Mitglied der Helmholtz-Gemeinschaft

JÜLICH FORSCHUNGSZENTRUM

KU LEUVEN

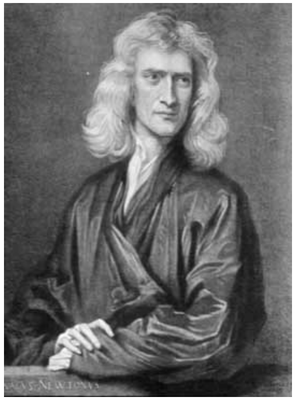
Probing microstructural origin of complex flow behavior

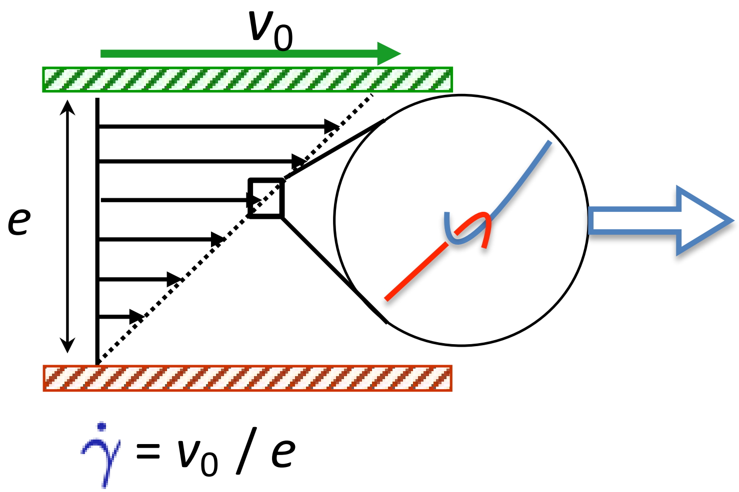
Pavlik Lettinga

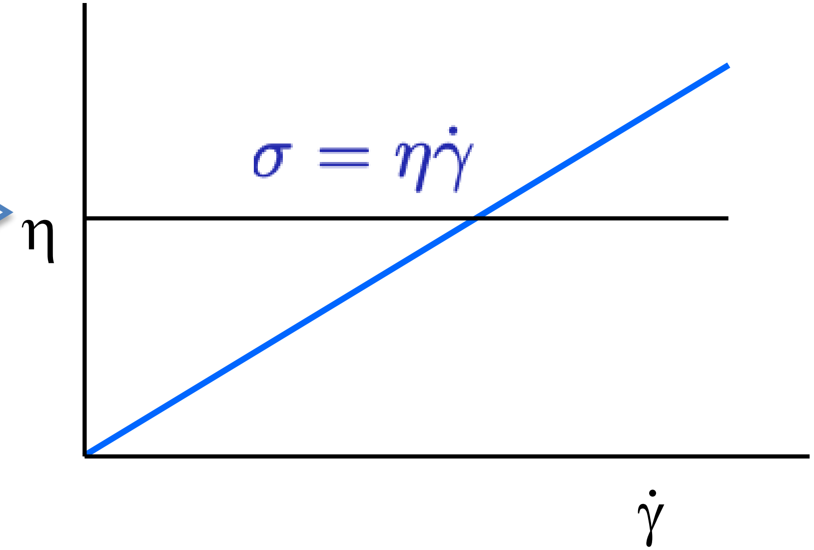
UCSB, 2nd February 2018

Complex flow: high inertia

Ideal Newtonian fluids



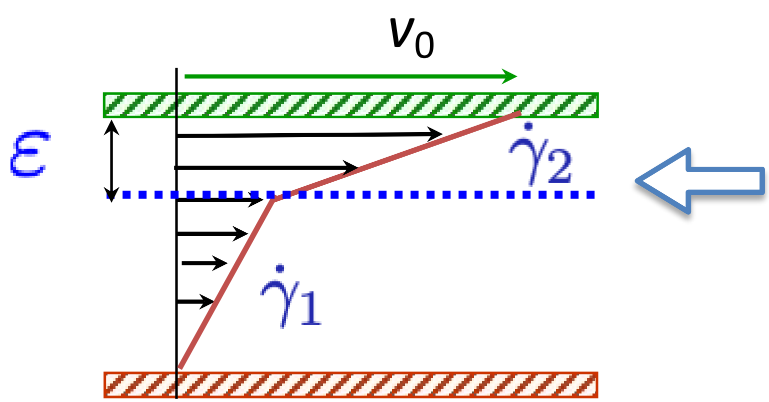


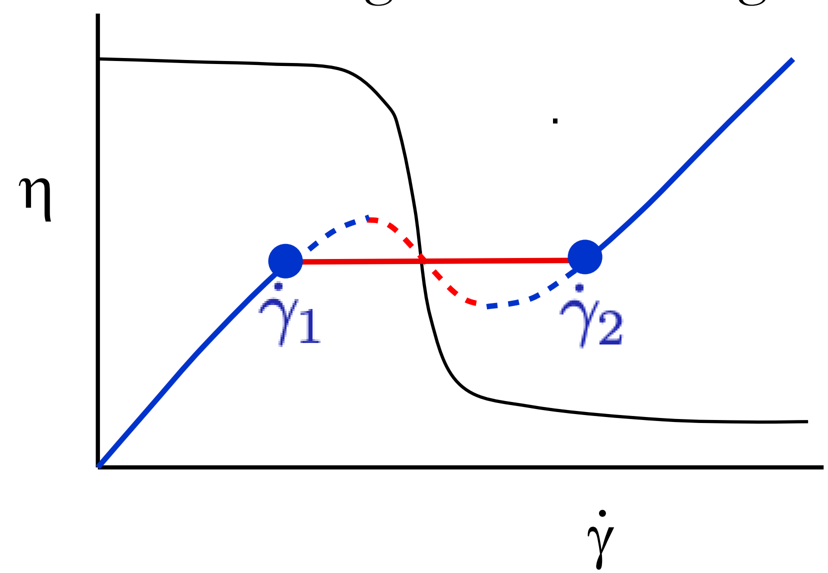


Non-linear Newton: shear thinning fluids

Flow instabilities: shear banding

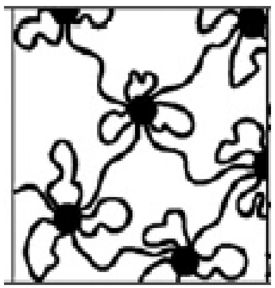
strong shear-thinning





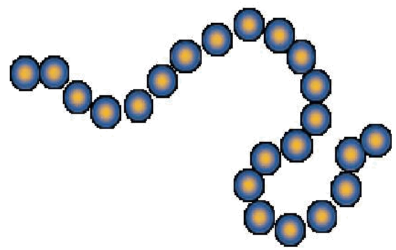
Possible shear thinners

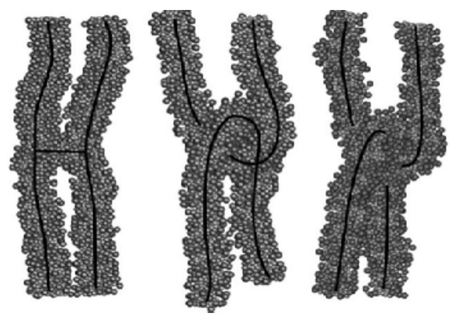
Living gels:



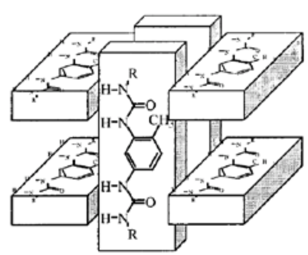
Sprakel et al, Soft Matter, **4**, (2008) 1696

Living polymers:



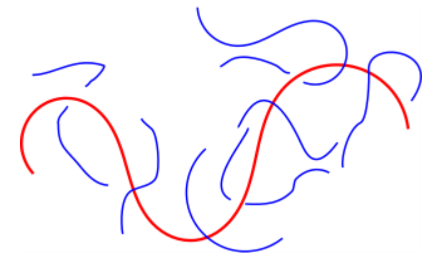


M. P. Lettinga and S. Manneville, *Phys. Rev. Lett.*, **103** 2009

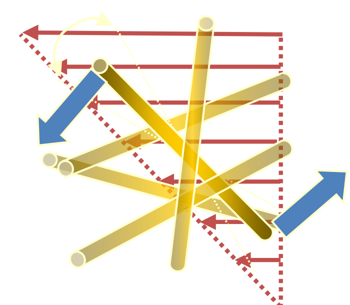


Van der Gucht et al Phys. Rev. Lett., **97**, (2006) 108301

Stiff Polymers:



Rods:



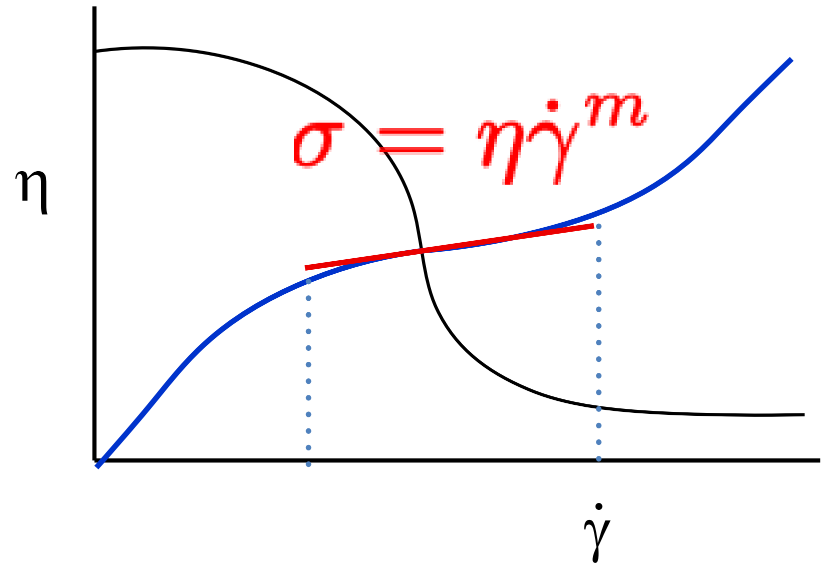
Main questions:

Molecular origin of shear band formation:

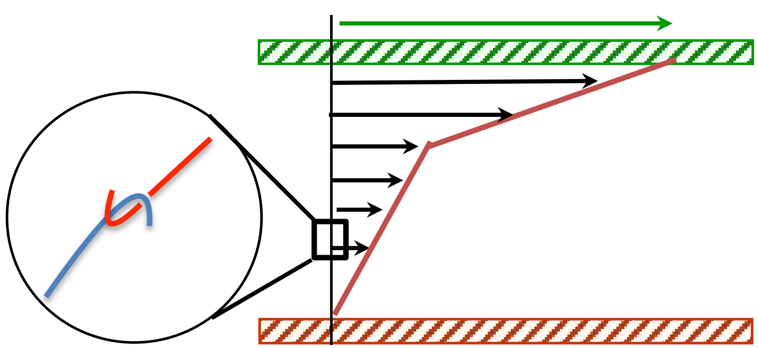
Can polymer shear band?

Can rods shear band?

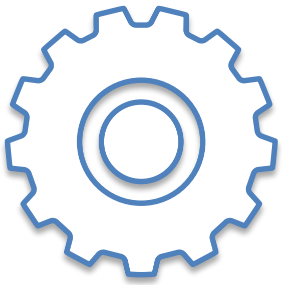
- How strong is strong?

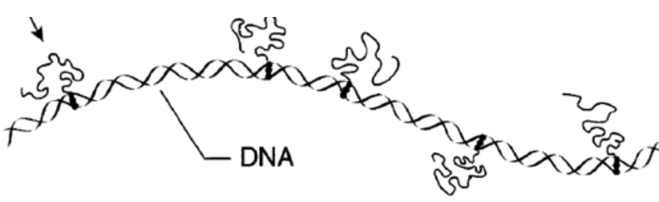


- Always shear banding for given *m*, or is it system dependent?



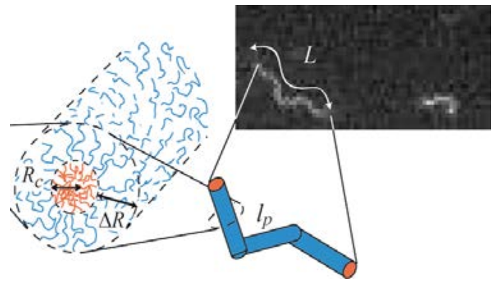
- Can we tune shear band formation?



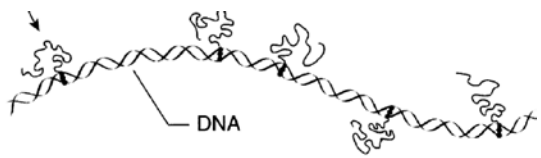


Contents: Tune stiffness, length and interaction

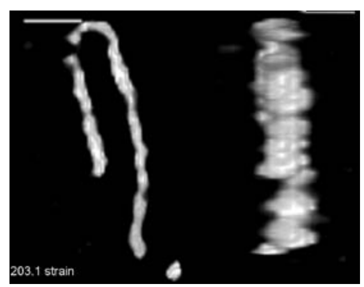
- **Pb-Peo worm-like micelles:**



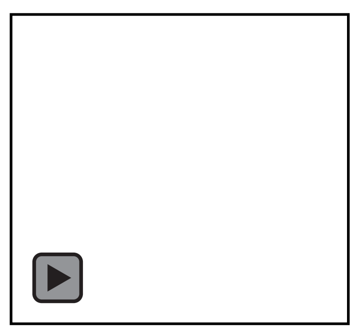
- **DNA**



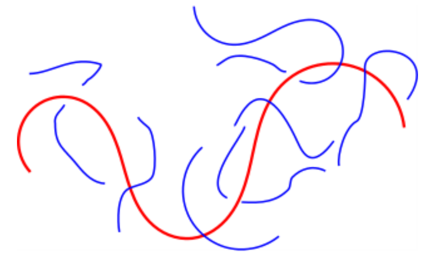
- **F-actin:**



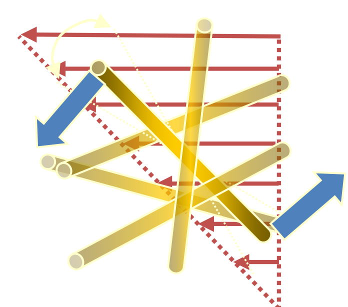
- **Filamentous viruses:**



Stiff Polymers:



Rods:



Smoluchowski theory for hard rods

Gives equation of motion for the orientational tensor **S**:

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

⇒ Link with macroscopic stress

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

Collective slowing down: Dynamic definition spinodal point

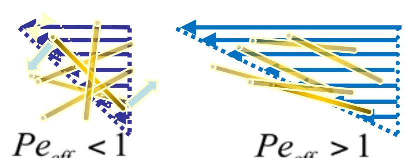
⇒ $$\delta S(t) = \exp(-6D_R^{eff}t)\delta S(t=0)$$

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

⟶ $$\Omega_{eff} = \omega/D_R^{eff}$$

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

D_R^0 : rotational at *infinite* dilution

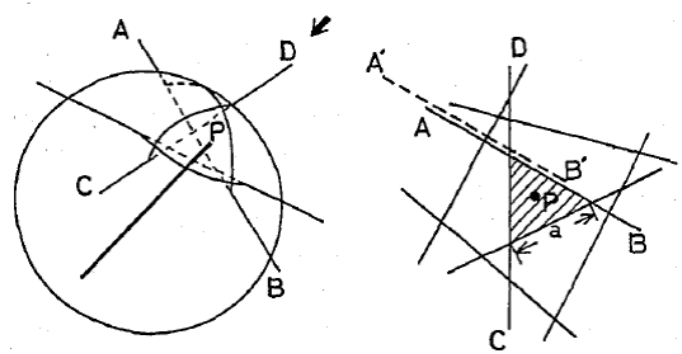


Dhont and Briels, *Coll. Surf A*, **213** *2003*

Topological slowing down:

Dois phenomenological rotational diffusion coefficient

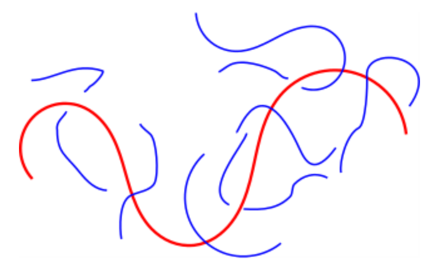
$$D_r = cD_r^0(\nu L^3)^{-2}$$



Monotonic constitutive theory for polymeric liquids

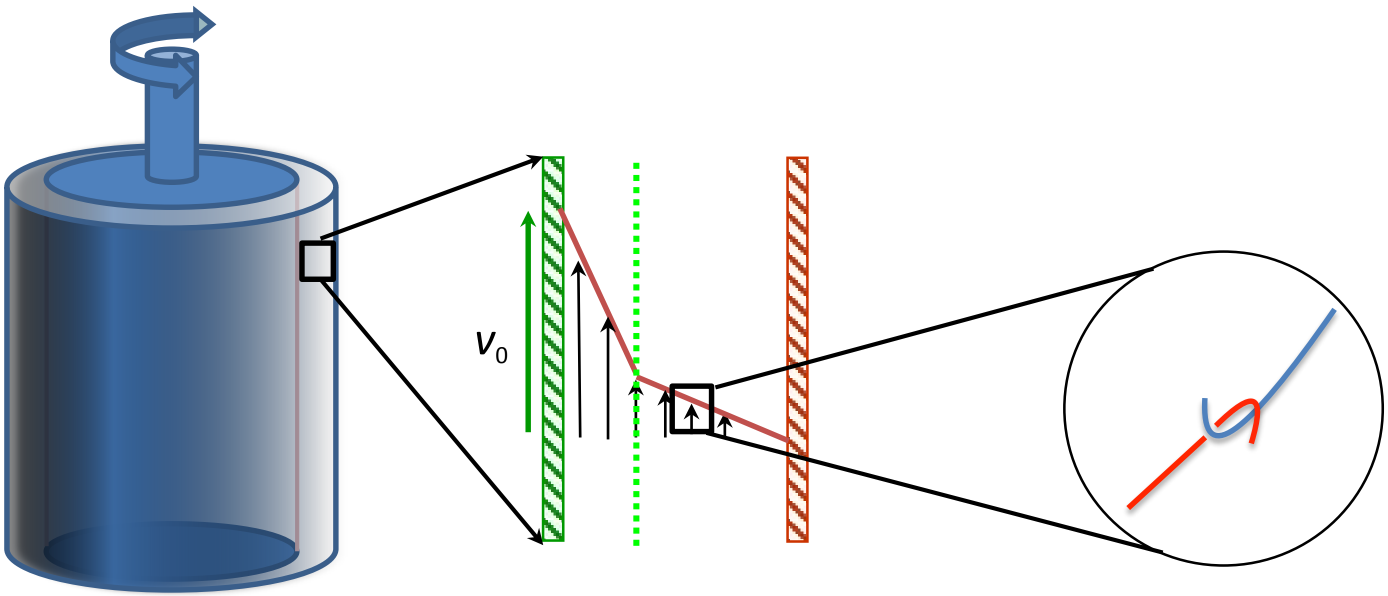
Competition of shear flow with Rouse and reputation time

non-monotonic behavior due to concentration coupling



Cromer et al, *Phys. Fluids, 2013*

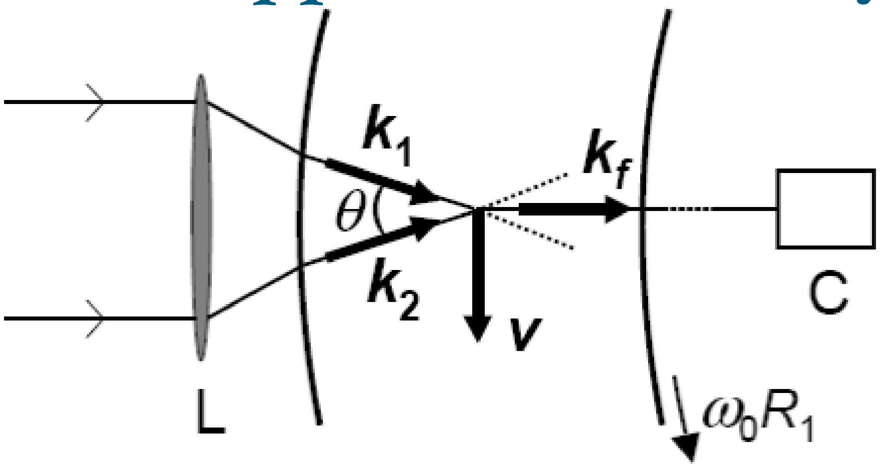
Experimental input needed:

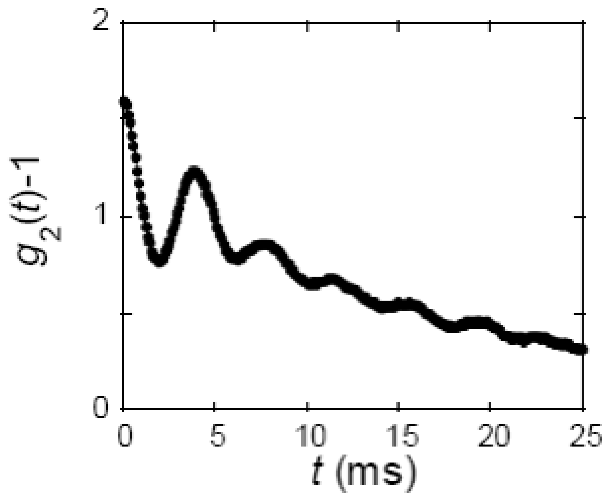


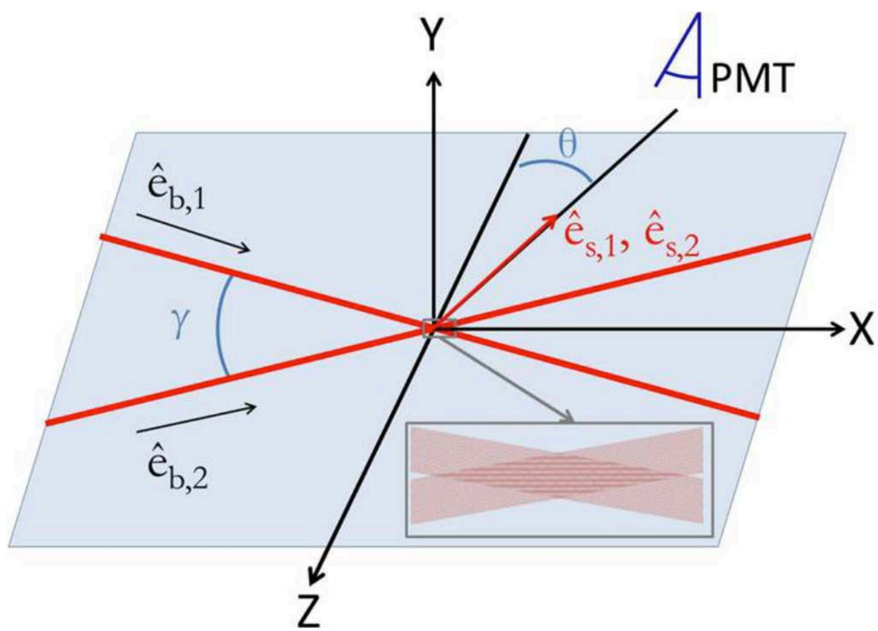
Information needed:

- 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



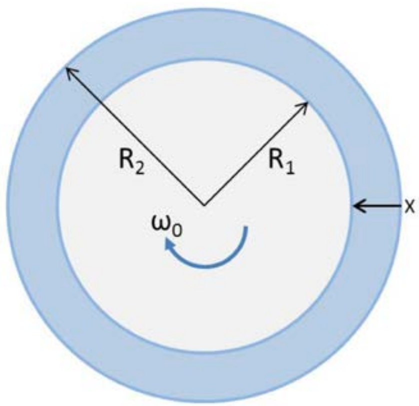


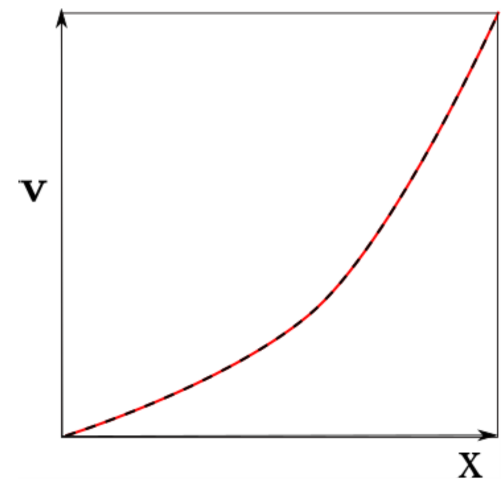


Analyse velocity profiles

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

Account for curvature cell:

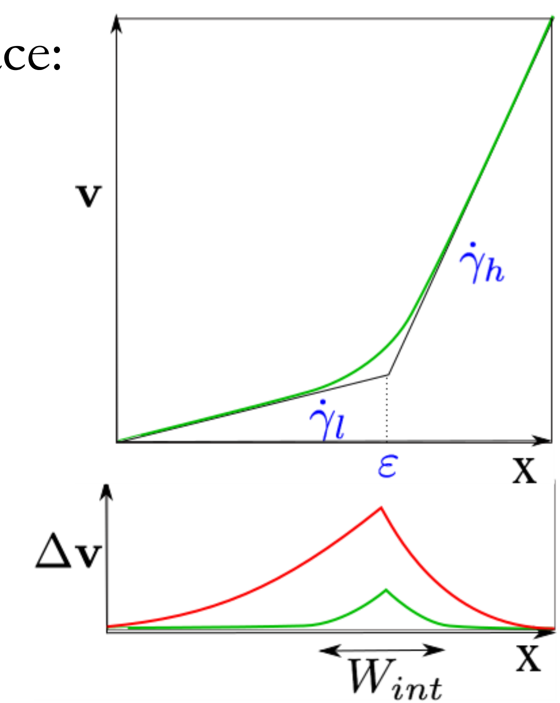




m

compare with m_{fc}

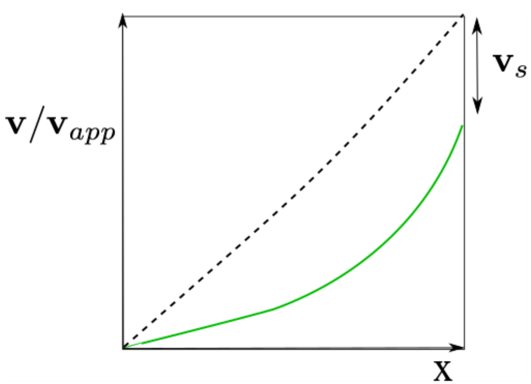
Shear banding with interface:



$\dot{\gamma}_h \; \dot{\gamma}_l \; \varepsilon$

W_{int}

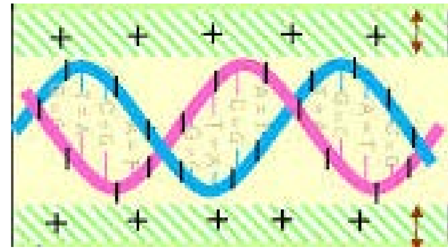
Wall slip:

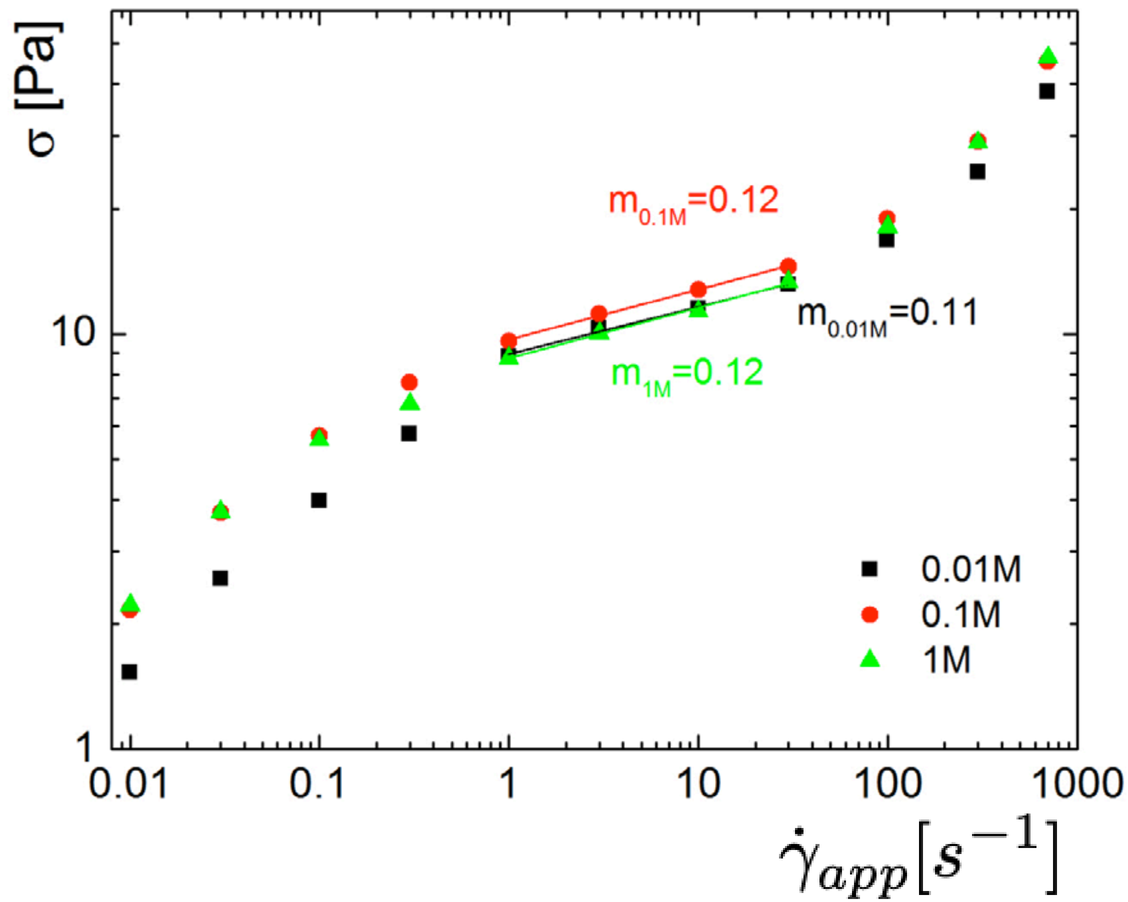


DNA, the tuneable polymer part I

$<L>\approx 20\ \mu m$, $d=7$ nm, $l_p=50$ nm

Tune repulsion by adding salt:





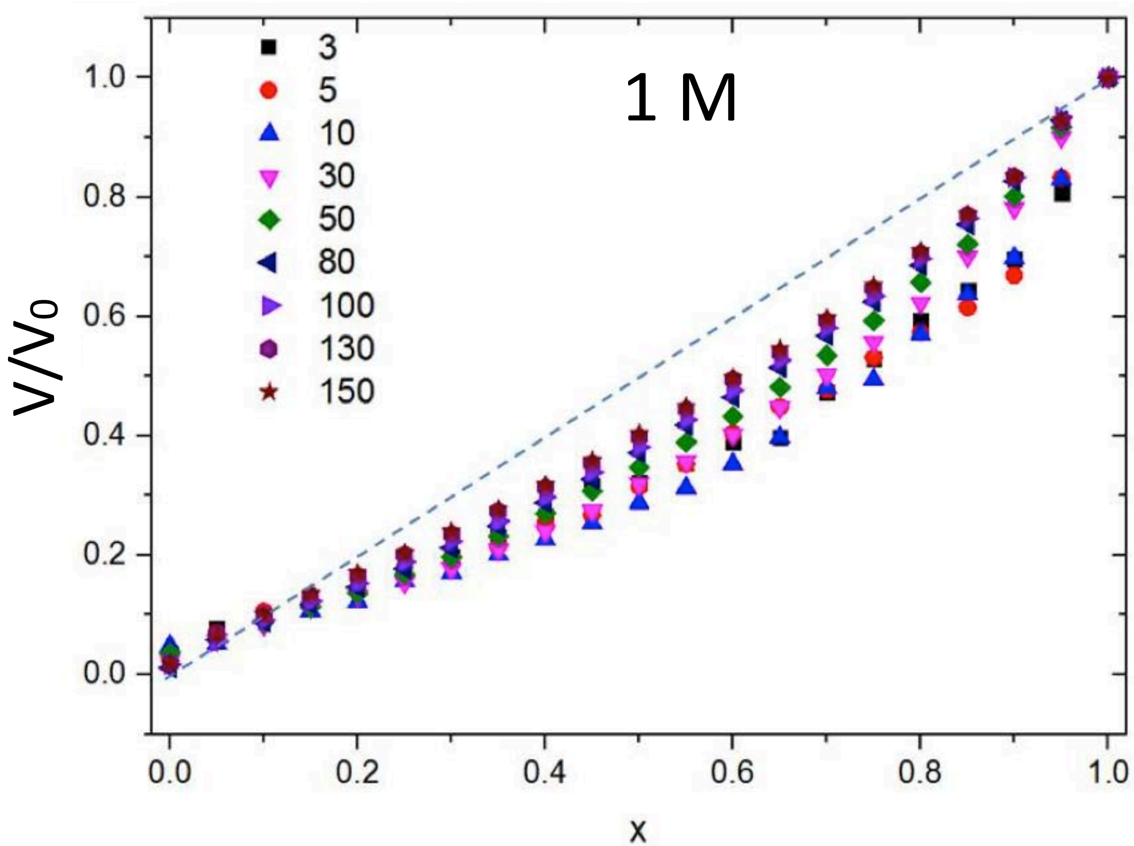
concentration: 0.7 mg/ml

Tuning by addition of salt

0.01 M

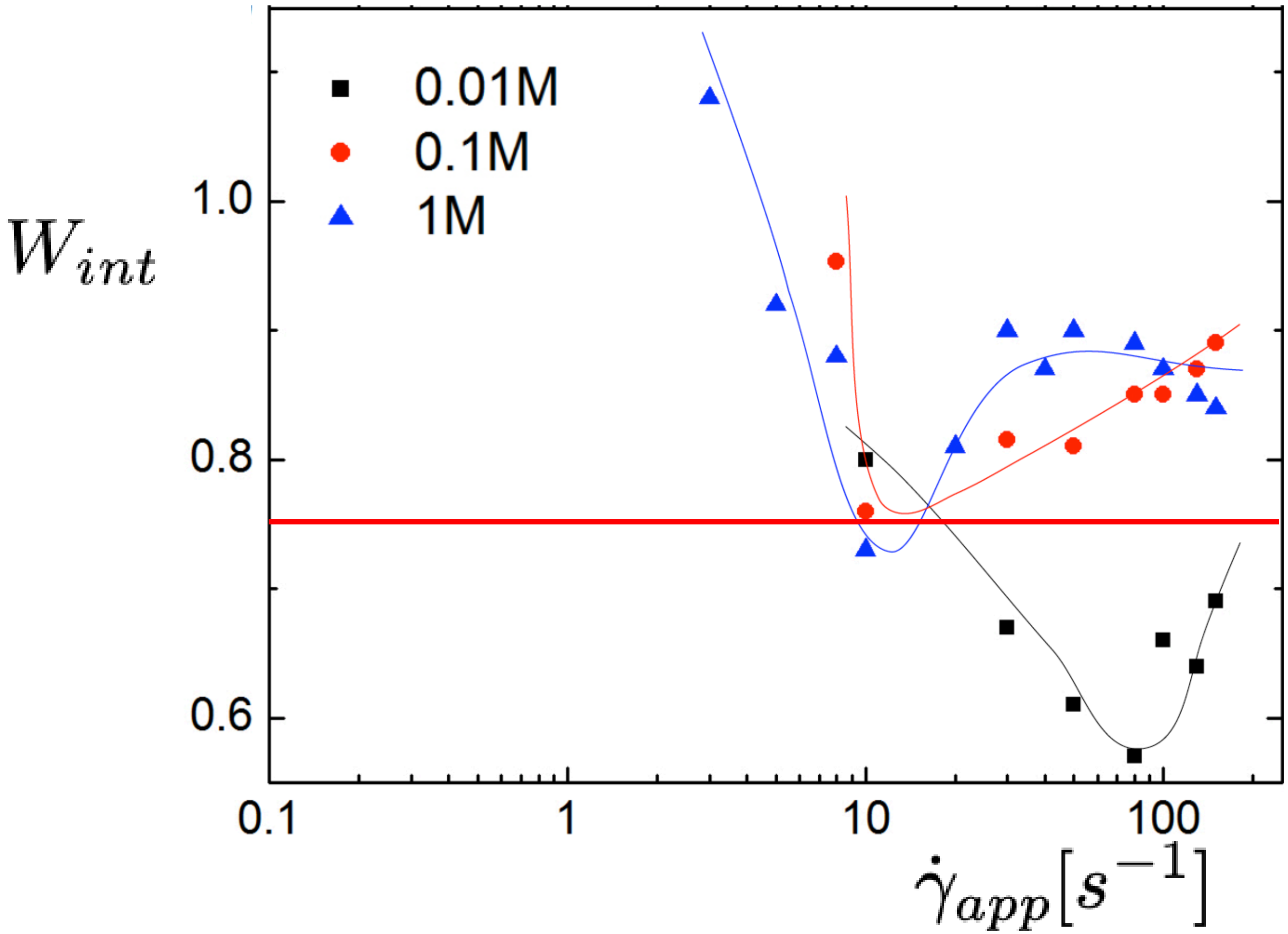
0.1 M

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

Some conclusions I

- How strong is strong?

- Always shear banding for given m, or is it system dependent? Depends on system

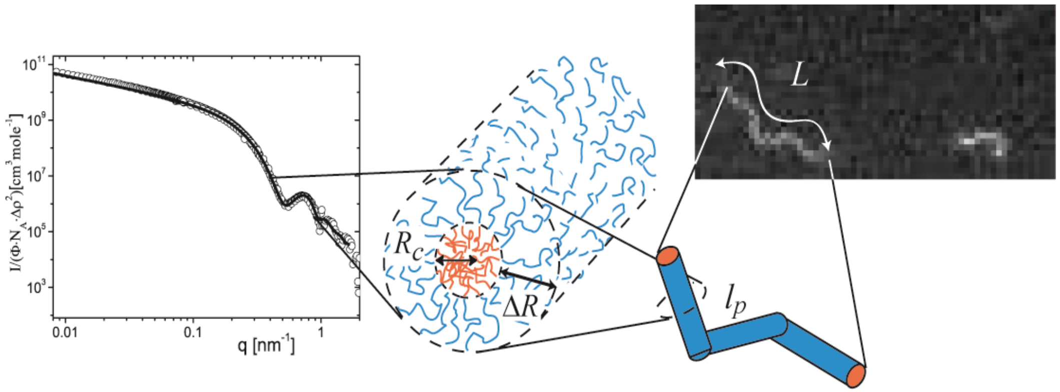
- Suppression shear banding via widening interface,
  BUT: broad shear banding can exist with broad interface

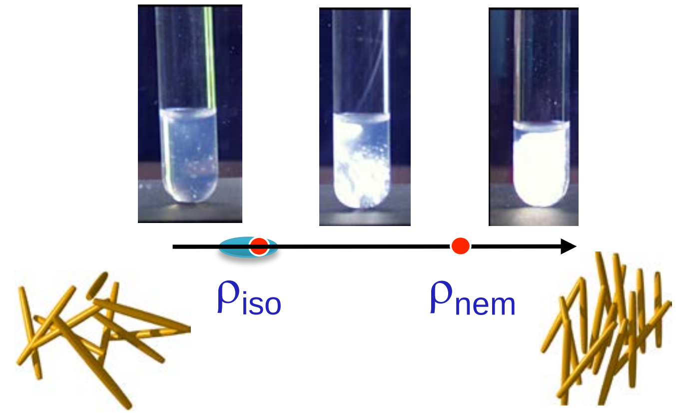
- Can we tune shear band formation? Yes, a bit

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

- New question: Is it charge or stiffness?

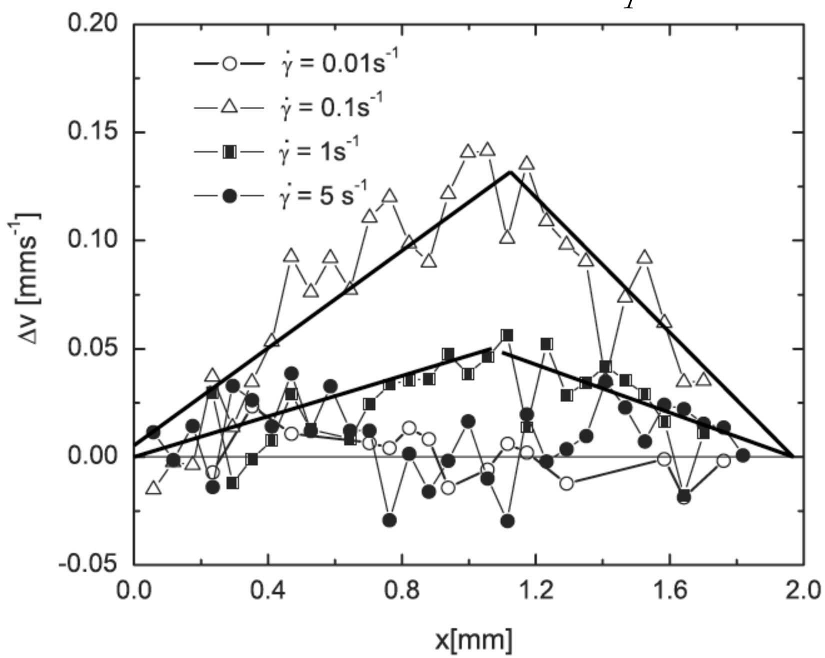
Neutral Rods close to I-N: Giant PB-PEO wormlike micelles

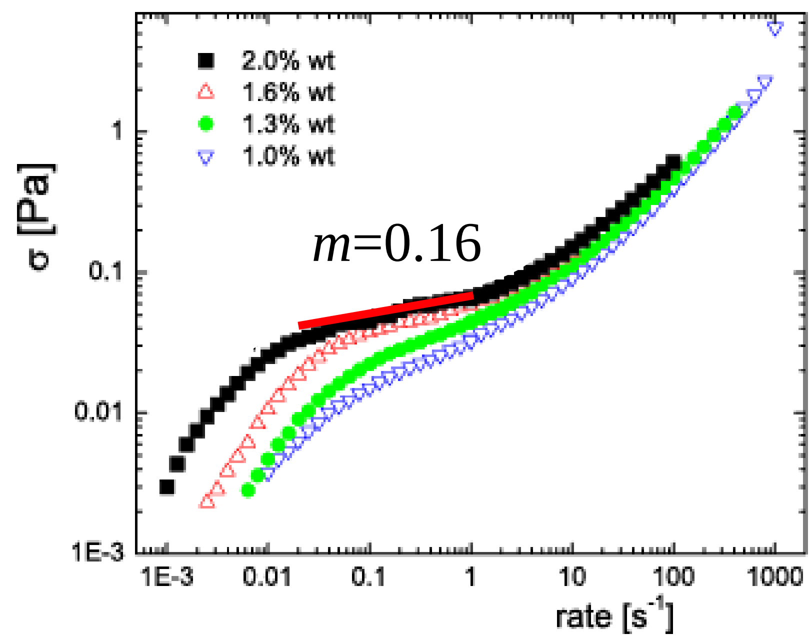




$\langle L \rangle$=800 nm, d=28 nm, l_p=500 nm

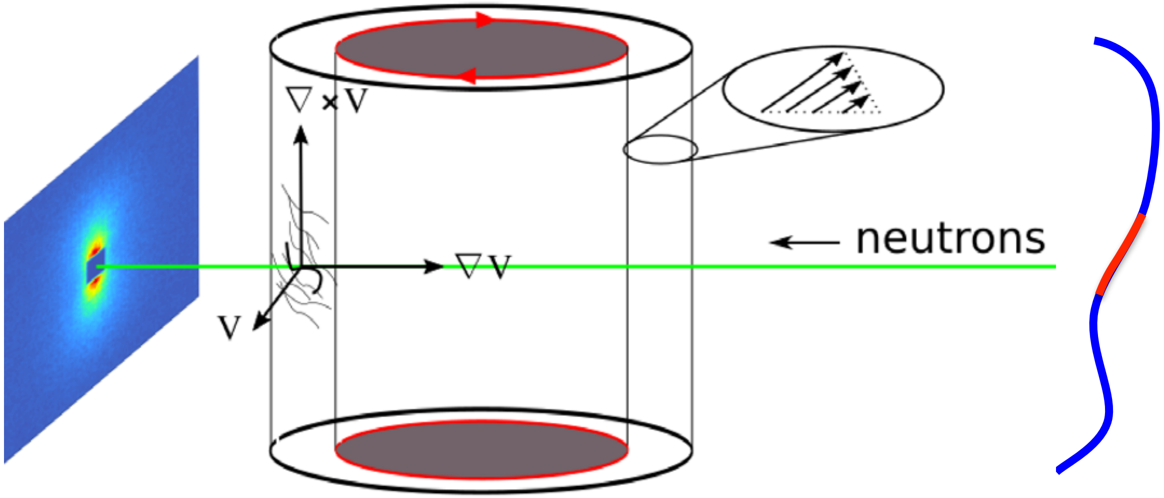
Y.-Y Won et al. , *Science*, **283** 1999

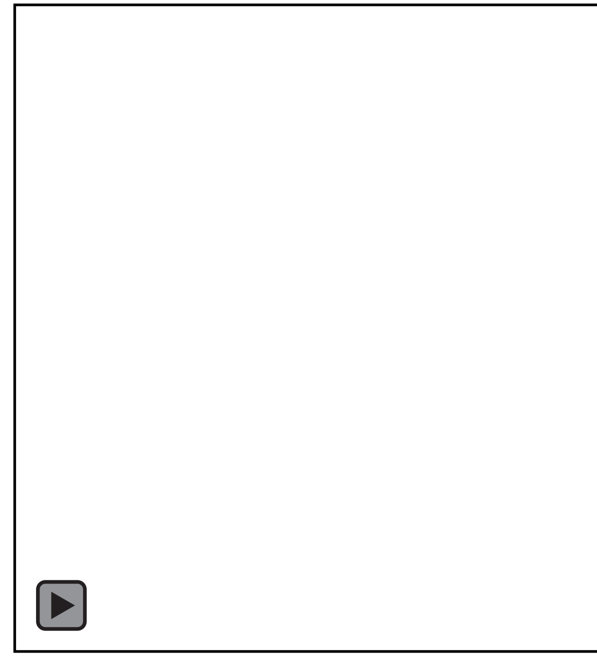




Lonetti, Kohlbrecher, Lettinga, *J. Phys. Cond. Matt.*, 2008

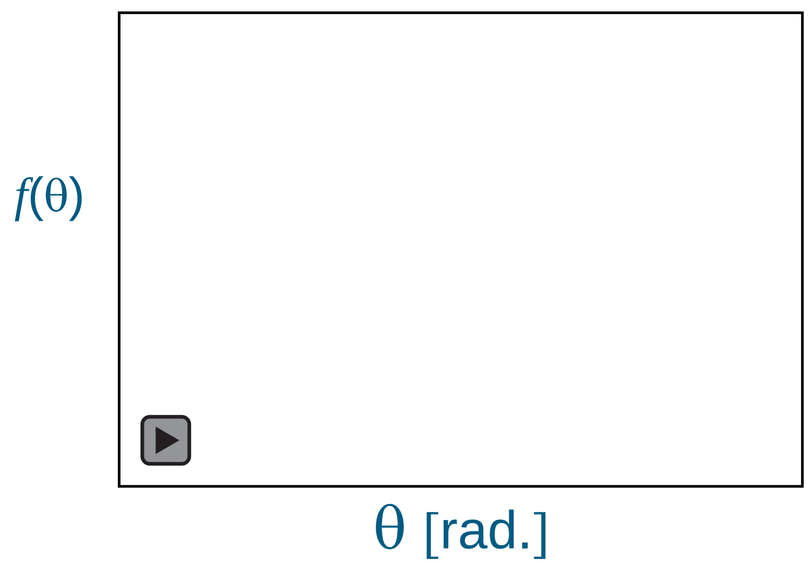
t-SANS to probe segment ordering dynamics





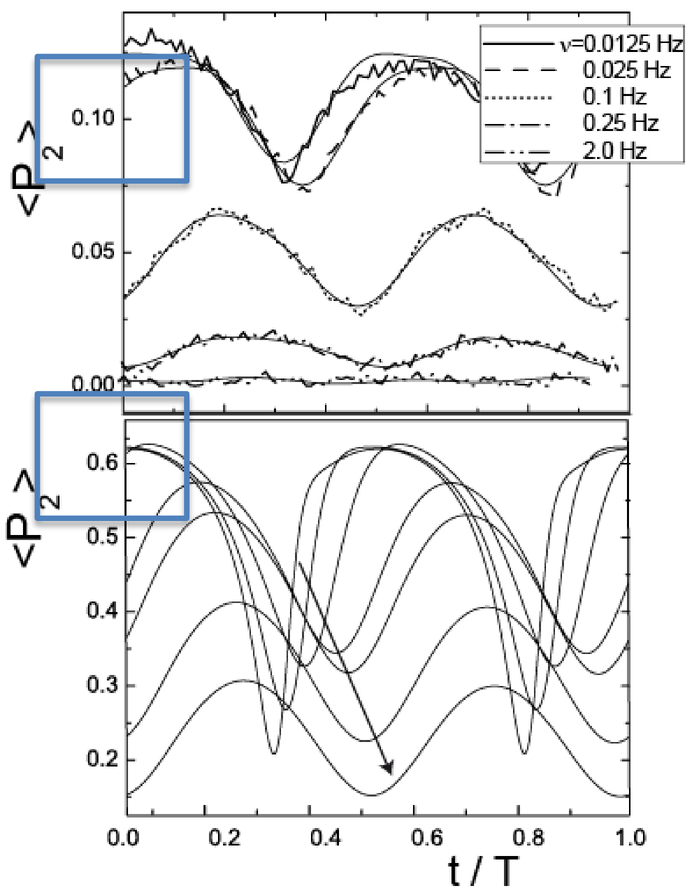
$$\langle P_2(t)\rangle = \frac{\int d\vartheta \sin(\vartheta)\, f(\vartheta) P_2(\vartheta))}{\int d\vartheta \sin(\vartheta)\, f(\vartheta)}$$

Orientational distribution function

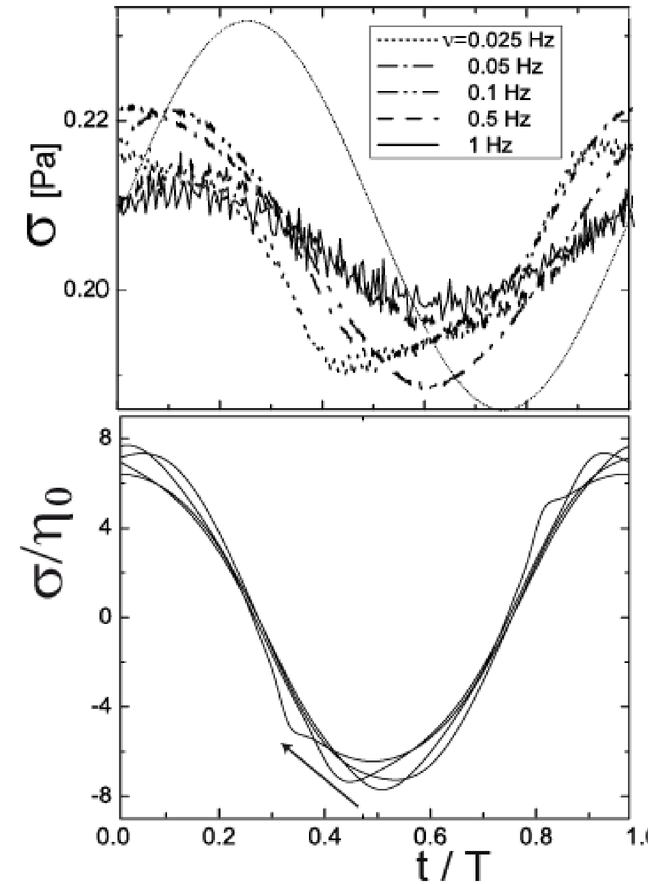


$$I(t_i,\vec{q}) = \sum_{n}^{Ncycle} I(t_i + n\Delta t, \vec{q}\ )$$

Micro & Macro



$$\Sigma_D(\mathbf{S})$$



Scaling frequency:

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

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

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

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

Some conclusions II

- Is it charge or stiffness? STIFFNESS

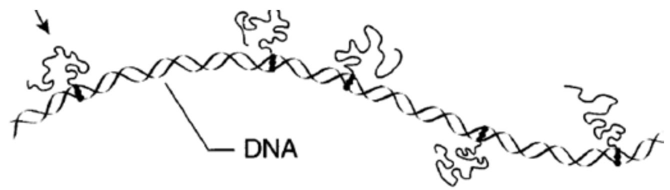
Suggestion:
Stiff systems don't collapse once disentangled

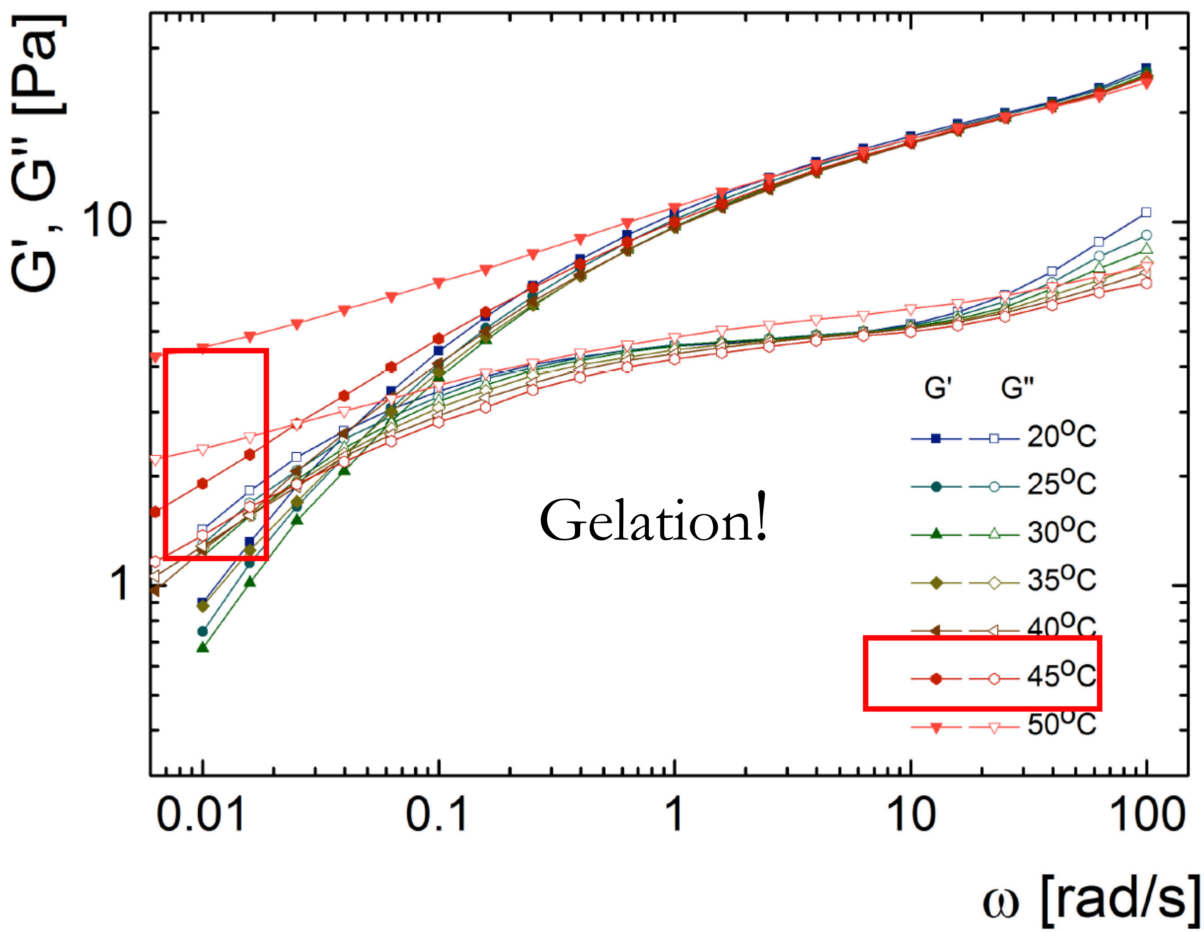
- New question: Can we force collapse?
- New question: Can we have a better look?

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

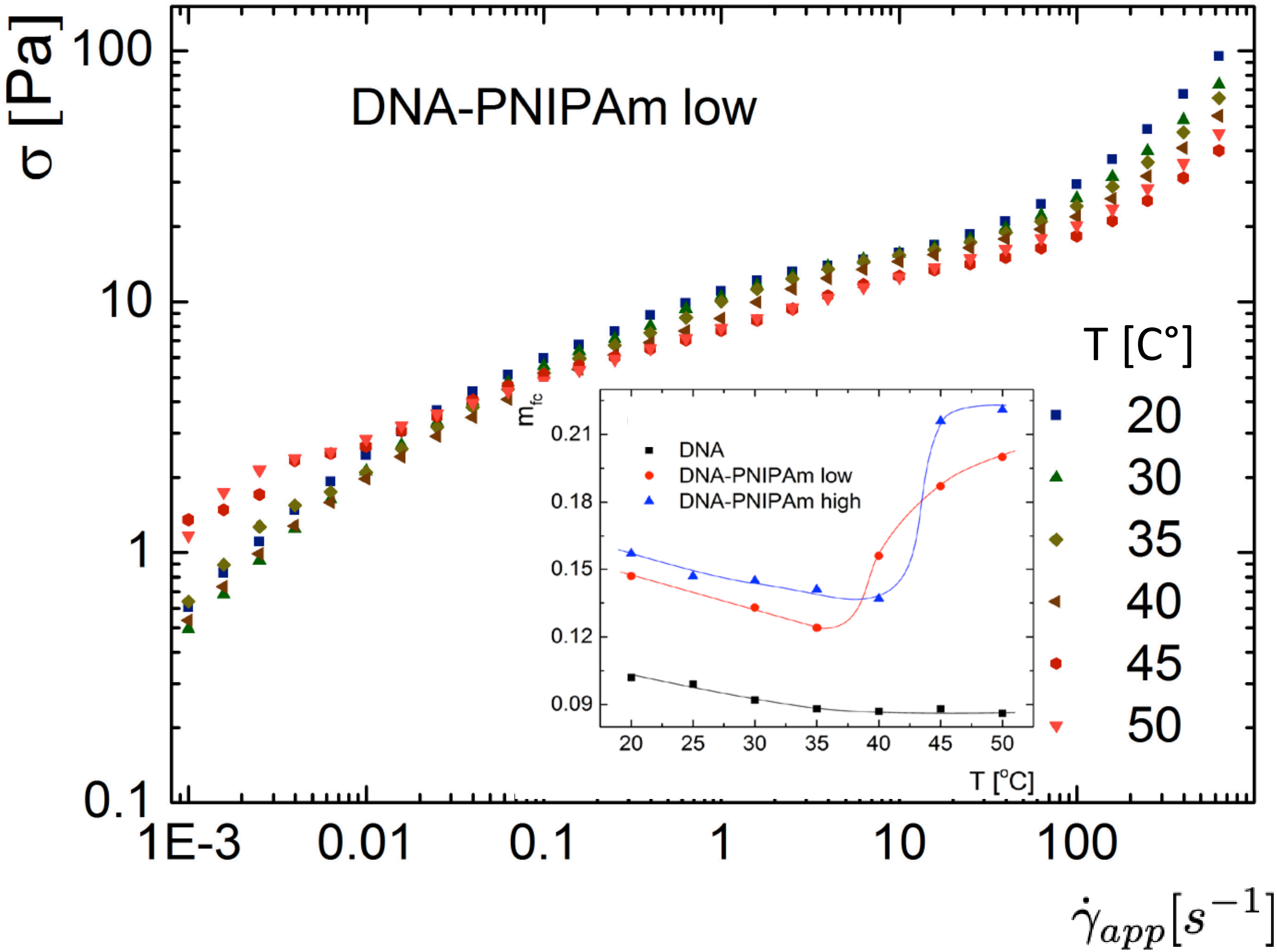
DNA, the tuneable polymer part II

Tune attraction by adding T-sensitive brush (PNIPAm)





Tuning by increasing attraction



Tuning by increasing attraction

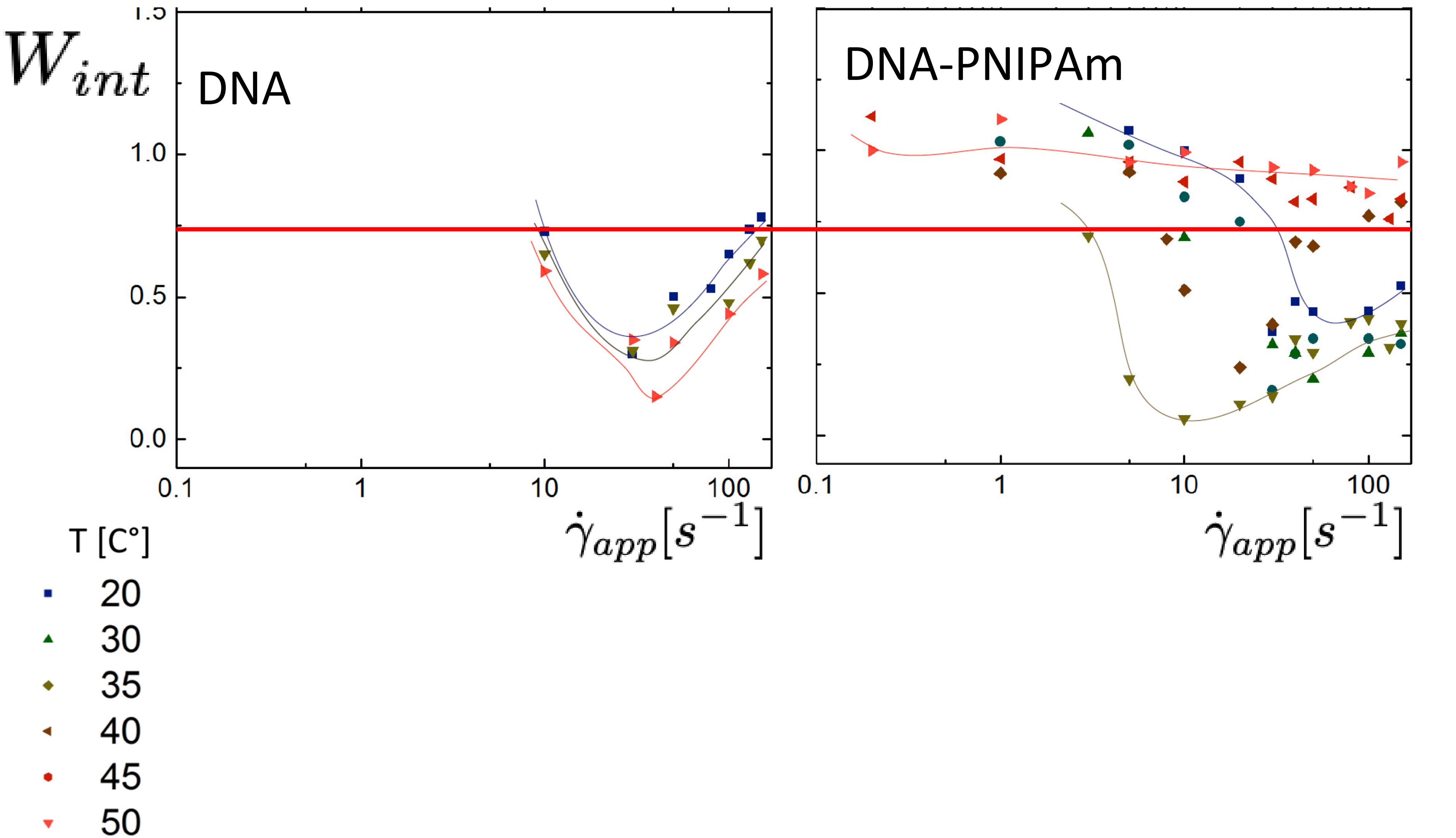
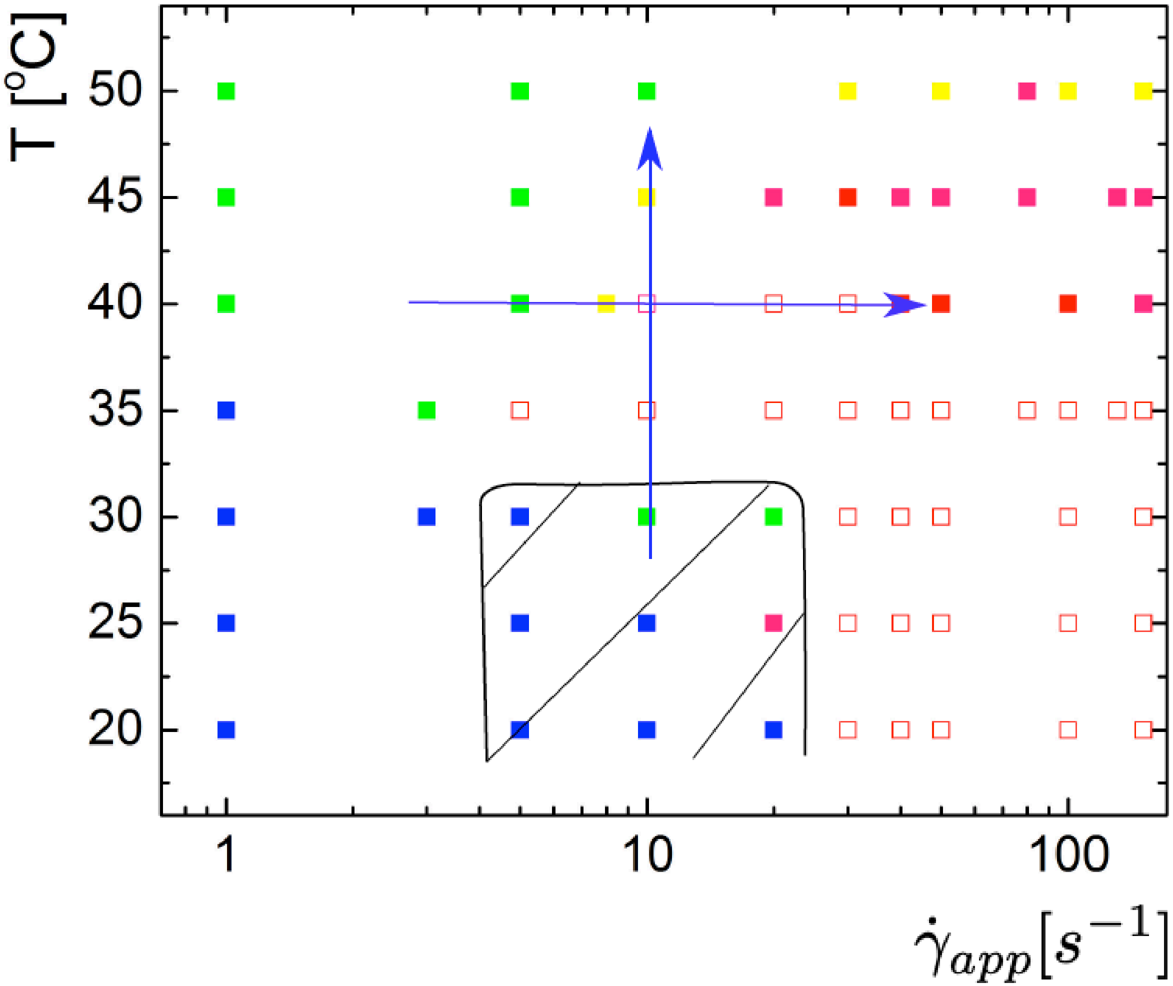


Diagram of states



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

Some conclusions III

- 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?

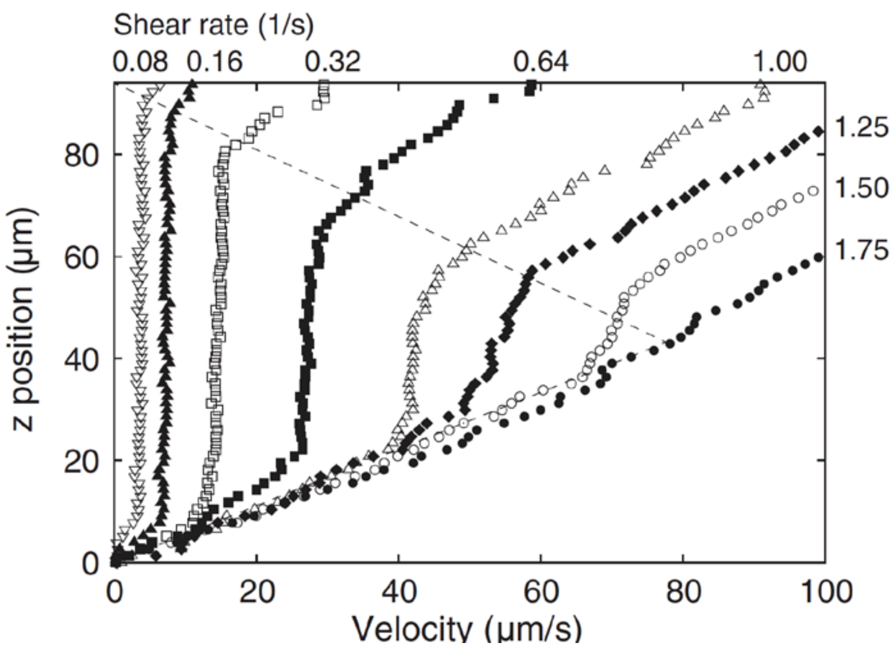
F-actin: stiffer and longer

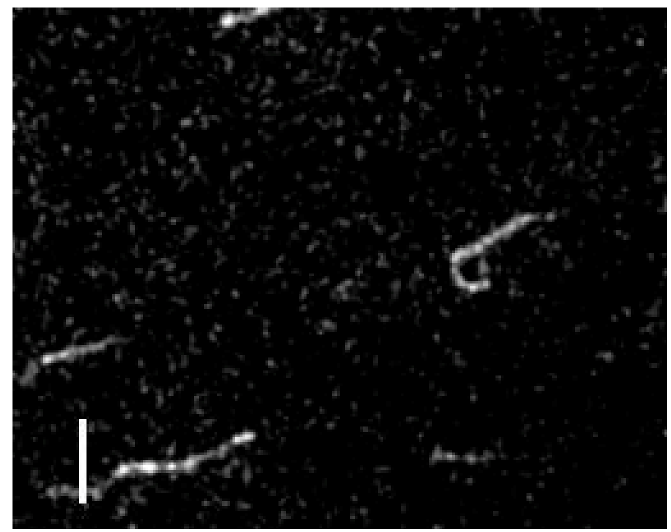
$<L> \approx 20\ \mu m$, $d = 7$ nm, $l_p = 17\ \mu m$

Shear banding has been identified by

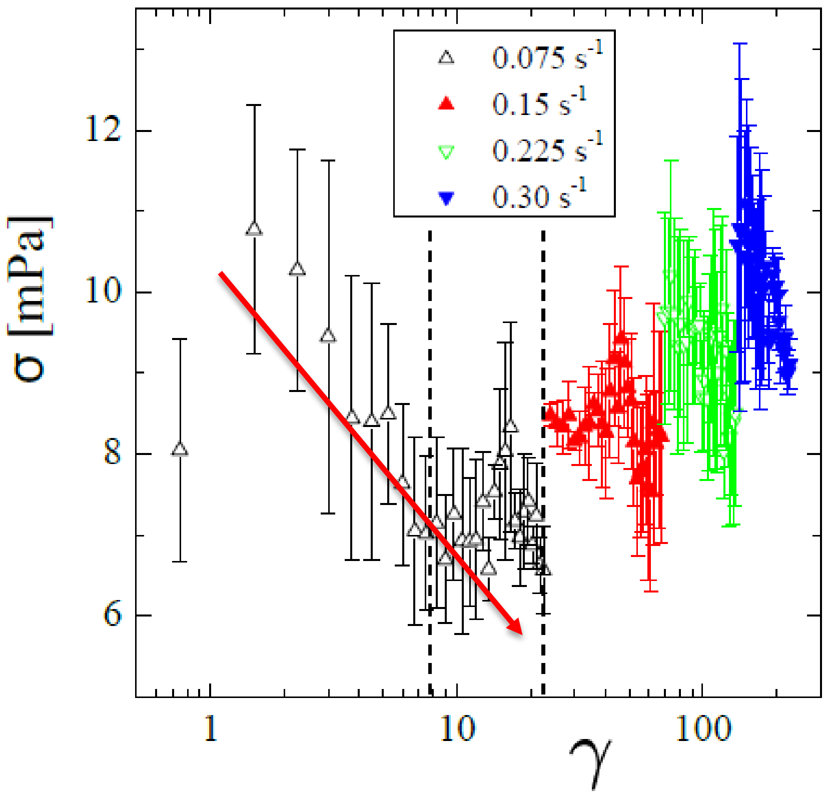
Kunita et al, PRL 109, 248303 (2012)

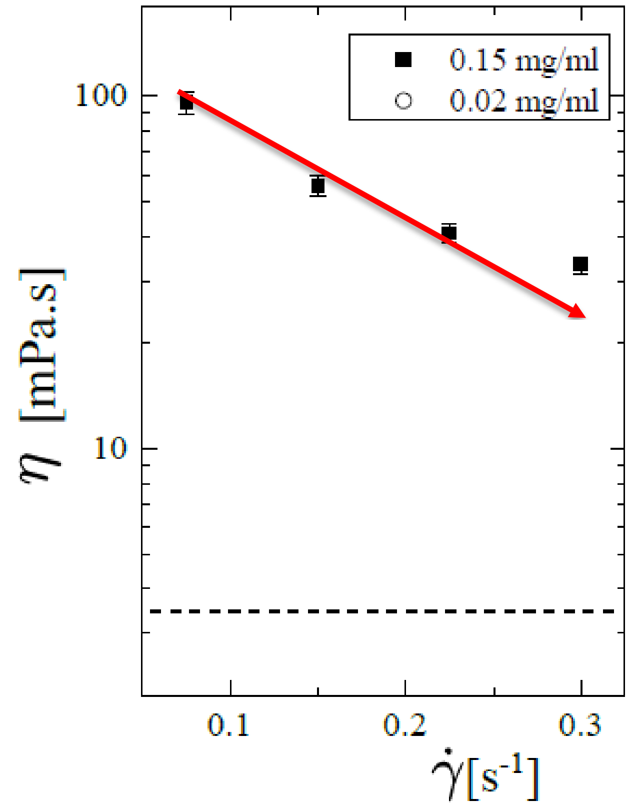
Goal: obtain 3-D structural information

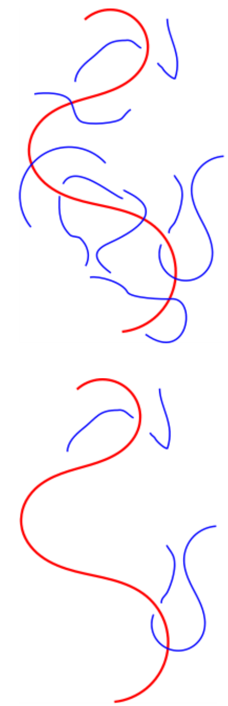




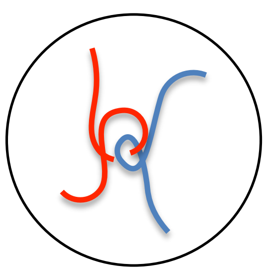
Rheological response of F-actin dispersions



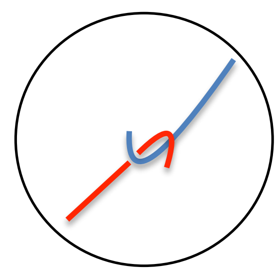




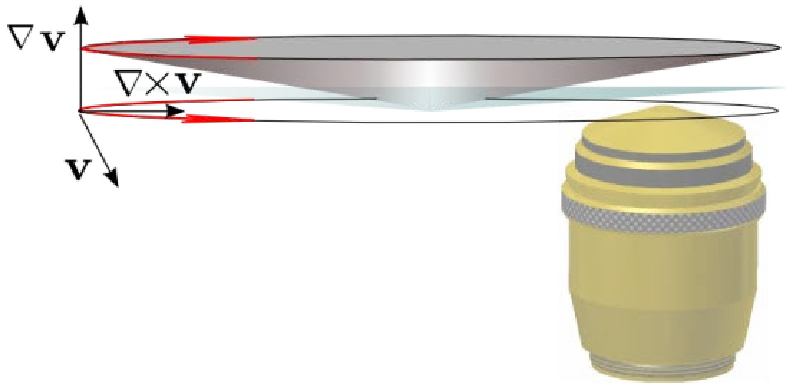
Strain softening

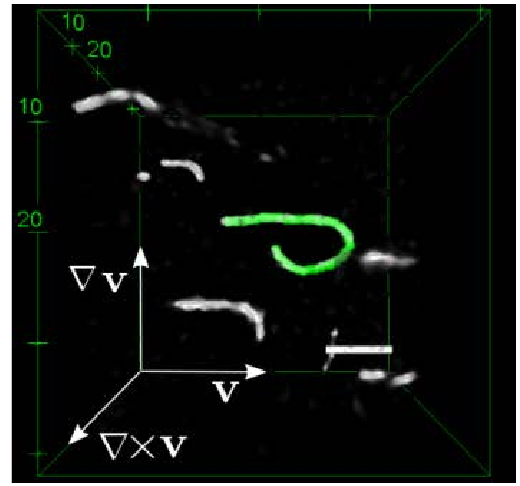


Shear thinning

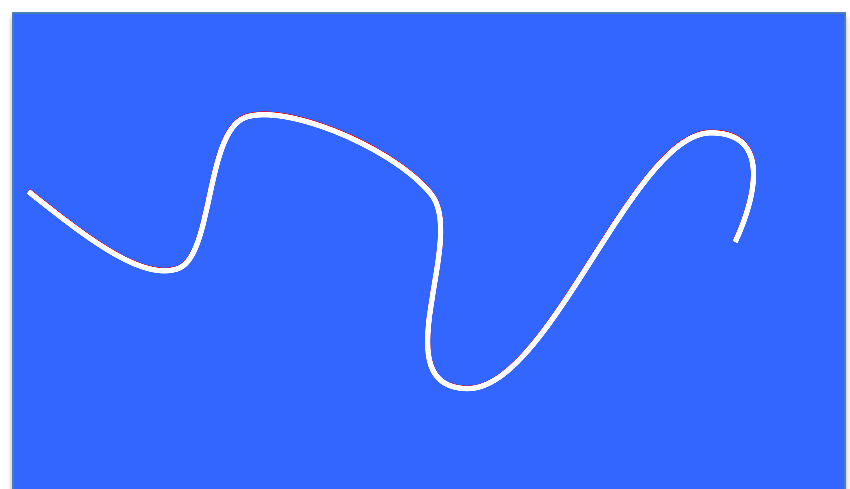


In situ confocal microscopy on entangled F-actin



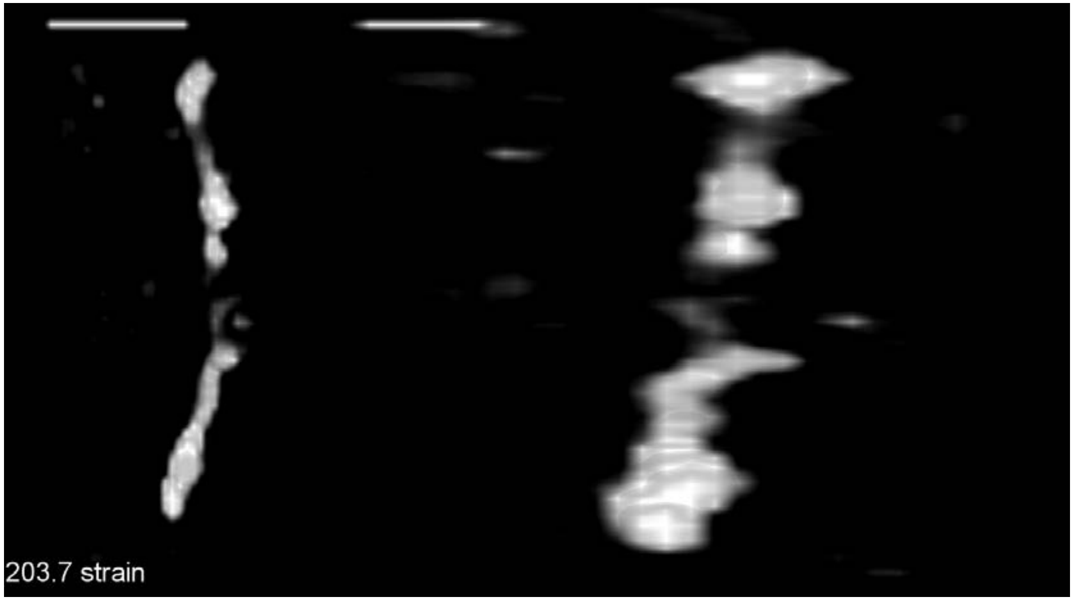


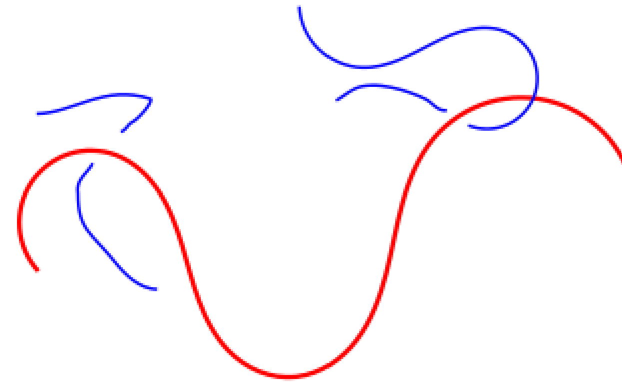
- Use three concentrations, label 1 per 100 filaments
- About 100 analyzed filaments per combination

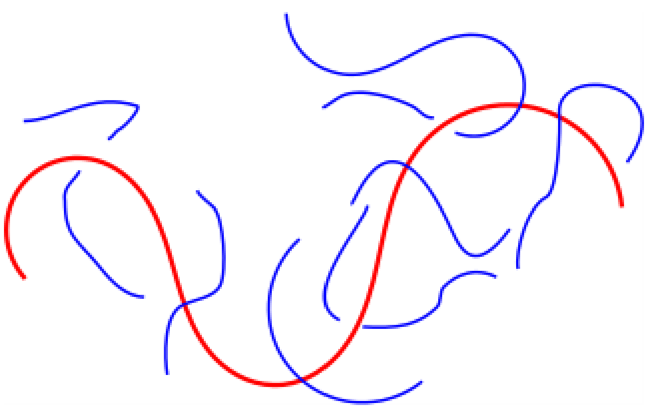


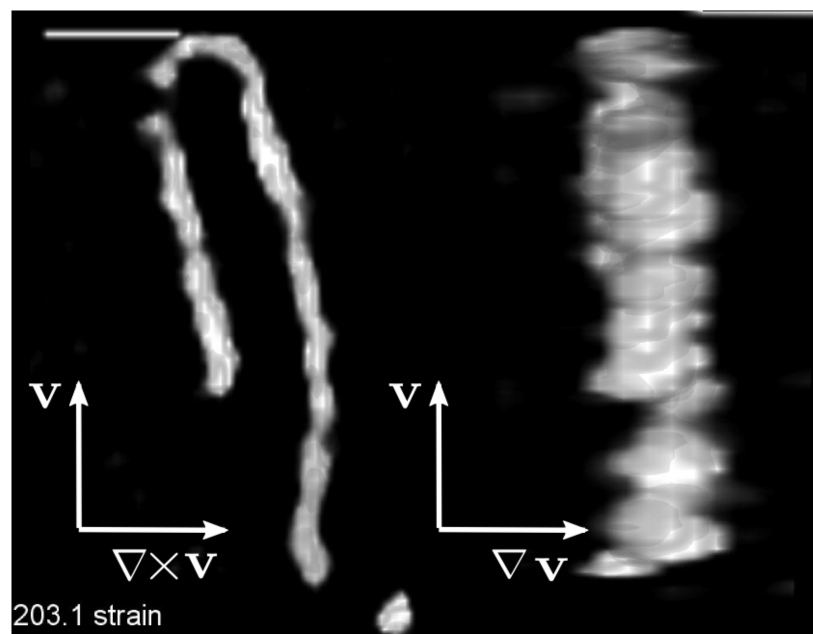
Kirchenbüchler et al *Nature Communications* 5:5060 (2014)

Sheared F-Actin in 3-D

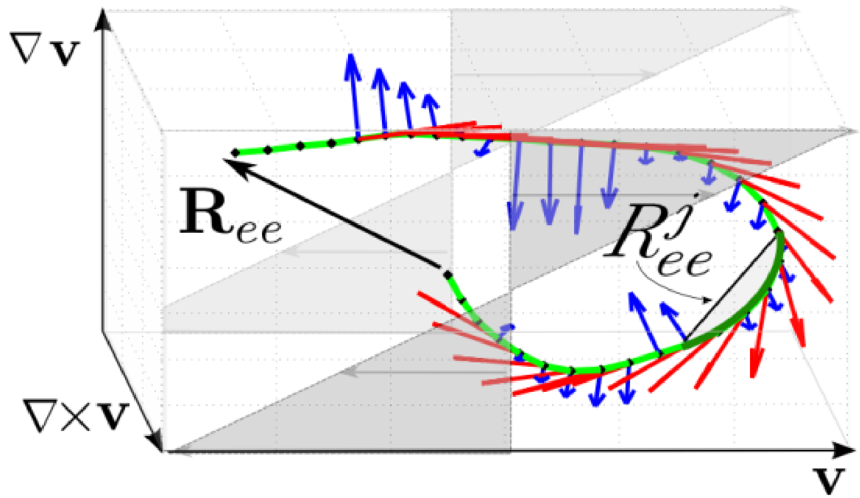


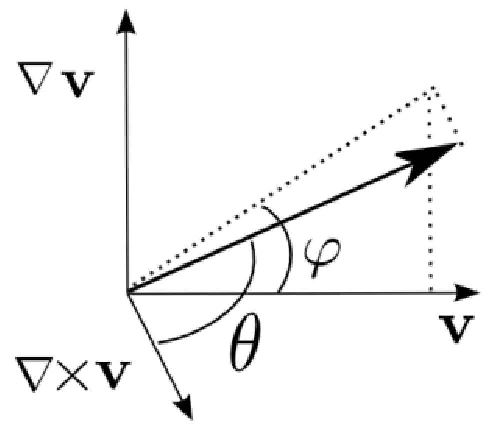




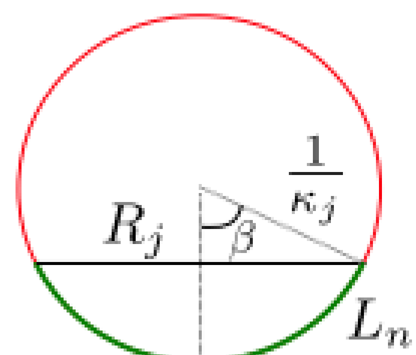


Analyze local bending and stretching:



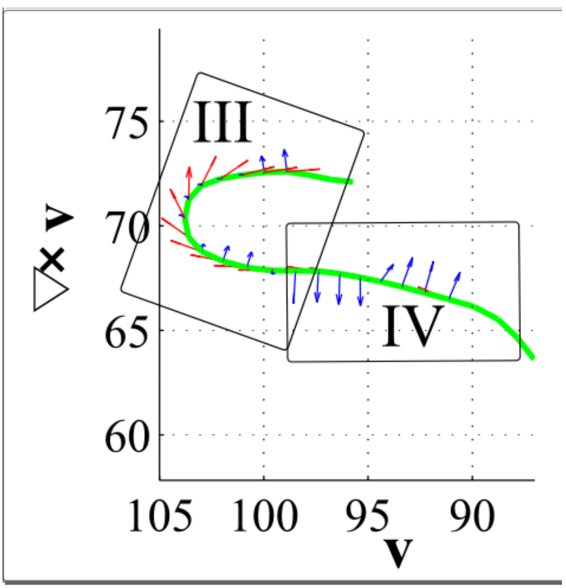


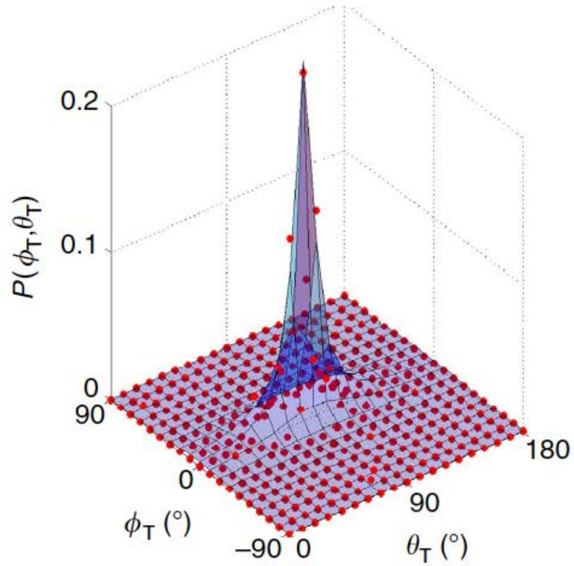
$$\hat{T}_j \equiv \frac{\dot{\mathbf{r}}_j}{|\dot{\mathbf{r}}_j|}; \hat{B}_j \equiv \frac{\dot{\mathbf{r}}_j \times \ddot{\mathbf{r}}_j}{|\dot{\mathbf{r}}_j \times \ddot{\mathbf{r}}_j|}; \kappa_j = \frac{|\dot{\mathbf{r}}_j \times \ddot{\mathbf{r}}_j|}{|\dot{\mathbf{r}}_j|^3}$$

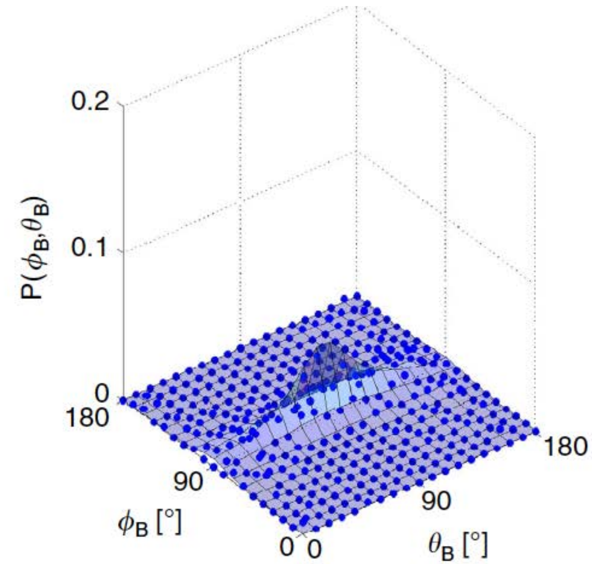


Distribution of angles

Stretched: IV

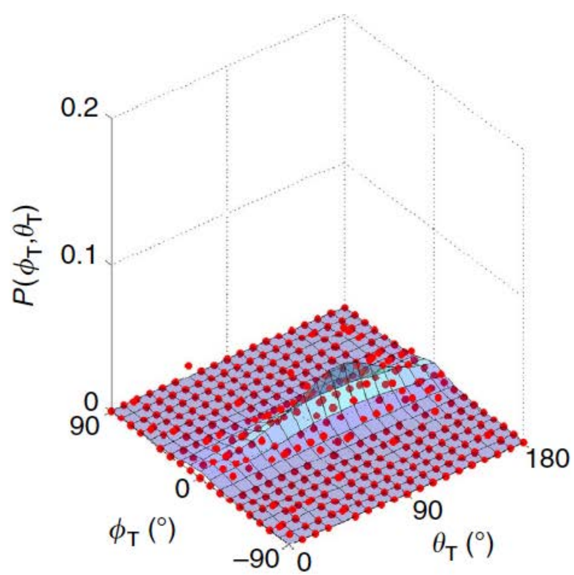


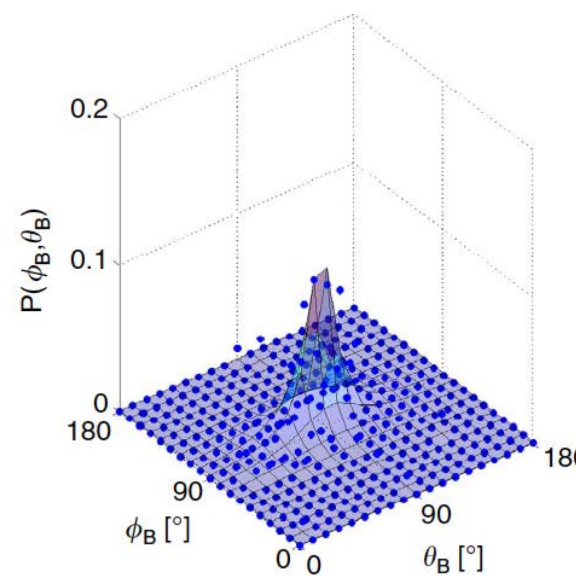




$$f(\theta,\phi) = a/\left((\frac{\theta-\Delta\theta}{w_\theta})^2 + (\frac{\phi-\Delta\phi}{w_\phi})^2 + 1\right)$$

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?

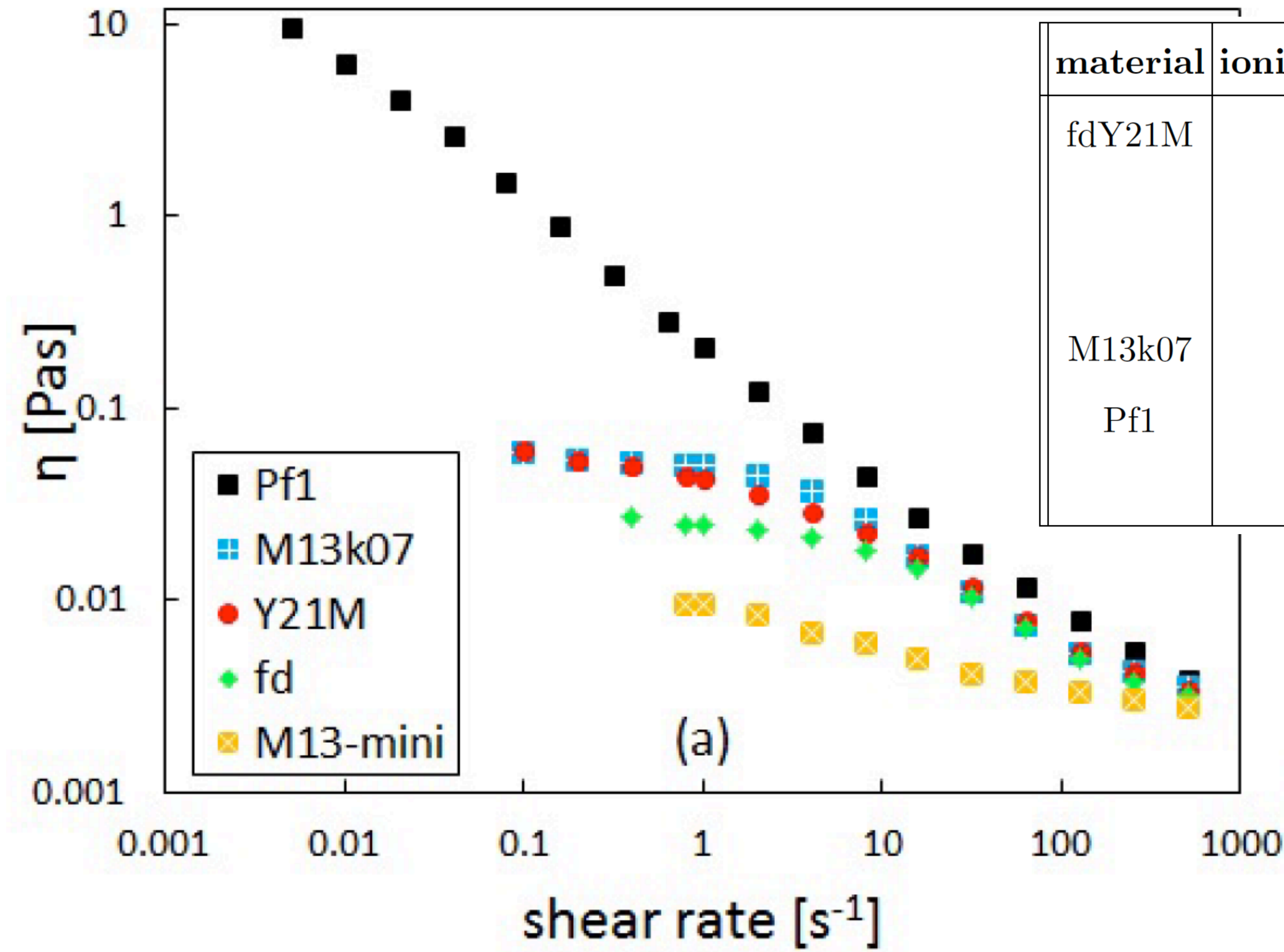
Stiff and mono-disperse rods

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

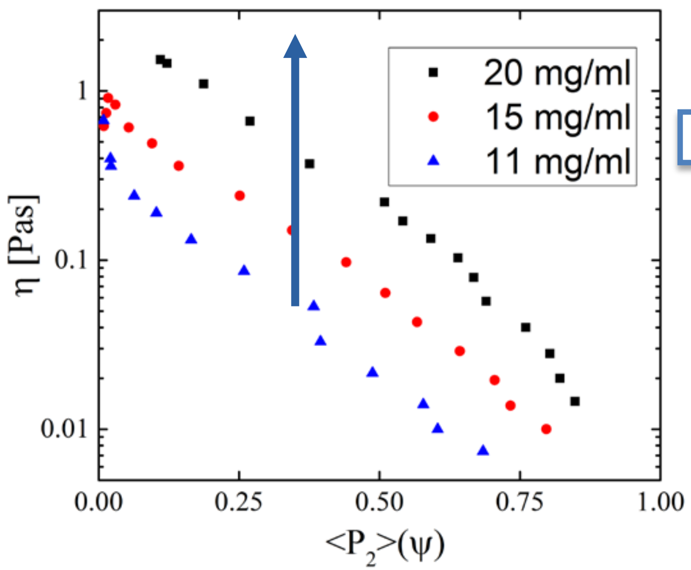


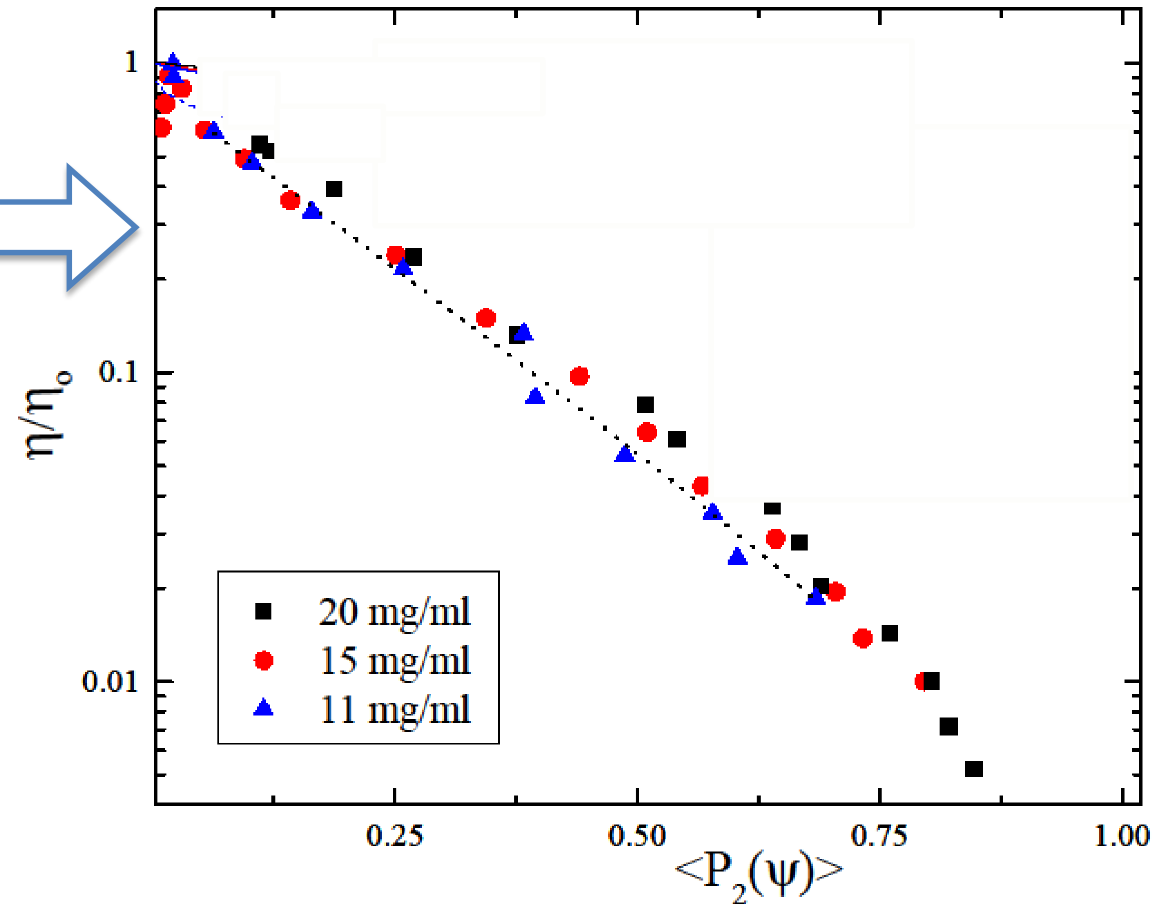
material	ionic strength	m
fdY21M	1	0.45
	20	0.36
	100	0.5
M13k07	100	0.4
Pf1	1	0.38
	100	0.27

Viscosity vs projected order parameter <$P_2(\psi)$>

Scale viscosity

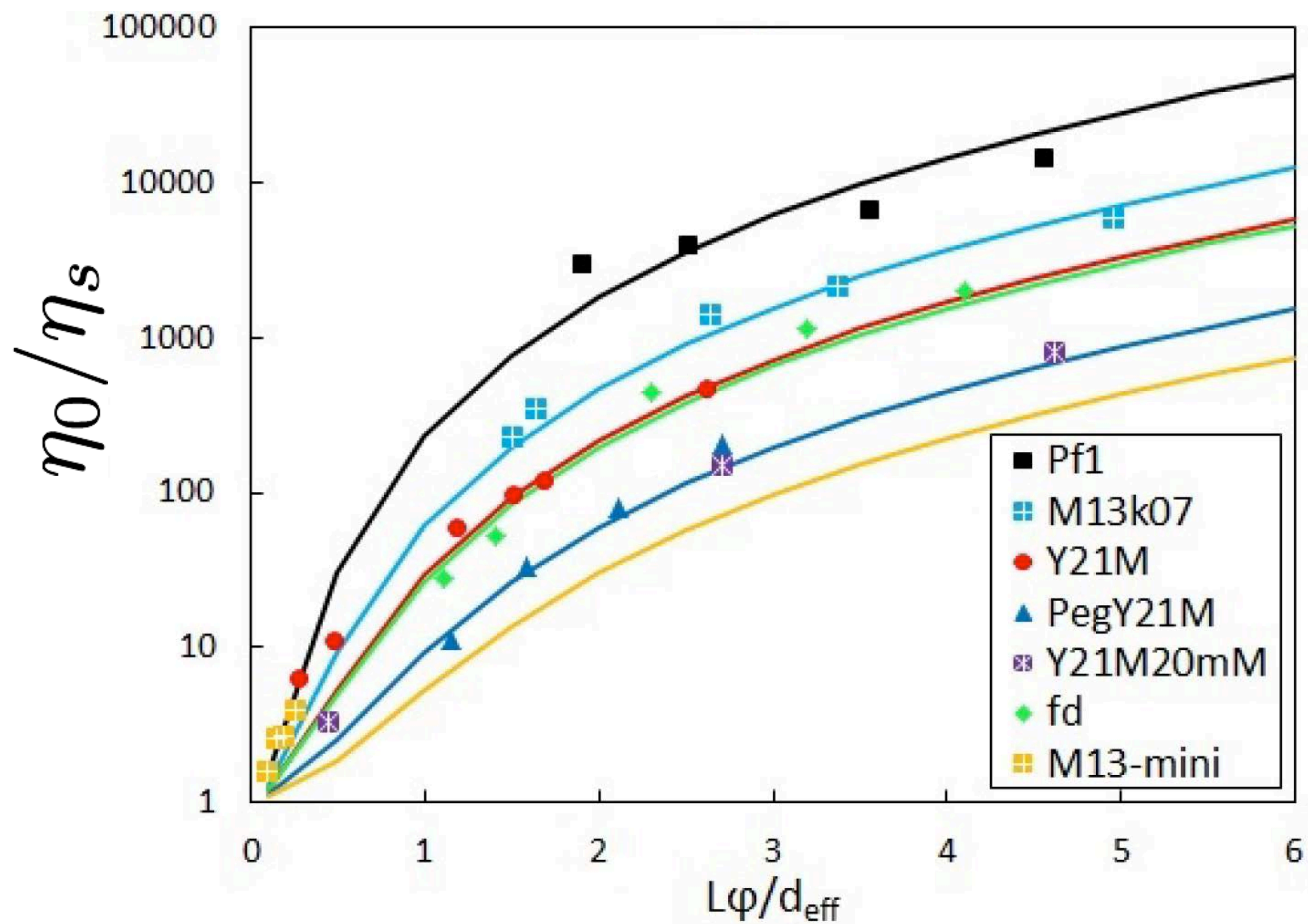
Assumption: shear thinning is caused by orientation





Lang et al, *Polymers*, 2016

Zero shear viscosity of rods



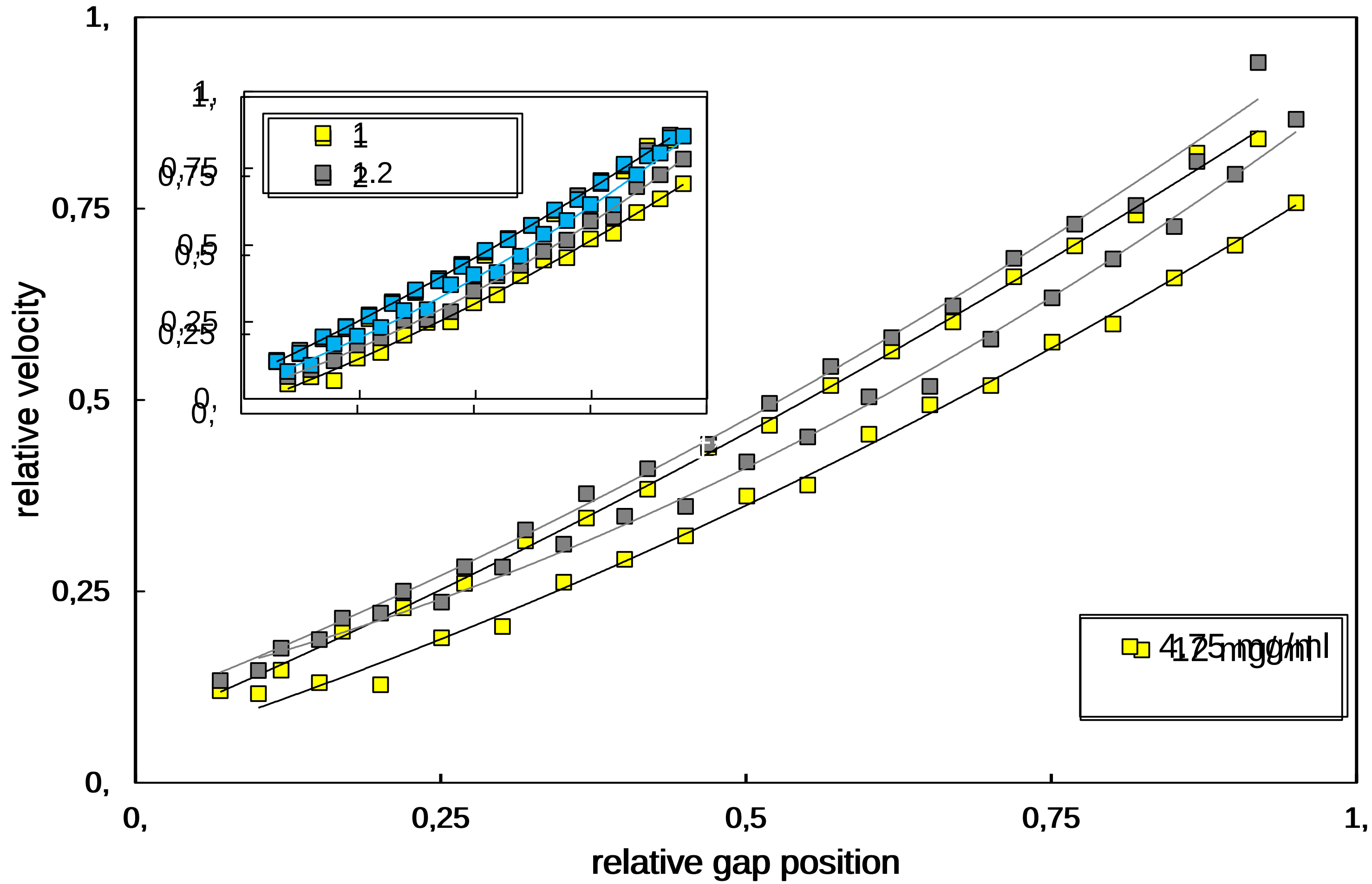
$$D_r = cD_r^0(\nu L^3)^{-2}$$

→ $c=3.10^3$

Velocity profiles of rods

JÜLICH FORSCHUNGSZENTRUM

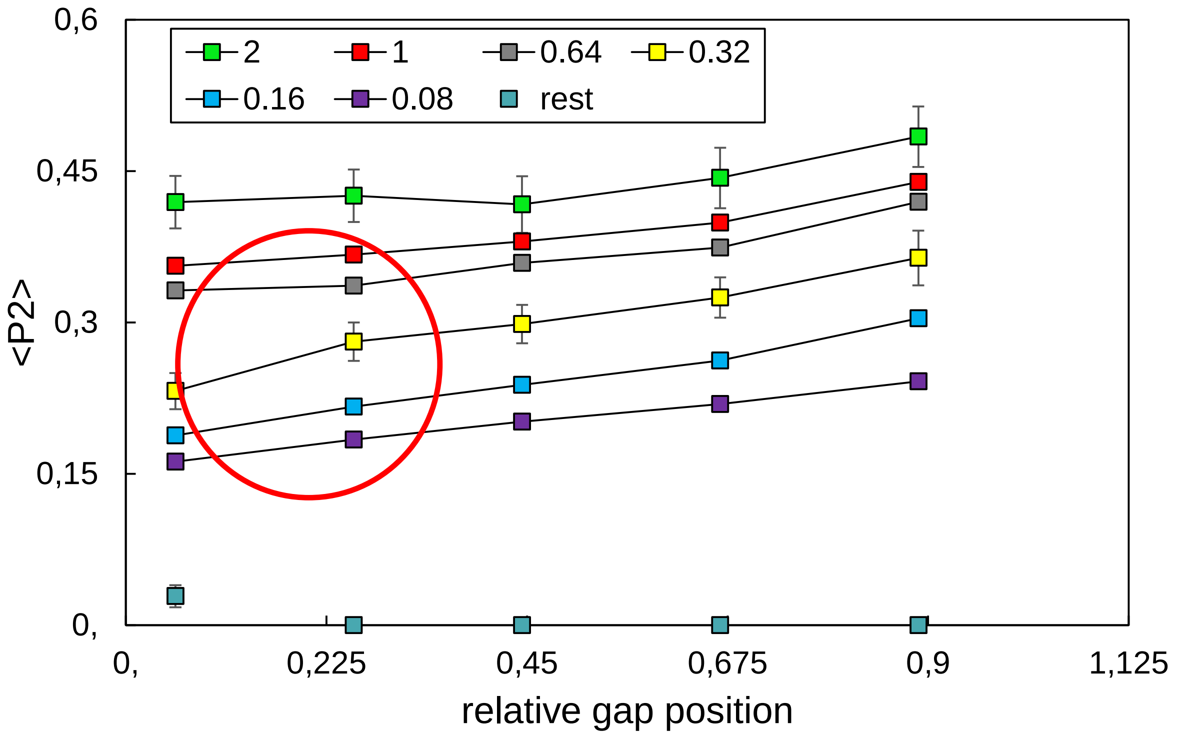
Velocity profile of M13k07 (L=1.2 µm, L_p=2.2 µm):

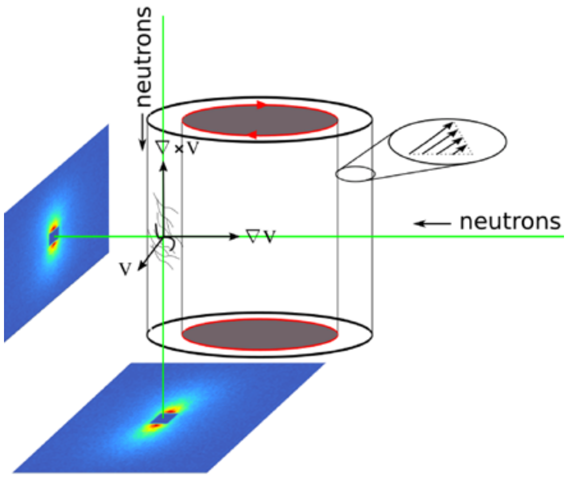


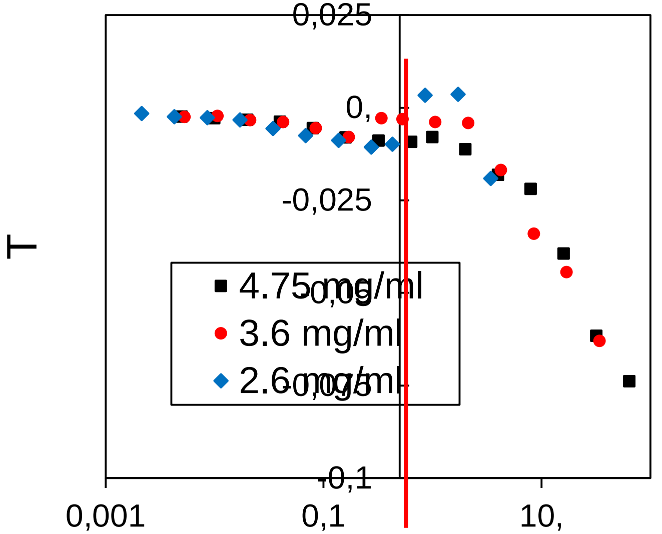
- very long and flexible rods show hints of shear banding

Zero shear viscosity of rods

Shear-banding and hairpin formation







- biaxiality reverses in a small shear rate range after "shear banding"

Lang et al, *Polymers*, 2016

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

FZ Jülich:
Chris Lang
Inka Kirchenbüchler
Manolis Stiakakis
Hu Tang
Lutz Willner
Barbara Lonetti

University of Urbain-Illinois:
Simon Rogers

PSI, Villigen:
Joachim Kohlbrecher

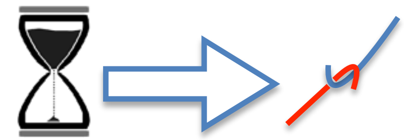
ILL, Grenoble:
Lionel Porcar

Amolf Amsterdam:
Gijsje Koenderink

DiStruc
Directed Structure at the meso-scale

Conclusions and Outlook

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

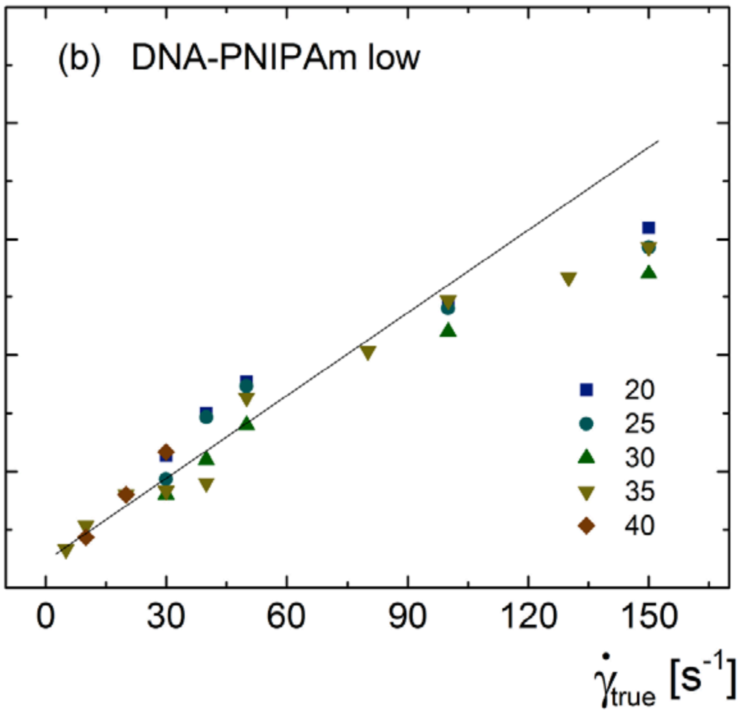
➢ no good handle on set flow instability

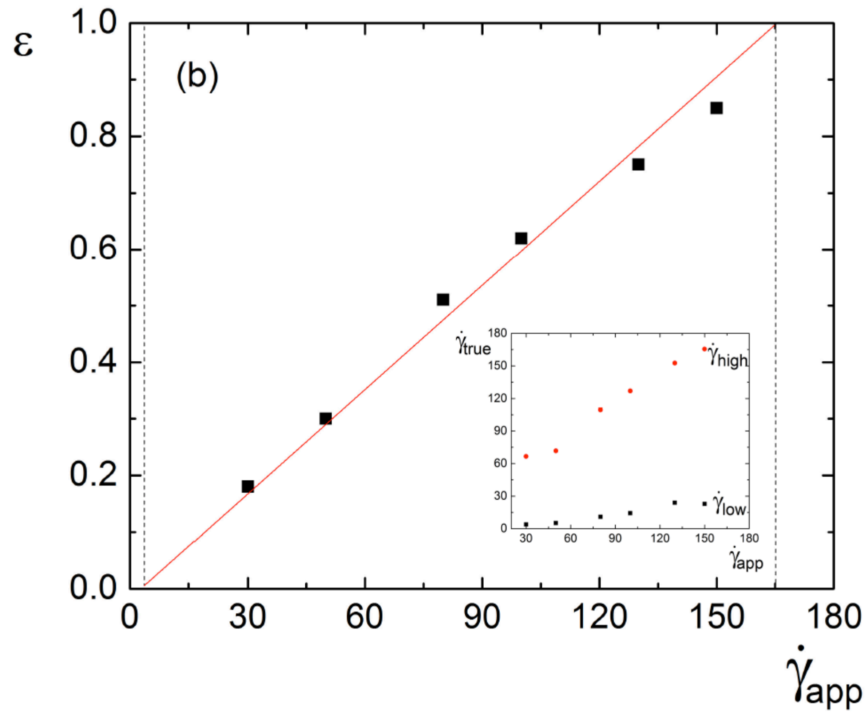
So:

➢ Improve theory

➢ Develop new systems:

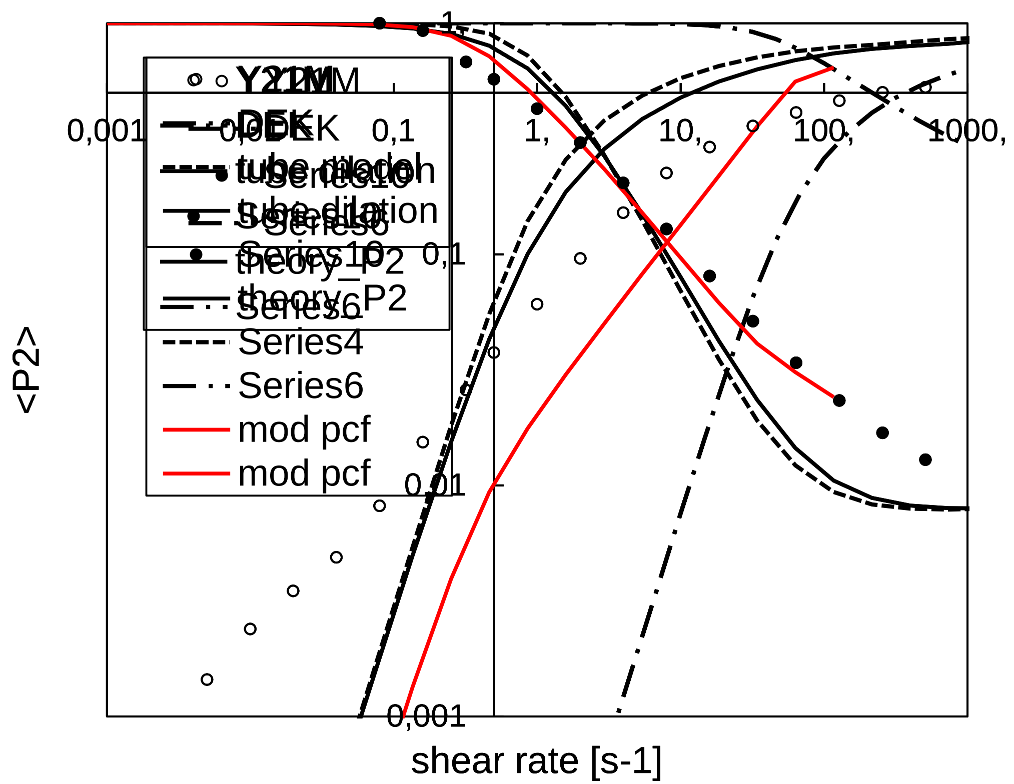
- Controlled polydispersity
- Controlled friction with grafted DNA
- Use labeled living stiff supra-molecular polymers


(b) DNA-PNIPAm low
20
25
30
35
40
0
30
60
90
120
150
$\dot{\gamma}_{true}$ [s^{-1}]


ε
1.0
0.8
0.6
0.4
0.2
0.0
(b)
0
30
60
90
120
150
180
$\dot{\gamma}_{app}$
$\dot{\gamma}_{true}$
$\dot{\gamma}_{high}$
$\dot{\gamma}_{low}$

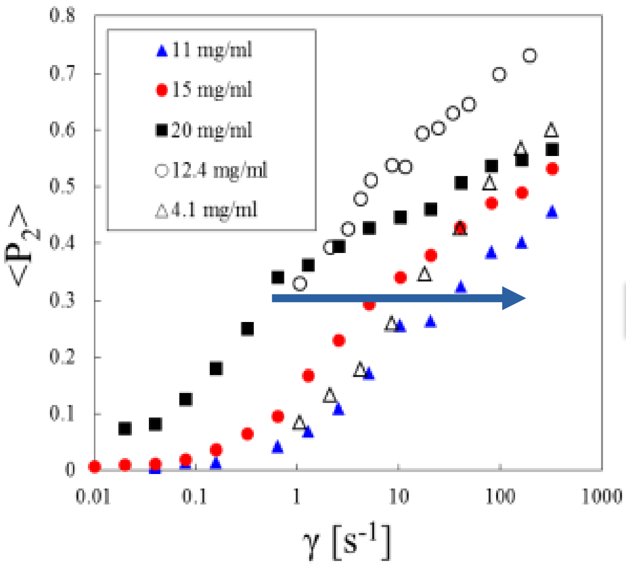
Advancements: pcf

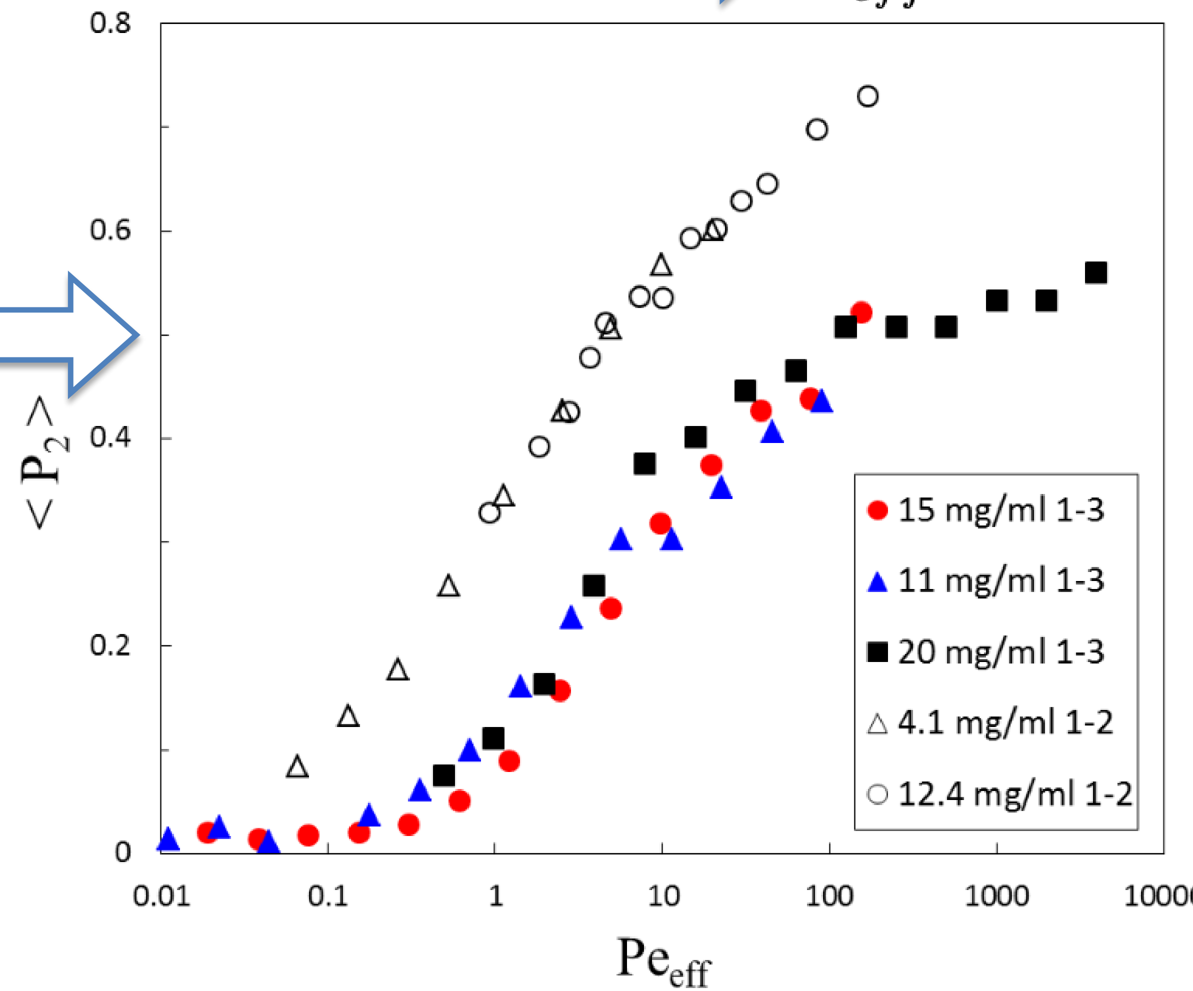
Nonlinear viscosity and ordering of the ideal rod



Obtain the I-N spinodal point

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

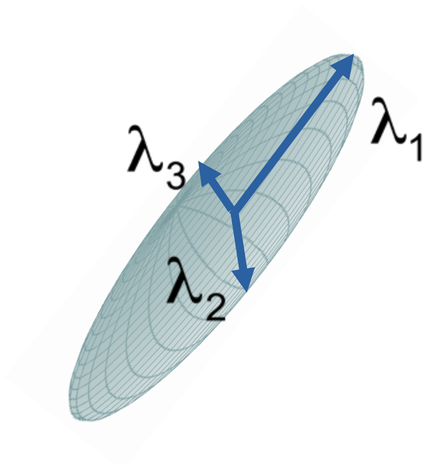


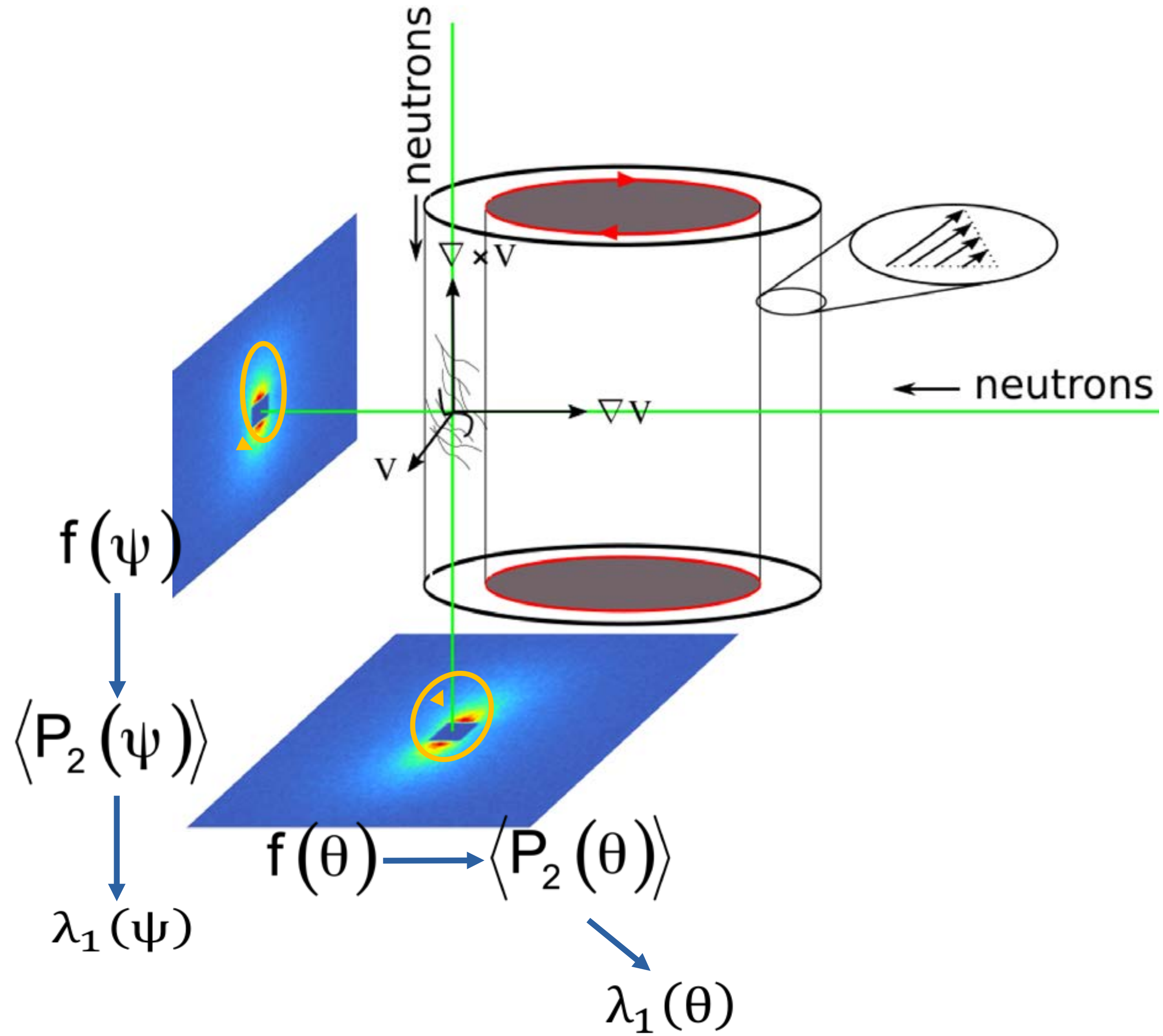


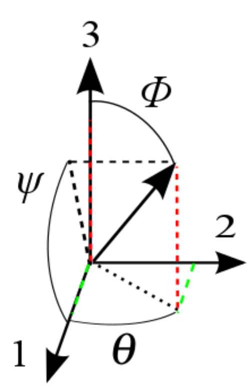
- Collective scaling works
- different ordering in different directions: Biaxiality!

Scattering in 3-D of actual rods

3-D SANS

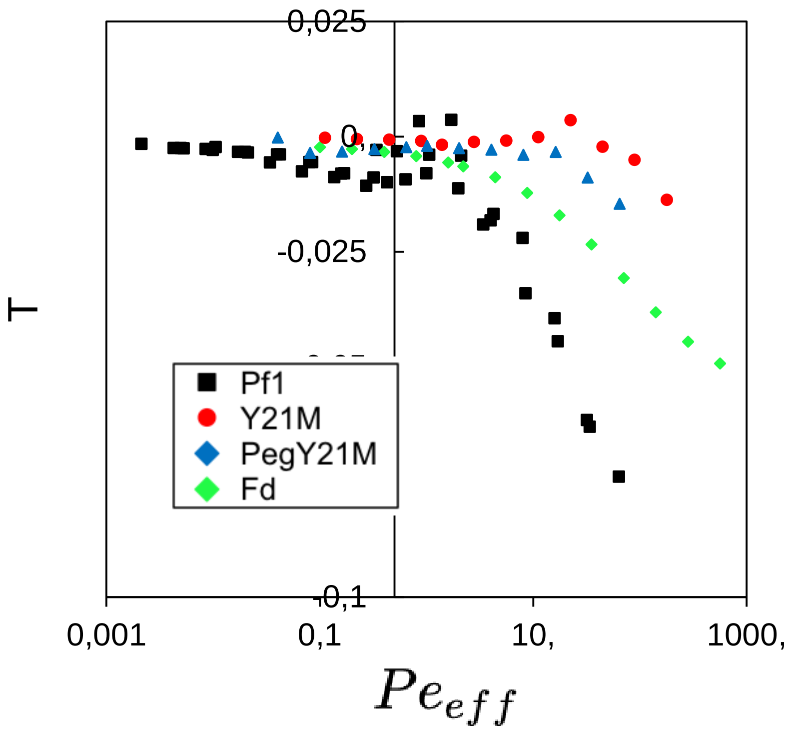


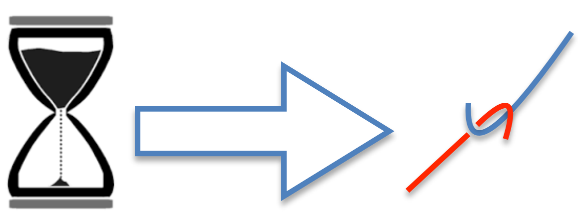




$$\lambda_1(\psi) \Rightarrow \psi_{max} \equiv 0$$

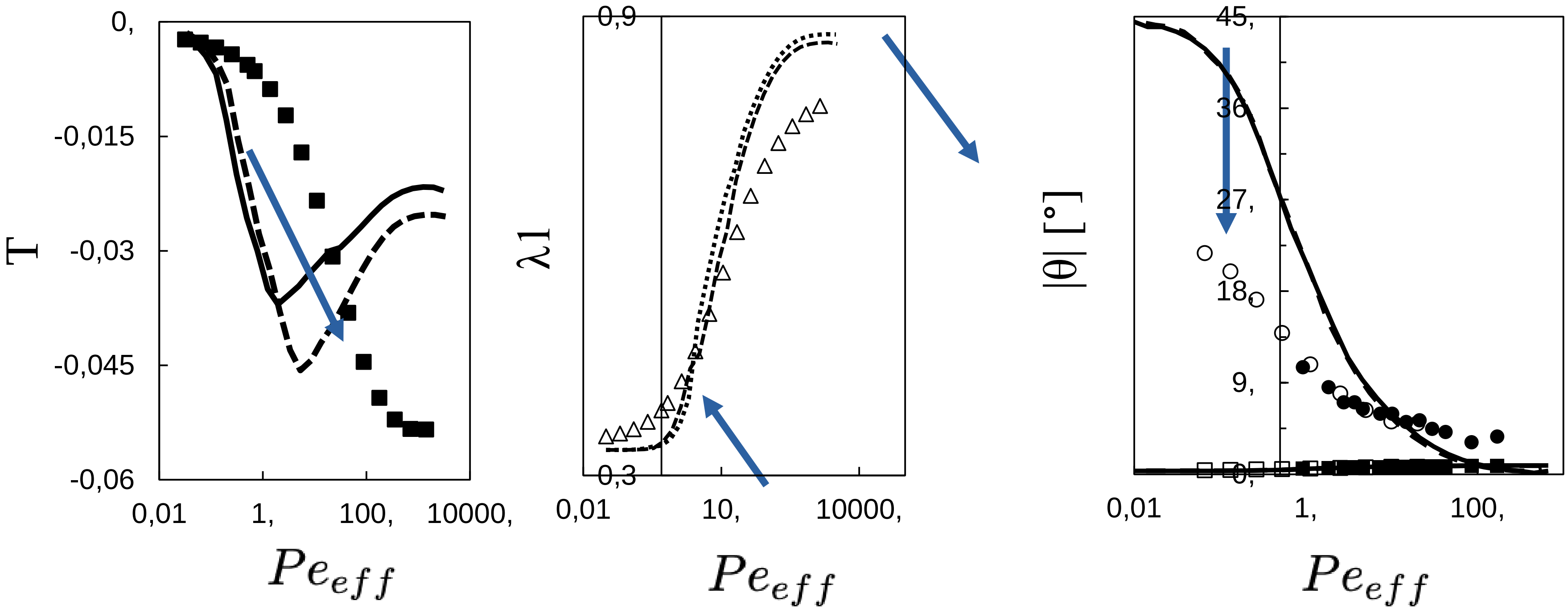
Biaxiality





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

Scaling other ordering parameters

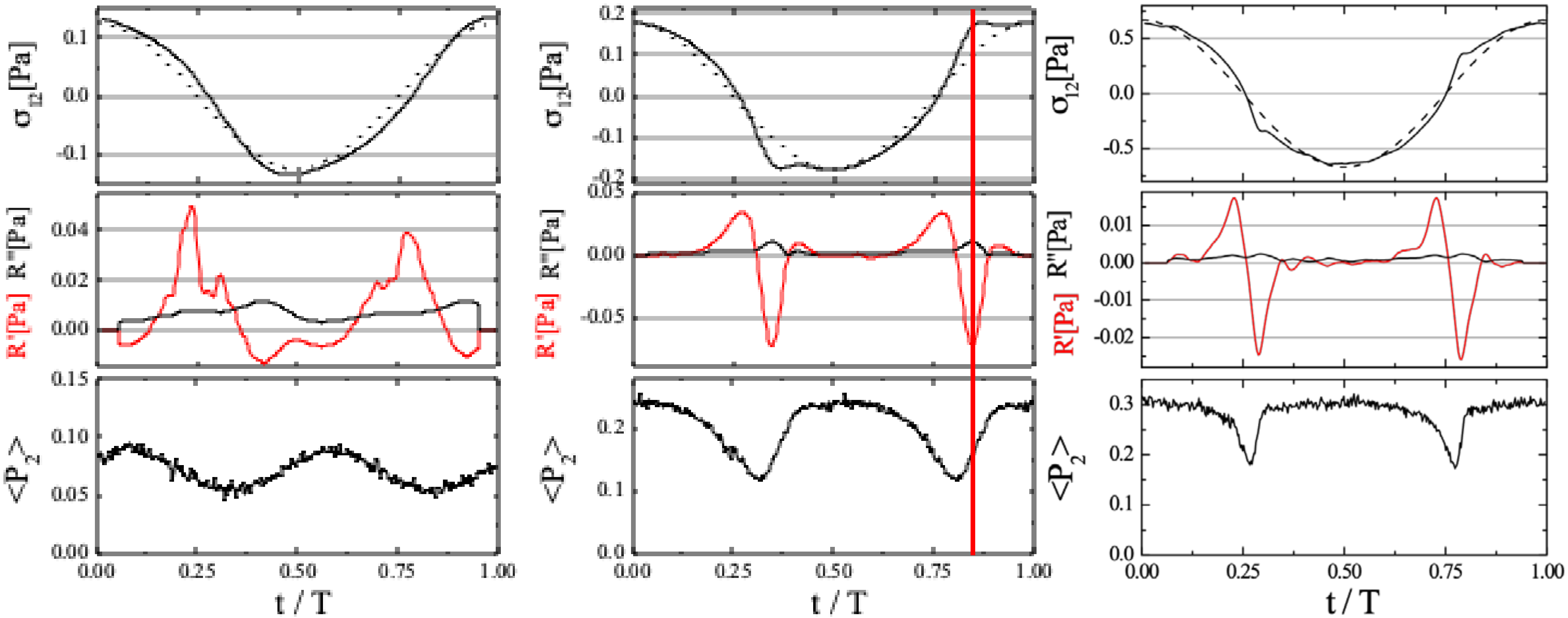


- **Strong dependence at low shear rate; weak dependence at high shear rate**

Lang, Kohlbrecher, Porcar, Lettinga, *Polymers* 2016, **8**, 291

Dynamic response fd virus in isotropic phase

$$f = 0.01 \ \ \mathrm{Hz}$$



$$\dot{\gamma}_0 = 3.2\ s^{-1} \qquad \dot{\gamma}_0 = 12.8\ s^{-1} \qquad \dot{\gamma}_0 = 102\ s^{-1}$$

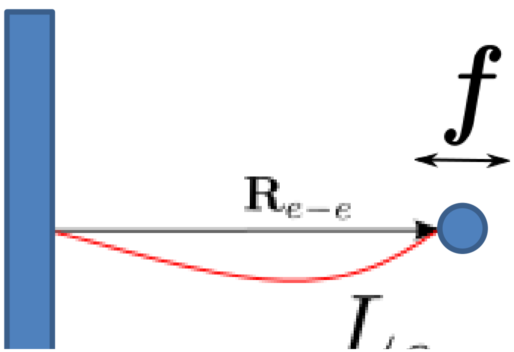
Push and pull experiments

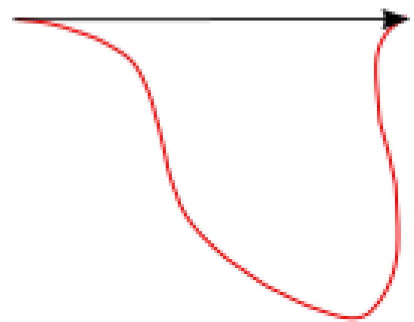
End-to-end vector $\mathbf{R}_{e-e}$ is the relevant parameter

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

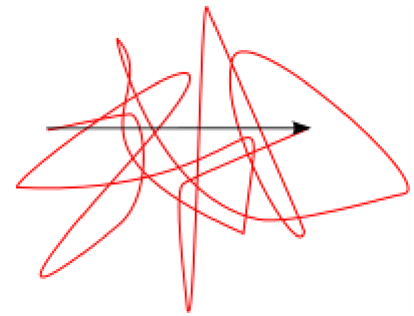
Semi-flexible: $\mathbf{R}_{\mathbf{e-e}} < L_c$

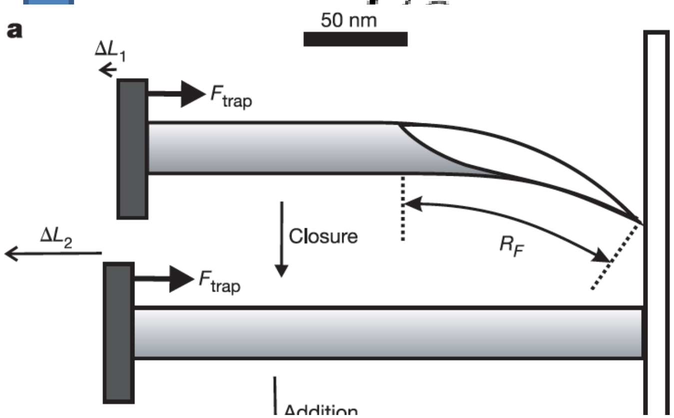
Flexible: $\mathbf{R}_{\mathbf{e-e}} << L_c$



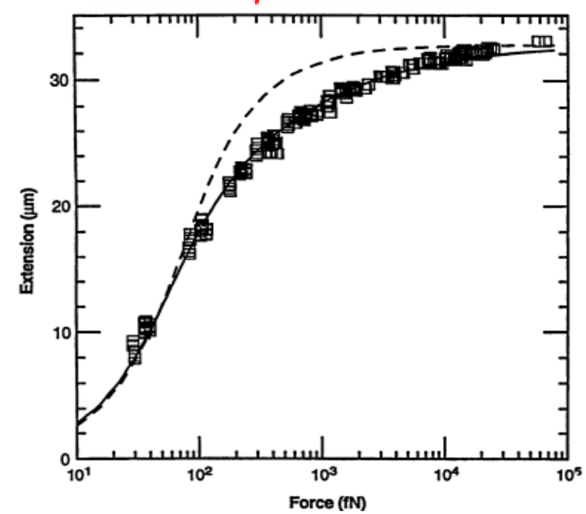


?





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

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

$$D_r^{coll}=D_r^0\left(\frac{L}{d}-\frac{L}{5d}\varphi\right)$$

(depending on U between 4 and 5)

- MPC:

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

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

- measurement:

$$\varphi_{IN} = 4.2$$

Introduction

Motivation:

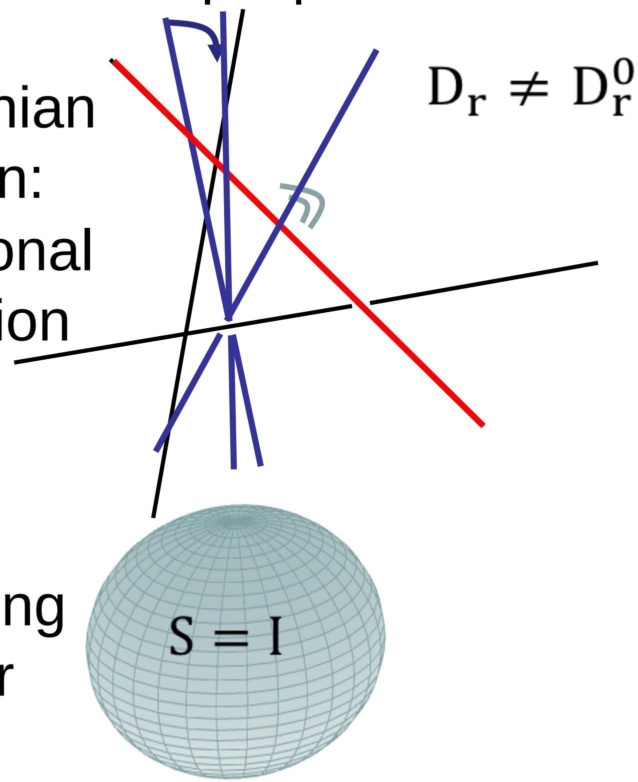
rod suspensions show strong shear thinning: microscopic reason

no shear

isotropic pdf

Brownian motion: rotational diffusion

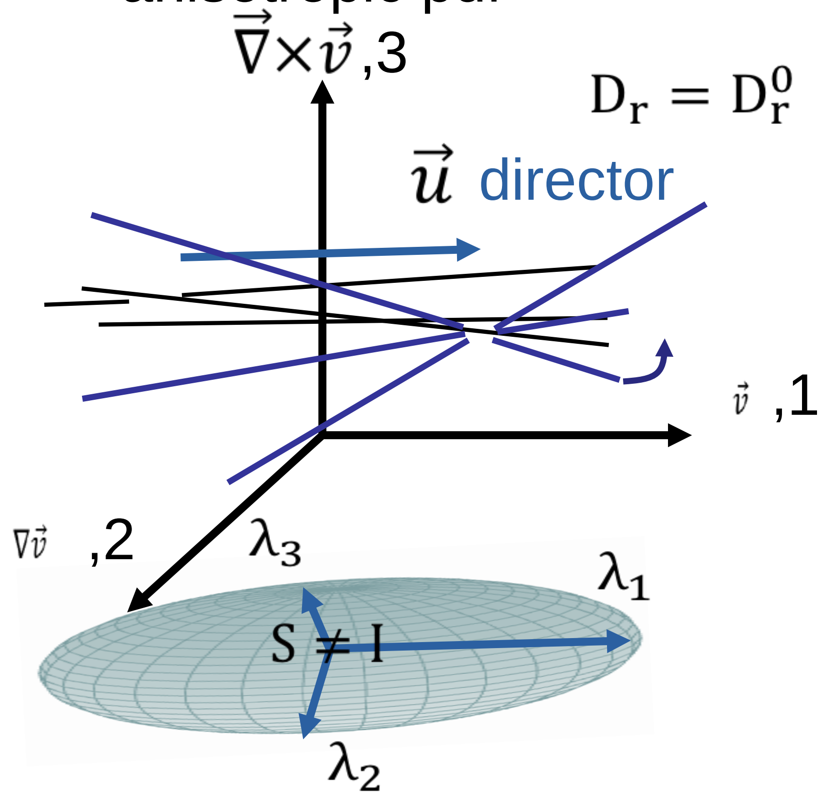
ordering tensor



high viscosity

shear

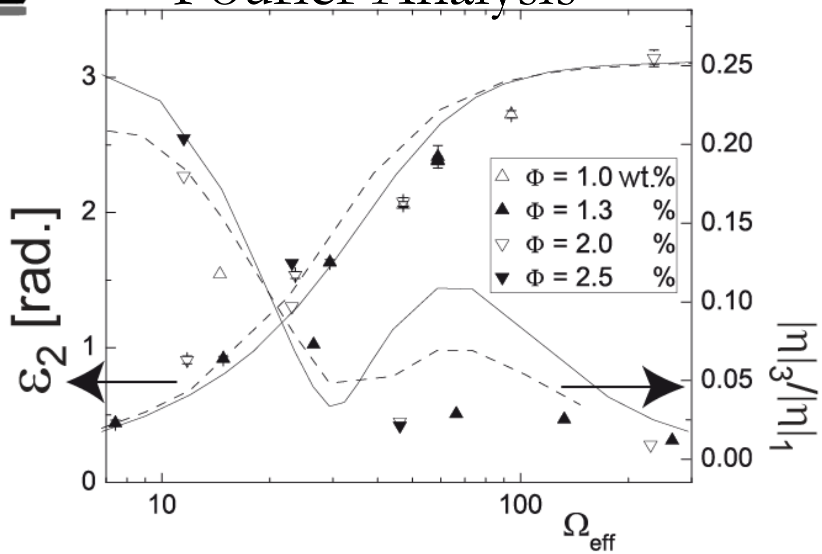
anisotropic pdf

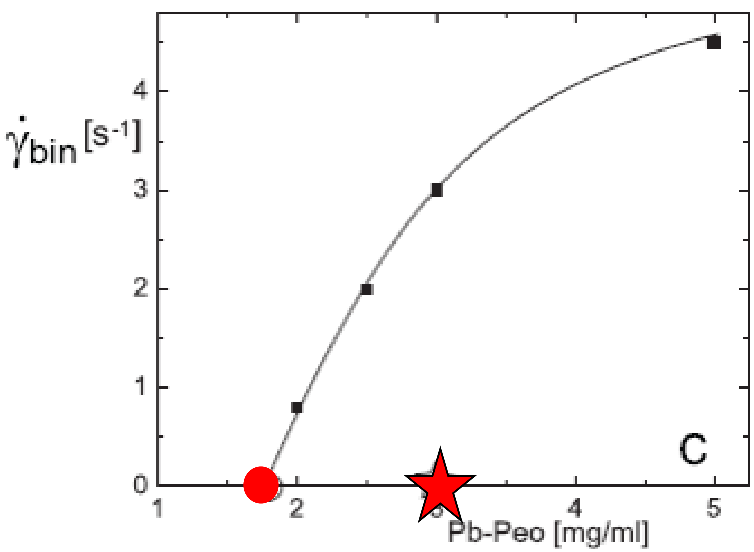


much lower viscosity

=?

Fourier Analysis





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

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

Scaling frequency:

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

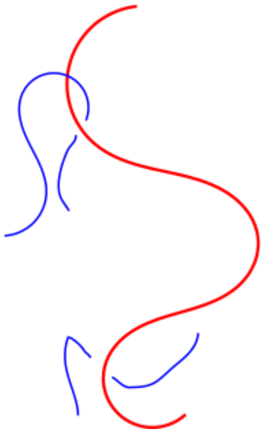
$$D_R^{eff} = D_R\,(1 - \varphi/\varphi_{IN})$$

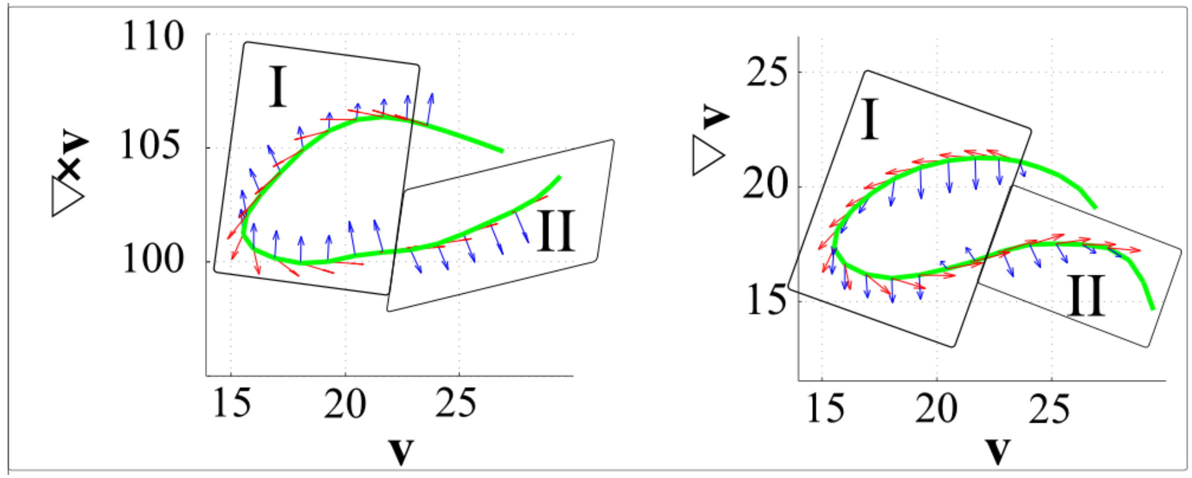
We obtained the I—N spinodal point!

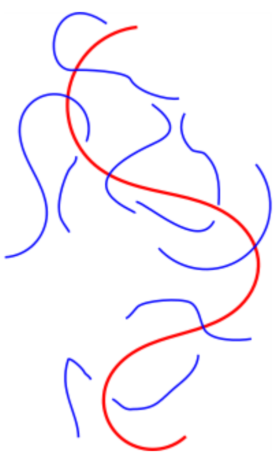
$$\frac{L}{d_{eff}}\varphi_{IN} = 3.0$$

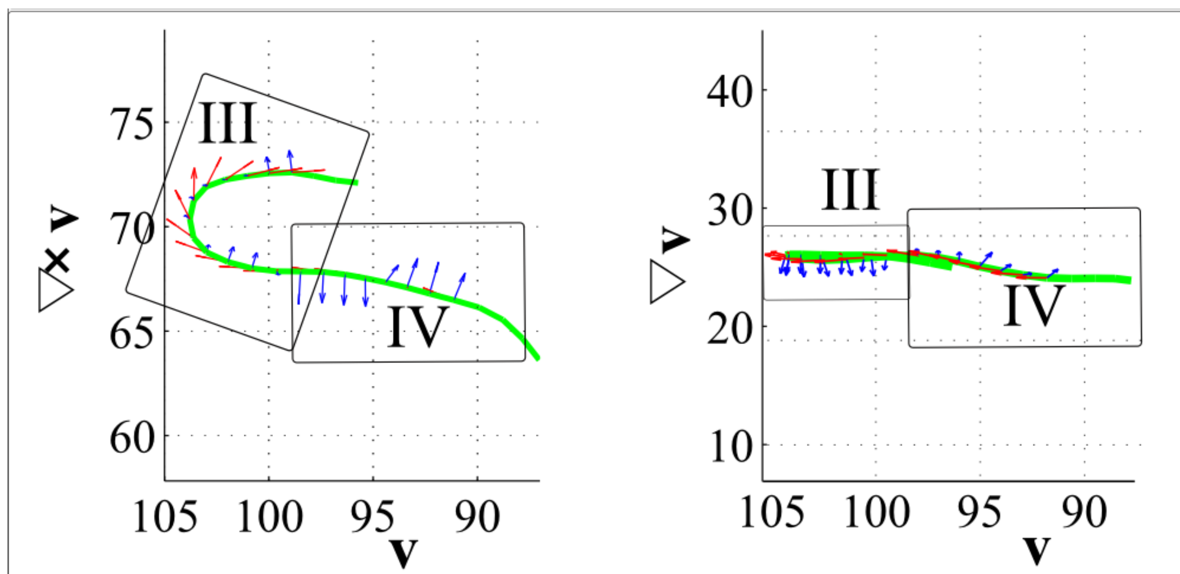
& $$D_R = 0.04\ s^{-1}$$

Typical examples:

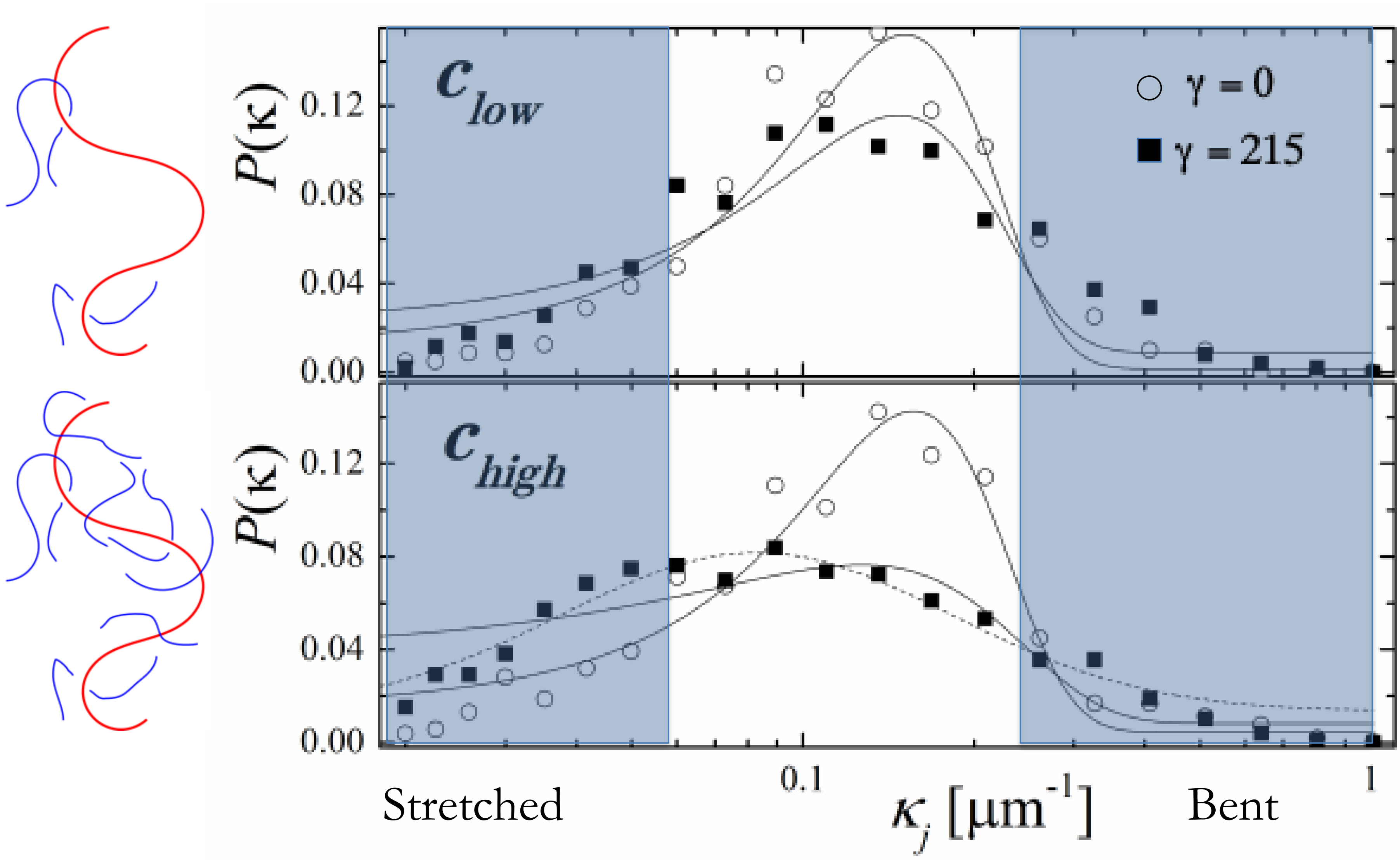








Distribution of curvatures:



Characterizing parameters

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

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

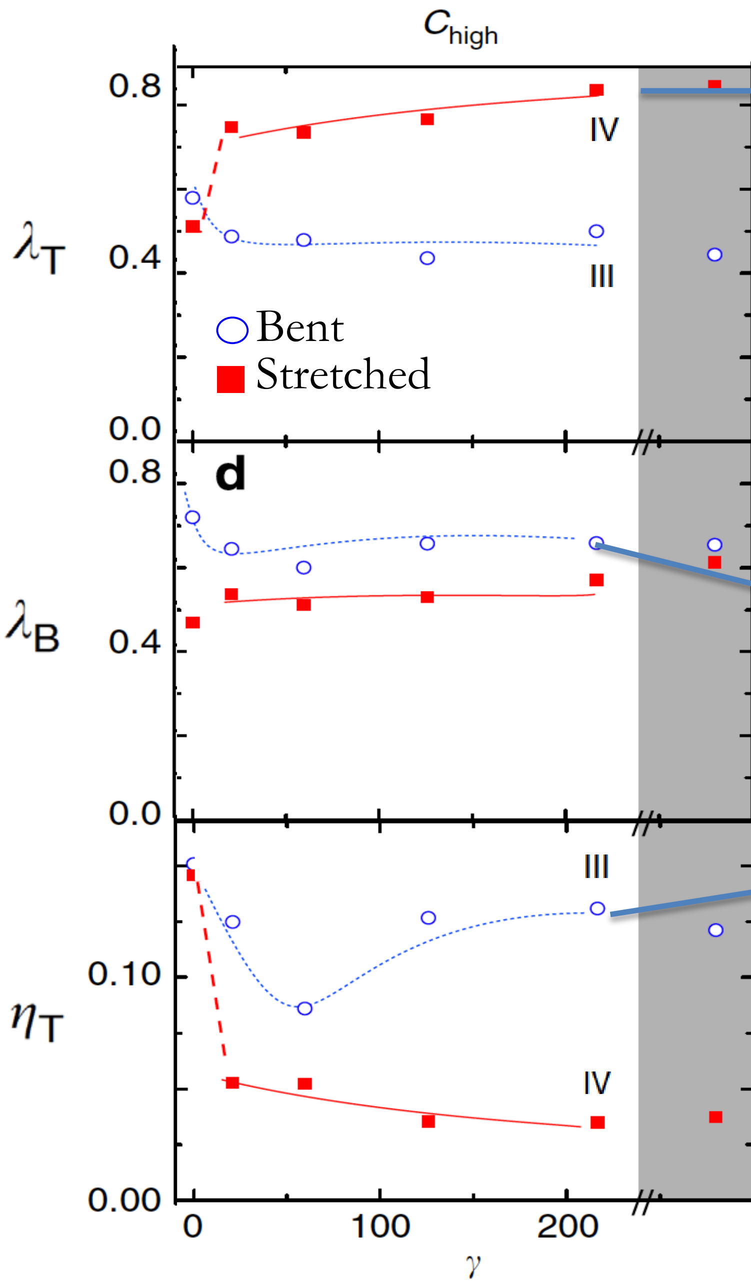
Biaxiality

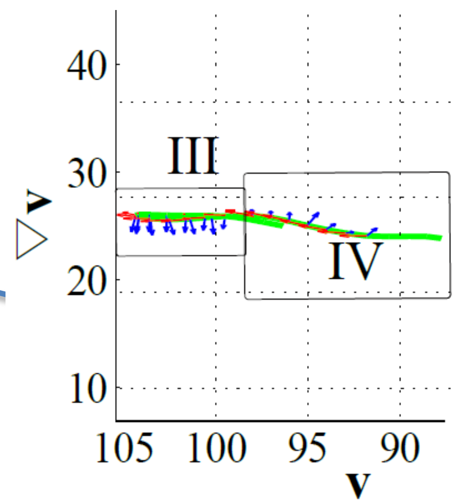
$$\bar{Q}_{T,B} = \begin{pmatrix} -\frac{1}{2}\lambda_{T,B} - \boxed{\eta_{T,B}} & 0 & 0 \\ 0 & -\frac{1}{2}\lambda_{T,B} + \eta_{T,B} & 0 \\ 0 & 0 & \boxed{\lambda_{T,B}} \end{pmatrix}$$

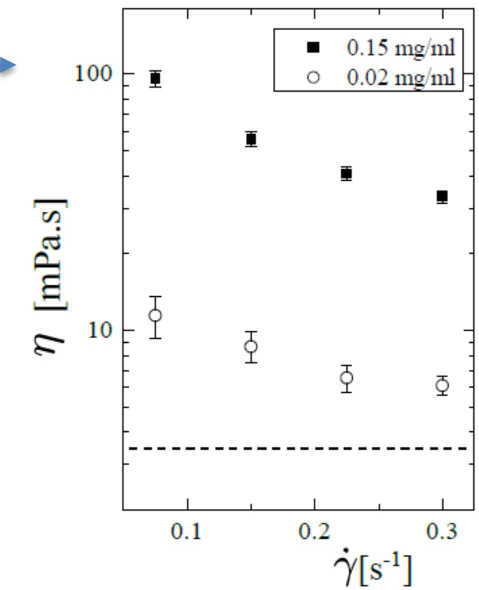
Orientational order parameter

Note: this is the input for calculating stress tensor

Connection between ordering and stress

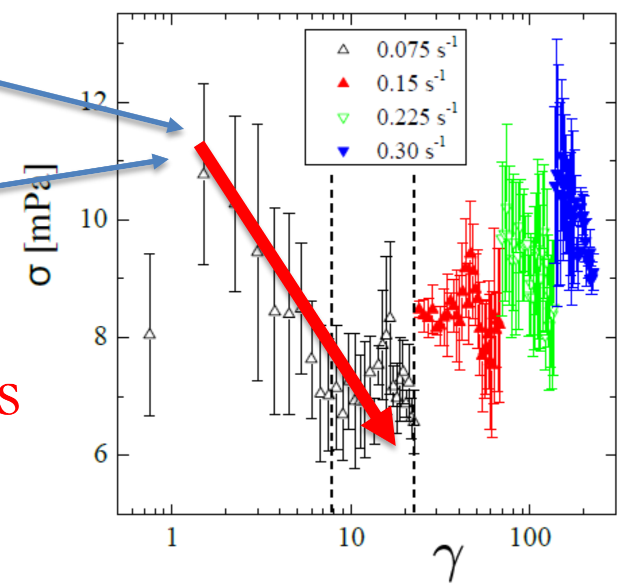






Shear thinning:

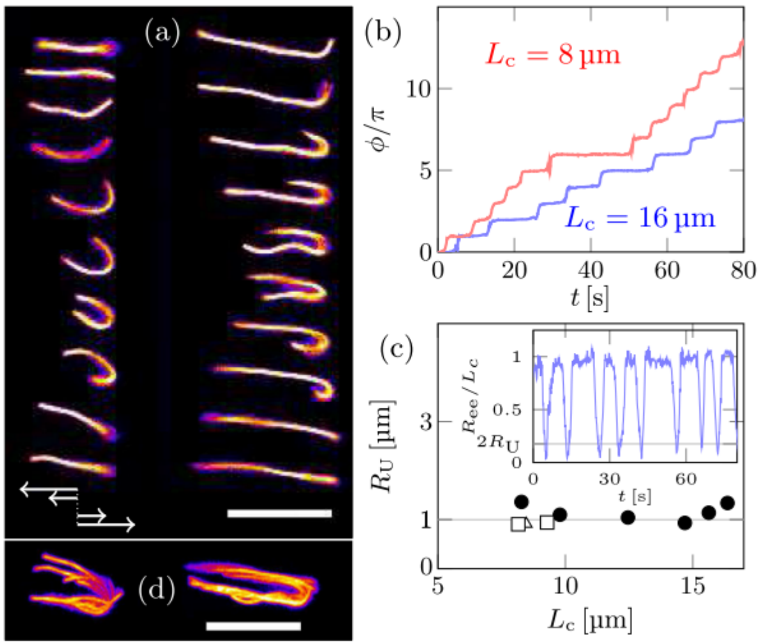
Nematic=more space



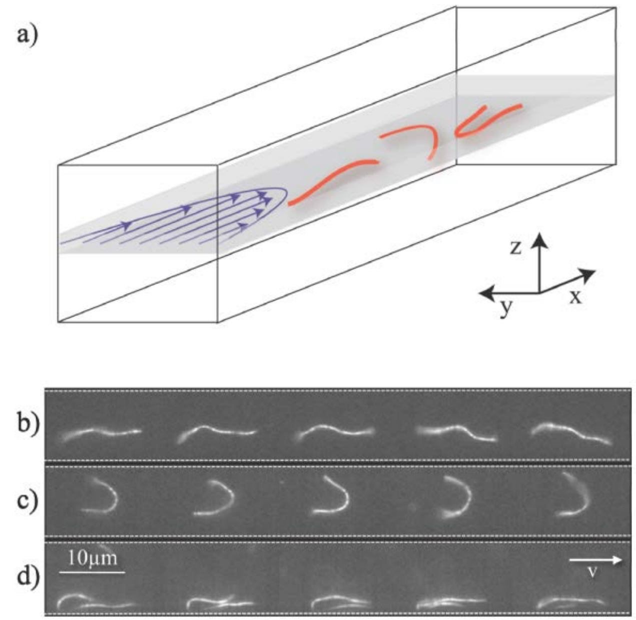
Strain softening :

Oriented hairpins

Shear experiments on F-Actin



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

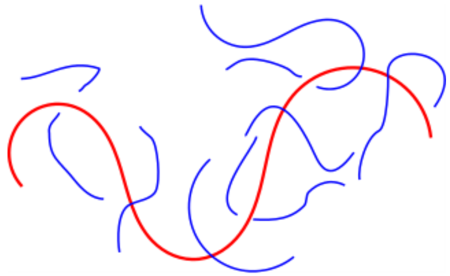


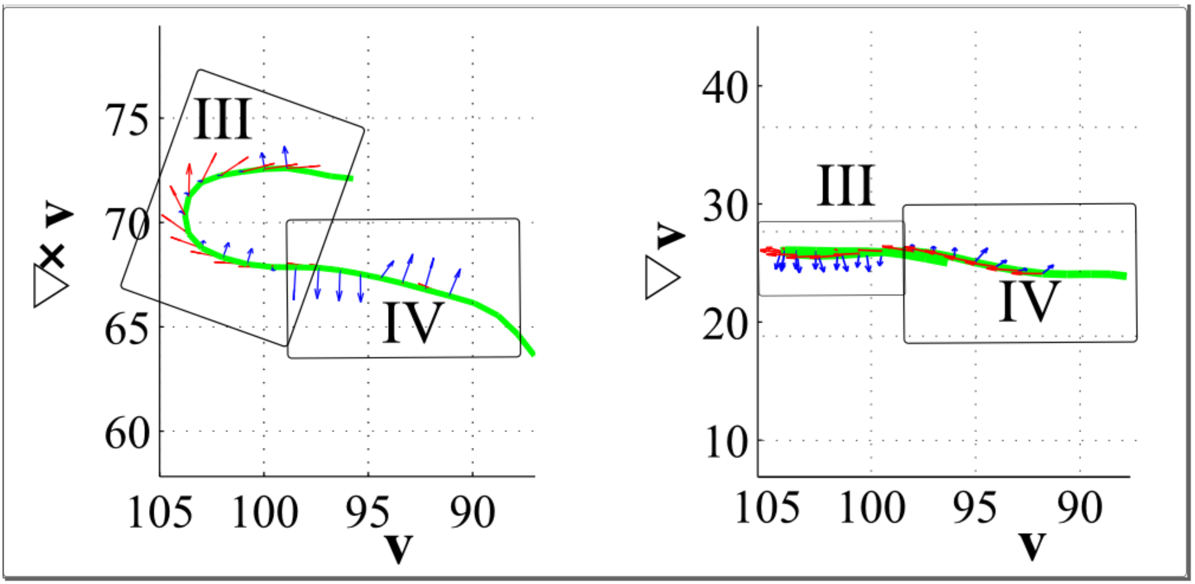
Mobility Gradient Induces Cross-Streamline Migration ofSemiflexible Polymers
Steinhauser et al, ACS Macroletters, p. 542 (2012)

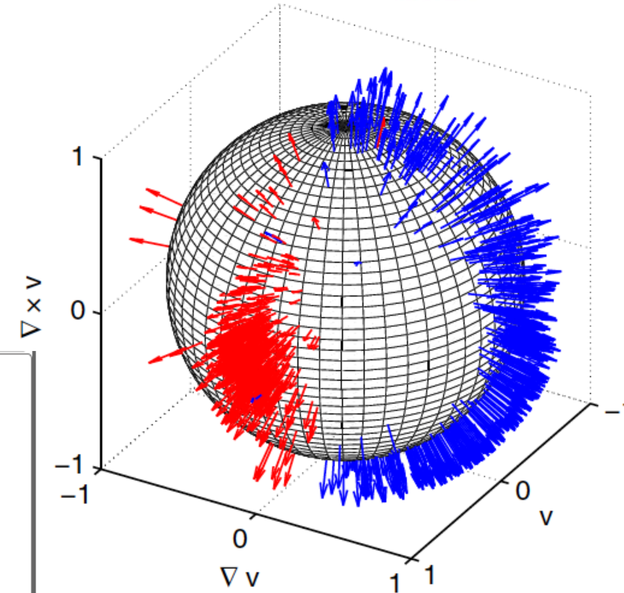
Ill defined geometries; Infinite dilute; 2-D imaging

Distribution of angles

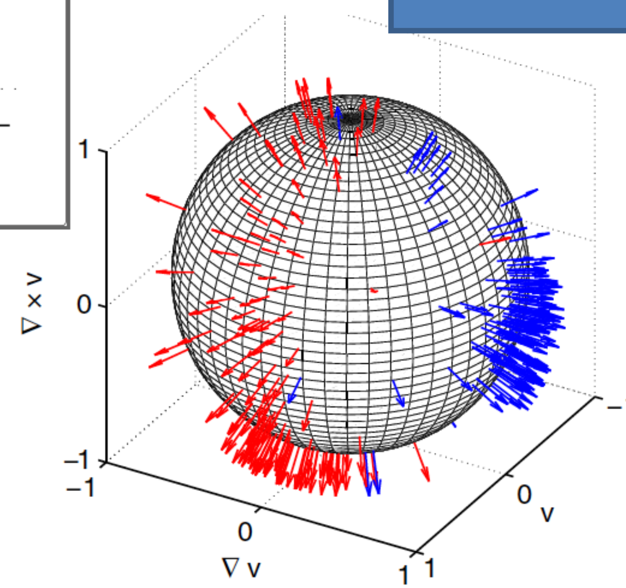
Stretched: IV



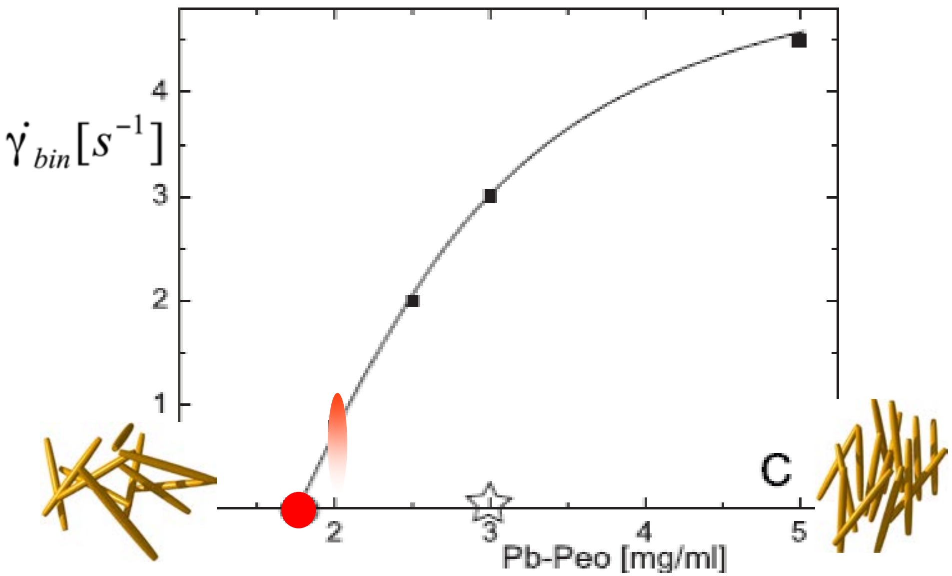


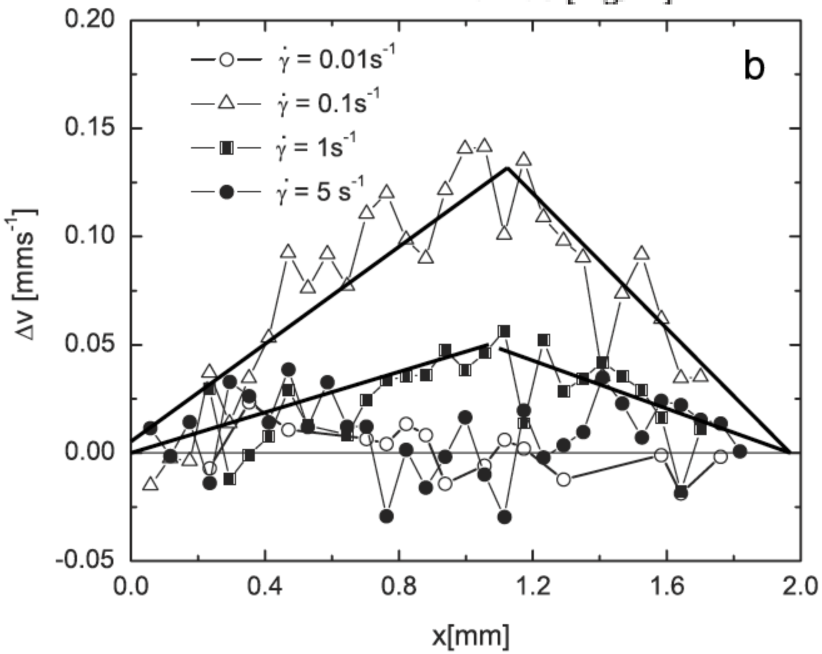


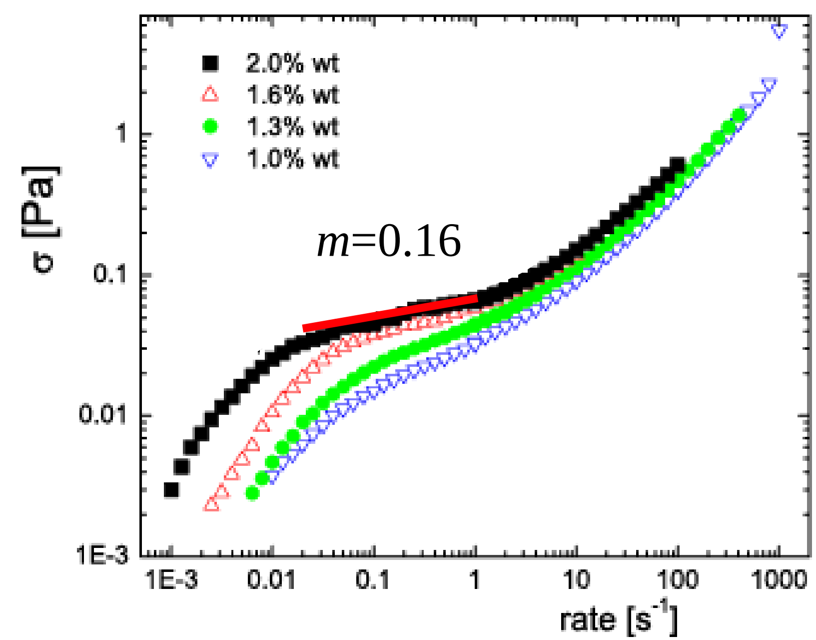
Bent: III



Non-equilibrium isotropic-nematic binodal

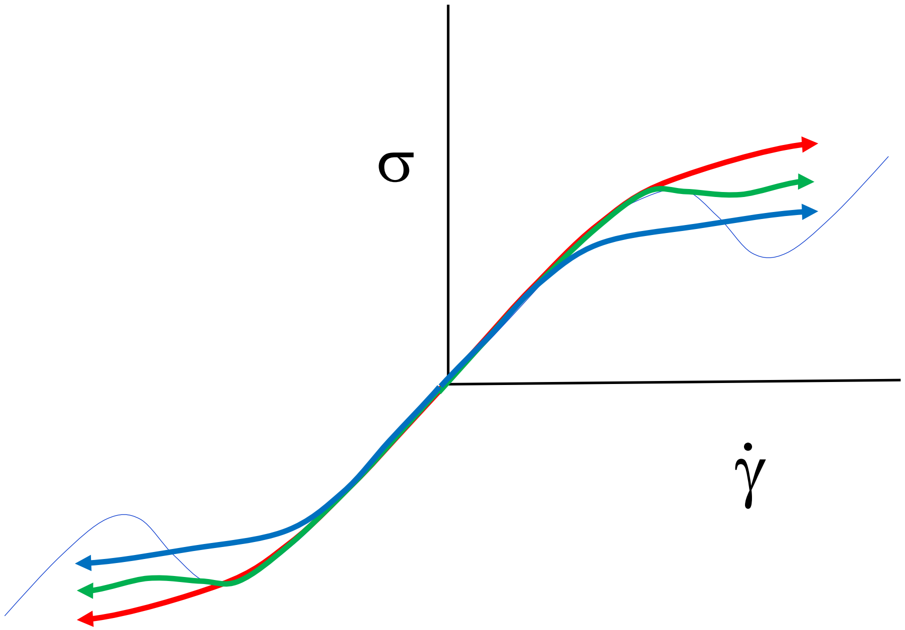


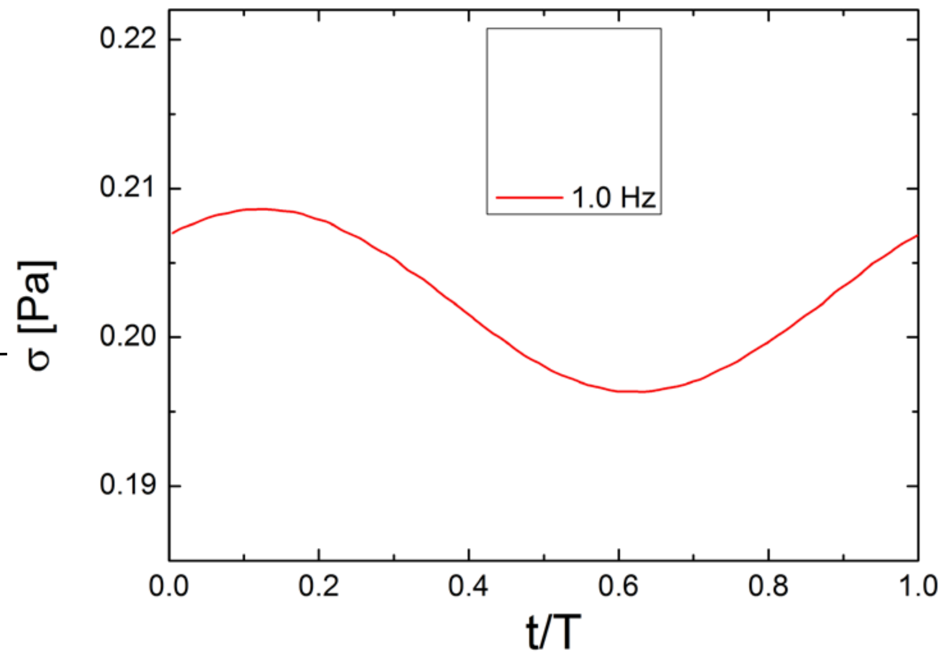




Probe dynamics

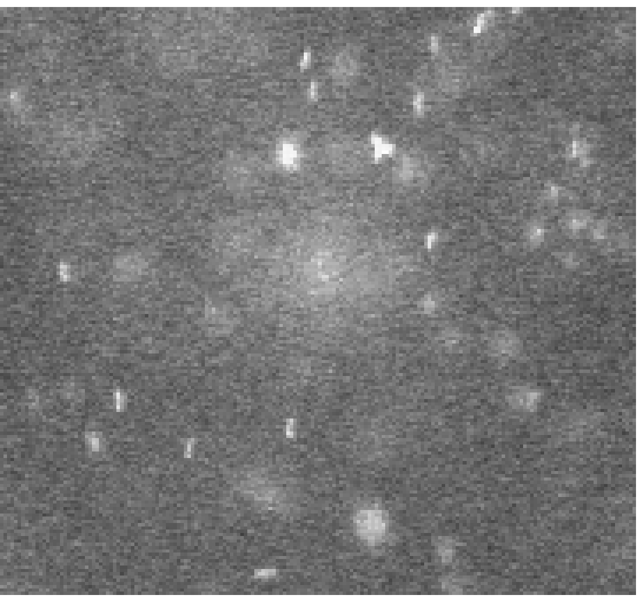
Probe dynamics with Large Amplitude Oscillatory Shear



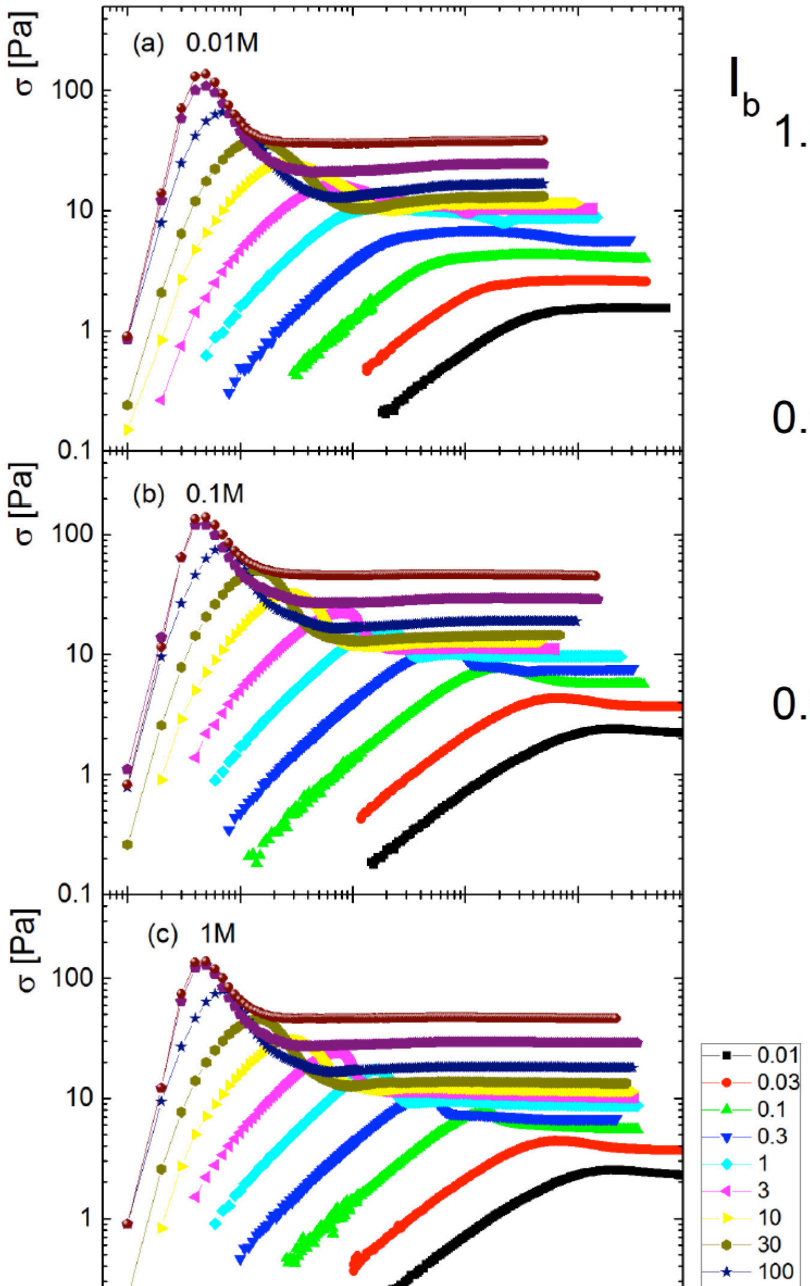


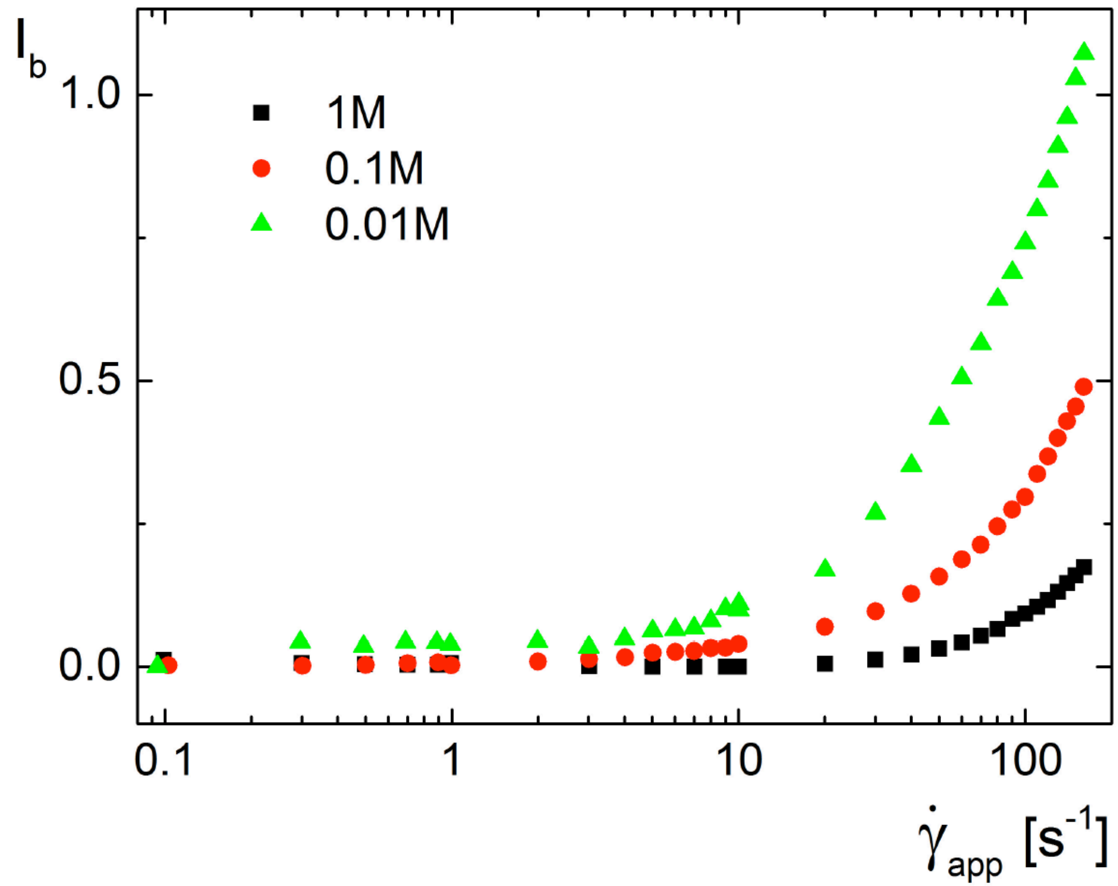
Probe structure with *in situ* scattering methods over broad range of length-scales and time-scales

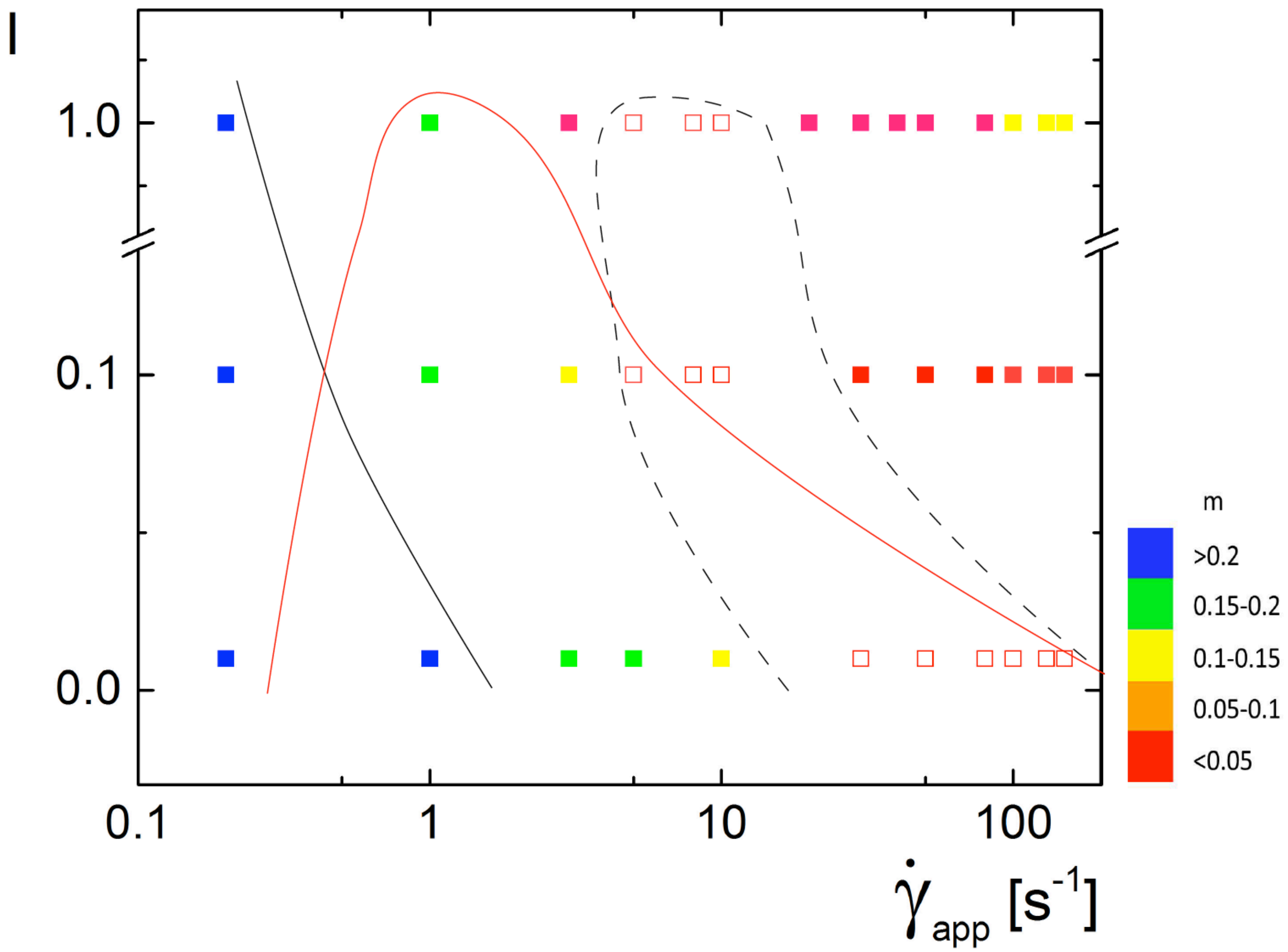
Complex flow: Complex fluids



start up on DNA at different ionic strngths







I
1.0
0.1
0.0
0.1
1
10
100
$\dot{\gamma}_{app}$ [s^{-1}]
m
>0.2
0.15-0.2
0.1-0.15
0.05-0.1
<0.05

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

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

Strong shear thinning does not mean that you will get Sms

F-actin, rod-to-polymer system

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 gamma_high and gamma 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 overstretche

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]

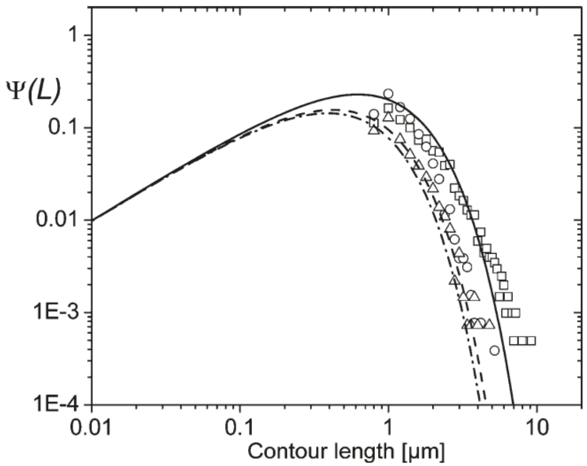


Figure 3. Probability density distribution of contour lengths for different molar fractions of DMF (solid line, square for $f = 0$; dashed line, circle for $f = 0.025$; dotted line, triangle for $f = 0.06$). The curves correspond to an exponential distribution with the parameters determined by DLS. The 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# (bp)	Range# (nm)	SD§ (bp)	M_w/M_n¶	$C_i^{\|}$ (mg/ml)
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