Nonlinear Stress - Strain Behavior of Nematic Elastomers using Relative Rotations

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Outline

Monodomain Side-Chain Nematic Elastomers

Experiment:

- linear anisotropic elasticity
- nonlinear stress-strain plateau for perpendicular stretching
- accompanied by a complete director reorientation

Description and Interpretation:
effective linear modulus and director relaxation under pre-strain?

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Results

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)
- 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

and

- this soft mode behavior is not related to the proposed Nambu-Goldstone mode ("soft-elasticity"), nor is any closeness to an ideal soft-elastic behavior ("semi-soft elasticity") required:
- the described scenario is found also for cases, where the plateau starts at very large applied strains

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Elastic and Orientational Degrees of Freedom

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

$\hat{\boldsymbol{n}} = \mathrm{S} \cdot \hat{\boldsymbol{n}}_{\mathbf{0}}$ and textures $(\nabla_j n_i)$

Relative Rotations

Coupling:

- rotations of the anisotropic network $\hat{\boldsymbol{n}}^{nw} = \mathrm{R}^{-1} \cdot \hat{\boldsymbol{n}}_0^{nw}$
  (there is no closed expression for R^{-1} in terms of $\partial u_j / \partial r_i$)
- rotations of the nematic director $\hat{\boldsymbol{n}} = \mathrm{S} \cdot \hat{\boldsymbol{n}}_0$
- relative rotations (projections)[1]

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

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

[1] 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 some order

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

$$
\begin{aligned}
F \;=\;& c_1\, \varepsilon_{ij}\varepsilon_{ij} + \tfrac{1}{2} c_2\, \varepsilon_{ii}\, \varepsilon_{jj} + \dots \\
& + \frac{1}{2} D_1\, \tilde{\Omega}_i \tilde{\Omega}_i + D_1^{(2)}\, (\tilde{\Omega}_i \tilde{\Omega}_i)^2 + D_1^{(3)}\, (\tilde{\Omega}_i \tilde{\Omega}_i)^3 \\
& + D_2\, n_i \varepsilon_{ij} \tilde{\Omega}_j + D_2^{nw}\, n_i^{nw} \varepsilon_{ij} \tilde{\Omega}_j^{nw} \\
& + D_2^{(2)} n_i \varepsilon_{ij} \varepsilon_{jk} \tilde{\Omega}_k + D_2^{nw,(2)} n_i^{nw} \varepsilon_{ij} \varepsilon_{jk} \tilde{\Omega}_k^{nw} \\
& - \tfrac{1}{2} \epsilon_a\, (n_i E_i)^2
\end{aligned}
$$

reduces in linear order to de Gennes' expression

Plateau for Perpendicular Stretch - Eulerian

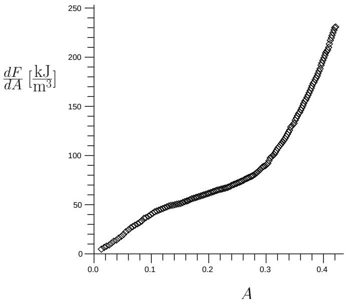


Fig.1: Stress-strain data measured by Urayama et al.[a] transferred to the representation in terms of the stretch amplitude $A = \partial u_z/\partial z$ and dF/dA.

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

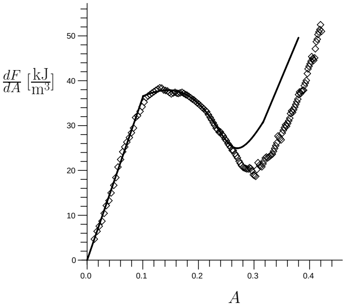


Fig.2: Same stress-strain data as in Fig.1 with nonlinear purely elastic contributions by the network of polymer backbones subtracted. The line is the result of the theoretical model [a]

[a] A. Menzel, H.P., and H.R. Brand, *J. Appl. Phys.* **105** (2009) 013503.

Plateau for Perpendicular Stretch - Lagrangian

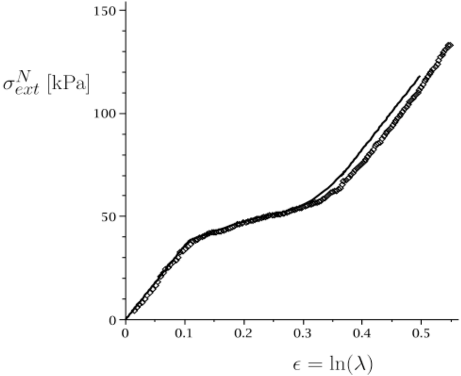


Fig.3: The same stress-strain data points of Urayama et al. and the theoretical line obtained by the present model (with the nonlinear elastic experimental contributions added) – now in the representation of the nominal stress as a function of the true strain.

Director Reorientation

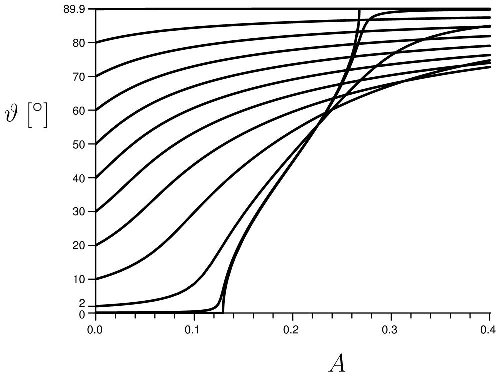


Fig.4: Angle ϑ between the director orientation and the x axis under the influence of an externally imposed strain A for various initial director orientations $\vartheta_0 = \vartheta(A = 0)$, e.g. 0°, 0.1°, 2°, 10°, ... 80°, and 89.9°, respectively. For $\vartheta_0 = 0°$ (perpendicular stretch) a singular threshold behavior is found.

Forward bifurcation

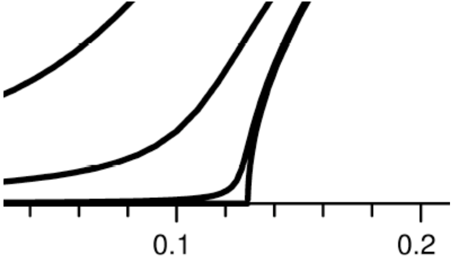


Fig.4a: $\vartheta = \vartheta(A)$; same as Fig.4 with the area around A_c enlarged

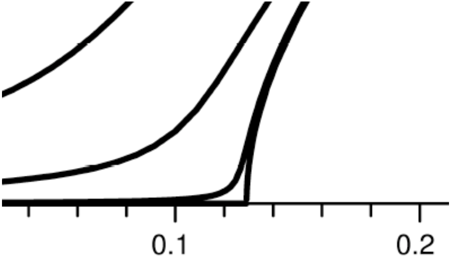
In the vicinity of A_c an amplitude equation can be derived analytically for the case $\vartheta_0 = 0$

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

$\longrightarrow$ 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 $\vartheta_0 > 0$ an imperfect bifurcation is obtained

Forward bifurcation



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for $\vartheta_0 > 0$ an imperfect bifurcation is obtained

Soft mode

- a forward bifurcation is similar to a second order phase transition
- an (effective) susceptibility vanishes at the phase transition (at onset)
- giving rise to diverging fluctuations (soft mode)
- in contrast to Nambu-Goldstone modes, where a susceptibility is identically zero throughout the whole phase due to symmetry reasons
- example: director rotations in a smectic C phase:
  azimuthal (on the cone) Nambu-Goldstone mode
  tilt angle: soft only at the smectic A to C transition
- for imperfect bifurcations no diverging fluctuations

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Homeotropic geometry

For a given prestrain *A* – that results in a given compression *B*, shear *S*, and tilt angle ϑ

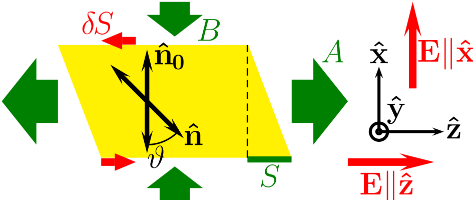

Fig.5: Homeotropic geometry

1. a small shear δS is added and the effective shear modulus is calculated
2. an external field is applied ($\|$ and $\perp$ to $\hat{\boldsymbol{n}}_0$) and the reorientability of the director is calculated

Effective linear shear modulus

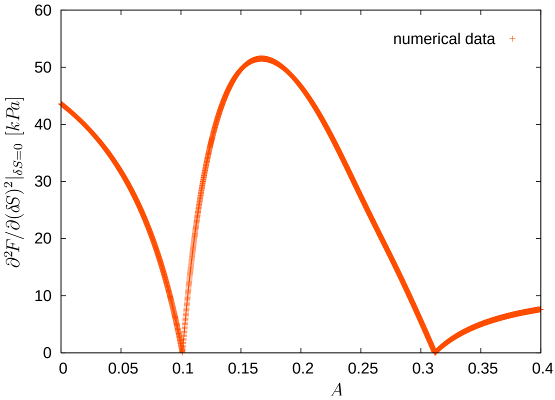

Fig.6: Effective shear modulus $\partial^2 F/\partial(\delta S)^2|_{\delta S=0}$ as a function of the prestretching amplitude A. Here, the system is prestretched in a direction perfectly perpendicular to the initial director orientation $\hat{\boldsymbol{n}}_0$. The zeroes of the effective shear modulus at the beginning and end of the plateau denote diverging fluctuations.

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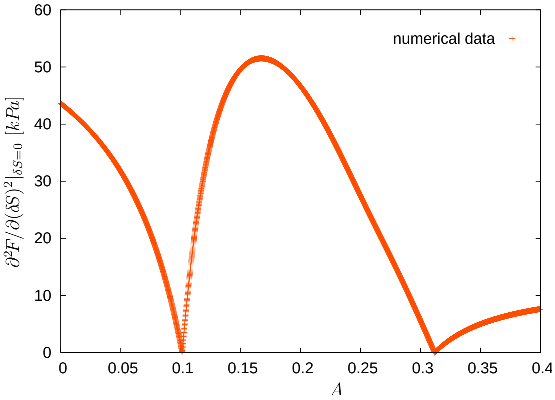

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Director reorientability

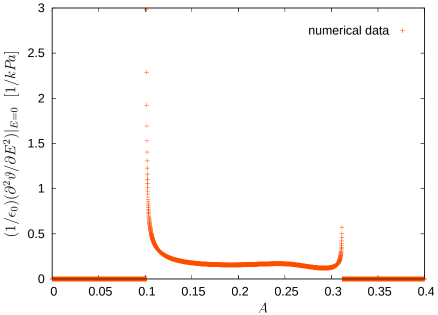

Fig.7: Reorientability $\partial^2\vartheta/\partial E^2|_{E=0}$ as a function of the prestretching amplitude A, where the divergencies take place at the beginning and end of the plateau ($\boldsymbol{E} \perp \hat{\boldsymbol{n}}_0$)

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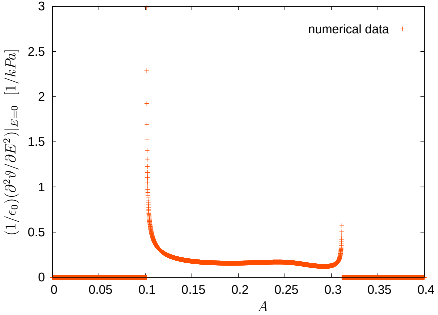

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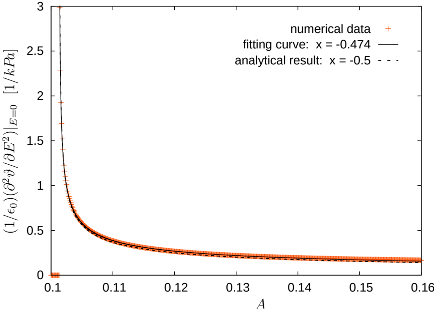

Fig.8: Same theoretical data fitted in the region $\vartheta \gtrsim 0$ by a curve $\propto (A - A_c)^x$ with $x \approx -1/2$, thus clearly indicating a soft mode behavior in mean field description

Oblique Pre-Strain

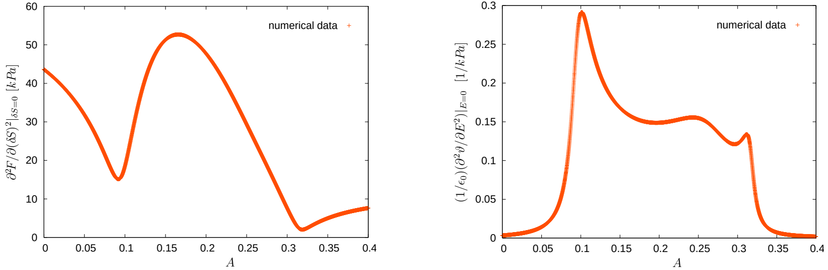

Fig.9: Effective shear modulus $\partial^2 F/\partial(\delta S)^2|_{\delta S=0}$ (left) and reorientability $\partial^2\vartheta/\partial E^2|_{E=0}$ (right) as a function of the prestretching amplitude A. Here, the initial director orientation $\hat{\boldsymbol{n}}_0$ slightly deviates from the perfectly perpendicular orientation by an angle of 0.01 rad (0.57°).

imperfect bifurcation: no divergent fluctuations[2]

[2] A. Petelin and M. Čopič, *Phys. Rev. Lett.* **103**, 077801 (2009); and presentations at the *European Conference on Liquid Crystals*, Colmar, April 2009

Remarks

the fluctuations at the bifurcation do not diverge (the effective linear modulus remains non-zero)

- for an oblique prestretch
- due to boundary induced director inhomogeneities (necking)
- due to macroscopic material inhomogeneities
- if the fluctuations are treated nonlinearly

there is no bifurcation (no diverging fluctuations)

- in the planar geometry (the small shear added is not in the director reorientation plane)
- for an external field in y direction (perpendicular to the director reorientation plane)

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Semisoftness

- the general scenario – elastic plateau with vanishing effective linear modulus at its beginning and end – has also been described by other methods[3]
- often, it is connected to semi-softness, where a small parameter α describes the (small) deviation from ideal softness;[4]

  the plateau starts at $\lambda_1 \approx 1 + \alpha$ and the slope of the plateau is $3\mu\alpha$ (cf. Chaps. 7.4 and 7.5 of Ref. 4)
- however, the smallness of $A_c \approx 0.1$ (corresponding to $\alpha \approx 0.1$) is not a necessary condition for the soft mode behavior at the beginning and end of the plateau

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

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High Plateau

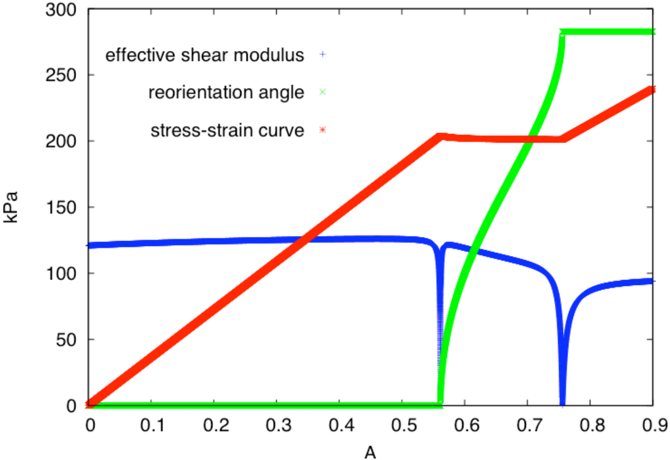

Fig.10: In this case the plateau starts at a rather large pre-strain $A_c \approx 0.56$ (or $\lambda \approx 2.3$) and ends at $A \approx 0.76$ (or $\lambda \approx 4.2$)
– the scenario is the same as for very small A_c.

Summary

- the scenario of an elastic plateau at finite perpendicular stretching, with a vanishing effective linear modulus and a divergent director reorientability at its beginning and end (soft mode), is a genuine manifestation of an instability due to nonlinear relative rotations;
- it requires two independent preferred directions and discriminates these systems from simple anisotropic solids;
- there is no need for a small parameter nor for the closeness to an ideal soft-elastic behavior (Nambu-Goldstone or almost Nambu-Goldstone mode)

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Lagrange description

Comparing the initial dimension l_0 to the actual dimension (in the direction of the external force F_{ext}), the ratio

$$\lambda = \frac{l}{l_0} \tag{1}$$

is taken as a measure of the induced strain.
Sometimes, the so called true strain $\epsilon = \ln(\lambda)$ is taken as a variable.
Stresses are recorded either as true stress

$$\sigma_{ext} = \frac{F_{ext}}{l_x l_y} \tag{2}$$

or as nominal stress

$$\sigma_{ext}^{N} = \frac{F_{ext}}{l_{x,0} l_{y,0}}, \tag{3}$$

From the experimental point of view the initial dimension l_0 is considered to be constant and the current sample dimension l is changed.

Eulerian description

In the hydrodynamic (Eulerian) picture the current dimension of the sample l is considered to be constant, and what changes is the initial dimension l_0. For the displacement field $u_z = Az$ (or $l_z - l_{z,0} = Al_z$) the strain is

$$\lambda = \frac{1}{1-A}. \tag{4}$$

and the stresses are

$$\sigma_{ext} \equiv \frac{F_{ext}}{l_x l_y} = \frac{dF}{dA}, \tag{5}$$

$$\sigma^N_{ext} \equiv \frac{F_{ext}}{l_{x,0} l_{y,0}} = (1-A)\frac{dF}{dA}. \tag{6}$$

Here, the expressions on the left of Eqs. (5) and (6) are given as functions of λ, the expressions on the right as functions of A.

The connection between both follows from Eq. (4).

Constrained equilibrium

As an ansatz we use for the displacement fields

$$u_z = Az + Sx, \quad (7)$$
$$u_x = Bx \quad (8)$$
$$u_y = Cy. \quad (9)$$

and for the director orientation

$$\hat{\boldsymbol{n}} = (\cos\vartheta, 0, \sin\vartheta) \quad (10)$$

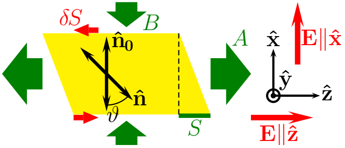
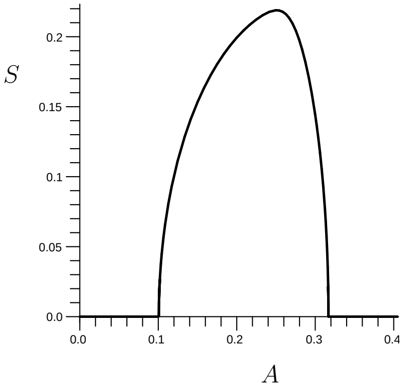


Fig.5: homeotropic geometry

For a given initial orientation ϑ_0 and external stretch A, the values $S(A)$, $B(A)$, and $\vartheta(A)$ follow from the equilibrium conditions $\partial F/\partial S = 0$, $\partial F/\partial B = 0$, and $\partial F/\partial\vartheta = 0$ (the compression C follows from the incompressibility condition).

Shear and compression



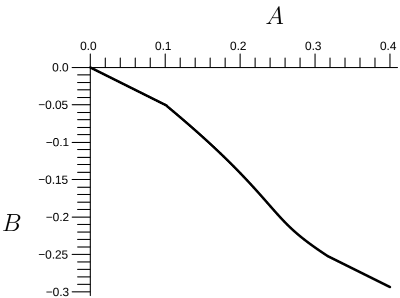


Fig.11: The shear $S(A)$ and the compression $B(A)$ as a function of the pre-strain amplitude A.

Effective linear modulus

For each given pre-strain A a small shear δS is added,

$$u_z = Az + [S(A) + \delta S]x \tag{11}$$

and the free energy (including δS) is again minimized w.r.t. ϑ and then calculated to lowest order in δS

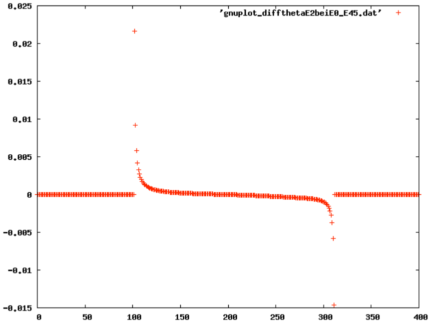
$$F_A = \frac{1}{2} c_{eff}(A)(\delta S)^2 + \mathcal{O}(\delta S)^3 \tag{12}$$

The effective linear modulus $c_{eff}(A) = \partial^2 F_A / \partial(\delta S)^2 \mid_{\delta S=0}$ is shown in Figs. 6 and 9.

Orientability

For given external field $\boldsymbol{E}$ in the x-z plane and a given pre-strain A, the system of constrained equilibrium conditions $\partial F/\partial\vartheta = \partial F/\partial B = \partial F/\partial S = 0$ is solved, resulting in $F = F(\boldsymbol{E}, A)$.
For each value of A, there is $\partial\vartheta/\partial E|_{E=0} = 0$ due to stability reasons.

Therefore, we take the second derivative $\partial^2\vartheta/\partial E^2|_{E=0}$ as a measure for the reorientability of the director $\hat{\boldsymbol{n}}$ in an external field for a given stretching amplitude A. In Fig.7 this reorientability is shown for $\boldsymbol{E} \perp \hat{\boldsymbol{n}}_0$, while for $\boldsymbol{E} \parallel \hat{\boldsymbol{n}}_0$ the sign of it is reversed. The case $E_x = E_z$ is shown on the right



Divergence of the orientability

- the coefficients of the amplitude equation close to the threshold ($E^2 = E^2_{x,z}$)

$$0 = \vartheta\left\{a(A_c - A) + g\vartheta^2\right\} + \mathcal{O}(\vartheta^5). \tag{13}$$

  generally acquire field contributions $\sim E^2$ due to the dielectric anisotropy energy
- in the limit $E \to 0$ one can write, e.g. $A_c(E) = A_c(1 + \zeta_A E^2)$
- for $A \gtrsim A_c$ this leads to the field dependence of the tilt angle

$$\vartheta = \sqrt{\tfrac{a}{g(E)}(A - A_c(E))} \approx \sqrt{\tfrac{a}{g}(A - A_c)}\left(1 + \zeta E^2 + \frac{\zeta_A}{2}\frac{A_c}{A_c - A}E^2\right) \tag{14}$$

- and to the orientability

$$\partial^2\vartheta/\partial E^2|_{E=0} \sim (A - A_c)^{-1/2} + \mathcal{O}((A - A_c)^{1/2})$$

  which is observed in Fig.8.