Rheology of Liquid Crystalline Polymers:

An Experimental View of Theoretical Needs

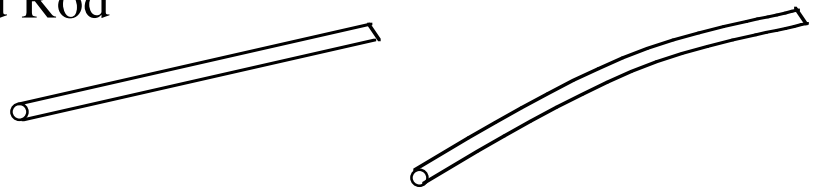
Pat Mather & Wes Burghardt

Outline

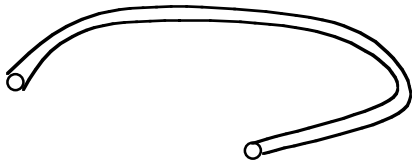
- Background
- Things we know: Lyotropic LCPs
  - Status of theory
  - Ongoing challenges
- Things we are learning: Thermotropic LCPs
  - Theoretical & computational opportunities
- New things we might want to know
  - Interfacial phenomena

LCP Molecular Architecture

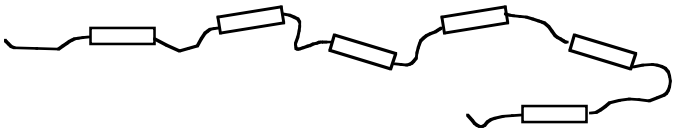
- Rigid Rod/Nearly Rigid Rod



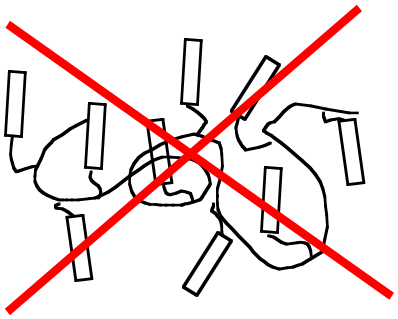
- Persistent/Semi-flexible chain



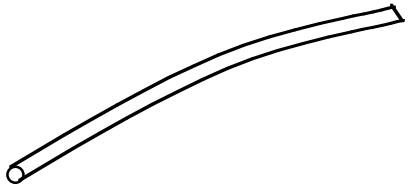
- Mesogen/Spacer Main-Chain

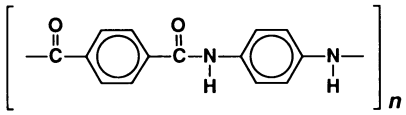
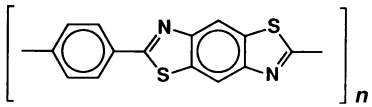
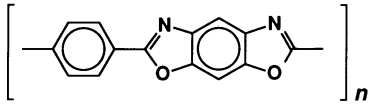


- Mesogen/Spacer Side-Chain



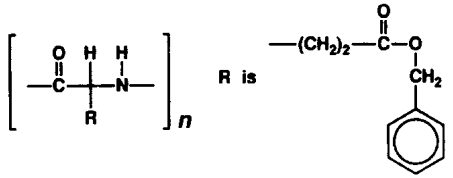
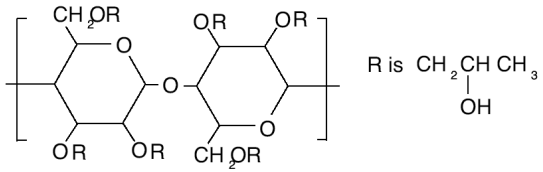
Typical LCP Molecules: Lyotropes



- **PPTA**  $\lambda_p = 29$ nm
- **PBZT**  $\lambda_p = 20$ nm
- **PBO** 

Commercial

- rigid
- chemically regular
- won't melt
- aggressive acid solvents
- moisture sensitive

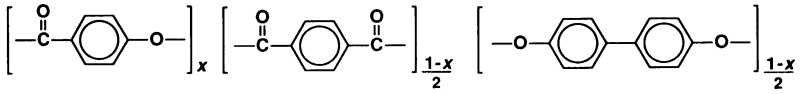
- **PBG**  $\lambda_p = 90$ nm
- **HPC**  $\lambda_p = 12$ nm

'Model'

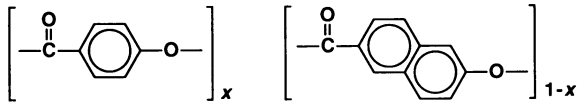
- rodlike owing to helix formation
- soluble in diverse organic solvents
- stable

Typical LCP Molecules: Thermotropes

- Xydar®

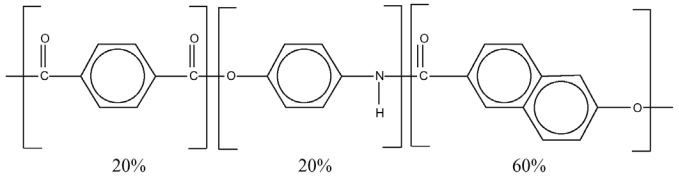


- Vectra A®



$\lambda_p = 12$ nm

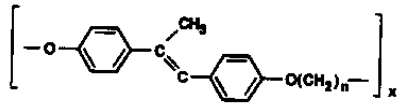
- Vectra B®



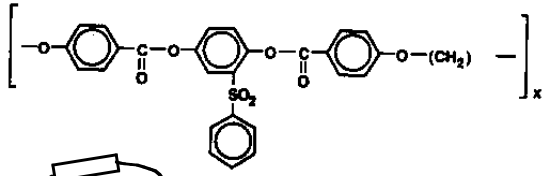
Commercial

- **copolymers to suppress melting point; melt at ~ 300˚C**
- **inaccessible isotropic phase**
- **poor stability in melt phase**

- DHMS-7,9



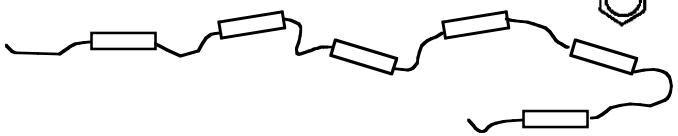
- PSHQ-n

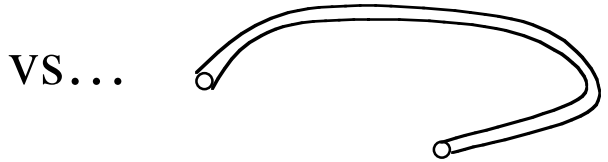


$\lambda_p = 6$ nm

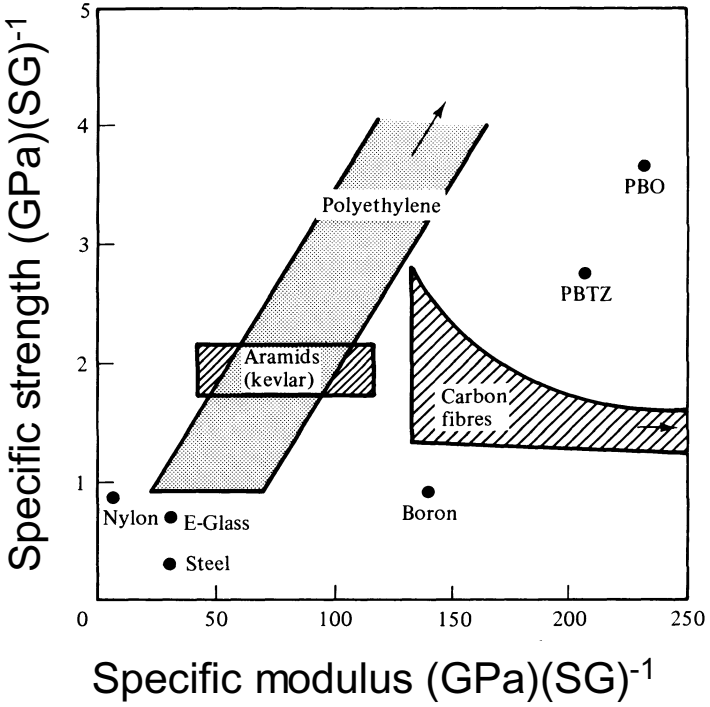
'Model'

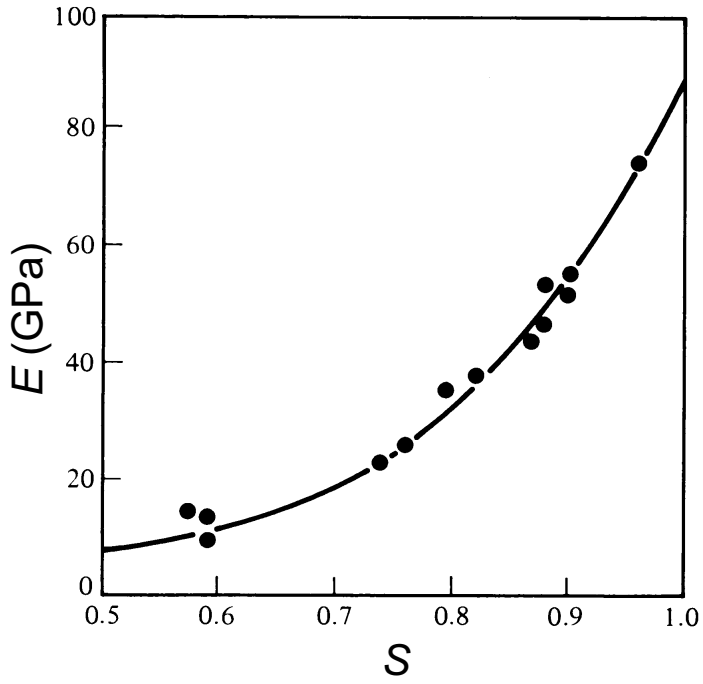
- **accessible isotropic phase**
- **convenient T range (~120-100˚C)**
- **thermally stable**



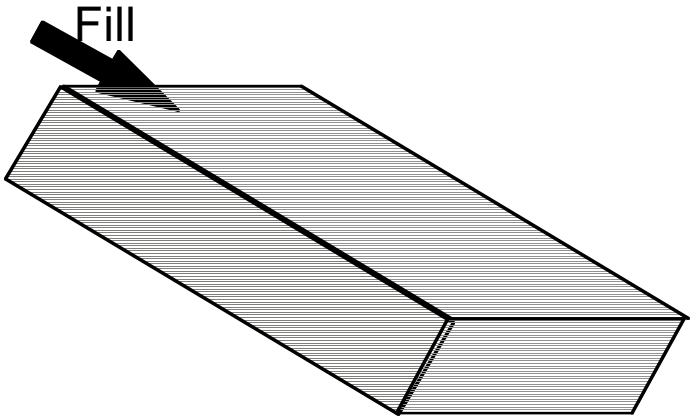


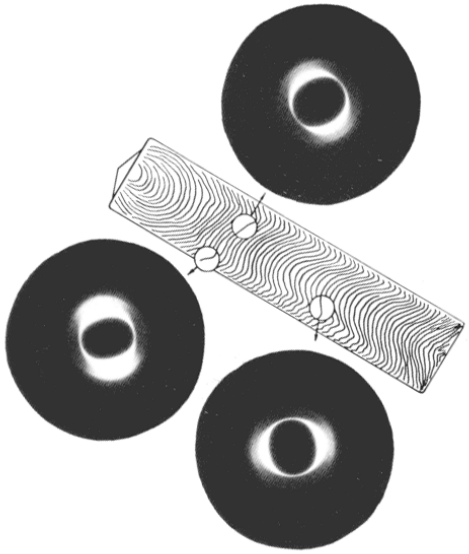
Technology: high strength fibers





Technology: Complex flows, complex structure





(Weng, et al., *J. Mater. Sci.*, **21**, 744, 1986)

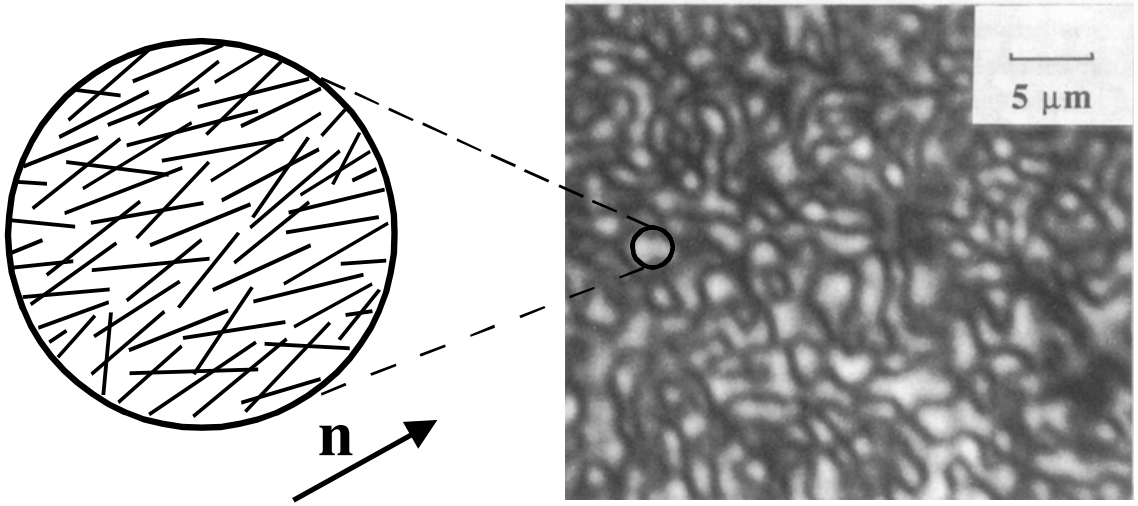
LCP Structure

(a) Microscopic

u = test molecule orientation

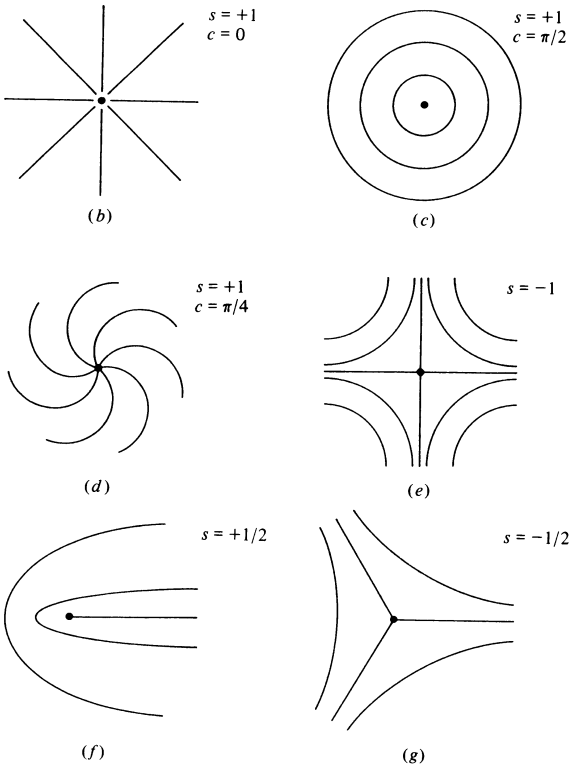
(b) Mesoscopic

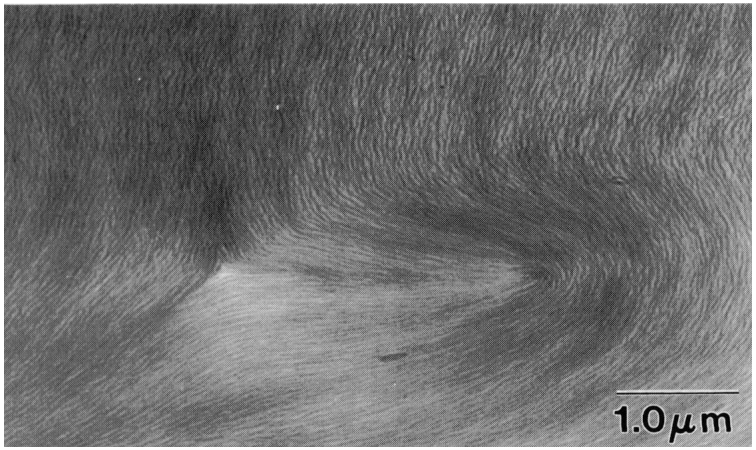
n = director orientation



$\Psi(\boldsymbol{u})$	**Orientation Distribution Function**	$\overline{\Psi}(\boldsymbol{n})$
$\boldsymbol{S}_m = \langle \boldsymbol{uu} \rangle - \boldsymbol{I}/3$	**Order Parameter Tensor**	$\overline{\boldsymbol{S}} = \langle \boldsymbol{nn} \rangle - \boldsymbol{I}/3$
S_m	**Scalar Order Parameter**	$\overline{S}$

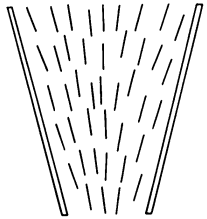
Disclinations in LCPs

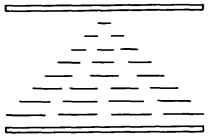


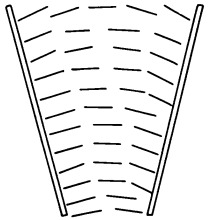


Fundamental LC Statics and Dynamics: Leslie-Ericksen Theory (nematics)

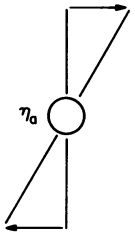
- 3 Elastic constants:

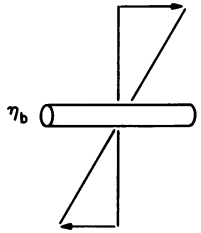
Splay K_1 

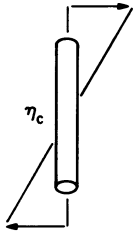
Twist K_2 

Bend K_3 

- **6 Viscosities: $\alpha_1 - \alpha_6$**
  eg, Miesowicz viscosities







$\eta_a = 1/2\ \alpha_4$ $\eta_b = 1/2\ (\alpha_3 + \alpha_4 + \alpha_6)$ $\eta_c = 1/2\ (-\alpha_2 + \alpha_4 + \alpha_5)$

Two levels of structure; Two sources of elasticity

- Gradient (distortional) elasticity
  - Free energy penalty for spatial variations in **n**(**r**)
  - Ericksen number:

$$Er = \frac{\eta V h}{K} = \frac{\dot{\gamma}\eta h^2}{K}$$

  - Ratio of hydrodynamic torques on **n** to distortional elastic torques on **n**
  - Distortional relaxation time:

$$\lambda_d = \frac{\eta h^2}{K}$$

- Molecular elasticity
  - Flow-induced changes in local molecular organization (e.g. *S*)
  - Deborah number:

$$De = \lambda_m \dot{\gamma}$$

  - λ_m = molecular relaxation time, ~ $1/D_r$.

Typical parameters for LCPs in rheological testing & processing

$\eta \sim 1000$ Poise; $K \sim 10^{-6}$ dyne; $h = 0.1$ cm

$\lambda_d \sim 10{,}000{,}000$ sec

$\lambda_m \sim 0.1$ sec

Shear Rate (1/s)	Ericksen Number	Deborah Number
0.001	10,000	0.0001
0.01	100,000	0.001
0.1	1,000,000	0.01
1	10,000,000	0.1
10	…	1
100	…	10

With thinner samples, can ‘tame’ Ericksen number somewhat, but…

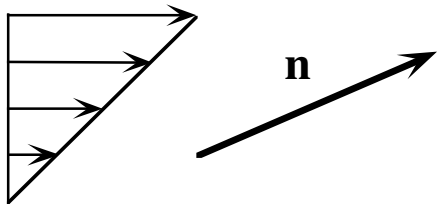
Here is an obvious problem for modeling

Some theories

- Leslie-Ericksen Theory
  - Continuum
  - Linear in velocity gradients; leading-order distortional effects
  - *Er* is critical parameter
- Ericksen TIF theory
  - L-E without distortional elasticity
  - Effectively set $Er = \infty$
- Larson-Doi model
  - Average of L-E theory over distribution of domain orientations in polydomain LCPs
- Doi molecular model (many flavors)
  - *Rigid* rod polymer *solutions*
  - No distortional elasticity
  - Molecular viscoelasticity
  - *De* is critical parameter
- Extensions of theory:
  - Effects of flexibility
    - Rodlike: Subbotin; Marrucci & Greco
    - Flexible but extended: Long & Morse (nematic Rouse)
    - High flexibility limit
      - Marrucci & Maffettone (nematic dumbbell)
      - Long & Morse (nematic Rouse)
  - Theories with gradient + molecular elasticity
    - Beris & Edwards
    - Rey
    - Feng
      - Both *De* and *Er*

Tumbling vs. Flow Alignment

- LCs may be classified according to alignment behavior under shear flow:



$$\frac{\partial \underline{n}}{\partial t} = \underline{n} \cdot \underline{\underline{\omega}} + \lambda(\underline{n} \cdot \underline{\underline{D}} - \underline{\underline{D}} : \underline{nnn})$$ ***Ericksen's Model***

λ = "tumbling parameter"

$|\lambda| > 1 \rightarrow$ "Flow Aligning"

$|\lambda| < 1 \rightarrow$ "Tumbling"

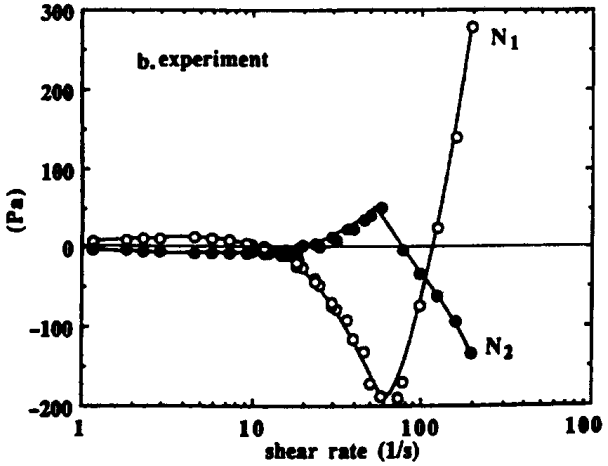
$$\lambda = \frac{-(\alpha_3 + \alpha_2)}{\alpha_3 - \alpha_2}$$

- To *begin* to understand rheology, texture & orientation development under shear, or processing, this is the most important question to answer.

Lyotropes: Complex Rheology

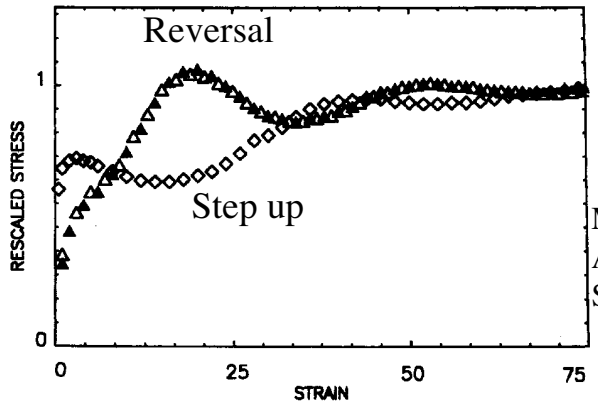
(All data for PBG)

Normal stresses: sign changes



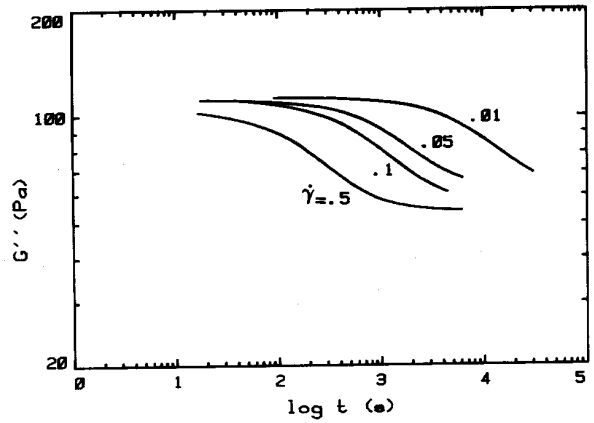
Magda et al. *Macromolecules*, **24**, 4460 (1991)

Stress oscillations in transient flows



Moldenaers et al. ACS Symposium Series 435 (1990)

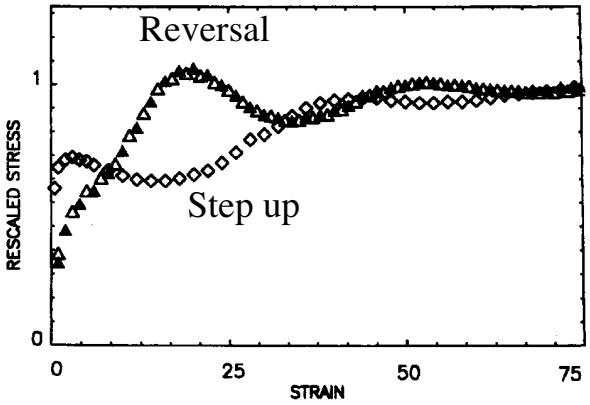
Slow structural evolution in relaxation

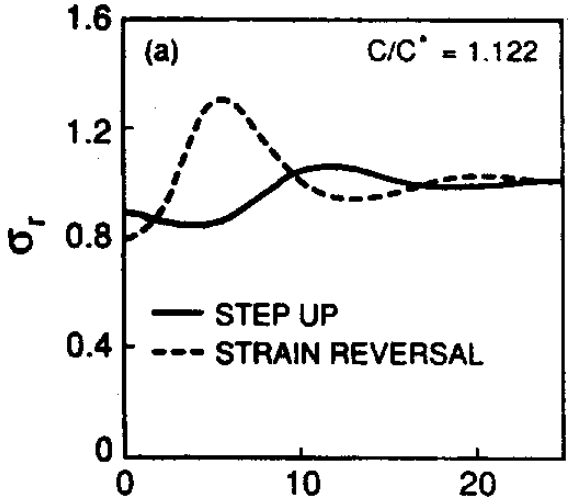


Moldenaers et al. *J. Rheol.* **30**, 567 (1986).

Lyotropes: We're doing pretty well...

Stress oscillations in transient flows at low rates

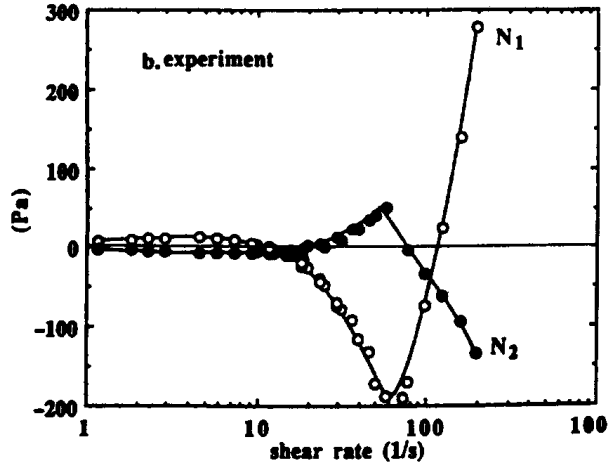


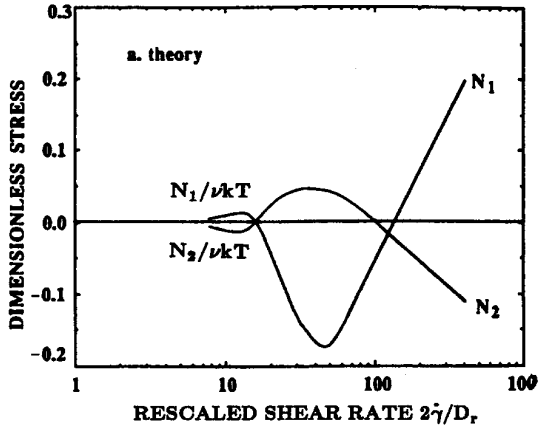


- Origin: director tumbling at low *De*.
- Strain scaling: follows directly from L-E theory
- Dampening: distortional elastic effects within polydomain structure
- Model: Larson-Doi polydomain

Lyotropes: We're doing pretty well...

Bizarre normal stresses...

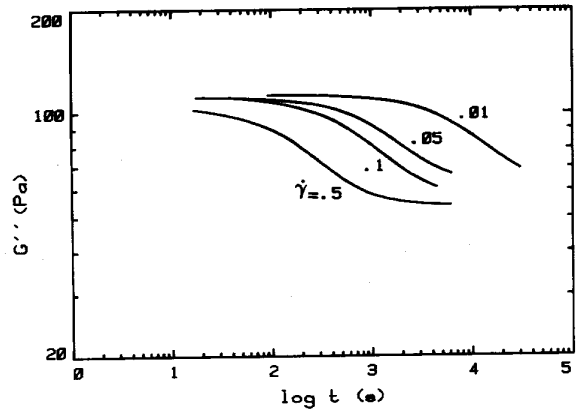


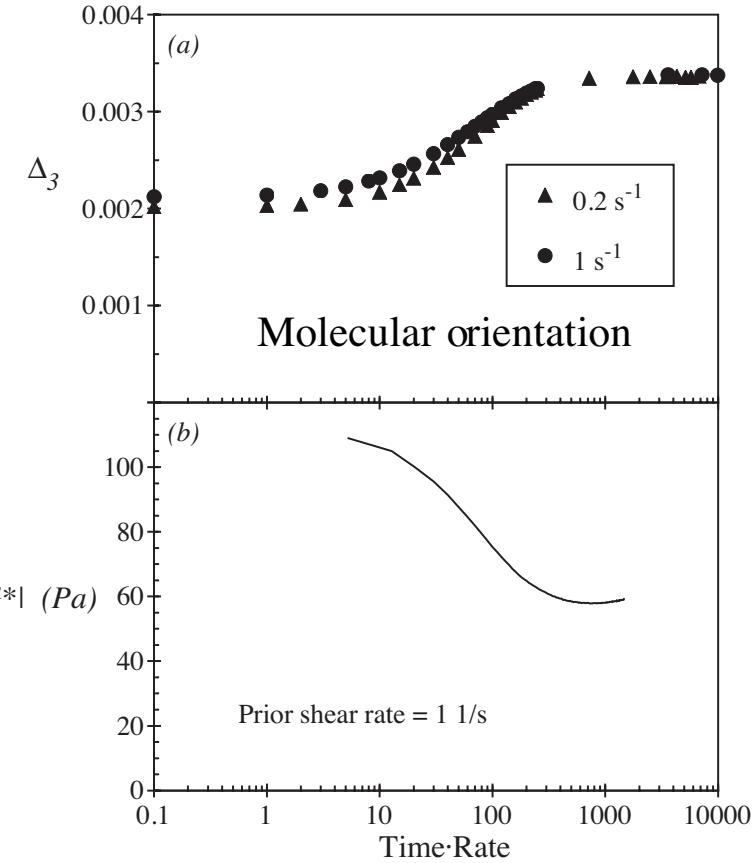


- Origin: Shear-induced *decrease* in local molecular order in certain shear rate range (Marrucci & Maffettone)
- Associated with predicted dynamic sequence:
  Tumbling --> 'Wagging' --> Flow alignment
- Model: Doi model (calculations of Larson et al.)

Lyotropes: We're doing pretty well...

Slow evolution of dynamic moduli





- Origin: Slow increase in average molecular orientation upon flow cessation.
- Relaxation scaling/Texture refinement:

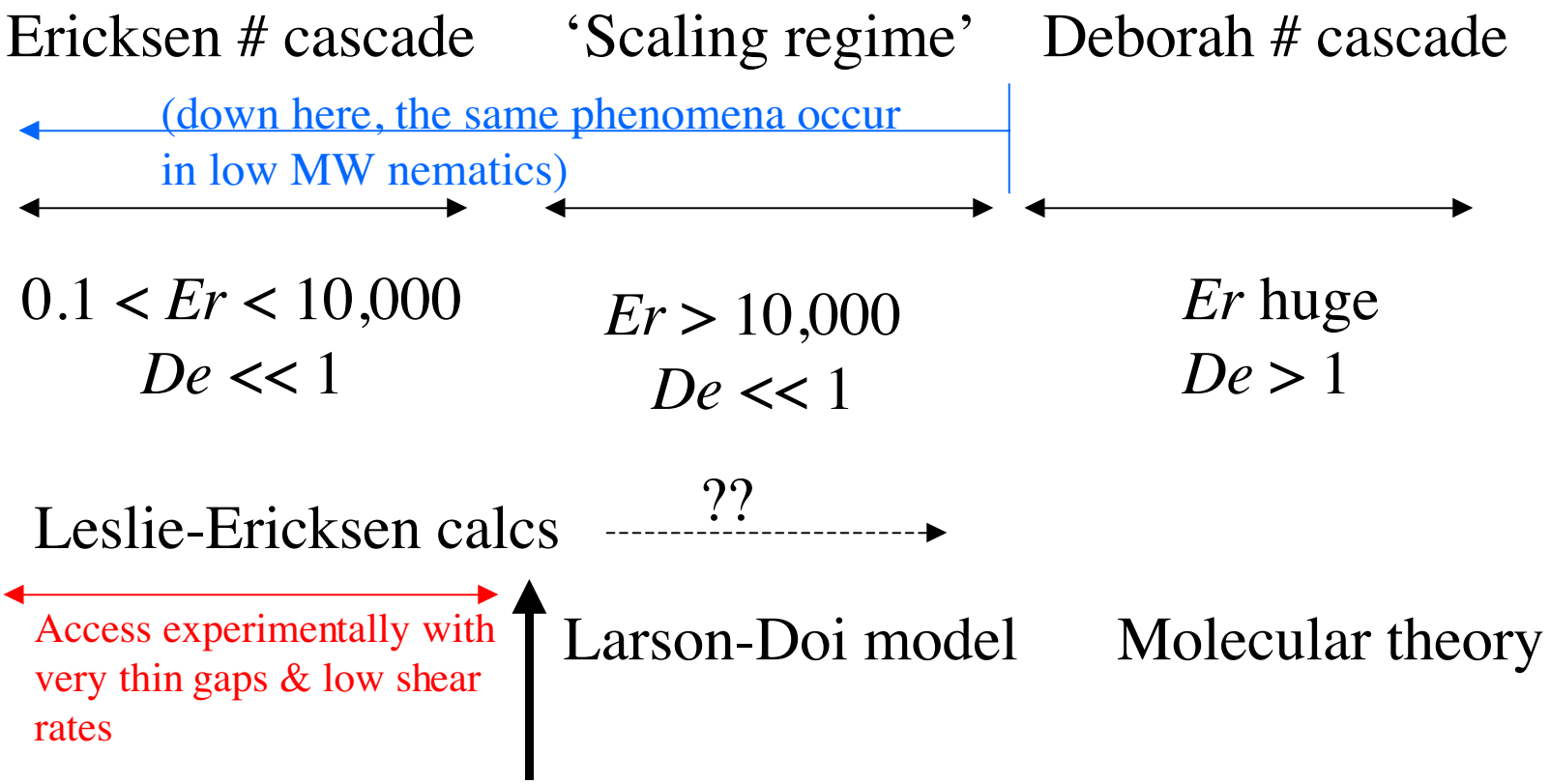
$$\lambda_d = \frac{\eta d^2}{K};\ \lambda \sim \frac{1}{\dot{\gamma}} \Rightarrow d \sim \dot{\gamma}^{-1/2}$$

- d = *texture* length scale, *not* flow dimension
- Model: these scaling arguments of are built into Larson-Doi model, but…
- Why does orientation go up? (It goes down in other systems…) Larson-Doi predicts it goes down.

Lyotropes: Ongoing challenges

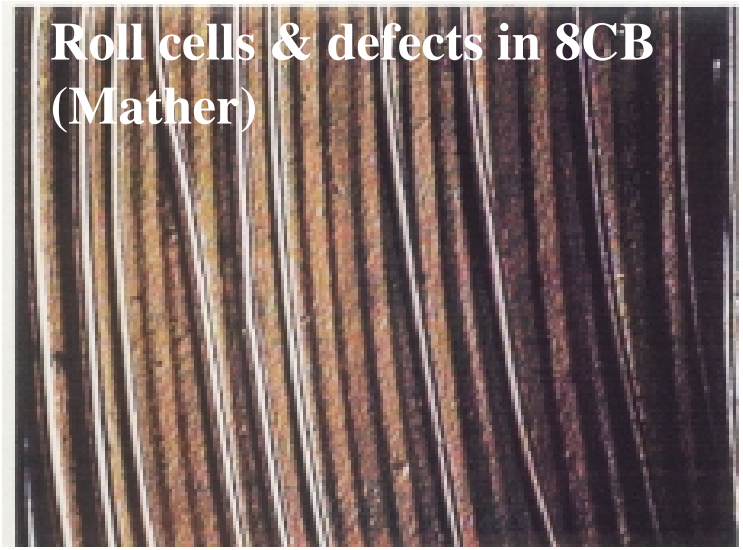
- Texture development in tumbling nematics
- Improved description of ‘scaling regime’

Texture development in tumbling LCPs (borrowing from Larson & Mead)



Texture development: moderate *Er*

- *Er* ~ 100s - 1000s
  - Primary phenomenon is 'roll-cell' instability, leading to defect nucleation
    - L-E Stability analyses by Manneville & Larson
    - L-E Simulations by Feng & Leal
    - Experiments by Mather, Larson, Srinivasarao...



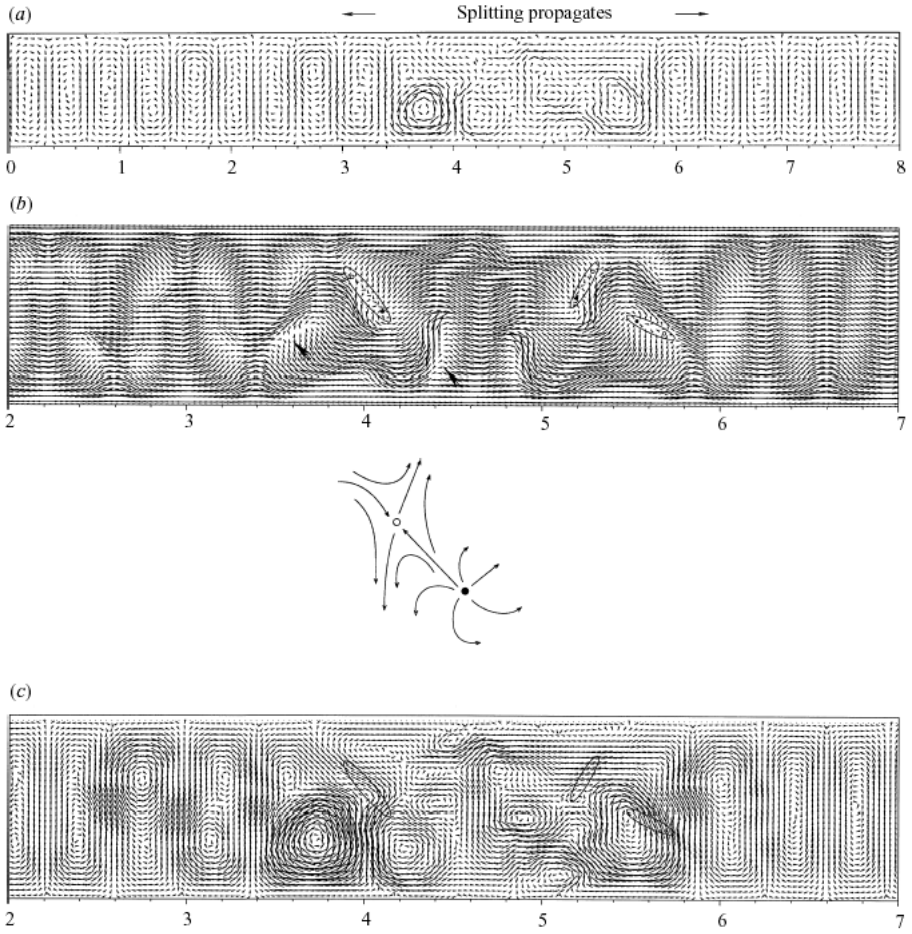


FIGURE 12. Cell splitting and secondary breakup lead to irregular patterns and three pairs of ± 1 disclinations at $t = 60$. (*a*) The whole flow field; (*b*) the director field. The large arrows point to two ridges, and the ellipses enclose pairs of defects, with open circles indicating -1 defect cores and filled circles $+1$ ones. At defect cores and the top of the ridges, $\boldsymbol{n}$ is in the flow direction, perpendicular to the page. The $\boldsymbol{n}$-field in the neighbourhood of one pair of defects is sketched. (*c*) Details of the flow field near the defects showing fast jet-like flows toward the $+1$ core.

Texture development: Issues

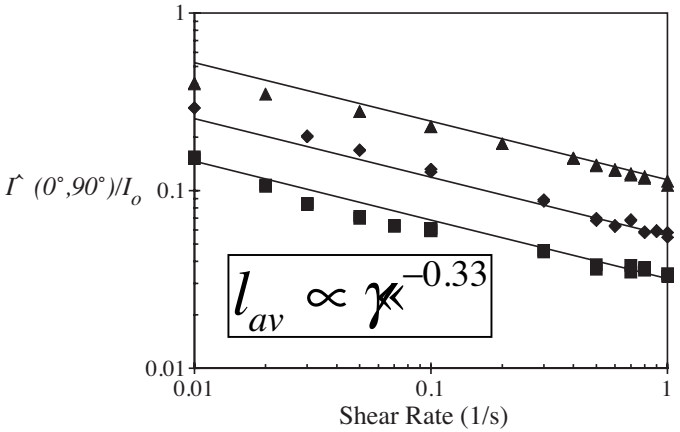
- L-E simulations can predict defect topology, but cannot give a realistic accounting of defect cores
  - Fix: Work with 'complete' models with molecular representation of gradient elasticity
    - Tsuji & Rey have worked along these lines; update?
    - Feng & Leal in progress?
- The problem of length scales:
  - Rheological testing: $h \sim 1$mm $d \sim 10$-$20\ \mu$ defect core: $0.1\ \mu$?
  - Even in roll cell experiments, $h \sim 100\ \mu$. If we want to resolve order parameter distribution within interior of defect core, need grid ~ 10 nm.
  - What to do?
    - No choice but to adopt unrealistically small gap sizes to bring characteristic length/time scales into closer coincidence.
    - Hopefully learn fundamental physics about defect generation, etc. Have to figure out a way (multi-scale?) to feed this information into coarser models.

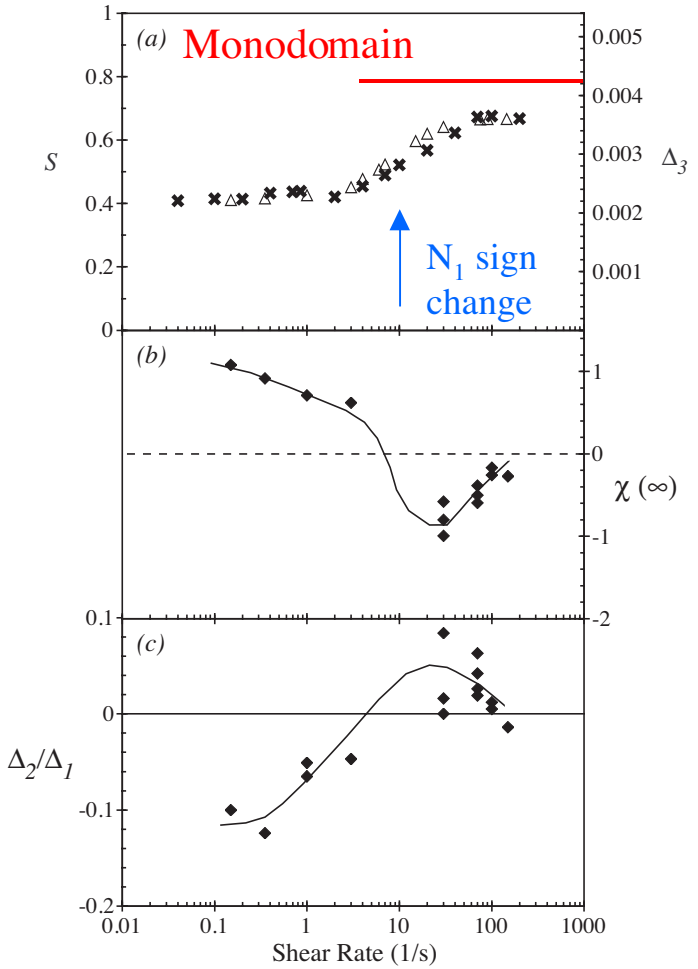
Texture development: Scaling regime

- Director tumbling, flow instabilities, defect generation, etc, lead to increasingly complex texture under shear ('director turbulence').
- Director & velocity are highly coupled, time-dependent and fully three-dimensional functions of position.
- As defects proliferate, 'communication' across sample via distortional elasticity is screened; macroscopic flow length scale no longer important (role of texture length scale).
- Texture refinement: increasing shear rate drives down texture size to maintain rough balance between hydrodynamic and elastic torques at texture scale.
- $Er \geq 10^4$; $De << 1$
- Currently out of reach of detailed simulation; for now, left with polydomain models (e.g. Larson-Doi).

Larson-Doi Model: Status

- Predicts orientation state is independent of shear rate.
- Predicts small positive orientation angle at low rates (positive 1-2 component of average orientation tensor)
- Predicts biaxial orientation state at low rates, with higher orientation in vorticity than gradient direction
- Predicts texture refinement





Orientation state in scaling regime

$$\langle \mathbf{nn} \rangle_{Larson-Doi} = \begin{bmatrix} 0.866 & 0.048 & 0 \\ 0.048 & 0.048 & 0 \\ 0 & 0 & 0.085 \end{bmatrix} \qquad \langle \mathbf{nn} \rangle_{Experiment} = \begin{bmatrix} 0.727 & 0.010 & 0 \\ 0.010 & 0.096 & 0 \\ 0 & 0 & 0.177 \end{bmatrix}$$

- Larson-Doi model *over predicts* anisotropy
- *Could* be consequence of quadratic closure approximation (Kawaguchi & Denn: 'kinetic domain' version of polydomain model in two dimensions, without closure)

- Low-hanging fruit: Evaluate the 3-D orientation state predictions of the Larson-Doi without closure approximations?

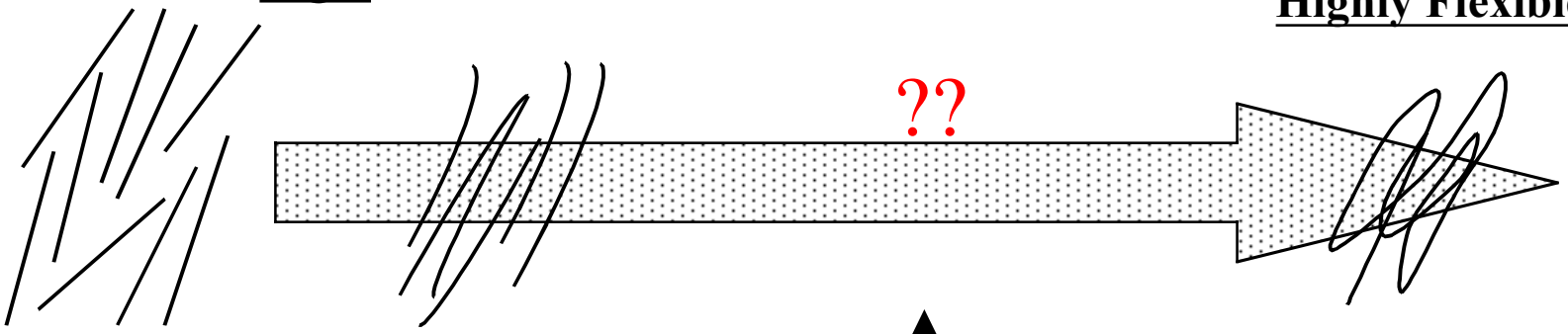
- Moderate-hanging fruit: Try using Larson-Doi model in more complex flow field/structure calculations?

Future needs in scaling regime

- Brute force? LE calculations might be pushed up in dimension & sufficiently far in Ericksen number to enter scaling regime (can evaluate **<nn>** to compare with data).
- 'Complete' models? Computers won't be big enough anytime soon to directly attack problem.
- But…
  - Remember that in scaling regime, LCP determines its *own* texture size; macroscopic dimension irrelevant.
  - Note that scaling regime ends when texture size approaches molecular dimensions: this is exactly conditions under which 'complete' models may be plausibly applied. Target *high* end of scaling regime directly.
  - *Proposal*:
    - 'Complete' theory. No director BCs (3-D computational cell with period BC).
    - Quench into nematic; allow to coarsen until defect density is reasonable
    - Apply shear flow. Fully couple 3-D director and 3-D velocity profiles.
    - Use this detailed information to develop improved phenomenology for statistical polydomain models.
    - Larson-Doi analog for 'complete' theories??

Role of Chain Flexibility in LCP Dynamics

Rigid **Highly Flexible**



Rigid Rods

Doi Model

Tumbling

Slightly bent rods

Subbotin
Marrucci & Greco

Even *more* tumbling

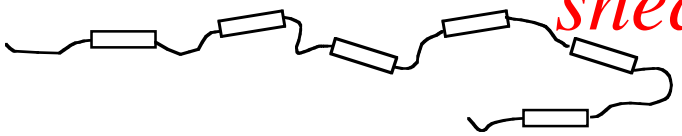
Wormlike chains, nematic dumbbell, nematic Rouse

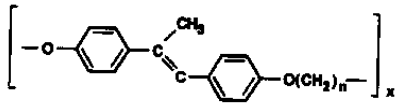
Semenov (1987), Maffettone & Marrucci (1992), Long and Morse (2000)

All predict flow-alignment

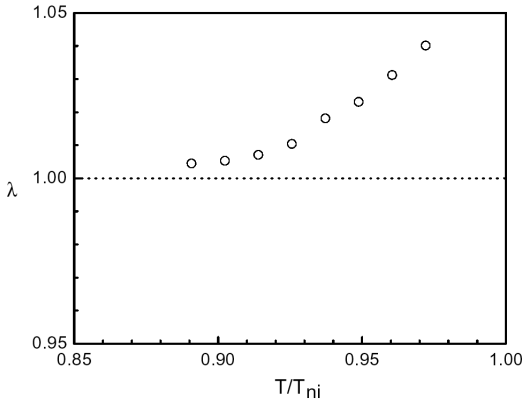
Hinged rigid rod
(Leal)

Mesogen-space main-chain LCPs appear to be *shear aligning* as rule

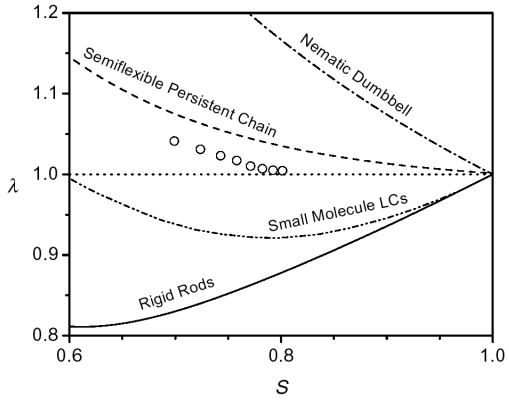


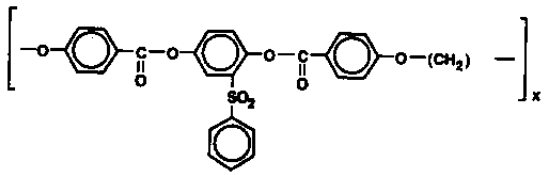
DHMS-7,9 

- Zhou & Kornfield
- Monodomain conoscopy
- Quantitative measurements of λ



Monodomain Δn to estimate S...



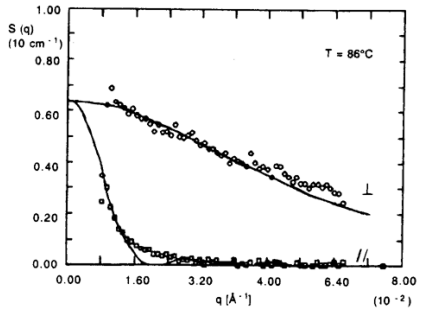
PSHQ-n 

- Han & Mather; Ugaz & Burghardt
- Rheology, orientation, texture; *indirect* evidence of alignment

Specific needs for molecular theory

- Have theories at opposite ends of flexibility spectrum
- However, no real thermotropes seem to fit in these limits
- Specific issues: hairpin defects:

Harduin et al (1995)

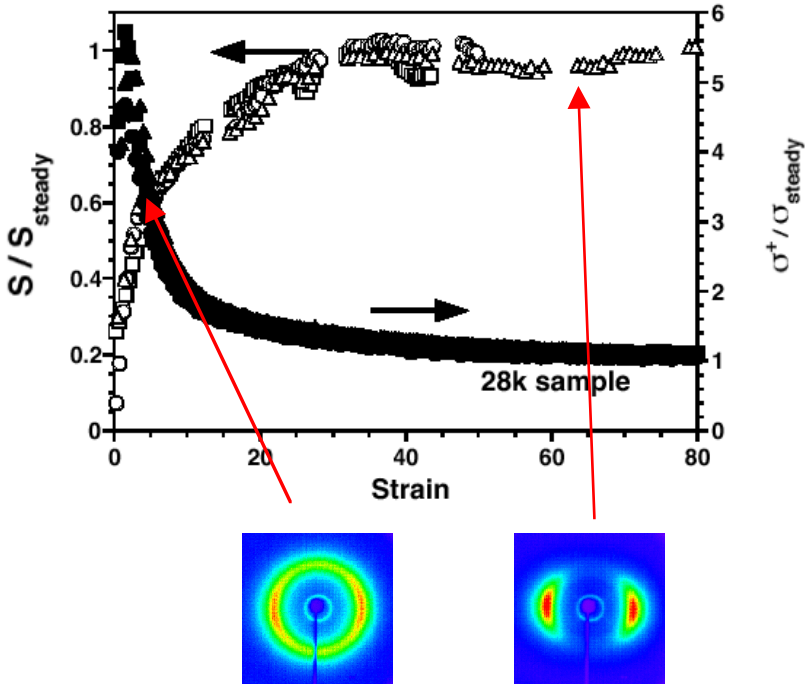


- *Many* hairpins/chain: nematic Rouse model (unentangled); Long & Morse

- 'Opportunities'
  - Does someone want to extend Semenov's semiflexible chain model to predict λ as one moves between rigid & high flexibility limits?
  - Does someone want to derive a molecular theory for λ for chains with 1 or 2 hairpin defects?
  - Are entanglements important?

Aligning LCPs are simpler!!

- Shear flow inception from random polydomain



- DHMS-7,9
  - Strain scaling (low *De*?)
  - Monotonic growth in orientation
  - Single shear stress overshoot

- Polydomain Ericksen modeling
  - Throw out everything *except* distribution of domain orientations.
  - Simulate initially random ensemble of director orientations
  - Compute orientation/stress from ensemble averages

$$\bar{S}_{11} - \bar{S}_{33} = \langle n_1^2 \rangle - \langle n_3^2 \rangle$$

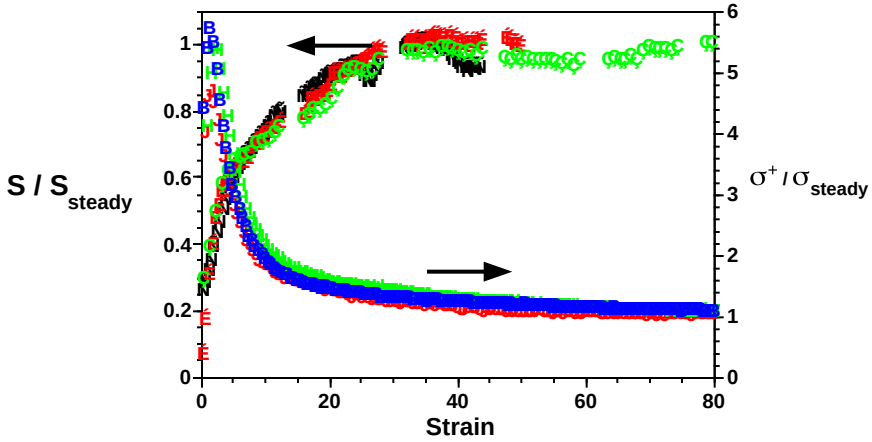
$$\sigma_{12} = \left[\mu + 2\mu_1 \langle n_1^2 n_2^2 \rangle + \frac{\mu_2}{2} \langle n_1^2 + n_2^2 \rangle \right] \dot{\gamma}$$

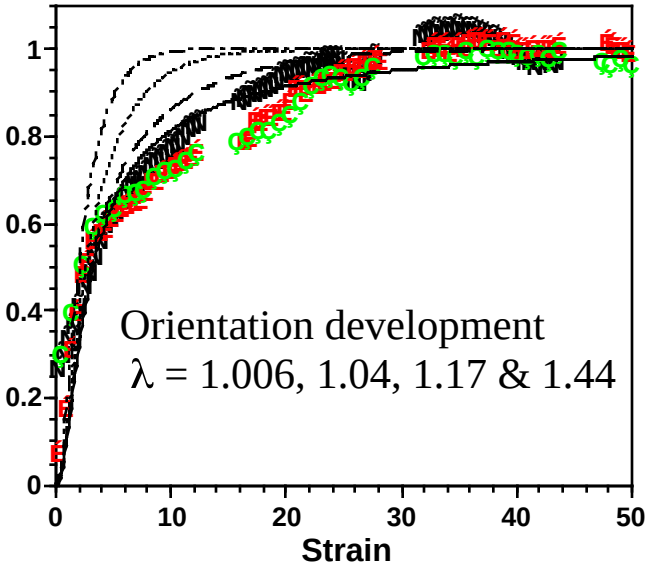
$$N_1 = 2\mu_1 \left[\langle n_1^3 n_2 \rangle - \langle n_1 n_2^3 \rangle \right] \dot{\gamma}$$

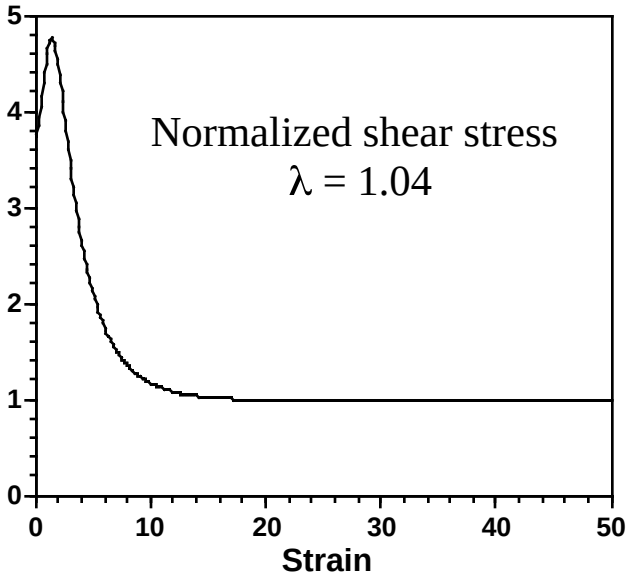
  - Parameters from nematic dumbbell/Rouse:

$$\frac{\mu_1}{\mu} = \frac{2\lambda}{\lambda - 1} \qquad \frac{\mu_2}{\mu} = -2$$

Polydomain Modeling: Shear Flow Inception







Polydomain Ericksen model: Heuristics for flow inception

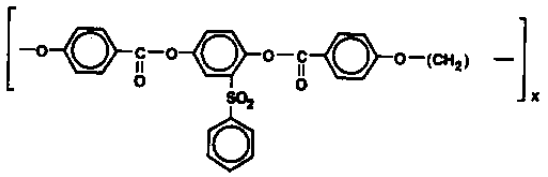
- Flow aligning dynamics:
  - Single shear stress overshoot
  - Monotonic orientation development
- At steady state, in flow-aligned condition
  - Using viscosity predictions of a wide range of molecular theories for LCPs:

$$\left.\frac{N_1}{\sigma}\right|_{SS} = \frac{2}{\sqrt{\lambda^2 - 1}}$$

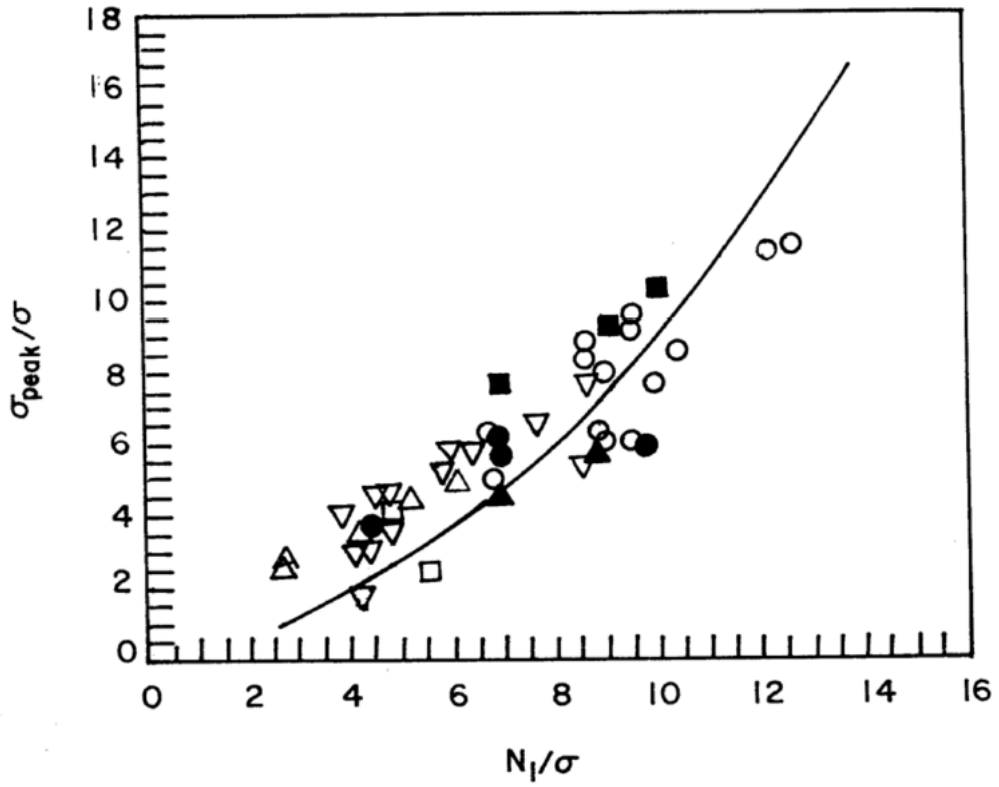
- At same time, relative magnitude of predicted stress overshoot also depends on λ:
  - As λ --> 1, shear stress overshoot becomes bigger.
- This suggests 'universal' correlation….

Polydomain Model in Inception: Broad Test in Other Polymers

- Collaboration with C.D. Han
- 'PxHQn' polymers of mesogen-spacer type



- Solid line is polydomain model prediction; no adjustable parameters
- Suggests that…
  - Shear aligning dynamics are typical of this architecture
  - Polydomain model captures basic physics of stress overshoot
  - Also supports nematic dumbbell/Rouse predictions

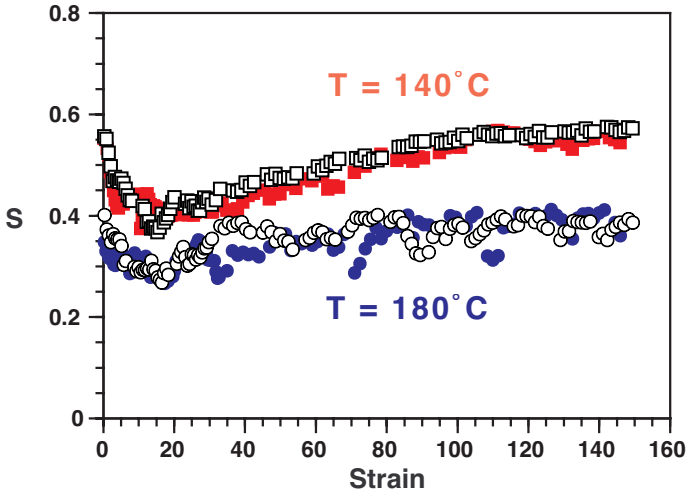


Opportunities for modeling

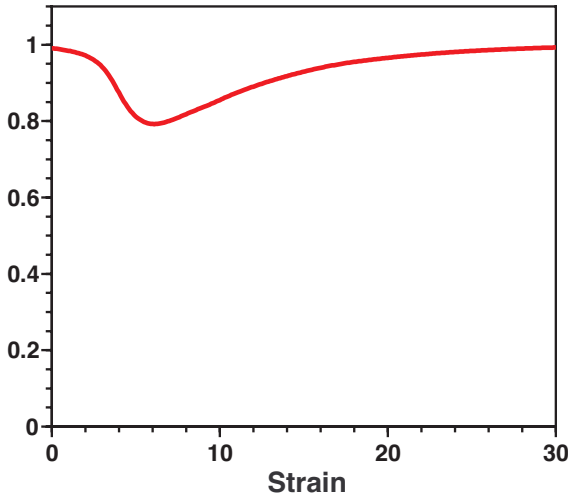
- Problems: Need real treatment of distortional elasticity and defects (for instance, bad N_1 predictions upon startup).
- Ideal opportunity for 'complete' models
  - Unlike tumbling systems, here the orientation evolves towards a final state that is *simple*.
  - Simulations in restricted dimension (e.g. 2-D) are probably *much* more realistic here than in texture development in tumbling lyotropes.
  - Fate of pre-existing defects when exposed to orienting effect of hydrodynamic torques in shear-aligning nematic?
  - How about an extended nematic dumbbell model with molecular description of gradient elasticity?
    - Quench into nematic phase; let defects form & anneal until you're happy
    - Start-up shear flow --> watch & see what happens!
    - Dare we hope for 3 regions?

Reversals: More complex, more need for detailed texture simulations

X-ray measurements of average orientation (DHMS-7,9):



Modest extension of polydomain Ericksen model:



Reversal in main-chain thermotropes:

- Single undershoot in average orientation (but, see below!)
- Polydomain models capture undershoot, but fail to predict long duration of transient
- Re-orientation hindered by texture?

Reversal of TLCPs: Flow-aligning PSHQ10