The Elasticity of Nematic Liquid Crystalline Elastomers
- are symmetry arguments always right?

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http://www.mpip-mainz.mpg.de/~pleiner/lcpe.html
Plateau for perpendicular stretch

The stress-strain data points of Urayama et al.¹ in the representation of the nominal stress as a function of the true strain.

Monodomain side-chain nematic elastomers

Experimental results for the usual twice cross-linked elastomers:
3 regimes

1. (ordinary) linear anisotropic elasticity
   director is clamped by the network and does not reorient
   soft elasticity? Goldstone mode?

2. Nonlinear stress-strain 'plateau' for perpendicular stretching
   accompanied by a complete director reorientation
   where does it come from and what happens at the beginning/end?

3. Above a second threshold (ordinary) nonlinear anisotropic
   elasticity without director reorientation
No soft elasticity (linear)

- Warner & Terentjev\(^2\): "soft elasticity" ↔ \(\tilde{c}_{44} = 0\) \((C^R_5 = 0)\)
- corresponds to a Goldstone mode due to spontaneous shape change\(^3\)
- however, experimentally no vanishing linear shear modulus
- semisoft (almost soft): small imperfections prevent \(\tilde{c}_{44}\) from being exactly zero,
- instead \(\tilde{c}_{44} = \mu \alpha \frac{r}{r-1}\) small,\(^4\) since the semisoftness parameter \(\alpha \approx 0.1\) is small


\(^4\)Warner and Terentjev, cit. op., Chap. 7.4 and 7.5
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\textsuperscript{2}M. Warner and E. Terentjev, \textit{Liquid Crystal Elastomers}, Oxford University Press 2003, Chap. 7.1 - 7.3
\textsuperscript{4}Warner and Terentjev, cit. op., Chap. 7.4 and 7.5
No semisoft elasticity (linear)

- however, experimentally the linear shear modulus is of the same order as in the isotropic phase\(^5\)
- \(G' \sim \tilde{c}_{44}\) as a function of temperature

ordinary, linear Hookean elasticity of uniaxial anisotropic type

Semisoftness (nonlinear)

- the general scenario of semisoftness – *ideal softness plus some disturbance* – has been used to describe the elastic plateau (in the nonlinear domain)\(^6\)
- as a result, the effective, or apparent linear elastic coefficient vanishes at the beginning and end of the plateau
- at the same points, director orientational fluctuations diverge
- general symmetry arguments are used to show that ’ideal softness plus some disturbance’ always leads to this soft mode behavior\(^7\)
- does this mean ’semisoftness’ is the reason for the plateau and the soft mode behavior?

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Different viewpoint

- first, one should differentiate between the linear semisoftness (small linear elastic coefficient) and the nonlinear plateau behavior
- the latter is a genuine nonlinear feature independent of the linear behavior
- it is unfortunate to give two separate phenomena the same name
- the linear (semi-)softness describes an (almost) Goldstone mode related to a broken symmetry [not present in nematic LC elastomers], while the nonlinear semisoftness gives a soft mode, a phase transition-type phenomena based on the special free energy
- Goldstone mode and soft mode are completely independent objects (cf. smectic C liquid crystals)
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- **Goldstone mode and soft mode are completely independent objects** (cf. smectic C liquid crystals)
Different viewpoint (cont.)

our viewpoint:

- the soft mode behavior at the beginning and end of the elastic plateau can be obtained \textit{without} the assumption of the existence of semisoftness
- it can be obtained by, and is based on the coupling between elasticity and director reorientation via ‘relative rotations’
- there is \textit{no small parameter} involved (no linear semisoftness)

our description (de Gennes approach):

- nematic LC elastomers are solid, elastic bodies with relative rotations between director and network
- all ingredients are highly nonlinear
Experiments

there are basically two experiments:

- light scattering experiments probing the nematic director fluctuations


(almost) critical slowing down
Experiments (cont.)

2. Direct rheological measurements of the effective shear modulus


No sign of a vanishing effective shear elastic coefficient

Conflicting outcome !!!
Experiments (cont.)

- direct rheological measurements of the effective shear modulus

\[ G\text{(Pa)} \]

\[ \sigma_{\text{nom}}(40^4 \text{Pa}) \]

\[ \lambda = 1.27, 1.43 \]

T = 82°C, f = 0.2 Hz

no sign of a vanishing effective shear elastic coefficient


conflicting outcome !!!
Elastic and orientational degrees of freedom

This description of the nematic elastomer elasticity has been done together with A. Menzel\textsuperscript{8,9}

Network: \[ da_\alpha = R_\alpha j \Xi_{jk} \, dr_k \]

Eulerian strain tensor
\[ \varepsilon_{ik} = \frac{1}{2} [\delta_{ik} - \Xi_{ij} \Xi_{ik}] \]
\[ = \frac{1}{2} [\delta_{ik} - (\partial a_\alpha / \partial r_k)(\partial a_\alpha / \partial r_i)] \]
\[ = \frac{1}{2} [\partial u_i / \partial r_k + \partial u_k / \partial r_i - (\partial u_j / \partial r_i)(\partial u_j / \partial r_k)] \]

Nematic: Director
\[ \hat{n} = S \cdot \hat{n}_0 \quad \text{and textures } (\nabla_j n_i) \]

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Relative rotations

Coupling:

- rotations of the anisotropic network \( \hat{n}_{nw} = R^{-1} \cdot \hat{n}_0 \)
  (there is no closed expression for \( R^{-1} \) in terms of \( \partial u_j / \partial r_i \))
- rotations of the nematic director \( \hat{n} = S \cdot \hat{n}_0 \)
- relative rotations (projections)\(^{10}\)
  \[
  \tilde{\Omega} \equiv \hat{n} - \gamma \hat{n}_{nw} \\
  \tilde{\Omega}_{nw} \equiv -\hat{n}_{nw} + \gamma \hat{n}
  \]
  with \( \gamma \equiv \hat{n} \cdot \hat{n}_{nw} \) resulting in
  \( \tilde{\Omega} \cdot \hat{n}_{nw} = 0 = \tilde{\Omega}_{nw} \cdot \hat{n} \)

Free energy

Power series expansion in $\varepsilon_{ij}$, $\tilde{\Omega}_i$, $\tilde{\Omega}_j^{nw}$, and $n_i$ and all its couplings up to third order (reduces to de Gennes’ expression in the linear theory\(^\text{11}\))

here: simplified model (analytical treatment) - elastic nonlinearities neglected

$$
F = \frac{1}{2} c_{44} \varepsilon_{ij} \varepsilon_{ij} + \ldots \\
+ \frac{1}{2} D_1 \tilde{\Omega}_i \tilde{\Omega}_i + D_1^{(2)} (\tilde{\Omega}_i \tilde{\Omega}_i)^2 + D_1^{(3)} (\tilde{\Omega}_i \tilde{\Omega}_i)^3 \\
+ D_2 n_i \varepsilon_{ij} \tilde{\Omega}_j + D_2^{nw} n_i^{nw} \varepsilon_{ij} \tilde{\Omega}_j^{nw} \\
+ D_2^{(2)} n_i \varepsilon_{ij} \varepsilon_{jk} \tilde{\Omega}_k + D_2^{nw, (2)} n_i^{nw} \varepsilon_{ij} \varepsilon_{jk} \tilde{\Omega}_k^{nw} \\
- \frac{1}{2} \varepsilon_{a} (n_i E_i)^2
$$

with the nonlinear rotation matrix to cubic order

$$
R_{ij} = \delta_{ij} + \varepsilon_{ij} + \frac{3}{2} \varepsilon_{ik} \varepsilon_{kj} + \frac{5}{2} \varepsilon_{ik} \varepsilon_{kl} \varepsilon_{lj} - (\partial_i u_j) - \varepsilon_{ik} (\partial_k u_j) - \frac{3}{2} \varepsilon_{ik} \varepsilon_{kl} (\partial_l u_j) + \ldots
$$

Plateau for perpendicular stretch

\[ \sigma^N_{\text{ext}} \text{ [kPa]} \]

\[ \epsilon = \ln(\lambda) \]

The stress-strain data points of Urayama et al. and the theoretical line obtained by the present model in the representation of the nominal stress as a function of the true strain.
Director reorientation

Theoretical curves of the director reorientation during stretch ($A$) for different stretch directions. For $\vartheta_0 = 0^\circ$ (perpendicular stretch) a singular threshold behavior is found.
Forward bifurcation

In the vicinity of $A_c$ an amplitude equation can be derived analytically for the case $\vartheta_0 = 0$ (perpendicular stretch)

$$0 = \vartheta \{ a(A_c - A) + g\vartheta^2 \} + O(\vartheta^5).$$

$\rightarrow$ forward bifurcation with exchange of stability between $\vartheta = 0$ for $A < A_c$ and $\vartheta \sim \sqrt{A - A_c}$ for $A > A_c$

for $\vartheta_0 > 0$ (oblique stretch) an imperfect bifurcation is obtained
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Shear response

For a given pre-strain $A$ – that results in a given compression $B$, shear $S$, and tilt angle $\vartheta$, a small shear $\delta S$ is added and the effective shear modulus is calculated.

Homeotropic geometry with a small shear $\delta S$ added.
Effective linear shear modulus

The system is pre-stretched in a direction perfectly perpendicular to the initial director orientation $\hat{n}_0$. The zeroes of the effective shear modulus at the beginning and end of the plateau denote diverging fluctuations.
Electric field response

For a given prestrain $A$ – that results in a given compression $B$, shear $S$, and tilt angle $\vartheta$, an external field $E$ is applied ($\parallel$ and $\perp$ to $\hat{n}_0$) and the reorientability of the director is calculated.

Homeotropic geometry with an external field applied
Director reorientability

Reorientability $\frac{\partial^2 \vartheta}{\partial E^2} \bigg|_{E=0}$ as a function of the pre-stretching amplitude $A$, where the divergencies take place at the beginning and end of the plateau ($\mathbf{E} \perp \hat{n}_0$).
Reorientability $\partial^2 \vartheta / \partial E^2 |_{E=0}$ as a function of the pre-stretching amplitude $A$, where the divergencies take place at the beginning and end of the plateau ($E \perp \hat{n}_0$)

Same theoretical data fitted in the region $\vartheta \gtrsim 0$ by a curve $\propto (A - A_c)^x$ with $x \approx -1/2$, thus clearly indicating a soft mode behavior in mean field description.
Effective shear modulus $\partial^2 F / \partial (\delta S)^2 |_{\delta S=0}$ (left) and reorientability $\partial^2 \vartheta / \partial E^2 |_{E=0}$ (right) as a function of the pre-stretching amplitude $A$. Here, the initial director orientation $\hat{n}_0$ slightly deviates from the perfectly perpendicular orientation by an angle of 0.01 rad ($0.57^\circ$).

imperfect bifurcation: no divergent fluctuations
Our interpretation

Stretching a mono-domain nematic elastomer perpendicularly, the resulting **elastic plateau** at finite strains

- comes with a vanishing effective linear modulus and a divergent director reorientability at its beginning and end (**soft mode** or **forward bifurcation** similar to a **second order phase transition**)

- the critical behavior is related to the **kink in the director reorientation**

- this bifurcation-type behavior is a genuine manifestation of the role of **nonlinear relative rotations**

- it requires **two independent preferred directions** and discriminates nematic LSCEs from simple anisotropic solids
Our interpretation (contin.)

- although this **soft mode behavior** is the same as found by the (nonlinear) semisoft approach, our description does not make use of any linear ideal soft-elastic behavior **Nambu-Goldstone mode** ("soft-elasticity"), nor of any closeness to an ideal soft-elastic behavior ("semisoft elasticity")
- we find this soft-mode scenario also for cases, where the plateau starts at **very large applied strains**

![Graph showing effective shear modulus, reorientation angle, and stress-strain curve.]

Soft mode behavior for large pre-strain \( A_c \approx 0.56 \) (or \( \lambda \approx 2.3 \)) – in the semisoftness picture this corresponds to \( \alpha \approx 1.3 \)
Theory vs. experiment

- both types of theory show the soft mode behavior
- fitting to the light scattering measurements, but contradicting the rheological shear elastic measurements
- our description cannot exclude the possibility of plateaus without a soft mode behavior, since we cannot explore the complete parameter space
  – however, the soft mode behavior seems to be related to the kink behavior of the director reorientation
- the semisoft description makes a strong statement that there must always be a soft mode due to symmetry arguments
- therefore the rheological shear elastic measurements must be wrong
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are symmetry arguments always correct ??
**Lehmann effect**

Lehmann: director rotations when a temperature gradient is applied

\[ \mathbf{n} \times \frac{\partial}{\partial t} \mathbf{n} = \psi' \nabla \perp \Theta \]

- works also for concentration gradients and electric fields
- there are inverse effects\(^1\)
- these effects are dissipative
  (although there are contributions originating from the statics)
- these effects are chiral: \( \psi' = q \psi \) (de Gennes’ symmetry argument), where \( q \) is the helical pitch

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Chirality at the compensation point

what happens at the compensation point?

- some mixtures of chiral molecules and at least one pure compound show a compensation point (no helix or \( q = 0 \))
- therefore, Lehmann has to vanish due to symmetry arguments\(^{13}\)
- however, experiments show non-vanishing Lehmann effects\(^{14,15}\)

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Chirality at the compensation point

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are symmetry arguments always correct ??


Lehmann effect experiments

- experiments show a non-vanishing Lehmann coefficient

![Graph showing temperature vs. angular velocity](image)

- answer: not necessarily, since the symmetry argument is not applicable
  - it starts from a description that is not general enough\footnote{H. Pleiner and H.R. Brand, Europhys. Lett. 89, 26003 (2010)}
Lehmann effect experiments

- experiments show a non-vanishing Lehmann coefficient

experiment wrong, since it violates a symmetry argument?

answer: not necessarily, since the symmetry argument is not applicable
- it starts from a description that is not general enough!\(^{16}\)

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Free energy

(achiral) nematics: $f_{nema} = \frac{1}{2} K_1 S^2 + \frac{1}{2} K_3 B^2 + \frac{1}{2} K_2 T^2$ with
- splay $S = \text{div} \ n$ - scalar
- bend $B = n \times \text{curl} \ n$ - vector
- twist $T = n \cdot \text{curl} \ n$ - pseudoscalar

equilibrium state: $S = B = T = 0$, homogeneous $n = \text{const.}$, $f_{nema}^{eq} = 0$

(chiral) cholesterics: $f_{chol} = f_{nema} + K'_2 T$
- a linear twist term $\sim T$ is allowed\textsuperscript{17,18}
- $K'_2$ has to be a pseudoscalar

\textsuperscript{17} $K'_2$ is called $k_2$ in F.C. Frank, *Discuss. Faraday Soc.*, 25 (1958) 19.
\textsuperscript{18} in addition, bilinear terms $\sim T \delta \sigma$, $\sim T \delta \rho$, and $\sim T \delta c$ are possible
Free energy

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Helix

\[ f_{\text{chol}} = \frac{1}{2} K_1 S^2 + \frac{1}{2} K_3 B^2 + \frac{1}{2} K_2 T^2 + K'_2 T \]

is minimized by a helix with the (pseudoscalar) coefficient \( q \)

\[ n = e_x \cos qz + e_y \sin qz \]

(implying \( S = B = 0 \) and \( T = -q \)), if

\[ q \to q^{eq} = \frac{K'_2}{K_2} \]

leading to the maximum energy reduction

\[ f^{eq} = -\frac{1}{2} \left( \frac{K'_2}{K_2} \right)^2 / K_2 \]
since $K'_2$ is a pseudoscalar, it has to vanish in an achiral system,

$$\rightarrow K'_2 \sim q$$

A) de Gennes’ choice: $K'_2 = qK_2$, resulting in $q^{eq} = q$
(only one pseudoscalar quantity)

$$f_{chol} = \frac{1}{2}K_2(n \cdot \text{curl}n + q)^2 + \ldots$$

B) generally: $K'_2 = qL_2$, resulting in $q^{eq} = q\frac{L_2}{K_2}$
($q^{eq}$ and $q$ are not identical)

$$f_{chol} = \frac{1}{2}K_2(n \cdot \text{curl}n + q^{eq})^2 + \ldots$$
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A) de Gennes’ choice: \( K' = qK \), resulting in \( q^{eq} = q \)
(only one pseudoscalar quantity)

\[ f_{chol} = \frac{1}{2}K_2(n \cdot \text{curl} n + q)^2 + \ldots \]

B) generally: \( K' = qL \), resulting in \( q^{eq} = q\frac{L}{K} \)
(\( q^{eq} \) and \( q \) are not identical)

\[ f_{chol} = \frac{1}{2}K_2(n \cdot \text{curl} n + q^{eq})^2 + \ldots \]
Resolution

A) if the vanishing helix at the compensation point means \( q = 0 \)
\[ \rightarrow \] there is no Lehmann effect, since \( \psi' = q \psi = 0 \)

B) if the vanishing helix at the compensation point means \( q^{eq} = 0 \),
this can be obtained by \( L_2 = 0 \), with \( q \) still being finite
\[ \rightarrow \] there is a Lehmann effect possible and there is no contradiction between experiment and theory\(^{19}\)

starting from a more general description resolves the contradiction between experiment and symmetry argument

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\(^{19}\) A non-vanishing \( q \) at the compensation point means the system is still chiral, i.e. can show optical rotatory power.
Resolution in the LCE case?

- **Is ideal softness**, the starting point of the (nonlinear) semisoft description, **general enough**?
- **If not**, the symmetry arguments were not applicable and there were **no contradiction** with the rheological shear elastic measurements.
- (semi-)softness approach assumes Gaussian properties of the network - not present for the twice crosslinked elastomers (cf. talk by P. Martinoty)
- (semi-)softness approach assumes affine deformations - not present for realistic polymer networks (cf. next page)
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- (semi-)softness approach assumes affine deformations - not present for realistic polymer networks (cf. next page).
No affine deformations

- no affine deformations under stretch
  (simulations by R. Everaers and K. Kremer)

- this might also be the reason for intrinsic inhomogeneities, even in the single domain samples
Announcement

Welcome to the 24th International Liquid Crystal Conference
ILCC2012
August 19 - 24, Mainz, Germany
http://www.ilcc2012.de