Lyotropic nematic liquid crystals: interplay between a small twist elastic constant and chirality effects under confined geometries

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ABSTRACT
There are two classes of liquid crystals (LCs): Thermotropic LCs where the organic molecule represents the anisotropically shaped mesogen and lyotropic LCs, where the mesogens are nonspherical supramolecular assemblies dispersed in a solvent. Various kinds of lyotropic nematic liquid crystals (LLCs) exist, differing in shape and composition of the aggregates: Chromonic, polymeric or micellar LLCs. However, micellar LLCs are the most ubiquitous kind of LLCs, occurring in soaps and biological systems. Although these nematic lyotropics are so different, they exhibit – contrary to thermotropic nematics – spontaneous reflection symmetry breaking under confinement. We discuss spontaneous mirror symmetry breaking under capillary confinement for a standard micellar N\textsubscript{p} phase and give a detailed director field structure of the twisted polar configuration. Furthermore, we measure for the first time a complete set of viscoelastic properties of a micellar nematic LLC, finding a small twist elastic constant \(K_{22}\), which is at least one order of magnitude smaller than \(K_{11}\) and \(K_{33}\). As demonstrated by the following work, a small \(K_{22}\) and therefore spontaneous mirror symmetry breaking under confinement is rather the rule than the exception in lyotropic nematics and constitutes a unique difference between lyotropic and typical thermotropic nematics, for which the well-known one-constant approximation holds.

Abbreviations: LC: Liquid Crystal; LLC: Lyotropic liquid crystal; TER: twisted escaped radial director configuration; TP: twisted polar director configuration; \(\alpha\): director; \(K_{11}\): splay elastic constant of the nematic phase; \(K_{22}\): twist elastic constant of the nematic phase; \(K_{33}\): bend elastic constant of the nematic phase; \(s\): strength of a defect/dischlination; ER: escaped radial director configuration; CDEAB: \(N, N\)-ethyhexadecylammonium bromide; DOH: decan-1-ol; \(N_2\): nematic phase of disk-shaped building blocks; \(N_2^o\): nematic phase of rod-shaped building blocks; H-field: magnetic field; PR: planar radial director configuration; PP: planar polar director configuration; RR: right handed – right handed; LL: left handed – left handed; RL: right handed – left handed; LR: left handed – right handed.

Introduction
Chirality is a phenomenon in nature that appears across all disciplines of natural science, from biology to mathematics. The spontaneous formation of chiral structures in a system of achiral components is known as spontaneous reflection symmetry breaking and is by itself of fundamental interest. The current status and understanding of reflection symmetry breaking in liquid crystals has been summarised in a number of reviews [1–4]. Recently, the appearance of spontaneous reflection symmetry breaking in achiral chromonic LLCs under confinement was reported [5–10]. The nematic phase of lyotropic chromonic liquid crystals (LLCs) is formed by long range orientationally ordered columnar stacks of flat dye molecules dispersed in water [11,12]. In contrast to thermotropic \(N\textsubscript{C}\) phases, the chromonic \(N_2\) phase has an exceptionally small twist elastic constant [13,14]. Under confinement, the relative values of the elastic moduli (splay, twist and bend) determine the nematic director field structure, and with an extremely small twist elastic constant, nematic LLCs can release external stresses as far as possible into twist deformations [5,9,15,16], leading to reflection symmetry breaking structures under confinement. Before discussing chiral director configurations, here is a short introduction to the well-known achiral director configurations of nematics in cylinders [17–20]. If a nematic LC is confined to a capillary with homeotropic boundary conditions, there is frustration between the uniform director field of an undeformed nematic LC and the radial director field given by the boundary conditions. The simplest solution is the planar radial configuration (PR), shown in Figure 1(a). Here, the director only splays and a disclination line of \(s = + 1\) is formed along the axis of the capillary. Because the energy per unit length (the line tension) is proportional to \(s^2\), the +1 disclination line is unstable upon splitting into two disclination lines of \(s = + \frac{1}{2}\). This leads to the planar polar...
The nematic liquid crystal (LLC) used in this study is a ternary system containing N,N-ethylhexadecylammonium bromide (CDEAB) as the surfactant, decan-1-ol (DOH) as the co-surfactant, and doubly distilled water as the solvent. The composition is 32.0 wt. % CDEAB, 4.8 wt % DOH and 63.2 wt % water, as used in ref [24]. At this concentration, the surfactant and co-surfactant molecules assemble themselves into disk-shaped micelles forming a broad nematic Nd phase around room temperature [25]. The short axes of the disk-shaped micelles are long-range-ordered along the director $\hat{n}$, which coincides with the optical axis of the uniaxial Nd phase, having positive optical anisotropy and negative magnetic anisotropy [26,27], see Figure 2.

In the following a detailed study of this lyotropic micellar Nd phase confined to cylindrical capillaries with homeotropic boundary conditions is given, analysing the occurring structures by polarised optical microscopy and proposing corresponding director fields of the configurations [24]. Furthermore, the addition of intrinsic chirality to this system is studied [28]. Last but not least, depolarised dynamic light scattering was performed to measure the viscoelastic properties of this micellar Nd phase [29]. The content of this paper is based on Ref. [24,28,29].

Chiral configurations under capillary confinement

Twisted escaped radial configuration

Figure 3 shows the time-dependent development of the director field in the absence of a magnetic field [24]. After directly filling the capillaries with the micellar lyotropic Nd phase, a typical Schlieren-like texture was observed. The capillary walls provide homeotropic boundary conditions, i.e., the director $\hat{n}$ aligns normal to the capillary walls without any surface modification needed. After 2–3 days at room temperature, a configuration with TER domains of alternating twist sense was observed. In the TER configuration some twist is added to the pure splay-bend director field of the non-chiral ER configuration. The superimposed twist goes along all directions of the capillary diameter. Under crossed polarisers this is indicated by a brightening of the dark brush along the axis of the capillary. In the Mauguin limit, where the total twist angle is much smaller than the retardation caused by the anisotropy of the refractive indices, the director field serves as a waveguide to the incident polarised light. This results in a brightening of the centre part of the capillary under crossed polarisers in the TER due to a rotation of the plane of polarisation in addition to the retardation of travelling light. In contrast to the TER structure observed by Jeong et al [5], this TER structure under study is defect-free and the alternating senses of twist are separated by twist-free escaped radial (ER) regions. Figure 4 confirms the regions of opposite twist sense by de-crossing the polarisers. Overall, the LLC is inherently non-chiral, so domains of opposite handedness occur with the same probability.

As illustrated in Figure 3, after waiting for some weeks, the TER configuration relaxes into the non-chiral ER configuration. This indicates that the state of lowest energy, at least at room temperature, is not the TER, but simply the ER. There can be several reasons for that, e.g. the diameter
is nearly one millimetre, and the wavelength of deformations along the axis could be some millimetres too, which in itself should give a slow dynamic behaviour [24].

**Twisted polar configuration**

The second chiral configuration which appeared for this micellar $N_{D}$ phase under homeotopic capillary confinement is the so-called twisted polar (TP) configuration [24]. The TP configuration is characterised by two half-unit disclination lines twisting around each other and forming a double helix along the capillary axis. In the SI of ref. [24] videos of the two twist disclination lines moving along the capillary are shown when rotating the capillary around its axis.

If an external magnetic field is applied along the long capillary axis during very slow cooling from the isotropic to the nematic phase, the observed configuration is shown in Figure 5. Figure 5(a) depicts an approximately 23 mm long section of the capillary. Typically the capillaries were 50 mm long. Starting at the left end of the capillary in Figure 5(a), a fine dark line in the middle is observed. This is a field distorted ER configuration, where the director configuration gets squeezed into a more planar configuration. Due to the negative magnetic susceptibility of the $N_{D}$ phase, the director orients perpendicular to the direction of the applied magnetic field. Further along the capillary, there is a transition to a configuration with two disclination lines emerging from a point on the cylinder axis, see Figure 5(b). These disclination lines form a double helix with a period of roughly 5 mm. Additionally, the handedness of the double helix is changing several times. Even though the number of full turns is few, it appears that the pitch is the same for both senses of handedness. Figure 5(c–d) shows enlarged sections of the double helix with opposite twist senses. The handedness of the double helix can be determined by rotating the capillary about its axis and checking whether the crossover points move to the left or to the right. Figure 5(c–h) illustrates that the double helix does not appear dark between crossed polarisers along and perpendicular to the capillary axis. This indicates that it is not a planar structure. A slight decrossing of the polarisers shows that the configuration contains not only the obvious axial twist along the long capillary axis, but also an additional transverse twist running across the two $\pm \frac{1}{2}$ disclination lines parallel to the capillary diameter. There are two different ways how a $\pm \frac{1}{2}$ disclination can be performed by the director field. Either the director stays in plane normal to the disclination line and contains solely splay and bend deformations, this is a so-called wedge disclination (Figure 6(a)) [30,31]. Or the director rotates out of plane; this is then called twist disclination (Figure 6(b)) [30–33]. Due to the fact, that in twist disclinations
a director twist is introduced, the reflection symmetry is broken. According to Ranganath, Anisimov, and Dzyaloshinskii, in usual nematic LCs the non-chiral wedge dislocation is energetically favoured upon the chiral twist disclination, except a very small twist elastic constant comes into play [34,35].
disclinations in a capillary confinement, a director field profile suggested as in Figure 6(d–f) emerges, with an additional transverse twist along the capillary diameter between the two twist disclinations. In the double-helix TP configuration, the twist deformations around the two disclination lines have the same sense of chirality, so each pair of disclinations are right handed-right handed (RR) or left handed-left handed (LL) [28]. Since the system under study is achiral, RR and LL must occur with the same probability. But, if the two disclinations are formed without mutual coupling, combinations right handed-left handed or left handed-right handed can occur as well, meaning that the two lines have opposite chirality. This is what is happening in the region where the twist sense of the double helix is changing. Figure 7 enlarges a region of changing twist sense and sharp kinks in the disclination lines are revealed. By de-crossing the polarisers slightly, local optical activity can be detected, the area at one side of a kink gets blue/orange depending on the sign of de-crossing. If the two disclination lines have opposite chirality, they tend to spiral in opposite directions, therefore no double helix is formed in these regions of changing handedness. In this case, the two lines head towards each other as they move along the capillary. But, when the two
Figure 6. Schematic illustration of the reflection symmetry breaking in the vicinity of the $+\frac{1}{2}$ disclination lines (marked as red dots/lines) in the twisted polar configuration. (a) Top view of the director field (here represented by cylinders) of an achiral $+\frac{1}{2}$ wedge disclination. The director lies in a plane normal to the disclination line and contains only splay and bend deformations. (b) Top view of the director field of a chiral $±\frac{1}{2}$ twist disclination, the director twists out of the paper plane and around the disclination line following the plane in which the molecules lie. The twist disclination is obtained by rotating the director field from the wedge disclination by an angle of 90° about a vertical axis in the plane of the page (axis is indicated as an orange arrow in (b). (c) Oblique side view on a $+\frac{1}{2}$ twist disclination. (d) – (f) two $\frac{1}{2}$ twist disclinations interconnected in the cylindrical confinement of a capillary. The director twist around the twist disclinations has the opposite handedness compared to the transverse and axial twists going along and perpendicular to the diameter of the capillary, respectively. Figure adapted with permission from Langmuir from ref. [24].
lines are getting closer together, the total elastic energy increases. In order to avoid this, the respective chiralities (from RL to LR) are flipped at these kinks, see Figure 8. This is repeated more or less regularly and therefore the lines are approximately kept at a maximum distance. If only one of the disclination lines flips its chirality, e.g. LR → RR or LR → LL.

Figure 7. (a and b) Close up of the kinks of the disclination lines in a non-TP region. De-crossing ± 10° of the polarisers (c and d) reveals opposite sign (orange/blue, blue/orange appearance) of optical activity between kinks. Figure reprinted with permission from Langmuir from ref. [28].

Figure 8. Illustrations of proposed structures in a TP capillary. Top: experimentally observed TP structure with polarising optical microscopy. Smooth double helix domains and regions with closely spaced kinks in the two disclination lines are observable. Middle: cylindrical capillary where the disclination lines are schematically indicated. Two oppositely twisted TP double helix domains, with disclination chiralities RR and LL, respectively, are separated by a mixed region with RL chiralities. RR gives a right-handed, while LL gives a left-handed TP helix. Bottom: Illustration of the corresponding director configurations in the RR, RL, and LL cases. Blue cylinders represent the local director, placed on strings in a circular frame representing the cylinder walls. This way of illustrating 3D director structures is inspired by the work of Y. Bouligand [37]. Figure reprinted with permission from Langmuir from ref. [28].
\[ \rightarrow \text{LL}, \text{the structure is changed into the pure TP configuration with smooth disclination lines and a well-defined period of the double helix. Because it seems like the smooth double helix TP structure is predominate, one could draw the conclusion, that the RR and LL configurations are lower in energy than the mixed RL and LR configurations. However, it is interesting, that RR, LL, RL and LR structures coexist. The reason for forming either RR/LL or RL/LR regions in an applied magnetic field could be related to the degree of the mutual elastic interaction between the twist disclinations during their formation. In the squeezed ER under an axial magnetic field, the splay-bend region is, in contrast to the ER without magnetic field action, confined to a narrow region approximately at the centre of the capillary. Due to a small twist elastic constant, the energetically costly splay and bend deformations are partly replaced by twist deformation. This would result into reflection symmetry breaking with a certain TER handedness. If the further branching into two \( \frac{1}{2} \) disclinations occurs from this field-induced chiral TER state [36], one might think that the chirality around both disclination lines would have the same sign (RR or LL). However, if the branching occurs starting from a field-induced planar radial plane (which is achiral), the (chiral) interaction between the two lines forming should be smaller than in the “squeezed” state. Therefore, the chirality adopted by each of the two singularities is more mutually independent, so LR and RL configurations might be allowed. The field-induced PR state should have (achiral) wedge disclinations, which should transform by removing the magnetic field, into (chiral) twist disclinations. To understand what really happens, it would be necessary to observe the capillaries with a microscope while the magnetic field is applied. Furthermore, such investigations might also provide new information about the fundamental question of the nature of the \( s = +1 \) defect core [28]. The TP configuration also occurs in the LLC Sunset Yellow under capillary confinement, although in this system the TER configuration seems to be the predominant configuration, and of lowest energy, since the TP configuration only forms spontaneously at arbitrary positions like a watersprinkler [5]. The difference of the TP formation between the micellar \( N_D \) phase under study and the chromonic \( N_C \) phase of Sunset Yellow probably originates in the different relative values of the other elastic constants in those two systems. However, the TP formation process in both these systems still needs to be further investigated.

Adding intrinsic chirality

Adding intrinsic chirality via (R)-mandelic acid as chiral dopant to the micellar \( N_D \) phase leads to various new structures with which the interplay between confinement, twist elasticity and intrinsic chirality can be studied [28]. In the TP case, the topological constraints of the twist disclinations facilitate stable heterochiral systems even in the presence of a small amount of chiral dopant, with unusual regions of rapidly reversing handedness between homochiral domains. At moderate dopant concentrations, the TP structure becomes homochiral. At high dopant concentrations, for which the induced cholesteric pitch is much smaller than the diameter of the capillary, the cholesteric fingerprint texture develops in a chevron-like way. In the TER case, no heterochiral domains while adding chiral dopant are observed. Instead, a homochiral TER immediately develops and by increasing the dopant concentration, a doubly twisted escaped radial (DTER) configuration is formed, in which the escape direction spirals along the capillary axis. Since the structure is now twisted along the diameter and along the cylinder axis, we refer to this configuration as the doubly twisted escaped radial (DTER) configuration. Although there has been a certain concentration of chiral dopant at which the TP structure turns from heterochiral to homochiral, there can be no sharp threshold for chiral induction identified, because the TP configuration is topologically constrained. In this sense, the escaped radial configuration is much more sensitive than the TP configuration to chiral doping, because neither topological constraints nor an energy barrier in going from the achiral ER to the chiral TER structure exists for the micellar \( N_D \) phase [28].

Extremely small twist elastic constants in lyotropic nematic LCs

In thermotropic nematics, the well-known one constant approximation is widely applied in experimental and theoretical advances, assuming that all three bulk elastic constants of the nematic phase (splay \( K_{11} \), twist \( K_{22} \), and bend \( K_{33} \)) are within the same order of magnitude [38]. The confinement-induced reflection symmetry breaking of the lyotropic \( N_D \) phase [24] discussed in the previous section, suggests that a one constant approximation does not hold true for this lyotropic micellar system. Some years ago, a similar scenario was reported for a lyotropic chromonic nematic LC exhibiting reflection symmetry breaking under cylindrical as well as under droplet confinement [5,9,39]. And, in this particular case the twist elastic constant \( K_{22} \) has been measured to be one order of magnitude smaller than \( K_{11} \) and \( K_{33} \) [13,14]. A LLC consists of rod-like stacks of dye molecules being orientationally ordered and suspended in typically water [11]. LLCs are rather a special class of lyotropic LCs, whereas the most ubiquitous class of LLCs is formed by surfactants that in water assemble into rod- or disk-like micelles. Actually, micellar LLCs have been
known for a long time since they are used in soaps and detergents, and they are abundant in biological structures (e.g. phospholipid membranes) [40,41]. Searching the literature very little is known about the viscoelastic properties of lyotrophic nematic phases of disk- (N\textsubscript{D}) or rod-like (N\textsubscript{C}) micelles, giving either just relative values or the splay (K\textsubscript{11}) or bend (K\textsubscript{33}) elastic constant [42–44]. However, it has been neither a single complete set of elastic constants nor a single K\textsubscript{22} value reported for micellar lyotropic nematics.

In 1985 the lyotropic polymeric nematic phase of poly-\(\gamma\)-benzyl-glutamate (PBG) was investigated via depolarised dynamic light scattering [45]. In addition with an independent measurement of K\textsubscript{33} via the magnetic Freedericksz transition using the diamagnetic anisotropy of PBG [46], absolute values for the three bulk elastic constants (splay K\textsubscript{11}, twist K\textsubscript{22} and bend K\textsubscript{33}) and the corresponding viscosities (\(\eta\text{_{splay}}, \eta\text{_{twist}}\) and \(\eta\text{_{bend}}\)) were reported [45,47]. It was found, that K\textsubscript{22} of the N\textsubscript{C} phase of polymeric lyotropic PBG is one order of magnitude smaller than K\textsubscript{11} and K\textsubscript{33}. Zhou et al. measured the viscoelastic properties of the chromonic nematic LC disodium cromoglycate (DSCG) by depolarised dynamic light scattering [14]. They enhanced the method by introducing a calibration step using the standard thermotropic nematic SCB, for which all viscoelastic properties are well known. By this calibration step, absolute measurements of the elastic constants and the corresponding viscosities of the lyotropic chromonic N\textsubscript{C} phase of DSCG were possible. We used the same light-scattering technique of Zhou et al [14], to measure a complete set of elastic constants and viscosities for the micellar lyotropic N\textsubscript{D} phase under study. Very different elastic moduli were found: The twist elastic constant K\textsubscript{22} = (0.300 ± 0.018) pN is one order of magnitude smaller than

### Table 1. Overview of the measured elastic constants and the corresponding viscosities of the N\textsubscript{D} phase of the micellar LLC CDEAB/DOH/H\textsubscript{2}O (indicated in red) compared to what is known from the literature for splay (K\textsubscript{11}), twist (K\textsubscript{22}) and bend (K\textsubscript{33}) elastic constants and viscosities (\(\eta\text{_{splay}}, \eta\text{_{twist}}\) and \(\eta\text{_{bend}}\)) for thermotropic (grey) and other lyotropic (blue) nematic phases. Values listed for the thermotropic N\textsubscript{D} phase refer to hexakis(p-hexyloxybenzoyloxy)triphenylene [51]. The volume fraction of the lyotropic polymeric racemic PBG system is 0.2 and the polymer chains have a length to diameter ratio of 36 (see Ref [45,47]). The concentration of the lyotropic chromonic DSCG is c = 16 wt\% [14], whereas c = 29 wt\% for SSY [13]. The N\textsubscript{D} phase of the lyotropic micellar CsPFO/H\textsubscript{2}O contains 49 wt\% CsPFO and 51 wt\% water [42]. The two investigated mixtures of the N\textsubscript{D} phase of the lyotropic micellar decahydronaphthalene chloride (DACl)/H\textsubscript{2}O/NH\textsubscript{4}Cl are either 7 mol\% DACl, 2.5 mol\% NH\textsubscript{4}Cl, and 90.5 mol\% H\textsubscript{2}O or 7.57 mol\% DACl, 2.73 mol\% NH\textsubscript{4}Cl, and 89.70 mol\% H\textsubscript{2}O [44]. The table is reprinted with permission from Ref. [29].

| Building block shape | Rod-shaped (N\textsubscript{C} phases) | Disk-shaped (N\textsubscript{D} phases) |
|----------------------|--------------------------------------|--------------------------------------|
|                      | Thermotropic | Lyotropic | Thermotropic | Lyotropic |
| Building block       | Single molecules | Polymer | Single molecules | Molecules |
| Liquid crystal       | 5CB | PBG | DSCG | SSY | Triphenylene | CsPFO | DACI | CDEAB |
| Concentr.            | - | 0.2 vol. fraction | 16 wt\% | 29 wt\% | - | 49 wt\% CsPFO | 7 mol\% DACI | 7.6 mol\% DACI | 32 wt\% | CDEAB |
| Temp.                | 298 K | 298 K | 298 K | 298 K | 527 K | 309 K | 313 K | 320 K | 298 K |
| K\textsubscript{11} (pN) | 6 | 10 | 12 ±1 | 4.3 ±0.4 | 7 | 1.5 | - | - | 1.54 ±0.08 |
| K\textsubscript{22} (pN) | 3 | 0.6 | 0.7 ±0.1 | 0.70 ±0.07 | - | - | - | - | 0.300 ±0.018 |
| K\textsubscript{33} (pN) | 8 | 10 | 27 ±5 | 6.1 ±0.6 | 2 | 8 | - | - | 20.8 ±1.3 |
| K\textsubscript{11}/K\textsubscript{22} | 2 | 16.7 | 17.1 | 6.1 | - | - | - | - | 5.1±0.1 |
| K\textsubscript{33}/K\textsubscript{22} | 2.7 | 16.7 | 38.6 | 8.7 | - | - | - | - | 69±2 |
| K\textsubscript{11}/K\textsubscript{11} | 1.3 | 1 | 2.3 | 1.4 | 0.3 | 5.3 | 5.3 | 18.9 | 13±0.4 |
| \(\eta\text{_{splay}}\) (kgm\textsuperscript{-3}s\textsuperscript{-1}) | 0.078 | 5 | 18±1 | - | - | - | - | - | 1.65 ±0.09 |
| \(\eta\text{_{twist}}\) (kgm\textsuperscript{-3}s\textsuperscript{-1}) | 0.08 | 5 | 14±1 | - | - | - | - | - | 5.28 ±0.32 |
| \(\eta\text{_{bend}}\) (kgm\textsuperscript{-3}s\textsuperscript{-1}) | 0.028 | 0.03 | 0.01 ±0.002 | - | - | - | - | - | 87±6 |
$K_{11} = (1.54 \pm 0.08)$ pN and almost two orders of magnitude smaller than the bend elastic constant $K_{33} = (20.8 \pm 1.3)$ pN [29]. With that, the corresponding viscosities of the splay, twist and bend deformations $\eta_{\text{splay}}$, $\eta_{\text{twist}}$ and $\eta_{\text{bend}}$ are calculated. A value of $(1.65 \pm 0.09)$ kg m$^{-1}$ s$^{-1}$ is found for $\eta_{\text{splay}}$ ($5.28 \pm 0.32$) kg m$^{-1}$ s$^{-1}$ for $\eta_{\text{twist}}$ and $(87 \pm 6)$ kg m$^{-1}$ s$^{-1}$ for $\eta_{\text{bend}}$ [29]. Note that the measurements were performed at room temperature.

Table 1 summarises the elastic moduli and viscosities of different thermotropic and lyotropic nematics from the literature along with the data for the micellar lyotropic N$_D$ phase of CDEAB/DOH/H$_2$O (indicated in red). Even for thermotropic N$_D$ phases only few literature data are available on the viscoelastic properties. In a discotic thermotropic LC with the normal phase sequence (crystalline-columnar-N$_D$-isotropic) it is proposed that $K_{33} < K_{11} \leq K_{22}$, which is the opposite of thermotropic NC phases where $K_{22} < K_{11} < K_{33}$ [48–53]. However, in lyotropic N$_D$ phases the above mentioned trend is not observed. Actually, $K_{33}$ is of highest value when the nearby more ordered phase is a lamellar phase which allows only splay deformation. $K_{33}$ and $K_{22}$ tend to diverge while approaching the phase transition to the lamellar phase [42]. This results in a high $K_{33}/K_{11}$ ratio which was found for several N$_D$ phases of LLCs [42–44]. The relatively high $K_{33}$ of the CDEAB/DOH/H$_2$O N$_D$ phase can be explained with the same argument, since a lamellar phase is nearby. In LCLCs, the nearby more ordered phase is a columnar phase that excludes splay and twist deformations, which might explain that the $K_{33}/K_{11}$ ratios for these systems are much smaller. Theoretically, twist deformations should also be inhibited by a nearby lamellar or columnar phase. But instead, in all lyotropic nematic phases, independent of whether the building blocks are rod or disk shaped, $K_{22}$ is around one order of magnitude smaller than the other two elastic moduli. With this, it is not only shown that a small $K_{22}$ is independent of the shape of the building block, but also that the composition of the building block, and therefore the intermolecular forces being responsible for the aggregation behaviour seem to have little effect on this phenomenon. For all LLCs for which a one order of magnitude smaller $K_{22}$ was measured (compared to $K_{11}$ and $K_{33}$), either chromonic, polymeric or micellar [13,14,29,45,47], reflection symmetry-breaking director configurations under confinement are reported [5,24,54]. In other words, confinement induced chiral structures, like the TER or the TP configuration under capillary confinement, point to a small $K_{22}$. This demonstrates that an order of magnitude smaller $K_{22}$ value in lyotropic nematic phases is rather the rule than the exception, constituting a unique difference between lyotropic and thermotropic nematics. In comparison to the single-molecule building blocks of thermotropic nematics, the building blocks of lyotropic nematics are larger supramolecular assemblies, the nanoscale dimensions of which allow long wavelength fluctuations and lend these assemblies certain flexibility. In the Onsager case of hard-rod nematics, a distinct difference of elastic constants depending on the aspect ratio of the building blocks and the steric repulsion between them is predicted by theory [55]. However, flexible assemblies can accommodate a specific elastic deformation of the phase up to a certain extent so that the steric repulsion between the assemblies is lowered while reducing the elastic energy of that deformation [56]. That means that the actual values of the elastic constants depend on how flexibly the building blocks distort accommodating a specific elastic deformation of the nematic phase.

Taking the flexibility of the aggregates into account, this leads to the following considerations for the micellar N$_D$ phase under study. It is well known that micelles dispersed in water repel each other on the nanometre length scale via effective solvent-mediated interactions, namely hydration interactions [57–59]. Those interactions decay exponentially with the intermicellar distance. Apart from their rim, disk-shaped micelles are essentially a flat, finite and fluid amphiphile bilayer with a surface area of few square nanometres. Let us assume that disk-shaped micelles distort like a single amphiphilic bilayer would do. First, any change in bilayer thickness is energetically very costly and is therefore prohibited [60]. Second, bending the bilayer by increasing the curvature of the bilayer requires less energy. Third, a (small) twist of the bilayer directed parallel to its surface should be the least energy-costly deformation since neither the thickness nor the mean curvature of the bilayer is changed. Figure 9 illustrates how the disk-shaped micelles of an N$_D$ phase could accommodate the fundamental elastic deformations of a nematic phase. The elastic energy for a bend deformation can be reduced only very little, since accommodating this deformation would require an energetically expensive change in bilayer thickness. On the other hand, the elastic energy for twist deformation can be reduced most significantly, since it is the least energy-costly distortion of the micelles. Reducing the elastic energy of splay deformation by accommodating the distortion is for the micelles energetically in between those two cases. With these arguments, the extremely large $K_{33}$ and the anomalously small $K_{22}$ of a micellar lyotropic N$_D$ phase can be understood at least qualitatively [29].
Figure 9. (a)–(c) Elastic deformations of a micellar lyotropic N\(_c\) phase and (d)–(f) the corresponding distortions of the disk-shaped micelles. All three kinds of deformations are associated with close approaches between micelles, the repulsive interactions between which increase the elastic energy. As a result, flexible micelles may distort their disk-like shape to accommodate the specific deformation and lower the elastic energy. To accommodate the splay deformation in (a), the micelles distort into a bent shape, as indicated by the red arrows at the centre of the micelle. The schematic cross-section of a bent micelle (d) illustrates the corresponding change in the bilayer structure, the non-zero curvature of which requires energy to vary the distances between the surfactant headgroups from their equilibrium distance in the undistorted state. To accommodate the bend deformation in (b), the micelles splay into a wedge-like shape. The schematic cross-section of a splayed micelle (e) shows that the splay of the micelle is associated with variations in the bilayer thickness, an energetically expensive distortion which, like for thermotropic smectics, requires a good deal of energy to change the density of amphiphile tails inside the bilayer. To accommodate the twist deformation in (c), the micelle twists along its long axis parallel to the local twist axis of the N\(_c\) phase. In (f) the bilayer structure of a twisted micelle is approximated by a twisted stack of thin bilayer slices. Since in each slice neither the thickness nor the curvature of the bilayer is changed, this is a soft deformation which requires less energy than the distortions in (d) and (e). Twist deformations are thus the least energy costly fluctuations in a lyotropic N\(_c\) phase while bend deformations are the most energy costly fluctuations. Figure reprinted with permission from PNAS from ref. [29]

Although a nematic LC appears to flow as easily as a liquid, understanding the viscosities is rather complicated due to the anisometric shape of the building blocks and the alignment of the mesogens in the LC, given by the director \( \mathbf{n} \). The flow depends on the angles between the director and the velocity gradient, as well as between director and flow direction. Additionally, the shear-flow causes a rotation of the director since translational and orientation motions are coupled. Finding a qualitative explanation for the viscous behaviour involving the viscosities \( \eta_{\text{splay}} \), \( \eta_{\text{twist}} \), and \( \eta_{\text{bend}} \) is a bit more difficult than the rather straightforward qualitative explanation for the elastic behaviour given above. It is important to point out that the elastic constants and their corresponding viscosities describe different phenomena. On the one hand the elastic constants give the energy necessary to distort the nematic director and on the other hand the viscosity represents the resistance there is in the system when the distortion is taking place. First, the viscosities \( \eta_{\text{splay}} \), \( \eta_{\text{twist}} \), and \( \eta_{\text{bend}} \) for thermotropic SCB are of the same order of magnitude, whereas the viscosities of all lyotropic nematics investigated so far (chromonic, polymeric and micellar) have very different viscosities that span a range of two or three orders of magnitude. The viscosity \( \eta_{\text{splay}} \) is the largest in the N\(_c\) phase of chromonic DSCG, whereas in the micellar N\(_D\) phase \( \eta_{\text{bend}} \) is the largest. The reverse behaviour of N\(_c\) and N\(_D\) phases regarding \( \eta_{\text{splay}} \) vs. \( \eta_{\text{bend}} \) can be explained according to the Ericksen-Leslie model with the backflow mechanism [61–69]. It seems that backflow lowers \( \eta_{\text{splay}} \) but not \( \eta_{\text{bend}} \) in lyotropic N\(_D\) phases. Second, the relatively high \( \eta_{\text{bend}} \) indicates that bend deformations of the N\(_D\) phase are highly dissipative. The reason behind this may be that the bend deformation cannot relax via an internal elastic mode of the micelle and instead requires the rotational diffusion of the entire entity [29]. Furthermore, the ratios of elastic constants in lyotropic nematics are significantly larger than in thermotropic nematics. However, since elastic constants and their corresponding viscosities describe different phenomena, it is difficult to draw conclusions from the elastic behaviour. Overall, a detailed analysis on
the viscous behaviour of lyotropic nematics is still to
be accomplished, as well as a comprehensive study of
the physics behind a small twist elastic constant inter-
connecting the elastic behaviour of all different kinds
of lyotropic nematics (micellar, chromonic, polymeric)
still has to be elaborated.

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References

[1] Pérez-García L, Amabilino DB. Spontaneous resolution,
whence and whither: from enantiomorphic solids to
chiral liquid crystals, monolayers and macro- and
supra-molecular polymers and assemblies. Chem Soc
Rev. 2007;36:941–967.
[2] Takezoe H. Spontaneous achiral symmetry breaking in
liquid crystalline phases. In: Tschierske C, editor. Liquid
crystals. Vol. 318; Topics in Current Chemistry. Berlin:
Springer; 2011. p. 303–330.
[3] Tschierske C, Ungar G. Mirror symmetry breaking by
chirality synchronisation in liquids and liquid crystals
of achiral molecules. ChemPhysChem. 2016;17:9–26.
[4] Walba DM. Ferroelectric liquid crystal conglomerates.
In: Green MM, Olte RJM, Meijer EW, editors. Materials-
chirality. Vol. 24. Hoboken, NJ: John Wiley & Sons, Inc;
2003. p. 457–518.
[5] Jeong J, Kang L, Davidson ZS, et al. Chiral structures
from achiral liquid crystals in cylindrical capillaries. Proc Natl
Acad Sci U S A. 2015;112:E1837–44.
[6] Davidson ZS, Kang L, Jeong J, et al. Chiral structures and
defects of lyotropic chromonic liquid crystals induced by
saddle-splay elasticity. Phys Rev E. 2015;91:50501.
[7] Nayani K, Chang R, Fu J, et al. Spontaneous emergence of
chirality in achiral lyotropic chromonic liquid crystals
confined to cylinders. Nat Commun. 2015;6:8067.
[8] Nayani K, Fu J, Chang R, et al. Using chiral tactoids as optical
probes to study the aggregation behavior of chromonics.
Proc Natl Acad Sci U S A. 2017;114:3826–3831.
[9] Tortora L, Lavrentovich OD. Chiral symmetry breaking by
spatial confinement in tactoidal droplets of lyotropic
chromonic liquid crystals. Proc Natl Acad Sci U S A.
2011;108:5163–5168.
[10] Nych A, Ognysta U, Mušević I, et al. Chiral bipolar collo-
oids from nonchiral chromonic liquid crystals. Phys Rev
E. 2014;89:62502.
[11] Lydon J. Chromonic liquid crystalline phases. Liq Crist.
2011;38(11–12):1663–1681.
[12] Collings PJ, Goldstein JN, Hamilton EJ, et al. The nature of
lyotropic chromonic liquid crystals probed by director
reorientation in a magnetic field. Phys Rev Lett.
2012;109:37801.
[13] Zhou S, Nastishin YA, Omelchenko MM, et al. Elasticity of
lyotropic chromonic liquid crystals probed by director
reorientation in a magnetic field. Phys Rev Lett.
2011;106:6571–6581.
[14] Williams RD. Two transitions in tangentially anchored
nematic droplets. J Phys A: Math Gen. 1986;19:3211–3222.
[15] Lavrentovich OD, Sergan VV. Parity-breaking phase transi-
tion in tangentially anchored nematic drops. Nuovo
Cimento Soc Ital Fis. D. 1990;12:1219–1222.
[16] Saupe A. Disclinations and properties of the directorfield
in nematic and cholesteric liquid crystals. Mol Cryst Liq
Cryst. 1973;21:211–238.
[17] Kralj S, Zumer S. Saddle-splay elasticity of nematic struc-
tures confined to a cylindrical capillary. Phys Rev E.
1995;51:366–379.
[18] Meyer RB. On the existence of even indexed disclinations
in nematic liquid crystals. Philos Mag. 1973;27:405–424.
[19] Williams C, Bouligand Y. Fils et disinclinaisons dans un
nématique en tube capillaire. J Phys. 1974;35:589–593.
[20] Shams A, Yao X, Park JO, et al. Theoretical predictions of
disclination loop growth for nematic liquid crystals
under capillary confinement. Phys Rev E. 2014;90:42501.
[21] Williams C, Pierański P, Cladis PE. Nonsingular S=1
screw disclination lines in nematics. Phys Rev Lett.
1972;29:90–92.
[22] Cladis PE, Kléman M. Non-singular disclinations of
strength S = + 1 in nematics. J Phys. 1972;23:591–598.
[23] Dietrich CF, Rudquist P, Lorenz K, et al. Chiral structures
from achiral micellar lyotropic liquid crystals under capi-
lary confinement. Langmuir. 2017;33:5852–5862.
[24] Görgens C. Strukturelle Charakterisierung lyotroper Mesophasen,
insbesondere lytop-nematischer und lytop-cholesterischer
Phasen, mittels Röntgenkleinwinkel-rtersuchungen in binären,
temären und quaternären Systemen. Dissertation,Technical
University of Dresden, Dresden, Germany; 1996.
[25] Amaral LQ. Magnetic orientation of nematic lyomesophases.
Mol Cryst Liq Cryst. 1983;100:85–91.
[26] Boden N, Radley K, Holmes MC. On the relationship
between the micellar structure and the diamagnetic
anisotropy of amphiphilic nematic mesophases. Mol
Phys. 1981;42:493–496.
[27] Dietrich CF, Rudquist P, Collings PJ, et al. Interplay
between confinement, twist elasticity, and intrinsic
chirality in micellar lyotropic nematic liquid crystals.
Langmuir. 2021;37:2749–2758.
[28] Dietrich CF, Collings PJ, Sottmann T, et al. Extremely small
twist elastic constants in lyotropic nematic liquid crystals.
Proc Natl Acad Sci U S A. 2020;117:27238–27244.
[30] Ranganath GS. Twist disclinations in elastically anisotropic nematic liquid crystals. Mol Cryst Liq Cryst. 1982;87:187–195.
[31] Ranganath GS. Defects in liquid crystals. Curr Sci. 1990;59:1106.
[32] Frank FC. On the theory of liquid crystals. Discuss Faraday Soc. 1958;25:19.
[33] Lavrentovich OD. Nematic liquid crystals: defects. In: Buschow KHJ, Cahn RW, Flemings MC, eds., editors. Encyclopedia of materials science and technology. 2nd ed. New York: Elsevier Science Ltd; 2001. p. 6071–6076.
[34] Anisimov SI, Dzyaloshinskii IE. A new type of disclination in liquid crystals and the stability of disclinations of various types. Soviet Phys JETP. 1973;36:774–779.
[35] Ranganath GS. Energetics of disclinations in liquid crystals. Mol Cryst Liq Cryst. 1983;9:77–94.
[36] Shams A, Yao X, Park JO, et al. Theory and modeling of nematic disclination branching under capillary confinement. Soft Matter. 2012;8:11135–11143.
[37] Bouligand Y. Geometry and topology of defects in liquid crystals. In: Balian R, Kleman M, Poirier J-P, editors. Physics of defects. New York: North-Holland Publishing Company; 1981. p. 695.
[38] de Gennes P-G. The physics of Liquid Crystals. Oxford: Clarendon Press; 1974.
[39] Jeong J, Davidson ZS, Collings PJ, et al. Chiral symmetry breaking and surface faceting in chroomic liquid crystal droplets with giant elastic anisotropy. Proc Natl Acad Sci U S A. 2014;111:1742–1747.
[40] Stegemeyer H, editor. Lyotrope Flüssigkristalle: grundlagen, Entwicklung, Anwendung. Heidelberg: Springer-Verlag; 1999.
[41] Laughlin RG. The aqueous phase behaviour of surfactants. London, San Diego: Academic Press; 1994.
[42] Bajc J, Hillig G, Sause A. Determination of elastic constants and rotational viscosity of micellar liquid crystals by conductivity measurements. J Chem Phys. 1997;106:7372–7377.
[43] Pinto AVA, Amaral LQ. Bend and splay elastic constants in two nematic lyomesophases with sodium decyl sulfate and potassium laurate. J Phys Chem. 1990;94:3186–3188.
[44] Haven T, Armitage D, Sause A. Bend and splay elastic constants and the rotational viscosity of nematic decylammonium chloride and ammonium chloride water mixtures. J Phys Chem. 1981;75:352–355.
[45] Taratuta VG, Hurd AJ, Meyer RB. Light-scattering study of a polymer nematic liquid crystal. Phys Rev Lett. 1985;55:246–249.
[46] Murthy NS, Knox JR, Samulski ET. Order parameter measurements in polypeptide liquid crystals. J Phys Chem. 1976;65:4835–4839.
[47] Lee S-D, Meyer RB. Light scattering measurements of anisotropic viscoelastic coefficients of a main-chain polymer nematic liquid crystal. Liq Cryst. 1990;7:15–29.
[48] Sidky H, Whitmer JK. Elastic properties of common Gay–Berne nematogens from density of states simulations. Liq Cryst. 2016;43:2285–2299.
[49] Ospov MA, Hess S. The elastic constants of nematic and nematic discotic liquid crystals with perfect local orientational order. Mol Phys. 1993;78:1191–1201.
[50] Cui M, Kelly JR. Temperature dependence of visco-elastic properties of SCB. Mol Cryst Liq Cryst. 1999;331:49–57.
[51] Warmerdam TW, Zijlstra RJJ, Frenkel D. Measurements of the ratio of the Frank constants for splay and bend in nematics consisting of disc-like molecules 2,3,6,7,10,11-hexakis(p-alkoxybenzoyloxy)triphenylenes. Liq Cryst. 1988;3:369–380.
[52] Bisoyi HK, Kumar S. Discotic nematic liquid crystals: science and technology. Chem Soc Rev. 2010;39:264–285.
[53] Warmerdam T, Frenkel D, Zijlstra R. Measurements of the ratio of the Frank constants for splay and bend in nematics of disc-like molecules. J Phys. 1987;48:319–324.
[54] Chang R. Chiral configurations from achiral lyotropic chromonic liquid crystals under confinement. PhD dissertation, Georgia Institute of Technology, Atlanta, 2018.
[55] Odijk T. Elastic constants of nematic solutions of rod-like and semi-flexible polymers. Liq Cryst. 1986;1:553–559.
[56] Meyer RB. Macroscopic phenomena in nematic polymers. In: Ciferri A, Krigbaum W, Meyer RB, editors. Polymer liquid crystals. New York: Elsevier Science; 1982. p. 133–163.
[57] Cheng J-X, Pautot S, Weitz DA, et al. Ordering of water molecules between phospholipid bilayers visualized by coherent anti-Stokes Raman scattering microscopy. Proc Natl Acad Sci U S A. 2003;100:9826–9830.
[58] Leikin S, Parsegian VA, Rau DC, et al. Hydration forces. Ann Rev Phys Chem. 1993;44:369–395.
[59] LeNeveu DM, Rand RP, Parsegian VA. Measurement of forces between lecithin bilayers. Nature. 1976;259:601–603.
[60] Helfrich W. Elastic properties of lipid bilayers: theory and possible experiments. Z Naturforsch C. 1973;28:693–703.
[61] Risi CLS, Figueiredo Neto AM, Akpinar E, et al. Dynamic light scattering and viscosity measurements in a ternary and quaternary discotic lyotropic nematic liquid crystal: tuning the backflow with salt. Phys Rev E. 2013;88:22506.
[62] Santos MBL, Oliveira EA, Neto AMF. Rayleigh scattering of a new lyotropic nematic liquid crystal system: cross-over of propagative and diffusive behaviour. Liq Cryst. 2000;27:1485–1495.
[63] Lacerda Santos MB, Galerne Y, Durand G. Orientational diffusivities in a disk-like lyotropic nematic phase a strong backflow effect. J Phys. 1985;46:933–937.
[64] Lacerda Santos MB, Amato MA. Orientational diffusivities measured by Rayleigh scattering in a lyotropic calamitic nematic () liquid crystal phase: the backflow problem revisited. Eur Phys J B. 1999;7:393–400.
[65] Stewart LW. The static and dynamic continuum theory of liquid crystals: a mathematical introduction. London, New York: CRC Press; 2005.
[66] Ericksen JL. Anisotropic fluids. Arch Ration Mech Anal. 1959;4:231–237.
[67] Miesowicz M. The three coefficients of viscosity of anisotropic liquids. Nature. 1946;158:27.
[68] Leslie FM. Some constitutive equations for liquid crystals. Arch Ration Mech Anal. 1968;28:265–283.
[69] Leslie FM. Continuum theory for nematic liquid crystals. Contin Mech Thermodyn. 1992;4:167–175.