Numerical Simulations of Flow and Microstructure in Nematic Liquid Crystalline Materials

by

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Abstract

Liquid crystals are known for their anisotropic characteristics, which lead to a preferred orientation of their molecules in the vicinity of solid surfaces. The ability of liquid crystalline materials to form ordered boundary layers with good load-carrying capacity and outstanding lubricating properties has been widely demonstrated. In order to study the advantages of implementing liquid crystals as lubricants, the steady state / time transient isothermal flow of thermotropic / lyotropic, nematic / chiral nematic liquid crystals between two concentric / eccentric cylinders and in planar Couette geometries were studied numerically. To consider the influence of the microstructure formation / evolution on the macro-scale attributes of the flow, the Leslie–Ericksen and Landau–de Gennes theories were employed. Simplicity of the Leslie–Ericksen theory in capturing the orientational alignment angle of the molecules makes it a viable candidate for modelling the flow of flow-aligning nematic liquid crystals. On the other hand, the Landau–de Gennes nematodynamics equations are well suited for predicting texture formation since defects and disclinations are non-singular solutions of the governing equations. The Landau–de Gennes theory for the liquid crystalline microstructure along with continuity and momentum equations were solved simultaneously using General PDE and Laminar Flow modules of COMSOL Multiphysics. The investigation of flow characteristics and orientation of liquid crystalline molecules for different rotational velocities / shear rates and anchoring angles at the boundaries were presented. Furthermore, nucleation and evolution of singularities in texture of the liquid crystalline materials were tracked over the simulation time. Moreover, alterations in the macro-scale attributes of the flow such as velocity profile, pressure distribution and first normal stress difference along with the evolution of defects were studied inside the liquid crystalline domain.

The implementation of Landau–de Gennes nematodynamic governing equations for LCs flow simulations offered an insight in application of these materials as lubricants. It was shown the LCs could provide protection against the wearing mechanism by forming a shielding layer in the vicinity of solid surfaces. Three-dimensional simulations of a simplified prosthetic hip joint...
Abstract

suggested that liquid crystalline materials should be considered as potential bio–lubricants.
Preface

The following desertion is the result of my graduate study performed at the Mechanical Engineering Department, University of British Columbia during the period of September 2008—September 2013. All of the work presented henceforth was conducted in the Advanced Numerical Simulation Lab (ANS), Institute for Computing, Information and Cognitive Systems at the University of British Columbia, Point Grey campus.

A version of Chapter 2 has been published online [Noroozi N, Grecov D. Flow modelling and rheological characterization of nematic liquid crystals between concentric cylinders. Liquid Crystals 40:871-883, 2013] and presented [Flow modelling and rheological characterization of nematic liquid crystals between two concentric cylinders. 23rd Canadian Congress of Applied Mechanics, 2011, Vancouver, BC, Canada]. I was the lead investigator, responsible for all major areas of concept formation, data collection and analysis, as well as manuscript composition. Dr. Dana Grecov was the supervisory author on this project and was involved throughout the project in concept formation and manuscript composition.

A version of Chapter 3 has been accepted to the Liquid Crystal journal [Noroozi N, Grecov D, Shafiei-Sabet S. Estimation of Viscosity Coefficients and Rheological Functions of NanoCrystalline Cellulose Aqueous Suspensions, June 2013]. I was the lead investigator, responsible for all major areas of concept formation, data collection and analysis, as well as the majority of manuscript composition. Shafiei-Sabet S. was involved in the early stages of concept formation, experimental data collection and contributed to manuscript edits. Dr. Dana Grecov was the supervisory author on this project and was involved throughout the project in concept formation and manuscript edits.

A version of Chapter 4 was presented as [Numerical simulation of flow induced structure in nematic liquid crystalline materials between two cylinders, 24th International Liquid Crystal Conference, Mainz, Germany, ILCC 2012, 5551-0386]. I was the lead investigator, responsible for all major areas of concept formation, data collection and analysis, as well as manuscript composition. Dr. Dana Grecov was the supervisory author on this project.
and was involved throughout the project in concept formation and manuscript composition.

I was the lead investigator for the projects located in Chapters 2 to 4 where I was responsible for all major areas of concept formation, data collection and analysis, as well as the majority of manuscript composition.
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G \quad \text{External director body force \([N]\)}
N \quad \text{Angular velocity of director vector with respect to velocity field \([s^{-1}]\)}
A \quad \text{Rate of deformation tensor \([s^{-1}]\)}
W \quad \text{Vorticity tensor \([s^{-1}]\)}
Q \quad \text{Order parameter tensor}
F \quad \text{Flow contributions}
H^{sr} \quad \text{Short-range elasticity contributions}
H^{lr} \quad \text{Long-range elasticity contributions}
v \quad \text{Velocity \([m/s]\)}
f \quad \text{Body force \([N]\)}
t \quad \text{Leslie-Ericksen total stress tensor \([Pa]\)}
g \quad \text{Intrinsic director body force \([N]\)}
n \quad \text{Eigenvector of } Q \text{ corresponds to largest eigenvalue, director vector}
m \quad \text{Eigenvector of } Q \text{ corresponds to second largest eigenvalue}
l \quad \text{Eigenvector of } Q \text{ corresponds to smallest eigenvalue}
I \quad \text{Second order unity tensor}
p \quad \text{Pressure \([Pa]\)}
\dot{s} \quad \text{Rate of entropy generation \([J/K.kg.s]\)}
S_d \quad \text{Defect strength}
F_d \quad \text{Frank elasticity free energy function \([Pa]\)}
k_{ii} \quad \text{Frank elasticity constants \([N]\)}
T \quad \text{Resistant torque \([N.m]\)}
S \quad \text{First scalar order parameter}
P \quad \text{Second scalar order parameter}
U \quad \text{Nematic potential}
k_B \quad \text{Boltzmann constant \([J/K]\)}
T \quad \text{Temperature \([K]\)}
H \quad \text{Flow characteristics length scale \([m]\)}
L_1 \quad \text{First Landau elastic coefficient \([N]\)}
L \quad \text{Isotropic long-range elasticity length scale \([m]\)}
L^* \quad \text{Non-dimensional Landau elastic coefficient}
P_2 \quad \text{Second order Legendre’s polynomial}
P_4 \quad \text{Fourth order Legendre’s polynomial}
**Nomenclature**

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<tr>
<td>$l$</td>
<td>Length of LC molecules</td>
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<tr>
<td>$d$</td>
<td>Diameter of LC molecules</td>
<td>$[m]$</td>
</tr>
<tr>
<td>$r$</td>
<td>Variable radius</td>
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<td>$S_{eq}$</td>
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<td>$R$</td>
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**Greek Letters**

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<td>$\mathcal{B}$</td>
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<td>$\pi$</td>
<td>Intrinsic director surface stress tensor</td>
<td>$[Pa]$</td>
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<tr>
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<td>$\tau_v$</td>
<td>Landau-de Gennes’ viscous stress tensor</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$\tau_e$</td>
<td>Landau-de Gennes’ elastic stress tensor</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$\tau_{Er}$</td>
<td>Landau-de Gennes’ Ericksen stress tensor</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$\tau_w$</td>
<td>Wall shear stress</td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Reactive parameter</td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>$[kg/m^3]$</td>
</tr>
<tr>
<td>$\rho_1$</td>
<td>Material constant</td>
<td>$[kg/m]$</td>
</tr>
<tr>
<td>$\mu_i$</td>
<td>Leslie viscosity coefficients</td>
<td>$[Pa.s]$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Orientational angle of molecular director</td>
<td></td>
</tr>
<tr>
<td>$\theta^0$</td>
<td>Anchoring angle of the molecules on the wall boundaries</td>
<td></td>
</tr>
<tr>
<td>$\omega$</td>
<td>Rotational velocity</td>
<td>$[s^{-1}]$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Material shape factor</td>
<td></td>
</tr>
<tr>
<td>$\Theta$</td>
<td>Ratio of anisotropic distortional elasticity to the isotropic one</td>
<td></td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Levi-Civita symbol</td>
<td></td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>Shear rate</td>
<td>$[s^{-1}]$</td>
</tr>
<tr>
<td>$\mathcal{L}$</td>
<td>Anisotropic long-range elasticity length scale</td>
<td>$[m]$</td>
</tr>
<tr>
<td>$\nu_i$</td>
<td>Landau viscosity coefficients</td>
<td>$[Pa.s]$</td>
</tr>
<tr>
<td>$\eta_s$</td>
<td>Solvant viscosity</td>
<td>$[Pa.s]$</td>
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# Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$\gamma$</td>
<td>Molecular aspect ratio correction parameter</td>
<td></td>
</tr>
<tr>
<td>$\eta_{al}$</td>
<td>Alignment viscosity $[Pa.s]$</td>
<td></td>
</tr>
<tr>
<td>$\eta_a$</td>
<td>Miesowicz viscosity along the flow direction $[Pa.s]$</td>
<td></td>
</tr>
<tr>
<td>$\eta_b$</td>
<td>Miesowicz viscosity along velocity gradient $[Pa.s]$</td>
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</tr>
<tr>
<td>$\eta_c$</td>
<td>Miesowicz viscosity along vorticity axis $[Pa.s]$</td>
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# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>MUMPS</td>
<td>MUltifrontal Massively Parallel sparse direct Solver</td>
</tr>
<tr>
<td>FEA</td>
<td>Finite Element Analysis</td>
</tr>
<tr>
<td>COF</td>
<td>Coefficient Of Friction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>ROI</td>
<td>Relative Optical Interference Intensity</td>
</tr>
<tr>
<td>RCD</td>
<td>Reciprocating Cylinder on Disc</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>RA</td>
<td>Rheumatoid Arthritis</td>
</tr>
<tr>
<td>PAA</td>
<td>Para−Azoxyanisole</td>
</tr>
<tr>
<td>DDA9</td>
<td>Poly(4, 4′−dioxy−2, 2′−dimethylazoxybenzene−dodeccanediyl)</td>
</tr>
<tr>
<td>AZA9</td>
<td>22−dimethyl−3−hydroxy−8−methyl−azaspiracid</td>
</tr>
<tr>
<td>MBBA</td>
<td>N−(4−Methoxybenzylidene)−4−butylaniline</td>
</tr>
</tbody>
</table>
Acknowledgements

I would like to express my eternal gratitude to my supervisor, Associate Prof. Dana Grecov for her influential guidance, encouragement, patience and tremendous concern for the success of this research. Additionally, I would like to acknowledge my supervisory committee members, Professor Ian Frigaard and Professor Savvas G. Hatzikiriakos. Also, I’d like to express my gratitude to Dr. Hatzikiriakos for many helpful discussions and guidance throughout the preparation of the thesis.
Dedication

I dedicate my dissertation work to my family, friends. A special feeling of gratitude to my loving parents, Saeid and Homera Noroozi and my sister Nazbanoo for believing in me. I also dedicate this dissertation to my many friends who have supported me throughout this process especially Farhang, Arash, Meygan, Forasad, Mehdi, Farazmorx and Sherin. I dedicate this work and give special thanks to my fiancé Azin Jahanafroz for nonstop support and for the many hours of proofreading. Without the moral support of any of you this work would never reach the end.
Chapter 1

Introduction

1.1 Background

In 1888, Austrian botanist Friedrich Reinitzer encountered a new phase of matter while performing physicochemical experiments on derivatives of cholesterol. Although at that time he was not confident about his discovery, he reported his observations to one of his colleagues, Otto Lehmann. Reinitzer observed a reversible phenomenon during the process of warming cholesterol benzoate; a new phase with distinct cloudy colour had occurred between 145.5°C and 178.5°C. This intermediate phase was also observed in other materials; for example, although his samples drifted as liquids, they exhibited crystallinity. It was the peculiar properties of these meso−phases that led to the term Liquid Crystals [1]. Although not much progress was originally done following the discovery of the liquid crystalline state and of materials with liquid crystalline characteristics, more recent times have seen an exponential increase in the interest in studying static and dynamic behaviour of the liquid crystalline materials.

In short, the liquid crystal (LC) phase is a state of matter that has properties between those of a conventional liquid and a solid crystal. LCs do not inherently possess positional order but they keep the orientational order of solids and the flowing properties of liquids while exhibiting strong anisotropic properties. A schematic representation of the transition from the solid crystal phase to the liquid crystalline meso−phase is presented in figure 1.1.

LC molecules can be classified into several different categories based on origin, shape, molecular arrangement and also their formation process. They are classified as organic and non−organic in terms of origin, and rod−like and disk−like in terms of shape. Furthermore, based on their arrangement, LCs are further categorized into nematic, cholesteric, smectic A, smectic C, columnar etc. [2]. A schematic representation of the arrangement of LC molecules is presented in figure 1.2.
1.1. Background

Crystal Liquid Crystal (Mesophases) Liquid

- Anisotropic
- 3D Lattice
- Positional Order
- Orientational Order
- Anisotropic
- No Lattice
- No Positional Order
- Orientational Order
- Isotropic
- No Lattice
- No Positional Order
- No Orientational Order

Figure 1.1: Schematic representation of transition from solid crystal to liquid crystalline meso−phases

Nematic Smectic A Smectic C

Columnar Cholesteric

Figure 1.2: Schematic representation of various configurations of LC molecules based on the molecular arrangement

Nematic liquid crystal (NLCs) is the simplest liquid crystalline phase and although it was generally assumed that its properties were uniaxial [3], nematic LCs with biaxial properties have been observed [4]. In fact, cholesteric
meso–phases can be considered a specific type of nematic LCs that have a twist in their molecular orientation about an axis normal to the preferred orientation of the molecules. As mentioned above, nematic and cholesteric liquid crystalline materials possess orientational order but no translational order, however, as smectic LCs maintain a degree of translational order, they stratify a vast number of structures.

Smectic C demonstrates a tilted molecular orientation at different layers, contrary to the upright molecular orientation of smectic A. Several different classes of discotic liquid crystalline materials have been introduced based on the orientation of the molecular director and degree of translational order (columnar LCs is only one example of these classifications). However, the main focus of this thesis was limited to the rod–like LC molecules and as such, discotic / disk–like liquid crystalline molecules are not further discussed in this document.

In addition to the above classes, liquid crystalline materials are further categorized according to the process that leads to the formation of the liquid crystalline meso–phase, namely thermotropics and lyotropics. With thermotropic liquid crystalline materials, changes in temperature affect the molecular motion and the level of free energy, leading to a phase transition. By melting a crystalline solid or cooling an isotropic liquid to a specific temperature, a thermotropic phase that exists only within a limited temperature range can be reached. In contrast, lyotropic LCs are obtained by changing the concentration of a particular amphiphilic substance in a solvent such as water. Although generally, particle shape, size and charge play the primary role in the phase transition from an isotropic mixture to a lyotropic suspension / solution, temperature remains an important factor in this transition.

Frank [5] proposed the term "disinclination" to describe unique patterns of liquid crystalline materials under polarized light microscopy in analogy with dislocations in solid crystalline materials; this term was later changed to "disclination". Any local breakage in symmetric patterns of the orientation of liquid crystalline molecules can be described as a defect. In static liquid crystalline samples between two glass plates under polarized light microscopy, defect points and brushes around them can be easily spotted since the position of defects remain constant while the orientation of disclination lines (brushes) changes with respect to the polarized light angle. Figure 1.3 depicts experimental results on defect patterns in a nematic LC sample (Oleg D. Lavrentovich, Kent University).

According to Chandrasekhar [6], defect strength can be calculated by knowing the number of disclination brushes attached to the defect point,
1.1. Background

Figure 1.3: An experiment by Oleg D. Lavrentovich from Kent University on defect patterns in a nematic LCs

\[ S_d = \frac{1}{4} (\text{# of brushes}) \]. Defects with \( S_d = \pm \frac{1}{2} \) and \( S_d = \pm 1 \) are mostly observed in the literature [6]. The importance of these patterns has been known since the discovery of liquid crystalline states by Reinitzer and Lehmann [7], however, the mathematical study and formulation of these textures were conducted many years later by Oseen [8] and Frank [5] for static samples of liquid crystalline molecules. Frank suggested various types of defects and disclination lines according to the definition of defect strength, presented in figure [1.4].

Additional studies were conducted on the dynamic patterns of LCs flowing in encapsulated domains. Figure [1.5] depicts the liquid crystalline patterns under the flow-induced structure for 5 wt% nanocrystalline cellulose aqueous suspension under steady shear rate of 0.01 and 0.05 [s\(^{-1}\)] [9]. In this figure, cross polarized light microscopy has been implemented to capture the isotropic and anisotropic subdomains.
1.2 Motivation

Liquid crystalline materials have a potential to be used in different applications. Structurally, liquid crystalline materials can be used as precursors in the fabrication of films, fibers and foams and their transformation into high-performance materials using conventional processing operations. Different studies have been conducted on the application of liquid crystalline microstructure as precursors and the influence of rheological properties such as viscoelastic modules, anisotropic viscosity and flow-induced structure on
1.3 Literature Review

the processing of liquid crystalline materials \[10\]. However, this study was focused on the functionality of LC meso—phases, based on their flow—induced texture evolution.

In terms of function, LC’s have also been used as lubricating agents \[11\]; for example, one of the functional applications of rod—like liquid crystalline materials is implementing them as lubricants or as performance boosting additives to standard lubricants, which take advantage of the unique anisotropic rheological characteristics of LCs. The intrinsic properties of LCs allow them to enhance their orientation—dependent viscosity and customize it for any application. Anisotropic characteristics of liquid crystalline materials also lead to complex flow properties; thus, several different attempts have been made to propose a general continuum model in order to predict the flowing characteristics of LC materials.

The subject of employing liquid crystalline materials as lubricants, or as additives to other standard lubricants to enhance their performance in journal bearings, requires an examination of their flowing characteristics, which was the main motivation for this study. Moreover, overcoming the challenges raised by simulating the flow between two eccentric cylinders (as a simplified model for journal bearings) due to the existence of shear, rotational and extensional forces, provided additional incentives for this study.

1.3 Literature Review

In the previous section the role of liquid crystalline meso—phases as lubricating agent have been stated as the main motivation for this study; unfortunately, the complex anisotropic characteristics of liquid crystalline materials made their flowing properties intensely complicated, which limits the range of predictions for applying LCs as lubricants.

Flow of liquid crystalline materials contains a unique micro—scale texture that evolves in time and space and interacts with macro—scale flow characteristics. Investigating the formation and evolution of LC’s textures (liquid crystalline finger—prints) was the objective of many studies; several different continuum models were suggested trying to capture all different aspects of this phenomenon.

This study was focused on illustrating various aspects of the complicated flow characteristics of liquid crystalline materials based on the different continuum models to have a better understanding from flow of LC materials as lubricants. In the following sub—sections, details of other researchers’ accomplishments are presented; starting by the achievements on the contin-
uum model, which was proposed by Frank Matthews Leslie and Jerald Ericksen; followed by the contributions of other researchers on the more complex continuum model that was proposed by Nobel prize winner Pierre-Gilles de Gennes and Lev Davidovich Landau. At the end, application of liquid crystalline meso-phases as lubricants were discussed.

1.3.1 The Leslie–Ericksen Theory

LCs are anisotropic viscoelastic materials; the combination of fluid-like flow with crystal-like anisotropy makes their phases interesting as modifiers of interfacial behaviour when applied as lubricants. The anisotropy of the viscosity coefficient, with respect to different flow directions, is a unique property of the liquid crystalline phase. The ability of liquid crystalline materials to form ordered boundary layers with good load-carrying capacity, and to decrease the friction coefficients, wear rates and contact temperatures of sliding surfaces (contributing to increase the components service life and save energy) has been widely demonstrated [11–13]. Several authors have presented experimental, theoretical and numerical results for the tribology of LCs [11]. The effect of using liquid crystal as additive for mineral oil on the coefficient of friction, which resulted in major improvements, was investigated in [14]. Liquid crystals used as smart lubricants with an active control of friction coefficient, based on electrical and / or hydrodynamic field variation has been studied in [15].

Leslie and Ericksen [16, 17] formulated the conservation laws of mass, linear and angular momentum for nematic LCs using a director vector n. Atkin and Leslie [18] simplified the governing equations in the case of simple Couette flow of nematic LCs based on the assumption of constant Frank elasticity coefficients. Measurements of splay (k_{11}) and bend (k_{33}) Frank elasticity coefficients have been performed on nematic LCs by Bradshaw et al. [19].

Rey [20] revealed that in two-dimensional modelling of liquid crystals based on the Leslie–Ericksen model, the director escapes from the shear plane under particular conditions. Rey studied transition of the director of nematic LCs in radial flow and discovered that the out-of-plane orientation of the director was due to the high Ericksen number (the elastic and shear forces were incapable of keeping the director inside the shear plane). In 2000, Van Horn et al. [21] implemented a simplified version of the Leslie–Ericksen model to solve the start-up simple shear flow; Amar and Cummings [22] used the same Leslie–Ericksen model to study instabilities in thin layers of nematic LCs on rigid surfaces; however, classification of results based on the
Leslie–Ericksen model was performed by Lima and Rey [23]. They studied multiplicity and multistability of solutions of the Leslie–Ericksen model for Poiseuille flow of discotic LCs.

1.3.2 The Leslie Viscosity Coefficients

Liquid crystals are artificial and biological anisotropic viscoelastic textured material. Due to their properties, they can be used as functional materials, sensors, actuators, lubricants or as precursor materials in the manufacturing of fibers, films, foams or composites. Their flow behaviour can be described using the Leslie–Ericksen director vector ($\mathbf{n}$) theory [8, 16, 17], or the Landau–de Gennes tensor order parameter ($Q$) theory. The uniaxial director $\mathbf{n}$ represents the average orientation of the unit axis of the rod–like molecules. The degree of order for the unit normals along $\mathbf{n}$ is given by the scalar order parameter ($S$). The orientation variable is a slow long wave–length mode and the scalar order parameter is a fast short wave–length mode; thus, the selection of the theory depends on the purpose and use of the model. For fast flows and / or descriptions of short length scale phenomena such as defect nucleation, the Landau–de Gennes model must be used. The Leslie–Ericksen model is adequate for sufficiently slow flows, when the flow time scale slower than the internal one, in which the orientation dominates the rheology and the scalar order parameter reaches close to its equilibrium value, and long length scale phenomena. In the limit of slow flows the Landau–de Gennes theory converges to the Leslie–Ericksen theory [24], and thus the viscoelastic material parameters of the latter can be given in terms of parameters of the former.

The Leslie–Ericksen model incorporates a modified stress tensor in the Navier–Stokes equations to couple the microstructure with macro–scale attributes of the flow of Liquid crystalline materials [18]; therefore, six new coefficients have been introduced in the stress tensor. The evolution of order parameter tensor $Q$ in time has been the principal focus of the Landau–de Gennes theory in predicting complex patterns in the flow of LCs [25, 26]. In comparable manner to the Leslie–Ericksen model, the Landau–de Gennes nematodynamic theory introduces an asymmetric stress tensor to capture the complicated phenomenological aspects of the flow of liquid crystals. Total stress tensor for the Landau–de Gennes model has a viscous component that implements three viscosity coefficients ($\nu_i$) to model the anisotropy of rheological characteristics of LCs [25]. Grecov proposed a method for calculation of $\nu_i$ as a function of the Leslie viscosities and scalar order parameter by mapping the two stress tensors [24].
1.3. Literature Review

Anisotropic rheological characteristics of the liquid crystalline materials are well described by the Leslie viscosity coefficients $\alpha_i$, $i = 1, \ldots, 6$; where only five of these are independent due to the Parodi’s relation [27]. Marrucci [28] proposed a formulation to predict the values of Leslie coefficients assuming very thin, long and rigid rod–like molecules, and considering $\alpha_6 = 0$. Moreover, he correlated the Leslie coefficients only to the scalar order parameter. Doi [29] implemented Smoluchowski equation and equilibrium distribution of molecular unit vectors around the director. Furthermore, second and fourth order Legendre polynomials have been applied as 2nd and 4th moment of the bulk of molecules to express the Leslie viscosity coefficients of lyotropic liquid crystals with rod–like polymeric molecules under weak velocity gradients [30]. Larson proposed additional viscous contributions to the Leslie viscosity coefficients using a rod–solvent friction factor $\xi_{str}$ which is a function of rotational diffusivity of dilute suspension and temperature [31].

Nanocrystalline cellulose (NCC) is composed of nano–fibres with high aspect ratio cellulose and unique rheological characteristics [9, 32]. Due to the rod–like shape, size and surface charge of the particles, NCC aqueous suspension exhibits liquid crystalline state in its phase diagram [32], which display the influence of concentration and temperature on the phase change of NCC aqueous suspensions. Colloidal suspension of NCC molecules in water are known to possess chirality in their nematic phase [33]. Dynamics of chiral nematic liquid crystalline materials have been studied using the Landau–de Gennes theory by introducing an extra term in the evolution of order parameter tensor; the extra term regarding the chiral pitch of the cholesteric liquid crystals is related to the ratio of elasticity to the helical distortions of the molecules [34, 35].

As been discussed by many authors before, the Landau–de Gennes nematodynamic model is well suited to simulate texture formation since defects are non singular solutions to the governing equations; however, finding meaningful values for various parameters and variables in the model is problematic. In this study different methods that have been proposed by other researchers were gathered to shed light on the values of different variables of the Landau–de Gennes model with focus on capturing trends of the Landau coefficients in viscous component of the total shear stress ($\nu_i$) for lyotropic LCs e.g. NCC aqueous suspension.
1.3.3 The Landau–de Gennes Nematodynamics Governing Equations

Nematic liquid crystals are orientationally ordered, textured, anisotropic and viscoelastic materials. They are used as structural or functional materials. One example of their various functionalities is their application as lubricants, which is related to the anisotropy of the viscosity coefficient with respect to different flow directions; this is a unique property of the liquid crystalline phase. The remarkable rheological properties of these materials are due to the flow–induced evolution of molecular configurations. Independent studies indicate that LCs change their orientational state in the vicinity of a solid surface. The ability of liquid crystalline materials to form ordered boundary layers with good load–carrying capacity, and to lower the friction coefficients, wear rates and contact temperatures of sliding surfaces (contributing to increase the components service life and save energy) has been widely demonstrated \[12, 36–38\].

Modelling the flow of liquid crystals is a dynamic multidisciplinary area of research for experimental and numerical fluid flow researchers as well as applied mathematicians. Since 1888 that liquid crystals were examined for the first time by Friedrich Reinitzer, several continuum theories had been developed to capture different aspects of the rheology and structure formation in liquid crystals. The flow of liquid crystals has been investigated through numerical simulations, in several studies, using Landau–de Gennes theory, Doi–Marrucci–Greco theory and extensions of Doi theory for nematic polymers. In Doi theory, at any given point in space, the dynamics of rod–like molecules of nematic liquid crystalline polymers (NLCPs) can be found using a diffusion equation of their orientational distribution function by implementing the Maier–Saupe nematic potential function \[39\].

Start–up flow of lyotropic LCs between two eccentric cylinders has been studied using the Doi theory by \[40\]; defects generation and the coupling between the flow and the molecular structure has been investigated using quadratic closure approximation to estimate the evolution of molecules \[41\]. Six closure models considered for the Doi theory have been compared with each other to predict three regimes of director motion: steady alignment, wagging and tumbling. All of the closure models foresaw the same distinct attributes of the liquid crystals behaviour. Complex flow simulation of NLCPs has been performed along with comparison among different closure approximations of the Doi theory for rigid rod–like molecules by \[42\].

Essential elements in the pattern formation of the LCP was solved using the Doi–Marrucci–Greco and moment–averaged theory by \[43\]. Slow Cou-
1.3. Literature Review

The flow of NLCPs was modelled using the Doi–Marrucci–Greco tensorial theory by [44], extending the structural scaling laws which was developed based on the Leslie–Ericksen theory to incorporate the flow of NLCPs and molecular elasticity. Furthermore, the mesoscopic Doi–Marrucci–Greco theory and the transient Stokes flow of NLCPs were simulated by [45] to study unsteady structural and orientational transition in unsteady shear flow. The texture formation of discotic nematic carbon fibers during the thermal relaxation after the termination of extensional flow was studied by Hong and Chan [46]. The Landau–de Gennes free energy of molecules was used to predict the difference between molecular reorientation time scale and thermal relaxation [47].

The isothermal, incompressible flow of liquid crystalline polymers was formulated by Farhudi and Rey using tensors for the microstructure; the transient and steady simple shear flow of uniaxial NLCs was studied. Furthermore, the elastic contribution for the molecular field and the elastic stress tensors were neglected to simplify the model and a spatially homogenous director vector for the molecules were assumed. Two types of orientational modes were predicted according to the nematic potential, (a) simple aligning mode, (b) complex modes. Three different subdivision regimes of complex modes were further investigated via the change in shear rates, which resulted in describing two distinct critical shear rates that characterize the transition between tumbling, oscillatory and stationary regime [48, 49].

Tsuji and Rey solved constitutive equations for evolution of LCs in rectilinear simple shear flow. Both, short–range elasticity and long–range elasticity were considered in their model. The compatibility of this tensorial theory was tested with the Leslie–Ericksen and Doi theory for asymptotic cases of $De \to \infty$ and $Er \to \infty$ respectively. A mechanism for compatibility between the Doi’s tumbling effect and fixed anchoring angle of the molecules on the boundaries was suggested [50].

A generalized version of tensorial governing equation was proposed by Tsuji; in these governing equations, short–range elasticity, flow contributions and long–range elasticity were included. Shear flow of liquid crystalline materials as a function of the Ericksen and Deborah numbers and for a fixed anchoring angle of the molecules on the boundaries was investigated. In their study, the counter impact of the microstructure on flow characteristics of LC was neglected [51].

Grecov and Rey adapted the Landau–de Gennes theory to describe the flow of flow–aligning thermotropic LCs. Well known thermodynamic restrictions along with ordering of Miesowicz viscosities and flow–aligning angle of the director emerging from the Leslie–Ericksen theory were imple-
1.3. Literature Review

mented to characterize shear viscosity coefficients of NLCs [24]. Start—up shear responses for different anchoring angles of the director at the wall boundaries and various Ericksen and Deborah numbers were investigated [25]. Grecov and Rey implemented the Landau—de Gennes equations along with decoupling simplification and constant shear rate, to achieve an insight on defects nucleation in shear—induced flow of flow—aligning liquid crystalline polymers (LCPs). The understanding of defect—defect annihilation and defect—wall interactions resulted from this study was needed to achieve a defect—free monodomain melts of LCPs [52, 53].

In summary, the Landau—de Gennes theory is well suited to simulate texture formation since defects are non—singular solutions to the governing equations. However, solving the Landau—de Gennes model for realistic applications is computationally expensive; thus, numerous simplifications of this theory have been done in the past to make it simpler to solve. For example, neglecting the counter impact of the microstructure on the flow or neglecting the long—range contribution on the shear stress tensors for solving the fluid flow have been used as simplifying assumptions.

1.3.4 Introduction to COMSOL Multiphysics

COMSOL Multiphysics is a commercial FEA simulation package that has been developed to handle complex entangled multiphysics physical phenomenon. The very first version of the software was developed by Svante Littmarck and Farhad Saeidi as FEMLAB in KTH [2]. COMSOL uses Galerkin finite element method to discretize the continuum domain into several finite pieces. In Galerkin finite element, the solution is calculated at nodal points and interpolated between nodes using the test functions \( v(x) \). In this case the solution for an arbitrary variable \( u(x,t) \) can be written as,

\[
\mathbf{u}(x,t) = \sum_{i=0}^{\infty} \omega_i(x) u_i
\]

For the case of solving the Landau-de Gennes equations for the LC’s microstructure coupled with the Navier-Stokes equations for the LC’s flow, the system of partial differential equations can be discretized by the FEM method that results in a linear system of equations. For example, in Poisson’s equation with a Dirichlet boundary condition, weak formulation of the

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1 Finite Element Analysis
2 Royal Institute of Technology, Stockholm, Sweden
test functions can be written as,

\[ \int_{\Omega} \nabla u(x) \cdot \nabla v(x) \, ds = \int_{\Omega} f v(x) \, ds \]  

(1.2)

Which can be transformed to \( Au = R \) where \( A \) is a large, usually sparse matrix. COMSOL solves this system of equations using MUMPS\(^3\) MUMPS uses multifrontal \( LU \) decomposition to generate upper triangle and lower triangle matrices, \( A = LU \) that leads to calculating the inverse of matrix \( A \). By knowing \( A^{-1} \), the unknown nodal vectors can be calculated as \( u = A^{-1}r \). Moreover, COMSOL employs multi order Backward Differential Formula to calculate the time steps in any transient analysis and variable damping factor base on CFL numbers for fluid mechanic related problems.

### 1.3.5 Application of Liquid Crystals as Lubricant

Nature of liquid crystals leads to a preferred direction of molecules in the vicinity of solid surfaces that gives them outstanding tribological properties. It has been proved \([11, 12, 37, 38, 54-60]\) that liquid crystals can be used as lubricants or as additives to industrial lubricants. Studies performed by \([14, 55]\) on the influence of the molecular structure on the tribological performance of liquid crystalline meso–phase showed that not only the orientation of rigid part of the molecules but also the alignment of the flexible components of the molecular structure have contributions on the tribological characteristics of LCs; which also demonstrated a decrease in COF\(^4\) by increasing molecular mass of the mixture (mineral oil lubricant (SAE 10W/40) + LCs).

Influence of the implementation of LCs as additives to other types of lubricants was further investigated by \([54]\). In this study, structural formation in standard lubricants due to the presence of additives with liquid crystalline nature such as nematics, cholesteric and smectic were resulted in four regimes of relative COF based on increasing the load for different types of additives. Further investigations have been proved that lubricants enriched with liquid crystalline particles, capable of configuring planar microstructure close to a contact surface, exhibit anti–friction characteristics. After observing the self–aligning pattern of liquid crystalline molecules close to the solid surfaces using imaging techniques by \([60]\); optimum value of 1% weight addition of LCs to reach minimum COF and maximum wear resistance between two contact surfaces were reported.

\(^3\)MUltifrontal Massively Parallel sparse direct Solver

\(^4\)Coefficient Of Friction
1.3. Literature Review

Tribological properties of liquid crystals (LC 1 – 4, LC 5 – 8, LC 9 – 12, LC 13 and LC 14) as additives to common oil based lubricants (HN−95 – 10 and SAE 15 W/40) were explored by Bermúdez et al. [56]. Tribology studies using pin and disk friction tester were performed on aluminum−steel metal couple which is more difficult to lubricate using common lubricants. Weight loss during the wearing process was measured with an electronic balance and worn surfaces were separately analyzed by SEM. Using SEM imaging technique also showed the tangential alignment of the molecules’ orientation with respect to the solid surface. Additionally, in the case of implementing lyotropic LCs as lubricants on aluminum alloy surfaces, higher load carrying capacity was observed compared to the standard oil based lubricants [57]. This outcome was achieved by comparing the widths of the wear scars measured under microscope for lyotropic LCs and liquid crystalline−enriched lubricants.

Nano−tribological properties of liquid crystals as an additive were studied with ROI technique [13]. As been suggested before [61], orientational order of liquid crystalline meso−phase grants them long−range, quasi long−range and short−range elasticity that was discussed in chapter 4. The influence of long−range order of the molecules on film forming mechanism and thickness of the lubricating film was studied by [13]. Outstanding anisotropic rheological characteristics of liquid crystalline materials give them outstanding advantages over the isotropic liquids while being used as lubricants. Considering the studies performed by [15], not only the rheological properties of LCs make them a suited candidate to be used as lubricants but also the influence of electromagnetic fields on liquid crystalline meso−phases initiate a possibility of producing smart lubricants capable of being actively controlled to modify their viscosity and adjust any changes in operating parameters.

Electro−rheological characteristics of the mixture containing liquid crystalline molecules as additives were investigated, which resulted in a raise in the magnitude of viscosity and film thickness by increasing the strength of the electric field; which led to rearrangement of the molecular orientation. In 2005, dynamic characteristics of liquid crystals as lubricants in sliding bearings were measured under applied electric field [62]. Experimental data proved that the orientation of liquid crystalline molecules became tangential to direction of the electric field; the fact that the main axis of liquid crystalline molecules coincide with the shear direction on lubricated surfaces.

5 Scanning Electron Microscopy
6 Relative Optical Interference Intensity
1.4. Summary of the Gaps in Existing Knowledge

led to a decrease in the value of COF even in the absence of the electric field. Controlling the viscosity of liquid crystalline meso–phase by altering the voltage in an electromagnetic field was achieved in order to reach less friction forces.

Lately, ultra low friction fluid mixtures using mesomorphic materials were studied by [12]; SAE 10W−40 and paraffin oil were used as solvents, D1 and 07/10 mesogenics, which are discotic and rod−like LCs, as additives. Time dependent friction coefficient of such mixtures with various combination of different concentration of LCs in oil was examined using RCD\textsuperscript{7} tribometer.

In conclusion, the role of liquid crystalline materials as lubricants or as additives to other type of lubricants has been established. It also should be taken into account that most LCs have intrinsic presence in living organisms [63], with lowest energy dissipation associated with their ordered layers; which make them a viable candidate as bio−lubricants. Waters et al. [38] performed experiments on wear of the artificial hip−joint materials by using normal aqueous saline, aqueous sodium azide, pure ethanol, aqueous hyaluronan acid and cholesterol palmitate as lubricants in ball and disk tribometer. After performing the examination on worn disks with SEM, significant decrease in wear scars and formation of liquid crystalline protection shield on the counter−face surfaces were detected.

1.4 Summary of the Gaps in Existing Knowledge

The flow between two eccentric cylinders, used as the basis of the flow model in journal bearings, is particularly complex in nature since shear, extensional and rotational flow features are present. When used in combination with liquid crystals, the model becomes even more elaborate. In fact, to the best of our knowledge no numerical studies have been able to tackle the lubrication of liquid crystalline materials. Despite this, a number of phenomenological continuum models have been proposed and several studies have been performed on the simple shear flow of NLCs.

As such, the flow of liquid crystalline materials in the complicated geometry of two eccentric cylinders was one of the challenges that needed to be addressed. Moreover, the Landau−de Gennes theory, which is one of the most sophisticated theories in predicting the flow properties of liquid crystalline materials has an additional intrinsic complexity for numerical simulation due to the presence of second and fourth order gradients of order

\textsuperscript{7}Reciprocating Cylinder on Disc
1.5. Objectives and Approach

parameter tensor. As the literature review suggests, many studies conducted in the past on the numerical analysis of LC materials using the Landau–de Gennes theory present a variety of shortcomings, namely:

- The counter–impact of the microstructure on the flow properties have been commonly neglected and by consequence, microstructure and flow field were separately modelled. In other words, the evolution equation and the Navier–Stokes equations were segregated in the solving process.

- Little attention has been paid to the influence of third dimensions of LC molecular shape and flow. Most of the studies in this field were performed on 2–dimensional models, which lead to lower accuracy compared to 3–dimensional models. This is particularly evident in trying to capture specific aspects of liquid crystalline behaviour such as tumbling or a director escaping from shear plane.

- The Landau–de Gennes theory has not been used to address the flow of liquid crystalline materials between two eccentric cylinders, which is induced by the rotation of the inner cylinder and therefore has inherent shear, rotational and extensional features that result in more complex flow patterns.

- The idea of implementing liquid crystalline materials as lubricants / lubricating agents has been explored by many experimental studies but has not been investigated by numerical simulations.

In order to accurately predict the nucleation and evolution of the LC’s texture, and understand the implications of LC patterns on its rheological and tribological characteristics (by using LCs as lubricating agents), the unabridged Landau–de Gennes theory coupled with the Navier–Stokes equations has to be implemented to model the start–up flow of NLCs between two eccentric cylinders (as a simplified model for journal bearings).

1.5 Objectives and Approach

Our understanding of the macro–scale attributes of the flow of liquid crystalline materials as lubricants is relatively lacking compared to that of Newtonian fluids. As a result, this study focused mainly on the flow of liquid crystalline materials. The following list presents the primary objectives of this study, in an order of noteworthiness.
1.5. Objectives and Approach

**Texture and Macro–Scale Flow Attributes**

The nucleation and evolution of the liquid crystalline texture (finger prints) / defects under flow–induced microstructure due to the presence of the orientational order of LC molecules has to be modelled; any interactions between the liquid crystalline microstructure and the macro–scale flow attributes have to be taken into account to achieve a better understanding of the nature of the rheological and tribological features as lubricating agents.

**Molecular Orientation vs. Rheology**

The alteration of the molecular orientation under simple shear flow and its impact on the apparent viscosity and resistant torque has to be studied, so that the intrinsic rheological characteristics of LCs can be effectively employed in the development of high performance / smart lubricating agents.

**Rheological Functions**

A semi–empirical methodology to predict the anisotropic viscosity coefficients and the rheological functions of lyotropic liquid crystalline materials with cholesteric nature has to be proposed.

When exploring the implementation of liquid crystalline materials as lubricating agents, a number of complexities need to be taken into account. They are associated with the flow of liquid crystalline materials, as well as the interaction between microstructure / texture / defects and macro–scale flow characteristics. The following is a listing of detailed objectives, each of which corresponds to a dedicated chapter in the remainder of this text.

- Initially, the Leslie–Ericksen theory was implemented to model the steady flow–induced microstructure of several flow–aligning liquid crystals between two concentric cylinders with a very small gap. The chief objective in this part of the study was to capture and investigate the multiplicity and multistability of results produced by the Leslie–Ericksen theory. An additional goal was set to explore how the anchoring angle of molecules on the wall boundaries influence the rheological characteristics of LCs, and to compare the resistance torque generated by Newtonian fluid between two rubbing surfaces and the one of LCs.

- Analyzing the connection between the Leslie–Ericksen and Landau–de Gennes theories was the objective of the third chapter. By taking into account the significance of several viscosity coefficients in the
Leslie—Ericksen and Landau—de Gennes governing equations, it was possible to define a methodology to calculate the values of Leslie / Landau viscosity coefficients by combination of theoretical / experimental methods. To test the accuracy of the proposed method, the rheological data on the shear stress and the apparent viscosity of certain lyotropic LCs was compared with numerical simulations of the start–up simple shear flow using the Landau—de Gennes theory and the proposed Landau viscosity coefficients.

In the final stage of the study, the leading objective was to understand the formation and evolution of LC microstructures in the vicinity of solid surfaces as a protective layer against wearing processes, as well as its implications on the macro–scale flow attributes between two rubbing surfaces of eccentric cylinders. In order to achieve this goal, transient flow–induced microstructures and microstructure–induced flow were numerically simulated by implementing the Landau—de Gennes theory fully–coupled with the Navier–Stokes equations. The flow of lubricants in journal bearings was modelled by the flow between two eccentric cylinders.

The final and most critical objective of this thesis was a numerical study of a 3–dimensional start–up flow of liquid crystalline materials between two eccentric semi–spheres (as a simplified model of prosthetic hip joint), which provided a comprehensive understanding of the intricacies involved in the application of LCs as bio–lubricants.

1.6 Thesis Layout

In chapter 2 governing equations of the Leslie—Ericksen theory was presented for steady flow of liquid crystalline materials between two concentric cylinders; alignment angle, entropy generation, free energy per unit volume, apparent viscosity and resistant torque was presented and also compared with rheological characteristics obtained from rheometry tests.

In chapter 3, rheological functions and the Leslie / Landau viscosity coefficients were theoretically predicted for various concentration of NCC aqueous suspensions; chiral patterns of the molecular orientation under start–up simple shear flow were explored. Shear stress and apparent shear viscosity were numerically calculated and compared with rheological data.

In chapter 4, governing equations of the Landau—de Gennes theory were presented for 2–dimensional (3–dimensional) transient flow of liquid crystalline materials between two eccentric cylinders (two eccentric semi–spheres)
1.6. Thesis Layout

under start—up flow by rotation of inner cylinder. Flow—induced microstructure and microstructure—induced flow were investigated; schematic representation of LC molecules, scalar order parameter as a measure for distribution of LC molecules, pressure, flow streamlines and first normal stress difference were calculated and compared with the related one of the hypothetical similar Newtonian fluids.

In chapter 5 highlights and summary of the previous sections were illustrated, followed by a short discussion on the potential future research directions; at the end references based on the order of appearance in the text and the appendix were arrayed.
Chapter 2

Flow Modelling and Rheological Characterization of Nematic LCs Using Leslie–Ericksen Theory

The present chapter aims at simulating the steady flow of thermotropic flow-aligning nematic liquid crystalline materials (NLCs) between two concentric cylinders with small gap size, which is the preliminary geometry for journal bearings (modelled usually by eccentric cylinders). Using concentric cylinders rather than eccentric cylinders significantly reduces the computational cost of numerical simulations due its symmetric nature. Furthermore, using rheological characterization and simulations, the viscous torque corresponding to a NLC is compared to the torque for a Newtonian fluid.

This chapter is restricted to orientation flow processes where the flow time scale is always slower than the order parameter time scale. In this chapter we characterize the flow aligning rod-like NLCs and show that the rheology is solely driven by orientation processes. The orientation variable is a slow, long wave-length mode. Thus the selection of the theory depends on the purpose and use of the model. For sufficiently slow flows, when the flow time scale is slower than the internal time scale such that the orientation dominates the rheology and long length scale phenomena, the Leslie-Ericksen theory is sufficient. In this chapter we use the Leslie-Ericksen vector theory to extract a clear rheological characterization of NLCs.

The main objective of the present chapter is to describe the rheology and orientation of the molecules of representative thermotropic rod-like nematic liquid crystals that aligns under weak flow with the average molecules unit normal close to the velocity directions. Generalizations to other flow conditions will require special considerations to the material parameters appearing in the constitutive equations.

The particular objectives of this chapter are:
2.1 Governing Equations of the Leslie-Ericksen Theory

- characterize the orientation of flow-aligning NLCs and how this affects the rheology
- compare the viscous torque for a liquid crystal and an equivalent Newtonian fluid

The organization of this chapter is as follow: In the next section we present the governing equations that describe the microstructure for rod-like nematic liquid crystals under arbitrary shear flow. Numerical and experimental setup for various NLCs are explained in the following sections. In the results section, multiplicity and multistability of numerical results for different boundary conditions and initial guesses are presented. Comparison between numerical and experimental results for viscosity and resistant torque for different liquid crystals are shown in the following subsection.

2.1 Governing Equations of the Leslie-Ericksen Theory

The shear flow behaviour and rheology of nematic liquid crystals (NLCs) depends on the sign and magnitude of the reactive parameter $\lambda = f(\mu)$ (considered as one of the material properties), which is the ratio of the flow aligning effect of the deformation rate and the tumbling (rotational) effect of the vorticity. For rod-like NLCs it is known that $\lambda > 0$ [64]. When $\lambda > 1$, the material flow-aligns close to the velocity direction since the rotational effect of vorticity is overcome by deformation. When $0 < \lambda < 1$, the director does not align close to the velocity direction because the rotational effect of vorticity dominates over the aligning effect of deformation. Materials with $\lambda > 1$ display the flow-aligning mode. The flow-alignment angle is known as the Leslie angle and for rod-like NLCs exists for $\lambda > 1$. For shear-aligning rod-like molecules, flow tends to align the average molecular unit normals along the velocity direction. The theoretical alignment angle is $2\theta_0 = \cos^{-1}\left(\frac{1}{\lambda}\right)$.

The governing equations based on the Leslie-Ericksen theory for the isothermal flow of liquid crystals, including the conservation of mass, and linear momentum and Oseen equations, are presented below [6][8].

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \]  
(2.1)

\[ \rho \frac{D\mathbf{v}}{Dt} = f + \nabla \cdot \mathbf{t} \]  
(2.2)
2.1. Governing Equations of the Leslie-Ericksen Theory

\[ \rho_1 \frac{D^2 n}{Dt^2} = G + g + \nabla \cdot \pi \]  

(2.3)

where \( \rho \) is density, \( v \) is velocity, \( f \) is the body force, \( \rho_1 \) is a material constant that has dimension of inertia per unit volume \([ML^{-1}]\), \( G \) is the external director body force, \( g \) is the intrinsic director body force, \( \pi \) is the intrinsic director surface stress tensor \([6]\), \( n \) is a dimensionless vector, which represents the direction of the preferred orientation for the LC molecules, also \( t \) is the total stress tensor. Figure 2.1 shows a schematic of the uniaxial rod-like nematic liquid crystalline phase. It consists of flat, rod-like molecules more or less aligned along a common direction, represented by the uniaxial director \( n \).

The major difference between isotropic liquids and LCs is the effect of orientational movement of the director \( n \) in the equations represented by the Frank elasticity function \( F_d \) \([5, 6]\), which is the free energy per unit volume, that can be defined as,

\[ 2F_d = k_{11} (\nabla \cdot n)^2 + k_{22} (n \cdot \nabla \times n)^2 + k_{33} | n \times \nabla \times n |^2 \]  

(2.4)

where \( k_{ii} \) for \( i = 1, 2, 3 \) are Frank elasticity constants. Schematic representations of major deformations related to each one of the Frank elasticity constants \([6, 19]\) are shown in figure 2.2. As the free energy has to be positive definite, it can be proved that \( k_{ii} \geq 0 \) for \( i = 1, 2, 3 \).

Thus, by knowing the asymmetric total stress tensor \( t \), the model is complete. The total stress tensor is \( t = t^0 + t' \) where the superscript "0" denotes the isothermal static deformation and the prime one denotes the hydrodynamic component.

\[ t^0 = -p \cdot I - \left( \frac{\partial F_d}{\partial n} \right) \cdot \nabla n^T \]  

(2.5)
2.1. Governing Equations of the Leslie-Ericksen Theory

Figure 2.2: Principal deformation of liquid crystal molecules, (a) bend, (b) twist, (c) splay

\[ t' = \mu_1 (\mathbf{nn} : \mathbf{A}) \mathbf{nn} + \mu_2 \mathbf{nnN} + \mu_3 \mathbf{Nn} + \mu_4 \mathbf{A} + \mu_5 \mathbf{nn} \cdot \mathbf{A} + \mu_6 \mathbf{A} \cdot \mathbf{nn} \quad (2.6) \]

Here, \( p \) is an arbitrary (indeterminate) constant, \( \mu_i \) for \( i = 1, 2, \ldots, 6 \) are the Leslie viscosities, \( \mathbf{A} \) is the rate of deformation tensor, \( 2\mathbf{A} = \nabla \mathbf{v} + (\nabla \mathbf{v})^T \), and \( \mathbf{N} \) is the angular velocity of the director relative to the velocity of the fluid, \( \mathbf{N}_j = \mathbf{n}_j - W_{jk} \mathbf{n}_k \) and \( \mathbf{W} \) is the vorticity tensor, \( 2\mathbf{W} = \nabla \mathbf{v} - (\nabla \mathbf{v})^T \). The flow of rod-like nematic liquid crystals between two concentric cylinders can be modelled using the equations 2.1--2.3. The director \( \mathbf{n} \) was assumed to be a function of \( \theta \), which represents the angle between the molecules’ director and streamlines and can be considered as a function of the radius, \( \tilde{r} \).

\[ \mathbf{n} = [\sin \theta, \cos \theta, 0] \quad (2.7) \]

Therefore, equations 2.1--2.6 can be simplified and velocity vector can be written as,

\[ \mathbf{v} = \left[ 0, r \omega (r), 0 \right] \quad (2.8) \]

By introducing \( \mathbf{n} \) and \( \mathbf{v} \) in equations 2.1--2.6, the governing equations in dimensionless form can be defined as,

\[ \tilde{f}(\theta) \left[ \frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \frac{\partial \tilde{\omega}}{\partial \tilde{r}} \right] + \frac{1}{2} \frac{\partial \tilde{f}(\theta)}{\partial \theta} \left[ \frac{1}{\tilde{r}^2} + \left( \frac{\partial \theta}{\partial \tilde{r}} \right)^2 \right] + \left( \tilde{\gamma}_1 + \tilde{\gamma}_2 \cos 2\theta \right) \frac{\tilde{r} \partial \tilde{\omega}}{2 \partial \tilde{r}} = 0 \quad (2.9) \]

\[ \frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left[ \tilde{r}^3 \tilde{g}(\theta) \frac{\partial \tilde{\omega}}{\partial \tilde{r}} \right] = 0 \quad (2.10) \]

where the definitions of \( \tilde{f}(\theta) \) and \( \tilde{g}(\theta) \) are as follow,

\[ \tilde{f}(\theta) = \cos^2 \theta + \varepsilon \cdot \sin^2 \theta \quad (2.11) \]
2.2. Numerical Setup and Validation

\[2\tilde{g}(\theta) = 2\tilde{\mu}_1 \sin^2 \theta \cdot \cos^2 \theta + (\tilde{\mu}_5 - \tilde{\mu}_2) \sin^2 \theta + (\tilde{\mu}_6 - \tilde{\mu}_3) \cos^2 \theta + \tilde{\mu}_4 \quad (2.12)\]

The dimensionless parameters in this set of equations are presented in Table 2.1.

<table>
<thead>
<tr>
<th>(\tilde{\omega})</th>
<th>(\tilde{\tau})</th>
<th>(\tilde{\gamma}_1)</th>
<th>(\tilde{\mu}_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega L^2 \gamma /k_{11})</td>
<td>(L)</td>
<td>(\tilde{\gamma}_2)</td>
<td>(\tilde{\eta})</td>
</tr>
</tbody>
</table>

Table 2.1: List of dimensionless variables

Here, \(\tilde{\gamma}_1 = \tilde{\mu}_2 - \tilde{\mu}_3\) and \(\tilde{\gamma}_2 = \tilde{\mu}_5 - \tilde{\mu}_6\); the gap size between two cylinders is \(L\); \(\tilde{\mu}_i\) for \(i = 1, 2, \ldots, 6\) are the dimensionless Leslie viscosity coefficients; \(\tilde{\eta}\) is the average of the three Miesowicz shear viscosities that describe anisotropic liquids and \(\varepsilon = k_{33}/k_{11}\) [6, 64].

2.2 Numerical Setup and Validation

Equations 2.9 and 2.10 are a set of fully non-linear, non-homogeneous and second order unidimensional ODEs that should be solved numerically. Two of the most general methods of solving ODEs are shooting and relaxation methods. Due to the nature of these equations and the high probability of reaching multiplicity in the results, the relaxation method was selected to solve these equations. The continuous domain between two concentric cylinders was discretized using finite difference schemes in order to transform the set of ODEs to finite difference equations or FDEs, which can be expressed as a block diagonal mass matrix for discretized domain. In relaxation method the final solution is determined by starting from a random predication and improving and evolving it, iteratively [65]. In this study, variant of Newton–Raphson method was used for improving the predication. By knowing the fact that, relaxation method allow us to use not only the dependent variables but also any algebraic correlations of the dependent variables; thus, gradients of the main variables such as \(\theta\) and \(\omega\) can be determined as part of the solution, which speed up the calculation of apparent viscosity and torque on the inner cylinder.

Four rod-like NLCs have been used in this study: DDA9 8 8, AZA9 9 9 2, PAA10 10, and MBBA11 11. Alignment angles of all liquid crystalline materials that have

---

8poly(4,4′-dioxo-2,2′-dimethyazoxybenzene-dodecane-diyldiyl)
922′-dimethyl-3-hydroxy-8-methyl-azaspiracid
10para-Azoxyanisole
11N-(4-Methoxybenzylidene)-4-butylaniline
2.2. Numerical Setup and Validation

Table 2.2: Alignment angles for the LCs used in this study

<table>
<thead>
<tr>
<th></th>
<th>DDA9</th>
<th>AZA9</th>
<th>PAA</th>
<th>MBBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_0^\circ$</td>
<td>6.1980</td>
<td>7.1291</td>
<td>8.4175</td>
<td>5.7003</td>
</tr>
</tbody>
</table>

Table 2.3: List of the Leslie viscosities [Pa · s] and tumbling factors for the LCs used in this study [66]

been employed in this study were provided in table 2.2. The Leslie viscosities of all liquid crystalline materials implemented in this study were presented in table 2.3 and Frank elasticity constants of selected LCs have been shown in table 2.4.

In order to validate the simulation code we compared the numerical results for the bulk angle at high rotational velocities with the theoretical alignment angle of liquid crystalline molecules. For high rotational velocities of inner cylinder the orientational angle of the bulk of molecules reached to its alignment value, $2\theta_0 = \cos^{-1} \left( \frac{1}{\lambda} \right)$, that verified the fact that numerical simulation is accurate.

Two liquid crystals have been chosen to test our model, DDA9 and AZA9. For the numerical simulations, the gap size was chosen to be $10^{-4}$ m. Grid

Table 2.4: Frank elasticity constants [6, 67]
independency study was performed for 160, 200, 300, 400 and 550 nodes between the two cylinders on distribution of the orientational angle of the molecules.

Since the 300 node grid exhibited high enough accuracy in capturing the
gradient of orientational angle distribution close to the wall boundaries, it was chosen to present the results. Infinity-norm of error, \( L_\infty \) was used as convergence criterion, where \( \|E_i\|_\infty = \max_i |E_i| \) and threshold of acceptable relative error was set to \( 10^{-8} \). Figure 2.3 illustrates the distribution of the orientation angle (\( \theta \)) for anchoring angle of 0.0 [rad] on the wall boundaries and an initial distribution was set to \( \theta = \pi/10 \) [rad] for DDA9 and AZA9. The results are presented for different dimensionless rotational velocities, \( \tilde{\omega} \). By increasing the dimensionless rotational velocity, the orientation of the molecules reached the exact alignment angle that was predicted theoretically (see table 2.2).

2.3 Experimental Method

A commercial MBBA (98%) supplied by Sigma–Aldrich (Oakville, Canada), a translucent yellow thermotropic LC with rod-like molecules was used to validate numerical simulations. A rotational rheometer (Kinexus Ultra Rheometer Malvern Instruments Ltd., Worcestershire, UK) was implemented to perform the rheological experiments in this study. Steady shear flow was used to characterize the rheological behaviour of the liquid crystalline mesophase. A fixture consisting of two stainless steel concentric cylinders with 25 mm diameter and a gap between cylinders of 1 mm, at a controlled temperature of 23\(^\circ\)C was used. The rheometer was first calibrated with Cannon Certified Viscosity Standard oil (Bellefonte, USA). In the steady shear test, shear rates from \( 10^{-1} \) to \( 10^3 \) [s\(^{-1}\)] were applied to the samples. It is important to note that in some industrial applications (e.g. journal bearing) the shear rates in a normal regime are sometimes well over \( 10^3 \) [s\(^{-1}\)].

2.4 Results

2.4.1 Multiplicity and Multistability

Previously, the accuracy of the model for capturing the alignment angle of different liquid crystals was assessed. Results were calculated for numerous types of boundary conditions, only few were presented here. Different studies confirmed the fact that LC molecules orient themselves completely parallel to the solid surface or with a certain angle, which depends on the several different factors. Study of different mechanism for obtaining diverse anchoring angle of molecules near solid surfaces was not in the scope of this study. However, five distinct orientational angles were implemented on
2.4. Results

the inner and outer cylinders to study the impact of anchoring angle of the
molecules on the bulk of fluid that have been presented in table 2.5. Figures

<table>
<thead>
<tr>
<th>Boundary Condition</th>
<th>B.C. 1</th>
<th>B.C. 2</th>
<th>B.C. 3</th>
<th>B.C. 4</th>
<th>B.C. 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta^\circ$ (rad)</td>
<td>0 (0)</td>
<td>5.73 (0.1)</td>
<td>-5.73 (-0.1)</td>
<td>11.46 (0.2)</td>
<td>-11.46 (-0.2)</td>
</tr>
</tbody>
</table>

Table 2.5: The anchoring angles of molecules on the inner and outer cylinders for the boundary conditions used in this study

2.4, 2.5, 2.6, 2.7 and 2.8 present the orientational angles of MBBA and PAA molecules vs. different dimensionless rotational velocities and $\theta = \pi/10$ as initial guess for the distribution of molecules, and corresponding to boundary conditions B.C. 1, B.C. 2, B.C. 3, B.C. 4 and B.C. 5 respectively. The positive initial guesses for distribution of the molecules were chosen close to the stable solutions.

At very low rotational velocities elasticity is dominant and the orientational angle of the molecules in the bulk of fluid depends on the anchoring angle at the wall boundaries rather than the viscous terms. On the other hand, as the rotational velocity increases there is a competition between the contributions of elastic and viscous terms to dominate the orientation of molecules. By increasing the dimensionless rotational velocity of the inner cylinder a considerable part of the domain between the cylinders has been affected and a larger number of molecules reached the alignment angle.

At high rotational velocities, the viscous terms become dominant and the director reaches the alignment angle, exception a thin boundary layer close to the boundaries. The alignment angles obtained from numerical results are consistent with the theoretical values.

Figures 2.9, 2.10 and 2.11 present the orientational angles for MBBA and PAA for different dimensionless rotational velocities and initial guess for the distribution of molecules $\theta = -\pi/10$, for boundary conditions corresponding to B.C. 1, B.C. 2 and B.C. 3 respectively.

For both liquid crystals, it was observed that changing the sign of the initial guess for the orientational angle from positive to negative would cause instabilities in results, and even divergence for high dimensionless rotational velocities. This phenomenon has been reported by other authors as well [23].

The negative initial guesses for distribution of the molecules were chosen close to the unstable solutions. As illustrated in figure 2.12 positive ini-
2.4. Results

Figure 2.4: Distribution of orientational angle $\theta$ between two concentric cylinders for different dimensionless rotational velocities $\tilde{\omega}$ of inner cylinder for (a) MBBA and (b) PAA; initial distribution was set to $\theta = \pi/10$ and for boundary conditions case B.C. 1 was implemented.
2.4. Results

Figure 2.5: Distribution of orientational angle $\theta$ between two concentric cylinders for different dimensionless rotational velocities $\tilde{\omega}$ of inner cylinder for (a) MBBA and (b) PAA; initial distribution was set to $\theta = \pi/10$ and for boundary conditions case B.C. 2 was implemented.
2.4. Results

Figure 2.6: Distribution of orientational angle $\theta$ between two concentric cylinders for different dimensionless rotational velocities $\tilde{\omega}$ of inner cylinder for (a) MBBA and (b) PAA; initial distribution was set to $\theta = \pi/10$ and for boundary conditions case B.C. 3 was implemented
2.4. Results

Figure 2.7: Distribution of orientational angle $\theta$ between two concentric cylinders for different dimensionless rotational velocities $\tilde{\omega}$ of inner cylinder for (a) MBBA and (b) PAA; initial distribution was set to $\theta = \pi/10$ and for boundary conditions case B.C. 4 was implemented.
2.4. Results

Figure 2.8: Distribution of orientational angle $\theta$ between two concentric cylinders for different dimensionless rotational velocities $\tilde{\omega}$ of inner cylinder for (a) MBBA and (b) PAA; initial distribution was set to $\theta = \pi/10$ and for boundary conditions case B.C. 5 was implemented.
2.4. Results

Figure 2.9: Distribution of orientational angle $\theta$ between two concentric cylinders for different dimensionless rotational velocities $\tilde{\omega}$ of inner cylinder for (a) MBBA and (b) PAA; initial distribution was set to $\theta = -\pi/10$ and for boundary conditions case B.C. 1 was implemented
Figure 2.10: Distribution of orientational angle $\theta$ between two concentric cylinders for different dimensionless rotational velocities $\tilde{\omega}$ of inner cylinder for (a) MBBA and (b) PAA; initial distribution was set to $\theta = -\pi/10$ and for boundary conditions case B.C. 2 was implemented.
2.4. Results

Figure 2.11: Distribution of orientational angle $\theta$ between two concentric cylinders for different dimensionless rotational velocities $\tilde{\omega}$ of inner cylinder for (a) MBBA and (b) PAA; initial distribution was set to $\theta = -\pi/10$ and for boundary conditions case B.C. 3 was implemented.
2.4. Results

The initial distribution of molecules has better chance of reaching stable alignment angle while negative initial distribution of molecules are more probable to reach unstable alignment angle.

At very low rotational velocities the elastic term was dominant and the contribution of the anchoring angle of the molecules at the boundaries was more significant. Increasing the dimensionless rotational velocity, the viscous terms became more significant and unstable alignment angles were reached. This was an anomaly that observed for all different liquid crystalline materials and every boundary condition that had been tested using the model. In all of these figures orientational director of the molecules of MBBA and PAA oscillate between their intrinsic stable alignment angle and the unstable angle. By further increase of the dimensionless rotational velocities $\tilde{\omega} \geq 10^{-1}$ these fluctuations propagated inside the system with higher frequencies.

Unstable solutions are also the answer to the Leslie-Ericksen equations but do not possess the minimum amount of Frank elasticity energy nor the maximum amount of entropy generation through the process. The rate of entropy generation in the process of flowing a liquid crystalline material between two concentric cylinders can be calculated by equation 2.13 [6, 27].

$$\text{Temp} \cdot \dot{s} = t'_i A_{ij} - g_i^i N_i$$  \hspace{1cm} (2.13)

Where $\text{Temp}$ is the absolute temperature, $t'$ can be evaluated using equation 2.6 and $g$ is the intrinsic director body force. Equation 2.13 in dimensionless
2.4. Results

form can be simplified to,

\[
\text{Temp} \cdot \dot{S} = \frac{1}{2} \left( \vec{r} \cdot \frac{d\vec{\omega}}{d\vec{r}} \right)^2 \cdot \left[ 2 \tilde{g}(\theta) \right]
\]  \hspace{1cm} (2.14)

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
 & MBBA & & MBBA & PAA \\
 & N. I. \(^a\) & & P. I. \(^b\) & N. I. & P. I. \\
\hline
\(F_d \left( \frac{J}{m^3} \right)\) & 0.00125 & 1.6417 \times 10^{-4} & 0.00120 & 4.2638 \times 10^{-4} \\
\(s' \left( \frac{J}{kgKm^3s} \right)\) & 14.573 & 14.602 & 0.2476 & 0.2512 \\
\hline
\end{tabular}
\end{table}

\(^a\) Positive initial distribution of molecules
\(^b\) Negative initial distribution of molecules

Table 2.6: Frank elasticity and rate of entropy generation for negative / positive initial distribution of molecules

Amount of Frank elasticity energy and rate of entropy generation were presented in table 2.6 for dimensionless rotational velocity \(\tilde{\omega} = 1\) and different initial guesses for the distribution of molecules of MBBA and PAA based on the equations 2.4 and 2.14 respectively. It can be concluded that stable solutions always possess minimum amount of Frank elasticity energy while generating the higher amount of entropy.

2.4.2 Viscosity and Torque

The theoretical apparent viscosity \([18]\) of selected liquid crystalline materials can be calculated using equation 2.15:

\[
\eta = \frac{r_2 - r_1}{\int_{r_1}^{r_2} \frac{d\theta}{g[\theta(s)]}}
\]  \hspace{1cm} (2.15)

Where \(g(\theta)\) is the dimensional form of equation 2.12. Different types of surface treatments achieved various anchoring angles of the molecules on the solid boundaries, which led to different flow curves. According to the numerical experimentation that had been done on MBBA samples, it revealed that shear thinning and shear thickening behaviour of the material were functions of anchoring angles of the molecules on the solid surface. In order to verify the accuracy of the model in capturing the apparent viscosity of different liquid crystalline materials, set of experiments was performed
2.4. Results

in order to measure the apparent viscosity of MBBA. Two different rheological characterization tests with two concentric cylinders as geometry have been performed as described before. The non-isotropic behaviour of liquid crystals lead to non-repeatability in results of viscosity.

In figure 2.13 the apparent viscosity of MBBA for different anchoring angles of molecules on the wall boundaries along with the measured apparent viscosity were presented. A good agreement between the apparent viscosity obtained from numerical and experimental approaches with the error of less than 6% for relatively high shear rates was demonstrated. It was observed that at lower shear rates the amount of torque produced due to the resistance in the material is within the range of the rheometer’s error (10^{-7} N.m). It should be noted that steady shear measurements are only reported for shear rates higher than 10^{-1} s^{-1}, given that at lower shear rates the signals were too noisy due to torque limitations and inertia of the rheometer. The torque per unit of length in the z-direction applied on the inner cylinder can be calculated from the contributions of shear stress and director surface stress as follow, [18].

\[
T = 2\pi \left[ r^2 t_{r\phi} + r (\epsilon_{zp} n_p \pi_{rq}) \right] \tag{2.16}
\]

where \( t \) is the total shear stress tensor, \( \pi \) is the director stress tensor and \( \epsilon_{ijk} \) are the components of the altering tensor. By using equation 2.6, applied torque on the inner cylinder can be calculated by,

\[
T = 2\pi r^3 \left( \frac{d\omega}{dt} \right) g (\theta) \tag{2.17}
\]

Comparison between the torque on the inner cylinder estimated by numerical simulation and that obtained from the experiment was illustrated in figure 2.14. Good agreement between numerical and experimental results were observed for high shear rates. For low shear rates, fluctuations in the experimental data due to physical limitations of the rotary rheometer imposed difficulty on obtaining accurate comparison between results.

In order to compare the behaviour of liquid crystal material to Newtonian fluid, simulations had been performed on MBBA and a hypothetical Newtonian fluid with a viscosity having the same value of \( \mu_4 \). According to the Leslie Ericksen theory, \( \mu_4 \) is the Leslie viscosity equivalent to the Newtonian viscosity of a fluid. Resistance torque exerted on the inner cylinder by the Newtonian fluid was compared with that exerted by MBBA, as presented in figure 2.14. Up to 60% reduction on the resistance can be obtained using a liquid crystal in comparison with a hypothetical Newtonian fluid.
2.4. Results

Figure 2.13: (a) Apparent viscosity of MBBA for different boundary conditions (b) Comparison between apparent viscosity of MBBA derived from the Leslie-Ericksen theory and the measured apparent viscosity.
Figure 2.14: (a) The torque on the inner cylinder measured for MBBA and from numerical simulations for B.C. 1 as a function of shear rate (b) Ratio between the computed torque for MBBA and the computed torque for the hypothetical Newtonian fluid as a function of shear rate
2.5 Summary and Remarks

The Leslie-Ericksen theory was implemented to predict the evolution of alignment angle of PAA, AZA9, DDA9 and MBBA between two concentric cylinders. Multiplicity and multistability of results for the Leslie-Ericksen theory was observed as a function of the initial state of LC molecules. Unstable state for alignment angle of molecules were detected, which did not possess the minimum free energy nor the maximum rate of entropy generation in comparison with stable solutions.

Investigation of the influence of rotational velocity of the inner cylinder on evolution of the alignment angle of molecules were performed which resulted in following conclusions. At high rotational velocities, viscous terms became dominant and the director reached the alignment angle for stable solutions, for the case of unstable solution fluctuations in the alignment angle was observed that propagated inside the system with larger frequencies at rotational velocities \( \bar{\omega} \geq 10^{-1} \).

Finally, viscosity and resistance torque exerted on the inner cylinder were estimated using the Leslie-Ericksen theory and compared with the data from rheological experiments, that has been indicating a good agreement.
Chapter 3

Estimation of Viscosity Coefficients and Rheological Functions

The objective of the chapter is to propose a methodology to calculate different rheological functions and viscosity coefficients for lyotropic liquid crystals using analytical and experimental rheological data. The validation of the procedure has been done using numerical simulations of the Landau–de Gennes equations for start up shear flow of 7 wt% NCC aqueous suspensions and experimental rheological data. In addition, based on concentration and size of molecules, different characteristic parametric values and dimensionless numbers from the Landau–de Gennes theory have been calculated for NCC aqueous suspension.

The organization of this chapter is as follows: In the section 3.1 we present an overview of Landau–de Gennes model for cholesteric nematics under arbitrary flow and introduce various parameters and variables in the model. In section 3.2 we present the estimation of Landau viscosity coefficients and rheological functions based on the Leslie–Ericksen theory. In section 3.3 we present the experimental methods. The calculation of different rheological parametric values for aqueous suspensions of NCC is presented in section 3.4. In section 3.5 we present the numerical methods for solving the Landau–de Gennes microstructure equation. In section 3.6 we present the numerical results for 7 wt% NCC aqueous suspension and the validation of the calculated Landau viscosity coefficients using experimental data.

3.1 Nematodynamic Governing Equations

In the Landau–de Gennes theory the microstructure of cholesteric liquid crystals is described conveniently in terms of a second order, symmetric and traceless tensor order parameter (Q). The tensor order parameter Q can be
3.1. Nematodynamic Governing Equations

expressed as a function of its main eigenvalues and eigenvectors,

\[ Q = S (n n - \frac{1}{3} I) + \frac{1}{3} P (m m - I) \]  (3.1)

In equation 3.1, \( I \) is the unit tensor, \( S = \frac{3}{2} \mu_n \) and \( P = \frac{3}{2} \mu_n + \frac{3}{2} \), where \( \mu_n, \mu_m \) and \( \mu_l \) are the largest, second largest and smallest eigenvalues of \( Q \), corresponding to the eigenvectors \( n \) (uniaxial director), \( m \) and \( l \) respectively.

The uniaxial director, \( n \) is a dimensionless vector, which represents the direction of the preferred orientation of the liquid crystals’ molecules.

The evolution equation describes the dynamics of cholesteric liquid crystals through the following equation 3.1 [25, 35].

\[ \dot{Q} = F (\nabla v, Q) + H^{sr} (D_r, Q) + H^{lr} (D_r, \nabla Q) + \mathcal{P} (\nabla Q) \]  (3.2)

where \( \dot{Q} \) is the Jaumann derivative of the tensor order parameter,

\[ \dot{Q} = \frac{\partial Q}{\partial t} + (\bar{v} \cdot \nabla) Q - \bar{W} \cdot Q + Q \cdot \bar{W} \]  (3.3)

\( F \) is the flow contribution,

\[ F = \frac{2}{3} \beta \bar{A} + \beta \left[ \bar{A} \cdot Q + Q \cdot \bar{A} - \frac{2}{3} \left( \bar{A} : Q \right) I \right] - \frac{1}{2} \beta \left\{ \left( \bar{A} : Q \right) Q + \bar{A} \cdot Q \cdot Q + Q \cdot \bar{A} \cdot Q + Q \cdot Q \cdot \bar{A} - \left[ (Q \cdot Q) : \bar{A} \right] I \right\} \]  (3.4)

Short–range elasticity (\( H^{sr} \)) arises from the inter–molecular forces and long–range elasticity (\( H^{lr} \)) transmits the surface anchoring effects from the wall boundaries to the bulk of the fluid.

\[ H^{sr} = \frac{1}{2 \nu} \left[ \left( \frac{U}{3} - 1 \right) Q + U Q \cdot Q - U (Q : Q) \cdot (Q + \frac{I}{3}) \right] \]

\[ H^{lr} = \frac{1}{E} \left\{ \nabla^2 Q + L^* \left[ \nabla(\nabla \cdot Q) + [\nabla(\nabla \cdot Q)]^T - 2 \frac{3}{3} tr(\nabla(\nabla \cdot Q)) \right] \right\} \]  (3.5)

\( \mathcal{P} \) is the chiral term and is related to the ratio of elasticity to the helical distortions of molecules tending to increase the twist pattern of the directors [35].

\[ \mathcal{P} = \frac{\Theta}{E} \left( \epsilon_{mik} Q_{mj,k} + \epsilon_{mjk} Q_{mi,k} \right) \]  (3.6)

In the above equations, \( \bar{A} \) is the dimensionless rate of deformation tensor, \( \bar{W} \) is the dimensionless vorticity tensor, \( \beta \) is the molecular shape factor, \( U \) is the nematic potential, \( \epsilon \) is the Levi–Civita symbol, \( L^* \) is the ratio of Landau elastic coefficients, \( L^* = L_2/L_1 \) where, \( L_1 = K_{22}/2S^2 \) and \( L_2 = (K_{11} - K_{22})/S^2 \); \( K_{ii} \) are Frank elasticity constants that depend on principal
deformation of molecules and $S$ is the scalar order parameter. Moreover, four dimensionless numbers are defined in this set of governing equations and can be described as follows: Ericksen number ($Er$), represents the ratio of viscous flow effects to long-range order elasticity, Deborah number ($De$), indicates the ratio of viscous flow effects to short-range order elasticity, energy ratio ($R$), measures the ratio of short-range order to long-range order elasticity and $\Theta$ quantify the ratio of anisotropic distortional elasticity to the isotropic one.

$$Er = \frac{ck_B T \gamma H^2}{6L_1 Dr}; \quad De = \frac{\dot{\gamma}}{6Dr}; \quad R = \frac{ck_B TH^2}{L_1}; \quad \Theta = \frac{L^2}{L^2}; \quad (3.7)$$

In equation $3.7$, $c$ is the concentration of molecules per unit volume, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\dot{\gamma}$ is the shear rate, $H$ is the flow characteristic length scale, $L$ ($L$) is the isotropic (anisotropic) long-range length scale $[34]$ and $D_r$ is the pre-averaged rotational diffusivity $[68]$ that is a process by which the equilibrium statistical distribution of the overall orientation of molecules is preserved.

The Landau–de Gennes model incorporates the influence of microstructure on macro-scale attributes of the flow by modifying the total stress tensor. Evolution of tensor order parameter along with mass balance and modified momentum balance (using total stress tensor) are the governing equations for the flow of liquid crystals.

The total stress tensor has two main components, symmetric and asymmetric. The symmetric component contains viscous and elastic terms. Dimensionless viscous, component of total stress tensor can be expressed as a function of tensor order parameter $Q$ and dimensionless rate of deformation tensor $\tilde{\dot{A}}$ as follows,

$$\tilde{\tau}_v = \tilde{\nu}_1 \tilde{A} + \tilde{\nu}_2 \left[ Q \cdot \tilde{A} + \tilde{A} \cdot Q - \frac{2}{3} \left( Q : \tilde{A} \right) I \right] + \tilde{\nu}_4 \left\{ \left( \tilde{A} : Q \right) Q + \tilde{A} \cdot Q \cdot Q + Q \cdot \tilde{A} \cdot Q + \left[ (Q : Q) \tilde{A} \right] I \right\} \quad (3.8)$$

In equation $3.8$, $\tilde{\nu}_i$ for $i = 1, 2$ and $3$ are dimensionless Landau viscosity coefficients. The other components of the total stress tensor were implemented the same as $[25]$.

An important challenge related to the Landau–de Gennes model is the difficulty to find the characteristic parametric values including the viscosity coefficients for a specific liquid crystalline material, connect the experimental data to the model and provide meaningful values for various parameters and coefficients. In the next section we use the Leslie–Ericksen theory.
3.2 Estimation of Rheological Functions and Landau Viscosity Coefficients

and Doi and Larson models for reactive parameter for lyotropic nematic liquid crystals, to calculate analytically different rheological functions and the Landau viscosity coefficients.

3.2 Estimation of Rheological Functions and Landau Viscosity Coefficients

The Leslie–Ericksen theory applies to uniaxial nematic flows neglecting the short-range order elasticity, and hence being unable to describe the changes of the scalar order parameter due to the imposition of sufficiently strong flow. Consequently, in this theory, the microstructure is described by the director vector \( \mathbf{n} \) and the scalar order parameter \( S \) is assumed to remain constant, that is, unaffected by the flow, and always equal to its value at equilibrium: \( S = S_{eq} \), while the biaxial order parameter \( P \) is equal to zero. The total extra-stress tensor is \( \mathbf{t} = \mathbf{t}^0 + \mathbf{t}' \) where the superscript "0" indicates the isothermal static deformation and the prime one contains hydrodynamic terms [6, 17].

\[
\mathbf{t}' = \alpha_1 (\mathbf{n} \cdot \mathbf{A}) \mathbf{n} n + \alpha_2 \mathbf{n} \mathbf{N} + \alpha_3 \mathbf{N} \mathbf{n} + \alpha_4 \mathbf{A} + \alpha_5 \mathbf{n} \cdot \mathbf{A} + \alpha_6 \mathbf{A} \cdot \mathbf{n} \quad (3.9)
\]

In correlations (3.9), \( \mathbf{n} \) is the director of LC molecules, \( \alpha_i \) for \( i = 1, 2, \ldots, 6 \) are the Leslie viscosities, \( \mathbf{N} \) is the angular velocity of the director relative to the velocity of the fluid [6], \( \mathbf{N}_j = \dot{\mathbf{n}}_j - \mathbf{W}_{jk} \cdot \mathbf{n}_k \), where \( \mathbf{W} \) is the vorticity tensor, \( 2\mathbf{W} = \nabla \mathbf{v} - (\nabla \mathbf{v})^T \) and \( \mathbf{A} \) is the rate of deformation tensor, \( 2\mathbf{A} = \nabla \mathbf{v} + (\nabla \mathbf{v})^T \).

The anisotropy of liquid crystals leads to numerous viscosity coefficients in order to describe the flow properties. These coefficients strongly depend on the concentration of the LC molecules in the solvent and are sensitive to molecular structure. The qualitative flow behaviour of a nematic liquid crystal depends on the sign and magnitude of the reactive parameter or equivalently on the Leslie viscosity coefficients \( \alpha_2 \) and \( \alpha_3 \). When shearing a nematic liquid crystal two different types of flow behaviour are possible, depending on the signs of \( \alpha_2 \) and \( \alpha_3 \). For rod-like molecules, \( \alpha_2 \) is always negative, while \( \alpha_3 \) can be negative for flow alignment systems (\( \lambda > 1 \)) or positive for non-alignment systems (\( 1 > \lambda > 0 \)) [6].

Leslie viscosities can be expressed in terms of two main components, elastic and viscous, \( \alpha_i = \alpha_i^E + \alpha_i^V \). Viscous components of Leslie viscosities
3.2. Estimation of Rheological Functions and Landau Viscosity Coefficients

are given by \[1, 31\].

\[
\begin{align*}
\alpha_1^V &= 10 C \bar{\eta} \beta^*_V S_4 \\
\alpha_2^V &= \alpha_3^V = 0 \\
\alpha_4^V &= \alpha_5^V = \frac{4}{21} C \bar{\eta} \beta^*_V (7 - 10 S_2 + 3 S_4) \\
\alpha_6^V &= \frac{20}{7} C \bar{\eta} \beta^*_V (S_2 - S_4)
\end{align*}
\]

(3.10)

Elastic components of Leslie viscosities have been formulated by \[29, 30\] as expressed in equations 3.11.

\[
\begin{align*}
\alpha_1^E &= -2 \bar{\eta} \beta^*_S S_4 \\
\alpha_4^E &= \bar{\eta} \beta^* \left( \frac{2}{35} \right) (7 - 5 S_2 - 2 S_4) \\
\alpha_2^E &= -\bar{\eta} \beta \left( 1 + \frac{1}{\lambda} \right) S_2 \\
\alpha_5^E &= \bar{\eta} \beta \left[ \frac{1}{7} \beta (3 S_2 + 4 S_4) + S_2 \right] \\
\alpha_3^E &= -\bar{\eta} \beta \left( 1 - \frac{1}{\lambda} \right) S_2 \\
\alpha_6^E &= \bar{\eta} \beta \left[ \frac{1}{7} \beta (3 S_2 + 4 S_4) - S_2 \right]
\end{align*}
\]

(3.11)

According to \[1\], \(C\) is the dimensionless concentration, \(C = \frac{c}{c^*}\) where \(c\) is the number of molecules per unit volume and \(c^*\) is a characteristics concentration proposed by Doi et al. \[30\] to be a function of the molecular dimensions, \(c^* = 16/\pi d l^2\), where \(l\) and \(d\) are length and diameter of the LC molecules respectively. Moreover, \(\beta^*_V\) is a dimensionless group equal to the ratio of viscous to elastic contributions, \(\beta^*_V = (\xi_{str} D^*_r) / k_B T\), where \(\xi_{str}\) has a nature of drag coefficient, \(\xi_{str} = (k_B T / 2 D_{r0})\); \(\bar{\eta}\) is the characteristic viscosity that can be expressed as, \(\bar{\eta} = c^* k_B T / (10 D^*_r)\), where \(k_B\) is the Boltzmann constant, \(T\) is the temperature and \(D^*_r\) represents the microstructural rotational diffusivity at concentration equal to \(c^*\). According to \[69\] for rod like molecules, \(D^*_r\) is a function of the rotational diffusivity in dilute solutions, \(D_{r0}\),

\[
\tilde{D}^*_r = B D_{r0} (c^* \beta^*)^{-2} \\
\text{where} \quad D_{r0} = \frac{3 k_B T \ln (p) - \gamma}{\pi \eta_s l^3}
\]

(3.12)

In equation 3.12, \(B\) is the numerical correction parameter, \(\eta_s\) is the apparent viscosity of the solvent, \(\gamma\) is a constant to correct the edge effect which is a function of the molecular aspect ratio \((p)\) and is equal to 0.8 through this study \[68\].

In equations 3.10 and 3.11, \(S_2\) and \(S_4\) can be obtained using second and forth order Legendre polynomials, \(P_2\) and \(P_4\) respectively \[1\].

\[
\begin{align*}
S_2 &= \langle P_2 (x) \rangle \\
P_2 (x) &= \frac{1}{2} (3 x^2 - 1) \\
S_4 &= \langle P_4 (x) \rangle \\
P_4 (x) &= \frac{1}{8} (35 x^4 - 30 x^2 + 3)
\end{align*}
\]

(3.13)
3.2. Estimation of Rheological Functions and Landau Viscosity Coefficients

Various correlations have been proposed to estimate the value of reactive parameter as a function of dimensionless concentration. According to [30], reactive parameter can be expressed as,

\[ \lambda = 1 - \frac{0.0129 C^4 - 0.00129 C^6}{C^2 - 0.091875 C^4 - 0.02765 C^6} \]

and according to [1] the value of reactive parameter as a function of molecular aspect ratio, \( n^{\text{2nd}} \) and \( n^{\text{4th}} \) order Legendre polynomials was reported as,

\[ \lambda = \frac{\beta (5S_2 + 16S_4 + 14) / (35S_2)}{(p^2 - 1) / (p^2 + 1)} \]

where \( \beta \) is the effective aspect ratio of LC molecules; for rod-like molecules \( p = l/d \). Both of them converge to one for high concentration of molecules in solvent. In this study, the first reactive parameter was referred as \( \lambda_D \) and second one was referred as \( \lambda_L \) for the sake of simplicity. For the case of lyotropic LCs \( S_2 \) and \( S_4 \) can be simplified and expressed as a function of dimensionless concentration [29, 30].

\[
S_2 = 1 - 0.14726C^{-2} - 3.344 \times 10^{-1}C^{-4} - 1.49 \times 10^{-1}C^{-6} + \ldots \\
S_4 = 1 - 0.49087C^{-2} - 2.713 \times 10^{-1}C^{-4} - 1.56 \times 10^{-1}C^{-6} + \ldots 
\]

Doi [30] implemented equation 3.12 to 3.14 to simplify correlations 3.11 as follows,

\[
\frac{\alpha_i^E}{\bar{\eta}} = a_{i1}C + a_{i2}C^{-1} + a_{i3}C^{-3} \quad \text{for} \quad i = 1, 2, \ldots, 6 
\]

where, \( a_{i1} \), \( a_{i2} \) and \( a_{i3} \) from equation 3.15 were presented in table 3.1.

<table>
<thead>
<tr>
<th>( i )</th>
<th>( a_{i1} )</th>
<th>( a_{i2} )</th>
<th>( a_{i3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-( \frac{5}{2} )</td>
<td>0.767</td>
<td>0.182</td>
</tr>
<tr>
<td>2</td>
<td>-( \frac{7}{3} )</td>
<td>-0.215</td>
<td>-0.011</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0.123</td>
<td>0.051</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.123</td>
<td>0.038</td>
</tr>
<tr>
<td>5</td>
<td>( \frac{5}{7} )</td>
<td>-0.153</td>
<td>-0.081</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>-0.245</td>
<td>-0.041</td>
</tr>
</tbody>
</table>

Table 3.1: Coefficients \( a_{i1} \), \( a_{i2} \) and \( a_{i3} \) used to calculate Leslie viscosities [30]

According to [17, 70], requiring the entropy production to be positive,
3.2. Estimation of Rheological Functions and Landau Viscosity Coefficients

![Diagram of shear rates and director orientations]

Figure 3.1: The Miesowicz viscosities, corresponding to the orientation of the director along one of the three axis \( \eta_a \), for the director along the flow direction, \( \eta_b \) for the director along the velocity gradient direction, and \( \eta_c \) for the vorticity axis.

the following thermodynamic inequalities must be satisfied:

\[
\begin{align*}
\alpha_4 & \geq 0 \\
2\alpha_1 + 3\alpha_4 + 2\alpha_5 + 2\alpha_6 & \geq 0 \\
2\alpha_4 + \alpha_5 + \alpha_6 & \geq 0 \\
-4\gamma_1 (2\alpha_4 + \alpha_5 + \alpha_6) & \geq (\alpha_2 + \alpha_3 - \gamma_2)^2 
\end{align*}
\]  

(3.16)

In equation (3.16) \( \gamma_1 \) is rotational viscosity, \( \gamma_1 = \alpha_2 - \alpha_3 \) and \( \gamma_2 \) is irrotational torque coefficient, \( \gamma_2 = \alpha_5 - \alpha_6 \) [6].

Besides Leslie viscosities, Miesowicz viscosities are important for describing the anisotropic behaviour and the rheology of liquid crystalline states. [71]. The three Miesowicz viscosities correspond to three primary orientations of the director of LC molecules fixed with an external force field as shown in figure 3.1.

- Director parallel to the flow direction, \( \eta_a \)
- Director parallel to the velocity gradient direction, \( \eta_b \)
- Director parallel to the vorticity axis, \( \eta_c \)

\[
\begin{align*}
\eta_a & = \frac{1}{2} (\alpha_3 + \alpha_4 + \alpha_6) \\
\eta_b & = \frac{1}{2} (\alpha_4 + \alpha_5 - \alpha_2) \\
\eta_c & = \frac{1}{2} \alpha_4 
\end{align*}
\]  

(3.17)

Theoretically, in high enough shear rates, viscous forces are dominant and align all the molecules approximately parallel to the flow direction and the value of apparent viscosities is equal to the alignment viscosity, \( \eta_{al} \) [24, 72, 73]. Dimensionless alignment viscosity was presented in equation (3.18):

\[
\tilde{\eta}_{al} = \tilde{\eta}_a + \frac{1}{2} (\tilde{\eta}_b - \tilde{\eta}_a) \left( 1 - \frac{1}{\lambda} \right) + \frac{\tilde{\alpha}_1}{4} \left( 1 - \frac{1}{\lambda^2} \right)
\]  

(3.18)
3.3 Experimental Method

Where, \( \tilde{\alpha}_i \) \((i = 1, \ldots 6)\) are the dimensionless Leslie viscosity equal to \( \alpha_i/\tilde{\eta} \) and \( \tilde{\eta}_i \) are the dimensionless Miesowicz viscosity equal to \( \eta_i/\tilde{\eta} \).

Finally, the values of viscosity coefficients from the Landau–de Gennes model can be obtained by mapping the total stress tensor from the Landau–de Gennes model by the one from the Leslie–Ericksen model \([24]\). Based on Grecov’s calculations,

\[
\begin{align*}
\tilde{\alpha}_1 &= 2\tilde{\nu}_4 S^2 - \beta^2 S^2(\frac{8}{9} - \frac{8}{9} S + \frac{S^2}{147}) \\
\tilde{\alpha}_2 &= -\frac{1}{3}\beta S(2 + S - \frac{S^2}{2}) - S^2 \\
\tilde{\alpha}_3 &= -\frac{1}{3}\beta S(2 + S - \frac{S^2}{2}) + S^2 \\
\tilde{\alpha}_4 &= \tilde{\nu}_1 - \frac{2}{3}\tilde{\nu}_2 S + \frac{1}{3}\tilde{\nu}_4 S^2 + \frac{4}{3}\beta^2(1 - S - \frac{S^2}{7}) \\
\tilde{\alpha}_5 &= \tilde{\nu}_2 + \frac{4}{3}\beta S[2 + S - \frac{S^2}{2} + (4 - S - S^2)] \\
\tilde{\alpha}_6 &= \tilde{\nu}_2 - \frac{1}{3}\beta S[2 + S - \frac{S^2}{2} - (4 - S - S^2)]
\end{align*}
\] (3.19)

By rearranging equations [3.19], values of \( \tilde{\nu}_1, \tilde{\nu}_2 \) and \( \tilde{\nu}_4 \) can be obtained as a function of Leslie viscosity coefficients \( \alpha_i \), scalar order parameter \( S \) and \( \beta \).

3.3 Experimental Method

Freeze-dried NCC, produced according to \([9]\), has been dispersed in DI water to prepare 5, 7 and 10 wt% concentrations of NCC aqueous suspensions. To ensure proper dispersion, the samples were sonicated (Ultrasonic processor VCX-130, Sonics and Materials Inc.) for 1000 \( Jg^{-1} \) of NCC. Ultrasonic treatment was carried out in an ice bath to avoid sample overheating.

The rheological measurements were performed using a rotational rheometer (MCR-501 Anton Paar Physica) with a parallel plate glass geometry of 43 \( [mm] \) in diameter. The steady state shear viscosity versus shear rate curves were generated for all samples for shear rates in the range from 0.01 to 100 \( [s^{-1}] \). For each sample, the time required to reach steady state at 0.01 \( [s^{-1}] \) was determined by a transient test; the sampling time used to generate the flow curves was decreased with increasing shear rate. To avoid sample evaporation, a small amount of silicone oil was placed on the periphery of samples together with an evaporation blocker. All rheological measurements were performed at temperature of 25\(^\circ\)C.
3.4 Calculation of Rheological Material Functions and Landau Viscosity Coefficients for Aqueous Suspensions of NCC

In this section we present the calculation of rheological material functions from the Leslie–Ericksen theory and Landau viscosity coefficients for aqueous suspensions of NCC for a range of concentrations, 4 to 22 wt%. Beside the concentrations, the most important input data is the size of the molecules. Aspect ratio and size of the particles were obtained by [9] through TEM imaging techniques.

Ureña et al. [32] reported the concentration of the NCC aqueous suspension in liquid crystalline phase consistent with the results of Shafiei et. al [9]. As discussed in previous section Leslie viscosities can be expressed as a function of dimensionless concentration of molecules per unit volume of their suspensions. In figure 3.2, 3.3 and 3.4 values of dimensionless Leslie viscosities \( \tilde{\alpha}_1 \), Miesowicz viscosities \( \tilde{\eta}_1 \), alignment \( \tilde{\eta}_{al} \) and Landau \( \tilde{\nu}_i \) viscosity coefficients as a function of dimensionless concentration have been reported for NCC aqueous suspension.

![Figure 3.2: Dimensionless Leslie viscosities \( \tilde{\alpha}_1 \) as a function of dimensionless concentration \( \frac{c}{c^*} \) for NCC aqueous suspension](image-url)

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3.4. Calculation of Rheological Material Functions and Landau Viscosity Coefficients for Aqueous Suspensions of NCC

![Graph of Dimensionless Miesowicz viscosities $\tilde{\eta}_i$ and alignment viscosity, $\tilde{\eta}_{al}$ vs. dimensionless concentration $c^*$ for NCC aqueous suspension](image1)

Figure 3.3: Dimensionless Miesowicz viscosities $\tilde{\eta}_i$, and alignment viscosity, $\tilde{\eta}_{al}$ vs. dimensionless concentration $c^*$ for NCC aqueous suspension

![Graph of Dimensionless Landau viscosity coefficients $\tilde{\nu}_i$ vs. dimensionless concentration $c^*$ for NCC aqueous suspension](image2)

Figure 3.4: Dimensionless Landau viscosity coefficients $\tilde{\nu}_i$ vs. dimensionless concentration $c^*$ for NCC aqueous suspension
3.4. Calculation of Rheological Material Functions and Landau Viscosity Coefficients for Aqueous Suspensions of NCC

Figure 3.5: Reactive parameter, rotational diffusivity vs. $C$ of NCC aqueous suspension for different values of the numerical correction parameter, $B$

Figure 3.6: Characteristic viscosity $\bar{\eta}$ vs. $C$ of NCC aqueous suspension for different values of the numerical correction parameter, $B$
3.4. Calculation of Rheological Material Functions and Landau Viscosity Coefficients for Aqueous Suspensions of NCC

Beside the aspect ratio and concentration of NCC molecules that has a huge impact on the magnitude of characteristic viscosities, the value of numerical correction parameter $B$ is equally important. In order to estimate the value of $B$, a series of trial and error numerical experiments have been performed; in figures 3.5 and 3.6 values of reactive parameter ($\lambda$), rotational diffusivity ($\bar{D}_r$) and characteristic viscosity coefficient ($\bar{\eta}$) for different values of numerical correction parameter $B$ have been reported. Viscosity of lyotropic liquid crystalline state as a function of shear rate has three regions [31], starting with a shear thinning followed by plateau and second shear thinning regions. For aqueous suspensions of NCC, the experimental value of apparent viscosity in the plateau region represents the flow–alignment mode; the qualitative alignment state of liquid crystalline phase of the NCC aqueous suspension captured by polarized light microscopy imaging technique employed by Shafiei et al. [9]. The alignment viscosity of aqueous suspensions of NCC based on Doi model for reactive parameter has been matched with the experimental apparent viscosity of the same suspensions in high shear rate ($\dot{\gamma} \approx 10$) for concentrations of 5, 7 and 10 wt% NCC suspensions and the results have been reported in figure 3.7.

![Alignment Viscosity and Apparent Viscosity](image)

Figure 3.7: Alignment viscosity of 5, 7 and 10 wt% NCC aqueous suspension, from experimental [9] and analytical calculations for different values of the numerical correction factor, $B$
Alignment viscosity with $B = 5 \times 10^4$ had shown good agreement with experimental results and for this value of $B$ dimensionless ratio of viscous to elastic contributions $\beta^*_V$ was equal to 0.003.

3.5 Numerical Methods

In order to verify the procedure of obtaining Leslie viscosities, Landau viscosity coefficients and the other calculated parametric characteristic values, series of numerical experimentation were performed for shear flow of 7 wt% NCC aqueous suspension. A set of partial differential equations (3.1) consisting of five equations and five unknowns was solved simultaneously for transient simple shear flow between two parallel plates using COMSOL Multiphysics 4.3b. A linear velocity profile between the two plates was implemented (distance between the plates is one tenth of the length of the domain), where the upper plate was moving and the bottom plate was fixed.

COMSOL is a commercial package that uses finite element methods to discretize continuously the liquid crystalline material domain. General PDE ($G$) module was used to predict evolution of flow—induced microstructure inside the domain. Parallel sparse direct solver ($PARDISO$) with adaptive relaxation factor and second order backward differentiation formula ($BDF$) for time stepping were used to solve these set of equations. Acceptable relative error was set to be equal to $10^{-6}$, mesh independency of the final solutions were accepted based on the standard methods. The final mesh consists of 4000 quadrilateral elements with average element quality of 0.963 and 21105 number of degree of freedom ($DOFs$).

In each one of these tests, start—up simple shear flow was numerically simulated under different shear rates; initial condition was set to be equal to absolute randomness between the molecules and periodic condition with zero flux was set for the inlet and outlet of the domain. Moreover, the anchoring angle of NCC molecules was set to be parallel to the wall boundaries which was reflected in order parameter tensor as follows,

$$Q_B = S_{eq} \cdot \begin{bmatrix} \frac{2}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{bmatrix}$$

(3.20)

In equation (3.20) $S_{eq}$ represented the equilibrium state of the scalar order parameter, $S_{eq} = \frac{1}{4} + \frac{3}{4} \sqrt{1 - \frac{8}{37}}$. In table 3.2, the list of all the characteristic parametric values and viscosity coefficients that has been used for 7 wt% NCC aqueous suspension was given.
3.6 Selected Results

The values were calculated based on the size of particles and concentration. All the results from next section pertain to insignificant $De$ numbers where flow only affects macroscopic orientation.

<table>
<thead>
<tr>
<th>$Er$</th>
<th>$De$</th>
<th>$R$</th>
<th>$\Theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^2 - 10^8$</td>
<td>$10^{-7} - 10^{-1}$</td>
<td>$10^9$</td>
<td>2.2</td>
</tr>
<tr>
<td>$l [nm]$</td>
<td>$d [nm]$</td>
<td>$L_1 [pN]$</td>
<td>$L_2 [pN]$</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>43.29</td>
<td>6.687</td>
</tr>
<tr>
<td>$\lambda_D$</td>
<td>$c^* [#/m^4]$</td>
<td>$Dr^*$</td>
<td>$Dr$</td>
</tr>
<tr>
<td>0.8792</td>
<td>$1.02 \times 10^{25}$</td>
<td>1041.8</td>
<td>1334</td>
</tr>
<tr>
<td>$\tilde{\nu}_1$</td>
<td>$\tilde{\nu}_2$</td>
<td>$\tilde{\nu}_4$</td>
<td>$U$</td>
</tr>
<tr>
<td>0.5057</td>
<td>0.3138</td>
<td>-0.4383</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3.2: List of all characteristic parametric values for 7 wt% NCC aqueous suspension implemented in the Landau–de Gennes model and extra–stress tensor for the start up shear flow simulations

3.6 Selected Results

The modified shear stress was calculated using the Landau viscosity coefficients $\tilde{\nu}_1 = 0.5057$, $\tilde{\nu}_2 = 0.3138$ and $\tilde{\nu}_4 = -0.4383$ in viscous contribution of the stress. The shear stress and apparent viscosity were compared with experimental results in figure 3.8. Acceptable agreement between numerical and experimental results was observed validating the analytical predictions for Leslie viscosity coefficients [31] and for Landau viscosity coefficients [24]. In figure 3.8, the numerical predictions of shear stress were slightly underestimating the experimental results. For relatively low viscosity materials, the resistant torque, which is a basis of calculation in rheometry, is very small and measurement error due to the sensitivity of torque sensor is a viable source of error. Furthermore, the calculation of the Landau viscosity coefficients was based on analytical correlations and moreover on the numerical parameter $B$, selected to match the experimental alignment viscosity; a slight change in $B$ has considerable influence on the value of Landau viscous coefficients followed by change in shear stress magnitude, that potentially could be another source of the disparity between numerical and experimental shear stress. Moreover, the counter influence of the microstructure on the macro–scale attributes of the flow (change in velocity profile and pressure
Figure 3.8: Shear stress tensor and apparent viscosity as a function of shear rate, from numerical simulations and from rheological experiments for 7 wt% NCC aqueous suspension.

distribution) was not considered. A better prediction of apparent viscosity and shear stress would be expected by considering this interaction. Finally, another source of error could be the absence in the total stress of any extra term related to the chiral elasticity.

In figure 3.9, scalar order parameter, $S = \frac{3}{2} \mu_n$ was presented for three different shear rates, $\dot{\gamma} = 1, 5$ and $10 \text{ [s}^{-1}]$. For low shear rates chiral behaviour of NCC aqueous suspension was observed; although, by increasing the shear rate, flow aligning model was dominant inside the system. In order to have a better understanding of the orientational order of 7 wt% NCC aqueous suspension, magnified snapshots of schematic representation of molecules were presented in figure 3.10 for different shear rates at $t = 100 \text{ [s]}$. Once again the transition from chirality to flow aligning by increasing shear rate is evident. Due to the fact that tensor order parameter has negative eigenvalues, for the schematic representation of molecules, a new tensor $M$ was introduced; where $M = Q + \frac{1}{3} I$. Triaxial ellipsoids were used to represent NCC molecules. Major axis of ellipsoids was selected to comply the direction of the eigenvector corresponding to the largest eigenvalue of $M$; while, first and second minor axes of the ellipsoids were aligning to the
3.6. Selected Results

Figure 3.9: Scalar order parameter $S$ at $t = 100$ [s] for shear rate $\dot{\gamma}$ a) 1 b) 5 and c) 10 [s$^{-1}$]

direction of eigenvectors corresponding to the second largest and smallest eigenvalues of $M$ at any given point in space [74]. The aspect ratio of three axes of each ellipsoids were obtained relative to the first, second and third eigenvalues of the modified tensor order parameter $M$.

According to the polarized light microscopy tests performed by Shafiei et al [9] for 5 wt% concentration of NCC aqueous suspension, cholesteric fingerprints of liquid crystalline state was observed at low shear rates followed by flow alignment at higher shear rate. The same behaviour was observed in numerical experiments for 7 wt% NCC suspension in the bulk of the fluid, although close to the wall boundaries, a small layer of molecules was under the influence of the strong anchoring. The cholesteric helix uncoiled and became flow aligned when the viscous flow torque has overcome the chiral elastic energy.
Figure 3.10: Schematic representation of NCC molecules at $t = 100 \, [s]$ for shear rate $\dot{\gamma}$ (top) 1 (middle) 5 and (bottom) 10 $[s^{-1}]$
3.7 Summary and Remarks

A methodology was proposed to calculate the rheological functions and Leslie / Landau viscosity coefficients in order to solve Landau–de Gennes governing equations for NCC aqueous suspension which is a cholesteric lyotropic liquid crystals.

By adjusting the numerical correction parameter $B$, theoretical alignment viscosity of NCC aqueous suspension has been matched with the experimental apparent viscosity of the 5, 7 and 10 wt% NCC aqueous suspensions. Evolution of the microstructure of the liquid crystalline state had been studied by implementing the Landau–de Gennes theory for transient simple shear flow between two parallel plates on 7 wt% NCC aqueous suspension under known velocity profile. Values of the Landau viscosity coefficients ($\tilde{\nu}_i$) were calculated based on the Leslie viscosity coefficients and were implemented in the total stress tensor in the Landau–de Gennes model.

Apparent viscosity and shear stress were calculated and compared with the experimental results for the same concentration. Scalar order parameter and schematic representation of the molecules were presented for three different shear rates that exhibited transition from chirality to flow aligning by increasing the value of the shear rate. Therefore, due to the chiral nature of NCC aqueous suspensions, a cholesteric pattern was observed at low shear rates, however by increasing the shear rates flow–alignment regime were achieved.
Chapter 4

Landau–de Gennes Nematodynamics Theory

The main objective of this chapter was to numerically simulate the behaviour of nematic LCs in a geometry similar to a journal bearing, in relation to the application of LCs as lubricants. Therefore, a complete set of equations for the evolution of the microstructure coupled with 2–D Navier–Stokes equations has been solved. In this chapter, the evolution of the microstructure modelled using the Landau–de Gennes theory, was linked with the Navier–Stokes equations using a modified total stress tensor established in the momentum equations. The flow characteristics and the orientation of the liquid crystal molecules for different rotational velocities of the inner cylinder were investigated. Flow and rheological properties, defects nucleation and their evolution inside the domain have been studied. The flow–induced structural changes and the orientation–induced flow were analyzed for different Reynolds numbers and Energy ratios. At the end, 3–d analysis of the flow of liquid crystalline materials vs. synovial fluid diagnosed with rheumatoid arthritis was chosen in a simplified geometry of a prosthetic hip joint.

This chapter was organized as follows. First we presented the governing equations that describe the microstructure and flow for lyotropic nematics. Then the numerical procedure was presented. Following this, the numerical results for start–up shear flow was investigated, the effect of the Reynolds number and the Energy Ratio on the microstructure and rheological properties are presented. Numerical methods, selected results for 3–dimensional flow of LC materials in a simplified prosthetic hip joint were presented. Finally conclusions were given.

4.1 Theory and Governing Equations

In this paper we study the flow of lyotropic liquid crystals between eccentric cylinders. The Landau-de Gennes nematodynamics equations are well suited for predicting texture formation since defects are non-singular solutions of
4.1. Theory and Governing Equations

the governing equations. The evolution equations based on the Landau-de Gennes theory and the Navier Stokes equations have been used to model the isothermal flow of lyotropic liquid crystals.

The evolution equation describes the microstructure of liquid crystalline state using a traceless and symmetric second order tensor order parameter, \( Q \). Based on the definition which has been given by de Gennes and Prost

\[
Q = \int (uu - \frac{1}{3}) \omega d^2 u \quad [61],
\]

where \( u \) is the unit vector that is either normal to the surface of disk-like molecules or parallel to the long chain of rod-like molecules of LCs and \( I \) represent the identity tensor (see Figure 2.1) and \( \omega \) is the orientation distribution function.

Furthermore, the tensor order parameter \( Q \) can also be expressed as a function of its main eigenvalues and eigenvectors,

\[
Q = S (mm - \frac{1}{3}I) + \frac{1}{3}P (mm - lI)
\]  

In equation \([4.1]\), \( S = \frac{3}{2} \mu_n \) and \( P = 3 \mu_n + \frac{3}{2} \mu_m \), where \( \mu_n \), \( \mu_m \) and \( \mu_l \) are the eigenvalues corresponding to the largest eigenvector \( n \) (uniaxial director), the second largest eigenvector \( m \) and smallest eigenvector \( l \) respectively.

The uniaxial director, \( n \) is a dimensionless vector, which represents the direction of the preferred orientation of the liquid crystals’ molecules. Figure 2.1 shows the orientation vector of each molecule with respect to \( n \) and the orientation angle \( \theta \).

The evolution equation describes the dynamics of liquid crystals through the following equation,

\[
\ddot{Q} = F (\nabla v, Q) + H^{sr} (\overrightarrow{D}_r, Q) + H^{fr} (\overrightarrow{D}_r, \nabla Q)
\]  

In equation \([4.2]\) \( F \) is the flow contributions,

\[
F = \frac{3}{2} \beta A + \beta \left[ A \cdot Q + Q \cdot A - \frac{2}{3} (A : Q) I \right] - \frac{1}{2} \beta \left\{ (A : Q) Q + A \cdot Q \cdot Q + Q \cdot A + Q \cdot Q \cdot A - (Q : Q) A I \right\}
\]

where \( \beta \) is a shape parameter; \( A = \frac{1}{2} [\nabla v + (\nabla v)^T] \) is the rate of deformation tensor and \( v \) is the velocity profile. Short-range elasticity (\( H^{sr} \)) arises from the inter-molecular forces and can be expressed as,

\[
H^{sr} = 6D_r \left[ \left( \frac{U}{3} - 1 \right) Q + UQ \cdot Q - U (Q : Q) \cdot (Q + \frac{1}{3}I) \right]
\]

Where \( U \) is the nematic potential and \( \overrightarrow{D}_r \) represents the microstructural rotational diffusivity \([68]\), a process by which the equilibrium statistical distribution of the overall orientation of molecules is preserved and it is defined
4.1. Theory and Governing Equations

by,

\[ \mathcal{D}_r (Q) = D_r \left[ 1 - \frac{3}{2} (Q : Q) \right]^{-2} \] (4.5)

In equation [4.5] \( D_r \) is the pre-averaged rotational diffusivity.

Long-range elasticity \( (H^{lr}) \), transmits the surface anchoring effects from the wall boundaries to the bulk of the fluid.

\[ H^{lr} = \frac{6D_r L_1}{ck_BT} \left\{ \nabla^2 Q + L^* \frac{1}{2} \left[ \nabla (\nabla \cdot Q) + \left[ \nabla (\nabla \cdot Q) \right]^T - \frac{2}{3} tr(\nabla (\nabla \cdot Q)) \right] \right\} \] (4.6)

In equation [4.6], \( L^* = L_2/L_1 \) where \( L_i \) are Landau coefficients; \( c \) represents the concentration of molecules in liquid crystalline state; \( k_B \) is the Boltzmann constant; \( T \) is the absolute temperature. \( Q \) is the Jaumann derivatives of the order parameter tensor that can be defined as,

\[ \hat{Q} = \frac{\partial Q}{\partial t} + (v \cdot \nabla) Q - W \cdot Q + Q \cdot W \] (4.7)

where \( W \) is the vorticity tensor, \( W = \frac{1}{2} [\nabla v - (\nabla v)^T] \).

The evolution of the microstructure has a considerable impact on the velocity profile and pressure distribution that brings up the necessity to modify the liquid crystals’ stress tensor for completing the model and to take into account the complexity of the physical phenomenon. The total stress tensor for the nematic liquid crystalline materials has three main components; the symmetric components, containing viscous and elastic terms, \( \tau_v \) and \( \tau_e \) respectively, \( \tau_s = \tau_v + \tau_e \); asymmetric component, \( \tau_a \) and Ericksen stress tensor, \( \tau_{Er} \).

\[ \tau_t = \tau_a + \tau_s + \tau_{Er} \] (4.8)

\[ \tau_v = \nu_1 A + \nu_2 \left[ Q \cdot A + A \cdot Q - \frac{2}{3} (Q : A) I \right] + \nu_3 \left\{ (A : Q) Q + A \cdot Q \cdot Q \right. \]
\[ + Q \cdot A \cdot Q + Q \cdot Q \cdot A + \left[ (Q : Q) A \right] I \} \] (4.9)

\[ \tau_e = ck_BT \left\{ \frac{-2\beta}{3} H - \beta \left[ H \cdot Q + Q \cdot H - \frac{2}{3} (H : Q) I \right] \right\} + \frac{\beta}{2} \left\{ (H : Q) Q \right. \]
\[ + H \cdot Q \cdot Q + Q \cdot H \cdot Q + Q \cdot Q \cdot H + \left[ (Q : Q) I \right] \} \] (4.10)

\[ \tau_a = ck_BT \left\{ H \cdot Q - Q \cdot H \right\} \] (4.11)

\[ \tau_{Er} = ck_BT L_1 \left\{ L^* (\nabla \cdot Q) \cdot (\nabla Q)^T - \nabla Q \cdot (\nabla Q)^T \right\} \] (4.12)
In the above equations, $H$ represents the combination of short-range and long-range elasticity, $H = H^{sr} + H^{lr}$; $\nu_i$ are Landau viscosity coefficients that can be derived from mapping the shear stress of the Landau-de Gennes theory with the one of Leslie-Ericksen theory [24]. For solving numerically the evolution equation along with modified Navier-Stokes equations, a set of dimensionless variables was introduced to simplify the equations; (a) Ericksen number, $Er$, the ratio of viscous flow effect to long-range elasticity (b) Deborah number, $De$, the ratio of viscous flow effect to short-range elasticity and (c) energy ratio, $R$, the ratio of short-range elasticity to long-range elasticity.

\[ Er = \frac{Vhck_BT}{6L_1D_r} \quad De = \frac{V}{6hD_r} \quad R = \frac{ck_BT h^2}{L_1} \quad (4.13) \]

In equation [4.13] $V$ is the characteristic velocity or sliding velocity of the inner cylinder and $h=R_2-R_1$, where $R_1$ is the inner cylinder radius and $R_2$ is the outer cylinder radius. By introducing the Ericksen and the Deborah numbers, the dimensionless form of the evolution equation is,

\[ \hat{Q} = F + \left( \frac{1}{De} \right) H^{sr} + \left( \frac{1}{Er} \right) H^{lr} \quad (4.14) \]

Moreover, a new Reynolds number was defined as, $Re_n = \rho V^2 / (ck_BT)$, where $\rho$ is a characteristic density. Thus, the dimensionless modified Navier-Stokes equation for the isothermal flow of nematic liquid crystalline material can be defined as,

\[ \frac{\partial \mathbf{v}^*}{\partial t^*} + (\mathbf{v}^* \cdot \nabla^*) \mathbf{v}^* = -\nabla^* p^* + \nabla^* \cdot \tau^*_t \quad (4.15) \]

Where,

\[ \tau^*_t = \frac{\tau_t}{ck_BT} = \tau^*_a + \tau^*_e + \left( \frac{E_r}{R} \right) \cdot \tau^*_v + \left( \frac{1}{R} \right) \cdot \tau^*_Er \quad (4.16) \]

Where, $\tau^*_t$ described dimensionless shear stress for each component of the total shear stress.

### 4.2 Computational Methods

Continuity equation along with equations 4.14 and 4.15 are a set of six coupled non-linear PDEs that inherited the parabolic nature from evolution equation and hyperbolic and elliptic nature from Navier-Stokes equations. The governing equations of liquid crystalline state in two dimensions were
4.2. Computational Methods

solved using Laminar flow module (*SFP*) and PDE general module (*G*) of COMSOL Multiphysics 4.3b. COMSOL uses Galerkin FEM method and a Multifrontal Massive Parallel sparse direct Solver (*MUMPS*) with adaptive relaxation factor and variable backward differentiation formula (*BDF*) for time stepping to solve these set of equations. Acceptable relative error was set to be equal to $10^{-8}$, absolute convergences and mesh independency of the final solutions were established based on the standard methods; in this case, wall shear stress on the inner cylinder were calculated for fine, finer, extra fine and extremely fine automatic meshing options in the software, since wall shear stress value was exactly the same for both extra fine and extremely fine methods, extra fine option was implemented to generate the final mesh. Final mesh has 48042 elements with minimum element quality equal to 0.7475 and average element quality equal to 0.9862.

The initial orientation of the molecules was set to be random in the flow plane, which was set by implementing the scalar order parameter, $S = 0$. In this case, if $U \leq \frac{8}{3}$ the state of the fluid is considered isotropic. For $\frac{8}{3} \leq U \leq 3$, dual phase of the nematic and isotropic states are predicted. Moreover, for higher values of nematic potential, uniaxial nematic phase of liquid crystals is expected. In this article, $U = 4$ was chosen for the numerical simulations.

![Figure 4.1: Numerical domain and boundary conditions](image-url)
4.2. Computational Methods

Numerical domain was presented in figure 4.1 with the outer cylinder fixed and the inner cylinder rotating with a velocity $V$. The boundary conditions for velocity and pressure are shown in figure 4.1. The eccentricity ratio is $\varepsilon/(R_2 - R_1) = 0.5$, where $\varepsilon$ is the eccentricity. The boundary condition for the tensor order parameter corresponding to a tangential orientation of molecules with respect to the wall boundaries was set using $Q = Q_B$,

$$Q_B = S_{eq} \cdot \begin{bmatrix} \frac{y^2}{x^2+y'^2} - \frac{1}{3} & \frac{-xy}{x^2+y^2} & 0 \\ \frac{-xy}{x^2+y^2} & \frac{x^2}{x^2+y^2} - \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{bmatrix}$$ (4.17)

In equation 4.17, the equilibrium scalar order parameter is, $S_{eq} = \frac{1}{4} + \frac{3}{4} \sqrt{1 - \frac{8}{3\eta}}$; the simulation parameters that have been used in this study are: $\beta = 0.99$, $L^* = 0.45$, $\nu_1^* = 1$, $\nu_2^* = -1$ and $\nu_4^* = 6$, [25].

![Figure 4.2: Orientation angle of MBBA as a function of the dimensionless gap between the inner and outer cylinder at the centreline, $Re_n = 1.4 \times 10^{-4}$, $De = 1.3$ and $Er = 2.4 \times 10^4$ for different dimensionless times](image)

In order to evaluate the accuracy of the numerical method, transient two dimensional flow of MBBA\textsuperscript{12} between two concentric cylinders was solved \textsuperscript{12}N-(4-Methoxybenzylidene)-4-butylaniline
4.3. Results and Discussion

using the Landau-de Gennes theory. The anchoring angle of the molecules on wall boundaries was set to zero or the molecules were aligned perpendicular to the surface normal vector; initial condition was set to be complete randomness [75].

For MBBA the Leslie coefficients at 30°C were tabulated by [66, 76] in table 2.3. In general, for any flow-aligning nematic liquid crystals the alignment angle is a function of rotational viscosity \( \gamma_1 = \mu_3 - \mu_2 \) and irrotational torque coefficient \( \gamma_2 = \mu_6 - \mu_5 \) [23] and can be expressed as \( \theta_0 = \frac{1}{2} \cos^{-1} (-\gamma_1/\gamma_2) \). By calculating rotational viscosity and irrotational torque coefficients based on the data presented in table 2.3, we found for MBBA an alignment angle \( \theta_0 = 5.7^\circ \).

Figure 4.3: Molecular orientation of MBBA, \( Re_n = 1.4 \times 10^{-4}, De = 1.3, Er = 2.4 \times 10^4, t = 10^5 \) at the centreline for \( t = 10^5 \)

Figure 4.2 shows the orientation angle, \( \theta \), of MBBA molecules at the centreline, from numerical simulations based on the Landau-de Gennes theory. The results are consistent with the theoretical value for the alignment angle, with an error less than 1%. Based on these results, the orientation of molecules between two concentric cylinders at the centreline was illustrated in figure 4.3.

4.3 Results and Discussion

The start-up shear flow of nematic liquid crystals between two eccentric cylinders was modelled using the Landau-de Gennes nematodynamics model for \( 10^{-4} \leq Re_n \leq 10^2, Er = 10^6 \) and \( 10^8 \), \( De = 10 \) and \( R = 10^5 \) and \( 10^7 \).

This section is divided into three sub-sections. In the first sub-section, different flow properties and the microstructure are illustrated for different time steps for two different Reynolds numbers. In the second sub-section the same properties and microstructure are presented as a function of the
Reynolds number for two time steps. Finally the impact of the Energy ratio (R) on the microstructure of LCs is discussed.

4.3.1 Start-up Flow

Flow, rheological properties and microstructure of liquid crystalline materials were presented for $De=10$, $Er=10^8$ and $Re_n=10^{-2}$ and $10^2$.

Before presenting the results, it is important to mention some significant aspects related to the flow of liquid crystals, already known from previous studies, that will contribute to our understanding of the flow between eccentric cylinders:

1. The flow between eccentric cylinders is very complex as it is a combination of shear, rotational and extensional flows, which occur in different regions of the domain [40].

2. The flow of liquid crystalline materials is governed by the balance between the inertial forces and viscous forces, and the structure is governed by the balance between long/short-range elasticity and viscous contributions.

3. For high Ericksen numbers ($Er$) the influence of long-range elasticity contributions is relatively small compared to viscous contribution.

4. For Deborah number $De \geq 1$ we have a molecular process and the flow affects the eigenvalues and eigenvectors of $Q$.

5. Based on the set of experiments performed by Larson et al. [77, 78] for large Ericksen numbers and $De \geq 5$, shear flow uniform texture-free samples are expected.

6. Extensional flow aligns the molecules along the streamlines [40].

In figures 4.4 and 4.5 the streamlines for start-up flow of liquid crystalline material between two eccentric cylinders were presented for $Re_n=10^{-2}$ and $10^2$ respectively. For $Re_n=10^{-2}$, the magnitude of viscous forces was small compared with the elastic contribution. The recirculations region was stretched for dimensionless time, $t=50$. By further marching in time quasi-steady state condition was reached; the flow streamlines became more and more stable and the impact of microstructure evolution on the streamlines was decaying in time. Moreover, the occurrence of instabilities was limited to the central part of the recirculations region that was illustrated at $t=500$ and 1000.
Figure 4.4: Flow streamlines for $De=10$, $Er=10^8$ and $Re_n=10^{-2}$ at dimensionless times: a) $t=50$, b) $t=100$, c) $t=500$ and d) $t=1000$

Figure 4.5: Flow streamlines for $De=10$, $Er=10^8$ and $Re_n=10^2$ at dimensionless times: a) $t=50$, b) $t=100$, c) $t=500$ and d) $t=1000$
Figure 4.6: Dimensionless pressure contours for $De=10$, $Er=10^8$ and $Re_n=10^{-2}$ at dimensionless times: a) $t=50$, b) $t=100$, c) $t=500$ and d) $t=1000$

Figure 4.7: Dimensionless pressure contours for $De=10$, $Er=10^8$ and $Re_n=10^2$ at dimensionless times: a) $t=50$, b) $t=100$, c) $t=500$ and d) $t=1000$
4.3. Results and Discussion

For $Re_n=10^2$, the magnitude of viscous forces was higher and became dominant. The amplitude and frequency of the instabilities for the recirculations streamlines were smaller and the quasi-steady state was reached earlier than for $Re_n=10^{-2}$. It should be noted that for both Reynolds numbers, the streamlines contours at steady state were qualitatively similar to the Newtonian case, showing that the impact of microstructure was not very significant.

In order to further study the impact of microstructure on the macro-scale attributes of the flow of liquid crystalline material pressure distribution for various times was illustrated in figures 4.6 and 4.7. For $Re_n=10^{-2}$, by marching in time, quasi-steady state was reached after $t=100$. However, the absolute maximum and minimum values of pressure did not change with time. For $Re_n=10^2$, the quasi-steady state was reached earlier in time.

In order to compare further the macro-scale attributes of the flow of liquid crystalline materials with Newtonian fluids, a hypothetical Newtonian fluid was chosen as follows: $\nu_1^*$ from the liquid crystal viscous stress expression from Landau-de Gennes theory represents the isotropic segment of the viscosity coefficients, therefore viscosity of the hypothetical Newtonian fluid was set to $\nu_1=Dev_1^*ck_BTh/V$. For each one of the cases with $Re_n=10^{-2}$ and $Re_n=10^2$, flow of a hypothetical Newtonian fluid was simulated in the same geometry; for the hypothetical Newtonian fluid, $Re = \rho V h/\nu_1$.

Certainly, the start-up flow regime is important for journal bearings, for example with respect to the initial load carrying capacity or the overshoot of the friction torque. The figures 4.8, 4.9, 4.10, 4.11, 4.12 and 4.13 present dimensionless pressure, dimensionless first normal stress difference ($N_1^* = \tau_{xx}^* - \tau_{yy}^*$), and dimensionless wall shear stress along the inner cylinder for various times, showing the approach to steady state values. All the above figures show the liquid crystalline material behaviour compared with the hypothetical Newtonian fluid behaviour.

The maximum value of dimensionless pressure, dimensionless first normal stress difference and dimensionless wall shear stress for LC materials had an overshoot around $t = 100$ for the low Reynolds number and $t = 5$ for the high Reynolds number. From solid design point of view, information regarding the maximum amount of stress or pressure inside the system is very important.
4.3. Results and Discussion

Figure 4.8: Dimensionless first normal stress difference $N_1^*$ vs. dimensionless rotational angle along the inner cylinder for various dimensionless times, $De=10$, $Er=10^8$ and $Re_n=10^{-2}$ (left), for Newtonian fluid, $Re=10^{-3}$ (right).

Figure 4.9: Dimensionless first normal stress difference $N_1^*$ vs. dimensionless rotational angle along the inner cylinder for various dimensionless times, $De=10$, $Er=10^8$ and $Re_n=10^2$ (left), for Newtonian fluid, $Re=10$ (right).
4.3. Results and Discussion

Figure 4.10: Dimensionless pressure $p^*$ vs. dimensionless rotational angle along the inner cylinder for various dimensionless times, $De=10$, $Er=10^8$ and $Re_n=10^{-2}$ (left), for Newtonian fluid, $Re=10^{-3}$ (right).

Figure 4.11: Dimensionless pressure $p^*$ vs. dimensionless rotational angle along the inner cylinder for various dimensionless times, $De=10$, $Er=10^8$ and $Re_n=10^2$ (left), for Newtonian fluid, $Re=10$ (right).
4.3. Results and Discussion

Figure 4.12: Dimensionless wall shear stress $\tau_{w}^* \text{ vs. dimensionless rotational angle along the inner cylinder for various dimensionless times, } D_{e}=10, E_r=10^8 \text{ and } Re_n=10^{-2} \text{ (left), for Newtonian fluid, } Re=10^{-3} \text{ (right)}$

Figure 4.13: Dimensionless wall shear stress $\tau_{w}^* \text{ vs. dimensionless rotational angle along the inner cylinder for various dimensionless times, } D_{e}=10, E_r=10^8 \text{ and } Re_n=10^2 \text{ (left), for Newtonian fluid, } Re=10 \text{ (right)}$
4.3. Results and Discussion

By comparing the difference between maximum and minimum amount of dimensionless pressure, it can be concluded that the liquid crystalline material has a greater pressure difference hence higher load carrying capacity. Not only the magnitude of the maximum pressure for LC was higher for both Reynolds numbers comparing with hypothetical Newtonian fluid under the same conditions, but the ratio between the maximum pressure of LC material with $Re_n=10^2$ to $Re_n=10^{-2}$ was also larger comparing with the same ratio for hypothetical Newtonian fluid.

The quasi-steady state condition for the region close to the inner cylinder was achieved by marching in time. In the case of LC, for $Re_n=10^2$ flow properties converged after few simulation time steps (around $t=55$) and for $Re_n=10^{-2}$ they converged close to time step $t=550$. On the other hand, for the hypothetical Newtonian fluid for the low Reynolds number, the convergence to the steady state condition occurred faster compared with the one of high Reynolds number. Indeed, considering the impact of elasticity at $Re_n=10^{-2}$ for LC can explain this difference. Qualitatively, all the flow properties are similar for LC and Newtonian fluid, although the magnitude is different. These results are consistent with the results for flow streamlines.

As discussed before, by marching in time, quasi-steady state was reached for all the flow properties, and a balance between elastic, viscous and inertial forces was reached. Therefore, the stability of liquid crystalline microstructure under the same elastic, viscous and inertial forces was foreseeable through the simulation time. For rod-shape molecules of the liquid crystalline material, stability is accessible through the alignment of director vector with respect to the local velocity vectors.

In order to analyze the order of the liquid crystalline molecules, the contours of the scalar order parameter ($S$) were presented for $Re_n=10^{-2}$ and $10^2$ in figures 4.14 and 4.15 at different dimensionless time frames. Scalar order parameter corresponds to the largest eigenvalue of the order parameter tensor and confines between zero and one. Higher values of scalar order parameter indicates higher degree of orientational order in the domain with one indicating absolute ideal order between molecules and lower values of $S$ indicates lower degree of orientational order with zero corresponds to absolute randomness between molecules or isotropic state. Furthermore, lower value of scalar order parameter occurs in vicinity of disclination lines and defect points. Nucleation and evolution of defects depends on various factors related to intrinsic properties of liquid crystals and the shape of domain.
4.3. Results and Discussion

Figure 4.14: Distribution of scalar order parameter $S$ between two eccentric cylinders for $D_e=10$, $Er=10^8$ and $Re_n=10^{-2}$ for dimensionless time $s)$ $t=1$, b) $t=10$, c) $t=50$, d) $t=100$, e) $t=500$, and f) $t=1000$
4.3. Results and Discussion

Figure 4.15: Distribution of scalar order parameter $S$ between two eccentric cylinders for $De=10$, $Er=10^8$ and $Re_n=10^2$ for dimensionless times a) $t=1$, b) $t=10$, c) $t=50$, d) $t=100$, e) $t=500$, and f) $t=1000$
4.3. Results and Discussion

Viscous contributions in evolution of the microstructure tend to align all the molecules in the direction of flow; on the other hand, the elastic contributions transmit the surface anchoring effects from the wall to the bulk of the fluid. For the case of lower Reynolds number $Re_n=10^{-2}$, the orientation of the molecules evolved from absolute randomness at $t=0$ to nearly ordered at $t=100$ due to the viscous forces obtained from rotation of the inner cylinder. Formation of a disclination line close to the outer rim of the gap was observed along with the development of the orientational order, that was stretched through the centre of the recirculation zone between the upward flow and downward flow.

However, for the higher value of Reynolds number $Re_n=10^2$ the pattern was more complicated; at $t=20$ nearly all the molecules in the domain were aligned except the vicinity of the disclination line; however, by marching in time, the disclination line became more and more unstable and small defect zones were generated and evolved through the simulation time.

Through the simulation time, the flow in the small gap has been primarily shear flow that reached the flow-alignment mode in the early stages of simulation; no defect point or stretch of disclination lines have been observed in the small gap region through the simulation time. Despite the fact that microstructure was evolving in time as it had been illustrated in figures 4.14 and 4.15, the macro-scale attributes of the flow reached a quasi-steady state at time step $t=1000$, even though the quasi-steady state of the microstructure only occurred at the low Reynolds number. At high Reynolds number, the directors were essentially unsteady as it was observed at $t=1000$ and $Re_n=10^2$; this phenomenon has been observed before by other researchers [79].

In order to obtain a broad understanding and exploring the interconnection of flow and microstructure of liquid crystalline materials, molecular representation of LCs was illustrated in figures 4.16 and 4.17 for the Reynolds numbers equal to $10^{-2}$ and $10^2$. Due to the complexity of the flow close to the outer rim of the domain, magnified snapshots have been presented solely for the sake of better visualization of the microstructure. The fingerprint texture of LCs was demonstrated and defects in the texture of the fluid were tracked over the simulation time. Due to the fact that tensor order parameter has negative eigenvalues, for the schematic representation of molecules, a new tensor $M = Q + \frac{1}{3}I$ was introduced. Triaxial ellipsoids were used to represent LC molecules. Major axis of ellipsoids was selected to comply the direction of the eigenvector corresponding to the largest eigenvalue of $M$; while, first and second minor axes of the ellipsoids were aligning to the direction of eigenvectors corresponding to the second largest and smallest.
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eigenvalues of $M$ at any given point in space [74]. The aspect ratio of three axes of each ellipsoids were obtained relative to the first, second and third eigenvalues of the modified tensor order parameter $M$.

In this study the initial condition was set to be absolute randomness for the LC molecules; at first few dimensionless time steps the spatial derivative of the eigenvalues of the tensor order parameter was negligible which resulted in degradation of the triaxial ellipsoids to spheres. For the sake of visualization, the time steps with complete randomness were omitted from this report. In figure 4.16 for $Re_n=10^{-2}$ at $t=50$, part of the domain close to the inner cylinder was in liquid crystalline state (shown by the ellipsoidal shape); however, part of the domain close to the outer rim was in isotropic state. At $t=100$, two different domains were observed. One was close to the inner cylinder under the influence of viscous contributions with alignment of the LC molecules along the flow streamlines. The second domain was located close to the outer cylinder under the influence of the large-elasticity contributions and the curvature of the wall boundary. In the darker region, these two contributions were both present. At time $t=500$ and particularly at $t=1000$ a disclination line and later defect points were nucleated between these two domains.

In order to categorize defects, the number of brushes [6], $(N_d)$ connected to the defect point has to be counted, $S_d=\frac{1}{4} (N_d)$. Most of the defects that have been observed in this study could be categorized with strength, $S_d=\pm \frac{1}{2}$. Schematic representation of each category was illustrated in figure 4.16. For the high value of Reynolds number, the texture pattern was more complex. LC molecules aligned with smaller alignment angles with respect to the velocity vector and two distinctive domains under the influence of viscous and elastic contributions occurred earlier in simulation time; the disclination line developed as a result of their encounter. At $t=500$ the disclination line was dissembled into smaller domains containing defects; the interactions of these domains resulted in several different smaller defect domains that propagated inside the gap between the cylinders.
4.3. Results and Discussion

Figure 4.16: Magnified snapshots of the ellipsoidal representation of the LC molecules for $De=10$, $Er=10^8$ and $Re_n=10^{-2}$ for dimensionless times a) $t=50$, b) $t=100$, c) $t=500$, d) $t=1000$ and schematic representation of defect points with strength $S_d=\pm \frac{1}{2}$.
Figure 4.17: Magnified snapshots of the ellipsoidal representation of the LC molecules for $De=10$, $Er=10^8$ and $Re_n=10^2$ for dimensionless times a) $t=50$, b) $t=100$, c) $t=500$, d) $t=1000$ and schematic representation of defect points with strength $S_d=\pm\frac{1}{2}$. 
4.3. Results and Discussion

4.3.2 Effect of Re on Microstructure—Flow Properties

In this section, two simulation time steps were selected to compare the effect of the Reynolds number on the flow and microstructure of NLCs. Other dimensionless groups were set as follows, $De=10$ and $Er=10^8$. The comparison range for Reynolds number was set to $10^{-4} \leq Re \leq 10^2$; two time steps ($t=100$ and $t=1000$) were chosen to make sure the start-up and quasi-steady states that have been described previously were captured and compared for different values of the Reynolds numbers.

![Figure 4.18: Dimensionless first normal stress difference $N_1^*$ vs. dimensionless rotational angle along the inner cylinder for various dimensionless Reynolds numbers, $De=10$, $Er=10^8$ at $t=1000$](image)

The dimensionless first normal stress difference, dimensionless pressure and dimensionless wall shear stress on the inner cylinder vs. dimensionless rotational angle along the inner cylinder for various Reynolds numbers were illustrated in figures 4.18, 4.19 and 4.20 at $t=1000$. By increasing the magnitude of the Reynolds number, value of dimensionless first normal stress difference and dimensionless pressure were increased; the antisymmetry that was observed for the dimensionless first normal stress difference at low Reynolds numbers was disturbed at higher Reynolds numbers. With respect to the lubrication problem in journal bearings, the region with higher magnitude of wall shear stress is probable to be more affected by the
Figure 4.19: Dimensionless pressure $p^*$ vs. dimensionless rotational angle along the inner cylinder for various dimensionless Reynolds numbers, $Re_n$ for $De=10$, $Er=10^8$ at $t=1000$

wear process.

The influence of the Reynolds number on the scalar order parameter was presented in figures 4.21 and 4.22. At $t=100$ and $Re_n=10^{-4}$, the weak viscous forces resulted in less orientational order in the most part of the domain. However, by increasing the Reynolds number, the disclination line occurred in the vicinity of the outer rim and the width of the domain that was occupied by defects decreased due to the viscous contributions. At $t=100$ and $Re_n=10^2$, only a small portion of the domain was not ordered. The $t=1000$ case was more complicated, since the disclination line became more and more unstable by increasing the Reynolds number and it was divided into several different groups of defects. Propagation and evolution of the defects inside the domain was discussed in the previous section.

Based on the results for scalar order parameter, the evolution of microstructure was highly dependent on the value of the Reynolds number. It was expected to find the same influence for the schematic representation of the molecules. In figures 4.23 and 4.24 the schematic representation of LC molecules between the eccentric cylinders was illustrated using ellipsoids for $t=100$ and $t=1000$. The same method that was described in the previous
4.3. Results and Discussion

Figure 4.20: Dimensionless wall shear stress $\tau^*$ vs. dimensionless rotational angle along the inner cylinder for various dimensionless Reynolds numbers, $Re_n$ for $De=10$, $Er=10^8$ at $t=1000$

section was implemented to visualize LC molecules. For the sake of easier detection of all minor alterations in orientation of the molecules, magnified snapshots of domain were presented.

As expected for $t=100$ and $Re_n=10^{-4}$ most of the domain was not affected by the rotation of the inner cylinder. However, by increasing the Reynolds number, viscous contribution became predominant; at $t=100$ and $Re_n=10^{-2}$ two distinct regions co-existed for a period of simulation time. One was under the influence of the viscous contributions due to the rotation of the inner cylinder and the other region was located close to the outer rim more likely to be under the influence of the anchoring angle of the molecules on the wall boundary due to the long-range elasticity contributions. The darker zone in between, exhibited isotropic state, in other words, the balance between elastic and viscous contributions prevented the dark zone to exhibit any alteration from isotropic state.

A polydomain structure was observed by increasing the Reynolds number; the darker portion of the domain became thinner and turned into a disclination line. As observed in 4.23, two distinct flow-aligned domains co-existed at the same time inside the gap between the cylinders. One domain
which was predominant, had smaller alignment angle that tends to zero by increasing the Reynolds number. The second domain kept the initial orientational angle between the director and the flow streamlines through the simulation time. For $t=1000$ and $Re_n=10^2$ the groups of defects predicted by scalar order parameter, were detected inside the domain; the director became more unstable and an onset of defect nucleation was observed in the schematic representation of the molecules. Furthermore, the ordered layer of liquid crystalline molecules in vicinity of solid surfaces formed a protective layer against wear for the two rubbing surfaces that makes the liquid crystalline materials potentially a viable candidate to be used as lubricants.
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Figure 4.21: Scalar order parameter contours for $D_e=10$, $E_r=10^8$ at $t=100$ for various Reynolds numbers a) $Re_n=10^{-4}$, b) $Re_n=10^{-2}$, c) $Re_n=10^{-1}$, d) $Re_n=1$, e) $Re_n=10$, f) $Re_n=10^2$
4.3. Results and Discussion

Figure 4.22: Scalar order parameter contours for $De=10$, $Er=10^8$ at $t=1000$ for various Reynolds numbers a) $Re_n=10^{-4}$, b) $Re_n=10^{-2}$, c) $Re_n=10^{-1}$, d) $Re_n=1$, e) $Re_n=10$, f) $Re_n=10^2$
Figure 4.23: Magnified snapshots of the ellipsoidal representation of the LC molecules, $D_e=10$, $E_r=10^8$ at $t=100$ vs. Reynolds numbers a) $Re_n=10^{-4}$, b) $Re_n=10^{-2}$, c) $Re_n=10^{-1}$, d) $Re_n=1$, e) $Re_n=10$, f) $Re_n=10^2$.
Figure 4.24: Magnified snapshots of the ellipsoidal representation of the LC molecules, $D_e=10$, $Er=10^8$ at $t=1000$ vs. Reynolds numbers a) $Re_n=10^{-4}$, b) $Re_n=10^{-2}$, c) $Re_n=10^{-1}$, d) $Re_n=1$, e) $Re_n=10$, f) $Re_n=10^2$
4.3. Results and Discussion

4.3.3 Effect of Energy Ratio on Microstructure–Flow Properties

In order to investigate the influence of the Energy ratio $R$ on the micro/macroscale attributes of the flow, the following dimensionless variables were used: $Re_n=10^{-2}$ and 1, $De=10$ and $Er=10^6$ and $10^8$ which resulted in $R=10^5$ and $10^7$. As discussed before, by decreasing the Ericksen number, long-range elasticity contribution was increased comparing to viscous contribution.

In figures [4.25] and [4.26], the flow streamlines and pressure distributions between the eccentric cylinders were presented at $t = 150$. The time step was chosen to emphasize on the differences between the two energy ratios. For lower value of Energy ratio, long-range elasticity contributions became more important in comparison with short-range elasticity; therefore, numerous vortices were occurred inside the system due to the contribution of elasticity over the viscous contribution in transient mode.

Figure 4.25: Flow streamlines at $t=150$, a) $R=10^7$, $Re_n=10^{-2}$, b) $R=10^5$, $Re_n=10^{-2}$, c) $R=10^7$, $Re_n=1$ and d) $R=10^5$, $Re_n=1$
Figure 4.26: Dimensionless pressure contours at $t=150$, a) $R=10^7$, $Re_n=10^{-2}$, b) $R=10^5$, $Re_n=10^{-2}$, c) $R=10^7$, $Re_n=1$ and d) $R=10^5$, $Re_n=1$

Figure 4.27: Scalar order parameter at $t=150$, a) $R=10^7$, $Re_n=10^{-2}$, b) $R=10^5$, $Re_n=10^{-2}$, c) $R=10^7$, $Re_n=1$ and d) $R=10^5$, $Re_n=1$
4.3. Results and Discussion

Although, these vortices gradually disappeared by marching in time, for both Reynolds numbers the streamlines exhibited the same type of vortices for the lower value of energy ratio; however, for $Re_n=1$ these vortices occurred close to the outer rim comparing with the central location of the vortices for $Re_n=10^{-2}$. Moreover, in transient mode of $R=10^5$ and $Re_n=10^{-2}$ the viscous contributions could not stabilize the flow even in the small gap between the two cylinders and a group of vortices occurred in this region. That was not observed in any other combination of dimensionless variables.

Influence of the flow for two energy ratios ($R$) on the scalar order parameter was presented in figure 4.27; as observed before, the disclination line and centre of the recirculation zone were co-located inside the domain through the simulation time. At $t=150$ for $Re_n=10^{-2}$ by decreasing the energy ratio, several different defect domains were nucleated inside the system. The same polydomain structure was observed in schematic representation of the molecules in figure 4.28. Four isotropic domains along with ordered domains co-existed to generate a remarkable texture. Inside the ordered domain, several sub-domains with different orientations of the director were observed for $Re_n=10^{-2}$ and $R=10^5$. By increasing the Reynolds number, the ordered sub-domains were unified under the dominant viscous forces and the orientation of the directors coalesced mainly to the direction of the velocity vectors. In other words, for transient mode when the elasticity is dominant, the flow was induced by evolution of microstructure.
Figure 4.28: Schematic representation of molecules at $t=150$, a) $R=10^7$, $Re_n=10^{-2}$, b) $R=10^5$, $Re_n=10^{-2}$, c) $R=10^7$, $Re_n=1$ and d) $R=10^5$, $Re_n=1$
4.4 3-D Analysis of NLC Flow in a Simplified Prosthetic Hip Joint

Isothermal flow of lyotropic nematic LCs under start—up flow between two eccentric semi—spheres as a model for prosthetic hip joint’s capsular space has been numerically simulated by solving mass, momentum and evolution of order parameter equations (see equations 4.14 and 4.16). In order to study the flow—induced texture of liquid crystalline microstructure, formation and evolution of defects, Landau—de Gennes model has been implemented.

4.4.1 Numerical Methods for 3—Dimensional Model

The governing model that has been described by equations 4.14 to 4.16 is a set of ten coupled non—linear partial differential equations (PDEs) that inherited their intrinsic parabolicity from the evolution equation, and the hyperbolic and elliptic nature from Navier—Stokes equations. Three—dimensional governing equations of an isothermal liquid crystalline material in simplified capsular domain of an artificial hip joint for transient shear flow induced by rotation of the artificial head of femur was numerically simulated with laminar flow module (SPF) and PDE general module (G) embedded in COMSOL Multiphysics. COMSOL is a commercial CFD package that discretize continuous domain using Finite Element methods and implements MUltifrontal Massive Parallel sparse direct Solver (MUMPS) with adaptive relaxation factor and variable backward differentiation formula to find time steps.

The space and time evolution of six components of the tensor order parameter \( Q_{11}, Q_{12}, Q_{13}, Q_{22}, Q_{23}, Q_{33} \) were incorporated as a set of six parabolic equations in G module; at each time step, evolution equations have been solved, and the components of the total stress tensor were evaluated and incorporated in SPF module, which resulted in alteration of the velocity profile and pressure distribution. At the next time step, modified velocity and pressure were implemented in evolution equations to apply the counter impact of macro-scale attributes of the flow on microstructure.

Mesh independency and convergence of the final solution was established according to the standard procedures. Acceptable relative infinity—norm of error \( (L_\infty) \) was used as convergence criterion and threshold of acceptable relative error was set to \( 10^{-6} \). The grid that was implemented in this study has 1,808,947 tetrahedral elements with minimum element quality of 0.2555,
average element quality of 0.7681 and 4,728,250 degrees of freedom (DOF).

The numerical domain was represented in figure 4.29, all the measurements were in dimensionless format using the radius of the outer concave of acetabulum as characteristic length; furthermore, geometry of the numerical domain was characterized by two dimensionless parameters, $\mu = (R_2 - R_1)/R_1 \approx 0.055$ and $\epsilon = \varepsilon/(R_2 - R_1) = 0.2$, where, $R_1$ is the radius of the head of femur, $R_2$ is the radius of acetabulum and $\varepsilon$ is the eccentricity along $x$–axis. All the dimensions were selected based on [80, 81].

Initial condition of molecules was set to absolute randomness or an isotropic state and for boundary conditions at the solid walls, rotational velocity of the head of artificial femur was selected to be equal to slow forward rotation. The boundary condition for tensor $\mathbf{Q}$ was set to ensure the tangential orientation of the anchoring angle of the molecules with respect to the wall boundaries as follows,

$$
\mathbf{Q}_B = \frac{S_{eq}}{A} \begin{bmatrix}
(y \cos \psi)^2 - \frac{A}{3} & yz \sin \psi \cos \psi - xy \cos^2 \psi & -y^2 \sin \psi \cos \psi \\
yz \sin \psi \cos \psi - xy \cos^2 \psi & (z \sin \psi - x \cos \psi)^2 - \frac{A}{3} & xy \sin \psi \cos \psi - yz \sin^2 \psi \\
-y^2 \sin \psi \cos \psi & xy \sin \psi \cos \psi - yz \sin^2 \psi & (y \sin \psi)^2 - \frac{A}{3}
\end{bmatrix}
$$

(4.18)

In equation 4.18, dummy variable $A = y^2 + (z \sin \psi - x \cos \psi)^2$; where, $x$, $y$ and $z$ are spacial coordinates of the boundaries, and $\psi$ is the transverse angle of the acetabular inlet plane [82]. Some other parameters that have been used
in this study were set to certain values according to [25] as follows, $\beta=0.99$, $L_2^*=0.45$, $\nu_1^*=1$, $\nu_2^*=-1$ and $\nu_4^*=6$.

### 4.4.2 Selected Results for 3–Dimensional Model

The three–dimensional model which is a set of 10 equations and 10 unknowns has 4,728,250 number of degrees of freedom. Therefore, due to the computational cost of solving those equations, a parametrical study would have been very long and difficult. Thus, a set of dimensionless variables was chosen in order to match the isotropic segment of viscosity coefficient ($\nu_1$) with the viscosity of synovial fluid from patients diagnosed with RA\textsuperscript{14}, which is a Newtonian fluid. The dimensionless variables for nematic liquid crystals (NLCs) were selected as follows $Re_n=1$, $Er=9.756 \times 10^5$ and $De=10$. In the case of Newtonian fluids Reynolds number, $Re = \rho V h/\nu_1$, was implemented. It has been proven that for large Ericksen numbers and $De \geq 5$, shear flow uniform texture–free samples are expected \cite{77, 78}.

In the following three figures, in order to illustrate the magnitude of different flow attributes inside the domain, ten slices perpendicular to the $x$–axis in $y$–$z$ plane were presented. In figures 4.30 and 4.31 dimensionless pressure and first normal stress difference ($N_1^*=\tau_{xx}^* - \tau_{yy}^*$) for LC and for synovial fluid affected by RA at dimensionless time $t=1000$ were presented and compared. The increase in the value of pressure across the gap suggests an increase in the load carrying capacity. In figure 4.31, the raise in the value of the first normal stress difference from synovial fluid affected by RA to liquid crystalline material was observed due to the viscoelastic nature of LC materials.

Dimensionless hydrodynamic wall shear stress on the surface of the prosthetic head of femur was calculated for liquid crystalline material and synovial fluid affected by RA and presented in figure 4.32. According to this figure, the magnitude of wall shear stress was higher for the case of liquid crystalline material and the region with higher magnitude of wall shear stress is probable to be more affected by the wear process. However, for LC the distribution of shear stress was more uniform, indicating that the prediction of life cycle for the head of femur will be more accurate.

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\textsuperscript{14}Rheumatoid Arthritis
4.4. 3–D Analysis of NLC Flow in a Simplified Prosthetic Hip Joint

Figure 4.30: Contour slices of the dimensionless pressure for a) lyotropic liquid crystal with $Er=9.756 \times 10^5$, $De=10$ and $Re_n=1$ b) synovial fluid diagnosed with RA, $Re=0.1$
4.4. 3-D Analysis of NLC Flow in a Simplified Prosthetic Hip Joint

Figure 4.31: Contour slices of the dimensionless first normal stress difference for a) lyotropic liquid crystal with $Er=9.756 \times 10^5$, $De=10$ and $Re_n=1$ b) synovial fluid diagnosed with RA, $Re=0.1$
Figure 4.32: Contours of the dimensionless wall shear stress on the head of artificial femur for a) lyotropic liquid crystal with $Er=9.756 \times 10^5$, $De=10$ and $Re_h=1$ b) synovial fluid affected by RA, $Re=0.1$
Figure 4.33: Contours slices of the scalar order parameter, $Er=9.756 \times 10^5$, $De=10$ and $Re_n=1$ at dimensionless times a) $t=10$ b) $t=1000$
4.4. 3-D Analysis of NLC Flow in a Simplified Prosthetic Hip Joint

As a measure to describe the average orientational distribution of LC molecules around the director for uniaxial liquid crystals, scalar order parameter was presented for two dimensionless time steps, \( t = 10 \) and 1000 in figure [4.33]. By marching in time more molecules align themselves with the orientation of the director vector that forms a protective layer close to the rubbing surfaces that not only reduce the COF but also increase the durability of surfaces by decreasing the wear rate.

Due to the fact that the tensor order parameter has negative eigenvalues, for the schematic representation of molecules, a new tensor \( \mathbf{M} \) was introduced; where \( \mathbf{M} = \mathbf{Q} + \frac{1}{3} \mathbf{I} \). Triaxial ellipsoids were used to represent LC molecules. Major axis of ellipsoids was selected to comply the direction of the eigenvector corresponding to the largest eigenvalue of \( \mathbf{M} \); while, first and second minor axes of the ellipsoids were aligning to the direction of eigenvectors corresponding to the second largest and smallest eigenvalues of \( \mathbf{M} \) at any given point in space [74]. Aspect ratio between transverse diameter and conjugate diameters of the ellipsoids were defined using the ratio of eigenvalues of \( \mathbf{M} \) as presented in figure [4.34].

Magnified snapshots of schematic representation of liquid crystalline molecules were presented in figure [4.35] for the narrow and wide gap of the capsular space of simplified prosthetic hip joint at dimensionless times \( t = 10 \) and 1000. The surface selected to present the molecular representation results had a normal vector of equal to \((\cos \psi, 0, \sin \psi)\), which was parallel to the base cross section of the joint. For \( t = 10 \) only a small portion of the liquid crystalline molecules were under the influence of the inner cylinder rotation and the rest of the domain was in isotropic state. However, by marching in time more and more molecules joined the formation of microstructure in the vicinity of solid boundary acting as a shielding layer against wearing mechanism.
4.4. 3–D Analysis of NLC Flow in a Simplified Prosthetic Hip Joint

Figure 4.34: Schematic of three–axes ellipsoids representing liquid crystalline molecules

Figure 4.35: A magnified slice of schematic representation of liquid crystalline molecules, a) (left) narrow gap (right) wide gap at $t=10$; b) (left) narrow gap (right) wide gap at $t=1000$; $Re_n=1$, $Er=9.756 \times 10^5$ and $De=10$
4.5 Conclusion and Summary

The start–up flow of nematic liquid crystalline molecules were numerically simulated in a capsular space between two eccentric cylinders for various Reynolds numbers and energy ratios. The macro–scale attributes of the NLC’s flow such as, flow streamlines, dimensionless pressure and first normal stress difference along with microstructure characteristics of liquid crystalline meso–phase such as, scalar order parameter and schematic representation of LC molecules were exhibited as a function of time, Reynolds number and energy ratio.

Based on the results for comparison between the Reynolds numbers, for the case of high Reynolds numbers, the flow reached quasi–stationary condition while the microstructure evolution was at unsteady state. As observed in chapter 4 for the case of high values of Ericksen number or lower magnitude of long–range elasticity, the counter influence of microstructure on the flow is negligible, while the flow contributions affect the microstructure indisputably.

Co–existence of aligned and non–aligned domains along with aligned domain with several subdomains with different orientational angle for the director was observed in the liquid crystalline texture. Moreover, nucleation and evolution of disclination line and defect points were tracked through the simulation time. Furthermore, quasi–steady state of macro–scale attributes of the flow was observed in the same time that microstructure was going through unstable mode.

In the vicinity of solid surfaces, liquid crystalline molecules formed an ordered layer, which can be considered as a protective layer for the two rubbing surfaces that reduces the wear scars and decrease the coefficient of friction at the same time; the formation of this layer prove the hypothesis that consider liquid crystalline molecules as a viable candidate to be used as lubricants or bio–lubricants in specific applications. Although, the gap size that has been used in this numerical analysis is considerably larger than the actual gap size in journal bearings; the overall pattern of the flow follow the same behaviour. Thus, it is been expected to observe nucleation of ordered molecular structure in vicinity of the smaller gap region as the same phenomenon has been observed in this study. By considering the fact that this study has been conducted in dimensionless format, any other analysis with the same non-dimensional variables has to follow the same flow and microstructure pattern for any LC material.

Numerical simulation that has been presented for 2–dimensional flow of LC materials between two eccentric cylinders did not considered the con-
tributions of the third components of velocity profile on the molecular microstructure. In order to have a better understanding of the interactions between flow and microstructure of LC materials, running simulations in 3D geometries are believed to be necessary. The 3-dimensional analysis on the flow of liquid crystalline materials in a simplified prosthetic hip joint geometry was performed using the Landau–de Gennes nematodynamics governing equations, showing the formation of LC microstructure inside the domain. Moreover, increase in the values of dimensionless pressure across the head of femur indicated the better load-carrying capacity of liquid crystalline materials as bio-lubricants comparing with Newtonian fluids.
Chapter 5

Conclusion, Contributions and Future Research Directions

In the following section, a summary of different steps taken during this study toward investigating the implementation of liquid crystalline meso−phases as lubricating agents is briefly presented, followed by a list of contributions to this field of research and several suggestions for future research direction.

5.1 Summary and Conclusion

The numerical study of flow−aligning nematic LCs between two concentric cylinders with a very small gap was performed using the Leslie−Ericksen theory. The distribution of the orientational angles of PAA, AZA9, DDA9 and MBBA were investigated for various dimensionless rotational velocities of the inner cylinder. In each case, the orientational angle reached the theoretical alignment angle for the specific LC, which proved the accuracy of the simulation. Moreover, the study of the multiplicity and multistability of the results for MBBA and PAA revealed unstable orientational angles for certain initial treatments. Although the unstable results were legitimate solutions to the Leslie−Ericksen governing equations, they fulfill neither the minimum Frank elasticity energy nor the highest amount of entropy generation rate in comparison with the stable solutions. Therefore, they should not be considered as a physical valid state in nature for those liquid crystalline materials. At the high rotational velocities, viscous terms became dominant and the director reached the alignment angle for the stable solutions; for the case of unstable solutions fluctuations in the alignment angle was observed to propagate inside the system with larger frequencies for the dimensionless rotational velocities $\tilde{\omega} \geq 0.1$.

Finally, viscosity and resistance torque exerted on the inner cylinder were estimated using the Leslie−Ericksen theory and compared to the experi-
mental results, that has been indicating a good agreement. The ratio of the resistance torque for LCs over the one of hypothetical Newtonian fluid was reported, which showed up to 60% energy saving. Thus, as it has been predicted, the preferred orientation of the molecules of liquid crystalline materials in the vicinity of solid surfaces gives them an advantage over isotropic Newtonian fluids by reducing the amount of resistance torque on the inner cylinder.

By implementing the Doi and Larson models for anisotropic viscosity coefficients and reactive parameters of lyotropic nematic liquid crystals, the Leslie viscosity coefficients for various concentration of NCC aqueous suspensions have been calculated. Miesowicz viscosities and the Landau viscosity coefficients used in symmetric viscous stress tensor of the Landau–de Gennes nematodynamics theory have been presented based on the mapping of Landau–de Gennes total stress tensor with the one of the Leslie–Ericksen theory. By adjusting the numerical correction parameter $B$, the theoretical alignment viscosity of NCC aqueous suspension has been matched with the experimental apparent viscosity of the 5, 7 and 10 wt% NCC aqueous suspensions. Evolution of the liquid crystalline microstructure had been studied by implementing the Landau–de Gennes theory for transient simple shear flow between two parallel plates on 7 wt% NCC aqueous suspension under known velocity profile. Values of the Landau viscosity coefficients ($\tilde{\nu}_i$) were calculated based on the Leslie viscosity coefficients, and also were implemented in the total stress tensor in the Landau–de Gennes model. Apparent viscosity and shear stress were determined and compared with the experimental results for the same concentration. Scalar order parameter and schematic representation of the molecules were demonstrated for three different shear rates that exhibited transition from chirality to flow–aligning by increasing the value of the shear rate. Therefore, due to the chiral nature of NCC aqueous suspensions, a cholesteric pattern was observed at the low shear rates; however, flow–alignment regime were achieved by increasing the shear rates.

In conclusion, a methodology has been proposed to calculate different rheological functions and viscosity coefficients for lyotropic liquid crystals using analytical calculations and experimental rheological data. The validation was done using numerical simulations of the Landau–de Gennes equations for start up shear flow of 7 wt% NCC aqueous suspensions and rheological data. Ultimately this study helps connecting the experimental data to the Landau–de Gennes theory and provides meaningful values for its various parameters and coefficients while using the link between Leslie–Ericksen and Landau–de Gennes theories.
5.1. Summary and Conclusion

In the last chapter, the start-up shear flow of nematic liquid crystals between two eccentric cylinders was modelled using the Landau-de Gennes nematodynamics model for $10^{-4} \leq Re \leq 10^2$, $10^4 \leq Er \leq 10^9$ and $1 \leq De \leq 10^2$. The accuracy of the model was tested by comparison with the Leslie-Ericksen theory for flow of MBBA between two concentric cylinders. Flow streamlines, dimensionless pressure distribution, first normal stress difference and wall shear stress, scalar order parameter and schematic representation of the molecules were illustrated as a function of simulation time, the Reynolds number and the Energy ratio, $R$. Interconnection and impact of the texture and defects formation/evolution on velocity profile and pressure distribution was observed; nucleation and evolution of disclination line and defect points were detected and pursued over the simulation time. Based on the results from comparison between the Reynolds numbers, for the case of high Reynolds numbers, the flow reached quasi-stationary condition while the microstructure evolution was at unsteady state. For the higher Ericksen number or lower magnitude of long-range elasticity, the counter influence of microstructure on the flow was negligible, while the flow contributions affected the microstructure indisputably.

Polydomain structure with different orientations of the director was observed in the liquid crystalline texture based on the magnitude of Reynolds number. Moreover, the influence of the Energy ratio and the Reynolds number on the formation and evolution of polydomains was studied.

Furthermore, some of the results from the thesis are related to the lubrication application of LCs and suggest some advantages for using LCs as lubricants:

- the ordered layers of liquid crystalline molecules in vicinity of solid surfaces may reduce the wear and decrease the friction
- the pressure distribution with higher pressure values compared to the Newtonian fluid shows a better load–carrying capacity

Future work involving simulations using realistic parameters for the journal bearing, specific LCs, calculation of the coefficient of friction and the impact of the defects on its value is required to resolve the lubrication problem using LCs.

Flow and microstructure of liquid crystalline state for LCs were investigated in 3-dimensional domain similar to the capsular space of prosthetic hip joint by implementing nematodynamics governing equations of the Landau–de Gennes theory. The modified total stress tensor containing asymmetric, viscous, elastic and Ericksen components was implemented in
5.2. Contributions

Navier–Stokes equations in order to connect the microstructure formation to macro-scale attributes of the flow. Increase in the magnitude of first normal stress difference and pressure difference across the inner semi-sphere was observed for LC comparing with the synovial fluid affected by RA in the same geometry with the same isotropic viscosity segment ($\nu_1$). Higher magnitude of pressure difference across the head of femur will result in higher load-carrying capacity for the proposed liquid crystalline materials compared with synovial fluid affected by RA.

Formation of molecular microstructure in vicinity of solid surfaces with perpendicular orientation to the normal surface vector, which has been already proposed by many studies, was observed. Theoretically, the formation of the microstructure of molecules tangential to the solid surface decreases the wear rate for the two rubbing surfaces and reduces the dissipation rate of energy.

To the best of our knowledge, this is the first study to simulate LCs in a prosthetic hip geometry. Future work involving numerical simulations using different rotational velocities and calculation of specific parameters related to lubrication performance is required.

5.2 Contributions

This section presents the contributions made to the field of Liquid Crystals, as published in several journal / conference articles.

- The application of the Leslie–Ericksen theory for the prediction of the orientation-dependent viscosity for flow-aligning NLCs has been addressed.

- It has been shown that NLCs exhibit less energy dissipation compared to a hypothetical Newtonian fluid with the same isotropic segment of viscosity, by reducing the magnitude of the resistance torque due to the ordered molecular structure.

- A methodology that is based on a semi-empirical model was proposed to predict the rheological functions and variables embedded in the Landau–de Gennes model for lyotropic liquid crystalline materials. The missing link between rheology and the nematodynamics governing equations of liquid crystalline materials has been restored.

- The complex flow of liquid crystalline materials between two eccentric cylinders was studied using the unabridged Landau–de Gennes ne-
matodynamics governing equations coupled with the Navier–Stokes equations. Three types of contribution to the evolution of the microstructure (namely flow, short–range and long–range), as well as four components of the total stress tensor in the Navier–Stokes equations (namely viscous, elastic, asymmetric and Ericksen) were solved simultaneously to derive the unique texture of liquid crystalline materials.

- A parametric study on the influence of texture formation, defect nucleation and evolution upon macro–scale flow attributes of the liquid crystalline materials has been performed; since this was the first time that all characteristics of the Landau–de Gennes theory was implemented at the same time on a complex flow with shear, rotational and extensional features, results should be considered as the chief novelty of this investigation.

- The Landau–de Gennes nematodynamics theory was applied to model the 3–dimensional flow of liquid crystalline materials in the capsular space of the simplified prosthetic hip joint, as a potential enhancement of prosthetic implants design.

5.3 Future Research Directions

Based on the complexity and computational costs associated with the numerical simulation of liquid crystalline meso–phases, a number of potential research directions can be explored by future research:

- Conduct a complete investigation and parametric study of the dimensionless variables of a 3–dimensional flow of liquid crystalline materials in a confined space.

- Investigate the flow of a specific liquid crystalline lubricant between two eccentric cylinders with a gap size comparable to that of journal bearings.

- Explore the rheological and tribological characteristics of a healthy synovial fluid in order to understand its rheological functions.

- Perform an analytical study of the cholesteric texture of chiral liquid crystalline materials and its influence on the elastic components of the total stress tensor.
5.3. Future Research Directions

- Investigate the electro–rheological characteristics of liquid crystalline materials under weak flow contributions as a step toward designing smart liquid crystalline bio–lubricants.
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Appendix A

Leslie–Ericksen Derivations

As mentioned in equation 2.3, $g$ is the intrinsic director body force,

$$g = an - \beta \nabla n + \dot{g} = an - \beta \nabla n - \frac{\partial F_d}{\partial n} + \gamma_1 N + \gamma_2 n \cdot A$$  \hspace{1cm} (A.1)

where $a$ and $\beta$ are arbitrary constants, \[18\] and \[6\],

$$\dot{g}_1 = -(k_{33} - k_{22}) \left[ \sin \theta \left( \frac{d\theta}{dr} \right)^2 - \frac{\cos \theta}{r} \frac{d\theta}{dr} \right] + (\gamma_1 + \gamma_2) \frac{\xi}{r} \cos \theta \frac{d\omega}{dr}$$

$$\dot{g}_2 = (k_{33} - k_{22}) \left[ \frac{\sin \theta}{r} \frac{d\theta}{dr} - \frac{\cos \theta}{r^2} \right] + (\gamma_2 - \gamma_1) \frac{\xi}{r} \sin \theta \frac{d\omega}{dr}$$  \hspace{1cm} (A.2)

and $\pi$ is the intrinsic director surface stress tensor and can be explained as follow,

$$\pi = \beta n + \hat{\pi} = \beta n + \frac{\partial F_d}{\partial \nabla n}$$  \hspace{1cm} (A.3)

where,

$$\hat{\pi}_{11} = \left[ k_{11} + (k_{33} - k_{22}) \sin^2 \theta \right] \cos \theta \frac{d\theta}{dr} + \left[ k_{11} - k_{22} - (k_{33} - k_{22}) \cos^2 \theta \right] \frac{\sin \theta}{r}$$

$$\hat{\pi}_{12} = -\left[ k_{22} + (k_{33} - k_{22}) \sin^2 \theta \right] \sin \theta \frac{d\theta}{dr} + \left[ k_{33} - k_{22} \right] \sin^2 \theta \frac{\cos \theta}{r}$$

$$\hat{\pi}_{21} = (k_{33} - k_{22}) \sin \theta \cos^2 \theta \frac{d\theta}{dr} - \left[ k_{22} + (k_{33} - k_{22}) \cos^2 \theta \right] \frac{\cos \theta}{r}$$

$$\hat{\pi}_{22} = \left[ k_{11} - k_{22} - (k_{33} - k_{22}) \sin^2 \theta \right] \cos \theta \frac{d\theta}{dr} + \left[ k_{11} + (k_{33} - k_{22}) \cos^2 \theta \right] \frac{\sin \theta}{r}$$  \hspace{1cm} (A.4)
Appendix A. Leslie–Ericksen Derivations

For the case of couette flow of liquid crystalline materials between two concentric cylinders, shear stress terms in equation (2.5) can be simplified to,

\[
\begin{align*}
t_{11}^0 &= -f(\theta) \left( \frac{d\theta}{dr} \right)^2 + \frac{1}{2r} \frac{df(\theta)}{d\theta} \frac{d\theta}{dr} \\
t_{12}^0 &= \frac{1}{r} f(\theta) \frac{d\theta}{dr} - \frac{1}{2r} \frac{df(\theta)}{d\theta} \\
t_{21}^0 &= \frac{1}{r} \left[ f(\theta) + \frac{1}{2} \frac{d^2 f(\theta)}{d\theta^2} \right] \frac{d\theta}{dr} - \frac{1}{2} \frac{df(\theta)}{d\theta} \left( \frac{d\theta}{dr} \right)^2 \\
t_{22}^0 &= -\frac{1}{r^2} f(\theta) + \frac{1}{2r} \frac{df(\theta)}{d\theta} \frac{d\theta}{dr}
\end{align*}
\] (A.5)

and,

\[
\begin{align*}
t_{11}' &= \frac{r}{2} \frac{d\omega}{dr} \left[ 2\alpha_1 \sin^3 \theta \cos \theta + (\alpha_2 + \alpha_3 + \alpha_5 + \alpha_6) \sin \theta \cos \theta + \alpha_4 \right] \\
t_{12}' &= \frac{r}{2} \frac{d\omega}{dr} \left[ g(\theta) \right] \\
t_{21}' &= \frac{r}{2} \frac{d\omega}{dr} \left[ 2g(\theta) + \gamma_1 + \gamma_2 \cos 2\theta \right] \\
t_{22}' &= \frac{r}{2} \frac{d\omega}{dr} \left[ 2\alpha_1 \sin \theta \cos^3 \theta + (\alpha_5 + \alpha_6 - \alpha_2 - \alpha_3) \sin \theta \cos \theta + \alpha_4 \right]
\end{align*}
\] (A.6)

where, \( f(\theta) = k_{11} \cos^2 \theta + k_{33} \sin^2 \theta \), and \( 2g(\theta) = 2\alpha_1 \sin^2 \theta \cos^2 \theta + (\alpha_6 + \alpha_3) \cos^2 \theta + (\alpha_5 - \alpha_2) \sin^2 \theta + \alpha_4 \)
Appendix B

Landau–de Gennes Derivations

In evolution equation \([4,7]\) Jaumann derivatives of order parameter tensor can be described as follow,

\[ \dot{Q}_{11} = \frac{\partial Q_{11}}{\partial \tilde{t}} + \tilde{u} \frac{\partial Q_{11}}{\partial \tilde{x}} + \tilde{v} \frac{\partial Q_{11}}{\partial \tilde{y}} + \tilde{w} \frac{\partial Q_{11}}{\partial \tilde{z}} - 2 \tilde{W}_{12} Q_{12} - 2 \tilde{W}_{13} Q_{13} \]

\[ \dot{Q}_{22} = \frac{\partial Q_{22}}{\partial \tilde{t}} + \tilde{u} \frac{\partial Q_{22}}{\partial \tilde{x}} + \tilde{v} \frac{\partial Q_{22}}{\partial \tilde{y}} + \tilde{w} \frac{\partial Q_{22}}{\partial \tilde{z}} + 2 \tilde{W}_{12} Q_{12} - 2 \tilde{W}_{23} Q_{23} \]

\[ \dot{Q}_{12} = \frac{\partial Q_{12}}{\partial \tilde{t}} + \tilde{u} \frac{\partial Q_{12}}{\partial \tilde{x}} + \tilde{v} \frac{\partial Q_{12}}{\partial \tilde{y}} + \tilde{w} \frac{\partial Q_{12}}{\partial \tilde{z}} - \tilde{W}_{12} (Q_{22} - Q_{11}) - \tilde{W}_{13} Q_{23} - \tilde{W}_{23} Q_{12} \]

\[ \dot{Q}_{13} = \frac{\partial Q_{13}}{\partial \tilde{t}} + \tilde{u} \frac{\partial Q_{13}}{\partial \tilde{x}} + \tilde{v} \frac{\partial Q_{13}}{\partial \tilde{y}} + \tilde{w} \frac{\partial Q_{13}}{\partial \tilde{z}} - \tilde{W}_{13} (Q_{33} - Q_{11}) - \tilde{W}_{12} Q_{23} + \tilde{W}_{23} Q_{12} \]

\[ \dot{Q}_{23} = \frac{\partial Q_{23}}{\partial \tilde{t}} + \tilde{u} \frac{\partial Q_{23}}{\partial \tilde{x}} + \tilde{v} \frac{\partial Q_{23}}{\partial \tilde{y}} + \tilde{w} \frac{\partial Q_{23}}{\partial \tilde{z}} - \tilde{W}_{23} (Q_{33} - Q_{22}) + \tilde{W}_{12} Q_{13} + \tilde{W}_{13} Q_{12} \]  

(B.1)

Short-range elasticity can be defined as follows,

\[ H_{11}^{\text{sr}} = \frac{1}{D_e}\left[ \left( \frac{U}{3} - 1 \right) Q_{11} + U \left( Q_{11}^2 + Q_{12}^2 + Q_{13}^2 \right) + U \left( Q : Q \right) \cdot (Q_{11} + \frac{1}{3}) \right] \]

\[ H_{22}^{\text{sr}} = \frac{1}{D_e}\left[ \left( \frac{U}{3} - 1 \right) Q_{22} + U \left( Q_{12}^2 + Q_{22}^2 + Q_{23}^2 \right) + U \left( Q : Q \right) \cdot (Q_{22} + \frac{1}{3}) \right] \]

\[ H_{12}^{\text{sr}} = \frac{1}{D_e}\left[ \left( \frac{U}{3} - 1 \right) Q_{12} + U \left( Q_{11} Q_{12} + Q_{12} Q_{22} + Q_{13} Q_{23} \right) + U \left( Q : Q \right) Q_{12} \right] \]

\[ H_{13}^{\text{sr}} = \frac{1}{D_e}\left[ \left( \frac{U}{3} - 1 \right) Q_{13} + U \left( Q_{11} Q_{13} + Q_{12} Q_{23} + Q_{13} Q_{33} \right) + U \left( Q : Q \right) Q_{13} \right] \]

\[ H_{23}^{\text{sr}} = \frac{1}{D_e}\left[ \left( \frac{U}{3} - 1 \right) Q_{23} + U \left( Q_{12} Q_{13} + Q_{22} Q_{23} + Q_{23} Q_{33} \right) + U \left( Q : Q \right) Q_{23} \right] \]  

(B.2)
Appendix B. Landau–de Gennes Derivations

Long-range elasticity can be defined as follows,

\[ H_{11}^r = \frac{1}{E_r} \left[ \nabla^2 Q_{11} + \frac{L^*}{3} \left( \frac{\partial^2 Q_{11}}{\partial \tilde{x}^2} + \frac{\partial^2 Q_{12}}{\partial \tilde{x} \partial \tilde{y}} + \frac{\partial^2 Q_{13}}{\partial \tilde{x} \partial \tilde{z}} - \frac{\partial^2 Q_{22}}{\partial \tilde{y}^2} + 2 \frac{\partial^2 Q_{23}}{\partial \tilde{y} \partial \tilde{z}} - \frac{\partial^2 Q_{33}}{\partial \tilde{z}^2} \right) \right] \]

\[ H_{22}^r = \frac{1}{E_r} \left[ \nabla^2 Q_{22} + \frac{L^*}{3} \left( \frac{\partial^2 Q_{12}}{\partial \tilde{x} \partial \tilde{y}} - \frac{\partial^2 Q_{11}}{\partial \tilde{x}^2} - 2 \frac{\partial^2 Q_{13}}{\partial \tilde{x} \partial \tilde{z}} + 2 \frac{\partial^2 Q_{22}}{\partial \tilde{y}^2} + \frac{\partial^2 Q_{23}}{\partial \tilde{y} \partial \tilde{z}} + \frac{\partial^2 Q_{33}}{\partial \tilde{z}^2} \right) \right] \]

\[ H_{12}^r = \frac{1}{E_r} \left[ \nabla^2 Q_{12} + \frac{L^*}{2} \left( \frac{\partial^2 Q_{11}}{\partial \tilde{x} \partial \tilde{y}} + \frac{\partial^2 Q_{12}}{\partial \tilde{x}^2} + \frac{\partial^2 Q_{13}}{\partial \tilde{x} \partial \tilde{z}} + \frac{\partial^2 Q_{22}}{\partial \tilde{y} \partial \tilde{z}} + \frac{\partial^2 Q_{23}}{\partial \tilde{y}^2} + \frac{\partial^2 Q_{33}}{\partial \tilde{z}^2} \right) \right] \]

\[ H_{13}^r = \frac{1}{E_r} \left[ \nabla^2 Q_{13} + \frac{L^*}{2} \left( \frac{\partial^2 Q_{11}}{\partial \tilde{x} \partial \tilde{z}} + \frac{\partial^2 Q_{12}}{\partial \tilde{x} \partial \tilde{y}} + \frac{\partial^2 Q_{13}}{\partial \tilde{x}^2} + \frac{\partial^2 Q_{22}}{\partial \tilde{y} \partial \tilde{z}} + \frac{\partial^2 Q_{23}}{\partial \tilde{y}^2} + \frac{\partial^2 Q_{33}}{\partial \tilde{z}^2} \right) \right] \]

\[ H_{23}^r = \frac{1}{E_r} \left[ \nabla^2 Q_{23} + \frac{L^*}{2} \left( \frac{\partial^2 Q_{12}}{\partial \tilde{x} \partial \tilde{z}} + \frac{\partial^2 Q_{13}}{\partial \tilde{x} \partial \tilde{y}} + \frac{\partial^2 Q_{22}}{\partial \tilde{y} \partial \tilde{z}} + \frac{\partial^2 Q_{23}}{\partial \tilde{y}^2} + \frac{\partial^2 Q_{33}}{\partial \tilde{z}^2} \right) \right] \]

(B.3)
Flow contributions can be described as follows,

\[
F_{11} = \frac{2}{3} \beta \left( A_{11} + 2A_{11}Q_{11} + A_{12}Q_{12} + A_{13}Q_{13} - A_{22}Q_{22} - 2A_{23}Q_{23} - A_{33}Q_{33} \right) \\
- \frac{1}{2} \beta \left[ A_{11} (3Q_{11}^2 + Q_{12}^2 + Q_{13}^2) + 4A_{12}Q_{11}Q_{12} + 4A_{13}Q_{11}Q_{13} + A_{22} (Q_{11}Q_{22} - Q_{12}^2 - Q_{23}^2) + 2A_{23}Q_{23} (Q_{11} - Q_{22} - Q_{33}) \\
+ A_{33} (Q_{11}Q_{33} - Q_{23}^2 - Q_{33}^2) \right]
\]

\[
F_{22} = \frac{2}{3} \beta \left( A_{22} - A_{11}Q_{11} + A_{12}Q_{12} - 2A_{13}Q_{13} + 2A_{22}Q_{22} + A_{23}Q_{23} - A_{33}Q_{33} \right) \\
- \frac{1}{2} \beta \left[ A_{22} (3Q_{22}^2 - Q_{11}^2 - Q_{13}^2) + 4A_{12}Q_{12}Q_{22} + 4A_{23}Q_{23}Q_{22} + A_{11} (Q_{11}Q_{22} - Q_{12}^2 - Q_{13}^2) + 2A_{13}Q_{13} (Q_{22} - Q_{11} - Q_{33}) \\
+ A_{33} (Q_{22}Q_{33} - Q_{13}^2 - Q_{33}^2) \right]
\]

\[
F_{12} = \frac{2}{3} \beta A_{12} + \beta \left[ A_{11}Q_{12} + A_{12} (Q_{11} + Q_{22}) + A_{13}Q_{13} + A_{22}Q_{22} + A_{23}Q_{23} \right] \\
- \frac{1}{2} \beta \left[ A_{11} (3Q_{11}Q_{12} + Q_{12}Q_{22} + Q_{13}Q_{23}) + 4A_{13}Q_{12}Q_{13} + 4A_{23}Q_{12}Q_{23} + A_{22} (3Q_{12}Q_{22} + Q_{11}Q_{12} + Q_{13}Q_{23}) + A_{33} (Q_{12}Q_{33} + Q_{13}Q_{23}) \\
+ A_{12} (Q_{11}^2 + 5Q_{12}^2 + Q_{13}^2 + Q_{22}^2 + Q_{23}^2 + Q_{11}Q_{22}) \right]
\]

\[
F_{13} = \frac{2}{3} \beta A_{13} + \beta \left[ A_{11}Q_{13} + A_{12}Q_{23} + A_{13} (Q_{11} + Q_{33}) + A_{23}Q_{13} + A_{33}Q_{13} \right] \\
- \frac{1}{2} \beta \left[ A_{11} (3Q_{11}Q_{13} + Q_{12}Q_{23} + Q_{13}Q_{33}) + 4A_{12}Q_{12}Q_{13} + 4A_{23}Q_{13}Q_{23} + A_{22} (Q_{13}Q_{22} + Q_{12}Q_{23}) + A_{33} (3Q_{13}Q_{33} + Q_{11}Q_{13} + Q_{12}Q_{23}) \\
+ A_{13} (Q_{11}^2 + Q_{13}^2 + 5Q_{13}^2 + Q_{23}^2 + Q_{33} + Q_{11}Q_{33}) \right]
\]

\[
F_{23} = \frac{2}{3} \beta A_{23} + \beta \left[ A_{12}Q_{13} + A_{13}Q_{12} + A_{22}Q_{23} + A_{23} (Q_{22} + Q_{33}) + A_{33}Q_{23} \right] \\
- \frac{1}{2} \beta \left[ A_{22} (3Q_{22}Q_{23} + Q_{12}Q_{13} + Q_{23}Q_{33}) + 4A_{12}Q_{12}Q_{23} + 4A_{13}Q_{13}Q_{23} + A_{11} (Q_{11}Q_{23} + Q_{12}Q_{13}) + A_{33} (3Q_{23}Q_{33} + Q_{12}Q_{13} + Q_{22}Q_{23}) \\
+ A_{23} (Q_{12}^2 + Q_{13}^2 + Q_{22}^2 + 5Q_{23}^2 + Q_{33}^2 + Q_{22}Q_{33}) \right]
\]

\[(B.4)\]
Appendix B. Landau–de Gennes Derivations

For total stress tensor \( \mathbf{T} \), symmetric viscous component can be described as follows,

\[
\tau_{v11} = \nu_1 \tilde{A}_{11} + 2 \nu_2 \left[ \tilde{A}_{11} Q_{11} + \tilde{A}_{12} Q_{12} + \tilde{A}_{13} Q_{13} - \frac{Q A}{3} \right] \\
+ \nu_1 \left[ Q Q \tilde{A} + Q \tilde{A} Q_{11} + \tilde{A}_{11} \left( 3 Q_{11}^2 + 2 Q_{12}^2 + 2 Q_{13}^2 \right) + 2 \tilde{A}_{12} \left( Q_{12} \left( Q_{11} + Q_{22} \right) + Q_{13} Q_{23} \right) \\
+ 2 \tilde{A}_{13} \left( Q_{13} \left( Q_{11} + Q_{33} \right) + Q_{12} Q_{23} \right) + \tilde{A}_{22} Q_{12}^2 + 2 \tilde{A}_{23} Q_{12} Q_{13} + \tilde{A}_{33} Q_{13}^2 \right] \\
+ \nu_2 \left[ \tilde{A}_{12} Q_{12} + \tilde{A}_{22} Q_{22} + \tilde{A}_{33} Q_{23} - \frac{Q A}{3} \right]
\]

\[
\tau_{v12} = \nu_1 \tilde{A}_{12} + \nu_2 \left[ \tilde{A}_{11} Q_{12} + \tilde{A}_{12} Q_{22} + \tilde{A}_{13} Q_{23} + \tilde{A}_{12} Q_{11} + \tilde{A}_{22} Q_{12} + \tilde{A}_{23} Q_{13} \right] \\
+ \nu_1 \left[ Q \tilde{A} Q_{12} + \tilde{A}_{11} \left( Q_{12} \left( Q_{11} + Q_{22} \right) + Q_{13} Q_{23} \right) + 2 \tilde{A}_{12} \left( Q_{12} \left( Q_{22} + Q_{11} \right) + Q_{13} Q_{23} \right) \\
+ \tilde{A}_{12} \left( 3 Q_{12}^2 + Q_{11}^2 + Q_{22}^2 + Q_{13}^2 + Q_{23}^2 + Q_{11} Q_{22} \right) \\
+ 2 \tilde{A}_{13} Q_{12} Q_{13} + \tilde{A}_{22} \left( Q_{12} \left( Q_{22} + Q_{11} \right) + Q_{13} Q_{23} \right) \right]
\]

\[
\tau_{v13} = \nu_1 \tilde{A}_{13} + \nu_2 \left[ \tilde{A}_{11} Q_{13} + \tilde{A}_{12} Q_{23} + \tilde{A}_{13} Q_{33} + \tilde{A}_{12} Q_{11} + \tilde{A}_{23} Q_{12} + \tilde{A}_{33} Q_{13} \right] \\
+ \nu_1 \left[ Q \tilde{A} Q_{13} + \tilde{A}_{11} \left( Q_{13} \left( Q_{11} + Q_{33} \right) + Q_{12} Q_{23} \right) + 2 \tilde{A}_{13} \left( Q_{13} \left( Q_{23} + Q_{11} \right) + Q_{12} Q_{23} \right) \\
+ \tilde{A}_{13} \left( 3 Q_{13}^2 + Q_{11}^2 + Q_{33}^2 + Q_{12}^2 + Q_{23}^2 + Q_{11} Q_{33} \right) \\
+ 2 \tilde{A}_{12} Q_{12} Q_{13} + \tilde{A}_{33} \left( Q_{13} \left( Q_{23} + Q_{11} \right) + Q_{12} Q_{23} \right) \right]
\]

\[
\tau_{v23} = \nu_1 \tilde{A}_{23} + \nu_2 \left[ \tilde{A}_{12} Q_{13} + \tilde{A}_{22} Q_{23} + \tilde{A}_{23} Q_{33} + \tilde{A}_{12} Q_{12} + \tilde{A}_{23} Q_{22} + \tilde{A}_{33} Q_{23} \right] \\
+ \nu_1 \left[ Q \tilde{A} Q_{23} + \tilde{A}_{22} \left( Q_{23} \left( Q_{22} + Q_{33} \right) + Q_{12} Q_{13} \right) + 2 \tilde{A}_{12} Q_{12} Q_{23} + \tilde{A}_{11} Q_{12} Q_{13} \\
+ \tilde{A}_{23} \left( 3 Q_{23}^2 + Q_{22}^2 + Q_{33}^2 + Q_{12}^2 + Q_{13}^2 + Q_{22} Q_{33} \right) \\
+ 2 \tilde{A}_{13} Q_{13} Q_{23} + \tilde{A}_{33} \left( Q_{23} \left( Q_{23} + Q_{22} \right) + Q_{12} Q_{13} \right) \right]
\]

(B.5)
Appendix B. Landau–de Gennes Derivations

Where, \( \mathbf{Q} \mathbf{A} \) and \( \mathbf{Q}\mathbf{Q}\mathbf{A} \) can be defined as follows,

\[
\mathbf{Q}\mathbf{A} = Q_{11} \mathbf{A}_{11} + Q_{22} \mathbf{A}_{22} + Q_{33} \mathbf{A}_{33} + 2(Q_{12} \mathbf{A}_{12} + Q_{13} \mathbf{A}_{13} + Q_{23} \mathbf{A}_{23})
\]
\[
\mathbf{Q}\mathbf{Q}\mathbf{A} = (Q_{11}^2 + Q_{12}^2 + Q_{13}^2) \mathbf{A}_{11} + (Q_{22}^2 + Q_{23}^2 + Q_{23}^2) \mathbf{A}_{22} + (Q_{33}^2 + Q_{33}^2 + Q_{33}^2) \mathbf{A}_{33} + 2(Q_{11} Q_{12} + Q_{12} Q_{22} + Q_{13} Q_{23}) \mathbf{A}_{12} + 2(Q_{11} Q_{13} + Q_{12} Q_{23} + Q_{13} Q_{33}) \mathbf{A}_{13} + 2(Q_{12} Q_{13} + Q_{22} Q_{23} + Q_{23} Q_{33}) \mathbf{A}_{23}
\]

(B.6)

For the anisotropic component of the total stress tensor, \( \mathbf{\tau}_{a11} = \mathbf{\tau}_{a22} = \mathbf{\tau}_{a33} = 0 \) and the rest of the components of \( \mathbf{\tau}_{a} \) can be expressed as follows,

\[
\mathbf{\tau}_{a12} = (Q_{22} - Q_{11}) H_{12} + (H_{11} - H_{22}) Q_{12} + H_{13} Q_{23} - H_{23} Q_{13}
\]
\[
\mathbf{\tau}_{a21} = (Q_{11} - Q_{22}) H_{12} + (H_{22} - H_{11}) Q_{12} + H_{23} Q_{13} - H_{13} Q_{23}
\]
\[
\mathbf{\tau}_{a13} = (Q_{33} - Q_{11}) H_{13} + (H_{11} - H_{33}) Q_{13} + H_{12} Q_{23} - H_{23} Q_{12}
\]
\[
\mathbf{\tau}_{a31} = (Q_{11} - Q_{33}) H_{13} + (H_{33} - H_{11}) Q_{13} + H_{23} Q_{12} - H_{12} Q_{23}
\]
\[
\mathbf{\tau}_{a23} = (Q_{33} - Q_{22}) H_{23} + (H_{22} - H_{33}) Q_{23} + H_{12} Q_{13} - H_{13} Q_{12}
\]
\[
\mathbf{\tau}_{a32} = (Q_{22} - Q_{33}) H_{23} + (H_{33} - H_{22}) Q_{23} + H_{13} Q_{12} - H_{12} Q_{13}
\]

(B.7)

By taking into consideration the fact that, \( \mathbf{QH} \) and \( \mathbf{QQH} \) can be defined as follows,

\[
\mathbf{QH} = Q_{11} H_{11} + Q_{22} H_{22} + Q_{33} H_{33} + 2(Q_{12} H_{12} + Q_{13} H_{13} + Q_{23} H_{23})
\]
\[
\mathbf{QQH} = (Q_{11}^2 + Q_{12}^2 + Q_{13}^2) H_{11} + (Q_{22}^2 + Q_{23}^2 + Q_{23}^2) H_{22} + (Q_{33}^2 + Q_{33}^2 + Q_{33}^2) H_{33} + 2(Q_{11} Q_{12} + Q_{12} Q_{22} + Q_{13} Q_{23}) H_{12} + 2(Q_{11} Q_{13} + Q_{12} Q_{23} + Q_{13} Q_{33}) H_{13} + 2(Q_{12} Q_{13} + Q_{22} Q_{23} + Q_{23} Q_{33}) H_{23}
\]

(B.8)

Elastic and the Ericksen component of total stress tensor can be described in correlation [B.9] and [B.10].
\[ \begin{align*}
\tau_{e11} & = -\frac{2}{3} \beta H_{11} - 2 \beta \left[ H_{11} Q_{11} + H_{12} Q_{12} + H_{13} Q_{13} - QH3 \right] \\
& \quad + \frac{1}{2} \beta \left[ QHQ_{11} - QQH + H_{11} \left( 3Q_{11}^2 + 2Q_{12}^2 + 2Q_{13}^2 \right) \\
& \quad + 2H_{12} \left( Q_{12} (2Q_{11} + Q_{22}) + Q_{13} Q_{23} \right) + 2H_{13} \left( Q_{13} (2Q_{11} + Q_{33}) + Q_{12} Q_{23} \right) \\
& \quad + H_{22} Q_{12}^2 + 2H_{23} Q_{12} Q_{13} + H_{33} Q_{13}^2 \right] \\
\tau_{e22} & = -\frac{2}{3} \beta H_{22} - 2 \beta \left[ H_{12} Q_{12} + H_{22} Q_{22} + H_{23} Q_{23} - QH/3 \right] \\
& \quad + \frac{1}{2} \beta \left[ QHQ_{22} - QQH + H_{22} \left( 3Q_{22}^2 + 2Q_{12}^2 + 2Q_{23}^2 \right) \\
& \quad + 2H_{12} \left( Q_{12} (2Q_{22} + Q_{11}) + Q_{13} Q_{23} \right) + 2H_{23} \left( Q_{23} (2Q_{22} + Q_{33}) + Q_{12} Q_{13} \right) \\
& \quad + H_{11} Q_{12}^2 + 2H_{13} Q_{12} Q_{23} + H_{33} Q_{23}^2 \right] \\
\tau_{e12} & = -\frac{2}{3} \beta H_{12} - \beta \left[ H_{11} Q_{12} + H_{12} Q_{22} + H_{13} Q_{23} + H_{12} Q_{11} + H_{22} Q_{12} + H_{23} Q_{13} \right] \\
& \quad + \frac{1}{2} \beta \left[ H_{11} \left( Q_{12} (2Q_{11} + Q_{22}) + Q_{13} Q_{23} \right) + 2H_{13} Q_{12} Q_{13} \\
& \quad + H_{12} \left( 3Q_{12}^2 + Q_{11}^2 + Q_{22}^2 + Q_{13}^2 + Q_{23}^2 + Q_{11} Q_{22} \right) \\
& \quad + H_{22} \left( Q_{12} (2Q_{22} + Q_{11}) + Q_{13} Q_{23} \right) + 2H_{23} Q_{12} Q_{23} + H_{33} Q_{13} Q_{23} + QHQ_{12} \right] \\
\tau_{e13} & = -\frac{2}{3} \beta H_{13} - \beta \left[ H_{11} Q_{13} + H_{12} Q_{23} + H_{13} Q_{33} + H_{13} Q_{11} + H_{23} Q_{12} + H_{33} Q_{13} \right] \\
& \quad + \frac{1}{2} \beta \left[ H_{11} \left( Q_{13} (2Q_{11} + Q_{33}) + Q_{12} Q_{23} \right) + 2H_{12} Q_{12} Q_{13} \\
& \quad + H_{13} \left( 3Q_{13}^2 + Q_{11}^2 + Q_{33}^2 + Q_{12}^2 + Q_{23}^2 + Q_{11} Q_{33} \right) \\
& \quad + H_{33} \left( Q_{13} (2Q_{33} + Q_{11}) + Q_{12} Q_{23} \right) + 2H_{23} Q_{13} Q_{23} + H_{22} Q_{12} Q_{23} + QHQ_{13} \right] \\
\tau_{e23} & = -\frac{2}{3} \beta H_{23} - \beta \left[ H_{12} Q_{13} + H_{22} Q_{23} + H_{23} Q_{33} + H_{13} Q_{12} + H_{23} Q_{22} + H_{33} Q_{23} \right] \\
& \quad + \frac{1}{2} \beta \left[ H_{22} \left( Q_{23} (2Q_{22} + Q_{33}) + Q_{12} Q_{13} \right) + 2H_{13} Q_{13} Q_{23} \\
& \quad + H_{23} \left( 3Q_{23}^2 + Q_{22}^2 + Q_{33}^2 + Q_{12}^2 + Q_{13}^2 + Q_{22} Q_{33} \right) \\
& \quad + H_{33} \left( Q_{23} (2Q_{33} + Q_{22}) + Q_{12} Q_{13} \right) + 2H_{12} Q_{12} Q_{23} + H_{11} Q_{12} Q_{13} + QHQ_{23} \right] \\
& \quad \text{(B.9)}
\end{align*}\]
\[ \tau_{Er_{11}} = -\left\{ \left( \frac{\partial Q_{11}}{\partial \tilde{x}} + \frac{\partial Q_{11}}{\partial \tilde{y}} + \frac{\partial Q_{11}}{\partial \tilde{z}} \right) \right\} \left( 1 + L^* \right) \left( \frac{\partial Q_{11}}{\partial \tilde{x}} + \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{13}}{\partial \tilde{z}} \right) \\
+ L^* \left( \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{22}}{\partial \tilde{y}} + \frac{\partial Q_{23}}{\partial \tilde{y}} \right) + L^* \left( \frac{\partial Q_{23}}{\partial \tilde{y}} + \frac{\partial Q_{23}}{\partial \tilde{z}} + \frac{\partial Q_{33}}{\partial \tilde{z}} \right) \right\} \\
+ \frac{\partial Q_{12}}{\partial \tilde{x}}^2 + \frac{\partial Q_{13}}{\partial \tilde{x}}^2 + \frac{\partial Q_{23}}{\partial \tilde{x}} \left( \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{13}}{\partial \tilde{y}} \right) + \frac{\partial Q_{12}}{\partial \tilde{y}} \frac{\partial Q_{22}}{\partial \tilde{y}} + \frac{\partial Q_{13}}{\partial \tilde{z}} \frac{\partial Q_{23}}{\partial \tilde{y}} \right\} \\
\tau_{Er_{22}} = -\left\{ \left( \frac{\partial Q_{22}}{\partial \tilde{x}} + \frac{\partial Q_{22}}{\partial \tilde{y}} + \frac{\partial Q_{22}}{\partial \tilde{z}} \right) \right\} \left( 1 + L^* \right) \left( \frac{\partial Q_{11}}{\partial \tilde{x}} + \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{23}}{\partial \tilde{z}} \right) \\
+ L^* \left( \frac{\partial Q_{11}}{\partial \tilde{x}} + \frac{\partial Q_{12}}{\partial \tilde{x}} + \frac{\partial Q_{13}}{\partial \tilde{x}} \right) + L^* \left( \frac{\partial Q_{13}}{\partial \tilde{z}} + \frac{\partial Q_{23}}{\partial \tilde{z}} + \frac{\partial Q_{33}}{\partial \tilde{z}} \right) \right\} \\
+ \frac{\partial Q_{12}}{\partial \tilde{y}}^2 + \frac{\partial Q_{13}}{\partial \tilde{y}}^2 + \frac{\partial Q_{23}}{\partial \tilde{y}} \left( \frac{\partial Q_{12}}{\partial \tilde{x}} + \frac{\partial Q_{13}}{\partial \tilde{x}} \right) + \frac{\partial Q_{12}}{\partial \tilde{x}} \frac{\partial Q_{22}}{\partial \tilde{x}} + \frac{\partial Q_{13}}{\partial \tilde{z}} \frac{\partial Q_{23}}{\partial \tilde{y}} \right\} \\
\tau_{Er_{12}} = -\left\{ \left( \frac{\partial Q_{12}}{\partial \tilde{x}} + \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{12}}{\partial \tilde{z}} \right) \right\} \left( 1 + L^* \right) \left( \frac{\partial Q_{11}}{\partial \tilde{x}} + \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{13}}{\partial \tilde{z}} \right) \\
+ L^* \left( \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{22}}{\partial \tilde{y}} + \frac{\partial Q_{23}}{\partial \tilde{y}} \right) + L^* \left( \frac{\partial Q_{13}}{\partial \tilde{z}} + \frac{\partial Q_{23}}{\partial \tilde{z}} + \frac{\partial Q_{33}}{\partial \tilde{z}} \right) \right\} \\
+ \frac{\partial Q_{23}}{\partial \tilde{x}} \left( \frac{\partial Q_{13}}{\partial \tilde{x}} + \frac{\partial Q_{23}}{\partial \tilde{x}} + \frac{\partial Q_{22}}{\partial \tilde{x}} \right) + \frac{\partial Q_{23}}{\partial \tilde{x}} \frac{\partial Q_{33}}{\partial \tilde{x}} + \frac{\partial Q_{22}}{\partial \tilde{y}} \left( \frac{\partial Q_{12}}{\partial \tilde{x}} + \frac{\partial Q_{22}}{\partial \tilde{y}} \right) \right\} \\
\tau_{Er_{13}} = -\left\{ \left( \frac{\partial Q_{13}}{\partial \tilde{x}} + \frac{\partial Q_{13}}{\partial \tilde{y}} + \frac{\partial Q_{13}}{\partial \tilde{z}} \right) \right\} \left( 1 + L^* \right) \left( \frac{\partial Q_{11}}{\partial \tilde{x}} + \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{13}}{\partial \tilde{z}} \right) \\
+ L^* \left( \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{22}}{\partial \tilde{y}} + \frac{\partial Q_{23}}{\partial \tilde{y}} \right) + L^* \left( \frac{\partial Q_{13}}{\partial \tilde{z}} + \frac{\partial Q_{23}}{\partial \tilde{z}} + \frac{\partial Q_{33}}{\partial \tilde{z}} \right) \right\} \\
+ \frac{\partial Q_{23}}{\partial \tilde{x}} \left( \frac{\partial Q_{12}}{\partial \tilde{x}} + \frac{\partial Q_{33}}{\partial \tilde{x}} + \frac{\partial Q_{23}}{\partial \tilde{x}} \right) + \frac{\partial Q_{23}}{\partial \tilde{y}} \frac{\partial Q_{33}}{\partial \tilde{x}} + \frac{\partial Q_{33}}{\partial \tilde{z}} \left( \frac{\partial Q_{13}}{\partial \tilde{x}} + \frac{\partial Q_{33}}{\partial \tilde{z}} \right) \right\} \\
\tau_{Er_{23}} = -\left\{ \left( \frac{\partial Q_{23}}{\partial \tilde{x}} + \frac{\partial Q_{23}}{\partial \tilde{y}} + \frac{\partial Q_{23}}{\partial \tilde{z}} \right) \right\} \left( 1 + L^* \right) \left( \frac{\partial Q_{11}}{\partial \tilde{x}} + \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{23}}{\partial \tilde{z}} \right) \\
+ L^* \left( \frac{\partial Q_{11}}{\partial \tilde{x}} + \frac{\partial Q_{12}}{\partial \tilde{x}} + \frac{\partial Q_{13}}{\partial \tilde{x}} \right) + L^* \left( \frac{\partial Q_{13}}{\partial \tilde{z}} + \frac{\partial Q_{23}}{\partial \tilde{z}} + \frac{\partial Q_{33}}{\partial \tilde{z}} \right) \right\} \\
+ \frac{\partial Q_{13}}{\partial \tilde{y}} \left( \frac{\partial Q_{33}}{\partial \tilde{x}} + \frac{\partial Q_{12}}{\partial \tilde{y}} + \frac{\partial Q_{13}}{\partial \tilde{y}} \right) + \frac{\partial Q_{11}}{\partial \tilde{y}} \frac{\partial Q_{13}}{\partial \tilde{y}} + \frac{\partial Q_{33}}{\partial \tilde{y}} \left( \frac{\partial Q_{23}}{\partial \tilde{y}} + \frac{\partial Q_{33}}{\partial \tilde{y}} \right) \right\} \]

(B.10)