Abstract

Liquid crystalline states of matter provide a useful testing ground for statistical mechanical theories of ordered states, since a variety of ordered phases can be accessed in experiments and computer simulations. They also constitute simple model systems for studying the interplay between internal structure and an externally imposed flow, thus illuminating rheological studies of a large class of complex fluids.

In this thesis, we study some problems in the statics and dynamics of nematic liquid crystals. Nematics, typically formed in solution by rod-like molecules with an aspect ratio which deviates sufficiently from unity, exhibit orientational order in the absence of translational order. Such orientational order is quantified through a traceless, symmetric tensor $Q_{\alpha\beta}$. The free energy which quantifies the cost of deformations is the Ginzburg-Landau-de Gennes (GLdG) free energy functional, obtained via a gradient expansion in $Q$.

This thesis studies two broad classes of problems using the GLdG approach. The first class deals with the static properties of the isotropic-nematic interface. The problem of interface structure for the nematic is particularly interesting since it provides a simple illustration of how the structure of an interface can differ substantially from structure in the bulk.

The second class of problems involves the study of the dynamics of $Q_{\alpha\beta}$ for a nematic fluid in an external shear flow. Our study of the dynamics of $Q_{\alpha\beta}$ impacts experiments on the flow behaviour of fluids with orientational order, a prototypical model for the understanding of complex fluid rheology, in particular of chaos associated with unsteady rheological response or “rheochaos”. Such rheochaos is a consequence of constitutive and not convective non-linearities, originating in the coupling of the flow to structural or orientational variables describing the local state of the fluid.

A powerful approach to understanding complex spatio-temporal dynamics is based on the study of coupled map lattices, a numerical scheme in which maps placed on the sites of a lattice evolve both via local dynamics as well as through couplings to neighbouring sites. However, the utility of this methodology in a specific context is often severely limited by the availability of local maps able to comprehensively describe the spatially uniform case. In this thesis, we discuss this
requirement in the context of a model for rheochaos, proposing a local map as well as a coupled map description of the regular and chaotic states obtained in sheared nematics.

The thesis is organized as follows. In the first chapter, the Introduction, we briefly review the GLdG order parameter theory of the isotropic-nematic transition. We survey the literature which deals with the isotropic-nematic interface and briefly describe methodologies for studying the rheology of complex fluids, in particular nematogenic fluids. The results presented in the chapters which follow are summarized in more detail below, chapterwise. Finally, we end this thesis with a conclusion and point to further work.

**Isotropic-Nematic interface with Planar Anchoring**
In the second chapter of this thesis we revisit the classic problem of the structure of the isotropic-nematic interface within Ginzburg-Landau-de Gennes theory, refining previous analytic treatments of biaxiality at the interface. We present results for the uniaxial and biaxial profiles, specialized to the case of planar anchoring, showing how a term in the Euler-Lagrange equations neglected in previous work contributes substantially to determining the structure of the interface. We use results from a fast and highly accurate spectral collocation scheme for the solution of the Landau-Ginzburg-de Gennes equations to test these analytic results. In comparison to earlier work, we obtain improved agreement with numerics for both the uniaxial and biaxial profiles, with our results being increasingly accurate as $\kappa$ is reduced. We also provide accurate asymptotic results for the decay of the $S$ and $T$ order parameters deep into the nematic and isotropic phases.

**Isotropic-Nematic Interface with an Oblique Anchoring Condition**
In the third chapter of this thesis, we study the case where a general anchoring condition is imposed on the nematic side of the interface, reproducing results of previous work in the limit in which this anchoring condition reduces to the planar or homeototropic case. Our approach uses variational methods, based on physically motivated and computationally flexible variational profiles for uniaxial and biaxial order, as well as for the variation of the angle between the nematic axis
and the coordinate normal to the interface. Results from our analysis are compared to numerical results obtained from a direct numerical minimization of the Ginzburg-Landau-de Gennes free energy. While spatial variations of the uniaxial and biaxial order parameters are approximately confined to the neighbourhood of the interface, nematic elasticity requires that the director orientation interpolate smoothly between planar anchoring at the location of the interface and the imposed boundary condition at infinity. Our variational results are in close agreement with numerical results as well as results from molecular simulations. Our methods access the nontrivial structure of the biaxiality at the interface including the large tail towards the isotropic side and the change in the sign of the biaxial order parameter across the interface. This approach also captures the inversion of the profile of biaxiality as the elastic coefficient $L_2$ crosses zero.

**Local Map Description of Nematic Liquid Crystals**

In chapter four of this thesis, we propose and study a local map capable of describing the full variety of dynamical states, ranging from regular to chaotic, obtained when a nematic liquid crystal is subjected to a steady shear flow. The map is formulated in terms of a quaternion parametrization of rotations of the local frame described by the axes of the nematic director, subdirector and the joint normal to these, with two additional scalars describing the strength of ordering. Our model yields kayaking, wagging, tumbling, aligned and coexistence states, in agreement with previous formulations based on coupled ordinary differential equations. The phase diagram we obtain using our methods contains all non-trivial dynamical states obtained in previous work. Moreover, it closely resembles, even at the quantitative level, phase diagrams obtained in previous work which used ordinary differential equations formulated in continuous time. Our approach makes an extension to the case in which the shear rate is periodically modulated, possible. Our work thus supplies a crucial ingredient required for the construction of coupled map lattice approaches to the spatio-temporal aspects of rheological chaos, a problem currently at the boundaries of our understanding of the dynamics of complex fluids.
A Coupled Map Lattice Model of Rheological Chaos.
In chapter five of this thesis we devise and study a coupled map lattice model for a nematogenic fluid in a passive shear flow. We begin with a local map which contains all the states predicted using a ODE-based methodology. We then couple these maps together spatially, using standard techniques, in one and two dimensions. Our results provide evidence for spatially and temporally uniform states, as well as states which are spatially uniform but temporally periodic. In a restricted regime of parameter space, we find evidence for spatio-temporally chaotic behaviour, which we characterize in detail. We obtain a phase diagram in the space of the coupling constant for the spatial coupling of sites as well as a parameter which enters our map, illustrating how the different spatio-temporal phases are connected to each other. Previous work on rheochaos has been based on methodologies which use partial differential equations, which are then solved (typically in one dimension) in the passive advection approximation. Our results here obtain the same states found in approaches which use PDE’s, but allow a numerically tractable extension to two and higher dimensions. Our results for this model indicate that behaviour in the one dimensional and two dimensional cases are qualitatively similar, although the larger number of neighbours in two dimensions suppresses spatial irregularity. We have checked that our results are qualitatively similar for different choices of spatial coupling schemes. Our results include the complete characterization of phases and the phase diagram as well as the demonstration of spatio-temporal intermittency in this system. More centrally, our work shows that coupled map lattice models of rheological chaos can provide accurate yet computationally tractable descriptions of the steady state behaviour of driven complex fluids.

List of publications/preprints

1 Regular and Chaotic States in a Local Map description of Nematic Liquid Crystals,
(arXiv:0801.3876v2)

2 Biaxiality at the Isotropic-Nematic Interface with Planar Anchoring.
S. M. Kamil, A. K. Bhattacharjee, R. Adhikari and Gautam I. Menon
(http://arxiv.org/abs/0906.2899)

3 **The isotropic-nematic interface with an oblique anchoring condition.**
S. M. Kamil, A. K. Bhattacharjee, R. Adhikari and Gautam I. Menon
(http://arxiv.org/abs/0908.2517)

4 **A Coupled Map Lattice Model for Rheological Chaos in Sheared Nematic Liquid Crystals.**
S.M. Kamil, Gautam I. Menon and Sudeshna Sinha
*Chaos* **20** 043123 (2010)
(http://arxiv.org/abs/1005.2041)