JÜLICH FORSCHUNGSZENTRUM

Probing the microstructural origin of complex flow behaviour with in situ Small Angle Neutron and X-ray Scattering

Pavlik Lettinga

What is Rheologie?

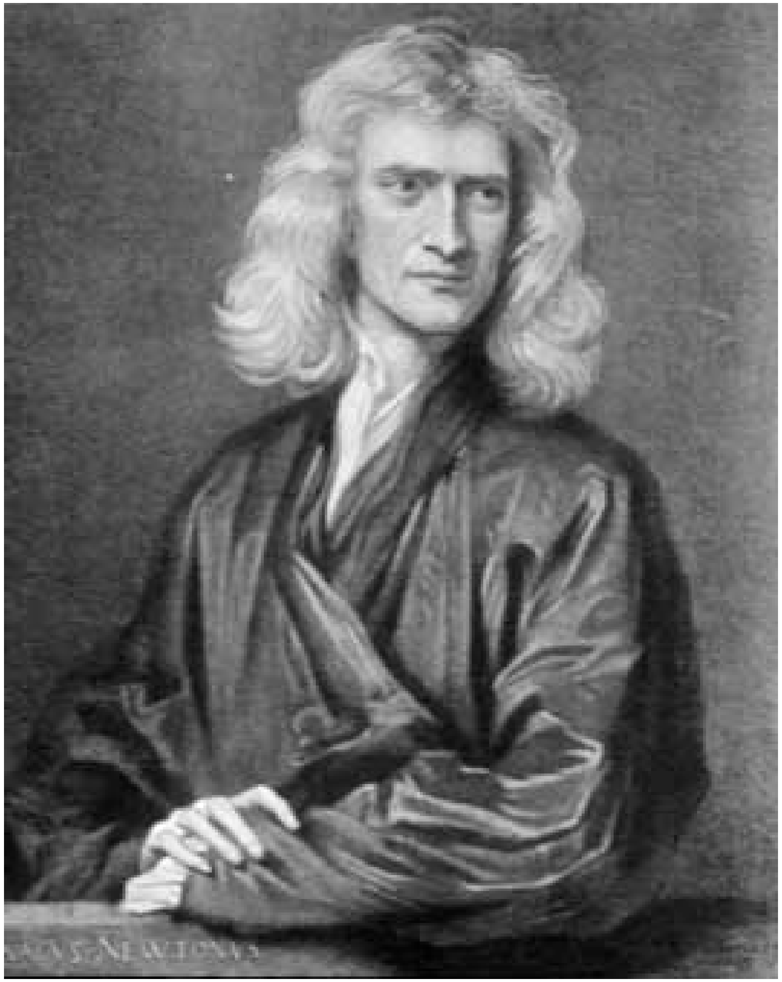
« Science of deformation and flow »

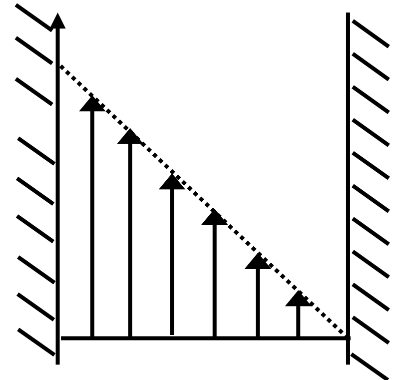
Heraklites : Παντα ρει (= everything flows)

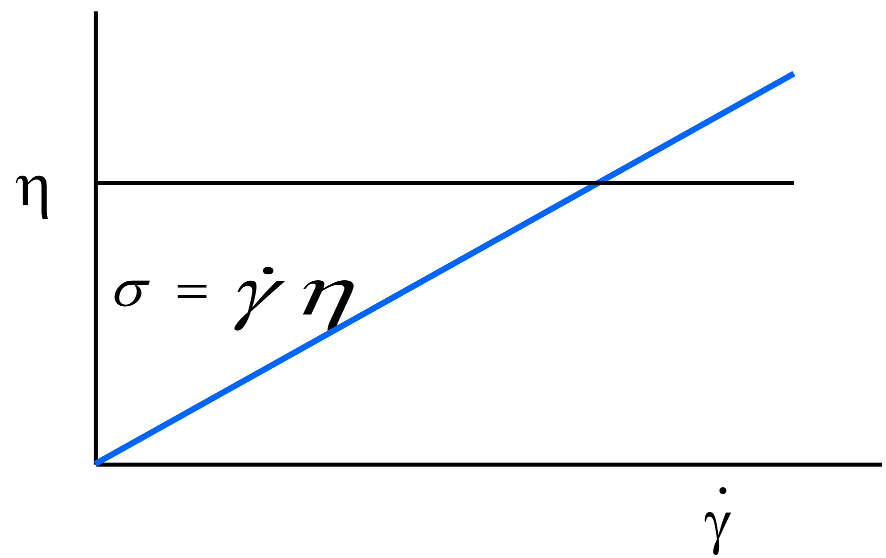
Deborah: "The mountains flowed before the Lord"

in a song by prophetess Deborah (Judges 5:5).

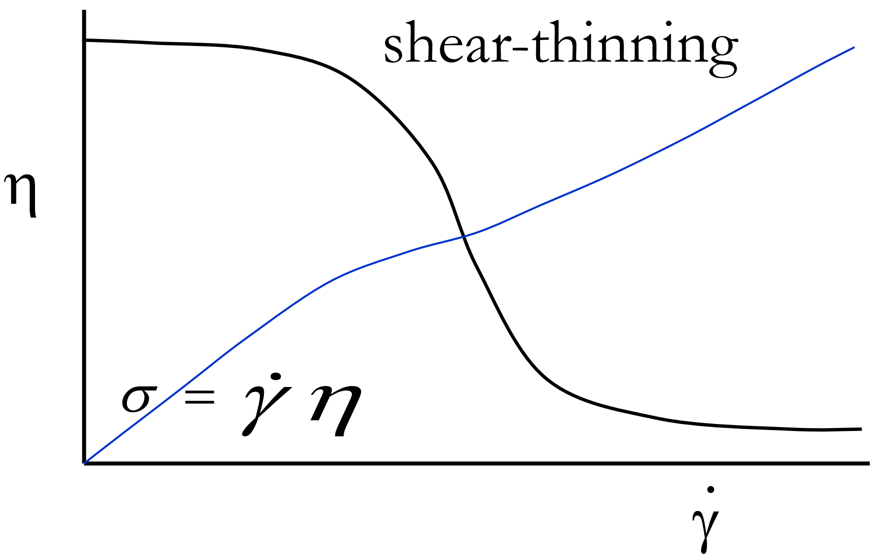
The ideal Newtonian world

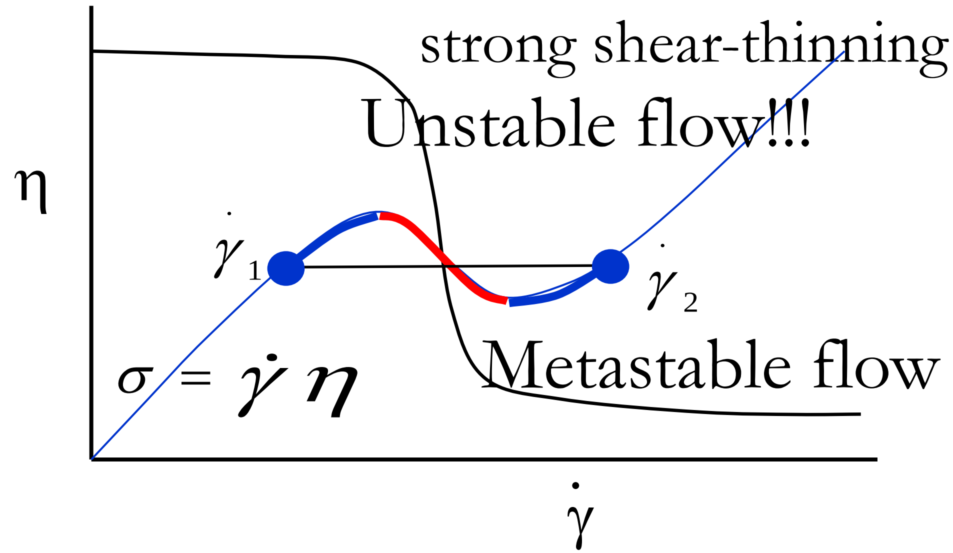




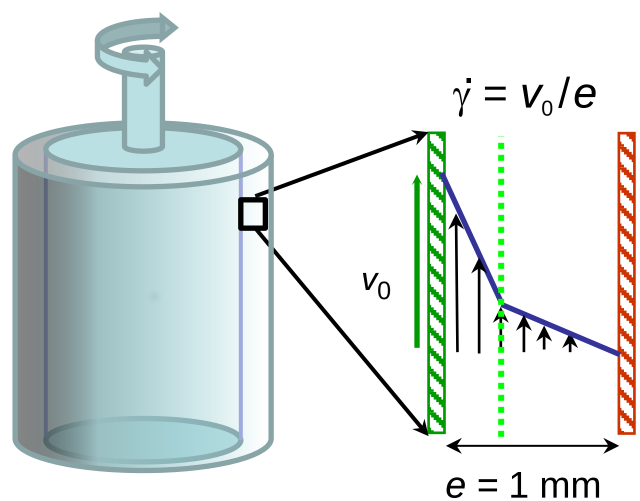


Our real world

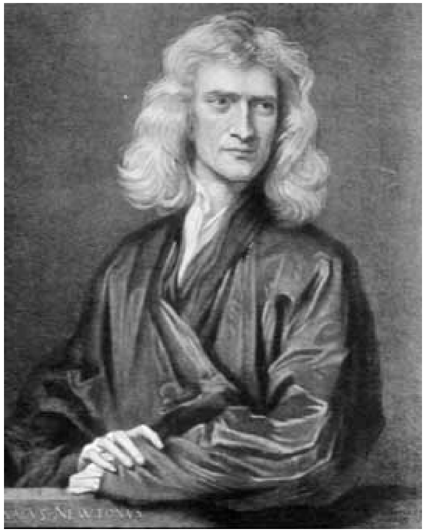


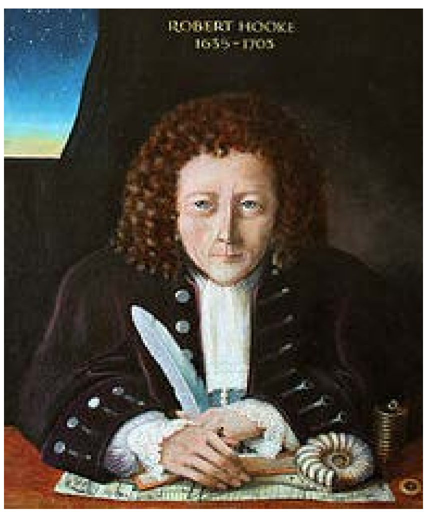


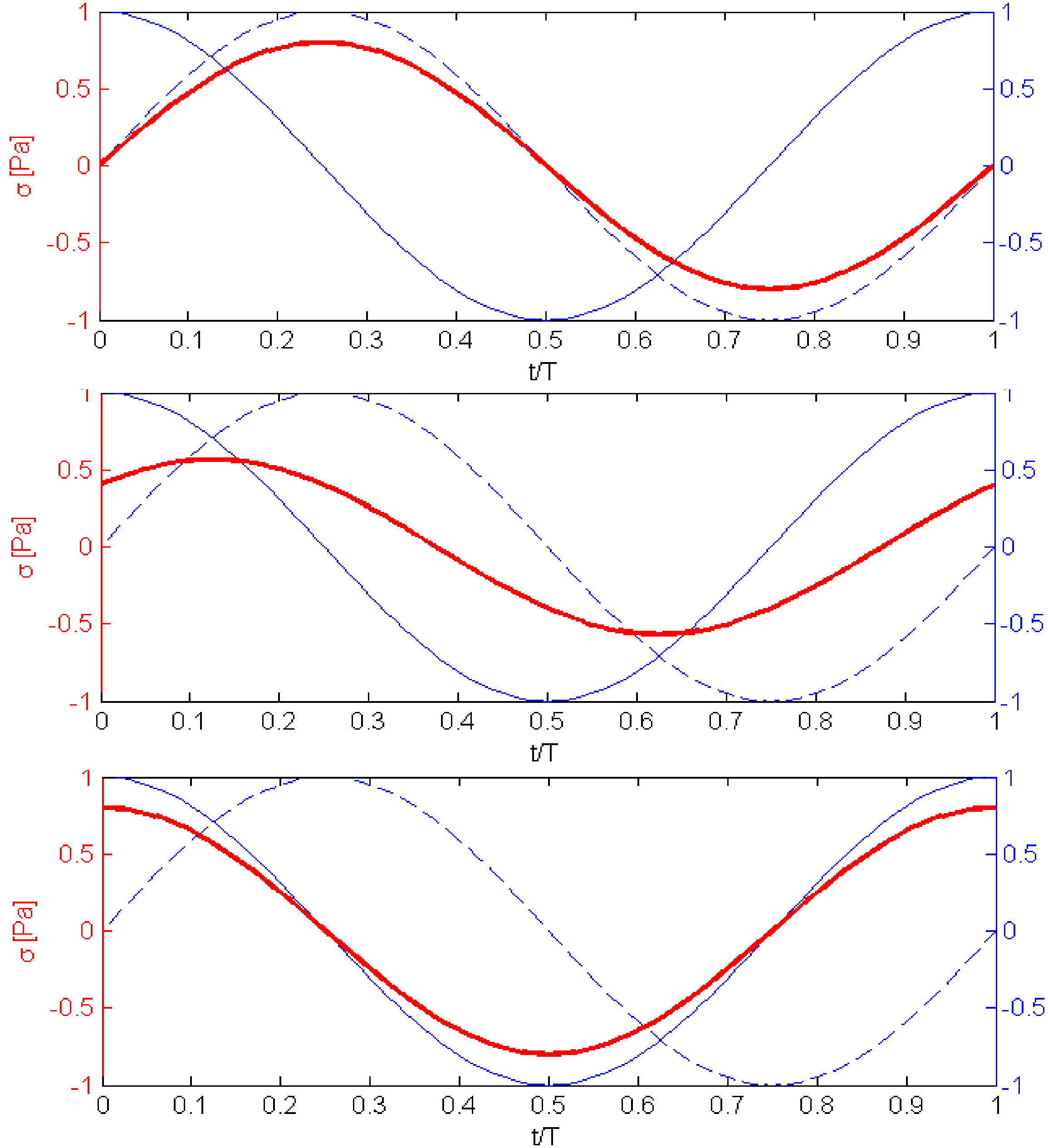
Flow instabilities:
gradient shear banding



The ideal visco-elastic world: $\sigma = G' \sin(\omega t) + G'' \cos(\omega t)$







$G' >> G''$

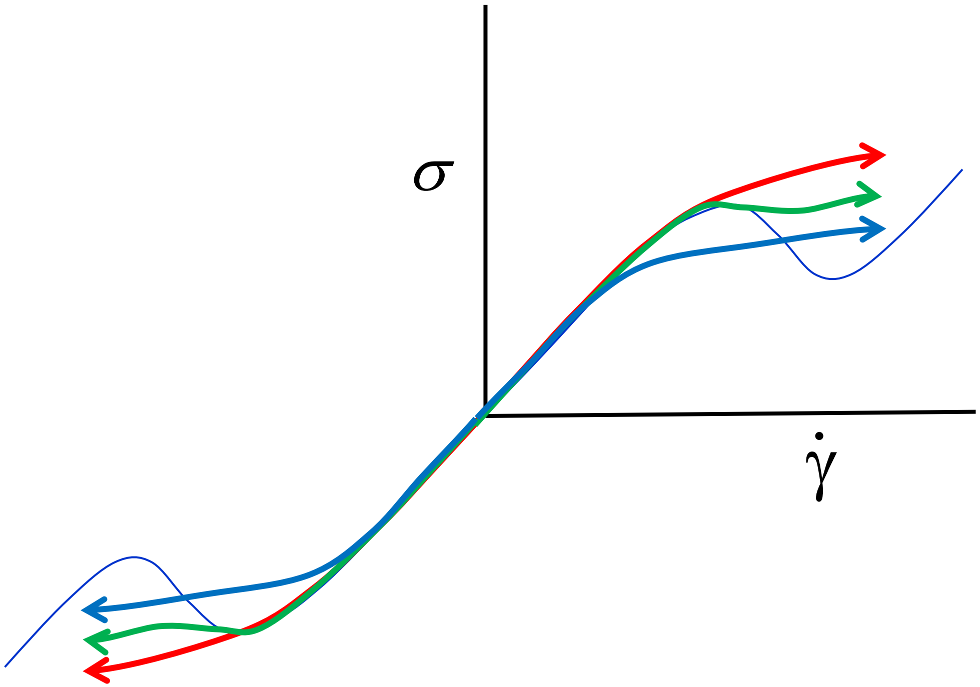
$G' \approx G''$

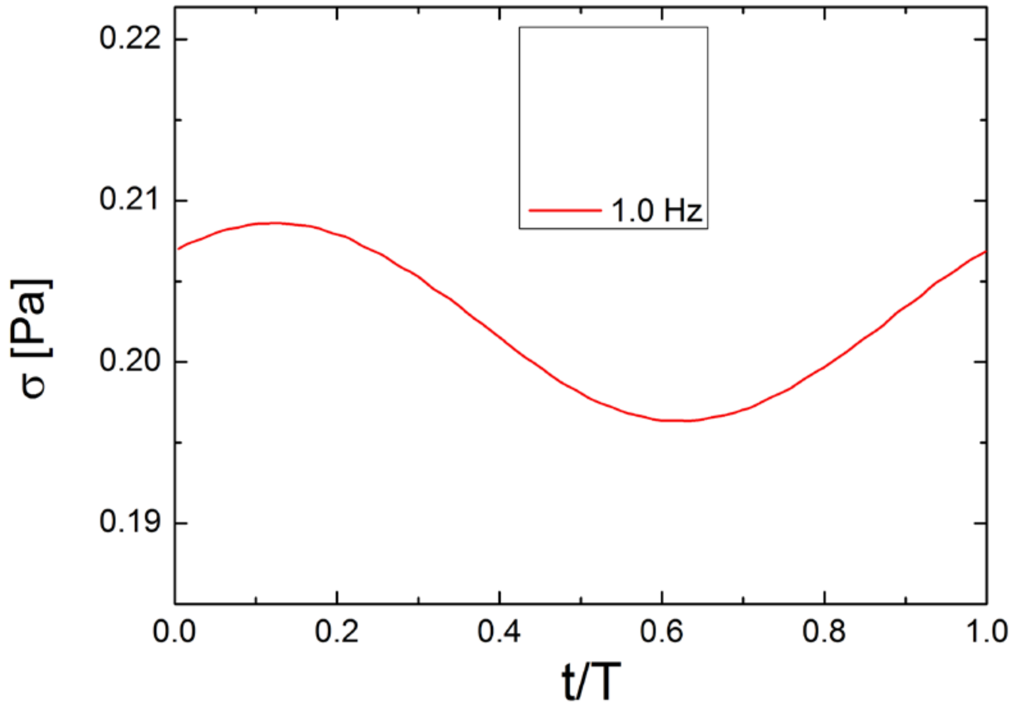
$G' << G''$

The non-ideal visco-elastic world

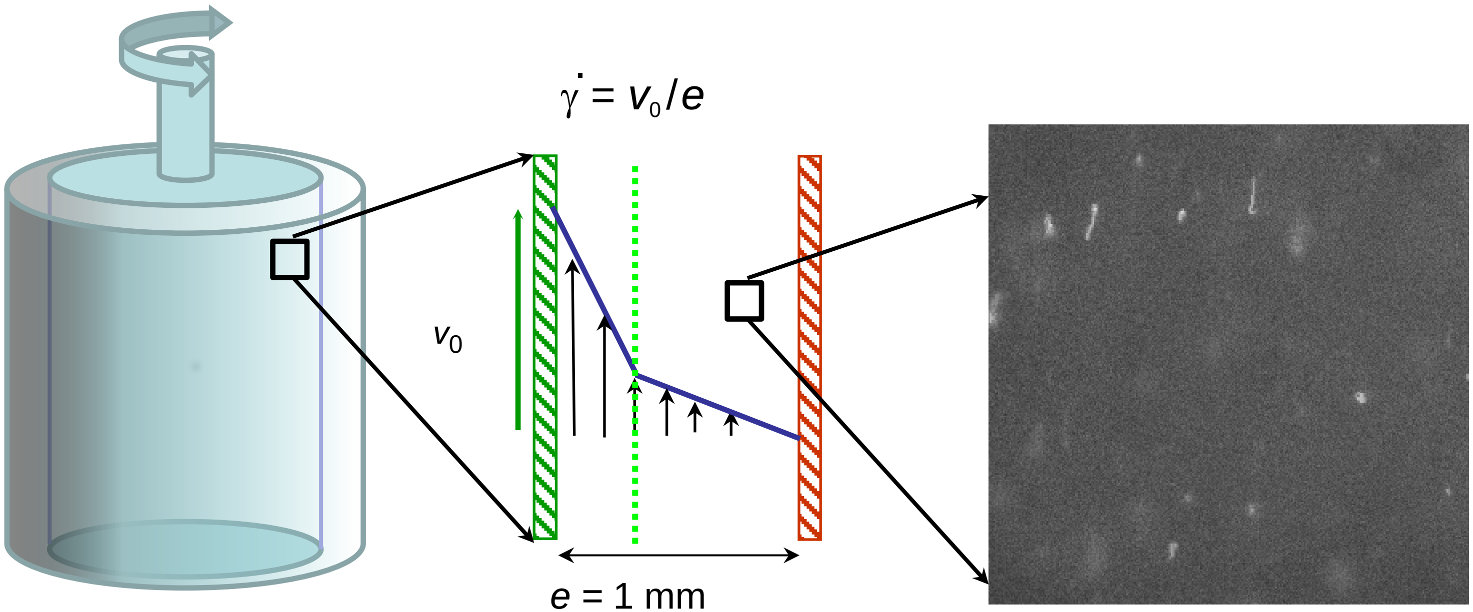
- Probe dynamics with Large Amplitude Oscillatory Shear

$$\dot{\gamma}(t) = \frac{A}{l}\omega\cos(\omega t)$$



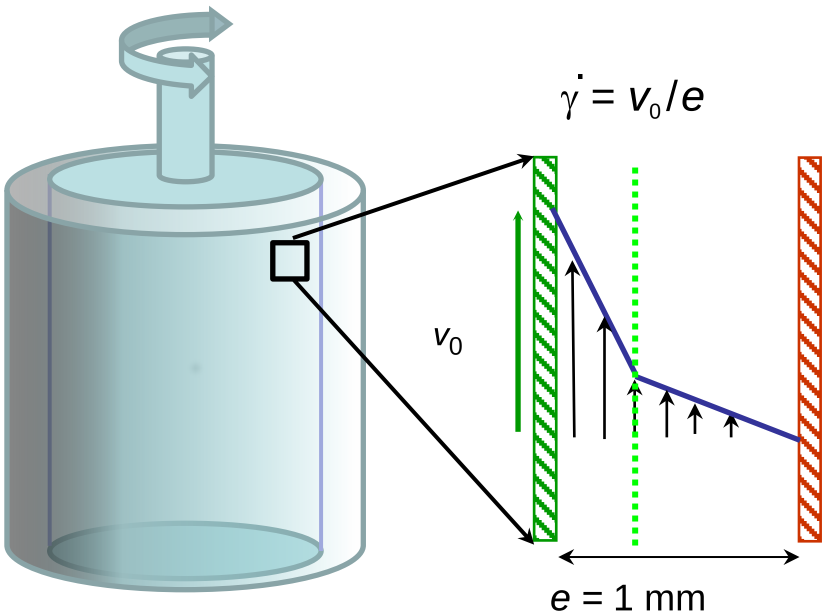


Information needed:



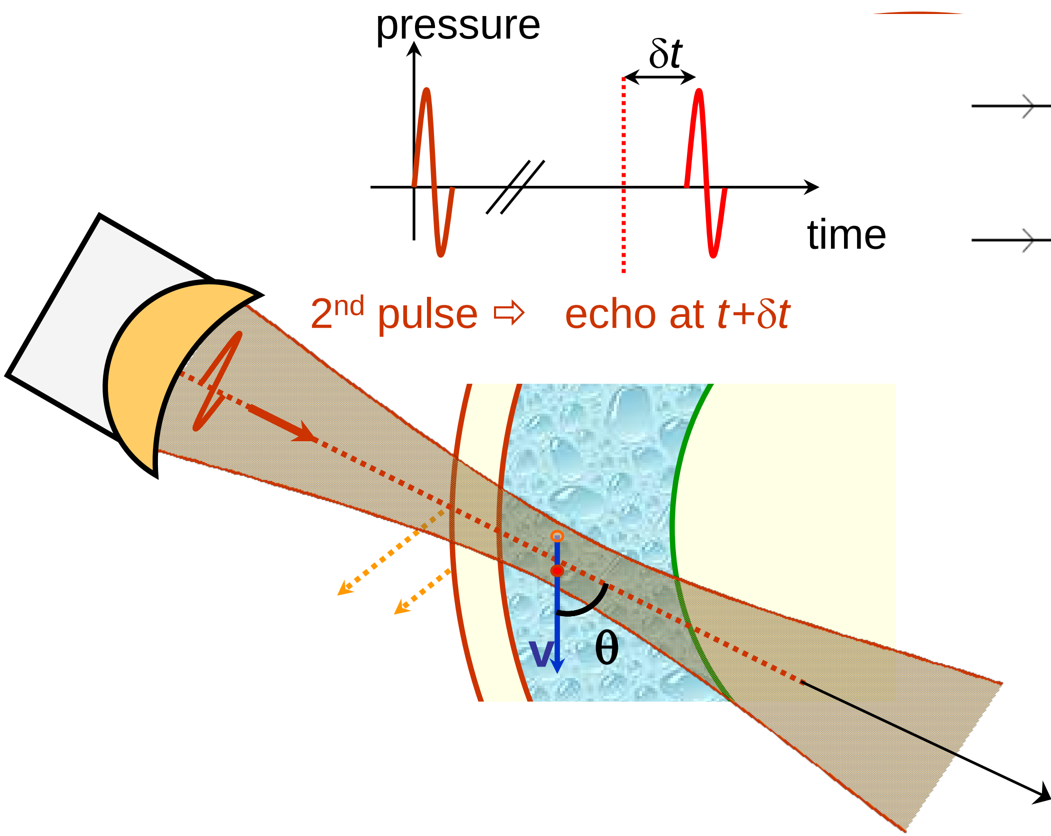
- Probe the mechanical response of the system.
- Probe the stability of the flow.
- Probe structure with *in situ* scattering or imaging methods over broad range of length-scales and time-scales.

Part I: Shear thinning and shear banding systems

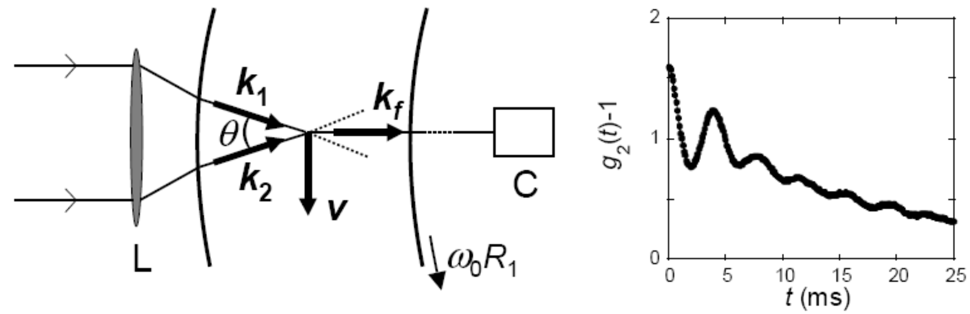


Measuring velocity profiles

Ultra-sound velocimetry



Heterodyne dynamic light scattering:



- Echography: arrival time t ⇔ depth

$$z = \frac{c_0 t}{2}$$

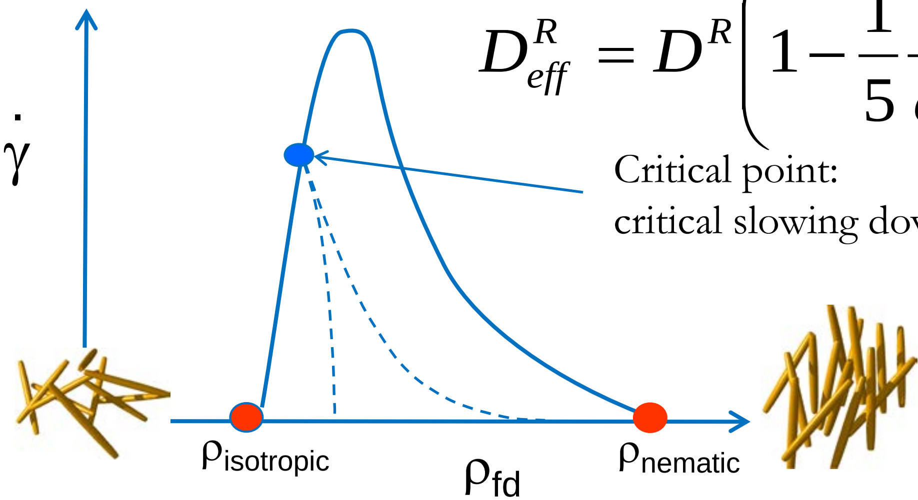
- Velocimetry: time-shift δt ⇔ displacement

$$\delta z = \frac{c_0 \delta t}{2}$$

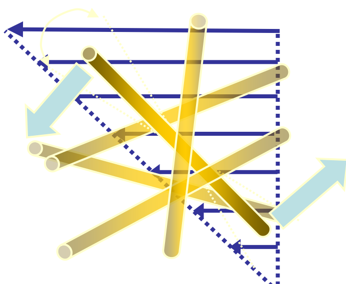
Possible scenarios for shear thinning

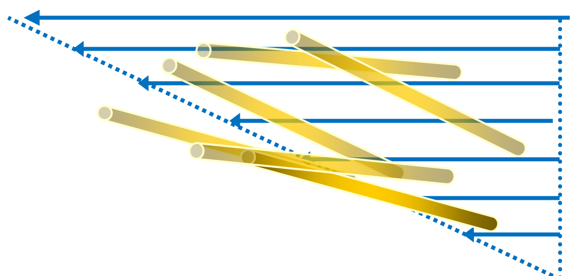
Rods close to I-N coexistence:

$$D_{eff}^{R} = D^{R}\left(1-\frac{1}{5}\frac{L}{d_{eff}}\varphi\right)$$



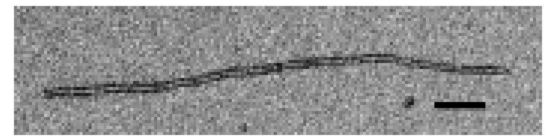
$$Pe_{eff} = \dot{\gamma}_0 / D_{eff}^{R}$$

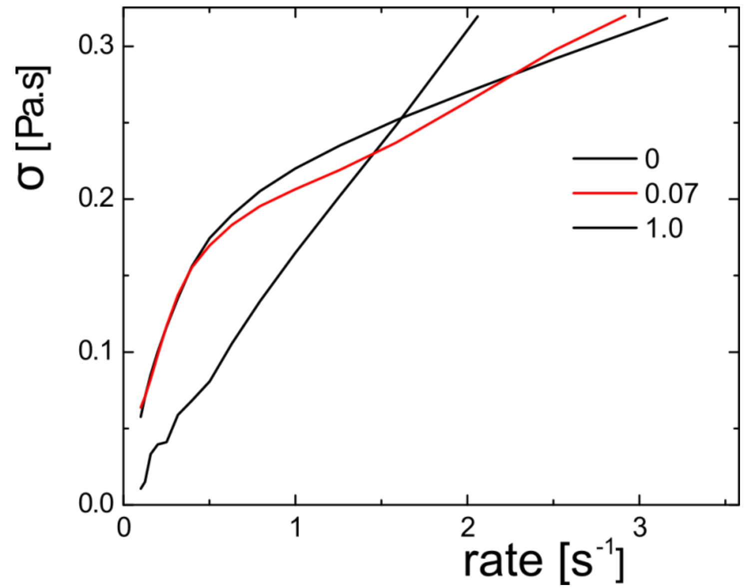




$Pe_{eff} < 1$ $\qquad$ $Pe_{eff} > 1$

Fd virus: L=880 nm
D=6.6 nm
P=3.0 μm



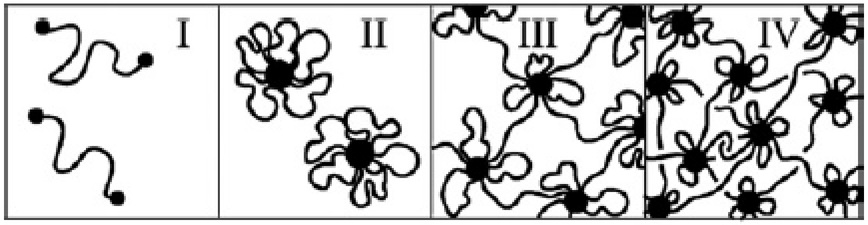


No gradient shear banding!

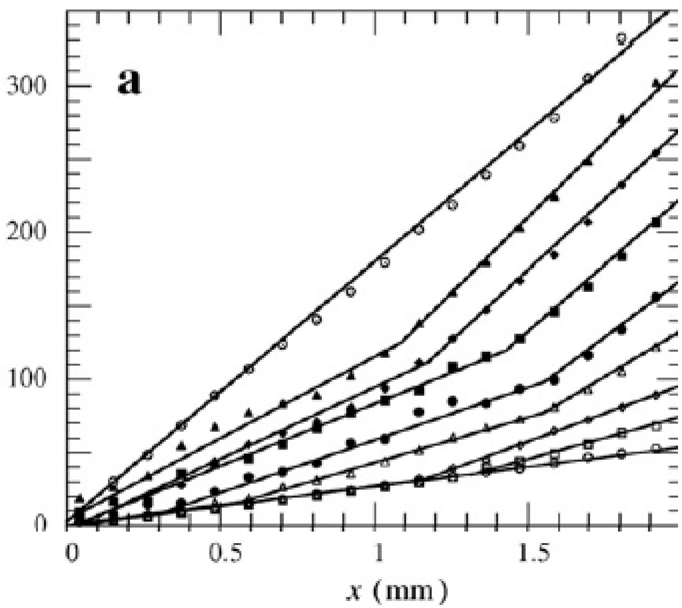
Ripoll et al, Phys. Rev. Lett., **101**, (2008) 168302

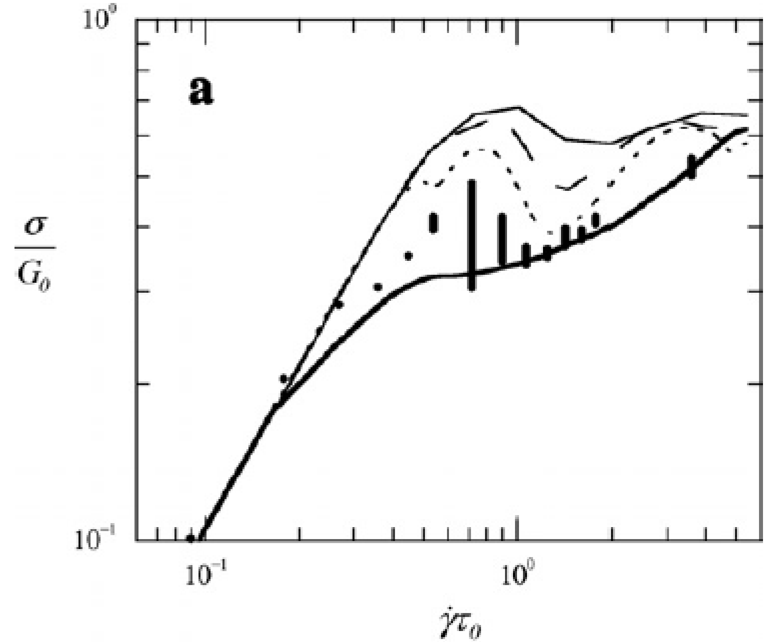
Possible scenarios for shear thinning

Living networks: tri-block copolymers



$$\tau = \tau_0 \exp\left(\frac{-f\delta}{k_B T}\right)$$

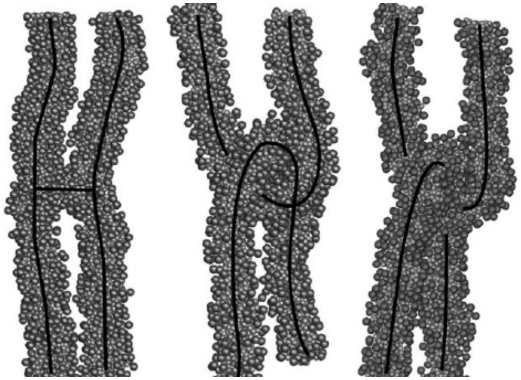




Sprakel et al, Soft Matter, **4**, (2008) 1696

Possible scenarios for shear thinning

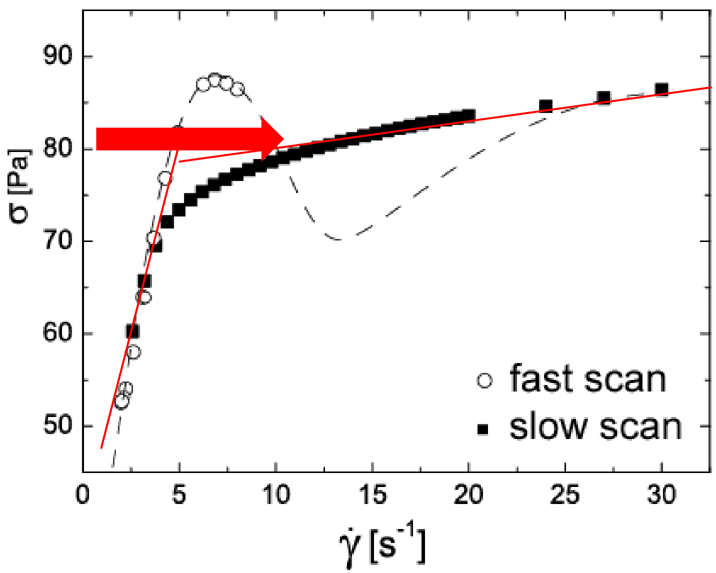
Living polymers: surfactant wormlike micelles

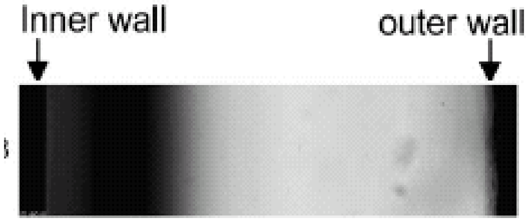


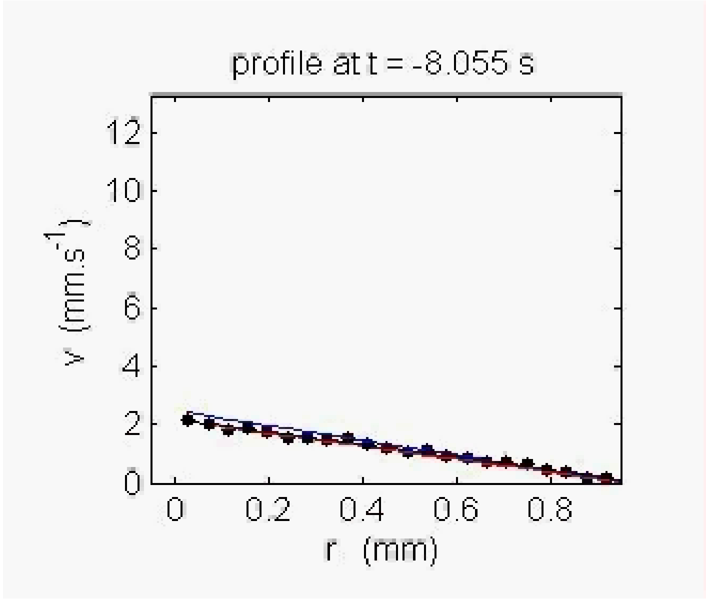
W J Briels, P Mulder and W K den Otter
J. Phys.: Condens. Matter **16** (2004) S3965–S3974

6% ww cetylpyridinium chloride/
sodium salicylate

- Single relaxation time $\lambda = \sqrt{\tau_{rep.}\tau_{break}}$
- (I-N at about 14 % ww)



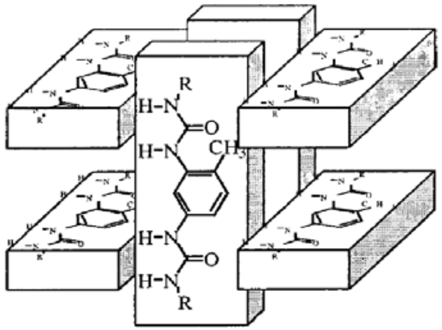




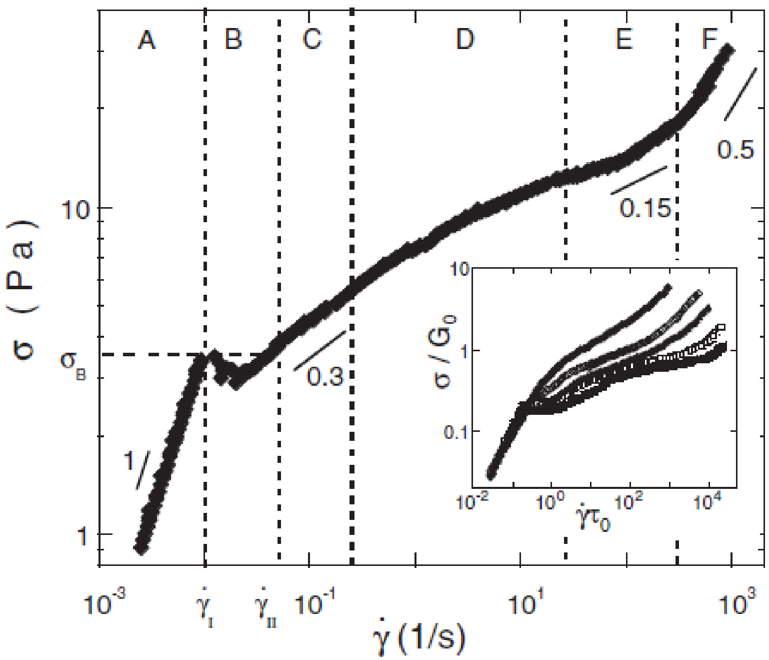
M. P. Lettinga and S. Manneville, PRL, 2009

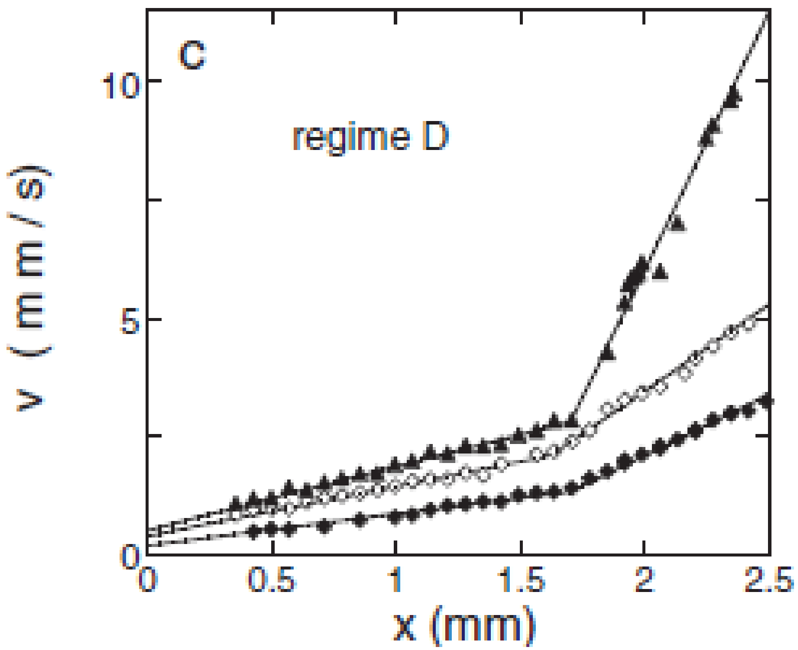
Possible scenarios for shear thinning

Living polymers: supra-molecular polymers



$$\lambda = \sqrt{\tau_{rep.}\tau_{break}}$$

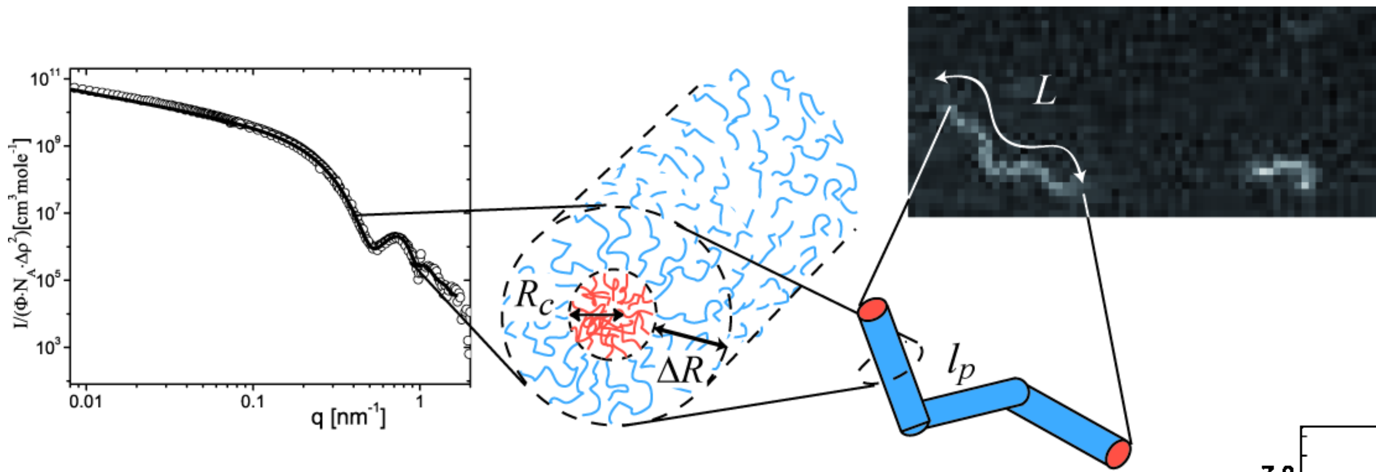




Van der Gucht, Phys. Rev. Lett., **97**, (2006) 108301

Possible scenarios for shear thinning

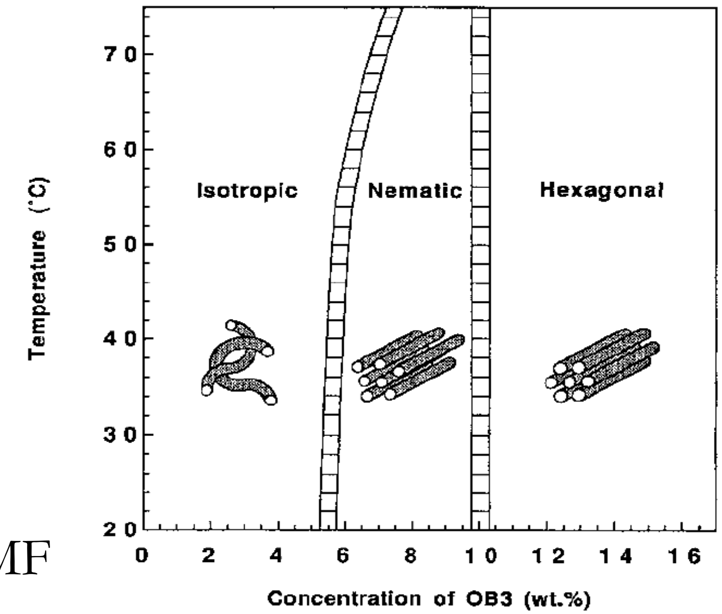
Rods close to I-N coexistence: PB-PEO wormlike micelles



Poly-(butadiene) 2.5 kd – Poly-ethylene glycol 2.5 kd

Advantage Pb-PEO:

- Displays I-N transition
- Wormlike micelles at size ratio of 1:1
- Detectable with fluorescence microscopy
- Tunable system at different length scales using D_2O:DMF

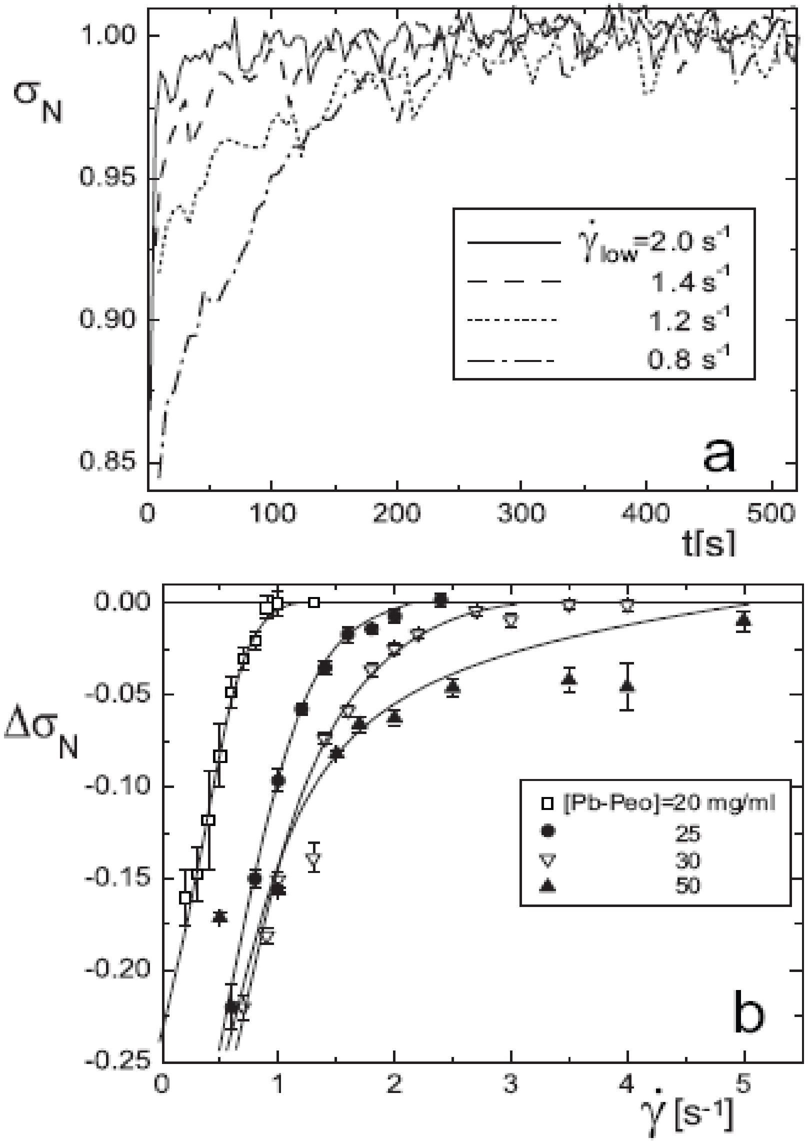


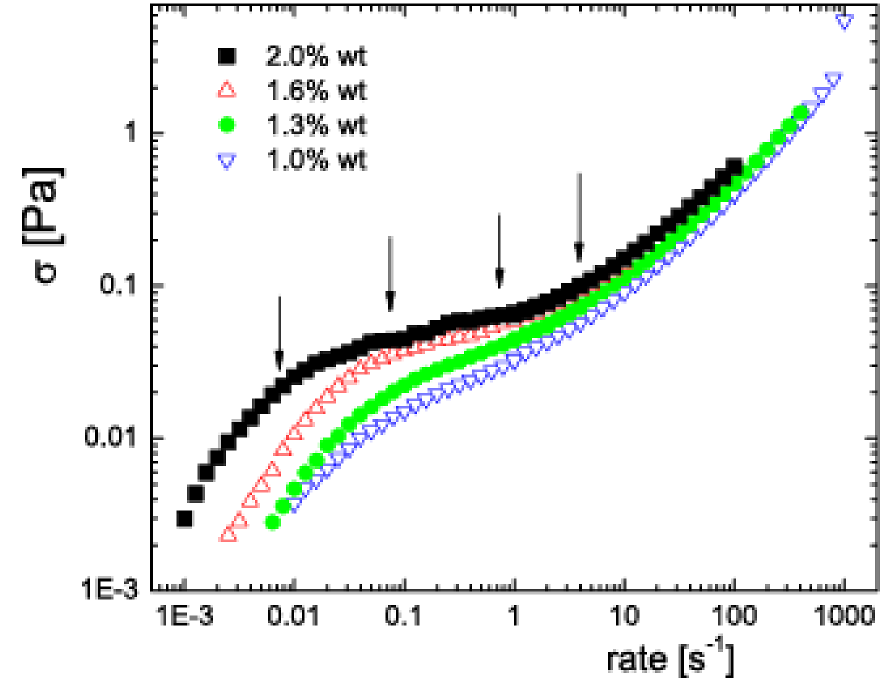
You-Yeon Won, H. Ted Davis, Frank S. Bates*

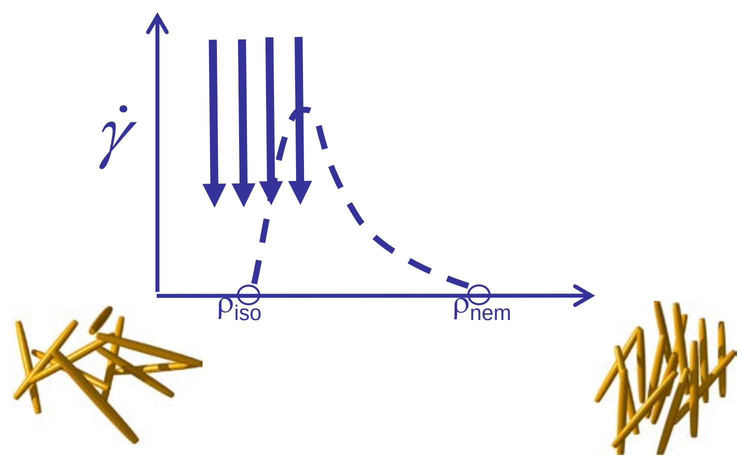
12 FEBRUARY 1999 VOL 283 SCIENCE

Possible scenarios for shear thinning

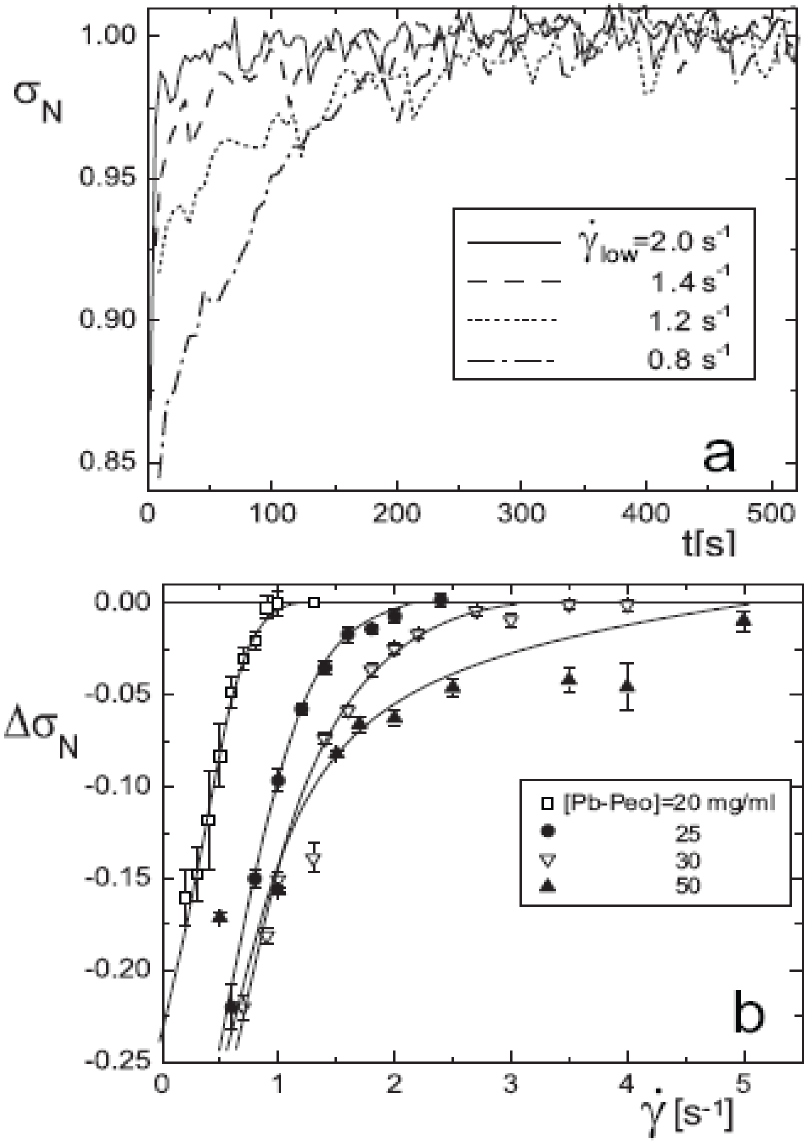
Test dynamics: quench down experiments

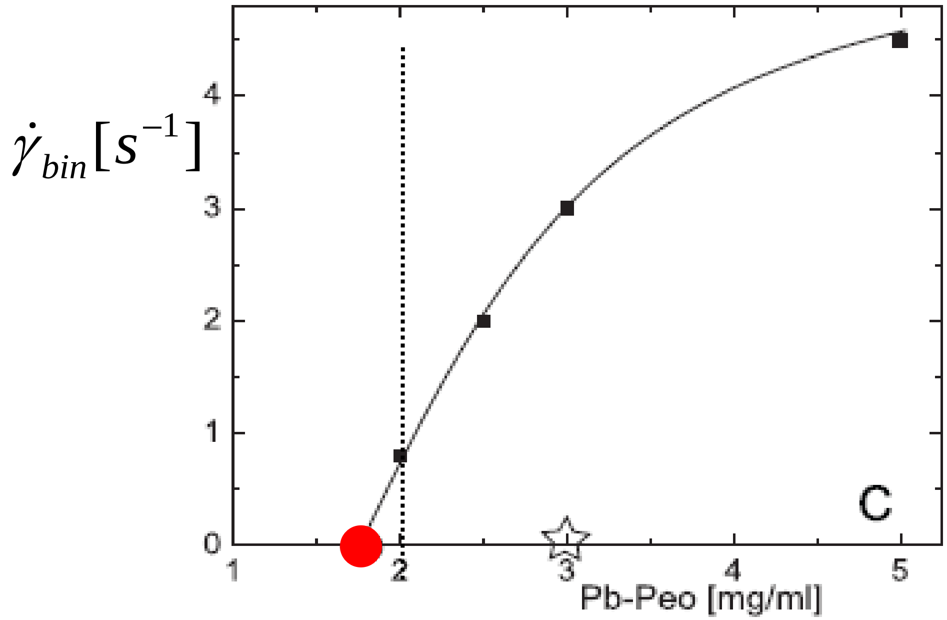






Possible scenarios for shear thinning

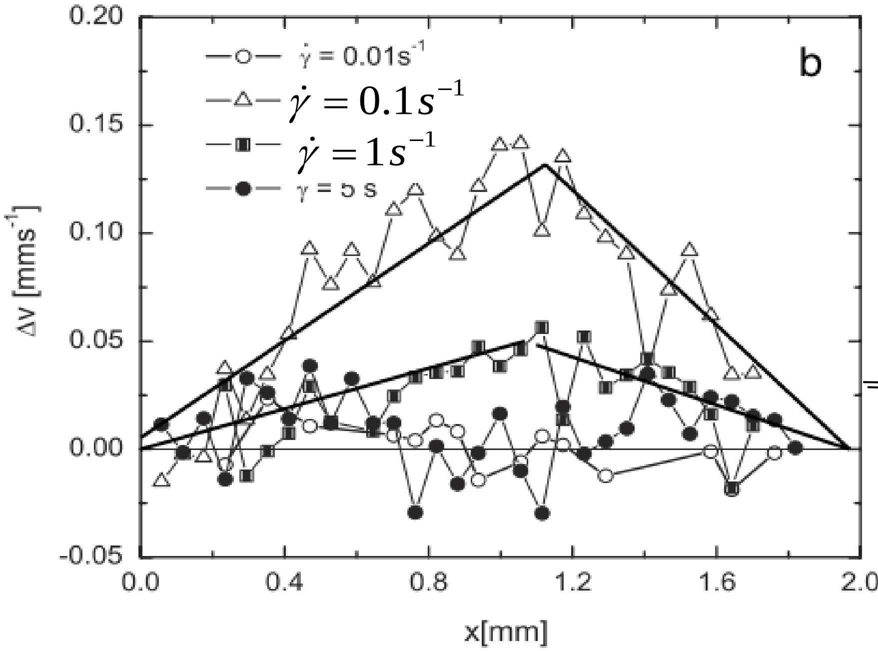


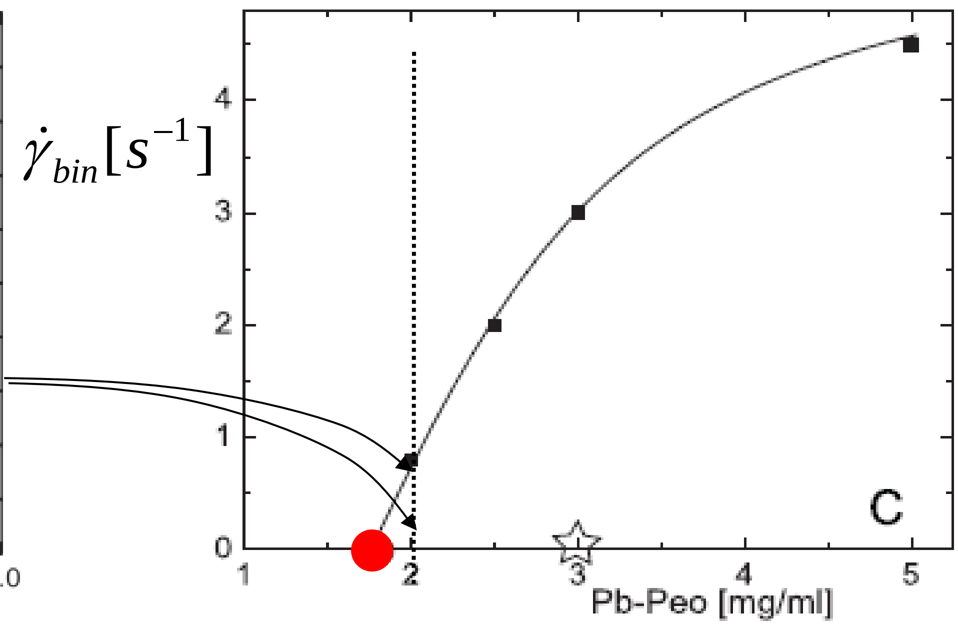


➢ **First determination equilibrium binodal**

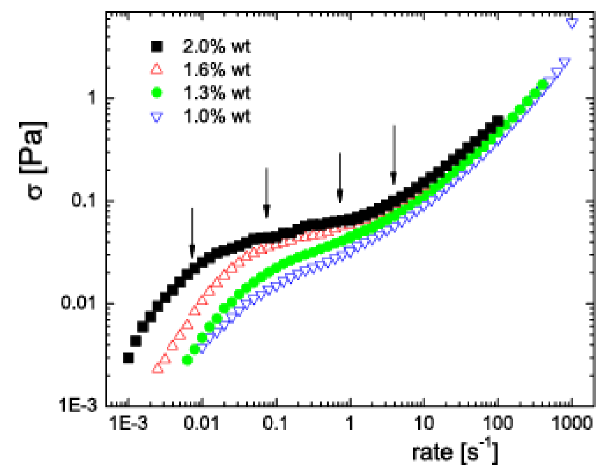
Possible scenarios for shear thinning

Rods close to I-N coexistence: PB-PEO wormlike micelles

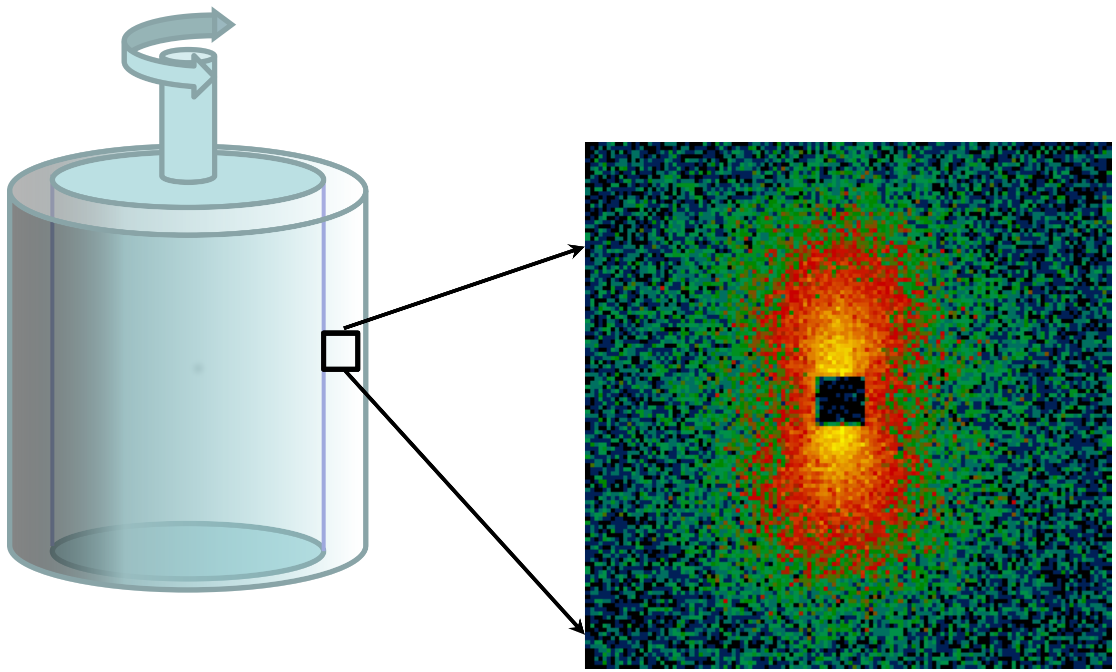




➢ Polydispersity enhances shear banding

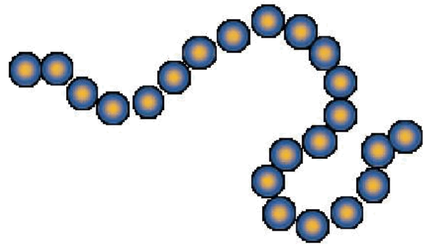


Part II: Molecular origin shear thinning using *in situ* LAOS

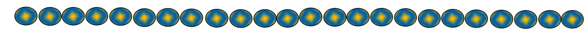


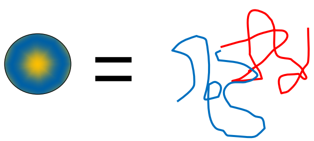
Focus on three systems:

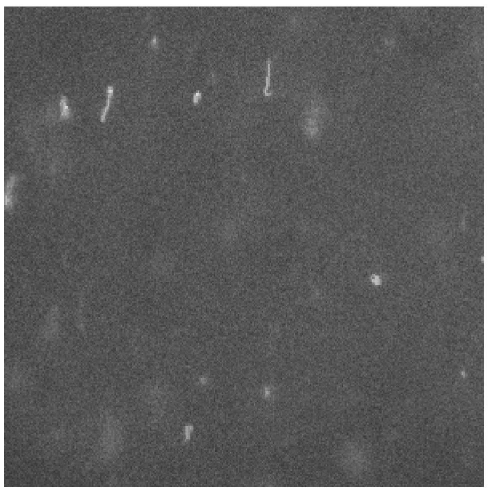
Living Polymers

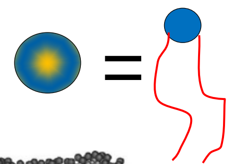


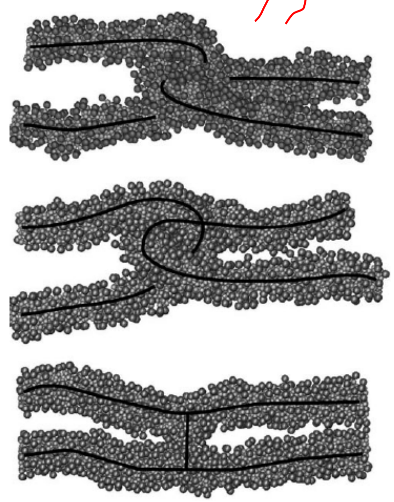
Rods



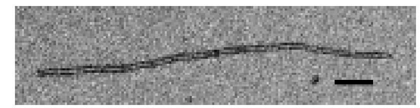


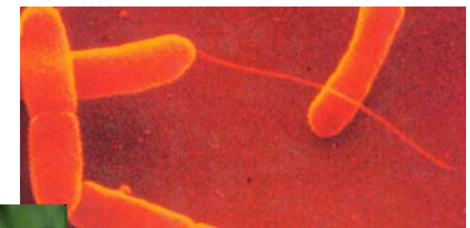






L=880 nm
D=6.6 nm
P=3.0 μm





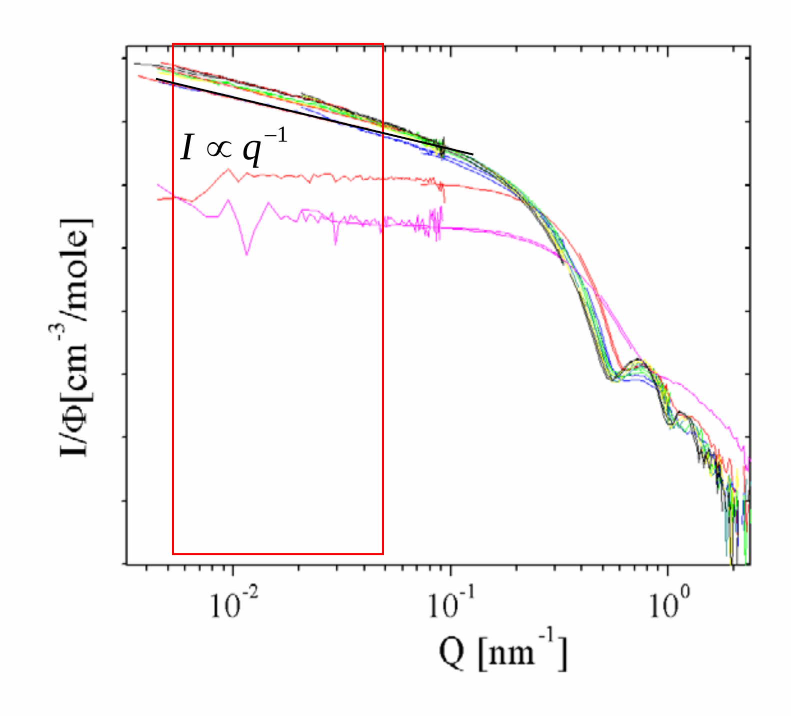
Pb-PEO
= Giant

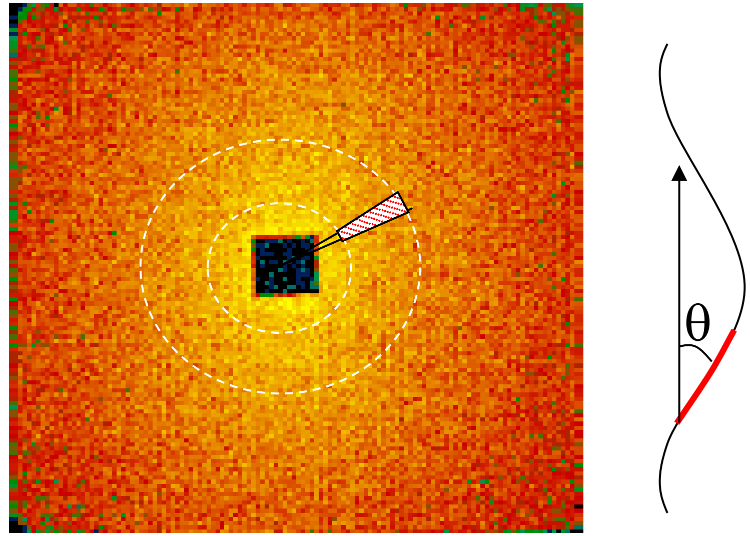
CpCl/NaSyl
= Dwarf

Fd virus

t-SANS to probe segment ordering

Scattering of a rod: $I \propto q^{-1}$

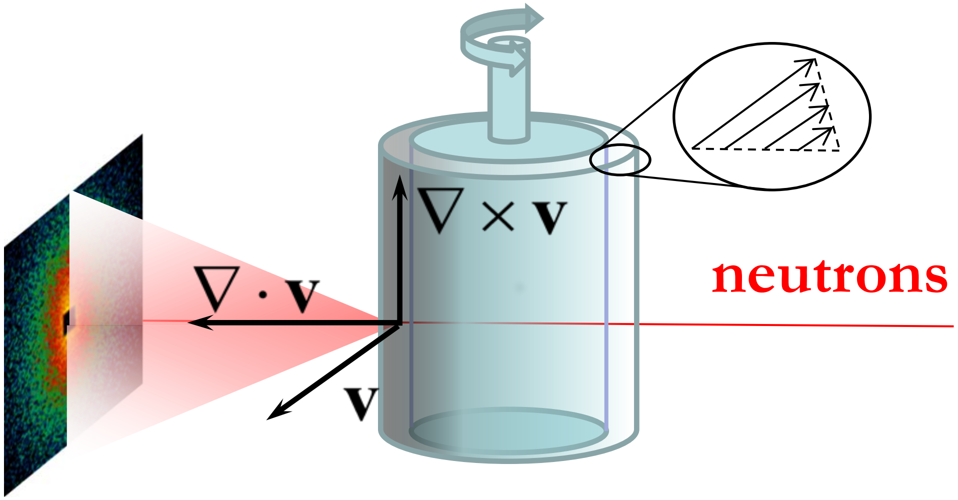




For the really soft matter (polymers and protein clusters) it is best to use neutrons:

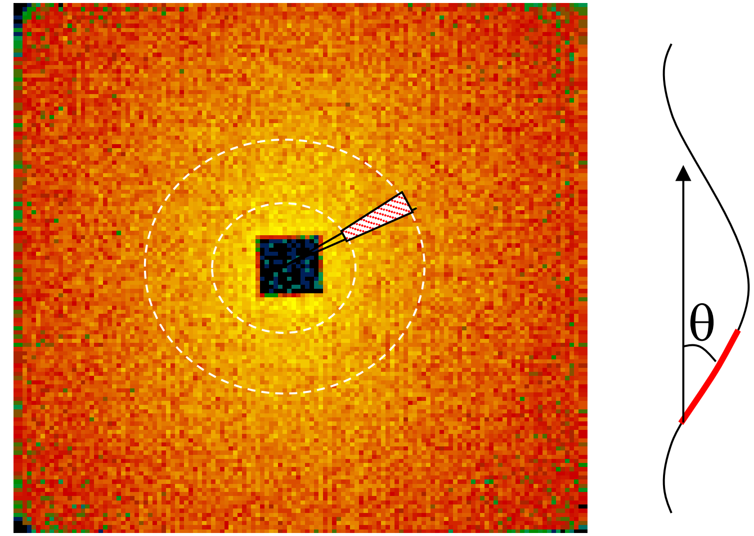
- Better contrast
- No beam damage

t-SANS to probe segment ordering

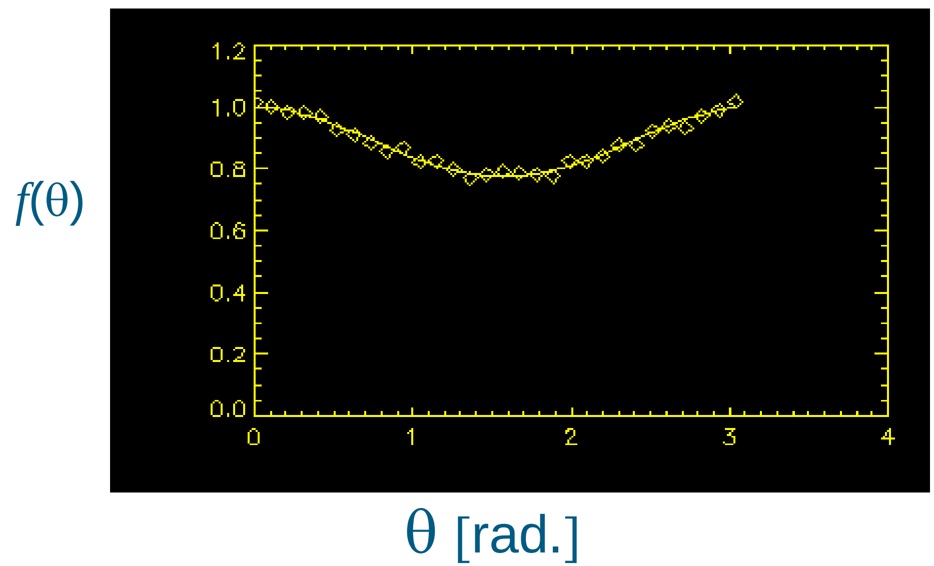


flow-vorticity plane probed

$$\langle P_2(t)\rangle = \frac{\int d\vartheta \sin(\vartheta)\ f(\vartheta) P_2(\vartheta))}{\int d\vartheta \sin(\vartheta)\ f(\vartheta)}$$



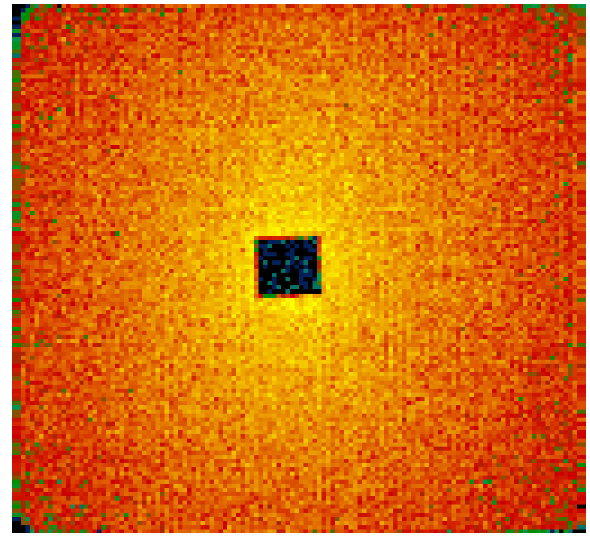
Orientational disitribution function



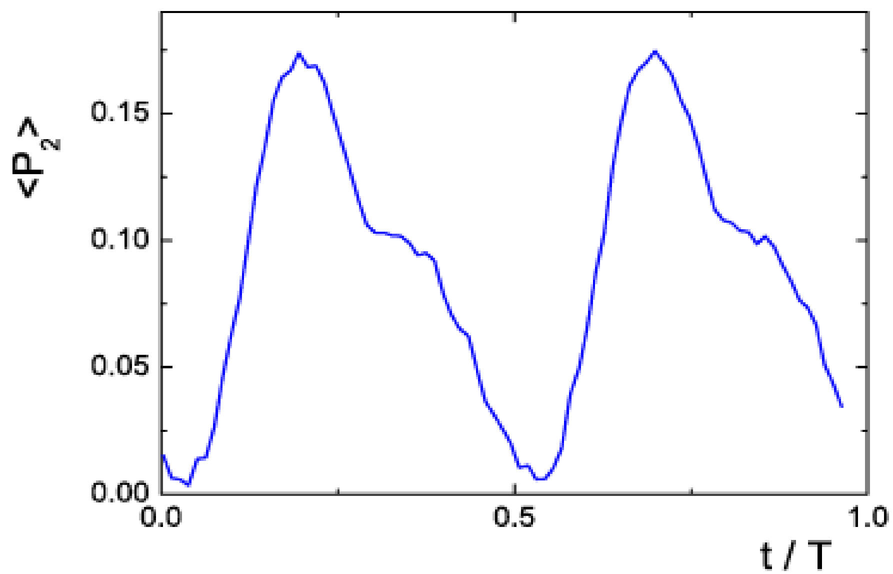
SANS in stroboscopic mode

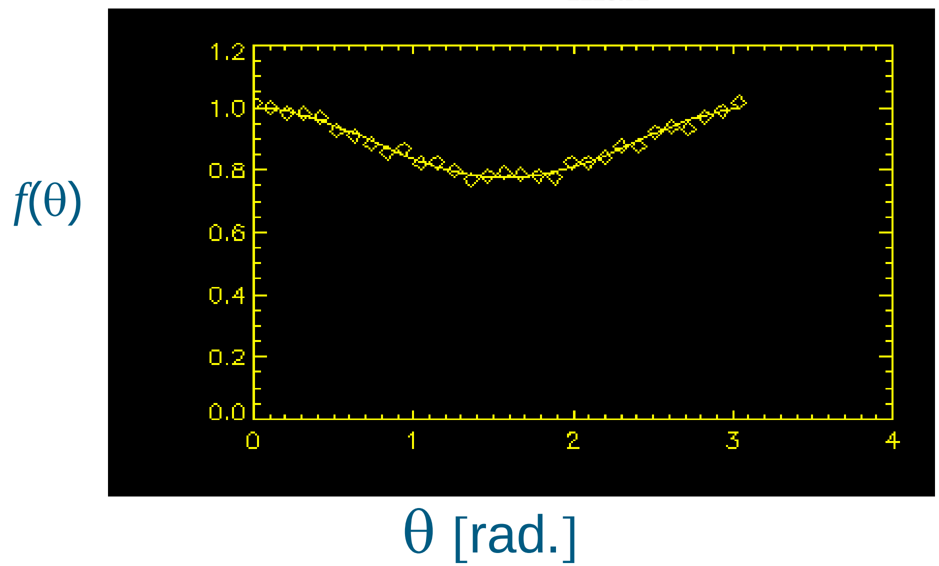
$$I(t_i,\vec{q}) = \sum_{n}^{Ncycle} I(t_i + n\Delta t, \vec{q}\ )$$

- at least n = 100 time channels of widths $\Delta t = (nw/2p)^{-1}$
- trigger is sent when the maximum shear rate is reached
- Summed over an interval of time ranging from one hour to fifteen minutes

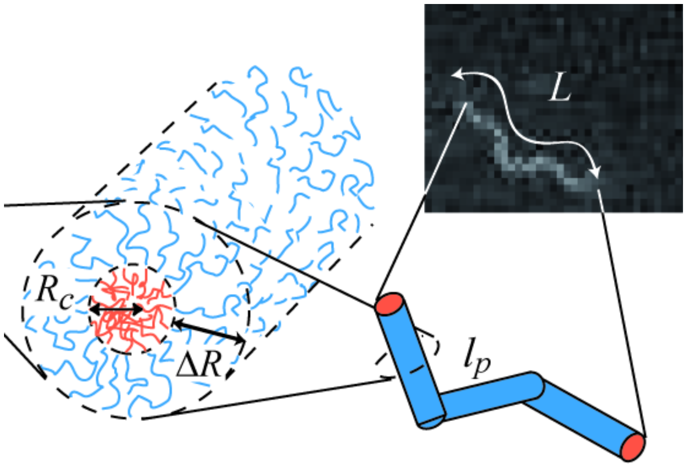


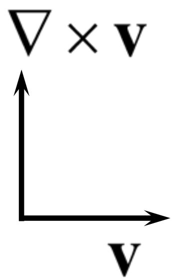
$f = 0.25\ \mathrm{Hz};\ \dot{\gamma}_{max} = 18\ \mathrm{s}^{-1}$

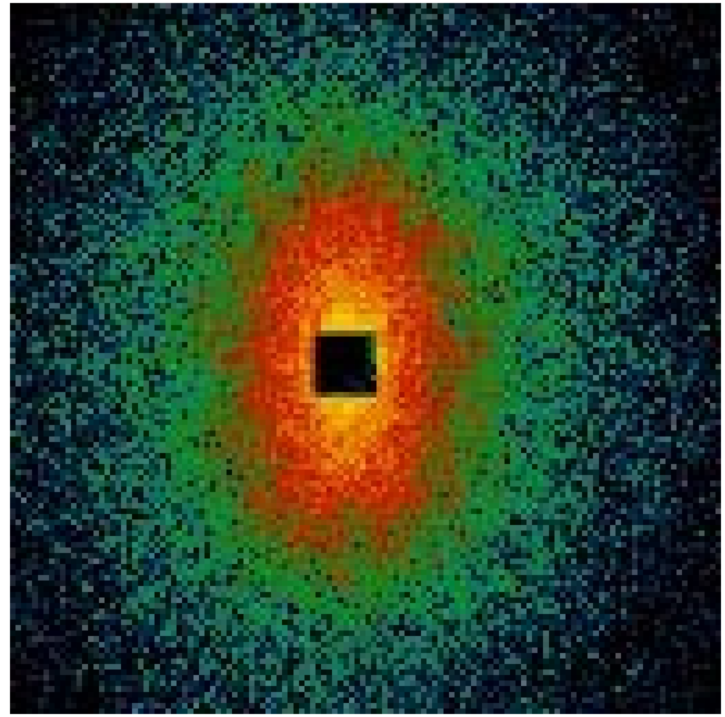




Dynamic response Pb-Peo wormlike micelles



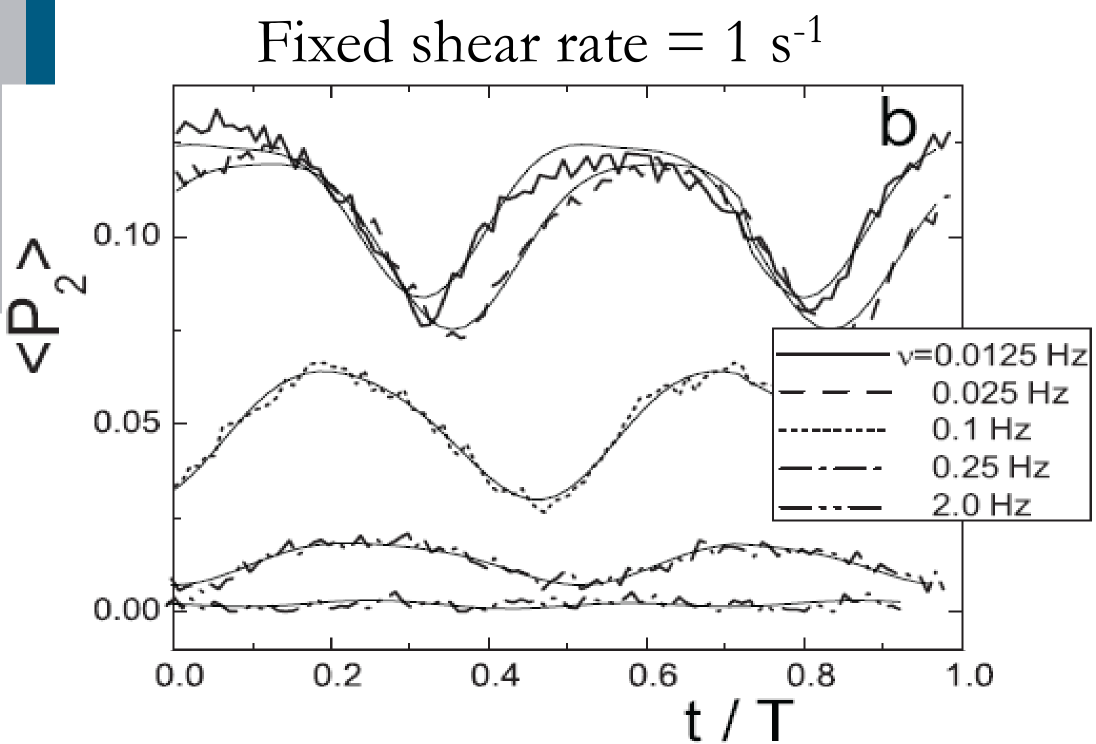


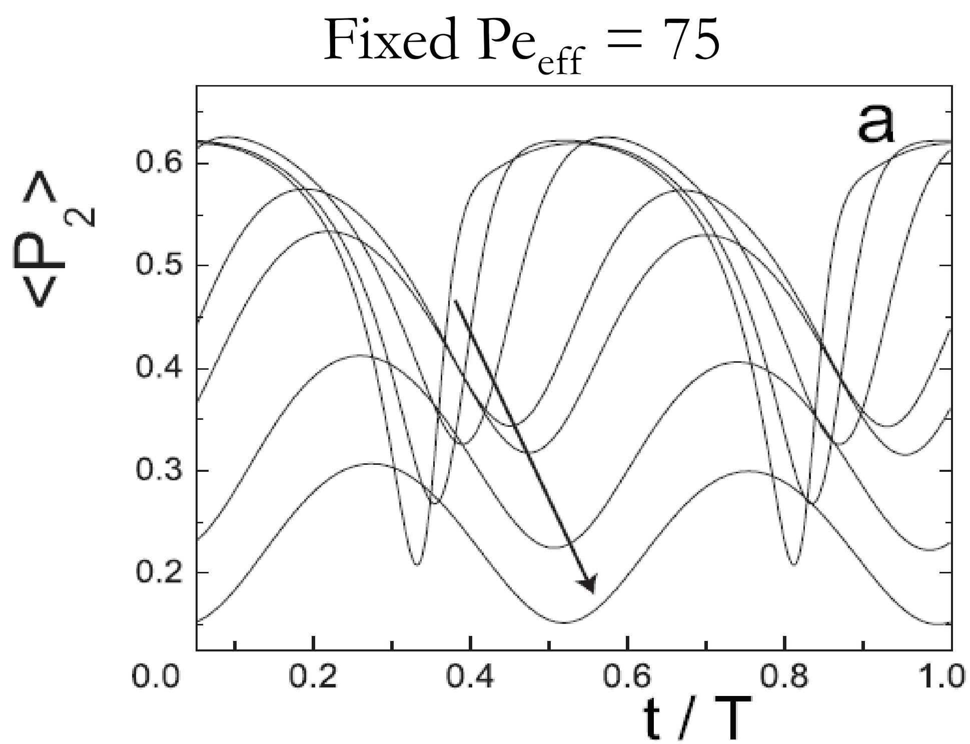


t-SANS @ PSI

f=0.025, γ=7.3

Oscillatory flow: compare P_2

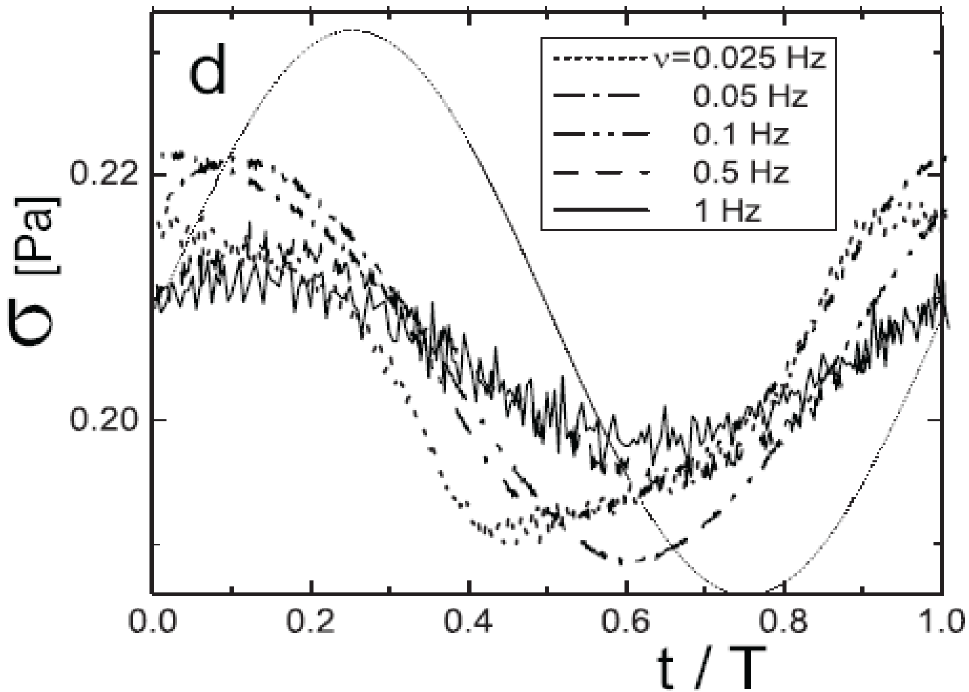


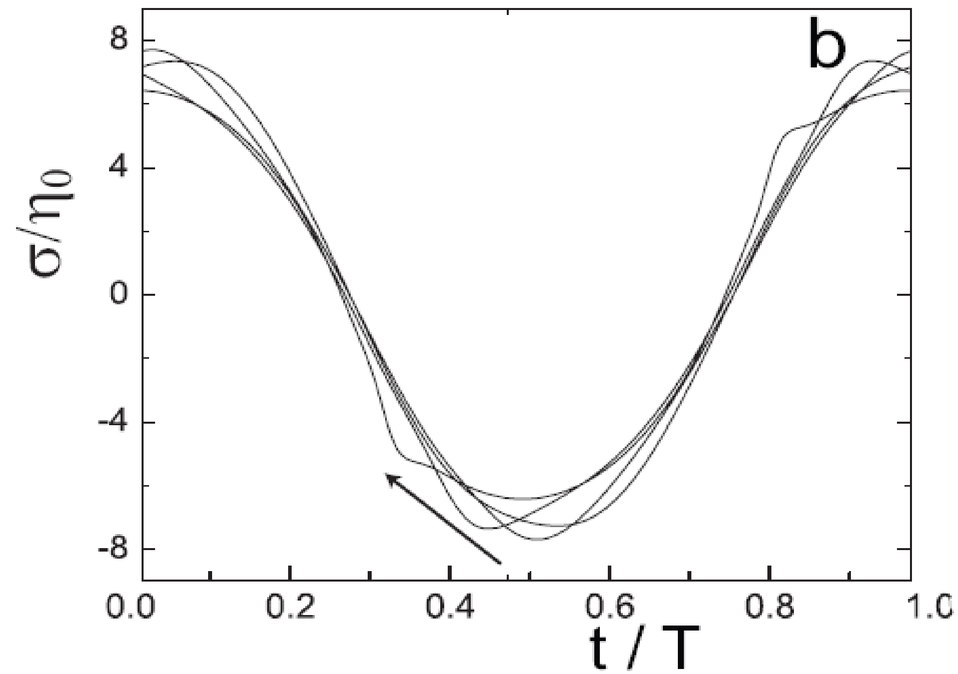


$$\frac{d}{dt}\mathbf{S} = -6D_r\left\{\mathbf{S} - \tfrac{1}{3}\hat{\mathbf{I}} + \tfrac{L}{D}\varphi\left(\mathbf{S}^{(4)} : \mathbf{S} - \mathbf{S}\cdot\mathbf{S}\right)\right\} + \dot{\gamma}\left\{\hat{\mathbf{\Gamma}}\cdot\mathbf{S} + \mathbf{S}\cdot\hat{\mathbf{\Gamma}}^T - 2\mathbf{S}^{(4)} : \hat{\mathbf{E}}\right\}$$

Lonetti, Kohlbrecher, Lettinga, *J. Phys. Cond. Matt.*, 2008

Oscillatory flow: compare stress

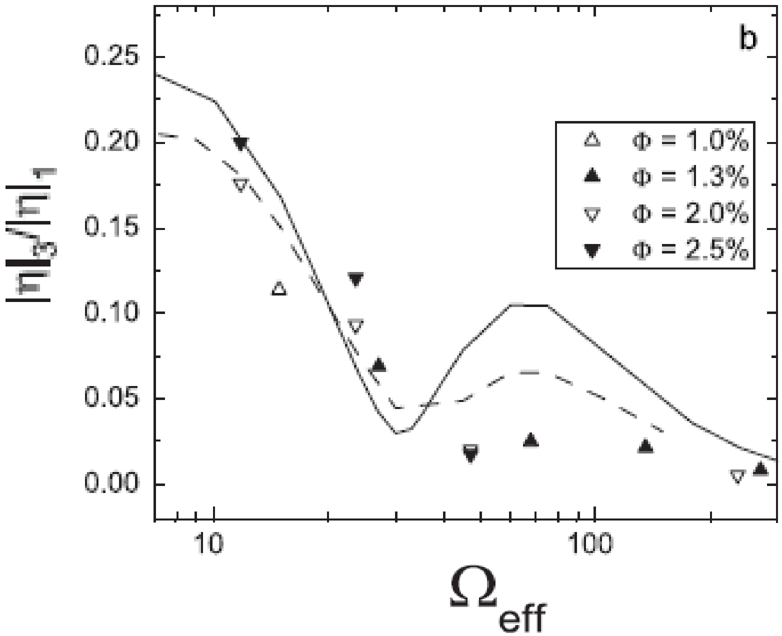


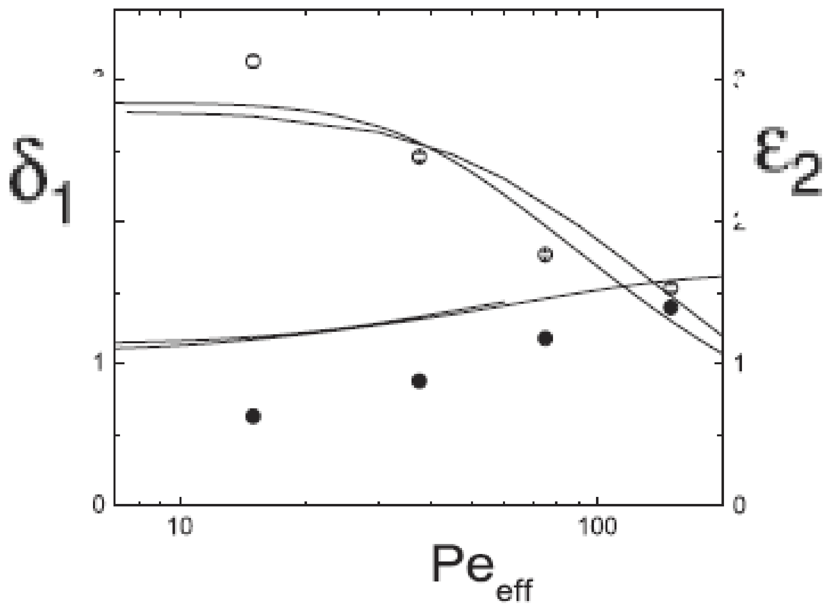


$$\Sigma_D = 2\eta_0\dot{\gamma}\left[\hat{\mathbf{E}} + \frac{(L/D)^2}{3\ln\{L/D\}}\varphi \times \left\{\hat{\mathbf{\Gamma}}\cdot\mathbf{S} + \mathbf{S}\cdot\hat{\mathbf{\Gamma}}^{\mathrm{T}} - \mathbf{S}^{(4)}:\hat{\mathbf{E}} - \frac{1}{3}\hat{\mathbf{I}}\mathbf{S}:\hat{\mathbf{E}} - \frac{1}{\dot{\gamma}}\frac{\mathrm{d}\mathbf{S}}{\mathrm{d}t}\right\}\right]$$

Lonetti, Kohlbrecher, Lettinga, *J. Phys. Cond. Matt.*, 2008

Fourier Analysis





$$\Sigma_D = 2\,\dot{\gamma}_0\,\hat{\mathbf{E}} \sum_{n=0}^{\infty} |\eta|_n \sin(n\omega t + \delta_n)$$

$$P_2(t) = \sum_{n}^{\infty} |P_2|_n \cos(\omega t + \epsilon_n)$$

Find scaling for…

$$Pe_{eff} = \dot{\gamma}_0 / D_r^{eff} \qquad \Omega_{eff} = \omega / D_r^{eff}$$

Using…

$$D_r^{eff} = D_r \{1 - [Pb - Peo]/C\}$$

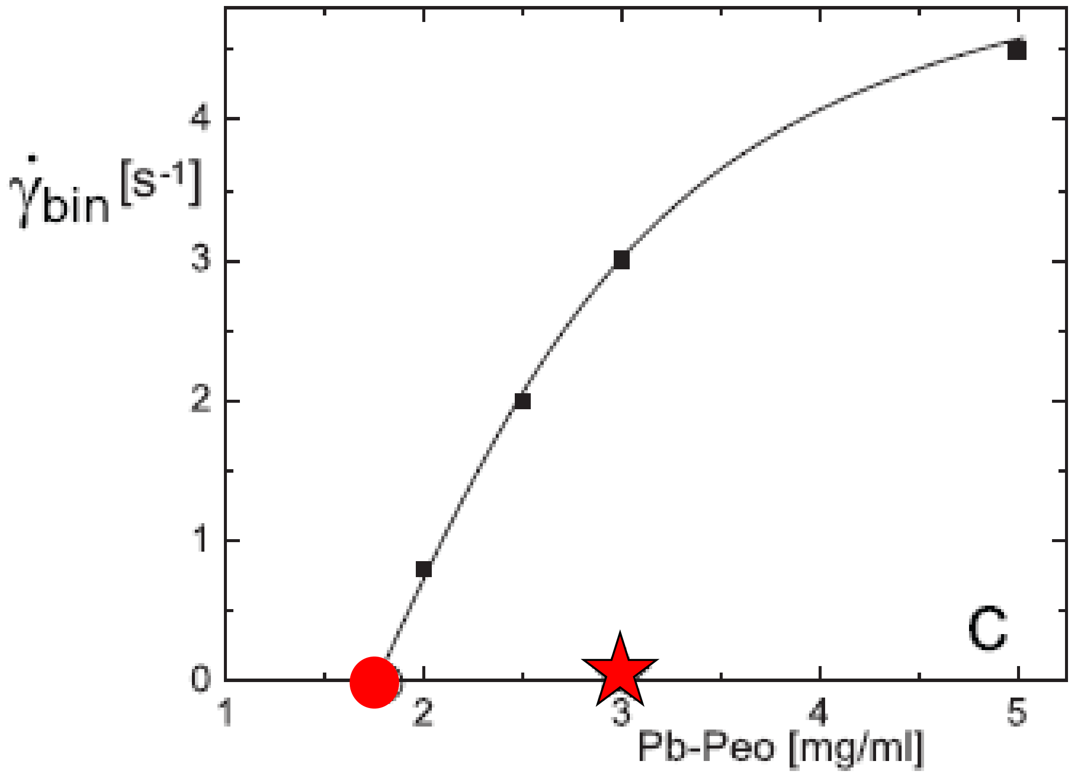
with fit parameters:

$$D_r = 0.04\ s^{-1} \text{ and } C = 3$$

Consequences for equilibrium phase diagram

C=3 mg/ml, so $\phi_{I-N} = 4\dfrac{L}{d} = 3$

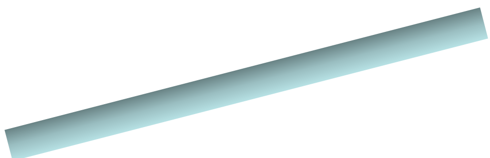
We obtained the I—N spinodal point!



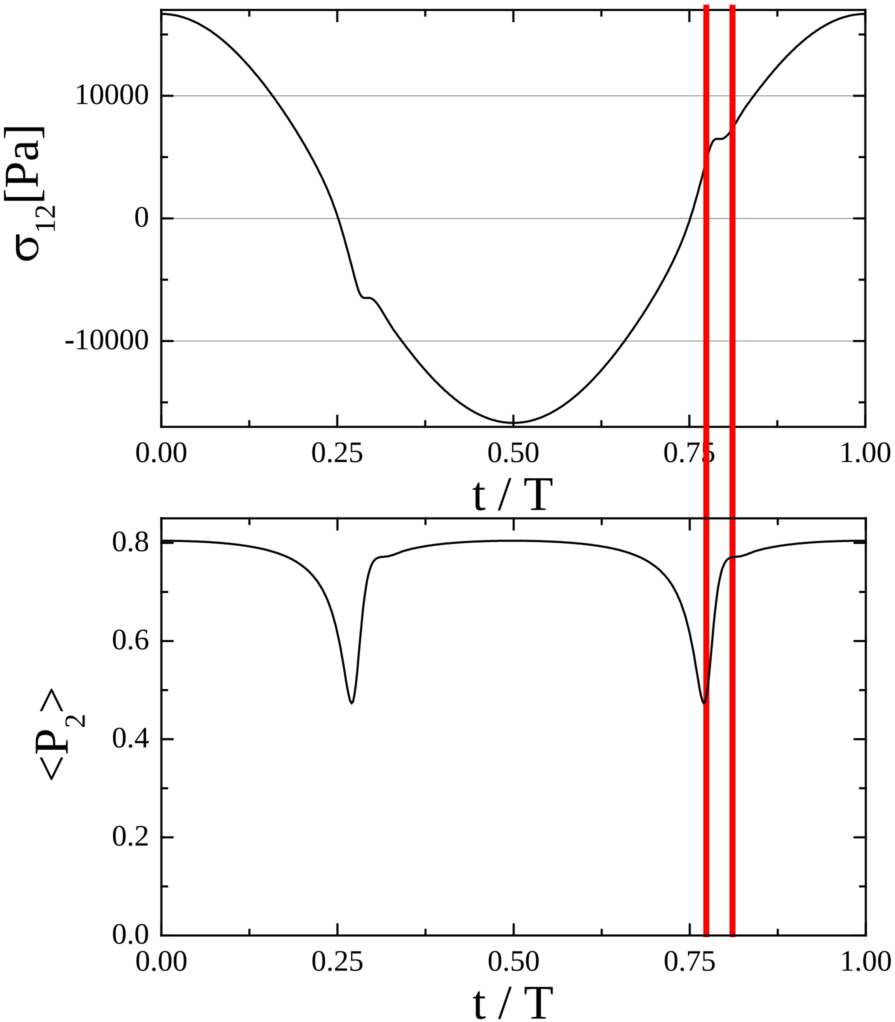
Lonetti, Kohlbrecher, Lettinga, *J. Phys. Cond. Matt.*, 2008

Smoluchowski Theory for hard rods

$$\boldsymbol{\Sigma}_D = 2\eta_0\dot{\gamma}\left[\hat{\mathbf{E}} + \frac{(L/D)^2}{3\ln\{L/D\}}\varphi \times \left\{\hat{\boldsymbol{\Gamma}}\cdot\mathbf{S} + \mathbf{S}\cdot\hat{\boldsymbol{\Gamma}}^{\mathrm{T}} - \mathbf{S}^{(4)}:\hat{\mathbf{E}} - \frac{1}{3}\hat{\mathbf{I}}\mathbf{S}:\hat{\mathbf{E}} - \frac{1}{\dot{\gamma}}\frac{\mathrm{d}\mathbf{S}}{\mathrm{d}t}\right\}\right]$$



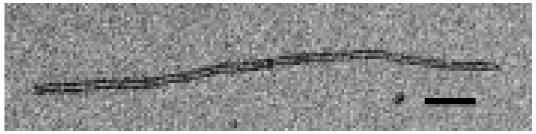
$$\frac{d}{dt}\mathbf{S} = -6D_r\left\{\mathbf{S} - \tfrac{1}{3}\hat{\mathbf{I}} + \tfrac{L}{D}\varphi\left(\mathbf{S}^{(4)}:\mathbf{S} - \mathbf{S}\cdot\mathbf{S}\right)\right\} + \dot{\gamma}\left\{\hat{\boldsymbol{\Gamma}}\cdot\mathbf{S} + \mathbf{S}\cdot\hat{\boldsymbol{\Gamma}}^T - 2\mathbf{S}^{(4)}:\hat{\mathbf{E}}\right\}$$

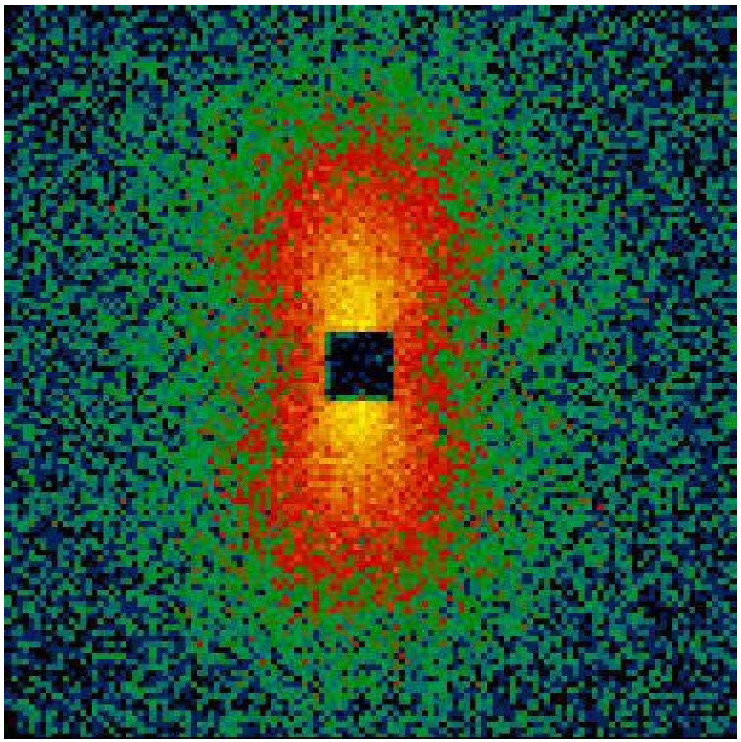


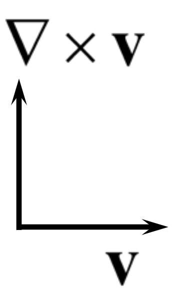
$-\gamma_0$ $-\dot{\gamma}_0$ γ_0 $\dot{\gamma}_0$

Dynamic response fd virus in isotropic phase

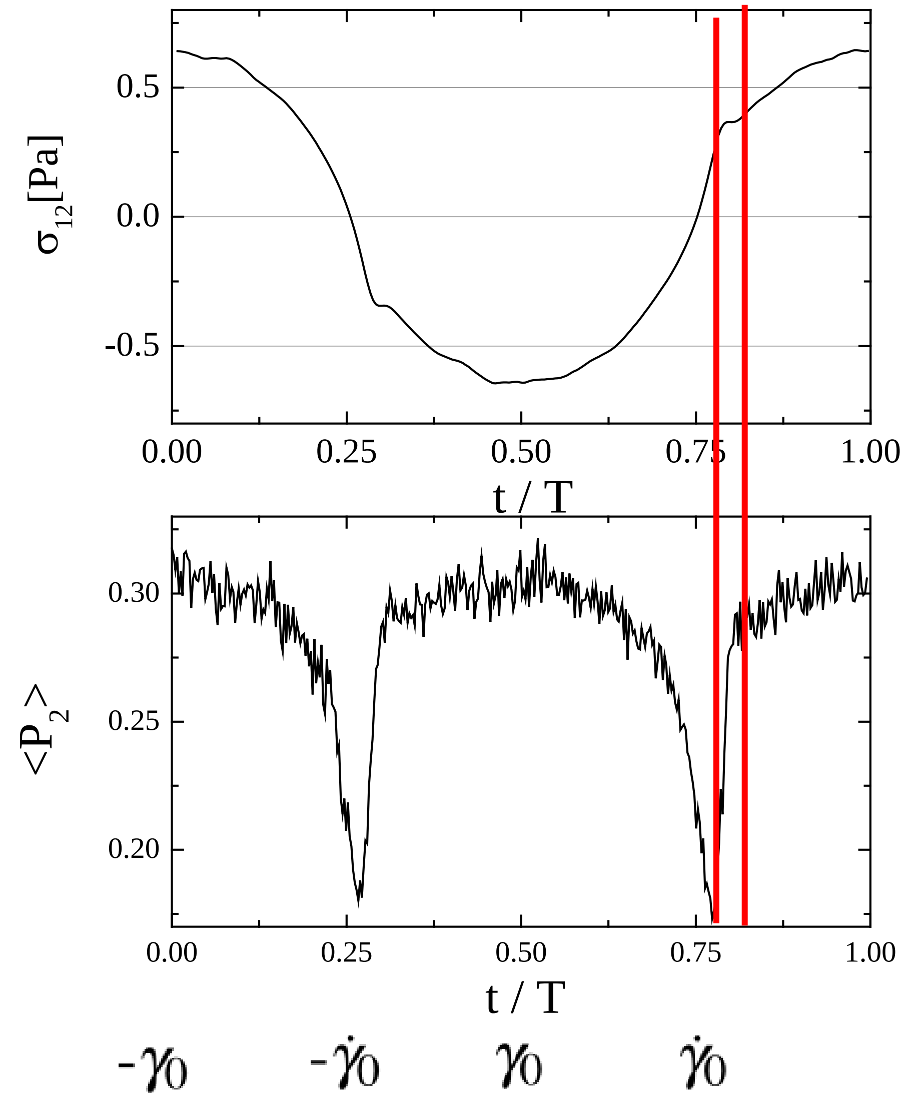
L=880 nm
D=6.6 nm
P=3.0 µm



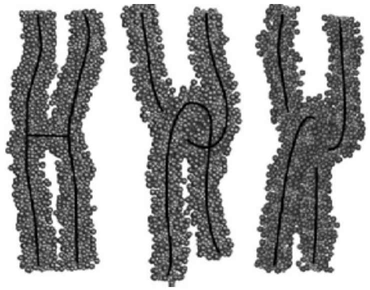


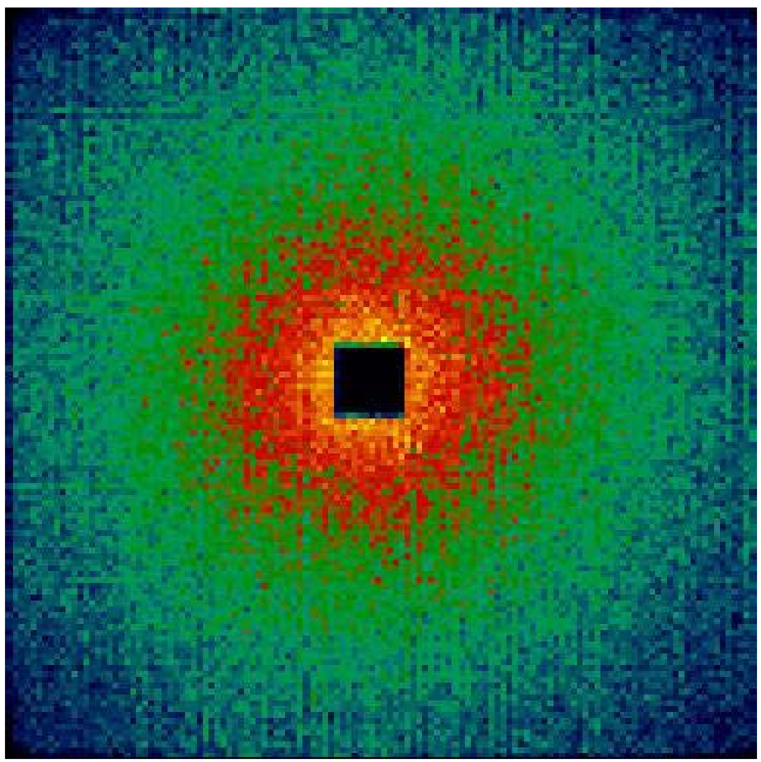


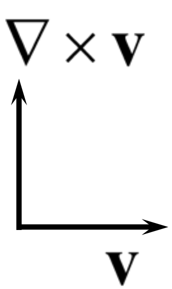
t-SANS @ PSI
f=0.01, γ=25.6



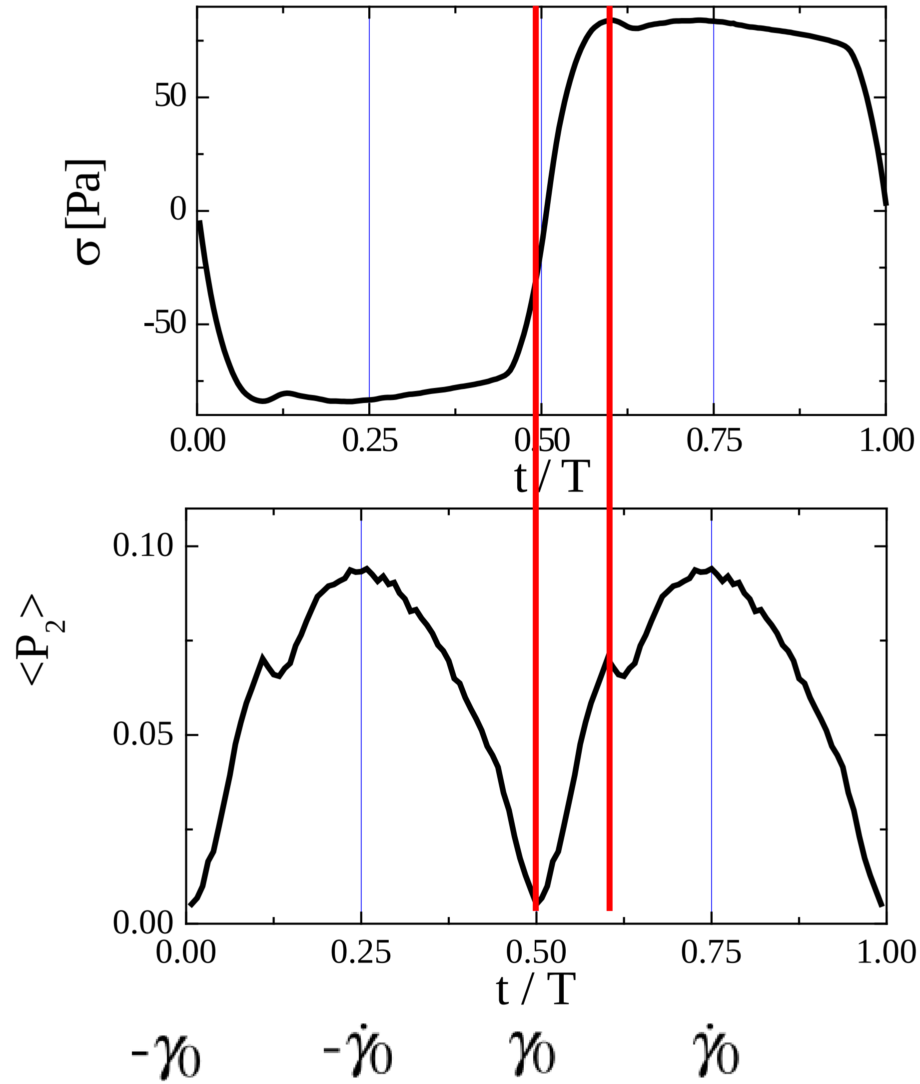
Dynamic response CpCl wormlike micelles





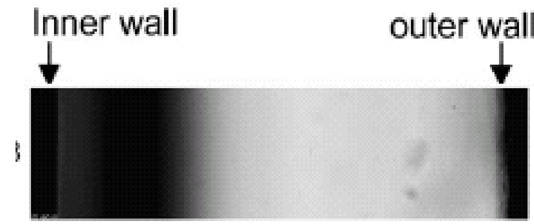


t-SANS @ PSI
f=0.0037, γ=766

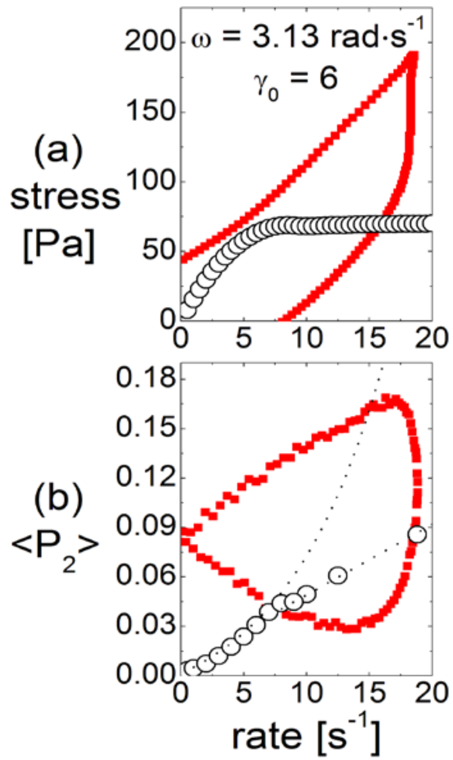


Dynamic response CpCl wormlike micelles

@ constant applied shear rate amplitude = $\gamma_0\omega$



Rate dependence (positive rate only)



Rogers, Kohlbrecher, and Lettinga, *Soft Matter*, 2012, **8**, 7831-7839

Dynamic response CpCl wormlike micelles

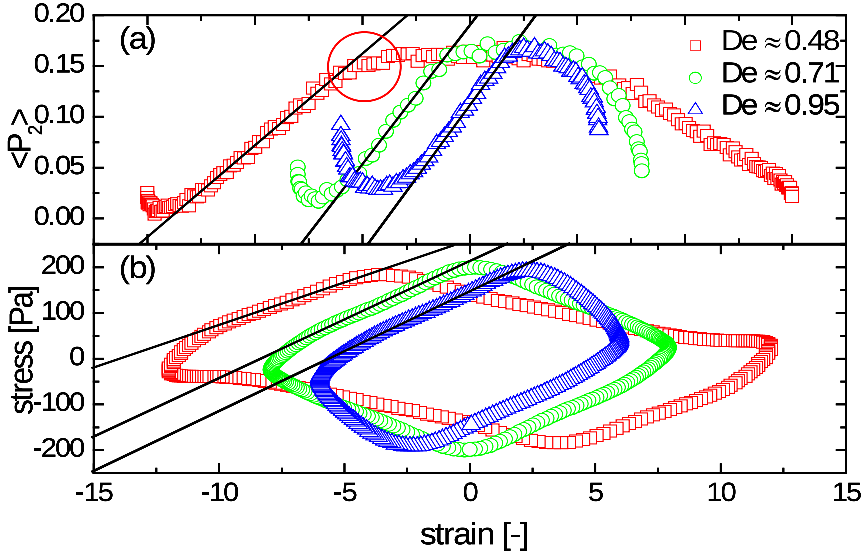
@ constant applied shear rate amplitude = $\gamma_0\omega$

Strain dependence

$\omega >> 1/\lambda \rightarrow$ elastic

Stress-optical relation

for $\gamma < 2\dot{\gamma}_0\lambda$: $\dfrac{\partial P_2}{\partial \sigma} = \dfrac{S_K}{G_K}$



$\omega < 1/\lambda \rightarrow$ yielding

Transform from solid into liquid

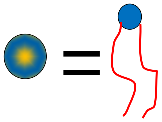
Critical strain:

γ @ $\sigma_{max} \approx 2\dot{\gamma}_0\lambda$

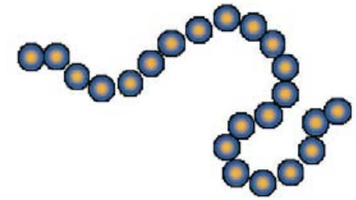
$<P_2>_{max} \sim 2<P_2>_{stationary}$

Rogers, Kohlbrecher, and Lettinga, *Soft Matter*, 2012, **8**, 7831-7839

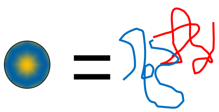
Conclusions part I and II



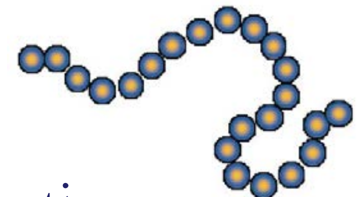
CpCl/NaSyl = Dwarf = Living



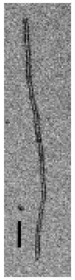
- strong shear thinning, fast shear band formation
- stress relexation probably through break up
- maximum orientation at maximum stress



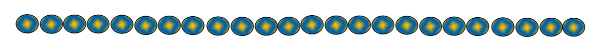
Pb-PEO = Giant = Dead



- strong shear thinning close to I-N, some shear band formation
- stress relexation probably through alignment Kuhn segment

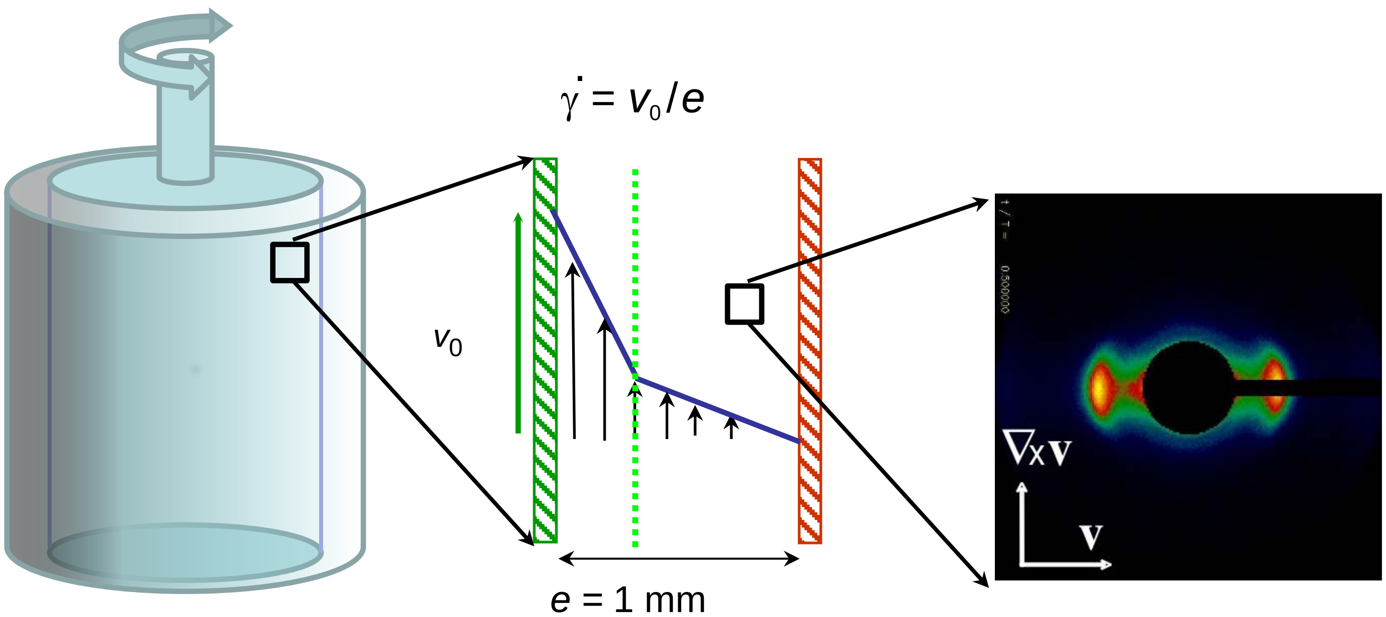


Fd virus = Rods



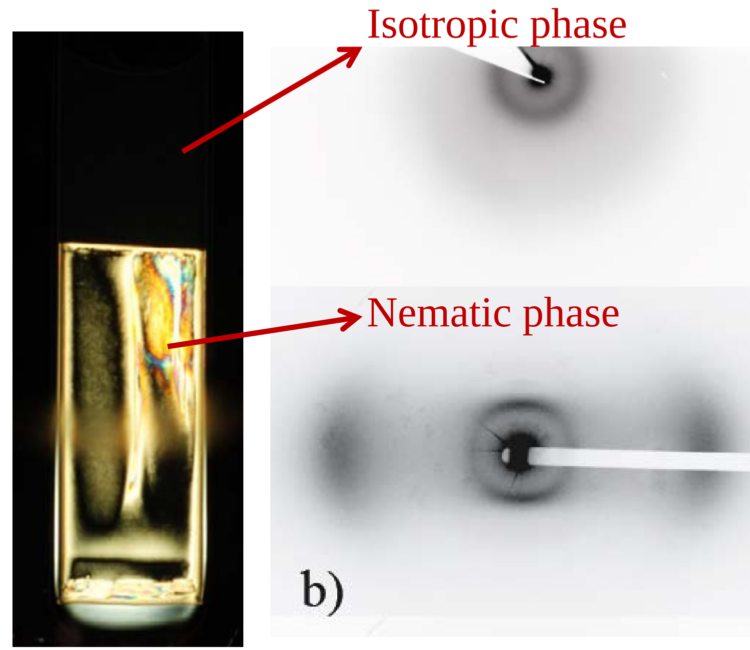
- moderate shear thinning close to I-N, no shear band formation
- stress relexation probably through alignment rods
- minimum orientation at maximum stress

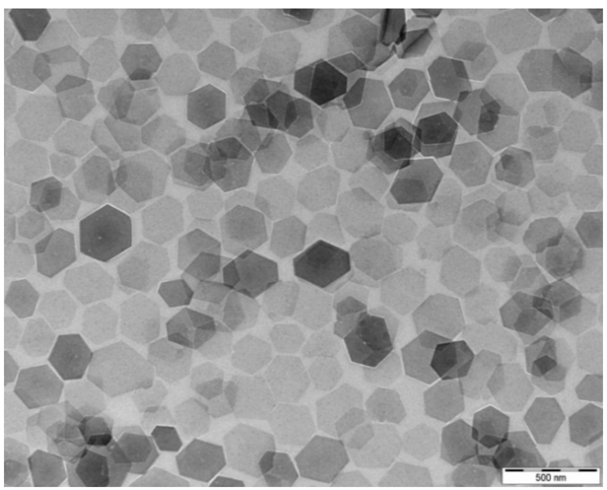
Part III: 3D reorientational motion in sheared nematic platelet dispersions

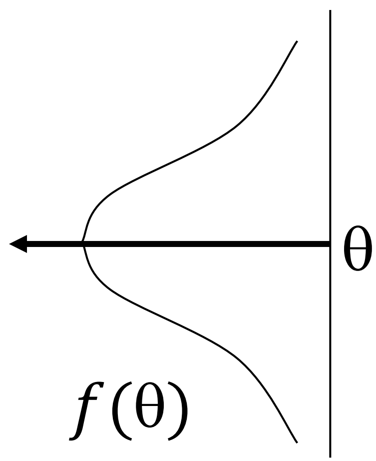


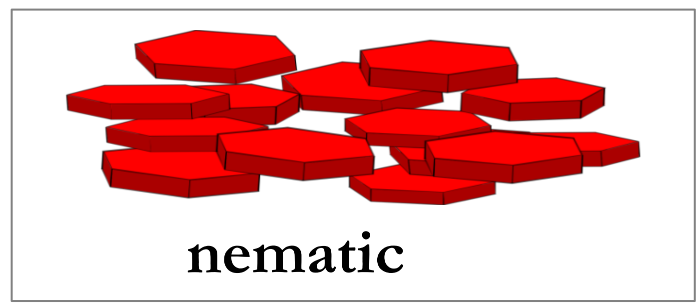
System: Gibbsite (AlOOH)

- Charged ,
- Relatively thick (R=125 ± 16 nm, d=11 ± 4 nm)
- Relatively monodisperse (~ 13–20%)
- Sides and faces carry the same charges (positive)
- Dispersed in glycerol







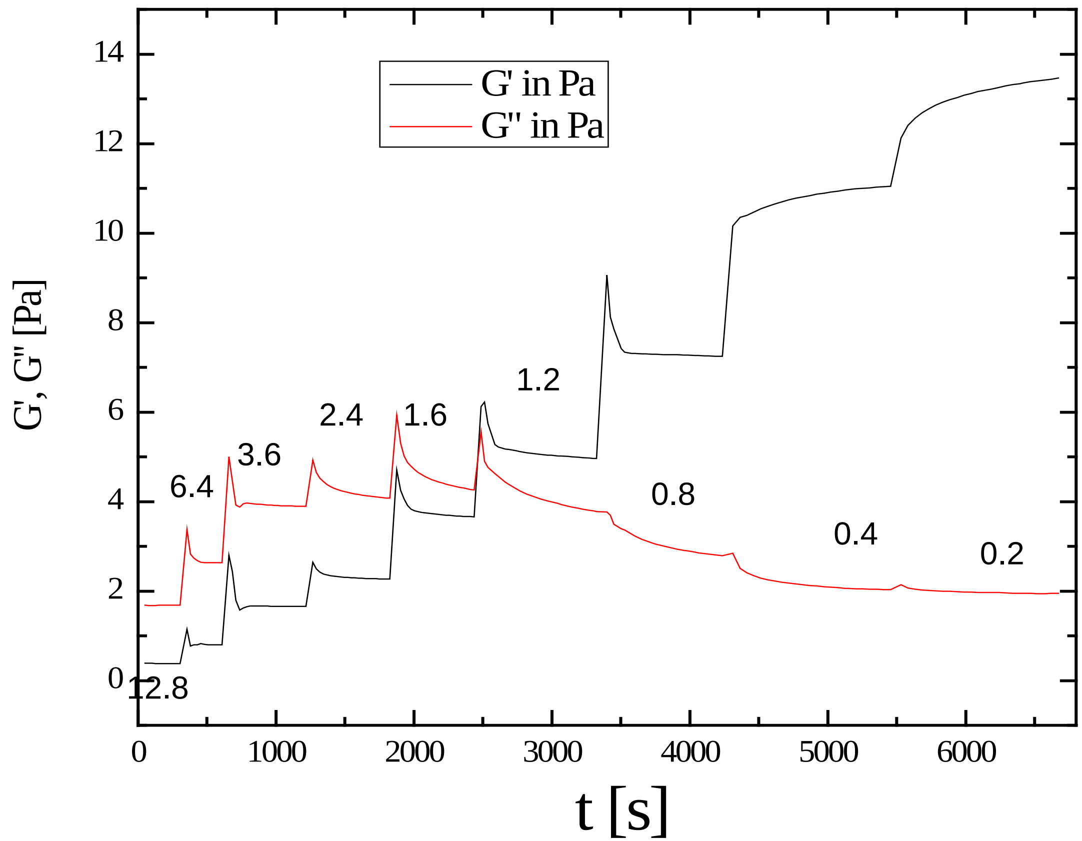


Lettinga et al, *PRL* (2012) **109**, 246001

How liquid is a liquid crystal?

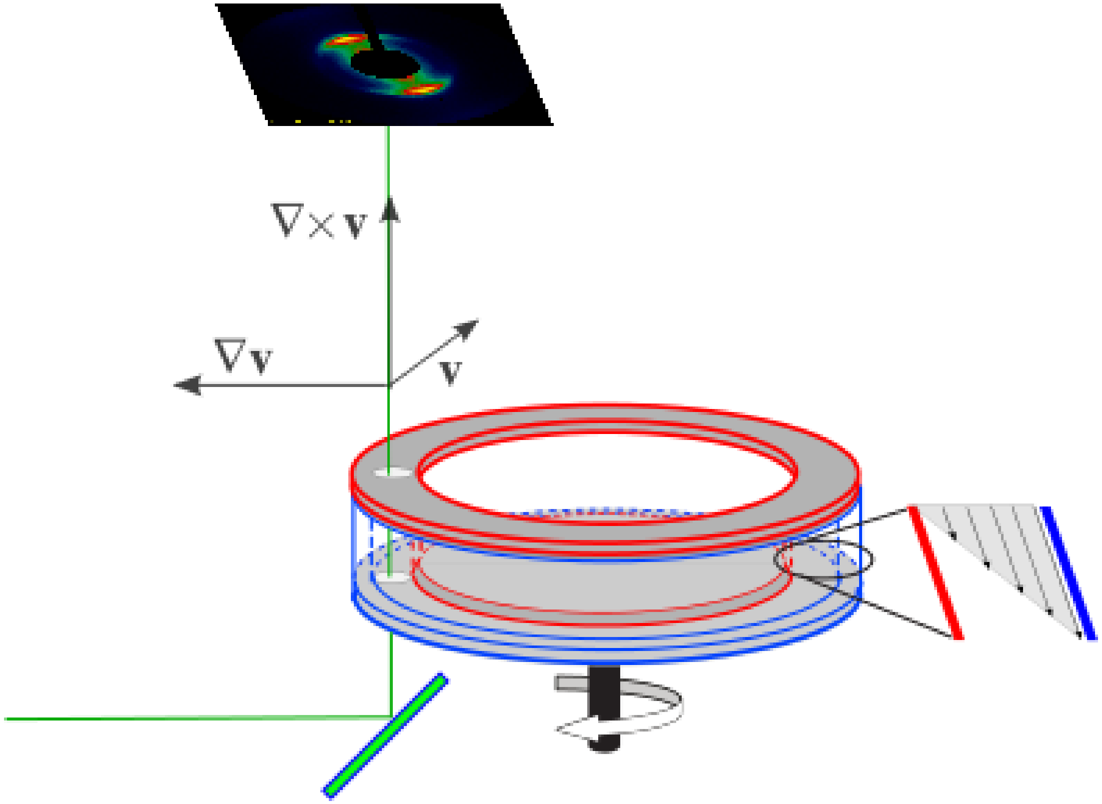
JÜLICH
FORSCHUNGSZENTRUM

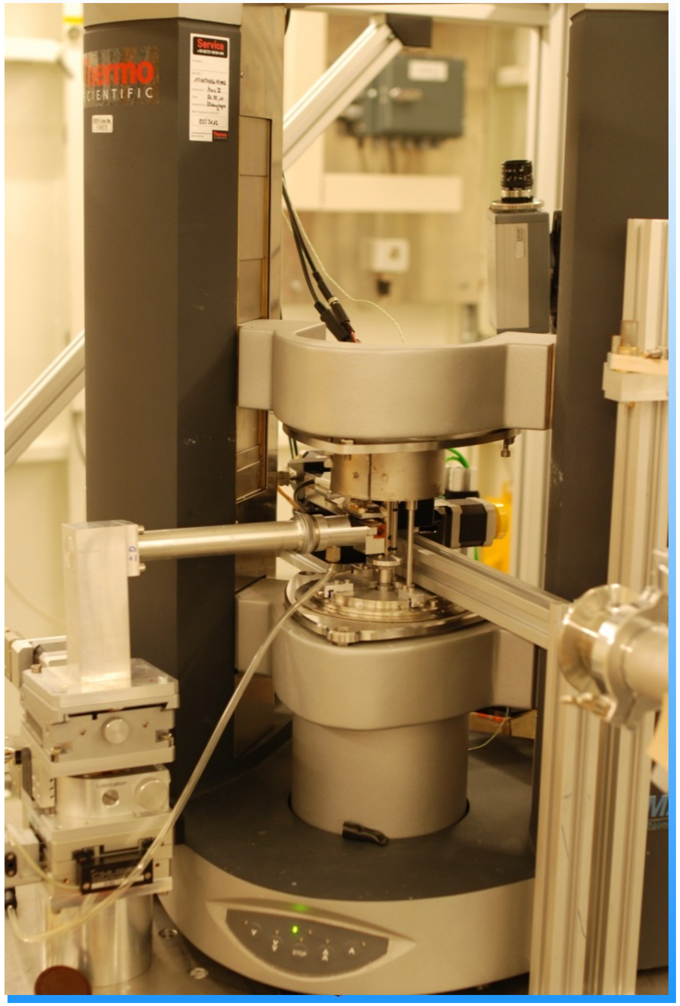
The Experiment: strain sweep at f=0.04 Hz



12.8 ← γ_0 — 0.2

Structure with Rheo-SAXS @ DESY

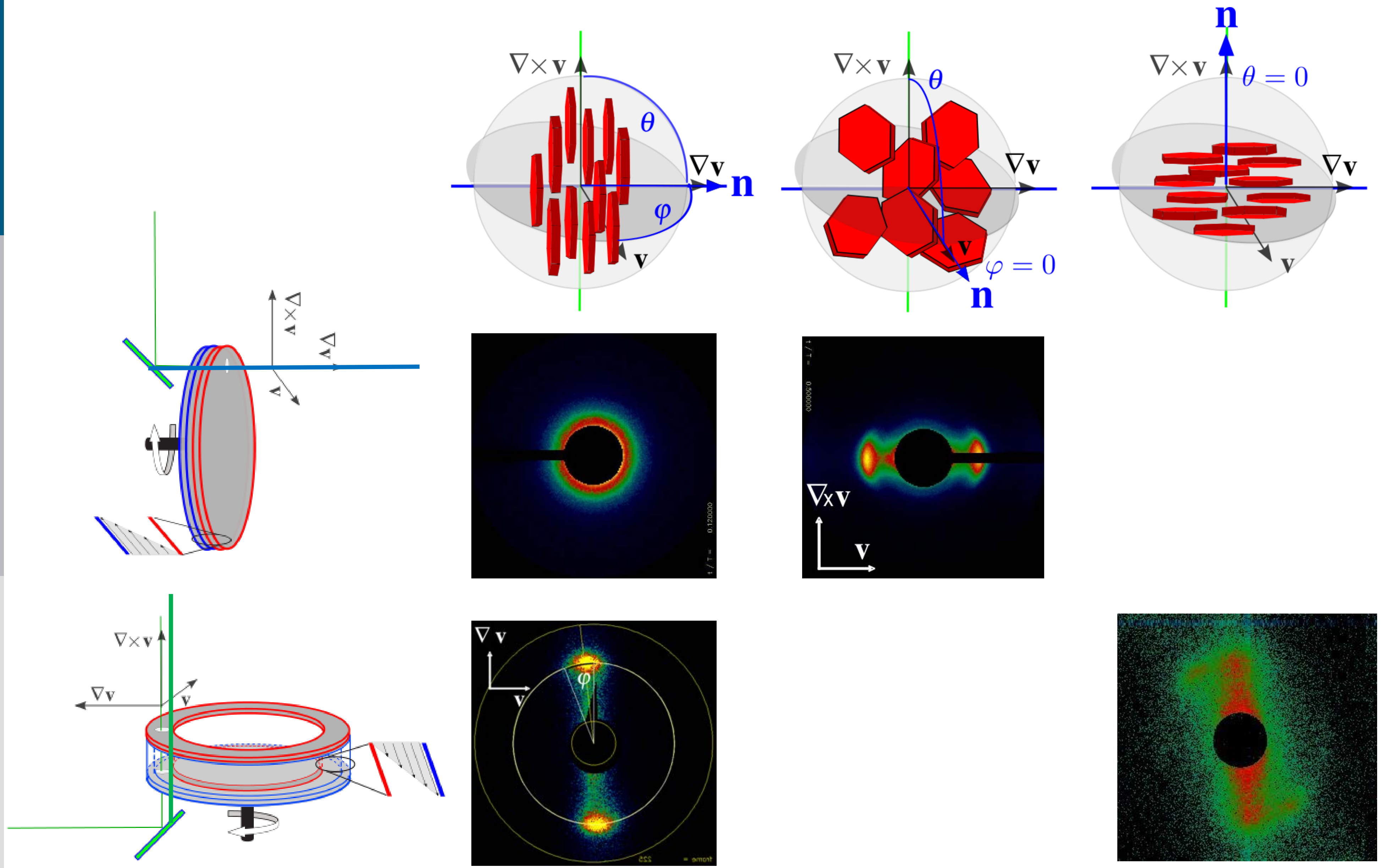




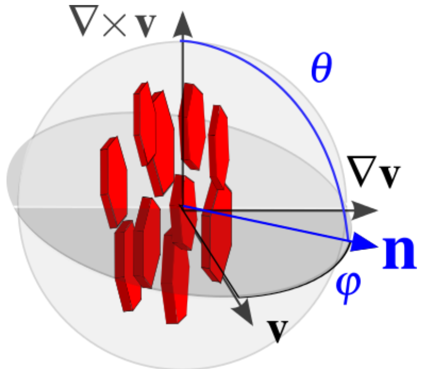
Is flow homogeneous?

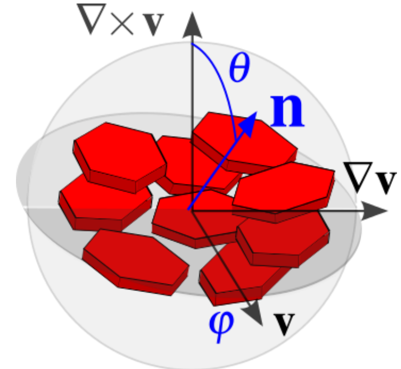
What is the total 3D motion?

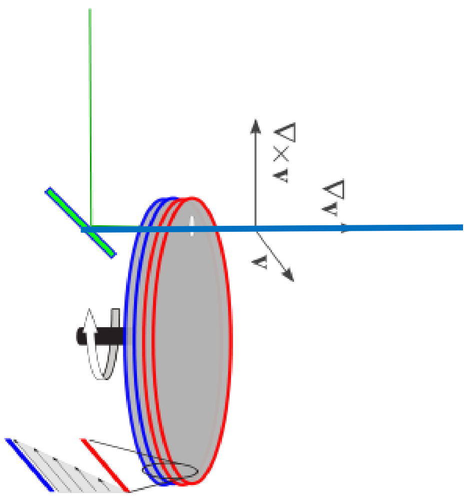
Possible configurations

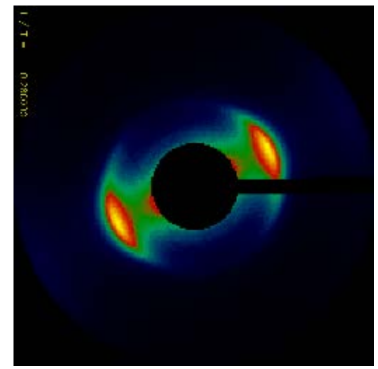


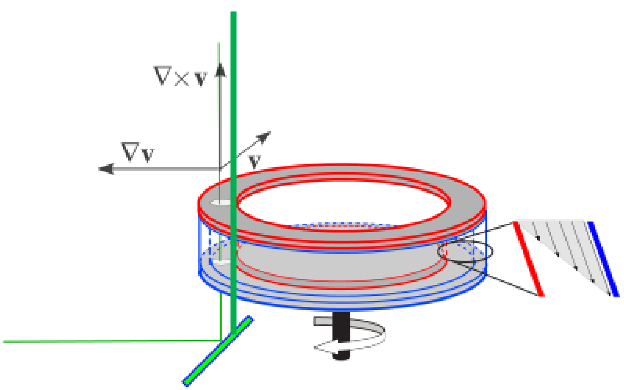
Possible configurations

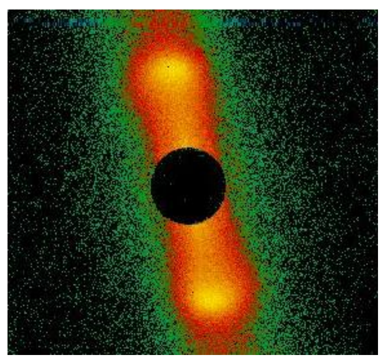




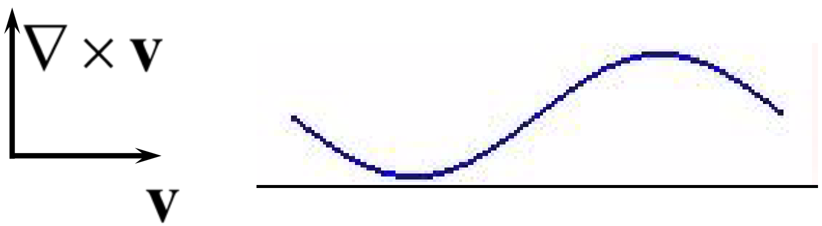


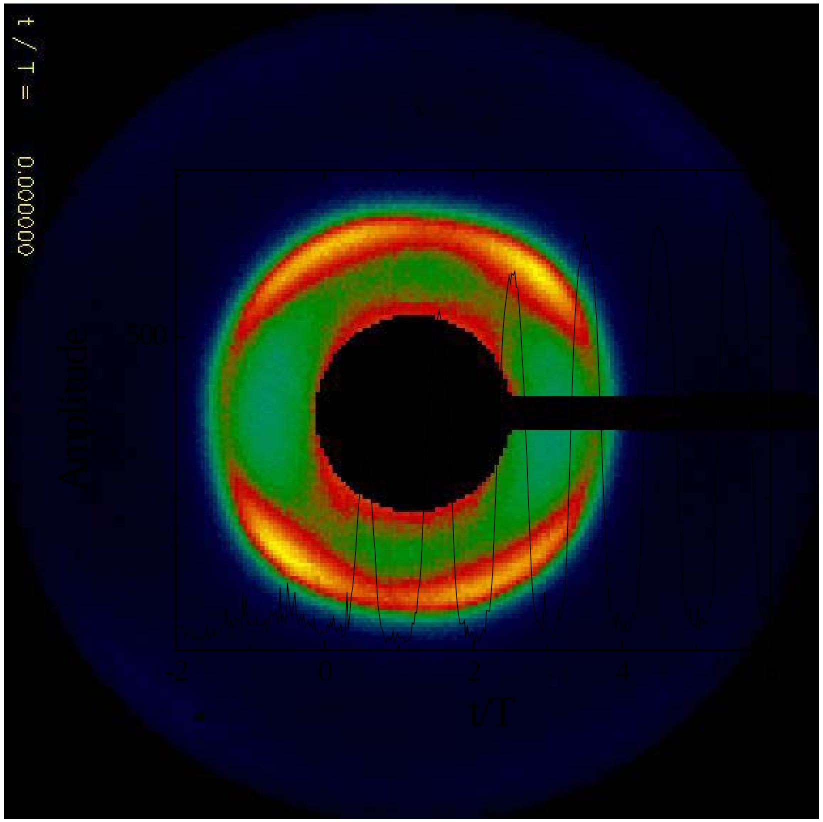




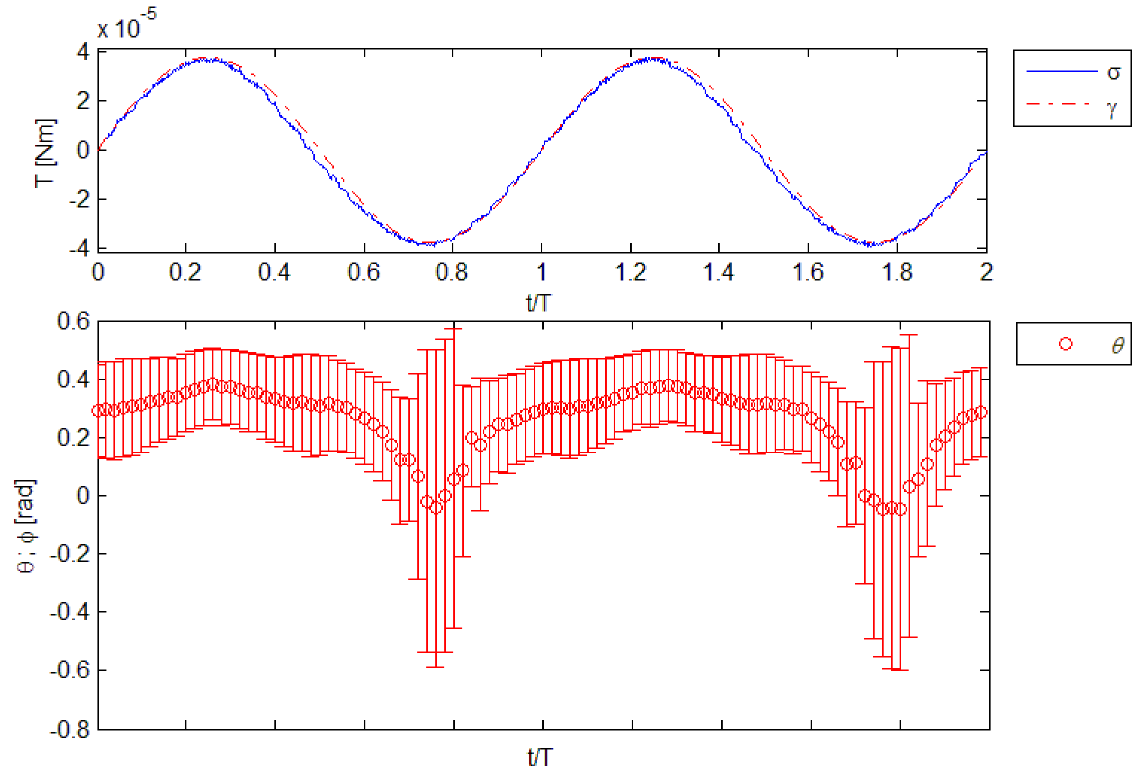


Low strain response: γ=0.4

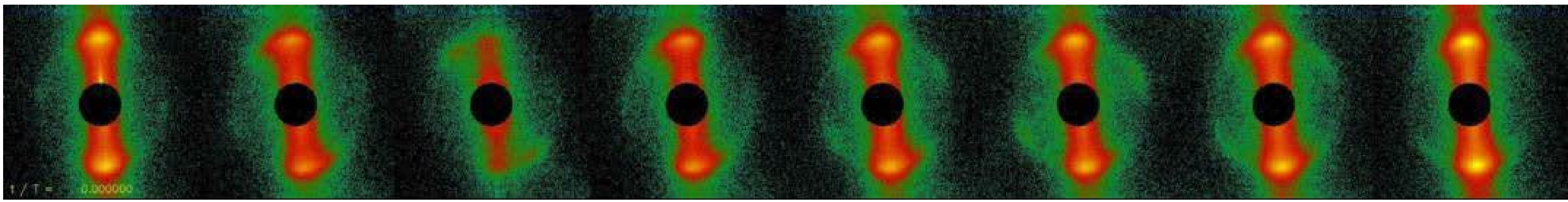


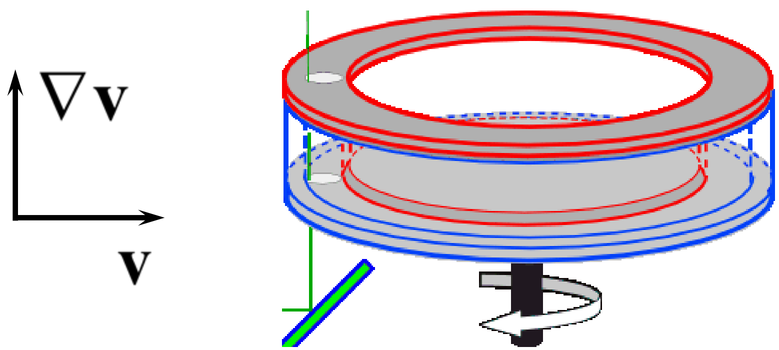


1st harmonic response→ Preferential direction of deformation→ Symmetry breaking→ Dynamic bifurcation



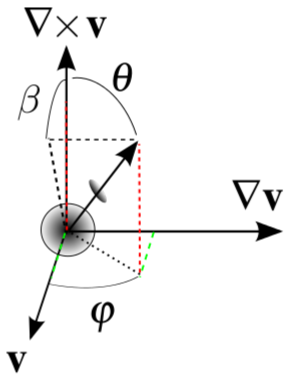
Low strain response: γ=0.4

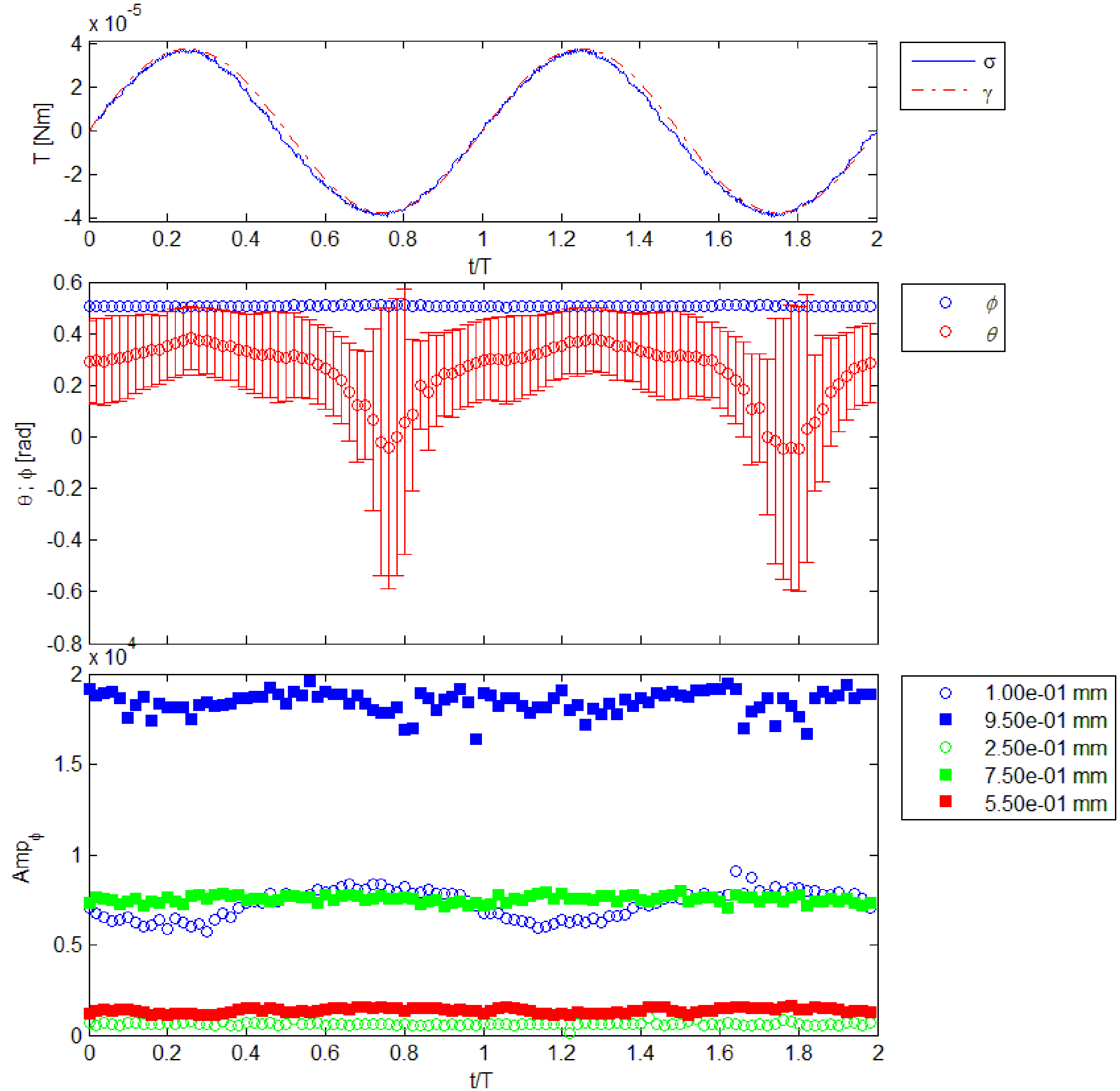




Low strain response: γ=0.4

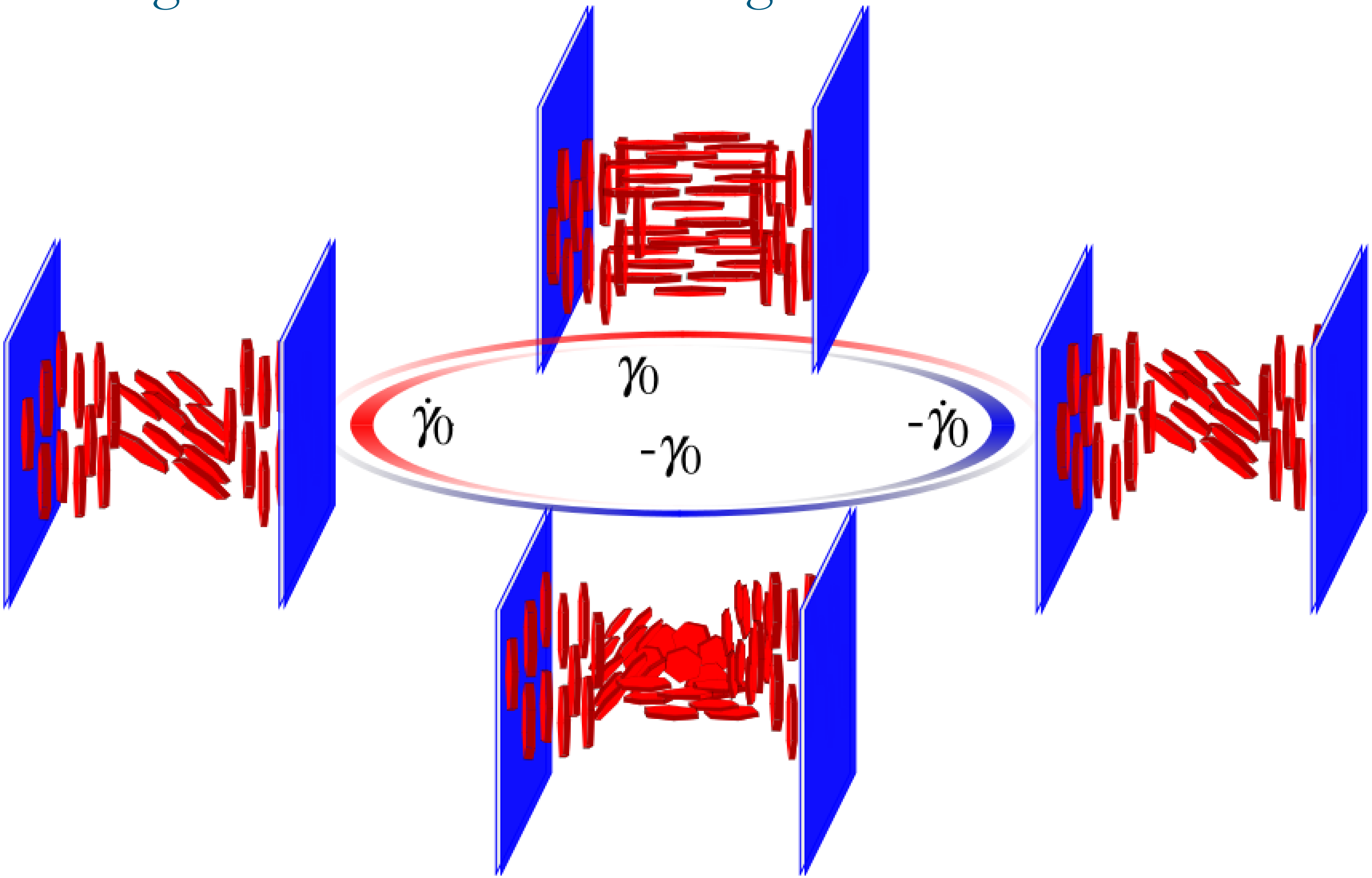
No clear structure in middle of gap



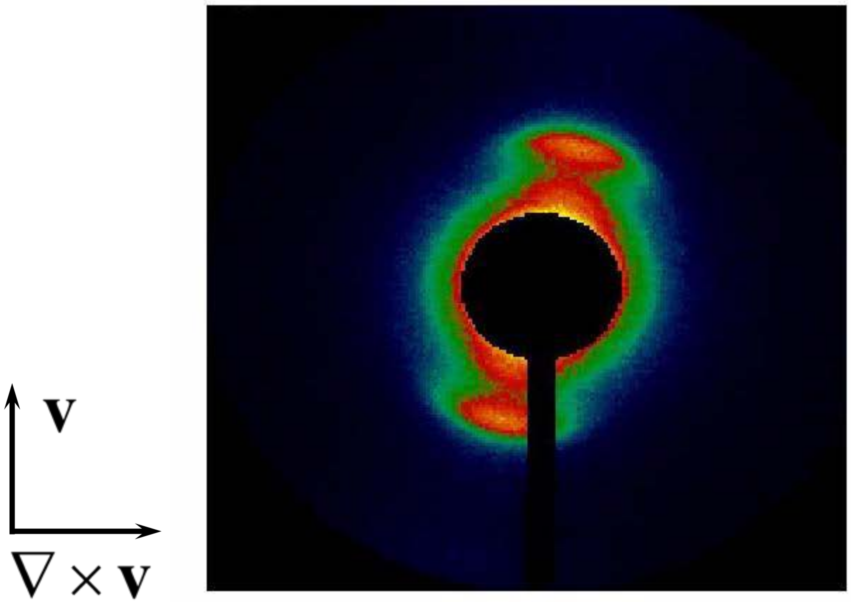


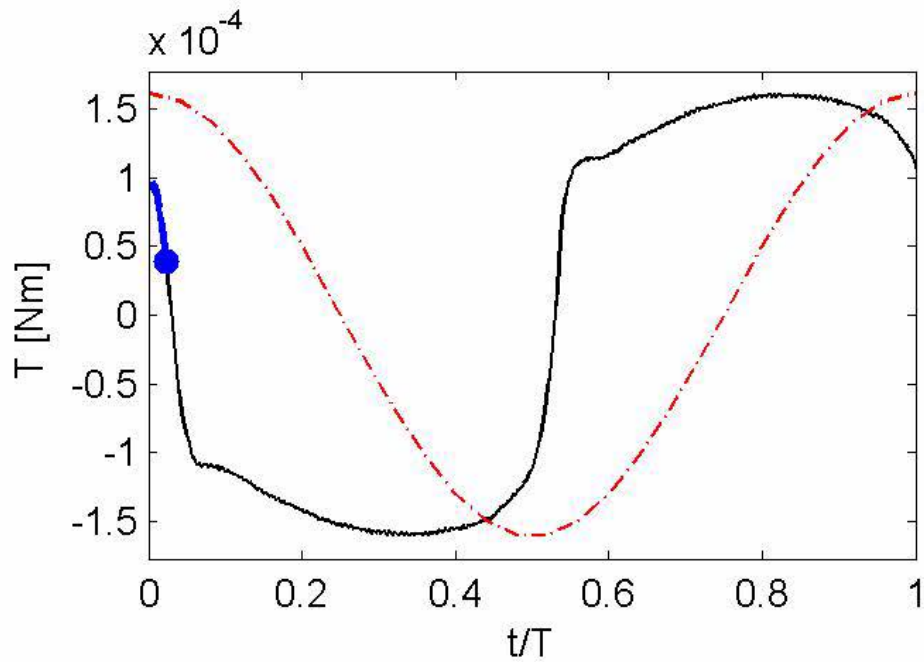
Cartoon low strain response:

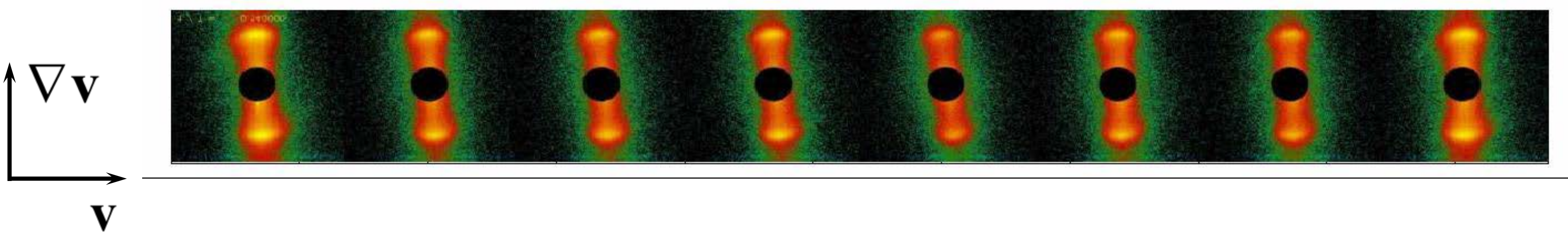
- 1st harmonic response =Dynamic bifurcation
- Huge effect of wall anchoring



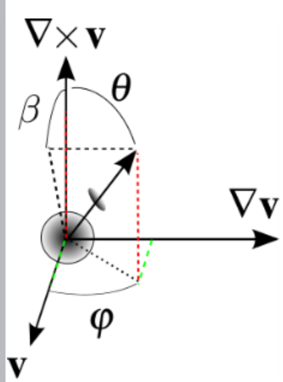
High strain response: γ=12.8

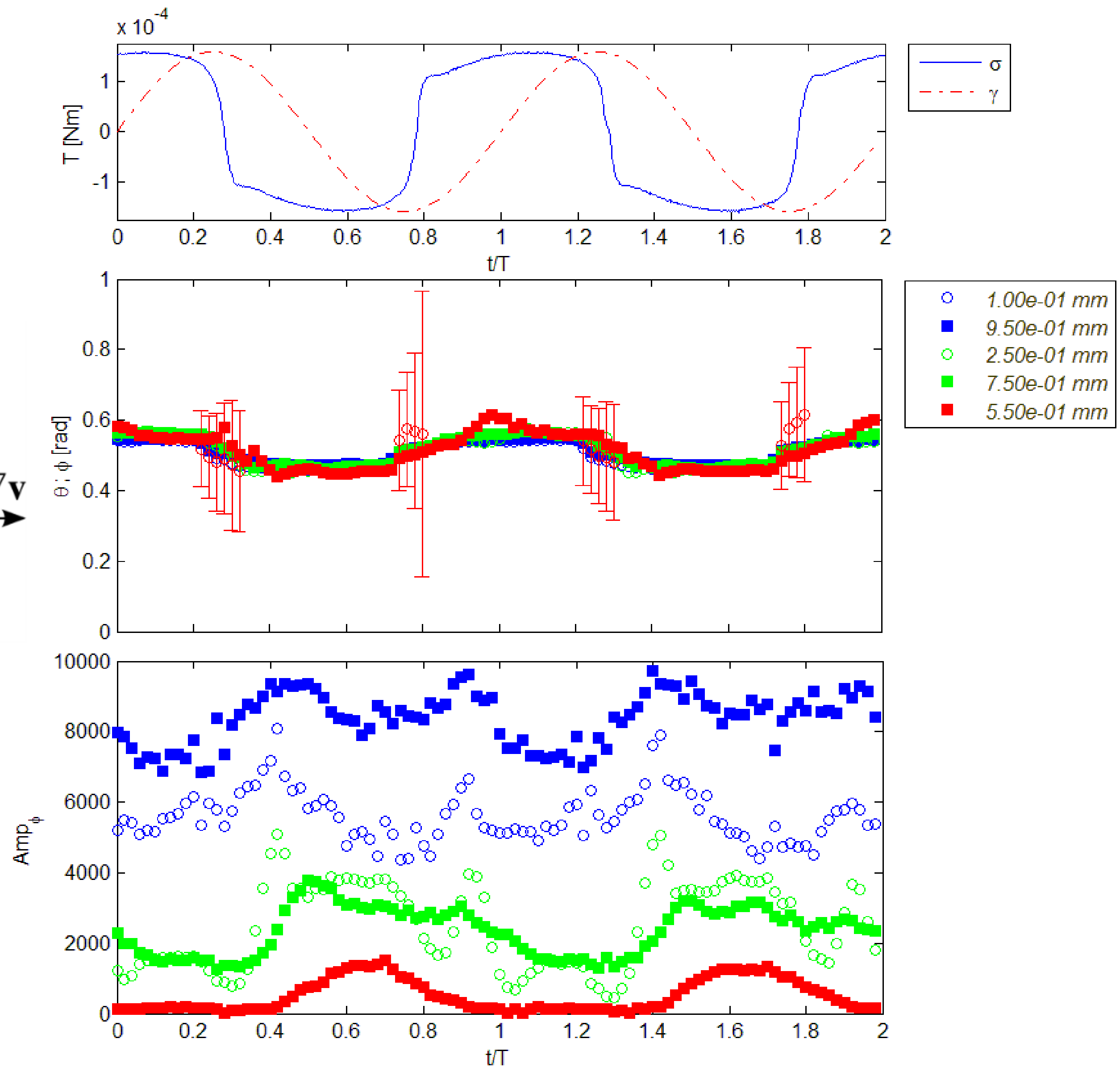






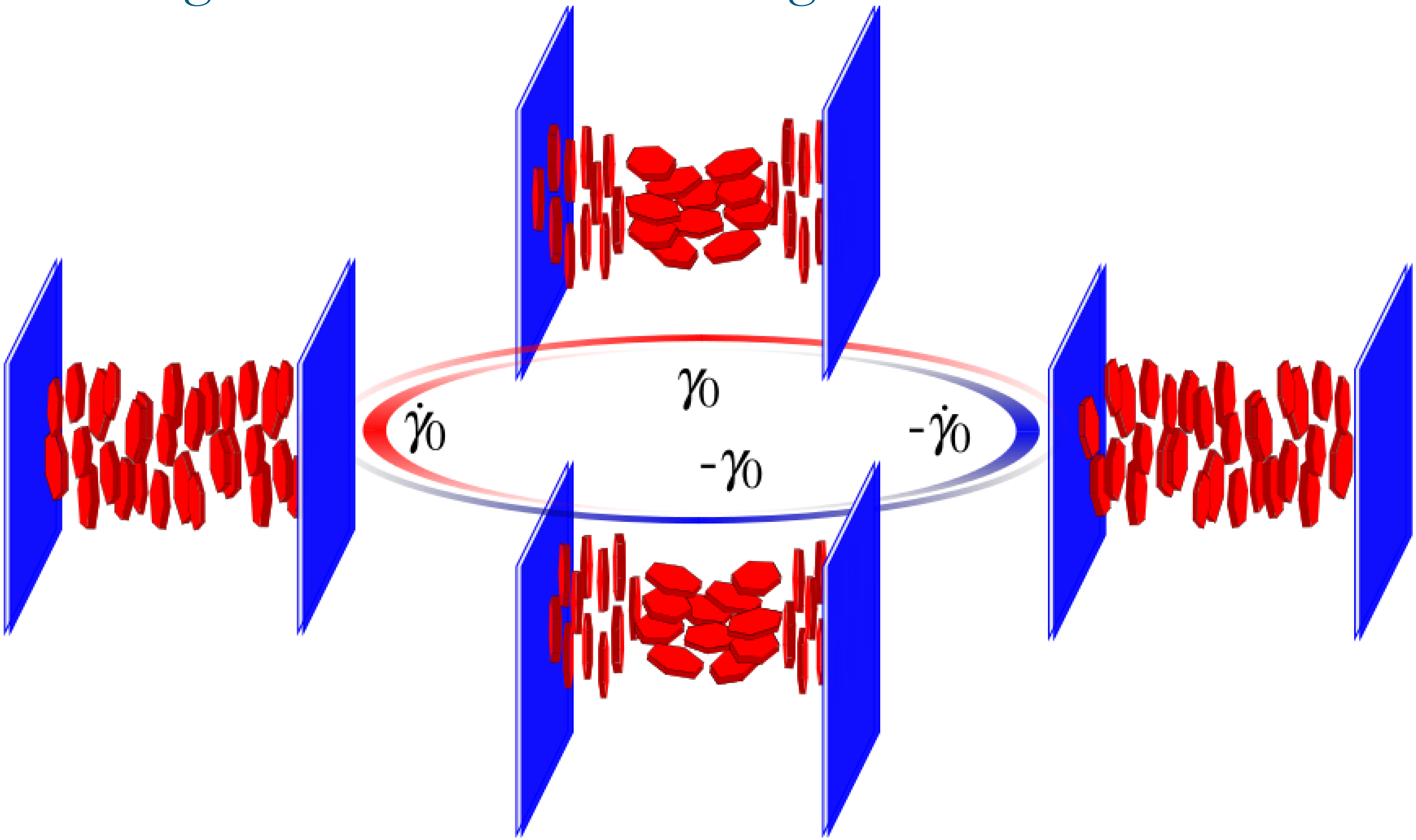
High strain response: γ=12.8



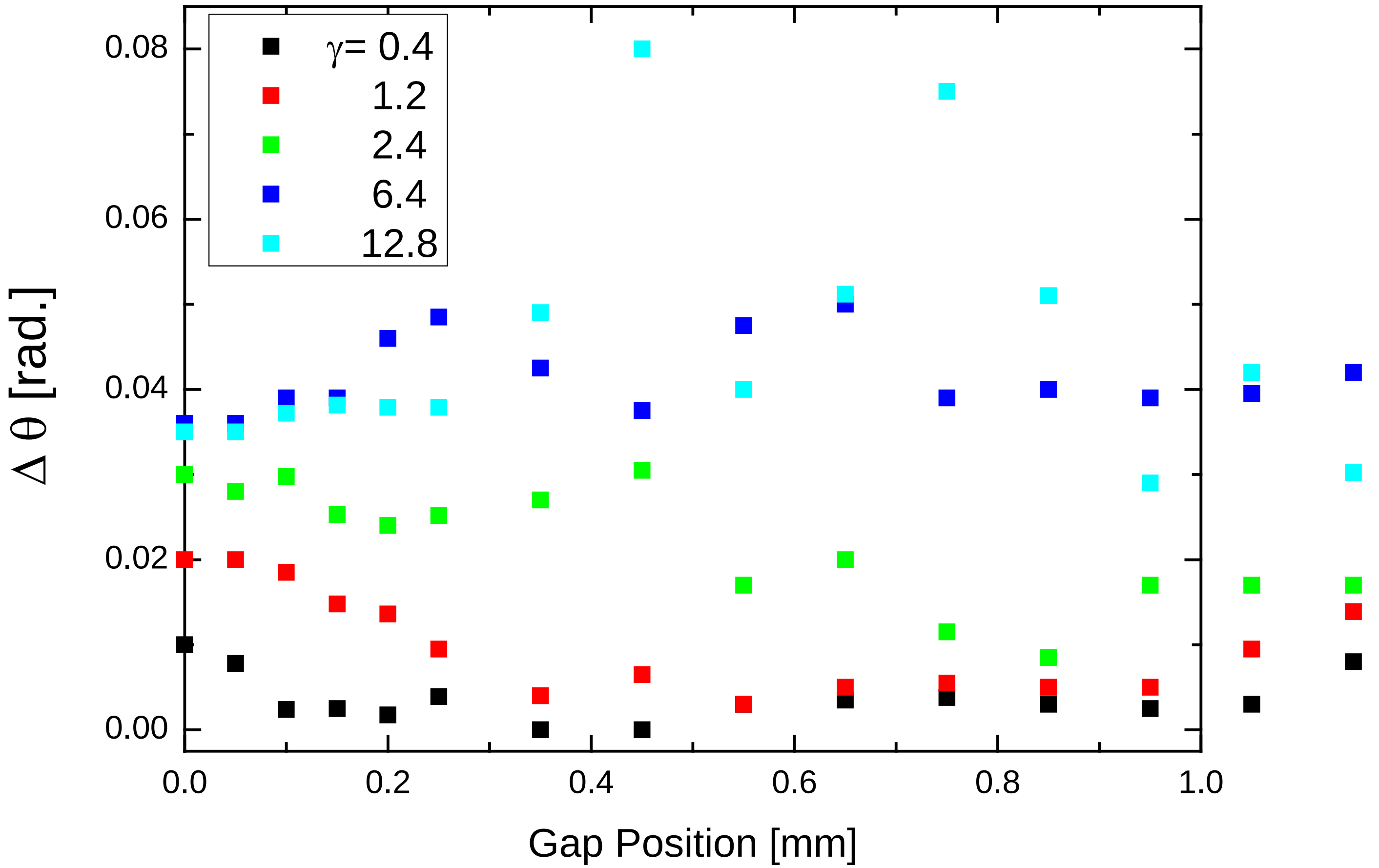


Cartoon high strain response:

- 2nd harmonic response
- Widening followed by flipping
- Huge effect of wall anchoring



How soft is the inside of a shear cell? Wall anchoring vs Director motion

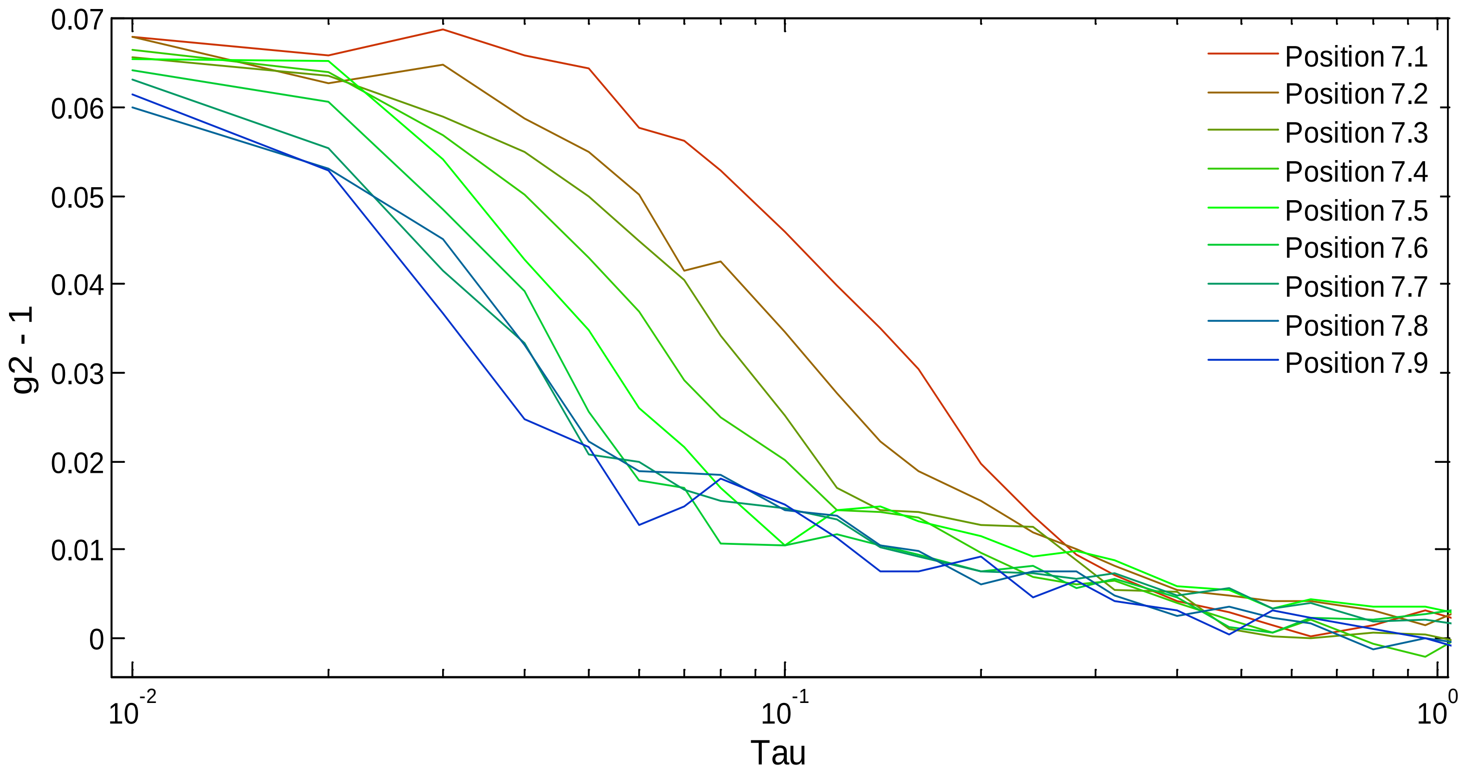


Outlook

- Use the coherence of the squeezed X-rays AND very fast

New Lambda Detector!

Silica particles in highly viscous medium, at shear rate 0.005 s^{-1}



Conclusions Part III

- Low strain: Hookean stress response, **but**

  structure response has same frequency as shear field→

  Dynamic bifurcation

- High strain: normal double frequency response of structure; on average flow alignment, but system flips at flow reversal.

- BUT: response depends highly on location in the cell:

  Strong competition between wall anchoring and director tumbling

Acknowledgements:

<u>Stroboscobic SANS:</u>

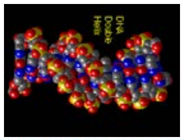
Simon Rogers,Barbara Lonetti, Joachim Kohlbrecher[PSI]

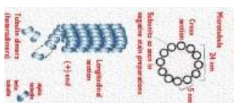
<u>Platelets:</u>

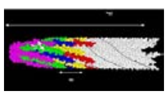
Peter Holmqvist, Pierre Ballesta, Simon Rogers,
Bernd Struth, Fabian Westermeier, Heinz Graafsma[DESY]

Extra: Molecular origin shear thinning using imaging

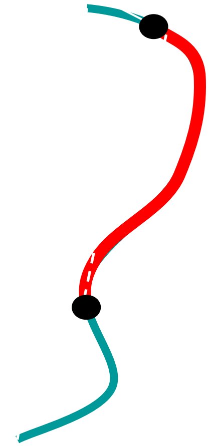
What about semi-flexible systems?



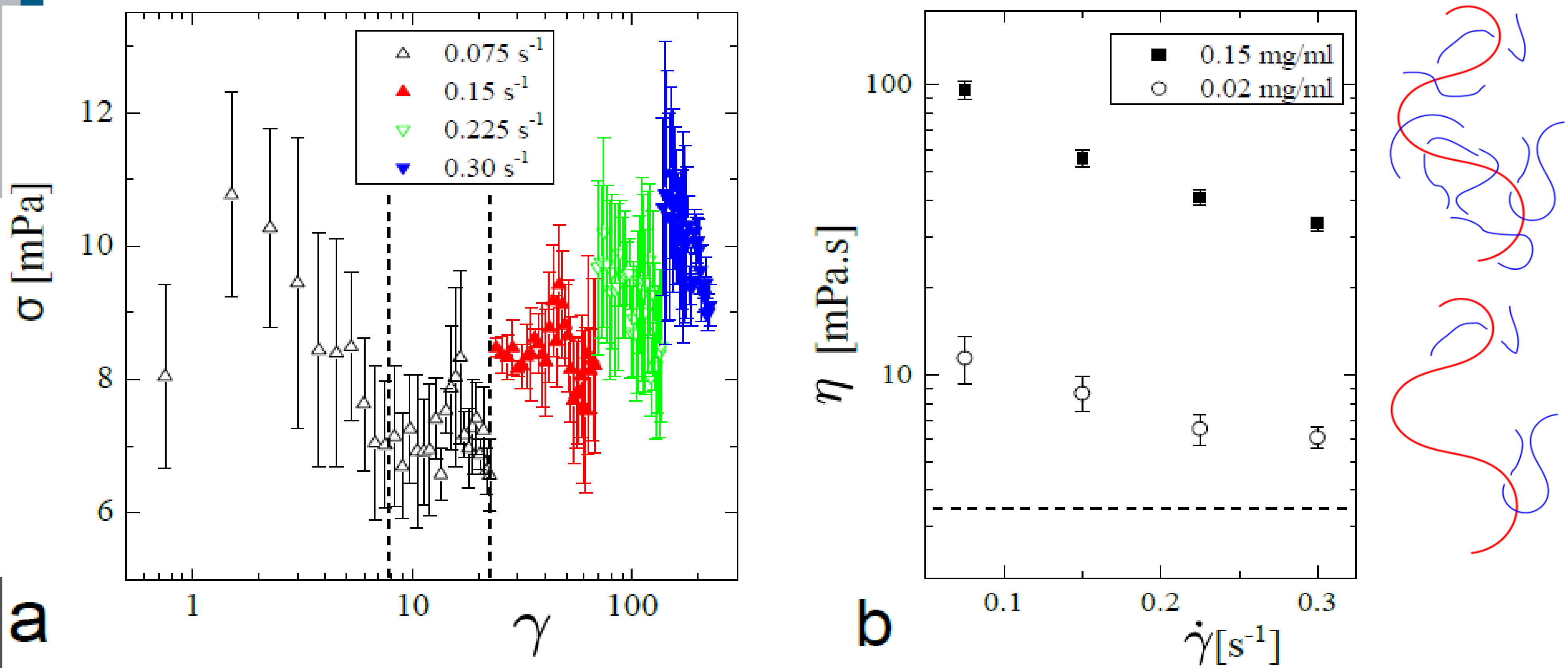




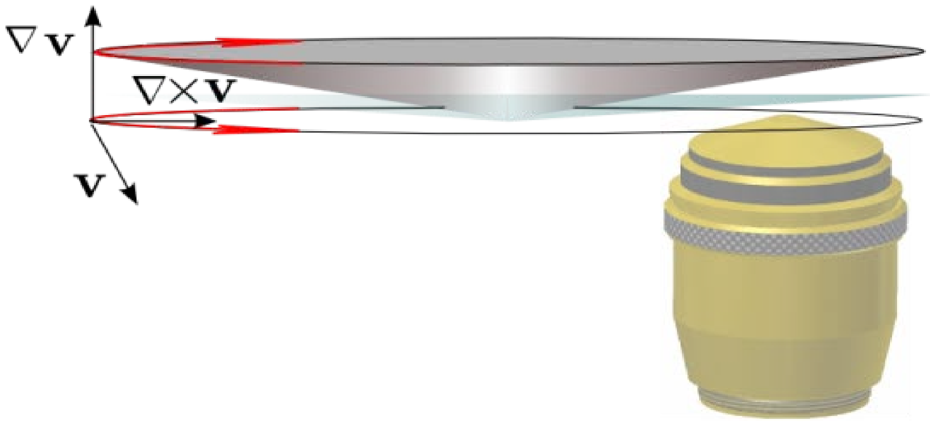
	L	D	P
DNA	variable	3 nm	50 nm
F-actin	variable	7 nm	17 μm
Microtubuli	variable		>>
Fd virus	880 nm	6.6 nm	1.8 μm

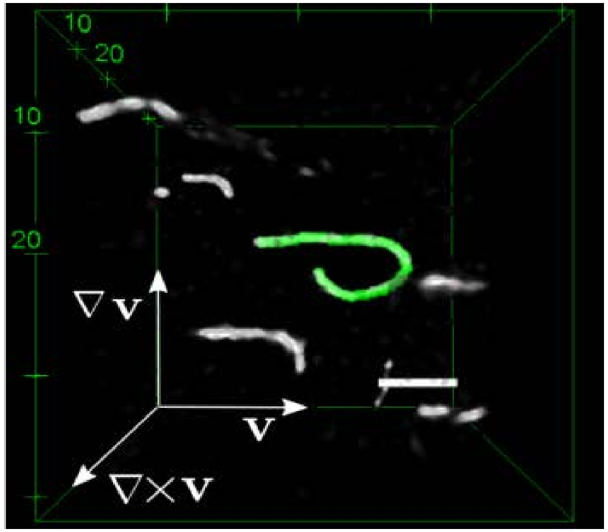


Rheological response of F-actin dispersions



Fast confocal microscopy on F-Actin

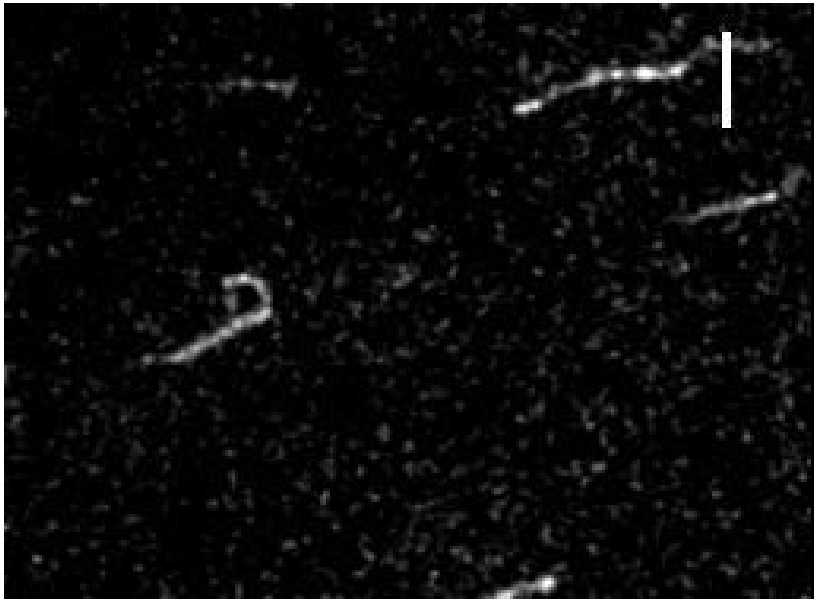




- Image at increasing strain
- Use three concentrations, label 1 per 100 filaments

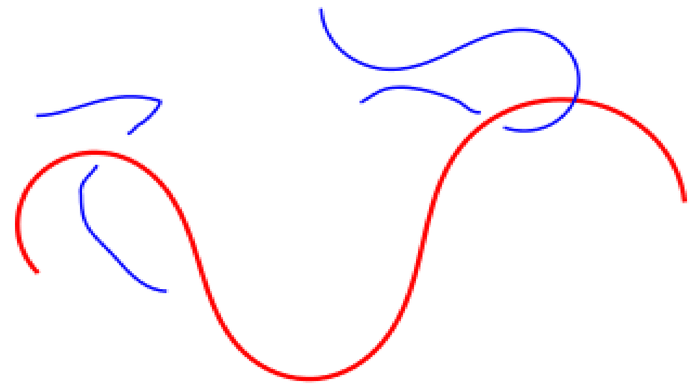
$L_c > 21\ \mu m$

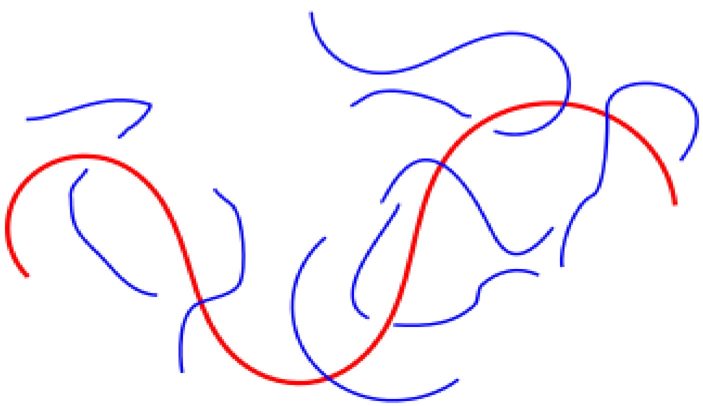
- About 100 analyzed filaments per combination

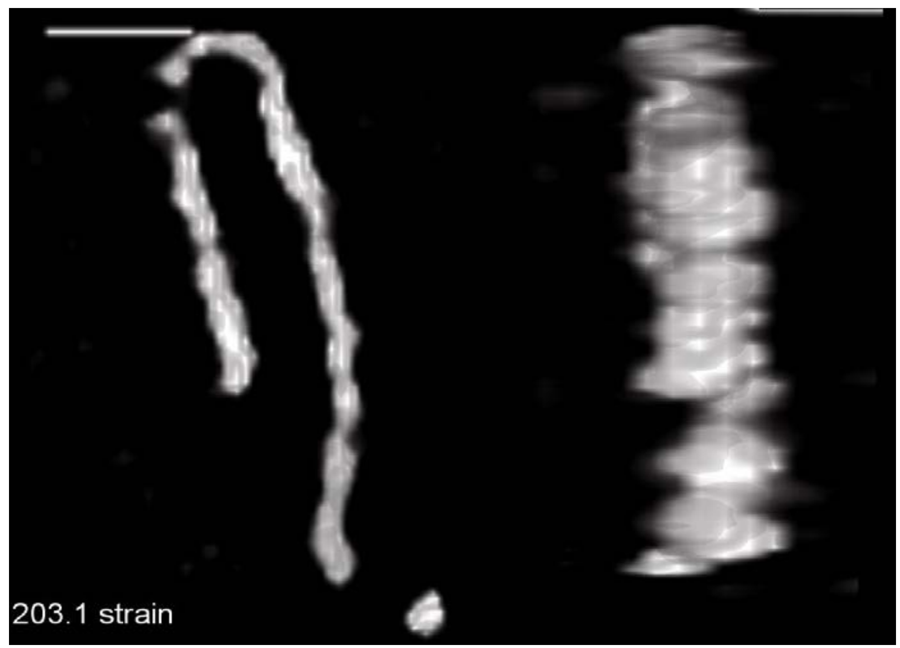


Space bar 10 µm

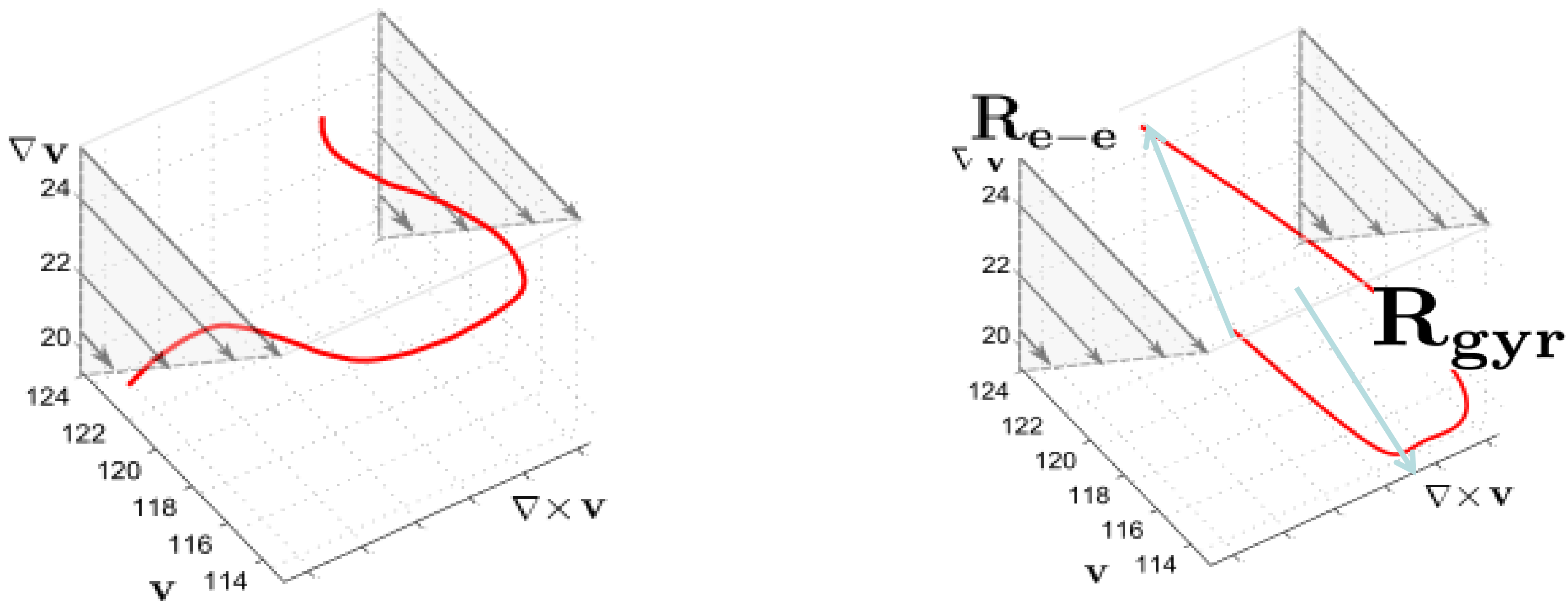
Sheared F-Actin in 3-D







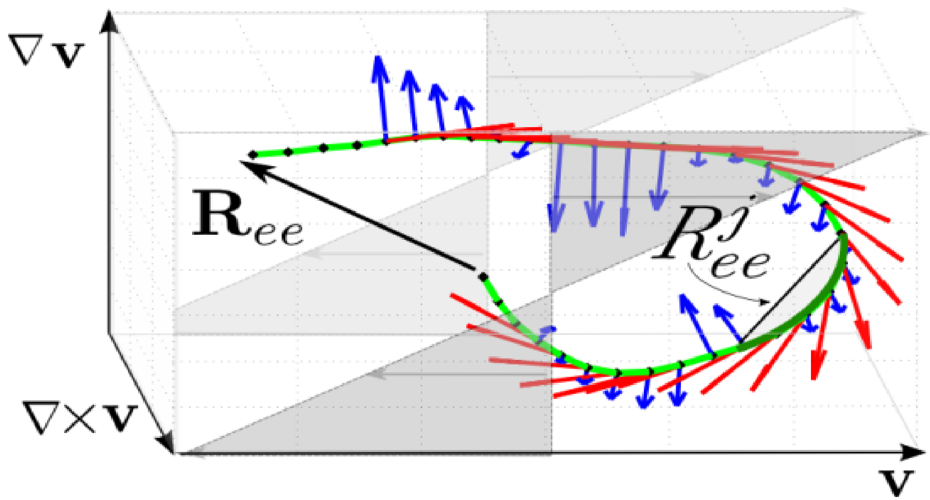
How to analyze?

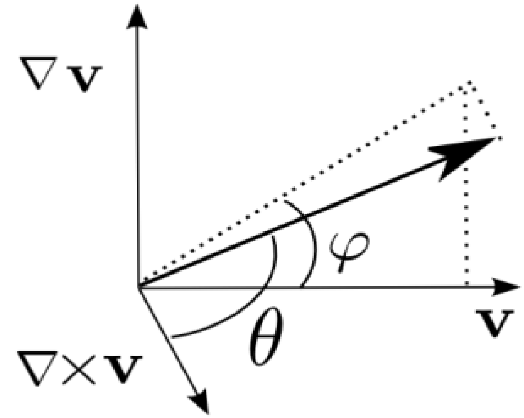


End-to-end vector $\mathbf{R}_{e-e}$: NOT the relevant parameter

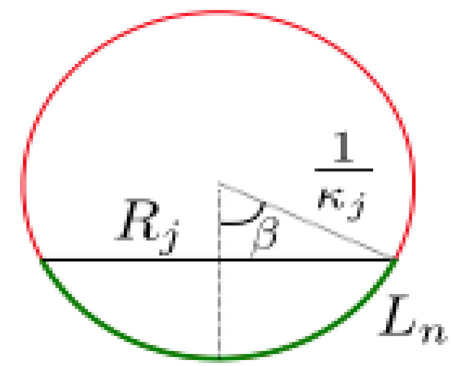
Inertia tensor $\mathbf{R}_{gyr}$ might NOT be the relevant parameter

Analyze local bending and stretching:



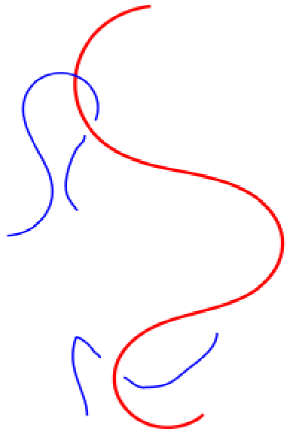


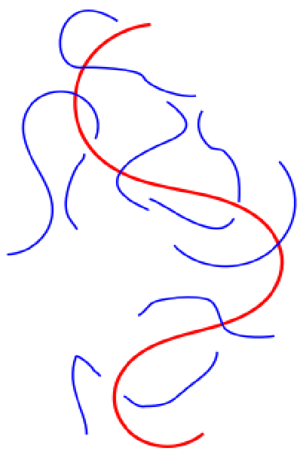
$$x_t(\kappa_t) = \frac{2\sin(\frac{\pi\kappa_t\langle L_n\rangle}{2})}{\pi\kappa_t\langle L_n\rangle}.$$

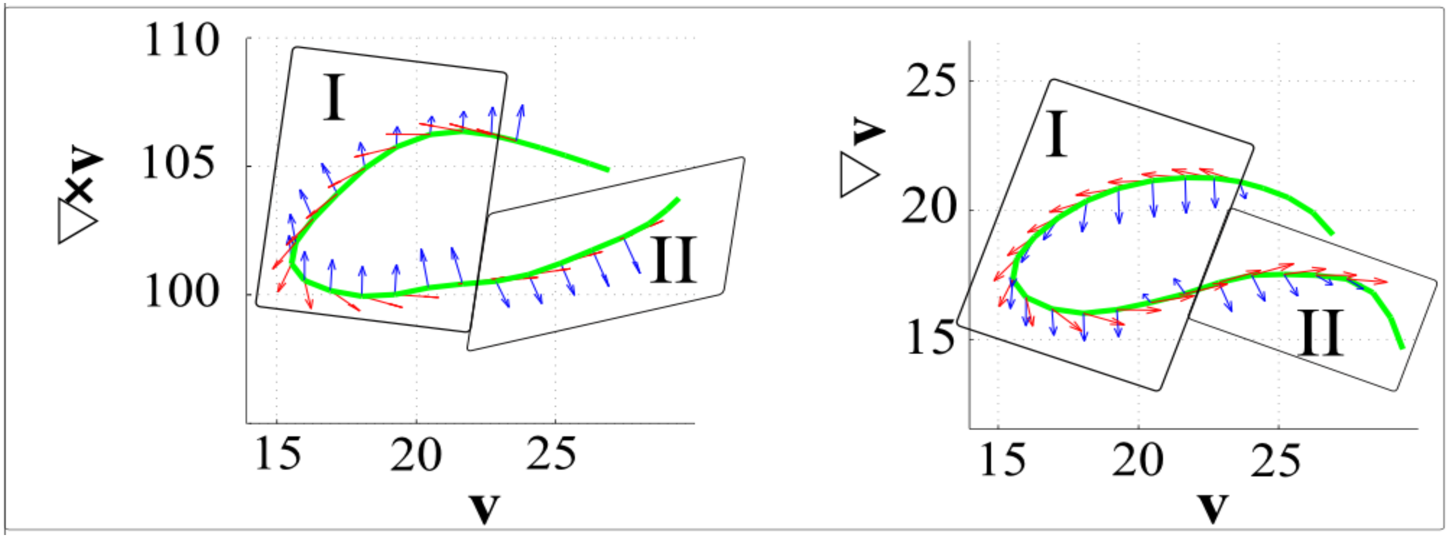


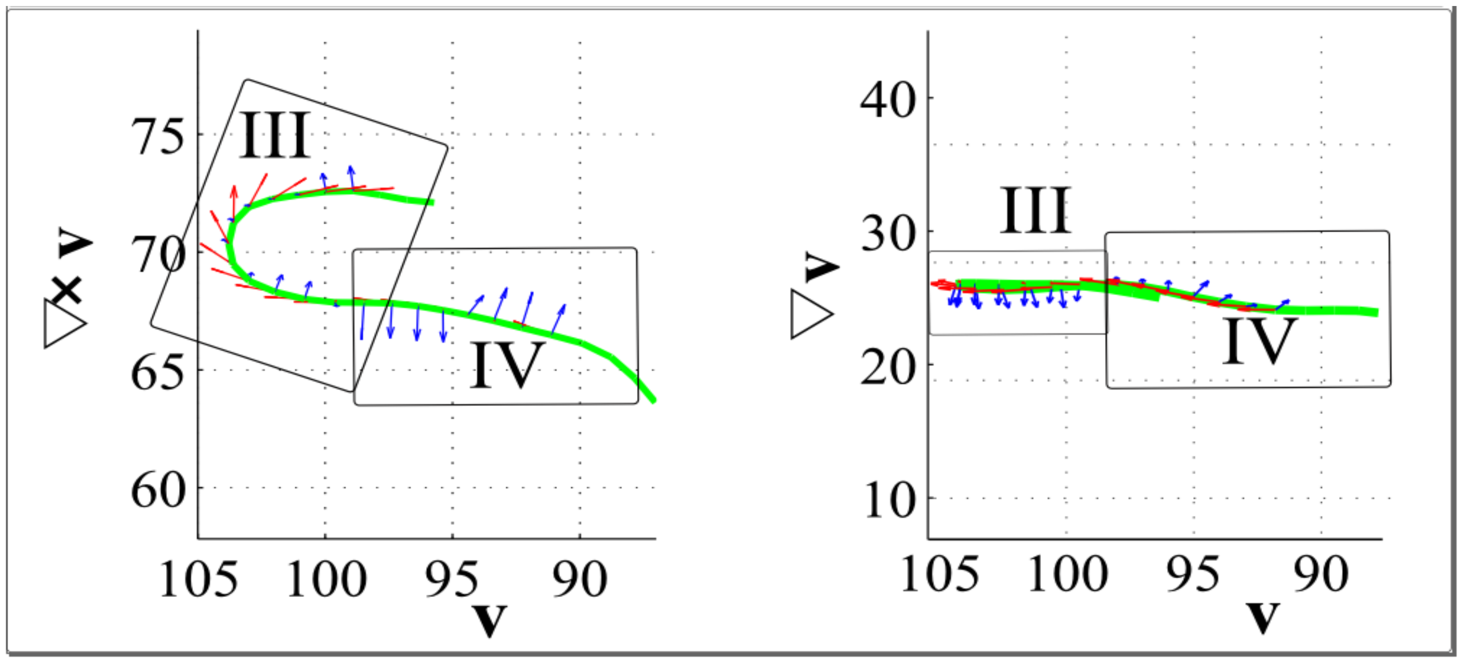
$$\hat{T}_j \equiv \frac{\dot{\mathbf{r}}_j}{|\dot{\mathbf{r}}_j|};\hat{B}_j \equiv \frac{\dot{\mathbf{r}}_j\times\ddot{\mathbf{r}}_j}{|\dot{\mathbf{r}}_j\times\ddot{\mathbf{r}}_j|};\kappa_j = \frac{|\dot{\mathbf{r}}_j\times\ddot{\mathbf{r}}_j|}{|\dot{\mathbf{r}}_j|^3}$$

Typical examples:

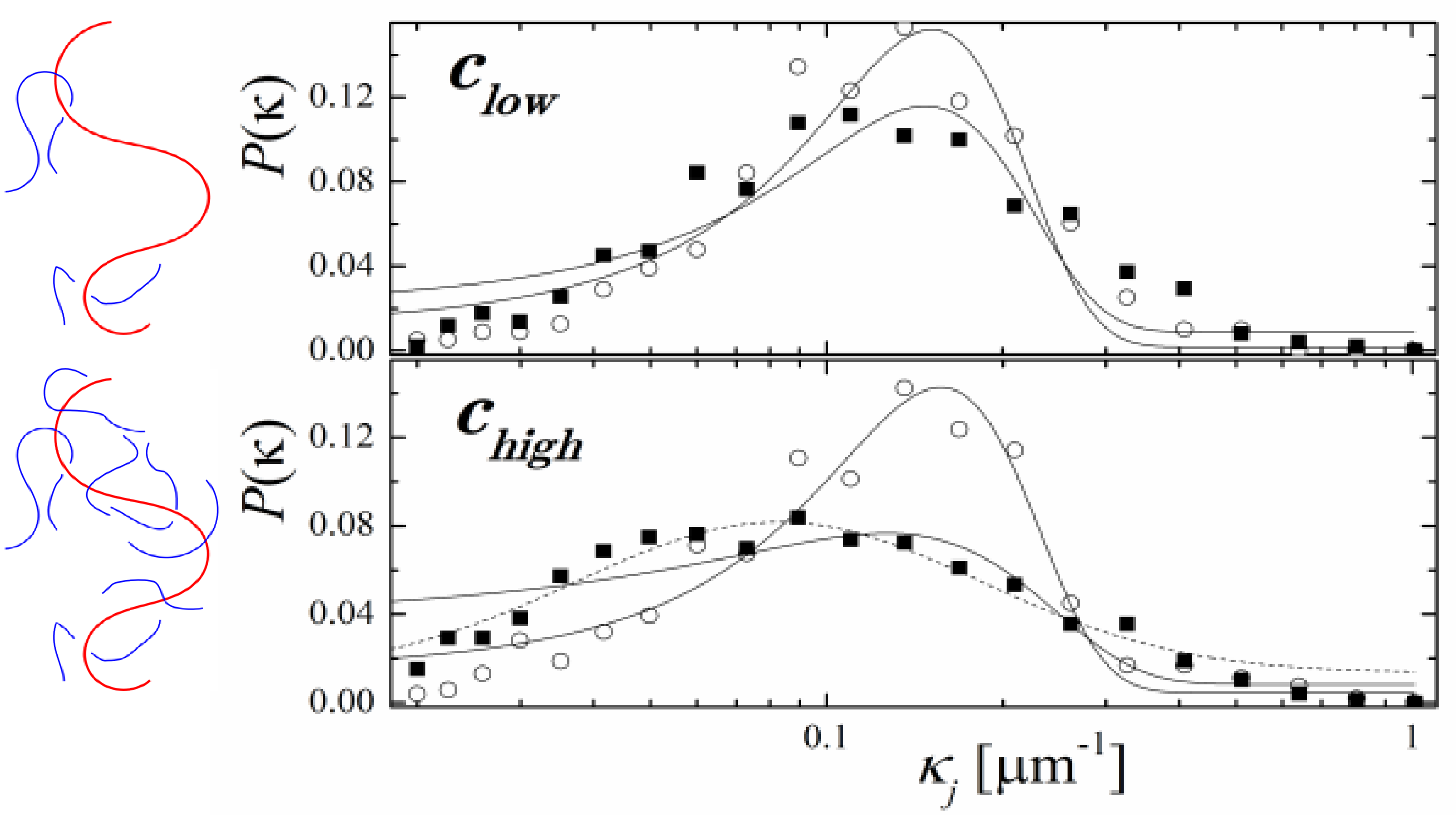






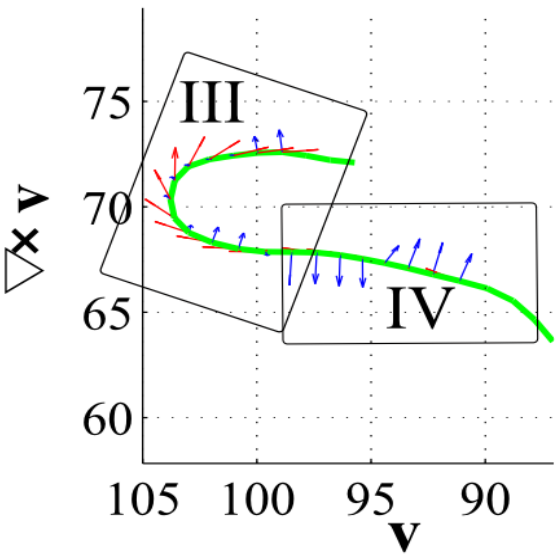


Distribution of curvatures:

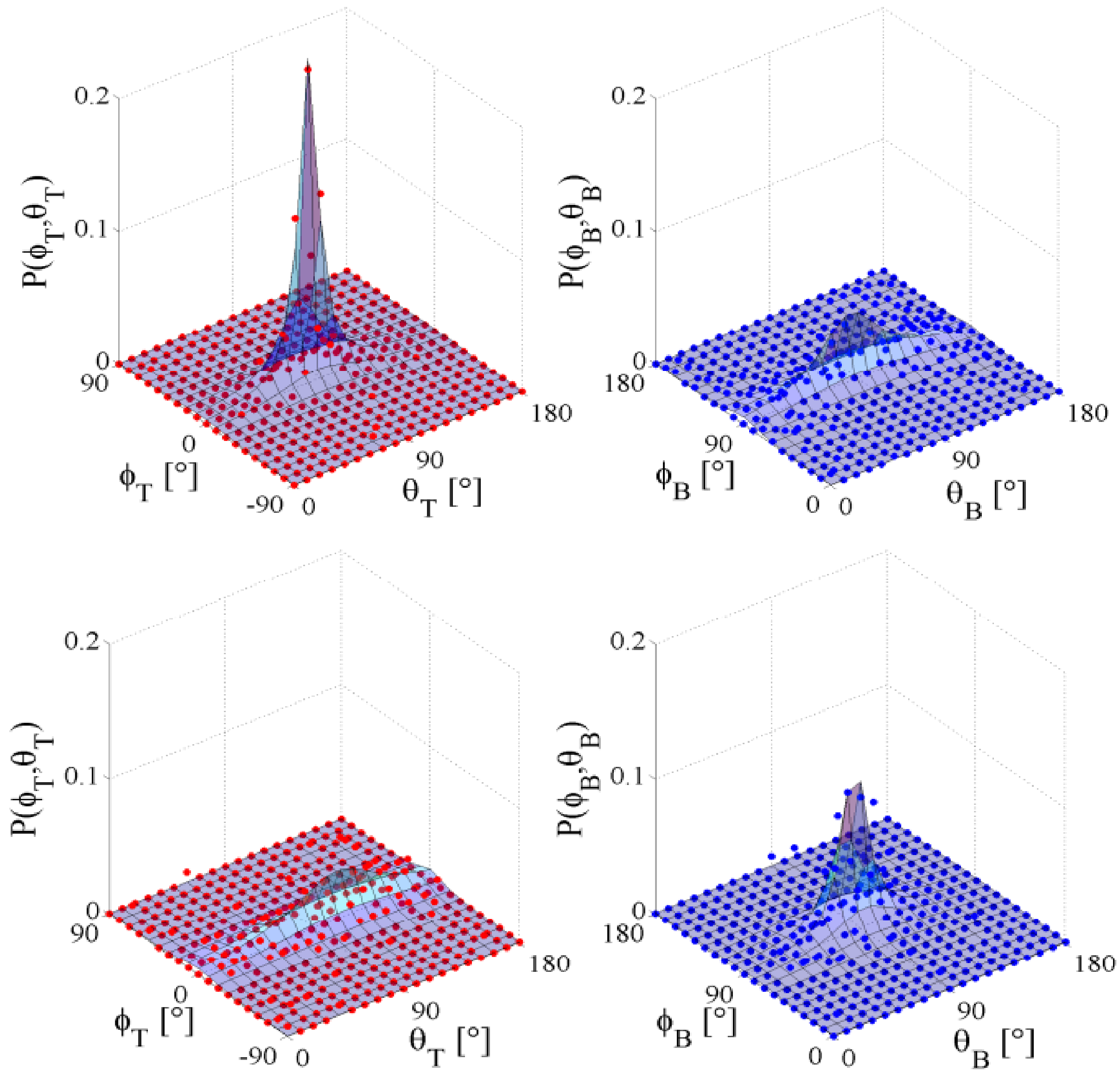


Distribution of angles

IV



III



Characterizing parameters

$$f(\theta,\phi) = a/\left((\frac{\theta-\Delta\theta}{w_\theta})^2 + (\frac{\phi-\Delta\phi}{w_\phi})^2 + 1 \right)$$

$$\bar{S}_T = \int_0^{\pi}\int_0^{2\pi} d\theta d\phi \sin(\phi) f(\theta_T,\phi_T)\hat{T}\hat{T}$$

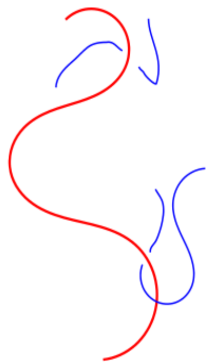
$$\bar{Q} = \frac{1}{2}(3\bar{S} - \mathbf{I})$$

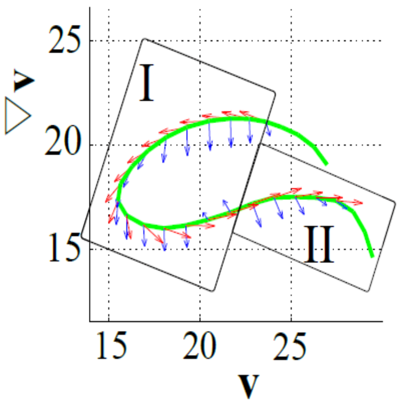
biaxiality

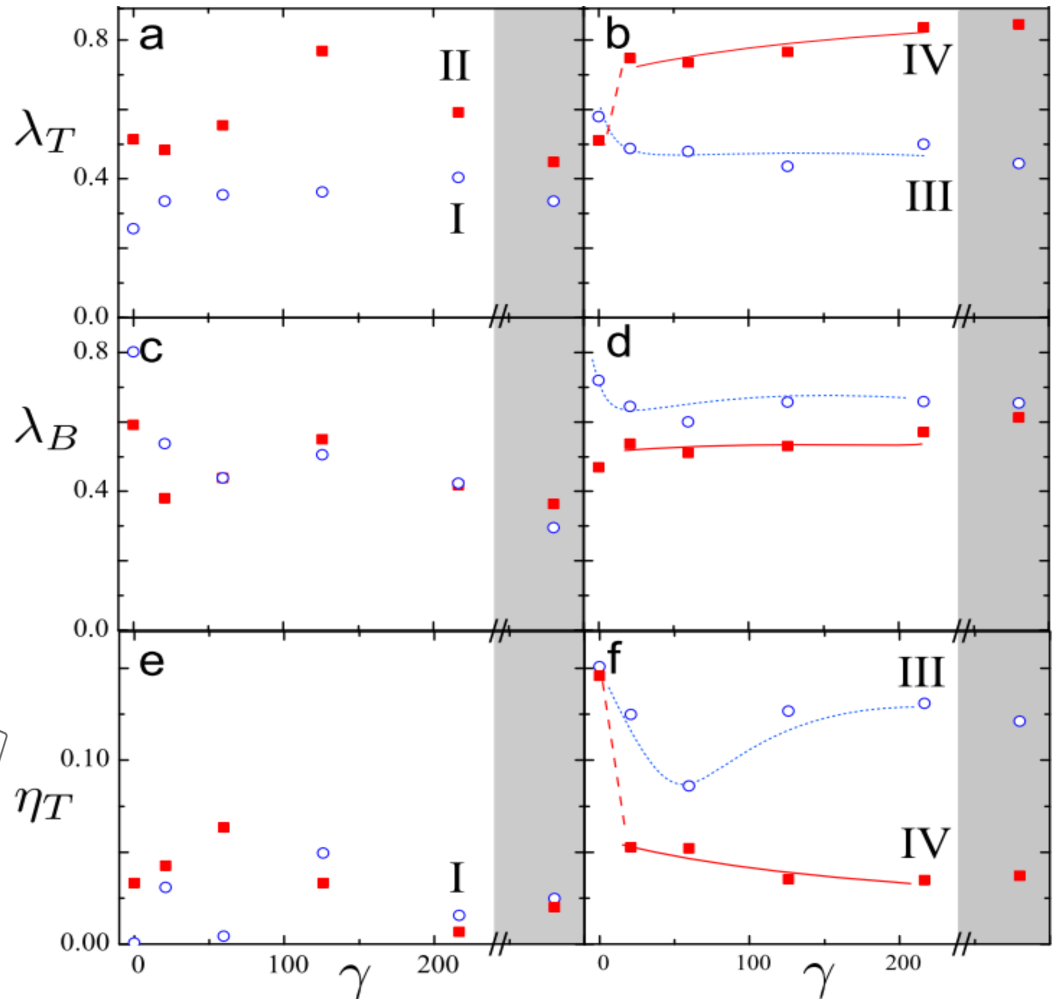
$$\bar{Q}_{T,B} = \begin{pmatrix} -\frac{1}{2}\lambda_{T,B} - \boxed{\eta_{T,B}} & 0 & 0 \\ 0 & -\frac{1}{2}\lambda_{T,B} + \eta_{T,B} & 0 \\ 0 & 0 & \boxed{\lambda_{T,B}} \end{pmatrix}$$

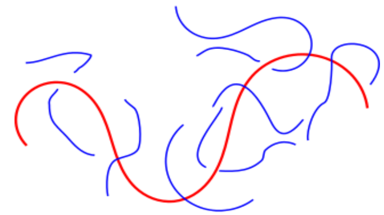
Highest order parameter

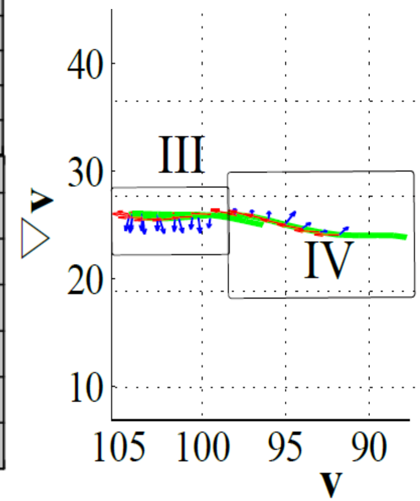
Ordering and biaxiality











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Conclusions Extra

- We obtain stored energy from microscopic data by analysis on smalles lengthscale

- Alignment higher at high concentration and more along the flow vector

- Orientation does not show strong dependence due to slow relaxation after loading

- Effect of strain mainly in curvature, less in orientation