The Elasticity of Nematic Liquid Crystalline Elastomers

- are symmetry arguments always right?

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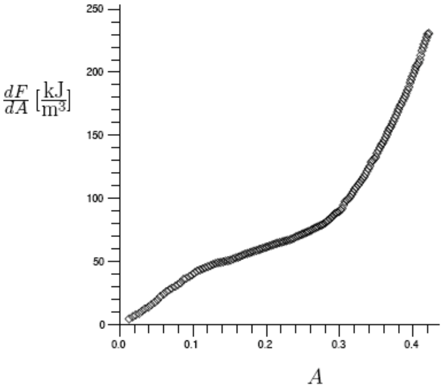
http://www.mpip-mainz.mpg.de/∼pleiner/lcpe.html

Outline

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.

[1] K. Urayama, R. Mashita, I. Kobayashi, and T. Takigawa, *Macromol.* **40** (2007) 7665.

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" $\leftrightarrow$ $\tilde{c}_{44} = 0$ ($C_5^R = 0$)
- 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

[2] M. Warner and E. Terentjev, *Liquid Crystal Elastomers*, Oxford University Press 2003, Chap. 7.1 - 7.3

[3] L. Golubovic and T.C. Lubensky, *Phys. Rev. Lett.* **63** (1989) 1082.

[4] Warner and Terentjev, cit. op., Chap. 7.4 and 7.5

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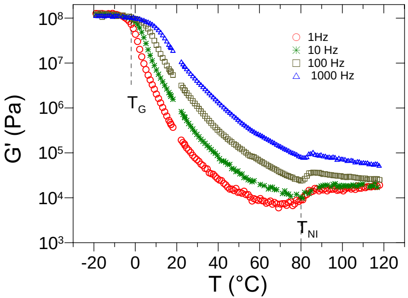
No semisoft elasticity (linear)

- 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
- small dip explained by P.G. de Gennes in *Liquid Crystals of One- and Two-Dimensional Order*, eds. W. Helfrich and G. Heppke, Springer, New York, p. 231 (1980).



ordinary, linear Hookean elasticity of uniaxial anisotropic type

[5] P. Martinoty, P. Stein, H. Finkelmann, H. P., and H.R. Brand, *Eur. Phys. J. E*, **14** (2004) 311.

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?

[6] J. S. Biggins, E. M. Terentjev, and M. Warner, *Phys. Rev. E* **78** (2008) 041704
[7] F. F. Ye and T. C. Lubensky, *J. Phys. Chem. B* **113** (2009) 3853.

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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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Different viewpoint (cont.)

our viewpoint:

- the soft mode behavior at the beginning and end of the elastic plateau can be obtained 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 no small parameter involved (no linear semisoftness)

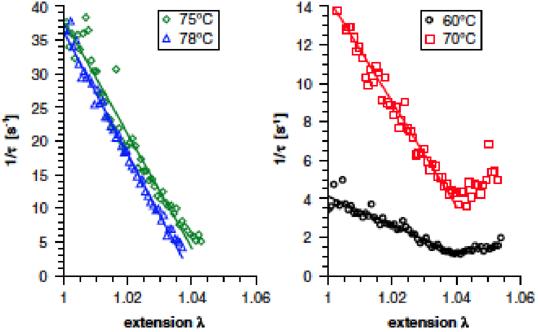
our description (de Gennes approach):

- 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:

1. light scattering experiments probing the nematic director fluctuations

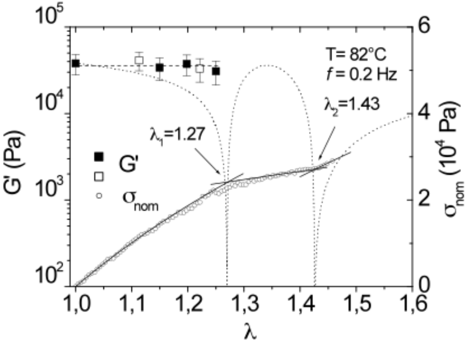


(almost) critical slowing down

A. Petelin and M. Čopič, *Phys. Rev. Lett.* **103**, 077801 (2009)

Experiments (cont.)

2. direct rheological measurements of the effective shear modulus



no sign of a vanishing effective shear elastic coefficient

D. Rogez and P. Martinoty, *Eur. Phys. J. E*, **34**, 69 (2011)

conflicting outcome !!!

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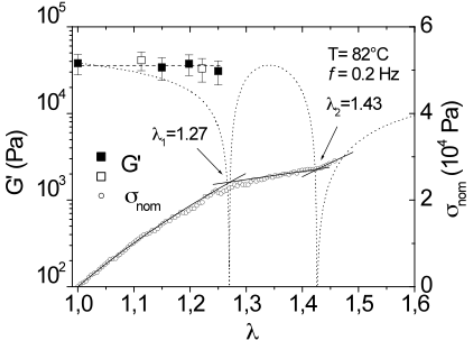

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Elastic and orientational degrees of freedom

This description of the nematic elastomer elasticity has been done together with A. Menzel[8,9]

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

Eulerian strain tensor

$$\begin{aligned}\varepsilon_{ik} &= \tfrac{1}{2}[\delta_{ik} - \Xi_{ij}\Xi_{ik}] \\ &= \tfrac{1}{2}[\delta_{ik} - (\partial a_\alpha/\partial r_k)(\partial a_\alpha/\partial r_i)] \\ &= \tfrac{1}{2}[\partial u_i/\partial r_k + \partial u_k/\partial r_i - (\partial u_j/\partial r_i)(\partial u_j/\partial r_k)]\end{aligned}$$

Nematic: Director

$\hat{\boldsymbol{n}} = \mathsf{S} \cdot \hat{\boldsymbol{n}}_0$ and textures $(\nabla_j n_i)$

[8] A. Menzel, H.P., H.R. Brand, *J. Appl. Phys.* **105**, 013503 (2009) and *Eur. Phys. J. E* **30**, 371 (2009)

[9] address starting October 1, 2011: Inst. Theor. Phys., Univ. Düsseldorf, Germany

Relative rotations

Coupling:

- rotations of the anisotropic network $\hat{\boldsymbol{n}}^{\boldsymbol{nw}} = \mathrm{R}^{-1} \cdot \hat{\boldsymbol{n}}_{\mathbf{0}}^{\boldsymbol{nw}}$

  (there is no closed expression for R^{-1} in terms of $\partial u_j/\partial r_i$)

- rotations of the nematic director $\hat{\boldsymbol{n}} = \mathrm{S} \cdot \hat{\boldsymbol{n}}_{\mathbf{0}}$

- relative rotations (projections)[10]

$$\tilde{\boldsymbol{\Omega}} \equiv \hat{\boldsymbol{n}} - \gamma\, \hat{\boldsymbol{n}}^{\boldsymbol{nw}}$$
$$\tilde{\boldsymbol{\Omega}}^{\boldsymbol{nw}} \equiv -\hat{\boldsymbol{n}}^{\boldsymbol{nw}} + \gamma\, \hat{\boldsymbol{n}}$$

with $\gamma \equiv \hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{n}}^{\boldsymbol{nw}}$ resulting in $\tilde{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{n}}^{\boldsymbol{nw}} = 0 = \tilde{\boldsymbol{\Omega}}^{\boldsymbol{nw}} \cdot \hat{\boldsymbol{n}}$

[10] A. M. Menzel, H. Pleiner and H. R. Brand, *J. Chem. Phys.* **126** (2007) 234901.

Free energy

Power series expansion in ε_{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[11])

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

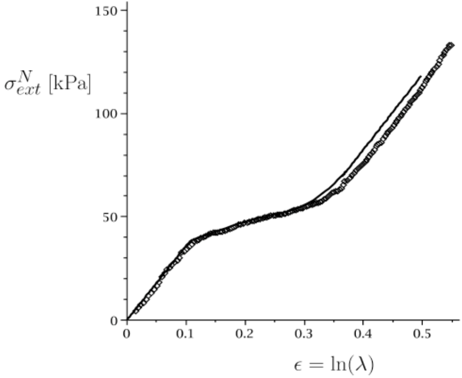
$$\begin{aligned} F \;=\;& \tfrac{1}{2} c_{44}\, \varepsilon_{ij}\varepsilon_{ij} + \dots \\ & + \tfrac{1}{2} D_1\, \tilde{\Omega}_i\tilde{\Omega}_i + D_1^{(2)}\, (\tilde{\Omega}_i\tilde{\Omega}_i)^2 + D_1^{(3)}\, (\tilde{\Omega}_i\tilde{\Omega}_i)^3 \\ & + D_2\, n_i\varepsilon_{ij}\tilde{\Omega}_j + D_2^{nw}\, n_i^{nw}\varepsilon_{ij}\tilde{\Omega}_j^{nw} \\ & + D_2^{(2)} n_i\varepsilon_{ij}\varepsilon_{jk}\tilde{\Omega}_k + D_2^{nw,(2)} n_i^{nw}\varepsilon_{ij}\varepsilon_{jk}\tilde{\Omega}_k^{nw} \\ & - \tfrac{1}{2}\epsilon_a\, (n_i E_i)^2 \end{aligned}$$

with the nonlinear rotation matrix to cubic order

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

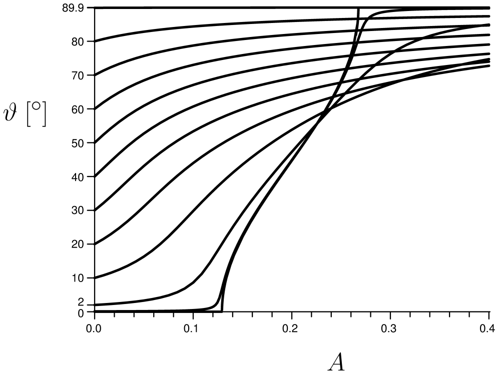
[11] P.G. de Gennes, in *Liquid Crystals of One- and Two-Dimensional Order*, eds. W. Helfrich and G. Heppke, Springer, New York, p. 231 (1980).

Plateau for perpendicular stretch



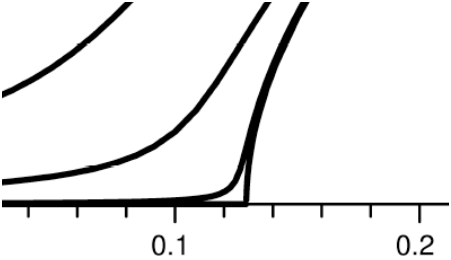
The stress-strain data points of Urayama et al. and the theoretical line obtained by the present model in the representation of the nominal stress as a function of the true strain.

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



the curve $\vartheta(A)$ as before, but with the area around A_c enlarged

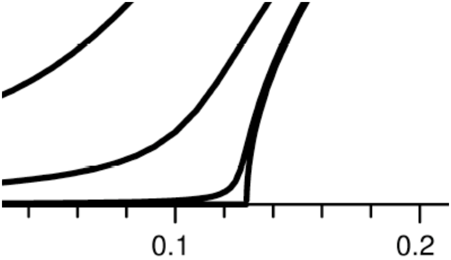
In the vicinity of A_c an amplitude equation can be derived analytically for the case $\vartheta_0 = 0$ (perpendicular stretch)

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

$\longrightarrow$ 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

Forward bifurcation



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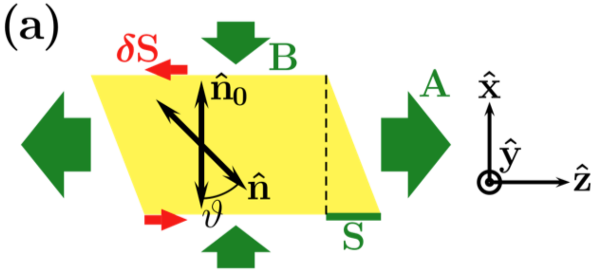
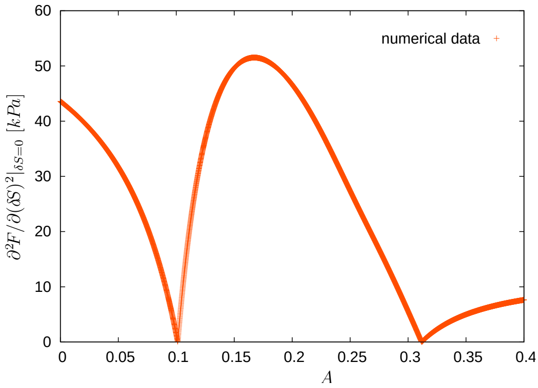
Shear response

For a given pre-strain *A* – that results in a given compression *B*, shear *S*, and tilt angle ϑ,
a small shear δS is added and the effective shear modulus is calculated



Homeotropic geometry with a small shear δS added

Effective linear shear modulus

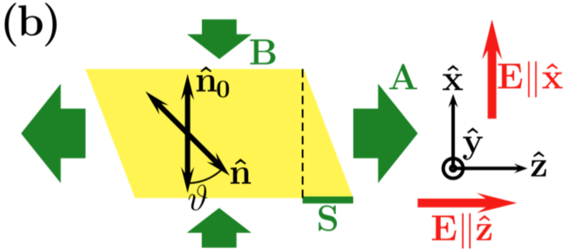


Effective shear modulus $\partial^2 F/\partial(\delta S)^2|_{\delta S=0}$ as a function of the pre-stretching amplitude A

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

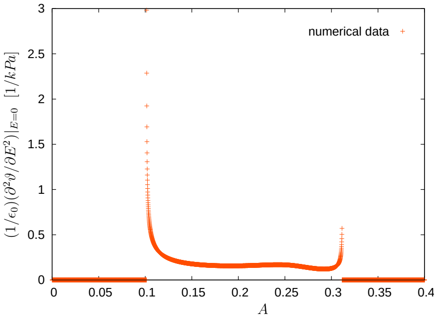
Electric field response

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



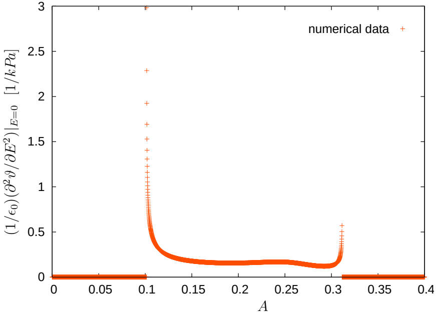
Homeotropic geometry with an external field applied

Director reorientability



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 ($\boldsymbol{E} \perp \hat{\boldsymbol{n}}_0$)

Director reorientability



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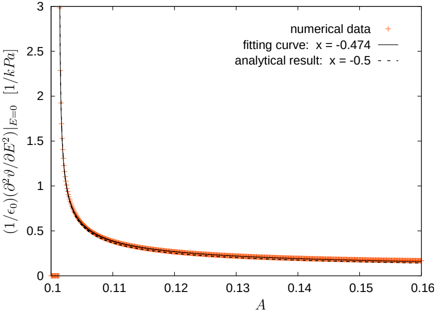
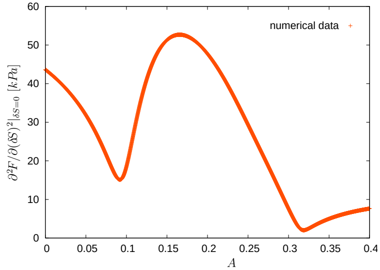
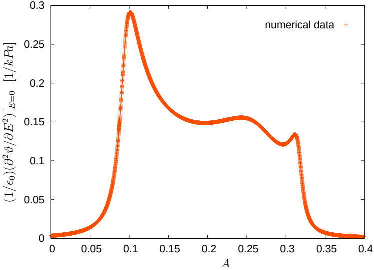


Same theoretical data fitted in the region $\vartheta \gtrsim 0$ by a curve $\propto (A - A_c)^x$ with $x \approx -1/2$, thus clearly indicating a soft mode behavior in mean field description

Oblique pre-strain





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 $\hat{\boldsymbol{n}}_0$ slightly deviates from the perfectly perpendicular orientation by an angle of 0.01 rad (0.57°).

imperfect bifurcation: no divergent fluctuations

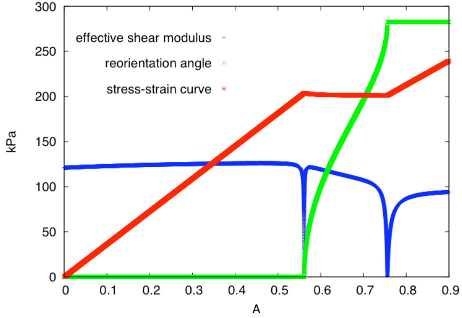
Our interpretation

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



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

$$\boldsymbol{n} \times \frac{\partial}{\partial t}\boldsymbol{n} = \psi' \boldsymbol{\nabla}_\perp \Theta$$

- works also for concentration gradients and electric fields
- there are inverse effects[12]
- 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

[12] D. Svenšek, H. Pleiner, and H.R. Brand, Phys. Rev. E **78**, 021703 (2008)

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]

[13] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford) 1995.

[14] P. Oswald and A. Dequidt, *Europhys. Lett.*, **83** (2008) 16005; **80** (2007) 26001; *Phys. Rev. Lett.* **100** (2008) 217802.

[15] N. Éber and I. Jánossy, *Mol. Cryst. Liq. Cryst.*, **72** (1982) 233; **102** (1984) 311; and *Mol. Cryst. Liq. Cryst. Lett.*, **5** (1988) 81.

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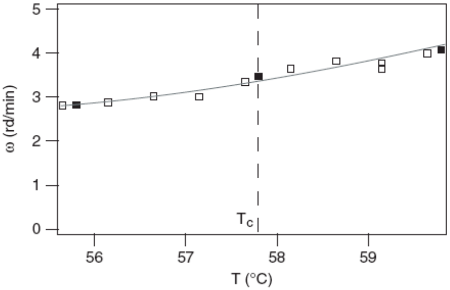
Lehmann effect experiments

- 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]

[16] H. Pleiner and H.R. Brand, Europhys. Lett. **89**, 26003 (2010)

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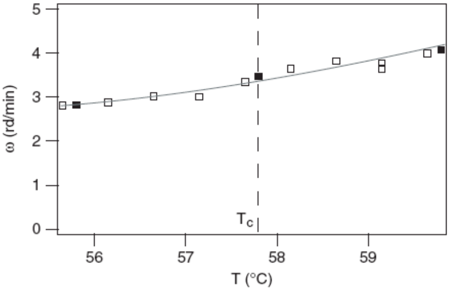

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Free energy

(achiral) nematics: $f_{nema} = \frac{1}{2}K_1 S^2 + \frac{1}{2}K_3 \boldsymbol{B}^2 + \frac{1}{2}K_2 T^2$ with

- splay $S = \mathrm{div}\boldsymbol{n}$ - scalar
- bend $\boldsymbol{B} = \boldsymbol{n} \times \mathrm{curl}\boldsymbol{n}$ - vector
- twist $T = \boldsymbol{n} \cdot \mathrm{curl}\boldsymbol{n}$ - pseudoscalar

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

(chiral) cholesterics: $f_{chol} = f_{nema} + K_2' T$

- a linear twist term $\sim T$ is allowed[17,18]
- K_2' has to be a pseudoscalar

[17] K_2' is called k_2 in F.C. Frank, *Discuss. Faraday Soc.*, **25** (1958) 19.

[18] in addition, bilinear terms $\sim T\delta\sigma$, $\sim T\delta\rho$, and $\sim T\delta c$ are possible

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- twist $T = \boldsymbol{n} \cdot \mathrm{curl}\boldsymbol{n}$ - pseudoscalar

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

(chiral) cholesterics: $f_{chol} = f_{nema} + K_2' T$

- a linear twist term $\sim T$ is allowed[17,18]
- K_2' has to be a pseudoscalar

[17] K_2' is called k_2 in F.C. Frank, *Discuss. Faraday Soc.*, **25** (1958) 19.
[18] in addition, bilinear terms $\sim T\delta\sigma$, $\sim T\delta\rho$, and $\sim T\delta c$ are possible

Helix

$$f_{chol} = \frac{1}{2}K_1 S^2 + \frac{1}{2}K_3 \boldsymbol{B}^2 + \frac{1}{2}K_2 T^2 + K_2' T$$

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

$$\boldsymbol{n} = \boldsymbol{e}_x \cos qz + \boldsymbol{e}_y \sin qz$$

(implying $S = \boldsymbol{B} = 0$ and $T = -q$), if

$$q \to q^{eq} = K_2'/K_2$$

leading to the maximum energy reduction

$$f^{eq} = -\frac{1}{2}(K_2')^2/K_2$$

Symmetry

- since K_2' is a pseudoscalar, it has to vanish in an achiral system,

$$\longrightarrow K_2' \sim q$$

A) de Gennes' choice: $K_2' = qK_2$, resulting in $q^{eq} = q$
(only one pseudoscalar quantity)

$$f_{chol} = \frac{1}{2}K_2(\boldsymbol{n} \cdot \mathrm{curl}\boldsymbol{n} + q)^2 + \dots$$

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

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Resolution

A) if the vanishing helix at the compensation point means $q = 0$
$\longrightarrow$ 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
$\longrightarrow$ 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

[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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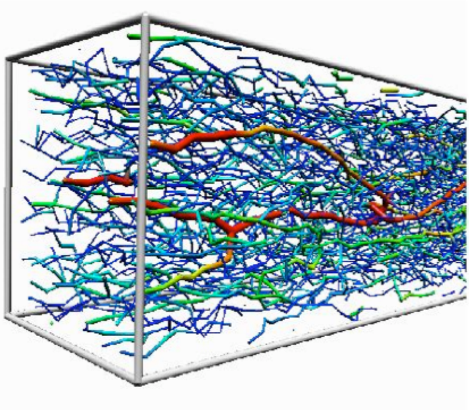
No affine deformations

- 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

24^{th} International Liquid Crystal Conference

ILCC2012

August 19 - 24, Mainz, Germany

http://www.ilcc2012.de