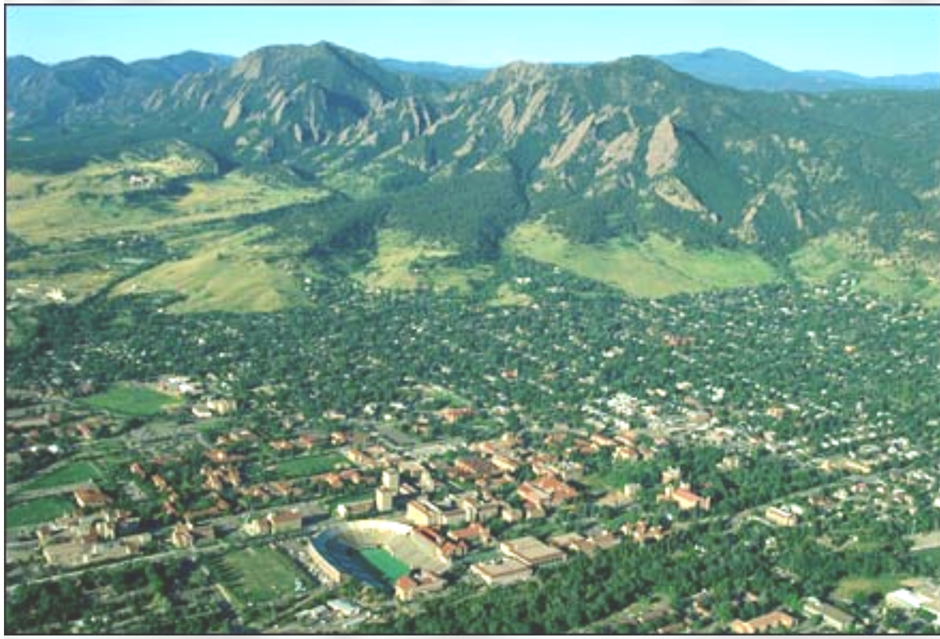
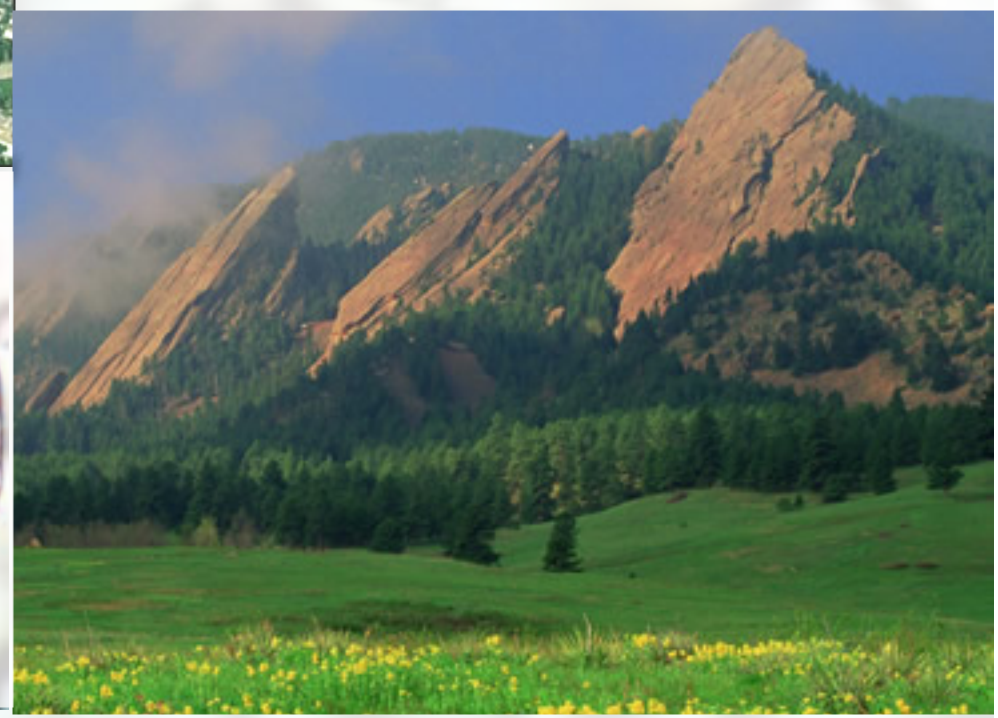
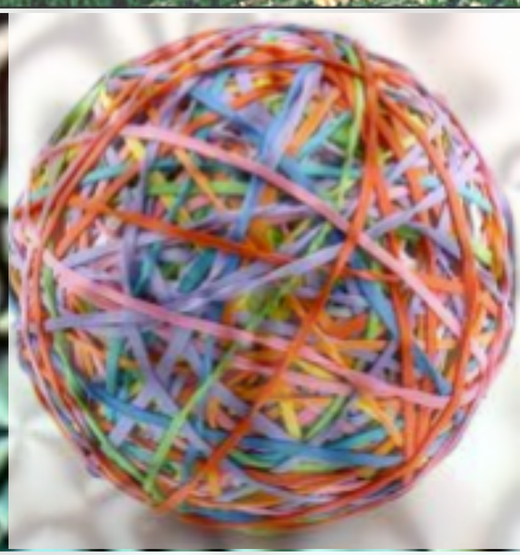
Strange elasticity of liquid-crystal rubber



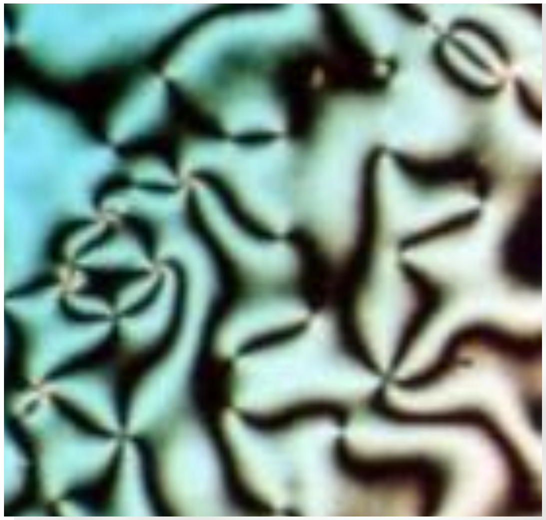
University of Colorado
Boulder





$ ***NSF-MRSEC, Materials Theory, Packard Foundation***

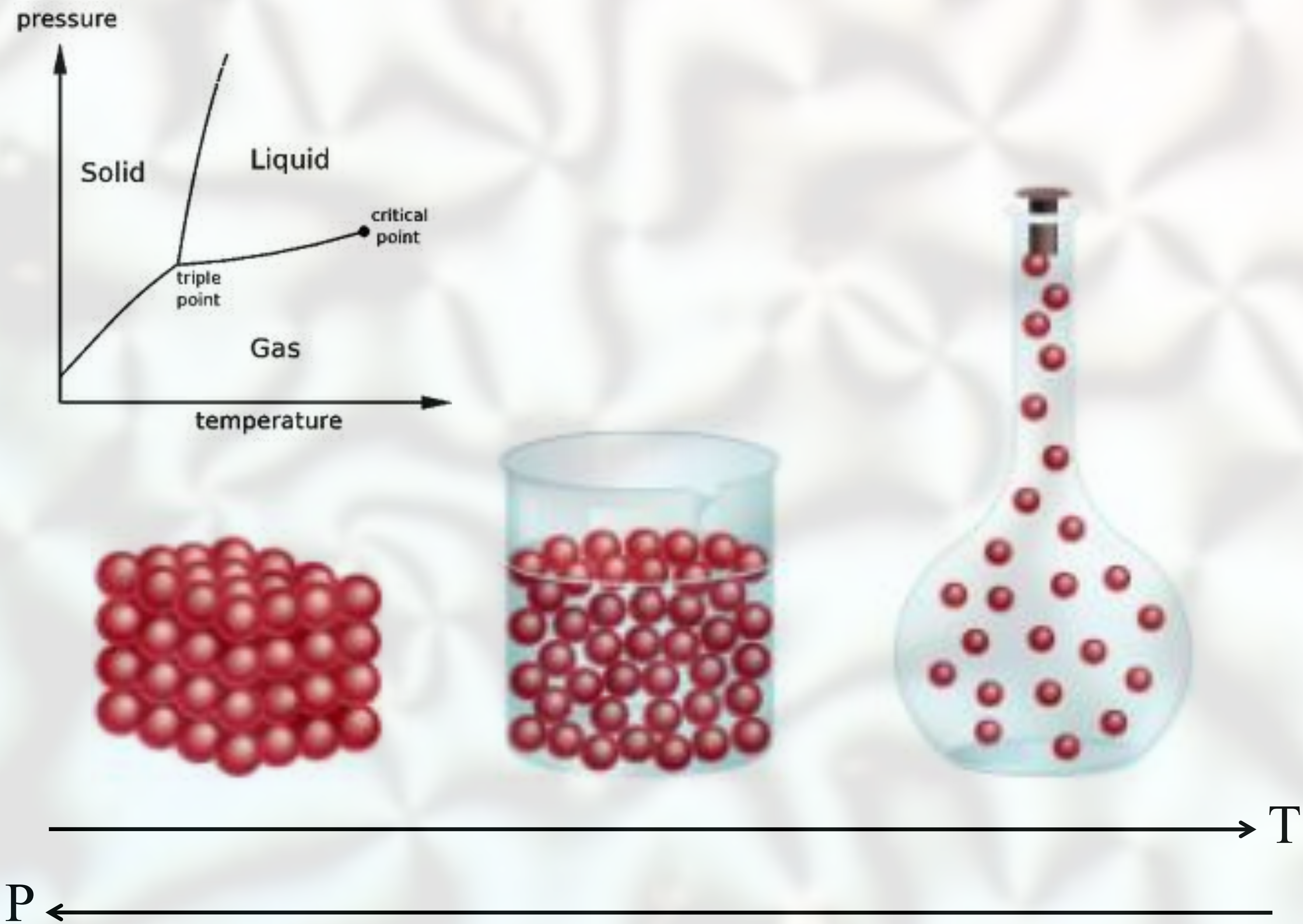
UMass, April 2011



Outline

- Diversity of phases in nature
- Liquid-crystals
- Rubber
- Liquid-crystal elastomers
- Phenomenology
- Theory (with ***Xing, Lubensky, Mukhopadhyay***)
- Challenges and future directions

"White lies" about phases of condensed matter

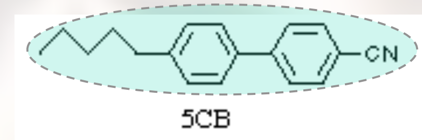


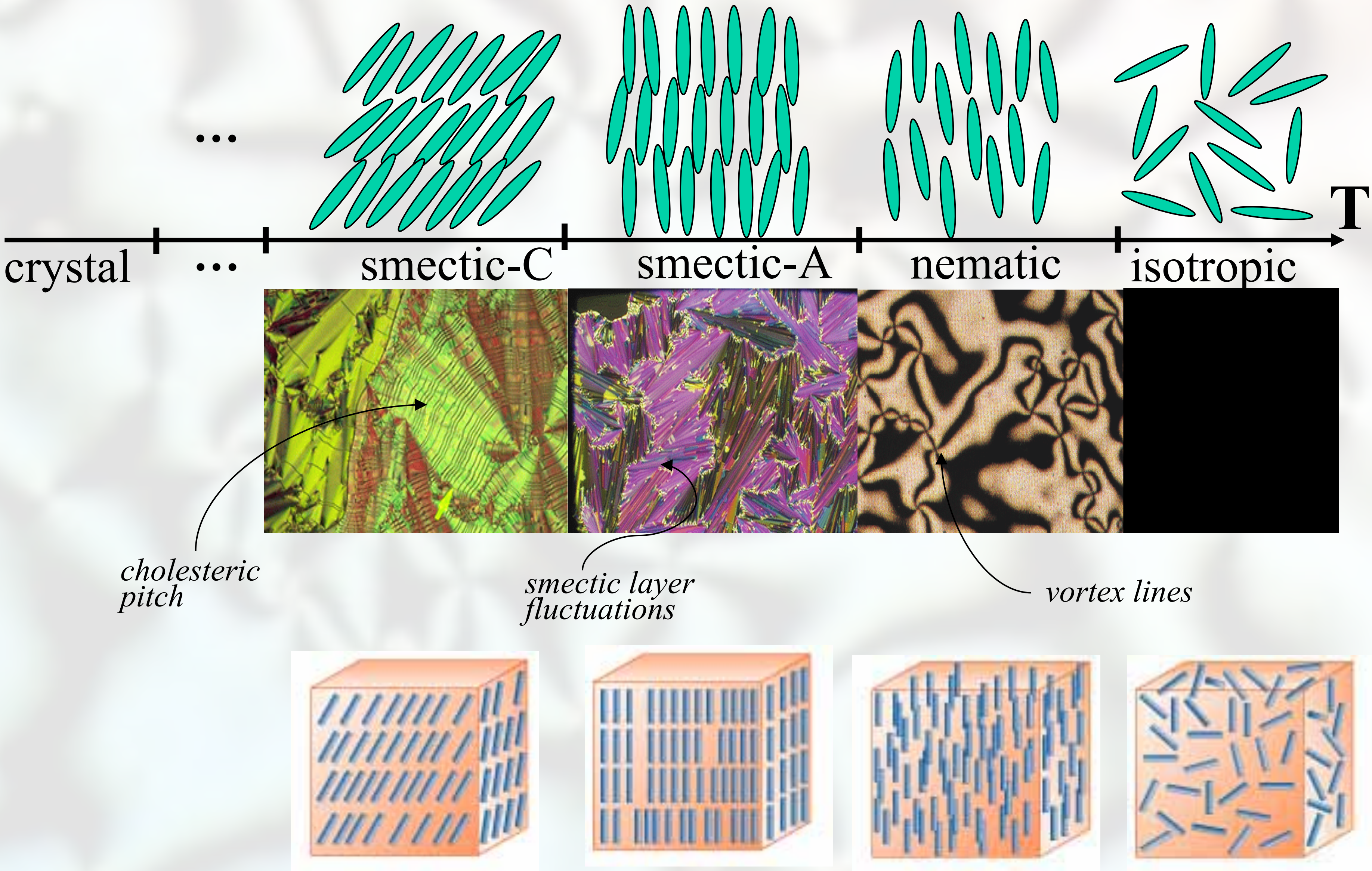
States of condensed matter in nature

- magnets, superconductors, superfluids, liquid crystals, rubber, colloids, glasses, conductors, insulators,...

Reinitzer 1886
(nematic, Blue phase)

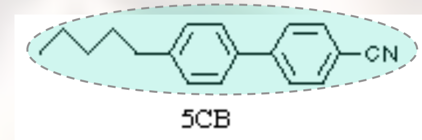
Liquid Crystals

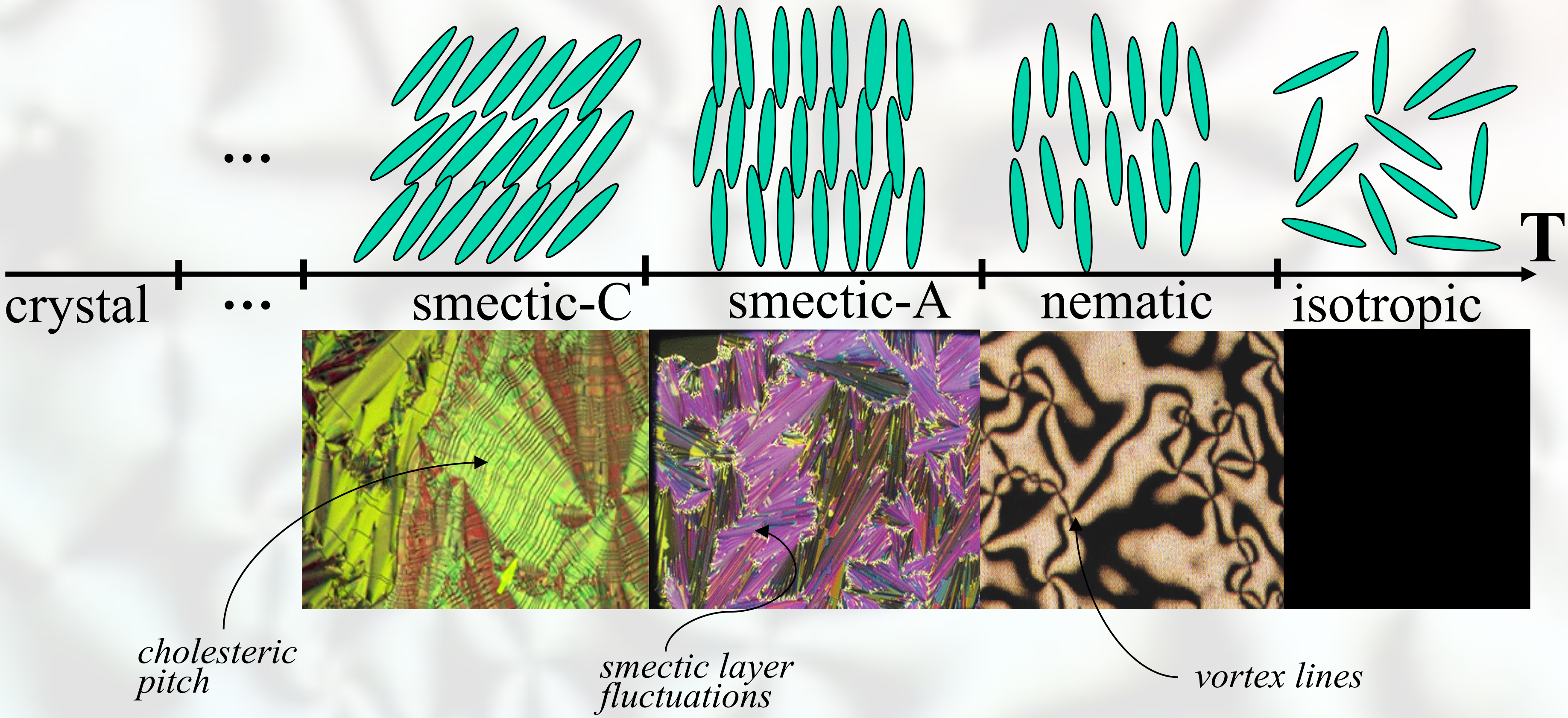




Reinitzer 1886
(nematic, Blue phase)

Liquid Crystals





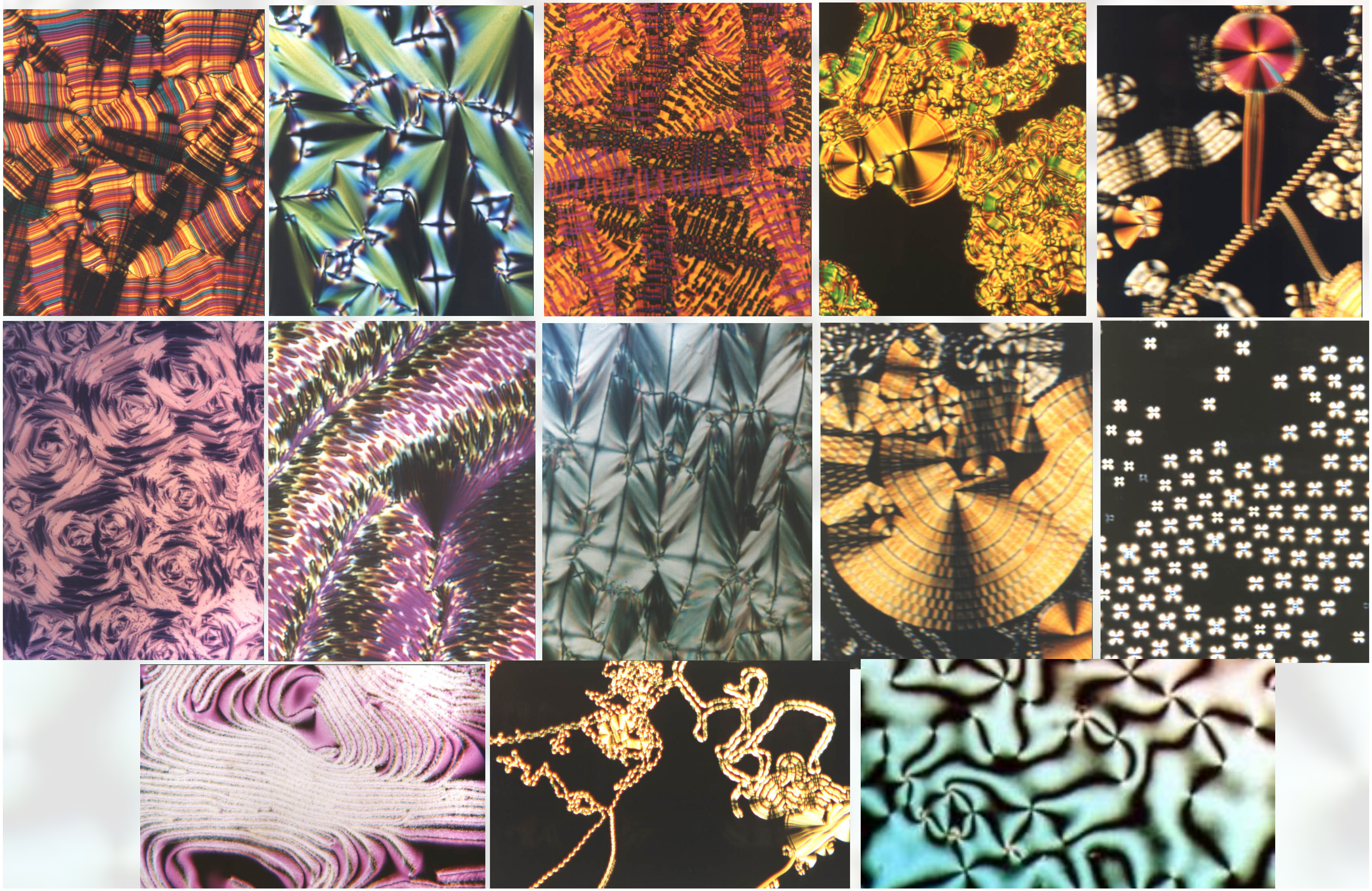
- **Rich basic physics** – *critical phenomena, hydrodynamics, coarsening, topological defects, `toy` cosmology,…*

- **Important applications** – *displays, switches, actuators, electronic ink, artificial muscle,…*

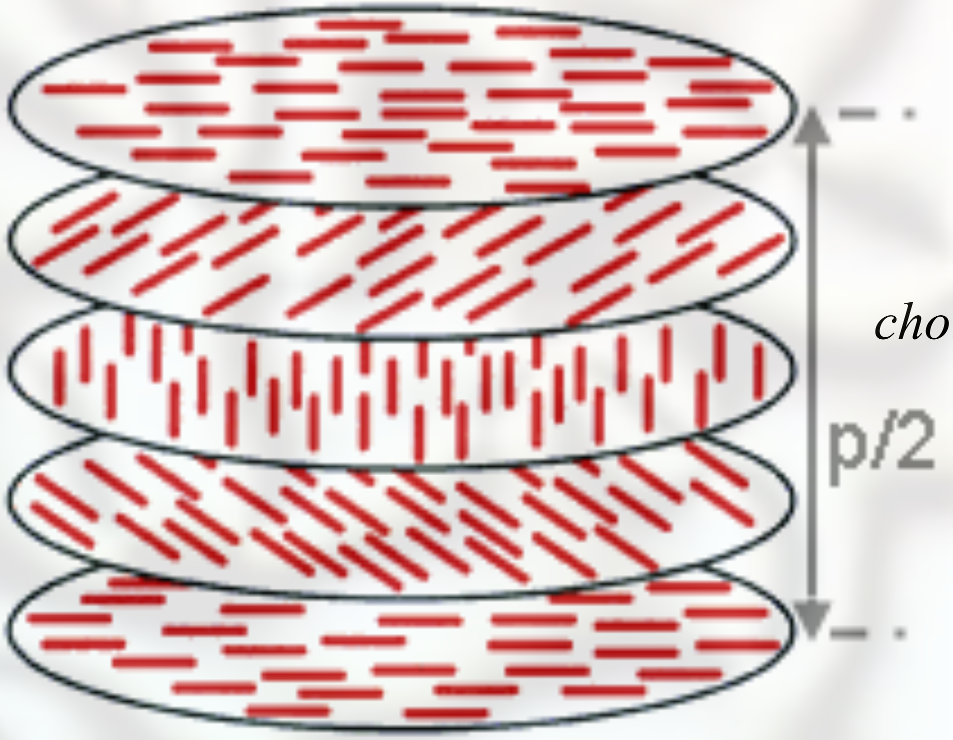
Liquid-crystal beauty

N. Clark

"Liquid crystals are beautiful and mysterious; I am fond of them for both reasons." – P.-G. De Gennes

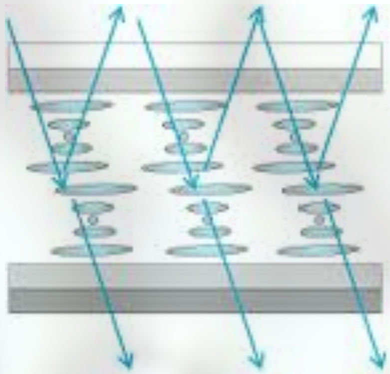


Chiral liquid crystals: cholesterics



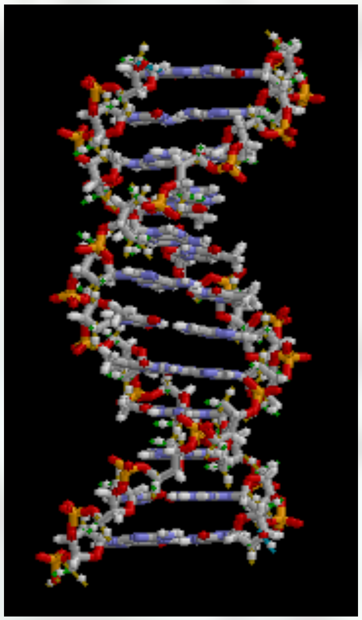
cholesteric pitch

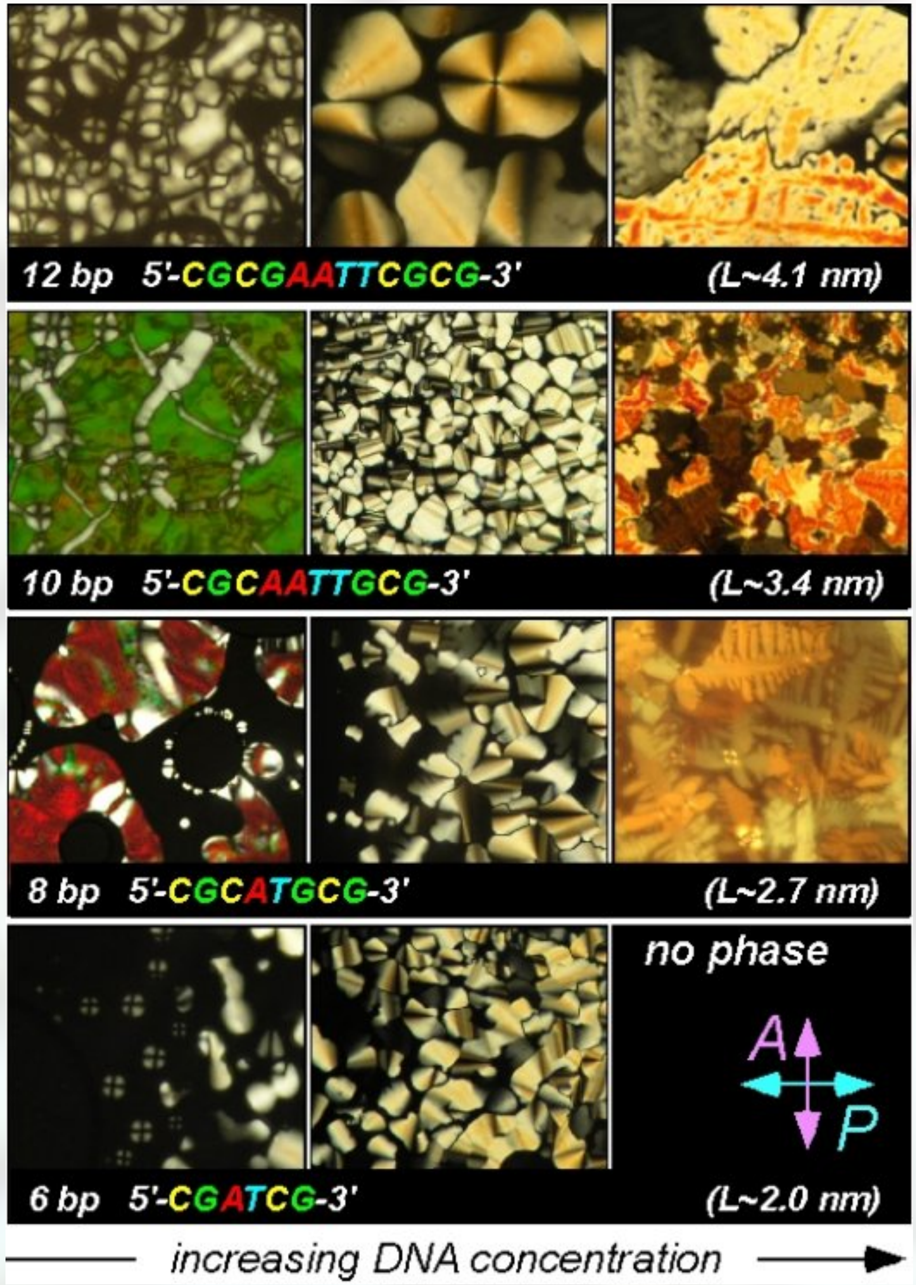
- color selective Bragg reflection from cholesteric planes



- temperature tunable pitch → wavelength

Bio-polymer liquid crystals: DNA





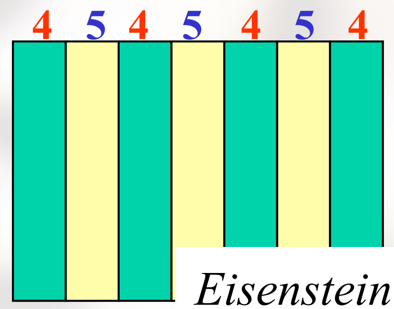
M. Nakata,
N. Clark, et al

Nonconventional liquid crystals

- electron liquid in semiconductors under strong B field

    half-filled high Landau levels

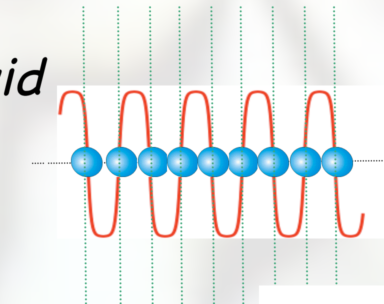
$\nu=4+\frac{1}{2}$



Eisenstein

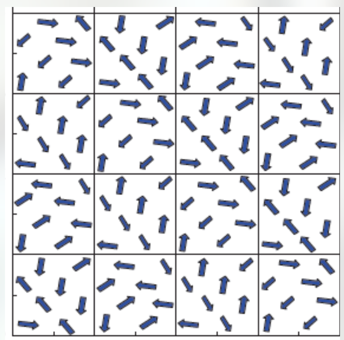
- two-species degenerate atomic Fermi gases:

    Fulde-Ferrell-Larkin-Ovchinnikov superconductor/superfluid



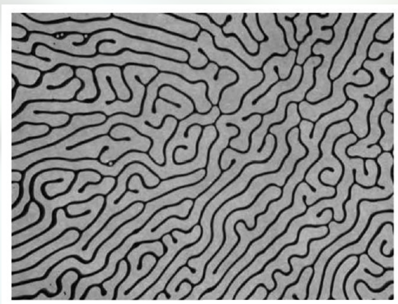
L.R.

- frustrated magnets



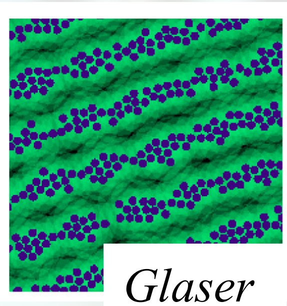
Balents

- ferrofluids



Dorsey

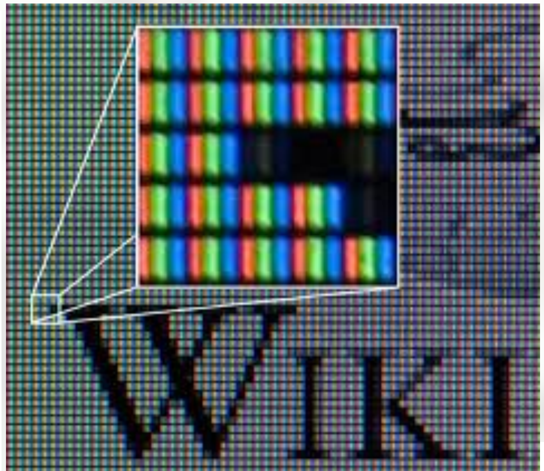
- colloids

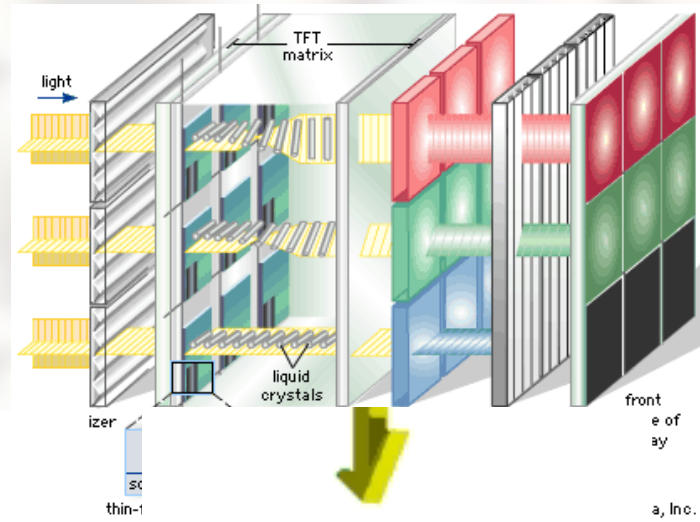


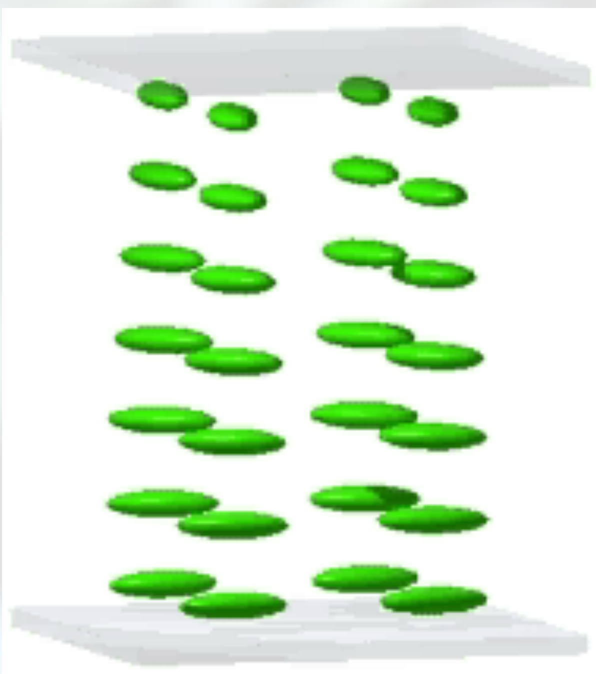
Glaser

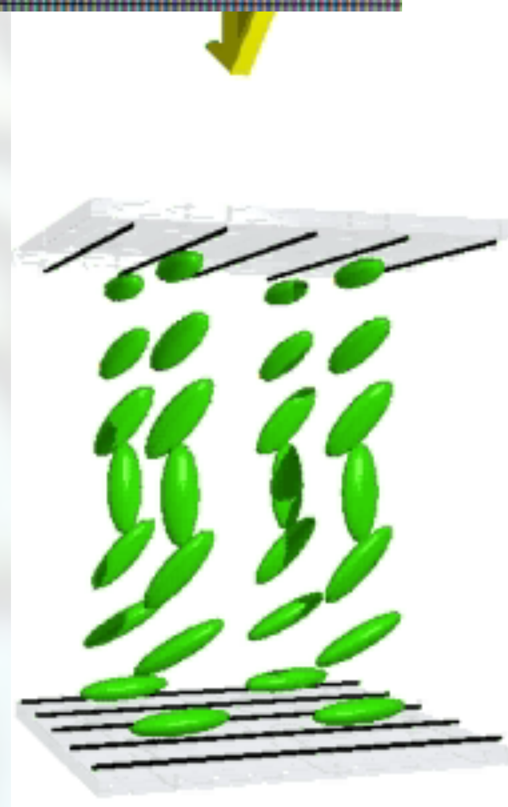
...anything orientationally or spatially partially ordered (layered)

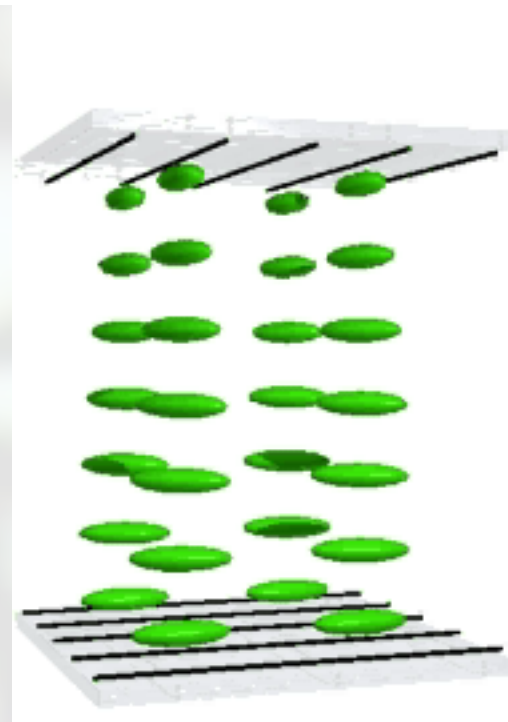
Liquid-crystal display applications



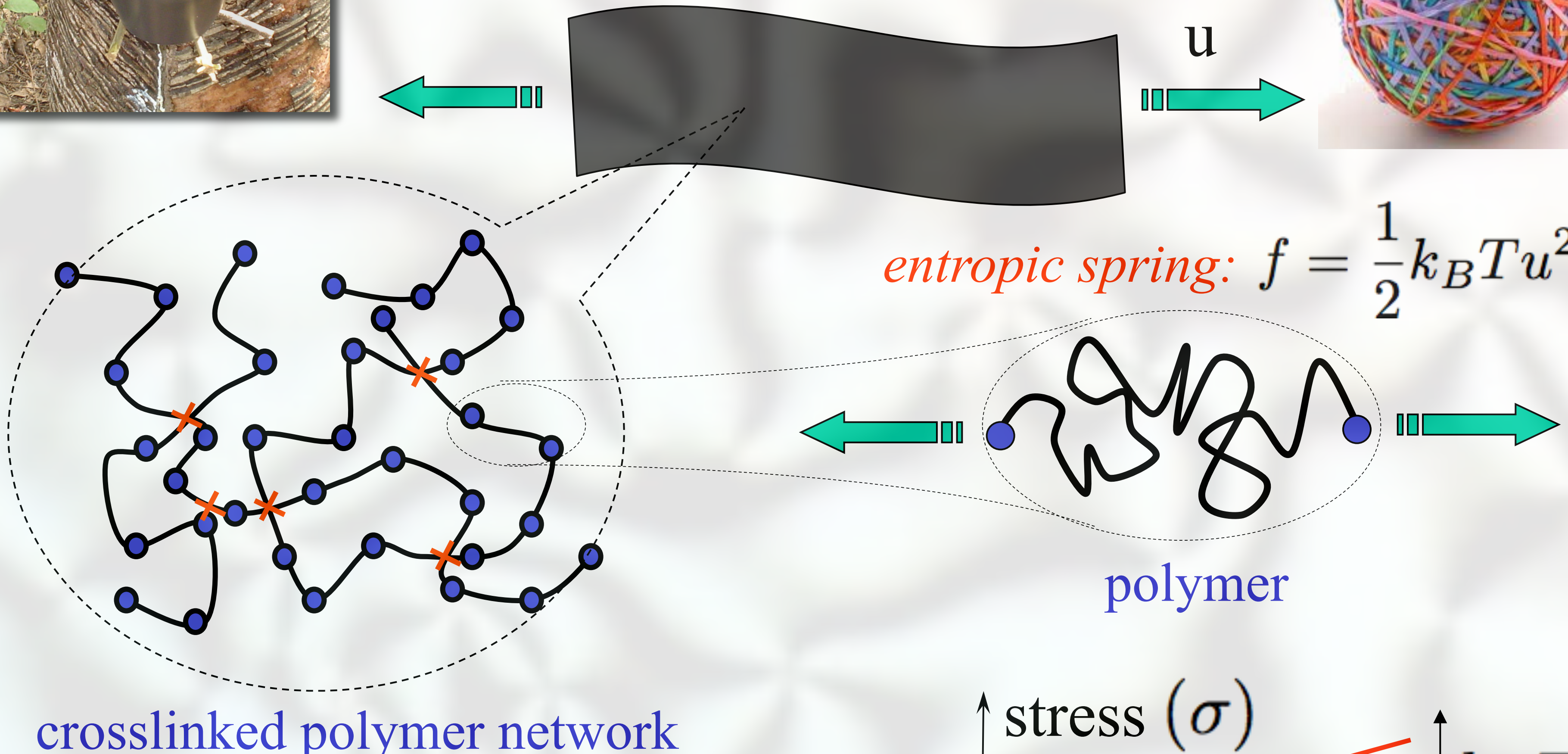








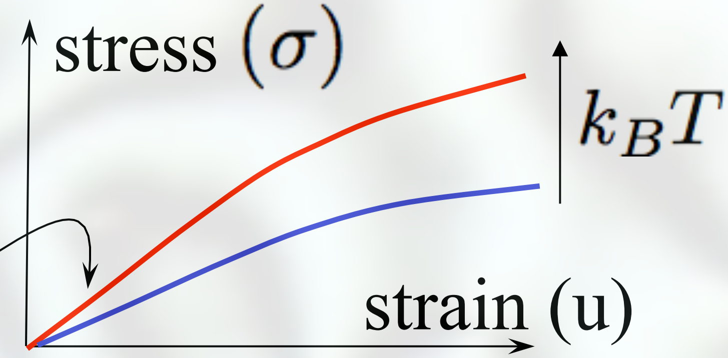
Conventional Rubber



Entropic spring

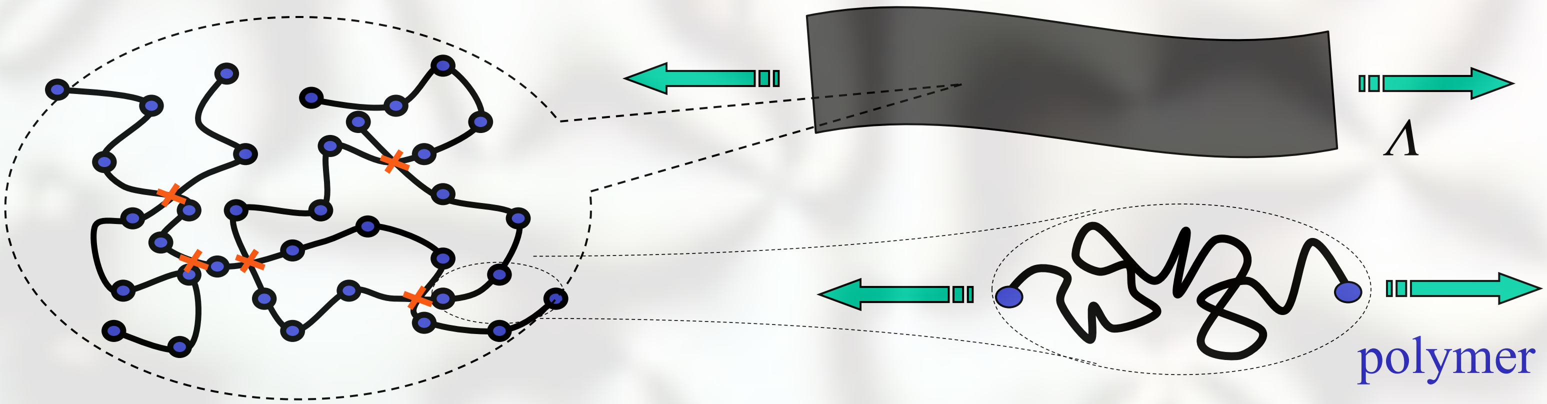
→ *stiffens/shrinks on heating*

but still obeys Hooke's law



Classical theory of rubber elasticity

Kuhn, Wall, Flory, Treloar (1940's)



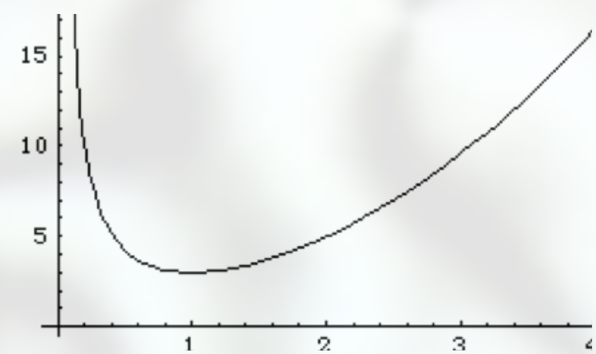
• crosslinked polymer network:

- *affine deformation:* $r = \lambda x$
- *incompressible*
- *fixed, non-fluctuating crosslinks*
- *"phantom" (noninteracting, nonentangled) polymers)*
- $\delta f = \frac{1}{2}\frac{k_B T}{\xi^3} Tr \Lambda^T \Lambda = \frac{\mu_0}{2}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)$
- *uniaxial:* $\lambda_x = \lambda$, $\lambda_y = \lambda_z = \lambda^{-1/2}$

• single chain: $P \sim e^{-R^2/R_0^2}$

$$\delta F = k_B T \log P \sim k_B T (R/R_0)^2$$

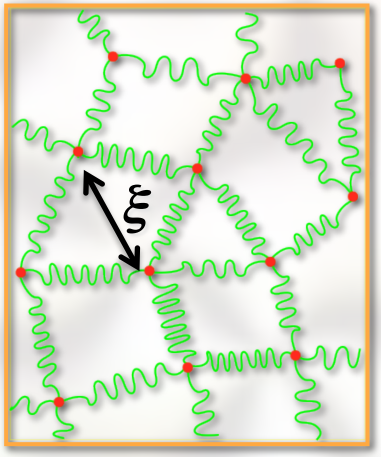
Hookean entropic spring



$$\boxed{\delta f = \frac{\mu_0}{2}(\lambda^2 + \frac{2}{\lambda})}$$

What's missing? k_BT fluctuations beyond ξ

Xing, Goldbart, L.R., (PRL'06)



- want to include long scale polymer network fluctuations

- finite compressibility is crucial: $\vec{\nabla} \cdot \vec{u} = 0$

- integrate over phonons u(x):

$$f(\lambda) = f_{class.}(\lambda) + \mu_1 \left[\frac{\tanh^{-1}\sqrt{1-\lambda^{-3}}}{\sqrt{1-\lambda^{-3}}} - \ln \lambda \right]$$

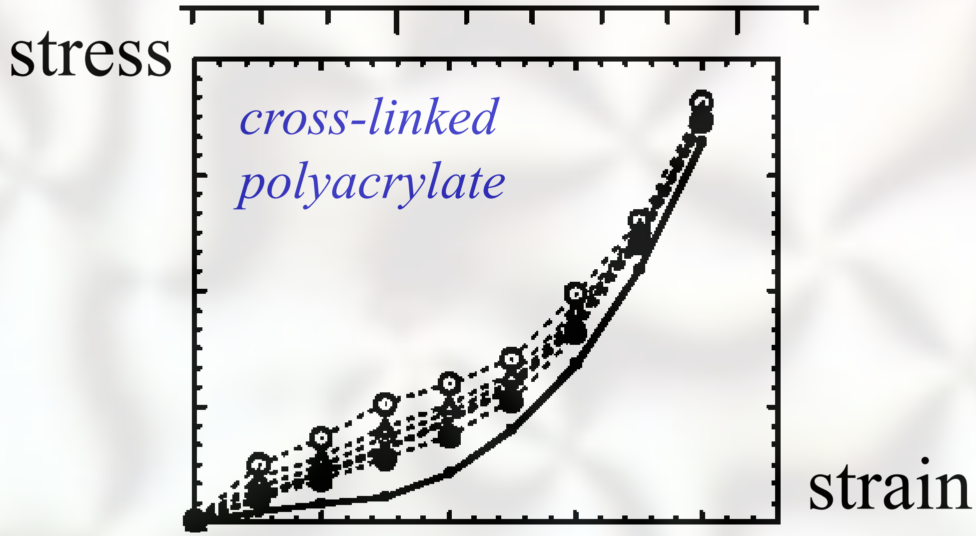
- anisotropic, L-dependent phonon correlations

$$\mu_1 \approx \mu_0 \approx k_B T/\xi^3$$

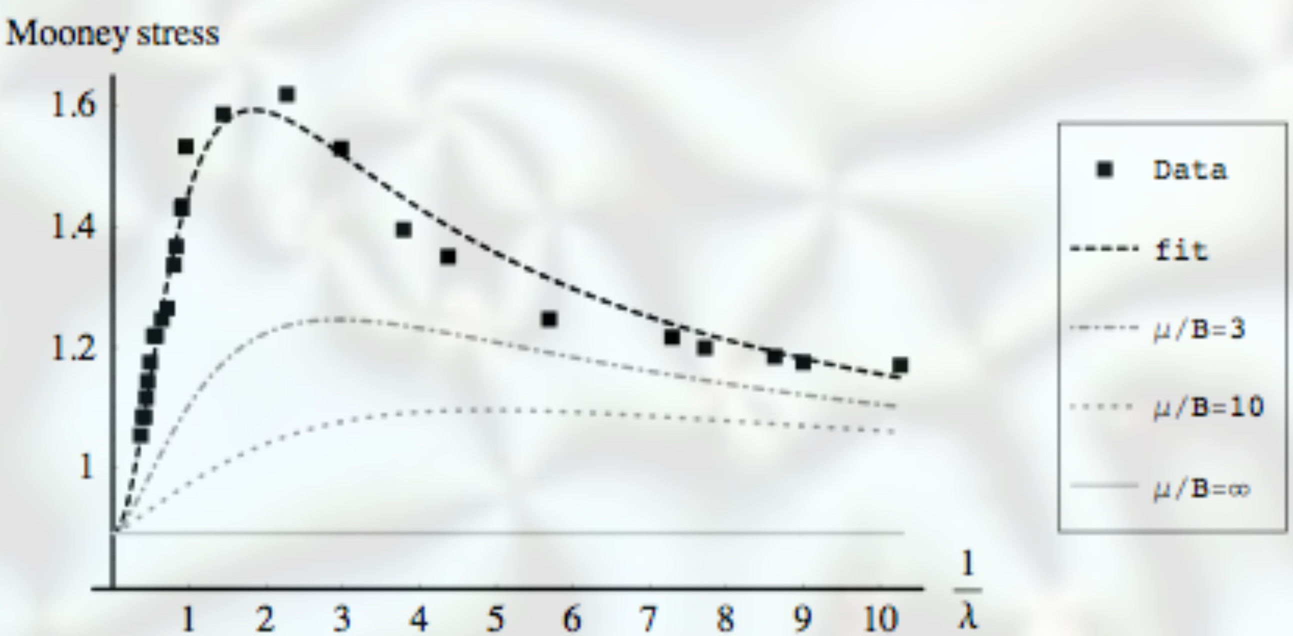
$$\langle u_i(q) u_j(-q) \rangle \approx \frac{k_B T/\mu_0}{\vec{q} \cdot \Lambda \Lambda^T \cdot \vec{q}} P^T_{ij}(q)$$

Mooney-Rivlin stress-strain relation

Xing, Goldbart, L.R., (PRL'06)



$$\sigma_{MR} = \frac{\partial f/\partial\lambda}{\lambda - \lambda^{-2}}$$



Xu and Mark (1990)
Rubber Chem. Technol.
Data provided by
M. Rubinstein

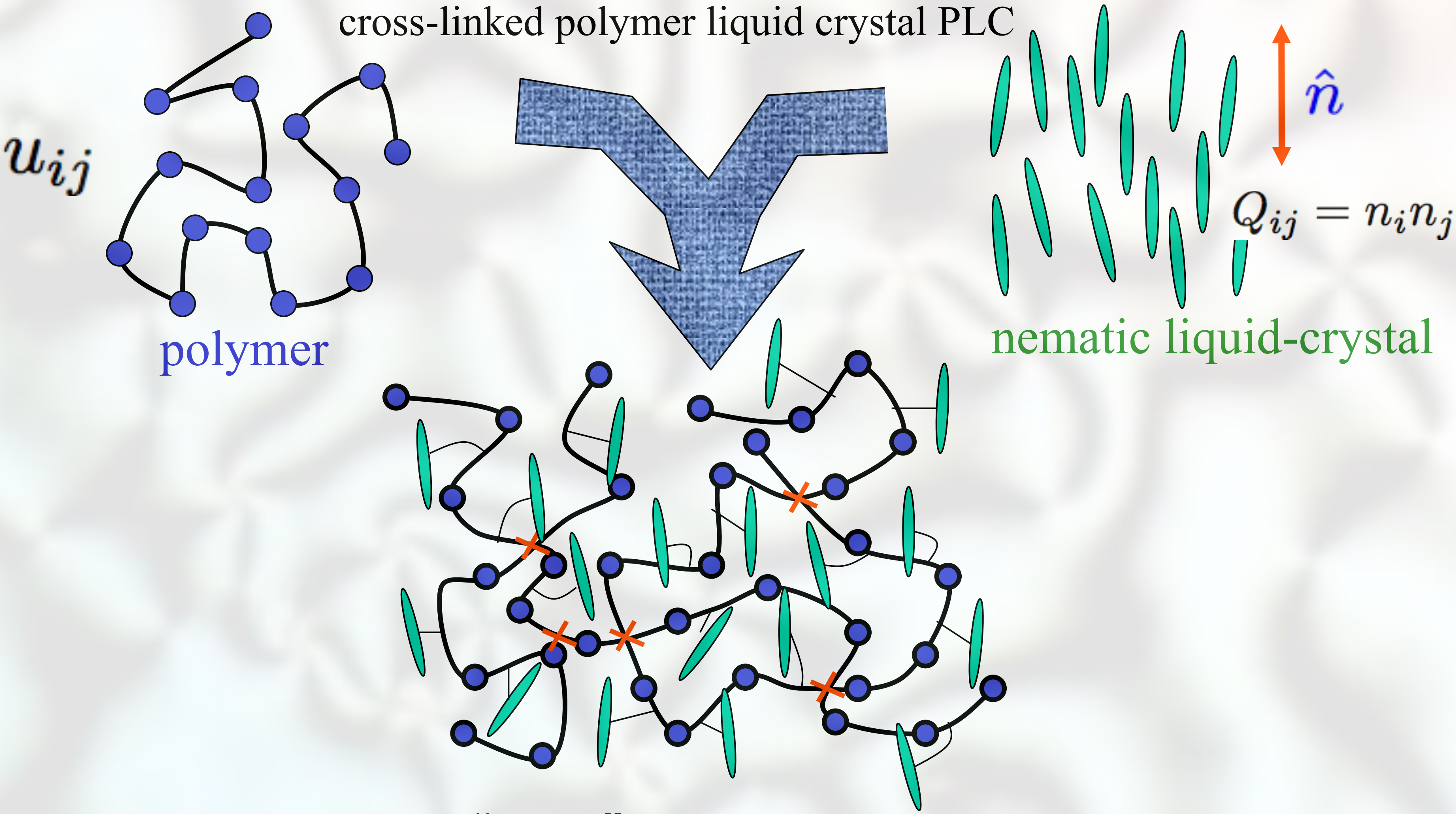
Open questions

- physical picture of the peak?
- universality of the stress-strain relation?
- beyond harmonic phonon approximation?
- frozen heterogeneity and nonaffine distortion?
- biaxial and shear distortions?
- effects of entanglement, non-ideal chain?
- key experiments?

Nematic Elastomer

Terentjev
Finkelmann
Ratna

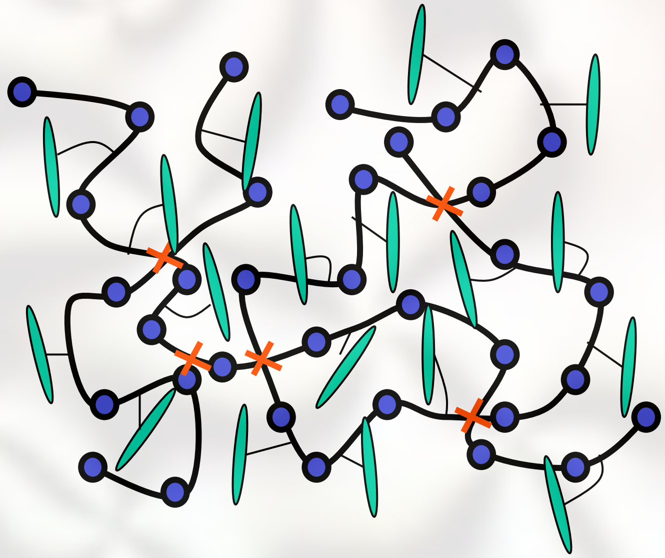
cross-linked polymer liquid crystal PLC



"Solid" Liquid-Crystal

exhibits most conventional liquid-crystal phases (I, N, Sm-A, Sm-C,…)

Questions of interest



• **Effects of polymer matrix on liquid crystal order**

cf. liquid crystals in random matrix (e.g., aerogel)

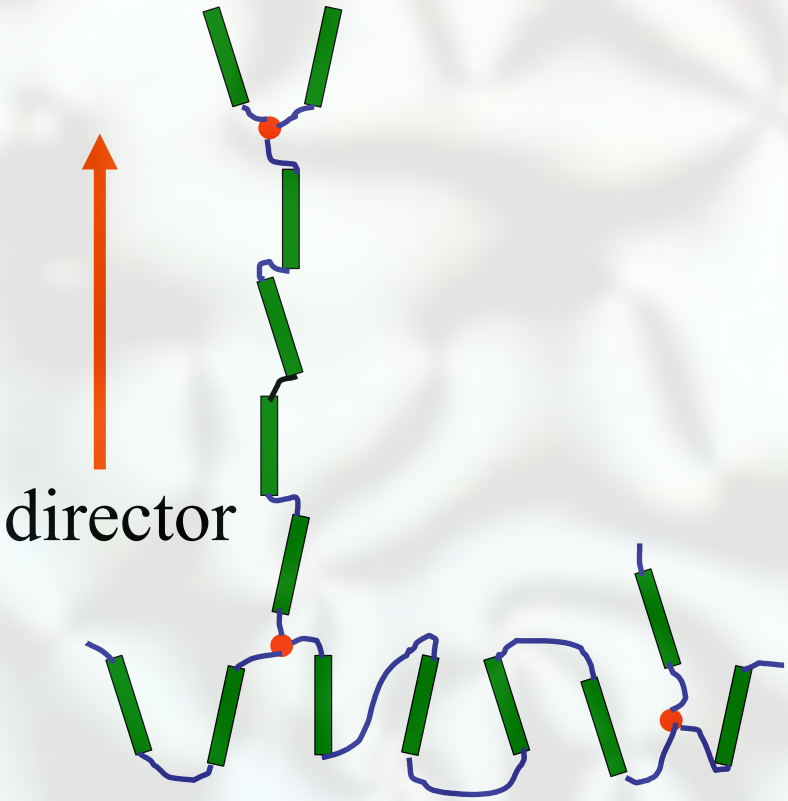
(L.R.+Toner; Feldman; Gingras; Clark, Garland, Birgeneau)

• **Effect of liquid crystal order on rubber (gel) elasticity**

(de Gennes, Golubovic+Lubensky, Warner, Terentjev)

Must understand both questions self-consistently to understand liquid crystal elastomers and gels

Main-chain nematic elastomer



If orientational order increases

expansion

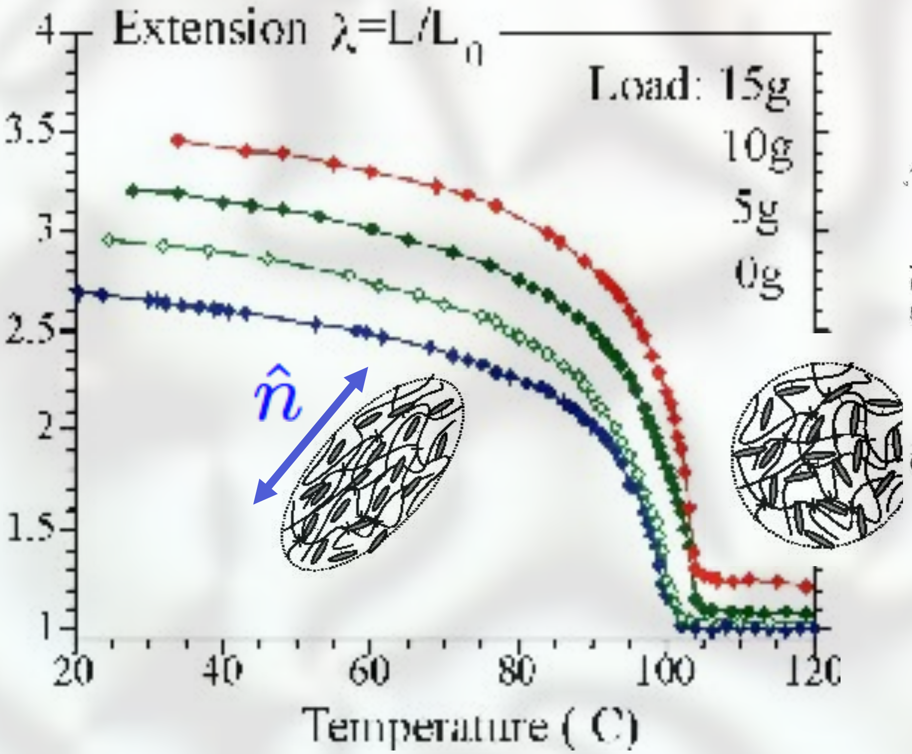
contraction

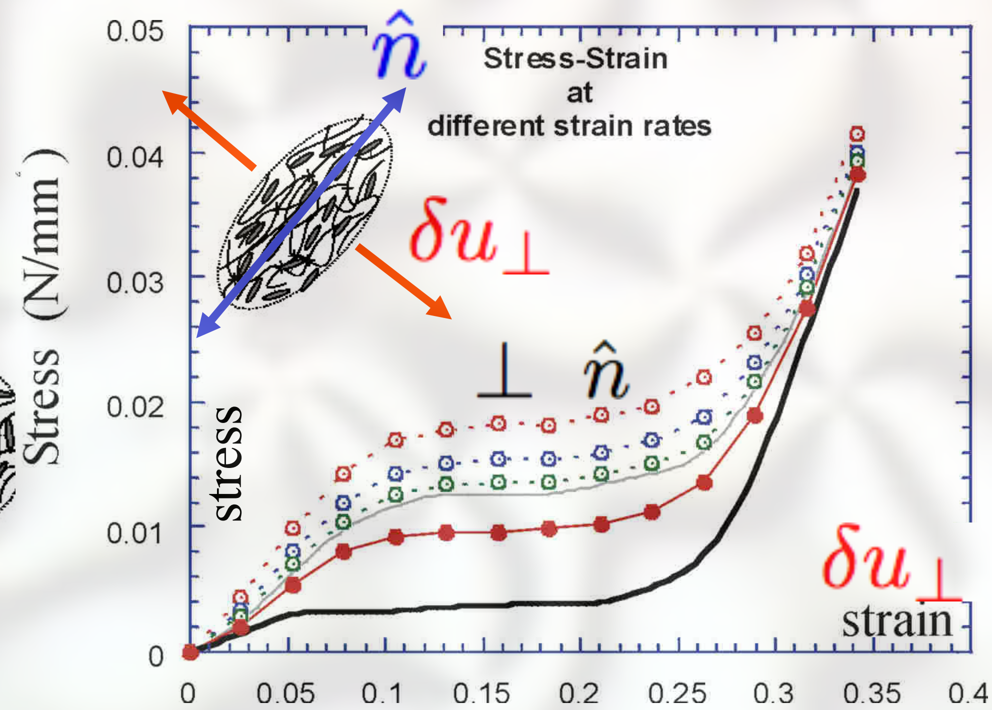
If orientational order decreases

contraction

expansion

Thermal response and stress-strain relation



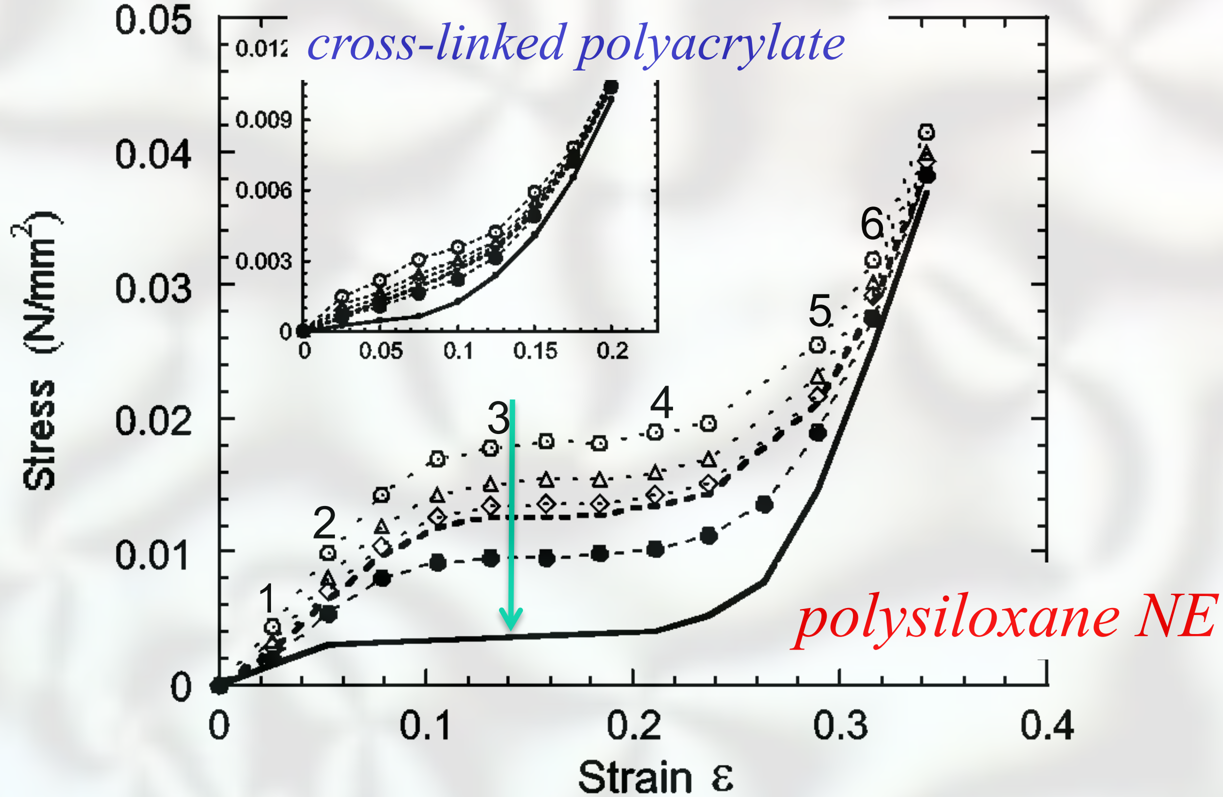


Properties: • *spontaneous distortion (~ 400%) at T_{IN}, thermoelastic*
• *"soft" elasticity*
• *giant electrostriction*

Applications: • *plastic displays*
• *switches*
• *actuators*
• *artificial muscle*

Terentjev, et al

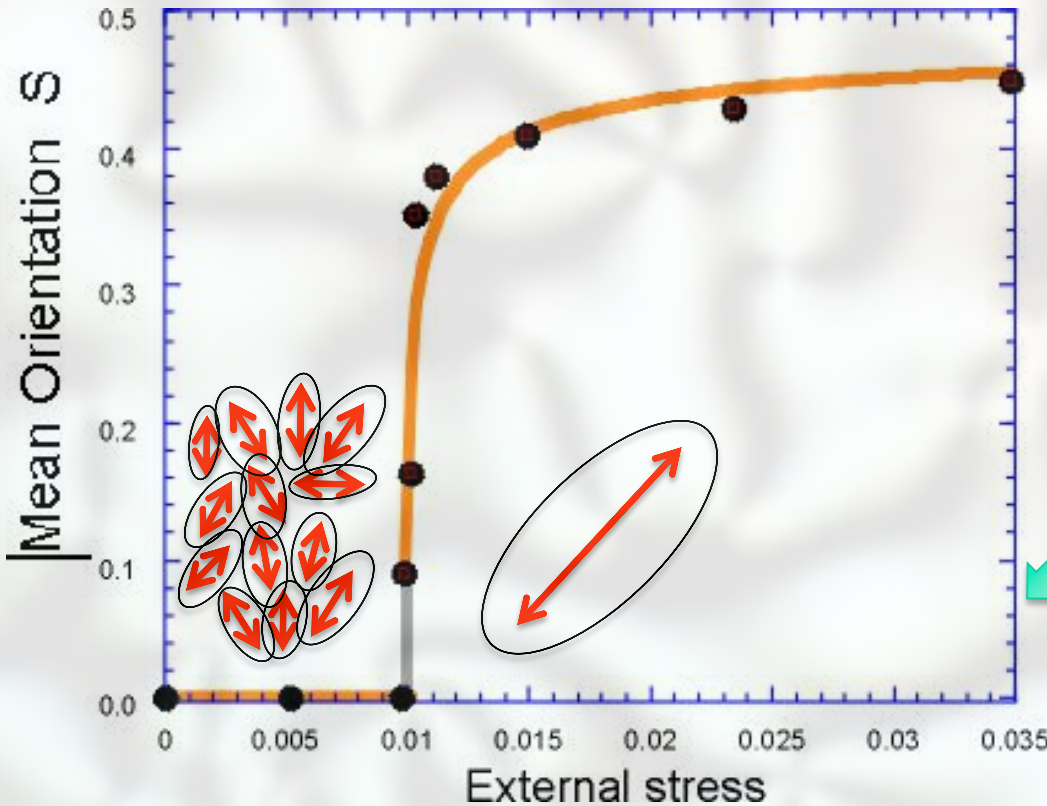
Stress-strain relation (relaxation)

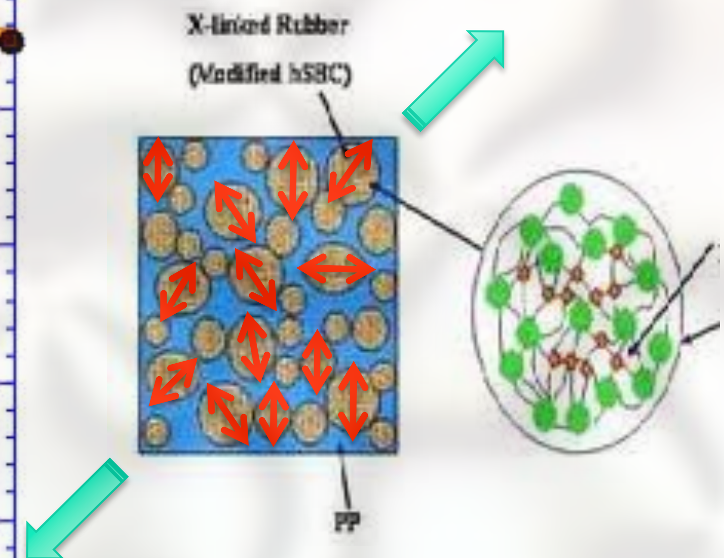


- extended stress plateau contrasting ordinary rubber
- small threshold

Clarke, Terentjev, PRL '98

Glass-like threshold stress response

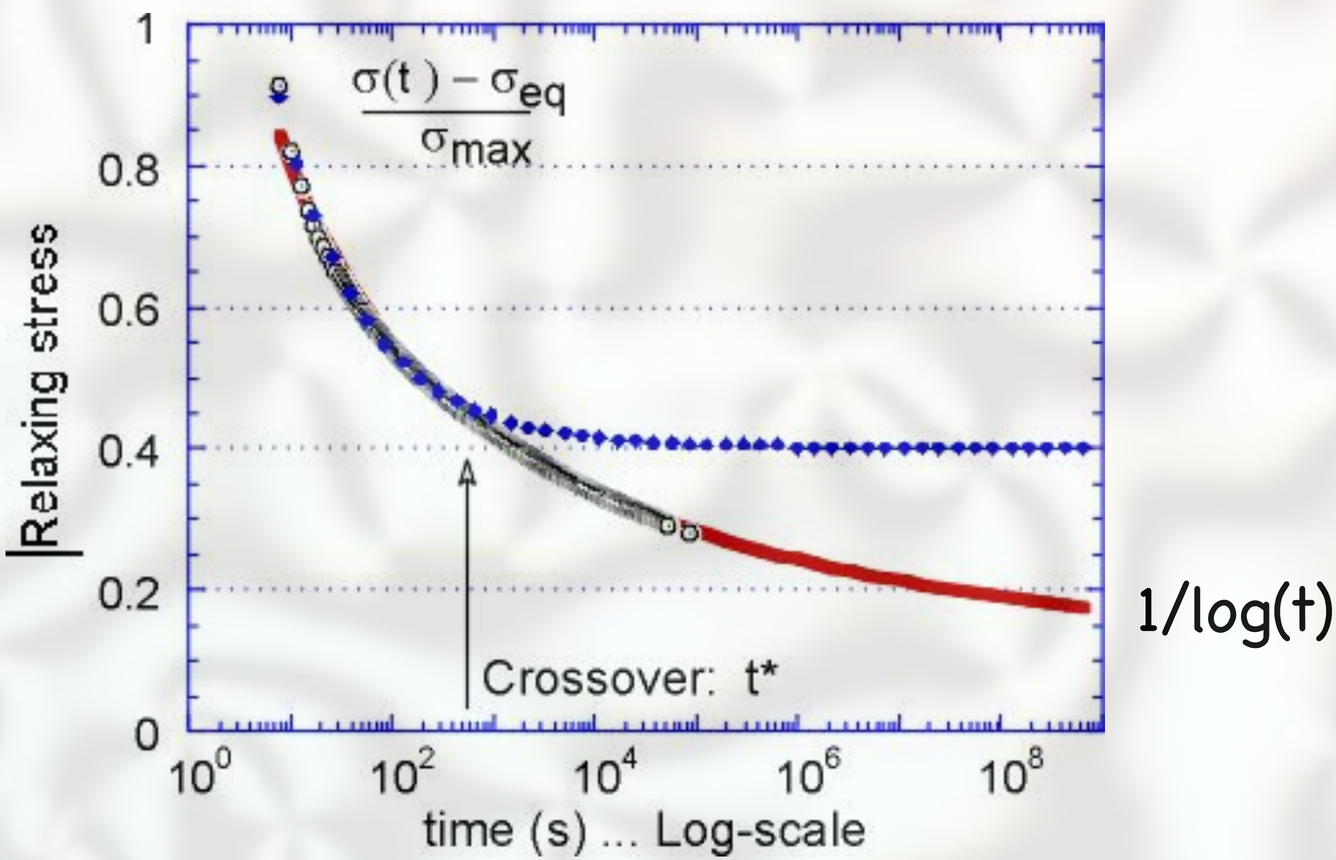




- polydomain – monodomain transition
- threshold set by domain size and heterogeneity

Clarke, Terentjev, PRL ‘98

Glass-like slow stress relaxation

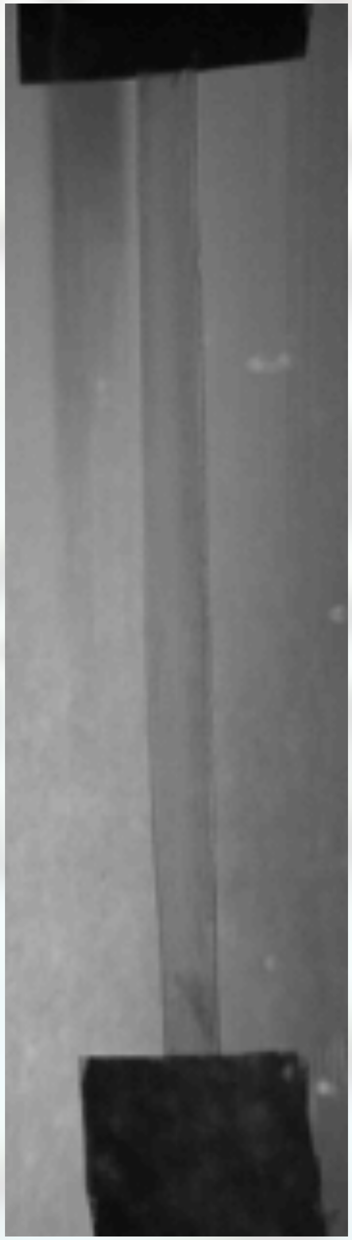


- crossover from $1/t^{1/2}$ to slow 1/log(t) stress relaxation reminiscent of glasses

Clarke, Terentjev, PRL '98

Nematic elastomer as heat engine

n



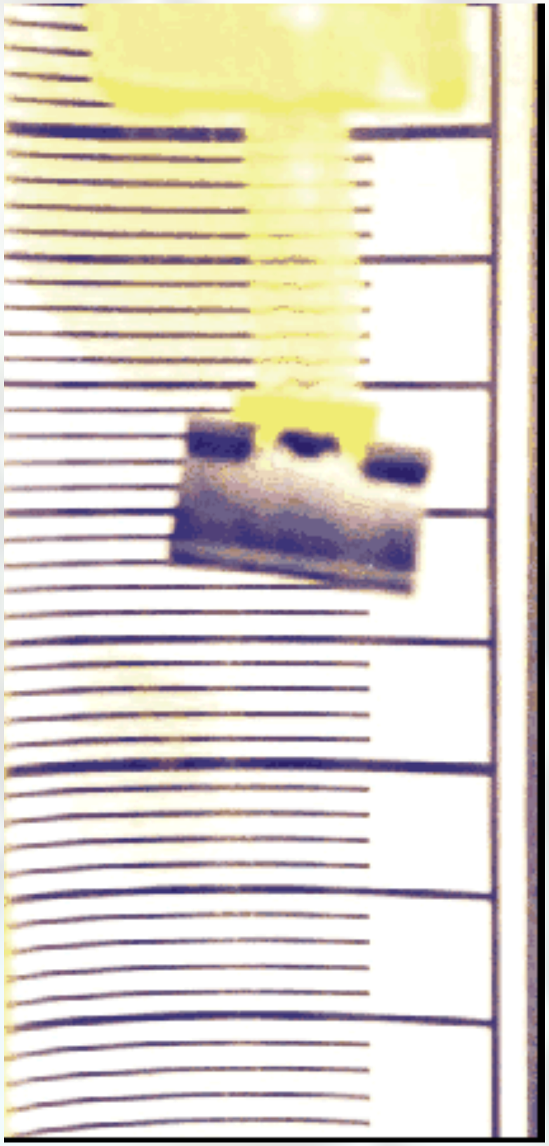
- monodomain nematic LCE
- 5cm x 5mm x 0.3mm
- lifts 30g wt. on heating, lowers it on cooling
- large strain (>400%)

(P. M-Palffy)

H. Finkelmann, Shahinpoor, et al

Nematic elastomer as heat engine

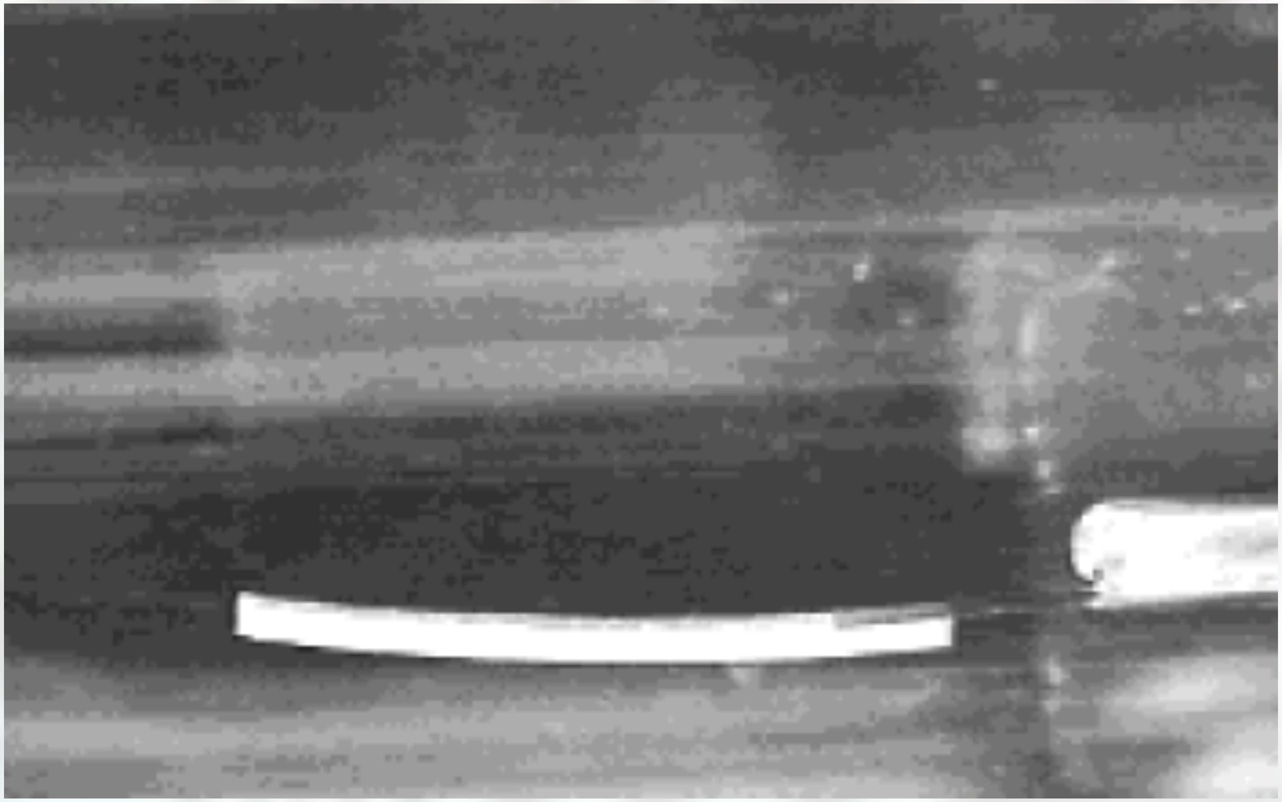
n



Terentjev, et al (Cambridge)

Ratna, et al (NRL)

Nematic elastomer as heat engine



n

Terentjev, et al

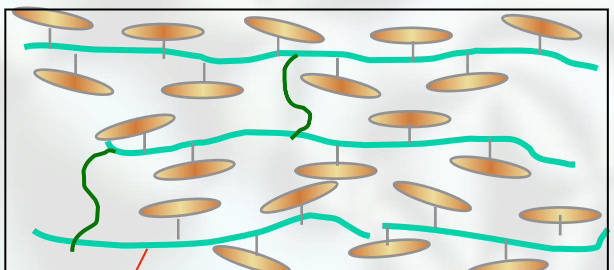
Liquid crystal elastomer as a muscle concept

Nematic liquid crystal phase

Order in liquid crystal units

Ordered backbone

Elongation



Polymer backbone Liquid crystal units

External stimulus

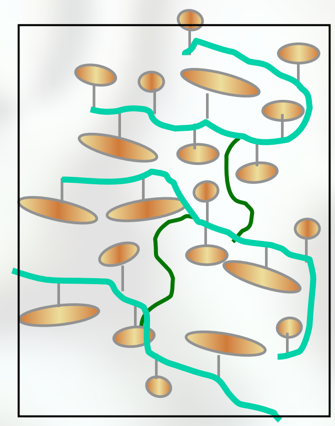
Temperature
Light
E-field

Isotropic phase

Disorder of liquid crystal units

Disordered backbone

Contraction



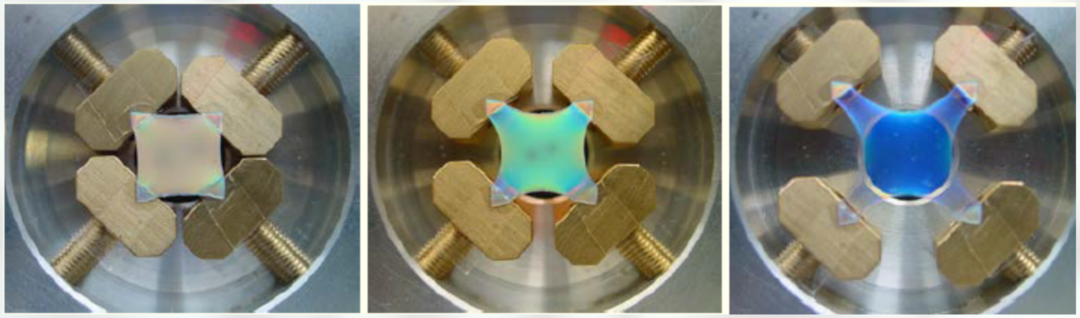
Memory effect:
- Reversible extension/contraction
- Director alignment

Ratna (NRL)

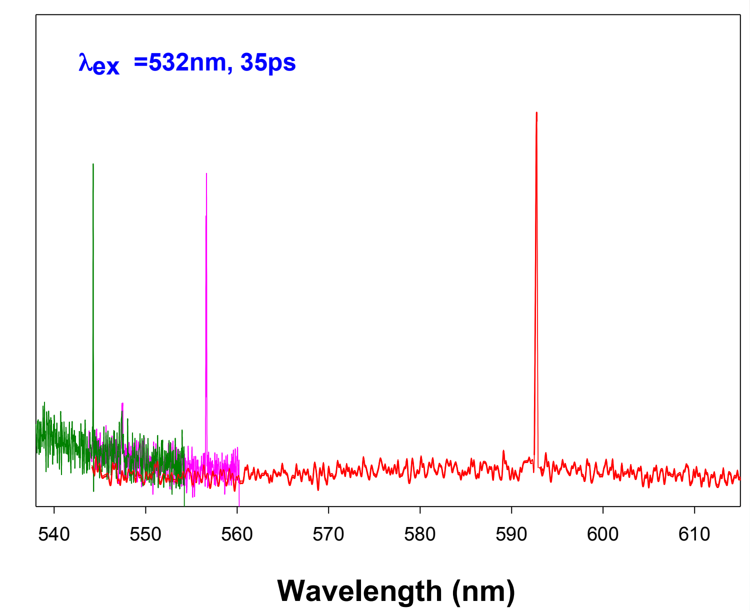
Sensors: strain changes optical properties

- changing sample shape changes Q and
  - magnetic permeability, dielectric permittivity
  - optical properties: cholesteric pitch

cholesteric elastomer



-mechanically tunable material



-mirrorless 'rubber' laser

H. Finkelmann, S-T. Kim, A. Munoz, P. Palffy-Muhoray and B. Taheri, Adv. Mat. ***13****, 1069 (2001)*

Mechanism of optomechanical effects in LCE

- optomechanical coupling:

light

↓

orientational order

↓

mechanical strain

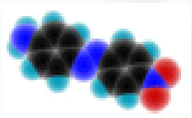
↓

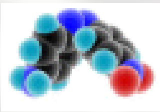
shape change

Mechanism of optomechanical effects in LCE

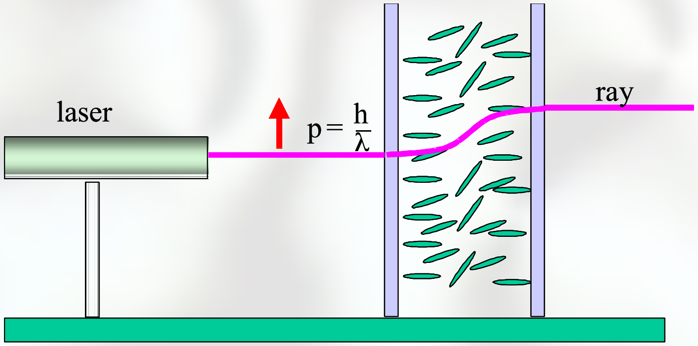
- optical field changes liquid crystal order via:
  - direct heating
    - absorption

  - disruption of order
    - photoisomerization

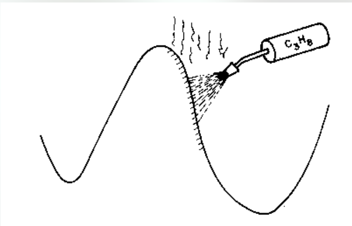




  - direct optical torque
    - angular momentum transfer from light

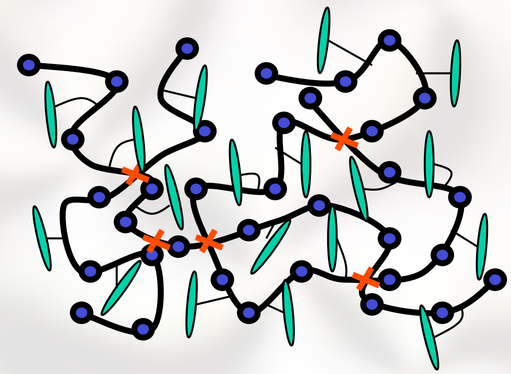


  - indirect optical torque
    - Landauer's blowtorch
    - orientational Brownian ratchet
      - no angular momentum transfer from light;
      - light drives molecular motor

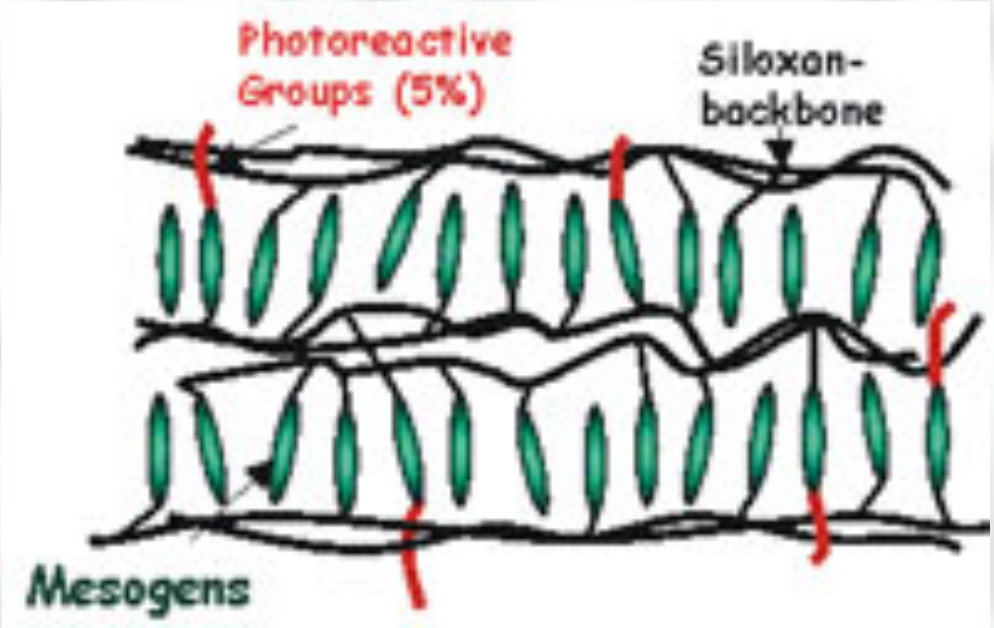


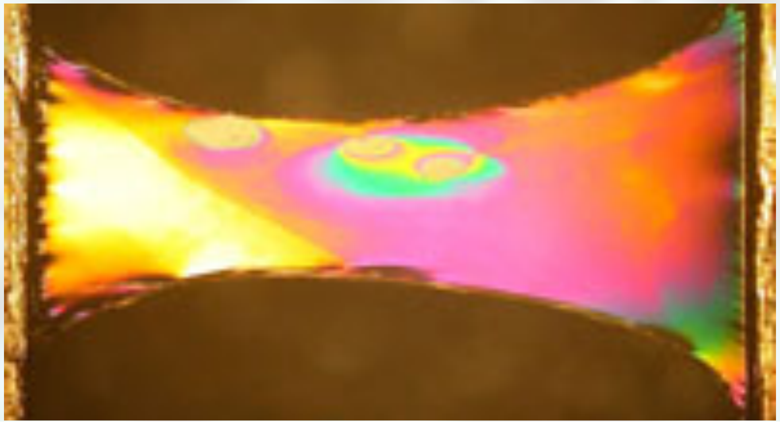
P. Palffy-Muhoray

Other liquid crystal elastomers



- has also been generalized to:
  - o smectic-A
  - o smectic-C
  - o biaxial nematic
  - o cholesterics
  - o nematic membranes

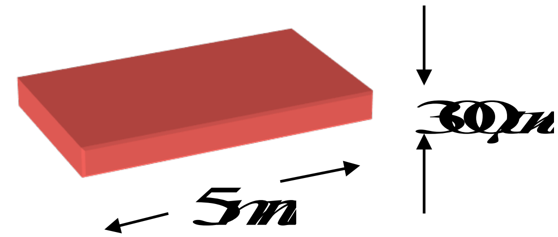


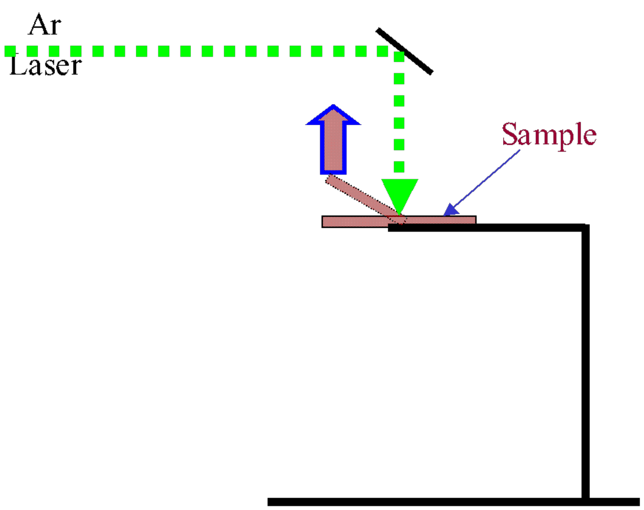


smectic elastomers:
W. Lehmann, et al, Nature '01

Mechanism of optomechanical effects in LCE

sample: nematic elastomer EC4OCH3
+ 0.1% dissolved
Disperse Orange 1 azo dye

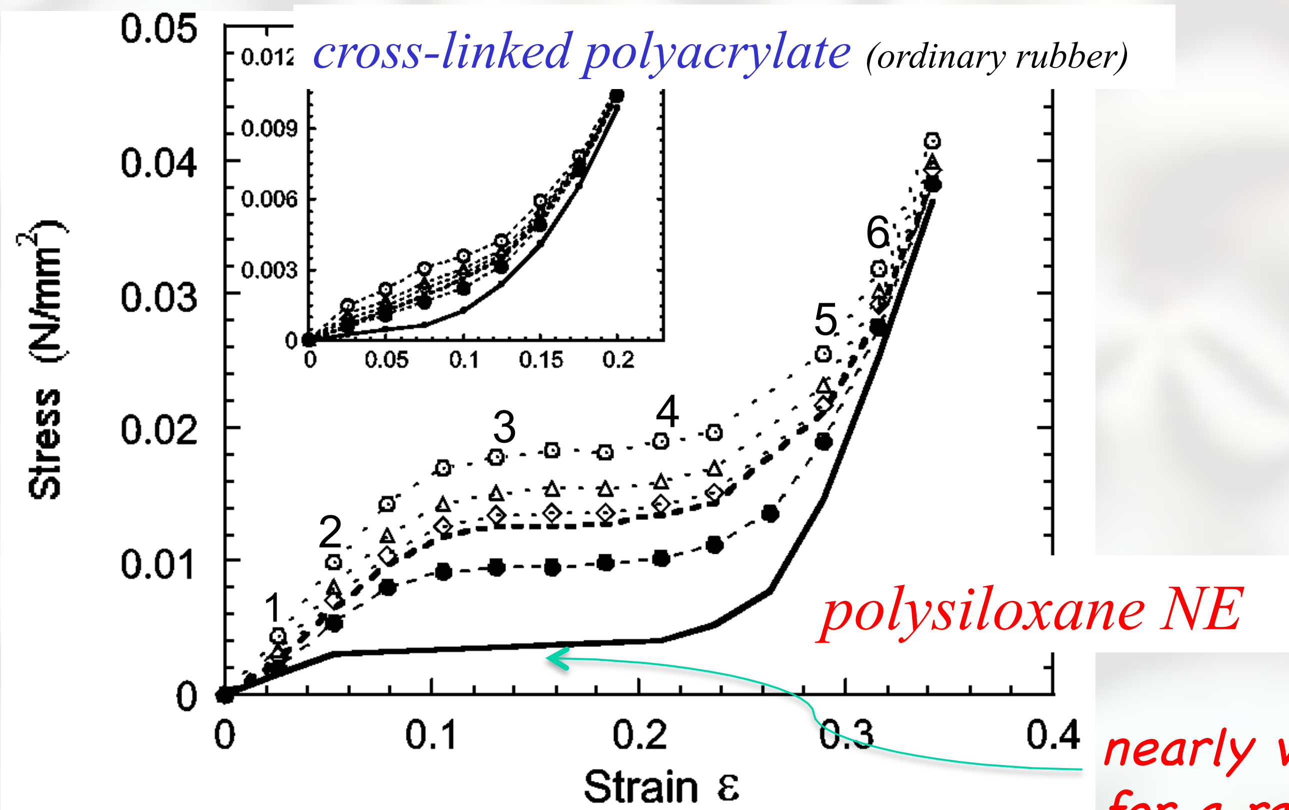




Response time: 70ms

M. Chamacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, M. Shelley, Nature Mat. ***3****, 307, (2004)*

Soft elasticity



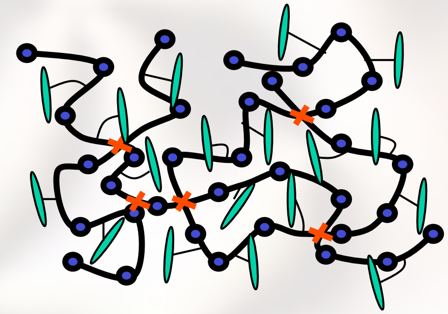
nearly vanishing stress for a range of strain

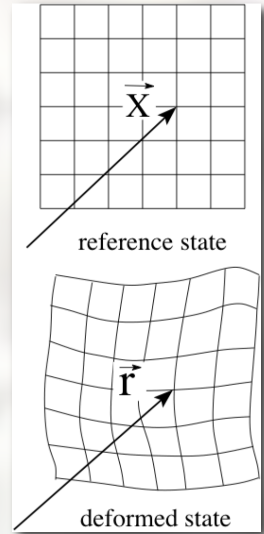
(cf Josephson effect,...)

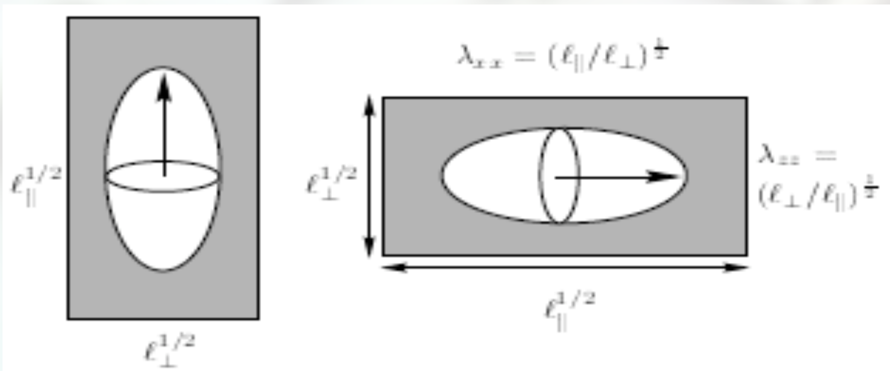
- extended <u>stress plateau</u> contrasting ordinary rubber
- small threshold

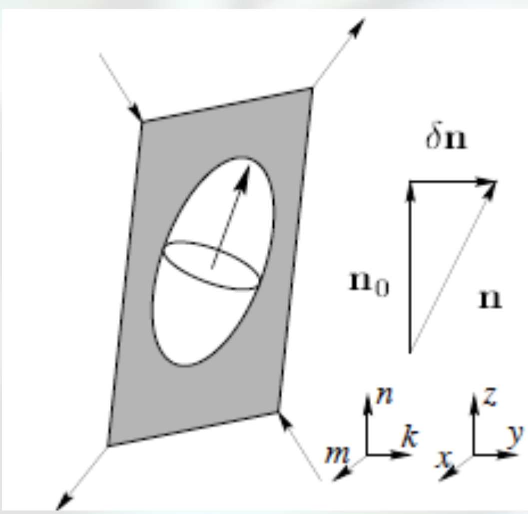
Clarke, Terentjev, PRL '98

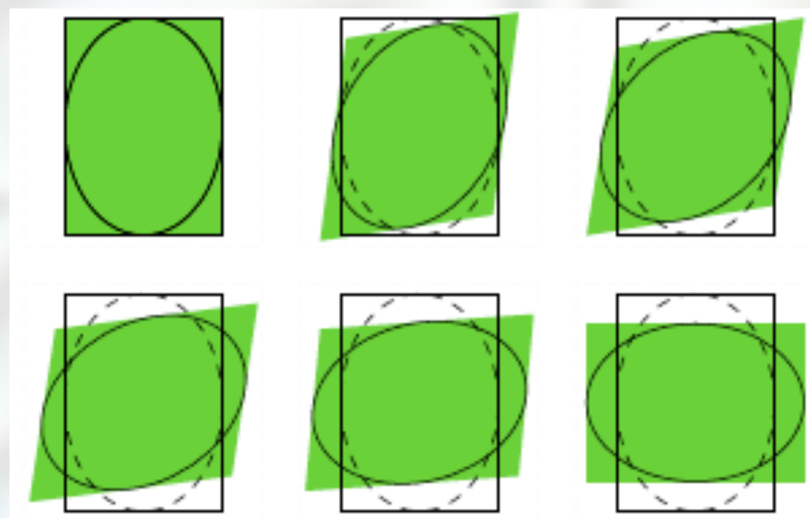
Visualization of soft deformation











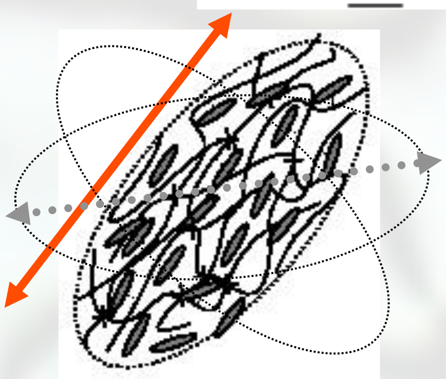
Warner, Terentjev '90
Olmsted

Nematic elastomer elasticity

Xing, Mukhopadhyay, Lubensky, L.R. 2001

- **Isotropic phase:** $\mathcal{H}_{elastic}[\underline{\underline{u}}] = \mu\, \underline{\underline{u}}^2$ *(conventional)*

- **IN transition:** $\mathcal{H}[\underline{\underline{u}}, \underline{\underline{Q}}] = \mathcal{H}_{elastic}[\underline{\underline{u}}] + \mathcal{H}_N[\underline{\underline{Q}}] - \underline{\underline{u}} \cdot \underline{\underline{Q}}$

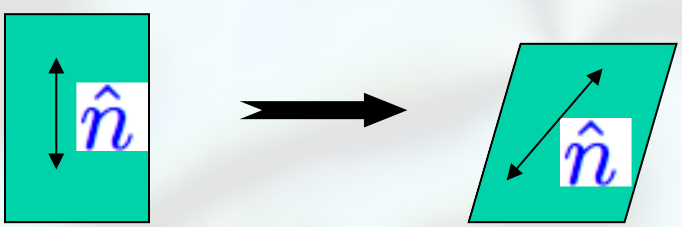


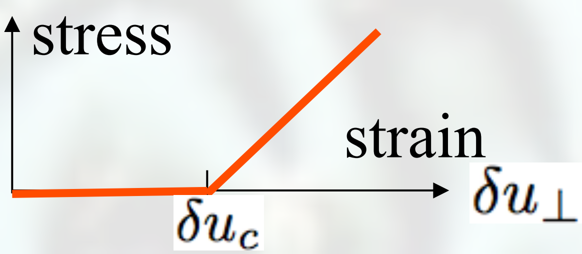
$\langle \underline{\underline{Q}} \rangle \neq 0 \neq \langle \underline{\underline{u}} \rangle$ $\quad T_{IN} \quad$ $\langle \underline{\underline{Q}} \rangle = 0 = \langle \underline{\underline{u}} \rangle$ $\quad$ T

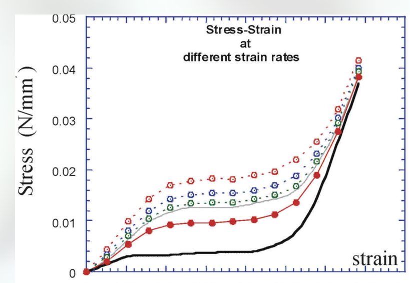
- **Nematic phase:** $\mathcal{H} = \mu(\underline{\underline{u}} - \underline{\underline{Q}})^2 + \mathcal{H}_{lc}[\underline{\underline{Q}}]$

nemato-elastic Goldstone mode
"Higg's mechanism"

$\delta \underline{\underline{u}}^{\perp} = u_{zi}$ *can be compensated by* $\delta \underline{\underline{Q}}^{\perp} = \delta \hat{n}_i$

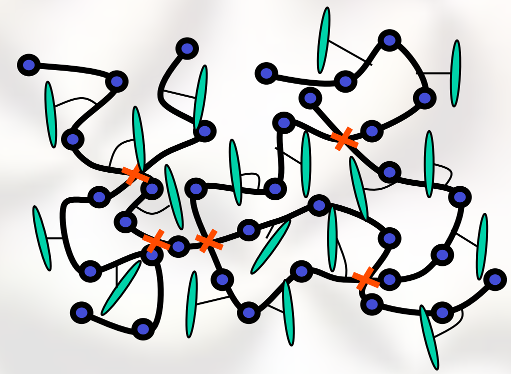




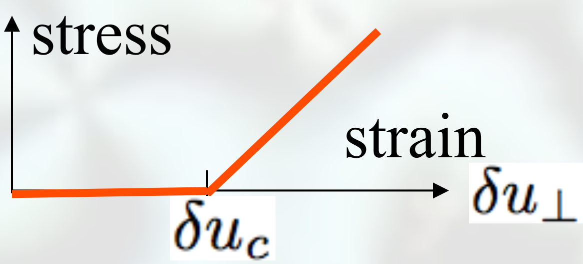


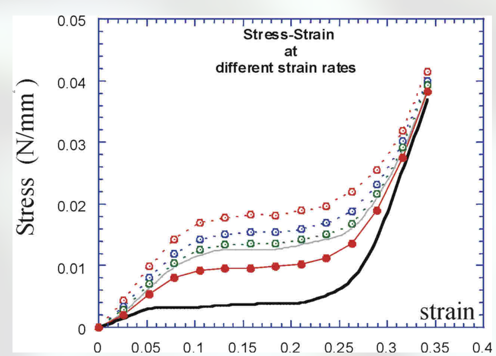
Neoclassical theory of nematic elastomers

Warner, Terentjev '90



- $F \approx k_B T\, R^T L^{-1} R \quad (L = N\,\ell)$
- affine deformation: $R = \Lambda R_0$ *(e.g.,* $\Lambda \approx 1 + u$*)*
- $F \approx k_B T\, \mathrm{Tr}\,(\ell_0\, \Lambda^T \ell^{-1} \Lambda)$
- incompressible $\det \Lambda = 1 = \lambda_x \lambda_y \lambda_z$
- soft mode (zero energy deformation): $\Lambda = \ell^{-1/2}\; O\; \ell_0^{-1/2}$
  restore to isotropic state, rotate, deform along new axis n
- $$\ell = \begin{pmatrix} \ell_\perp & 0 & 0 \\ 0 & \ell_\perp & 0 \\ 0 & 0 & \ell_{||} \end{pmatrix} = \ell_\perp \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & r \end{pmatrix} = \ell_{||} \hat{n}_i \hat{n}_j + \ell_\perp (\delta_{ij} - \hat{n}_i \hat{n}_j)$$
- soft elasticity:





Elastic theory of NE

Xing + L.R., PRL, EPL, AOP
Lubensky + Stenull, EPL (2003)

- Construct rotationally invariant elastic theory of deformations about $\underline{\underline{u}}_0$
- Study fluctuations and heterogeneities about $\underline{\underline{u}}_0$

Must incorporate underlying rotational invariance of the nematic state

$\Longrightarrow$ *some distortions cost no energy:* ***"soft" uniaxial solid***

$$f[\vec{R}(\mathbf{x})] = f[O_T \vec{R}(O_R \mathbf{x})]$$

- Vanishing energy cost for: $\delta \underline{\underline{u}} = \underline{\underline{O}} \cdot \underline{\underline{u}}_0 \cdot \underline{\underline{O}}^T - \underline{\underline{u}}_0$

- Harmonic elasticity about nematic state: $\underline{\underline{\varepsilon}} = \underline{\underline{u}} - \underline{\underline{u}}_0$

$$\mathcal{H}^0_{NE} = \cancel{\mu_{zi}}\varepsilon^2_{zi} + B_z \varepsilon^2_{zz} + \mu_\perp \varepsilon^2_{ij} + \lambda \varepsilon^2_{ii} + \lambda_{zi} \varepsilon_{zz} \varepsilon_{ii}$$

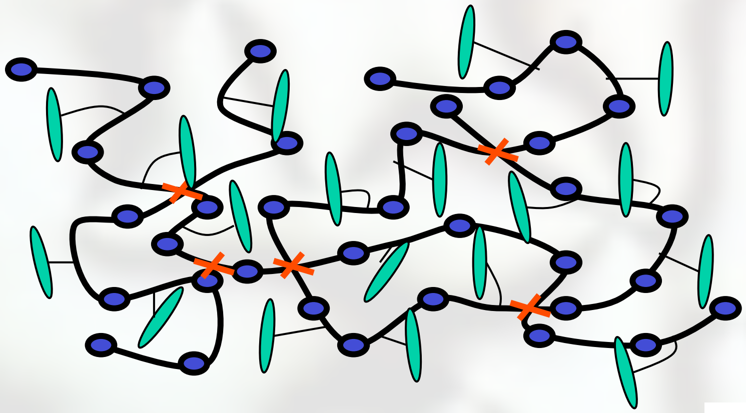
0 , *required by rotational invariance*

- Nonlinear elasticity about nematic state:

$$\mathcal{H}_{NE} = B_z w^2_{zz} + \mu_\perp w^2_{ij} + \lambda w^2_{ii} + \lambda_{zi} w_{zz} w_{ii}$$

$$w_{zz} = \partial_z u_z + \frac{1}{2}(\nabla u_z)^2 \qquad w_{ij} = \frac{1}{2}(\partial_{(i} u_{j)} - \partial_i u_z \partial_j u_z)$$

Fluctuations and heterogeneity



- Thermal fluctuations: $\mathcal{Z} = \mathrm{Trace}_u[e^{-\beta\mathcal{H}[u]}]$

- Heterogeneity ⇨ random torques and stresses:

nematic elastomers are only statistically homogeneous and isotropic

$$\mathcal{H}_{NE}^{real} = \mathcal{H}_{NE}[\underline{\underline{u}}] - \underbrace{\underline{\underline{u}} \cdot \underline{\underline{\sigma}}(\mathbf{r}) - (\hat{n} \cdot \vec{g}(\mathbf{r}))^2}_{\text{encodes heterogeneity}}$$

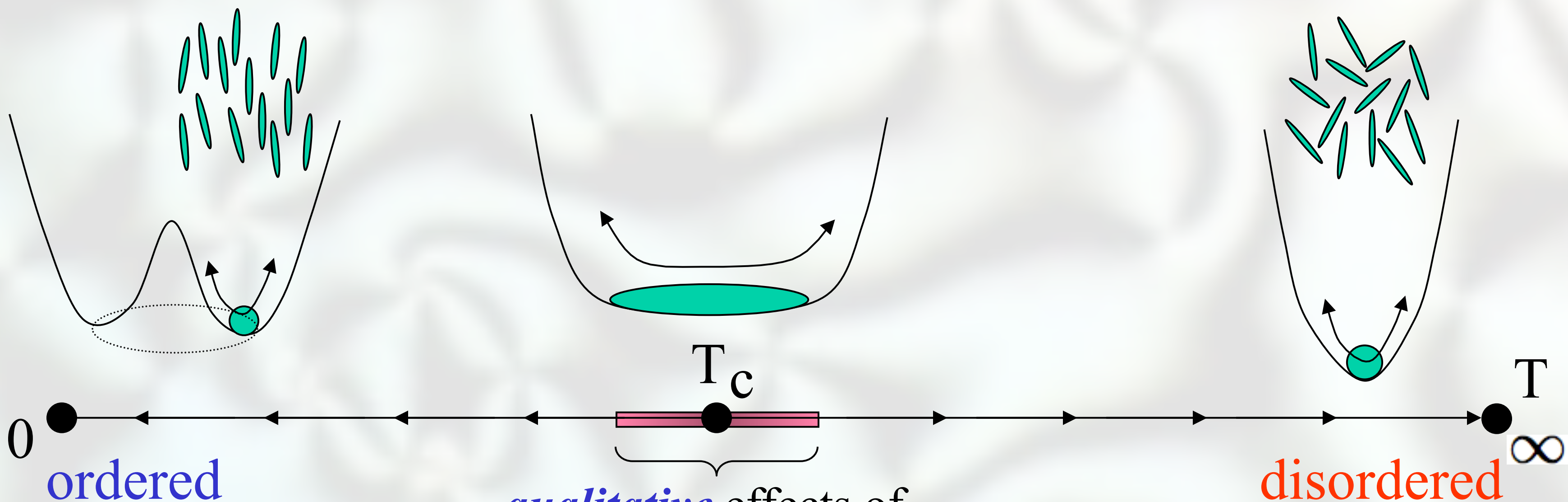
Elastic "softness" leads to strong qualitative effects of thermal fluctuations and network heterogeneity

Fluctuations, nonlinearities and phase transitions

Upshot of 40 years of research on fluctuations and critical phenomena:

usually

Fluctuations and nonlinearities are only important near isolated critical points (continuous phase transition)



(e.g. ferromagnet)

$H = (\nabla S)^2$

qualitative effects of fluctuations and nonlinearities

$$H = (\nabla S)^2 + \cancelto{0}{r} S^2 + S^4$$

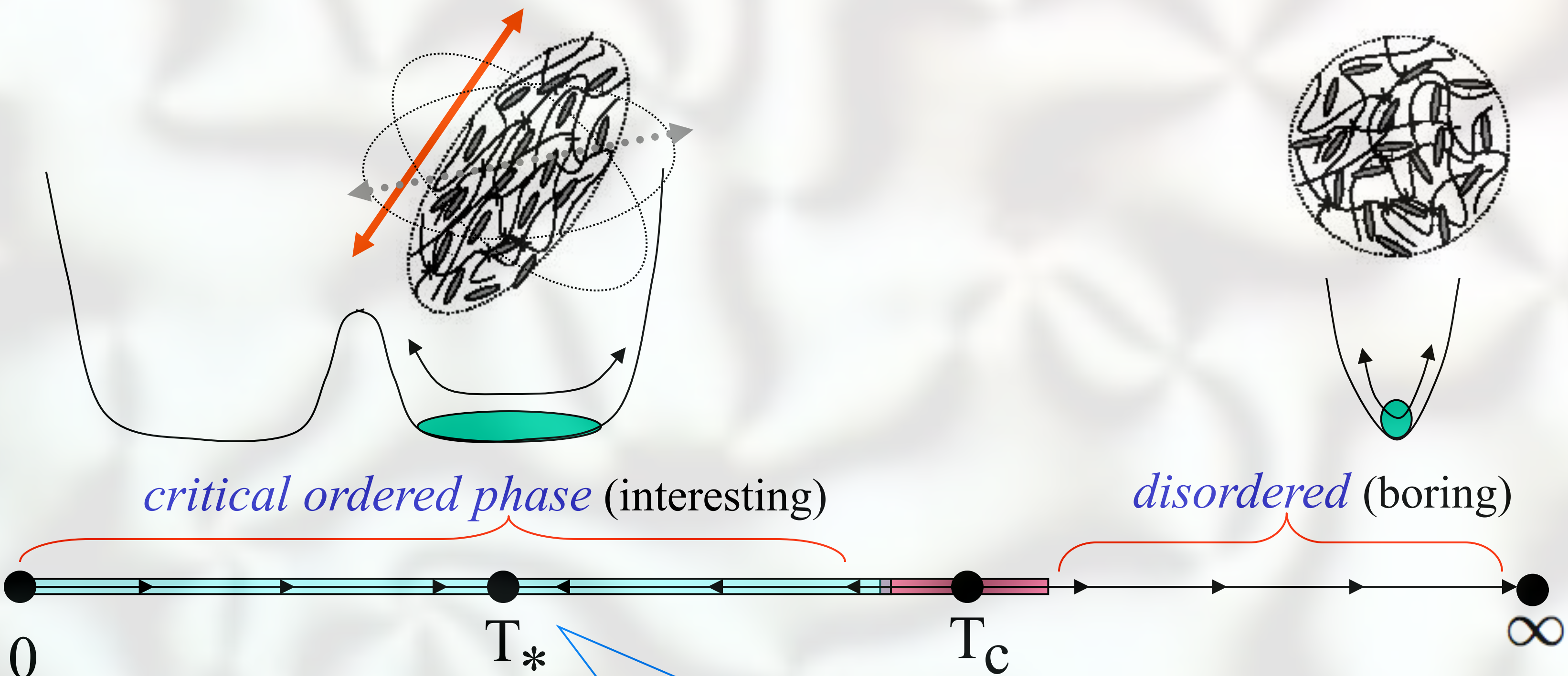
(e.g. paramagnet)

$H = S^2$

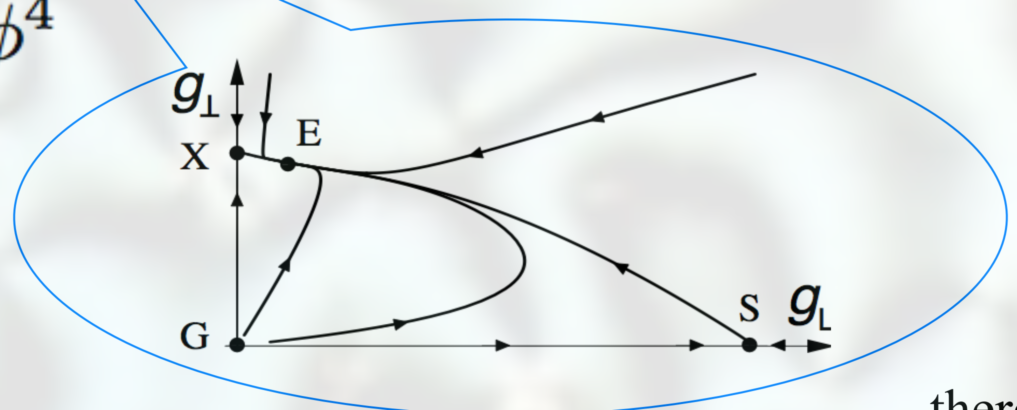
well-known exception: **FQHE**

Critical phase in nematic elastomer

Xing + L.R.,
PRL (2003)



$$H = (\nabla\phi)^2 + \phi^4$$



…there are others

Predictions

Xing + L.R., PRL (2003)

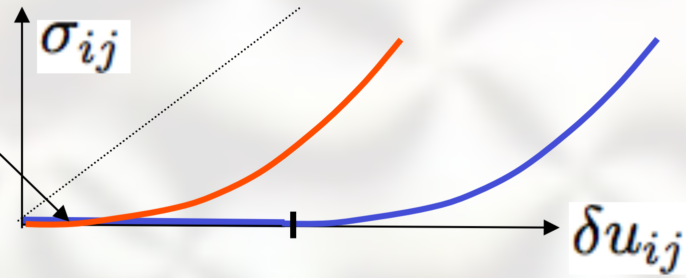
- *Universal* elasticity: $\overline{\langle|\delta u(q)|^2\rangle} \sim q_\perp^{-4+\eta}, \text{ for } r_\perp > \xi_\perp \sim K^2/\Delta$

- Non-Hookean elasticity: $\sigma_{zz} \sim (u_{zz})^\delta \;, \quad \delta > 1$

  (cf. non-Fermi liquid)

  vanishing slope

  no linear response

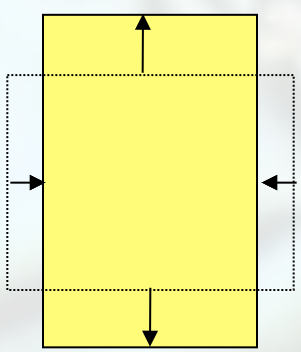


- Length-scale dependent elastic moduli:

$$K_{\text{eff}}(L) \sim L^\eta, \quad \mu_{\text{eff}}(L) \sim L^{-\eta_\mu}, \quad B_{\text{eff}}(L) \sim B_0$$

- Macroscopically incompressible: $\kappa_{\text{eff}} \sim \mu_{\text{eff}}(L)/B_{\text{eff}}(L) \to 0$

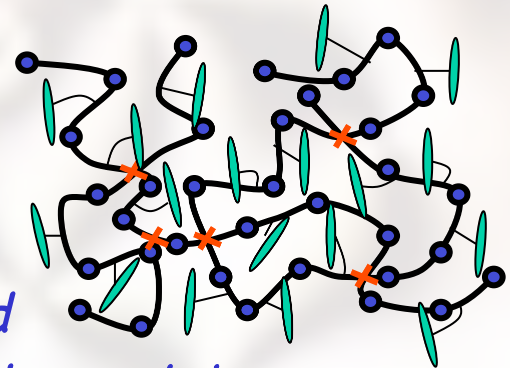
- Universal Poisson ratios:



$$u_{xx} > 0 \Rightarrow \begin{cases} u_{yy} = \frac{5}{7} u_{xx} \\ u_{zz} = -\frac{12}{7} u_{xx} \end{cases}$$

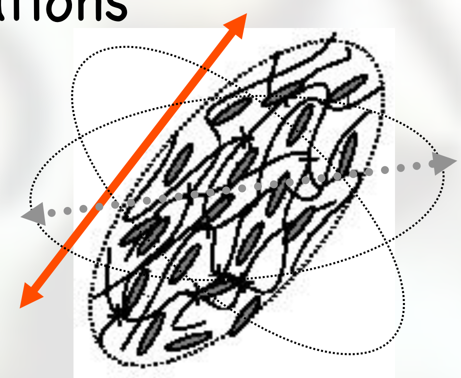
$$u_{zz} > 0 \Rightarrow u_{xx} = u_{yy} = -\frac{1}{2} u_{zz}$$

Summary and Conclusions



- Amazing liquid-crystal rubber --- *a "liquid" solid*
  a "solid" liquid-crystal

- Dramatic influence of thermal fluctuations and heterogeneities on macroscopic elasticity and orientational correlations



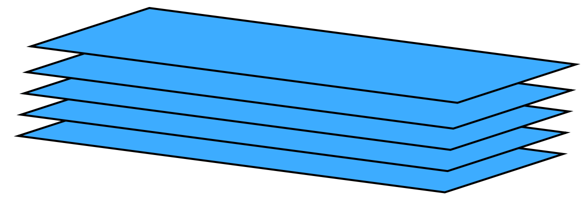
- Critical phases in "soft" condensed matter

Open questions:

- *More sophisticated model of heterogeneity?*
- *"Plastic" deformation?*
- *Other liquid crystal phases (e.g., smectic rubber)?*
- *Dynamics?*
- *Quantum realizations of critical phases?*

"Soft" elastic systems: critical phases

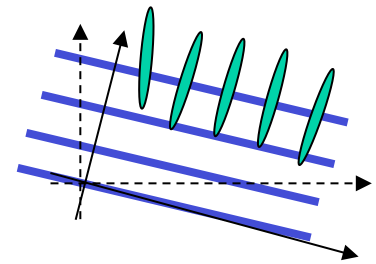
guiding principle: ***partial breaking of spatial symmetry***



- **Smectic phase** (*Grinstein + Pelcovits*)

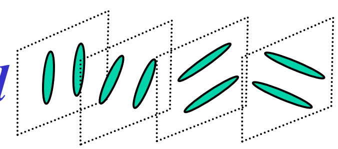
$$H = K(\nabla^2 u)^2 + B(\partial_z u + \frac{1}{2}(\nabla u)^2)^2$$

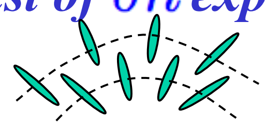
harmonic $\boxed{\textit{rotational invariance}}$ nonlinear

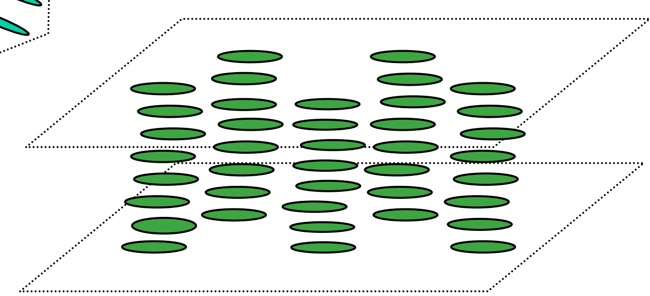


$$H = B_\perp(\nabla_\perp u - \delta n)^2 + B_z(\partial_z u)^2 + K_s(\nabla \cdot n)^2 + K_{tb}(\nabla \times n)^2$$

Higgs mechanism $\longrightarrow$ ***twist of $\delta\hat{n}$ expelled***
but not splay







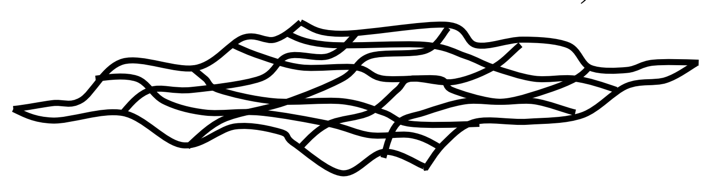
- **Columnar phase** *(L.R. + Toner)*

  (spontaneous vortex lattice in FM superconductor)

- **Tensionless polymerized membrane** *(Nelson+Peliti, Aronovitz +Lubensky, Le Doussal + L.R.)*

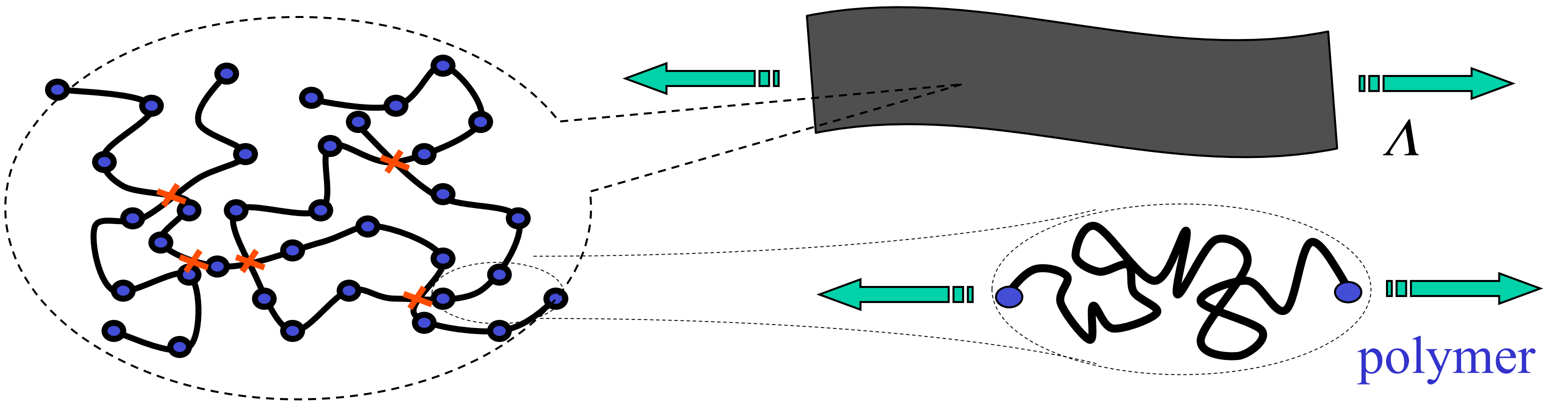
$$H = \frac{\kappa}{2}(\nabla^2 h)^2 + \mu u_{ij}^2 + \frac{\lambda}{2} u_{ii}^2$$

$$u_{ij} = \frac{1}{2}(\partial_i u_j + \partial_j u_i + \partial_i h \partial_j h)$$



Classical theory of rubber elasticity

Kuhn, Wall, Flory, Treloar (1940's)



- crosslinked polymer network:
  - affine deformation: $R = \Lambda R_0$

$$\Lambda = \begin{matrix} \lambda_x & 0 & 0 \\ 0 & \lambda_y & 0 \\ 0 & 0 & \lambda_z \end{matrix}$$

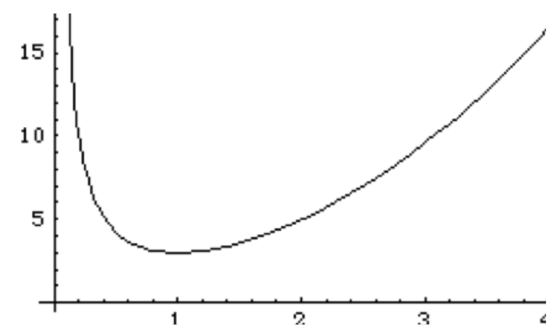
  - *incompressible* $\det \Lambda = 1 = \lambda_x \lambda_y \lambda_z$
  - *fixed, non-fluctuating crosslinks*
  - *"phantom" (noninteracting, nonentangled polymers)*
  - $\delta f = \frac{1}{2}\frac{k_B T}{\xi^3} Tr \Lambda^T \Lambda = \frac{\mu_0}{2}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)$
  - *uniaxial* $\lambda_x = \lambda$, $\lambda_y = \lambda_z = \lambda^{-1/2}$

$$\delta f = \frac{\mu_0}{2}(\lambda^2 + \frac{2}{\lambda})$$

- single chain: $P \sim e^{-R^2/R_0^2}$

$$\delta F = k_B T \log P \sim k_B T (R/R_0)^2$$

Hookean entropic spring



What's missing? *k_BT fluctuations beyond ξ*

Xing, Goldbart, L.R., (PRL'06)

- want $F[\Lambda] = -kT \ln Tr\, e^{-H/kT}$ with $H = \frac{\mu_0}{2} \int |\nabla r(X)|^2$

- approximate by small thermal fluctuations about imposed affine distortion:

$$\vec{r}(\vec{X}) = \Lambda \cdot e^{\mathbf{u}(\vec{\mathbf{X}})\cdot\nabla} \vec{X} \approx \Lambda \cdot (\vec{X} + \vec{u}(\vec{X}) + \ldots)$$

- finite compressibility is crucial:

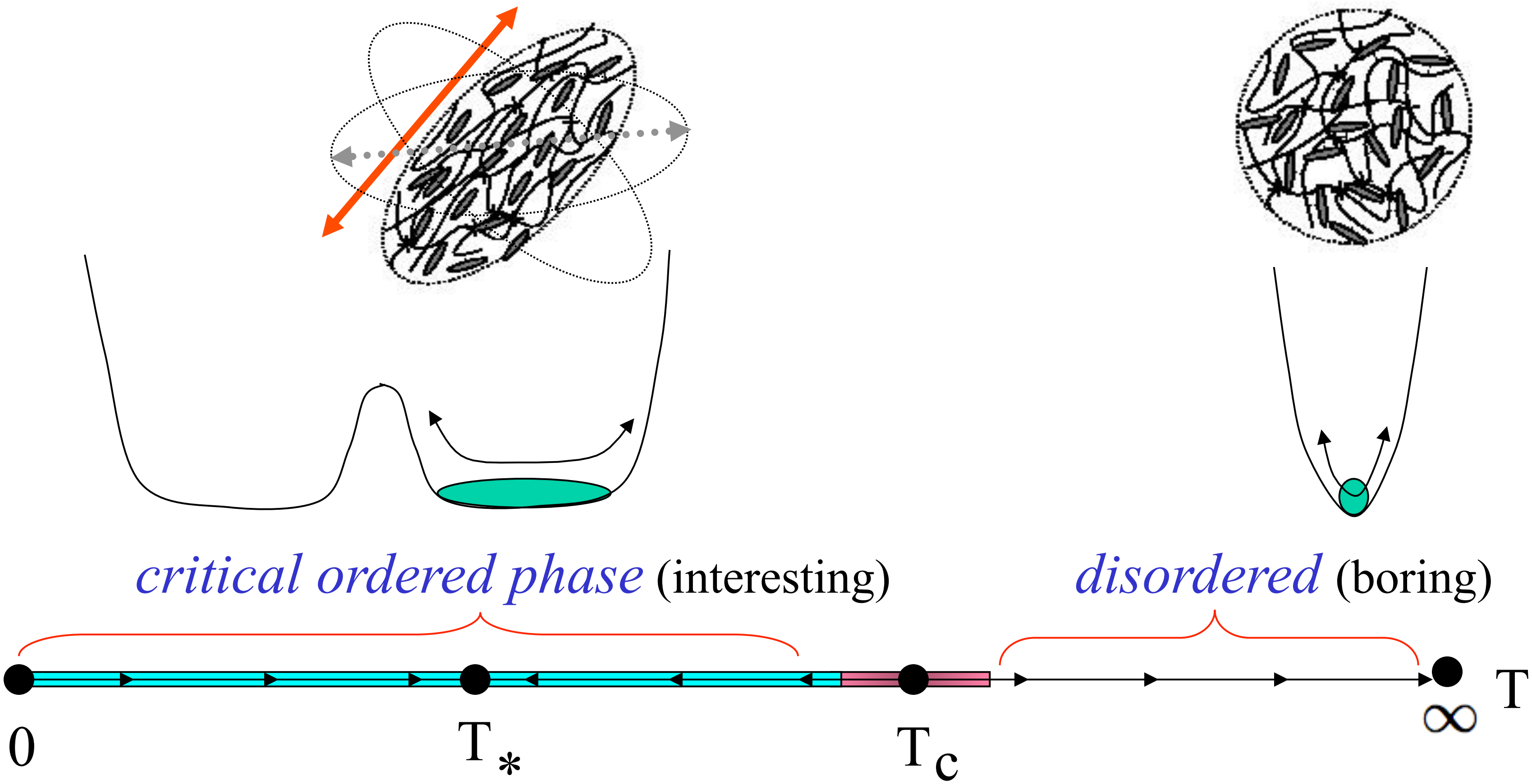
$$\vec{\nabla} \cdot \vec{u} = 0$$

- integrate over phonons u(x): $f(\lambda) = f_{class.}(\lambda) + \mu_1 \left[\frac{\tanh^{-1}\sqrt{1-\lambda^{-3}}}{\sqrt{1-\lambda^{-3}}} - \ln\lambda \right]$

$$\mu_1 \approx \mu_0 \approx k_B T/\xi^3$$

- anisotropic, Λ-dependent phonon correlations $\langle u_i(q) u_j(-q) \rangle \approx \frac{k_B T/\mu_0}{\vec{q}\cdot\Lambda\Lambda^T\cdot\vec{q}} P^T_{ij}(q)$

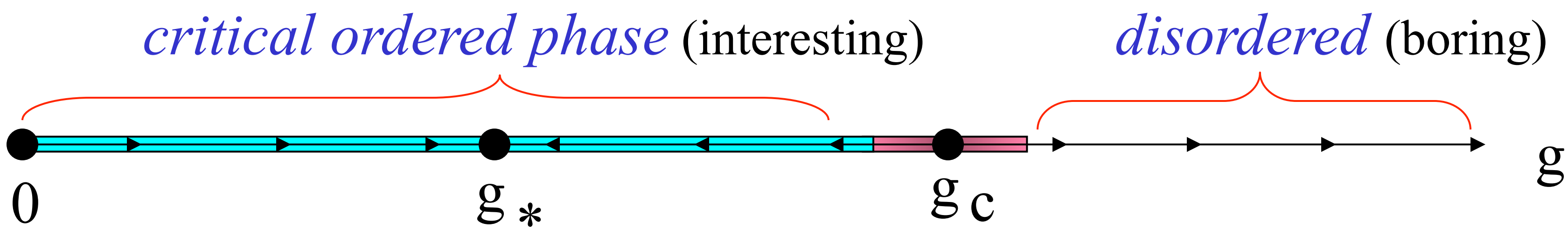
Critical phases



$$H = (\nabla\phi)^2 + \phi^4$$

…there are others

Properties of critical phases



$$H = (\nabla^2 u)^2 + (\partial_z u + (\nabla u)^2)^2$$

- *spontaneously broken continuous symmetry*
- *nontrivial fixed point of strongly interacting Goldstone modes (c.f. nonlinear O(N) sigma-model)*
- *universal power-law correlation functions and amplitude ratios (throughout the phase)*
- *no fine-tuning to a critical point required*
- *quantum analogs? road to 3d "Luttinger liquids"?*

Strange elasticity of liquid-crystal rubber