Smectic Liquid Crystal Elastomers

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Related interests:
Main chain LCEs: Mechanics and Polarization mechanisms
Shear banding in viscoelastic liquids
1 Background
   - Liquid crystals
   - Elastomers

2 Smectic A elastomers
   - Experiment
   - Modelling

3 Smectic C elastomers
   - Properties
   - Microstructure and ferroelectric properties

4 Conclusions
LC Phases

- Typical rod length 30Å
- Thermotropic liquid crystal $\rightarrow$ nematic on cooling
- Short range forces $\rightarrow$ smectic phase on further cooling
- Order described by order parameter $Q$
- Change in layer spacing has modulus $B \sim 10^7$ Pa
**LC applications**

- Deep fundamental science
- Widely used in displays
- New uses e.g. fast microbial sensor
Gaussian Polymer Models

- Gaussian chain $\rightarrow$ entropic spring: $F = \frac{3k_B T}{2Na^2} r^2$
- Consequently, rubber shear modulus $\mu \sim T$
Phantom Network Model

- Length scale $\gg l\sqrt{L}$ (Cross link spacing)
- Crosslinks deform affinely: $\mathbf{x} = \lambda \cdot \mathbf{x}_0$
- Elongation of $\sim 100s\%$
- High molecular mobility: almost liquid
- Bulk modulus $\gg \mu$ so volume conserving
Orientational order of the rods affect the backbone conformation (intimately coupled)

Connection point and spacer length affect shape

Rod coupling to network has profound consequences for rubbers

Average shape described by $\ell \left( \langle RR \rangle = \frac{1}{3} L \ell \right)$
Nematic Liquid Crystalline Elastomers

- Spontaneous elongation/contraction at phase transition
- Bi-rubber strip curls on heating
- Strip can lift significant weight, and be actuated thermally or equivalently by light
- For applications as artificial muscles, values of 25% strain and 350kPa stress are attainable
Smectic liquid crystal elastomer films

Elongation \( \perp \) to the layer normal:
- Modulus similar to isotropic phase
- 2D rubber response
- Poisson ratios: \( 0 \parallel e_3, 1 \parallel e_1 \)
- Remains transparent on elongation

Elongation \( \parallel \) to the layer normal:
- Higher elastic modulus \( \times 10^2 \)
- Threshold at \( \sim 5\% \)
- Poisson ratios: \( \frac{1}{2} \) in all directions
- Opaque after threshold (reversible)
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Smectic elastomer free energy density

\[ f = \frac{1}{2} \mu \text{Tr} \left[ \Lambda \cdot \ell_0 \cdot \Lambda^T \cdot \ell^{-1} \right] + \frac{1}{2} B \left( \frac{d}{d_0} - 1 \right)^2 \]  

nematic rubber

layer spacing

- Polymer spans deform as vectors
- Smectic layers deform as normals \((\mathbf{k} = \Lambda^{-T} \cdot \mathbf{k}_0)\)
- Layer spacing \(\frac{d}{d_0} = \frac{1}{|\lambda^{-T} \cdot \mathbf{k}_0|}\)
Theoretical Curve:

\[ \sigma_{\text{nom}} = 1 + \frac{r \mu}{B} \lambda \]

Threshold is determined by the ratio of the two slopes.

The mode of deformation changes after the threshold to a shearing mode.

If the sample is clamped then microstructure must form (Convexify energy).
Smectic C phase

- Director $\mathbf{n}$ tilted w.r.t. layer normal $\mathbf{k}$
- Director is free to rotate about layer normal

Smectic C elastomer properties
- Exhibits soft modes (shape change at low energy cost)
- Symmetry $\rightarrow$ piezo-, pyro- and ferroelectric
Spontaneous shears

- Monodomain at high temperature is in SmA phase
- SmC phase forms on cooling
- Tilt of the molecules cause the polymer conformation to change
- Network develops a spontaneous shear
- Magnitude of $\sim 0.4$ shear has been achieved
Model predicts multiple ground states of equivalent energy

Microstructure forms as in microstructure of Martensitic transition (continuum of wells here)

More general deformations can be achieved by assembling these states
Microstructure of soft shear deformation

- Simple laminate microstructure from soft modes
- Director rotates in opposite sense in alternating phases
- Polarization direction also rotated by mechanical deformation
Summary

- Developed model of smectic elastomer from microscopic principles
- Applied model to Smectic A elastomers, predicting threshold behaviour
- Accompanying microstructure predictions (yet to be tested)
- Smectic C elastomer model predicts soft elasticity and spontaneous shearing
- Microstructures from simple laminates calculated
- Some of the consequences for ferroelectric rubber explored
Future work

- Wide spread experimental interest developing (Groups in UK, Germany, Japan and US) — Refine model accordingly
- Refine Smectic model, detailed numerical calculation
- Finite element analysis of SmC microstructure
- Calculate full quasiconvexification of SmC free energy
- Model chiral phases of SmC elastomers
- Improve ferroelectric modelling
- Potential applications of smectic elastomers
- Acuation using light by embedding azo-dyes
Suggested experimental work

- Simplest to carry out experiments under extension
- $K^{qc}$ used to suggest experimental geometry

- Predict different amplitudes of soft mode depending on polymer anisotropy ($r$) and $\theta$