

Probing microstructural origin of complex flow behavior

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UCSB, 2nd February 2018

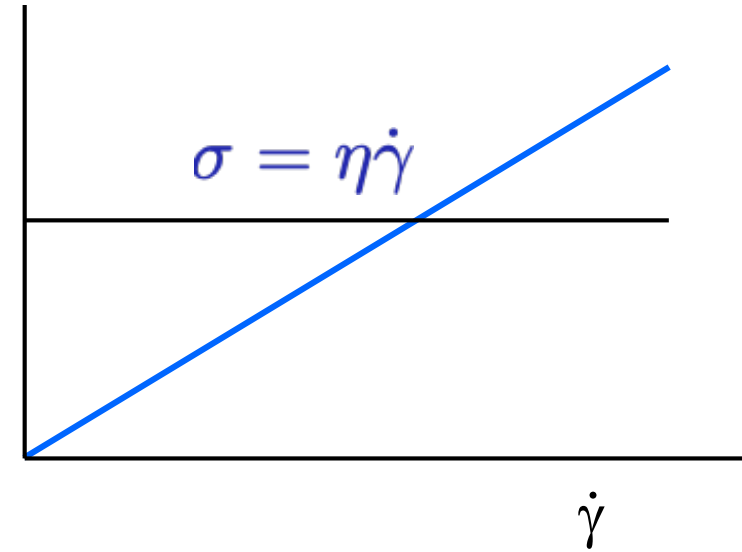
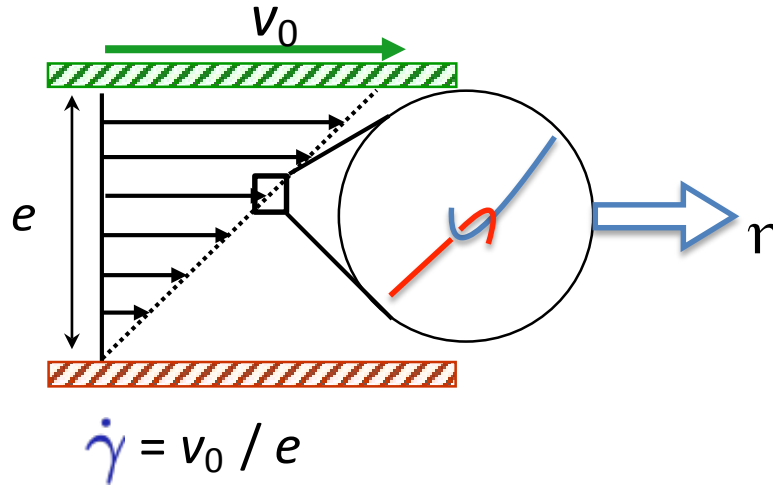
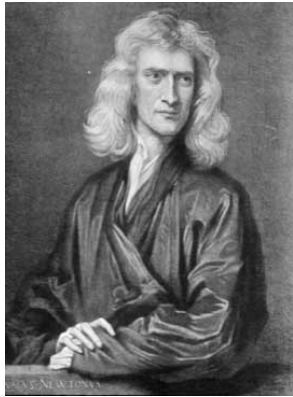
Complex flow: high inertia



Ideal Newtonian fluids

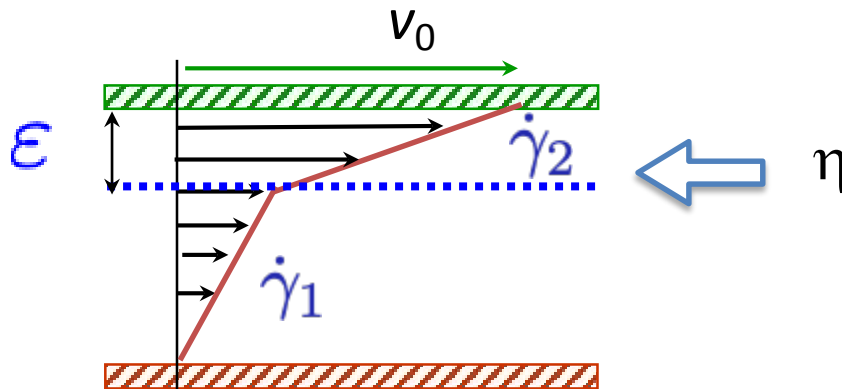


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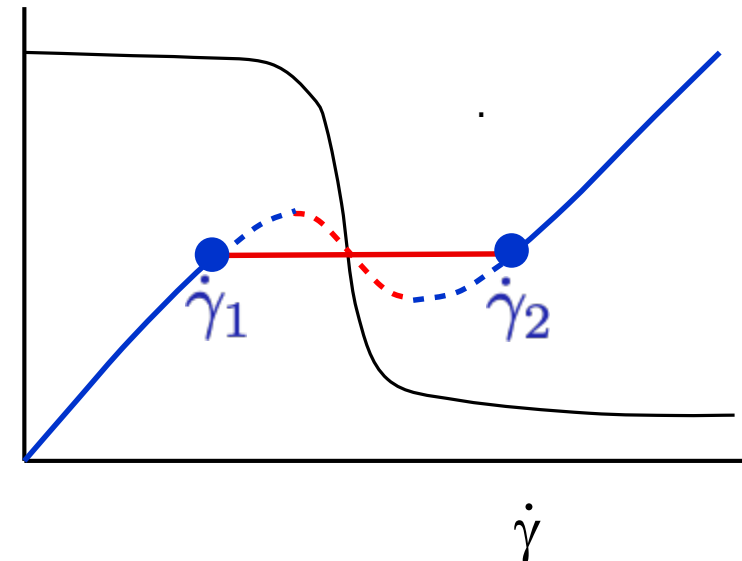


Non-linear Newton: shear thinning fluids

Flow instabilities: shear banding

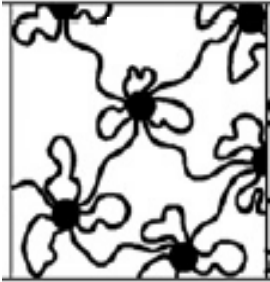


strong shear-thinning



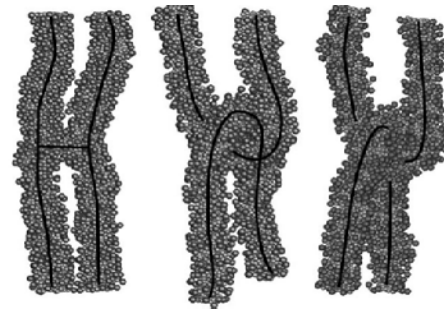
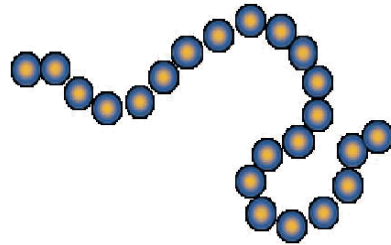
Possible shear thinners

Living gels:

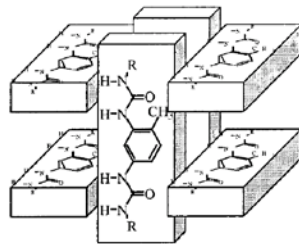


Sprakel et al, *Soft Matter*, **4**, (2008) 1696

Living polymers:

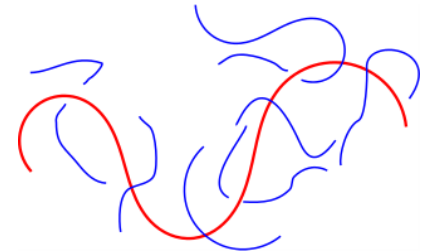


M. P. Lettinga and S. Manneville, *Phys. Rev. Lett.*, **103** 2009

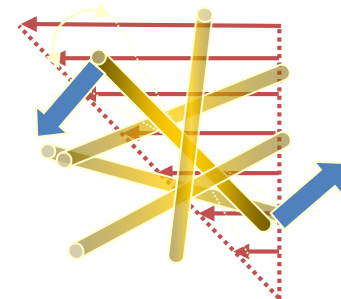


Van der Gucht et al *Phys. Rev. Lett.*, **97**, (2006) 108301

Stiff Polymers:



Rods:





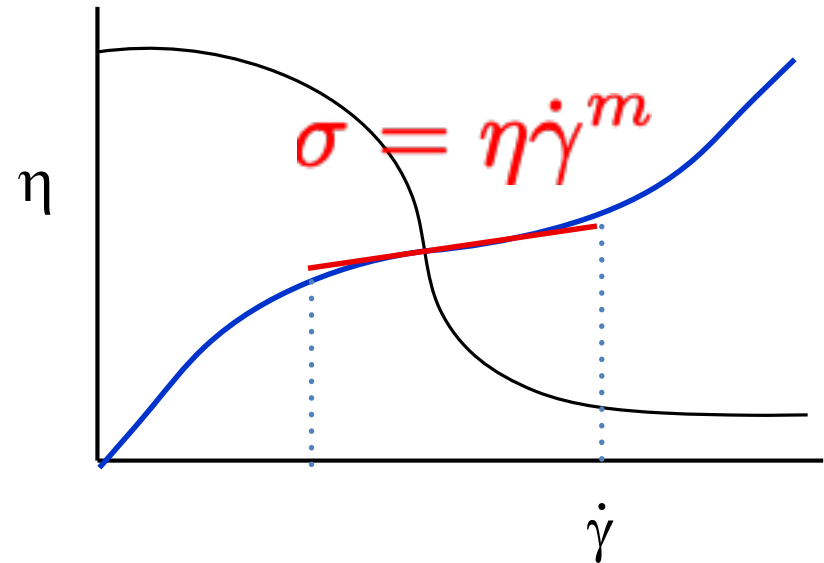
Main questions:

Molecular origin of shear band formation:

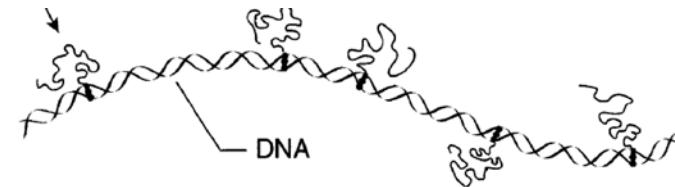
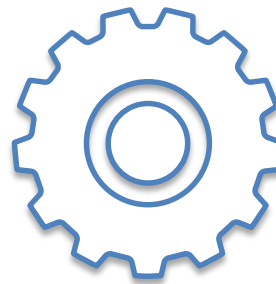
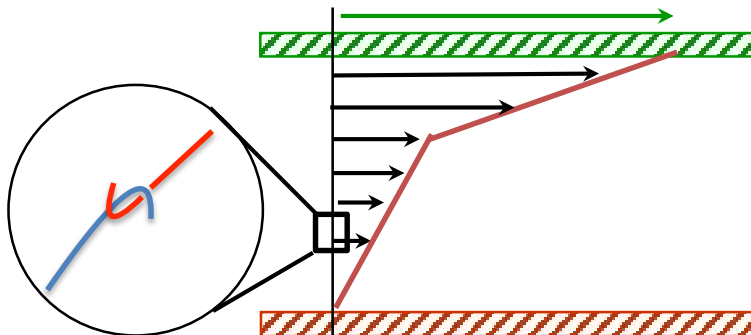
Can polymer shear band?

Can rods shear band?

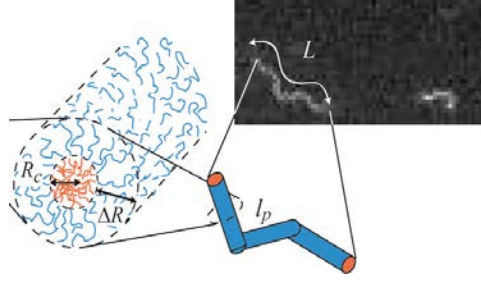
- How strong is strong?



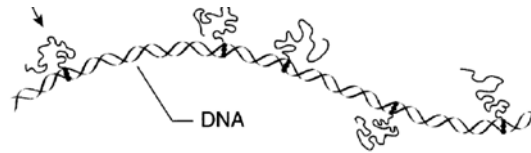
- Always shear banding for given m , or is it system dependent?
- Can we tune shear band formation?



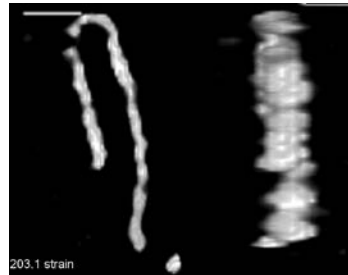
- Pb-Peo worm-like micelles:



- DNA



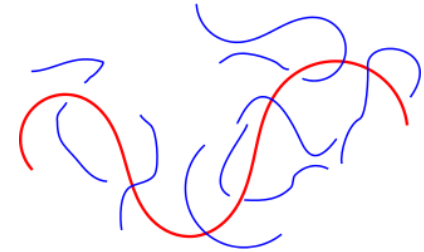
- F-actin:



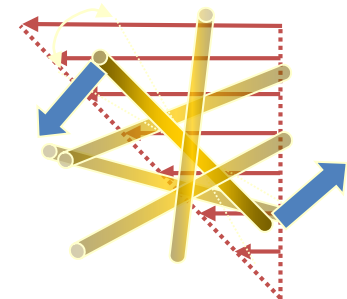
- Filamentous viruses:



Stiff Polymers:



Rods:



Gives equation of motion for the orientational tensor $\mathbf{S}$:

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

➡ Link with macroscopic stress

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

Collective slowing down: Dynamic definition spinodal point

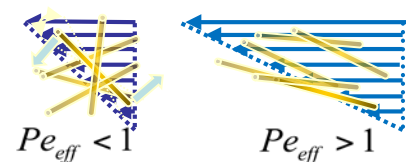
$$\Rightarrow \delta S(t) = \exp(-6D_R^{eff}t)\delta S(t=0)$$

$$D_R^{eff} = D_R^0 \left(1 - \frac{1}{4} \frac{L}{d_{eff}} \varphi \right) \longrightarrow \Omega_{eff} = \omega / D_R^{eff}$$

$$\downarrow \longrightarrow Pe_{eff} = \dot{\gamma}_0 / D_R^{eff}$$

D_R^0 : rotational at *infinite* dilution

D_R^0 : rotational at *infinite* dilution

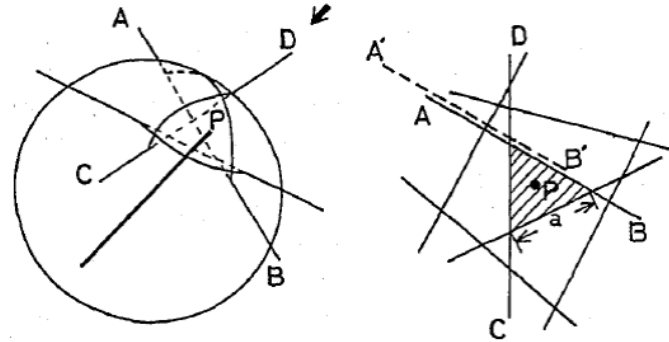




Topological slowing down:

Does phenomenological rotational diffusion coefficient

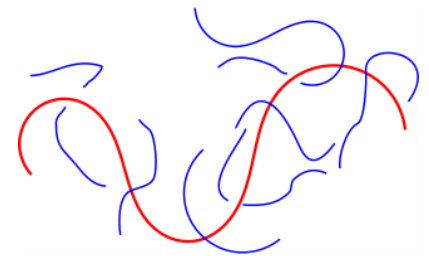
$$D_r = cD_r^0(\nu L^3)^{-2}$$



Monotonic constitutive theory for polymeric liquids

Competition of shear flow with Rouse and reptation time

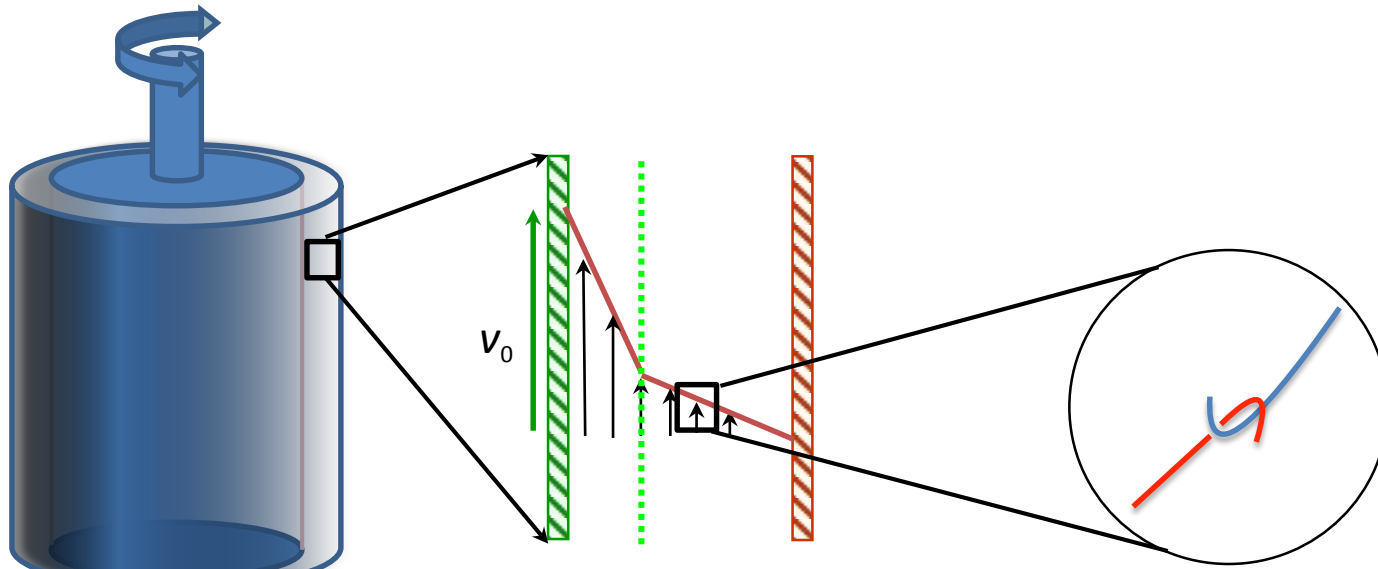
non-monotonic behavior due to concentration coupling



Cromer et al, *Phys. Fluids*, 2013



Experimental input needed:

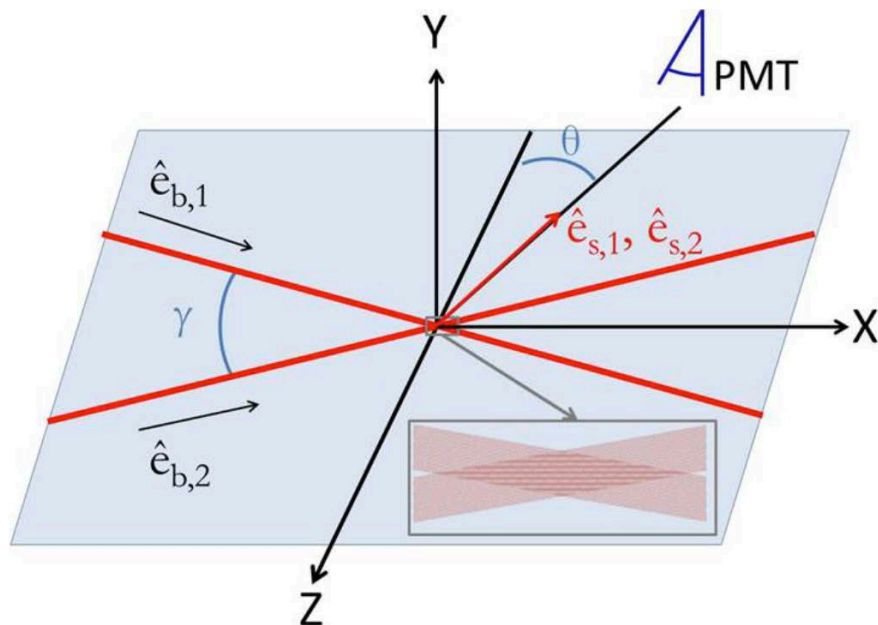
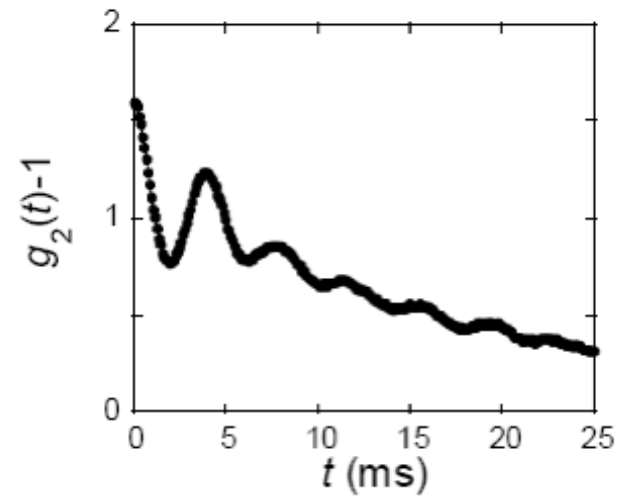
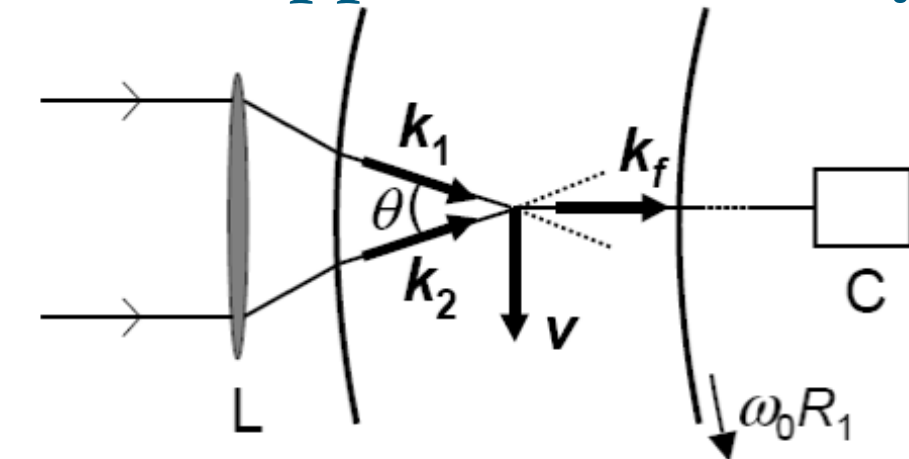


Information needed:

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

Probe the stability of flow with

Laser Doppler Velocimetry



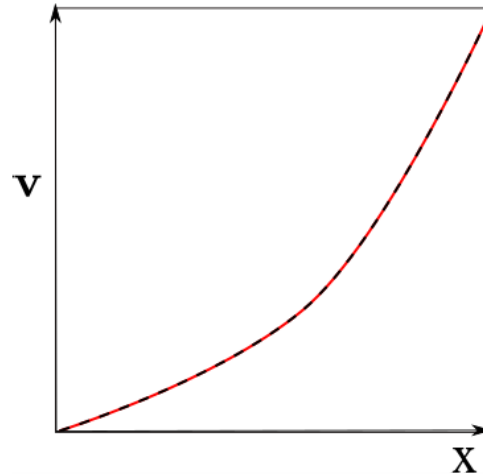
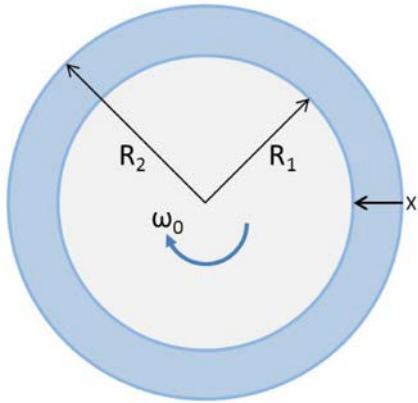
Analyse velocity profiles



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$$V(x) = \omega_0 R_1 [(R_2 - x)^{1-2/m} - R_2^{1-2/m}] / [R_1^{1-2/m} - R_2^{1-2/m}]$$

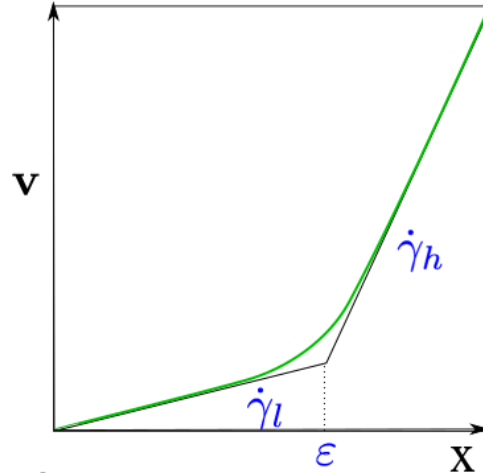
Account for curvature cell:



m

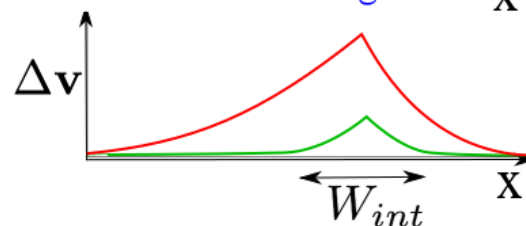
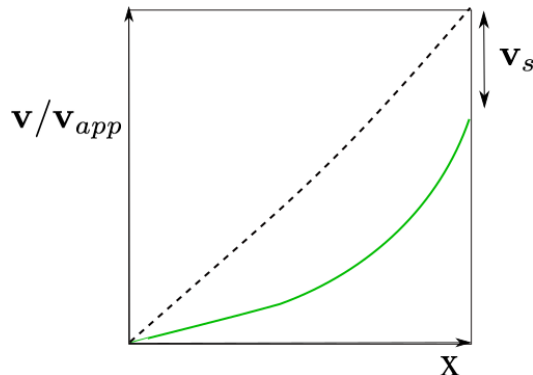
compare with m_{fc}

Shear banding with interface:



$\dot{\gamma}_h \dot{\gamma}_l \epsilon$

Wall slip:



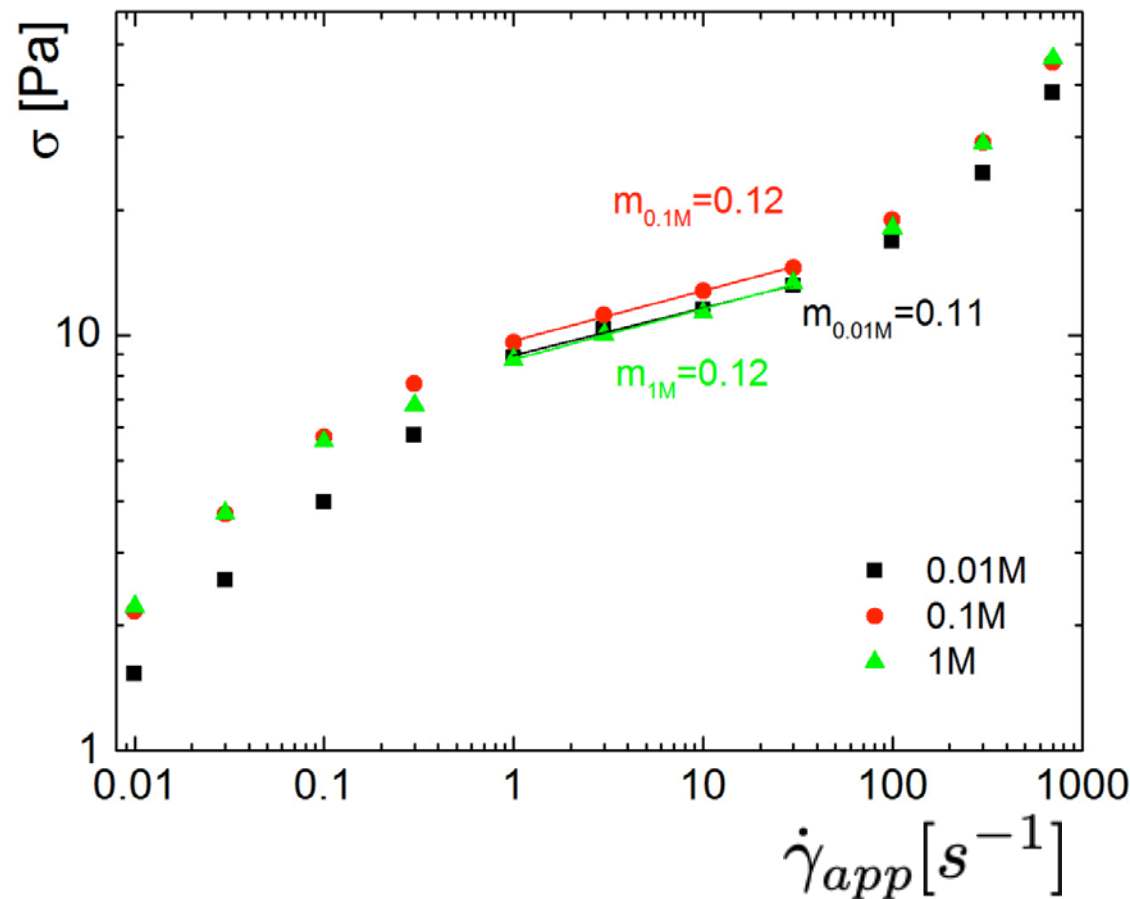
W_{int}



DNA, the tuneable polymer part I

$$\langle L \rangle \approx 20 \mu\text{m}, d = 7 \text{ nm}, l_p = 50 \text{ nm}$$

Tune repulsion by adding salt:



concentration: 0.7 mg/ml

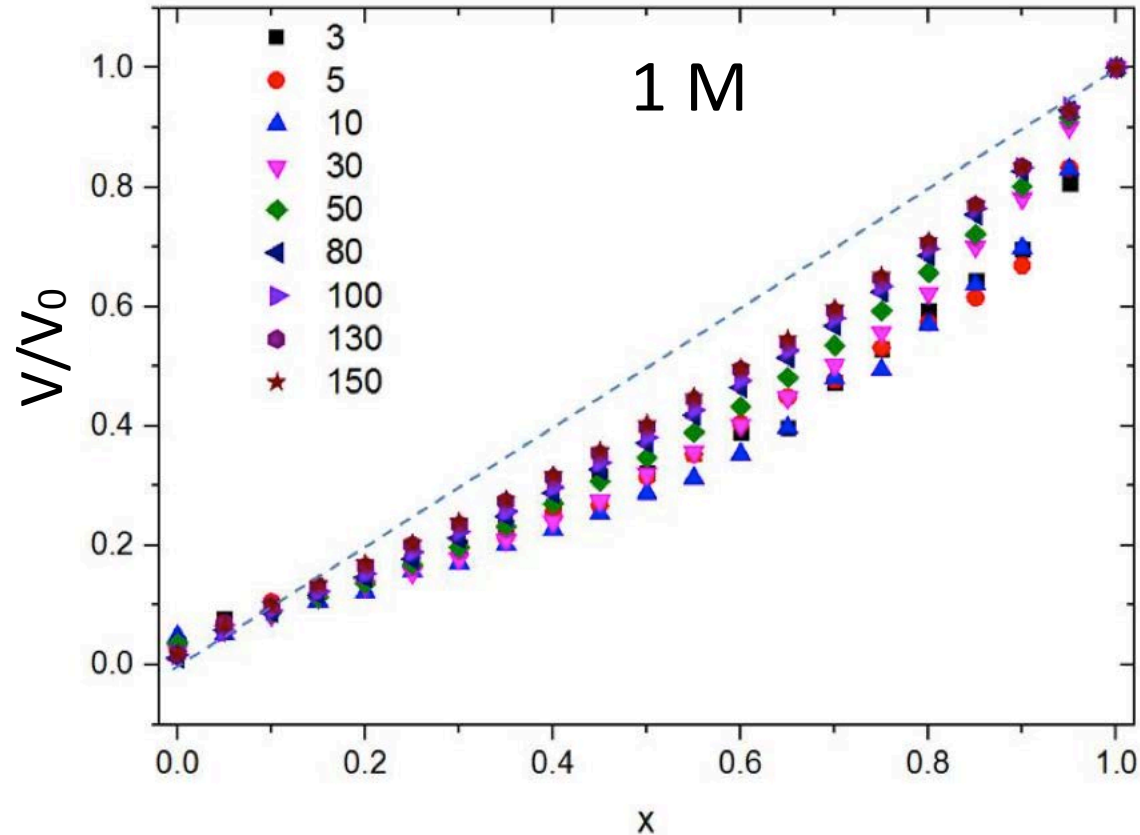
Tuning by addition of salt



0.01 M

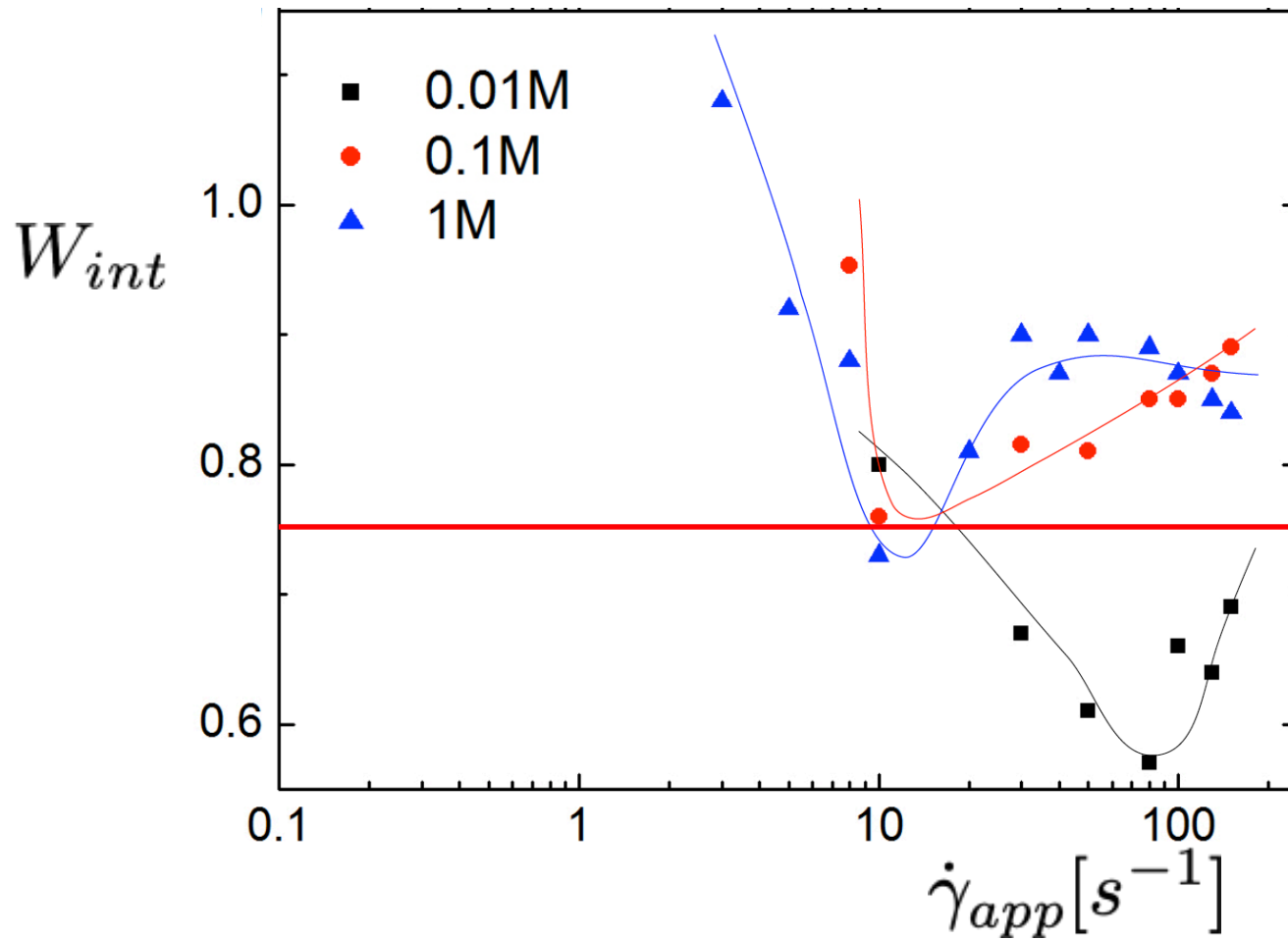
0.1 M

1 M



- Bands disappear at equal thinning m_{fc}
- Birefringence disappears along with the bands

Tuning by addition of salt



- Bands disappear via widening of the interface

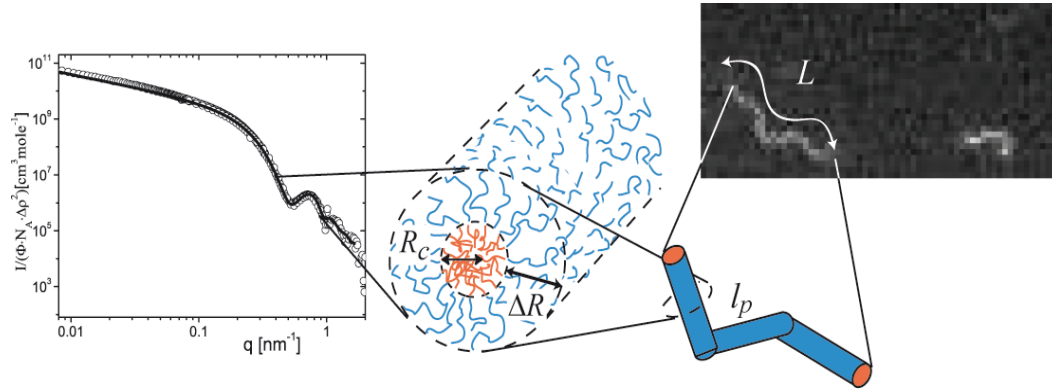
- How strong is strong?
- Always shear banding for given m , or is it system dependent? Depends on system
- Suppression shear banding via widening interface, BUT: broad shear banding can exist with broad interface
- Can we tune shear band formation? Yes, a bit

Also seen for Xanthan, with $m_{fc} = 0.21$
Tang et al, Soft Matter 2018

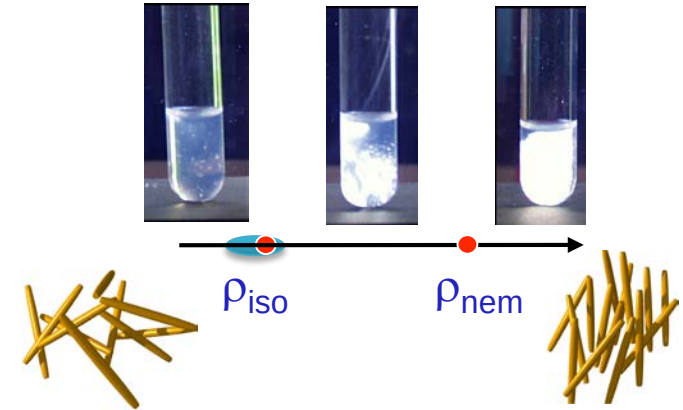
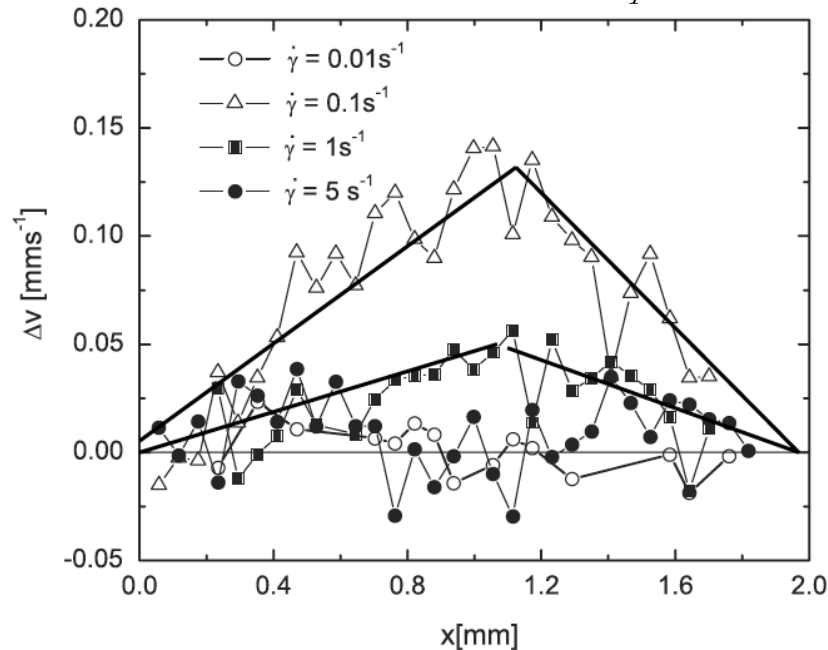
- New question: Is it charge or stiffness?



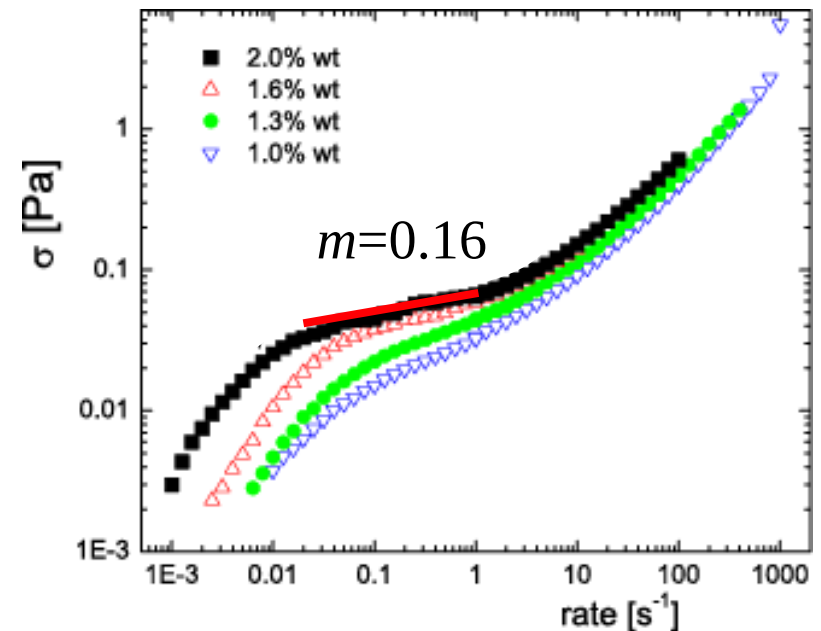
Neutral Rods close to I-N: Giant PB-PEO wormlike micelles



$$\langle L \rangle = 800 \text{ nm}, d = 28 \text{ nm}, l_p = 500 \text{ nm}$$



Y.-Y Won et al., *Science*, 283 1999

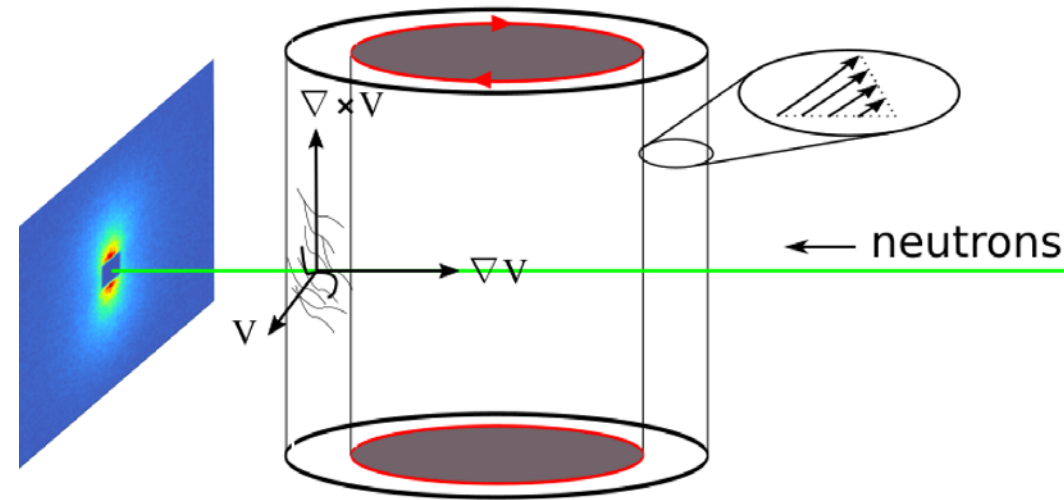




t-SANS to probe segment ordering dynamics

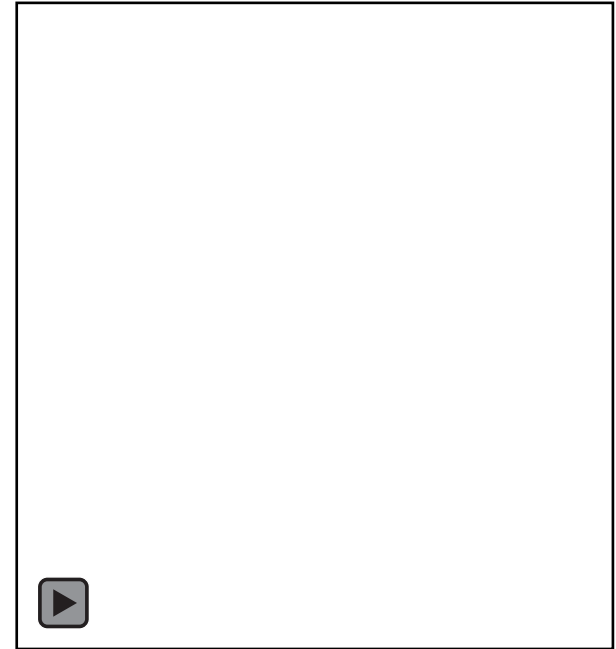
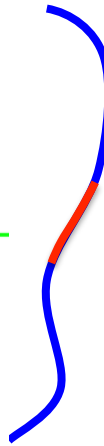


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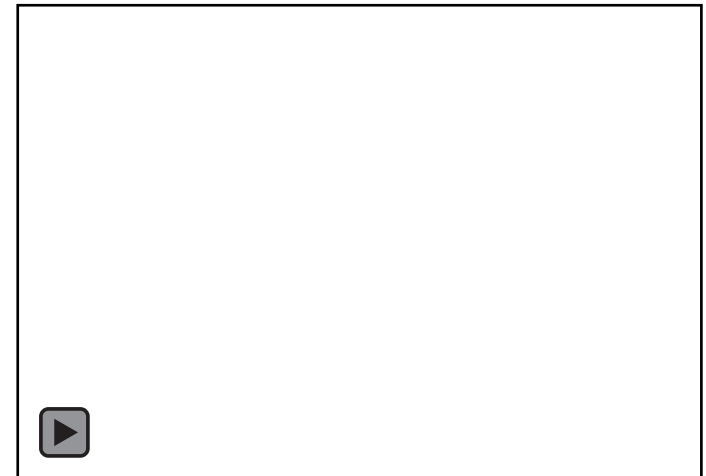
$$\langle P_2(t) \rangle = \frac{\int d\vartheta \sin(\vartheta) f(\vartheta) P_2(\vartheta)}{\int d\vartheta \sin(\vartheta) f(\vartheta)}$$

$$I(t_i, \vec{q}) = \sum_n^{N_{\text{cycle}}} I(t_i + n\Delta t, \vec{q})$$



Orientational distribution function

$f(\theta)$



θ [rad.]



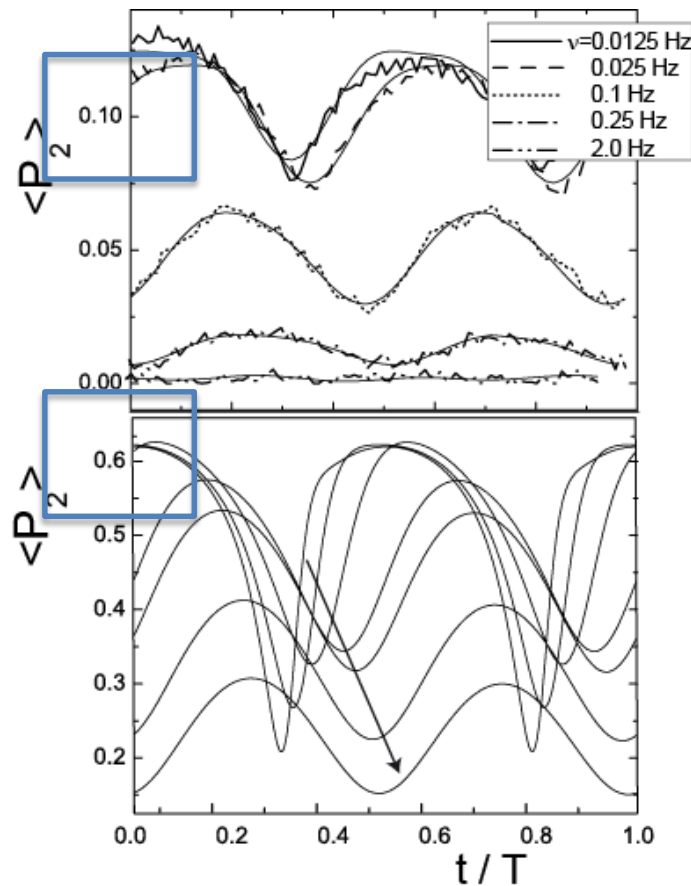
Micro

&

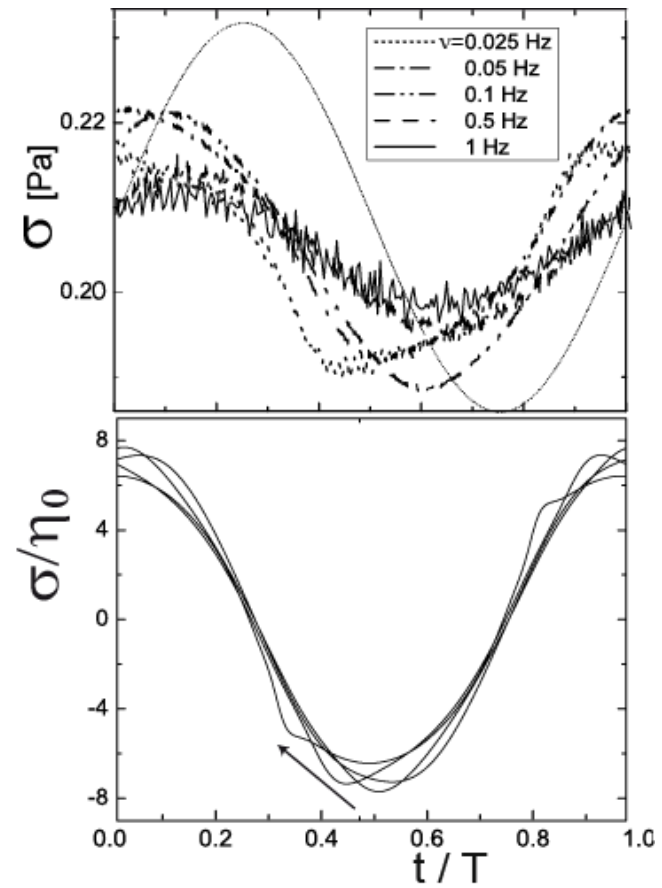
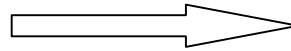
Macro



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$\Sigma_D(\mathbf{S})$



Scaling frequency:

$$\Omega_{eff} = \omega / D_R^{eff}$$

$$D_R^{eff} = D_R (1 - \varphi / \varphi_{IN})$$

$$D_R = 0.04 \text{ s}^{-1} \ll D_R^0$$

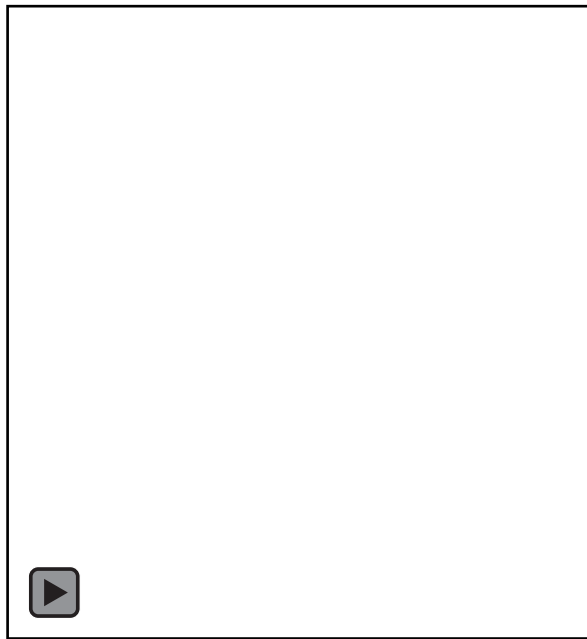
$$\frac{L}{d_{eff}} \varphi_{IN} = 3.0$$

- Is it charge or stiffness? **STIFFNESS**

Suggestion:

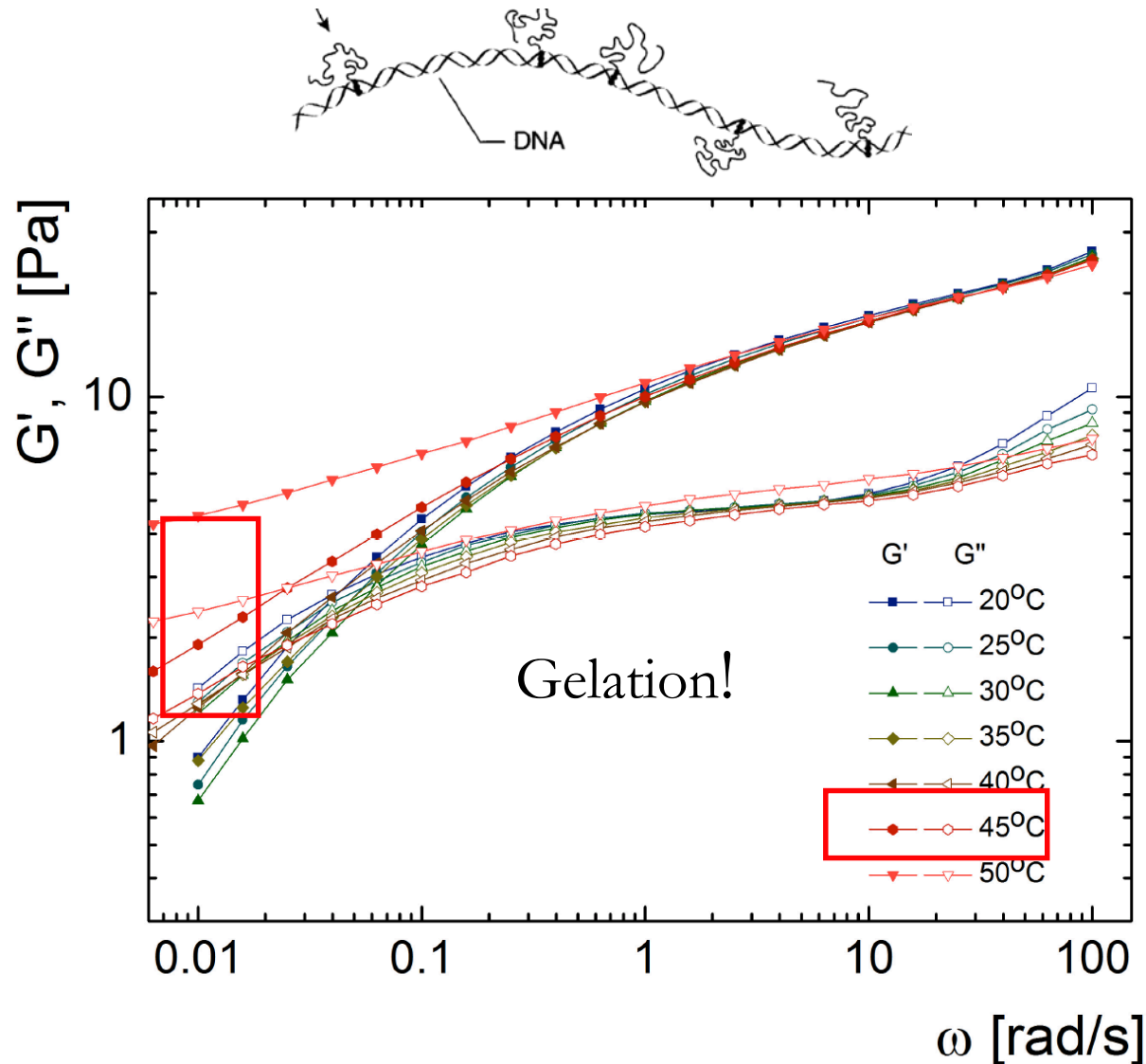
Stiff systems don't collapse once disentangled

- New question: Can we force collapse?
- New question: Can we have a better look?

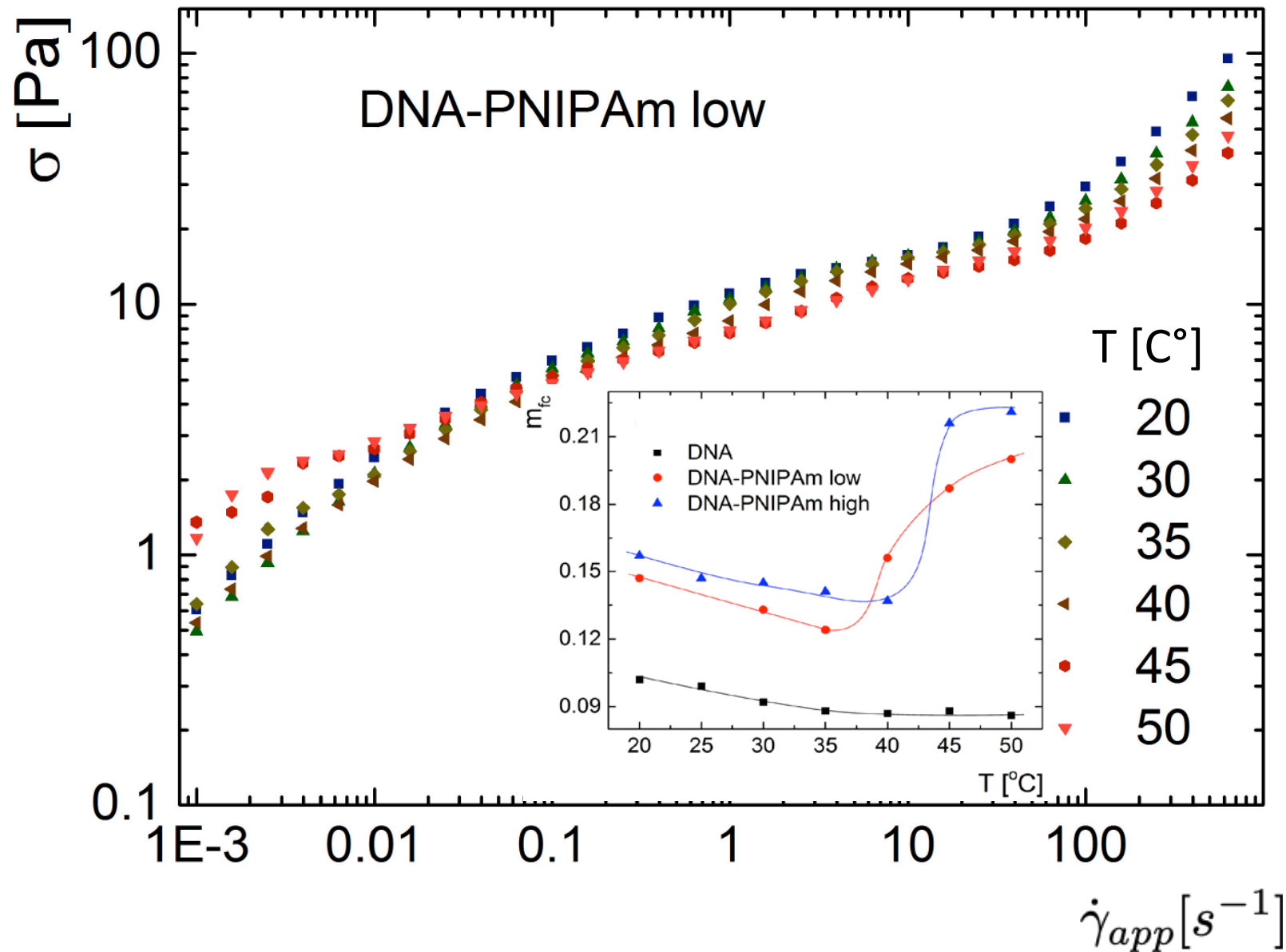


DNA, the tuneable polymer part II

Tune attraction by adding T-sensitive brush (PNIPAm)



Tuning by increasing attraction



Tuning by increasing attraction

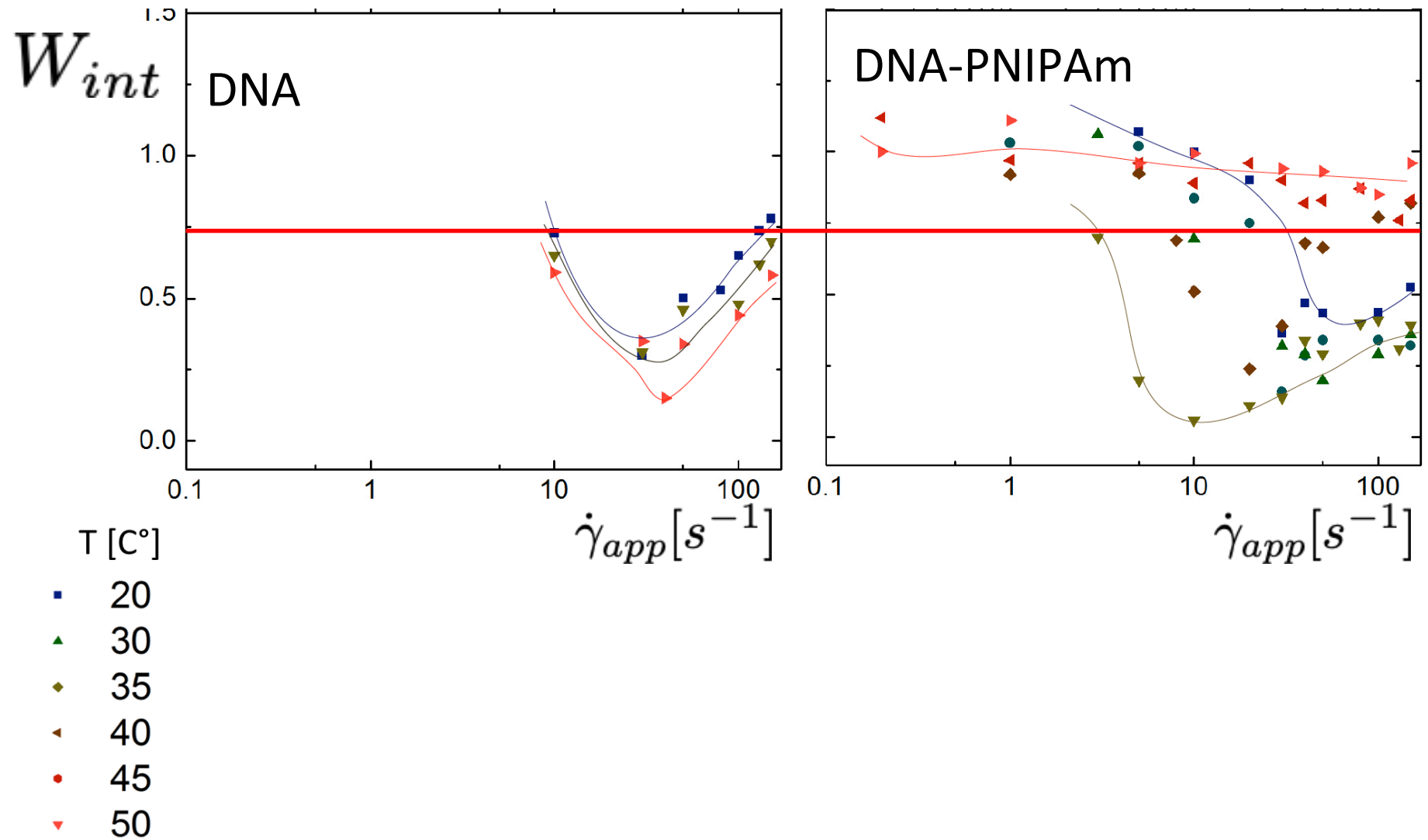
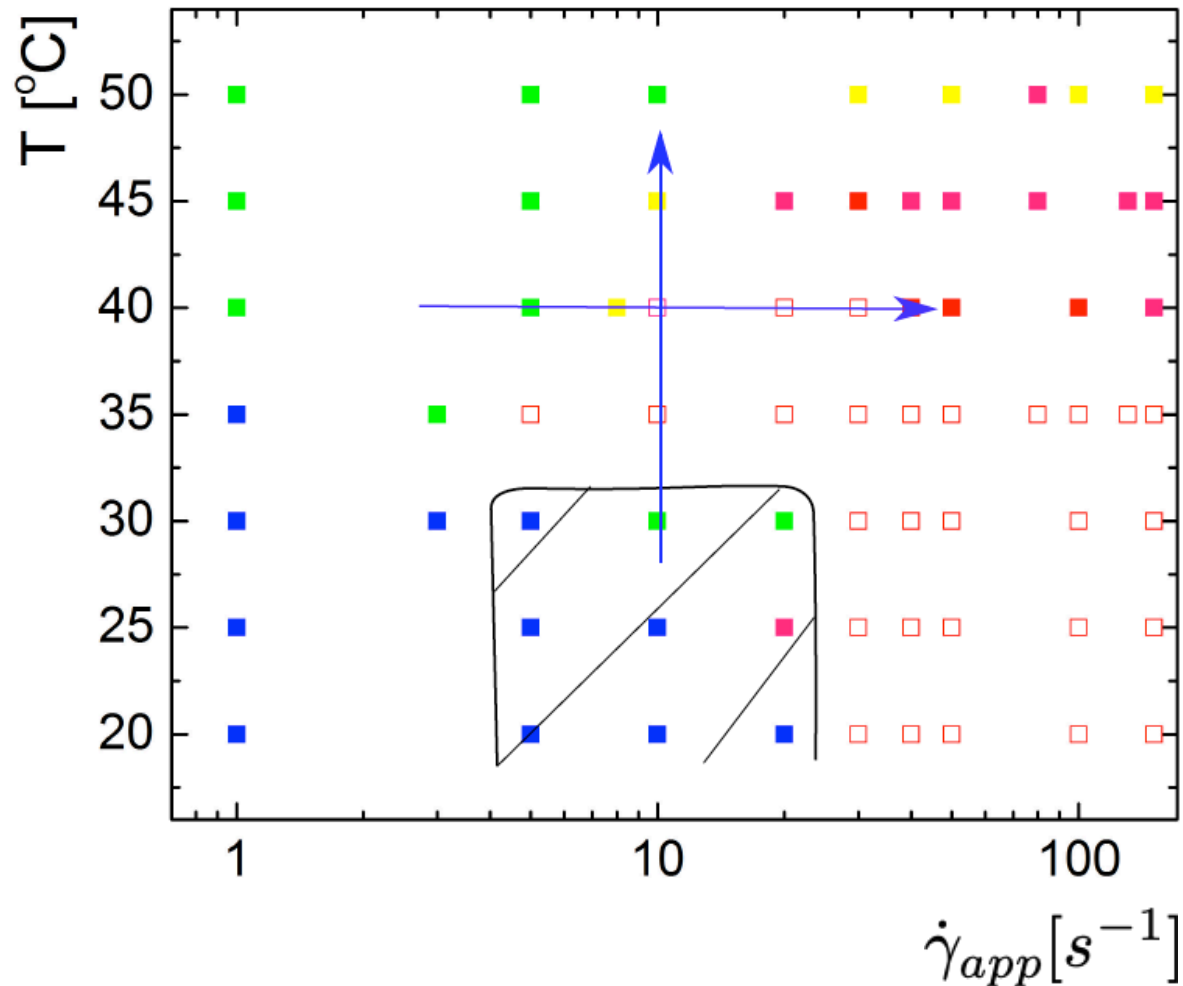


Diagram of states



- Attraction suppresses shear band formation (and orientation)
- Re-entrant behavior in two directions

- How strong is strong?
- Always shear banding for given m ,
or is it system dependent? Depends on system
- Is it charge or stiffness? STIFFNESS
- Suppression shear banding via widening interface,
BUT: broad shear banding can exist with broad interface
- Can we tune shear band formation? YES
- New question: Can we have a better look?

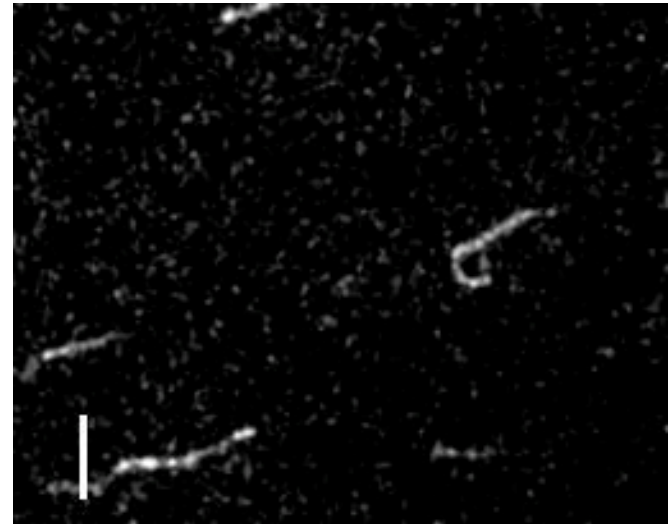
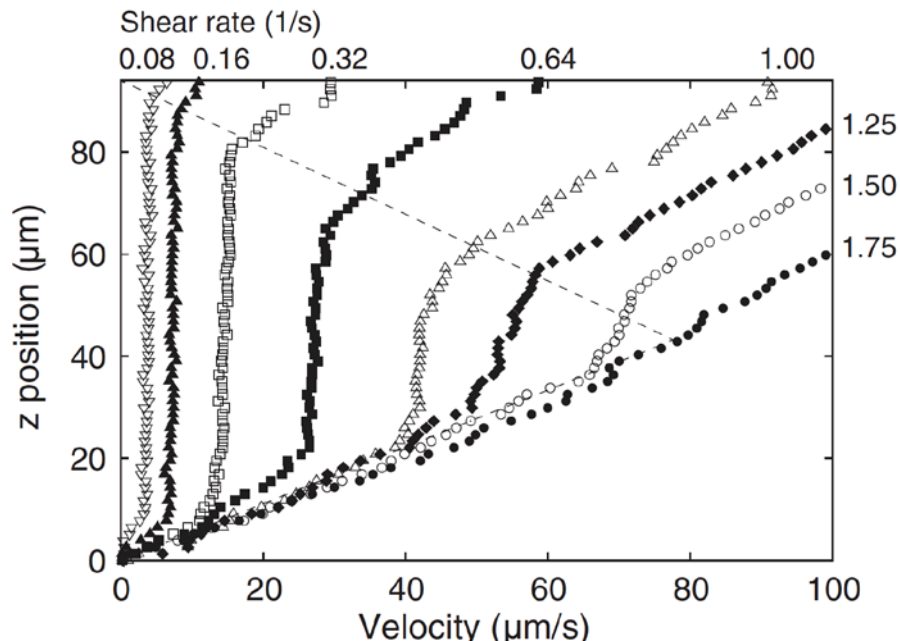
F-actin: stiffer and longer

$$\langle L \rangle \approx 20 \mu\text{m}, d = 7 \text{ nm}, l_p = 17 \mu\text{m}$$

Shear banding has been identified by

Kunita et al, PRL 109, 248303 (2012)

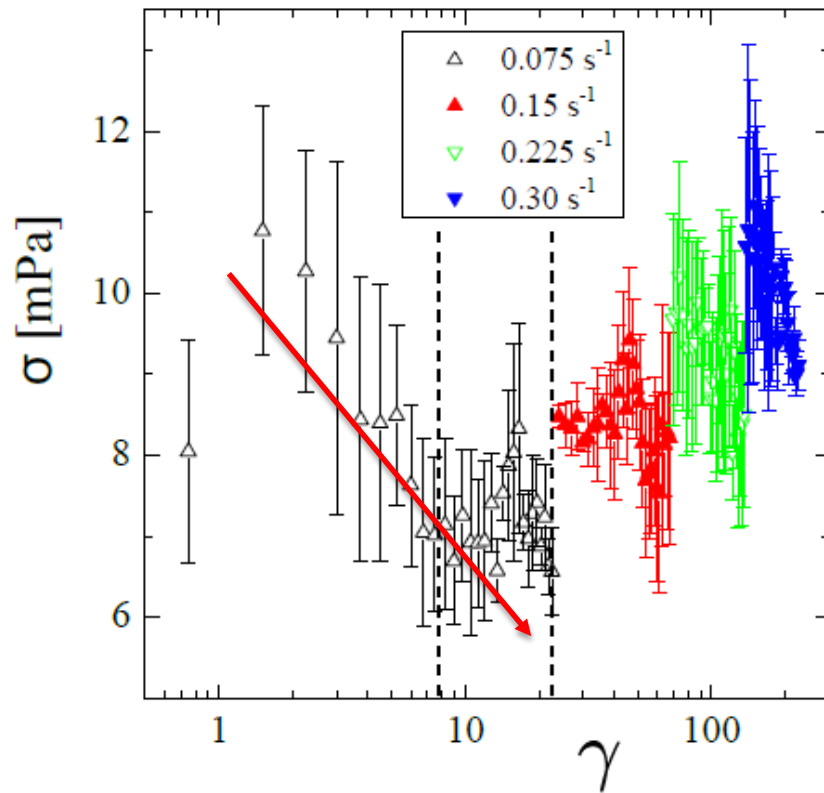
Goal: obtain 3-D structural information



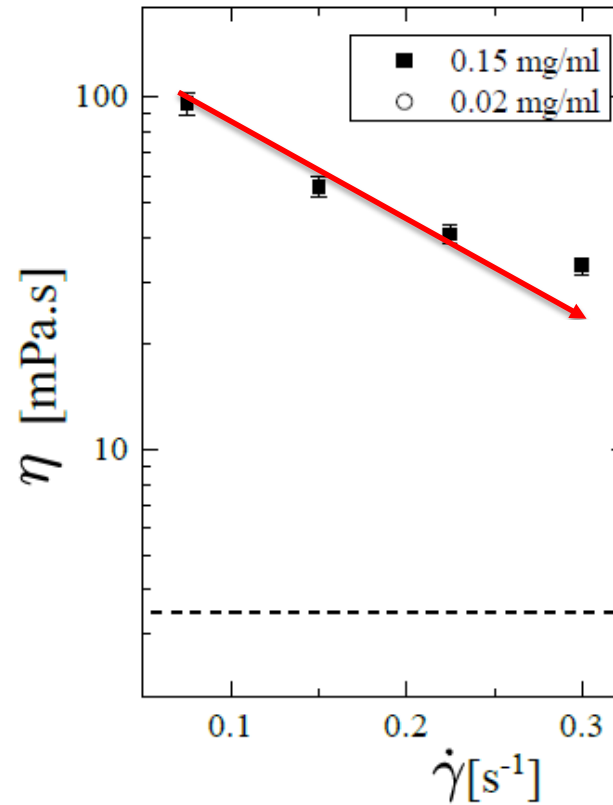
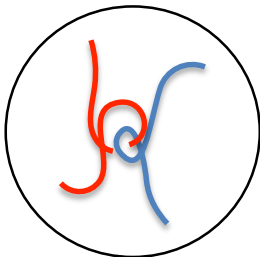
Rheological response of F-actin dispersions



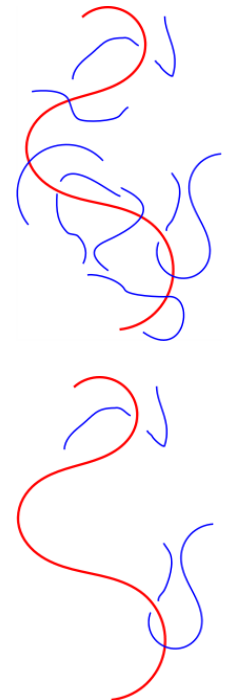
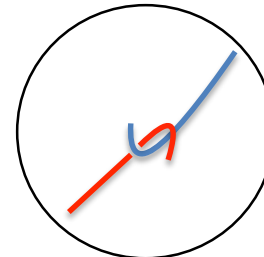
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Strain softening



Shear thinning

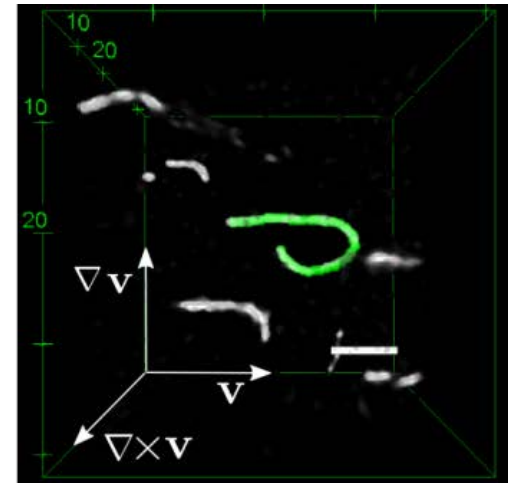
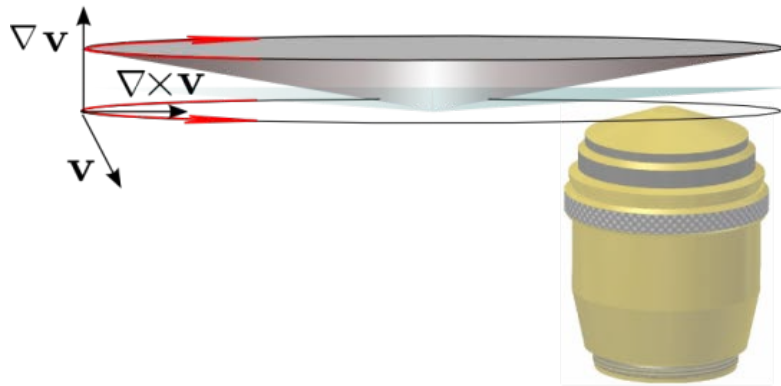




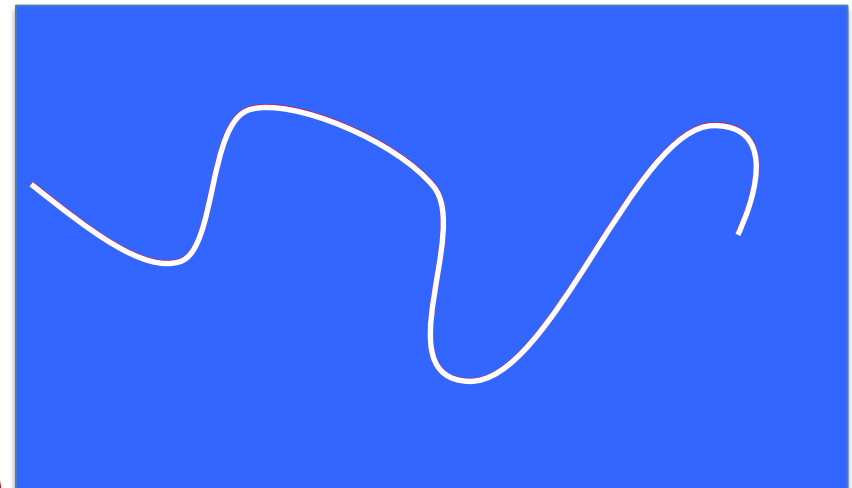
In situ confocal microscopy on entangled F-actin



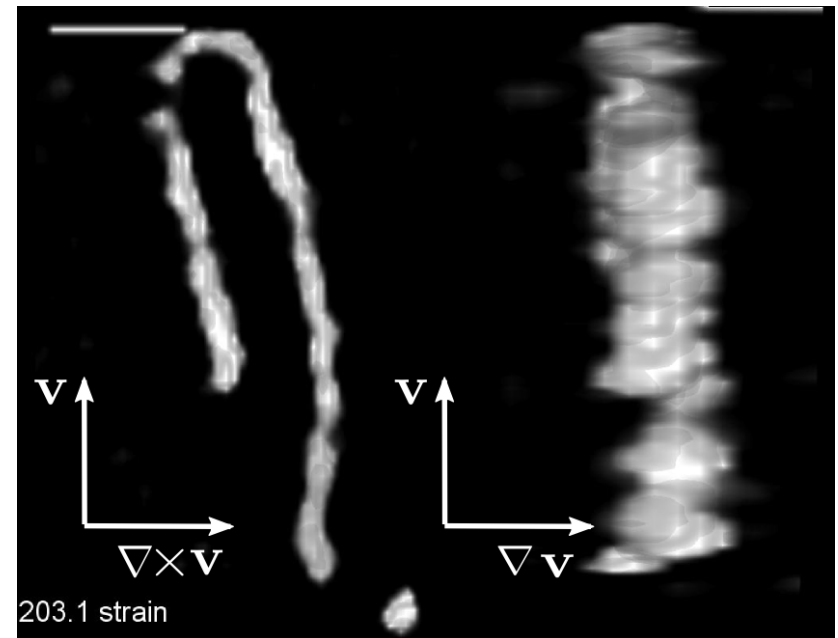
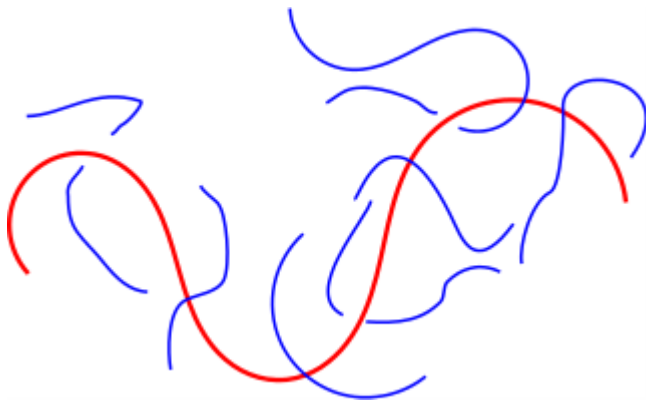
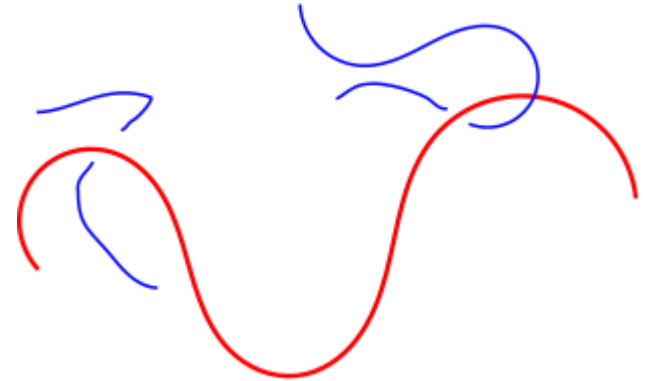
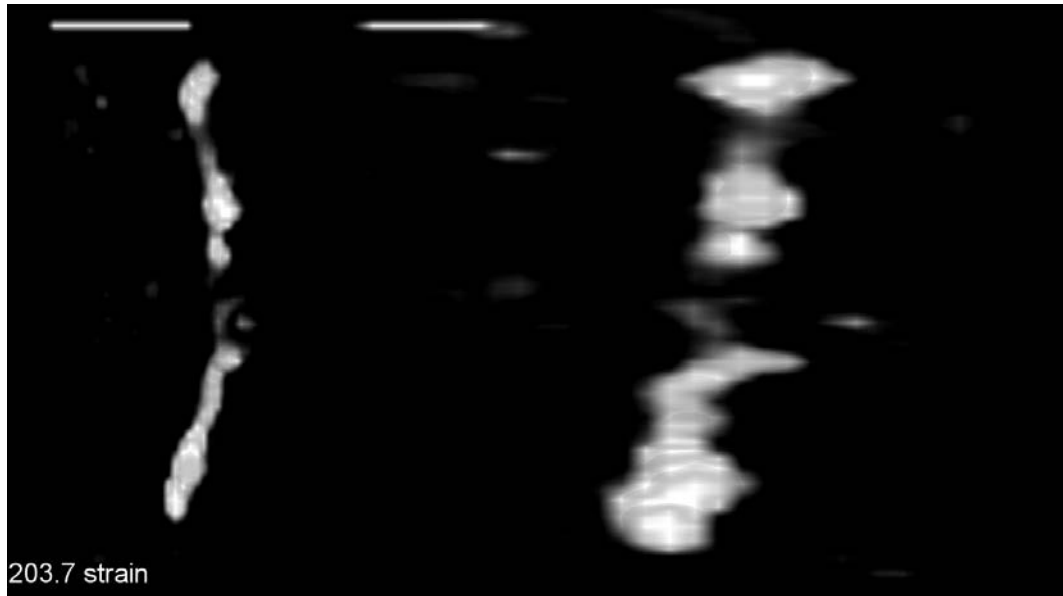
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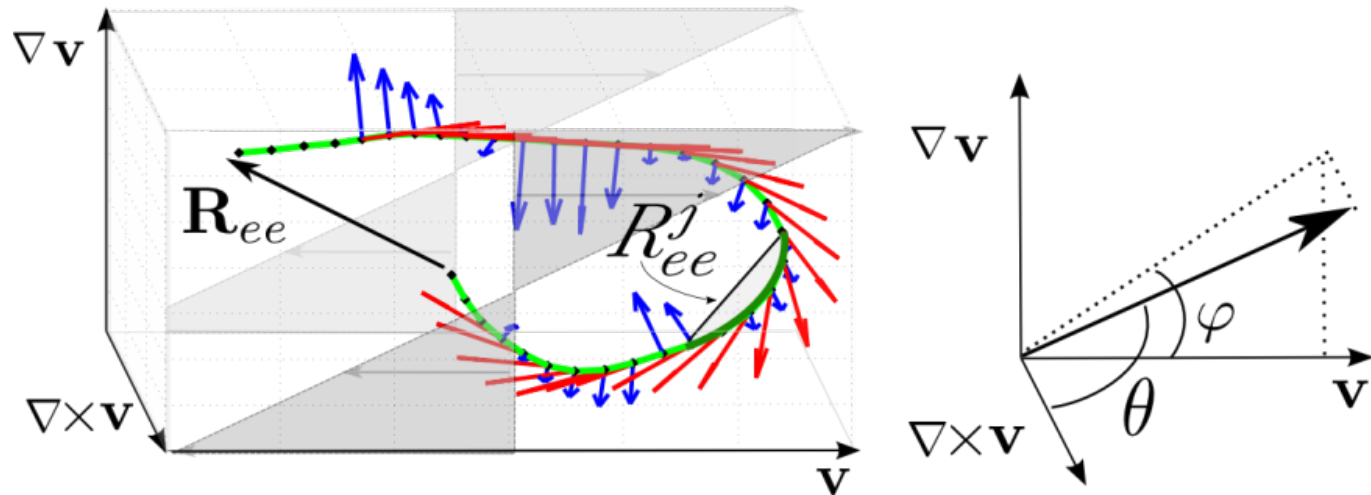
- Use three concentrations, label 1 per 100 filaments
- About 100 analyzed filaments per combination



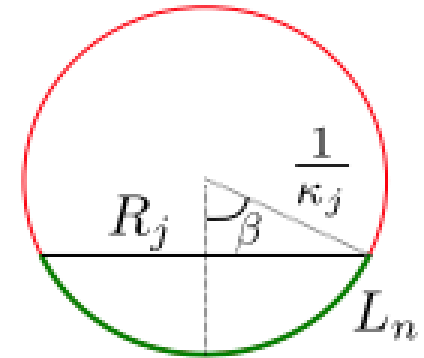
Sheared F-Actin in 3-D



Analyze local bending and stretching:



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



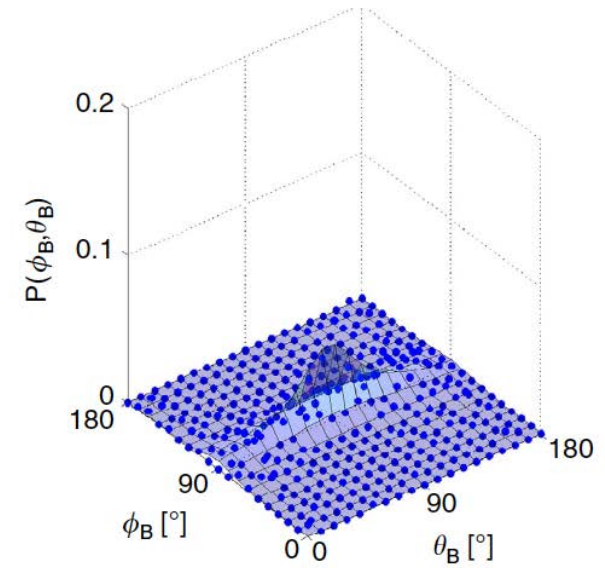
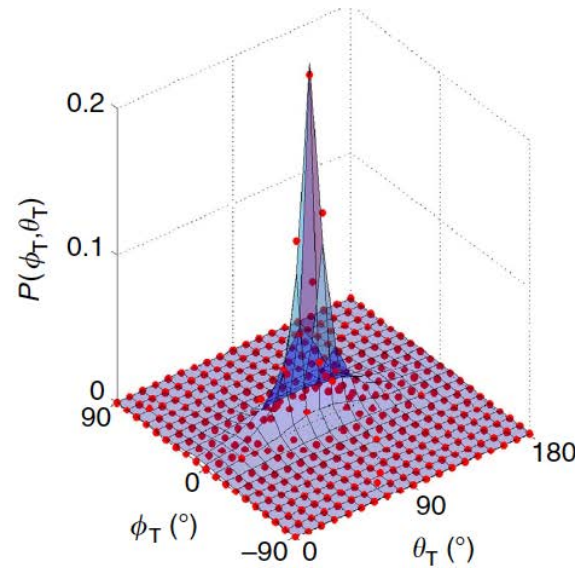
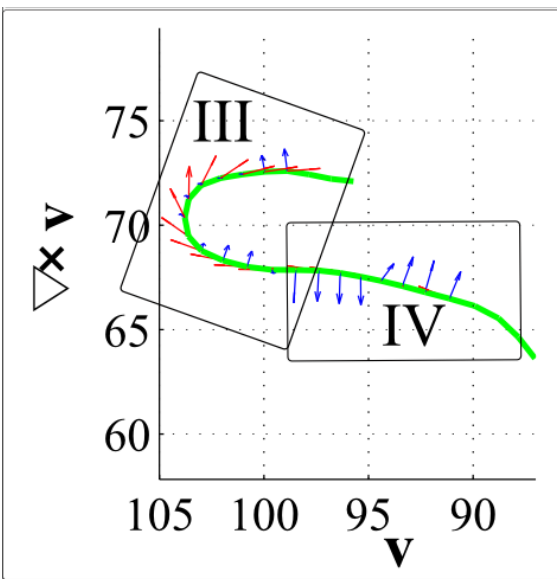


Distribution of angles



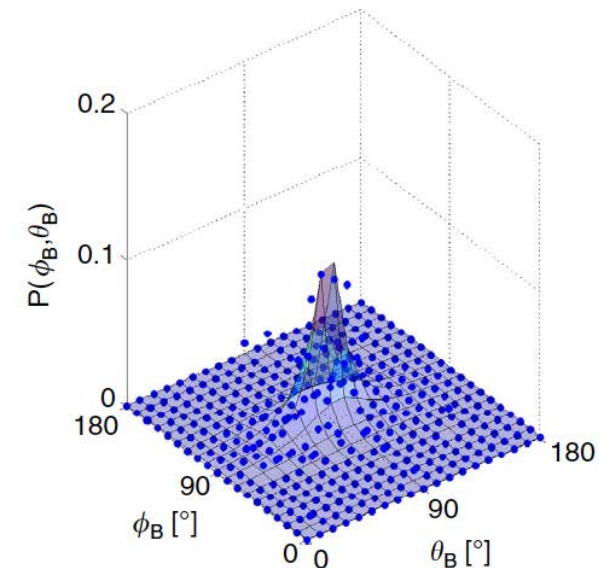
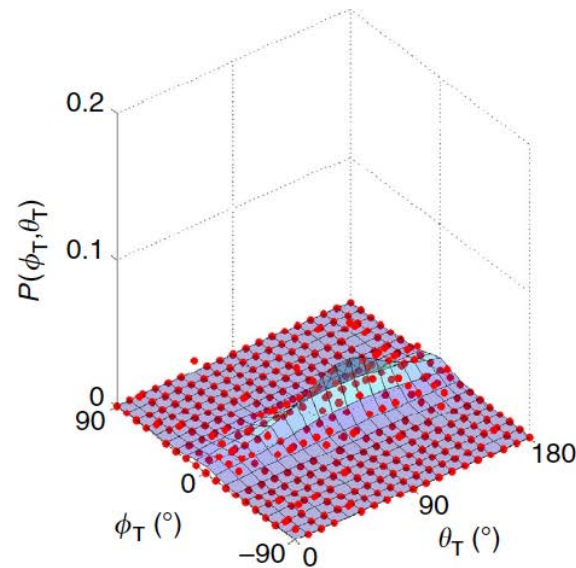
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Stretched: IV



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

Bent: III



Some conclusions IV

- How strong is strong?
- Always shear banding for given m ,
or is it system dependent? Depends on system
- Can we tune shear band formation? YES
- Is it charge or stiffness? STIFFNESS
- Suppression shear banding via widening interface
- Long stiff filaments form ordered hair pins
- So what about real rods?

Stiff and mono-disperse rods

Materials Bio-Engineered Phage Systems (varying morphology)

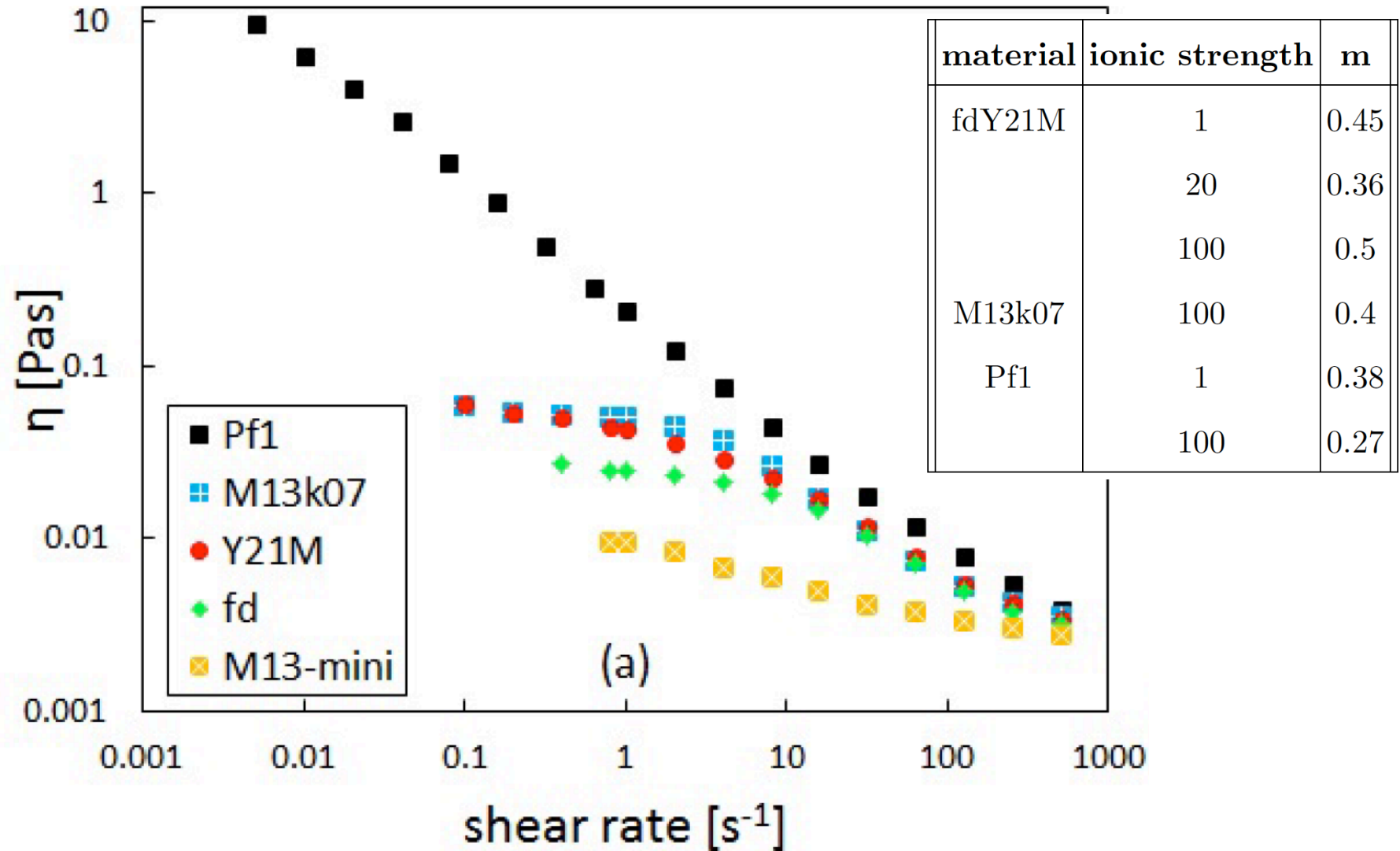
$d=6.6$ nm, but effective thickness depends on ionic strength



system	L [μm]	L_p [μm]
fd wild type	0.88	2.8
fd Y21M	0.91	9.9
Pf1	1.96	2.8
M13k07	1.2	2.8



Shear thinning rods





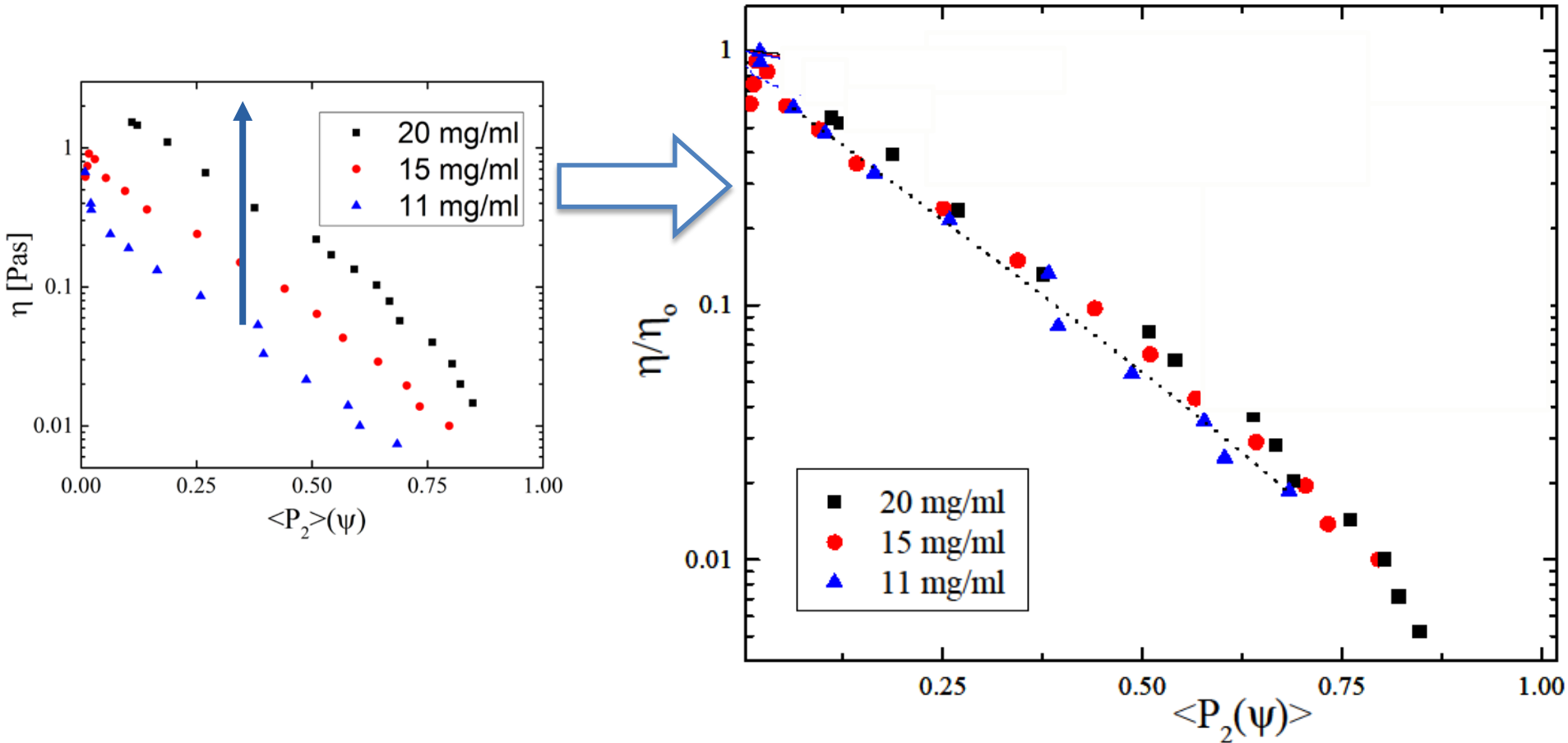
Viscosity vs projected order parameter $\langle P_2(\psi) \rangle$



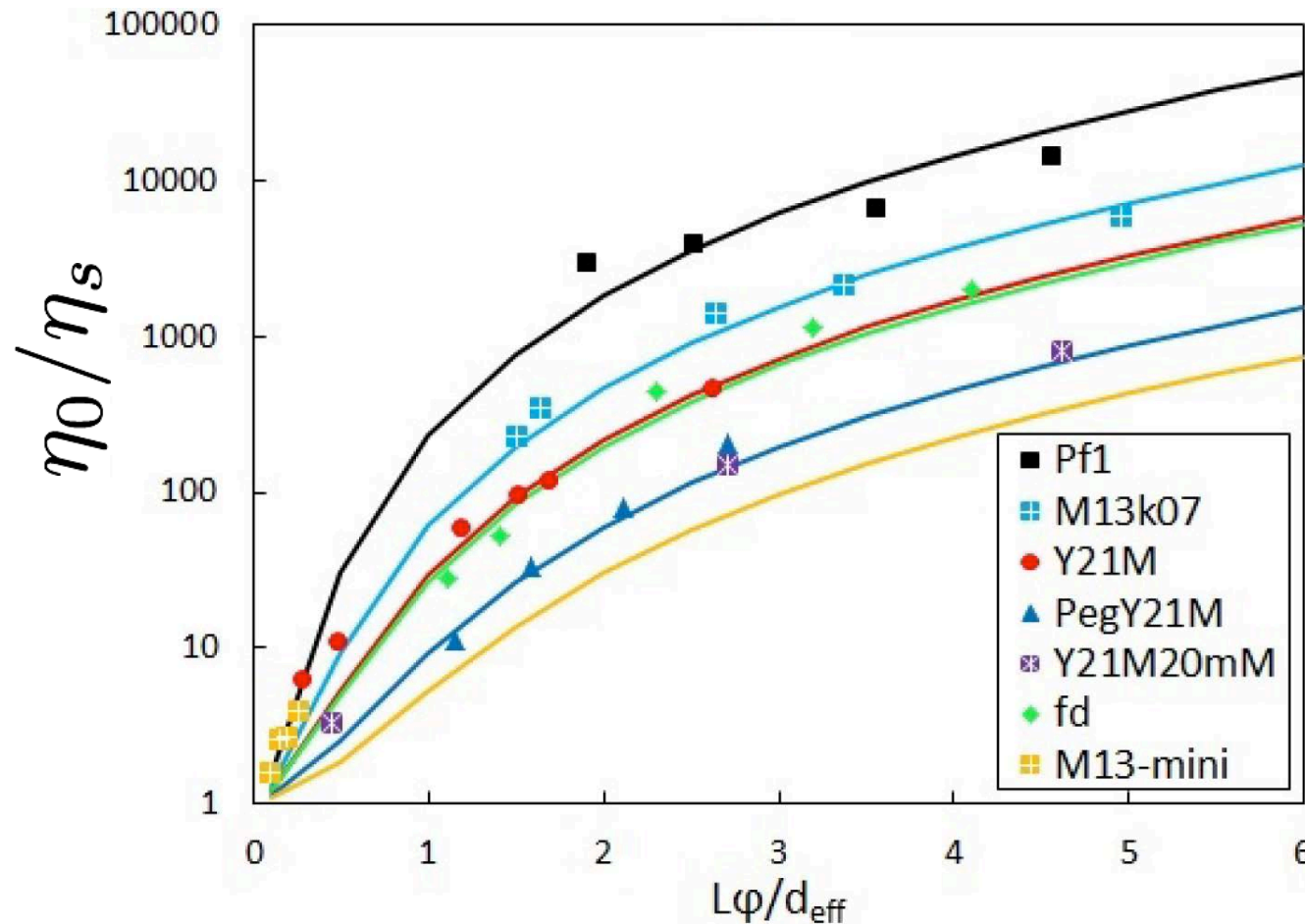
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Scale viscosity

Assumption: shear thinning is caused by orientation



Zero shear viscosity of rods

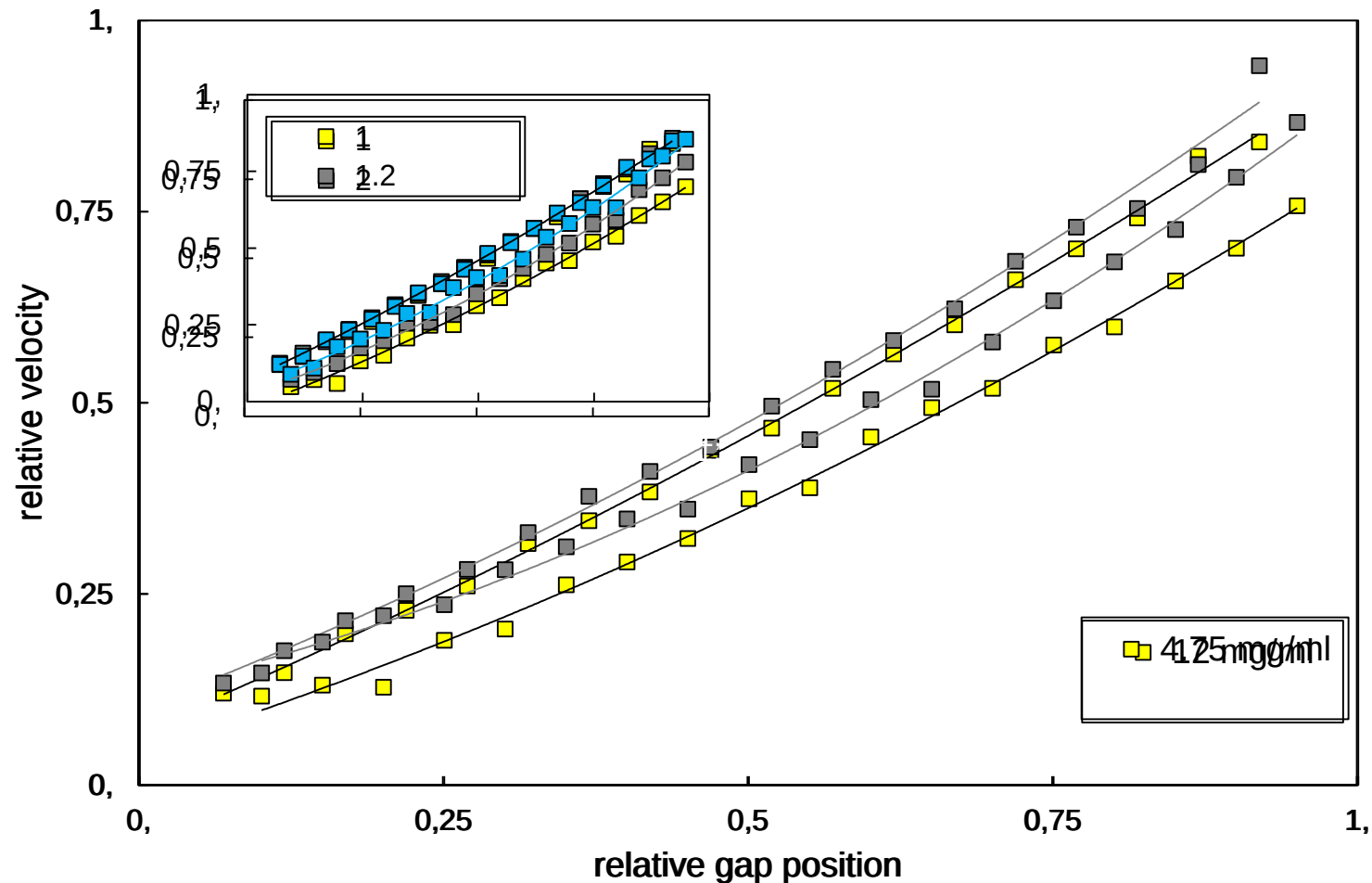


$$D_r = cD_r^0(vL^3)^{-2}$$



$$c=3 \cdot 10^3$$

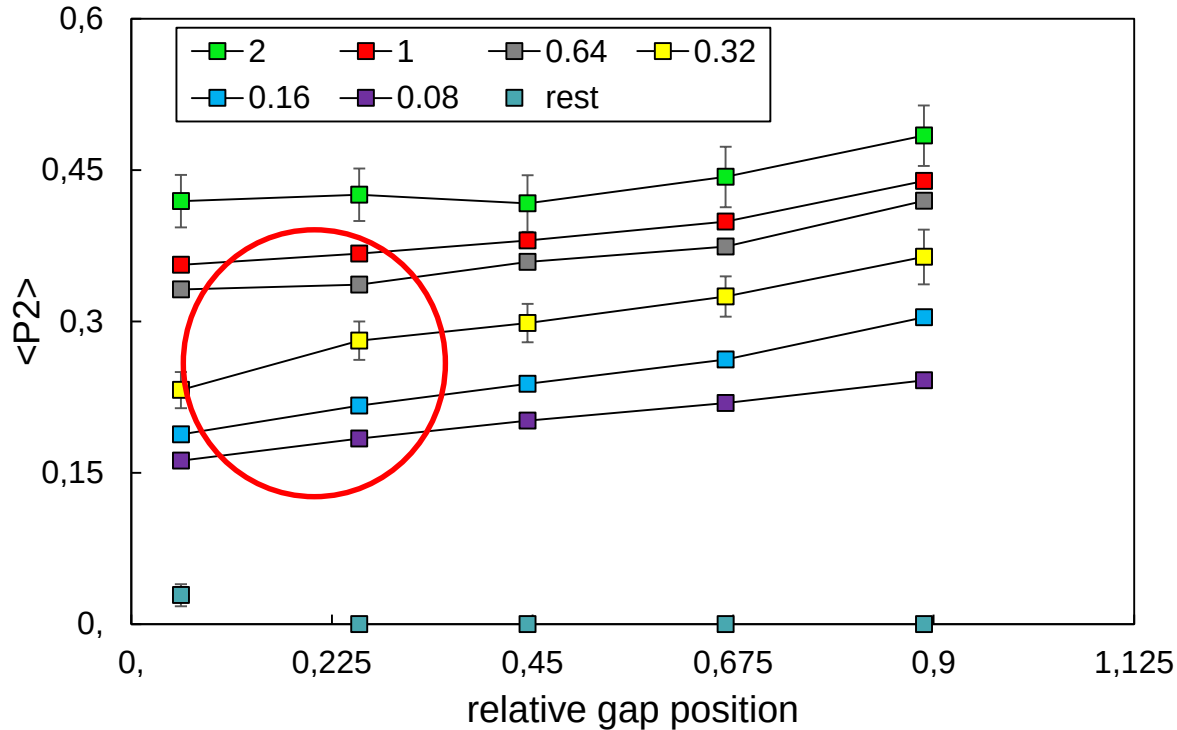
Velocity profile of M13k07 ($L=1.2\ \mu\text{m}$, $L_p=2.2\ \mu\text{m}$):



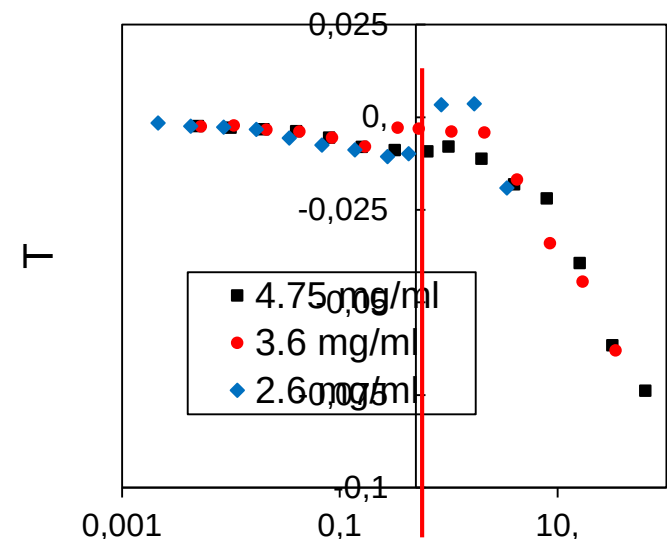
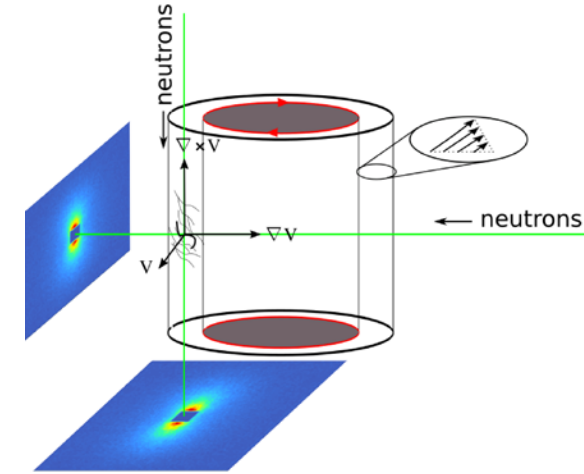
- very long and flexible rods show hints of shear banding

Zero shear viscosity of rods

Shear-banding and hairpin formation



- biaxiality reverses in a small shear rate range after “shear banding”



Final conclusion

- Always shear banding for given m ,
or is it system dependent? Depends on system
- Can we tune shear band formation? YES
- How strong is strong? $m_{fc} < 0.25$
- Suppression shear banding via widening interface,
BUT: broad shear banding can exist with broad interface

Suggestions:

- Shear banding is suppressed when chain collapses after disentanglement
- Collapse affects the shear-curvature viscosity
- Shear banding is suppressed when system is not long enough

Acknowledgements

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Simon Rogers

PSI, Villigen:

Joachim Kohlbrecher

ILL, Grenoble:

Lionel Porcar

Amolf Amsterdam:

Gijsje Koenderink



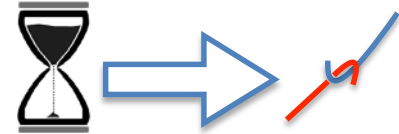


Conclusions and Outlook



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We find the connection between ordering and stress for *semi-flexible polymers* to *stiff rods* :



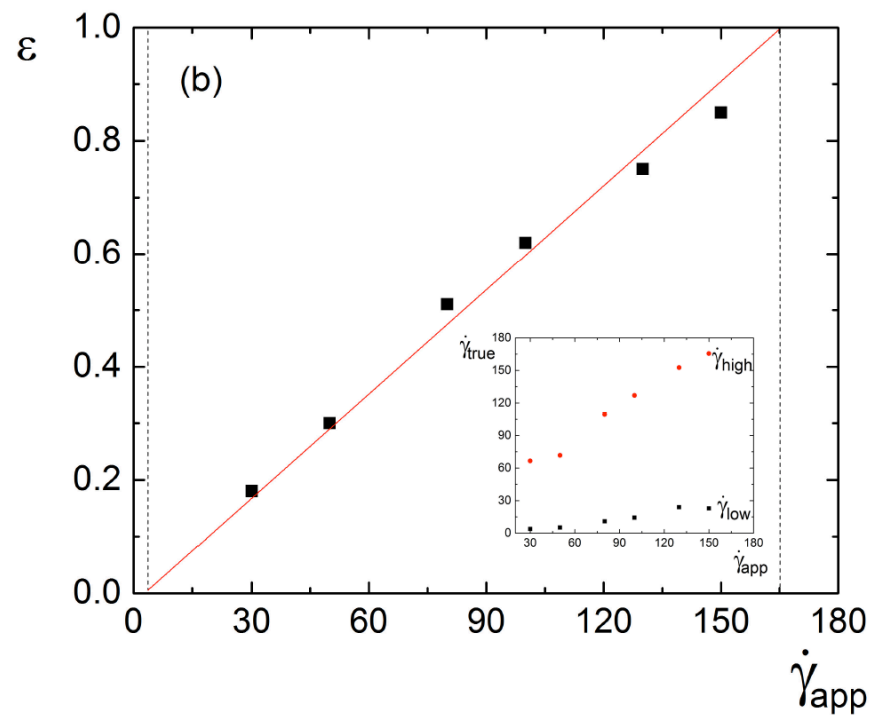
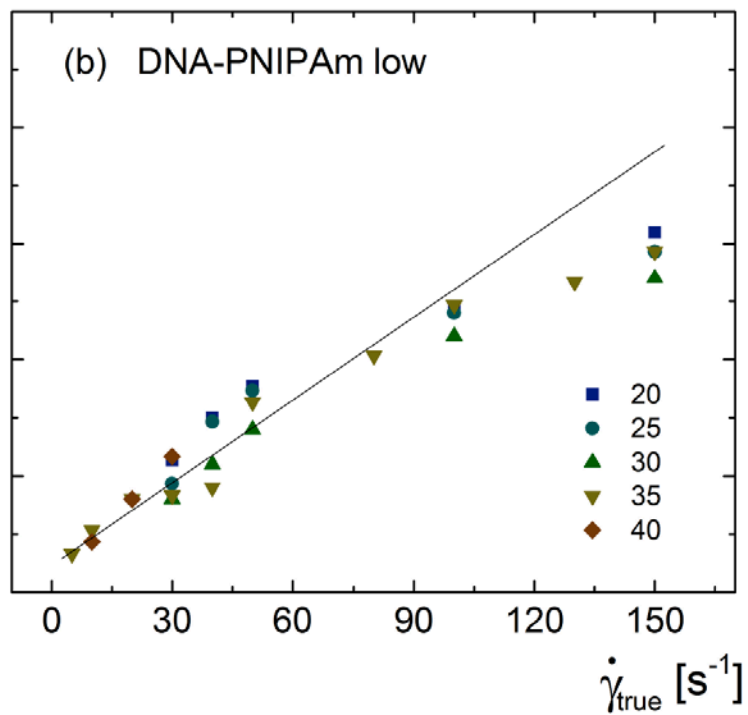
- Shear induced biaxial alignment of stiff segments

But:

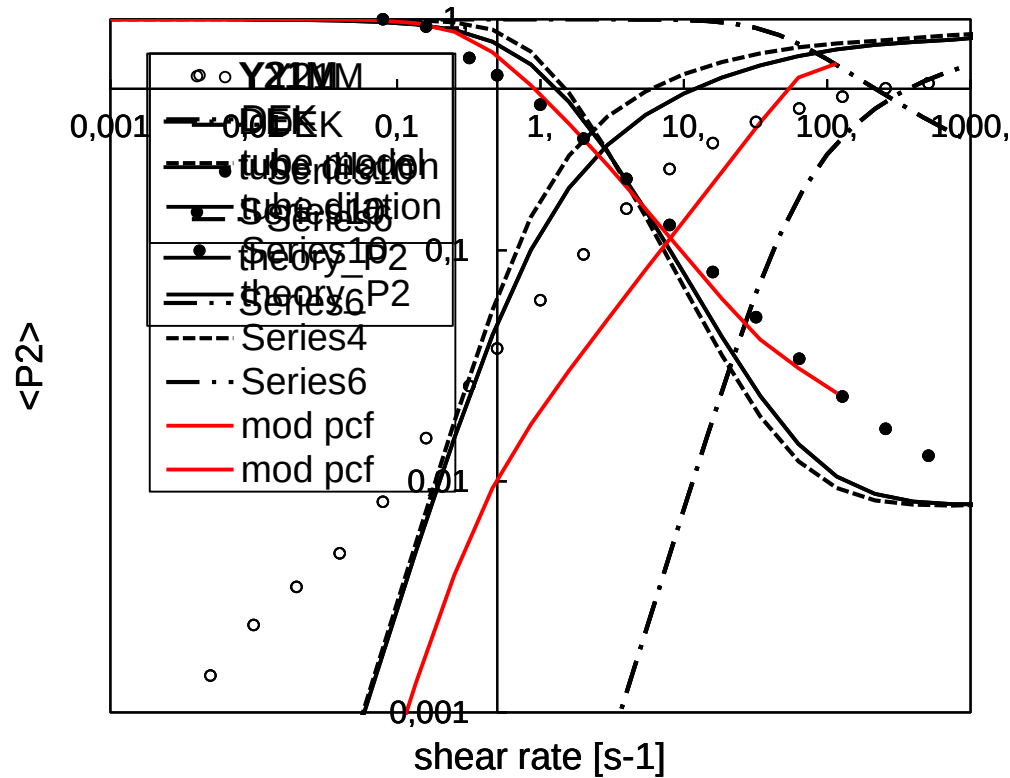
- big flaws in theory for sheared rods, no non-linear theory for sheared semi-flexible polymers
- no good handle on set flow instability

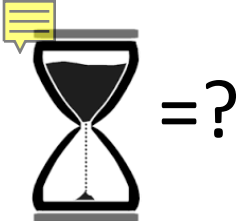
So:

- Improve theory
- Develop new systems:
 - Controlled polydispersity
 - Controlled friction with grafted DNA
 - Use labeled living stiff supra-molecular polymers



Nonlinear viscosity and ordering of the ideal rod



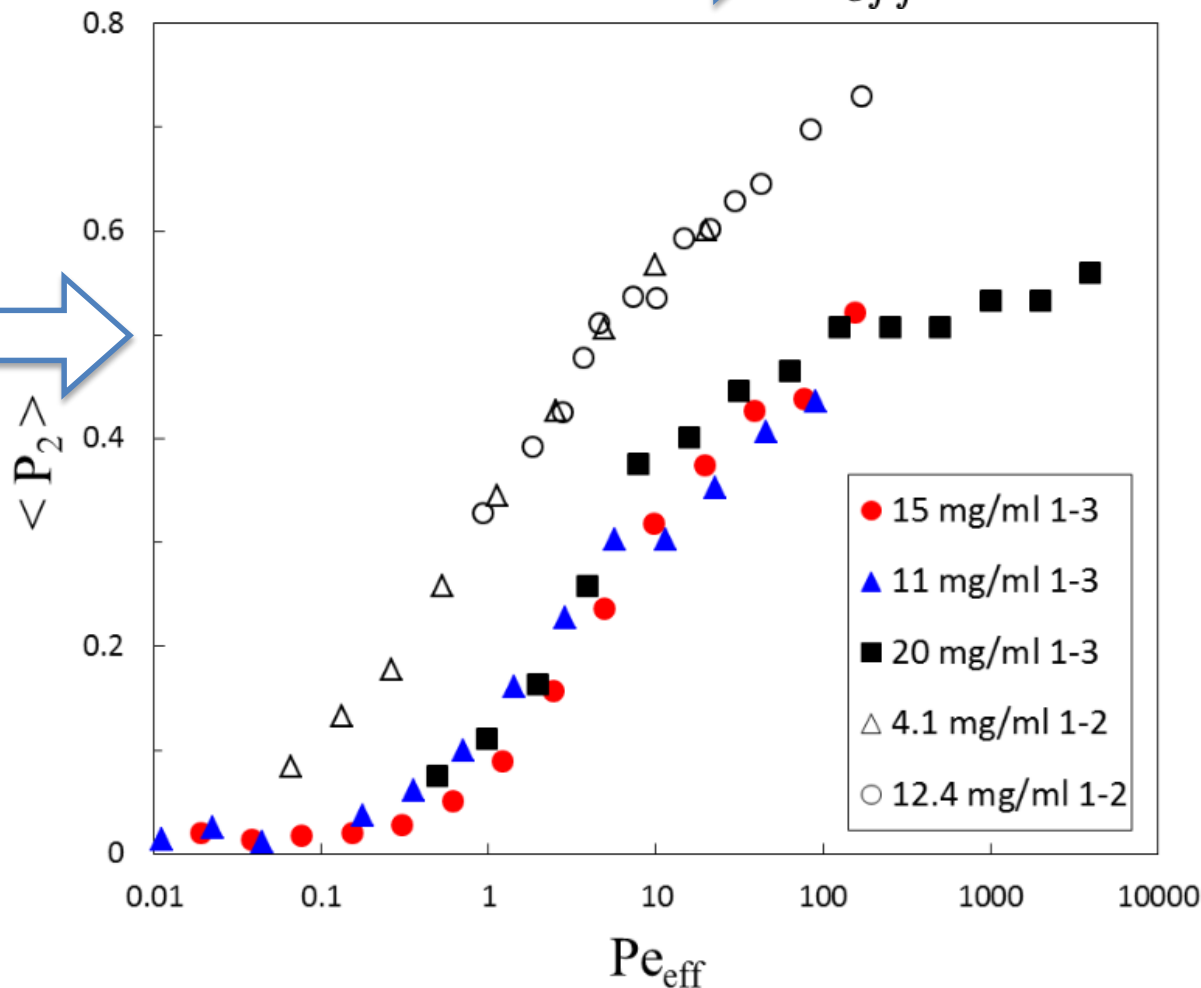
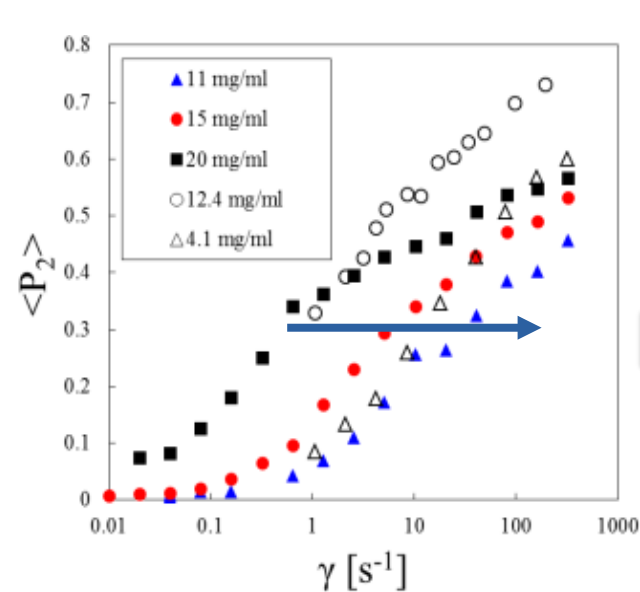


Obtain the I-N spinodal point



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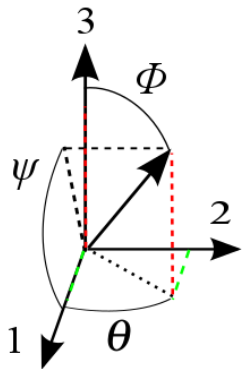
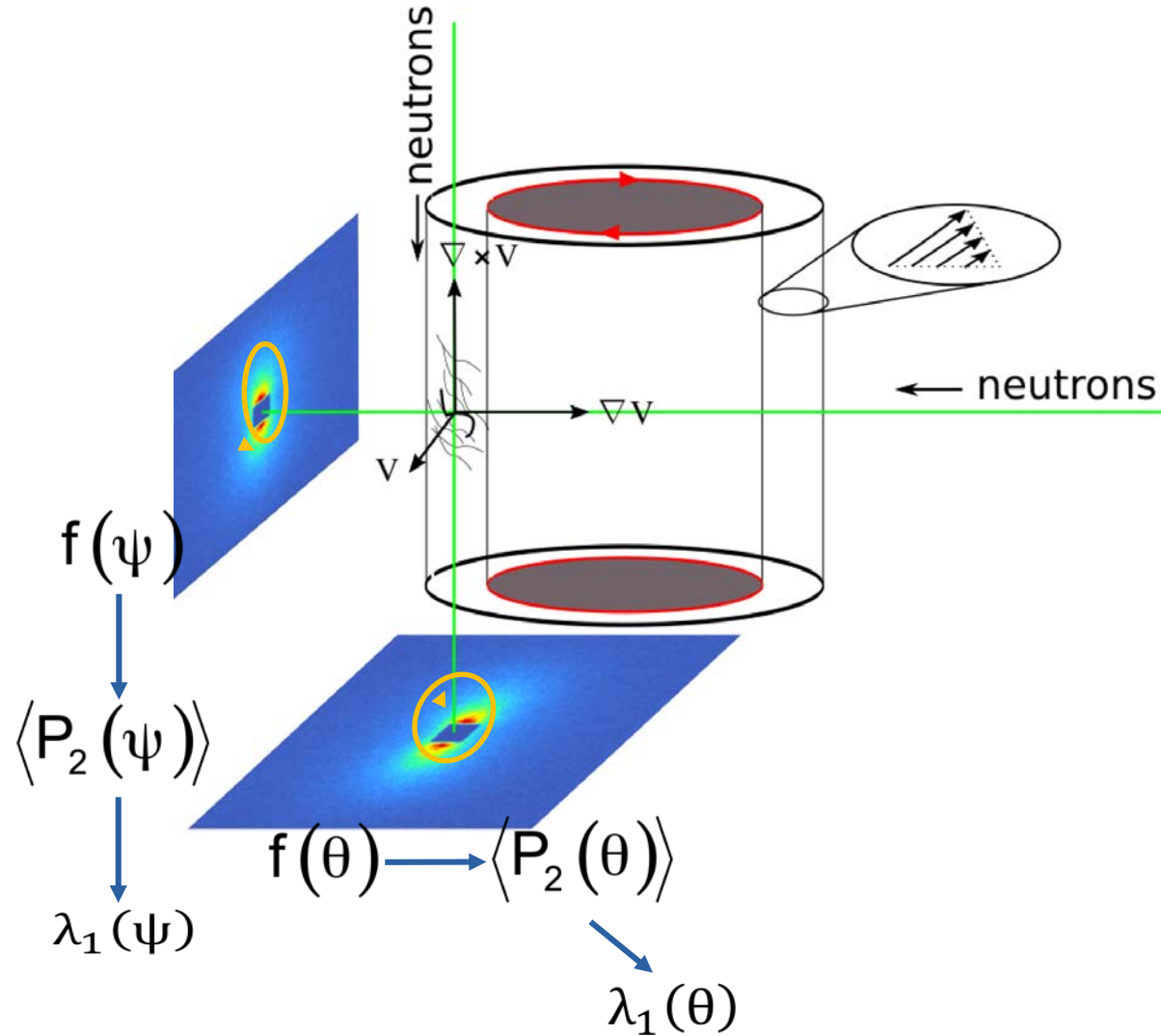
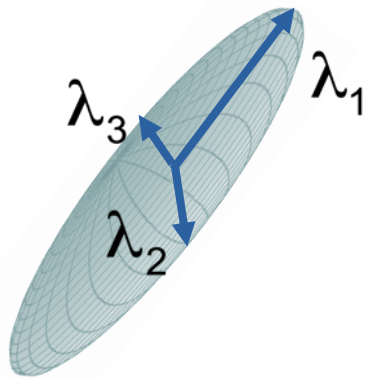
Scale shear rate: $Pe_{eff} = \dot{\gamma}_0 / D_R^{eff} \Rightarrow \frac{L}{d_{eff}} \varphi_{IN} = 4.2$



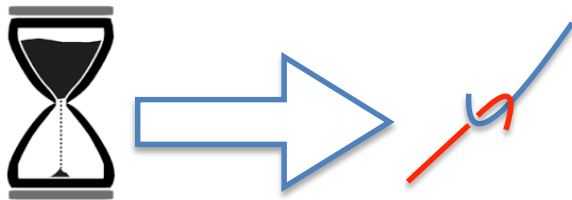
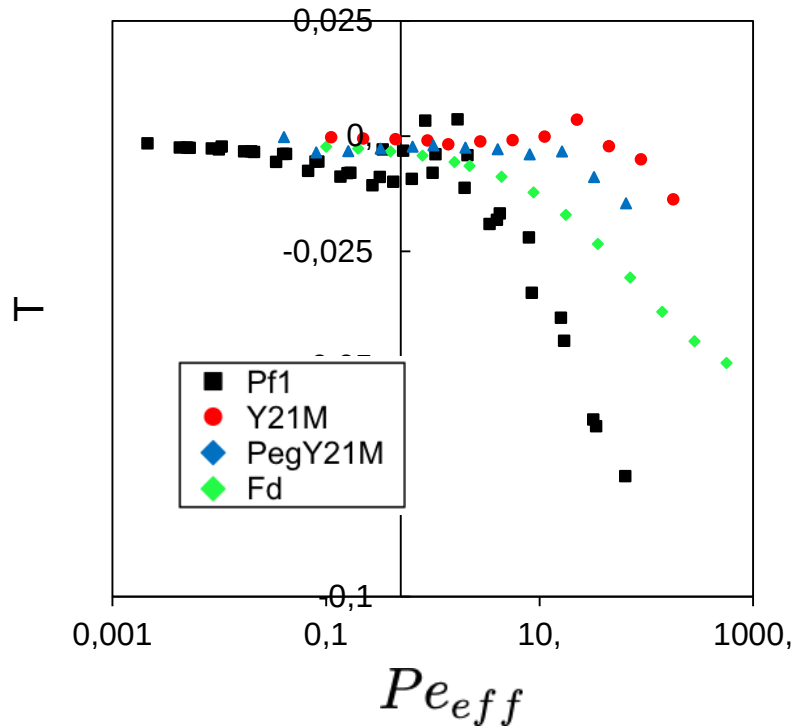
- Collective scaling works
- different ordering in different directions: Biaxiality!

Scattering in 3-D of actual rods

3-D SANS



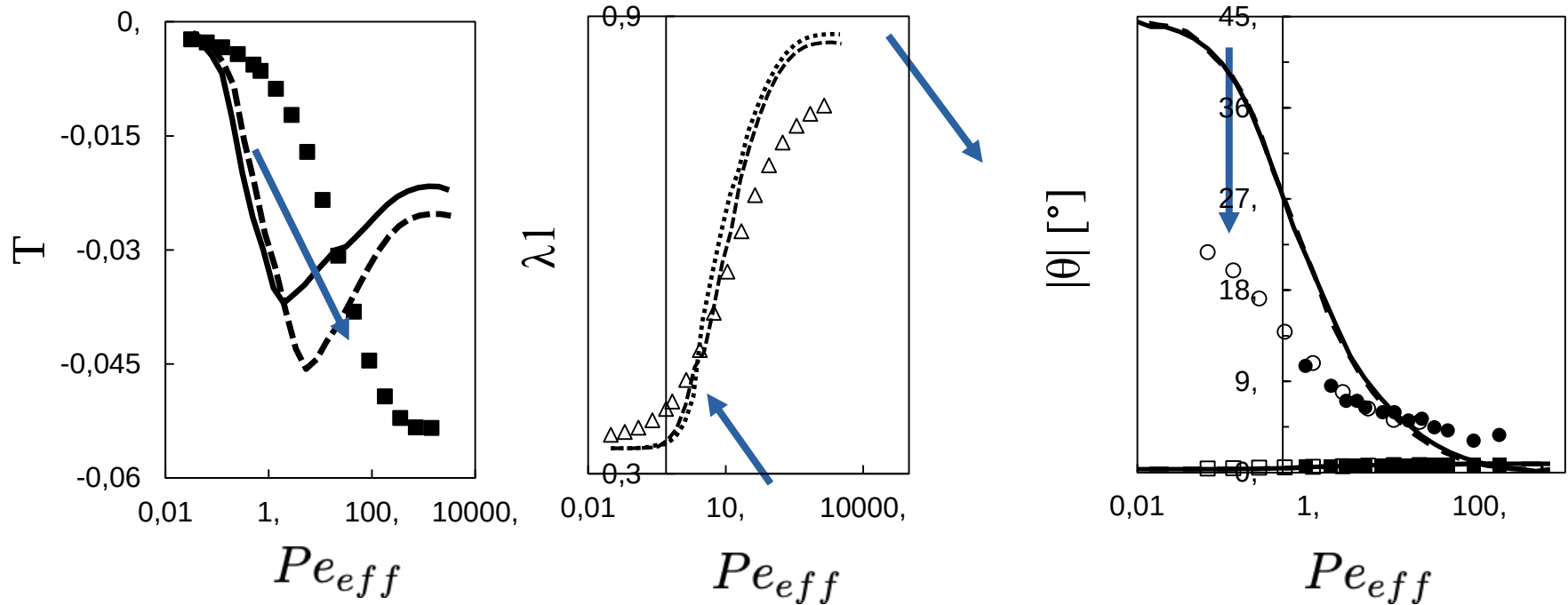
$$\lambda_1(\psi) \Rightarrow \psi_{\max} \equiv 0$$



- **Collective scaling works**
- But no good handle on topological effect and biaxiality.



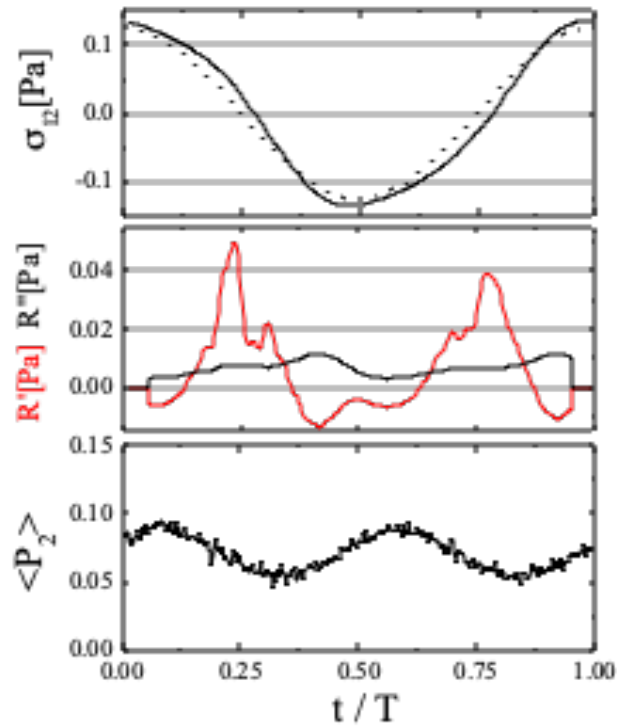
Scaling other ordering parameters



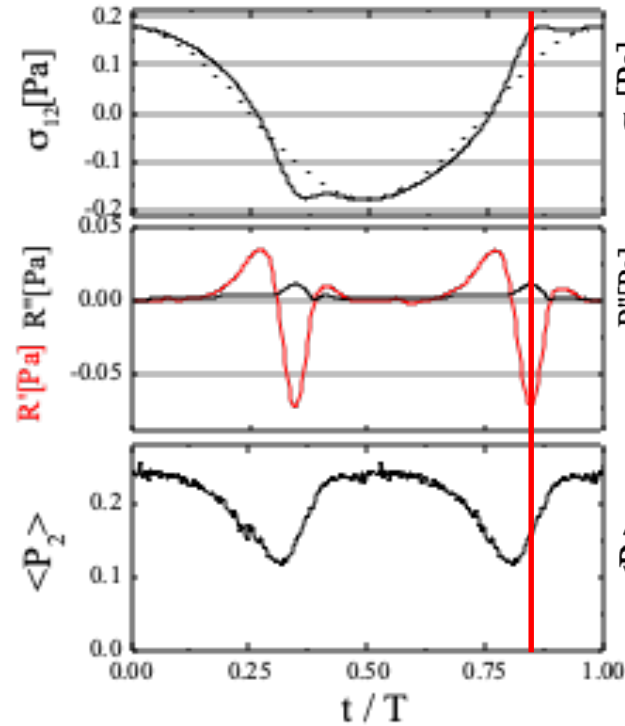
- Strong dependence at low shear rate; weak dependence at high shear rate

Dynamic response **fd virus** in isotropic phase

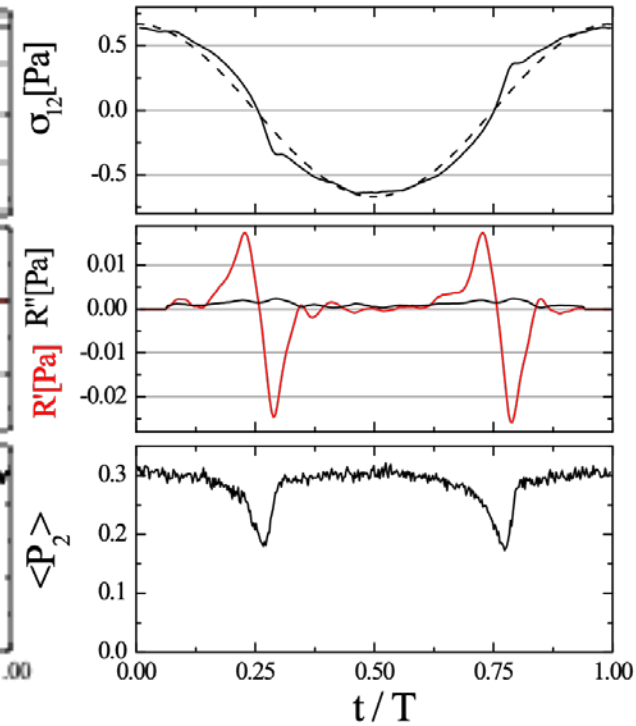
$f = 0.01 \text{ Hz}$



$$\dot{\gamma}_0 = 3.2 \text{ s}^{-1}$$



$$\dot{\gamma}_0 = 12.8 \text{ s}^{-1}$$



$$\dot{\gamma}_0 = 102 \text{ s}^{-1}$$

Push and pull experiments

End-to-end vector $\mathbf{R}_{e-e}$ is the relevant parameter

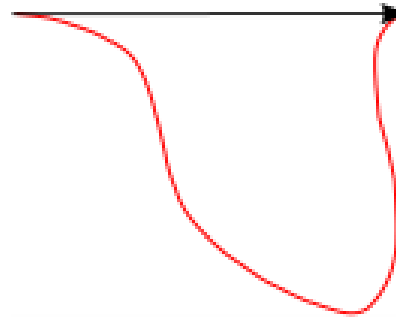
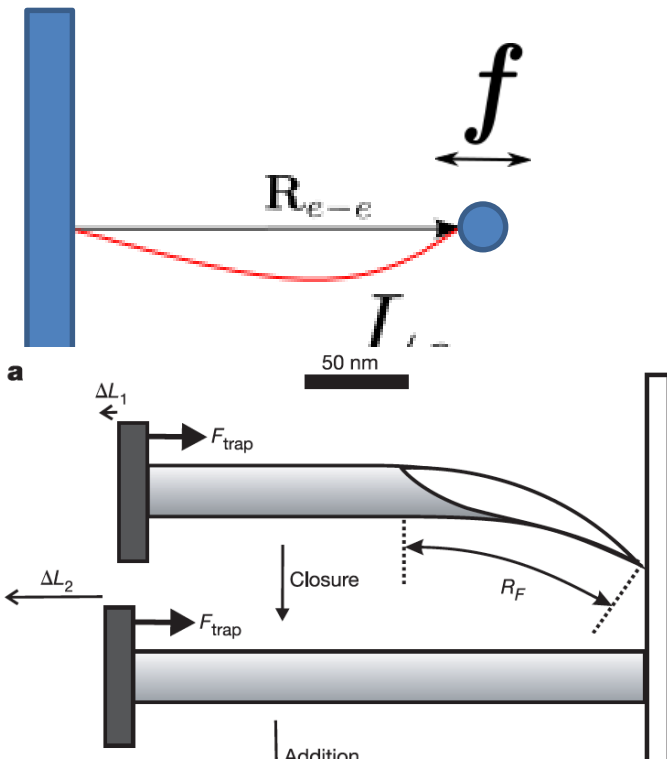
Stiff: $\mathbf{R}_{e-e} \approx L_c$

Semi-flexible:

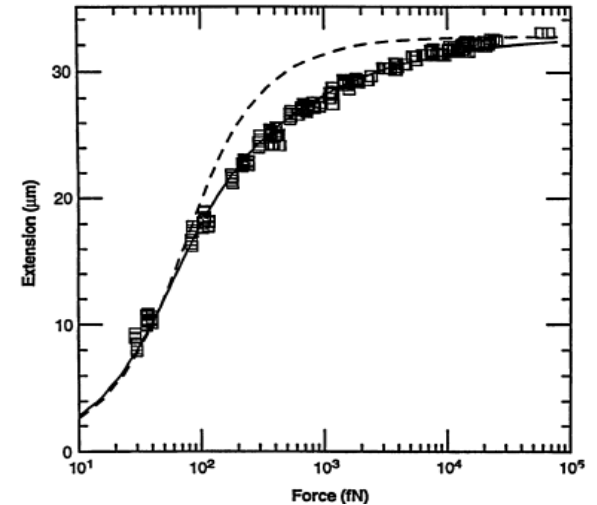
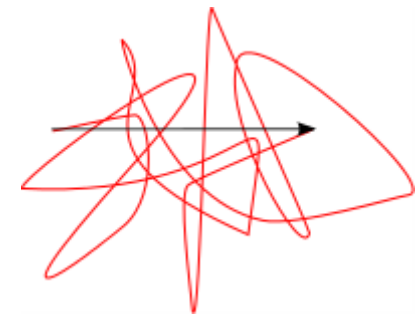
$$\mathbf{R}_{e-e} < L_c$$

Flexible:

$$\mathbf{R}_{e-e} \ll L_c$$



?



Assembly dynamics of microtubules at molecular resolution
Kerssemakers et al, Nature, 442 (2006)

Entropic elasticity of λ -DNA
Bustamante, Science 265(1994)

Introduction

Scaling the effective Peclet number by an apparent rotational diffusion coefficient (MPC calculation):

- effective Peclet number:
- at the I-N transition: $Pe_{\text{eff}} = \dot{\gamma} / D_r^{\text{coll}}$ (lower spinodal point)
- Smoluchowski theory: $\varphi_{\text{IN}} \Rightarrow D_r^{\text{coll}} \equiv 0$

$$\frac{\partial}{\partial t} \delta S = -6 D_r^{\text{coll}} \delta S$$

$$D_r^{\text{coll}} = D_r^0 \left(\frac{L}{d} - \frac{L}{5d} \varphi \right) \quad \text{(depending on } U \text{ between 4 and 5)}$$

- MPC:

$$D_r^{\text{coll}} = D_r^0 A \left(\frac{L}{d_{\text{eff}}} \varphi_{\text{IN}} - \frac{L}{d_{\text{eff}}} \varphi \right)^v$$

Tao et al., *J. Chem. Phys.*, 2006

- measurement:

$$\varphi_{\text{IN}} = 4.2$$

Introduction

Motivation:

rod suspensions show strong shear thinning: microscopic reason

no shear

isotropic pdf

Brownian motion:
rotational diffusion

$$D_r \neq D_r^0$$

ordering tensor

$$S = I$$

high viscosity

shear

anisotropic pdf

$$\vec{\nabla} \times \vec{v}, 3$$

$$D_r = D_r^0$$

$\vec{u}$ director

$\vec{v}, 1$

$\vec{v}, 2$

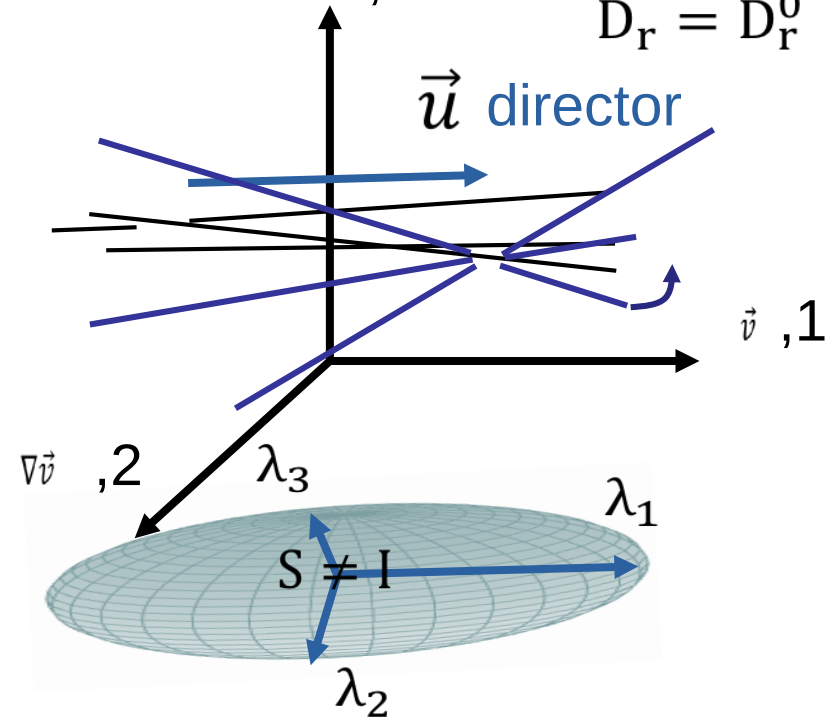
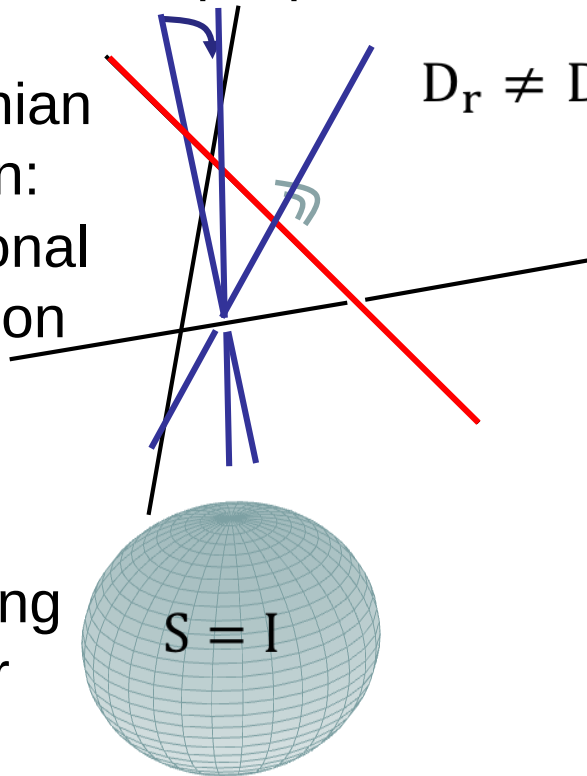
λ_3

λ_1

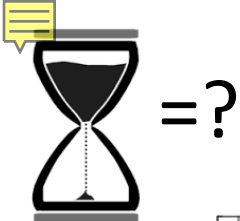
$$S \neq I$$

λ_2

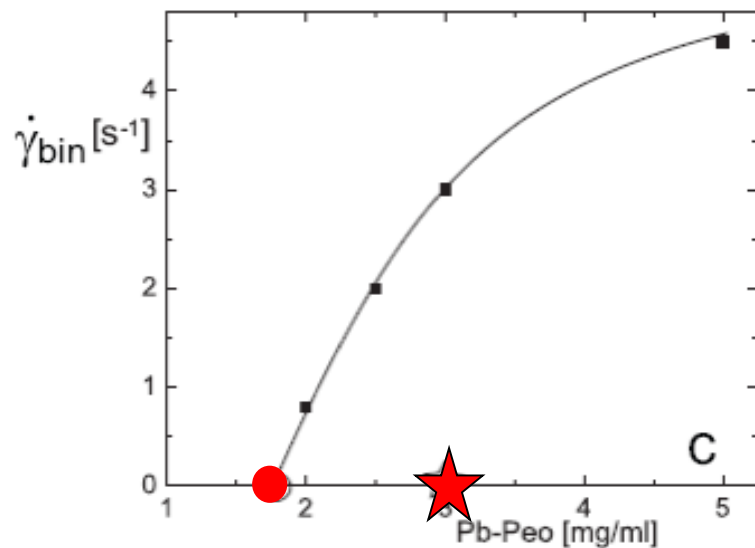
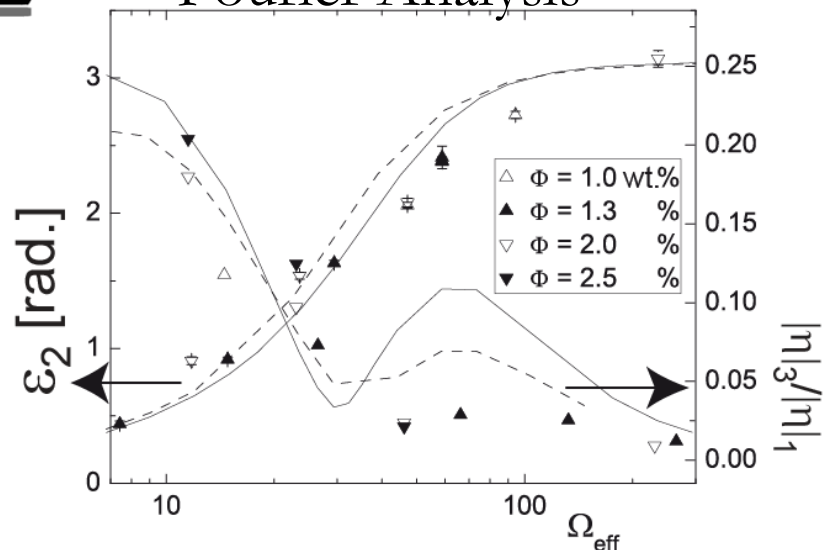
much lower viscosity







Fourier Analysis



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

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

Scaling frequency:

$$\Omega_{eff} = \omega / D_R^{eff}$$

$$D_R^{eff} = D_R (1 - \varphi / \varphi_{IN})$$

We obtained the I—N spinodal point!

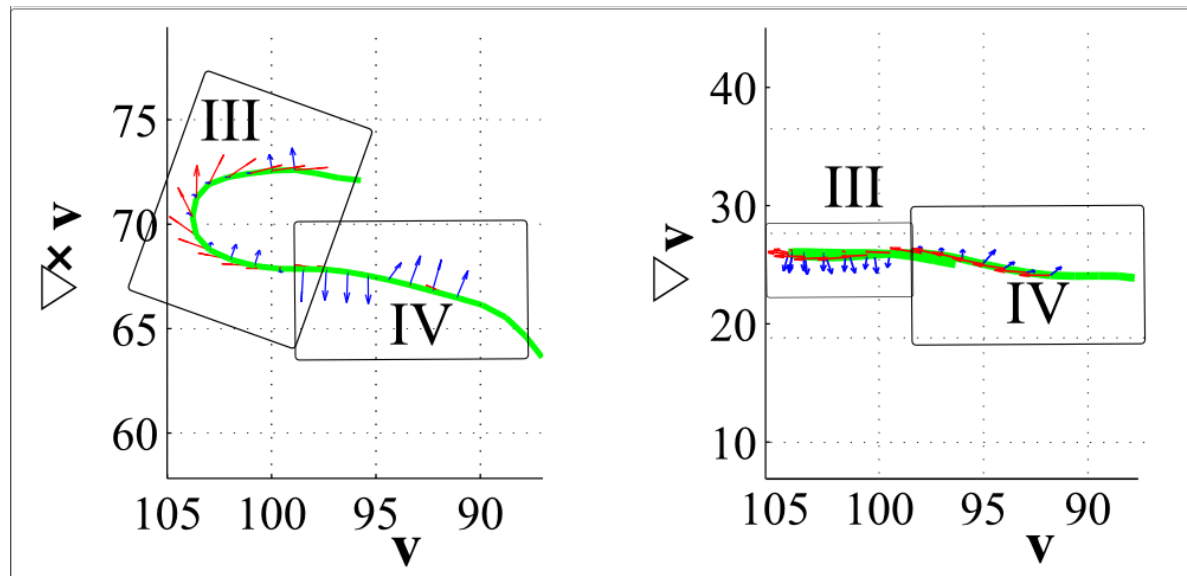
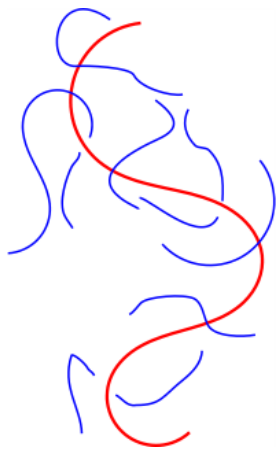
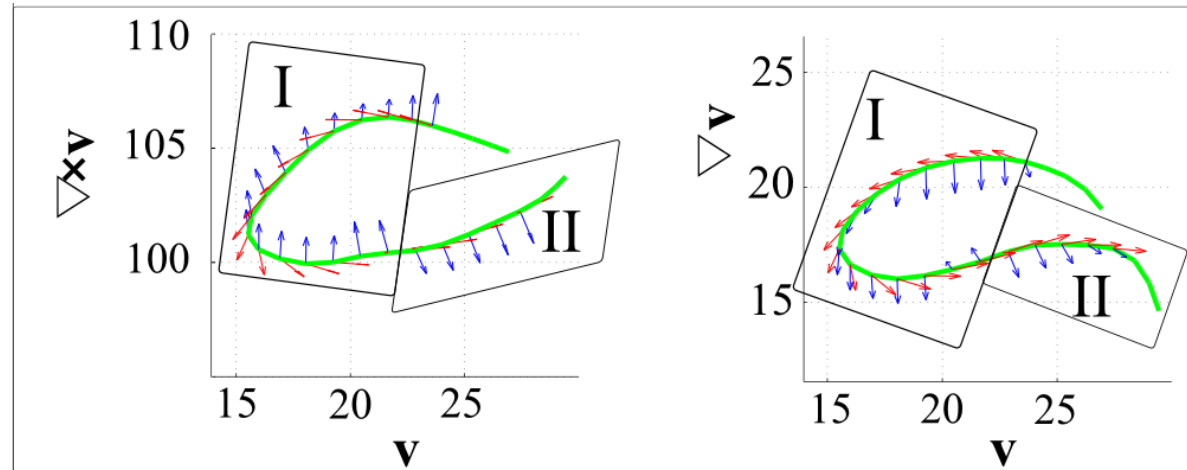
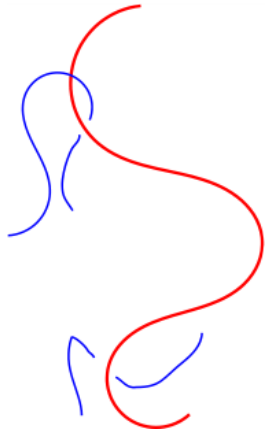
$$\frac{L}{d_{eff}} \varphi_{IN} = 3.0$$

& $D_R = 0.04 \text{ s}^{-1}$

Typical examples:

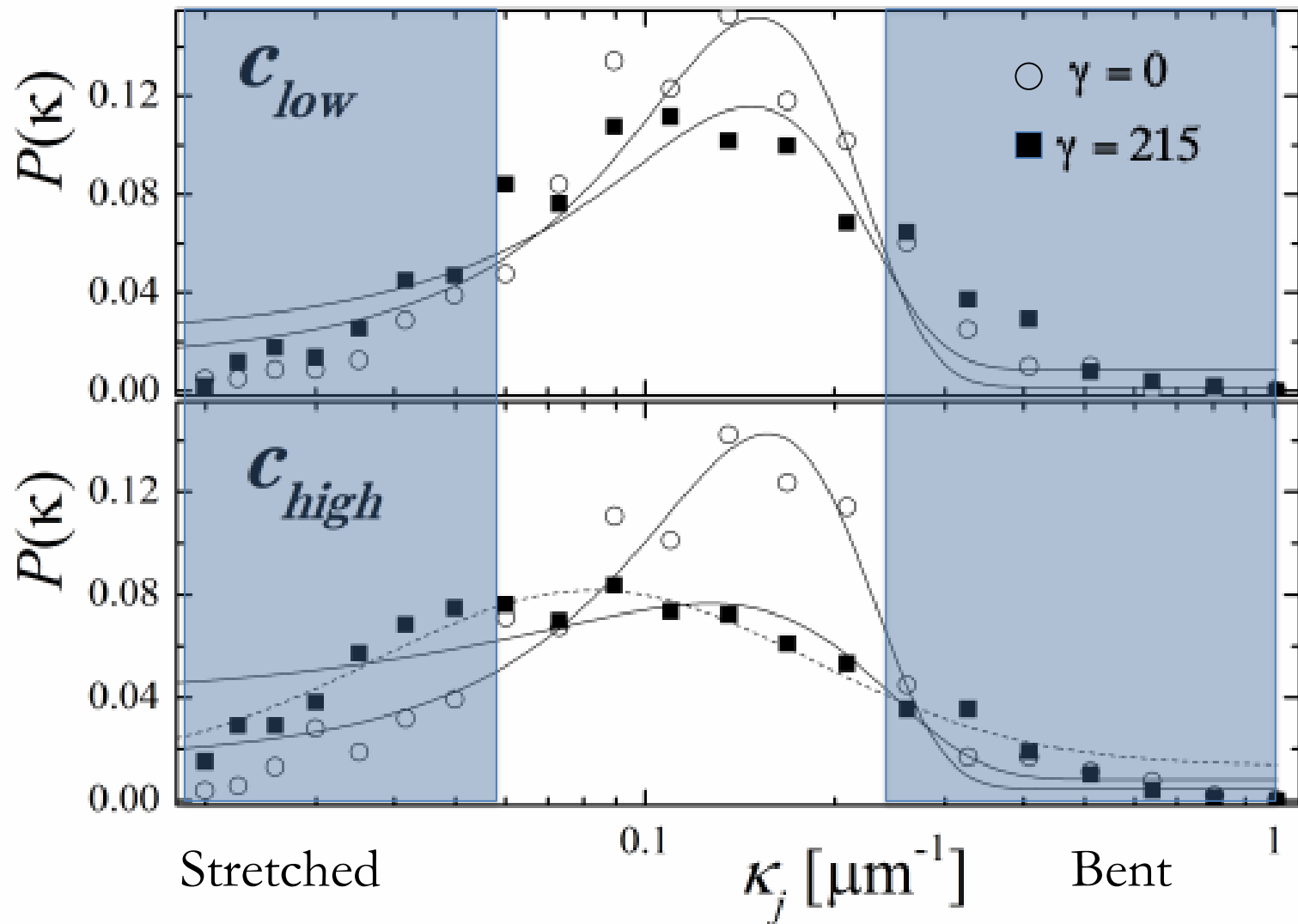
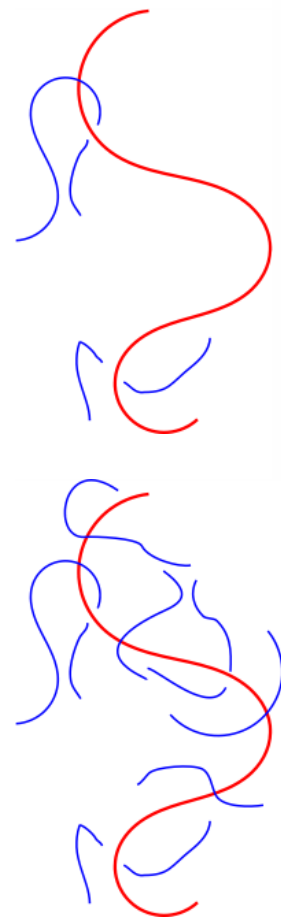


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Distribution of curvatures:





Characterizing parameters

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

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

Biaxiality

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

Orientational order parameter

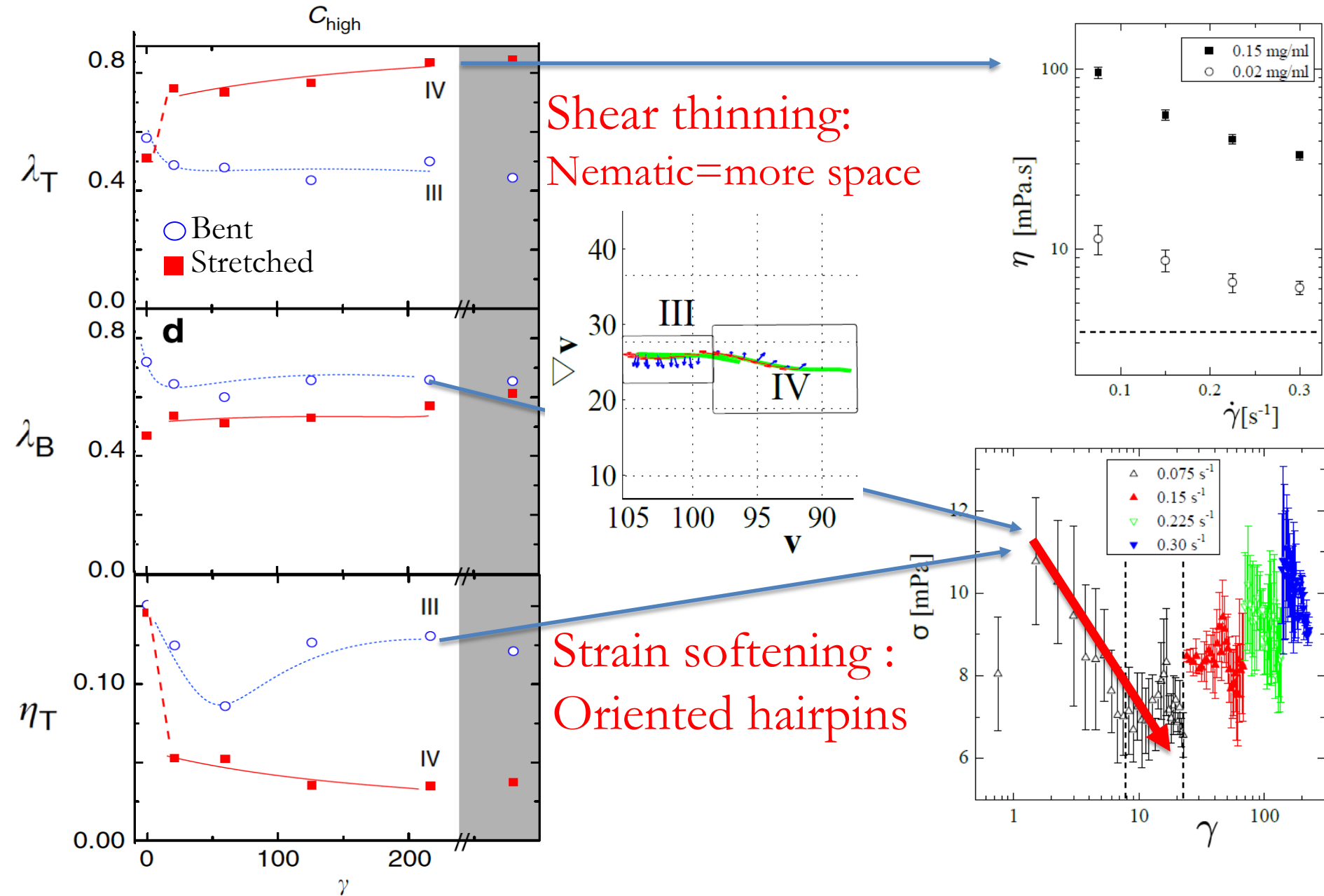
Note: this is the input for calculating stress tensor



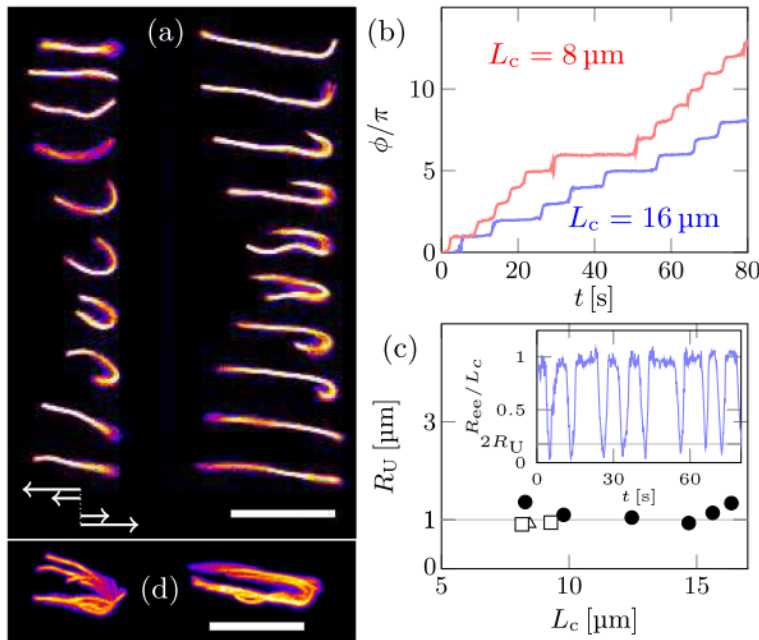
Connection between ordering and stress



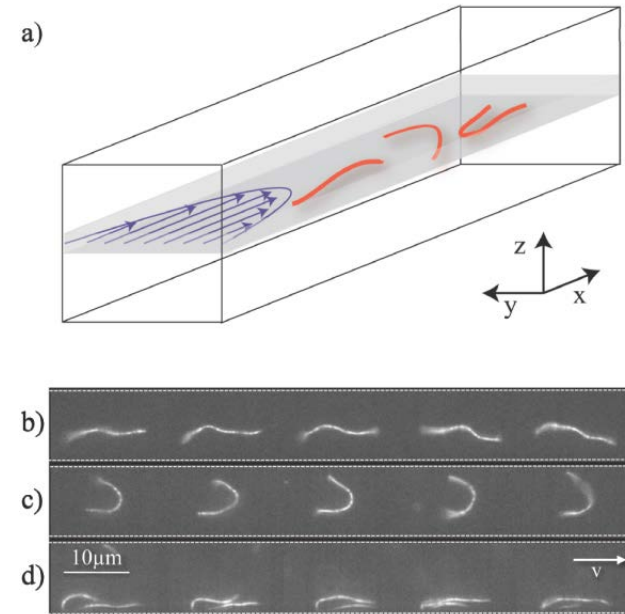
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Shear experiments on F-Actin



Direct Observation of the Dynamics of Semiflexible Polymers in Shear Flow
Harasim et al, PRL, 110 (2013)



Mobility Gradient Induces Cross-Streamline Migration of Semiflexible Polymers
Steinhauser et al, ACS Macroletters, p. 542 (2012)

Ill defined geometries; Infinite dilute; 2-D imaging

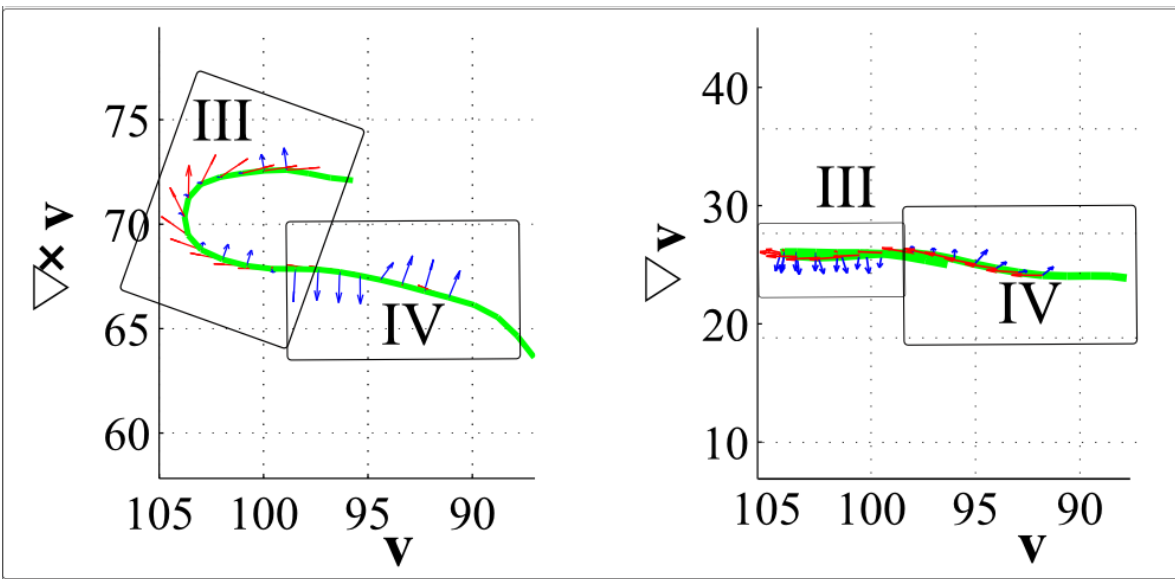
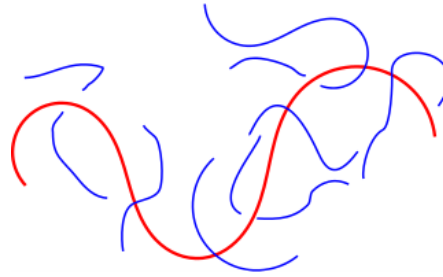


Distribution of angles

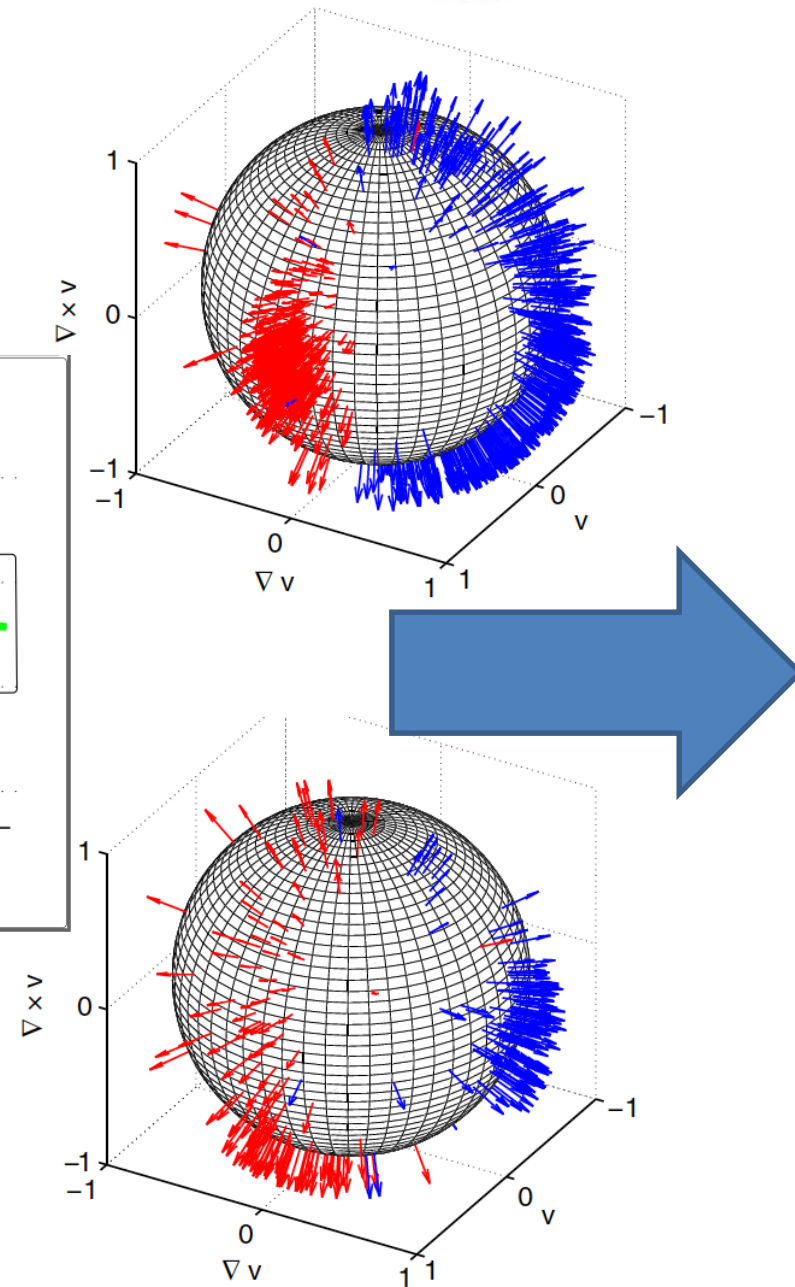


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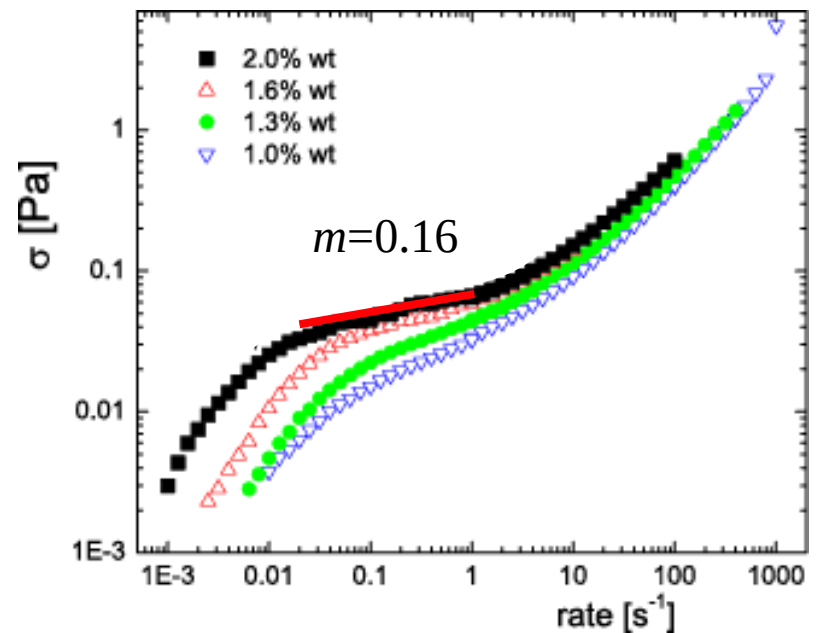
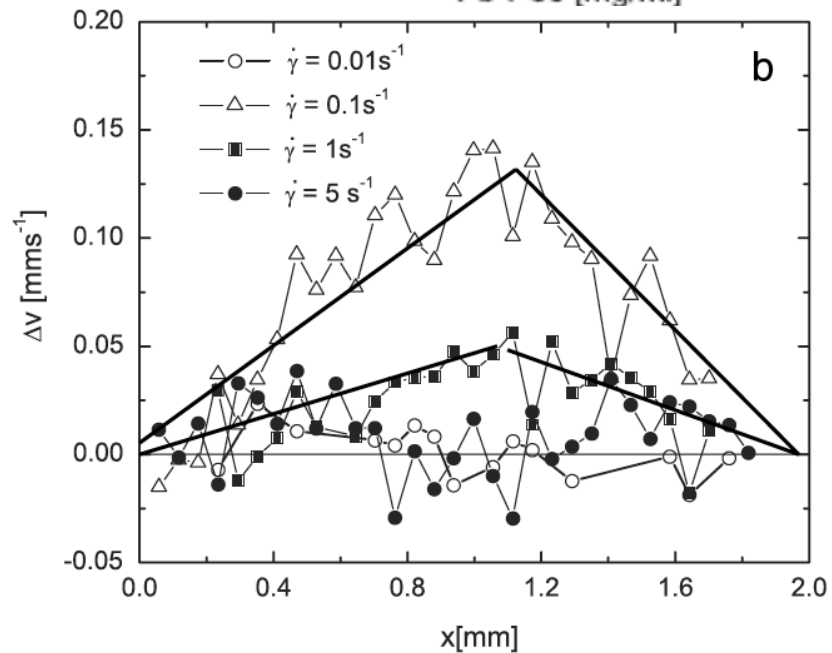
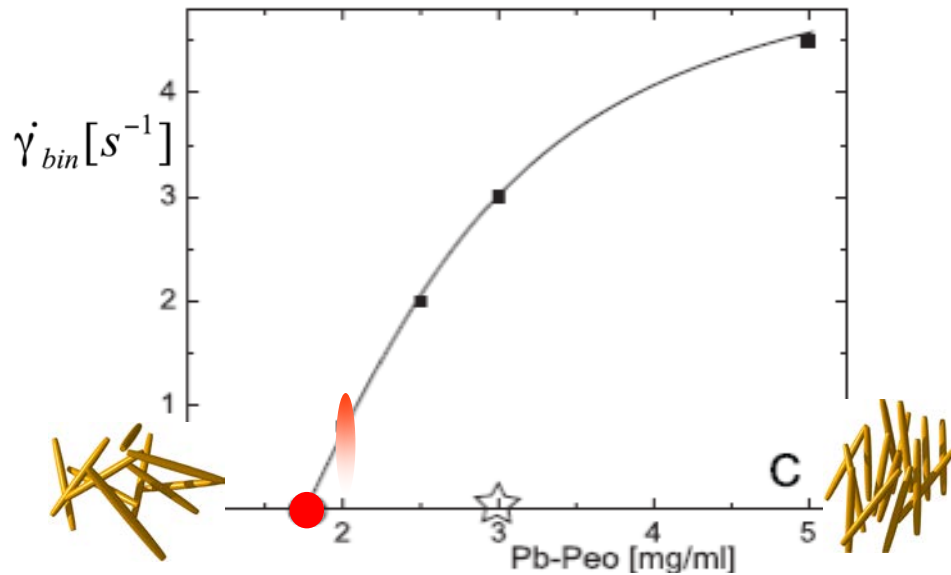
Stretched: IV



Bent: III



Non-equilibrium isotropic-nematic binodal



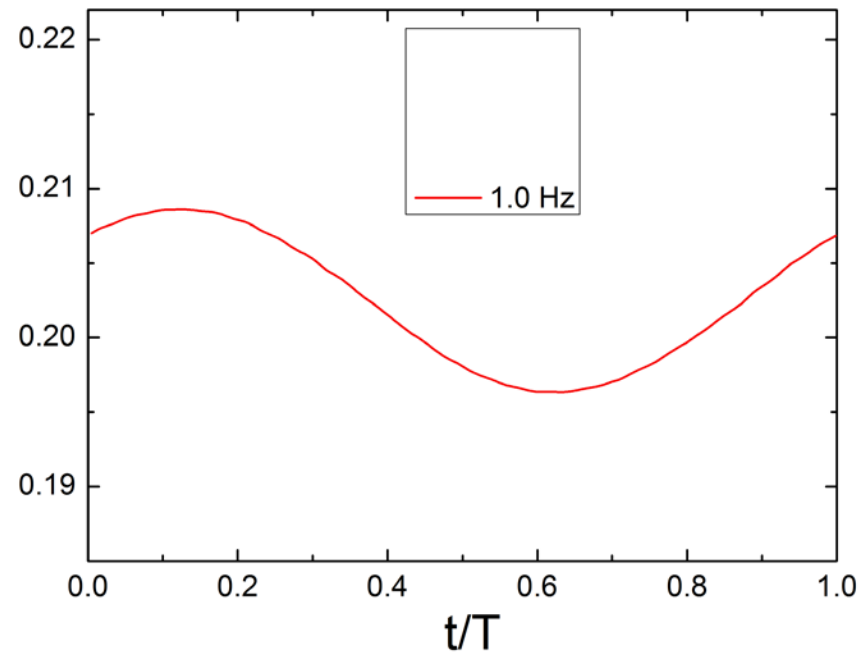
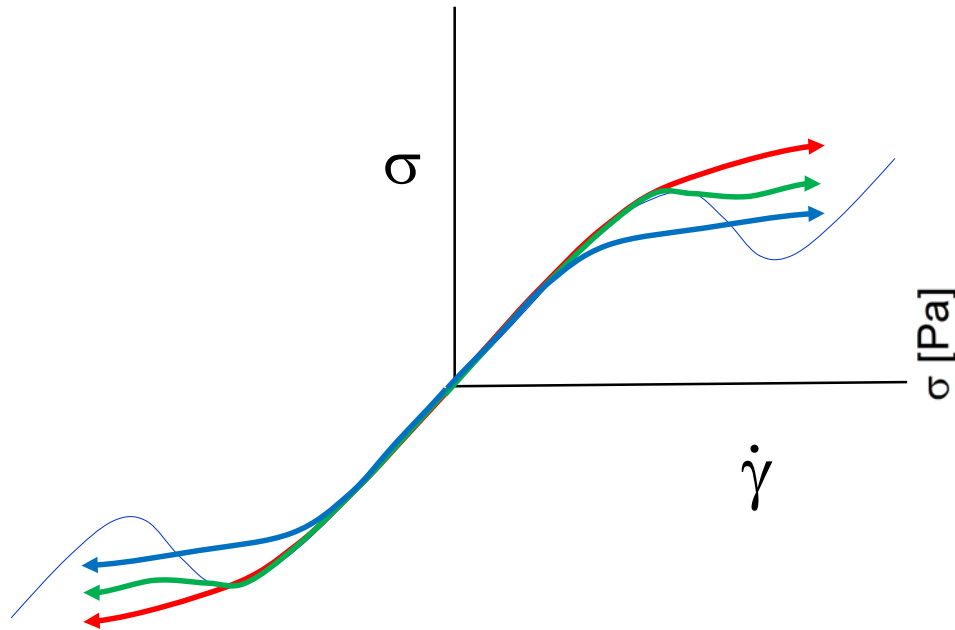


Probe dynamics



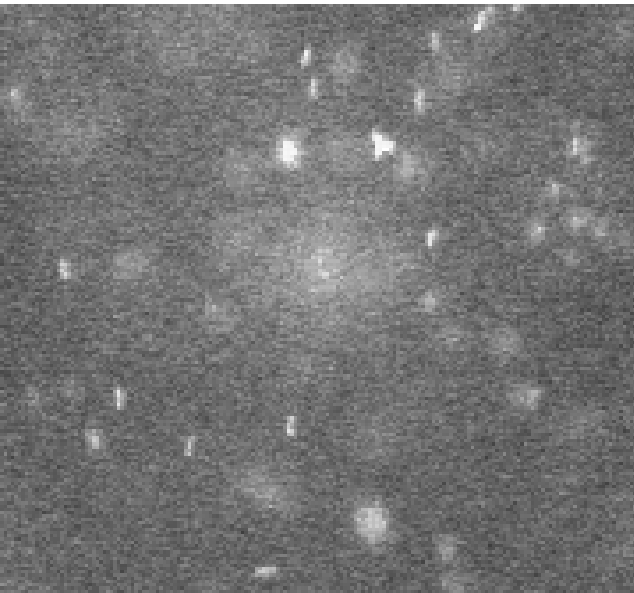
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Probe dynamics with Large Amplitude Oscillatory Shear

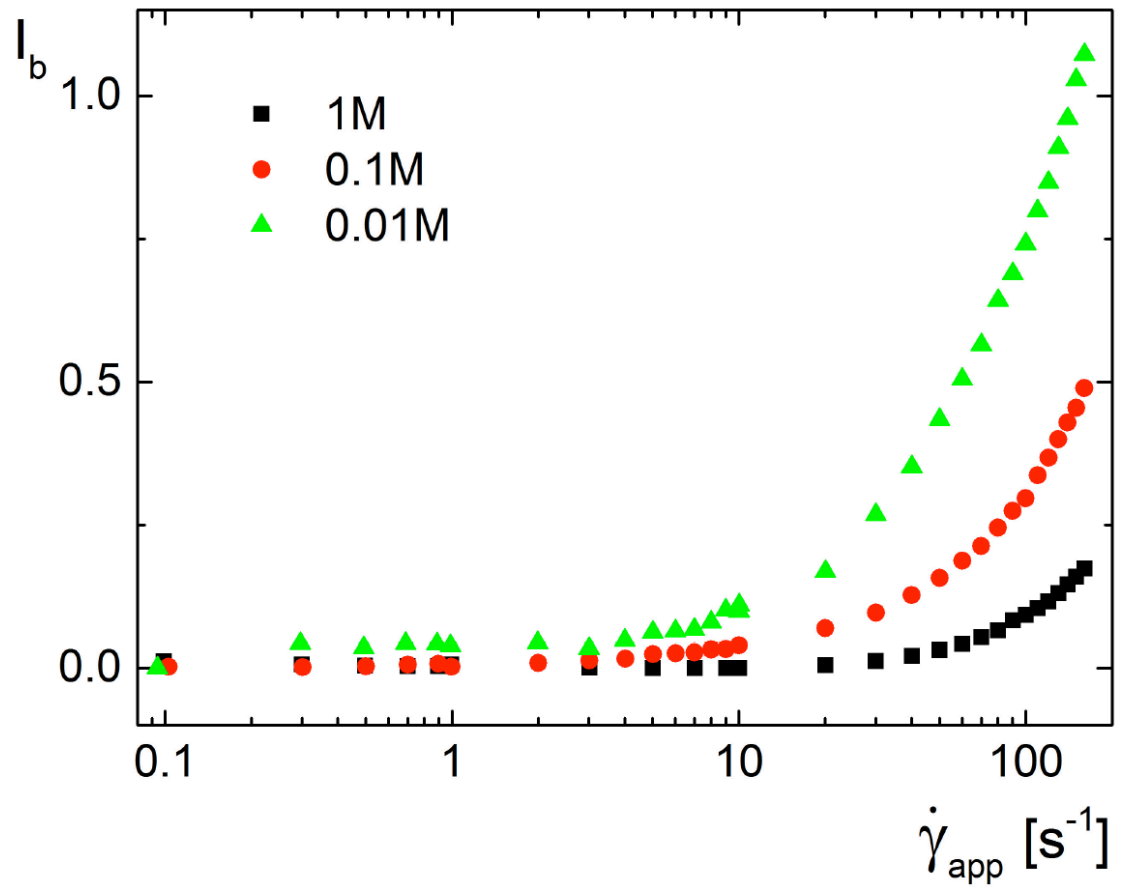
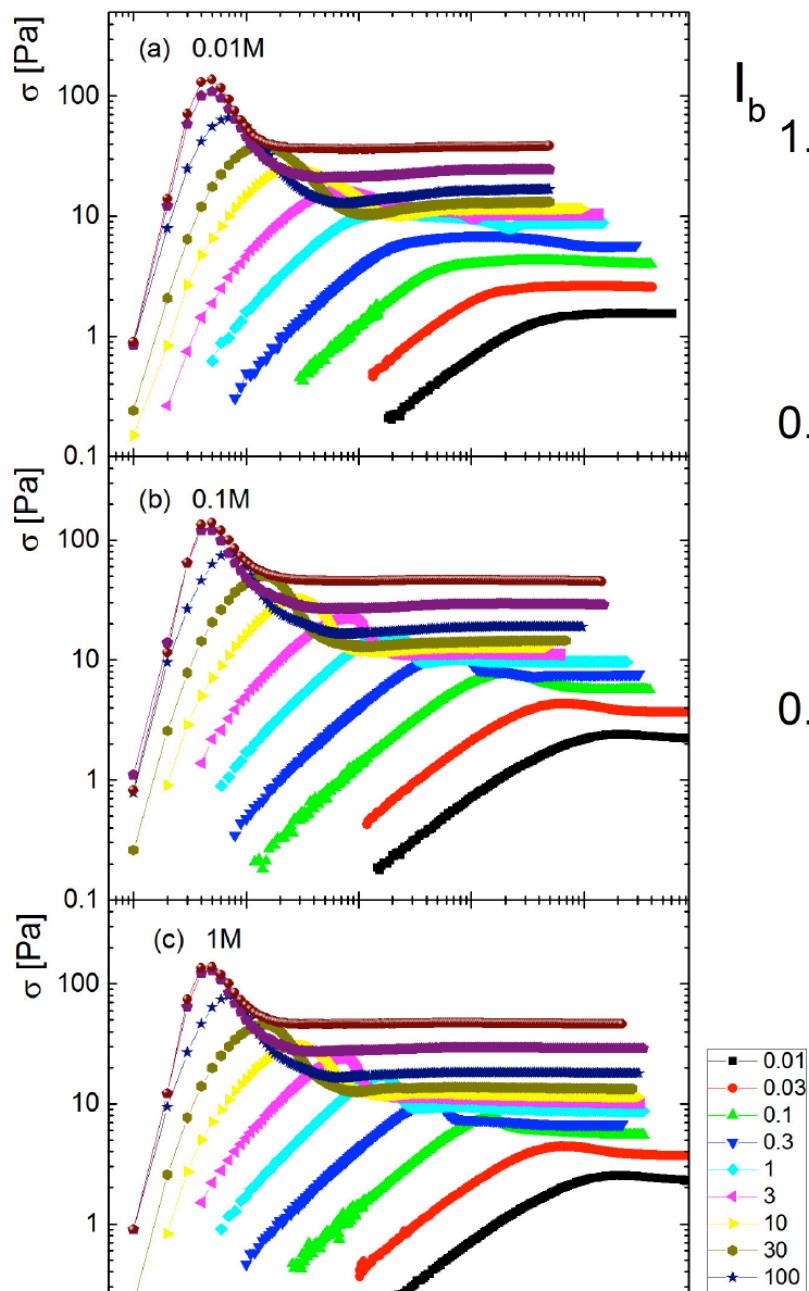


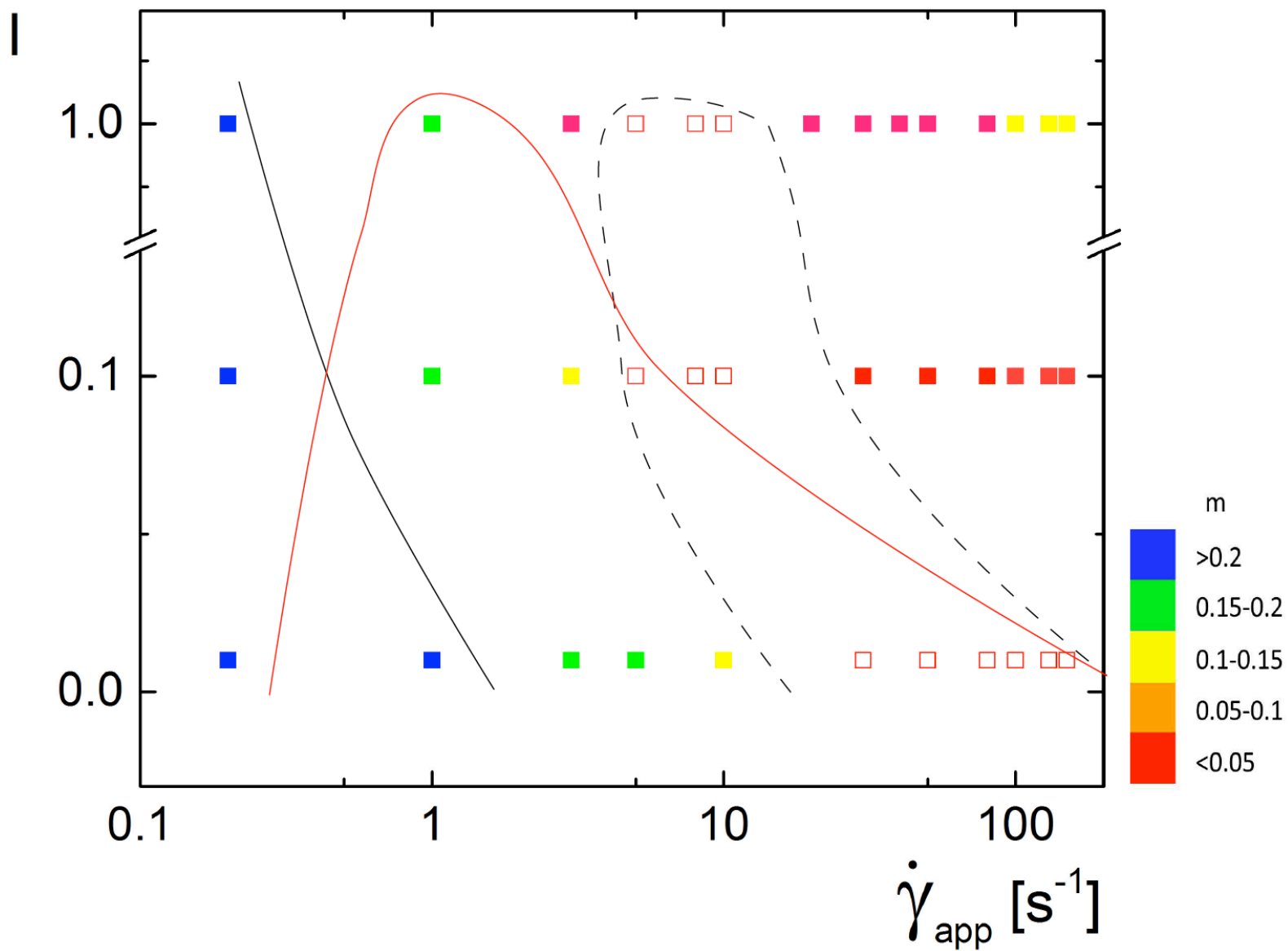
Probe structure with *in situ* scattering methods over broad range of length-scales and time-scales

Complex flow: Complex fluids



start up on DNA at different ionic strengths





We see a reentrant behavior in shear thinning:
Far away from I-N $\rightarrow$ nothing
around I-N but flexible $\rightarrow$ shear banding
towards ideal rod $\rightarrow$ loose it
Ideal $\rightarrow$ nothing

Systems:
high salt DNA/xanthan
low salt DNA/xanthan AND pb-peo
pf1 / F-actin
fd-y21m

Strong shear thinning does not mean that you will get Sms

done:

Open:
effect of salt works different directions, comparing DNA with pf1
How does system sustain orientation after disentanglement?
—> shear rate should now be scaled by local rotation motion and not reptation time.

For the how strong is strong question we have that indeed systems that have $m > 0.3$ don't band
Possible reason could be that γ_{high} and γ_{low} are too close to each other.

Suggestion:

stiff rods go into nematic before reaching really high concentration
but

0.7% xanthan is not that high

0.5 mg/ml DNA also not that high

2 mg/ml for pb-Peo

- We see a link between I-N and shear banding

Is it the charge?

Screening charge aids SB for DNA

screening charge reduces SB pf1 (if at all)

PbPeo is uncharged.

—> no

But: both very long contour length!

xanthin, DNA and pb-peo are all long. F-actin also.

Is it the length or is it polydispersity?

What tuning tells us:

collateral understanding: understand stiff polymers and rods

- we got hold on shear thinning using new theory and ideal r
- We understand shear thinning stiff polymers. No theory!

Hint:

stress overshoot in LAOS when WLMs are overstretch

PHYSICS OF FLUIDS 25, 051703 (2013)

Shear banding in polymer solutions

Michael Cromer,^{1,2} Michael C. Villet,³ Glenn H. Fredrickson,^{1,2,4}
and L. Gary Leal^{1,4,5}

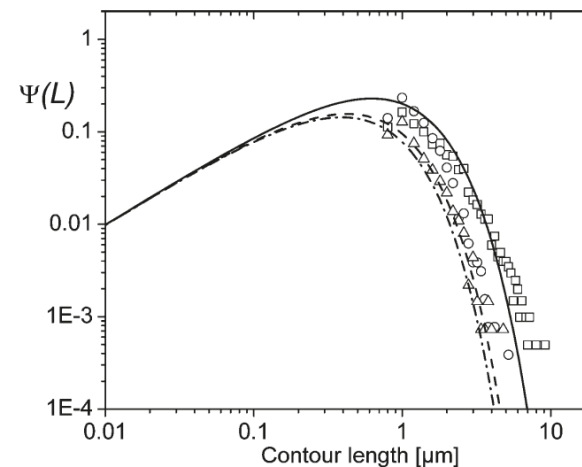


Figure 3. Probability density distribution of contour lengths for different molar fractions of DMF (solid line, square for $f = 0$; dashed line, circle for $f = 0.025$; dotted line, triangle for $f = 0.06$). The curves correspond to an exponential distribution with the parameters determined by DLS. The symbols are the data obtained from microscopy.

Merchant and Rill

DNA Phase Transitions

TABLE 1 Lengths, length distributions, and critical concentrations of DNA samples

DNA (bp)	Length* (nm)	Range*		SD [§] (bp)	$M_w/M_n^¶$	$C_i^ $ (mg/ml)
		(bp)	(nm)			
147	50	135–162	46–55	± 12	1.07	135
170	58	131–210	44–71	± 32	1.07	122
336	114	311–355	105–120	± 19	1.01	48
570	190	257–1140	87–386	NA	1.23	23
1450	490	766–2400	262–804	± 690	1.14	13
8000	2700	4k–>23k	1352–7774	NA	ND	13