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# Normal Complex Tensor Order Parameter for Smectics in 3D

MPhys Project Report

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## **Abstract**

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Supervisor: Tyler N Shendruk

**Personal statement**

**Acknowledgments**

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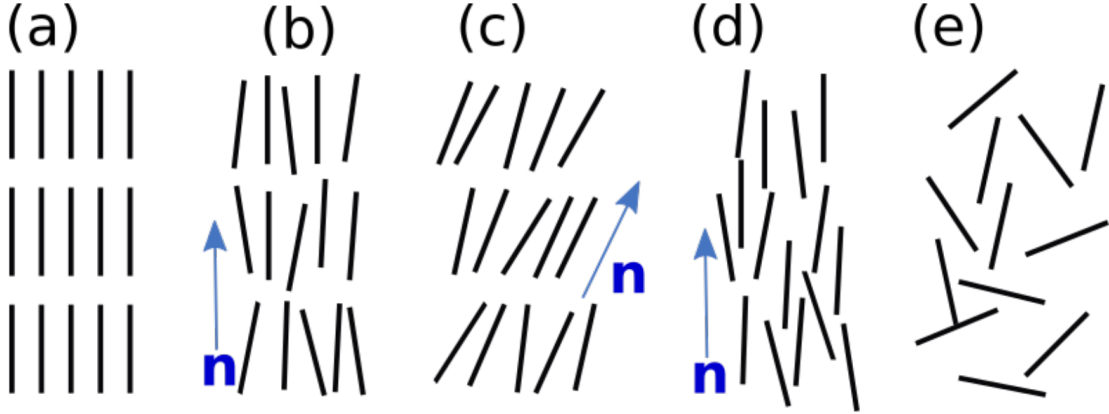


Figure 1. Illustrative structures of a substance made up from rod-like molecules. In order from (a) to (e) they are a fully crystallized phase, a smectic A, smectic C, nematic and an isotropic liquid.

## 1 Smectic Liquid Crystals

All, physicists will be well familiar with the ordered crystalline phase, in which the relative positions and possibly orientation of molecules is ordered, predictable and often repeating. Liquid crystals (LC) lay between this state and a typical liquid, some aspects of the phase are ordered, but others are not. This is best illustrated as a transition from an unordered (isotropic) liquid state as in fig. 1.

In an isotropic liquid the molecules have random, uncorrelated positions and orientations. Note that we talk about orientations, these are naturally only present if the molecules themselves are not spherical/symmetric. Depending on just how asymmetric they are they can have one or two orientation directions (in 3D), here we mainly look at rod-like molecules which have one, the axis of symmetry. The first step in ordering is usually a transition to a nematic liquid crystal in which the orientations of nearby molecules align, see fig. 1. An important detail of nematic liquid crystals is that the constituent molecules are symmetric along their length as well (there is no head and tail) as this changes the physics, a nematic phase which does not have this symmetry is called a polar nematic.

Next can come partial positional order, while different classification exist, in essence there are two ways this can happen in 3D. Either the symmetry is broken along one axis, these are the smectic phases, or along two in the columnar phases[1]. In the columnar phases there remains only local one direction along which the system is not ordered. As such these phases are composed of separated columns of flowing liquid which are at ordered positions much like a 2D crystal. In the smectic phases, a broken symmetry along one axis results in a layered structure, the system is isotropic and flows within the layers but is organized along the layer normal. As such, smectics are fundamentally a layered phase, and that is what we focus on in this project, in essence we create a mesoscopic model for layering.

There are various types of smectic phases, the simplest being the smectic A and C shown in fig. 1. It is worth pointing out that the smectic layering coexists with a nematic order of the molecules. In smectic A phases the nematic orientation is always perpendicular to the layering, whereas in smectic C phases these are at an angle. Besides these there is a class of hexatic smectic phases, in which the molecules within layers locally arrange in a hexagonal lattice. However, while the lattice itself is only maintained for short distances, these local hexatic lattices have an orientation to them as well and this is aligned over large distances. Thus these feature yet more order than the smectic A and C phases, they include the  $B_{\text{hex}}$  phase which has the nematic director perpendicular to the layering, along with the F and I phases which have an angle between the two. There are also smectic-like crystals which feature fully ordered often hexatic layers, among these are the B and E phases. For more details on these structures see [1–3].

This could be extended pretty much indefinitely, given the twist data we have perhaps the TGB would be the next thing worth mentioning

Paragraph on why are they important/useful etc, the usual are soap, displays and hopefully something new? Bacteria! that might need a citation

The model presented in this thesis is in its early stages and so we mainly aim to capture the physics of the A and perhaps C phases. Though as we have extended the model into 3D it further highlighted that it captures the general concept of layers, and it does not currently have any concept of the underlying nematic order of smectics. There is a way to add that and it is perhaps the next step in developing this theory, however it also shows that the model might be used in other fields which require a mesoscopic model for layering.

I don't like this paragraph but want to mention some of it somehow

## 1.1 Ginzburg-Landau theory and the nematic $\underline{\underline{Q}}$ tensor

Ginzburg-Landau theory is a powerful recipe to build phase transition theories, the work in this thesis being one of them. As such we start by introducing these on the example of an isotropic liquid to nematic LC transition for two reasons. Because nematic order often underlays smectic order and so the two need to be considered simultaneously, and because the  $\underline{\underline{Q}}$  tensor theory for nematics has heavily inspired the  $\underline{\underline{E}}$  tensor theory for smectics this thesis is based on.

### 1.1.1 The order parameter

The central concept of Ginzburg-Landau theory is the order parameter, this is usually some mathematical object such as a scalar, vector or tensor that has known values for each of the phases and varies in between them in mostly a smooth manner. If a single order parameter is used to describe the entire system in question as a whole, it is a Landau theory, one can extract useful information using this alone. However, Ginzburg-Landau theory goes a step

further and promotes the order parameter to a field. This way one may have a part of the system be in one phase and a different part in the other.

Going back to our example of a nematic LC, this order parameter needs to capture how aligned the molecules are at each point, accounting for the nematic symmetry. The way to do this is using the  $\underline{\underline{Q}}$  tensor which can be obtained from a system of discrete molecules via

$$\underline{\underline{Q}}_{\text{mol}} = \underline{N}_{\text{mol}}\underline{N}_{\text{mol}} - \frac{\delta}{d} \quad (1)$$

where  $\underline{N}_{\text{mol}}$  is a unit vector denoting the orientation of a molecule,  $\underline{\delta}$  the identity and  $d$  the dimensionality of the system (2 or 3). Throughout this thesis, if two tensors appear side by side then it means a dyadic/tensor product and any contractions are denoted by dots  $\cdot$  (their order usually does not matter). Note that  $\underline{\underline{Q}}_{\text{mol}}$  immediately satisfies the nematic symmetry of to  $\underline{N}_{\text{mol}}$  being the same as  $-\underline{N}_{\text{mol}}$ . So each molecule has a  $\underline{\underline{Q}}_{\text{mol}}$  and we take a local average of these to arrive at the tensor field  $\underline{\underline{Q}}$  (taking these local minima numerically can be quite tricky). Given the form of  $\underline{\underline{Q}}$  we can then reexpress it as the following

$$\underline{\underline{Q}} = S \left( \underline{N}\underline{N} - \frac{\delta}{d} \right) + \text{possibly more terms, ignore for simplicity here} \quad (2)$$

where  $S$  is a number between 0 and 1,  $\underline{N}$  is a unit vector and both are fields along with  $\underline{\underline{Q}}$ . From there it is easy to see that an isotropic liquid would have  $\underline{\underline{Q}} = S = 0$  and a fully nematic one would have  $S = 1$  and  $\underline{N}$  be the orientation of the phase. From this it is clear that  $\underline{\underline{Q}}$  is a valid order parameter to describe the isotropic to nematic transition, it is in fact the most widely used such parameter due to it respecting the orientational symmetry.

### 1.1.2 The free energy density and deformations

Now that we have an order parameter, the next step in forming a Ginzburg-Landau theory is to find a suitable free energy, physics then follow through minimization of it. This will be a volume integral of a free energy density  $f(\underline{r})$  over the system and potentially surface contributions  $\mathcal{F}(\underline{r})$

$$F = \int f(\underline{r})dV + \int \mathcal{F}(\underline{r})dS \quad (3)$$

though the surface is often dealt with separately.  $f(\underline{r})$  should only depend on the order parameter  $\underline{\underline{Q}}$  and elastic constants, it must be local, and crucially it must maintain any symmetries of the system[4, 5]. This can be done in two ways, if one know the underlying microscopic interactions then these can be coarse-grained to obtain  $f(\underline{r})$ . However, this can be very difficult or not possible at all, and one might not know all the microscopic interactions. This is where the power of Ginzburg-Landau theories lays as one may instead start taking all possible symmetry-allowed terms of  $f(\underline{r})$  increasing in power of the order parameter and stop once all the physics is captured.

In the example of  $\underline{\underline{Q}}$ , that already contains the  $\underline{N} \leftrightarrow -\underline{N}$  symmetry and the bulk free energy density (which does not account for gradients) should only depend on  $S$  as it should be the

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Figure 2. Diagrams of the splay, twist and bend nematic deformation types respectively. Image taken from [8].

same regardless of the orientation direction. As such we have  $f_{\text{bulk}}(r)$  being a power series of  $S$  and given eq. (2) that translates to a series of suitably contracted terms of  $\underline{Q}$ . Generally, the following form is used

$$f_{\text{bulk}}(r) = \frac{a}{2} \text{Tr}(\underline{Q}^2) - \frac{b}{3} \text{Tr}(\underline{Q}^3) + \frac{c}{4} \text{Tr}(\underline{Q}^2)^2 = \frac{a}{2} Q_{ij} Q_{ij} - \frac{b}{3} Q_{ij} Q_{jk} Q_{ki} + \frac{c}{4} Q_{ij} Q_{ij} Q_{kl} Q_{kl} \quad (4)$$

where  $b$  and  $c$  are positive constants and  $a$  can have either sign, the terms correspond to  $S^2$ ,  $S^3$  and  $S^4$  terms[6, 7]. The repeated indices in the second form of eq. (4) being Einstein summation indices which are assumed throughout this thesis unless otherwise specified. This form can have one or two minima for  $S \geq 0$ , this is determined by the coefficients which are set relative to a critical temperature or concentration. Without going through the details, generally one takes enough terms to allow for a suitable number of minima (each of which corresponds to a stable or metastable phase), then one extra term with a positive coefficient is added to make sure that  $f_{\text{bulk}}(r)$  keeps growing at very large order parameter.

However,  $f_{\text{bulk}}(r)$  does not account for any deformation energy costs, which is naturally a key ingredient to describing a system. To add these we introduce terms to  $f(r)$  which depend on the gradients of the order parameter. This gets more complex, though the same rule still applies, take as many allowed terms in increasing powers of the order parameter and  $\underline{\nabla}$  as is needed. However, here finding the correct form can get tricky and one generally starts considering specific geometries of the system and what their deformation terms should be like. If one is to work analytically or on a constrained system, it might also be that certain terms are negligible and others are not, as such, which terms are used varies in literature.

For the nematic case, in the simplest case of constant  $S$  but varying  $\underline{N}$  we get the Frank-Oseen deformation energy terms[3, 6, 9]

$$K_1(\underline{\nabla} \cdot \underline{N})^2 \quad K_2(\underline{N} \cdot \underline{\nabla} \times \underline{N})^2 \quad K_3(\underline{N} \times \underline{\nabla} \times \underline{N})^2 \quad (5)$$

where the  $K$ s are positive elastic constants. These three terms correspond to three type of deformation of the director  $\underline{N}$ : splay, twist and bend respectively, as shown in fig. 2. Adapting these to be in terms of  $\underline{Q}$  has proven difficult, first attempted by de Gennes[3] using the terms

$$L_1 Q_{ij,k} Q_{ij,k} \quad L_2 Q_{ij,j} Q_{ik,k} \quad L_4 \epsilon_{ijk} Q_{il} Q_{jl,k} \quad (6)$$

is this okay?



with  $L_s$  being elastic constants and  $\epsilon$  the Levi-Civita tensor. However, these have later been shown to imply  $K_1 = K_3$ [10], which is contradicted by experiment. Since then additional terms have been added to account for this[11] though that is going beyond the scope of this summary. What is worth noting however is the one constant approximation, where all the  $K$  elastic constants are taken to be equal which leads to all the terms collapsing to

$$L_1 Q_{ij,k} Q_{ij,k} \quad (7)$$

While this is the simplest possible approximation, it has been used widely for both numerical and analytical studies, and historically it has been the starting point before the different terms have all been discovered. In many ways it highlights the idea of Ginzburg-Landau theory in that it is the simplest possible term one can construct using  $\underline{\underline{Q}}$  and  $\underline{\nabla}$  and it captures all the possible deformation terms. In the work on smectics presented in this thesis we start from a similar approximation, still using it but also trying to go a step beyond and develop more specific terms which collapse to the approximation.

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true...

### 1.1.3 Biaxiality of $\underline{\underline{Q}}$

There is one additional bit of complexity worth introducing and that is biaxiality of nematics. We have been talking about the orientation of molecules as being a single direction, which is correct for rod-like molecules. However, if the molecules are completely asymmetric then there can be order in two perpendicular directions. Say we have long cuboid molecules, they can first order by aligning their longest axes and then also rotate around those axes so that the next longest axes also align. The same applies to any asymmetrical shaped molecules in 3D.

It demonstrates the power of  $\underline{\underline{Q}}$  that we can still use it to describe this dual order, we can still calculate it exactly the same way through  $\underline{\underline{Q}}_{\text{mol}}$  and  $\underline{\underline{Q}}$  will still be symmetric and traceless, however we now allow it to take the more general form

$$\underline{\underline{Q}} = S_1 \left( \underline{\underline{N}} \underline{\underline{N}} - \frac{\delta}{d} \right) + S_2 \left( \underline{\underline{M}} \underline{\underline{M}} - \frac{\delta}{d} \right) \quad (8)$$

where  $\underline{\underline{N}}$  and  $\underline{\underline{M}}$  are mutually orthogonal unit vectors which describe the directions of the two orders, with  $S_1$  and  $S_2$  acting as their corresponding order parameters.

This needs more, cite/use[7] mention how final states for uniaxial nematics have a uniaxial  $\underline{\underline{Q}}$  even when using eq above, aka  $S_2 = 0$ , though I need a thing to cite for that

## 1.2 Describing smectics[2]

Fundamentally, the layered positional order corresponds to a wave-like density fluctuation. Following [2] in the approach suggested by de Gennes, if we first only consider a single wave throughout the entire system, then the density field is

$$\rho(\underline{r}) = \rho_0 + \rho_1 \cos(\underline{q_0} \cdot \underline{r} + \phi) = \rho_0 + \text{Re}(\rho_1 e^{i(\underline{q_0} \cdot \underline{r} + \phi)}) \quad (9)$$

where  $\rho_0$  is the average density,  $\rho_1$  is the wave amplitude,  $\phi$  an arbitrary phase (determined by boundary conditions) and  $\underline{q}_0$  its wavevector containing both the wave direction ( $\underline{N} = \frac{\underline{q}_0}{q_0}$  being the layer normal, the smectic director) and spacing ( $\frac{2\pi}{q_0}$ ). This is a very simple start, however already one can take  $\rho_1$  as an order parameter (not a field here, making this a Landau theory) with 0 corresponding to no wave and so an isotropic liquid. To then build a bulk free energy in terms of  $\rho_1$  we need to identify any symmetries. The only relevant symmetry here is that of  $\rho_1 \leftrightarrow -\rho_1$  as such a change only leads to a change in the phase  $\phi$  which is not a physical change. Such a change would keep the same wave amplitude and spacing and as such the smectic phase is unchanged and so should be its free energy. The implication of this is that the free energy may only have even power terms of  $\rho_1$  becoming

$$F_{\text{bulk}} = \frac{A}{2}\rho_1^2 + \frac{B}{4}\rho_1^4 + \frac{C}{6}\rho_1^6 + \quad (10)$$

with  $A, B, C$  being constants which determine the order of the isotropic-smectic phase transition[2].

The natural next step is to promote  $\rho_1$  to a field and the free energy to a free energy density, this leads to equivalent bulk terms but also deformation terms. In that case the layering direction and spacing is uniform throughout the system, however the ordering can be perfectly smectic or perfectly isotropic in different areas. To account for local changes to layering direction and spacing one must allow some part of the phase of eq. (9) to change in space.

Different choices can be made in that regard, the first and most commonly used being to keep  $\underline{q}_0$  constant but make  $\phi$  a field. This allows the layers to locally contract, dilate and tilt in small magnitudes as the phase changes through  $\phi$ . This is a particularly good approach to study near equilibrium configurations, their stability and energetics as it contains enough information yet is simple enough for analytical work. Going a step further,  $\underline{q}_0$  need not be constant throughout the system as long as we keep it fixed in time. This way more interesting geometries can be studied through an imposed  $\underline{q}_0$  and solving for  $\rho_1$  and  $\phi$ .

It is worth elaborating a little on what exactly  $\phi$  means once we have made it a field. It is difficult to quantify how exactly it may alter the layering direction and so we do not discuss that here, however there is a clear correspondence between gradients in  $\phi$  and contractions and dilations. For simplicity, consider a 1D system with  $\phi = sx$  where  $s$  is a constant gradient, then clearly we have  $e^{i(q_0x+sx)} = e^{i(q_0+s)x}$  or in other words we simply have a modified wavelength of  $\frac{2\pi}{q_0+s}$ . For a more complex example see fig. 3 where we have a spherically symmetric setup of  $\underline{q}_0 = \frac{2\pi}{2L}\hat{r}$  with  $L$  being an arbitrary unit of length and

$$\phi(r) = \begin{cases} 0 & \text{if } r \leq 5L \\ s(r - 5L) & \text{if } r \geq 5L \end{cases} \quad (11)$$

In other words,  $\phi$  has a constant gradient of  $s$  in the layering normal direction for  $r \geq 5L$  which results in a constant change to layer spacing. The key point here being that gradients of  $\phi$  in the direction of layering correspond to contractions and dilations.

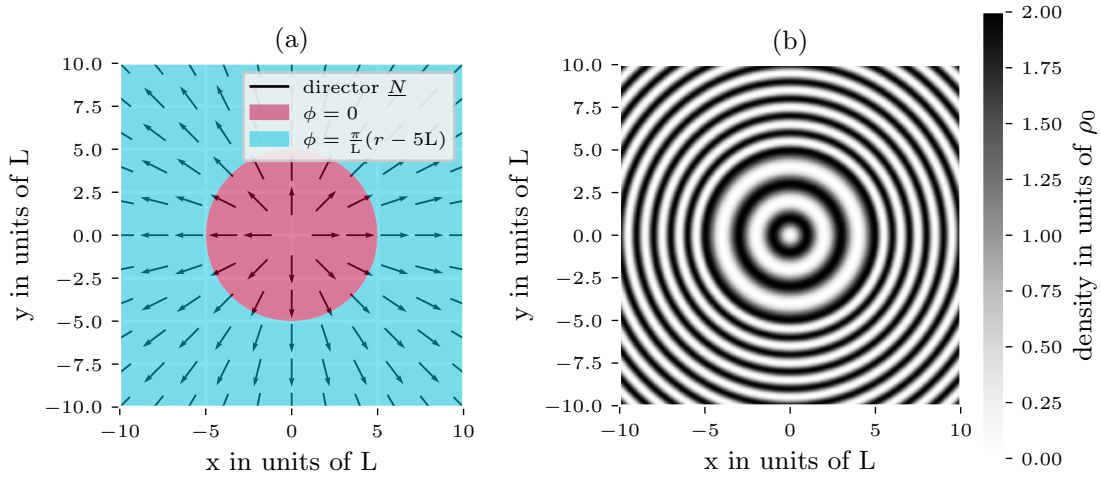


Figure 3. Diagrams of how eq. (9) behaves for a 2D, spherically symmetric system with a non-uniform but fixed  $q_0 = \frac{2\pi}{2L}\hat{r}$ , constant  $\rho_1 = \rho_0$  (so a fully smectic phase) and  $\phi$  given by eq. (11) with  $s = \frac{\pi}{L}$ .  $L$  here is an arbitrary unit of length. (a) shows the layer normal direction  $\underline{N}$  and highlights the two zones for  $\phi$ . (b) shows the resulting density having constant wavelengths of  $2L$  and  $\frac{2\pi}{\frac{2\pi}{2L} + \frac{\pi}{L}} = 1L$  in each of the zones from (a).

In these approaches a complex order parameter  $\psi = \rho_1 e^{i\phi}$  is used to simplify eq. (9) to  $\rho(\underline{r}) = \rho_0 + \text{Re}(\psi(\underline{r})e^{iq_0 \cdot \underline{r}})$ , this is known as the de Gennes order parameter. In essence, it replaces the degrees of freedom of two real parameters by a single complex one. It is using this theory that de Gennes has demonstrated an analogy between smectic liquid crystals and superconductors[12], a particularly fruitful contribution leading to better understanding of the twist-grain boundary phase[13] among others.

### 1.3 Smectic (and nematic) defects

### 1.4 Limitations of $\psi$ and the $\underline{N} \leftrightarrow -\underline{N}$ symmetry

The theoretical framework described in section 1.2 has been very successfully used since the second half of the 20th to understand many of the smectic and other liquid crystalline phases. However, it also comes with some significant shortcomings, two of which have been highlighted by Pevnyi, Selinger and Sluckin in 2014[14] and which have sparked renewed interest in smectic studies. As a response a new smectic order parameter  $\underline{E}$  has been developed along with a corresponding free energy form by Paget et al[15, 16] and this thesis continues that work.

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The main issue arises when studying the dynamics of more complex systems as when studying a how different domains may form during the isotropic to smectic transition and how they

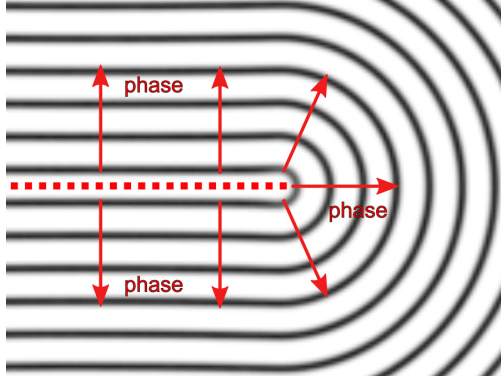


Figure 4. Diagram of a  $+\frac{1}{2}$  defect in the smectic phase to demonstrate the double-valuedness of the de Gennes complex order parameter, taken from [14]. Black lines correspond to smectic layers, red arrows point in the direction of increasing (or decreasing, this is a choice)  $\phi$ . Dotted red line is where the gradient of  $\phi$  discontinuously changes (this can be chosen to be elsewhere) even though the layering there is uniform.

then merge and defects annihilate[17, 18]. In these cases the mentioned approach of keeping  $q_0$  fixed and only working with  $\rho_1$  and  $\phi$  from eq. (9) cannot work. In theoretical studies this can often be circumvented by separating the system into domains manually, however this is not feasible for numerical studies. If one is to model such a complex system using a single set of fields, a slightly different complex order parameter is used which replaces all the degrees of freedom from eq. (9)[19, 20]. Mathematically this is equivalent to setting  $\underline{q}_0 = 0$  with us now having

$$\rho(r) = \rho_0 + \text{Re}(\psi(r)) \quad (12)$$

and  $\phi$  carrying all of the phase information including the layering direction and spacing. The layering wavevector can then be recovered via  $\underline{q}_0 = \underline{\nabla}\phi$  and so the layering normal direction is  $\underline{N} = \frac{\underline{\nabla}\phi}{|\underline{\nabla}\phi|}$ .

This is the order parameter that Pevnyi et al discuss and the main problem they bring up is that  $\psi$  is fundamentally double-valued, or in other words ill-defined. Why this is perhaps best shown on the example of a smectic system with a  $+\frac{1}{2}$  defect, as in fig. 4. In order to obtain such layering in the model of eq. (12) there must be an increasing or decreasing  $\phi$  perpendicular to the layering. Now consider it is increasing downwards in the bottom half of fig. 4, then as  $\phi$  ought to be smooth in the defect free region to its right and around the defect, we end up with an upwards increasing  $\phi$  in the upper region of fig. 4. This then gives a line of a discontinuous change in  $\underline{N} = \underline{\nabla}\phi$  in the middle left, along the highlighted line, which is also defect free and so any fields should be changing smoothly.

Ultimately this double-valuedness is a result of the smectic  $\underline{N} \leftrightarrow -\underline{N}$  symmetry as layering upwards and downwards is physically the same. This is exactly what we see in the left part of fig. 4 where we get  $\underline{N}$  pointing downwards in the bottom half and upwards in the upper half. The problematic middle line is unclear, however in a physical sense both directors are equivalent and the phase is continuous. This problem is not a purely formal one either,

unless accounted for it leads to unphysical line defects appearing between point defects[14] and associated unphysical energy costs. This is the key problem that  $\underline{E}$  theory aims to solve.

## 1.5 Other approaches and recent smectic results

Naturally, other approaches to these problems have been developed as well. Pevnyi et al themselves suggest working with the density directly instead of using a coarse-grained mesoscopic order parameter[14, 21–23]. There  $\delta\rho(\underline{r}) = \rho(\underline{r}) - \rho_0 = \text{Re}(\psi(\underline{r}))$  is used as the order parameter and a free energy constructed in terms of it. In essence this resolves the symmetry problem by switching to a more microscopic picture whereas  $\underline{N}$  only appears through  $\delta\rho$  as a macroscopic variable. Of course the free energy must be carefully crafted so that layering does appear, one way to do this is to relate  $\delta\rho$  to  $\psi$  and use the same free energies that have been developed for  $\psi$ [14].

Another benefit of this microscopic treatment is that individual layers in the smectic are resolved, unlike in the approaches using  $\psi$  where the focus is on the degree of ordering and layer normal direction. This is a notable feature as precise layer positioning plays a role in dislocation defects and it also allows to obtain the preferred layer spacing  $q_0$  through simulations instead of considering it as an outside parameter like in most  $\psi$  based approaches.

cref to figure of defect

However, the microscopic nature of this density-based approach is also its largest limitation at it severely limits the size of systems that can be numerically solved for. Given that the individual layers need to be captured, in a naive numerical solver many numerical grid points are needed per wavelength  $\frac{2\pi}{q_0}$ . In a comparable study using a mesoscopic order parameter only a single grid point might well be sufficient, even less in more uniform areas and perhaps more near defects.

Additionally, a completely different approach to modelling smectics has also been developed since the end of the last century based on dynamical density functional theory and phase field crystal methods[24–28]. This is a rather complex approach which starts at the individual particles, their positions, orientations and interactions and coarse-grains these. As such these at a fundamental level describe a more general liquid crystal system of non-spherical (mainly rod-like) particles which may have both nematic and smectic order. In the methods of [24] one ends up with three fields: the particle density field  $\psi_1$ , a nematic order parameter  $\psi_2$  and the nematic director field  $\underline{u}_0$ . The nematic order fields  $\psi_2$  and  $\underline{u}_0$  vaguely corresponding to the  $S$  and  $\underline{N}$  parameters from section 1.1.1.

This is a promising method, in particular when considering its generality when it comes to different types of order, physical insight and mathematical rigour. However, for simulating large mesoscopic systems it shares the same limitations of the density based methods using  $\delta\rho$ . Similarly to those, the smectic ordering is fully captured by a density field (though how that is done is very different) and so it is a microscopic picture of the smectic which limits the scope of numerical simulations.

Maybe add something about Monderkamp simulation results?

## 2 Introduction to E theory

Firstly, to revise the main objectives and motivations for E. The goal is to develop a mesoscopic order parameter for smectics (and possibly other layered systems) that is suitable for large numerical simulations. Mesoscopic meaning that it does not resolve individual layers but only their overall ordering, direction and spacing. To start, the focus is in particular on the smectic A and perhaps C phases. It follows in the approach of de Gennes by using a complex number field, however it must account for the  $\underline{N} \leftrightarrow -\underline{N}$  symmetry in order to avoid unphysical defects.

As we continue in the spirit of the de Gennes parameter, we start at the density wave equation

$$\rho(\underline{r}) = \rho_0 + \text{Re}(\rho_1 e^{i(\underline{q}_0 \cdot \underline{r} + \phi)}) \quad (9 \text{ revisited})$$

with the layer normal being  $\underline{N} = \frac{\underline{q}_0}{q_0}$ . We want to build a model capable of describing complex smectic systems, and so we require full flexibility in both the wave amplitude and phase throughout space. However, unlike previously when the entire phase of eq. (9) was replaced by a phase field  $\phi(\underline{r})$  here we keep both  $\underline{q}_0$  and  $\phi$  as they are and make them both fields. Specifically, we take the magnitude of the wavevector  $q_0$  to be a constant physical parameter (perhaps dependent on temperature or other macroscopic variables, though that is not considered here) but allow its direction  $\underline{N}$  to vary in space.

So we have three independent fields  $\rho_1(\underline{r})$ ,  $\underline{N}(\underline{r})$  and  $\phi(\underline{r})$ , and we would like to form a complex order parameter as before, though to be completely clear it is worth noting the units.  $\underline{N}$  is a dimensionless unit vector,  $\phi$  a dimensionless phase but  $\rho_1(\underline{r})$  has units of density whereas we would like the complex order parameter be dimensionless. To do that we define  $\psi(\underline{r}) = \frac{\rho_1(\underline{r})}{\rho_1} e^{i\phi(\underline{r})}$  where  $\rho_1$  is a constant with units of density which defines the amplitude of the density wave for a fully ordered smectic. This leads to

$$\rho(\underline{r}) = \rho_0 + \rho_1 \text{Re}(\psi(\underline{r}) e^{iq_0 \underline{N}(\underline{r}) \cdot \underline{r}}) = \rho_0 \left(1 + \frac{\rho_1}{\rho_0} \text{Re}(\psi(\underline{r}) e^{iq_0 \underline{N}(\underline{r}) \cdot \underline{r}})\right) \quad (13)$$

where all the fields are written explicitly,  $\psi$  is a dimensionless complex order parameter with magnitude between 0 and 1 and  $\rho_0$ ,  $\rho_1$  and  $q_0$  are all physical constants defining what a smectic phase would look like. For a further, but reasonable, simplification we may use  $\rho_1 = \rho_0$  which is the largest value it may take and it corresponds to a fully smectic phase having the density  $\rho$  reach zero in the layer gaps.

Now we are left with a complex field  $\psi(\underline{r})$  and a unit vector field  $\underline{N}(\underline{r})$ , from now on the explicit field notation will be dropped. The magnitude of  $\psi$  describes how smectic the system is at a particular point and  $\underline{N}$  is the layer normal of the dominant wave. What is meant by that is that because we also have  $\phi$  (the phase of  $\psi$ ) varying, this may change the layering to not be precisely that described by  $\underline{N}$ . There is a degree of redundancy between the two as we need both. We need an explicit  $\underline{N}$  so that we can account for the layering symmetry, and we need an explicit  $\phi$  to account for layer compressions and dilations. This means that technically the precise layer normal may differ from  $\underline{N}$  though we do not expect that to play a role and it does not in our simulations. Specifically, this will not be an issue as long as  $\phi$  varies slowly compared to  $\underline{N}$  in the directions perpendicular to  $\underline{N}$ .

### 3 New perspectives on $\underline{\underline{E}}$ in 3D

#### 3.1 Constraints

#### 3.2 Biaxiality

#### 3.3 Properties of biaxial $\underline{\underline{E}}$

$$\underline{\underline{E}} = \psi_1(\underline{N}\underline{N} - \frac{\underline{\underline{\delta}}}{d}) + \psi_2(\underline{M}\underline{M} - \frac{\underline{\underline{\delta}}}{d}) \quad (14)$$

$$|\underline{\underline{E}}|^2 = \underline{\underline{E}} : \underline{\underline{E}}^* = (|\psi_1|^2 + |\psi_2|^2)(1 - 2\frac{1}{d} + \frac{d}{d^2}) + (\psi_1\psi_2^* + \psi_1^*\psi_2)(-2\frac{1}{d} + \frac{d}{d^2}) \quad (15)$$

$$= \frac{d-1}{d}(|\psi_1|^2 + |\psi_2|^2) - \frac{1}{d}(\psi_1\psi_2^* + \psi_1^*\psi_2) \quad (16)$$

$$= (|\psi_1|^2 + |\psi_2|^2) - \frac{1}{d}(|\psi_1|^2 + |\psi_2|^2 + \psi_1\psi_2^* + \psi_1^*\psi_2) \quad (17)$$

$$= |\psi_1|^2 + |\psi_2|^2 - \frac{|\psi_1 + \psi_2|^2}{d} \quad (18)$$

$$|\underline{\underline{E}}_{eq}|^2 = \frac{d-1}{d} \quad (19)$$

### 4 Dynamics of $\underline{\underline{E}}$

#### 4.1 Ginzburg-Landau

#### 4.2 Free Energy

$$f_{\text{bulk}} = A|\underline{\underline{E}}|^2 - \frac{C}{2}|\underline{\underline{E}}|^4 \rightarrow |\underline{\underline{E}}_{eq}|^2 = \frac{A}{C} \quad (20)$$

### 4.3 Projection operators

### 4.4 Taking the functional derivatives

### 4.5 Lagrange multipliers

## 5 Numerical considerations

### 5.1 Approximating $\Pi$

### 5.2 System boundaries

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## 6 Numerical Results

### 6.1 Imposed twist

#### 6.1.1 Fitting $\frac{\theta}{\Delta\theta}$

We now want to quantify the shapes of the azimuthal angle  $\theta$  as a function of height. To do that, we first of all non-dimensionalize these quantities and instead look at  $\frac{\theta}{\Delta\theta}$  as a function of  $\frac{h}{H}$ . That way all the plots will have the same end points and so can be compared, notably these endpoints will be at  $(0,0)$  and  $(1,1)$  and by symmetry they also ought to go through  $(\frac{1}{2}, \frac{1}{2})$ . Further as the shape is clearly a sigmoidal one, we attempted a fit using both the arctan and the tanh functions, both of which only leave one parameter once the endpoints are fixed. As the arctan method performed qualitatively better (see [for an example comparison](#) of the two), we only use that from now on. Its exact form is

do cref

$$\frac{\theta}{\Delta\theta} = \frac{\arctan(a(\frac{h}{H} - \frac{1}{2}))}{2 \arctan(\frac{a}{2})} + \frac{1}{2} \quad (21)$$

and we also quote that the slope of this function evaluated at  $\frac{h}{H} = \frac{1}{2}$  is

$$\left. \frac{d\frac{\theta}{\Delta\theta}}{d\frac{h}{H}} \right|_{\text{middle}} = \frac{a}{2 \arctan(\frac{a}{2})} \quad (22)$$



## 7 Current limitations of $\underline{\underline{E}}$

### 7.1 Dealing with the biaxiality

### 7.2 The smectic symmetries

Earlier, in the motivational part of this thesis I have mentioned that one of the advantages of  $\underline{\underline{E}}$  is that it respects the symmetry of reversing the layering direction  $\underline{N}$  both globally and locally. While this is the true symmetry of a layered system, it is not a symmetry of the established relation between  $|\psi|$ ,  $\phi$ ,  $\underline{N}$  and the density modulation

$$\rho(\underline{r}) = \rho_0 + \text{Re}(|\psi|e^{i(q_0\underline{N}\cdot\underline{r}+\phi)}), \quad |\psi|, \underline{N} \text{ and } \phi \text{ being fields} \quad (23)$$

which we did not directly use in this work, but it heavily guided our interpretation of the field. The only symmetry of eq. (23) is under simultaneously exchanging  $\underline{N}, \phi \leftrightarrow -\underline{N}, -\phi$  locally or globally. There are naturally two ways to resolve this issue. Either modify  $\underline{\underline{E}}$ , in particular its complex phase, such that it respects the symmetry of eq. (23). Or find a different way to interpret the fields from  $\underline{\underline{E}}$  as it is, or perhaps a combination of both approaches.

For modifying  $\underline{\underline{E}}$ , I suspect this would be very difficult to the point where any suitable form of  $\underline{\underline{E}}$  would likely be so different it should be called something else. This is as one would need to somehow couple the complex phase  $\phi$  and  $\underline{N}$ , an eigenvector of  $\underline{\underline{E}}$ , which is only accessible numerically. This is as the only symmetry of eq. (23) is when the signs of both flip, not just one. Regardless, if one was to find a form for  $\underline{\underline{E}}$  that satisfied both symmetries independently the interpretation of  $\phi$  would not hold anymore. Currently, using eq. (23), we interpret  $\frac{d\phi}{dx}$  (with  $x$  being the direction along  $\underline{N}$  at any point) as a contraction if it is positive and dilation if negative. However, the change of  $\phi \rightarrow -\phi$  will change the sign of these and so clearly this is not a physical symmetry of the system.

Thus, it seems the more natural way to move forward is to adapt eq. (23) to respect the symmetry in  $\underline{N}$  only. Starting from a wave resembling  $e^{i(q_0\underline{r})}$  of which we want to adjust the wavelength locally. Given the addition in eq. (23) using  $e^{i(q_0\underline{r})(1+s(\underline{r}))}$  might be a good starting point, where  $s = 0$  corresponds to equilibrium spacing,  $s > 1$  to a contraction and  $s < 1$  to a dilation. This form has the required symmetry and can be expanded as

$$e^{i(q_0\underline{r})(1+s(\underline{r}))} = e^{i(q_0\underline{N}\cdot\underline{r}+s(\underline{r})q_0\underline{N}\cdot\underline{r})} \quad (24)$$

which now has the same form as eq. (23) with  $\phi(\underline{r}) = s(\underline{r})q_0\underline{N}\cdot\underline{r}$ , however it is very important to stress that that would no longer be the  $\phi$  from  $\underline{\underline{E}}$  as that would not change anything. However,  $s$  and  $\phi$  from  $\underline{\underline{E}}$  are both dimensionless quantities and perhaps we can find a way to map them onto each other. The only reasonable values for  $s$  are from  $-1$ , where the wavelength becomes infinite, to  $+\text{inf}$  where wavelength goes to 0. Any values  $< -1$  would just correspond to a different  $s$  and a flipped  $\underline{N}$ . On the other hand  $\phi$  from  $\underline{\underline{E}}$  belongs to any set interval of length  $2\pi$ . So if we use  $\phi \in (-\pi, \pi]$  and let  $s = \frac{\phi}{\pi}$  then the model could account for any dilation and a contraction of up to half the natural wavelength. However, this would fundamentally change what  $\phi$  from  $\underline{\underline{E}}$  is and would require more work to investigate the free energy costs to contractions and dilations, among other considerations.

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