STATE UNIVERSITY OF MARINGÁ CENTER OF EXACT SCIENCES DEPARTAMENT OF PHYSICS DOCTORAL THESIS

**Renan Lafayete Biagio** 

## A Study of Pattern Formation in Confined Cholesteric Samples by Monte Carlo Simulations

Advisor: **Rafael Soares Zola, PhD** Co-advisor: **Rodolfo Teixeira de Souza, PhD** 

Maringá, February 2020.

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## A Study of Pattern Formation in Confined Cholesteric Samples by Monte Carlo Simulations

Doctoral thesis submitted to State University of Maringá in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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Maringá, February 2020.

Dados Internacionais de Catalogação-na-Publicação (CIP) (Biblioteca Central - UEM, Maringá - PR, Brasil)

Г

B576s	Biagio, Renan Lafayete A study of pattern formation in confined cholesteric samples by Monte Carlo simulations / Renan Lafayete Biagio Maringá, PR, 2020. 135 f.: il. color., figs., tabs.
	Orientador: Prof. Dr. Rafael Soares Zola. Coorientador: Prof. Dr. Rodolfo Teixeira de Souza. Tese (Doutorado) - Universidade Estadual de Maringá, Centro de Ciências Exatas, Departamento de Física, Programa de Pós-Graduação em Física, 2020.
	1. Método de Monte Carlo. 2. Cristais líquidos colestéricos. 3. Gotas colestéricas. 4. Potencial aditivo de Luckhurst. 5. Modulação espontânea. I. Zola, Rafael Soares, orient. II. Souza, Rodolfo Teixeira de, coorient. III. Universidade Estadual de Maringá. Centro de Ciências Exatas. Departamento de Física. Programa de Pós-Graduação em Física. IV. Título.
	CDD 23.ed. 530.429

Elaine Cristina Soares Lira - CRB-9/1202

### **RENAN LAFAYETE BIAGIO**

### A STUDY OF PATTERN FORMATION IN CONFINED CHOLESTERIC SAMPLES BY MONTE CARLO SIMULATIONS

Tese apresentada à Universidade Estadual de Maringá, como requisito parcial para a obtenção do título de doutor.

Aprovado em: Maringá, 27 de fevereiro de 2020.

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Dedicated to my parents.

## Acknowledgments

I thank God for the gift of life and for all the opportunities He has given me.

I thank Capes and CNPq for the financial support.

I shall acknowledge my advisor, professor Rafael Soares Zola, for all the support, patience, conversations, advice and incentives given throughout the PhD process. I'll take it with me for a lifetime!

I would also like to thank my co-advisor, professor Rodolfo Teixeira de Souza, for all the support, patience and teachings transmitted for the developments in simulations.

I would like to give special thanks to professor Luiz Roberto Evangelista for providing great support during the master's and PhD days, and advice on the conferences I was able to attend.

I thank all the professors in my thesis committee for accepting the invitation.

I thank my parents, Pascoal and Selma, for everything. I have no words to describe all things they did for me without any effort.

I thank all my friends for their support and conversations on this journey. Long years my friends!

I thank professor Cristina Mott Fernandez for all the support and work she has done in correcting and revising English. Thank you for all the conversations.

## Abstract

A study of pattern formation in confined cholesteric samples by Monte Carlo simulations is performed. It is carried out by approaching the local director as a headless spin, respecting the symmetry property of nematics. The supramolecular architecture of cholesterics is obtained by interacting the directors via the Metropolis-Hasting algorithm to find energetically favorable configurations randomly drawing accessible microstates. The spins energy is evaluated according to the Hamiltonian proposed by the Luckhurst model for cholesterics, a pairwise additive potential including the chirality as parameter. The director profile is studied by taking snapshots of configurations in the lattice and observing simulated textures, produced by the Müller matrix method, to compare with experimental results. Different kinds of configurations can appear along the volume depending on the chirality, surface anchoring, elastic constants and external influences. In a hybrid aligned cell, the surface anchoring energy is crucial to determine the director field. A variety of anchoring energies in the homeotropic substrate is set to investigate the role of surface anchoring energy in the director configuration. Simulations in this confinement show spontaneous modulated pattern formation for intermediate anchoring energies, and structural transitions could be reached by changing the anchoring energy values. The spontaneous modulation also appears in cases of planar anchoring on both substrates. By heating the cholesteric liquid crystal to the isotropic phase, and slightly decreasing the temperature through the isotropic-nematic phase transition, the sample may experience the wetting phenomenon at the surfaces under specific conditions. After the wetting layer reaches a critical thickness, the striped pattern spontaneously takes place in the thin layer. Two different situations of modulated structure are reported both with experiments and simulations: the growing modulation and the developable-modulation. The situation of spherical environments mimicking liquid crystal droplets are also investigated in the simulations by applying thermal quenches. Several sets of elastic constant ratios were analyzed under homeotropic and planar boundaries, considering weak and moderate surface anchoring energy. The thermal quench process is reported to be an efficient technique to reach stable and metastable states by the simulation perspectives, for whatever choice of anchoring energies.

**Key-words:** Monte Carlo simulations, cholesteric liquid crystals, Luckhurst pairwise additive potential, spontaneous modulations, cholesteric droplets.

## Resumo

Um estudo da formação de padrões em amostras de colestéricos confinados é realizado por simulações de Monte Carlo. Tal estudo é realizado aproximando o diretor local como um spin, respeitando as propriedades de simetria dos nemáticos. A arquitetura supramolecular dos colestéricos é obtida pela interação dos diretores via algoritmo Metropolis-Hasting para encontrar configurações energeticamente favoráveis sorteando aleatoriamente microestados acessíveis. A energia entre os spins é calculada de acordo com a Hamiltoniana porposta pelo modelo de Luckhurst para os colestéricos, um potencial aditivo entre pares que inclui a quiralidade como um parâmetro. O perfil do diretor é estudado por figuras das configurações na rede e observando as texturas simuladas, produzidas pelo método das matrizes de Müller, para comparar com resultados experimentais. Diferentes tipos de configurações podem aparecer ao longo do volume, dependendo da quiralidade, ancoramento da superfície, constantes elásticas e influências externas. Em uma célula híbrida, a energia de andoramento da superfície é crucial para determinar o campo do diretor. Várias energias de ancoragem no substrato homeotrópico são definidas para investigar o papel da energia de ancoramento da superfície na configuração do diretor. Simulações neste confinamento mostram formação espontânea de padrões modulados para energias de ancoramento intermediárias, e transições estruturais podem ocorrer alterando os valores da energia de ancoramento. A modulação espontânea também aparece nos casos de ancoramento plana em ambos os substratos. Aquecendo o cristal líquido colestérico até a fase isotrópica e diminuindo suavemente a temperatura através da transição de fase isotrópicanemática, a amostra pode sofrer o fenômeno de molhamento nas superfícies sob condições específicas. Após a camada de molhamento atingir uma espessura crítica, o padrão de listras surge espontaneamente na camada fina. Duas situações diferentes de modulação são relatadas com experimentos e simulações: a "growing-modulation" e a "developable-modulation". A situação de confinamentos esféricos que imitam gotas de cristal líquido também é investigada nas simulações usando o resfriamento térmico. Vários conjuntos de razões de constantes elásticas foram analisadas em ancoramentos homeotrópicos e planares, considerando energias de superfície fraca e moderada. O processo de resfriamento térmico é relatado como uma técnica eficiente para alcançar estados estáveis e metaestáveis pelas perspectivas da simulação, para qualquer escolha de energias de ancoramento.

**Palavras-chave:** Simulações de Monte Carlo, cristais líquidos colestéricos, potencial aditivo entre pares de Luckhurst, modulações espontâneas, gotas colestéricas.

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## **List of Abbreviations**

BS	bipolar structure
bTBS	bent-TBS
CLCs	cholesteric liquid crystals
CPL	circularly polarized light
DSS	diametrical spherical structure
FC	focal conic
GH	Gruhn-Hess
НТР	helical twisting power
LdG	Landau-de Gennes
LH	lying helix
LL	Lebwohl-Lasher
LPL	linearly polarized light
LS	Lyre structure
MH	Metropolis-Hasting
MS	Maier-Saupe
PBS	planar bipolar structure
POM	polarizing optical microscope
RP	Rapini-Papoular
RSS	radial spherical structure
SH	standing helix
TBS	twisted bipolar structure
ULH	uniform LH
YS	Yeti structure

# **List of Symbols**

$\Delta \varepsilon$	dielectric anisotropy
n <sub>eff</sub>	effective refractive index
$\vec{E}$	electric field
γ	extrapolation length
G	Gibbs free energy
h <sub>eff</sub>	effective molecular field
Η	Hamiltonian of the system
H <sub>mf</sub>	Hamiltonian of mean-field
С	concentration of dopant
ε	exchange energy parameter
k <sub>B</sub>	Boltzmann constant
$\overleftarrow{M}$	Müller matrix
$\Delta n$	optical anisotropy
S	orientational order parameter
Ζ	canonical partition function
δ	phase difference
$arPsi_{jk}$	interaction energy between a pair of neighbor molecules
р	natural pitch of cholesteric
$T^*$	scaled temperature
$T_{IN}^*$	isotropic-nematic transition temperature
$\mathrm{d}arOmega$	solid angle
$c_h$	specific heat at constant external field
$\vec{S}_{inc}$	normalized incident Stokes vector
Т	temperature of the system
$\vec{k}$	wave vector

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## Chapter 1

### Introduction

Understanding liquid crystals (LCs) director fields in complex confination systems can be advantageous for efficiently applying them in several burgeoning technological applications. Such configurations are the ones that minimize the system's free energy density. Determining the aforesaid supramolecular architecture can be a challenging task due to the complex math needed to describe the system. In the past years, finding numerical solutions for self-consistent equations within theoretical models has been a useful tool to solve such problems. In many cases, an alternative solution could be obtained by treating molecular behavior as interacting spins, under an effective potential, in a discretized lattice. To put it differently, the system discretization can exchange a many interacting body system into a many independent body system. The elastic energy density of an achiral nematic, given by the expression proposed by Frank [1], was firstly discretized in the isotropic elastic form by Lebwohl and Lasher [2], and in an explicit elastic constant manner under the influence of an external field by Gruhn and Hess [3]. Since then, the anisotropic potential was parameterized in terms of splay, twist and bend elastic constants by Romano [4]. Besides nematics, cholesteric liquid crystals (CLCs) have several industrial applications, such as supertwisted nematic displays. The anisotropic potential extension with the inclusion of a chiral term also allows to efficiently simulate CLCs devices [5]. However, there are many open problems concerning the use of simulation models unable to connect the elastic constants with the interpretation of results. In addition, the lack of simulations using models considering the temperature as the director fluctuation controller drives the interest in the studies here realized.

In Chap. 2, we present the fundamental concepts of nematic and CLC phase, as well as significant properties to explore molecular interactions by a pairwise potential. The Ising model is briefly commented to introduce concepts of spins located in a discretized lattice and interacting by a pairwise potential. Finally, we describe the extension for spins representing nematic directors in the lattice model, their pairwise interaction being connected with splay, twist, and bend elastic constants, and the chiral term to represent cholesteric interactions.

Behaviors such as phase transition in LCs are extensively studied by numerical models. One of them, which has been potentially used for LCs, is the Monte Carlo (MC) method. In physical science, this method consists of calculating observable properties by a probability distribution to obtain numerical results by randomness in deterministic systems.<sup>1</sup> The idea in LCs consists of simulating thermal fluctuations in the system and see how it behaves along the changes from state to state. The main goal of this thesis is to use the MC method to study CLCs under different confinements, which are open problems both from the LC point of view and from the MC point of view.

Treated surfaces in contact with LCs can induce a preferred orientation in the director field, consequently changing the bulk organization. If the surface influences the LC directors to keep the perpendicular alignment, the anchoring is said to be homeotropic, while parallel surface alignments are so-called planar anchoring. Different kinds of supramolecular helix structure can be achieved depending on the combinations of surface alignments. Recently, experiments have shown that CLCs under hybrid aligned confinements (planar – homeotropic) spontaneously form a uniform striped pattern along the bulk [6]. With the aim to investigate the surface influence on the LC organization, we studied CLCs in hybrid boundary conditions by means of MC simulations. Experimentally, the thickness of slab to cholesteric pitch ratio  $(d/p_0)$  is fundamental to describe how the stripes will behave, but no deep studies on the role of anchoring energy have been reported to date. According to simulation results, reported in Chap. 3, it is possible to observe a textural transition that depends both on the material's physical parameters and the anchoring strength. Such transition, from planar to a spontaneous striped pattern structure, occurs when the anchoring energy at the homeotropic surface reaches a critical value  $J_{crit}$ . Moreover, the oscillation amplitudes of directors immediately below the top surface changes with anchoring energy and with the physical parameters of the liquid crystal host.

CLCs feature a structural director arrangement in the form of a helix throughout the volume. The control of this helix is often difficult, however, under certain experimental conditions it is possible to orient them with a purpose, either by applying an electric field or changing the anchoring conditions of the substrates, for example. Cholesterics confined between two substrates (typically called slab) form a system in which the symmetry is broken by surfaces. If such surfaces are treated with materials that favor high LC ordering when in contact with them, a type of anchoring may arise according to the their treatments. After cooling, it provides that the cholesteric phase takes place at the surface, creating a system which has three interfaces, the solid-isotropic phase, the solid-cholesteric phase and the cholesteric phase, the wetting phenomenon can emerge due to the preferred surface alignment, and there is no more contact between the cholesteric phase and the substrate tends to zero. As a consequence, a phase separation is induced by the surface treated with planar anchoring. In this case, the more ordered phase appears at the substrates due to the higher affinity with the surface material.

<sup>&</sup>lt;sup>1</sup>A system is considered deterministic if its development is not random and the final properties are the same, independent of initial conditions.

So, after the wetting phenomenon, a phase confined between the isotropic phase (generating a tilted weak anchoring) in the sample volume and the substrates (strong planar anchoring) may appear. If the temperature keeps decreasing, the ordered phase continues to get thicker, since the isotropic phase looses space. After the thickness grows and reaches a critical value, which may depend on the cholesteric pitch, a dynamic, rotative temperature-dependent striped pattern appears and changes the orientation of the induced layer. Such modulated pattern takes place due to the chiral nature of the LC, the weak and inclined anchoring at the interface (which separates the nematic and isotropic phases), and the elastic anisotropy present in the material [7]. We report in Chap. 4 novel experimental and simulation results showing two different manners of stripes emergence after wetting phenomenon when transiting the sample from isotropic to chiral phase. They are named growing and developable modulation.

The striped pattern is not limited just to rectangular confinements, usually used for display applications, but it stretches far beyond manifesting in spherical geometries like droplets. Unlike the cases in which the LC is confined between rigid surfaces, the droplets generally take spherical shape when dispersed in aqueous solution, for example. In this case, the boundaries between the drop and the external environment form an interface offering a certain type of alignment. The inner structure must be governed by a subtle balance between several factors, such as elasticity, chirality, in addition to the type of spherical interface anchoring. Due to the sensitive for physical and chemical interactions at the interface, CLCs change the optical configuration allowing them to work as biosensors [8,9]. One of most important factors in LC ordering is the temperature, since thermal quenches can be used to achieve supramolecular architecture remote control. There are few experiments that link thermal quenching with chirality, surface alignment and anchoring energy [10, 11]. Furthermore, understanding the mechanism that governs droplet relaxation to a specific stable states is still an open problem. Recently, simulations using the Landau-de Gennes (LdG) model found stable states in planar droplets for different cholesteric pitch values. On the other hand, stable structures were found to change according to surface anchoring energy variations. In droplets with homeotropic alignment, only metastable states have been observed in quenching process. In order to address this gap in the literature, we report in Chap. 5 MC simulations of thermal quench process reaching stable and free-standing metastable states by considering a pairwise additive interaction between directors in the bulk. Also, a wealth of stable states may appear by changing the LC elastic constants in droplets with intermediate chirality.

Briefly summarizing, we discuss in Chap. 2 the main properties of nematic and cholesterics to analyze LCs near molecular level. In Chap. 3, we study the results for simulations of CLCs confined in hybrid cells, observing the role of surface anchoring energy at the bulk. In Chap. 4, we report two different modulations in experiments and demonstrate them occurring in simulations. Also, thermal quench simulations in CLC droplets setting several combinations of interface anchoring, elastic constants and chirality is described in Chap. 5. Finally, in Chap. 6, we join the main observed aspects on the chiral pairwise additive potential performance in the studied simulations.

## Chapter 2

## **Elementary Concepts**

Phase transition and critical phenomena are common events extensively present in nature. Generally, a system behavior is described by thermodynamic quantities, which bring information such as the state of matter, including stable states. These quantities can be related to specific features of the physical system which depend on the range of microscopic interactions [12].

Furthermore, it can be useful to relate the macroscopic behavior to the microscopic one. In this case, the connection can be given by the canonical partition function (Z), which measures the number of accessible microstates in the system, supplying a good understanding of statistical properties describing systems in thermodynamic equilibrium. There are a few physical systems for which it is quite simple to find an exact solution for Z. On the other hand, if we take LCs as an example, it can be complicated to find an analytical solution. It happens because the degrees of freedom of a LC molecule are enormous due to the continuum of states. Although this bias is a difficult task, the MC method has been used to treat this problem [2, 13–15].

The MC method is a computational algorithm based on a massive random sample to generate numerical results by means of average. There are several methods to produce MC simulations, however for the purpose of this work, we focused only on the Metropolis-Hasting (MH) algorithm, which is a rejection method [16, 17]. As written before, the LC molecule can assume any state in the bulk. So, the reasoning for choosing this algorithm is that the possibility to access a specific state is evaluated according to the Boltzmann distribution. A more detailed description of MH algorithm in the LC shall be given in the next sections.

This chapter is dedicated to present elementary concepts in which this research is based on. In order to understand how the mechanism of simulations works, firstly we introduce the basic properties of nematic and cholesteric liquid crystals (CLCs), followed by the mean-field theory and its applications in Ising model and nematic LCs. For the second part, we describe molecular interaction and how it can be useful to understand macroscopic LC properties and their connection with theoretical and experimental behaviors. Furthermore, interface interactions, light transmission behavior and how to simulate them in a LC media are briefly discussed.

### 2.1 Notions of Liquid Crystalline Phase

Discovered in 1888, LCs were firstly noted by F. Reinitzer during an analysis of cholesteryl benzoate, a compound that presented an unusual phase transition with two different melting points between the solid and the liquid phase [18]. Thereafter, O. Lehmann observed that this intermediate phase (mesophase) of the substance showed both mechanical properties of liquids and optical features of crystals [19].

LCs present specific behaviors which resemble crystals due to their elastic and optical anisotropies, besides being light scatterers and, in some cases, reflective materials. Crystalline solids have high positional order structure and the molecules are fixed in a three-dimensional array, as it can be seen in Fig. 2.1-(a). On the contrary, in the LC mesophase, the molecules are not completely fixed and, at the same time, they are not disordered as the gas molecules. Besides positional order, LCs, when under specific conditions, present orientational order because the molecular shape is not spherical, but rather anisometric. A mesophase between solid–isotropic liquid may arise because the organic molecules of LCs are composed of a rigid core and flexible tail [20,21]. Without these two compositions, no orientational order neither intermediate phase would prevail. In a certain instance, the combinations of these orders may lead LCs to be classified in at least three different phases according to G. Friedel: smectic, nematic and cholesteric phases [22]. They are different phases of thermotropic LCs, since phase transitions are mainly driven by temperature [23].

The first classification is the "smectic" phase, where the molecules are ordered side by side pointing to an average direction, in a series of quite flexible layers about one molecule thick distant [24]. The molecules have high orientational order but partial positional one (correlation between the center of mass of the molecules) in the structure [23]. Fig. 2.1-(b) illustrates this phase. In general, such phase is a layered structure with well-defined interlayer spacing, where the interlayer attractions are weak compared with lateral interactions between molecules, allowing the layers to be similar to a two-dimensional liquid [25]. Different from crystals, that possess high positional and orientational orders, smectics have high orientational order but partial positional one (correlation between the center of mass of the molecules) in the structure.

The second great class of LCs is so-called "nematic" phase because of the typical line defects often observed in this mesophase, hence the name, which in Greek means thread. In particular, the most common kind of LC molecule which is composed of a longer axis and two other shorter perpendicular ones are named calamitics. If there is a preference for orientation just in the longer axis, the LC is defined as uniaxial [26].<sup>1</sup> The uniaxial feature happens due to thermal motion producing a high-frequency rotation around the long molecular axis. Here, the lack of positional order in the nematic phase happens because they are found in a temperature higher than the smectic phase.<sup>2</sup> This additional thermal agitation allows the molecules to diffuse

<sup>&</sup>lt;sup>1</sup>For both long and short axes with an orientational tendency, the LC is called biaxial.

<sup>&</sup>lt;sup>2</sup>It implies that nematic phase is less ordered than smectic one.



**Fig. 2.1:** Molecular structures for different phases. (a) Solid crystalline – the molecules are fixed within the lattice. (b) Smectic phase – after increment in temperature, the molecules can diffuse within each layer like 2D liquid. (c) Nematic phase – increasing even more the temperature from the smectic phase, the molecules loose positional order but still have orientational order. (d) Cholesteric phase – the supramolecular architecture forms a helical structure through space; the distance p, known as the pitch, is defined as the required distance in which the helix twists  $360^{\circ}$ .

through the space, decreasing the apparent viscosity of the substance. Despite this, there is still orientational order for the long axis. This phase is schematically represented in Fig. 2.1-(c). The preferred average direction of molecules in a small region is denoted by the unit vector  $\vec{n}$ , the so-called director. Further increments of temperature lead the LCs to the isotropic state where both positional and orientational orders are not present. At this state, the molecular long axis can point to any direction in space with equal probability.

The third class, according to Friedel, is called chiral nematics, also known as cholesterics, because of the similarity with compounds that contain cholesterol molecules. Chirality is remarkable in nature because of the lack of mirror symmetry under rotations or translations, differentiating systems in all length scales, from microscopic to macroscopic levels, biological and chemical systems or even in astronomical scales [27–34]. CLC structure with short pitch (or high twisting ratio) resembles smectics due to the presence of pseudolayered organization. The difference here is that the layers where the molecules are organized rotate along the space. The characteristic distance of  $360^{\circ}$  rotation is defined as the natural pitch of cholesteric (p), shown in Fig. 2.1-(d). In this case, the molecules are arranged systematically with long axes parallel to the layer, but the flexible tail points upward from the layer causing a slight displacement in adjacent layer. It happens because the chiral molecules have a carbon atom with four different bonds that are not in the same plane (although axial chirality also exists in LCs), but



**Fig. 2.2:** (a) Illustration of cholesterol molecule; it is represented by groups of methyl chain (in blue color) dislocated out from the plane of the molecule (black bonds); the CH bonds (in red lines) are below the plane. (b) Typical rod-like LC molecule; its structure is composed by groups which affect the features of supramolecular structure, like the formation of nematic phase (benzene rings) with a linking group (L), the elastic deformations (group X) and the responses to electric field influences (group Y).

forming a tetrahedron [30, 35–37], as illustrated in Fig. 2.2-(a). As a result, the molecules form a helical supramolecular architecture in a mesoscopic region. The helical arrangement is an optical active structure because the electric field vector of linear polarized light is deflected along the helical arrangement rotating the plane of polarization of light traveling perpendicularly to the layers.<sup>3</sup> This peculiar optical characteristic of CLCs happens due to the so-called circular dichroism, which separates light in two components, one rotating clockwise-sense and the other counterclockwise. If a white light passes through the cholesteric material, a dispersion can occur resulting in different colors according to the combination of temperature, angle of incidence of the light beam and the pitch size. So, a specific color of light dispersion can be reached in cholesteric materials by combining these parameters as desired.

#### **Properties of nematics**

A general molecular structure of a typical rod-like LC molecule is illustrated in Fig. 2.2-(b). It is composed of two terminal groups (X and Y), and a linking group L between the ring systems. The rings can be both of benzenes, cyclohexanes or a combination between them. Their presence affects the short range intermolecular force responsible to form the nematic phase. The terminal group X, often called side chain, strongly influences the elastic constants of nematic phase and the phase transition temperatures. On the other hand, the group Y acts for the most part on the dielectric anisotropy ( $\Delta \varepsilon$ ), which dictates the behavior of the threshold voltage.<sup>4</sup> Physically, this voltage goes with the inverse to the square root of  $\Delta \varepsilon$ .

If there is absence of external forces, LCs behaves as a viscous media. Nevertheless, applied torques disturb the orientation in the bulk, so the material tries to elastically restore its preferred direction. These features cause LCs to be classified as viscoelastic materials [38]. Theories for dynamic of LCs were developed by Ericksen and Leslie [39–43]. Distortions in the bulk provided by external influences, like electric field or geometric confinement for example, makes the director  $\vec{n}$  to be position dependent, which means its derivatives are not zero. Frank developed the curvature-elasticity theory [1] for nematic LCs, proposing that the free energy in

<sup>&</sup>lt;sup>3</sup>Materials that rotate the light polarization plane are often called optically active.

<sup>&</sup>lt;sup>4</sup>The threshold voltage is defined as the minimum voltage required to reorient the LC molecules.



Fig. 2.3: Representation of distortions in a nematic sample. (a) Splay, (b) twist and (c) bend type.

a small unit of volume can be written as

$$f = \frac{1}{2}K_{11} \left[\vec{\nabla} \cdot \vec{n}\right]^2 + \frac{1}{2}K_{22} \left[\vec{n} \cdot \left(\vec{\nabla} \times \vec{n}\right)\right]^2 + \frac{1}{2}K_{33} \left[\vec{n} \times \left(\vec{\nabla} \times \vec{n}\right)\right]^2,$$
(2.1)

where the  $K_{ii}$ 's are the elastic constants and  $\vec{n}$  is the director. In fact, the elastic constants, or the curvature components, dictates how much each kind of distortion (splay –  $K_{11}$ , twist –  $K_{22}$  and bend –  $K_{33}$ ) will contribute to the total energy. Fig. 2.3 shows these three kinds of distortion in a nematic media. In addition to dynamical fluidity, optical and mechanical properties, the anisotropy in LC molecules brings electric and magnetic responses, making them easily influenced by external electric and magnetic fields. Besides, LCs are mechanical-stress responsive materials.

#### Cholesterics

Generally speaking, CLCs are nematics with chiral molecules (dopant) dissolved in the LC media.<sup>5</sup> From the mesoscopic point of view, the directors are nematics, but in the macroscopic level its architecture features a helical distortion along the bulk. The pitch p is frequently defined as the distance in which the directors rotate 360°. Arising from optical isomerism, the sense of the pitch rotation depends on whether the dopant molecules are dextrogyres or levogyres. The efficiency of chiral dopants for inducing the twisted order in the media is related to the dopant helical twisting power (HTP). Significant HTP is often found in chiral dopants with structure similar to the host [44]. Considering  $\delta$  as the HTP of the chiral dopant, the magnitude of p, the concentration of dopant (c) and its facility in twisting the superstructure are connected by

$$p = \frac{1}{|\delta|c}.\tag{2.2}$$

Naturally, the minimum energy state for cholesterics demands a smooth distortion in a small region. This finite twist in the curvature-elasticity theory for cholesterics proposed by

<sup>&</sup>lt;sup>5</sup>In some cases, chirality is intrinsic in the material, such as cholesterols, for example.

Frank generates an energetic cost that can be written as [1]

$$f = \frac{1}{2}K_{11} \left[\vec{\nabla} \cdot \vec{n}\right]^2 + \frac{1}{2}K_{22} \left[\vec{n} \cdot \left(\vec{\nabla} \times \vec{n}\right) + q_0\right]^2 + \frac{1}{2}K_{33} \left[\vec{n} \times \left(\vec{\nabla} \times \vec{n}\right)\right]^2,$$
(2.3)

where  $q_0$  is the modulus of wave vector of the CLC helix. Since the helical structure is periodically repeated along a certain direction, as illustrated in Fig. 2.1-(d), a wave vector can be related with the pitch as  $q_0 = 2\pi/p$ . The elastic theory actually depends on the sample size to pitch ratio (L/p). Also, L can be interpreted as the characteristic scale of deformations. Cholesterics that admits  $L/p \ll 1$  are considered weakly twisted (similar to nematics), while  $L/p \gg 1$ is the strongly twisted regime (forming a layered structure similar to smectics) [45].

Depending on the cells microenvironment and the relation L/p, the intriguing helical pattern in cholesterics can generate different kinds of textures. In the intermediate regime of  $L \sim p$  and  $L/p \gg 1$ , the oily streaks edge dislocation can appear. It is a network-like defect line where the directors are not well defined and the lines appear as long bands dividing domains of flat layers. While the lines have a confusing orientation, the big uniform domains are composed of a helical arrangement where the directors rotate around the field of view.<sup>6</sup> For planar anchoring at the surfaces, it suggests that the helix axis is normal to substrates. This configuration is known as Grandjean texture, or standing helix (SH) orientation, and it can be seen in Fig. 2.4-(a). The unclear orientation in oily streaks is due to the mismatch of helix rotation in adjacent domains. On the other hand, boundary conditions like environment or external disturbance may induce other kinds of frequent orientation in directors. When the helix axis lies in-plane, in other words parallel to the substrates, the commonly designated fingerprint configuration takes place in the bulk. This assembly is recognized as the lying helix (LH) orientation or as modulated state. It can be non-uniform, or with high-aligned stripes, as illustrated in Figs. 2.4-(b) and (c).

In addition to the SH and LH equilibrium orientation, there are other common intermediate states for CLCs. One of them is the focal conic (FC) alignment, in which there are many local domains with helical axis approximately parallel to the substrates, but oriented in different directions. In the regime of  $L/p \gg 1$ , or very small pitches, the FC texture appears getting space through the field of view [45].<sup>7</sup> Fig. 2.4-(d) shows this kind of texture. Another one is the Helfrich pattern, shown in Fig. 2.4-(e), where a 2D arrangement is formed by bending the cholesteric layered structure.

Transitions between the states mentioned above are common if an external field is applied on the sample. So, switches from FC to planar structure can be achieved if an electric field acts in the parallel direction of the substrates. The same FC state can change to homeotropic state if the electric field is perpendicular to the substrates.<sup>8</sup> It makes CLCs of great importance

<sup>&</sup>lt;sup>6</sup>The color in the sample depends on the pitch and on the phase retardation.

<sup>&</sup>lt;sup>7</sup>For  $L/p \ll 1$  the cholesteric textures are similar to nematics.

<sup>&</sup>lt;sup>8</sup>In the homeotropic state the directors point parallelly to the normal of substrates while in the planar case, they are parallel to the surface.



**Fig. 2.4:** Common experimental structures (above) with their respective director schematic representation (below). (a) Standing helix (SH) orientation with oily streaks forming wall defects. (b) Non-uniform and (c) uniform finger print textures. (d) Focal conic (FC) domain and (e) the 2D Helfrich pattern where the cholesteric layers are bending in the bulk. Note that in (b) the schematic representation shows the top view of the in-plane cholesteric helix, while the FC illustration in (d) is from a lateral point of view, showing that the helices are not in the plane of substrates. (b) and (e) Reproduced with permission of Zola et al. (2012) [46].)

for technological applications such as displays [47,48], switchable mirrors [49], lasers [50] and so on because they are stimuli-responsive, so their helical arrangement is readily modulated by reacting to external influences [51–68]. One interesting property that is potentially applied in display industries, for example, is the optical activity due to the variation of dielectric tensor along the twisted structure.

#### 2D and 3D helical axis control by different stimuli

Mediated by some boundary conditions, CLCs can rearrange the helix alignment perpendicular to the plane of observation. Changes in the helix assembly are mediated by the energetic balance between elasticity and external influences in the system. Recently, changes in the helical superstructure is burgeoning through different stimuli offering to CLCs the possibility to be used as smart materials. Patterns like grating field can be obtained under the change of confinement size, direct-current field, temperature, and light irradiation [7,57,60,64,69–73], for example. It is worth mentioning that the modulated pattern, or LH state, can appear for hybrid-aligned cells [60]. The sample thickness to pitch ratio d/p plays an important role for the uniform LH orientation in the bulk. Researches have demonstrated that the grating field pattern rotates in relation to the rubbing direction by comparing cells filled with CLCs assuming different values of d/p [60], as shown in Fig. 2.5-(a).<sup>9</sup> Besides that, the easiest form to obtain the uniform LH (ULH) is by applying electric field in the sample [74]. The uniform LH is rotative-responsive when electric field is applied in a cell with modulated pattern.<sup>10</sup> The angle between the stripes and the rubbing direction on the surfaces changes if the voltage increases for a fixed d/p ratio [60], as shown in Fig. 2.5-(b).

Other manner to change the angle of grating field involves temperature [7]. By de-

<sup>&</sup>lt;sup>9</sup>The rubbing direction is the preferred orientation in the substrate with planar anchoring.

<sup>&</sup>lt;sup>10</sup>The electric field is usually applied from one surface to the other due to the glass treatment with ITO.



**Fig. 2.5:** Cholesteric textures showing a controllable grating pattern in slabs (a) with different d/p ratios; (a).i – d/p = 1.5, (b) (a).ii – d/p = 2.2, (a).iii – d/p = 2.5, (a).iv – d/p = 2.7, (a).v – d/p = 3.0 and (a).vi – d/p = 4.0. (b) The direction of helix alignment rotates as the electric field strength changes in a sample where d/p = 2.4. (Lin et al. (2012) [60]. Reproduced with permission of The Optical Society.)



**Fig. 2.6:** (a) Striped pattern controlled by temperature reductions. (Zola et al. (2013) [7]. Reproduced with permission of American Physical Society.) (b) Cholesteric nanomachines controlled by photochemical isomerization; (b).i molecular motor structure, (b).ii-iii striped pattern and its rotation under UV illumination and (b).iv the surface microscopy image of the CLC. (Eelkema et al. (2006) [75]. Reproduced with permission of Nature Publishing Group.)

creasing the temperature of a LC in the isotropic to the CLC phase, a wetting transition occurs if the surfaces are coated with a material which favors the planar ordination. Consequently, a thin layer with size h of chiral nematic assembly appears at each surfaces, growing while temperature decreases. After h/p reaches a critical value the grating field takes place instead of SH orientation. This pattern rotates due to the increasing of layer thickness h followed by further sample cooling. Fig. 2.6-(a) shows its behavior.

Another different configuration for the system, where the LC doped with a fluorenederived molecular motor is trapped between a planar coated surface and the air, shows the ability for CLCs working as nanomachines driven by thermal and also by photochemical isomerization [57].<sup>11</sup> Items thousand times larger than the molecular motor can turn due to this

<sup>&</sup>lt;sup>11</sup>An isomerization process typically happens when a compound is switched to an isomeric form (same atoms with different structure).



**Fig. 2.7:** Reversible process of 3D helical axis control switching under UV and visible light illumination. (a) Schematic illustration of the changing in the helix behavior after shining visible light. (b) Experimental results showing the rotation and the helix unwinding in the bulk, inverting its handedness. (Zheng et al. (2016) [64]. Reproduced with permission of Nature Publishing Group.)

induced helix rotation (Fig. 2.6-(b)). Indeed, the impressive rotational reorganization is intenser for electromagnetic irradiation than for thermal effect. The control over the helical behavior is a challenging task, and the previous commented stimuli are 2D effects, where the grating field dynamically rotates in the plane parallel to the surfaces. A reversible dynamic, remote and 3D manipulation of the helical axis of CLCs has been demonstrated using only light stimulus in the LC E7 doped with a synthesized dithienylcyclopentene-based dopant [64]. Fig. 2.7 shows this dynamical phenomenon. The UV illumination turns the ring-open structure into a ring-closed one changing the chiral dopant conformation, leading to a handedness inversion. Under visible light irradiation the reversible process occurs.<sup>12</sup> When the CLC is filled in a planar cell the SH state appears due to the surface anchoring, then after some seconds of UV illumination, the structure switches for the unwound nematic phase, and then after further seconds the SH arrangement with opposite handedness takes place. The photostationary state is reached around a minute later with the uniform LH orientation. A complete continuous handedness inversion process is illustrated in Fig. 2.7-(b), where the left-handed striped pattern becomes a righthanded LH state achieved by visible light illumination. This effect is exclusively obtained by light, but a coupling of light and electric external field has been recently studied [67], showing a controllable dynamic zigzag pattern, making CLCs candidates for optical elements in photonic circuits.

<sup>&</sup>lt;sup>12</sup>The handedness inversion in the helix is due to the changing in the chiral dopant HTP.

#### Defects in nematics and cholesterics

Defects in LCs are recognized as the regions where the director field suffers abruptly changes [23, 76]. The theories about disclinations, manifested as points or lines, are done to describe the director orientation around points of topological singularities. The defects are often characterized by having an associated strength s, which defines the director rotation angle along a closed path around the undefined orientation [45]. Half-integer strength s nematic disclinations are featured by a  $\pi$  director rotation around a fictitious closed loop, while integer-strength defects makes a  $2\pi$  rotation. The value of strength is obtained by considering the common one-constant approach for the Frank free energy in Eq. (2.1), although it can be a complicate dependence on the elastic constants [77]. Fig. 2.8-(a) shows some common nematic disclinations of positive and negative strength. Similarly, the cholesterics also present discontinuity in



**Fig. 2.8:** (a) Nematic defects with positive and negative, half and integer strength. The strength has positive signal if the directors rotate in the same sense as the closed loop taken around the defect, otherwise, opposite rotation senses make the strength negative. The strength has half-integer or integer value if the total rotation angle of directors is  $\pi$ , or  $2\pi$ , respectively. (b) Common cholesteric disclination lines with positive and negative winding number *s*. Note that the  $\chi$  defect line is perpendicular to the plane of cholesteric layers.

the director field in large scales. For describing the irregularities in cholesterics, it is conventional to adopt three mutually perpendicular directors,  $\vec{\lambda}$ ,  $\vec{\tau}$  and  $\vec{\chi}$ . The  $\lambda$  lines have no core due to their continuous director field, while the  $\tau$  and  $\chi$  disclinations have the core (black points in Fig. 2.8) representing undefined director organization. The vector  $\vec{\lambda}$  is along the director direction  $\vec{n}$ ,  $\vec{\chi}$  is pointed towards the helix direction, and they are related by  $\vec{\tau} = \vec{\lambda} \times \vec{\chi}$  [45,78]. In this case, if two out of three directors make a  $\pi$  rotation around the disclination core, the defect is classified as half-integer strength defect, and  $2\pi$  rotation determines integer-strength disclinations. The  $\lambda^{\pm s}$  defects are considered to be continuous since they are coreless disclinations (there are not escaped configuration). On the other hand, the  $\tau^{\pm s}$  and  $\chi^{\pm}$  defects have core, where the order parameter has low values similar to isotropic phase. Fig. 2.8-(b) illustrates some cholesteric disclinations that can appear in experimental observations. Besides the bulk, irregularities in the director order can also appear at the boundaries of the geometry where the LC is confined. In this case, topological defects that often exist on surfaces of ordered media are named boojum [79].

#### Dielectric and optical anisotropy in the LC media

Different effects may arise when an electric field  $(\vec{E})$  is applied, reorienting the molecules in the bulk due to the presence of natural and induced dipole moments. As the LC is an anisotropic media, the polarization parameters are different depending on the bulk orientation. For the uniaxial symmetry, the dielectric constant along the preferred axis ( $\varepsilon_{\parallel}$ ) is different from the perpendicular axis ( $\varepsilon_{\perp}$ ). It means that there is a dielectric anisotropy, and it is defined as

$$\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}. \tag{2.4}$$

The dielectric contribution to the free energy is

$$f_d = -\frac{1}{2}\vec{P}\cdot\vec{E},\tag{2.5}$$

where  $\vec{P}$  is the polarization in the LC media. In fact,  $\vec{P}$  has a parallel and a perpendicular components [26],

$$\vec{P}_{\parallel} = \varepsilon_0 \chi_{\parallel} \left( \vec{E} \cdot \vec{n} \right) \vec{n}, \qquad (2.6)$$

$$\vec{P}_{\perp} = \varepsilon_0 \chi_{\perp} \left[ \vec{E} - \left( \vec{E} \cdot \vec{n} \right) \vec{n} \right], \qquad (2.7)$$

where  $\chi_{\parallel}$  and  $\chi_{\perp}$  are the dielectric permittivity of the media and  $\varepsilon_0$  is the dielectric constant in the vacuum. As  $\vec{P} = \vec{P}_{\parallel} + \vec{P}_{\perp}$ , then

$$\vec{P} = \varepsilon_0 \Delta \chi \left( \vec{E} \cdot \vec{n} \right) \vec{n} + \varepsilon_0 \chi_\perp \vec{E}.$$
(2.8)

Considering that  $\varepsilon_{\parallel} = 1 + \chi_{\parallel}$  and  $\varepsilon_{\perp} = 1 + \chi_{\perp}$ , which leads to  $\Delta \chi = \Delta \varepsilon$ , and that just the first
term on the right hand side of Eq. (2.8) depends on the director, the contribution on the free energy  $f_d$  can be rewritten as [26]

$$f_d = -\frac{1}{2}\varepsilon_0 \Delta \varepsilon \left(\vec{E} \cdot \vec{n}\right)^2.$$
(2.9)

So, if  $\Delta \varepsilon > 0$ , the directors tend to orient parallel to the electric field trying to minimize the energy, whereas if  $\Delta \varepsilon < 0$  the directors orient perpendicular to  $\vec{E}$ .

It is convenient to understand how light propagates through a LC material. For an isotropic media, light propagates with the same speed v = c/n in any direction, where *c* is the light speed in vacuum and *n* is the refractive index of the material. Light propagation in LCs may behave differently due to the anisotropy present in the medium. Specifically in uniaxial LC media, where the optical axis coincides with the director  $\vec{n}$ , the light beam splits into two rays traveling at different speeds.<sup>13</sup> The reason is that the refractive index along the optical axis has a distinct value compared with the normal to the optical axis. The refractive index attributed along the optical axis is given by  $n_{\parallel}$ , while the other two short axes are related to  $n_{\perp}$ . Fig. 2.9 shows the schematic representation of a linearly polarized light (LPL) passing through a material oriented parallel (a) and (b) perpendicular to the light polarization sense. Similar to dielectric anisotropy, these birefringence properties generate the optical anisotropy ( $\Delta n$ ) defined as

$$\Delta n = n_{\parallel} - n_{\perp}. \tag{2.10}$$

The material is classified as optically positive (negative) if  $\Delta n > 0$  ( $\Delta n < 0$ ). One can observe that for optically positive materials, light propagates faster in the short axes than in the longer one, since  $n_{\perp} < n_{\parallel}$ . The reciprocal situation holds valid. The wave vector ( $\vec{k}$ ) indicates the direction of light propagation.



**Fig. 2.9:** A linearly polarized wave can observe the  $n_{\parallel}$  refractive index if the polarization is (a) parallel to the optical axis or observe  $n_{\perp}$  for (b) polarization perpendicular to the material alignment, in which there are two possibilities. The red lines are the electric field changing as the wave propagates, and the blue line represents the direction of the wave propagation  $\vec{k}$ .

Supposing that there is no free charge in the material, the Maxwell equations show that the electric field of light beam must be always perpendicular to  $\vec{k}$ , lying parallel to the plane of propagation. If light passes through an isotropic media, the electric component is just

<sup>&</sup>lt;sup>13</sup>Biaxial LCs split light in three components, one in each perpendicular axis due to the three different refractive indexes.



**Fig. 2.10:** Indicatrix of an (a) isotropic media, where the refractive index is the same in any direction ( $n_o$  reduces to the refractive index n), and an (b) anisotropic one, like the LC molecules (which slip in two components). (c) Particular case for a plane wave traveling in  $\vec{k}$  direction parallel to z axis, which observes the  $n_o$  refractive index.



Fig. 2.11: Schematic representation for the general propagation of an extraordinary wave, where the direction of propagation  $\vec{k}$  makes an angle  $\theta$  with the optical axis  $\vec{a}$ , observing an effective refractive index  $n_{eff}$ .

influenced by the ordinary refractive index  $n_o$ , regardless the material alignment direction and how the way the electric field vibrates, as illustrated by the indicatrix in Fig. 2.10-(a). For an anisotropic media, if  $\vec{k}$  is parallel to the material orientation, no matter where the electric field is, in the plane of propagation, the refractive index influencing the electric field will be just  $n_o$ . In the perpendicular propagation,  $n_e$  or  $n_o$  can influence the light performance depending on the direction in which the electric field oscillates [45, 80], as shown in Fig. 2.10-(b) and (c). The phase difference ( $\delta$ ) generated between the two rays in a general case, where  $\vec{k}$  and the material orientation represented by  $\vec{a}$  makes an angle  $\theta$ , as illustrated in Fig. 2.11, is given by [21,45]

$$\delta = \frac{2\pi}{\lambda} \left( n_{eff} - n_o \right) d, \qquad (2.11)$$

where  $\lambda$  is the vacuum wavelength, *d* is the sample thickness and  $n_{eff}$  is the effective refractive index influencing light propagation. According to Fig. 2.10-(b), using the relation  $k = n_{eff}\omega/c$ , and considering that the electric field components of the wave vector  $k_x$  and  $k_y$  "feel" the refractive index  $n_e$ , while  $k_z$  is influenced by  $n_o$ , the ellipse equation allows us to rewrite the

relation for the effective refractive index  $(n_{eff})$  as [81]

$$\frac{k^2}{n_{eff}^2} = \frac{k_x^2 + k_y^2}{n_e^2} + \frac{k_z^2}{n_o^2}.$$
(2.12)

By geometrical relations,

$$\sin \theta = \frac{\sqrt{k_x^2 + k_y^2}}{k}, \ \cos \theta = \frac{k_z}{k}$$

So, it is possible to find that

$$n_{eff} = \frac{n_o n_e}{\sqrt{n_o^2 \sin^2 \theta + n_e^2 \cos^2 \theta}}.$$
(2.13)

If a nematic sample is observed between crossed polarizers, and  $\beta$  is the angle between the polarizer and the optical axis of the material, the normalized intensity of the transmitted light when  $\vec{k}$  and  $\vec{a}$  are arbitraries, like sketched in Fig. 2.11, is given by [45]

$$I = \sin^2 \left(2\beta\right) \sin^2 \left[\frac{\pi d}{\lambda} \left(\frac{n_o n_e}{\sqrt{n_o^2 \sin^2 \theta + n_e^2 \cos^2 \theta}} - n_o\right)\right].$$
 (2.14)

#### **Optical properties of cholesterics**

The optical properties of cholesterics are quite different from nematics and there is a relation between the pitch p and the light wavelength  $\lambda$ . Notably, p is much larger than the molecular dimension and light transmission properties can be dictated by three kinds of regimes. Firstly, for cases where  $p \gg \lambda$ , known as Mauguin limit, the cholesteric behaves as a thin nematic where light is transmitted by rotating through the helix. This is the regime which happens for twisted-nematic displays.<sup>14</sup> Due to the molecule anisotropic nature and the continuous rotation of the director  $\vec{n}$ , cholesterics can act as one-dimensional Bragg reflectors if the pitch is comparable with the light wavelength passing through the sample,  $(p \sim \lambda)$ . It is known as photonic bandgap which may exist only for circularly polarized light (CPL) with the same handedness of helix rotation sense. To put it differently, the photonic bandgap is a narrow region in the light spectrum in which polarized light with the same rotation sense of the helix is reflected [23, 82]. Polarized light in opposite handedness of helix is completely transmitted because the instantaneous component of electric field in the light is not identical to the cholesteric helix shape [23]. By means of Maxwell's equations, both theoretical and experimental studies could be combined to explain this phenomena in a certain group of LC [83, 84], mainly found in derivates of cholesterol. Considering normal incidences for the light, the maximum reflectivity of an incident CPL in a sample with thickness described by l is given by [26]

$$R_{max} = \tanh^2 \left[ \pi \Delta n \frac{l}{\lambda_{max}} \right], \qquad (2.15)$$

<sup>&</sup>lt;sup>14</sup>In a typical twisted-nematic display, the surfaces with planar anchoring are with the rubbing 90° twisted.

where the maximum wavelength is written as [26, 85]

$$\lambda_{max} = p\langle n \rangle = p \frac{(n_e + n_o)}{2}, \qquad (2.16)$$

where  $\langle n \rangle$  is the refraction index average. The main responsible wavelengths for determining the region of wide plateau in Bragg reflection are determined by  $\lambda_o = pn_o$  and  $\lambda_e = pn_e$ . So the width of reflection band is

$$\Delta \lambda = p \Delta n. \tag{2.17}$$

Cases of light oblique incidence have some quite different features. It causes a displacement of maximum Bragg reflexion and emergence of high order reflections with complicate spectral and angular dependence [25, 82]. Although the changes in theory are not simple, the oblique incidence is useful for studying polydomain planar structure [23]. Finally, the third case where  $p \ll \lambda$ , the light is again transmitted as if it was in an isotropic media with speed  $c/\langle n \rangle$ . CLCs become unique materials in nature with high variety of applications for presenting such a diversified optical properties.

To briefly summarize, LCs are anisotropic media that present optical, electrical and mechanical properties which allow them to be applied in many optical devices beyond LCDs. Such properties are better understood if the order in the medium is well described. Previously mentioned, the Frank elastic theory indicates the energetic cost of nematic LCs distorted in the space. An alternative form of energy is described by the Landau theory, where the energy is expanded in terms of the system order and predicts first and second order phase transitions [86]. Second-order transitions are characterized by continuous change of the order while phase transition occurs, for example the transition between paramagnetic and ferromagnetic phases. The LC medium is composed by molecules which interact via van der Waals potential. Considering the molecules such as represented in Fig. 2.2, they have anisotropic shape. It implies that the interaction is anisotropic and the molecules may arrange the longer axis in a different form of the shorter axes. The average under a considerable number of molecules may bring information such as the order in a small region in the volume. Such information can be better understood by molecular theories, such as the theory of Maier and Saupe linked with mean-field approximation. To make it easier to understand the molecular order in the system, the next section will introduce the mean-field theory and explore its applications in LCs.

### 2.2 Mean-field theory

The mean-field theory provides, in a first approach, great results to explain critical phenomena like phase transition by introducing an orientational order parameter (S). For LCs, the molecules tend to be oriented at the same direction of their neighbors. For this reason, in a mesoscopic perspective, we can represent, on average, an specific direction represented by a

vector named "director". Notably, the nematic phase in LC possesses a high orientational order of directors over the space in the bulk, but it does not happen when the LC is in the isotropic phase, where the molecules are totally disordered [26].

The procedure to develop the theory is made up of some fundamental steps. Hamiltonians of molecular systems are not quite simple to be used for analytical purposes. One of the reasons is that larger systems usually have impracticable solutions for desired physical quantities. The first step is to approximate the many interacting-body problem in a system of many independent interactions of the same type. Then, if one knows how to solve the calculus for a unique independent Hamiltonian, it is possible to extend the results for the whole system. It is convenient to notice that in the linearization, the fluctuations which arise by the transformations accomplished are neglectable. The unknown inserted parameters are now obtained by the self-consistency relation. To put it differently, it is possible to find out the mean of the unknown quantity in terms of a complicated self-consistent function and consequently to estimate its value. Superconductors and LCs are physical examples of a successful description of phase transition by the self-consistency relation coming from the mean-field theory [87].

#### Ising model

Before coming to details concerning the order in LCs, it is convenient to study the Ising model, a simpler system from the accessible states point of view. Although its complexity seems small, the analytical solution for phase transition is known for just one- [88] and two-dimensions [89, 90]. The three-dimensional case is still open despite efforts already made [91, 92]. Nevertheless, numerical methods have been used to estimate the nature of phase transition for the 3D case [93]. For the aim of this study just the unidimensional case will be discussed here.

The Ising model is constituted by *N* spins localized in sites of a *d*-dimensional lattice. Each one of them can adopt just one of the two accessible states available, the up state or the down one. The variable  $\sigma_i$  contains the information about how the spin is situated in the *i*-th position of lattice. If the *l*-th spin is in the up state,  $\sigma_l$  receives the value +1, while the down state assumes -1. Supposing the spins are distributed with random values ±1 in the lattice. The affinity between two neighbor spins *i* and *j* is represented by the interaction energy  $J_{ij}$ . In this case, it is equal for any pair of interaction, or merely  $J_{ij} = J$ . If the spins tend to be oriented in the same state as their neighbors, the system has a ferromagnetic ordination and J > 0. For J < 0, the state is anti-ferromagnetic. Supposing that an external field with intensity *h* is presented in this paramagnetic system, the total Hamiltonian of the system (*H*) can be written as

$$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_{i=1}^N \sigma_i.$$
(2.18)

The first summation comes from the nearest-neighbor sites and the second one includes the couple spin-external field.

The model statistical mechanics can be developed considering the canonical partition function Z(T, h, N) given by

$$Z_N(T,h) = \sum_{\{\sigma_i\}} e^{-\beta H}$$
(2.19)

$$= \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \sum_{\sigma_3=\pm 1} \dots \sum_{\sigma_N=\pm 1} \exp\left(\beta J \sum_{\langle i,j \rangle} \sigma_i \sigma_j + \beta h \sum_{i=1}^N \sigma_i\right), \quad (2.20)$$

where the sum in Eq.(2.19) is over the combination of all accessible states of the system. The Boltzmann constant ( $k_B$ ) and the temperature of the system (T) are included in  $\beta = 1/(k_B T)$ .

It must be remembered that in this physical problem both entropy and magnetization are extensive parameters while temperature and external field are intensive ones.<sup>15</sup> According to Legendre transformations, each extensive parameter has one intensive conjugate. As Z is external field- and temperature-dependent,<sup>16</sup> the connection to thermodynamics comes with Gibbs free energy (G)

$$G(T,h) = -k_B T \ln Z_N(T,h),$$
 (2.21)

in which the magnetization of the system per spin is given by the state equation

$$m(T,h) = -\left(\frac{\partial g}{\partial h}\right)_T.^{17}$$
(2.22)

Taking the limit of zero external field, the quantity above gives m(0, T) entitling the spontaneous magnetization of the system. The challenge is to find out an analytical expression for *Z*. Several approaching techniques have been elaborated to succeed in obtaining a result. Some of them are not relatively complicated and can acceptably describe the quantitative behaviors. One specific technique that makes it possible to find the exact solution for unidimensional case is the matrix formalism defining a transfer matrix for *Z*, for example.

At this instance, after expanding the summation in Eq. (2.20), it is possible to rewrite  $Z_N$  as hyperbolic functions. Using Eq. (2.21), g is found to be

$$g(T,h) = -\frac{1}{\beta} \ln \left[ e^{\beta J} \cosh\left(\beta h\right) + \sqrt{e^{2\beta J} \cosh^2\left(\beta h\right) - 2\sinh\left(2\beta J\right)} \right], \qquad (2.23)$$

and consequently,

$$m(h,T) = \frac{\sinh\left(\beta h\right)}{\sqrt{\sinh^2\left(\beta h\right) + e^{-4\beta J}}}.$$
(2.24)

From Eq. (2.23), it is possible to obtain an expression that explains the behavior of the specific

<sup>&</sup>lt;sup>15</sup>Extensive parameters depend on the size of each part in the system, while the intensive ones have the same value.

<sup>&</sup>lt;sup>16</sup>Both external field and temperature are intensive parameters.

<sup>&</sup>lt;sup>17</sup>Here, g represents the Gibbs free energy density. The Helmholtz free energy density is obtained by the transformation f(T, m) = g(T, h) + mh. The other state equation provides the entropy  $s(T, h) = -(\partial g/\partial T)_h$ .

heat at constant external field  $(c_h)$ , but it is not able to explain the ferromagnetism because m(0,T) furnishes trivial solution.<sup>18</sup>

#### Mean-field method

The mean-field method, known as Bragg-Williams method [94], is a molecular field approach which presupposes disregarding fluctuations in the dynamic variables  $\sigma_i$  and  $\sigma_j$ . The Hamiltonian in Eq. (2.18) is bilinear in  $\sigma$ . The mean-field approach allows the linearization in  $\sigma$ . Supposing the variance in  $\sigma$  is negligible, so

$$(\sigma_i - \langle \sigma_i \rangle)(\sigma_j - \langle \sigma_j \rangle) \approx 0, \tag{2.25}$$

or simply,

$$\sigma_i \sigma_j \approx \langle \sigma_j \rangle \sigma_i + \langle \sigma_i \rangle \sigma_j - \langle \sigma_i \rangle \langle \sigma_j \rangle.$$
(2.26)

Due to translational invariance,  $\langle \sigma_i \rangle = \langle \sigma_j \rangle = \langle \sigma \rangle$ , the Hamiltonian of mean-field  $(H_{mf})$  can be rewritten as

$$H_{mf} = -(zJ\langle\sigma\rangle + h)\sum_{i=1}^{N}\sigma_i + \frac{1}{2}zNJ\langle\sigma\rangle^2.$$
(2.27)

The summation  $\sum_{\langle i,j \rangle}$  over the first neighbors in Eq.(2.18) can be written as  $\frac{1}{2}z \sum_{i=1}^{N}$ , where z is the number of first neighbors and the factor 1/2 appears to avoid repeated counting. The term multiplying the summation can be understood as the effective molecular field ( $h_{eff}$ ) that the neighbors make over the *i*-th spin. If the Eq.(2.27) is rewritten just with one summation, we have

$$H_{mf} = \sum_{i=1}^{N} \left( -h_{eff} \,\sigma_i + \frac{1}{2} z J \langle \sigma \rangle^2 \right) = \sum_{i=1}^{N} H_i.$$
(2.28)

It is important to realize that by the process of linearization,  $H(\sigma_i, \sigma_j)$  becomes  $H(\sigma_i)$ . This technique changes a Hamiltonian of interacting kind (Eq. (2.18)) to a system of N independent Hamiltonians (Eq. (2.28)). The problem consists of exchanging the interaction field of molecules by N of them being influenced by a new mean field, excluding their own. The penalty for this is the introduction of a new unknown variable  $\langle \sigma \rangle$ .

Furthermore, in a system of independent Hamiltonians, Z can be written as  $Z_0^N$  where  $Z_0$  is the partition function of only one spin. The Gibbs free energy in Eq. (2.21) furnishes

$$G(T,h) = N\left(\frac{1}{2}zJ\langle\sigma\rangle^2 - \frac{1}{\beta}\ln\left[2\cosh\left(\beta(zJ\langle\sigma\rangle + h)\right)\right]\right).$$
(2.29)

Evaluating the average in the ensemble of  $\langle \sigma \rangle$ , we find

$$\langle \sigma \rangle = \langle \sigma_i \rangle = \frac{1}{Z} \sum_{i=1}^{N} \sigma_i e^{-\beta H_i} = \tanh \left[\beta \left(zJ \langle \sigma \rangle + h\right)\right].$$
(2.30)

<sup>&</sup>lt;sup>18</sup>The specific heat at constant external field is  $c_h = T (\partial s / \partial T)_h$ .

Based on the definition of magnetization, the state equation (2.22) gives

$$m = \tanh\left[\beta\left(zJ\langle\sigma\rangle + h\right)\right]. \tag{2.31}$$

Thus, it is possible to explain  $\langle \sigma \rangle$  as being the average magnetization of the system, and finally,

$$m = \tanh\left[\beta\left(zJm + h\right)\right],\tag{2.32}$$

which is a self-consistence relation. After a detailed analysis, this result shows solutions for  $m \neq 0$ , even in the absence of external field and therefore, the existence of spontaneous magnetization under some conditions around critical temperature. Furthermore, the energy density and its first derivative are continuous functions, but the specific heat represented by the second derivative presents a discontinuous behavior surrounding the region of phase transition.<sup>19</sup> Indeed, the Bragg-Williams method can explain ferromagnetism and can predict a discontinuity for the specific heat, but it fails when explaining critical exponents that displays universal features. Two years after the Bragg-Williams theory, R. Peierls discovered that the Ising theory for ferromagnetism [88] and a more sophisticated Bragg-Williams model proposed by Bethe [95] were equivalent [96].<sup>20</sup>

#### **Maier-Saupe theory**

After the Ising model has been briefly discussed, it is possible to point out how the LC behaves, and similarly to develop a mean-field theory, accomplished by Maier and Saupe [97, 98]. Some features of uniaxial LCs need to be considered. Differently from the Ising model, where the spins could reach just two accessible states, the calamitic molecule can point out to any direction in the continuum space. If the temperature is high enough to allow changes in the LC phase, the molecules loose their preferred ordination presented in the nematic phase, behaving as an isotropic liquid. Properties like anisotropy or sensible responses to external electro or magnetic fields can be understood by the introduction of the orientational order parameter. The order is lost in isotropic phase, but is non-zero in the nematic phase. Besides, the rod-like molecules may have permanent dipoles. Considering the region which defines the director, the number of dipoles pointed to the same sense to  $\vec{n}$ , is practically the same of the ones pointed to the sense of  $-\vec{n}$ . So, the properties of  $\vec{n}$  must be equivalent to  $-\vec{n}$  (non-polar). An order parameter which satisfies all the previous discussed conditions and is non-polar was proposed by Tsvetkov [99] as

$$S = \langle P_2(\cos\theta) \rangle = \frac{1}{2} \left( 3 \langle \cos^2\theta \rangle - 1 \right), \tag{2.33}$$

where  $P_2$  is the second-order Legendre polynomium and  $\theta$  is the angle between one specific molecule pointed to a direction  $\hat{a}$  and the average molecular direction in the same region dictated

<sup>&</sup>lt;sup>19</sup>These conditions for derivatives are characteristics of second-order phase transition.

<sup>&</sup>lt;sup>20</sup>The Bethe model is an enhanced version of Bragg-Williams theory for order-disorder transitions in alloys with Bravais lattice.

by  $\vec{n}$ .

Let  $\rho(\theta, \phi)$  be the orientational distribution function of  $\hat{a}$ . The probability of finding one molecule with an angle in the range  $\theta$  and  $\theta + d\theta$  and with azimuthal angle between  $\phi$  and  $\phi + d\phi$  is given by

$$dP = \rho(\theta, \phi) d\Omega, \qquad (2.34)$$

where the derivative is considered over the solid angle  $(d\Omega)$ . So,

$$S = \langle P_2(\cos\theta) \rangle = \int d\Omega \,\rho(\theta,\phi) P_2(\cos\theta) \bigg| \int d\Omega \,\rho(\theta,\phi).$$
(2.35)

It is important to realize that for the isotropic phase, the molecules have equal probability to point to any direction, so  $\rho(\theta, \phi)$  is a constant and *S* becomes zero. For uniaxials, there may be no preferential distribution for azimuthal angle, then  $\rho(\theta, \phi) = \rho(\theta)$  and the order parameter reduces to

$$S = \int_0^{\pi} d\theta \sin \theta \rho(\theta) P_2(\cos \theta) \bigg| \int_0^{\pi} d\theta \sin \theta \rho(\theta).$$
(2.36)

The Maier-Saupe (MS) theory is a molecular field or mean-field treatment which predicts the orientation of nematics. It is based on a weakly anisotropic long-range interaction potential. The long-range orientational order is annihilated in isotropic phase, so this effective single molecule potential V must disappear if the LC has S = 0. Furthermore, the more aligned the molecules are, the greater is the influence of potential over them. Correspondingly, V must be proportional to  $\langle P_2 \rangle \equiv S$ . Also, the energetic cost is lower when the molecular alignment is parallel or anti-parallel. So, V must be proportional to  $P_2$ . The potential suggested by the MS theory is

$$V(\theta) = -\vartheta SP_2(\cos\theta), \qquad (2.37)$$

where  $\vartheta$  is a constant interpreted as a combination of the average anisotropic interaction parameters. According to statistical mechanics, the probability of a single molecule to be oriented by an angle  $\theta$  regarding the director is given by the Boltzmann distribution

$$\rho(\theta) = \frac{1}{Z} e^{-\beta V(\theta)}, \qquad (2.38)$$

where the single molecule canonical partition function Z is defined by

$$Z = \int_0^{\pi} d\theta \sin \theta e^{-\beta V(\theta)}.$$
 (2.39)

Using Eq. (2.38) in (2.36) one can obtain the expression

$$S = \frac{1}{Z} \int_0^{\pi} d\theta \sin \theta P_2(\cos \theta) e^{\beta \vartheta S P_2(\cos \theta)},$$
(2.40)

which is a self-consistence relation that needs to be solved numerically. Introducing the variable

 $a = 3\beta \vartheta S/2$ , and taking the parametrization  $\cos \theta = x$ , the order parameter becomes

$$S = \frac{1}{Z} \int_0^1 dx P_2(x) e^{ax^2} = -\frac{1}{2} + \frac{3}{2} \frac{1}{Z} \frac{\partial Z}{\partial a}.$$
 (2.41)

Each value of x furnishes a value for S and T. The connection to thermodynamics comes with Helmholtz energy  $F = U - T\Sigma$ , where the internal energy  $U = -N\langle V \rangle/2$  and the entropy  $\Sigma = -Nk_B \ln Z$  [26]. So

$$f = \frac{1}{2}\vartheta S^2 - \frac{1}{\beta} \ln\left(\int_0^1 \mathrm{d}x P_2(x) e^{ax^2}\right).$$
 (2.42)

According to Maier and Saupe analysis [97, 98], there are at least four interesting regimes to be examined for the reduced temperature parameter  $\tau = k_B T / \vartheta$ . We clarify each one in Fig. 2.12. The first of them (Fig. 2.12-(a)) occurs when  $\tau > 0.222$ ; only S = 0 satisfies the self-consistence relation and the LC is in the isotropic phase. For the second regime (Fig. 2.12-(b)),  $\tau = 0.222$  both S = 0 and S = 0.3235 are solutions, however S > 0 provides an unstable equilibrium. So, the LC still prefers the isotropic phase. The third regime (Fig. 2.12-(c)) happens when  $0.2 < \tau < 0.222$ . In this case, there are at least three solutions for S, in which one of them is S = 0 and the two others with S > 0. Supposing  $S_1$  and  $S_2$  are the other solutions and  $S_1 < S_2$ , the intermediate value  $S_1$  is the unstable equilibrium for the energy and both S = 0 and  $S_2$  are stable ones. Within this interval, if  $\tau_c = 0.2202$ , the variation of Helmholtz free energy must vanish, and the MS theory predicts a phase transition with  $S_2 = 0.429$  [98]. As mentioned before, S = 0 and  $S_2$  are stable solutions, but  $S_2$  gives lower energy than S = 0. So, the LC prefers to organize in such a way that  $S = S_2$  rather than S = 0. The last regime (Fig. 2.12-(d)) happens for  $\tau < 0.2$ , where there are just two solutions, S = 0 and  $S > S_2$ , but the case for S = 0 is an unstable equilibrium. Therefore, the order parameter  $S > S_2$  may be the solution for nematic phase, while S = 0 becomes unstable. To summarize, the order parameter decreases in the nematic phase from 1.00 (perfect order in absolute zero) to 0.429 while T increases till  $\tau_c$ . Then, it passes through a gap directly to 0 when  $\tau > \tau_c$ , transiting to isotropic phase, characterizing a first order phase transition, since the order parameter has a discontinuity in its derivative.

Some points about the MS theory are highlighted in this study. This is a long-range interaction model that seems to be in good agreement with experimental results for phase transitions [100, 101] and for the temperature dependence of S [102, 103] in LCs. On the other hand, the theory disregards short-range repulsive forces that play an important role for fluid organization [104]. In contrast, other theories only based on short-range repulsive interactions, like the Onsager approximation, do not exhibit consistent results with parameters found in experimental phase transition [89, 105]. An alternative solution for this impasse could be considering both the long and short range forces together in a theory. The disadvantage for such model would be determining  $\vartheta$  because both forces have influence over it. Furthermore, it would not be possi-



**Fig. 2.12:** Graphic representations for different temperature regimes according to the MS theory. The curve (I) is given by  $S = 2\tau a/3$  coming from the parametrization and the curve (II) is dictated by Eq. (2.41). (a) The first illustrated situation is the regime for high temperatures, or  $\tau > 0.222$ , where just the intersection point M is the solution, or S = 0. (b) In the second case,  $\tau = 0.222$ ; the curve (I) sloping is smaller in such a way that (I) intersects the (II) in both points M and N; in M the order parameter S = 0, and in N, S > 0; S = 0 is the stable solution. (c) The third regime, where the reduced temperature  $\tau = 0.2202$  is a bit smaller, there are three intersections, M (S = 0), N ( $S = S_1$ ) and O ( $S = S_2$ ); the intersection N represents an unstable solution and O gives a less energetic costing solution than M; so the nematic ordering prefers the solution O. (d) The last case happens for  $\tau < 0.2$  where the interception N is the stable solution and the nematic prefers S > 0.

ble to know which anisotropic force would indeed dominate the molecular organization [106]. Luckhurst and Zannoni suggested that the solution for such apparent controversy would be considering that both forces are important for determining the organization of LC molecules, but each one would be acting in different levels [107].

## 2.3 Lattice model and pairwise additive potentials for LCs

Molecular theories allow a better understanding of the crystalline order in microscopic level. In contrast, intermolecular interaction potentials are not exactly known. Besides, statistical mechanics for such theories are difficult because of the complexity of calculations. An alternative which can help on the interpretation of molecular theory, but cannot replace it, is the computational simulation. Such tool could still require a hard interpretation of results, but it can be a source of important additional information about the LC properties and structure.

The first key point to be introduced is how the LC will be represented in the simulations. The simplest form to simulate the LC by computer methods is supposing the bulk as a lattice headless spin system [108], where the spins represent long axis of molecular orientation. Here, the significant change is that the model is not governed by continuous theory anymore, since the lattice is now discretized. It is worth noting that a simple spin model becomes a vividly convenient and easily modified tool to simulate realistic situations. In fact, the lattice model approach for LCs agrees with experiments if rotational invariance is maintained [109, 110]. Studies of self-organized supramolecular architectures, like LC droplets with different boundary conditions at the surface, have been performed by this technique [111–117].

#### Lebwohl-Lasher model

The first work that implemented the lattice model was developed by Lasher [110]. Lasher model supposes that nearby spin interaction is proportional to  $P_2(\cos \theta_{jk})$  where  $\theta_{jk}$  is the angle between the symmetry axes of spins at sites j and k.<sup>21</sup> This model supposes that the spins could just assume positions along the center of a dodecahedron towards the center of each face. Results for this show a first-order phase transition of the order parameter, but a critical value of 0.82. Whereas, MS theory predicts a transition around 0.43. Lasher suggested this disagreement could happen because the accessible states of spins linked to the faces of dodecahedron do not present enough points for converging it into a sphere [110]. On the other hand, Lebwohl and Lasher improved this first model allowing the spins to adopt any direction in space [2]. This significant change makes the number of accessible states in the Lebwohl-Lasher (LL) model sufficiently large and thereupon a weak first-order phase transition is found, where the critical value for the order parameter is around 0.33.

In LL model, the interaction energy between a pair of neighbor molecules  $(\Phi_{jk})$  is given by

$$\Phi_{j,k} = -\varepsilon P_2 \left( \hat{a}_j \cdot \hat{a}_k \right) = -\varepsilon P_2 \left( \cos \theta_{jk} \right), \qquad (2.43)$$

where the exchange energy parameter ( $\varepsilon$ ) is a positive nonzero number for the nearest neighbors of *j*-th spin, and 0 for the others. Since the interaction is over the nearest neighboring, the total energy of a single molecule can be written as

$$\Phi_j = -\varepsilon \sum_{\langle k \rangle} P_2\left(\cos \theta_{jk}\right),\tag{2.44}$$

where the summation is over the k-ths first neighbors. The N-particle standard canonical function (constant number of spins N, volume V and temperature T) is

$$Z_N = \int \left\{ \prod_{j=1}^N \frac{\mathrm{d}\Omega_j}{4\pi} \right\} \exp\left\{\beta\varepsilon \sum_{\langle j,k \rangle} P_2(\cos\theta_{jk}) \right\}.$$
(2.45)

Originally, the purpose of the potential was to describe phase transition and order parameter at molecular levels. In contrast, LL model gives a good representation of orientation properties for real nematics, suggesting an alternative interpretation for spins as being directors if the system has a scaled temperature ( $T^*$ ), defined as  $T^* = k_B T/\varepsilon$ , quite bellow the isotropic-nematic transition temperature ( $T^*_{IN}$ ) [116, 118–121]. It would be convenient to know how the LL model can be connected with the continuous theoretical model proposed for the nematics. For one-constant approximation ( $K_{ii} = K$ ), the Frank energy density in Eq. (2.1) can be rewritten as [122]

$$f = \frac{1}{2}K ||\nabla \vec{n}||^2.$$
 (2.46)

That is, this approach effectively gives an energy which depends only on the variation of  $\vec{n}$ 

<sup>&</sup>lt;sup>21</sup>Each spin represents the long axis of a single molecule.

through the surrounding space, since each elastic constant is not distinguished. Likewise, LL model has an energy dependence on the spin relative orientation around a specific region, and hence, it corresponds to the one-constant approximation for nematics. Although the model satisfactorily explains the nematic behavior for systems with temperature quite far from  $T_{IN}^*$ , it has a limitation in discerning splay, twist and bend deformations.

#### **Gruhn-Hess model**

In order to investigate the microscopic behavior in the bulk, it is possible to construct a pairwise additive interaction in different ways, which roughly mimics the elastic energy density [3, 123]. In contrast with the aforementioned model, Gruhn and Hess firstly proposed the discretization of the Frank free energy [3]. From another perspective, the Gruhn-Hess (GH) model rewrites the energy in a tensorial form where nematic symmetry is preserved and derivatives are appropriately taken in the difference of neighbor values. The dimensionless expression for the energy  $f^*$  in three dimensions for nematics in the absence of external field is defined as [3]

$$f^{*}(i,j,k) = \frac{1}{8} \sum_{r,s,t=\pm 1} \left[ \frac{1}{2} K_{22}^{*} \sum_{\alpha,\gamma=1}^{3} \sum_{d=1}^{3} \left( \mathcal{D}_{d\alpha\gamma}^{(r,s,t)}(i,j,k) \right)^{2} + \left( K_{11}^{*} - K_{22}^{*} \right) \sum_{\gamma=1}^{3} \left( \sum_{d=1}^{3} \mathcal{D}_{dd\gamma}^{(r,s,t)}(i,j,k) \right)^{2} + \frac{1}{2} \left( K_{33}^{*} - K_{11}^{*} \right) \sum_{\alpha,\gamma=1}^{3} \left( \sum_{d=1}^{3} n_{d}(i,j,k) \mathcal{D}_{d\alpha\gamma}^{(r,s,t)}(i,j,k) \right)^{2} \right],$$

$$(2.47)$$

where  $f^*$  is given by the arithmetic average over the eight asymmetrical discretizations of the derivatives

$$\mathcal{D}_{1\alpha\gamma}^{(r,s,t)}(i,j,k) = n_{\alpha}n_{\gamma}(i+r,j,k) - n_{\alpha}n_{\gamma}(i,j,k),$$
  

$$\mathcal{D}_{2\alpha\gamma}^{(r,s,t)}(i,j,k) = n_{\alpha}n_{\gamma}(i,j+s,k) - n_{\alpha}n_{\gamma}(i,j,k),$$
  

$$\mathcal{D}_{3\alpha\gamma}^{(r,s,t)}(i,j,k) = n_{\alpha}n_{\gamma}(i,j,k+t) - n_{\alpha}n_{\gamma}(i,j,k),$$

with  $r, s, t \in \{1, -1\}$ . It is convenient to point out that the indexes  $\alpha$  and  $\gamma$  are related to the three components of the director, while *d* is related to the dimension of the grid system. Pursuing the one-constant approach for Eq. (2.47), the interaction energy between two neighbor spins located at the positions  $\vec{r}_l$  and  $\vec{r}_m$  can be written as

$$f^*(\vec{r}_l, \vec{r}_m) = \frac{KL}{2} \sum_{\langle l, m \rangle} \left[ 1 - (\vec{n}_l \cdot \vec{n}_m)^2 \right], \qquad (2.48)$$

where L is the length between the neighbors in the grid. Although Eq. (2.47) cannot be divided into interaction pairs, the result in Eq. (2.48) differs from Hamiltonian of LL in Eq. (2.44) by a constant in the energy and by the object interpretation in the lattice. From the LL model, molecules are considered to compose the sites while the GH model supposes the sites are set with directors. Besides, the interpretation of the energetic parameter  $\varepsilon$  can be made with elastic constant and unit cell size by  $\varepsilon = Kl/3$ , where *l* is interpreted as the average distance between the sites.

Under the circumstances of elastic anisotropy, GH model offers possibilities for extending the interaction energy of LL model between two directors  $\vec{n}_j$  and  $\vec{n}_k$  in the grid. Let us consider  $\vec{r}_{jk} (\equiv (\vec{r}'_j - \vec{r}'_k)/|\vec{r}'_j - \vec{r}'_k|)$  as the unit intermolecular vector linking the center of mass of both neighboring objects. After expressing Eq. (2.47) for neighbor directors and identifying terms like  $\vec{n}_j \cdot \vec{r}_{jk} = a_j$ ,  $\vec{n}_k \cdot \vec{r}_{jk} = a_k$ , and  $\vec{n}_j \cdot \vec{n}_k = b_{jk}$ , the pair potential can be written as

$$E_{jk} = j_2 \left( 1 - b_{jk}^2 \right) + (j_1 - j_2) \left( a_j^2 + a_k^2 - 2a_j a_k b_{jk} \right) + \frac{1}{2} \left( j_3 - j_1 \right) \left( a_j^2 + a_k^2 \right) \left( 1 - b_{jk}^2 \right).$$
(2.49)

Looking for some specific configurations for the directors, the authors in [3] concluded that the meaning for  $j_1$ ,  $j_2$  and  $j_3$  are related to the splay, twist, and bend energies, respectively. Also, simulations carried out with GH model reproducing Fréederickz transitions and Schadt-Helfrich cell with perpendicular boundary conditions showed good agreement with analytic solutions [3]. Estimates of threshold fields for several  $K_{11}/K_{33}$  and  $K_{22}/K_{33}$  ratios, and how the director changes the tilt angle while increasing external fields, were found to be different from theoretical predictions by an order of magnitude near few tenths of a percent.

By writing Eq. (2.49) with second rank Legendre polynomial, we obtain

$$E_{jk} = \frac{2}{9} [2j_1 - 3j_2 + j_3] (P_2(a_j) + P_2(a_k)) + 2 [j_2 - j_1] (a_j a_k b_{jk}) + \frac{2}{9} [j_1 - 3j_2 - j_3] P_2(b_{jk}) + \frac{2}{9} [j_1 - j_3] (P_2(a_j) + P_2(a_k)) P_2(b_{jk}).$$
(2.50)

Romano expressed the energy parameters as linear combination of elastic constants and rewrote the energy as [124]

$$W_{jk} = \lambda \left[ P_2(a_j) + P_2(a_k) \right] + \mu \left[ a_j a_k b_{jk} - \frac{1}{9} \right] + \nu P_2(b_{jk}) + \rho \left[ P_2(a_j) + P_2(a_k) \right] P_2(b_{jk}), \quad (2.51)$$

$$\lambda = \frac{1}{3}l\left(2K_{11} - 3K_{22} + K_{33}\right), \qquad (2.52)$$

$$\mu = 3l(K_{22} - K_{11}), \qquad (2.53)$$

$$\nu = \frac{1}{3}l(K_{11} - 3K_{22} - K_{33}), \qquad (2.54)$$

$$\rho = \frac{1}{3}l(K_{11} - K_{33}), \qquad (2.55)$$

where Eq. (2.51) differs from Eq. (2.50) just by a multiplicative factor and by an energy constant.

#### Anisotropic elastic pairwise potential for nematics

Potentials describing molecule-molecule interactions have been very required to aggregate relevant information about systems, like attractive and repulsive forces in Lennard-Jones potential for a molecular field [125], or the electric multipole expansions in Van der Meer potential in CLCs [126]. In details, these potentials can depend on the distance between the molecules or their orientation as well.

According to Stones, a scalar function involving the interaction among a pair of molecules (independently of their shape) can be expanded in terms of S-functions [127]. For LCs, a pairwise additive potential between two directors, which is descendant from S-functions, and includes spatial orientation information by means of scalar invariants have already been studied [4, 128].

There are at least three primary geometric relations involved in an interaction between two spins. The first to be treated is the position of objects relative to each other, expressed by  $b_{jk} = \vec{n}_j \cdot \vec{n}_k$ . This is the unique geometric information on LL model. The second and third kind are given by the relative position between the objects and the direction of unit intermolecular vector  $\vec{s}_{jk}$ , where  $a_j = \vec{n}_j \cdot \vec{s}_{jk}$  and  $a_k = \vec{n}_k \cdot \vec{s}_{jk}$ . So, the potential is defined by the expansion

$$\Phi_{jk} = \sum_{i_1, i_2, i_3} c_{i_1, i_2, i_3} a_j^{i_1} a_k^{i_2} b_{jk}^{i_3}, \qquad (2.56)$$

where the  $c_{i_1,i_2,i_3}$ 's are the arbitrary coefficients and the  $i_m$ 's represents the expansion order.

Considering nematic symmetry ( $\vec{n}$  equivalent to  $-\vec{n}$ ), it is possible to express  $\Phi_{jk}$ , by expanding Eq. (2.56) till terms of second order, as

$$\Phi_{jk} = \lambda Y_{jk} + \mu \left( a_j a_k b_{jk} - \frac{1}{9} \right) + \nu P_2(b_{jk}) + \rho Y_{jk} P_2(b_{jk}), \qquad (2.57)$$

where  $Y_{jk} = P_2(a_j) + P_2(a_k)$ . For small angular displacements between two neighbor objects, Eqs. (2.1) and (2.57) allow relating the parameters  $\lambda$ ,  $\mu$ ,  $\nu$ , and  $\rho$  to elastic constants  $K_{11}$ ,  $K_{22}$ and  $K_{33}$  by means of [4]

$$\begin{cases}
\Lambda K_{11} = \frac{3}{2}(\lambda - \nu + 2\rho), \\
\Lambda K_{22} = \frac{3}{2}(-\nu + \rho), \\
\Lambda K_{33} = -\left[\frac{3}{2}(\lambda + \nu) + \mu + \frac{9}{2}\rho\right],
\end{cases}$$
(2.58)

where  $\Lambda$  has the same interpretation of l in Eq. (2.51), meaning the length of unit cell filled by the spin. This is a linear system that relates three elastic constants to four energetic parameters. Some assumptions must be made to solve these equations. Each kind of assumption may lead to a specific interpretation. If we take  $\rho = 0$ , *e.g.*, terms of fourth and high orders are dropped from Eq. (2.57), but this can be useful for some set of configurations. Although this parametrization gives a moderately good qualitative agreement for theoretical predictions, like order parameter, the deviations seem to arise from neglecting the high order terms of scalar invariants [4]. One can expect that another parametrization keeps this description in the potential. Supposing that the energy  $\Phi_{jk}$  may be independent of absolute orientation of two parallelly aligned directors, thus  $b_{jk} = 1$ ,  $a_j = a_k = a$ . Hence,

$$\Phi_{jk} = a^2 \left[ 3(\lambda + \rho) + \mu \right] - \left[ \frac{\mu}{9} + (\lambda + \rho) \right] + \nu$$
(2.59)

is independent of *a* if  $\mu = -3(\lambda + \rho)$ .<sup>22</sup> This assumption is essential for describing elastic interaction between two directors [128]. So, the energetic parameters in Eq. (2.58) can be solved in function of elastic constants as

$$\lambda = \frac{1}{3}\Lambda \left(2K_{11} - 3K_{22} + K_{33}\right), \tag{2.60}$$

$$\mu = 3\Lambda (K_{22} - K_{11}), \qquad (2.61)$$

$$v = \frac{1}{3}\Lambda (K_{11} - 3K_{22} - K_{33}), \qquad (2.62)$$

$$\rho = \frac{1}{3}\Lambda \left(K_{11} - K_{33}\right). \tag{2.63}$$

One can conclude that the parametrization  $\mu = -3(\lambda + \rho)$  is implicit in the obtained expression by the GH model in Eq. (2.50).

The richness of this potential is that it connects the cell size with reduced temperature by  $T_R \equiv k_B T/|v|$ , which is similar to the LL interpretation of  $T^*$ . As the cell size changes in function of  $T_R$ , it can be of considerable interest to establish the range where director fluctuation is connected to continuous theory without loss of generality. The cell size is inversely dependent on the reduced temperature. So, if  $T_R$  increases,  $\Lambda$  decreases, and vice versa. If  $\Lambda$  reaches molecular dimensions, the elastic behavior and the director interpretation for sites no longer hold valid. Lets assume a real LC at 300 K with average elastic constants of  $1.0 \times 10^{-12}$  N. If the reduced temperature  $T_R = 3k_BT/\Lambda|K_{11} - 3K_{22} - K_{33}|$  is 0.20, the cell size is approximately  $6.2 \times 10^{-8}$  m. For this value, it is necessary around 15 sites to amount near  $1.0 \ \mu$ m in the bulk and it is around 10 times bigger than the molecule size. So, the site includes considerable fluctuation of molecules and can be interpreted as a director.<sup>23</sup> Experimental results have shown that the coherence length  $\xi$  for director fluctuations varies from 200 nm at 41°C to 1.0  $\mu$ m at 29°C [129]. This is the same scale of cell size in regimes of  $T_R$  near 0.10 in simulations of anisotropic potential scheme, providing support for interpreting the site in lattice as a director [116, 118– 121, 128].

<sup>&</sup>lt;sup>22</sup>Consequently,  $\Phi_{j||k} = -\Lambda(K_{11} + K_{22} + K_{33})/3$ . For single elastic constant approach,  $\Phi_{j||k} = -\Lambda K$  is the expected minimum value for interaction.

<sup>&</sup>lt;sup>23</sup>If  $T_R = 0.10$ , the cell size is near 0.1  $\mu$ m and around 10 sites describes 1.0  $\mu$ m. Of course, this is a simple analysis to illustrate that the regime of  $T_R$  far from the transition temperature furnishes interpretation of director for the spins in the lattice.

#### Anisotropic elastic pairwise potential for cholesterics

Supported by the previous section, the extension of pairwise additive potential for cholesterics is reached by the elastic free energy density for a chiral nematic in Eq. (2.3). As mentioned before, a modified LL model has been used for analyzing the LC properties with an elastic anisotropic pair potential for ordinary nematics. It was derived by evaluating the gradients in Eq. (2.1) as finite increments written in terms of symmetry elements, thus mapping the pair potential onto the Frank free energy [3,128,130]. Saieli and Luckhurst have generalized this potential for cholesterics by adding a chiral term scalar invariant  $c_{jk}$  to the Hamiltonian [5]

$$\Phi_{jk} = \sum_{i_1, i_2, i_3, i_4} c_{i_1, i_2, i_3, i_4} a_j^{i_1} a_k^{i_2} b_{jk}^{i_3} c_{jk}^{i_4}, \qquad (2.64)$$

where  $c_{jk} = \vec{n}_j \cdot (\vec{n}_k \times \vec{s}_{jk})$ . After considering the expansion till first order correction in  $c_{jk}$ , and correlating the discretization of Eq. (2.3), the pairwise additive potential between a pair of spins,  $\Phi_{jk}$ , is given by

$$\Phi_{jk} = \lambda Y_{jk} + \mu \left( a_j a_k b_{jk} - \frac{1}{9} \right) + \nu P_2(b_{jk}) + \rho Y_{jk} P_2(b_{jk}) + \sigma P_1(c_{jk}) \frac{b_{jk}}{|b_{jk}|}.$$
 (2.65)

Now,  $\sigma$  represents the energetic parameter of chirality meaning how powerful the system is to rotate the helical superstructure. The parameters  $\lambda$ ,  $\mu$ ,  $\nu$ ,  $\rho$  and  $\sigma$  in Eq. (2.65) are related to the elastic constants as

$$\lambda = \frac{1}{9}\Lambda \left(2K_{11} - 3K_{22} + K_{33}\right), \tag{2.66}$$

$$\mu = \Lambda (K_{22} - K_{11}), \qquad (2.67)$$

$$\nu = \frac{1}{9}\Lambda \left(K_{11} - 3K_{22} - K_{33}\right), \qquad (2.68)$$

$$\rho = \frac{1}{9}\Lambda (K_{11} - K_{33}), \qquad (2.69)$$

$$\sigma = -K_{22}q_0 \Lambda^2, \tag{2.70}$$

where  $\Lambda$  is the lattice parameter.<sup>24</sup> In the limit of  $\sigma \rightarrow 0$ , the potential must describe nematics. Two recent works with the pairwise potential for cholesterics were developed in good qualitative agreement describing the spontaneous stripes formation under the interaction with interfaces [131, 132].

## 2.4 Interaction with interfaces

LCs are often limited by interfaces. Such interfaces may be originated by the contact between the LC with other medium. This medium can be a rigid solid or an aqueous substance

<sup>&</sup>lt;sup>24</sup>The parameter  $\Lambda$  differs from nematic model by a multiplicative factor for convenient representation of  $\sigma$  in function of elastic constants in Eq. (2.70).

or even a gas. These limitations between LC and interfaces may induce organization or frustration in the system. In other words, the bulk will be influenced by the interfaces, thus creating ordered patterns, defect lines, or boojums according to the conditions on the boundaries.

As interfaces break the LC symmetry, the director assembly depends on the competition between elastic anisotropy and surface distortion. If there is no external torque acting over the system, the total energy density should be the sum of distortions in the bulk  $f_0$  with distortions on the interface. The distortion around the interface depends on the medium features in contact with LC. Different phenomena are found due to effects of interfaces in LCs. At least three of them can be distinguished [133]: critical adsorption, wetting or the imposition of a preferable orientation. The last one is so-called anchoring phenomenon.

Boundary effects of interfaces are often generated in several LC systems by solid surfaces. As previously mentioned, the bulk distortions may be influenced by the surface anchoring state. This reaction in the volume will depend on the alignment strength along the easy axis at the wall. The extrapolation length ( $\gamma$ ) is defined as the distance which the system should have beyond the surface for the anchoring to be strong [134]. Namely, if the strength of alignment is infinity, the directors near the surface are precisely in the same alignment direction commanded by the surface. On the contrary, if the surface imposes a weak anchoring strength, the deformations in the bulk may be strong enough to disrupt the surface alignment and  $\gamma$  should be huge related to molecular size [23].

Interactions with surfaces are commonly represented by the Rapini-Papoular (RP) theory [135]. This potential energy is characterized by the energetic cost of switching the director from the preferred direction imposed by the surface. The surface density energy in RP model is

$$f_s = -\frac{1}{2} W_s \left( \vec{n} \cdot \vec{n}_s \right)^2, \tag{2.71}$$

where  $W_s$  is the anchoring energy, which can be physically interpreted as the work required to rotate the director  $\vec{n}$  from the easy axis  $\vec{n}_s$  [136]. Measurements by continuum theory and other procedures like high-electric-field technique have demonstrated that strong anchoring energy should be from the order of  $10^{-4}$  J/m<sup>2</sup> [137–140].

Normally, elastic theory in LC systems is not viable in local regions where the directors and the order parameter change drastically. So, it is convenient to treat nematic-interface interactions in simulations considering the anchoring conditions. The lattice model has some advantages and one of them is the facility to add external interactions with directors. The total energy of a system where any interface contributes for distortion is given by

$$\Phi_t = \Phi_{bulk} + \Phi_{int} \tag{2.72}$$

The nematic-interface interaction can be locally summarized for a *j*-th spin neighbor to the

interface as

$$\Phi_{j,int} = -J_{int}P_2\left(\vec{n}_j \cdot \vec{n}_{int}\right),\tag{2.73}$$

where  $J_{int}$  is the anchoring energy and  $\vec{n}_{int}$  is the easy axis along the interface. The intensity of surface alignment depends on the energy of wall-nematic interaction. For the pairwise additive anisotropic model previously treated, the nematic-nematic interaction is given by  $\nu$ , and the wall-nematic one is now represented by  $J_{int} = J_s$ . So, for  $J_s \sim \nu$ , the anchoring is considered strong and the surface imposes its alignment over the region where it is presented. If  $J_s$  is relatively smaller than  $\nu$  the anchoring strength is considered weak.

## 2.5 Textures

Computer simulations have proved to be a good technique for analyzing observables like polarized light [116, 132, 141–143]. As LCs are birefringent, the molecules change light propagation. As a result, the process to get analytical expressions for optical properties could be quite difficult, because the refraction index is not uniform through space. It can be interesting to know how the optical textures would be in the simulations. Calculations to find textures are done by a matrix approach in which the optic ray in each site is detailed by a Müller matrix. It is a numerical method to study optical properties where the spins are treated as retardants that modify the polarization of the incoming light beam.

If the beam of light is not monochromatic, the phase amplitude changes in the perpendicular axes to the propagation over the time. This suggests that the polarization state of a polychromatic plane wave may continuously change. If the change in this state occurs faster than the speed of observation, the light is partially polarized or unpolarized, depending on the behavior time-average of the polarization state [26]. This kind of incident light is described by the normalized incident Stokes vector ( $\vec{S}_{inc}$ ) which has four components, given by

$$\vec{S}_{in} = \begin{pmatrix} 1\\0\\0\\0 \end{pmatrix}.$$
 (2.74)

Hence, the beam will interact with all directors along with a straight line, inside the lattice, modifying the direction of polarization. This change happens because of the optical element named retarder, which is responsible for dividing the light into two perpendicular beams (one time-shifted phase later than the other). As the LC is optically anisotropic, or birefringent, it can be considered as a light retarder. The incident light interaction with the LC directors is represented by the Müller matrix  $(\widetilde{M})$  operating in the incident Stokes vector, creating a new

Stokes vector outing the sample, it means

$$\vec{S}_{out} = \overleftarrow{M} \cdot \vec{S}_{in}.$$
(2.75)

The Müller matrix responsible for this procedure is defined as [144]

$$\widehat{M}_{k} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \sin^{2}(2\phi_{k})\cos(\delta_{k}) + \cos^{2}(2\phi_{k}) & \sin(2\phi_{k})\cos(2\phi_{k})(1 - \cos(\delta_{k})) & \sin(2\phi_{k})\sin(\delta_{k}) \\ 0 & \sin(2\phi_{k})\cos(2\phi_{k})(1 - \cos(\delta_{k})) & \sin^{2}(2\phi_{k}) + \cos^{2}(2\phi_{k})\cos(\delta_{k}) & -\cos(2\phi_{k})\sin(\delta_{k}) \\ 0 & -\sin(2\phi_{k})\sin(\delta_{k}) & \cos(2\phi_{k})\sin(\delta_{k}) & \cos(\delta_{k}) \end{pmatrix}$$

where  $\delta_k$  is the retarder angle given by

$$\delta_k = \frac{2\pi h}{\lambda'} \Delta n = \frac{2\pi h}{\lambda'} n_o \left( \frac{n_e}{\sqrt{n_o^2 \sin^2(\theta_k) + n_e^2 \cos^2(\theta_k)}} - 1 \right), \tag{2.76}$$

and  $\theta_k$  is the angle between the *k*-th particle and the light propagation, and  $\phi_k$  is its azimuthal angle in the plane perpendicular to the incident beam direction. In Eq. (2.76),  $n_o$  is the ordinary refractive index,  $n_e$  is the extraordinary refractive index,  $\lambda'$  is the light wavelength of the incident beam and *h* is considered the thickness of a layer [116].

Beams of light propagating through space are represented by its electric field vector vibrating in the plane of propagation. For transverse waves, there are two independent directions of vibration. If these components are uncorrelated, the beam light is unpolarized. If the direction of vibration happens in a particular direction and the electric field components differ by a phase angle  $\pi$ , the beam light is linearly polarized. Otherwise, circularly polarization happens if the electric field vector components are mutually perpendicular, in other words, they are always phase-shifted by  $\pi/2$ . In case of linear polarization, the polarizer and analyzer,  $\tilde{P}_{in}$  and  $\tilde{P}_{out}$  are respectively represented by

while for circular light polarization, the polarizer and analyzer are represented by

$$\widehat{P}_{in,out}^{(circ)} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & \pm 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \pm 1 & 0 & 0 & 1 \end{pmatrix}.$$
(2.78)

After the light interacts with the sample, the resulting Stokes vector should be given by [142,

144]

$$\vec{S}_{out} = \overleftarrow{P}_{out} \cdot \prod_{k} \overleftarrow{M}_{k} \cdot \overleftarrow{P}_{in} \cdot \vec{S}_{in}, \qquad (2.79)$$

where  $\overleftrightarrow{P}_{in}$  and  $\overleftrightarrow{P}_{out}$  are the Müller matrix representing the polarizer and the analyzer, respectively. Pondering to avoid noises in the signal, it is convenient to get the average over a considerable number  $N_i$  of equilibrated states [116], so that

$$\langle \vec{S}_{out} \rangle = \frac{1}{N_i} \sum_{i} \vec{S}_{out}^{(i)}.$$
(2.80)

The choice for linear or circular polarization may depend on the way we desire to observe the light transmission in the medium. In fact, the problem of light transmission is reduced to a linear superposition of monochromatic plane waves transmitted through the LC assembly [81]. Fig. 2.13 shows examples of simulations for Müller texture productions in a (a) nematic and (b) cholesteric samples under specific anchoring conditions. In Fig. 2.13-(a) the nematic sample is confined between a hybrid-aligned cell with degenerated (random alignment) planar anchoring, showing the Schlieren texture as resulting configuration. In such pattern, when the LC sample is observed between crossed polarizers, dark and white brushes can be seen, representing extinction and presence of light intensity, respectively. Regions where two or four alternative dark and white brushes meet correspond to director singularities in the medium, which can be featured, *e. g.*, by a point defect or a disclination line. In Fig. 2.13-(b) there is a cholesteric sample sandwiched between a uniform planar anchoring and a tilted weak anchoring in boundaries of isotropic phase, where the organization shows a uniform striped pattern with a  $\lambda^{+1/2}$  kind defect indicated by the black arrow.<sup>25</sup>



**Fig. 2.13:** (a) Schlieren textures in simulations for nematic sample in a hybrid-aligned cell with planar degenerated anchoring. (b) Simulations for a CLC sandwiched between a uniform planar alignment and isotropic phase showing a uniform modulated pattern with a  $\lambda^{+1/2}$  defect in the black arrow.

<sup>&</sup>lt;sup>25</sup>Other textures can be seen in Refs. [132, 145].

## 2.6 Metropolis-Hasting algorithm

During the simulations, we use the MH algorithm [16] to update the evolution of the system. A spin  $\vec{n}_j$  is randomly selected and its energy

$$U_j = \sum_{\langle k \rangle} U_{jk},\tag{2.81}$$

is evaluated, in which the sum is performed over the nearest neighbors of j. Then, it is raffled to a new configuration  $\vec{n}'_j$  according to the BW technique [146], and its new energy  $U'_j$  is also evaluated. If  $\Delta U = U'_j - U_j \le 0$  the new state  $\vec{n}'_j$  is accepted. If  $\Delta U > 0$ , a number  $0 \le w \le 1$ is raffled; if

$$w \le p = e^{(-\Delta U/k_B T)},\tag{2.82}$$

the state  $\vec{n}'_{j}$  is accepted, on the contrary, it is rejected. After each spin in the bulk has been visited to interact with its neighbors at least once, on average, the algorithm completes one cycle, or one MC step (MCs). The evolution of the process is given with an acceptance rate around 0.50 to improve time-simulation without loss of generality in statistical mechanics.

## Chapter 3

# **Hybrid Aligned CLCs: Role of Anchoring Energy on the Texture Transitions**

#### 3.1 Introduction

As a burgeoning field of study, both from the basic science and the applications point of view, the behavior of CLCs in thin hybrid aligned cells, a common situation where one of the substrates promotes planar orientation whereas the opposite substrate imposes homeotropic anchoring, has drawn considerable attention in the past few years. Such configuration often results in a modulated structure (stripe pattern) due to an energetic competition that occurs between the substrates and the bulk parameters.

Stripe patterns, as they are often referred to, have attracted a great deal of attention because they can be readily applied as Raman-Nath diffraction gratings [64, 67, 147]. There are several ways of generating such patterns, including by applying an external field [72, 147–150], light irradiation [64], or by using hybrid aligned cells [60, 70]. Recently, hybrid aligned CLCs were shown to act as nanomotors that can move objects 10.000 larger than the chiral dopant itself when the CLC is fabricated with a photosensitive chiral dopant [**?**, 57]. In another study, hybrid aligned CLCs were demonstrated to form striped patterns that continuously rotate upon UV and visible light irradiation, reaching up to 690° rotation of the grating vector [6].

When dealing with nematic LCs, several studies have been reported in order to understand the bulk and surface organization of the directors depending on the elastic properties of the materials [151–154]. On the other hand, when the material is a CLC, several works report on the importance of the thickness to pitch  $(d/p_0)$  ratio for forming the striped pattern [72]. It is quite astonishing however that the literature lacks of studies on the effect of surface anchoring energy on the stripe pattern formation of CLCs, even when considering that hybrid aligned cells are often used to generate such patterns. This is likely due to the complexness of the equations governing the system, which involves a minimization process of the Frank free density energy in Eq. (2.1) combining the different kinds of deformation, splay, twist and bend [1]. In certain cases, depending on the complexity of the system, analytical profiles of the director field become troublesome. One possible solution is to deal with the molecular interactions characterizing the material by discretizing the sample into small domains placed in sites of a lattice. An important example is the GH model for a conventional nematic, in which the elastic anisotropy is involved, discussed in Sec. 2.3. This model was parametrized by Romano *et al.* [4, 124], resulting in Eq. (2.51), and then extended for cholesterics, Eq. (2.65), later proposed by Luck-hurst *et al.* [5]. The extra term that aggregates the chiral interaction in Eq. (2.65) makes two neighboring spins to be slightly twisted with respect to each other.

Such models are often used in combination with MC simulations. When studying confined cells with hybrid alignment, there are some works that report the behavior of nematic samples by means of MC simulations [121, 145, 155–157]. Nonetheless, to the best of our knowledge, there are no reports of CLCs in hybrid aligned cells explored by MC simulations with the anisotropic potential proposed by Luckhurst et al. [5] and no studies of the role of surface anchoring energy on the stripe pattern formation of CLCs.

In this work we present simulations by the MC method in a lattice of headless spins that represent a cell with hybrid anchoring at the surfaces, considering strong planar anchoring on the bottom substrate but taking into account the finite energy on the top, homeotropically aligned surface. Fig. 3.1 shows a schematic representation of the expected periodic modulated pattern of directors near the homeotropic surface alignment with finite anchoring energy [6]. It is possible to observe three kinds of arrangement of spins in the bulk when the anchoring energy at the homeotropic surface changes. Depending on the value of this energy we can find a planar organization (or Grandjean texture), an undulated modulation or a frustrated, conical structure. These arrangements seems to be valid for more than one host LC, and the strength of the anchoring energy which promotes the structural transition changes according to the host characteristics. In this chapter we present the simulations aspects to reproduce the hybrid cell and the results for structure transitions in the simulations.



**Fig. 3.1:** Schematic representation for the directors bulk alignment. Near the finite homeotropic surface a modulated pattern of period L may appear in a cholesteric of pitch P. (Ryabchun et al. (2015) [6]. Adapted and reproduced with permission of Wiley Online Library.)

## **3.2** Simulation Aspects

Let us consider the Hamiltonian for cholesterics where the pairwise potential between a pair of spins,  $\Phi_{jk}$ , is given by Eq. (2.65). In this case,  $\vec{n}_j$  is the orientation of the *j*-th spin,  $\vec{n}_k$ is its neighbor spin on the lattice and  $\vec{s}_{jk}$  is the unit vector joining them. The parameters  $\lambda$ ,  $\mu$ ,  $\nu$ ,  $\rho$  and  $\sigma$  in Eq. (2.65) can be written in terms of elastic constants ratio as

$$\lambda = \frac{1}{9}\Lambda K_{22} \left( 2\frac{K_{11}}{K_{22}} - 3 + \frac{K_{33}}{K_{22}} \right), \tag{3.1}$$

$$\mu = \Lambda K_{22} \left( 1 - \frac{K_{11}}{K_{22}} \right), \tag{3.2}$$

$$\nu = \frac{1}{9}\Lambda K_{22} \left( \frac{K_{11}}{K_{22}} - 3 - \frac{K_{33}}{K_{22}} \right), \tag{3.3}$$

$$\rho = \frac{1}{9}\Lambda K_{22} \left( \frac{K_{11}}{K_{22}} - \frac{K_{33}}{K_{22}} \right), \tag{3.4}$$

$$\sigma = -\Lambda K_{22} q_0^*, \tag{3.5}$$

where  $\Lambda$  is the lattice parameter and  $q_0^* (= q_0 \Lambda)$  is the reduced wave vector of cholesteric helix.

In order to reproduce experimental conditions, some parameters are fixed for all the simulation runnings. We scale the potential by v (and set it to -1) in such way that the pairwise additive potential, Eq. (2.65), recovers the LL model in the so-called isotropic (or spherical) approach, in which all elastic constants assume the same value [128, 145].

The simulations take place in a rectangular lattice with dimensions  $N_x \times N_y \times N_z$ , with  $N_x = N_y$ . Periodic boundary conditions are applied in  $x^*$  and  $y^*$  scaled directions. For  $z^*$  scaled direction, the quantity  $N_z$  gives the number of planes that effectively represents the sample, with  $d = N_z$  being its thickness. Apart from  $N_z$ , there are two fixed boundary layers that imposes the easy axis direction of each surface.

The interaction of the bulk spins immediately near of both surfaces in  $z^*$  axis is considered to be the LL potential, where

$$\Phi_{j,s} = -J_s P_2(b_{js}). \tag{3.6}$$

In this equation,  $b_{js} = \vec{n}_j \cdot \vec{n}_s$ , and  $\vec{n}_s$  is the easy axis of anchoring at the surface, and  $J_s$ , is the strength of the anchoring energy scaled by v. This potential supplies an isotropic potential describing the surface anchoring, equivalent to RP anchoring energy [135]. At the bottom surface,  $J_{bot} = 1.00$  to reproduce a relatively strong anchoring energy with its easy axis aligned with  $x^*$  direction (planar) and small pretilt of 3° in  $z^*$  direction related with the  $x^*y^*$  plane to avoid the degenerescence of states [158]. At the top surface, we set the easy axis pointed to  $z^*$  direction (homeotropic) and the values of  $J_{top}$  ranging from a weak (0.10) to strong (1.00) anchoring to observe the behavior of the directors in the volume as the anchoring energy changes.

We set the reduced temperature to  $T_R (= k_B T/|v|) = 0.10$ . This temperature is relatively far from the reduced transition temperature of LL model (1.1232 [118]), but it is high enough to induce some thermal fluctuations of spins [5]. At beginning of the simulations, all spins in the bulk are aligned parallel to the direction of the bottom surface and the anchoring parameter is the weakest one ( $J_{top} = 0.100$ ). Then, the sample evolves for 100 kMC steps and a small increment of the top anchoring parameter is performed in order to observe some textural transition depending on the anchoring energy. A MC step is counted when, in average, all spins in the bulk are raffled to a new state at least once. To analyze if a new state will be accepted, the Metropolis algorithm was applied [16]. The maximum rotation allowed for directors was updated with the BW technique, where the acceptance rate is kept around 0.5 [146].

#### **3.3 Results and Discussions**

In our simulations, we used four different set of physical parameters, representing four different LC hosts: E44, E7, TL203 and ZLI4330. We shall describe the main results using the E44 parameters, and later summarize the results for each host in table form. The nematic E44 has the ratio between the elastic constants given by  $K_{11}/K_{22} = 1.19$  and  $K_{33}/K_{22} = 2.15$ . Besides, the term  $p_0^* (= p_0/\Lambda)$  typifying the doping by a chiral agent was fixed in 20 lattice sites. Then, the numerical parameters of the potential in Eqs. (3.1)-(3.5) are given by

$$\lambda = 0.38641, \mu = -0.43187, \nu = -1, \rho = -0.24245, \sigma = -0.714.$$
 (3.7)

The mesh size was set up in such way that the length along  $x^*$  and  $y^*$  direction is three times the reduced pitch, and  $d/p_0 = 0.50$  in  $z^*$  direction. So, the lattice was performed with a dimension of  $61 \times 61 \times 10$  spins along  $x^*$ ,  $y^*$  and  $z^*$  axes.

It is quite remarkable how much the surface energy parameter influences the bulk organization of the stripe pattern. In the range of top anchoring energies analyzed, there are three kinds of ordering for the spins in the lattice. When  $J_{top}$  is small enough that the top surface influence is almost unnoticed by the bulk, the spins prefer to maintain the cholesteric helix axis in the  $z^*$  direction (Grandjean texture). This quoted situation happens for  $J_{top}$  less than 0.290. In this region, the simulated results for the pitch is roughly the theoretical pitch (10 sites to complete half pitch), as illustrated in Fig. 3.2 for  $J_{top} = 0.260$ .

We define as  $J_{crit}$  the value for  $J_{top}$  that makes the arrangement of directors in the bulk change from planar to the striped pattern. When  $J_{top}$  grows and it becomes bigger than 0.290, the striped pattern emerges in the bulk by forming undulations, as shown in Fig. 3.3, for an illustrative value of  $J_{top} = 0.400$ . In this case, the easy axis of the top surface has a considerable influence. Near to the top surface, splay and twist deformations [7] take place, induced by the easy axis parallel to  $z^*$ . Due to the balance between bulk elastic energy and surface anchoring, these deformations becomes energetically unfavorable, so the system prefers to lay down the CLC helix in-plane, with the wave vector perpendicular to the  $z^*$  direction. Here, the helical axis direction forms an angle of approximately 45° with respect to the rubbing direction at the bottom surface, as seen in the top view configuration illustrated in Fig. 3.3-(c). Also, a Müller matrix texture is shown in Fig. 3.3-(d) representing the light interaction with the sample along the  $z^*$  axis. The procedure to calculate such texture is described in Sec. 2.5. The texture is taken from directors in the bulk, calculated over an average of the last 500 cycles considering  $n_0 = 1.50$  and  $n_e = 1.66$ , an incident light with wavelength  $\lambda' = 545 n$ m and layers of 0.20  $\mu$ m.

For simulations in which  $J_{top}$  begins greater than 0.430, the modulated pattern is not energetically favorable at the given  $d/p_0$  ratio. We define this value as  $J_{max}$ , in other words, the value of  $J_{top}$  that no longer favors the stripe pattern. At this regime of  $J_{top} > J_{max}$ , the system is not able to get rid of the configuration imposed by the surface and the spins close to the top surfaces tends to orient homeotropically, following the easy axis, as illustrated in Fig. 3.4 for the case of  $J_{top} = 0.600$ . Therefore, for  $d/p_0 = 0.5$  and the set of parameters aforementioned, the system will adopt a frustrated configuration, without pattern formation.

In order to investigate the pattern formation observed for intermediate values of  $J_{top}$ , we analyzed the oscillating behavior of spins in  $z^*$  axis. In fact, the profile of  $n_z^2$  as a function of spin position at the layer immediately below the homeotropic surface ( $z^* = 10$ ) can be used to measure the amplitude of the pattern. The measured wavelength of the stripes is around twice the natural pitch for all the host materials. Hence, we established a fit in the quadratic sinusoidal form, given by

$$n^{2} = n_{0z}^{2} \sin\left(\frac{2\pi}{p^{*}}r^{*} + \delta\right), \tag{3.8}$$

with maximum amplitude given by  $n_{0z}$ , with the directors on the diagonal of the plane, in a trace



**Fig. 3.2:** Snapshots for  $J_{top} = 0.260$  from the side view in the middle of the sample after run 100 kMC steps. (a) and (b) are showing the plane  $x^*z^*$  and  $y^*z^*$ , respectively. The cholesteric helix lies in  $z^*$  direction and the simulated pitch seems to agree with the theoretical one.



**Fig. 3.3:** Snapshots for  $J_{top} = 0.400$ . Again, (a) and (b) are the side view and (c) the top view in  $z^* = 10$ . In this case, it is clear to see how the directors are organizing itself to forming the stripes. From figure (c), the simulated pitch is 43.21, what is approximately twice greater than the theoretical one. (d) Müller matrix texture showing from the top view the light interaction with the sample.

perpendicular to the stripes direction, named  $r^*$  direction. An example of this fitting adjust is illustrated in Fig. 3.5-(a) for  $J_{top} = 0.430$ , where the abscissa axis is scaled by the length of the sample  $N_x$ . By this graphic, it is possible to observe how the long axis of the spins are oscillating in the  $z^*$  direction, with quadratic modulus of  $n_{0z}$  near 0.80, through the diagonal of the sample. We have plotted in Fig. 3.5-(b) a graphic to observe the behavior of  $n_{0z}^2$  when  $J_{top}$  increases, crossing  $J_{crit}$  represented as the vertical black dashed line, and the planar to striped pattern transition occurs. The small fluctuations observed on Fig. 3.5-(a) and 3.5-(b) is directly linked to the thermal agitation of the directors, similar to the behavior of order parameter reported by Masurier [128] at the same reduced temperature.

Similar results can be verified for the other liquid crystal hosts, as E7, TL203 and



**Fig. 3.4:** Snapshots for  $J_{top} = 0.600$  of the side view. The top surface imposes a vertical force in  $z^*$  direction that the system cannot relieve the splay distortion for this  $d/p_0$  ratio.



**Fig. 3.5:** (a) Square of maximum amplitude for  $J_{top} = 0.430$  in function of the director position in the diagonal of the plane  $x^*y^*$  for  $z^* = 10$ . (b) Behavior of the square of oscillation amplitude as the homeotropic anchoring energy increases.

**Tab. 3.1:** Table containing the parameter values for other LCs in addition to E44, keeping fixed  $\sigma^* = 0.714$ .

Nematic LC	$K_{11}/K_{22}$	$K_{33}/K_{22}$	$p_0^*$	d/p	$N_z$	λ	μ	ρ	J <sub>crit</sub>	$J_{max}$
E44	1.19	2.15	20.00	0.50	10	0.38641	-0.43187	-0.24245	0.288	0.430
E7	1.48	2.28	20.84	0.53	11	0.58937	-1.13664	-0.21049	0.364	0.460
TL203	1.97	2.23	24.29	0.49	12	0.97249	-2.67817	-0.07976	0.426	0.510
ZLI4330	2.00	2.92	20.20	0.50	10	1.00004	-2.29600	-0.23470	0.520	0.570

ZLI4330. Again, the investigated values are those that keep the energetic ratio between the natural twist and the nematic ordering energies  $\sigma^* (= \sigma/\nu)$  equals to 0.714, for the same scaled temperature  $T_R = 0.10$ . Tab. (3.1) brings the values for elastic constants and the respective parameters for each nematic host.

The amplitude of directors for the other nematic hosts are shown in Fig. 3.6. By comparing the nematics E44 in Fig. 3.5-(b) with E7, TL203 and ZLI4330, in Fig. 3.6, it is possible to see that the value of  $J_{crit}$  is related with the increasing value of  $K_{11}$ . This would make sense because the homeotropic anchoring at the top surface induces a splay distortion in the bulk,



**Fig. 3.6:** Square of amplitude oscillations for nematics (a) E7, (b) TL203 and (c) ZLI4330. According to results reported on Tab. (3.1), the critical value for  $J_{crit}$  to the structural transition occurs is 0.364, 0.426 and 0.520, respectively. Each point was collected after the sample was evolved with 100 kMC steps for the values of  $J_{top}$ .

since the anchoring at the bottom surface is planar.

If the anchoring is considerable weak ( $J_{top} < J_{crit}$ ), the spins prefer to hold the cholesteric helix rotating along of the  $z^*$  direction. When  $J_{top}$  increases passing the critical value ( $J_{top} > J_{crit}$ ), the effects of top surface have more influence over the bulk, mainly in planes near the surfaces, and the splay distortion starts to be imposed by the homeotropic alignment. This energetic coast provided by this vertical force starts to compete with the chirality of the medium, so the undulated pattern takes place in the planes  $x^*y^*$  near the top surface. A similar situation about the role of splay elastic constant in this pattern formation was reported in reference [7] when a CLC confined in treated planar substrates suffers the wetting transition phenomena forming the undulated pattern. When  $K_{11}/K_{22}$  grows, the directors try to avoid the energetically unfavorable distortions, hence, the value  $J_{crit}$  increases. Crucially, all nematics except E44 present a high discontinuous change in amplitude of oscillations resulting in a sudden structural transition.

In this chapter we discussed the results found by applying the Luckhurst model in a rectangular hybrid cell geometry with periodic boundary conditions. However, besides experimental behaviors, in the next chapter we will investigate how such model performs in simulations for describing the striped pattern formation in a dynamic thin cholesteric layer, which appears in experiments after wetting phenomenon.

## Chapter 4

# **Striped Pattern Formation After Wetting Transition in Monte Carlo Simulations**

## 4.1 Introduction

Spatially repeated arrangements frequently occur in nature. Such orderly outcomes are formed in consequence of one or more driving forces, yielding beautiful and, more important, functional patterns in self-organized systems [159]. Snow flakes, body segmentation in animals, sand dunes, complex organization of cell fates, the circumpolar hexagonal storm in Saturn [160], Belousov-Zhabotinsky chemical reaction [161] and Rayleigh-Bénard convection [162] patterns are just a few examples of pattern formation. In many cases, replicating a naturally occurring pattern in a synthetic system is key for understanding the physics involved in a determined system [163]. Due to the multifaceted structures and phenomena LCs might present, they are terrific candidates to be used as synthetic, stimuli responsive media for simulating naturally occurring systems [164]. In this context, LCs have been extensively studied for their incredible patterns. Such patterns may arise as equilibrium arrangements resulting from external forces such as applied field, light illumination, confinement (anchoring mediated) [26,66,67,165,166] or as dynamical instabilities frequently observed in electroconvective patterns [167] and surface driven non-equilibrium patterns [168]. The correct connection between naturally occurring patterns and the ones fabricated in a LC system can only be made if the synthetic system is well understood, which is often done through numerical simulations.

Supramolecular heliconical arrangements in soft condensed matter such as CLCs are in the limelight center of scientific attention. In such materials, as in condensed matter in general, interface and surface phenomena play very important role [140,169–173], determining the bulk directors orientation and are of fundamental importance for LC devices [140, 174, 175]. In general, when a CLC sample is added to a planar treated cell, the helical axis is oriented perpendicular to the substrates, with the twist happening from one substrate to the other. This configuration is often called standing helix (SH). Upon certain stimuli, the helix might be induced to form with helical axis parallel to the substrates, forming a striped pattern often called lying helix (LH). Recently, stripe pattern formations were studied in a mixture of nematic LC with chiral dopant under wetting transition [7, 176, 177]. In [7], as to the system studied here, after the wetting transition a thin CLC layer is formed between the planar oriented substrate and the isotropic state at which the director weakly anchors with large tilting angle with respect to the interface. Fig. 4.1 illustrates the process of surface induced phase transition. Fig. 4.1-(a) shows the usual phase transition that occurs in the bulk while Fig. 4.1-(b) shows the layer that forms at the surfaces.<sup>1</sup>



Fig. 4.1: Illustration of (a) a usual phase transition in the bulk and (b) a surface induced phase transition.

The stripes appear as the result of chirality, wetting, elasticity and surface strength interplaying, generating a beautiful and dynamic pattern of defects and rotating stripes, that may be use to mimic biological structures [180]. In reference [7], the experimental results were interpreted with the **Q**-tensor relaxation method [26]. However, this method is purely elastic and no information about thermodynamical quantities, such as thermal fluctuations, are taken into account.

Here, we explore experimentally and by MC simulations the pattern formation in a CLC sample during a wetting transition. Experimentally, we observed that the transition from the uniform state (no pattern) to the striped state may happen in two distinct ways: the stripes might appear uniformly everywhere simultaneously or the stripes may nucleate one by one until the whole field of view is filled with the striped pattern. Indeed, this dual behavior depends on the d/p (thickness to pitch) ratio. This behavior has been observed before in planar oriented cells under an applied external field [181]. The nucleating type of stripe was called growing modulation (GM) while the homogeneous case was called developable modulation (DM). As reported in reference [72], the GM type happens typically for d/p > 1.5 while the DM type happens for 0.5 < d/p < 1. For 1 < d/p < 1.5, reference [72] reports a non-uniform texture. In reference [7] was reported that the stripes are formed for  $d/p \ll 1$ , but no further study was conducted on this matter. In a recent publication [9], distinct behavior of stripes that form in CLC shells under weak anchoring strength was reported, including nucleation of new stripes. Here, we report on the formation of patterns occurring for much lower values of d/p, for both types of modulation (GM and DM), indicating that surface anchoring plays a major

<sup>&</sup>lt;sup>1</sup>In this case, the wetting transition occurs when the contact angle between the LC and the surface goes to  $0^{\circ}$  by the change of temperature [178, 179].

role in the LH formation, since such behavior is not observed in conventional studies of lying helix in strongly anchored cells. Hence, it is important to explore the problem by considering simultaneously, the elastic anisotropy, anchoring strength, and thermal fluctuation effects during the pattern formation. Our model is based on the MC method with the MH algorithm [16]. A discretized pairwise additive potential between domains is used [5]. This potential with the MC method combines altogether the main ingredients to describe the experimental data: elastic anisotropy, chirality, thermal fluctuations (necessary for the GM type modulation) and variable anchoring strength. To the best of our knowledge, this is the first application of the potential to this kind of phenomena. Furthermore, we report GM and DM instabilities happening for d/p < 0.5. By using the Müller matrix approach, textures are built to compare the experimental images observed between crossed polarizers with the optical images calculated from the simulation. We verify that this simple model is able to reproduce many features of the pattern formation process, including the type of modulation; and can be very useful in describing the mechanisms that conduce the system to this particular molecular organization. In this chapter, we describe the experimental setup and the experimental discussions, the simulation details and its results, and finally the discussions.

## 4.2 **Experimental Procedure**

E7 (Merck) was used as the nematic host. The CLC mixture was made by doping the nematic LC with the chiral dopant S811 (Merck). Here we discuss the wetting phenomenon after the isotropic to chiral nematic transition (IN\*) transition for two different concentrations of S811. In one of them, E7 was doped with 0.76% (weight) of S811 generating a pitch of 13.00  $\mu$ m, while the other was made with 1.24% (weight) which leads to 8.00  $\mu$ m of pitch.<sup>2</sup> The material was accommodated between two glass plates forming a slab with measured cell gap of approximately 10  $\mu$ m. The cell's substrates, which have an area of approximately 1.0 cm<sup>2</sup>, were coated with the polyimide PI2555 and homogeneously rubbed, producing a strong planar anchoring. PI2555 is crucial for the work developed here. It has high affinity with LC molecules, favoring the contect with the LC phase rather than the isotropic phase. The use of this polyimide to favor wetting transition was first described in reference [7]. The cells were filled by capillary force in the isotropic state and were studied under a polarizing optical microscope (POM); the temperature was controlled with a hot stage (HCS402 Instec).

First, the temperature is increased a few degrees above the IN<sup>\*</sup> phase transition. Then, the sample is cooled from the isotropic to the CLC phase with cooling ratio of 0.10 °C/min. The textures were observed under a POM and textures (photographies) were taken in 30 s interval. When the temperature drops below the critical value  $T_{IN}$ , the LC phase occurs near the substrates first, induced by the surface and thus wetting the substrate and forming a thin layer because the polyimide has great affinity with LC. As reported in [7], the thickness layer can be

<sup>&</sup>lt;sup>2</sup>The experimental pitches were also confirmed by the microscope ruler.

determined from the transmitted light intensity vs. temperature. It is important to stress here that if the cooling process is stopped, the observed pattern remains still untill any further change in temperature occurs. Therefore, thermal gradients can be neglected in our analysis.

Initially, we discuss the phenomenon that emerges just after the wetting transition, at which the thin LC layer forms. Fig. 4.2-(a)–(d) shows the POM textures for the sample with pitch of 13.00  $\mu$ m as the temperature is decreasing. As discussed in [7], after the wetting transition ( $T_{IN} \approx 60.10 \text{ °C}$ ), the LC layer is too thin so no modulation is observed. We observed that light extinction is no longer possible as the sample is rotated, although the intensity of transmitted light is much lower than the sample with smaller pitch cell. It indicates that a small amount of twist develops with helical axis perpendicular to the substrates, thus allowing a small amount of light to get through the crossed polarizers, which is shown in Fig. 4.2-(a).

As the temperature of the system is continuously decreased, the wetting layer grows. When a critical value for d/p is reached, stripes start to nucleate from defects and spacers, spreading over in the field of view; this is characteristic of a growing modulation (GM), as shown in Fig. 4.2-(b) and 4.2-(c). As the temperature is further decreased, the stripes tile the whole field of view, leaving the undulated pattern shown in Fig. 4.2-(d). The entire process of undulated pattern formation happens within 1.40 °C. Notice that the overall direction of the stripes rotates as the temperature is lowered.

The second kind of structural transition is illustrated in Fig. 4.3 for the sample with pitch of 8.00  $\mu$ m. The initial process of cooling is similar to the previous case. Here the wetting transition happens in  $T_{IN} = 59.20$  °C. Initially, as in the previous case, only a very thin layer forms, Fig. 4.3-(a). At this stage, light extinction occurs since the rubbing direction is parallel to the polarizer direction. However, as the layer grows, light extinction occurs only upon large rotation of the cell, since twist starts to develop across the layer. This effect is more subtle for the cell presenting GM type, meaning that very small twist occurs prior the formation of the stripe pattern. This fact is corroborated by our simulations, as we shall discuss latter. As the LC layer thickness reaches a critical value, the undulated pattern emerges homogeneously everywhere across the sample, just like the developable modulation (DM) reported in reference [72]. In this



**Fig. 4.2:** GM type textures. (a) The wetting transition produces a thin ordered layer that increases under the decrement of temperature. (b) The striped pattern formation is energetically favorable after d/p reaches a critical value. The stripes nucleate in different points and spread continuously. (c)–(d) Under further cooling, the stripes connect and form the undulated pattern. In the figures, A stands for analyzer, P is polarizer and R is the rubbing direction, which is parallel to the polarizer axis.



**Fig. 4.3:** DM type textures. (a) Under cooling the system's temperature, a thin, pattern free layer is formed. (b)–(c) When d/p reaches a critical value, the striped pattern suddenly forms in a short range (0.20 °C) of temperature. (d) As the temperature keeps decreasing, the LH orientation changes and defects move through the sample, as described in reference [7]. In the figures, A stands for analyzer, P is polarizer and R is the rubbing direction, which is parallel to the polarizer axis.

case, the process of undulated pattern formation in the field of view is completed in a range of 0.20 °C, as illustrated in Fig. 4.3-(b) and 4.3-(c), while for GM the stripes need around 0.60 °C to be consolidated. As to the first sample, the orientation of the stripes rotate as the wetting layer grows. Notice that for the first kind of modulation, as shown in Fig. 4.2, the stripes form at approximately 45° with respect to the rubbing direction. The second modulation, shown in Fig. 4.3, upon appearing in field of view, is almost parallel to the rubbing direction. Both stripes rotate counterclockwise.

### 4.3 Simulation Model

In order to get some information on the mechanism behind both kinds of modulations, we used a computer simulation analysis based on the Monte Carlo method in a cubic lattice. In the experiment reported in Sec. 4.2, the thickness of the ordered phase is increasing from plates to the bulk as the temperature decreases, in the vicinity of the IN phase transition. Regarding the simulation, the lattice is set to be similar to an experimental slab. Each lattice point contains an interacting spin describing the director's orientation within a small volume of the sample. The axes are set in Cartesian coordinates  $x^*$ ,  $y^*$ , and  $z^*$  ( $x^* = x/\Lambda$ ,  $y^* = y/\Lambda$ ,  $z^* = z/\Lambda$ ), where  $\Lambda$  is an arbitrary length representing the dimension of the unit cell. The whole sample dimension was taken as  $150 \times 150 \times 20$  sites along the  $x^*$ ,  $y^*$  and  $z^*$ , respectively. We set up empty boundary conditions in  $x^*$  and  $y^*$  directions because, upon the formation of stripes, there is a break in symmetry from one side to the other [5]. This means that spins on the borders interact with just 5 near neighbors. Inspired on the model with **Q**-tensor relaxation described in [7], the simulations are started with a reduced number of planes in  $z^*$  direction ( $z^* = 2$ ), in which the spins are free to rotate. Then, the LC layer growth effect is realized by periodically releasing a new plane of spins in the  $z^*$  direction.

With respect to the potential, we set the scalar function for CLCs previously developed in Chap. 2, in Eq. (2.65). In this case,  $\vec{n}_j$  is the orientation of the *j*-th spin and  $\vec{n}_k$  is the neighbor spin on the lattice,  $\vec{s}$  is the unit vector joining them. By assuming that  $\lambda = \mu = \rho = 0$ , the interaction potential reduces to

$$\Phi_{jk} = \nu P_2(b_{jk}) + \sigma P_1(c_{jk}) sgn(b_{jk}), \qquad (4.1)$$

that is an elastically isotropic potential with the chiral term analogous to the potential obtained by van der Meer [126] and recovers the Lebwohl-Lasher (LL) potential [2] when  $\sigma = 0$ .

From now on, we scale the potential by  $\nu$ , thus we define the reduced temperature by  $T_R = k_B T/|\nu|$ . In our simulations, the reduced temperature was adjusted to  $T_R = 0.20$ , far enough from the isotropic phase transition, which for the LL model is around 1.1232 [118]. Although the temperature of the experimental setup is near  $T_{IN}$ , we are more interested in the molecular organization of the ordered phase (elastic effects) and for this reason such a low temperature is crucial.

In the experiment, the temperature close to the IN phase transition is necessary due the phase coexistence regime. This low reduced temperature in the simulation guarantees enough order so elasticity plays an important role, but thermal fluctuations are still present. In essence, the model proposed in Eq. (4.1) captures the main aspects of the phenomenon, and, it is able to reproduce quite well many of them. In the experimental situation, the LC is confined between the substrate and the isotropic interface. Both of them represent a surface energy term which can be, from the elastic point of view, described by the LL isotropic potential represented by

$$\Phi_{j,int} = -J_{int}P_2(\vec{n}_j \cdot \vec{n}_{int}), \qquad (4.2)$$

in which the subindex *int* = {*sub*, *IN*} refers to the bottom surface (named as substrate) and IN interface, respectively. The bottom surface is located at  $z^* = 0$ , in which the spins lay parallel to the  $x^*$  direction, thus mimicking the strong, rubbed planar orientation on the substrate. We set  $J_{sub} = 1.00$  to reproduce a relatively strong anchoring, and the direction of  $\vec{n}_{sub}$  with a small pretilt of 3° with respect to the *x* direction, in agreement with experimental results [7] and for avoiding degenerated states [158]. It has been measured and theoretically confirmed [182, 183] that LCs anchor at the IN interface with high pretilt (~ 50 to 70° with respect to the interface's normal) and weak anchoring strength. Therefore, in our model, the spins located in  $z^* = d^* = d/A$  interact with their fixed neighbor according to Eq. (4.2), where weak anchoring strength is achieved with  $J_{IN} = 0.10$  and the easy axis  $\vec{n}_{IN}$  tilted in the  $x^*$  direction (50° with respect to the normal). In the region of the bulk with thickness  $d^*$  (1  $\leq z^* \leq d^*$ ), the spins are free to gyrate and are initially set with components in the same direction of substrate alignment to reproduce the thin layer ordered of nematic phase after the wetting transition. The initial reduced thickness is  $d^* = 2$ .

We have set 50 kMCs, and after this, the interface rises one plane making the thickness  $d^* \rightarrow d^* + 1$ , liberating sites of easy axis above to be part of the bulk, increasing the CLC layer. Again, 50 kMCs are completed and the previous procedure is repeated. Screenshots from Müller matrix approach are taken from directors below the IN interface each 2 kMCs, calculated
over an average of the last 500 cycles considering  $n_0 = 1.50$  and  $n_e = 1.66$ , an incident light with wavelength  $\lambda' = 545 nm$  and layers of 0.20  $\mu$ m.

## 4.4 Simulation results

As mentioned in the previous section, Eq. (2.65) is a pairwise additive potential with intrinsic chiral contribution provided by  $\sigma$ . Apart from this term, we investigated several sets of values of the physical parameters contained in Eq. (2.65), each of them representing a different LC. The selected values for the parameters that appear to best describe the experimental results were

$$\lambda = -0.35484, \, \mu = 1.16129, \, \nu = -1, \, \rho = -0.03226. \tag{4.3}$$

According to Luckhurst [5],  $\sigma$  can be rewritten as a function of the reduced wave vector  $q^* (= q\Lambda)$  as  $\sigma = -3q^*(\rho - \nu)$ , where  $q^* = 2\pi/p^*$ . We investigated the behavior of the system for several values of the reduced pitch  $p^* (= p/\Lambda)$ , ranging from 12.00 to 30.00 in steps of 2.00. First we discuss what happens with spins for two specific values of  $\sigma^* (= \sigma/\nu)$ , 1.140 and 0.608, where the reduced pitch is 16.00 and 30.00, respectively.

The first situation studied is for  $\sigma^* = 1.140$ . In this case, the spins start to organize themselves spontaneously in such a way that the stripes begin to spread over the field of view by nucleating new stripes. As discussed before, this is the GM type. The process of pattern formation occurs in the same way as the experimental situation, starting from a homogeneous texture and eventually developing the stripped pattern as the thickness grows. Fig. 4.4-(a)–(d) shows the Müller textures at different d/p ratios while Fig. 4.5-(a)–(d) illustrates the directors inside the small region delimited by the white square in the textures (Fig. 4.4), plotted in a 3D view. To clarify what is happening with the directors, each 3D plot has a lateral perspective from the plane  $x^*z^*$  showing the black dashed square region.

Initially, when  $d^* = 2 (d/p = 0.125)$  and, after the evolution of 50 kMCs, the texture is uniform. The material has no space to twist, so the sample behaves essentially as a nematic



**Fig. 4.4:** Müller textures showing the GM type. (a) d/p = 0.125 (50 kMCs) – the sample is pattern free. (b) d/p = 0.188 (50 kMCs) – stripes start to nucleate and grow across the field of view. (c) d/p = 0.250 (50 kMCs) – the pattern is consolidated in the LH orientation. (d) d/p = 0.312 (50 kMCs) – under the increase of the thickness to pitch ratio, the pattern fills the whole field of view. As to the experiment, defects move across the cell.

#### **4.4 Simulation results**



**Fig. 4.5:** Vectorial field of spins in the white square of the Müller textures of Fig. 4.4. (a) d/p = 0.125 (50 kMCs) – the thickness is thin so the sample is not allowed to form the SH configuration by the bottom surface. (b) d/p = 0.188 (50 kMCs) – the system starts to nucleate stripes. (c) d/p = 0.250 (50 kMCs) – and (d) d/p = 0.312 (50 kMCs) – the LH orientation is well defined.

Figs. 4.4-(a) and 4.5-(a). The striped pattern is not formed at this moment because the strong anchoring energy at the bottom surface overlaps any other energetic competition. After the addition of one plane in the  $z^*$  direction,  $d^* = 3$  and d/p becomes 0.188. At this ratio, after 50 kMCs, black lines starts to appear in the textures, which results from the different refractive index of the forming stripes with respect to the uniform texture, as illustrated in Fig. 4.4-(b). Here, in different regions, the spins change their orientation, forming periodically distributed orientations of the director where the helix lies down in the plane so that its direction become parallel to the substrate, as shown in Fig. 4.5-(b). Notice how the stripes "end" at the isotropic interface, which is not the case if the anchoring energy is high [181]. When  $d^* = 4$  and d/preaches 0.250, after 50 kMCs again, the system has enough space so the stripes form the LH orientation and adjust themselves according to the characteristics of the box simulated, as illustrated in Figs. (4.4c) and (4.5c). For  $d^* = 5$ , d/p = 0.312, the stripes in simulation follow the same behavior as experimentally, where the defects move through the plane  $x^*y^*$ . Figs. (4.4d) and (4.5d) show the configuration after 50 kMCs. Although the system in the simulation does not include nucleation seeds in the bulk, it presents the stripes emerging from different areas. The system is able to spontaneously reproduce this experimental behavior because of the random nature of MC simulation.

In the second situation,  $\sigma^* = 0.608$ , which implies  $p^* = 30.00$ . As the first case discussed previously, Figs. (4.6a–d) and (4.7a–d) shows the Müller textures and the 3D plot of spins in the lattice inside the white square of the textures. The behavior found for the evolution of the system in the simulation is quite similar to the DM. We report on the simulation mimicking this pattern with qualitative agreement to the experimental results discussed in Fig. 4.3. Here, while  $d^*$  is smaller than 7, the spins just keep the SH orientation. When  $d^* = 7$ , and

$p^*$	12.00	14.00	16.00	18.00	20.00	22.00	24.00	26.00	28.00	30.00
$\sigma^*$	1.520	1.303	1.140	1.013	0.912	0.829	0.760	0.702	0.651	0.608
d/p	0.167	0.143	0.188	0.222	0.200	0.227	0.208	0.231	0.214	0.233
type	GM	GM	GM	CM	CM	СМ	CM	DM	DM	DM

**Tab. 4.1:** Table containing values of the reduced pitch, the respective values for  $\sigma^*$ , the critical ratio d/p under which the stripes form and the kind of modulation for the energy parameters used.

consequently d/p = 0.233, the system starts to evolve. After just 2 kMCs, Fig. 4.6-(a), an undulated modulation subtly forms, Fig. 4.7-(a), which is confirmed with a smooth indicative of modification in the spins orientation. Contrarily to what happens with GM, after accumulating 10 kMCs, the system shows the stripes quite well defined. The pattern suddenly appears as the MCs increase, even for d/p fixed, as illustrated in Figs. (4.6b) and (4.7b). When the system reaches 50 kMCs, Figs. 4.6-(c) and 4.7-(c), the spins do not present any significant change, just a small adjustment on the displacement of stripes. Finally, we show in Fig. 4.6-(d)  $d^* = 9$  and d/p = 0.300. The lateral perspective shows in Fig. 4.7-(d) a structure modulated quite different from GM type. The spins change their orientation smoothly. In addition, Fig. 4.8-(a)–(b) shows the spins of a slice of the plane  $x^*y^*$  overlapping the Müller texture. Fig. 4.8-(a) is the same region of the white square in Fig. 4.4-(c), and the Fig. 4.8-(b) is the region around the defect in Fig. 4.6-(d). In both of them, it is possible to compare the result of the texture with the directors orientation.

Table 4.1 shows the values for each  $p^*$ , the values for  $\sigma^*$ , the critical values for d/p in which the system starts to suffer the structural transition and the respective kind of modulation. For values of  $p^* \leq 16.00$ , the spins present the GM. When  $p^* \geq 26.00$ , the system presents the DM. Values between 16.00 and 26.00 present both GM and DM in the field of view for the same critical value of d/p; in this case we say that there is a coexistence between both modulations (CM), like reported by Fuh et al. when the CLC is under a specific voltage [72].



**Fig. 4.6:** Müller textures showing the DM type. (a) d/p = 0.233 (2 kMCs) – the pattern starts to develop. (b) d/p = 0.233 (10 kMCs) – the striped pattern emerges homogeneously in the field of view. (c) d/p = 0.233 (50 kMCs) – the system organizes the stripes according to the parameters and the characteristics of the lattice. (d) d/p = 0.300 (50 kMCs) – the defect (dislocation) changes as d/p increase.



**Fig. 4.7:** Vectorial field of spins in the white square of Müller textures of Fig. 4.6. (a) d/p = 0.233 (2 kMCs) – the spins are in the SH orientation. (b) d/p = 0.233 (10 kMCs) – as the system is in the critical ratio just 10 kMCs is enough to develop homogeneously. (c) d/p = 0.233 (50 kMCs) – after the pattern is formed, no significant change is found because the system has already reached the equilibrium configuration. (d) d/p = 0.300 (50 kMCs) – as the ratio d/p increases even more, the stripes just organize themselves according to the pitch and the lattice size.

## 4.5 Discussions

We first discuss the rotation of the stripes. Such rotation occurs due to the continuous change in d/p ratio as the temperature is lowered. Since the LC layer has a structure similar to a hybrid aligned cell (one substrate favors planar anchoring while the opposite favors homeotropic anchoring), near the planar side the CLC forms a SH structure to follow the substrate's imposition. This small elastic boundary layer dictates the overall direction of the stripes that are formed right above. As d/p grows, the amount of twist of this standing helix portion also increases, which, consequently, twists more and impose the observed rotation of the stripes. The observed defects result from the rotation without a fixed point [7]. Such phenomenon has been explored before under applied electric field [70], light irradiation [6] and thermal stimulus [60]. From the simulation point of view, the rotation of the stripes is also observed. However, they require large meshes and are difficult to work with. We therefore will explore this effect on both GM and DM type of modulations in a future work.

From the experimental data, we observe that both, the GM and DM type take roughly the same temperature interval from the first appearance of the phase (wetting transition) until the formation of the stripes, thus indicating that the thickness of the layers are about the same in both situations [7]. Therefore, the critical thickness to pitch ratio, experimentally, is different



**Fig. 4.8:** Horizontal slice of the plane  $x^*y^*$  showing the behavior of spins (a) the GM and (b) for the DM. As background the Müller textures are contrasting the light interaction with spins below the interface.

mainly due to the values of pitch length of both samples. Clearly, the GM type possess smaller d/p value than the DM type. The simulations agree well with the experimental results when one looks only at the critical d/p ratio required to the striped pattern formation, that is, it is smaller for GM in comparison with DM type. In the simulations, the critical ratio for GM is 0.188 while for the DM is 0.233.

The phenomenon reported here occurs experimentally while the temperature changes. Since the temperature change in the experiments is small ( $10^{-3}$  in terms of the reduced temperature), in the simulations the reduced temperature is fixed, so the connection with experimental facts is done by the ratio d/p. From the statistical mechanics point of view, for  $T_R = 0.2$ , this interval can be negligible without loss of generality. Therefore, the experimental change in d/pcan be directly connected with the simulated change in d/p.

In order to understand the two types of modulation and the connection between the experimental and simulated results, we propose the following explanation: as previously discussed, the fact that CLCs anchor with very low energy strength on the isotropic interface allows a director distribution in which the stripes form within the interface. In fact, the low anchoring strength at the top interface allows the director to use the interface as part of the stripes themselves, rather than keeping them in the bulk. This fact favors the formation of stripes for very thin layer, a phenomenon that would not happen in the strong anchoring situation. As shown in Fig. 4.5-(a), but also in reference [7], the initial layer is under strong influence of the bottom substrate, in such a way that the LC layer in the initial moments is essentially nematic. Clearly, as the temperature decreases, the system eventually forms the stripe pattern, but how it does is directly related to the d/p ratio. If the system does not form SH in the initial moments, it will try to form GM type. Therefore, it requires very small d/p ratios where no twist is allowed to form in the initial moments, due to the strong influence made by the bottom substrate, but, upon thermal fluctuations, each stripe is allowed to nucleate, jumping from the nematic-like arrangement to the LH organization. There is, therefore, an energy barrier between the no twist arrangement

and the striped pattern that is overcome by thermal fluctuations. In the simulations, the stripes form for very thin layers, before any twist perpendicular to the substrate occurs. Therefore, only for smaller pitches the GM type is observed. Experimentally, on the other hand, the larger pitch cell (in comparison to the DM type) makes this nematic layer to continue as large as the DM forming layer, which is expected since larger pitches samples require more space to form any twist (SH structure). Since the sample becomes frustrated, it thus forms the pattern by nucleating stripes one by one. This process therefore is analogous to the finger formation under external stimuli often found in surface frustrated CLCs [166, 184]. Hence, in both experiments and simulation the small d/p ratio is required. For the DM type, on the other hand, a small amount of twist occurs perpendicular to the substrates. In the simulations due to the larger layer while in the experiments due to smaller pitch. Eventually, as discussed in reference [7], the elastic penalty, which results from strong splay deformation at the IN interface and twist deformation from the system's frustration, makes the helix to form parallel to the substrates, thus explaining the larger d/p needed.

The pattern formation and the critical parameters for its appearance was analyzed in reference [7] with  $\mathbf{Q}$ -tensor and relaxation methods. The MC technique has stochastic features aggregated in the numerical simulations. Thereby, the simulation done here is performed from the statistical mechanics point of view. The potential in Eq. (2.65) provided both growing and developable modulations whereas the  $\mathbf{Q}$ -tensor method has found just the developable one.

Altogether, a discussion on why the critical layer thickness of both modulations are different in the simulations whereas in the experimental cases they are the similar is necessary. In other words, although the d/p ratios agree well for the formation of the modulations, when layer thickness and pitch are looked separately the experiments and simulation fail to agree. We believe a few facts might be responsible for this: first, it is not very clear what values the pretilt and anchoring strengths assume at the isotropic interface, since there are few experiments on the subject and the number of liquid crystal hosts used in such experiments is very limited. Furthermore, the experimental sample has many nucleation seeds such as defects and spacers that are not accounted for in the simulations. More drastically, CLCs are known to present different behaviors depending on the elastic anisotropy. The LL pairwise potential does not have anisotropy included in its interaction, whereas Gruhn and Hess proposed a spatially anisotropic pair potential. The process is done by discretizing the Frank energy by small displacements, where the elastic constants (splay, twist and bend) can be distinguished [3]. Recently, several works have been done with the potential in Eq. (2.65) which represents an extension of the LL potential that aggregates elastic anisotropy [4,5,124,128,130,131,158,185–187]. One possible link between the energy parameters  $\lambda$ ,  $\mu$ ,  $\nu$ ,  $\rho$  and  $\sigma$  with the elastic constants is obtained by the condition of  $\mu = -3(\lambda + \rho)$  [128]. It leads to the following connection:

$$\lambda = \frac{1}{9}\Lambda (2K_{11} - 3K_{22} + K_{33}),$$
  

$$\mu = \Lambda (K_{22} - K_{11}),$$
  

$$\nu = \frac{1}{9}\Lambda (K_{11} - 3K_{22} - K_{33}),$$
  

$$\rho = \frac{1}{9}\Lambda (K_{11} - K_{33}),$$
  

$$\sigma = -K_{22}q^*\Lambda.$$
(4.4)

For the purpose of this work, the values used in Eq. (4.4) imply elastic constants values given by  $K_{11}/K_{22} = 0.60$  and  $K_{33}/K_{22} = 0.70$ . These values do not represent any known LC but, in our tests, represent the best set of energetic parameters (in Eq. (2.65)) to describe the experimental results. It is, therefore, important to stress that the simulations and experiments might not be represented by the same elastic parameters. Further investigation is being carried out to better understand the connection between the simulation parameters and the experimental elastic constants. However, the simulation model used here is a pairwise potential and the connection with continuous models is valid in a limited regime with very low temperature and small deformations [128]. Out of this regime, this connection seems to be still a challenging task.

Remarkably, this simple simulation procedure is able to qualitatively reproduce most of the experimental results. For example, the same LC with different pitches can present, after the wetting transition, stripes formation of GM and DM type. In the pairwise additive potential studied here, the same process is observed when the theoretical pitch is changed. Furthermore, both kinds of pattern formation are observed in the simulations. In addition, the experimental results indicate that the periodicity of the stripes corresponds to roughly half of the pitch. For  $\sigma^* = 1.140$ , Eq. (4.4) gives  $p^*(= p/\Lambda) = 16.00$ . It means the theoretical natural pitch in this sample needs at least 14 sites to the spins rotate 360°. The periodicity found after the sample stabilizes the stripes (keep equally spaced) is  $\approx 8.08$ . For the case of  $\sigma^* = 0.608$ , the theoretical pitch is 30.00. The periodicity found in the simulation was  $\approx 17.5$ .

## Chapter 5

# Thermal Quench in Liquid Crystal Droplets

## 5.1 Introduction

A typical thermodynamic stable phase is often described by an order parameter that varies continuously through space, except in singular regions, known as defects, where the order is not well defined [188]. In some cases, these topological defects can appear in LC even when it is in the ground state, for example, confined in a spherical geometry like a droplet. The topology in the sphere can not be quite simple since it is not a rule the ground state to assume the simplest solution [189]. The features of a defect can affect macroscopic characteristics and the interplay between topological limitations and energy minimization is crucial to determine the structures of some systems. Viruses and spherical bacterial surface layers are some examples of how the environment and minimum energy state affect on each other [190–193]. Controlling topological defects can be important for electro-optical material science in polymer-dispersed LCs [194–196], since the LC internal order in the droplets can either change from an opaque or diffracting state to a transparent one. Besides, droplets are interesting because the inner structure is ordered, and they are small, so bulk and surface are directly competing, making the droplets more complex and distinctive than continuous liquid crystalline media.

The spherical cavity provides different complicated arrangements according to the combination of several factors, like the anchoring at the surface, the LC elastic properties, the droplet size and external influences [197]. Among these considerations, the kind of surface anchoring should be used to classify the LC drop. The director field  $\vec{n}$  tends to follow the easy axis imposed in the sphere boundaries. The alignment at the surface can be in the radial line, perpendicular to the surface, called homeotropic anchoring. In this case, configurations like sea hedgehog, a twisted version of this one, beyond the axial drop (when bend distortions are favorable) can usually be found as stable states in nematic droplets [189]. The Gauss theorem requires that this kind of anchoring generates structures with total topological charge in the bulk

equals to +1. On the other side, the surface can be tangentially aligned, called planar or parallel anchoring. The bipolar drop, the twisted bipolar or the concentric arrangement (also formed when bend distortion are favorable) are possible equilibrium configurations for this case. A tangential anchoring may generate topological defects at the surface and the total topological charge on the surface, required by the Poincaré-Hopf theorem, is +2 [188, 198].

After new applications of nematic and cholesteric droplets in functional, responsive materials boost researches in this subfield of physics, several works were developed to better understand physical properties, formations of topological defects in ground states and the droplet responses to temperature, external stimuli and chemical reactions. The complex behaviors that appear in LC droplets are resulting from intrinsic topology in the space curvature in a sphere. Although little explored, effects of induced interaction between the droplets and the LCs confined in more complex geometries may be worth studying in order to find new features.

In 1931, Dirac theoretically proved that the existence of magnetic monopoles would be consistent according to the symmetry in Maxwell equations [199], but they are really hard to be detected in experiments and it remains an open research problem. Notwithstanding, other fields of physics, like the LCs, have observed interesting similarities in topological charges with the Dirac monopole (hypothetical magnetic charge). Fascinatingly, monopole defects have demonstrated stability in layered structure like CLC droplets if the pitch is considerably smaller than the droplet radius [200, 201].

Boundary conditions often break the symmetry of an ideal CLC structure. For spherical environments like droplets, the geometric frustration can generate equilibrium states with stable topological defects. The resulting structure depends on several parameters of the system, like size of the droplet radius (*R*), kind of surface anchoring, pitch length (*p*), external influences, among other aspects, as well. To measure the intensity of helix rotation inside the droplet, it is convenient to define a parameter relating the droplet size and the cholesteric pitch. The definition N = 4R/p counts how many times the helix completes half pitch, or the number of  $\pi$ -turns along the droplet diameter, and it does not have to assume integer values. In particular, after thermal quench in droplets with homeotropic anchoring, single disclination loops are expected if  $N \leq 3$ , but many metastable states and complex linked knots can emerge if the chiral regime is driven by  $N \geq 4$  [10,202]. On the other hand, low chirality regimes (N < 4) in a planar surface anchoring may produce the twisted bipolar configuration, while high chirality ( $N \geq 4$ ) leads to spiral arrangements [203].

Although some simulations have reproduced thermal quenches in cholesteric droplets, they have accomplished the quenching process by the continuum mean field LdG free energy approach. The procedure to carry out the relaxation in this model consists of moving the directors according to the Frank free energy minimization. In 2012, Seč *et al.* used the LdG numerical model to find equilibrium states in droplets with parallel alignment at the surface, by changing the cholesteric pitch, starting the simulations in structures organized by Ansatze [204]. Still considering the planar alignment, in 2016, Zhou *et al.* reproduced transitions between stable

structures for intermediate cholesteric pitches using the LdG model by considering random director field as initial condition [11]. On the other hand, the LdG relaxation process in cholesteric droplets with homeotropic surface alignment and random initial orientation showed a variety of metastable configurations for a  $N \ge 4$  pitch regime [202]. There is a lack of simulations in frustrated cholesteric droplets, with homeotropic or planar surface anchoring, successfully describing stable and metastable states considering different pitch regimes and starting the relaxation process by random organizations. Besides, simulations really involving the temperature in relaxation procedures have not been reported yet. The understanding of state stability and its relation to system parameters is still a challenging and open task. To the best of our knowledge, this is the first report of thermal quench simulations by the Monte Carlo method using the MH algorithm, which includes the temperature as a real parameter in the system. In the context of such scarce simulation state of the art, we performed simulations of thermal quench in CLC droplets to investigate the equilibrium states to compare the Monte Carlo (MC) method with other commonly available tools for studying these systems. The simulations are based on spins in a discretized lattice interacting with the nearest neighbors by means of the chiral pairwise additive potential proposed by Luckhurst [5]. We report common experimental macrostructures for both homeotropic and planar degenerate anchoring, as well as states featured by new linked knots, not previously found in the literature. In this chapter we describe the expected stable states for homeotropic and planar surface alignment, the aspects of simulations, followed by the results and discussions.

## 5.2 Basic properties, kinds of anchoring and stable states

Generally, nematic supramolecular droplets have the order parameter approximately constant in the bulk, but they suffer a considerable change near the surface and defect lines, due to the sharply increment on the elastic energy [205–207]. As previously mentioned, the structure of the droplet depends on factors like the competition between elasticity, kind of anchoring and the surface tensions. In general, an equilibrium state is defined by the minimum of the free energy functional given by

$$F = F_v + F_s = \int_V f_v dV + \int_{\Sigma} f_s d\Sigma, \qquad (5.1)$$

where V is the droplet's volume,  $f_v$  is the bulk free energy density,  $\Sigma$  is the area of the surface, and  $f_s$  is the surface free energy per unit area [208]. However, it is relatively difficult to find solutions for this minimization problem, because the bulk and surface energies are often comparable, and  $f_s$  depends on the orientation of directors at the surface, for example. Terms of surface, usually omitted in the minimization process, do not change considerably the stability of the supramolecular architecture [207].<sup>1</sup>

<sup>&</sup>lt;sup>1</sup>As a first approach,  $f_s$  is considered to be a constant.

LC droplets are practically spherical in real cases. The structure inside the droplet depends strongly on its size. In the small size regime,  $R \ll l_w (\equiv K/W_a)$ , where  $l_w$  is the characteristic anchoring length,  $W_a$  is the anchoring energy and K is the elastic constant for one-constant approach, the bulk energy outweigh the surface terms, and no variations on the director profile happen. On the contrary, the directors in large droplets ( $R \gg l_w$ ) respect the imposition required by the surface anchoring, making a distorted field with topological defects taking place inside the droplet. Droplets where the surface terms are dominant ( $R > K/W_a$ ) contain topologically stable defects. In some cases, they are unusual, *e.g.*, monopoles analogues of Dirac monopole.

Typically,  $W_a \sim (10^{-6} - 10^{-5}) Jm^{-2}$  for the liquid crystalline cyanobiphenyls-glycerin [208], which leads to an extrapolation length  $l_w$  of the order of micrometers if  $K \sim 10^{-11}$  N. The large regime of *R* provides defects in equilibrium. So, the directors make a polar angle  $\alpha$  with the radial direction  $\vec{r}$  normal to the surface. If this angle is fixed, there is no need to solve the minimization of energy to find topological properties inside the droplet. This is possible due to the differential geometry and it can be better understood by the Gauss and Poincaré theorems, which establish connections to the topological charge. Significantly, the conservation of the topological charge guarantees the defect stability, so the conservation laws dictate the defect creation, annihilation or mutual transformation [208].

Lets consider the normal molecular anchoring over the interface, where the directors are perpendicular to the surface. Although it is a simple case of surface alignment, the director field in the bulk can adopt complex configurations such as equatorial disclination for low chirality [209], twisted disclination around the sphere [210], bulk defects like Skyrmions [211], or even hidden constellations of monovalent and polyvalent singular point defects [212]. On the other hand, the planar anchoring requires a special attention concerning the defects that the intrinsic topology of the system generates. There are different ways the directors can be aligned at the surface. The first to be mentioned is the bipolar anchoring. In this case, the easy axis at the surface is fixed and, in each point of the surface, it points towards the pole of the respective hemisphere where the director is located. So, the director field forms two diametrically opposite boojums and the anchoring is similar to the Earth's magnetic field. The second case is the toroidal boundary conditions. This case is similar to the bipolar boundaries, but here the directors are, beyond be tangential of the surface, perpendicular to the axis which connects the two opposite boojums at the surface. So, the alignment at the surface is similar to the concentric rings around the diameter line of the droplet. Although once reported [213], this kind of anchoring is not so common because the bend elastic constant is very often larger than splay constant in LCs. The third and most common parallel anchoring at the surface is the planar degenerated anchoring [66, 68, 203, 214, 215]. In this case, the directors are free to rotate in the tangent plane to the surface. Consequently, the planar degenerate alignment is a result that minimizes the bulk energy driven by the competition between elastic anisotropy, thermal energy, chirality and anchoring energy at the surface.

#### Nematics

For nematic droplets under homeotropic anchoring, the radial alignment is the preferred configuration depending on the splay and bend distortions. Variations like the twisted radial configuration can be found for  $K_{33}/K_{11} < 6$ , since it reduces the bulk energy near the point defect. It is important to mention that the previous states have stability driven by the relation between the elastic constants. Still for homeotropic anchoring, if bend distortions are favorable over the splay ones, a structure with a defect ring located near the surface can be seen. This is the axial structure. In addition, there is a critical droplet radius in which the surface anchoring is no longer kept, making a transition possible from the radial to axial configuration.

In the case of a tangential anchoring, the bipolar structure (BS) experiments splay distortions near the boojums at the surface and bend distortions in the bulk. If the twist distortion appears in the bulk, the twisted bipolar distortion is formed given an specific relation between the elastic constants. Besides, it is possible to find the concentric structure according to the elastic constants ratio. The concentric drop is an unstable state due to the nonexistence of defect line of integer strength in nematics [23].

#### Cholesterics

Different from nematics, that form singular defect lines, the disclinations in cholesterics are of type  $\lambda$ ,  $\tau$  and  $\chi$ , but this latter class is unstable. The chirality in LC droplets breaks the symmetry of the nematic orientation in the bulk. As a result, more complex configurations may appear. Since the helix rotates inside the droplet, the director field should be driven by the twisting power and boundary conditions.

Droplets with homeotropic anchoring can present several different metastable states with disclination lines knotted in the bulk [202]. This bulk disclinations can also be understood as an intermediate state between the homogeneous nematic and the non-trivial blue phase structures under complex confinement [216, 217]. Considering the homeotropic anchoring and high values of qR, the Frank-Pryce model prevails since the anchoring energy of the surface does not exert a force to unpack the cholesteric layers [209]. According to the literature, if qR < 5 ( $N \leq 3.3$ ), the probable structure is the axial configuration with a twist between the layers [189, 209]. For smaller values of qR, a ring defect can be observed around the surface, and even smaller values furnish the radial structure in a very similar way to the nematic configuration [209].

For cholesteric droplets with planar anchoring, at least three kinds of structures can be found in experiments depending on the radius to pitch ratio R/p. The molecular organization can easily become complex when chirality is competing with other parameters. Understanding the behavior of supramolecular architecture is a difficult task that can help applications like color displays, biosensors, cross-communication between droplets and generation of 3D omnidirectional microlasers [8, 218–220]. The low chirality regime (N < 2) in tangential anchoring generates the BS [207, 209], similar to the nematic case. If the chirality parameter obeys 2 < N < 3, the twisted bipolar structure (TBS) appears and the sample exhibits the twisted bipolar transmission pattern. When this cylindrical symmetric configuration is observed with its axis perpendicular to the light and parallel to one polarizer, an elliptical ring pattern forms in the field of view. As the helix in the bulk is rotating in the perpendicular plane to the light ray, the chirality is revealed by dark regions across the bulk appearing due to the birefringence of LC. If the parameter N keeps increasing, the boojums become nonantipodal and are located in the same droplet hemisphere. This is an intermediate state between the TBS and the high chirality regime, also found in experiments and theory, known as bent-TBS (bTBS). For the regime of high chirality (p < R or N > 4), experiments exhibit droplets arranged in the spiral pattern, while the perpendicular plane manifests a concentric ring pattern. The Frank-Pryce model describes this concentric ring pattern as a  $\chi^{+2}$  defect line going from the surface to the center of the droplet, which does not allow the rings to connect completely. Xu and Crooker explained that the Frank-Pryce structure could be better understood if the escaped model (describing the defect line) were implemented as a non-singular disclination line [203]. On the other side, Seč et al. has recently proposed that the Frank-Pryce structure is the radial spherical structure (RSS) with no singular bulk defects and with the director escaping in two separate regions corresponding to two  $\lambda^{+1}$  lines winding around itself finishing in two very closed boojums in the same hemisphere at the surface [204]. In their simulations with the numerical LdG model in planar degenerate cholesteric droplets, they found the structure stability in function of the pitch [204]. For such, Ansatze were used to generate initial conditions and the elastic anisotropy was not considered. The equilibrium configurations RSS, diametrical spherical structure (DSS) and planar bipolar structure (PBS), previously known in the literature, were reported. The theoretical predictions show the DSS as one of the solutions for a possible structure, with cylindrical symmetry and two defect lines terminating on the surface with two s = 1defects. In agreement to the stability diagram of the structures, the experiments show that for large pitches the TBS is the most stable state, due to the helix unwinding, while in high chirality regimes the most observed equilibrium state is the RSS. Additionally, two new proposed structures with appropriate values of N, Lyre structure (LS) and Yeti structure (YS), were found to be highly metastable. Due to the high energetic difference of the structures for large values of N, it is not expected that thermal fluctuations in the director could induce transition between the configurations. For all these structures, the gap in the energy can achieve an order of magnitude of  $10^4 k_B T$ . Small values of  $N (\leq 2)$  always present the TBS as the stable state, while for  $N \geq 3$ the RSS is the most stable compared to all the other structures. For N = 4, the highest energetic structure is the YS, followed by LS, though such structures do not have singular defect because the cholesteric layers are highly deformed along the bulk. Furthermore, the internal energy of PBS increases with N, becoming the most unfavorable configuration for N > 7.

Uncommon structures and thermodynamic phase transitions also happen since the droplet is strongly influenced by parameters, such as temperature, external fields, elastic con-

stant and chirality, but the relation between them and these controlling parameters are not well known.

## 5.3 Aspects of simulations

#### **Classification of points**

In order to accomplish the simulations, it is necessary to represent the system in the discretized space, choosing the Cartesian coordinates. For such, let us suppose the droplet has a radius occupying  $R^* \equiv R/\Lambda$  sites in the discretized system.<sup>2</sup> If a point located by the vector  $\vec{r}^* = x^*\hat{i} + y^*\hat{j} + z^*\hat{k}$  has its modulus  $|\vec{r}^*| \leq R' (= R^* + R_{\text{ext}})^3$  this point is considered to be inside the sphere. To represent the spherical shell where the spins at the surface are, an interval of points between R' and  $R^* + 2$  was delimited to avoid risks of some point to be interacting with points outside the sphere. Finally, points in which are distant in a value greater than  $R^* + 2$  are considered out of the sphere for the simulations. So, an sphere with radius  $R^*$  must have a diameter of  $2(R^* + 2)$  eligible points belonging to the sphere and, consequently, must be contained in a cube with side length  $2(R^* + 2)$ . Given this configuration, there is no need to access points outside the sphere.<sup>4</sup> To know if the points are from the bulk, the following analyses were made. Points located between the center of the sphere and R' are classified as point of the bulk, or points of the type 1 (pt = 1).<sup>5</sup> Points belonging between R' and R<sup>\*</sup> + 2 are points at the surface, or pt = 3. Points farther than  $R^* + 2$  are outside the sphere, and they are considered as pt = 0. After these points are characterized, the lattice is scanned again. If a point of type 1 has one or more neighbors of type 3, it is a point beside the surface and it is classified as a point of type 2.

#### Lattice size and kinds of interaction

As previously mentioned, the morphological behavior of the sample in the bulk is sensitive to the R/p ratio. Determining the lattice size is not a simple task, because it depends on the material, *e. g.*, if the LC is a nematic or cholesteric, beyond other factors acting in the system. If the droplet radius is very small, the surface can no longer perform its function since the extrapolation length becomes the same order of magnitude as the radius, thus representing an extremely weak anchoring. In case the material is a cholesteric, it is necessary to consider a minimum quantity of sites to appropriately typify the intrinsic helix in the phase. As the pairwise potential involves energetic parameters competitions, it is convenient to consider the

<sup>&</sup>lt;sup>2</sup>As the error to represent the sphere in the Cartesian system tends to zero only when *R* goes to infinity, the radius in some points on the boundaries can variate in  $\pm \sqrt{2}$ , and in other points  $\pm \sqrt{3}$ .

 $<sup>{}^{3}</sup>R_{\text{ext}}$  is a small value to correct the sphericity near regions coinciding with the axes x, y, and z.

<sup>&</sup>lt;sup>4</sup>During the simulation, it is not efficient to calculate the distance between a raffled point in the bulk and the center of the sphere several times to know if such point belongs to the bulk. It is convenient to classify the lattice points by kinds. So, the distance between each point and the center of the sphere is calculated just once to know the type of the point.

<sup>&</sup>lt;sup>5</sup>The center of the droplet is located in the position  $(R^* + 2, R^* + 2, R^* + 2)$  in the lattice.

values of the chirality parameter in comparison to the other terms of nematic phase and the surface interaction energy. As an example, suppose the chiral elastic one-constant approach case. The terms that do not vanish in Eq. (2.65) are

$$\Phi_{ik} = \nu P_2(b_{ik}) + \sigma P_1(c_{ik}) \operatorname{sgn}(b_{ik}).$$
(5.2)

Considering that the cholesteric is a locally quasi-nematic, it is useful to propose that  $|\sigma| < |\nu|$ , where  $\nu$  represents the interaction energy between the directors in the nematic phase. Supposing  $\sigma^* (\equiv \sigma/\nu) = 0.500$ , the Luckhurst model shows that

$$p^* = -K\Lambda \frac{2\pi}{\sigma} = 3\nu \frac{2\pi}{\sigma} = \frac{6\pi}{\sigma^*} = 12\pi.$$
(5.3)

Such value of  $\sigma^*$  generates a reduced pitch  $p^*$  near 38 sites. Thus,  $R^*$  around 40 sites can be a suggestive value for the lattice in the simulations, since under the  $T_R = k_B T/|\nu| \sim 10^{-1}$  temperature regime, each site represents around  $\sim 10^{-1} \mu$ m, which designates an experimental droplet with diameter between 1 and 10  $\mu$ m.

#### Interaction with surface

The spins interactions of type 1-1, 1-2 and 2-2 normally occur via Luckhurst potential, given by the Eq. (2.65). On the other hand, spins of type 2 that have at least one or more type 3 neighbors have 2-3 interactions given by the LL elastic isotropic potential, where the main factor determining the interaction is the angle between the spin and the surface easy axis  $\vec{n}_{surf}$  together with its anchoring energy  $J_s$ . Therefore,

$$\Phi_{j,surf} = -J_s P_2(\vec{n}_j \cdot \vec{n}_{surf}).$$
(5.4)

#### Homeotropic and planar degenerate anchoring

To impose homeotropic molecular alignment at the interface between the bulk and the outside matrix is quite simple, one just needs to align the directors at the surface in the radial direction of the sphere. In other words, the easy axis is pointed towards the unit vector connecting the center of the droplet and the point at the surface.

The planar degenerate anchoring setup is not quite simple, because the surface needs to be dynamic and adjusted until the volume reaches a stable equilibrium configuration. So, the easy axis moves just in the tangential plane to the sphere containing the point at the surface. The configuration of spins at the surface with planar anchoring is made as follows. Firstly, the spins of type 3 are set in the radial direction, forming a unit vector  $\vec{u}$ . Using spherical coordinates, each point in the space can be represented with three coordinates: the radius *R*, the polar angle  $\theta$  and the azimuthal angle  $\phi$ . For each point where the angle  $\theta \neq 0$  or  $180^{\circ}$ , we take the cross product between  $\vec{u}$  and the *z* axis in  $\hat{k}$  direction, in order to obtain a vector  $\vec{a} = \vec{u} \times \hat{k}$  perpendicular to both vectors. If it is carried out for all spins at the surface with exception to the poles, the surface will have a toroidal anchoring, since the spins are tangent to the surface and do not possess components in  $\hat{k}$  direction.<sup>6</sup> In principle, the droplet surface alignment starts from the bipolar alignment condition. To obtain such surface configuration, it is required to take the cross product  $\vec{n}_s = (\vec{u} \times \vec{a}) / |\vec{u} \times \vec{a}|$  also perpendicular to both vectors  $\vec{u}$  and  $\vec{a}$ .<sup>7</sup> Considering  $\vec{u} = (u_x, u_y, u_z)$ , the unit vector in the direction  $\vec{n}_s$  is given by

$$\vec{n}_{s} = \frac{1}{\sqrt{u_{x}^{2}u_{z}^{2} + u_{y}^{2}u_{z}^{2} + (u_{x}^{2} + u_{y}^{2})^{2}}} \left[ u_{x}u_{z}\hat{i} + u_{y}u_{z}\hat{j} - (u_{x}^{2} + u_{y}^{2})\hat{k} \right].$$
(5.5)

Therefore, given a unit vector in the radial direction in a certain point of the surface, the direction of bipolar, tangential alignment at the surface is given by  $\vec{n}_s$  in Eq. (5.5), as illustrated in Fig. (5.1). According to the movements of type 2 spins in the bulk, the type 3 neighbors must follow the volume progress, forming the degeneration at the surface. Once the surface must sustain the planar anchoring, the projection of type 2 spin in the bulk  $\vec{n}_b$  should be passed to the type 3 spin  $\vec{n}_s$  at the surface. Supposing that  $\alpha$  is the angle between  $\vec{n}_b$  and the radial direction  $\hat{R}$ , the angle  $\beta = \alpha - \pi/2$  may be the angle between the surface tangential plane and  $\vec{n}_b$ . Using the definitions of 3D rotation matrix, it is possible to rotate  $\vec{n}_b$  and project it on the tangential plane to the surface, finding a vector which is going to update the spin at the surface to  $\vec{n}'_s$ , making  $\vec{n}_s \rightarrow \vec{n}'_s$ . Being  $\vec{e}$  perpendicular to both the spin in the bulk  $\vec{n}_b$  and the radial vector  $\hat{R}$ , it means,  $\vec{e} = \vec{n}_b \times \hat{R}$ . The matrix  $\vec{M}(\hat{e}, \beta)$  which rotates a vector by an angle  $\beta$ , around the axis

<sup>&</sup>lt;sup>7</sup>The vectors  $\vec{a}$  and  $\vec{n}_s$  form the axis of the tangential plane at the surface in such point.



**Fig. 5.1:** Illustration of planar anchoring at the surface of sphere. The final result for the vector parallel to the surface is obtained by  $\vec{n}_s = (\vec{u} \times \vec{a}) / |\vec{u} \times \vec{a}|$ , where  $\vec{u}$  is a unit vector parallel to the radial direction  $\hat{R}$ , and  $\vec{a} = \vec{u} \times \hat{k}$ .

<sup>&</sup>lt;sup>6</sup>The planar anchoring for the spins at the poles are separetly imposed, just choosing a director planar aligned at the surface.

 $\hat{e} = x\hat{i} + y\hat{j} + z\hat{k}$  is given by

$$\overleftrightarrow{M}(\hat{e},\beta) = \begin{pmatrix} \cos\beta + x^2(1-\cos\beta) & xy(1-\cos\beta) - z\sin\beta & xz(1-\cos\beta) + y\sin\beta \\ xy(1-\cos\beta) + z\sin\beta & \cos\beta + y^2(1-\cos\beta) & yz(1-\cos\beta) - x\sin\beta \\ xz(1-\cos\beta) - y\sin\beta & yz(1-\cos\beta) + x\sin\beta & \cos\beta + z^2(1-\cos\beta) \end{pmatrix}$$

where the angle  $\beta$  is defined as

$$\beta = \arccos\left(\frac{\vec{n}_b \cdot \hat{R}}{|\vec{n}_b|| \hat{R}|}\right) - \frac{\pi}{2}$$

So, given an updated vector in the bulk  $\vec{n}_b$ , the updated vector in the surface can be written as

$$\vec{n}_{s}^{'} = \overleftrightarrow{M}(\hat{e},\beta) \cdot \vec{n}_{b} = \begin{pmatrix} M_{00} & M_{01} & M_{02} \\ M_{10} & M_{11} & M_{12} \\ M_{20} & M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} n_{x}^{(b)} \\ n_{y}^{(b)} \\ n_{z}^{(b)} \end{pmatrix}.$$
(5.6)

Fig. (5.2) illustrates how the director projection is at the surface. This updating process is performed every time the type 2 spin is modified in the bulk.



Fig. 5.2: Process of spins update at the surface. (a) Side view of the system showing the axis  $\hat{e}$  where the spin  $\vec{n}_b$  rotates an angle  $\beta$ . The vector  $\hat{R}$  is the radial direction and  $\vec{n}_s$  is the director at the surface, parallel to the tangential plane of the sphere. (b) Schematization of top view showing how the spins are aligned before the surface update, and how  $\vec{n}_s \rightarrow \vec{n}'_s$  after the projection.

#### Thermal quench in droplets

The LC droplets are made by using a glass capillary-based microfluidic device, inserting them in a surfactants matrix that interacts with the droplet boundaries, generating an anchoring at the interface according to the matrix material. After the droplets are formed, the system may reach a resultant equilibrium configuration due to all the energetic competitions. These stable states can be reached by photoincidence, electric field application, or thermal operations on the droplet. In special, heating the LC in the nematic phase above a temperature higher than the melting point to isotropic phase cleans any kind of order memory which the droplet had before [10]. As the system has a topological richness, the thermal quench allows several metastable states. It happens due to the thermal agitation providing energy gaps to the system leaping energetic barriers around the local minima. According to LL model, the reduced isotropic-nematic phase transition temperature is 1.123 [118]. This is the reference  $T_R^{IN}$  for simulations with the chiral potential proposed by Luckhurst. The first attempt in reproducing the experiments is supposing that initially, the system temperature in the simulation is fixed and the director configuration in the lattice is random. On average, the order parameter is zero in the isotropic phase. Following the MH algorithm [16], the MC method is able to eliminate the defects along the bulk due to the intrinsic thermal agitation in the simulations. The BW method efficaciously introduce the thermal agitation in the system [146]. Indeed, when the chirality is not present, the system relaxation occurs more efficiently compared to chiral systems that may have local helix rotating in different directions generating disclination lines. Consequently, if the LC has high chirality and the thermal quench is carried out very fast, these disclination lines can form complex links and knots which are very difficult to disrupt. This complication occurs because the disclination lines stabilizes in a locally trapped state [202]. So, it can be expected that keeping the reduced temperature  $T_R$  fixed in the simulations should work only for nematics and low twisting power cholesterics (N < 4). The reason is that keeping  $T_R$  fixed makes the director maximum rotation angle  $\theta_{max}$  to tend to a small fixed value.<sup>8</sup> Small values of  $\theta_{max}$ are not enough to switch the whole structure and escape from undesirable metastable states. If the system starts from random states with a temperature quite below the considered transition temperature, then the complex configurations reached by the directors could be hardly undone due to the complicated spherical topology. As LC droplets with low chirality easily relax in low temperature regimes, it is reasonable to think that the higher the chirality is, the higher the temperature needs to be for the system to get rid of bulk defects energetically unfavorable. Only then, after the system is kept in a certain temperature for several MC cycles, its change can be convenient. We selected *a posteriori*, an initial temperature near  $T_i = 0.700$  even for chiral droplets with  $N \leq 2$ . In this temperature, the  $\theta_{\text{max}}$  of directors tends to be near 45°. Choosing an ideal step size of temperature is crucial, because the sphere volume increases with the cube of R, so short steps can considerably enhance the simulation time. In order to choose the step magnitude, it is convenient to observe some experimental facts. If the droplets are too large, the relaxation can take hours after a thermal quench is done due to the increment in the combinations of accessible states in the system. A solution for such problem is performing a very slow thermal quench, with very short steps in the temperature, or to accomplish several thermal quenches in an intermediate speed. Looking for the range in the temperature in which the final point is  $T_f = 0.100$ , instead of doing  $dT \sim 10^{-2}$ , it is plausible to consider dT = 0.100. As mentioned before, whether the system is in a temperature near 0.200 in the high chirality regime, it is important to consider that the droplet will form a linked and knotted director field,

<sup>&</sup>lt;sup>8</sup>Such maximum rotation angle is updated in each cycle. Each temperature has a value in which  $\theta_{\text{max}}$  tends to keep the acceptance rate of BW method around 0.50. If  $T_R \to 0$ ,  $\theta_{\text{max}} \to 0$ , while if  $T_R \to T_R^{IN}$ , so  $\theta_{\text{max}} \to \pi/2$ .

and it remains because of the insufficient thermal agitation needed to relieve it.<sup>9</sup> In this case, *a posteriori* has been selected that, after the system reaches  $T_R = 0.400$ , an analyses is done in the directors. If the structure has not got rid of the undesirable disclinations, the system temperature is increased to  $T_R = 0.700$  or around and a new thermal quench is performed. It makes that the thermal agitation in the system increases to try to eliminate the defects which appear through the bulk. This procedure is done as many times as necessary, until the system has eliminated the defect lines, reaching an energetically most favorable structure. If the structure appropriately got rid of the defects, the system goes to  $T_f$ . Considering that the thermal quench process was carried out just once, the sample should have relaxed in at least 7 different temperatures. For each temperature, 200 *k*MCs are performed for the interaction of directors. No type of transient is considered in order to obtain the director field evolution in the lattice and to observe how the defects behave in the bulk. The order parameter *S* is evaluated according to Eq. (2.33), taking averages each 1 *k*MCs. The Müller matrix is taken each 10 *k*MCs, calculated over an average of 5 *k* cycles considering  $n_0 = 1.50$ ,  $n_e = 1.66$ , an incident light with wavelength  $\lambda' = 545 nm$  and layers of 0.20  $\mu$ m.

### 5.4 **Results and discussions**

In this section, we show the different organizations of droplets by performing thermal quenches under several combinations of elastic constants, chirality and anchoring energy. The elastic one-constant approach is given when  $K_{11} = K_{22} = K_{33} = K$ , but real elastic constants in common LCs respect the inequality  $K_{22} < K_{11} < K_{33}$ . When considering the complexity of chiral LL potential, we simplified both homeotropic and planar degenerate anchoring for isotropic case using the chiral LL potential. Also, for both kinds of anchoring, we used the elastic anisotropic approach using the Luckhurst potential with chirality.

Primarily, we describe the low chirality regime and then increase the number of rotations in the cholesteric helix. Before we mention the results, it is convenient to rewrite the cholesteric parameter  $\sigma$  in terms of N. By using the definition of  $N = 4R^*/p^*$  and Eq. (2.68) to substitute  $\Lambda$ , according to Eq. (2.70),

$$\sigma^* = -\frac{9\pi K_{22}N}{2R^*(K_{11} - 3K_{22} - K_{33})}.$$
(5.7)

We investigated the thermal quench in strong and weak homeotropic droplets for different pitches with elastic one-constant approach and the  $K_{11}/K_{22} = 1.20$  and  $K_{33}/K_{22} = 1.60$  elastic constant ratios, similar to CCN-37 LC [221, 222]. Due to the lack of experiments in droplets with weak planar anchoring, we investigated only strong anchoring energy cases for elastic one-constant approach and some different cases of elastic anisotropy, also for different chirality

<sup>&</sup>lt;sup>9</sup>The known structures in the literature have defect lines near the surface, which are eliminated in the central part of the droplet.

levels. All the droplets are set to have  $R^* = 40$  sites.

#### N = 0.00

In order to make a complete study of thermal quench, we start by discussing the nonchiral case N = 0 in the simulations, which implies  $\sigma^* = 0$ . The potential simply reduces to the LL model. Besides, we set the strong surface anchoring energy in  $J_s = 1.00$ , initial temperature  $T_i = 0.700$ , final temperature  $T_f = 0.100$  and steps of dT = 0.100. For each temperature, we run 200 kMC steps. As  $T_i$  is smaller than the transition temperature, there is a trend of alignment which favors the nematic phase. In a few cycles, compared to the whole range of simulations, the expected nematic structure takes place showing the known patterns in the literature for the two different kinds of anchoring. In Fig. 5.3 we show results for elastic one-constant approach in strong (a) homeotropic and (b) planar anchoring, both at  $T_R = 0.100$ . The directors are colored according to the order parameter S, so regions in blue scale are near defects where the spins suffer abrupt changing in the direction. In a transparent blue sphere representing the LC droplet, we plot red isosurface of order parameter S = 0.74 to observe how the defects are arranged in the bulk.<sup>10</sup> In case of Fig. 5.3-(a), the hedgehog pattern appears in the homeotropic anchoring, since the surface energy overlaps the bulk energy. So, the directors follow the radial field towards the center of the droplet. As the method used in the simulations is stochastic, it is difficult to exactly obtain a point defect located in the middle of the lattice. Instead, we observe a short length ring defect oscillating in the center of the droplet. As the ring can be considered a regular circle with radius near 2 sites, its scaled length  $C^*$  is around  $4\pi$ .

<sup>10</sup>An isosurface shows the resulting structure where a specific parameter assumes a certain value.



(a) Homeotropic anchoring.

(b) Planar degenerate anchoring.

**Fig. 5.3:** Simulations for one-constant approach with N = 0 (nematic sample) in (a) strong homeotropic anchoring, and (b) strong planar degenerate anchoring. In both cases,  $T_R = 0.100$ . (a) The directors align radially and a small ring defects is formed in the center of the droplet, forming the hedgehog pattern. Their colors are scaled by the value of order parameter. The red ring is the order parameter isosurface with S = 0.74. On the right hand side, the C Müller matrix represents the circular polarized light passing through the droplet while the L is the linear polarized light. (b) As expected by the Poincaré-Hopf theorem, the BS is formed, since two boojums with topological charge s = +1 are localized diametrically opposed. Near the boojums, the sample suffers an accentuated splay distortion. Again, the red isosurfaces are the region in which the order parameter *S* is smaller than 0.74.

Even setting weak anchoring,  $J_s = 0.25$ , the elastic isotropic case presents the same behavior for both kinds of surface alignment. Also, simulations for CCN-37 show the same results for both strong and weak homeotropic anchoring, and the strong planar anchoring case. The Müller matrix results in Fig. 5.3-(a) show regular circles of minimum intensity for circular (C) polarized light. For linear (L) polarized light, an alternating pattern of dark and bright brushes appear in the sample, similar to experiments [223–230]. As the directors are radially aligned and the polarizer is perpendicular to the analyzer, the brushes maximum and minimum intensities oscillate each 45°. When the anchoring is planar, Fig. 5.3-(b), the one constant approach shows the formation of BS with antipodal boojums appearing in the droplet surface, as expected by the Poincaré-Hopf theorem. The boojums have topological charge s = +1, and are located by the blue arrows. The directors in the bulk follow the imaginary lines similar to electric field lines created by two opposite charges. The bend distortion propagates near the surface while the splay distortion surrounds the defects. The resulting structure is cylindrically symmetric around the axis connecting the boojums and shows elliptical rings in the Müller textures, similar to experimental results [227, 229–232]. These elliptical dark brush rings are formed due to the total optical retardation effect. According to Eq. (2.14), the transmittance, or light intensity, is proportional to  $\sin^2(\pi\Delta L/\lambda')$  with

$$\Delta L = \int_{-R}^{R} \Delta n \, \mathrm{d}l,\tag{5.8}$$

where l is the axis parallel to the light propagation [232]. So, dark regions appear for

$$\frac{\Delta L}{\lambda'} = m, \text{ with } m \text{ integer.}$$
(5.9)

The simulations for CCN-37 also show the same results in the planar anchoring.

#### *N* = 1.00

Considering that the system is chiral in such a way that N = 1.00, Eq. (5.7) may return different values of  $\sigma^*$  depending on the elastic constants.<sup>11</sup> Setting  $R^* = 40$ , the chiral therm in the potential for elastic one-constant approach may be  $\sigma_{iso}^* = 0.118$ , while for CCN-37,  $\sigma_{AES}^* = 0.104$ . Fig. 5.4 shows the strong homeotropic anchoring with  $J_s = 1.00$  for (a) the one constant approach and (b) the CCN-37 LC. The isotropic elastic case is shown in Fig. 5.4-(a) and CCN-37 in Fig. 5.4-(b). As N = 1.00 is still a low chirality regime, the evolution from the initial random state in  $T_i = 0.700$  to the final state in  $T_f = 0.100$  occurs reasonably fast, in the first 100 k cycles. Equally to the nematic case (N = 0), just one ramp in the temperature is enough to observe the bulk reaching the stable structure with ring defect oscillating in the bulk. Here, the hedgehog pattern also takes place for both samples, but the final structure in

<sup>&</sup>lt;sup>11</sup>According to Ref. [5], the anisotropy in the pairwise additive potential should not influence the theoretical pitch, once  $\sigma$  does not depend on the elastic constants in the procedure to obtain Eq. (2.65).



**Fig. 5.4:** Droplets with low chirality, N = 1.00, in moderate homeotropic anchoring  $J_s = 1.00$  for (a) one-constant approach and (b) CCN-37. The ring defect appears in both cases, however in (a) it is dislocated from the center with scaled length  $C^* \simeq 5\pi$ , as it can be seen in the *z* axis direction. (b) On the other hand, the CCN-37 keeps the ring centered forming the hedgehog structure, with scaled length slightly smaller, approximately equals to  $4\pi$ . The green, blue and yellow isosurfaces in the top are related to the parameters  $n_x^2$ ,  $n_y^2$  and  $n_z^2$ , respectively, equal to 0.90.

the isotropic elastic case is slightly distorted, dislocating the ring defect from the center to near the surface, as shown in Fig. 5.4-(a). Isosurfaces of parameters  $n_x^2$ ,  $n_y^2$  and  $n_z^2$  corresponding to 0.90 and represented by the green, blue and yellow, respectively, reveal this distortion. They are met in the center of the ring, but just one component has the isosurface going into the red ring defect. This dislocation breaks the cylindrical symmetry of the structure as the chirality starts emerging in the bulk, as it can also be seen in the Müller textures of Fig. 5.4-(a). On the other hand, the anisotropy shows no difference compared to the achiral case and the ring holds centered in the bulk, as shown in Fig. 5.4-(b). In this case, the square of director components shows isosurfaces also meeting in the center. Here, we notice the Luckhurst potential presents a difference on the ring position compared to the chiral isotropic potential. The bulk "feels" some resistance when changing the defect position since the surface keeps imposing its strong anchoring on the boundaries of the droplet.

We performed simulations for weak anchoring to observe if the ring defect in the bulk remains the same as in the strong anchoring case. Different from the strong anchoring, in both cases the defect becomes larger and moves to the surface, as illustrated in Fig. 5.5. The isosurface for the order parameter reveals the regions where the directors abruptly change. As shown by the director components isosurfaces, when surrounding the ring defect we observe the directors practically changing their direction by 90° in some regions. It explains the reason why in some points around the defect line the isosurfaces are one beside the other, just separated by the order parameter isosurface. In considering the ring as a regular circle in the first approach, the defect line length can be estimated as the base circumference of a cone where the opening angle is given by  $\beta/2$ . Here,  $\beta$  is the angle formed between the two points in which the defect line crosses the sliced plane and the center of the droplet. So, the scaled length is approximately



**Fig. 5.5:** Chiral samples in low chirality regime with N = 1.00 in a droplet with weak homeotropic anchoring  $(J_s = 0.25)$ . Also, both samples are equilibrated in  $T_R = 0.100$  and run 200 kMCs. The top inset shows the components and the order parameter isosurfaces. (a) The elastic isotropic case presents an opening angle of  $\beta = 140.0^\circ$ , while (b) the CCN-37 opens the ring in a smaller angle  $\beta = 101.1^\circ$  due to the presence of anisotropy in the potential. The Müller matrix textures for circular polarized light (C) and linear polarized light (L) are represented in the bottom. The estimated scaled length is  $C_{iso}^* = 5.90R^*$  for isotropic case and  $C_{CCN-37}^* = 4.85R^*$  for CCN-37.

given by

$$C^* = 2\pi R^* \sin\left(\frac{\beta}{2}\right). \tag{5.10}$$

The estimative for the scaled length in the elastic isotropic case with  $\beta = 140.0^{\circ}$  and  $R^* = 40$  is  $C_{iso}^* = 5.90R^*$ . For the CCN-37 sample  $\beta = 101.1^{\circ}$ , which leads to  $C_{CCN-37}^* = 4.85R^*$ . As the ring length in the strong anchoring keeps stable in the center of the droplet and its length is smaller than isotropic elastic case for weak homeotropic anchoring, we can observe that anisotropy imposes a certain resistance on acting over the ring defect movement.

The thermal quench results in the CCN-37 droplet with strong planar anchoring, where  $J_s = 2.00$ , are shown in Fig. 5.6. Both the isotropic and the CCN-37 samples form the TBS pattern. likewise the achiral case, two point defects are formed diametrically opposed in the sphere. Fig. 5.6-(a) shows the directors in the xz slice in the middle of the droplet, and the blue arrows indicate where the boojums are located. Contrary to the achiral case, the optical retardation effect shown in Figs. 5.6-(b) and (c) forms flat elliptic rings with the longer axis coinciding with the axis direction connecting the boojums. This difference happens because the helix rotates 180° in the perpendicular direction to the droplet symmetry axis. Elliptical ring in Muller matrix may also appear for both circular (C) and linear (L) light polarization, as shown in Figs. 5.6-(b) and (c). The reason for such pattern is that the directors near the surface in z direction differ 90° from directors in the middle of the droplet, as shown in Fig. 5.6-(a). The isosurfaces of  $n_x^2$ ,  $n_y^2$  and  $n_z^2$  equal 0.90, in green, blue and yellow color, respectively, shown in Fig. 5.6-(d) help on visualizing the director rotation near the surface. In this case, the green



**Fig. 5.6:** Droplet in low chirality regime with N = 1.00, assuming elastic constants of CCN-37, conditioned upon strong planar anchoring ( $J_s = 2.00$ ). The reduced temperature is  $T_R = 0.100$  with 200 k cycles. (a) The equilibrium configuration is the TBS, with two boojums indicated by the blue arrows. (b)–(c) Müller matrix textures for circular (C) and linear (L) polarized light, respectively, forming flat elliptical rings. (d) Red isosurfaces of S = 0.74 show the boojums while the green ( $n_x^2$ ), blue ( $n_y^2$ ) and yellow ( $n_z^2$ ) ones show isosurfaces of  $n_x^2 = n_y^2 = n_z^2 = 0.90$ . One component connects the boojums while the others form perpendicular circle shape surrounding the surface.

isosurface connects the two boojums, while the two others form perpendicular circles crossing one another in the boojums.

N = 2.00

The third case studied is N = 2.00 where the theoretical prediction considers that the helix may rotate  $360^{\circ}$  along the bulk. Using the same procedures as in the previous case, we set the initial random condition submitting the droplet to a temperature ramp from  $T_i = 0.700$ to  $T_f = 0.100$  in steps of dT = 0.100 (in each temperature, the sample runs 200 kMCs). Let's first consider the homeotropic aligned case with anchoring energy given by  $J_s = 1.00$ . Fig. 5.7 summarizes the spins behavior in the bulk forming the equatorial ring defect in an elastic isotropic sample. According to Eq. (5.7),  $\sigma_{iso}^* = 0.236$ . The formed stable structure has cylindrical symmetry around z axis. Fig. 5.7-(a) shows the director configuration in a slice in the xz plane, the defect line resulting in the S = 0.74 red isosurface and the resulting Müller matrix textures. For a better comprehension, isosurfaces of  $n_x^2 = n_y^2 = n_z^2 = 0.90$  are shown in Fig. 5.7-(b). The green isosurface of  $n_x^2$  and the blue one of  $n_y^2$  are intertwined around the equatorial ring defect while the yellow isosurface of  $n_z^2$  crosses in the middle of the ring. In the strong homeotropic anchoring, the surface forces the spins to assume a radial orientation. The chirality expels the ring defect to the surface as observed for N = 1.00. Since the surface anchoring energy hinder the cholesteric twisting power, the ring defect has a smaller radius compared to the droplet one. It is possible to observe in Fig. 5.7-(c) the ring defect inside the droplet. The sphere coloration in Fig. 5.7-(c) is given according to the values of  $n_x^2$ , where minimum values are blue, and high ones are red. In addition, Fig. 5.7-(d) clearly shows the directors radially aligning in the boundaries, and the ring defect line in a bright color due to low values of order parameter S. The ring defect radius is around 35 sites, so the estimative for



**Fig. 5.7:** Isotropic approach of a CLC droplet with N = 2.00 and strong homeotropic anchoring ( $J_s = 1.00$ ) in  $T_R = 0.100$  (200 kMCs). (a) The director field of structure forms an equatorial ring defect (red isosurface of S = 0.74). (b) Isosurfaces of  $n_x^2$  (green) and  $n_y^2$  (blue) equal 0.90 show that the components are intertwined around the ring defect, while  $n_z^2$  (yellow) crosses the bulk in the middle of the sample. (c) The surface is colored by the parameter  $n_x^2$ , where low values represent are in blue tones and high values are in red tones. (d) Due to the strong anchoring, the directors are radially aligned at the surface, so the ring radius is smaller than  $R^*$ ; it is near 35 sites, which generates a scaled length ring defect about 5.50 $R^*$ .

the defect length is  $C_{iso}^* = 5.50R^*$ . Investigations of CCN-37 provide similar results related to the final structure. Also, both the one-constant approach and the CCN-37 present the equatorial ring defect for weak anchoring, where the difference is in the defect size. Considering the surface has weak anchoring energy, the bulk forces the ring to open even more, overlapping the impositions done by the alignments at the boundaries. In this case, the ring defect rounds the droplet at the surface, so the scaled length in the weak anchoring is around  $2\pi R^*$ .

Simulations for N = 2.00 in a droplet with strong planar degenerate alignment ( $J_s =$ 2.00) at the surface reveals the TBS if quenching the sample from  $T_i = 0.700$  to  $T_f = 0.100$  in steps of dT = 0.100, as shown in Fig. 5.8 for the elastic isotropic sample. A well known configuration in the literature is observed when carried out a single thermal quench. Two antipodal boojums at the surface, highlighted by blue arrows, form a cylindrical symmetric structure that coincides with z axis (denoted as bipolar axis) as shown in Fig. 5.8-(a). By observing the perpendicular plane to the bipolar axis, it is possible to notice that the directors almost completing two  $\pi$  turns along the black line x direction. The director field also shows a  $\lambda^{+1}$  disclination line connecting both the boojums. New maximum and minimum optical retardation points emerge near the surface thus forming elliptical rings even flatter, as shown in Figs. 5.8-(b) and (c). In this case, the central ellipse is smaller than the N = 1.00 case due to the higher chirality in the system. It happens because more cholesteric layers bend in the bulk along z direction. Isosurfaces of  $n_x^2$ ,  $n_y^2$  and  $n_z^2$  equal to 0.90 are shown in Figs. 5.8-(d) and (e), with the green, blue and yellow colors, respectively. Although the boojums are in a different axis from the N = 1.00case, the isosurfaces shape are similar. It makes the isosurfaces connecting the boojums through the droplet center different. Instead of two regular circle which form isosurfaces (Fig. 5.6-(d)),



**Fig. 5.8:** Chiral isotropic elastic sample in low chirality regime with N = 2.00 in a droplet with strong planar anchoring ( $J_s = 2.00$ ) at  $T_R = 0.100$  (200 kMCs). (a) The cholesteric layers bend in the bulk forming the TBS, with two s = +1 diametrically opposed boojums, and a  $\lambda^{+1}$  line connecting them along the *z* direction. (b)-(c) Müller textures reveal new maximum and minimum points in the transmittance, so decreasing the elliptical rings size. (d)-(e) Isosurfaces of  $n_x^2$  (green) and  $n_y^2$  (blue) show an oscillated elliptical structure, while  $n_z^2$  (yellow) follows the  $\lambda^{+1}$ .

here they become perpendicular ellipses passing through the boojums, as shown in Fig. 5.8-(d), but forming an oscillated structure, as shown in Fig. 5.8-(e) along the z axis observation. Also, the TBS pattern is found in simulations for CCN-37 sample.

#### N = 3.00

The N = 3.00 case is quite interesting for CLC droplets having normal molecular anchoring at the surface. From the previous droplets already mentioned, we observe the ring defect morphology being modified in function of  $\sigma$ . By changing the anchoring energy and the number of turns inside the droplet, it was expected that the structure could be different. As an example, while increasing the chirality level under low values of  $J_s$  for homeotropically aligned droplets, the ring changed its central position and size, moving towards the surface, forming a ring similar to the base of a central cone, and it finally appeared as an equatorial defect. We performed the simulations following the same setup as the previous droplets. Firstly, we mention the isotropic elastic case with strong ( $J_s = 1.00$ ) and weak ( $J_s = 0.25$ ) anchoring energies in the droplets with perpendicular alignment at the surface, shown in Fig. 5.9. The chiral term  $\sigma_{iso}^* = 0.353$  in the system begins to influence the director organization in such a way that the equatorial ring defect is not adopted anymore. The strong anchoring case, illustrated by a snapshot in Fig. 5.9-(a) reveals a truncated and disorganized loop defect organization in the sample (red order parameter isosurface of S = 0.74), due to the surface orientational imposition to overcome the radial alignment near the borders. Curiously, when the weak anchoring is



**Fig. 5.9:** Simulations of isotropic sample at  $T_R = 0.100 (200 \text{ kMCs})$  with N = 3.00. (a) Moderate homeotropic anchoring  $J_s = 1.00$  showing the directors forming a metastable state with a single non-uniform loop defect, as revealed by the red isosurface of S = 0.74. (b) Different from moderate anchoring, the weak anchoring case  $(J_s = 0.25)$  shows that the director field forms the twisted loop defect around the surface. In this case, the structure bipolar axis does not match with any Cartesian axis, thus, creating false impression of non-uniform cholesteric layers separation. The (C) and (L) Müller textures are the results for circular and linear polarized light passing through the sample, respectively.

considered, the bulk is able to determine the ground state for cholesterics by forming the helix configuration inside the droplet, as shown in Fig. 5.9-(b). The cholesteric layers, determining the bipolar axis of the droplet, bend along the bulk because of the spherical geometry, and the twisted loop defect (red isosurfaces with S = 0.74) takes place at the surface. As the twisted loop defect is regular spaced, it is possible to conclude that the bipolar axis does not coincide with any Cartesian axis.

In the anisotropic case, Fig. 5.10 shows the final structure of both strong ( $J_s = 1.00$ ) and weak ( $J_s = 0.25$ ) homeotropic anchoring for CCN-37 chiral droplet with  $R^* = 40$ . Eq. (5.7) shows that  $\sigma^*_{\text{CCN-37}} = 0.312$ . The equilibrium state has abrupt change of the director field near the surface, thus forming a bipolar distribution of the cholesteric helix in the bulk. This configuration is the so-called twisted loop defect since there is a twisted ring defect line (red isosurface of S = 0.74) encircling the droplet near the surface. In such supramolecular conformation, the cholesteric layers organize in isocline lines related to the bipolar axis (green line), as shown in Figs. 5.10-(a) and (c), for strong and weak anchoring, respectively. The perpendicular plane, shown in Fig. 5.10-(b), reveals that the bipolar axis does not perfectly coincide with a Cartesian axis, but is regularly distributed in space. Also, the Müller textures confirm the slight inclination of the structure related to the point of view. It happens because initially, the sample is randomly oriented and the MC method allows the bulk to visit different states with similar structures and energy levels, since there is not a bias in the structure inducing the alignment in a specific direction. Such structure has no rotational symmetry around the bipolar axis once the shape of twisted ring is antisymmetric concerning a cut done in any slice passing through the middle of the droplet. For the weak homeotropic anchoring, the twisted ring reaches the surface, consequently changing the easy axis orientation where it passes. These points are highlighted



**Fig. 5.10:** Simulations of cholesteric CCN-37 droplet at  $T_R = 0.100$  (200 kMCs) with N = 3.00 and  $J_s = 1.00$  in the (a)-(b) strong homeotropic anchoring and  $J_s = 0.25$  in the (c)-(d) weak homeotropic anchoring. The bulk forms the twisted loop defect near the surface. (a) The directors settle in cholesteric layers forming isoclinal lines which are perpendicular to the bipolar axis (green line). (b) As the bipolar axis does not match with a Cartesian axis, the perpendicular plane does not show symmetry along the observation point (it also can be confirmed by the Müller textures), however the structure is regularly spaced in the bulk and it has cylindrical symmetry along the bipolar axis. (c)-(d) In the weak anchoring case, the directors overlap the surface alignment, oscillating to the parallel orientation following the defect line (highlighted by gray arrows). Due to the coincidence between the bipolar axis and a Cartesian axis, the structure has the cylindrical symmetry along the y direction. The twisted loop defect is illustrated by the red order parameter isosurfaces in S = 0.74.

in gray arrows indicating the regions where the bulk orientation overlaps the surface easy axis imposition, as shown in Figs. 5.10-(c) and (d). This trend is in accordance with experimental results [210]. The droplet stabilizes the bipolar axis in y axis, as revealed by the Müller textures showing a symmetric structure in the plane of view. To obtain the estimative defect line scaled length for such stable state, it is necessary to know how the defect line varies in space. Given a curve described by the vector  $\vec{r}^*(t) = x^*(t)\hat{i} + y^*(t)\hat{j} + z^*(t)\hat{k}$  in space, if its parametrization in function of t is known, it is possible to obtain the length C<sup>\*</sup> from a point A to B by

$$C^* = \int_A^B \left| \frac{\mathrm{d}\vec{r}^*}{\mathrm{d}t} \right| \mathrm{d}t.$$
 (5.11)

The twisted loop defect is also known as loxodrome curve.<sup>12</sup> Considering the condition that

 $<sup>^{12}</sup>$ A loxodrome is the path created in the surface of a sphere when the path crosses the meridians with a fixed angle.

 $z^*$  has maximum value when  $x^* = y^* = 0$ , the loxodrome describing the twisted loop defect having *M* isocline lines in a sphere of radius  $R_{lox}$  can be parametrized as

$$\begin{cases} x^{*}(t) = R_{\text{lox}}(-1)^{k+1}\sin(t)\sin((M+1)t), \\ y^{*}(t) = R_{\text{lox}}(-1)^{k}\sin(t)\cos((M+1)t), \\ z^{*}(t) = R_{\text{lox}}\cos(t), \end{cases} \quad 0 \le t \le \pi, \ k = 1, 2.$$
(5.12)

The parameter k = 1 describes half of the complete curve, while k = 2 refers to the other one. As the loxodrome is regular, one can integrate over just half length of the curve, since the other part has the same length. So, for k = 1, and considering that for integer values of N the number of isocline lines is M = N - 2, the estimative of complete scaled length of the twisted loop defect, according to Eq. (5.11) and (5.12), can be written as

$$C^* = 2R_{\text{lox}} \int_0^{\pi} \sqrt{1 + (N-1)^2 \sin^2(t)} \, \mathrm{d}t.$$
 (5.13)

Therefore, numerical calculations for the integral in Eq. (5.13) with N = 3.00 show that in the strong anchoring case (where the radius  $R_{\text{lox}} \sim 36.5\Lambda$ )  $C_{\text{str}}^* = 9.62R^*$ , while for the weak anchoring  $C_{\text{weak}}^* = 10.54R^*$ , since  $R_{\text{lox}}$  coincides with  $R^*$ .

Results for parallel surface alignment in isotropic sample curiously present two distinct final equilibrium configurations, depending on the surface anchoring energy. For  $J_s = 1.00$ , the sample reaches the TBS, as shown in Figs. 5.11-(a) and (b). The directors alignment in the droplet generates a  $\lambda^{+1}$  disclination line connecting the boojums, and the cholesteric layers bend in the volume following the field line as if the boojums were opposite electric charges. Interestingly, for  $J_s = 2.00$ , only one boojum appears with a winding number -1/2 nematic disclination line, as shown in Figs. 5.11-(c) and (d). It seems an incomplete-bTBS taking place over the bulk. The splay distortion formed around the s = +1 boojum has higher energetic cost for  $J_s = 2.00$  than for the case of  $J_s = 1.00$ . So, the reason for appearing the incomplete-bTBS should be that it is easier for the bulk to bend the cholesteric layers, instead of keeping the  $\lambda$  line connecting the two opposite boojums straight. A similar behavior of this structure transition was found by Zhou et al., showing the bTBS taking place over the bulk after increasing the surface anchoring energy in cholesteric droplets with N = 3.5 [11]. Contrary to the isotropic case, by carrying out simulations for exploring the strong planar anchoring case of CCN-37 for N = 3.00, we just observe the TBS as the stable state structure for both anchoring energies  $J_s = 1.00$  and  $J_s = 2.00$ . This can be verified by Fig. 5.12 which shows the sample with  $J_s = 2.00$  at  $T_R = 0.100$  (200 kMCs). The sample holds the TBS even for higher surface energy cases, and the reason for that should be related to the CCN-37 bend elastic constant. As in this case  $K_{33}$  is bigger than the isotropic one, the bulk still prefers to keep the boojums antipodally aligned, instead of bending the cholesteric layers to form the bTBS, which would cost more energy for the bulk than paying for the penalty for increasing the energy in the surface. Again, just one thermal quench is enough to find the two boojums raising in the sample (red



**Fig. 5.11:** Chiral isotropic sample for N = 3.00 at  $T_R = 0.100$  (200 kMCs). (a) The case for  $J_s = 1.00$  shows the TBS with two opposite boojums, while (b) the  $J_s = 2.00$ , the directors form an incomplete-bTBS, where just one boojum appear with a nematic disclination line. The (C) and (L) Müller textures are the results for circular and linear polarized light passing through the sample, respectively.



**Fig. 5.12:** Chiral CCN-37 with N = 3.00 in a droplet with strong planar anchoring  $(J_s = 2.00)$  at  $T_R = 0.100$  (200 kMCs). (a) The TBS pattern is formed by a  $\lambda^{+1}$  line connecting two s = +1 diametrically opposed boojums (red isosurfaces of S = 0.74). (b)-(c) Isosurfaces of  $n_x^2$  (green) and  $n_z^2$  (yellow) show an oscillated elliptical structure, while  $n_y^2$  (blue) follows the  $\lambda^{+1}$  line in y direction. (d)-(e) Müller textures show flat elliptical ring pattern in the transmittance like the cases for N = 1.00 and 2.00, differing just near the surface in the axis perpendicular to the bipolar axis.

isosurfaces of S = 0.74) with topological charge s = +1 antipodally located at the surface, generating a cylindrical symmetry structure that matches with y axis, as shown in Fig. 5.12-(a). In the first instance, this structure is similar to the one obtained for N = 2.00. Also, when observing the textures formed by the circularly and linearly polarized light, in Figs. 5.12-(d) and (e), respectively, the flat elliptical rings of minima in transmittance aspects are very similar to the N = 2.00 case in the central part of the droplet, but slightly differs near the surface in the plane perpendicular to the bipolar axis. To clearly outline this difference, it is necessary to investigate how the director field is distributed in the sphere. Isosurfaces of  $n_x^2$ ,  $n_y^2$  and  $n_z^2$  equal to 0.90 are shown in Figs. 5.12-(b) and (c), with the green, blue and yellow colors, respectively. The oscillating elliptic shaped isosurfaces of  $n_x^2$  and  $n_z^2$  are perpendicular and they meet in the boojums. The blue isosurface representing the  $n_y^2$  component links the boojums through the  $\lambda^{+1}$  defect line. However, this isosurface reveals that the  $n_y$  component is practically completing two  $\pi$ -turns along the droplet diameter in z direction. The probable reason for existent discrepancy in the number of  $\pi$  rotation is that the anchoring energy is strong enough to overlap the twisting power of the bulk, so keeping the supramolecular architecture constrained.

#### N = 4.00

Finally, we report the distinguished behaviors for N = 4.00. This value of N is considered to be in a region of transition between the low and high number of possible states, because values greater than 4.00 allow the disclination lines to get trapped in several different local minima. Fig. 5.13 shows the results of simulations considering the one-constant case in a droplet with moderate homeotropic anchoring  $J_s = 1.00$ , where  $\sigma_{iso}^* = 0.471$ . Unlike the previous results, the bulk allocates an entanglement of linked disclination loops randomly organized. Even performing the procedure of thermal quench for several times by heating the droplet, the LC sample gets stuck in metastable states. Also, the droplet with  $J_s = 0.25$ , weak anchoring at the surface presents similar results. The stability of defects in a LC has high dependence on the surface geometry. In the case discussed here, a slice in the droplet reveals that the defects are nematic disclinations with winding number -1/2, since the director field rotates a  $\pi$  angle in the counterclockwise sense when the defect is surrounded by a  $2\pi$  clockwise turn (or vice-versa), as shown in the snapshot of Fig. 5.13-(a). When  $N \ge 4.00$ , the disclination loops can assume different stabilized arrangement, such as single or multiple unlinked loops, the Solomon or a three-component link, both with an extra loop, the Whitehead link, and the Hopf link, for example. If N = 4.00 multiple unlinked loops and Hopf links are found after thermal quench [202]. Isosurfaces of order parameter S = 0.74 are shown in Fig. 5.13-(b)-(c). By carefully analyzing the disclination network, it is possible to observe the formation of Hopf links (two linked



**Fig. 5.13:** Chiral isotropic sample with N = 4.00 in a droplet with moderate perpendicular anchoring ( $J_s = 1.00$ ) at  $T_R = 0.100$  (200 kMCs). (a) The bulk keeps trapped in metastable states, forming nematic disclination lines with winding number -1/2. The Müller textures with circular (C) and linear (L) polarized light show the resulting chaotic configuration. (b)-(c) The linked and knotted structure forms the Hopf-link with an extra loop, as can be seen by the red order parameter isosurfaces of S = 0.74.

circles) with an extra loop.

We carried out simulations of nematic CCN-37 ( $\sigma_{\text{CCN-37}}^* = 0.416$ ) with strong ( $J_s =$ 1.00) and weak ( $J_s = 0.25$ ) homeotropic anchoring. Interestingly, instead of random organizations of disclinations, in both cases the results have the same behavior where the defect lines arrange in a single loop forming the twisted loop defect (red isosurfaces of S = 0.74), just differing from each other only in the loxodrome radius. Fig. 5.14 shows the results for CCN-37 in the droplet with strong homeotropic anchoring. Unlike the case for N = 3.00, just one thermal quench is not enough. Even repeating the procedure three times, the structure in the strong anchoring still remains constrained in metastable states. By setting up  $T_i = 0.900$ , we observe that the thermal quench is efficient at reaching the single loop defect surrounding the surface. Starting the relaxation in a higher temperature makes it possible for the spins to access locally unfavorable energetic states, but that are macroscopically advantageous to form up structures with a well defined pattern. This extra thermal agitation allows the system to access similar energy level states, but separated by an energetic barrier. On the contrary, just one thermal quench is enough when considering weak anchoring and  $T_i = 0.700$ , since the bulk can relieve the defect line to the surface easier than the moderate anchoring. The cholesteric layers twist around the bipolar axis forming 2 isocline lines beyond the poles in z direction, as shown in Fig. 5.14-(a). It is also possible to observe the Müller textures similar to experimental results [210]. Fig. 5.14-(b) shows the resulting configurations when rotating the droplet by



**Fig. 5.14:** CCN-37 sample with N = 4.00 in moderate homeotropic anchoring ( $J_s = 1.00$ ) at  $T_R = 0.100$  (200 kMCs). (a) The snapshot reveals the ground state in the bulk, with regular space cholesteric layers along z direction. It is also possible to observe the twisted loop defect by red isosurfaces of the order parameter S = 0.74, and the Müller textures for circular (C) and linear (L) polarized light showing a resulting image similar to experiments. (b) Cross-section snapshot showing the xz plane. (c) The  $n_x^2 = 0.90$  (green), (d)  $n_y^2 = 0.90$  (blue) and (e)  $n_z^2 = 0.90$  (yellow) isosurfaces, show the component behavior along the bulk.

90° around the z axis. The isosurfaces of  $n_x^2$  (green),  $n_y^2$  (blue) and  $n_z^2$  (yellow) set equal 0.90, shown in Fig. 5.14-(c)-(e), confirm that the structure alternates the components  $n_x^2$  and  $n_y^2$  along z direction, and  $n_z^2$  takes place just near the poles. As the number of isocline lines between the two opposite poles is M = 2, respecting M = N - 2, according to Eq. (5.13) the first approach scaled length of twisted loop defect with  $R_{lox} = 38$  is given by  $C^* = 13.28R^*$ .

The quenching process of planar surface anchoring promotes an intriguing morphological behavior depending on the elastic constants for N = 4.00. Firstly, we mention the elastic one-constant approach case ( $\sigma_{iso}^* = 0.471$ ) with  $J_s = 1.00$  and  $J_s = 2.00$  to check if they have similar or different behavior. As shown in Fig. 5.15, nematic defect lines with winding -1/2appear in the bulk, but do not close the loop. Since both  $J_s = 1.00$  and  $J_s = 2.00$  cases show the same results, we illustrate just the  $J_s = 1.00$  in Fig. 5.15. Several thermal quenches, considering dT = 0.100, show that the one-constant approach is not efficient on completely annihilating disclinations (red isosurfaces of S = 0.74) along the droplet volume. The disclination line behavior is chaotic like the isotropic elastic sample in droplets with homeotropic surface. The intricate topology and the pitch near the chaotic regime make the system complex and hard to reach any known pattern. We set a different procedure for quenching the droplet, selecting the number of MC cycles in 500 k and a smaller temperature step in dT = 0.025. Interestingly, when the elasticity is slightly changed for  $K_{11}/K_{22} = 1.10$  and  $K_{33}/K_{22} = 1.20$  ( $\sigma^* = 0.456$ ), the stable structure is completely modified, as shown in Fig. 5.16, while in the isotropic case the disordered disclinations still remain. For low chirality (p > R), the CLC droplets present the TBS pattern while for high chirality (p > R) the RSS is predominant. The final structure



**Fig. 5.15:** Chiral isotropic sample with N = 4.00 also forming an incomplete-bTBS in moderate anchoring energy  $J_s = 1.00$  (at  $T_R = 0.100 - 200 \text{ kMCs}$ ). (a) The cross-section snapshot shows that the cholesteric layers are bent, but it is incomplete to form the spiral pattern due to the disclination lines passing through the central plane (red isosurfaces of S = 0.74). Boojums do not appear in this case, instead, two disclination lines are formed and they are not annihilated, even performing several thermal quenches. (b) Snapshot showing the director field at marked continuous and (c) dashed line cross-section in (a). Also, the onion-like pattern is incomplete. The (C) and (L) Müller textures are the results for circular and linear polarized light passing through the sample, respectively.



**Fig. 5.16:** Slightly anisotropic sample with  $K_{11}/K_{22} = 1.10$  and  $K_{33}/K_{22} = 1.20$  with N = 4.00 forming the bTBS as equilibrium state. (a) The cross-section snapshot shows the onion-like pattern formation, where the cholesteric layers bend in the bulk. In this stable state, the two boojums (red isosurfaces of S = 0.74) are in the same droplet hemisphere. Again, the Müller textures of circular (C) and linear (L) confirm similarity with experimental results. (b) Snapshot showing the director field at marked continuous and (c) dashed line cross-section in (a).

after one thermal quench is the bTBS, the intermediate state between TBS and RSS, where the boojums (red isosurfaces of S = 0.74) are not opposite anymore. Figs. 5.16-(a)-(c) are snapshots showing different slices of the director field in the droplet, with the respective Müller textures with circularly (C) and linearly (L) polarized light. The boojums are located in the same hemisphere and make an angle of  $63.34^{\circ}$  with the droplet center, which only differs in approximately 5° from the angle found in simulations by the LdG method [11]. In the bTBS, the cholesteric layers bend in the bulk following the surface curvature and breaking the cylindrical symmetry, creating the so-called onion-like pattern (Fig. 5.16-(a)) or the double spiral arrangement (Fig. 5.16-(b)), depending on the observation point. We highlight the situation found in Fig. 5.16-(c), where the directors perpendicularly oriented to the plane of observation form an arc shape arrangement near the droplet center. The first emerged impression is that such arc does not connect to the boojums, like it happens when observing the xy plane in Fig. 5.16-(a). For a better understanding, we plotted isosurfaces of square components  $n_x^2$  (green),  $n_y^2$  (blue) and  $n_z^2$ (yellow), as shown in Fig. 5.17. The incomplete arc in yz plane happens because the boojums are far apart in a considerable distance compared to the droplet radius. When observing regions of  $n_x^2 = 0.90$ , it is possible to see that the arc shape connects the boojums in a fish hoop-like arc shape, beyond a ring surrounding the surface boundaries passing between the boojums, as shown in Figs. 5.17-(a) and (b). Looking at the isosurface of  $n_z^2 = 0.90$  in Fig. 5.17-(c) and (d), we observe that the formed structure also emerges from both boojums and coincides with perpendicular directors in the cross-section of xy plane in Fig. 5.16-(a). The last isosurface representing  $n_v^2 = 0.90$  also demonstrates the spiral pattern taking form from the boojums, but



**Fig. 5.17:** Squared components isosurfaces in the bTBS showing the director field along the bulk. The  $n_x^2$  (green),  $n_y^2$  (blue)  $n_z^2$  and (yellow) isosurfaces are set in 0.90. (a)-(b) The  $n_x^2$  component shows the fish hoop-like isosurface connecting the two boojums, together with a ring isosurface surrounding the surface and passing between them. (c)-(d) The  $n_z^2$  component reveals two isosurfaces originating in one boojum and finishing in the other. (e)-(f) The  $n_y^2$  component shows two distinct symmetric isosurfaces starting in the boojums and finishing near the surface. Such isosurface shows (g) two  $\lambda^{+1}$  lines starting near the boojums, as shown in the plane snapshot close to the boojums. (h)-(j) The isosurfaces are inset together in pairs to observe their complements the director distribution along the bulk.

in this case, the  $n_y^2$  component creates two similar structures in which none of them connects the surface defects, as shown in Fig. 5.17-(e) and (f). In addition, after slicing the droplet close to the poles, we observe two cholesteric  $\lambda^{+1}$  disclination lines arising from the boojums, as shown in Fig. 5.17-(g). For larger values of *N*, the expected RSS presents two  $\lambda^{+1}$  lines winding towards the droplet center [204]. It did not happen here because the chirality level for N = 4.00 is not enough to form the helicoidal shape of disclinations, and it is still the bTBS. Considering the CCN-37 elastic constants ( $\sigma_{\text{CCN-37}}^* = 0.416$ ), the two s = +1 boojums also appear in just one hemisphere, but the double spiral pattern seems to organize in square layers as if the bulk did not feel the droplet curved surface.

As noted in the diversity of structures found while changing the chirality by controlling N, we tested another LC, supposing the ZLI4330 elastic constant, given by  $K_{11}/K_{22} = 2.00$  and  $K_{33}/K_{22} = 2.92$  [7] ( $\sigma_{ZLI}^* = 0.361$ ) in the strong planar anchoring ( $J_s = 2.00$ ) droplet. Such LC has the higher  $K_{33}$  elastic constant compared to all the other samples previously studied. We would expect that the supramolecular architecture would not arrange in a structure with

cholesteric layers bending in the bulk. Indeed, Fig. 5.18 shows the PBS as stable state after performing one thermal quench from  $T_i = 0.700$  to  $T_f = 0.100$  in steps of dT = 0.100, running 200 kMCs for each temperature. Unlike the double spiral pattern, the PBS presents two diametrically opposed boojums with topological charge s = +1, demonstrated by the two blue arrows in Fig. 5.18-(a). Once the bipolar axis connecting the boojums does not coincide with a Cartesian axis, a perpendicular slice (gray line) related to the bipolar axis can be useful for understanding the director orientation. Fig. 5.18-(b) shows the directors forming two cholesteric  $\lambda^{+1/2}$  disclination lines in the bulk. Differently from TBS, where the cholesteric layers bend towards the boojums near the poles, in PBS they remain perpendicular to the bipolar axis including near the poles. This is confirmed by the isosurfaces of  $n_x^2$  (green),  $n_y^2$  (blue) and  $n_z^2$ (yellow), equal 0.90 shown in Figs. 5.18-(c) and (d). These isosurfaces of TBS presented a pair of perpendicular rings passing through the boojums, and one component coinciding with the bipolar axis. Contrary to TBS, the isosurfaces in PBS exhibited just one oscillated ring in the component  $n_z$  following the boundaries, while an elliptical ring-like is formed by two different components ( $n_x$  and  $n_y$ ). Also, there is not a single isosurface directly connecting the boojums



**Fig. 5.18:** Simulations for ZLI4330 nematic LC sample with N = 4.00 at  $T_R = 0.100$  (200 kMCs). (a) This LC presented the PBS as equilibrium state, where the two boojums (red isosurfaces of S = 0.74) are kept antipodally aligned (located by the blue arrows) forming the droplet bipolar axis. It is different from the bTBS case, where the boojums are in the same hemisphere. The circular (C) and linear (L) light polarization in the Müller textures show bright and dark circles and elliptical rings. (b) The marked line in (a) presents the cross-section perpendicular to the droplet bipolar axis, showing the two  $\lambda^{+1/2}$  lines appearing in the bulk. (c)-(d) The green, blue and yellow isosurfaces, related to  $n_x^2$ ,  $n_y^2$  and  $n_z^2$  components, respectively, show the director field along the bulk; in this case, all the three components have isosurfaces connecting the boojums.
through the bipolar axis, so the  $\lambda^{+1}$  line may not appear. The behavior is similar as if the  $\lambda^{+1}$  has split in two  $\lambda^{+1/2}$  lines, since the cholesteric layers are perpendicular to the bipolar axis instead of bending along the bulk. We also observe the optical retardation phenomenon in the Müller textures forming regular circle patterns in the center of the droplet, surrounded by bright and dark elliptical rings.

## Discussions

The director configurations in cholesteric droplets is size-driven, so the changing of R/p ratio provides transition between stable structures. We reported the formation of different structures after thermal quench in cholesteric droplets, where the pitch ranges from N = 0to N = 4.00, considering the elastic isotropy and anisotropy, in droplets with parallel and perpendicular surface alignment (also testing the weak and moderate anchoring energy). In the N = 0 regime, the found stable states are the well-known hedgehog pattern in the homeotropic anchoring. For N = 1.00 at this same boundaries, the strong anchoring case also forms the hedgehog pattern, but a surface ring defect is reported in the weak anchoring case. Keeping the chirality increasing, the N = 2.00 case shows a director field forming the equatorial loop disclination. The structural pattern for N = 3.00 presented a twisted or a non-uniform loop defect, depending on the combinations between the elastic constants and surface anchoring energy. In the N = 4.00 regime, besides the twisted loop defect pattern, metastable states could be also found. Considering the parallel anchoring, N = 0, 1.00 and 2.00 presented structures with two opposite boojums at the surface, forming the BS for the nematic case, and TBS for both N = 1.00 and 2.00. The N = 3.00 case presented the TBS, but an incomplete-bTBS also appeared, depending on the set of parameters chosen. For N = 4.00, we reported the formation of incomplete-bTBS, the bTBS, and the PBS. We summarize the discussed structures of this chapter in Tab. 5.1, associating the pitch parameter N, the elastic constant set, and the kind of anchoring.

Droplets pattern configuration as a function of N				
Chirality level	LC	weak H anc.	moderate H anc.	moderate P anc.
N = 0	ISO	hedgehog pattern	hedgehog pattern	BS
	CCN-37	hedgehog pattern	hedgehog pattern	BS
<i>N</i> = 1.00	ISO	surface ring defect	dislocated hedgehog pattern	TBS
	CCN-37	surface ring defect	hedgehog pattern	TBS
<i>N</i> = 2.00	ISO	equatorial ring defect	equatorial ring defect	TBS
	CCN-37	equatorial ring defect	equatorial ring defect	TBS
<i>N</i> = 3.00	ISO	twisted loop defect	metastable state	TBS/incomplete-bTBS
	CCN-37	non-uniform loop defect	twisted loop defect	TBS
<i>N</i> = 4.00	ISO	metastable state	metastable state	incomplete-bTBS
	Slight Aniso	twisted loop defect	metastable state	bTBS
	CCN-37	twisted loop defect	twisted loop defect	squared bTBS
	ZLI4330	twisted loop defect	metastable state	PBS

**Tab. 5.1:** Table containing different stable and metastable states for several combinations of chirality, elastic constants, surface alignment and anchoring energy.

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According to the results, the elastic one-constant approach has demonstrated to be insufficient in reproducing stable states after thermal quench in chiral droplets of moderate surface anchoring with N = 3.00 and 4.00. It may happen because the helix rotates in several different directions inside the bulk, and the surface energetic contribution becomes insignificant to impose any kind of change. As the LC has elastic isotropy in the one-constant approach, the directors can not get rid of defects made in points of space where the cholesteric helices are rotating in different directions. Splay, twist and bend deformations may equally contribute for the director distribution along the bulk. Thus, the high degree of spherical geometry complexity prevails in cases of elastic isotropy with high chirality. For both homeotropic and planar degenerate anchoring the chiral LL potential could just reproduce structures in low chirality regime. When N assumes a value near 4.00, the thermal quench easily makes the director organization chaotic, due to the raising in the number of metastable states, and the cholesteric disclination lines remain resistant to the relaxation process. When the surface is homeotropically aligned, linked and knotted metastable structures look similar to the results found in simulations with the LdG method [202]. Even after performing several thermal quenches, they could not be disrupted. In the planar boundaries, the system presents a certain difficulty to gap to states like the bTBS predicted with the LdG model [11, 204]. Droplets for both homeotropic and planar anchoring easily relieved the chaotic initial configuration when p > R, since the pitch becomes practically equal or bigger than the droplet diameter. It is important to mention that the stable states diversity, in a certain chirality level, was possible to be achieved just when considering elastic anisotropy, mainly for N = 4.00.

Simulations carried out by Seč et al. [204] concludes that thermal agitation may not induce transitions between structures. Also, by calculating the total free energy for chiral droplets with N = 4.00, their results reveal that RSS seems to be a most favorable stable state than PBS. Besides, given a fixed value of N, all structures in planar surface alignment, are found to be stable states by initial configurations generated by Ansatz, even when having different internal energies. In contrast, our thermal quench simulations, made by the MC method, has the sample starting from initially random director field and a well-ordered equilibrium states can be reached. Such ordered configurations attain the most stable equilibrium state for each set of elastic constants. The final results in the MC method may not depend on the initial configuration, even when starting the quenching process by other random states. Considering this situation, other well-ordered structures will hardly ever be found in systems driven by the stochastic Metropolis algorithm. Such interchange between well-ordered states would happen only if they were practically in the same energy levels, so that thermal agitation could induce that modification. While the LdG model is able to find RSS and PBS by considering initial ordered Ansatz, we succeeded on describing the bTBS as the final state for droplets of the slightly elastic anisotropic LC ( $K_{11}/K_{22} = 1.10$  and  $K_{33}/K_{22} = 1.20$ ) with planar degenerate anchoring, and the PBS pattern for droplets of ZLI4330 ( $K_{11}/K_{22} = 2.00$  and  $K_{33}/K_{22} = 2.92$ ).

Notwithstanding the lattice is discretized in simulations, all energetic parameters in

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Eq. (2.65) have continuous function properties, once they are elastic constant and chirality dependent. Such parameters directly influence the system energy minimum behavior. The chiral additive pairwise potential showed that the stability of states for a LC changes as the chiral parameter  $\sigma^*$  shifts its value. Furthermore, given a fixed N, it is also possible to observe macrostructural switches by changing elastic constants and anchoring energy. A multidimensional diagram would be necessary to better understand two aspects. Firstly, the new energy minima arise from variating  $\sigma^*$  but keeping all the other parameters fixed. Secondly, the energy minima may bifurcate while fixing N and changing elastic constants. We highlight that maintaining R/p fixed for different values of R does not mean keeping  $\sigma^*$  fixed, since it is pitch dependent. We mentioned that  $p^* = 40.00$  must be a considerable value for the validation of Luckhurst chiral potential. If considering a small droplet with  $R^* = 20$ ,  $p^*$  is bigger than  $R^*$ , but the chiral parameter keeps its value, and its magnitude is enough for annihilating and expelling defects from the volume to the surface. Although  $\sigma$  has low values compared to the nematic interaction energy  $\nu$ , it can be enough for presenting chaotic regimes in droplets respecting  $p^* \leq R^*$ . Precise and refined simulations are required to better investigate the energy dependence, their sensitive changes with chirality, elasticity and anchoring conditions, and how the macrostructures are influenced by surface energy in regions of N near structural transitions.

The considered droplet radius  $R^* = 40$  required some extra thermal quenches for N =4.00. By keeping the pitch fixed, simulations of bigger lattices generating N > 4.00 may require even more thermal quenches due to the high increment in the number of metastable states. As the sample reaches states with truncated loop defects for a given temperature, the trapped state stabilization is totally dependent on the thermal agitation in the system. Let us consider a multidimensional graphic of energy levels in the phase space of accessible states as a function of  $\sigma^*$ . If  $\sigma^*$  is fixed in zero, a homeotropic droplet may organize in a hedgehog structure as the accessible state of global energy minima, for example. The bigger the chiral parameter becomes, the bigger is the number of new energy minima which may emerge in energy landscape. The thermal energy is a function of the system temperate, it means  $E_T$  =  $E_T(T_R)$ . Let us suppose that all the spin changes have occurred with maximum angle of rotation (according to the BW method) during the cycles. So,  $E_T$  must assume a maximum value of thermal energy  $E_T^{(max)}$  for such a temperature that the system has to make changes of states. If  $T_R$  decreases, the maximum angle of rotation  $\theta_{max}$  for the spins also decreases in similar way by a complicated arcsine function of  $T_R$ , where the limits are  $\theta_{max} = 0$  when  $T_R \rightarrow 0$  and  $\theta_{max} = \pi$ when  $T_R \rightarrow T_{IN}$ . Between the range of  $T_R = 0.400$  and  $T_R = 0.700$ , we can consider, as a first approach, that  $\theta_{\text{max}}$  linearly decays with  $T_R$ , but it is not true supposing that  $E_T^{(\text{max})}$  respects the same behavior as a function of  $\theta_{\text{max}}$ . If N is near 4.00, several energy minima may rise. Let us suppose that the system is in a temperature  $T_R$ , accessing the *i*-th state with local minimum energy  $U_i$ , and it needs to overcome an energetic barrier  $U_b$  to access the global state g of minimum energy. The energetic barriers may drastically and complexly increase as N increases, so decreasing the temperature in steps of dT = 0.100 makes the thermal energy decreases in such a way that the system can not get rid of states featured by local energy minima, in other words,  $U_i + E_T^{(\text{max})} < U_b$ . Thus, in case the droplet is trapped in an unexpected metastable state, it could access other lower energy states only by suffering an external disturbance, either thermally by a new thermal quench, by light illumination if the chiral dopant is photoresponsive, or by electric field application which favors some kinds of alignment. As the annihilation of defects is related to the system's accessibility to lower energy states, it can easily occur if dTassumes smaller values, since the free energy is related to the disclination length. Besides that, this annihilation behavior due to thermal agitation should be simpler for smaller values of  $\sigma^*$ , since  $U_b$  also reduces with decrements of chiral term.

The values of order parameter isosurfaces in the MC simulations were taken in  $S_{MC}$  = 0.74, while the values obtained by the LdG model form all the point and line defects with  $S_{LdG} = 0.48$  [204]. The common values of order parameter for LC in nematic phase changes in the region between 0.40 and 0.70 [233], in which 0.40 is near the critical value of isotropicnematic phase transition, and 0.70 is near the limits of nematic to smectic phase. The order parameter near the nematic-smectic phase transition was theoretically obtained in good agreement with experiments by the McMillan-de Gennes approach [234–236]. According to the McMillan criteria, the nematic-smectic temperature  $(T_{NS})$  to isotropic-nematic temperature  $(T_{IN})$  ratio has a value generally greater than 0.87. By considering the Maier-Saupe theory, this ratio determines an upper value of  $S_{upp} = 0.70$  where the order parameter for nematic phase is still valid, once this theory can not be hold for temperatures much lower than isotropic-nematic phase transition temperature [26]. The pairwise potential used in our MC simulations does not describe smectic behavior, as the procedure on obtaining the molecular model, which is elastic constants dependent, consists of small director field distortions considering the Frank free energy for nematics [3,4]. Figs. 5.19-(a) and (b) show, for example, high ordered regions in the bulk with weak and strong homeotropic anchoring for CCN-37 LC, respectively. Even near the surface, the order parameter attains values near  $S_{MC} = 1.00$ , indicating an almost perfect order. Actually, the nematic phase does not have perfect alignment, so this value for the order parameter is a good representation for the well ordered regions in this phase, since the simulations are performed with lattice model of spins allowed to change their orientation but fixed in the space. As the high order representation happens near S = 0.70 in real cases, which is 70% of values found in high ordered regions in the MC simulations, the isosurfaces carried out with  $S_{MC} = 0.74$ would have an equivalent order parameter given by  $S_{equiv} = 0.52$ . This value is near the one found by the LdG model ( $S_{LdG} = 0.48$ ), but the lowest value  $S_{low}$  would have problems after considering 70% of S near the isotropic-nematic phase transition ( $S_{IN} = 0.42$ ). It would lead to a value near  $S_{low} = 0.30$ . Since defect regions, where the order parameter is low, are complex to be described for theoretical models, one can use  $S_{low} = 0.40$  as a first approach, where the isotropic-nematic transition occurs. So, associating  $S_{\text{low}} = 0.40$  in real cases for  $S_{\text{MC}} = 0.40$  in the MC simulations, and  $S_{upp} = 0.70$  in real situations for  $S_{MC} = 1.00$  in MC simulations, by a simple proportion, it is possible to assume that  $S_{MC} = 0.74$  in MC simulations may correspond



**Fig. 5.19:** Order parameter near the surface in the CCN-37 homeotropic droplet. (a) The weak anchoring energy  $(J_s = 0.25)$  shows that the bulk expels the defects to the surface, forming the twisted loop defect, similar to the loxodrome curve. It is possible to observe that the defect line influences the order in the surface, where red regions have high alignment and blue color are low order regions of order parameter *S*. However, (b) the moderate anchoring energy  $(J_s = 1.00)$  also presents the twisted loop defect near the surface, but it is inside the droplet, which means that the surface still keeps the homeotropic order at the surface. So, the penetration depth of twisted loop defect in the surface is related to the anchoring energy.

to  $S_{\text{equiv}} = 0.57$  in real cases. Indeed, this last value still seems to disagree with  $S_{\text{LdG}} = 0.48$ , but the estimative made here is simple and it is complicated to find a correct value of  $T_{NS}/T_{IN}$ . According to McMillan-de Gennes approach, bigger values for this ratio makes the upper value  $S_{\text{upp}}$  smaller than 0.70, which decreases the representation range of order parameter in real nematics. Moreover, the lower value  $S_{\text{low}}$  is closer of 0.43, instead of 0.40 taken in the approach. Supposing these corrections, and that  $S_{\text{MC}} = 0.72$  in MC simulations also presents the same isosurfaces in the most part of the cases studied, the value to represent real nematics approaches would be  $S_{\text{equiv}} = 0.53$ , which now seems to be in better agreement with  $S_{\text{LdG}}$ , minimizing the error.

Linked and knotted fields play important significance in classic and quantum field theories [237, 238], dynamics of vortices in fluid mechanics [239], proteins [240] and liquid crystals [202, 211, 241, 242]. Theoretical analysis of nontrivial tangled loop configurations are complex and difficult to predict because continuum space allows infinite possibilities of arrangements. The elastic one-constant approach of CLC droplets in homeotropic surface anchoring presented chaotic configurations of loop defects forming Hopf links with an extra loop. It can be related to the thermal quench speed associated with magnitude of dT. We do not rule out the possibilities in spherical geometry. Interestingly, the elastic anisotropy plays an important role in homeotropic droplets acting over disclination lines like Meissner effect in superconductors.<sup>13</sup> The similarity to this effect is given when magnetic field lines expelled outside the material is associated with the single twisted loop defect formed and forced towards the droplet surface, since in both cases the phenomenon is temperature dependent. Notably, chirality ensures that

<sup>&</sup>lt;sup>13</sup>The Meissner effect is associated with expulsion of magnetic field from internal part of superconductive materials when below the superconductivity critical temperature.

the nematic disclination lines keep a certain minimum length in stabilized configurations. It is observed in homeotropic droplets, cause planar anchoring just showed point defects at the surface, as predicted by the Poincaré-Hopf theorem. The dependence only on N of loxodrome parametrization in Eq. (5.13) fits the estimative well for scaled length in homeotropic droplets with N = 3.00 and N = 4.00. In case of N = 2.00, the number of isocline lines is zero and the loxodrome curve is similar to an infinite symbol, but droplets did not show this kind of disclination loop. On the other hand, it presented a simple single equatorial ring defect, where its estimative size is performed by the circle length equation. The estimates for twisted loop defect length holds valid for  $N \ge 3.00$  in homeotropic anchoring cases.

Nontrivial topology of CLC droplets is a burgeoning field in soft matter science due to the complex and intriguing chiral sensitive energy landscape. While the well-ordered configurations in CLC droplets can be used as filters, biosensors, optical cross-communicators, and Bragg resonators, droplets with metastable states are unique and can be used as storing information. Structural modifications provide changes in the media optical properties in such a way that droplets in different stable states can serve as photonic elements in optical systems. Boundary and initial conditions besides procedures of system relaxation are fundamental factors that lead to specific states and director fields. Researches exploring these aspects in cholesteric droplets under Metropolis algorithm point of view can bring new relevant information on how simple changes in the chiral anisotropic pairwise additive potential affect regions of structural transitions.

## Chapter 6

## Conclusions

CLCs confined in different systems were studied by means of MC method and Metropolis algorithm. The relaxation process considered that spins in the lattice interact via chiral pairwise additive potential. We succeed on studying three different, important physical phenomena in CLCs: the role of surface anchoring in hybrid aligned cells, the striped pattern formation after wetting transition, and the formation of stable and metastable states after thermal quenches in spherical droplets.

Firstly, we analyzed a hybrid cell filled with a CLC and investigated the role of the anchoring energy on the director organization by using MC simulations. We verified three kinds of behavior by varying this quantity: a planar arrangement, a striped pattern and a conic-like structure. We emphasized that the pairwise additive potential proposed for CLCs is able to aggregate anisotropic effects on the interactions, so that the striped pattern can structurally reproduce CLCs in a similar fashion to what is found in experimental samples. In our MC simulations, the surface plays a very important role on determining the orientation of the directors through the volume according to the anchoring energy, therefore, being one of the key parameters on the striped pattern formation. We identified a structural transition-like behavior by changing the anchoring energy parameter and verified that it is different for each of the liquid crystals host studied. We hope that the results found here may lay the bedsheets for deeper studies, both experimentally and theoretically, on the stripe pattern formation of CLCs.

Secondly, we have used the MC method and the MH algorithm to model pattern formation during a wetting transition in CLCs. We used a pairwise potential proposed by Luckhurst [5] and a good qualitative agreement with experiments was found. Experimental samples have shown that while the stripe pattern is under formation, it is possible to control them with temperature [7], including the orientation of the stripes and the way they develop. Both experiments and simulations show that the way the stripe modulation forms depend on the pitch to thickness ratio. In other words, different pitch length in the temperature controlled sample (thickness) might produce different manner of development, in a similar way of planar oriented CLC samples under an applied field. We have verified that the elastic anisotropy is an important parameter for the appearance of the pattern. The simulated textures predict both, GM and DM modulations. We interpreted the formation of either GM or DM stripes in terms of the initial moments of the growing layer. Accordingly, if the layer is too small to accommodate the formation of the SH configuration, the sample is essentially nematic and the only way of developing stripes is by a nucleation process, where new stripes are formed one by one by transposing an energy barrier. On the other hand, if there is enough space for the CLC layer to form the SH configuration, the stripe formation occurs once elastic distortions become too high, so the LH configuration becomes more viable, a homogeneous process described in [7]. Further analysis are being undertaken to improve the model, especially on the elastic anisotropy matter. The results presented here might be used for better understanding the grating formation (with applications in optics and photonics) in CLC, and to model bio-systems with homogeneous to periodic deformation transitions [180].

Finally, we have studied MC simulations of thermal quenches in spherical CLC droplets, by interacting the spins via Luckhurst chiral pairwise potential. Since the potential is anisotropic, and links the energetic parameters to LC elastic constants, we analyzed the quenching process simulations for several combinations of elastic constants, droplet size to pitch ratio regimes, strong and weak anchoring energy in both homeotropic and planar boundary conditions. We clearly observe the elastic anisotropy directly modifying the defect morphology and the facilities on annihilating them. Results show that for low chirality in the system both the LL and the Luckhurst chiral potential were successful in describing the formation of stable states that appear in experiments. For N = 3.00, the metastable states start to manifest if the elastic constants are considered to be equal. On the contrary, elastic anisotropy included in the potential could well reproduce stable states known in the literature. Mainly for N = 4.00, the relaxation process in homeotropic droplets gets the director configuration to stick in metastable states when considering the chiral LL potential. Again, setting different ratios for elastic constants in the Luckhurst chiral potential is the key for reaching the stable states diversity. We highlight the possibility on finding different stable states configuration by exploring other sets of elastic constants ratios, anchoring energy, chirality level and temperature steps.

Trying to reproduce the spherical geometry in a small rectangular lattice can potentialize the irregularities of a squared border, since there are not points enough at the surface to mimic a sphere. In fact, the droplets radius in our MC simulations is near half-size or smaller when compared to conventional simulations made by explicit finite difference method. Some structures that we found are exactly aligned with some axes. The first impression is that small lattices may induce a bias in the Cartesian axes direction, but it is discard this possibility because more than one stable structure was found to be with symmetry axis pointed to a random direction in the space, for example the BS (N = 0), the twisted loop defect (N = 3.00), or even the PBS (N = 4.00).

Systems where the spins do not interact with all the six first neighbors in the boundaries have complex connections with real elastic constants. We consider that a system is closed if all spins in the bulk always interact with their six first neighbors. Better results of elastic constants,

in agreement with real values, were obtained when the system is closed, since the pairwise interaction can better reproduce the director field variations in continuous media, if considering a well balance between small deformations and thermal agitation. In the hybrid-aligned cell system, all spins in the bulk have six neighbors, including the borders in the x and y direction, since the periodic boundary condition was taken in account. On the contrary, to reproduce the striped modulation after wetting transition, no periodic boundary conditions were implemented. In the third studied system, the spherical geometry system is considered to be closed system. In the hybrid-cells and the droplet systems, closed systems, real elastic constants ratio were used in the simulations, and could successfully reproduce experimental behaviors. Even the second system not being closed, the chiral pairwise potential reproduced the striped pattern in good qualitative agreement as experimental results.

To the best of our knowledge, we firstly reported the use of the anisotropic chiral pairwise additive potential, defined in Eq. (2.65), to describe stable and (in some cases) metastable configurations in environments like cells with different kinds of anchoring, and droplets. The main advantage to perform Monte Carlo simulations over other techniques is the inclusion of temperature as a real parameters that controls the thermal fluctuations in the system. Even keeping  $T_R$  fixed, or changing it, cholesteric structures can be successfully reached according to the interplay between the chirality and other parameters involved in the geometric confinement. Besides, as the additive potential does not explicitly depend on the space derivatives magnitude (the interaction energy just depends on the spins orientation and their relative position to each other), smaller systems can be designed when compared to the system size treated by other simulation models. Consequently, it makes possible the analysis of mesoscopic and macroscopic systems with low computational power consumption. In the future, such Monte Carlo technique opens opportunities to study several problems of industrial interests by using the relatively simple pairwise interaction.

## **Bibliography**

- [1] F. C. Frank, "I. Liquid crystals. On the theory of liquid crystals," *Discussions of the Faraday Society*, vol. 25, pp. 19–28, 1958.
- [2] P. A. Lebwohl and G. Lasher, "Nematic-liquid-crystal order—a Monte Carlo calculation," *Phys. Rev. A*, vol. 6, no. 1, p. 426, 1972.
- [3] T. Gruhn and S. Hess, "Monte Carlo simulation of the director field of a nematic liquid crystal with three elastic coefficients," *Z. Naturforsch. A*, vol. 51, no. 1-2, pp. 1–9, 1996.
- [4] G. R. Luckhurst and S. Romano, "Computer simulation study of a nematogenic lattice model based on an elastic energy mapping of the pair potential," *Liq. Cryst.*, vol. 26, no. 6, pp. 871–84, 1999.
- [5] G. R. Luckhurst and G. Saielli, "A pairwise additive potential for the elastic interaction energy of a chiral nematic," *Mol. Cryst. Liq. Cryst.*, vol. 395, no. 1, pp. 183–92, 2003.
- [6] A. Ryabchun, A. Bobrovsky, J. Stumpe, and V. Shibaev, "Rotatable diffraction gratings based on cholesteric liquid crystals with phototunable helix pitch," *Adv. Opt. Mater.*, vol. 3, no. 9, pp. 1273–1279, 2015.
- [7] R. Zola, L. Evangelista, Y.-C. Yang, and D.-K. Yang, "Surface induced phase separation and pattern formation at the isotropic interface in chiral nematic liquid crystals," *Phys. Rev. Lett.*, vol. 110, no. 5, p. 057801, 2013.
- [8] H.-G. Lee, S. Munir, and S.-Y. Park, "Cholesteric liquid crystal droplets for biosensors," ACS Appl. Mater. Interfaces, vol. 8, no. 39, pp. 26407–26417, 2016.
- [9] L. Tran, M. O. Lavrentovich, G. Durey, A. Darmon, M. F. Haase, N. Li, D. Lee, K. J. Stebe, R. D. Kamien, and T. Lopez-Leon, "Change in stripes for cholesteric shells via anchoring in moderation," *Phys. Rev. X*, vol. 7, no. 4, p. 041029, 2017.
- [10] T. Orlova, S. J. Aßhoff, T. Yamaguchi, N. Katsonis, and E. Brasselet, "Creation and manipulation of topological states in chiral nematic microspheres," *Nat. Commun.*, vol. 6, p. 7603, 2015.

- [11] Y. Zhou, E. Bukusoglu, J. A. Martínez-González, M. Rahimi, T. F. Roberts, R. Zhang, X. Wang, N. L. Abbott, and J. J. de Pablo, "Structural transitions in cholesteric liquid crystal droplets," ACS nano, vol. 10, no. 7, pp. 6484–6490, 2016.
- [12] S. R. A. Salinas, "The Ising Model," in *Introduction to Statistical Physics*, pp. 257–276, Springer, 2001.
- [13] K. Binder, Monte Carlo Methods in Statistical Physics. Springer, 1986.
- [14] K. Binder and D. W. Heermann, *Monte Carlo Simulation in Statistical Physics*. Springer, 1997.
- [15] M. P. Allen and D. J. Tildesley, *Computer simulation of liquids*. Oxford University Press, 2017.
- [16] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, "Equation of state calculations by fast computing machines," *J. Chem. Phys.*, vol. 21, no. 6, pp. 1087–1092, 1953.
- [17] I. Beichl and F. Sullivan, "The Metropolis algorithm," *Computing in Science & Engineering*, vol. 2, no. 1, pp. 65–69, 2000.
- [18] F. Reinitzer, "Beiträge zur kenntniss des cholesterins," Monatsh. Chem., vol. 9, no. 1, pp. 421–441, 1888.
- [19] O. Lehamnn, "Über fliessende krystalle," Z. Phys. Chem., vol. 4, no. 1, pp. 462–72, 1889.
- [20] P. J. Collings, *Liquid crystals: Nature's delicate phase of matter*. Princeton University Press, 2002.
- [21] A. Jákli and A. Saupe, One-and two-dimensional fluids: properties of smectic, lamellar and columnar liquid crystals. CRC Press, 2006.
- [22] G. Friedel, "Les états mésomorphes de la matière," in Ann. Phys., vol. 9, pp. 273–474, 1922.
- [23] P. G. de Gennes and J. Prost, *The physics of liquid crystals*, vol. 83. Oxford university press, 1995.
- [24] J. L. Fergason, "Liquid crystals," Sci. Am., vol. 211, no. 2, pp. 76–85, 1964.
- [25] S. Chandrasekhar, *Liquid Crystals*. Cambridge University Press, 1992.
- [26] D.-K. Yang, Fundamentals of liquid crystal devices. John Wiley & Sons, 2014.
- [27] R. Noyori, "Centenary Lecture. Chemical multiplication of chirality: Science and applications," *Chem. Soc. Rev.*, vol. 18, pp. 187–208, 1989.

- [28] R. A. Hegstrom and D. K. Kondepudi, "The handedness of the universe," Sci. Am., vol. 262, no. 1, pp. 108–115, 1990.
- [29] B. Yurke, A. J. Turberfield, A. P. M. Jr, F. C. Simmel, and J. L. Neumann, "A DNAfuelled molecular machine made of DNA," *Nature*, vol. 406, no. 6796, p. 605, 2000.
- [30] C. Bahr and H.-S. Kitzerow, *Chirality in liquid crystals*. Springer, 2001.
- [31] Y. Sofue and V. Rubin, "Rotation curves of spiral galaxies," *Annu. Rev. Astron. Astro-phys.*, vol. 39, no. 1, pp. 137–174, 2001.
- [32] R. P. Goodman, I. A. T. Schaap, C. F. Tardin, C. M. Erben, R. M. Berry, C. F. Schmidt, and A. J. Turberfield, "Rapid chiral assembly of rigid DNA building blocks for molecular nanofabrication," *Science*, vol. 310, no. 5754, pp. 1661–1665, 2005.
- [33] B. A. McGuire, P. B. Carroll, R. A. Loomis, I. A. Finneran, P. R. Jewell, A. J. Remijan, and G. A. Blake, "Discovery of the interstellar chiral molecule propylene oxide (CH3CHCH2O)," *Science*, vol. 352, no. 6292, pp. 1449–1452, 2016.
- [34] I. Kocsis, M. Sorci, H. Vanselous, S. Murail, S. E. Sanders, E. Licsandru, Y.-M. Legrand,
  A. V. D. Lee, M. Baaden, P. B. Petersen, *et al.*, "Oriented chiral water wires in artificial transmembrane channels," *Sci. Adv.*, vol. 4, no. 3, p. eaao5603, 2018.
- [35] E. L. Eliel, S. H. Wilen, and L. N. Mander, *Stereochemistry of Organic Compounds*, vol. 13. Wiley & Sons, Inc. New York, Cap, 1994.
- [36] D. Nasipuri, *Stereochemistry of organic compounds: principles and applications*. New Age International, 1994.
- [37] A. N. Collins, G. N. Sheldrake, and J. Crosby, *Chirality in industry II: Developments in the commercial manufacture and applications of optically active compounds*, vol. 2. John Wiley & Sons, 1997.
- [38] R. A. L. Jones, *Soft condensed matter*, vol. 6. Oxford University Press, 2002.
- [39] J. L. Ericksen, "Anisotropic fluids," Arch. Ration. Mech. Anal., vol. 4, no. 1, pp. 231–237, 1959.
- [40] J. L. Ericksen, "Conservation laws for liquid crystals," *Trans. Soc. Rheol.*, vol. 5, no. 1, pp. 23–34, 1961.
- [41] J. L. Ericksen, "Hydrostatic theory of liquid crystals," Arch. Ration. Mech. Anal., vol. 9, no. 1, pp. 371–378, 1962.
- [42] F. M. Leslie, "Some constitutive equations for liquid crystals," *Arch. Ration. Mech. Anal.*, vol. 28, no. 4, pp. 265–283, 1968.

- [43] F. M. Leslie, "Continuum theory of cholesteric liquid crystals," *Mol. Cryst. Liq. Cryst.*, vol. 7, no. 1, pp. 407–431, 1969.
- [44] G. Solladié and R. G. Zimmermann, "Liquid crystals: A tool for studies on chirality," Ang. Chem. Int. Ed. Eng., vol. 23, no. 5, pp. 348–362, 1984.
- [45] M. Kleman and O. D. Lavrentovich, Soft matter physics: an introduction. Springer Science & Business Media, 2007.
- [46] R. S. Zola, *Effects of electric field, surface alignment and guest materials in cholesteric liquid crystals.* PhD thesis, Kent State University, 2012.
- [47] D.-K. Yang, X.-Y. Huang, and Y.-M. Zhu, "Bistable cholesteric reflective displays: Materials and drive schemes," *Annu. Rev. Mater. Sci.*, vol. 27, no. 1, pp. 117–146, 1997.
- [48] H. Nemati, D.-K. Yang, K.-L. Cheng, C.-C. Liang, J. Shiu, C.-C. Tsai, and R. S. Zola, "Effect of surface alignment layer and polymer network on the helfrich deformation in cholesteric liquid crystals," J. Appl. Phys., vol. 112, no. 12, p. 124513, 2012.
- [49] H. Nemati, S. Liu, R. S. Zola, V. P. Tondiglia, K. M. Lee, T. White, T. Bunning, and D.-K. Yang, "Mechanism of electrically induced photonic band gap broadening in polymer stabilized cholesteric liquid crystals with negative dielectric anisotropies," *Soft Matter*, vol. 11, no. 6, pp. 1208–1213, 2015.
- [50] H. Finkelmann, S. T. Kim, A. Munoz, P. Palffy-Muhoray, and B. Taheri, "Tunable mirrorless lasing in cholesteric liquid crystalline elastomers," *Adv. Mater.*, vol. 13, no. 14, pp. 1069–1072, 2001.
- [51] M. Schadt and W. Helfrich, "Voltage-dependent optical activity of a twisted nematic liquid crystal," *Appl. Phys. Lett.*, vol. 18, no. 4, pp. 127–128, 1971.
- [52] W. M. Gibbons, P. J. Shannon, S.-T. Sun, and B. J. Swetlin, "Surface-mediated alignment of nematic liquid crystals with polarized laser light," *Nature*, vol. 351, no. 6321, p. 49, 1991.
- [53] D.-K. Yang, L.-C. Chien, and J. W. Doane, "Cholesteric liquid crystal/polymer dispersion for haze-free light shutters," *Appl. Phys. Lett.*, vol. 60, no. 25, pp. 3102–3104, 1992.
- [54] R. B. Meyer, F. Lonberg, and C.-C. Chang, "Cholesteric liquid crystal smart reflectors," *Mol. Cryst. Liq. Cryst. A*, vol. 288, no. 1, pp. 47–61, 1996.
- [55] M. Xu and D.-K. Yang, "Dual frequency cholesteric light shutters," Appl. Phys. Lett., vol. 70, no. 6, pp. 720–722, 1997.

- [56] M.-H. Lu, "Bistable reflective cholesteric liquid crystal display," J. Appl. Phys., vol. 81, no. 3, pp. 1063–1066, 1997.
- [57] R. Eelkema, M. M. Pollard, N. Katsonis, J. Vicario, D. J. Broer, and B. L. Feringa, "Rotational reorganization of doped cholesteric liquid crystalline films," *J. Am. Chem. Soc.*, vol. 128, no. 44, pp. 14397–14407, 2006.
- [58] Y. Matsuhisa, Y. Huang, Y. Zhou, S.-T. Wu, Y. Takao, A. Fujii, and M. Ozaki, "Cholesteric liquid crystal laser in a dielectric mirror cavity upon band-edge excitation," *Opt. Express*, vol. 15, no. 2, pp. 616–622, 2007.
- [59] Q. Li, Y. Li, J. Ma, D.-K. Yang, T. J. White, and T. J. Bunning, "Directing dynamic control of red, green, and blue reflection enabled by a light-driven self-organized helical superstructure," *Adv. Mater.*, vol. 23, no. 43, pp. 5069–5073, 2011.
- [60] C.-H. Lin, R.-H. Chiang, S.-H. Liu, C.-T. Kuo, and C.-Y. Huang, "Rotatable diffractive gratings based on hybrid-aligned cholesteric liquid crystals," *Opt. Express*, vol. 20, no. 24, pp. 26837–26844, 2012.
- [61] Y. Wang and Q. Li, "Light-driven chiral molecular switches or motors in liquid crystals," *Adv. Mater.*, vol. 24, no. 15, pp. 1926–1945, 2012.
- [62] N. Katsonis, E. Lacaze, and A. Ferrarini, "Controlling chirality with helix inversion in cholesteric liquid crystals," J. Mater. Chem., vol. 22, no. 15, pp. 7088–7097, 2012.
- [63] J. Xiang, Y. Li, Q. Li, D. A. Paterson, J. M. D. Storey, C. T. Imrie, and O. D. Lavrentovich, "Electrically tunable selective reflection of light from ultraviolet to visible and infrared by heliconical cholesterics," *Adv. Mater.*, vol. 27, no. 19, pp. 3014–3018, 2015.
- [64] Z.-G. Zheng, Y. Li, H. K. Bisoyi, L. Wang, T. J. Bunning, and Q. Li, "Three-dimensional control of the helical axis of a chiral nematic liquid crystal by light," *Nature*, vol. 531, no. 7594, p. 352, 2016.
- [65] Y. Wang, Z.-G. Zheng, H. K. Bisoyi, K. G. Gutierrez-Cuevas, L. Wang, R. S. Zola, and Q. Li, "Thermally reversible full color selective reflection in a self-organized helical superstructure enabled by a bent-core oligomesogen exhibiting a twist-bend nematic phase," *Mater. Horiz.*, vol. 3, no. 5, pp. 442–446, 2016.
- [66] L. Wang, D. Chen, K. G. Gutierrez-Cuevas, H. K. Bisoyi, J. Fan, R. S. Zola, G. Li, A. M. Urbas, T. J. Bunning, D. A. Weitz, and Q. Li, "Optically reconfigurable chiral microspheres of self-organized helical superstructures with handedness inversion," *Mat. Horiz.*, vol. 4, no. 6, pp. 1190–1195, 2017.

- [67] Z.-G. Zheng, R. S. Zola, H. K. Bisoyi, L. Wang, L. Yannian, T. J. Bunning, and Q. Li, "Controllable dynamic zigzag pattern formation in a soft helical superstructure," *Adv. Mater.*, vol. 29, no. 30, p. 1701903, 2017.
- [68] P. Sleczkowski, Y. Zhou, S. Iamsaard, J. J. de Pablo, N. Katsonis, and E. Lacaze, "Lightactivated helical inversion in cholesteric liquid crystal microdroplets," *PNAS*, vol. 115, no. 17, pp. 4334–4339, 2018.
- [69] J. S. Patel and R. B. Meyer, "Flexoelectric electro-optics of a cholesteric liquid crystal," *Phys. Rev. Lett.*, vol. 58, no. 15, p. 1538, 1987.
- [70] T. Nose, T. Miyanishi, Y. Aizawa, R. Ito, and M. Honma, "Rotational behavior of stripe domains appearing in hybrid aligned chiral nematic liquid crystal cells," *Jpn. J. Appl. Phys.*, vol. 49, no. 5R, p. 051701, 2010.
- [71] R. Hamdi, G. Petriashvili, M. P. de Santo, G. Lombardo, and R. Barberi, "Electrically controlled 1D and 2D cholesteric liquid crystal gratings," *Mol. Cryst. Liq. Cryst.*, vol. 553, no. 1, pp. 97–102, 2012.
- [72] A. Y.-G. Fuh, C.-H. Lin, and C.-Y. Huang, "Dynamic pattern formation and beamsteering characteristics of cholesteric gratings," *Jpn. J. Appl. Phys.*, vol. 41, no. 1R, p. 211, 2002.
- [73] L.-L. Ma, W. Duan, M.-J. Tang, L.-J. Chen, X. Liang, Y.-Q. Lu, and W. Hu, "Light-driven rotation and pitch tuning of self-organized cholesteric gratings formed in a semi-free film," *Polym. J.*, vol. 9, no. 7, p. 295, 2017.
- [74] R. S. Zola and Q. Li, "Stimuli-directed helical axis switching in chiral liquid crystal nanostructures," in *Functional Organic and Hybrid Nanostructured Materials: Fabrication, Properties, and Applications*, John Wiley & Sons, 2018.
- [75] R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. M. Bastiaansen, D. J. Broer, and B. L. Feringa, "Nanomotor rotates microscale objects," *Nature*, vol. 440, no. 7081, pp. 163–163, 2006.
- [76] S. Chandrasekhar and N. V. Madhusudana, "Molecular statistical theory of nematic liquid crystals," *Acta Cryst.*, vol. A 27, no. 4, pp. 303–13, 1970.
- [77] D. Demus, J. W. Goodby, G. W. Gray, H. W. Spies, and V. Vill, *Handbook of liquid* crystals, volume 1: Fundamentals. John Wiley & Sons, 2011.
- [78] I. I. Smalyukh and O. D. Lavrentovich, "Three-dimensional director structures of defects in Grandjean-Cano wedges of cholesteric liquid crystals studied by fluorescence confocal polarizing microscopy," *Phys. Rev. E*, vol. 66, no. 5, p. 051703, 2002.

- [79] Q. Liu, B. Senyuk, M. Tasinkevych, and I. I. Smalyukh, "Nematic liquid crystal boojums with handles on colloidal handlebodies," *PNAS*, vol. 110, no. 23, pp. 9231–9236, 2013.
- [80] I. Dierking, Textures of liquid crystals. John Wiley & Sons, 2003.
- [81] P. Yeh and C. Gu, Optics of liquid crystal displays, vol. 67. John Wiley & Sons, 2010.
- [82] L. M. Blinov, Structure and properties of liquid crystals, vol. 123. Springer Science & Business Media, 2010.
- [83] H. de Vries, "Rotatory power and other optical properties of certain liquid crystals," Acta Cryst., vol. 4, no. 3, pp. 219–226, 1951.
- [84] V. A. Belyakov, V. E. Dmitrienko, and V. P. Orlov, "Optics of cholesteric liquid crystals," *Sov. Phys. Uspekhi*, vol. 22, no. 2, p. 64, 1979.
- [85] L. M. Blinov and V. G. Chigrinov, *Electrooptic effects in liquid crystal materials*. Springer Science & Business Media, 1996.
- [86] L. D. Landau and E. M. Lifshitz, "Statistical Physics, Part 1: Volume 5 (Course of Theoretical Physics)," *Publisher: Butterworth-Heinemann*, vol. 3, 1980.
- [87] B. I. Halperin, T. C. Lubensky, and S.-K. Ma, "First-order phase transitions in superconductors and smectic-A liquid crystals," *Phys. Rev. Lett.*, vol. 32, no. 6, p. 292, 1974.
- [88] E. Ising, "Beitrag zur theorie des ferromagnetismus," Z. Phys., vol. 31, no. 1, pp. 253– 258, 1925.
- [89] L. Onsager, "Crystal statistics. I. A two-dimensional model with an order-disorder transition," *Phys. Rev.*, vol. 65, no. 3-4, p. 117, 1944.
- [90] H. A. Kramers and G. H. Wannier, "Statistics of the two-dimensional ferromagnet. Part I," *Phys. Rev.*, vol. 60, no. 3, p. 252, 1941.
- [91] C. Domb, "On the theory of cooperative phenomena in crystals," Adv. Phys., vol. 9, no. 35, pp. 245–361, 1960.
- [92] M. E. Fisher, "The theory of equilibrium critical phenomena," *Rep. Prog. Phys.*, vol. 30, no. 2, p. 615, 1967.
- [93] A. M. Ferrenberg and D. P. Landau, "Critical behavior of the three-dimensional Ising model: A high-resolution Monte Carlo study," *Phys. Rev. B*, vol. 44, no. 10, p. 5081, 1991.
- [94] W. L. Bragg and E. J. Williams, "The effect of thermal agitation on atomic arrangement in alloys," *Proc. R. Soc. Lond. A*, vol. 145, no. 855, pp. 699–730, 1934.

- [95] H. A. Bethe, "Statistical theory of superlattices," *Proc. R. Soc. Lond. A*, vol. 150, no. 871, pp. 552–575, 1935.
- [96] R. Peierls, "On Ising's model of ferromagnetism," in *Math. Proc. Camb. Philos. Soc.*, vol. 32, pp. 477–481, Cambridge University Press, 1936.
- [97] W. Maier and A. Saupe, "Eine einfache molekular-statistische theorie der nematischen kristallinflüssigen phase. Teil I.," *Z. Naturforsch. A*, vol. 14, no. 10, pp. 882–889, 1959.
- [98] W. Maier and A. Saupe, "Eine einfache molekular-statistische theorie der nematischen kristallinflüssigen phase. Teil II.," Z. Naturforsch. A, vol. 15, no. 4, pp. 287–292, 1960.
- [99] V. Tsvetkov, "On molecular order in the anisotropic liquid phase," *Acta Physicochim. URSS*, vol. 16, pp. 132–147, 1942.
- [100] A. Saupe, "Recent results in the field of liquid crystals," Angew. Chem. Int., vol. 7, no. 2, pp. 97–112, 1968.
- [101] T. E. Faber and G. R. Luckhurst, "Chapter 3. Liquid Crystals," Annu. Rep. Prog. Chem., Sect. A. Inorg. and Phys. Chem, vol. 72, pp. 31–65, 1975.
- [102] R. L. Humphries, P. G. James, and G. R. Luckhurst, "Molecular field treatment of nematic liquid crystals," J. Chem. Soc. Faraday Trans., vol. 68, pp. 1031–1044, 1972.
- [103] R. L. Humphries and G. R. Luckhurst, "On the molecular field theory of the nematic mesophase," *Chem. Phys. Lett.*, vol. 17, no. 4, pp. 514–515, 1972.
- [104] H. C. Andersen, D. Chandler, and J. D. Weeks, "Roles of repulsive and attractive forces in liquids: The equilibrium theory of classical fluids," *Adv. Chem. Phys.*, vol. 34, pp. 105– 156, 1976.
- [105] M. A. Cotter, "Hard-rod fluid: Scaled particle theory revisited," *Phys. Rev. A*, vol. 10, no. 2, p. 625, 1974.
- [106] G. R. Luckhurst, C. Zannoni, P. L. Nordio, and U. Segre, "A molecular field theory for uniaxial nematic liquid crystals formed by non-cylindrically symmetric molecules," *Mol. Phys.*, vol. 30, no. 5, pp. 1345–1358, 1975.
- [107] G. R. Luckhurst and C. Zannoni, "Why is the Maier–Saupe theory of nematic liquid crystals so successful?," *Nature*, vol. 267, no. 5610, p. 412, 1977.
- [108] P. Pasini and C. Zannoni, *Advances in the computer simulatons of liquid crystals*, vol. 545. Springer Science & Business Media, 2013.
- [109] R. G. Priest, "Comments on the lattice model of liquid crystals," *Phys. Rev. Lett.*, vol. 26, no. 8, p. 423, 1971.

- [110] G. Lasher, "Monte Carlo results for a discrete-lattice model of nematic ordering," *Phys. Rev. A*, vol. 5, no. 3, p. 1350, 1972.
- [111] C. Chiccoli, P. Pasini, F. Semeria, and C. Zannoni, "A computer simulation of nematic droplets with radial boundary conditions," *Phys. Lett. A*, vol. 150, no. 5-7, pp. 311–314, 1990.
- [112] C. Chiccoli, P. Pasini, F. Semeria, and C. Zannoni, "Monte Carlo simulations of model nematic droplets," *Mol. Cryst. Liq. Cryst.*, vol. 212, no. 1, pp. 197–204, 1992.
- [113] C. Chiccoli, P. Pasini, F. Semeria, and C. Zannoni, "Computer simulations of nematic droplets with toroidal boundary conditions," *Mol. Cryst. Liq. Cryst.*, vol. 221, no. 1, pp. 19–28, 1992.
- [114] E. Berggren, C. Zannoni, C. Chiccoli, P. Pasini, and F. Semeria, "Monte Carlo study of the molecular organization in model nematic droplets. Field effects," *Chem. Phys. Lett.*, vol. 197, no. 3, pp. 224–230, 1992.
- [115] E. Berggren, C. Zannoni, C. Chiccoli, P. Pasini, and F. Semeria, "Monte Carlo study of the effect of an applied field on the molecular organization of polymer-dispersed liquidcrystal droplets," *Phys. Rev. E*, vol. 49, no. 1, p. 614, 1994.
- [116] E. Berggren, C. Zannoni, C. Chiccoli, P. Pasini, and F. Semeria, "Computer simulations of nematic droplets with bipolar boundary conditions," *Phys. Rev. E*, vol. 50, no. 4, p. 2929, 1994.
- [117] C. Chiccoli, P. Pasini, F. Semeria, E. Berggren, and C. Zannoni, "Can spin models reproduce or predict experimental results in PDLC?," *Mol. Cryst. Liq. Cryst.*, vol. 266, no. 1, pp. 241–262, 1995.
- [118] U. Fabbri and C. Zannoni, "A Monte Carlo investigation of the Lebwohl-Lasher lattice model in the vicinity of its orientational phase transition," *Mol. Phys.*, vol. 58, no. 4, pp. 763–788, 1986.
- [119] Z. Zhang, O. G. Mouritsen, and M. J. Zuckermann, "Weak first-order orientational transition in the Lebwohl-Lasher model for liquid crystals," *Phys. Rev. Lett.*, vol. 69, no. 19, p. 2803, 1992.
- [120] C. Chiccoli, P. Pasini, S. Guzzetti, and C. Zannoni, "A Monte Carlo simulation of an inplane switching liquid crystal display," *Int. J. Mod. Phys. C*, vol. 9, no. 03, pp. 409–419, 1998.
- [121] C. Chiccoli, O. D. Lavrentovich, P. Pasini, and C. Zannoni, "Monte Carlo simulations of stable point defects in hybrid nematic films," *Phys. Rev. Lett.*, vol. 79, no. 22, p. 4401, 1997.

- [122] I. W. Stewart, *The static and dynamic continuum theory of liquid crystals: A mathematical introduction.* CRC Press, 2019.
- [123] S. E. Bedford and A. H. Windle, "Modelling of microstructure in mesophases," *Liq. Cryst.*, vol. 15, no. 1, pp. 31–63, 1993.
- [124] S. Romano, "Elastic constants and pair potentials for nematogenic lattice models," *Int. J. Mod. Phys. B*, vol. 12, no. 22, pp. 2305–2323, 1998.
- [125] J. E. Jones, "On the determination of molecular fields.—II. From the equation of state of a gas," in *Proc. R. Soc. Lond. A*, vol. 106, pp. 463–477, The Royal Society, 1924.
- [126] B. W. Van der Meer, G. Vertogen, A. J. Dekker, and J. G. J. Ypma, "A molecularstatistical theory of the temperature-dependent pitch in cholesteric liquid crystals," J. *Chem. Phys.*, vol. 65, no. 10, pp. 3935–3943, 1976.
- [127] A. J. Stone, "The description of bimolecular potentials, forces and torques: the S and V function expansions," *Mol. Phys.*, vol. 36, no. 1, pp. 241–256, 1978.
- [128] P. J. Le Masurier, G. R. Luckhurst, and G. Saielli, "Monte Carlo lattice simulations of the elastic behaviour of nematic liquid crystals," *Liq. Cryst.*, vol. 28, no. 5, pp. 769–778, 2001.
- [129] D. J. Pusiol and F. V. Chávez, "NMR study of the director fluctuations coherence length in the nematic phase of butylcyano-phenylcyclohexane," *Chem. Phys. Lett.*, vol. 312, no. 2-4, pp. 91–95, 1999.
- [130] S. Romano, "Computer simulation study of a two-dimensional nematogenic lattice model based on the Gruhn–Hess interaction potential," *Phys. Lett. A*, vol. 302, no. 4, pp. 203– 210, 2002.
- [131] R. L. Biagio, R. T. Teixeira-Souza, L. R. Evangelista, and R. S. Zola, "Role of the surface anchoring energy on the spontaneous modulated pattern formation of hybrid aligned cholesteric liquid crystals," *Mol. Cryst. Liq. Cryst.*, vol. 657, no. 1, pp. 107–115, 2017.
- [132] R. L. Biagio, R. T. de Souza, L. R. Evangelista, R. R. R. de Almeida, and R. S. Zola, "Spontaneous striped pattern formation in thin chiral nematic liquid crystal layers," *J. Mol. Liq.*, vol. 269, pp. 703–711, 2018.
- [133] B. Jerome, "Surface effects and anchoring in liquid crystals," *Rep. Prog. Phys.*, vol. 54, no. 3, p. 391, 1991.
- [134] A. A. Sonin, *The surface physics of liquid crystals*. Taylor & Francis, 1995.

- [135] A. Rapini and M. Papoular, "Distorsion d'une lamelle nématique sous champ magnétique conditions d'ancrage aux parois," *J. Phys. Colloq.*, vol. 30, no. C4, pp. C4–54, 1969.
- [136] G. Barbero and L. R. Evangelista, *Adsorption phenomena and anchoring energy in nematic liquid crystals.* CRC Press, 2005.
- [137] H. Yokoyama and H. A. Van Sprang, "A novel method for determining the anchoring energy function at a nematic liquid crystal-wall interface from director distortions at high fields," *Journal of applied physics*, vol. 57, no. 10, pp. 4520–4526, 1985.
- [138] Y. A. Nastishin, R. D. Polak, S. V. Shiyanovskii, V. H. Bodnar, and O. D. Lavrentovich, "Nematic polar anchoring strength measured by electric field techniques," *J. Appl. Phys.*, vol. 86, no. 8, pp. 4199–4213, 1999.
- [139] F. Yang, J. R. Sambles, Y. Dong, and H. Gao, "Fully leaky guided wave determination of the polar anchoring energy of a homogeneously aligned nematic liquid crystal," *J. Appl. Phys.*, vol. 87, no. 6, pp. 2726–2735, 2000.
- [140] X. Nie, R. Lu, H. Xianyu, T. X. Wu, and S.-T. Wu, "Anchoring energy and cell gap effects on liquid crystal response time," *J. Appl. Phys.*, vol. 101, no. 10, p. 103110, 2007.
- [141] R. Ondris-Crawford, E. P. Boyko, B. G. Wagner, J. H. Erdmann, S. Žumer, and J. W. Doane, "Microscope textures of nematic droplets in polymer dispersed liquid crystals," *J. Appl. Phys.*, vol. 69, no. 9, pp. 6380–6386, 1991.
- [142] F. Xu, H.-S. Kitzerow, and P. P. Crooker, "Electric-field effects on nematic droplets with negative dielectric anisotropy," *Phys. Rev. A*, vol. 46, no. 10, p. 6535, 1992.
- [143] A. Kilian, "Computer simulations of nematic droplets," *Liq. Cryst.*, vol. 14, no. 4, pp. 1189–1198, 1993.
- [144] J. A. Schellman, "Polarized Spectroscopy of Ordered Systems, eds. B. Samori' and E. W. Thulstrup," 1988.
- [145] C. Chiccoli, P. Pasini, L. R. Evangelista, R. Teixeira de Souza, and C. Zannoni, "Lattice spin simulations of topological defects in nematic films with hybrid surface alignments," *Int. J. Mod. Phys. C*, vol. 22, no. 05, pp. 505–516, 2011.
- [146] J. A. Barker and R. O. Watts, "Structure of water; A Monte Carlo calculation," *Chem. Phys. Lett.*, vol. 3, no. 3, pp. 144–145, 1969.
- [147] D. Subacius, P. J. Bos, and O. D. Lavrentovich, "Switchable diffractive cholesteric gratings," *Appl. Phys. Lett.*, vol. 71, no. 10, pp. 1350–1352, 1997.

- [148] T. Ishikawa and O. D. Lavrentovich, "Dislocation profile in cholesteric finger texture," *Phys. Rev. E*, vol. 60, no. 5, p. R5037, 1999.
- [149] D. Subacius, S. V. Shiyanovskii, P. Bos, and O. D. Lavrentovich, "Cholesteric gratings with field-controlled period," *Appl. Phys. Lett.*, vol. 71, no. 23, pp. 3323–3325, 1997.
- [150] S.-W. Kang, S. Sprunt, and L.-C. Chien, "Structure and morphology of polymerstabilized cholesteric diffraction gratings," *Appl. Phys. Lett.*, vol. 76, no. 24, pp. 3516– 3518, 2000.
- [151] G. Barbero and R. Barberi, "Critical thickness of a hybrid aligned nematic liquid crystal cell," *J. Phys. (Paris)*, vol. 44, no. 5, pp. 609–616, 1983.
- [152] S. Matsumoto, M. Kawamoto, and K. Mizunoya, "Field-induced deformation of hybridaligned nematic liquid crystals: New multicolor liquid crystal display," J. Appl. Phys., vol. 47, no. 9, pp. 3842–3845, 1976.
- [153] S. Ponti, P. Ziherl, C. Ferrero, and S. Zumer, "Flexoelectro-optic effect in a hybrid nematic liquid crystal cell," *Liq. Cryst.*, vol. 26, no. 8, pp. 1171–1177, 1999.
- [154] A. Sparavigna, O. D. Lavrentovich, and A. Strigazzi, "Periodic stripe domains and hybrid-alignment regime in nematic liquid crystals: Threshold analysis," *Phys. Rev. E*, vol. 49, no. 2, p. 1344, 1994.
- [155] R. Memmer and O. Fliegans, "Monte Carlo simulation of twisted nematic and supertwisted nematic liquid crystal cells," *Phys. Chem. Chem. Phys.*, vol. 5, no. 3, pp. 558– 566, 2003.
- [156] C. Chiccoli, P. Pasini, A. Šarlah, C. Zannoni, and S. Žumer, "Structures and transitions in thin hybrid nematic films: A Monte Carlo study," *Phys. Rev. E*, vol. 67, no. 5, p. 050703, 2003.
- [157] R. T. Teixeira-Souza, C. Chiccoli, P. Pasini, L. R. Evangelista, and C. Zannoni, "Nematic liquid crystals in planar and cylindrical hybrid cells: Role of elastic anisotropy on the director deformations," *Phys. Rev. E*, vol. 92, no. 1, p. 012501, 2015.
- [158] C. Chiccoli, L. R. Evangelista, E. K. Omori, P. Pasini, R. T. Teixeira-Souza, and C. Zannoni, "Computer simulation of a nematic hybrid cell: The effects of elastic anisotropy," *Mol. Cryst. Liq. Cryst*, vol. 649, no. 1, pp. 86–93, 2017.
- [159] P. Ball, "Pattern formation in nature: Physical constraints and self-organising characteristics," *Archit. Design*, vol. 82, no. 2, pp. 22–27, 2012.

- [160] R. Morales-Juberías, K. M. Sayanagi, A. A. Simon, L. N. Fletcher, and R. G. Cosentino, "Meandering shallow atmospheric jet as a model of saturn's north-polar hexagon," *Astrophys. J. Lett.*, vol. 806, no. 1, p. L18, 2015.
- [161] L. B. Smolka, B. Marts, and A. L. Lin, "Effect of inhomogeneities on spiral wave dynamics in the Belousov-Zhabotinsky reaction," *Phys. Rev. E*, vol. 72, no. 5, p. 056205, 2005.
- [162] A. V. Getling, Rayleigh-Bénard Convection: Structures and Dynamics, vol. 11. World Scientific, 1998.
- [163] A. C. B. Aguiar, P. L. Read, R. D. Wordsworth, T. Salter, and Y. H. Yamazaki, "A laboratory model of Saturn's north polar hexagon," *Icarus*, vol. 206, no. 2, pp. 755–763, 2010.
- [164] I. Chuang, R. Durrer, N. Turok, and B. Yurke, "Cosmology in the laboratory: Defect dynamics in liquid crystals," *Science*, vol. 251, no. 4999, pp. 1336–1342, 1991.
- [165] U. A. Hrozhyk, S. V. Serak, N. V. Tabiryan, and T. J. Bunning, "Periodic structures generated by light in chiral liquid crystals," *Opt. Express*, vol. 15, no. 15, pp. 9273–9280, 2007.
- [166] I. I. Smalyukh, Y. Lansac, N. A. Clark, and R. P. Trivedi, "Three-dimensional structure and multistable optical switching of triple-twisted particle-like excitations in anisotropic fluids," *Nat. Mater.*, vol. 9, no. 2, p. 139, 2010.
- [167] D. Wiant, J. T. Gleeson, N. Éber, K. Fodor-Csorba, A. Jákli, and T. Toth-Katona, "Nonstandard electroconvection in a bent-core nematic liquid crystal," *Phys. Rev. E*, vol. 72, no. 4, p. 041712, 2005.
- [168] A. Martinez and I. I. Smalyukh, "Light-driven dynamic archimedes spirals and periodic oscillatory patterns of topological solitons in anisotropic soft matter," *Opt. Express*, vol. 23, no. 4, pp. 4591–4604, 2015.
- [169] V. G. Guimaraes, H. V. Ribeiro, Q. Li, L. R. Evangelista, E. K. Lenzi, and R. S. Zola, "Unusual diffusing regimes caused by different adsorbing surfaces," *Soft Matter*, vol. 11, no. 9, pp. 1658–1666, 2015.
- [170] I. Jánossy, "Molecular interpretation of the absorption-induced optical reorientation of nematic liquid crystals," *Phys. Rev. E*, vol. 49, no. 4, p. 2957, 1994.
- [171] Y. Cui, R. S. Zola, Y.-C. Yang, and D.-K. Yang, "Alignment layers with variable anchoring strengths from polyvinyl alcohol," *J. Appl. Phys.*, vol. 111, no. 6, p. 063520, 2012.

- [172] R. F. de Souza, D.-K. Yang, E. K. Lenzi, L. R. Evangelista, and R. S. Zola, "Effect of surface viscosity, anchoring energy, and cell gap on the response time of nematic liquid crystals," *Ann. Phys.*, vol. 346, pp. 14–21, 2014.
- [173] R. F. de Souza, E. K. Lenzi, R. T. Teixeira-Souza, L. R. Evangelista, Q. Li, and R. S. Zola, "Surface induced twist in nematic and chiral nematic liquid crystals: Stick-slip-like and constrained motion," *Soft Matter*, vol. 14, no. 11, pp. 2084–2093, 2018.
- [174] G. Hegde and L. Komitov, "Periodic anchoring condition for alignment of a short pitch cholesteric liquid crystal in uniform lying helix texture," *Appl. Phys. Lett.*, vol. 96, no. 11, p. 113503, 2010.
- [175] D. Liu and D. J. Broer, "Self-assembled dynamic 3D fingerprints in liquid-crystal coatings towards controllable friction and adhesion," Ang. Chem., vol. 126, no. 18, pp. 4630– 4634, 2014.
- [176] N. R. Bernardino, M. C. F. Pereira, N. M. Silvestre, and M. M. T. da Gama, "Structure of the cholesteric–isotropic interface," *Soft Matter*, vol. 10, no. 47, pp. 9399–9402, 2014.
- [177] N. M. Silvestre, M. C. F. Pereira, N. R. Bernardino, and M. M. T. da Gama, "Wetting of cholesteric liquid crystals," *Eur. Phys. J. E*, vol. 39, no. 2, p. 13, 2016.
- [178] H. Nakanishi and M. E. Fisher, "Multicriticality of wetting, prewetting, and surface transitions," *Phys. Rev. Lett.*, vol. 49, no. 21, p. 1565, 1982.
- [179] J. W. Cahn, "Critical point wetting," J. Chem. Phys., vol. 66, no. 8, pp. 3667–3672, 1977.
- [180] G. de Luca and A. D. Rey, "Chiral front propagation in liquid-crystalline materials: Formation of the planar monodomain twisted plywood architecture of biological fibrous composites," *Phys. Rev. E*, vol. 69, no. 1, p. 011706, 2004.
- [181] O. D. Lavrentovich, S. V. Shiyanovskii, and D. Voloschenko, "Fast beam steering cholesteric diffractive devices," in *P. Soc. Photo-Opt. Ins.*, vol. 3787, pp. 149–156, International Society for Optics and Photonics, 1999.
- [182] S. Faetti and V. Palleschi, "Nematic-isotropic interface of some members of the homologous series of 4-cyano-4'-(n-alkyl) biphenyl liquid crystals," *Phys. Rev. A*, vol. 30, no. 6, p. 3241, 1984.
- [183] R. Holyst and A. Poniewierski, "Director orientation at the nematic-phase-isotropicphase interface for the model of hard spherocylinders," *Phys. Rev. A*, vol. 38, no. 3, p. 1527, 1988.
- [184] P. Ribiere and P. Oswald, "Nucleation and growth of cholesteric fingers under electric field," J. Phys. Fr., vol. 51, no. 16, pp. 1703–1720, 1990.

- [185] Y. Zhang and Z. Zhang, "Monte Carlo simulations of intrinsic anchoring in nematic liquid crystals based on spatially anisotropic pair potential," *Molec. Phys.*, vol. 105, no. 1, pp. 85–94, 2007.
- [186] Z.-D. Zhang and Y.-J. Zhang, "Study of intrinsic anchoring in nematic liquid crystals based on modified Gruhn–Hess pair potential," *Phys. Lett. A*, vol. 372, no. 4, pp. 498– 509, 2008.
- [187] Y.-J. Zhang, Z.-D. Zhang, and L.-Z. Zhu, "Computer simulation study of the twodimensional nematic lattice model based on the modified Gruhn-Hess pair potential model," *Mol. Phys.*, vol. 109, no. 3, pp. 419–427, 2011.
- [188] N. D. Mermin, "The topological theory of defects in ordered media," *Rev. Mod. Phys.*, vol. 51, no. 3, p. 591, 1979.
- [189] T. Lopez-Leon and A. Fernandez-Nieves, "Drops and shells of liquid crystal," *Colloid Polym. Sci.*, vol. 289, no. 4, pp. 345–359, 2011.
- [190] D. L. D. Caspar and A. Klug, "Physical principles in the construction of regular viruses," in *Cold Spring Harbor symposia on quantitative biology*, vol. 27, pp. 1–24, Cold Spring Harbor Laboratory Press, 1962.
- [191] J. Lidmar, L. Mirny, and D. R. Nelson, "Virus shapes and buckling transitions in spherical shells," *Phys. Rev. E*, vol. 68, no. 5, p. 051910, 2003.
- [192] U. B. Sleytr and P. Messner, "Crystalline surface layers on bacteria," Ann. Rev. Microbiol., vol. 37, no. 1, pp. 311–339, 1983.
- [193] M. Sára and U. B. Sleytr, "S-layer proteins," J. Bacteriol., vol. 182, no. 4, pp. 859–868, 2000.
- [194] J. W. Doane, N. A. Vaz, B.-G. Wu, and S. Žumer, "Field controlled light scattering from nematic microdroplets," *Appl. Phys. Lett.*, vol. 48, no. 4, pp. 269–271, 1986.
- [195] S. Zumer and J. W. Doane, "Light scattering from a small nematic droplet," *Phys. Rev.* A, vol. 34, pp. 3373–3386, 1986.
- [196] S. C. Jain and D. K. Rout, "Electro-optic response of polymer dispersed liquid-crystal films," J. Appl. Phys., vol. 70, no. 11, pp. 6988–6992, 1991.
- [197] P. S. Drzaic, Liquid crystal dispersions, vol. 1. World Scientific, 1995.
- [198] H. Poincaré, "Sur les courbes définies par les équations différentielles," J. Math. Pures Appl., vol. 4, pp. 167–244, 1885.

- [199] P. A. M. Dirac, "Quantised singularities in the electromagnetic field," Proc. R. Soc. Lond. A Contain. Pap. Math. Phys. Character, vol. 133, no. 821, pp. 60–72, 1931.
- [200] C. Robinson, "Liquid-crystalline structures in solutions of a polypeptide," *Trans. Faraday Soc.*, vol. 52, pp. 571–592, 1956.
- [201] C. Robinson, J. C. Ward, and R. B. Beevers, "Liquid crystalline structure in polypeptide solutions. Part 2," *Disc. Faraday Soc.*, vol. 25, pp. 29–42, 1958.
- [202] D. Seč, S. Čopar, and S. Žumer, "Topological zoo of free-standing knots in confined chiral nematic fluids," *Nat. Commun.*, vol. 5, p. 3057, 2014.
- [203] F. Xu and P. P. Crooker, "Chiral nematic droplets with parallel surface anchoring," *Phys. Rev. E*, vol. 56, no. 6, p. 6853, 1997.
- [204] D. Seč, T. Porenta, M. Ravnik, and S. Žumer, "Geometrical frustration of chiral ordering in cholesteric droplets," *Soft Matter*, vol. 8, no. 48, pp. 11982–11988, 2012.
- [205] S. Kralj, S. Žumer, and D. W. Allender, "Nematic-isotropic phase transition in a liquidcrystal droplet," *Phys. Rev. A*, vol. 43, no. 6, p. 2943, 1991.
- [206] I. Vilfan, M. Vilfan, and S. Žumer, "Orientational order in bipolar nematic microdroplets close to the phase transition," *Phys. Rev. A*, vol. 40, no. 8, p. 4724, 1989.
- [207] J. Bezić and S. Žumer, "Structures of the cholesteric liquid crystal droplets with parallel surface anchoring," *Liq. Cryst.*, vol. 11, no. 4, pp. 593–619, 1992.
- [208] O. D. Lavrentovich, "Topological defects in dispersed liquid crystals, or words and worlds around liquid crystal drops," *Liq. Cryst.*, vol. 24, no. 1, pp. 117–126, 1998.
- [209] M. V. Kurik and O. D. Lavrentovich, "Negative-positive monopole transitions in cholesteric liquid crystals," *JETP Lett.*, vol. 35, no. 9, pp. 444–447, 1982.
- [210] M. N. Krakhalev, A. P. Gardymova, O. O. Prishchepa, V. Y. Rudyak, A. V. Emelyanenko, J.-H. Liu, and V. Y. Zyryanov, "Bipolar configuration with twisted loop defect in chiral nematic droplets under homeotropic surface anchoring," *Sci. Rep.*, vol. 7, no. 1, p. 14582, 2017.
- [211] G. Posnjak, S. Čopar, and I. Muševič, "Points, skyrmions and torons in chiral nematic droplets," *Sci. Rep.*, vol. 6, p. 26361, 2016.
- [212] G. Posnjak, S. Čopar, and I. Muševič, "Hidden topological constellations and polyvalent charges in chiral nematic droplets," *Nat. Commun.*, vol. 8, p. 14594, 2017.
- [213] P. Drzaic, "A new director alignment for droplets of nematic liquid crystal with low bend-to-splay ratio," *Mol. Cryst. Liq. Cryst.*, vol. 154, no. 1, pp. 289–306, 1988.

- [214] M. V. Kurik and O. D. Lavrentovich, "Topological defects of cholesteric liquid crystals for volumes with spherical shape," *Mol. Cryst. Liq. Cryst.*, vol. 72, no. 7-8, pp. 239–246, 1982.
- [215] J. Bajc, J. Bezić, and S. Žumer, "Chiral nematic droplets with tangential anchoring and negative dielectric anisotropy in an electric field," *Phys. Rev. E*, vol. 51, no. 3, p. 2176, 1995.
- [216] J.-I. Fukuda and S. Žumer, "Quasi-two-dimensional Skyrmion lattices in a chiral nematic liquid crystal," *Nat. Commun.*, vol. 2, p. 246, 2011.
- [217] J.-I. Fukuda, S. Žumer, *et al.*, "Ring defects in a strongly confined chiral liquid crystal," *Phys. Rev. Lett.*, vol. 106, no. 9, p. 097801, 2011.
- [218] P. P. Crooker and D.-K. Yang, "Polymer-dispersed chiral liquid crystal color display," *Appl. Phys. Lett.*, vol. 57, no. 24, pp. 2529–2531, 1990.
- [219] J. Fan, Y. Li, H. K. Bisoyi, R. S. Zola, D.-K. Yang, T. J. Bunning, D. A. Weitz, and Q. Li, "Light-directing omnidirectional circularly polarized reflection from liquid-crystal droplets," *Angew. Chem.*, vol. 54, no. 7, pp. 2160–2164, 2015.
- [220] M. Humar and I. Muševič, "3D microlasers from self-assembled cholesteric liquidcrystal microdroplets," *Opt. Express*, vol. 18, no. 26, pp. 26995–27003, 2010.
- [221] G. Poy, F. Bunel, and P. Oswald, "Role of anchoring energy on the texture of cholesteric droplets: Finite-element simulations and experiments," *Phys. Rev. E*, vol. 96, no. 1, p. 012705, 2017.
- [222] P. Oswald, G. Poy, and A. Dequidt, "Lehmann rotation of twisted bipolar cholesteric droplets: role of Leslie, Akopyan and Zel'dovich thermomechanical coupling terms of nematodynamics," *Liq. Cryst.*, vol. 44, no. 6, pp. 969–988, 2017.
- [223] O. D. Lavrentovich and E. M. Terent'ev, "Phase transition altering the symmetry of topological point defects (hedgehogs) in a nematic liquid crystal," *Zh. Eksp. Teor. Fiz.*, vol. 91, pp. 2084–2096, 1986.
- [224] E. Brasselet, N. Murazawa, S. Juodkazis, and H. Misawa, "Statics and dynamics of radial nematic liquid-crystal droplets manipulated by laser tweezers," *Phys. Rev. E*, vol. 77, no. 4, p. 041704, 2008.
- [225] M. Humar, M. Ravnik, S. Pajk, and I. Muševič, "Electrically tunable liquid crystal optical microresonators," *Nat. photonics*, vol. 3, no. 10, p. 595, 2009.

- [226] S. Sivakumar, K. L. Wark, J. K. Gupta, N. L. Abbott, and F. Caruso, "Liquid crystal emulsions as the basis of biological sensors for the optical detection of bacteria and viruses," *Adv. Funct. Mater.*, vol. 19, no. 14, pp. 2260–2265, 2009.
- [227] L. N. Tan, G. J. Wiepz, D. S. Miller, E. V. Shusta, and N. L. Abbott, "Liquid crystal droplet-based amplification of microvesicles that are shed by mammalian cells," *Analyst*, vol. 139, no. 10, pp. 2386–2396, 2014.
- [228] M. Humar, "Liquid-crystal-droplet optical microcavities," *Liq. Cryst.*, vol. 43, no. 13-15, pp. 1937–1950, 2016.
- [229] A. V. Dubtsov, S. V. Pasechnik, D. V. Shmeliova, A. S. Saidgaziev, E. Gongadze, A. Iglič, and S. Kralj, "Liquid crystalline droplets in aqueous environments: Electrostatic effects," *Soft Matter*, vol. 14, no. 47, pp. 9619–9630, 2018.
- [230] A. Eremin, H. Nádasi, M. Kurochkina, O. Haba, K. Yonetake, and H. Takezoe, "Lightresponsive microstructures in droplets of the twist-bend nematic phase," *Langmuir*, vol. 34, no. 48, pp. 14519–14527, 2018.
- [231] I.-H. Lin, D. S. Miller, P. J. Bertics, C. J. Murphy, J. J. de Pablo, and N. L. Abbott, "Endotoxin-induced structural transformations in liquid crystalline droplets," *Science*, vol. 332, no. 6035, pp. 1297–1300, 2011.
- [232] J. Jiang and D.-K. Yang, "Bipolar to toroidal configuration transition in liquid crystal droplets," *Liq Cryst.*, vol. 45, no. 1, pp. 102–111, 2018.
- [233] D. Demus, J. W. Goodby, G. W. Gray, H. W. Spies, and V. Vill, Handbook of liquid crystals, volume 2A: Low molecular weight liquid crystals I: Calamitic liquid crystals. John Wiley & Sons, 2011.
- [234] W. L. McMillan, "Simple molecular model for the smectic A phase of liquid crystals," *Phys. Rev. A*, vol. 4, no. 3, p. 1238, 1971.
- [235] C. W. Garland, M. Meichle, B. M. Ocko, A. R. Kortan, C. R. Safinya, L. J. Yu, J. D. Litster, and R. J. Birgeneau, "Critical behavior at the nematic-smectic-A transition in butyloxybenzylidene heptylaniline (40. 7)," *Phys. Rev. A*, vol. 27, no. 6, p. 3234, 1983.
- [236] J. Thoen, H. Marynissen, and W. V. Dael, "Nematic-smectic-A tricritical point in alkylcyanobiphenyl liquid crystals," *Phys. Rev. Lett.*, vol. 52, no. 3, p. 204, 1984.
- [237] L. Faddeev and A. J. Niemi, "Stable knot-like structures in classical field theory," *Nature*, vol. 387, no. 6628, p. 58, 1997.
- [238] T. H. R. Skyrme, "A non-linear field theory," in *Selected Papers, With Commentary, Of Tony Hilton Royle Skyrme*, pp. 195–206, World Scientific, 1994.

- [239] D. Kleckner and W. T. M. Irvine, "Creation and dynamics of knotted vortices," *Nat. Phys.*, vol. 9, no. 4, p. 253, 2013.
- [240] P. Dabrowski-Tumanski and J. I. Sulkowska, "Topological knots and links in proteins," *PNAS*, vol. 114, no. 13, pp. 3415–3420, 2017.
- [241] M. Tasinkevych, M. G. Campbell, and I. I. Smalyukh, "Splitting, linking, knotting, and solitonic escape of topological defects in nematic drops with handles," *PNAS*, vol. 111, no. 46, pp. 16268–16273, 2014.
- [242] J.-S. B. Tai and I. I. Smalyukh, "Three-dimensional crystals of adaptive knots," *Science*, vol. 365, no. 6460, pp. 1449–1453, 2019.