Capillary models for liquid crystal films, membranes, and fibers

Alejandro D. Rey

Department of Chemical Engineering
McGill University, Montreal, Quebec, Canada

Isaac Newton Institute for Mathematical Sciences
University of Cambridge
Mathematical Modeling and Analysis of Complex Fluids and Active Media in Evolving Domains, 1/8/2013


Funding: NSERC, PRF, FQNRT, DOE
Capillary Models

1-5

Liquid Crystal Landau - de Gennes Model

Surface Euler Equations

6

Shape Equations

7

Leslie-Ericksen Nematodynamics

Applications

Films
- Film stability
- Forced wetting

Membranes
- Flexoelectric membranes
- 2D anisotropic soft matter

Fibres
- Carbon fibres
- Rayleigh instabilities

Drops

Thermodynamics of Shape and Structure
I. Liquid Crystals: Anisotropic Soft Matter

**Crystal 230 point groups**

- **smectic**
- **nematic**
- **columnar**
- **cholesteric**

**Liquid crystal phases**

- **50 liquid crystal phases**
- **orientational order**
- **orientational & 1D/2D positional order**
- **disorder**

**Anisotropic elastic**

- \( E_{ijkl} \)
- \( P=1, Q=1 \)
- **order**

**Anisotropic visco-elastic**

- \( E_{ijkl} \)
- \( \eta_{ijkl} \)
- \( P>0, Q>0 \)
- **orientational order**

**Viscous**

- \( \eta \)
- \( P=0, Q=0 \)
- **disorder**
Bulk Nematodynamics

\[ \Delta = T^s : A - \frac{\delta F}{\delta Q} : \left( \frac{dQ}{dt} \right) \]

\[ T^s \frac{dQ}{dt} = \begin{pmatrix} a & -\alpha^T \\ \alpha & b \end{pmatrix} \otimes \left( \frac{A}{\delta F/\delta Q} \right) \]

\( \alpha: \) shape parameter

Flow-Induced Orientation/Back-Flow Cycle

Flow velocity

\( \mathbf{v} \Rightarrow \mathbf{A} = (\nabla \mathbf{v})^s \)

Flow-induced orientation

\[ \frac{dQ}{dt} = \left( \begin{array}{cccc} \lambda_1 & \alpha \\ \alpha & \lambda_2 \end{array} \right) \otimes \left( \begin{array}{c} \beta \end{array} \right) \]

Defects

Back-flow

Q-velocity

\[ \frac{dQ}{dt} \Rightarrow \frac{\delta F}{\delta Q} \]

4D Parametric Space

\[ \frac{U}{C^*} = \frac{E}{R} \Rightarrow E = \frac{\tau_e}{\tau_f}; R = \left( \frac{H}{\ell} \right)^2; \beta \]

Rey and Denn (2001)
Computational Bulk Nematodynamics

Phase Transitions: \( Q(x,y,z,t), \dot{\gamma} \)

T. Tsuji and ADR

2D transient sheared nematics: 
\( p(x,y,t), v(x,y,t), Q(x,y,t) \)
ADR and NSF-CAEFF (2008)
Nemato-capillarity: Structure-Shape-Stability

Films/Foams/Coatings

Active/Anisotropic Membranes

Fiber/Filaments

Drops
**Order Parameters**

**Bulk**

\[ \Psi(u) = \frac{1}{4\pi} + \frac{3 \times 5}{4\pi x 2} Q : (uu - I / 3) + ... \]

\[ Q = S \left( \frac{nn - I}{3} \right) + \frac{P}{3} (mm - ll) \]

**Interfaces and Membranes**

**Filaments and Contact Lines**

\[ s = \frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{2} \]

\[ b = H I_s + D q; K = H^2 - D^2 \]

\[ K = c^2 \quad K = 0 \quad K = -c^2 \]

\[ \frac{dt}{ds} = \begin{bmatrix} 0 & \kappa & 0 \\ -\kappa & 0 & \tau \\ 0 & -\tau & 0 \end{bmatrix} \begin{bmatrix} t \\ p \\ b \end{bmatrix} \]
1. **Order Parameters: Q-tensor and Curvature Tensors**
2. **Q-tensor Ordering Triangle: Trajectories in Phase Space**
   - bulk defects
   - interfaces
   - interfacial defects
3. **Free Energies**
   - nematic homogeneous, gradient and anchoring energies
   - free energies for surfactant-laden interfaces and membranes
   - energy ratios: extrapolation length
   - energy ratios: tactoids
4. **Bulk, Surface and Line Nematostatics**
   - force balances
   - Q-tensor balances
   - junction forces and couples
   - number of independent shape equations
5. **Stress Tensors**
   - orientational Marangoni flow
   - capillary rise: role of gradient elasticity
   - partial wetting: three modes
6. **Shape Equations**
   - Cahn-Hoffman capillary vector
   - surface shape equation
   - Cahn-Hoffman line tension vector
   - line shape equation
7. **Thermodynamics**
   - Euler equations: easy axis and easy shape
   - morphactant and linealant effects
Shapes of Nematic Spherulites

\[ \gamma = \gamma_{iso} + \frac{W}{2} (Q : kk) \]

\[ f_b = \frac{L}{2} (\nabla Q)^2 \]

Prinsen/van der Schoot PRE (2003)

\[ V^{1/3} = L \left( \frac{W}{\gamma_{iso}} \right)^{1/6} / W \]

Cahn-Hoffman Capillary Vector: $X_s(Q, k)$

$$f_s = f_s(Q, k)$$

$$X_s = f_s \left( \frac{k}{X_{s\perp}} \right) + I_s \cdot \frac{\partial f_s}{\partial k}$$

$$A = A_k$$

$$-\left( \frac{\partial \gamma}{\partial k} \right)$$

Main frame: \( \{ k, t_o = \frac{n_{///}}{n_{/://}}, b_o = t_o \times k \} \)

Torque on \( k \): \( \sigma = X_{s\perp} \times k \)

Surface Bending Stress $\mathbf{T}^b_s$ and Surface Force $\mathbf{\sigma}$

\[
\mathbf{T}^b_s = - \mathbf{I}_s \cdot \frac{\partial \mathbf{f}_s}{\partial \mathbf{k}} \mathbf{k} = - \mathbf{X}_{s/\mathbf{k}}
\]

\[
\begin{bmatrix}
0 & 0 \\
0 & 0 \\ 1
\end{bmatrix}
\]

force on $\mathbf{t}$: $\mathbf{\sigma} = \mathbf{X}_s \times \mathbf{t} = \mathbf{f}_s \mathbf{k} \times \mathbf{t} + \left( \mathbf{I}_s \cdot \frac{\partial \mathbf{f}_s}{\partial \mathbf{k}} \right) \times \mathbf{t}$

Cheong and Rey, JCP (2004), Wincure and Rey, Nanoletters (2007)
Nematic Surface Shape Equation: Normal Stress Balance

\[-[kk : T_b] = \{\nabla_s \cdot T_s\} \cdot k = -p_c\]

\[\Psi_s = kI_s - I_s k, \quad T_s = X_s \cdot \Psi_s + T_s^D\]

Capillary stress

Ericksen stress

\[X_s(k, Q) = f_s k + I_s \cdot \frac{\partial f_s}{\partial k}\]

Nematic Capillary Pressure

\[-p_c = -\nabla_s \cdot X_s + T_s^D : b = \left\{ \begin{array}{c}
\frac{\partial X_s}{\partial k} \\
\frac{\partial X_s}{\partial k}
\end{array} \right\} : b - \nabla \cdot X_s^s \bigg|_b + T_s^D : b\]

Area size change

Area rotation

Surface Q-curvature

GradQ

Herring Pressure

\[\Delta p = \left\{ -f_b - kk : T_b^D \right\} + \left\{ f_s I_s + \frac{\partial^2 f_s}{\partial k^2} + T_s^D \right\} : b - \left\{ \frac{\partial X_s^s}{\partial Q} : (\nabla_s Q)^T + \frac{\partial X_s^s}{\partial \nabla_s Q} : (\nabla_s \nabla_s Q)^T \right\} \]
**Wulff Plot of Nematic Spherulite**

\[ \text{CP}(\varphi) = \{ f_s I_s \} : b \]

**LdG model**

\[
\begin{align*}
  f_h &= \frac{a(T)}{2} Q : Q - \frac{b}{3} Q : (Q \cdot Q) + \frac{c}{4} (Q : Q)^2 \\
  f_g &= \frac{L_1}{2} \nabla Q : (\nabla Q)^T + \frac{L_2}{3} (\nabla \cdot Q) (\nabla \cdot Q) + \frac{L_3}{4} Q : (\nabla Q : (\nabla Q)^T)
\end{align*}
\]

\[ f_s(\varphi) = b^3 \sqrt{3L_1 + \frac{L_2}{2} + 3L_2 (n \cdot k)^2} / 486c^{5/2} \]

**Surface Gradient Elasticity: interfacial defect shedding**

\[ QP = -\nabla_s \cdot X_{s//} = - \left\{ \frac{\partial X_{s//}}{\partial Q} : (\nabla_s Q)^T + \frac{\partial X_{s//}}{\partial \nabla_s Q} : (\nabla_s \nabla_s Q)^T \right\} \]
Rayleigh-Herrings Instabilities

Cahn–Hoffman Vector: $X = f_s k + \frac{\partial f_s}{\partial k}$

Rayleigh–Herrings Instabilities

$$A_f = A_i \left\{ 1 + \frac{\xi^2}{4a^2} \left[ (ka)^2 + m^2 - 1 \right] \right\}$$

Peristaltic

$A_f < A_i$

$m = 0$

$m = +1$

$m = -1$

$m = +2$

$m = -2$

$m = +9$

$m = -9$

Chiral

$A_f > A_i$

Liquid Crystal Fiber
1. Order Parameters: $Q$-tensor and Curvature Tensors
2. $Q$-tensor Ordering Triangle: Trajectories in Phase Space
   - bulk defects
   - interfaces
   - interfacial defects
3. Free Energies
   - nematic homogenous, gradient and anchoring energies
   - free energies for surfactant-laden interfaces and membranes
   - energy ratios: extrapolation length
   - energy ratios: tactoids
4. Bulk, Surface and Line Nematostatics
   - force balances
   - $Q$-tensor balances
   - junction forces and couples
   - number of independent shape equations
5. Stress Tensors
   - orientational Marangoni flow
   - capillary rise: role of gradient elasticity
   - partial wetting: three modes
6. Shape Equations
   - Cahn-Hofman capillary vector
   - surface shape equation
   - Cahn-Hoffman line tension vector
   - line shape equation
7. Thermodynamics
   - Euler equations: easy axis and easy shape
   - morphactant and linealant effects
Interfacial Thermodynamics

$$\tilde{U} = T \tilde{S} + \sum_{j} \mu_j \tilde{\rho}_j + \gamma(Q, k)$$

Preferred Anchoring Angle = Easy Axis

$$g = -\left( \frac{\partial \gamma}{\partial Q} \right)^{[s]}$$

$$\frac{\partial \tilde{U}}{\partial Q}^{[s]} \text{energy} - \frac{\partial^2 g}{\partial Q^2}^{[s]} \text{work} \cdot \left\{ T \frac{\partial Q}{\partial T}^{\text{entropy}} + \sum_{j} \mu_j \frac{\partial Q}{\partial \mu_j}^{\text{adsorption}} \right\} + g_i \text{intrinsic force} = 0$$

Preferred Shape=Easy Shape

Blanc et al. PCB 2008, 112, 4157-4160

Elasticity and anchoring, hydrodynamic flows, or external fields. Molecules adsorbed specifically at LC interfaces are known to orient LC molecules (anchoring effect), but other induced effects have been poorly explored. Using specifically designed amphitropic surfactants, we demonstrate that large-shape transformations can be achieved in direct LC/water emulsions. In particular, we focus on unusual nematic filaments formed

\[ \tilde{U} = T\tilde{S} + \sum_j \mu_j \tilde{\rho}_j + \gamma(Q,k) \]

\[ \nabla_s \left( I_s \cdot \frac{\partial \tilde{U}}{\partial k} \right) - \nabla_s \left( I_s \cdot \frac{\partial (X_{//})}{\partial k} \right) = \sum_i \frac{T}{\partial T} \frac{\partial k}{\partial \mu_i} + \sum_{i=3}^{N} \mu_i \frac{\partial k}{\partial \mu_i} \]

\[ \nabla_s \cdot X_{//} = 0 \]

\[ X = \gamma k_{//} + I_s \cdot \frac{\partial \gamma}{\partial k} \]

CTAB

\[ CH_3(CH_2)_mCH_2--\overset{\text{N}}{\text{--}}CH_3 \]

\[ CH_3(CH_2)_mCH_2--\overset{\text{N}}{\text{--}}CH_3 \]

40µm

\[ 20µm \]

\[ T=20°C \]

\[ T=25°C \]

\[ T(°C) \]

\[ (5.8K/Ro) dA \]

\[ (3.2K/Ro) dA \]
Concentration profile showcasing the adaptive grid structure

Crystalline order parameter without the adaptive grid structure

Gurevich, Soule, Provatas, Reven and Rey (2013)

Thermodynamics of LC nano-colloids

N+C, T=30°C
Quench. Initial seed oriented in x-direction
Capillary Models

- Liquid Crystal Landau - de Gennes Model
- Surface Euler Equations

Shape Equations

Applications

Leslie-Ericksen Nematodynamics

- Films
  - Film stability
  - Forced wetting

- Membranes
  - 2D anisotropic soft matter
  - Flexoelectric membranes

- Fibres
  - Carbon fibres
  - Rayleigh instabilities

- Drops

Thermodynamics of Shape and Structure
Structural LC Film Pressure:

\[ P_m = P_0 - \frac{\gamma}{R} = P_f = P_0 - \Pi_s \]

Hybrid Strong Anchoring

\[ \nabla n \neq 0 \]

Flat film shape equation (b=0)

\[ \Pi_s = \left\{ -\left( f_g + f_h \right) I + \frac{\partial f_g}{\partial \nabla n} : (\nabla n)^T \right\} : kk \]

pN Frank elasticity

\[ \Pi_{s, \text{max}} \approx \frac{L}{L_{\text{ex}}^2} = \frac{W^2}{L} \]
Structural Pressure in Symmetric Films

\[ \nabla n = 0 \]

Fig. 2. MBBA thin film formation observed between cross nicols. The figure shows the boundary conditions at the free surface and the structural transition due to hydrodynamic flow. a) initial structure. b) equilibrium structure. n. is the direction.

Fig. 3. Critical thickness of “black spots” formation versus film radius. a) pentylcyanobiphenyl. b) octylpolyoxyethylene 10^{-5} M solutions in KCl 0, 1 M

Symmetric Strong Anchoring

\[ \Pi_s = -\left\{ \frac{\partial^2 \gamma}{\partial Q \partial k} \right\} : \nabla_s Q - \left\{ f_h + \frac{\partial f_g}{\partial z} \right\} \]

Free Energy Density (kcal/m^2)

5CB
Nematic Fiber Coating Film Flow

Landau-Levich-Derjaguin coating scaling law

\[ \frac{h}{r} \propto C_a^{2/3} = \left( \frac{\eta V}{\gamma} \right)^{2/3} \]

Experimental section

We have used a eutectic liquid crystal mixture, E7, in the nematic phase (at room temperature) and in the isotropic phase (at 100 °C). E7 is composed of K15 (4-pentyl-4'-cyanobiphenyl), K21 (4-heptyl-4'-cyanobiphenyl), M24 (4-octyloxy-4'-cyanobiphenyl), and T15 (4-pentyl-4'-cyanoterphenyl), and is a homogeneous mixture (single thermodynamic phase) with a single nematic–isotropic transition temperature of 60–61 °C. A polypropylene fiber of diameter 200 μm is dragged through a Teflon tube reservoir (inner radius = 0.24 cm, length = 1.5 cm) containing E7. The fiber passes through the tube in the horizontal direction.


Shear and Normal Stresses

\[ t_{ij} = \eta_{ijkl} A_{lk} + \mu_{ijk} N_k \]

\[ t_{ii} = \eta_{iikl} A_{lk} + \mu_{iik} N_k \]

\[ t_{xy} = \eta_{xykl} A_{lk} + \mu_{xyk} N_k \]

\[ N_1 = t_{xx} - t_{yy} = \gamma n_x n_y \left( \gamma_2 + \alpha_1 \left( n_y^2 - n_x^2 \right) \right) \]

\[ \frac{N}{t_{xy}}_{\text{flow-alignment}} = \frac{\sqrt{\lambda^2 - 1} \left( \frac{\gamma_2 - \alpha_1}{\lambda} \right)}{2 \gamma_1 + \alpha_2 \left( \frac{\lambda^2 - 1}{\lambda^2} \right)} \]

Cone & plate \( N_1/t_{xy} \) data & simulation for a sheared thermotropic discotic nematic

Experiments: \( N_D \)

Simulations

Rey, Advances in Rheology (2010)
**Leslie-Ericksen Film Formation Model**

\[
\frac{\partial t_{yx}}{\partial y} + \frac{\partial}{\partial x} \int_y^h t_{xy,x} \, dy + \frac{\partial N_1}{\partial x} = -\gamma \frac{\partial^3 h}{\partial x^3}
\]

**shear force**

\[t_{yx} = \alpha_1 \left( \frac{V}{\lambda} \right) + \alpha_2 \left( \frac{V}{h} \right) + \alpha_3 \left( \frac{Vh}{\lambda^2} \right)\]

\[N_1 = \alpha_4 \left( \frac{V}{\lambda} \right) + \alpha_5 \left( \frac{V}{h} \right) + \alpha_6 \left( \frac{Vh}{\lambda^2} \right)\]

**Generalized LLD-LE Coating Scaling Law**

\[\frac{h}{r} \approx C_1^a\]

\[Ca = \frac{(h/r)^{3/2}}{\left[ \alpha_{145} (h/r)^{1/2} + \alpha_{23} (h/r) + \alpha_2 + \alpha_{16} (h/r)^{3/2} + \alpha_3 (h/r)^2 \right]}\]

LLD=Newtonian Fluids
**Capillary Models**

- **Liquid Crystal Landau - de Gennes Model**
  - **Shape Equations**
  - **Applications**
    - Films
      - Disjoining Pressure
      - Anchoring transitions
      - Forced wetting
    - Membranes
      - Flexoelectric membranes
      - 2D anisotropic soft matter
    - Fibres
      - Carbon fibres
      - Silk fibres
  - **Surface Euler Equations**
    - Thermodynamics of Shape and Structure
Nematic Textures under Cylindrical Confinement

disclinations lines, escaped lines, point defects, rings

Planar Radial

Planar Polar (PP)

Axial Rings (AR)

Point Defect (PD)

Escape (E)

Radial Rings
Spider Silk Fiber Biospinning Process

**Table 1.** $^{13}$C labelling percentages of silk samples from 3 kinds of spider species

<table>
<thead>
<tr>
<th>AA</th>
<th>DOGSY, $^{13}$C Ala, %</th>
<th>DOGSY, $^{13}$C Gly, %</th>
<th>DOGSR, $^{13}$C Ala, %</th>
<th>DOGSR, $^{13}$C Gly, %</th>
<th>Relative abundance of amino acids, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ala</td>
<td>27.2 (7)</td>
<td>10.0 (7)</td>
<td>11.8 (6)</td>
<td>10.1 (4)</td>
<td>29</td>
</tr>
<tr>
<td>Gly</td>
<td>3.9 (18)</td>
<td>59.4 (2)</td>
<td>19.6 (6)</td>
<td>16.1 (2)</td>
<td>40</td>
</tr>
<tr>
<td>Pro</td>
<td>1.9 (13)</td>
<td>1.6 (8)</td>
<td>1.8 (6)</td>
<td>1.4 (6)</td>
<td>3</td>
</tr>
<tr>
<td>Tyr</td>
<td>1.5 (28)</td>
<td>1.0 (25)</td>
<td>1.0 (16)</td>
<td>1.5 (5)</td>
<td>4</td>
</tr>
<tr>
<td>Glu</td>
<td>4.0 (9)</td>
<td>3.5 (2)</td>
<td>3.9 (3)</td>
<td>2.9 (4)</td>
<td>10</td>
</tr>
</tbody>
</table>

The absolute biological composition of the five most abundant amino acids in silk is given in percentage, together with the relative abundance of the respective amino acids in mol%. The title of each column refers to the experiment and the intended labeling. SDs are given in brackets.

**1. synthesis  2. self-assembly  3. flow-process  4. solidification**

Three Spider and Silworm Duct Textures

Silkworm

Spider

Escaped

weak converging flow

Random shear flow

Silk Spinning

deluca and ADR, JCP (2007), Gupta and Rey PRL (2005)

Carbon Fiber Spinning

ADR, Adv in Rheology (2008)
Mesophase Pitch-based Carbon Fiber Processing

discotic mesophases precursors for high performance carbon fibers

<table>
<thead>
<tr>
<th></th>
<th>Tensile Strength (GPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Strain %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>2.4</td>
<td>830</td>
<td>0.3</td>
</tr>
<tr>
<td>PR</td>
<td>3.0</td>
<td>590</td>
<td>0.5</td>
</tr>
</tbody>
</table>

$\rho$ defects orientation
Carbon Fiber Texture Engineering
Temperature + Extensionsal Flow + Elasticity

Experiments
Simulations
First Principles

Strong Anchoring

High T  Low T

Die Geometry

Extrusion Flow

Die Geometry

Extrusion Flow

planar extensional flow

elastic instability

\[ \tilde{T} = 3/8 - \left( \frac{H}{\ell} - 37 \right)^{0.65} \]

\[ A = \begin{bmatrix}
-\frac{1}{2} \dot{\gamma} (1 + b) & 0 & 0 \\
0 & -\frac{1}{2} \dot{\gamma} (1 - b) & 0 \\
0 & 0 & \dot{\gamma}
\end{bmatrix} \]

ADRey, Advances in Rheology (2010); Sonnet, Killian, Hess, PRE (1995)
Capillary Models

- Liquid Crystal
  - Landau - de Gennes Model
  - Shape Equations
  - Applications
  - Membranes
    - Anchoring transitions
    - Forced wetting
    - 2D anisotropic soft matter
    - Flexoelectric membranes
  - Fibres
    - Carbon fibres
    - Rayleigh instabilities

- Surface Euler Equations
  - Thermodynamics of Shape and Structure
References

Review Papers


