3D structures

Top: chiral nematic skyrmions

Side: Smalyukh, Nat. Mat. (2011)

Discotic nematics

H. Chen, JMC (2012)

Molecules

Iso - Smectics - Xtal

Iso - Xtal

J. Goodby (York)

Pathways to LCs - fluid interfaces (positional ordering)

Smectic A
smectic A textures

between clean glass plates (n parallel to the glass, unconstrained in-plane)

smectic A focal conic domains

Georges Friedel 1922

cyclides of Dupain - parabolic

cyclides of Dupain – ellipse / hyperbola

J.C. Maxwell from amazon.com
textures - what do they depend on?

- the phase
- cell thickness
  - optics
  - structure
- surface treatment
- thermal history
  - cooling rate
  - increasing or decreasing $T$
- adjacent phases
- Impurities
- flow
- inhomogeneities
  - quenched disorder
  - particles

freely suspended smectic films

**smectic C**

$\Phi_{(r)}$

3D XY model

de Gennes (1972)

layers parallel to plates

single-layer films - polar smectic A (Sm AP)

W586

$p$

highest symmetry polar fluid
Observation and Analysis of Smectic Islands in Space

- Island emulsions
- Side view
- Top view in reflection

Structure vs. Handedness

- Homochiral dipolar
- Heterochiral quadrupolar

Real Time

Calamitic Liquid Crystal Phases

<table>
<thead>
<tr>
<th>Orthogonal Phases</th>
<th>Twisted Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smectic A</td>
<td>Smectic C (pynoline)</td>
</tr>
<tr>
<td>Smectic A</td>
<td>Smectic C (antiphase)</td>
</tr>
<tr>
<td>Hexatic Smectic B</td>
<td>Hexatic Smectic I</td>
</tr>
<tr>
<td>Hexatic Smectic I</td>
<td>Hexatic Smectic F</td>
</tr>
<tr>
<td>Crystal B</td>
<td>Crystal J</td>
</tr>
<tr>
<td>Crystal E</td>
<td>Crystal H</td>
</tr>
</tbody>
</table>
molecular origins of nematics, smectics

\[ \phi_c = \frac{V_{rod}n_s}{V} \sim \left( NLD^2 \right) / \left( NL^2 D \right) = D/L \]

\[ \rho_c \sim 1/(L^2 D) \]

\[ \Delta S_{tr} = -k_B \ln \left( 1 - V_{rod}/V \right) \sim k_B p L^2 D \]

\[ \Delta S_{sw} = k_B \ln \Omega \sim k_B \]

\[ \Delta S_{tr} = 0 \]

hard spherocylinders

Bolhuis, Frankel, JCP (1997)

Onsager (1949)

\[ k_b = 1/4, \beta PD^3 = 6 \]

\[ k_b = 1, \beta PD^3 = 5 \]

\[ k_b = 4, \beta PD^3 = 1.8 \]

\[ k_b = 16, \beta PD^3 = 1.2 \]

\[ k_b = 64, \beta PD^3 = 0.4 \]

adding flexible tails...

- soft spherocylinder polymer with rigid core and flexible chains
- molecular flexibility controlled by bond angle bending spring constant \( K_{bend} \)
- studied using NPT MD simulation

phase diagram of flexible-tail spherocylinders

\[ \log_2(\beta k_{bend}) \]

increasing flexibility

\[ \text{SmF} \]

\[ \text{SmI} \]

\[ \text{SmC} \]

\[ \text{SmA} \]

\[ \text{N} \]
**discotic columnar phases**

IB2-C6  
Triphenylene-C6

**pathways - fluid interfaces generate anisotropy**

G. Srinivas, IBM Almaden  

**block copolymers**

Spheres  Cylinders  Gyroid  Lamellar  Gyroid  Cylinders

PMMA  polystyrene

**triblock copolymers**

Hexagonal cylinders  Lamellar  Hexagonal cylinders  Spheres  Spheres (BCC)  Cylinders  Gyroid  Lamellar  Hexagonal cylinders  Spheres (BCC)  Cylinders  Gyroid  Lamellar  Hexagonal cylinders
lyotropics

nanoporous silica from lyotropic liquid crystals

lyotropic variations

hierarchical self assembly

~ 10 of the 20 most cited liquid crystal papers
**bola-amphiphiles**

*Myongsoo Lee (Seoul)*

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**amphiphilic rings**

*Myongsoo Lee (Seoul)*

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**aggressive amphiphilics**

*Myongsoo Lee (Seoul)*
polymers and elastomers

photoactuated cilia

photopolymerized side chain polymer network with azo-based mesogens

D. Broer, Nat. Mat. (2009)

chromonic liquid crystals

M. Wilson, JACS (2012)

chromonic liquid crystals

nematic columnar

Spada, JACS (1989)

Lavrentovich (Kent State)

guanine quartets

DNA
Maier – Saupe model of the isotropic / nematic transition

\[ S = \frac{1}{2} (3 \cos^2 \theta - 1) \]

\[ V(\theta, S) = -\frac{A}{kT} \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \] \[ \times \exp \left[ -\frac{V(\theta, S)}{kT} \right] \sin \theta d\theta \]

\[ Z = 2\pi \int_0^\pi \exp \left[ -\frac{V(\theta, S)}{kT} \right] \sin \theta d\theta \]

\[ S = \frac{3}{4} \left[ \exp(x^2) - 1 \right] - \frac{1}{2} \]

\[ kT/A = \frac{3}{2} \frac{S}{x^2} \]

\[ g = \frac{1}{2} k_{11} (\nabla \cdot n)^2 + \frac{1}{2} k_{22} (n \cdot \text{curl } n)^2 + \frac{1}{2} k_{33} (n \times \text{curl } n)^2 \]

Oseen / Frank (1930s – 1950s)
1911

- constructs nematic cells
- surface alignment by rubbing glass with paper
- observes that polarization follows optic axis if \( \lambda \ll p \)

Charles Mauguin

Mauguin limit

1931:

Freedericksz transition...

\[
\begin{align*}
g & = \frac{1}{2} k \int_{0}^{d/2} \frac{dz}{dz} \left[ \left( k_{11} \sin^2 \theta + k_{33} \cos^2 \theta \right) \left( \frac{\partial \theta}{\partial z} \right)^2 - \chi \alpha H \sin \theta \right] \\
g & = 2 \int_{0}^{d/2} \frac{dz}{dz} \left[ \xi^2 \left( \frac{\partial \theta}{\partial z} \right)^2 - \sin^2 \theta \right] \\
\xi & = \frac{\sqrt{k/\chi \alpha H^2}}{\sin \theta - \sin \theta_m}
\end{align*}
\]

\[\frac{1}{2} \left( \frac{\partial \theta}{\partial z} \right)^2 + \sin^2 \theta = \sin^2 \theta_m
\]

\[\frac{1}{2} d - z = \int_{0}^{d} \frac{d\theta'}{\sin^2 \theta_m - \sin^2 \theta'} \left( \frac{1}{2} \right) = \frac{\sqrt{k_33 \pi}}{\chi \alpha d}
\]

\[\frac{1}{2} k \cdot \frac{1}{2} d \cdot \xi \cot \theta_m F(\cot \theta_m, \theta) = \frac{\xi K}{\sin \theta_m}
\]

Freedericksz transition

\[
\theta_m \sim 2 \left( \frac{H}{H_c} - 1 \right)^{1/2}
\]

\[H_c = \sqrt{\frac{k_33 \pi}{\chi \alpha d}}
\]

\[\nabla \cdot n = -\sin \theta \frac{\partial \theta}{\partial z}, \quad \nabla \times n = \frac{\partial \theta}{\partial z} \cos \theta, \quad n \cdot (\nabla \times n) = 0, \quad \n \cdot \nabla \times n = (kn_x - n_x) \cos \theta \frac{\partial \theta}{\partial z}
\]
**dynamics**

static equilibrium: torque unbalance \(= \xi^2 \frac{\partial^2 \theta}{\partial z^2} + \sin \theta \cos \theta = 0\)

dynamic torque unbalance \(= \gamma \frac{\partial \theta}{\partial t} = K \frac{\partial^2 \theta}{\partial z^2} + \varepsilon \Delta E^2 \sin \theta \cos \theta\)

reorientation time \(\tau = \frac{\gamma d^2}{\pi^2 K (1 - (E/E_c)^2)}\)

**flexoelectricity**

\(P = \varepsilon_1 n (\nabla \cdot n)\) for splay

\(P = e_3 (\nabla \times n) \times n\) for bend

for bend in an electric field:
\[g = K/2 \left[(\nabla \times n) \times n \right]^2 + E \left[(\nabla \times n) \times n \right] \sim E\]


**chirality - blue phases**