Pattern Formation in Confined Nematic Liquid Crystals

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Liquid Crystals – what are they?

- Mesogenic phases of matter

- Intermediate between solids and liquids
Discovered by Reinitzer in 1888: two melting points for cholesterol!

**Diagram:**
- Solid crystal
- Hazy liquid
- Clear liquid
- Isotropic liquid

**Image:**
- Courtesy: Peter Palffy-Muhoray Lectures at Colorado - Boulder
Different Liquid Crystal Phases

nematic

cholesteric

+ ferroelectric, blue, TGB, bananas, etc...

smectic A

smectic C

Courtesy: Peter Palffy-Muhoray Boulder Lectures 2011
Nematic Liquid Crystals

- Anisotropic rod-like molecules with directional properties

- Long-range orientational ordering: molecules line up with one another
Key word: anisotropy!!!

*stimulus*
- chemical
- electric field
- light
- magnetic field
- temperature
- mechanical stress

*response: change in*
- compressibility
- conductivity
- electric susceptibility
- magnetic susceptibility
- refractive index
- modulus
- viscosity

Courtesy: Images from Peter Palffy-Muhoray’s lectures at Colorado – Boulder (Physics Today 60 (9), 54 (2007))
Nematic Anisotropy to Applications ...

- Best known as the working material of the multi-billion dollar liquid crystal display (LCD) industry.
New Applications and New Research

• New Materials and Colloid Science


• Photonics, Actuators, Security Applications

• Microfluidics and Biomimetic Systems

Why Liquid Crystals - Rich Mathematical Landscape

- Partial Differential Equations
- Calculus of Variations
- Scientific Computation
- Algebra and Topology, Functional Analysis
- Dynamical Systems
Questions that interest me...

The mathematics of

Orientational Order/Partial Order

Hierarchy of continuum theories and their predictions.

Material imperfections and defect-mediated structural transitions (F. Duncan M. Haldane and J. Michael Kosterlitz 2016 Nobel Prize in Physics)

Microscopic to Macroscopic Derivations?

Applications.
Liquid Crystals are a fascinating playground for mechanics, geometry, modelling and analysis to meet physics and real-life applications.

- Real opportunity for new mathematics-driven approaches to new materials, optimal design, optimal performance and efficient methodologies.
How do we mathematically model nematic liquid crystals?

Three popular “continuum” approaches -

- Oseen-Frank theory: assume that constituent molecules have a single direction of locally preferred alignment with “constant degree of orientational order”.

- Ericksen theory: assume that constituent molecules have a single distinguished direction with “variable degree of orientational order”.

- Landau-de Gennes theory: account for primary and secondary directions of alignment and “variable degrees of orientational order”.

\[ n(r) \]
The Nobel Prize in Physics in 1991 was awarded to Pierre-Gilles de Gennes for "for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers".
The Landau-De Gennes Theory

- General continuum theory that can account for all nematic phases and physically observable singularities.

- Define macroscopic order parameter that distinguishes nematic liquid crystals from conventional liquids, in terms of anisotropic macroscopic quantities such as the magnetic susceptibility and dielectric anisotropy.

- The $\mathbf{Q}$ – tensor order parameter is a symmetric, traceless $3\times3$ matrix.

\[
\mathbf{Q} = \begin{pmatrix}
Q_{11} & Q_{12} & Q_{13} \\
Q_{12} & Q_{22} & Q_{23} \\
Q_{13} & Q_{23} & -Q_{11} - Q_{22}
\end{pmatrix}
\]

Five degrees of freedom.
Eigenvalues of the Q-tensor and LC Phases

\[ Q = \lambda_1 n \otimes n + \lambda_2 m \otimes m + \lambda_3 p \otimes p \]

\[ \sum_{i=1}^{3} \lambda_i = 0 \]

• isotropic – triad of zero eigenvalues

\[ \lambda_1 = \lambda_2 = \lambda_3 = 0 \implies Q = 0 \]

• uniaxial – a pair of equal non-zero eigenvalues

\[ \lambda_2 = \lambda_3 = \lambda; \lambda_1 = -2\lambda \implies Q = -3\lambda \left( n \otimes n - \frac{1}{3} I \right) \]

• biaxial – three distinct eigenvalues and two locally preferred directions of molecular alignment.
The Landau-de Gennes Energy

The physically observable configurations correspond to minimizers of the Landau-de Gennes energy subject to the imposed boundary conditions.

\[ I[Q] = \int \frac{f_B(Q)}{L} + w(Q, \nabla Q) \, dV \]

The thermotropic potential:

\[ f_B(Q) = \frac{A}{2} tr Q^2 - \frac{B}{3} tr Q^3 + \frac{C}{4} (tr Q^2)^2 \]

\[ A = \alpha(T - T^*) \quad \alpha, b, c, T^* > 0 \]

- non-convex, non-negative potential with multiple critical points
- dictates preferred phase of liquid crystal – isotropic/ uniaxial as function of temperature?

The elastic energy density:

\[ w(Q, \nabla Q) = L|\nabla Q|^2 \]

\[ w(Q, \nabla Q) = L_1 |\nabla Q|^2 + L_2 Q_{ij,j} Q_{ik,k} \]
\[ f_B(Q) = \frac{A}{2} trQ^2 - \frac{B}{3} trQ^3 + \frac{C}{4} (trQ^2)^2 + M(A,B,C) \]

\[ A = \alpha(T - T^*) \quad \alpha, b, c, T^* > 0 \]

The bulk potential can be explicitly written as a function of two eigenvalues (from the tracelessness constraint) and we can compute the bulk minimisers explicitly as pairs of minimising eigenvalues, depending on the temperature regime.

*Introduction to Q-tensor theory 2014*

*Nigel J. Mottram, Christopher J.P. Newton*
The Landau-de Gennes Euler Lagrange Equations

The physically observable configurations correspond to minimizers of the Landau-de Gennes liquid crystal energy functional subject to the imposed boundary conditions.

The Euler-Lagrange equations in the one-constant case:

\[ w(Q, \nabla Q) = L |\nabla Q|^2 \]

\[ \Delta Q_{ij} = \frac{1}{L} \left( A Q_{ij} - B \left( Q_{ip} Q_{pj} - \frac{1}{3} (\text{tr} Q^2) \delta_{ij} \right) + C (\text{tr} Q^2) Q_{ij} \right) \quad i, j = 1, 2, 3 \]

- Energy minimizers are classical solutions of the Euler-Lagrange equations.

- Multiple solutions.

- Smooth and analytic (standard results in elliptic regularity)
Why is this a hard problem?

- Qualitative properties of energy minimizers in asymptotic limits: can we recover structure of defect cores?

- Exact solutions of Euler-Lagrange equations

\[ \Delta Q_{ij} = \frac{1}{L} \left( A Q_{ij} - B \left( Q_{ip} Q_{pj} - \frac{1}{3} (trQ^2) \delta_{ij} \right) + C (trQ^2) Q_{ij} \right) \quad i, j = 1, 2, 3 \]


- Non-minimising solutions?

A Toy Problem: The Planar Bistable LC Device

- Micro-confined liquid crystal system.

- Array of nematic liquid crystal-filled square / rectangular wells with dimensions between 20×20×12 microns and 80×80×12 microns.

- Surfaces treated to induce planar or tangential anchoring.

Boundary Conditions

• Top and bottom surfaces treated to have tangent boundary conditions – liquid crystal molecules in contact with these surfaces are in the plane of the surfaces.

Chong Luo, Apala Majumdar and Radek Erban, 2012 "Multistability in planar liquid crystal wells", Physical Review E, Volume 85, Number 6, 061702
Bistability: two experimentally observed states

Diagonal state: liquid crystal alignment along one of the diagonals.
Defects pinned along diagonally opposite vertices.

Tsakonas, Davidson, Brown, Mottram 2007

Also see
Rotated state: vertical liquid crystal alignment in the interior.
Defects pinned at two vertices along an edge.

Tsakonas, Davidson, Brown, Mottram 2007
Optical contrast?

Theoretical and experimental optical textures:

Theory:

Experiment:

Tsakonas, Davidson, Brown, Mottram 2007
Our work on this device....


- C.Luo, A.Majumdar and R.Erban 2012 Multistability in planar liquid crystal wells. Physical Review E, 85,Number 6, 061702
Our Approach to this Toy Problem

• Step 1: Model Reduction

Can rigorously prove using Gamma-convergence techniques (see below) that for sufficiently shallow three-dimensional wells, with particular surface energies on top and bottom that allow for planar anchoring and Dirichlet uniaxial conditions on lateral sides, (i) LdG energy minimizers have a fixed eigenvector in the z-direction and (ii) it suffices to study the variational problem on the square cross-section i.e. we can neglect the third dimension.

\[ Q = (q_3 + q_1) \epsilon_x \otimes \epsilon_x + (q_3 - q_1) \epsilon_y \otimes \epsilon_y + q_2 (\epsilon_x \otimes \epsilon_y + \epsilon_y \otimes \epsilon_x) - 2q_3 \epsilon_z \otimes \epsilon_z, \]

Reduced a problem with five degrees of freedom to a problem with three degrees of freedom!

• Restrict ourselves to:

\[ Q = q_1(x,y)(n_1 \otimes n_1 - n_2 \otimes n_2) + q_2(x,y)(n_1 \otimes n_2 + n_2 \otimes n_1) + q_3(x,y)(2e_z \otimes e_z - n_1 \otimes n_1 - n_2 \otimes n_2) \]

• Dirichlet boundary conditions on square edges

\[ q_1 = \begin{cases} 
-s_+/2 & C_1 \cup C_3, \\
+s_+/2 & C_2 \cup C_4, \\
g(y) & S_1 \cup S_3, \\
g(x) & S_2 \cup S_4 
\end{cases} \]

\[ q_2 = 0, \quad q_3 = -\frac{s_+}{6} \quad \text{on} \quad \partial \Omega \]

• Uniaxial boundary conditions that minimize the bulk potential for low temperatures.

\[ f_B(Q_b) = \frac{A}{2} tr Q_b^2 - \frac{B}{3} tr Q_b^3 + \frac{C}{4} (tr Q_b^2)^2 \]

\[ S_+ = \frac{B + \sqrt{B^2 - 24AC}}{4C} \]

\[ A = \alpha(T - T^*) < 0 \]
A Special Temperature

\[ A = -\frac{B^2}{3C} < 0 \]

• Existence of unique solution branch with

\[ Q = q_1(e_x \otimes e_x - e_y \otimes e_y) + q_2(e_x \otimes e_y + e_y \otimes e_x) - \frac{B}{6C}(2e_z \otimes e_z - e_x \otimes e_x - e_y \otimes e_y) \]

compatible with the Dirichlet conditions on square edges which are equivalent to

\[
\begin{align*}
q_1 &= \frac{S_+}{2} = \frac{B}{2C} & C_1 \cup C_3 & q_2 = 0 \\
q_1 &= -\frac{S_+}{2} = -\frac{B}{2C} & C_2 \cup C_4 & q_3 = -\frac{S_+}{6} = -\frac{B}{6C}
\end{align*}
\]

• Reduced a problem with five degrees of freedom to a problem with two degrees of freedom!!

\[
Q_{\text{red}} = \begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix} \quad \Delta Q_{ij} = \frac{1}{L}(aQ_{ij} - c(\text{tr} Q^2)Q_{ij}) \quad i,j = 1,2
\]
Special solutions with Two Degrees of Freedom at Special Temperature as critical points of ....

\[ J[q_1, q_2] := \int_{\Omega} |\nabla q_1|^2 + |\nabla q_2|^2 + \frac{\lambda^2}{L} \left\{ -\frac{B^2}{2C} (q_1^2 + q_2^2) + C (q_1^2 + q_2^2)^2 \right\} \, dA \]

\[ q_1 = \begin{cases} 
-s_+/2 & C_1 \cup C_3, \\
{s_+/2} & C_2 \cup C_4, \\
g(y) & S_1 \cup S_3, \\
g(x) & S_2 \cup S_4 
\end{cases} \quad q_2 = 0 \quad \text{on } \partial \Omega
\]

- Classical solutions of –
  \[ \frac{L}{\lambda^2} \Delta q_1 = -\frac{B^2}{2C} q_1 + 2C (q_1^2 + q_2^2) q_1 \]
  \[ \frac{L}{\lambda^2} \Delta q_2 = -\frac{B^2}{2C} q_2 + 2C (q_1^2 + q_2^2) q_2 \]

- Always have the existence of a solution branch with
  \[ q_2 = 0 \quad \text{on } \Omega. \]
The Small $\lambda$ Limit and the new Well Order Reconstruction Solution

Uniqueness of solutions for sufficiently small squares from convexity of the Landau-de Gennes energy

• Can construct a solution has two key properties:
  
  \[ q_2 = 0 \quad \forall (x, y) \]
  
  \[ q_1 = 0 \quad y = \pm x \]

• What does this mean for the actual Landau-de Gennes critical point

\[
Q = q_1(e_x \otimes e_x - e_y \otimes e_y) + q_2(e_x \otimes e_y + e_y \otimes e_x) - \frac{B}{6C} (2e_z \otimes e_z - e_x \otimes e_x - e_y \otimes e_y)
\]

• Constant eigenframe

• Uniaxial diagonal cross with negative order parameter

• Ring of maximal biaxiality

Well Order Reconstruction Solution
• How do we construct a solution of the form

\[
Q = q_1 (e_x \otimes e_x - e_y \otimes e_y) - \frac{B}{6C} (2e_z \otimes e_z - e_x \otimes e_x - e_y \otimes e_y)
\]

\[
q_1 = 0 \quad \text{on} \quad y = \pm x
\]

• Minimize the following functional on a quadrant of the rotated square

\[
H[q] = \int_{Q} \left( |\nabla q|^2 + \frac{\lambda^2}{L} \left( Cq^4 - \frac{B^2}{2C} q^2 \right) \right) dA
\]

• existence of minimizer, \( h(x,y) \), from direct methods in calculus of variations;

• extend minimizer to truncated square by odd reflection about the lines \( x=0 \) and \( y=0 \) (the rotated diagonals);

• this defines a function

\[
\Delta q_s = \frac{2C\lambda^2}{L} \left( q_s^3 - \frac{B^2}{4C^2} q_s \right)
\]

\[
q_s(x, y); \quad (x, y) \in \Omega
\]

\[
q_s(x,0) = q_s(0, y) = 0
\]
The Well Order Reconstruction Solution (WORS)

We have defined a Landau-de Gennes critical point, labelled as the WORS

\[ Q_{OR} = q_s(x, y)(n_1 \otimes n_1 - n_2 \otimes n_2) - \frac{B}{6C}(2e_z \otimes e_z - n_1 \otimes n_1 - n_2 \otimes n_2) \]

\[ \Delta q_s = \frac{\lambda^2}{L} \left( 2Cq_s^3 - \frac{B^2}{2C}q_s \right) \]

- exists for all \( \lambda \);
- the eigenvectors are constant and fixed and
- has the negatively-uniaxial diagonal cross
- The WORS is the UNIQUE critical point for

\[ \lambda^2 = O\left(\frac{CL}{B^2}\right) \approx 100 \text{ nm} \]

- The WORS solution is an UNSTABLE critical point for sufficiently large \( \lambda \). Construct perturbation for which second variation is negative by using key idea from: M. Schatzman, Proceedings of the Royal Society of Edinburgh: Section A Mathematics / Volume 125 / Issue 06 / January 1995, pp 1241-1275

The large $\lambda$ regime.

What can we say about critical points of the form

$$Q_\lambda = q_1(e_x \otimes e_x - e_y \otimes e_y) + q_2(e_x \otimes e_y + e_y \otimes e_x) - \frac{B}{6C}(2e_z \otimes e_z - e_x \otimes e_x - e_y \otimes e_y)$$

at $A = -\frac{B^2}{3C} < 0$? Look at minimizers of

$$J[q_1, q_2] := \int_\Omega |\nabla q_1|^2 + |\nabla q_2|^2 + \frac{\lambda^2}{L} \left\{-\frac{B^2}{2C} (q_1^2 + q_2^2) + C (q_1^2 + q_2^2)^2\right\} dA$$

- For small $\lambda$, we recover the Well Order Reconstruction Solution.
- For large $\lambda$, readily apply Ginzburg-Landau techniques to show that

$$q_1^2 + q_2^2 \to \frac{B^2}{4C^2}$$

almost everywhere

- and the LdG critical points of the form above, converge (in an appropriately defined sense) to

$$Q_\lambda \to \frac{B}{C} \left(n \otimes n - \frac{I_z}{2}\right) - \frac{B}{6C}(2e_z \otimes e_z - e_x \otimes e_x - e_y \otimes e_y) \quad \lambda \to \infty$$

$$n = (\cos \theta, \sin \theta) \quad \Delta \theta = 0, \quad \text{away from corners.}$$

Also see G. Canevari, Biaxiality in the asymptotic analysis of a 2D Landau-de Gennes model for liquid crystals, ESAIM: COCV 21 (2015), 101–137.

The large $\lambda$ regime.

\[ J[q_1, q_2] := \int_\Omega |\nabla q_1|^2 + |\nabla q_2|^2 + \frac{\lambda^2}{L} \left\{ -\frac{B^2}{2C} \left( q_1^2 + q_2^2 \right) + C \left( q_1^2 + q_2^2 \right)^2 \right\} dA \]

- As $\lambda \to \infty$, the problem effectively reduces to

\[ (q_1, q_2) = \frac{B}{2C} (\cos \theta, \sin \theta) \]

\[ \Delta \theta = 0 \]

The large $\lambda$ regime.

- As $\lambda \to \infty$, the problem effectively reduces to

$$ (q_1, q_2) = \frac{B}{2C} (\cos \theta, \sin \theta) $$

$$ \Delta \theta = 0 \quad J[\theta] := \int_{\tilde{\Omega}} |\nabla \theta|^2 \, dA $$

\[ \tilde{E}_D = \ln \left( \frac{2}{\pi} \right) + s_1(1) - s_2(1) \]

\[ \tilde{E}_{U_1} = \tilde{E}_{U_2} = \ln \left( \frac{2}{\pi} \right) + s_1(1) + s_2(1) \]

\[ s_1(1) = 2 \sum_{n=0}^{\infty} \frac{\coth \left( \frac{(2n+1)\pi}{2} \right) - 1}{2n+1} \]

\[ s_2(1) = 2 \sum_{n=0}^{\infty} \frac{\cosech \left( \frac{(2n+1)\pi}{2} \right)}{2n+1} \]

---

A detailed bifurcation plot

Unique solution for small squares; six distinct solution branches for large squares – two diagonal and four rotated.

From molecular to continuum modelling of bistable liquid crystal devices
Martin Robinson, Chong Luo, Patrick E. Farrell, Radek Erban & Apala Majumdar.
Look for critical points (not just minimizers) of

\[ J[q_1, q_2] := \int_{\Omega} \left( |\nabla q_1|^2 + |\nabla q_2|^2 \right) dA + \]
\[ + \int_{\Omega} \frac{\lambda^2}{L} \left( -\frac{B^2}{2C} (q_1^2 + q_2^2) + C \left(q_1^2 + q_2^2\right)^2 \right) dA \]

21 other critical points found using numerical deflation techniques for intermediate values of \( \lambda \).
• Adapt similar methods to hexagons or arbitrary polyhedra – observe generic trends

• Joint work with Lei Zhang (Peking), Yucen Han (Peking), Lingling Zhao (Dalian), Giacomo Canevari (Spain), Yiwei Wang (Chicago)
• What have we learnt?

➢ A specific problem with a rich solution landscape.

\[
Q = q_1(e_x \otimes e_x - e_y \otimes e_y) + q_2(e_x \otimes e_y + e_y \otimes e_x) - \frac{B}{6C}(2e_z \otimes e_z - e_x \otimes e_x - e_y \otimes e_y)
\]

• The blue points/lines correspond to \( S=0 \) i.e. they extend as negatively ordered uniaxial lines through a three-dimensional domain.

• These interfaces are globally stable for small systems.

• Solutions with interfaces are unstable for larger systems but only in certain directions \( \Rightarrow \) control problems!

• Numerically, known that they act as transition states for larger systems.

• Add flow to the problem and study response and evolution of interfaces \( \Rightarrow \) mean curvature flow with forcing terms!
• Bigger Picture?

The Well Order Reconstruction Solution – specific example of a negatively-uniaxial interface separating the square into four quadrants.

• Lessons learnt

- study of NLC interfaces in high-dimensional systems i.e. problems of a vectorial or tensorial nature;

- Connections between entire solutions of the Allen Cahn equation and critical points of the Landau-de Gennes energy i.e. construct non-minimizing critical points with interfaces;

- Location of interfaces determined by a Toda lattice ⇒ new connections with integrability!

• Stronger conjectures:

- Nematic defects are contained in special NLC interfaces which have a generic structure!

- Understanding the structure and location of NLC interfaces as a function of temperature, material constants \( \Rightarrow \) much better understanding of NLC defects

- Bringing together cutting-edge problems in geometric measure theory, nonlinear PDE and integrability!

• See work by Majumdar, Henao & Pisante; Lamy et.al, Ignat et.al, Canevari
• Stronger conjectures:

➢ Dynamics of NLC interfaces ⇒ mathematics of self-assembly!!

• Connections to Smales’ open 7th problem.

• Nematodynamics with different boundary conditions ⇒ open questions on Navier Stokes with added complexities from nemato-fluid coupling stresses!


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