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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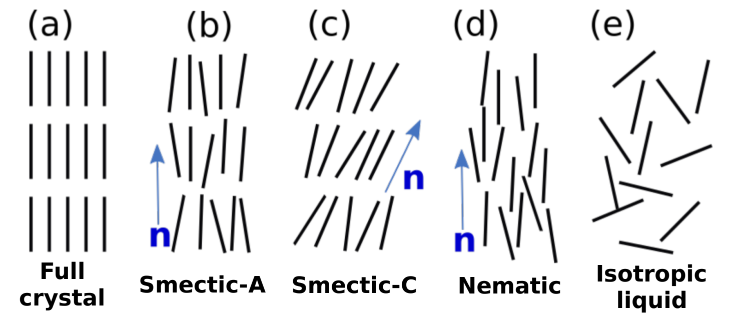
Main goals: adapt it for 3D & new free energy form

Liquid crystals – partial order in rod-like molecules



Phases of a substance of rod-like molecules, in order of decreasing phase order[1].

Nematic $\sim$ alignment, broken rotational symmetry

Smectic $\sim$ layering, broken translational symmetry in 1 direction

[1] J. Paget, **"Complex tensors and simple layers: A theory for smectic fluids"**, PhD thesis (The University of Edinburgh, Apr. 2023).

Liquid crystals – why do we care?

Physicists playground

- Fascinating interplay of order and disorder
- Topological matter, various symmetries at play etc.
- Analogy between smectics and superconductivity[1]

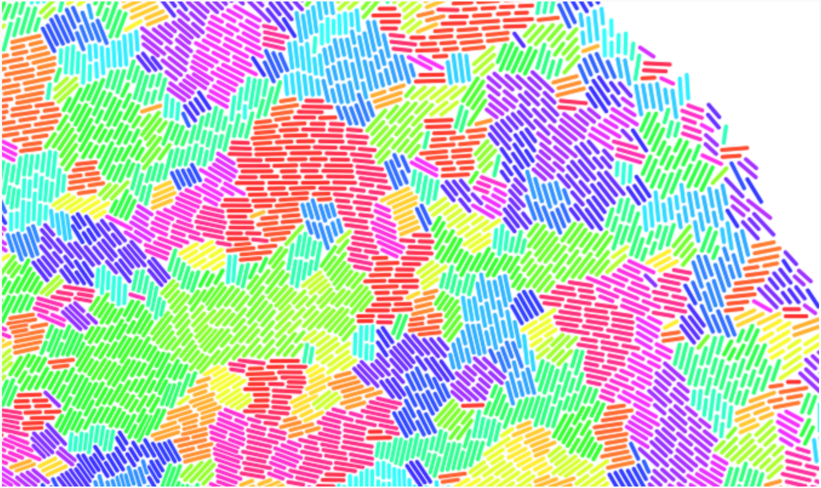
Real-world applications

- Liquid crystal displays
- Organic electronics[2]
- Biological and living matter[2]

[1] P. de Gennes, **"An analogy between superconductors and smectics A",** Solid State Communications **10**, 753–756 (1972).

[2] J. P. F. Lagerwall and G. Scalia, **"A new era for liquid crystal research: Applications of liquid crystals in soft matter nano-, bio- and microtechnology",** Current Applied Physics **12**, 1387–1412 (2012).

Bacterial colonies have nematic and smectic order



Example snapshot of a bacteria situation within the group. Colour shows the orientation of each bacterium. Domains of clear nematic and limited smectic order.

Outline

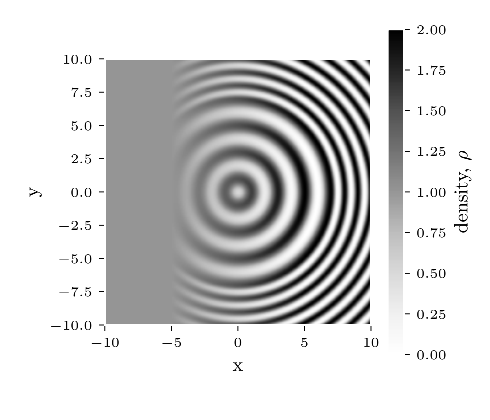
- Smectics as a density wave
- Problems of current approaches
- Our complex tensor $\underline{\underline{E}}$ and why it solves the issue
- Redefining $\underline{\underline{E}}$ in 3D – biaxiality
- Ginzburg-Landau dynamics
- New free energy
- Simulation results

Layering is determined by three quantities

Smectic $\sim$ layered

3 quantities (fields)

- Degree of layering
- Direction of layering
- Spacing of layers



Example of a layering structure

Layering as a density wave

$$\begin{aligned}\rho(\underline{r}) &= \rho_0 + \rho_1 \cos\big(\underline{q_0} \cdot \underline{r} + \phi\big) \\ &= \rho_0(1 + \mathrm{Re}(|\psi| e^{i(\underline{q_0} \cdot \underline{r} + \phi)}))\end{aligned}$$

where

- $|\psi|$ is the wave amplitude – degree of layering
- $\underline{q_0}$ determines layering direction and spacing
  - Layer normal direction $\underline{N} = \frac{\underline{q_0}}{q_0}$
  - Layer spacing is $\frac{2\pi}{q_0}$
- Here ϕ is an arbitrary phase
- ρ_0 is the average density and $\rho_1 = \rho_0 |\psi| \leq \rho_0$

Complex number field order parameter $\psi(\underline{r})$

$$\begin{aligned}\rho(\underline{r}) &= \rho_0(1 + \mathrm{Re}(|\psi| e^{i(\underline{q_0}\cdot\underline{r}+\phi)})) \\ &= \rho_0(1 + \mathrm{Re}(\psi e^{i\underline{q_0}\cdot\underline{r}}))\end{aligned}$$

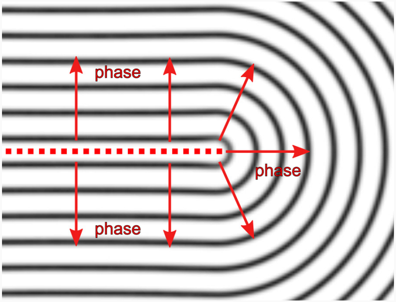
- More interesting systems – need to promote parameters to fields
- Promoting $|\psi|(\underline{r})$ is simple
- $\phi(\underline{r})$ also taken to be a field
- $\psi(\underline{r}) = |\psi|(\underline{r})e^{i\phi(\underline{r})}$ is the de Gennes complex order parameter

Established approaches have limitations

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

Two options, both limited

- Fixed $\underline{q_0}$, solve for $\psi(\underline{r})$ – near equilibrium systems only
- Remove $\underline{q_0}$ – does not capture the smectic $\underline{N} \leftrightarrow -\underline{N}$ symmetry[1]



Example density wave where the red arrows show directions of increasing ϕ. Black corresponds to layers of increased density. Figure from [1].

[1] M. Y. Pevnyi, J. V. Selinger, and T. J. Sluckin, **"Modeling smectic layers in confined geometries: Order parameter and defects"**, Physical Review E **90**, 032507 (2014).

E theory – have varying $\underline{N}$ as well

Still use

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

- Keep the $\psi(\underline{r})$ field, and make $\underline{N}(\underline{r}) = \frac{\underline{q_0}(\underline{r})}{q_0}$ a field.
- Leave ρ_0, q_0 as microscopic constants

Package these as

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

where d is the number of dimensions, 2 or 3

E theory – Mesoscopic theory respecting the layering symmetry

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

Benefits/motivation for $\underline{\underline{E}}$

- Incorporates $\underline{N} \leftrightarrow -\underline{N}$ symmetry
- Captures all three quantities – degree of order, layer direction and spacing through $|\psi|$, $\underline{N}$ and ϕ
- Numerically convenient – one object, it can numerically melt
- Mesoscopic theory – does not directly resolve density

What is $\underline{\underline{E}}$ in 3D

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

- Treat $\underline{\underline{E}}$ as general complex tensor
- Need arrive at the form above
- Inspiration from real symmetric tensors leads us to diagonalization
- Require $\underline{\underline{E}}$ be unitarily diagonalizable (<u>normal</u>), <u>symmetric</u> and <u>traceless</u>

What is $\underline{\underline{E}}$ in 3D

Normality and tracelessness give

$$\underline{\underline{E}} = \underline{\underline{U}} \cdot \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 = -\lambda_1 - \lambda_2 \end{pmatrix} \cdot \underline{\underline{U}}^\dagger$$

where the λ_i are eigenvalues of $\underline{\underline{E}}$ and $\underline{\underline{U}}$ some unitary matrix

Our constraints lead to biaxial $\underline{\underline{E}}$ in 3D

Also using symmetry this leads to

$$\underline{\underline{E}} = \cdots = \psi_1(\underline{N}\,\underline{N} - \frac{\underline{\underline{\delta}}}{3}) + \psi_2(\underline{M}\,\underline{M} - \frac{\underline{\underline{\delta}}}{3})$$

where

$$\psi_1 = \lambda_1 - \lambda_3 \qquad\qquad \psi_2 = \lambda_2 - \lambda_3$$

and $\underline{N}$ and $\underline{M}$ are real, mutually orthogonal unit eigenvectors of $\underline{\underline{E}}$ associated to λ_1 and λ_2

Biaxial $\underline{\underline{E}}$ could mean two density waves

$$\underline{\underline{E}} = \cdots = \psi_1(\underline{N}\,\underline{N} - \frac{\underline{\underline{\delta}}}{3}) + \psi_2(\underline{M}\,\underline{M} - \frac{\underline{\underline{\delta}}}{3})$$

- Symmetry, tracelessness, normality lead to biaxial $\underline{\underline{E}}$
- No simple way to force uniaxiality
- We interpret each term as a density wave
- This may allow $\underline{\underline{E}}$ to model more ordered, columnar phases

Evolve $\underline{\underline{E}}$ in time via local free energy minimization

- $\underline{\underline{E}}$ is a Ginzburg-Landau theory
- Need a free energy in terms of $\underline{\underline{E}}$

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

- F must be real
- Then evolve $\underline{\underline{E}}$ to minimize F using the functional derivative

$$\frac{\partial \underline{\underline{E}}}{\partial t} = -\mu \frac{\delta F}{\delta \underline{\underline{E}}^*}$$

- Model A like dynamics using Wirtinger derivatives
- Plus Lagrange multipliers to enforce constraints

The one constant approximation free energy

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

$$f_{\mathsf{bulk}} = A|\underline{\underline{E}}|^2 + \frac{C}{2}|\underline{\underline{E}}|^4$$

$$f_{\mathsf{comp}} = b_1|\underline{\nabla}\,\underline{\underline{E}}|^2 = b_1 E_{ij,k}E^*_{ij,k}$$

$$f_{\mathsf{curv}} = b_2|\nabla^2\underline{\underline{E}}|^2 = b_2 E_{ij,kk}E^*_{ij,ll}$$

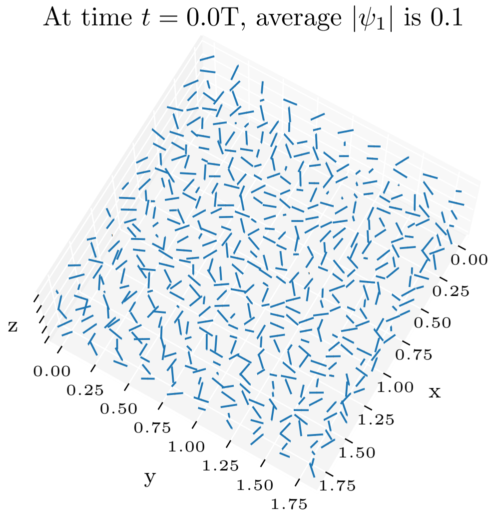
- f_{bulk} – base free energy, determines the phase
- f_{comp} – layer compression/compression energy costs
- f_{curv} – layer curvature/bending energy costs
- With $|?_{ij\dots k}|^2 = ?_{ij\dots k}?^*_{ij\dots k}$ being the Frobenius norm

New F using projection operators

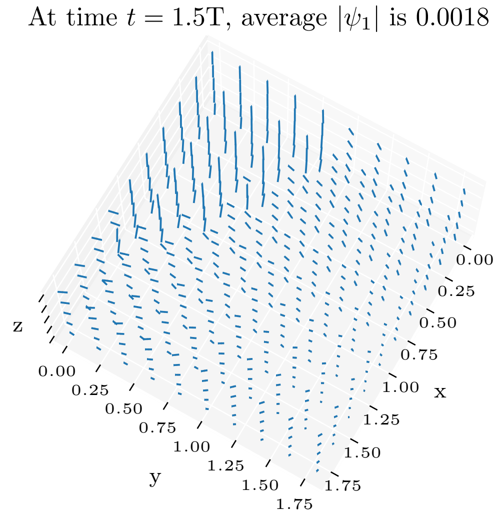
- Gradients in different directions have different energy costs
- Uniaxial $\underline{\underline{E}}$ – special direction is $\underline{N}$
- Projection operator $\underline{\underline{\Pi}} = \underline{N}\underline{N}$, rest is $\underline{\underline{T}} = \underline{\underline{\delta}} - \underline{\underline{\Pi}}$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

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

Quench-like system – smectic forming from isotropic



Quench-like system – smectic forming from isotropic



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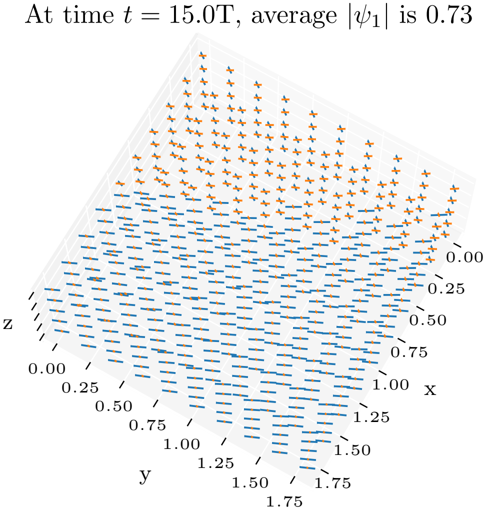

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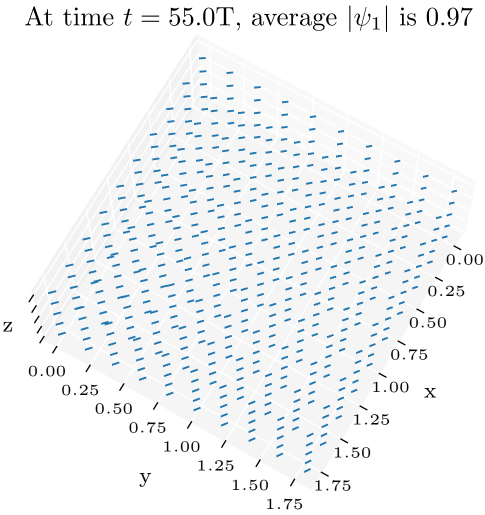
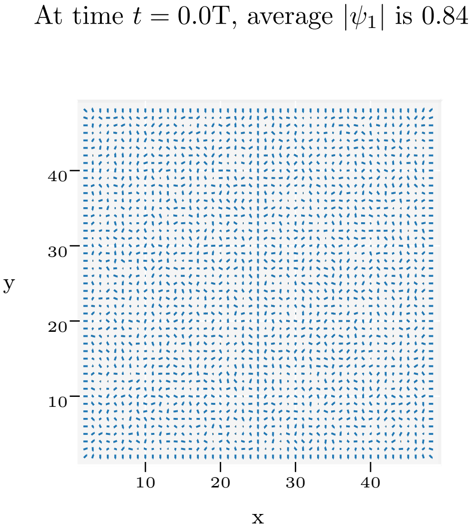
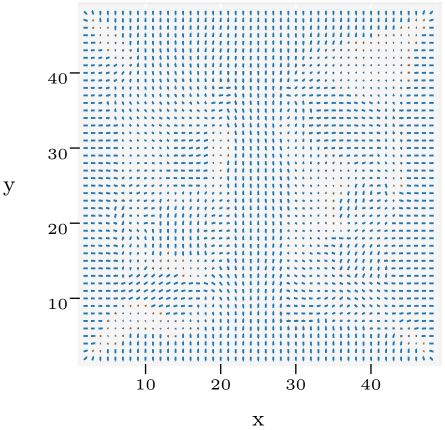


$\underline{\underline{E}}$ escapes into the third dimension



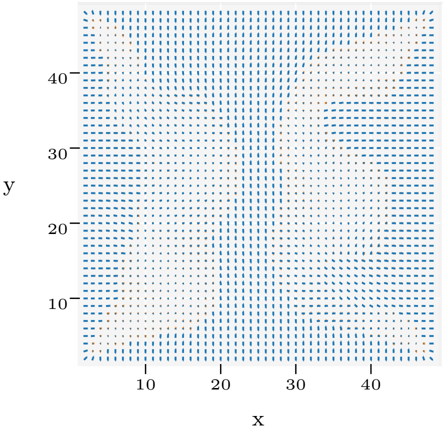
$\underline{\underline{E}}$ escapes into the third dimension

At time $t = 5.0\mathrm{T}$, average $|\psi_1|$ is 0.79

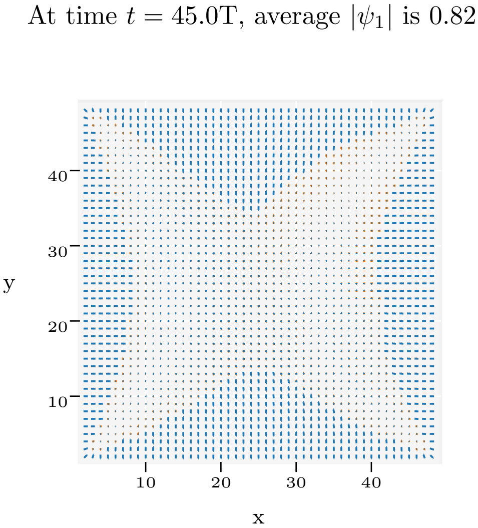


$\underline{\underline{E}}$ escapes into the third dimension

At time $t = 15.0\mathrm{T}$, average $|\psi_1|$ is 0.82

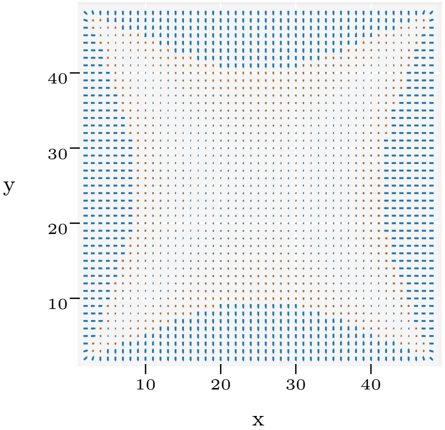


$\underline{\underline{E}}$ escapes into the third dimension



$\underline{\underline{E}}$ escapes into the third dimension

At time $t = 195.0$T, average $|\psi_1|$ is 0.81



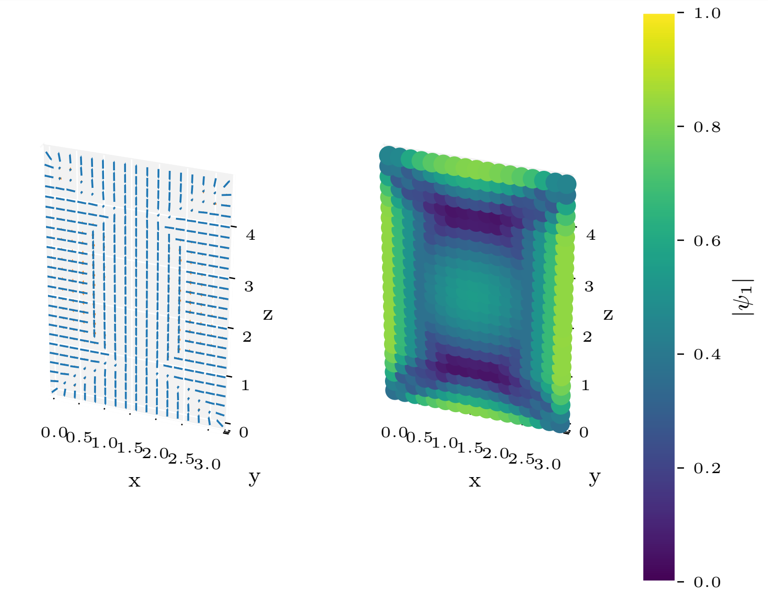
Main conclusions of the project

- In 3D a symmetric, traceless and normal $\underline{\underline{E}}$ gains a biaxial term
- We observe significant biaxiality in simulations
- Escaping into the third dimension is a major effect in our simulations

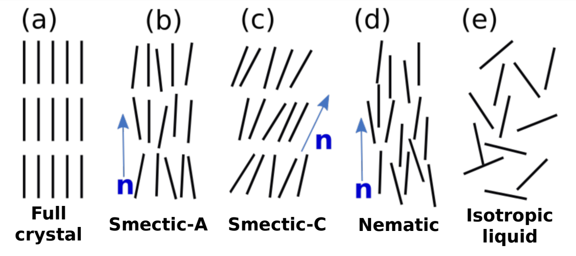
Thank you for your attention

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

More complex simulation



Liquid crystals – partial order in rod-like molecules



Phases of a substance of rod-like molecules, in order of decreasing phase order[1].

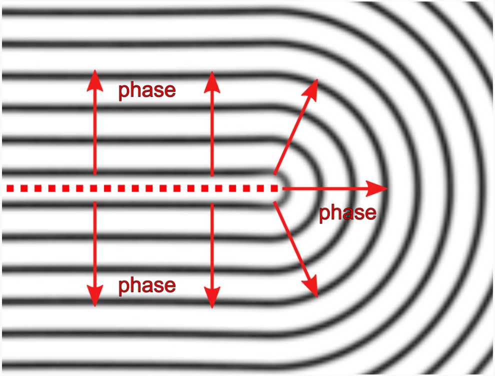
Different LC phases determined by their order/symmetries

Phase	Order	Broken symmetry
Isotropic liquid	No order	None
Nematic	Orientational	Rotational
Smectic	Positional	Translational in one direction
Full crystal	Both	Rotational and translational in all directions

[1] J. Paget, **"Complex tensors and simple layers: A theory for smectic fluids",** PhD thesis (The University of Edinburgh, Apr. 2023).

$\psi(\underline{r})$ alone does not respect smectic symmetry

here use $\quad \rho(\underline{r}) = \rho_0(1 + \mathrm{Re}(|\psi|e^{i\phi})$



Example density wave where the red arrows show directions of increasing ϕ. Black corresponds to layers of increased density. Figure from [1].

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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:

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

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

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

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

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

Physical quantities

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

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

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

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

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