Liquid crystal shells
What is left to learn? How can we apply them?

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¹University of Luxembourg, Physics & Materials Science Research Unit Luxembourg
²Cambridge University, Institute for Manufacturing, Cambridge, United Kingdom
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Inspiration and guidance at the right time

David Weitz
Alberto Fernandez-Nieves
Teresa Lopez-Leon
Before shells, there were drops

Oleg Lavrentovich  Slobodan Zumer  Yves Bouligand
A GREAT TEAM

Johanna Bruckner
Mathias Bourg
Larry Honaker
Catherine Reyes
Martin Urbanski
Vanessa Schmidt-Barbé
Camila Honorato Rios
Nina Schwarz

Anshul Sharma
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Rao Jampani

Zory Tosheva
Johanna Bruckner
Junghyun Noh
Larry Honaker
Catherine Reyes
Vanessa Schmidt-Barbé
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Camila Honorato Rios
Nina Schwarz

Yong Geng
Benjamin Henz
Kevin Resueng De Sousa
THE SHELL TEAM

HSIN-LING LIANG

RAO JAMPANI

BENJAMIN HENX

JUNGHYUN NOH

YONG GENG

KEVIN REGUENGO DE SOUSA
A liquid crystal shell

- Isotropic internal phase, immiscible with LC
- Liquid crystal
- Isotropic continuous phase, immiscible with LC

~10 µm

~100 µm
A liquid crystal shell

- Isotropic continuous phase, immiscible with LC
- Isotropic internal phase, immiscible with LC
- Liquid crystal

~10 µm

~100 µm

Gravity
A liquid crystal shell

~10 µm

~100 µm

Isotropic internal phase, immiscible with LC

Liquid crystal

Gravity

Isotropic continuous phase, immiscible with LC
Cylindrical capillary outer diameter = inside length of square capillary

Capillary microfluidics

Concept developed in group of David Weitz; illustration by H.-L. Liang
Emulsion (shells)

Middle fluid (LC)

Outer fluid (water + stabilizer; continuous phase)

Inner fluid (water + stabilizer)

Capillary microfluidics

Concept developed in group of David Weitz; illustration by H.-L. Liang
We produce the shells using microfluidics

YONG GENG
Some possible tangential director fields on a nematic shell, all with +2 total defect strength.
From liquid crystal shells to colloids with directional bonding?

- Energy minimization (distortion minimization) ➞ tetrahedral arrangement of four \( s = + \frac{1}{2} \) defects
- Added linker molecules attracted to defects ➞ Carbon atom-like colloidal particle: diamond structure
From liquid crystal shells to colloids with directional bonding?

**Reality**

- Most nematic shells have all four disclinations close to top or bottom
Non-uniformity of shell thickness affects defect configuration

- Disclinations move to thinnest region to minimize global energy
  ➔ tetrahedral symmetry is lost

  - *Even for perfect density matching, the defects drive the shell asymmetric!*

- Which defect configuration do we get in a smectic phase and what happens at phase transition?

Spontaneous symmetry breaking in liquid crystals

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</table>

- nematic
  - orientational order ($\mathbf{n}$)
  - uniaxial: $\varepsilon = \begin{pmatrix} \varepsilon_\perp & 0 & 0 \\ 0 & \varepsilon_\perp & 0 \\ 0 & 0 & \varepsilon_\parallel \end{pmatrix}$

- smectic A
  - orientational order ($\mathbf{n}$)
  - 1-D translational order ($\mathbf{k}$)
  - uniaxial: $\varepsilon = \begin{pmatrix} \varepsilon_\perp & 0 & 0 \\ 0 & \varepsilon_\perp & 0 \\ 0 & 0 & \varepsilon_\parallel \end{pmatrix}$

- smectic C
  - orientational order ($\mathbf{n}$)
  - 1-D translational order ($\mathbf{k}$)
  - tilt ($\theta$)
  - biaxial: $\varepsilon = \begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix}$
Textures of nematic shells with varying boundary conditions

- Planar outside, planar inside
- Homeotropic outside, homeotropic inside
- Hybrid: homeotropic outside, planar inside (or vice versa)
Textures of nematic shells with varying boundary conditions

Planar outside, planar inside
(aqueous PVA solution on both sides)

Homeotropic outside, homeotropic inside
(aqueous surfactant solution on both sides)

Hybrid: homeotropic outside, planar inside (or vice versa)
(PVA on one side, surfactant on the other)
N – SmA transition

Planar alignment

Thickness < 5 µm
Diameter < 100 µm

Bend defects
Splay defects
Splay defect

H.-L. Liang, et al.,
Defects start at thinnest shell part, but move to equator to expel director bend.

X. Xing,
**134** 487 (2009)
Below phase transition texture breaks up in spherical lunes, later decorated with chevrons.
In the smectic phase, the change in curvature from out- to inside yields frustration.

- To accommodate curvature with the requirement of constant layer thickness, the layers buckle => spherical lunes

- Buckling increases continuously towards the outside

Others came to the same conclusion and developed rigorous models for the lunes


But chevron texture remains to be properly modeled!

• Our proposal:
  • Buckling solves frustration along original director orientation \( n_0 = u \)
  • But shells curve also along \( v \), perpendicular to \( u \)
    • No problem initially, when positional order only along \( u \)
    • But layer buckling rotates layer normal with component in \( v \)
  ➔ Secondary buckling instability

N-SmA transition in hybrid shells
Planar outside, homeotropic inside or v.v.

Average thickness ≈ 13 µm
Diameter ≈ 200 µm

N-SmA transition in hybrid shells

Planar outside, homeotropic inside or v.v.

Average thickness $\approx 6 \, \mu m$
Diameter $\approx 350 \, \mu m$

N-SmA transition in hybrid shells
Planar outside, homeotropic inside or v.v.

SmA-SmC transition in homeotropic shell

Nematic-isotropic transition in hybrid 5CB shell

Heating at 0.01K/min.

Nematic-isotropic transition in planar 5CB shell

Heating at 0.01K/min.
Nematic-isotropic transition in homeotropic 5CB shell

Heating at 0.01K/min.
Two possible reasons for 2-stage clearing transition in hybrid shells

- Bend gives elastic energy cost that outweighs anchoring energy ➟ first stage is just a realignment

- But why should anchoring energy decrease more rapidly than elastic energy close to transition?

- Radially aligned surfactant layer stabilizes nematic phase to higher temperature than on planar side
Radially aligned surfactant layer stabilizes nematic phase

CMC $\approx 0.3\%$

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OPPORTUNITY FOR COLLABORATION ??
ADD 5% OF RM257

CAN WE LOCK A DESIRED CONFIGURATION IN PLACE BY PHOTOPOLYMERIZING AT THE RIGHT TEMPERATURE?
Photopolymerization at high temperature locks defects in place

7CB phase sequence: Cr 30 N 42.8 Iso

Photopolymerization close to $T_{N-SmA}$ triggers phase transition

4x real time

Photopolymerization in smectic phase locks in undulated structure

Liquid crystal elastomer shell

E.-K. Fleischmann, H.-L. Liang, N. Kapernaum, F. Giesselmann, J.P.F. Lagerwall, R. Zentel
At n-Iso transition, the rubber contracts along director, expands perpendicular to it.
Polymer stabilization renders shells mechanically robust

Also spheres with different pitch communicate, at distinct wavelengths.

Abstract. The extraordinary responsiveness and large diversity of self-assembled structures of liquid crystals are well documented and they have been extensively used in devices like displays. For long, this application route strongly influenced academic research, which frequently focused on the performance of liquid crystals in display-like geometries, typically between flat, rigid substrates of glass or similar solids. Today a new trend is clearly visible, where liquid crystals confined within curved, often soft and flexible, interfaces are in focus. Innovation in microfluidic technology has opened for high-throughput production of liquid crystal droplets or shells with exquisite monodispersity, and modern characterization methods allow detailed analysis of complex director arrangements. The introduction of electrospinning in liquid crystal research has enabled encapsulation in optically transparent polymeric cylinders with
Conclusions

N-SmA transition in shells induces modulated textures due to frustration from curvature and/or conflicting boundary conditions.

Shell stabilizers have effects beyond aligning and stabilizing, for instance affecting phase sequence.

Polymerization locks defect configurations in place and makes shells long-term stable, but it can also induce phase transitions.
Visualizing the director field