Orientation and Flow in Liquid Crystals

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Outline

Introduction

Nematic Elasticity

Nematic Hydrodynamics
**Liquid Crystals**

**Timeline**

- **1880**: Discovery, Reinitzer, Lehmann
- **1900**: Characterization, Friedel
- **1920**: Twist cells, Helfrich
- **1940**: Room-T nematics, Gray
- **1960**: Discotics, Chandrasekhar
- **1980**: Elastic Theory
- **2000**: Hydrodynamics, Simulations

**Additional References**

Liquid Crystal Simulations

Coarse-Grained Models

Discs, Rods, Ellipsoids
Liquid Crystal Simulations
Interaction Potentials

The Gay-Berne Potential

Liquid Crystals
Orientational Order

- Short-ranged positional order.
- Long-ranged orientational order.
- The director $\mathbf{n}$: a unit vector.
- Second-rank order: $\mathbf{n} \leftrightarrow -\mathbf{n}$.
- Magnitude of ordering: $S$.

- Global reorientation of $\mathbf{n}$ costs zero free energy.
- Quasi-conserved: influences hydrodynamics.
- Molecular simulation:
  - orientational elasticity;
  - effect on nematic flow.
Outline

Introduction

Nematic Elasticity

Nematic Hydrodynamics
Spatial deformations of director $\mathbf{n}$ incur free energy penalty.

**Elastic Free Energy**

\[
\Delta F = \int d\mathbf{r} f[\mathbf{n}(\mathbf{r})]
\]

\[
f[\mathbf{n}] = \frac{1}{2} K_1 (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2} K_3 \left| \mathbf{n} \times (\nabla \times \mathbf{n}) \right|^2
\]

- Description valid at long wavelengths.
- Elastic constants $K_1$, $K_2$, $K_3$.
- Fourier transform: $\nabla \rightarrow i\mathbf{k}$. 
Director Fluctuation Modes

Splay-Bend and Twist-Bend

\[ \mathbf{n} = (0, 0, 1) \]
\[ \delta \mathbf{n} = (n_1, n_2, 0) \]
\[ \mathbf{k} = (k_1, 0, k_3) \]
Free Energy in Fourier Space

$$\Delta \mathcal{F} = \frac{1}{V} \sum_{\mathbf{k}} f(\mathbf{k})$$

$$f(\mathbf{k}) = \frac{1}{2} (K_1 k_1^2 + K_3 k_3^2) |\tilde{n}_1(\mathbf{k})|^2 + \frac{1}{2} (K_2 k_1^2 + K_3 k_3^2) |\tilde{n}_2(\mathbf{k})|^2$$

splay-bend

twist-bend

Equipartition of (free) energy:

Splay-bend:  \( W_{13} \propto \langle |\tilde{n}_1(\mathbf{k})|^2 \rangle^{-1} \propto K_1 k_1^2 + K_3 k_3^2 \)

Twist-bend:  \( W_{23} \propto \langle |\tilde{n}_2(\mathbf{k})|^2 \rangle^{-1} \propto K_2 k_1^2 + K_3 k_3^2 \)
Inverse Orientational Fluctuations

$N = 5 \times 10^5$ Molecules

Colloidal Platelets
Elastic Constant Measurements


Sterically stabilized *gibbsite* $\text{Al(OH)}_3$ platelets (hexagons).

- Diameter $D \approx 230\text{nm}$.
- Thickness $H \approx 18\text{nm}$.
- $H/D \approx 1/13$.
- 20% polydispersity in both dimensions.

- Alignment dictated by container walls.
- Magnetic field: Freedericksz transition.
- Gives bend elastic constant $K_3 = 6 - 8 \times 10^{-14}\text{N}$. 

Tactoids in Magnetic Field

Tactoids ≈ droplets.

Low magnetic field: radial director structure, “hedgehog”, splay.

High magnetic field: director structure deforms, tactoid elongates.

- Theory balances surface, elastic, and magnetic forces.
- Gives splay elastic constant $K_1 = 9 - 26 \times 10^{-14} \text{N}$. 

Colloidal Platelets
Elastic Constant Simulations

Experiment, Theory and Simulation


Outline

Introduction

Nematic Elasticity

Nematic Hydrodynamics
The director is effectively conserved on large length scales. Coupled director $\tilde{n}(k, t)$ and velocity $\tilde{v}(k, t)$ fields. Two Goldstone modes associated with director motion.
Nematic Hydrodynamics

Balance Equations

\[ \rho \dot{v}_i = \tau_{ji,j} \]
\[ \rho' \ddot{n}_i = g_i + \pi_{ji,j} \]

\( i, j = x, y, z \)
\( f, j \equiv \frac{\partial f}{\partial r_j} \)

▶ We use the Einstein convention.
▶ Incompressible fluid.
▶ \( \rho \) = mass density, \( \rho' \) = director moment of inertia density.
▶ \( v_i(r, t) \) = velocity field, \( n_i(r, t) \) = director field.
▶ \( \tau_{ji} \) = stress tensor, \( \pi_{ji} \) = couple stress tensor.
▶ \( g_i \) = intrinsic director body force.
Nematic Hydrodynamics

Reactive Coefficients

Elastic Effects

\[ \tau_{ji}^R = -P \delta_{ji} - \frac{\partial f}{\partial n_{k,j}} n_{k,i} \]

\[ g_i^R = \gamma n_i - \beta_j n_{i,j} - \frac{\partial f}{\partial n_i} \]

\[ \pi_{ji}^R = \beta_j n_i + \frac{\partial f}{\partial n_{i,j}} \]

- \( f \) = Frank free energy density.
- \( P, \beta_j \) and \( \gamma \) are constants.
- \( \delta_{ij} \) is the Kronecker delta.
Nematic Hydrodynamics
Dissipative Coefficients

Viscous Effects

\[
\tau_{ji}^D = \alpha_1 \, n_k n_m d_{km} n_i n_j + \alpha_2 \, n_j N_i + \alpha_3 \, n_i N_j + \alpha_4 \, d_{ji} + \alpha_5 \, n_j n_k d_{ki} + \alpha_6 \, n_i n_k d_{kj}
\]
\[
g_i^D = -\gamma_1 \, N_i - \gamma_2 \, n_j d_{ji}
\]
\[
\pi_{ji}^D = 0
\]

- \( \alpha_1 \ldots \alpha_6 \) = Leslie coefficients (viscosities)
- \( \gamma_1 = \alpha_3 - \alpha_2, \gamma_2 = \alpha_6 - \alpha_5 = \alpha_3 + \alpha_2 \).
- \( N_i = \dot{n}_i - \omega_{ij} n_j \) = co-rotational time flux of the director
- \( d_{ij} = \frac{1}{2}(v_{i,j} + v_{j,i}) \) = symmetric strain rate
- \( \omega_{ij} = \frac{1}{2}(v_{i,j} - v_{j,i}) \) = antisymmetric strain rate, vorticity
Drop $\rho'\vec{n}_i$ term; $\dot{n}_i$ still appears through $N_i = \dot{n}_i - w_{ij} n_j$.

- Adopt same axis system as before.
- Set $\vec{n} = (0, 0, 1) + \delta n$; drop nonlinear terms in $\delta n$.
- Use incompressibility: $\nabla \cdot \vec{v} = 0$, $k \cdot \vec{\tilde{v}} = k_1 \tilde{v}_1 + k_3 \tilde{v}_3 = 0$.

Define $k = k(\sin \varphi, 0, \cos \varphi)$ and let $\tilde{v}_\perp = \tilde{v}_1 \cos \varphi - \tilde{v}_3 \sin \varphi$. 
Splay-Bend Fluctuation Dynamics

\[
\left( \gamma_1 \frac{\partial}{\partial t} + K k^2 \right) \tilde{n}_1 + i k \alpha \tilde{v}_\perp = 0 \\
-ik\alpha \frac{\partial}{\partial t} \tilde{n}_1 + (\rho \frac{\partial}{\partial t} + \eta k^2) \tilde{v}_\perp = 0
\]

\[
K = K_1 \sin^2 \varphi + K_3 \cos^2 \varphi \\
\alpha = \alpha_2 \cos^2 \varphi - \alpha_3 \sin^2 \varphi \\
\eta = \eta_1 \sin^2 \varphi + \eta_2 \cos^2 \varphi + \eta_{12} \sin^2 \varphi \cos^2 \varphi
\]
Nematic Hydrodynamics

Twist-Bend Fluctuation Dynamics

\[
\begin{align*}
(\gamma_1 \frac{\partial}{\partial t} + K k^2) \tilde{n}_2 + i k \alpha \tilde{v}_2 &= 0 \\
-ik\alpha \frac{\partial}{\partial t} \tilde{n}_2 + (\rho \frac{\partial}{\partial t} + \eta k^2) \tilde{v}_2 &= 0
\end{align*}
\]

\[
K = K_2 \sin^2 \varphi + K_3 \cos^2 \varphi
\]

\[
\alpha = \alpha_2 \cos \varphi
\]

\[
\eta = \eta_3 \sin^2 \varphi + \eta_2 \cos^2 \varphi
\]
Linear Response Theory

- Consider perturbation coupling to $A(r, p)$.
- Measure response in $B(r, p)$.
- Define $B$ such that $\langle B \rangle = 0$.

The Response Function

Hamiltonian Perturbation: $\Delta \mathcal{H} = -\phi(t)A(r, p)$

Response: $\langle B(t) \rangle_A = \int_{-\infty}^{t} dt' \chi_{BA}(t - t')\phi(t')$

Response function: $\chi_{BA}(t) = 0$ for $t < 0$

Nonequilibrium response: $\langle B(t) \rangle_A$.

Equilibrium time correlation: $C_{AB}(t) \equiv \langle AB(t) \rangle$. 
Nonequilibrium Response

**Response and Correlation**

\[
\chi_{BA}(t) = -\frac{1}{k_B T} \langle A \dot{B}(t) \rangle = -\frac{1}{k_B T} \dot{C}_{AB}(t), \text{ for } t > 0
\]

**Impulsive perturbation:** \( \phi(t) = \text{constant} \times \delta(t) \)

\[
\langle B(t) \rangle_A \propto \chi_{BA}(t) \propto -\dot{C}_{AB}(t)
\]

**Preparation and relaxation:** \( \phi(t) = \begin{cases} \text{constant} & (t \leq 0) \\ 0 & (t > 0) \end{cases} \)

\[
\langle B(t) \rangle_A \propto \int_t^\infty dt' \chi_{BA}(t') \propto C_{AB}(t)
\]
Director fluctuations, and time correlation functions or spectra, are investigated by light scattering experiments.


*For each mode the power spectrum (or frequency distribution) has the form of one single Lorentzian, centred on the incident beam frequency. This means that the behaviour of the fluctuations is purely viscous (no oscillations).*


*The orientation fluctuations of the director are coupled to the fluid velocity by viscous effects, and in fact are overdamped: the modes which the elastic theory … predicts do not propagate.*
Twist Dynamics

Director and Velocity Fluctuations

Hydrodynamic Equations

\[
\begin{align*}
\left( \gamma_1 \frac{\partial}{\partial t} + K_2 k^2 \right) \tilde{n} &= 0 \\
\left( \rho \frac{\partial}{\partial t} + \eta_3 k^2 \right) \tilde{v} &= 0
\end{align*}
\]
Twist Dynamics

Director and Velocity Fluctuations

\[ \mathbf{n} \]

Hydrodynamic Equations

\[
\begin{align*}
\left( \gamma_1 \frac{\partial}{\partial t} + K_2 k^2 \right) \mathbf{n} &= 0 \\
\left( \rho \frac{\partial}{\partial t} + \eta_3 k^2 \right) \mathbf{v} &= 0
\end{align*}
\]

\[ \mathbf{n} \sim e^{-\left(\frac{K_2 k^2}{\gamma_1}\right)t} \]

no coupling
director rotation
elastic constant
Hydrodynamic Equations

\[ \left( \gamma_1 \frac{\partial}{\partial t} + \mathbf{k}_2 \mathbf{k}^2 \right) \tilde{n} = 0 \]
\[ \left( \rho \frac{\partial}{\partial t} + \eta_3 \mathbf{k}^2 \right) \tilde{v} = 0 \]

no coupling
density
shear viscosity
\[ \tilde{v} \sim e^{-\left(\eta_3 k^2/\rho\right)t} \]
Twist Dynamics
Simulation Results

Director and Velocity Correlation Functions

\[ \langle \tilde{n}(k, t) \tilde{n}(-k, 0) \rangle \]

\[ \langle \tilde{v}(k, t) \tilde{v}(-k, 0) \rangle \]
Twist Dynamics
Simulation Results

Director and Velocity Correlation Functions

\[ \langle \tilde{n}(k, t) \tilde{n}(-k, 0) \rangle \]

\[ \langle \tilde{v}(k, t) \tilde{v}(-k, 0) \rangle \]
Splay Dynamics

Director and Velocity Fluctuations

\[ \tilde{n} + \frac{i \alpha_3}{k} \tilde{v} = 0 \]

\[ \frac{\partial}{\partial t} \tilde{n} + \left( \rho \frac{\partial}{\partial t} + \eta_1 k^2 \right) \tilde{v} = 0 \]
Hydrodynamic Equations

\[
\left( \gamma_1 \frac{\partial}{\partial t} + K_1 k^2 \right) \tilde{n} + i k \alpha_3 \tilde{v} = 0 \\
-ik \alpha_3 \frac{\partial}{\partial t} \tilde{n} + \left( \rho \frac{\partial}{\partial t} + \eta_1 k^2 \right) \tilde{v} = 0
\]
Splay Dynamics
Simulation Results

Director and Velocity Correlation Functions

\[ \langle \tilde{n}(k, t) \tilde{n}(-k, 0) \rangle \]

\[ \langle \tilde{v}(k, t) \tilde{v}(-k, 0) \rangle \]
Splay Dynamics
Simulation Results

Director and Velocity Correlation Functions

\[ \langle \tilde{n}(k, t) \tilde{n}(-k, 0) \rangle \]

\[ \langle \tilde{v}(k, t) \tilde{v}(-k, 0) \rangle \]
Hydrodynamic Equations

\[
\left( \gamma_1 \frac{\partial}{\partial t} + K_3 k^2 \right) \tilde{n} + ik\alpha_2 \tilde{v} = 0
\]

\[
-ik\alpha_2 \frac{\partial}{\partial t} \tilde{n} + \left( \rho \frac{\partial}{\partial t} + \eta_2 k^2 \right) \tilde{v} = 0
\]
Bend Dynamics

Director and Velocity Fluctuations

Hydrodynamic Equations

\[
\begin{align*}
\left( \gamma_1 \frac{\partial}{\partial t} + K_3 k^2 \right) \tilde{n} + ik\alpha_2 \tilde{v} &= 0 \\
-ik\alpha_2 \frac{\partial}{\partial t} \tilde{n} + (\rho \frac{\partial}{\partial t} + \eta_2 k^2) \tilde{v} &= 0
\end{align*}
\]

strong coupling
Bend Dynamics

Simulation Results

Director and Velocity Correlation Functions

\[ \langle \tilde{n}(k,t) \tilde{n}(-k,0) \rangle \]

\[ \langle \tilde{v}(k,t) \tilde{v}(-k,0) \rangle \]

The diagrams show the correlation functions over time, indicating behavior for larger \( k \) values.
Bend Dynamics
Simulation Results

Director and Velocity Correlation Functions

\[ \langle \tilde{n}(k,t) \tilde{n}(-k,0) \rangle \]

\[ \langle \tilde{v}(k,t) \tilde{v}(-k,0) \rangle \]
Orders of Magnitude

\[ \rho \sim 10^3 \text{ kg m}^{-3} \]
\[ \eta \sim \alpha \sim \gamma_1 \sim 10^{-3} - 10^{-2} \text{ Pa s} \]
\[ K \sim 10^{-11} \text{ N} \]
\[ (K/\gamma_1)k^2 \]
\[ (\eta/\rho)k^2 \]
\[ \mu = \frac{\rho K}{\gamma_1 \eta} \sim 10^{-4} - 10^{-2} \]

densities
viscosities
elastic constants
director decay rate
velocity decay rate
time scale separation
Solving the Hydrodynamics

Secular Equations for Bend Fluctuations

\[ \tilde{n}(k, t) \sim e^{-\lambda k^2 t} \quad \text{and} \quad \tilde{v}(k, t) \sim -\lambda k^2 t \]

\[ \lambda^2 \rho \gamma_1 + \lambda\left(\alpha^2 - \gamma_1 \eta_2 - \rho K_3\right) + K_3 \eta_2 = 0 \]

small or large?

Define \( \mu = \frac{\rho K_3}{\gamma_1 \eta_2} \), \( \xi = 1 - \frac{\alpha^2}{\gamma_1 \eta_2} \),

\[ \xi^2 \lesssim 4\mu \Rightarrow \text{complex } \lambda \]
What Did We Learn?

- Simulations agree with hydrodynamics.

- \(\mu = \frac{\rho K_3}{\gamma_1 \eta_2}\) is small (de Gennes), typically \(\mu \approx 10^{-4} - 10^{-2}\).

- \(\alpha_2^2 \approx \gamma_1 \eta_2\) (de Gennes again!).

- \(\xi = 1 - \frac{\alpha_2^2}{\gamma_1 \eta_2}\) also small, typically \(\xi \approx 0.2\).

- Propagating modes if \(\xi^2 \lesssim 4\mu\) \(\Rightarrow\) \[
\begin{align*}
\mu &\approx 10^{-4}, & |\xi| &\lesssim 0.02 \\
\mu &\approx 10^{-2}, & |\xi| &\lesssim 0.2
\end{align*}
\]

- Experimentally observable for low viscosity liquid crystals?


Conclusions

- Liquid crystalline properties
  - Molecular structure
- Occasional surprises require a rethink
- Insight from statistical mechanical theories
- Stimulate new experiments

Simulations can be useful!
Conclusions

- Liquid crystalline properties and molecular structure:
  - Simulations can be useful!
  - Insight from statistical mechanical theories
  - Occasionally, surprises require a rethink
  - Stimulate new experiments
Acknowledgements

PhD students:
- Anja Humpert
- Paul O’Bien

Collaborators:
- David Cheung (Galway)
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Funding:
- EPSRC
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AND THANK YOU FOR YOUR ATTENTION!