Mesoscale models for soft layered materials: 
the role of curvatures in topological defect motion, 
flows and instabilities

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To my wife and parents
Abstract

Curvature driven phenomena in soft matter involves both complex geometry at small scales and anisotropies associated with material symmetries. In particular, the class of soft modulated materials present molecules that are organized in layers, so that material properties significantly vary between the direction normal to the layer and those of the layers. This is the case of smectic liquid crystals, which behave as a solid in the direction normal to the molecular layers, while each of their layers behave as a two-dimensional fluid. Under appropriate boundary conditions, smectic layers are known to bend and form focal conic defects, whose curvatures significantly increase in magnitude as the tip of the cone is approached. Intriguingly, experiments on smectic films presenting arrays of focal conics have shown that these materials undergo unexpected morphological transitions, which are not explained by classical local equilibrium thermodynamics. For example, annealing of focal conic domains can lead to conical pyramids, changing the sign of both mean and Gaussian curvatures and exposing smectic layers at the interface. In order to understand the role played by high order curvature terms on the stability and evolution of a smectic film interface, we propose a phase-field model for a smectic-isotropic system. Through an asymptotic analysis, we generalize the classical condition of local equilibrium, the Gibbs-Thomson equation, to include contributions from surface bending and torsion and a dependence on the layer orientation at the interface. Numerical results for a diffusive evolution of the interface reproduce the focal conic to conical pyramid transition in smectic films, and we show that such morphologies can be explained in light of the derived interface equations. We then generalize this model to include flows and to allow each phase to have a different density. We derive both a quasi-incompressible and a weakly compressible smectic-isotropic model from this approach, explaining their applicability and limitations. Finally, we investigate the role of flows and defect interactions in two-dimensional active smectics, known as the spiral defect chaos state in Rayleigh-Bénard convection.
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6.2 Left: Two clockwise rotating spirals with cores located at approximately $(104, 56)$ and $(156, 81)$. The blue line has a length of 58, which is roughly the distance between the cores. Right: Azimuthal component of the force $f = -\nabla^2 \psi \nabla \psi$ (solid line), with $r = 0$ at the $(104, 56)$ core. The dashed line is a guide to the eye showing the approximate $0.44/r$ decay of the force amplitude.
6.3 Schematics of the two domains used for the numerical simulations of the Boussinesq equations. The Cartesian coordinates \((x, y, z)\) are in the directions shown and gravity acts in the direction opposing \(z\). (a) The box domain with a square planform of side length \(L\) and a depth \(d\) with an aspect ratio of \(\Gamma = L/d = 100\). The sidewall boundary conditions are periodic and the bottom and top walls are no-slip surfaces. This domain was used to generate a state of spiral defect chaos, with a sample flow field shown in Fig. 6.4. (b) The cylindrical domain of radius \(r_0\) and depth \(d\) with an aspect ratio of \(\Gamma = r_0/d = 40\). All material surfaces are no-slip boundaries and the sidewalls are heated as part of the procedure to develop a giant rotating spiral as described in the text. A sample flow field image is shown in Fig. 6.10 (left). Both schematics are drawn to scale and are shown slightly tilted with respect to the horizontal for perspective.

6.4 Left: Temperature field at the mid plane of the convection cell obtained by integrating the Boussinesq fluid model in time with periodic boundary conditions. The convection cell is a box domain with \(\Gamma = 100\), \(\epsilon = 0.7\) and \(Pr = 1\). The temperature field is shown at time \(t = 914.69\). Right: A close-up view of a rotating spiral.

6.5 (Part 1) Azimuthal velocity for the spiral located at \((104, 56)\) in Fig. 6.2 with \(r = 0\) at its core, for \(g_m = 50\), \(\sigma = 1\), and \(\epsilon = 0.7\). Left column compares numerical results with our analytic predictions, and right column is in logarithmic scale. First row: \(c^2 = 0\), using \(v_\phi = -1.3 r \ln(r/30)\) for the analytic curve. Second row: \(c^2 = 0.1\), using \(\alpha = 5/\sigma\) and \(\beta = -1.75\). For all the cases of \(c^2 > 0\), \(r_b = 35\) is used.

6.6 (Part 2) Azimuthal velocity for the spiral located at \((104, 56)\) in Fig. 6.2 with \(r = 0\) at its core, for \(g_m = 50\), \(\sigma = 1\), and \(\epsilon = 0.7\). Left column compares numerical results with our analytic predictions, and right column is in logarithmic scale. First row: \(c^2 = 0.4\), using \(\alpha = 5/\sigma\) and \(\beta = -0.5\). Second row: \(c^2 = 2\), using \(\alpha = 5/\sigma\) and \(\beta = -0.1\). For all the cases of \(c^2 > 0\), \(r_b = 35\) is used.
6.7 Azimuthal velocity between two spirals of opposite topological charge using the generalized Swift-Hohenberg equation. At $r = 0$ we find the core of the spiral located at $(104, 56)$ from Fig. 6.2, and at $r = 47$ the core of the spiral is located at $(139, 25)$. Using this same order parameter configuration, we compute the instantaneous velocity for $c^2 = 0$ (middle panel) and $c^2 = 2$ (right panel), and plot the azimuthal velocity between the two spirals.

6.8 Ratios of advection and roll unwinding [the RHS of Eq. (6.1)] to the overall time variation $\partial_t \psi$, as a function of the damping coefficient $c^2$ and the rescaled Prandtl number $\sigma$. Values are computed based on the spiral located at $(104, 56)$ in Fig. 6.1a, with $\epsilon = 0.7$ and $g_m = 50$. The blue line with circle symbols shows the ratio for the spiral's characteristic advection contribution $(v \cdot \nabla \psi)$, and the red line with square symbols shows the ratio for its characteristic roll unwinding contribution (RHS). Left: Ratios are plotted as a function of $c^2$, for $\sigma = 2$. Right: Ratios are plotted as a function of $\sigma$, for $c^2 = 1$.

6.9 Patterns of order parameter field $\psi$ obtained from the generalized Swift-Hohenberg model for $\epsilon = 0.7$, $\sigma = 2$, and $c^2 = 0$, at time $t = 2 \times 10^3$. Left: $g_m = 50$, showing a chaotic state without the emergence of spirals. Right: $g_m = 5$, showing spiral defect chaos.

6.10 Left: Temperature field at the midplane for a cylindrical convection cell obtained by time integration of the Boussinesq (BSQ) equations where $q_c = 3.1165$, $\Gamma = 40$, $\epsilon = 0.4637$, and $Pr = 1$. Middle: Rescaled azimuthal velocity $v_\varphi$ from the Boussinesq model with $r = 0$ at the spiral core (solid line). The straight dashed line illustrates the power law fit $v_\varphi \sim r^{-2}$. The red dashed line is the result of Eq. (6.14), using $c^2 = 1$, $\sigma = 2$, $\alpha = 1.4383$, $\beta = -0.04328$, and $r_b = 35q_c$. Right: $v_\varphi$ as a function of $q_c r$ obtained from the generalized Swift-Hohenberg model (SH) with $c^2 = 1$, $\sigma = 2$, $\epsilon = 0.7$, and $g_m = 50$, for the spiral located at $(104, 56)$ in Fig. 6.2, as compared to that of the Boussinesq equations. The $x$ axis is scaled with $q_c = 3.1165$ for the Boussinesq result, and $q_c = q_0$ for the Swift-Hohenberg model. No adjustable parameters have been used.
6.11 Rescaled azimuthal velocity for the enlarged spiral in Fig. 6.4 obtained from the Boussinesq model (BSQ), with \( r = 0 \) at its core. The corresponding rescaled parameters are \( \sigma = 2, \beta^2 = 1, \) and \( \epsilon = 0.7. \) Left: Comparison of numerical results with analytic predictions. Right: The same results using a logarithmic scale. Parameters of \( \beta^2 = 1, \alpha = 5/\sigma, \beta = -0.1 \) and \( r_b = 4.5 \) are used for the analytic curve.
Chapter 1

Introduction

Microstructural engineering was introduced in our society more than three thousand years ago. It started with the blacksmith trade, where those working on the forging and tempering of iron were able to achieve great progress in developing sturdy tools and sharp weapons, despite being clueless about concepts such as dislocations, grain boundaries and atomic packing. After the advent of thermodynamics in the XIX century, it was possible to formalize a theory of phase transformations, and start understanding how thermomechanical treatments, phases and material properties were related. When Taylor [1], Orowan [2] and Polanyi [3] proposed the idea of crystalline imperfections, defects that could move and explain the origin of plastic deformation at low stresses, it finally became possible to envision a fine microstructure control that was not chained to empirical knowledge. At surface or interface level, however, such control becomes more intricate, since geometry at small scales plays a major role in nonequilibrium evolution and properties. The implication is that, in many cases, microstructure and shape become entangled at interfaces, relying on nanotechnology and sophisticated treatments to achieve the desired designs.

Thermodynamics started with the study of bulk infinite systems, though progress towards developing a treatment for surfaces has slowly caught up. A major result in this treatment is that deviations in local intensive thermodynamic variables at curved surfaces determine the forces that govern their motion outside of thermodynamic equilibrium. Equilibrium at curved surfaces [4], initially studied to address capillary phenomena at fluid interfaces, has subsequently played a key role in broad classes of moving
boundary problems. Notable examples include nucleation theory and curvature driven growth in phase transformations [5], grain growth [6], sintering of ceramics [7], crystal growth in metal alloys, semiconductor, and high temperature superconducting materials [8, 9], including dendritic growth [10], polymer [11] and protein crystal growth [12], or the related field of pattern formation in Geochemical systems [13]. More recently, attention has shifted to more complex physico-chemical and biological systems in which interfaces and the phases they bound include complex constituents and interactions, and often spontaneously broken symmetries. In these systems, the interplay between microscopic processes and mesoscopic shape is much richer and difficult to elucidate.

![Phases of a liquid crystalline material](image)

(a) Isotropic  
(b) Nematic  
(c) Smectic

Figure 1.1: Phases of a liquid crystalline material. Isotropic is the high temperature phase, nematic is the mid temperature phase where molecules present a broken rotational symmetry, and smectic is the low temperature phase where molecules present both rotational and translational broken symmetries.

Soft matter is one particular class of materials where such interplay appears. Soft matter is of particular interest due to the versatility of their ordered phases, and the ability to control of morphology, defects and topology, leading to potential novel applications in both materials science and biology. Among prominent soft materials we mention modulated phases in block copolymers [14] and smectic liquid crystals [15], which are one of the main topics of this thesis. The latter are formed by anisometric molecules that present collective orientational order along a director axis \( \mathbf{n} \), and are organized in periodically spaced layers, so that they exhibit broken rotational and translational symmetries. Contrast smectics in Fig. 1.1 with a liquid crystalline nematic phase, which presents molecules aligned to \( \mathbf{n} \) without spatial ordering, and an
isotropic phase, whose molecules are randomly oriented. While in the longitudinal direction smectic layers behave rigidly as a solid, in the transverse direction (in the two dimensional manifolds defined by the smectic layers) smectics exhibits fluidity; hence both elasticity and hydrodynamics are important when modeling smectics. Both effects have a major role in the orientational control of smectics, a fact that has prompted recent experimental studies of mesoscopic patterning of liquid crystal films by thermal and surface treatments 16 17 18, and also by manipulating the geometry of the interface via inclusions 19. This combination of elasticity and hydrodynamics becomes key not only to the engineering of surface properties, but also to controlling the structure of self-induced flows.

One feature observed in some of the experiments with smectic liquid crystals is surface defects with large curvatures. Interfacial curvature effects, and in particular those related to the Gaussian curvature, are under active investigation in the emerging field of shape engineering of surfaces and interfaces 20 21 22 23. The goal is to leverage interfacial curvature distributions to affect controllable and reversible changes in surface morphology, or to use curved substrates to control crystalization, defect formation, and motion. Examples include shape control through the application of external stimuli 24, the use of curvature to localize defects and control hierarchical bending, buckling or folding of multilayered surfaces 25 26, the control of fracture by constraining elastic sheets to adopt fixed curvature distributions 27, or nucleation and growth 28 and elastic instabilities 29 on curved surfaces.

Interfacial geometry, and hence interfacial energy, are described by the local mean and Gaussian curvatures, \( H \) and \( G \) respectively. Define a differentiable surface \( \Gamma \subset \mathbb{R}^3 \) where for each point \( p \in \Gamma \) we can assign an unit normal \( \hat{n} \) to the tangent plane. In an infinitesimal neighborhood of \( p \), there are infinite choices of a plane defined by the normal \( \hat{n} \) and a vector in the tangent plane. Each of them define locally a normal curvature, where the minimum and maximum values among all such curvatures are the principal curvatures, \( c_1 \) and \( c_2 \). Physically, they tell us about the minimum and maximum bending at each point of the surface. The mean and Gaussian curvatures are defined as the average and product of the principal curvatures, that is,

\[
H = \frac{c_1 + c_2}{2}, \quad G = c_1 c_2. \tag{1.1}
\]
The notion of “positive” normal curvature depends on the adopted convention. Here, we set that the normal curvatures and mean curvature of a sphere are positive, so that bending against the outward normal $\hat{n}$ is positive. In particular, the mean curvature and the normal are related by the surface divergence of $\hat{n}$,

$$H = \frac{1}{2} \nabla \cdot \hat{n}.$$  \hspace{1cm} (1.2)

The mean curvature has been the quantity of primary physical interest in expressing interfacial energy, as it is directly related to the change in interfacial area for a small displacement of the interface. The classical manifestation of this result is the Gibbs-Thomson equation, which relates the change in chemical potential $\delta \mu$ relative to planarity to the mean curvature as

$$\delta \mu = 2H \sigma_h,$$  \hspace{1cm} (1.3)

where $\sigma_h$ is the thermodynamic excess free energy (surface tension for a fluid interface). Indeed, this equation has been central to all studies of equilibrium morphology and interfacial motion. If the interface is endowed with its own elasticity, the additional energy is described by the Canham-Helfrich free energy functional [30], with dependence on $H^2$ and $G$, and coefficients given by the so called bending moduli.

However, while the Gaussian curvature appears in energy formulations and has been associated to different various experimental observations in soft matter, it is generally neglected in equations for interfacial dynamics and flows. Through the development of transport models for soft modulated materials, this thesis aims to investigate the role of both mean and Gaussian curvature on morphological transitions and pattern formation in soft matter systems. The energy functional we propose for a smectic is similar to the one found in Amundson and Helfand [31] for the study of lamellar block copolymer microstructures. Their functional was based on the Hamiltonian derived by Leibler [32] for composition patterns in weak segregation using mean-field theory. This class of polymers present the same translational and rotational symmetries as the smectics we study, so that the free energy in both these materials and smectics will be affected in an analogous way when the molecular planes are distorted (by splay or elongation).

In particular, we use transport models to theoretically and numerically investigate...
two different problems. The first problem concerns a modulated phase in contact with a disordered phase, with the goal to reproduce equilibrium results observed in smectic-isotropic systems, and be able to model some of the nonequilibrium features previously described. From such a model, one of the main goals will be to derive interface equations in which corrections due to the Gaussian curvature appear, and that are able to account for effects associated with the modulated microstructure of these materials. From there, we will be able to relate curvatures to the motion of interfaces and topological defects, flows, and instabilities. The second problem concerns an active modulated system, presenting a persistent dynamics that induces a continuous nucleation and annihilation of spiral defects. We will investigate azimuthal flows in this regime, induced by curvatures and topological charges. Some background on these problems (smectic thin films and spiral defect chaos) are described below.

1.1 Experiments in smectic thin films

While we propose to develop a general framework for modeling soft modulated materials, the particular systems and geometries we investigate numerically are motivated by recent experiments on smectic-A (SmA) films by Kim et al. [33, 18]. In SmA liquid crystals, rod like molecules are organized in planes with a distinct inter-layer spacing, where the normal to the layers is parallel to the director $\mathbf{n}$ almost everywhere. When thin films of a liquid crystal in its smectic phase are deposited on a treated substrate (e.g. using polyethyleneimine), so that molecules align parallel to the substrate, focal conic defects may be formed. That is, instead of a film comprising of flat smectic layers, layers can bend into conical defects on the film surface, which have been known as equilibrium structures since Bragg in the 1930s [34].

These defects form in the presence of antagonistic boundary conditions when the molecules prefer to align perpendicularly to the interface with some isotropic phase, such as air in the experiments, while remaining parallel to the substrate. Periodic arrays of thesis defects can be obtained at the film surface, as shown in Fig. 1.2 (left) extracted from Ref. [18], which are called focal conic domains (FCDs). When these FCDs are axially symmetric about the main vertical axis, they are called toroidal focal conic domains (TFCDs). Another fundamental reason for the origin of FCDs is that
they minimize an elastic energy associated with bending of the layers: they minimize
the integral of the mean curvature squared over layers, which is known as the Willmore
problem. Among the minima for this problem are Dupin cyclides, and, in particular, the
Clifford torus for the axially symmetric case. Hence, the internal structure of a TFCD
shown in Fig. 1.2 (right) is mathematically described by a family of Clifford tori.

Figure 1.2: Smectic-A film presenting an array of TFCDs, extracted from Ref. [18]. Left
figure presents a top view of the TFCDs, which are equilibrium structures, and the scale
of the bar in white is 10 µm. Image is obtained through scanning electron microscopy.
Right figure illustrates the internal structure of a TCFD, which mathematically can be
approximately described by a family of Clifford tori.

Techniques for obtaining smectic films with arrays of FCDs are well known, and,
more recently, such films have been of interest for nanotechnology applications. How-
ever, Kim et al. [33, 18] have shown that not only can periodic patterns of focal conics be
obtained, but also that these structures can undergo morphological transitions through
sintering (i.e., reshaping of a SmA at elevated temperatures for an amount of time, with
subsequent cooling), leading to new and unexpected patterns. They observed that at
temperatures above the smectic region, layers would evaporate in a curvature driven
fashion, resulting in a variety of transient film structures. By sintering a sample of
TFCDs at 130°C for 120 h evaporation of the layers resulted in tiny spheres or little
Udumbara flower structures at the core of the focal conics, as observed in Fig. 1.3 (a).
When sintering at 160°C for 40 min, evaporation of layers removed even more of the
outer layers, and at the core of the focal conics a structure of concentric rings appeared,
as in Fig. 1.3 (b). By increasing the temperature to 180°C, sintering for about 8 min
resulted in a fast removal of layers at the periphery of each focal conic, sculpting conical
pyramids in the process (centered at the axes of the TFCDs), shown in Fig. 1.3 (c).
Finally, when sintering at 190°C for less than 2 min, films lost most of their volume and dome-like structures appeared (temperature becomes too close to the melting point), as shown in Fig. 1.3 (d).

Figure 1.3: Resulting morphologies for sintering experiments on smectic thin films presenting arrays of TFCDs, from Ref. [18]. (a) Udumbara flower structures; (b) Concentric rings; (c) Conical pyramids; (d) Domes.

An interesting aspect of these morphological transitions is that some of them cannot be understood by classic interface theories, such as the Gibbs-Thomson equation (1.3). For instance, let us focus on the case of focal conic to conical pyramid transition. Using Eq. (1.3), we think of the change in energy at the interface by emitting or absorbing molecules. Emission is favored in regions of positive mean curvature, which are the peripheral ones in a focal conic, while in regions close to the core, of negative mean curvature, we expect emission to be suppressed. This reasonably agrees with initial observations, that layers evaporate away from the core. However, classic theories fail to explain why the region near the core, of negative $H$ and $G$, is later restructured into a conical pyramid, of positive $H$ and $G$. That is, what is the process that actually takes place near the macroscopic conic singularity? Why are structures of positive mean curvature formed if from Eq. (1.3) they are expected to enhance evaporation? Also, what are the implications of changing the sign of the Gaussian curvature for the
resulting morphologies? The interplay between mean and Gaussian curvatures in the FCD is key to the complex instabilities and film morphologies under heat treatment that are observed in the experiments.

Smectic films displaying arrays of FCDs constitute a potential platform for surface engineering through heat treatment. Indeed, arrays of focal conics are being investigated as building-blocks for soft lithography patterning [35, 36], base structures for the fabrication of superhydrophobic films [37], guides for the self-assembly of nanoparticles [38, 39], and optically selective microlens photomasks [40], which make for an efficient way to produce patterns through photolithography. It has also been observed that when domains of focal conics are formed through morphological transformations in the nematic-smectic transition, they retain the geometric memory of how boojum defects in nematics were organized [41, 42]. Further, these structures present dual scale features, since the scale of the original defects is usually in micrometers, while the details of the formed layers are nano-sized. This dual roughness gives them superhydrophobicity, which is an essential ingredient for self-cleaning surfaces [16]. Nevertheless, there is very limited understanding at present of the role of curvatures on the thermal processes and stability of these arrays, which would be fundamental to fine tune the morphological transitions and properties of resulting patterns.

1.2 Phase-field modeling of liquid crystals

Modeling of liquid crystals started with the Oseen-Frank theory, which describes the free energy of a liquid crystal through a functional of the director. A standard procedure in modeling a smectic-A is tying the director to the same direction as the layer normal, so that only three possible molecular distortions appear in smectic free energy: compression, splay (bending of layers) and saddle-splay. This topic is covered in detail in Chapter 2. For small local distortions it becomes possible to describe the smectic layers through a configuration variable $u$, which represents normal displacements of the layers with respect to planarity. This theory has been successful in describing equilibrium configurations, such as focal conics (the splay term, in particular, contains the mean curvature squared).

However, modeling the dynamics of a smectic-isotropic interface that undergoes
morphological transitions is much more challenging. First of all, the model needs to be able to dynamically handle macroscopic singularities (such as a focal conic), which is an issue for a model based on the $u$ variable. For instance, near the conic singularity the interface becomes highly deformed, where the director and the layer normal diverge, so that additional terms become necessary in the energy. Also, we would like a model to represent a two-phase system in which we could have both coexistence between phases and a regime that could induce a continuous evaporation of smectic layers.

Phase-field models have been introduced as a convenient and versatile mathematical description of complex interfacial morphologies. The use of phase-fields or Ginzburg-Landau type equations in the study of interfacial motion became widespread since the pioneering work of Cahn and Hilliard [43] who, instead of a sharp interface, described the interface between two neighboring phases as a continuous transition in composition (i.e. a diffuse interface). For this, they proposed an energy functional for the two phase system whose energy density was function of the composition and gradients of the composition. By expanding the energy density in Taylor series and using symmetry arguments, they expressed the energy of the system through a polynomial describing the energy landscape plus a gradient squared of the composition, which implies in a smooth transition of the composition between phases. This work was later extended by Allen and Cahn [44] who showed that the method could be used to study the unstable motion of a two phase interface outside of thermodynamic equilibrium. The classical result involving motion driven by mean interfacial curvature emerges from the Allen-Cahn equation as the singular limit in which the width of the initially diffuse interface is taken to zero [45]. The methodology has been subsequently generalized to the case of a conserved order parameter [46], to interfaces separating fluid phases [47, 48, 49, 50], and to interfaces bounding phases that are modulated in equilibrium [51].

Therefore, a phase-field model can be suitable for describing the evolution of a two-phase interface between a smectic and an isotropic phase. We will represent the smectic layering by a real order parameter $\psi$, which is adapted from previous work using a complex order parameter for smectics [52, 53]. The parameter $\psi$ can be written in terms of a complex amplitude, whose phase connects to the configuration variable $u$. From the phase-field model, in the macroscopic limit of a thin interface, it is possible to derive interface equations such as conditions for local equilibrium [54]. One challenge
in the case of a modulated phase is that spatial modulations are also present at the interface, so that deriving thermodynamic relations at the interface is not as simple as in the case of Allen-Cahn or Cahn-Hilliard equations. We overcome this problem by using a multiscale expansion, from which we derive the amplitude equation for a smectic-isotropic interface. This equation describes the motion of the amplitude that envelopes the modulated phase, which gives us a coarse-grained representation of the interface and assists us in deriving interface equations. Our results, present in Chapter 3, lead to an extended Gibbs-Thomson relation governing local equilibrium at a distorted interface that depends not only on its mean curvature but also on interfacial bending and torsion, and on the alignment of the modulated phase with respect to the interface.

A complete transport model of an isothermal smectic film of the type described above requires consideration of an appropriate smectic order parameter (non conserved), as well as mass and momentum conservation relations. With an internal energy provided by the phase-field, we are able to derive all the required governing equations with appropriate choices of constitutive relations from the Coleman-Noll procedure. We will study both a smectic-isotropic system of constant density, so the isotropic phase is essentially unstructured liquid crystal. We also study a system where the phases have different densities, so that the isotropic phase can represent some other fluid (e.g. water, air). When phases have distinct density, we explore in Chapter 4 a limiting case of quasi-incompressibility, where local density is tied to the order parameter constitutively, indirectly forcing conservation of the order parameter. In Chapter 5 we relax this condition, presenting a weakly compressive smectic-isotropic model, where the density becomes independent. In this model the energy presents an energy penalty for deviations from equilibrium density values, which leads to a coupling between density and order parameter in the dynamical equation for the latter.

1.3 Spiral Defect Chaos: a case of active smectic

Rayleigh-Bénard convection appears from buoyancy driven instabilities in a layer of confined fluid submitted to a temperature gradient in the vertical direction \( \hat{z} \) to the convection box, leading to convective patterns known as Bénard cells. At the midplane (in \( z \)) of the box, the temperature and the vertical velocity fields form roll structures.
This pattern presents relaxational dynamics, and its two-dimensional motion can be interpreted as a diffusive dynamics of a smectic. Classical stability theory is based on the Boussinesq model of thermal convection in a simple fluid [55], and motion near the onset of Rayleigh-Bénard convection is predicted to be variational, a fact that would preclude persistent dynamics.

However, an unexpected chaotic state near the onset of convection in a Rayleigh-Bénard configuration was discovered in CO\textsubscript{2} gas (a low Prandtl number fluid) by Morris et al. [56], in which rolls bend and spiralize forming rotating spirals, that are continuously nucleated and eliminated, yielding a state with persistent dynamics (i.e., “spiral defect chaos”), as shown in Fig. 1.4. Experimental evidence also suggests that, as the fluid Prandtl number decreases or the aspect ratio of the experimental cell increases, the chaotic state may emerge as the first bifurcation from the quiescent, conduction state [57], contrary to well established theory [58, 55, 59]. As was recognized early on, the chaotic state is enabled through the coupling between the primary vertical velocity field mode that becomes unstable at threshold, and weakly damped, long wavelength rotational flows on the horizontal plane. That such near-marginal flows could be relevant in convection in large aspect ratio systems had been proposed earlier by Siggia and Zippelius [60].

A class of theoretical and computational analyses focused on two-dimensional (2D) models (generalized Swift-Hohenberg models) that explicitly include the coupling between the vertical vorticity and an order parameter field appropriate for the convective instability (proportional to the vertical velocity or temperature deviation on the mid plane of the convection cell) [61, 62, 63]. Following the discovery of spiral defect chaos, numerical analysis of these models confirmed the importance of the coupling to vortical flows to model the transition to chaos [64, 65, 66, 67, 68, 69], although it remains unclear what its precise role actually is in sustaining the chaotic state. Extensive computational work also included direct numerical solution of the governing equations for a Boussinesq fluid in a Bénard configuration [70, 65, 71, 68, 69], and also of the related problem of a single rotating spiral pattern filling the entire convection cell [72, 73, 74]. In particular, a detailed numerical investigation by Karimi \textit{et al.} [68, 69] has shown that the flow structure around a spiral core in a fully three-dimensional (3D) numerical solution of the Boussinesq equations is qualitatively similar to that of the simpler generalized
Swift-Hohenberg models that incorporate 2D rotational flows. Yet, the main question as to the mechanisms underlying the appearance of the chaotic state and, in particular, the role of any hydrodynamic interactions among rotating spirals in an extended systems remain unanswered.

In Chapter 6, we present results based on both a generalized Swift-Hohenberg model using a 2D order parameter field $\psi(x, t)$, which represents the vertical velocity of the fluid at the convection box's mid-plane, and a full 3D solution of the Boussinesq equations. We begin by examining approximate solutions of the 2D model that correspond to a rotating spiral pattern, focusing on the rotational horizontal flow induced by an effective body force $f = -\nabla^2 \phi \nabla \psi$ (where $\nabla$ is the 2D gradient operator on the horizontal plane) that plays the role of the driving force of the vortical flow \[ \text{(64) 66} \]. It is through this term that the curved convective rolls generate vertical vorticity, which in turn advects convective rolls. From the form of the $\psi$ field corresponding to a spiral pattern, we obtain an asymptotic form for the body force, independent of modulations. This form allows us to make a parallel with active matter: although it is a force whose form coincides with the one derived from a coarse grained energy of the system, the coefficients do not match, i.e., it is not the divergence of a stress derived from the energy. This implies
that there is an internally generated active stress contributing to flows and the persistent dynamics.

We show that there exists an irrotational contribution to $f$ that leads to a long-ranged azimuthal velocity field around the core of the spiral. We rely on amplitude equation for curved smectics in order to find this contribution. For a laterally unbounded configuration, the azimuthal velocity decays as $v_\varphi \sim 1/r$ away from the core. If, instead, the azimuthal velocity is required to vanish at a finite distance $r_b$ from the core, we show that this asymptotic dependence is never attained for typical spiral sizes. Furthermore, if damping at the bottom and top bounding walls is neglected, we find $v_\varphi \sim r \ln(r/r_b)$, where $r_b$ is a cutoff distance at which the velocity vanishes. These results are verified numerically for both a rigidly rotating spiral pattern and the spiral defect chaotic state that are generated in the 2D generalized Swift-Hohenberg model and the 3D Boussinesq equations.

### 1.4 Thesis organization

The present thesis seeks to develop and interpret results from mesoscale models for soft layered materials. One of its main achievements is to propose solutions for modeling a two-phase interface where one side presents a modulated phase. In particular, it addresses the issue of how to derive thermodynamic relations at a modulated interface, and how to model a transient density field with distinct values at the bulk of each phase, but independent of modulations. The goal is to combine analytic predictions and numerical results to understand unstable interface motion, morphological transitions, and the role of curvatures on pattern formation and flow structure. The physical systems that motivate our investigations, as explained, are the sintering of smectic films presenting arrays of TFCDs and active smectics in the Rayleigh-Bénard convection.

- Chapter 2 starts with a historical background of the mechanics of liquid crystals. After a review of continuum thermomechanics, the Coleman-Noll procedure is covered in details, with a few examples. The chapter ends discussing the evolution of thermodynamics of highly curved interfaces, since early attempts in generalizing Gibbs theory in 1950s up to modern days.
• A diffusional model for a smectic-isotropic system of uniform density is introduced in Chapter 3, based on our publication from Ref. [75]. By using the amplitude equation for the order parameter model, we derive a generalized Gibbs-Thomson equation and an equation for interface kinematics, which are function of both mean and Gaussian curvature, and depend on layer orientation with respect to the interface. Numerical results are shown, including focal conic to conical pyramid transitions, which is explained in light of the derived interface equations.

• Chapter 4 adopts the same energy for a smectic-isotropic system from Chapter 3 and uses it to derive a full transport model through the Coleman-Noll procedure, where the order parameter, density and velocity are coupled. We work in the quasi-incompressible limit, where the density is given constitutively as a function of the order parameter. A decay rate for transverse perturbations to flat layers is derived, and used to verify the numerical implementation. We show numerical results for the velocity field on perturbed smectic layers and on a focal conic, and interpret them based on local curvatures. This chapter is based on our article in Ref. [76].

• In Chapter 5 we further generalize the smectic-isotropic model for the case of weak compressibility, relaxing the strong constraint of quasi-incompressibility. We add a term to the energy that penalizes deviations from preferred density values on both phases. By controlling the constant associated with this term, we are able to set the strength of the coupling between the order parameter and the density, which acts as a correction to the bifurcation parameter. We show that if this constant is high enough, the system reaches the quasi-incompressible limit ($\psi$ becomes approximately conserved), and that if the constant is too low, $\psi$ moves almost independently of the density. Numerical results explore the possibility of coalescence between two cylindrical stacks of smectic layers, and also interactions between focal conics due to the flow. An article presenting these results is currently in preparation.

• Chapter 6 changes the discussion to active smectics in the Rayleigh-Bénard convection, in the Spiral Defect Chaos regime. We adopt a two-dimensional order
parameter model coupled to a velocity equation for the mean flow, which is derived from the three-dimensional Boussinesq equations. Our goal is to understand azimuthal flows generated by the topological defects, their implications for interactions between spirals, and the role of flows in sustaining the regime. Finally, we show a correlation between a balance of unwinding dynamics (due to curvature of rolls) and advection of order parameter, and the appearance of the spiral chaos regime. This chapter is based on our article in Ref. [77].

- Chapter 7 concludes the thesis with a summary of the main findings.
Chapter 2

Thermomechanics of soft materials

The existence of nematic, cholesteric and smectic phases was first recognized by Friedel [78] in 1922. Since then, researchers have been interested in understanding liquid crystalline materials from a thermomechanical point of view. Many soft materials such as liquid crystals present a microstructure and broken symmetries that differ from those in typical solids, which has implications for mechanical balances (and microbalances): for instance, due to restoring torques in a molecular configuration that deviates from equilibrium, the stress tensor in a liquid crystal may not be asymmetric. Moreover, the mixed behavior between a solid and a fluid implies that flows are of importance for such materials, which often presents non-classical stresses and complicated viscous tensors.

This chapter starts with a historical overview of the development of continuum theories for liquid crystals. Section 2.1 discusses the origins of the well known Oseen-Frank energy for nematic liquid crystals, and how a theory for nematodynamics progressed since the pioneering works of Jerald Ericksen. The mechanics of smectics is introduced in Sec. 2.2, which is built on the work for nematics. In particular, we discuss the mean curvature squared and Gaussian curvature terms that are present in the energy, and how their minimization is connected to the appearance of focal conic domains in smectic films. Before introducing the Coleman-Noll procedure, through which we derive constitutive relations and obtain the governing equations of a smectic, we briefly review
continuum mechanics and thermodynamics in Sec. 2.3 (Euler’s laws of mechanics, thermodynamics axioms). The Coleman-Noll procedure is then applied for three different examples: a simple material, theory of microforces, and a smectic described by the layer displacement variable \( u \). The chapter ends in Sec. 2.4 with a digression on thermodynamics of highly curved interfaces, describing efforts since the 1950s to generalize the Gibbs-Kelvin (and Gibbs-Thomson) equation for surfaces whose local equilibrium is not a linear function of the mean curvature.

## 2.1 Mechanics of nematics

We begin with a discussion of nematic liquid crystals. Recall from Fig. 1.1 that a nematic presents long-range orientational order along a director axis, but does not present a long-range spatial organization such as a smectic. The foundations of the curvature-elasticity theory of liquid crystals was formulated by Oseen in 1933 [79], motivated by the observation that forces causing molecules to combine and align were weak intermolecular forces, and not of the valence type. Oseen argued that the force and energy for a liquid crystal were functions of a vector of unit length which has the same direction as the axis of symmetry of the molecule, which later became known as the director \( n \).

In 1958, Frank [80] revised Oseen’s theory for hydrostatics of liquid crystals, with particular interest in curvatures and equilibrium forms. When bending an elastic solid, we consider that changes in distance between material points are opposed by restoring forces, while in a simple fluid, no such forces are present. For a bent liquid crystal, since molecules tend to align according to the director, Frank proposed that there would be restoring torques opposing changes in curvatures. He labels them as torque-stresses, which are assumed to be proportional to curvature-strains in the limit of small distortions. This motivated him to write a free energy density as a quadratic function of these curvature-strains, in terms of the director \( n \) and its gradient \( \nabla n \), where each possible distortion of the molecular arrangement is associated with an elastic modulus, known as Frank’s constants. The key requirements for the distortion free energy density \( w_d \) of a liquid crystal are the following:
• $w_d(\mathbf{n}, \nabla \mathbf{n})$ presents a quadratic form;

• Frame indifference: $w_d(Q\mathbf{n}, Q\nabla \mathbf{n}Q^T) = w_d(\mathbf{n}, \nabla \mathbf{n}), Q \in SO(3)$;

• $w_d(-\mathbf{n}, -\nabla \mathbf{n}) = w_d(\mathbf{n}, \nabla \mathbf{n})$.

The total elastic energy, known as the Oseen-Frank free energy, is then a nonlinear functional of $\mathbf{n}$ and $\nabla \mathbf{n}$, of the form

$$W_d[\mathbf{n}] = \int w_d(\mathbf{n}, \nabla \mathbf{n})d\mathbf{x}. \quad (2.1)$$

In a nematic liquid crystal, the energy density which satisfies all the previous requirements and accounts for the different distortion penalties has the form

$$2 w_d(\mathbf{n}, \nabla \mathbf{n}) = K_1(\nabla \cdot \mathbf{n})^2 + K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2 + K_{24} [\text{tr}(\nabla \mathbf{n})^2 - (\nabla \cdot \mathbf{n})^2], \quad (2.2)$$

where the $K_i \geq 0$ are Frank’s elastic constants, with $K_1$ the splay constant, $K_2$ the twist constant, and $K_3$ the bend constant. All these possible distortions of a molecular field are sketched in Fig. 2.1.

![Elastic distortions of the director field in a liquid crystal.](image)

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

Figure 2.1: Elastic distortions of the director field in a liquid crystal.

In the 1960s, Ericksen [81, 82, 83, 84] made significant contributions to the continuum theory of liquid crystals, in particular by formulating conservation laws for nematics. As pointed out by Truesdell and Toupin [85], there is no general requirement that a stress tensor needs to be symmetric, so that liquid crystals became alluring for the
continuum mechanics community as a theory with an asymmetric stress tensor. This is a consequence of their molecular orientation being correlated macroscopically, so that the restoring torques (which appear when molecules deviate from the director) enter in the balance of angular momentum, adding asymmetrical contributions to the stress. In this continuum theory, Ericksen considered that the director $\mathbf{n}(\mathbf{x})$ at a certain point described the orientation of a packet of rodlike molecules, and that $\mathbf{n}$ changes in a systematic way as we move from one packet to another. In a packet, molecules are parallel to each other and reasonably free to move in this parallel direction. The reversible second-rank tensor (distortion stress [86]) derived from this theory is typically called the Ericksen stress, which has the form

$$ T_E = - (\nabla \mathbf{n})^\top \frac{\partial \mathbf{w}_d}{\partial \nabla \mathbf{n}}. \quad (2.3) $$

This stress represent the work done by the displacement of the molecules while keeping the director $\mathbf{n}$ unchanged. This stress is generally asymmetric, an effect that, for instance, describes changes in the energy by pure rotation about the centers of gravity of molecules, with $\mathbf{n}$ fixed. This stress can only become symmetric if $K_1 = K_2 = K_3$ [86].

In the same decade, Leslie (1966) [87] worked on constitutive equations for anisotropic fluids, completing Ericksen dynamical theory for nematics. The theory born from their efforts is known as the Ericksen-Leslie theory for nematic liquid crystals. Leslie was responsible for proposing a form for the viscous stress $\mathbf{T}$ with six coefficients of viscosity $\alpha_i$, the Leslie viscosities. In order to show its form, define the rate of strain tensor $\mathbf{E}$ and the vorticity tensor $\mathbf{W}$ as

$$ \begin{align*}
\mathbf{E} &= \frac{1}{2} \left[ \nabla \mathbf{v} + (\nabla \mathbf{v})^\top \right], \\
\mathbf{W} &= \frac{1}{2} \left[ \nabla \mathbf{v} - (\nabla \mathbf{v})^\top \right]
\end{align*} \quad (2.4) $$

where $\mathbf{v}(\mathbf{x}, t)$ is the fluid velocity. Also, define the co-rotational time flux of the director $\mathbf{N}$ as

$$ \mathbf{N} = \mathbf{n} - \mathbf{W} \mathbf{n}. \quad (2.5) $$

We note that the tensors $\mathbf{N}$, $\mathbf{W}$ and $\mathbf{n}$ are all objective, i.e., they are physically the same in all frames of reference (material frame-indifferent). In the Ericksen-Leslie theory, $\mathbf{T}$
becomes a function of these three tensors, and, consequently, it also satisfies material frame-indifference. By accounting for nematic symmetries and from the imposition that dissipation should be greater or equal than zero, Leslie proposed the following dissipative part for the stress in an incompressible nematic:

\[ \tilde{T}_{ij} = \alpha_1 n_k E_{kl} n_i n_j + \alpha_2 N_i n_j + \alpha_3 n_i N_j + \alpha_4 E_{ij} + \alpha_5 n_j E_{ik} n_k + \alpha_6 n_i E_{jk} n_k. \]  

(2.6)

Using the Onsager reciprocal relations, Parodi (1960) [88] derived the following relation between the Leslie viscosities:

\[ \alpha_2 + \alpha_3 = \alpha_6 - \alpha_5, \]  

(2.7)

reducing the number of independent viscosities in a nematic to five. For the general compressible case of nematodynamics, there are a total of eight independent viscosity coefficients [86].

Under isothermal conditions, and assuming incompressibility of the fluid \( \nabla \cdot \mathbf{v} = 0 \), the Ericksen-Leslie dynamic equations for a nematic in local form, obtained from the conservation laws, are [89, 90]

\[ \rho \dot{\mathbf{v}} = -\nabla p + \mathbf{F}_{\text{ext}} + \nabla \cdot (\mathbf{T}_E + \tilde{T}) , \]

\[ = -\nabla(p + w_d) + \mathbf{F}_{\text{ext}} + (\nabla n) \tilde{T}(\mathbf{g} + F_g) + \nabla \cdot \tilde{T} , \]  

(2.8)

\[ \lambda \mathbf{n} = \nabla \cdot \left( \frac{\partial w_d}{\partial \nabla n} \right) - \frac{\partial w_d}{\partial n} + \dot{\mathbf{g}} + F_g , \]  

(2.9)

where \( \lambda \) is a Lagrange multiplier due to the \( |n| = 1 \) constraint on the director, \( p \) is the pressure, \( \mathbf{F}_{\text{ext}} \) is an external body force, and \( \mathbf{F}_g \) is a generalized body force. Equation 2.8 is the balance of linear momentum, while Eq. 2.9 is the balance of angular momentum. In Eq. 2.8 we can also add an inertia term \( \dot{n} \) multiplied by a constant to the left hand side, to account for the rotational kinetic energy of a material element (negligible in most cases [90]). Finally, the expression for \( \dot{\mathbf{g}} \) is

\[ \dot{\mathbf{g}} = (\alpha_2 - \alpha_3) \mathbf{N} + (\alpha_5 - \alpha_6) \mathbf{E} n. \]  

(2.10)
These equations have been studied extensively, with particular interest in the coupling between flow in nematic liquid crystals and their director field (e.g. flow-aligning and non-flow-aligning nematics), and have also been extended to account for gravity, magnetic fields and others. Once nematodynamics was established, efforts in the sense of developing continuum theories and dynamical equations for smectics appeared, based on ideas from the Oseen-Frank energy and the Ericksen-Leslie theory.

2.1.1 Geometric interpretation of splay and saddle-splay

When considering the special case of an interface where the director $\mathbf{n}$ approximately coincides with the interface normal $\hat{n}$, the splay and saddle-splay term acquire particular geometric meanings. For such an interface, the splay term multiplied by $K_1$ represents the variation in energy due to a change in mean curvature, since $\nabla \cdot \mathbf{n} \approx 2H$. In the case of the saddle splay term, it becomes connected to the Gaussian curvature, as will be explained next.

The saddle-splay term in Eq. (2.2) associated with $K_{24}$ often presents different forms in literature, and it is not always evident that they are the same. Moreover, this term corresponds to the Gaussian curvature, since a classic result in differential geometry \cite{91} is

$$G = \frac{1}{2} \nabla \cdot [\mathbf{n}(\nabla \cdot \mathbf{n}) + \mathbf{n} \times \mathbf{n}] .$$

In order to show the equivalence between the previous expression for the Gaussian curvature and the saddle-splay term in Eq. (2.2), we start by rewriting the latter in another commonly found divergence form \cite{92},

$$\left[\text{tr}(\nabla \mathbf{n})^2 - (\nabla \cdot \mathbf{n})^2\right] = \nabla \cdot \left[(\mathbf{n} \cdot \nabla)\mathbf{n} - \mathbf{n}(\nabla \cdot \mathbf{n})\right] .$$

Then, the task now is to prove that Eq. (2.11) can be written as the previous divergence expression in Eq. (2.12). Using Einstein notation, we can write the expression for the Gaussian curvature as

$$G = \frac{1}{2} \partial_i \left[(\partial_k n_k)n_i + \epsilon_{ijk}n_j(\epsilon_{klm}\partial_l\partial_m n_i)\right] .$$

(2.13)
Further, from the identity
\[ \epsilon_{ijk} \epsilon_{lmn} = \delta_{il} \delta_{jm} - \delta_{im} \delta_{jl} \]  
(2.14)
we find,
\[ G = \partial_i [(\partial_k n_k) n_i + n_j \partial_i n_j - n_j \partial_j n_i] . \]  
(2.15)
Since the director has the property \(|n| = 1\), the last term in the divergence \(n_j \partial_i n_j = \frac{1}{2} \partial_i (n_j n_j)\) is zero, so that
\[ G = -\frac{1}{2} \nabla \cdot [(n \cdot \nabla) n - n (\nabla \cdot \hat{n})] , \]  
(2.16)
which proves the equality.

### 2.2 Mechanics of smectics

In the following discussion, we restrict our attention to non-chiral smectics, which is the case for smectic-A. Smectic liquid crystals behave like a solid in the direction of layer modulation, while each of its molecular layers behave as a two-dimensional fluid, manifolds in which molecules present a higher mobility. In a smectic-A, the solid axis is closely aligned to the normal to the layers, whereas in a smectic-C the solid axis is tilted with respect to the normal. The stack of fluid layers in a smectic present a characteristic period \(\lambda_0 = \frac{2\pi}{q_0}\), where \(q_0\) is a wave number, and their molecular density \(M\), using Fourier series, can be written as \[ M(x) = M_0 + \sum_n \left[ \langle \psi_n \rangle e^{i q_0 \cdot x} + \text{c.c.} \right] \approx M_0 + \left[ \langle \psi_1 \rangle e^{i q_0 \cdot x} + \text{c.c.} \right] . \]  
(2.17)
That is, the smectic layering is well defined by the first harmonic, and higher harmonics are generally not experimentaly visible. Note that \(M\) is different from the macroscopic material density \(\rho\), as it describes how molecules are spaced and organized. On the other hand, the density \(\rho\) is approximately constant in the bulk of a smectic and does not depend on the layering order. \(\langle \psi_1 \rangle\) is a complex amplitude of the molecular density,
where for smectic layers with $q_0 = q_0 \hat{z}$ and normal displacements $u$, it can be written in terms of a real amplitude and a phase as $\langle \psi_1 \rangle = |\langle \psi_1 \rangle| e^{-iq_0 u}$. The broken symmetry variable $u(x)$ represents layer displacements with respect to a flat configuration, and has been used extensively in the description of smectic phases as mentioned in Sec. 1.2.

By using rectangular Cartesian coordinates, smectic layers normal to the solid axis $\hat{z}$ can be represented as planes of constant phase $\phi$, given by

$$\phi = \frac{\nabla \phi}{|\nabla \phi|} \approx (-\partial_x u, -\partial_y u, 1) \quad (2.18)$$

where $n \in \mathbb{Z}$ corresponds to different level sets ($n^{th}$ layer). This allows us to define the normal to the layers, which is,

$$\hat{n} = \frac{\nabla \phi}{|\nabla \phi|} \approx (-\partial_x u, -\partial_y u, 1) .$$

An elastic free energy for a smectic should account for the fact that the smectic breaks both rotational and translational symmetry. Therefore, it should be invariant under rotations as well as translations. The Oseen-Frank free energy density from Eq. (2.2) is written in terms of the director $n$, which, for a smectic-A, only differs from the normal $\hat{n}$ by a high energy mode with respect to the ideal layering [94]. If we assume that the layer normal changes instantaneously with the director, constraining $\hat{n} = n$, we are able to evaluate which distortions from Oseen-Frank are allowed for a smectic-A. From the definition of the phase $\phi$ in Eq. (2.18), we have that $n \cdot \nabla \times n = 0$ in the absence of defects. As twist and bend of molecules cannot occur while preserving a uniform interlayer spacing, thus implies that they cost much more energy for a smectic-A than splay ($\lambda_0$ preserving), as illustrated in Fig. 2.1. Therefore, in most works twist and bend are neglected from the energy of a smectic, although close to singularities and regions of large deformation of layers (compression) they may play a role in the smectic energy [95, 94].

In addition, in smectics there is an energetic cost associated with compression of the layers, given by the strain $\partial^2_z u$, a deformation that maintains an uniform layer spacing, and is always accounted for alongside splay when writing a smectic free energy. Note that the splay term is a function of the mean curvature of the layers, since $\nabla \cdot n = 2H$, which can also be written in terms of the small displacements $u(x)$ (trace of the Hessian).
Further, the saddle-splay term is proportional to the Gaussian curvature, so that we can also write it as a function of displacements (determinant of the Hessian). Therefore, when constraining $\mathbf{n}$ to the normal direction to the layers, the smectic energy \[96\] is given by

$$W_s = \frac{1}{2} \int \left\{ B (\partial_z u)^2 + K (\partial_x^2 u + \partial_y^2 u)^2 + \tilde{K} \left[ (\partial_{xy} u)^2 - \partial_x^2 u \partial_y^2 u \right] \right\} dx , \quad (2.19)$$

where $K$ and $\tilde{K}$ are the splay and saddle-splay constants for a smectic, respectively (in physics of lamellar media, typically $K = K_1$ and $\tilde{K} = -2K_{24}$). This energy is also found in the literature written directly in terms of $H$ and $G$ \[97, 91\] as

$$W_s = \frac{1}{2} \int \left\{ B \left( \frac{\lambda}{\lambda_0} - 1 \right)^2 + K (2H)^2 + 2\tilde{K}G \right\} dx . \quad (2.20)$$

where $\lambda$ is interlayer spacing. Since mean and Gaussian curvature appear in the energy density, this equation describes a system with various smectic layers, where curvatures may change from one to another. Without the compression term, we can also think of a layer-wise surface energy, which has the form of a Canham–Helfrich energy \[98\].

### 2.2.1 Saddle-splay term in smectics

The last term in Eq. (2.19) is a divergence (surface term) \[86\], which does not contribute to the associated Euler-Lagrange equation, and it is often overlooked. That is, it is a null Lagrangian (labeled as nilpotent energy by Ericksen \[83\]), and does not contribute to bulk equilibrium equations when considering variations of the smectic layers, as long as the topology, singularities and the boundaries are fixed. This observation connects to the Gauss-Bonnet theorem, according to which the integral of the Gaussian curvature over a compact orientable surface $\Gamma$ is a constant. That is,

$$\int_{\Gamma} G d\mathcal{A} = 2\pi \chi(\Gamma) , \quad (2.21)$$

where $\chi(\Gamma)$ is the Euler characteristic of $\Gamma$, which in terms of the genus $g$ of the surface is $\chi = 2 - 2g$, and $d\mathcal{A}$ is a surface element. This statement can be generalized for the case of a surface presenting a boundary $\partial\Gamma$ and also cone singularities, which are points on
the interior of the surface with angle $\theta \neq 2\pi$. Defining $\Gamma_0 = \Gamma / \{x_1, ..., x_n\}$ as the surface with the singularities $x_i$ removed (each with an associated $\theta_i$), and $k_g$ as the geodesic curvature on the boundary (which measures how far the curve is from a geodesic, the “shortest path” between two points), the generalized Gauss-Bonnet becomes

$$\int_{\Gamma} G dA + \int_{\partial \Gamma} k_g dl + \sum_{i=1}^{n} (2\pi - \theta_i) = 2\pi \chi(\Gamma).$$

(2.22)

Note that in case a cone singularity appears on the boundary, the term in the sum associated with this singularity should be $(\pi - \theta_i)$.

Schief et al. [97] present a discussion on the signs of $K$ and $\bar{K}$, describing scenarios where one would expect the stabilization of planar layers, spherical layers (micelles) or a minimal surface shape. However, work on smectics appears to neglect cone singularities, which matter for focal conic domains. While the internal layers of a focal conic could be regarded as a series of Clifford tori (conformally equivalent to Dupin cyclides), the surfaces defined by the outer intersecting layers can be described by the apple segment of a spindle torus [100]. Although a spindle torus presents the same Euler characteristic, $\chi = 2$, as a 2-sphere, the integral of the Gaussian curvature over these two different closed surfaces is not the same due to the cone singularity, as described by Eq. (2.22). Therefore, in morphological transitions of smectic surfaces, including focal conic to conical pyramids transition (annihilation of singularity), the saddle-splay term in Eq. (2.19) can lead to a change in energy, and should be treated carefully.

2.2.2 Focal conics and the Willmore problem

When bending a smectic-A (splay of molecules) or introducing perturbations, we expect the interlayer spacing to remain close to the equilibrium distance (approximately $\lambda_0$), such that the layers stay parallel when curving. When fixing the director to be the same as the normal to the layers, we have seen that Eq. (2.19) is appropriate to describe a smectic elastic energy. Therefore, the appearance of focal conic defects in smectic films should, in some sense, be explained by a minimization of $W_s$. While these defects are known to form when antagonistic boundary conditions are present, with molecules tending to align parallel to a substrate and perpendicular to the interface with a neighboring phase (e.g. air in experiments [18]), there is also an important energetic component that
explains why the focal conic shape is chosen.

When restricting Eq. (2.19) to the splay term (no layer compression, fixed topology), the energy becomes solely dependent of the mean curvature squared of the layers. The question of which shape minimizes this energy is then connected to the Willmore problem: Given the Willmore functional for a smooth, orientable surface $\Gamma$,

$$W_h = \int_{\Gamma} \left\{ H^2 - G \right\} d\mathcal{A},$$

what are the minima of $W_h$? For a fixed topology, this variational problem can be simplified to the minimization of the $L^2$ norm of the mean curvature. The variation of this functional with respect to perturbations on the surface leads to the Willmore flow [101], with an interface normal velocity $v_n$ (gradient flow leading to energy minimization) of the form

$$v_n = \nabla^2 H + 2H(H^2 - G)$$

Surfaces that satisfy $v_n = 0$ are Willmore surfaces, which is the case for minimal surfaces, spheres and Dupin cyclides [97]. For any compact surface $\Gamma$ immersed in $\mathbb{R}^3$, Willmore proved that $W_h \geq 4\pi$, and the only surface satisfying $W_h = 4\pi$ is a round sphere [101]. The problem becomes more intricate for a surface presenting boundaries and other constraints. Still, since the pioneering work of Bragg (1934) [34] it has been known that the geometry of focal conic domains in smectic films has the form of Dupin cyclides, in particular as a Clifford torus in the axially symmetric case (TFCD). Therefore, the combination of minimization of mean curvature and antagonistic boundary conditions for molecules explain why focal conic domains appear as equilibrium structures.

Note that the Willmore flow is different from the simple minimization of the surface area (membrane energy)

$$E_\Gamma = \int_{\Gamma} d\mathcal{A}$$

which leads to an interface velocity $v_n = -H$, at least to leading order in curvature. Hence, shapes evolving through flow by mean curvature present a remarkably different evolution than those evolving by the Willmore flow [102].
2.3 Continuum thermomechanics

The objective in this section is to introduce the Coleman-Noll procedure \[103\], a systematic way to derive constitutive relations, that will be used to derive the governing equations for a smectic liquid crystal. We start by reviewing the balance laws from continuum mechanics, and, by introducing state variable fields, we discuss the local form of the first and second laws of thermodynamics. Sections 2.3.1 and 2.3.2 present a summary of classical results on continuum thermomechanics, based on the books by Truesdell \[104, 105\], Tadmor et al. \[106\], and Gurtin et al. \[107\]. From the specific entropy production inequality, the Coleman-Noll procedure can be applied to derive constitutive relations by imposing that this inequality should be satisfied for every admissible process. We show three different applications, including a way to derive the dynamics equations for a smectic, based on the configuration variable energy description from Eq. (2.19).

2.3.1 Basics of continuum mechanics

Start with a body \( B \), which occupies a domain of space at time \( t \), and whose reference configuration is \( B_0 \). A particle \( X \in B_0 \) (reference description) is mapped into \( x \in B \) (spatial description) through a bijection \( \varphi \). This deformation mapping is

\[
x = \varphi(X, t), \quad -\infty < t < \infty ,
\]

which is the motion of \( B \). The rate of change of position of a particle is defined as the velocity \( \mathbf{v} = \dot{x} \), where

\[
\dot{x} := \partial_t \varphi(X, t) = \dot{x}(x, t) .
\]

This is called the material time derivative, since it is the rate of change that follows a particle \( X \) of the reference body. For a field \( h = h(x, t) \), by the chain rule, its material time derivative is

\[
\dot{h} = \partial_t h + \nabla h \cdot \mathbf{v} ,
\]
where $\nabla$ is the gradient in the spatial description. Throughout this work, the *dot* $\dot{}$ notation will always be used for the material time derivative.

The total mass of a closed system should be conserved. Defining $\rho(x, t)$ as the non-negative mass-density, the integral $\int_B \rho \, dx$ should not change in time, and the same applies for the integral over any subset $\mathcal{H} \subset B$. By differentiating this integral with respect to time, *Reynolds transport theorem* states that the resulting integral is

$$\frac{d}{dt} \int_B \rho \, dx = \int_B \left[ \partial_t \rho + \nabla \cdot (\rho \mathbf{v}) \right] \, dx . \quad (2.29)$$

The result on the right hand side can be localized, so that for every point where $\rho$ and $\mathbf{v}$ are sufficiently smooth the following holds for any $\mathbf{x} \in B$:

$$\dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0 . \quad (2.30)$$

In the present configuration $B$, the linear momentum $\mathfrak{L}$ and angular momentum $\mathfrak{H}$ (about a fixed point $\mathbf{x}_0$ point) are

$$\mathfrak{L} = \int_B \rho \mathbf{v} \, dx , \quad \mathfrak{H} = \int_B (\mathbf{x} - \mathbf{x}_0) \times (\rho \mathbf{v}) \, dx . \quad (2.31)$$

For every body, the material time derivative of these quantities should be equal to the total force and total torque acting upon the body. For a *body force* $\mathbf{b}$ (acting at distance) and *traction* $\mathbf{t}$ (mutual action of neighboring parts of the material, or forces across the boundary $\partial B$ from interaction with the body’s surrounding), we write Euler’s laws of mechanics as

$$\dot{\mathfrak{L}} = \int_B \rho \mathbf{b} \, dx + \int_{\partial B} \mathbf{t} \, dA , \quad (2.32)$$

$$\dot{\mathfrak{H}} = \int_B (\mathbf{x} - \mathbf{x}_0) \times \rho \mathbf{b} \, dx + \int_{\partial B} (\mathbf{x} - \mathbf{x}_0) \times \mathbf{t} \, dA , \quad (2.33)$$

where $A$ is a piece of the boundary $\partial B$.

Cauchy’s relation gives us $\mathbf{t} = \mathbf{Tn}$, where $\mathbf{n}$ is the outward normal to $\partial B$, and $\mathbf{T}$ is the *Cauchy stress tensor*. This stress is a second order tensor that maps a vector in spatial description into another spatial vector. Assuming that the fields are sufficiently smooth, it is possible to localize the principle of linear momentum from Eq. (2.32).
which is Cauchy’s first law of motion

\[ \rho \ddot{x} = \nabla \cdot T + \rho \mathbf{b} . \] (2.34)

The consequence of localizing the principle of angular momentum from Eq. (2.33) is that the stress tensor \( T \) should be symmetric, \( T = T^\top \), which is Cauchy’s second law of motion. However, this conclusion is not always true, as observed in the case of Ericksen stress from Eq. (2.3), since depending on the microstructure of a material additional torques may be present. For instance, if molecules in a liquid crystal deviate from the director alignment, restoring torques may appear. These torques must enter Eq. (2.33), and from Cauchy’s second law of motion it will no longer hold that the stress should be symmetric.

### 2.3.2 Local form of the thermodynamic laws

In order to bring thermodynamics to a continuum framework and introduce state variable fields, we assume that in a system out of equilibrium both local and instantaneous thermodynamic relations are the same as for a system in equilibrium \[108\] (postulate of thermodynamic equilibrium). This is a reasonable assumption for a nonequilibrium process, as long as at least locally the process is sufficiently close to thermodynamic equilibrium.

To reach this goal, we need to derive the local form of the thermodynamic laws. The kinetic energy \( \mathcal{K} \) and internal energy \( \mathcal{U} \) for the body \( B \) in spatial description are

\[ \mathcal{K} = \frac{1}{2} \int_B \rho v^2 d\mathbf{x} , \quad \mathcal{U} = \int_B \rho u d\mathbf{x} , \] (2.35)

where \( u \) is the specific internal energy. Further, we define the power \( \mathcal{P} \) as the work per unit time of all forces acting on \( B \),

\[ \mathcal{P} = \int_B \rho \mathbf{b} \cdot \mathbf{v} d\mathbf{x} + \int_{\partial B} \mathbf{t} \cdot \mathbf{v} dA , \] (2.36)

and the heat transfer rate \( \mathcal{R} \) as the sum of the body heating and the contact heating,

\[ \mathcal{R} = \int_B \rho r d\mathbf{x} - \int_{\partial B} \mathbf{q}_t \cdot \mathbf{n} d\mathbf{A} . \] (2.37)
The body heating is the volume integral of the heating supply \( r(x,t) \), generally used for describing radiation or chemical reactions, while the contact heating is the surface integral of the outward heat flux \( q_t \cdot n \).

The balance of energy, or first law of thermodynamics, can be written as

\[
\dot{\mathcal{E}} + \dot{\mathcal{U}} = \mathfrak{P} + \mathfrak{R}.
\]  

(2.38)

The left hand side of this equation is the derivative with respect to time of the total energy \( \mathcal{E} \) of the body \( \mathcal{B} \), since \( \mathcal{E} = \mathcal{K} + \mathcal{U} \). As in Sec. 2.3.1, assuming that all fields in Eq. (2.38) are sufficiently smooth, it is possible to localize the first law. First, using Cauchy’s relation, note that the surface integral in the power \( \mathfrak{P} \) can be rewritten as

\[
\int_{\partial \mathcal{B}} t \cdot v \, dA = \int_{\mathcal{B}} \nabla \cdot (Tv) \, dx = \int_{\mathcal{B}} [(\nabla \cdot T) \cdot v + T : \nabla v] \, dx.
\]  

(2.39)

Therefore, using the local balance of linear momentum, Eq. (2.34), we can also write the power \( \mathfrak{P} \) as

\[
\mathfrak{P} = \int_{\mathcal{B}} (\nabla \cdot T + \rho b) \cdot v \, dx + \int_{\mathcal{B}} T : \nabla v \, dx = \dot{\mathcal{K}} + \int_{\mathcal{B}} T : \nabla v \, dx.
\]  

(2.40)

By substituting Eq. (2.40) into the first law, Eq. (2.38), and using the divergence theorem for the heat flux, we obtain a single volume integral containing all the terms in the expression. This integral must be satisfied for any subbody \( \mathcal{H} \subset \mathcal{B} \), so that first law can be expressed locally for any \( x \in \mathcal{B} \) as

\[
\rho \dot{u} = T : \nabla v - \nabla \cdot q_t + \rho r.
\]  

(2.41)

In addition to formulating the first law in local form, we can also derive the second law in local form, which is the axiom of irreversibility. Similarly to the internal energy, we define the entropy \( S \) of a body \( \mathcal{B} \) as the integral of the specific entropy (the entropic) over the body

\[
S = \int_{\mathcal{B}} \rho s \, dx.
\]  

(2.42)
In the Clausius-Planck form, the second law of thermodynamics states

$$\theta \dot{S} \geq R,$$  \hspace{1cm} (2.43)

where $\theta(x,t)$ is the positive-valued absolute temperature. By substituting the rate of heat transfer from Eq. (2.37) in Eq. (2.43), and using Reynolds transport theorem, for any subbody $\mathcal{H} \subset \mathcal{B}$ the following must hold:

$$\int_{\mathcal{H}} \rho \dot{s} \, dx \geq \int_{\mathcal{H}} \frac{\partial \theta}{\partial t} \, dx - \int_{\partial \mathcal{H}} q_t \cdot n \, dA. \hspace{1cm} (2.44)$$

For sufficiently smooth fields, using the divergence theorem we localize this last expression, resulting in the **Clausius-Duhem inequality**:

$$\dot{s} \geq \frac{r}{\theta} - \frac{1}{\rho} \nabla \cdot \left( \frac{q_t}{\theta} \right). \hspace{1cm} (2.45)$$

A simpler form to express the Clausius-Duhem inequality is by writing $\dot{s}^d$ as the internal dissipation, which is the amount by which the entropic production rate exceeds external entropic input rate - defined as the right hand side of Eq. (2.45). In this case, the local form of the second law becomes

$$\dot{s}^d \geq 0. \hspace{1cm} (2.46)$$

This inequality is fundamental in our treatment of deriving constitutive relations in a continuum theromomechanical system, as it must be satisfied for every admissible process.

### 2.3.3 Coleman-Noll procedure

The field equations that describe a continuum thermomechanical system require constitutive relations, which describe the response of a material to external stimuli. These relations must be compatible with the material’s structure and satisfy physical constraints. The most fundamental thermodynamic constraint is the entropy principle, which has been used as a guiding principle to derive constitutive equations \[^{[109]}\]. The two well known mathematical procedures based on the dissipation inequality are the
Coleman-Noll [110] and the Liu procedures [111], with the former discussed at length here.

The idea behind the Liu procedure is to add the local balance of energy from Eq. (2.38) (and other additional constraints) multiplied by a Lagrange multiplier into the entropy inequality from Eq. (2.43), finding the constitutive relations based on necessary and sufficient conditions to satisfy the inequality.

The Coleman-Noll procedure originates from a simple idea by Walter Noll, in the early 1960s. He shared with Bernard Coleman that the Clausius-Duhem inequality is a restriction on all processes that are admissible in a material of which a body is composed, and, as each material is defined by a set of constitutive relations, the inequality must hold for all processes compatible with these relations [112]. His proposal combined restrictions on constitutive equations (admissibility) with general principles of the theory of materials, which include the principle of objectivity (constitutive equations need to be frame indifferent), of determinism (current state only depends on the history of the material), and of local action (neighboring processes to a material point have a stronger influence to it than distant one). This procedure was initially applied for simple materials, and was later applied to continuum theories including Ginzburg-Landau and Cahn-Hilliard.

2.3.4 Simple materials

Assume we have an internal specific energy given by \( u = u(s, F) \). Here, \( F \) is the deformation gradient tensor defined by \( F = \partial \varphi / \partial X \), which describes the deformation in the neighborhood of a material point. An important distinction for the constitutive relations is that some can be decomposed into reversible (elastic) and dissipative parts. For instance, a reversible stress \( T^R \) is the thermodynamic conjugate to strain, associated with the equilibrium state of a material, which can be derived from \( u \). However, when out of equilibrium, there is also a dissipative part of the stress \( T^D \) which has no connection to the equilibrium state (associated with an irreversible process), and explains why in many experiments it is observed that the stress is not a state variable.

In order to derive constitutive relations, we start from the Clausius-Duhem inequality
multiply it by $\rho \theta$, and explicitly write the dissipation as

$$
\rho \dot{s} = \rho \dot{s} - \rho \dot{r} + \theta \nabla \cdot \left( \frac{q_t}{\theta} \right) \\
= \rho \dot{s} - \rho \dot{r} + \nabla \cdot q - \frac{1}{\theta} q_t \cdot \nabla \theta \geq 0 \quad (2.47)
$$

By substituting the local balance of energy from Eq. (2.38) into Eq. (2.47), we find

$$
\rho \dot{s} - \rho \dot{u} + T : \nabla v - \frac{1}{\theta} q_t \cdot \nabla \theta \geq 0 \quad . (2.48)
$$

From the constitutive relation defined for $u(s, F)$ and the chain rule, we write

$$
\rho \left( \dot{\theta} - \frac{\partial u}{\partial s} \right) \dot{s} + \left( T : \nabla v - \rho \frac{\partial u}{\partial F} : \dot{F} \right) - \frac{1}{\theta} q_t \cdot \nabla \theta \geq 0 \quad (2.49)
$$

In Eq. (2.49), $\dot{F}$ can substituted by a product containing $\nabla v$. From Eqs. (2.26) and (2.27), observe that the material time derivative of the deformation gradient can be recast as

$$
\dot{F} = \frac{\partial v}{\partial X} = \frac{\partial v}{\partial x} \frac{\partial \varphi}{\partial X} = (\nabla v)F \quad . (2.50)
$$

Therefore, the inequality from Eq. (2.49) becomes

$$
\rho \left( \dot{\theta} - \frac{\partial u}{\partial s} \right) \dot{s} + \left( T - \rho \frac{\partial u}{\partial F} F^\top \right) : \nabla v - \frac{1}{\theta} q_t \cdot \nabla \theta \geq 0 \quad . (2.51)
$$

Admissible constitutive relations require the inequality (2.51) to hold for all possible thermomechanical processes [106]. The Coleman-Noll procedure meticulously investigates each of the terms in the inequality, asking (in this case) for necessary conditions on $\theta$, $T$ and $q_t$ so that Eq. (2.51) is (i) exactly satisfied, and/or (ii) products on the left hand side are necessarily positive.

For example, one can imagine a scenario where the temperature in the body is constant, with a deformation gradient that does not change in time, so that the constraint
that needs to be satisfied is

\[
\left( \theta - \frac{\partial u}{\partial s} \right) \dot{s} \geq 0 .
\] (2.52)

Therefore, the form of the temperature which always satisfies this inequality, so since \( \dot{s} \) can have any sign, requires

\[
\theta = \frac{\partial u}{\partial s} .
\] (2.53)

This local relation for the temperature has the same form as the entropy relation for a homogeneous system, which is the partial derivative of the \( \mathcal{U} \) with respect to \( S \) when the number of particles and kinematic state variables are fixed. Therefore, classic thermodynamic results naturally appear from the Coleman-Noll procedure. Note that if we assumed that \( u \) had a dependence on the gradient of the temperature, an extra term containing a derivative of \( u \) with respect to \( \nabla \theta \) would appear in Eq. (2.51). By inspection, we would require this derivative to be zero, so that under the current assumptions the specific internal energy cannot depend on \( \nabla \theta \).

While keeping the temperature constant and using Eq. (2.53) any admissible deformation should satisfy

\[
\left( T - \rho \frac{\partial u}{\partial F} F^\top \right) : \nabla v \geq 0
\] (2.54)

By enforcing zero dissipation for any possible deformation, we find the reversible part of the stress tensor

\[
T^R = \rho \frac{\partial u}{\partial F} F^\top .
\] (2.55)

A material whose stress tensor is solely defined by \( T^R \) is called hyperelastic. More generally, materials present a stress tensor with \( T = T^R + T^D \), where the dissipative part \( T^D \) is nonzero and \( T^D : \nabla v \geq 0 \). For example, the classic isotropic dissipative stress for fluids is given by

\[
T^D = \eta \left[ \nabla v + (v)^\top \right] + \lambda (\nabla \cdot v) I,
\] (2.56)
where \( \eta \) and \( \lambda \) are viscosity coefficients that satisfy the inequality. Finally, the other source of dissipation in Eq. (2.51) would be the heat flux when the temperature is nonuniform, as only \( \mathbf{q}_t = 0 \) implies in reversibility for any possible process. To ensure a positive entropy production rate, the heat flux \( \mathbf{q}_t \) should then be proportional to \( -\nabla T \), so that besides depending on \( \mathbf{s} \) and \( \mathbf{F} \) it should also depend on \( \nabla T \), \( \mathbf{q}_t = \mathbf{q}_t(\mathbf{s}, \mathbf{F}, \nabla T) \).

### 2.3.5 Generalization to the theory of microforces

The Coleman-Noll procedure has been successfully applied for other continuum theories, including strain gradient theory, micromorphic theory and theory of microforces [113]. The latter is a generalization of order parameter theories such as Ginzburg-Landau and Cahn-Hilliard, and is relevant to the phase-field model proposed in the present work. The basic idea is that the internal energy for such systems depends on an order parameter \( \psi \) and also on gradients of \( \psi \). For instance, assume we have the following energy density (per unit of mass)

\[
u = u(s, \psi, \nabla \psi). \tag{2.57}
\]

In order for \( u \) and \( T \) to depend on gradients, they must already appear in the local balance of energy (2.38), otherwise we have the same situation as \( \nabla \theta \) in the previous Sec. 2.3.4. Since in the total energy is conserved (absence of external source), this new order parameter term should enter in the power \( \mathcal{P} \) as a flux of mechanical power, with the form \( \mathbf{q}_m = \xi \dot{\psi} \), where \( \xi \) is known as a microstress (or, simply, a generalized force [114]). The local balance of energy then takes the following form:

\[
\rho \ddot{u} = \mathbf{T} : \nabla \mathbf{v} + \nabla \cdot (\mathbf{q}_m - \mathbf{q}_t) + \rho r. \tag{2.58}
\]

Similar to Eq. (2.51), the entropy inequality in this case can be cast into the following form:

\[
\rho \left( \theta - \frac{\partial u}{\partial s} \right) \dot{s} + \left( \mathbf{T} + \rho \nabla \psi \otimes \frac{\partial u}{\partial \nabla \psi} \right) : \nabla \mathbf{v} + \left( \nabla \cdot \mathbf{q} - \rho \frac{\partial u}{\partial \psi} \right) \dot{\psi} + \left( \xi - \rho \frac{\partial u}{\partial \nabla \psi} \right) \cdot \nabla \dot{\psi} - \frac{1}{\theta} \mathbf{q}_t \cdot \nabla \theta \geq 0. \tag{2.59}
\]
Note that many of the terms in Eq. (2.59) appear from the chain rule on \( \dot{u} \), and that \( \nabla \dot{\psi} \) appears from the material time derivative \( \dot{\nabla} \psi \), which is rewritten as we later explain in Eq. (2.64).

Defining \( \pi \) as a microforce, the balance of microforce can be written as

\[
\nabla \cdot \xi + \pi = 0.
\]

(2.60)

Based on this balance and Eq. (2.59), the constitutive relations for the reversible microstres and microforce necessary for the validity of all admissible processes are

\[
\xi = \rho \frac{\partial u}{\partial \nabla \psi}, \quad \pi = -\rho \frac{\partial u}{\partial \psi}.
\]

(2.61)

Depending on boundary conditions, it is possible to rearrange terms from Eq. (2.59), by moving the negative divergence of the terms in parenthesis contracting with \( \nabla \dot{\psi} \) to the parenthesis multiplying \( \dot{\psi} \), so that \( \xi \) is eliminated. This way, the chemical potential (the thermodynamic conjugate to \( \psi \) in the sense of a functional derivative) explicitly appears in the inequality. In Chapters 4 and 5 we give further details about applications for this theory when developing a continuum model for the dynamics of a smectic-isotropic interface.

### 2.3.6 Strain gradient theory for a smectic

In this section, we derive the governing equations for an incompressible smectic based on the configuration variable \( u \) (scalar), which accounts for layer displacements, and so is a strain gradient theory. From Eq. (2.19), assume for simplicity that \( u = u(s, \nabla u) \), so that the energy only depends on gradients of \( u \) and is invariant under simple translations of the structure. Further, \( u \) is now defined as a volumetric energy density, to connect our results with others in the literature [86]. As in the microforce theory, we introduce a flux of mechanical power \( q_m = \xi \dot{u} \), where \( \xi \) is a generalized force analogous to the microstres (since \( u \) is a displacement normal to the layers, \( \xi \) can be thought of as the result of a stress operating on the normal). Therefore, the local balance of internal energy is given by

\[
\dot{u} = T : \nabla \mathbf{v} + \nabla \cdot (\xi \dot{u}) + \rho r.
\]

(2.62)
From here, the local balance of entropy can be obtained by first expanding the material time derivative of $u$ as 

$$
\dot{u} = \frac{\partial u}{\partial s} \dot{s} + \frac{\partial u}{\partial \nabla u} \cdot \dot{\nabla u}.
$$

(2.63)

The overline notation means that the derivative applies to the entire term. Hence, we can write it as 

$$
\bar{\dot{\partial}} u = \partial_t \partial_t u + v_j \partial_t \partial_j u = \partial_t (\partial_t u + v_j \partial_j u) - \partial_t v_j \partial_j u.
$$

(2.64)

By substituting Eqs. (2.62) and (2.64) into Eq. (2.62), and using the fact that the partial derivative of $u$ with respect to $s$ gives the temperature $\theta$, we obtain the following entropy inequality 

$$
\theta \dot{s} = \left( T + \nabla u \otimes \frac{\partial u}{\partial \nabla u} \right) : \nabla v + \left( \xi - \frac{\partial u}{\partial \nabla u} \right) : \nabla \dot{u} + \nabla \cdot \xi \dot{\nabla} + \rho r \geq 0.
$$

(2.65)

Using the Coleman-Noll procedure, we obtain the reversible currents by setting the entropy production rate to zero, so that 

$$
T^R = -\nabla u \otimes \frac{\partial u}{\partial \nabla u},
$$

(2.66)

$$
\xi = \frac{\partial u}{\partial \nabla u}.
$$

(2.67)

The expression obtained for the reversible part of the generalized force $\xi$ is the thermodynamic conjugate to $\nabla u$. This derivative plays the role of a molecular field in smectics, which is commonly labeled as $h$, and whose divergence is a thermodynamic force (in nematics, the molecular field is conjugate to the director $n$, and at equilibrium $n$ should be at each point parallel to $h$ [86]).

Since $u$ is a symmetry variable associated to the translational broken symmetry of the smectic, its dynamic equation will be of the form [115]

$$
\partial_t u + \nabla \cdot \nabla u + Y = 0
$$

(2.68)

where $Y$ is a quasi-current, which we write as $Y = Y^R + Y^D$. Since from Eq. (2.67)
there is no restriction on $\xi$ to be solenoidal, based on Eq. \ref{2.65} we require $\dot{u} = 0$ for reversibility, which implies that $Y^R = 0$. For deriving the irreversible quasi-current $Y^D$ that satisfies $\dot{s} > 0$, we propose a dissipation function $R$. This is a bilinear expression function, a positive definite form of the thermodynamic forces, from which irreversible currents (and quasi-currents) can be derived by taking derivatives. Accounting for restrictions on symmetry \cite{116, 115}, and using Einstein notation, we find the following bilinear form

\[
R = \frac{1}{2} \Gamma \partial_i h_i \partial_j h_j + c_j \partial_i h_i \partial_j \theta + \frac{1}{2} \kappa_{ij} \partial_i \theta \partial_j \theta + \frac{1}{2} \eta_{ijkl} \partial_i v_j \partial_k v_l . \tag{2.69}
\]

where $h$ is the molecular field defined by $h = \partial u / \partial \nabla u$. If the temperature field is kept at a constant uniform value, we find

\[
Y^D = - \frac{\partial R}{\partial \nabla \cdot h} = - \Gamma \nabla \cdot h , \text{ so that } \dot{u} = \Gamma \nabla \cdot \left( \frac{\partial u}{\partial \nabla u} \right) . \tag{2.70}
\]

The viscous part of the stress tensor is written in terms of the viscosity tensor as $T^D = \eta : \nabla \mathbf{v}$, and will later be specialized for the case of an uniaxial phase (see Chapter 4). From the derived expression, we obtain the following system of governing equations

\[
\dot{\rho} = - \rho \nabla \cdot \mathbf{v} , \tag{2.71}
\]

\[
\rho \dot{\mathbf{v}} = - \nabla p + \nabla \cdot \left( - \nabla u \otimes \frac{\partial u}{\partial \nabla u} \right) + \nabla \cdot T^D , \tag{2.72}
\]

\[
\dot{u} = \Gamma \nabla \cdot \left( \frac{\partial u}{\partial \nabla u} \right) . \tag{2.73}
\]

In Eq. \ref{2.19} we have shown the form of the commonly adopted elastic energy for a smectic \cite{96}, as a function of gradients of the configuration variable $u$. This energy is given by $W_s = \int u \, d\mathbf{x}$, where $u$ is an energy density per unit of volume. While we assumed $u = u(s, \nabla u)$ when deriving the governing equations, with this choice of energy we have a different dependence on derivatives of $u$, that is $u = u(s, \partial_z u, \nabla^2 u)$). Similar to Chaikin and Lubensky \cite{93}, we account for this difference and compute the molecular...
field as a functional derivative of $W_s$ with respect to $\nabla u$, so that we find

$$h = \frac{\delta W_s}{\delta \nabla u} = B \partial_z u \hat{k} - K \nabla_\perp \nabla^2 u .$$

Therefore, we obtain the following equation for the configuration variable

$$\dot{u} = \Gamma B \partial_z^2 u - \Gamma K \nabla^4 u ,$$

where the first and second terms on the right hand side are associated to the permeation and undulation modes, respectively. In de Gennes and Prost notation, $\Gamma = \lambda_p$ is the permeation constant (see Eq. (8.37) in Ref. [86]). Therefore, the balance of linear momentum, the dynamic equation for $u$ and the balance of mass obtained in this section agree with established results from the literature [86, 93].

It is also easily shown that our derived reversible stress is the same one found in the previous references. For instance, if we have $\nabla u \sim \hat{k}$, then

$$T^R = -\nabla u \otimes \frac{\partial u}{\partial \nabla u} , \quad \text{so that} \quad T_{zz} = K \partial_z \nabla^2 u ,$$

which is the same as in Eq. (8.7) from de Gennes and Prost [86].

### 2.4 Thermodynamics of curved interfaces

Focal conics and the nonequilibrium morphologies observed in smectic liquid crystals have curved interfaces where the curvature not only changes in sign throughout the surface but also shows regions of high magnitude, especially near macroscopic singularities. The subject of thermodynamics at curved interfaces was initially studied by Gibbs [117], in his work on capillary phenomena at surfaces of curved interface. In this theory, the mean curvature $H$ has been the quantity of primary interest, being directly related to the change in interfacial area while keeping the curvatures constant. A classical manifestation of this result is the Gibbs-Thomson equation,

$$\delta \mu = 2H \sigma_h ,$$

(2.76)
which relates the change in chemical potential \( \mu \) relative to planarity to the mean curvature, where \( \sigma_h \) is the \textit{surface tension} for a fluid interface (thermodynamic excess free energy). An analogous result (the “mechanical counterpart”) is the Gibbs-Kelvin, or Young-Laplace, equation, which relates the change in pressure \( \delta p \) at the interface to the same right hand side as in Eq. \ref{eq:2.76}.

While these results have been largely successful in describing curvature driven phenomena, from the formation of menisci to coalescence of droplets and solid particles, Gibbs theory is insufficient to describe the experimental observations discussed in Chapter 1 in smectic thin films. Efforts on expanding Gibbs theory for curved fluid interfaces, which would account for higher order curvature terms such as the Gaussian \( G \), started with Buff \cite{118} in 1956. By describing a point close to the interface as a function of surface coordinates and of the normal coordinate to the interface, Buff derived a generalized Gibbs-Kelvin equation through two different methods: one from mechanical balances, and another starting from the total derivative of a thermodynamic potential. Later, Murphy \cite{119} in 1966 followed the previous work of Eliassen \cite{120} (both students of Laurence Scriven, at the University of Minnesota) and expanded Buff’s theory on thermodynamics of highly curved interfaces. He further derived an equilibrium conditions for a curved interface from mechanical and thermodynamical viewpoints, showing necessary conditions for the equivalence between the interface equations derived from each of them. Additionally, Murphy defined the \textit{bending stress} \( \sigma_b \) and the \textit{torsion stress} \( \sigma_t \), which enter the Gibbs-Kelvin equation alongside the surface tension \( \sigma_h \).

The generalized Young-Laplace equation according to Buff-Murphy theory, which gives the difference in pressure between bulk phases separated by a curved interface, has the form

\[
\delta p = 2H\sigma_h + (4H^2 - 2G)\sigma_b - 2HG\sigma_t .
\]  

(2.77)

While the surface tension is associated with stretching an interface, increasing its area at a constant mean and Gaussian curvature, the bending stress \( \sigma_b \) is associated with a change in mean curvature by interfacial bending (keeping area and Gaussian curvature constants), and the torsion stress \( \sigma_t \) is connected to a change in Gaussian curvature by
interfacial torsion (maintaining area and mean curvature constants). All these definitions can be calculated analytically through integrals across the transition zone at the interface: $\sigma_b$ and $\sigma_t$ are the first and second moment of the excess pressure distribution about the reference surface, respectively. Figure 2.2 presents the drawing made by Murphy in his thesis to illustrate these concepts. The Buff-Murphy theory was initially well received, and has been carefully reviewed by Melrose [121].

However, in 1977 Boruvka and Neumann [122] reconsidered the problem of generalizing Gibbs theory to highly curved interfaces, arguing that Buff, Murphy and Melrose did not solve the problem. Their argument was that the subdivision between extensive and intensive variables was not made properly, leading to a wrong generalization of the Young-Laplace equation. According to them, the condition for mechanical equilibrium
for a dividing surface is

\[ \delta p = 2H\gamma_{bn} - 2G\sigma_1 - 2\nabla_s^2 \sigma_1 - G\nabla_s^* \cdot (\nabla_s \sigma_2), \]

(2.78)

where \( \gamma_{bn} \) is the surface tension, \( \sigma_1 \) and \( \sigma_2 \) are called as the first and second “bending moments” (the same as \( \sigma_b \) and \( \sigma_t \), as we later explain), and \( \nabla_s \) and \( \nabla_s^* \) are surface differentials \[122\]. In many cases, \( \gamma_{bn}, \sigma_1 \) and \( \sigma_2 \) are approximately constant throughout a surface, and the generalized Young-Laplace equation reduces to

\[ \delta p = 2H\gamma_{bn} - 2G\sigma_1, \]

(2.79)

which is still remarkably different when compared to Buff-Murphy result in Eq. (2.77).

Boruvka and Neumann’s work was well accepted by the scientific community, overshadowing Buff and Murphy past efforts for about ten years. During this period, in 1983 Rowlinson \[123\] was the first to express doubts about the correctness of some equations in Boruvka-Neumann theory. In 1988, Markin et al. \[124\] reassessed the Boruvka and Neumann criticisms against the results obtained by Buff, Murphy and Melrose, and were able to prove that the criticisms were baseless. Markin et al. noticed that the Boruvka-Neumann theory used a definition of surface tension \( \gamma_{bn} \) which is different from the one given by Gibbs, without noticing it. Hence, they analyzed the different definitions of surface tension, and have shown that the results obtained by all the previous authors were the same when defining the surface tension properly.

Markin et al. start by reviewing how the generalized local equilibrium condition for the curved interface is derived by Buff, Murphy and Melrose from a thermodynamic approach. The equation for the grand thermodynamics potential \( \Omega^* \) for a two-phase system, on a surface \( \Gamma \) whose area is \( \mathcal{A} \), presents the following total derivative:

\[ d\Omega^* = -S^* d\theta - N_i^* d\mu_i + \sigma_h d\mathcal{A} + 2.\mathcal{A} \sigma_0 dH + \mathcal{A} \sigma_t dG, \]

(2.80)

where \( N_i \) and \( \mu_i \) are the number of particles and chemical potential for constituent \( i \), and no external fields are present. In the thermodynamics framework, surface tension
σ_h, bending stress σ_b and torsion stress σ_t are the following conjugates:

\[ \sigma_h = \left( \frac{\partial \Omega^*}{\partial A} \right)_{\theta, \mu_i, H, G}, \]  
\[ \sigma_h = \frac{1}{A} \left( \frac{\partial \Omega^*}{\partial H} \right)_{\mu_i, A, G}, \]  
\[ \sigma_h = \frac{1}{A} \left( \frac{\partial \Omega^*}{\partial G} \right)_{\mu_i, A, H}. \]  

(2.81)  
(2.82)  
(2.83)

The minimum of the grand potential from Eq. (2.80) gives the equilibrium condition of the surface. The minimization of this potential at constant \( \theta \) and \( \mu_i \) leads exactly to the generalized Young-Laplace equation (2.77) as obtained by Buff, Murphy and Melrose.

Next, Markin et al. compared this derivation with the one performed by Boruvka and Neumann. They believed that Boruvka and Neumann made a mistake by choosing intensive variables \( H \) and \( G \), so, instead, they introduced the following extensive ones:

\[ \tilde{H} = \int_{\Gamma} H d\mathcal{A}, \quad \tilde{G} = \int_{\Gamma} G d\mathcal{A}. \]  

(2.84)

These equations become simply \( \tilde{H} = H A \) and \( \tilde{G} = G A \) for a small surface element. Therefore, the total derivative of the grand potential becomes

\[ d\Omega^* = -S^* d\theta - N^*_i d\mu_i + \gamma_{bn} d\mathcal{A} + 2\sigma_b d\tilde{H} + \sigma_t d\tilde{G}, \]  

(2.85)

The issue with Boruvka and Neumann’s approach is that they considered \( \gamma_{bn} \) to be the same surface tension as \( \sigma_h \), which is not true. From Eq. (2.85), observe that \( \gamma_{bn} \) is defined as

\[ \gamma_{bn} = \left( \frac{\partial \Omega^*}{\partial \mathcal{A}} \right)_{\mu_i, \tilde{H}, \tilde{G}}. \]  

(2.86)

Since Eq. (2.80) and Eq. (2.85) should be the same, by substituting \( \tilde{H} = H A \) and \( \tilde{G} = G A \) into Eq. (2.85), and comparing the two total derivatives, the relation between the Gibbs’ surface tension \( \sigma_h \) and \( \gamma_{bn} \) should be

\[ \sigma_{bn} = \gamma_h - 2\sigma_b H - \sigma_t G. \]  

(2.87)
Therefore, by substituting this expression into the Young-Laplace equation (2.78) we find the exact same expression as Eq. (2.77) obtained by Buff, Murphy and Melrose (for an interface of constant $\sigma_h$, $\sigma_b$ and $\sigma_t$). This observation was fundamental for unifying the different treatments on thermodynamics of highly curved interfaces. Further, Markin et al. note that it is easier to interpret Gibbs definition of surface tension, and that Eq. (2.77) is more convenient for practical use (a sentiment that later is reinforced by Oversteegen et al. [125]).

Since then, this theory has been of interest in curvature problems in thin films and membranes. For example, Kralchevsky and Ivanov [126, 127], and Ljugreen et al. [128], revisited Buff-Murphy theory and some of Boruvka and Neumann’s additions, and discussed that these previous results would be limited for surfaces presenting slowly varying curvatures (quasi-uniform surfaces). One important contribution from these works, which is also emphasized on a review article by Rusanov [129], is the argument that the thermodynamic shearing tension $\eta_s$ is important for biomembranes, and should appear in the interface equations. The generalized Young-Laplace equation then becomes

$$\delta p = 2H\sigma_h + 2\eta_s(H^2 - G)^{1/2} + (4H^2 - 2G)\sigma_b - 2HG\sigma_t.$$  \hspace{1cm} (2.88)

In soft matter, due to the molecular structure and presence of local curvature of high magnitude, interfacial dynamics is a subject in which the generalized thermodynamic theory for curved interfaces finds many potential applications, both in theory and experiments [130]. In this work, the Gibbs-Thomson equation, which is the chemical counterpart to Young-Laplace, will be systematically derived from the proposed phase-field model for a smectic-isotropic interface. We will show that our theory for highly curved interfaces connects to the legacy of Buff and Murphy: in addition to the surface tension, we find a bending stress $\sigma_b$ and a torsion stress $\sigma_t$ in the interface equations, whose definition in our theory is analogous to the one proposed by Murphy fifty years ago.
Chapter 3

Diffusive model for a smectic-isotropic system of uniform density

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3.1 Introduction

In this chapter we focus on the study of a diffusive smectic-isotropic interface of uniform density, which is sufficient to obtain equilibrium conditions at a distorted interface, and the kinetic equation for the interface that follows from the relaxation of smectic fluctuations. Direct isotropic to smectic transitions are predicted in systems with sufficiently large intermolecular anisotropic interactions [131], and have been observed in a number of systems including virus-polymer mixtures, liquid crystalline polymers and elastomers [132] [133]. Similarly to a smectic-air interface, the smectic-isotropic interface involves smectic layers that are parallel to the interface, and we will choose boundary conditions on a substrate so that smectic layers are perpendicular to it. Therefore, our model system also exhibits stationary toroidal focal conic configurations. Shrinkage and
growth of the smectic will be interpreted in the sense of evaporation and condensation, respectively.

In Sec. 3.2 we briefly summarize the phase-field model used and its relation to the more common description based on the smectic layer displacement field. Section 3.3 studies weakly nonlinear solutions of the model, including the one dimensional, stationary smectic-isotropic profile at coexistence, and the amplitude equation for weakly distorted smectic layers. The amplitude equation helps us to derive analytic equations for the interface without dealing with the oscillatory nature of the phase-field associated with the smectic layering. Through it, we construct a front solution connecting smectic and isotropic phases. With this result we derive a generalized Gibbs-Thomson and interface velocity equations, and find that these equations are different depending on whether the smectic planes are parallel to the interface, or perpendicular (as in exposed smectic layers). In Sec. 3.4, we present our numerical results for a three dimensional configuration in order to verify both stationary solutions and our asymptotic results. We also examine kinetic phenomena that are not restricted to weak interfacial curvatures. Starting from a TFCD, we show how curvature induced evaporation and condensation of SmA planes leads to morphological change and the formation of conical pyramids. Away from regions of large curvature or interfacial cusps, surface evolution is well described by the generalized Gibbs-Thomson equation. In some cases mean curvature driven growth is sufficient to describe interface motion, whereas in others, Gaussian and mean curvature terms are both needed to fully describe interfacial motion.

### 3.2 Model

The smectic phase of a liquid crystal has uniaxial symmetry: a layered structure along one direction, and liquid like properties along the two transverse directions. We describe such a phase with a scalar order parameter $\psi(x, t)$, function of the three dimensional space $x$ and time $t$, that also accounts for an isotropic phase when its value is zero. At a microscopic scale on the order of the smectic layer separation, the two phase interface is not sharp, but rather has a finite characteristic width which is larger than the smectic layer wavelength. The free energy associated with the order parameter is given by
\[
\mathcal{F}_s = \frac{1}{2} \int \left\{ \epsilon \psi^2 + \alpha \left( (q_0^2 + \nabla^2) \psi \right)^2 - \frac{\beta}{2} \psi^4 + \frac{\gamma}{3} \psi^6 \right\} d\mathbf{x}. \tag{3.1}
\]

The liquid crystal elastic moduli are proportional to the coefficient \(\alpha\): the term associated with \(\alpha\) in Eq. (3.1) is the one influenced by distortions, as it penalizes the energy when the SmA layers move away from a parallel alignment with constant interlayer spacing, where \(q_0\) is the layer wavenumber. The advantage of adopting a phase-field model for interface problems in modulated phases is the regularization it introduces, which allows for topological changes to occur smoothly and hence can dynamically deal with macroscopic singularities.

The coefficients \(\alpha\), \(\beta\) and \(\gamma\) are three constant, positive parameters, and \(\epsilon\) is a small bifurcation parameter that describes the distance away from the SmA-isotropic transition temperature. The constants \(\beta\) and \(\gamma\) are chosen to give a triple well energy (smectic layers and isotropic phase). Although the temperature does not explicitly shows in this form of free energy, it can be adjusted through \(\beta\) and \(\gamma\) in the sense that they change the relative stability of the smectic and isotropic phases. The term proportional to \(\psi^6\) is necessary for coexistence between isotropic and smectic phases \([134]\), which occurs at the coexistence point \(\epsilon_c = 27\beta^2/160\gamma\). For \(\epsilon > \epsilon_c\), the equilibrium phase is isotropic, \(\psi = 0\), whereas for \(\epsilon < \epsilon_c\), the smectic phase \(\psi \approx \frac{1}{2} [Ae^{i\mathbf{q} \cdot \mathbf{x}} + c.c.]\) is in equilibrium. Here \(\|\mathbf{q}\| \approx q_0\), where \(\mathbf{q}\) has an arbitrary orientation.

Spatially localized and periodic states are found not only exactly at \(\epsilon_c\), but in a neighborhood of \(\epsilon_c\) that grows as \(\epsilon_c\) increases \([134]\). This is due to a frustration effect \([135]\), as for \(\epsilon\) just above \(\epsilon_c\) there is compression of the localized states with respect to the wavelength at \(\epsilon_c\), while for \(\epsilon\) just below \(\epsilon_c\) there is a stretching of the localized states. Beyond this neighborhood, the front between the two solutions will move towards either the isotropic or smectic phase.

We consider relaxational evolution of the order parameter away from equilibrium to be solely driven by free energy minimization,

\[
\partial_t \psi = -\frac{\delta \mathcal{F}_s}{\delta \psi} = -\epsilon \psi - \alpha (q_0^2 + \nabla^2)^2 \psi + \beta \psi^3 - \gamma \psi^5. \tag{3.2}
\]

While \(\psi\) is not conserved, in this chapter we assume a smectic-isotropic system of
uniform density, so that mass conservation is automatically satisfied. The model defined by Eqs. (3.1) and (3.2) forms the basis of our analytic and numerical analyses described below. It is rotationally invariant, and allows tracking of arbitrarily distorted smectic planes, as well as smectic-isotropic fronts.

A more common description of weakly distorted smectic phases is in terms of the layer displacement field away from a reference planar configuration \(u(x,t)\), as detailed in Sec. 2.2. The order parameter and displacement field descriptions coincide when there is a preferred direction of the smectic planes, and for weak distortions away from planarity. This is accomplished by defining smectic layers as the surfaces of constant phase of \(\psi\). For reference layers perpendicular to the \(z\) direction, from Eq. 2.18, a weakly distorted smectic plane is

\[
\psi = \frac{1}{2} (A e^{i q_0 (z - u(x,t))} + c.c). 
\]

In this limit, the free energy follows from the Oseen-Frank energy and is given by Eq. 2.19, or, equivalently, Eq. 2.20. Recall that the surface has a normal \(n = (-\partial_x u, -\partial_y u, 1)\) to first order in the distortion, \(K\) is the splay modulus of the smectic, \(\bar{K}\) is the so called saddle-splay modulus, and \(B\) is the compressibility modulus.

It is possible to relate parameters in Eq. (3.1) to the Oseen-Frank constants of Eq. (2.19) [31]. Consider a longitudinal distortion field \(u(x) = \delta z\), with \(\delta \ll 1\). From Eq. (2.19), the resulting Oseen-Frank free energy density is \(f_d = \frac{1}{2} B \delta^2\). Then, by computing the change in free energy through Eq. (3.1), where we take \(f'_s\) to be the free energy density for a distorted \(\psi(x') = A \cos[q_0 (z + \delta z)]\) and subtracting the undistorted free energy \(f_x\), one finds \(\Delta f_x = \delta^2 \alpha q_0^4 A^2\). Therefore \(B = 2 \alpha q_0^4 A^2\). Similarly, by considering a transverse distortion field \(u(x) = \delta \cos(Qx)\) and \(u(x) = \delta [\cos(Q_x x) + \cos(Q_y y)]\), one can compute the change in free energy density according to Oseen-Frank and the phase-field model. In the limit of small distortions, one finds that \(K = \frac{1}{2} \alpha q_0^2 A^2\) and \(\bar{K} = 0\). Even though it would be required to consider higher order distortions to find an expression connecting \(\bar{K}\) to the phase-field model parameters, we note that the saddle-splay term in Eq. (2.19) is a null Lagrangian, and from the Gauss-Bonnet theorem it follows that the energy contribution of this term depends only on the topology of the smectic domain and boundary conditions [136].
3.3 Local equilibrium thermodynamics and kinetics of weakly perturbed smectic layers

Before presenting a fully numerical study of the evolution of a TFCD in Sec. 3.4, we discuss in this section the equilibrium conditions at a weakly curved smectic-isotropic front (the Gibbs-Thomson equation), and the equation of motion for the front. Both can be derived from an asymptotic expansion of Eqs. (3.1) and (3.2) about the isotropic to smectic transition point. Our analysis serves to both generalize the classical Gibbs-Thomson equation, and to verify the numerical calculations of Sec. 3.4 for fronts that have small curvature and are away from singularities. We also seek to understand how the orientation of the smectic layers with respect to the interface affects these equilibrium conditions, and how this is related to the experimentally observed nonequilibrium structures [18]. We first use a multiple scale expansion to derive an amplitude equation for Eq. (3.2) near two phase coexistence, such that we can describe the interface between the two phases without the oscillatory behavior of the order parameter associated with the modulated phase. We then obtain a particular solution of the amplitude equation that corresponds to a planar and stationary front connecting bulk regions of smectic and isotropic phases. Third, we extend this calculation to curved fronts by projecting the amplitude equation into a local frame on the curved front, and derive both the chemical potential and law of motion as a function of front curvatures alone.

3.3.1 Weakly nonlinear analysis

A weakly nonlinear expansion valid near the smectic-isotropic transition is introduced to describe the slow relaxation of modulated configurations. We set \( \epsilon \) to be a small expansion parameter, and conduct a standard multiple scale analysis [137, 138]. Here \( \epsilon > 0 \) since our study lies in the region where both \( \psi = 0 \) and periodic \( \psi \) solutions are linearly stable. The order parameter \( \psi \) is expanded in powers of \( \epsilon \) as

\[
\psi(x, t) = \epsilon^{1/4} \psi_1 + \epsilon^{3/4} \psi_2 + \epsilon^{5/4} \psi_3 \ldots ,
\]  
(3.3)
and slow spatial and temporal variables are introduced according to

\[ X = \epsilon^{1/4} x, \quad Y = \epsilon^{1/4} y, \quad Z = \epsilon^{1/2} z \quad \text{and} \quad T = \epsilon t. \tag{3.4} \]

The weakly nonlinear analysis will capture smectic-isotropic fronts when the amplitude of the order parameter in the smectic phase is small.

Since we are interested in analytic results for the front when the phases are close to coexistence, and \( \epsilon_c = 27 \beta^2 / 160 \gamma \), one needs to account for the scaling of the parameters \( \beta \) and \( \gamma \). We follow Sakaguchi and Brand [134], so that we fix \( \gamma = 1 \) and let \( \beta \) control the width of the coexistence region. Therefore, \( \beta \) must scale as \( \beta \sim \Theta(\epsilon^{1/2}) \), and numerically we will only vary \( \epsilon \) and \( \beta \) in order to control the structure of the triple well energy. The resulting expansion of Eq. (3.2) is solved order by order in \( \epsilon \). Note that the powers of \( \epsilon \) in the expansion of \( \psi \) come from the fact that the amplitude of the oscillatory phase is given by \( \sqrt{3\beta / 5\gamma} \), and that we collect terms coming from the expansion of a Laplacian and a biharmonic operator. At \( \Theta(\epsilon^{1/4}) \) we obtain the equation defining the stationary and one dimensional solution in the bulk smectic phase, \( \psi_1 = \frac{1}{2} [Ae^{i\sigma_0} + \text{c.c.}] \). At order \( \epsilon^{5/4} \) a solvability condition appears that leads to an equation for the amplitude \( A \), which when written in the original \( x \) and \( t \) variables, reads (details are given in Appendix A),

\[ \partial_t A = -\epsilon A + 4\alpha q_0^2 \partial_z^2 A - 4i\alpha q_0 \partial_z \nabla_{xy}^2 A - \alpha \nabla_{xy}^4 A + \frac{3}{4} \beta |A|^2 A - \frac{5}{8} \gamma |A|^4 A \tag{3.5} \]

where \( \nabla_{xy}^2 = \partial_x^2 + \partial_y^2 \) and \( \nabla_{xy}^4 = \nabla_{xy}^2 \cdot \nabla_{xy}^2 \). This amplitude equation is accurate up to terms of \( \Theta(\epsilon^{5/4}) \). Even though this equation was derived for small \( \epsilon \), we will later show numerically that it remains accurate for finite values of this parameter. In our simulations we use \( \epsilon_c \gtrsim 0.5 \) in order to have a coexistence region of finite width, sufficient for stable numerical computation [134], and also to have a sufficiently large range of \( \epsilon \) to perform thermal treatment studies.

The amplitude equation can be written in variational form as \( \partial_t A = -\delta \mathcal{F}_A / \delta A^* \), where \( A^* \) is the complex conjugate of \( A \), and the associated free energy is,

\[ \mathcal{F}_A [A, A^*] = \int \left[ \alpha |(2q_0 \partial_z - i \nabla_{xy}^2)A|^2 + \epsilon |A|^2 - \frac{3}{8} \beta |A|^4 + \frac{5}{24} \gamma |A|^6 \right] dx. \tag{3.6} \]
Equation (3.6) describes up to $\Theta(\epsilon^{5/4})$ the relaxation of slowly varying bulk smectic modulations. The relationship between the parameters of the phase-field and Oseen-Frank free energies can be obtained from the energy $\mathcal{F}_A$ as well. In terms of a small displacement $u$, we can write $A = \frac{1}{2}|A|e^{-iq\phi u}$ and similarly for the complex conjugate $A^*$. By substituting into Eq. (3.6), we obtain the compressibility term as $\frac{1}{4}\alpha q^2|A|^2|\partial_z u|^2$, which when compared to the Oseen-Frank free energy leads to $B = 2\alpha q^2|A|^2$. Also from this substitution we obtain $\frac{1}{4}\alpha q^2|A|^2|\partial_x^2 u + \partial_y^2 u|^2$ for the splay part, and hence $K = \frac{1}{2}\alpha q^2|A|^2$.

### 3.3.2 Stationary, one dimensional, smectic-isotropic front

The amplitude equation, Eq. (3.5), describes the relaxation of weakly distorted smectic planes. Near coexistence, however, it can also be used to describe a continuous front solution connecting smectic and isotropic regions. In order to find such a one dimensional solution $A = A(z)$ for a planar front perpendicular to the $z$ direction, we substitute $A = |A|e^{i\phi}$ into Eq. (3.5), where $\phi$ is the phase of the complex amplitude. The stationary phase equation leads to

$$\partial_z(|A|^2\partial_z \phi) = 0,$$

so that $|A|^2\partial_z \phi = \text{constant}$. (3.7)

Since $|A| = 0$ for the isotropic phase (at $z \to \infty$) and $|A|$ has a constant value in the smectic phase ($z \to -\infty$), this implies that $\partial_z \phi = 0$. The equation for the amplitude $|A|$ ($A$ for simplicity) becomes independent of the phase and is given by

$$-\epsilon A + 4\alpha q^2\partial_z^2 A + \frac{3}{4}\beta A^3 - \frac{5}{8}\gamma A^5 = 0$$

(3.8)

The constant amplitude $A$ in the smectic phase is

$$A^2 = \frac{3\beta + \sqrt{9\beta^2 - 40\epsilon\gamma}}{5\gamma}$$

(3.9)

By denoting $A = A_p(z)$, Eq. (3.8) can be solved to yield a planar smectic-isotropic front exactly at $\epsilon = \epsilon_c$ [139], given by,
\[ A_p(z) = \sqrt{\frac{18\beta}{5\gamma}} \left[ 4 + \exp\left( \pm \frac{z - z_0}{2\sqrt{\alpha_s/3}} \right) \right]^{-1/2}. \] (3.10)

The front is centered around \( z_0 \) (arbitrary) and has width proportional to \( \alpha_s = 40\alpha\gamma/9\beta^2 \).

If the smectic-isotropic interface is not planar, the amplitude \( A \) will deviate from Eq. (3.10). We expect, however, that for weakly curved interfaces, Eq. (3.10) will be a good approximation when \( z \) is replaced by the coordinate along the local normal to the interface. For example, Fig. 3.1 shows \( A_p \) and the order parameter \( \psi \) found from direct numerical solution of Eq. (3.2), plotted along the local normal direction for the cyclide shown in Fig. 3.2 at time \( t = 2 \). Other than the location of the front, \( z_0 \), there are no adjustable parameters. The agreement between the two is excellent despite the fact that \( \epsilon_c = 0.675 \) is of order one. We also observed numerically that for values of \( \epsilon \) up to 0.85 the front solution from Eq. (3.10) still agrees with the interface obtained from the order parameter, even though it is no longer stationary.

![Figure 3.1](image)

Figure 3.1: Phase-field order parameter profile \( \psi \) along the normal direction \( \lambda \) in a SmA-isotropic phase curved interface compared with the amplitude solution \( A_p \) for \( t = 2 \). We have chosen \( \epsilon_c = 0.675 \). Further numerical details are given in Sec. 3.4. The function \( A_p \) accurately captures the envelope of the field \( \psi \).

Note that \( A_p \) is not symmetric around \( z_0 \). In what follows, we will refer to the “smectic-isotropic interface” as the locus of points of constant \( A_p \), or, equivalently, of constant phase of \( \psi \) in the front region. Section 4.3 discusses in detail how the location of the interface is obtained numerically from the order parameter \( \psi \), and how
the curvatures on the interface are computed.

### 3.3.3 Local equilibrium at curved front and kinetic law of motion

In this section, we derive a generalized Gibbs-Thomson relation for the case where smectic layers are parallel to the interface, and also show the generalized relation for the case where layers are perpendicular to the interface (whose derivation is analogous). The amplitude equation is described by Eq. (3.5), and has an analytical stationary solution given by Eq. (3.10) in coexistence. Our procedure for deriving a a generalized Gibbs-Thomson relation is based on the analysis by Langer for the Cahn-Hilliard model [54].

Consider an idealized surface that corresponds to the smectic-isotropic interface, and let \( p = (s_1, s_2) \) be a point on the surface parametrized by \( s_1 \) and \( s_2 \). If \( \lambda \) is the coordinate along the local normal to the surface (\( \lambda = 0 \) on the surface), the coordinates of a point \( r \) near the surface can be written as
\[
  r(\lambda, s_1, s_2) = p(s_1, s_2) + \lambda n(s_1, s_2),
\]
where \( n \) is the local normal at \( p \). The coordinates \( s_1 \) and \( s_2 \) are aligned with the principal directions, associated with the principal curvatures \( c_1 \) and \( c_2 \). We now seek solutions of Eq. (3.5) of the form
\[
  A(r) = A_p(\lambda(r, t)).
\]

### Generalized equations for layers parallel to the interface

We first compute the difference in chemical potential between a planar SmA-isotropic interface and a configuration with a weakly distorted interface, where the smectic layers remain parallel to the interface (perpendicular to the \( \lambda \) direction). As previously noted, the phase \( \phi \) of the amplitude is a constant near \( \epsilon_c \), and the amplitude is a real quantity. The chemical potential \( \mu \) in terms of the slowly varying amplitude \( A \), is given by the variational derivative \( \mu = \delta F_A / \delta A \), and so
\[
  \mu = \epsilon A - 4\alpha q_0^2 \partial_z^2 A + \alpha \nabla_{xy}^4 A - \frac{3}{4} \beta A^3 + \frac{5}{8} \gamma A^5. \tag{3.11}
\]
For a flat interface perpendicular to the \( z \) direction, the chemical potential \( \mu_f \) is simplified by assuming a front \( A \) aligned with \( z \), \( A = A_p(z) \), as in Eq. (3.10). That
is,

\[ \mu_f = \epsilon A - 4\alpha q_0^2 \partial_z^2 A - \frac{3}{4} \beta A^3 + \frac{5}{8} \gamma A^5. \quad (3.12) \]

In order to obtain the chemical potential \( \mu_c \) associated with a curved interface, it is necessary to solve the corresponding amplitude equation. The scaling in \( \epsilon \) for the coordinates transverse to the smectic-isotropic interface is \( X = \epsilon^{1/4} x \) and \( Y = \epsilon^{1/4} y \). We assume that the same scaling applies to \( s_1 \) and \( s_2 \). The induced scaling of the principal curvatures is \( c_1, c_2 \sim \Theta(\epsilon^{1/2}) \), which follows from the fact that for small curvatures the mean curvature is half the trace of the Hessian matrix. The second derivative in the \( z \) direction in Eq. (3.11) generalizes to a second derivative in the normal direction \( \lambda \). Additional contributions come from the curvatures, and are obtained by expanding the differential operators on local interface coordinates (Appendix B details their expansion in terms of mean \( H \) and Gaussian \( G \) curvatures).

As the interface in the normal direction conserves the shape of the solution \( A_p \) when the SmA layers are curved (see Fig. 3.1), we consider the front to be described by \( A = A_p(\lambda) \). Hence, the amplitude is aligned with the normal direction \( \lambda \) to the interface. We find,

\[ \mu_c = \epsilon A - \frac{3}{4} \beta A^3 + \frac{5}{8} \gamma A^5 \]

\[ -4\alpha q_0^2 \left[ \partial_\lambda - 2H - (4H^2 - 2G) \lambda + 2H(3G - 4H^2) \lambda^2 \right] \partial_\lambda A. \quad (3.13) \]

For consistency, we have retained curvature terms below order \( \epsilon^{7/4} \), the same order used in the derivation of Eq. (3.5). Note that \((4H^2 - 2G) = c_1^2 + c_2^2 \) is known as the bending curvature, and that \( 2H(3G - 4H^2) = -(c_1^3 + c_2^3) \).

By multiplying both sides by the derivative of the amplitude \( A \) with respect to \( \lambda \) and integrating the result from a point before the transition zone (say, the smectic region)
to another one after the transition zone (say, the isotropic region), we obtain
\[- \int_{-\infty}^{\infty} \mu_c \partial_\lambda A \, d\lambda = \int_{-\infty}^{\infty} \left\{ -\epsilon A + \frac{3}{4} \beta A^3 - \frac{5}{8} \gamma A^5 \right\} \partial_\lambda A \, d\lambda. \tag{3.14}\]

Hence, the difference between the chemical potentials of a curved and flat interface is given by
\[- \int_{-\infty}^{\infty} \partial_\lambda (\mu_c A - \mu_f A) \, d\lambda = 4\alpha q_0^2 \left\{ -2H \int_{-\infty}^{\infty} (\partial_\lambda A)^2 \, d\lambda - (4H^2 - 2G) \int_{-\infty}^{\infty} (\partial_\lambda A)^2 \lambda \, d\lambda + 2H(3G - 4H^2) \int_{-\infty}^{\infty} (\partial_\lambda A)^2 \lambda^2 \, d\lambda \right\}. \tag{3.15}\]

The integrals on the right hand side have been defined in Sec. 3.3, Eq. (3.17), see also [119]. They are the interfacial tension $\sigma_h$, the bending stress $\sigma_b$ and the torsion stress $\sigma_t$, respectively. We now write the generalized Gibbs-Thomson equation as,
\[\delta \mu \Delta A = 2H \sigma_h + (4H^2 - 2G) \sigma_b - 2H(3G - 4H^2) \sigma_t. \tag{3.16}\]

This equation is the condition of local equilibrium, or the generalized Gibbs-Thomson equation in our model. The chemical potential difference between a curved and a planar surface $\delta \mu$ is given as a function of the surface curvatures, the discontinuity in amplitude between bulk smectic and isotropic phases, $\Delta A$, and three coefficients that depend explicitly on the one dimensional planar front solution $A_p$:
\[
\sigma_h = 4\alpha q_0^2 \int_{-\infty}^{\infty} (\partial_\lambda A_p)^2 \, d\lambda,
\]
\[
\sigma_b = 4\alpha q_0^2 \int_{-\infty}^{\infty} (\partial_\lambda A_p)^2 \lambda \, d\lambda,
\]
\[
\sigma_t = 4\alpha q_0^2 \int_{-\infty}^{\infty} (\partial_\lambda A_p)^2 \lambda^2 \, d\lambda. \tag{3.17}\]

The first coefficient $\sigma_h$ is the standard surface tension coefficient that relates the change in chemical potential to the mean curvature of the surface. For weakly curved surfaces,
this is the dominant term as it is inversely proportional to the radii of curvature. The second and third terms are of second and third order in the inverse radii of curvature, and describe deviations from the classical form of the Gibbs-Thomson equation. They represent interface bending ($\sigma_b$) and torsion ($\sigma_t$) contributions respectively, and are usually neglected. We retain all three terms in the expansion of the chemical potential in what follows because domains bounded by toroidal focal conics include regions in which the mean curvature vanishes, as well as regions of large curvature near the conic center. We will investigate numerically the accuracy of Eq. (3.16) in those regions. More generally, surface curvatures become large near regions of morphological singularities, and our result may extend the range of validity of the Gibbs-Thomson equation in the vicinity of the singularities. Finally, we stress that all three coefficients can be obtained from $A_p$ given in Eq. (3.10), and therefore are completely determined by the parameters of the model, Eq. (3.1). Note in particular that $\sigma_b \neq 0$ because the solution $A_p$ is not symmetric around $z_0$.

A generalized Gibbs-Thomson equation similar to Eq. (3.16) has been previously given by Buff [118] and Murphy [119] in the context of curved fluid interfaces, albeit using different methods [124]. The curvature terms in Eq. (3.16) coincide with theirs, except we have $2H(3G - 4H^2) = -(c_1^2 + c_2^2)$ instead of $2HG$ alongside the interface torsion. Also, their curvature terms are associated with similarly defined coefficients $\sigma_h$, $\sigma_b$ and $\sigma_t$ (in fact, the terminology comes from the work of Murphy [119]).

A kinetic equation for the smectic-isotropic surface can be derived with a similar projection operation. For this, we assume that the kinetic equation of the envelope Eq. (3.5) describes a motion predominantly aligned with the normal direction $\mathbf{n}$. From the chain rule, the left hand side of Eq. (3.5) is then given by $\partial_t A = \partial_\lambda A \partial_\lambda r \cdot \mathbf{n}$. Since the expansion of the right hand side of Eq. (3.5) is the same as the right hand side of Eq. (3.11), we have

$$\partial_\lambda A \partial_t r \cdot \mathbf{n} = \epsilon A + \frac{3}{4} \beta A^3 - \frac{5}{8} \gamma A^5$$

$$+ 4\alpha q_0^2 \left[ \partial_\lambda - 2H - (4H^2 - 2G) \lambda + 2H(3G - 4H^2) \lambda^2 \right] \partial_\lambda A$$

Note in particular that $\sigma_b \neq 0$ because the solution $A_p$ is not symmetric around $z_0$. A generalized Gibbs-Thomson equation similar to Eq. (3.16) has been previously given by Buff [118] and Murphy [119] in the context of curved fluid interfaces, albeit using different methods [124]. The curvature terms in Eq. (3.16) coincide with theirs, except we have $2H(3G - 4H^2) = -(c_1^2 + c_2^2)$ instead of $2HG$ alongside the interface torsion. Also, their curvature terms are associated with similarly defined coefficients $\sigma_h$, $\sigma_b$ and $\sigma_t$ (in fact, the terminology comes from the work of Murphy [119]).
for curved SmA layers (with a constant phase \( \phi \)). For \( A \approx A_p \), the right hand side of the previous equation reduces to

\[
\partial_\lambda A \partial_t \mathbf{r} \cdot \mathbf{n} = 4\alpha q_0^2 \left\{ -2H - (4H^2 - 2G) \lambda + 2H(3G - 4H^2) \lambda^2 \right\} \partial_\lambda A.
\]  
\( (3.19) \)

Since the interface velocity \( V_n \) is taken as positive when the SmA surface moves in the direction of the isotropic phase (and negative otherwise), \( V_n = \partial_t \mathbf{r} \cdot \mathbf{n} \). Then, multiplying both sides of Eq. \( (3.19) \) by \( \partial_\lambda A \) and integrating, we obtain

\[
\int_{-\infty}^{\infty} (\partial_\lambda A)^2 V_n d\lambda = 4\alpha q_0^2 \left\{ -2H \int_{-\infty}^{\infty} (\partial_\lambda A)^2 d\lambda - (4H^2 - 2G) \int_{-\infty}^{\infty} (\partial_\lambda A)^2 \lambda d\lambda + 2H(3G - 4H^2) \int_{-\infty}^{\infty} (\partial_\lambda A)^2 \lambda^2 d\lambda \right\}.
\]  
\( (3.20) \)

Recalling the definitions for \( \sigma_h \), \( \sigma_b \) and \( \sigma_t \), the interfacial velocity is

\[
V_n = -4\alpha q_0^2 \left\{ 2H + (4H^2 - 2G) \frac{\sigma_b}{\sigma_h} - 2H(3G - 4H^2) \frac{\sigma_t}{\sigma_h} \right\}.
\]  
\( (3.21) \)

The lowest order term is the classical law relating the normal velocity to the local mean curvature, while the remaining terms are the higher order contributions (below \( \epsilon^{7/4} \)). As is the case with Eq. \( (3.16) \), all coefficients are determined by the parameters of the model.

**Generalized equations for layers perpendicular to the interface**

The generalized Gibbs-Thomson equation \( (3.16) \), and the kinetic law, Eq. \( (3.21) \), have been derived under the assumption that the smectic layers are parallel to the smectic-isotropic interface. However, some of the configurations observed out of equilibrium in the experiments of Kim et al. [18] involve pyramidal structures in which smectic layers are exposed, so that they are aligned perpendicularly to the interface. In this case, for a planar interface the smectic layers are perpendicular to \( z \) whereas the front normal is along \( x \) (or \( y \)). The equation describing the planar front for this configuration is,

\[
-\epsilon A - \alpha \partial_x^4 A + \frac{3}{4} \beta A^3 - \frac{5}{8} \gamma A^5 = 0.
\]  
\( (3.22) \)
We cannot find an analytic solution for this front analogous to Eq. (3.10), but it can be obtained numerically. For a weakly curved interface, a similar analysis to the previous case can be carried out, where the biharmonic from the amplitude equation (3.5) is expanded when perturbations off coexistence are introduced in the weakly curved surface description (details given in Appendix B). This calculation gives the change in chemical potential at a curved interface relative to planarity as,

\[ \delta \mu \Delta A = \left[ \frac{1}{2} \nabla_s^2 H + 2H(H^2 - G) \right] \frac{\sigma_h}{q_0^2}. \]  

(3.23)

The coefficient \( \sigma_h \) is again given by Eq. (3.17), although in this case it must be computed approximately from the numerically determined solution of Eq. (3.22). Importantly, however, the coefficient \( \sigma_h / q_0^2 \) is not a surface tension (energy per unit surface) due to the fact that the smectic layers are perpendicular to the interface in this configuration. In order to compute \( \sigma_h \) for specific parameter values so as to carry out comparisons with the numerical solutions of the full phase-field model (in Sec. 3.4), we have obtained a numerical solution of \( A \) in Eq. (3.22) through a finite difference relaxation method. For the parameter values of the model used (\( q_0 = 1, \alpha = 1, \beta = 2, \epsilon = 0.675 \) and \( \gamma = 1 \)) we find that \( (\sigma_h) \parallel / (\sigma_h) \perp \approx 2.28 \), which means that the effective tension for layers perpendicular to the interface is more than 100% larger than for layers parallel to the interface (see also Ref. [18]).

In analogy to the case with layers parallel to the interface, we can derive a kinetic law for the perpendicular interface. We find,

\[ V_n = -4\alpha \left[ \frac{1}{2} \nabla_s^2 H + 2H(H^2 - G) \right]. \]  

(3.24)

One remark about the derivation of Eqs. (3.32) and (3.24) is that integrals across the interface of the form \( \sigma_{h2} = 4\alpha q_0^2 \int (\partial^2 \lambda A_p)(\partial \lambda A_p) d\lambda \) and \( \sigma_{h3} = 4\alpha q_0^2 \int (\partial^3 \lambda A_p)(\partial \lambda A_p) d\lambda \) that appear in the derivation vanish in the limit of small \( \epsilon \) since \( \sigma_{h2} / \sigma_h \) and \( \sigma_{h3} / \sigma_h \) scale as \( \epsilon^{1/4} \) and \( \epsilon^{1/2} \) respectively. The kinetic equation (3.24) that results has a form similar to that of a Willmore flow [101], although it differs by a factor of 1/2 in the surface Laplacian. Similar kinetic laws (also called fourth order flows) in which the biharmonic operator plays a role in the dynamics [140, 141] have been examined in connection with.
the biharmonic heat equation and the Willmore flow [142].

3.4 Numerical study of toroidal focal conic instabilities

We use the phase-field model given by Eqs. (3.1) and (3.2) to study the evolution of a single focal conic domain of a smectic phase in contact with an isotropic phase. The computational cell is a three dimensional cubic mesh of size $512^3$ or $1024^3$. Boundary conditions of the computational domain are zero normal derivatives of $\psi$, and zero normal derivative of the Laplacian of $\psi$. Focal conic domains, when present, are compatible with these boundary conditions, since they favor parallel alignment of the molecules with respect to the boundaries. Unless otherwise noted, we use $\alpha = 1$, $\beta = 2$ and $\gamma = 1$ in our calculations. These parameters yield a coexistence value of $\epsilon_c = 0.675$. We also use $q_0 = 1$ as the reference wavenumber. The focal conic configuration used for initial conditions (e.g., Fig. 3.2) is defined by $\psi(\lambda) = A \cos(q_0 \lambda)$ in the smectic, where $\lambda$ is the normal direction, $q_0 = 1$, and then amplitude $A$ is given by Eq. (3.8). This phase is in contact with an isotropic phase $\psi = 0$.

Equation (3.2) is solved numerically by a pseudo-spectral method, in which gradient terms are computed in Fourier space and nonlinear terms in real space. Space discretization, based on 16 points per wavelength, is $\Delta x = 2\pi/(16q_0)$. Integration in time is of second order with a Crank-Nicholson algorithm for the linear part of the equation, and a second order Adams-Bashforth method for the nonlinear terms. The time step used is $\Delta t = 5 \cdot 10^{-4}$. We have developed a custom C++ code based on the parallel FFTW library and the standard MPI passing interface for parallelization. In order to accommodate the stated boundary conditions, we use the Discrete Cosine Transform. Further details on the computational method, tracking of the smectic-isotropic surface, and calculation of the interfacial curvatures can be found in Sec. 4.3.

As discussed earlier, the value that we choose for $\epsilon_c$ allows for a reasonably large region of coexistence. This is advantageous from a numerical standpoint, as for small $\epsilon_c$ it is a challenging task to maintain coexistence in three dimensions. At the same time, since the interface equations were derived for small values of $\epsilon$, we had to perform a numerical check to confirm that we were still within the limit of validity of the asymptotic analysis. We observed that while the solution $A_p$ from Eq. (3.10) was derived for
small $\epsilon$, it still accurately describes the envelope for $\epsilon_c = 0.675$, as observed along the curved interface of a focal conic in Fig. 3.1. Even when displacing the system from coexistence, the solution $A_p$ remains an approximate description of the interface, up to $\epsilon \sim 0.85$. The validity of the interface equations for this value of $\epsilon_c$ is further confirmed by our numerical results for the interface velocity, as will be presented in this section.

### 3.4.1 Computational methodology

We employ a hybrid spectral-finite difference scheme in space owing to the fourth-order spatial derivatives in Eq. (3.2). All gradient terms are computed in Fourier space. Unstable or nonlinearly active modes in this model are contained in a finite band around $q_0$, which is an input parameter for the model. Therefore it is possible to use controlled Fourier filtering to ensure stability of the high $q$ Fourier modes in the decomposition, and thus avoid subharmonic instability arising from modes that are strongly damped in the physical model.

All nonlinear terms are computed in real space. By using real space operations we avoid having to compute Fourier mode convolutions. We employ a second order accurate scheme in time. Because both characteristic spatial and temporal scales derive from model parameters, it is relatively easy to maintain accuracy and stability. This is in marked contrast with the difficulties inherent in evolving macroscopic singular distributions.

Our FFT based code solves the evolution equation for the order parameter through an in-house developed C++ code (PFSmA) which relies on the FFTW library [143, 144] and standard MPI libraries for parallelization. Each core receives one to several two-dimensional slabs of real (DP) three-dimensional data sets when computing forward and inverse FFTs. The main performance bottleneck in FFT computation is communication, so the global transposition of post-processed data is a downside that compromises the parallel performance.

The PFSmA code computes the order parameter after each time step using a combination of Crank-Nicolson and Adams-Bashforth schemes in Fourier space. For such task, we define the linear operator $L_q$ and the Fourier transform $N_q$ of the nonlinear
We then use a combination of the implicit Crank-Nicolson scheme for the linear terms with an explicit, second order Adams-Bashforth scheme for the non-linear terms in Fourier space to integrate Eq. (3.2) and obtain \( \psi \) for the new time,

\[
\psi(q(t + \Delta t)) = (1 + \frac{\Delta t}{2} \omega(t))\psi(t) + \frac{\Delta t}{2} (3N_q(t - N_q(t - \Delta t)) - (1 - \frac{\Delta t}{2} \omega(t + \Delta t)).
\]

(3.27)

For all numerical solutions shown in this work, we use Neumann and zero normal third order derivatives as boundary conditions for the order parameter field, in order to make contact with the focal conic domains of [18]. In this case we use the cosine Fourier transform (DCT) for the even order derivatives of the order parameter. Our computational domain is \( \Omega = [0, L]^3 \), where \( L \) is the domain length. We fix \( q_0 = 1 \) in all simulations, such that the grid spacing is \( h = 2\pi/16q_0 \), \( N \) is the number of nodes (generally 512^3 or 1024^3) and \( L = (N^{1/3} - 1)h \).

### 3.4.2 Surface tracking and curvatures computation

The surface is tracked by searching for points where \( \psi(x) = \text{const.} \) and \( |\nabla \psi(x)| \neq 0 \) in the transition region. Since we acquire the curvatures from this rapidly varying phase-field, we need to implement an algorithm to smoothly and accurately compute them. Here, based on Megrabov’s work [145], we use the following implicit expressions

\[
H = \frac{1}{2} \nabla \cdot \left( \frac{\nabla \psi}{|\nabla \psi|} \right)
\]

(3.28)

\[
G = -\frac{1}{2} \nabla \cdot \left[ \nabla (\ln |\psi|) - \nabla^2 \psi \frac{\nabla \psi}{|\nabla \psi|^2} \right].
\]

(3.29)

Since at each node on the mesh we are able to compute the order parameter derivatives, we rework the previous expressions to better accommodate them in the algorithm. By writing first and second derivatives of \( \psi \) as \( \psi_i \) and \( \psi_{ij} \) respectively, where
i, j = \{x, y, z\}, we can numerically obtain the mean and Gaussian curvatures through

\[ H = (2|\nabla \psi|^3)^{-1} \left[ (\psi_y^2 + \psi_z^2)\psi_{xx} + (\psi_x^2 + \psi_z^2)\psi_{yy} + (\psi_x^2 + \psi_y^2)\psi_{zz} \right. \]

\[ \left. -2(\psi_x\psi_y\psi_{xy} + \psi_x\psi_z\psi_{xz} + \psi_y\psi_z\psi_{yz}) \right] \]  

(3.30)

and

\[ G = |\nabla \psi|^{-4} \left\{ \psi_z^2(\psi_{xx}\psi_{yy} - \psi_{xy}^2) + \psi_y^2(\psi_{xx}\psi_{zz} - \psi_{xz}^2) + \psi_x^2(\psi_{yy}\psi_{zz} - \psi_{yz}^2) \right. \]

\[ +2[\psi_y\psi_{xy}(\psi_z\psi_{xz} - \psi_x\psi_{zz}) + \psi_x\psi_{xz}(\psi_y\psi_{yz} - \psi_z\psi_{yy})] \]

\[ \left. + \psi_z\psi_{yz}(\psi_x\psi_{xy} - \psi_y\psi_{xx}) \right\}. \]  

(3.31)

### 3.4.3 Stationary Clifford torus

In order to verify the accuracy of the numerical scheme, we first consider a toroidal configuration at coexistence \( \epsilon = \epsilon_c \), and examine smectic planes bent in the shape of a focal conic. Friedel [78] was the first to associate focal conic domains with Dupin cyclides, arguing that smectic molecular layers would bend in this geometrical fashion while remaining parallel to the interface. Later, these cyclides were also shown to be stable configurations of a SmA via energy minimization of the Oseen-Frank energy given by Eq. (2.19) [34, 80, 97]. If the layer spacing of the smectic in equilibrium is assumed to remain approximately constant, and given that the term proportional to the Gaussian curvature is a null Lagrangian, minimization of Eq. (2.19) reduces to the minimization of \( \int d\chi (K/2)H^2 \), where \( K \) is the splay elastic modulus. This is the classical Willmore problem. Surfaces that minimize this energy are Willmore surfaces, which include minimal surfaces, spheres, and Dupin cyclides (in particular, the axially symmetric Clifford torus), and are obtained by an evolution that follows the Willmore flow [101].

We have verified that stationary solutions of the phase-field model agree with this result. We consider an initial condition with layers bent in a cyclide configuration, as a half-torus, in which there is no self-intersection of layers; hence, we have a disk of isotropic phase inside the torus and in contact with the substrate. We then compute the evolution of this configuration by integrating Eq. (3.2). The evolution leads to
the stationary Clifford torus shown in Fig. 3.2. Every cross section along the radial
direction will display two sections of the torus. We show our numerical results in Fig.
3.3 for both mean and Gaussian curvatures of a cross section of the surface. They agree
very well with the curvatures obtained from an analytic Clifford torus of the same size.

The circular arrangement of the planes seen from a cross section in the radial direc-
tion is known as a target pattern in the phase-field literature [146], such that we can
observe two quarter circle targets in a cross section, one on each side of the center hole.
The target pattern is a stationary solution of Eq. (3.2) in two dimensions. This can be
seen by writing Eq. (3.5) in polar coordinates, with \( r \) the radial coordinate and \( r = 0 \)
at the center of the target. The solution for \( r \gg 1 \) is \( A(r) = \sqrt{1 - 1/r^2} A_s \), where \( A_s \) is the
solution for the polynomial part of the amplitude equation given by Eq. (3.9). Since the
Clifford torus is an axially symmetric cyclide, this observation about the target patterns
implies that such a torus should also be a solution for Eq. (3.2), as verified in Fig. 3.2.

![Figure 3.2: (a) Clifford torus configuration as represented by the phase-field. (b) For
reference, we show internal segments for a family of Clifford tori.](image)

### 3.4.4 Evolution of focal conic domains at coexistence

We consider a focal conic at coexistence involving a macroscopic cusp where smectic
layers self intersect. This initial configuration is no longer stationary, and the evolution
of the order parameter is shown in Fig. 3.4. Near the cusp, where the mean curvature is
negative, a small smectic region nucleates, whereas in the outer region of positive mean
curvature, smectic layers near the interface evaporate. A stationary configuration is
reached which is shown in the figure. Smectic condensation at the cusp like depression
Figure 3.3: Stationary values of the (a) mean and (b) Gaussian curvatures computed for the SmA surface from the phase-field in Fig. 3.2. They are plotted along the radial direction ($r = 0$ at the center of the torus), and compared with the analytic curvatures of a Clifford torus. We use $N = 512^3$ and coexistence parameters, with $\alpha = 1$, $\beta = 2$, $\gamma = 1$ and $\epsilon = 0.675$.

is also observed by experiments, where material transfers along the interface owing to the variation of the local vapor pressure at the interface [18].

Figure 3.5 shows results for a similar initial configuration, but with a larger number of smectic layers. This configuration is closer to the focal conics observed in SmA films, and illustrates the instability of the layer cusps deep inside the smectic domain. Curvatures are smaller in magnitude when compared to the previous case, in particular close to the singularity, which slows down the dynamics. We still observe some condensation at the core under coexistence, but no evaporation is seen near the boundaries. This chevron pattern has also been observed in phase-field models of low angle grain boundaries [147].

3.4.5 Evolution of focal conic domains away from coexistence

We next study the evolution of a toroidal focal conic initial condition away from coexistence. We take $\epsilon > \epsilon_c$, which corresponds to a thermal treatment in which the isotropic phase has lower free energy than the smectic. The initial configuration is similar to one considered in Fig. 3.5 but with more smectic layers. We observe that smectic layers in the outer region evaporate, leading to a conical pyramid in the center, as shown in
Figure 3.4: (a) Three dimensional phase-field and (b) cross section for a focal conic which is unstable at its core, extracted from time $t = 150$. Parameters are set within the coexistence region ($\alpha = 1$, $\beta = 2$, $\gamma = 1$ and $\epsilon = \epsilon_c = 0.675$).

Fig. 3.6 The evaporation of each layer stops once the layer border aligns with the one above, creating an interface of stacked layers. The pyramid has positive Gaussian curvature, in contrast to the initial layers of negative Gaussian curvature. Similar pyramidal morphologies are observed experimentally [18].

During the evaporation of the smectic film, we compare the numerically computed interface normal velocity, given by $V_n = \partial_t \psi / |\nabla \psi|$ with the asymptotic predictions of Eqs. (3.21) and (3.24). We consider first the case of smectic layers parallel to the interface, with velocity described by Eq. (3.8). The initial configuration adopted is the same as the one used to generate Fig. 3.5. We take $\epsilon = 0.75$, and all numerical data shown corresponds to the initial stages of evolution ($t = 5$) so that the SmA layers remain parallel to the interface across the entire surface outside a small neighborhood around the cusp. The values of the coefficients $\sigma_h$, $\sigma_b$ and $\sigma_t$ used are given in Eq. (3.17) with $A_p$ defined in Eq. (3.10). Local mean and Gaussian curvatures are directly obtained from the evolving phase-field as discussed in Sec. 4.3. Figure 3.7 shows the normal velocity computed from the full phase-field model, the normal velocity predicted by Eq. (3.21), and the normal velocity that follows from mean curvature motion alone (i.e., with $\sigma_b = \sigma_t = 0$). The system size is $N = 1024^3$ so that $0 < x < 401$. The interface singularity is located at $x \approx 200$ in the figure. While there is good agreement among all three results away from the center, differences appear in the high curvature.
Figure 3.5: Cross section of the phase-field order parameter representation for a TFCD at coexistence ($\alpha = 1$, $\beta = 2$, $\gamma = 1$ and $\epsilon = 0.675$). (a) Numerical solution for the starting stage. (b) Later stage, time $t = 50$, we see some deposition at the core of the defect.

Figure 3.6: (a) Three dimensional phase-field and (b) cross section for a conical pyramid that appears due to the localized evaporation of smectic layers around the edges, extracted from time $t = 50$. Parameters are set such that the isotropic phase is thermodynamically favored ($\alpha = 1$, $\beta = 2.0$, $\gamma = 1.0$ and $\epsilon = 0.8$).

region towards the center of the domain. Specifically, motion driven by mean curvature alone near the focal conic center deviates from the computed interface velocity, including its sign. On the other hand, the normal velocity predicted by the higher-order velocity equation agrees with the numerical value until very close to the center of the focal conic. We note that there are no adjustable parameters in the results shown in Fig. 3.7 except
for a uniform velocity shift owing to the lower energy of the isotropic phase, as \( \epsilon > \epsilon_c \). We observe that the region in which mean curvature driven growth deviates from the full numerical calculation is rather small. We estimate that the radius of this region would be on the order of 30 nm in the experiments of Ref. 18, and hence below the resolution of optical detectors. Nevertheless, our calculation is consistent with the experimental observation that pyramids form due to smectic layer evaporation away from the focal conic center, not nucleation of new smectic layers at the center.

Figure 3.7: Local normal velocity of SmA-isotropic interface, extracted from a focal conic under sintering (\( \epsilon = 0.75 > \epsilon_c \)). The numerically determined surface velocity is plotted against the generalized velocity prediction for planes parallel to the interface, and compared to the classical prediction of mean curvature driven motion. \( N = 1024^3 \), defect core at \( x \approx 200 \).

As mentioned previously, the results shown in Fig. 3.7 were taken early in the evolution, so that the pyramidal structure was just beginning to form. As the pyramidal structure grows to macroscopic size, as in Fig. 3.6, the smectic planes in the pyramid are perpendicular, not parallel, to the smectic-air interface. This agrees with the observed morphological reconstruction of smectic films during thermal sintering 18. As a consequence, the local normal velocity in this case should be given by Eq. (3.24). Consider a large pyramidal structure, shown in Fig. 3.8, taken from a calculation with \( N = 512^3 \), \( \epsilon = 0.8 \) and after a fairly long time of \( t = 200 \). As observed, the pyramidal surface is smooth enough for the curvatures to be computed without issues, and the corresponding interfacial velocity is shown in Fig. 3.9 (left). We find that the normal
velocity is approximately constant and slightly negative over the entire pyramid, meaning that the structure shown is uniformly evaporating, albeit slowly. The curvatures of the moving interface are shown in Fig. 3.9 (right). The mean curvature squared $H^2$ is almost identical to the Gaussian curvature $G$, which, given the interfacial kinetic equation Eq. (3.24), accounts for the small and almost constant normal velocity over the entire pyramid interface. The constant rate of evaporation is due to the difference in bulk energy between the two phases when $\epsilon > \epsilon_c$, and does not depend on local curvatures.

Figure 3.8: (a) Cross section and (b) interface location for a pyramidal morphology obtained from a focal conic under thermal sintering, extracted from time $t = 200$. Coloring of the interface location indicates the height $z$. Initial condition was composed of a focal conic with layers reaching almost the top ($z = 200$) of the domain, using $N = 512^3$. Parameters are such such that the isotropic phase is thermodynamically favored ($\alpha = 1, \beta = 2.0, \gamma = 1.0$ and $\epsilon = 0.8$).

We conclude by presenting numerical results for a larger system ($N = 1024^3$), with $\epsilon = 0.8$, so that we can examine the different interface orientations within a single numerical solution. The initial configuration is a focal conic domain. As the configuration evolves, smectic layers away from the middle (and parallel to the interface) evaporate while a pyramid (with layers perpendicular to the interface) forms at the center. The transient morphology obtained at $t = 50$ is shown in Fig. 3.10. The local normal velocity in the outer region is given by Eq. (3.21), whereas the inner region local normal velocity is given by Eq. (3.24). As was the case in the experiments of Ref. [18], the
conical pyramid forms due to curvature induced evaporation of layers in the outer region, whereas evaporation is essentially negligible in the pyramidal region owing to the balance of mean and Gaussian curvatures. Our numerically obtained normal velocities for this interface are shown in Fig. 3.11(left). As before, there is a constant background shift of both curves arising from the constant energy difference between the bulk phases, but there are otherwise no adjustable parameters. The agreement between the numerical solution and the predictions of the asymptotic analysis is excellent.

Finally, we show in Fig. 3.11(right) the interfacial normal velocity that would result from mean curvature driven growth alone. The agreement with the numerical result is quite good in the outer region of small curvature, where the effects of bending and torsion are negligible. Near the center, however, mean curvature driven growth fails to describe the numerical results.

3.5 Chapter conclusions

In this chapter we have introduced a model for a smectic-isotropic system from which we have derived a generalized Gibbs-Thomson and interfacial motion equations, revealing the role of the Gaussian curvature and the orientation of a modulated phase on local
Figure 3.10: (a) Expanded cross section blow up and (b) interface location right for a focal conic during thermal sintering, showing a pyramid of appreciable size, extracted from time $t = 50$. We used $N = 1024^3$, for which the numerical solution reveals the pyramidal structure being formed at the core around layers that remain parallel to the interface. Parameters are such that the isotropic phase is thermodynamically favored ($\alpha = 1, \beta = 2.0, \gamma = 1.0$ and $\epsilon = 0.8$).

Figure 3.11: Interface velocity for a middle cross-section. (a) The numerically determined surface velocity is plotted against the two generalized kinetic laws, one for each region. (b) The evolution by mean curvature velocity prediction strongly diverges in the central pyramidal region.

equilibrium thermodynamics and kinetics of the interface. The computational challenges of tracking a complex and moving smectic-isotropic phase boundary have been addressed by using a phase-field model. We have presented an asymptotic analysis of the solutions
of the model, valid near smectic-isotropic coexistence, and for weakly curved interfaces. Through this analysis we obtain a dynamical equation for the amplitude that modulates the periodic smectic layering. This procedure allows us to obtain physical insights about local equilibrium thermodynamics and evaporation-condensation dynamics of the smectic-isotropic interface without dealing with the oscillatory nature of the layering description.

The work is directly motivated by recent experiments in the sintering of TFCDs in thin films of smectic liquid crystals [18, 148], which show novel morphologies, including conical pyramids and concentric rings. By both simulating the sintering of focal conics and comparing the results to an asymptotic analysis of the governing equations, we reproduce the evaporation process that takes place in the experiments, while clarifying the limitations of classical interface equations. Our results portray how focal conics evolve to conical pyramids through evaporation and condensation of the smectic layers, as observed in the experiments. The analysis also shows that when smectic planes are parallel to the interface, three surface energy coefficients are necessary to describe local equilibrium thermodynamics and kinetics to the order of approximation considered. These coefficients can be computed analytically within the model, from Eq. 3.17. For the case of planes perpendicular to the interface, the chemical potential at a curved interface is not proportional to the local mean curvature, but rather a Willmore type problem emerges.

Our findings expand the range of understanding and control of micropatterning of smectic films, as templates for superhydrophobic surfaces [37], guides for colloidal dispersion [38, 39] and soft lithography [35, 36]. More broadly, the present results can guide future experiments in other modulated phases such as block copolymers. Our generalized theory should also benefit research in biomembranes, which have already reported connections between the Gaussian curvature and protein binding [149], as well as work on nucleation and growth on curved surfaces [28].

We mention finally that our analysis focuses on the smectic-isotropic interface, whereas the experiments in thin films concern a smectic-air interface instead, and does not contain any hydrodynamic stresses at the smectic-air boundary, or any resulting mass flows. Although velocity fields were not measured in the experiments, and the results were interpreted in terms of the same evaporation-condensation mechanisms that
we have examined here, the excess energies that introduce corrections to the Gibbs-Thomson equation will also lead to normal stresses at the boundary. This topic will be discussed in Chapters 4 and 5.
Chapter 4

Quasi-incompressible model for a smectic phase in contact with an isotropic phase of distinct density

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[https://journals.aps.org/prfluids/abstract/10.1103/PhysRevFluids.5.073302](https://journals.aps.org/prfluids/abstract/10.1103/PhysRevFluids.5.073302)

4.1 Introduction

In the previous chapter we introduced a diffuse interface model of a smectic-isotropic system [75] with uniform density, and focused our attention on the resulting thermodynamic relations and kinetic laws in the macroscopic limit of a thin interface. While the model describes diffusive evaporation-condensation, a proper study of a smectic film interface requires consideration of mass flow and stresses at the interface when the smectic is in contact with an isotropic fluid phase of different density. We present here a detailed derivation of a phase-field model for a system where a smectic phase is in contact with an isotropic phase of different density. In this chapter, we further consider the quasi-incompressible limit (following Lowengrub and Truskinovsky [114]), in which the density is defined by a constitutive relation function of the order parameter.
In liquid crystals, particular interest lies in how the fluid flow connects to the director field and geometry of such systems, and the role played by hydrodynamics in the interaction of defects. Hydrodynamics is also key in studies of active matter transport, since active particles and microswimmers, such as bacteria, can be guided by the fluid flow induced by an anisotropic medium [150, 151]. However, a theory for the coupled evolution of a smectic liquid crystal with a two phase interface and the resulting hydrodynamic flows, including macroscopic singularities associated to topological defects, is still under active development. The modulated nature of smectic phases requires one to distinguish between the motion of the surfaces defining the modulation in the bulk phase, and the interface separating this phase from a neighboring isotropic fluid phase.

Phase-field models have been extended to include hydrodynamic flows [48, 49] through a coupled Navier-Stokes and Cahn-Hilliard problem, also known as Model H in the critical dynamics literature. Lowengrub and Truskinovsky [114] proposed a phase-field model for a binary mixture with phases of different density, and derived thermodynamically consistent equations that account for the effects of such a varying density field. While they considered both bulk phases of the binary to be incompressible, they show that compressibility effects take place at the interface, where the velocity becomes non-solenoidal. Since the density can be calculated by a constitutive equation from any point where the composition is known, and compressibility is restricted to the interface, their model is known as the quasi-incompressible Cahn-Hilliard model. Diffuse-interface models and numerical schemes for quasi-incompressible two-phase flows with distinct densities have been actively developed since then [152, 153, 154, 155], with particular interest in large density ratios [156, 157], for which the stability of the derived numerical schemes becomes a problem due to nonlinear terms coupled to the density. These latter developments may be extended beyond uniform bulk phase binaries. For the case of a modulated-isotropic interface, however, the oscillatory nature of the order parameter introduces challenges that we explore in the present work. For example, we have an energy density with a dependence on higher order derivatives, and a less intuitive choice of constitutive equation for the density. In this case, we need to extract from a non-uniform oscillatory order parameter a density field that is homogeneous in both phases, and we also need to carefully define pressure fields. Here we use a Coleman-Noll procedure [106, 114, 157] to derive a set of governing equations that couple the phase-field equation...
for the order parameter representation of a smectic-isotropic system to a momentum transport equation, and accounts for a varying density between the two phases. We specialize our discussion to the analog of quasi-incompressible smectic-isotropic fluid, once again motivated by recent experiments in smectic A thin films \cite{18, 148}.

In Sec. 4.2 we briefly show how hydrodynamics can be incorporated into the model for a smectic-isotropic system of uniform density of Chapter 3. A fully compressible model for smectic-isotropic two phase interface is derived in Sec. 4.3: reversible currents are obtained by imposing zero entropy production in the Second Law of Thermodynamics, while irreversible currents are derived by asserting the Clausius-Duhem inequality holds in case of dissipation. We next specialize this model to a quasi-incompressible case, in which the density of the modulated phase is given constitutively. The density is independent of the pressure but depends on the amplitude of the order parameter. As a consequence, bulk phases are incompressible, but we allow a non-solenoidal velocity in the interfacial region. Compressibility effects are of importance for fluid flow on the surface of the smectic in diffuse-interface treatments, which arise from the difference in density between the two phases. A numerical scheme suitable to study the evolution equation of the order parameter is introduced in Sec. 4.4 which is based on existing schemes for phase-field models with varying mobilities. A stability analysis for transverse interfacial perturbations is presented in Sec. 4.5 which is then used to verify the numerical code. Finally, in Sec. 4.6 we show numerical results concerning flows originating from perturbed smectic layers, and also for layers bent in a focal conic configuration. We discuss the consequences of the varying density field on flow structure, and how curvatures determine interfacial flows through the normal stress balance.

4.2 Order parameter model of a smectic-isotropic interface: Incompressible limit

We first expand the model of Chapter 3 for a smectic-isotropic two phase system of uniform density, showing how hydrodynamics can be included. The scalar order parameter $\psi(x, t)$ describes both an isotropic phase with $\psi = 0$, and a smectic phase where $\psi$ is a periodic function of space. This function represents the smectic layered structure, and $\psi$ smoothly changes at the interface between the two phases. A free energy functional
of the order parameter $F_s$ was introduced in Eq. (3.1). Relaxational evolution for the order parameter $\psi$ is assumed through minimization of the free energy

$$\partial_t \psi + v \cdot \nabla \psi = -\Gamma \frac{\delta F_s}{\delta \psi} = -\Gamma \mu$$ (4.1)

where $v$ is the mass velocity, $\mu$ is the chemical potential conjugate to $\psi$, and $\Gamma$ is a constant mobility (chosen as $\Gamma = 1$ below). Gradient terms in the free energy functional lead to non-classical (reversible) stresses of the form,

$$T = \frac{\delta F_s}{\delta \nabla u} = \nabla \psi \otimes \nabla \left( \frac{\partial f}{\partial \nabla^2 \psi} \right) - \frac{\partial f}{\partial \nabla^2 \psi} D \psi$$ (4.2)

where $D \psi$ is a shorthand for $\partial_i \partial_j \psi$. The stress is defined as the variation of the energy with respect to an independent distortion $\psi(x) \to \psi(x + u)$ (see Appendix C). Adding dissipative stresses appropriate for an isotropic, Newtonian fluid, lead to the following governing system of equations for an incompressible fluid,

$$\nabla \cdot v = 0$$ (4.3)

$$\rho (\partial_t v + v \cdot \nabla v) = -\nabla p + \nabla \cdot T + \eta \nabla^2 v$$ (4.4)

$$\partial_t \psi + v \cdot \nabla \psi = -\epsilon \psi - \alpha (\nabla^2 + q_0^2)\psi + \beta \psi^3 - \gamma \psi^5.$$ (4.5)

In this system, $\rho$ is the constant density, and $\nu$ is the isotropic shear viscosity. It is straightforward to replace the Newtonian viscous dissipation introduced with that of an uniaxial fluid. In the incompressible case, this amounts to considering three independent viscosities. For simplicity, we restrict our analysis here to isotropic viscous dissipation, while noting that the reversible part of the stress does contain the uniaxial symmetry of the smectic phase.

Equation (4.5) as a model of a smectic-isotropic configuration was investigated in Chapter 3, albeit without advection ($v = 0$). We analyzed the role of Gaussian curvature on local thermodynamics at the two phase interface (the Gibbs-Thomson equation), and on the evolution of a smectic-isotropic interface, including the effects of local equilibrium thermodynamics from layer alignment with respect to the interface. By examining focal conic instabilities under heat treatment, we showed that conical pyramids of smectic
layers could be obtained as observed in experiments [18], and that their formation could
be explained through the interplay between Gaussian curvature, mean curvature and
layering alignment. We expect these results to hold qualitatively for a smectic-isotropic
fluid interface in terms of the main mechanism of smectic evaporation and condensation.
However, in order to fully develop a model that connects to experiments in smectic thin
films, we need to account for hydrodynamics and a varying density field between the
phases. This way, one can capture the role of surface flows and compressibility effects at
the interface, which are relevant not only for the evolution of smectic-isotropic interface,
but may also be important for interactions between topological defects in smectics.

4.3 Order parameter model of a smectic-isotropic inter-
face: Compressible phases

We derive in this section a diffuse interface model for a smectic phase in contact with
an isotropic fluid when they have different densities. Earlier work by Brand and Pleiner
[158] considered a hydrodynamic theory for smectics and other mesophases exhibiting
broken symmetries. They introduced an energy density $u$ that depends on mass density,
momentum, entropy, and on a variable representing the broken symmetry of the system
(e.g. the director $\hat{n}$ and its derivatives in nematics). We use the same methodology but
focus on a real variable $\psi$ representing the layering order. Our energy density depends
on the Laplacian $\nabla^2 \psi$, which leads to layer formation, and accounts for the energy
involved in layer distortions.

4.3.1 Compressible model

We write the internal energy of the system in terms of the energy per unit mass $u$ and
the mass density $\rho$ as

$$\Omega = \int_{\Omega} \rho u \, d\mathbf{x}.$$  (4.6)

We first obtain the local form of the internal energy and entropy balances from Eq.
(2.38), as detailed in Sec. 2.3.2. The relations derived in this section are obtained in
the absence of thermal radiation and heat flux though the boundary, so that we neglect
\( R \) for the rest of this section. When deriving the governing equations, we set no-flux boundary conditions: Neumann condition for the order parameter \( \psi \) (which forces the smectic planes to be perpendicular to the domain outer boundary) and zero normal velocity on the boundary, such that

\[
\nabla \psi(\mathbf{x}) \cdot \mathbf{n} = \nabla^2 \psi(\mathbf{x}) \cdot \mathbf{n} = 0, \quad \mathbf{v}(\mathbf{x}) \cdot \mathbf{n} = 0, \quad \mathbf{x} \in \partial \Omega. \quad (4.7)
\]

Accounting for the balance of linear momentum \( \rho \dot{\mathbf{v}} = \nabla \cdot \mathbf{T} \) and balance of mass \( \dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0 \), the local form of the balance of internal energy \([107]\) is obtained as in Eq. (2.58), so that

\[
\rho \dot{e} = \mathbf{T} : \nabla \mathbf{v} + \nabla \cdot (\mathbf{G} \dot{\psi}). \quad (4.8)
\]

In order to derive the balance of entropy for the specific internal entropy \( s \), we assume \( e \) has a dependence not only on \( \nabla \psi \), but also on \( \nabla^2 \psi \), so \( \mathbf{u} = \mathbf{u}(\rho, s, \psi, \nabla \psi, \nabla^2 \psi) \). This dependence on \( \nabla^2 \psi \) does not appear for binary systems, but is fundamental to model the smectic phase. Hence, by the chain rule

\[
\dot{\mathbf{u}} = \frac{\partial \mathbf{u}}{\partial \rho} \dot{\rho} + \frac{\partial \mathbf{u}}{\partial s} \dot{s} + \frac{\partial \mathbf{u}}{\partial \psi} \dot{\psi} + \frac{\partial \mathbf{u}}{\partial \nabla \psi} \cdot \nabla \psi + \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \nabla^2 \psi. \quad (4.9)
\]

where the overbar notation denotes the material time derivative of the entire term below the bar. Given that the temperature \( \theta = \partial u/\partial s \), we rewrite Eq. (4.8) as a local balance of entropy

\[
\rho \dot{s} = \left\{ \mathbf{T} + \rho^2 \frac{\partial \mathbf{u}}{\partial \rho} \mathbf{I} + \rho \nabla \psi \otimes \frac{\partial \mathbf{u}}{\partial \nabla \psi} - \nabla \psi \otimes \nabla \left( \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \right) + \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \mathbf{D} \psi \right\} : \nabla \mathbf{v}
\]
\[
+ \left[ \mathbf{t} - \rho \frac{\partial \mathbf{u}}{\partial \nabla \psi} + \nabla \left( \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \right) \right] \cdot \nabla \dot{\psi} - \left[ \rho \frac{\partial \mathbf{u}}{\partial \psi} - \nabla \cdot \mathbf{G} \right] \dot{\psi}, \quad (4.10)
\]

where \( \mathbf{D} \) stands for \( \partial_i \partial_j \), so that \( \mathbf{D} \psi \) is a second order tensor. In deriving the previous
expression, the boundary conditions from Eq. (4.7) allow us to write
\[ \rho \frac{\partial u}{\partial \nabla^2 \psi} \nabla^2 \dot{\psi} = \rho \frac{\partial u}{\partial \nabla^2 \psi} \nabla^2 \dot{v} \cdot \nabla \psi - 2\rho \frac{\partial u}{\partial \nabla^2 \psi} \nabla v : \mathbf{D} \psi \]
and also
\[ \rho \frac{\partial u}{\partial \nabla \psi} \cdot \nabla \dot{\psi} = \rho \frac{\partial u}{\partial \nabla \psi} \cdot \nabla \dot{\psi} - \rho \nabla \psi \otimes \frac{\partial u}{\partial \nabla \psi} : \nabla v . \tag{4.11} \]

The terms in square brackets proportional to \( \dot{\psi} \) and \( \nabla \dot{\psi} \) in Eq. (4.10) are both related to variations of \( \psi \) and can be grouped together. By using the boundary conditions, we write
\[ \rho \dot{s} = \left\{ \mathbf{T} + \rho \frac{\partial u}{\partial \rho} + \rho \nabla \psi \otimes \frac{\partial u}{\partial \nabla \psi} - \nabla \psi \otimes \nabla \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right) + \rho \frac{\partial u}{\partial \nabla^2 \psi} \mathbf{D} \right\} : \nabla v \]
\[ + \left[ - \rho \frac{\partial u}{\partial \psi} + \nabla \frac{\partial u}{\partial \nabla \psi} - \nabla^2 \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right) \right] \dot{\psi} . \tag{4.13} \]

In order to obtain the required constitutive relations, we use the Coleman-Noll procedure, which defines necessary conditions for them by imposing a strict requirement on the entropy production. Based on the Clausius-Duhem inequality, the condition for the specific internal entropy \( \dot{s} \geq 0 \) implies that Eq. (4.13) must be satisfied for every admissible thermomechanical process. Hence, by splitting the stress into reversible and dissipative parts, \( \mathbf{T} = \mathbf{T}^R + \mathbf{T}^D \), we can derive the reversible parts from Eq. (4.13) in the limit of zero entropy production, while dissipative parts are obtained by enforcing positive entropy production.

For deriving \( \mathbf{T}^R \), which is a reversible current for the balance of linear momentum, we set the terms in brackets associated with the rates \( \nabla v \) equal to zero, so that
\[ \mathbf{T}^R = -\rho^2 \frac{\partial u}{\partial \rho} \mathbf{I} - \rho \nabla \psi \otimes \frac{\partial u}{\partial \nabla \psi} + \nabla \psi \otimes \nabla \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right) - \rho \frac{\partial u}{\partial \nabla^2 \psi} \mathbf{D} \psi . \tag{4.14} \]
The expression in square brackets multiplying $\dot{\psi}$ is the thermodynamic conjugate to $\psi$, $\mu = \delta \Omega / \delta \psi$. That is,

$$\mu = \rho \frac{\partial u}{\partial \psi} - \nabla \cdot \left( \rho \frac{\partial u}{\partial \nabla \psi} \right) + \nabla^2 \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right). \quad (4.15)$$

Since $\dot{s} = 0$ for reversible motions, and $\mu$ is arbitrary, we must have $\dot{\psi} = 0$. The order parameter $\psi$ is a slowly relaxing variable, which is not associated with any conservation law. Hence, its dynamic equation is of the form

$$\partial_t \psi + \mathbf{v} \cdot \nabla \psi + Z = 0 \quad (4.16)$$

where $Z$ is a quasi-current (that is, its surface integral is not a flux), which can be decomposed into $Z = Z^R + Z^D$. Since in the reversible limit $\dot{\psi} = 0$, this implies that $Z^R = 0$, and we are only left with the dissipative part $Z^D$.

To obtain the form of the irreversible currents, we need to impose the condition $\dot{s} > 0$ to Eq. (4.13) (one can also derive these functions from derivatives of a generalized function with respect to thermodynamic forces [116, 115]). This implies that $\dot{\psi}$ must be proportional to the negative of the chemical potential times a constant $\Gamma$, so that $Z^D$ has the form

$$Z^D = \Gamma \mu. \quad (4.17)$$

Physically, the dissipative contribution to $\dot{\psi}$ is a permeation mode [86]; it is nonzero when there is mass transport relative to the smectic layers.

We finally introduce the dissipative contribution to the stress. When $\dot{s} > 0$, only $\mathbf{T}^D$ remains inside the curly brackets contracted with $\nabla \mathbf{v}$ in Eq. (4.13), so that to enforce positive entropy production we require

$$\mathbf{T}^D = \eta : \nabla \mathbf{v}. \quad (4.18)$$

For an uniaxial phase with an optical axis $\mathbf{n}$ (normal direction to the smectic layers), by defining the rate of deformation tensor as $\mathbf{E} = (\nabla \mathbf{v} + \nabla \mathbf{v}^T)/2$, this viscous term
presents five independent viscosities $\alpha_{i(j)}$.

$$\eta_{ijkl}\partial_t v^k = \alpha_0 \delta_{ij} E_{kk} + \alpha_1 \delta_{in} \delta_{jn} E_{nn} + \alpha_4 E_{ij}$$

$$+ \alpha_5 (\delta_{in} E_{nj} + \delta_{jn} E_{ni}) + \alpha_6 (\delta_{in} \delta_{jn} E_{kk} + \delta_{ij} E_{nn}) . \hspace{1cm} (4.19)$$

For simplicity, we will restrict our study to the case of a Newtonian fluid for both phases, although the extension to a uniaxial fluid is straightforward. Therefore, instead of working with the full fourth order viscosity tensor $\eta$, we consider only the viscosity coefficient $\eta$, and the second coefficient of viscosity $\lambda$, which are also assumed to be the same for both phases. Because we account for compressibility effects on the interface, the velocity is non-solenoidal, which adds a contribution of $\nabla \cdot v$ to the viscous stress

$$T^D = \eta (\nabla v + \nabla v^T) + \lambda (\nabla \cdot v) I . \hspace{1cm} (4.20)$$

While out of equilibrium the two viscosities are generally independent, in our numerical investigations we follow Stokes’ hypothesis and set the bulk viscosity to zero. That is, we set trace $(T^D) = 0$, which gives $\lambda = -\frac{2}{3} \eta$. The choice of $\lambda$ has an important impact on the fully compressible model, as it controls the magnitude of the longitudinal part of the flow. When one accounts for the viscous term with all five viscosity coefficients, the longitudinal flow also depends on derivatives of the velocity field with respect to the direction of $\nabla \psi$, damping oscillations of the flow along the optical axis. A full analysis would require extensive numerical study on the role of each viscosity coefficient, as well as evaluation of the ratios among these coefficients to best connect to empirical data.

The equations governing the evolution of the quasi incompressible system now read

$$\dot{\rho} = -\rho \nabla \cdot v , \hspace{1cm} (4.21)$$

$$\rho \dot{v} = \nabla \cdot (T^R + T^D) , \hspace{1cm} (4.22)$$

$$\dot{\psi} = -\Gamma \mu , \hspace{1cm} (4.23)$$

with $T^R$ defined in Eq. (4.14), $T^D$ in Eq. (4.20) and $\mu$ in Eq. (4.15). Boundary conditions on the outer boundaries are specified by Eqs. (4.7).
4.3.2 Quasi-incompressible model

We next assume that the density does not depend on pressure in the bulk phases (quasi incompressible assumption), but depends constitutively on $\psi$, so that $\rho = \rho(\psi)$ in the two phase system. Due to the modulated nature of $\psi$, the choice of constitutive relation is not as straightforward as in the Cahn-Hilliard model of a binary mixture in which there is a transition between two regions of uniform composition. We write in the present case $\rho$ as a function only of the slowly varying envelope of the order parameter, $A(x)$, as defined in Ref. [75] (see Fig. 3.1),

$$\rho[A(x)] = \kappa A(x) + \rho_0,$$  \hspace{1cm} (4.24)

where $\kappa$ is a constant that controls the density ratio between the bulk smectic and isotropic phases, and $\rho_0$ is the density of the isotropic phase where $A = 0$. In practice, we compute the amplitude by using $A = (\psi^2 + q_0^2 |\nabla \psi|^2)^{1/2}$. For the form of the energy that we introduce below, we have numerically confirmed that for smectic layers that are not severely distorted this expression accurately captures the amplitude of $\psi$.

While both bulk fluids are incompressible, the velocity field becomes non-solenoidal at the interface. From the balance of mass in Eq. (4.21), we find that

$$\nabla \cdot \mathbf{v} = -\frac{\partial \rho}{\partial A} \frac{\dot{A}}{\rho} = -\kappa \frac{\dot{A}}{\rho}.$$  \hspace{1cm} (4.25)

We note that Eq. (4.25) is similar to that used for the Cahn-Hilliard model of a quasi-incompressible binary fluid, which becomes more clear by expressing it in terms of $\psi$. The material time derivative of $A$ is connected to permeation, that is mass motion relative to smectic planes, so that the divergence of the velocity in a quasi-incompressible diffusive-interface model is linked to the order parameter chemical potential, as discussed in Refs. [114, 157]. From $\rho = \rho(\psi)$, one can also write

$$\nabla \cdot \mathbf{v} = -\frac{\partial \rho}{\partial \psi} \frac{\dot{\psi}}{\rho} = \frac{\partial \rho}{\partial \psi} \frac{\Gamma \mu}{\rho}.$$  \hspace{1cm} (4.26)

Finally, we make explicit the dependence of the chemical potential on pressure by decomposing the velocity gradient $\nabla \mathbf{v} = \mathbf{S}_v + \frac{1}{3}(\nabla \cdot \mathbf{v})\mathbf{I}$, where $\mathbf{S}_v$ is its deviatoric part.
We can rewrite the local balance of entropy from Eq. (4.13), so that the stress contracts with the deviatoric tensor \( S_v \). Since \( \mathbf{I} : S_v = 0 \), any scalar multiplying the identity in the stress satisfies the Clausius-Duhem inequality. Therefore, we introduce the pressure \( p \), which is not uniquely defined, and write the reversible part of the stress as

\[
T^R = -p\mathbf{I} - \rho \nabla \psi \otimes \frac{\partial \mathbf{u}}{\partial \nabla \psi} + \nabla \psi \otimes \nabla \left( \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \right) - \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \mathbf{D} \psi .
\] (4.27)

When the identity contracts with the stress terms inside the curly brackets from Eq. (4.13), we get exactly \( 3p \) from the resulting trace. Using this result and substituting \( \nabla \cdot \mathbf{v} \) from Eq. (4.26) in the local balance of entropy, we write

\[
\rho \dot{\theta} = \left\{ T + \rho \nabla \psi \otimes \frac{\partial \mathbf{u}}{\partial \nabla \psi} - \nabla \psi \otimes \nabla \left( \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \right) + \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \mathbf{D} \psi \right\} : S_v
\]

\[
+ \left[ p \rho^{-1} \frac{\partial \rho}{\partial \psi} - \rho \frac{\partial \mathbf{u}}{\partial \psi} + \nabla \cdot \left( \rho \frac{\partial \mathbf{u}}{\partial \nabla \psi} \right) - \nabla^2 \left( \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \right) \right] \dot{\psi} .
\] (4.28)

Therefore, the order parameter chemical potential per unit volume now exhibits an explicit dependence on the kinematic pressure, that is

\[
\mu = -p \rho^{-1} \frac{\partial \rho}{\partial \psi} + \rho \frac{\partial \mathbf{u}}{\partial \psi} - \nabla \cdot \left( \rho \frac{\partial \mathbf{u}}{\partial \nabla \psi} \right) + \nabla^2 \left( \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \right) .
\] (4.29)

The governing equations are given by Eqs. (4.22) and (4.23), with the definitions for the chemical potential and reversible stress as given by Eqs. (4.29) and (4.27) respectively.

### 4.3.3 Choice of energy functional

In order to study a system comprising a smectic and an isotropic phase which can achieve coexistence, based on the energy density from Chapter 3 we choose \([75]\),

\[
u(\psi, \nabla^2 \psi) = \frac{1}{2} \left\{ \epsilon \psi^2 + \alpha \left[ (\nabla^2 + \quad 3 \psi) \right] - \frac{\beta}{2} \psi^4 + \frac{\gamma}{3} \psi^6 \right\} . \]

(4.30)

The coefficients \( \alpha, \beta \) and \( \gamma \) are three constant, positive parameters, and \( \epsilon \) is a bifurcation parameter that describes the distance away from the smectic-isotropic transition. The values of the constants \( \beta \) and \( \gamma \) are chosen to give a triple well energy function with minima representing smectic and isotropic phases \([134]\). Coexistence
occurs at \( \epsilon_c = 27\beta^2/160\gamma \), when both phases present the same energy density. For \( \epsilon > \epsilon_c \), \( \psi = 0 \) becomes the equilibrium phase, whereas for \( \epsilon < \epsilon_c \), a modulated phase \( \psi \approx \frac{1}{2}(A e^{i\mathbf{q} \cdot \mathbf{x}} + c.c.) \) is stable. Here \(|\mathbf{q}| \approx q_0\), with \( \mathbf{q} \) along an arbitrary direction.

The chemical potential from Eq. (4.29) is now,

\[
\mu = -p \rho^{-1} \frac{\partial \rho}{\partial \psi} + p \left[ \epsilon \psi + \alpha q_0^2 (\nabla^2 + q_0^2) \psi - \beta \psi^3 + \gamma \psi^5 \right] + \alpha \nabla^2 \left[ \rho (\nabla^2 + q_0^2) \psi \right].
\] (4.31)

One important remark about computing \( \mu \) is that \( \rho \) in Eq. (4.24) is given as a function of the amplitude \( A \), so we do not actually have an expression for \( \rho(\psi) \). By the chain rule, a simple calculation of \( \partial \rho/\partial \psi \) from the way we obtain \( A \) from a \( \psi \) would give \( \kappa \psi / A \).

Since we set \( \rho \) as constant in the bulk of the two phases, its derivative with respect to \( \psi \) should only be nonzero at the interface. Due to this, we interpret \( \psi \) that shows in the previous derivative as the average of the order parameter, \( \langle \psi \rangle \), computed over a unit cell defined by the wavelength (which is zero outside the interface). For parallel computations, it becomes costly to perform such averaging after every iteration, so that an alternative is to approximate \( \langle \psi \rangle / A \) by \( |\nabla A| / A \), or similarly \( |\nabla \rho| / \rho \).

The balance of linear momentum for the choice of energy given by Eq. (4.30) is

\[
\rho \dot{\mathbf{v}} = -\nabla p + \nabla^2 \left( \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \right) \nabla \psi - \rho \frac{\partial \mathbf{u}}{\partial \nabla^2 \psi} \nabla^2 \nabla \psi + \eta \nabla^2 \mathbf{v} + (\lambda + \eta) \nabla (\nabla \cdot \mathbf{v}).
\] (4.32)

By focusing only on overdamped or Stokes flow, we further assume that the fluid velocity everywhere satisfies

\[
0 = -\nabla p + \alpha \nabla^2 \left[ \rho (\nabla^2 + q_0^2) \psi \right] \nabla \psi - \alpha \rho (\nabla^2 + q_0^2) \psi \nabla^2 \nabla \psi
+ \eta \nabla^2 \mathbf{v} + (\lambda + \eta) \nabla (\nabla \cdot \mathbf{v}).
\] (4.33)

Taking the divergence of Eq. (4.33), once \( \psi \) is known, \( p \) can be immediately obtained through a modified pressure Poisson equation.
4.3.4 Governing equations in dimensionless form

By using the constitutive law Eq. (4.24) we summarize here the complete set of governing equations for the smectic-isotropic fluid system,

\[
\nabla \cdot \mathbf{v} = -\frac{\hat{A}}{\rho},
\]

\[
0 = -\nabla p + \alpha \nabla^2 \left[ \rho (\nabla^2 + q_0^2) \psi \right] \nabla \psi - \alpha \rho (\nabla^2 + q_0^2) \psi \nabla^2 \nabla \psi
+ \eta \nabla^2 \mathbf{v} + (\lambda + \eta) \nabla (\nabla \cdot \mathbf{v}),
\]

\[
\dot{\psi} = -\Gamma \mu,
\]

\[
\rho = \kappa A + \rho_0.
\]

To introduce dimensionless variables, let U and L represent characteristic scales for the velocity and length, and \( \hat{\rho} \), \( \tilde{\psi} \) and \( \tilde{\mu} \) represent typical values for \( \rho \), \( \psi \) and \( \mu \) in the modulated phase. Then, we introduce the dimensionless variables \( \mathbf{v}^* = \mathbf{v}/U \), \( x^* = x/L \), \( t^* = Ut/L \), \( \rho^* = \rho/\hat{\rho} \), \( \psi^* = \psi/\tilde{\psi} \) and \( \mu^* = \mu/\tilde{\mu} \). The resulting equations have the same form as Eqs. (4.34)-(4.37), replacing constants and variables by dimensionless constants and variables. The dimensionless constants one finds are \( \hat{\kappa} = \kappa/\hat{\rho} \), \( \hat{\Gamma} = \Gamma L \tilde{\mu}/\tilde{\psi} U \), \( \tilde{\eta} = \eta UL^3/\tilde{\psi} \tilde{\psi}^2 \) and \( \tilde{\lambda} = \lambda UL^3/\tilde{\psi} \tilde{\psi}^2 \), where the last two are proportional to the capillary number. In the following discussion, we use the non-dimensional set of governing equations, dropping the tilde from constants and star from variables.

4.4 Numerical Method

We solve Eqs. (4.34)-(4.37) numerically, with boundary conditions specified in Eq. (4.7), by using a pseudo-spectral method, in which linear and gradient terms are computed in Fourier space and nonlinear terms in real space. Space discretization depends on \( n_w \), the number of points per base wavelength, and is given by \( \Delta x = 2\pi/(n_w q_0) \). The appropriate choice of time step will be later analyzed in the context of the scheme stability. We have developed custom C++ codes based on the parallel FFTW library and the standard MPI passing interface for parallelization. In order to accommodate
the boundary conditions, we use both the Discrete Cosine Transform of \((\psi, \rho)\) and the Discrete Sine Transform of \((\nabla \psi, \nu)\). The source codes containing the implementation of this model \((\text{smaiso}\text{-}\text{quasi})\) can be found in Ref. \[160\], and the codes for the simpler uniform density model \((\text{smaiso}\text{-}\text{uniform})\) described in Sec. 4.2 are found in Ref. \[161\].

In Chapter 3 when working with an uniform density system \[75\], we integrated the dynamic equation for \(\psi\) in time employing a Crank-Nicolson algorithm for the linear part of the equation, and a second order Adams-Bashforth method for the nonlinear terms. However, we cannot deal with Eq. (4.36) in the same way (splitting it into linear and nonlinear parts), as now the right hand side is multiplied by a varying density. Therefore, we rewrite Eq. (4.36) as
\[
\partial_t \psi = \Gamma (\rho L \psi + N) ,
\]
where \(L\) is a linear operator, and \(N\) is a collection of nonlinear terms. Note that \(\Gamma \rho\) plays the role of a spatially varying mobility (this is why we cannot treat this equation as in Ref. \[75\]). We follow a scheme already introduced for phase-field models with variable mobility \[162\] \[163\]: We split the density as \(\rho \rightarrow \rho_m + (\rho - \rho_m)\), where \(\rho_m = \frac{1}{2}(\rho_s + \rho_0)\). Here, \(\rho_s\) is the density of the smectic bulk, which can be obtained from the system parameters by \(\rho_s = \kappa A_s + \rho_0\), where \(A_s = 2A_0\) is the amplitude of the sinusoidal phase, with \(A_0\) given by Eq. (4.47). The idea behind the split is that the term associated to \(\rho_m\) can be treated implicitly, and \((\rho - \rho_m)\) explicitly, with a choice of \(\rho_m\) that satisfies \(|\rho - \rho_m| \leq \rho_m\).

In Fourier space, we use a second order discretization in time, and compute \(\psi\) at time \(n + 1\) by
\[
\frac{3}{2}\psi^{n+1}_k - 2\psi^n_k + \frac{1}{2}\psi^{n-1}_k = \frac{\Gamma \rho_m L \psi^{n+1}_k - \rho_m L \psi^n_k + (\rho^n L \psi^n + N^n)_k}{\Delta t} .
\]
The term \(\rho^n L \psi^n\) is nonlinear, so we include it in the definition of \(N\). Instead of solely accounting for the nonlinear terms \(N\) at time \(n\), we treat \(N\) with a second order multistep
Adams-Bashforth scheme. In frequency space, $\psi_k$ for the new time is then obtained by

$$(3/2 - \Delta t \Gamma \rho_m L)^n_{k+1} = (2 - \Delta t \Gamma \rho_m L)n^n_{k} - \frac{1}{2} \Delta t \Gamma \frac{1}{2} (3N^n_k - N^n_{k-1}). \quad (4.41)$$

Overall, our model—as well as the physical system—is only concerned with a slowly varying density, on the scale of variations of the envelope $A = (\psi^2 + q_0^{-2} |\nabla \psi|^2)^{1/2}$, but not changing on the scale of the smectic layers, $1/q_0$. While this approximation for $A$ gives us an adequate approximation for the amplitude of $\psi$ in regions where the smectic layers are well formed and only weakly distorted, it becomes noisier on the interface and also in regions where layers are highly distorted or break up. Therefore in our numerical calculations we smooth the computed amplitude with a Gaussian filter in Fourier space, given by the operator $F_\zeta = \exp(-\zeta^2 q^2/2)$, where $q$ is the wavenumber and $\zeta$ the filtering radius, chosen as $1/q_0$. For large density ratios, $(\rho_s - \rho_0)/\rho_0 > 5$, we also observe for numerical instabilities originating from terms containing gradients of $\rho$ in Eqs. (4.31) and (4.35), due to fast oscillatory terms that should be compensated by an oscillatory pressure. Therefore, while in such cases we use a spatially varying density in the numerical integration, we neglect higher order terms in terms $\nabla \rho$ and $\nabla^2 \rho$ from Eqs. (4.35) and (4.36).

### 4.5 Stability analysis

In order to elucidate the role of hydrodynamics on interfacial motion, as well as to validate the numerical algorithm, we first address the linear stability of a stack of smectic layers as shown in Fig. 4.1 and derive the dispersion relation for transverse perturbations of the smectic layers as a function of the distortion wavelength. Consider a reference configuration comprising a set of parallel smectic planes that span the whole domain, aligned along a reference wave vector $q$. The base solution is $\psi_0 = A_0e^{i\mathbf{q} \cdot \mathbf{x}} + c.c.$, and homogeneous density $\rho = \rho_s$. We introduce a perturbation of wave vector $Q$ while leaving the density constant,

$$\psi = A_0e^{i\mathbf{q} \cdot \mathbf{x}} + A_1e^{i(q+Q) \cdot \mathbf{x}} + A_2e^{i(q-Q) \cdot \mathbf{x}} + c.c. , \quad (4.42)$$
where $A_1, A_2 \ll A_0$ are small amplitudes. Since the density is constant, the order parameter equation reduces to

$$\partial_t \psi + v \cdot \nabla \psi = -\Gamma \mu = \Gamma \rho_s \left[ -\epsilon \psi - \alpha q_0^2 (\nabla^2 + q_0^2)^2 \psi + \beta \psi^3 - \gamma \psi^5 \right]. \quad (4.43)$$

The mobility $\Gamma = 1$ in all our simulations. Define

$$l_0 = |\mathbf{q}|^2 - q_0^2, \quad l_1 = |\mathbf{q} + \mathbf{Q}|^2 - q_0^2, \quad l_2 = |\mathbf{q} - \mathbf{Q}|^2 - q_0^2.$$

Then, by keeping only modes $\exp(\pm i \mathbf{q} \cdot \mathbf{x})$ and $\exp(\pm i (\mathbf{q} \pm \mathbf{Q} \cdot \mathbf{x}))$ when expanding $\mu$ in terms of the perturbation, we find

$$\mu \rho_s^{-1} = M_0 e^{i \mathbf{q} \cdot \mathbf{x}} + M_1 e^{i (\mathbf{q} + \mathbf{Q}) \cdot \mathbf{x}} + M_2 e^{i (\mathbf{q} - \mathbf{Q}) \cdot \mathbf{x}} + c.c.$$ 

with

$$M_0 = \epsilon A_0 + l_0^2 A_0 - 3 \beta |A_0|^2 A_0 + 10 \gamma |A_0|^4 A_0,$$

$$M_1 = \epsilon A_1 + l_1^2 A_1 - 6 \beta |A_0|^2 A_1 - 3 \beta A_0^2 A_2^* + 30 \gamma |A_0|^4 A_1 + 20 \gamma |A_0|^2 A_0^2 A_2^*,$$

$$M_2 = \epsilon A_2 + l_2^2 A_2 - 6 \beta |A_0|^2 A_2 - 3 \beta A_0^2 A_1^* + 30 \gamma |A_0|^4 A_2 + 20 \gamma |A_0|^2 A_0^2 A_1^*.$$
Since the density is uniform in the smectic layer, the velocity field is solenoidal. Also, the pressure in Eq. (4.35) can be redefined so that the momentum balance equation can be written in terms of a forcing term \( f = \mu \nabla \psi \),

\[
0 = -\nabla \bar{p} + f + \eta \nabla^2 \mathbf{v}, \tag{4.44}
\]

\[
\bar{p} = p + \frac{\alpha \rho_s}{2} [ (\nabla^2 + q_0^2) \psi ]^2 + \frac{\rho_s e}{2} \psi^2 - \frac{\rho_s \beta}{4} \psi^4 + \frac{\rho_s \gamma}{6} \psi^6. \tag{4.45}
\]

That is, \( \bar{p} = p + \rho_s e \). Since for planar smectic layers the chemical potential \( \mu \) is zero in equilibrium, the velocity field \( \mathbf{v}_0 \) for the base \( \psi \) solution is also exactly zero.

In order to obtain an expression for the perturbed flow velocity, we set the base state of the smectic layers to be aligned along \( z \), \( \mathbf{q} = q_0 \hat{z} \), so that \( \mathbf{Q} \) is orthogonal to \( z \). By applying the Fourier transform, we obtain the following terms from \( f \) for frequencies \( Q \) and \( 2q \), in Fourier space,

\[
f_Q = \rho_s \left[ -i M_0 (\mathbf{q} - \mathbf{Q}) A_2^* + i M_2 q A_0 - i M_1 q A_0^* + i M_0 (\mathbf{q} + \mathbf{Q}) A_1 \right]
\]

\[
f_{2q} = -i \rho_s A_0 q_0
\]

The remaining modes that are required for the leading order expansion of the order parameter equation are given by \( f^*_Q = f_Q \) and \( f^*_{2q} = f_{2q} \). By taking the divergence of Eq. (4.44), we find a pressure Poisson equation, which allows us to calculate the pressure in terms of the frequency \( \mathbf{k} \) as

\[
p_k = \frac{i \mathbf{k} \cdot \mathbf{f}_k}{|\mathbf{k}|^2}.
\]

Then, by substituting the pressure into Eq. (4.44), we obtain an expression for the flow velocity in terms of the Fourier modes

\[
\mathbf{v} = \sum_{\mathbf{k} \neq \mathbf{Q}} \frac{1}{\eta |\mathbf{k}|^2} \left( \mathbf{I} - \frac{\mathbf{k} \otimes \mathbf{k}}{|\mathbf{k}|^2} \right) \mathbf{f}_k e^{i \mathbf{k} \cdot \mathbf{x}}, \tag{4.46}
\]

for which the longitudinal modes, \( \mathbf{v}_{\pm 2q} \), drop out, since the velocity is solenoidal in the smectic. Hence, the flow velocity \( \mathbf{v} \) will only couple to the transverse part of the perturbation in \( \psi \). Hydrodynamic effects do not affect the stability of \( \psi \) for longitudinal
distortions of the layers.

As we are interested in the transverse stability through modulations of the phase, we impose a perturbation in the plane orthogonal to the layering normal, say \( Q = Q \hat{x} \). By substituting \( f_Q \) into Eq. (4.46), we find a velocity in the longitudinal direction \( \hat{z} \) that only depends on the Fourier transform on the \( z \) component of the forcing term, \( (f_z)_{\pm Q} \). Finally, by substituting this expression for the velocity into Eq. (4.43) and gathering terms associated with modes \( \exp(\pm i (q \pm Q \cdot x)) \), we obtain the amplitude equations that govern the evolution of \( A_1 \) and \( A_2 \),

\[
\frac{\partial}{\partial t} A_1 = (6\beta A_0^2 - 30\gamma A_0^4 + \epsilon - l_1^2 - H_c(l_1^2 - l_0^2))A_1 \\
+ (H_c(l_2^2 - l_0^2) + 3\beta A_0^2 - 20\gamma A_0^4)A_1^*,
\]

\[
\frac{\partial}{\partial t} A_2 = (6\beta A_0^2 - 30\gamma A_0^4 + \epsilon - l_2^2 - H_c(l_2^2 - l_0^2))A_2 \\
+ (H_c(l_1^2 - l_0^2) + 3\beta A_0^2 - 20\gamma A_0^4)A_1^*.
\]

where \( H_c \) is a hydrodynamic coupling coefficient obtained from Eq. (4.46), and is given by

\[
H_c = \frac{1}{\eta|Q|^2} \left( |q|^2 - \frac{(q \cdot Q)^2}{|Q|^2} \right) A_0^2.
\]

As previously argued, there is no hydrodynamic coupling for longitudinal perturbations, so that \( H_c = 0 \) when \( q \) and \( Q \) are parallel. However, for the case of transverse perturbations, the coupling coefficient can have an significant role in the stability. To derive the dispersion relation we need a solution for \( A_0^2 \) (note that \( A_0 \) is constant and real), found by gathering terms in the base wavenumber \( q_0 \),

\[
0 = -\epsilon A_0 - \alpha l_0^2 A_0 + 3\beta A_0^3 - 10\gamma A_0^5
\]

which gives us

\[
A_0^2 = \frac{3\beta + \sqrt{9\beta^2 - 40\epsilon\gamma}}{20\gamma}.
\]
For transverse modulations of the phase, considering a base frequency $q = q_0 \hat{z}$ and perturbation $Q = Q \hat{x}$, we can write the order parameter as

$$\psi = 2A_0 \cos(q_0 z + \phi \sin(Qx)),$$

where $\phi$ is the amplitude of the initial perturbation. In the limit of $\phi \ll 1$, this is equivalent to setting $A_1 = A_0 \phi/2$ and $A_2 = A_0 \phi/2$ in Eq. (4.42). By substituting $A_0, A_1,$ and $A_2$ into the amplitude equation for $A_1$ above, we find

$$\sigma_\perp = \frac{\partial \phi}{\phi}.$$  \hspace{1cm} (4.48)

The decay rate for the transverse perturbation is given by $\sigma_\perp = \partial_t \phi/\phi$. Therefore, while in the absence of hydrodynamics the growth rate is proportional to $Q^4$, hydrodynamic effects lead to a decay proportional to $Q^2$ at low wavenumbers.

### 4.5.1 Code validation

We compare the numerical solution of the model using the numerical method described in Sec. 4.4 to the dispersion of Eq. (4.48). We set the viscosity to be small, $\eta = 0.1$, so that we are able to distinguish the effects from order parameter relaxation and flow. The parameters of the model used are $\beta = 0.4$, $\gamma = 3$, and $\epsilon = \epsilon_c = 0.009$. The base amplitude $A_0$ is computed from Eq. (4.47), and the perturbation amplitude is $\phi = 0.1$. We use $N = 512^3$ and $\Delta x = 0.7854$ (8 grid nodes per wavelength) and $\Delta t = 5 \times 10^{-4}$.

We use an initial condition of the form of Eq. (4.42) with $A_1 = A_0 \phi/2, A_2 = -A_0 \phi/2,$ and set the density of the smectic $\rho_s = 1$. The base and perturbation wavenumbers are $q = q_0 \hat{z}$ and $Q = Q \hat{x}$. Equations (4.35) and (4.36) are integrated in time, and the growth rate is computed after a few time steps ($\approx 10$). Since we employ the discrete cosine transform for $\psi$, the growth rate is obtained from the spectrum of the transformed $\psi$, by computing the time derivative of the amplitude associated with the frequency $q \pm Q$ and dividing by the same amplitude. The results are shown in Fig. 4.2, where we include, as a reference, the decay rate in the absence of hydrodynamic coupling.

We observe that in both cases numerical results agree very well with the analytic prediction from Eq. (4.48). In the absence of hydrodynamics, numerical results for the decay rate follow the $-Q^4$ dependence. When hydrodynamic coupling is included, we also obtain a good agreement between numerical results and the derived dispersion
Figure 4.2: Logarithmic plot for the transverse growth rate $\sigma_\perp$ as a function of the perturbation frequency $Q$, showing how numerical results match the analytic predictions. The solid curve represents the hydrodynamic free case, and the dashed curve the case when hydrodynamics is turned on, with viscosity $\eta = 0.1$. Parameters are $\epsilon = 0.009$, $\beta = 0.4$, $\gamma = 3$ and $q_0 = 1$.

relation for all values of $Q$. The amplitude 0.6 in the figure follows from substitution of the given model parameters into Eq. (4.48). There are no adjustable parameters in this figure.

4.5.2 Energy relaxation and stability of the algorithm

The stability of the numerical integration with respect to time step is now investigated by monitoring the decay of the total energy of the system, Eq. (6.22), with $e$ as defined in Eq. (4.30). The case investigated concerns a slab of distorted smectic planes surrounded by an isotropic fluid at coexistence. We take the smectic layers aligned along the $z$ direction, and perturbed along $Q = Q_\perp \hat{x}$ as in Eq. (4.42), and as shown in Fig. 4.3a. The density of the bulk smectic is chosen as $\rho_s \approx 0.67$, and the density of the isotropic fluid $\rho_0 = 0.05$. The parameters in the energy are $q_0 = 1$, $\alpha = 1$, $\beta = 2$, $\gamma = 1$, $\epsilon = \epsilon_c = 0.675$ so that the two phases have approximately the same energy.
coexistence). Up to a certain finite value of the perturbation amplitude, we expect the reference planar configuration to be stable, so that the perturbed smectic planes relax as shown in Fig. 4.3b.

![Figure 4.3: Two dimensional cross section of an initially perturbed stack of smectic layers in contact with an isotropic fluid relaxing towards a planar configuration while decreasing the total energy of the system.](image)

We set $\Delta x = 2\pi/8 = 0.7854$ and $N = 256^3$. Time steps are chosen for each of the runs, and we let the system evolve in time, so that the total energy decay can be monitored. Results are shown in Fig. 4.4 for three different time steps: $\Delta t = 5 \times 10^{-4}$, $\Delta t = 1 \times 10^{-3}$, and $\Delta t = 5 \times 10^{-3}$. We observe that the curves match for $\Delta t = 5 \times 10^{-4}$ and $\Delta t = 1 \times 10^{-3}$, and both exhibit the expected monotonic decay. We obtain the same curves for smaller values of $\Delta t$. However, the curve $\Delta t = 5 \times 10^{-3}$ diverges from the previous ones, and fails to be monotonic. For $\Delta t \geq 1 \times 10^{-2}$, the numerical scheme becomes unstable and numerical solutions diverge.

These results show that the scheme introduced in Sec. 4.4 for dealing with a dynamic equation for the order parameter with phases of varying density does not impose overly severe restrictions on time step. For instance, for a smectic density $\rho_s \approx 1$, the time step is of the same order as in the semi-implicit scheme employed for purely diffusive decay in Ref. [75]. While $\Delta t = 1 \times 10^{-3}$ is an appropriate choice for the time step in this case, some factors may require this choice to be altered. For example, increasing
Figure 4.4: Energy \( \int \rho \, dx \) decay in time for different values of the time step \( \Delta t \). The curves agree for \( \Delta t \leq 1 \times 10^{-3} \), while for larger steps the curves deviate.

the resolution to have more points representing the base wavelength requires \( \Delta t \) to be decreased. Another factor is associated with the balance of mass from Eq. (4.34): by increasing the difference between the smectic and disordered phase densities, numerical instabilities may arise from the way \( \nabla \cdot \mathbf{v} \) is computed from the material time derivative of the amplitude over the density. Hence, the appropriate choice of \( \Delta t \) and \( \Delta x \) must be done on a case to case basis.

Finally, we conclude this section by mentioning that we have checked that the numerical method conserves mass at coexistence of phases. For the same initial condition (i.e., transversely perturbed smectic layers), parameters as above, and \( \Delta t = 1 \times 10^{-3} \), we have followed how the mass fraction \( m/m_0 \) changes in time, where \( m_0 \) is the initial mass, and \( m = \int \rho \, dV \) is computed after every time step. While there is a slight decay of mass (approx. 2%) at the start due to relaxation of the imposed initial condition, mass gradually returns towards its initial value. For long times \( (t > 60) \), mass reaches a constant value, at a mass fraction \( m/m_0 \) of 99.8%. 
4.6 Flow structure in smectic-isotropic fluid configurations

The balance of linear momentum can be written in terms of a body force \( f = \mu \nabla \psi \), as seen in Eq. (4.44). The force \( f \) is zero either for planar smectic layers, or at coexistence with the isotropic fluid across a planar interface. For curved layers parallel to a curved interface, the change in chemical potential with respect to planarity \( \delta \mu \) becomes a function of the curvatures of the surfaces of constant \( \psi \), and is given by an extension of the Gibbs-Thomson equation \[75\], found in Eq. (3.16). The factor \( \nabla \psi \) in \( f \) ensures that the force is normal to the smectic layers. At the interface, a positive normal points outwards away from smectic, and the sign of \( H \) is such that it is positive for a sphere. At the interface, given that the amplitude \( A \) goes from its finite value in the bulk smectic to zero in the isotropic phase, to lowest order in curvature the force \( f \) is directed towards (resp. away) from the nearest center of curvature when \( \delta \mu > 0 \) (resp. \( \delta \mu < 0 \)), so that at an interface it points towards the smectic phase in regions of positive \( H \).

With these considerations in mind, we present results on the structure of the flow for two different configurations: a transversely modulated smectic layer in contact with the isotropic fluid as in Sec. 4.5.2, and a smectic domain in the form of a focal conic. We consider the following values of the model parameters: \( \kappa = 0.5, \rho_0 = 0.05 \) (density ratio above 10:1), \( q_0 = 1, \alpha = 1, \beta = 2, \gamma = 1, \epsilon = \epsilon_c = 0.675 \), and viscosity is \( \eta = 10 \). For this value of the viscosity, the non-solenoidal velocity has a strong contribution to the resulting interfacial flows. Figure 4.5 shows the transient mass flux, \( v_m = \rho \mathbf{v} \), alongside the density field (green for high density smectic, and blue for low density fluid), for time \( t = 2 \). On the interface, we observe that mass flows outward from smectic regions of negative mean curvature (growth), while in regions of positive mean curvature mass flows inwards towards the smectic phase and also towards regions of negative mean curvature. This is in agreement with our discussion about the direction of the force \( f \) as a function of curvatures.

One of the main motivations of our study is to understand the stability and evolution of focal conic domains in smectics films. A focal conic exhibits a macroscopic singularity at its center, hence the phase-field approach is well suited to study this configuration. Three important effects relevant to focal conics are captured by our model. First, non-classical stresses are present at the interface between the conic and the isotropic fluid
Figure 4.5: Mass flow $\rho \mathbf{v}$ and density field $\rho$ at time for a transversely perturbed smectic at $t = 2$, with a density ratio of approximately 10:1. The right image is a magnification of the left one, showing the flow structure near the interface. We use $N = 256^3$, $\Delta t = 5 \times 10^{-4}$, and parameters $\kappa = 0.5$, $\rho_0 = 0.05$, $q_0 = 1$, $\eta = 10$, $\epsilon = 0.675$, $\alpha = 1$, $\beta = 2$ and $\gamma = 1$.

that depend on both mean and Gaussian curvatures. Second, given a density contrast between the smectic and surrounding fluid, a non-solenoidal velocity field at the interface can introduce significant changes to mass transport and therefore to flow structure and stability. Finally, as shown in Chapter 3 (but not in the example below), instability of a smectic-fluid interface can result in exposed smectic layers at the interface. Their local evolution is governed by Willmore type flows instead of capillarity driven flows.

We show in Fig. 4.6 an initial configuration comprising a focal conic domain in three dimensions surrounded by an isotropic fluid of different density. We use the same model parameters as in the previous case except that $\rho_0 = 0.005$, so that we have a density ratio greater than 100:1 between the smectic and the isotropic fluid. We also set $\eta = 1$. Figure 4.7 shows the transient velocity field at time $t = 5$ at the center cross section, with average velocity $\mathcal{O}(10^{-1})$, alongside the density in the background (green for high density, blue for low). The flow pushes the smectic outwards near the conic center, which is a region of negative mean curvature, while away from the core it
Figure 4.6: Smectic layers bent in a focal conic configuration. (a) The color code represents the order parameter $\psi$ ranging between $\psi_{\text{max}}$ (red) and $\psi_{\text{min}}$ (blue). (b) Middle cross-section displaying the values the order parameter field.

pushes inwards, as it is a region of positive mean curvature. This is in agreement with the dependency of the force $\mathbf{f}$ with respect to Eq. (3.16) to lowest order in curvatures. Hence within the incompressible smectic we observe a recirculating toroidal flow. Given the large density contrast between the phases, the flow velocity exhibits a large variation for most of the interface (away from the center). For comparison, we also show results for the same focal conic for a smectic-isotropic interface when the density is uniform, and for the same dimensionless time $t = 5$. For an uniform density system, it is clear that the flow is continuous on the smectic-isotropic interface since the velocity is solenoidal. While we also observe the flow moving outward on regions of negative mean curvature, and inward on regions of positive mean curvature, it does so continuously through the smectic-isotropic transition creating advection rolls that span the two phases, as expected for this fully incompressible case.

When the focal conic configuration evolves for long times, we observe that the flow considerably slows down in the smectic, away from the central vertical axis where layers self-intersect. In the case of purely diffusional dynamics (relaxational motion of $\psi$), the focal conic slowly evolves toward a steady state configuration [75], creating rings
Figure 4.7: Comparison between the transient fluid flow $\mathbf{v}$ on smectic-isotropic fluid system with approximately 100:1 density contrast ($\kappa = 0.5$, $\rho_0 = 0.005$) and on a smectic-isotropic system of homogeneous density, where the dashed lines mark the location of the interface. The density is represented by the background color: green for high density and blue for low density. We use $N = 256^3$, $\Delta t = 5 \times 10^{-4}$, and parameters $q_0 = 1$, $\eta = 1$, $\epsilon = 0.675$, $\alpha = 1$, $\beta = 2$ and $\gamma = 1$.

at the surface and filling the singularity with smectic. In contrast, in the presence of flow, we observe flow-induced corrections to the resulting morphologies. Fig. 4.8 shows the morphology obtained by letting the focal conic from Fig. 4.7 evolve up to time $t = 310$, keeping the approximate 100:1 density contrast. In addition to the creation of rings at the smectic-isotropic interface (small blue disks in the cross-section), we find that flow induces the breaking of layers right below the rings, which we did not observe in the absence of flow. Also, we see that different layers break in the vicinity of their self-intersection point, which again does not happen for purely diffusional dynamics. This observation is connected to the high curvatures and deviations from the layering wavenumber in regions where layers self-intersect, generating stress and inducing flows that lead to ruptures in these internal layers. While the dynamics at this stage becomes very slow, fluid flow is still relevant, with average velocity $\Theta(10^{-2})$, and advection of the order parameter may induce more rupture of layers for even longer times.
Figure 4.8: Focal conic configuration at time $t = 310$, using the same parameters as in Fig. 4.6 for a density ratio of approximately 100:1. As in the purely diffusional dynamics, rings are formed at the top of the focal conic. Additional breakage of layers close to the interface and regions of self-intersection are due to the order parameter advection. The dynamics are very slow at this stage, but it is not a steady state configuration.

An application for this model is the case where the isotropic phase represents a fluid that the smectic transitions into at sufficiently high temperatures. In thermotropic low molecular weight materials, the density difference for such isotropic - smectic A transitions is very low, ranging between 0.5% and 2% [164]. Therefore, using the same parameters as in Fig. 4.7, we also studied a system where a smectic A phase with $\rho_s = 1$ of a thermotropic material coexists with its isotropic phase with $\rho_0 = 0.99$, so that we have a density jump of 1% between them. In Fig. 4.9 we show both the perturbed smectic A (at $t = 2$) configuration used in Fig. 4.5 and the focal conic configuration (at $t = 5$) used in Fig. 4.7 for the case of a 1% density jump. Due to the small density ratio between phases, the flow is very similar to the fully incompressible case. For the perturbed smectic, we observe advection rolls generated by the flow moving outward on regions of negative mean curvature, and inward on regions of positive mean curvature. The magnitude of the mass flux does not change in the transition between the phases, in contrast to Fig. 4.5 where it decays in the isotropic phase. For the focal conic, the
flow can be described similarly to the uniform density case from Fig. 4.7. However, for 1% density jump we observe a stronger tangential flow at the interface, and advection rolls start bending closer to the smectic. As mentioned in Sec. 4.4, gradients of the density do not pose a problem to numerical stability for such small density differences.

Figure 4.9: Fluid flow on a smectic-isotropic fluid system with a density jump of 1%, a value in the empirical range of transitions in thermotropic low molecular weight materials. The density is represented by the background color: green for high density and blue for low density. We use $\rho_0 = 0.99$, $\rho_s = 1$, and the remaining parameters are the same as in Fig. 4.6.

4.7 Chapter conclusions

We have derived a compressible phase-field model for a two phase smectic-isotropic fluid of varying density by introducing an energy density functional of the smectic order parameter and its gradients. Reversible and irreversible currents are derived from the second law of thermodynamics, leading to the governing dynamical equations. We have specialized our analysis to the case in which the bulk fluids in coexistence are incompressible, but compressibility effects are allowed near the two phase interface. In order to accomplish this, we have introduced a constitutive relation for the density
which depends only on the amplitude of the smectic order parameter. Therefore the velocity field is non solenoidal only in the interfacial region.

A semi-implicit numerical method was developed to integrate the governing equations which is based on an earlier scheme for phase-field models with varying mobilities. The algorithm has been implemented in a parallel code so that we can examine relatively large three dimensional configurations. We have also conducted a stability analysis of weakly perturbed smectic planes, and derived the corresponding dispersion relation, Eq. (4.48), for transverse modes. At long wavelengths, hydrodynamic effects dominate the dispersion relation, with a $Q^2$ wavenumber dependence, instead of the $Q^4$ expected for diffusive decay. We have validated our code against this dispersion relation.

We have presented numerical results concerning fluid flows for a smectic film surrounded by an isotropic fluid of different density. When the initial configuration comprises a set of smectic layers that are weakly perturbed along the transverse direction, we observe that in regions of negative mean curvature at the interface the flow is outward away from the smectic, while those of positive mean curvature push the flow inward toward the smectic, as expected from the dependence of the surface stress on curvature. In a focal conic configuration, flow in the bulk smectic is, for the parameters considered, a convective roll as expected in an incompressible fluid. In both configurations, there is a large variation in velocity across the interface due to the density variation associated with the local gradient of order parameter. Hydrodynamic flows are expected to introduce long-range interactions between focal conics, a subject of considerable interest in applications of arrays of focal conics in smectic films, which will be discussed in Chapter 5.
Chapter 5

Weakly compressible model for a smectic-isotropic system

5.1 Introduction

In Chapter 4, we derived a phase-field model for a smectic-isotropic interface where both phases are compressible and have distinct densities. We then restricted this model to the quasi-incompressible limit, where both phases are considered as incompressible but a non-solenoidal velocity is allowed at the interface \[114\]. In order to do so, we considered the internal energy \[\mathcal{U} = \int \rho u \, dx\], and from an specific choice of the energy density \(u\) we used the Coleman-Noll procedure to obtain the constitutive relations required by the governing equations. In the quasi-incompressible case, a constitutive equation for the density as a function of the amplitude of the order parameter was proposed, so that the density had a constant value in the bulk of the smectic (\(\rho_s\)) and in the bulk of the isotropic phase (\(\rho_0\)). When parameters are chosen such that phases are in coexistence, curvature driven growth and dissolution of the smectic was observed at the interface, in a way that conservation of mass was satisfied. However, this model is not suited for situations, out of coexistence, where one phase can grow at the expense of other, as would be the case of sintering of smectic films (as in experiments \[18\]). The reason is that in the quasi-incompressible limit, if the smectic continuously evaporated, balance of mass would not be satisfied because the density of the isotropic phase is not allowed to increase, since it is determined constitutively by the local order parameter (which is...
zero for the isotropic phase).

While the quasi-incompressible model presents this limitation, it has the advantage of tying the density in each phase to the order parameter, in a way that we are able to have control over its value in each bulk phase and also control of the density ratio between phases. In order to combine these features of the quasi-incompressible model with the possibility of allowing phases to grow outside coexistence, we here propose a more flexible and general model than the quasi-incompressible one. We call it the weakly compressible model for a smectic-isotropic system, since we now add to the energy a penalty term for deviations from the expected smectic and isotropic equilibrium bulk densities. This model directly enforces mass conservation, and is numerically stable even in presence of a large density ratio between phases, which was an issue for the quasi-incompressible model.

For introducing the energy density, we use a similar methodology as Brand and Pleiner [158], who developed a hydrodynamic theory for smectics and other mesophases exhibiting broken symmetries. Their proposed energy density depended on a variable representing the broken symmetry of the system, such as the director $\hat{n}$ and its derivatives in nematics. In our case, we adopt the periodic order parameter $\psi$ representing the smectic layering order, and we account for an additional dependency of $u$ on $\nabla^2 \psi$ (energy involved in layer distortions). We derive the governing equations and constitutive relations from restrictions on the local balance of entropy.

### 5.2 Weakly Compressible model

We derive in this section a diffuse interface model for a weakly compressible smectic phase in contact with an isotropic fluid when they have different equilibrium densities. We write the internal energy $\mathcal{U}$ of the system in terms of the energy per unit mass $u$ and the mass density $\rho$, where $u = u(s, \psi, \nabla \psi, \nabla^2 \psi)$ and $s$ is the specific internal entropy. The energy also has an explicit dependence on the amplitude $A$ of the periodic order parameter $\psi$, which is approximately constant in both smectic and isotropic phases. This internal energy is written as

$$\mathcal{U} = \int_{\Omega} \left\{ \rho u + \frac{\zeta}{2} \left( \rho - \rho_0 - \kappa A \right)^2 \right\} dx. \quad (5.1)$$
The second term inside the integral penalizes density values that deviate from equilibrium values in the smectic and isotropic phases, where $\zeta$, $\rho_0$ (the equilibrium density for the isotropic phase) and $\kappa$ are constants. In the limit of $\zeta \to \infty$, the density becomes constitutively governed by $A$, as $\rho = \rho_0 + \kappa A$, and the energy reduces to $U = \int_\Omega \rho u \, dx$. This is the quasi-incompressible limit, which we have previously studied [76] and imposes a strict constraint on the evolution of the non-conserved order parameter $\psi$. However, when $\zeta$ is finite, the density is an independent parameter, and, for smaller values of $\zeta$, $\psi$ becomes able to evolve more freely as it is less energetically expensive for density to deviate from equilibrium values. The main difference between the derivation shown in Chapter 4 and the present one is the presence of this density penalty term.

The relations we derive in this section are obtained in the absence of a heating supply, so that we neglect $\mathcal{R}$ for the rest of this section. When deriving the governing equations, we set no-flux boundary conditions: Neumann condition for the order parameter $\psi$ (which forces the smectic planes to be perpendicular to the domain outer boundary) and zero normal velocity on the boundary, such that

$$\nabla \psi(x) \cdot n = \nabla^2 \psi(x) \cdot n = 0, \quad v(x) \cdot n = 0, \quad x \in \partial \Omega. \quad (5.2)$$

Accounting for the balance of linear momentum $\rho \dot{v} = \nabla \cdot T$ and balance of mass $\dot{\rho} + \rho \nabla \cdot v = 0$, the local form of the balance of internal energy [107] is obtained as in Eq. (2.58), so that

$$\rho \dot{u} - \kappa \zeta \left( \rho - \rho_0 - \kappa A \right) \dot{A} = \left\{ T + \frac{\zeta}{2} \left[ \rho^2 - (\rho_0 + \kappa A)^2 \right] \right\} : \nabla v + \nabla \cdot (t \dot{\psi}) \quad (5.3)$$

The local balance of entropy can be derived from the previous equation, by accounting for the following dependence of the energy density: $u = u(s, \psi, \nabla \psi, \nabla^2 \psi)$. Note that $u$ is an energy per unit mass independent of the density. The dependence on $\nabla^2 \psi$ does not appear for binary systems, but is fundamental to model the smectic phase. Hence, by the chain rule

$$\dot{u} = \frac{\partial u}{\partial s} \dot{s} + \frac{\partial u}{\partial \psi} \dot{\psi} + \frac{\partial u}{\partial \nabla \psi} \cdot \nabla \psi + \frac{\partial u}{\partial \nabla^2 \psi} \cdot \nabla^2 \psi \cdot (5.4)$$

Given that the temperature $\theta = \partial u / \partial s$, we rewrite Eq. (5.3) as a local balance of
entropy

$$
\rho \dot{s} = \frac{1}{2} \left( T + \frac{e}{2} - (\rho_0 + \kappa A)^2 \right) + \rho \nabla \psi \otimes \frac{\partial u}{\partial \nabla \psi} - \nabla \psi \otimes \nabla \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right) + \rho \frac{\partial u}{\partial \nabla^2 \psi} \mathbf{D} \psi \right) : \nabla \mathbf{v} \\
+ \left[ t - \rho \frac{\partial u}{\partial \nabla \psi} + \nabla \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right) \right] \cdot \nabla \cdot \dot{\psi} + \left[ \kappa \zeta \left( \rho - \rho_0 - \kappa A \right) \frac{\partial A}{\partial \psi} - \rho \frac{\partial u}{\partial \psi} + \nabla \cdot t \right] \dot{\psi}, \quad (5.5)
$$

where $\mathbf{D}$ stands for $\partial_i \partial_j$, so that $\mathbf{D} \psi$ is a second order tensor. In deriving the previous expression, the boundary conditions from Eq. (5.2) allow us to write

$$
\rho \frac{\partial u}{\partial \nabla^2 \psi} \nabla^2 \psi = \rho \frac{\partial u}{\partial \nabla^2 \psi} \nabla^2 \psi - \rho \frac{\partial u}{\partial \nabla^2 \psi} \nabla \psi \cdot \nabla - 2 \rho \frac{\partial u}{\partial \nabla^2 \psi} \nabla \cdot \mathbf{v} : \mathbf{D} \psi \\
= -\nabla \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right) \cdot \nabla \dot{\psi} + \left[ \nabla \psi \otimes \nabla \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right) - \rho \frac{\partial u}{\partial \nabla^2 \psi} \mathbf{D} \psi \right] : \nabla \mathbf{v}, \quad (5.6)
$$

and also

$$
\rho \frac{\partial u}{\partial \nabla \psi} \cdot \nabla \dot{\psi} = \rho \frac{\partial u}{\partial \nabla \psi} \cdot \nabla \dot{\psi} - \rho \nabla \psi \cdot \frac{\partial u}{\partial \nabla \psi} : \nabla \mathbf{v}. \quad (5.7)
$$

The terms in square brackets proportional to $\dot{\psi}$ and $\nabla \dot{\psi}$ in Eq. (5.5) are both related to variations of $\psi$ and can be grouped together. By using the boundary conditions, we write

$$
\rho \dot{s} = \frac{1}{2} \left( T + \frac{e}{2} - (\rho_0 + \kappa A)^2 \right) + \rho \nabla \psi \otimes \frac{\partial u}{\partial \nabla \psi} - \nabla \psi \otimes \nabla \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right) + \rho \frac{\partial u}{\partial \nabla^2 \psi} \mathbf{D} \psi \right) : \nabla \mathbf{v} \\
+ \left[ \kappa \zeta \left( \rho - \rho_0 - \kappa A \right) \frac{\partial A}{\partial \psi} - \rho \frac{\partial e}{\partial \psi} + \nabla \cdot \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right) \right] \dot{\psi}. \quad (5.8)
$$

As in the previous chapter, we use the Coleman-Noll procedure to derive constitutive relations. Equation (5.8) must be satisfied for every admissible thermomechanical process, so that we enforce the positive-definiteness of $\mathbf{\dot{s}}$. Hence, by splitting the stress into reversible and dissipative parts, $\mathbf{T} = \mathbf{T}^R + \mathbf{T}^D$, we can derive the reversible parts from Eq. (5.8) in the limit of zero entropy production, while dissipative parts are obtained
by enforcing positive entropy production.

For deriving $T^R$, which is a reversible current for the balance of linear momentum, we set the terms in brackets associated with the rates $\nabla v$ equal to zero, so that

$$
T^R = -\frac{\zeta}{2} \left[ \rho^2 - (\rho_0 + \kappa A)^2 \right] I - \rho \nabla \psi \otimes \frac{\partial u}{\partial \nabla \psi} \\
+ \nabla \psi \otimes \nabla \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right) - \rho \frac{\partial u}{\partial \nabla^2 \psi} D \psi.
$$

(5.9)

Note that the non-classical stresses appear in Eq. (5.9), not only due to the dependence of $u$ on $\nabla^2 \psi$, but also because of the presence of the term multiplied by $\zeta$. Generally, we will expect this term to be zero for the bulk smectic and isotropic phases, since $\rho$ will approach $\rho_0 + \kappa A$ there due to energy minimization. However, this term can potentially become large for compressible flows near the smectic-isotropic interface, an effect that does not appear for incompressible flows.

The expression in square brackets multiplying $\dot{\psi}$ is the thermodynamic conjugate to $\psi$, $\mu = \delta U/\delta \psi$. That is,

$$
\mu = -\kappa \zeta \left( \rho - \rho_0 - \kappa A \right) \frac{\partial A}{\partial \psi} + \rho \frac{\partial u}{\partial \psi} \cdot \nabla \left( \rho \frac{\partial u}{\partial \nabla \psi} \right) + \nabla^2 \left( \rho \frac{\partial u}{\partial \nabla^2 \psi} \right).
$$

(5.10)

Since $\dot{s} = 0$ for reversible motions, and $\mu$ is arbitrary, we must have $\dot{\psi} = 0$. The arguments for writing the dissipative part of the quasi-current $Z$ in the dynamical equation for $\psi$ and the dissipative part of the stress $T$ are the same as in Chapter 4, so that we have

$$
Z^D = \Gamma \mu,
$$

(5.11)

$$
T^D = \eta (\nabla v + \nabla v^T) + \lambda (\nabla \cdot v) I.
$$

(5.12)

While we previously assumed the Stokes’ hypothesis and set $\lambda = -\frac{2}{3} \eta$, we will now allow the second coefficient of viscosity $\lambda$ to be independent of $\eta$. 
The equations governing the evolution of the weakly compressible system now read

\[
\begin{align*}
\dot{\rho} &= -\rho \nabla \cdot \mathbf{v} , \\
\rho \dot{\mathbf{v}} &= \nabla \cdot \left( T^R + T^D \right) , \\
\dot{\psi} &= -\Gamma \mu ,
\end{align*}
\]

with \( T^R \) defined in Eq. (5.9), \( T^D \) in Eq. (5.12) and \( \mu \) in Eq. (5.10). Boundary conditions on the outer boundaries are specified by Eqs. (5.2).

### 5.2.1 Choice of energy functional

The form of the specific energy \( u \) is the same as in Eq. 4.30, as we are still interested in a rotationally invariant energy that can represent a modulated phase in contact with an isotropic phase, under both coexistence and non-coexistence conditions. The chemical potential from Eq. (5.10) is now,

\[
\mu = -\kappa \zeta \left( \rho - \rho_0 - \kappa A \right) \frac{\partial A}{\partial \psi} + \rho \left[ \epsilon \psi + \alpha q_0^2 (\nabla^2 + q_0^2) \psi - \beta \psi^3 + \gamma \psi^5 \right] \\
+ \alpha \nabla^2 \left[ \rho (\nabla^2 + q_0^2) \psi \right] .
\]

One important remark about computing \( \mu \) from Eq. (5.16) is that while we are able to numerically extract the amplitude from \( \psi \), the dependence of \( A \) as a function of \( \psi \) is unknown, and so is its derivative with respect to \( \psi \). In this work, since the order parameter \( \psi \) has a sinusoidal form, we compute the amplitude \( A \) through \( A = \sqrt{\psi^2 + q_0^{-2} |\nabla \psi|^2} \).

Inspired by this calculation, we compute the chemical potential \( \mu = \delta \Omega / \delta \psi \) accounting for \( A = A(\psi, \nabla \psi) \), which slightly modifies the result from Eq. (5.16). That is, from the functional derivative of \( \Omega \) with respect to \( \psi \) we find

\[
\mu = -\kappa \zeta \left( \rho - \rho_0 - \kappa A \right) \frac{\psi}{A} + \kappa \zeta q_0^{-2} \nabla \cdot \left[ \left( \rho - \rho_0 - \kappa A \right) \frac{\nabla \psi}{A} \right] \\
+ \rho \left[ \epsilon \psi + \alpha q_0^2 (\nabla^2 + q_0^2) \psi - \beta \psi^3 + \gamma \psi^5 \right] + \alpha \nabla^2 \left[ \rho (\nabla^2 + q_0^2) \psi \right] .
\]

Due to the dominance of viscous effects in smectics over inertia, and using the
definition of the energy density in Eq. (4.30), the balance of linear momen
tum from Eq. (5.14) becomes

\[
0 = -\frac{\zeta}{2} \nabla \left[ \rho^2 - (\rho_0 + \kappa A)^2 \right] + \alpha \nabla^2 \left[ \rho (\nabla^2 + q_0^2) \right] \nabla \psi \\
- \alpha \rho (\nabla^2 + q_0^2) \psi \nabla^2 \psi + \eta \nabla^2 v + (\eta + \lambda) \nabla (\nabla \cdot v).
\] (5.18)

By denoting \( \bar{\mu} \) as the chemical potential from Eq. (5.16) without the term containing
the derivative of \( A \) with respect to \( \psi \), we can rewrite the two terms in Eq. (5.18)
containing \( \psi \) as \( \bar{\mu} \nabla \psi - \rho \nabla u \). In particular, \( \bar{\mu} \nabla \psi \) is known as the osmotic stress, and
is exactly the forcing term that appears for an incompressible smectic-isotropic system,
where both phases have the same density. Therefore, \(-\rho \nabla u\) is a force that originates
from compressibility effects.

### 5.2.2 Governing equations in dimensionless form

We summarize here the complete set of governing equations for the weakly compressible
smectic-isotropic fluid system,

\[
\dot{\rho} = -\rho \nabla \cdot \mathbf{v}, \quad (5.19)
\]

\[
0 = -\frac{\zeta}{2} \nabla \left[ \rho^2 - (\rho_0 + \kappa A)^2 \right] + \bar{\mu} \nabla \psi - \rho \nabla u + (\eta + \lambda) \nabla (\nabla \cdot \mathbf{v}), \quad (5.20)
\]

\[
\dot{\psi} = -\Gamma \mu, \quad (5.21)
\]

with the chemical potential \( \mu \) given by Eq. (5.17).

To introduce dimensionless variables, let \( U \) and \( L \) represent characteristic scales for
the velocity and length, and \( \tilde{\rho}, \tilde{\psi} \) and \( \tilde{\mu} \) represent typical values for \( \rho, \psi \) and \( \mu \) in the
modulated phase. Then, we introduce the dimensionless variables \( \mathbf{v}^* = \mathbf{v}/U, \mathbf{x}^* = \mathbf{x}/L, \)
\( t^* = Ut/L, \rho^* = \rho/\tilde{\rho}, \psi^* = \psi/\tilde{\psi} \) and \( \mu^* = \mu/\tilde{\mu} \). The resulting equations have the same
form as Eqs. (5.19)-(5.21), replacing constants and variables by dimensionless constants
and variables. The dimensionless constants one finds are \( \tilde{\kappa} = \kappa/\tilde{\rho}, \tilde{\Gamma} = \Gamma L \tilde{\mu}/\tilde{\psi} U \) and
\( \tilde{\eta} = \eta UL^3/\tilde{\rho} \tilde{\psi}^2 \), where the latter is proportional to the capillary number. In the following
discussion, we use the non-dimensional set of governing equations, dropping the tilde
from constants and star from variables.

5.3 Numerical scheme

We solve Eqs. (5.19)-(5.21) numerically, with boundary conditions specified in Eq. (5.2), by using a pseudo-spectral method, in which linear and gradient terms are computed in Fourier space and nonlinear terms in real space. Space discretization depends on $n_w$, the number of points per base wavelength, and is given by $\Delta x = 2\pi/(n_wq_0)$. We have developed custom C++ codes based on the parallel FFTW library and the standard MPI passing interface for parallelization. In order to accommodate the boundary conditions, we use both the Discrete Cosine Transform of $(\psi, \rho)$ and the Discrete Sine Transform of $(\nabla\psi, \nu)$.

Numerically, due to the periodic nature of the order parameter, we compute its amplitude $A$ by $A = (\psi^2 + q_0^{-2}|\nabla\psi|^2)^{1/2}$. While this approximation gives us an adequate value for the amplitude of $\psi$ in regions where the smectic layers are well formed and only weakly distorted, it becomes noisier on the interface and also in regions where layers are highly distorted or break up. Therefore in our numerical calculations we smooth the computed amplitude with a Gaussian filter in Fourier space, given by the operator $F_{\omega} = \exp(-\omega^2q^2/2)$, where $q$ is the wavenumber and $\omega$ the filtering radius, chosen as $1/q_0$.

5.3.1 Order parameter equation

The numerical scheme for integrating Eq. (5.21) has been detailed in Chapter 4, and here we will summarize it. Due to the variable density multiplying the RHS of Eq. (5.21), it cannot be dealt with in the same form as the uniform density case [75]. Instead, we follow a scheme previously employed for phase-field models with variable mobility [162, 163]. First, we split Eq. (5.21) as $\partial_t\psi = \Gamma(L\psi + N)$ with

$$L = -\left[\epsilon + (\nabla^2 + q_0^2)^2\right]$$

$$N = \kappa\zeta(\rho - \rho_0 - \kappa A)\frac{\psi}{A} + \kappa\zeta q_0^{-2}\nabla \cdot \left[(\rho - \rho_0 - \kappa A)\frac{\nabla\psi}{A}\right]$$

$$-2\alpha\nabla \rho \cdot (\nabla^2 + q_0^2)\nabla\psi - \alpha\nabla^2 \rho (\nabla^2 + q_0^2)\psi + \beta\psi^3 - \gamma\psi^5 - \Gamma^{-1}\nu \cdot \nabla \psi$$

(5.23)
where \( L \) is a linear operator, and \( N \) is a collection of nonlinear terms. We split the density as \( \rho \rightarrow \rho_m + (\rho - \rho_m) \), where \( \rho_m = \frac{1}{2}(\rho_s + \rho_0) \). Here, \( \rho_s \) is the density of the smectic bulk, which can be obtained from the system parameters by \( \rho_s = \kappa A_s + \rho_0 \), where \( A_s \) is the amplitude solution of the sinusoidal phase. The idea behind the split is that the term associated to \( \rho_m \) can be treated implicitly, and \( (\rho - \rho_m) \) explicitly, with a choice of \( \rho_m \) that satisfies \( |\rho - \rho_m| \leq \rho_m \).

As detailed in Chapter 4, we treat the linear term \( L \) implicitly, while the nonlinear term \( N \) is treated with a second order Adams-Bashforth scheme. In Fourier space, the order parameter \( \psi_q \) for the new time step \( n+1 \) can be obtained from

\[
(3/2 - \Delta t \Gamma \rho_m L)\psi^{n+1}_k = \left(2 - \Delta t \Gamma \rho_m L\right)\psi^n_k - \frac{1}{2} \psi^{n-1}_k + \frac{\Delta t \Gamma}{2} (3N^n_k - N^{n-1}_k).
\] (5.24)

The stability of this scheme has been studied in Sec. 4.5, and we found that for \( n_w = 8 \) a time step of \( \Delta t = 1 \cdot 10^{-3} \) or less was necessary to guarantee stability.

### 5.3.2 Velocity decomposition

Based on the Helmholtz Decomposition, the velocity field \( v \) can be written as the sum of an irrotational vector field with a solenoidal vector field. That is,

\[
v = \nabla \Phi + \nabla \times A,
\] (5.25)

where \( \Phi \) is a scalar potential and \( A \) is a vector potential. By substituting this decomposition of the velocity into the balance of linear momentum from Eq. (5.20), we obtain

\[
0 = -\frac{\zeta}{2} \nabla \left[ \rho^2 - (\rho_0 + \kappa A)^2 \right] + f + \eta \nabla^2 \nabla \times A + (2\eta + \lambda) \nabla \nabla^2 \Phi.
\] (5.26)

where \( f = \bar{\mu} \nabla \psi - \rho \nabla u \). Numerically, since the gradient of the density is computed at every time step, one can avoid computing the gradient of the energy density \( u \) by adding \( \rho u \) inside the gradient from the first term in Eq. (5.26) and rewriting \( f \) as \( \bar{f} = \bar{\mu} \nabla \psi + u \nabla \rho \).

The solenoidal field can be obtained from the transverse part of Eq. (5.26). In Fourier space, by eliminating irrotational terms through an orthogonal projection (and,
consequently, modulations due to the layering), we can compute $\nabla \times A$ from

$$\nabla \times A_q = \frac{1}{\eta q^2} \left( I - \frac{q \otimes q}{q^2} \right) f_q . \quad (5.27)$$

Similarly, the longitudinal component of Eq. (5.26) eliminates the solenoidal terms, and allows us to compute $\nabla \Phi$. By substituting Eq. (5.27) into Eq. (5.26), we obtain

$$\nabla \Phi_q = \frac{1}{(2\eta + \lambda) q^2} \left\{ \frac{\zeta q^2}{2} \left[ \rho^2 - \left( \rho_0 + \kappa A \right)^2 \right] + \frac{q \otimes q}{q^2} f_q \right\} . \quad (5.28)$$

Note that the density does not change in the scale of the smectic layering modulations, and also that the force $f$ contains both resonant terms on the same scale as the amplitude, and modes $\pm 2iq_0$ or higher. As we do not want the irrotational flow to oscillate along smectic layers, we dampen contributions from the higher order frequencies by applying a filter $F_\omega = \exp(-\omega^2 q^2/2)$ to the $f_q$ term in Eq. (5.28).

### 5.3.3 Balance of mass

The balance of mass from Eq. (5.19) can be easily integrated by a multistep method such as Adam-Bashforth. Here, we compute the density at the new time step $n + 1$ through

$$\rho^{n+1} = \rho^n - \Delta t \left[ \frac{3}{2} (v^n \cdot \nabla \rho^n + \rho^n \nabla \cdot v^n) \ight. - \left. \frac{1}{2} (v^{n-1} \cdot \nabla \rho^{n-1} + \rho^{n-1} \nabla \cdot v^{n-1}) \right] , \quad (5.29)$$

where the divergence of the velocity is computed from $\nabla \cdot v = \nabla^2 \Phi$.

### 5.4 The density effect on the order parameter equation

We now investigate the role of the first term that appears on the expression for the chemical potential $\mu$ (RHS of Eq. (5.17)) on the motion of $\psi$ governed by Eq. (5.21). Recall that this term appears from the energy penalty due to density deviations from equilibrium values. For an analytic interpretation, assume we have a region of constant
density and amplitude. By setting $\Gamma = 1$ as in our computations, the order parameter equation can be written as

$$\dot{\psi} = \frac{\kappa \zeta}{A} \left( \rho - \rho_0 - \kappa A \right) \left( 1 - q_0^2 \nabla^2 \right) \psi - \rho \left[ \epsilon \psi + \alpha (\nabla^2 + q_0^2) \psi - \beta \psi^3 + \gamma \psi^5 \right]. \tag{5.31}$$

Under these conditions, we observe that the first term on the RHS becomes linear, and for simplicity we define the constant $c_1 = \kappa \zeta / A$. Since the order parameter has a solution which is approximately $\psi \approx A \cos(q_0 \cdot x)$, note that $(1 - q_0^2 \nabla^2) \psi \approx 2\psi$. By combining this first term with the term containing the bifurcation parameter $\epsilon$, we have approximately $[2c_1(\rho - \rho_0 - \kappa A) - \rho \epsilon] \psi$. Therefore, the term with the amplitude can be regarded as a correction to the bifurcation parameter.

The way this correction acts can be understood by considering a stack of flat smectic layers in contact with an isotropic phase, where the layers have a normal in the $\hat{z}$ direction. When both phases are in coexistence ($\epsilon = \epsilon_c$), and in equilibrium, we have a density profile $\rho = \rho_0 + \kappa A$, as illustrated in Fig. 5.1. The velocity is $v = 0$, and the interface is stationary with $\partial_t \psi = 0$. By decreasing the bifurcation parameter, so that $\epsilon < \epsilon_c$, the smectic phase becomes energetically favored, and without the correction term the smectic would grow and move towards the isotropic phase. As the smectic advances, the amplitude of $\psi$ grows in regions where we previously had the isotropic phase, so that in these regions we now have $\rho < \rho_0 + \kappa A$. Therefore, while $-\rho \epsilon$ increases by decreasing $\epsilon$, the term $2c_1(\rho - \rho_0 - \kappa A)$ will decrease in the regions we described, so that it acts as a resistance to movements of $\psi$ from equilibrium. This analysis is analogous for the case of $\epsilon > \epsilon_c$, when the smectic would try to shrink due to being energetically disfavored, while the amplitude term in Eq. (5.31) would once again act in the sense of counteracting this effect.

We numerically investigate this effect by using the order parameter and density profiles from Fig. 5.1 as initial condition, which is the middle $xz$ cross-section of a cubic computational domain with $N = 64^3$ nodes. Governing equations are integrated using time step $\Delta t = 0.001$ and grid spacing $\Delta x = \pi/4$ (8 points per wavelength). These equilibrium profiles are obtained setting $q_0 = 1$, $\beta = 2$, $\gamma = 1$, $\nu = 1$, $\lambda = 1$, $\zeta = 1$, $\rho_0 = 0.5$ and $\kappa = 0.3727$, so that the equilibrium density of the smectic is $\rho_s = 1$ (density ratio 2:1). We set $\epsilon = \epsilon_c$, where the coexistence parameter for the chosen values
Figure 5.1: Middle cross section $xy$ of a stack of flat smectic layers with normal in the $z$ direction, showing the order parameter field $\psi$ and density field $\rho$ used as initial condition. Simulations employing this initial conditions use parameters $\beta = 2, \gamma = 1, \nu = 1, \lambda = 1, \rho_0 = 0.5$ and $\kappa = 0.3727$. For this choice, the coexistence parameter is $\epsilon_c = 0.675$.

is $\epsilon_c = 0.675$. Then, by changing only $\epsilon$ and $\zeta$, we let the initial condition evolve in time. First, we change the bifurcation parameter to $\epsilon = 0.5$, favoring the smectic phase, and keep $\zeta = 1$. Fig. 5.2a shows that at time $t = 90$ the smectic has grown from its initial size, and that the density has spread and decayed from its initial $\rho_s = 1$ value in the smectic (conserving mass). However, in case we set $\epsilon = 0.5$ and $\zeta = 100$, we show in Fig. 5.2b that for the same time $t = 90$ the smectic and the density change very little from the initial condition. That is, the amplitude term in the chemical potential becomes large enough to counter the tendency of the smectic to grow for $\epsilon < \epsilon_c$, so that even out of coexistence the smectic-isotropic interface does not move. Similarly, we show in Fig. 5.2c that, for $\epsilon = 0.8$ and $\zeta = 1$, at $t = 90$ the smectic has shrunk, increasing the density of the isotropic phase to satisfy the balance of mass. By increasing $\zeta$ to 100, we see in Fig. 5.2d that for $t = 90$ the smectic shrinks more slowly than in the $\zeta = 1$ case. For longer times, while the smectic layering disappears for $\zeta = 1$, the layering shown in Fig. 5.2d does not vanish.
Figure 5.2: Order parameter (top) and density (bottom) configuration at time $t = 90$, starting from the initial condition in Fig. 5.1. For $\epsilon = 0.5$, the smectic phase is energetically favored, while for $\epsilon = 0.8$, the isotropic phase is energetically favored. For $\zeta = 100$, the interface does not move with respect to the initial condition for $\epsilon = 0.5$.

5.5 Morphological evolution and flows in focal conics

In this section, we investigate the velocity field in a smectic-isotropic system presenting layers bent in a focal conic configuration. Our numerical results show the effect of $\zeta$ and different density ratios between phases on the velocity. We also revisit the morphological transition studied in Ref. [75], which was initially investigated with a purely diffusional model (governed by the order parameter equation) and uniform density. First, we show that for a certain range of parameters, the transition from focal conic defects to conical pyramids or concentric rings can also be observed from the weakly compressible model with density contrast. This is an important feature of this model, as it relaxes the strong constraint imposed on the order parameter in the quasi-incompressible model [76], and allows the non-conserved $\psi$ to move more freely while conserving mass, as discussed in the previous section. Also, we discuss how the velocity field changes out of coexistence during these morphological transitions, when layers change their orientation with respect to the interface.
5.5.1 Flows in focal conics under coexistence

For small density ratios $\rho_s : \rho_0$ (up to 2:1) and coexistence, we have shown in Ref. [76] that for a focal conic in a quasi-incompressible smectic-isotropic system, the solenoidal part of the velocity dominates, creating vortices between regions of negative and positive mean curvature of the focal conic at initial times. For a large density ratio (100:1), the vortices at initial times became localized inside the smectic. We now show the velocity field obtained from the weakly compressible model for coexistence and different values of $\zeta$. The computational domain is a box with $N = 256^3$ number of points, with approximately 8 points per $\psi$ wavelength and $q_0 = 1$, so that $L_x = 200$, $L_y = 200$ and $L_z = 200$. Parameters used are $\beta = 2$, $\gamma = 1$, and $\nu = \lambda = 1$.

We start with a scenario in which both phases have the same bulk density $\rho_s = \rho_0 = 1$, with $\kappa = 0$. In the quasi-incompressible limit, this is the same as uniform density for the system, and the potential part of the velocity becomes zero. In Fig. 5.3 we plot the middle cross section of the box at $y = L_y/2$, and compare the velocity $v$ at $t = 4$ for the cases $\zeta = 100$ and $\zeta = 0.01$. As expected, for large $\zeta$ the flow behaves similarly to an uniform density, and we observe the formation of vortices between the smectic-isotropic interface, where the flow moves outward from the smectic in regions of negative mean curvature, and inward towards the smectic in regions of positive mean curvature. However, for $\zeta = 0.01$, we observe a more localized flow inside the smectic in the form of vortices, while the flow in the isotropic phase simply points upwards. The reason is that the density is smaller than $\rho = 1$ at the interface due to the small value of $\zeta$, which undermines the creation of vortices between phases (a similar effect was observed in the quasi-incompressible limit for large density ratios between phases [76]).

Next, we change the density ratio $\rho_s : \rho_0$ to 2:1, using $\kappa = 0.3727$ and $\rho_0 = 0.5$. Figure 5.4 once again compares the velocity $v$ at time $t = 4$ for the cases of $\zeta = 100$ and $\zeta = 0.01$. Observe that, when compared to Fig. 5.3, the velocity for $\zeta = 100$ form vortices that are much closer to the smectic, and quickly decay in the isotropic phase away from the interface, due to the density contrast. For the case of $\zeta = 0.01$, the velocity points upwards in the whole system, implying that the density gradient dominates the orientation of the flow.

When changing the density ratio to $\rho_s : \rho_a = 100 : 1$, using $\kappa = 0.7379$ and
Figure 5.3: Comparison between the transient fluid flow $v$ on smectic-isotropic fluid system for different $\zeta$, at an early time $t = 4$, where both phases have the same bulk density ($\kappa = 0$ and $\rho_0 = 1$). Background color is the order parameter $\psi$. We use $N = 256^3$, $\Delta t = 1 \times 10^{-3}$, and parameters $q_0 = 1$, $\eta = 1$, $\epsilon = 0.675$ (coexistence), $\alpha = 1$, $\beta = 2$ and $\gamma = 1$.

For $\rho_0 = 0.01$, some significant changes in the velocity for large $\zeta$ are observed. Figure 5.5a shows that the flow in the smectic becomes dominated by the potential part of the velocity for $\zeta = 100$ at $t = 4$, pointing in the radial direction to the layers, in the sense of the density gradient. The velocity in the isotropic phase is smaller in magnitude, and points towards the smectic. We also show in Fig. 5.5c the transient flow for $\zeta = 100$ at a later time, $t = 25$, where the flow in the smectic calmed down, and only remains significant in the isotropic phase (going towards the smectic) and tangentially at the interface. Since the density of the isotropic phase is small, the mass flux in this case becomes very small in magnitude and continuously slows down. In contrast, for $\zeta = 0.01$ Fig. 5.5b shows that the velocity at $t = 4$ once again points upwards as in Fig. 5.4. In Fig. 5.5d, we see that the velocity at $t = 25$ is still mostly pointing upwards, and that a significant growth of smectic layers at the interface took place when compared to $t = 4$. Indeed, since the energy penalty for deviations of the preferred bulk density is small for a small $\zeta$, the mass flux $\rho v$ from the bulk smectic towards the interface led to the
growth of layers. That is, deviations from \( \rho_s = 1 \) and \( \rho_a = 0.01 \) are less penalized for \( \zeta = 0.01 \), so that growth of the smectic by mass flow may occur (at the cost of reducing the bulk smectic density, which is necessary to satisfy mass conservation).

### 5.5.2 Flows in focal conics under thermal sintering

The transition from focal conic defects to conical pyramids in smectic thin films has been experimentally observed by Kim et al. [18, 148], when sintering films containing arrays of focal conics. The coexistence point \( \epsilon_c \) in our model physically represents the coexistence temperature between the smectic and the isotropic phase, and by increasing \( \epsilon \) and moving towards the isotropic region we can simulate the sintering of a smectic. We set an initial condition as shown in Fig. 5.6 (left), with smectic layers bent in a focal conic configuration, in a box with \( N = 256^3 \) number of points, so that \( L_x = 200 \), \( L_y = 200 \) and \( L_z = 200 \). Parameters used are \( \beta = 2 \), \( \gamma = 1 \), \( \nu = \lambda = 100 \), \( \rho_0 = 0.5 \), \( \rho_s = 1 \) and \( \zeta = 0.01 \). Since the transition involves a melting of smectic layers away
Figure 5.5: Comparison between the transient fluid flow $v$ on smectic-isotropic fluid system for different $\zeta$, at times $t = 4$ and $t = 25$, with 100:1 density ratio between bulk phases ($\kappa = 0.7379$ and $\rho_0 = 0.01$). Background color is the order parameter $\psi$. We use $N = 256^3$, $\Delta t = 1 \times 10^{-3}$, and parameters $q_0 = 1$, $\eta = 1$, $\epsilon = 0.675$ (coexistence), $\alpha = 1$, $\beta = 2$ and $\gamma = 1$.

from the core of the focal conic, we set $\epsilon = 0.8$, in the isotropic state ($\epsilon_c = 0.675$), so that the initial $\psi$ field can slowly melt at the interface with the isotropic phase. We
choose a small value for $\zeta$ in order to allow the transition to take place - if $\zeta \geq 1$, the focal conic remains, for the reasons detailed in Sec. 5.4. Figure 5.6 (right) shows the resulting conical pyramid at time $t = 80$.

In the transition from focal conics to conic pyramids, the layers become exposed at the interface. An interesting question is if there is any effect on the flow when layers become perpendicular to the interface. As previously discussed [75], the Gibbs-Thomson equation for this alignment of layers is different from the classical equation found in literature, even at leading order. The difference in chemical potential between flat and curved interfaces in this case is given by

$$
\delta \mu \Delta A = \left[ \frac{1}{2} \nabla^2 H + 2H(H^2 - G) \right] \frac{\sigma_h}{q_0} \tag{5.32}
$$

where the terms in the RHS are similar to Willmore-type flows [101]. Here $\Delta A$ is the difference in amplitude between the two phases (that is, the amplitude of the smectic phase), and $\sigma_h$ is the surface tension.

Since we choose a small $\zeta$, there is a delay in the density response after the order parameter moves, so that when the conical pyramids are formed, the density at the interface between phases is roughly constant. Based on the balance of linear momentum from Eq. (5.20), under these conditions the velocity is governed by the force $\bar{\mu} \nabla \psi$. We have previously shown [75] that conical pyramids are surfaces that satisfy Eq. (5.32),

[Figure 5.6: Focal conic (initial condition) transforms into a conical pyramid ($t = 80$). Red and blue planes represent $+1$ and $-1$ values of $\psi$, respectively. Parameters used are $\epsilon = 0.8$ ($> \epsilon_c$), $\beta = 2$, $\gamma = 1$, $\nu = 1$, $\lambda = 1$, $\rho_0 = 0.5$, $\kappa = 0.3727$, and $\zeta = 0.01$.]
where the values of $H^2$ and $G$ are close to each other. When layers are perpendicular to the interface, $\nabla \psi$ has both a tangential and a normal component at this interface, where the latter is the same as the gradient of the amplitude $\nabla A$ for this interface. Since Eq. (5.32) is derived from the amplitude equations, $\delta \mu \Delta A$ gives the asymptotic form of $\bar{\mu} \nabla \psi$ in the normal direction to the interface.

The fact that the RHS of Eq. (5.32) is equals zero for a conical pyramid then implies that $\mathbf{v} \cdot \mathbf{n}$ at the interface is zero, as there is no force in the normal direction, and the flow becomes tangential. In Fig. 5.7, we show the middle cross section of the $\psi$ field for a conical pyramid alongside the velocity field. As we concluded, the flow indeed becomes tangential to the interface for the surface of the pyramid, indicating that the expression with mean and Gaussian curvatures in the RHS of Eq. (5.32), the normal stress balance, must be zero.

![Figure 5.7: Order parameter field for a conical pyramid (mid cross section) at $t = 80$ obtained from an initial focal conic configuration. The velocity field $\mathbf{v}$ is also plotted, showing that the velocity becomes tangential to the interface of the pyramid. Parameters are $\epsilon = 0.8$ (> $\epsilon_c$), $\beta = 2$, $\gamma = 1$, $\nu = 1$, $\lambda = 1$, $\rho_0 = 0.5$, $\kappa = 0.3727$, and $\zeta = 0.01.$](image)
5.6 Domain interactions in smectic-isotropic systems

5.6.1 Coalescence of smectic cylinders

Coalescence of viscous objects driven by capillarity is a widely studied phenomenon, ranging from the coalescence of droplets and bubbles to fluid cylinders. For two infinite isotropic fluid cylinders with the same radius, Hopper [165, 166] developed an exact theory based on the assumption of creeping planar viscous flow, parameterizing the coalescing form in the plane through a 1-parameter family of closed inverse ellipses of constant area. This theory has been shown to be qualitatively consistent with a bridge growing between two smectic islands [167, 168], although presenting a slower temporal evolution. Nguyen et al. [168, 169] point out that permeation through the molecular layers of the merging islands, a source of dissipation not included in Hopper’s model, is the responsible for the slower dynamics. Coalescence of smectic islands [167, 168] and holes [170] has been observed in freely-suspended smectic films, which are formed by smectic layers parallel to the surface of the film, and whose thickness can range from two layers up to thousands of layers. In this context, islands are regions with more smectic layers than the embedding film, resulting in smectic cylinders enveloped by outer layers, with associated dislocations. The line tension of these dislocations is argued to drive the initial bridge expansion in the coalescence process.

Here we present a numerical study of the interaction between two smectic cylinders, which are initially touching, and are surrounded by an isotropic phase of different density. This geometry is much simpler than the one for freely-suspended smectic films, but connects to Hopper’s works on the coalescence of two fluid cylinders, and also helps us elucidate some of the roles played by irrotational flows from the model. As an uniaxial phase, we expect to observe different features in the interaction between two smectic cylinders when compared to isotropic fluids.

We start with a $N = 256^2 \times 32$ box, so that $L_x = 200$, $L_y = 200$ and $L_z = 25$, containing two tangent smectic cylinders with radius $R_0 = 37.5$ of five layers each, at the middle of the box. Parameters used are $\beta = 2$, $\gamma = 1$, $\nu = \lambda = 1$, $\rho_0 = 0.5$, and $\zeta = 100$. We choose $\epsilon = 0.3$, deep in the smectic state ($\epsilon_c = 0.675$), so that we enhance the order parameter $\psi$ dynamics in the sense of smectic growth. At the same time, $\zeta = 100$ is high enough to guarantee a weak conservation of $\psi$, a necessary condition for
coalescence to take place (if $\zeta$ is too small, $\psi$ would grow and occupy the whole domain for $\epsilon = 0.3$). Figure 5.8 shows the two smectic cylinders creating a bridge between each other at time $t = 2.5$, and also the resulting stationary cylinder at time $t = 200$ after coalescence takes place. Note that not only we have a two-dimensional coalescence process in the plane of the smectic layers, but also the number of layers grows in their normal direction $\hat{z}$, moving from five initial layers to eight in the resulting cylinder (filling the whole $L_z$).

Figure 5.8: Coalescence of smectic cylinders inside a box with $L_x = L_y = 200$ and $L_z = 25$. Besides coalescence, the number of layers of the final cylinder grow with respect to the initial ones. Parameters are $\epsilon = 0.3$ (smectic region), $\beta = 2$, $\gamma = 1$, $\nu = 1$, $\lambda = 1$, $\rho_s = 1$, and $\rho_0 = 0.5$ ($\kappa = 0.3727$).

In order to focus on the two-dimensional dynamics, we change the initial condition from five to eight smectic layers, so that both cylinders occupy bottom to top of the domain. This way the two cylinders are constrained, a condition closer to Hopper’s assumption of infinity cylinders or the smectic islands constrained by enveloping layers in experiments. Figure 5.9 shows the evolution of order parameter for the midplane $(L_z/2)$ of the box, and we observe that in this case the evolving area is conserved, with final radius approximately $R_f = 53$. Analogous results are observed for the midplane density, but are not shown here. While capillarity driven coalescence is well understood for objects such as droplets or cylinders of isotropic fluids, the modulated nature of a smectic introduces a few peculiarities.

First, we note that the interface between the cylinder and the isotropic phase is
Figure 5.9: Order parameter at the mid height $xy$ plane of a box with $L_x = L_y = 200$ and $L_z = 25$ showing coalescence of smectic cylinders, at times $t = 0.5$, $t = 10$ and $t = 50$. Initial conditions present two tangential smectic cylinders with layers filling the whole height $L_z$, so that the area in the plots is conserved in the process. Parameters are $\epsilon = 0.3$ (smectic region), $\beta = 2$, $\gamma = 1$, $\nu = 1$, $\lambda = 1$, $\rho_s = 1$, and $\rho_0 = 0.5$ ($\kappa = 0.3727$).

composed of layers perpendicularly oriented to the interface. According to the equations derived in Ref. [75], the diffusion driven interface motion of the smectic for such orientation is proportional to $v_n \sim -H^3$ for zero Gaussian curvature (as in a cylinder), which by itself leads to coalescence at a slower rate than the classical motion by mean curvature. The smectic motion also depends on the evolution of the density, governed by Eq. (5.19). Note that the divergence of the velocity depends on the irrotational flow, $\nabla \cdot \mathbf{v} = \nabla^2 \Phi$. Equation (5.28) gives us $\nabla \Phi$ in Fourier space, and that the first term on the RHS is proportional to the normal $\mathbf{n}$ at the interface when $\rho \neq \rho_0 + \kappa A$. Since $\nabla \cdot \mathbf{n} = 2H$, this implies that $\dot{\rho}$ is proportional to the negative of the mean curvature, that is, a mean curvature flow of the mass from regions of positive to negative curvature. To verify this statement, we plot the divergence of the velocity for time $t = 5$ in Fig. 5.10. Observe that regions of positive $\nabla \cdot \mathbf{v}$ correspond to an interface of positive mean curvature, while regions of negative $\nabla \cdot \mathbf{v}$ have an interface of negative mean curvature. Figure 5.10 shows a blow-up of the bridge region, and also displays the velocity field $\mathbf{v}$. During coalescence, the flow in the left cylinder moves toward the right, and vice-versa, and at the bridge the flow sinks in the region of negative mean curvature, as expected from the coalescence process.

In our numerical calculations with vertically constrained smectic cylinders, we observed coalescence from deep inside the smectic region $\epsilon = 0.2$ up to the coexistence
Figure 5.10: Divergence of the velocity $\nabla \cdot \mathbf{v}$ at the mid height $xy$ plane of a box with $L_x = L_y = 200$ and $L_z = 25$ at time $t = 5$. Initial conditions and parameters are the same as in Fig. 5.9. The right figure is a blow up at the bridge region, showing that the velocity field $\mathbf{v}$ moves from regions of positive $\nabla \cdot \mathbf{v}$ ($H > 0$) towards regions of negative $\nabla \cdot \mathbf{v}$ ($H < 0$).

Point $\varepsilon_c = 0.675$. In Fig. 5.11 we plot the normalized bridge length between the smectic stacks as a function of time, for different values of $\varepsilon$. Note that coalescence becomes faster as we decrease the bifurcation parameter from the coexistence value, that is, as we further decrease the energy of the smectic in comparison to the isotropic phase (which physically translates into a decrease of temperature). Every curve closely follows a logarithmic equation, and qualitatively these curves and the numerical evolution of the order parameter resemble the bridge width evolution shown in experiments and Hopper’s theoretical model. The phase-field model also allows for more intricate order parameter morphologies, and future work is planned to simulate freely-suspended smectic films and study the role of permeation on coalescence.

Finally, we mention that for non-constrained smectic cylinders, coalescence is not always observed. For example, using a box with $N = 256^2 \times 64$, and the same parameters as before, the cylinders did not coalesce when $\varepsilon$ is close to the coexistence value $\varepsilon_c = 0.675$. From the midplane order parameter in Fig. 5.12, we see that, after creating an initial thin bridge ($t = 2.5$), the two stacks start moving apart from each other, until the bridge breaks ($t = 25$). When compared to the constrained cylinders, this suggest that there is a process in the normal direction to the smectic layers competing with coalescence, that leads the cylinders to move apart from each other. In order to
investigate this, we plot in Fig. 5.13 the velocity $v$ alongside the order parameter for the $xz$ plane at $L_y/2$. Note that we multiply the scale of the height $z$ by four times, for the sake of flow visualization. At the initial stage $t = 2.5$, the two cylinders are still closely in contact (at $x = 100$), but we see a flow between the two that acts to tear them apart from each other. The flow moves from the lateral regions of layers perpendicular to the interface towards the top and bottom of the cylinder, where layers are parallel to the interface. That is, flow enters the smectic in regions of negative mean curvature, and moves out at the flat top and bottom. The reason for the latter is the irrotational flow, as from Eq. (5.28) we observe that when $\rho \neq \rho_0 + \kappa A$ there is a force normal to the smectic layers at the interface. In a later stage, $t = 25$, the flow continues to point oppositely to the bridge (which is very thin at this point, as seen in Fig. 5.12), leading cylinders to further distance from each other. At the top and bottom of the cylinders, we observe the formation of target structures [171], which are interfacial rings induced by the circular geometry of the order parameter (the bottom and top droplets shown in the cross-section). Therefore, while we argue that the diffusional motion leads to a slow coalescence process, in this case the flow dominates the motion of the smectic.

Another scenario in which coalescence does not take place is when we move further into the isotropic region $\epsilon > \epsilon_c$. This applies to any of the geometries shown in this
Figure 5.12: Order parameter at the mid height $xy$ plane of a box with $L_x = L_y = 200$ and $L_z = 50$ showing separation of smectic cylinders, at times $t = 2.5$ and $t = 25$. Initial conditions present two smectic tangential cylinders with approximately five layers. Parameters are $\epsilon = 0.675$ (coexistence), $\beta = 2$, $\gamma = 1$, $\nu = 1$, $\lambda = 1$, $\rho_s = 1$, and $\rho_0 = 0.5$ ($\kappa = 0.3727$).

section, even for the constrained cylinders in the $N = 256^2 \times 32$ box. Numerical results for the latter are shown in Fig. 5.14, using the same parameters as before and $\epsilon = 0.9$. While in the constrained geometry the flow was shown to promote coalescence, following Eq. (5.21) the smectic tends to shrink for $\epsilon > \epsilon_c$, and the order parameter dynamics dictates the observed results. No bridge is initially formed, and the cylinders’ cross-section start to melt in a target fashion, as seen for $t = 7.5$. At time $t = 20$ the target cross-section further disintegrate into droplets, and at time $t = 200$ we show the stationary form of the order parameter field, with droplets spread all over the domain. This is strikingly different when compared to classical Swift-Hohenberg dynamics (pure diffusional dynamics of the order parameter $\psi$), for which the order parameter in the isotropic region would simply disappear in time. We conclude that, coalescence requires a synergy between flow and dynamics of the order parameter and density, and it may not occur if one of them becomes antagonistic to the coalescence process.

5.6.2 Interactions between focal conic defects

While topological defects are known to interact in various soft matter systems, not much is known about interactions between focal conics. For instance, Kim et al. [18]...
Figure 5.13: Order parameter and velocity field at the mid cross-section $xz$ for the same simulation described by Fig. 5.12. Note that the axis $z$ is distorted by four times $x$ for better visualizing the flow. Left: two smectic cylinder in contact at $x = 100$, and time $t = 2.5$. Right: smectic cylinders are almost separating due to the flow, time $t = 25$.

experiments on sintering of TFCDs present resulting morphologies in which one observe thin tunnel like structures connecting a few of the original focal conics. The reason behind their appearance is unknown, which motivates us to perform a preliminary a numerical study on the circumstances that can lead focal conics to communicate with each other through the mass flux.

The most straightforward investigation is to double the computational domain used in Sec. 5.5 and place two focal conics side by side (no overlapping). For both coexistence and non-coexistence values of $\epsilon$, no interaction was observed from the velocity field, and each of two focal conics evolved independently from the other. A second investigation was to place two focal conics of different sizes side by side, and once again their associated velocity fields remained isolated from the other. Therefore, we concluded from these preliminary test that it is necessary to introduce gradients on existing fields or set focal conics at a closer distance in order to make them interact. Here we show three different scenarios which resulted in interaction between neighboring defects: a difference in strain between two focal conics, a density gradient in the isotropic phase from one defect to another, and overlapping focal conics. For all simulations we use a computational domain with $N = 512 \times 256^2$ number of points, 8 points per $\psi$ wavelength and $q_0 = 1$, so that $L_x = 400$, $L_y = 200$ and $L_z = 200$, and we set the density ratio between phases
Figure 5.14: Order parameter at the mid height $xy$ plane of a box with $L_x = L_y = 200$ and $L_z = 25$ showing disintegration of smectic cylinders, at times $t = 7.5$, $t = 20$ and $t = 200$ (steady state). Initial conditions present two smectic tangential cylinders with layers filling the height $L_z$. Parameters are $\epsilon = 0.9$ (isotropic region), $\beta = 2$, $\gamma = 1$, $\nu = 1$, $\lambda = 1$, $\rho_s = 1$, and $\rho_0 = 0.5$ ($\kappa = 0.3727$).

$\rho_s : \rho_0 = 2 : 1$ (with $\rho_s = 1$ and $\rho_0 = 0.5$). Other parameters used are $\beta = 2$, $\gamma = 1$, $\nu = \lambda = 1$, and $\zeta = 1$

5.6.3 Varying strain field

While smectics present a preferred equilibrium layer spacing $\lambda_0/2$, the layer thickness may change by straining a sample of the liquid crystal [172]. Also, for arrays of TFCDs, due to boundary conditions and proximity of the defects, it is possible that some regions will present layers with thickness deviating from $\lambda_0/2$, so that strain gradients may be present between neighboring defects. Here we impose a linear strain gradient in the $x$ direction, with an initial wavenumber for the layers that changes from $1.2q_0$ at $x = 0$ up to $0.8q_0$ at $x = L_x$. This way, the left focal conic is initially in compression, and the right one in tension.

In Fig. 5.15 (using $\epsilon = \epsilon_c$) we plot the middle cross section of the box at $y = L_y/2$, presenting the velocity $v$ and the order parameter $\psi$ on the background. For time $t = 0.5$, close to the start of the simulation, we have two focal conics of the same size, and we can clearly see that the velocity circulates between the two focal conics. The velocity is shown to be clockwise, going inwards the focal conic in tension and outwards from the focal conic in compression at the interface. At time $t = 15$ we can see a strong flux in the bulk of the smectic from the right to the left focal conic. The left focal conic
(that was initially in compression) expands, increasing the interlayer spacing, while the right focal conic (that was initially in tension) contracts, decreasing the interlayer spacing. This difference in expansion/contraction alongside a bulk mass flux towards the left focal conic leads to resulting focal conics of different shapes, where the right one becomes deeper and with fewer layers than the left one.

Figure 5.15: Two neighboring focal conics with a varying strain field, showing both the velocity field $\mathbf{v}$ and the order parameter $\psi$. Left focal conic is initially in compression and right focal conic in tension.
5.6.4 Density gradient in the isotropic phase

In a situation where one injects molecules of the liquid crystal in the isotropic phase in one side of the domain, or a side of the smectic sample melts/evaporates quicker than the other, a density gradient can be appear in the isotropic phase. The question then is if this gradient would promote any kind of interaction between the focal conics below it. In order to answer this, we start with two neighboring focal conics of the same size and introduce a density gradient in the isotropic phase only. The density only changes in $x$, starting at $\rho = 0.7$ for $x = 0$, and decays linearly up to $\rho = 0.2$ for $x = L_x$.

Figure 5.16 (a) and (b) shows the velocity field with the density on the background, for times $t = 0.5$ and $t = 25$, obtained using $\epsilon = 0.8$. Not only does the velocity field initially points to the right in the isotropic phase (the direction opposite to the density gradient), but it also does so in the smectic, which presents an approximately uniform density of $\rho_s = 1$. At time $t = 25$, the velocity calms down in the smectic, but at the isotropic phase it still points to the right, since the density there is still not homogeneous.

Figure 5.16 presents the order parameter field $\psi$ at time $t = 25$, in which we observe that the left focal conic expanded towards the right one due to the strong flow that was initially present. Note that the center of the cross-sectional target structure that starts at $x = 200$ moved to the right due to the flow, and also observe the difference between the core structures in the left and the right (squished) focal conics.

5.6.5 Overlapping focal conics

A third way to make two focal conics interact is to move them closer, so that the flow generated by each focal conic will necessarily overlap with each other. In Fig. 5.17 (using $\epsilon = \epsilon_c$) we show the middle cross section at $y = L_y/2$ for two focal conics whose minimum non-overlapping distance from one core to another would be $L_c = 200$. We move these two defects, so that the initial distance between their cores is $\Delta L = 150$. This creates a region of high positive mean curvature between them, inducing the flow to move from the isotropic phase towards the smectic in such areas. When comparing times $t = 5$ to $t = 38$ in Fig. 5.17, we observe that the region between the two defects smoothens, reducing local curvatures. Still, for both times the flow is predominantly concentrated between the two focal conics.
Figure 5.16: Two neighboring focal conics in contact with an isotropic phase presenting a density gradient. Figures show the velocity field $\mathbf{v}$ alongside (a), (b) the density $\rho$, (c) the order parameter $\psi$. 
Figure 5.17: Two neighboring focal conics that overlap at $x = 200$, showing both the velocity field $\mathbf{v}$ and the order parameter $\psi$. The minimum non-overlapping between their cores is $L_c = 200$, while the distance employed as initial condition is $\Delta L = 150$. 

(a) $t = 5$

(b) $t = 38$
Chapter 6

Spiral Defect Chaos

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6.1 Introduction

In the previous chapters we developed models to study a smectic liquid crystal in contact with an isotropic phase, which under favorable thermodynamic conditions could relax towards equilibrium. However, there exists some intrinsically nonequilibrium systems, where such relaxation is not observed (including phases whose symmetry is equivalent to a smectic). This is the case of *active matter*, which are formed by a large number of “self-propelled particles”, that is, particles that continuously consume energy in order to exert forces and move. While common examples appear in systems whose particles are spread in a discrete sense, such as swimming bacteria [173], flock of birds [174] and active nematics [175], it is also possible for modulated phases, such as a smectic, to behave in an active sense [176]. As explained in Sec. 1.3 this is the case of Spiral Defect Chaos in the Rayleigh-Bénard convection, where the modulated phase that develops at the midheight of the convection box can be described as a smectic with persistent dynamics (due to the coupling between the diffusive motion of the order parameter with its advection due to the mean flow). Here we investigate the origin of the force that leads to the continuous motion of spiral defects and the role of azimuthal flows, induced
by this force, in sustaining spiral chaos.

In Sec. 6.2.1 we introduce the generalized Swift-Hohenberg model, which is the starting point of our asymptotic analysis. We expand the order parameter $\psi$ as a function of a small parameter in Sec. 6.2.2, which allows us to express the force $f$ in terms of gradients of the complex amplitude $A$ of the $\psi$ field. Based on a dynamic equation for the amplitude, we obtain the asymptotic form of $f$ which exhibits both rotational and irrotational terms. We derive in Sec. 6.2.3 different components of the azimuthal velocity from the asymptotic form of $f$, and show that they are dominated by the contribution from the irrotational force term. The numerical methods used for both generalized Swift-Hohenberg and Boussinesq models are detailed in Secs. 6.3.1 and 6.3.2, respectively. In Sec. 6.4, we confirm the analytic results for the dependence of the azimuthal velocity $v_\phi$ on damping by computing it for a range of damping coefficients. While for relatively large damping the azimuthal flows are largely confined near the core of each spiral, as damping decreases a hydrodynamic interaction between neighboring spirals arises through the cutoff length $r_b$. In Sec. 6.5.2 we discuss the role of advection versus spiral arm unwinding in the rotation of the spiral. Finally, in Sec. 6.5.3 we present a comparison of the azimuthal velocity computed from the generalized Swift-Hohenberg model and the full Boussinesq equations.

6.2 Azimuthal flow induced by a rotating spiral

6.2.1 The generalized Swift-Hohenberg model

The Swift-Hohenberg model for Rayleigh-Bénard convection [61] follows from a 2D projection of the governing fluid equations in the Boussinesq approximation that eliminates the dependence of the temperature, pressure, and velocity fields on the vertical coordinate $z$ near the onset of convection. This results in a gradient model for an order parameter field $\psi(x, t)$ [with $x = (x, y)$] that represents the vertical velocity on the mid-plane of the convection cell [62, 177, 178]. The model was later generalized to account for the coupling between the unstable mode at the onset of convection and 2D mean
flows \[62, 63\], and is associated with the equations

\[
\frac{\partial}{\partial t} \psi + \mathbf{v} \cdot \nabla \psi = \epsilon \psi - (\nabla^2 + q_0^2)^2 \psi - \psi^3,
\]

(6.1)

\[
\left[ \frac{\partial}{\partial t} - \sigma (\nabla^2 - c^2) \right] \nabla^2 \zeta = g_m \left[ \nabla (\nabla^2 \psi) \times \nabla \psi \right] \cdot \hat{z},
\]

(6.2)

where \(\epsilon\) is a bifurcation parameter that measures the dimensionless distance to the convection threshold (in terms of the Rayleigh number), \(\mathbf{v}(x, t)\) is the 2D incompressible mean flow velocity, and \(\sigma\) is a rescaled Prandtl number. The mean flow velocity is obtained from the vertical vorticity potential \(\zeta(x, t)\) via \(\mathbf{v} = \nabla \times (\zeta \hat{z})\), such that the vertical vorticity \(\Omega_z = (\nabla \times \mathbf{v}) \cdot \hat{z} = -\nabla^2 \zeta\). A momentum damping coefficient \(c^2\) is introduced to model viscous friction at the top and bottom bounding walls, and appears from averaging derivatives of the flow in the vertical direction over the thickness of the convection cell. In the case of free-slip (i.e., stress-free) boundary conditions, one would have \(c^2 = 0\), while \(c^2 > 0\) for no-slip boundary conditions. The coefficient \(g_m\) controls the magnitude of the flow coupling \[63, 177\], which increases as the Prandtl number decreases and also appears from the averaging process.

The right hand side of Eq. (6.2) can be written as \(-g_m (\nabla \times \mathbf{f}) \cdot \hat{z}\), with \(\mathbf{f} = - (\nabla^2 \psi) \nabla \psi\). This effective body force appears from projecting the advection nonlinearity in the Boussinesq model onto the 2D order parameter model, so it does not originate from the divergence of a physical stress \[76\]. This force has a functional analog in models of active matter in which an active stress breaks equilibrium symmetry relations \[179, 180, 181\] and hence directly allows non-variational flows.

### 6.2.2 Effective body force induced by a rotating spiral

Rotating spiral and target solutions are well known to emerge from Eq. (6.1) \[182\]. Away from the core, the solution for the order parameter field in polar coordinates \((r, \varphi)\) has the form \(\psi = Ae^{i\theta_0 r} + \text{c.c.}\), where \(A\) is a slowly-varying complex amplitude that can be written as \(A(r, \varphi, t) = \rho(r)e^{i\theta}\), with phase \(\theta = m\varphi - \omega t\) and a real amplitude \(\rho\). Here \(\omega\) is the angular frequency of the spiral, and the topological charge \(m\) is an integer representing the index of the singularity \[183\] (which is the number of arms in the spiral in this case). While target patterns with \(m = 0\) present a single-valued \(\theta\), rotating spirals have a multivalued phase \(\theta\) as \(m \neq 0\). This has implications for their topological
stability \[183\] as the circulation of \(\theta\) around a contour \(\gamma\) enclosing the spiral core has a quantized value that depends on the topological charge, i.e., \(\oint_\gamma \nabla \theta \cdot dl = 2\pi m\), where \(l\) is the vector function that defines the path. Velocity fields induced by rotating spirals have been argued to decay with distance as \(1/r\), and to be negligible for spiral rotation as compared to motion induced by wavevector frustration [66]. This implies that direct hydrodynamic interactions among rotating spirals are negligible, and therefore the role of mean flows in inducing and sustaining the chaotic state remains to be understood.

We reexamine this issue by investigating the azimuthal velocity generated by a rotating spiral by both asymptotic and numeric analyses.

We derive the asymptotic form of the body force \(f\) that appears in the 2D momentum Eq. (6.2). Near the convection threshold \(\epsilon \ll 1\), we expand the order parameter \(\psi\) into a periodic base state in terms of a slowly varying amplitude of the form

\[
\psi = \epsilon \left[ A(X,T)e^{ik \cdot x} + \text{c.c.} \right],
\]

(6.3)

where \((X,T)\) denotes slow spatial and time scales upon which the amplitude \(A\) depends. Assuming an isotropic expansion in which \(\nabla \rightarrow \pm ik + \epsilon \nabla\), \(|k| = k\), and the gradient only acts on the slow \(X\) scale, we find

\[
\nabla^2 \left[ \epsilon A(X,T)e^{ik \cdot x} \right] = -\epsilon k^2 A e^{ik \cdot x} + 2i \epsilon^2 k \cdot \nabla A e^{ik \cdot x} + \epsilon^3 \nabla^2 A e^{ik \cdot x},
\]

which leads to the following resonant terms in the amplitude expansion of the force \(f\) (those originated from a combination of wavevectors whose result is zero)

\[
\nabla^2 [\epsilon A(X,T)e^{ik \cdot x}] \nabla [\epsilon A^*(X,T)e^{-ik \cdot x}] = i \epsilon^2 k^2 |A|^2 k - \epsilon^3 k^2 A \nabla A^* + 2 \epsilon^3 (\mathbf{k} \cdot \nabla A) A^* k
+ 2i \epsilon^4 (\mathbf{k} \cdot \nabla A) \nabla A^* - i \epsilon^4 A^* \nabla^2 A k + \epsilon^5 \nabla^2 A \nabla A^*.
\]

Explicitly adding the complex conjugate terms, we find

\[
(\nabla^2 \psi) \nabla \psi = -\epsilon^3 k^2 \nabla |A|^2 + 2 \epsilon^3 \left[ (\mathbf{k} \cdot \nabla A) A^* + (\mathbf{k} \cdot \nabla A^*) A \right] \mathbf{k}
+ 2i \epsilon^4 \left[ (\mathbf{k} \cdot \nabla A) \nabla A^* - (\mathbf{k} \cdot \nabla A^*) \nabla A \right] + i \epsilon^4 (A \nabla^2 A^* - A^* \nabla^2 A) \mathbf{k}
+ \epsilon^5 \left( \nabla^2 A \nabla A^* + \text{c.c.} \right).
\]
This expression can be further simplified by noting that in the radial direction the rigid rotating spiral is approximately a solution of the governing equation for the order parameter. That is, we adopt the solution \( k = k \hat{r} \) and \( A = \rho(r)e^{i\theta} \), where \( \theta = m\varphi - \omega t \). This leads to \( (A \nabla^2 A^* - A^* \nabla^2 A) = \nabla \cdot (A \nabla A^* - A^* \nabla A) = 0 \). By gathering terms up to order \( \epsilon^5 \) and rescaling all the quantities back to the original scales \((x,t)\), we find that the force can be written as

\[
f = -\nabla^2 \psi \nabla \psi = k^2 \nabla (|A|^2 - 2\rho^2) - 4k \frac{\rho \rho'}{r} \hat{\varphi} - (\nabla^2 A \nabla A^* + c.c.) . \tag{6.4}
\]

The first term in the RHS is of gradient form and does not contribute to Eq. (6.2). In a pressure-velocity formulation, it can be absorbed into the pressure term. The other two terms contribute to the mean flow.

We begin with the last term of Eq. (6.4), which can be written as a function of the angular frequency of the spirals. From Eq. (6.1), the corresponding amplitude equation \[178, 184\] can be written in polar coordinates for curved rolls (targets or spirals) \[75, 146\],

\[
\partial_t A = \epsilon A + 4q_0^2 (\partial_r^2 + r^{-1} \partial_r) A - 2i q_0 r^{-2} (2 \partial_r + r^{-1}) \partial_\varphi^2 A - r^{-4} \partial_\varphi^4 A - 3 |A|^2 A . \tag{6.5}
\]

This amplitude equation appears from a solvability condition at \( O(\epsilon^3/2) \) of the expansion, with \( \psi \) expanded in power of \( \epsilon \) similarly to Eq. (6.3). Rearranging terms, we obtain the following expressions for a rigidly rotating spiral with \( \partial_t A = -i \omega A \),

\[
(\partial_r^2 + r^{-1} \partial_r) A = \frac{1}{4q_0^2} \left[ - (i \omega + \epsilon) A + 2i q_0 r^{-2} (2 \partial_r + r^{-1}) \partial_\varphi^2 A \\
+ r^{-4} \partial_\varphi^4 A + 3 |A|^2 A \right] . \tag{6.6}
\]

For the complex amplitude of a spiral given by \( A = \rho(r)e^{i\theta} \), we have \( \nabla A = (\rho' \hat{r} + imr^{-1} \rho \hat{\varphi})e^{i\theta} \) and \( |\nabla \theta| = m/r \). Hence, from Eqs. (6.4) and (6.6) we obtain

\[
f = -\frac{1}{2q_0^2} \left[ (3\rho^2 - \epsilon + |\nabla \theta|^4 - 4q_0^2 |\nabla \theta|^2) \rho \rho' \hat{r} + \left( -\frac{\rho^2 m \omega}{r} + \frac{8kq_0^2 \rho \rho'}{r} \right) \hat{\varphi} \right] . \tag{6.7}
\]

This is the central result of this section. The radial component in the RHS of Eq. (6.7)
is irrotational and can be included in a redefinition of the pressure. The azimuthal component vanishes for targets with \( m = 0 \) (i.e., no angular dependence). It also vanishes near the core (\( r \rightarrow 0 \)) since the real amplitude \( \rho \) and the wavenumber \( k \) decay to zero linearly in \( r \) as the core is approached \[ 182 \]. However, away from the core where \( \rho \) is approximately constant and \( k \approx q_0 \), the term \( -(\rho^2 m \omega / r)\hat{\varphi} \) can be written as \( -\rho^2 m \omega \nabla \varphi \). This is an azimuthal body force induced by the rotating spiral that is irrotational. This irrotational force term cannot be eliminated by subsuming it into the pressure as the latter would become multivalued. That is, the observed pressure is continuous, without a direct dependence on \( \varphi \), which would lead to a jump of \( 2\pi \) (see Fig. 6.1). The curl of this irrotational force corresponds to a vorticity point source at the origin. No true divergence exists in this term as both \( \rho, k \) ∼ \( r \) for \( r \ll 1 \), vanishing at the core. We will retain this irrotational force, and calculate its contribution to the azimuthal velocity explicitly.

### 6.2.3 Azimuthal velocity field

In order to compute the velocity field that results from the force given in Eq. (6.7), we first obtain an asymptotic expression for the amplitude \( \rho \) by substituting \( A = \rho(r)e^{i\theta} \) in the amplitude equation (6.5); in the stationary limit we find

\[
4q_0^2 (\partial_r^2 + r^{-1} \partial_r) \rho + (\epsilon - |\nabla \theta|^2 - 3\rho^2) \rho = 0.
\]

For \( r \gg 1 \), using \( \theta = m\varphi - \omega t \) we obtain

\[
\rho^2 = \frac{1}{3} \epsilon - \frac{1}{3} |\nabla \theta|^2 = \frac{4}{3} \epsilon - \frac{4m^4}{3r^4}, \quad 2\rho \rho' = \frac{4m^4}{3r^5}.
\]

Substituting Eq. (6.9) into Eq. (6.7), with \( k = q_0 \), yields

\[
f_\varphi = \frac{1}{2q_0^2} \left( \frac{\rho^2 m \omega}{r} - 8q_0^3 m \rho \rho' \right) = \frac{1}{6q_0^2} \left[ \frac{\epsilon m \omega}{r} - \frac{m^5 \omega}{r^5} - \frac{16q_0^3 m^5}{r^6} \right].
\]

The radial component of \( f \) given in Eq. (6.7) can be written in a gradient form and absorbed into the pressure term; thus we only need to consider \( f = f_\varphi \hat{\varphi} \). As shown in Eq. (6.10), this azimuthal force consists of an irrotational contribution (the first term)
and two rotational contributions.

The calculation of the azimuthal velocity is simplified by using a pressure-velocity representation of Eq. (6.2) for Stokes flow,

$$ -\nabla p + \sigma (\nabla^2 - c^2)\mathbf{v} + g_m\mathbf{f} = 0. \quad (6.11) $$

Since this equation is linear in $\mathbf{v}$ we solve separately for the three components of $f_\phi$ in Eq. (6.10), which leads to the three velocity contributions $v_1$, $v_2$, and $v_3$. The component $v_1$ satisfies

$$ -\nabla p + \sigma (\nabla^2 - c^2)v_1 + \frac{\epsilon g_m m \omega}{6q_0^2} r \hat{\varphi} = 0. \quad (6.12) $$

This flow component is induced by the irrotational part of the azimuthal force. In the vorticity and stream function formulation of Eq. (6.2), the corresponding term is zero except for a point source of vorticity at the origin. In this configuration, the pressure changes only along the radial direction (as observed in Fig. 6.1c), so that the azimuthal component of the velocity satisfies an inhomogeneous modified Bessel equation

$$ \partial_r^2 v_1 + \frac{1}{r} \partial_r v_1 - (c^2 + \frac{1}{r^2})v_1 = -\frac{\epsilon g_m m \omega}{6q_0^2} r. \quad (6.13) $$

Assuming Dirichlet boundary conditions, so that the velocity approaches zero at the spiral’s core $r = 0$ and vanishes at some distance $r_b$, we find

$$ v_1 = \frac{m \omega e g_m}{6q_0^2 \sigma c^2} \left[ \frac{1}{r} + \left( c K_1(r_b c) - \frac{1}{r_b} \right) \frac{I_1(c r)}{I_1(r_b c)} - c K_1(c r) \right], \quad (6.14) $$

where $I_1$ and $K_1$ are modified Bessel functions of first and second type, respectively. In the limit of $c^2 \to 0$, for which damping at the top and bottom bounding walls is negligible (free-slip), the solution for $v_1$ reduces to

$$ v_1 = -\frac{m \omega e g_m}{12q_0^2 \sigma} r \ln(r/r_b). \quad (6.15) $$

For $c^2 > 0$, in the limit $r_b \to \infty$ the contributions from the parts containing the modified Bessel functions in Eq. (6.14) become negligible at long distance, so that $v_1 \sim 1/r$, in
agreement with the result in Ref. [66]. Recall that several approximations made here hold only away from the spiral core, and therefore this solution must be regarded as an outer solution for the flow.

It is possible to obtain analytically a solution for the rotational component of the flow $v_{2\phi}$, although only when $c^2 = 0$. The corresponding flow equation is given by

$$- \nabla p + \sigma (\nabla^2 - c^2) v_2 - \frac{g_m m^5 \omega}{6d_0^2 r^3} \dot{\phi} = 0. \tag{6.16}$$

It can be rewritten in terms of $\zeta$ in polar coordinates, i.e.,

$$\partial_r^4 \zeta + \frac{2}{r} \partial_r^3 \zeta - \frac{1}{r^2} \partial_r^2 \zeta + \frac{1}{r^3} \partial_r \zeta + \frac{1}{r^3} \partial_{\phi} \zeta + \frac{1}{r^2} \partial_r \partial_{\phi}^2 \zeta - c^2 \left( \frac{1}{r} \partial_r \zeta + \partial_r^2 \zeta \right) = \frac{2g_m m^5 \omega}{3d_0^2 \sigma r^5}, \tag{6.17}$$

where $\zeta = \zeta(r)$ due to $v_2 = v_{2\phi} \dot{\phi}$. At large distances and $c^2 = 0$, we find

$$\zeta(r) = \frac{g_m m^5 \omega}{96d_0^2 \sigma r^2}. \tag{6.18}$$

Therefore, since $v_{2\phi} = -\partial_r \zeta$ we obtain

$$v_{2\phi} = \frac{g_m m^5 \omega}{48d_0^2 \sigma r^3}. \tag{6.19}$$

Similar to $v_{2\phi}$, we are able to obtain a solution for the other rotational component $v_{3\phi}$ generated by the last term in Eq. (6.10), also for $c^2 = 0$. Following the same steps, we obtain

$$v_{3\phi} = \frac{8g_m m^5 q_0}{45\sigma r^4}. \tag{6.20}$$

In summary, the azimuthal flow induced by a rotating spiral can be decomposed into two separate contributions arising from irrotational and rotational force components respectively. The former, $v_{1\phi}$ as given by Eq. (6.14), leads to a long ranged logarithmic dependence of the azimuthal velocity when $c^2 = 0$, and to a $1/r$ decay at finite damping with $c^2 > 0$ as $r_b \to \infty$. Rotational forces lead to azimuthal velocities $v_{2\phi}$ and $v_{3\phi}$ that decay as power laws ($1/r^3$ and $1/r^4$) for $c^2 = 0$, as shown in Eqs. (6.19) and (6.20), and therefore decay much faster than the flow $v_{1\phi}$ created by the irrotational component of the force. We will use these results to interpret the numerical calculations in the next
section.

### 6.3 Numerical methods

#### 6.3.1 2D generalized Swift-Hohenberg model

Computations of the generalized Swift-Hohenberg model were based on the vorticity formulation, Eqs. (6.1) and (6.2). We also conducted spot checks with an equivalent 2D pressure-velocity formulation based on Eqs. (6.1) and (6.11), and computed the effective pressure field as shown in Fig. 6.1c. The results obtained for the velocity field are identical within numerical accuracy. For all the results presented, the equations have been solved on an equally spaced, square grid of $512^2$ nodes, with $q_0 = 1$ and the grid spacing $\Delta x = 2\pi/16$. We used a pseudo-spectral method, where gradient terms are computed in Fourier space with a second-order implicit iteration scheme, and nonlinearities are computed in real space through an explicit second-order Adams-Bashforth scheme. The time step used is $\Delta t = 10^{-3}$. The algorithm was implemented by using the parallel FFTW routine with associated MPI libraries. Periodic boundary conditions were used throughout. In our calculations the parameters were chosen as $g_m = 50$, $\sigma = 1$, and $\epsilon = 0.7$. Further details about the influence of the various parameters on the qualitative nature of the patterns obtained have been given in Refs. [66, 68].

From the pressure-velocity formulation, the pressure has been computed through the pressure Poisson equation which follows from the longitudinal projection of the underlying momentum conservation equation (by taking the divergence of Eq. (6.11) and accounting for incompressibility $\nabla \cdot \mathbf{v} = 0$). The same grid setup, model parameters, and boundary conditions were used in this case.

Figure 6.1a shows a typical configuration of the $\psi$ field inside the regime of spiral defect chaos. It is obtained by time integration of the model equations from a random initial condition of uniformly distributed $\psi \in (-0.05, 0.05)$ and zero initial velocity. The figure shows multiple one-armed spirals, obtained at time $t = 10^5$ for $c^2 = 2$. Following the algorithm of Egolf et al. [186], we show in Fig. 6.1b the corresponding spatial distribution of phase $\theta$, and observe the expected discontinuity of $2\pi$ when enclosing a full circle around the core of each spiral. Although the phase is multivalued, the body force is continuous and the resulting pressure (illustrated in Fig. 6.1c) is also continuous.
Note that the pressure is mostly radially symmetric, with its local maximum near the core of every spiral.

![Figure 6.1: Spatial pattern of (a) the order parameter field \( \psi \) comprising several one-armed spirals, (b) the corresponding local phase \( \theta \), and (c) the pressure. The model parameters used are \( \epsilon = 0.7, g_m = 50, c^2 = 2 \), and \( \sigma = 1 \).](image)

From each spatial configuration, such as the one shown in Fig. 6.1a, we extract the locations of spiral cores by plotting the magnitude of the velocity \( v \) and searching for the location inside the vortices where \( |v| = 0 \). The flow generated by each spiral has the form of a vortex \([68, 69]\); hence well-formed spirals are detectable through axially symmetric rings in \( |v| \) or smooth spikes in the vorticity potential (for which the core is located at the maximum of \( \zeta \)).

Figure 6.2 shows two neighboring spirals rotating in the same direction, with cores located at positions (104, 56) and (156, 81) of Fig. 6.1a. By setting the origin, \( r = 0 \), of a polar coordinate system at the core of the left spiral at (104, 56), the figure also shows the radial dependence of the azimuthal component of the force \( f \) up to the edge of the spiral. The amplitude of the force decays slowly with distance \( r \), and for \( r > 5 \) oscillates with periodic wavelength slightly larger than \( \pi/q_0 \), half of the approximate stripe/roll periodicity \( \lambda_0 \) from the linear solution, as expected from \( f = -\nabla^2 \psi \nabla \psi \). The velocity generated by this rotating spiral will be investigated in Sec. 6.2.3.

### 6.3.2 3D Boussinesq equations

Rayleigh-Bénard convection is the buoyancy driven convection that occurs when a shallow and horizontal layer of fluid is heated from below. The fluid motion is described by
Figure 6.2: Left: Two clockwise rotating spirals with cores located at approximately (104,56) and (156,81). The blue line has a length of 58, which is roughly the distance between the cores. Right: Azimuthal component of the force $f = -\nabla^2 \psi \nabla \psi$ (solid line), with $r = 0$ at the (104,56) core. The dashed line is a guide to the eye showing the approximate $0.44/r$ decay of the force amplitude.

the Boussinesq equations [59], which represent the conservation of momentum, energy, and mass, and are given as

$$\text{Pr}^{-1} \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \nabla^2 \mathbf{u} + Ra \hat{z},$$  \hspace{1cm} (6.21)$$

$$\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T = \nabla^2 T,$$  \hspace{1cm} (6.22)$$

$$\nabla \cdot \mathbf{u} = 0.$$  \hspace{1cm} (6.23)$$

In these equations, $\mathbf{u}(x,y,z,t) = (u,v,w)$ is the velocity vector with components $(u,v,w)$ in the $(x,y,z)$ directions, respectively. The pressure is given by $p(x,y,z,t)$, the temperature field is denoted by $T(x,y,z,t)$, and $\hat{z}$ is a unit vector in the positive $z$ direction which opposes the direction of gravity. Equations (6.21)–(6.23) have been nondimensionalized using the depth of the convection layer $d$ as the length scale and the vertical heat diffusion time $d^2/\kappa$ as the time scale, where $\kappa$ is the thermal diffusivity. The vertical diffusion time represents the time required for heat to diffuse from the bottom to the top of the convection layer. Additionally, the constant temperature difference between the bottom and top boundaries, $\Delta T$, is set as the temperature
scale. Using this convention, \(0 \leq T \leq 1\) where \(T(z = 0) = 1\) at the bottom boundary and \(T(z = 1) = 0\) at the top boundary. The Rayleigh number \(Ra = \beta gd^3\Delta T/(\nu\kappa)\) is often the control parameter used in experiments and represents the ratio of buoyancy to thermal and viscous dissipation, where \(\beta\) is the thermal expansion coefficient and \(\nu\) is the kinematic viscosity. It is often convenient to use the reduced Rayleigh number \(\epsilon = (Ra - Ra_c)/Ra_c\) to describe the degree of driving beyond the convective threshold, where \(Ra_c\) is the critical Rayleigh number. The way this number rescales to \(\epsilon\) in Eq. (6.1) is detailed in Appendix D. For an infinite layer of fluid with no-slip boundaries \(Ra_c = 1707.76\) and the nondimensional critical wave number of the convection rolls is \(q_c = 3.1165\). Therefore, the width of a single convection roll will be approximately unity after the nondimensionalization.

The Prandtl number of the fluid \(Pr = \nu/\kappa\) is the ratio of the momentum diffusivity to the thermal diffusivity. The connection between \(Pr\) and the rescaled Prandtl number \(\sigma\) used in the generalized Swift Hohenberg equation is described in Appendix A. The Prandtl number is inversely related to the magnitude of the mean flow [187, 188] which has been shown to have a significant effect upon the state of spiral defect chaos [189, 71, 190, 191]. In the numerical simulations presented here, we use \(Pr = 1\) which is typical of the compressed gases often used in Rayleigh-Bénard convection experiments [191, 56].

The aspect ratio of the domain \(\Gamma\) is the ratio of the lateral extent of the convection layer to its depth. We have used two different geometries in our exploration reported here: a periodic box domain with \(\Gamma = 100\) to study spiral defect chaos and a cylindrical domain with \(\Gamma = 40\) to study a single rotating giant spiral. Schematics of these two domains are shown in Fig. 6.3(a) and Fig. 6.3(b) for the box and cylindrical domains, respectively. We note that the spatial scale in this figure is different from the one used for Fig. 6.1 by a factor of \(1/q_c\), as later detailed in the text and Appendix D.

For the box domain, we used periodic boundary conditions at all the sidewalls while the bottom and top walls are no-slip surfaces. For the thermal driving we used \(\epsilon = 0.7\). In this case, our intention was to study the state of spiral defect chaos in a domain where the effects of the sidewall boundary conditions were reduced. For a box geometry with a square platform it is typical to define the aspect ratio as \(\Gamma = L/d\), where \(L\) is the length of the side of square domain. Using this convention we have \(\Gamma = 100\) for the results presented here for the box domain. We used initial conditions composed of
Figure 6.3: Schematics of the two domains used for the numerical simulations of the Boussinesq equations. The Cartesian coordinates \((x, y, z)\) are in the directions shown and gravity acts in the direction opposing \(z\). (a) The box domain with a square planform of side length \(L\) and a depth \(d\) with an aspect ratio of \(\Gamma = L/d = 100\). The sidewall boundary conditions are periodic and the bottom and top walls are no-slip surfaces. This domain was used to generate a state of spiral defect chaos, with a sample flow field shown in Fig. 6.4. (b) The cylindrical domain of radius \(r_0\) and depth \(d\) with an aspect ratio of \(\Gamma = r_0/d = 40\). All material surfaces are no-slip boundaries and the sidewalls are heated as part of the procedure to develop a giant rotating spiral as described in the text. A sample flow field image is shown in Fig. 6.10 (left). Both schematics are drawn to scale and are shown slightly tilted with respect to the horizontal for perspective.

small random thermal perturbations of magnitude \(\delta T = 0.01\) to an otherwise quiescent layer of fluid. We then evolved the dynamics forward in time for approximately 930 time units to allow initial transients to decay.

We note that this duration of time is less than a nondimensional horizontal heat diffusion time \(\tau_h\) which is often used as a rough benchmark for determining the length of time required for a simulation to achieve a sufficient reduction of transients [187]. \(\tau_h\) is the amount of time required for heat to diffuse from the center of the domain to a sidewall. For the box domain this yields \(\tau_h = (L/2)^2 = 2500\). A simulation of this duration requires significant computational expense. We found that a duration of
930 time units was sufficient to establish a steady state of spiral defect chaos. We are interested in the instantaneous features of the patterns, in particular in the features of the relatively short lived spiral structures, and not in the long time statistics of the global pattern dynamics. As a result, we anticipate that a time of 930 time units is sufficient to study the mean flow field and the azimuthal flows that are generated around the spiral structures. An example flow field from a numerical simulation is shown in Fig. 6.4.

In order to study a single rotating spiral we used a cylindrical domain of aspect ratio \( \Gamma = \frac{r_0}{d} = 40 \), where \( r_0 \) is the radius of the domain. To generate a large spiral in this domain we follow the approach used in the experiment of Plapp et al. [192]. We initialize the simulation by starting with a quiescent layer of fluid where the lateral sidewalls are slightly heated while the thermal driving of the layer is just above threshold at \( \epsilon = 0.054 \). Specifically, the temperature at the sidewalls are set to the constant value of \( T = 0.1 \) for all \( z \), i.e., a hot sidewall boundary condition. The hot sidewall creates an up-flow at the wall which initializes the formation of a curved convection roll that aligns with the sidewall boundary. We then evolve the system forward in time for approximately 500 time units; during this time curved convection rolls grow inward towards the geometric center of the domain, resulting in a stable and stationary target pattern. We next restart the simulation further from threshold with \( \epsilon = 0.405 \) and allow it to evolve for approximately 300 time units. During this time, the center of the target pattern slowly drifts away from the geometric center of the domain to yield a stationary and time-independent skewed target-like pattern. We then restart the simulation further from threshold with \( \epsilon = 0.464 \) and let the system evolve for another 800 time units. This causes the center of the target-like pattern to drift further from the geometric center of the domain where the pattern eventually undergoes a complex transition of instabilities that eventually yield the giant one-armed spiral with a single dislocation as shown in Fig. 6.10. Both the giant spiral and the dislocation are rotating in the clockwise direction for these results. This procedure appears to be a flexible and reliable way to generate giant spirals. However, the specific parameters and sequence we used were determined by trial and error with the goal of generating a giant spiral and are by no means meant to describe a unique procedure.

All of our numerical simulations of Eqs. (6.21)–(6.23) were conducted using the high-order, highly parallelized, and open-source spectral element solver nek5000 [193]...
The code uses a semi-implicit operator splitting approach that is third-order accurate in time and converges exponentially in space. A hallmark of the approach is its geometric flexibility while also permitting explorations of large spatially extended systems. The nek5000 solver has been used to explore a broad range of fluids problems. More details regarding its use to study spatiotemporal chaos in Rayleigh-Bénard convection can be found in Refs. [194, 195].

Figure 6.4: Left: Temperature field at the mid plane of the convection cell obtained by integrating the Boussinesq fluid model in time with periodic boundary conditions. The convection cell is a box domain with $\Gamma = 100$, $\epsilon = 0.7$ and $Pr = 1$. The temperature field is shown at time $t = 914.69$. Right: A close-up view of a rotating spiral.

6.4 Azimuthal flows in the chaotic regime

We address in this section the extent to which the asymptotic results of Sec. 6.2.3 can shed some light on the role of hydrodynamic flows on spiral defect chaos. There are a number of factors that preclude a precise comparison between these analytic predictions and our numerical results. First, the typical size of a spiral in the chaotic state is relatively small (a few rolls), making a determination of the asymptotic decay of the azimuthal velocity questionable. Second, the results of Sec. 6.2.3 have been derived for the generalized Swift-Hohenberg model, and they exhibit a strong dependence on the damping parameter $c^2$. This makes a comparison with results from the Boussinesq model difficult as this parameter is largely phenomenological, although it has been estimated for the case of no-slip boundary conditions (see Ref. [177] and Appendix D). Third,
we have not explored the dynamics using the Boussinesq model for the case of free-slip
(stress-free) boundary conditions. In this case $c^2 = 0$, and the logarithmic dependence of
Eq. (6.15) might be apparent, and with it strong mean flows and interactions between
spirals. Nevertheless, we will argue that the azimuthal velocity field within a given
spiral depends strongly on the cutoff radius $r_b$ for small values of $c^2$, thereby providing
a mechanism for the hydrodynamic interaction of spirals.

We first use a chaotic configuration obtained from the solution of the the generalized
Swift-Hohenberg model, to analyze the $r$-dependence of the azimuthal velocity $v_\phi$ as
given in Eqs. (6.14)-(6.15). We use the same spiral configuration of Fig. 6.1a obtained
with the following values of model parameters: $\epsilon = 0.7, g_m = 50, c^2 = 2$, and $\sigma = 1$. We
then compute the corresponding $v_\phi$ from Eq. (6.2) from the instantaneous velocity field,
for a range of values of $c^2$. That is, by setting the time derivative of Eq. (6.2) to zero
(or equivalently, from the curl of Eq. (6.11), we obtain the velocity field in the Stokes
limit for various values of $c^2$ from the same order parameter $\psi$ configuration. This way,
we are able to follow the evolution of $v_\phi$ as a function of $c^2$ only, and evaluate if the
transition from the $-\ln(r/r_b)$ behavior based on Eq. (6.15) to the damped profiles
of Eq. (6.14) is observed. Note, however, that for these parameter values we do not
observe spirals in the simulation transients when $c^2 \leq 0.1$; rather, we observe target
defects (see also discussions in Sec. 6.5.2).

Figures 6.5 and 6.6 show the azimuthal velocity $v_\phi$ away from $r = 0$ at the core of
the spiral located at coordinate (104, 56) in Fig. 6.2 up to the midpoint between this
spiral and the other one at (156, 81). The figure shows the numerical solution for
$c^2 = 0$, $c^2 = 0.1$, $c^2 = 0.4$ and $c^2 = 2$ (solid lines). In order to compare the numerical solution
with the analytic result of Eq. (6.14) with $c^2 > 0$, we define

$$g(r) = \frac{1}{c^2} \left[ \frac{1}{r} + \left( cK_1(r_b c) - \frac{1}{r_b} \right) \frac{I_1(c r)}{I_1(r_b c)} - cK_1(c r) \right] ,$$  (6.24)

and fit the function $v_\phi = \alpha g(r) + \beta$, where $\alpha$ and $\beta$ are two fitting coefficients. The
function $g(r)$ depends on two parameters, the damping parameter $c^2$ and a cutoff radius
$r_b$ which is taken to be of the order of the spiral size.

For $c^2 = 0$ and the two rotating spirals of Fig. 6.2 we set $r_b = 30$, the mid point
between the two spirals (we see that $v_\phi$ changes sign approximately at $r = 30$). The
asymptotic relation \( v_\phi = -1.3 r \ln(r/30) \) is shown in the top two panels of Fig. 6.5 (dashed lines), where the constant \(-1.3\) is the single fitting parameter. There is good agreement away from the core. Figures 6.5 and 6.6 also show our results for \( c^2 > 0 \). We have set \( r_b = 35 \) in all these cases, and fit the parameters \( \alpha \) and \( \beta \). From Eq. (6.14) we note that \( \alpha = m \omega \epsilon g_m / 6q_0^2 \sigma \), where the only unknown is the angular frequency of rotation \( \omega \). Using our current parameter values, we have \( \alpha = 5.83 \omega \), where \( \omega \) is not known \textit{a priori}. The order of magnitude of the angular frequency will be further discussed in Sec. 6.5.2, where we find it to be on the order of \( 10^{-1} - 1 \). We have assumed that the constant \( \alpha \) is largely independent of \( c^2 \), and chosen \( \alpha = 5/\sigma \) for all the values of \( c^2 > 0 \) in Fig. 6.5 where the rescaled Prandtl number is \( \sigma = 1 \). Therefore the only fitting parameter used in Figs. 6.5 and 6.6 for \( c^2 > 0 \) is the constant \( \beta \). We note that Eq. (6.14) is valid away from the core, and is obtained with the boundary condition of vanishing velocity at the core. Hence the constant \( \beta \) can be rationalized as being related to the velocity near the core that should be used as a known boundary condition for the outer solution. The fitted \( \beta \) value also contributes to the large radius at which \( v_\phi \) vanishes. For finite damping, the azimuthal velocity does not completely decay to zero, so that we need a negative \( \beta \) to capture such effect. For small values of \( c^2 \), the value of \( r_b \) is relatively easy to determine, and is closely related to \( \beta \) in order to obtain a good fit. As \( c^2 \) increases, the velocity field decays quickly, and the fitting becomes less dependent on the value of cutoff \( r_b \) as long as \( r_b \) remains greater than the size of the spiral.

By increasing the damping coefficient from \( c^2 = 0 \) to \( c^2 = 0.1 \), the magnitude of the azimuthal velocity diminishes by a factor of four, and its asymptotic decay changes from convex to concave, as expected from Eq. (6.14). Figures 6.5 and 6.6 show that our analytic prediction from Eq. (6.14) appropriately describes the behavior of \( v_\phi \) far enough from the spiral core for all the \( c^2 > 0 \) cases. We also note that in every case \( v_{1,\phi} \) is sufficient to describe the form of the numerical curves, while \( v_{2,\phi} \) and \( v_{3,\phi} \) do not provide any major contribution to the observed results.

As \( c^2 \) increases, the flow field becomes increasingly localized within the vicinity of the spiral cores, thereby reducing any interaction between velocity fields generated by different spirals. This is illustrated in Fig. 6.6 when comparing the cases of \( c^2 = 0.4 \) and \( c^2 = 2 \). As the flow damping increases, the velocity becomes more short-ranged,
Figure 6.5: (Part 1) Azimuthal velocity for the spiral located at (104, 56) in Fig. 6.2 with $r = 0$ at its core, for $g_m = 50$, $\sigma = 1$, and $\epsilon = 0.7$. Left column compares numerical results with our analytic predictions, and right column is in logarithmic scale. First row: $c^2 = 0$, using $v_\phi = -1.3r \ln(r/30)$ for the analytic curve. Second row: $c^2 = 0.1$, using $\alpha = 5/\sigma$ and $\beta = -1.75$. For all the cases of $c^2 > 0$, $r_b = 35$ is used.
Figure 6.6: (Part 2) Azimuthal velocity for the spiral located at (104, 56) in Fig. 6.2 with \( r = 0 \) at its core, for \( g_{\text{m}} = 50, \sigma = 1, \) and \( \epsilon = 0.7. \) Left column compares numerical results with our analytic predictions, and right column is in logarithmic scale. First row: \( c^2 = 0.4, \) using \( \alpha = 5/\sigma \) and \( \beta = -0.5. \) Second row: \( c^2 = 2, \) using \( \alpha = 5/\sigma \) and \( \beta = -0.1. \) For all the cases of \( c^2 > 0, \) \( r_b = 35 \) is used.
and the magnitude of the azimuthal velocity decreases significantly: for \( c^2 = 2 \), the flow magnitude is only 4% of the flow obtained for \( c^2 = 0 \). Note that while \( r_b \) is of the order of the spiral’s size, the velocity for larger values of \( c^2 \) reaches zero well before \( r = 30 \), and that due to the small size of the spirals we do not observe a \( 1/r \) decay at long distances. In this range of \( c^2 \), the velocity field within each spiral is largely independent of the existence of other spirals, and does not depend on the value of \( r_b \).

In summary, we have observed the transition of the azimuthal velocity from a \(-r\ln(r/r_b)\) profile to the damped convex profiles when the damping coefficient \( c^2 \) increases, as suggested by our predictions in Sec. 6.2.3. As \( c^2 \) approaches zero, given the longer range of the flows the cutoff parameter \( r_b \) has the same value as the spiral’s radius when there are spirals of the same topological charge in the vicinity. By increasing \( c^2 \), as long as \( r_b \) is greater than this radius, varying the cutoff makes little quantitative difference to the fits, since the azimuthal velocity decays quickly to zero. In addition, the azimuthal velocity field within a spiral strongly depends on the existence of neighboring spirals, and their presence affects the fit parameters \( r_b \) and \( \beta \). The topological charge of the spirals also plays a role in this observation, as will be discussed in Sec. 6.5.1 for the case of neighboring counter-rotating spirals.

### 6.5 Discussion

#### 6.5.1 Azimuthal flow between two counter rotating spirals

In the spiral chaos regime the flow field within each spiral depends on the spiral size, which in turns is determined by the presence of neighboring spirals and other defects through the cutoff parameter \( r_b \). In particular, the decay of \( v_\phi \) with distance \( r \) is faster than the asymptotic \( 1/r \). For stress free boundary conditions, \( c^2 = 0 \), or small damping (e.g., \( c^2 = 0.1 \)) there is a strong and long ranged azimuthal velocity component spanning the entire spiral, which decays to zero at a scale determined by neighboring spirals of the same topological charge. For low damping, \( r_b \) is approximately the spiral’s radius. We present here an analysis of the flow between two counter rotating spirals (with opposite topological charge), as the flow would interact constructively along a line connecting them. Figure 6.7 shows the azimuthal velocity between two neighboring counter rotating spirals, centered at coordinates (104, 56) and (139, 25) in Fig. 6.1a. We again use the
same \( \psi \) configuration shown in Fig. 6.1a to compute the azimuthal velocities in the absence of inertia for two different values of the damping coefficient \( c^2 \). In the absence of damping, \( c^2 = 0 \), the azimuthal velocity is nonzero in the region between the two spirals, as the vorticity generated by the two cores adds up constructively. For \( c^2 = 2 \), the flow once again becomes concentrated at each spiral, with small or no flow interaction between them.

Figure 6.7: Azimuthal velocity between two spirals of opposite topological charge using the generalized Swift-Hohenberg equation. At \( r = 0 \) we find the core of the spiral located at \((104, 56)\) from Fig. 6.2 and at \( r = 47 \) the core of the spiral is located at \((139, 25)\). Using this same order parameter configuration, we compute the instantaneous velocity for \( c^2 = 0 \) (middle panel) and \( c^2 = 2 \) (right panel), and plot the azimuthal velocity between the two spirals.

### 6.5.2 Advection versus roll unwinding in spiral dynamics

We address here the possible relevance of the mean flows discussed to the chaotic state itself, based on the generalized Swift-Hohenberg model. It has been established that spiral defect chaos is only observed for a specific range of \( c^2 \) and scaled Prandtl number \( \sigma \). For the parameter set used here, \( g_m = 50, \epsilon = 0.7 \) and \( \sigma = 1 \sim 2 \), spiral defect chaos has been found in the range \( 0.1 < c^2 < 5 \) [68, 64, 66]. For \( c^2 > 4 \), the leading-order Lyapunov exponent of the flow approaches zero [68]. In the opposite range of small damping, \( c^2 \leq 0.1 \), spiral defects are no longer observed while the system dynamics is chaotic. In our calculations, if \( c^2 = 0 \) the magnitude and range of the mean flow increase significantly and we are only able to achieve spiral defect chaos for this free-slip condition by reducing \( g_m \) significantly to \( g_m \sim 5 \) (or, similarly, by increasing \( \sigma \)).
We examine here the relative contribution to the overall time variation rate \( \partial_t \psi \) from the mean flow advection \( \mathbf{v} \cdot \nabla \psi \), and the diffusive pattern dynamics given by the RHS of Eq. (6.1), leading to roll unwinding [200, 66]. The magnitude of the latter depends on the value of the local wavenumber when it is maintained away from the critical value (i.e., wavevector frustration) [66, 67], and also from the curvature of the rolls [75]. Both contributions have been estimated theoretically [201, 66].

We use the same configuration of the order parameter field shown in Fig. 6.2 and analyze the flow field around the spiral with core located at (104, 56). We obtain the velocity field by solving Eq. (6.2) with the time derivative set to zero, and for a range of values of \( c^2 \) and \( \sigma \). The overall time variation \( \partial_t \psi \), advection \( \mathbf{v} \cdot \nabla \psi \), and the relaxational part (i.e., the RHS of Eq. (6.1) yielding diffusive dynamics) oscillate nonuniformly as a function of the radial coordinate \( r \). We extract the characteristic magnitude of each quantity by finding its maximum absolute value between \( r = 5 \) (away from the core) and \( r = 28 \) (the approximate radius of the spiral). Other measures, such as choosing the values from the first peak of these functions, lead to similar results. Our results are shown in Fig. 6.8 for a range of values of \( c^2 \) for fixed \( \sigma = 2 \), and also as a function of \( \sigma \) for fixed \( c^2 = 1 \). As described in Appendix D, the value of \( \sigma = 2 \) corresponds to a Prandtl number of \( \text{Pr} = 1 \) (consistent with the CO \(_2 \) experiments of Ref. [56]). We have conducted calculations across the range \( 0 \leq c^2 \leq 100 \), and find that advection and diffusion contributions are of similar value around \( c^2 = 1 \). When rescaling the critical wavenumber to \( q_0 = 1 \), the value \( c^2 = 1 \) is the one estimated for no-slip boundary conditions on the cell’s plates, as detailed in Ref. [177] and Appendix D. Next, we fix \( c^2 = 1 \) and compute the same ratios for a range of \( 0.125 \leq \sigma \leq 64 \). Interestingly, both advection and diffusion contributions have approximately the same magnitude at \( \sigma = 2 \) (i.e., at the experimentally used Prandtl number \( \text{Pr} = 1 \)).

These results indicate three distinct regimes which can be correlated with the qualitative nature of the system dynamics obtained from the generalized Swift-Hohenberg model. (i) For very small \( c^2 \) (\( \lesssim 0.1 \)) at \( \sigma = 2 \), the observed defect patterns are chaotic but without any observable spirals, other than some transient target defects (similarly for \( \sigma \lesssim 0.25 \) at \( c^2 = 1 \)). As seen in the left panel of Fig. 6.8 when \( c^2 \leq 0.1 \) the dynamics are mainly driven by advection and the diffusive dynamics contribution from the RHS of Eq. (6.1) to \( \partial_t \psi \) becomes very small. At \( c^2 = 0 \) we still observe a few transient
Figure 6.8: Ratios of advection and roll unwinding [the RHS of Eq. (6.1)] to the overall time variation $\partial_t \psi$, as a function of the damping coefficient $c^2$ and the rescaled Prandtl number $\sigma$. Values are computed based on the spiral located at $(104, 56)$ in Fig. 6.1a with $\epsilon = 0.7$ and $g_m = 50$. The blue line with circle symbols shows the ratio for the spiral’s characteristic advection contribution $(\mathbf{v} \cdot \nabla \psi)$, and the red line with square symbols shows the ratio for its characteristic roll unwinding contribution (RHS). Left: Ratios are plotted as a function of $c^2$, for $\sigma = 2$. Right: Ratios are plotted as a function of $\sigma$, for $c^2 = 1$.

(i) At the other extreme with large $c^2$, the calculations in Ref. [68] showed that the leading-order (and positive) Lyapunov exponent of the flow approaches zero, indicating very weak or even non chaotic state. The patterns are dominated by slowly coarsening, large target and spiral defects, mixing with small spirals or targets. Similar results can be obtained for large enough $\sigma$ at $c^2 = 1$ in the right panel of Fig. 6.8. In this regime, diffusive roll unwinding mainly determine spiral rotation, as can be seen in Fig. 6.8 (ii) In the intermediate parameter range (e.g., around $0.1 < c^2 < 5$ for $\sigma = 1 \sim 2$ or in the mid-range values of the $\sigma$ dependence at $c^2 = 1$) spiral defect chaos is observed in the numerical solutions. In this range the contributions from advection and diffusive relaxation are comparable. In particular, both contributions are nearly the same around $c^2 = 1$ and $\sigma = 2$, the parameter values that correspond to the experiment of Ref. [56], and to the previous study of the Boussinesq equations [196, 71, 70, 68]. These results also help explain why spiral defect chaos was not observed when $c^2 = 0$ and $g_m = 50$, but did appear by reducing the latter to $g_m = 5$, as shown in Fig. 6.9.
That is, reducing \( g_m \) would roughly translate into moving the curves shown in Fig. 6.8 to the left. In summary, the results suggest a correlation between the existence of spiral defect chaos and the relative balance between advection and order parameter diffusion.

Figure 6.9: Patterns of order parameter field \( \psi \) obtained from the generalized Swift-Hohenberg model for \( \epsilon = 0.7, \sigma = 2, \) and \( c^2 = 0, \) at time \( t = 2 \times 10^3 \). Left: \( g_m = 50, \) showing a chaotic state without the emergence of spirals. Right: \( g_m = 5, \) showing spiral defect chaos.

Characteristic values of the spiral rotation rate \( \omega \) can be obtained from the numerical solutions. We estimate \( \omega \sim \mathcal{O}(10^{-1}) \) in dimensionless units, with its maximum value close to 1. This is consistent with the values of \( \alpha \) used in the fits of Figs. 6.5 and 6.6.

6.5.3 Comparison with spirals obtained from the Boussinesq equations

We have explored spiral defect chaos in the Boussinesq model only for no-slip boundary conditions. From the numerical results, as in Fig. 6.4, we observed that the size of the spirals in the range of parameters where chaos exists is fairly small, as is the case in experiments. Therefore, we cannot examine the asymptotic decay of \( v_\varphi \sim 1/r \) as has been predicted for large \( r, \) nor can we conclusively obtain the spatial dependence of long-range flows at small damping as argued above. We do present, however, results for a large, single rotating spiral (see Sec. 6.3.2), and evidence that the azimuthal velocity field obtained agrees, without any adjustable parameters, with \( v_\varphi \) obtained from direct integration of the generalized Swift-Hohenberg equation and in the regime of spiral defect chaos. We therefore expect that the asymptotic behavior of Figs. 6.5 and 6.6 at small damping would carry over to the full Boussinesq model.
A configuration comprising a single rotating spiral as given by the Boussinesq model with Prandtl number $Pr = 1$ is shown in Fig. 6.10. It has been obtained by adding a lateral forcing thermal boundary term in a cylindrical cell (a hot sidewall) while setting no-slip boundary conditions at all material surfaces, as described in Sec. 6.3.2. The temperature field at mid cell of a slowly rotating spiral and an accompanying dislocation is shown in Fig. 6.10. Lengths are made dimensionless by the cell thickness, so that the critical wavenumber is $q_c = 3.1165$, which can be obtained from the marginal stability problem at the critical Rayleigh number. The size of the spiral in Fig. 6.10 is 14 wavelengths, before reaching the dislocation. According to the derivation by Manneville [177], given no-slip boundary conditions and a cell with dimensionless thickness $h = 1$, a Galerkin expansion of the flow indicates that the mean flow becomes Poiseuille-like at lowest order. By averaging the governing equations over the height, a vorticity equation analogous to Eq. (6.2) can be obtained, with a damping coefficient $c^2 = 10$ corresponding to $q_c = 3.1165$. More details are given in Appendix D including how the length, time and various parameters are mapped from the Boussinesq model with no-slip conditions and $q_c = 3.1165$, to the generalized Swift-Hohenberg model, Eqs. (6.1) and (6.2) with $q_0 = 1$. The value of $c^2$ is further rescaled by $1/q_c^2$, so that $c^2 \approx 1$. Since the length scales as $1/q_c$ and for $Pr = 1$ the time scale is $2.05/q_c^2$, the Boussinesq velocity is rescaled by $2.05/q_c$ to agree with our dimensionless units. Finally, based on the Prandtl and Rayleigh numbers of the Boussinesq solution, we have $\sigma = 2$, $\epsilon = 0.7$, and $g_m = 50$, with scaling also given in Appendix D.

Figure 6.10 (middle) shows the rescaled azimuthal velocity $v_\phi$ computed at the mid plane of the cell as a function of $q_c r$, so that we can compare it directly with the result from the generalized Swift-Hohenberg model. The coordinate origin has been placed at the spiral’s core. Following an initial rise from zero at the core, the velocity appears to decay with distance as $r^{-2}$ between $q_c r = 3$ and $q_c r = 20$, until it quickly decays to zero at about $q_c r = 46$. This decay is faster than the expected asymptotic behavior of $1/r$, although we must note that for the time shown, there still is a difference between the rotation velocities of the core and the dislocation given in the simulation.

Figure 6.10 (right) compares the azimuthal velocity of the large spiral obtained from the Boussinesq model with that of a rotating spiral in the fully chaotic regime given by
Figure 6.10: Left: Temperature field at the midplane for a cylindrical convection cell obtained by time integration of the Boussinesq (BSQ) equations where $q_c = 3.1165$, $\Gamma = 40$, $\epsilon = 0.4637$, and $Pr = 1$. Middle: Rescaled azimuthal velocity $v_\phi$ from the Boussinesq model with $r = 0$ at the spiral core (solid line). The straight dashed line illustrates the power law fit $v_\phi \sim r^{-2}$. The red dashed line is the result of Eq. (6.14), using $c^2 = 1$, $\sigma = 2$, $\alpha = 1.4383$, $\beta = -0.04328$, and $r_b = 35q_c$. Right: $v_\phi$ as a function of $q_c r$ obtained from the generalized Swift-Hohenberg model (SH) with $c^2 = 1$, $\sigma = 2$, $\epsilon = 0.7$, and $g_m = 50$, for the spiral located at $(104, 56)$ in Fig. 6.2, as compared to that of the Boussinesq equations. The $x$ axis is scaled with $q_c = 3.1165$ for the Boussinesq result, and $q_c = q_0$ for the Swift-Hohenberg model. No adjustable parameters have been used.
the generalized Swift-Hohenberg model. We have mapped the physical values of the parameters in the Boussinesq model to the parameters of the generalized Swift-Hohenberg model, as explained in Appendix A. Therefore there are no adjustable parameters. The Swift-Hohenberg result was obtained by computing the adiabatic flow (by eliminating the time derivative in Eq. (6.2)) associated with $\psi$ in Fig. 6.1a for $c^2 = 1$, $\sigma = 2$, $\epsilon = 0.7$, and $g_m = 50$, and the spiral located at the coordinate (104, 56). The azimuthal velocity obtained from the Boussinesq model agrees quantitatively with the result of the generalized Swift-Hohenberg model, even when comparing an isolated spiral in the former to one in the chaotic regime in the latter. This lends credence to the observation that the asymptotic calculation of Sec. 6.2.3, which is based on a rigidly rotating spiral, is a good approximation to the flow induced by a spiral in the chaotic state, albeit in the range of moderate to large values of the damping parameter $c^2$. For the value of $c^2 = 1$ used in the comparison, the azimuthal velocity within a rotating spiral depends only weakly on whether the spiral is isolated or surrounded by other spirals.

Figure 6.11: Rescaled azimuthal velocity for the enlarged spiral in Fig. 6.4 obtained from the Boussinesq model (BSQ), with $r = 0$ at its core. The corresponding rescaled parameters are $\sigma = 2$, $c^2 = 1$, and $\epsilon = 0.7$. Left: Comparison of numerical results with analytic predictions. Right: The same results using a logarithmic scale. Parameters of $c^2 = 1$, $\alpha = 5/\sigma$, $\beta = -0.1$ and $r_b = 4.5$ are used for the analytic curve.

We finally analyze the azimuthal velocity in the chaotic regime of the Boussinesq model, with results presented in Fig. 6.11. We show the azimuthal velocity of the spiral of Fig. 6.4 with $r = 0$ centered at the core of the spiral. This result is compared with our analytic prediction of Eq. (6.14), with $c^2 = 1$, $g_m = 50$, $\sigma = 2$, and $\epsilon = 0.7$. Instead
of fitting both $\alpha$ and $\beta$ as previously discussed in Sec. 6.3.1, we set $\alpha = 5/\sigma$ (the same value used in Figs. 6.5 and 6.6). Since $\alpha = m \omega g_m / 6 q_0^2 \sigma$, all the parameters used in Sec. 6.3.1 are the appropriate ones for the Boussinesq model with no-slip boundary conditions as described in Sec. 6.3.2. In both cases we obtain one-armed spirals ($m = \pm 1$). Here we use $r_b = 4.5$ (the approximate size of the spiral) and $\beta = -0.1$. Note that due to the small size of the spiral, $v_\varphi$ does not reach zero at the edge of the spiral, as this is a small defect constrained by other features of the disordered pattern. Even under these circumstances, there is good agreement between the result of the Boussinesq model and the analytic solution, when using the same parameters estimated from the data fit with the generalized Swift-Hohenberg model.

6.6 Chapter conclusions

An irrotational azimuthal body force proportional to $\hat{\varphi}/r$ in the generalized Swift-Hohenberg model induces an azimuthal velocity $v_\varphi$ for a configuration of a rigidly rotating spirals. At zero damping (free-slip), this force leads to long ranged flows proportional to $-r \ln(r/r_b)$, where $r_b$ needs to be determined independently. For the more realistic case of no-slip boundary conditions, the azimuthal velocity would be expected to decay as $1/r$ instead at a scale $r \gg 1$ when $r_b \to \infty$. For realistic spiral sizes in the regime of spiral defect chaos, $q_0 r_b$ is of order one, and this asymptotic regime is never reached. Instead, the velocity flow depends strongly on the value of $r_b$, which in turn depends on the characteristic separation between neighboring spirals.

This dependence of the azimuthal velocity has been compared with direct numerical solution in a chaotic state both for the 3D Boussinesq equations and for the 2D generalized Swift-Hohenberg equations. For free-slip boundary conditions in the latter, the velocity behaves as $-r \ln(r/r_b)$, which is long-ranged and necessarily crosses zero between neighboring spirals of the same topological charge, while for neighboring spirals of opposite charge the velocity interacts constructively. When no-slip conditions are considered (with a finite damping parameter), the velocity profile qualitatively changes. This agrees with our predictions that the velocity decay is governed by a combination of modified Bessel functions. When damping is sufficiently high, we confirm the earlier suggestions that the flow within a spiral is largely independent of the background in
which it is immersed. For moderate damping the flow within a spiral is a function of the spiral’s size, and hence of the distance to neighboring spirals and their topological charges. This observation is consistent with an earlier suggestion of spiral defect chaos as a form of invasive chaos \[66\], except that hydrodynamic flows also play a role.

For the 2D generalized Swift-Hohenberg model, we identify two contributions to the spiral rotating dynamics: Mean flow advection and diffusive dynamics with wavevector frustration and roll unwinding. We have performed a series of calculations by varying the damping coefficient and the Prandtl number to identify three distinct regimes: Chaos without spiral patterns, diffusive pattern dynamics with extremely weak or no chaos, and spiral defect chaos. The latter appears in the range in which order parameter advection and diffusive relaxation are of similar magnitude. In particular, we find that both contributions are approximately the same at a damping coefficient about $c^2 = 1$, and a rescaled Prandtl number of $\sigma = 2$ (with $Pr = 1$), which correspond to the experimental conditions for convection in CO$_2$ gas.

The 3D Boussinesq equations have been integrated in a rectangular geometry with periodic sidewalls and no-slip conditions at top and bottom surfaces. By analyzing the flow field around a small spiral in the chaotic state, we found that the analytic result based on a rigidly rotating spiral agrees reasonably well with the Boussinesq azimuthal velocity, and that the remaining fit coefficients are consistent with those used with the generalized Swift-Hohenberg results under corresponding values of the physical parameters. Finally, we obtained a large spiral using the Boussinesq model in a cylindrical configuration, and analyzed the azimuthal flow around the core of the spiral. The azimuthal velocity agrees with the generalized Swift-Hohenberg result without any adjustable parameters. We conclude that for large values of the damping parameter, the flow field induced by a rotating spiral is the same regardless of whether it is isolated or surrounded by other spirals. When the damping parameter is reduced, the flow field depends on the distance to neighboring spirals and the relative sign of their topological charge, therefore providing a means for their interaction.
Chapter 7

Conclusion and Discussion

One of the main motivations of this thesis was to understand morphological changes experimentally observed in modulated soft materials, that could not be explained by classic interface thermodynamics. These modulated phases present large curvatures at the mesoscale, so that it was necessary to develop an interface theory that could both incorporate higher order curvatures, such as the Gaussian curvature, and anisotropic effects due to the uniaxial structure. By introducing a phase field model for a smectic-isotropic system, in Chapter 3 we have derived a generalized Gibbs-Thomson and interfacial motion equations, revealing the role of the Gaussian curvature and the orientation of a modulated phase on local equilibrium thermodynamics and kinetics of the interface. These equations present the classic surface tension, but also interface bending and tension constants, which can be calculated from parameters of the model. The smectic order parameter equation was integrated in time, and numerical results have shown the same focal conic to conical pyramid transition observed in experiments. Our analytic equations show that conical pyramids are formed because their layers become exposed to the interface, and satisfy the equation we derived for this scenario. Local equilibrium at such interface is governed by a different condition when compared to focal conics (layers parallel to the interface), and remarkably the leading order curvature terms are of third order, including a product between Gaussian and mean curvatures.

Using the proposed energy for a smectic-isotropic system, in Chapter 4 we expanded the model to include flows and possibility of distinct densities for each phase. For this, we
employed the Coleman-Noll procedure to derive constitutive relations and a set of governing equations: balance of mass, balance of linear momentum and an order parameter equation. We proposed a model for which the density is given as a constitutive function of the amplitude of the smectic order parameter, which is the quasi-incompressible limit. That is, the density presents a constant value for both the bulk smectic and the isotropic phases. This model allows for compressibility effects at the interface, since for a diffusive-interface the density smoothly changes in the transition between phases. A semi-implicit numerical method was developed to integrate the governing equations, based on an earlier scheme for phase-field models with varying mobility. We have also conducted a stability analysis of weakly perturbed smectic planes, and derived a dispersion relation for transverse modes. As predicted by the dispersion relation, we show that hydrodynamic effects dominate over the diffusive decay at low wavelength. We presented numerical results for weakly perturbed smectic layers and for focal conics in coexistence with an isotropic phase, revealing that the velocity field behaves accordingly to the dependence of the surface stress on curvatures. The velocity field and formation of convective rolls have also been shown to depend on the density ratio between the two phases.

Due to the balance of mass requirement, the quasi-incompressible model limits how much the smectic may grow or shrink, since the density is constant in the bulk of each phase. Therefore, this model is not suitable to study morphological transitions during sintering, or a scenario of continuous smectic growth. Seeking to develop a more versatile model, in Chapter 6 we proposed a weakly compressible model, which is derived in a similar way to the quasi-incompressible model. The difference is that the density becomes an independent variable, and we change the energy by adding a term that penalizes deviations from preferred density values for the smectic and the isotropic phases. We studied the role played by a density term that appears in the order parameter equation, coupling order parameter to density. Our results showed that this term affects the bifurcation structure of the problem, so that it may restrain the evolution of the smectic-isotropic interface if it becomes too large (quasi-incompressible limit). When the coupling constant is small enough, we observed the focal conic to conical pyramids transition, and showed that the flow becomes tangential to the interface, which is
expected from the dependence of the stress on curvatures for the case of layers perpendicular to the interface. Motivated by experiments on coalescence of smectic cylinders, we use the weakly compressible model to show under which circumstances coalescence is observed numerically, and we discuss the mechanisms behind our observations. This model has also been applied to study domain interactions between two neighboring focal conics, which has been observed under three different scenarios: density gradient in the isotropic phase, strain gradient between the two focal conics, and the case of overlapping focal conics.

Finally, we explored in this thesis Spiral Defect Chaos, a state that appears in the Rayleigh-Bénard convection (using a low Prandtl number fluid), where at the mid-height of a convection cell the vertical velocity or temperature form two-dimensional spiral structures that are continuously nucleated and annihilated. This state can be described as an active smectic, since rolls and spirals are modulated structures with the same elasticity (compression, splay moduli), symmetry and dispersion relation as the smectic, and are spontaneously kept outside thermodynamic equilibrium. Using a generalized Swift-Hohenberg model, whose dynamical equation for the order parameter is akin to the one employed for the smectic-isotropic problem, we derived the irrotational azimuthal body force generated by the topological defects. This force induces an azimuthal velocity, which has an important role in sustaining the spiral chaos regime. We showed that the magnitude and range of the velocity generated by each spiral strongly depends on mean flow damping due to boundary conditions of the convection cell, and that numerical results from integration of the generalized Swift-Hohenberg model agrees with the derived azimuthal equation away from the core. These results were also compared with velocity plots obtained from the numerical integration of the 3D Boussinesq equations, revealing a reasonable agreement with the derived azimuthal velocity equation (under the appropriate scaling). We concluded that for large damping the flow field induced by each rotating spiral is mostly independent neighboring spirals, while for low to moderate damping the flow depends on distance and topological charges of neighboring spirals, providing a means of interaction. Finally, we identified and compared two contributions to the spiral rotating dynamics: Mean flow advection and diffusive dynamics with wavevector frustration and roll unwinding. We found a correlation between the ratio of these contributions to the spiral dynamics and the emergence of spiral
chaos. For very low Prandtl numbers or low damping, mean flow advection dominates and we only observed chaos without spiral defects, while for high Prandtl numbers or high damping the diffusive dynamics dominate, and we did not observe chaos. Spiral chaos for parameter values in between these two regimes, and explain experimental observations.

The models developed in this thesis present many other applications in soft modulated matter, as well as possible problems that have not been explored here. Among them, we cite:

- Understanding the equilibrium distance between focal conics. For which distance the smectic-isotropic system minimizes its energy?

- Studying the nucleation of focal conics in the nematic to smectic transition, in particular how focal conic domains are formed and organized away from boojum defects in nematics [41]. This can be done by introducing a nematic variable, such as the director \( \mathbf{n} \) or the \( \mathbf{Q} \)-tensor, which should be coupled to the smectic order parameter.

- Using the same approach from Chapters 4 and 5 for developing an isotropic-columnar phase model. This can be done by introducing an internal energy that properly translates the symmetry of a columnar phase, which presents a translational invariance broken in two different directions. The columnar phase order parameter would describe tubes instead of planes in 3D, and parameters of the model would be able to capture elasticity and thermodynamics of the columnar system, such as in the present smectic case.
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Note that the flow itself is rotational, i.e., $\nabla \times \mathbf{v}_1 \neq 0$. While the force component $\mathbf{f}_\phi = - (\rho^2 m \omega / r) \hat{\phi}$ is irrotational, its curl is nonzero, since $\nabla \times (\mathbf{f}_\phi) \propto \delta(0) \hat{z}$. Hence, it leads to a nonzero vorticity, and consequently to the rotational $\mathbf{v}_1$. 


Appendix A

Amplitude equation

The phase field order parameter introduced in Sec. 3.2 is driven by energy minimization, with the following dynamical equation

\[
\partial_t \psi = -\epsilon \psi - \alpha (q_0^2 + \nabla^2) \psi + \beta \psi^3 - \gamma \psi^5. \tag{A.1}
\]

Our goal is to derive an amplitude equation [137, 138, 135] describing the motion of the envelope that describes the SmA-isotropic front without the oscillatory behavior of the phase field. We perform this analysis for small positive values of \( \epsilon \), \( \epsilon \ll 1 \) such that the amplitude of the order parameter is also small. Assuming the SmA layers are perpendicular to the \( z \) direction, the solution representing this phase is approximately

\[
\psi(x, t) \approx \frac{1}{2} (A e^{i q_0 z} + c.c.).
\]

Space and time can be separated in fast and slow scales, where the fast variables are \( \{x, y, z, t\} \), and the slow variables are \( \{X, Y, Z, T\} \). If we consider this amplitude to be slowly modulated along the perpendicular direction to the layers, we can set a distinction between the fast varying carrier \( \exp(i q_0 z) \), and the slowly varying the amplitude \( A(X, Y, Z, T) \).

The slow variables scaling can be obtained by introducing small perturbations in the different directions. Although the energy is rotationally invariant, perturbations in \( x, y \) and \( z \) will scale differently. For instance, take perturbations in \( z \), \( \psi = \psi(x, y, z + \delta_z, t) \), and linearize Eq [A.1]
\[ \partial_t \psi = \left[ -\epsilon - \alpha (2q_0 \delta_z + \delta_z^2) \right] \psi = \left[ -\epsilon - \alpha (4q_0^2 \delta_z^2 + 4q_0 \delta_z^3 + \delta_z^4) \right] \psi . \] 

(A.2)

Now, compare it to perturbations along \( x \) (or \( y \)), \( \psi = \psi(x + \delta_x, y, z, t) \):

\[ \partial_t \psi = ( -\epsilon - \alpha \delta_x^4 ) \psi \]

(A.3)

From Eqs. (A.2) and (A.3), we observe that the consistency condition between the lowest order terms acting on the slowly modulated envelope should be

\[ \partial_t A \sim \epsilon A \sim \partial_z^2 A \sim \partial_x^4 A \sim \partial_y^4 A . \] 

(A.4)

Hence, the slow variables scale as

\[ X = \epsilon^{1/4} x, \quad Y = \epsilon^{1/4} y, \quad Z = \epsilon^{1/2} z, \quad T = \epsilon t . \] 

(A.5)

Note that \( \beta \sim \epsilon^{1/2} \), since at the coexistence point \( \epsilon_c = 27 \beta^2 / 160 \gamma \). Also, one can show that both \( \psi = 0 \) and the non-trivial solution are stable for \( \epsilon > 0 \) up to the turning point \( \epsilon_{tp} = 9 \beta^2 / 40 \). For larger \( \epsilon \) only the trivial solutions exists and is stable. For small values of \( \epsilon \) these two points become very close, and they are also within the range of small perturbations from the bifurcation point \( \epsilon = 0 \).

From the proposed scaling and the chain rule, the derivatives from Eq. (A.1) can be recast as

\[ \partial_z \rightarrow \partial_z + \epsilon^{1/2} \partial_Z, \quad \partial_x \rightarrow \epsilon^{1/4} \partial_X, \quad \partial_y \rightarrow \epsilon^{1/4} \partial_Y, \quad \partial_t \rightarrow \epsilon \partial_T \] 

(A.6)

The dynamical equation for the order parameter can then be expanded in terms of these fast and slow variables. By writing its linear part as the operator \( L \), we have that

\[ L - \partial_t = -\epsilon - \alpha (\nabla^2 + q_0^2 \xi^2) - \partial_t \]

\[ = -\epsilon - \alpha ((\partial_z + \epsilon^{1/2} \partial_Z)(\partial_z + \epsilon^{1/2} \partial_Z) + \epsilon^{1/2} \partial_X^2 + \epsilon^{1/2} \partial_Y^2 + q_0^2 \delta_z^2) - \epsilon \partial_T \]

\[ = L_c + \epsilon^{1/2} L_1 + \epsilon L_2 + \epsilon^{3/2} L_3 + \epsilon^2 L_4 . \] 

(A.7)
The phase field order parameter $\psi$ can be expanded in terms of $\epsilon$ about the zero solution as

$$\psi = \epsilon^{1/4}\psi_1 + \epsilon^{3/4}\psi_2 + \epsilon^{5/4}\psi_3 + \ldots \quad \text{(A.8)}$$

By substituting these expansions back into the phase field dynamical equation, we collect the different terms according to their order in $\epsilon$. Starting with order $\epsilon^{1/4}$, we have

$$L_c\psi_1 = 0 \Rightarrow \psi_1(x, t) = \frac{1}{2} \left[A_{11} e^{i\eta_0 z} + \text{c.c.}\right]. \quad \text{(A.9)}$$

For order $\epsilon^{3/4}$, the following is satisfied

$$L_c\psi_2 + L_1\psi_1 = 0 \Rightarrow \psi_2(x, t) = \frac{1}{2} \left[A_{21} e^{i\eta_0 z} + \text{c.c.}\right]. \quad \text{(A.10)}$$

Finally, for order $\epsilon^{5/4}$ we find extra contributions owing to the nonlinear terms in Eq. (A.1),

$$L_c\psi_3 = -L_1\psi_2 - L_2\psi_1 - \beta\psi_1^3|\pm i\eta_0 + \gamma|\psi_1^5|\pm i\eta_0$$

$$= -\left[-\epsilon + 4\alpha q_0^2 \partial_2^2 - i4\alpha q_0 \partial_Z (\partial_X^2 + \partial_Y^2) - \alpha(\partial_X^4 + 2\partial_X^2 \partial_Y^2 + \partial_Y^4)ight] + \frac{3}{4}\beta|A_{11}|^2 \frac{5}{8}\gamma|A_{11}|^4 \partial_T \right] \left[A_{11} e^{i\eta_0 z} + \text{c.c.}\right]. \quad \text{(A.11)}$$

From the solvability condition (Fredholm’s Alternative), this equation has a solution if

$$\partial_T A_{11} = -\epsilon A_{11} + 4\alpha q_0^2 \partial_2^2 A_{11} - i4\alpha q_0 \partial_Z (\partial_X^2 + \partial_Y^2) A_{11}$$

$$+ \frac{3}{4}\beta|A_{11}|^2 A_{11} - \alpha(\partial_X^4 + 2\partial_X^2 \partial_Y^2 + \partial_Y^4) A_{11} - \frac{5}{8}\gamma|A_{11}|^4 A_{11}. \quad \text{(A.12)}$$

Since the fast-varying carrier is now removed from this equation, we can rescale it back to the original variables $\{x, y, z, t\}$. Expanding $A$ as

$$A = \epsilon^{1/4} A_{11} + \epsilon^{3/4} A_{21} + \ldots \quad \text{(A.13)}$$

and going back to the original variables, we find the amplitude equation for $A$ in complex
form,

\[ \partial_t A = -\epsilon A + 4\alpha q_0^2 \partial_z^2 A - 4i \alpha q_0 \partial_z \nabla_{x,y}^2 A - \alpha \nabla_{x,y}^4 A + \frac{3}{4} \beta |A|^2 A - \frac{5}{8} \gamma |A|^4 A. \]  

(A.14)

Although the current analysis was performed around small positive values of \( \epsilon \), we observe numerically that this amplitude equation and its stationary solutions (discussed in Sec. 3.3) accurately describe the two phases and the front between them at least up to \( \epsilon_c \approx 1 \).
Appendix B

The Laplace-Beltrami operator for a curved surface

Let $S \subset \mathbb{R}^3$ be a regular orientable surface, where $T_p(S)$ is the tangent plane to $S$ at $p \in S$. Define the following sets of orthogonal frames

\[ \{t_1, n, b_1\} \quad , \quad t_1 \in T_p(S) \quad (B.1) \]
\[ \{t_2, n, b_2\} \quad , \quad t_2 \neq t_1, \quad t_2 \in T_p(S). \quad (B.2) \]

The differential $dN_p : T_p(S) \rightarrow T_p(S)$ of the Gauss map $N : S \rightarrow S^2$ of $S$, where $n \in N(S)$, is a self-adjoint linear map. Therefore, for each $p \in S$ there exists an orthonormal basis $\{t_1, t_2\}$ of $T_p(S)$ such that

\[ dN_p(t_1) = -c_1 t_1, \quad dN_p(t_2) = -c_2 t_2. \quad (B.3) \]

See Do Carmo [202] for a proof of this theorem. Hence, $t_1$ and $t_2$ in our frames are defined as the eigenvectors at $p$, with eigenvalues (principal curvatures) $c_1$ and $c_2$. Since $t_1$ and $t_2$ are orthonormal, we can simply set an orthonormal frame aligned with the principal directions

\[ \{t_1(p), t_2(p), n(p)\} \quad , \quad p \in S. \quad (B.4) \]
Writing the surface coordinates as \( s_1 \) and \( s_2 \), we have \( p = (s_1, s_2) \in S \). For a point near the surface \( S \), we write the position vector as

\[
\mathbf{r}(\lambda, s_1, s_2) = \mathbf{p}(s_1, s_2) + \lambda \mathbf{n}(s_1, s_2)
\]  

(B.5)

where \( \lambda \) is the normal coordinate. Therefore, we obtain the following set of derivatives

\[
\frac{d\mathbf{r}}{ds_1} = \frac{d\mathbf{p}}{ds_1} + \lambda \frac{d\mathbf{n}}{ds_1} = (1 - \lambda c_1)\mathbf{t}_1
\]  

(B.6)

\[
\frac{d\mathbf{r}}{ds_2} = \frac{d\mathbf{p}}{ds_2} + \lambda \frac{d\mathbf{n}}{ds_2} = (1 - \lambda c_2)\mathbf{t}_2
\]  

(B.7)

\[
\frac{d\mathbf{r}}{d\lambda} = \mathbf{n}
\]  

(B.8)

The covariant metric tensor (first fundamental form) can now be computed by

\[
g_{ij} = \langle \mathbf{r}_i, \mathbf{r}_j \rangle = \begin{bmatrix}
1 & 0 & 0 \\
0 & (1 - \lambda c_1)^2 & 0 \\
0 & 0 & (1 - \lambda c_2)^2
\end{bmatrix}.
\]  

(B.9)

From the orthogonality of the covariant and contravariant metric tensors, the contravariant form is

\[
g_{ij}g^{ij} = \delta^i_j \Rightarrow g^{ij} = \begin{bmatrix}
1 & 0 & 0 \\
0 & (1 - \lambda c_1)^{-2} & 0 \\
0 & 0 & (1 - \lambda c_2)^{-2}
\end{bmatrix}.
\]  

(B.10)

For this principal coordinate system \((\lambda, s_1, s_2)\), the infinitesimal distance with respect to a point on the surface is

\[
d\mathbf{r} = \frac{\partial \mathbf{r}}{\partial \lambda} d\lambda + \frac{\partial \mathbf{r}}{\partial s_1} ds_1 + \frac{\partial \mathbf{r}}{\partial s_2} ds_2 = \mathbf{n} d\lambda + (1 - \lambda c_1)\mathbf{t}_1 ds_1 + (1 - \lambda c_2)\mathbf{t}_2 ds_2.
\]  

(B.11)

With the metric tensor at our disposal, it is possible to obtain the Laplace-Beltrami operator for the Riemannian manifold associated with the coordinate system \((\lambda, s_1, s_2)\).
The operator has the following form

\[ \nabla^2 = \frac{1}{g^{1/2}} \partial_i \left( g^{1/2} g^{ij} \partial_j \right). \]  \hspace{1cm} (B.12)

where \( g = \det(g) = (1 - \lambda c_1)^2(1 - \lambda c_2)^2 \). We expand further as

\[ \nabla^2 = g^{ij} \partial_{ij} + \partial_i (g^{ij}) \partial_j + \frac{1}{g^{1/2}} \partial_i (g^{1/2}) g^{ij} \partial_j \]  \hspace{1cm} (B.13)

\[ g^{ij} \partial_{ij} = \partial_\lambda^2 + (1 - \lambda c_1)^{-2} \partial_{s_1}^2 + (1 - \lambda c_2)^{-2} \partial_{s_2}^2 \]  \hspace{1cm} (B.14)

\[ \partial_i (g^{ij}) \partial_j = \frac{2\lambda \partial s_1 c_1}{(1 - \lambda c_1)^3} \partial s_1 + \frac{2\lambda \partial s_2 c_2}{(1 - \lambda c_2)^3} \partial s_2 \]  \hspace{1cm} (B.15)

\[ \frac{1}{g^{1/2}} \partial_i (g^{1/2}) g^{ij} \partial_j = \frac{1}{g^{1/2}} \left\{ \left[ -(c_1 + c_2) + 2\lambda c_1 c_2 \right] \partial_\lambda \\
+ \left[ -\lambda \partial s_1 (c_1 + c_2) + \lambda^2 \partial s_1 (c_1 c_2) \right] (1 - \lambda c_1)^{-2} \partial s_1 \\
+ \left[ -\lambda \partial s_2 (c_1 + c_2) + \lambda^2 \partial s_2 (c_1 c_2) \right] (1 - \lambda c_2)^{-2} \partial s_2 \right\} \]  \hspace{1cm} (B.16)

For a weakly distorted interface, derivatives in the normal and the tangential direction scale differently in terms of curvatures: \( \partial_\lambda \sim 1, \partial_{s_1} \sim c_1 \) and \( \partial_{s_2} \sim c_2 \). Hence, by neglecting the higher order curvature contributions for tangential derivatives, the Laplace-Beltrami operator can be reduced to

\[ \nabla^2 \approx \partial_\lambda^2 + \partial_{s_1}^2 + \partial_{s_2}^2 + \frac{-(c_1 + c_2) + 2\lambda c_1 c_2}{1 - \lambda(c_1 + c_2) + \lambda^2 c_1 c_2} \partial_\lambda \\
= \partial_\lambda^2 + \partial_{s_1}^2 + \partial_{s_2}^2 + \partial_\lambda (\ln(1 - \lambda(c_1 + c_2) + \lambda^2 c_1 c_2)) \partial_\lambda. \]  \hspace{1cm} (B.17)

By expanding \( \ln(1 + x) = x - (1/2)x^2 + (1/3)x^3 + ... \) with \( x = (-2\lambda H + \lambda^2 G) \), where \( H = \frac{1}{2}(c_1 + c_2) \) is the mean curvature and \( G = c_1 c_2 \) the Gaussian curvature, the previous
equation becomes

$$\nabla^2 = \partial^2_\lambda + \partial^2_{s_1} + \partial^2_{s_2} + \partial_\lambda \left[ -2\lambda H + \lambda^2 G \right. \\
\left. - \frac{1}{2}(4\lambda^2 H^2 - 4\lambda^3 GH + \lambda^4 G^2) + \frac{1}{3}(-8\lambda^3 H^3 + ...) \right] \partial_\lambda + h.o.t. \quad (B.18)$$

By rearranging the terms, Eq. (B.18) may be cast with respect to its leading order terms as

$$\nabla^2 \approx \partial^2_\lambda + \nabla^2_s + (-2H - (4H^2 - 2G)\lambda + 2H(G - B)\lambda^2) \partial_\lambda \quad (B.19)$$

where $\nabla^2_s = \partial^2_{s_1} + \partial^2_{s_2}$. Note that $B = 4H^2 - 2G = (c_1^2 + c_2^2)$ is known as the bending curvature, and that $2H(3G - 4H^2) = -(c_1^3 + c_2^3)$. We don’t substitute $B$ for second order curvature term to leave the Gaussian curvature explicit in it.

The biharmonic $\nabla^4$ can similarly be expanded in curved coordinates from the Laplace-Beltrami operator in Eq. (B.18). This operator is needed to derive the Gibbs-Thomson equation for the case of layers perpendicular to the interface. We collect all terms up to third order in curvatures. We find the term $(\partial^2_\lambda + \partial^2_{s_1} + \partial^2_{s_2})^2$ as well as additional terms associated with the first, second and third derivatives with respect to $\lambda$. As we are unable to say anything about the possible order and role of derivatives in $\lambda$, we keep all of these terms; however we keep only the lowest order term in curvature associated with each of them. This yields,

$$\nabla^4 \approx (\partial^2_\lambda + \partial^2_{s_1} + \partial^2_{s_2})^2 - (2\nabla^2_s H + 4H(2H^2 - 2G)) \partial_\lambda - 4(H^2 - G) \partial^2_\lambda \\
-4H(\partial^2_\lambda + \partial^2_{s_1} \partial_\lambda + \partial^2_{s_2} \partial_\lambda) - 4(\partial_{s_1} H \partial_{s_1} \partial_\lambda + \partial_{s_2} H \partial_{s_2} \partial_\lambda). \quad (B.20)$$
Appendix C

Stress tensor for a smectic

Assume a space distortion at constant order parameter $\psi$ [93], where $\mathbf{r}$ is a position vector and $\mathbf{u}$ is a small distortion. That is, assume

$$\psi(\mathbf{r}') = \psi(\mathbf{r}) \quad \mathbf{r}' = \mathbf{r} + \mathbf{u}(\mathbf{r}) .$$  \hspace{1cm} (C.1)

Then,

$$\frac{\partial \psi(\mathbf{r}')}{\partial r_i} = \frac{\partial \psi(\mathbf{r})}{\partial r_i} \quad \frac{\partial \psi(\mathbf{r}')}{\partial r_j} = \frac{\partial \psi(\mathbf{r})}{\partial r_j} - \frac{\partial u_j}{\partial r_i} \frac{\partial \psi(\mathbf{r})}{\partial r_j} .$$  \hspace{1cm} (C.2)

Using a linear strain approximation and Einstein notation, we write

$$\frac{\partial \psi(\mathbf{r}')}{\partial r_i} = \frac{\partial \psi(\mathbf{r})}{\partial r_i} - \frac{\partial u_j}{\partial r_i} \frac{\partial \psi(\mathbf{r})}{\partial r_j} .$$  \hspace{1cm} (C.4)

We will denote this result as $\partial'_{ij} = \partial_i - (\partial_i u_j) \partial_j$. Similarly, one can compute the second derivative,

$$\partial'_{ij} \psi(\mathbf{r}') = (\partial_i - \partial_i u_l) (\partial_j \psi - \partial_j u_k \partial_k \psi) .$$  \hspace{1cm} (C.5)
Linearizing again one finds,

\[ \partial'_{ij} \psi(r') = \partial_i \partial_j \psi - \partial_i \left[ \partial_j u_k \partial_k \psi \right] - \partial_i u_l \partial_l \partial_j \psi. \]  

(C.6)

The change in free energy \( \mathcal{F} \) (with density \( f \)) due to the distortion is then,

\[ \mathcal{F}[\psi(r')] - \mathcal{F}[\psi(r)] = \int f \left( \partial'_{i} \psi, \partial'_{ij} \psi \right) dr' - \int f \left( \partial_i \psi, \partial_{ij} \psi \right) dr. \]  

(C.7)

The contribution from \( f \) that does not depend on gradients does not enter the change in energy by assumption (\( \psi \) is held constant). For an incompressible system \( dr' = dr \), and linearizing again

\[ \delta \mathcal{F} = \int \left[ \frac{\partial f}{\partial (\partial_i \psi)} (\partial'_{i} \psi) + \frac{\partial f}{\partial (\partial_{ij} \psi)} (\partial'_{ij} \psi) - f (\partial_i \psi, \partial_{ij} \psi) \right] dr. \]  

(C.8)

We now substitute the two derivatives computed above, and cancel the undistorted contribution to obtain,

\[ \delta \mathcal{F} = \int \left\{ \frac{\partial f}{\partial (\partial_i \psi)} (-\partial_i u_j \partial_j \psi) \right. \\
\left. + \frac{\partial f}{\partial (\partial_{ij} \psi)} (-\partial_i [\partial_j u_k \partial_k \psi] - \partial_i u_l \partial_l \partial_j \psi) \right\} dr. \]  

(C.9)

The term in square brackets is a divergence term, and can be integrated by parts. We find (rearranging indices as well),

\[ \delta \mathcal{F} = \int \left\{ - \frac{\partial f}{\partial (\partial_i \psi)} (\partial_j \psi) + \partial_k \left[ \frac{\partial f}{\partial (\partial_k \psi)} \right] (\partial_j \psi) - \frac{\partial f}{\partial (\partial_{ij} \psi)} (\partial_j \partial_l \psi) \right\} (\partial_i u_j) dr \\
- \int \frac{\partial f}{\partial (\partial_{ij} \psi)} (\partial_j u_k) (\partial_k \psi) \hat{n}_i dA. \]  

(C.10)
This expression allows one to identify a stress tensor,

\[
T_{ij} = \frac{\delta F}{\delta (\partial_j u_i)}
\]

\[
= -\frac{\partial f}{\partial (\partial_j \psi)} (\partial_i \psi) + \partial_k \left[ \frac{\partial f}{\partial (\partial_{kj} \psi)} \right] (\partial_i \psi) - \frac{\partial f}{\partial (\partial_{jl} \psi)} (\partial_i \partial_l \psi) .
\] 

(C.11)
Appendix D

Parameter values of the generalized Swift-Hohenberg model

A generalized Swift-Hohenberg model that includes advection by the solenoidal mean flow velocity $v$ has been derived by Manneville [62,177] from the Boussinesq equations, which has the following form

$$
\tau_0 \left( \frac{\partial \psi}{\partial t} + v \cdot \nabla \psi \right) = \left[ \epsilon - \frac{\xi_0^2}{4q_c^2} (\nabla^2 + q_0^2)^2 \right] \psi - g(Pr)N[\psi], \tag{D.1}
$$

$$
\left[ \frac{\partial}{\partial t} - Pr(\nabla^2 - c^2) \right] \nabla^2 \zeta = g_{qc} \left[ \nabla(\nabla^2 \psi) \times \nabla \psi \right] \cdot \hat{z}, \tag{D.2}
$$

where

$$
v = \nabla \times (\zeta \hat{z}) = (\partial_y \zeta, -\partial_x \zeta). \tag{D.3}
$$

In Manneville’s model, the nonlinearity $N[\psi]$ has the form $N[\psi] = |\nabla \psi| \psi + q_c^2 \psi^3$. However, the threshold expansion of the Boussinesq equations leads to the cubic sum of Fourier modes, with no counterpart in real space [203]. Therefore, there is no systematic way for which $N[\psi]$ can be derived for a real-space expression, and its form depends on boundary conditions and arbitrariness of expansions [204]. In this work we use the simplest form $N[\psi] = q_c^2 \psi^3$. The model parameters depend on boundary conditions for
the top and bottom of the convection cell. In the case of no-slip (rigid) boundary conditions, where \( c^2 > 0 \) accounting for hard-mode oscillatory instabilities, these parameters are given by \[177\]

\[
\epsilon = \frac{(Ra - Ra_c)}{Ra_c}, \quad Ra_c = 1750 \text{ (exact value: 1708),} \quad c^2 = 10
\]

\[
g_c = 3.1165 \text{ (∼ exact value),} \quad \zeta_0^2 = 0.1497 \text{ (exact value : 0.148),}
\]

\[
\tau_0 = \frac{(1.9425 + Pr^{-1})}{38.2927} \text{ [exact value: (1.9544 + Pr^{-1})/38.4429],}
\]

\[
g_q = \frac{2}{(21q_c)}, \quad g(Pr) = \alpha_0 + \beta_0/Pr + \gamma_0/Pr^2;
\]

where \( \alpha_0, \beta_0, \gamma \) are some unknown expansion coefficients. Note that the above parameters such as \( R_c, q_c, \xi_0, \) and \( \tau_0 \) were derived from the Galerkin expansion by Manneville \[62, 177\] and well agree with the known exact values; also the length scale used above should be the vertical thickness \( d \), and hence the dimensional \( q_c \rightarrow q_c d \) and \( c^2 \rightarrow c^2 d^2 \) after rescaling.

In our simulations (and most other research), the dimensionless model equations are used. Setting a length scale \( 1/q_c \), a time scale \( 4\tau_0/(\xi_0^2 q_c^2) \), the rescaled variables \( \psi' = \psi \sqrt{4g(Pr)/\xi_0^2}, \zeta' = \zeta(4\tau_0/\xi_0^2) \), as well as

\[
\epsilon' = \epsilon \frac{4}{\xi_0^2 q_c^2} \frac{Ra - Ra_c}{Ra_c} \left( \frac{4}{\xi_0^2 q_c^2} \right), \quad c'^2 = c^2/q_c^2,
\]

and omitting all the primes, the generalized Swift-Hohenberg model equations \[D.1\] and \[D.2\] can be rescaled as

\[
\partial \psi/\partial t + v \cdot \nabla \psi = \left[ \epsilon - (\nabla^2 + q_0^2) \right] \psi - N[\psi], \quad (D.6)
\]

\[
[\partial/\partial t - \sigma(\nabla^2 - c^2)] \nabla^2 \zeta = g_m \left[ (\nabla^2 \psi) \times \nabla \psi \right] \cdot \hat{z}, \quad (D.7)
\]

as used in our study. Here

\[
q_0^2 = 1, \quad \sigma = \frac{4\tau_0}{\xi_0^2} Pr, \quad g_m = \frac{4\tau_0^2}{g(Pr)\xi_0^2 g_q c}.
\]

From the values given in Eq. \[D.4\], the parameters in the above equations \[D.6\] and
(D.7) can be estimated as

\[ \epsilon = 2.7511 \frac{(Ra - Ra_c)}{Ra_c}, \quad c^2 = \frac{10}{q_c^2} = 1.03, \]

\[ \sigma = 0.6978(1 + 1.9425Pr), \quad g_m = 1.7868 \times 10^{-4} \frac{(1.9425 + Pr^{-1})^2}{g(Pr)}. \quad (D.9) \]

If the Prandtl number \( Pr = 1 \) as set in experiments and the simulations of the Boussinesq model, we have \( \sigma \simeq 2 \). Also if choosing \( g(Pr) = 3.0941 \times 10^{-5} \), we get \( g_m = 50 \) as used in our calculations. In many calculations \( \epsilon \) is set as 0.7, which corresponds to \( (Ra - Ra_c)/Ra_c = 0.2544 \). This choice started from the first theoretical paper of spiral defect chaos \{64\}, based on the experimental results showing the onset of spiral chaos at \( (Ra - Ra_c)/Ra_c \geq 0.25 \) for \( Pr = 1 \) and in systems of large enough aspect ratio \{56, 57\}. The value of \( c^2 \) \([= 10 \text{ (unscaled) or equivalently } \simeq 1 \text{ after rescaling}]\) comes from the approximation process based on no-slip boundary condition \{177\}; after rescaling it is independent of the Prandtl number or the length scale chosen. Values of \( g(Pr), g_{qc}, \) and hence \( g_m \) also depend on the approximation of expansion (or the averaging over vertical thickness). As pointed out by Manneville \{177\}, their values would be different if using a different averaging procedure (e.g., the unscaled \( c^2 \) would change from 10 to 12, and \( g_{qc} \) from \( 2/21q_c \) to \( 4/35q_c \)).

We note that in most of previous studies using the generalized Swift-Hohenberg equations, usually \( \sigma \) is set as 1 which actually corresponds to \( Pr \simeq 0.22 \); also \( c^2 = 2 \) was first chosen in Ref. \{64\} and then followed in almost all the later work except for Ref. \{68\} which explored a range of possible \( c^2 \) values.