

Chiral Colloidal Membranes: effects of curvature and dynamics of π -walls

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This dissertation by Zifei Liu is accepted in its present form
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Abstract of “Chiral Colloidal Membranes: effects of curvature and dynamics of π -walls” by Zifei Liu, Ph.D., Brown University, May 2026

Colloidal membranes are monolayers of rod-like particles and provide a model system of liquid crystals to study chirality, elasticity, and geometry. In this thesis, we study chiral colloidal membranes in both curved and planar geometries. We consider the competition between Frank elasticity and tilt coupling determining how chiral membranes respond to curvature and director dynamics of skyrmions in planar colloidal membranes. In the case of curved surface, we study the interplay of curvature, the tilt coupling favoring alignment of the directors to the normal of the surface, and liquid crystal elasticity on a cylinder. We show that when the tilt coupling is sufficiently large, the curvature of the cylinder leads to a discontinuous transition between the twisted state and the state with all directors normal to the surface. We also study the metastable twisted conformations above the transition corresponding to two sharp twist domain walls (π -walls) that wrap around the cylinder in helical paths. Our numerical work is supported by analytic calculations that approximately capture the transition as well as the trend of increasing pitch with increasing penalty for tilt away from the surface normal. Finally, we explore the role of the Gaussian curvature of the surface by determining the conformation of a chiral liquid crystal on a family of unduloids, which smoothly vary from the cylinder to a string of spheres. In the case of planar membranes, we analyze a phenomenological model for the dynamics of a skyrmion in a colloidal membrane, disregarding membrane and solvent flow. The skyrmion corresponds to a configuration with a circular twist wall. Numerically solving this model, we find that chirality determines whether a circular twist wall expands or contracts. The transition point is consistent with the criteria for the formation of a straight twist wall in the plane. By fitting the numerical calculation with the results

of experiments, we estimate the rotational viscosity of the rods. Our results match well with other theoretical approximations, giving a more precise range of chirality to form a colloidal skyrmion. We also perform simulations based on Landau–de Gennes theory using *FEniCS*. We find two mechanisms that make the straight π -walls relax faster than the curved π -walls. One is the anisotropy in the elastic constants. Another is that the dissipation is confined to the ends of the straight π -wall but takes place all along the length of the curved π -wall.

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Chapter 1

Introduction

1.1 Liquid crystal and fluid membrane

Liquid crystals and fluid membranes represent two distinct types of soft matter systems. Liquid crystals are typically described using orientational order parameters, whereas fluid membranes are mainly characterized by their shape, curvature, and dynamic behavior. In this work, I study colloidal membranes composed of chiral liquid crystals that also exhibit fluid-like properties, and investigate the interplay of orientational order and the curvature of such chiral membranes as well as the dynamics of topological defects in planar membranes.

Unlike conventional liquids, the particles in liquid crystals are typically elongated rod-like or disk-like molecules which can exhibit a certain degree of orientational organization [17]. They tend to align along preferred directions that can be described by a director field or corresponding order parameters, while still maintaining fluid-like properties. Variations in this orientational order lead to an elastic energy cost, which in turn influences the configuration and dynamics of the system. In chiral liquid crystals, the breaking of mirror symmetry causes the particles to favor a twisted arrangement, creating a competition between alignment and distortion. This interplay can give rise to complex structures and even topological defects.

Liquid crystals can exhibit several phases depending on the director orientation and possible partial translational ordering of the particles. The simplest and most common one is the nematic phase, where the system is spatially homogeneous and the directors align along a common direction. Although the material remains fluid, this phase breaks rotational symmetry. When the constituent particles are chiral, the director alignment can rotate in space, forming the cholesteric phase. In this phase, the directors twist and rotate around a pitch axis. Another important phase is the smectic phase, which resembles the nematic phase but with an additional layered structure. In the smectic-A phase, the layers are perpendicular to the average alignment direction, while in the smectic-C phase the particles are tilted within the

layers. Transitions between these phases can occur under different conditions, such as the application of an external magnetic field.

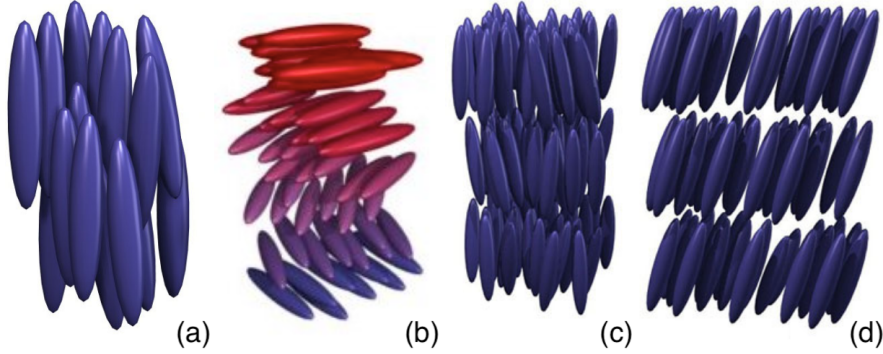


Figure 1.1: Nematic, cholesteric, and smectic phases of liquid crystals [89]. (a) Nematic phase: homogeneous with orientational order. (b) Cholesteric phase: orientational order in each layer, with a twist between layers. (c,d) Smectic phases: molecules form layers; the director is perpendicular to the layers in smectic-A and tilted in smectic-C (reproduced from Ref. [89] under GNU Free Documentation License).

A fluid membrane can be viewed as a two-dimensional surface that can adopt a variety of shapes, such as saddles or catenoids. It is essentially a thin film in which particles are free to move within the membrane surface. A fluid membrane may have open edges or form closed structures such as vesicles, and it can transition between different shapes. Because of this flexibility, researchers study how bending elasticity and membrane curvature interact with the orientational order of the particles, as well as with the overall shape of the membrane, both in equilibrium and during dynamical processes.

In a liquid crystal membrane, the particles are confined to a two-dimensional surface while maintaining orientational order. As a result, the shape of the surface and the director field become coupled and influence each other. This framework allows researchers to study systems such as colloidal membranes, which are two-dimensional thin films composed of rod-like particles.

1.2 Colloidal membranes

In contrast to short-rod liquid crystals, we focus on monodisperse micron-sized rod-like colloids, such as fd viruses, which have well-defined diameter, length, rigidity, charge, and chirality [29]. These particles can be viewed as giant molecules in a solution containing polymers, known as depletants, that induce effective depletion interactions (see Fig 1.4) between them. This system offers several advantages: the structures are visible at the colloidal scale under a microscope, they can be readily manipulated using experimental techniques, and their relatively slow dynamics make it possible to track their behavior over time.

The fd viruses have a contour length of 880 nm and a diameter of 6 nm, giving them a large aspect ratio of about 130 [64] [9]. They also possess a long persistence length, ranging from $2.8 \pm 0.7 \mu\text{m}$ for fd-wt viruses to $9.1 \pm 1.6 \mu\text{m}$ for fd-Y21M viruses [7], which indicates their strong rigidity. Because of these properties, these viruses can be regarded as a model liquid crystal system.

As the concentration of colloidal rods increases from low to high, the system undergoes a transition from a purely isotropic phase to a coexistence of isotropic and nematic phases separated by an interface [69] [26]. However, due to their intrinsic chirality, fd viruses form a cholesteric phase at room temperature. The chirality originates from the major coat proteins of the viruses [34], and it can be tuned either by changing the temperature or by mixing viruses with opposite handedness at controlled ratios.

In Fig. 1.2(a), the striped pattern indicates the cholesteric phase of fd-wt. In this phase, the director rotates along a pitch axis that is perpendicular to the local director orientation, and the pitch is defined as the distance along the pitch axis over which the director rotates by 360° [30]. As the temperature increases, the pitch becomes larger and eventually diverges, leading to an achiral nematic phase. In Fig. 1.3, when the concentration of fd-wt is increased in a mixture of right-handed fd-Y21M and

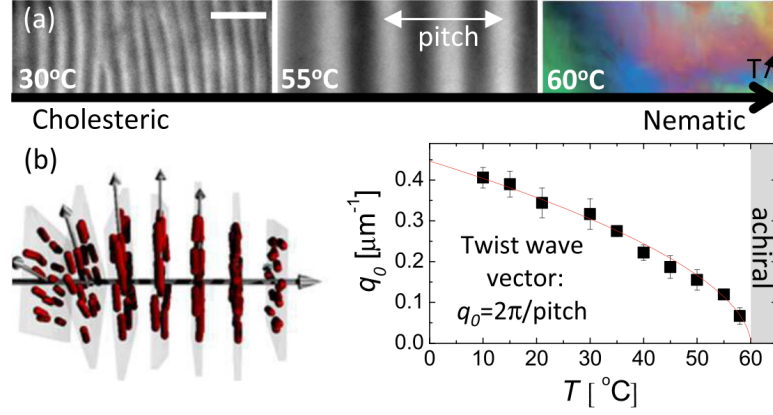


Figure 1.2: Temperature dependence of chirality in fd-wt suspensions at $c_v = 100 \text{ mg ml}^{-1}$ [30]. (a) Cross-polarized images of nematic and cholesteric phases (scale bar: $30 \mu\text{m}$). (b) Twist wave vector q_0 as a function of temperature. As $q_0 \rightarrow 0$, the cholesteric pitch diverges and the system transitions to an achiral nematic phase.(reproduced from Ref. [29])

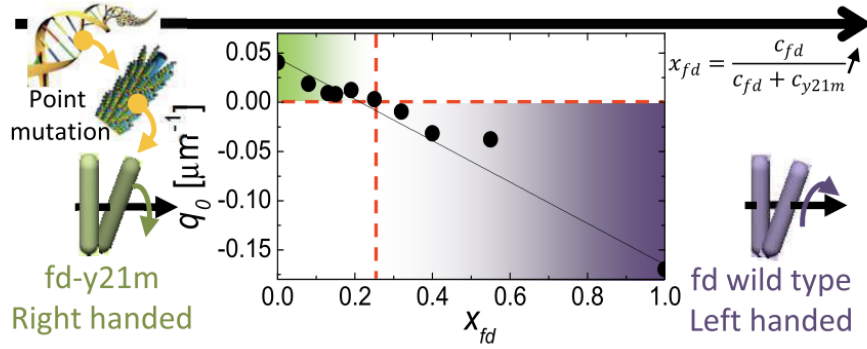


Figure 1.3: Effect of the fd-wt to fd-y21m ratio on chirality in aqueous mixtures at $c_v = 55 \text{ mg ml}^{-1}$ and $T = 22^\circ\text{C}$ [8]. The twist wave vector is measured as a function of $x_{fd} = c_{fd} / (c_{fd} + c_{fd-y21m})$. Side figures illustrate the chiral interactions of fd-wt rods and the point mutation in fd-y21m that leads to opposite handedness.(reproduced from Ref. [29])

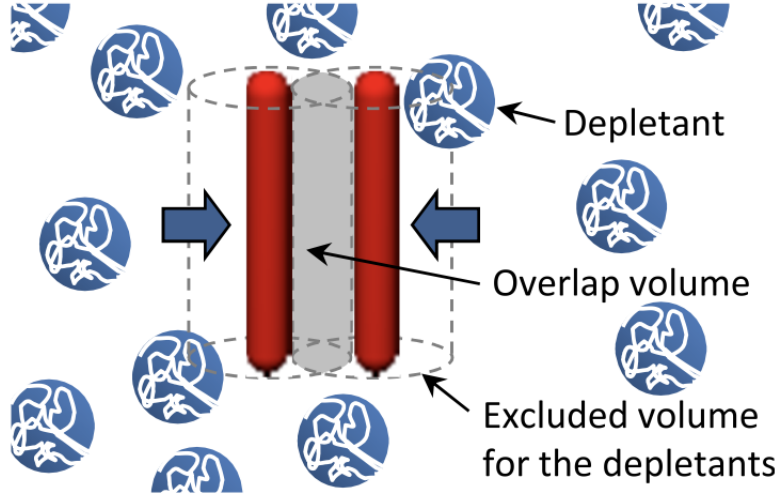


Figure 1.4: Sketch of the depletion interaction (reproduced from Ref. [29]).

left-handed fd-wt viruses, the overall chirality of the system changes from positive to negative [30] [7].

Depletants such as Dextran in solution introduce depletion interactions between colloids. Since the smaller depletant polymers do not directly interact with the colloids, they can be approximately treated as hard spheres surrounding the colloidal rods. However, an excluded volume region forms around each colloid where the depletants cannot penetrate. This excluded volume effect makes it entropically favorable for the colloids to align with each other and overlap their excluded volumes, which increases the free volume available to the polymers to increase the total entropy of the system [5].

Due to this depletion effect, when the concentration of Dextran becomes sufficiently high, the colloidal rods condense into a two-dimensional monolayer structure known as a colloidal membrane. In this structure, the rods are aligned perpendicular to the membrane plane. The membrane thickness is approximately one rod length, while its lateral diameter can vary over a wide range. On a coarse-grained level, this colloidal membrane shares many similarities with lipid bilayers [6].

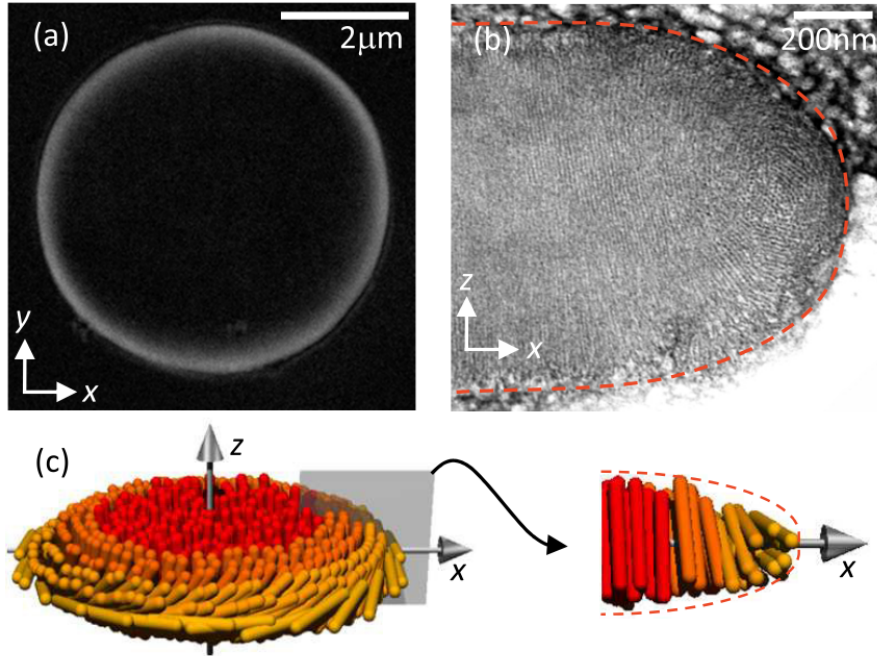


Figure 1.5: Structure of a colloidal membrane at $T = 22^\circ\text{C}$ and Dextran concentration $Dext = 45 \text{ mg ml}^{-1}$ [30]. (a) A 2D LC-PolScope retardance map showing a bright edge band due to rod tilting. (b) Electron micrograph cross section revealing the tilted rods and curved edge profile. (c) Schematic illustrating the curved edge and the resulting local twist of the rods (reproduced from Ref. [29]).

The 2D-LC-PolScope image reveals the twisted edge structure of the colloidal membrane (see Fig. 1.5). The dark bulk region inside the membrane indicates that the rods are aligned along the z -axis, while at the bright edge region the rods become tilted. It is confirmed that the tilt reaches 90° , changing from the normal direction in the bulk to a tangential orientation at the edge [53] [48] [68]. The formation of this curved edge structure can be understood as a result of the competition between reducing interfacial tension and the energetic cost of twist distortions.

The twisted edge gives the colloidal membrane an effective chirality determined by the chirality of the virus suspension and the diameter of the membrane. If the membrane diameter is smaller than the virus length, the twisted edge does not appear and the rods remain aligned along the z -axis. Otherwise, if the virus suspension is chiral, the edge adopts the same chirality. If the suspension is achiral, the edge is equally likely to be left-handed or right-handed.

When two membranes with the same handedness coalesce, various structures can emerge, such as π -walls, pores, Möbius anchors, and colloidal skyrmions. During this homo-chiral coalescence process, thermal fluctuations of the approaching edges can form a bridge that traps a 180° twist of the rods. This trapped twist can either be expelled to the edge, forming a defect-free daughter membrane, or grow into a one-dimensional line defect known as a π -wall [91] [31].

Depending on the interfacial tension between the π -wall and the membrane edge, the π -wall can further evolve into an alternating bridge-pore array (ABPA) (see Fig. 1.6). This structure can transform back into a π -wall as the temperature changes, since temperature controls the effective chirality of the system [31].

Colloidal skyrmions are another important structure that we focus on. In experiments on a colloidal membrane, the laser spot of optical tweezers rotates the rods normal to the beam, so that the laser spot traces out a π -wall when it is moved across the surface, and the two ends of the π -wall can then be quickly joined to form a closed

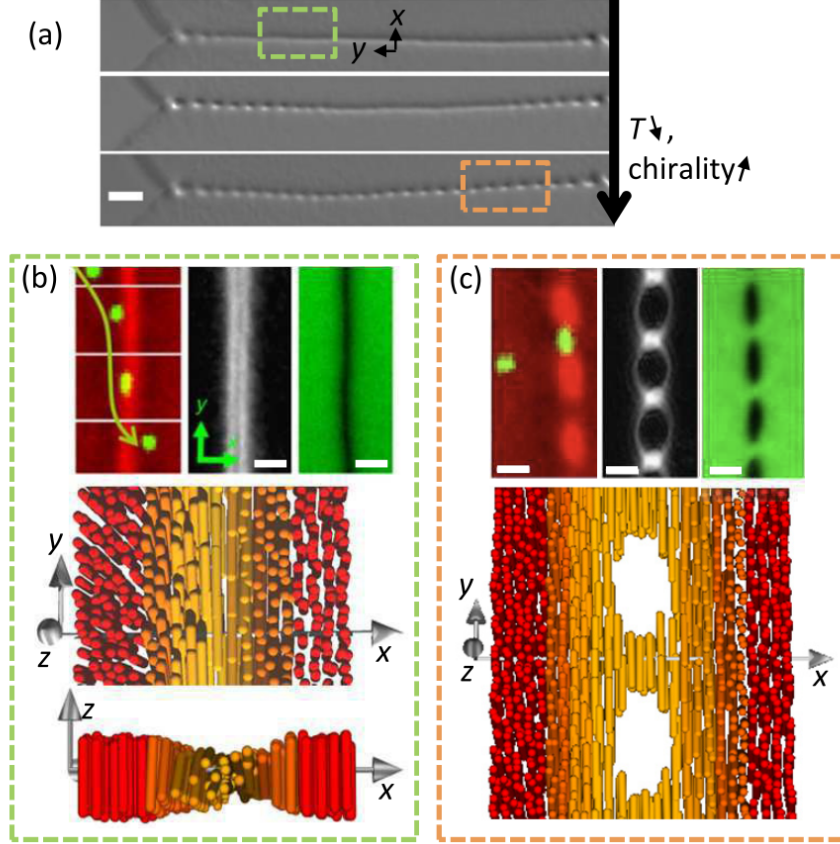


Figure 1.6: Reconfigurable self-assembly in fd-wt colloidal membranes: the transition from a π -wall to an alternating bridge-pore array (ABPA) [32]. (a) A temperature quench from 55°C to 22°C at $D_{\text{ext}} = 45 \text{ mg ml}^{-1}$ drives the transformation of a π -wall into an ABPA. This process is reversible; DIC images, scale bar $5 \mu\text{m}$. (b) π -wall structure: time-lapse fluorescence images show a 180° rotation of labeled rods across the wall, consistent with LC-PolScope measurements. The defect appears thinner at its center. (c) ABPA structure: combined fluorescence and phase-contrast imaging shows 180° twist within bridges, while pores are devoid of rods. LC-PolScope confirms the twist; scale bars $2 \mu\text{m}$ (reproduced from Ref. [29]).

ring (see Fig. 4.1). This ring gradually shrinks and reaches an equilibrium diameter of about $\sim 1 \mu\text{m}$ [30] [91].

The colloidal skyrmion is metastable and shares similarities with skyrmion excitations studied in hard condensed matter systems. We will discuss this structure in more detail in Chapter 4.

1.3 Theory

1.3.1 Frank–Oseen theory

The Frank–Oseen elastic theory is commonly used to describe the orientational distortions of the director field in liquid crystals. In this description, the local orientation of the rod-like particles is represented by a unit director field $\mathbf{n}(\mathbf{r})$. When the director field varies in space, the system pays an elastic free energy cost.

In general, the director field can undergo three basic types of distortions: splay, twist, and bend (see Fig. 1.7). These deformation modes are characterized by three elastic constants K_1 , K_2 , and K_3 , respectively [77]. The Frank elastic free energy of a nematic liquid crystal can be written as

$$F = \int d^3r \left[\frac{1}{2} K_1 (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2} K_3 |\mathbf{n} \times (\nabla \times \mathbf{n})|^2 \right]. \quad (1.1)$$

When the saddle-splay contribution is included, the full expression becomes

$$\begin{aligned} f &= \frac{1}{2} K_1 (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2} K_3 |\mathbf{n} \times (\nabla \times \mathbf{n})|^2 \\ &+ \frac{1}{2} K_{24} \nabla \cdot [(\mathbf{n} \cdot \nabla) \mathbf{n} - \mathbf{n} (\nabla \cdot \mathbf{n})], \end{aligned} \quad (1.2)$$

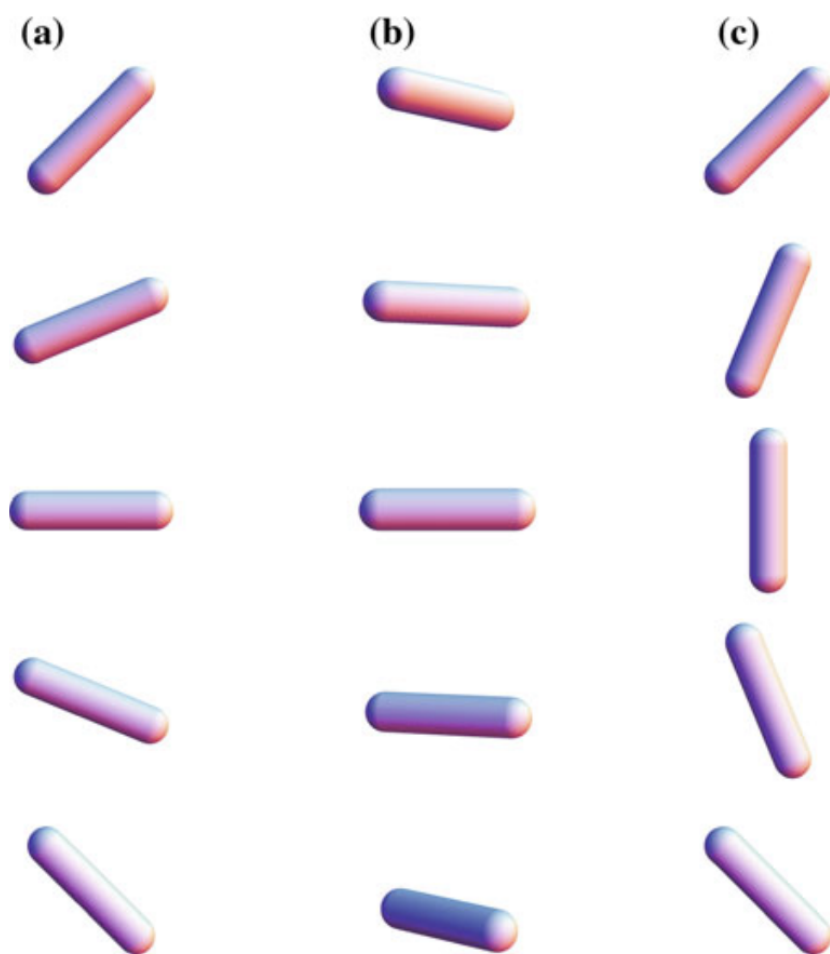


Figure 1.7: Three nematic modes of distortion: (a) Splay. (b) Twist. (c) Bend (reproduced from Ref. [77]).

where the last term corresponds to the saddle-splay deformation mode which is a total divergence and can be written as a surface term in the free energy.

In the one-constant approximation, the elastic free energy can be simplified to

$$F = \int d^3r \frac{1}{2} K (\partial_\gamma n_\alpha) (\partial_\gamma n_\alpha). \quad (1.3)$$

This expression represents the simplest form of the Frank elastic energy, where any spatial variation of the director field costs elastic free energy.

For chiral liquid crystals, the twist deformation has a preferred handedness. This preference is characterized by the chiral wave number q_0 . In this case, the Frank free energy density becomes

$$F = \int d^3r \left[\frac{1}{2} K_1 (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n} - q_0)^2 + \frac{1}{2} K_3 |\mathbf{n} \times (\nabla \times \mathbf{n})|^2 \right]. \quad (1.4)$$

Here $q_0 = 2\pi/p$ represents the intrinsic twist of the chiral liquid crystal, where p is the cholesteric pitch.

1.3.2 Landau-de Gennes theory

Another commonly used theoretical description is the Landau-de Gennes theory. In this theory, the orientational order of liquid crystals is described by a second-rank tensor order parameter called the $\mathbf{Q}$ tensor. The $\mathbf{Q}$ tensor is symmetric and traceless, and it vanishes in the isotropic phase.

In the uniaxial nematic phase, the $\mathbf{Q}$ tensor can be written as

$$Q_{\alpha\beta} = \frac{3}{2} S \left(n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta} \right), \quad (1.5)$$

where S is the scalar order parameter and $\mathbf{n}$ is the director field. In this way, the $\mathbf{Q}$

tensor describes both the direction and the magnitude of orientational order. Compared with the director description, the $\mathbf{Q}$ tensor provides a more general framework because the magnitude of the order parameter can vary in space. This feature becomes important near defects or strongly distorted regions.

In the Landau–de Gennes theory, the total free energy is written as a functional of the $\mathbf{Q}$ tensor. Here we consider the bulk and distortion contributions,

$$F = \int d^3r (f_{\text{bulk}} + f_{\text{distortion}}). \quad (1.6)$$

The bulk free energy density describes the tendency of the system to develop orientational order. It is written in terms of rotational invariants of the $\mathbf{Q}$ tensor,

$$f_{\text{bulk}} = \frac{1}{2}A \text{tr}(\mathbf{Q}^2) + \frac{1}{3}B \text{tr}(\mathbf{Q}^3) + \frac{1}{4}C (\text{tr}(\mathbf{Q}^2))^2. \quad (1.7)$$

For a uniaxial state this expression becomes

$$f_{\text{bulk}} = \frac{3}{4}AS^2 + \frac{1}{4}BS^3 + \frac{9}{16}CS^4. \quad (1.8)$$

Minimizing the bulk free energy gives either $S = 0$ for the isotropic phase or

$$S = S_0 = \frac{-B + \sqrt{B^2 - 24AC}}{6C}, \quad (1.9)$$

which determines the preferred magnitude of orientational order.

The distortion free energy describes the energetic cost of spatial variations of the orientational order. In the simplest approximation, it can be written as

$$f_{\text{distortion}} = \frac{1}{2}L(\partial_k Q_{ij})(\partial_k Q_{ij}), \quad (1.10)$$

where L is an elastic coefficient.

A more general description includes several independent elastic coefficients. In

this case the distortion free energy can be written as

$$f_{\text{distortion}} = \frac{1}{2}L_1 \frac{\partial Q_{ij}}{\partial x_k} \frac{\partial Q_{ij}}{\partial x_k} + \frac{1}{2}L_2 \frac{\partial Q_{ij}}{\partial x_j} \frac{\partial Q_{ik}}{\partial x_k} + \frac{1}{2}L_3 \frac{\partial Q_{ik}}{\partial x_j} \frac{\partial Q_{ij}}{\partial x_k} \quad (1.11)$$

$$+ \frac{1}{2}L_4 \epsilon_{lik} Q_{lj} \frac{\partial Q_{ij}}{\partial x_k} + \frac{1}{2}L_6 Q_{lk} \frac{\partial Q_{ij}}{\partial x_l} \frac{\partial Q_{ij}}{\partial x_k}. \quad (1.12)$$

Here L_1 , L_2 , L_3 , L_4 , and L_6 are elastic coefficients. The first three terms describe different gradient contributions to the elastic energy. The L_4 term introduces chirality, and the L_6 term allows different splay and bend elastic constants.

If the $\mathbf{Q}$ tensor is assumed to be uniaxial with constant scalar order parameter, the Landau–de Gennes distortion free energy reduces to the Frank–Oseen elastic free energy density described in last section. In this limit the Frank elastic constants can be expressed in terms of the Landau–de Gennes coefficients as

$$K_1 = \frac{9}{4}S^2(2L_1 + L_2 + L_3 - SL_6), \quad (1.13)$$

$$K_2 = \frac{9}{4}S^2(2L_1 - SL_6), \quad (1.14)$$

$$K_3 = \frac{9}{4}S^2(2L_1 + L_2 + L_3 + 2SL_6), \quad (1.15)$$

$$K_{24} = -\frac{9}{4}S^2(-2L_1 - L_3 + SL_6), \quad (1.16)$$

$$q_0 = -\frac{L_4}{2(2L_1 - SL_6)}. \quad (1.17)$$

Conversely, the Landau–de Gennes coefficients can be written in terms of the Frank elastic constants [85],

$$L_1 = \frac{2}{27S^2}(K_3 - K_1 + 3K_2), \quad (1.18)$$

$$L_2 = \frac{4}{9S^2}(K_1 - K_{24}), \quad (1.19)$$

$$L_3 = \frac{4}{9S^2}(K_{24} - K_2), \quad (1.20)$$

$$L_4 = -\frac{8}{9S^2}q_0K_2, \quad (1.21)$$

$$L_6 = \frac{4}{27S^3}(K_3 - K_1). \quad (1.22)$$

The preferred twist of a chiral nematic is characterized by the chiral wave number

$$q_0 = \frac{2\pi}{p}, \quad (1.23)$$

where p is the cholesteric pitch.

Chapter 2

The theory of colloidal membranes

2.1 Flat membrane

As mentioned in Chapter 1, planar colloidal membranes are monolayers formed by rod-like colloidal particles such as fd viruses in the presence of non-adsorbing polymers through the depletion interaction [6] [90] [5] [4]. Experiments show that planar colloidal membranes exhibit a variety of structures and defects. For example, the rods near the edge tilt and twist, forming a narrow twisted boundary layer. When two membranes partially coalesce, the rods rotate by 180° across a narrow region called a π -wall. In addition, other structures such as pores and skyrmion-like textures have also been observed in these systems [8] [30] [92] [91].

To understand these structures, several theoretical models have been proposed. In this chapter, I review two theories that describe the structure of planar colloidal membranes. The first is the entropy-based theory developed by Kang et al. [44], which describes the membrane structure by considering depletion interactions, Frank elastic energy, and rod fluctuation entropy. The second is the theory proposed by Kaplan and Meyer [45], which treats the membrane as a system containing both smectic-A-like and cholesteric regions and introduces an order parameter to describe the transition between these phases.

In the Kang-Lubensky model, it is assumed that once a membrane is formed, rods do not exchange with the surrounding solution, so the total membrane volume is fixed. The membrane structure is described using two variables in Cartesian coordinates assuming the radius of large membranes is much greater than the penetration depth of edge twist. The first variable is the tilt angle of the rods $\theta(x)$ (see Fig. 2.1) relative to the membrane normal which describes the local orientation of the rods. The second variable is the effective membrane half-thickness

$$h(x) = t \cos \theta(x) + b(x), \quad (2.1)$$

where t is the half-length of the rods and $b(x)$ represents the height fluctuations of the rods perpendicular to the membrane plane. In this description, the membrane thickness arises from both the geometric projection of tilted rods and the protrusion fluctuations of rods [90].

Within this framework, the total free energy of the membrane can be written as

$$\frac{F}{2nak_{\text{B}}TL_y} = F_{\text{dep}} + F_{\text{Frank}} + F_{\text{rod}}, \quad (2.2)$$

where n is the depletant concentration, a is the characteristic depletant radius, T is the temperature, and k_B is the Boltzmann constant. In Cartesian coordinates, the large twisted membrane is regarded as a rectangular membrane of length $L_y \rightarrow \infty$ along the y -direction and length $2L_x$ along the x -direction with rods rotating along (see Fig. 2.1). Here the three contributions correspond to depletion interactions, liquid-crystal elasticity, and rod protrusion fluctuations, respectively.

The depletion contribution to the free energy is written as

$$F_{\text{dep}} = \int_0^{L_x} dx \left[\sqrt{1 + (\partial_x h)^2} - \frac{h}{t + b_0} \right] + h(0), \quad (2.3)$$

which describes the depletion interaction between the rods and the non-adsorbing polymers [5] [4]. Here b_0 is the preferred amplitude of rod height fluctuations in the membrane interior.

The first term,

$$\sqrt{1 + (\partial_x h)^2}, \quad (2.4)$$

represents the surface area of the membrane edge. Since the excluded volume accessible to the polymers depends on the membrane surface area, this term effectively acts as a surface tension that penalizes large surface area. The second term arises from the constraint of fixed membrane volume. The final term $h(0)$ accounts for the free

boundary condition at the membrane edge.

The second contribution to the free energy is the Frank elastic energy with chirality,

$$F_{\text{Frank}} = \frac{kt}{2} \int_0^{L_x} dx h [(\partial_x \theta)^2 + 2q \partial_x \theta]. \quad (2.5)$$

Here k is a dimensionless parameter related to the Frank elastic constant K of the liquid crystal and q is the preferred twist wavenumber of the cholesteric phase.

The final contribution describes fluctuations of rods perpendicular to the membrane plane,

$$F_{\text{rod}} = \frac{2\pi}{\sqrt{3}\xi^2} \int_0^{L_x} dx \cos \theta (h - t \cos \theta - b_0)^2. \quad (2.6)$$

Here ξ is a characteristic length scale related to the spacing between neighboring rods in the membrane. This term couples the membrane thickness $h(x)$ to the rod tilt angle $\theta(x)$. When the rods are nearly perpendicular to the membrane plane ($\theta \approx 0$), fluctuations are suppressed and the membrane thickness is approximately $h \approx t \cos \theta$. When the rods tilt strongly, the coupling becomes weaker and larger fluctuations become possible.

By minimizing the total free energy with respect to $h(x)$ and $\theta(x)$, the theory predicts the profile of edge and π -wall qualitatively and quantitatively. In the membrane interior the rods remain nearly aligned with the membrane normal. Near the membrane edge, however, the rods tilt and twist over the twist penetration length. The model also predicts a curved edge profile resulting from the competition between depletion and liquid-crystal elasticity. The model can also describe the structure of a π -wall. The theory predicts that the tilt angle varies smoothly across the wall and reaches approximately $\theta = \pi/2$ at the center of the wall, where the rods lie nearly parallel to the membrane plane. The membrane thickness also varies across the wall due to various Frank-to-depletion ratios and chirality.

One advantage of this model is that the physical origin of each contribution to the

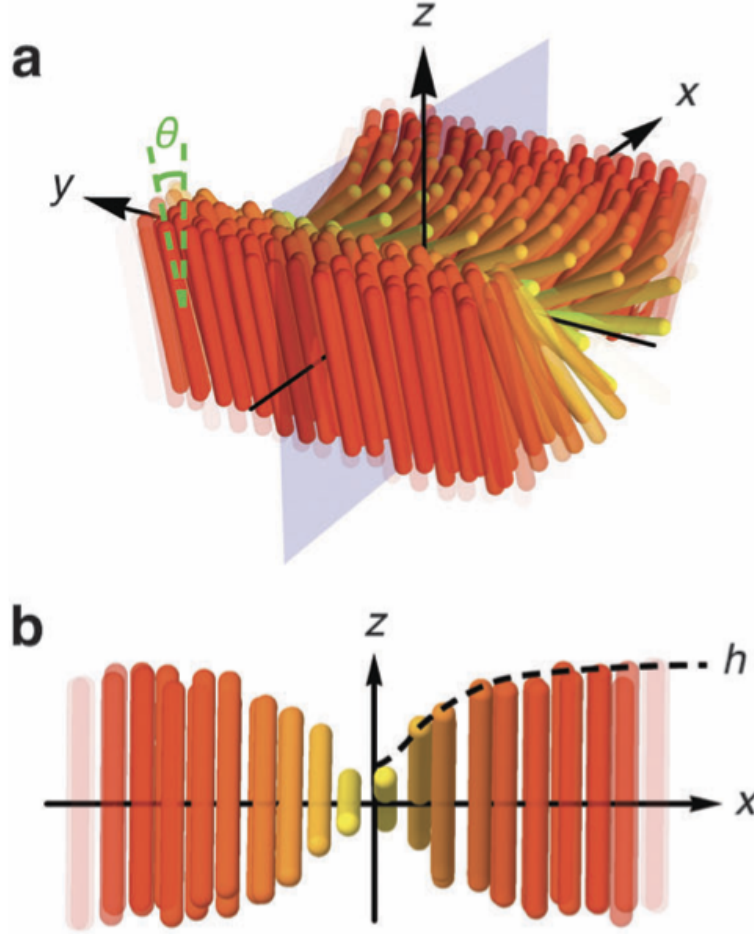


Figure 2.1: Vertical π -wall profiles. (a) Perspective and (b) cross-sectional schematics illustrate the parameterization of the π -wall and the Cartesian coordinate system. The cross section (b) shows rods intersecting the plane in (a). Here h is the membrane half-thickness, and θ is the rod tilt angle (modified from Ref. [44] Fig. 7).

free energy is clearly identified. The theory explicitly incorporates depletion interactions, liquid-crystal elasticity, and rod protrusion entropy, allowing it to describe the twisted edge structure, the dependence of line tension on chirality, and the structure of π -walls.

However, the model also has limitations. It describes the membrane using only two coarse-grained variables and does not explicitly include an order parameter describing smectic ordering in the membrane. In addition, some approximations used in the model may become less accurate in regions where the rods are strongly tilted.

Another theoretical description of planar colloidal membranes was proposed by Kaplan and Meyer [45]. In this approach, the membrane is treated as a liquid-crystalline system composed of two regions: a smectic-A-like phase in the membrane interior and a cholesteric phase that appears near the membrane edge or inside a π -wall. To describe the transition between these two regions, the theory introduces a scalar order parameter Ψ , which represents the local concentration of the smectic-A phase. When $\Psi = \Psi_0$, the rods are perfectly aligned and the membrane behaves like a smectic-A layer. When $\Psi = 0$, the smectic order disappears and the region behaves like a cholesteric liquid crystal.

In addition to the order parameter Ψ , the theory also includes the rod tilt angle θ , which measures the angle between the rod orientation and the membrane normal, and the local membrane thickness t , which describes variations in the membrane thickness near interfaces. In this description, Ψ and θ are non-conserved fields, while the thickness t is a conserved field because the total membrane volume remains fixed.

The total free energy of the system is written as

$$\begin{aligned}
F = & \int dx |t| \left[f_{\text{Ch-A}} + \frac{C_t}{2} \Psi^2 (t^2 - (t_0 \cos \theta)^2)^2 - \nu \right] \\
& + \oint ds \left[\sigma_{\parallel} (\hat{\mathbf{N}} \cdot \mathbf{n})^2 + \sigma_{\perp} (\hat{\mathbf{N}} \times \mathbf{n})^2 + k \kappa^2 \right].
\end{aligned} \tag{2.7}$$

Here t is the local membrane thickness and t_0 is the rod length. The C_t term couples the membrane thickness to the rod tilt angle. When the smectic order parameter Ψ is large, the membrane thickness is constrained to follow $t_0 \cos \theta$. When Ψ approaches zero, this constraint becomes weaker, allowing the thickness to vary more freely in the cholesteric region. The parameter ν is a Lagrange multiplier enforcing the constraint of constant membrane volume. The second integral represents the surface energy, where $\hat{\mathbf{N}}$ is the unit normal of the membrane surface and $\mathbf{n}$ is the director describing the rod orientation. The coefficients $\sigma_{\parallel}$ and $\sigma_{\perp}$ represent anisotropic

surface tensions associated with depletion interactions, and κ is the curvature of the membrane edge with bending modulus k [37] (see Fig. 2.2).

The bulk free energy density is given by

$$f_{\text{Ch-A}} = -\frac{r}{2}\Psi^2 + \frac{u}{4}\Psi^4 + \frac{C_1}{2}(\nabla\Psi)^2 + \frac{C_2}{2}(\Psi\sin\theta)^2 + \frac{K_2}{2}(\mathbf{n}\cdot\nabla\times\mathbf{n}-q_0)^2 \quad (2.8)$$

representing the de Gennes free energy for the Ch-Sm-A transition [74] [16] [17].

By minimizing the free energy, Kaplan and Meyer obtained the structure of both the membrane edge and the π -wall. In the membrane interior the rods remain aligned with the membrane normal and the smectic order parameter is close to Ψ_0 . Near the membrane edge the smectic order gradually decreases, forming a narrow cholesteric band in which the rods tilt and twist.

The theory predicts that the membrane thickness changes continuously near the edge due to the competition between liquid-crystal elasticity and depletion-induced surface tension.

The same model can also describe the structure of a π -wall formed when two membranes coalesce. In this case the cholesteric region appears between two smectic domains, and the rods rotate by approximately 180° across the wall. The tilt angle reaches its maximum at the center of the wall, while the smectic order parameter is strongly reduced in this region. The theory predicts both the tilt profile and the thickness variation across the π -wall and allows the line tension of the defect to be calculated.

The advantage of the Kaplan Meyer model is that it introduces an order parameter to describe the transition between smectic-A and cholesteric regions. This allows the theory to capture the structural crossover at the membrane edge and inside π -walls in a continuous way. The model also naturally incorporates thickness variations and anisotropic surface tension. However, the model introduces several phenomenological

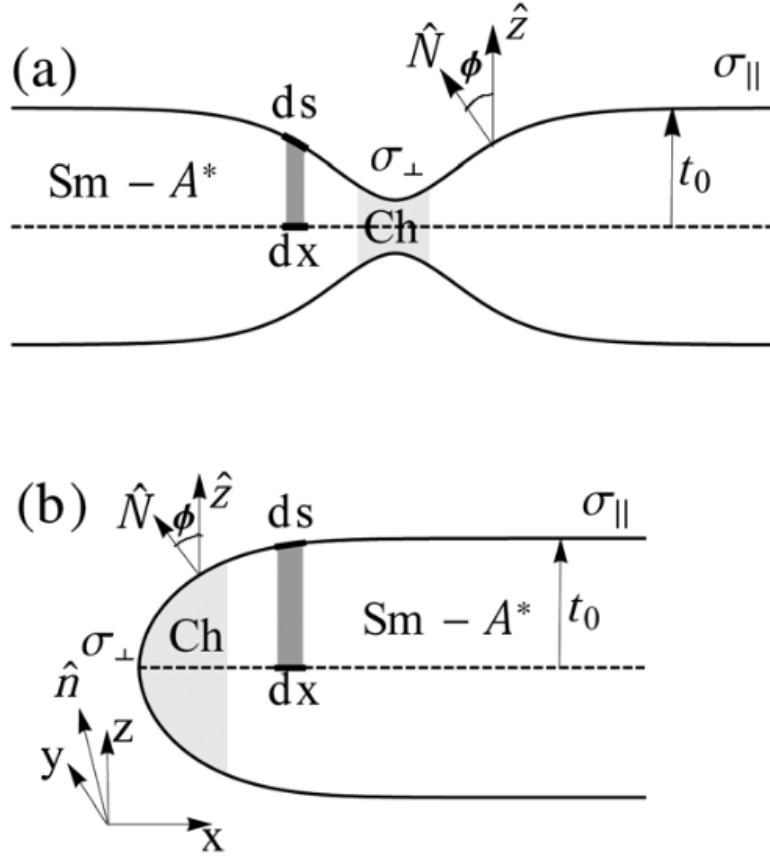


Figure 2.2: Kaplan & Meyer model: Schematics of the π -wall and membrane edge. Side views of (a) the π -wall and (b) the edge. Dashed lines indicate the mid-plane. The light-shaded region denotes the cholesterics, while the dark-shaded region represents the projection ds to dx . The surface normal $\hat{\mathbf{N}}$ lies in the (x, z) -plane, with ϕ the angle between $\hat{\mathbf{N}}$ and the z -axis. The nematic director $\hat{\mathbf{n}}$ lies in the (y, z) -plane. (modified from Ref. [45] Fig. 3).

parameters that are not always directly measurable.

These theories motivate the work in the following two chapters. In contrast, our approach incorporates depletion interactions together with the tilt interaction term to describe the system.

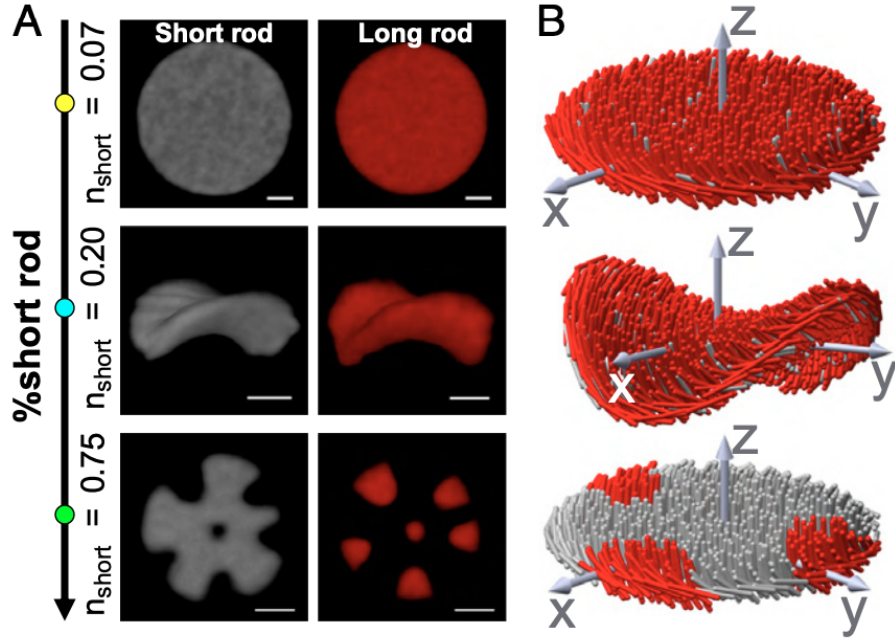


Figure 2.3: Phase diagram of binary colloidal membranes. (a) Membranes composed of long (red) and short (gray) rods at $Dext = 50 \text{ mg mL}^{-1}$. Increasing the short-rod fraction n_{short} drives a transition from flat mixed membranes to saddle-shaped structures, followed by phase separation and a return to flat membranes at higher n_{short} (scale bar $2 \mu\text{m}$). (b) Schematic showing rod arrangement and orientation at different n_{short} (modified from Ref. [46] Fig. 3).

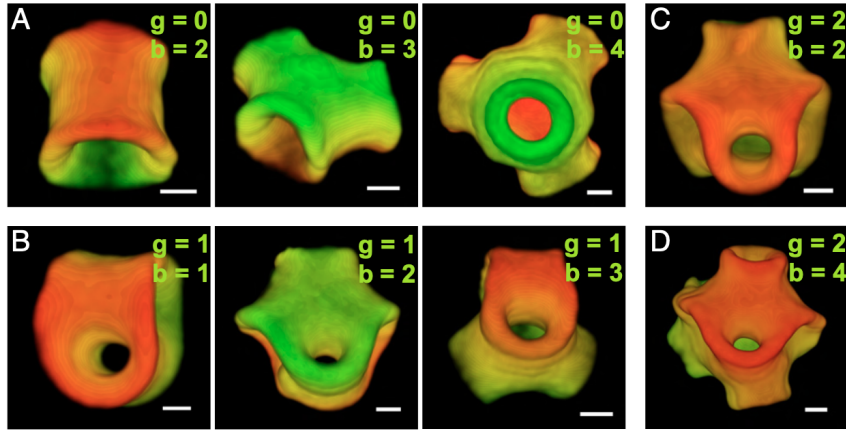


Figure 2.4: Topologically complex colloidal membranes characterized by genus g and number of boundaries b . (a) Catenoid-like membranes and their derivatives, including three-noid and four-noid structures. (b) Shapes with additional handles, such as saddles and catenoids with handles. (c,d) Genus-two surfaces with $b = 2$ and $b = 4$, respectively. Experiments were performed at $Dext = 50 \text{ mg mL}^{-1}$ and $n_{\text{short}} = 0.2$ (scale bar $2 \mu\text{m}$) (modified from Ref. [46] Fig. 3).

2.2 Curved geometry

Curved colloidal membranes were experimentally observed in two-component systems composed of rod-like viruses with different lengths [22] [34] [7]. In these experiments, mixtures of filamentous viruses M13KO7 (length ~ 1200 nm) and M13-wt (length ~ 880 nm) were assembled into membranes in the presence of the non-adsorbing polymer dextran through depletion interactions [6] [90] [5]. Both types of rods have the same chirality and can coassemble into a single membrane phase over a range of concentrations. The relatively large length scale of these colloidal membranes, typically on the order of micrometers, enables direct visualization of their three-dimensional shapes and dynamical pathways using optical microscopy [30] [8].

The experiments were performed by varying the number fraction of short rods [46], denoted as n_{short} , while keeping the polymer concentration fixed (see Fig. 2.3). At small values of n_{short} , the system assembled into flat disk-shaped membranes similar to those observed in single-component systems. However, as the fraction of short rods increased to an intermediate range ($0.2 < n_{\text{short}} < 0.35$), the membranes spontaneously adopted three-dimensional saddle-like shapes with negative Gaussian curvature. When the fraction of short rods becomes even larger ($n_{\text{short}} > 0.35$), the system undergoes phase separation between the long and short rods, and the membranes revert to flat disk-like shapes.

Time-resolved microscopy also revealed how curved membranes evolve through coalescence events [92]. Initially, small saddle-shaped membranes form and grow in size as they merge with neighboring membranes. Depending on the coalescence pathway, the resulting structures can remain saddle-shaped or transform into topologically distinct surfaces. In particular, fusion of two saddle membranes can produce catenoid-like structures with two openings. Subsequent fusion events can generate more complex shapes such as trinoids, four-noids, and structures with multiple handles (see Fig. 2.4). These assemblies exhibit predominantly negative Gaussian curvature over

large regions of the membrane surface.

The experiment results inspired us to work on curved membranes especially cylindrical surface [41]. We choose a cylindrical surface as an example of curved membrane for simplification.

Here we define the various geometric quantities [73] and introduce calculations of the membrane free energy on a curved surface. If $\mathbf{X} = \mathbf{X}(\xi^1, \xi^2)$ describes a surface in three-dimensional space, then the tangent vectors along the coordinate directions are $\mathbf{t}_\mu = \partial \mathbf{X} / \partial \xi^\mu$, and the normal to the surface is $\hat{\mathbf{n}} = \mathbf{t}_1 \times \mathbf{t}_2 / |\mathbf{t}_1 \times \mathbf{t}_2|$. Distances along the surface are computed using the metric tensor $g_{\mu\nu} = \mathbf{t}_\mu \cdot \mathbf{t}_\nu$. For example, the area element of the surface is $dA = \sqrt{g} d\xi^1 d\xi^2$, where g is the determinant $g_{\mu\nu}$. As usual, the inverse of the metric tensor is written as $g^{\mu\nu}$, where $g^{\mu\lambda} g_{\lambda\nu} = \delta_\nu^\mu$, and the inverse of the metric tensor is used to raise indices, as in $\mathbf{t}^\mu = g^{\mu\nu} \mathbf{t}_\nu$. Some useful identities are $\mathbf{t}_\mu \times \mathbf{t}_\nu = \epsilon_{\mu\nu} \hat{\mathbf{n}}$ and $\mathbf{t}_\mu \times \hat{\mathbf{n}} = \epsilon_\mu^\nu \mathbf{t}_\nu$, where $\epsilon_{\mu\nu}$ is totally antisymmetric with $\epsilon_{12} = \sqrt{g}$.

We define the surface gradient of function $f(\xi^1, \xi^2)$ on the surface by

$$\nabla_S f \equiv \mathbf{t}^\mu \partial_\mu f. \quad (2.9)$$

The surface gradient of a director $\hat{\mathbf{d}}$, which in general has tangential and normal components, is given by

$$(\nabla_S)_i d_j = t_{\mu i} g^{\mu\nu} \partial_\nu d_j, \quad (2.10)$$

where the Latin indices i and j label the three Cartesian components.

We can define the surface gradient using intrinsic coordinates only as just described, or by using the Cartesian coordinates of the ambient space and projecting the three-dimensional gradient onto the tangent plane of the surface. In the second case, we extend the domain of f by imagining that the surface has a finite thickness, with f defined across that thickness such that $f(\mathbf{X}(\xi^1, \xi^2)) = f(\xi^1, \xi^2)$. There is

no prescription for how $f(X_1, X_2, X_3)$ should vary in the normal direction $\hat{\mathbf{n}}$, but the choice made is of no importance because we define the surface gradient by subtracting off the normal part:

$$\nabla_S f \equiv \frac{\partial f}{\partial \mathbf{X}} - \hat{\mathbf{n}} \hat{\mathbf{n}} \cdot \frac{\partial f}{\partial \mathbf{X}} \quad (2.11)$$

To see that the two definitions are equivalent, use the chain rule, $\partial_\mu f = \partial_\mu \mathbf{X} \cdot \partial f / \partial \mathbf{X}$, and the relationship

$$\frac{\partial \mathbf{X}}{\partial \xi^\mu} g^{\mu\nu} \frac{\partial \mathbf{X}}{\partial \xi^\nu} = \mathbf{I} - \hat{\mathbf{n}} \hat{\mathbf{n}}. \quad (2.12)$$

Derivatives of the tangent vectors along the coordinate directions have tangential and normal components given by the Christoffel symbol and the curvature tensor, respectively:

$$\partial_\mu \mathbf{t}_\nu = \Gamma_{\mu\nu}^\lambda \mathbf{t}_\lambda + K_{\mu\nu} \hat{\mathbf{n}}, \quad (2.13)$$

where $\Gamma_{\mu\nu}^\lambda = g^{\lambda\sigma}(\partial_\mu g_{\sigma\nu} + \partial_\nu g_{\sigma\mu} - \partial_\sigma g_{\mu\nu})/2$. Note that $\hat{\mathbf{n}} \cdot \mathbf{t}_\mu = 0$ and eqn (2.13) imply $\partial_\mu \hat{\mathbf{n}} = -K_\mu^\nu \mathbf{t}_\nu$. The components of the derivative of a *tangential* vector field $\mathbf{V} = V^\mu \mathbf{t}_\mu$ projected onto the surface is conveniently represented by the covariant derivative $\nabla_\mu V^\lambda$:

$$\partial_\mu \mathbf{V} - \hat{\mathbf{n}} \hat{\mathbf{n}} \cdot \partial_\mu \mathbf{V} = (\nabla_\mu V^\lambda) \mathbf{t}_\lambda, \quad (2.14)$$

where $\nabla_\mu V^\lambda = \partial_\mu V^\lambda + \Gamma_{\mu\nu}^\lambda V^\nu$. The invariants of the curvature tensor give the mean curvature $H = g^{\mu\nu} K_{\mu\nu}/2 = (1/R_1 + 1/R_2)/2$ and the Gaussian curvature $K_G = \det K^\mu{}_\nu = 1/(R_1 R_2)$, where R_1 and R_2 are the principal radii of curvature.

There are only four independent degrees of freedom of the director gradient on a curved surface for a director field with tangential and normal components. We show that these components are splay, twist, and the two components of the bend vector. We make use of a generalization of Selinger's reformulation[78] of eqn (3.3), the central idea of which is to describe the configuration of a nematic liquid crystal in terms of the irreducible representations of gradients of the director field.[52, 78] Before applying

Selinger's reformulation to a curved surface, we review the simple case of a two-dimensional vector field on a flat surface, as described in the appendix of Selinger's article.[78] The standard decomposition would be to write the gradient of a vector field $\partial_\mu m_\nu$ as a sum of terms involving a symmetric traceless tensor, an antisymmetric tensor, and the trace of the gradient tensor, giving a total of $2 + 1 + 1 = 4$ degrees of freedom. However, since $\hat{\mathbf{m}}$ is a unit vector, there are two constraints, $m_\nu \partial_\mu m_\nu = 0$, leaving a total of two degrees of freedom, in contrast with the six degrees of freedom of the gradient of the unit director field in three dimensions. Decomposing the gradient $\partial_\mu m_\nu$ into parts in which the first leg is either parallel or perpendicular to the director, we find

$$\partial_\mu m_\nu = -m_\mu B_\nu + S(\delta_{\mu\nu} - m_\mu m_\nu), \quad (2.15)$$

where $\mathbf{B} = -(\hat{\mathbf{m}} \cdot \nabla)\hat{\mathbf{m}} = \hat{\mathbf{m}} \times (\nabla \times \mathbf{m})$ is the bend vector, $S = \nabla \cdot \hat{\mathbf{m}}$ is the splay scalar, and $\delta_{\mu\nu}$ is the Kronecker delta.[78] Since the bend vector is perpendicular to the director, it has one degree of freedom. The splay accounts for the other degree of freedom of the director gradient in two dimensions. On a curved surface with tangential directors, the natural generalization is to replace the gradients with the covariant derivative, [75] so that

$$\nabla_\mu m_\nu = -m_\mu B_\nu + S(g_{\mu\nu} - m_\mu m_\nu), \quad (2.16)$$

where the bend vector is $B_\nu = -m^\mu \nabla_\mu m_\nu$ and the splay is $S = \nabla_\mu m^\mu$.

To apply this formulation to directors with a normal component on a curved surface, we replace the three-dimensional ordinary derivative in the director gradient, eqn (3.2),

$$(\nabla_S)_i d_j = t_{\mu i} g^{\mu\nu} \partial_\nu d_j. \quad (2.17)$$

At first sight, this tensor may seem to have nine degrees of freedom for a general vector field $\mathbf{d}$, but because the surface derivative is a linear combination of the two deriva-

tives ∂_μ , it only has at most six degrees of freedom. Likewise, since the constraint $d_j (\nabla_S)_i d_j = 0$ follows from $d_j \partial_\mu d_j = 0$, there are only two independent constraints, leading to total of four degrees of freedom.

We decompose the surface gradient of the director field in the same way as the gradient of a director field in three dimensional space is decomposed:[78]

$$(\nabla_S)_i d_j = -d_i B_j + \frac{1}{2} \epsilon_{ijk} T d_k + \frac{S}{2} (\delta_{ij} - d_i d_j) + \Delta_{ij}, \quad (2.18)$$

where ϵ_{ijk} is the Levi-Civita symbol,

$$\mathbf{B} = -(\hat{\mathbf{d}} \cdot \nabla_S) \mathbf{d} = \hat{\mathbf{d}} \times (\nabla_S \times \hat{\mathbf{d}}) \quad (2.19)$$

is the bend vector,

$$T = \hat{\mathbf{d}} \cdot (\nabla_S \times \hat{\mathbf{d}}) \quad (2.20)$$

is the twist pseudoscalar,

$$\mathbf{S} = (\nabla_S \cdot \hat{\mathbf{d}}) \hat{\mathbf{d}} = S \hat{\mathbf{d}} \quad (2.21)$$

is the splay vector, and

$$\begin{aligned} \Delta_{ij} &= \frac{1}{2} \left[(\nabla_S)_i d_j + (\nabla_S)_j d_i + d_i B_j + d_j B_i \right. \\ &\quad \left. - S (\delta_{ij} - d_i d_j) \right] \end{aligned} \quad (2.22)$$

is the biaxial splay.

The bend vector has two degrees of freedom, since it is perpendicular to the director. The twist pseudoscalar and splay scalar have one degree of freedom each, and the traceless symmetric biaxial splay tensor has two degrees of freedom once we account for the constraint $\Delta_{ij} d_j = 0$. Since the surface gradient of the director field has only four degrees of freedom, the bend, twist, splay, and biaxial splay for

directors on a surface must not all be independent. To find the relation between these quantities, we use the fact that the first leg of the surface gradient has no normal component,

$$(\hat{\mathbf{n}} \cdot \nabla_S) \hat{\mathbf{d}} = -(\hat{\mathbf{n}} \cdot \hat{\mathbf{d}}) \mathbf{B} + \frac{1}{2} T \hat{\mathbf{d}} \times \hat{\mathbf{n}} + \frac{1}{2} S (\hat{\mathbf{n}} - d_n \hat{\mathbf{d}}) + \hat{\mathbf{n}} \cdot \Delta = 0, \quad (2.23)$$

where $d_n = \hat{\mathbf{n}} \cdot \hat{\mathbf{d}}$ is the normal component of the director. Note that eqn (2.23) is only two constraints, since the component along the director automatically vanishes. To understand the implications of the constraints, eqn (2.23), it is convenient to introduce an orthonormal frame in the plane perpendicular to the director.[42] We define $\hat{\mathbf{e}}_1 = \hat{\mathbf{n}} \times \hat{\mathbf{d}}$ and $\hat{\mathbf{e}}_2 = \hat{\mathbf{d}} \times \hat{\mathbf{e}}_1 = \hat{\mathbf{n}} - d_n \hat{\mathbf{d}}$. Note that the bend vector and the biaxial splay tensor only have components in the $\hat{\mathbf{e}}_1$ - $\hat{\mathbf{e}}_2$ plane, i.e. $\mathbf{B} = B_\alpha \hat{\mathbf{e}}_\alpha$ and $\Delta = \hat{\mathbf{e}}_\alpha \Delta_{\alpha\beta} \hat{\mathbf{e}}_\beta$. In the $\hat{\mathbf{e}}_\alpha$ basis, the constraints become

$$-d_n B_1 - \frac{1}{2} T (1 - d_n^2) + \Delta_{12} (1 - d_n^2) = 0 \quad (2.24)$$

$$-d_n B_2 + \frac{1}{2} S (1 - d_n^2) - \Delta_{11} (1 - d_n^2) = 0. \quad (2.25)$$

We see that as long as there is a tangential component to the director ($d_n \neq 1$), we may use the constraints to eliminate the biaxial splay and describe the director gradient on a curved surface in term of the four quantities B_α , T , and S only. In contrast, when the director is everywhere normal to surface, the constraints imply that there is no bend. Of course, the bend and the twist vanish for a normal director field since the surface curl of the normal vanishes, $\nabla_S \times \hat{\mathbf{n}} = 0$. In this case the splay and the biaxial splay are the only potentially nonzero components of the director gradient:

$$S = -2H \quad (2.26)$$

$$\Delta_{ij} = -(K^{\mu\nu} - H g^{\mu\nu}) t_{\mu i} t_{\nu j}. \quad (2.27)$$

When the director is always normal to the surface, the director gradients depend only on the curvature of the surface.

In the general case in which the director has both tangential and normal components, $\hat{\mathbf{d}} = d^\mu \mathbf{t}_\mu + d_n \hat{\mathbf{n}}$, direct calculation shows that

$$\begin{aligned} \mathbf{B} = & \left[-d^\mu \nabla_\mu d^\nu + d_\mu \nabla^\nu d^\mu + d_n g^{\mu\nu} (\partial_\mu d_n + K_{\mu\lambda} d^\lambda) \right] \mathbf{t}_\nu \\ & - d^\mu (\partial_\mu d_n + K_{\mu\nu} d^\nu) \hat{\mathbf{n}} \end{aligned} \quad (2.28)$$

$$T = d_n \epsilon^\mu{}_\nu \nabla_\mu d^\nu - \epsilon^\mu{}_\nu (\partial_\mu d_n) d^\nu + d^\mu \epsilon_\mu{}^\nu K_{\nu\lambda} d^\lambda \quad (2.29)$$

$$S = \nabla_\mu d^\mu - 2d_n H, \quad (2.30)$$

where $\epsilon_{\mu\nu}$ is the covariant Levi-Civita symbol, with $\epsilon_{12} = \sqrt{g}$ and $g = \det g_{\mu\nu}$. As a check on our formulas, we see that when the director lies wholly in the tangent plane, we recover expressions that have appeared in the literature many times before:[38, 93, 63, 72, 76, 88]

$$\mathbf{B} = -(d^\mu \nabla_\mu d^\nu) \mathbf{t}_\nu - d^\mu K_{\mu\nu} d^\nu \hat{\mathbf{n}} \quad (2.31)$$

$$T = d^\mu \epsilon_{\mu\nu} K_\lambda{}^\nu d^\lambda. \quad (2.32)$$

Although we will not require it, for completeness we include a discussion of the saddle-splay term. Recall that in three-dimensions, if the director field $\hat{\mathbf{d}}$ of a nematic phase is normal to a family of surfaces, then the saddle-splay term at a point is twice the Gaussian curvature of the surface that passes through that point. [42] A key step in the derivation of this fact is that partial derivatives commute:

$$f_{\text{ss}}^{3\text{D}} = \frac{\partial}{\partial x_i} \left(d_i \frac{\partial d_j}{\partial x_j} - d_j \frac{\partial d_i}{\partial x_j} \right) \quad (2.33)$$

$$= \frac{\partial d_i}{\partial x_i} \frac{\partial d_j}{\partial x_j} - \frac{\partial d_i}{\partial x_j} \frac{\partial d_j}{\partial x_i} + d_i \left[\frac{\partial}{\partial x_i}, \frac{\partial}{\partial x_j} \right] d_j \quad (2.34)$$

$$= \frac{\partial d_i}{\partial x_i} \frac{\partial d_j}{\partial x_j} - \frac{\partial d_i}{\partial x_j} \frac{\partial d_j}{\partial x_i}. \quad (2.35)$$

If we were to define the saddle-splay of a director field on a single two-dimensional surface by the analogous expression with surface derivatives, we do not get the same relation with the Gaussian curvature, since the surface gradients do not commute:

$$\begin{aligned} & \nabla_S \cdot \left[\hat{\mathbf{d}} \nabla_S \cdot \hat{\mathbf{d}} - \hat{\mathbf{d}} \cdot \nabla_S \hat{\mathbf{d}} \right] \\ &= (\nabla_{S_i} d_i) (\nabla_{S_j} d_j) - (\nabla_{S_i} d_j) (\nabla_{S_j} d_i) + d_i [\nabla_{S_i}, \nabla_{S_j}] d_j. \end{aligned} \quad (2.36)$$

Indeed, when $\hat{\mathbf{d}}$ is purely normal to the surface, the term $\hat{\mathbf{d}} \cdot \nabla_S \hat{\mathbf{d}} = 0$, and $\nabla_S \cdot [\hat{\mathbf{d}} \nabla_S \cdot \hat{\mathbf{d}} - \hat{\mathbf{d}} \cdot \nabla_S \hat{\mathbf{d}}] = 4H^2$. To maintain the relation between saddle-splay and the Gaussian curvature for director fields that are purely normal, we define the two-dimensional saddle-splay to be [62]

$$f_{ss}^{2D} = (\nabla_{S_i} d_i) (\nabla_{S_j} d_j) - (\nabla_{S_i} d_j) (\nabla_{S_j} d_i). \quad (2.37)$$

A short calculation shows that the saddle-splay is related to the splay, twist, and biaxial splay via

$$f_{ss}^{2D} = \frac{1}{2} S^2 + \frac{1}{2} T^2 - \Delta_{ij} \Delta_{ij}, \quad (2.38)$$

just as in three dimensions. [78] Also, if the director field is purely normal to the surface, the same steps presented in Kamien's review article [42] show that $f_{ss}^{2D} = 2K$. Alternatively, the same result follows from eqns (2.26), (2.27), (2.38), and the Cayley-Hamilton theorem applied to K_ν^μ , which implies $K_\nu^\mu K_\mu^\nu = 4H^2 - 2K$.

Chapter 3

Competition between Frank
elasticity and tilt coupling
determines how chiral membranes
respond to curvature

3.1 Introduction

The work of this chapter is published in Soft Matter [41].

Cholesteric liquid crystals are fluids with orientational order where the chiral constituents or dopants promote a locally twisted configuration. The interplay of chirality and geometry leads to complex ordered structures.[43] In confined geometries, commensurability requirements lead to additional constraints and geometric frustration where the boundary conditions and chiral order favor incompatible configurations.[25] Confining the cholesteric to a 2D surface further frustrates the liquid crystal, and can result in the self-assembly of non-planar structures such as tubules.[39, 79, 28, 76] In liquid crystalline shells,[51] nematic [60, 59] and cholesteric textures [11, 61, 87] arise from the interaction of curvature and liquid crystalline order.[66] Early studies of colloidal membranes focused on flat disk-shaped membranes, [23, 6] whose thickness—the twist penetration depth—is determined by a balance of liquid crystal elasticity and the depletion effect. [8, 1, 45, 44] When two flat disk-shaped colloidal membranes are pressed together, the edges fuse, leading to a narrow wall in the interior of the membrane in which the rods twist through 180° .[91] This wall is called a π -wall. Meanwhile, recent numerical simulations suggest that curved membranes with π -walls may form if the chirality is sufficiently strong.[20, 21]

To untangle the effects of curvature on colloidal membranes, in this chapter we elucidate the director configurations of a curved liquid crystalline membrane using a combination of numerical modeling and analytic calculations in simple limits. We also exploit an analogy between the effect of the tilt coupling in curved cholesteric membranes and the alignment of a thermotropic cholesteric by a magnetic field.[55, 56, 14] Allowing the director configuration and membrane shape to be variable leads to a daunting theoretical problem. To simplify the calculations, we fix the shape of the membrane and focus on axisymmetric surfaces such as the cylinder, which possesses extrinsic but not intrinsic curvature. Since the shape is fixed, our model

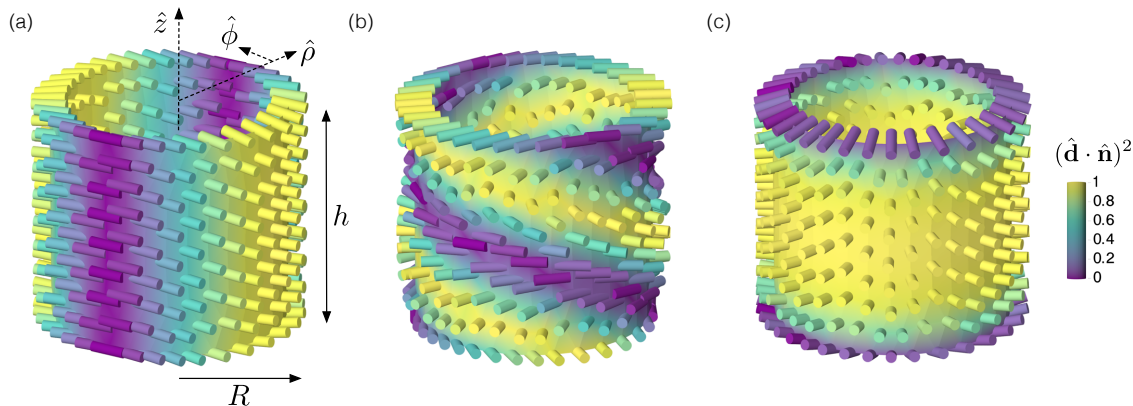


Figure 3.1: Possible equilibrium configurations adopted by a colloidal membrane in a cylindrical geometry simulated using *Morpho* for $R = 1$ and $h = 2$. Color indicates alignment of the director $\hat{\mathbf{d}}$ with the local surface normal $\hat{\mathbf{n}}$. (a) Nematic configuration where the director is spatially uniform, with $q_0 R = 0$, $CR^2/K = 1$; (b) Cholesteric configuration showing rotating director with $q_0 R = 2.5$, $CR^2/K = 1$. (c) Single-layer smectic configuration where the director is largely parallel to the normal, with $q_0 R = 0$, $CR^2/K = 5$. Here, q_0 is the preferred pitch wave-vector of the cholesteric, K is the nematic elastic constant, and C is the strength of the aligning interaction; see eqn (3.3).

could also apply to the case of a very thin cholesteric film deposited on a solid surface with a homeotropic anchoring potential. Some possible configurations that emerge for cylindrical membranes are displayed Fig. 3.1 together with coordinate definitions. To understand the role of intrinsic curvature, we also consider the family of unduloids that interpolates between a cylinder and a string of spheres; these surfaces possess spatially varying Gaussian curvature that depends on the location along the axis of the unduloid.

In this chapter, we introduce the free energy of our system, which we derive by projecting the 3D Frank free energy onto our surface. In Section 3.3, we discuss the two methods we use to determine the minima of the free energy: a numerical approach implemented using *Morpho*, a programmable environment for shape optimization,[19, 40] and analytical techniques valid in particular limits of the parameters of the free energy. We apply both methods to study the two surfaces of interest, presenting results for the cylinders and unduloids respectively.

3.2 Liquid crystal free energy on a curved surface

To see how curvature affects cholesteric order, we begin with the three-dimensional liquid crystal energy and project it onto a curved surface. The standard form of the elastic free energy of a chiral nematic liquid crystal with director $\hat{\mathbf{d}}$ is [15]

$$\begin{aligned} F = \int d^3x & \left\{ \frac{K_1}{2} (\nabla \cdot \hat{\mathbf{d}})^2 + \frac{K_2}{2} (\hat{\mathbf{d}} \cdot \nabla \times \hat{\mathbf{d}} - q_0)^2 \right. \\ & + \frac{K_3}{2} [\hat{\mathbf{d}} \times (\nabla \times \hat{\mathbf{d}})]^2 \\ & \left. - K_{24} \nabla \cdot [\hat{\mathbf{d}}(\nabla \cdot \hat{\mathbf{d}}) + \hat{\mathbf{d}} \times (\nabla \times \hat{\mathbf{d}})] \right\}, \end{aligned} \quad (3.1)$$

where K_1 , K_2 , K_3 and K_{24} are the elastic moduli associated with splay, twist, bend and saddle-splay deformations, respectively, and q_0 is the preferred twist rate. With our sign convention, a positive value of q_0 favors a left-handed cholesteric twist.

On a curved surface, the free energy cost of a configuration is described using gradients of the directors and the curvature of the membrane. Since the director varies only along the surface, but is not constrained to be parallel to it, it is natural to write the free energy for directors on a curved surface in terms of the surface gradient,

$$(\nabla_S)_i d_j = t_{\mu i} g^{\mu\nu} \partial_\nu d_j, \quad (3.2)$$

where i and j label the coordinates of the three-dimensional ambient space, μ and ν label the coordinates of the surface, $g_{\mu\nu}$ is the metric tensor, and $\mathbf{t}_\mu$ is the tangent vector along the coordinate direction μ . The many different ways to construct low-order scalars from the gradient of the director and the curvature lead to many possible terms. In fact, the free energy for a chiral nematic on a curved surface has more terms in general than the three-dimensional case shown in eqn (3.1), because all the low-order combinations could have different coefficients. [65]

To keep the number of terms manageable, we adopt a minimal model in which we

replace the three-dimensional gradients in the bulk energy by the surface gradient, and integrate over the surface rather than three dimensional space. We use a single elastic constant for the splay, twist, and bend moduli, $K_1 = K_2 = K_3 = K$, and also assume $K_{24} = 0$. To model the effect of the depletion force, we also include a potential that promotes local alignment of the director with the surface normal $\hat{\mathbf{n}}$. This term, $C[1 - (\hat{\mathbf{n}} \cdot \hat{\mathbf{d}})^2]/2$, is a generalization of the interaction used for flat membranes, $C \sin^2 \beta/2$, [1] where β is the angle that the director makes with the membrane normal. Since (positive) C penalizes tilt of the rods away from the surface normal, we call it the tilt coupling. Note that this term is effectively a homeotropic anchoring potential since it favors alignment with the surface normal.

The resulting free energy which we will use throughout this work is then given by

$$\begin{aligned}
F = & \int dA \left\{ \frac{K}{2} \left(\nabla_s \cdot \hat{\mathbf{d}} \right)^2 + \frac{K}{2} \left(\hat{\mathbf{d}} \cdot \nabla_s \times \hat{\mathbf{d}} - q_0 \right)^2 \right. \\
& \left. + \frac{K}{2} \left[\hat{\mathbf{d}} \times \left(\nabla_s \times \hat{\mathbf{d}} \right) \right]^2 + \frac{C}{2} \left[1 - \left(\hat{\mathbf{n}} \cdot \hat{\mathbf{d}} \right)^2 \right] \right\}. \quad (3.3)
\end{aligned}$$

We emphasize again that even though this energy is defined on a 2D surface, the director $\hat{\mathbf{d}}$ is fully three-dimensional and has no restricted degrees of freedom with respect to the surface normal, in contrast with nematics that are in-plane or lie at a fixed angle relative to the surface normal.

We first describe the cylindrical geometry. The cylinder is fixed, of radius R and height h and we assume no-torque boundary conditions on the director field at the cylinder's edges. We use R to non-dimensionalize both the twist penetration length $\lambda_t = \sqrt{K/C}$ and the preferred twist wave vector q_0 , obtaining the dimensionless parameters $CR^2/K = R^2/\lambda_t^2$ and q_0R , respectively. These dimensionless parameters allow us to identify possible structures based on competition between the terms appearing in the energy functional, eqn (3.3). Prototypical examples of such states are displayed in Fig. 3.1.

The Frank elasticity and tilt coupling favor incompatible states and hence tend to produce geometric frustration.[43] Where elasticity dominates, it favors a *nematic* state with a spatially uniform director for $q_0R = 0$ (Fig. 3.1a) and a *cholesteric* state, whereby the director rotates perpendicular to $\hat{\mathbf{z}}$, when q_0R is finite (Fig. 3.1b). In contrast, the tilt coupling promotes a radial configuration in the cylindrical geometry and hence when the tilt coupling is dominant we obtain radially aligned single-layer smectic-A states like that shown in Fig. 3.1(c). We will simply denote these states as *smectic*. We therefore anticipate a transition from the nematic or cholesteric configuration to the smectic configuration above some threshold value of CR^2/K as a function of q_0R . To determine the transition point, we must first consider how the cholesteric state is affected by the tilt coupling, which we shall do in subsection 3.4.1. We will return to the transition further in subsection 3.4.2.

Before doing so, we conclude our discussion of the cylindrical geometry by deriving expressions for splay, twist, and bend for a director $\hat{\mathbf{d}} = d_n\hat{\mathbf{n}} + d^\phi\mathbf{t}_\phi + d^z\mathbf{t}_z$ on a cylindrical surface that are required for our analytical calculations. In Appendix B, extending a recent reformulation of liquid crystal elasticity theory [78, 52], we show that these quantities completely determine the director gradient for a general director field on a curved surface, and we also give the expressions for an arbitrary curved surface. For a cylinder, the surface normal is $\hat{\mathbf{n}} = \hat{\boldsymbol{\rho}}$, and the tangent vectors along the coordinates ϕ and z are $\mathbf{t}_\phi = R\hat{\boldsymbol{\phi}}$ and $\mathbf{t}_z = \hat{\mathbf{z}}$. Note that $d_n = d^\rho$ and $d^\phi = \hat{\mathbf{d}} \cdot \hat{\boldsymbol{\phi}}/R$. The metric tensor is diagonal with $g_{\phi\phi} = R^2$ and $g_{zz} = 1$. The only nonzero element of the second fundamental form is $K_{\phi\phi} = -R$. Splay is given by the usual formula for divergence in cylindrical coordinates, with the derivatives with respect to ρ set to zero and evaluated at $\rho = R$:

$$S = \boldsymbol{\nabla}_S \cdot \hat{\mathbf{d}} = \partial_\phi d^\phi + \partial_z d^z + d^\rho/R. \quad (3.4)$$

Likewise, the curl of the director field is also given by the usual formula in cylindrical coordinates, restricted to a cylinder:

$$\nabla_S \times \hat{\mathbf{d}} = \hat{\rho} (\partial_\phi d^z / R - R \partial_z d^\phi) + \hat{\phi} \partial_z d^\rho + \hat{z} (d^\phi - \partial_\phi d^\rho / R). \quad (3.5)$$

Thus, the twist $T = \hat{\mathbf{d}} \cdot \nabla_S \times \hat{\mathbf{d}}$ is

$$T = d^\rho (\partial_\phi d^z / R - R \partial_z d^\phi) - [(\partial_\phi d^\rho) d^z - R (\partial_z d^\rho) d^\phi] + d^z d^\phi / R. \quad (3.6)$$

Writing $\mathbf{B} = B_n \hat{\mathbf{n}} + B^\phi \mathbf{t}_\phi + B^z \mathbf{t}_z$, we find that the components of the bend vector $\mathbf{B} = \hat{\mathbf{d}} \times (\nabla_S \times \hat{\mathbf{d}})$ are

$$B^\rho = -d^\phi (\partial_\phi d^\rho - R d^\phi) - d^z \partial_z d^\rho \quad (3.7)$$

$$B^\phi = -R d^z \partial_z d^\phi + d^z \partial_\phi d^z / R + d^\rho (\partial_\phi d^\rho / R - d^\phi) \quad (3.8)$$

$$B^z = -d^\phi \partial_\phi d^z + R^2 d^\phi \partial_z d^\phi + d^\rho \partial_z d^\rho. \quad (3.9)$$

3.3 Morpho simulation

We use two approaches to determine the director configuration on a cylinder. The first approach is using *Morpho*, a programmable environment for optimization in soft matter,[19, 40] where the surface is discretized as a simplicial complex and the director configuration $\hat{\mathbf{d}}$ is discretized using linear Lagrange elements on the simplices. In this formulation, the gradient operator is a surface gradient. Since in this discretization the elements are locally flat, no curvature terms arise. The free energy eqn (3.3) is numerically minimized with respect to $\hat{\mathbf{d}}$ subject to the normalization constraint $\hat{\mathbf{d}} \cdot \hat{\mathbf{d}} = 1$. To identify the ground state, a technique known as *continuation* can be used, where parameters are slowly changed and the system re-optimized to explore the behavior of a particular solution as a function of parameters.

Morpho can be applied to a director field on any curved surface, or indeed to geometries of different dimensionality. To gain simple physical insight, however, we restrict our study to axisymmetric surfaces such as a cylinder and an unduloid, the latter allowing us to study the role of Gaussian curvature. We perform optimization on a number of cylindrical meshes of different length h/R (see Fig. 3.1). Optimization is performed from an initial configuration using a conjugate gradient algorithm, incorporating global refinement and nested iterations to improve convergence.[19, 3] A sample code is provided as supplementary material.

Our second approach is analytical: we construct and solve the Euler-Lagrange equations associated with the free energy eqn (3.3) using appropriate *ansätze* for the solutions valid in special limits of the energy parameters. We obtain results that we then compare with the numerical results found using *Morpho* in appropriate limiting cases.

3.4 Results

3.4.1 Helical cholesteric states

When the tilt coupling vanishes, the cholesteric state can be constructed as shown in the cartoon displayed in Fig. 3.2. Starting with a bulk 3d cholesteric, where the director $\hat{\mathbf{d}}$ lies in the (x, y) plane and rotates uniformly about the z axis,

$$\hat{\mathbf{d}} = \hat{\mathbf{x}} \cos(q_0 z) - \hat{\mathbf{y}} \sin(q_0 z) \quad (3.10)$$

we insert a cylindrical surface also oriented along z as shown. The director at every point on the cylinder is then simply obtained from the bulk cholesteric. It is possible to identify places where the director is tangential to the surface; these form helices and an example is shown in Fig. 3.2 in blue. More generally, level sets of the scalar

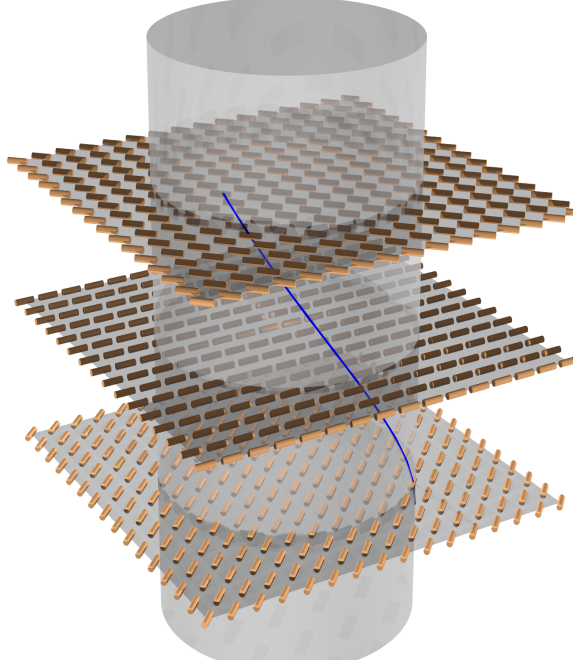


Figure 3.2: Cartoon illustrating construction of the cholesteric state with $C = 0$. Three slices of are shown of a bulk cholesteric state in 3D with the wavevector aligned along the z axis. The directors on the cylinder in the cholesteric state are given by retaining only the directors from the bulk structure on the cylinder. Contours of constant $\mathbf{n} \cdot \mathbf{d}$ form helices; an example is indicated in blue.

$\hat{\mathbf{n}} \cdot \hat{\mathbf{d}}$, where $\hat{\mathbf{n}}$ is the surface normal, form similar helices.

To provide an initial insight into the effect of the tilt coupling on the cholesteric state, we display numerically minimized structures from *Morpho* varying $q_0 R$ and CR^2/K in Fig. 3.3. These structures were obtained using *continuation*: we begin with an initially uniform nematic state $\hat{\mathbf{d}} = \hat{\mathbf{x}}$ at $q_0 R = 0$ and $CR^2/K = 0$. Note that although any uniform nematic state minimizes the free energy when $C = 0$ and $q_0 = 0$, we choose the initial state to have no z component since any nonzero C favors nematic states with $d_z = 0$. We then slowly adjust q_0 upwards, obtaining the optimized solution set as we do so. From optimized solutions at each value of q_0 , we continue from $C = 0$ upwards in C , again obtaining optimized solutions as we do. In this way, we map out the cholesteric solution set as a function of $(q_0 R, CR^2/K)$. Note that these solutions, while optimal, are not necessarily stable nor do they necessarily

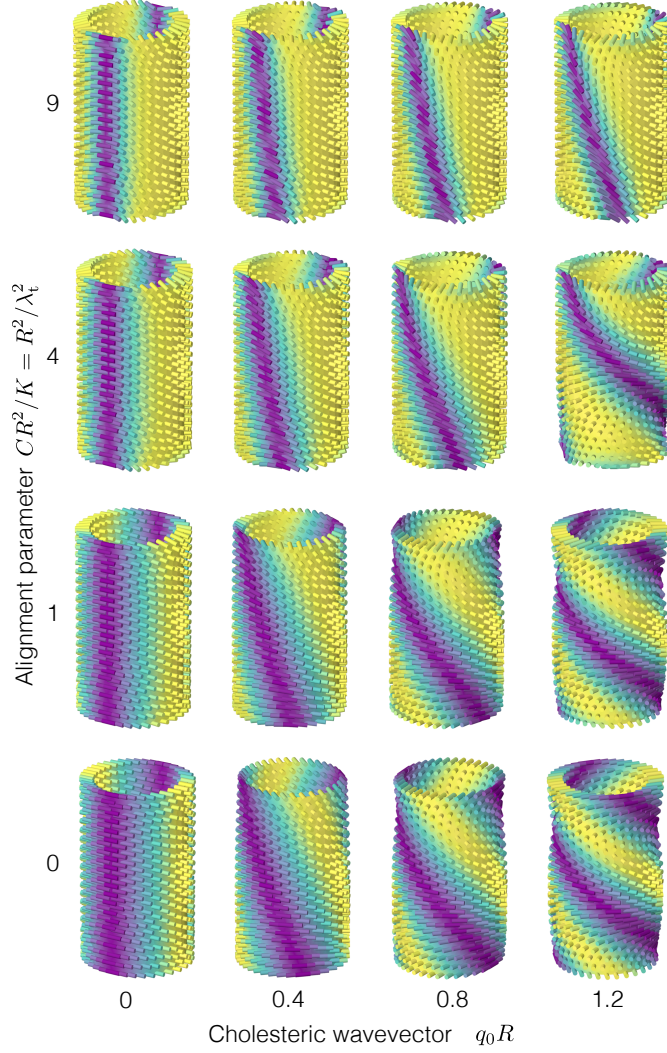


Figure 3.3: Numerically minimized cholesteric structures produced with *Morpho* on cylinders of height $h = 8$, $R = 1$ with varying cholesteric wavevector q_0R and alignment parameter CR^2/K as shown. Solutions show increasingly helical states with increasing q_0R . Increasing the alignment parameter CR^2/K localizes twist into domain walls and increases the helical pitch relative to the $CR^2/K = 0$ state. Note that these configurations do not necessarily represent the ground state since at sufficiently high values of CR^2/K , the smectic state has lower free energy than the state with two domain walls.

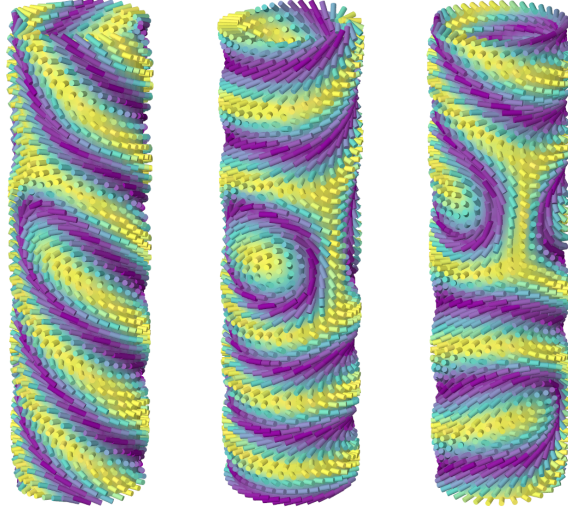


Figure 3.4: Non-ground state cholesteric structures on cylinders of height $h = 8$, $R = 1$ with $q_0R = 2.5$ and $CR^2/K = 0$. Each structure was produced by starting from a random initial director configuration and optimizing.

represent the ground state. Rather, the continuation technique allows us to examine the behavior of the cholesteric branch.

From the results, we observe several interesting phenomena: For $CR^2/K = 0$, as q_0R increases the cholesteric state emerges from the nematic with a decreasing pitch. Increasing CR^2/K at fixed q_0R tends to increase the pitch of the cholesteric relative to the $CR^2/K = 0$ state as we shall confirm analytically momentarily. Finally, for $q_0R = 0$ and increasing CR^2/K , the region where the director is tangential to the surface becomes localized (purple); we return to this effect in section 3.4.3.

As well as the cholesteric and smectic structures produced by continuation, we also note the existence of many additional solutions. As was shown in,[25] cholesterics in confined environments tend to have very rich solution landscapes, and we find similar results here. A few illustrative examples are shown in Fig. 3.4 for just one set of parameter values, $(q_0R, CR^2/K) = (2.5, 0)$. To produce these, the director field is initialized with randomized values drawn from a normal distribution and subsequently normalized. The solutions produced have energies significantly higher than the ground state solutions and exhibit phenomena such as dislocations. The deflation technique

described in [25] could be used to map the solution set more systematically, but we did not attempt to do so here.

We now perform an analytical variational calculation that allows for nonuniform azimuthal rotation of the director. To do so, we retain the assumption that the director has no z -component and hence can be parametrized as

$$\hat{\mathbf{d}} = \hat{\boldsymbol{\rho}} \cos \beta(\phi, z) + \hat{\boldsymbol{\phi}} \sin \beta(\phi, z). \quad (3.11)$$

Comparing with eqn (3.10), we see that $\beta = -\phi - q_0 z$ when $C = 0$ and the state is the pure cholesteric. While the tilt angle β in Fig. 3.3 depends on both ϕ and z for nonzero q_0 , close inspection of the figure suggests that the director field only varies along the direction perpendicular to the purple bands of constant tilt angle, i.e. the dependence on position is one-dimensional. Therefore we unroll the surface of the cylinder and choose coordinates ϕ' and z' such that z' is parallel to the lines of constant β (Fig. 3.5), and look for a solution in which the tilt angle β depends only on the coordinate ϕ' . Denoting by α the angle between the z -axis and a line in which $\beta = \pi/2$, we have

$$R\phi' = R\phi \cos \alpha + z \sin \alpha \quad (3.12)$$

$$z' = -R\phi \sin \alpha + z \cos \alpha. \quad (3.13)$$

We also assume that around the cylinder circumference, $\hat{\mathbf{d}}$ rotates by -2π relative to $\hat{\boldsymbol{\rho}}$. Thus $\beta(\phi = 2\pi, z) - \beta(\phi = 0, z) = -2\pi$, and there are two lines (blue) on the unrolled cylinder where $\mathbf{d}$ is purely azimuthal (Fig. 3.5). As we shall show in the next subsection, when the dimensionless tilt coupling CR^2/K is increased, these lines will become the sites of twist walls between radially aligned domains and hence we refer to them as “domain walls” for brevity.

We calculate the free energy per unit area of a configuration by computing the

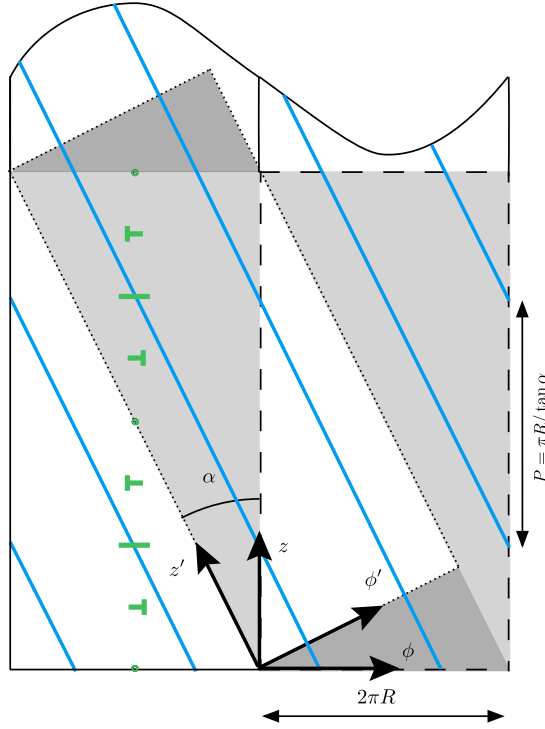


Figure 3.5: Coordinate system for a cholesteric configuration on a cylinder. The surface of the cylinder is unrolled with the dashed rectangle indicating the unit cell associated with the cylindrical coordinates ϕ and z . Vertical edges are identified and the directors (green) rotate in a left-handed sense about z through 2π as z increases from the bottom to the top of the rectangle. We use Kléman's nail notation to represent the tilt angle of the directors, with the point of the nail above the plane of the diagram, and the head of the nail below. [47]. Solid blue lines represent regions where the director is purely azimuthal. The pitch P is also indicated. Coordinate axes ϕ' and z' are chosen so that the z' -axis is parallel to the level sets of the tilt angle β in this unrolled representation. The dotted rectangle is the unit cell associated with the rotated coordinates ϕ' and z' . Since the light gray triangles represent the same region on the cylinder, and the dark gray triangles are equivalent regions, the two unit cells are equivalent.

free energy of a unit cell and dividing by its area. The unit cell corresponding to the ϕ - z coordinates has height $P = \pi R / \tan \alpha$, where P is the pitch of the configuration, and area $2\pi RP$ (Fig. 3.5). We may also deduce from Fig. 3.5 that the spacing $b'/2$ between domain walls is given by $b' = 2\pi R \cos \alpha$. Thus, the unit cell corresponding to the ϕ' - z' coordinates must have height $h' = 2\pi R / \sin \alpha$ to make the area of the two unit cells the same. The free energy of a unit cell is then given by

$$\begin{aligned} F_{\text{unit cell}} &= \int_0^{2\pi \cos \alpha} R d\phi' \int_0^{2\pi R / \sin \alpha} dz' f(\phi') \\ &= \frac{2\pi R^2}{\sin \alpha} \int_0^{2\pi \cos \alpha} d\phi' f(\phi'). \end{aligned} \quad (3.14)$$

Since β depends only on ϕ' , we find

$$\begin{aligned} f &= \frac{K}{2} \left[\frac{1}{R^2} \left(1 + \cos \alpha \frac{d\beta}{d\phi'} \right)^2 + \frac{1}{R^2} \left(q_0 R + \sin \alpha \frac{d\beta}{d\phi'} \right)^2 \right] \\ &+ \frac{C}{2} \sin^2 \beta, \end{aligned} \quad (3.15)$$

and a corresponding Euler-Lagrange equation

$$\frac{d^2 \beta}{d\phi'^2} - \frac{R^2}{\lambda_t^2} \cos \beta \sin \beta = 0, \quad (3.16)$$

with boundary conditions $\beta(\phi' = 0) = 0$ and $\beta(\phi' = 2\pi \cos \alpha) = -2\pi$. Note that the Euler-Lagrange equation is independent of q_0 . We will solve for the tilt angle $\beta(\phi')$, first perturbatively for small dimensionless tilt coupling $CR^2/K = R^2/\lambda_t^2 \ll 1$, and then exactly, as De Gennes did for a cholesteric subject to a uniform magnetic field. [14]

Perturbative solution

When the tilt coupling vanishes, $C = 0$, the directors take on the cholesteric configuration described earlier with pitch $P_0 = \pi/q_0$. We will show that the effect of a positive tilt coupling is to increase the pitch. We expand the tilt angle for small tilt coupling,

$$\beta(\phi') = \beta^{(0)}(\phi') + \frac{R^2}{\lambda_t^2} \beta^{(1)}(\phi') + \frac{R^4}{\lambda_t^4} \beta^{(2)}(\phi') + O\left(\frac{R^4}{\lambda_t^4}\right). \quad (3.17)$$

Solving (3.16) with boundary conditions $\beta^{(0)}(\phi' = 0) = 0$ and $\beta^{(0)}(\phi' = 2\pi \cos \alpha) = -2\pi$, and $\beta^{(m)}(\phi' = 0) = 0$ and $\beta^{(m)}(\phi' = 2\pi \cos \alpha) = 0$ for $m > 0$, we find

$$\begin{aligned} \beta(\phi') &= -\frac{\phi'}{\cos \alpha} + \frac{1}{8} \frac{R^2}{\lambda_t^2} \cos^2 \alpha \sin\left(\frac{2\phi'}{\cos \alpha}\right) \\ &\quad - \frac{1}{256} \frac{R^4}{\lambda_t^4} \cos^4 \alpha \sin\left(\frac{4\phi'}{\cos \alpha}\right). \end{aligned} \quad (3.18)$$

A short calculation shows that the corrections to the pure cholesteric state when C is nonzero lead to some splay and bend. We determine the pitch angle α by minimizing the free energy over α . Writing ϕ' in terms of ϕ and z and integrating the free energy from $\phi = 0$ to $\phi = 2\pi$ yields the free energy per unit length

$$F/L \approx \frac{K}{R} \left[\pi(q_0 R - \tan \alpha)^2 + \frac{\pi}{2} \frac{R^2}{\lambda_t^2} - \frac{\pi}{32} \frac{R^4}{\lambda_t^4} \cos^2 \alpha \right]. \quad (3.19)$$

Minimizing over α and using $P = \pi R / \tan \alpha$ yields

$$\tan \alpha \approx q_0 R \left[1 - \frac{1}{32} \frac{R^4}{\lambda_t^4} \frac{1}{(1 + q_0^2 R^2)^2} \right] \quad (3.20)$$

$$\frac{P}{P_0} \approx 1 + \frac{1}{32} \frac{R^4}{\lambda_t^4} \frac{1}{(1 + q_0^2 R^2)^2} \quad (3.21)$$

Note that a positive tilt coupling both decreases the pitch angle α and increases the pitch, as observed in the numerical results shown in Fig. 3.3. The alignment term tends to untwist the cholesteric because it gives the greatest penalty to regions where

the director is tangential to the surface; the area of these regions is reduced if the cholesteric untwists a bit. In Appendix C, we carry out the perturbative expansion to higher order.

Exact solution

To find the ϕ' -dependent solutions to eqn (3.16), we follow De Gennes' treatment of twist π -walls in three dimensions [14] and integrate to find

$$\frac{d\beta}{d\phi'} = -\frac{R}{\lambda_t k} \sqrt{1 - k^2 \cos^2 \beta}, \quad (3.22)$$

where $k > 0$ is an integration constant and we have chosen the negative root to make β decrease with increasing ϕ' . To determine k , note from Fig. 3.5 that the spacing between π -walls is $\pi R \cos \alpha$. Thus we take $\beta(\phi' = \pi \cos \alpha) - \beta(\phi' = 0) = -\pi$ to find

$$\begin{aligned} \cos \alpha &= -\frac{2\lambda_t k}{\pi R} \int_0^{-\pi/2} \frac{d\beta}{\sqrt{1 - k^2 \cos^2 \beta}} \\ &= \frac{2\lambda_t k}{\pi R} K(k), \end{aligned} \quad (3.23)$$

where $K(k)$ is the complete elliptic integral of the first kind.

To determine the pitch we need an additional relation between α and k which is found by minimizing the free energy per area $F/A = F_{\text{unit cell}}/[(2\pi R)^2 \cot \alpha]$ over α , or equivalently, k . Dividing the free energy of a unit cell by the area of the unit cell,

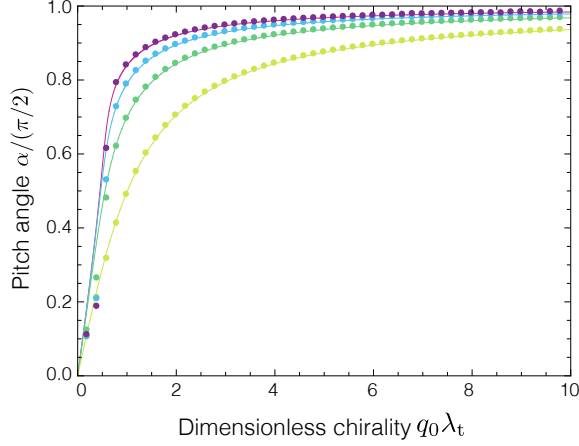


Figure 3.6: Plot of pitch angle α versus dimensionless chirality $q_0\lambda_t$ for $R/\lambda_t = 1$ (yellow-green), $R/\lambda_t = 2$ (green), $R/\lambda_t = 3$ (cyan), and $R/\lambda_t = 4$ (magenta). The dots are the numerical results from *Morpho* for a cylinder with $h/R = 8$; the solid lines are the analytical results for an infinite cylinder calculated from eqns (3.26) and (3.28).

we find that the free energy per area A is

$$\begin{aligned}
F/A &= \frac{C}{4\pi \cos \alpha} \int d\phi' \left[2 \frac{\lambda_t^2}{R^2} (\cos \alpha + q_0 R \sin \alpha) \frac{d\beta}{d\phi'} \right. \\
&\quad \left. + \frac{\lambda_t^2}{R^2} \left(\frac{d\beta}{d\phi'} \right)^2 + 1 - \cos^2 \beta \right] + \frac{K}{2R} (1 + q_0^2 R^2) \\
&= -\frac{K}{R^2} q_0 R \tan \alpha + \frac{2C\lambda_t}{\pi R \cos \alpha} \frac{E(k)}{k} + \frac{C}{2} \left(1 - \frac{1}{k^2} \right) \\
&\quad + \frac{K}{2R^2} (q_0^2 R^2 - 1).
\end{aligned} \tag{3.24}$$

Note that we have used eqn (3.22) to eliminate $(d\beta/d\phi')^2$ and to convert an integral over ϕ' to an integral over β . Minimizing F/A over k (taking care to note that α depends on k) yields the desired relation between α and k :

$$\sin \alpha = \frac{\pi}{2} q_0 \lambda_t \frac{k}{E(k)}. \tag{3.25}$$

Equations (3.23) and (3.25) can be combined and rearranged to yield

$$q_0 \lambda_t = \frac{2}{\pi} \frac{E(k)}{k} \sqrt{1 - \frac{4}{\pi^2} \frac{\lambda_t^2}{R^2} k^2 K^2(k)} \quad (3.26)$$

$$\frac{P}{P_0} = \left(\frac{2}{\pi}\right)^2 K(k)E(k), \quad (3.27)$$

where the pitch $P = \pi R / \tan \alpha$, and $P_0 = \pi / q_0$ is the pitch in the case of zero tilt modulus. If we take $R \rightarrow \infty$ in eqn (3.26), we recover de Gennes' result for the flat case. [14] Furthermore, eqn (3.27) is the same as what de Gennes found. Since $K(k)$ diverges at $k = 1$, and $E(1) = 1$, the critical value of $q_0 \lambda_t$ to completely unwind the cholesteric in the flat case is $2/\pi$. [14] Note that some care must be taken in the limit $R \rightarrow \infty$, since the pitch P need not diverge when R diverges because $\alpha \rightarrow \pi/2$. To see why, note that eqns (3.23) and (3.25) imply

$$\tan \alpha = \left(\frac{\pi}{2}\right)^2 \frac{q_0 R}{E(k)K(k)}. \quad (3.28)$$

Figure 3.6 shows the pitch angle α vs. $q_0 \lambda_t$ plotted parametrically for various R/λ_t (solid lines). As promised, the trend is that $\alpha \rightarrow \pi/2$ as R/λ_t increases, except in a thin boundary layer near $q_0 \lambda_t$. We also plot the numeric results from *Morpho* for a cylinder with dimensions $h/R = 8$, and find excellent agreement for larger $q_0 \lambda_t$. For small values of $q_0 \lambda_t$, we expect the discrepancy to be due to the finite extent of the cylinder; calculations on longer cylinders show improvements.

Integrating eqn (3.22), we find

$$\phi' = -\frac{\lambda k}{R} \int_0^\beta \frac{d\beta'}{\sqrt{1 - k^2 \cos^2 \beta'}}, \quad (3.29)$$

or

$$\beta(\phi') = \text{am} \left(-\frac{\phi' R}{\lambda_t} \frac{\sqrt{1 - k^2}}{k} \middle| -\frac{k^2}{1 - k^2} \right), \quad (3.30)$$

where $\text{am}(u|k')$ is the Jacobi amplitude function, and k is given by eqn (3.26). Our analytic solution has the same behavior as our numerics: as the tilt coupling C increases, the pitch angle α decreases. For large values of C , or equivalently, $\lambda_t/R \rightarrow 0$, eqn (3.26) indicates that $k \rightarrow 1$. In this limit, the dominant term of the free energy per unit area (3.24) is the second term. Noting that the arclength s of the domain wall is related to z via $s = z/\cos \alpha$ we see that the second term of eqn (3.24) corresponds to a free energy $\gamma_{\text{DW}} \int ds$ for each of the two domain walls, with $\gamma_{\text{DW}} = 2\sqrt{KC}$. When $C \rightarrow \infty$, $\alpha \rightarrow 0$ and the domain walls align with meridians to minimize their length. An alternative way to arrive at the same conclusion is to realize that for any finite R/λ , eqn (3.26) implies that $k < 1$, unlike de Gennes' case. In other words, when R is finite, the only way to completely unwind the cholesteric structure is to send C to infinity.

3.4.2 Smectic to Cholesteric transition

We now aim to predict the threshold value of CR^2/K as a function of q_0R for the smectic to cholesteric transition. To provide contrast, we begin by noting an instructive analogy between the tilt energy term in eqn (3.3) and the interaction energy of a liquid crystal with an external magnetic field $\mathbf{H}$,

$$F_H = -\frac{1}{2} \int d^3x \chi_a \left(\mathbf{H} \cdot \hat{\mathbf{d}} \right)^2, \quad (3.31)$$

where $\chi_a = \chi_{\parallel} - \chi_{\perp}$ is the diamagnetic anisotropy, and $\chi_{\parallel}$ and $\chi_{\perp}$ are the magnetic susceptibilities parallel and perpendicular to the local director axis, respectively. Meyer[55] and de Gennes [14] independently showed that a 3D cholesteric with a positive diamagnetic anisotropy undergoes a pitch-unwinding phase transition at a finite critical magnetic field H_c beyond which the average director completely aligns with

the field, resulting in an infinite pitch.[15] The critical magnetic field is given by

$$H_c = \frac{\pi}{2} \left(\frac{K_2}{\chi_a} \right)^{\frac{1}{2}} q_0. \quad (3.32)$$

In the limit where the curvature of the surface is small $q_0 R \gg 1$ and $\lambda_t/R \ll 1$ (with fixed $q_0 \lambda_t$), the tilt interaction is almost spatially uniform and hence we can determine a critical value C^* , analogous to the critical magnetic field eqn (3.32), where the cholesteric unwinds due to the aligning interaction,

$$C^* = \chi_a H_c^2 = \left(\frac{\pi}{2} \right)^2 K_2 q_0^2 \approx 2.47 K_2 q_0^2. \quad (3.33)$$

In the limit of infinite radius the transition from a twisted state when $\chi_a H_c^2 < C^*$ to a nematic state when $\chi_a H_c^2 > C^*$ is continuous. [14]

The case of a finite radius is different since as we noted in the previous section, the critical value of CR^2/K at which the cholesteric on a cylinder unwinds completely is infinite for finite R . Furthermore, there is a discontinuous transition from the cholesteric state to the smectic state that happens at a finite threshold value of CR^2/K . First, we estimate this value for case of no chirality, $q_0 = 0$. Consider the free energies of the nematic configuration with uniform directors and the radially aligned smectic configuration. In contrast to the aligned state in the magnetic scenario just examined, the smectic state is *not* distortion-free, but possesses splay due to the curvature. For the cylindrical geometry, the smectic state has a splay cost of K/R per unit length of the cylinder, compared to the tilt cost $\sim CR/2$ per unit length for the nematic state. (In the following we again assume $K_1 = K_2 = K_3 = K$.) Considering the ratio of these two quantities, $(CR/2)/(K/R) = CR^2/2K$, we expect that for $CR^2/K > 2$, the smectic state will be favorable while the nematic state will be favorable otherwise. We therefore expect the phase boundary between the smectic and uniform nematic states to approach the $CR^2/K \approx 2$ line at low chirality

$q_0 R \rightarrow 0$. Although the smectic state can be continuously deformed to the nematic state via escape to the third dimension, [54] i.e. rotating each director about the $\hat{\phi}$ direction, the smectic-nematic transition is discontinuous.

A more general version of this argument valid for finite q_0 was previously made by Ding and coauthors[21] by comparing the free energies per unit length of a (long) cylinder of length h for the smectic configuration, $F_{\text{sm}}/h = \pi K/R + \pi K q_0^2 R$, with that of the cholesteric state with uniform twist rate q_0 , $F_{\text{chol}}/h = \pi C R/2$. Equating these produces a phase boundary at $C R^2/K = 2(1 + q_0^2 R^2)$. Again, the cholesteric to smectic transition is discontinuous although there is a continuous path in configuration space between the two states. For example, we could unwind the cholesteric to get a nematic state along $\hat{\mathbf{x}}$, then rotate the directors by $\pi/2$ about $\hat{\mathbf{y}}$ to get all the directors along $\hat{\mathbf{z}}$, and then rotate each director about $\hat{\phi}$ to get the smectic state.

To obtain a more accurate estimate of the threshold value of C at which the free energy of the cholesteric state equals the free energy of the smectic state, we may use the perturbative results of the previous section. Substituting the minimizing value of α , eqn (3.20), into eqn (3.19) yields the free energy of the cholesteric state,

$$F_{\text{chol}}/h \approx \frac{K}{R} \left[\frac{\pi R^2}{2 \lambda_t^2} - \frac{\pi R^4}{32 \lambda_t^4} \frac{1}{(1 + q_0^2 R^2)} \right]. \quad (3.34)$$

The free energy of the smectic state ($\beta = 0$) is $F_{\text{sm}}/h = \pi(K/R)(1 + q_0^2 R^2)$. Equating F_{chol} and F_{sm} yields the formula for the phase boundary between the cholesteric and smectic states:

$$\left(\frac{R^2}{\lambda_t^2} \right)_{\text{crit}} - \left(\frac{R^4}{\lambda_t^4} \right)_{\text{crit}} \frac{1}{16} \frac{1}{1 + q_0^2 R^2} = 2(1 + q_0^2 R^2). \quad (3.35)$$

To solve for $(R/\lambda_t^2)_{\text{crit}}$, we formally treat the terms $1 + q_0^2 R^2$ appearing on the right-hand side of eqn (3.35) as small and perform a reversion of the series to get $(R/\lambda_t^2)_{\text{crit}}$

as a series in $1 + q_0^2 R^2$. The result is

$$C_{\text{crit}} R^2 / K \approx \frac{9}{4} (1 + q_0^2 R^2) = 2.25 (1 + q_0^2 R^2). \quad (3.36)$$

As mentioned earlier, we also performed a higher order perturbative calculation expanding β to eighth order R/λ_t in Appendix C, and obtain the following result by similar manipulations:

$$C_{\text{crit}} R^2 / K \approx \frac{1}{128} (297 + 301 q_0^2) \approx 2.32 + 2.35 q_0^2 R^2. \quad (3.37)$$

We now compare these estimates with numerical results using the continuation approach described earlier to characterize the cholesteric branch. We now also investigate the smectic branch (Fig. 3.1(c)) by starting with large C and continuing *downwards*, slowly reducing C and obtaining optimized structures as before.

In Fig. 3.7(a), we display a phase diagram obtained by comparing the energies of the minimized structures on both smectic and cholesteric branches at each point in the parameter space $(q_0 R, C R^2 / K)$ for several values of h/R . As the cylinder becomes longer, we observe that the transition lines converge on a common profile, while for lower aspect ratio cylinders, the smectic-cholesteric occurs at lower $C R^2 / K$, indicating that finite-size effects are strong for cylinder lengths comparable to the radius. Further, in the limit where chirality vanishes, the transition occurs at $C R^2 / K \simeq 2$, in agreement with our approximate estimates. Also shown in Fig. 3.7(a) are the phase boundaries predicted from the perturbative calculation, eqns (3.36) and (3.37). These estimates are close to one another, illustrating that the second order estimate is very good, and agree well with the numerical results from longer cylinders, $h/R > 16$.

We also display in Fig. 3.7(b), (c) and (d) quantities that measure the degree of alignment with each of the local cylindrical coordinate basis vectors over the whole

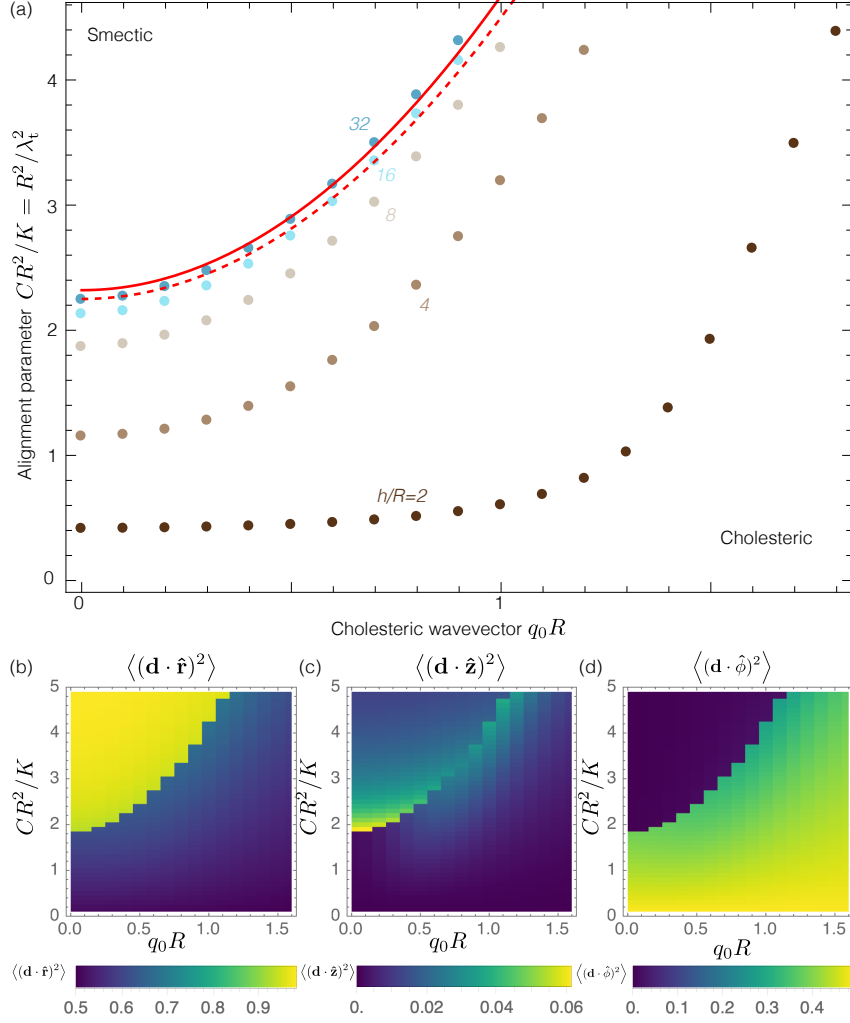


Figure 3.7: Phase diagram for the cholesteric membrane indicating regions where the smectic and cholesteric states are energetically preferred as a function of the alignment parameter CR^2/K and the dimensionless cholesteric wavenumber q_0R . Numerically obtained transition lines are displayed as dots for cylinders of increasing length h/R . The predicted phase boundary from an analytical second order perturbation theory is shown as a dashed red line; the corresponding fourth order perturbation theory is shown as a solid red line. (b-d) Average squared (b) radial, (c) vertical and (d) azimuthal component for the ground state configuration on cylinders of $h/R = 16$ as a function of CR^2/K and q_0R . Notice that the approximation $d_z \approx 0$ remains valid for both smectic and cholesteric states in regions where each is the respective ground state. The projection of the director onto the azimuthal direction is smaller than 0.05 in the smectic state.

structure,

$$\langle (\mathbf{d} \cdot \hat{\mathbf{n}})^2 \rangle = \frac{\int (\mathbf{d} \cdot \hat{\mathbf{n}})^2 dA}{\int dA}, \quad (3.38)$$

$$\langle (\mathbf{d} \cdot \hat{\mathbf{z}})^2 \rangle = \frac{\int (\mathbf{d} \cdot \hat{\mathbf{z}})^2 dA}{\int dA}, \quad (3.39)$$

$$\langle (\mathbf{d} \cdot \hat{\phi})^2 \rangle = \frac{\int (\mathbf{d} \cdot \hat{\phi})^2 dA}{\int dA}, \quad (3.40)$$

where the integrals are taken over the surface area of the cylinder. The transition in the radial order parameter Fig. 3.7(b) is very sharp and clearly distinguishes the two states.

The vertical and azimuthal quantities provide an important *a posteriori* cross-check on central assumptions of the analytical work in the previous section. As is shown in Fig. 3.7(c), the vertical component of the director remains quite small on average over the whole phase diagram. Regions of parameter space where $\hat{\mathbf{d}}_z$ is largest are found to be around the transition line: If the smectic state is continued *below* the transition line, the vertical component of the director continues to increase further, while the same effect occurs if the cholesteric state is continued above the transition line. Fortuitously, $\hat{\mathbf{d}}_z \approx 0$ remains valid in the regime where each state is stable. Meanwhile, the azimuthal projection of $\mathbf{d}$ shown in Fig. 3.7(d) remains very small in the smectic state. We examined the corresponding solution set carefully and found that directors with non-zero azimuthal component occur only near the boundaries of the cylinder, while in the center the director is exclusively radial. We will examine the structure of the boundary region in the smectic phase further in section 3.4.4.

3.4.3 Alignment induced localization into domain walls

We now turn to another phenomenon visible in Fig. 3.3, that increasing the value of the alignment term tends to localize distortions of the director into domain walls.

Restricting our attention to the nematic case $q_0 = 0$, the angle β is independent of z and the domain walls are aligned with the z axis, i.e., $\alpha = 0$. Thus, the tilt angle is given by eqn (3.30) with ϕ' replaced by ϕ ,

$$\beta(\phi) = \text{am} \left(-\frac{\phi R}{\lambda_t} \frac{\sqrt{1-k^2}}{k} \middle| -\frac{k^2}{1-k^2} \right), \quad (3.41)$$

where k is given by the $\alpha = 0$ limit of eqn (3.23),

$$\pi/2 = \frac{\lambda_t k}{R} K(k). \quad (3.42)$$

Figure 3.8 shows the tilt angle β vs. ϕ as R/λ_t is varied from 0.1 to 10. In the small curvature limit, when $R \gg \lambda_t$ (rightmost panel), we see sharp domain walls. This small curvature limit is equivalent to having a single splay-bend wall of width λ_t on a flat surface, as studied by Helfrich. [36] Of course, our cylinder has two splay-bend domain walls when the curvature is small, but they get infinitely far apart when $R \rightarrow \infty$. In Helfrich's case, the splay-bend wall has higher energy than the uniform state; we show below that the smectic state has lower free energy than the state with two domain walls when $R/\lambda_t > 1.522$. As the curvature increases and approaches λ_t , we see that the domain walls become less sharp, and the configuration becomes the uniform nematic state when $\lambda_t \gg R$. Also shown in Fig. 3.8 are tilt profiles extracted from numerically minimized solutions; these show excellent agreement with the predicted profiles.

To calculate the free energy difference per length $\Delta\mathcal{F}_0$ between the splay-bend domain wall state and the smectic state using the first integral, subtract the free energy of the smectic state from the $q_0 = 0$, $\alpha = 0$ limit of eqn (3.24) to find

$$\Delta F/A = -\frac{2C\lambda_t}{\pi R} \frac{E(k)}{k} + \frac{C}{2} \left(1 - \frac{1}{k^2} - \frac{2\lambda_t^2}{R^2} \right). \quad (3.43)$$

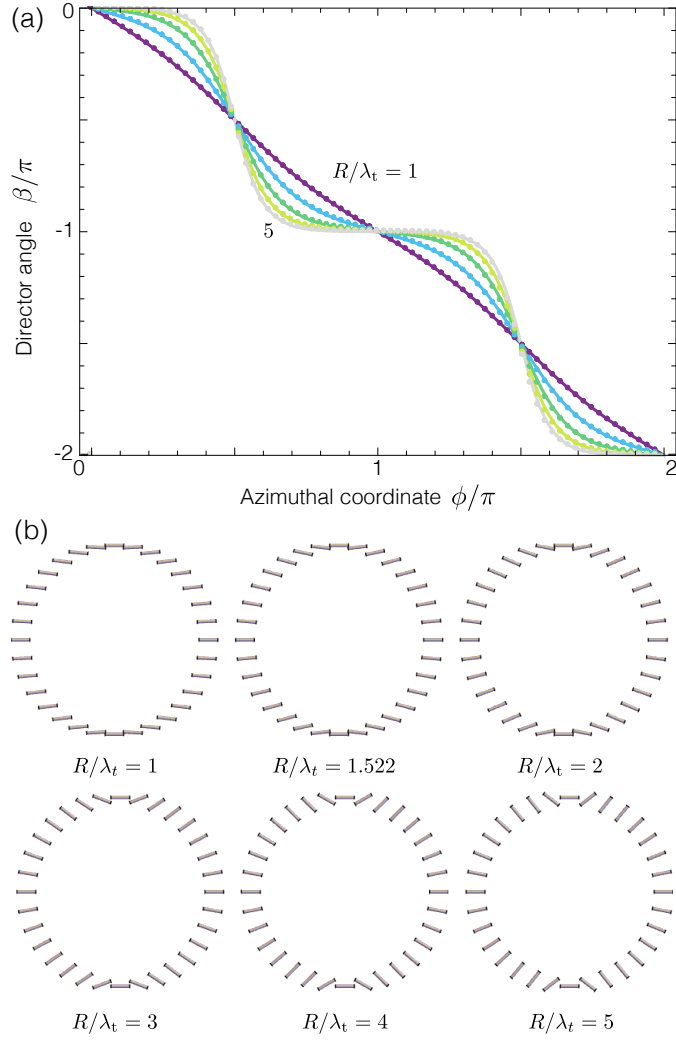


Figure 3.8: Localization of splay-bend walls. (a) Tilt angle vs. ϕ on a cylinder for the achiral case, $q_0 = 0$, and $R/\lambda_t \in [1, 5]$. When the curvature is high, $R \ll \lambda_t$, the director distribution is uniform. When the curvature is low, $R \gg \lambda_t$, there are two sharp splay-bend domain walls. Solid lines are the predictions of analytical theory eqn 3.41, while points are reconstructed tilt profiles from numerically optimized solutions. (b) Corresponding profiles of the director field viewed down the axis of the cylinder for the achiral case showing localization of a wall with increasing R/λ_t , a phenomenon also visible in Fig. 3.3. Since the smectic state has lower energy than the domain wall state when $R/\lambda_t > 1.522$, the configurations with sharp domain walls are metastable.

We find that $\Delta F/A = 0$ when $k = 0.9435$ and $R/\lambda_t = 1.522$. In other words, when the curvature is high enough so that $R/\lambda_t < 1.522$, splay-bend walls are favorable over the smectic state. When the curvature is low enough that $R/\lambda_t > 1.522$, the smectic state has lower energy. Note that this threshold value is greater than the value $R/\lambda_t = \sqrt{2}$ from the $q_0 = 0$ limit of the simple estimate of Ding et al. [21] mentioned above, since the exact calculation accounts for the non-uniform rotation of the directors, which is disregarded in the simple estimate. The perturbative result from eqn (3.37), $R/\lambda_t \approx \sqrt{2.32} \approx 1.52$, agrees very well with the exact result. Note also that as R/λ_t increases from a very small value, the lowest energy state evolves from a pure nematic state to a state with two splay-bend walls on opposite sides of the cylinder, although the domain walls do not get sharp before the lowest energy state is a smectic (Fig. 3.8).

3.4.4 Boundary layers in smectic structures

For low aspect ratio cylinders, we noticed significant variation of the director near the boundaries of the cylinder in our numerically optimized solutions (these are visible, for example, in Fig. 3.1(a)). This observation parallels a phenomenon that occurs experimentally in flat membranes where rods in the bulk are largely aligned with the surface normal except near the boundaries where twist is expelled.[8] Theoretical calculations show that the alignment occurs at the expense of elastic energy because the twist distortion favored by chirality is not accommodated.[16] As the chirality vanishes, i.e. $q_0 R \rightarrow 0$, the the cost in elastic energy similarly tends to zero.

For the cylindrical geometry in question, however, the smectic state $\hat{\mathbf{d}} = \hat{\rho}$ incurs a *splay* energy cost even in the absence of chirality. Without the aligning interaction, the nematic would tend to assume a spatially uniform configuration $\hat{\mathbf{d}} = \hat{\mathbf{z}}$ to avoid the cost of splay. A competition arises between these two states in the presence of the aligning term, and hence the splay distortion causes the director to *escape* towards

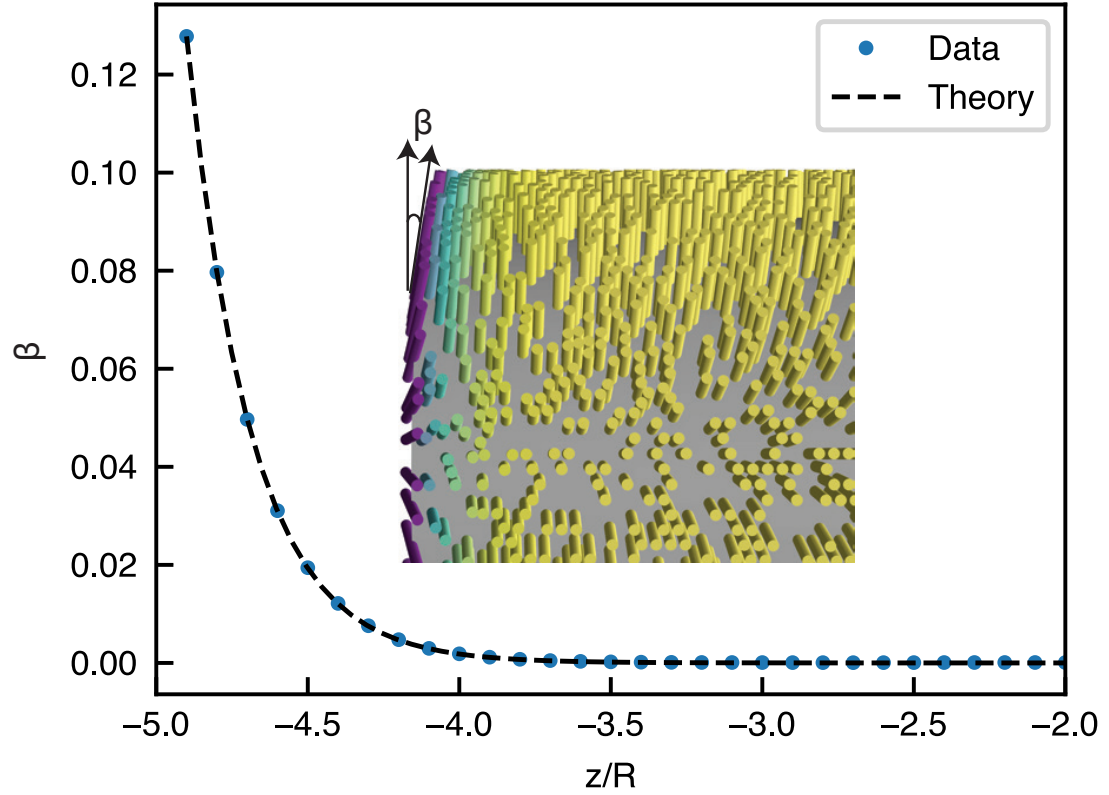


Figure 3.9: Splay escape at the boundary of the cylinder, showing the radially averaged tilt angle β as a function of the z coordinate on the cylinder for $h/R = 10$, $q_0 R = 0.1$ and $CR^2/K = 23.36$. The twist penetration length, $\lambda_t \sim 0.2$. The black dashed line is the corresponding estimate (eqn(3.49)) for a semi-infinite cylinder: $\beta = 2 \arctan(\tan(\beta_0/2) \exp(-z/\lambda_s))$, where $\lambda_s = \lambda_t / \sqrt{1 - \lambda_t^2/R^2}$.

the z -axis at the edge(s) of the cylinder forming a boundary layer.

We can study this analytically using techniques similar to those used in the previous section by constructing an *ansatz* solution for the director field on a semi-infinite cylinder with axis in the z direction and end at $z = 0$. In contrast to eqn (3.11) where the director is confined to the (ρ, ϕ) plane, here the director is assumed to lie in the (ρ, z) plane,

$$\mathbf{d} = \cos \beta(z) \hat{\rho} + \sin \beta(z) \hat{z} \quad (3.44)$$

Substituting this ansatz into the free energy, eqn (3.3), and taking variations with respect to $\beta(z)$, we obtain the Euler-Lagrange equation,

$$\beta''(z) = \frac{(CR^2 - K)}{KR^2} \cos \beta \sin \beta, \quad (3.45)$$

where the prime denotes differentiation with respect to z . Integrating this equation once, and using the boundary condition $\beta(z \rightarrow \infty) = \beta'(z \rightarrow \infty) = 0$, we find,

$$\frac{1}{2} \beta'(z)^2 = \frac{1}{2} \frac{(CR^2 - K)}{KR^2} \sin^2 \beta. \quad (3.46)$$

We define a new length scale associated with relaxation of splay distortions,

$$\lambda_s^2 = \frac{KR^2}{(CR^2 - K)} = \frac{\lambda_t^2}{(1 - \lambda_t^2/R^2)}, \quad (3.47)$$

which simplifies the equation for $\beta'(z)$,

$$\beta'(z)^2 = \frac{1}{\lambda_s^2} \sin^2 \beta. \quad (3.48)$$

We note that this is the same differential equation as for the *twist* angle at an edge in a flat smectic disk with chirality,[8] except with a different length scale λ_s instead

of λ_t . The solution to this equation is[8]

$$\beta(z) = 2 \arctan [\tan(\beta_0/2) \exp(-z/\lambda_s)] . \quad (3.49)$$

Using numerical solutions for a cylinder of modest aspect ratio $h/R = 10$, we display in Fig. 3.9 an estimate of β as a function of z/R the distance from the edge of a cylinder, computed from the solution by averaging azimuthally around the cylinder in a narrow band around z (points). The semi-infinite result, eqn (3.49) (dashed line) gives a very good fit to the simulation data. A zoomed-in section of a solution highlighting the boundary layer is shown as an inset.

3.4.5 Influence of intrinsic curvature

So far we have only considered the effects of *extrinsic* curvature on the cholesteric liquid crystal, because the cylindrical geometry studied is locally isomorphic to the plane and hence does not possess intrinsic curvature. To explore how intrinsic curvature affects the results of the previous section, we consider a family of surfaces, the unduloids, with constant mean curvature and shape depending continuously on a single parameter $\epsilon \in [0, 1]$. Unduloids interpolate between a cylinder for $\epsilon = 0$ and an infinite “necklace” of touching spheres as $\epsilon \rightarrow 1$. [33] Hence, by adjusting ϵ , we can change the Gaussian curvature continuously. In this section, we do not attempt an analytic calculation of the director field because we expect the $d_z = 0$ assumption to break down as soon as $\epsilon \neq 0$ for any $C > 0$, since the surface normal has a z -component when $\epsilon > 0$. However, we can interpret some of our numerical results with analytic observations.

It is standard to parametrize the family of unduloids [58, 33] with a coordinate u which increases along the the axis of symmetry of the surfaces, and the azimuthal

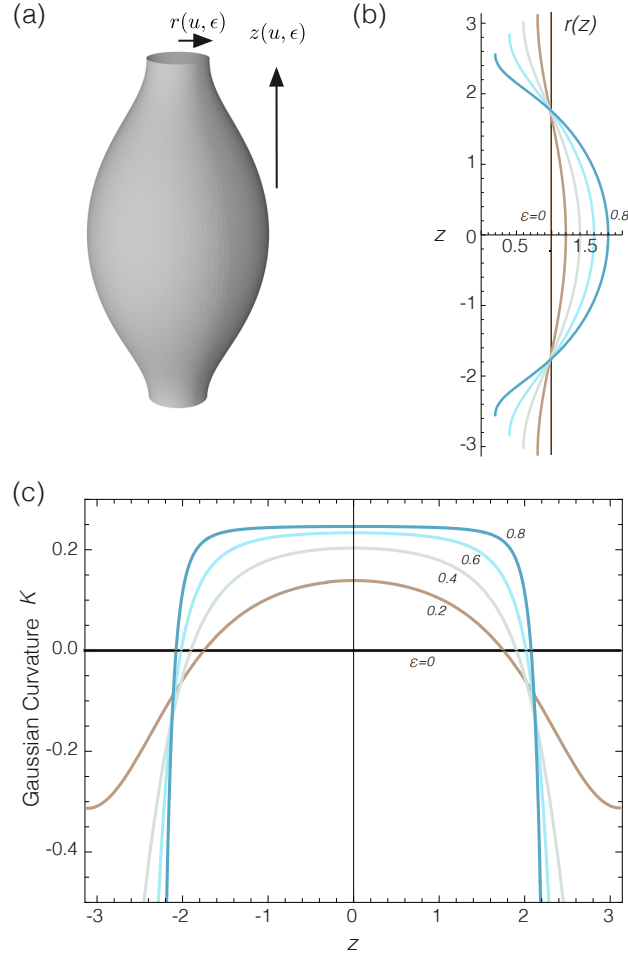


Figure 3.10: Unduloid geometry. (a) Coordinate system for the height $z(u, \epsilon)$ and the radius $r(u, \epsilon)$ as given by eqns (3.52) and (3.51) respectively. (b) Unduloid profiles for values of $\epsilon \in [0, 0.8]$ (c) Corresponding Gaussian curvature profiles K_G as a function of the height z from eqn (3.54) assuming $R = 1$. Note that the z values are shifted by constants to align the centers of the unduloids.

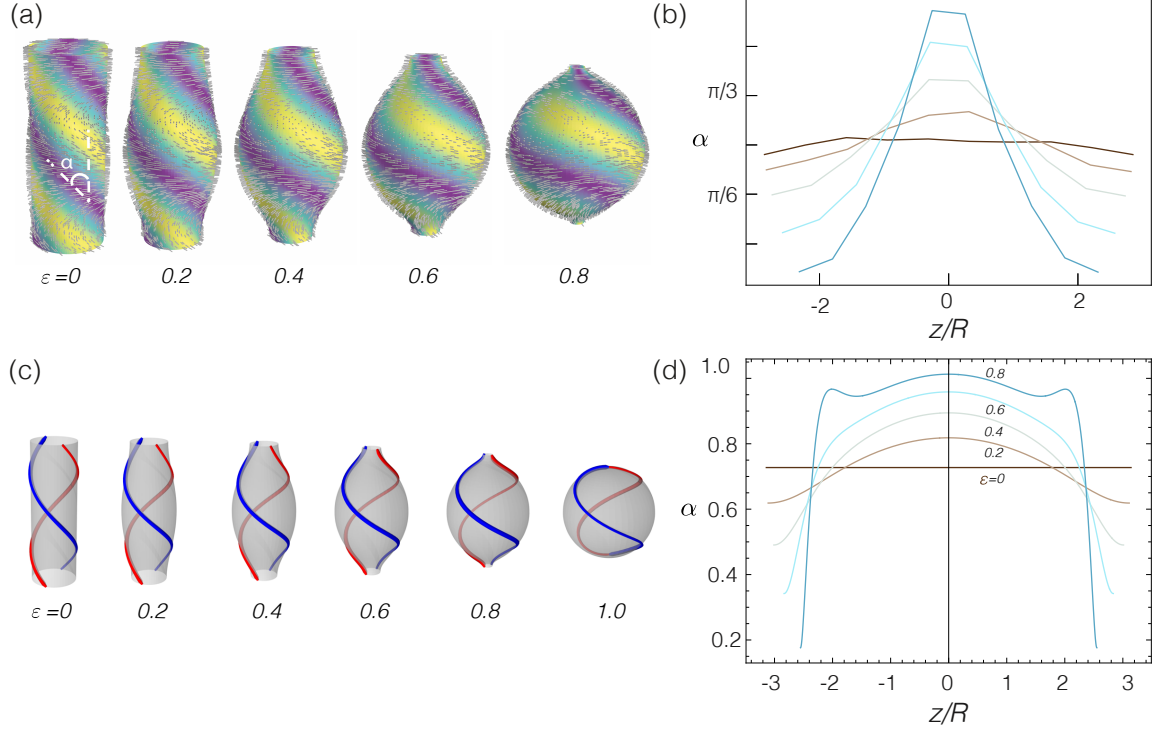


Figure 3.11: Unduloid cholesteric membranes. (a) Solutions for the cholesteric state with $CR^2/K = 0.48$ and $q_0R = 0.89$ are produced by a continuation process whereby the free energy, eqn (3.3) is optimized with respect to $\mathbf{d}$ on a cylindrical surface, then projected onto an unduloid with finite ϵ and reminimized; the process is then successively repeated onto unduloids with larger ϵ . (b) Variation of α along the height z from the optimized solutions for the states in (a). (c) Domain walls for $CR^2/K = 0$ and $q_0R = 0.89$ obtained from the intersection of a unduloid and a helicoid. (d) Variation of α for the domain walls in (c).

angle ϕ :

$$\mathbf{X}(u, \phi; \epsilon) = (r(u, \epsilon) \cos \phi, r(u, \epsilon) \sin \phi, z(u, \epsilon)), \quad (3.50)$$

with $u \in [-\pi/2, 3\pi/2]$ and $\phi \in [-\pi, \pi]$, and where

$$r(u, \epsilon) = R\sqrt{1 + 2\epsilon \sin u + \epsilon^2} \quad (3.51)$$

gives the variable radius, and

$$z(u, \epsilon) = R \int_{\pi/2}^u dt \frac{1 + \epsilon \sin t}{\sqrt{1 + 2\epsilon \sin t + \epsilon^2}}. \quad (3.52)$$

Figure 3.11(a) shows an example of an unduloid with $\epsilon = 0.5$ together with coordinates, and Fig. 3.11(b) shows profiles of unduloids for various values of ϵ . It can be shown[35] that the mean curvature of these surfaces is constant,

$$H = \frac{1}{2R}, \quad (3.53)$$

and the Gaussian curvature is

$$K_G = \frac{1}{4R^2} \left[1 - \frac{R^2(1 - \epsilon^2)^2}{r(u, \epsilon)^2} \right] \quad (3.54)$$

The spatial dependence of the Gaussian curvature for various values of ϵ is shown in Fig. 3.11(c).

We use *Morpho* to simulate cholesterics confined on an unduloid by minimizing the free energy of eqn (3.3). We adapt the continuation approach used earlier to track the behavior of a particular branch of the solutions as a function of intrinsic curvature: For a given set of parameters we first find an optimized solution on the cylindrical mesh, and then project the solution onto a mesh with a slightly higher value of ϵ and re-optimize. This procedure is repeated with each increment of ϵ .

Figure 3.11(a) shows the solutions for a few values of ϵ and $q_0R = 0.89$ and $CR^2/K = 0.48$. As in the case of the cylinder, α denotes the angle the domain wall makes with the z axis. It is evident that α in the central region near $z = 0$ decreases as ϵ increases. Plotting α versus z [Fig. 3.11(b)] reveals that α depends on z , indicating that except for the case of the cylinder, $\epsilon = 0$, the domain walls are no longer helices.

To understand why α depends on z in our numerical solution, note that when CR^2/K is small, the conformation will be close to the pure cholesteric state that occurs when $C = 0$. When $C = 0$, the domain walls are given by the positions where $\beta = -\pi/2$ or $\beta = -3\pi/2$, i.e. the intersection of the unduloid and the helicoids $q_0z + \phi = \pi/2$ and $q_0z + \phi = 3\pi/2$. These curves are shown in Fig. 3.11(c) for the unduloids with $\epsilon = 0, 0.2, 0.4, 0.6$, and 0.8 . The corresponding angles α are shown in Fig. 3.11(d). We note that while helices are geodesics on the cylinder ($\epsilon = 0$), the domain walls on the shapes close to spheres ($\epsilon = 0.8$) are not close to great circles and are therefore not geodesics. In fact, we have checked that when $\epsilon \neq 0$, the curves in Fig. 3.11(c) do not satisfy Clairaut's relation [84] and are therefore not geodesics. However, just as in the case of the cylinder, the free energy cost of the length of the domain walls dominates when the tilt modulus C becomes large, and the domain walls approach meridians of the unduloid, which are geodesics.

3.5 Conclusion

We studied the configurations of a chiral liquid crystal on cylinders and unduloids with a tilt interaction that favors alignment with the surface normal. When Frank elasticity dominates, a cholesteric state emerges with a pitch depending on the strength of the chirality. The smectic state in which the directors are purely normal occurs when the tilt interaction is strong enough to untwist the cholesteric. We studied the transition between the cholesteric and untwisted states, as well as the metastable states that

emerge above the transition. In particular we have shown how sharp domain walls develop in the metastable twisted states when the tilt penalty C is high, and we have determined how the pitch angle associated with these domain walls depends on the system parameters. Our work has several limitations that could be addressed in future studies. The analytical approximations are based on the assumption that the directors have no component along the axis of symmetry of the surface, which is largely appropriate for the cylinder, but not the unduloid. We have also limited the configurations to those that are continuously connected to the uniform nematic configuration (see Fig. 3.3); *Morpho* is well-suited for analyzing more complex states with multiple domain walls or defects. In particular, it would be interesting to study the interplay of defects with Gaussian curvature using the unduloids. Finally, in our work we have frozen the geometry of the surface to simplify the analysis. However, real colloidal and lipid bilayer membranes are deformable, and it is desirable to study how in-plane order affects shape.

Chapter 4

Director dynamics of skyrmions in planar colloidal membranes

4.1 Introduction

Skyrmions in magnetic [57, 10] or liquid crystalline systems [12, 13, 27, 18, 70] are vortex-like configurations in which the spin or director field is ordered everywhere but is topologically nontrivial. These structures have been extensively observed in magnetic systems as a crystal lattice form [86]. Similar topological defects can form in chiral nematic liquid crystal systems under applied electric fields due to the interplay between chirality and anisotropy [82]. In such systems, two-dimensional or “baby” skyrmions can be driven to move under orthogonal low-voltage electric fields, behaving like particles [2]. To describe their dynamics, Long and Selinger developed a coarse-grained theoretical model [50]. Further analogies between magnetic and liquid crystal skyrmions have been explored by Duzgun, Selinger, and Saxena [24], who proposed a simple theoretical framework for planar nematic systems in electric fields.

A related class of systems in which similar topological phenomena occur is colloidal membranes. These are single-layer, quasi-two-dimensional structures composed of aligned chiral filaments, such as rod-like fd viruses [29] or DNA origami filaments [80], suspended in a non-adsorbing depletant solution. Due to competition between chirality and depletion-induced attractive forces, these membranes exhibit diverse morphologies—ranging from flat disks and twisted ribbons [30] to saddles, catenoids, and trinoids [46]. In flat disk-shaped membranes, the rods align perpendicular to the membrane plane in the center and twist at the edges. Under optical manipulation, this twist can also be imposed at interior regions to form π -walls—structures across which the rods rotate by 180 degrees [29].

In these two-dimensional colloidal membranes, skyrmions can be engineered by cleaving a π -wall with optical tweezers and reconnecting its ends [92, 29]. The resulting skyrmion configuration relaxes slowly over thousands of minutes, eventually shrinking to a radius of approximately $1\,\mu\text{m}$. The dynamics of this shrinkage has not been well studied. In this chapter, we present a phenomenological model that

captures the dynamics and final equilibrium state of such colloidal skyrmions. Our model incorporates a tilt potential analogous to the electric field in previous studies of three-dimensional liquid crystals. We compare our theoretical predictions with experimental data and propose a new method for estimating the rotational viscosity of the constituent rods. Additionally, we compare our approach with those of other theoretical models [24] and find consistency with those results.

4.2 Phenomenological model

We consider the structure and dynamics of a skyrmion formed in a planar colloidal membrane lying in the $z = 0$ plane (see Fig. 4.1). The center of the skyrmion is located at the origin of our coordinate system. Outside a radius R which is large compared to the equilibrium radius r_{eq} of the skyrmion (and thus larger than the dimensions of the sketch shown in Fig. 4.1), the colloidal rods are assumed to be aligned along the z direction.

Motivated by the experimental observation of circular skyrmions in colloidal membranes [29], we assume a rotationally symmetric skyrmion configuration with no radial component, parameterized by the angle $\theta(\rho, t)$ that a rod located a radial distance ρ from the center of the skyrmion makes with the z axis at time t . Using cylindrical coordinates, the long axis $\hat{\mathbf{n}}$ of a rod is then given by

$$\hat{\mathbf{n}} = \hat{\boldsymbol{\phi}} \sin \theta(\rho, t) + \hat{\mathbf{z}} \cos \theta(\rho, t). \quad (4.1)$$

The skyrmionic boundary conditions are $\theta(\rho = 0) = 0$ and $\theta(\rho = R) = \pi$, which will produce a 180° rotation of the rods between the center of the skyrmion and r_{eq} .

We assume that the free energy of a planar membrane is the sum of the Frank

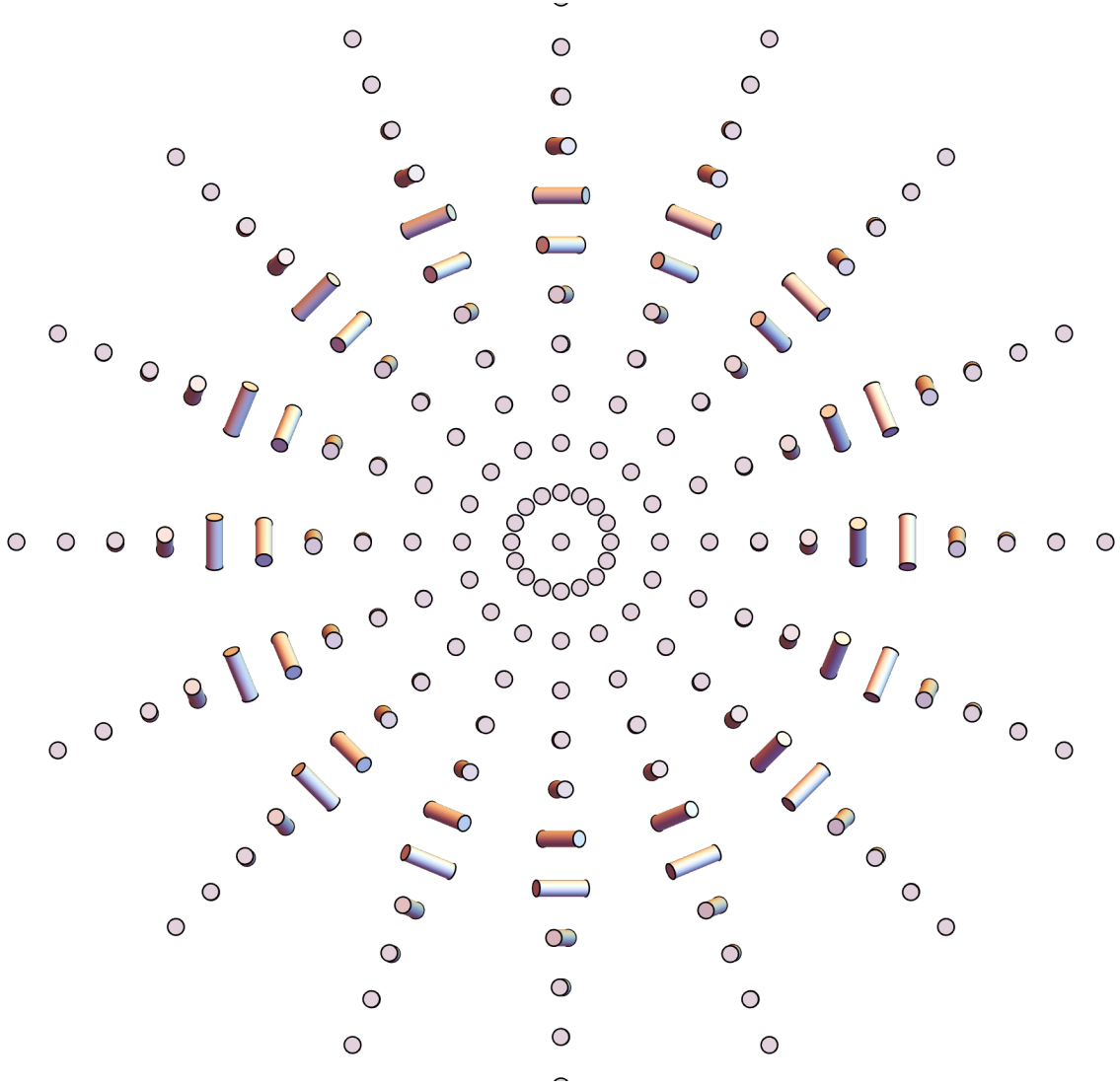


Figure 4.1: Schematic of a skyrmion in a planar membrane. The rods rotate through an angle π along the radial directions. The circle where the rods lie in the plane of the sketch is the center of a π -wall. The location of this wall depends on the parameters in the energy and the dynamics of the skyrmion (see Fig. 4.2).

chiral nematic free energy plus the cost for tilt relative to the membrane normal $\hat{\mathbf{z}}$ [8]

$$E = \frac{1}{2} \int 2\pi\rho \, d\rho \left\{ K_2 [\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}}) - q]^2 + K_3 [\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}})]^2 + C [1 - (\hat{\mathbf{n}} \cdot \hat{\mathbf{z}})^2] \right\}, \quad (4.2)$$

where K_2 and K_3 are the Frank twist and bend constants, respectively, q is the chirality of the rods and C is the tilt modulus. The Frank splay term does not appear because our assumed form Eq. (4.1) for $\hat{\mathbf{n}}$ satisfies $\nabla \cdot \hat{\mathbf{n}} = 0$.

To study the dynamics of the skyrmion, we consider the simplest model where we disregard fluid flow and assume that as the skyrmion expands or contracts, the directors simply rotate in place and do not generate any flow in the membrane or the surrounding solvent. The same assumption has been made to study skyrmions in chiral nematic fluids [2, 50]. Thus, we consider the director dynamics without any coupling to the flow velocity, and the equation of nematodynamics is reduced to [49]

$$\frac{\partial \mathbf{n}}{\partial t} = \frac{1}{\nu} \mathbf{h}, \quad (4.3)$$

where $\mathbf{h} = \mathbf{H} - (\mathbf{H} \cdot \hat{\mathbf{n}})\hat{\mathbf{n}}$ is the transverse part of the molecular field $\mathbf{H} = -\delta f / \delta \mathbf{n}$, where f is the energy density inside the integral of Eq. 4.2 and ν is the rotational viscosity of the rods.

Using Eqs. (4.1) - (4.3), we find that the angle θ satisfies the dynamical equation

$$\begin{aligned} \nu \frac{\partial \theta}{\partial t} &= K_2 \left[\frac{\partial^2 \theta}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial \theta}{\partial \rho} - \frac{1}{4\rho^2} \sin 4\theta - 2\frac{q}{\rho} \sin^2 \theta \right] \\ &- \frac{2K_3}{\rho^2} \cos \theta \sin^3 \theta - \frac{C}{2} \sin 2\theta \end{aligned} \quad (4.4)$$

Here, positive q corresponds to a left-handed cholesteric twist. Note that the right-hand side agrees with the Euler-Lagrange equation of Pelcovits and Meyer [71] who studied the energetics of membranes in the shape of a flat disk. In the following we

will measure length in units of the twist penetration length $\lambda = \sqrt{K_2/C}$ [16], and time in units of the diffusive time scale $\nu\lambda^2/K_2$.

4.3 Results

We solve Eq. (4.4) using the Matlab routine *pdepe* with boundary conditions $\theta(\rho = 0) = 0$ and $\theta(\rho = R) = \pi$. The initial condition for the director field is given by

$$\theta(\rho) = \pi \frac{1 + \text{erf}(\rho - r_0)}{1 + \text{erf}(R - r_0)} \quad (4.5)$$

with $R = 30$ and the initial radius of the skyrmion given by $r_0 = 12$. First, we solve for the equilibrium radius r_{eq} and equilibrium width w_{eq} of the skyrmion. We will provide a quantitative definition of the width later in this section. We determine the equilibrium radius and width as functions of the two dimensionless quantities $q\lambda$ and $k \equiv K_3/K_2$. After studying the equilibrium properties of the skyrmion, we consider its dynamics. We solve the dynamics of the skyrmion and find the time it takes to evolve to equilibrium. By comparing with experimental results, we are able to estimate the rotational viscosity of the rods.

4.3.1 Equilibrium state of the skyrmion

For $k = 1$, we find the skyrmion contracts at relatively low values of $q\lambda$ and expands to the radius R of our simulation domain at high values of $q\lambda$, as shown in Fig. 4.2. The equilibrium radius r_{eq} increases with $q\lambda$ as shown in Fig. 4.3, reaching a point $q\lambda \approx 0.636$, after which r_{eq} grows slowly reaching R , the size of our simulation domain. For larger values of R (not shown in the figure), we have found this critical point occurs at a slightly larger value of $q\lambda$. The equilibrium width w_{eq} of the skyrmion increases as $q\lambda$ almost linearly and then decreases slightly when $q\lambda$ exceeds the critical point.

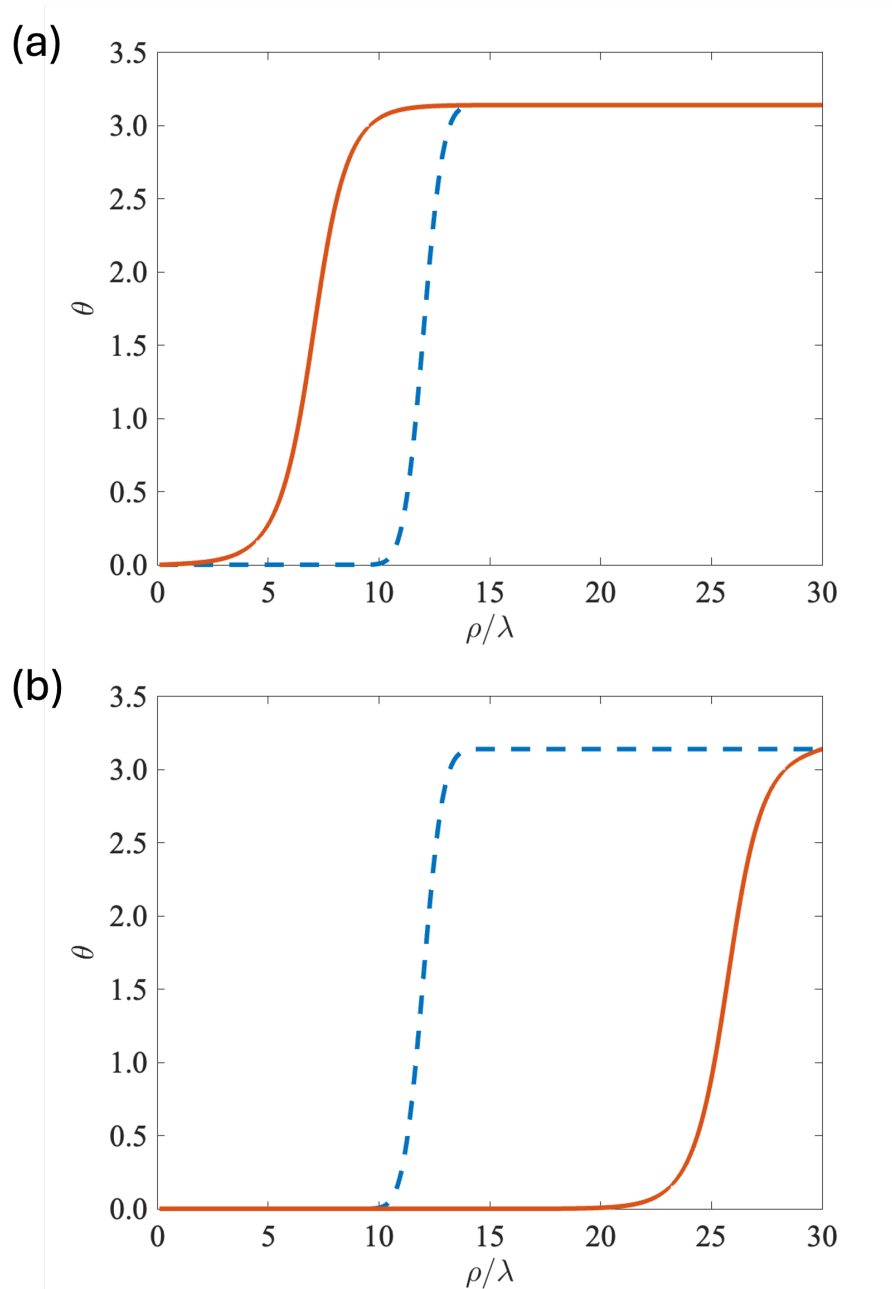


Figure 4.2: Angle θ of the rods with the $\hat{z}$ axis as a function of the radial coordinate ρ (in units of the twist penetration depth λ) for two different values of the dimensionless chirality: (a) $q\lambda = 0.63$, and (b) $q\lambda = 0.65$. In both figures, $k = 1$ and $R = 30$. The blue dashed line is the initial configuration of the skyrmion and the red solid line is the final equilibrium state. In (a) the skyrmion shrinks, while in (b), the skyrmion expands to the radius R of the domain and would expand further if R were increased.

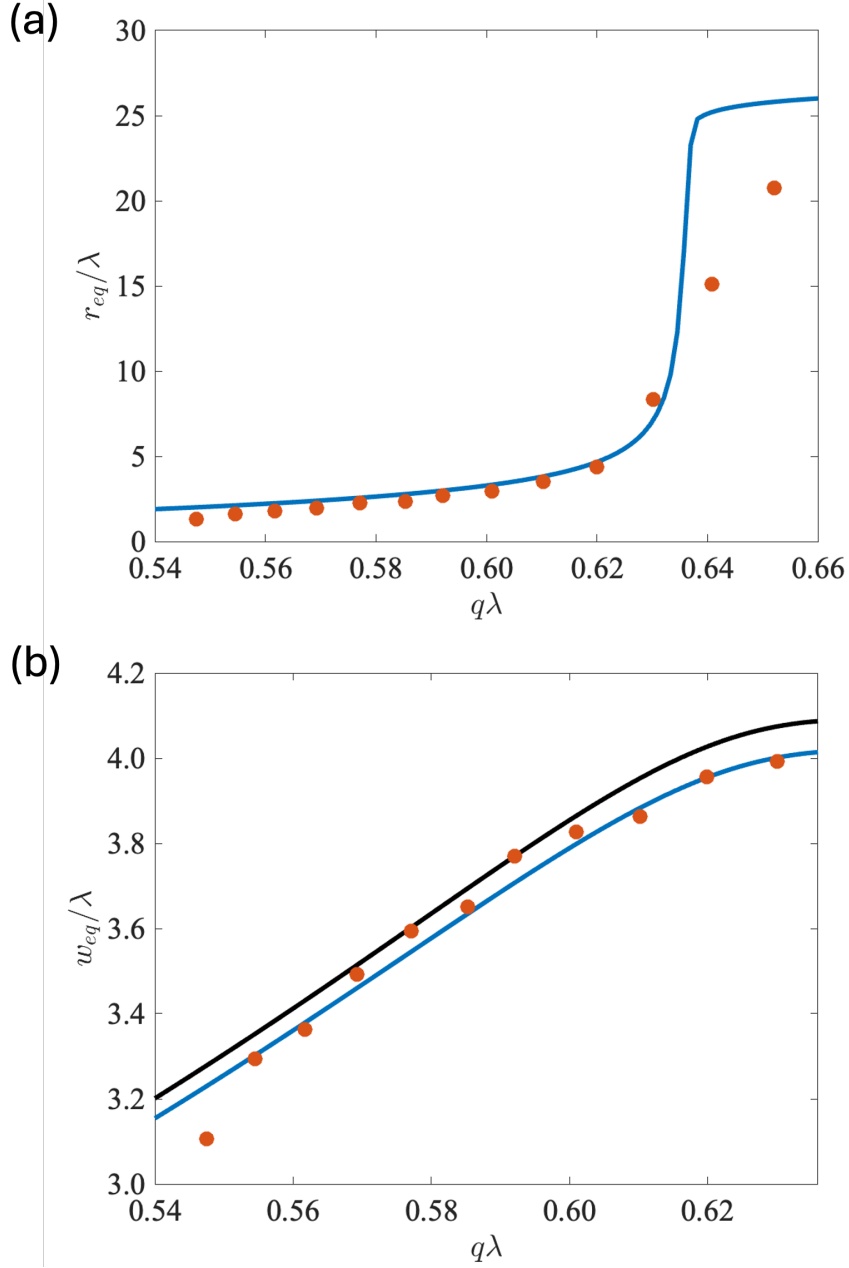


Figure 4.3: (a) Equilibrium radius r_{eq} and (b) width w_{eq} (both in units of the twist penetration depth λ) of the skyrmion as functions of the dimensionless chirality $q\lambda$. Here $k = 1$ and $R = 30$. Both r_{eq} and w_{eq} increase with $q\lambda$. The blue and black lines are numerical solutions from our model corresponding respectively to two choices for the definition of the skyrmion width: $0.085\pi < \theta < 0.915\pi$ and $0.082\pi < \theta < 0.918\pi$. The red dots are results of the Monte Carlo simulations in Ref.[24] for which no explicit definition of skyrmion width was given.

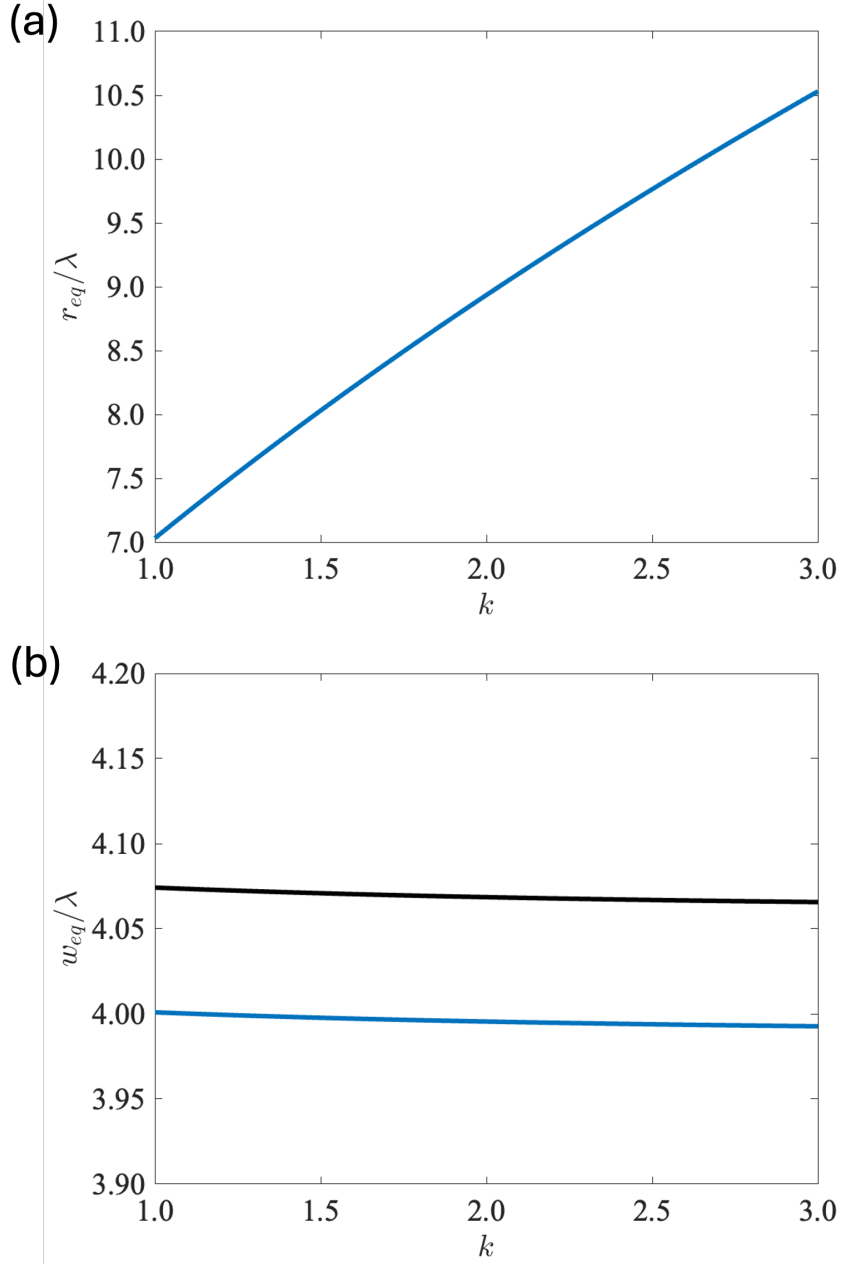


Figure 4.4: (a) Equilibrium radius r_{eq} and (b) width w_{eq} of the skyrmion as functions of $k = K_3/K_2$ with $q\lambda = 0.63$ and domain $R = 30$. The equilibrium radius r_{eq} increases with k since the Frank bending energy cost is minimized for a skyrmion with a larger radius of curvature. The equilibrium width w_{eq} barely changes with k . The blue and black lines in (b) correspond to the two definitions of width shown in 4.3(b).

We now compare our results with the theoretical and computational work of Duzgun, Selinger and Saxena [24] who studied skyrmions in two-dimensional chiral liquid crystals in the presence of an electric field. With the field oriented perpendicular to the two-dimensional plane, the interaction of the nematic directors with the field (assuming a positive dielectric anisotropy $\Delta\epsilon$) is analogous to our tilt interaction, the last term in Eq. (4.2). Duzgun et al. used the full Landau-de Gennes free energy density with a single Frank elastic constant

$$\begin{aligned}
f_Q &= \frac{1}{2}a \text{Tr}(Q^2) + \frac{1}{3}b \text{Tr}(Q^3) + \frac{1}{4}c (\text{Tr}(Q^2))^2 \\
&+ \frac{1}{2}L(\partial_\nu Q_{\alpha\beta})(\partial_\nu Q_{\alpha\beta}) - 2Lq\epsilon_{\alpha\beta\nu}Q_{\alpha\delta}\partial_\nu Q_{\beta\delta} \\
&- \Delta\epsilon E^2 Q_{zz},
\end{aligned} \tag{4.6}$$

where $Q_{ij} = S(\frac{3}{2}n_i n_j - \frac{1}{2}\delta_{ij})$, $i, j = x, y, z$. The elastic constant L and the dielectric coupling $\Delta\epsilon E^2$ correspond to our free energy parameters as follows:

$$\begin{aligned}
\frac{9}{2}LS^2 &\rightarrow K_2 = K_3 \\
S\Delta\epsilon E^2 &\rightarrow \frac{C}{3}
\end{aligned} \tag{4.7}$$

The chirality q is the same in both free energy expressions.

Duzgun et al. carried out Monte Carlo simulations and found metastable skyrmions within the range $0.55 \lesssim q\lambda \lesssim 0.65$. Our numerical results for the radius of the skyrmion (see Fig. 4.3(a)) compare well with Duzgun's Monte Carlo simulation results except for values of $q\lambda$ near the upper range of metastability. Duzgun et al. noted that their simulation results are not accurate for small C (i.e., large λ) because the simulated skyrmion develops four-fold anisotropy in this limit, arising from the square lattice used in the simulation. Our model assumes a circular skyrmion and thus will not exhibit this anisotropy. When $q\lambda$ is smaller than 0.63, the equilibrium

radius slowly increases with increasing $q\lambda$ and the width of the skyrmion grows linearly (see Fig. 4.3(b)) until nearing the value of chirality where the skyrmion is no longer stable. Duzgun et al. did not provide a quantitative definition of the skyrmion width (i.e., a range of θ). We have computed the width using two slightly different choices for the definition to obtain good fits to the Monte Carlo data. The kink appearing in the blue line in Fig. 4.3 (a) indicates that the upper limit of metastability is $q\lambda \simeq 0.63$. Beyond that value the radius grows rapidly and approaches the domain size, even if we increase the domain size to 100.

Fixing $q\lambda = 0.63$, we also examined how k influences the equilibrium state (see Fig. 4.4)) in the same domain. We find that larger values of k yield larger equilibrium radii. Since a larger k makes the Frank bending energy dominate over the twist energy, the skyrmion will prefer to have a larger radius. On the other hand, the equilibrium width is barely influenced by the value of k , as it is the value of the twist constant K_2 that determines the width and this value is set by the twist penetration depth which is a constant in Fig. 4.4(b).

Skyrmions have been formed in experiments by Gibaud et al. on colloidal membranes [29] by cleaving a π wall in two places and then joining the ends to form a ring. This ring resembles the π wall shown in Fig. 4.1 and a skyrmion has thus been formed. Gibaud et al. [92] determined the equilibrium radius r_{eq} of the skyrmion comparing the interfacial and bending energies of the π wall ring. The former energy is given by $2\pi\gamma_\pi r$ where γ_π is the line tension of the π wall. The latter energy is given by $2\pi\kappa_\pi/r$ where κ_π is the bending rigidity of the wall. Minimizing the energy leads to the prediction $r_{\text{eq}} = \sqrt{\kappa_\pi/\gamma_\pi}$. Figure 6(c) of Ref. [92] shows that the line tension γ_π increases with temperature leading to a decrease in the equilibrium radius of the ring, which is consistent with our model.

4.3.2 Skyrmion dynamics

Next we solve numerically for the dynamics of the skyrmion at fixed values of k and $q\lambda$. Fig. 4.5 shows examples of finite-sized metastable and unstable skyrmions depending on the value of $q\lambda$. For domain size $R = 30$, the skyrmion shrinks from its initial size of 12 to a smaller but nonzero radius when chirality is smaller than the critical value (approximately 0.63), and tends to expand to the boundary of the domain when chirality is larger as we already noted in Fig. 4.3 (a). We have checked that this result does not change if we increase the radius of the domain to 100.

Around the critical value $q\lambda \approx 0.63$, we find that the time for the skyrmion to reach equilibrium increases rapidly and approaches infinity (see Fig. 4.6). This indicates that the skyrmion is no longer metastable) and will expand indefinitely and grow to a straight π -wall in an infinite system.

Skyrmions have been formed in experiments on colloidal membranes [29] by cleaving a π wall in two places and then joining the ends to form a ring. This ring resembles the π wall shown in Fig. 4.1 and a skyrmion has thus been formed in a highly nonequilibrium state [29]. The radius of this skyrmion was found to shrink from about $6\mu\text{m}$ to $1\mu\text{m}$ in approximately 1000 min.

We have been able to obtain a good fit of our dynamical model Eq. (4.3) to the experimental data (see Fig. 4.7) choosing $q\lambda = 0.58$ and $\lambda = 0.6\mu\text{m}$. The resulting value of q is $0.97\mu\text{m}^{-1}$ which is of the order of magnitude of the corresponding experimental value [44]. We relate the Frank elastic constant K_2 of our two-dimensional energy Eq. (4.2) to the experimental estimate of the *bulk* value 0.5 pN [44] by multiplying the latter quantity by the thickness of the colloidal membrane which is approximately $1\mu\text{m}$.

From these values we find a rotational time unit $\nu\lambda^2/K_2 = 80\text{ s}$. This time unit in turn yields an estimate of the rotational viscosity of $\nu \simeq 111\text{ Pa}\cdot\text{s}$, which is approximately 3000 times greater than the viscosity of a typical short rod nematic [81].

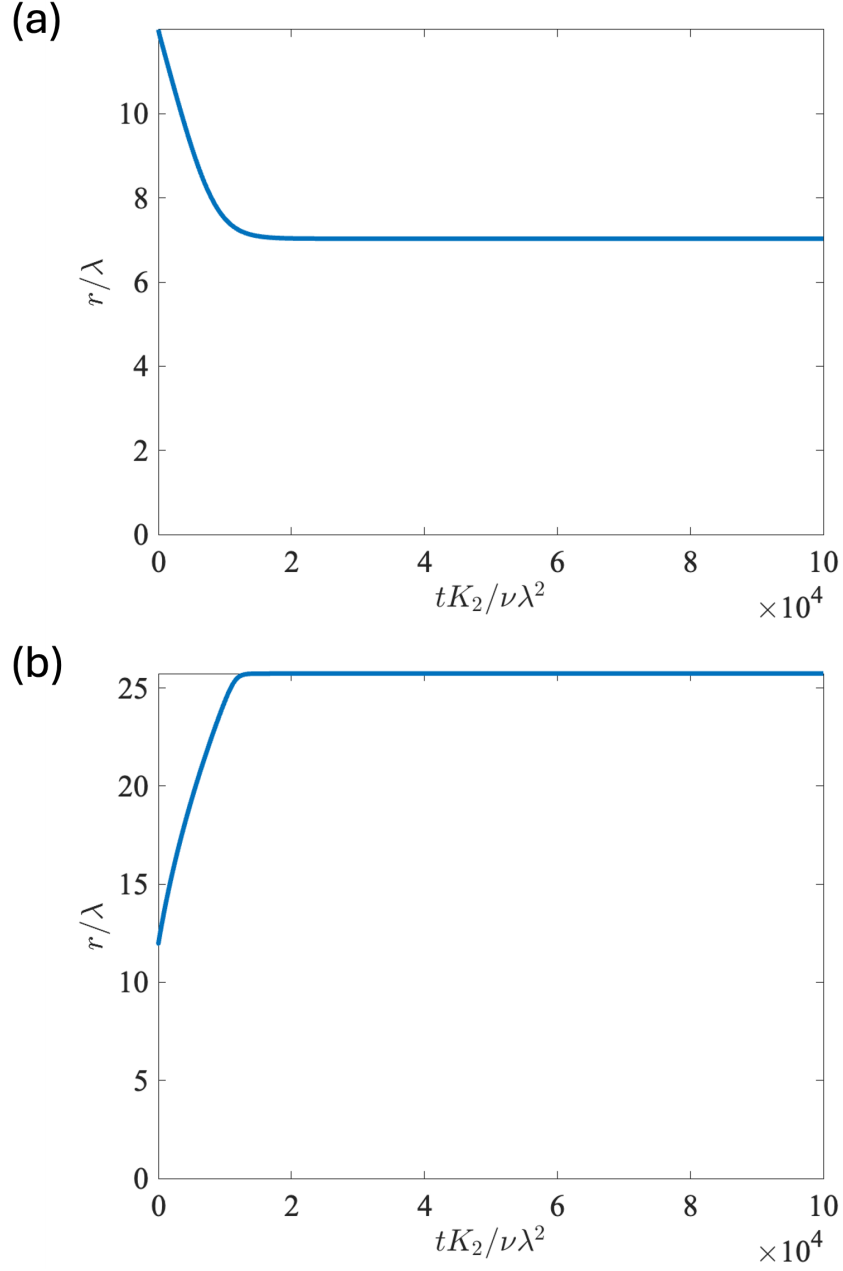


Figure 4.5: Radius r (in units of the twist penetration depth λ) of (a) a finite-sized metastable skyrmion and (b) an unstable skyrmion of unbounded radius, as functions of time t (in units of $\nu\lambda^2/K_2$) for $k = 1$ and $R = 30$. The initial radius is 12. The finite-sized skyrmion has chirality $q\lambda = 0.63$, while the unbounded one has $q\lambda = 0.65$.

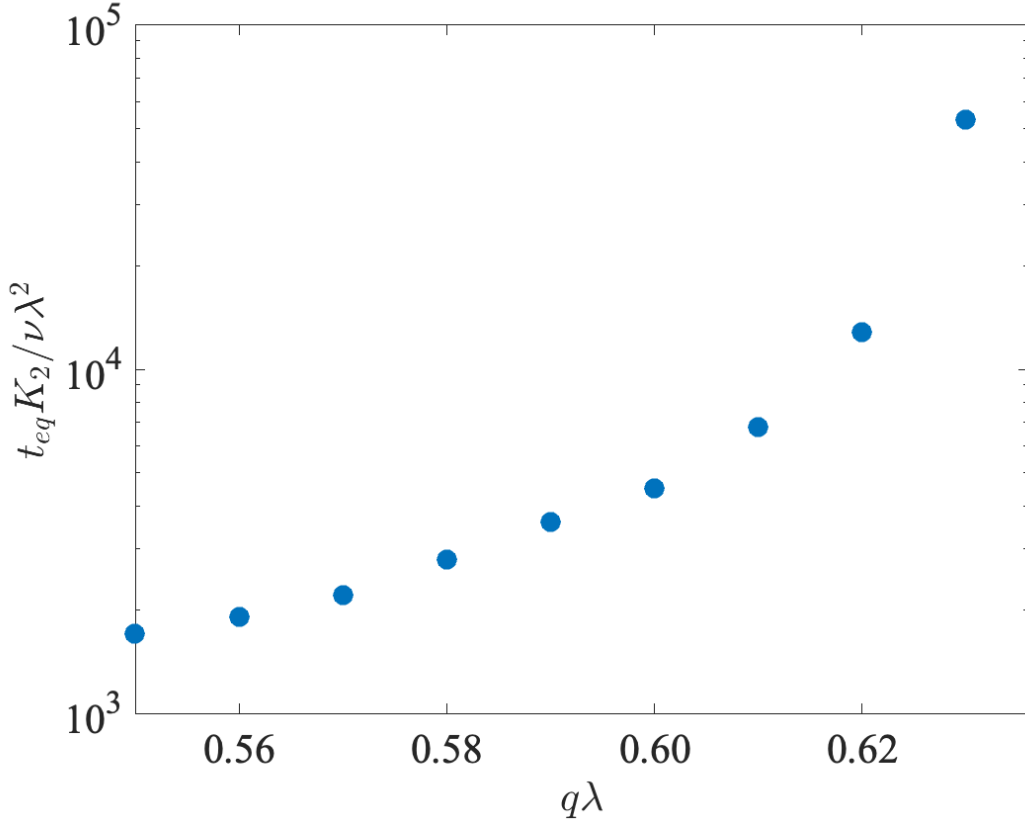


Figure 4.6: The time t_{eq} (in units of $\nu\lambda^2/K_2$) to reach equilibrium as a function of $q\lambda$ for a skyrmion initialized as in Eq. (4.5) with $r_0 = 18$, $R = 30$, and $k = 1$. For $q\lambda \approx 0.636$, t_{eq} approaches infinity, indicating that the skyrmion continues expanding indefinitely.

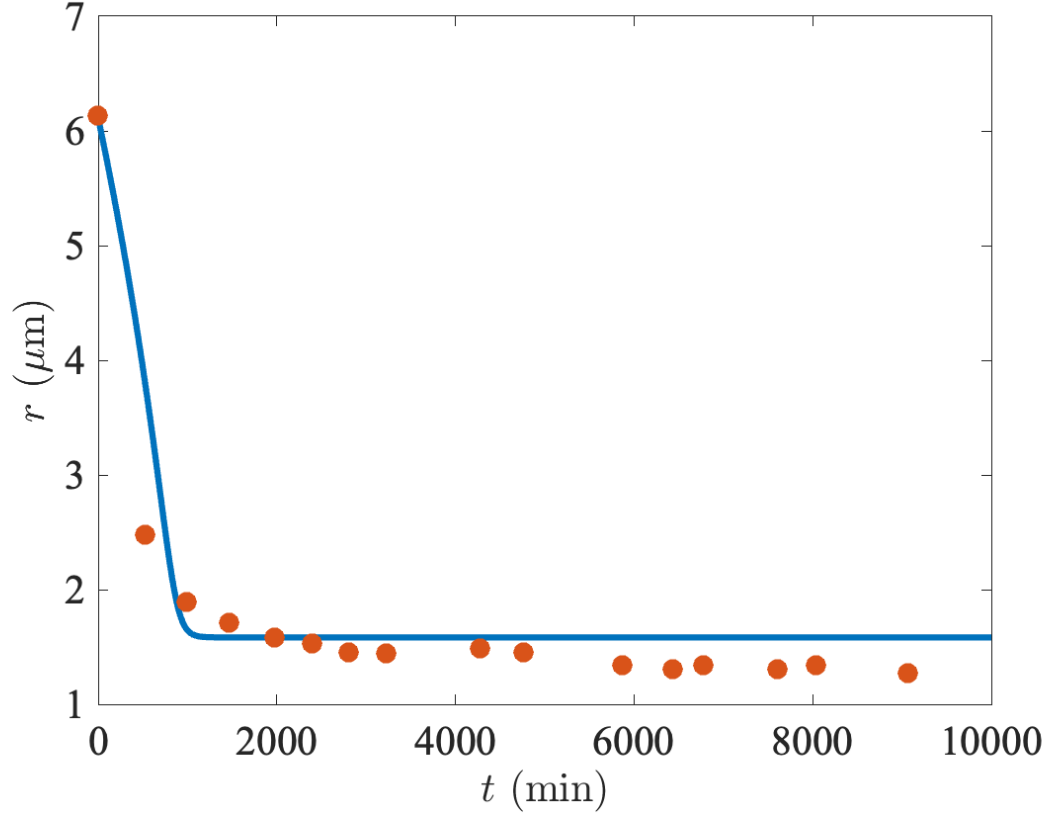


Figure 4.7: Time evolution of a skyrmion with initial radius $6\mu\text{m}$. Unlike our earlier figures where dimensionless units were used, here the radius is measured in microns and time in minutes to allow comparison of our numerical results (blue line) with the experimental data (red dots) of Ref.[29]. Our fit was obtained with penetration length $\lambda = 0.60\mu\text{m}$, $q\lambda = 0.58$, and time unit $\nu\lambda^2/K_2 = 80\text{ s}$.

The retraction of a straight π -wall has been observed experimentally [29] and it occurs at a much greater speed ($6.2\mu\text{m/s}$) compared with the shrinkage of the skyrmion. This can be explained by noting that the retraction of a straight π -wall is dominated by the splay term K_1 and the bend term K_3 in the Frank energy, while the skyrmion is dominated by the twist term K_2 . For long, hard rods, it is expected on the basis of Onsager theory[83] that $K_2 = K_1/3 = K_3/3$, providing weaker driving force of shrinkage.

4.3.3 Numerical simulations using FEniCS

We perform numerical simulations of the Landau–de Gennes model using the finite element package *FEniCS* to further investigate the relaxation dynamics of π -walls and skyrmions in more general cases. The simulations are based on the finite element method (FEM), which solves the partial differential equations by generating the weak form of the equations and solving the nonlinear variational problem.

The total free energy consists of bulk, elastic, and tilt contributions

$$F = \int (f_{\text{bulk}} + f_{\text{elastic}} + f_{\text{tilt}}) dA. \quad (4.8)$$

The bulk Landau–de Gennes energy is

$$f_{\text{bulk}} = \frac{A}{2} \text{Tr}(Q^2) + \frac{B}{3} \text{Tr}(Q^3) + \frac{C}{4} (\text{Tr}(Q^2))^2, \quad (4.9)$$

where A , B , and C are material parameters controlling the magnitude of the nematic order, and $Q = \frac{3}{2}S(\mathbf{n}\mathbf{n} - \frac{1}{3}I)$ is the order parameter tensor which is traceless. Here we choose $A = -796/27$, $B = -320/27$, $C = 1920/81$ to have a steep potential well and have $S = S_0 \approx 1$ to make the minimum potential.

The tilt coupling favors alignment of the director with the membrane normal,

$$f_{\text{tilt}} = -C_t Q_{zz}, \quad (4.10)$$

where C_t denotes the tilt strength and $C_t = 1/3S$.

The elastic energy is written as

$$f_{\text{elastic}} = \frac{1}{2} (L_1 I_1 + L_2 I_2 + L_3 I_3 + L_4 I_4 + L_6 I_6), \quad (4.11)$$

where L_i are elastic coefficients and I_i denote the gradient invariants constructed from spatial derivatives of the Q tensor. The invariants used in the simulation are

$$I_1 = (\partial_k Q_{ij})(\partial_k Q_{ij}), \quad (4.12)$$

$$I_2 = (\partial_j Q_{ij})(\partial_k Q_{ik}), \quad (4.13)$$

$$I_3 = (\partial_j Q_{ik})(\partial_k Q_{ij}), \quad (4.14)$$

$$I_4 = \epsilon_{lik} Q_{lj} \partial_k Q_{ij}, \quad (4.15)$$

$$I_6 = Q_{lk} (\partial_l Q_{ij})(\partial_k Q_{ij}), \quad (4.16)$$

where repeated indices imply summation. Here Q_{ij} is the Landau–de Gennes order parameter tensor, ∂_k denotes spatial derivatives, and ϵ_{ijk} is the Levi-Civita antisymmetric tensor. These parameters are related to the Frank elastic constants K_1 , K_2 , K_3 , and K_{24} through

$$K_1 = \frac{9}{4}S_0^2(2L_1 + L_2 + L_3 - L_6S_0), \quad (4.17)$$

$$K_2 = \frac{9}{4}S_0^2(2L_1 - L_6S_0), \quad (4.18)$$

$$K_3 = \frac{9}{4}S_0^2(2L_1 + L_2 + L_3 + 2S_0L_6), \quad (4.19)$$

$$K_{24} = -\frac{9}{4}S_0^2(-2L_1 - L_3 + S_0L_6). \quad (4.20)$$

We choose $L_1 = 2/9S_0^2$ without other terms for one constant case and add $L_2 = 4/3S_0^2, L_3 = -2L_1, L_4 = -4L_1q_0, q_0 = 0.6$ to have $K_1 = 3K_2 = K_3 = 3$ for different constant case. We define $\lambda_Q = L/C_{\text{tilt}}$ as our length unit, and $\nu\lambda_Q^2/L$ as our time unit, which can be well converted to units of director model.

The system is simulated on a rectangular domain representing a flat membrane. We impose Dirichlet boundary conditions corresponding to uniform vertical alignment of the rods

$$Q_{xx} = Q_{yy} = -\frac{S_0}{2}, \quad Q_{xy} = Q_{xz} = Q_{yz} = 0. \quad (4.21)$$

For the π -wall simulation (see Fig. 4.8), the director field is initialized with two opposite defects separated by $24\sqrt{2/3}\pi\lambda_Q$ which equals $24\pi\lambda$ to be comparable with the skyrmion initial circumference. The initial director angle is constructed as

$$\beta(x, y) = \frac{1}{2} \left[\tan^{-1} \left(\frac{x-d}{y} \right) - \tan^{-1} \left(\frac{x+d}{y} \right) \right], \quad (4.22)$$

where d represents half of the separation between the two defects. The total defect separation is therefore $d = 12\sqrt{2/3}\pi\lambda_Q$.

The director field is then constructed from the angle β as

$$\mathbf{n} = (\sin \beta, 0, \cos \beta), \quad (4.23)$$

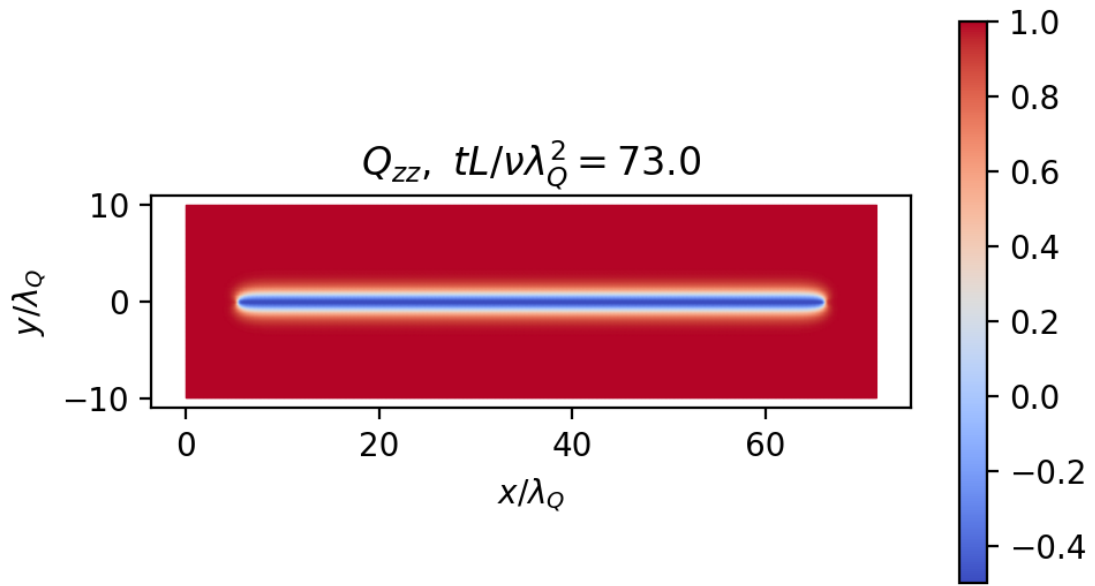


Figure 4.8: Q_{zz} configuration of the straight π -wall at time $tL/\nu\lambda_Q^2 = 73.0$, $K_3/K_2 = 1$.

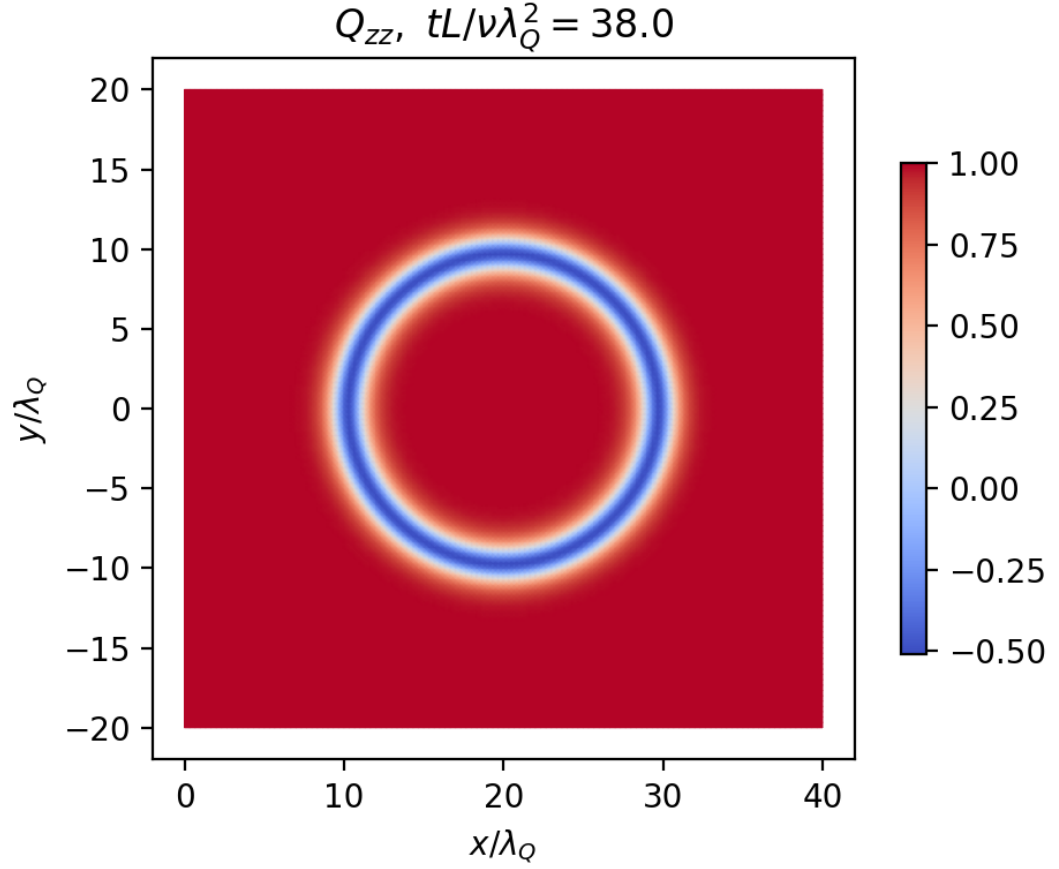


Figure 4.9: Q_{zz} configuration of the skyrmion at time $tL/\nu\lambda_Q^2 = 38.0$, $K_3/K_2 = 1$.

which corresponds to a π rotation of the director across the wall. This initial condition generates a configuration in which the director rotates by approximately π across the center of the domain, mimicking the structure of a π -wall observed in experiments. For the skyrmion simulations, the director field is initialized using a radially symmetric profile. The polar angle of the director relative to the membrane normal is defined as

$$\theta(r) = \frac{\pi}{2} \left(1 - \operatorname{erf} \left(\frac{r - r_0}{\delta} \right) \right), \quad (4.24)$$

where $r = \sqrt{(x - x_0)^2 + (y - y_0)^2}$ is the radial distance from the skyrmion center (x_0, y_0) . The parameter $r_0 = 12\sqrt{2/3}\lambda_Q$ sets the initial radius of the skyrmion,

while $\delta = \sqrt{2/3}\lambda_Q$ controls the width of the transition region over which the director rotates.

The azimuthal angle is defined as

$$\phi = \tan^{-1} \left(\frac{y - y_0}{x - x_0} \right). \quad (4.25)$$

The director field is then constructed as

$$\mathbf{n} = (-\sin \phi \sin \theta, \cos \phi \sin \theta, \cos \theta). \quad (4.26)$$

The time evolution is governed by relaxational dynamics

$$\nu \frac{\partial Q}{\partial t} = -\frac{\delta F}{\delta Q}, \quad (4.27)$$

where ν is a rotational viscosity. The equation is solved using an implicit time stepping scheme implemented in *FEniCS*.

The simulations show that the π -wall length decreases approximately linearly in time as the system relaxes. This behavior is shown in Fig. 4.10. Similarly, the skyrmion radius decreases over time until it approaches a stable equilibrium radius, indicating that the skyrmion relaxes toward a metastable localized configuration.

The numerical results show that the shrinkage of a straight π -wall occurs much faster than that of a skyrmion, which is qualitatively consistent with experiments. This difference can be understood from the spatial distribution of dissipation. For the π -wall configuration, dissipation is localized near the two ends of the wall, where the director field varies rapidly. As a result, the wall shortens efficiently as these end defects move toward each other. In contrast, for a skyrmion, the dissipation is distributed along the entire circular domain wall surrounding the core. The relaxation therefore involves motion of the whole ring, leading to a slower decrease of the skyrmion radius.

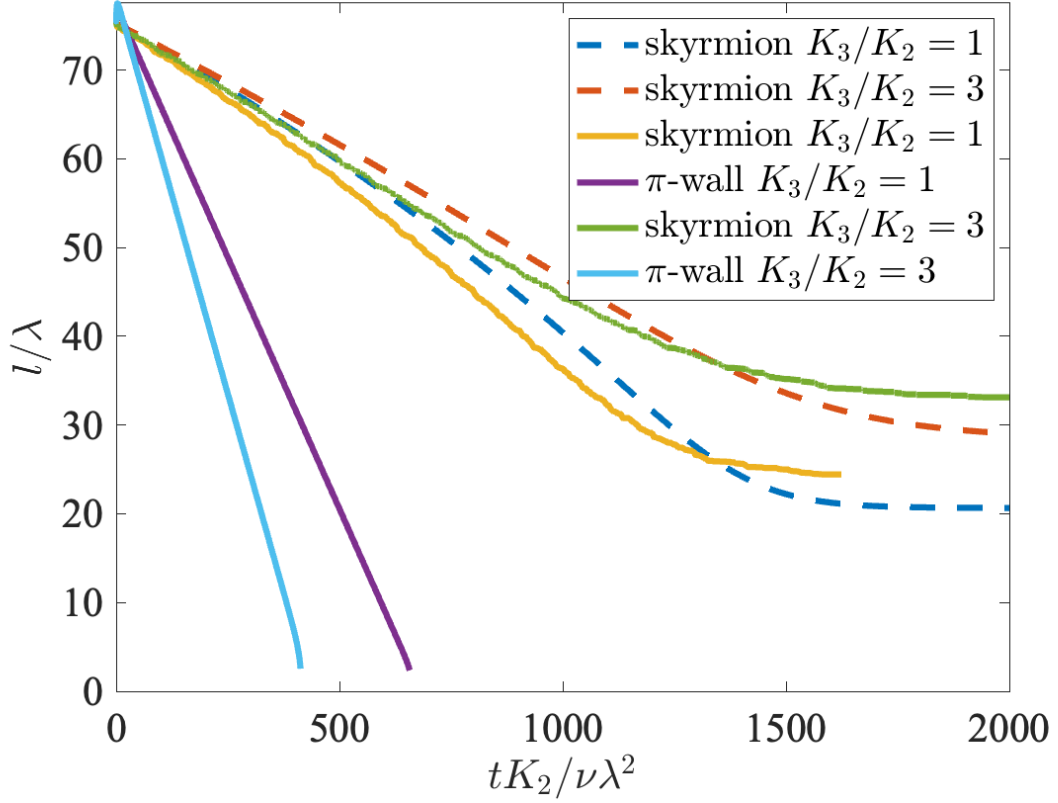


Figure 4.10: Time evolution of circumference of a skyrmion or length of a straight π -wall normalized as $24\pi\lambda$. Here the dashed lines from the first two legends are derived from director model, while others are derived from Landau-de Gennes model with different ratios of K_3/K_2 .

In Odijk theory [67], the Frank constants satisfy approximately $K_1 = 3K_2$. We choose $K_1 = 3K_2 = K_3 = 3$. For the skyrmion, the splay contribution is negligible. A larger K_3/K_2 ratio increases the bending energy cost, which suppresses the shrinkage of the skyrmion. As a result, the equilibrium radius becomes larger and the shrinkage velocity decreases (see Fig. 4.10). In contrast, for a straight π -wall, although the interior of the wall is dominated by twist, significant splay and bend deformations arise near the two ends. Increasing K_1 and K_3 therefore enhances the energetic penalty at the wall ends, effectively driving the two ends together and accelerating the shrinkage of the π -wall.

4.4 Conclusion

We proposed a phenomenological model for colloidal skyrmions in planar membranes by combining Frank elastic energy with a tilt potential. Numerical solutions show that the equilibrium radius grows with chirality $q\lambda$ and the elastic ratio $k = K_3/K_2$. A critical value $q\lambda \simeq 0.63$ marks the boundary between metastable finite skyrmions and expanding states that evolve into straight π -walls.

By fitting to experimental data, we estimated a rotational viscosity of $\nu \approx 111$ Pa-s, much higher than in short-rod nematics. The slow shrinkage of skyrmion compared with straight π -wall is explained that skyrmion dynamics are twist-driven (K_2), while wall retraction is dominated by splay and bend elasticity ($K_{1,3} \gg K_2$).

In addition, we performed numerical simulations using the finite element package *FEniCS* to study the relaxation dynamics of π -walls and skyrmions within the Landau-de Gennes framework. The simulations reproduce the qualitative difference in the relaxation behavior of the two structures. In particular, a straight π -wall shrinks significantly faster than a skyrmion. This difference can be understood from the spatial distribution of dissipation. Beyond the one-constant approximation, increasing the ratio K_3/K_2 further enhances the difference in shrinkage velocity observed in experiments, providing additional support for the phenomenological model. However, quantitatively our theoretical models do not fully explain the experiments. For the future work, we will investigate other modes of dissipation.

Chapter 5

Summary

5.1 Summary

In this thesis, we studied chiral liquid crystals on curved and planar colloidal membranes, focusing on the roles of curvature, chirality, and elasticity.

In Chapter 3, for curved geometries, we investigated director configurations on cylinders and unduloids with a tilt coupling that favors alignment with the surface normal. When Frank elasticity dominates, the system forms a cholesteric state with a pitch determined by chirality. As the tilt coupling increases, the cholesteric state is untwisted, leading to a transition to the smectic state in which the directors are purely normal. We also examined metastable twisted configurations above the transition and showed that sharp domain walls develop when the tilt penalty is large. The pitch associated with these domain walls depends on system parameters.

Our analytical results rely on the assumption that the director has no component along the axis of symmetry, which is appropriate for cylinders but less accurate for unduloids. In addition, we restricted our study to configurations continuously connected to the uniform nematic state. More complex states involving multiple domain walls or defects could be explored using *Morpho*. It would also be interesting to study the interplay between defects and Gaussian curvature on unduloid surfaces. Finally, we have treated the membrane shape as fixed, while real colloidal and lipid membranes are deformable, and the coupling between in-plane order and shape remains an important direction for future work.

In Chapter 4, for planar membranes, we proposed a phenomenological model for colloidal skyrmions by combining Frank elasticity with a tilt potential. Numerical solutions show that the equilibrium skyrmion radius increases with chirality and with the elastic ratio K_3/K_2 . A critical value $q\lambda \simeq 0.63$ separates metastable finite skyrmions from expanding states that evolve into straight π -walls. By fitting to experimental data, we estimated a rotational viscosity of $\nu \approx 111$ Pa·s, which is significantly larger than that of short-rod nematics.

We also compared the relaxation dynamics of skyrmions and straight π -walls using Landau–de Gennes simulations implemented in *FEniCS*. We reproduced the qualitative difference in relaxation behavior seen in experiments, with π -walls shrinking significantly faster than skyrmions. This difference can be understood from the spatial distribution of dissipation. Beyond the one-constant approximation, increasing the ratio K_3/K_2 further enhances the difference in shrinkage velocity, consistent with experimental observations. For the future work, we will investigate other modes of dissipation to better explain the experiments quantitatively.

Overall, these results demonstrate how curvature, chirality, and elastic anisotropy govern the structure, stability, and dynamics of defects in colloidal membranes.

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