Mitglied der Helmholtz-Gemeinschaft

JÜLICH FORSCHUNGSZENTRUM

KU LEUVEN

Probing microstructural origin of complex flow behavior

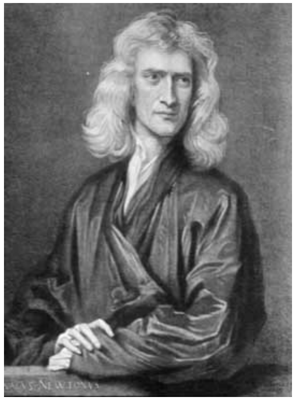
Pavlik Lettinga

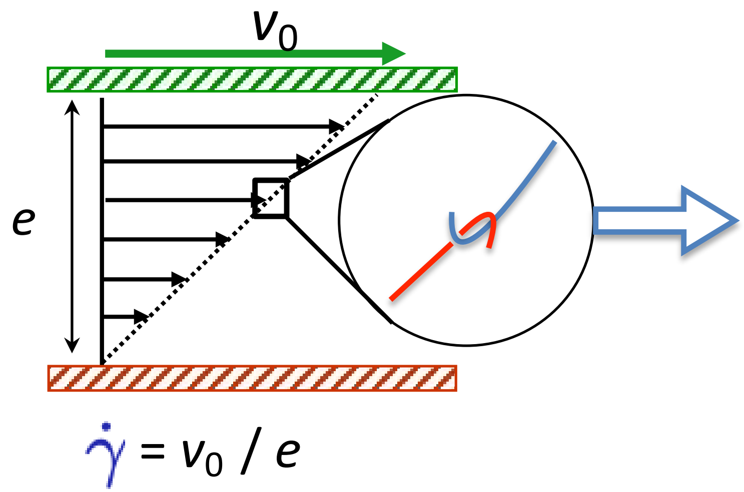
UdL, 2nd February 2018

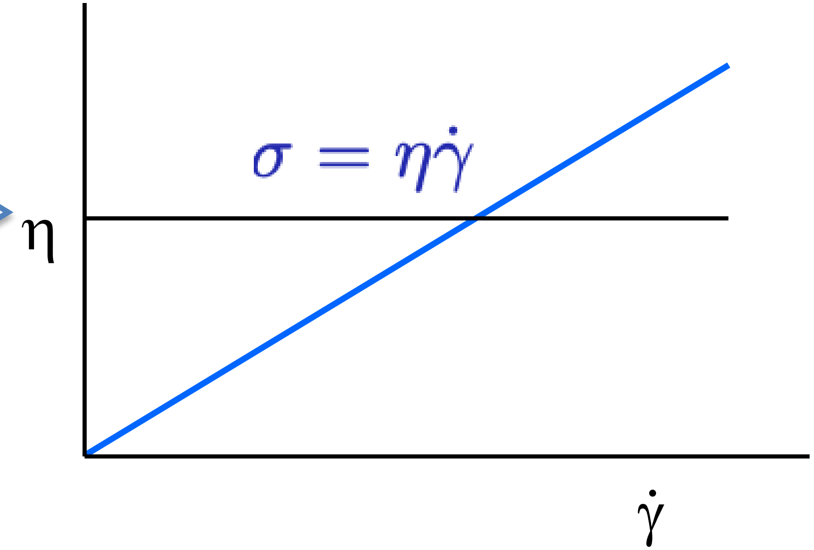
Acknowledgements

Hu Tang
Manolis Stiakakis
Tatjana Kochetkova

Ideal Newtonian fluids

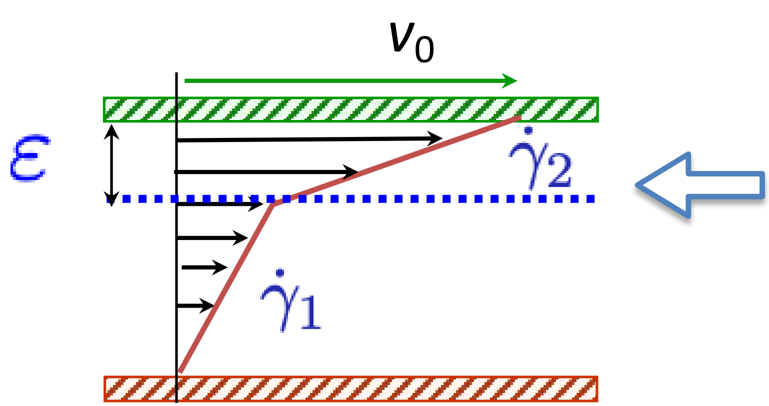




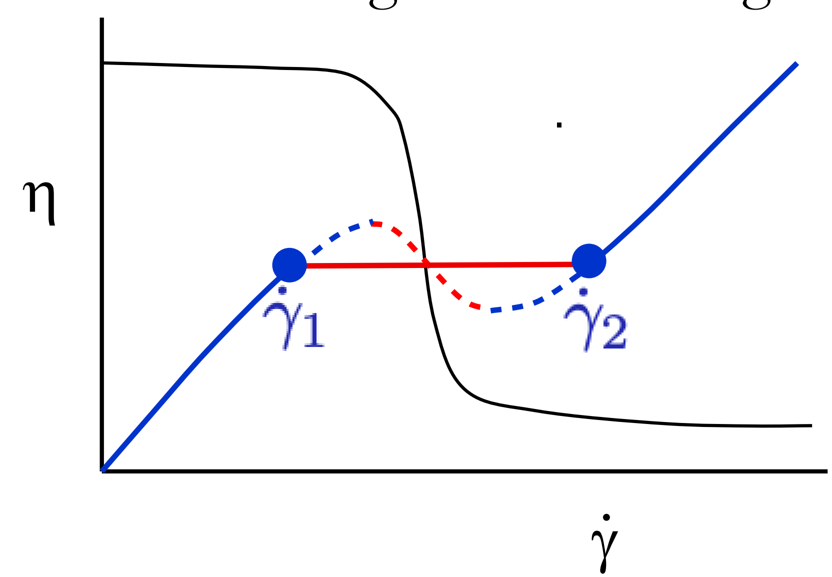


Non-linear Newton: shear thinning fluids

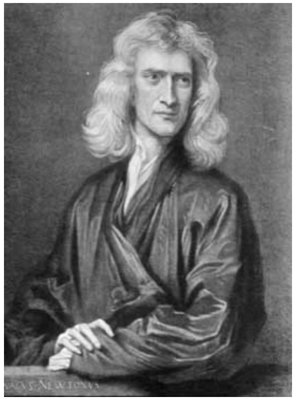
Flow instabilities: shear banding

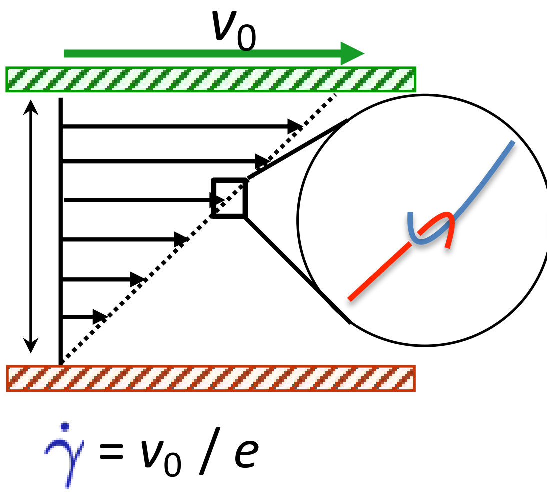


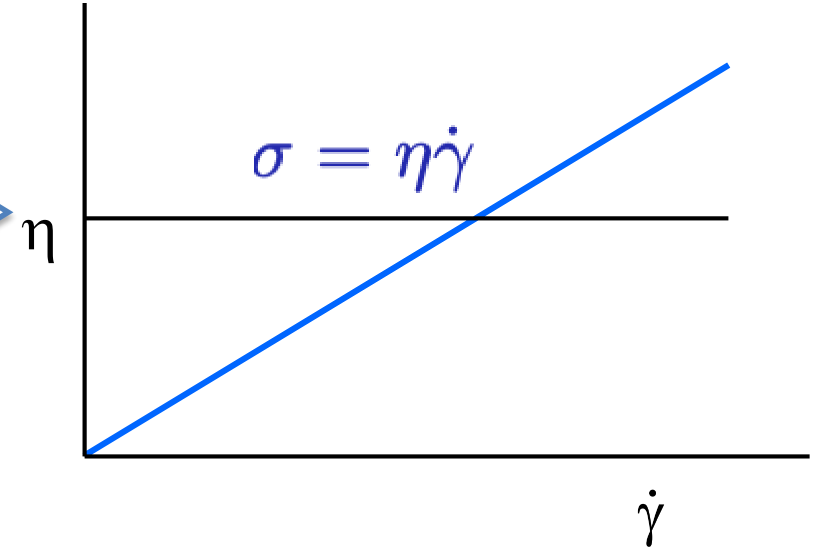
strong shear-thinning



Ideal Newtonian fluids

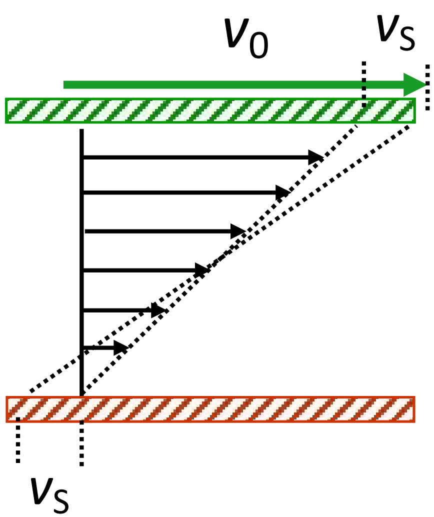




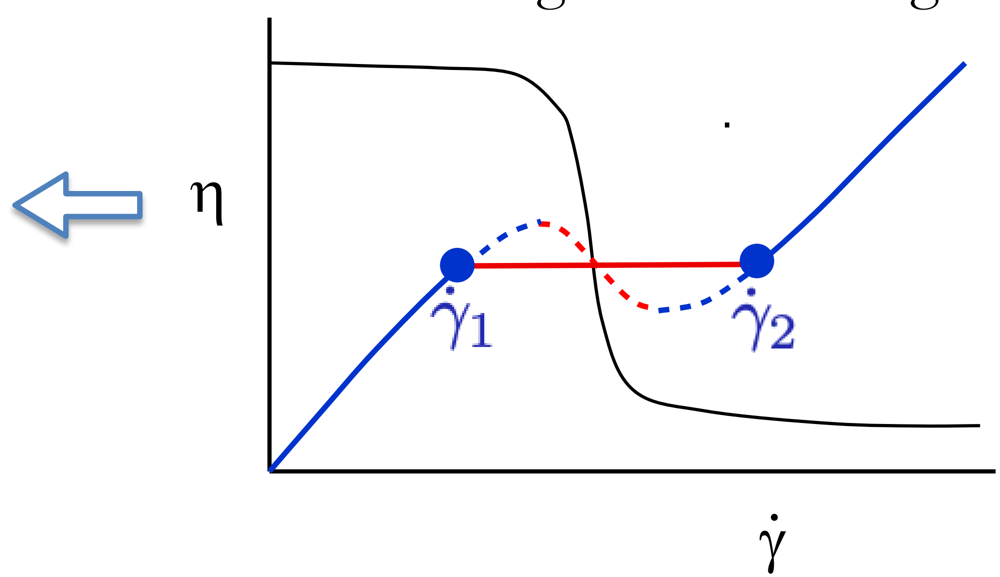


Non-linear Newton: shear thinning fluids

…or slip

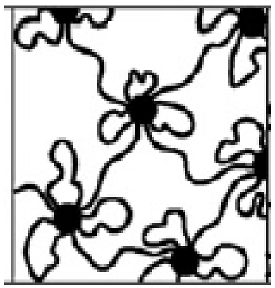


strong shear-thinning



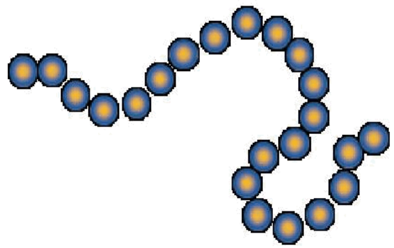
Possible shear thinners

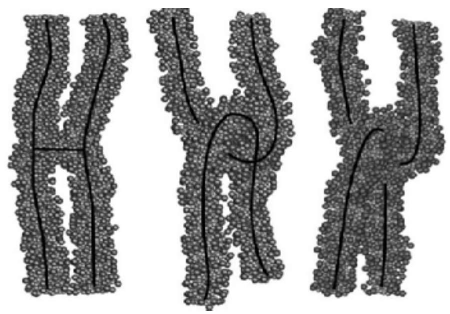
Living gels:



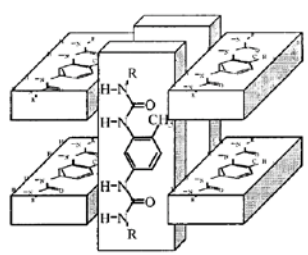
Sprakel et al, Soft Matter, **4**, (2008) 1696

Living polymers:



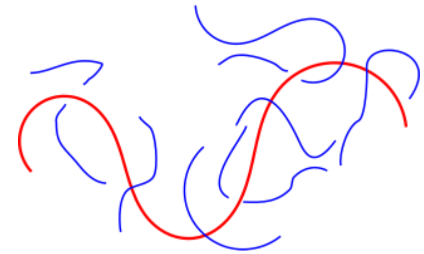


M. P. Lettinga and S. Manneville, *Phys. Rev. Lett.*, **103** 2009

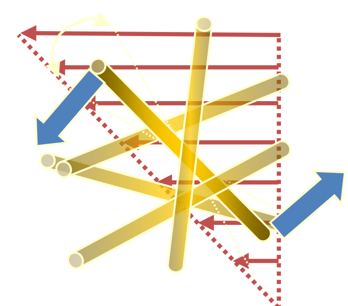


Van der Gucht et al Phys. Rev. Lett., **97**, (2006) 108301

Stiff Polymers:



Rods:



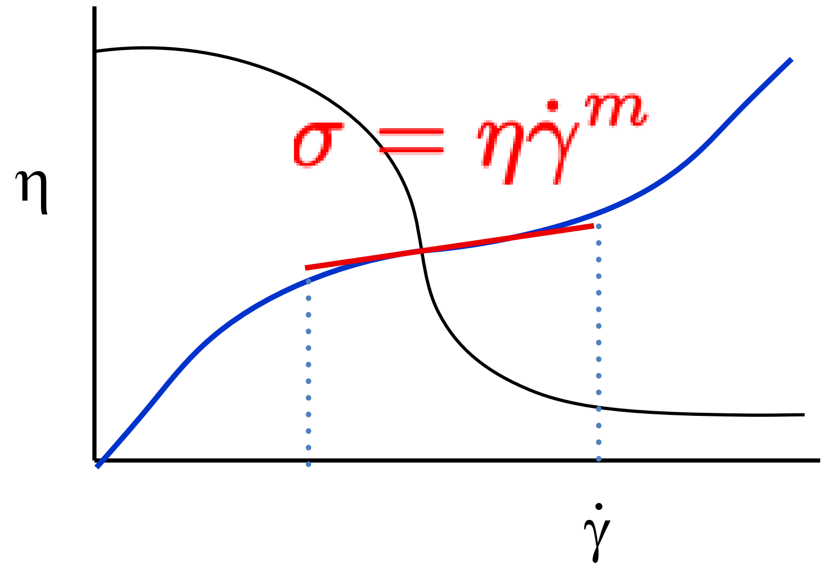
Main questions:

Molecular origin of shear band formation:

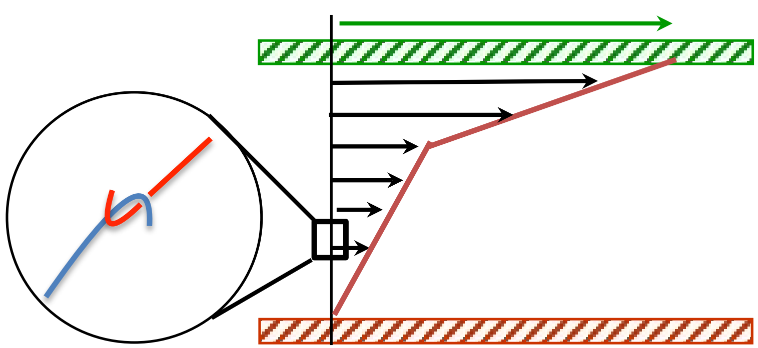
Can polymer shear band?

Can rods shear band?

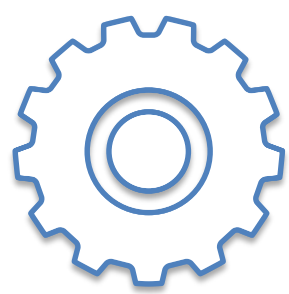
- How strong is strong?

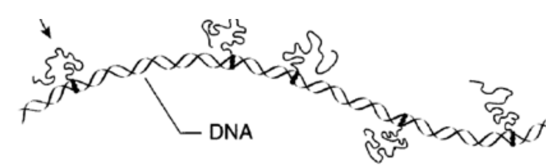


- Always shear banding for given *m*, or is it system dependent?



- Can we tune shear band formation?





Main questions:

Molecular origin of shear band formation:

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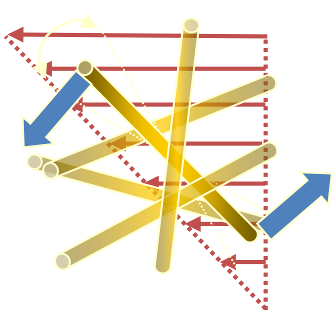
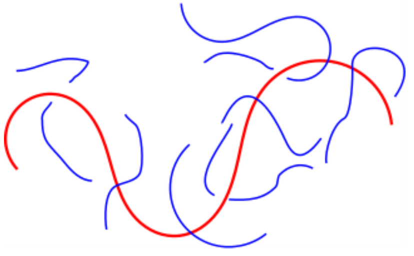
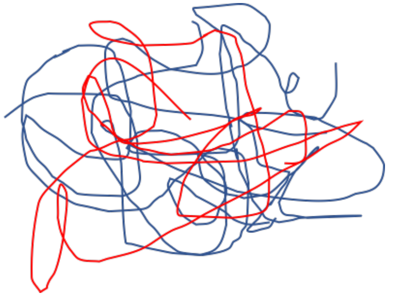
Rods:



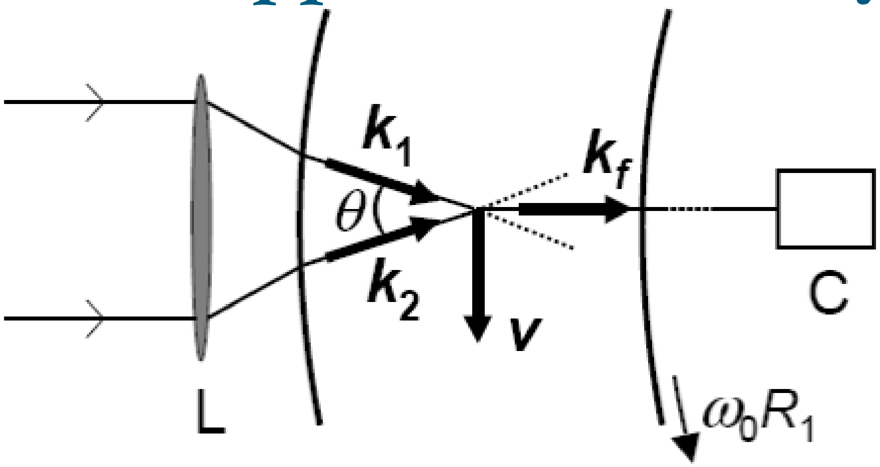
Stiff Polymers:

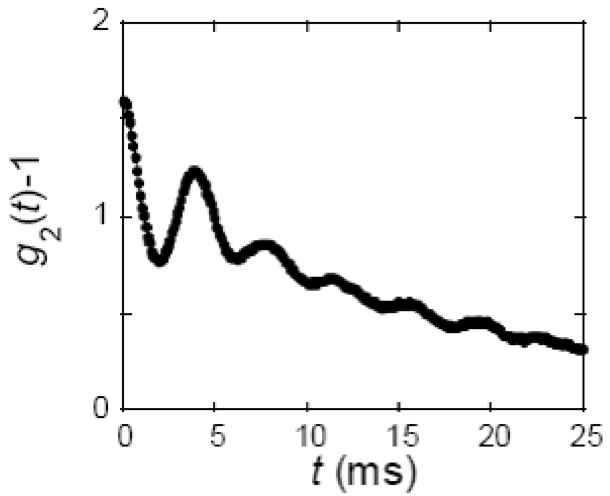


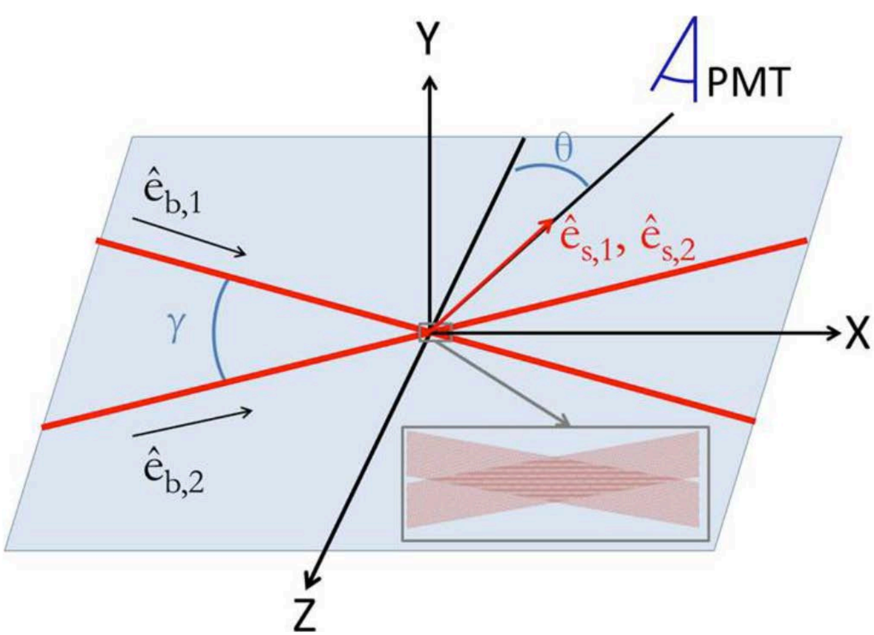
flexible Polymers:



Probe the stability of flow with Laser Doppler Velocimetry



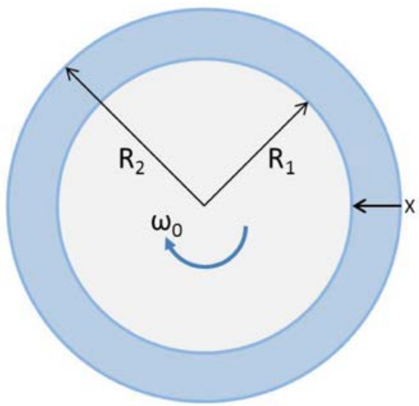


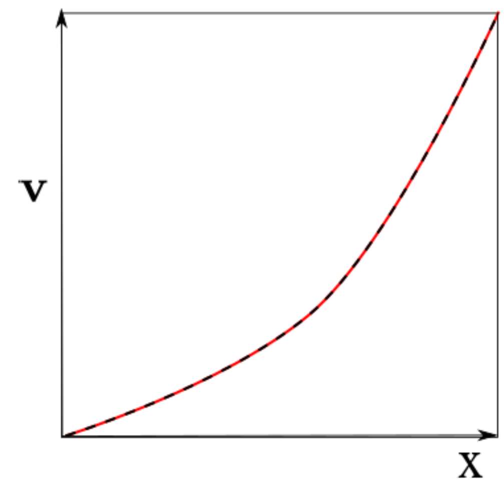


Analyse velocity profiles

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

Account for curvature cell:

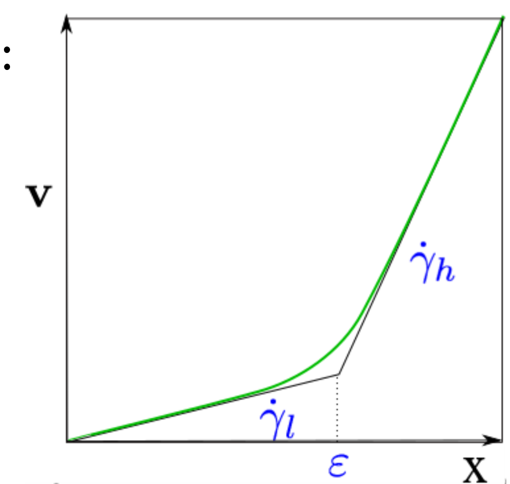




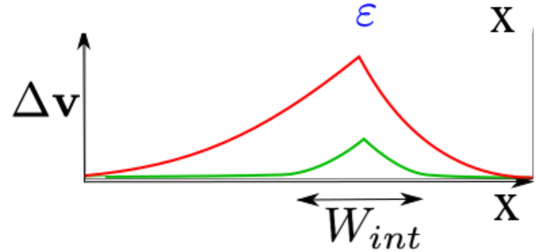
m

compare with m_{fc}

Shear banding with interface:

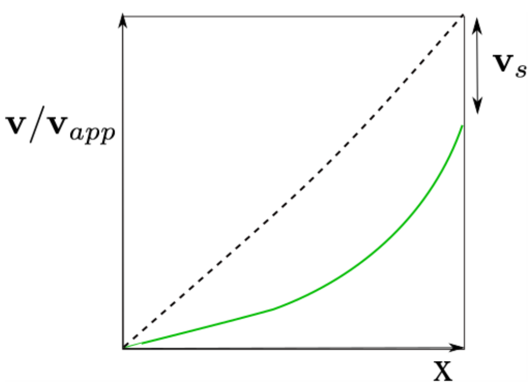


$\dot{\gamma}_h \; \dot{\gamma}_l \; \varepsilon$



W_{int}

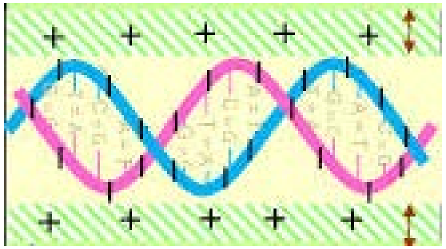
Wall slip:

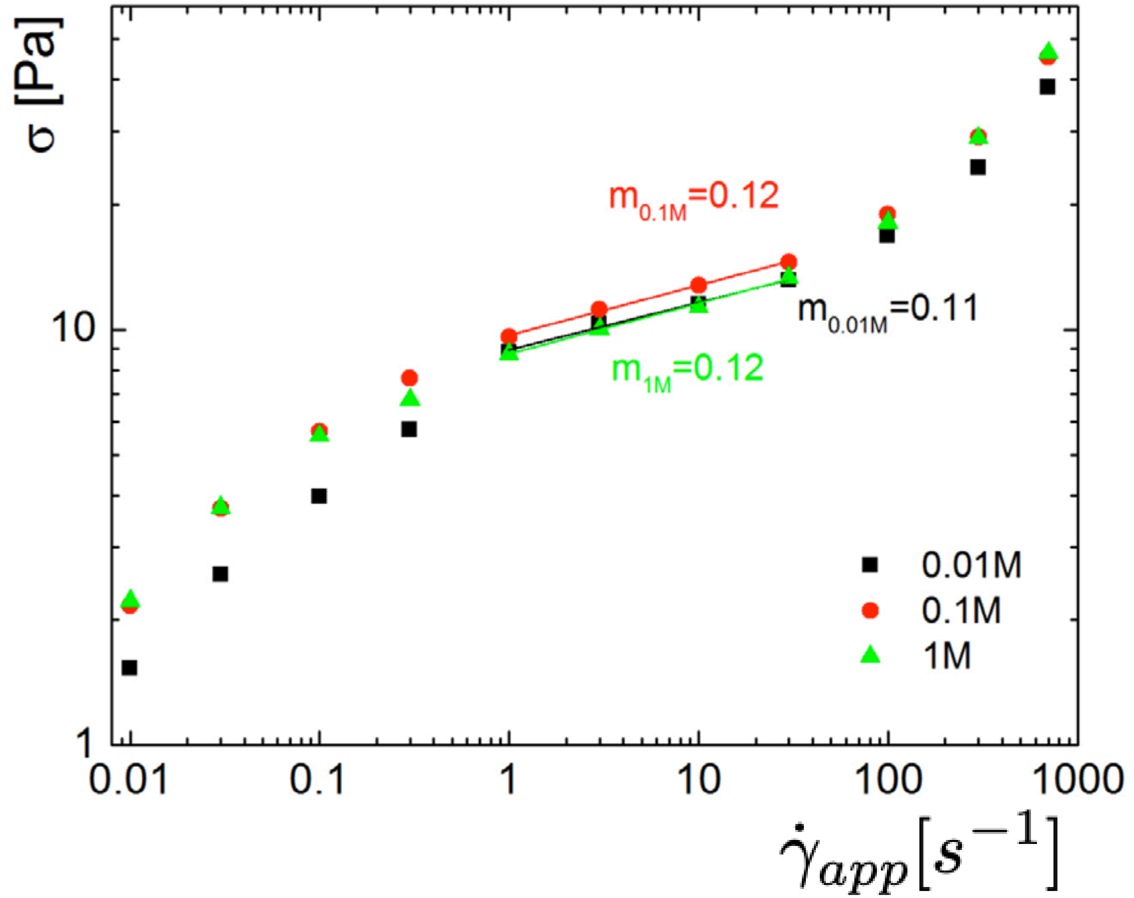


DNA, the tuneable polymer part I

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

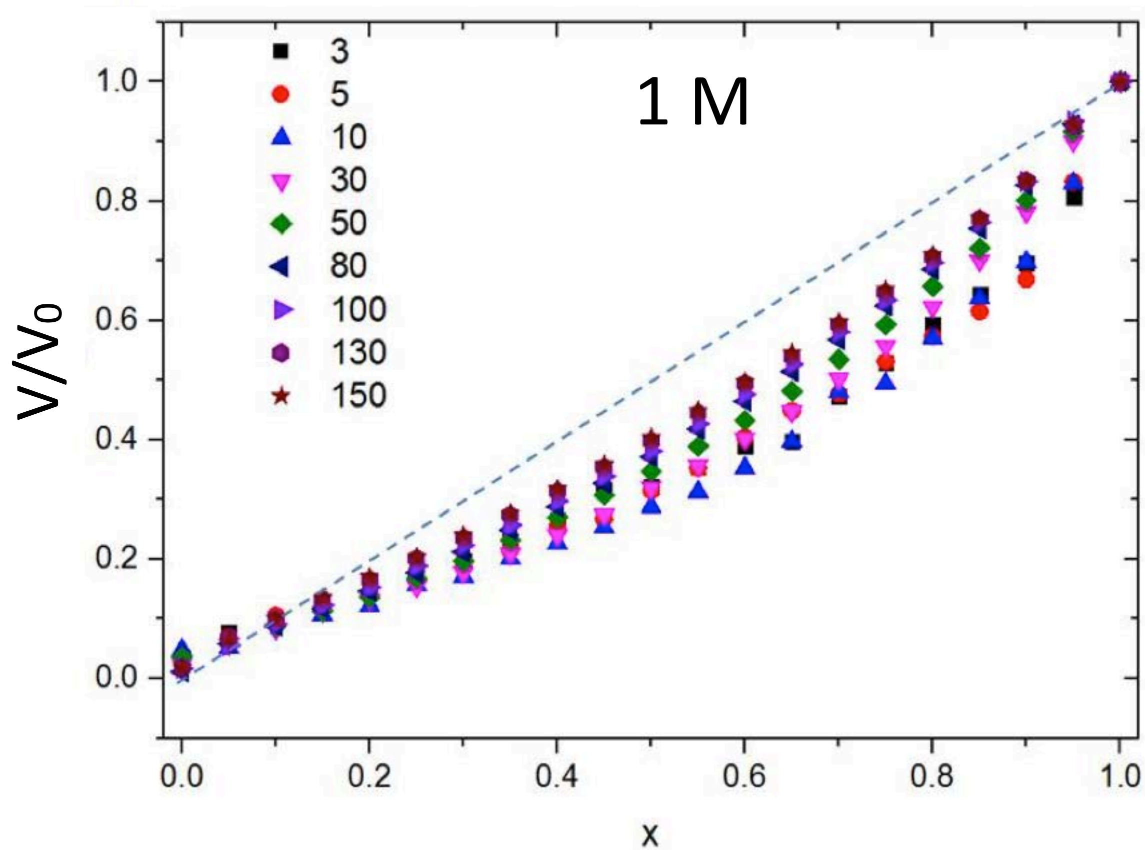
Tune repulsion by adding salt:





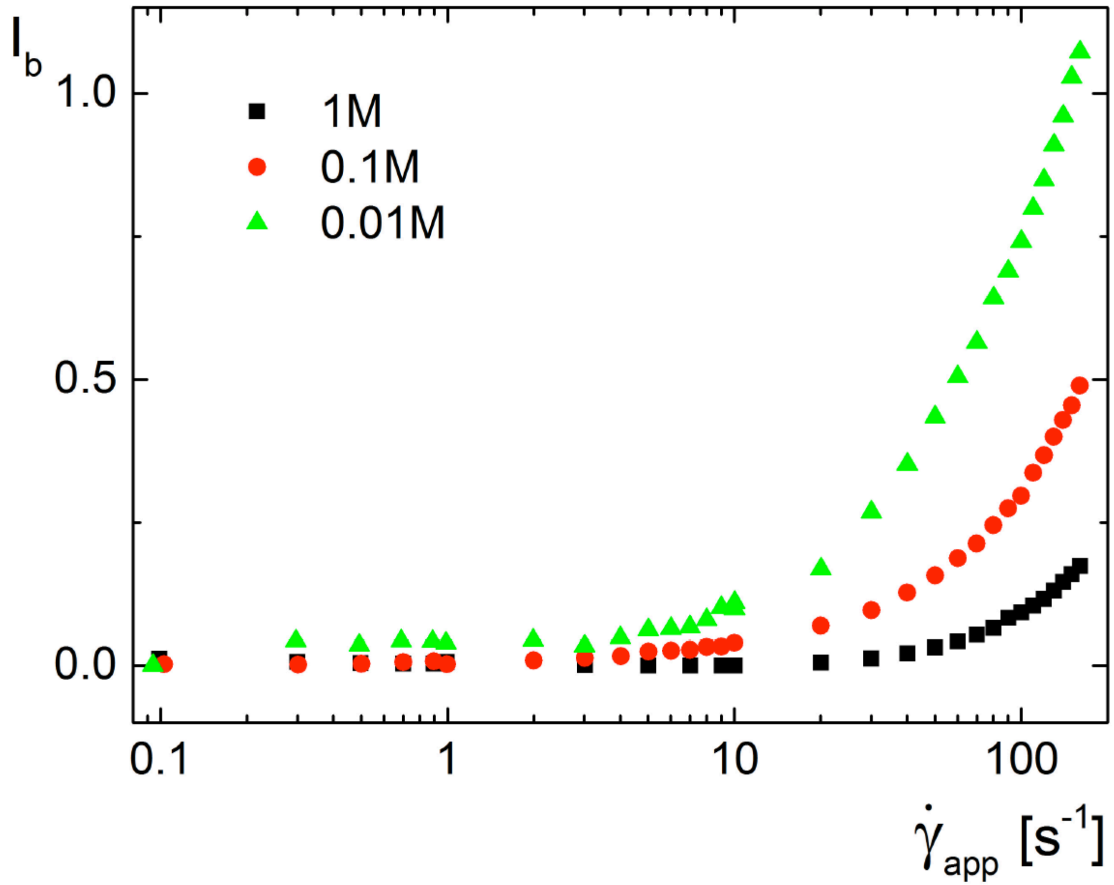
concentration: 0.7 mg/ml

Tuning by addition of salt



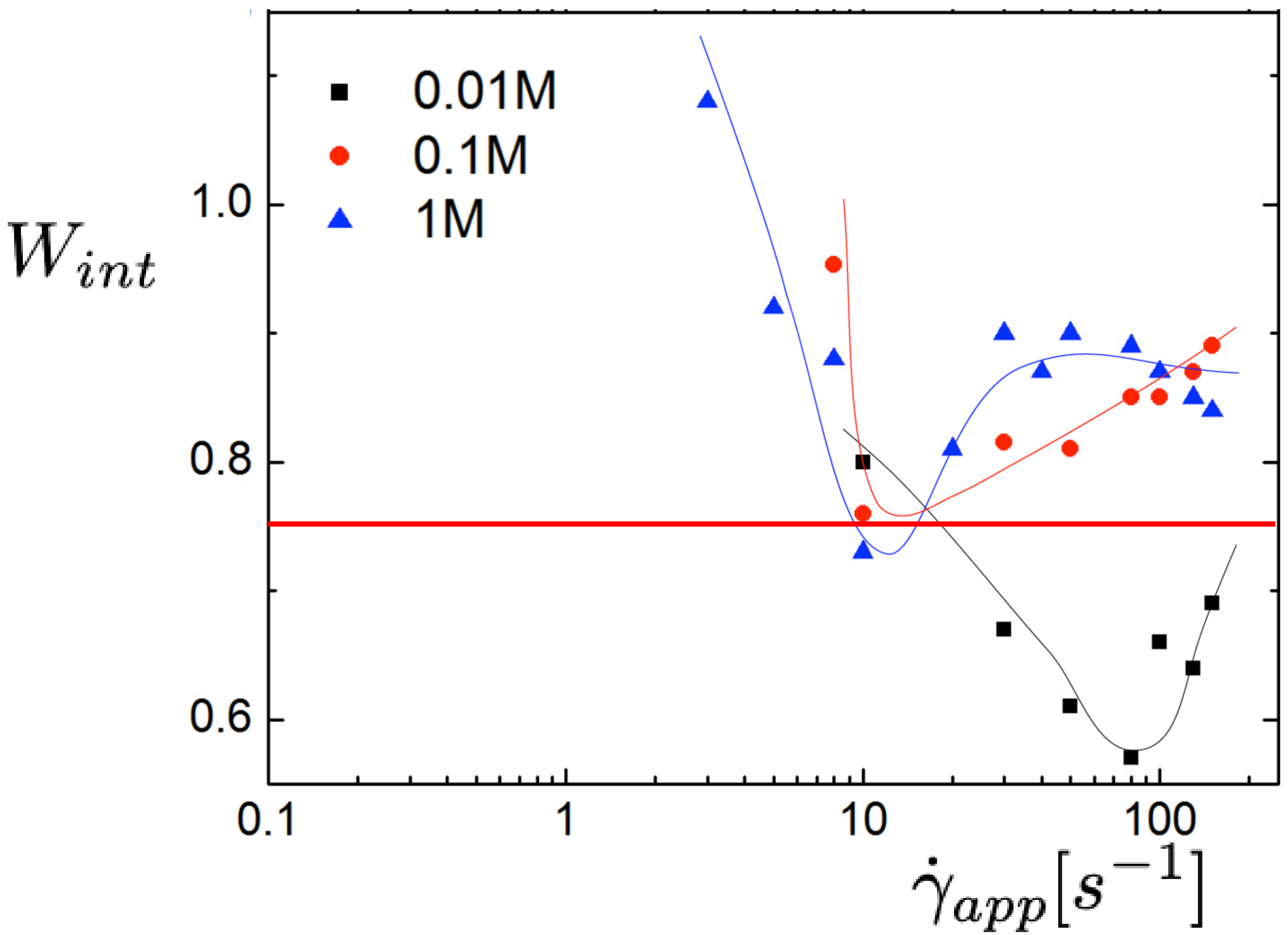
- Bands disappear at equal thinning m_{fc}

Tuning by addition of salt



- 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…

- 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: shear banding can exist with broad interface when $m<m_{fc}$

- Can we tune shear band formation?

Yes, a bit

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

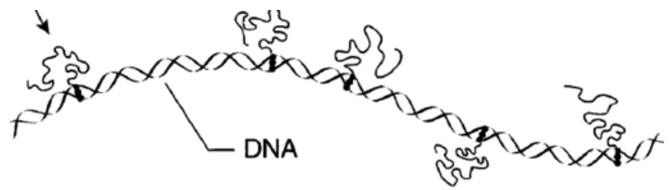
- Is it charge or stiffness?

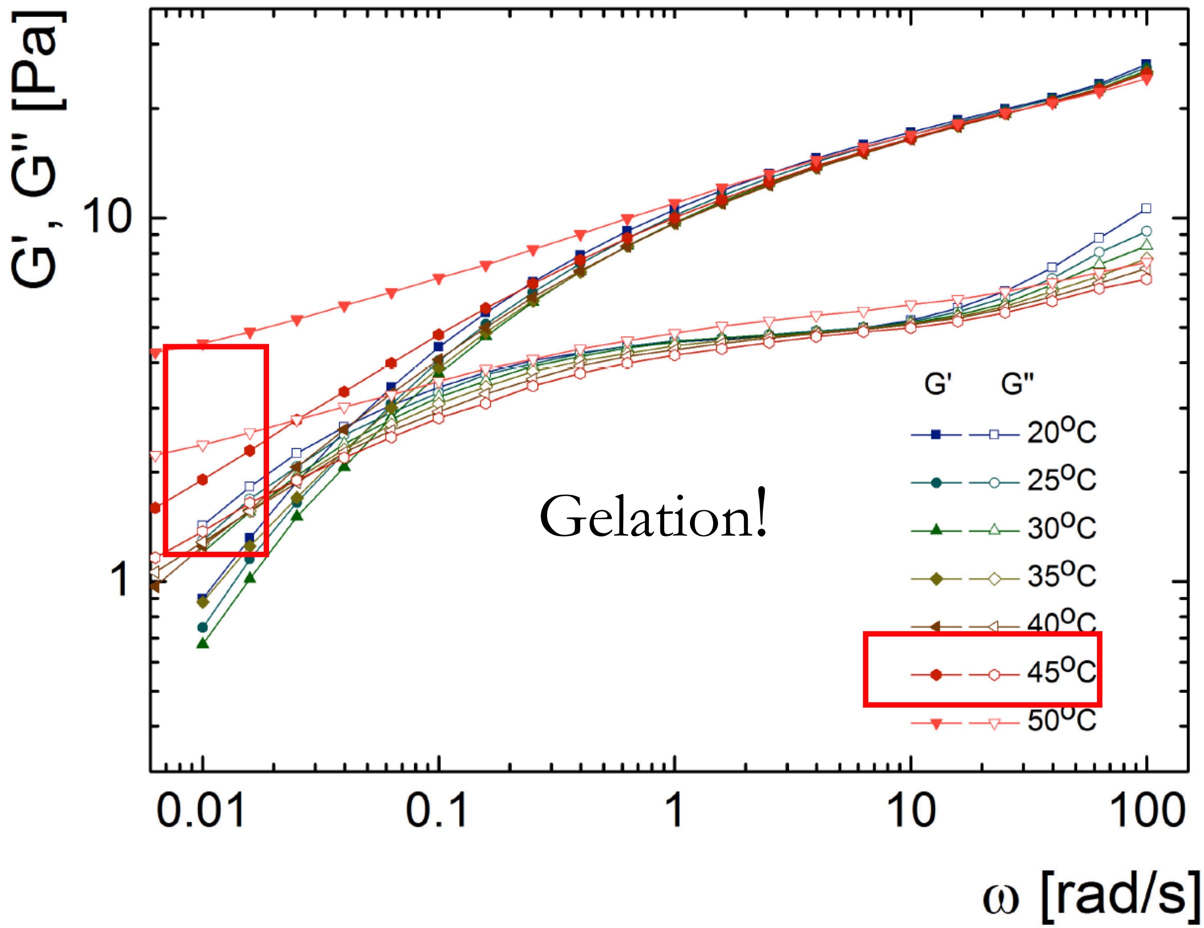
It is stiffness because SB observed for neutral PB-PEO micelles Lonetti et al, J. Phys. Rond. Matt. 2011

- New question: Can we force collapse?

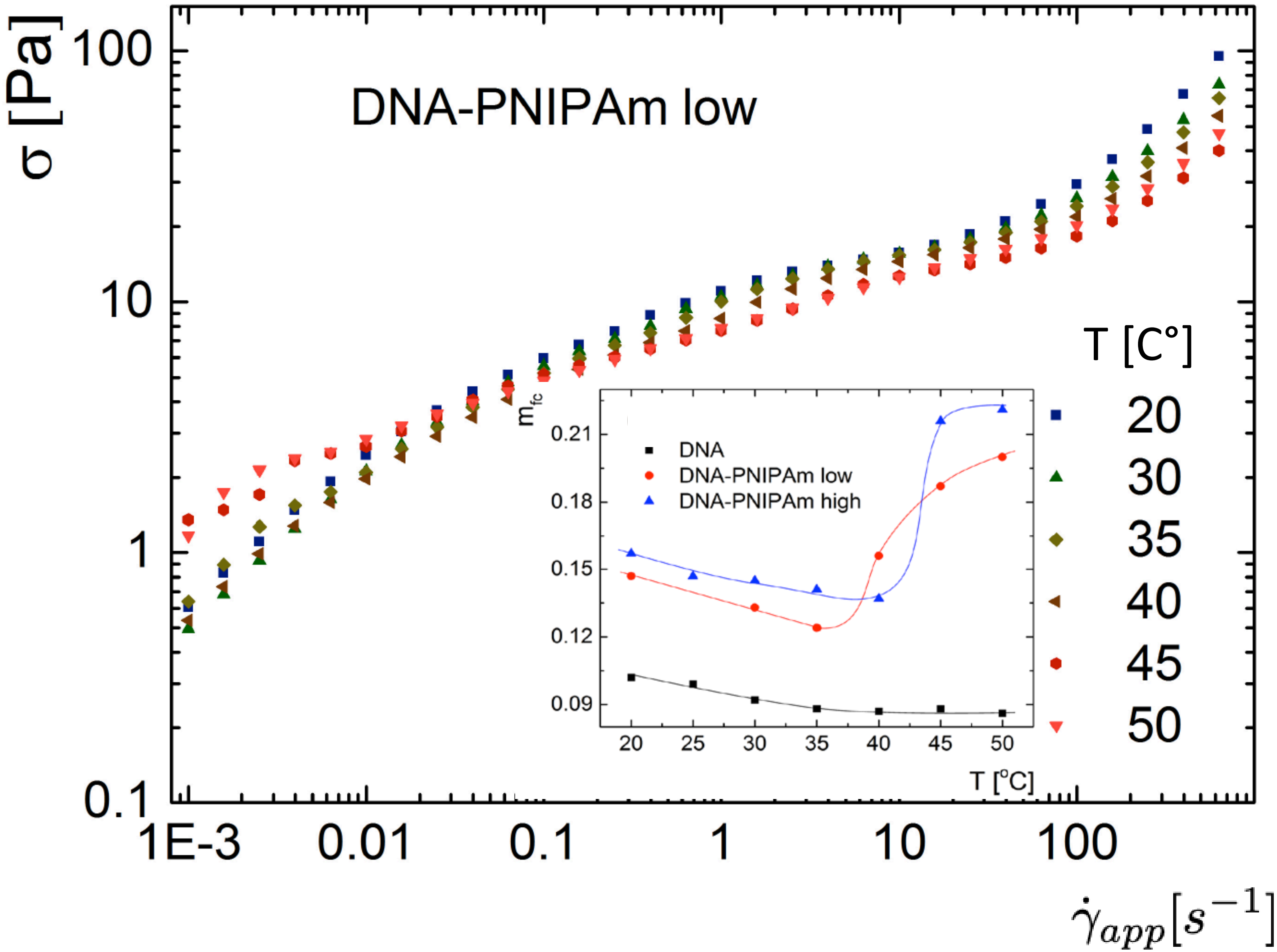
DNA, the tuneable polymer part II

Tune attraction by adding T-sensitive brush (PNIPAm)





Tuning by increasing attraction



Tuning by increasing attraction

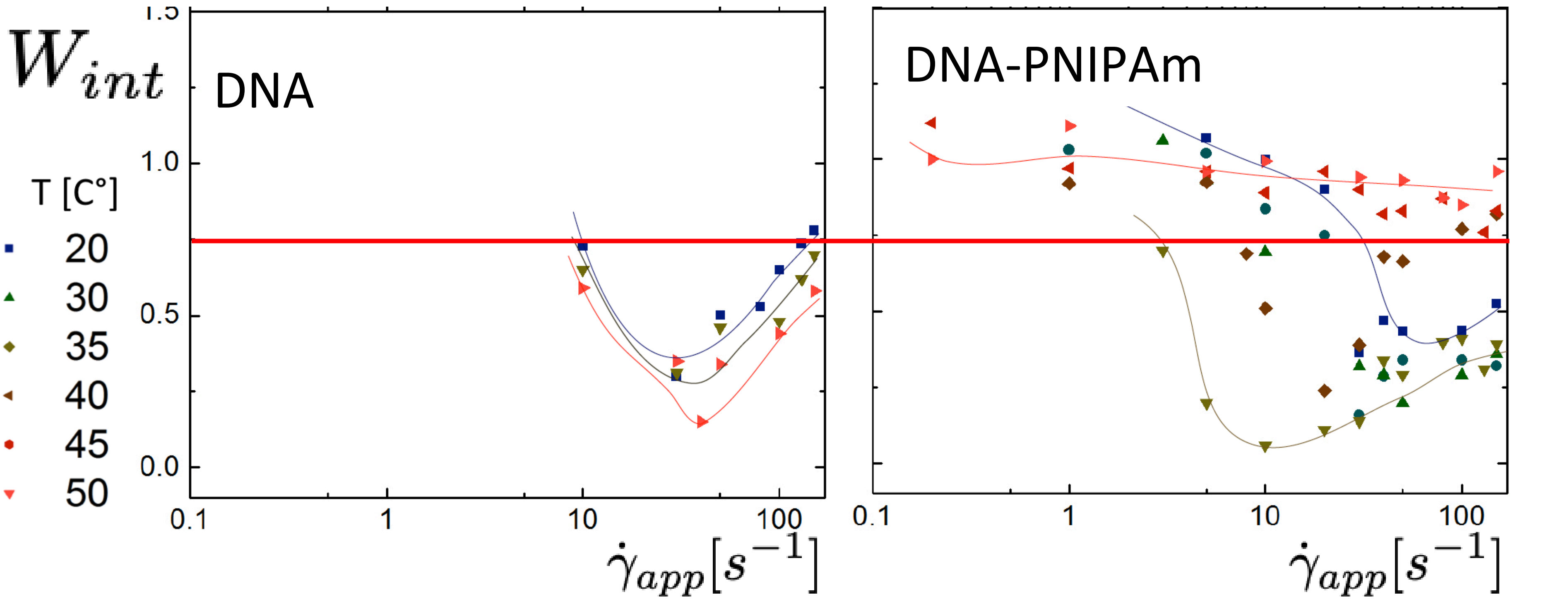


Diagram of states

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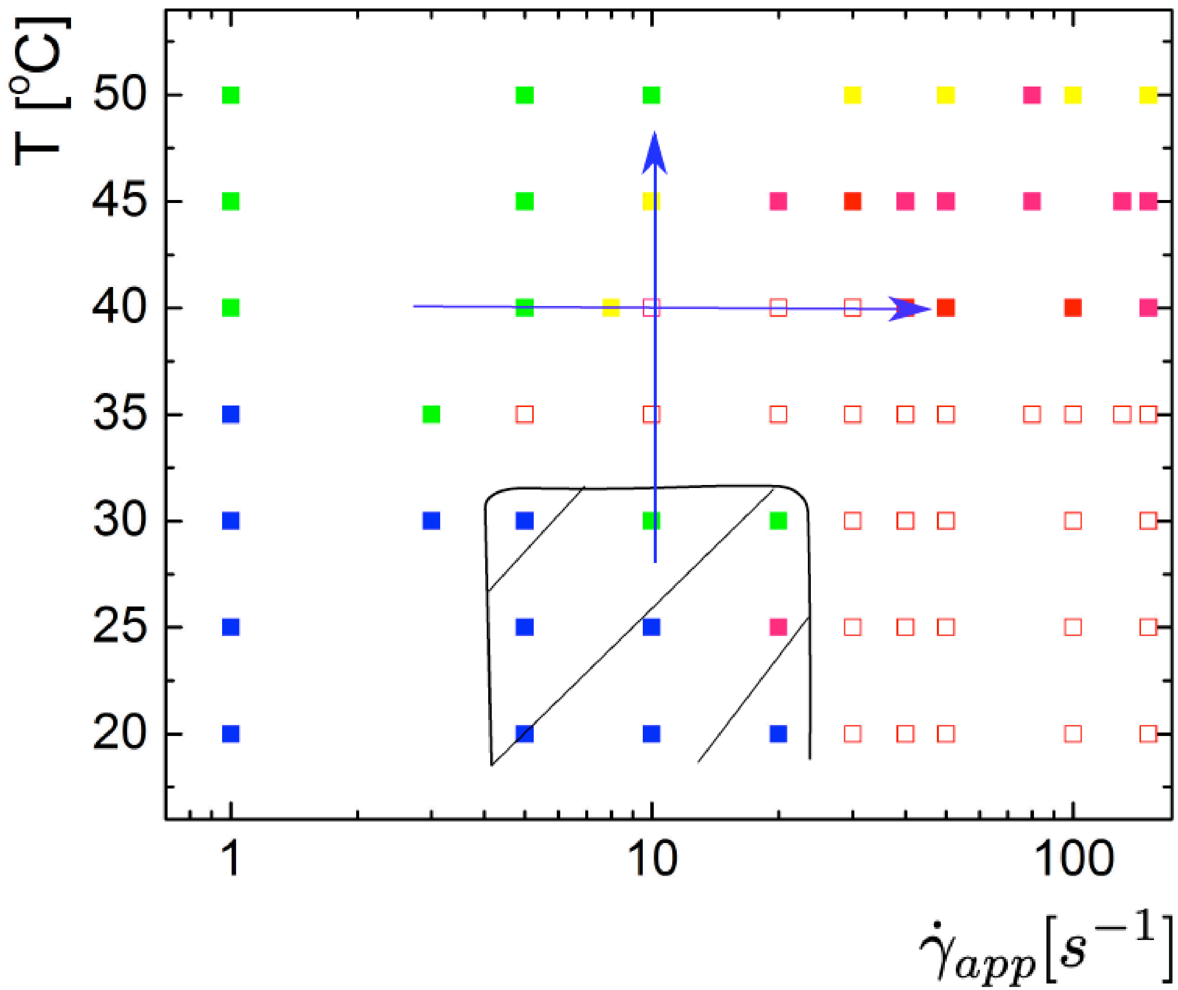
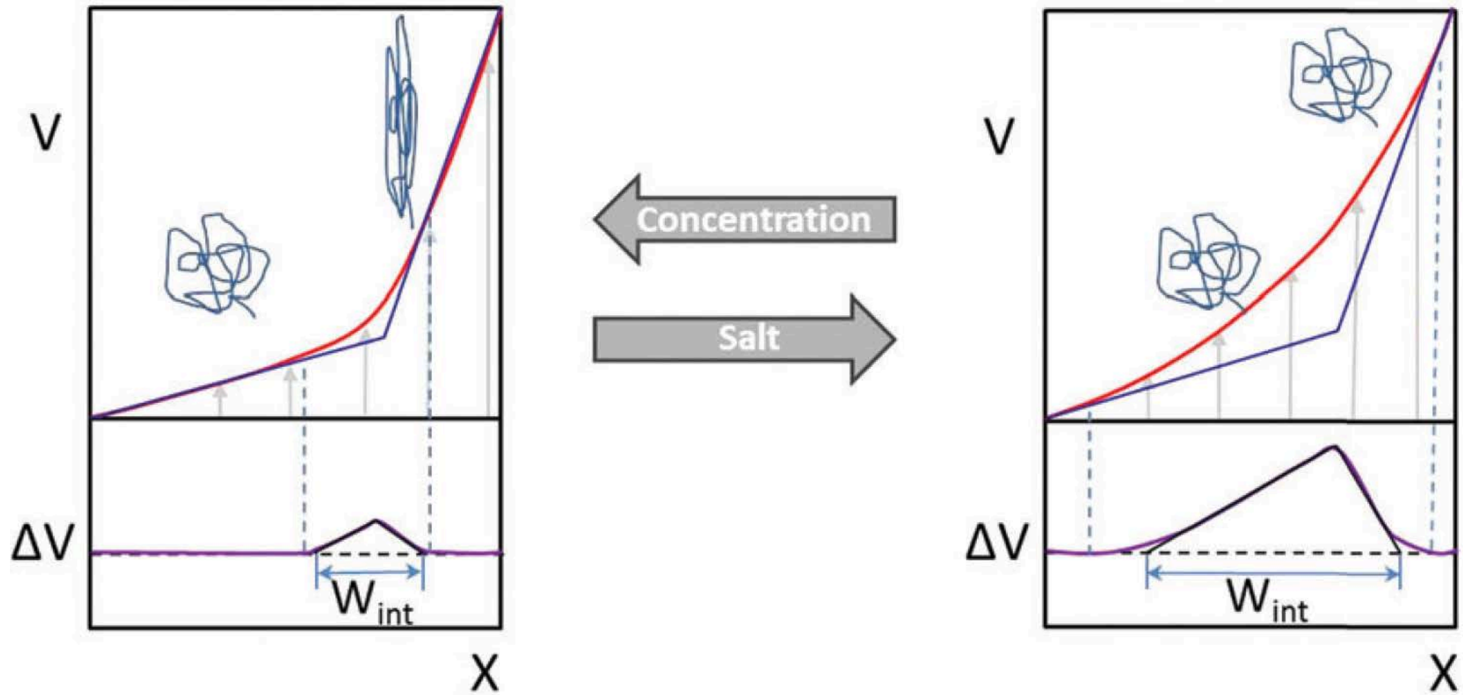


- Attraction suppresses shear band formation (and orientation)
- Re-entrant behavior in two directions

Conclusions

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

Mechanism?



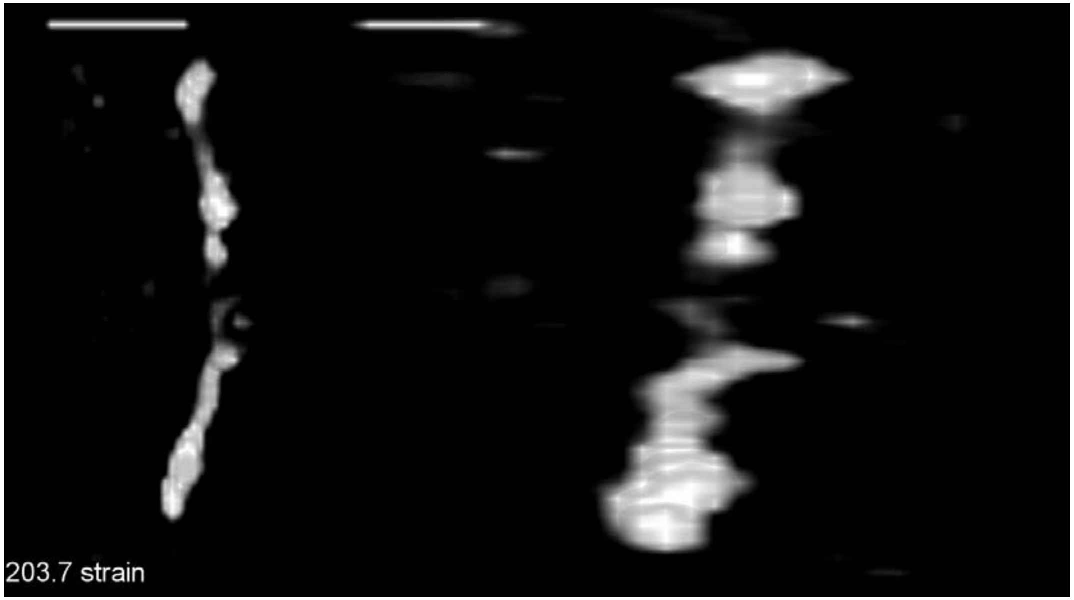
Adams&Olmsted , PRL, 2009

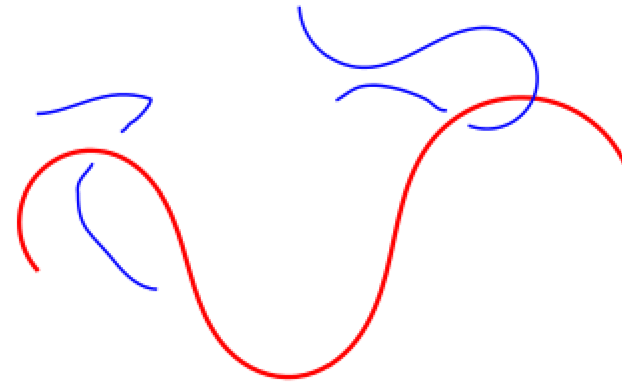
$$(\partial_t + \mathbf{v}\cdot\nabla)\boldsymbol{\Sigma} - (\nabla\mathbf{v})\cdot\boldsymbol{\Sigma} - \boldsymbol{\Sigma}\cdot(\nabla\mathbf{v})^T + \frac{1}{\tau_d}\boldsymbol{\Sigma} = 2\mathbf{D} - \frac{2}{\tau_R}(1 - A)[\mathbf{I} + \boldsymbol{\Sigma}(1 + \beta A)] + \mathcal{D}\nabla^2\boldsymbol{\Sigma}$$

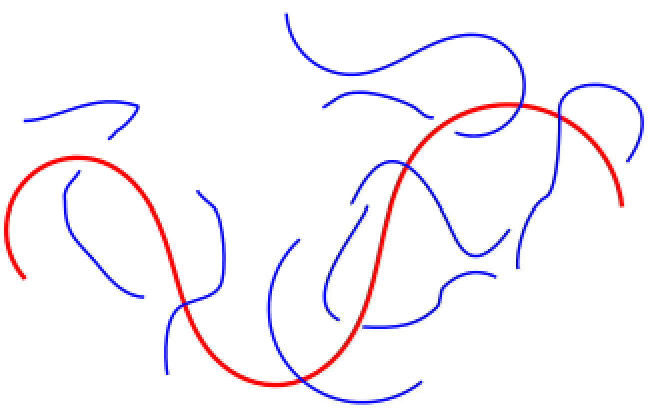
- Shear banding is suppressed when chain collapses after disentanglement , *or* alignment supports interface
- Collapse affects the shear-curvature viscosity

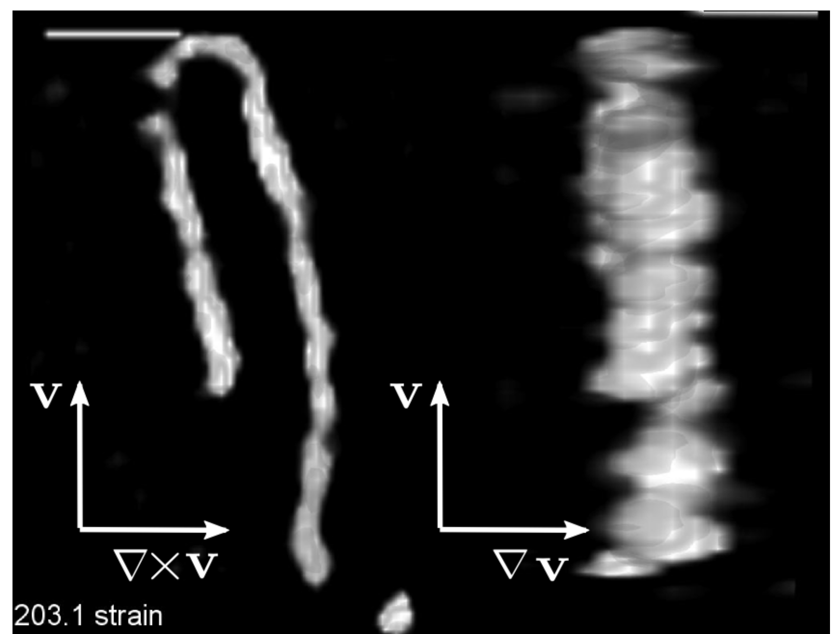
- Shear banding is suppressed when system is not long enough

Sheared F-Actin in 3-D



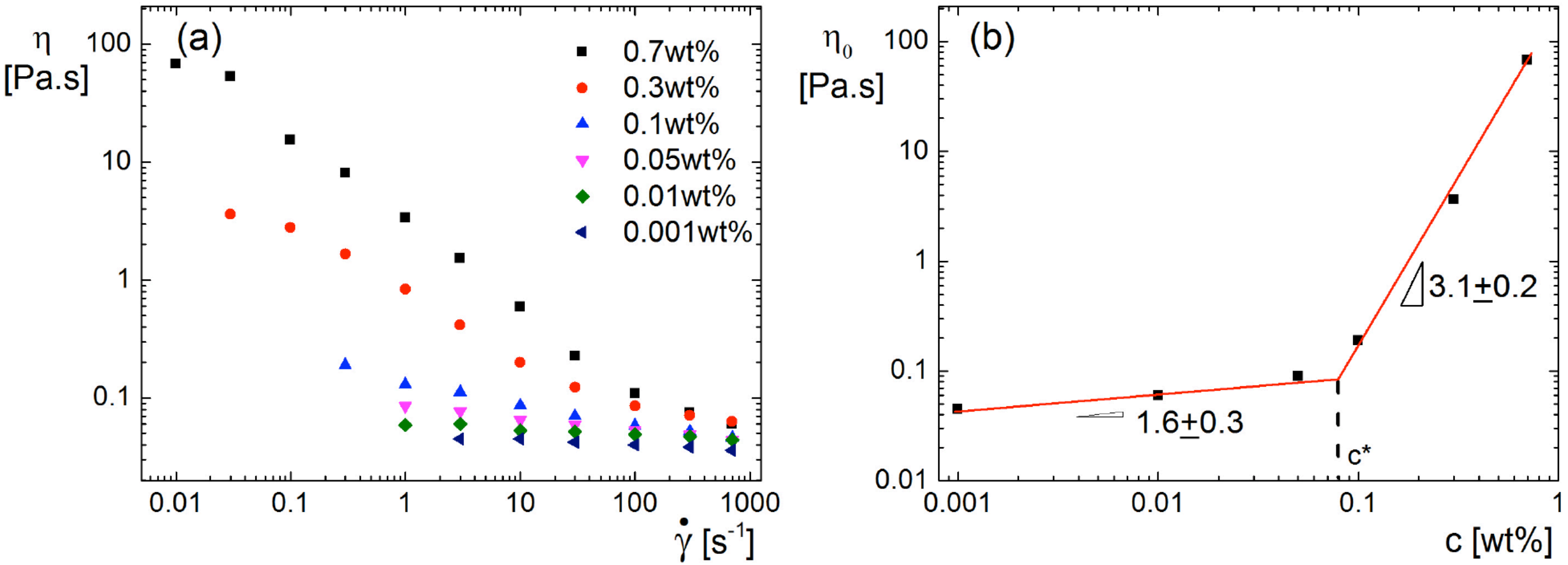




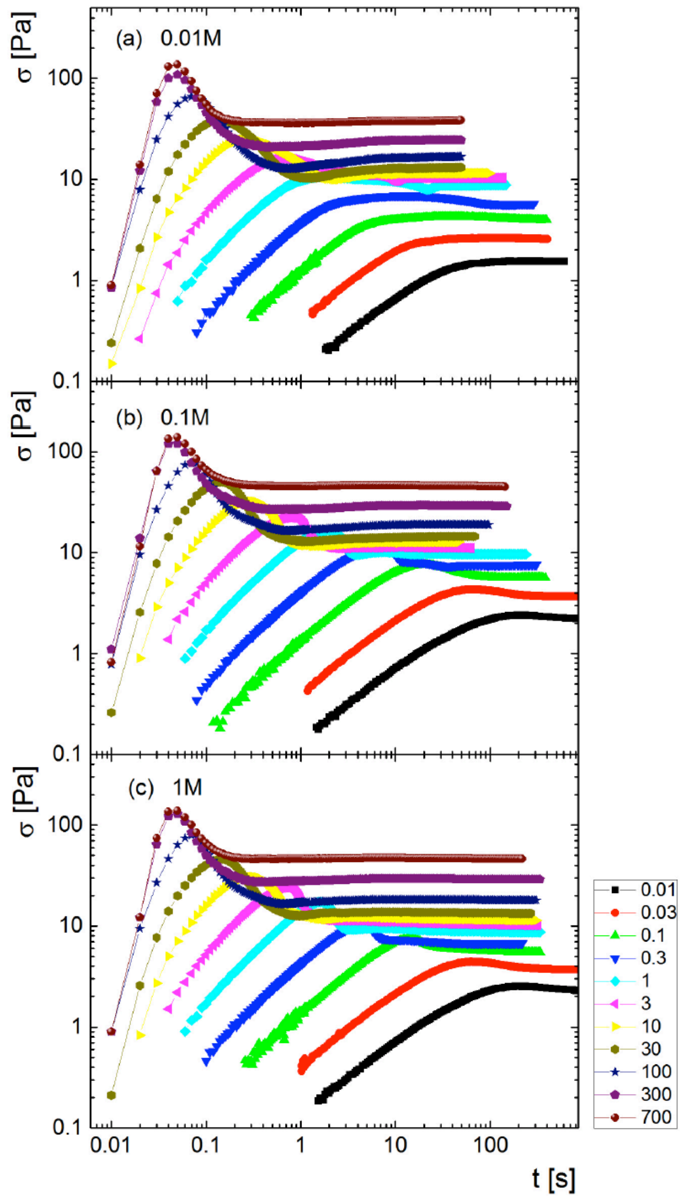


Kirchenbüchler et al *Nature Communications* 5:5060 (2014)

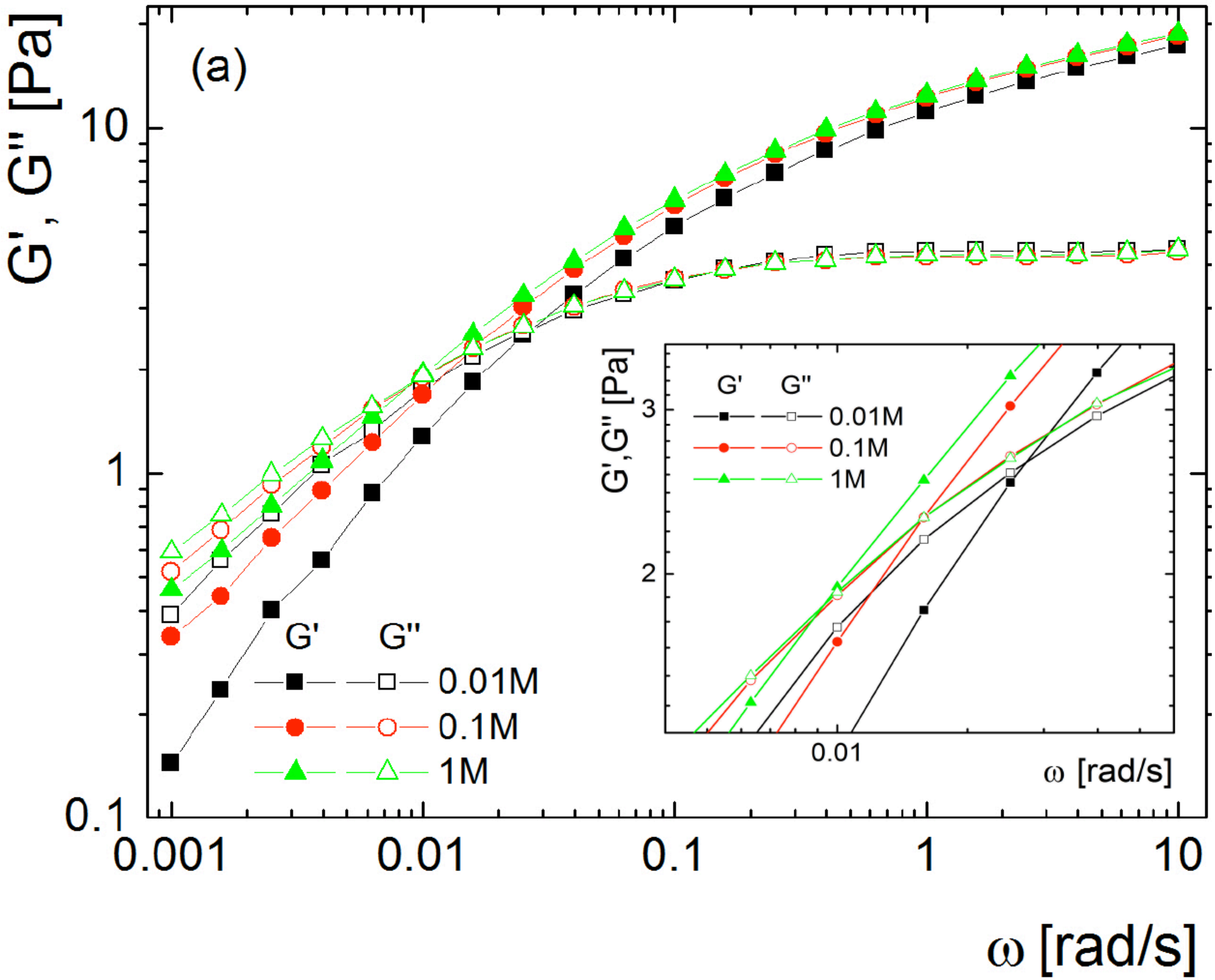
Entangled DNA



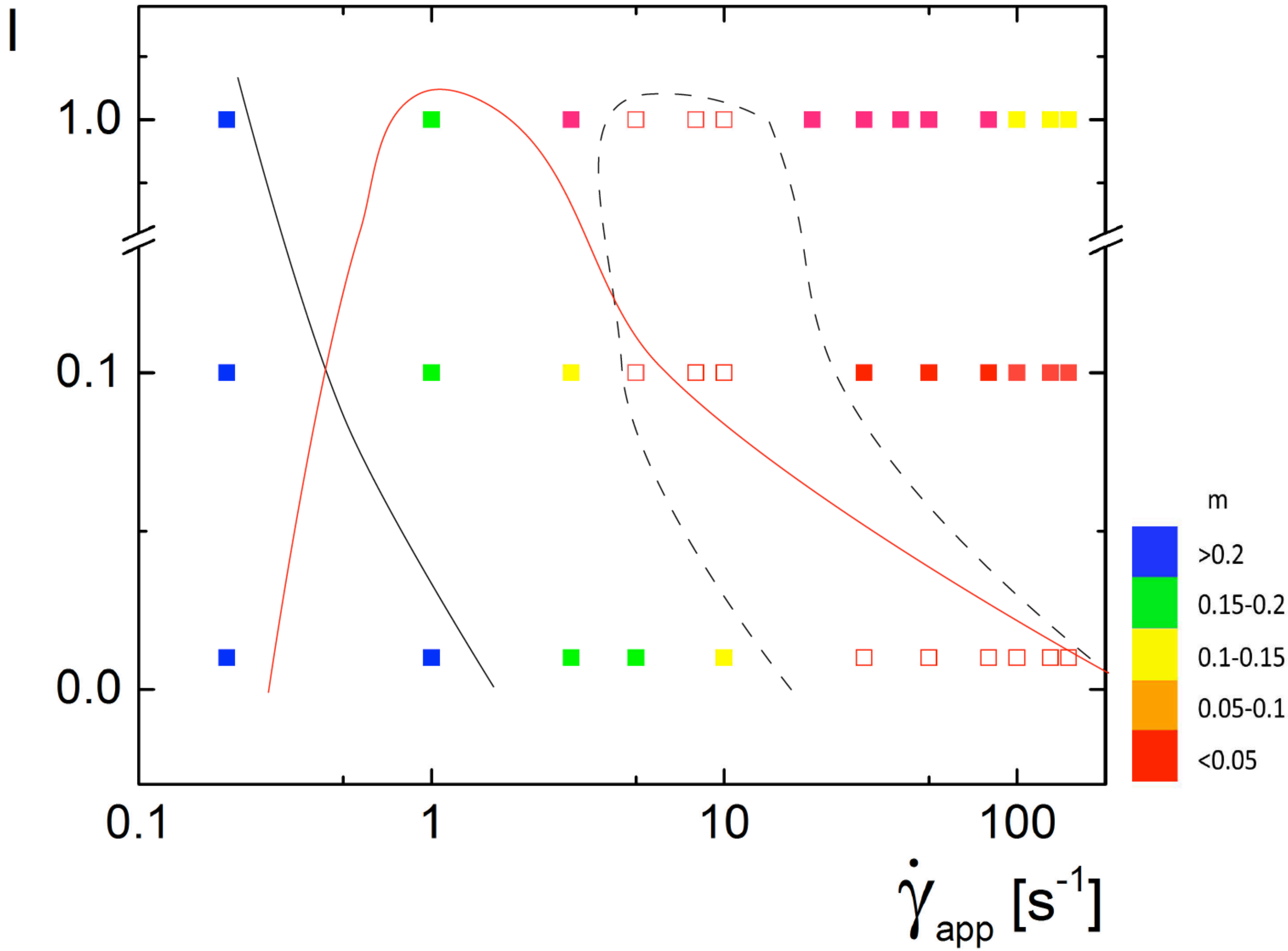
Start up on DNA at different ionic strengths



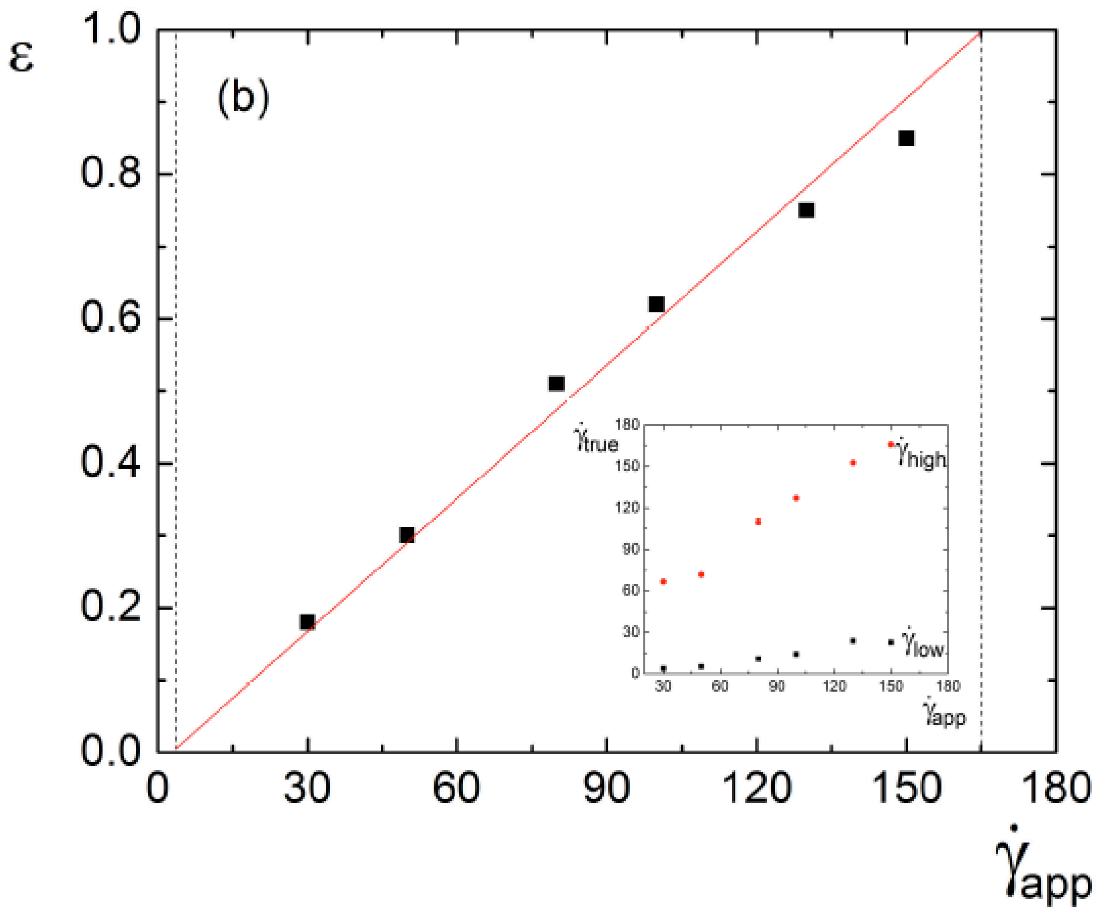
Linear rheology on DNA at different ionic strengths



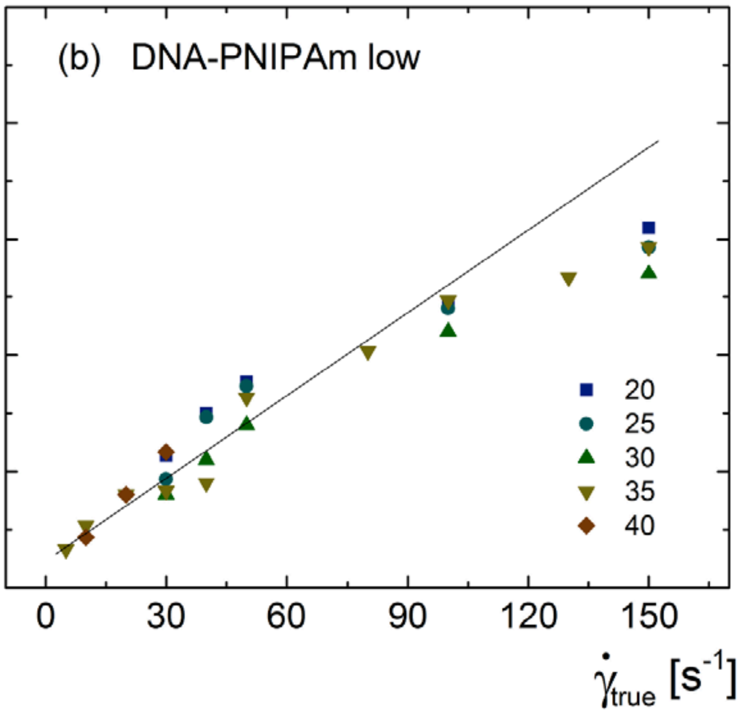
DNA diagram of states

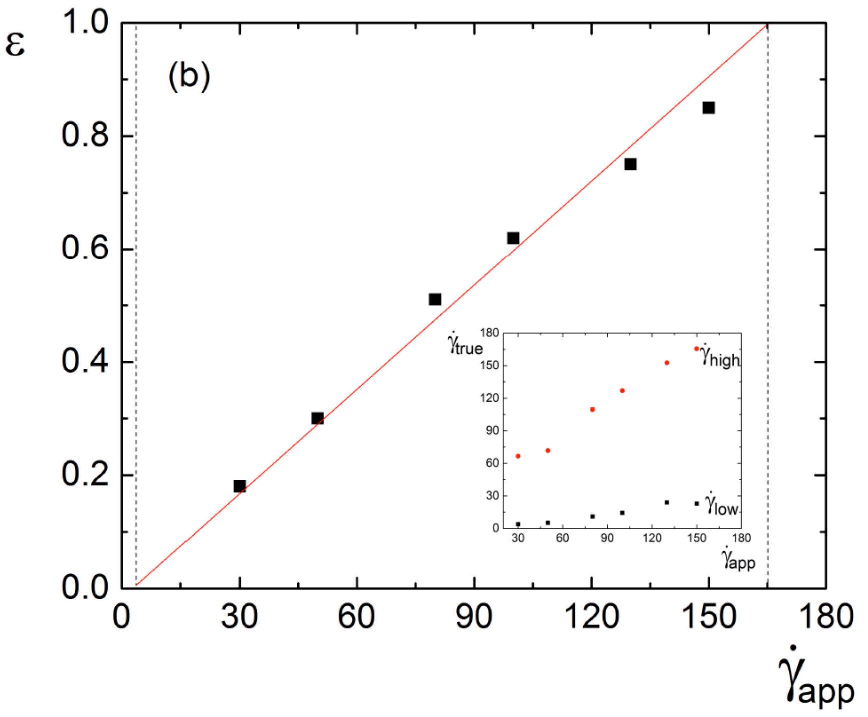


banding results for DNA

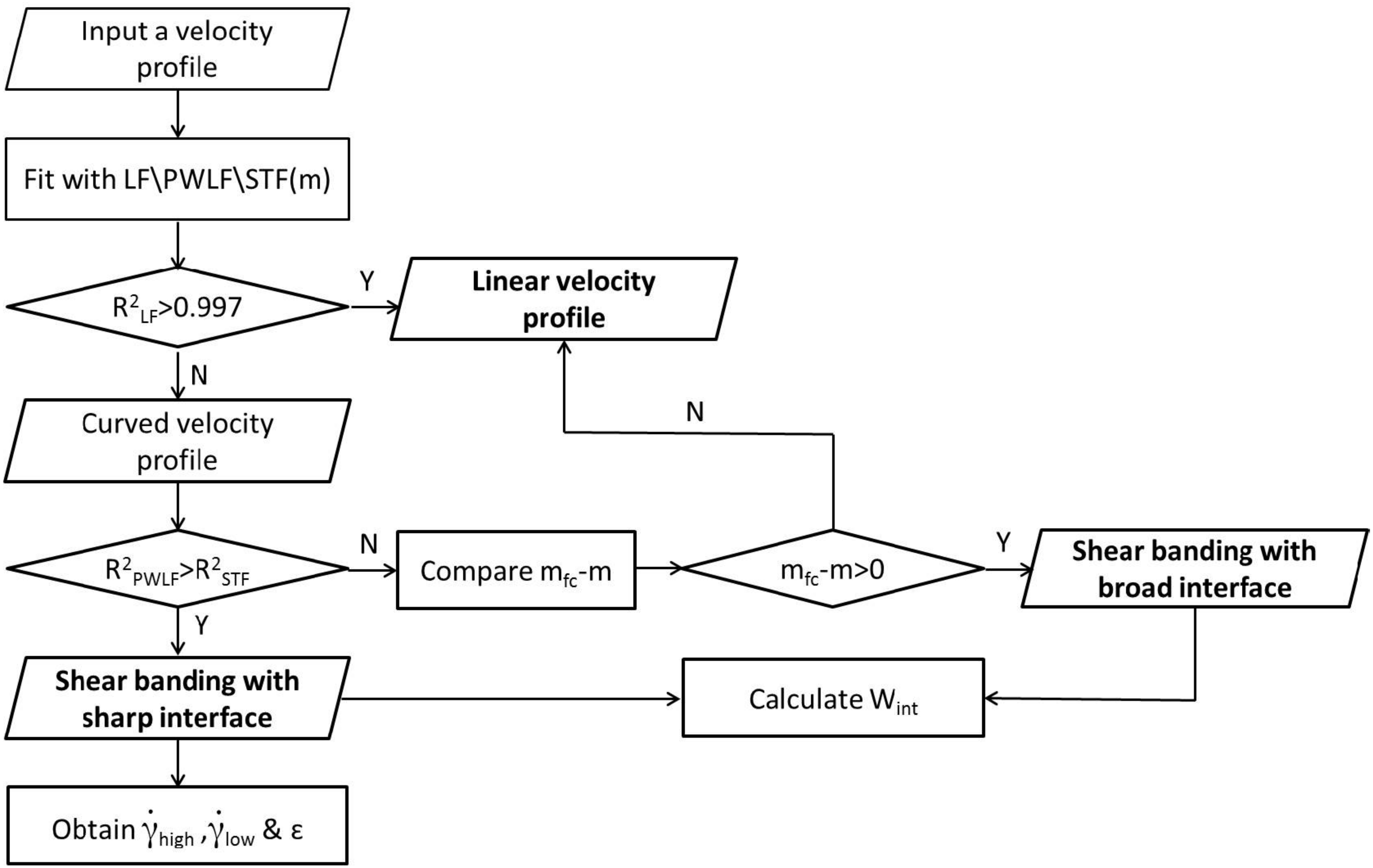


banding results for DNA-pnipam



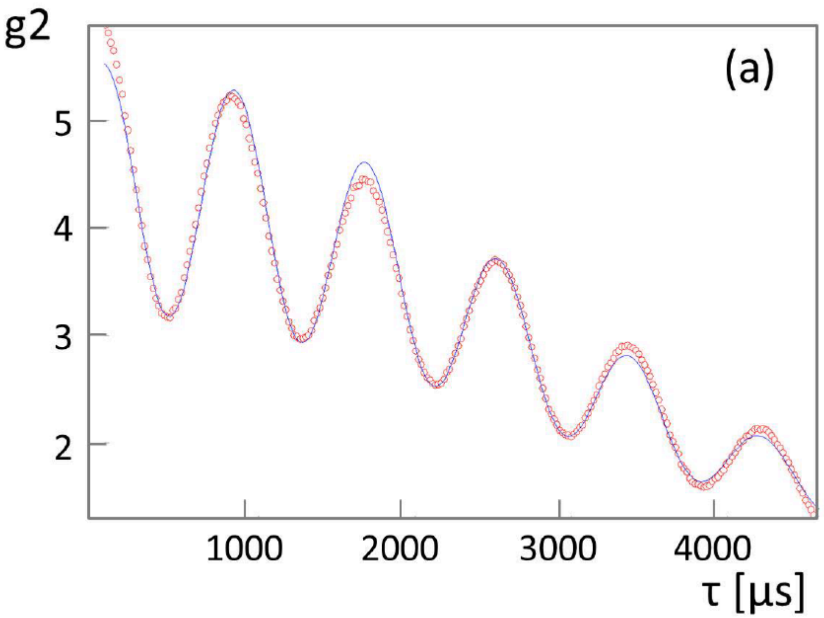


Analysis procedure

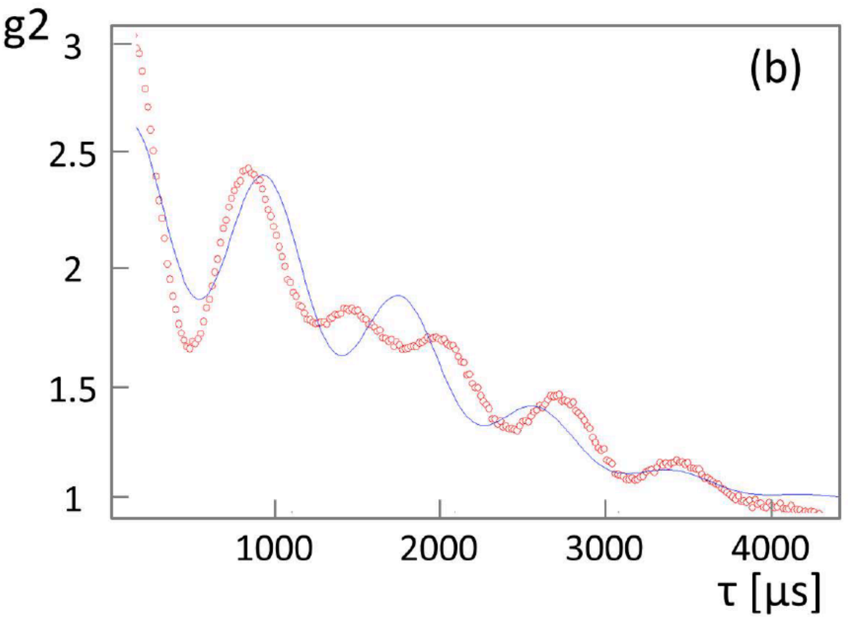


Stability of the profile

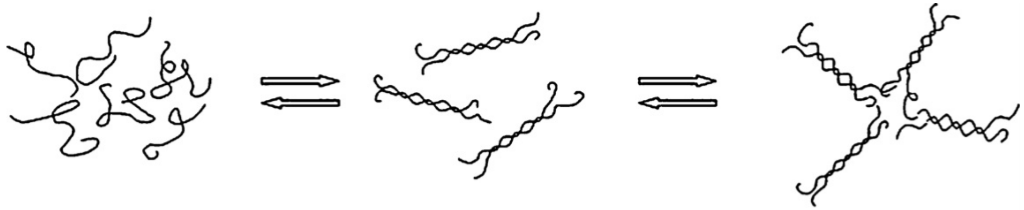
Away from the banding region

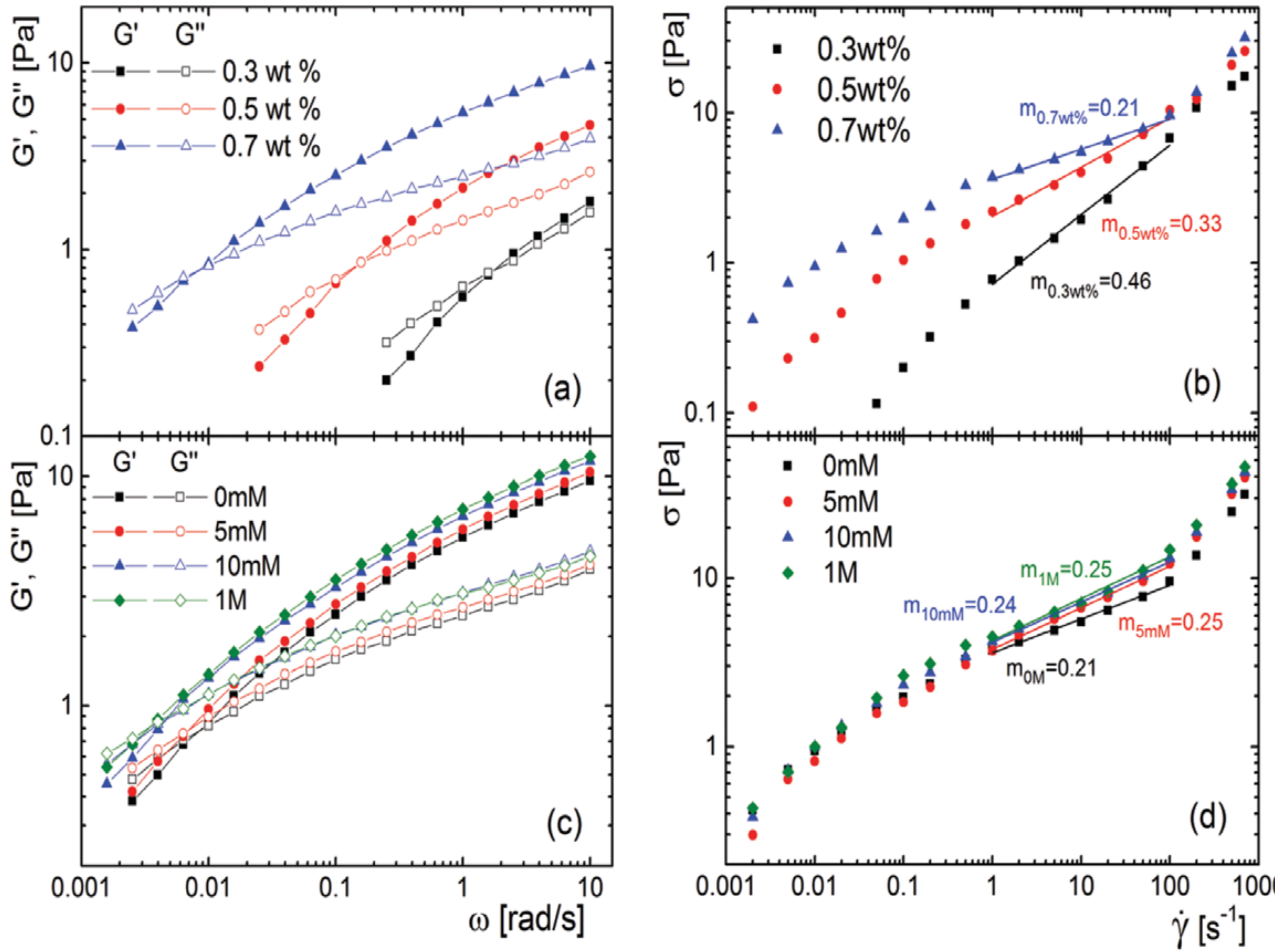


In the banding region



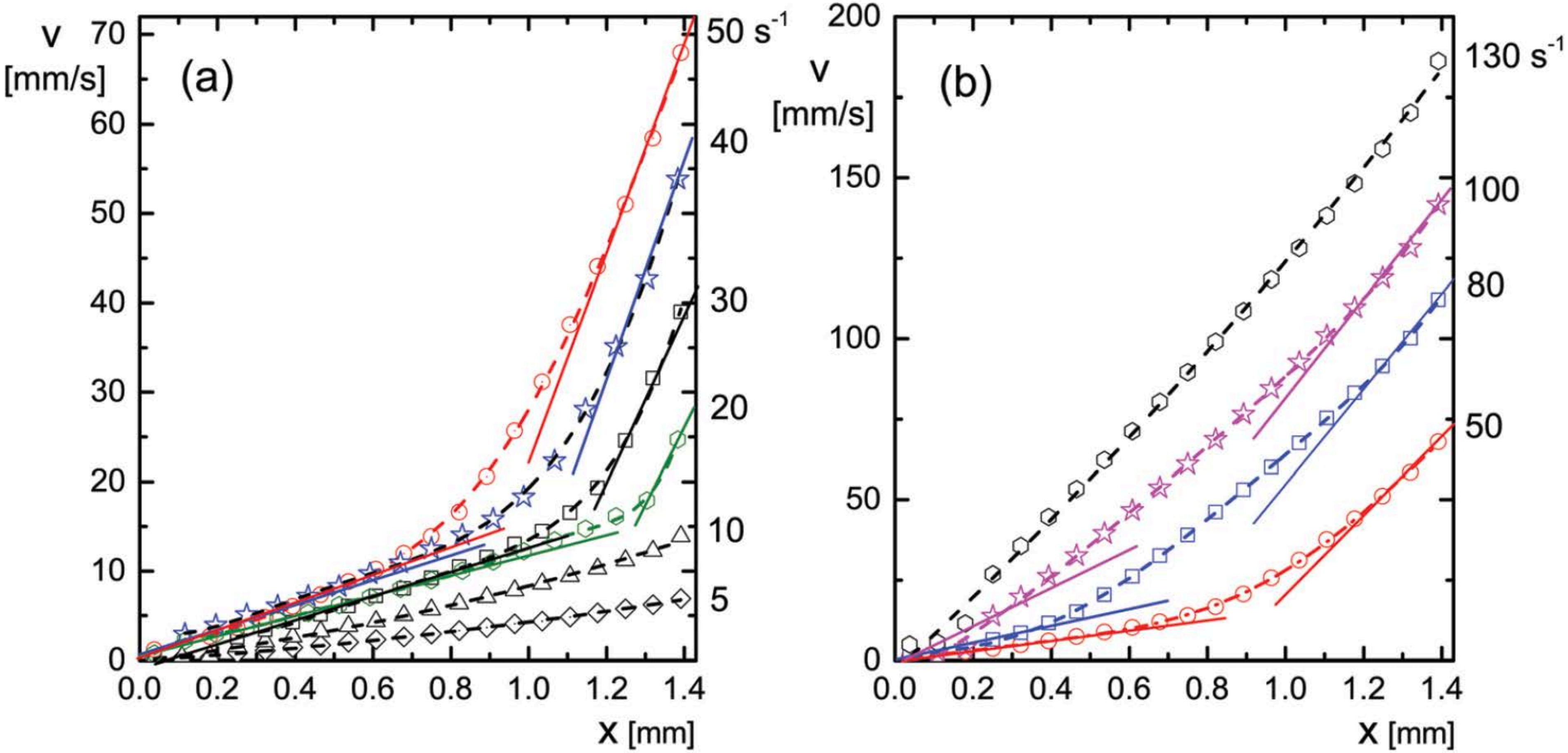
Xanthan…



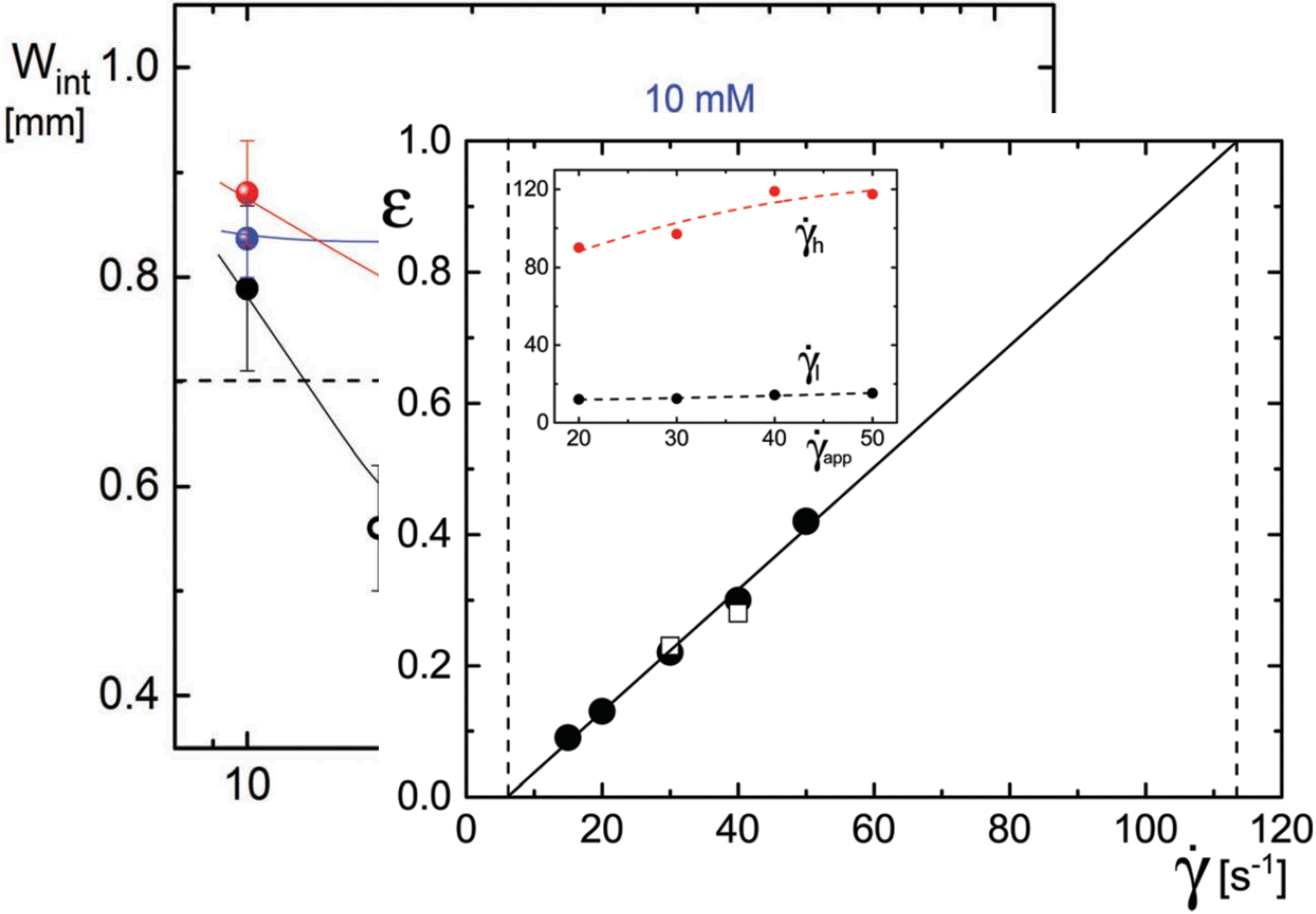


G'
G''
0.3 wt %
0.5 wt %
0.7 wt %
G', G'' [Pa]
(a)
0.3wt%
0.5wt%
0.7wt%
σ [Pa]
m0.7wt%=0.21
m0.5wt%=0.33
m0.3wt%=0.46
(b)
0mM
5mM
10mM
1M
(c)
ω [rad/s]
m1M=0.25
m10mM=0.24
m5mM=0.25
m0M=0.21
(d)
γ̇ [s-1]

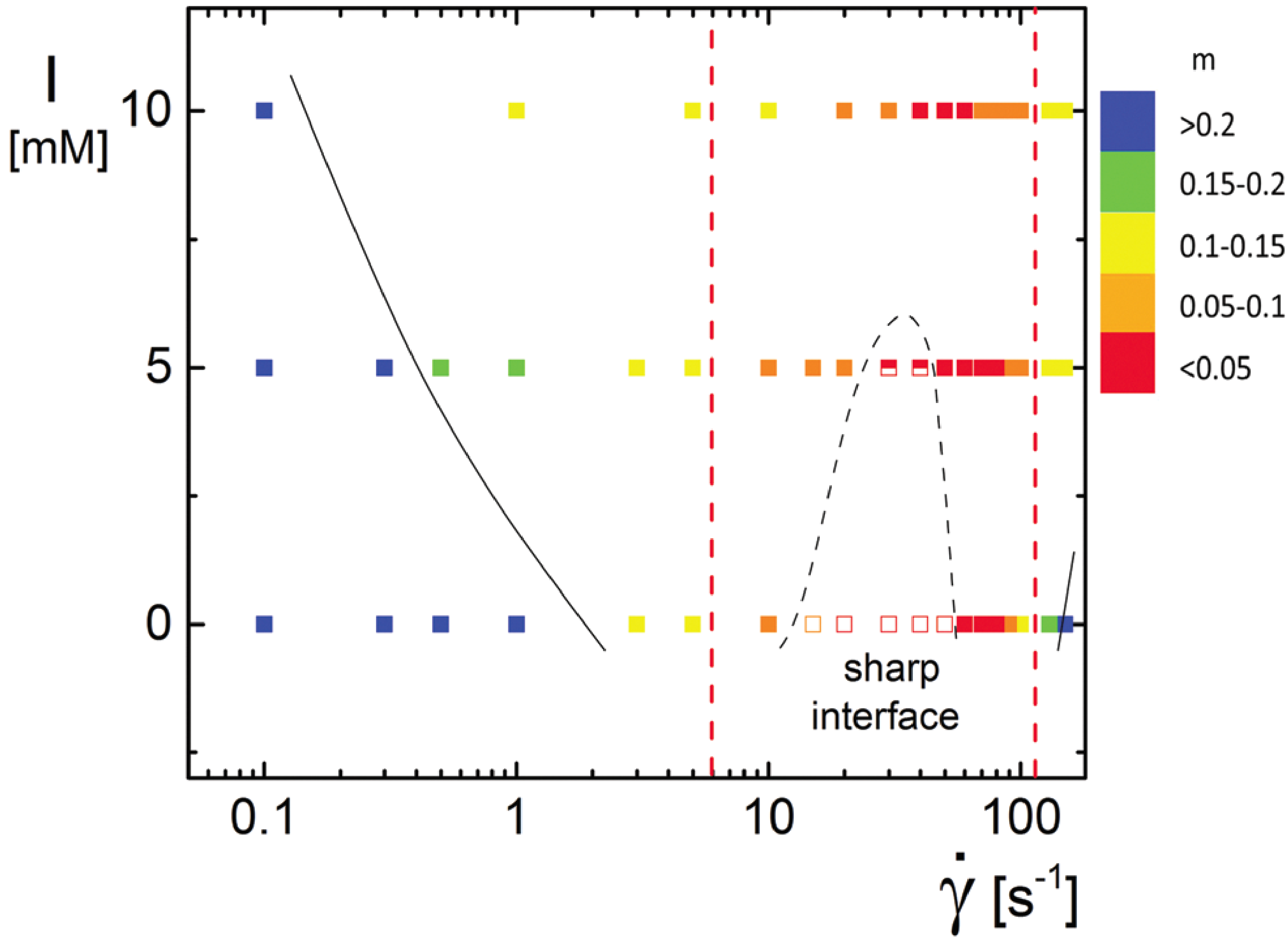
Xanthan… the profiles



Xanthan… the results



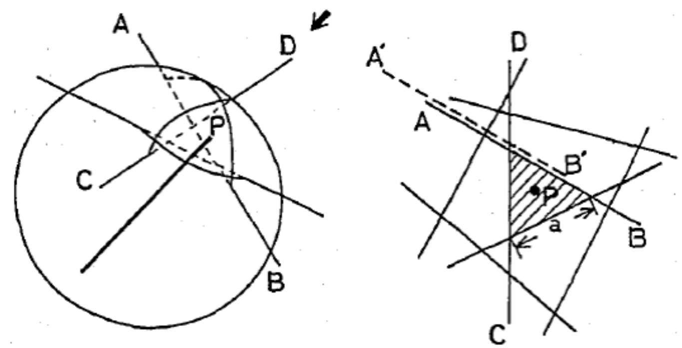
Xanthan… the diagram of states



Topological slowing down:

Dois phenomenological rotational diffusion coefficient

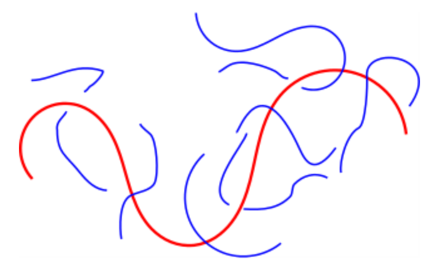
$$D_r = cD_r^0(\nu L^3)^{-2}$$



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*

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

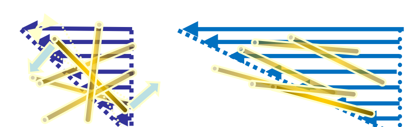
⇨ $$\delta S(t) = \exp(-6D_R^{eff}t)\delta S(t=0)$$

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

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

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

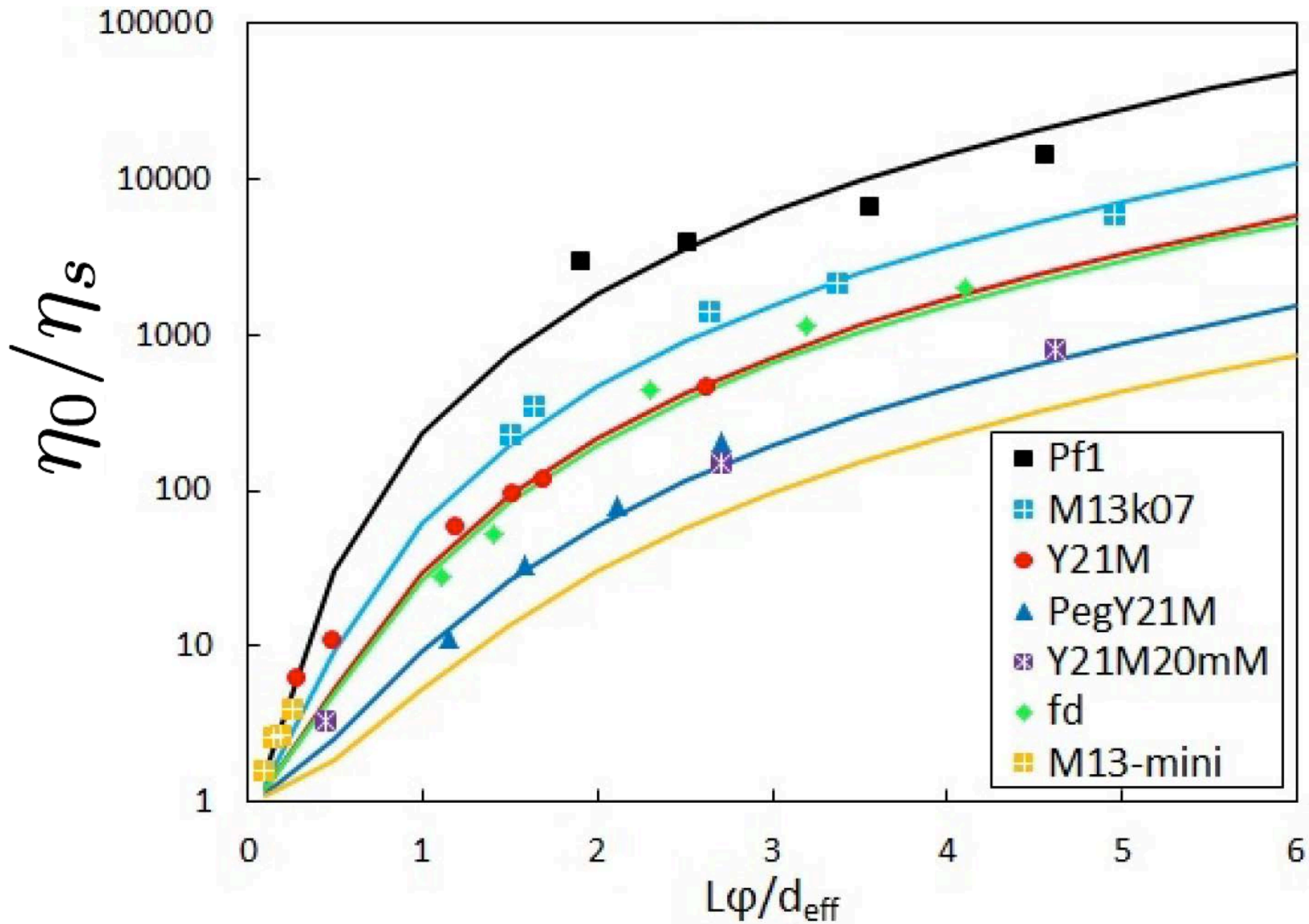
D_R^0 : rotational at *infinite* dilution



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

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

Zero shear viscosity of rods

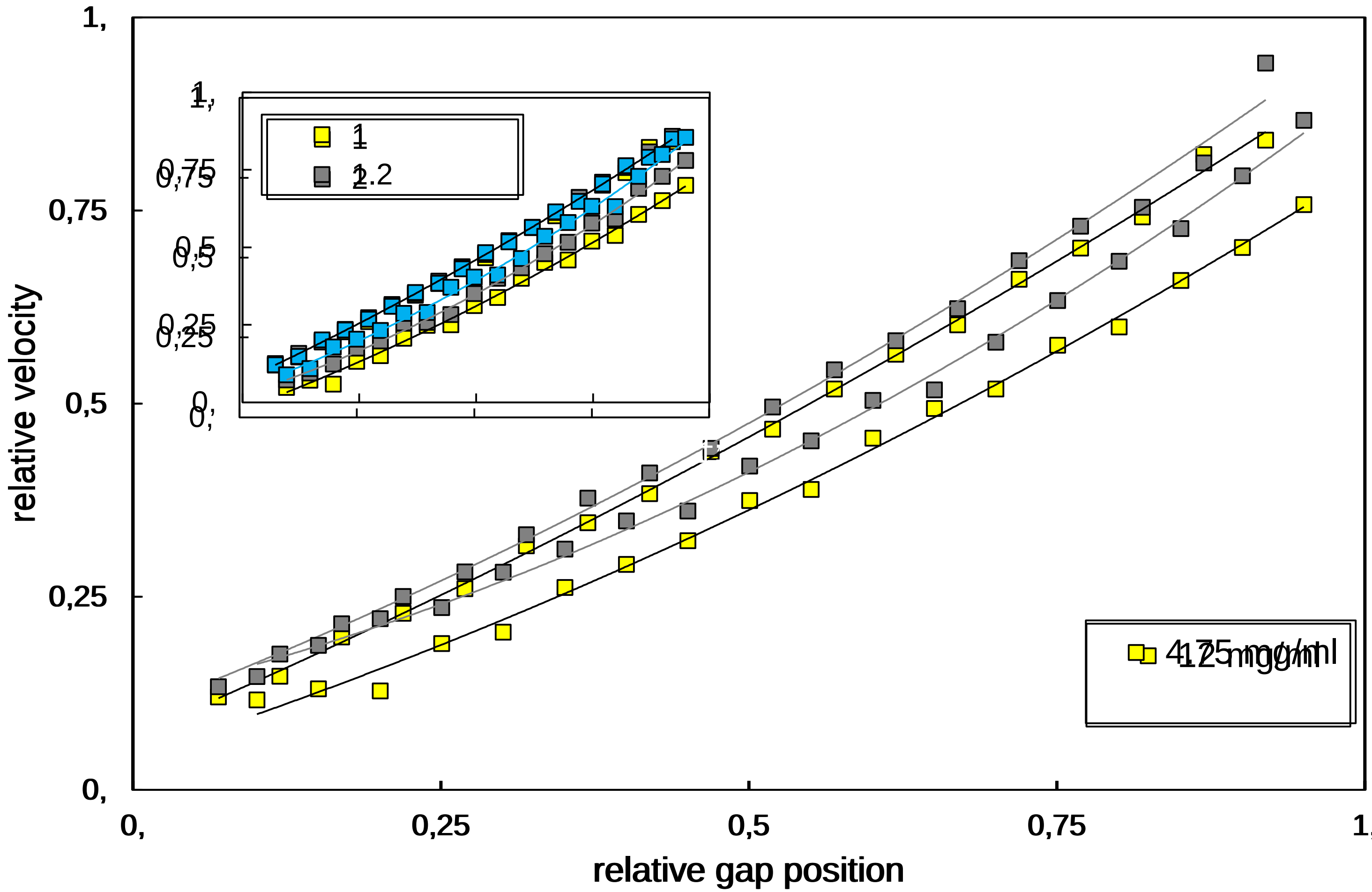


$$D_r = c D_r^0 (\nu L^3)^{-2}$$

c=3.10^3

Velocity profiles of rods

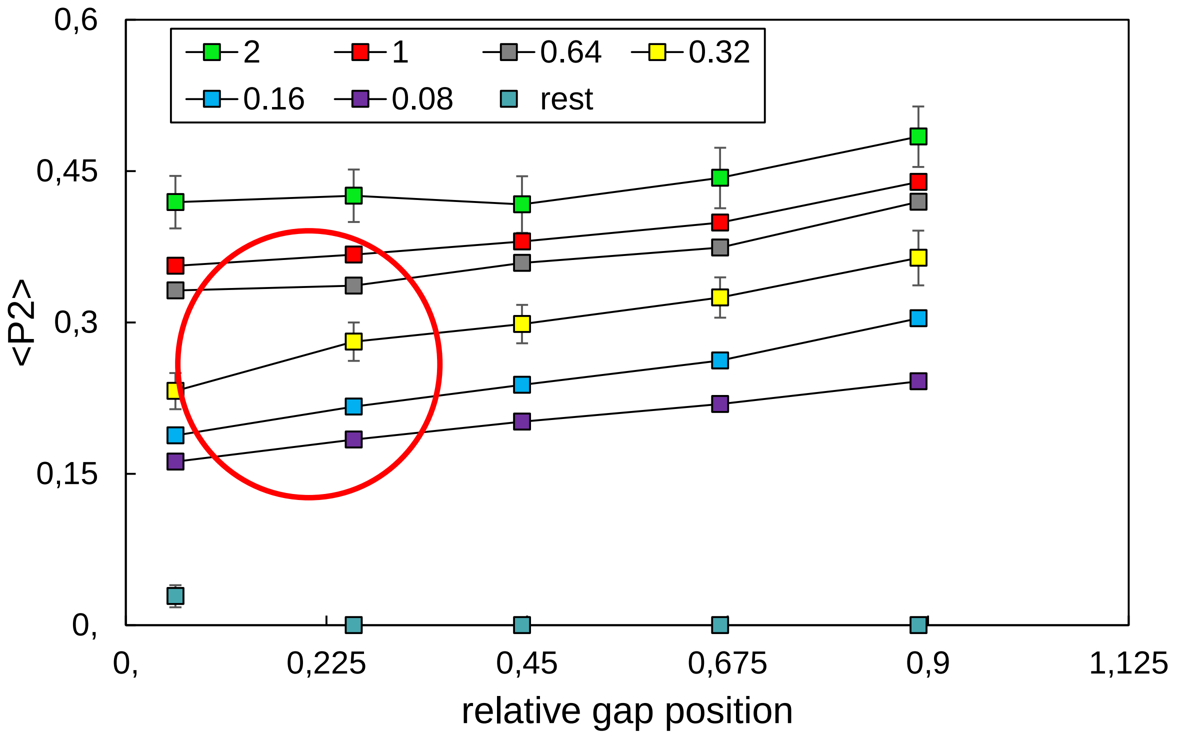
Velocity profile of M13k07 (L=1.2 μm, L_p=2.2 μm):

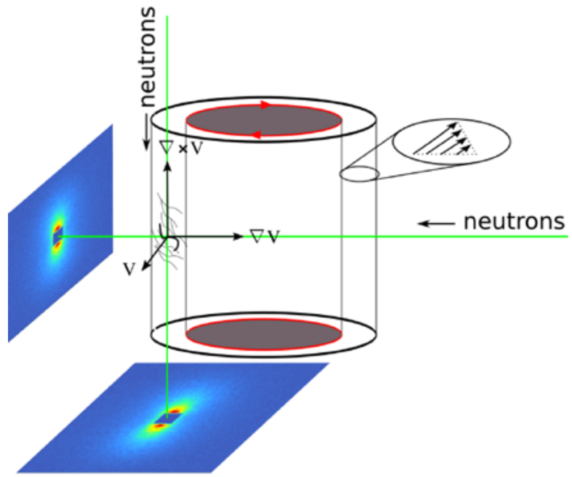


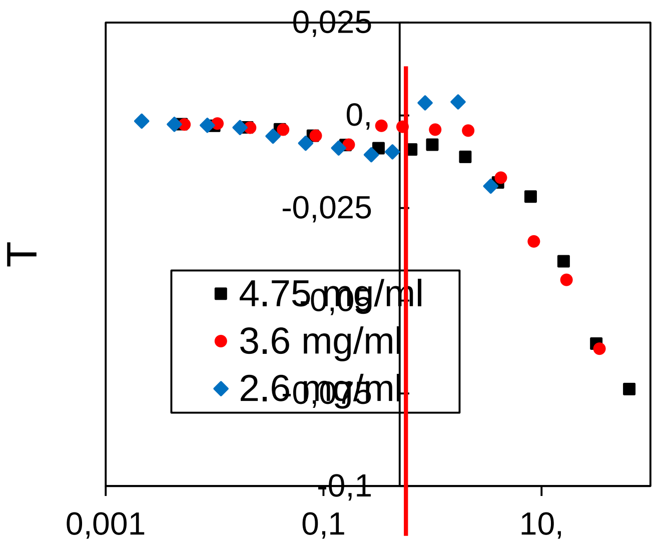
- very long and flexible rods show hints of shear banding

Zero shear viscosity of rods

Shear-banding and hairpin formation



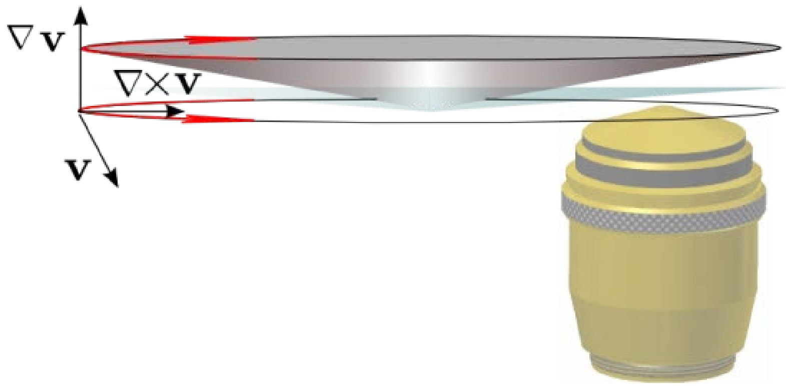


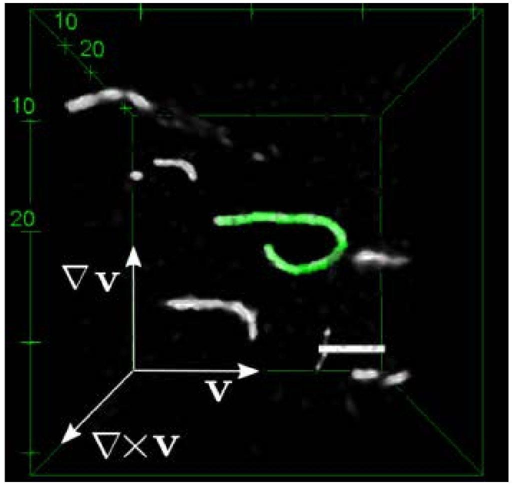


- biaxiality reverses in a small shear rate range after “shear banding”

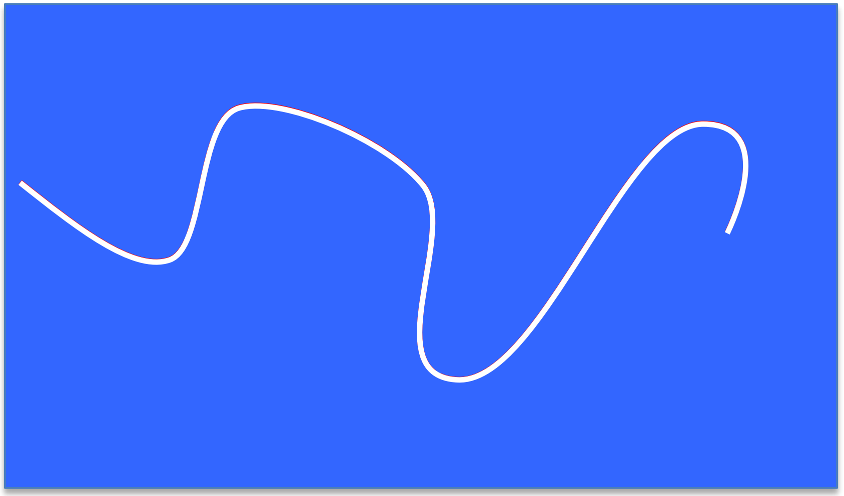
Lang et al, *Polymers*, 2016

In situ confocal microscopy on entangled F-actin



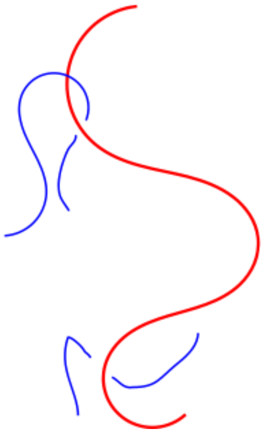


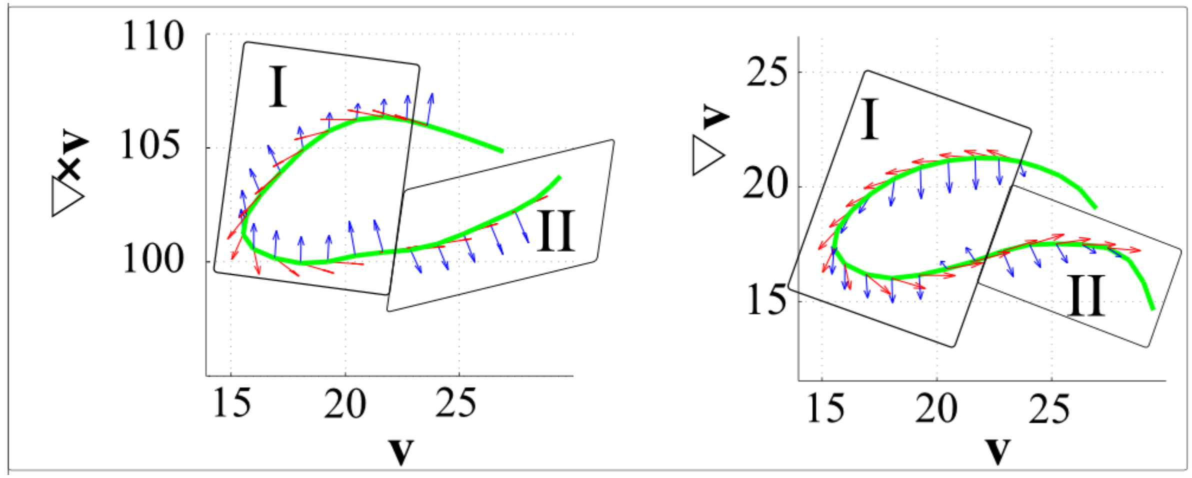
- ➢ Use three concentrations, label 1 per 100 filaments
- ➢ About 100 analyzed filaments per combination

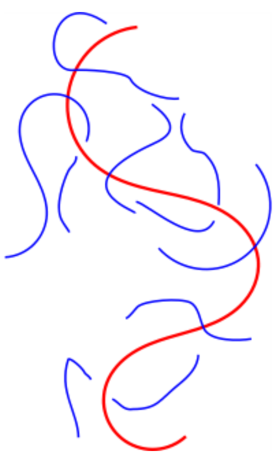


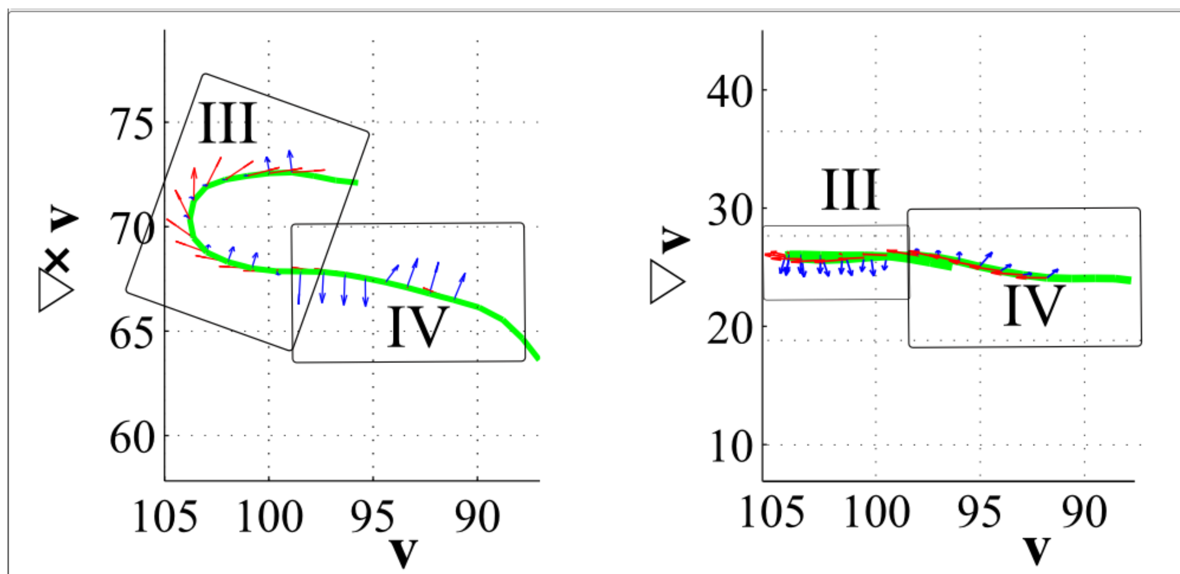
Kirchenbüchler et al *Nature Communications* 5:5060 (2014)

Typical examples:









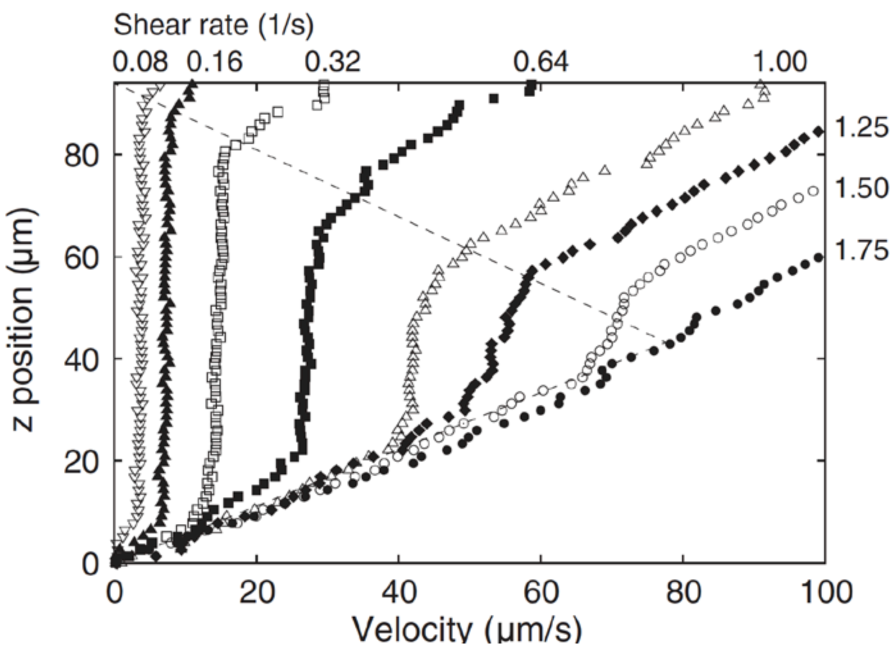
F-actin: stiffer and longer

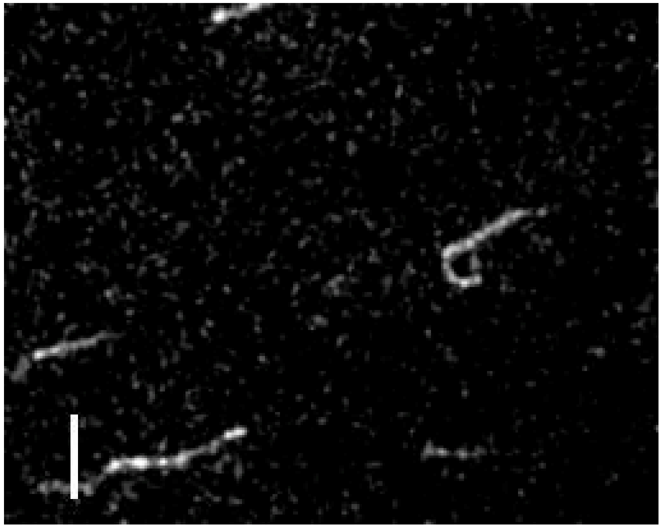
$<L> \approx 20\ \mu m$, $d = 7$ nm, $l_p = 17\ \mu m$

Shear banding has been identified by

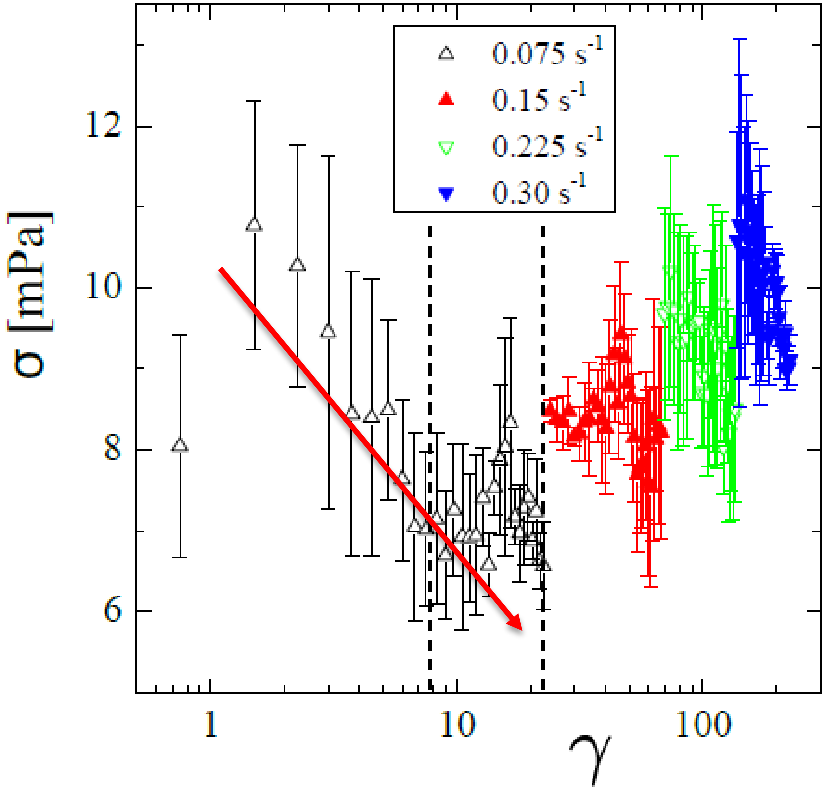
Kunita et al, PRL 109, 248303 (2012)

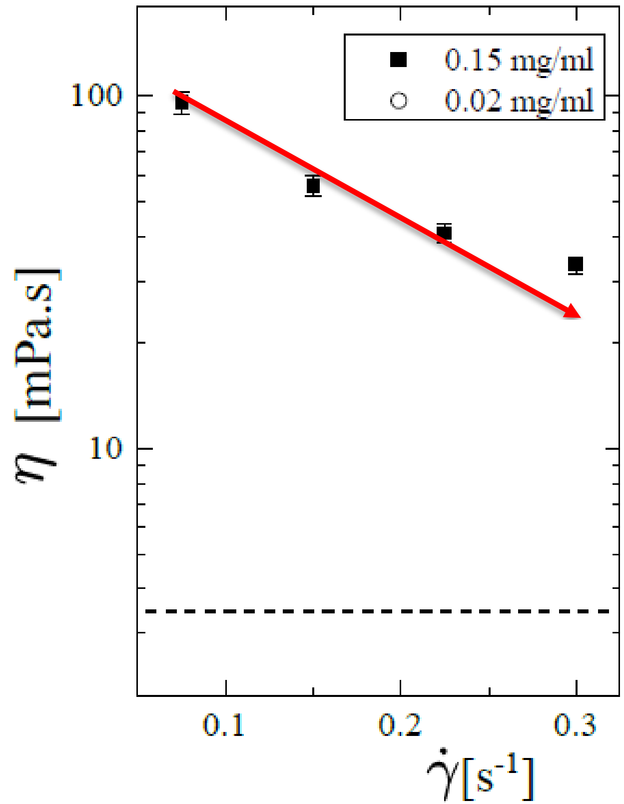
Goal: obtain 3-D structural information

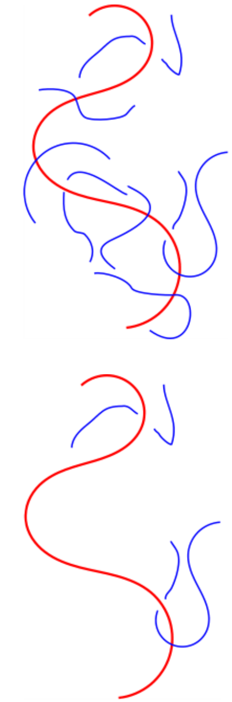




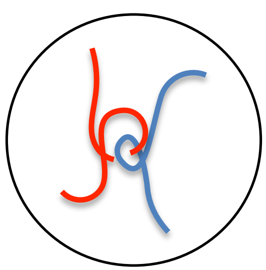
Rheological response of F-actin dispersions



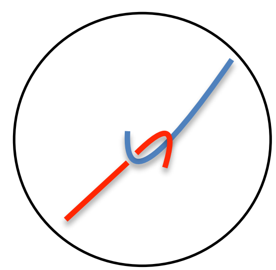




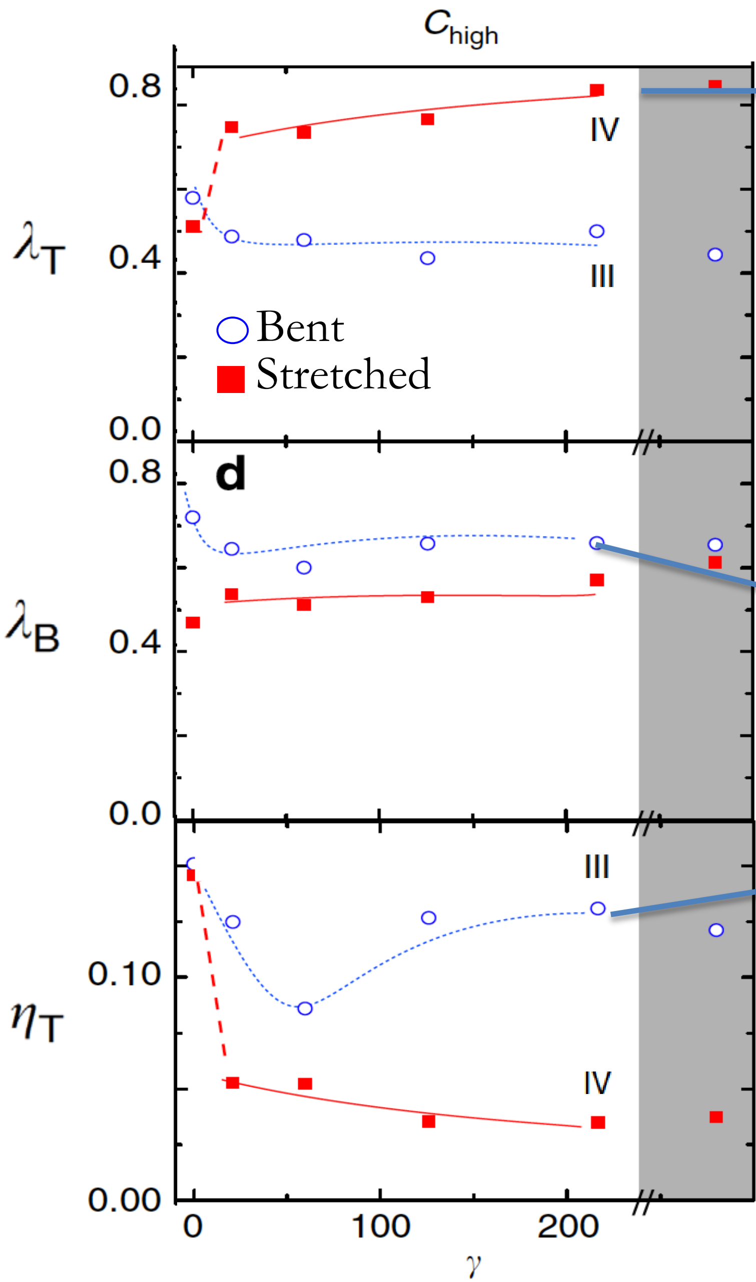
Strain softening



Shear thinning

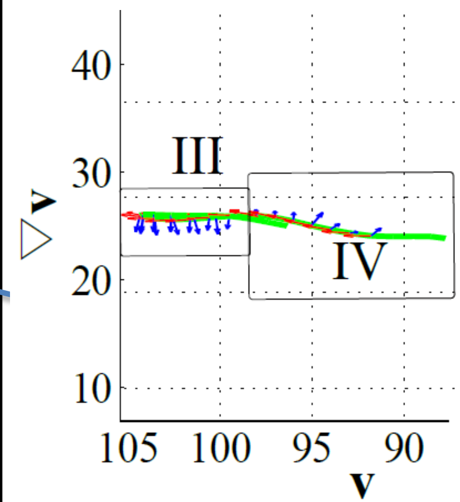


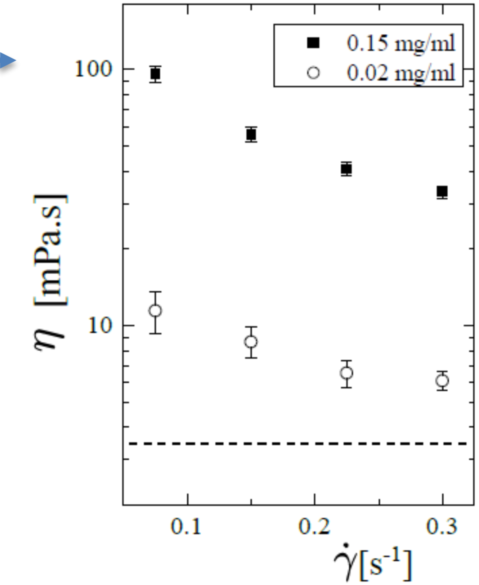
Connection between ordering and stress

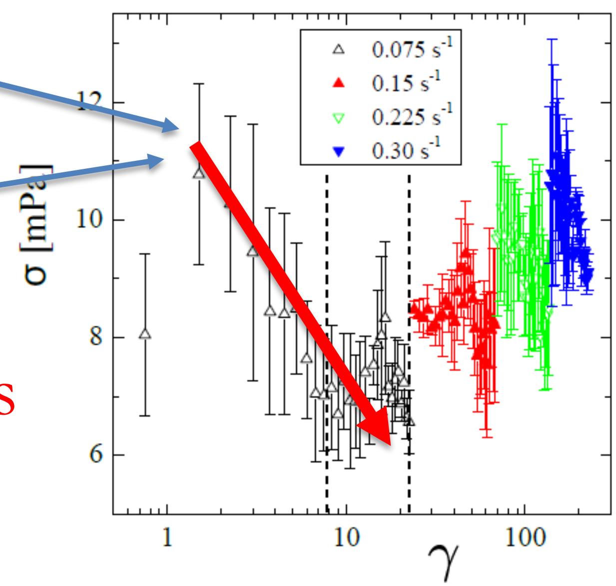


Shear thinning:

Nematic=more space



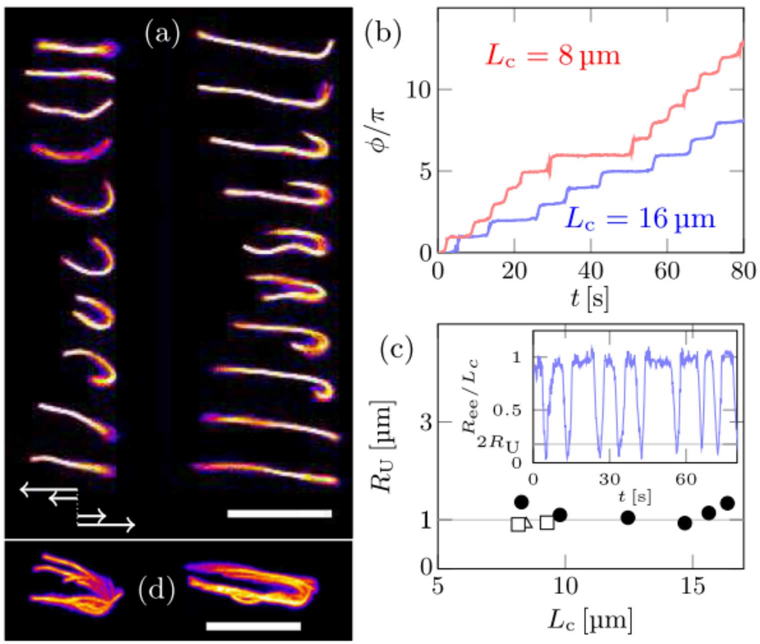




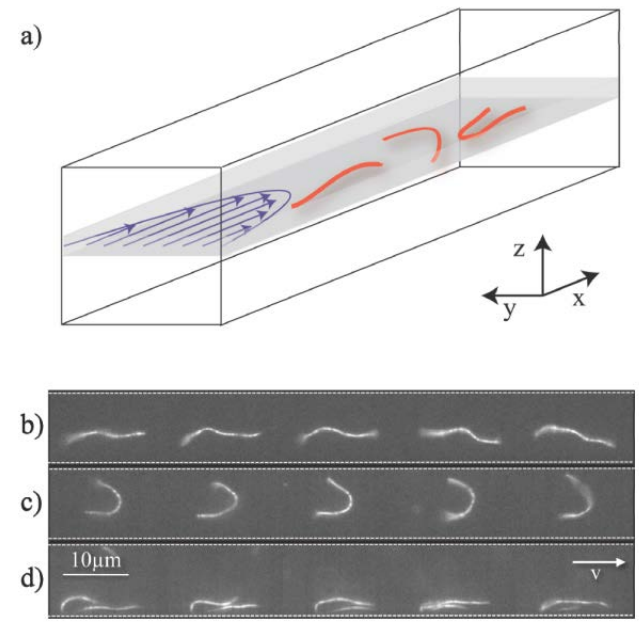
Strain softening :

Oriented hairpins

Shear experiments on F-Actin



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

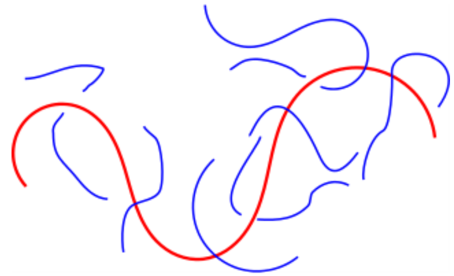


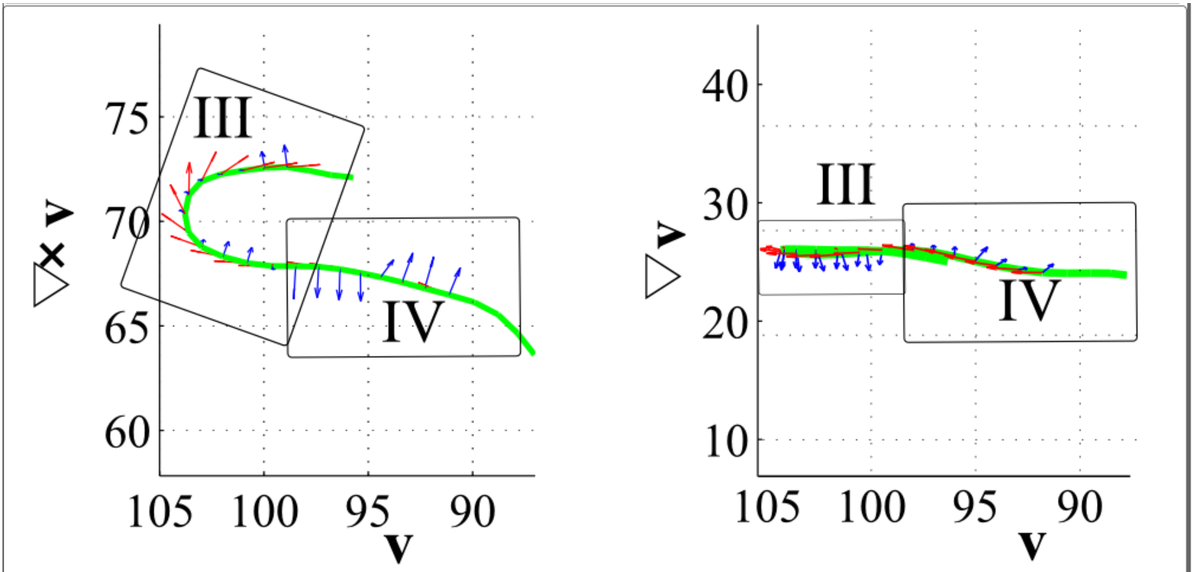
Mobility Gradient Induces Cross-Streamline Migration ofSemiflexible Polymers
Steinhauser et al, ACS Macroletters, p. 542 (2012)

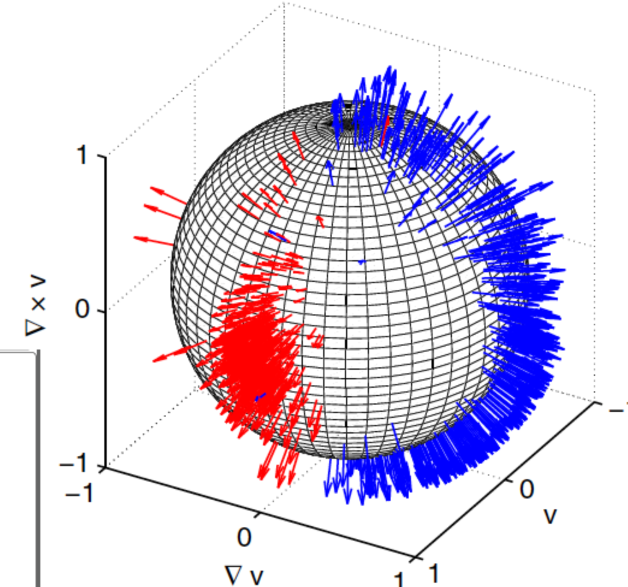
Ill defined geometries; Infinite dilute; 2-D imaging

Distribution of angles

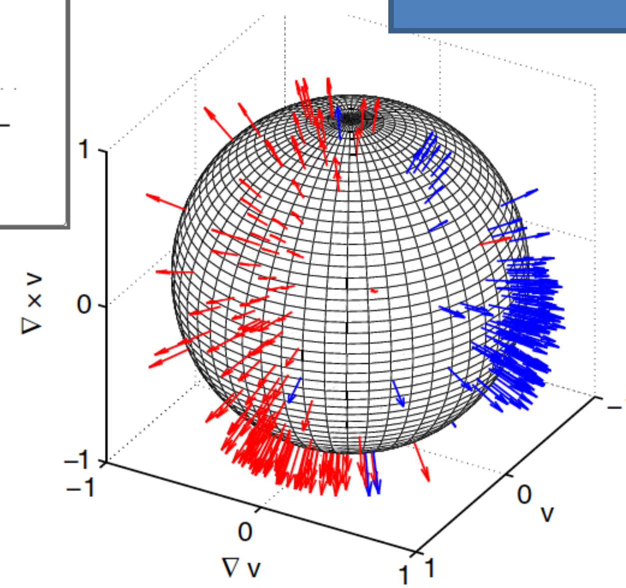
Stretched: IV



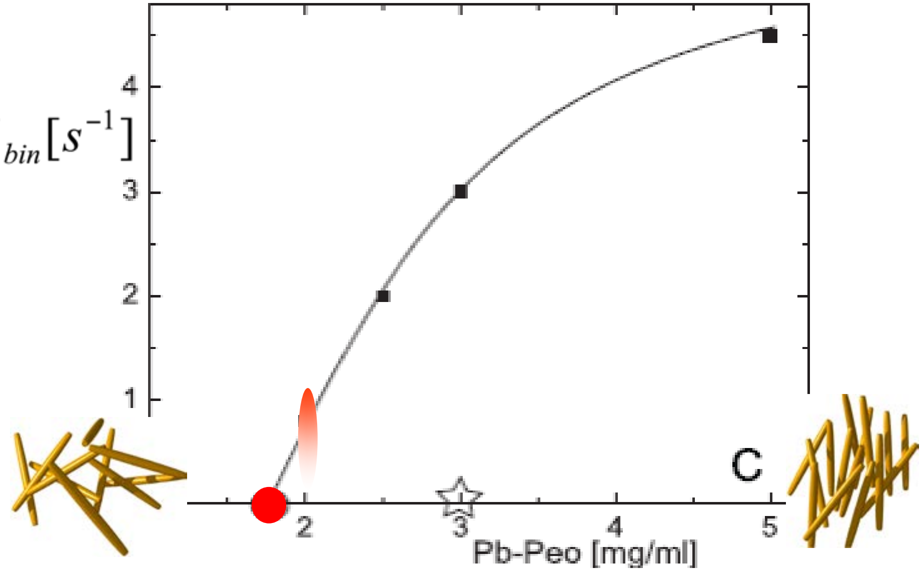


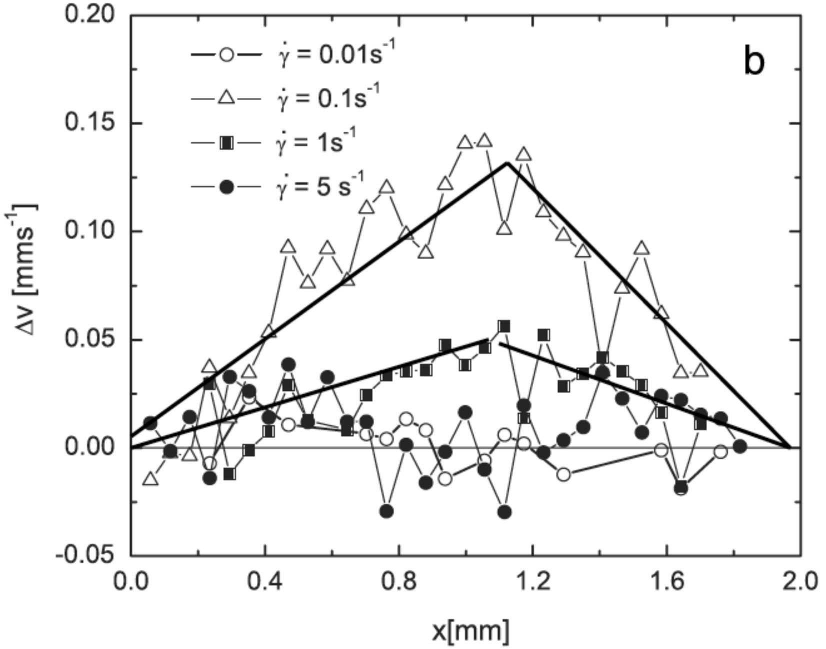


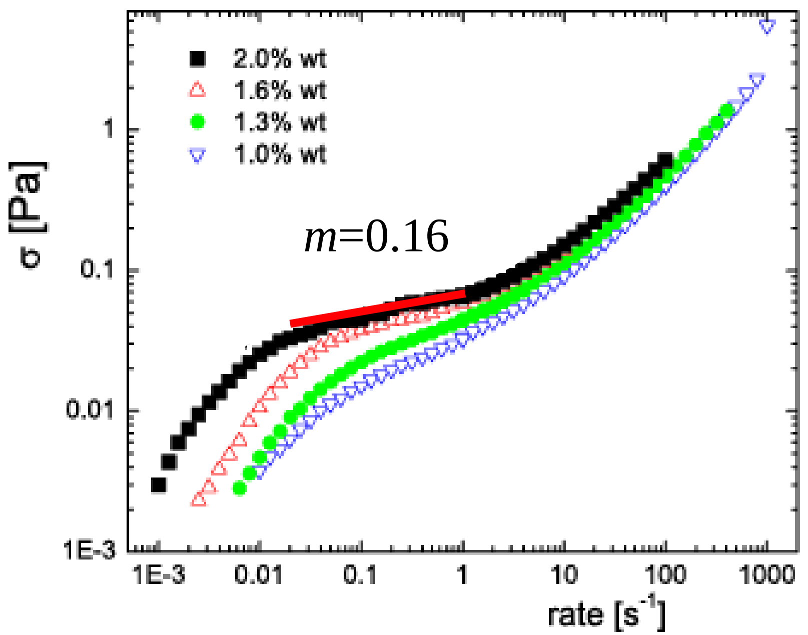
Bent: III



Non-equilibrium isotropic-nematic binodal

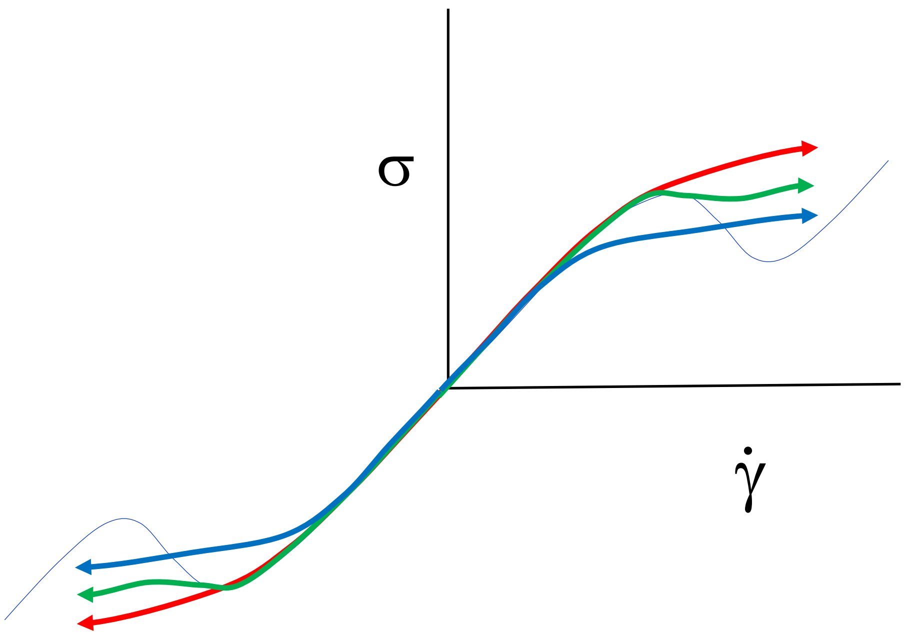


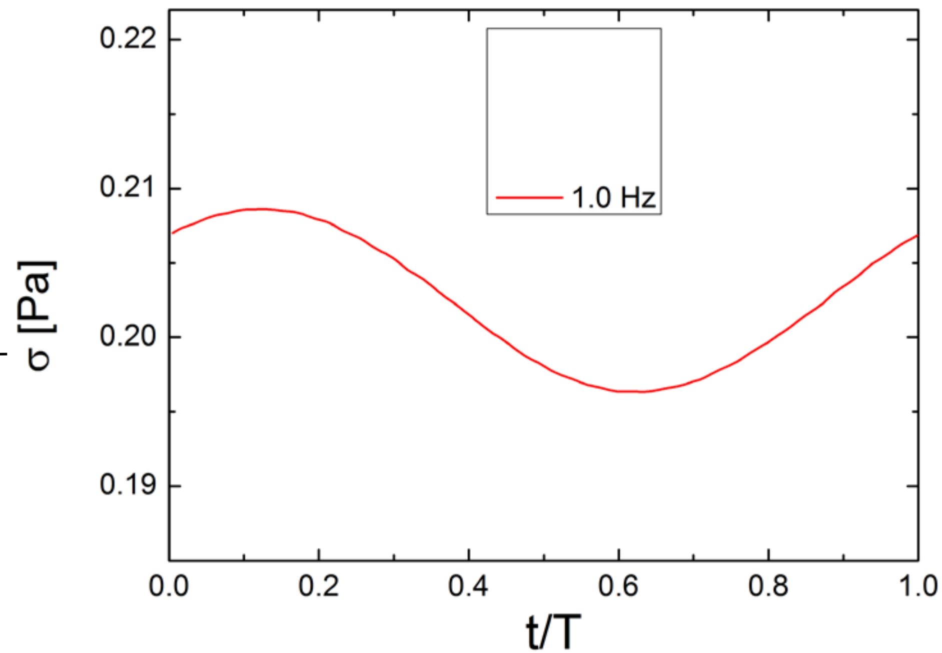




Probe dynamics

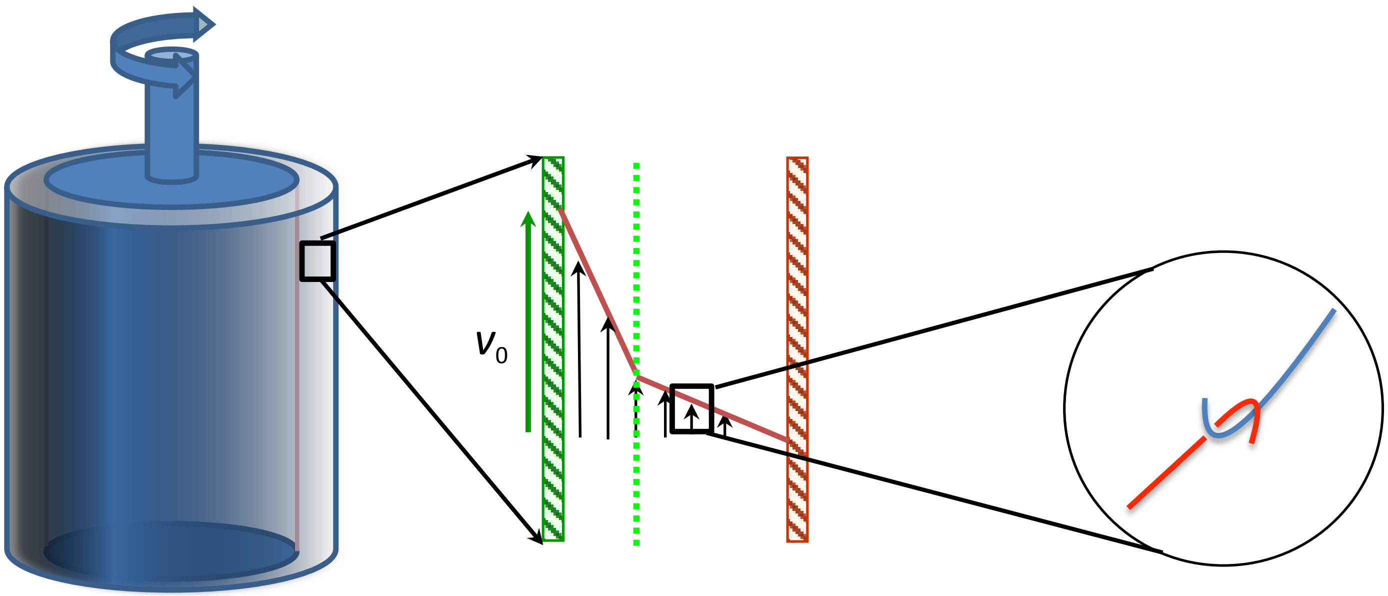
Probe dynamics with Large Amplitude Oscillatory Shear





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

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.

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 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]

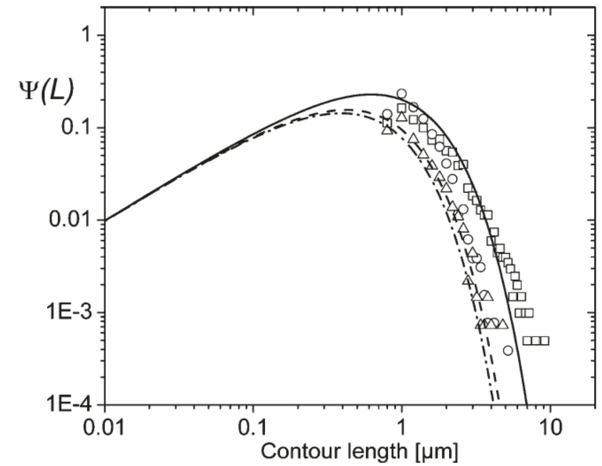


Figure 3. Probability density distribution of contour lengths for different molar fractions of DMF (solid line, square for $f = 0$; dashed line, circle for $f = 0.025$; dotted line, triangle for $f = 0.06$). The curves correspond to an exponential distribution with the parameters determined by DLS. The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