April 2016

Simulation of Heterogeneous Colloidal Particles Immersed in Liquid Crystals

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A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

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This thesis describes an investigation of interactions between colloidal particles immersed in a liquid crystal. The presence of colloidal particles in the liquid crystal distorts the director field distorted from its uniform orientation. These elastic distortions produce topological defects around the particles, which induce anisotropic interactions between them, and these anisotropic interactions can be used to manufacture non-closed packed colloidal crystals, such as diamond lattices, which are interesting in photonic applications. First, different types of liquid crystals, the mathematical tools to describe the anisotropic nature of liquid crystals, the Landau-de Gennes free-energy model to investigate the particle’s interaction, and different kinds of topological defects are described. Moreover, previous work regarding the interaction of particles with the same applied boundary conditions in both nematic and cholesteric liquid crystal are discussed. Second, the lattice Boltzmann method is introduced in order to couple the molecular dynamics particles to the computational fluid mesh, and the simulation is performed in the open source molecular dynamics package, LAMMPS. Next, we explore anisotropic interactions with minima at specific orientations of particles with heterogeneous boundary conditions inside both nematic and cholesteric liquid crystals, which have not been observed so far. The results show that when particles are put at different distances and angles with respect to each other, new types of defect structures are produced, depending on the relative distances and directions. In the cholesteric liquid crystal, the value of pitch affects the defect structures and induced forces.

Keywords: Liquid Crystal, Lattice Boltzmann
Co-Authorship Statement

The work presented in this thesis was done in collaboration with my supervisor, Prof. Colin Denniston. Chapter 3 will form the basis for a publication that will be co-authored with my supervisor.
Acknowledgements

First and foremost, I am deeply grateful to my supervisor, Professor Colin Denniston, for his guidance and support throughout my graduate studies at the University of Western Ontario. It was a great honor for me to work with such creative, brilliant, and knowledgeable supervisor. I also would like to extend my gratitude and affection to my beloved parents, Fatemeh and Mohsen, and my two brothers Saeed and Hamid, who supported me throughout my academic life. To them, I owe all I have ever accomplished.
## Contents

Abstract i

Co-Authorship Statement ii

Acknowledgements iii

List of Figures vi

List of Tables viii

List of Appendices ix

List of Abbreviations x

1 Introduction 1
    1.1 Liquid Crystal Classes ............................................. 2
    1.2 Liquid Crystal Phases ............................................. 2
        1.2.1 Nematic ...................................................... 2
        1.2.2 Cholesteric .................................................. 4
    1.3 Order Parameter .................................................. 5
    1.4 Landau-de Gennes Theory of Liquid Crystals ....................... 6
    1.5 Liquid Crystal Hydrodynamics .................................... 10
    1.6 Topological Defects ............................................... 11
    1.7 Colloidal Particles ............................................... 13

2 Methodology 19
    2.1 Introduction ..................................................... 19
    2.2 Lattice Boltzmann Method: Historical Background ................ 20
    2.3 The Boltzmann Equation ........................................... 21
    2.4 Lattice Boltzmann Method ........................................ 23
    2.5 Modeling a Liquid Crystal Through LBM Algorithm ............... 27
    2.6 Coupled LB-MD Method ............................................. 29
        2.6.1 Particle-Fluid Interaction .................................. 29
    2.7 Summary .......................................................... 32

3 Results 33
    3.1 Individual Spheres in Nematic .................................. 35
# List of Figures

1.1 Different states of matter .............................................. 2
1.2 Chemical structure of 4pentyl-4-cyanobiphenyl (5CB). ............ 3
1.3 Shear flow. ................................................................. 4
1.4 Cholesteric Liquid Crystal ............................................ 4
1.5 The distribution of molecular axes around the average alignment direction n. . 5
1.6 The Landau free energy of a nematic liquid crystal as a function of the scalar order parameter S. ......................................................... 7
1.7 Elastic distortions in liquid crystal .................................... 8
1.8 Different Surface Boundary Conditions ............................... 9
1.9 Topological defects of different strengths ........................... 12
1.10 Hyperbolic Hedgehog. .................................................... 13
1.11 Possible defects around the colloidal particles depending on molecule anchoring on their surfaces. In a) the sphere has planar anchoring and in b) the sphere has perpendicular anchoring. The pink lines correspond to contour plot of positions around the colloidal particles where the scalar order parameter drops 15% of the bulk value. In both a) and b) the director is shown at the surface of spheres. ................................................................. 14
1.12 Boojums on the surface of the colloidal particles when they get close each other along the director in nematic. [1] ................................................. 15
1.13 Defect structures around the colloidal particles in cholesteric liquid crystal . . 16
1.14 Defect-bonded chain [2] .................................................... 17
1.15 a) Free energy as a function of their particle-particle separation b) Angular separation of defect points [2] ......................................................... 17
1.16 Free energy as a function of the angular positioning of the particles relative to the twist axis [2] ......................................................... 18
2.1 Different lattice configurations ........................................ 25
2.2 Spherical objects with different number of nodes .................. 29
2.3 $P1$ is affected by node i by the ratio $\frac{Ai}{(Ax)^2}$ ................. 30
3.1 Schematic of our system where the periodic boundary conditions are imposed in the x and y directions, the fixed walls are located in the z direction, and the liquid crystal molecules are set to be parallel on the walls. .................... 34
3.2 The defects and their images for isolated particles in a nematic liquid crystal. In (a) and (c) the sphere has planar anchoring and in (b) and (d) the sphere has perpendicular anchoring. The director is shown on the surface of the sphere in (a) and (b) and the sphere is not shown in (c) and (d), so that the image defects are visible.

3.3 Defect structures of particles at distance of 0.125μm.

3.4 Plot of interaction energy for the particles immersed in the nematic liquid crystal in a) 2D and b)3D.

3.5 Plot of director field around the particles inside nematic with separation of 0.125μm.

3.6 Defect structures of particles at distance of 0.125μm in the cholesteric LC(pitch=1.5μm).

3.7 Defect structures of particles at distance of 0.25μm in the cholesteric LC(pitch=1.5μm).

3.8 Defect structures of particles at distance of 0.375μm in the cholesteric LC(pitch=1.5μm).

3.9 Defect structures of particles at distance of 0.375μm in the cholesteric LC(pitch=1.5μm) with different perspective.

3.10 Defect structures of particles at distance of 0.5μm in the cholesteric LC(pitch=1.5μm).

3.11 Plot of interaction energy for the particles immersed in the cholesteric liquid crystal with pitch value of 1.5μm in a) 2D and b)3D.

3.12 Defect structures of particles at distance of 0.125μm in the cholesteric LC(pitch=3μm).

3.13 Plot of interaction energy for the particles immersed in the cholesteric liquid crystal with pitch value of 3μm in a) 2D and b)3D.

3.14 Defect structures of particles at distance of 0.125μm in the cholesteric LC(pitch=1.125μm).

3.15 Different perspective of defect structures of particles at distance of 0.125μm in the cholesteric LC(pitch=1.125μm).

3.16 Defect structures of particles at distance of 0.1875μm in the cholesteric LC(pitch=1.125μm).

3.17 Different perspective of defect structures of particles at distance of 0.1875μm in the cholesteric LC(pitch=1.125μm).

3.18 Different perspective of defect structures of particles at distance of 0.25μm in the cholesteric LC(pitch=1.125μm).

3.19 Different perspective of defect structures of particles at distance of 0.25μm in the cholesteric LC(pitch=1.125μm).

3.20 Plot of interaction energy for the particles immersed in the cholesteric liquid crystal with pitch value of 1.125μm in a) 2D and b)3D.

3.21 Generated defects around the particles in nematic liquid crystal onto XZ plane while separated 0.125μm from each other.

3.22 2D contour plot of interaction energy of 2 particles in nematic LC.

3.23 Plot of director field for different particle-particle separations when θ = 0° and the particles are confined in XZ plane.

3.24 Generated defects around the particles in nematic liquid crystal onto XZ plane while separated 0.125μm from each other.

3.25 2D contour plot of interaction energy of 2 particles in the cholesteric LC(pitch=1.125μm).
List of Tables

3.1 Parameters .......................................................... 35
List of Appendices

Appendix A Copyright Permissions ........................................ 77
List of Abbreviations

LBM  Lattice Boltzmann Method
MD   Molecular Dynamics
LAMMPS  Large-Scale Atomic/Molecular Massively Parallel Simulator
Chapter 1

Introduction

Solid, liquid and gas are three distinct phases which most of people learn about in elementary school. There are more than these three phases, and one important for this thesis is called a liquid crystal. A new and promising research area in physics and chemistry was established by the discovery of an Austrian botanist, Friedrich Reintizer [3]. In the process of melting a certain compound, he realized that the solid had a transition toward a muddy liquid at about $145.5^\circ C$, and as he increased the temperature, it transformed to a clear liquid at about $178.5^\circ C$. This implied a new state of matter existed, which he called a liquid crystal, which is shown in figure 1.1. Liquid crystal is considered as a mesophase, meaning an intermediate phase existing between solid and liquid [4].

Colloidal crystals are composed of an array of micro- or nano-particles, which can be represented as a medium with a periodic structure of dielectric constant. Therefore, they can be used as photonic crystals. One of the ideal methods to fabricate such crystals is self-assembly of colloidal particles[5]. In an isotropic (simple) fluid, the colloidal particles create close-packed crystals such as fcc and hcp, which do not show a “complete band gap”, meaning light with specific frequencies cannot be propagated through the crystal. However, the particles must experience a non-isotropic interaction to form non-close-packed structures such as a diamond lattice, which show a complete band gap. As a result, we are motivated to investigate colloids
in a liquid crystal due to its anisotropic nature. This kind of nature generates distortions which induce forces between the particles that do not exist in an isotropic fluid [6].

1.1 Liquid Crystal Classes

Liquid crystals have been classified into two different groups: thermotropic and lyotropic. In a thermotropic liquid crystal, temperature is the most important factor. It controls the liquid crystal behavior, which is mainly focused on in our work. On the other hand, when amphiphilic molecules are added into a solvent like water, a lyotropic liquid crystal is formed. Each molecule has a hydrophobic tail and a hydrophilic head. So when they are mixed into water, the hydrophilic heads attracts water, but the hydrophobic tails avoids water [3]. If the concentration is high enough, a liquid crystal state is achieved.

1.2 Liquid Crystal Phases

1.2.1 Nematic

In a nematic liquid crystal, the average direction of the long molecular axes is along a common direction, called the director, $\hat{n}$, but the center of masses are distributed randomly, so the
molecules show long range orientational order, however there is no translational order [7]. This kind of behavior dictates anisotropic properties, which cannot be observed in simple fluids. Most molecules that form a nematic look like a rod. One of the common rod-like liquid crystal compounds is 4-Pentyl-4’-cyanobiphenyl (5CB). Its chemical structure is shown in figure 1.2. In our work, the material we have chosen to model has the similar properties of 5CB.

![Chemical structure of 4pentyl-4-cyanobiphenyl (5CB).](image)

In a nematic, the directions -\(\mathbf{n}\) and \(\mathbf{n}\) are equivalent. The properties of liquid crystals have different responses in different directions, as demonstrated by Miesowicz viscosity coefficients [8].

In 1935, Meisowicz decided to find the viscosity of a nematic liquid crystal. As is shown in figure 1.3, the nematic liquid crystal is confined by two parallel walls in y-z plane and a shear flow is applied in a way that the velocity is in the z direction and the velocity gradient is in the x direction. He performed his experiment for different director orientations with respect to the velocity and velocity gradient. Then, he recognized there would be three distinct viscosities for a nematic, which are labelled by \(\eta_a, \eta_b, \eta_c\). The three different viscosity values correspond to these three cases, indicating the anisotropic nature of liquid crystal:

\[\eta_a \rightarrow \mathbf{n} \parallel \bar{\nabla} \mathbf{V} \quad (\theta=90, \phi = 0).\]

\[\eta_b \rightarrow \mathbf{n} \parallel \bar{\mathbf{V}} \quad (\theta=0, \phi = 0).\]

\[\eta_c \rightarrow \mathbf{n} \perp \text{shear plane (along y axis)} \quad \bar{\mathbf{V}} \quad (\theta=0, \phi = 90).\]


1.2.2 Cholesteric

The cholesteric phase looks similar to the nematic, except that there is a helical twist in the medium when chiral molecules are dissolved in the nematic. The characteristic of a cholesteric liquid crystal is determined by its pitch, which is the distance along the twist axis that the director rotates by $360^\circ$ [9], as illustrated in figure 1.4. We can regard a nematic liquid crystal as a cholesteric with infinite pitch. The cholesteric liquid crystal has applications in electronics, such as producing displays with color flexibility.
1.3 Order Parameter

The magnitude of the orientational ordering of molecules separates the anisotropic and isotropic phase behavior and there must be a mathematical tool to describe this difference and that is the order parameter which is zero for an isotropic liquid and non-zero for a liquid crystal phase in which the molecules are more ordered. In a nematic liquid crystal, thermal fluctuations make the molecules not exactly orient along the director, and they skew off the director. So a scalar order parameter $S$ is used to quantify these fluctuations.

In a nematic with rotational symmetry, called a uniaxial nematic, the scalar order parameter can be defined as the ensemble average of the second Legendre polynomial $\{10, 7\}$ as,

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

(1.1)

where $\theta$ is the angle between the director and the long axis of a molecule. In the isotropic phase, where the rods are randomly oriented, $S$ vanishes as $\langle \cos^2(\theta) \rangle = \frac{1}{3}$, and is unity when the rods are parallel to $\hat{n}$ ($\theta = 0$ or $\pi$). On the other hand, when the rods are perpendicular to $\hat{n}$ ($\theta = \frac{\pi}{2}$), $S = -\frac{1}{2}$. As a result, $S$ is a good quantity to measure the alignment of rods.

However, the definition of $S$ is based on the uniaxial nematic which has rotational symmetry,
so in general, the order parameter is defined as a tensor:

\[
Q_{ij} = \langle \frac{3}{2} \hat{m}_i \hat{m}_j - \frac{1}{2} \delta_{ij} \rangle ,
\]

(1.2)

where \( \hat{m} \) gives the local orientations of the individual molecules. This tensor is symmetric and traceless. The director \( \hat{n} \) is associated with the eigenvector with the largest eigenvalue, which is equal to the scalar order parameter [11].

In a uniaxial nematic liquid crystal, which is the focus in the thesis, the tensor order parameter and its diagonalized form is [12]:

\[
Q_{ij} = S \left( \frac{3}{2} \hat{n}_i \hat{n}_j - \frac{1}{2} \delta_{ij} \right),
\]

(1.3)

\[
Q = \begin{bmatrix}
-S/2 & 0 & 0 \\
0 & -S/2 & 0 \\
0 & 0 & S
\end{bmatrix}.
\]

(1.4)

This form of the diagonalized tensor corresponds to rotation of a uniform system in a way that \( \hat{n} || e_z \).

### 1.4 Landau-de Gennes Theory of Liquid Crystals

The Landau theory is a general description of phase transitions [13]. It assumes that there is an order parameter, which is zero for disordered and non-zero for the ordered state. It is based on this idea that the free energy of the system can be expanded as a power series in the order parameter. Examples of an order parameter can be regarded as electric polarization in a ferroelectric state[14], magnetization in a ferromagnetic state [15], etc. In Landau theory, a first order transition from disordered to ordered state is a transition in which the order parameter changes discontinuously from zero to a non-zero value.

Later, de Gennes, a French physicist, developed a model to describe the nematic to isotropic
1.4. Landau-de Gennes Theory of Liquid Crystals

transition based on Landau theory. According to this model, known as Landau de Gennes theory, the free energy of the liquid crystal can be expanded in powers of the order parameter $Q$ as follows [7]:

$$F = F_0 + \frac{1}{2} A(T - T^*_c)Q_{\alpha\beta}Q_{\beta\alpha} + \frac{1}{3} BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \frac{1}{4} C(Q_{\alpha\beta}Q_{\alpha\beta})^2 + O(Q^5).$$  (1.5)

In the uniform aligned state, using 1.3, equation 1.5 becomes:

$$F = F_0 + \frac{3}{4} A(T - T^*_c)S^2 + \frac{B}{4} S^3 + \frac{9C}{16} S^4 + O(S^5),$$  (1.6)

where $A$, $B$, and $C$ are constants and $T^*_c$ is a temperature, a little bit smaller than the critical temperature, $T_c$, at the transition. As the positive and negative values of the scalar parameter correspond to different molecular alignments, the free energy must contain odd power of $S$, so that $F(S) \neq F(-S)$.

The reason for the discontinuity in the order parameter is shown in figure 1.6. In this figure,

Figure 1.6: The Landau free energy of a nematic liquid crystal as a function of the scalar order parameter $S$.

when $T > T_c$, the absolute minimum in energy occurs at $S = 0$, indicating the isotropic phase.
Chapter 1. Introduction

(a) Bend
(b) Splay
(c) Twist

Figure 1.7: Elastic distortions in liquid crystal

is the stable phase above the critical temperature. However, there is a coexistence of nematic and isotropic phases at $T = T_c$, and at $T_c^* < T < T_c$ the absolute minimum in energy occurs at a non-zero value of order parameter. This corresponds to the first order phase transition, as the order parameter, where the free energy is minimum, is changing discontinuously.

It should be emphasized that the Landau free energy is applicable to the situation in which there are no external effects acting on the nematic liquid crystal, which rarely happens. Often, to accommodate boundaries or other external effects, the director locally undergoes elastic distortions. Typically, the distortions are categorized into 3 different cases: splay, twist, and bend distortions. These cases can be seen in figure 1.7. These distortions can be described by the Frank elastic free energy [16, 17]:

$$F_e = \frac{1}{2}K_1(\nabla \cdot \hat{n})^2 + \frac{1}{2}K_2(\hat{n} \cdot \nabla \times \hat{n})^2 + \frac{1}{2}K_3(\hat{n} \times (\nabla \times \hat{n}))^2.$$  (1.7)
Splay is parameterized by $K_1$, showing an outward widening, twist is represented by $K_2$, and bend by $K_3$. This energy can be written in terms of the tensor order parameter as follows:

\[
F_e = \frac{L_1}{2} (\partial_{\alpha} Q_{\beta\gamma})^2 + \frac{L_2}{2} (\partial_{\alpha} Q_{\alpha\gamma})(\partial_{\beta} Q_{\beta\gamma}) + \frac{L_3}{2} Q_{\alpha\beta}(\partial_{\alpha} Q_{\gamma\epsilon})(\partial_{\beta} Q_{\gamma\epsilon}) + \frac{4\pi L_1}{P} \varepsilon_{\alpha\beta\gamma} Q_{\alpha
\epsilon
\gamma}(\partial_{\beta} Q_{\gamma\nu}). \tag{1.8}
\]

$L_1$, $L_2$, and $L_3$ can be mapped onto $K_1$, $K_2$, and $K_3$. $P$ is the value of pitch if the medium is a cholesteric liquid crystal [18].

In addition to the bulk energy of the liquid crystal, its interaction with surfaces must be considered as well. This should be characterized by the preferred orientation of the liquid crystal, applied by the surface boundary, and the anchoring strength $\alpha_s$. This interaction can be described by [1, 19]:

\[
F_{\text{surface}} = \frac{\alpha_s}{2} (Q_{ij} - Q^0_{ij})^2 \rightarrow \text{Perpendicular anchoring} \tag{1.9}
\]

\[
F_{\text{surface}} = \frac{\alpha_s}{2} (\tilde{Q}_{ij} - \tilde{Q}^\perp_{ij})^2 \rightarrow \text{Planar anchoring}, \tag{1.10}
\]

where $\tilde{Q}_{ij} = Q_{ij} + \frac{1}{3} S_0 \delta_{ij}$ and $\tilde{Q}^\perp_{ij} = (\delta_{ik} - \hat{n}_i^0 \hat{n}_k^0) \tilde{Q}_{kl}(\delta_{lj} - \hat{n}_l^0 \hat{n}_j^0)$ is the projection of $\tilde{Q}_{ij}$ onto the tangent plane of the surface. Also $Q^0_{ij} = S_0(\hat{n}_i^0 \hat{n}_j^0 - \frac{1}{3} \delta_{ij})$, and $\hat{n}^0$ is the normal to the surface, and $S_0$ is the equilibrium scalar order parameter in the undistorted state.

![Diagram](a) Planar (b) Perpendicular

Figure 1.8: Different Surface Boundary Conditions
1.5 Liquid Crystal Hydrodynamics

The evolution of the order parameter can be tracked using the Beris-Edwards formulation [20]:

\[
(\partial_t + u \cdot \nabla)Q - S(W, Q) = \Gamma H,
\]

(1.11)

with

\[
S(W, Q) = (\xi D + \Omega)(Q + I/3) + (Q + I/3)(\xi D - \Omega) - 2\xi(Q + I/3)Tr(QW),
\]

(1.12)

where \(D = (W + W^T)/2\) and \(\Omega = (W - W^T)/2\) correspond to the symmetric and antisymmetric parts of the velocity gradient tensor \(W_{\alpha\beta} = \partial_{\beta}u_{\alpha}\), and the effective aspect ratio of liquid crystal molecules is described by \(\xi\), and \(\Gamma\) is the collective rotational diffusion constant. The right hand side of equation 1.11 drives the system towards the minimum of the free energy, and \(H\) is related to the functional derivative of the free energy:

\[
H = -\frac{\delta F}{\delta Q} + \left(\frac{I}{3}\right) \frac{\delta F}{\delta Q}.
\]

(1.13)

As the liquid crystal is considered a fluid, it should satisfy the continuity and Navier-Stokes equations. However, the stress tensor in these equations contains the additional complexities of the liquid crystal which has both symmetric

\[
\sigma_{\alpha\beta} = -P_0\delta_{\alpha\beta} - \xi H_{\alpha\gamma}(Q_{\gamma\beta} + 1/3\delta_{\alpha\beta}) - \xi(Q_{\alpha\gamma} + 1/3\delta_{\alpha\gamma})H_{\alpha\beta}
\]

\[+ 2\xi(Q_{\alpha\beta} + 1/3\delta_{\alpha\beta})Q_{\gamma\epsilon}H_{\gamma\epsilon} - \partial_{\beta}Q_{\gamma\nu}(\frac{\delta F}{\delta \partial_{\alpha}Q_{\gamma\nu}}),
\]

and antisymmetric

\[
\tau_{\alpha\beta} = Q_{\alpha\gamma}H_{\gamma\beta} - H_{\alpha\gamma}Q_{\alpha\beta},
\]

(1.14)
1.6 Topological Defects

Topological defects are created when there is a local singularity in the order parameter of the system. They are observed in crystalline solids [21], superfluid helium [22], and cosmology [23].

Defect structures can exist in a liquid crystal medium as well. In fact, the name of "nematic" liquid crystals comes from the thread-like defect, which was observed under a microscope in the medium of LC by Friedel [24]. Defects can be produced by applying a specific boundary condition at the surface in a liquid crystal. Imposing the boundary conditions creates spots within the liquid crystal where the director field changes its direction discontinuously, so these spots are considered as a singularity or discontinuity. When defects are present within the sample, the whole free energy of the system increases. Therefore, there is no defect in an ideal ordered system. The singularities can be in the form of points or lines, the later are called disclinations.

Categorizing the defect structure involves specifying the strength of the defect, which is an integer or half integer. In order to determine the defect strength, a closed path must be traversed counter clockwise around the defect and then the strength is obtained by finding the angle the director is rotated and dividing by $2\pi$

$$m = \frac{\phi}{2\pi}, \ m = 0, \pm \frac{1}{2}, \pm 1, \ldots$$  \hspace{1cm} (1.16)

Figure 1.9 shows some examples of defect of different strengths. It can be shown that the elastic energy of defects is proportional to $m^2$ [25]. Also, the defects whose strengths have the same sign repel one another, while those with opposite strengths are attracted [25].
Figure 1.9: Topological defects of different strengths

(a) \( m = -1/2 \)  
(b) \( m = +1/2 \)  
(c) \( m = -1 \)  
(d) \( m = +1 \)
1.7 Colloidal Particles

If colloidal particles are present in the liquid crystal medium, due to preferred anchoring of molecules on the surface of particles, the director becomes distorted from its uniform orientation. Therefore, topological defects are generated around the particles [26]. It has been observed that the preferred anchoring of fluid molecules on the surface of particles is typically parallel (planar anchoring), or perpendicular (normal or homeotropic anchoring).

If the fluid molecules prefer to have tangential anchoring on the surface of the colloidal, two small radius $+\frac{1}{2}$ disclination loops are formed at the poles of spheres, called boojums. [27]. On the other hand, in the case of normal anchoring, two possible defect structures may be produced. One structure can be a -1 point defect, called a hyperbolic hedgehog, located near the surface of the colloidal, as illustrated in figure 1.10.

![Hyperbolic Hedgehog](image)

Another possibility is a disclination ring surrounding the particle which is called Saturn-ring defect, shown in figure 1.11b. The radius of the particle dictates which defect structure is generated in normal anchoring. It has been seen that the Saturn ring is the stable structure for small particles while the hedgehog point defect is produced for large particles [28, 6].

These topological defects induce long range interactions between the particles [26]. When the particles are far from each other, the interaction energy between them is dictated by the long range orientational field. For instance, particles with boojums in planar anchoring or particles with Saturn rings in normal anchoring induce elastic “quadrupolar” distortions, so the interac-
Figure 1.11: Possible defects around the colloidal particles depending on molecule anchoring on their surfaces. In a) the sphere has planar anchoring and in b) the sphere has perpendicular anchoring. The pink lines correspond to contour plot of positions around the colloidal particles where the scalar order parameter drops 15% of the bulk value. In both a) and b) the director is shown at the surface of spheres.

...tion energy between two particles, which are separated by distance $r$ and far from each other, decays like $r^{-5}$. Their interaction is repulsive when $r$ is perpendicular or parallel to the background director field, and attractive for $r$ oriented at about $50^\circ$ to $\hat{n}$ [29]. Considering colloidal particles with hyperbolic hedgehog defects in the nematic liquid crystal, there is a different kind of interaction. In the far-field approximation, the particle-defect pair is considered as a “dipole” and the effective interaction between two particles separated by $r$ is proportional to $r^{-3}$ [26]. When the particles get close to each other, the interactions deviate from far-field interactions due to local distortions around the defect structures [30]. Experimentally, it was observed when two particles with planar anchoring approach each other, they attract each other at $\theta = 30^\circ$ with respect to $\hat{n}$ and there is a repulsion at $75^\circ < \theta < 90^\circ$, which is different from the far-field interaction [31]. Moreover, it has been found when particles with hyperbolic defects are aligned parallel along the director field, there is an attractive interaction for large particle separation, producing a chain of particles, but a short-range repulsion is generated when they are separated a few tenths of a micron, so the particles do not touch each other in the chain [26]. Another example is that when a pair of boojums are getting close to each other along the director field. Assuming $\hat{n}$ is along the x axis, the boojums, which are getting close, are driven...
1.7. Colloidal Particles

Figure 1.12: Boojums on the surface of the colloidal particles when they get close each other along the director in nematic. [1]

away from the x-axis. As the defects become displaced from the x axis, there would be an induced attraction between the particles. This attraction is energetically favorable as the volume of the distorted region reduces. So the particles with planar anchoring attract each other at close distances, while they repel when they are far from each other [1]. Generally, attracting particles, when they are close to each other, in order to minimize the elastic energy, produce self-assembled structures such as linear chains [6] and 2D crystals [32].

However, in a cholesteric liquid crystal the defect lines become twisted. These structures can be controlled by the value of pitch in the cholesteric. In both cases of planar and normal anchoring, the defect lines wind around the particle, as the pitch decreases [33]. This is illustrated in figure 1.13

Furthermore, the interactions produced by colloidal particles with planar anchoring, with diameter to pitch ratio of $\frac{2}{3}$ was investigated by Mackay and Denniston in ref. [2]. In this case,
the defects on adjacent particles connect to each other when they are close to each other, and a defect-bonded particles chain is generated, which is shown in figure 1.14.

![Figure 1.13: Defect structures around the colloidal particles in cholesteric liquid crystal](image)

In figure 1.15(a), it is seen that there are two distinct regions in the free energy of two particles when they are put together in a cholesteric liquid crystal. The particles are connected by defect lines up to a particle-particle separation of 0.41\( \mu \text{m} \). But the defect bonds between the particles break at 0.41\( \mu \text{m} \) and the defects get close at the surface of each particle. The force needed to separate these particles at this distance corresponds to the jump in the free energy where the defect bonds break. At this separation, the length of the handle defect is getting longer than the defect bond, and as the longer defect costs more energy, it is energetically
1.7. Colloidal Particles

Figure 1.14: Defect-bonded chain [2]

Figure 1.15: a) Free energy as a function of their particle-particle separation b) Angular separation of defect points [2]

favorable that bonding happens.

Moreover, the free energy of the system is expected to be linear in particle separation, as the length of defect lines is proportional to particle separation and the dominant term in the free energy is related to defect lines, which is not seen in the figure 1.15(a) and in fact it is quadratic. The reason can be understood by focusing on the graph of angular separation of defects on the surface of the particles as a function of particle separation, which is shown in figure 1.15(b). It is seen that when the defect lines are shared in a bond, the $+\frac{1}{2}$ defects move apart from each other and this lowers the surface energy as the defects with strengths of the same sign repel each
other. As a result, this compensates for the longer defect lines as they are pulled apart and there is a quadratic dependence of free energy vs. particle separation. When particles are moved out of plane (so one particle is at a different part of the background twist in the cholesteric), as seen in figure 1.16, it can be seen that defect bonding still happens for $0 < \theta < 25^\circ$. However, the bond breaks at about $25^\circ$ and the energy levels off for $\theta > 25$. It also shows that there is a preference for alignment in a plane perpendicular to the twist axis, since the free energy is minimized at $\theta = 0$.

In the next chapter, a computational method is described in order to couple the particles to the liquid crystal, which is considered on a mesh. It is also explained how the interactions between the particles and liquid crystal are modelled by applying a conservative force on both of them. In chapter 3, a computer simulation of two heterogeneous particles immersed in both nematic and cholesteric liquid crystal, is presented. The results show new defect structures around the particles, leading to induction of different kinds of particle-particle interactions.
Chapter 2

Methodology

2.1 Introduction

One of the computational methods to describe the motion of particles, at the microscopic level, is molecular dynamics (MD). In this approach, Newton’s equation of motion for each individual particle is solved to track the trajectories of particles [34]. On the other hand, the fluid can be regarded as a continuous medium at the macroscopic level, in which the Navier-Stokes and continuity equations [35] are solved to evaluate the fluid flow. Navier-Stokes equations are partial differential equations which can be solved by a variety of methods, such as finite difference methods [36].

Each of these two methods has its own difficulties. At the macroscopic level, the potential numerical instability of methods to solve complicated non-linear partial equations is a problem that is a concern that can limit the size of the timesteps. Also, these numerical methods involve discretization of the equations and truncation errors which raise the question of whether physical quantities are conserved or not [37]. On the other hand, considering the system with colloidal particles immersed in the fluid, the MD algorithm is an impractical approach to simulate the motion of fluid molecules as the solvent, since the majority of the particles consists of solvent. Therefore, tracking the position of a large number of individual fluid particles costs
time and computer resources.

As a result, one considers a mesoscopic level, which is between the microscopic and macroscopic level [38]. One of the common and popular methods at this level, is the lattice Boltzmann method, which evaluates the collective behavior of fluid particles based on a collision procedure and does not involve solving Navier-Stokes and continuity equations directly. In this chapter, this method is described for a simple fluid and then generalized to model the motion of a liquid crystal.

### 2.2 Lattice Boltzmann Method: Historical Background

The lattice gas cellular automata is often described as the historical origin of lattice Boltzmann methods. In lattice gas automata, introduced by Hardy, Pomeau, and de Pazzis (HPP), the terms “lattice” and “gas” imply a gas is moving on a lattice, and “automata” suggests a set of rules governing the evolution of the gas. In this method, boolean particles (0 or 1) are used to represent the gas. Further, the fluid is regarded as a set of particles present on a square lattice with discrete velocities, and each step involves collision and streaming of particles [39]. However, the motion of particles does not satisfy Navier-Stokes equations in the long wavelength limit, which is considered one of the deficiencies of this method. This problem is due to the insufficient degree of rotational symmetry of the square lattice, which does not generate an isotropic lattice tensor (composed of moments of lattice vectors) [40, 37].

The correct form of Navier-Stokes equation in the long wavelength limit can be produced by using a hexagonal lattice, which has enough symmetry to reproduce Navier-Stokes equation, as shown by Frisch, Hasslachor and Pomeak [41]. Their FHP model is similar to the HHP model, but involves more collision rules due to its hexagonal symmetry [37]. This model still suffers from some drawbacks such as the existence of large statistical noise due to boolean variables, velocity dependence of fluid pressure, and a few other problems.

Later, the mentioned drawbacks were resolved through a new method, called the lattice Boltz-
2.3 The Boltzmann Equation

As the basic idea of LBM is replacing the discrete particles by particle distribution functions, this method can be explained through kinetic theory. This theory deduces the macroscopic properties of a large number of particles such as pressure, temperature, energy, etc, based on the Hamilton’s equation of motion of particles:

\[ \frac{\partial H}{\partial p_i} = \frac{dx_i}{dt}, \]
\[ \frac{\partial H}{\partial x_i} = -\frac{dp_i}{dt}, \tag{2.1} \]

where H is the Hamiltonian. In a system of N particles, if the position \( x_i \) and momentum \( p_i \) of all the particles are specified, then the micro-state of this system can completely be determined, corresponding to a point in phase space, a space where the coordinates are given by position and momentum vectors, and time [44].

Following the statistical approach, the single-particle distribution \( f(x, p, t) \) can be introduced in a way that \( f(x, p, t)d^3x d^3p \) gives the total number of particles positioned in a range between \( x \) and \( x + d^3x \) and momentum in the range between \( p \) and \( p + d^3p \). Assuming there are no collisions existing in the system, if an external force is applied to a particle, then the single particle distribution function, before and after applying the force, satisfies [45]:

\[ f(x + \frac{P}{m} \Delta t, p + F \Delta t, t + \Delta t) - f(x, p, t) = 0 \tag{2.2} \]
This type of evolution is referred to as streaming. But, the number of particles can differ from its value predicted by simple streaming if collisions occur between the particles. In this case, some particles can be added to, or removed from the small volume. So, the evolution of the distribution of the number of particles can be written as:

\[ f(x + \frac{P}{m} \Delta t, p + F \Delta t, t + \Delta t) - f(x, p, t) = \psi_{12} \Delta t, \quad (2.3) \]

where \( \psi_{12} \) is the rate of change between final and initial distribution function due to collisions, and is called the collision integral. Using a Taylor expansion of \( f(x + \frac{P}{m} \Delta t, p + F \Delta t, t + \Delta t) \),

\[ f(x + \frac{P}{m} \Delta t, p + F \Delta t, t + \Delta t) = f(x, p, t) + \frac{\partial f}{\partial x} \cdot \frac{P}{m} \Delta t + \frac{\partial f}{\partial p} \cdot F \Delta t + \frac{\partial f}{\partial p} \Delta t + \ldots \quad (2.4) \]

Now the Boltzmann equation can be written as:

\[ \left[ \frac{\partial}{\partial t} + \frac{P}{m} \cdot \frac{\partial}{\partial x} + F \cdot \frac{\partial}{\partial p} \right] = \psi_{12}, \quad (2.5) \]

where the left hand side is equal to the material derivative of \( f(x, p, t) \) which we denote by \( D_t f(x, p, t) \) and call the streaming term, while the right hand side is the collision integral. The collision integral has the following form, assuming the particles are completely uncorrelated prior to a collision [44, 46]:

\[ \psi_{12} = \frac{1}{m} \int d^3 p_2 d\Omega \left| p_2 - p_1 \right| \sigma(\Omega) \left[ f(x_1, p'_{1}, t) f(x_1, p'_{2}, t) - f(x_1, p_1, t) f(x_1, p_2, t) \right], \quad (2.6) \]

where \( \sigma(\Omega) \) is the differential crosssection for 2-particles collisions in the center of mass frame, which can be calculated by considering the laws of mechanics. The collision term can be regarded as the probability of finding a particle at position \( x_1 \) with momentum \( p_1 \) being changed by experiencing a collision with a particle with momentum \( p_2 \) at time \( t \) [44].
fact, \( f(x_1, p_1, t) \) \( f(x_2, p_2, t) \) indicates the loss of particles taken out, and \( f(x_1, p'_1, t) \) \( f(x_2, p'_2, t) \) describes the gain of particles taken in \( dx^3 \, dp^3 \) [40].

In many cases, the Boltzmann equation can be simplified using the BGK (Bhatnagar-Gross-Krook) collision operator [47]:

\[
\psi_{12} = -\frac{f - f^{eq}}{\tau},
\]

which indicates that collisions tend to relax toward an equilibrium distribution function \( f^{eq} \), and the time scale \( \tau \) can be regarded as the “collision time”. The equilibrium distribution function corresponds to a Maxwell-Boltzmann equation [44].

The macroscopic quantities can be obtained by calculating the moments of distribution function \( f(x, p, t) \):

\[
\int f(x, v, t) \, d^3v = \rho, \\
\int f(x, v, t) \, v\alpha \, d^3v = \rho \, u\alpha,
\]

where \( \rho \) is the fluid density and \( u\alpha \) is the fluid velocity.

### 2.4 Lattice Boltzmann Method

The lattice Boltzmann equation can be obtained directly from the continuous Boltzmann equation by discretizing time, space, and velocity [48]. So the discretized Boltzmann equation can be written as:

\[
f_i(x_\alpha + e_{i\alpha} \Delta t, t + \Delta t) - f_i(x_\alpha, t) = -\frac{\Delta t}{\tau_f} (f_i(x_\alpha, t) - f_i^{eq}(x_\alpha, t)) + p_i \Delta t,
\]
where \( p_i \) is a forcing term, \( e_i \) is a discrete velocity vector, and \( f_i \) is the partial distribution corresponding to \( e_i \).

Analogous to 2.8 we have:

\[
\sum_i f_i \equiv \rho , \\
\sum_i f_i e_i \equiv \rho u_\alpha .
\] (2.10)

In LBM, equation 2.9 is solved on a lattice. At each node of the lattice, the particle distributions move along the specified velocity direction to the neighboring nodes. The lattice Boltzmann equation can also reproduce the continuity and Navier-Stokes equations in the long wavelength limit [38]. The number of directions is indicated by the lattice configuration. These configurations can be determined by the dimension of the problem and the number of velocity directions which is labeled by \( D_nQ_m \), where \( n \) refers to the dimension and \( m \) indicates the number of velocity directions. Typical cases are illustrated in figure 2.1. In 2D, the common model is \( D_2Q_9 \), and the velocity directions are:

\begin{align*}
e_0 &= (0,0) , & e_1 &= (1,0) , & e_2 &= (0,1) , \\
e_3 &= (-1,0) , & e_4 &= (0,-1) , & e_5 &= (1,1) , \\
e_6 &= (-1,1) , & e_7 &= (-1,-1) , & e_8 &= (1,-1).
\end{align*}

In 3D, \( D_3Q_{15} \) is used as a common model:

\begin{align*}
e_i^{(0)} &= (0,0,0) , \\
e_i^{(1)} &= (\pm 1,0,0) , (0,\pm 1,0) , (0,0,\pm 1) , \\
e_i^{(2)} &= (\pm 1,\pm 1,\pm 1) ,
\end{align*}

where \( i = 0 \) corresponds to \( e_i^{(0)} \), \( i = 1, \ldots, 6 \) correspond to the \( e_i^{(1)} \), and \( i = 7, \ldots, 14 \) correspond to the \( e_i^{(2)} \).
The following equations are used to constrain the equilibrium distribution and to control the stress tensor:

\[
\begin{align*}
\sum_i f_{i}^{eq} &= \rho, \\
\sum_i f_{i}^{eq} e_{i\alpha} &= \rho u_{\alpha}, \\
\sum_i f_{i}^{eq} e_{i\alpha} e_{i\beta} &= -\sigma_{\alpha\beta} + \rho u_{\alpha} u_{\beta}.
\end{align*}
\] (2.11)

The continuous equilibrium distribution function is the Maxwell-Boltzmann distribution which has the following form in 3-dimensions:

\[
\begin{align*}
f^{eq} &= \rho \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp\left( -\frac{m(v - u)^2}{2k_B T} \right), \\
&= \rho \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp\left( -\frac{mv^2}{2k_B T} \right) \exp\left( \frac{m(v \cdot u)}{k_B T} \right) \left( \frac{m}{2k_B T} \right). 
\end{align*}
\] (2.12)
Then the indicated function can be expanded in a Taylor series as follows with small velocity:

\[
f_{\text{eq}} = \rho \left( \frac{m}{2\pi k_B T} \right)^2 \exp \left( \frac{-mv^2}{2k_B T} \right) \left[ 1 + \left( \frac{m(\mathbf{v} \cdot \mathbf{u})}{k_B T} - \frac{mu^2}{2k_B T} \right) + \frac{1}{2} \left( \frac{m(\mathbf{v} \cdot \mathbf{u})}{k_B T} - \frac{mu^2}{2k_B T} \right)^2 \right] + \ldots
\]

\[(2.13)\]

where \( \rho \left( \frac{m}{2\pi k_B T} \right)^2 \exp \left( \frac{-mv^2}{2k_B T} \right) \) is related as the weight function. Therefore, the general discretized form of the equilibrium distribution function, using discrete weights \( w_i \) associated with each of velocity directions, can be given as follows [49, 48]:

\[
f_{\text{eq}}^i = \rho w_i [A + Bu_i e_i + Cu^2 + Du_i u_\beta e_\alpha e_\beta + E_\alpha e_\alpha e_\beta].
\]

\[(2.14)\]

The constants can be obtained by the above constraints, and the weighting coefficients are given as [37]:

\[
D_2 Q_9 \rightarrow w_i = \begin{cases}
4/9 & i = 0 \\
1/9 & i = 1, \ldots, 4 \\
1/36 & i = 5, \ldots, 8
\end{cases},
\]

\[
D_3 Q_{15} \rightarrow w_i = \begin{cases}
2/9 & i = 0 \\
1/9 & i = 1, \ldots, 6 \\
1/72 & i = 7, \ldots, 14
\end{cases}.
\]

It should be taken into account that this method is only valid for an incompressible fluid, meaning the density of fluid is not varied significantly.

To sum up, the Boltzmann equation is solved in 2 steps:

- **Collision step:**

\[
f_i(x_\alpha, t + \Delta t) = f_i(x_\alpha, t) - \frac{\Delta t}{\tau_f} (f_i(x_\alpha, t) - f_{\text{eq}}^i(x_\alpha, t)) + p_i \Delta t,
\]

\[(2.15)\]
which indicates that the distribution function tends to relax towards the equilibrium distribution function.

- **Streaming step:**

\[
f_i(x_\alpha + e_\alpha \Delta t, t + \Delta t) = f_i(x_\alpha, t + \Delta t),
\]

(2.16)

showing the particles are moving from one site to the neighboring site.

### 2.5 Modeling a Liquid Crystal Through LBM Algorithm

So far, LBM has been described only for a simple fluid, which is defined in terms of a single set of particle distribution functions, the scalar \( f_i(x) \). As liquid crystal hydrodynamics involve the evolution of a tensor order parameter, a second set of distribution functions, the tensors \( G_i(x) \) which are related to the tensor order parameter \( Q \) [20, 50] must be considered as well. Again \( G_i \) corresponds to a lattice vector \( e_i \). Here, we work on a cubic lattice with the \( D_3Q_{15} \) model, which was described in previous sections.

The order parameter \( G_i \) also evolves as:

\[
G_i(x_\alpha, t + \Delta t) - G_i(x_\alpha, t) = -\frac{\Delta t}{\tau_{\text{G}}} (G_i(x_\alpha, t) - G_i^{\text{eq}}(x_\alpha, t)) + M_i \Delta t,
\]

(2.17)

where \( M_i \) is a forcing term. The first moment of \( p_i \) control the antisymmetric part of the stress tensor:

\[
\sum_i p_i = 0, \quad \sum_i p_i e_{i\alpha} = \partial_\beta \tau_{\alpha\beta}, \quad \sum_i p_i e_{i\alpha} e_{i\beta} = 0.
\]

(2.18)

Now the moments of the equilibrium order parameter distribution can be chosen as:

\[
\sum_i G_i^{\text{eq}} = Q, \quad \sum_i G_i^{\text{eq}} e_{i\alpha} = Q u_\alpha, \quad \sum_i G_i^{\text{eq}} e_{i\alpha} e_{i\beta} = Q u_\alpha u_\beta.
\]

(2.19)
Also, the forcing term satisfies:

\[ \sum M_i = \Gamma H(Q) + S(W, Q), \quad \sum M_i e_{ia} = \left( \sum M_i \right) u_a. \tag{2.20} \]

Now, both equilibrium distribution functions and forcing terms can be written as polynomial expansions in velocity:

\[
\begin{align*}
    f_i^{eq} &= A_s + B_s u_a e_{ia} + C_s u^2 + D_s u_a u_\beta e_{ia} e_{i\beta} + E_s e_{ia} e_{i\beta}, \\
    G_i^{eq} &= J_s + K_s u_a e_{ia} + L_s u^2 + N_s u_a u_\beta e_{ia} e_{i\beta}, \\
    p_i &= T_s \partial_\beta \tau_{ia} e_{ia}, \\
    M &= R_s + S_s u_a e_{ia},
\end{align*}
\]

where \( s \in \{0, 1, 2\} \) indicates the coefficients for vectors \( e_i^s \). By using the constraints 2.11, 2.18, 2.19, and 2.20, all the coefficients can be determined as follows [20]:

\[
\begin{align*}
    A_2 &= -\frac{1}{10} \left( \text{Tr} \left( \frac{1}{3} \sigma \right) \right), \quad A_1 = A_2, \quad A_0 = \rho - 14A_2, \\
    B_2 &= \frac{1}{24} \rho, \quad B_1 = 8B_2, \\
    C_2 &= -\frac{1}{24} \rho, \quad C_1 = 2C_2 \quad C_0 = -\frac{2}{3} \rho, \\
    D_2 &= \frac{1}{16}, \quad D_1 = 8D_2, \\
    E_{2\alpha\beta} &= \frac{1}{16} \left( -\sigma + \text{Tr} \left( \frac{1}{3} \sigma \right) \delta_{\alpha\beta} \right), \quad E_{1\alpha\beta} = 8E_{2\alpha\beta}, \\
    J_0 &= Q, \quad K_2 = \frac{1}{24} Q, \quad K_1 = 8K_2, \\
    L_2 &= -\frac{1}{24} Q, \quad L_1 = 2L_2, \quad L_0 = -\frac{2}{3} Q, \\
    N_2 &= \frac{1}{16} Q, \quad N_1 = 8N_2, \\
    R_2 &= \frac{1}{15} \hat{H}, \quad R_1 = R_0 = R_2, \\
    S_2 &= \frac{1}{24} \hat{H}, \quad S_1 = 8S_2, \\
    T_2 &= \frac{1}{24}, \quad T_1 = 8T_2
\end{align*}
\]
2.6 Coupled LB-MD Method

In order to model a system of colloidal particles immersed in a liquid crystal, as mentioned previously, LBM is an efficient method to simulate the motion of a large number of liquid crystal molecules as solvent. In addition, a MD algorithm is used to model the motion of colloidal particles based on solving Newton’s equations of motion. Therefore, these two methods are combined to model the whole system. The coupled LBM and MD algorithm have a lot of applications such as polymers in solution [51], colloidal suspensions [52].

2.6.1 Particle-Fluid Interaction

In our work, the colloidal particles are considered as spherical objects, and must be mapped onto the computational fluid mesh. In order to couple the object to the fluid lattice, the surface of the object must be discretized into a set of nodes and each node behaves as an individual MD particle, as shown in figure 2.2.

![Spherical objects with different number of nodes](image)

Figure 2.2: Spherical objects with different number of nodes
Figure 2.3 shows a finite object in two dimension. According to this figure, the finite object is interpolated on the fluid mesh and its surface nodes are distributed to the corners of the lattice site where they exist by assigning the ratio $\xi_{\alpha j}$ of the opposing area to the total area of the lattice cell to the corresponding mesh site [53]. As we work in three dimension, the ratio of areas are replaced by volumes: $\xi_{\alpha j} = \phi_j(x_{\alpha})\phi_j(y_{\alpha})\phi_j(z_{\alpha})$. Figure 2.2 shows some examples of spherical objects which are discretized by a set of nodes. This method is called the trilinear interpolation method, or trilinear stencil and the weights assigned to each of the nearest lattice sites is [54, 55]:

$$\phi_j(r_{\alpha}) = 1 - |\Delta r|,$$

(2.23)

where $\Delta r = \frac{r_{\alpha} - r_j}{\Delta x}$. Here, the position of the fluid mesh site is labeled by $r_j$, the position of the node is labeled by $r_{\alpha}$, and the lattice spacing is indicated by $\Delta x$. Now the interaction between the object and fluid must be considered by applying the forces to particle nodes and fluid mesh sites. So the force exerted on a lattice site $j$ due to particle node $\alpha$ is:

$$F_{ja} = \gamma(v_n - u_f)\xi_{ja}$$

(2.24)

Figure 2.3: P1 is affected by node i by the ratio $\frac{A_1}{(\Delta x)^2}$

Here, $\gamma$ is a proportionality constant, $u_f = \sum u_j\xi_{ja}$ is the interpolated velocity of fluid at the
2.6. Coupled LB-MD Method

particle node location and \( v_n \) is the particle velocity.

Now the total force applied to the fluid by the node \( \alpha \) can be calculated as \( \gamma (v_n - u_f) \), as \( \sum_j \xi_{ja} = 1 \). According to Newton’s third law, there is an equal and opposite force applied to particle node \( \alpha \):

\[
F_\alpha = -\gamma (v_n - u_f) .
\] (2.25)

Through the elastic collision between the particle nodes and mesh sites in discrete time, it can be shown that \( \gamma \) is calculated as [55],

\[
\gamma = \frac{2m_v m_v}{m_u + m_v} \left( \frac{1}{\Delta t_{coll}} \right) ,
\] (2.26)

where \( \Delta t_{coll} \) is the time of collisions between the fluid and particles, \( m_v \) is the particle mass, and \( m_u \) is the representative mass fluid on the particle node. As \( \tau \) indicates the time between the collisions in the fluid, it can be assumed that the collision time between fluid and particles is equal to the fluid relaxation time \( (\frac{\tau}{\Delta t} = 1) \)

In order to calculate the contribution of surface energy due to the applied boundary conditions on the surface of particles, an area per node, which can be determined by dividing the total surface of spherical particles by the total number of their nodes, must be found, and then interpolated to each nodes’ nearest lattice sites as follows:

\[
(\Delta A)_j = \sum_\alpha (\Delta A)_\alpha \xi_{ja} ,
\] (2.27)

where \( (\Delta A)_\alpha = 4\pi R^2 / \text{number of the nodes} \), and \( (\Delta A)_j \) is the interpolated of area per node on the lattice site \( j \), and \( R \) is the radius of spherical particles. Using 1.10 and 1.9, the surface energy interpolated on the mesh site \( j \) can be calculated as:

\[
(F_{\text{surface}})_j = \frac{\alpha_s}{2} (Q_{ln} - Q_{ln}^0)^2 (\Delta A)_j \rightarrow \text{Perpendicular anchoring} .
\] (2.28)

\[
(F_{\text{surface}})_j = \frac{\alpha_s}{2} (\bar{Q}_{ln} - \bar{Q}_{ln}^\perp)^2 (\Delta A)_j \rightarrow \text{Planar anchoring} .
\] (2.29)
2.7 Summary

In this chapter, the lattice Boltzmann method was introduced to solve the discretized Boltzmann equation. In this method, the particle and tensor distribution functions are used, and the surface of the particles are discretized to a set of nodes, which are distributed to the nearest mesh sites through the use of trilinear interpolation. Based on the assumption of an elastic collision between the interpolated mass of fluid at the particle location, and the particle nodes, the particle-fluid interaction can be modeled by using the conservative forces applied on both the fluid and the particles.
Chapter 3

Results

So far, studies have been focused on the defect structures, and interactions, produced by colloidal particles with the same kind of boundary conditions on their surfaces, such as the defect-bonded chain generated by colloidal particles with planar anchoring inside a cholesteric liquid crystal [2]. As many semiconductors are composed of two different elements and are considered as compound materials such as GaAs or InSb, we are motivated to investigate compound colloidal structures in order to search for potential photonic materials. Therefore, in the following chapter, we mainly investigate possible induced interactions between particles with different sorts of anchoring on their surfaces in both nematic and cholesteric liquid crystals.

At the first step, we consider two spherical colloidal particles with a radius of 0.625µm in a nematic liquid crystal inside a simulation box with dimensions of $L_x \times L_y \times L_z$. There are periodic boundary conditions imposed in the x and y directions, and fixed walls located in the z direction, and the liquid crystal molecules are set to be parallel on the walls as shown in the figure 3.1. In our work, we use planar anchoring on the surface of one of the spherical particles, and perpendicular anchoring on the surface of the other one. The distance between the particles and the boundaries are large enough to reduce the effect of the boundaries on the particles, and the particles are put in the XY plane at $z = \frac{L_y}{2}$. 

33
Here, we have chosen the one elastic constant approximation as $K_1 = K_2 = K_3$. The constants $A$, $B$, and $C$, used in the bulk free energy, are chosen as: $A = \frac{A_0}{2}(1 - \gamma^3)$, $B = A_0 \frac{\gamma^3}{3}$, and $C = A_0 \frac{\gamma^4}{4}$. The value of $\gamma$ controls the transition from isotropic to liquid crystal phase, $\gamma > 2.7$ corresponds to the nematic phase. All the simulation parameters are shown in table 3.1.

As described in the previous chapter, the surface of colloidal particles must be discretized into a set of nodes to be coupled to the computational mesh of the liquid crystal. In our work, all the particles are discretized into 540 nodes. The simulation of these particle nodes in the liquid crystal is performed in the open source molecular dynamics package, LAMMPS, and integrated through the verlet-velocity algorithm; however, we freeze the particle nodes in the simulation by setting the forces to zero, so they are not allowed to move. This way we can investigate the equilibrium energy at many different spacings and orientations.

In addition, a new package is added to create the lattice Boltzmann grid fluid for the liquid crystal on the whole simulation box. This is analogous to the package added to LAMMPS by Frances Mackay in reference [54]. As each computational step needs only information about the nearest neighbors, the code is implemented in parallel (OpenMPI). Simulations were performed on a variety of clusters, such as saw, orca, and redfin on SHARCNET (Shared Hierarchical Academic Research Computing Network), jasper on WestGrid, and GPC on SCINET. For instance, the saw cluster has 2712 cores, with 16GB memory and DDR InifiBand interconnection, and orca has 8880 cores, with QDR InfiniBand interconnection. Simulations were
implemented for a total of 30000 timesteps, and the total number of simulations that we performed was about 440. Each job used 16 processors and took 2 days to be completed.

<table>
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<th>Value</th>
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<tr>
<td>$P_0$</td>
<td>1.0</td>
<td>atm</td>
</tr>
</tbody>
</table>

### 3.1 Individual Spheres in Nematic

Before considering two spheres, the defect structures of each of the individual spheres were investigated separately. Figure 3.2 shows the defect structure for planar and perpendicular anchoring for isolated spheres in a nematic. In this figure, the pink lines correspond to defects, and show a contour plot of the positions around the particles where the scalar order parameter has decreased about 15% from the bulk value.

When we see inside the sphere, there is an inner defect line which can be considered as the image of the outer defect lines in both cases. So the surface of particle acts analogous to a conductor in electrostatics. This can be justified by considering the analogy between the defect
structures around the particles in a liquid crystal and charges in electrostatics. As the director field satisfies the linear Laplace’s equation far from the colloidal particles, where deviations from uniformity are small [6, 7], it can be concluded that it is analogous to electrostatics in which the electrostatic potential satisfies Laplace’s equation as well. Therefore, the defects in liquid crystal can be analogous to electric charges in electrostatics.

![Diagram of liquid crystal defects](image)

Figure 3.2: The defects and their images for isolated particles in a nematic liquid crystal. In (a) and (c) the sphere has planar anchoring and in (b) and (d) the sphere has perpendicular anchoring. The director is shown on the surface of the sphere in (a) and (b) and the sphere is not shown in (c) and (d), so that the image defects are visible.

### 3.1.1 Interaction of Two Particles Immersed in a Nematic Liquid Crystal

Next, we consider these two particles put together inside the nematic liquid crystal, and investigate the possible defects when the particle with planar anchoring is rotated around the other
one, and located at different distances with respect to each other. The angles are measured with respect to the x axis. In this case, completely new defect configurations have been observed. As can be seen in 3.3, while the sphere is being rotated, the defect lines between the particles get connected to each other at about 35° and become disconnected at $\theta \geq 39°$. This kind of behavior can be seen up to a specific separation of about 0.375µm. The defect lines do not connect to each other at larger distances.

The interaction of these particles can be explored through a 2D and 3D contour of the interaction energy of system. As is shown in figure 3.4, the energy is maximized at $\theta \sim 35°$, where the defect lines are joined together, and there is a minimum at $\theta \sim 90°$ at small particle-particle separations.

There are several factors affecting the total energy of system. One is the length of the defect line. The presence of defect line inside the liquid crystal medium costs energy and as it gets longer, the total energy of system increases. In addition to the length of defect lines, the energy of system can be decreased by reducing the volume of distortion in the director field. Moreover, it is energetically favorable to have defect lines with strength of half integer instead of integral strength, since the energy of defect lines is proportional to $m^2$ [7]. There is also the surface energy of the director configuration on the particles surface. For the boojums (3.2a), this makes the two $m = \frac{1}{2}$ defects on the surface repel each other. The surface energy would be minimized by moving the defects as far apart as possible ($\sim 109°$ for tetrahedral symmetry [56]). The defects do not adopt this configuration as it would lengthen the defect line extending into bulk.

The maximum in energy at $\theta \sim 35°$ corresponds to the configuration where the defect lines get connected to each other, so it seems they become longer and since the defect lines cost energy, which is proportional to their length, the interaction energy becomes increased at this configuration. This is in contrast to the case done by Mackay and Denniston in reference [2]. In this paper, the interactions of two particles, both with planar anchoring, was investigated inside a cholesteric liquid crystal. Since the length of defect bond got shorter than a single defect bond, it was energetically favorable for particle bonding to occur, which led to attraction. Also figure
3.5, which is the plot of director field around the particles, shows that there is a slightly higher distorted volume around the particles at this angle. Therefore, the particles tend to repel each other at $35^\circ$ to prevent increasing the distortion in the medium. On the other hand, when the particles are close to each other at $\theta \sim 90^\circ$, the plot of the director field indicates a less distorted region exists between the particles. As a result the particles prefer to become attracted to this position. There is also another local minimum at $\theta \sim 0^\circ$ and at a distance of 0.125µm, indicating an attraction between the particles.

3.2 Interaction of Particles Immersed in a Cholesteric Liquid Crystal

Now the medium is switched from nematic to cholesteric liquid crystal. As the properties of a cholesteric liquid crystal can be dependent on the value of its pitch, several pitch values have been tried to measure the interaction energy. The values that were selected, 1.5 µm, 3 µm, and 1.125 µm, are close to the size of the particle, larger and smaller than the particle size, respectively.

Again two spheres with binary applied boundary conditions, i.e. one planar and one perpendicular are put inside the cholesteric, starting with the pitch value of 1.5 µm, and the particle with planar anchoring is rotated around the other sphere while they are separated at a variety of distances. In this case, a completely different kind of defect structures was observed from that seen in the nematic. Since the medium is cholesteric, the defect lines are twisted around the particles, as it is shown in figure 1.15 in chapter 1. As can be seen in figure 3.6, when the particles are separated 0.125µm from each other, the boojum defect lines and the Saturn ring are joined together from both sides of particles. While the particle is being rotated, the Saturn ring gets connected to the surface of other particle in the middle at $\theta \sim 25^\circ$. This kind of structure is observed up to $\theta \sim 55^\circ$. At this configuration, there is a point where the defect
3.2. Interaction of Particles Immersed in a Cholesteric Liquid Crystal

Figure 3.3: Defect structures of particles at distance of 0.125\(\mu\)m
Figure 3.4: Plot of interaction energy for the particles immersed in the nematic liquid crystal in a) 2D and b) 3D.
Figure 3.5: Plot of director field around the particles inside nematic with separation of 0.125µm
lines of both particles are joined together. At $\theta \sim 60^\circ$, the defect lines are only connected on one side. The most fascinating defect structure happens at $\theta \sim 85^\circ$. At this position, the defect lines are connected not only on both sides, but also at two points in the middle of the particles, which looks like a symmetric defect structure. At $\theta \sim 90^\circ$, this symmetric defect model is not seen.

Next, the particle-particle separation is increased to 0.25$\mu$m with the same value of pitch, shown in figure 3.7. At $\theta = 0^\circ$, the defect lines of boojums and Saturn ring are shared in the middle of particles. At larger angles, they are connected at both sides again, and at $\theta \sim 37^\circ$, the ring gets connected in the middle as well. At $\theta \geq 43^\circ$, they become disconnected at one side, while joined at one common point on the other side.

In figure 3.8 and 3.9, when the particles are separated 0.375$\mu$m from each other, no defect lines are connected between the particles up to $\theta \sim 43^\circ$. At $\theta \sim 43^\circ$ the defect lines are connected at two points at one side of the particles. At $\theta \geq 55^\circ$, the lines are not joined at any points but there is a connection of defect lines at one side and in between the spheres. Furthermore, at $\theta \sim 90$, there is one point where the defects are connected as well. At a separation of 0.5$\mu$m, no connection occurs, while the boojum defect lines become different in shape at $\theta \sim 60^\circ$, as is exhibited in figure 3.10. At larger separations, no defect lines are joined together. In the plot of the interaction energy of particles, figure 3.11, there is a sharp maximum in energy at $\theta \sim 90^\circ$, where the particles are separated about 0.375$\mu$m from each other and the defect lines are joined at one common point at one side and there is a defect line connected to other sphere which is passed in between the particles. It seems that the defect lines get more stretched at this specific configuration, so it can be concluded that the total length of defect lines is higher than other positions, which leads to increase in the energy. So there is a repulsion when the particles approach each other from far distances.

Then, we increase the value of the pitch to 3 $\mu$m and see the defect lines are less twisted around the particles. When the particles are separated 0.125$\mu$m, it is observed in figure 3.12 that the defect lines of particles start to get connected at $\theta \sim 15^\circ - 25^\circ$, and disconnected for $\theta \geq 60^\circ$. 
Figure 3.6: Defect structures of particles at distance of 0.125µm in the cholesteric LC (pitch=1.5µm)
Figure 3.7: Defect structures of particles at distance of 0.25μm in the cholesteric LC (pitch=1.5μm)
3.2. Interaction of Particles Immersed in a Cholesteric Liquid Crystal

Figure 3.8: Defect structures of particles at distance of 0.375µm in the cholesteric LC (pitch=1.5µm)
Figure 3.9: Defect structures of particles at distance of 0.375\(\mu\)m in the cholesteric LC (pitch=1.5\(\mu\)m) with different perspective
3.2. Interaction of Particles Immersed in a Cholesteric Liquid Crystal

Figure 3.10: Defect structures of particles at distance of 0.5µm in the cholesteric LC (pitch=1.5µm)
Figure 3.11: Plot of interaction energy for the particles immersed in the cholesteric liquid crystal with pitch value of 1.5\( \mu \)m in a) 2D and b) 3D.
3.2. *Interaction of Particles Immersed in a Cholesteric Liquid Crystal*

The same sort of structure is observed up to the specific particle separation of 0.375µm. So it seems the defect structure in cholesteric liquid crystal with higher value of pitch looks similar to the defects in nematic. As it can be seen in figure 3.13, the interaction energy is maximized at about $15^\circ - 25^\circ$, corresponding to the configurations where the defect lines start to be connected to each other in between the particles, so the particles tend to repel each other, as the distortion of director field between the particles increases at this configuration. Also there is a minimum in energy when the particles are very close to each other at $\theta \sim 90^\circ$. In this case, like the particles inside a nematic, there is a lower distorted volume in between the particles, which makes them attract each other.

Next, the defect structures and interaction of two particles is investigated in a cholesteric with the lower pitch value of 1.125µm. In this case, the defect lines are much more twisted around the particles. Figure 3.14 and 3.15, show the defect structure of particles when they are kept at a distance of 0.125µm. At $\theta \sim 0^\circ$, two twisted defect lines are joined together from both sides and a defect in a shape of handle appears on the surface of the particle with planar anchoring. At $\theta = 25^\circ$, the Saturn ring starts to join to the mentioned handle defect, so the defect in between the particles does not look like a handle any more. If we look at the particle at $\theta = 30^\circ$, it can be recognized that the twisted line is surrounding the particles and the Saturn ring gets connected to the surface of the other particle in between. This structure is seen up to $\theta = 45^\circ$. At this angle, there is a point on one side of particles, where the defect lines are joined together. This kind of defect can be observed up to $\theta = 85^\circ$. At $\geq 85^\circ$, the defect lines are only connected around the particles. Then the particle separation is increased to 0.1875µm. As it is seen in figure 3.16 and 3.17, one of the twisted defect lines cycles around the particles at this point. This structure is seen up to $\theta \sim 15^\circ$. At this angle, again the defect lines are joined at a point on one side of the particles; however, the Saturn ring is only connected to the other particle at $\theta \sim 25^\circ$ in between the particles, and the same structure remains for larger angles.

At $\theta \geq 55^\circ$, there is a point where three defect lines are joined on one side and we can see a symmetric defect structure in between the particle at $\theta = 90^\circ$. At a particle separation of 0.25
μm, seen in figure 3.18 and 3.19, the same sort of defects are seen but at different values of angles. At 0 ≤ θ < 55°, there is a defect line surrounding the particles. At θ ~ 55°, again we see a point where the defect lines are joined at one side and the symmetric defect structure is observed at 75 ≤ θ ≤ 90°. There is no connection in defect lines for larger distances.

If we look at the plots of the energy of the particles, as shown in figure 3.20, we see that the interaction energy increases at θ >~ 55° at a particle separation of about 0.25μm, in which the defect lines get connected between the particles as well and the total length of lines is higher, leading to increase the distortion volume. This indicates that there is a repulsion between the particles when they approach each other from further distances. Also the energy is minimized at θ ~ 0° when they are close to each other, as there is a less distorted volume in the medium. So the particles become attracted to this position.

So far the spheres have been confined on the XY plane. Now, the next step is investigating the possible induced interactions between the particles, with produced defect structures, when they are rotated only on the XZ plane and the spheres are located at y = L_y/2.

First, the same particles are put in the nematic, and again the particle with planar anchoring is rotated around the other particle, separated at different distances. Figure 3.21 shows the configuration of particles in which they are kept at the distance of 0.125μm with respect to each other. Unlike the spheres confined on XY plane, the defect lines do not get connected to each other any more. According to the contour plot of interaction energy in figure 3.22, we see the energy is much lower when they are close to each other (up to a separation of about 0.5μm). The energy gets increased as they are pulled apart from each other, meaning they become attracted to the small separations. This can be justified by focusing at the plot of director field around the particles which is illustrated in figure 3.23. According to this figure, when the particles are close to each other, there is a small region around the particles where the director field becomes distorted from its uniform orientation. On the other hand, if they are kept at larger distances with respect to each other, the distorted volume surrounding the particles gets increased, leading to an increase in the interaction energy.
Next, the particles are placed into a cholesteric with pitch value of 1.5µm. Figure 3.24 shows the defect structures of two particles when they are separated by 0.125µm from each other. At \( \theta = 0^\circ \), we see that the boojums and the Saturn ring are joined together into one defect line, which is surrounding both particles. At \( \theta = 15^\circ \), the defect lines get disconnected at one side of the particles; however, they are joined in between. Moreover, the ring and the boojums are connected to each other at two points at one side of particles at \( \theta = 30^\circ \). At \( \theta = 37^\circ \), there is only one point where they are joined together. Also, no connection happens in between the particles at \( \theta = 45^\circ \). At \( \theta = 60^\circ \) the defect lines are joined from both sides and the boojums get connected to the ring at the pole of particle with perpendicular anchoring. No defect lines are joined together for greater angles. This kind of behavior is not seen for particles separations greater than 0.25 µm.

As it can be seen in figure 3.25, the energy is maximized at \( \theta \sim 15^\circ \), while it is minimized at \( \theta \sim 60^\circ \). This can be described by considering this point that the defect lines start to connect to each other at two points in between the particles at \( \theta \sim 15^\circ \); however, the defect lines are twisted in a way that no extra defect appears in between the particles at \( \theta \sim 60^\circ \). So they prefer to repel each other at \( \theta \sim 15^\circ \), while there is an attraction between the particles at \( \theta \sim 60^\circ \).

Now, it is worthwhile to compare the results obtained for both XY and XZ planes. If we focus on the interaction energy of particles, we recognize that its total range in the nematic liquid crystal, on both XY and XZ plane, is much lower than the cholesteric liquid crystal. Moreover, if we compare the particles, for nematic medium, placed on the XY plane and the XZ plane, we notice that the lowest minimum in energy occurs on the XY plane rather than the XZ plane. Therefore, it can be concluded that the minimum in energy may be in XY plane for particles inside a nematic liquid crystal.

Now considering the particles immersed in cholesteric liquid crystal with pitch value of 1.5µm, we recognize that the total range of interaction energy gets lower when the particles are confined on the XY plane. Comparing the energy of different pitch values for the XY plane, we see that the lower the pitch value is, the higher the interaction energy we have, so the minimum
of the energy happens for a pitch value of 3µm. As a result, most probably the minimum in energy is located on the XY plane for cholesteric liquid crystals as well.

![Defect structures of particles at distance of 0.125µm in the cholesteric LC(pitch=3µm)](image)

Figure 3.12: Defect structures of particles at distance of 0.125µm in the cholesteric LC(pitch=3µm)
3.2. Interaction of Particles Immersed in a Cholesteric Liquid Crystal

Figure 3.13: Plot of interaction energy for the particles immersed in the cholesteric liquid crystal with pitch value of 3\(\mu\)m in a) 2D and b)3D.

(a)

(b)
Figure 3.14: Defect structures of particles at distance of 0.125 µm in the cholesteric LC (pitch = 1.125 µm)
3.2. Interaction of Particles Immersed in a Cholesteric Liquid Crystal

Figure 3.15: Different perspective of defect structures of particles at distance of 0.125µm in the cholesteric LC (pitch = 1.125µm)
Figure 3.16: Defect structures of particles at distance of 0.1875\( \mu \text{m} \) in the cholesteric LC(pitch=1.125\( \mu \text{m} \))
3.2. Interaction of Particles Immersed in a Cholesteric Liquid Crystal

Figure 3.17: Different perspective of defect structures of particles at distance of 0.1875\(\mu\)m in the cholesteric LC(pitch=1.125\(\mu\)m)
Figure 3.18: Defect structures of particles at distance of 0.25µm in the cholesteric LC(pitch=1.125µm)
3.2. Interaction of Particles Immersed in a Cholesteric Liquid Crystal

Figure 3.19: Different perspective of defect structures of particles at distance of 0.25\(\mu\)m in the cholesteric LC(pitch=1.125\(\mu\)m)
Figure 3.20: Plot of interaction energy for the particles immersed in the cholesteric liquid crystal with pitch value of 1.125µm in a) 2D and b)3D.
3.2. Interaction of Particles Immersed in a Cholesteric Liquid Crystal

Figure 3.21: Generated defects around the particles in nematic liquid crystal onto XZ plane while separated 0.125µm from each other
Figure 3.22: 2D contour plot of interaction energy of 2 particles in nematic LC
3.2. Interaction of Particles Immersed in a Cholesteric Liquid Crystal

Figure 3.23: Plot of director field for different particle-particle separations when $\theta = 0^\circ$ and the particles are confined in XZ plane.
Figure 3.24: Generated defects around the particles in nematic liquid crystal onto XZ plane while separated 0.125µm from each other.
3.3 Discussion

Even though we predict the energy is minimized on the XY plane, it is likely that the particles experience local minima at other positions. Therefore, our future plan is to perform the same simulation, but with particles which are free to move in the medium to see where they move. Now it must be mentioned why we are motivated to scan through all possible positions in order to find the full energy landscape. The point is that we want to put more particles together inside the liquid crystal to see what positions they prefer to move inside the total volume of liquid crystal and see what kind of possible crystals the particles will self assemble to. The
presence of multiple local minima in the two particle interaction energy suggests potential locations for other particles to sit on.
Chapter 4

Conclusions

In the preceding thesis, we have investigated the possible anisotropic interactions induced by defect structures around colloidal particles inside both nematic and cholesteric liquid crystals. This work was done using the lattice Boltzamnn method to model the liquid crystal and trilinear interpolation to couple the particles to the computational liquid crystal mesh.

In the first chapter, the liquid crystal mesophase is described, as well as its different classes such as nematic and cholesteric. As liquid crystals show anisotropic behavior and are more ordered than an isotropic fluid, the tensor order parameter is introduced to distinguish these two phases. Then Landau de Gennes theory was presented to describe the free energy of the system in terms of the order parameter. After emphasizing the hydrodynamics equations of liquid crystals, the topological defects were described, which are generated when colloidal particles are present inside the liquid crystal. These defect structures induce anisotropic forces between the particles, which do not exist in a simple fluid such as defect-bonded chains produced by particles with planar anchoring in a cholesteric liquid crystal.

In chapter 2, the method of coupling the particles onto the lattice Boltzmann fluid is presented. In this method, the surface of a particle is discretized to a set of nodes, and the fluid is considered as a computational mesh; therefore, the particle nodes are distributed onto the fluid mesh using an interpolating scheme. It is worthwhile to mention that the particle distribution func-
tion \( f \) and the distribution function for the tensor order parameter \( G \) are used in this method. Moreover, the fluid coupling involves conservative forces based on the assumption of elastic collisions between the particle nodes and the interpolated fluid mass at the position of the particle.

In chapter 3, we have investigated the interaction of two particles with different sorts of anchoring, planar and perpendicular, in both nematic and cholesteric liquid crystals. Considering the defect structures of particles separately, we see that there is an image of the outer defect lines inside the particles, which can be justified by the analogy of electrostatics, in which the potential satisfies the Laplace’s equation and liquid crystal, in which the director field satisfies the Laplace’s equation in a linearized limit as well.

First the interaction of two particles was explored when they are put in a nematic, confined on the XY plane, and one of the particles is rotated around the another one at different distances with respect to each other. In this case, there is a maximum in the interaction energy when \( \theta \sim 35^\circ \), corresponding to the configuration where the defect lines are joined together from both particles, so the particles experience repulsion at this configuration and the energy is minimized when \( \theta \sim 90^\circ \), where the distorted region inside the nematic has the least volume, indicating an attraction between the particles.

Next, the medium is changed to cholesteric with different pitch values, which were close to, larger and smaller than the particle size, and in this case, the defect lines get connected to each other and produce a new set of structures due to the twist of defect lines. Considering \( R \) as particle radius, at the pitch value of 1.5\( \mu \)m (2.4\( R \)), we see that there is a sharp maximum in energy when the particles are kept at a distance of about 0.375\( \mu \)m, corresponding to the configuration where the total length of connected defect lines is higher, which indicates that the particles repel each other at this location when they approach each other from far distances.

At higher pitch value of 3\( \mu \)m (4.8\( R \)), the defect structures are approximately the same as the nematic. It is seen that particles repel each other at \( \theta \sim 15^\circ – 25^\circ \), where the defect lines start to be connected and the distorted volume gets larger in this case, while particles attract each
other at $\theta \sim 90^\circ$, where the director field becomes less distorted in the bulk. On the other hand, the defect lines are more twisted as the pitch value decreases to 1.125\(\mu\)m (1.8R), leading to different defect structures. Now the particles prefer to attract each other at $\theta \sim 0^\circ$ when they are so close to each other. At this configuration, there is a less distorted region in the bulk which reduces the interaction energy. On the other hand, there is a repulsion at $\theta >\sim 55^\circ$ at a distance of 0.25\(\mu\)m, where the get connected between the particles and the length of lines is higher, which increases the interaction energy.

Next, the rotation of particle is only confined on XZ plane. In the nematic, no defect lines are connected while the particle is being rotated; however, the particles tend to attract each other to reduce the distorted volume between them. In a cholesteric liquid crystal with pitch value of 1.5\(\mu\)m, the particles repel each other at $\theta \sim 15^\circ$, while they tend to attract each other at $\theta \sim 60^\circ$. At $\theta \sim 60^\circ$ the defect lines are joined together from both particles in a way that there is no extra defect generated in between the particles, but the defect lines get connected to each other at two points in between the particles at $\theta \sim 15^\circ$. This leads to more defect in the medium, so they repel each other at this position.

Comparing the interaction energy of particles on the XY and XZ planes, it can be recognized that in the nematic the total energy is much less than particles in the cholesteric on both planes. Also, the lowest minimum of energy is located on the XY plane in the nematic liquid crystal. In a cholesteric liquid crystal, the total energy is lowered when the particles are only confined on the XY plane. On this plane, as the pitch value decreases, the interaction energy increases, and as a result, the lowest minimum of energy occurs for pitch value of 3\(\mu\)m.

In a previous published paper [57], the stability of a diamond colloidal crystal in a cholesteric liquid crystal was investigated, suggesting the crystal stays stable when such a colloidal structure is formed. In that paper, the same kind of boundary condition was applied on the surface of all particles; however, we have used particles with different applied boundary conditions on their surfaces, since many of semiconductors are compound materials and we are interested to see if we can find such a compound for photonic crystals. Also, we intend to investigate the
impact of interaction energy on the potential for producing different types of crystals. As our future work, we will implement the simulation for particles which are free to move in order to see what positions they prefer to be attracted to.
Bibliography


Appendix A

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