THE UNIVERSITY *of* EDINBURGH
School of Physics
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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 N
- Spacing of layers

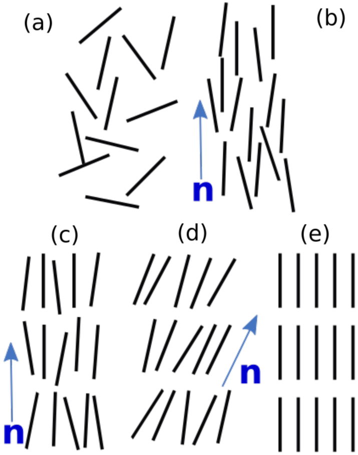


Figure: Isotropic, nematic, Smectic-A, Smectic-C and crystalline phases

Describing smectics – de Gennes

- The layering is a wavelike density fluctuation

$$\rho(\underline{r}) = \rho_0(1 + |\psi| \cos\big(\underline{q_0} \cdot \underline{r} + \phi\big)) = \rho_0(1 + \mathrm{Re}(|\psi| e^{i(q_0 \cdot r + \phi)}))$$

- 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

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

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

d is the number of dimensions, 2 or 3

E theory numerics

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

- 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 (normal), symmetric and traceless

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

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

- 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 $\underline{\underline{E}}$

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

The free energy – one constant approximation

$$F = \int f_{\mathsf{bulk}} + f_{\mathsf{comp}} + f_{\mathsf{curv}} \, \mathrm{d}V$$

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

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

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

- Choose suitable gs and treat λs as variables

Lagrange multipliers

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

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

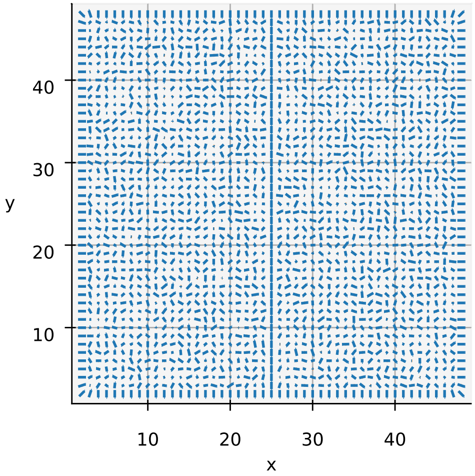
- Two options for λs – soft constraints or approximate analytic form
- $\underline{\underline{E}}$ is normal iff $[\underline{\underline{E}}, \underline{\underline{E}}^*] = 0$

Some preliminary results

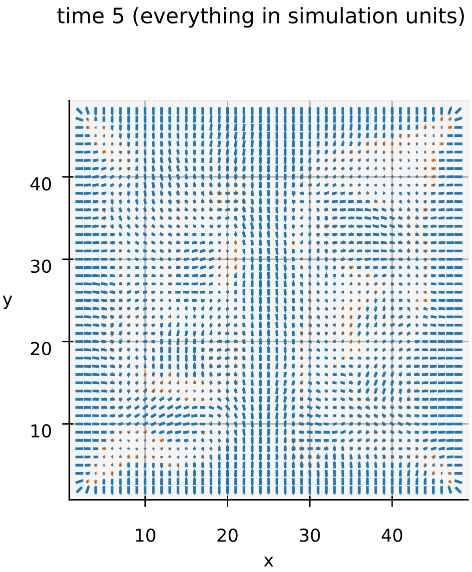
- Fixed boundaries along the sides
- I show a single slice
- Systems starts isotropic with an ordered streak

Some preliminary results

time 0 (everything in simulation units)

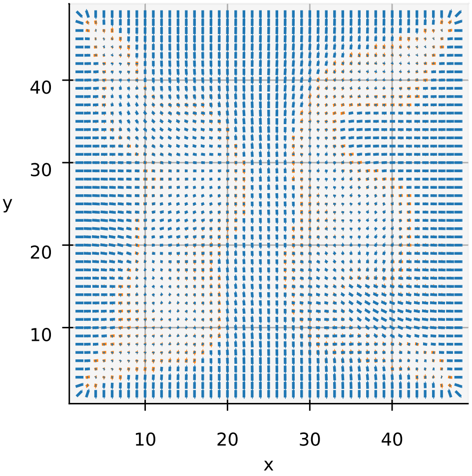


Some preliminary results

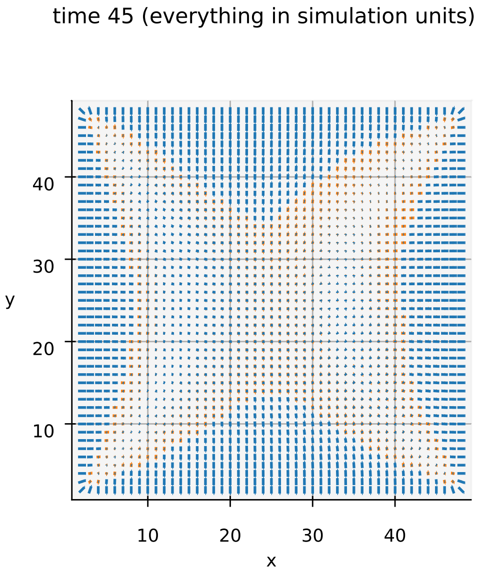


Some preliminary results

time 15 (everything in simulation units)

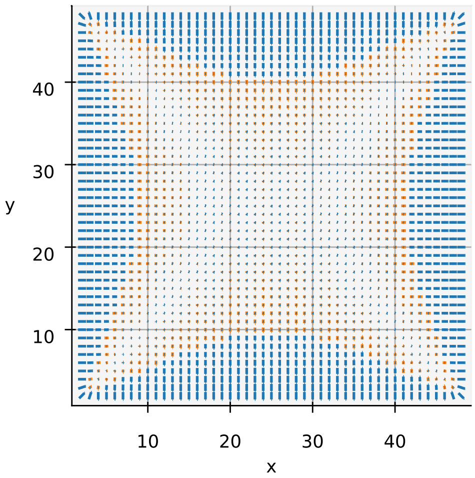


Some preliminary results



Some preliminary results

time 195 (everything in simulation units)



Thank you for your attention

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

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

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

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

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

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