Geometry, Topology, and Liquid Crystals: their Materials Applications

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Geometry: geo (earth) and metron (measure)

“Geometry is perhaps the most elementary of the sciences that enable man, by purely intellectual processes, to make predictions (based on observation) about physical world.”

Harold Scott MacDonald Coxeter (1907-2003)

It is concerned with the properties of configurations of points, (straight) lines, and circles

Topology: place and study

It is concerned with the properties of space that are preserved under continuous deformation such as stretching, twisting, crumpling and bending, but not tearing or gluing.

Topological equivalence (homeomorphism)

https://en.wikipedia.org/wiki/Topology
Embedding Intelligence: Materials with Intrinsic Anisotropy

- Liquid crystals (LCs)
- Nanorods
- Nanotubes
- 2D Nanosheets
- Nanoprisms
- Janus particles

Arthur Losquin
The Fourth Phase of Matter: Liquid Crystals (LCs)

- Thermotropic and lyotropic LCs
- Anisotropy
  - Orientational ordering
  - Structure and properties influenced by
    - External fields: electric and magnetic fields, temperature
    - Surfaces: confined geometry, chemistry

Liquid Crystals Are Everywhere in Our Life

Fibers, ropes, cables

Detergent

Beetle scale

Displays

Kevlar

Cell membrane

Food dyes, cosmetics, drugs

Mood ring

Liquid crystal collection of physicist Otto Lehmann (ca. 1925)

Fishing line
Anisotropy and Alignment

- optical properties (birefringence)
- mechanical properties
- dielectric constants
- magnetic susceptibility
- viscosity
- diffusion coefficients

Maximizing the translational entropy!
**Defect type**: point defect, line defect (disclination)

**Winding number**: \( S = \frac{\theta}{2\pi} \)
Elastic Deformation of LCs on Surface

Here, LC molecules are depicted as rods

Frank-Oseen free energy density

\[
f = \frac{1}{2} \left\{ K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3 [(\mathbf{n} \cdot \nabla)\mathbf{n}]^2 \right\}
\]
Topological Defects Formed on Geometric Surfaces: Effect of Surface Topography

\[ \Delta F = \Delta F_{\text{elastic}} + \Delta F_{\text{air}} + \Delta F_{\text{substrate}} \]


Collaboration with Randall Kamien & Kathleen Stebe
Topological Defects Formed On Geometric Surfaces: Effect of Chemically Patterning + Topography

Planar anchoring: SU8

Homeotropic anchoring:
N,N-dimethyl-n-octadecyl-3-amino-propyltrimethoxysilyl chloride (DMOAP)

4-Cyano-4′-octylbiphenyl (8CB)

C₈H₁₇-CN

21.5°C 33.5°C 40.5°C
Cr SmA N Iso

Pinwheel
Radial
Single Boojum
Uniform
Adaptive and Foldable Soft Materials

Voxelated liquid crystal elastomers

Folding thermo-responsive half-tone patterns

Biomimetic 4D Printing

Self-folding polymer sheets

Shaping Non-Euclidean Elastic Sheets

Ware, T. H., et al. Science, 2015, 347, 982


Liu, Boyles, Genzer and Dickey, Soft Matter, 2012
Nematic to Isotropic Transition

in small molecule liquid crystals

\[ \bar{a} = \begin{pmatrix} 10 \\ 01 \end{pmatrix} \]

Anisotropic strain

in liquid crystal elastomers (LCEs)

\[ \bar{a} = \begin{pmatrix} \lambda^2 & 0 \\ 0 & \lambda^{-2\nu} \end{pmatrix} \]

Actuated by heat, light, electric field...

• Up to 400% strain
• Reversible shape memory effect
• Load lifting 100-1000x of its own mass

Blueprint Desired Shape Transformation

Design of Topological Defects

+1 defect

Topological Equivalence: Materials Could Appear in Different Forms

\[ s = +1 \]


\[ Ware, T. H., et al. Science, 2015, 347, 982 \]
Patterning Topological Defects in NLCEs via Photoalignment

Ware, T. H., et al. Science, 2015, 347, 982


- Requires highly specialized equipment;
- Resolution limits the size of each unit.

Use surface patterns to align LCs?
Sample Preparation Procedure

Yu Xia, et al., SY, Adv. Mater. 2016, 28 (43), 9637

1. Replica Molding
2. Surface treatment

Ware, T. H., et al. Science, 2015, 347, 982

LC Monomer Chemistry

Crosslink

Chain extender

Mesogen

Ware, T. H., et al. Science, 2015, 347, 982
Confining LCs within Micromolded 1D Channels

To minimize $\theta$: mold epoxy substrate

Surface anchoring strength:
- Ideal anchoring: $\theta=0$, $\phi=0$
- Goal: to minimize $\theta$ and $\phi$

$\phi$: dependent on surface chemistry
$\theta$: dependent on surface topography

Free energy density:
$$\rho_{\phi} = \frac{K}{2 \sum_{i=1}^{N} \frac{1}{(2i-1)\pi}} A^2 [(2i-1)k]^3 \sin^2 \phi$$

$$k = \frac{2\pi}{\lambda}$$

$$\rho_{\phi} \propto A^2 \lambda^{-3} \propto d^2 w^{-3}$$

Large depth (d)
Small width (w)

Yu Xia, et al., SY, Adv. Mater. 2016, 28 (43), 9637
**Programmed Actuation in Liquid Crystal Elastomers**


Unusual weight lifting capacity:
up to **734 x** its own weight by ~ 1mm vertically (stroke ~1000%)

**Work capacity:** 2.36J/kg, or ~ **370 W/kg/m²**

**Gaussian Curvature and Mean Curvature**

**Principal Curvatures, \( \kappa_1 \) and \( \kappa_2 \)**

**Gaussian Curvature** \[ \kappa = \kappa_1 \kappa_2 \]

- \( \kappa_1 \kappa_2 > 0 \): Positive
- \( \kappa_1 \kappa_2 < 0 \): Negative
- \( \kappa_1 \kappa_2 = 0 \): zero

**Mean Curvature**

\[ H = \frac{1}{2} (\kappa_1 + \kappa_2) \]

- Origami: paper folding
  - Bend: Mean Curvatures
  - Stretch: Gaussian Curvatures
Curvature and Strength

Folding Paper
- √ Bend
- × Stretch

Mean Curvatures
- √

Gaussian Curvatures
- ×

\[ H = \frac{1}{2} (\kappa_1 + \kappa_2) \]
\[ \kappa = \kappa_1 \kappa_2 \]

Holding a weighing Paper

Holding a pizza slice

http://www.chem.ucla.edu/

Growth, Geometry, and Mechanics of a Blooming Lily

Differential lateral growth —> local control of strain!

Reverse Design of an Arbitrary 3D Shape

- General design problem: Need to search for director field coordinates
- Taking the design to practice:
  - Need to accurately and faithfully imprint the design onto a thin LCE sheet and obtain the correct local stimulus-responsiveness
    - Top-down fabrication of micro-channels with strong surface anchoring
    - Nematic phase should be stable
    - Photochemistry needs to be efficient to lock the LC director field
  - Control over additional degrees of freedom
    - there are many different isometric embeddings in space;
    - the system might be stuck in a non-isometry or undesired configuration.
Varying director field coordinates \( \theta(u,v) \)

\[
\bar{a}(u,v) = R[\theta(u,v)] \begin{pmatrix} \lambda^2 0 \\ 0 \lambda^{-2\nu} \end{pmatrix} R[\theta(u,v)]^T
\]

Reference Gaussian Curvature:

\[
\bar{K}_\Sigma = (\lambda^{2\nu} - \lambda^{-2}) \left[ \left( \frac{\theta_v^2 - \theta_u^2 - \theta_{uv}}{2} \right) \cos 2\theta + \left( 2\theta_u\theta_v + \frac{\theta_{vv} - \theta_{uu}}{2} \right) \sin 2\theta \right]
\]

assuming constant principal strains across the film

Hillel Aharoni, Sharon and Kupferman 2014.
A Local/Global Approach to Mesh Parameterization

Original 3D mesh | flattened triangles | 2D parameterization

Tissot Indicatrix World Map Projection

in a Mollweide projection

https://commons.wikimedia.org/wiki/File:Tissot_indicatrix_world_map_Mollweide_proj.svg
Equirectangular projection

https://en.wikipedia.org/wiki/Tissot%27s_indicatrix
Reserve Engineering of General Shapes

Input a 3D shape (face)

Numerical calculation of the 2D coordinates

Ellipse-map of the deformation

Circle-map on the 2D film
Two-step Polymerization via Click Chemistry

**Step 1: Synthesis oligomers**

RM (reactive mesogenic monomer) + DT (dithiol)

- **Molar ratio:**
  - DBU: 1,8-Diazabicycloundec-7-ene
  - RM82-1,3-dithiol
  - \( T_{NI} = 78\, ^\circ C \)
  - Large nematic window: \( \sim 120\, ^\circ C \)

**Step 2: Photopolymerization in the presence of \( O_2 \)**

RM-DT + RM

- **Molar ratio:**
  - 1

20 s @ \( \sim 50 \text{ mw/cm}^2 \), reaching 85% gel fraction

Spatial Alignment of LCs

Channel width: 1 µm
Spacing: 1 µm
Depth: ~ 600 nm

Yu Xia, Xinyue Zhang, Hillel Aharoni, Randall Kamien, SY, PNAS 2018, 115 (28) 7206
Achieving Simple Gaussian Curvatures

Negative Curvature

On a hot plate, ~ 170°C

Positive Curvature

Yu Xia, Xinyue Zhang, Hillel Aharoni, Randall Kamien, SY, PNAS 2018, 115 (28) 7206
Combination of Gaussian Curvatures

Leaf: combination of negative curvatures

Face: positive + negative + zero curvatures

Yu Xia, Xinyue Zhang, Hillel Aharoni, Randall Kamien, SY, PNAS 2018, 115 (28) 7206
Geometry is Scale Invariant
and it can be Wearable and Smart
“Humans are tool builders”
Smart Garments

Breathable, Comfortable, Personal, & Responsive
Geometry is Materials Independent
MXenes: a few atoms thick layers of transition metal carbides, nitrides, or carbonitrides. Conductivity close to multi-layer graphene ~$10^5$ S/m

M: Early transition metal (e.g., Ti)
A: a group IIIA or IVA element (e.g., Al)
X: C or N

Surface rich with OH groups; dispersible in aq. solutions


- Mxene layer ~1nm;
- Layer spacing ~1nm.
How to Vertically Align Atomically Thin MXene up to 100 µm Thick?

- Aspect ratio of a Mxene “paper”: ~ 1,000 (1 µm wide and 1 nm thick)
- Aspect ratio of a piece of Letter-sized paper: > 2,000 (215.9 x 279.4 x 0.1 mm)
How Do We Stack Papers?

A stack of papers

A heap/pile of papers
How About Stacking Books?
Discotic Liquid Crystal Phases

Different nematic phases

- discotic nematic (ND)
- nematic lamellar (NL)
- chiral nematic (N*D)
- columnar nematic (Ncol)

Vertical Alignment of MXene LLCs

Y Xia, TS Mathis, MQ Zhao, B Anasori, A Dang, Z Zhou, H Cho, Y Gogotsi, SY, Nature 557 (7705), 409–412
- **Nearly thickness independent rate performance** up to 200 μm
- **Unprecedented capacitance retention:**
  - all MXLLC electrodes < 200 μm retaining over 200 F/g at the high scan rate of 2,000 mV/s
  - retaining almost 100 % capacitance after 20,000 cycles of galvanostatic cycling at 20 A/g

Xia, Yu; Mathis, Tyler; Zhao, Meng-qiang; Anasori, Babak; Dang, Alei; Zhou, Zehang; Cho, Hyesung; Gogotsi, Yury*; and Yang, S.*. *Nature*, 2018, 557, 409-412
“Geometry is perhaps the most elementary of the sciences that enable man, by purely intellectual processes, to make predictions (based on observation) about physical world.”

Harold Scott MacDonald Coxeter (1907-2003)

“Liquid crystals are beautiful and mysterious; I am fond of them for both reasons.”

– P.G. De Gennes