expression to describe the average length $\bar{L}$ of the LCLC aggregates, by noticing that in the latter case, $\bar{L} = \bar{n}a_z$, 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. [9]. The result is

$$\bar{L} = \frac{2}{\pi^{2/3}} \sqrt{D a_z} \phi^{5/6} \left(\frac{\lambda_p}{D} \right)^{1/3} \exp \frac{E + \kappa \phi}{2k_B T} \quad (2.6)$$

which is rewritten as Eq. (2.1) in the beginning of this chapter.

2.5.2 Measurement of Diamagnetic Anisotropy $\Delta\chi$

We used a superconducting quantum interference device to determine the mass diamagnetic susceptibility of the sample as described in Ref. [33]. The LC sample, flame-sealed in a glass NMR tube (2 cm length, 5 mm 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 800 Pa taken from the liquid He bath.

In the sample space, the glass tube with SSY was heated to 67–83 °C (well above nematic-biphasic transition for $c = 29$ –31.5%) and slowly cooled down to the nematic phase at 25 °C with 5T field applied. At 25 °C, a strong field aligns $\hat{\mathbf{n}} \perp \mathbf{B}$, thus we measured $\chi_{\perp}$ after monitoring the magnetization for over 10 h until its value saturated, indicating an equilibrium state of a homogeneous nematic phase. At high temperatures well above nematic-biphasic transition, the measurements of magnetization yield $\chi_{iso}(t)$ as a function of temperature, for example (67–47) °C for 29%. Following Stefanov and Saupe [17], 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 χ_{av} , we calculated $\Delta\chi = 3(\chi_{av} - \chi_{\perp})$ [17], Fig. 2.5. An independent measurement of $\Delta\chi$ done under 1T field gave only a small difference of 1%, indicating that the

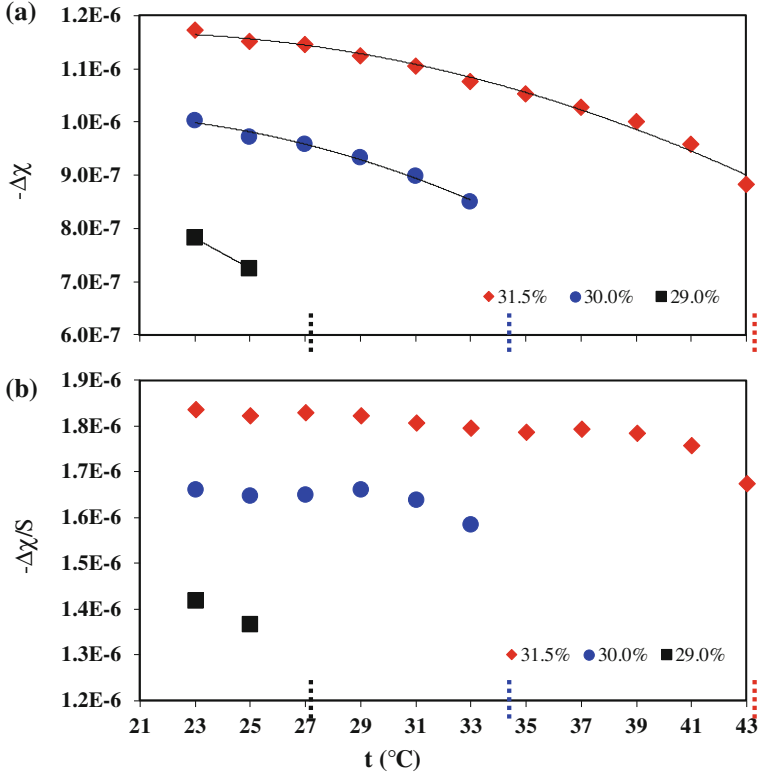


Fig. 2.5 Temperature and concentration dependences of **a** $\Delta\chi$ and **b** $\Delta\chi/S$ of SSY. Note that $\Delta\chi/S$ remains practically constant when temperature is more than 2 – 3 °C below $T_{N \rightarrow N+I}$ for each concentration. In the vicinity of $T_{N \rightarrow N+I}$, $\Delta\chi$ deviates from $\Delta\chi \propto S$ behavior, likely due to pretransitional effects [34]. We estimate the accuracy of $\Delta\chi$ measurements to be $\pm 10\%$

magnetic field induced changes in the degree of orientational order are negligible, in agreement with the Luoma's data on the Cotton-Mouton constant [18].

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 [33]. 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 χ_{iso} to obtain χ_{av} and measuring directly $\chi_{||}$) and found it to be about 10% lower than the value reported previously [33]. We thus estimate the accuracy of our measurements as $\pm 10\%$.

2.5.3 Measurements of Density ρ and Volume Fraction ϕ

In previous studies [14, 16], volume fraction of SSY was calculated by taking the SSY mass density $\rho_{SSY} = 1.4 \times 10^3 \text{ kgm}^{-3}$ from Ref. [14] and assuming both volume and mass are additive quantities, as if water is a continuous medium and ρ_{SSY} is the mass density of individual aggregate. However, the second assumption is 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. 2.6) and with the obtained data determined volume fraction ϕ . As water molecules (typically 0.15 nm) are much smaller than SSY aggregates (~ 1.1 nm diameter, ~ 7 nm length [14, 16]), we approximate water as a continuous medium. Given the weight concentration of SSY c , one can calculate the volume fraction of water ϕ_w :

$$\phi_w = \frac{(1 - c)/\rho_w}{1/\rho_{sol}} = (1 - c) \frac{\rho_{sol}}{\rho_w} \quad (2.7)$$

where ρ_w and ρ_{sol} are the densities of water and solution, respectively. $\phi_{SSY} = 1 - \phi_w$ is shown in Fig. 2.6.

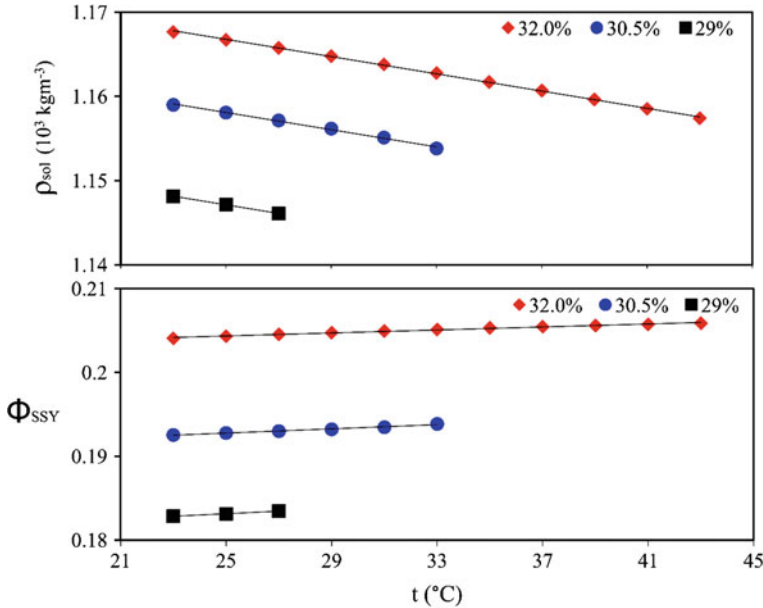


Fig. 2.6 Mass density measurements and calculated volume fraction

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

$$\rho_{SSY} = \frac{c}{\frac{1}{\rho_{sol}} \phi_{SSY}} \quad (2.8)$$

which yields $\rho_{SSY} = (1.82 \pm 0.02) \times 10^3 \text{kgm}^{-3}$, significantly different from the value of $\rho_{SSY} = 1.4 \times 10^3 \text{kgm}^{-3}$ presented in Ref. [18]. If one takes the typical parameters of SSY aggregates, the outer diameter $D = 1.1$ nm, repeating distance $a_z = 0.34$ nm, and molar mass $M_{SSY} = 0.452 \text{kgmol}^{-1}$, one estimates the mass density for individual aggregates as $\rho_{SSY} = \frac{4M_{SSY}/N_A}{\pi D^2 a_z} = 2.32 \times 10^3 \text{kgm}^{-3}$ (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 1.1 to 1.4 nm in literatures [14, 16, 18]), and from the assumption that water is a continuous medium.

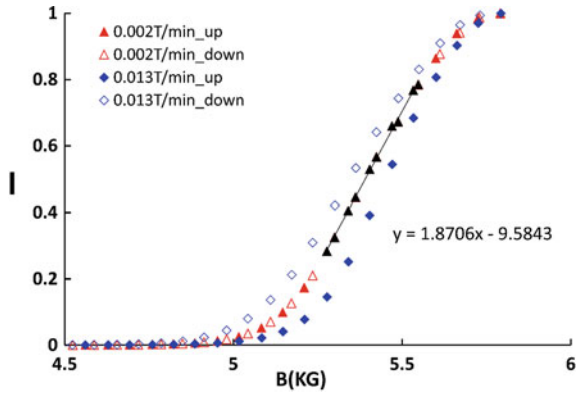
2.5.4 Optical Response in Bend Frederiks Transition

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:

$$I = I_0 \sin^2 \frac{R}{2} \quad (2.9)$$

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 $I(B)$

Fig. 2.7 Intensity versus $\mathfrak{B}$ for bend deformation. *Inset* equation is the fitting from linear part (black triangles) of the curve



curve shows no hysteresis, Fig. 2.7. 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. 2.7. From the linear part of the $I(B)$ curve, we found the critical field intensity B_3 .

2.5.5 Optical Simulation to Determine Splay Constant K_1

When the LC is distorted by the magnetic field $\mathfrak{B}$, the free energy density in the general form writes [24]:

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

In our cases, the deformation is always uniform in the xy plane parallel to the cell, thus we express the director $\hat{\mathbf{n}}$ as a function of the normal $\mathfrak{Z}$ coordinate only: $\hat{\mathbf{n}}(z) = (n_x, n_y, n_z) = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$, 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 Sect. 2.2, Eq. (2.10) becomes:

$$f = \frac{1}{2} (K_1 \sin^2 \theta + K_3 \cos^2 \theta)^2 \left(\frac{d\theta}{dz} \right)^2 + \frac{1}{2} (K_2 \sin^2 \theta + K_3 \cos^2 \theta)^2 \sin^2 \theta \left(\frac{d\varphi}{dz} \right)^2 - \frac{1}{2} \frac{\Delta\chi}{\mu_0} B^2 (\cos \alpha \cos \theta + \sin \alpha \sin \theta \cos \varphi)^2 \quad (2.11)$$

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 mid-plane, for 0.3 T field, director orientation changes from $\theta(d/2) = 90^\circ$ to $\theta(d/2) = 80^\circ$ but $\varphi(z)$ remains 0, as follows from the numerical minimization of the energy Eq. (2.11) for $\varphi(z) = 0$ simplifies to Eq. (2.3).

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,

$$\frac{\partial f}{\partial \theta} - \frac{d}{dz} \left(\frac{\partial f}{\partial \theta'} \right) = 0 \quad (2.12)$$

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. (2.12), one can calculate the effective extraordinary refractive index $n_{eff}(z, B)$ in the cell:

$$n_{eff}(z, B) = \frac{n_e n_o}{\sqrt{n_e^2 \cos^2(\beta - \theta(z, B)) + n_o^2 \sin^2(\beta - \theta(z, B))}} \quad (2.13)$$

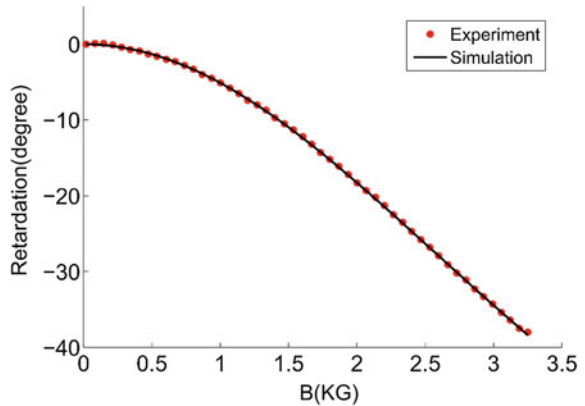
where n_e and n_o are the extraordinary and ordinary refractive indices, respectively; we also take into account that the light propagation direction $\hat{\mathbf{k}}$ within the LC, characterized by the polar angle β measured with respect to $\hat{\mathbf{z}}$, is different from $\mathbf{B}$ direction (polar angle α), 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 $\beta = \sin^{-1}\left(\frac{\sin \alpha}{n_{av}}\right)$.

Integration over the cell thickness gives the total phase retardation of the splayed director field [22]:

$$R(B) = \frac{2\pi}{\lambda \cos \beta} \int_0^d (n_{eff}(z, B) - n_o) dz \quad (2.14)$$

Using this equation to fit the experimental data of $R(B)$ with an independently measured $\frac{K_3}{\Delta\chi}$, we obtain $\frac{K_1}{\Delta\chi}$, as shown in Fig. 2.8.

Fig. 2.8 Experimental measurement and numerical simulation of $R(B)$ which result in $\frac{K_1}{\Delta\chi} = 13.2 \mu\text{N}$ for a cell of 31.5% SSY with $\Delta n = -0.0768$ for $\lambda = 633 \text{ nm}$ 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 [10], including the case of LCLCs [11]. We observed the same phenomenon in SSY. When $\mathbf{B}$ is applied at $\alpha = 90^\circ$ direction, it causes "bamboo" patterns, Fig. 2.9, similar to that presented in Ref. [11]. As pointed in Ref. [11], the periodic patterns does not appear when $\mathbf{B}$ is tilted away from $\hat{\mathbf{n}}_0$ direction. In our experiments, we used a 15° tilt away from $\hat{\mathbf{n}}_0$ to avoid non-uniform twist, $\alpha = 75^\circ$.

When $\mathbf{B}$ 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. 2.10. 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 α 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. $\theta(z) = \frac{\pi}{2} + \delta \sin(\frac{\pi}{d}z)$, where δ 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

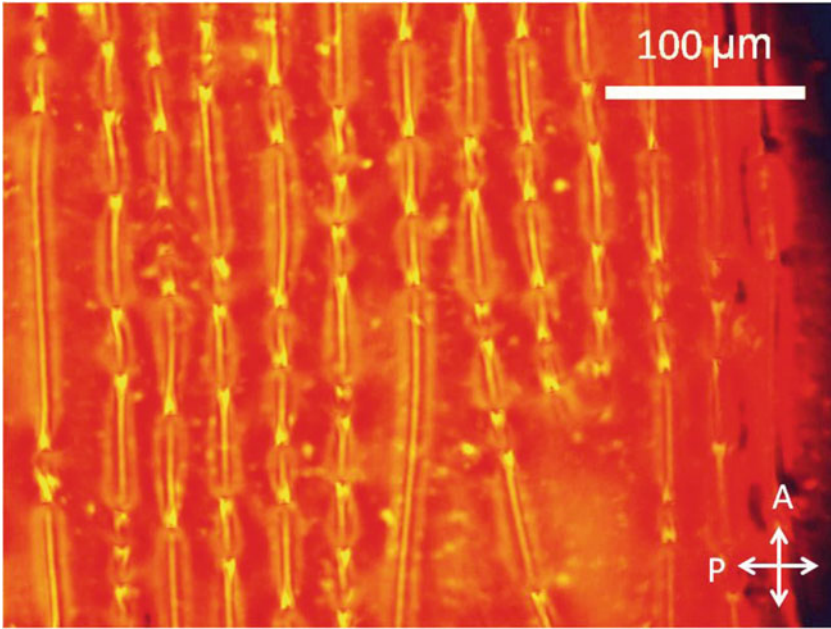


Fig. 2.9 Periodic pattern in a planar SSY cell induced after abruptly applying a magnetic field of 0.4 T at $\alpha = 90^\circ$

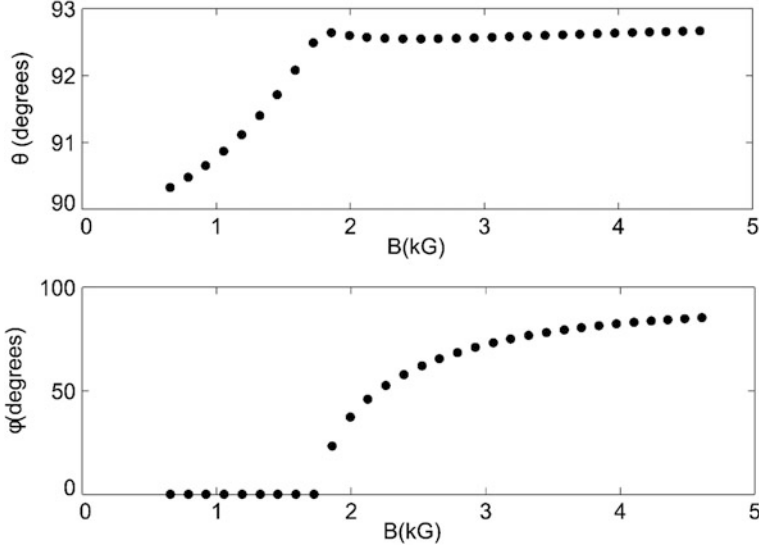


Fig. 2.10 Numerically simulated dependencies $\theta(d/2)$ and $\varphi(d/2)$ versus B representing maximum deformations in the mid-plane of cell, for a cell with $d = 23.8 \mu\text{m}$, $\frac{K_2}{-\Delta\chi} = 1.22 \mu\text{V}$, $\frac{K_1}{-\Delta\chi} = \frac{K_3}{-\Delta\chi} = 9.8 \mu\text{V}$

$\varphi(z) = 0 + \gamma(z) = \varphi_m \sin(\frac{\pi}{d}z)$, ($\varphi(0) = \varphi(d) = 0$ fixed at two boundaries). If the twisted state is preferred as compared to pure splay, then the following integral should be negative:

$$J = \int_0^d \left(\frac{\partial f}{\partial \varphi} \gamma + \frac{\partial f}{\partial \varphi'} \gamma' \right) dz < 0 \quad (2.15)$$

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 δ):

$$J \approx \varphi_m^2 \frac{d}{2} \left[\frac{\Delta\chi}{\mu_0} B^2 \left(\sin^2 \alpha - \frac{8}{3\pi} \delta \sin \alpha \cos \alpha \right) + \left(\frac{\pi}{d} \right)^2 K_2 \right] < 0 \quad (2.16)$$

Thus,

$$B_2 = \frac{\pi}{d \sin \alpha} \sqrt{\frac{\mu_0 K_2}{-\Delta\chi \left(1 - \frac{8}{3\pi} \delta \cot \alpha \right)}} \quad (2.17)$$

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,

$$B_2 = \frac{\pi}{d \sin \alpha} \sqrt{\frac{\mu_0 K_2}{-\Delta\chi}} \quad (2.18)$$

to determine $\frac{K_2}{\Delta\chi}$, as indicated in Sect. 2.3.3.

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