Boulder 2002

Liquid Crystal Gels

Liquid & Rubber in one material!

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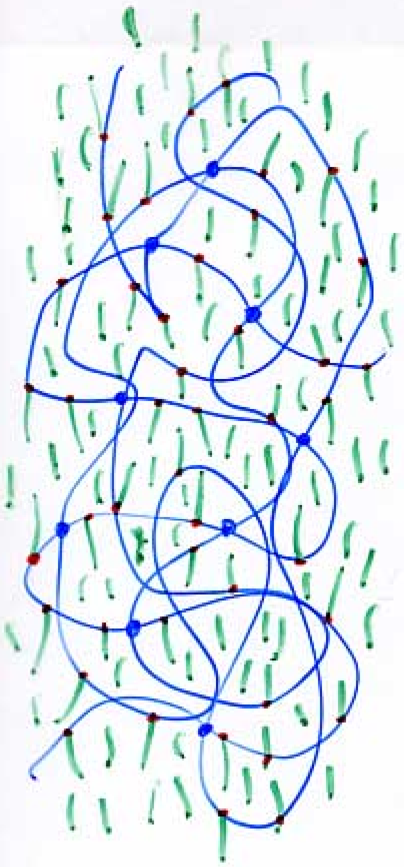
Nematic Gels

"Hyper-Complex Fluids"



* Cross-linked polymer coils
* Nematogenic molecules bound to polymer (~10%)
* Nematogenic molecules as solvent (~90%).

Look for new properties __not__ found in either component — some co-operation of the gel & the nematic.

Length Scale: $\sqrt{\frac{K}{\mu}}$

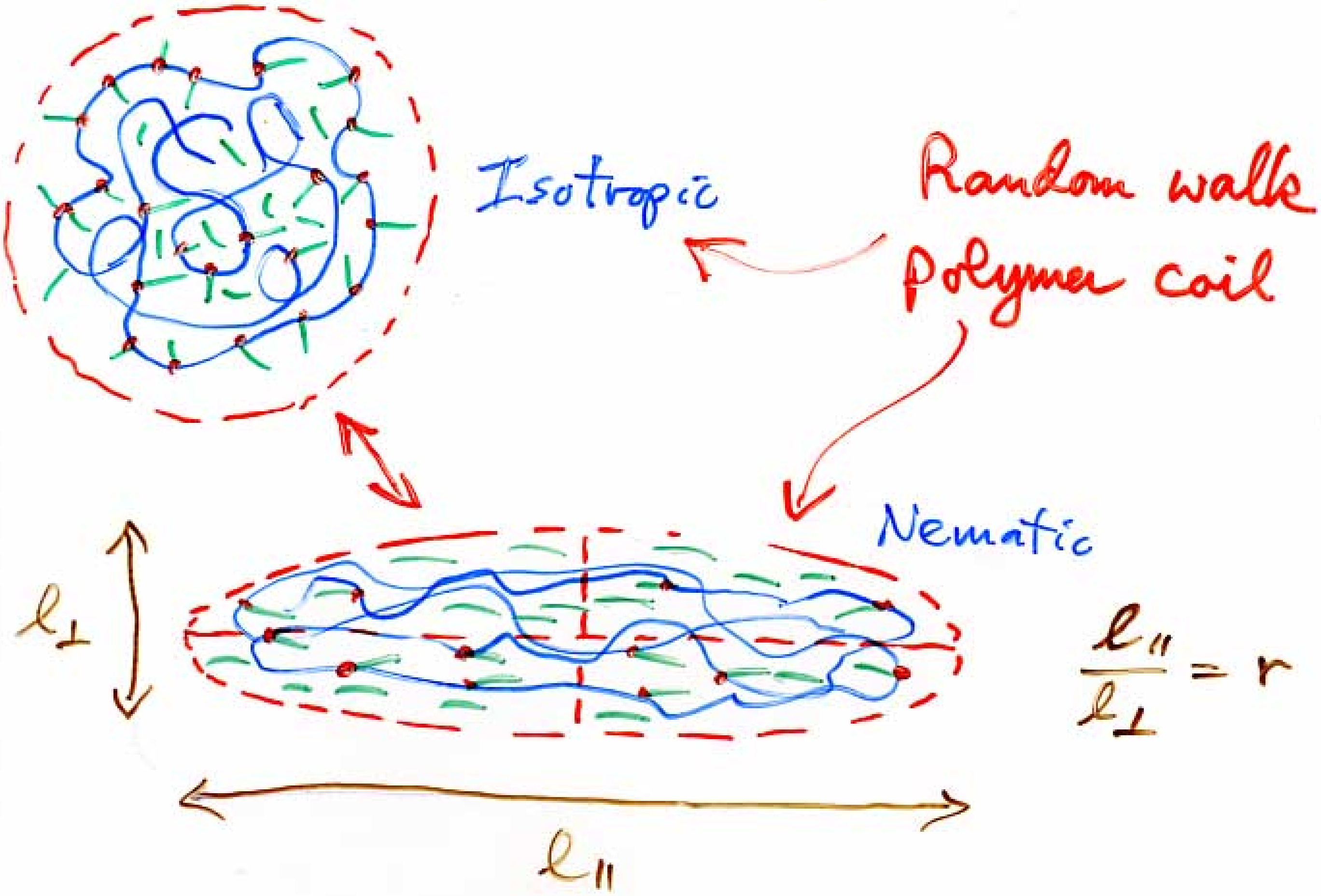
$K \sim 10^{-11}\, J/m \quad \mu \sim 10^{2} \to 10^{5}\, J/m^{3}$

$\sqrt{\frac{K}{\mu}} \sim 10^{-8} \to 3\times 10^{-7}\, m. \; (100\,Å \to 3000\,Å)$

Basic Interaction

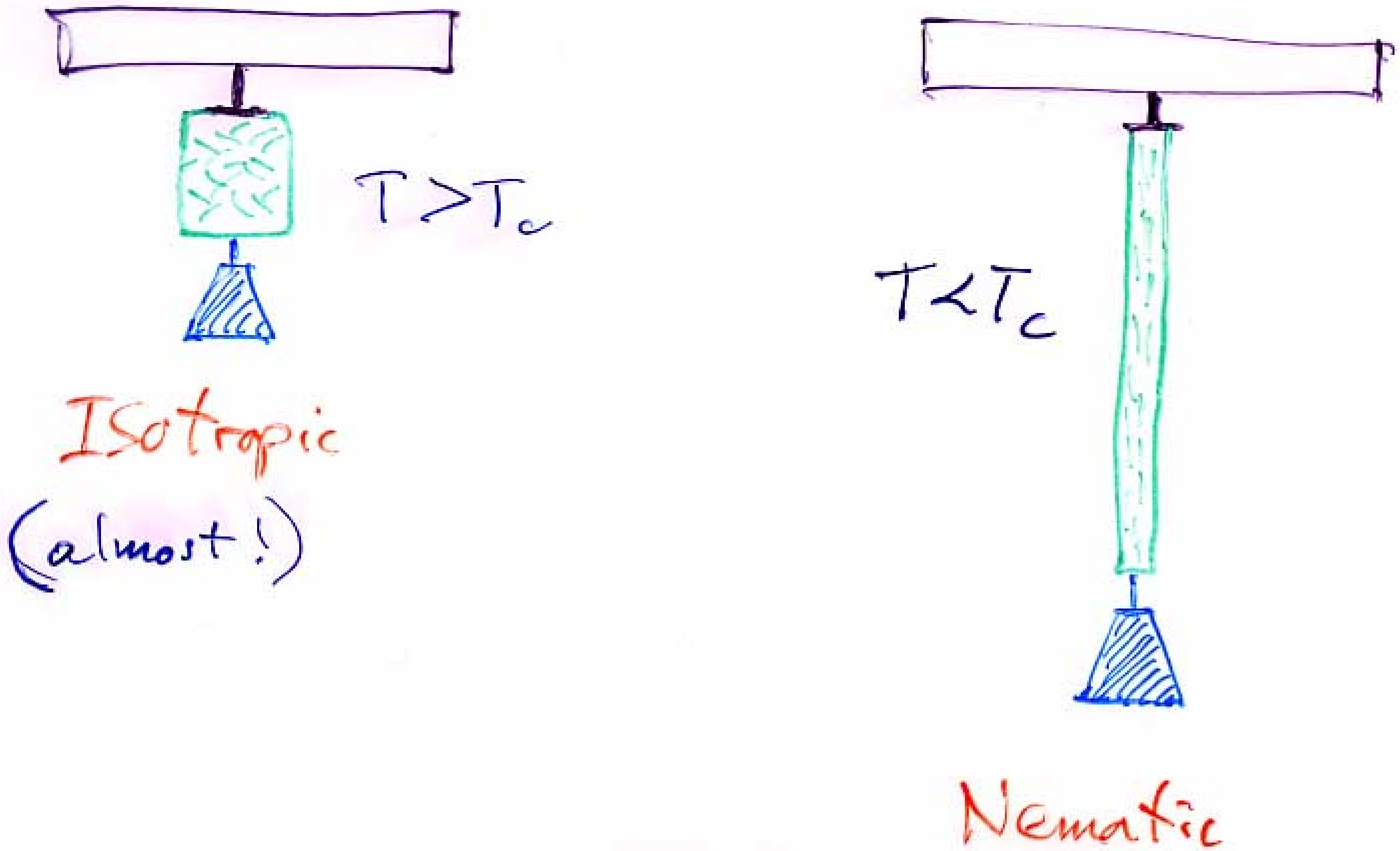
Polymer chains tend to align **parallel** to nematic molecules

[Some materials perpendicular]



$$\frac{\ell_{\parallel}}{\ell_\perp} = r$$

Rubber band Heat Engine
("Artificial Muscle")



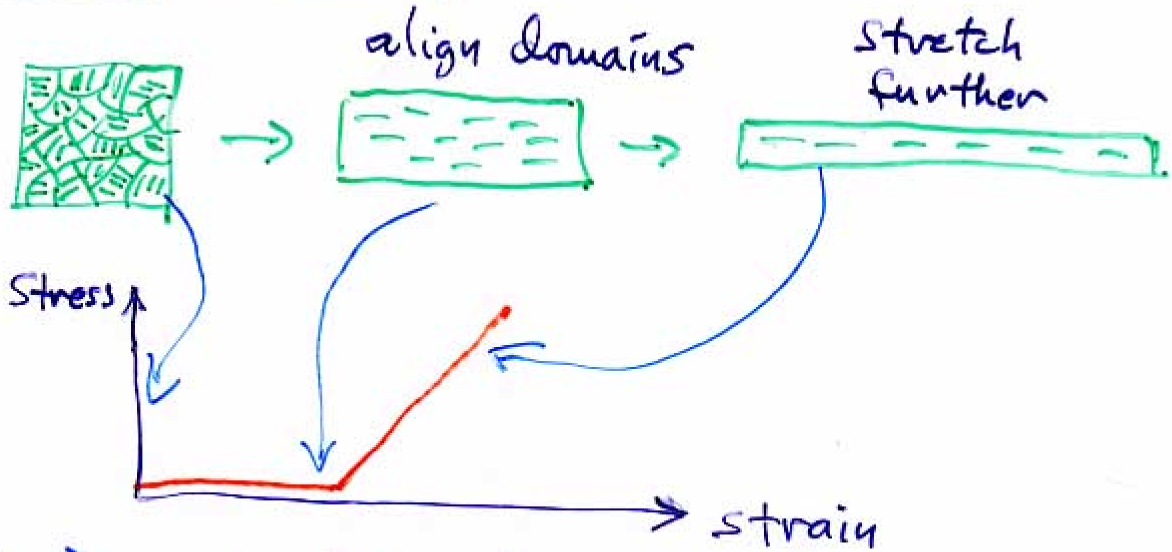
Heat of transition converted to work.

<u>Trick</u>: To specify a single axis for <u>elongation</u> of the nematic phase one must <u>bias</u> the polymer network.

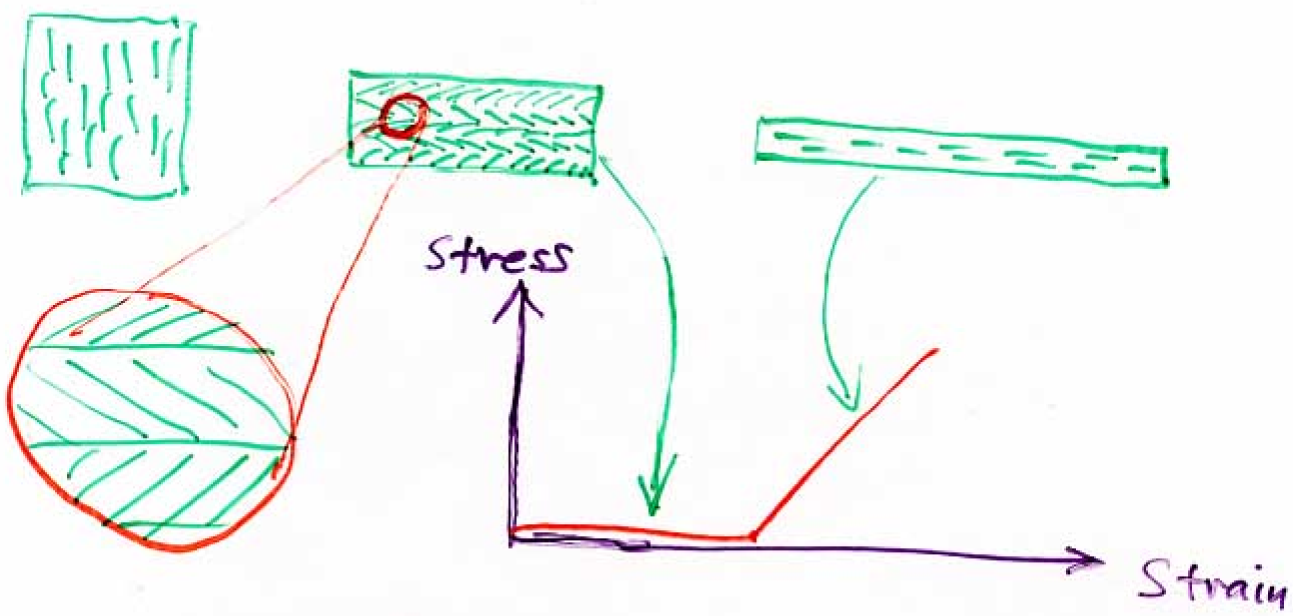
* gel in the nematic phase
* crosslink while stretching the isotropic phase.

Stretching Experiments

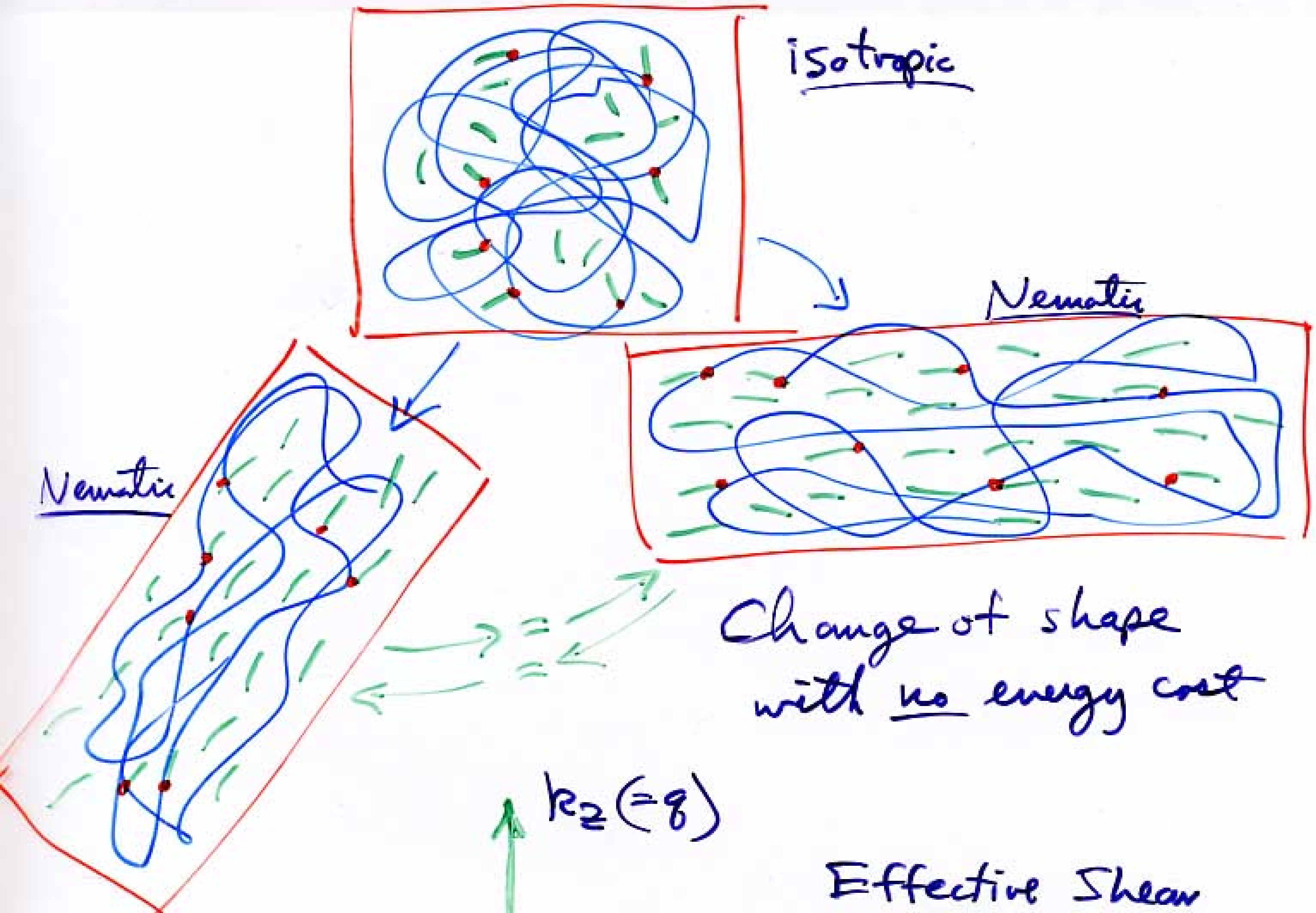
Polydomain Nematic



Single Domain Nematic

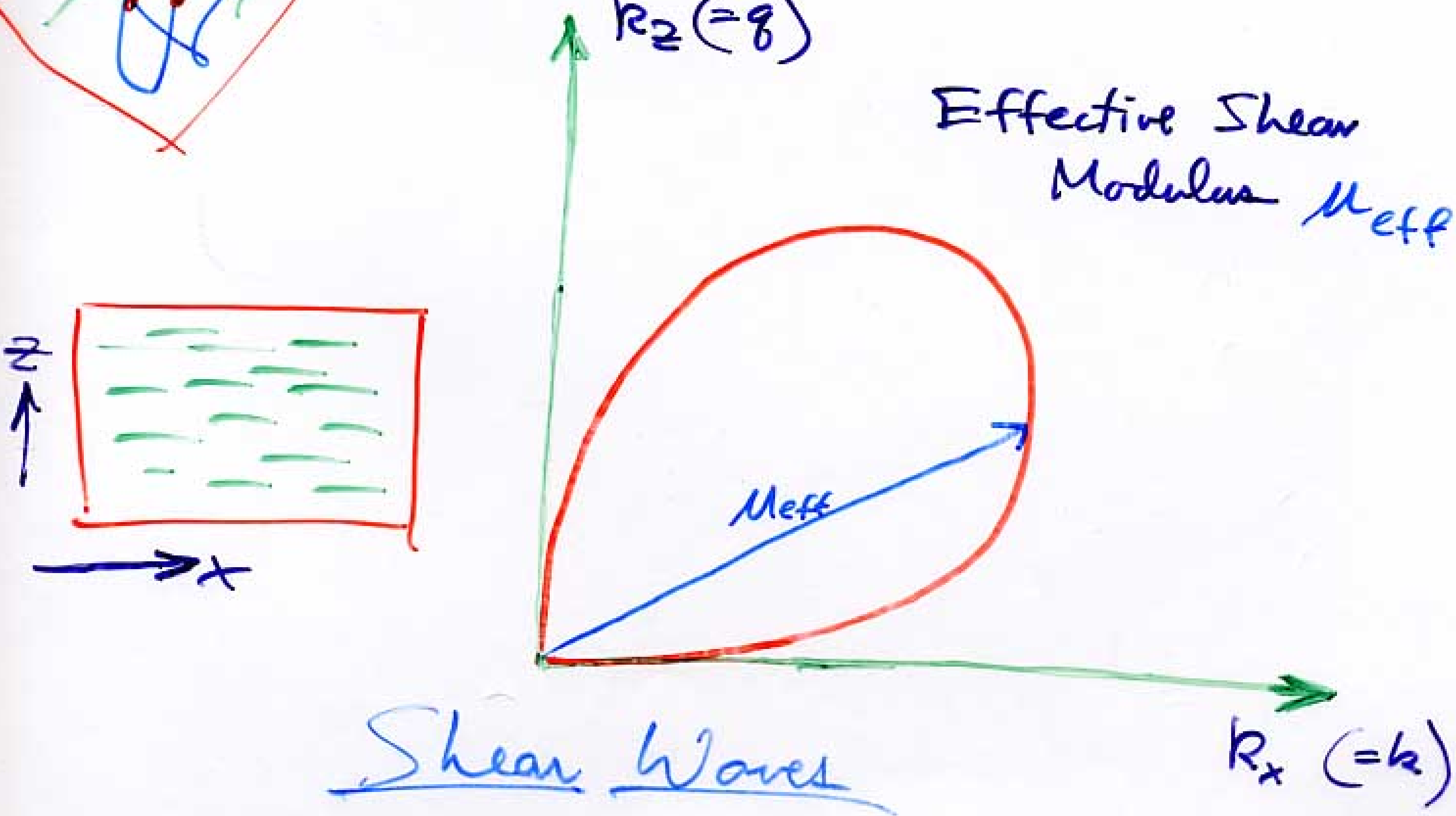


Soft Elasticity



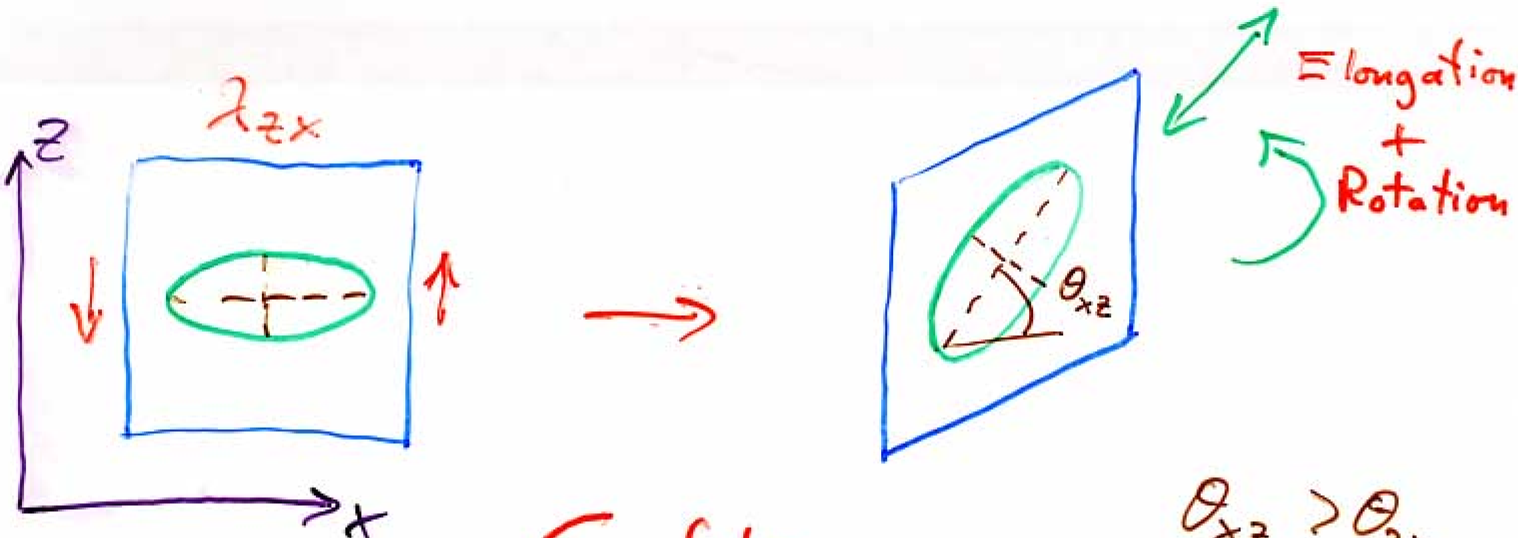
Change of shape with no energy cost

Effective Shear Modulus μ_{eff}



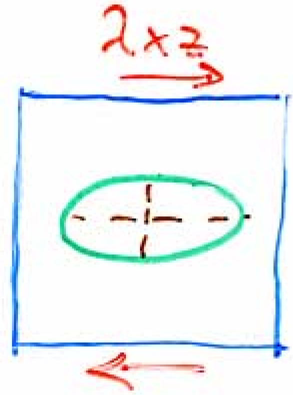
Shear Waves

Simple Shear



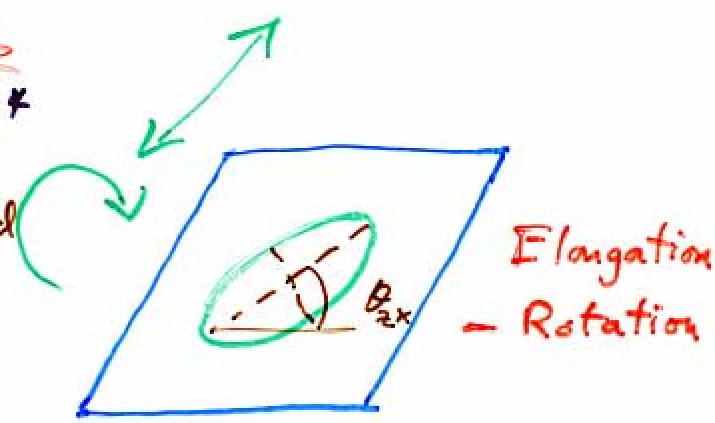
$\theta_{xz} > \theta_{zx}$

Soft

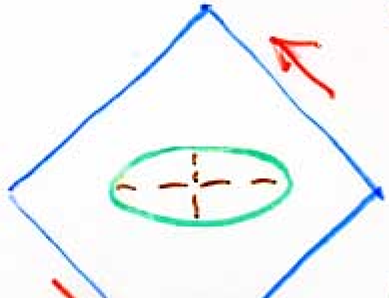


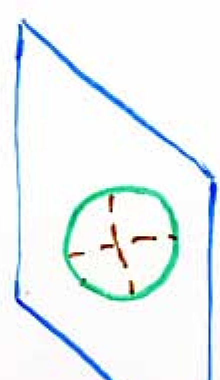
$E \sim \lambda^4 \sim \theta^4$

r conserved



Hard



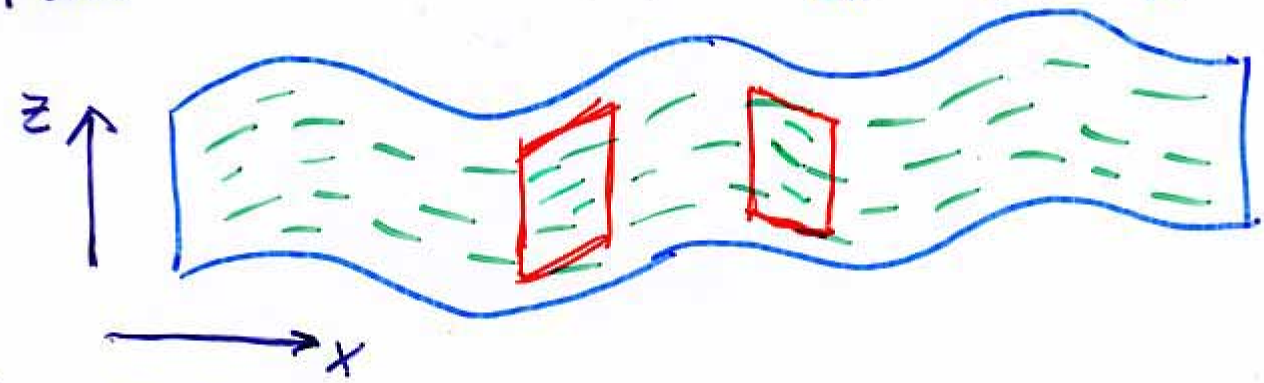


$E \sim \lambda^2$

r <u>not</u> conserved

Soft Shear Waves = Director Rotation Waves

Pure Bend: Strain = λ_{zx} ($\lambda_{xz}=0$)



Pure Splay

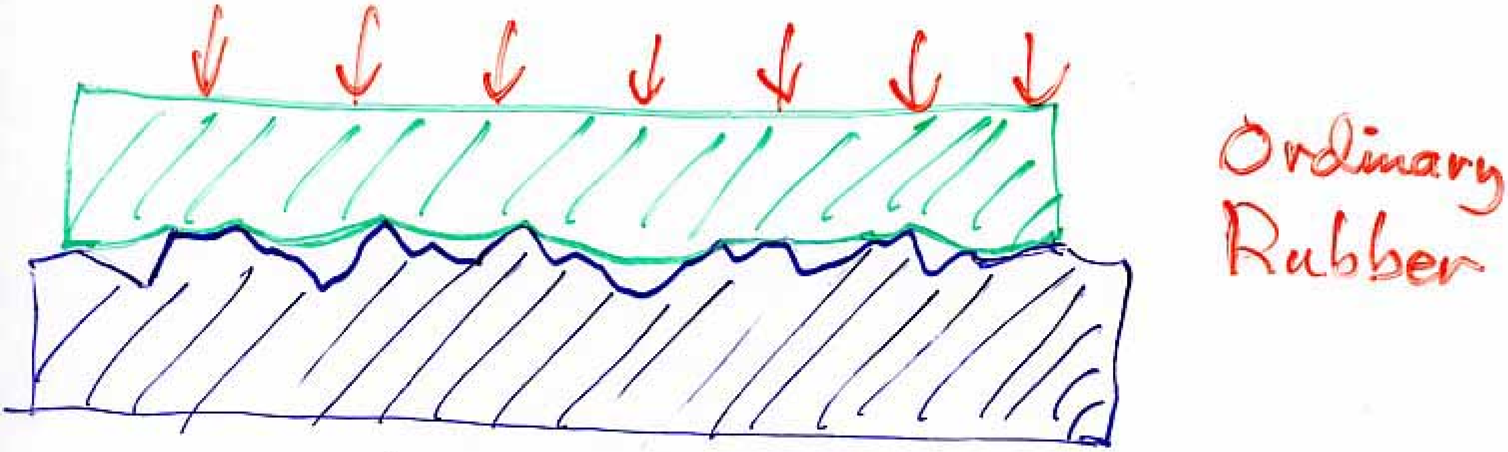
Strain $= \lambda_{xz}$ ($\lambda_{zx}=0$)

"Hard" Shear Wave

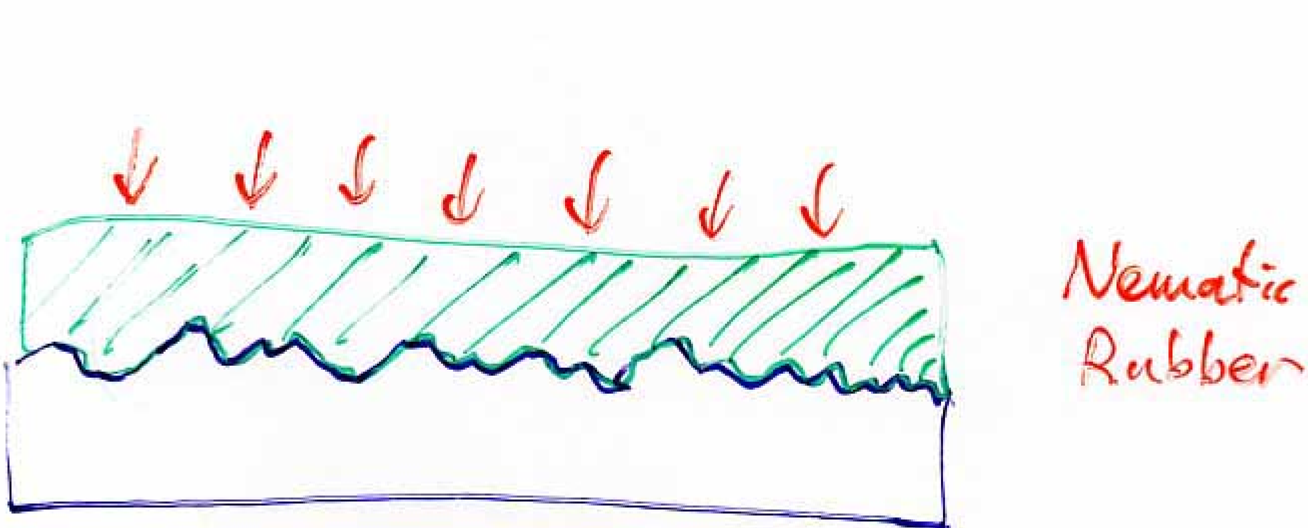
Strain

Both λ_{xz} & λ_{zx}

Contact with a Rough Surface



elastic contact



liquid-like contact

"Semi-Soft" Gels

* Crosslink polymers in 2 stages
  - first to make a gel
  - second under elongational strain
* Crosslink polymers in the ordered phase
  - in a nematic mono-domain
  - in a cholesteric
  - in any "pre-strained" configuration to produce a "memory" of that state.
* Produces a kind of "internal field" along the <u>initial</u> director during cross-linking

<u>Zero Strain</u> $\underset{\approx}{\lambda} = 0$

$$F_{semi} = \frac{1}{2}\mu A \left(\sin(\theta - \theta_0) \right)^2$$

θ_0 = initial director angle

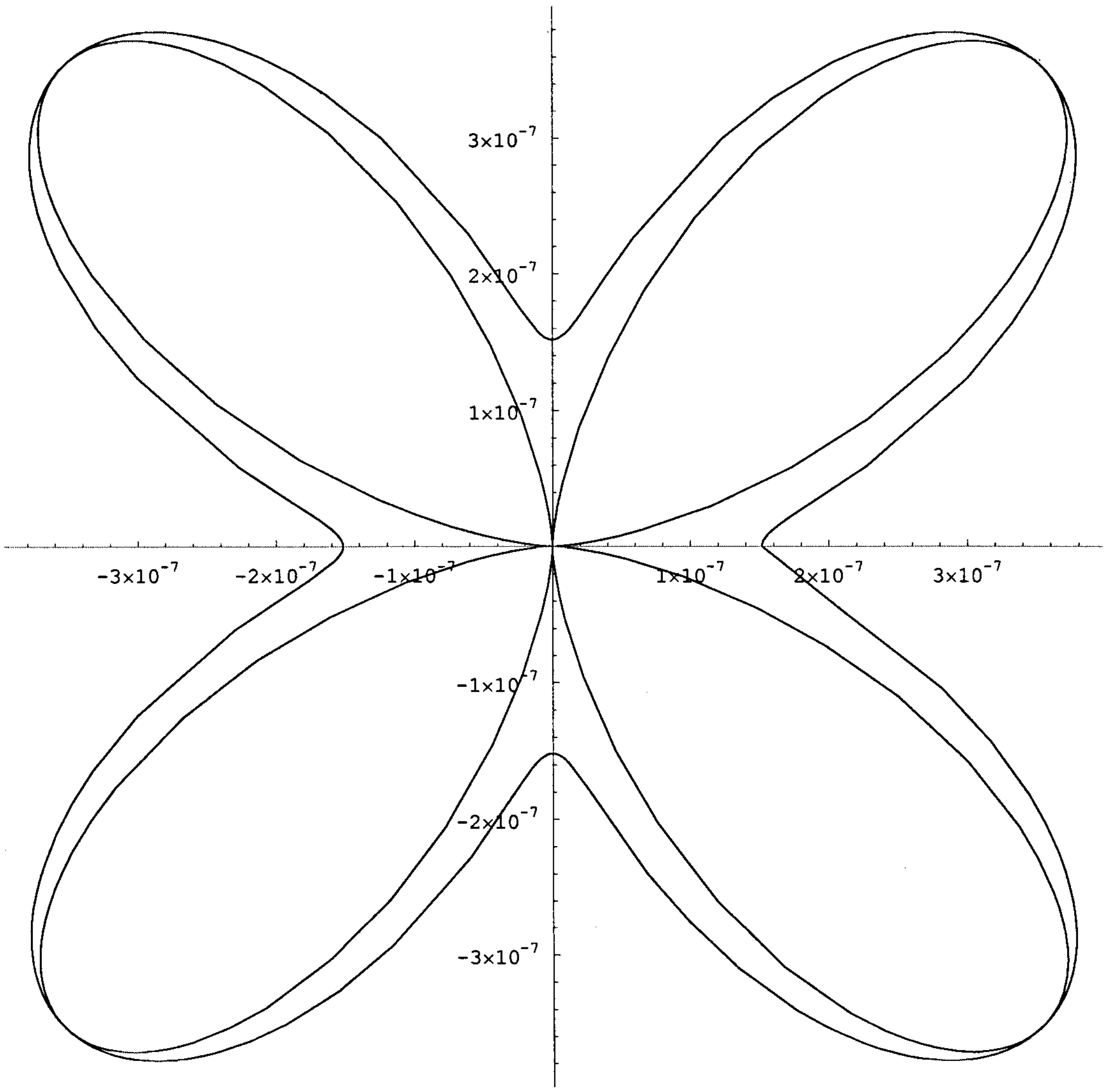
<u>If</u> θ_0 is <u>fixed</u> & <u>unchanging</u>

<u>Non-Zero Strain</u>

$$F_{semi} = \frac{1}{2}\mu A \left(f(\theta, \theta_0(\underset{\approx}{\lambda})) \right) \sim \frac{1}{2}\mu A \left(\theta - \theta_0(\underset{\approx}{\lambda}) \right)^2$$

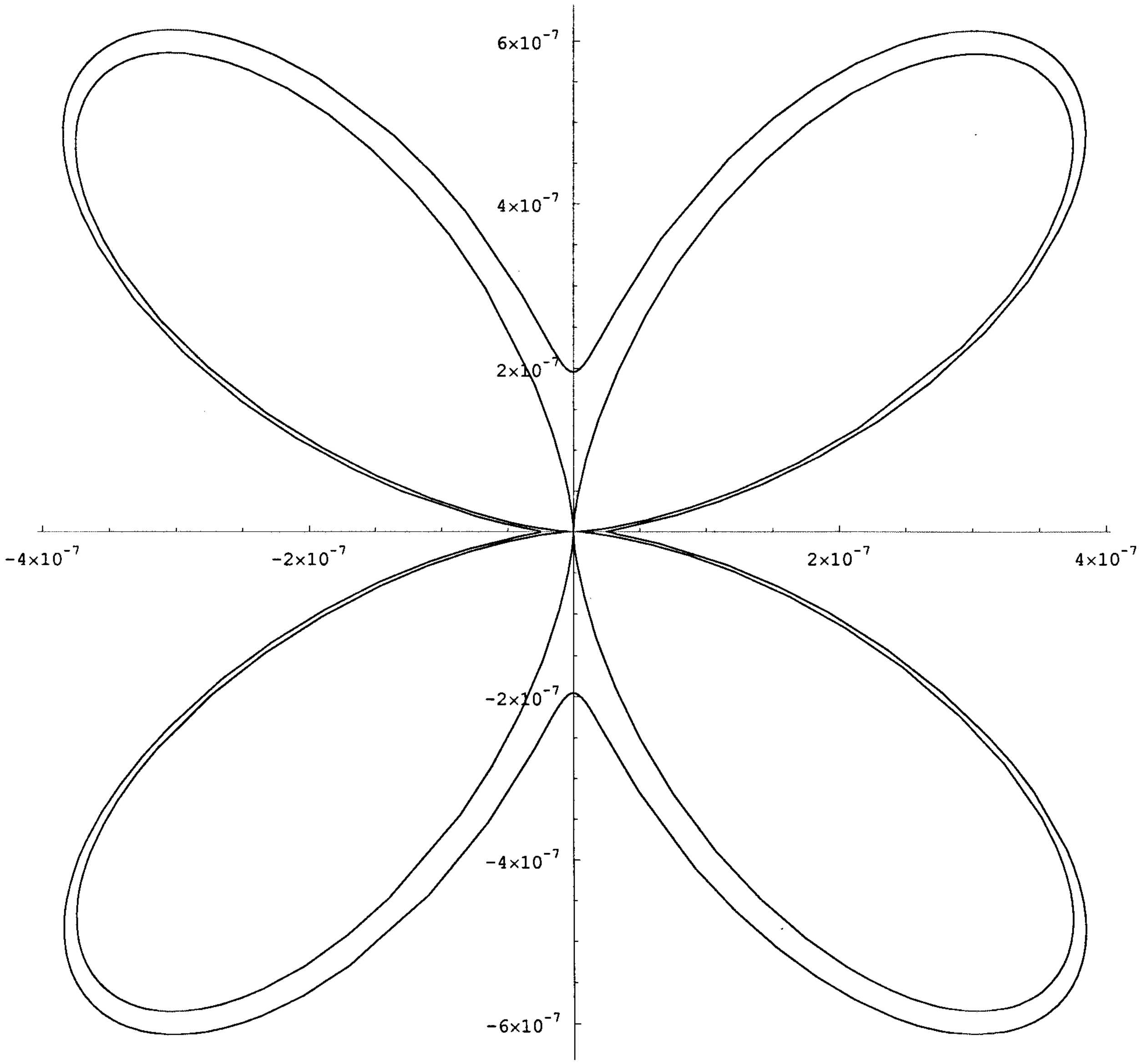
$\theta_0(\underset{\approx}{\lambda})$ <u>rotated</u> by strains $\underset{\approx}{\lambda}$

```
num = gchi /. {d → 0.001, r → 3, A → 0.15};
numsoft = gchi /. {d → 0.001, r → 3, A → 0};
fx = num * Cos[χ];
fy = num * Sin[χ];
fxsoft = numsoft * Cos[χ];
fysoft = numsoft * Sin[χ];
ParametricPlot[{{fx, fy}, {fxsoft, fysoft}}, {χ, 0, 2 * Pi}, AspectRatio → 1.0]
```



- Graphics -

```
In[105]:= num = g /. {θ → 0.001, r → 3, A → 0.05};
          numsoft = g /. {θ → 0.001, r → 3, A → 0};
          fx = num * Cos[χ];
          fy = num * Sin[χ];
          fxsoft = numsoft * Cos[χ];
          fysoft = numsoft * Sin[χ];
          ParametricPlot[{{fx, fy}, {fxsoft, fysoft}}, {χ, 0, 2 Pi}, AspectRatio → 1.0]
```

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Out[111]= - Graphics -
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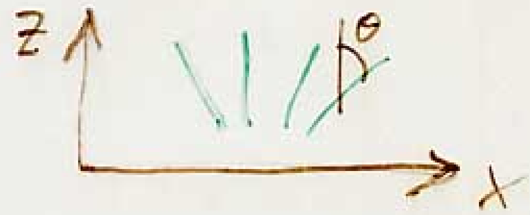
Nematic Elasticity

Curvature Elasticity



$$E \sim \frac{1}{2} K \left(\frac{\partial \theta}{\partial x}\right)^2$$

$$[K] = \frac{[\text{Energy}]}{[\text{length}]} \sim \frac{10^{-11} J}{m}$$

Gel Elasticity

$$E \sim \frac{1}{2} \mu \left(\frac{\partial u}{\partial z}\right)^2$$

$$[\mu] = \frac{[\text{Energy}]}{[\text{length}]^3} \sim \frac{10^3 J}{m^3}$$

Length scale: equal energies

$$\xi = \sqrt{\frac{K}{\mu}} \sim 10^{-7} m \quad , 1000 \text{ Å}$$

But, for soft modes, $\mu_{eff} \to 0$, $\xi \to$ larger!

Complex Fluids Group
Brandeis University

Preparation of Nematic Gel Material

Chemical Composition for Mixture:

Nematic Liquid Crystal: K15 (89.78%)

$CH_3–(CH_2)_4–C_6H_4–C_6H_4–CN$

Acrylate Monomer: (9%)

$CH_2=CH–CO_2–(CH_2)_4–O–C_6H_4–C_6H_4–CN$

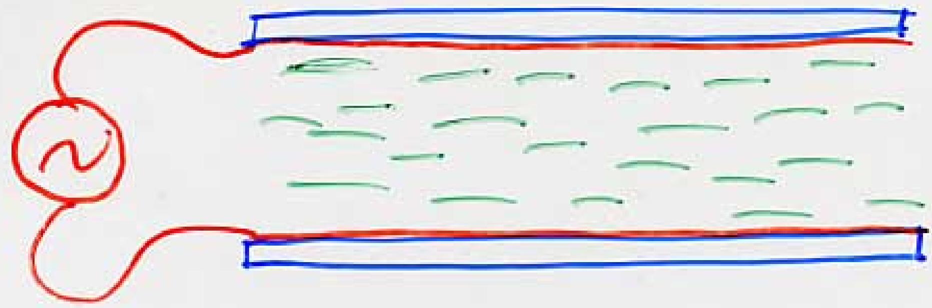
Diacrylate Monomer: 4,4'-bis(acryloyloxy) biphenyl(1%)

$CH_2=CH–CO_2–C_6H_4–C_6H_4–O_2C–CH=CH_2$

Photoactive Initiator: BME (Benzoin Methyl Ether) (0.2%)

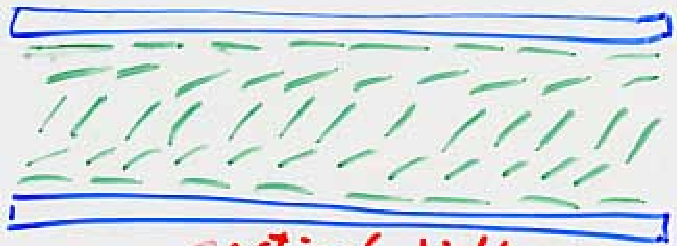
Slow polymerization under UV light for 4 hours

Electro-Optic Experiment



Initial state

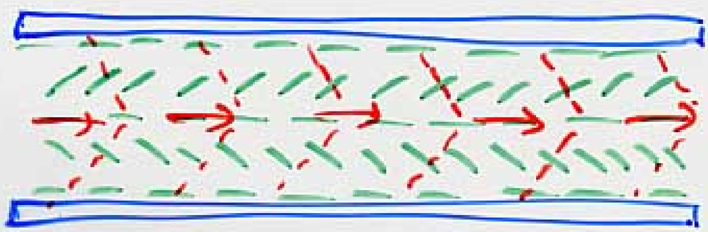
Nematic



Ordinary Frederiks transition

Critical Voltage

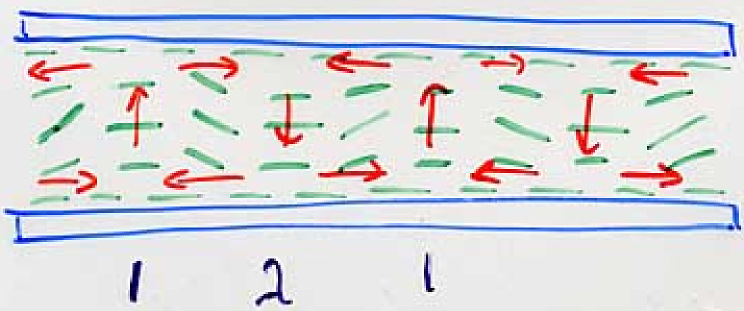
Thick Gel



Full wave "Frederiks" transition

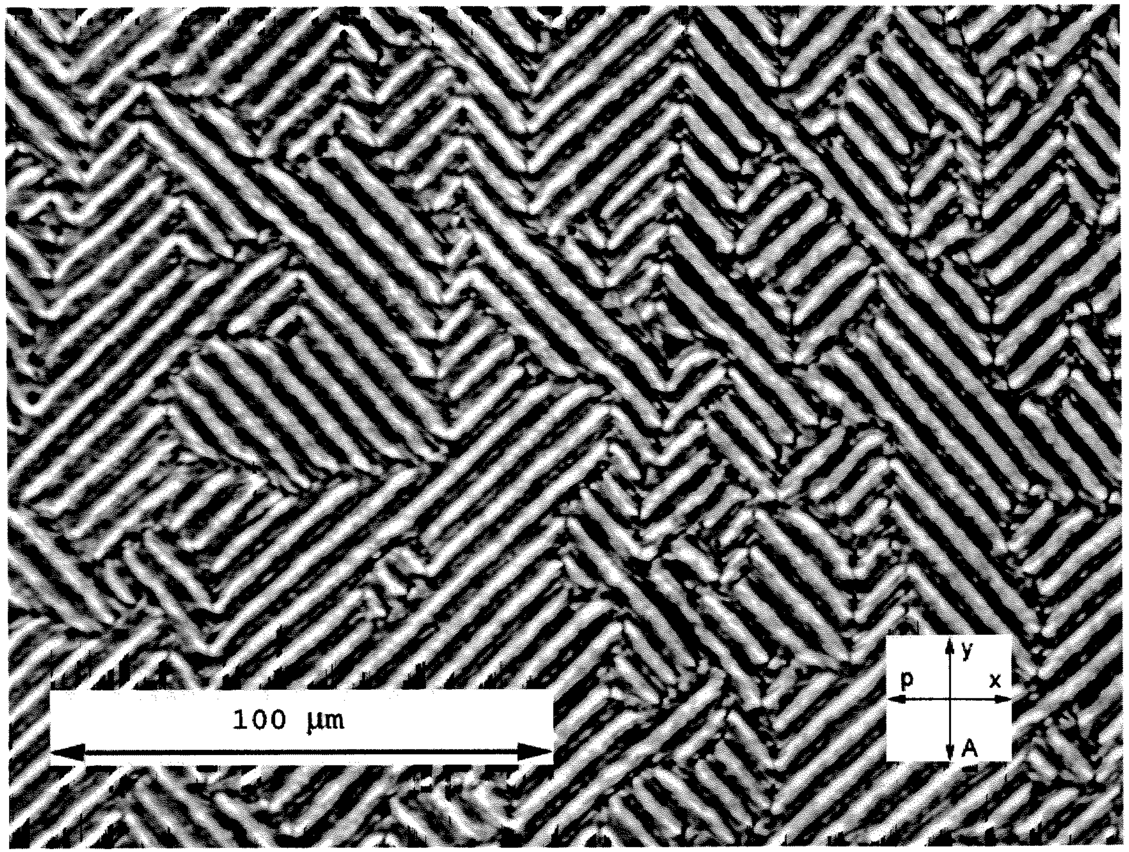
Critical Field

thin Gel

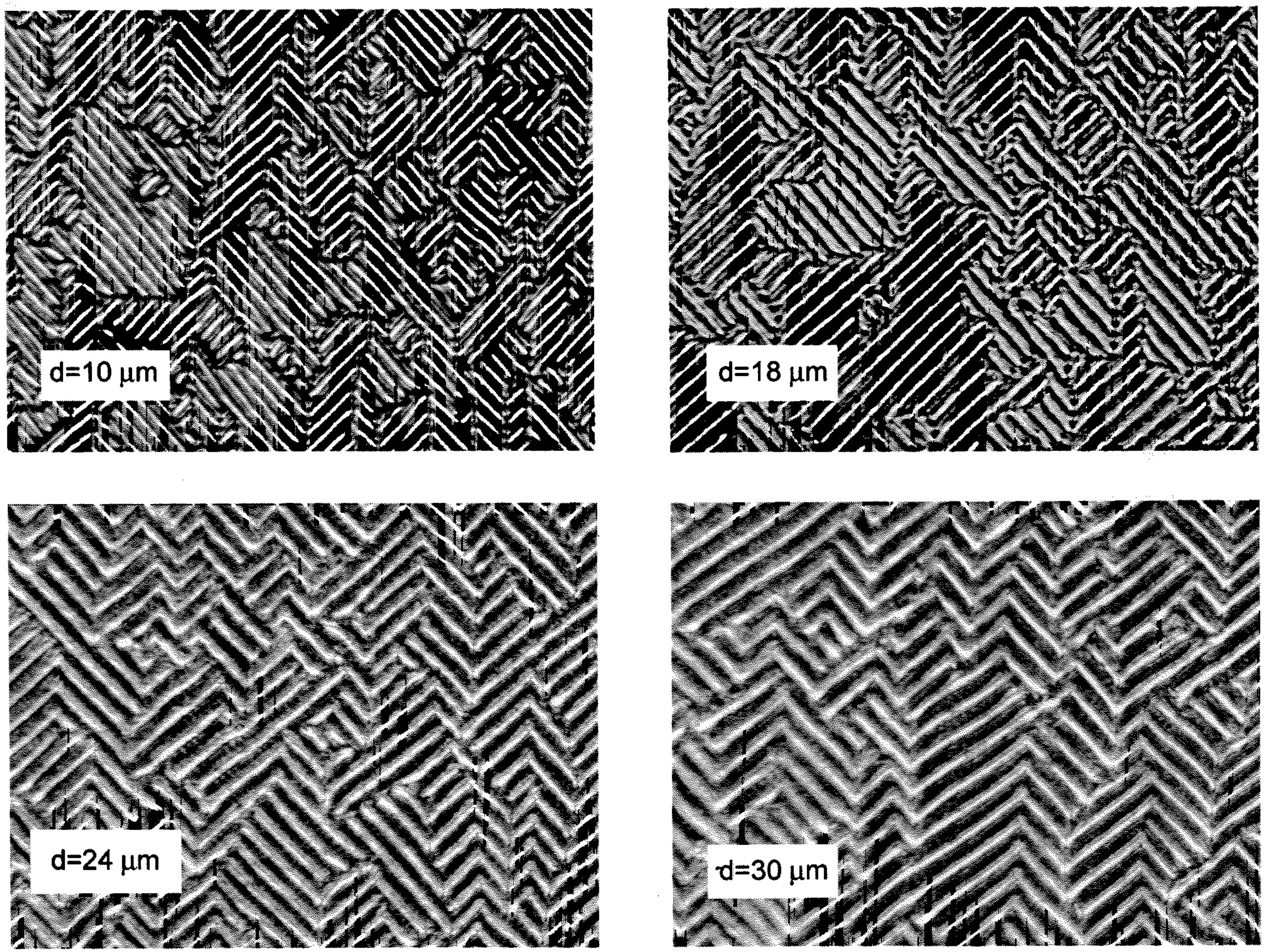


Periodic Frederiks transition

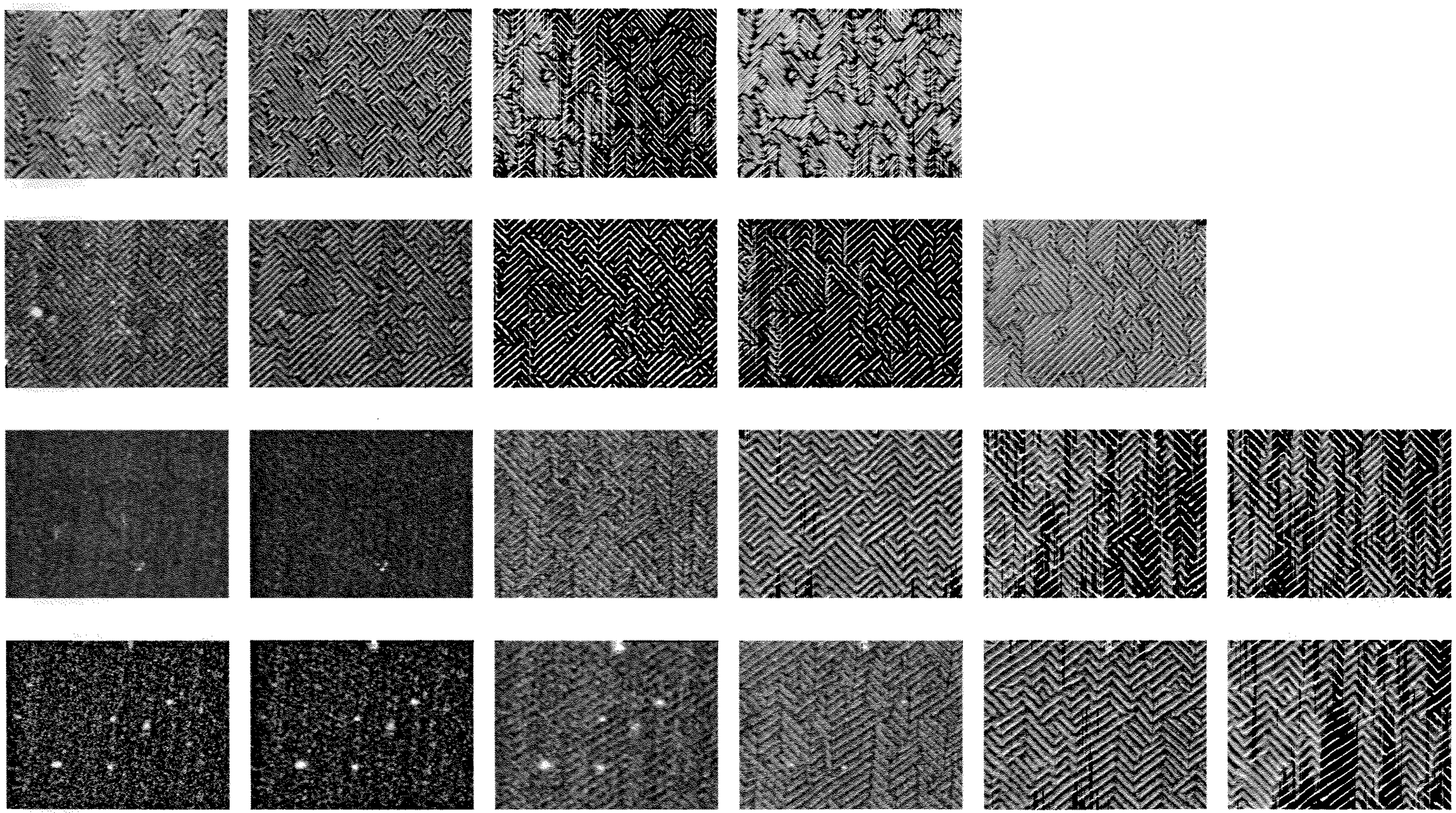
Stripe Pattern Observed



Thickness Dependence of the Pattern



Thickness and Voltage Dependence



10 μm

18 μm

24 μm

30 μm

16V 25V 35V 45V 55V 70V

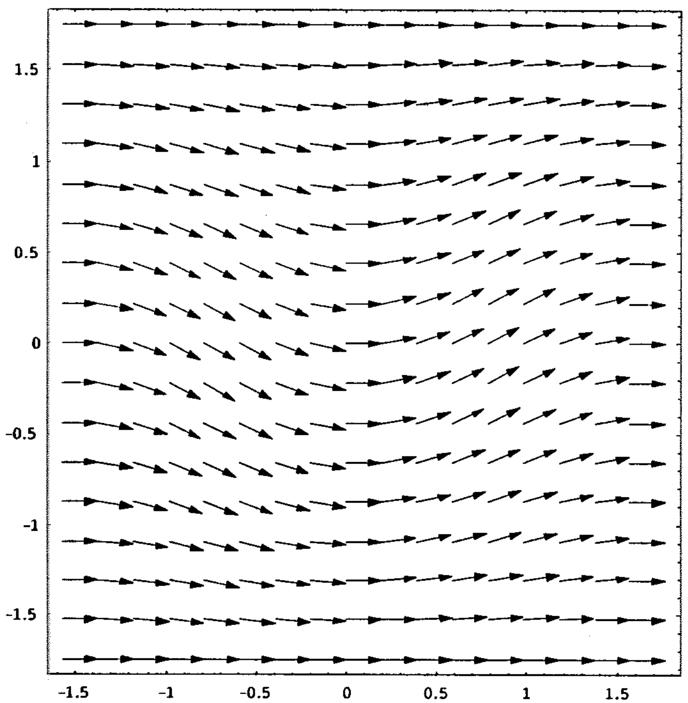
A Simple Model

For Stripes Perpendicular to the Rubbing Direction

Director Field after Transition

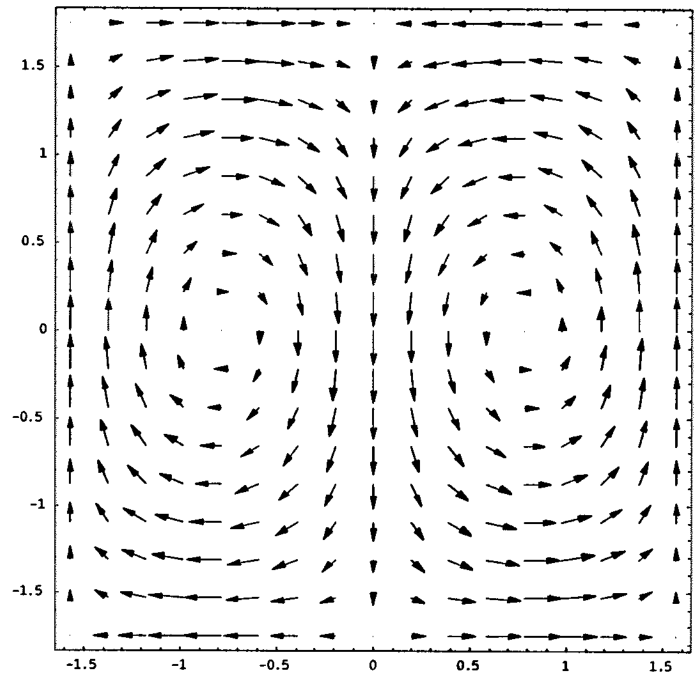
$$\theta(x, y, z) = \theta_0 \cdot Sin[k \cdot y] \cdot Cos[q \cdot z]$$

Where $q = \pi / d$



Displacement Field after Transition

$$\begin{cases} d_x(x, y, z) = d_1 \cdot Sin[k \cdot y] \cdot Sin[q \cdot z] \\ d_z(x, y, z) = d_2 \cdot Cos[k \cdot y] \cdot Cos[q \cdot z] \end{cases}$$



Elasticity in Nematic Elastomers and Gels

$$F = \frac{1}{2}\mu \cdot Tr\left[l_0 \cdot \lambda^T \cdot l^{-1} \cdot \lambda\right]$$

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

$$\propto \delta_{ij} + (r-1) n_i n_j, \text{ where } r = \frac{l_{//}}{l_\perp}$$

$$\lambda_{ij} = \frac{\partial R_i}{\partial R_j^0}$$

The free energy density F of a deformed nematic elastomer is proportional to the shear modulus μ. l_0 and l describe the ellipsoidal polymer coil, with principle axis parallel to the director n, before and after deformation. The Cauchy strain tensor is λ, derived from R^0 and R, the positions of a material point before and after the deformation.

$$F \propto Tr\left[\lambda^T : \lambda\right]$$

In an ordinary rubber, only symmetric components of strain tensor contribute to the free energy density.

$\mu = n k T$

8

Free Elastic and Dielectric Free Energy Density

$$F = \frac{1}{2}\cdot\mu\cdot Tr\left[l_0\cdot\lambda^T\cdot l^{-1}\cdot\lambda\right]$$ Ideal Nematic Rubber Elasticity;

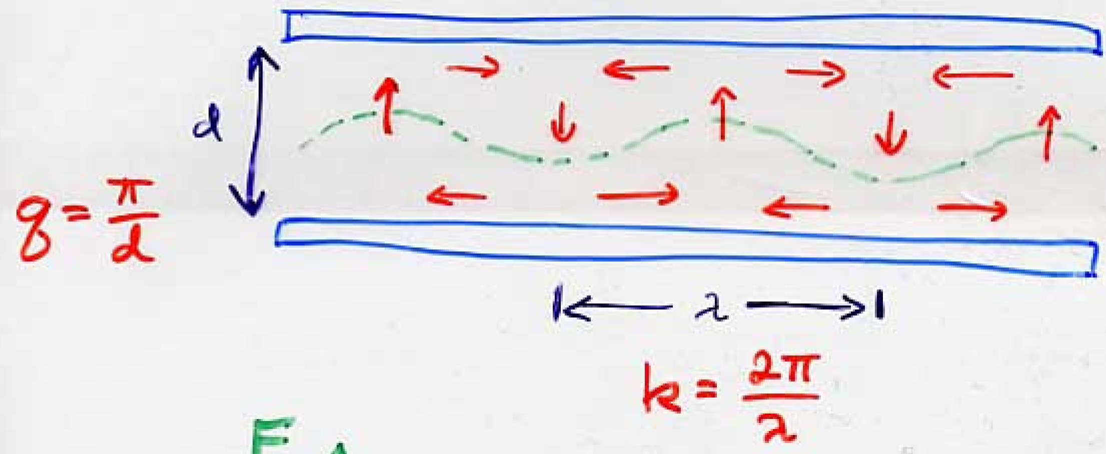
$$+\frac{1}{2}\cdot\mu\cdot A\cdot\left[\lambda_{zz}\cdot Sin\theta+\lambda_{yz}\cdot Cos\theta\right]^2$$ "Semisoft" Contribution;

$$-\frac{1}{2}\cdot\Delta\varepsilon\cdot E^2\cdot Sin^2\theta$$ Dielectric Term;

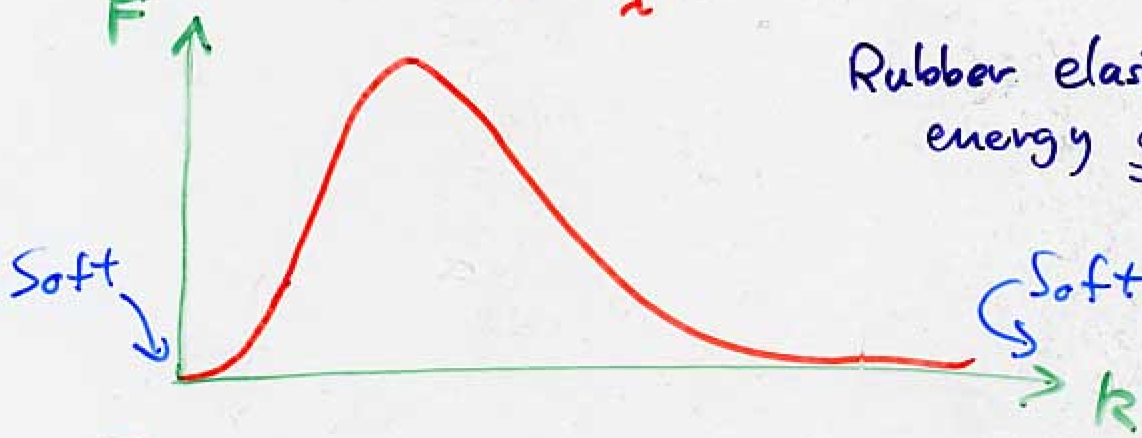
$$+\frac{1}{2}\cdot K_S\cdot[\nabla\cdot n]^2+\frac{1}{2}\cdot K_B\cdot[n\times(\nabla\times n)]^2$$ Frank Elasticity.

Director rotation angle: θ

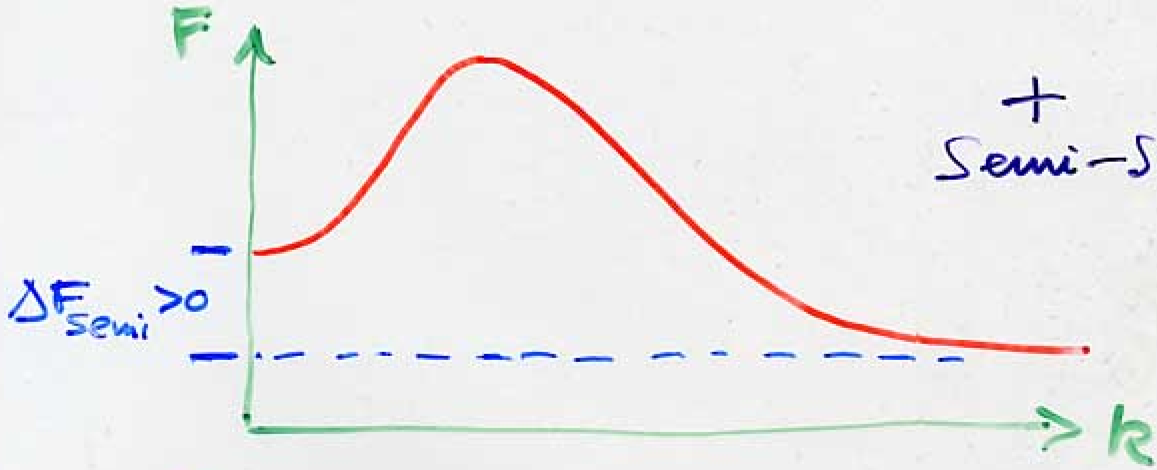
Energetics of the Periodic Response



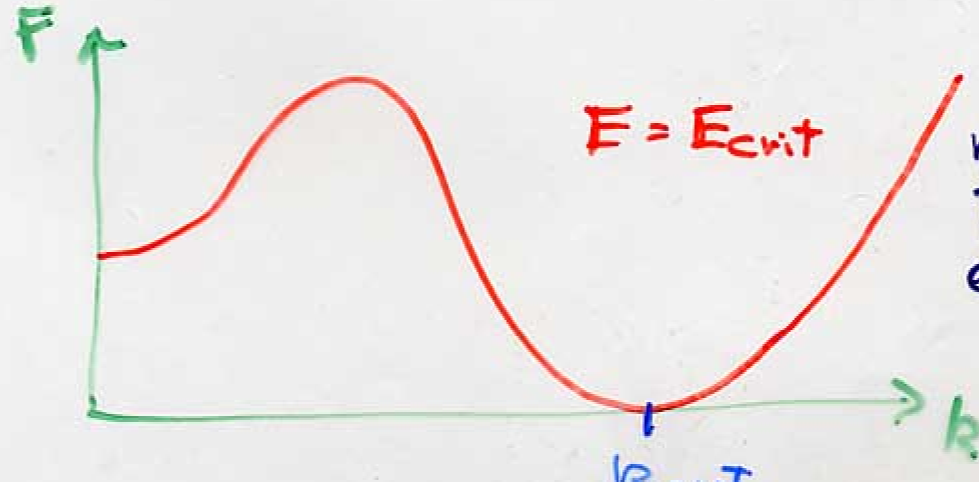
Model



Rubber elastic energy only



\+ Semi-Soft



\+ nematic Bend energy

\+ dielectric energy

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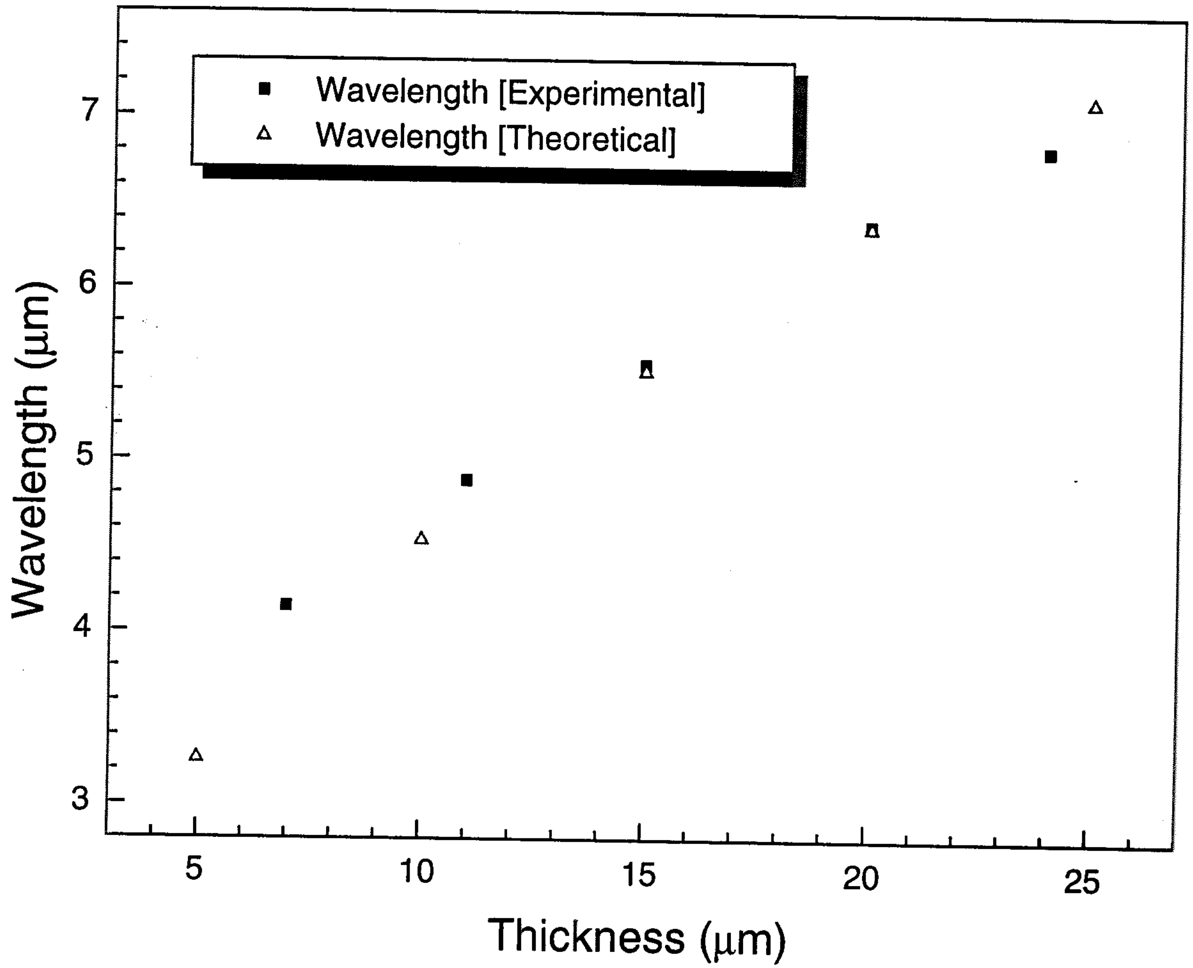
Results from Simple 2-D Model [Wavelength]

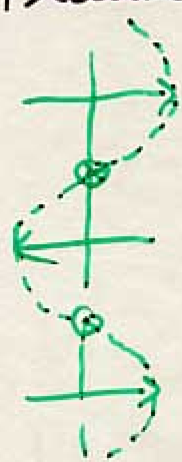


Problem: Isotropic to multidomain nematic.

Compatibility: local strains must all come from a continuous displacement field.

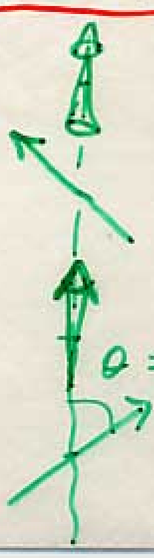
How do local domains elongate parallel to the nematic director, and preserve compatibility?

More specific problem: Isotropic to cholesteric transition: try to elongate parallel to director at each plane in the helix.



Every 1/4 Pitch, elongations at right angles! Clearly not compatible.

Possible Solution: conical helix



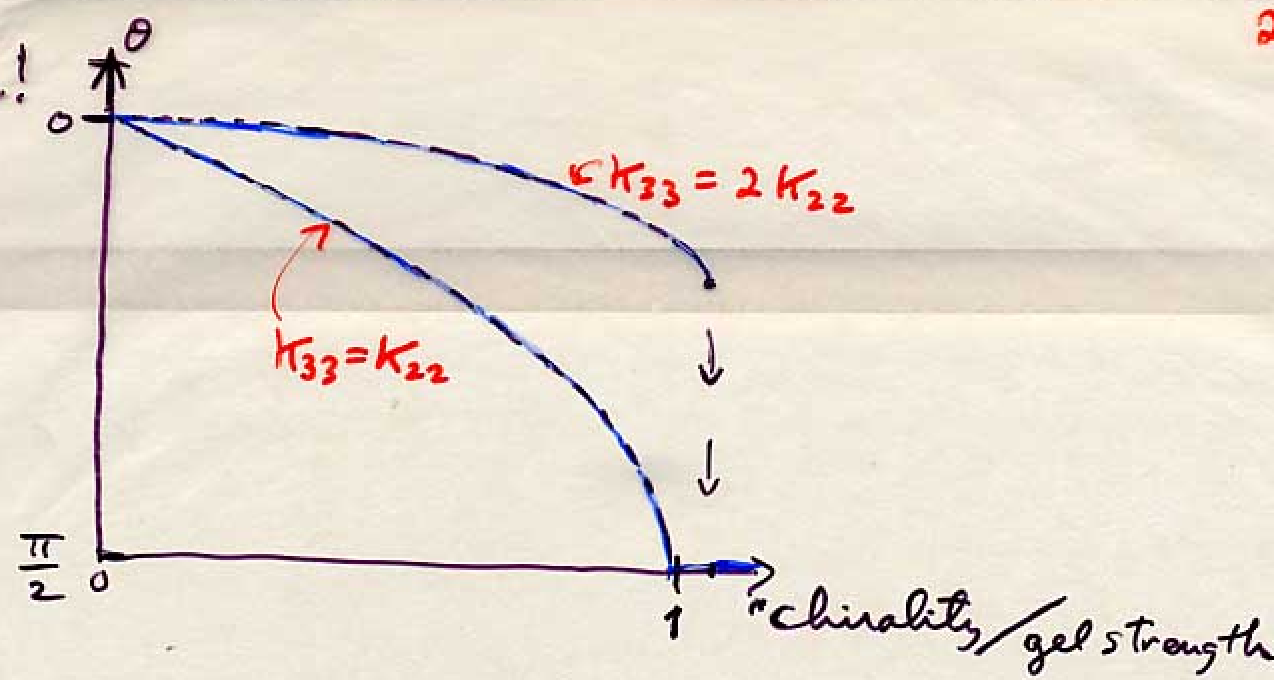
$\theta = \frac{\pi}{2}$ ordinary cholesteric helix incompat.

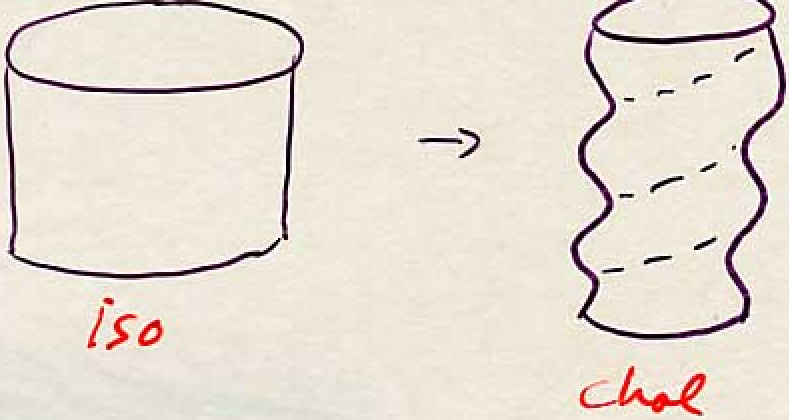
$\theta = 0$ ordinary nematic. compat. (elongate parallel to helix axis

θ = cone angle.

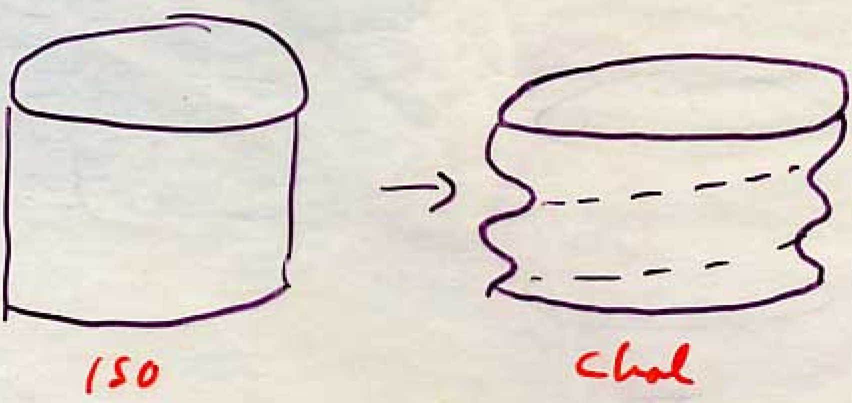
Oblique θ: Some elongation, and some twisting. Will it minimize the free energy??

Yes!

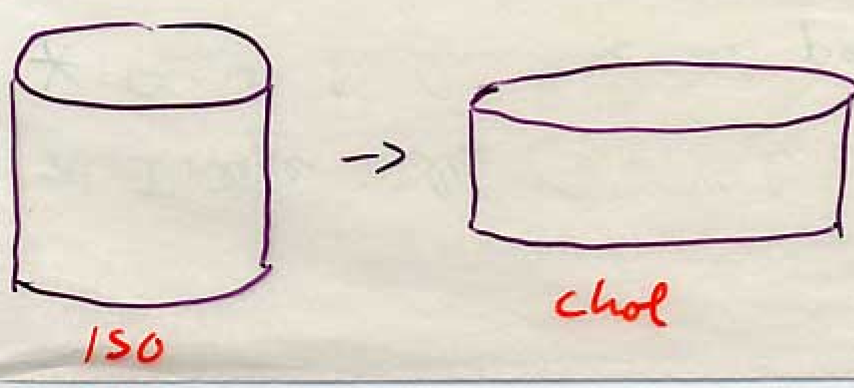




small cone angle



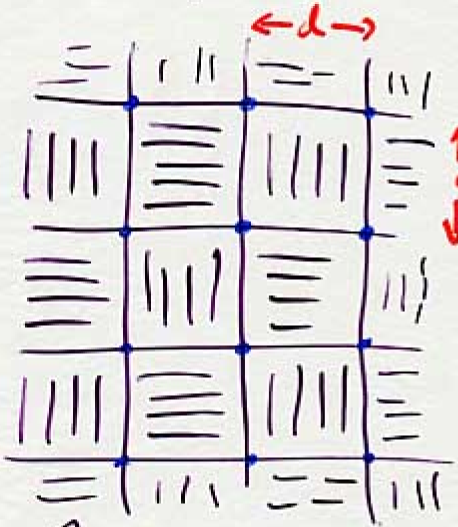
large cone angle



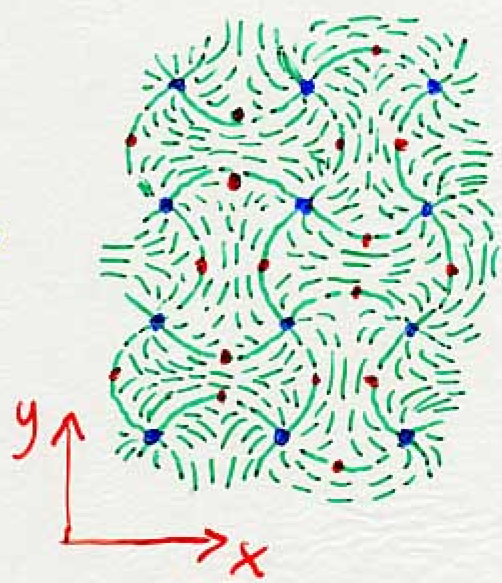
$\theta = \frac{\pi}{2}$

More general isotropic to multidomain nematic transition. Preserving <u>compatibility</u> <u>and</u> allowing <u>elongation</u>. (In a random strain situation.)

Example in 2D (not random)



strain or stress field
isotropic phase



$x \to x + A\cos kx \sin ky$

$y \to y - A\sin kx \cos ky$

$k = \frac{\pi}{d}$

Local elongation in one domain is correlated with $\perp$ elongations in neighboring cells.