Landau Theory and Simulation for Columnar Liquid Crystals

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Columnar liquid crystals are a phase characterised by two-dimensional positional order in three spatial dimensions. They can be pictured as a lattice of fluid columns. We develop a Landau theory for the columnar liquid crystal, using the columnar density wave coupled to nematic order. Applying this, we reproduce the known result for the linear elasticity of a uniaxial solid. We then create a computer simulation of the columnar phase based on the theory we developed. The simulation successfully reproduces known behaviour of the columnar phase and so verifies our model.

I. Introduction

Matter can exist in different states or phases, the most familiar being solids, liquids and gases. There are in fact a great many intermediate phases that can exist 'between' liquids and solids [1]. To say more, it's useful to characterise phases by the type of 'order' present in them. Liquids (or more generally, fluids) are very disordered, whereas solids have a great deal of order. As temperature is reduced the intermediate or 'mesomorphic' phases with progressively more order can form, resulting eventually in the most highly ordered phase - a crystalline solid. The type of order present in a phase determines its mechanical properties [1, 2]. Mesomorphic phases have order, and therefore mechanical properties, intermediate to liquids and crystals and so are also called 'liquid crystal' phases.

This paper is concerned with one particular mesomorphic phase - the 'columnar' phase. Columnar phases are characterized by crystalline positional order in two dimensions and fluid like order in one dimension. They can be pictured as an array of fluid columns in a two-dimensional (2d) crystal lattice (Fig.1). They were first identified in liquid crystals

consisting of disc-like molecules [3] in 1977, and have been observed in highly concentrated suspensions of biofilaments, including DNA [4, 5, 6].

Other liquid crystal phases (nematic, smectic) have been very well studied [2] but historically columnar liquid crystals have had less attention, due in large part to their relatively recent discovery. Work has however been done to understand their elasticity, they are typically described as a two-dimensional linear elasticity coupled to column bending [7]. The mechanical properties of columnar liquid crystals are common to that of other fibrous materials composed of tightly packed columns. This has meant that recent efforts to describe filament bundles has renewed interest in a geometric description of the columnar phase [8, 9].

In this paper we develop a new theoretical model for the columnar phase using the spatially modulated density coupled to nematic order. This takes the form of a Landau theory for the nematic to columnar phase transition. Using our model, we reproduce the known linear elasticity associated with uniaxial solids [7]. We then apply our model to create a numerical code for the simulation of the columnar phase. This successfully reproduces known behaviour of columnar phases, including the formation of helical columns when subject to an appropriately constrained director field [10]. The simulation then not only verifies the validity of our theoretical model, but provides a robust and flexible tool with which further study of columnar phases can be carried out. This extends to the study of topological defects and elastic instabilities [11, 12] including behaviour under external fields, e.g. the Helfrich-Hurault instability [13, 14, 11].

II.   Liquid Crystals

Before discussing the columnar phase, we will identify what differentiates phases from each other and, in doing so, define them.

We start with the most familiar examples, isotropic fluids (liquids and gasses) and crystalline solids. The obvious property that differentiates the two phases is the presence of positional order. In crystals the mass is distributed on some lattice - knowledge of the position of some constituent particle (and the crystal's lattice vectors) gives the positions of *all* particles in the lattice. Fluid phases have no long range positional order - knowing the position of a given fluid particle provides no additional information about the positions of distant fluid particles.

Formally we can say that, for a perfect crystal, the density-density correlation function

$\langle \rho(\mathbf{r})\rho(\mathbf{r}')\rangle$ (where $\rho(\mathbf{r})$ is the mass density at position $\mathbf{r}$ and $\langle \cdots \rangle$ represents the ensemble average) is some periodic function of the separation, which stays finite in the limit of large separations,

$$\lim_{|\mathbf{r}-\mathbf{r}'|\to\infty} \langle \rho(\mathbf{r})\rho(\mathbf{r}')\rangle = F(\mathbf{r}-\mathbf{r}'). \qquad (1)$$

Note that F is written not as a function of $|\mathbf{r}-\mathbf{r}'|$, but of $(\mathbf{r}-\mathbf{r}')$, to wit, our correlation function is anisotropic; there is *orientational* as well as positional order present.

For an isotropic fluid, however, we can express this limit only in terms of the average density [2],

$$\lim_{|\mathbf{r}-\mathbf{r}'|\to\infty} \langle \rho(\mathbf{r})\rho(\mathbf{r}')\rangle = \tilde{\rho}^2, \qquad (2)$$

since there exists some finite length scale over which correlations are lost.

We see that we can use the order present in a system to define its phase. It is possible then to imagine intermediate phases *between* fluid and crystalline, where the system has some intermediate degree of order. These intermediate phases exist in nature and are known as liquid crystals [2]. We will define three:

1. Nematic: A phase with orientational order but no positional order. The correlation function, now of molecular orientations, is anisotropic in that its decay length scale differs depending on direction. Alternatively we can say that the constituent particles that make up the phase do not have spherical symmetry (typically we picture rods) and so they themselves can be oriented in some common direction. We can define a 'director' field, $\mathbf{n}$ - a vector field giving the local average orientation. The director field then is non-zero in the nematic phase, see Fig.2 (a) and (b).

2. Smectic: One dimensional positional order in three dimensional space, giving 2d fluid planes spaced on a one-dimensional lattice. Smectic liquid crystals also demonstrate the orientational alignment of their constituent molecules, much like in the nematic. See Fig. 2(c) and (d).

3. Columnar: Two dimensional positional order in three dimensions. The result is a 2d lattice of columns with liquid like order in the positions of the particles along the column axis - an array of liquid tubes which can glide with respect to each other (Fig.1). Columnar liquid crystals are typically formed from disc-like molecules, which share a common orientation. The columns orient themselves along the director field $\mathbf{n}$.
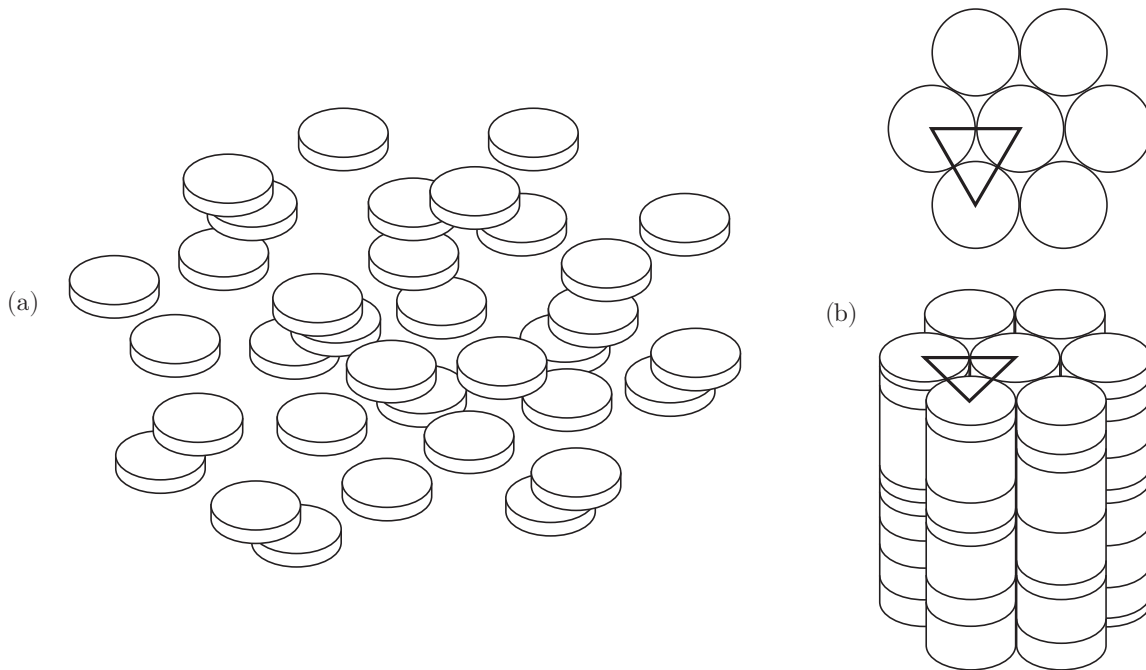
Figure 1: (a) The discotic (disc-like) molecules, arranged with some common orientation but no positional order. (b) The columnar phase. There exists no positional order within the columnar columns, and so they behave like a fluid in the column direction. The columns are situated here in a hexagonal lattice, but can form in any of the 2d lattices [1]. In this paper we deal entirely with the case of the 2d hexagonal lattice.

For our discussion of the columnar phase we aim to develop a Landau theory - a theoretical framework for describing ordered phases.

III.   Landau Theory

In 1937 soviet physicist L.D. Landau noted that it is natural to distinguish phases by their respective symmetries [15], and that phase transitions can therefore be understood in terms of changes from states with one symmetry group, to states with another. The order present in a system corresponds to the symmetries that the system possesses. For example, lack of positional order (as described in eq(2)) implies that the system is invariant under all spatial translations; the system has continuous translational symmetry. Isotropic fluids then have a great deal of symmetries, solids have comparatively few. As the temperature is reduced, a system undergoes transitions to phases with progressively more order and hence fewer symmetries. Phenomenological Landau theory uses ideas about the symmetries of phases to describe ordered phases and phase transitions quantitatively.

For a phase transition from some high temperature phase to a lower temperature, lower entropy phase we construct the following argument. We can describe all dynamical
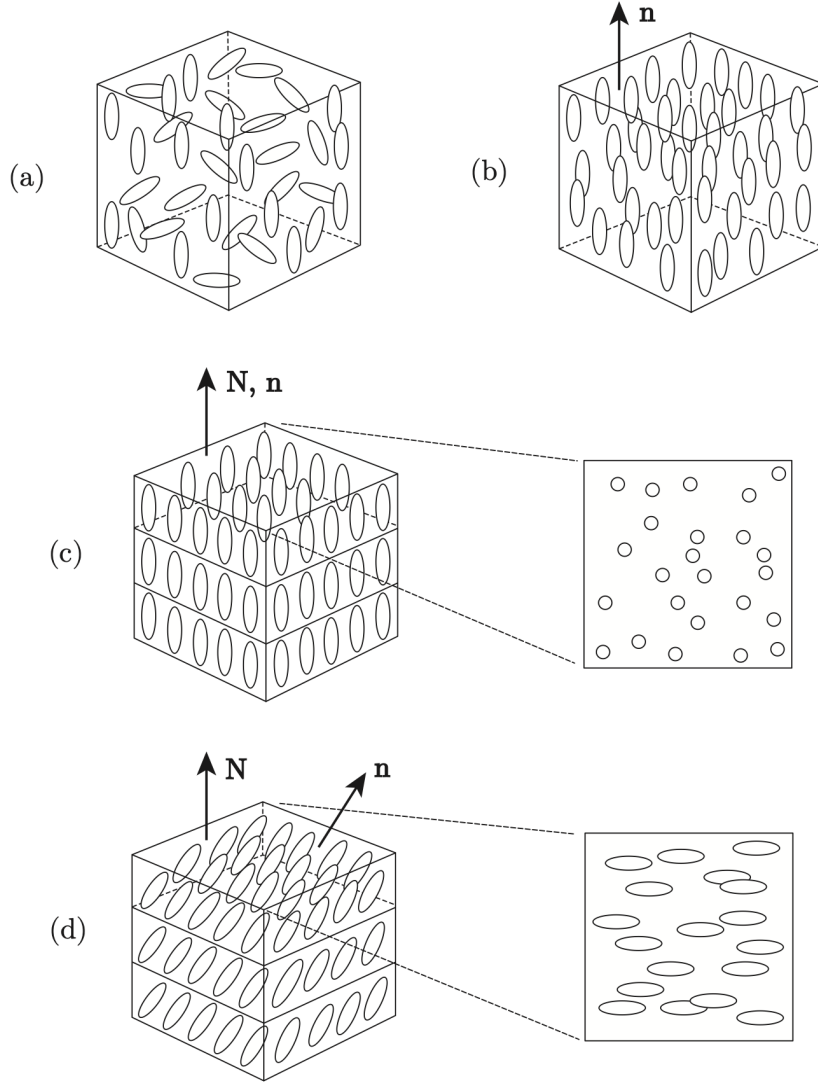
Figure 2: (a) 'rod-like' molecules arranged with no positional or orientational order - an isotropic fluid. (b) The nematic phase. We can define some common orientation, represented locally by the director field, **n**. (c) The smectic-A phase. Molecules have one-dimensional positional order, forming a one dimensional lattice of fluid-like planes, in which there exists no positional order. The smectic-A phase has the director aligned normal to the fluid layers. We write the normal vector as **N**. (d) Smectic-C phase. A smectic phase in which the director is not parallel to **N**.

properties of the system by its Hamiltonian, $\mathcal{H}$. $\mathcal{H}$ has some associated symmetry group $\mathcal{G}$ i.e. it is invariant under all transformations in $\mathcal{G}$. For an isotropic fluid, $\mathcal{G}$ includes the Euclidean group: arbitrary rotations, translations and reflections. High temperature phases, including fluids, are themselves invariant under the same group as their Hamiltonian, this means that any quantity which describes the fluid is invariant under all transformations in $\mathcal{G}$. These 'quantities' could be thermodynamic averages of functions of dynamical variables e.g. correlation functions. When transitioning to a

lower temperature phase, the thermodynamic average $\langle \phi \rangle$ of some function of dynamical variables, ϕ, which does *not* share the symmetry of the Hamiltonian, becomes non-zero. That is to say, the low temperature phase is not invariant under $\mathscr{G}$ but only under some subgroup of $\mathscr{G}$, whereas the symmetry of its Hamiltonian remains unchanged - we have 'broken' the symmetry of the Hamiltonian [1]. The quantity $\langle \phi \rangle$ is a measure of the order of the system - an 'order parameter', since at the moment it becomes non-zero we break the symmetry of $\mathscr{H}$ and the formation of the ordered phase has begun. As the temperature continues to lower, more phase transitions may occur, meaning new order parameters grow from zero and we break the symmetry further.

In our ordered phase, we can now identify some unique states of the system which are degenerate in the free energy because our order parameter transforms under some operations in $\mathscr{G}$ under which the Hamiltonian, and hence free energy of the system, is invariant. We will have multiple equivalent minima in the free energy corresponding to different values of the order parameter, where transformations of the order parameter under $\mathscr{G}$ represents transformations between equivalent equilibrium states [1].

If our system has spatial dimensionality, we could describe it with an order parameter that varies spatially, $\langle \phi(\mathbf{r}) \rangle$. We can choose $\langle \phi(\mathbf{r}) \rangle$ so that, for a uniform system, it takes the same value everywhere.

Equilibrium thermodynamics is determined completely by the temperature and the form of the function $\langle \phi(\mathbf{r}) \rangle$ for some choice of order parameter $\langle \phi(\mathbf{r}) \rangle$ - that is to say, by the free energy functional $F[T, \langle \phi(\mathbf{r}) \rangle]$.

Suppose now that we choose $\langle \phi(\mathbf{r}) \rangle$ to be uniform when the system is uniformly ordered and hence has uniform energy density. Then the local free energy density of the system, when in this uniform state, can be expressed as a function, f, of the local value of $\langle \phi(\mathbf{r}) \rangle$. This suggests, then, that we can express the free energy functional of some general system in terms of this local free energy density (as a *function* of the local evaluation of $\langle \phi(\mathbf{r}) \rangle$) and a part, F_{change}, which accounts for any deviations from uniformity. For this choice of $\langle \phi(\mathbf{r}) \rangle$, F_{change} includes only gradient terms in $\langle \phi(\mathbf{r}) \rangle$ [1]. We write

$$F = F_{change}[\langle \phi(\mathbf{r}) \rangle] + \int d^d x f(T, \langle \phi(\mathbf{r}) \rangle). \tag{3}$$

F shares the symmetry group of $\mathscr{H}$, so can depend only on those combinations of $\langle \phi(\mathbf{r}) \rangle$ that are invariant under all transformations in $\mathscr{G}$. One implication of this is that we may include only scalar combinations of $\langle \phi(\mathbf{r}) \rangle$ [1]. In Landau theory, we attempt to describe

systems near the phase transition ($T \approx$ critical temperature, T_C), thus $\langle \phi(\mathbf{r}) \rangle$ is small and we can expand F in a power series in our invariant scalar combinations of $\langle \phi(\mathbf{r}) \rangle$. The simplest form for the F_{change} functional in eq(3) is then

$$F_{change} = \int d^d x \frac{K}{2} (\nabla \langle \phi(\mathbf{r}) \rangle)^2, \tag{4}$$

for some constant K (the factor of $\frac{1}{2}$ is convention). And, for f,

$$f(T, \langle \phi(\mathbf{r}) \rangle) = \sum_{p=2}^{n} a_p \Phi^p. \tag{5}$$

Here Φ^p represents the scalar combinations of $\langle \phi(\mathbf{r}) \rangle$ evaluated locally, that form terms of order p. a_p are the coefficients of terms p in the power series, and are in general some function of temperature and pressure. We could have multiple invariant scalar combinations of the same order, but typically these are not independent and we need only include one.

When constructing our Landau expansion, n is chosen to be even so that the equilibrium state remains bounded in $\langle \phi(\mathbf{r}) \rangle$ (we typically include terms up to $n = 4$). We also set all a_p to be constants for $p > 2$, and a_2 to have the form $a(T - T_C)$. This way, in equilibrium, $\langle \phi \rangle$ is zero when $T > T_C$. This ensures the desired emergence of degenerate minima in F as T drops below the critical temperature. Note finally that we do not include terms with $p = 1$, since we must have that our high temperature equilibrium phase correspond to $\Phi = 0$ [1].

The way in which the symmetry of the order parameter differs from the Hamiltonian is important. It is this difference that determines which combinations of $\langle \phi(\mathbf{r}) \rangle$ must be made in order to restore the symmetry of the Hamiltonian and be included in the free energy. The form of the free energy, and hence the behaviour of the system, is then a direct result of the difference in symmetry between phases.

To construct the Landau free energy, we need to know how different combinations of our order parameter transform under $\mathscr{G}$.

IV.   The Nematic-Columnar Transition

We now present a new treatment of the columnar phase in the form of a Landau theory for the nematic to columnar (N-C) transition.

A. Columnar Free Energy

Columnar phases are characterised by 2d positional order, but they share some orientational order with nematics [1], namely the alignment of the constituent molecules. We choose to study the nematic to columnar (N-C) transition, this way we focus on the emergence of the positional order.

The first task is to identify an appropriate order parameter. It must be some property of the system which becomes non-zero at the transition into the ordered phase. Since the formation of the columnar phase is marked by the breaking of 2d continuous translational symmetry (the emergence of a 2d lattice), our order parameter must transform under all translations that can not be expressed as a linear combination of the lattice vectors. That way we get, at the N-C transition, a new continuum of unique states which share the symmetry group of the columnar phase. These states are degenerate in the free energy since $\mathscr{H}$ is invariant to all translations.

In the nematic phase there exists no positional order and we can say only that $\langle \rho(\mathbf{r}) \rangle$ takes the value of the average density (see eq(2)). In the columnar (ordered) phase $\langle \rho(\mathbf{r}) \rangle$ has some periodicity,

$$\langle \rho(\mathbf{r}) \rangle = \tilde{\rho} + \langle \delta\rho(\mathbf{r}) \rangle, \tag{6}$$

where $\langle \delta\rho(\mathbf{r}) \rangle$ accounts for any periodic variations from the average. Note that $\langle \delta\rho(\mathbf{r}) \rangle$ varies only in the plane of the columnar lattice vectors, and does so with the periodicity of the lattice. It remains invariant to all translations normal to this plane (along the columnar 'columns').

Since it has the appropriate symmetries, we choose as an order parameter the spatially modulating density $\Psi = \langle \delta\rho(\mathbf{r}) \rangle$. This is a typical choice for phase transitions involving the breaking of continuous translational symmetries [16, 17], see for example the liquid-solid transition and the nematic-smectic transition [1].

We should, however, be aware of some implications of this choice. The fact that the order parameter is spatially varying (even when describing the ordered phase) departs from the description of Landau theory given in section (III.). We can still use the same ideas but must proceed with caution.

We can now look to construct the Landau free energy for the N-C transition by writing a power law expansion of the form eq(5) in Ψ, ensuring that we restore the symmetry of the Hamiltonian. Typically we choose to expand in the scalar combinations of the order parameter that are themselves invariant under all operations in $\mathscr{G}$. In our treatment of

the columnar phase, however, we expand directly in the order parameter,

$$F = \int d^d x (a_2 \Psi^2 - a_3 \Psi^3 + a_4 \Psi^4) + F_{change}. \tag{7}$$

F still has the required symmetry after the integration. F_{change} serves to favour the spatially modulated state. In section (III.), we said simply that F_{change} should penalise spatial deviations from order, but here we must again take care to properly acknowledge the inherent spatial variation in Ψ.

We want our ordered phase to exhibit spatial modulations in the lattice planes with a wavenumber, q_0, that matches that of the desired hexagonal lattice. Clearly then, we do not want to include a term $|\boldsymbol{\nabla}\Psi|^2$ as described in section (III.), since this will indiscriminately penalise all spatial modulations. We *do* want to suppress any gradients along the column direction, (to reflect the 1 dimension of translational symmetry present in columnar phases). We might then include a term $|\boldsymbol{\nabla}_\parallel \Psi|^2$, where $\boldsymbol{\nabla}_\parallel$ represents gradients taken in the direction parallel to the columns. We want also to selectively suppress any gradients in the lattice planes that are not the desired modulations. That is to say, we want to penalise all Fourier modes with wavevectors perpendicular to the column direction that do not have wavenumber q_0. The appropriate term to include has the form $|(\nabla_\perp^2 + q_0^2)\Psi|^2$, where $\nabla_\perp^2$ is constructed from $\boldsymbol{\nabla}_\perp$, which represents some gradient operator taken the plane perpendicular to the columns. The object $|(\nabla^2 + q_0^2)\Psi|^2$ is used in the descriptions of other spatially modulating systems [16, 17]; here we make the distinction of using $\nabla_\perp^2$.

To explicitly justify the use of $|(\nabla_\perp^2 + q_0^2)\Psi|^2$, we note that it is sufficient to expand $\langle \delta\rho(\mathbf{r}) \rangle$ in a Fourier series in the reciprocal lattice vectors of the 2d columnar lattice and retain only the 'fundamental set'. This is the set of terms in the expansion for which the wavevectors are the primitive reciprocal lattice vectors,

$$\Psi(\mathbf{r})_{fund} = \sum_{\mathbf{G}} \psi_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}. \tag{8}$$

The primitive reciprocal lattice vectors $\mathbf{G}$ can be obtained from the real lattice vectors $\mathbf{R}$ by the relation $G_i \cdot R_i = 2\pi\delta_{ij}$ [1], such that $|\mathbf{G}| = q_0$. Equation (8) is all that is needed to describe the ordering with the periodicity of the crystal lattice. Let us write an integration by parts on eq(4),

$$F_{change} = \int \boldsymbol{\nabla} \cdot (\Psi\boldsymbol{\nabla}\Psi) - \Psi\nabla^2\Psi d^d x. \tag{9}$$

The first term corresponds to boundary effects, and so the simplest choice we can make is to include only $\nabla^2 \Psi$. Clearly $\nabla^2 \Psi_{fund} = -q_0^2 \Psi_{fund}$, and so we conclude naturally that $|(\nabla_\perp^2 + q_0^2)\Psi|^2$ suppresses the relevant Fourier modes.

We write F_{change} then in the form

$$F_{change} = \int d^d x \left(\frac{K_0}{2} |(\nabla_\perp^2 + q_0^2)\Psi|^2 + \frac{K_1}{2} |\boldsymbol{\nabla}_\parallel \Psi|^2 \right), \qquad (10)$$

where we have included separate elastic constants K_0, K_1. Note that each term in the integrand has the symmetry of the Hamiltonian (the object $|(\nabla_\perp^2 + q_0^2)\Psi|^2$ is translationally invariant when Ψ is in the ordered phase). This is consistent with the usual development of a Landau theory.

Reducing Ψ to the fundamental set is common in the analysis of spatially modulated states [2, 1] as it helps simplify calculations - we use this form again in section (V.) and section (VII.). Using $G_i \cdot R_i = 2\pi \delta_{ij}$ we find that the reciprocal lattice of a 2d-hexagonal lattice is itself a (rotated) hexagonal lattice. Going forward, we will use $\mathbf{G}_n = q_0(\cos(\frac{n\pi}{3})\hat{\mathbf{e}}_x + \sin(\frac{n\pi}{3})\hat{\mathbf{e}}_y)$ where subscript n denotes the n'th reciprocal lattice vector ($n = 0, 1, 2...5$).

Since the form for F_{change} is invariant under all translations in $\mathscr{G}$, we can (in line with the typical Landau model outlined in section (III.)) think of the integrand as representing the local contribution to F caused by spatial deviations from order.

We have said that our operators $\nabla_\perp^2$ and $\boldsymbol{\nabla}_\parallel$ that appear in eq(10) act in directions defined relative to the column direction. In columnar liquid crystals, the columns form along the nematic director (see Fig.1) and so we define $\nabla_\perp^2$ and $\boldsymbol{\nabla}_\parallel$ as acting perpendicular and parallel to the director field, $\mathbf{n}$ respectively. This model produces columnar ordering relative to the local director field, and so should be equipped to describe columnar phases with the nematic's director distortions. We have a geometric, coordinate-free model of the columnar phase using the spatially modulating density, coupled to the nematic director field. Finally, since we allow for non-uniform director fields, $\mathbf{n}$, we ought to include the appropriate term for the relaxation of the director. For this we borrow the 'Frank free energy' [18] taken from the study of nematic liquid crystals (the director fields for the columnar and nematic phases are, of course, the same),

$$F_{\mathbf{n}} = \int d^d x \left(\frac{K_{\mathbf{n}1}}{2} (\nabla \cdot \mathbf{n})^2 + \frac{K_{\mathbf{n}2}}{2} [\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 + \frac{K_{\mathbf{n}3}}{2} [\mathbf{n} \times (\nabla \times \mathbf{n})]^2 \right). \qquad (11)$$

We have then our final form for the Landau free energy for the N-C transition,

$$F[\Psi, \mathbf{n}] = \int \left(\frac{A}{2}\Psi^2 - \frac{B}{3}\Psi^3 + \frac{C}{4}\Psi^4 + \frac{K_0}{2}[(\nabla_\perp^2 + q_0^2)\Psi]^2 + \frac{K_1}{2}[\nabla_\parallel \Psi]^2 + F_\mathbf{n} \right) d^3x. \quad (12)$$

The model is coordinate free and accounts for the coupling between Ψ and $\mathbf{n}$.

B. The Form of $\nabla_\perp^2$ and $\boldsymbol{\nabla}_\parallel$

We mentioned that the object $\nabla_\perp^2$ is constructed from gradients in the plane perpendicular to the director, and implied that its behaviour is analogous to the Laplacian operator, ∇^2, taken in this plane. We will now detail exactly the form of $\nabla_\perp^2$.

Since $\boldsymbol{\nabla}_\parallel$ represents gradients along the column direction ($\mathbf{n}$), we say simply that

$$\boldsymbol{\nabla}_\parallel = \hat{\mathbf{n}}(\mathbf{n} \cdot \boldsymbol{\nabla}), \text{ or, } (\nabla_\parallel)_k = (n_k)(n_i \partial_i), \quad (13)$$

and so

$$(\nabla_\perp)_i = \nabla_i - (\nabla_\parallel)_i = (\delta_{ij} - n_i n_j)\partial_j. \quad (14)$$

For $\nabla_\perp^2$ we can make two choices. We can think of $\nabla_\perp^2$ as $\boldsymbol{\nabla}_\perp \cdot \boldsymbol{\nabla}_\perp$. Then

$$\nabla_\perp^2 = (\nabla_\perp)_i(\nabla_\perp)_i = (\delta_{ij} - n_i n_j)\partial_j[(\delta_{ik} - n_i n_k)\partial_k]$$
$$= (\delta_{ij} - n_i n_j)(\delta_{ik} - n_i n_k)\partial_j\partial_k - (\delta_{ij} - n_i n_j)\partial_j[n_i n_k]\partial_k. \quad (15)$$

Now $\mathbf{n}$ is a normalised vector field, so that $n_i n_i = 1$, and $\partial_j[n_i n_i] = 2n_i(\partial_j n_i) = 0$. We can therefore make the simplifications

$$(\delta_{ij} - n_i n_j)(\delta_{ik} - n_i n_k)\partial_j\partial_k = \delta_{ij}(\delta_{ik} - n_i n_k)\partial_j\partial_k = (\delta_{jk} - n_j n_k)\partial_j\partial_k, \quad (16)$$

and

$$(\delta_{ij} - n_i n_j)\partial_j[n_i n_k]\partial_k = (\delta_{ij} - n_i n_j)(n_i(\partial_j n_k) + n_k(\partial_j n_i))\partial_k = n_k(\partial_j n_j)\partial_k. \quad (17)$$

So that

$$\nabla_\perp^2 = (\delta_{jk} - n_j n_k)\partial_j\partial_k - n_k(\partial_j n_j)\partial_k. \quad (18)$$

Thus $\boldsymbol{\nabla}_\perp \cdot \boldsymbol{\nabla}_\perp$ mixes derivatives in Ψ and $\mathbf{n}$. We choose instead to keep them seperate

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and use

$$\nabla_\perp^2 = (\delta_{jk} - n_j n_k)\partial_j\partial_k. \tag{19}$$

This choice still gives the desired behaviour and $\frac{K_0}{2}[(\nabla_\perp^2 + q_0^2)\Psi]^2$ suppresses the intended Fourier modes.

V.   Distortions and Elasticity

We now demonstrate how our Landau theory reproduces the linear elasticity of the columnar phase [7]. Typically columnar phases are modelled as having a 2d linear elasticity coupled to column bending. This is often written in terms of a two-dimensional displacement field, $\mathbf{u}(\mathbf{r})$, which represents displacements of the columns from the lattice sites in the plane perpendicular to the column direction, see Fig.3. The elasticity of the columnar phase is that of a uniaxial solid [7],

$$f_{el} = \frac{a}{2}(\partial_x u_x + \partial_y u_y)^2 + \frac{b}{2}[(\partial_x u_x - \partial_y u_y)^2 + (\partial_y u_x + \partial_x u_y)^2] + \frac{c}{2}[(\partial_z^2 u_x)^2 + (\partial_z^2 u_y)^2]. \tag{20}$$

This includes a part which represents bulk dilations, $(\boldsymbol{\nabla} \cdot \mathbf{u})^2$, and a part representing shear terms. Column bending is accounted for by gradients along the column direction,
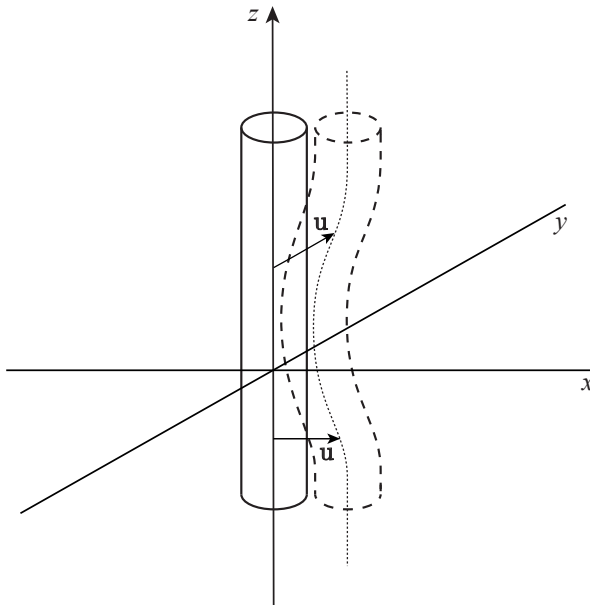
Figure 3: A columnar column and its distorted image. For the undistorted column, director $\mathbf{n}$ points uniformly in the z direction. We can interpret the displacement field $\mathbf{u}(\mathbf{r})$ as a vector displacement of the column's axis in the x-y plane [2]. Geometrically, $\mathbf{n} = [\partial_z u_x, \partial_z u_y, 1]$.

z. Note that we write the second order contribution; first derivatives of $\mathbf{u}$ in z represent rotations of the columns and so cannot enter the free energy.

We will try to recover the dilation and shear terms in eq(20) from the elastic contributions to our Landau free energy. We again choose to approximate Ψ in the ordered phase as being the fundamental set, eq(8). We can then include the displacement field $\mathbf{u}(\mathbf{r})$ as

$$\Psi(\mathbf{r}) = \sum_{\mathbf{G}} \psi e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{u}(\mathbf{r}))}. \tag{21}$$

This gives $\mathbf{u}$ the same interpretation as in eq(20). The displacement field represents a displacement of our mass density in the 2d plane of the lattice.

The calculation of changes in f_{el} in terms of the displacement field $\mathbf{u}(\mathbf{r})$, then, is simply a case of evaluating our elastic energy contributions eq(10) with our distortion included. Here we will deal with the contribution from the K_0 term, which should give the dilation and shear terms in eq(20) (the elasticity relative to the lattice plane). We reduce to a two-dimensional treatment in the lattice plane, the x-y plane, with $\mathbf{n}$ uniformly pointing in the z direction. We will write $\nabla_\perp^2$ as ∇^2, with the interpretation that it is the Laplacian taken in the x-y plane (with a uniform director aligned along the z-axis, eq(19) reduces to this form). We wish to evaluate then,

$$f_{elastic} = |(\nabla^2 + {q_0}^2) \sum_{\mathbf{G}} \psi e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{u}(\mathbf{r}))}|^2. \tag{22}$$

The calculation proceeds as follows:

First we deal with the Laplacian term, $\nabla^2\Psi(\mathbf{r})$. Using an index notation, where indices are taken over the spatial components x and y, we can express the gradient of $\Psi(\mathbf{r})$ as

$$(\nabla\Psi)_a = \sum_{\mathbf{G}} \psi_{\mathbf{G}}(iG_a - iG_b\partial_a u_b)e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{u}(\mathbf{r}))}. \tag{23}$$

Since we are taking gradients in the x-y plane, with $\mathbf{n}$ uniform and normal to the plane we can write $\nabla^2\Psi(\mathbf{r})$ simply as $\partial_a(\nabla\Psi(\mathbf{r}))_a$. Let $m_a = (iG_a - iG_b\partial_a u_b)$ so that (with

summation convention over repeated indices)

$$\nabla^2 \Psi(\mathbf{r}) = \partial_a (\nabla \Psi(\mathbf{r}))_a \tag{24}$$

$$= \sum_{\mathbf{G}} \psi_{\mathbf{G}} [\partial_a e^{(\cdots)} m_a + \partial_a m_a e^{(\cdots)}] \tag{25}$$

$$= \sum_{\mathbf{G}} \psi_{\mathbf{G}} (m_a m_a + i G_b \nabla^2 u_b) e^{i\mathbf{G} \cdot (\mathbf{r} - \mathbf{u}(\mathbf{r}))}, \tag{26}$$

where $m_a m_a = -G_a G_a + 2 G_a G_b \partial_a u_b - G_a G_b \partial_c u_a \partial_c u_b$. Now the $q_0^2 \Psi$ term in eq(22) is simply $G_a G_a \sum_{\mathbf{G}} \psi_{\mathbf{G}} e^{i\mathbf{G} \cdot (\mathbf{r} - \mathbf{u}(\mathbf{r}))}$ (it was included for the purpose of cancelling the $G_a G_a$ term in eq(26)). We are left with

$$\nabla^2 \Psi + q_0^2 = \sum_{\mathbf{G}} \psi_{\mathbf{G}} L e^{i\mathbf{G} \cdot (\mathbf{r} - \mathbf{u}(\mathbf{r}))}, \tag{27}$$

where the scalar L is

$$L = (2 G_a G_b \partial_a u_b - G_a G_b \partial_c u_a \partial_c u_b + i G_b \nabla^2 u_b). \tag{28}$$

Taking the product of eq(27) with its complex conjugate, we get a double sum over the set of reciprocal lattice vectors, which we write as being over $\mathbf{G}_1$ and $\mathbf{G}_2$,

$$f_{elastic} = \sum_{\mathbf{G}_1 \mathbf{G}_2} \psi_{\mathbf{G}_1} \psi_{\mathbf{G}_2}^* L_1 L_2^* e^{i(\mathbf{G}_1 - \mathbf{G}_2) \cdot (\mathbf{r} - \mathbf{u}(\mathbf{r}))}. \tag{29}$$

This can be simplified if we make the assumption that $\mathbf{u}(\mathbf{r})$ varies on scales larger than the lattice spacing, so that it can be taken as a constant here. We can then exploit the fact that we intend to integrate the energy contribution, and so need only to keep terms where $\mathbf{G}_1 = \mathbf{G}_2 = \mathbf{G}$ (the Fourier terms where $\mathbf{G}_1 \neq \mathbf{G}_2$ integrate to zero),

$$f_{elastic} = \sum_{\mathbf{G}} \psi_{\mathbf{G}} \psi_{\mathbf{G}}^* L L^*. \tag{30}$$

$\psi_{\mathbf{G}} = \psi_0$ for all $\psi_{\mathbf{G}}$ and so we need not keep it for this analysis. We wish then to evaluate $\sum_{\mathbf{G}} L L^*$. Cross terms in the product $L L^*$ of course cancel, leaving the real scalar

$$L L^* = (2 G_a G_b \partial_a u_b - G_a G_b \partial_c u_a \partial_c u_b)^2 + (G_b \nabla^2 u_b)^2. \tag{31}$$

We want to recover terms quadratic in $\mathbf{u}$, and so will look only at the term $2 G_a G_b \partial_a u_b$.

Expanding gives $4G_aG_bG_cG_d\partial_au_b\partial_cu_d$, where we have extended our indices appropriately. We are interested then in the sum,

$$\sum_{\mathbf{G}} G_aG_bG_cG_d\partial_au_b\partial_cu_d, \tag{32}$$

where we can take $\partial_au_b\partial_cu_d$ outside the sum over $\mathbf{G}$ and write (32) as a sum over two rank four tensors, $\mathbf{J}$ and $\mathbf{T}$,

$$\partial_au_b\partial_cu_d\sum_{\mathbf{G}} G_aG_bG_cG_d = J_{abcd}\sum_{\mathbf{G}} G_aG_bG_cG_d = J_{abcd}T_{abcd}. \tag{33}$$

The evaluation of $\mathbf{T}$ is best done by explicitly writing the terms for each of the reciprocal lattice vector of our hexagonal lattice. For example, for $\mathbf{G}_{n=0} = \hat{\mathbf{e}}_x$, we get a contribution $\mathbf{G}^4 = (\hat{\mathbf{e}}_x)^4$, that is, a contribution of 1 to the element T_{0000}. When summing the contributions from each $\mathbf{G}_n$, terms with odd powers of $\hat{\mathbf{e}}_x$ or $\hat{\mathbf{e}}_y$ cancel due to the symmetry of the hexagon, leaving

$$\mathbf{T} = 9/4(\hat{\mathbf{e}}_x^4 + \hat{\mathbf{e}}_y^4) + 3/4(\hat{\mathbf{e}}_x^2\hat{\mathbf{e}}_y^2 + \hat{\mathbf{e}}_x\hat{\mathbf{e}}_y\hat{\mathbf{e}}_x\hat{\mathbf{e}}_y + \hat{\mathbf{e}}_x\hat{\mathbf{e}}_y\hat{\mathbf{e}}_y\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y\hat{\mathbf{e}}_x\hat{\mathbf{e}}_x\hat{\mathbf{e}}_y + \hat{\mathbf{e}}_y\hat{\mathbf{e}}_x\hat{\mathbf{e}}_y\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y^2\hat{\mathbf{e}}_x^2), \tag{34}$$

where, for example, $\hat{\mathbf{e}}_x\hat{\mathbf{e}}_y\hat{\mathbf{e}}_x\hat{\mathbf{e}}_y$ corresponds to the element T_{0101}. We then simply evaluate the sum $J_{abcd}T_{abcd}$, which after some straightforward manipulation yields finally

$$f_{elastic} = J_{abcd}T_{abcd} = 2(\partial_xu_x + \partial_yu_y)^2 + [(\partial_xu_x - \partial_yu_y)^2 + (\partial_yu_x + \partial_xu_y)^2]^2. \tag{35}$$

We have recovered the dilation and shear terms in the linear elasticity, eq(20). Of course, our free energy, eq(12), accounts also for an energy contribution arising from frustrations in the director field.

We have verified that our model developed in section (IV.) behaves as expected for the simple case illustrated above. Computer simulations often prove invaluable when trying to understand complex systems. To take our analysis of columnar phases further we now look to develop a computer simulation of the phase, using our Landau theory.

VI.   Computational Method

In this section we outline the computational method used to simulate the columnar phase using the Landau free energy, eq(12), derived in section (IV.). We do, however, make one

simplification - we assume one elastic constant for the Frank free energy, eq(11), which we write K_2. The Frank free energy contribution can then be reduced to the form $\frac{K_2}{2}|\boldsymbol{\nabla}\mathbf{n}|^2$. This simplifies the following calculations without omitting any of the essential physics.

We restate, with this modification, the free energy for the columnar phase that we will use going forward,

$$F[\Psi, \mathbf{n}] = \int \left(\frac{A}{2}\Psi^2 - \frac{B}{3}\Psi^3 + \frac{C}{4}\Psi^4 + \frac{K_0}{2}[(\nabla_\perp^2 + q_0^2)\Psi]^2 + \frac{K_1}{2}[\nabla_\parallel \Psi]^2 + \frac{K_2}{2}|\boldsymbol{\nabla}\mathbf{n}|^2 \right) d^3x, \tag{36}$$

with $\nabla_\perp^2$ and $\boldsymbol{\nabla}_\parallel$ having the forms given in equations (19) and (13) respectively.

A. Set-up

In equilibrium, the form of the density and director fields, $\Psi(\mathbf{r})$ and $\mathbf{n}(\mathbf{r})$ respectively, correspond to some minima in the free energy functional $F[\Psi, \mathbf{n}]$, eq(36). It is, therefore, possible to create a computer simulation of the columnar liquid crystal's equilibrium state by finding, for some boundary conditions, the form of $\Psi(\mathbf{r})$ and $\mathbf{n}(\mathbf{r})$ that minimise F. In fact, we can simulate the dynamical evolution of the system by performing gradient descents of the free energy. The method proceeds as follows:

We want to find the functions $\Psi(x, y, z)$ and $\mathbf{n}(x, y, z)$ that, together, minimise the functional $F[\Psi, \mathbf{n}]$. For this we can of course use the calculus of variations [19]. We will split the problem into two parts, first minimising $F[\Psi]$ for fixed $\mathbf{n}$, and then $F[\mathbf{n}]$ for fixed Ψ.

We vary Ψ by adding to it some arbitrary, small function ($\epsilon f(x, y, z)$, where $\epsilon \ll 1$), which we write $\delta\Psi$ so that F becomes $F[\Psi + \delta\Psi]$. The form of Ψ that extremises F, which we write Ψ_{ex}, satisfies $F[\Psi_{ex} + \delta\Psi] = F[\Psi_{ex}]$ to first order in $\delta\Psi$ (the definition of the extremum). To find Ψ_{ex}, then, it is sufficient to expand $F[\Psi + \delta\Psi]$ in powers of $\delta\Psi$, and choose Ψ such that the terms first order in $\delta\Psi$ are equal to zero. That is to say, we set the functional derivative, $\frac{\delta F}{\delta \Psi}$, to zero so that, to first order, there is no change in F given some small change in Ψ.

Our form for $F[\Psi]$ contains spatial derivatives of Ψ of first and second order, which we can write as an explicit dependence on Ψ' and Ψ'' respectively,

$$F[\Psi] = \int L(\Psi, \Psi', \Psi'') d^3x. \tag{37}$$

Expanding $F[\Psi + \delta\Psi]$ is a case of expanding the resulting integrand $L(\Psi + \delta\Psi, \Psi' +$

$\delta\Psi', \Psi'' + \delta\Psi'')$. Keeping only changes in F first order in $\delta\Psi$ we write the 'functional differential', δF, as

$$\delta F = F[\Psi + \delta\Psi]_{first\ order} - F[\Psi] = \int d^3x \left(\frac{\partial L}{\partial \Psi} \delta\Psi + \frac{\partial L}{\partial \Psi_i} \delta\Psi_i + \frac{\partial L}{\partial \Psi_{ij}} \delta\Psi_{ij} \right)$$
$$= \int d^3x \left(\frac{\partial L}{\partial \Psi} \delta\Psi + \frac{\partial L}{\partial \Psi_i} \partial_i \delta\Psi + \frac{\partial L}{\partial \Psi_{ij}} \partial_i \partial_j \delta\Psi \right). \quad (38)$$

Here subscripts of the field Ψ denote spatial derivatives taken with respect to index i. To identify terms linear in the change, we move the derivatives from $\delta\Psi$ using integration by parts, once on the $\partial_i\delta\Psi$ term and twice on the $\partial_i\partial_j\delta\Psi$ term. We have

$$\delta F = \int d^3x \left(\frac{\partial L}{\partial \Psi} \delta\Psi - \delta\Psi \partial_i \frac{\partial L}{\partial \Psi_i} + \delta\Psi \partial_i \partial_j \frac{\partial L}{\partial \Psi_{ij}} \right) + boundary\ terms$$
$$= \int d^3x \left(\frac{\partial L}{\partial \Psi} - \partial_i \frac{\partial L}{\partial \Psi_i} + \partial_i \partial_j \frac{\partial L}{\partial \Psi_{ij}} \right) \delta\Psi \quad (39)$$
$$= \int d^3x \frac{\delta F}{\delta\Psi} \delta\Psi, \quad (40)$$

where we have ignored the boundary terms. We identify the functional derivative $\frac{\delta F}{\delta\Psi}$ as the coefficient of $\delta\Psi$,

$$\frac{\delta F}{\delta\Psi} = \frac{\partial L}{\partial \Psi} - \partial_i \frac{\partial L}{\partial \Psi_i} + \partial_i \partial_j \frac{\partial L}{\partial \Psi_{ij}}. \quad (41)$$

It represents the rate of change in F with respect to a local change $\delta\Psi(\mathbf{r})$ at some point $\mathbf{r}$ in the domain.

Setting $\frac{\delta F}{\delta\Psi}$ to zero imposes the condition that changes in F are zero, to first order in $\delta\Psi$. This is the condition that Ψ extremises F. $\frac{\delta F}{\delta\Psi} = 0$ is known as an Euler-Lagrange equation. Our computational method might be then to solve this Euler-Lagrange equation as a boundary value problem. It is, however, computationally simpler to perform a gradient descent of the functional derivative of the kind

$$\frac{\partial\Psi}{\partial t} = -\gamma \frac{\delta F}{\delta\Psi}, \quad (42)$$

and instead solve an initial value problem. Then, at each point in space, $\Psi(\mathbf{r})$ descends the gradient of its local contribution to F and the system converges to an equilibrium configuration, $\frac{\delta F}{\delta\Psi} = 0$.

In fact, eq(42) models the physical time evolution of the system [1]. To see this, consider a system that evolves in accordance with Newton's second law as $m\ddot{x} = -\frac{\partial V}{\partial x} - \beta\dot{x}$,

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where V is some potential and β the coefficient of some drag term. In the viscous regime we set accelerations to zero and recover $\dot{x} = -\frac{1}{\beta}\frac{\partial V}{\partial x}$ as in eq(42). By updating Ψ in accordance with eq(42) then, we can simulate the evolution of the columnar phase over time.

Let us now deal with the director field, $\mathbf{n}$. We have

$$F[\mathbf{n}] = \int L(\mathbf{n}, \mathbf{n}')d^3x, \tag{43}$$

and so, in the same manner,

$$\delta F = \int d^3x \left(\frac{\partial L}{\partial n^i}\delta n^i + \frac{\partial L}{\partial n^i_j}\delta n^i_j \right),$$

where superscripts n^i correspond to the i'th component of n, and subscripts denote the derivative with respect to coordinate x^i.

Again we remove derivatives from δn^i with an integration by parts, this time only once since we have only first derivatives in δn.

$$\delta F = \int d^3x \left(\frac{\partial L}{\partial n^i}\delta n^i - \delta n^i \partial_j \frac{\partial L}{\partial n^i_j} \right) + boundary\ terms = \int d^3x \left(\frac{\partial L}{\partial n^i} - \partial_j \frac{\partial L}{\partial n^i_j} \right) \delta n^i.$$

We identify our functional derivative $\frac{\delta F}{\delta n^i}$, now for each component i of $\mathbf{n}$,

$$\frac{\delta F}{\delta n^i} = \frac{\partial L}{\partial n^i} - \partial_j \frac{\partial L}{\partial n^i_j}, \tag{44}$$

and perform a gradient descent with the same form as eq(42),

$$\frac{\partial n^i}{\partial t} = -\gamma \frac{\delta F}{\delta n^i}. \tag{45}$$

B.   Evaluating Functional Derivatives

B..1   Evaluating $\frac{\delta F}{\delta \Psi}$

First we will evaluate eq(41). Writing L using eq(18) and eq(13),

$$L(\Psi, \Psi_i, \Psi_{ij}) = \frac{A}{2}\Psi^2 - \frac{B}{3}\Psi^3 + \frac{C}{4}\Psi^4 + \frac{K_0}{2}[(\delta_{ij} - n^i n^j)\Psi_{ij} + q_0^2\Psi]^2 + \frac{K_1}{2}[n^i n^j \Psi_j]^2. \tag{46}$$

$\mathbf{n}$ is a normalised vector field, so that evaluating each term in eq(41) we have

$$\frac{\partial L}{\partial \Psi} = A\Psi - B\Psi^2 + C\Psi^3 + K_0[(\delta_{ij} - n^i n^j)\Psi_{ij} + q_0^2 \Psi]\frac{\partial}{\partial \Psi}[(\delta_{ij} - n^i n^j)\Psi_{ij} + q_0^2 \Psi]$$

$$= A\Psi - B\Psi^2 + C\Psi^3 + K_0 q_0^2 (\nabla_\perp^2 \Psi + q_0^2 \Psi), \tag{47}$$

$$\frac{\partial L}{\partial \Psi_\alpha} = \frac{K_1}{2}\frac{\partial}{\partial \Psi_\alpha}[(n^i n^j \Psi_j)(n^i n^k \Psi_k)] = \frac{K_1}{2}\frac{\partial}{\partial \Psi_\alpha}[(n^j \Psi_j)(n^k \Psi_k)] = K_1(n^\alpha n^j \Psi_j), \tag{48}$$

and

$$\frac{\partial L}{\partial \Psi_{\alpha\beta}} = K_0[(\delta_{ij} - n^i n^j)\Psi_{ij} + q_0^2 \Psi]\frac{\partial}{\partial \Psi_{\alpha\beta}}[(\delta_{ij} - n^i n^j)\Psi_{ij} + q_0^2 \Psi]$$

$$= K_0(\nabla_\perp^2 \Psi + q_0^2 \Psi)(\delta_{\alpha\beta} - n^\alpha n^\beta). \tag{49}$$

Our functional derivative w.r.t. Ψ is then, using eq(41),

$$\frac{\delta F}{\delta \Psi} = A\Psi - B\Psi^2 + C\Psi^3 + K_0 q_0^2 (\nabla_\perp^2 \Psi + q_0^2 \Psi) - K_1 \partial_\alpha[n^\alpha n^j \Psi_j]$$
$$+ K_0 \partial_\alpha \partial_\beta[(\nabla_\perp^2 \Psi + q_0^2 \Psi)(\delta_{\alpha\beta} - n^\alpha n^\beta)]. \tag{50}$$

B..2 Evaluating $\frac{\delta F}{\delta \mathbf{n}}$

Now we evaluate eq(44), where L is now

$$L(n, n') = \frac{K_0}{2}[\nabla_\perp^2 \Psi + q_0^2 \Psi]^2 + \frac{K_1}{2}[\boldsymbol{\nabla}_\parallel \Psi]^2 + \frac{K_2}{2}|\boldsymbol{\nabla}\mathbf{n}|^2$$
$$= \frac{K_0}{2}[(\delta_{ij} - n^i n^j)\Psi_{ij} + q_0^2 \Psi]^2 + \frac{K_1}{2}(n^j \Psi_j)(n^k \Psi_k) + \frac{K_2}{2}(\partial_i n^j)(\partial_i n^j). \tag{51}$$

We have again used $n_i n_i = 1$ in expanding $[\boldsymbol{\nabla}_\parallel \Psi]^2$ (keeping the factor of $n_i n_i$ when evaluating the functional derivative yields additional terms parallel to $\mathbf{n}$. These terms are removed by the constraint $|n| = 1$ giving the same result as that reached in the following calculation). The terms in the functional derivative equation, eq(44), are calculated as follows.

$$\frac{\partial L}{\partial n^\alpha} = K_0[(\delta_{ij} - n^i n^j)\Psi_{ij} + q_0^2 \Psi]\frac{\partial}{\partial n^\alpha}[(\delta_{ij} - n^i n^j)\Psi_{ij} + q_0^2 \Psi] + K_1(n^j \Psi_j)\frac{\partial}{\partial n^\alpha}[n^k \Psi_k]$$

$$= -2K_0 n^j \Psi_{j\alpha}(\nabla_\perp^2 \Psi + q_0^2 \Psi) + K_1 n^j \Psi_j \Psi_\alpha \tag{52}$$

and

$$\frac{\partial L}{\partial n_\beta^\alpha} = \frac{K_2}{2}\frac{\partial}{\partial n_\beta^\alpha}[(\partial_j n^i)(\partial_j n^i)] = \frac{K_2}{2}\frac{\partial}{\partial n_\beta^\alpha}[(n_j^i)(n_j^i)] = K_2 n_\beta^\alpha. \tag{53}$$

So our functional derivatives w.r.t. n^α then are, using eq(44),

$$\frac{\delta F}{\delta n^\alpha} = -2K_0(\nabla_\perp^2\Psi + q_0^2\Psi)(n^j\Psi_{j\alpha}) + K_1 n^j\Psi_j\Psi_\alpha - K_2\partial_\beta\partial_\beta n^\alpha. \tag{54}$$

An alternative method would be to directly expand F in $\delta\Psi$ and δn^α and collect terms first order in the changes to identify the respective functional derivatives.

We now look to devise a computational scheme to perform the gradient descents eq(42) and eq(45) with $\frac{\delta F}{\delta\Psi}$ and $\frac{\delta F}{\delta\mathbf{n}}$ given by eq(50) and eq(54) respectively. First, we explicitly write the dynamical equations.

C. Summary of the Dynamical Equations

To summarise, we have the following PDE's to describe the time evolution of the columnar phase, in the density field Ψ and director field $\mathbf{n}$,

$$\begin{aligned}\frac{\partial\Psi}{\partial t} &= -\gamma(A\Psi - B\Psi^2 + C\Psi^3 + K_0 q_0^2(\nabla_\perp^2\Psi + q_0^2\Psi) - K_1\partial_\alpha[n^\alpha n^j\Psi_j]) \\ &\quad + K_0\partial_\alpha\partial_\beta[(\nabla_\perp^2\Psi + q_0^2\Psi)(\delta_{\alpha\beta} - n^\alpha n^\beta)],\end{aligned} \tag{55}$$

$$\frac{\partial n^\alpha}{\partial t} = -\gamma\left(-2K_0(\nabla_\perp^2\Psi + q_0^2\Psi)(n^j\Psi_{j\alpha}) + K_1 n^j\Psi_j\Psi_\alpha - K_2\partial_\beta\partial_\beta n^\alpha\right). \tag{56}$$

D. Numerical Scheme

The dynamical equations were discretised and solved using a finite difference method with forward Euler time stepping. The numerical scheme is as follows.

First let us define a shift operator, S_a^s, which acts on an element $P_{i,j,k}$ in some three-dimensional array (or rank 3 tensor), $\mathbf{P}$, to give the element in $\mathbf{P}$, s positions shifted in the dimension a,

$$S_a^s(P_{i,j,k}) = \begin{cases} P_{i+s,j,k} & \text{if } a = 1 \\ P_{i,j+s,k} & \text{if } a = 2 \\ P_{i,j,k+s} & \text{if } a = 3 \end{cases}. \tag{57}$$

And the grid space tensor,

$$
\Delta_a = \begin{cases} \Delta x & \text{if } a = 1 \\ \Delta y & \text{if } a = 2 \\ \Delta z & \text{if } a = 3 \end{cases}.
\tag{58}
$$

We then define the first centered difference operator, $\boldsymbol{D}_a^1$, which acts on some 3 dimensional array, $\mathbf{P}$, to give the array of centered differences. $\boldsymbol{D}_a^1$ is a fourth rank tensor, where index a gives the 3d array of centered differences taken in the a'th dimension.

$$
(\boldsymbol{D}_a^1(\mathbf{P}))_{i,j,k} = \frac{1}{2\Delta_a}[S_a^1(P_{i,j,k}) - S_a^{-1}(P_{i,j,k})].
\tag{59}
$$

Finally we define the second centered difference operator, $\boldsymbol{D}_{ab}^2$, as

$$
(\boldsymbol{D}_{ab}^2(\mathbf{P}))_{i,j,k} = \begin{cases} \frac{1}{\Delta_a \Delta_a}[S_a^1(P_{i,j,k}) + S_a^{-1}(P_{i,j,k}) - 2P_{i,j,k}] & \text{if } a = b \\ \frac{1}{4\Delta_a \Delta_b}[S_a^1(S_b^1(P_{i,j,k})) + S_a^{-1}(S_b^{-1}(P_{i,j,k})) \\ \quad - S_a^1(S_b^{-1}(P_{i,j,k})) - S_a^{-1}(S_b^1(P_{i,j,k}))] & \text{if } a \neq b \end{cases}.
\tag{60}
$$

We now discretise the PDE's eq(55) and eq(56) onto a three dimensional grid. We represent the discretised arrays for Ψ and $\mathbf{n}$ as the tensors $\boldsymbol{\Psi}$ and $\mathbf{N}$ respectively. $\boldsymbol{\Psi}$ then is a rank three tensor and $\mathbf{N}$ a rank four tensor, with $\mathbf{N}_\alpha$ the α component of $\mathbf{N}$, where $\alpha = 1, 2, 3$ for the x, y and z components of the vector field. The raised index inside parenthesis, (t), denotes the time step of the array tensors. Summations over repeated indices has been written explicitly for clarity. The discretised PDE's are then as follows

For the scalar field, Ψ:

$$
\frac{\boldsymbol{\Psi}^{(t+1)} + \boldsymbol{\Psi}^{(t)}}{\Delta t} = -\gamma\Big(A\boldsymbol{\Psi}^{(t)} - B(\boldsymbol{\Psi}^{(t)} * \boldsymbol{\Psi}^{(t)}) + C(\boldsymbol{\Psi}^{(t)} * \boldsymbol{\Psi}^{(t)} * \boldsymbol{\Psi}^{(t)}) + K_0 q_0^2 \mathbf{M}^{(t)} \\
- K_1 \sum_{\alpha=1}^3 \boldsymbol{D}_\alpha^1(\mathbf{B}_\alpha^{(t)}) + K_0 \sum_{\alpha=1}^3 \sum_{\beta=1}^3 \boldsymbol{D}_{\alpha\beta}^2(\mathbf{F}_{\alpha\beta}^{(t)})\Big),
\tag{61}
$$

where $*$ represents elementwise multiplication and

$$
\mathbf{M} = \sum_{\alpha=1}^3 \sum_{\beta=1}^3 \big((\boldsymbol{\delta}_{\alpha\beta} - \mathbf{N}_\alpha * \mathbf{N}_\beta) * \boldsymbol{D}_{\alpha\beta}^2(\boldsymbol{\Psi})\big) + q_0^2 \boldsymbol{\Psi}),
\tag{62}
$$

$$\mathbf{F}_{\alpha\beta} = \mathbf{M} * (\boldsymbol{\delta}_{\alpha\beta} - \mathbf{N}_\alpha * \mathbf{N}_\beta), \tag{63}$$

$$\mathbf{B}_\alpha = \mathbf{N}_\alpha * \sum_{\beta=1}^{3} \mathbf{N}_\beta * \boldsymbol{D}_\beta^1(\boldsymbol{\Psi}). \tag{64}$$

For the scalar field, $\mathbf{n}$:

$$\begin{aligned}
\frac{\mathbf{N}_\alpha^{(t+1)} - \mathbf{N}_\alpha^{(t)}}{\Delta t} = -\gamma\Big(&-2K_0 \mathbf{M}^{(t)} * \sum_{\beta=1}^{3} \mathbf{N}_\beta^{(t)} * \boldsymbol{D}_{\alpha\beta}^2(\boldsymbol{\Psi}^{(t)}) \\
&+ K_1 \boldsymbol{D}_\alpha^1(\boldsymbol{\Psi}^{(t)}) * \sum_{\beta=1}^{3} \mathbf{N}_\beta * \boldsymbol{D}_\beta^1(\boldsymbol{\Psi}^{(t)}) - K_2 \sum_{\beta=1}^{3} \boldsymbol{D}_{\beta\beta}^2(\mathbf{N}_\alpha^{(t)})\Big).
\end{aligned} \tag{65}$$

Next time steps are solved for using vectorised NumPy arithmetic in Python. For the majority of cases, periodic boundary conditions were imposed. The arrays are written to a .vtk file after some chosen multiple of iterations. This allows for the data to be imported into the visualisation software 'ParaView'. All three-dimensional figures in section (VII.) were produced using ParaView.

VII. Simulation

With the numerical scheme detailed in section (VI.), a computer simulation of the dynamical evolution of the columnar liquid crystal phase was produced. The simulation successfully reproduced expected behaviour of the columnar phase. This includes the full coupling between Ψ and $\mathbf{n}$ - seen notably in the formation of helical columnar columns. The simulation also demonstrates crystal growth and appropriate response to external field forcing.

In this section we continue to use the notation $\boldsymbol{\Psi}$ and $\mathbf{N}$ to refer to the discretised arrays for Ψ and $\mathbf{n}$.

A. Initialisation and Seeding

In order to produce the columnar phase as desired, we must make appropriate choices for the constants in eq(55) and eq(56), and for the initialisation of the arrays $\boldsymbol{\Psi}$ and $\mathbf{N}$. One trivial example is that, to give the ordered phase, we must have $A < 0$ (otherwise the free energy minima corresponds to $\boldsymbol{\Psi} = 0$). Generally, the simulation should produce the ordered phase if all other constants in the dynamical equations are positive, provided stability criteria are met and that we initialise the arrays appropriately.

The term $\frac{K_0}{2}|(\nabla_\perp^2 + q_0^2)\Psi|^2$ in the free energy (eq(12)) penalises variations with wavenumbers not equal to q_0. By seeding Ψ with a hexagonal lattice with the appropriate lattice spacing, we can introduce variations in the scalar field with this wavenumber. The full Fourier modes corresponding to the hexagonal lattice can then grow, as the system minimises the contributions to the term $|(\nabla_\perp^2 + q_0^2)\Psi|^2$. In fact, seeding Ψ with only random noise (which can in theory introduce any Fourier modes with wavelengths from the grid spacing to the domain length) will result in the formation of the hexagonal crystal lattice, provided the coefficient K_0 is large enough. It is, however, still fruitful to develop methods for seeding with a lattice directly as this enables the system to rapidly form a columnar phase without deformations. (Generally, the system will form columns around seeded points quickly. The timescales on which deformations and defects, such as grain boundaries, relax are much longer, and so if a well structured lattice is desired it is often best to seed it.) It is also interesting to seed only part of Ψ with a lattice as it is then possible to study the growth and propagation of the columnar crystal, see section (VII.B.).

A straightforward method to seed a hexagonal lattice is to simply alter, in some way, those points in Ψ that map most closely to the sites of a discrete Bravais lattice. For example, suppose we have a finite hexagonal lattice described by $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit lattice vectors of the hexagonal lattice, and n_1 and n_2 are integers over some chosen range. We change the value of the elements $\Psi_{i,j,k}$ that satisfy $(j,k) \approx d(R_x, R_y)$, for some lattice spacing d (as seen in Fig.4(a)). This simple initialisation provides enough structure for the simulation to rapidly form ordered columnar columns around the initialised region.

When lattice spacing, d, approaches the grid size (typically $d < 4\Delta x$), or when the number of seeded sites is too small, errors introduced in the mapping of the lattice to the discretised grid can prevent the forming of the proper structure. It is, in these cases, preferable to instead initialise Ψ with the entire fundamental set, eq(8). To introduce the desired Fourier modes the lattice spacing should satisfy $q_0 = \frac{4\pi}{d\sqrt{3}}$, for a hexagonal lattice.

B. Crystal Growth and Fourier Spectra

The examples in this subsection have the director field initialised and fixed to point uniformly along the column direction, $\mathbf{n} = \hat{\mathbf{e}}_z$. Since the initialisation introduces no gradients in Ψ along the columns, coupling plays no role. This allows us to focus on the
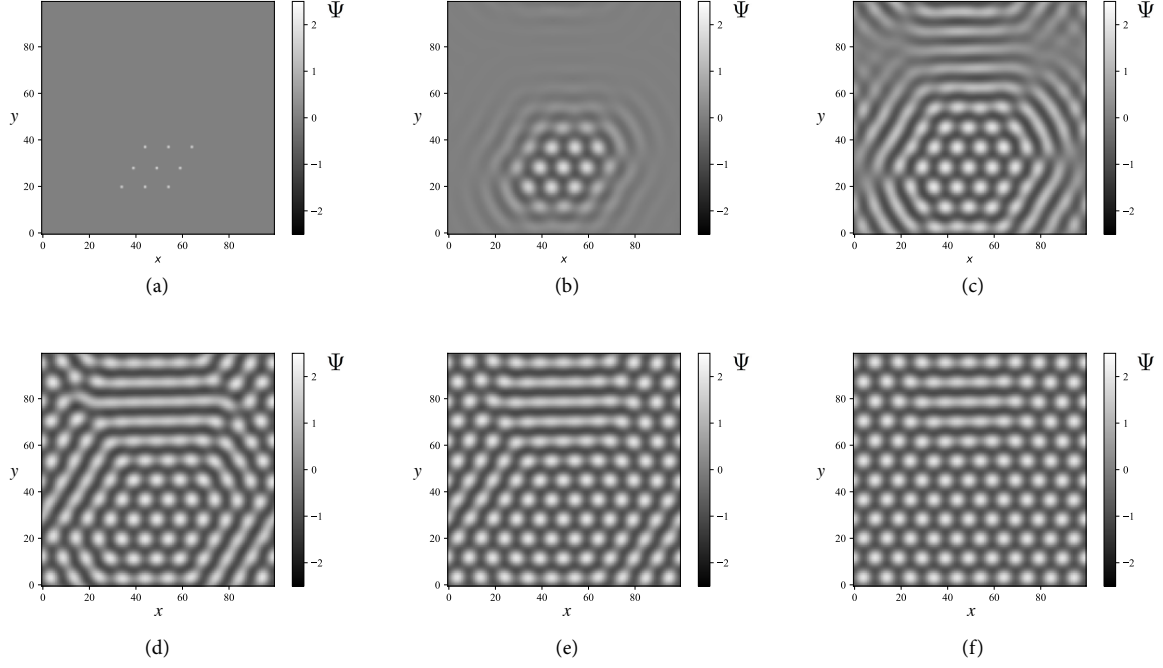
Figure 4: The time evolution of a cross section of the density array $\mathbf{\Psi}$. Grid size: 100×100. $\Delta x = \Delta y = 1$, therefore the length scales shown on the axes also represent the grid points. Director field $\mathbf{N}$ is held fixed in the form $\mathbf{n} = \hat{\mathbf{e}}_z$, so that coupling plays not role. (a) Iteration 0. Seeding with a map from the hexagonal Bravais lattice with lattice spacing $d = \frac{4\pi}{q_0\sqrt{3}}$. Array elements that map closely to lattice points are altered. (b) Iteration 2800. Density waves form rapidly around seeded region and begin to propagate. (c) Iteration 5000. Crystal growth can be seen to wrap around the grid due to periodic boundaries. (d) Iteration 10000. Grain boundaries form. (e) iteration 150000. Grain boundaries and defects relax but are still present. (f) Iteration 20000. Hexagonal lattice is well formed but some non-uniformities persist beyond these timescales.

formation of the 2d lattice structure in the plane normal to $\mathbf{n}$. Figures in this subsection represent cross sections taken in this plane.

As mentioned in the previous subsection, if we initialise only part of $\mathbf{\Psi}$ with a hexagonal lattice, the time evolution of the columnar phase should show the growth of the columnar crystal over the rest of the grid (naturally when in the ordered state the free energy is minimised by having the crystal formed everywhere). The simulation successfully demonstrates this behaviour, see Fig.4. When crystal domains meet, grain boundaries can be seen to form (Fig.4(d)). The timescale over which these fully relax is generally very large relative to that of other system behaviour.

We see in figure 4(a) and (b) that the expected density waves form rapidly around the seeded region. To examine the evolution of Fourier modes it is perhaps better to initialise the entire grid with the fundamental set, eq(8), using some small value for the initial amplitude, $\psi_{\mathbf{G}}$, that is far from the equilibrium value. This initialisation is shown in figure 5(a) where we have included the addition of random noise. The six corresponding
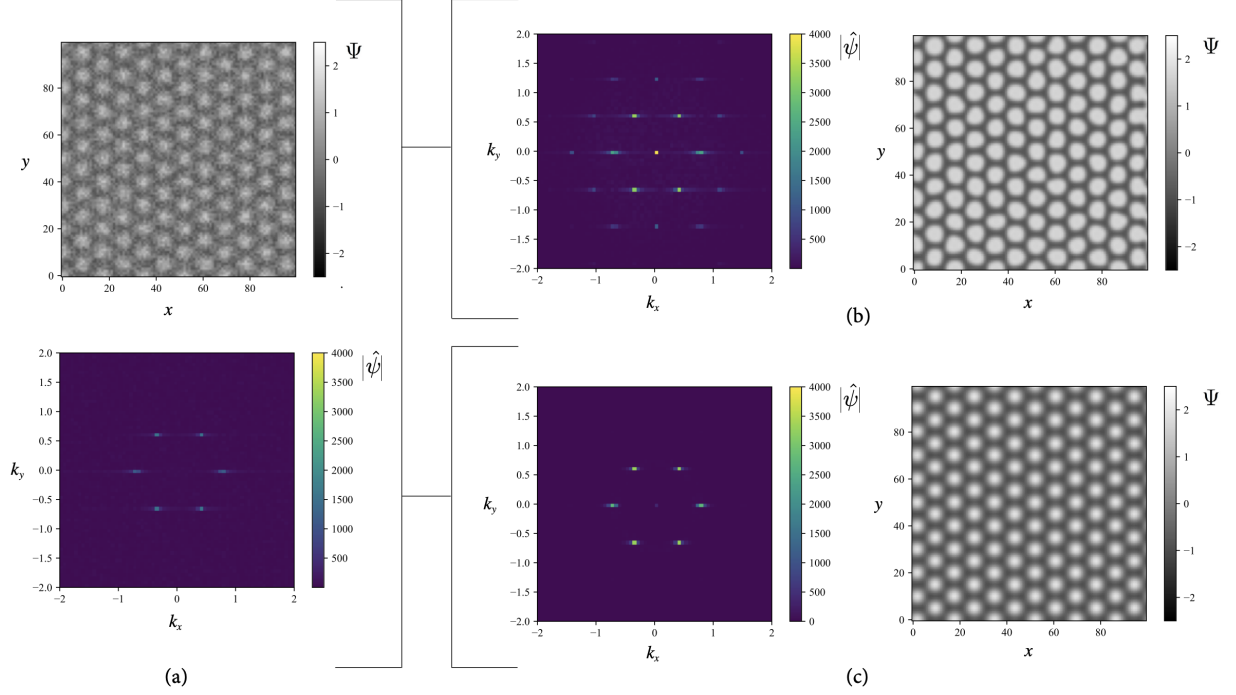
Figure 5: Two examples of Fourier mode evolution from the same initialisation. Grid sizes: 100×100. $\Delta x = \Delta y = 1$, therefore the length scales shown on the axes also represent the grid points. Grey-scale figures show cross sections of $\boldsymbol{\Psi}$ in the plane normal to the column direction. Colour figures show the absolute value of the Fourier transform of this cross section, $|\hat{\psi}|$. $\mathbf{N}$ is held fixed at $\mathbf{n} = \hat{\mathbf{e}}_z$. (a) Iteration 0. Initialisation with fundamental set and random noise. Fourier modes corresponding to the reciprocal lattice are visible but faint. (b) Iteration 2400 with K_0 chosen to be small ($K_0 = 0.4$). $\boldsymbol{\Psi}$ maintains hexagonal structure but harmonics beyond the fundamental set are not properly suppressed. This is seen explicitly the Fourier transform (left) and manifests as a 'softening' of the hexagonal lattice in $\boldsymbol{\Psi}$ (right). (c) Iteration 2400 with larger value for K_0 ($K_0 = 20$). This is sufficient to effectively suppress all but the fundamental set, as seen in the Fourier transform of $\boldsymbol{\Psi}$ (left). This results in a well ordered hexagonal lattice in $\boldsymbol{\Psi}$ (right). Lattice separation d is 10 units. Wavenumber q_0 seen in the Fourier transform satisfies the relation $q_0 = \frac{4\pi}{d\sqrt{3}}$.

Fourier modes are then represented faintly in the Fourier transform of $\boldsymbol{\Psi}$. Figure 5(b) demonstrates the evolution of the system with a small value for the elastic constant, $K_0 = 0.4$. Though sufficient to maintain a hexagonal lattice structure, the K_0 term cannot effectively suppress higher harmonics of the reciprocal lattice, which grow appreciably and can be seen in the Fourier transform. This manifests in a softening of the lattice structure in $\boldsymbol{\Psi}$. We repeat the simulation with a factor of 50 increase in the value of the elastic constant, $K_0 = 20$ (Fig.5(c)). The Fourier modes grow rapidly to the equilibrium values. The timescales over which this happens are generally much shorter than that of any other system behaviour. All modes but the fundamental set are suppressed effectively, resulting in a well defined hexagonal lattice in $\boldsymbol{\Psi}$. This demonstrates the expected behaviour from the term $\frac{K_0}{2}|(\nabla_\perp^2 + q_0^2)\Psi|^2$.

In the limit of large K_0 we can expect all Fourier modes with wavenumbers not equal

to q_0 to be crushed. We should therefore be able to recover the equilibrium value for $\psi_{\mathbf{G}}$, in this limit, by substituting the fundamental set, eq(8), into the functional

$$F = \int d^3x \left(\frac{A}{2} \Psi^2 - \frac{B}{3} \Psi^3 + \frac{C}{4} \Psi^4 \right), \tag{66}$$

and minimising with respect to $\psi_{\mathbf{G}}$.

C. Coupling of Ψ with the Director Field

In the previous section, the behaviour demonstrated was under a uniform director field, which was set to align with the columns initialised in $\boldsymbol{\Psi}$. In order to demonstrate the full behaviour of the coupling between the fields, we now introduce some frustration by initialising $\mathbf{N}$ so as to be misaligned with the columns.

First we hold $\mathbf{N}$ fixed with some deformation in order to examine the dependence

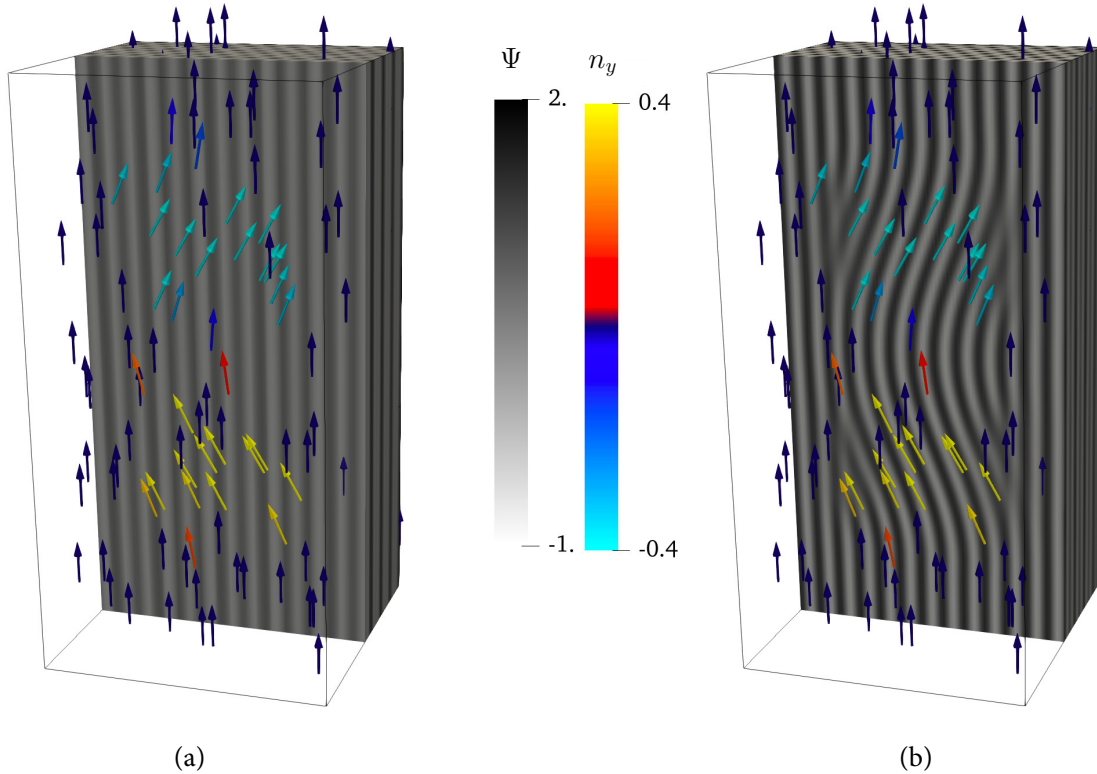(a)   (b)

Figure 6: Cross section of grid at iteration 0 (a) and 6000 (b). Grid dimension: 160×80×80. Glyphs represent random samples of the director field, which is held static in the form $\mathbf{n} \approx \sin(kz)\hat{\mathbf{e}}_y + \hat{\mathbf{e}}_z$ within a centered internal region of size 140×60×60, and $\mathbf{n} = \hat{\mathbf{e}}_z$ elsewhere. k is chosen to give one period. We initialise with the fundamental set (a), and watch the deformation grow. (b) represents near equilibrium, where columns lie for the most part along the director. Note the columns themselves appear more defined (higher contrast) in (b) due Fourier amplitudes growing from the initialisation value.
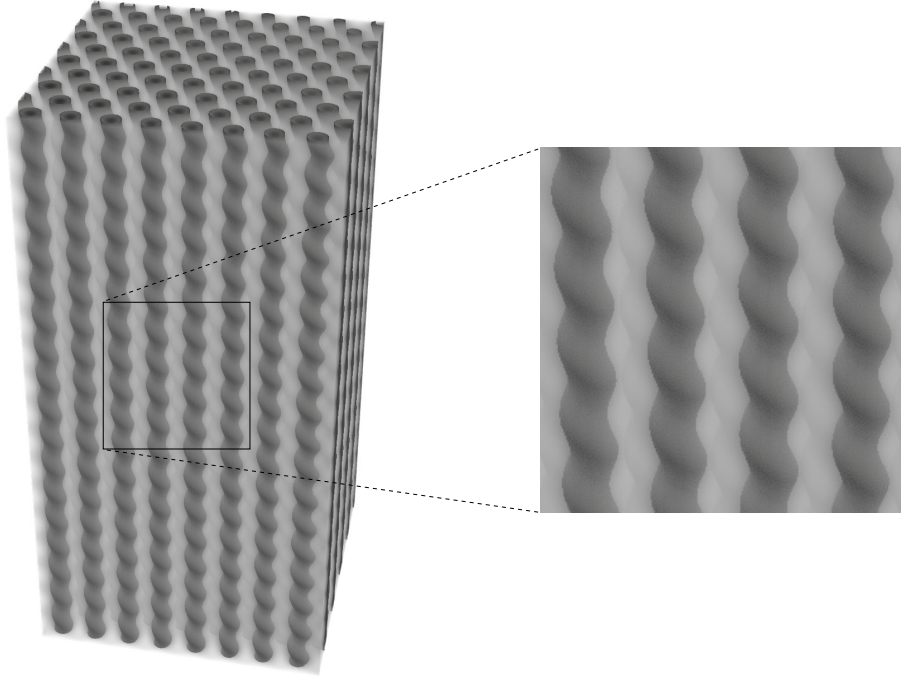
Figure 7: Helical columns resulting from constraints on the director field. Grid size: $200\times100\times100$. We show a contour plot of $\mathbf{\Psi}$, superimposed on a volume filter. This allows us to clearly isolate the form of the columns. The simulation reproduces the expected result from the literature [10].

of $\mathbf{\Psi}$ on the director. The equilibrium state now corresponds to some energetic balance between minimising gradients in $\mathbf{N}$ and maintaining the lattice structure. The coupling of $\mathbf{\Psi}$ to $\mathbf{N}$ in the simulation continues to behave as expected under these frustrations, see Fig.6. See also Fig.7 for a notable example, where the columns form the expected helices associated with the chiral director field, $\mathbf{n} = \sin(\theta)[\cos(kz)\mathbf{e}_x + \sin(kz)\mathbf{e}_y] + \cos(\theta)\mathbf{e}_z$ [10].

Of course, for the complete simulation of the columnar phase we must include also the dependence of $\mathbf{N}$ on $\mathbf{\Psi}$. We should expect the K_0 and K_1 terms to encourage the alignment of $\mathbf{n}$ normal to any gradients in Ψ, that is to say, along the local column direction as defined by the values in $\mathbf{\Psi}$. We also included the Frank free energy term with coefficient K_2. This should penalise all spatial gradients in $\mathbf{N}$ and act to relax any deformations in the director. When including the gradient descent of $\frac{\delta F}{\delta \mathbf{n}}$ the simulation demonstrates exactly this behaviour, and so fully realises the coupling of $\mathbf{\Psi}$ to $\mathbf{N}$, with the appropriate Frank free energy contribution.

To summarise, the simulation of the columnar phase demonstrates the full two way dependency of the fields Ψ and $\mathbf{n}$. The fact that we see the expected behaviour not only

verifies that the numerical scheme was appropriate, but crucially it suggests that the Landau theory developed in section (IV.) describes the phase as intended.

D. Constraints and Coupling to External Fields

Generally, when simulating the columnar phase we have been initialising $\mathbf{\Psi}$ and $\mathbf{N}$ with some frustration. The resulting evolution of the phase (if including the time evolution of the director) tends to show a relaxation to a uniformly ordered state. By imposing constraints on the system we can instead force the equilibrium state to be frustrated. (Fig.6 and Fig.7 show equilibrium under constraints on the director field.) We want to study frustrated equilibrium states without 'turning off' the time evolution of $\mathbf{\Psi}$ or $\mathbf{N}$. We could, for example, introduce constraints in the form of Dirichlet boundary conditions.

When studying deformations in equilibrium it can be useful to include some additional forcing to the system. This allows us to initialise without deformations and then create the deformed state by applying this forcing. The system then evolves towards an equilibrium configuration that represents a balance between the external forcing and the tendency for uniform order, subject to the imposed constraints.

One particularly interesting and well studied property of liquid crystals is their response to external electric and magnetic fields. We can model the interaction as a coupling with the director field, having an associated energy contribution $-\frac{\epsilon}{2}(\mathbf{E} \cdot \mathbf{n})^2$, where the external field $\mathbf{E}$ is here an electric field, and ϵ the dielectric anisotropy of the constituent columnar molecules [1, 2]. $\epsilon > 0$ favours alignment of the director field with $\mathbf{E}$.

We include $-\frac{\epsilon}{2}(\mathbf{E} \cdot \mathbf{n})^2$ when solving for the functional derivative $\frac{\delta F}{\delta n^\alpha}$. The resulting contribution to our gradient descent of $\mathbf{n}$ is in the amount $-\epsilon(E^\alpha E^i n^i)$.

In the simulation the coupling to $\mathbf{E}$ demonstrates the expected behaviour, showing a forcing on $\mathbf{n}$ to align along $\mathbf{E}$ when the dielectric anisotropy is positive. This enables further study of deformations and extends to the study of elastic instabilities in columnar phases when subject to external fields [11].

E. Further Applications and Future Work

Up to this point, it has been demonstrated that the simulation appears to successfully reproduce the behaviour of the columnar phase. There remains, however, a wealth of interesting phenomena associated with the phase that we have yet to explore and reproduce.

The implementation of external field coupling was successful. This should enable the simulation of the Helfrich-Hurault elastic instability in the columnar phase, for which there exists a prediction of the associated deformations wavenumber [11]. Reproducing this result would further validate the accuracy of our model and simulation, and could provide invaluable insight into the nature of the instability, about which there remains many unanswered questions [1, 11]. Finding the appropriate initial conditions to reproduce the instability has proved challenging, but should be achieved with more experimentation. We also expect that our simulation should reproduce buckling instabilities that occur in columnar phases when subject to strain [12]. It may be possible to simulate the appropriate strains by imposing constraints on the wavenumber of the crystal lattice.

VIII. Conclusion

To summarise, we have introduced a new theoretical model describing the columnar phase in terms of a spatially modulating density coupled to nematic ordering, eq(12). This was developed in the form of a Landau theory for the nematic to columnar transition. Using this model, we successfully reproduced the known result for the linear elasticity of uniaxial solids [7]. We then developed a numerical code for the simulation of the dynamical behaviour of the columnar phase, using gradient descents of the free energy derived in our model, eq(55) and eq(56). The resulting simulation demonstrated a full realisation of the intended coupling between the density and director fields, and successfully reproduced the expected behaviour of the columnar phase. This includes the formation of chiral structures under an appropriately constrained director field [10]. We also successfully incorporated coupling of the director to external fields, which enables further work on elastic instabilities including the reproduction of the Helfrich-Hurault instability [13].

The simulation could, in its own right, prove an invaluable tool in furthering the understanding of columnar liquid crystals, but, perhaps more importantly, its success validates our theoretical model.

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