THE UNIVERSITY *of* EDINBURGH
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Normal Complex Tensor Order Parameter for Smectics in 3D

MPhys Project Report

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March 12, 2024

Abstract

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Supervisor: Tyler N Shendruk

Personal statement

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also discuss Pevniy

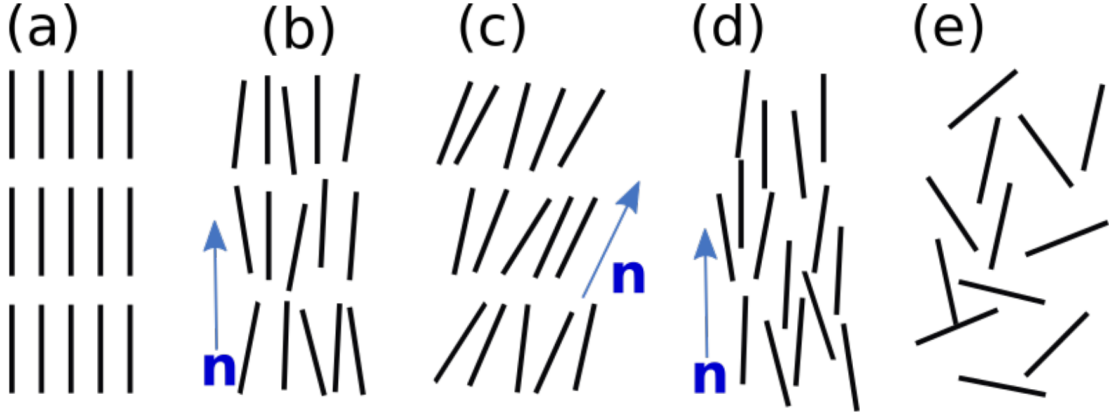mention the sqrt thing! And the small E thing

mix of Dirichlet and von Neumann

Figure 1. Illustrative structures of a substance made up from rod-like molecules. In order from (a) to (e) they are a fully crystalized 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 (the 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_{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 as there are many similarities to our smectic model.

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

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

where $\underline{N}_{\text{mol}}$ is a unit vector denoting the orientation of a molecule, $\underline{\underline{\delta}}$ 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 · (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

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

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

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

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.

could use a citation, got this from StatPhys notes

In the example of $\underline{\underline{Q}}$, that already contains the $\underline{N} \leftrightarrow -\underline{N}$ symmetry and the bulk free energy (which does not account for gradients) should only depend on S as it should be the same regardless of the orientation direction. As such we have $f_{\text{bulk}}(\underline{r})$ being a power series of S

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

and given eq. (2) that translates to a series of suitably contracted terms of $\underline{\underline{Q}}$. Generally, the following form is used

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

$$(4)$$

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 $S \geq 0$ and the coefficients are often chosen 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 $f_{\text{bulk}}(\underline{r})$ grows at very large order parameter.

However, $f_{\text{bulk}}(\underline{r})$ 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 $f(\underline{r})$ 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 ∇ 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]

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

where the Ks 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 $\underline{\underline{Q}}$ has proven difficult, first attempted by de Gennes[3] using the terms

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

with Ls being elastic constants and ϵ 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

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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

$$L_1 Q_{ij,k} Q_{ij,k} \tag{7}$$

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.

Not sure the second part is 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 decribe 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

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

where $\underline{N}$ and $\underline{M}$ 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 Q even when using eq above, aka S2 = 0, though I need a thing to cite for that

1.2 Describing/modelling smectics[2]

Fundamentally, the layered positional order corresponds to a wave-like density fluctuation. If we only consider a single wave throughout the system we have

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

where ρ_0 is the average density, ρ_1 is the wave amplitude, q_0 its wavevector containing both the wave direction and spacing and ϕ an arbitrary phase (determined by boundary conditions).

1.3 The Problems

also discuss Pevniy

1.4 Other approaches and recent smecic results

2 Introduction to the $\underline{\underline{E}}$ tensor

We start by considering the density fluctuation as we have before

$$\rho \simeq \rho_0 + 2\,\mathrm{Re}(\psi e^{iq_0 \cdot \underline{r}}) \tag{10}$$

but we allow the complex ψ and the direction of q_0 both to be vary as fields leading to the wave part of the density being

$$|\psi(\underline{r})|e^{i(q_0 \underline{N}(\underline{r}) \cdot \underline{r} + \phi(\underline{r}))} \tag{11}$$

with q_0 corresponding to the natural spacing of the wave. Both $\underline{N}$ and ϕ influence the phase, as before a constant gradient in ϕ corresponding to a constant contraction/dilation.

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

3.1 Constraints

3.2 Biaxiality

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

$$\underline{\underline{E}} = \psi_1(\underline{N}\,\underline{N} - \frac{\underline{\underline{\delta}}}{d}) + \psi_2(\underline{M}\,\underline{M} - \frac{\underline{\underline{\delta}}}{d}) \tag{12}$$

$$|\underline{\underline{E}}|^2 = \underline{\underline{E}} : \underline{\underline{E}}^* = (|\psi_1|^2 + |\psi_2|^2)(1 - 2\frac{1}{d} + \frac{d}{d^2}) + (\psi_1\psi_2^* + \psi_1^*\psi_2)(-2\frac{1}{d} + \frac{d}{d^2}) \tag{13}$$

$$= \frac{d-1}{d}(|\psi_1|^2 + |\psi_2|^2) - \frac{1}{d}(\psi_1\psi_2^* + \psi_1^*\psi_2) \tag{14}$$

$$= (|\psi_1|^2 + |\psi_2|^2) - \frac{1}{d}(|\psi_1|^2 + |\psi_2|^2 + \psi_1\psi_2^* + \psi_1^*\psi_2) \tag{15}$$

$$= |\psi_1|^2 + |\psi_2|^2 - \frac{|\psi_1 + \psi_2|^2}{d} \tag{16}$$

$$|E_{eq}|^2 = \frac{d-1}{d} \tag{17}$$

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

4.1 Ginzburg-Landau

4.2 Free Energy

$$f_{\text{bulk}} = A|\underline{\underline{E}}|^2 - \frac{C}{2}|\underline{\underline{E}}|^4 \to |E_{eq}|^2 = \frac{A}{C} \tag{18}$$

4.3 Projection operators

4.4 Taking the functional derivatives

4.5 Lagrange multipliers

5 Numerical considerations

5.1 Approximating $\underline{\underline{\Pi}}$

mention the sqrt thing! And the small E thing

5.2 System boundaries

mix of Dirichlet and von Neumann

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 θ 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 [do cref] of the two), we only use that from now on. Its exact form is

$$\frac{\theta}{\Delta\theta} = \frac{\arctan\left(a\left(\frac{h}{H} - \frac{1}{2}\right)\right)}{2\arctan\left(\frac{a}{2}\right)} + \frac{1}{2} \tag{19}$$

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

$$\left.\frac{\mathrm{d}\frac{\theta}{\Delta\theta}}{\mathrm{d}\frac{h}{H}}\right|_{\text{middle}} = \frac{a}{2\arctan\left(\frac{a}{2}\right)} \tag{20}$$

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

7.1 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

$$\rho(\underline{r}) = \rho_0 + \mathrm{Re}(|\psi|e^{i(q_0\underline{N}\cdot\underline{r}+\phi)}), \quad |\psi|, \underline{N} \text{ and } \phi \text{ being fields} \tag{21}$$

which we did not directly use in this work, but it heavily guided our interpretation of the field. The only symmetry of eq. (21) 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. (21). 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 ϕ and $\underline{N}$, an eigenvector of $\underline{\underline{E}}$, which is only accessible numerically. This is as the only symmetry of eq. (21) 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 ϕ would not hold anymore. Currently, using eq. (21), we interpret $\frac{\mathrm{d}\phi}{\mathrm{d}x}$ (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 $\phi \to -\phi$ 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. (21) 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. (21) using $e^{i(q_0\cdot\underline{r})(1+s(\underline{r}))}$ 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

$$e^{i(q_0\cdot\underline{r})(1+s(\underline{r}))} = e^{i(q_0\underline{N}\cdot\underline{r}+s(\underline{r})q_0\underline{N}\cdot\underline{r})} \tag{22}$$

which now has the same form as eq. (21) 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 ϕ from $\underline{\underline{E}}$ as that would not change anything. However, s and ϕ 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 $+\inf$ where wavelength goes to 0. Any values < -1 would just correspond to a different s and a flipped $\underline{N}$. On the other hand ϕ from $\underline{\underline{E}}$ belongs to any set interval of length 2π. 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 ϕ from $\underline{\underline{E}}$ is and would require more work to investigate any free energy costs to contractions and dilations, among other considerations.

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