# Surface Pattern Formation in Plant-based Plywoods and Biological Liquid Crystal Membranes

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# Dedication

To my lovely mother, Parvin Kahrizi

# **Contributions of the Author**

The author chooses the manuscript-based thesis option following the guidelines stipulated by the Faculty of Graduate and Postdoctoral Studies:

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The contents of Chapters 2-5 of the present thesis are adopted from articles published in or to-be submitted to scientific journals under the normal supervision of my research supervisor, Prof. Alejandro D. Rey, and co-supervisor, Prof. Damiano Pasini, who are also co-authors. All the theoretical and computational work described in this thesis has been done by the present author.

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# Abstract

This thesis provides a comprehensive theoretical framework to elucidate the principles and mechanisms that govern the formation of periodic nano-structured surfaces in biological and synthetic anisotropic soft materials. A new physical model is presented to characterize the interface wrinkling in chiral/achiral open and closed liquid crystal surfaces using the Cahn-Hoffman capillary vector. A nemato-capillary shape equation is derived using the well-known cellulose chiral liquid crystals (LC) material model system that displays the ubiquitous twisted plywood architecture. To analyze the origin of periodic surfaces, all possible capillary pressures and corresponding surface energies are systematically investigated. A scaling law is formulated to derive the explicit relation between the wrinkling's amplitude to the wave-length ratio as a function of the anisotropic surface tension, which is then validated with experimental values.

Then, the shape equation is applied to investigate the surface structural changes and the corresponding color changes in response to humidity. The formation of the water-induced surface undulations is investigated through the interaction of anisotropic interfacial tension, swelling through hydration, and capillarity at free surfaces. The optical responses of the periodic nano-structured surfaces are studied through finite difference time domain simulations (FDTD). A novel colorimetric humidity sensor model based on the self-assembly formation of the chiral surface structures together with the water-induced multiple structural colors is established.

The model is further extended to include both liquid crystal anisotropy of biological materials, bending elasticity of surfactant-like biomolecules, and substrate cholesteric order. The results elucidate a natural setting for the creation and control of complex real surface patterns such as spatial period-doubling, period-tripling, and quasi-periodicity. A morphology phase diagram is presented, which allows us to determine what characteristic pattern will appear on the surface based on the interaction of the three primitive shapes (folding, creasing, and flat). The model is shown to be analogous to a driven pendulum, a connection that enables generic pattern classification as a function of bending elasticity, liquid crystal chirality and anchoring strength.

Finally, the model is extended to understand the deformation of closed liquid crystal cell membranes. A comprehensive morphological phase diagram of the closed membrane surface patterns, in which we classify the characteristic regimes of membrane shapes based on the interaction of the three primitive shapes (ellipse, spindle-like shape, and n-fold) is presented. The

results indicate that, depending on the bending elasticity of the membrane, the liquid crystal anisotropy might be able to deform the cell resulting in anisotropic asymmetric shapes.

All these findings provide a foundation to understand the nano-structured surface patterns, and corresponding structural color phenomena in Nature. Furthermore, the coupling between the order and the curvature of the membrane opens up new opportunities to design novel functional soft materials.

# Résumé

Cette thèse fournit un cadre théorique approfondi expliquant les principes et mécanismes qui régissent la formation des surfaces nanostructurées périodiques dans les matériaux biologiques anisotropes. Un nouveau modèle physique qui caractérise les surfaces planes et cylindriques des cristaux liquides en utilisant le vecteur de capillarité Cahn-Hoffman est présenté. Une équation nemato-capillaire est dérivée en utilisant le modèle de l'architecture des parois cellulaires de plantes. Toutes les pressions capillaires et les énergies de surface correspondantes sont systématiquement étudiées, afin d'analyser l'origine des surfaces périodiques. Une loi d'échelle qui permet d'établir une relation explicite entre l'amplitude et la longueur d'onde des ondulations est formulée. Par la suite, cette loi est validée expérimentalement. L'équation de forme est ensuite appliquée pour étudier les changements structuraux de surface et les changements de couleurs correspondantes en fonction de l'humidité. La formation d'ondulations induite par l'humidité est étudiée au travers des interactions de la tension superficielle anisotrope, du gonflement d'hydratation, et de l'instabilité capillaire. Les propriétés optiques des surfaces sont étudiées grâce aux simulations des différences finies dans le domaine temporel (FDTD : Finite Difference Time Domain).

Le modèle est ensuite étendu pour inclure à la fois les propriétés anisotropes des cristaux liquides, les propriétés élastiques des surfactants (OR tensioactifs), et l'ordre cholestérique du substrat. Un diagramme de phase morphologique basé sur l'interaction de trois formes primitives (pliage, plissage, et plat) OR ('folding', 'creasing', et 'flat') est présenté. Ce diagramme permet de déterminer le motif (OR structure) caractéristique qui apparaîtra sur la surface. Le modèle est présenté comme l'analogue dynamique du pendule, une connexion qui permet la classification des motifs en fonction de l'élasticité des membranes et des propriétés anisotropes des cristaux liquides.

Enfin, le modèle est étendu pour comprendre la déformation des membranes biologiques cylindriques. Un diagramme de phase morphologique basé sur l'interaction de trois formes primitives (ellipse, fusiforme, et n-pli) OR ('ellipse', 'spindle-like shape', et 'n-fold') est présenté, et permet de déterminer le motif (OR structure) caractéristique qui apparaîtra sur la surface. Les résultats montrent que, dépendamment de l'élasticité de la membrane, l'anisotropie du cristal liquide pourrait être capable de déformer la cellule, ce qui entrainerait des formes asymétriques anisotropes. Tous ces résultats fournissent une base pour comprendre les motifs des surfaces

nanostructurées et les couleurs associées (OR les phénomènes de couleur associés) à ces structures observées dans la nature. De plus, le couplage entre l'ordre et la courbure des membranes (permet d'ouvrir) OR offre de nouvelles opportunités pour construire de nouveaux matériaux fonctionnels.

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# Chapter 1

#### **1** General Introduction

# 1.1 Thesis motivation

Liquid crystalline phases, found in many biological materials such as collagen, cellulose and chitin, are formed through an efficient entropy-driven self-assembly process. Biological liquid crystals (BLCs) are functional materials that display several unique important properties such as nano-scale surface ultrastructures. Relationships between the architecture of the biological liquid crystal materials and surface wrinkling is widely recognized but it is currently poorly understood. These surface patterns that form spontaneously on the free surface of BLCs are responsible for iridescence and structural colors, observed in some beetles and plants. The study of the formation of these surface undulations is fundamental in understanding structural color in nature and can inspire the design of optical devices with novel functionalities. Moreover, living systems can respond to external environmental changes by adapting their shapes. Lipid vesicles show a wide variety of complex topographies and morphological instabilities in response to chemical and physical stimuli. There is great interest in industry to efficiently mimic this behavior to develop bio-materials in applications such as artificial muscles and drug delivery. This thesis focuses on the formation mechanism of surface wrinkling and morphological patterns observed in biological materials, and investigates the role of external stimuli such humidity and osmotic pressure in the surface deformation patterns and the morphological changes. The integration of anisotropic material physics, pattern formation, and differential geometry developed in this thesis yields fundamental properties-structure-surface shape relations of wide applicability to biomimetic engineering.

## **1.2 Liquid crystals**

Liquid crystallinity is an intermediate state between stable crystalline solids and isotropic liquids. Hence this state possesses both the mechanical properties of liquid such as fluidity and the structural properties of crystalline solids such anisotropic molecular order [1]. Liquid crystals (LCs) are anisotropic soft materials formed by calamitic (rod-like), discotic (disc-like), and v-shaped molecules/mesogens that possess long-range orientational order and varying degrees of positional order. Liquid crystalline phases can be classified on the basis of the controlling self-assembly driving force (temperature and/or solvents) and average molecular order. When liquid crystals exhibit phase transitions due to temperature changes, it is defined as a thermotropic liquid crystal and when the phase transitions occur due to solvent concentration, it is known as lyotropic. The phase transition in thermotropic LCs is mainly driven by van der Waals interactions [2]. While, the formation mechanism of lyotropic phases is an entropy driven process; the phase transition is governed by excluded volume interactions [3]. The lyotropic phase is essentially formed in aqueous solutions of amphiphilic molecules such as soaps, detergents, and phospholipids which tend to self-assemble to form spherical and cylindrical bilayers, vesicles, and micelles. As the concentration of amphiphilic molecules increases, various lyotropic structures can be obtained (see Figure 1-1). When the concentration of amphiphile in aqueous solution exceeds ~10% by weight, the simple spherical and cylindrical micelles undergo conversion to hexagonal, cubic and lamellar phases [4]. These LCs are abundant in Nature, specifically in living systems.



**Figure 1-1.** Schematics of lyotropic liquid crystals: (a) spherical micelles, (b) cylindrical micelles, (c) hexagonal phases, (d) cubic phase (e) lamellar phase. Adapted from ref [5].

Thermotropic LCs are generally classified based on the average molecular orientation into three main phases known as (1) nematics, (2) cholesterics, and (3) smectics (see Figure. 1-2). The nematic phase possesses partial orientational order and lack of positional order; in this phase the long axes of the molecules are preferably oriented along a particular direction [6]. The preferred average molecular orientation known as the "director" is represented by the unit vector **n**. When the molecules are intrinsically chiral, or when a chiral dopant is added to nematic LC phases, the nematic phase undergoes a macroscopic helical distortion around an axis perpendicular to the director resulting in the cholesteric LC phase, also known as the twisted nematic phase (N\*) [7].



**Figure 1-2.** Schematics of the classification of the liquid crystal mesophases in terms of average molecular orientation: (a) nematic, (b) cholesteric, and (c) smectic. **n** represents the director field towards which the molecules show preferred orientation. **H** is the helix unit vector showing the rotation axis of director, and  $p_0$  is the pitch.

Cholesteric LCs can be portrayed by a multi-layered configuration where the molecules are laid down parallel in each layer, whereas the orientation of molecules between layers changes by a slight constant angle. The periodic structure can be characterized by a length scale known as the pitch P<sub>0</sub>, which is defined as the distance through which the molecules undergo a  $2\pi$  rotation. The pitch is generally of the order of few micrometres and it is affected by physicochemical factors and external stimuli. Smectic phases exhibit both orientational order of long molecular axis and translational order which is partial positional order along the vertical axis. In this phase, the director **n** shows the average orientation of the long molecular axes in each layer; the molecules are free to move within the plane of each layer. As within each layer a variety of molecular arrangement is possible, different types of smectic LCs can be classified e.g. when the average orientation of the long axis is perpendicular to the layer plane results in smectic A phase and when the average orientation is tilted results in the smectic C phase [8]. This thesis only considers cholesteric and nematic liquid crystals.

## **1.3 Biological liquid crystals**

Biological liquid crystals (BLCs) are anisotropic structural and functional materials displaying long range orientational order and partial positional order [1]. Liquid crystallinity is abundantly

found in living systems such as DNA in human cells [9], cellulose in plant cell walls [10], chitin in arthropods cuticles [11], and collagen in human compact bones [12]. Some examples of liquid crystalline analogues observed in nature are presented in Table 1-1. BLCs can be classified into [13]: (i) solid liquid crystal analogues, (ii) in vitro solutions, and (iii) in vivo liquid crystals. Biological liquid crystals are generally formed by self-assembly (plant-based plywoods) and/or flow processes (silk), exhibit multiple length scales and multifunctionality, are responsive to changing environments, and are capable of healing and regeneration [14]. The multiple length scale nature of biological materials arises from the typical sequential assembly of molecular chains, microfibrils, filaments, and fibers, as found in cellulose, collagen, and chitin. Multifunctionality of biological liquid crystals is found by the combination of mechanical and optical properties as in insect eye lenses, bird cornea, and certain beetle cuticle optics. The liquid crystalline order and topological defects in biological analogues are typically that of cholesteric and hence they are referred as biological helicoidal plywoods, also known as the Bouligand structure [15]. Helicoidal plywoods are found in plant cell walls, insect cuticles, bones, corneal tissues and eggshells, and are formed by directed self-assembly when the elongated molecules or filaments with a high aspect ratio align spontaneously above a critical volume fraction, the Onsager threshold [15]. Hence, understanding the self-assembly mechanism through which the biological liquid crystalline phases arise in fibrous composites is crucial in unravelling the fundamental mechanisms of nature's material synthesis. The response of biological liquid crystals to environmental stimuli includes structure adaptation to changing in mechanical stress, chemical composition, and pH; for example helix pitch in cholesterics is a function of chemical composition [14]. Examples of healing and wounding recovery are found in the epidermal lamella where initial random collagen fibrils become oriented into a laminated structure [11]. These multi-scale nature and multifunctionality in biological liquid crystals are expected to open up novel opportunities for biomimetic design of bio-inspired materials and devices. This thesis focuses on biological cholesteric liquid crystals (BCLCs) as the representative liquid crystalline analogues in plant cell wall and biological nematic liquid crystals (BNLCs) as the representative liquid crystalline analogues in living cell membranes. In the following section, the microstructure, properties, and functionalities of plant cell wall and biological cell membranes are discussed.

Solid Biological Analogues	In vitro	In vivo liquid crystals
	solutions	
Exoskeleton of insects [10, 11, 16, 17]	Collagen [18-20]	DNA [21, 22]
Plant cell wall [23-26]	Cellulose [27-29]	Spider silk [30-32]
Bone osteons [11, 12]	DNA [33-35]	Collagen in egg shell & glands of dog fish [36, 37]
Epidermis of fish [38, 39]	Actin [40, 41]	Sickle-Cell hemoglobin [42]
Membranes of animal eggs [11, 43]	Mucin [44, 45]	Microtubule [46]
Cornea [11, 47, 48]	Chitin [49-51]	Chromosomes of dinoflegallate and bacteria [52]

Table 1-1. Biological liquid crystals observed in living systems (adapted from ref. [14, 15]).

# 1.4 Plant cell wall

The plant cell wall is a stiff and viscoelastic composite, behaves as a supporting structure and allows surface expansion [53]. The main components of the cell wall are cellulose, hemicellulose, lignin, protein, and pectin. The typical thickness of plant cell walls is about hundred times thinner than the cell thickness (0.1 to 0.3  $\mu$ m). As shown in Figure 1-3 plant cell wall is a layered structure with a primary cell wall (p) laid down during growth on the outside and three secondary cell walls (S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>) that formed when the cell has reached its final size and shape [54]. The primary and secondary wall layers differ in detailed chemical composition (cellulose and hemicellulose content is greater in secondary walls than primary wall) and structural organization (cellulose microfibril (CMF) in primary wall is organized in a loose interwoven texture, while CMF is well oriented in secondary layers). But, their basic structure is the same: hemicellulose and lignin matrix reinforced by cellulose fibers. The thickness of S<sub>2</sub> layer is generally much higher than that of S<sub>1</sub>, S<sub>3</sub>, and primary layers. Each cellulose fiber has about 3-4 nm diameter and several hundred nanometers length. The angle between the cellulose fibers and the cell axis is known as the MFA (microfibril angle). Generally, the measurement of MFA for the whole cell wall is based on the approximation of MFA in the S<sub>2</sub> layer. The MFA usually varies between 0 to  $40^{\circ}$  in the S<sub>2</sub> layer [55]. The cell wall structure controls the complex shape of plants and their mechanical behavior [56]. The important characteristics of plant cell walls are explained as follows.



**Figure 1-3.** Schematic of multilayered plant cell wall structure. P is primary cell wall;  $S_1$ ,  $S_2$ , and  $S_3$  are secondary cell wall layers [54].

The primary and secondary walls can be regarded as a biological composite with cellulose fibers embedded in a matrix of hemicellulose and lignin. In the plant cell wall, CMF in the polysaccharide matrix are oriented in strategic directions to form an anisotropic structure, generally a plywoodlike laminated architecture with the goal of attaining good mechanical properties in all directions. The twisted plywood structure also known as helicoidal structure is the most abundant architecture in living systems. In many skeletal support systems of plants and animals, cellulose, chitin, and collagen occur in the form of microfibrils ordered in a chiral nematic fashion (helicoids). In nature, the twisted plywood organization can be found in planar and cylindrical configurations. The planar twisted plywood structure is characterized by a series of planes with parallel CMF in each layer where the CMF direction changes from layer to layer by a regular angle ( $10^{\circ}$  to  $20^{\circ}$ ) as in the stairs of a spiral staircase (Figure 1-4a). One of the most distinctive characteristics of the helicoidal structure is the series of superimposed nested arcs observed in any oblique cross section (Figure 1-4b). The helicoidal plywood is a unidirectional periodic structure in which the arced pattern repeats over a length  $P_0/2$ , where  $P_0$  is the helix pitch (Figure 1-4c). In the cylindrical twisted plywood structure, the parallel and equidistant planes become a set of coaxial cylinders, and fiber orientation represented by parallel helices. The fiber orientation slightly changes from one cylinder to the next (Figure 1-4d).



**Figure 1-4.** Twisted plywood structure; a) planar twisted plywood structure b) oblique cross section c) length scale (pitch) d) cylindrical plywood structure [12].

Plant cell wall can be considered as an extracellular component that shows complex hierarchical organization from the macroscopic scale to the nanometer scale, each level involving of analogous molecular components, but giving rise to different and independent functional properties and adaptions [57]. At these levels of hierarchy, plants manifest a wide variety of adaptable parameters such as cell shape, the orientation of cellulose microfibrils within cell wall, arranging the constituents in layers of varied thickness and chemical composition. This organization enables plants to structurally adapt with high efficiency on every hierarchical level, because all levels of organization are tightly integrated. The hierarchical organization found in a woody tissue is depicted in Figure 1-5. Typical magnitudes of the different structures are given based on the information from bamboo emphasizing the hierarchical nature found from the molecular scale of cellulose fibrils to the micron scale of plywood helicoids found in the plant cell wall, up to the millimetre scale of plant cellular structure. This hierarchy makes it possible to extract scientific and engineering principles of plant-based biomimetic at different length scales [58].



Figure 1-5. Hierarchical organization in bamboo as a woody tissue [59].

The plant cell wall is a multifunctional, dynamics structure that provides mechanical strength to the plant tissue, maintains cell shape, controls cell expansion, and regulates transport [54]. Because of the limited chemical composition (C, H, O, etc) and processing conditions (low temperature and pressure), plants have evolved the water actuation mechanisms that rely on their internal heterogeneous architecture. In fact, the sophisticated structure of the plant cell wall is the basis of the actuation systems in plants [60]. This actuation system can be divided into two forms: surface and bulk actuations. Although, the anisotropic structure of plant cell walls is the source of both actuation forms, different mechanisms are involved in each. This thesis deals with surface actuation mechanism in plant-based plywoods.

### 1.5 Biological and synthetic membranes

Biological membranes generally contain an oriented bilayer of phospholipids, the basic structure of all living cells, such that the hydrophobic tails face each other and the hydrophilic phosphate heads the aqueous phase [61]. Although cell membranes including a set of proteins, phospholipids, and cholesterols are complex structures, they all share the basic membrane structure (see Figure 1-6). Different types of proteins are linked to extracellular or intracellular surfaces of the cell membrane, cholesterol is situated among the phospholipids (close to hydrophilic heads), and carbohydrates are placed in the outer surface.

Despite their simple flat configuration, biological membranes can vary to a wide variety of complex topographies and display morphological instabilities in response to different physical and

chemical conditions [62, 63]. Several membrane models have been presented to study the fundamental properties of lipid bilayers such as unilamellar and multilamellar vesicles [64], supported bilayers [65], and nano-discs [66]. Lipid bilayers in water (analogous to lyotropic liquid crystals) generally form vesicles which are well-known examples of closed biomembranes and act as the simple representation of cell membranes. The diameter of vesicles is in a range between 50 nm to tens of micrometers, and the thickness of the vesicles is a few nanometers [67]. Larger vesicles commonly referred to as Giant Unilamellar Vesicles, GUVs) are large enough biomimetic models (tens of microns in size) of cellular membranes that have played a prominent role in studying biophysical characteristics of living cells. As quantifying the membrane shape variations in nucleated cells is experimentally challenging, shape selection of single isolated membranes is typically studied in red blood cells (RBCs) and in model systems, typically giant unilamellar vesicles (GUVs) [68]. A healthy blood cell typically has a biconcave shape, known as discocyte. By changing several system parameters such as osmotic pressure, cholesterol content, and pH, the cell shape can be changed into other shapes. Shape variations in red blood cells, known as poikilocytosis, can be correlated to pathological conditions and can be used in clinical diagnosis of diseases, such as trauma, infections, and cancer [69, 70].

As the lipid bilayers exhibit long range ordering [71], they might be regarded as liquid crystals. Besides, liquid crystalline phase and topological defects are found in numerous biological materials, such as DNA [9], cellulose [10], chitin [11], and collagen [12]. Liquid crystallinity not only governs most physical aspects of biological morphogenesis, but it also contributes in the detailed organization of cells and living tissues [72]. A cell membrane can exhibit anisotropic behavior due to lipid tilt, lipid rotation, and chirality [74] or due to external macromolecules like proteins [75].



**Figure 1-6.** The schematic of cell, a phospholipid bilayer with embedded cholesterols, proteins, and carbohydrate chains [73].

Liquid crystallinity of actin or tubulin polymer networks can also contribute in controlling shape deformation in biological cells. Besides, it has been shown that the morphological patterns of some lyotropic liquid crystal droplets closely resemble the geometries and symmetries of living tissues and cell membranes [76]. Lipid-forming bilayers can be biological or synthetic, and bilayer elements are not necessarily always lipids, as new liposomes known as polymersomes can also be formed from polymers. Polymersomes are macromolecular synthetic analogs of phospholipids nanostructures composed of amphiphilic block copolymers that have a size range between 50 nm and 5 µm [77]. Polymersomes exhibit a large variety of morphologies that can be controlled by copolymer composition and subsequently respond to chemical or physical stimuli such as pH, osmotic pressure, and temperature [78]. Abdelmohsen et al. recently reported the osmotically induced shape transformation of spherical poly (ethylene glycol)-b-poly(styrene) (PEGPS) polymersomes into stomatocytes through reduction of the inner volume [79]. Polymersomes have revealed a great potential in biomedical applications from drug delivery to artificial organelles due to their higher stability and membrane integrity compared to liposomes [78]. This thesis presents a systematic modeling approach to derive the equations coupling topology, elastic free energy, and anchoring conditions that can be used in analyzing the surface morphologies observed in liposomes or phospholipid bilayer, surfactant-coated nematic liquid crystal droplet or liquid-crystalline lipid monolayers, and polymersomes (see figure 1-7).



**Figure 1-7.** Anisotropic drops with complex coatings. (a) Liposome, (b) surfactant-coated nematic liquid crystal droplet, and (c) polymersome.

### 1.6 Free surface patterns

Surface ultrastructures are found in many biological materials such as periodic undulations observed in films of concentrated collagen [19], silk gland ducts of golden orb-web spider *Nephilaclavipes* [31], exoskeleton of the beetle *Chrysinagloriosa* [17], and cellulosic materials [28, 29]. The interaction of liquid crystal self-assembly and free surface capillarity is manifested in beetle exocuticles and spiders duct interfaces. It has been shown that the surface patterns in the exoskeleton of beetle *Chrysina gloriosa* and in the duct of silk secreting glands in spider *Nephila clavipes* closely resemble the atomic force microscopy image of the focal conic domains that spontaneously arise on the free surface of cholesteric liquid crystals, CLCs (see Figure 1-8) [17, 82]. The well-organized near hexagonal packing and spiral structure observed in each cell on the beetle exoskeleton correlates nicely with the conical form [17]. The duct of silk secreting glands in spider silk has similar surface undulations of periodicity 270 nm, the defect disclinations, and fiber orientation close to the surface which are like the defect patterns near the free surface of a siloxane oligomer-based cholesteric liquid crystal and the beetle exocuticle [17, 31, 81].



**Figure 1-8.** Surface patterns in the exoskeleton of beetle Chrysina gloriosa and in the duct of silk secreting glands in comparison with the free surface of cholesteric liquid crystals a) SEM image shows the nested arcs and a waxy top layer the beetle C. gloriosa b) bright-field TEM images of sections taken from the silk gland ducts of N. clavipes c) orientation distribution of cholesteric with surface defects. Adapted from [17, 31, 81].

Furthermore, the surfaces of plants show a variety of micro/nano periodic structures that can be observed on seed, leaf and most frequently on flower petals (Figure 1-9) [83]. These surface patterns are responsible for several fascinating mechanical and optical properties observed in some plants. They can provide super hydrophobicity and functional support for the cell, and they can act as a diffraction grating [84]. The surface wrinkling can be parallel to or perpendicular to the long axis of the cell, or can lie in more complex patterns.



**Figure 1-9.** Surface wrinkling in flower petals. (a) Tulip 'queen of the night', (b) Scanning electron microscope image of the outer (abaxial) epidermis of the tulip, (c) The Venice mallow (Hibiscus trionum) flower (d) Scanning electron microscope image of the upper surface of the purple patch, (e) The Yunnan rhododendron flower, (f) Scanning electron microscope image of the epidermal cells of the petals, (g) The daisy Ursinia calendulifolia flower, (h) Scanning electron microscope images. Scale bars: 10  $\mu$ m. Adapted from [84].

The surface undulations in living systems are not limited to single-wavelength sinusoidal patterns, and a rich variety of multi-scale and complex patterns, such as folding, creasing, spatial period-doubling, and quasi-periodicity arise on surfaces of plant tissues, animal organs, and spatially confined membranes. Figure 1-10 illustrates some examples of the fascinating morphological patterns found in various types of living systems across multiple size scales, such as period-doubling spatial patterns in the *esophageal mucosa* [85], period-doubling spatial patterns in the *esophageal mucosa* [85], period-doubling spatial patterns in the pulmonary airway [86], creases on the cerebral cortex [87], and the multi-lengthscale undulations in the tulip "Queen of the Night" [88]. Although the formation of these morphological patterns is governed by several complex genetic and biochemical processes, the general formation mechanism has been believed to be the growth-induced mechanical instabilities that produced by the compressive strain between biological layers with different swelling or shrinking rates [89].



**Figure 1-10.** Complex surface wrinkling in living membranes. (a) a typical ring cut from a bovine esophagus b) normal and asthmatic airways, (c) human cerebral cortex d) multi-scale surface grating of tulip "Queen of the Night" petals that reflect the double wavelength periodic wrinkling. The grating of short wavelength,  $\lambda_2 \approx 1.2 \mu m$ , are superimposed on longer waves of length  $\lambda_1 \approx 29 \mu m$ . Adapted from [85].

These patterns can be categorized into wrinkles, folds, creases, and period-doubling (see Figure 1-11). The type of surface morphological patterns can be associated with pathological and physiological conditions of biological tissues and be used in clinical diagnosis of diseases such as trauma, asthma, infections, and cancer. For instance, deeper folds have been observed in asthmatic airways in comparison with healthy airways [90].

In addition to these in vivo observations, concentrated collagen solution (20 mg/ml) forming cholesteric films are known to exhibit periodic undulations of similar scales at the free surface with amplitude of the order of 150 nm, an order of magnitude smaller than its cholesteric pitch of the order of  $3.5 \mu m$  [19]. Similar surface topography and undulations of the order 500 nm is known to arise in 18 wt.% solutions of cellulose [29].

Although, considerable efforts have been directed in formulating and validating theoretical models that attempt to explain these complex surface wrinkling in biological soft materials,

previous studies have been restricted to bilayer elastic models where a stiff film resting on a compliant elastic substrate. There are few studies considering other chemical and biological mechanisms coupled with the compression-induced elastic deformation contributing to the wrinkling behavior in biological surfaces and membranes. One of the objectives of this thesis is to develop a physical model that includes liquid crystal anisotropy of biological materials, bending elasticity of surfactant-like biomolecules, and substrate helicoidal structure to describe the complex real surfaces.





# **1.7 Structural color**

Structural color is widespread in animals and plants. The primary purposes of structural colors in Nature are the ability to camouflage against variety of backgrounds, mating and social signaling [91]. The helicoidal plywood has been reported as the structure directly responsible for generating structural color and iridescence in several plants [92], beetles [17], and fruits [93]. The iridescence and structural color in plants are typically associated with diffraction grating, multilayered interference, and helicoidal architecture (see Figure 1-12). Structural color in floral plants originates mainly from ordered surface diffraction gratings [94]. When the periodicity of the

surface undulations is of the same order of the incident light wavelength, the structure has the potential to generate iridescence through the diffraction grating mechanism. The ordered surface gratings scatter incident light in the plane perpendicular to the direction of the periodic undulations based on the grating equation [94]:

$$m\lambda = \frac{p_0}{2}(\sin\theta_i - \sin\theta_d)$$
(1.1)

where  $\theta_i$  and  $\theta_d$  are angles of incidence and diffraction which govern the angular locations of the principal intensity maxima for the diffracted incident light with wavelength  $\lambda$ , and *m* is the diffraction order. When the incident light is along the surface, mainly first order reflection occurs. While, for oblique incidence of light higher order reflections can happen [95]. Considering Eq. 1.1, for any given value of the angle of incidence  $\theta_i$ , each wavelength  $\lambda$  scatters into different angular directions. When the incident light is white light, different colors disperse in the perpendicular direction of the periodic structure, making the surface iridescent. One of the outstanding examples of diffraction grating in flowers is the iridescent purple color of the tulip "Queen of the night" [94].

Structural color in leaves originates mainly from multilayer interference of materials with different refractive indexes or from helicoidal structure of the plant cell wall [94]. When incident light reflects at each interface between materials with different refractive indices, based on the wavelength and the angle of incidence, the reflected beams might have interfered constructively or destructively [96]. In fact, the multilayer acts as a filter and reflect a certain wavelength. Consider a multilayer made of two materials with thicknesses  $d_1$  and  $d_2$  and refractive indices  $n_1$  and  $n_2$  respectively (see Figure 1-12b). For  $(n_1 > n_2)$ , constructive interference occurs when the phase difference of a beam traversing both materials is a multiple of the wavelength [96]:

$$m\lambda = n_1 d_1 \cos \theta_1 + n_2 d_2 \cos \theta_2 \tag{1.2}$$

If the phase difference of two beams reflected at the interface between two materials equals to  $(m' + \frac{1}{2})\lambda$  where m' < m, Eq. 1.2 becomes:

$$(m' + \frac{1}{2})\lambda = 2n_1 d_1 \cos \theta_1 \tag{1.3}$$

At a normal incidence of light and m' = 0, Eq. 1.3 equals to  $n_1 d_1 cos \theta_1 = \frac{\lambda}{4}$ , hence the quarter-

wave stack is ideal for multilayer interference [96].

The helicoidal architecture in plant cell wall can also generate iridescent colors. As the orientation of the cellulose microfibrils in helicoids changes between layers, the refractive index also changes from one layer to the next, which generates the reflection of polarized light in the opposite direction of the helix axis [94]. In the case that the difference between the refractive index of the cellulose microfibrils and the matrix is insignificant, the maximum reflectivity is obtained for  $\lambda = 2np_0$ , where n is the refractive index of the cellulose microfibrils, and P<sub>0</sub> is the helix pitch (see Figure 1-12c). One of the outstanding examples of helicoid architecture in producing iridescent blue color in leaves happens in the tropical plant "Selaginella willdenowii" [97].

Numerous efforts have been made to capture the helicoidal architecture in solid films to create colored iridescent films [98-100]. In the preparation of a lyotropic cholesteric mesophase, *Werbowyi* and *Gray* discovered that concentrated aqueous solutions of hydroxypropyl cellulose (HPC) displayed iridescent colors that changed with concentration and viewing angle [101]. *Fernandes et al.* fabricated iridescent solid cellulosic films with tunable mechanical and structural color properties, which mimic the structures found in the surface of the "Queen of the Night" tulip petals [102]. They indicated that the formation and periodicity of the surface structure are governed by the helicoidal structure.

#### 1.7.1 Color change in response to environmental stimuli

Color change in response to environmental stimuli is ubiquitous in plants and animals. The iridescent blue color in the fish *Chrysiptera cyanea* can change to ultraviolet (see Figure 1-13a) by the simultaneous change in spacing of the adjoining reflecting plates [104]. It has also been observed that the beetles *Dynastes Hercules* and *Coptocycla* can vary their coloration in response to humidity [105,106]. The elytra of longhorn beetles *Tmesisternus isabellae* reacts to water absorption by color change, from golden in the dry state to red in the wet state (see Figure 1-13b). The factors controlling color change are the swelling of the multilayer pitch (from about 175 nm in the dry state to about 190 nm in the fully wet state) and the water infiltration [107].


**Figure 1-12.** Schematics of three main mechanisms responsible for producing iridescence and structural color: (a) diffraction grating (b) multilayer interference (c) helicoidal structure. Adapted from [94, 103].

Structural colors in some plants can also be the result of a response to humidity, light, and touch through the change of bulk and surface nanostructures, among other external stimuli. One of the interesting examples is a tropical rainforest plant, *Selaginella willdenowii* that possesses iridescent blue leaves that can dynamically respond to hydration and dehydration. It has been shown that the iridescent blue color turns to green when the leaves are immersed in water, with blue color reappearing when the leaves are dry [108]. Electron microscopy of iridescent blue leaves show that optical effects upon humidity changes are mediated by altering the twisted plywood structure (helix pitch) in the plant cell walls (see Figure 1-13c). The reported lamellar spacing in green leaves is  $268 \pm 2.2$  nm, which is larger than the lamellar spacing in blue leaves,  $141 \pm 2.4$  nm [92].



**Figure 1-13.** Structural color change in response to environmental stimuli: (a) the iridescent blue color and ultraviolet in the fish Chrysiptera cyanea (b) color change in the beetle Tmesisternus isabellae from golden in the dry state to red in the wet state (c) color change in the tropical plant Selaginella willdenowii from iridescent blue color to green through hydration; scale bars: 0.5  $\mu$ m. Adapted from [104], [107], [108].

Similar behavior is observed in a hygroscopic liquid crystal polymer film that responds to temperature and humidity by changing its color [109]. It has been proved that that when humidity is high, the film swelling results in a pitch increase as opposed to the case of low humidity, which causes a decrease in the pitch with consequent film shrinkage. Such structural colors observed in the animal and plant kingdoms [96] offer an interesting area for biomimetic design of optical sensors because of its quite simple mechanism, limited biomaterial resources (cellulose, chitin, keratin, and collagen), ambient conditions (low temperature and pressure), and multi-scale domain. Understanding the formation of the surface gratings is crucial in understanding structural color in nature and can inspire optical devices with novel functionality.

## **1.8** Cylindrical shapes of cell membranes

Biological membranes exhibit a variety of complex shapes including elliptocyte, discocytes, stomatocytes, pear-shaped, echinocyte, and starfish. Figure 1-14 illustrates some of the morphological patterns observed in giant vesicles and red blood cell as the typical examples of lipid bilayers. By varying the chemical and physical parameters such as osmotic pressure and chemical concentration across the membrane, transitions from one configuration to another can be observed. Several mechanisms can be considered as the sources of the membrane curvature [75]: 1) different composition of phospholipids on either side of the bilayer 2) helix insertion 3) shape of proteins 4) scaffolding by proteins, and 6) Cytoskeletal proteins. Figure 1-15 shows a number of possible examples induces the membrane curvature.



**Figure 1-14.** Confocal images of giant vesicles (a-e) and red blood cell (f) with the schematic vesicle shape configurations: (a) elliptocyte, (b) discocyte, (c) stomatocyte, (d) pear-shaped, (e) starfish, and (f) echinocyte. Adapted from [110].

As shown in Figure 1-15, the cytoskeleton of the membrane plays a significant role in changing membrane tension and resultant curvature. It has been shown that the actin filaments or tubulin polymer networks are involved in the generation of high membrane curvature. Moreover, liquid crystallinity can be also responsible in controlling shape deformation in cells, vesicles, and liquid droplets. For example, spontaneous assembly of phospholipids at the interface between liquid crystals and aqueous phases results in dynamic spatial patterns typical of phospholipids [111]. Another example of coupling between membrane elasticity and liquid crystal anisotropy responsible for the generation of complex surface morphologies, occurs in giant unilamellar

vesicles (GUVs) suspended in a liquid crystal [112, 113]. Moreover, the three-dimensional architectures of some liquid crystal colloids closely resemble the geometries and symmetries of living tissues and cell membranes [114], such as starfish morphology, an instance that confirms the analogy that can be drawn between liquid crystal anisotropy and amphiphilic surfactants [115].



**Figure 1-15.** Different mechanisms of membrane curvature formation. a) changes in phospholipid composition b) shape of membrane proteins c) changes in cytoskeleton of the membrane d) direct and indirect scaffolding of the bilayer e) active amphipathic helix insertion. Adapted from [75].

The morphological patterns are mostly governed by the elastic energy of the membrane, and the membrane shape can be characterized by changes in volume and/or changes in area. A systematic attempt has been made to identify different configurations of deformable vesicles as a function of reduced area and bending energy [116]. Figure 1-16 shows the bending energy of the vesicles versus the reduced area for two families of the equilibrium cylindrical shapes (two-lobed and three-lobed vesicles), together with some representative configurations. It can be noted that the bending energy increases with increasing number of lobes and decreasing reduced area and the number of lobes. The variety of shapes shown in Figure 1-16 can be obtained through changing a single physical parameter such as the surface tension. Increasing the surface tension can result in a reduction of the vesicle area and correspondingly can buckle the membrane shapes.



**Figure 1-16.** Bending energy as a function of the reduced area for two-lobed and three-lobed vesicles. The bending energy increases with increasing number of lobes and decreasing reduced area [116].

#### 1.9 Theoretical background on modelling

In the previous sections, the general background information for the material model systems, the characterization of the surface patterns, and their unique optical properties were described. It is now helpful to briefly describe the theoretical background of the modeling approaches adopted in this thesis.

## **1.9.1** Anisotropic elastic soft matter model for nanostructured free surfaces in biological plywoods

Although, the chiral surface structures are extensively studied by microscopy methods including atomic force microscopy (AFM) [117-120], the complementary theoretical analysis of CLC surface wrinkling is rarely studied. The formation of the surface undulations in CLC interfaces is a complex problem that includes surface tension, anchoring energy and bulk elasticity. In order to explore the free surface relief, the total system energy including surface energy and the bulk elastic energy should be minimized. All the equations that govern the shape of interfaces coupling bulk and surface phases have been presented in [121]. However, the analytical and/or numerical solutions of the problem with the usual formalism is very complicated. In this thesis, it is assumed that the surface undulations in cellulose-based plywoods formed through modulation in surface energy at the anisotropic-air interface and influenced by the chirality of the cellulose fibers. The coupling mechanism between the surface geometry and cellulose fiber orientation can be demonstrated through the shape equation that couples the plywood structure with free surface capillarity. In the following section, a general framework of the shape equation based on the previously used Cahn-Hoffman formalism for anisotropic liquid crystals surfaces is presented.

Liquid crystals generally exhibit anisotropic interfacial properties which play a significant role in capillary instabilities. A capillarity vector thermodynamics for anisotropic materials was first developed by Cahn-Hoffman [122], and then was applied to analyze nematic liquid crystalline surfaces [123, 124]. The capillarity vector  $\boldsymbol{\xi}$  is a fundamental quantity which provides a direct way to take into account the orientation dependences of the surface tension. The capillary vector is a function of the surface unit normal **k** and director **n** and is defined by the gradient of the scalar field r $\gamma$ . Where r is the distance from the origin in a fixed reference frame and is denoted by the surface position vector **r**=r**k**.  $\gamma$  is the surface free energy:

$$\boldsymbol{\xi}(\mathbf{n},\mathbf{k}) = \nabla[r\gamma(\mathbf{n},\mathbf{k})] \tag{1.4}$$

For isotropic interfaces, the capillary vector  $\boldsymbol{\xi}$  reduces to a normal vector  $\boldsymbol{\xi} = \gamma \mathbf{k}$ . The decomposition of the surface director field into normal and tangential components yields  $\mathbf{n}_{\perp} = \mathbf{k}\mathbf{k}$ .  $\mathbf{n}$  and  $\mathbf{n}_{\parallel} = \mathbf{I}_{s}$ .  $\mathbf{n}$ , where  $\mathbf{I}_{s}$  is the 2×2 unit surface dyadic  $\mathbf{I}_{s}=\mathbf{I}-\mathbf{k}\mathbf{k}$ , and  $\mathbf{I}$  is the 3×3 unit tensor. Calculating the gradient of the field r $\gamma$  appearing in Eq. 1.4, using  $\boldsymbol{\xi} \cdot \mathbf{k} = \gamma(\mathbf{n},\mathbf{k}), \boldsymbol{\xi} \cdot \mathbf{d}\mathbf{k} = d\gamma(\mathbf{n},\mathbf{k})$ , and  $d(r\gamma)=(r\gamma).d\mathbf{r}$  gives:

$$\xi(\mathbf{n},\mathbf{k}) = \gamma \frac{\partial r}{\partial \mathbf{r}} + r \frac{\partial \gamma}{\partial \mathbf{r}} = \gamma \mathbf{k} + I_s \frac{\partial \gamma}{\partial \mathbf{k}}$$

$$\xi_{\perp} \qquad (1.5)$$

where the normal component  $\xi_{\perp}$  describes the increase in the surface energy through area dilation and the tangential component  $\xi_{\parallel}$  is the change in the surface energy through rotation of the unit normal. Assuming that the surface is uniaxial, the total surface free energy can be expressed using the Rapinin-Papoular anchoring energy density [125], and the Helfrich free energy [126]:

$$\gamma(\mathbf{n}, \mathbf{k}) = \gamma_0 + \gamma_{an}(\mathbf{n}, \mathbf{k}) + \gamma_{mem}(\mathbf{n}, \mathbf{k}), \qquad (1.6)$$
  
$$\gamma_{an}(\mathbf{n}, \mathbf{k}) = \frac{W}{2} (\mathbf{n}. \mathbf{k})^2, \ \gamma_{mem}(\mathbf{n}, \mathbf{k}) = 2k_c (H - H_0)^2 + \overline{k_c} K$$

where W is the anchoring coefficient. When W<0 (W>0), the easy axis or preferred orientation is normal (tangential) to the interface, and is known as homeotropic (planar) anchoring.  $\gamma_0$  is the

surface tension at zero curvature (H =K=0),  $k_c$  is bending elastic moduli, H<sub>0</sub> is the spontaneous curvature,  $\overline{k_c}$  is the torsion elastic moduli, H is the average curvature, K is the Gaussian curvature. Substituting Eq. 1.6 into Eq. 1.5 yields the normal and tangential components of the capillarity vector:

$$\boldsymbol{\xi}_{\perp}(\mathbf{n},\mathbf{k}) = (\gamma_0 + \frac{W}{2}(\mathbf{n},\mathbf{k})^2) - \frac{k_c}{2}\kappa^2$$

$$\boldsymbol{\xi}_{\parallel}(\mathbf{n},\mathbf{k}) = W((\mathbf{n},\mathbf{k})(\mathbf{n}\cdot\mathbf{t})) + k_c \frac{\partial\kappa}{\partial s}$$
(1.7 a,b)

where s is the surface arc-length and  $\mathbf{t}$  is the surface unit tangent. To derive the shape equation, the following capillary pressure definition is used:

$$\Delta p = -\nabla_s \xi = -\nabla_s (\xi_\perp + \xi_\parallel) \tag{1.8}$$

The divergence of the capillary vector yields the capillary shape equation:

$$\Delta \mathbf{p} = -\mathbf{t} \cdot \frac{\partial \mathbf{\xi}}{\partial \mathbf{s}} = \mathbf{\xi}_{\perp} \kappa - \frac{\partial \mathbf{\xi}_{\parallel}}{\partial \mathbf{s}} = \frac{\partial \mathbf{\xi}_{\perp}}{\frac{\partial \mathbf{k}}{\operatorname{area \ size \ change}}} : \nabla_{\mathbf{s}} \mathbf{k} + \frac{\partial \mathbf{\xi}_{\parallel}}{\frac{\partial \mathbf{k}}{\operatorname{area \ rotation}}} : \nabla_{\mathbf{s}} \mathbf{n} + \frac{\partial \mathbf{\xi}_{\parallel}}{\frac{\partial \mathbf{n}}{\operatorname{crea \ curvature}}} : \nabla_{\mathbf{s}} \mathbf{n}$$

$$(1.9)$$

where  $\Delta p$  is the pressure jump across the interface and  $\kappa$  is the surface curvature. The contribution from the normal component of the capillary vector  $\xi_{\perp}$  is from surface area reduction (the classical Laplace pressure), and the contribution from the tangential component of the capillary vector  $\xi_{\parallel}$ is from surface area rotation (Herring's pressure). Moreover, as for anisotropic interfaces the capillary vector is a function of both the director field **n** and the unit normal **k**, an additional contribution to the capillary pressure arises from director curvature due to orientation gradients (director curvature pressure). By substituting the normal  $\xi_{\perp}$  and tangential  $\xi_{\parallel}$  components of the capillarity vector (Eq. 1.7a,b), the capillary pressure is:

$$\Delta \mathbf{p} = \underbrace{\left\{ \gamma_{o} - \frac{\mathbf{W}}{2} \left( \mathbf{n} \cdot \mathbf{k} \right)^{2} + \mathbf{W} \left( \mathbf{n} \cdot \mathbf{t} \right)^{2} \right\} \kappa}_{\text{tension}} - \underbrace{\mathbf{W} \left\{ \left( \mathbf{k} \cdot \mathbf{n} \right) \left( \nabla_{s} \cdot \mathbf{n} \right) + \mathbf{k} \mathbf{n} : \nabla_{s} \mathbf{n} \right\}}_{\text{anchoring}} - \underbrace{\mathbf{K}_{c} \left( \kappa_{ss} + \frac{1}{2} \kappa^{2} \right)}_{\text{bending}}$$
(1.10)

This equation shows that the surface shape is the balance between tension, anchoring and bending. The anchoring term can drive the surface undulations in helicoidal plywoods where the helix axis is along the interface. In fact, for a helicoidal plywood with a fixed fiber orientation the only way to minimize the surface energy is to deform the interface to avoid energetically costly mismatch between the director and the easy axis. Since the director field is periodic then the surface undulations are also periodic. Figure 1-18 shows the simple schematic representing the formation mechanism of the surface undulations. Periodic changes in the orientation of director **n** result in a periodic surface energy profile which is the origin of the surface curvature.



**Figure 1-17.** Surface undulations in planar helicoidal plywood due to the fixed chirality of the director **n**. a) the helicoidal architecture of fibers along the interface b) the periodic anchoring energy c) the surface profile. Adapted from [127].

## 1.9.2 Modeling the cylindrical shapes of biological membranes

To elucidate the morphological variety of biological membranes, several theoretical studies were undertaken with the goal of minimizing membrane-bending energy subjected to area and volume constraints (Helfrich model, also known as the spontaneous curvature model) [116, 128-131]. In the Helfrich models, the membrane is assumed to exhibit purely elastic behavior and the equilibrium shape of membranes is determined by minimizing the elastic bending energy:

$$f = \frac{k_c}{2} \int (2H + H_0)^2 dA + \overline{kc} \int K dA + \alpha \int dA + \beta \int dV$$
(1.11)

Here  $\alpha$  and  $\beta$  are the Lagrange multipliers corresponding to the constraints of area A and volume V.  $\alpha$  physically represents the surface tension and  $\beta$  represents the pressure difference between the

outer and inner sides of the membrane. Setting Eq. 1.11 to zero, the Euler–Lagrange equation which is referred to as the membrane shape equation reads [132]:

$$2k_{c}\Delta H + k_{c}(2H + H_{0})(2H^{2} + H_{0}H - 2K) - 2\alpha H + \beta = 0$$
(1.12)

where  $\Delta$  is the Laplace–Beltrami operator on the surface arclength *s*. Although Helfrich models can well capture numerous cell membrane morphological deformations, they fail to reproduce membrane shapes that are asymmetric, such as the echinocyte [70]. While the area-differenceelastic models (ADE), which minimize the energy associated with the area difference between the inner and outer leaflet of the membrane, can represent the top-bottom asymmetric shapes [133, 134]. In the ADE model, the areas of the inner and outer layers of the membrane are not fixed; each layer has a preferred area ( $A_0^{inn}$  or  $A_0^{out}$ ) determined by the number of lipid molecules. This adds an extra contribution to the Helfrich model due to the difference between the actual and the preferred areas [129]:

$$f_{ADE} = \frac{k_m}{2} \frac{\pi}{AD^2} (\Delta A - \Delta A_0)^2 \tag{1.13}$$

where  $k_m$  is a material parameter and D is the monolayer thickness. Further, numerical simulations such coarse-grained molecular dynamics (CGMD) [135, 136], spherical harmonics parameterization (SHP)[137], and dissipative particle dynamics [138] were proposed to provide a detailed description of pattern formation occurring in both symmetric and asymmetric deformation. Although significant progress has been made in formulating theoretical and numerical models that attempt to explore the complex surface morphologies in biological closed membranes, previous studies have been restricted to bilayer elastic models. There are few studies that consider other chemical and biological mechanisms (such as the presence of multiple components or in-plane order) contributing to the formation of top-bottom asymmetric membrane shapes [114, 139-141]. Of particular interest of the present thesis is to study the role of liquid crystal anisotropy in formation of complex surface patterns observed in biological and synthetic membranes.

## **1.10** Thesis objectives

The motivation of this thesis is to present a theoretical model that includes liquid crystal anisotropy of biological materials to explain the surface wrinkling and the morphological patterns

observed in living systems, to provide a foundation to understand structural color phenomena in Nature, and to demonstrate the potential biomimetic mechanism for the design of optical sensor devices. The following list summarizes the specific objectives of this thesis:

1. To derive a non-linear nemato-capillarity shape equation that considers the membrane curvature-fiber order contributions and describes the main mechanisms driving nano-scale surface undulations in chiral nematic liquid crystals as shown in plant-based plywoods (chapter 2).

2. To present a theoritical scaling law expressing the explicit relation between the surface profile amplitude and the model parameters, and to validate the scaling formula with a number of experimental values available in literature for surface undulations observed in chiral nematic liquid crystals and biological plywoods (chapter 2).

To study the role of humidity in deforming the surface undulations through the interaction of anisotropic interfacial tension, swelling through hydration, and capillarity at free surfaces (chapter 3).

4. To investigate the optical responses of the surface wrinkling, and to suggest a potential biosensor that can respond to different ranges of relative humidity depending on the the reflection peak of the surface nanostructure (chapter 3).

5. To propose a physical model that can describe more complex real surfaces such as creasing, folding, and period-doubling through interaction of liquid crystal anisotropy of biological materials and bending elasticity of surfactant-like biomolecules (chapter 4).

6. To explore the effect of liquid crystal anisotropy in the formation of complex top-bottom asymmetric complex topographies observed in biological and synthetic closed membranes (chapter 5).

7. To establish a new paradigm for characterizing the morphological patterns in nematic liquid crystal closed membranes and to elucidate a natural setting for the creation and control of the emerging complex patterns (chapter 5).

## 1.11 Methodology and thesis organization

The thesis organization is shown in Figure 1-18 and a detailed description is presented in the following pages.



**Figure 1-18.** Thesis organization chart. Contents in round rectangles represent the models developed (chapters 2,3,4,5) in this thesis, the rectangles present the objectives, and the dashed line rectangles illustrate the outputs and the key parameters of the models.

## Chapter 2: Modeling nanostructured free surfaces in plant-based plywoods driven by chiral capillarity

In this chapter, focusing on the cellulose-base helicoidal plywood, a generalized shape equation for anisotropic interfaces using the Cahn-Hoffman capillarity vector and the well-known Rapini-Papoular anchoring energy is developed. The nemato-capillary shape equation expresses the coupling mechanism between the surface geometry and cellulose fiber orientation for CLC/air interface in rectangular (x,y,z) coordinates. The key mechanisms that induce and resist the surface undulations are identified and discussed. Finally, a theoretical scaling law expressing surface profile amplitude as a function of model parameters is presented and validated.

## Chapter 3: Modeling nano-wrinkling of chiral surfaces in response to humidity: structure and diffraction optics

In this chapter, the nemato-capillary shape equation formulated in chapter 2 is extended to investigate the surface wrinkling in plant-based plywoods with water-induced spatially varying pitch through interaction of anisotropic interfacial tension and chirality changes through hydration. The role of three capillary pressure contributions (surface area change, surface area rotation, and director gradient curvature), and bulk stress jump are characterized and the impacts of the system parameters on the surface profile are investigated. A scaling law for the chirality-humidity driven surface wrinkling expressing the spatially-varying surface profile amplitude as a function of model parameters is presented. To investigate the optical responses of the surface wrinkling, finite difference simulations in the time domain (FDTD) is implemented and the corresponding planar reflection of light is calculated. The optical properties of the free surface gratings with water-induced varying pitch and the free surface gratings with constant pitch are compared and finally a potential biosensor is presented that can respond to different ranges of relative humidity depending on the amplitude and wavelength of the grating structure.

# Chapter 4: Multiple-wavelength surface patterns in models of elastic biological chiral liquid crystal membranes

In chapter 4, a novel physical model that includes liquid crystal anisotropy of biological materials, bending elasticity of surfactant-like biomolecules, and substrate cholesteric order is proposed to study multi-scale complex patterns, such as spatial period-doubling, period-tripling, and quasi-periodicity that no longer can be described by the shape equation used in chapter 2 and 3. Two system length scales and two key dimensionless numbers that control the surface morphogenesis are presented. The proposed model is compared and linked to a driven pendulum, that connects the ratio of the two system length scales to the winding number used in dynamics of elastic pendulums. Moreover, a general morphological phase diagram is presented that allow us to characterize the surface patterns based on the interaction of the three primitive shapes (folding, creasing, and flat).

# Chapter 5: Cylindrical shapes of nematic liquid crystal membranes: a model for 2D anisotropic biological cells

In this chapter, the governing shape equation is presented for a nematic liquid crystal closed membrane with quite weak homeotropic anchoring where the radius of the membrane is always significantly less than the extrapolation length scale, resulting in homogenous director field. The role of liquid crystal anisotropy in the formation of anisotropic asymmetric cylindrical shapes is established. A comprehensive morphological phase diagram of liquid crystal membrane configurations as a function of the system physical parameters is illustrated, which allows us to select the membrane shape through the interaction of the three primitive shapes (folded-shape, spindle-like, and ellipse). Finally, the system capillary pressures associated with the bending-anchoring morphological patterns are presented and discussed.

## Chapter 6: General conclusions and original contribution to knowledge

The key findings of this work are presented in this chapter along with a list of contributions to original knowledge.

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## Chapter 2

## 2 Modeling Nanostructured Free Surfaces in Plant-Based Plywoods Driven by Chiral Capillarity

## **2.1 Preface**

In this chapter, focusing on the cellulose-base helicoidal plywood, a generalized shape equation for anisotropic interfaces using the Cahn-Hoffman capillarity vector and the well-known Rapini-Papoular anchoring energy is developed. The key mechanisms that induce and resist the surface undulations are identified, and a theoretical scaling law expressing surface profile amplitude as a function of model parameters is presented. This chapter is reproduced from two published papers with the titles "Nano-scale surface wrinkling in chiral liquid crystals and plant-based plywoods", and "Nanostructured free surfaces in plant-based plywoods driven by chiral capillarity" which are co-authored with Prof. Damiano Pasini and Prof. Alejandro. D. Rey; Colloids Interface Sci. Commun., 2014, 1, 23–26 and Soft Matter, 2015, 11, 1127–1139.

### 2.2 Summary

We present theoretical scaling and computational analysis of nano-structured free surfaces formed in chiral liquid crystals (LC) and plant-based twisted plywoods. A nemato-capillary model is used to derive a generalized equation that governs the shape of cholesteric free surfaces. It is shown that the shape equation includes three distinct contributions to the capillary pressure: area dilation, area rotation, and director curvature. To analyze the origin of periodic reliefs in plywood surfaces, these three pressure contributions and corresponding surface energies are systematically investigated. It is found that for weak homeotropic surface anchoring, the nano-wrinkling is driven by the director curvature pressure mechanism. Consequently, the model predicts that for a planar surface with a uniform tangential helix vector no surface nano-scale wrinkling can be observed since the director curvature pressure is zero. Scaling is used to derive the explicit relation between the wrinkling's amplitude to the wavelength ratio as a function of the anisotropic surface tension, which is then validated with experimental values. These new findings can be used to characterize plant-based twisted plywoods as well as to inspire the design of biomimetic chiro-optical devices.

## **2.3 Introduction**

Biological liquid crystals (BLCs) are anisotropic viscoelastic materials exhibiting long range orientational order and partial positional order [1]. The liquid crystalline phase and topological

defects in biological analogues are usually those of chiral nematics (cholesteric) and hence they are referred to as biological helicoidal plywoods [2,3], also known as the Bouligand architecture [4-7]. Helicoidal plywoods are found in many biological materials, such as DNA in human cells [8], cellulose in plant cell walls [9], chitin in arthropods cuticles [2], and collagen in human compact bones [10]. BLCs are functional materials that display several unique properties [11] such as nano-scale surface wrinkling observed in LC DNA [12], cellulose [13], and collagen [14]. Cholesteric films of concentrated collagen solutions exhibit periodic undulations at the free surface with an amplitude of the order of 150 nm, and a periodicity of the order of 3.5 µm [14]. Undulations of similar scales are also observed in silk gland ducts of golden orb-web spider *Nephilaclavipes* [15], the exoskeleton of the beetle *Chrysinagloriosa* [16], and cellulosic materials [13]. These nano-scale structures that formed spontaneously on the free surface of BLC are responsible for their particular optical responses resulting in structural colors, observed in beetles [16], mollusk shells [17], and some plants [18]. The study of the formation of these surface undulations is fundamental in understanding structural color in nature and can inspire the design of optical devices with novel functionalities [19].

Photonic structures in many floral plants are associated with the shape and the anatomy of the plant surface topography. It has been reported that certain floral plant species, such as *Hibiscus trionum* and *Tulipakaufmanniana* petals, use ordered striation or ridges to obtain iridescence with a striking metallic appearance [20]. Although the formation of these micro- and nanostructures during the development of the petals is not well-understood yet, it is believed that cellulosic CLCs are responsible for plant surface undulations and iridescent colors. In the preparation of a lyotropic cholesteric mesophase, *Werbowyi* and *Gray* discovered that concentrated aqueous solutions of (hydroxypropyl) cellulose (HPC) displayed iridescent colors that changed with concentration and viewing angle [21]. Efforts have been made to trap the CLC structure in solid films to create colored iridescent films [22-24]. *Fernandes et al.* fabricated iridescent solid cellulosic films with tunable mechanical and structural color properties, which mimic the structures found in the surface of the "Queen of the Night" tulip petals, which display periodic striation of about 1.5 µm, responsible for petal iridescence [25]. They indicated that the formation and periodicity of the surface structure are governed by the CLC structure.

Although, the chiral surface structures are extensively studied by microscopy methods including atomic force microscopy (AFM) [26-29], the complementary theoretical analysis of CLC surface

wrinkling is rarely studied. The formation of surface nanostructures in CLC interfaces is a complex phenomenon involving interfacial tension, surface anchoring energy, and LC Frank elasticity [11] that requires integrated multi-scale modelling of bulk and surface [30]. In a study of cholesteric liquid crystal free surface, *Meister et al* described the periodic relief of a cholesteric liquid crystal interface by minimization of surface free energy composed of the anchoring energy and the surface tension [31, 32]. They found that for relatively strong and finite anchoring, the surface deformation energy arises due to director surface gradient and elastic constants [31]. The director distributions in the distorted region coupled with anchoring energy create nano-scale undulations in the free surface.

The plant cell wall is a multifunctional viscoelastic structure made of cellulose microfibrills (CMFs) coated with hemicelluloses and embedded in a matrix of lignin/pectin [33]. Plant cell wall includes a primary cell wall (p) laid down during growth on the outside and three secondary cell walls (S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>) that formed when the cell has reached its final size and shape [34]. Although the primary and secondary wall layers differ in the specific chemical composition (cellulose and hemicellulose contents are greater in secondary walls than primary walls) and structural organization (CMFs in primary layers are organized in a loose interwoven texture, while are well-oriented in secondary layers). Overall, CMFs in the polysaccharide matrix are oriented in strategic directions to form twisted plywood architecture for optimal mechanical efficiency. The proof that plant cell wall is formed through a liquid crystalline self-assembly process is the presence of the microstructure, textures and defect patterns observed in secondary cell wall of some plan species [11, 35, 36]. The plant cell wall helicoidal plywoods can be characterized by the helix axis **H**, the pitch length P<sub>0</sub>, which is the distance through which the fibers undergo a  $2\pi$  rotation and handedness (sign of P<sub>0</sub>), and the average fiber orientation **n** which is normal to **H** (see Figure 2-1).

In this chapter, we present the main mechanism that operate in chiral capillarity using a plantbased plywood as a model material system. We demonstrate a comprehensively analysis of the nano-scale structures observed in chiral surfaces in full detail and predict the response of the surface structure to chirality and anisotropic tension changes. We restrict our attention to the case in which the helix axis remains always parallel to the surface; other complex structures arising when the helix axis is tilted are beyond the scope of this study. Focusing on the cellulosic CLCs material model, we use the generalized shape equation for anisotropic interfaces using the Cahn-Hoffman capillarity vector developed for LCs [37] and the well-known Rapini-Papoular anchoring energy [38] for the anisotropic part of the interfacial tension, to analyze periodic nano-wrinkling in plant-based plywood free surfaces. The objective of this chapter is to identify the key mechanisms that induce and resist nano-wrinkling in CLC, and to formulate nano-wrinkling scaling laws of biomimetic utility for the design of optical gratings and as a tool to characterize plant-based plywoods.

The organization of this chapter is as follows. Section 2.4 presents the governing nematocapillary shape equation expressing the coupling mechanism between the surface geometry and cellulose fiber orientation for CLC/air interface in rectangular (x,y,z) coordinates. The capillary shape equation is derived and described in terms of three capillary pressures. Appendix A presents the details of the derivation of the Cahn-Hoffman capillary vector thermo-dynamics for CLC interfaces. Appendix B derives the generic conditions under which the director curvature pressure is zero. Appendix C formulates the capillay shape equation for the splay-bend director field relevant to nano-wrinkling. Section 2.5 analyses the effect of model parameters on the surface profile. The leading mechanism controlling chiral wrinkling is determined and the generic sufficient condition that results in flat and non-flat surfaces is derived. Furthermore, the surface energies associated with the CLC interface are presented and discussed. Finally, based on a standard order of magnitude analysis, a scaling formula expressing surface profile amplitude as a function of model parameters is presented and validated with a number of experimental biological CLC surface undulations and with numerical results. Section 2.6 presents the conclusions.

#### 2.4 Capillary shape equation

We assume that the surface undulations in plant cell walls are formed through modulation in surface energy at the anisotropic-air interface and are influenced by the macroscopic chirality of the cellulose fibers. The coupling mechanism between the surface geometry and cellulose fiber orientation can be demonstrated through the shape equation. In this section, the capillarity shape equation using the capillary vector  $\xi$  [39] is presented for the CLC free interfaces in rectangular (x,y,z) coordinates and the resulting surface pressures are formulated.

For isotropic interfaces, the capillary pressure,  $p_c$ , based on the well-known Young-Laplace equation, is proportional to the surface tension  $\gamma$  and vanishes for plane surfaces ( $\nabla_s$ . **k** = 0) [40]:

$$-\mathbf{p}_{c} = -\nabla_{s} \mathbf{k} \boldsymbol{\gamma} \tag{2.1}$$

where  $\nabla_s = \mathbf{I}_s$ .  $\nabla$  is the surface gradient,  $\mathbf{I}_s = \mathbf{I} - \mathbf{k}\mathbf{k}$  is the 2×2 unit surface dyadic, and  $\mathbf{k}$  is the surface unit normal. For a cholesteric liquid crystal (CLC) surface, however, the anisotropic

surface tension contributes additional modes to the capillary pressure. The interfacial surface tension  $\gamma$  for anisotropic surfaces is a function of the surface unit normal **k** and the director **n**:  $\gamma$  (**k**, **n**) and is given by Rapini and Papoular [38]:

$$\gamma(\mathbf{n},\mathbf{k}) = \gamma_0 + \gamma_{\text{aniso}}(\mathbf{n},\mathbf{k}); \quad \gamma_{\text{aniso}}(\mathbf{n},\mathbf{k}) = \frac{W}{2}(\mathbf{n}.\mathbf{k})^2$$
(2.2)

where  $\gamma_0$  is the isotropic contribution,  $\gamma_{aniso}$  is the anisotropic anchoring energy contribution, and W is the anchoring energy coefficient. The anisotropic surface tension appears as the property that renormalizes the isotropic component of the interfacial tension and promotes the rotation of the interface. The anchoring energy contribution is associated with the director deviations from its preferred orientation due to bulk distortions or external fields. The preferred orientation or easy axis corresponding to Eq. 2.2 can be parallel to the unit normal **k** (homeotropic), perpendicular to the unit normal **k** (planar). In the present study, we restrict the discussion to homeotropic anchoring (W<0), because for planar surface anchoring (W>0, **n.k**=0) the helicoidal structure, in which helix axis is perpendicular to the surface, will remain undistorted as it is the most stable and lowest energy state [41]; the undistorted helix results in a flat surface [31].

As the nematic director in CLCs continuously rotates along the helical axis, the helix structures (helixes perpendicular (**H.k=0**) and parallel (**H.k=1**) to the surface) for strong homeotropic anchoring (W<0) is not fully compatible with any uniform aligning surface [42]. As the result, the average orientational order is disrupted due the frustration that leads to sub-surface defect nucleation, which can be resolved by changing the interface shape. The appearance of inclusions and formation of defects in the bulk can change the director orientation in the CLC and results in a periodicity at the free surface whose wave length can vary from half helical pitch  $P_0/2$  to  $P_0$  or even greater [27, 43]. Here we assume that the pitch of the distorted region is equal to the bulk  $P_0$ . The effect of  $\mathbf{n}(\mathbf{x})$  on surface relief of two CLC structures is shown in Figure 2-1. The distorted surface layer can be generated by either vertical or tangential helixes in the bulk (note that only a horizontal helix alignment  $\mathbf{H}$  is presented in Figure 2-1).

The Cahn-Hoffman capillary vector  $\xi$  [39] is the fundamental quantity that provides a direct and clear way to explain the role of anisotropy in capillary pressure and its role in surface shape determination. The capillary vector  $\xi$  takes into account the changes in surface energy due to surface dilation (change in area) and surface rotation (change in unit normal **k**) in one single vectorial quantity. In this section, the key formulations of the capillary vector thermodynamics are

presented. Appendix A gives the details of the derivation of the Cahn-Hoffman capillary vector thermodynamics for anisotropic interfaces [37]. The capillary vector  $\xi$  for nematic surfaces and interfaces has two components:

$$\boldsymbol{\xi}(\mathbf{n},\mathbf{k}) = \boldsymbol{\xi}_{\perp}(\mathbf{n},\kappa) + \boldsymbol{\xi}_{\parallel}(\mathbf{n},\mathbf{k})$$

$$\boldsymbol{\xi}_{\perp}(\mathbf{n},\mathbf{k}) = \boldsymbol{\gamma}\mathbf{k}; \ \boldsymbol{\xi}_{\parallel}(\mathbf{n},\mathbf{k}) = \mathbf{I}_{s} \cdot \frac{d\boldsymbol{\gamma}}{d\mathbf{k}}$$
(2.3 a,b)

The normal component  $\xi_{\perp}$  describes the increase in surface energy through dilation and the tangential component  $\xi_{\parallel}$  is the change in surface energy through rotation of the unit normal. For isotropic surfaces,  $\xi_{\parallel} = 0$  and no rotational effects appear since W=0. It is important to note that at the free surface we have two independent fields: the director **n** and the unit normal **k**. A soft surface describes the case when its shape adapts to a given director orientation, as considered in this chapter.



**Figure 2-1.** Schematic of a cholesteric liquid crystal (plywood architecture) and surface structures. H is the helix unit vector, and P<sub>0</sub> is the pitch. (a) The surface director has an ideal cholesteric twist and the surface is flat. (b) Bend and splay orientation distortions with  $\lambda$ + disclination [44] for W<0 create surface undulations. Adapted from ref [31]. Note that the director field is continuous everywhere and  $\lambda$  lines are non-singular core.

The normal component of the interfacial stress boundary conditions at the CLC/air interface is:

$$-\mathbf{k}\mathbf{k}: (\mathbf{T}^{a} - \mathbf{T}^{b}) = (\nabla_{s} \cdot \mathbf{T}_{s}) \cdot \mathbf{k}$$
(2.4)

where  $\mathbf{T}^{a/b}$  is the total stress tensor in the air and cholesteric bulk phase, and  $\mathbf{T}_s$  is the interface stress tensor. The air and bulk stress tensors are given by:

$$\mathbf{T}^{\mathrm{b}} = -(\mathbf{p}^{\mathrm{b}} - \mathbf{f}_{\mathrm{b}})\mathbf{I} + \mathbf{T}^{\mathrm{E}}; \quad \mathbf{T}^{\mathrm{E}} = -\frac{\partial \mathbf{f}_{\mathrm{b}}}{\partial \nabla \mathbf{n}} . (\nabla \mathbf{n})^{\mathrm{T}}$$
(2.5)

where p <sup>a/b</sup> are the hydrostatic pressures,  $f_b$  is the bulk Frank energy density, and  $\mathbf{T}^E$  is the Ericksen stress tensor. The projection of Eq. 2.4 along **k** results in the shape equation:

$$\underbrace{\left(p^{a}-p^{b}\right)+\left(f_{b}\right)-\mathbf{k}\mathbf{k}:\left(\frac{\partial f_{b}}{\partial \nabla \mathbf{n}}.\left(\nabla \mathbf{n}\right)^{T}\right)}_{\text{bulk normal stress jump, SJ}}=\underbrace{\left(\nabla_{s}\cdot\mathbf{T}_{s}\right)\cdot\mathbf{k}}_{-\text{capillary pressure, }-\mathbf{p}_{c}}$$
(2.6)

where SJ is the total normal stress jump and  $p_c$  is the capillary pressure. The bulk free energy density of a cholesteric in the one constant approximation reads:

$$\mathbf{f}_{b} = \frac{1}{2} \mathbf{K} \left( \left( \nabla \cdot \mathbf{n} \right)^{2} + \left( \mathbf{n} \cdot \nabla \times \mathbf{n} - \mathbf{q}_{0} \right)^{2} + \left( \mathbf{n} \times \nabla \times \mathbf{n} \right)^{2} \right)$$
(2.7)

where K is the Frank elasticity constant, and  $q_0$  is the wave vector which is equal to  $2\pi/P_0$ . The surface contribution  $(\nabla_s \cdot \mathbf{T}_s) \cdot \mathbf{k}$  is minus the divergence of the capillary vector decomposed naturally as [45]:

$$-\mathbf{p}_{c} = (\nabla_{s} \cdot \mathbf{T}_{s}) \cdot \mathbf{k} = -\nabla_{s} \cdot \boldsymbol{\xi} = -\nabla_{s} \cdot \left(\boldsymbol{\xi}_{\parallel} + \boldsymbol{\xi}_{\perp}\right)$$

$$= -\underbrace{\frac{\partial \boldsymbol{\xi}_{\perp}}{\partial \mathbf{k}} : \nabla_{s} \mathbf{k}}_{P_{\text{dilation}}} - \underbrace{\frac{\partial \boldsymbol{\xi}_{\parallel}}{\partial \mathbf{k}} : \nabla_{s} \mathbf{k}}_{P_{\text{rotation}}} - \underbrace{\frac{\partial \boldsymbol{\xi}_{\parallel}}{\partial \mathbf{n}} : \nabla_{s} \mathbf{n}}_{P_{\text{director}}} + \underbrace{\frac{\partial \boldsymbol{\xi}_{\parallel}}{\partial \mathbf{n}} : \nabla_{s} \mathbf{n}}_{P_{\text{director}}}$$

$$(2.8)$$

where  $P_{dilation}$  is the contribution from the normal component  $\xi_{\perp}$  which is the usual Laplace pressure and  $P_{rotation}$  is the contribution from the tangential component  $\xi_{\parallel}$  which is the anisotropic pressure due to preferred orientation and is known as Herring's pressure. The additional contribution to the capillary pressure,  $P_{director}$  appears from director curvature due to orientation gradients. The capillary pressure in CLC free interfaces includes a number of novel interfacial effects: i) capillary pressure even for flat surfaces, ii) Laplace-type capillary pressure due to director orientation curvature (i.e. gradients), iii) orientation-dependent renormalization of the surface tension coefficients due to anchoring energy [37].

For the case under consideration, in the absence of gravitation, semi-infinite media in the vertical direction and periodic in the horizontal direction, we take  $p^a - p^b = 0$ . The remaining contribution to SJ,  $\{f_b + \mathbf{kk}: \mathbf{T}^E\}$ , is known as the elastic correction in the liquid crystal literature. Using Eq. 2.6 and Eq. 2.7 the elastic correction is:

$$SJ = \{f_{b} + \mathbf{k}\mathbf{k} : \mathbf{T}^{E}\}$$

$$= \frac{1}{2}K \left( (\nabla \cdot \mathbf{n})^{2} + (\mathbf{n} \cdot \nabla \times \mathbf{n} - q_{0})^{2} + (\mathbf{n} \times \nabla \times \mathbf{n})^{2} \right)$$

$$- K (\mathbf{n} \cdot \nabla \times \mathbf{n} - q) \left( \mathbf{n} \cdot \left( ((\mathbf{k} \cdot \nabla) \mathbf{n}) \times \mathbf{k} \right) \right)$$

$$- K ((\mathbf{n} \cdot \nabla \mathbf{n}) (\mathbf{n} \cdot \mathbf{k})) \cdot ((\mathbf{k} \cdot \nabla) \mathbf{n}) - K (\nabla \cdot \mathbf{n}) ((\mathbf{k} \cdot \nabla) \mathbf{n}) \cdot \mathbf{k}$$

$$(2.9)$$

This expression can be greatly simplified. Using the director field of ref. [31], with  $\mathbf{n}=(n_x(x,y),n_y(x),n_z(x,y))$  and the interfacial torque balance equation, we find that the Ericksen stress projection is zero:

$$\mathbf{k}\mathbf{k}:\mathbf{T}^{\mathbf{E}} = \left( \left( (\mathbf{I} - \mathbf{n}\mathbf{n}) \cdot \frac{\partial \gamma}{\partial \mathbf{n}} \right) \cdot \left( \nabla \mathbf{n} \right)^{\mathbf{T}} \right) \cdot \mathbf{k} = 0$$
(2.10)

because  $\frac{\partial n_y}{\partial y} = 0$ . The elastic correction SJ in the present case is then only due to  $f_b$ . Using Eqs. (2.6, 2.9, 2.10) and  $\mathbf{n} = (n_x(x,y), n_y(x), n_z(x,y))$  we obtain [46]:

$$\frac{\mathrm{Kq_0}^2}{2} \left(1 + n_y^2\right) = \left(\gamma_0 - \frac{\mathrm{W}}{2} \left(\mathbf{n} \cdot \mathbf{k}\right)^2 + \mathrm{W}(\mathbf{n} \cdot \mathbf{t})^2\right) \kappa -$$

$$\mathrm{W}\left\{ \left(\mathbf{k} \cdot \mathbf{n}\right) \left(\mathbf{t} \cdot \frac{\mathrm{d}\mathbf{n}}{\mathrm{d}s}\right) + \mathbf{k}\mathbf{n} : \left(\mathbf{t}\frac{\mathrm{d}\mathbf{n}}{\mathrm{d}s}\right) \right\}$$
(2.11)

where  $k = \frac{d\varphi}{ds}$  is the surface curvature,  $\varphi$  is the normal angle, s is the arc-length (Appendix.C, Figure C-1) and **t** is the tangential surface unit vector. For significant anchoring that unravels the helix we find that the extrapolation length  $\ell_{ex}$  scales as:

$$\ell_{\rm ex} = \frac{K}{W} = cP_{\rm o}$$
(2.12)

where c is the ratio of the extrapolation length K/W to the cholesteric pitch  $P_0$ . Thus, the order of

magnitude of the stress jump (elastic correction) written in relation to anchoring (i.e. W/P<sub>o</sub>) gives:

$$o(SJ) = o\left(\frac{K}{P_o^2}\right) = o\left(W\frac{K}{WP_o^2}\right) = o\left(W\frac{\ell_{ex}}{P_o^2}\right) = o\left(c\frac{W}{P_o}\right)$$
(2.13)

For typical cholesteric liquid crystals, the internal length  $K/\gamma_0$  is usually in the range 1nm (an order of magnitude estimation of the elastic constant K and the surface tension  $\gamma_0$  gives  $K \approx 10^{-11}$  J/m and  $\gamma_0 \approx 10^{-2}$  J/m<sup>2</sup>). As the ratio of  $W/\gamma_0$  at the cholesteric-air interface with quite strong anchoring lies in the range (B=W/\gamma\_0=0.05), the extrapolation length scale K/W is about

$$\frac{K}{W} = \frac{K/\gamma_0}{W/\gamma_0} \approx \frac{1 \text{ [nm]}}{0.05} \approx 20 \text{ [nm]}$$
(2.14)

With these values, for a biological cholesteric liquid crystal with a typical pitch  $P_0 \sim 1 \,\mu m$ , the value of c is in order of  $\frac{K/W}{P_0} = \frac{20 \,[nm]}{1000 \,[nm]} = 0.02$ . Hence if c is of the order of 0.02, the SJ contributes 2% to the shape equation, and the elastic correction to the surface shape is not significant and can be neglected to describe nano-scale surface undulations. When P<sub>o</sub> increases beyond 1  $\mu$ m, the elastic correction essentially vanishes. When the elastic correction is essentially negligible, the shape Eq. 2.11, when the director field and geometry are as shown in Figure 2-1, reduces to a balance of dilation, rotation, and director pressures:

$$\underbrace{\left(1-\frac{B}{2}(\mathbf{n}\mathbf{k})^{2}+B(\mathbf{n}\mathbf{t})^{2}\right)}_{P_{\text{dilation}}+P_{\text{rotation}}}\kappa}\underbrace{-B\{(\mathbf{k}\cdot\mathbf{n})(\nabla_{s}\cdot\mathbf{n})+\mathbf{k}\mathbf{n}:\nabla_{s}\mathbf{n}\}}_{P_{\text{director}}}=0$$
(2.15)

where  $B = W/\gamma_0$  is the scaled anchoring coefficient. This equation shows that the surface shape is the balance between surface tension and anchoring. The anchoring term is the driving force for surface undulations and it originates from the fact that this anisotropic surface energy is minimized when the director **n** is aligned along the preferred "easy axis". For a fixed cholesteric helical orientation, the only way to minimize this energy is to deform the interface to avoid energetically costly mismatch between the director and the easy axis. Since the director of a cholesteric is periodic, then the surface undulations are also periodic. When the director orientation deviates from the easy axis and the deviation generates gradients in surface tension, which are comparable to the characteristic kinetic energy density, the orientational-driven Marangoni flow may appear [47-49]. In this study, we neglect this Marangoni effect and consider the shape instability as driven by elastic effects. One mechanism that may eliminate or reduce viscous effects when the helix is tangential to the surface is the high viscosity associated with permeation flow [50-52]. For flat planar interfaces ( $\kappa$ =0) the capillary pressure is driven only by director curvature:

$$\mathbf{p}_{c} = \mathbf{W}((\mathbf{k}.\mathbf{n})(\nabla_{s}.\mathbf{n}) + \mathbf{k}\mathbf{n}:\nabla_{s}\mathbf{n})$$
(2.16)

The director curvature pressure, Pdirector is zero when:

$$(\mathbf{k}.\mathbf{n})(\nabla_{\mathbf{s}}.\mathbf{n}) + \mathbf{k}\mathbf{n}: \nabla_{\mathbf{s}}\mathbf{n}) = 0 \longrightarrow \nabla_{\mathbf{s}}.\mathbf{n} = 0 \text{ and } \mathbf{k}\mathbf{n}: \nabla_{\mathbf{s}}\mathbf{n} = 0$$
(2.17)

In a rectangular (x,y,z) coordinate system, to satisfy the zero director curvature pressure condition (Eq. 2.17), we find that the director **n** must obey one of the following two conditions: 1)  $n_x=0$  and  $n_y=0$  or 2)  $n_xn_y=$ constant (the generic conditions under which the director curvature pressure is zero are derived in Appendix B). We note that the surface director field describing a planar surface with a uniform tangential helix vector is given by  $\mathbf{n}(x) = (0, \cos qx, \sin qx)$ , and since  $n_x=0$ , the director curvature pressure is zero and no surface wrinkling can be observed, as previosuly predicted using other approaches [31].

To describe 1D surface undulation in a CLC, we use a rectangular coordinate frame (x,y,z), where x is the undulation direction, and y the vertical axis (see Figure 2-1). The amplitude of the vertical undulation is h(x). For a 1D texture, the surface relief is constant in the z direction. The arc-length measure of the undulating surface is "s".

$$\frac{d\varphi}{dx} = \frac{p_c + q_0 B \sin(\varphi) \{\sin^2(\varphi - q_0 x) - \cos^2(\varphi - q_0 x)\}}{\sin(\varphi) \{1 - \frac{B}{2} \cos^2(\varphi - q_0 x) + B \sin^2(\varphi - q_0 x)\}}$$
(2.18)

Setting  $p_c=0$  and using the above-specified splay-bend director  $\mathbf{n}(x) = (\cos qx, \sin qx, 0)$  and surface unit normal  $\mathbf{k}(x)$  vectors gives the governing nonlinear first order ODE for the normal angle  $\varphi(x,B,P_0)$ , where -2 < B < 0,  $0 < P_0 < 100 \ \mu\text{m}$ , 0 < x < L where L is the given system length in the x direction. This nonlinear ODE with periodic coefficients is solved using the well-known AUTO nonlinear software [53]. The surface relief is then obtained from  $\mathbf{h}(x) = \int_0^x \cot \varphi \, dx'$ . The boundary condition at x=0, is  $\varphi|_{x=0} = \frac{\pi}{2}$ , consistent with the adopted sign of B.

## 2.5 Results and discussion

In this section we: (1) establish and quantify the effect of anchoring (B) and chirality (P<sub>0</sub>) on the normal angle  $\varphi(x, B, P_0)$  and on the amplitude profile h(x,B,P\_0), (2) use a pressure-energy analysis

to characterize wrinkling, and (3) formulate and validate scaling relations for  $h_{max}$  as a function of B and P<sub>0</sub>.

### 2.5.1 Free surface profile

The generic features of the amplitude profile h(x), its maximum value  $h_{max}$ , and its periodicity  $h(x)=h(x+\lambda)$  are the three relevant outputs of the model. The two significant parameters influencing h(x) are the scaled anchoring coefficient B and the micron scale length of the pitch P<sub>0</sub>. For the nematic-isotropic interface, the scaled anchoring coefficient B is of the order of magnitude of 0.01 [54]. The anchoring strength W at the nematic-air interface is about several orders of magnitude larger than the anchoring strength at the nematic-isotropic interface. However, as the surface tension at the nematic-air interface is higher than the surface tension at the nematic-isotropic interface [31],[55], the scaled anchoring coefficient B=W/ $\gamma$  is taken to be in the range -0.1<B<-0.01.

The plots of normal angle  $\varphi(x)$  and the corresponding surface reliefs h(x) as a function of the distance "x", for different B and P<sub>0</sub> are shown in Figure 2-2 and Figure 2-3, respectively. As expected, the periodicity,  $\lambda$  equals the pitch, P<sub>0</sub> and the amplitude are in the nanometer range, consistent with experimental findings [26, 56]. Increasing both parameters B and P<sub>0</sub> results in higher amplitudes.

#### 2.5.2 Pressure-curvature relations

As at the nematic-air interface, the anchoring strength (W $\approx 10^{-5}$  J/m<sup>2</sup>) is three orders of magnitudes smaller than the surface tension ( $\gamma \approx 10^{-2}$  J/m<sup>2</sup>) [54], it would seem that there is no driving forces to deform the CLC free interfaces and a flat interface would minimize the free surface energy. However, the director pressure curvature is shown here to be a driving force that wrinkles the surface under weak anchoring (i.e. small B) and typical values of chirality (i.e P<sub>0</sub> in the µm range). All pressures are scaled with the isotropic tension  $\gamma_0$  and have units of µm<sup>-1</sup>. Due to the orientational order of CLC interface, the capillary pressure contains three contributions: surface area reduction, surface area rotation, and director curvature (Eq. 2.8).



**Figure 2-2.** The numerical solutions  $\varphi(x)$  and h(x) for P<sub>0</sub>=1.2 µm and different values of B=-0.05, -0.1, and -0.2, showing the increase of the normal angle  $\varphi$  and the resultant surface amplitude h through increase in the anchoring constant B.



**Figure 2-3.** The numerical solutions  $\varphi(x)$  and h(x) for B=-0.05 and different values of P<sub>0</sub>=0.5,1 and 2 µm, showing the increase of the normal angle  $\varphi$  and the resultant surface.

The essential feature of chiral capillarity is the interaction of anisotropy (director **n** of fibers), micron-range chirality ( $P_0$ ), helix direction (**H**) and free surface topography. When the holesteric helix is parallel to a flat surface, frustration driven by the unavoidable (due to periodic **n**) presence of high surface energy drives the surface uncoiling of the helix and the periodic tilting of the interface. This is another example of pattern formation by frustration, ubiquitous in mesophases [11, 57].

A unique feature of liquid crystal surfaces is the presence of Laplace pressure (area dilation), Herrings pressure (area rotation), and director orientation gradients pressure, as revealed succinctly by the surface gradient of the capillary vector  $\xi$  (Eq. 2.15). Herring's pressure forms the basis of anisotropic crystal morphologies and is included here as P<sub>rotation</sub> [37]. As the Herring's pressure depends on curvature, it is only the orientation pressure P<sub>director</sub> that wrinkles the surface with a wavelength that reflects the periodicity of the director field. Extracting the curvature in Eq. 2.15 clearly shows that it is the ratio of a wrinkling driving force (-P<sub>director</sub>) to a resistance to wrinkling (capillary tension coefficients):

$$\kappa = \frac{\text{driving force}}{\text{resistance}} = \frac{-P_{\text{director}}}{\left(\gamma + \frac{\partial^2 \gamma}{\partial s^2}\right)} = \frac{B\left((\mathbf{k}.\mathbf{n})(\nabla_s.\mathbf{n}) + \mathbf{kn}:\nabla_s\mathbf{n}\right)}{1 - B\left(\frac{1}{2}(\mathbf{n}.\mathbf{k})^2 + (\mathbf{n}.\mathbf{t})^2\right)}$$
(2.19)

where the capillary tension coefficients are the usual Laplace terms plus the Herring's coefficient given by the second derivative  $\frac{\partial^2 \gamma}{\partial \mathbf{k}^2} = \mathbf{tt}: (\partial(\mathbf{tt}, \frac{\partial \gamma}{\partial \mathbf{k}}) \partial \mathbf{k})$ ; the last ratio is obtained by scaling with  $\gamma_0$ . Clearly as  $P_{director} = 0 \rightarrow \kappa = 0$  (see also Appendix C). This is illustrated in Figure 2-4 through 3-D representation of surface curvature,  $\kappa$ , and associated pressure directors,  $P_{director}$ , and normal angle,  $\varphi$ , for two anchoring coefficients and three chirality values. Figure 2-4 shows that for all values of the anchoring coefficients and chiralities, the zero pressure director results in a flat surface (zero curvature). The horizontal diameter corresponds to the zero pressure director ( $P_{director}=0$ ). Using scaling arguments, the  $P_{director}$  scales as:

$$\mathbf{P}_{\text{director}} = \text{order}\left(\frac{\mathbf{B}}{\mathbf{P}_0}\right) \tag{2.20}$$

Therefore, from Eq. 2.19 and Eq. 2.20 we see that the maximum curvature will increase with B and decrease with P<sub>0</sub>, in agreement with computations. This dependence is manifested in the 3-D plots of the surface curvature for different anchoring coefficients (B=-0.05, and -0.1) and chirality (P<sub>0</sub>=0.5, 1, and 5  $\mu$ m), as shown in Figure 2-4(a) and Figure 2-4(b) respectively.



**Figure 2-4.** 3-D representation of the surface curvature and associated pressure directors  $P_{director}$  and normal angle  $\varphi$ . (a)  $P_0=0.5 \mu m$ , B=-0.05, -0.1 and (b) B=-0.05,  $P_0=0.5$ , 1, and 5  $\mu m$ , showing the increase of the maximum curvature for higher values of B and lower values of  $P_0$ . The diameter corresponds to the zero pressure director ( $P_{director}=0$ ).

Figure 2-5 shows the three scaled surface pressures as a function of "x" for two anchoring coefficients and P<sub>0</sub>=0.5µm. The ellipsoids correspond to the director orientation. Pressure extrema (and surface relief extrema as in Figure 2-2 and Figure 2-3) occur at planar and homeotropic orientation. The Herring's pressure P<sub>rotation</sub> is always positive and alternates its phase along each cycle, such that when the director angle is  $\pi/4 < \theta < \pi/2$  dilation and rotation are in-phase and when  $0 < \theta < \pi/4$  rotation and director curvature are in-phase. Dilation and director curvature pressures are always out-of-phase. In addition, its amplitude also oscillates. Increasing the anchoring strength increases the magnitude of all pressures. The polar plots of the three scaled capillary pressures as a function of anchoring B and chirality P<sub>0</sub>, are shown in Figure 2-6 and Figure 2-7 respectively. The angular coordinate is the director field  $\theta$ . The fourfold symmetry reflects the facts that the pressure extrema are at 0,  $n\pi/2$ ;  $n=\{\pm 1,2,\ldots\}$  and that all pressures vanish at  $n\pi/4$ ;  $n=\{\pm 1,3\ldots\}$ . The figure shows that pressure asymmetry is strongest for the chiral component P<sub>rotation</sub>, but is essentially zero for the other two. Figure 2-7 shows polar plots of pressure as a function of P<sub>0</sub>. Decreasing chirality decreases all pressures as the wave-length of the undulation increases. Changing  $P_0$  does not affect the degree of asymmetry between the lobes of these pressures.



**Figure 2-5.** Pressure profiles for  $P_{dilation}$ ,  $P_{rotation}$ , and  $P_{director}$  as a function of distance "x". (a) B=-0.05 and  $P_0=0.5 \ \mu m$  and (b) B=-0.1 and P0=0.5  $\ \mu m$ . The ellipsoid corresponds to the director orientation. The figures display that pressure extrema occur at planar and homeotropic orientation. When the director angle is  $\pi/4 < \theta < \pi/2$  dilation and rotation are in-phase and when  $0 < \theta < \pi/4$ , rotation and director curvature are in-phase. Dilation and director curvature pressures are always out-of-phase.


**Figure 2-6.** Polar plots of the three scaled capillary pressures a)  $P_{dilation}(\mu m^{-1})$  b)  $P_{rotation}(\mu m^{-1})$  c)  $P_{director}(\mu m^{-1})$  for B=-0.05 and -0.1, and  $P_0$ =0.5  $\mu m$ . The angular coordinate is the director field  $\theta$ . The fourfold symmetry reflects the facts that the pressure extrema are at 0,  $n\pi/2$ ;  $n=\{\pm 1,2,...\}$  and that all pressures vanish at  $n\pi/4$ ;  $n=\{\pm 1,3...\}$ .



**Figure 2-7.** Polar plots of the three scaled capillary pressures a)  $P_{dilation}(\mu m^{-1})$  b)  $P_{rotation}(\mu m^{-1})$  c)  $P_{director}(\mu m^{-1})$  for  $P_0=0.5\& 1 \ \mu m$  and B=-0.5. The fourfold symmetry reflects the facts that the pressure extrema are at 0,  $n\pi/2$ ;  $n=\{\pm 1,2,...\}$  and that all pressures vanish at  $n\pi/4$ ;  $n=\{\pm 1,3...\}$ .

#### 2.5.3 CLC surface energies

The total surface energy is defined by  $F_s = \int \gamma dA$  [58], and for an initially flat surface of area  $L^2$ , the total scaled surface energy  $\varepsilon_T / \gamma_0 L^2$  is:

$$\frac{\varepsilon_{\rm T}}{\gamma_0 L^2} = \underbrace{\frac{1}{L^2} \int_0^L \int_0^L \frac{1}{\sin \phi} \, dx dz}_{\text{isotropic surface tension}} + \underbrace{\frac{B}{L^2} \int_0^L \int_0^L (\mathbf{n.k})^2 \frac{1}{\sin \phi} \, dx dz}_{\text{anchoring energy}}$$
(2.21)

Figure 2-8 shows the variations of the total surface energy with the two surface energy contributions for various B in comparison with the flat surface energy contributions. Figure 2-8(a) shows the total scaled surface energy of the wrinkled and flat surfaces as a function of anchoring B. Increasing the magnitude of B increases the energy difference between the flat and undulating

surfaces. The figure demonstrates that the total energy monotonically decreases by increasing the magnitude of B. Figure 2-8(b) shows the different contributions of the profiles shown in Figure 2-8(a). The undulation is driven by the anisotropic surface energy despite the increase in the isotropic energy. Also, the decrease in anisotropic energy is significantly augmented by the undulations.



**Figure 2-8.** a) The total surface energy and b) isotropic and anisotropic contributions in comparison with flat surface energies for  $P_0=0.5 \ \mu m$  and different values of B=-0.5 to -0.05. The system reduces its free energy by decreasing its anisotropic surface energy.

Figure 2-9 shows the corresponding energy contributions and behavior as a function of chirality.

The Figure shows that the isotropic surface tension energy and the anchoring energy for a

particular value of anchoring (B=-0.05) are almost independent of chirality. Although, the undulating surface has a higher isotropic energy compared to the flat surface, the lower anisotropic energy yields the undulating surface with a lower total surface energy compared to the flat surface reference line (Figure 2-9(a)).



**Figure 2-9.** a) The total surface energy and b) isotropic and anisotropic contributions in comparison with flat surface energies for B=-0.05 and different values of  $P_0=0.5 \ \mu m$  to  $10 \ \mu m$ , showing that the system free energy is almost insensitive to the variations of helix pitch  $P_0$ .

#### 2.5.4 Undulation scaling law and validation

Using a standard order of magnitude analysis based on Eq. 2.8, we find a revealing close form expression for the maximum amplitude  $h_{max}$  as a function of B and P<sub>0</sub>:

$$h_{\max} = \frac{BP_0}{1+\delta B}$$
(2.22)

The numerical results indicate that  $\delta = 10.71B^{-1.02}$ . The prediction is that the ratio of amplitude/periodicity is essentially a linear function of the scaled anchoring B:  $\frac{h_{max}}{P_0} = 0.085B$ .

Since the value of B for the interface between the chiral nematic and the isotropic phase/air usually is in the range -0.1 < B < -0.01, the estimated amplitude of surface undulation is about one percent of the undulation wavelength. The theoretical estimate, based on the shape equation, of the depthto-period ratio is consistent with the nano-scale surface structures that have been experimentally observed in a variety of polymeric and biological CLC. Periodic surface structures with amplitude of the order of hundred nanometers and a periodicity of the order of few micrometers that spontaneously appeared from evaporating droplets of collagen solutions on glass substrates were detected using an atomic force microscope (AFM) [14]. The periodic surface relief found in his work is very similar to the periodic undulations observed in a collagen film with twisted plywood architecture [59]. Besides, the AFM images of sheared nano crystalline cellulose thin films showed two periodic gratings with different scales: the primary periodic structure perpendicular to the shear direction and a smoother texture characterized by a secondary periodic structure which is very similar to the surface modulation found in the Tulip "Queen of the Night" petals [25]. The estimated values of the parameter B for several surface nano-undulations of CLC (refs. [14, 25, 26, 31, 56, 59]) are shown in Table 2-1. The results show that the predicted values of the parameter B using the scaling law are consistent with the anchoring energy coefficients for the CLC/air interface.

Experiments	h(nm)	λ(μm)	B fitted
Chiral polymer [26]	2.5	0.63	0.028
Collagen solution [59]	100	7.5	0.079
Liquid crystalline collagen [14]	150	8	0.110
Cellulosic cholesteric film [25]	5	0.5	0.059

Table	2-1.	Validation	of th	he scalir	g law	(Eq.	2.22	with	experimentally	observed	nano-scale
surface	undu	ulations in <b>(</b>	CLCs	and bio	ogica	l plyw	voods.				

## **2.6 Conclusions**

This study has used a non-linear nemato-capillarity shape equation to describe the main mechanisms driving nano-scale surface undulations in chiral nematic liquid crystals as shown in plant-based plywoods and various cholesteric liquid crystals. The generalized Laplace equation based on the Cahn-Hoffman capillarity vector formalism was formulated and used as an efficient tool to analyse surface reliefs in plant-based plywoods. The resulting chiral capillary equation admits stable spatially periodic solutions describing surface wrinkling, where the amplitude is in the order of few nms and the wave-length is in order of µms. The role of three capillary pressure contributions (surface area change, surface area rotation, and director curvature) have been elucidated and the influence of chirality and surface anchoring has been characterized. The director pressure has been identified as the fundamental driving force that generates the surface nano-scale undulations. The model predictions show that the director pressure vanishes for a planar surface with a uniform tangential helix vector and results in a flat surface. A scaling law for the chirality-driven surface wrinkling shows that the ratio of amplitude-to-period is a linear function of the ratio of anchoring strength to isotropic surface tension  $(0.085 \times W/\gamma_0)$ . The scaling law is validated with experimental values available in literature for surface undulations observed in CLCs and biological plywoods. Since the pitch P<sub>0</sub> of cholesteric liquid crystals and plywoods is sensitive to temperature, water content, pH, and external fields we expect new functional material surfaces that operate through the chiral capillarity mechanism described here. Further work is currently in progress to characterize water- based surface actuation mechanism through interaction of anisotropic interfacial tension and chirality changes through hydration.

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# Chapter 3

# **3** Modeling Nano-Wrinkling of Chiral Surfaces in Response to Humidity: Structure and Diffraction Optics

## **3.1 Preface**

In the previous chapter, a comprehensive shape equation that reflects the membrane curvaturefiber order contributions was developed and the main mechanisms driving nano-scale surface undulations in plant-based plywoods were described. In this chapter, the role of humidity in deforming the surface undulations through the interaction of anisotropic interfacial tension, swelling through hydration, and capillarity at free surfaces is established. The optical properties of the water-induced surface wrinkling are explored and compared with the optical responses of the free surface nanostructures presented in the previous chapter. This chapter is reproduced from a published paper with the title "Tunable nano-wrinkling of chiral surfaces: Structure and diffraction optics", and co-authored with Prof. Damiano Pasini and Prof. Alejandro. D. Rey; Journal of chemical physics, 2015, 143, 114701.

#### 3.2 Summary

Periodic surface nano-wrinkling is found throughout biological liquid crystalline materials, such as collagen films, spider silk gland ducts, exoskeleton of beetles, and flower petals. These surface ultrastructures are responsible for structural colors observed in some beetles and plants that can dynamically respond to external conditions, such as humidity and temperature. In this chapter, the formation of the surface undulations is investigated through the interaction of anisotropic interfacial tension, swelling through hydration, and capillarity at free surfaces. Focusing on the cellulosic cholesteric liquid crystal (CCLC) material model, the generalized shape equation for anisotropic interfaces using the Cahn-Hoffman capillarity vector and the Rapini-Papoular anchoring energy are applied to analyze periodic nano-wrinkling in plant-based plywood free surfaces with water-induced cholesteric pitch gradients. Scaling is used to derive the explicit relations between the undulations' amplitude expressed as a function of the anchoring strength and the spatially varying pitch. The optical responses of the periodic nano-structured surfaces are studied through finite difference time domain simulations (FDTD) indicating that CCLC surfaces with spatially varying pitch reflect light in a wavelength higher than that of a CCLC's surface suith spatially varying pitch. This structural color change is controlled by the pitch gradient through hydration.

All these findings provide a foundation to understand structural color phenomena in Nature and for the design of optical sensor devices.

## **3.3 Introduction**

A variety of surface ultrastructures can be found in many biological materials, such as the periodic undulations observed in films of concentrated collagen [1], silk gland ducts of the golden orb-web spider Nephila clavipes [2], the exoskeleton of the beetle Chrysina gloriosa [3], and other cellulosic materials [4,5]. It has been shown that the surface patterns in the exoskeleton of Chrysina gloriosa and in the duct of silk secreting glands in Nephila clavipes closely resemble the atomic force microscopy image of the focal conic domains that spontaneously arise on the free surface of cholesteric liquid crystals, CLCs [3, 6]. Besides, similar periodic patterns have been observed at the free surface of a nematic liquid crustal under a magnetic field [7] and a cholesteric under a homeotropic alignment [8]. Cholesteric liquid crystal self-assembly has been proposed to explain the surface structures of many fibrous composites ranging from plant cell walls to arthropod cuticles [9, 10]. Some of these periodic surface structures give rise to structural colors that are observed in beetles [3], mollusk shells [11], ostracods [12], large fishes [13], and some plants [14]. Although, minor light absorption effects have been reported in CLCs, the absorption of light by pigments in some beetle cuticles plays an important role in structural colors. The black melanin pigment present in a Japanese jewel beetle cuticle absorbs the light fraction scattered from inner layers, which contributes in determining the iridescent color [15]. Furthermore, the single iridescent colors observed in some beetles and butterflies result from color mixing of structurally different colors. The beetle *Calidea panaethiopica* shows a metallic green color that originates from a multilayer structure generating two different colors mixed to produce the single color [16]. Additionally, the complex green color of the butterfly Papilio palinurus results from an additive color mixing of yellow and blue [17].

Structural color and iridescence in plants are typically associated with diffraction grating, thin layered or multilayered interference, and often with contributions from pigmentation as well. Structural color in plant's leaves arises essentially from multilayers of cellulose microfibrils with differing orientations in the plant cell walls forming a cholesteric liquid crystal phase [18, 19]. Structural color in plant's flowers arises essentially from surface diffraction gratings. For example, the petals of *Hibiscus trionum* and *Tulipa kaufmanniana* feature ordered surface striation controlling iridescence with a striking metallic appearance [20].

Color change in response to environmental stimuli is ubiquitous in plants and animals. The iridescent blue color in the fish Chrysiptera cyanea can change to ultraviolet by the simultaneous change in spacing of the adjoining reflecting plates [21]. It has also been observed that the beetles Dynastes Hercules and Coptocycla can vary their coloration in response to humidity [22, 23]. The elytra of longhorn beetles Tmesisternus isabellae reacts to water absorption by color change, from golden in the dry state to red in the wet state. The factors controlling color change are the swelling of the multilayer pitch (from about 175 nm in the dry state to about 190 nm in the fully wet state) and the water infiltration [24]. Structural colors in some plants can also be the result of a response to humidity, light, and touch through the change of bulk and surface nanostructures, among other external stimuli. One of the interesting examples is a tropical rainforest plant, Selaginella willdenowii that possesses iridescent blue leaves that can dynamically respond to hydration and dehydration. It has been shown that the iridescent blue color turns to green when the leaves are immersed in water, with blue color reappearing when the leaves are dry [25]. Electron microscopy of iridescent blue leaves in four Malaysian rain forest understory plants show that optical effects upon humidity changes are mediated by altering the twisted plywood structure (helix pitch) in the plant cell walls. The reported lamellar spacing in green leaves is 268±2.2 nm, which is larger than the lamellar spacing in blue leaves, 141±2.4 nm.[18] Similar behavior is observed in a hygroscopic liquid crystal polymer film that responds to temperature and humidity by changing its color [26]. It has been proved that that when humidity is high, the film swelling results in a pitch increase as opposed to the case of low humidity, which causes a decrease in the pitch with consequent film shrinkage.

Understanding the mechanisms through which plants exhibit specific optical appearances is an illustration of "bio-inspiration" for the design of optical devices with novel functionalities [27], and as a tool to characterize plant-based plywoods. Although the formation of these surface ultrastructures during the plant development is not yet well understood, it is recognized that the formation and periodicity of the plant surface undulations are governed by the CCLC structure [28]. It has been shown that the change of the orientational order, the fiber orientation at the CCLC interface, defined by the average direction of preferred orientation called the director  $\mathbf{n}$ , and the presence of topological defects can cause the undulation on free interfaces through a process of surface energy minimization of the surface interface shape [29]. The interaction between the interface shape and the director  $\mathbf{n}$  is a complex phenomenon involving interfacial tension, surface

anchoring energy, and LC Frank elasticity, all factors requiring the integration of multi-scale modelling for bulk and surface structure properties [30]. In our recent study, we presented the main mechanisms driving nanoscale surface undulations in chiral nematic liquid crystals as shown in plant-based plywoods and various cholesteric liquid crystals [31, 32].

Of particular interest in the present chapter is the study the role of tangential water gradient in the formation of plant surface undulations. The insight gained from this study can be used to generate surface patterns and nano-scale actuation systems capable to autonomously respond to humidity. In this chapter, we seek to characterize the free surface relief of CCLC through the interaction of anisotropic interfacial tension, swelling through hydration, and capillarity at free surfaces. With a focus on the CCLC material model, we consider two-dimensional cholesteric films with a free interface subject to a tangential water gradient. To analyze periodic nanowrinkling in plant-based plywood free surfaces, we use the generalized shape equation for anisotropic interfaces using the Cahn-Hoffman capillarity vector developed for LCs [33], and the classical Rapini-Papoular anchoring energy [34] for the anisotropic part of the interfacial tension. To investigate the optical responses of the surface wrinkling, we implement finite difference simulations in the time domain (FDTD) and calculate the corresponding planar reflection of light. The FDTD method is established as an accurate numerical method to solve Maxwell's equations and as an efficient tool for simulation of light propagation in liquid crystals containing complex textures [35]. It has been shown that the FDTD method is capable of predicting optical responses to textured nematic liquid crystal films containing non-uniform orientation induced by variations in surface anchoring [36]. The interaction between the incident light and the nanoscale periodic structure shows bistructural color reflection through hydration and dehydration. The wavelength of the reflection peak strongly depends on the CCLC helical pitch. The self-assembly formation of the CLC surface ultrastructure together with the water-induced multiple structural colors suggests a potential mechanism to exploit in the design of colorimetric humidity sensors.

The organization of this chapter is as follows. Section 3.4 introduces the CCLCs material model system with water-induced spatially varying pitch. Section 3.5 presents the interfacial force balance equation, and the governing nemato-capillary shape equation expressing the coupling mechanism between the surface geometry and cellulose fiber orientation for CCLC/air interface in rectangular (x,y,z) coordinates. The capillary shape equation is derived and the unique role of the Cahn-Hoffman capillary vector is discussed. Section 3.6 presents the effect of model

parameters on the surface profile, the capillary pressures associated with the CCLC interface, the scaling formula expressing surface profile amplitude as a function of the anchoring strength and the water-induced varying helix pitch, and the optical response of the surface relief using the finite difference time domain simulation. In section 3.6, the reflection of light affected by the spatially varying pitch is also theoretically investigated and compared with the reflection of light at free surfaces of CCLCs with constant pitch. The role of key parameters such as the anchoring strength, and the helix pitch on the optical properties is discussed. Section 3.7 presents Conclusions.

## 3.4 Geometry and structure

Plant cell walls can be considered as a natural viscoelastic composite reinforced by cellulose microfibrills (CMFs) coated with hemicelluloses and embedded in a matrix of lignin/pectin [37]. CMFs in the extracellular polysaccharide matrix are oriented in strategic directions to form the twisted plywood architecture that provides mechanical strength, controls cell expansion, contributes to the morphology at the tissue, and functions in signaling [38]. A plant cell wall consists of a primary wall that is a thin layer laid down during cell growth, and three secondary walls, which are thick and rigid layers laid down when the cell has reached its final size and shape [38]. However, the mechanisms by which the CMFs are oriented in a specific direction are not well understood. Based on the microstructural and textural similarities between the plant cell walls and chiral liquid crystal phases, it is hypothesized that the formation of plant cell wall microstructure arises through liquid crystal self-assembly [39-41]. Plant cell walls can be characterized by a multi-layered structure where cellulose fibers are laid down parallel in each layer, whereas the CMF orientation between layers changes by a constant angle [10]. Figure 3-1(a) depicts the schematics of the helicoidal plant cell wall where ellipsoids indicate fiber orientation on each parallel layer. The fiber orientation at the interface is defined by the director **n**. The instantaneous axis of rotation is defined by the helix axis **H**. We assume that the helix axis remains parallel to the surface; other complex structures occurring when the helix axis H is distorted are beyond the scope of this study. The pitch length P is defined as the distance through which the fibers undergo a  $2\pi$  rotation. The handedness of the CLC in the whole study is assumed to be right-handed (P>0). For rectangular (x,y,z) coordinate system, the surface relief that is directed along the x axis can be described by a y(x,z) deviation from the xz plane. The amplitude of the vertical undulation is h(x). As the surface relief is constant in the z direction for a linear texture, the curvature in the z-direction is zero. The unit tangent,  $\mathbf{t}$  and the unit normal,  $\mathbf{k}$  to the surface can be expressed with the normal angle,  $\varphi:(\mathbf{x}) = (\sin \varphi(\mathbf{x}), -\cos \varphi(\mathbf{x}), 0)$ ,  $\mathbf{k}(\mathbf{x}) = (\cos \varphi(\mathbf{x}), \sin \varphi(\mathbf{x}), 0)$ . L is the given system length in the x direction. The arc-length measure of the undulating surface is "s".

The preferred fiber orientation or easy axis at the interface can be parallel to the unit normal **k** (homeotropic) or perpendicular to the unit normal  $\mathbf{k}$  (planar). Based on the surface anchoring type (planar or homeotropic) of CLCs, the director filed configuration close to the surface can be distorted or undistorted to reach the minimum-energy state. In the case of planar anchoring, as the helix axis H perpendicular to the surface is the most stable configuration, it will remain undistorted [42]. However, in the case of homeotropic anchoring (W<0), either the helix structures parallel to the surface or perpendicular to the surface is not fully compatible with any uniform aligning surface [43]. Therefore, to adapt the helix axis to uniformly aligning surface, a set of elastic distortion and sub-surface defect nucleation results in a disruption of the average orientational order and creation of topological defects, need to be formed at the interface. In this chapter, we restrict the discussion to homeotropic anchoring (W<0), because the undistorted helicoidal structure for planar surface anchoring (W>0, n.k=0) results in a flat surface [6]. It has been reported that the presence of elastic distortion near to the CLC interface can change the director field and its periodicity at the free surface [44,45]. Here we assume that the periodicity of the distorted region is constant and equal to the bulk pitch, P. Usually, the defect dissociates in a bulk  $\lambda^+$  and a surface  $\tau^-$  pair. The  $\tau^-$  defect lines disappear for the non-planar surface (see Figure 3-1).

The present study uses the cholesteric representation of the director field **n** developed by Meister *et al.* [6]:

$$\mathbf{n}(\mathbf{x}, \mathbf{y}) = (\cos q \mathbf{x} \cos q \mathbf{y}, \sin q \mathbf{x}, \cos q \mathbf{x} \sin q \mathbf{y}), \quad \mathbf{q}(\mathbf{x}) = \frac{2\pi}{\mathbf{P}(\mathbf{x})}$$
(3.1)

Topological defects in cholesteric liquid crystals include disclinations and dislocations. Disclination is a defect involving discontinuity in the director field, and dislocation is a translational defect corresponding to addition or removal of cholesteric layers. Disclinations are characterized by core type (singular,  $\tau$  lines or non-singular,  $\lambda$  lines), where in singular core the molecular order deviates from its homogenous value while in the non-singular core it does not. The strength of disclination is characterized by sense rotation (sign) and amount of rotation (amplitude) [46].



**Figure 3-1.** Schematic of a cholesteric liquid crystal (plywood architecture) and nano-wrinkled surface structures. Bend and splay orientation distortions with  $\lambda^+$  disclination for normal anchoring (W<0) create surface undulations. Note that the director field is continuous everywhere and the  $\lambda^+$  lines have a low energy non-singular core. (a) Surface structure of CCLC surface with constant pitch. **H** is the helix unit vector, and P<sub>dry</sub> is the constant pitch. (b) Surface structure of CCLC surface with water-induced varying pitch. P(x) is the local pitch which varies linearly over a range of x-values: P(x)=P<sub>dry</sub>+(P<sub>wet</sub>-P<sub>dry</sub>) x/L. Adapted with permission from Journal de Physique II,6, 827-844 (Ref. [6]). Copyright 1996 EDP Sciences.

We note that this director field is continuous everywhere and only contains non-singular core  $\lambda^+$ disclination lines, and that  $n_{y}(x) = \sin qx$  lacks "y" dependence. The latter is an important factor for the bulk normal stresses. The interfacial structure, with an array of  $\lambda^+$  lines at a distance P/4 from the surface, emerges from a sufficiently strong homeotropic anchoring. Figure 3-2(a) shows the director **n** trajectories on the unit sphere corresponding to Figure 3-1. It has been proved that for equal elastic constants, all the trajectories on the unit sphere are geodesic, i.e. circles whose plane passes through the center of the sphere. Geodesics are well known energy minimizers for liquid crystals [47, 48]. As depicted in Figure 3-2 (b), the continuous director field is the ABCD patch on the unit sphere limited by two meridians (pure twist A-B and splay-bend A-D) and the equator. The temperature and concentration dependence of the CLC helical pitch has been widely reported [7]. Recently Matsuyama [49, 50] showed that the helical pitch of a cholesteric phase is a function of the concentration and the orientation order parameter in a mixture of polymer and a liquid crystal. In the present study, we assume that the helix pitch changes in response to humidity level from the swelling and shrinking of the polysaccharide matrix through water sorption. As the stiffness of the crystalline cellulose microfibrils is approximately two orders of magnitude higher than the hygroscopic matrix, they do not swell whereas the hygroscopic matrix, which is embedded in, does [51].

It has been shown that some biological helicoidal structures when exposed to higher humidity, result in an increase of the pitch due to the swelling of the multilayer, and when exposed to lower humidity they result in a decrease of the pitch due to the shrinkage of the multilayer. Therefore, in the presence of the tangential water gradient at the CLC-air interface we consider a spatially varying pitch, where the director **n** rotates non-uniformly along the x-direction. The pitch gradient can be described by a power series or an exponential [52, 53]. To meet the objectives and remain within the scope of this work, we assume the pitch profile as linear. As shown in Figure 3-1(b), in the presence of the tangential water gradient, the pitch is assumed to grow from  $P_{dry}$  to  $P_{wet}$  along the x-direction:

$$P(x) = P_{dry} + (P_{dry} - P_{wet})\frac{x}{L}$$
(3.2)

#### **3.5 Governing equations**

The formation of the surface undulations in CLC interfaces is a complex multiple-coupling problem that includes surface tension, anchoring energy and bulk elasticity. To explore the free

surface relief, the total system energy including bulk surface energy and the bulk elastic energy should be minimized. All the equations that govern the shape of the interfaces coupling bulk and surface phases have been presented in Ref. [30]. However, the analytic solution of the problem with the usual formalism is very complicated. In the present study, to elucidate the bulk contribution to the shape equation, the interfacial stress boundary conditions at the CLC/air interface are considered. The surface undulations in plant cell walls are assumed to be formed through a modulation in the surface energy at the anisotropic-air interface.



**Figure 3-2.** (a) The director field used in this study is continuous everywhere in ABCD; adapted with permission from Journal de Physique II,6, 827-844 (Ref. [6]). Copyright 1996 EDP Sciences. (b) The corresponding orientation paths  $(n_y(x))$  are geodesics, well known energy minimizers [47,48].

The macroscopic chirality of the cellulose fibers emerges as the property that impacts the interfacial tension and stimulates the free surface relief. In this section, the coupling mechanism between the surface geometry and cellulose fiber orientation is presented through the shape equation based on the vector formalism of Cahn-Hoffman capillarity [54] for a cholesteric liquid crystal with a spatially varying pitch (Eq. 3.2).

## 3.5.1 Cahn-Hoffman capillarity vector

Cahn and Hoffman formulated the capillary vector  $\boldsymbol{\xi}$  [54] to describe interfacial surface energy anisotropy, which is known as the capillary vector formulation of interface energies. For anisotropic systems, the orientation-dependent surface energy can be categorized by: the director

n=n(r), the surface position vector r=rk, and the surface unit normal k. Cahn and Hoffman defined the nematic capillarity by the gradient of the scaler field  $r\gamma$  [55]:

$$\xi(\mathbf{n},\mathbf{k}) = \nabla[r\gamma(\mathbf{k})] \tag{3.3}$$

For isotropic interfaces, the capillary vector  $\boldsymbol{\xi}$  reduces to the form  $\boldsymbol{\xi} = \gamma \mathbf{k}$ . The decomposition of the surface director field into normal and tangential components yields:  $\mathbf{n}_{\perp} = \mathbf{k}\mathbf{k}$ .  $\mathbf{n}$  and  $\mathbf{n}_{\parallel} = \mathbf{I}_{s}$ .  $\mathbf{n}$  where  $\mathbf{I}_{s}$  is the 2×2 unit surface dyadic:  $\mathbf{I}_{s}=\mathbf{I}-\mathbf{k}\mathbf{k}$ ,  $\mathbf{I}$  is the 3×3 unit tensor. Calculating the gradient of the field r $\gamma$  using  $\boldsymbol{\xi}.\mathbf{k}=\gamma$  ( $\mathbf{k}$ ,  $\mathbf{n}$ ),  $\boldsymbol{\xi}.d\mathbf{k}=d\gamma$  ( $\mathbf{k}$ ,  $\mathbf{n}$ ), and  $d(r\gamma) = \nabla(r\gamma)$ . d $\mathbf{r}$  gives:

where the normal component  $\xi_{\perp}$  represents the change in surface energy by contraction of the surface unit normal, and the tangential component  $\xi_{\parallel}$  represents the change in surface energy by rotation of the surface unit normal. The classical Rapini and Papoular form of surface free energy can be used to derive the Cahn-Hoffman capillary vector  $\xi$  for cholesteric surfaces [34]:

$$\gamma(\mathbf{n},\mathbf{k}) = \gamma_0 + \gamma_{\text{aniso}}(\mathbf{n},\mathbf{k}); \quad \gamma_{\text{aniso}}(\mathbf{n},\mathbf{k}) = \frac{W}{2}(\mathbf{n}.\mathbf{k})^2$$
(3.5)

where  $\gamma_0$  is the isotropic surface tension,  $\gamma_{aniso}$  represents the anisotropic anchoring energy contribution due to the director field, and W is the surface anchoring strength. For strong anchoring, the director field is fixed as a function of temperature and does not change due to bulk distortions or external fields. However, for weak anchoring, the director field can be changed due to bulk director fields. As mentioned above, W>0 if the easy axis that is an energetically preferable direction for the surface orientation is tangential to the interface (planar), and W<0 if the easy axis is normal to the interface (homeotropic). Substituting Eq. 3.5 into Eq. 3.4 yields the following normal and tangential components of the capillarity vector:

$$\boldsymbol{\xi}_{\perp}(\mathbf{n},\mathbf{k}) = (\gamma_0 + \frac{W}{2}(\mathbf{n},\mathbf{k})^2)\mathbf{k}$$
(3.6)

$$\boldsymbol{\xi}_{\parallel}(\mathbf{n},\mathbf{k}) = \mathbf{W}(\mathbf{n},\mathbf{k})\mathbf{n} - \mathbf{W}(\mathbf{n},\mathbf{k})^{2}\mathbf{k} = \mathbf{W}(\mathbf{n},\mathbf{k})(\mathbf{n}-(\mathbf{n},\mathbf{k})\mathbf{k})$$
(3.7)

#### **3.5.2 Interfacial force balance equation**

In this section, we present the interfacial stress boundary conditions at the interface between air and cholesteric liquid crystal, denoted by phase (a) and phase (b) respectively. We assume that the system is isothermal, both phases are incompressible, and the interface is elastic. The interfacial force balance equation is the balance between interfacial forces and the bulk stress jump [56]:

$$-\mathbf{k}.(\mathbf{T}^{a}-\mathbf{T}^{b})=(\nabla_{s}.\mathbf{T}_{s})$$
(3.8)

where  $\nabla_s = I_s \cdot \nabla$  is the surface gradient. The surface stress tensor,  $\mathbf{T}_s$  is given by the sum of normal  $\mathbf{T}^N$ , bending  $\mathbf{T}^B$  and distortion stresses  $\mathbf{T}^D$ :

$$\mathbf{T}_{s} = \mathbf{T}^{N} + \mathbf{T}^{B} + \mathbf{T}^{D}; \mathbf{T}^{N} = \gamma \mathbf{I}_{s}, \mathbf{T}^{B} = -\mathbf{I}_{s}.\frac{\partial \gamma}{\partial \mathbf{k}} \mathbf{k}, \mathbf{T}^{D} = -\mathbf{I}_{s}.\frac{\partial \gamma}{\partial \nabla_{s} \mathbf{n}}.(\nabla_{s} \mathbf{n})^{T}$$
(3.9)

 $\mathbf{T}^{a}$  and  $\mathbf{T}^{b}$  is the total stress tensor in the air and cholesteric bulk phase respectively. The bulk stress tensor in air is pure pressure:

$$\mathbf{T}^{\mathbf{a}} = -\mathbf{p}^{\mathbf{a}}\mathbf{I} \tag{3.10}$$

The bulk stress tensor in CLC is given by [56]:

$$\mathbf{T}^{\mathrm{b}} = -(\mathbf{p}^{\mathrm{b}} - \mathbf{f}_{\mathrm{b}})\mathbf{I} + \mathbf{T}^{\mathrm{E}}; \quad \mathbf{T}^{\mathrm{E}} = -\frac{\partial \mathbf{f}_{\mathrm{b}}}{\partial \nabla \mathbf{n}} (\nabla \mathbf{n})^{\mathrm{T}}$$
(3.11)

where  $p^b$  is the hydrostatic pressure,  $T^E$  is the Ericksen stress tensor,  $f_b$  is the CLC bulk Frank energy density. Substituting Eq. 3.10 and Eq. 3.11 into Eq. 3.8 and project the result along **k** (normal component) results in:

$$\underbrace{\left(p^{a}-p^{b}\right)+\left(f_{b}\right)-\mathbf{kk}:\left(\frac{\partial f_{b}}{\partial \nabla \mathbf{n}}.\left(\nabla \mathbf{n}\right)^{T}\right)}_{\text{bulk normal stress jump, SJ}}=\underbrace{\left(\nabla_{s}\cdot\mathbf{T}_{s}\right)\cdot\mathbf{k}}_{-\text{capillary pressure, }-\mathbf{p}_{c}}$$
(3.12)

Simply by considering the semi-infinite media in the vertical direction and periodic in the horizontal direction neglecting gravity, the hydrostatic term,  $(p^a - p^b)$  becomes zero. The remaining contribution to SJ,  $\{f_b + \mathbf{kk}: \mathbf{T}^E\}$  is known as the elastic correction in the liquid crystal literature. The expression for the bulk elastic energy density of a cholesteric is:

$$\mathbf{f}_{b} = \frac{1}{2}\mathbf{K}_{1}(\nabla \cdot \mathbf{n})^{2} + \frac{1}{2}\mathbf{K}_{2}(\mathbf{n} \cdot \nabla \times \mathbf{n} - \mathbf{q}(\mathbf{x}))^{2} + \frac{1}{2}\mathbf{K}_{3}(\mathbf{n} \times \nabla \times \mathbf{n})^{2}$$
(3.13)

where K<sub>1</sub>, K<sub>2</sub>, and K<sub>3</sub> are the splay, twist, and bend Frank constants. q(x) is the variable wave vector equals to  $2\pi/P(x)$ . Considering one constant approximation for the Frank bulk energy and the director field expressed by Eq. 3.1, the corresponding Frank energy density f<sub>b</sub> becomes:

$$f_{b} = \frac{1}{2} K \left( 2(q(x))^{2} + \left(\frac{\partial n_{z}}{\partial y}\right)^{2} - 2\left(n_{x}\frac{\partial n_{z}}{\partial y}q(x)\right) \right) = \frac{1}{2} K (q(x))^{2} (1+n_{y}^{2})$$
(3.14)

 $f_b$  is out-of-phase with the surface energy density: when  $f_b$  increases  $\gamma$  decreases and vice versa. Using Eq. 3.14, we find the normal projection of the bulk Ericksen stress **kk** : **T**<sup>*E*</sup> :

$$\mathbf{k}\mathbf{k}:\mathbf{T}^{\mathrm{E}} = -\mathrm{K}\left((\mathbf{n}\cdot\nabla\mathbf{n})(\mathbf{n}\cdot\mathbf{k})\right)\cdot\left((\mathbf{k}\cdot\nabla)\mathbf{n}\right) - \mathrm{K}\left(\nabla\cdot\mathbf{n}\right)\left((\mathbf{k}\cdot\nabla)\mathbf{n}\right)\cdot\mathbf{k}$$
(3.15)

Having established the director field  $\mathbf{n}(\mathbf{x}, \mathbf{y})$ , its associated bulk energy  $f_b$ , and the interfacial surface tension  $\gamma$ , we find that the normal projection of the bulk Ericksen stress,  $\mathbf{kk} : \mathbf{T}^E$  is zero:

$$\mathbf{k}\mathbf{k}:\mathbf{T}^{\mathrm{E}} = \left( \left( (\mathbf{I} - \mathbf{n}\mathbf{n}) \cdot \frac{\partial \gamma}{\partial \mathbf{n}} \right) \cdot (\nabla \mathbf{n})^{\mathrm{T}} \right) \cdot \mathbf{k} = \mathbf{W}(\mathbf{n}.\mathbf{k}) \left( \left( \nabla_{\perp} \mathbf{n}_{\mathrm{y}} \right)^{\mathrm{T}} \right) = 0$$
(3.16)

 $\nabla_{\perp} n_y = 0$  because  $n_y$  depends only on x ( $\frac{\partial n_y}{\partial y} = 0$ ). Therefore, as the elastic correction SJ in the present case is only due to  $f_b$ :

$$\mathbf{f}_{\mathrm{b}} = (\nabla_{\mathrm{s}} \cdot \mathbf{T}_{\mathrm{s}}) \cdot \mathbf{k}$$
(3.17)

## 3.5.3 Liquid crystal shape equation

To derive the capillary shape equation, we use the definition  $-\mathbf{p}_c = -\nabla_s \cdot \mathbf{\xi} = -\nabla_s \cdot (\mathbf{\xi}_{\perp} + \mathbf{\xi}_{\parallel})$ . For isotropic surfaces, the contribution from the normal component of the capillary vector  $\mathbf{\xi}_{\perp}$  is the classical Laplace pressure, and the contribution from the tangential component of the capillary vector is a function of both the director filed, **n** and the unit normal, **k**, an additional contribution to the capillary pressure arises from director curvature due to orientation gradients. It is worth emphasizing that in this formulation the surface unit normal **k** and surface director **n** whereas independent are coupled, and hence their gradients are associated with different kinds of pressure. By substituting the normal  $\mathbf{\xi}_{\perp}$  and tangential  $\mathbf{\xi}_{\parallel}$  components of the capillarity vector (Eq. 3.6 and Eq. 3.7) we obtain:

$$(\nabla_{s} \cdot \mathbf{T}_{s}) \cdot \mathbf{k} = \left(\gamma_{0} - \frac{W}{2} (\mathbf{n} \cdot \mathbf{k})^{2} + W(\mathbf{n} \cdot \mathbf{t})^{2}\right) \kappa - W \left\{ (\mathbf{k} \cdot \mathbf{n}) \left(\mathbf{t} \cdot \frac{d\mathbf{n}}{ds}\right) + \mathbf{k} \mathbf{n} : \left(\mathbf{t} \frac{d\mathbf{n}}{ds}\right) \right\}$$
(3.18)

Where  $\kappa = d\phi/ds$  is the surface curvature, s is the arc-length, and t is the tangential surface unit vector. Replacing Eq. 3.18 into Eq. 3.17 and using the Frank energy (Eq. 3.14), the governing shape equation reads:

$$\frac{\mathbf{K}(\mathbf{q}(\mathbf{x}))^{2}}{2\gamma_{0}}\left(1+\mathbf{n}_{y}^{2}\right) = \left(1-\frac{\mathbf{W}}{2\gamma_{0}}(\mathbf{n}.\mathbf{k})^{2}+\frac{\mathbf{W}}{\gamma_{0}}(\mathbf{n}.\mathbf{t})^{2}\right)\kappa -\frac{\mathbf{W}}{\gamma_{0}}\left\{(\mathbf{k}\cdot\mathbf{n})\left(\mathbf{t}\cdot\frac{\mathbf{d}\mathbf{n}}{\mathbf{d}s}\right)+\mathbf{k}\mathbf{n}:\left(\mathbf{t}\frac{\mathbf{d}\mathbf{n}}{\mathbf{d}s}\right)\right\}$$
(3.19)

where  $K/\gamma_0$  represents the elasto-capillary length scale which compares bulk elasticity and surface tension, and  $W/\gamma_0$  represents the scaled anchoring coefficient. This equation shows that the surface

shape is the result of the balance between Frank elasticity, surface tension and anchoring. The anchoring term can derive the surface wrinkling in cholesteric liquid crystals since for a fixed director field, the surface energy can only be minimized by distorting the interface. The surface shape also depends on the relative importance of the elastic contributions to the capillary pressure. The relative importance of elastic contributions compared to anchoring can be evaluated by comparing the extrapolation length,  $\ell_{ex} = \frac{\kappa}{W}$  and the helix pitch P. For biological cholesteric liquid crystals with significant anchoring that unravels the helix and with a large enough pitch (order of micrometers), the elastic contribution to the shape equation is not significant as the extrapolation length is much less than the helix pitch:  $\ell_{ex} < P$ . By increasing the helix pitch through hydration, the bulk elastic contribution  $(\frac{K(1+n_Y^2)}{2\gamma_0})$  decreases and eventually vanishes. Nevertheless, to rigorously determine the surface profile, it is thus essential to consider the bulk elastic contribution together with the three surface capillary pressures in the shape equation (Eq. 3.19).

## 3.5.4 Chiral surface shape equation and material parameters

Considering the specified splay-bend director  $\mathbf{n}(x)=(\cos qx, \sin qx, 0)$ , surface unit normal  $\mathbf{k}(x)=(\cos \varphi(x), \sin \varphi(x), 0)$ , unit tangent  $\mathbf{t}(x)=(\sin \varphi(x), -\cos \varphi(x), 0)$  and using the definitions:

$$\frac{\mathrm{dx}}{\mathrm{ds}} = \sin\phi, \quad \frac{\mathrm{dn}}{\mathrm{ds}} = \frac{\mathrm{dn}}{\mathrm{dx}}\frac{\mathrm{dx}}{\mathrm{ds}} = \frac{\mathrm{dn}}{\mathrm{dx}}\sin\phi, \quad \kappa = \frac{\mathrm{d\phi}}{\mathrm{dx}}\sin\phi \tag{3.20a}$$

gives the governing shape equation:

$$\frac{d\varphi}{dx} = \frac{\frac{Kq^{2}(x)}{2\gamma_{0}}\left(1+n_{y}^{2}\right) + \frac{q(x)W}{\gamma_{0}}\sin(\varphi)\left\{\sin^{2}(\varphi-q(x)x) - \cos^{2}(\varphi-q(x)x)\right\}}{\sin(\varphi)\left\{1-\frac{W}{2\gamma_{0}}\cos^{2}(\varphi-q(x)x) + \frac{W}{\gamma_{0}}\sin^{2}(\varphi-q(x)x)\right\}}$$
(3.20b)

The shape equation is a nonlinear first order ODE for the normal angle  $\varphi(x, K/\gamma_0, W/\gamma_0, q(x))$ , where the surface length scale L, the elasto-capillary length  $K/\gamma_0$ , extrapolation length  $W/\gamma_0$ , wave-vector q and pitch P are:

$$0 < x < L = 4.8\mu m, \ 1 \ nm < \frac{K}{\gamma_0} < 100 \ nm, \ -2 < \frac{W}{\gamma_0} < 0,$$

$$q(x) = \frac{2\pi}{P(x)}; \ P(x) = P_{dry} + (P_{wet} - P_{dry}) \frac{x}{L}$$
(3.21)

The nonlinear ODE with periodic coefficients is solved using the AUTO software [57]. The surface relief is then obtained from:

$$h(x) = \int_{0}^{x} \cot \varphi \, dx'$$
 (3.22)

The boundary condition at x=0, is  $\varphi|_{x=0} = \frac{\pi}{2}$ , consistent with the adopted sign of W/ $\gamma_0$ . The generic features of the amplitude profile h(x) and its periodicity h(x)=h(x+ $\lambda$ ) are the important outputs of the model. The four significant parameters influencing h(x) are:

- (i) the scaled anchoring coefficient:  $W/\gamma_0$ ,
- (ii) the elasto-capillary length scale:  $K/\gamma_0$ ,
- (iii) the micron scale pitch in dry state:  $P_{dry}$ ,
- (iv) the hydration-driven pitch gradient: (P\_{wet}\!-\!P\_{dry})\!/L.

For the nematic-isotropic interface, the scaled anchoring coefficient  $W/\gamma_0$  is of the order of 0.01 [58]. The anchoring strength W at the nematic-air interface is about several orders of magnitude larger than the anchoring strength at the nematic-isotropic interface. However, as the surface tension at the nematic-air interface is higher than the surface tension at the nematic-isotropic interface [6, 29], the scaled anchoring coefficient  $W/\gamma_0$  is taken to be in the range  $-0.1 < W/\gamma_0 < -0.01$ . For typical cholesteric liquid crystals, the elasto-capillary length scale K/ $\gamma_0$  is usually in the order of few nanometers (an order of magnitude estimation of the elastic constant K and the surface tension  $\gamma_0$  gives K  $\approx 10^{-11}$  J/m and  $\gamma_0 \approx 10^{-2}$  J/m<sup>2</sup>). So, the elasto-capillary length scale, K/ $\gamma_0$  is taken to be in the range 1 nm< K/ $\gamma_0 < 100$  nm. The helix deformation through tangential water gradient is described by a linear pitch profile so that the pitch increases from P<sub>dry</sub> to P<sub>wet</sub> along the wave propagating direction. P<sub>dry</sub> and (P<sub>wet</sub>-P<sub>dry</sub>)/L are taken to be in the range 0.5 $\mu$ m  $< P_{dry} < 3 \mu$ m and 0.1< (P<sub>wet</sub>-P<sub>dry</sub>)/L<0.3 respectively.

## **3.6 Results and discussion 3.6.1 Free surface profile**

Figure 3-3 shows the amplitude  $h_{max}$  profile for increasingly scaled values of the anchoring W/ $\gamma_0$ . The amplitude increases with increasing W/ $\gamma_0$ . For constant pitch, the periodicity of the undulation is constant and equal to the helix pitch P [31]. In the case of a cholesteric with a linearly varying pitch P(x), the periodicity increases quadratically along x, due to the integral relation between surface relief h(x) and the cotangent of the normal angle  $\varphi$ . The h periodicity is independent of  $W/\gamma_0$ . Figure 3-4 shows the corresponding surface profiles h(x) as the elasto-capillary length scale  $K/\gamma_0$  increases. The surface amplitude and periodicity remain essentially constant. One can infer that for particular values of the anchoring coefficient and the helix pitch, the elastic contribution to the surface shape is not significant and can be neglected. Figure 3-5 illustrates the variation of the amplitude and periodicity with the initial helix pitch  $P_{dry}$ . The figure shows that higher  $P_{dry}$  increases the periodicity. Since this pitch sets the scale of the pattern, increasing the base pitch increases the amplitude, which is consistent with the constant pitch case (see Ref. [32] and Ref. [31]). The reason behind this fact is that the Laplace pressure scales with  $h\gamma_0/P^2$ , while the balancing director pressure scales with W/P. Figure 3-6 shows the corresponding surface profiles h(x) for increasing ( $P_{wet}-P_{dry}$ )/L. Both amplitude and periodicity increase but the effect increases with "x" since it is the gradient factor of the pitch.



**Figure 3-3.** Surface profile h(x) for  $K/\gamma_0=1$  nm,  $P_{dry}=1.2 \mu m$ ,  $(P_{wet}-P_{dry})/L=0.2$  and different values of  $W/\gamma_0=-0.05$ , -0.1, and -0.2, showing the increase of the resultant surface amplitude h(x) through increase in the anchoring strength  $W/\gamma_0$ .



**Figure 3-4.** Surface profile h(x) for  $W/\gamma_0=-0.05$ ,  $P_{dry}=1.2 \ \mu m$ ,  $(P_{wet}-P_{dry})/L=0.2$  and different values of  $K/\gamma_0=1 \ nm$ , 10 nm, and 100 nm, showing the small shift of the resultant surface amplitude h(x) through increase in the elasto-capillary length scale  $K/\gamma_0$ .



**Figure 3-5.** Surface profile h(x) for  $W/\gamma_0=-0.05$ ,  $k/\gamma_0=1$  nm,  $(P_{wet}-P_{dry})/L=0.2$  and different values of  $P_{dry}=0.6 \mu m$ , 1.2  $\mu m$ , and 2.4  $\mu m$ , showing the increase of the resultant surface amplitude h(x) through increase in the pitch at dry state  $P_{dry}$ .



**Figure 3-6.** Surface profile h(x) for  $W/\gamma_0=-0.05$ ,  $k/\gamma_0=1$  nm,  $P_{dry}=1.2 \mu m$  and different values of  $(P_{wet}-P_{dry})/L=0.1$ , 0.2, and 0.3, showing the increase of the resultant surface amplitude h(x) through increase in the pitch gradient rate  $(P_{wet}-P_{dry})/L$ .

#### **3.6.2 Pressure-curvature relations**

As mentioned above, the main contributions to the capillary pressure arise from the area reduction (Laplace pressure), area rotation (Herrings pressure), director curvature, and bulk stress jump [33]. The Laplace capillary pressure,  $P_{dilation}$  is the resistant term (increasing energy with increasing area). While, the Herring's capillary pressure,  $P_{rotation}$  and the director curvature pressure,  $P_{director}$  are the driving forces to undulate the interface.

Rearranging Eq. 3-20b gives the three surface pressures and the bulk stress jump as function of "x":

$$\underbrace{\frac{\sin(\varphi)\frac{d\varphi}{dx}}{P_{\text{dilation}}} - \underbrace{\left\{\frac{W}{2\gamma_{0}}\cos^{2}(\varphi - q(x)x) + \frac{W}{\gamma_{0}}\sin^{2}(\varphi - q(x)x)\right\}\frac{d\varphi}{dx}}_{P_{\text{rotation}}} - \underbrace{\frac{q(x)W}{\gamma_{0}}\sin(\varphi)\left\{\sin^{2}(\varphi - q(x)x) - \cos^{2}(\varphi - q(x)x)\right\}}_{P_{\text{director}}} = \underbrace{\frac{Kq^{2}(x)}{2\gamma_{0}}\left(1 + n_{y}^{2}\right)}_{\text{Stress Jump. SJ}}$$
(3.23)

where we have introduced the scaled pressures (divided by isotropic tension  $\gamma_0$ ). The director curvature term reflects the anisotropic nature of chiral liquid crystals through the orientation

contribution to the surface energy. The director variation in the bulk that contains orientation gradient contributions is the origin of the stress jump term.

Figure 3-7 illustrates the mechanisms behind chiral wrinkling using the three pressures and the bulk stress jump. The scaled surface pressure contributions and the stress jump are plotted as function of "*x*" for particular values of K/ $\gamma_0$ , W/ $\gamma_0$ , P<sub>dry</sub>, and (P<sub>wet</sub>–P<sub>dry</sub>)/L. For an increasing helix pitch, the amplitudes of all contributions decrease along x, because the director spatial periodicity increases. The Herring's capillary pressure, P<sub>rotation</sub> and the bulk stress jump, SJ are an order of magnitude smaller than the Laplace capillary pressure, P<sub>dilation</sub> and the director curvature, P<sub>director</sub>. The figure exhibits that the Herring's pressure P<sub>rotation</sub> is always positive, the stress jump is always negative, and they change their phase along each cycle, such that in the first circle, rotation and director curvature are in-phase while dilation and stress jump are out of phase. The stress jump, SJ decays along x, a contribution becoming insignificant when the helix pitch increases due to the tangential water gradient. The key observation from these pressure profiles is that dilation and director curvature pressures are always out-of-phase, and since dilation (increase area) resists wrinkling, the director curvature pressure is the driving force behind nano-wrinkling.



**Figure 3-7.** Pressure profiles for  $P_{dilation}$ ,  $P_{rotation}$ ,  $P_{director}$ , and SJ as a function of distance "x" for W/ $\gamma_0$ =-0.05, k/ $\gamma_0$ =1 nm,  $P_{dry}$ =1.2 µm and ( $P_{wet}$ - $P_{dry}$ )/L=0.2. The figure displays that pressure extrema occur at planar and homeotropic orientation. When the director angle is  $\pi/4 < \theta < \pi/2$  dilation and rotation are in-phase and when  $0 < \theta < \pi/4$  rotation and director curvature are in-phase.

Polar plots of pressure as a function of director angle reveal the intimate connection between forces and director orientation. The polar plots of the three scaled capillary pressures and stress jump as a function of the anchoring coefficient  $W/\gamma_0$ , the elasto-capillary length scale  $K/\gamma_0$  and the pitch gradient profile (Pdry, and (Pwet-Pdry)/L) are shown in Figure 3-8 to Figure 3-11 respectively. The angular coordinate is the director field  $\theta$ . Figure 3-8 shows that all surface capillary pressures grow as the anchoring increases, while the stress jump remains constant. Changing  $W/\gamma_0$  does not affect the degree of asymmetry between the lobes of the three pressures. Figure 3-9 shows that as the elasto-capillary length scale  $K/\gamma_0$  increases the Laplace pressure P<sub>dilation</sub>, Herring's pressure Protation, and stress jump increase, whereas the director pressure P<sub>director</sub> remains constant. This is due to the fact that the director pressure depends on the anchoring strength and chirality and is independent of the elasto-capillary length scale. Varying  $K/\gamma_0$  changes the degree of asymmetry between the lobes of the Laplace pressure P<sub>dilation</sub> and Herring's pressure P<sub>rotation</sub>. Figure 3-10 and Figure 3-11 illustrate that a decrease in chirality (increasing P(x)) through a raise of either  $P_{dry}$  or (Pwet-Pdry)/L, reduces all capillarity pressures and the stress jump as the wave-length of the undulation increases. Changing P(x) does not affect the degree of asymmetry between the lobes of the pressures and stress jump.



**Figure 3-8.** Polar plots of the three scaled capillary pressures and stress jump a)  $P_{dilation}(\mu m^{-1})$ , b)  $P_{rotation}(\mu m^{-1})$ , c)  $P_{director}(\mu m^{-1})$ , d) SJ for two different values of  $W/\gamma_0=-0.05$ , -0.1 where  $K/\gamma_0=1$  nm,  $P_{dry}=1.2 \mu m$ , and  $(P_{wet}-P_{dry})/L=0.2$ . The angular coordinate is the director field  $\theta$ .



**Figure 3-9.** Polar plots of the three scaled capillary pressures and stress jump a)  $P_{dilation}(\mu m^{-1})$ , b)  $P_{rotation}(\mu m^{-1})$ , c)  $P_{director}(\mu m^{-1})$ , d) SJ for two different values of K/ $\gamma_0$ =1, 10 nm where W/ $\gamma_0$ =-0.05,  $P_{dry}$ =1.2  $\mu$ m, and ( $P_{wet}$ - $P_{dry}$ )/L=0.2. The angular coordinate is the director field  $\theta$ .



**Figure 3-10.** Polar plots of the three scaled capillary pressures and stress jump a)  $P_{dilation}(\mu m^{-1})$ , b)  $P_{rotation}(\mu m^{-1})$ , c)  $P_{director}(\mu m^{-1})$ , d) SJ for two different values of  $P_{dry}=1.2$ , 2.4 $\mu$ m where K/ $\gamma_0=1$  nm, W/ $\gamma_0=-0.05$ , and ( $P_{wet}-P_{dry}$ )/L=0.2. The angular coordinate is the director field  $\theta$ .



**Figure 3-11.** Polar plots of the three scaled capillary pressures and stress jump a)  $P_{dilation} (\mu m^{-1})$ , b)  $P_{rotation} (\mu m^{-1})$ , c)  $P_{director} (\mu m^{-1})$ , d) SJ for two different values of  $(P_{wet}-P_{dry})/L=0.1$  and 0.3 where  $K/\gamma_0=1$  nm,  $W/\gamma_0=-0.05$ , and  $P_{dry}=1.2 \ \mu m$ . The angular coordinate is the director field  $\theta$ .

#### 3.6.3 Nano-wrinkling scaling law

For free surface relief of cholesteric liquid crystal with constant pitch, we previously presented a theoretical scaling law expressing for the maximum undulation amplitude  $h_{max}$  as a function of anchoring strength and chirality [31]:

$$h_{max} = \frac{\frac{WP}{\gamma_o}}{1 + \frac{WP}{\delta}}$$
(3.24)

The numerical results indicated that  $\delta = 10.71 (\frac{W}{\gamma_0})^{-1.02}$ . This prediction shows that the undulation amplitude is essentially a linear function of the scaled anchoring  $W/\gamma_0$  and the helical pitch:  $h_{max} = 0.085 P_0(\frac{W}{\gamma_0})$ , which is consistent with the nano-scale surface structures that have been experimentally observed in a variety of polymeric and biological CLC. Recently, Yoshioka et *al.* [59] showed that the amplitude and the period of interface distortions of cholesteric droplets are determined by the helical pitch and independent of the droplet size. They stated that the amplitude monotonically increases with the pitch length; we note that Bernardino et al. claimed that the cholesteric-isotropic interface undulations scale with square root of the pitch [60]. For the periodic surface relief found in cholesteric liquid crystal with water-induced varying pitch, we also find a revealing close form expression for the x-dependent profile amplitude A (A is the amplitude between the upper and the lower envelope of the periodic surface undulations) as a function of the scaled anchoring  $W/\gamma_0$ , the helix pitch at dry state  $P_{dry}$ , and the pitch gradient ( $P_{wet}-P_{dry}$ )/L:

$$\mathbf{A} = \alpha_1 \left(\frac{\mathbf{W}}{\gamma_0}\right) \mathbf{P}_{dry} + \alpha_2 \left(\frac{\mathbf{W}}{\gamma_0}\right) \left(\frac{\mathbf{P}_{wet} - \mathbf{P}_{dry}}{\mathbf{L}}\right) \mathbf{x}$$
(3.25)

where  $\alpha_1$ =-0.07 and  $\alpha_2$ =0.13, found from numerical simulations. In accordance with the scaling law presented for cholesteric liquid crystal with constant pitch (Eq. 3.24), the estimate is that the amplitude is essentially a linear function of the scaled anchoring and the variable helix pitch. As shown in Figure 3-12, this result is consistent with experimental data from optical and scanning force microscopy of free surface of a chiral liquid crystal, for which the ratio of period and depth is approximately constant [61].



**Figure 3-12.** Validation of the scaling law with experimentally observed nano-scale undulations at CLCs free surface [61].

## **3.6.4 Diffraction grating**

When the periodicity of the surface undulations is of the same order of the incident light wavelength, the structure has the potential to generate iridescence and colors through the diffraction grating mechanism. Structural color in floral plants originates mainly from ordered surface diffraction gratings that scatter incident light in the plane perpendicular to the direction of the periodic undulations according to the grating equation [14]:

$$m\lambda = \frac{P_0}{2}(\sin\theta_i - \sin\theta_d)$$
(3.26)

where  $\theta_i$  and  $\theta_d$  are angles of incidence and diffraction which govern the angular locations of the principal intensity maxima for the diffracted incident light with wavelength  $\lambda$ , and *m* is the diffraction order. When the incident light is along the helix axis, mainly first order reflection occurs. While, for oblique incidence of light or the distorted helical structures higher order reflections can happen [62]. According to Eq. 3.26, for any given value of the angle of incidence  $\theta_i$ , each wavelength  $\lambda$  scatters into different angular directions. When the incident light is white light, different colors disperse in the perpendicular direction of the periodic structure, making the surface iridescent. Changing the angle of incidence,  $\theta_i$  can yield a variation in the peak wavelength. It has been shown that increasing the angle of incidence in a jeweled beetle, *Chrysina gloriosa* causes a red shift in wavelength from 525 nm at normal incidence to 556 nm in oblique illumination [3]. Hence Eq. 3.26 provides an important new relation between functionality and

structure of nano-wrinkled chiral surfaces of plywoods. In this chapter, the interaction of light with the surface nanostructure is computationally investigated with FDTD simulation using the OptiFDTD12 software [63] that solves the differential form of Maxwell's equations by discretizing time and space on a finite rectangular grid. Diffraction from periodic nanostructures is simulated in two dimensions, while considering "perfectly matched layer", PML on top and bottom and "periodic boundary conditions", PBC on the sides of the computational domain. The near-zone scattered field on the top surface of the simulation domain determines the reflection intensity. We considered the refractive index n of the nanostructure scales to be 1.55. To determine the reflection and transmission intensity, observation lines are positioned on the top surface and the bottom of the diffracting interface (see Figure 3-13(a) and Figure 3-13(b)). For the surface structure with constant pitch, we assumed that the grating pitch is 1.2 µm, the grating depth is 20 nm, and the film thickness is 200 nm. For the surface structure with varying pitch, we assumed the grating pitch to grow from  $P_{dry}=1.2\mu m$  to  $P_{wet}=2.2\mu m$  along the x-direction, the grating depth and the film thickness is 20 nm and 200 nm, respectively. As shown in Figure 3-13(d) and Figure 3-13(e), the scattering patterns in the surface structure with constant pitch and with varying pitch are different. It should be noted that the electric field intensity in the surface structure with varying pitch, as compared with that in the flat surface structure (Figure 3-13(c)) and in the structure with constant pitch (Figure 3-13(d)), becomes weaker.



**Figure 3-13.** Optical FDTD simulations of the surface nanostructures. (a) 2D Schematic of the computational domain for air-CCLC interface with constant pitch. (b) 2D Schematic of the computational domain for air-CCLC interface with water-induced varying pitch. Perfectly matched layers are considered at the top and bottom of the grating structure; periodic boundary conditions are used on the left and right side of the structure. Scattered electric field of 480 nm normal incident light in the x-y plane for (c) CCLC-air flat surface, (d) CCLC-air surface nanostructure with constant pitch, and (e) CCLC-air surface nanostructure with variable pitch, illustrating differences in the scattering behavior.

This shows that the helix pitch growth through hydration could decrease light scattering, as the reflection energy is distributed over a wide wavelength range. Figure 3-14 shows the simulated optical reflectance for the nanostructures with constant and varying pitch as a function of wavelength  $\lambda$  for different observation angles  $\theta_D$ . The structure with constant helix pitch reflects a band of 440-525 nm of the incoming white light (see Figure 3-14(a)). The reflectivity peak red shifts at  $\theta_D$ = 15° for the nanostructure with constant pitch. The structure with water-induced varying pitch, however, shows a red shift for all observation angles (Figure 3-14(b)), and reflects

a band of 460-570 nm of the incoming white light. For the structure with the constant pitch the reflection increases sharply (around 50%) from  $\theta_D = 30^\circ$  to  $\theta_D = 45^\circ$ . However, the spectrum of the structure with water-induced varying pitch does not move towards the infrared region (IR) and undergoes less reduction in the reflected intensity, as observed by a change of the observation angle.

The reflection spectra of the surface nanostructures with constant and water-induced varying pitch are plotted in Figure 3-15(a) as a function of the wavelength  $\lambda$  under normal incidence for a reflection angle of 45°. The results show that the reflection peak of the surface nanostructure has a red shift at  $\theta_D$ = 45° driven by a tangential water gradient (from  $\lambda$ =477 nm to  $\lambda$ =507 nm). It should be noted that we assumed that the tangential water gradient would induce non-uniform swelling of the multi-layered structure along the helix axis parallel to the surface, leading to the linear expansion of the helix pitch along x-direction.



**Figure 3-14.** FDTD simulation results for the reflectivity of the two surface nanostructures with constant pitch and varying pitch as a function of the wavelength  $\lambda$ . The reflectance is numerically calculated for two different structures by measuring the scattered field power normalized by the incident power. Reflectivity as a function of observation angles at 480 nm for the nanostructures (a) with constant and (b) varying pitch. For CCLC with constant pitch, the reflectivity peak at  $\theta_D=15^\circ$  shifts but for CCLC with varying pitch the reflectivity peak does not shift.

As shown in Figure 3-15(a), the water-induced varying pitch grating structure displays a broader band spectrum and less intense reflection. The varying pitch structure reduces the spectrum by 44% and shifts 28nm towards IR region in comparison with the constant pitch structure for a reflection angle of 45°. In order to investigate the relation between the helix pitch and the reflection peak, the reflection spectra of the surface nanostructure are computed for different constant helix pitches. We assumed that the helix pitch swells from about 0.6  $\mu$ m in the dry state to about 2.4  $\mu$ m in the fully wet state. Figure 3-15(b) shows an almost linear correlation between the reflection peaks and the CCLC helix pitch. The visible reflection peak shifts from 460 nm to 520 nm, with a raise of the helix pitch from 0.6  $\mu$ m to 2.4  $\mu$ m through hydration. We can note that the reflection peak of the structure displays a red shift caused by an increase of the helix pitch (corresponding to higher levels of humidity), resulting in a structural color change from blue in the dry state to green in the dry state to green in the wet state through hydration. The results indicate that the reflection wavelength is directly related to the helix pitch P(x) and the structural color can be adjusted by controlling the humidity level.

Figure 3-16 shows the FDTD results for diffraction patterns observed in the reflection of the surface nanostructures with constant and water-induced varying pitch. The surface structure with constant pitch (dry state) gives rise to the specular reflection whose intensity reduces by moving towards longer wavelengths. Moreover, the structure includes the first order blazed diffraction grating for angles  $|\sin\theta|>0.4$  and a weak second order diffraction grating for angles  $|\sin\theta|>0.8$ . Most of the diffraction intensity are observed at the wavelengths  $\lambda$ <500 nm, which is in agreement with the blue color identified for the structure at dry state (Figure 3-16(a)).

The diffraction pattern detected for the structure with varying pitch (wet state) shows only the specular reflection for all wavelengths. Compared with the surface structure in the dry state, the specular reflection is broadened, a phenomenon that correlates with surface undulations with increasing periodicity. Therefore, we can infer that the iridescence occurring on the self-assembly CCLCs can be extinguished through wetting. The interplay of structure and hydration may also add to the functionality of the self-assembly CCLCs that can be used for the design of colorimetric biosensors.



**Figure 3-15.** Change of the reflection peaks of the CCLC free surface by humidity-driven helix pitch expansion. (a) Comparison of the FDTD simulation results for reflectivity spectrum of the surface ultrastructure in the dry and wet states under normal incidence for a reflection angle of  $45^{\circ}$ . The water-induced varying pitch grating structure shows broader band spectrum and less intense reflection (dashed line). The varying pitch reduces the spectrum by 44% and shifts 28nm towards IR region for a reflection angle of  $45^{\circ}$ . (b) The linear correlation between the reflection peaks and the CCLC helix pitch. The color changes from blue at pitch equals to 0.6  $\mu$ m to green at pitch equals to 0.6  $\mu$ m.

To quantitative investigate the role of key system parameters in the optical responses of the surface at dry and wet states; we plot in Figure 3-17 and Figure 3-18 the impact of the anchoring strength and the helix pitch profile on the diffracted orders. The influence of the anchoring strength on the diffracted orders for a CCLC with a fixed helix pitch ( $P_{dry}=1.2 \mu m$ ) is illustrated in Figure

3-17(a). As the surface undulation amplitude grows for increasingly higher values of the anchoring strength, the intensity of specular reflection (m=0) slightly decreases, and the first and second ordered diffraction gratings rise. We note that the increases of first and second ordered intensity do not significantly change with  $W/\gamma_0<0.1$ . This means that for the CCLCs with higher anchoring coefficients, a structural color may be reinforced as the number of diffraction orders increases, whereas the intensity of the specular reflection (m=0) decreases. As shown in Figure 3-17(b), similar trends are also observed through increasing the helix pitch. The results show that the decrease in the specular reflection intensity for the structures with longer pitches is very significant while the increase in first and second ordered diffraction intensities is very limited. It should be noted that the specular reflection intensity disappears for helix pitches larger than 0.9 µm.



**Figure 3-16.** FDTD simulation results for the diffraction patterns as a function of sin ( $\theta$ ) and  $\lambda$  observed in transmission of the surface structures with (a) constant pitch and (b) water-induced varying pitch. The central band is the signature of specular reflection. The diagonal bands in (a) are the first-order diffraction with weak second-order diffraction.
The influence of the anchoring strength for a fixed water-induced gradient pitch ( $P_{dry}=1.2\mu m$ , ( $P_{wet}-P_{dry}$ )/L=0.2) on the diffracted orders is assessed in Figure 3-18(a). As the surface undulation amplitude grows for increased anchoring strengths, the intensity of specular reflection (m=0) noticeably diminishes in a linear fashion. A similar trend is also observed in Figure 3-18(b) where the impacts of the helix pitch profile ( $P_{dry}$  and ( $P_{wet}-P_{dry}$ )/L) on the distribution of the diffracted light are plotted. The results show that the decrease in specular reflection intensity for the structures with the higher pitch gradients is very limited.



**Figure 3-17.** Impact of the anchoring strength (a) and the helix pitch (b) on the light intensity distribution for several diffraction orders at  $\lambda$ =490 nm and normal incident light for the surface nanostructures with constant pitch (dry state).



**Figure 3-18.** Impacts of the anchoring strength (a) and the helix pitch profile (b) on the light intensity distribution (m=0) at  $\lambda$ =490 nm and normal incident light for the surface nanostructures with water induced varying pitch (wet state).

### **3.7 Conclusions**

The formation of free surface nanostructures in cellulosic cholesteric liquid crystals with waterinduced varying pitch has been investigated using a non-linear nemato-capillarity shape equation. The generalized Laplace equation based on the Cahn-Hoffman capillarity vector formalism was formulated and used as an efficient tool to analyse nano-scale surface reliefs in plant-based plywoods with water-driven varying helical pitch through interaction of anisotropic interfacial tension and chirality changes through hydration. The spatially periodic solutions to the chiral capillary equation describe surface wrinkling, where the amplitude is on the order of nanometers and the periodicity is on the order of micrometers. The role of three capillary pressure contributions (surface area change, surface area rotation, and director gradient curvature), and bulk stress jump have been characterized and the impacts of the varying helical pitch, the elasto-capillary length scale, and the surface anchoring strength have been established.

The scaling law for the chirality-humidity driven surface wrinkling showed that the spatially-varying surface profile amplitude is mostly a function of the anchoring strength and the water-induced helix pitch gradient. Finally, the optical properties of the CCLCs free surface nanostructure with water-induced varying pitch have been investigated and compared with the CCLCs free surface nanostructure with constant pitch. The results show that the surface structure with non-uniform pitch distribution, where the pitch length changes in different regions, reflects normal incident light with a bandwidth wider than the constant pitch surface structure. The reflection peak of the surface nanostructure can be tuned through the change in the humidity level based on the plywood helix pitch expansion. We attributed the color transition to the swelling and shrinking of the multi-layered plant cell wall plywood, which cause the helicoidal pitch to increase, thereby leading to a red shift in the iridescence. In conclusion, plant-based cholesteric liquid crystals are of interest because their optical response can be controlled by self-assembly and their colorimetric humidity sensing can reduce the sensor cost. The potential biosensors can respond to different ranges of relative humidity depending on the amplitude and wavelength of the grating structure. Furthermore, as it is expected that the amount of water absorption in CCLC free surface nanostructure depends on the temperature, it is essential to consider the temperature-sensitivity of the biosensor response.

All these findings provide a foundation to understand structural color phenomena in Nature and for the design of optical sensor devices.

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# **Chapter 4**

# 4 Multiple-wavelength Surface Patterns in Models of Elastic Biological Chiral Liquid Crystal Membranes

### 4.1 Preface

In chapters 2 and 3, the nonlinear nemato-capillarity shape equations that describe the sinusoidal nano-scale surface undulations in plant-based plywoods were presented. In this chapter, to explore more complex real surfaces such as creasing, folding, and period-doubling, a novel physical model that includes liquid crystal anisotropy of biological materials, bending elasticity of surfactant-like biomolecules, and substrate cholesteric order is developed. This chapter is reproduced from a published paper with the title "Multiple-wavelength surface patterns in models of biological chiral liquid crystal membranes", and co-authored with Prof. Damiano Pasini and Prof. Alejandro. D. Rey; Soft Matter, 2017, 13, 541-545.

#### 4.2 Summary

We present a model to investigate the formation of surface patterns in biological materials through the interaction of anisotropic interfacial tension, bending elasticity, and capillarity at their free surfaces. Focusing on the cholesteric liquid crystal (CLC) material model, the generalized shape equation for anisotropic interfaces using the Rapini-Papoular anchoring and Helfrich free energies is applied to understand the formation of multi-length scale patterns, such as those found in floral petals. The chiral liquid crystal-membrane model is shown to be analogous to a driven pendulum, a connection that enables generic pattern classification as a function of bending elasticity, liquid crystal chirality and anchoring strength. The unique pattern-formation mechanism emerging from the model here presented is based on the nonlinear interaction between bending-driven folding and anchoring-driven creasing. The predictions are shown to capture accurately the two-scale wrinkling of certain tulips. These new findings enable not only to establish a new paradigm for characterizing surface wrinkling in biological liquid crystals, but also to inspire the design of functional surface structures.

### **4.3 Introduction**

Chiral liquid crystals (CLCs) have been widely found in Nature and living soft materials, such as DNA [1], collagen [2], cellulose and chitin [3]. These biological CLCs are functional materials that display unique properties [4] and specific geometric features, such as surface wrinkles, mostly

with nanoscale amplitudes and microscale single wavelength [5-11]. Chiral capillary pressure, known as director pressure [12] that reflects the anisotropic nature of CLC through the orientation contribution to the surface energy, has been identified as the fundamental driving force generating single-wave length surface wrinkling [12-14]. Similar single wavelength surface patterns are observed for elastic Euler buckling caused by external compression, differential swelling or constrained growth [15, 16]. In biological membranes, these surface patterns are mostly the result of compressive strain in a stiff film resting on a compliant elastic substrate [17, 18].

Moreover, surfactant-like biomolecules found in all living cells influence the elastic properties of the cell membrane, such as pulmonary surfactant which is essential to lower the surface tension in the lung and to facilitate inhalation [19]. In the presence of a layer of surfactant-like biomolecules, we expect that both surface bending elasticity and anisotropic energy play a role in the evolution of surface morphologies. The objective of this chapter is present a theoretical model that combines membrane elasticity and liquid crystal anchoringto explain the multiple-length-scale surface wrinkles, which are widely observed in flower petals [10, 20], plant leaves [21, 22], blood cells [23], cerebral cortex [24, 25], and several animal living tissues [26-28].

Although significant progress has been made in formulating and validating theoretical models that attempt to explain the multi-length scale surface wrinkling in biological soft materials, previous studies have been restricted to bi-layer elastic models [17, 18, 23, 28]. There are few studies taking into account other chemical and biological mechanisms coupled with the compression- induced elastic deformation contributing to the wrinkling behavior [29-32] in biological surfaces and membranes. Here, to describe more complex real surfaces [10, 20-28], we propose a physical model that includes liquid crystal anisotropy of biological materials, bending elasticity of surfactant-like biomolecules, and substrate cholesteric order; and for brevity we call it cholesteric liquid crystal membrane model (CLC-M). When the anchoring and bending effects are comparable, the surface profile may show a rich variety of multi-scale complex patterns, such as spatial period-doubling, period-tripling, and quasi-periodicity that no longer can be described by a single harmonic. In the absence of liquid crystal anchoring, the CLC-M model converges to the classical elastic membrane (M), and in the absence of an interfacial surfactant layer, it converges to the liquid crystal interface model (CLC). Table 4-1 lists the system length scales, the surface topographies, and main wrinkling mechanisms that are captured in the three models discussed below.

Model	Symbol	Energies	Wrinkling mechanisms	Length scales	Topography		
cholesteric surface	CLC	anchoring (W)	director pressure [12]	P <sub>0</sub>	sinusoidal		
elastic membrane	М	bending (k <sub>c</sub> )	compression stress [15]	$\sqrt{k_{c}/ T_{_{0}} }$	sinusoidal		
cholesteric- elastic membrane	CLC-M	anchoring (W)+ bending (k <sub>c</sub> )	director pressure + compression stress	$\sqrt{k_{c}^{/} T_{_{0}} }, P_{0}$	harmonic, sub- harmonic, chaotic		

**Table 4-1.** Energies, length scales, wrinkling mechanisms, and surface topographies for the three models: M, CLC, and CLC-M.

For a cholesteric of pitch P<sub>0</sub>, under compression stress T<sub>0</sub>, with surface anchoring W, and bending elasticity k<sub>c</sub>, we find two length scales,  $\ell_{chiral}$  and  $\ell_{mem}$ , and two key dimensionless numbers,  $\omega$  and  $\overline{W}$ , that control the surface morphogenesis:

$$\ell_{\rm chiral} = \frac{2\pi}{q_{_0}} = P_{_0}, \quad \ell_{\rm mem} = \frac{2\pi}{q_{_b}} = \sqrt{\frac{k_c}{|T_{_0}|}}$$
(4.1)

$$\omega = \frac{\ell_{\text{chiral}}}{\ell_{\text{mem}}} = \frac{P_{o}}{\sqrt{k_{c}/|T_{o}|}}, \quad \overline{W} = \frac{W}{T_{o}}$$
(4.2)

where  $\omega$  is the winding number and  $\overline{w}$  is the ratio of anchoring to compression, whose magnitudes control the pattern formation mechanisms in the CLC-M model. For the limiting CLC and M models we have: CLC:  $\omega \rightarrow \infty$ ,  $\overline{W} = W/\gamma_0$ , M:  $\omega = 0$ ,  $\overline{W} = 0$  and for the CLC-M complete model both  $\omega$  and  $\overline{W}$  are non-zero and finite;  $\gamma_0$  is the isotropic surface tension.

### 4.4 Geometry and structure

Schematics for the expected surface wrinkling of the CLC model and the CLC-M model are shown respectively in Figure 4-1(a) and Figure 4-1(b). In Figure 4-1(a) the cholesteric order of the substrate unwinds into a geodesic splay-bend field that interacts with the anchoring, which creates a periodic director capillary pressure that is balanced by isotropic capillarity, as reported in [12, 14]. This results in a single-wave length wrinkle (top left). In this chapter, we focus on the phenomenon shown in Figure 4-1(b), where the anchoring/chirality/bending interaction creates multiple periodic scales (top right). Unwinding a helix due to surface anchoring was first considered in [13].



**Figure 4-1.** Schematic of a cut of the layered membrane in the absence (a) and presence (b) of surfactants at a LC free surface. Bend and splay orientation distortions with  $\lambda$ + disclination for normal anchoring (W<0) create single-wavelength surface undulations [12]. The rods in the substrate layer denote average fiber (director) orientation, the top surfaces depict the surface morphologies, the surfactant molecules are denoted by the polar head and two tails, the cholesteric axis H is along the "x" axis, the surface normal is k, the surface tangent is t, the normal angle is  $\varphi$ , the  $\lambda$ 's on the top schematics denote wave-lengths, the cholesteric pitch is P<sub>0</sub>, and the compression direction is "x".

Next, we describe the essential elements of the CLC-M model. Liquid crystal orientation at the interface is defined by the director field **n**. We restrict the discussion to homeotropic anchoring (W<0) and a bend and splay director field:  $\mathbf{n}(\mathbf{x}) = (\cos\theta(\mathbf{x}), \sin\theta(\mathbf{x}), 0)$ , where the director angle,  $\theta = 2\pi \mathbf{x} / P_0$  has a domain of  $[0, 2\pi]$ . It should be noted that the presence of a layer of surfactant-like biomolecules can change the preferred surface anchoring, and the director field [33]. The arclength measure of the undulating surface is "s". We assume that the membrane is uniaxially compressed along the x direction (see Figure 4-1). Here we consider a single wave-vector and the amplitude of the vertical undulation is  $\mathbf{h}(\mathbf{x})$ . The unit tangent,  $\mathbf{t}$ , and the unit normal,  $\mathbf{k}$ , to the surface can be expressed with the normal angle,  $\varphi$ :  $\mathbf{t} = (\sin\varphi, -\cos\varphi, 0)$ ,  $\mathbf{k} = (\cos\varphi, \sin\varphi, 0)$ .

### 4.5 Governing equations

The interfacial surface tension  $\gamma$  for the cholesteric-elastic membrane (CLC-M) includes the anchoring energy given by Rapini and Papoular and the Helfrich free energy that describes the elasticity of membranes and surfactant-laden interfaces [34] such that:

$$\gamma = \gamma_{0} + \frac{\mathbf{k}_{c}}{2} \kappa^{2} + \frac{\mathbf{W}}{2} (\mathbf{n} \cdot \mathbf{k})^{2}$$
(4.3)

where  $\kappa$  is the surface curvature. The bulk Frank elastic contribution to the shape equation due to director gradients close to the surface is assumed to be negligible. The relative importance of the bulk elastic contributions compared to anchoring energy can be evaluated by comparing the extrapolation length,  $\ell_e = K / W$ , (K being the Frank elastic constant) and the helix pitch P<sub>0</sub>. For CLC-M with quite strong anchoring and large enough pitch (order of micrometers), the Frank elastic contribution is not significant as the extrapolation length is much less than the helix pitch:  $\ell_e < P_0$ [35].

The generalized Cahn-Hoffman capillary vector [34, 36] is the fundamental quantity that includes the curvature effects and liquid crystal orientation in one single vectorial quantity. The curvature gradient gives rise to the moment tensor, **M**, and the divergence of the moment tensor ( $\nabla_s$ .**M**) contributes to bending stresses. For curved anisotropic interfaces, the bending moment tensor ( $\nabla_s$ .**M**) and the changes in surface tilting ( $\partial \gamma$ (**n**,**k**)/ $\partial$ **k**) must be included into a generalized capillary vector. As the result, the capillary pressure includes the effects of bending ( $\nabla_s^2$ .**M**) and liquid crystal orientation ( $\nabla_s$ ( $\partial \gamma$ (**n**,**k**)/ $\partial$ **k**)) [34]. The generalized capillary vector  $\Xi$  for the elastic anisotropic interface (CLC-M) has two components [34] and in the 1D model considered here it reads:

$$\boldsymbol{\Xi} = \boldsymbol{\Xi}_{\perp} + \boldsymbol{\Xi}_{\parallel}, \quad \boldsymbol{\Xi}_{\perp} = \boldsymbol{\Xi}_{\perp} \boldsymbol{k} = \left( \boldsymbol{\gamma} - \boldsymbol{M} : \boldsymbol{\kappa} \boldsymbol{t} \boldsymbol{t} \right) \boldsymbol{k}, \quad \boldsymbol{\Xi}_{\parallel} = \boldsymbol{\Xi}_{\parallel} \boldsymbol{t} = \left( \boldsymbol{t} \cdot \frac{\partial \boldsymbol{M}}{\partial s} \right) \cdot \boldsymbol{t} \boldsymbol{t} + \boldsymbol{t} \boldsymbol{t} \cdot \frac{d \boldsymbol{\gamma}}{d \boldsymbol{k}}$$
(4.4)

The normal component  $\Xi_{\perp}$  describes the increase in the surface energy through dilation and the tangential component  $\Xi_{\parallel}$  is the change in the surface energy through rotation of the unit normal. Replacing the 1D Rapini-Papoular-Helfrich surface tension (Eq. 4.3) in (Eq. 4.4) yields:

$$\boldsymbol{\Xi}_{\perp} = \left(\gamma_0 + \frac{W}{2} \left(\mathbf{n} \cdot \mathbf{k}\right)^2 - \frac{k_c}{2} \kappa^2\right) \mathbf{k}, \ \boldsymbol{\Xi}_{\parallel} = \left(k_c \frac{\partial \kappa}{\partial s} + W\left((\mathbf{n} \cdot \mathbf{k}) \left(\mathbf{n} \cdot \mathbf{t}\right)\right)\right) \mathbf{t}$$
(4.5)

The shape equation is  $\Delta P = (\nabla_s \cdot \Xi) \equiv \mathbf{t} \cdot \partial \Xi / \partial s$  [34] where  $\Delta P$  represents the pressure difference between the inner and outer sides of the cell membrane and  $\nabla_s$  is the surface gradient. The capillary pressure has two contributions:

$$\mathbf{t} \cdot \frac{\partial \mathbf{\Xi}}{\partial \mathbf{s}} = \frac{\partial \mathbf{\Xi}_{\parallel}}{\partial \mathbf{s}} + \mathbf{\Xi}_{\perp} \boldsymbol{\kappa}$$
(4.6)

For the current case of  $\Delta P=0$ , the condition for which the capillary pressure is zero yields  $\Xi=C$ , where **C** is a constant vector. Considering the general case  $\kappa = \kappa_0$ ,  $\partial \kappa / \partial s = 0$ ,  $\theta=0$ ,  $\varphi=\pi/2$  at s=0, the constant vector is  $\mathbf{C} = (\gamma_0 - (\mathbf{k}_c / 2)\kappa_0^2) \, \boldsymbol{\delta}_x$ . Introducing the compression  $T_0 = (\gamma_0 - (\mathbf{k}_c / 2)\kappa_0^2)$  and replacing the curvature  $\kappa = d\varphi / ds$ , (Eq. 4.6) yields:

$$k_{c} \frac{\partial^{2} \varphi}{\partial s_{2}} + T_{0} \cos \varphi + W(\mathbf{n.k}) (\mathbf{n} \cdot \mathbf{t}) = 0$$
(4.7)

which is the equation of equilibrium for an elastica under a uniaxial compressive force  $T_0$ , and external anchoring force  $W(\mathbf{n.k})(\mathbf{n \cdot t})$ . The limits of  $k_c=0$  and W=0 yield the well-known models for liquid crystals and membranes, respectively. Our physical model for the elastic liquid crystal membrane is given by Eq. 4.7 and the two first order differential equations for the coordinates,  $dx/ds = \sin \phi$  and  $dy/ds = -\cos \phi$ , which have to be solved along with the four boundary conditions: x=0, y=0,  $\phi=\pi/2$ ,  $\kappa=\kappa_0$  at s=0. By scaling Eq. 4.7 with  $T_0$ , and by replacing the director field  $\mathbf{n}$  as per above we find the origin of Eq. 4.1 and Eq. 4.2. The model output is the height function h (x,  $\omega, \bar{w}$ ). Considering the infinite length of the membrane with all the boundary conditions applied at one point (s=0) is identical with an initial-value problem.  $\gamma_0$  is the Lagrange multiplier corresponding to the constraint of inextensibility of the membrane [17]. Here we consider local wrinkling in a membrane with infinite length [37]. We are dealing with a quite strong anchoring [13, 14],  $W \simeq -5 \times 10^{-5} \text{ J/m}^2$ , and a relatively small value of the bending elasticity,  $k_c \simeq 5 \times 10^{-18} \text{J}$ , which gives a micron-range bending/anchoring length,  $\ell_{b/a} = \sqrt{k_c/|W|} = 0.32 \mu$ .

## 4.6 Morphological phase diagram of the surface patterns for a helicoidal plywood

To include the limiting models (CLC, M), we present in Figure 4-2 the general morphological phase diagram of the surface patterns for a helicoidal plywood with a constant pitch,  $P_0=1.2 \mu m$  in the ternary parametric space (k<sub>c</sub>, W,  $\gamma_0$ ). The fundamental surface shapes at the corners of the triangle are: crease (top) with zero bending (CLC model), flat (lower right) with zero bending and

zero anchoring, and fold (lower left) with zero anchoring (M model). In the triangle's interior (CLC-M model), the LC anisotropy competes with the bending elasticity, creating a range of complex surface patterns. In the interior, we can identify two main surface patterns: single wavelength and multiple wavelengths. The first is located at the limiting cases of zero anchoring/zero bending elasticity. In the absence of anchoring (the base of the triangle), the pattern corresponds to the classical compression-induced buckling of an elastic membrane [17]. In the absence of bending elasticity (the right side of the triangle), the chirality-driven surface wrinkling is a single-wavelength periodic profile whose amplitude increases linearly with  $W / \gamma_0$  [12]. The multiple wavelengths pattern is observed in the regions where both bending elasticity and liquid crystal anisotropy are present. With the increase of anchoring, the surface profiles gradually change into profiles with high wavenumbers, resembling the experimentally observed multi-scale surface modulation found in the petals of the "Queen of the Night" tulip [20]. These surface patterns also reflect the two-wavelength periodic wrinkling experimentally observed at the free surface of cellulosic cholesteric liquid crystal films [10]. The wrinkling of short wavelength,  $\lambda_2 \simeq 0.8 \mu$ m, are superimposed on longer waves of length  $\lambda_1 \simeq 3.5 \mu$ m. The helix pitch and the anisotropic elastic constants of the cellulosic CLC film were suggested as the main parameters responsible for the short wavelength patterns, observed experimentally [10].

An increase of the bending elasticity  $k_c$ , increases the periodicity of the smoother wrinkles and leads to the lower wavenumber. The greater the value of  $k_c$ , the greater are the amplitudes of the wrinkles. The amplitude, h, can vary from few nanometers to few microns depending on the combination of the system parameters;  $k_c$ ,  $P_0$  and W. At higher bending elasticity ( $k_c \approx 10^{-18}$ J), folding may appear. In partial summary, if the effect of the bending elasticity is predominant, the profile is a fold. If the effect of anchoring is predominant, the profile is a crease, which mostly occurs at the surface of soft materials without hard skins [24]. When both effects are comparable, the surface exhibits multiple periodic wrinkles, as illustrated in Figure 4-2(b).



**Figure 4-2.** (a) The ternary phase diagram of wrinkling morphologies. (b) Pattern selection depending on anchoring strength W and bending elasticity kc. The folding appears at weak anchoring and high bending elasticity and the creasing occurs at strong anchoring and low bending elasticity. The multiple wavelengths pattern is observed where both bending elasticity and anchoring strength are comparable. MWW denotes multiple wavelength wrinkling.

#### 4.7 Pendulum analogy of the chiral elastic membrane

In this section, we show that the anchoring/bending/chiral model can be gainfully compared with a periodic forced pendulum, where the angular velocity of the pendulum is identical to the curvature  $\kappa$  of the elastic membrane. The natural frequency of the pendulum corresponds to the membrane wavenumber,  $2\pi \sqrt{|T_0|/k_c}$  and the frequency of the external force corresponds to director wave-vector q<sub>0</sub>. We first discuss linearized surface patterns in terms of length scales (P<sub>0</sub>,  $\ell_{mem}$ ) and anchoring ( $\overline{W}$ ) and then describe the general case in terms of ( $\omega, \overline{W}$ ). In the pure membrane and anchoring models, the normal angle can be expressed by a single sinusoid:  $\phi_a(s) = a_1 \overline{W} p_0 \sin(\frac{2\pi s}{p_0}), \phi_b(s) = a_2 \ell_{mem} \sin(2\pi s / \ell_{mem})$ , respectively. In each of those two cases the

system acts as a simple pendulum, with one degree of freedom (single frequency). In the presence of both surfactants and liquid crystals, the system acts as a periodically perturbed pendulum. In the presence of both anchoring and elasticity, for small amplitudes of the surface undulations, the normal angle can now be described by a linear combination of two sinusoids:  $\varphi(s) = P_0(a_1 \overline{W} \sin(2\pi s / P_0) + (a_2 / \omega) \sin(\omega s / P_0))$ . This linear approach valid for quite weak anchoring  $(|\bar{W}| < 0.1)$  yields the normal angle,  $\varphi$ , of periodic wrinkles as linear combination of two sinusoids with wave-lengths scales (P<sub>0</sub>, P<sub>0</sub>/ $\omega$ ) and amplitudes ( $a_1 \overline{W} P_{\alpha}$ ,  $a_2 P_{\alpha} / \omega$ ), where  $a_1=0.42$ , and  $a_2=0.99$ . Since the amplitude ratio of the two modes scales with  $\omega, \overline{W}$  we find that the dimensionless numbers that control the surface relief are:  $h=h(x, \overline{W}, \omega)$ . Furthermore, strong h-amplitude modulation will be found for  $\omega \approx o(1)$  and two-scale servated sinusoidal surfaces when  $\omega >> o(1)$ . The system can be completely described in the 3D toroidal phase ( $\phi$ ,  $\kappa$ ,  $\theta$ ) space, where  $\phi$ corresponds to the state of the pendulum,  $\kappa$  to the angular velocity, and  $\theta$  to time. Also, the trajectories in 2D phase space ( $\phi, \kappa$ ) are identical with the pendulum limit cycles. For two different values of the helix pitch, Figure 4-3 (a) and Figure 4-3 (c) illustrate the surface profiles corresponding to the pure elastic membrane (M) model (no anchoring, no chirality), the anchoring/chiral (CLC) model, the anchoring/bending/chiral (CLC-M) model, and the estimated profile that is obtained by using the linear combination of the two sinusoids; the latter shows a very good agreement with the complete CLC-M model. For the elastic membrane model and the CLC model, the phase space is a closed curve, resembling an ellipse. In the presence of both elasticity and LC chirality, the phase space ellipse gets distorted. As illustrated in Figure 4-3(b) and Figure 4-3(d), for particular values of the helix pitch ( $P_0=1.98 \& 0.79 \mu m$ ), the ellipse splits into five and two cycles respectively. The dynamic analogy clearly shows that the surface pattern selection depends on the system winding number  $\omega$ , or ratio between the number of times the trajectory rotates around the small cross section, and the large circumference of a torus.



**Figure 4-3.** Periodic surface profiles (a, c) and corresponding limit cycles (b, d) for the pure membrane (M), the pure CLC, and the elastic LC (CLC-M) models with W=-10<sup>-4</sup>J/m<sup>2</sup>,  $k_c=5\times10^{-18}$ J,  $T_0=-5\times10^{-3}$ J/m<sup>2</sup> (a, b) P\_0=1.98µm,  $\omega=10$  (c,d) P\_0= 0.79 µm,  $\omega=4$ . h is the amplitude of the surface wrinkles. The knots above the limits cycles show the 3D ( $\varphi$ ,  $\kappa$ ,  $\theta$ ) phase portraits of the system.

The 3D parametric curves  $(\kappa - \varphi - \theta)$  are the torus knots that illustrate the winding number dependence of the surface topographies (Figure 4-4) when  $\bar{w} = 0.2$ . For winding numbers,  $\omega = 2/3$ and 3/2, the torus knots are the well-known trefoil knots and the  $(\varphi - \theta)$  projections of the knots are the well-known Lissajous curves whose length depends on the length scales  $\bar{W}p_0$  and  $\ell_{mem}$ , and the ratio of the tangential and vertical lobes indicate the rotation number (Figure 4-4 (b and h)). The curves represent the trajectories of the commensurate anisotropic harmonic pendulum on a torus. When both wavenumbers are equal,  $\omega=1$ , the projection is a geodesic digon. The beating pattern is formed due to the interference of two sinusoids with slightly different wavenumbers (see Figure 4-4 (k)). The polar projections of the 3D curves are analogous to the rose curves which are strongly dependent on the winding number,  $\omega$  (Figure 4-4 (c, f, and i). If  $\omega$  is a half-integer, the curve is rose-shaped with 4 $\omega$  petals ( $\omega=3/2$ ) and if  $\omega$  can be expressed as n/3, the curve will be rose-shaped with 2n petals if n is even ( $\omega=2/3$ ). When  $\omega$  is odd, the entire graph of the rose will be traced out exactly once, when the value of the director angle,  $\theta$  changes from 0 to  $\pi$  ( $\omega=1$ ). At this level of anchoring, we observe sensitive amplitude h(x) modulation with changes in  $\omega$  around unity.



**Figure 4-4.** 3D torus knots, its projections on the  $\varphi$ - $\theta$ , polar  $\theta$ - $\kappa$  planes, and corresponding surface profiles for the structure with  $\bar{w} = 0.2$  and  $\omega = 2/3$  (a, b, c, j),  $\omega = 1$  (d, e, f, k), and  $\omega = 3/2$  (g, h, i, l). The polar  $\theta$ - $\kappa$  planes, typically a cycloid, with the bending wave number (q<sub>b</sub>) and the LC wave number (q<sub>0</sub>). For  $\omega < 1$ , the inward winding occurs, whereas for  $\omega > 1$  outward winding appears. For  $\omega \approx o(1)$  strong h-profile amplitude modulation is shown.

Figure 4-5(a) is a phase diagram in terms of pitch  $P_0$  and bending constant  $k_c$ , and illustrates the boundary lines in which a CLC-M has an integer winding number  $\omega$ ; the actual multiscale periodic surface profile is shown on the bottom right. If the winding number is not an integer, the LC elastic membrane has a periodic profile but the wrinkles are not perfectly periodic (quasiperiodic). The inset clearly shows the geometric impact of increasing  $\omega$  and confirms the relation between number of peaks and P<sub>0</sub>/2; for  $\omega$ =3 we have 3 peaks per P<sub>0</sub>/2 and when  $\omega$ =6 we find 6 peaks per P<sub>0</sub>/2. Hence the model clearly captures the mechanism of multiple wrinkling scales as a function of the magnitude of  $\omega = P_0 / \sqrt{k_c / |T_0|}$ . As described above, the surface patterns can be characterized by  $\omega$  and  $\overline{W}$ , and the wrinkling mode can be well characterized by limit cycles. The morphological transitions of the surface patterns are depicted in Figure 4-5 (b) with respect to the anchoring constant ( $\overline{W}$ ). When the cholesteric pitch becomes short (compared to the elasticity length scale), or the anchoring strength is insignificant, the system changes to an essentially unperturbed system, thus resulting in single-wavelength periodic patterns (limit cycle is an ellipse). As the anchoring strength tends to increase, the limit cycles expand, the number of rotations decreases, and the surface structures transform into single wavelength patterns. For small winding numbers, an increase in the anchoring may result in spatial quasi-periodicity and onset of chaotic patterns  $(\omega=4)$ . The reason why for  $\omega=3$  the quasi-periodic pattern is not formed is attributed to the oddeven effects described above. Not surprisingly, for weak anchoring the effect of nonlinearity is negligible and the limit cycles represent the system winding number. However, as we increase the anchoring  $\overline{W}$ , the nonlinearity gradually increases, thereby triggering period doubling, period tripling and other unique solutions that no longer represent the system winding number. If we increase the anchoring further ( $|\bar{W}| > 0.1$ ), nonlinear buckling (chaotic spatial patterns) can appear.



**Figure 4-5.** Limit cycle phase diagram (a) showing the system boundaries in which the integer winding number assumes values:  $\omega=3, 4, 5, 6$ . (b) Surface morphologies depending on the winding number  $\omega$  and the anchoring constant  $\overline{W}$ . The periodic patterns on the top of the limit cycles represent the surface membrane profile.

We validate our model with the two-scale surface pattern of the Queen of the Night tulip [20] in Figure 4-6, where for this specimen the amplitudes are:  $h_1=1 \ \mu m$ ,  $h_2=0.1 \ \mu m$ , and corresponding wave-lengths are  $\lambda_1=29 \ \mu m$ , and  $\lambda_2=1.2 \ \mu m$ . The corresponding model parameters are:  $W=-7 \times 10^{-5} \ J/m^2$ ,  $P_0=58 \ \mu m$ ,  $k_c=1.2 \times 10^{-17} \ J$ ,  $T_0=-3 \times 10^{-4} \ J/m^2$ ,  $\omega=46$ ,  $\overline{W}=0.23$ ; the origin of the

relatively large pitch can be rationalized by a pitch dilation process during the self-assembly precursor stage [4]. A relatively large pitch value can also be generated by chemical doping [38, 39]. The high rotation number  $\omega$ =46 and sufficiently low dimensionless anchoring  $\overline{W}$  yield a serrated sinusoidal surface profile, which is responsible for the tulip iridescence [35].



**Figure 4-6.** Model validation with 2-scales surface patterns of the queen of the night tulip [20] with permission from Science. Copyright 2009 AAAS.

### **4.8 Conclusions**

This chapter has analyzed the surface pattern formation in elastic LC membranes. We showed that the capillary shape equation provides a comprehensive quantitative description of surface pattern formation in biological and synthetic liquid crystal membranes. Through the combination of elasticity and orientation gradients, we elucidate a natural setting for the creation and control of complex surface patterns. Furthermore, the morphology phase diagrams allow us to determine what characteristic pattern will appear on the surface based on the interaction of the three primitive shapes (folding, creasing, and flat). The observation of similar patterns in biological membranes can now be understood in terms of liquid crystal anisotropy and we can conclude that the numerous surface patterns observed in living tissues might be formed through LC anisotropy. Design and fabrication of surface textures in ordered media is fundamental to the development of advanced multi-functional materials such as biosensors and actuators. These results can also provide promising techniques to fabricating surface patterns on soft thin film by means of surface anisotropy.

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# Chapter 5

# 5 Cylindrical Shapes of Nematic Liquid Crystal Membranes: A Model for 2D Anisotropic Biological Cells

### 5.1 Preface

In the previous chapter, the formation of complex surface patterns in planar biological materials was investigated. A comprehensive morphological phase diagram of the surface patterns for a helicoidal plywood was presented. In this chapter, the governing elasto-capillarity equations are extended to analyze the surface morphologies in cylindrical nematic liquid crystal elastic membranes. This study explores the formation of complex top-bottom asymmetric topographies in biological membranes in terms of liquid crystal anisotropy. This chapter is produced from a paper, currently in preparation, with the title "Morphology of closed neamtic liquid crystal membranes" and co-authored with Prof. Damiano Pasini and Prof. Alejandro. D. Rey.

### 5.2 Summary

Liquid crystalline phases found in many biological materials, such as actin, DNA, cellulose, and collagen can be responsible for the deformation of cell membranes. In this chapter, cell membrane deformation is investigated through the coupling between liquid crystal anisotropy and membrane bending elasticity. The generalized shape equation for anisotropic interfaces, which resort to the Cahn-Hoffman capillarity vector, the Rapini-Papoular anchoring energy, and the Helfrich elastic energy, is applied to gain insight into the deformation of closed liquid crystal membranes. This study presents a general morphological phase diagram of membrane surface patterns, in which two characteristic regimes of membrane shapes can be classified with respect to the most dominant factor between liquid crystal anisotropy and bending elasticity. The presented results indicate that, depending on the bending elasticity of the cell membrane, the liquid crystal might be able to deform the cell, thereby resulting in anisotropic asymmetric shapes. As liquid crystal anisotropy dominates the bending elasticity, spindle-like or tactoid shapes, which are extensively observed in experiments, can be formed. The findings provide a foundational framework to better understand membrane topologies in living soft matters. Furthermore, the coupling between order and curvature of membranes shed new light into the design of novel functional soft materials.

### **5.3 Introduction**

Biological membranes contain an oriented bilayer of phospholipids, the basic structure of all cell membranes, such that the hydrophobic tails face each other and the hydrophilic phosphate heads

the aqueous phase [1]. Although cell membranes including a set of proteins, phospholipids, and cholesterols, are complex structures, they all share the basic membrane structure. Despite their simple configuration, biological membranes generally show a wide variety of complex topographies and morphological instabilities, such as discocyte, stomatocytes, and echinocyte shapes observed in red blood cells [2, 3]. Shape variations in red blood cells, known as poikilocytosis, can be correlated to pathological conditions and can be used in clinical diagnosis of diseases, such as trauma, infections, and cancer [4, 5]. Moreover, the rich set of surface patterns formed in biological membranes can inspire the design and fabrication of biomimetic materials with novel functionalities [6, 7].

To elucidate the morphological variety of biological membranes, several theoretical studies were undertaken with the goal of minimizing membrane-bending energy subjected to area and volume constraints (Helfrich model, also known as the spontaneous curvature model) [8-12]. Although Helfrich models can well capture numerous cell membrane morphological deformations, they fail to reproduce membrane shapes that are asymmetric, such as the echinocyte [5]. While the area difference elastic models (ADE), which minimize the energy associated with the area difference between the inner and outer leaflet of the membrane, can represent the top-bottom asymmetric [13, 14]. Further, numerical simulations such coarse-grained molecular dynamics (CGMD)[15, 16], spherical harmonics parameterization (SHP)[17], and dissipative particle dynamics [18] were proposed to provide a detailed description of pattern formation occurring in both symmetric and asymmetric deformation. Although significant progress has been made in formulating theoretical and numerical models that attempt to explore the complex surface morphologies in biological closed membranes, previous studies have been restricted to bilayer elastic models. There are few studies that consider other chemical and biological mechanisms (such as the presence of multiple components or in-plane orders) contributing to the formation of top-bottom asymmetric membrane shapes [19-22].

As the lipid bilayers exhibit long range ordering [23], they might be regarded as liquid crystals. Furthermore, liquid crystalline phase and topological defects are found in numerous biological materials, such as DNA [24], cellulose [25], chitin [26], and collagen [27]. Liquid crystallinity not only is governed most physical aspects of biological morphogenesis, but it also contributes in the detailed organization of cells and living tissues [28]. A cell membrane can exhibit anisotropic behavior due to lipid tilt, lipid rotation, and chirality [29] or due to external macromolecules like

proteins [30]. Liquid crystallinity of actin or tubulin polymer networks can also contribute in controlling shape deformation in biological cells [31]. Besides, the morphological patterns of some lyotropic liquid crystal droplets closely resemble the geometries and symmetries of living tissues and cell membranes [32]. It is shown that spontaneous assembly of phospholipids at the interface between liquid crystals and aqueous phases results in dynamic spatial patterns typical of phospholipids [33],[34]. Another example of coupling between membrane elasticity and liquid crystal anisotropy responsible for the generation of complex surface morphologies, occurs in giant unilamellar vesicles (GUVs) suspended in a liquid crystal [35, 36]. Moreover, the threedimensional architectures of some liquid crystal colloids closely resemble the geometries and symmetries of living tissues and cell membranes [20], such as starfish morphology, an instance that confirms the analogy that can be drawn between liquid crystal anisotropy and amphiphilic surfactants [37]. Polymersomes can also exhibit a large variety of morphologies that can be controlled by copolymer composition and subsequently respond to chemical or physical stimuli such as pH, osmotic pressure, and temperature [38, 39]. This chapter presents a systematic modeling approach to derive the equations coupling topology, elastic free energy, and anchoring conditions that can be used in analyzing the surface morphologies observed in elastic anisotropic drops such as liposomes or phospholipid bilayer, surfactant-coated nematic liquid crystal droplet or liquid-crystalline lipid monolayers, and polymersomes (see Figure 5-1).

Several theoretical and experimental studies have been presented to model the coupling mechanism between the orientational order, topological defects, and the curvature in spherical vesicles [32, 40-42]. The presented theoretical studies illustrate the deformation of an isotropic droplet immersed in a liquid crystal phase [41] and the inverse problem, the deformation of a nematic liquid crystal droplet within an isotropic phase [42]. Recent studies have also explored the deformation of lyotropic chromonic liquid crystal (LCLC) drops [43] and active nematics [44]. For spherical nematic droplets, curvature generally drives formation of topological defects and disclinations, and correspondingly, defects and disclinations change curvature [36]. But, the nematic droplets do not necessarily have a distorted director field. If the droplet size is sufficiently small, the director field would be homogenous and the droplet would be defect free, while large nematic droplets favor the formation of topological defects. The type of surface anchoring may result in the formation of either a hedgehog point defect in the center [45], or a pair of surface point defects at the poles of the droplet known as boojums [46]. The results show that the shape of

nematic liquid crystal droplet is typically an ellipsoid in which the major axis of the shape lies along the director orientation [47]. The spindle-shaped droplet or tactoid have also been observed in suspensions where both isotropic and nematic phases exist [35, 41, 42].



**Figure 5-1.** Schematic of possible elastic anisotropic drops. (a) Liposome, (b) Surfactant-coated nematic liquid crystal droplet, and (c) Polymersome.

Significant progress has been made in developing theoretical models that couple the orientational order and curvature for anisotropic elastic interfaces [48-57]. In the previous chapter, it is shown that when the liquid crystal anisotropy and bending effects are comparable, the planar anisotropic interface may show a rich variety of multi-scale complex patterns, such as spatial period-doubling, period-tripling, and quasi-periodicity [56]. In this chapter, we seek to characterize the shape deformation of closed liquid crystal membranes through the interaction of anisotropic interfacial tension, bending elasticity, and capillarity at free surfaces. We theoretically consider a nematic liquid crystal droplet immersed in a passive isotropic phase in the presence of an interfacial layer of surfactants, which leads to an additional elastic contribution to the free energy of the system. The aim of this work is to develop an exclusive physical model based on the integration of the Cahn-Hoffman capillarity vector developed for liquid crystals [50], the classical Rapini-Papoular anchoring energy [58] for liquid crystals, and the Helfrich membrane energy [59]. We only consider 2D drops, with a constant director field in its interior and with a surface that displays bending elasticity and anisotropic surface tension; the outer phase is inert. Of particular interest here is to study the role of liquid crystal anisotropy in complex surface pattern formation.

Understanding the mechanisms through which biological membranes exhibit specific morphologies can be used as an illustration of "bio-inspiration" for the design of novel devices such as sensors.

The specific objectives of this chapter are: (a) to derive and solve a nemato-capillary shape equation that describes the surface deformation of an elastic liquid crystal membrane; (b) to characterize the possible deformation modes and investigate the effect of the system physical parameters on the surface morphologies; (c) to characterize the role of membrane elasticity and anisotropic surface tension on the surface deformation mode; and (d) to elucidate the mechanisms that drive surface deformations.

The organization of this chapter is as follows. Section 5.4 introduces the material model system, the different contributions to the free energy, and the governing nemato-capillary shape equation expressing the coupling mechanism between the surface geometry and director field in rectangular (x,y,z) coordinates. In this section, we assume a nematic liquid crystal membrane with quite weak homeotropic anchoring where the radius of the membrane is always significantly less than the extrapolation length scale, resulting in homogenous director field. Section 5.5 presents a phase diagram of liquid crystal membrane configurations as a function of the scaled pressure jump and the scaled LC anchoring, the effect of model parameters on the membrane shape. At the end of this section, a general morphological phase diagram of the surface patterns for the closed LC elastic membrane in the ternary parametric space (bending elasticity, anchoring, surface tension) is illustrated, which allows us to select the membrane shape that results from the interaction of the three primitive shapes (folded-shape, spindle-like, and ellipse). In section 5.6, we present the capillary pressures associated with the bending-anchoring morphological instabilities. Section 5.7 presents the conclusions.

### **5.4 Theory and governing equations**

In this section, we first present the material model system and the basic concepts of the membrane geometry. Then, we introduce the governing nemato-capillary equations based on the widely used Cahn-Hoffman formalism [44] of capillarity for anisotropic closed membranes expressing the coupling mechanism between the surface geometry, membrane bending elasticity, and liquid crystal director field.

### 5.4.1 Geometry and structure

The 2D shape of an elastic liquid crystal cell membrane can be characterized by a membrane profile with respect to reference coordinates "x-y" (Figure 5-2). For membranes with circular

cross-section, the curvature is constant through the surface and equals to R/2, where R is the radius of the membrane. As the membrane deviates from that of a circle, the curvature varies around the circumference and is a function of the polar angle. In this work, the turning angle of the normal vector **k** is used as a single scalar function  $\varphi(s)$  to characterize the membrane profile in the x-y coordinates. s is the surface arc-length and L is the total system length. Knowing  $\varphi(s)$ , the membrane profile can be obtained by the integrals:  $y = \int_0^L \cos \varphi \, ds$  and  $x = \int_0^L \sin \varphi \, ds$ .



**Figure 5-2.** Schematic of a 2D nematic liquid crystal membrane. The rods denote the nematic director field. The director field is along the vertical "y" axis, the surface normal is **k**, the surface tangent is **t**, the normal angle is  $\varphi$ , and the total membrane length is L. W denotes the liquid crystal anchoring strength, k<sub>c</sub> denotes the surface bending elasticity, and  $\Delta p=p_{out}-p_{in}$  represents the pressure jump across the membrane. Note that the director field is constant everywhere and for this condition to exists the radius of the membrane is much less than the extrapolation length, K/W.

The curvature is defined as the derivative of the normal angle:  $\kappa = \frac{d\varphi}{ds}$ . The area of the plane curve, A, can be computed as:  $A = \int_0^L x \cos \varphi \, ds$ . The unit tangent **t** and the unit normal **k** to the surface can be parametrized with the normal angle,  $\mathbf{t}(\mathbf{x}) = (\sin \varphi(\mathbf{x}), -\cos \varphi(\mathbf{x})), \mathbf{k}(\mathbf{x}) = (\cos \varphi(\mathbf{x}), \sin \varphi(\mathbf{x}))$ . The nematic liquid crystal orientation is defined by the director field **n**: **n** =  $(\cos \theta, \sin \theta)$ . The preferred orientation or easy axis at the interface can be parallel to the unit normal **k** (homeotropic) or perpendicular to the unit normal **k** (planar). It should be noted that the presence of surfactant-like biomolecules or phospholipids can change the preferred surface

anchoring, and the director field [60]. For nematic liquid crystals immersed in aqueous surfactant solutions, it is shown that the anchoring type can depend on the surfactant's concentration, and increasing the surfactant concentration can lead to adsorption-driven orientational transition [61]. In this study, and without loss of physical phenomena, we restrict the discussion only to homeotropic anchoring (W<0). To determine a closed surface profile for the membrane, a number of constraints must be imposed. Firstly, the membrane length L must satisfy the periodicity condition: x(0)=x(L) and y(0)=y(L). The smoothness of surface profile implies that  $\kappa(0) = \kappa$  (L) =  $\kappa_0$ . As the arc-length varies from 0 to L, the normal angle rotates from 0 to  $2\pi$  indicating that there exists an integer *m* such that:  $\oint k \, ds = 2m\pi$ .

# **5.4.2 Governing equations**

The shape deformation of a liquid crystal (LC) membrane is a complex multiple-coupling problem that includes anisotropic surface tension, membrane bending elasticity, and Frank bulk elasticity [62,63]. To explore the shape selection of a liquid crystal membrane, the total system energy including the surface energy and the bulk Frank elastic energy should be minimized. However, the analytical solution of the problem with the usual formalism is very complicated. In this study, the bulk Frank elastic contribution to the shape equation is assumed to be negligible. The relative importance of the bulk elastic contributions compared to the anchoring energy can be evaluated by comparing the extrapolation length, le=K/W, (K being the Frank elastic constant) and the liquid crystal membrane radius, R. For a liquid crystal membrane with quite weak anchoring and small enough radius (R  $\leq l_e$ ) the Frank elastic contribution is not significant as it scales as R, whereas the surface energy scale as  $R^2$ . Consequently, the elastic energy dominates over the anchoring energy for small membranes, and we can assume that the director field is undistorted and homogenous [41]. The typical size of biological membranes is about 1µ [8]. Taking typical values of Frank elastic constant for nematic liquid crystals (K  $\approx 10^{-12}$  -10<sup>-11</sup> N)[64], the extrapolation length scale  $l_e$  is in the range of few micrometers ( $l_e \approx 10 \mu m$ ). Thus, to neglect the contribution of the elastic distortion, we should set the size constraint on the membrane (R < 10 $\mu$ m). In this study, we are dealing with a quite weak anchoring, W $\simeq 10^{-6}$  J/m<sup>2</sup> [65], and a relatively small value of the bending elasticity,  $k_c \simeq 10^{-21} \cdot 10^{-18} J$  [66], typical values for biological membranes, which gives a micron-range bending/anchoring length. We assume that the interfacial surface tension is  $\gamma_0 = 10^{-7} - 10^{-5}$  Nm<sup>-1</sup> [8], and the pressure jump across the membrane is  $\Delta p \simeq 10^{-3} - 10^{-1}$  atm [67].

Several theoretical models incorporating Helfrich membrane energy were formulated to investigate the shape deformation of biological membranes and constrained soft materials [10, 11, 66, 68]. In this section, we develop a physical model of a nematic liquid crystal membrane where the coupling mechanism between surface geometry and liquid crystal order is presented through the shape equation that resorts to the vector formalism of Cahn-Hoffman capillarity [69]. The presented liquid crystal Laplace–Helfrich shape equation can be employed to predict shape of isotropic droplet embedded in a nematic liquid crystal phase or shape of nematic liquid crystal embedded in an isotropic phase.

### 5.4.2.1 Cahn-Hoffman capillarity vector

The generalized Cahn-Hoffman capillary vector  $\boldsymbol{\xi}$  [69] is the fundamental quantity that includes the curvature effects and liquid crystal orientation in one single vectorial quantity. The orientationdependent surface energy can be specified by the unit vector or director  $\mathbf{n}=\mathbf{n}(\mathbf{r})$  field, the surface position vector  $\mathbf{r}=\mathbf{r}\mathbf{k}$ , and the surface unit normal  $\mathbf{k}$ . Cahn and Hoffman defined the nematic capillarity by the gradient of the scalar field  $r\gamma$ :

$$\boldsymbol{\xi}(\mathbf{n},\mathbf{k}) = \nabla[r\gamma(\mathbf{n},\mathbf{k})] \tag{5.1}$$

For isotropic interfaces, the capillary vector,  $\xi$  reduces to a normal vector  $\xi = \gamma \mathbf{k}$ . The decomposition of the surface director field into normal and tangential components yields  $\mathbf{n}_{\perp} = \mathbf{k}\mathbf{k}$ .  $\mathbf{n}$  and  $\mathbf{n}_{\parallel} = \mathbf{I}_{s}$ .  $\mathbf{n}$ , where  $\mathbf{I}_{s}$  is the 2×2 unit surface dyadic  $\mathbf{I}_{s}=\mathbf{I}-\mathbf{k}\mathbf{k}$ , and  $\mathbf{I}$  is the 3×3 unit tensor. Calculating the gradient of the field r $\gamma$  appearing in Eq. 5.1, using  $\xi \mathbf{k} = \gamma(\mathbf{n}, \mathbf{k})$ ,  $\xi d\mathbf{k} = d\gamma(\mathbf{n}, \mathbf{k})$ , and  $d(r\gamma) = \nabla(r\gamma) d\mathbf{r}$  gives:

$$\boldsymbol{\xi}(\mathbf{n},\mathbf{k}) = \gamma \frac{\partial r}{\partial \mathbf{r}} + r \frac{\partial \gamma}{\partial \mathbf{r}} = \gamma \mathbf{k} + I_s \cdot \frac{\partial \gamma}{\partial \mathbf{k}}$$

$$\boldsymbol{\xi}_{\perp} \qquad \qquad \boldsymbol{\xi}_{\perp} \qquad \qquad \boldsymbol{\xi}_{$$

where the normal component  $\xi_{\perp}$  describes the increase in the surface energy through dilation and the tangential component  $\xi_{\parallel}$  is the change in the surface energy through rotation of the unit normal. The surface energy that includes anchoring energy given by Rapini and Papoular [58] and the Helfrich free energy [59] can be used to derive the Cahn-Hoffman capillary vector  $\xi$  for a composite nematic liquid crystal membrane:

$$\gamma = \gamma_0 + \overline{k_c} K + 2k_c (H - H_0)^2 + \frac{1}{2} W(\mathbf{n.k})^2$$
(5.3)

where  $\gamma_0$  is the isotropic surface tension,  $k_c$  is the membrane bending elastic moduli, H is the membrane surface curvature, H<sub>0</sub> is the spontaneous curvature of the membrane,  $\overline{k_c}$  is the torsion elastic moduli of the membrane, and K is Gaussian curvature; based on the Gauss–Bonnet theorem [70] for closed membranes without edges the integral over the Gaussian curvature K is a topological invariant and it can be ignored [12]. The term  $W(\mathbf{n.k})^2/2$  represents the anisotropic anchoring energy contribution due to the director field deviations from the preferred "easy axis", and W is the surface anchoring strength. If W>0, the easy axis or preferred orientation is tangential to the interface (planar), and if W<0 the easy axis is normal to the interface (homeotropic anchoring). When the director field deviates from the preferred orientation, the deviation causes gradients in surface tension, and may generate the orientational-driven tangential Marangoni elastic forces and as well as normal forces [71, 72]. In this study, this Marangoni effect is neglected.

Substituting Eq. 5.3 into Eq. 5.2 yields the normal and tangential components of the capillarity vector:

$$\boldsymbol{\xi}_{\perp}(\mathbf{n},\mathbf{k}) = (\gamma_0 + \frac{W}{2}(\mathbf{n},\mathbf{k})^2) - \frac{k_c}{2}\kappa^2$$

$$\boldsymbol{\xi}_{\parallel}(\mathbf{n},\mathbf{k}) = W((\mathbf{n},\mathbf{k})(\mathbf{n}\cdot\mathbf{t})) + k_c\frac{\partial\kappa}{\partial s}$$
(5.4 a,b)

These equations shows that when  $\mathbf{n.k}=1$ , the surface behaves like an isotropic membrane and that the degree of anisotropy is controlled by  $\mathbf{n.k}$ .

#### 5.4.2.2 Nemato-capillary shape equation

To derive the capillary shape equation required to determine the liquid crystal membrane shape, we use the capillary pressure definition  $\Delta p = -\nabla_s \cdot \xi = -\nabla_s \cdot (\xi_{\perp} + \xi_{\parallel}) = -\mathbf{t} \cdot \frac{\partial \xi}{\partial s}$ , where  $\frac{\partial \xi}{\partial s} = \frac{\partial \xi_{\parallel}}{\partial s}\mathbf{t}$  $+\xi_{\parallel}\kappa\mathbf{k} + \frac{\partial \xi_{\perp}}{\partial s}\mathbf{k} \cdot \xi_{\perp}\kappa\mathbf{t}$  yields:  $\Delta \mathbf{n} = -\mathbf{t} \cdot \frac{\partial \xi}{\partial s} = \xi_{\perp}\kappa_{\perp} - \frac{\partial \xi_{\parallel}}{\partial s}$  (5.5) By substituting the normal  $\xi_{\perp}$  and tangential  $\xi_{\square}$  components of the capillarity vector (Eq. 5.4) we obtain:

$$\Delta p = \left\{ \left( \gamma_0 + \frac{W}{2} (\mathbf{n} \cdot \mathbf{k})^2 \right) - \frac{k_c}{2} \kappa^2 \right\} \kappa - \left( k_c \frac{d^2 \kappa}{ds^2} + W(\mathbf{n} \cdot \mathbf{t})^2 \kappa \right)$$

$$-W \left\{ \left( \mathbf{k} \cdot \mathbf{n} \right) \left( \mathbf{t} \cdot \frac{d\mathbf{n}}{ds} \right) + \mathbf{k} \mathbf{n} : \left( \mathbf{t} \frac{d\mathbf{n}}{ds} \right) \right\}$$
(5.6)

In the absence of the liquid crystal order, the contribution from the normal component of the capillary vector  $\xi_{\perp}$  is the classical Laplace pressure, and the contribution from the tangential component of the capillary vector  $\xi_{\parallel}$ , is known as Herring's pressure. For liquid crystal membranes, since the capillary vector is a function of both the director field, **n** and the unit normal **k**, an additional contribution to the capillary pressure arises from director curvature due to orientation gradients. This equation shows that the membrane shape is the result of the balance between the membrane bending elasticity, surface tension, surface anchoring effects, and the pressure jump. Both anchoring term and bending elasticity can drive shape deformation of a nematic liquid crystal membrane. Rearranging Eq. 5.6, we obtain:

$$\frac{d^{2}\kappa}{ds^{2}} = \frac{-1}{2}\kappa^{3} + \frac{\gamma_{0}}{k_{c}}\kappa + \frac{-\Delta p}{k_{c}} + \frac{W}{2k_{c}}\left(\mathbf{n}\cdot\mathbf{k}\right)^{2}\kappa - \frac{W}{k_{c}}\left(\mathbf{n}\cdot\mathbf{t}\right)^{2}\kappa - \frac{W}{k_{c}}\left\{\left(\mathbf{k}\cdot\mathbf{n}\right)\left(\mathbf{t}\cdot\frac{d\mathbf{n}}{ds}\right) + \mathbf{k}\mathbf{n}:\left(\mathbf{t}\frac{d\mathbf{n}}{ds}\right)\right\}$$
(5.7)

For nematic liquid crystal with the fixed director field, the director pressure term,  $W\{(\mathbf{k} \cdot \mathbf{n}) (\mathbf{t} \cdot d\mathbf{n}/ds) + \mathbf{kn} : (\mathbf{t}d\mathbf{n}/ds)\}$  vanishes [73]. Integrating Eq. 5.7 with respect to curvature  $\kappa$ , gives:

$$\frac{1}{2}\left(\frac{d\kappa}{ds}\right)^{2} + \frac{1}{8}\kappa^{4} - \frac{\gamma_{0}}{2k_{c}}\kappa^{2} + \frac{\Delta p}{k_{c}}\kappa - \frac{W}{4k_{c}}\left(\mathbf{n}\cdot\mathbf{k}\right)^{2}\kappa^{2} + \frac{W}{2k_{c}}\left(\mathbf{n}\cdot\mathbf{t}\right)^{2}\kappa^{2}$$
(5.8)

In the absence of liquid crystal order, the integration can be reduced to:

$$\frac{1}{2} \left(\frac{d\kappa}{ds}\right)^2 + \frac{1}{8}\kappa^4 - \frac{\gamma_0}{2k_c}\kappa^2 + \frac{\Delta p}{k_c}\kappa$$
(5.9)

interpreting the quantity s as a time and  $\kappa$  as a position, Eq. 5.9 corresponds to the equation of motion of a particle with unit mass and kinetic energy T, moving in a potential U and whose total energy E is conserved:

$$E = \frac{1}{2} \left(\frac{d\kappa}{ds}\right)^2 + \frac{1}{8}\kappa^4 - \frac{\gamma_0}{2k_c}\kappa^2 + \frac{\Delta p}{k_c}\kappa,$$

$$T(\kappa) = \frac{1}{2} \left(\frac{d\kappa}{ds}\right)^2, U(\kappa) = \frac{1}{8}\kappa^4 - \frac{\gamma_0}{2k_c}\kappa^2 + \frac{\Delta p}{k_c}\kappa$$
(5.10)

The anchoring term in Eq. 5.8 acts as the correction term when the mass of the particle changes with time.

Considering the nematic director field  $\mathbf{n} = (\cos \theta, \sin \theta)$ , surface unit normal  $\mathbf{k}(s) = (\cos \varphi(s), \sin \varphi(s))$ , unit tangent  $\mathbf{t}(s) = (\sin\varphi(s), -\cos\varphi(s))$  and using the definitions:  $\frac{d\mathbf{x}}{ds} = \sin\varphi$ ,  $\frac{d\mathbf{n}}{ds} = \frac{d\mathbf{n}}{dx}\frac{dx}{ds} = \frac{d\mathbf{n}}{dx}\sin\varphi$ ,  $\kappa = \frac{d\varphi}{dx}\sin\varphi$  gives the governing shape equation:  $\frac{d^{3}\varphi}{ds^{3}} = -\frac{1}{2}\left(\frac{d\varphi}{ds}\right)^{3} + \frac{-\Delta p}{k_{c}} + \frac{W}{2k_{c}} (\mathbf{n}\cdot\mathbf{k})^{2}(\frac{d\varphi}{ds}) - \frac{W}{k_{c}} (\mathbf{n}\cdot\mathbf{t})^{2}(\frac{d\varphi}{ds})$ (5.11)

The shape equation is a nonlinear third order ODE for the normal angle  $\varphi$  (s,  $\Delta p$ , k<sub>c</sub>, W,  $\gamma_0$ ). In the absence of liquid crystal anisotropy, the Eq. 5.11 becomes the classical Euler-Lagrange equation. It represents the interfacial force balance between the surface forces and the bulk force,  $\Delta p \mathbf{k}$  due to the pressure jump across the membrane. The interfacial stress tensor  $\mathbf{T}_s$  can be expressed in terms of the capillary vector  $\boldsymbol{\xi}$  [74]:  $\mathbf{T}_s = \boldsymbol{\xi}.\mathbf{D}$  where  $\mathbf{D} = \mathbf{k}\mathbf{I}_s - \mathbf{I}_s\mathbf{k}$  is the geometric tensor that maps the capillary vector into the tangential stress  $\boldsymbol{\xi}_{\perp}\mathbf{I}_s$  and bending stress  $\boldsymbol{\xi}_{\parallel}\mathbf{k}$ . Then, the capillary pressure can be simply presented by:  $\Delta p = (\nabla_s \cdot \mathbf{T}_s).\mathbf{k} = \nabla \cdot \boldsymbol{\xi}$ .

The dot product of the interface stress tensor,  $\mathbf{T}_{s}$  with the unit tangent gives:

$$\mathbf{t} \cdot \mathbf{T}_{s} = \boldsymbol{\xi}_{\perp} \mathbf{t} - \boldsymbol{\xi}_{\parallel} \mathbf{k} \tag{5.12}$$

Besides, the normal vector, **k** can be expressed as an arc-length derivative of a vector field:  $\mathbf{k} = \frac{d}{ds} ((\mathbf{r} \cdot \mathbf{t})\mathbf{k} - (\mathbf{r} \cdot \mathbf{k})\mathbf{t}).$  Therefore, we can obtain:

$$\frac{\partial (\mathbf{t} \cdot \mathbf{T}_{s})}{\partial s} = \frac{\partial}{\partial s} (\boldsymbol{\xi}_{\perp} \mathbf{t} - \boldsymbol{\xi}_{\parallel} \mathbf{k}) = \Delta p \mathbf{k} = \Delta p \frac{d}{ds} ((\mathbf{r} \cdot \mathbf{t}) \mathbf{k} - (\mathbf{r} \cdot \mathbf{k}) \mathbf{t})$$
(5.13)

Thus, the capillary shape equation can be readily found to be:

$$\left(\boldsymbol{\xi}_{\perp}\mathbf{t} - \boldsymbol{\xi}_{\parallel}\mathbf{k}\right) - \Delta \mathbf{Pr} \cdot \left(\mathbf{tk} - \mathbf{kt}\right) = \mathbf{0}$$
(5.14)

Multiplying the Eq. 5.14 by  $(\mathbf{kt} - \mathbf{tk})$  and considering that  $(\mathbf{tk} - \mathbf{kt}) \cdot (\mathbf{kt} - \mathbf{tk}) = tt + kk$  results in:

$$\left(\boldsymbol{\xi}_{\perp}\mathbf{k} + \boldsymbol{\xi}_{\parallel}\mathbf{t}\right) = \left(-\Delta \mathbf{P}\right)\mathbf{r}$$
(5.15)

Substituting the normal and tangential components of the capillary vector, Eq. 5.4, we obtain:

$$\mathbf{r} = \frac{\xi_{\perp} \mathbf{k} + \xi_{\parallel} \mathbf{t}}{\left(-\Delta P\right)},$$

$$\mathbf{r} = \frac{\left(\gamma_{o} + \frac{W}{2} \left(\mathbf{n} \cdot \mathbf{k}\right)^{2} - \frac{k_{c}}{2} \kappa^{2}\right) \mathbf{k}}{\left(-\Delta p\right)} + \frac{\left(k_{c} \frac{\partial \kappa}{\partial s} + W\left((\mathbf{n} \cdot \mathbf{k})\left(\mathbf{n} \cdot \mathbf{t}\right)\right)\right) \mathbf{t}}{\left(-\Delta p\right)}$$
(5.16)

Thus, we can further find a notable polar formulation for computing the local radius of the nematic liquid crystal membrane:

$$\mathbf{r}^{2} = \mathbf{r} \cdot \mathbf{r} = \frac{\boldsymbol{\xi} \cdot \boldsymbol{\xi}}{\left(-\Delta P\right)^{2}},$$

$$\mathbf{r}^{2} = \frac{\left(\gamma_{o} + \frac{W}{2} \left(\mathbf{n} \cdot \mathbf{k}\right)^{2} - \frac{\mathbf{k}_{c}}{2} \kappa^{2}\right)^{2}}{\left(-\Delta P\right)^{2}} + \frac{\left(\mathbf{k}_{c} \frac{\partial \kappa}{\partial s} + W\left((\mathbf{n} \cdot \mathbf{k}) \left(\mathbf{n} \cdot \mathbf{t}\right)\right)\right)^{2}}{\left(-\Delta P\right)^{2}}$$
(5.17)

In the absence of liquid crystal anisotropy (W=0), Eq. 5.17 yields [12]:

$$r^{2} = \frac{k_{c}E + \gamma_{0}^{2}}{\Delta p^{2}} + \frac{2k_{c}k}{\Delta p}$$
(5.18)

Using this equation, we can determine the local radius of the membrane for a known total energy E.

## 5.5 Results and discussion

To investigate the effects of the system physical parameters on the membrane shape and to characterize the morphological surface patterns, the nonlinear differential equation with periodic coefficients is solved using the AUTO software [75]. The reduced area of the membrane, the local curvature of the membrane, and the number of membrane folds are the important outputs of the model. The two significant parameters influencing the membrane morphology are: (i) the scaled

anchoring coefficient,  $W/\gamma_0$  (ii) the bending elasticity number,  $\Delta p R_0^3/k_c$ . The scaled anchoring coefficient  $W/\gamma_0$  is taken to be in the range  $0 < |W/\gamma_0| < 2$ . The bending elasticity number,  $\Delta p R_0^3/k_c$  is taken to be in the range  $0.05 < \Delta p R_0^3/k_c < 50$ .

Table 5-1 lists the system length scales, the dimensionless numbers, and their definitions and physical descriptions, that are captured in the results discussed below.

Name	Symbol	Definition	Physical description
bending elasticity number	α	$\Delta p R_0^3 / k_c$	ratio of the pressure jump and surface bending elasticity
pressure bending number	β	$\gamma_0 R_0^2/k_c$	ratio of the surface tension and surface bending elasticity
anchoring bending number	ω	$WR_0^2/k_c$	ratio of the anchoring and surface bending elasticity
extrapolation length	le	K/W	relative importance of the bulk elasticity to anchoring
pressure bending length	$\ell_{pb}$	$\sqrt[3]{k_c/\Delta p}$	relative importance of the surface bending elasticity to pressure jump
anchoring bending length	$\ell_{ab}$	$\sqrt[2]{k_c/W}$	relative importance of the surface bending elasticity to anchoring
anchoring bending length	τ	$L/\ell_{ab}$	relative strength of the anchoring to the bending elasticity

**Table 5-1.** System dimensionless numbers, their definitions and physical descriptions.

## 5.5.1 Shape selection

To find the shape of a nematic liquid crystal membrane, we first make Eq. 5.11 dimensionless by taking  $\tilde{s} = s/R_0$ ,  $\alpha = \Delta p R_0^3/k_c$  (pressure bending number),  $\beta = \gamma_0 R_0^2/k_c$  (tension bending number),  $\omega = W R_0^2/k_c$  (anchoring bending number), where  $R_0$  is the spontaneous radius of the membrane. We then have:

$$-\frac{d^{3}\varphi}{d\tilde{s}^{3}} = \frac{1}{2} \left(\frac{d\varphi}{d\tilde{s}}\right)^{3} + \alpha - \beta \left(\frac{d\varphi}{d\tilde{s}}\right) - \frac{\omega}{2} (\cos^{2}(\varphi - \theta)) \left(\frac{d\varphi}{d\tilde{s}}\right) + \omega (\sin^{2}(\varphi - \theta)) \left(\frac{d\varphi}{d\tilde{s}}\right)$$
(5.19)

For each solution  $\varphi = \varphi(\tilde{s})$  of Eq. 5.19, there is a certain value of the variable  $\tilde{s}$  at which  $d^2\varphi/d\tilde{s}^2 = 0$ . We choose  $d^2\varphi/d\tilde{s}^2 = 0$  at  $\tilde{s} = 0$ . We also select  $d\varphi/d\tilde{s}|_{\tilde{s}=0} = d\varphi/d\tilde{s}|_{\tilde{s}=L/R_0}$  that gives closed solutions, and  $\varphi|_{s=0} = \frac{\pi}{2}$ , which is consistent with the homeotropic anchoring. Solving Eq. 5.19 with the specified boundary conditions, we can investigate the shape selection of the membrane based on the three dimensionless parameters:  $\alpha$ ,  $\beta$  and  $\omega$ . The spontaneous radius is
fixed to ( $R_0=0.5\mu m$ ) and the remaining system parameters are varied to investigate their effect on the membrane shape selection.

To study the effect of the pressure bending number,  $\alpha$  and the dimensionless anchoring number  $W/\gamma_0 = \omega/\beta$  (ratio of the two-other system dimensionless numbers  $\omega/\beta$ ) on the membrane shapes, the values for  $\gamma_0$ , and  $R_0$  are held fixed. The membrane shape can be characterized by the reduced area  $A_r = 4\pi A/L^2$ , where A is the membrane area and L is the membrane length and the dimensionless bending energy that is scaled by bending energy of the circular configuration,  $E_0$ , with the reduced area ( $A_r=1$ ). Figure 5-3 illustrates the dimensionless bending energy as a function of the reduced area for the n-fold membrane morphologies. For the morphologies shown in the beginning of each line (the left side of the lines), the corresponding scaled anchoring,  $W/\gamma_0$  is zero. Thus, we can note that in the absence of liquid crystal anisotropy as the pressure bending number,  $\alpha$  increases from 0.3 to 7, the membrane shape is transformed from 5-fold (starfish) deformation mode to 2-fold deformation mode (discocyte), which is energetically less expensive than the starfish shape. These membrane shapes can be also obtained by minimizing the Helfrich free energy [10, 12],  $\int_{s} (\gamma_0 + \frac{k_c}{2}\kappa^2) ds + \int_{s} \Delta p dA$ . All the shapes start as a circle for  $A_r = 1$  and transform to the folded modes as A, decreases from 1.

the folded modes as  $A_r$  decreases from 1.

In the presence of liquid crystal order with homeotropic anchoring, rising the dimensionless anchoring number, W/ $\gamma_0$ , results in deformation modes with increased number of folds and higher bending energies. The results show that the anchoring energy can control the surface tension. This demonstrates an analogy between the liquid crystal anisotropy and the surface bending elasticity that can change the interfacial tension and drive the formation of several polymorphic topologies such as starfish membranes. In fact, the anchoring energy can govern the interfacial energy and lessen the energetic cost of creating multi-fold shapes. It should be noted that the shape deformation will only be significant for values of the scaled anchoring coefficient, W/ $\gamma_0 \sim 1$  where the anchoring strength is of the same order, or larger, than the surface tension. For the morphologies shown in the beginning of the each line where the liquid crystal anisotropy is absent, increasing the surface tension,  $\gamma_0$  above a threshold results in the self-intersecting membrane shapes [76]. For instance, the discocyte shape intersects itself when the reduced area A<sub>r</sub> becomes less than 0.3 [68]. As the self-intersecting shapes are physically irrelevant [11], they are not discussed in the present work.



**Figure 5-3.** The scaled bending energy as a function of the reduced area for four different values of the pressure bending dimensionless number  $\alpha$ =0.3, 0.5, 1, and 7. Increasing W/ $\gamma_0$  results in deformation modes with increase the number of folds. The scaled bending energy increases with increasing number of folds. All the drops have a vertical mirror symmetry due to director axis orientation.

Figure 5-4 shows the dimensionless bending energy of the membrane shapes corresponding to the 2-fold, 3-fold, 4-fold, and 5-fold modes, shown in Figure 5-3 as a function of the total dimensionless length:  $L/\ell_{ab}+L/\ell_{pb}$ . The numerical results indicate that the bending energy of the folded membrane with constant surface tension is essentially a linear function of the scaled anchoring bending number,  $\omega L/R_0$  and the scaled pressure bending number,  $\alpha L/R_0$ .



**Figure 5-4.** Scaled bending energy as a function of total dimensionless length shows a linear scaling for the 2-fold, 3- fold, 4- fold, and 5- fold deformation modes.

### 5.5.2 Effect of anchoring

In the presence of the nematic liquid crystal orientation, the surface area might be increased or decreased for the case of homeotropic or planar anchoring, respectively. Then, the excess or lack of the length might buckle the membrane shape. As an example, Figure 5-5 shows the membrane shapes corresponding to the 2-fold, 3-fold, 4-fold, and 5-fold modes in the presence and absence of LC anisotropy. To investigate the effect of the liquid crystal anchoring W on the membrane shapes, for all the deformation modes the value of the surface tension,  $\gamma_0$  is fixed. The break in top-to-bottom symmetry of the shapes occurred in the membranes with the presence of liquid crystal orientation is due to the competition between the bending elasticity of the membrane and the anchoring of the nematic liquid crystals.



**Figure 5-5.** Membrane shapes in the presence and absence of liquid crystal anisotropy. (a) 2-fold symmetry, (b) 3-fold symmetry, (c) 4-fold symmetry, and (d) 5-fold symmetry. The scaled anchoring coefficient is  $W/\gamma_0=1.5$ . The pressure bending number,  $\alpha=\Delta pR_0^{3}/k_c$  and the tension bending number,  $\beta=\gamma_0R_0^{2}/k_c$  equal to ( $\alpha=2.5$ ,  $\beta=1.25$ ), ( $\alpha=0.15$ ,  $\beta=0.075$ ), ( $\alpha=0.08$ ,  $\beta=0.04$ ), and ( $\alpha=0.05$ ,  $\beta=0.025$ ) for figures 4(a) to 4(d), respectively. Adding the liquid crystal anchoring breaks the membrane top-to-bottom symmetry and results in high curvature on the top of the membrane shape.

It should be noted that adding the anchoring effect results in high curvature on the top of the membrane. The figure also illustrates that the 2-fold and 4-fold modes show the effect of greater top-to-bottom asymmetry with adding LC anisotropy. As the number of folds increases, the effect of anchoring in breaking the symmetry becomes insignificant. The reason is that the more folded modes corresponds to the higher bending energies where the anchoring energy has a slight effect on the membrane deformation shape. The 2-fold mode in the presence of the LC order shown in Figure 5-5a is the known stomatocyte shape observed in red blood cell vesicles [14] that could not be obtained using the two-dimensional Helfrich model. So, by combining the two deformation mechanisms, bending and anchoring, in theory it would be possible to obtain the novel top-bottom

asymmetric membrane shapes (Figure 5-5(a-d), dashed lines), which are not possible configurations that can be produced using classical single-layer membrane models.

## 5.5.3 Effect of bending elasticity

To explore the effect of bending elasticity on the membrane shape, we varied the bending number,  $\alpha = \Delta p R_0^3/k_c$  in a broad range from 0.05 to 50. It should be noted that the values for pressure jump  $\Delta p$ , and spontaneous radius  $R_0$  are held fixed while  $k_c$  is varied. This range maps out a wide variety of membrane configurations. As shown in Figure 5-6, a large part of the membrane shapes can be captured by varying a single parameter, the membrane bending elasticity,  $k_c$ . As the bending elasticity decreases, the number of membrane folds reduces and the morphology changes from 5fold to discocyte, ellipsoid, stomatocyte, umbonate, umbilicate, and undulate. In the limit  $k_c \rightarrow 0$ the shape of the membrane adapts to a spindle-like morphology. Table 5-2 lists the standard nomenclature of the membrane morphologies.

Shape	Name
	discocyte
	stomatocyte
	umbonate
	umbilicate
	undulate
	spindle-like shape

Table 5-2. Nomenclature of membrane morphologies.

By decreasing  $k_c$  the ratio of radius of the membrane curvature to the spontaneous radius,  $R/R_0$  which is also representative of the membrane reduced area, and the scaled bending energy decrease until the membrane shape adapts to the ellipsoid. Then, decreasing the bending elasticity further results in fixed reduced area ( $R/R_0$ ) and increased scaled bending energy. Figure 5-6 shows that

two starkly different classes of membrane deformation modes can be characterized: n-fold topographies and 1-fold topographies, respectively, corresponding to the right nearly horizontal branch when the bending energy is dominant and the vertical left branch when both anchoring and bending contribute in buckling the membrane. The curvature of the liquid crystal membranes shown in the left branch can be very well approximated by Airy functions (see Appendix. D). Earlier, boundary layer behavior of nematic liquid crystals in shear flows is analytically approximated in terms of Airy functions [77]. The results show that when both liquid crystal anisotropy and membrane elasticity contribute in the membrane deformation, the anchoring strength promotes shape anisotropy and top-to-bottom asymmetry while the membrane elasticity promotes symmetric shapes. Thus, the complex morphologies (shown in the left vertical branch of Figure 5-6) that emerge in numerous biological membranes can also be explored by another mechanism that couples liquid crystal orientational order and membrane elasticity and be well described by a fundamental function (Airy) of physics.



**Figure 5-6.** Bending energy as a function of the ratio of radius of the membrane curvature to the spontaneous radius for a wide range of bending number  $\alpha$ =0.05-50. The values for pressure jump  $\Delta p$ , and spontaneous radius R<sub>0</sub> are held fixed while k<sub>c</sub> is varied.

To explore the morphological patterns shown in the left vertical branch of Figure 5-6, we present in Figure 5-7 the dimensionless local curvature,  $r/R_0$  (see Eq. 5.17) as a function of the scaled membrane arclength, s/L for six membrane morphologies with the different values of the dimensionless number  $\tau$ . The dimensionless parameter,  $\tau$  is a measure of the relative strength of the liquid crystal anchoring to the bending elasticity. As the liquid crystal anisotropy can compete with the bending elasticity, a range of multiple wavelengths pattern can form. Through increasing the effect of liquid crystal anisotropy, first, the period-doubling pattern corresponding to the discocyte shape appears. Then, period-tripling, period-quadrupling, and the high wavenumber periodic wrinkling respectively corresponding to the umbonate, umbilicate, undulate appear. As the bending elasticity becomes insignificant, the surface undulations disappear and the membrane shape adopts the spindle-like morphology.



**Figure 5-7.** The dimensionless local curvature,  $r/R_0$  as a function of the scaled membrane arclength, s/L for six membrane morphologies with the different values of the dimensionless number  $\tau$ . Through increasing  $\tau$ , the dimensionless local curvature,  $r/R_0$  shows period-doubling, period-tripling, period-quadrupling, and the high wavenumber periodic wrinkling of respectively corresponding to the discocyte, umbonate, umbilicate, and undulate morphologies (see Table 5-2).

An increase of the effect of liquid crystal anisotropy decreases the periodicity of the wrinkles and leads to the higher wave-number periodic patterns. The greater the value of  $\tau$ , the smaller are the amplitudes and the wavelength of the smooth wrinkles, as shown in Figure 5-8.



**Figure 5-8.** Effect of the dimensionless number  $\tau$  on (a) the scaled amplitude and (b) the scaled wavelength of the smooth wrinkles.

### 5.5.4 Membrane elongation

The membrane elongation can be characterized by its aspect ratio  $\varepsilon$ =b/a. The effect of the dimensionless number  $\tau$  on the membrane elongation is shown in Figure 5-9. In the absence of LC anisotropy, for quite small bending elasticity the membrane will tend to be close to an ellipsoid so as to minimize their interfacial energy. In the presence of liquid crystal anisotropy, when the anchoring coefficient is of the same order, or larger than the surface tension, the nematic liquid crystal membrane has spindle-like shape. The aspect ratio of the membrane we obtained obeys  $\frac{b}{a} = 96.06\tau$  if  $\tau <<0.05$  and  $\frac{b}{a} = 1.27\tau$  if  $\tau >>0.05$ , which is quite close to the approximate results presented by [42].

In the absence of bending elasticity, the aspect ratio of the nematic liquid crystal droplet predicted using the Wulff construction shows a linear relationship,  $\frac{b}{a} = 1 + W/\gamma_0$  if  $W/\gamma_0 <<1$  and a power

function,  $\frac{b}{a} = (\frac{W}{\gamma_0})^{1/2}$  if  $W/\gamma_0 > 1$ . As we expect that by increasing the dimensionless number,  $\tau$ , the aspect ratio of the membrane becomes a weak function of the dimensionless anchoring. In Figure 5-9, the dashed black line illustrates the points where the membrane shape has a constant aspect ratio, in this case equals to b/a = 2. Regardless of whether the anchoring type is homeotropic or planar, the liquid crystal membrane favors elongated shapes.



**Figure 5-9.** Aspect ratio, b/a of a homogeneous nematic membrane as a function of the of the dimensionless number,  $\tau$ . The aspect ratio of the membrane shows a linear relationship,  $\frac{b}{a} = 96.06\tau$  if  $\tau << 0.05$  and  $\frac{b}{a} = 1.27\tau$  if  $\tau >> 0.05$ . The dashed black line illustrates the points where the membrane shape has a constant aspect ratio, b/a = 2.

The elongation follows the liquid crystal director field. Here, as homeotropic anchoring is preferred, any deviation from a spherical shape will result in an ellipsoid whose axis is perpendicular to the director field. However, in the case of planar anchoring (not treated here), the main axis of the membrane is parallel to the director field. Also, it should be noted that for small values of the scale anchoring coefficient,  $W/\gamma_0$  where the isotropic surface tension  $\gamma_0$ , dominates the anisotropic surface tension, the membrane tip becomes rounded. The increase in anisotropic surface energy compensates with the shorter total boundary length associated with rounded tips [78]. While for sufficiently large values of the scaled anchoring coefficient,  $W/\gamma_0$ , the opposite condition occurs and the tip becomes sharp. As reported in [41], the aspect ratio of the nematic liquid crystal droplet decreases with decreasing the dimensionless parameter,  $\beta = \gamma_0 R_0^2/k_c$  which is

a measure of the relative strength of the surface tension to bending elasticity. For membrane with spindle-like shapes, the effect of the membrane elasticity would be to remove the sharp discontinuity in curvature, which minimize the curvature energy. In agreement with the earlier works [42, 79], the membrane would be spherical if  $W/\gamma_0\approx 0$ , elongated if  $0 < W/\gamma_0 <= 1$ , and elongated with sharper ends if  $W/\gamma_0>1$ .

#### 5.5.5 Morphological phase diagram

To obtain a comprehensive atlas of morphological surface patterns, and to predict the membrane shapes depending on the system physical parameters, we present in Figure 5-10 the general morphological phase diagram of the surface patterns for a liquid crystal membrane with a constant pressure jump across the membrane,  $\Delta p = 10^{-2}$  atm, in a ternary parametric shape space (k<sub>c</sub>, W,  $\gamma_0$ ). The fundamental membrane shapes at the corners of the triangle are: spindle-like shape (top) with nearly zero bending elasticity (liquid crystal droplet), ellipse (lower right) with zero bending and zero anchoring, and n-fold pattern (lower left) with zero anchoring. In the triangle's interior, the liquid crystal anisotropy competes with the bending elasticity, and promotes formation of surface patterns with increased number of folds and higher bending energies. But, for the cases bending elasticity is higher than  $k_c > 5 \times 10^{-21}$  J, the effect of liquid crystal anchoring is insignificant, and the membrane practically adopts the conventional bending elastic shapes. For the minimum value of the bending elasticity,  $k_c = 5 \times 10^{-21}$  J (the right side of the triangle), the both liquid crystal anisotropy and membrane elasticity can equally contribute in the membrane deformation. The anchoring strength promotes the shape anisotropy and the top-to-bottom asymmetry, and creates the complex morphologies such as discocyte, ellipsoid, stomatocyte, umbonate, umbilicate, and undulate. With the increase of anchoring, the smooth surface undulations on the top of the membrane disappear and the membrane shape adopt the spindle-like morphology. Increasing the surface tension,  $\gamma_0$ particularly when the anchoring strength is insignificant results in the self-intersecting membrane shapes. In general, we can identify two main surface patterns: symmetric and asymmetric. The first is located at the limiting cases of zero anchoring/high bending elasticity.

In the absence of anchoring (the base of the triangle), the surface patterns correspond to the classical folded elastic membrane shapes. With the decrease of bending elasticity, the surface patterns change into modes with lower number of folds, while for the minimum value of the bending elasticity  $k_c=5\times10^{-21}$ J, the membrane in the absence of anchoring forms the ellipse (shown in the lower right corner of the ternary phase diagram). As the value of bending elasticity is nearly

zero (with  $k_c=0$ , the shape equation approaches infinity), the membrane shape is not a circle but ellipse. In partial summary, if the effect of the bending elasticity is predominant, the membrane shape is a n-fold pattern. If the effect of anchoring is predominant, the membrane shape is a spindle-like. When both effects are comparable, the membrane exhibits top-bottom asymmetric patterns, as illustrated in the right side of the triangle. We can conclude that the morphology phase diagram can allow us to determine what characteristic pattern will appear on the surface membrane based on the interaction of the three primitive shapes (n-fold, spindle-like shape, and ellipse). We can also gainfully compare the fundamental topographies of closed membrane with the three primitive surface wrinkling of planar liquid crystal membranes, where the n-fold, spindle-like, and ellipse shapes of the closed membrane are identical to folding, creasing, and flat patterns observed in the planar liquid crystal elastic membrane, respectively [49].



**Figure 5-10.** The ternary phase diagram ( $k_c$ , W,  $\gamma_0$ ) of the membrane surface morphologies. Surface pattern selection mostly depends on anchoring strength W and bending elasticity  $k_c$ . The n-fold pattern appears at high bending elasticity and weak anchoring, the spindle-like shape occurs at strong anchoring and low bending elasticity. The top-bottom asymmetric pattern is observed where both bending elasticity and anchoring strength are comparable.

#### 5.6 Pattern formation mechanism, pressure-curvature relations

To assign real forces behind shape selection we examine all the acting pressures across the surface. Rearranging Eq. 5.19 gives the four scaled surface pressures as function of the scaled membrane arc-length,  $\tilde{s} = s / R_0$ :

$$\frac{\Delta p R_0^3}{k_c} = -\underbrace{\left(\frac{d^3 \varphi}{d\tilde{s}^3} + \frac{1}{2} \left(\frac{d\varphi}{d\tilde{s}}\right)^3\right)}_{P_{bending}} + \underbrace{\frac{\gamma_o R_0^2}{kc} \left(\frac{d\varphi}{d\tilde{s}}\right)}_{P_{dilation}} + \underbrace{\frac{W R_0^2}{2kc} \left(\cos^2(\varphi - \theta)\right) \left(\frac{d\varphi}{d\tilde{s}}\right)}_{P_{rotation}} - \underbrace{\frac{W R_0^2}{kc} \left(\sin^2(\varphi - \theta)\right) \left(\frac{d\varphi}{d\tilde{s}}\right)}_{P_{rotation}} - \underbrace{\frac{W R_0^2}{kc} \left(\cos^2(\varphi - \theta)\right) \left(\frac{W R_0^2}{kc}\right)}_{P_{rotation}} - \underbrace{\frac{W R_0^2}{kc} \left(\cos^2(\varphi - \theta)\right) \left(\frac{W R_0^2}{kc}\right)}_{P_{rotation}} - \underbrace{\frac{W R_0^2}{kc} \left(\cos^2(\varphi - \theta)\right)}_{P_{rotation}} - \underbrace{\frac{W R_0^2}{kc}} - \underbrace{\frac{W R_0^2}{kc}}\right)}_{P_{rotation}} - \underbrace{\frac{W R_0^2}{kc}}_{P_{rotation}} - \underbrace{\frac{W R_0^2}{kc}}_{P_{rotation}} - \underbrace{\frac{W R_0^2}{kc}}_{P_{rotation}} - \underbrace{\frac{W$$

The bending elastic pressure, P<sub>bending</sub> is the resistant term for surface wrinkling (increasing energy with increasing area), while the Herring's capillary pressure, Protation is the driving force that undulates the membrane interface. To identify the mechanisms behind LC-elastic wrinkling, the four system scaled pressures: Pbending, Pdilation, Protation, and Pjump are illustrated as function of the scaled membrane arc-length, s/L for four membrane morphologies with different dimensionless numbers,  $\left(\sqrt[2]{WL^2/k_c}\right)$  (see Figure 5-11). The figure demonstrates that for the stomatocyte, umbilicate, and undulate morphologies, the scaled bending pressure and the scaled dilation pressure are quite out-of-phase while the rotation pressure changes its phase along the membrane arc-length, such that in some parts Protation and Pbending are in-phase while Protation and Pdilation are outof-phase, and in some parts, Protation and Pdilation are in-phase while Protation and Pbending are out-ofphase. The stress jump pressure is always negative, and as the dimensionless number  $\tau$  increases, its contribution to the surface wrinkling becomes insignificant. The key observation from these pressure profiles is that in the middle of the membrane arc-length (s/L=0.5) dilation and rotation pressures are always in-phase, and bending pressure are always out-of-phase with the dilation and rotation pressures. For the spindle-like shape morphology (Figure 5-11d), where the bending pressure is close to zero, the dilation pressure and rotation pressure is always out-of-phase. Figure 5-11 also illustrates that all surface capillary pressures grow as the dimensionless number  $\tau$ increases, while the stress jump remains constant. Increasing the dimensionless number  $\tau$  changes the degree of asymmetry between the top and bottom of the membrane (where the strong surface anchoring, top-bottom asymmetric membrane shapes emerge, and the surface energy increases by increasing the surface area) while for the spindle-like morphology, the wrinkles disappear and the membrane becomes symmetric.



**Figure 5-11.** The scaled pressures:  $P_{bending}$ ,  $P_{dilation}$ ,  $P_{rotation}$ , and  $P_{jump}$  are illustrated as function of the scaled membrane arclength, s/L for four membrane morphologies with the different dimensionless numbers, (a)  $\tau = 14.27$ , (b)  $\tau = 38.46$ , (c)  $\tau = 110.85$ , and (d)  $\tau = 500$ .

#### **5.7 Conclusions**

In this chapter, we have presented a physical model based on the elasto-capillary shape equations to study the surface pattern formation in closed liquid crystal elastic membranes. Using the presented model, we can obtain well-defined families of membrane morphologies. Besides, we showed that the complex morphologies that emerge in numerous biological membranes can be systematically explored by the mechanism that couples liquid crystal orientational order and membrane elasticity. The results show that when both liquid crystal anisotropy and membrane elasticity contribute in the membrane deformation, the anchoring strength promotes shape anisotropy and top-to-bottom asymmetry while membrane elasticity promotes symmetric shapes. We presented a general morphological phase diagram of the membrane surface patterns, in which we classify two characteristic regimes of membrane shapes based on whether the liquid crystal anisotropy or bending elasticity is dominant. The phase diagrams allow us to determine what

membrane shape will form based on the interaction of the three primitive shapes (ellipse, spindlelike shape, and n-fold). A one-to-one mapping of this primitive drop shapes with wrinklingcreasing-flat shape of open surfaces was established. The complex pressure balances behind shape selection was demonstrated. The observation of complex top-bottom asymmetric topographies in biological membranes can now be understood in terms of liquid crystal anisotropy and we can conclude that numerous surface morphologies observed in living cells might be formed through coupling between liquid crystal anisotropy and bending elasticity. All these findings provide a foundation to understand the pattern formation in biological cell membranes and open up new opportunities to design novel anisotropic soft materials with unique functionalities such as optical and wetting.

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# **Chapter 6**

### 6 Conclusions and Contributions to Original Knowledge

## **6.1** Conclusions

The purpose of this thesis is to contribute to the evolving understanding of nano-wrinkling in biological liquid crystal surfaces. Understanding the mechanisms through which living systems exhibit unique surface undulations and specific morphologies can inspire design and fabrication of bio-inspired structural and functional materials. This thesis explored the physics of wrinkling formation in cholesteric liquid crystal interfaces as the representative analogues in plant cell wall and nematic liquid crystal closed membranes as the representative analogues in living cell membranes. A compressive physical model using anisotropic soft matter models was developed to create new knowledge and principles for studying the role of liquid crystal anisotropy in the formation of surface morphologies. In this thesis, a detailed analysis of periodic structure formation and surface morphology evolution in liquid crystalline films and cylindrical membranes was performed by formulating and solving the governing nemato-capillary equations. By taking advantage of geometry and system material constraints, the key geometric and physical parameters that affect the formation of the surface morphologies were identified. Using standard order of magnitude analysis, the simple scaling law expressing the origin of surface wrinkling length scales is presented. Comprehensive phase diagrams of morphological surface patterns were illustrated that enable us to predict the surface patterns and membrane shapes depending on the system physical parameters. Moreover, potential biomimetic application of the surface ultrastructures was demonstrated. The following subsections highlight the main conclusions of each chapter in this thesis.

# 6.1.1 Modeling nanostructured free surfaces in plant-based plywoods driven by chiral capillarity

The Cahn-Hoffman capillary vector thermodynamics for curved interfaces was adapted to develop a nonlinear nemato-capillarity shape equation for plant-based plywoods surfaces. The main mechanisms that operate in chiral capillarity for generating nano-scale surface undulations in plant-based plywoods as shown in chiral nematic liquid crystals were elucidated. The essential feature of chiral capillarity was identified as the interaction of anisotropy (director **n** of fibers), micron-range chirality ( $p_0$ ), helix direction (**H**) and free surface topography. The results presented in this chapter indicate that when the plywood helix is parallel to a flat surface, frustration driven

by the unavoidable (due to periodic  $\mathbf{n}$ ) presence of high surface energy drives the surface uncoiling of the helix and the periodic tilting of the interface. The interfacial anchoring energy renormalizes the isotropic surface tension and promotes the rotation of the interface. The developed capillary pressure for chiral interfaces contains three main contributions: Laplace pressure (area dilation), Herrings pressure (area rotation), and director orientation gradients pressure. The role of the capillary pressure contributions was illuminated and the influence of chirality and surface anchoring was characterized. Herring's pressure forms the basis of anisotropic crystal morphologies, and depends only on curvature. The director orientation pressure was identified as the fundamental driving force that wrinkles the interface with a wavelength that reflects the periodicity of the director filed. It is shown that the director orientation vanishes for a planar surface with a uniform tangential helix vector and results in a flat surface. The resulting chiral capillary equation admits stable spatially periodic solutions describing surface wrinkling, where the amplitude is in the order of few nms and the wave-length is in order of µms. The ratio of amplitude/period of the chirality-driven surface wrinkling was estimated by a scaling law that expresses the ratio as a linear function of the ratio of anchoring strength to isotropic surface tension. The scaling law was validated with experimental values available in the literature for surface undulations observed in chiral nematic liquid crystals and biological plywoods. Diffraction gratings generated by chiral capillarity can be used for the characterization of plant-based plywoods and for Nature-inspired optical devices. Since the plywood pitch is sensitive to temperature, solvents, pH, and external fields, new functional material surfaces that operate through the chiral capillarity mechanism can be designed and fabricated.

# 6.1.2 Modeling nano-wrinkling of chiral surfaces in response to humidity: structure and diffraction optics

In this chapter, the formation of free surface nanostructures in plant-based plywoods with waterinduced varying pitch was investigated using a non-linear nemato-capillarity shape equation. The generalized Laplace equation based on the Cahn-Hoffman capillarity vector formalism was formulated and used as an efficient tool to analyse nano-scale surface reliefs in plantbased plywoods with water-driven varying helical pitch through interaction of anisotropic interfacial tension and chirality changes through hydration. The role of four capillary pressure contributions including surface area change, surface area rotation, director gradient curvature, and bulk stress jump was characterized. The influence of the varying helical pitch, the elasto-capillary length scale, and the surface anchoring strength on the surface wrinkling profile was characterized. Consistent with the scaling law presented in chapter 2 for the plywood structure with fixed pitch, it is shown that the spatially-varying surface profile amplitude is mostly a function of the anchoring strength and the water-induced helix pitch gradient. The optical properties of the plant-based plywood free surface nanostructure with water-induced varying pitch was investigated and compared with the plywood free surface nanostructure with constant pitch. The results showed that the surface structure with non-uniform pitch distribution, where the pitch length changes in different regions, reflects normal incident light with a bandwidth wider than the constant pitch surface structure. The reflection peak of the surface nanostructure can be altered through the change in the humidity level based on the plywood helix pitch expansion. The color transition is attributed to the swelling and shrinking of the multi-layered plant cell wall plywood, which cause the helicoidal pitch to increase, thereby leading to a red shift in the iridescence. Plantbased cholesteric liquid crystals are of interest because their optical response can be controlled by self-assembly and their colorimetric humidity sensing can reduce the sensor cost. The potential biosensors can respond to different ranges of relative humidity depending on the amplitude and wavelength of the grating structure. All these findings provide a foundation to understand structural color phenomena in Nature and for the design of optical sensor devices.

# 6.1.3 Multiple-wavelength surface patterns in models of elastic biological chiral liquid crystal membranes

A novel model that describes surface pattern formation in elastic liquid crystal membranes was formulated based on the integration of liquid crystal and membrane physics. The physical model combines the liquid crystal anisotropy of biological materials, the bending elasticity of surfactant-like biomolecules, and the substrate chirality. In the absence of liquid crystal anisotropy, the model converged to the classical elastic membrane, and in the absence of surface bending elasticity, the model converged to the liquid crystal interface model presented in chapter 2. The system length scales and key dimensionless numbers that control the surface morphogenesis are identified. A comprehensive morphological phase diagram of the surface patterns for a helicoidal plywood with a constant pitch was presented that enable us to determine what characteristic pattern will appear on the surface based on the interaction of the three primitive shapes (folding, creasing, and flat). Two main surface patterns, single wavelength and multiple wavelengths were classified. The

single wavelength patterns were located at the limiting cases of zero anchoring/zero bending elasticity. It is shown that in the absence of anchoring the surface patterns correspond to the classical compression-induced buckling of an elastic membrane. In the absence of bending elasticity, the surface patterns correspond to the chirality-driven surface wrinkling. When the effects of liquid crystal anchoring and bending elasticity are comparable, the surface profile shows a rich variety of multi-scale complex patterns, such as spatial period-doubling, period-tripling, and quasi-periodicity. The presented phase diagram illuminates a natural setting for the creation and control of complex surface patterns through the combination of membrane elasticity and orientation gradients. Furthermore, the chiral liquid crystal-membrane model was gainfully compared with a driven pendulum where the angular velocity of the pendulum is identical to the curvature of the membrane. The pendulum analogy demonstrates that the surface pattern selection depends on the system winding number, or ratio between the number of times the pendulum trajectory rotates around the small cross section, and the large circumference of a torus. Using the analogy, the surface patterns were portrayed in terms of the winding number and the liquid crystal anchoring, and the wrinkling mode was characterized by the dynamic limit cycles. In this chapter, we concluded that the observation of complex surface patterns in biological membranes and living tissues can be understood in terms of liquid crystal anisotropy. The coupling between the liquid crystal chirality, surface bending elasticity and the curvature of the membranes is fundamental for developing advanced multi-functional materials such as biosensors and actuators.

# 6.1.4 Cylindrical shapes of nematic liquid crystal membranes: a model for 2D anisotropic biological cells

In this study, a physical model based on the elasto-capillary shape equation that describes the surface deformation in closed nematic liquid crystal elastic membranes was derived and solved. It is assumed that the nematic liquid crystal membrane has a relatively weak homeotropic anchoring where the radius of the membrane is always significantly less than the extrapolation length scale, resulting in homogenous internal director field. Using the presented model, the possible families of complex membrane morphologies were obtained. It is shown that the complex morphologies that emerge in numerous biological membranes can be systematically explored by the mechanism that couples liquid crystal orientational order and membrane elasticity. The results showed that when both liquid crystal anisotropy and membrane elasticity contribute in the membrane deformation, the anchoring strength promotes shape anisotropy and top-to-bottom asymmetry

while membrane elasticity promotes symmetric shapes. The role of the system physical parameters on the surface morphologies was investigated, and the three key dimensionless numbers that control the surface morphogenesis were introduced. A general morphological phase diagram of the membrane surface patterns in the ternary parametric space (bending elasticity, anchoring, surface tension) was illustrated, in which two characteristic regimes of membrane shapes based on whether the liquid crystal anisotropy or bending elasticity is dominant were classified. The phase diagram enables us to determine what membrane shape will form based on the interaction of the three primitive shapes (ellipse, spindle-like shape, and n-fold). Furthermore, to elucidate the mechanisms that drive surface deformations, the complex pressure balances behind shape selection was demonstrated. In this chapter, we concluded that the observation of complex top-bottom asymmetric topographies in biological membranes can be understood in terms of liquid crystal anisotropy and the numerous surface morphologies observed in living cells might be formed through coupling between liquid crystal anisotropy and bending elasticity. The predictions of the model contribute the current effort to better understand the membrane topologies in living soft matters and synthetic phospholipids nanostructures.

## **6.2** Contributions to original knowledge

A summary of the original contributions to knowledge resulting from this thesis work are:

(1) A comprehensive nonlinear nemato-capillarity shape equation that reflects the membrane curvature-fiber order contributions is developed and the main mechanisms driving nano-scale surface undulations in chiral nematic liquid crystals as shown in plant-based plywoods are described.

(2) The possible surface profiles in capillary instabilities of plant-based plywoods are analyzed by solving the governing nemato-capillary equations. A theoritical scaling law expressing the explicit relation between the surface profile amplitude and the model parameters is presented and validated with a number of experimental values available in literature for surface undulations observed in chiral nematic liquid crystals and biological plywoods.

(3) The role of humidity in deforming the surface undulations through the interaction of anisotropic interfacial tension, swelling through hydration, and capillarity at free surfaces is established. A scaling law for the chirality-humidity driven surface wrinkling is proposed that derives the explicit relations between the undulations' amplitude as a function of the anchoring strength and

the spatially varying pitch.

(4) The optical properties of the surface wrinkling are explored, and a potential biosensor that can respond to different ranges of relative humidity depending on the the reflection peak of the surface nanostructure is suggested. The potential biosensor is of interest because its optical response can be controlled by self-assembly and its colorimetric humidity sensing can reduce the sensor cost.

(5) A novel physical model that can describe more complex real surfaces such as creasing, folding, and period-doubling is developed. The formation of complex surface patterns in biological membranes and living tissues is described through interaction of liquid crystal anisotropy of biological materials and bending elasticity of surfactant-like biomolecules.

(6) The elasto-capillary model is extended to cylindrical membranes. The effect of liquid crystal anisotropy in the formation of complex top-bottom asymmetric complex topographies observed in biological and synthetic closed membranes is explored. The main mechanism that drives the formation of complex cylindrical shapes is demonstrated. The morphology formation mechanism developed for closed nematic liquid crystal membranes has a remarkably wide range of biological and biomimetic relevance and biomedical applications.

(7) A new paradigm for characterizing the morphological patterns in biological and synthetic closed membranes is established and a natural setting for the creation and control of the emerging complex patterns is elucidated.

## 6.3 Recommendations for future work

Future research can continue in various directions based on the assumptions used in this thesis, the expansions and interests that have come about during the process of completion of this work are as follows:

• The 2D nemato-capillary model for liquid crystal membranes can be extended into a 3D model.

• The rule of water gradient presence across the membrane on formation of the complex cylindrical morphologies can be investigated. An energy density can be introduced that includes a chemical potential energy as a function of the water concentration. The water diffusion might be coupled to describe the rate of water absorption into the membrane.

• One multi-functionality example of biological membranes is flexoelectricity through coupling bending curvature and electric fields. The effect of flexoelectricity on formation of the complex cylindrical morphologies can be explored.

### Appendix A: Cahn-Hoffman capillarity vector thermodynamics for CLC interfaces

The purpose of this Appendix is to derive the Cahn-Hoffman capillarity vector formulations for CLC interfaces. The nematic capillarity vector is defined by the gradient of the scalar field ry [1]:

$$\boldsymbol{\xi}(\mathbf{n},\mathbf{k}) = \nabla[\mathbf{r}\boldsymbol{\gamma}(\mathbf{k})] \tag{A.1}$$

where **r** is the magnitude of surface position vector **r**: **r**=r**k**. Noting that  $d(r\gamma) = \nabla(r\gamma)$ . d**r**, the gradient of  $r\gamma$  yield:

$$\boldsymbol{\xi}(\mathbf{n},\mathbf{k}) = \nabla[\mathbf{r}\boldsymbol{\gamma}(\mathbf{k})] = \boldsymbol{\gamma}\frac{\partial \mathbf{r}}{\partial \mathbf{r}} + \mathbf{r}\frac{d\boldsymbol{\gamma}}{d\mathbf{r}} = \boldsymbol{\gamma}\mathbf{k} + \mathbf{I}_{\mathrm{s}} \cdot \frac{d\boldsymbol{\gamma}}{d\mathbf{k}}$$
(A.2)

Thus the normal and tangential components of capilarity vector for CLC interfaces are:

$$\xi_{\perp}(\mathbf{n},\mathbf{k}) = \gamma \mathbf{k}$$

$$\xi_{\parallel}(\mathbf{n},\mathbf{k}) = \mathbf{I}_{s} \cdot \frac{d\gamma}{d\mathbf{k}} = (\mathbf{I}_{s} \cdot \mathbf{n}) \frac{d\gamma}{d(\mathbf{n},\mathbf{k})} = \gamma' \mathbf{n}_{\parallel}$$
(A.3)

where  $\gamma' = \frac{d\gamma}{d(n.k)}$  and  $\mathbf{n}_{//} = \mathbf{I}_{s} \cdot \mathbf{n}$  is the tangential component of the surface director field. Noticing that  $\mathbf{I}_{s}$  is the 2×2 unit surface dyadic:  $\mathbf{I}_{s} = \mathbf{I} \cdot \mathbf{k}\mathbf{k}$  where  $\mathbf{I}$  is the 3×3 volumetric unit tensor, we have:

$$\xi_{\parallel}(\mathbf{n},\mathbf{k}) = \mathbf{I}_{s} \cdot \frac{d\gamma}{d\mathbf{k}} = (\mathbf{I} - \mathbf{k}\mathbf{k}) \cdot \frac{d\gamma}{d\mathbf{k}} = \mathbf{I} \cdot \frac{d\gamma}{d\mathbf{k}} - \mathbf{k}\mathbf{k} \cdot \frac{d\gamma}{d\mathbf{k}}$$
(A.4)

Using the Rapini-Papoular surface free energy  $\gamma = \gamma_0 + \frac{W}{2} (\mathbf{n}, \mathbf{k})^2$  [2], we get:

$$\frac{\mathrm{d}\gamma}{\mathrm{d}\mathbf{k}} = \mathbf{W}(\mathbf{n}.\mathbf{k})\mathbf{n} \tag{A.5}$$

Substituting Eq. A.5, we obtain the tangential component of the capillarity vector:

$$\boldsymbol{\xi}_{\parallel}(\mathbf{n},\mathbf{k}) = \mathbf{W}(\mathbf{n},\mathbf{k})\mathbf{n} - \mathbf{W}(\mathbf{n},\mathbf{k})^{2}\mathbf{k} = \mathbf{W}(\mathbf{n},\mathbf{k})(\mathbf{n}-(\mathbf{n},\mathbf{k})\mathbf{k}) \tag{A.6}$$

Hence the total capillary pressure  $p_c$  is defined by  $p_c = \nabla_s$ .  $\xi$ , the divergence of the capillary vector follows the rule [3]:

$$\mathbf{p}_{c} = \nabla_{s} \times \boldsymbol{\xi} = \nabla_{s} \times \left(\boldsymbol{\xi}_{\perp} + \boldsymbol{\xi}_{\parallel}\right) = \underbrace{\frac{\partial \boldsymbol{\xi}_{\perp}}{\partial \mathbf{k}} : \left(\nabla_{s}\mathbf{k}\right)}_{\text{area size change}} + \underbrace{\frac{\partial \boldsymbol{\xi}_{\parallel}}{\partial \mathbf{k}} : \left(\nabla_{s}\mathbf{k}\right)}_{\text{area rotation}} + \underbrace{\frac{\partial \boldsymbol{\xi}_{\parallel}}{\partial \mathbf{k}} : \nabla_{s}\mathbf{n}}_{\text{director curvature}}$$
(A.7)

Using Eq. A.3, the contribution from the normal component  $\xi_{\perp}$ , the area size change contribution becomes:

$$\frac{\partial \boldsymbol{\xi}_{\perp}}{\partial \mathbf{k}} : \nabla_{s} \mathbf{k} = \gamma \mathbf{I}_{s} : \nabla_{s} \mathbf{k} = -\gamma \kappa$$
(A.8)

where  $\nabla_{s} \mathbf{k} = -\kappa t \mathbf{t}$ . According to Eq. A.6, the area rotation contribution becomes:

$$\frac{\partial \boldsymbol{\xi}_{\parallel}}{\partial \mathbf{k}} : \left( \nabla_{s} \mathbf{k} \right) = -W \left( (\mathbf{n}.\mathbf{t})^{2} - (\mathbf{n}.\mathbf{k})^{2} \right) \kappa$$
(A.9)

The director curvature contribution is found using Eq. A.6, to obtain:

$$\frac{\partial \boldsymbol{\xi}_{\parallel}}{\partial \mathbf{n}} = \frac{\partial}{\partial \mathbf{n}} (\mathbf{W}(\mathbf{n}.\mathbf{k})(\mathbf{n} - (\mathbf{n}.\mathbf{k})\mathbf{k})) = \mathbf{W}\mathbf{k}\mathbf{n} - 2\mathbf{W}(\mathbf{k} \times \mathbf{n})\mathbf{k}\mathbf{k} + \mathbf{W}(\mathbf{n}.\mathbf{k})\mathbf{I}$$

$$\frac{\partial \boldsymbol{\xi}_{\parallel}}{\partial \mathbf{n}} : \nabla_{s}\mathbf{n} = \frac{\partial \boldsymbol{\xi}_{\parallel}}{\partial \mathbf{n}} : \mathbf{t}\frac{\partial \mathbf{n}}{\partial s} = \mathbf{W}(\mathbf{t} \times \mathbf{n})\left(\mathbf{k}.\frac{\partial \mathbf{n}}{\partial s}\right) + \mathbf{W}(\mathbf{n}.\mathbf{k})\left(\mathbf{t}.\frac{\partial \mathbf{n}}{\partial s}\right)$$
(A.10 a,b)

### **Appendix B: Director curvature pressure**

The purpose of this Appendix is: (i) to derive a general expression of the director curvature pressure  $p_N$ , (ii) to determine generic sufficient conditions under which  $p_N=0$ , and (iii) to use (i) and (ii) to show that for a planar surface with a uniform tangential helix vector then  $p_N=0$  and no surface wrinkling can be observed as predicted by [4] using other approaches.

## **B.1** General expression for the director curvature pressure (p<sub>N</sub>)

Using Eq. 2.8, the director curvature contribution to the capillary pressure,  $p_N$  appears due to orientation gradients:

$$p_{N} = \frac{\partial \boldsymbol{\xi}_{\parallel}}{\partial \mathbf{n}} : \nabla_{s} \mathbf{n}$$

$$p_{N} = W((\boldsymbol{k} \cdot \boldsymbol{n})(\nabla_{s} \cdot \boldsymbol{n}) + \boldsymbol{k}\boldsymbol{n} : \nabla_{s}\boldsymbol{n})$$
(B.1 a,b)

To analyze this expression further we need the covariant surface gradient of the director field  $\nabla_s n$  (for details see ref.[5]):

$$\nabla_{s}\mathbf{n} = \mathbf{a}^{\alpha}\mathbf{n}_{,\alpha} = \left(\mathbf{n}_{\beta;\alpha} - \mathbf{b}_{\beta\alpha}\mathbf{n}_{\perp}\right)\mathbf{a}^{\alpha}\mathbf{a}^{\beta} + \left(\mathbf{n}_{\perp,\alpha} + \mathbf{b}_{\beta\alpha}\mathbf{n}^{\beta}\right)\mathbf{a}^{\alpha}\mathbf{k}$$

$$= \left(\mathbf{n}_{\beta;\alpha}\mathbf{a}^{\alpha}\mathbf{a}^{\beta} - \mathbf{n}_{\perp}\mathbf{b}\right) + \left(\nabla_{s}\mathbf{n}_{\perp} + \mathbf{b}\cdot\mathbf{n}\right)\mathbf{k}$$
(B.2)

where a semicolon denotes covariant differentiation,  $\mathbf{a}_{\alpha}$  are the two tangential base vectors,  $\mathbf{a}^{\alpha}$  are the two reciprocal base vectors, the director field is  $\mathbf{n} = n_{\beta \mathbf{a}}{}^{\beta} + n_{\perp}\mathbf{k}$ , and the curvature tensor **b** is:

$$\mathbf{b} = -\frac{\partial \mathbf{k}}{\partial \mathbf{R}} = -\nabla_{s}\mathbf{k}, \ \nabla_{s}(*) = \mathbf{I}_{s} \cdot \nabla_{s}(*) = \frac{\partial(*)}{\partial \mathbf{R}} = \mathbf{a}^{\alpha} \frac{\partial(*)}{\partial \mathbf{u}^{\alpha}}$$
(B.3)

where **R** is the position vector given parametrically by  $\mathbf{R} = \mathbf{R}(u^{\alpha})$ ,  $\alpha = 1, 2$  and  $u^{\alpha}$  are the surface coordinates. The average curvature H and the Gaussian or total curvature  $\kappa$  are:

$$2\mathbf{H} = \mathbf{I}_{s} : \mathbf{b} = -\nabla_{s} \cdot \mathbf{k} = -\mathbf{a}^{\alpha} \frac{\partial \mathbf{k}}{\partial u^{\alpha}} = \mathbf{b}_{\alpha}^{\alpha} = (\mathbf{c}_{1} + \mathbf{c}_{2})$$
(B.4)

$$\mathbf{K} = -\frac{1}{2}\varepsilon_{s} : (\mathbf{b}.\varepsilon_{s}.\mathbf{b}) = \frac{1}{2}\varepsilon^{\alpha\beta}\varepsilon^{\gamma\delta}b_{\alpha\gamma}b_{\beta\delta} = (c_{1}c_{2})$$
(B.5)

where  $c_1$  and  $c_2$  are the radius of curvature and  $\varepsilon_s$  is the dyadic surface unit alternator:

$$\boldsymbol{\varepsilon}_{s} = -\mathbf{k} \times \mathbf{I}_{s} = -\mathbf{I}_{s} \times \mathbf{k} = -\mathbf{k} \times \mathbf{I} = -\mathbf{I} \times \mathbf{k} = \mathbf{a}^{\alpha} \mathbf{a}^{\beta} \boldsymbol{\varepsilon}_{\alpha\beta} = \mathbf{a}_{\alpha} \mathbf{a}_{\beta} \boldsymbol{\varepsilon}^{\alpha\beta}$$
(B.6)

The surface director gradient  $\nabla_s n$  can then be decomposed into the 2x2 symmetric surface gradient tensor **A**, the 2x2 antisymmetric surface gradient tensor **W**, and the 2x1 surface gradient tensor **R**:

$$\nabla_{\mathbf{s}}\mathbf{n} = \mathbf{A} + \mathbf{W} + \mathbf{R} \tag{B.7a}$$

$$\mathbf{A} = \mathbf{A}_{\alpha\beta} \mathbf{a}^{\alpha} \mathbf{a}^{\beta}; \tag{B.7b}$$

$$A_{\alpha\beta} = A_{\beta\alpha} = n_{(\beta;\alpha)} - n_{\perp} b_{\alpha\beta}; \ n_{(\beta;\alpha)} = \frac{1}{2} \left( n_{\beta;\alpha} + n_{\alpha;\beta} \right)$$
$$W = W_{\alpha\beta} a^{\alpha} a^{\beta};$$
(B.7c)

$$\mathbf{W}_{\alpha\beta} = -\mathbf{W}_{\beta\alpha} = \mathbf{n}_{[\beta;\alpha]}; \ \mathbf{n}_{[\beta;\alpha]} = \frac{1}{2} \left( \mathbf{n}_{\beta;\alpha} - \mathbf{n}_{\alpha;\beta} \right)$$

$$\mathbf{R} = \mathbf{R}_{\alpha n} \mathbf{a}^{\alpha} \mathbf{k}; \ \mathbf{R}_{\alpha n} = \mathbf{n}_{\perp,\alpha} + \mathbf{b}_{\alpha\beta} \mathbf{n}^{\beta}$$
(B.7d)

In addition, the surface divergence of the director is found from Eq. B.2 to be:

$$\nabla_{s}\mathbf{n} = \mathbf{a}^{\alpha}\mathbf{n}_{,\alpha} = \left(\mathbf{n}_{\beta;\alpha} - \mathbf{b}_{\beta\alpha}\mathbf{n}_{\perp}\right)\mathbf{a}^{\alpha}\mathbf{a}^{\beta} = \mathbf{I}_{s} : \mathbf{A} = \mathbf{n}_{\alpha;\alpha} - 2\mathbf{H}\mathbf{n}_{\perp}$$
(B.8)

Replacing Eq. B.7 and Eq. B.8 into Eq. B.1b) we find a general and detailed expression for the director pressure in terms of director component  $(n_{\alpha}, n_{\alpha:\alpha}, n_{\perp}, n_{\parallel})$  and curvatures (H,  $b_{\alpha,\beta}$ ):

$$\mathbf{p}_{\mathrm{N}} = \mathbf{W}\left(\left(\mathbf{n}.\mathbf{k}\right)\mathbf{I}_{\mathrm{s}}:\mathbf{A}+\mathbf{n}\cdot\mathbf{R}\cdot\mathbf{k}\right) = \mathbf{W}\left(\left(\mathbf{n}_{(\alpha;\alpha)}-2\mathbf{n}_{\perp}\mathbf{H}\right)\mathbf{n}_{\perp}+\left(\mathbf{n}_{\perp,\alpha}+\mathbf{b}_{\alpha\beta}\mathbf{n}^{\beta}\right)\mathbf{n}_{\alpha}\right)$$
(B.9)

## **B.2** Vanishing director curvature pressure (p<sub>N</sub>=0)

Here we analyze some likely cases of  $p_N=0$  for: (a) 2D surfaces and then (b) 1D planar lines. (a) For flat surfaces, Eq. B.9 it simplifies to:

$$\mathbf{p}_{N}\left(\mathbf{b}=\mathbf{0}\right) = \mathbf{W}\left(\mathbf{n}_{(\alpha;\alpha)}\mathbf{n}_{\perp} + \mathbf{n}\cdot\mathbf{a}^{\alpha}\mathbf{n}_{\perp,\alpha}\right) \tag{B.10}$$

If the director field is homeotropic,  $n_{(\alpha;\alpha)} = \mathbf{n} \cdot \mathbf{a}^{\alpha} = 0$  and  $p_N=0$ . If the director is tangential  $n_{\perp,\alpha} = n_{\perp} = 0$  and  $p_N=0$ .

(b) For 1D planar lines, the director pressure is:

$$P_{N} = W(t \cdot n) \left( k \cdot \frac{\partial \mathbf{n}}{\partial s} \right) + W(\mathbf{n} \cdot \mathbf{k}) \left( t \cdot \frac{\partial \mathbf{n}}{\partial s} \right)$$
(B.11)

where **t** is the unit tangent, **k** the unit normal and s the arc-length. For homeotropic and planar straight lines we find  $p_N=0$ . For straight lines with line gradients, using rectangular (x,y,z)

coordinates with unit vectors ( $\mathbf{\delta}_x = t, \mathbf{\delta}_y = \mathbf{k}, \mathbf{\delta}_z$ ) and a director filed  $\mathbf{n} = n_x \mathbf{\delta}_x + n_y \mathbf{\delta}_y + n_z \mathbf{\delta}_z$ , the pressure equation (Eq. B.11) becomes:

$$\mathbf{p}_{\mathrm{N}} = \mathbf{W} \left( \mathbf{n}_{\mathrm{y}} \mathbf{n}_{\mathrm{x},\mathrm{x}} + \mathbf{n}_{\mathrm{x}} \mathbf{n}_{\mathrm{y},\mathrm{x}} \right) \tag{B.12}$$

which vanishes when  $n_x n_y = C$  = constant. Hence under planar or homeotropic orientation there is no director pressure. Using the unit length of the director **n.n**=1, no director pressure is generated for director field satisfying:

$$n_{y}^{4} + n_{z}^{2}n_{y}^{2} - n_{y}^{2} + c^{2} = 0$$
(B.13)

# **B.3** Proof of zero director curvature pressure for planar surfaces (H=0) with tangential cholesteric helix (h=t)

When the cholesteric helix is tangential to the straight line then  $\mathbf{s} = x, \mathbf{t} = \mathbf{\delta}_x =$  constant,  $\mathbf{\delta}_x$ .  $\mathbf{n} = 0, \ \mathbf{\delta}_x$ .  $(\frac{dn}{dx}) = 0$ .

Using Eq. B.10 we find:

$$p_{N} = W \left\{ \left( \delta_{y} \cdot \mathbf{n} \right) \underbrace{\left( \delta_{x} \cdot \frac{d\mathbf{n}}{dx} \right)}_{=0} + \underbrace{\left( \delta_{x} \cdot \mathbf{n} \right)}_{=0} \left( \delta_{y} \cdot \frac{d\mathbf{n}}{dx} \right) \right\} = 0$$
(B.14)

No director pressure is generated because the director gradients and the director components have no projection on the x-axis.

### Appendix C: Derivation of shape and normal angle equations

The purpose of this Appendix is to formulate the capillay shape equation for the splaybend director.

The geometry of the free interface is characterized by a cylindrical surface such that its curvature in the z-direction is zero and focus on the projection  $\mathbf{x}(s)$  in the x-y plane (Figure C-1). The unit tangent **t** and the unit normal N to the surface are given by:

$$\mathbf{t}(s) = \frac{\partial \mathbf{x}(s)}{\partial s}; \quad \frac{\partial \mathbf{t}(s)}{\partial s} \equiv \frac{\partial^2 \mathbf{x}(s)}{\partial s^2} = \kappa \ \mathbf{k}(s) \tag{C.1}$$

Where  $\kappa$  is the curvature, quantifying the deviation from linearity.



**Figure C-1.** Geometry of the free surface, unit normal **k**, normal angle  $\varphi$ , unit tangent **t**, and (x,y,z) coordinate system.

Since **t** is a unit vector it can be expressed with the normal angle:  $\mathbf{t}(\mathbf{x}) = (\sin \varphi(\mathbf{x}), -\cos \varphi(\mathbf{x}), 0)$ . In the normal angle parameterization, the curvature is:  $\mathbf{\kappa} = \frac{d\varphi}{ds}$ . Using the definition:  $\frac{dx}{ds} = \sin \varphi$ , the director curvature pressure is  $\frac{dn}{ds} = \frac{dn}{dx} \frac{dx}{ds} = \frac{dn}{dx} \sin \varphi$ , and  $\mathbf{\kappa} = \frac{d\varphi}{dx} \sin \varphi$ . By substituting  $\kappa$  and  $\frac{dn}{ds}$  in eqn (5), the shape equation becomes:

$$\frac{\mathbf{p}_{c}}{\gamma_{o}} = \left\{ \left( 1 - \frac{\mathbf{B}}{2} \left( \mathbf{n} \cdot \mathbf{k} \right)^{2} + \mathbf{B} \left( \mathbf{n} \cdot \mathbf{t} \right)^{2} \right) \sin \phi \right\} \frac{d\phi}{dx}$$

$$- \left\{ \mathbf{B} (\mathbf{k} \cdot \mathbf{n}) \left( \frac{d\mathbf{n}}{dx} \cdot \mathbf{t} \right) + \mathbf{B} \left( \mathbf{n} \cdot \mathbf{t} \right) \left( \frac{d\mathbf{n}}{dx} \cdot \mathbf{k} \right) \right\} \sin \phi$$
(C.2)

Setting  $p_c=0$  and using the splay-bend director distribution  $\mathbf{n}(x)$ :  $\mathbf{n}(x) = (\cos qx, \sin qx, 0)$ and surface unit normal  $\mathbf{k}(x)$ :  $\mathbf{k}(x) = (\cos \varphi(x), \sin \varphi(x), 0)$ , gives the governing nonlinear first order ODE for the normal angle  $\varphi(x, B, q)$ :

$$\frac{d\varphi}{dx} = \frac{q_0 B \sin(\varphi) \{\sin^2(\varphi - q_0 x) - \cos^2(\varphi - q_0 x)\}}{\sin(\varphi) \{1 - \frac{B}{2} \cos^2(\varphi - q_0 x) + B \sin^2(\varphi - q_0 x)\}}$$
(C.3)

### **Appendix D: Airy function**

The Airy functions of the first and second kind, Ai and Bi which commonly appear in physics, especially in optics, quantum mechanics are the independent solutions to the homogenous second order differential equation, y'' - xy = 0[6]:

$$Ai(x) = \frac{1}{\pi} \int_{0}^{\infty} \cos(\frac{z^{3}}{3} + xz) dz$$
(D.1)

$$Bi(x) = \frac{1}{\pi} \int_{0}^{\infty} \left[ e^{-z^{3}/3 + xz} \sin(\frac{z^{3}}{3} + xz) \right] dz$$
(D.2)

The Airy function Gi is the independent solution to the inhomogeneous second order differential equation,  $y''-xy=\pm\pi^{-1}[6]$ :

$$Gi(x) = \frac{1}{\pi} \int_{0}^{\infty} \sin(\frac{t^{3}}{3} + xt) dt$$
(D.3)

The function can be defined based on the homogenous Airy functions:

$$Gi(x) = Bi(x) \int_{x}^{\infty} Ai(t)dt + Ai(x) \int_{0}^{x} Bi(t)dt$$
(D.4)

The general solution can be written as:

$$y(x) = aAi(x) + bBi(x) + Gi(x)$$
(D.5)

The shape equation (Eq. 5.19) in terms of curvature can be compared with the second Painleve equation,  $y'' = zy + by^3 + a$ :

$$\kappa'' = \underbrace{\left[\frac{\gamma_0}{k_c} - \frac{W}{2k_c}(\cos^2(\varphi - \theta)) - \frac{W}{k_c}(\sin^2(\varphi - \theta))\right]\kappa}_{f(s)\kappa} - \frac{1}{2}\kappa^3 + \frac{-\Delta p}{k_c}$$
(D.6)

The second Painleve equation can be considered as a non-linear generalization of the Airy equation. For the case a=1/2, the solution to the equation can expressed with the Airy function. The function K(x,y) is introduced as the solution to homogenous Painleve equation,  $y'' = zy + 2\sigma y^3$ [6]:

$$K(x, y) = rAi(\frac{x+y}{2}) + \sigma \frac{r^2}{4} \int_{x}^{\infty} \int_{x}^{\infty} K(x, z)Ai(\frac{z+s}{2})Ai(\frac{s+y}{2})dzds$$
(D.7)

where  $y \ge x$ ,  $\sigma = \pm 1$ , and r is a parameter. Under the condition that  $z \rightarrow \infty$ , W behaves like the Airy function:

$$y(z;r) \approx rAi(z)$$
 (D.8)

Under the condition that  $k_c \rightarrow 0$ , the shape equation (Eq. 5.26) behaves like an inhomogeneous Airy function, y'' = zy + a.

Figure D-1 and Figure D-2 clearly show the comparison between the dimensionless curvature of the liquid crystal membranes and the Airy transformations that can be defined as a family of functions:

$$\omega_{\alpha}(s) = \frac{c_1}{\alpha} Ai(\frac{s}{\alpha} + \frac{c_2}{\alpha}), \ \alpha \in \Box$$
 (D.9)

 $C_1$  and  $C_2$  are coefficient to be determined. We can readily realize that Airy functions are a good approximation for the membrane curvature.



**Figure D-1.** Comparison between scaled curvature of a liquid crystal membrane (stomatocyte morphology) and the Airy function.



**Figure D-2.** The comparison between scaled curvature of a liquid crystal membrane (undulate morphology) and Airy function.

# **References** (Appendices)

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