Thermo/Electro-Mechanical Instabilities
in Confined Samples of Nematic Gels

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Introduction & Background Knowledge
Complex Fluids — Liquid Crystals & Polymers
Liquid Crystalline Elastomer & Gel

Nematic Rubber Elasticity

Buckling Transition in Nematic Gels

Stripes in Electro-Optics Experiment

Conclusions & Future Works
Complex Fluids I — Liquid Crystals

Liquid Crystalline Phases
Intermediate phases between homogeneous isotropic liquid and anisotropic crystalline solid.

Long- & Short-Range Ordering
- Translational Order
- Orientational Order

Driving Forces for Phase Transition
- Temperature — *Thermotropic* LC;
- Concentration — *Lyotropic* LC.

Other Phases
Cholesteric, Columnar, Blue, TGB, Banana...
Curvature Elasticity & Fredericks Transition

Curvature Elasticity

\[ F = \frac{1}{2} \left( K_B (n \times (\nabla \times n))^2 + K_S (\nabla \cdot n)^2 + K_T (n \cdot \nabla \times n)^2 \right) \]

Fredericks Transition

\[ V = 0 \quad V > V_c \]
Polymeric Materials

- Polymers (poly-mer = many-parts) are the macro-molecules consisting of many elementary units (monomers).
- Elastomer (or Rubber) is the crosslinked polymer network with its $T_g$ below the room temperature.
- Gel is the crosslinked polymer network which is swollen in a solvent.
Free Energy of an Ideal Polymer Chain

End-to-end Vector:
\[
R = a_1 + a_2 + \cdots + a_N = \sum_{i=1}^{N} a_i
\]

Probability density:
\[
\lim_{N \to \infty} P(R, N) = \left( \frac{2\pi N a^2}{3} \right)^{-3/2} \exp\left( -\frac{3R^2}{2Na^2} \right)
\]

Configuration Entropy:
\[
S(R, N) = k_B \ln P(R, N) = -\frac{3k_B R^2}{2Na^2} + \text{Const.}
\]

Helmholtz Free Energy:
\[
F(R, N) = U - TS = \frac{3k_B T R^2}{2Na^2} + \text{Const.}
\]
\[
\Rightarrow \delta F \propto \delta r
\]
Entropic Elasticity of Polymeric Materials

Affine Deformation:
The relative deformation of each polymer strand is same as the macroscopic relative deformation applied on the whole polymer network.

Cauchy Strain Tensor:
\[ \lambda_{ij} = \frac{\partial R_i}{\partial R_j^0} = \delta_{ij} + \eta_{ij} \]

Classical Rubber Elasticity:
Free energy density (free energy per unit volume) of a general deformation for the isotropic elastomer becomes:
\[ F(\lambda) = F(R) - F(R^0) \]
\[ = \frac{n_s k_B T}{2} (\lambda_{ij} \lambda_{ji}) \equiv \frac{n_s k_B T}{2} \text{Tr}(\lambda^T \cdot \lambda) \]
Liquid Crystalline Elastomers

— Solid-Liquid Crystals

Liquid Crystalline Elastomer:
The elastic material freezing the liquid crystalline ordering into the crosslinked polymeric networks.

▶ Non-vanishing shear modulus — Solid instead of Fluid;
▶ Broken Symmetry — Anisotropic instead of Isotropic.
Nematic Phase I

Crosslinking in Isotropic Phase

Nematic Phase II
Solid rubber behaves like a liquid:

To make certain shear strain and to rotate the nematic director non-uniformly without any first order elastic energy cost, as long as the entropy of the polymer network doesn’t change during the transformation, e.g. liquid crystalline elastomer behaves like a classical liquid.
Solid rubber behaves like a liquid:
To make certain shear strain and to rotate the nematic director $\mathbf{n}$ non-uniformly without any first order elastic energy cost, as long as the entropy of the polymer network doesn’t change during the transformation, e.g. liquid crystalline elastomer behaves like a classical liquid.
**Solid** rubber behaves like a **liquid**: To make certain shear strain and to rotate the nematic director $\mathbf{n}$ non-uniformly without any first order elastic energy cost, as long as the entropy of the polymer network doesn’t change during the transformation, e.g. liquid crystalline elastomer behaves like a classical liquid.
Semi-Soft Elasticity

Internal field to memorize the crosslinking stage:

- To crosslink the polymer network in an ordered phase, e.g., a nematic mono-domain, cholesteric or other “pre-strained” configurations;
- To produce the “memory” effect of the polymer network about its thermomechanical history;
- e.g., For a uniaxial nematic elastomer crosslinked in the nematic state, there will be five independent semi-soft elastic modes in the elastic energy expression.


Free Energy Density:

\[ F_{\text{semi}} = \frac{1}{2} A \cdot \mu \cdot f(\theta, \theta^0(\lambda)) \]

where \( \mu \) is the shear modulus, \( \theta^0 \) and \( \theta \) are the director angle of the initial polymerization state and the final deformed state, \( A \) is the constant to tell the magnitude of semi-softness.
Introduction & Background Knowledge

Nematic Rubber Elasticity
  Nematic Rubber Elasticity
  Shear Waves in Nematic Elastomers
  Artificial Muscle Effect

Buckling Transition in Nematic Gels

Stripes in Electro-Optics Experiment

Conclusions & Future Works
Effects of LC Ordering on Polymer Network

Effective Step Length Tensor:
to define the anisotropic Gaussian distribution of the polymer chains:

$$l_{ij} = l_\perp \delta_{ij} + (l_\parallel - l_\perp) n_i n_j$$

$$= l_\perp (\delta_{ij} + (r - 1) n_i n_j)$$

in which $r = l_\parallel / l_\perp$ is a parameter to describe how anisotropic the polymer network is: $r = 1$ for an isotropic shape, $r > 1$ for a prolate ellipsoid and $r < 1$ for an oblate ellipsoid.

Analogy with the dielectric tensor:

$$D = \epsilon_\perp E + (\epsilon_\parallel - \epsilon_\perp)(n \cdot E)n;$$

$$D_i = \epsilon_{ij} E_j;$$

$$\epsilon_{ij} = \epsilon_\perp \delta_{ij} + (\epsilon_\parallel - \epsilon_\perp) n_i n_j.$$
Neo-Classical Rubber Elasticity Theory

Assumptions:

- The Gaussian Distribution of the Polymer Chains;
- The Affine Deformation of the Elastomers.

Free Energy Density for Nematic Elastomers:

\[
F = \frac{1}{2} \mu \cdot Tr(l^0 \cdot \lambda^T \cdot l^{-1} \cdot \lambda) - \frac{1}{2} A \cdot \mu \cdot Tr(\lambda^T \cdot n \cdot \lambda - n^0 \cdot \lambda^T \cdot n \cdot \lambda)
\]

in which \( \mu \) is the shear modulus, \( l^0 \) and \( l \) are the step length tensor before and after the deformation since the nematic director \( n \) rotates due to the applied mechanical strain \( \lambda \), and \( n_{ij} = n_i n_j \). \( A \) is the constant contribution from semi-soft elasticity.

Shear Waves

Bend Shear Wave $\Omega = 0$  \hspace{2cm} Splay Shear Wave $\Omega = \pi/2$

Shearing Displacement & Director’s Rotation

$$
\mathbf{d} = \left( d_x \sin(k_x x + k_y y), \quad d_y \sin(k_x x + k_y y) \right);
$$

$$
\mathbf{n} = \left( 1, \quad \xi \cos(k_x x + k_y y) \right).
$$

where $k_x = k \cos \Omega$, $k_y = k \sin \Omega$; and $\Omega$ is the angle measured away from the $x$-axis.
Shear Waves in Nematic Elastomers

Effective Shear Modulus:
The vector’s length is the free energy cost ($\mu_{\text{eff}}$) to propagate the shear waves of \textbf{unit amplitude} along the vector’s direction ($\mathbf{k}$).

\[ f_{\text{soft}} = \frac{\mu}{2r} \left( 1 + r(r - 2) - \frac{(1 + r(r - 2) + (r^2 - 1) \cos 2\Omega)^2}{4(r \cos^2 \Omega + \sin^2 \Omega)^2} \right); \]

\[ f_{\text{semi}} = \frac{\mu}{2r} \left( 1 + r(A + r - 2) - \frac{(1 + r(A + r - 2) + (r^2 - Ar - 1) \cos 2\Omega)^2}{4r^2 \cos^4 \Omega + 8r \cos^2 \Omega \sin^2 \Omega + (4 + 4Ar) \sin^4 \Omega} \right). \]
Liquid Crystalline Gels

— Hyper-Complex Fluids

Liquid Crystalline Gels
The crosslinked polymer network being swollen in the fluidic liquid crystals as the solvent.

**LC Curvature Elasticity:**
\[ F_{\text{Nematic}} \sim \frac{1}{2} K \left( \frac{\partial n}{\partial x} \right)^2 \]

\[ \Rightarrow [K] = \frac{[\text{Energy}]}{[\text{Length}]} \]

**Gel Entropic Elasticity:**
\[ F_{\text{Gel}} \sim \frac{1}{2} \mu \left( \frac{\partial d}{\partial x} \right)^2 \]

\[ \Rightarrow [\mu] = \frac{[\text{Energy}]}{[\text{Length}]^3} \]

**Length Scale of Competition:**
New properties not found in either components — co-operation of the gel and the liquid crystals, on the length scale of \( \sqrt{\frac{K}{\mu}} \) (\( \sim \) microns).
“Artificial Muscle” Effect

Shape Change at Nematic-Isotropic Transition — Nematic Ellipsoid vs. Isotropic Sphere

- Elongation along the direction parallel to the director $\mathbf{n}$;
- Shrinkage along the directions perpendicular to the director $\mathbf{n}$. 
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Strain–Temperature Measurements

Sample 10-wt%

$\Delta L_{\parallel}/L_{\parallel}^0$
$\Delta L_{\perp}/L_{\perp}^0$

Strain (%)

Temperature

I

II

III
Introduction & Background Knowledge

Nematic Rubber Elasticity

Buckling Transition in Nematic Gels
   Introduction & Description of Experiment
   Experimental Observations & Results
   Theoretical Interpretation

Stripes in Electro-Optics Experiment

Conclusions & Future Works
Introduction about Material

Molecular Structures:

Material Properties:

- **Self-Assembled** Liquid Crystalline Gel: insoluble end-blocks & well-solvated mid-blocks in LC host;

- The gelation temperature (or $T_{NI}$) is 37 °C for 5-wt% nematic gel, which is close to the $T_{NI}$ of 5CB (35.3°C).

Experiments in Homeotropic Cell:

- DMOAP coatings induce the nematic molecules anchored vertically on the surfaces;
- The nematic molecules can be aligned along the \( z \)-axis easily by applying the electric field across the cell, \( \mathbf{E} = E \mathbf{\hat{z}} \);
- The anisotropic properties of the polymer networks can be controlled by changing the sample’s temperature.

Experimental Steps:

1. Heat up the sample into the isotropic phase (45 °C) with the electric field applied (V=50 V);
2. Cool down the sample (at 2.5 °C/min) into the nematic phase (\( T < 37 \) °C) with the electric field applied (V=50 V);
3. Decrease the electric field down to zero (V=0 V) at temperature \( T \).
Buckling Under Confined Boundaries

Notes:
As the nematic gel becomes more ordered in lower temperature, the gel sample will finally buckle under the confined boundary conditions.

$T_i < T_{NI}$

$T_f < T_i < T_{NI}$
Temperature Dependence

Note:

As the temperature increases, the birefringence of the pattern decreases and the images become uniformly black when the temperature is above 30 °C.
Critical Voltage–Temperature Dependence

Voltage (V)

Temperature
Buckling Diagram

Initial Crosslinking State, $E > E_c$, $r^0$

Stressed State, $E > E_c$, $r > r^0$

Final Buckled State, $E < E_c$, $r > r^0$

$n^0 = (0, 0, 1)$;
$E = E^0 \hat{z}$;
$l_{ij}^0 = l^0_\perp (\delta_{ij} + (r^0 - 1)n_i^0 n_j^0)$.

$n = (0, 0, 1)$;
$E = E^0 \hat{z}$;
$l_{ij} = l_\perp (\delta_{ij} + (r - 1)n_i n_j)$.

$n = (\xi \cos kx \sin qz, 0, 1)$;
$d = (d_x \cos kx \cos qz, 0, d_z \sin kx \sin qz)$;
$E = 0$;
$l_{ij} = l_\perp (\delta_{ij} + (r - 1)n_i n_j)$.
Theoretical Calculation

Initial State:
\[
\begin{align*}
n^0 & = (0, 0, 1); \\
E & = E^0 \hat{z}; \\
l_{ij}^0 & = l_{\perp}^0 (\delta_{ij} + (r^0 - 1)n_i^0 n_j^0).
\end{align*}
\]

Final State:
\[
\begin{align*}
n & = (\xi \cos kx \sin qz, 0, 1); \\
d & = (d_x \cos kx \cos qz, 0, d_z \sin kx \sin qz); \\
E & = 0; \\
l_{ij} & = l_{\perp} (\delta_{ij} + (r - 1)n_i n_j).
\end{align*}
\]

Constrains & Approximations:

- Incompressibility: \( \nabla \cdot d = 0; \)
- Average energy density over the space;
- Minimize respect to \( \xi \) and \( d_z \);
- Ignore higher order terms \( o(d_x^2); \)
- Set \( k = 0 \) for the homogeneous birefringence transition as the basic mode.

Free Energy Expression:
\[
f = \mu \cdot d_x^2 q^2 \frac{r^0 (r + (r - 1)r^0 + r^2 (A - 1 + \epsilon_a E^2/\mu + K_B q^2/\mu))}{4r(1 - r^0 + r(A - 1 + r^0 + \epsilon_a E^2/\mu + K_B q^2/\mu))}
\]
Free Energy Plot of Buckling Transition

Notes:
Set \( q = \frac{\pi}{d} \), where \( d \) is the thickness of sample; the curve is plotted as \( r^0 = 2.0 \) and \( r = 3.0 \); the free energy decreases as the electric field \( E \) decreases, and perturbed state become stable \((f < 0)\) when the electric field is below critical field \((E < E_c)\).

Plotting Parameters:
\( d = 25 \mu m, \mu = 200 J/m^3, A = 0.1, K_S = K_B = 10^{-11} J/m, \) and \( \epsilon_a = 20 \epsilon_0 \).
Keeping $r^0 = 2.0$ as fixed, the critical field decreases as the value of $r$ decreases (corresponding to higher temperatures), which agrees qualitatively well with experimental observation, in which the critical voltage decreases as the temperature goes higher.

- $r = 2.5, \ V_C = 9.3\ V;$
- $r = 4.0, \ V_C = 46\ V.$

Note:
The quantitative relationship between $r$ and temperature is unknown, which makes it impossible to fit the critical field and temperature analytically.
Introduction & Background Knowledge

Nematic Rubber Elasticity

Buckling Transition in Nematic Gels

Stripes in Electro-Optics Experiment
  Simple Stripes in a Homogeneous Cell
  Experimental Description & Results
  Simplified Two Dimensional Model

Conclusions & Future Works
Simple Stripes in a Homogeneous Cell

Note:
The nematic director $\mathbf{n}$ is aligned parallel to the surfaces.
Simple Stripes in a Homogeneous Cell

$d=25 \mu m, T=25 ^\circ C$. Courtesy of J.A. Kornfield
Synthesis of Material

Molecular Structures:

- 89-wt% 5CB
- 9-wt% Monomer
- 0.8-wt% BME
- 1.2-wt% Crosslinker

Synthesis:

- Mixing the chemical components on vortex shaker for about four hours;
- Slow in-situ-polymerization under the UV light for four hours.
Stripe Pattern

Note:
An AC Sine voltage with frequency of 1 kHz applied.
Thickness Dependence of Stripes

d = 10 \mu m

d = 18 \mu m

d = 24 \mu m

d = 30 \mu m
\[ \theta = \xi \cos qz \sin kx, \quad \phi = 0 \]

\[ \mathbf{d} = (d_x \sin qz \sin kx, 0, d_z \cos qz \cos kx) \]

Note:

where \( \theta, \phi \) are respectively the tilt and azimuthal angles, into which the nematic director \( \mathbf{n} \) pointing, as \( \mathbf{n} = (\cos \theta \cos \phi, \cos \theta \sin \phi, \sin \theta) \); and \( q \) is determined by the sample thickness \( d \) as \( q = \frac{\pi}{d} \).
Free Energy Calculation of 2D Model

Free Energy Density Expression:

\[
F = F_{\text{Elastomer}} + F_{\text{Nematic}} + F_{\text{Dielectric}} \\
= \frac{1}{2} \mu \cdot \text{Tr}(I^0 \cdot \lambda^T \cdot I^{-1} \cdot \lambda) - \frac{1}{2} A \cdot \mu \cdot \text{Tr}(\lambda^T \cdot n \cdot \lambda - n^0 \cdot \lambda^T \cdot n \cdot \lambda) \\
+ \frac{1}{2} \left( K_B (n \times (\nabla \times n))^2 + K_S (\nabla \cdot n)^2 + K_T (n \cdot \nabla \times n)^2 \right) \\
- \frac{1}{2} \varepsilon_a E^2 \sin^2 \theta
\]

Other Constrains, Approximations:

- Incompressibility: \( \nabla \cdot d = 0 \);
- Average energy density over the space: \( f = \frac{k}{2\pi} \frac{q}{\pi} \int_0^{\frac{2\pi}{k}} \int_{-\frac{\pi}{2q}}^{\frac{\pi}{2q}} F \, dz \, dx \);
- Minimize respect to \( d_x \) and \( d_z \);
- Ignore the higher order terms \( o(\xi^2) \).
Free Energy Plot of 2D Model

Notes:
The total free energy is minimum at a finite value of $k$; The critical field can be found as the free energy at the minimum point reaches zero.

\[
f = f_{\text{elastomer}} + f_{\text{nematic}} + f_{\text{Dielectric}}
\]
\[
= \frac{\xi^2}{8} \left( \mu (A + (1 - \frac{1}{r})(r - 1) - \frac{(k^2(r - 1)r + q^2(1 + (A - 1)r))^2}{r(2k^2q^2r + k^4r^2 + q^4(1 + Ar))} \right)
\]
\[
+ K_S q^2 + K_B k^2 - \epsilon_a E^2
\]
Data Fitting of 2D Model

Fitting Parameters:

\( r = 3.17, \ A = 0.05, \ \mu = 160 J/m^3, \ K_S = 8.0 \times 10^{-12} J/m, \ K_B = 7.5 \times 10^{-12} J/m, \) and \( \epsilon_a = 20\epsilon_0. \)

Note:

The predicted values of critical voltage can not match with the experimental values, roughly five times smaller than the experimental ones.
Introduction & Background Knowledge

Nematic Rubber Elasticity

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Stripes in Electro-Optics Experiment

Conclusions & Future Works

Conclusions
Acknowledgments
- Buckling transition observed in homeotropic cell;
- Success of the simple model.

- Simple stripes observed in homogeneous cell;
- Stripe patterns observed in EO Experiments;
- Success of simple 2D calculation & Difficulty of 3D model.
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