Violation of Ericksen Inequalities in Lyotropic Chromonic Liquid Crystals

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Abstract
By analyzing elastic theory for nematic liquid crystals, we distinguish three regimes of elastic constants. In one regime, the Ericksen inequalities are satisfied, and the ground state of the director field is uniform. In a second regime, certain necessary inequalities are violated, and the free energy is thermodynamically unstable. Between those possibilities, there is an intermediate regime, where the Ericksen inequalities are violated but the system is still stable. Remarkably, lyotropic chromonic liquid crystals are in the intermediate regime. We investigate the nonuniform structure of the director field in that regime, show that it depends sensitively on system geometry, and discuss the implications for lyotropic chromonic liquid crystals.

Keywords Liquid crystal · Nematic · Lyotropic · Chromonic · Twist · Saddle splay

Mathematics Subject Classification 76A15 · 82D30

1 Introduction
In a nematic liquid crystal, the molecules have orientational order along an axis, which is called the nematic director and is represented by the unit vector \( \hat{n} \). The molecules are equally likely to orient up or down along this axis, and hence \( \hat{n} \) and \( -\hat{n} \) represent the same physical state. The axis of orientational order normally depends on position, so that the director becomes a position-dependent field \( \hat{n}(r) \). One fundamental problem of liquid-crystal elasticity theory is to determine how the free energy depends on spatial gradients of the director field. In early studies of liquid crystals, this problem was addressed by Oseen [1] and Frank [2], and further by Nehring and Saupe [3, 4]. Their work led to the Oseen-Frank free energy density, which includes terms representing three deformation modes—splay, twist, and bend—as well as a fourth term called saddle-splay. Hence, it has four independent elastic coefficients.

In any elasticity theory, there must be certain inequalities on the elastic coefficients so that the free energy is thermodynamically stable; i.e. no deformation can make the free energy more negative than it is in the ground state.
energy go to negative infinity. For example, in conventional elasticity for an isotropic solid, the bulk and shear moduli must both be positive. Soon after the development of the Oseen-Frank free energy density for liquid crystals, Ericksen [5] derived a corresponding set of four inequalities on the liquid-crystal elastic coefficients. These four inequalities will be presented in detail below.

The purpose of this paper is to re-examine the Ericksen inequalities. There are both theoretical and experimental reasons for this re-examination.

The theoretical reason is that our group has recently developed a reformulation of liquid-crystal elasticity theory [6], which is based on a mathematical decomposition of the director gradient tensor by Machon and Alexander [7]. This reformulation expresses the free energy density in terms of four director deformation modes—splay, twist, bend, and a less-well-known fourth mode represented as the tensor $\Delta$. It is mathematically equivalent to the Oseen-Frank free energy density, but it provides a conceptually simpler way to describe many elastic phenomena in liquid crystals. Using this reformulation, several groups have investigated geometric compatibility constraints on director deformations [8–11]. As we will show, this theoretical progress provides new insight into the Ericksen inequalities.

The experimental reason is that a violation of the Ericksen inequalities has actually been observed in certain liquid-crystal materials. These materials are lyotropic chromonic liquid crystals, such as Sunset Yellow (SSY) and disodium cromoglycate (DSCG). In these materials, the molecules self-organize into long stacks in aqueous solution, and the stacks form nematic orientational order. Several experiments have put these liquid crystals into cylindrical capillaries [12, 13], rectangular capillaries [14], or cylindrical shells [15], with degenerate planar anchoring on the surfaces. In these geometries, the director field spontaneously forms a twisted structure rather than a uniform, achiral state. The twisted structure has been modeled by the experimental groups using a twist elastic constant that is anomalously small, violating one of the Ericksen inequalities. Based on this observation, one must ask: Is the violation consistent with liquid-crystal elasticity theory? If so, are there any constraints on the elastic constants?

In Sect. 2 of this article, we present the four Ericksen inequalities, using both the standard form of the Oseen-Frank free energy and our recent reformulation. We point out that these inequalities are excessively strict, because of the geometric constraints on the director deformation modes. In the following sections, we investigate what happens if the Ericksen inequality on the twist elastic constant is violated. In Sect. 3, we consider a severe violation ($K_{22} < 0$), and show that the free energy can become arbitrarily negative. This violation is forbidden for reasons of thermodynamic stability (unless the free energy includes higher-order terms). In Sect. 4, we consider the intermediate regime ($0 < K_{22} < K_{24}$), as in the experiments on lyotropic chromonic liquid crystals, and show that the free energy does not become arbitrarily negative. Rather, the liquid crystal has a well-defined, non-uniform ground state, which depends on the system size. Finally, in Sect. 5, we discuss the implications of these results for studies of lyotropic chromonic liquid crystals.

When this article was being revised for publication, some closely related research by Paparini and Virga appeared in the literature [16, 17]. Their work considers the elasticity of lyotropic chromonic liquid crystals using different mathematical methods. We compare our results with theirs in Sect. 4.1.

2 Theoretical Background

Oseen-Frank theory shows all the ways that the free energy density can depend on spatial gradients of the director field, as allowed by symmetry, up to quadratic order in the gradients.

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The free energy density is conventionally written as

\[
F = \frac{1}{2} K_{11} S^2 + \frac{1}{2} K_{22} T^2 + \frac{1}{2} K_{33} |B|^2 - K_{24} \nabla \cdot \left[ \hat{n} (\nabla \cdot \hat{n}) + \hat{n} \times (\nabla \times \hat{n}) \right].
\]  

(1)

Here, \( S = \nabla \cdot \hat{n} \) is the splay, \( T = \hat{n} \cdot (\nabla \times \hat{n}) \) is the twist, and \( B = -(\hat{n} \cdot \nabla)\hat{n} = \hat{n} \times (\nabla \times \hat{n}) \) is the bend. These three deformation modes contribute to the free energy density with elastic constants \( K_{11}, K_{22}, \) and \( K_{33}, \) respectively. The fourth term is called the saddle-splay term. This expression for saddle-splay has been used, for example, by Burylov [18] to model transitions among different director configurations in a cylindrical capillary.

In the literature, there are some variations in the notation for the saddle-splay coefficient: it sometimes written as \( K_{24}, \frac{1}{2} K_{24}, (K_{22} + K_{24}) \), or \( \frac{1}{2} (K_{22} + K_{24}) \). We choose the notation of Eq. (1), because it seems to be the most common in recent articles, but our results can easily be translated into any of the other notations.

In Ref. [6], we argue that the elastic free energy for nematic liquid crystals can more easily be understood in terms of four bulk elastic modes, rather than three. This argument is based on a mathematical construction of Machon and Alexander [7], who decompose the director gradient tensor into four different types of mathematical objects as

\[
\partial_i n_j = -n_i B_j + \frac{1}{2} S (\delta_{ij} - n_i n_j) + \frac{1}{2} T \epsilon_{ijk} n_k + \Delta_{ij}.
\]  

(2)

Here, the scalar \( S \), pseudoscalar \( T \), and vector \( B \) are the splay, twist, and bend modes defined above. The fourth mode \( \Delta \) is a symmetric, traceless tensor in the plane perpendicular to \( \hat{n} \). It indicates how the director splays outward in one direction and inward in the orthogonal direction in that plane. All four modes are visualized in Ref. [6]. In this theoretical approach, pure splay is double splay, and pure twist is double twist. Planar single splay is a combination of pure splay and \( \Delta \) mode, while cholesteric single twist is a combination of pure twist and \( \Delta \) mode.

Using the four bulk elastic modes, the free energy can be written as

\[
F = \frac{1}{2} (K_{11} - K_{24}) S^2 + \frac{1}{2} (K_{22} - K_{24}) T^2 + \frac{1}{2} K_{33} |B|^2 + K_{24} \text{Tr}(\Delta^2).
\]  

(3)

We emphasize that Eq. (3) is mathematically equivalent to Eq. (1), so these expressions for the free energy can be used interchangeably. However, Eq. (3) has the special feature that it is a sum of squares of elastic modes. In the sum of squares, the elastic constant for splay is \( (K_{11} - K_{24}) \), the elastic constant for twist is \( (K_{22} - K_{24}) \), the elastic constant for bend is \( K_{33}, \) and the elastic constant for the \( \Delta \) mode is \( 2K_{24}. \) In this perspective, those four elastic constants are the fundamental parameters of the theory, while \( K_{11} \) and \( K_{22} \) are less fundamental: \( K_{11} = (K_{11} - K_{24}) + K_{24} \) applies to a combination of splay and \( \Delta, \) and \( K_{22} = (K_{22} - K_{24}) + K_{24} \) applies to a combination of twist and \( \Delta. \)

Ericksen [5] looked for conditions on the elastic constants such that the free energy would be positive definite. Translated into our current notation, his inequalities were

\[
K_{11} > |2K_{24} - K_{11}|, \quad K_{22} > |2K_{24} - K_{22}|, \quad K_{33} > 0.
\]  

(4)

These inequalities can be rewritten as

\[
K_{11} > K_{24}, \quad K_{22} > K_{24}, \quad K_{33} > 0, \quad K_{24} > 0.
\]  

(5)
Because Ericksen worked with the Oseen-Frank free energy in a form similar to Eq. (1),
the inequalities were not obvious; they required a significant derivation. However, with the
reformulated free energy of Eq. (3), the inequalities are almost trivial. They simply state that
the free energy is a sum of squares with positive coefficients.

Clearly the Ericksen inequalities are sufficient for the free energy to be thermodynamically
stable. If the inequalities are satisfied, then any director deformation has a positive free
energy. The ground state is a uniform director field, with $F = 0$. However, it is not clear
whether the Ericksen inequalities are necessary for the free energy to be thermodynamically
stable.

The main subtlety here is that the four director deformation modes $S$, $T$, $B$, and $\Delta$ are not
independent of each other. Rather, they must all be derived from the same director field $\hat{n}(r)$. Only certain combinations of $S$, $T$, $B$, and $\Delta$ can be derived from the same director field, and these combinations are called compatible, while other combinations are incompatible.

One way to see this issue is by counting degrees of freedom: $S$ has one degree of freedom
(as a scalar), $T$ has one (as a pseudoscalar), $B$ has two (as a vector perpendicular to $\hat{n}$), and $\Delta$ has two (as a traceless, symmetric tensor in the plane perpendicular to $\hat{n}$), for a total of six degrees of freedom in the deformation modes. By comparison, the director field has only two degrees of freedom (as a unit vector). Hence, we would expect four constraints among the director deformation modes.

An analogous issue occurs in the elastic theory of solids. The strain tensor is derived
from the displacement vector field, but the strain tensor has more degrees of freedom than
the displacement vector field. Hence, there must be compatibility constraints on the strain
tensor. Here, the director field of a liquid crystal is analogous to the displacement field of
a solid, and the deformation modes $S$, $T$, $B$, and $\Delta$ are analogous to the strain tensor of a solid.

In recent years, several groups have investigated how the compatibility constraints for
the director deformation modes are related to the geometry of space. Virga [8] found there
are only two ways to fill three-dimensional (3D) Euclidean space with constant director de-
f ormations: twist and $\Delta$, or bend, twist, and $\Delta$. Sadoc et al. [9] found that 3D non-Euclidean
curved space can be filled with a single director deformation mode, with the right correspon-
dence between the type of curvature and the type of deformation. Pollard and Alexander [10]
and da Silva and Efrati [11] developed general compatibility conditions for an arbitrary com-
bination of deformation modes and an arbitrary Euclidean or non-Euclidean geometry.

The compatibility conditions derived in Refs. [10, 11] are mathematically complex, and
we will not attempt to use them directly. Instead, we will construct director fields in 3D
Euclidean geometry, and determine what happens to these director fields if the Ericksen
inequalities are violated.

### 3 Necessary Inequalities

For a first step, consider a director field with the cholesteric helical structure

$$\hat{n} = (\cos qz, \sin qz, 0).$$

As shown in Ref. [6], this structure does not have pure twist; rather, it is a combination of the
twist and $\Delta$ deformation modes. It is one of the allowed constant combinations found
by Virga [8]. Inserting this director field into the free energy density of Eq. (1) or (3) gives
$F = \frac{1}{2} K_{22} q^2$. It involves $K_{22}$, which is a combination of the elastic constant $(K_{22} - K_{24})$ for
pure twist and the elastic constant $K_{24}$ for the $\Delta$ mode. Hypothetically, suppose that $K_{22} < 0$. In that case, minimizing the free energy would drive $q \rightarrow \pm \infty$, and hence $F \rightarrow -\infty$. That situation would be thermodynamically unstable. Hence, a necessary inequality is $K_{22} > 0$. Note that this inequality is weaker than the Ericksen inequality on $K_{22}$.

Next, consider a director field with the twist-bend heliconical structure

$$\hat{n} = (\sin \beta \cos qz, \sin \beta \sin qz, \cos \beta). \quad (7)$$

This structure is a combination of the bend, twist, and $\Delta$ deformation modes; it is the second allowed constant combination. Inserting this director field into Eq. (1) or (3) gives the free energy density

$$F = \frac{1}{2} \sin^2 \beta (K_{22} \sin^2 \beta + K_{33} \cos^2 \beta)q^2. \quad (8)$$

Hypothetically, suppose that $K_{33} < 0$. In that case, we can choose a cone angle $\beta$ such that the coefficient of $q^2$ is negative. Minimizing the free energy then drives $q \rightarrow \pm \infty$, and hence $F \rightarrow -\infty$, which is thermodynamically unstable. Hence, another necessary inequality is $K_{33} > 0$. That inequality is the same as one of the Ericksen inequalities.

When we construct director fields, we are not limited to constant combinations of deformation modes; we can also investigate non-uniform combinations. For example, consider the director wave

$$\hat{n} = (\sin \theta(r), 0, \cos \theta(r)), \text{ with } \theta(r) = \theta_0 \cos (q \cdot r), \quad (9)$$

for small $\theta_0$. By putting that wave into the free energy density of Eq. (1) or (3) and integrating over $r$, we obtain the average free energy density

$$F_{\text{average}} = \frac{1}{4} (K_{11}q_x^2 + K_{22}q_y^2 + K_{33}q_z^2)\theta_0^2 + O(\theta_0^4). \quad (10)$$

If any of the three coefficients $K_{11}$, $K_{22}$, or $K_{33}$ were negative, then minimization of the free energy would drive the corresponding component of $q$ to $\pm \infty$, and hence drive $F \rightarrow -\infty$, which would be thermodynamically unstable. Hence, all three of those coefficients must be positive, and the set of necessary inequalities becomes

$$K_{11} > 0, \quad K_{22} > 0, \quad K_{33} > 0. \quad (11)$$

At this point, some readers might object that there is actually an extensive literature on liquid crystals with $K_{33} < 0$, beginning with the work of Dozov [19]. However, that situation is different because Dozov uses a free energy with higher-order terms, involving either second derivatives or higher powers of first derivatives of the director field. These higher-order terms prevent the thermodynamic instability, and give a twist-bend nematic phase with finite values of wavevector $q$ and cone angle $\theta$. Likewise, in recent work by our group [20–23], an effective renormalized elastic constant ($K_{33}^R$, $K_{11}^R$, or $K_{22}^R$) is driven negative by interactions with another order parameter, and the free energy would be unstable, but it is stabilized by some higher-order couplings.

In elasticity theory, it is always possible to add higher-order terms to stabilize a free energy. When we search for stability conditions, the issue is whether the free energy is stable without higher-order terms. For a free energy with the form of Eq. (1) or (3), without higher-order terms, the conditions of Eq. (11) are necessary.
Summarizing the results of this section, we have derived a set of necessary inequalities (11), which are weaker than the Ericksen inequalities (5). If the necessary inequalities are violated, then the Ericksen inequalities are severely violated, and the free energy may go to negative infinity. This severe violation is forbidden (unless there are higher-order terms to stabilize the free energy). By comparison, in the previous section, we showed that the Ericksen inequalities are sufficient to prevent the free energy from going to negative infinity.

We must now ask: Are the necessary inequalities (11) also sufficient? In other words, what happens in the intermediate regimes, where the Ericksen inequalities are violated but the necessary inequalities are satisfied? In those regimes, does the liquid crystal have a well-defined ground state with a finite free energy? We will address these questions in the following section.

4 Intermediate Regimes

Figure 1 shows schematic diagrams of possible regimes for the elastic constants. The first row is expressed in terms of the fundamental elastic constants \((K_{11} - K_{24}), (K_{22} - K_{24}), \) and \(K_{24}\). The second row provides the same information expressed in terms of the conventional elastic constants \(K_{11}, K_{22}, \) and \(K_{24}\). In each case, we can see that there is a blue regime where the Ericksen and the necessary inequalities are both satisfied, and a red regime where the Ericksen and necessary inequalities are both violated. Between these regimes, there are intermediate regimes where the Ericksen inequalities are violated but the necessary inequalities are satisfied. In particular, there are three intermediate regimes, which we label as:

- Twist intermediate regime: \(0 < K_{22} < K_{24}\)
- Splay intermediate regime: \(0 < K_{11} < K_{24}\)
- \(\Delta \) intermediate regime: \(K_{24} < 0, K_{11} > 0, K_{22} > 0\)

In this section, we concentrate on the twist intermediate regime, because it occurs experimentally in lyotropic chromonic liquid crystals. At the end of the section, we briefly discuss the other two intermediate regimes, which have not yet been reported experimentally to our knowledge. (We do not consider regimes in which more than one of the Ericksen inequalities are violated simultaneously.)

4.1 Twist Intermediate Regime

Suppose we are in the twist intermediate regime, where \(0 < K_{22} < K_{24}\), as has been reported in lyotropic chromonic liquid crystals. In the free energy of Eq. (3), the coefficient of twist \(T^2\) is negative, while all the other coefficients are positive. Hence, the liquid crystal has a natural tendency toward twist; a twisted state should have a lower free energy than the uniform state. However, the amount of twist is limited by the compatibility conditions. If the director field has twist, it must have some of the other deformation modes, which have positive free energy. Those other modes may stabilize the system, and prevent the free energy from going to negative infinity.

To see these free energy considerations, suppose that the liquid crystal is in a cylindrical capillary with radius \(R_{\text{max}}\), and suppose the boundary conditions on the surface are totally free. Suppose the director field has the twisted structure shown in Fig. 2. As a simple ansatz, it can be described in cylindrical coordinates \((\rho, \phi, z)\) by the equation

\[
\hat{n} = \hat{z} \cos \theta(\rho) + \hat{\phi} \sin \theta(\rho),
\]
Fig. 1 Possible regimes of the elastic constants. (a,b) Expressed in terms of the fundamental elastic constants \((K_{11} - K_{24}), (K_{22} - K_{24}),\) and \(K_{24}\). (c,d) Expressed in terms of the conventional elastic constants \(K_{11}, K_{22},\) and \(K_{24}\). In parts (a,c), we vary \(K_{22}\) and \(K_{24}\), assuming that the splay and bend Ericksen inequalities are satisfied \((K_{11} > K_{24} \text{ and } K_{33} > 0)\). In parts (b,d), we vary \(K_{11}\) and \(K_{24}\), assuming that the twist and bend Ericksen inequalities are satisfied \((K_{22} > K_{24} \text{ and } K_{33} > 0)\).

with \(\theta(\rho) = \alpha \rho\), for small \(\alpha\). This director field has twist of order \(\alpha\), bend of order \(\alpha^2 \rho\), \(\Delta\) mode of order \(\alpha^3 \rho^2\), and zero splay. If we put this ansatz into the free energy density and average over the cylindrical geometry, we obtain

\[
F_{\text{average}} = 2(K_{22} - K_{24})\alpha^2 + \frac{1}{12} [3K_{33} - 8(K_{22} - K_{24})] \frac{R_{\text{max}}^2}{K_{33}} \alpha^4 + O(\alpha^6). \tag{13}
\]

This free energy has the usual form of a series expansion in powers of the twist order parameter \(\alpha\). When \((K_{22} - K_{24}) > 0\), the coefficient of the quadratic term is positive, and hence the minimum occurs at \(\alpha = 0\), which corresponds to an untwisted state. When \((K_{22} - K_{24}) = 0\), there is a critical point, where the untwisted state has a symmetry-breaking transition to right- or left-handed twist. Just below the critical point, the order parameter and free energy density scale as

\[
\alpha = \pm \frac{2}{R_{\text{max}}} \left[ \frac{K_{24} - K_{22}}{K_{33}} \right]^{1/2}, \quad F_{\text{average}} = -\frac{4(K_{24} - K_{22})^2}{K_{33} R_{\text{max}}^2}. \tag{14}
\]
The twist order parameter does not diverge, and the free energy does not go to negative infinity. Rather, the system is stabilized by the compatibility requirement: In order to have the favorable twist, the director field must also have some unfavorable bend (and a smaller amount of unfavorable $\Delta$ mode). These unfavorable deformation modes lead to a well-defined ground state, which has a free energy lower than the uniform state.

As a check on this simple variational calculation, we consider a director field with the form of Eq. (12), but with an arbitrary function $\theta(\rho)$. To minimize the free energy, we solve the Euler-Lagrange equation

$$4K_{22}\rho^2\theta''(\rho) + 4K_{22}\rho\theta'(\rho) - K_{22}\sin 4\theta(\rho) = 8K_{33}\sin^3\theta(\rho)\cos\theta(\rho),$$

with $\theta(0) = 0$ and the free boundary condition

$$2K_{22}R_{\text{max}}\theta'(R_{\text{max}}) = (2K_{24} - K_{22})\sin 2\theta(R_{\text{max}}).$$

Note that $K_{24}$ does not enter the Euler-Lagrange equation, but it does enter the boundary condition. We find numerical solutions with varying ratio $K_{22}/K_{24}$ from 1 down to 0.2, for fixed $K_{33}/K_{24} = 2$. The results are plotted in Fig. 3. When $K_{22}$ is just below $K_{24}$, the function is approximately linear, with the slope $\alpha$ as predicted in Eq. (14). When $K_{22}$ is substantially less than $K_{24}$, the shape of the function deviates from linearity, but still it has the same general form. We can see that there is a well-defined ground state, with a twist that does not diverge, even deep in the twist intermediate regime.

Using different mathematical methods, Paparini and Virga [16, 17] came to the same conclusion: A liquid crystal in a cylindrical geometry has a stable twisted ground state for $0 < K_{22} < K_{24}$.

From Eq. (14), we see that the free energy depends on the system radius $R_{\text{max}}$ in a surprising way. The average free energy density of the twisted state scales as $-1/R_{\text{max}}^2$, and it approaches the free energy density of the uniform state $F = 0$ in the limit of $R_{\text{max}} \to \infty$. Hence, the free energy per volume increases as the system size increases in the $(x, y)$ plane. (By contrast, the free energy per volume is constant as the system size increases in the $z$ direction.)

This dependence on system size is quite unusual in liquid-crystal physics. In typical liquid crystals, if we neglect surface effects, the free energy is extensive, meaning that the free energy per volume is constant as the system size increases. In typical liquid crystals, if we include surface tension and surface-induced director distortions, the free energy per
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Fig. 3 Numerical calculations of the director orientation $\theta(\rho)$ for a liquid crystal in a cylindrical capillary of radius $R_{\text{max}}$. The ratio $K_{33}/K_{24} = 2$ is fixed, and the ratio $K_{22}/K_{24}$ varies as indicated in the legend.

volume decreases as the system size increases; this behavior can be called sub-extensive. By contrast, we now see that the free energy in the twist intermediate regime is super-extensive. Meiri and Efrati [24] have recently argued that super-extensive scaling of the free energy is a general characteristic of geometrically frustrated systems. Our results for lyotropic chromonic liquid crystals provide an example of that phenomenon.

Whenever a system has super-extensive scaling of the free energy, one might ask whether it can reduce its total free energy by breaking into many smaller systems. Specifically, for a lyotropic chromonic liquid crystal in a cylindrical geometry, one might ask whether it can break into cylinders of smaller radius, with twist from the center to the edge of each cylinder. In principle, this breakup would provide a large negative free energy for each cylinder, and hence reduce the total free energy. Indeed, Paparini [16] considers this scenario as a “paradox,” which could lead to $F_{\text{average}} \to -\infty$ as $R_{\text{max}} \to 0$.

How can this paradox be resolved? Paparini suggests that the Oseen-Frank free energy may be supplemented with higher-order quartic terms in gradients of the director field. Such terms are certainly allowed by symmetry. As an alternative (and possibly simpler) explanation, we suggest that surface energy may provide a mechanism to prevent the instability.

In this argument, we must be careful about how the surface energy scales with $R_{\text{max}}$. If the total surface energy of a cylinder is proportional to the total surface area, then the average surface energy density per volume scales as $+1/R_{\text{max}}$. This surface energy density is not strong enough to overcome the Oseen-Frank free energy density, which scales as $-1/R_{\text{max}}^2$. However, the surface energy does not need to be proportional to surface area in the limit of small $R_{\text{max}}$. The surface can have an intrinsic length scale, such as a thickness or a persistence length. When $R_{\text{max}}$ is less than the intrinsic length scale, so that the surface is highly curved, then the cylinder can be regarded as a thin fiber with a constant surface energy $\tau$ per length. In that case, the average surface energy density would scale as $+1/R_{\text{max}}^2$. That scaling is strong enough to prevent the divergence, provided that $\tau$ is large enough compared with the Frank constants.

Rather than breaking into separate cylinders, a liquid crystal might form an array of half-skyrmions or merons, separated by disclinations. Figure 4 shows two possible structures for the director field, which are essentially two-dimensional versions of blue phases. In Fig. 4(a), all of the double-twist tubes have the same handedness and form a hexagonal lattice. In Fig. 4(b), the double-twist tubes have alternating handedness and are arranged in a square lattice. Half-skyrmion structures like Fig. 4(a) have been studied in the context of chiral liquid crystals, where they are stabilized by the favored twist arising from chirality [25, 26]. Here, we suggest that they might also form in achiral liquid crystals in the twist intermediate regime.

We can estimate the free energy of the structures in Fig. 4. The double-twist tubes in these lattices have approximately the same structure as the director field in the cylindrical capillary.
Possible structures for the director field in a liquid crystal where the disclination energy is low compared with \((K_{24} - K_{22})^2/K_{33}\), so that the free-energy benefit of the twist regions exceeds the free-energy cost of the disclinations between those regions. (a) Hexagonal lattice of double-twist tubes with uniform handedness. (b) Square lattice of double-twist tubes with alternating handedness.

of Fig. 2. Hence, the average free energy density should have the same scaling as Eq. (14), with the lattice constant \(a\) in place of \(R_{\text{max}}\), hence proportional to \(- (K_{24} - K_{22})^2/(K_{33}a^2)\). Note that the free energy can depend on \(K_{24}\) because the disclinations form internal surfaces for the director field. As in the previous case, one might worry that \(F_{\text{average}} \to -\infty\) as \(a \to 0\).

The disclination free energy provides a mechanism to prevent the instability. Each disclination has an energy of \(\tau\) per length, and hence the average disclination energy density per length scales as \(+1/a^2\). As in the previous problem, that scaling is strong enough to avoid the divergence, provided that \(\tau\) is large enough compared with the Frank constants. Indeed, these structures have not been observed in lyotropic chromonic liquid crystals, presumably because \(\tau\) is too large.

To summarize the results of this subsection, we see that the necessary inequalities (11) can be sufficient for thermodynamic stability, provided that the liquid crystal has a continuous director field inside a cylinder of fixed radius, as shown in Fig. 2. However, the situation becomes more complex if the liquid crystal is free to break into smaller cylinders, or to form disclinations as in Fig. 4, or perhaps to make other geometric changes. In those cases, thermodynamic stability may depend on specific parameters, such as the surface energy or the disclination energy, compared with the Frank constants.

### 4.2 Other Intermediate Regimes

So far, we have considered liquid crystals in the twist intermediate regime, because that regime corresponds to experiments on lyotropic chromonic liquid crystals. Two other theoretical possibilities are the splay intermediate regime and the \(\Delta\) intermediate regime. We do not know of any liquid-crystal materials in those regimes. However, we would like to make theoretical predictions for the director configurations, in case such materials should be discovered in the future.

First, consider the splay intermediate regime \(0 < K_{11} < K_{24}\). In the free energy of Eq. (3), the coefficient of splay \(S^2\) is negative, while all other coefficients are positive. Hence, the liquid crystal has a tendency toward splay; a splayed state has a lower free energy than the...
Fig. 5  (a) Director field in the splay intermediate regime $0 < K_{11} < K_{24}$. (b) Director field in the $\Delta$ intermediate regime $K_{24} < 0$. (This example is drawn with the parameter $\phi_0 = 0$)

uniform state. However, as with the twist case, the amount of splay is limited by compatibility conditions, which may stabilize the system.

As an example, suppose again that the liquid crystal is in a cylindrical capillary with radius $R_{\text{max}}$, with free boundary conditions, and suppose the director field has the splayed structure of Fig. 5(a). It can be represented in cylindrical coordinates by the ansatz

$$\hat{n} = \hat{z} \cos \theta(\rho) + \hat{\rho} \sin \theta(\rho),$$  \hspace{1cm} (17)

with $\theta(\rho) = \alpha \rho$, for small $\alpha$. This director field has splay of order $\alpha$, bend of order $\alpha^2 \rho$, $\Delta$ mode of order $\alpha^3 \rho^2$, and zero twist. By putting this ansatz into the free energy density and averaging over position in the cylinder, we obtain

$$F_{\text{average}} = 2(K_{11} - K_{24})\alpha^2 + \frac{1}{12} [3K_{33} - 8(K_{11} - K_{24})] R_{\text{max}}^2 \alpha^4 + O(\alpha^6).$$  \hspace{1cm} (18)

This free energy is a series expansion in powers of the splay order parameter $\alpha$. When $(K_{11} - K_{24}) > 0$, the quadratic coefficient is positive, and hence the minimum occurs at $\alpha = 0$, which is the uniform state. When $(K_{11} - K_{24}) = 0$, there is a critical point, where the uniform state has a symmetry-breaking transition to inward or outward splay, or equivalently, to splay up or down along the cylindrical axis. Just below the critical point, the order parameter and free energy density scale as

$$\alpha = \pm \frac{2}{R_{\text{max}}} \left[ \frac{K_{24} - K_{11}}{K_{33}} \right]^{1/2}, \hspace{1cm} F_{\text{average}} = -\frac{4(K_{24} - K_{11})^2}{K_{33} R_{\text{max}}^2}. \hspace{1cm} (19)$$

All of these predictions for splay are exactly analogous to the predictions for twist in the previous section.

The same considerations apply in the $\Delta$ intermediate regime $K_{24} < 0$. In the free energy of Eq. (3), the coefficient of $\text{Tr}(\Delta^2)$ is negative, and all other coefficients are positive. In this case, the liquid crystal has a tendency toward the $\Delta$ mode, so that a state with $\Delta \neq 0$ has a lower free energy than the uniform state. Because the favorable $\Delta$ deformation must be accompanied by other deformations, which are unfavorable, the system may still be thermodynamically stable.
To model the behavior in this regime, we again consider a liquid crystal in a cylindrical capillary with free boundary conditions, and now assume the director field

\[
\hat{n} = \hat{z} \cos \theta(\rho) + \hat{\rho} \sin \theta(\rho) \cos 2(\phi - \phi_0) - \hat{\phi} \sin \theta(\rho) \sin 2(\phi - \phi_0),
\]

(20)

with \( \theta(\rho) = \alpha \rho \), for small \( \alpha \). This structure is illustrated in Fig. 5(b); note that the outward tilt is at orientations of \( 2\phi_0 \) and \( 2\phi_0 + \pi \) with respect to the \( x \)-axis. It has \( \Delta \) mode of order \( \alpha \), bend of order \( \alpha^2 \rho \), and splay and twist of order \( \alpha^3 \rho^2 \). We put this ansatz into the free energy density, and average over position, to obtain

\[
F_{\text{average}} = 2K_{24} \alpha^2 + \frac{1}{12} (3K_{33} - 8K_{24}) R_{\text{max}}^2 \alpha^4 + O(\alpha^6).
\]

(21)

This free energy is a power series in \( \alpha \), which can now be regarded as an order parameter for the \( \Delta \) deformation. When \( K_{24} > 0 \), the minimum occurs at the uniform state \( \alpha = 0 \). When \( K_{24} = 0 \), there is a critical point, where the uniform state has a symmetry-breaking transition to some non-zero \( \Delta \) deformation, with an arbitrary orientation \( \phi_0 \). Just below the critical point, the order parameter and free energy density scale as

\[
\alpha = \pm \frac{2}{R_{\text{max}}} \left[ -\frac{K_{24}}{K_{33}} \right]^{1/2}, \quad F_{\text{average}} = -\frac{4K_{24}^2}{K_{33} R_{\text{max}}^2}.
\]

(22)

These predictions are quite analogous to the twist and splay cases.

All of our discussion about system-size dependence and geometric frustration in the twist intermediate regime applies also to the splay and \( \Delta \) intermediate regimes. In particular, if the disclination energy is very low, the liquid crystal might break up into domains of the favored mode separated by disclinations. For the splay case, we expect that the domain structure might resemble Fig. 4(a) or 4(b), but with the entire director field rotated by \( \pi/2 \) about the \( z \)-axis, so that twist is transformed into splay. For the \( \Delta \) case, we have not yet investigated the possible domain structures.

5 Discussion

In this article, we have identified three distinct regimes of elastic constants in nematic liquid crystals, which are indicated schematically in Fig. 1. In the regime where the Ericksen inequalities (5) are satisfied, all four director deformation modes cost some positive free energy. For that reason, the ground state of a bulk liquid crystal has a uniform director field. By contrast, in the forbidden regime where the necessary inequalities (11) are violated, some physically realizable director field has a negative free energy, and hence the free energy (1) or (3) is thermodynamically unstable. It can only be stabilized by extra terms with higher powers of the director gradients, or higher-order derivatives of the director field, or couplings with other order parameters. In this forbidden regime, the liquid crystal may form a modulated structure with no singularities in nematic order, such as a twist-bend nematic phase or a splay nematic phase, as studied in much recent research [19–23].

Between the Ericksen regime and the forbidden regime, there is an intermediate regime where the Ericksen inequalities are violated but the necessary inequalities are satisfied. In this intermediate regime, one of the director deformation modes—twist, splay, or \( \Delta \)—has a negative free energy. However, the total free energy is stabilized by geometric compatibility constraints, which require that any physically realizable director field must have a
combination of the favored mode with other, unfavorable modes. The intermediate regime
has surprising properties. In a finite cylindrical geometry, the liquid crystal minimizes its
free energy by forming a nonuniform director field, as shown in Fig. 2, 5(a), or 5(b). As
the cylinder radius increases, the total free energy increases super-extensively. The super-
extensive growth can only be avoided if the system adds disclinations, as in Fig. 4, provided
that the disclination energy is low enough.

Remarkably, the twist intermediate regime actually occurs in lyotropic chromonic liquid
 crystals, according to experimental measurements of the elastic constants [12–15]. Hence,
the behavior discussed here is not just a theoretical speculation, but can be studied in the
laboratory. In particular, we emphasize three consequences of this theory for experiments
on lyotropic chromonic liquid crystals.

First, these materials should be sensitive to the geometry of their container. In this article,
we have seen the effects of changing the radius $R_{\text{max}}$ of a cylindrical capillary. We would
expect equally important effects of changing the shape of the container. The favorable twist
deformation naturally fills up a region that is roughly circular in the plane perpendicular to
the director. If the cross section of the cell is not circular, then the director field must adapt
in a complex way, perhaps by forming circular domains of twist separated by untwisted
regions. As an example, the experiments of Ref. [14] put lyotropic chromonic liquid crystals
into capillaries of rectangular cross section and find complex director configurations.

Second, these materials have an unusual relationship between the free energies of double
twist, cholesteric single twist, and a uniform state. In typical chiral liquid crystals, double
twist is preferred over single twist, and single twist is preferred over a uniform state. By
contrast, in lyotropic chromonic liquid crystals, double twist is preferred over a uniform
state, and a uniform state is preferred over single twist. Hence, the materials should particu-
larly avoid cholesteric single twist. Indeed, the structures in Ref. [14] include double-twist
regions and monodomain uniform regions.

Third, we anticipate that these materials should be particularly compatible with impuri-
ties, such as dust or other colloidal particles. Any particles will break up the liquid crystals
into smaller volumes, and will allow the director field to break into more regions of double
twist. Effectively, the particles could play the same role as the disclinations in the structures
of Fig. 4. Hence, the negative free energy of the twist domains could offset the positive
free energy of contact between the particles and the liquid crystal. Distortions induced by
such particles could make these materials difficult to align. A recent study suspends rod-like
particles in a lyotropic chromonic liquid crystal, and finds an anomalous twisted alignment
of the rods with respect to the director field [27]. We speculate that the spontaneous twist
discussed here may be involved in that experiment.

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