THE UNIVERSITY of EDINBURGH
School of Physics
and Astronomy

Complex Tensor Order Parameter for Smectic Liquid Crystals

MPhys project 2023/24

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Main goals: adapt it for 3D & introduce a more complex free energy form

Smectic liquid crystals

- Layering of rod-like molecules (simplest case)
- Smectic-A is the simplest

3 quantities (fields)

- How ordered the phase is
- Direction of layering – director $\underline{N}$
- Spacing of layers

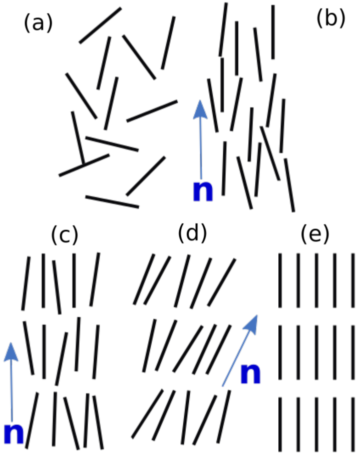


Figure: Isotropic, nematic, Smectic-A, Smectic-C and crystalline phases

Describing smectics

- The layering is a density fluctuation

$$\rho(\underline{r}, t) = \sum_{m=-\inf}^{+\inf} \psi_m e^{im\underline{q}\cdot\underline{r}} \simeq \rho_0 + 2\,\mathrm{Re}(\psi e^{i\underline{q_0}\cdot\underline{r}})$$

- Having $\psi = |\psi| e^{i\phi}$ gives
  - $|\psi|$ as the order parameter
  - Changes in ϕ lead to spacing differences
- $\underline{N} \propto \underline{q_0}$, can be an additional parameter or taken as $\underline{\nabla}\phi$

E theory – Motivations

Problems

- $\underline{N} \leftrightarrow -\underline{N}$ symmetry – $\underline{N}$ is not a vector
- Defects lead to undefined $\underline{N}$ and related problems

Requirements

- Incorporate the symmetry
- Combine parameters to allow "numerical melting"
- Enough degrees of freedom for $|\psi|, \phi$ and $\underline{N}$

E theory

- Inspiration from Q-tensor and complex ψ
- Replace the real order parameter S with complex ψ

$$\underline{\underline{Q}} = S_1(\underline{N}\,\underline{N} - \frac{\underline{\underline{\delta}}}{d}) \quad \text{uniaxial case}$$

$$\underline{\underline{E}} \sim \psi_1(\underline{N}\,\underline{N} - \frac{\underline{\underline{\delta}}}{d})$$

d is the number of dimensions, 2 or 3

E theory numerics

$$\underline{\underline{E}} \sim \psi_1(\underline{N}\,\underline{N} - \frac{\underline{\underline{\delta}}}{d})$$

- Want to evolve $\underline{\underline{E}}$ directly as a dxd complex tensor
- Enforce the form above?
- Inspiration from $\underline{\underline{Q}}$ – symmetric and traceless
  - real so can be diagonalized
- Require $\underline{\underline{E}}$ be unitarily diagonalizable (<u>normal</u>), <u>symmetric</u> and <u>traceless</u>

Constraints on E

Leads to the following form in 3D (equivalent in 2D, but only 1 term)

$$\underline{\underline{E}} = \underline{\underline{U}}^{\dagger} \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & -\lambda_1 - \lambda_2 \end{pmatrix} \underline{\underline{U}} \underbrace{= \cdots =}_{\text{also using symmetry}} \psi_1(\underline{N}\,\underline{N} - \frac{\underline{\underline{\delta}}}{3}) + \psi_2(\underline{M}\,\underline{M} - \frac{\underline{\underline{\delta}}}{3})$$

- With $\underline{N}$, $\underline{M}$ being real, orthogonal, unit vectors, and

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} \lambda_1 \\ \lambda_2 \end{pmatrix}$$

- A biaxial form of the E we want!
- $\underline{\underline{Q}}$ also has a biaxial form that is well studied

Ginzburg-Landau theory

- Dynamics using Ginzburg-Landau theory
- Need a free energy in terms of $\underline{\underline{E}}$
- Then evolve $\underline{\underline{E}}$ to minimize F

$$F = \int f(\underline{\underline{E}}, \underline{\nabla}\underline{\underline{E}}, \ldots)\,\mathrm{d}V$$

The free energy

- F must be real – need to match $\underline{\underline{E}}$ and $\underline{\underline{E}}^*$, simplest is

$$f_{\text{bulk}}(E_{ij}E^*_{ij} = \mathrm{Tr}\big(\underline{\underline{E}}\,\underline{\underline{E}}^*\big)) = AE_{ij}E^*_{ij} + \frac{C}{2}(E_{ij}E^*_{ij})^2$$

- In the uniaxial case $E_{ij}E^*_{ij} \propto |\psi|^2$, and f_{bulk} corresponds to work of de Gennes
- Take the simplest gradients terms in one $\underline{\underline{E}}$

$$|\underline{\nabla}\,\underline{\underline{E}}|^2 = E_{ij,k}E^*_{ij,k}$$
$$|\nabla^2\underline{\underline{E}}|^2 = E_{ij,kk}E^*_{ij,ll}$$

The free energy – simplest form

$$
\begin{aligned}
F &= \int f_{\mathsf{bulk}} + f_{\mathsf{comp}} + f_{\mathsf{curv}} \, \mathrm{d}V \\
f_{\mathsf{bulk}} &= A E_{ij} E^*_{ij} + \frac{C}{2} (E_{ij} E^*_{ij})^2 \\
f_{\mathsf{comp}} &= b_1 E_{ij,k} E^*_{ij,k} \\
f_{\mathsf{curv}} &= b_2 E_{ij,kk} E^*_{ij,ll}
\end{aligned}
$$

Projection operators for F, more complex

- Gradients in different directions have different energy costs
- For **uniaxial** $\underline{\underline{E}}$, special direction is $\underline{N}$
- Projection operator $\underline{\underline{\Pi}} = \underline{N}\,\underline{N}$, rest is $\underline{\underline{T}} = \underline{\underline{\delta}} - \underline{\underline{\Pi}}$
- Consider $\underline{\nabla} \to a\underline{\underline{\Pi}} \cdot \underline{\nabla} + b\underline{\underline{T}} \cdot \underline{\nabla}$ a, b being some constants

$$
\begin{aligned}
f_{\text{comp}} &\to b_1^{\parallel} \Pi_{kl} E_{ij,k} E^*_{ij,l} + b_1^{\perp} T_{kl} E_{ij,k} E^*_{ij,l} \\
f_{\text{curv}} &\to b_2^{\parallel} \Pi_{kl} E_{ij,lk} \Pi_{mn} E^*_{ij,nm} + b_2^{\perp} T_{kl} E_{ij,lk} T_{mn} E^*_{ij,nm} \\
&\quad + b_2^{\parallel\perp} \left(\Pi_{kl} E_{ij,lk} T_{mn} E^*_{ij,nm} + T_{kl} E_{ij,lk} \Pi_{mn} E^*_{ij,nm} \right)
\end{aligned}
$$

Projection operators – back to $\underline{\underline{E}}$

- Need a form for $\underline{\underline{\Pi}}$ in terms of $\underline{\underline{E}}$
- Have 2 forms which work for uniaxial $\underline{\underline{E}}$

$$\underline{\underline{\Pi}} = \sqrt{\frac{d-1}{d\underline{\underline{E}}:\underline{\underline{E}}}}\underline{\underline{E}} + \frac{\underline{\underline{\delta}}}{d}$$

$$\underline{\underline{\Pi}} = \frac{d-1}{d-2}\left(\frac{\underline{\underline{E}}\cdot\underline{\underline{E}}^*}{\underline{\underline{E}}:\underline{\underline{E}}^*} - \frac{\underline{\underline{\delta}}}{d(d-1)}\right)$$

- First is significantly easier to work with – currently used
- Lead to seemingly different functional derivatives – why?
- First form only has $\underline{\underline{E}}$, how about $\underline{\underline{E}} \to \underline{\underline{E}}^*$?
- How well do they work for biaxial $\underline{\underline{E}}$?

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

- Want $\frac{\partial E_{ij}}{\partial t} = -\mu \frac{\delta F}{\delta E^*_{ij}}$ Model A like, $\underline{\underline{E}}$ is not conserved
- But need constraints!
- Find extrema of G instead

$$G = \int f(\underline{\underline{E}}, \underline{\nabla} \underline{\underline{E}}, \dots) + \lambda_s g_s(\underline{\underline{E}}) + \lambda_t g_t(\underline{\underline{E}}) + \lambda_n g_n(\underline{\underline{E}}) \, \mathrm{d}V$$

- Choose suitable gs and treat λs as variables

Lagrange multipliers

- Choose real, non-negative $g_?(\underline{\underline{E}})$ that reflect the constraints:

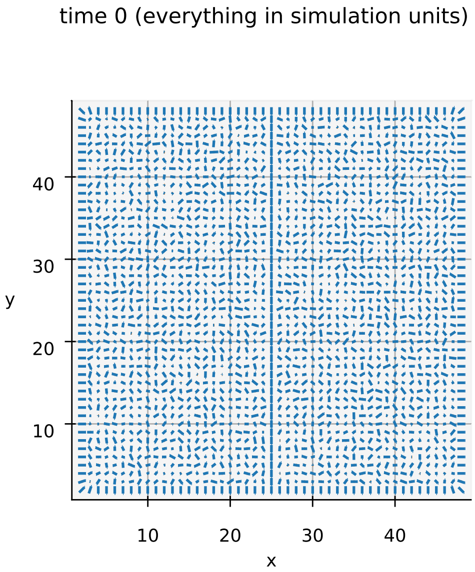
$$
\begin{aligned}
g_s &= |E_{ij} - E_{ji}|^2 \\
g_t &= |E_{ii}|^2 \\
g_n &= |[\underline{\underline{E}}, \underline{\underline{E}}^*]|^2 = |E_{ik}E^*_{kj} - E^*_{ik}E_{kj}|^2
\end{aligned}
$$

- Two options for λs – soft constraints or approximate analytic form
- $\underline{\underline{E}}$ is normal iff $[\underline{\underline{E}}, \underline{\underline{E}}^*] = 0$

Some preliminary results

- Fixed boundaries along the sides
- I show a single slice
- Systems starts isotropic with an ordered streak

Some preliminary results



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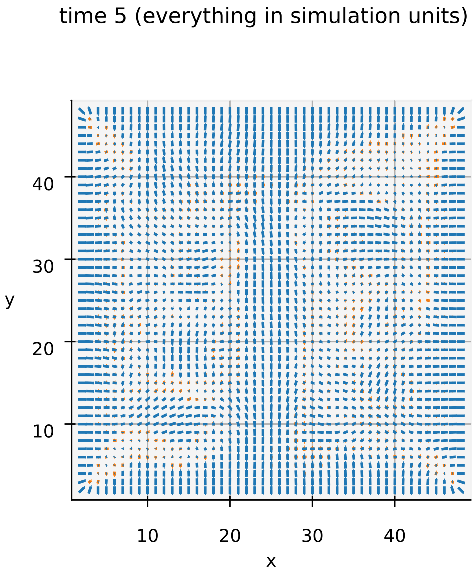
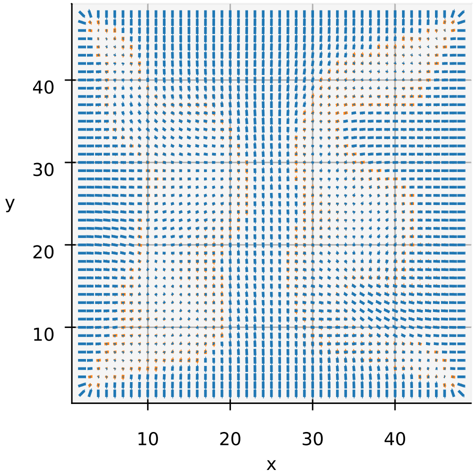


Some preliminary results

time 15 (everything in simulation units)



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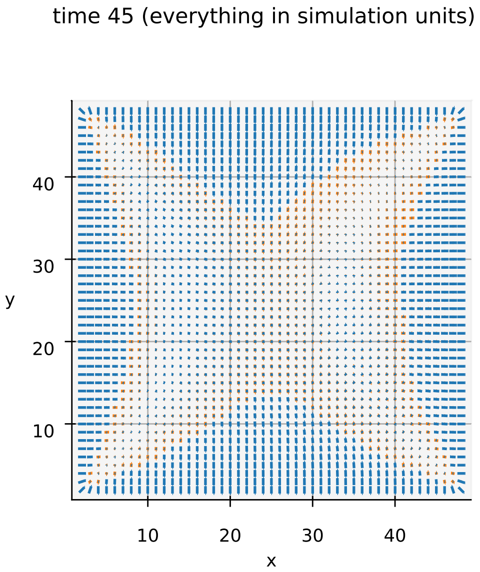

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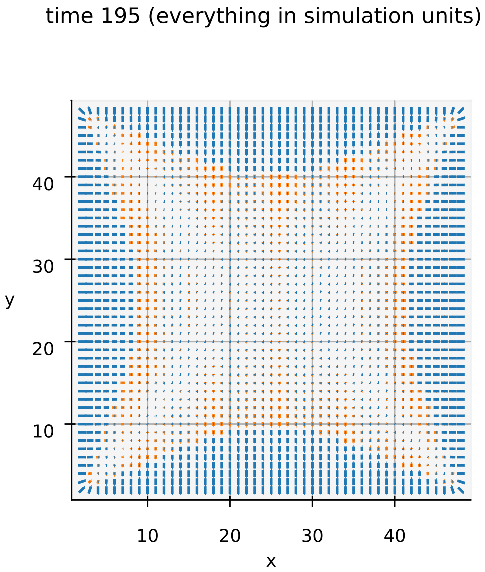

Thank you for your attention

$$
\begin{aligned}
\frac{\delta F_{\text{bulk}}}{\delta E^*_{ij}} &= \frac{1}{2}(A + CE_{ab}E^*_{ab})E_{ij} \\
\frac{\delta F_{\text{comp}}}{\delta E^*_{ij}} &= -(b_1^{\parallel} - b_1^{\perp})(\Pi_{kl,l}E_{ij,k} + \Pi_{kl}E_{ij,kl}) - b_1^{\perp}E_{ij,kk} \\
\frac{\delta F_{\text{curv}}}{\delta E^*_{ij}} &= (b_2^{\parallel} + b_2^{\perp} - 2b_2^{\parallel\perp})\Big((\Pi_{kl}\Pi_{po,po} + 2\Pi_{kl,o}\Pi_{po,p} + \Pi_{kl,po}\Pi_{po})E_{ij,lk} \\
&\qquad + 2(\Pi_{kl,o}\Pi_{po} + \Pi_{kl}\Pi_{po,o})E_{ij,lkp} + \Pi_{kl}\Pi_{po}E_{ij,lkpo}\Big) \\
&\quad + (b_2^{\parallel\perp} - b_2^{\perp})\Big(\Pi_{po,po}E_{ij,kk} + 2\Pi_{po,o}E_{ij,kkp} + \Pi_{po}E_{ij,kkpo} \\
&\qquad + \Pi_{kl,oo}E_{ij,lk} + 2\Pi_{kl,o}E_{ij,lko} + \Pi_{kl}E_{ij,lkoo}\Big) \\
&\quad + b_2^{\perp}E_{ij,kkoo}
\end{aligned}
$$

Gradients of $\underline{\underline{\Pi}}$

- Results using the square root version of $\underline{\underline{\Pi}}$

$$
\begin{aligned}
\Pi_{kl} &= \frac{sE_{kl}}{\sqrt{E_{ab}E_{ab}}} + \frac{\delta_{kl}}{d} \\
\Pi_{kl,m} &= \frac{s}{\sqrt{E_{ab}E_{ab}}}\left(E_{kl,m} - \frac{E_{kl}E_{cd}E_{cd,m}}{E_{ab}E_{ab}}\right) \\
\Pi_{kl,mn} &= \frac{s}{\sqrt{E_{ab}E_{ab}}}\Bigg(E_{kl,mn} \\
&\quad - \frac{E_{kl,n}E_{cd}E_{cd,m} + E_{kl,m}E_{cd}E_{cd,n} + E_{kl}(E_{cd,n}E_{cd,m} + E_{cd}E_{cd,mn})}{E_{ab}E_{ab}} \\
&\quad + 3\frac{E_{kl}E_{cd}E_{cd,m}E_{ef}E_{ef,n}}{(E_{ab}E_{ab})^2}\Bigg)
\end{aligned}
$$

Physical quantities

- Taking b_1 to be the order of magnitude of $b_1^{\parallel}$ and $b_1^{\perp}$
- Similarly for b_2

$$|\psi|_{eq} = \sqrt{\frac{3}{2} * \frac{-A}{C}}$$ The ideal smectic phase value, dimensionless

$$\varepsilon = \sqrt{\frac{b_1}{|A|}}$$ Lamellar in-plane coherence length, L

$$\lambda = \sqrt{\frac{b_2}{b_1}}$$ Penetration depth, L

$$\kappa = \frac{\lambda}{\varepsilon} = \sqrt{\frac{b_2|A|}{b_1^2}}$$ Ginzburg parameter, dimensionless