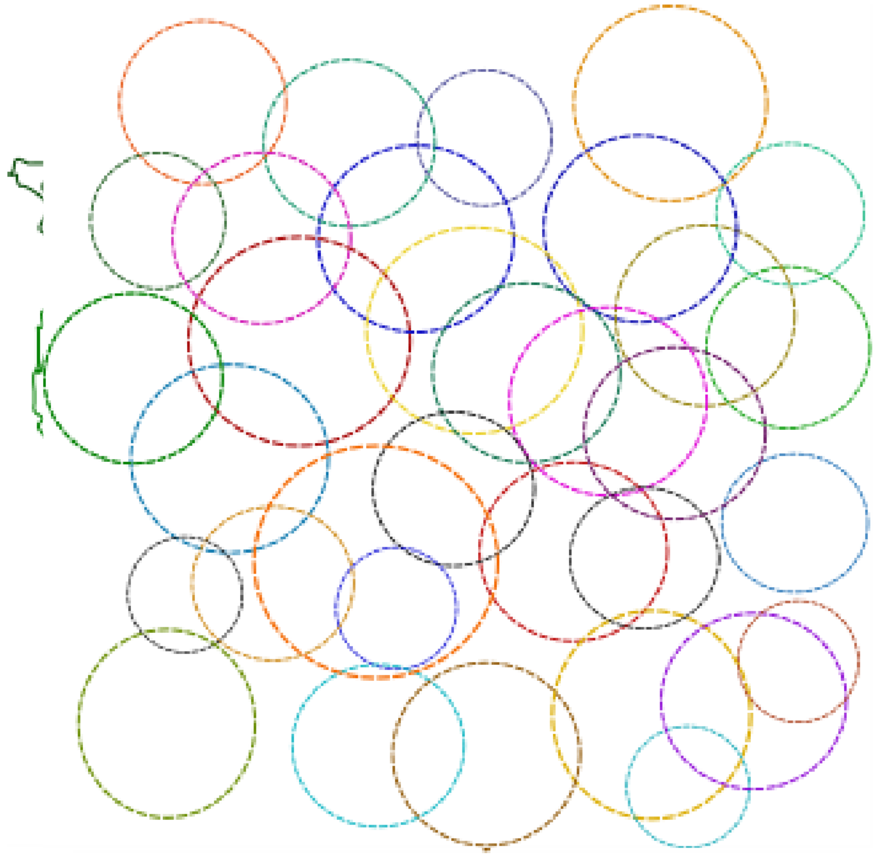
Mitglied der Helmholtz-Gemeinschaft

How rods give structure to fluids and how structure is distorted by flow

Pavlik Lettinga

ESPCI/Paris 7 or Diderot/Sorbonne/CNRS/…, September 2018

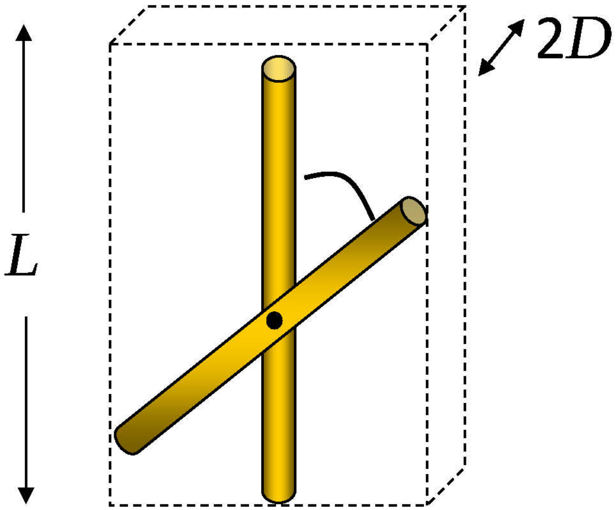
Rods: extremely effective in structuring a fluid

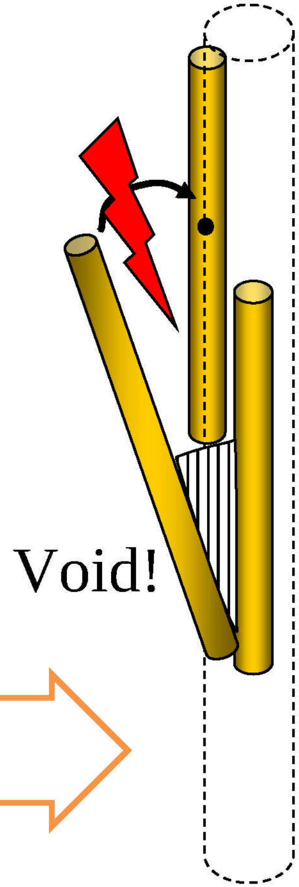


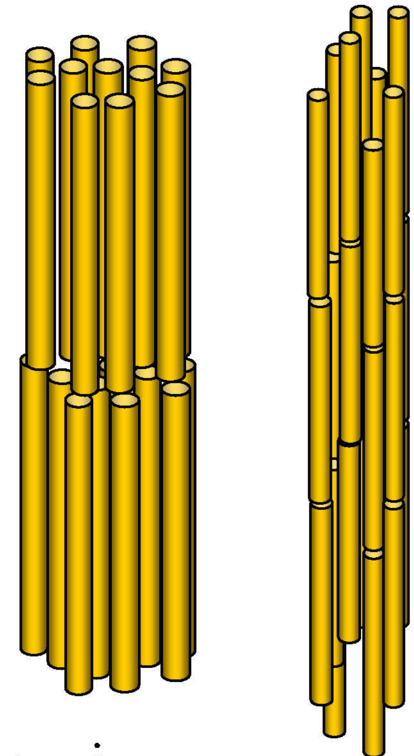
Rods: extremely effective in structuring a fluid

Phase transitions of colloidal rods

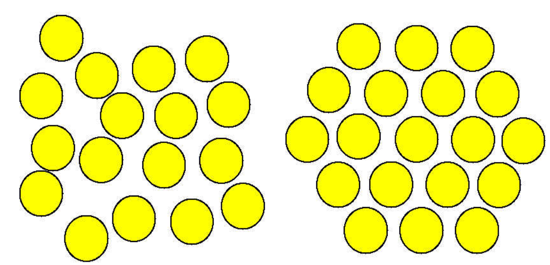
$$V_{ex} = 2DL^2 \sin\vartheta \qquad V_{ex} = \pi L D^2$$







top view:

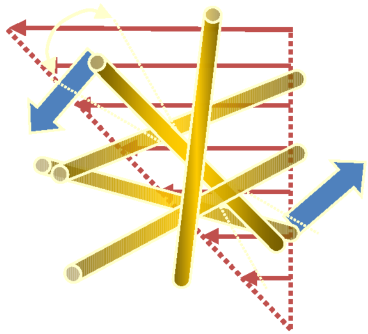


Onsager, 1949

$$\phi_{I-N} = 4\frac{L}{D_{eff}}$$

Isotropic | Nematic | Smectic | Columnar

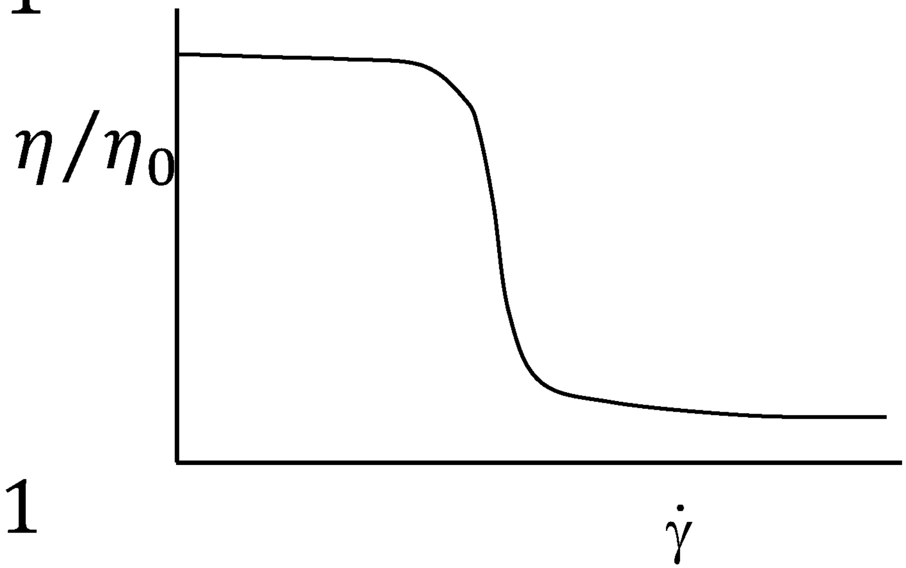
Colloidal rods in shear flow

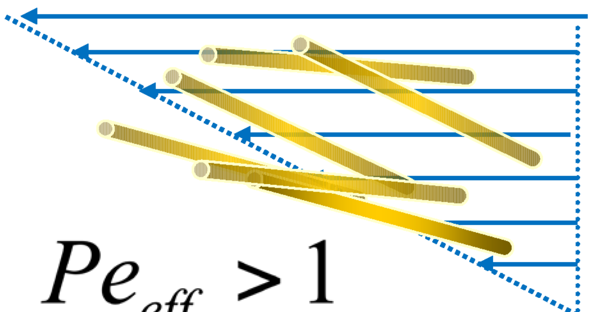


$$Pe_{eff} < 1$$

$$\eta/\eta_0 \gg 1$$

strong shear-thinning





$$Pe_{eff} > 1$$

$$\eta/\eta_0 \rightarrow 1$$

$$Pe_{eff} = \dot{\gamma}_0 / D^R_{eff}$$

Goal: understand shear thinning of systems like…

nano cellulose

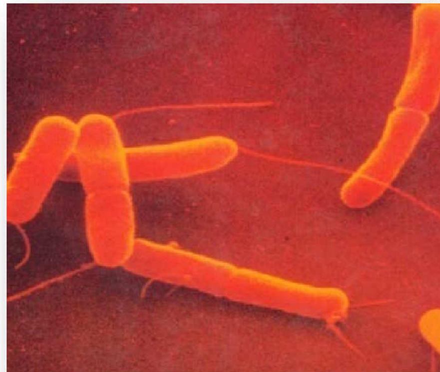
carbon nano tubes

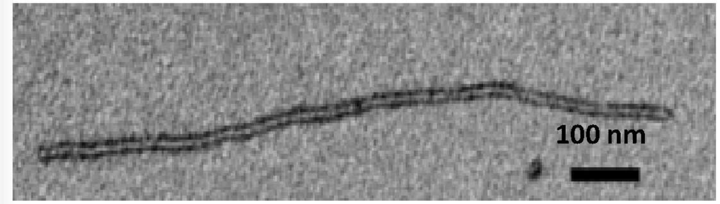
amyloid

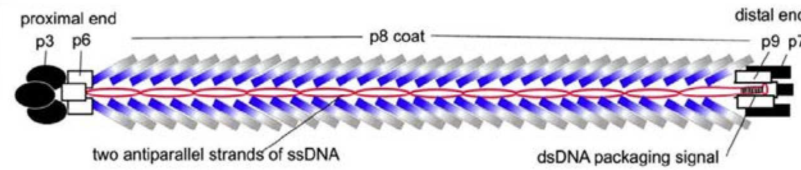
F-actin

Xanthan

Bacteriophages as model system



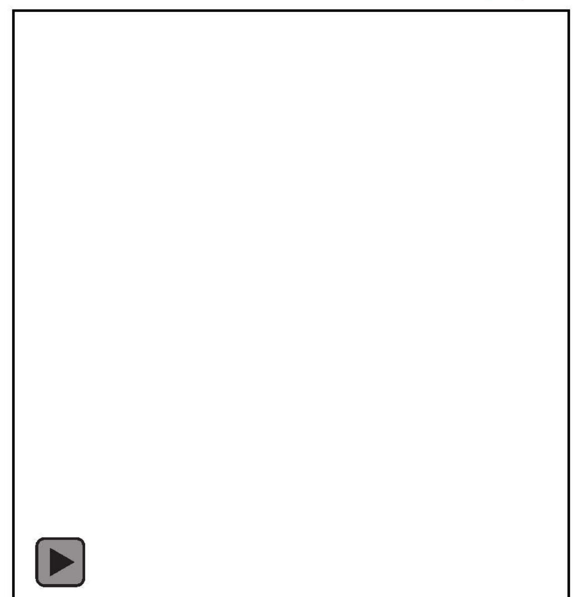




Genetic Modification

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

Fluorescent Microscopy



Lettinga *et al.,* Euro.Phys.Letter, **71**, 692 (2005)

Dynamics at increasing degree of ordering

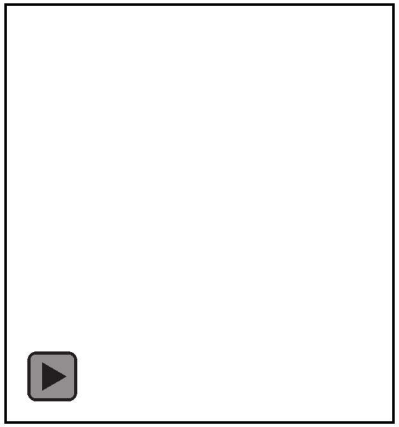
Connection between entropy and diffusion:

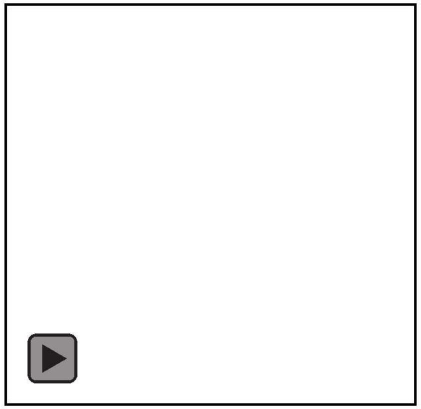
More free volume = More space per particle

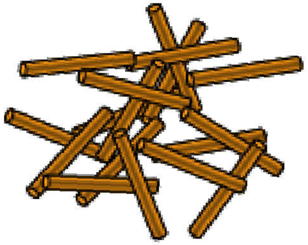
More space per particle= Higher positional entropy

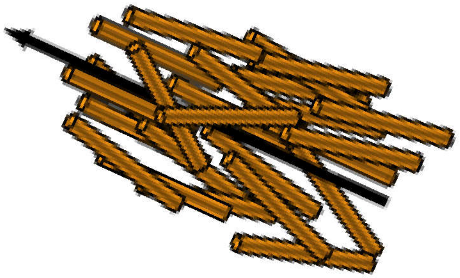
More space per particle= Faster diffusion

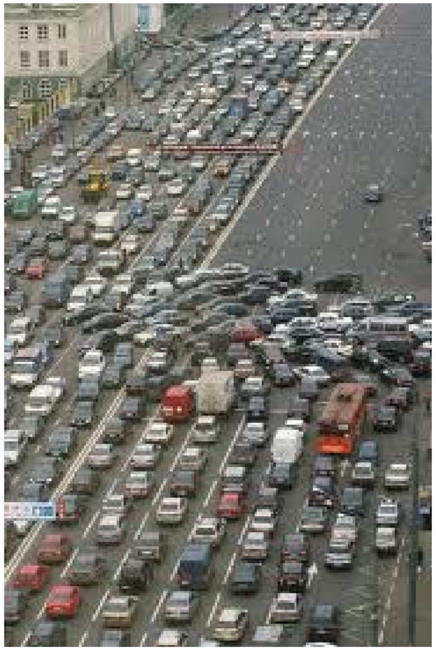
Faster diffusion = Signature for increase of translational entropy







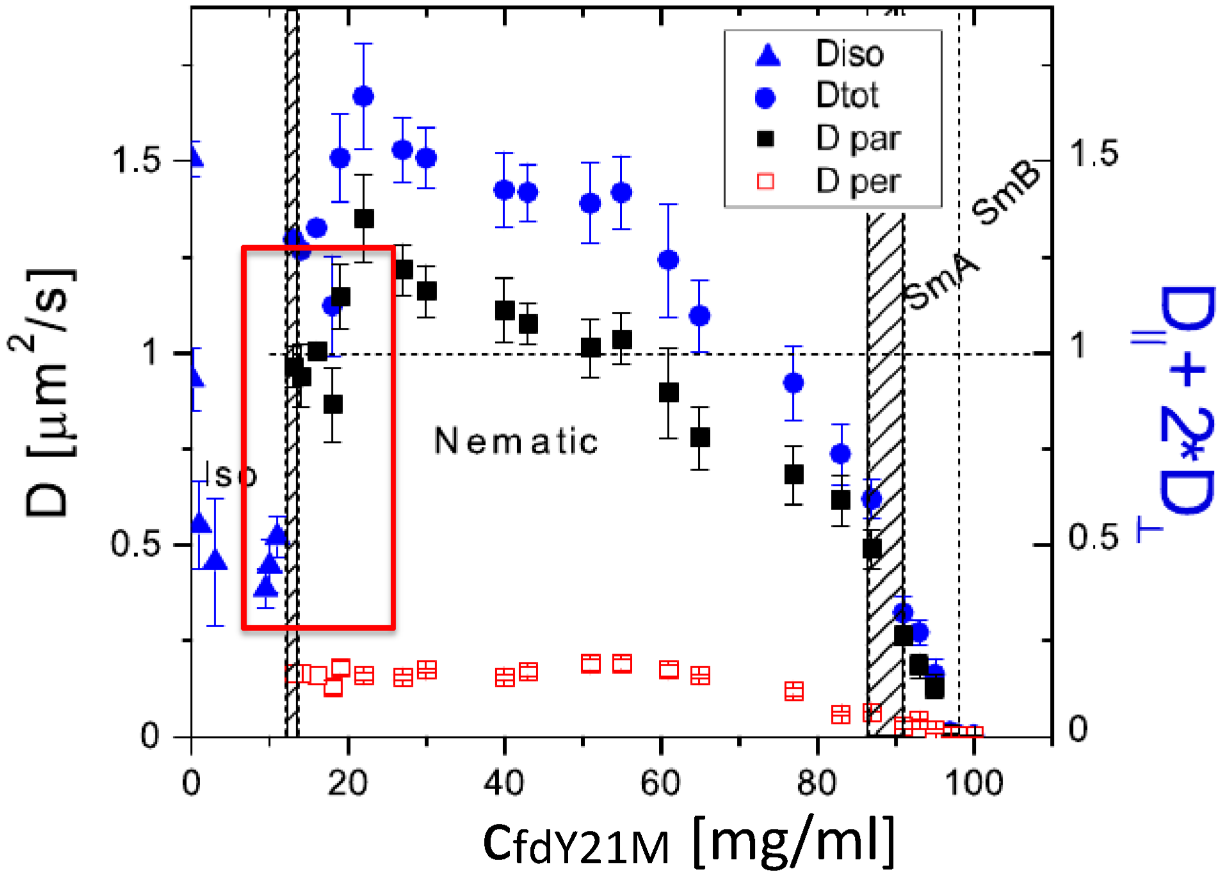




Isotropic

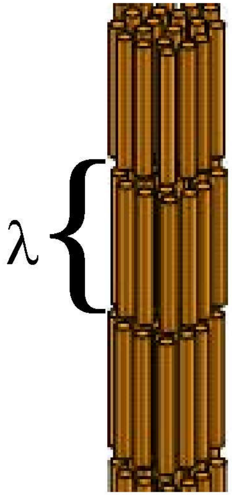
Nematic

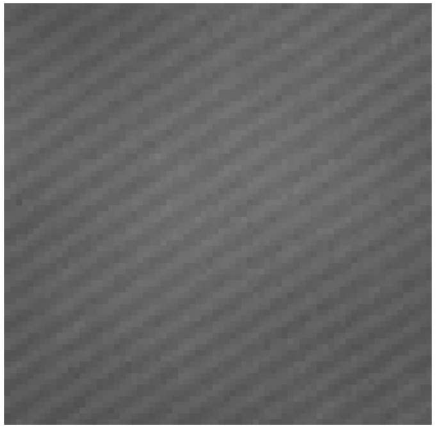
Dynamics at increasing degree of ordering

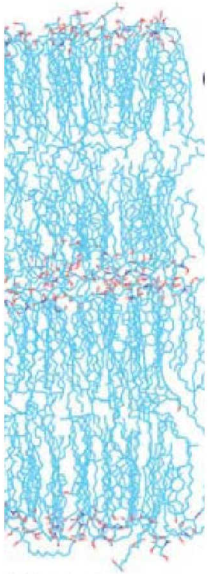


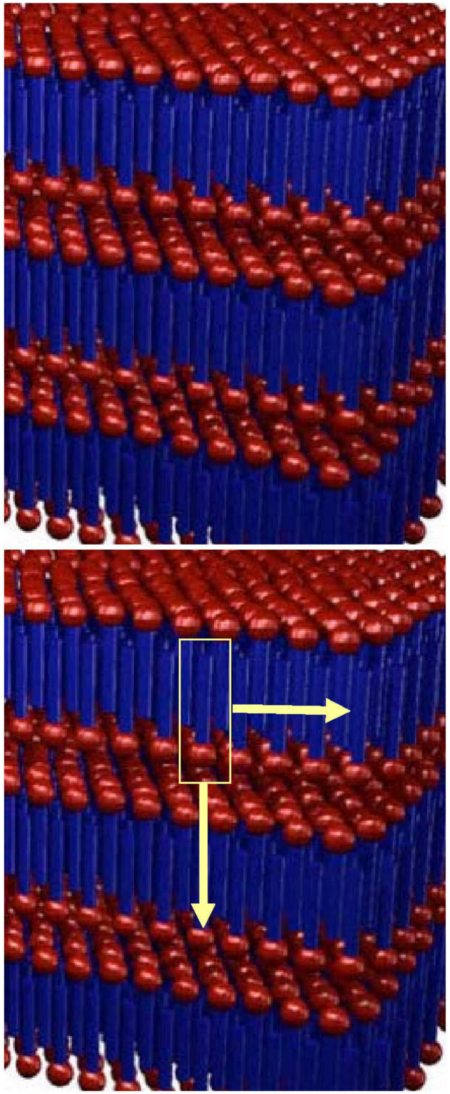
Signature increase entropy

Dynamics in the smectic phase





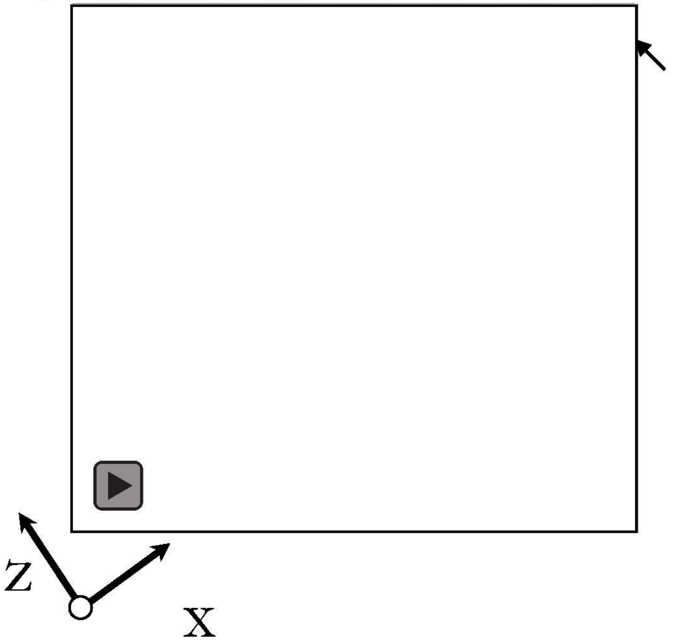


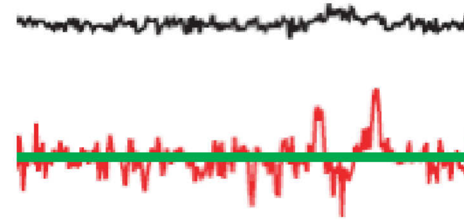


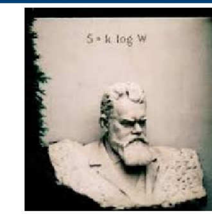
Permeation:

Transport through layers

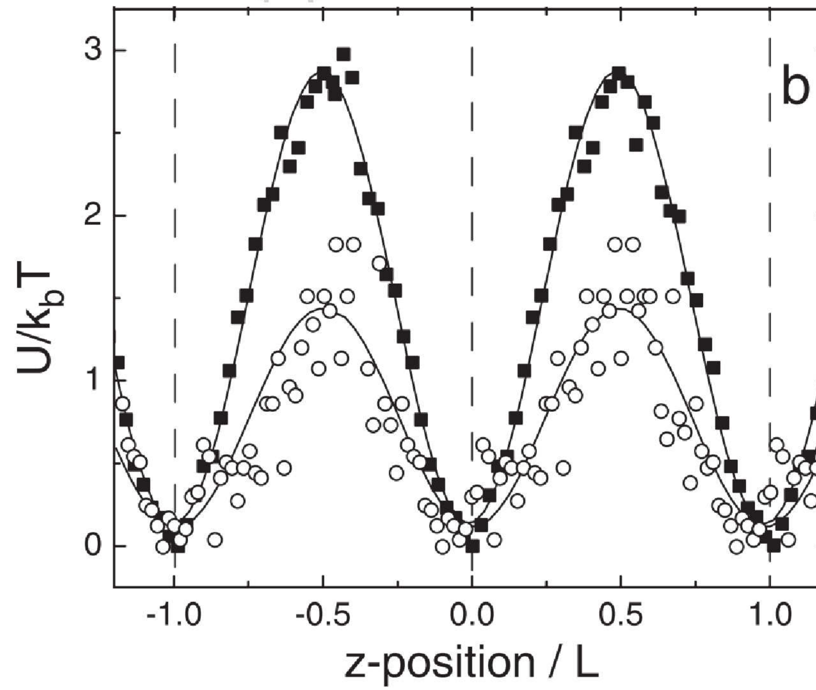
Dynamics in the smectic phase





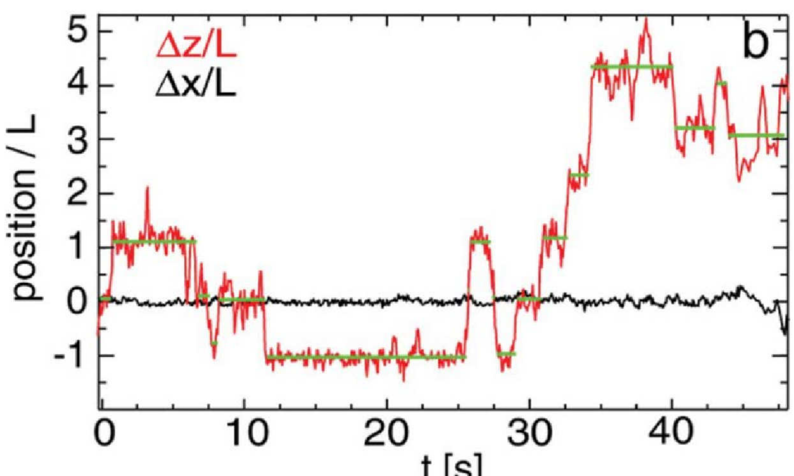


$$P(z) = e^{-U_{layer}(z)/kT}$$



Open: 110 mM
Solid: 20mM

Find jumps in trajectories:



Dynamics in the smectic phase

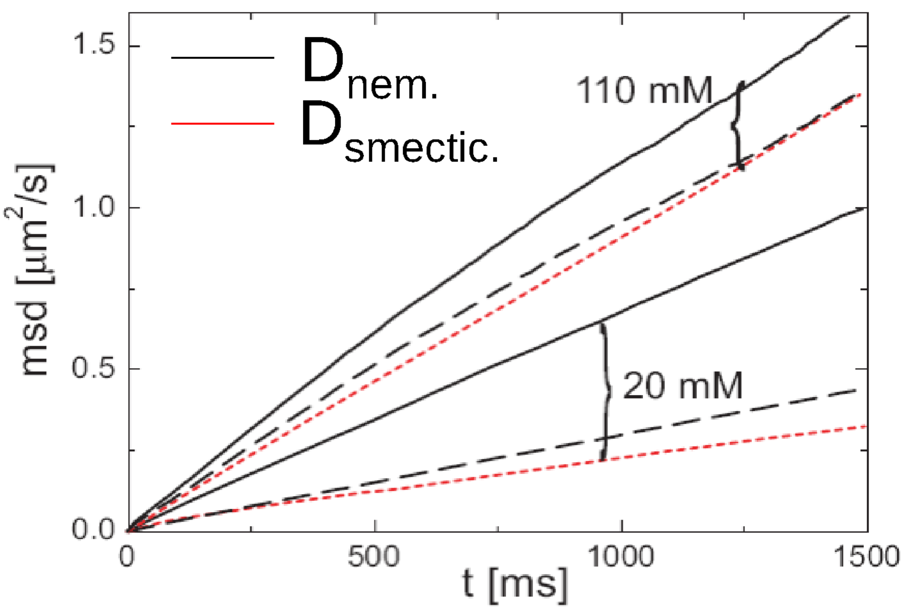
Physica **90A** (1978) 229–244

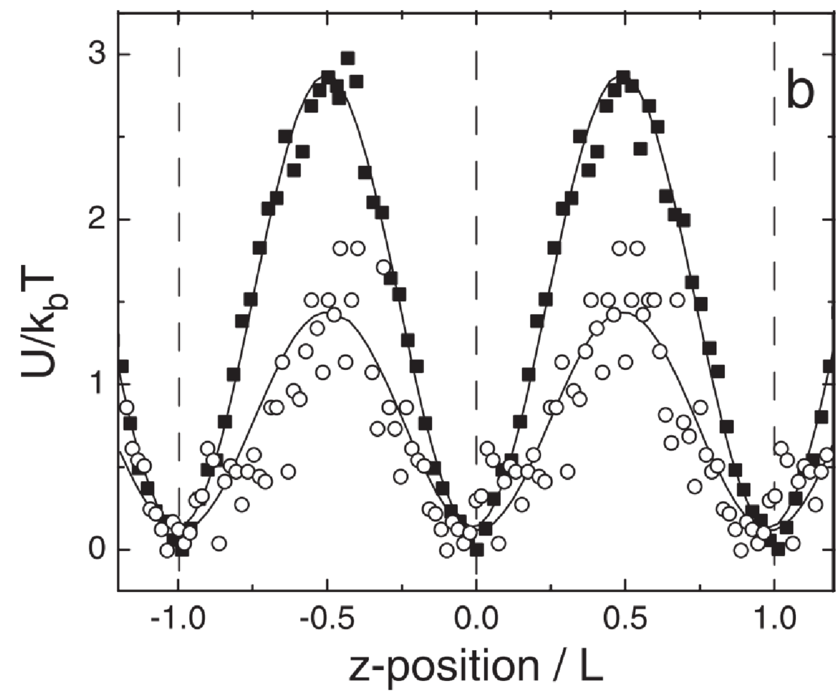
DIFFUSION COEFFICIENT FOR A BROWNIAN PARTICLE IN A PERIODIC FIELD OF FORCE

I. LARGE FRICTION LIMIT

R. FESTA and E. GALLEANI d'AGLIANO

$$D = \frac{D_0}{\langle e^{-U_{layer}(z)/kT}\rangle \langle e^{U_{layer}(z)/kT}\rangle}$$

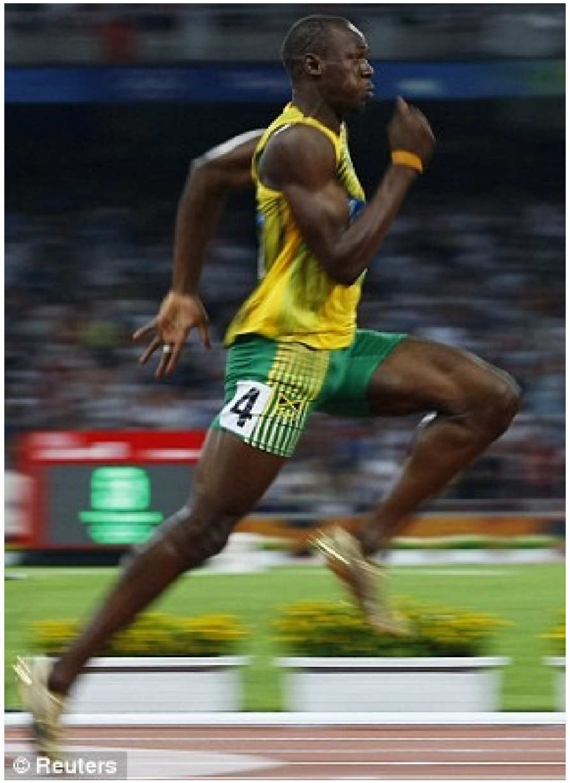




Diffusion in Smectic = jumping in 1D periodic potential

Lettinga and Grelet, PRL, 2007

So:



© Reuters

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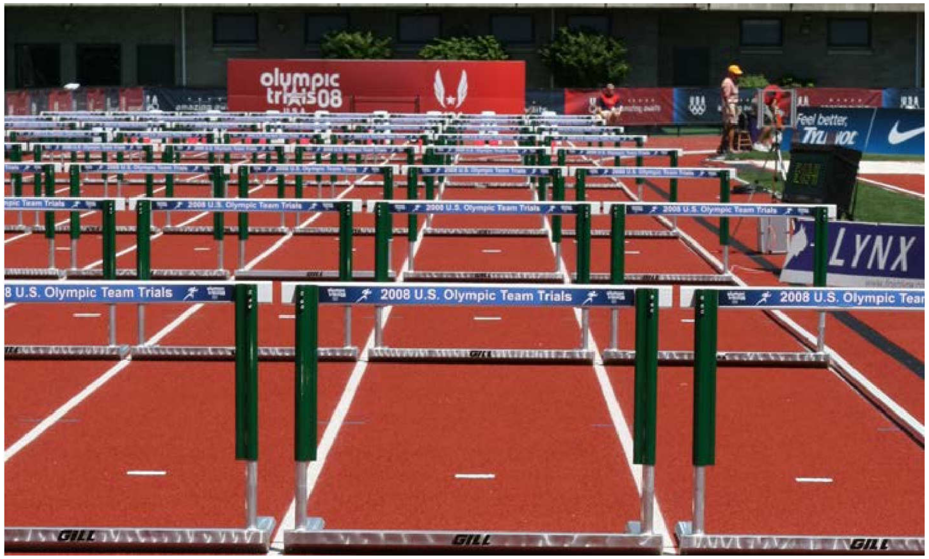
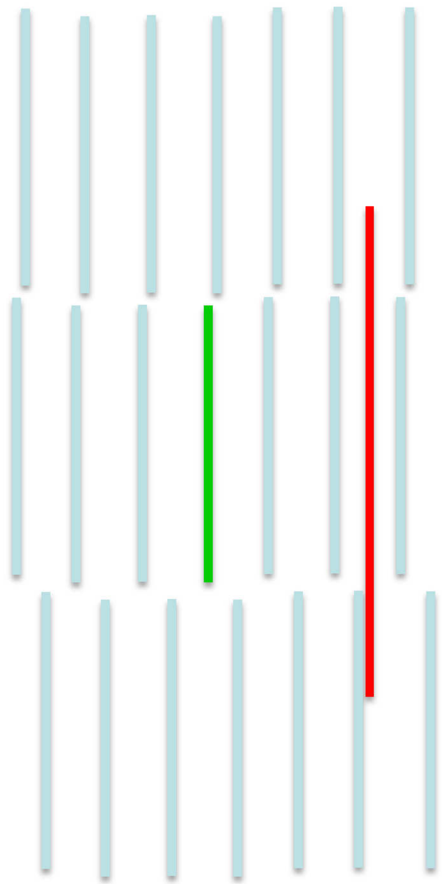


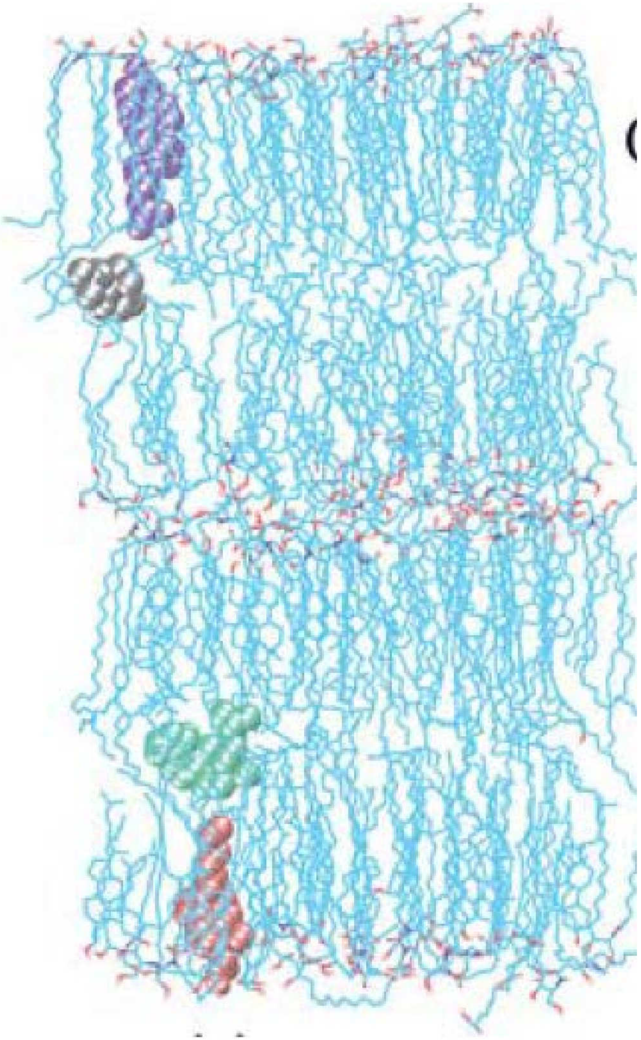
olympic trials 08
2008 U.S. Olympic Team Trials
LYNX
GILL

=

OSAKA NAGAI
NISHI

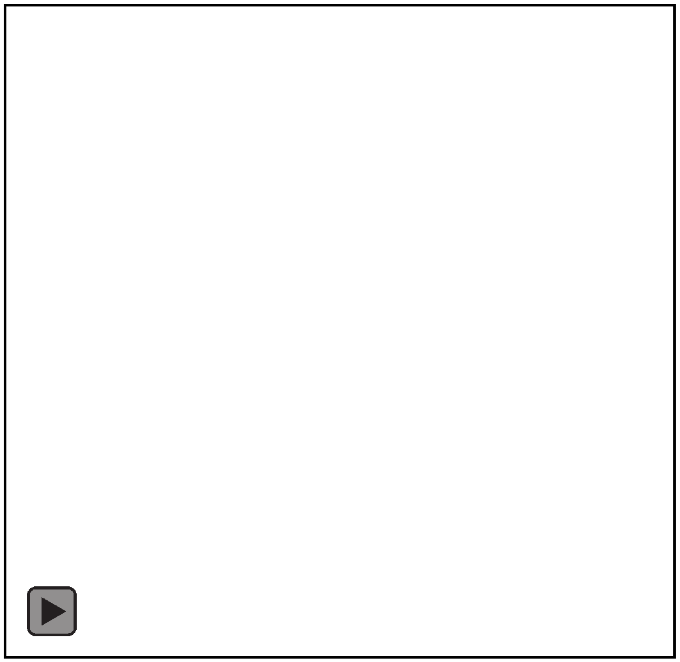
Put a guest in the layers

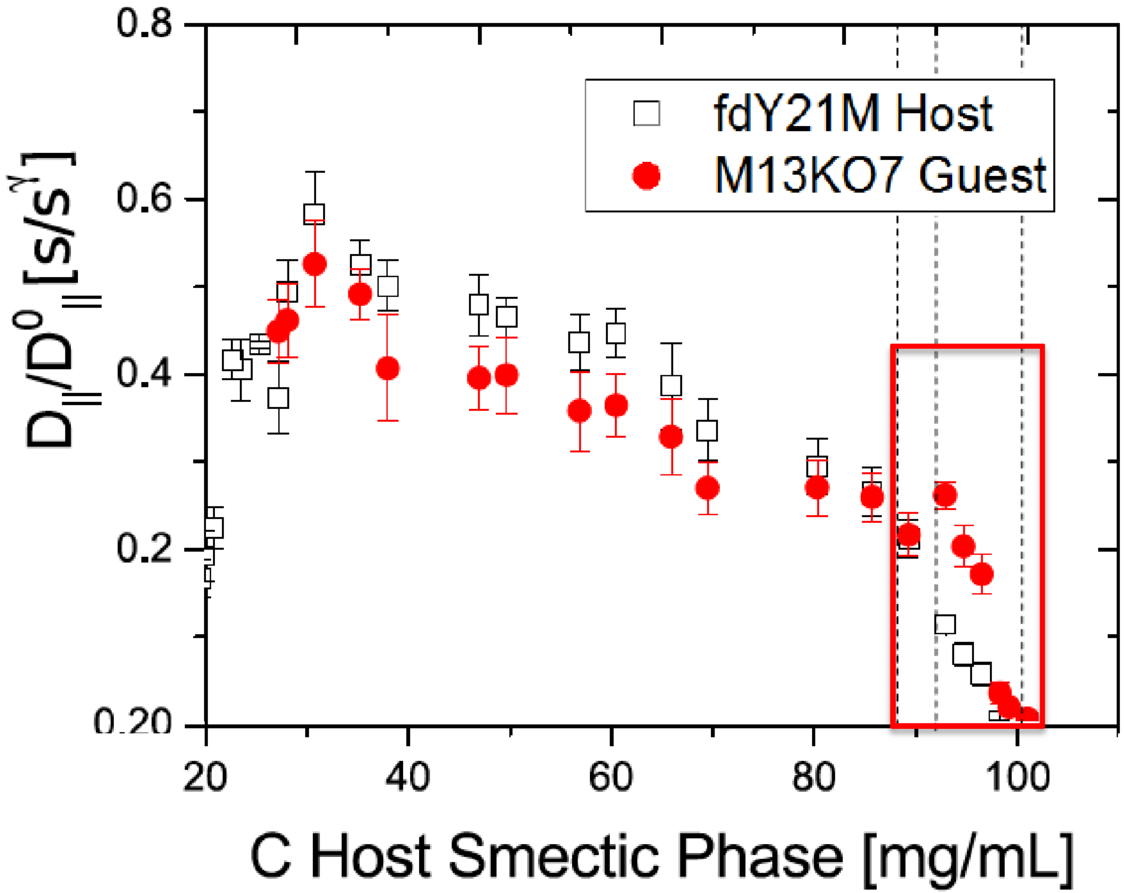




No fit

Longer is faster!

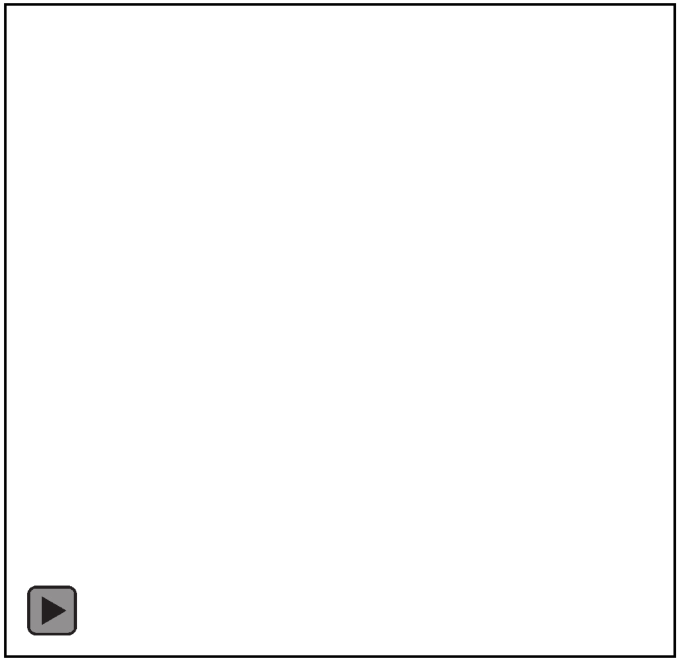


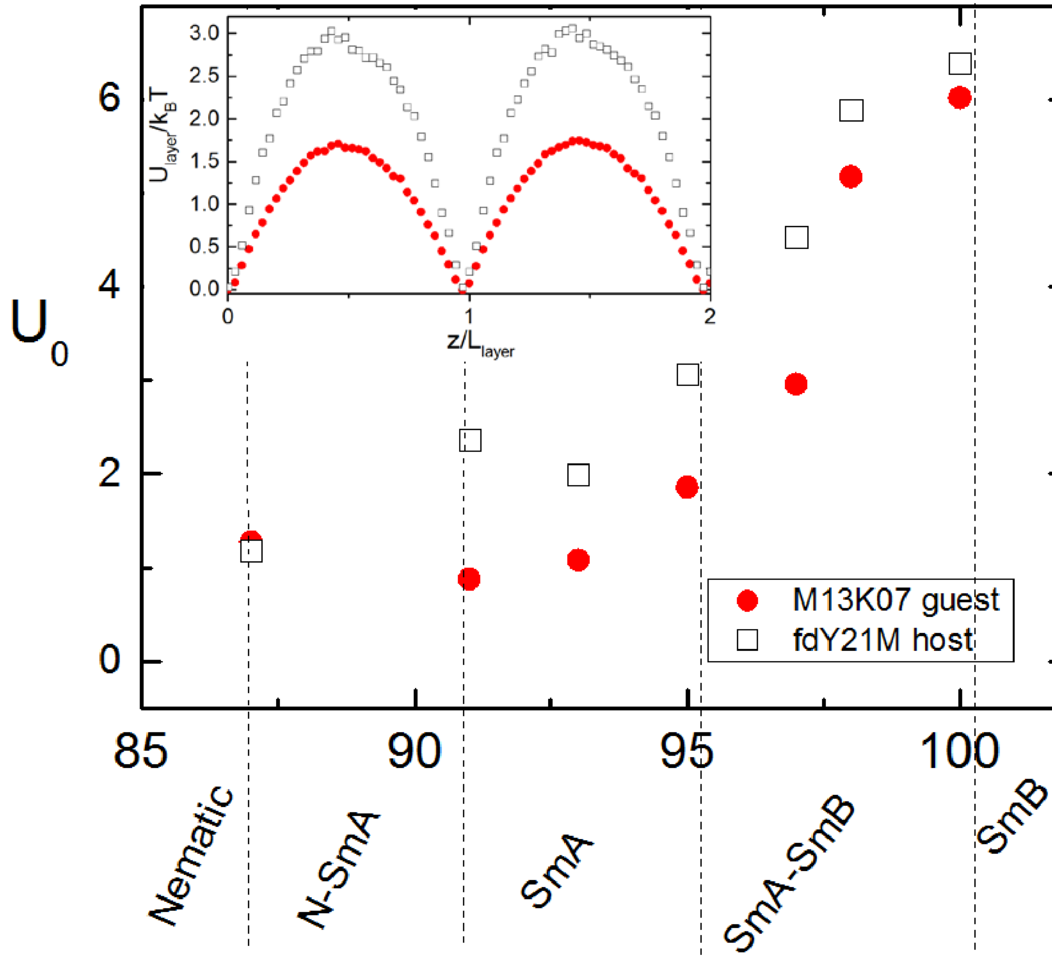


$$D = \frac{R\,T}{N}\,\frac{1}{6\,\pi\,k\,R} = \frac{k_b T}{6\pi\eta_0 a}$$

No fit

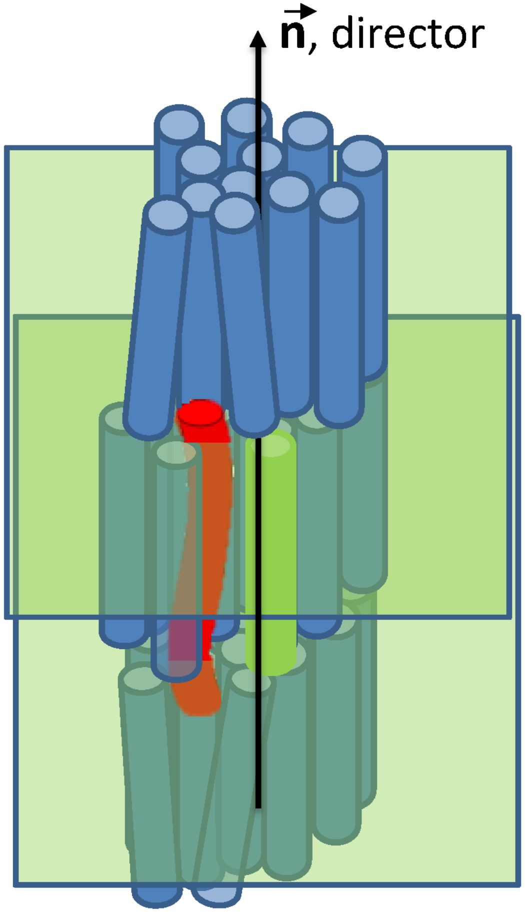
Longer is faster!



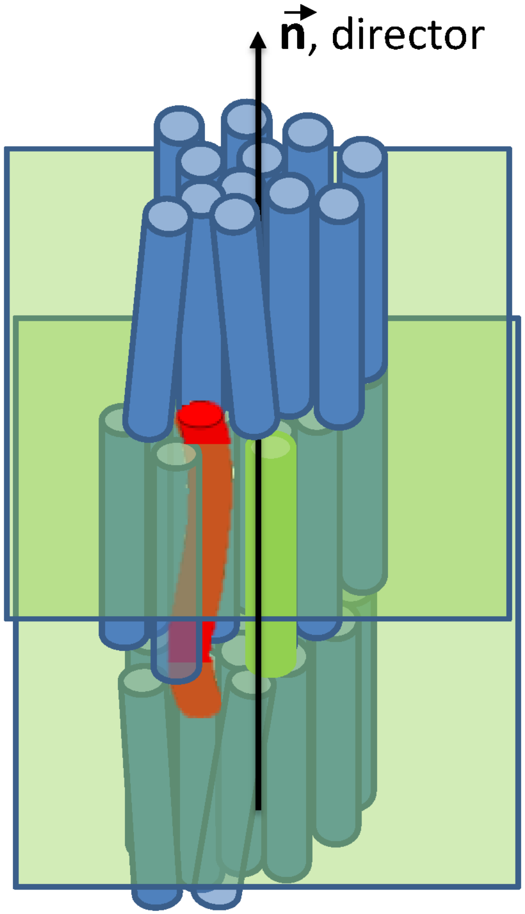


Alvarez et al PRL 2017

Some conclusions I



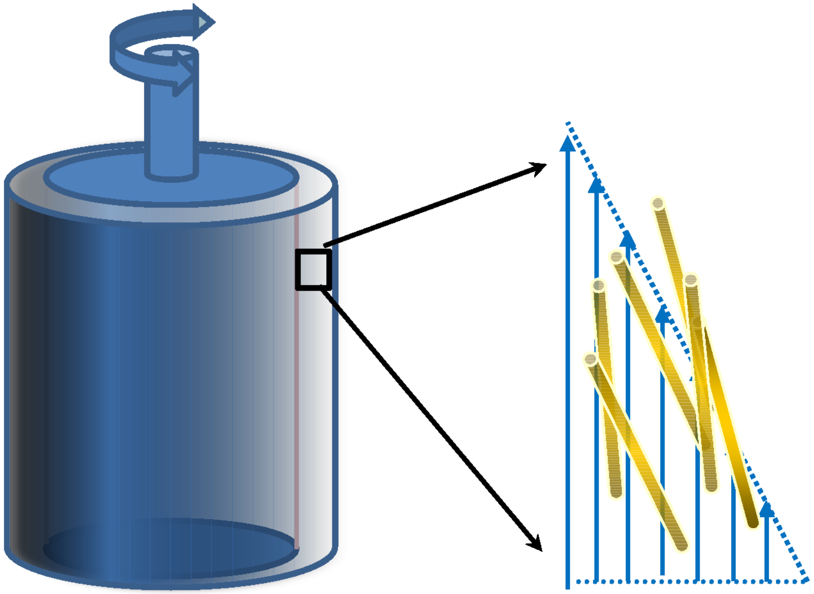
Some conclusions I



Vacancy needed to jump

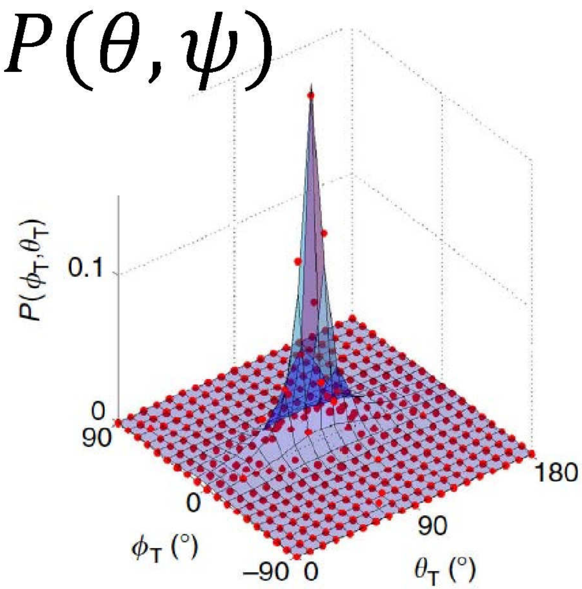
- Diffusion in Smectic = jumping in 1D periodic potential
- Long rods diffuse faster in a smectic layers of Short Host Particles…when size of particle does not fit length scale potential

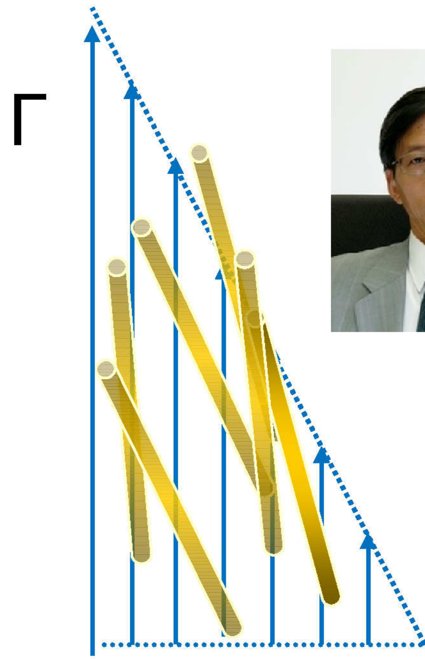
Flow behavior of isotropic rods

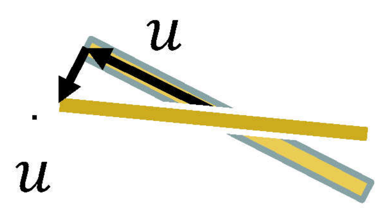


Goal: find connection between **mechanical response** and **orientational ordering**

Theory for sheared rods







DEH theory for rods in flow, equation of motion for pdf:

$$\frac{\partial \mathrm{P}}{\partial \mathrm{t}} = \langle \mathrm{D_r} \rangle \mathcal{R} \cdot \{\underbrace{\mathcal{R}\mathrm{P}}_{\text{Brownian Motion}} + \underbrace{\beta \mathrm{P} \mathcal{R} \mathrm{V_{scP}}}_{\text{Particle Interaction}}\} - \underbrace{\mathcal{R} \cdot \{\mathrm{u} \times (\Gamma \cdot \mathrm{u})\mathrm{P}\}}_{\text{Flow Field}}$$

Brownian Motion

Flow Field

Particle Interaction

Theory for sheared rods: the Smoluchowski

$$\frac{\partial P}{\partial t} = \langle D_r \rangle \mathcal{R} \cdot \{\mathcal{R}P + \beta P \mathcal{R} V_{scP}\} - \mathcal{R} \cdot \{u \times (\Gamma \cdot u) P\}$$

Use P(t,u) to calculate the orientational ordering tensor: $S(t) = \oint du\, uuP(u;t) = \langle uu$

S characterised by largest eigenvalue: $\max(\mathrm{eig}(S)) = \lambda_1 \sim \langle P_2 \rangle$

Use S to calculate stress tensor, this is the link!

$$\Sigma = -\eta I + 2\eta_s E \quad \Sigma = -pI + 2\eta_s E + 3\rho k_B T \left[S - \frac{I}{3} + \frac{L}{d} \varphi \left(S^{(4)} : S - S \cdot S \right) + \frac{1}{6D_r} \left(S^{(4)} : E - \frac{I}{3} S : E \right) \right]$$

$E = \frac{1}{2}\left(\nabla \vec{v} + \left(\nabla \vec{v}\right)^T\right)$ Excluded volume and inverse rotational diffusion $S^{(4)} = \oint d\vec{u}\vec{u}\vec{u}\vec{u}\vec{u} P(\vec{u})$

Stress tensor characterised by viscosity $\eta(S, \dot{\gamma}) = \Sigma_{21}(S)/\dot{\gamma}$

Typically plot zero shear viscosity $\eta_0 = \lim_{\dot{\gamma} \to 0} \eta$ and reduced viscosity η/η_0

Theory for sheared rods: rotational diffusion

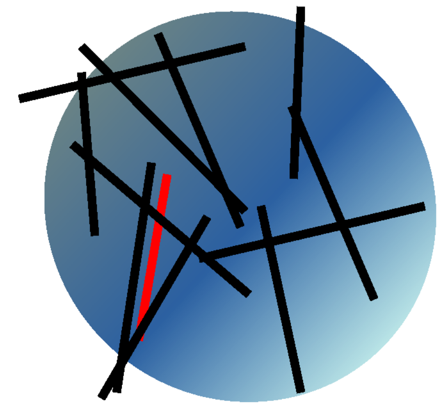
$$\frac{\partial P}{\partial t} = \langle D_r \rangle \mathcal{R} \cdot \{\mathcal{R}P + \beta P \mathcal{R} V_{scP}\} - \mathcal{R} \cdot \{u \times (\Gamma \cdot u) P\}$$

What is the relevant diffusion coefficient? $D_r^0 = \frac{3\ln(L/d)}{\beta \pi \eta_s L^3}$ $\sim L^{-3}$

Tube model for isotropic surrounding: $\bar{\bar{D}}_r = c D_r^0 (\rho L^3)^{-2}$ $\sim L^{-6}$

[Doi, Edwards, *J. Chem. Soc. Faraday Trans.* 2,1978]

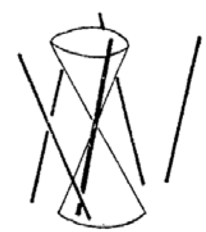
$c \approx 1.32 \times 10^3$



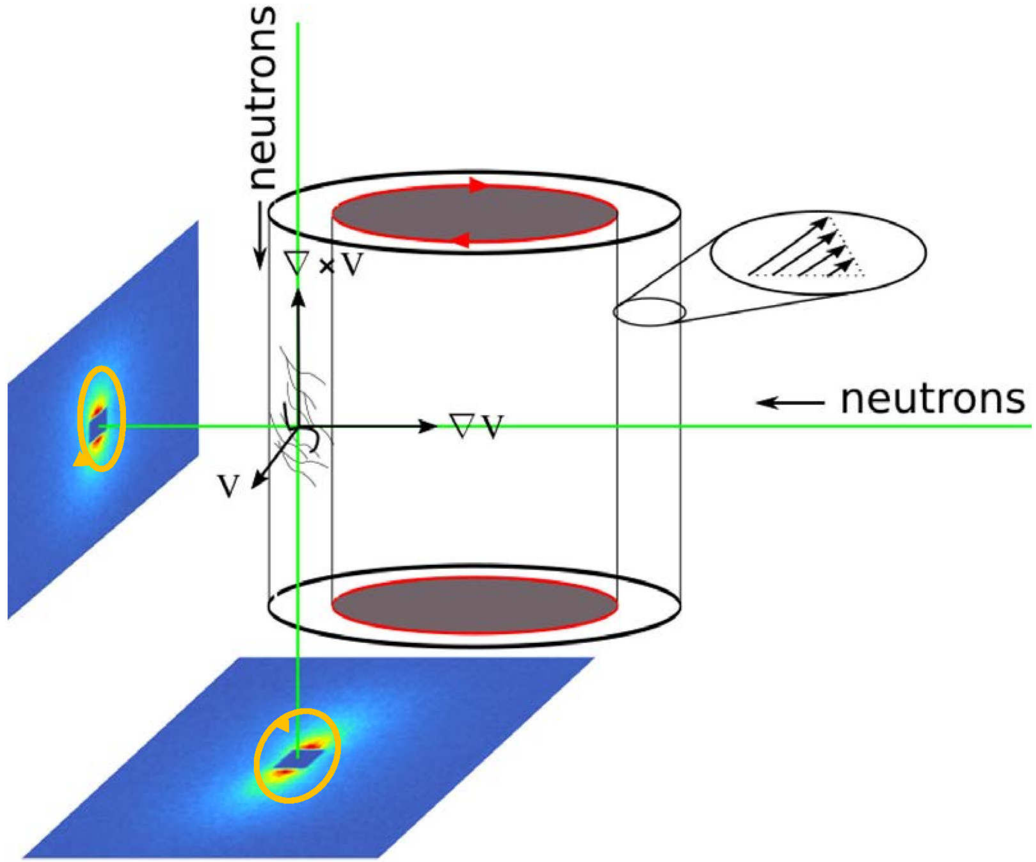
Teraoka et al. *J. Chem. Phys.* 91 1989]

Tube dilation for anisotropic surrounding:

$$\langle D_r \rangle = c D_r^0 \left(\frac{5}{4} \rho L^3 \left(1 - \frac{3}{5} S : S \right) \right)^{-2}$$



3-D SANS on rods



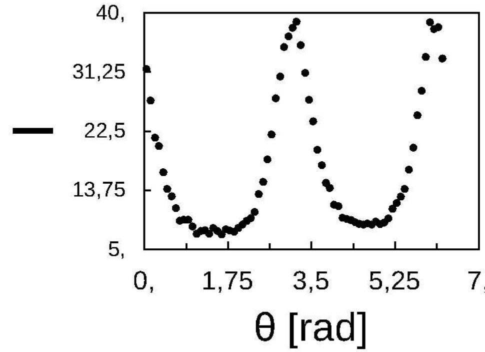
$P(\psi)$

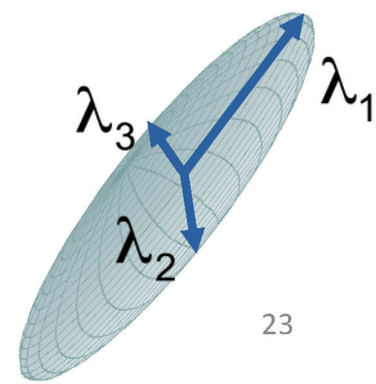
$\downarrow$

$\langle P_2(\psi) \rangle$

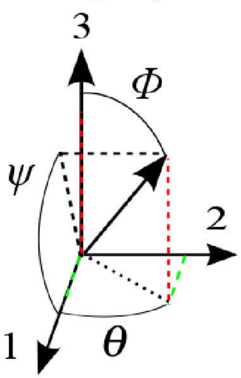
$\downarrow$

$\lambda_1(\psi)$



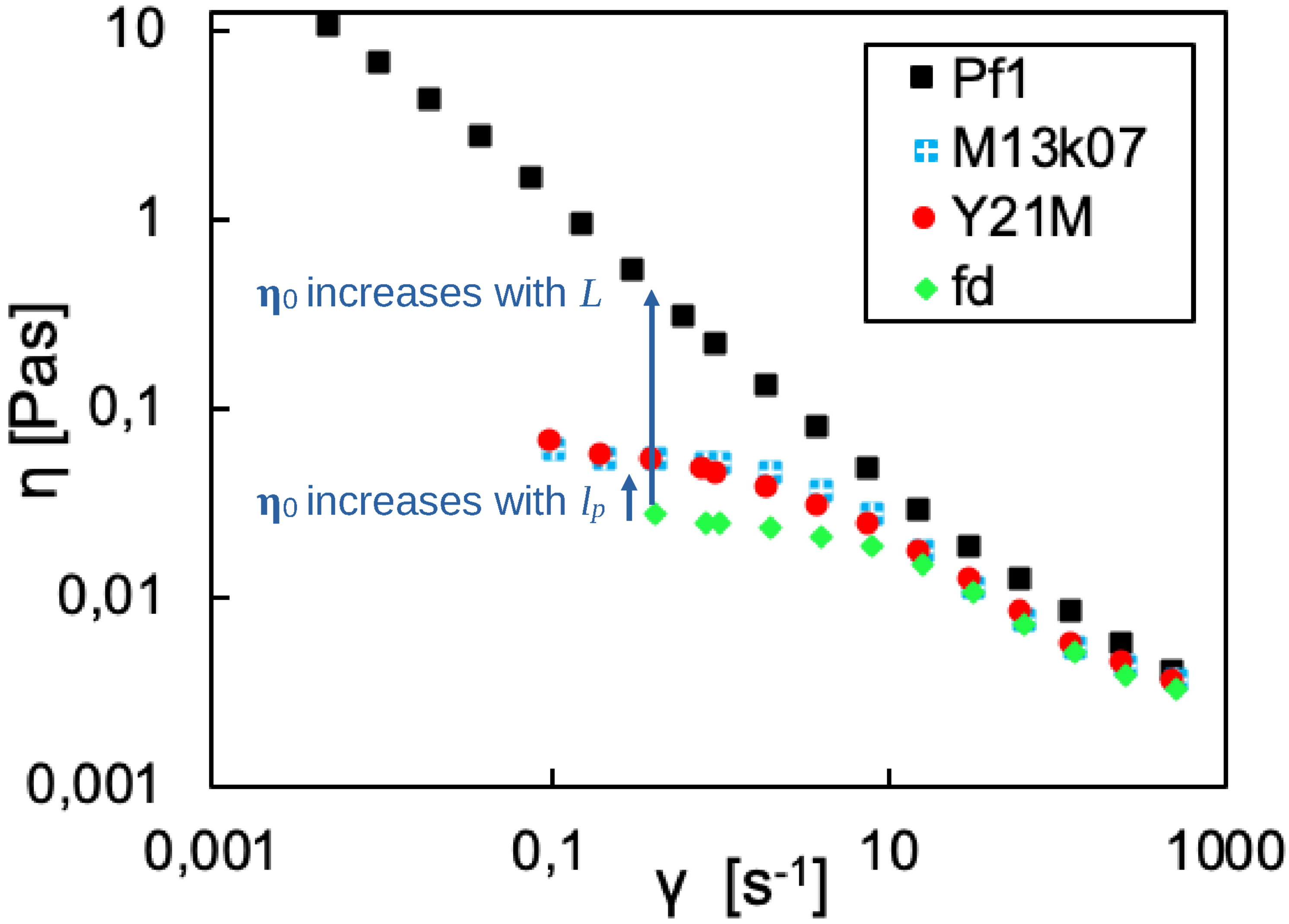


$P(\theta) \rightarrow \langle P_2(\theta) \rangle \rightarrow \lambda_1(\theta)$



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

Shear thinning rods: effect of length

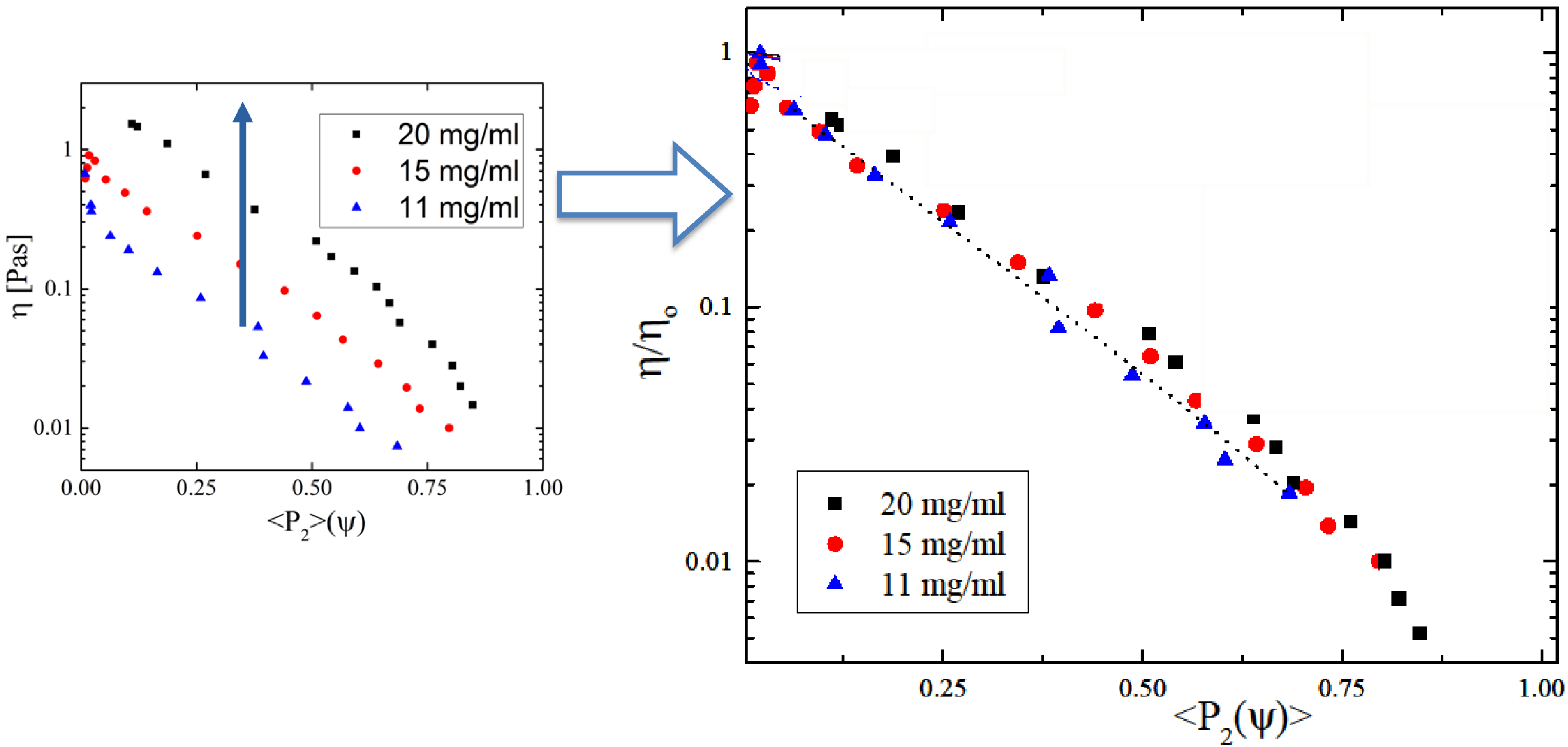


Viscosity vs projected order parameter <$P_2(\psi)$>

KU LEUVEN

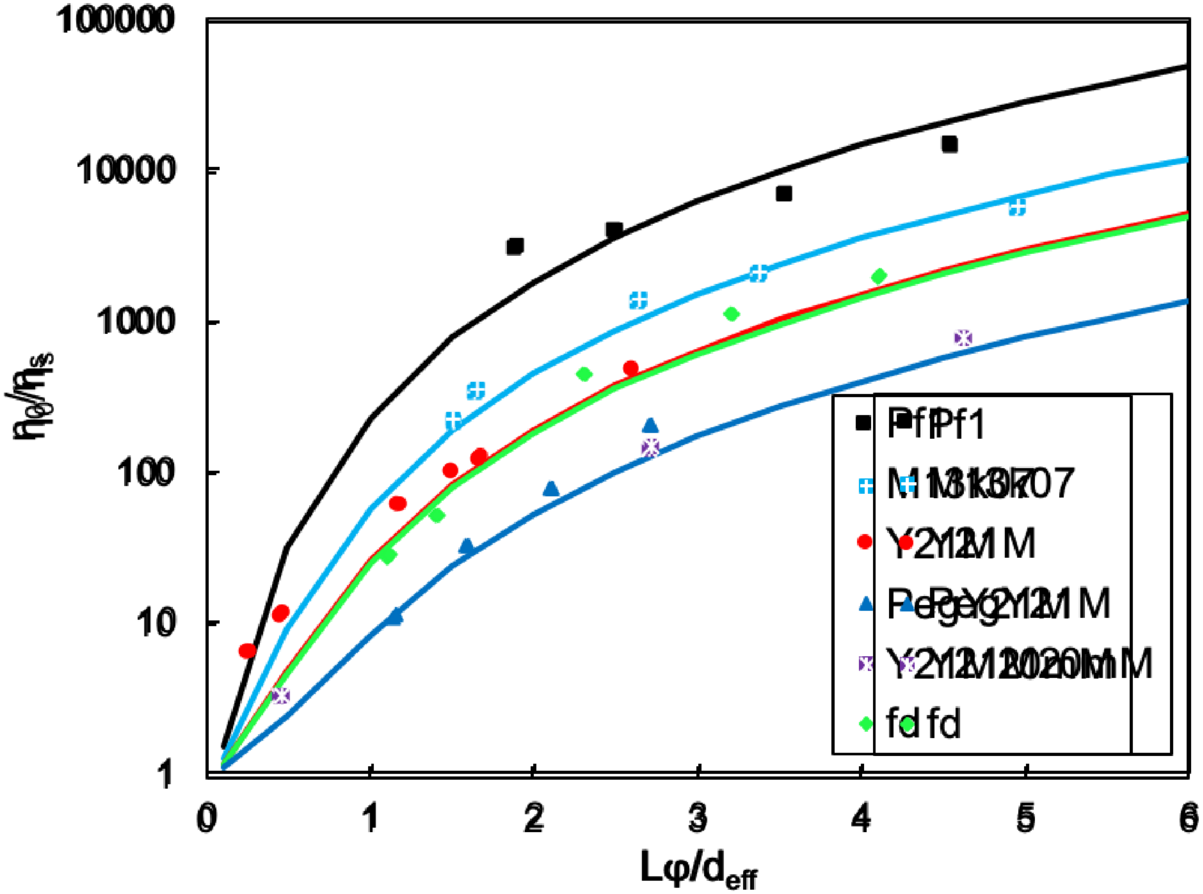
Use <$P_2(\psi)$> to scale viscosity

Assumption: shear thinning is caused by orientation



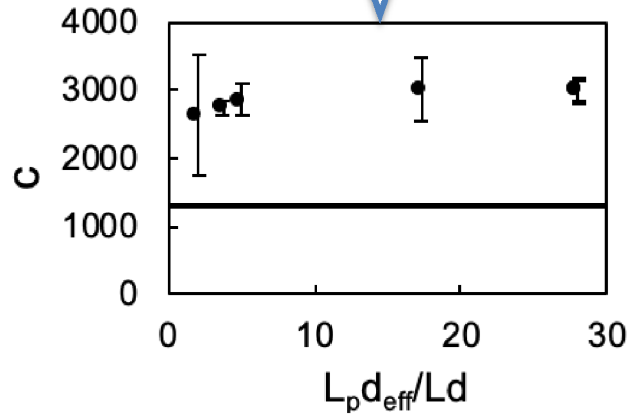
Lang et al, *Polymers*, 2016

Zero shear viscosity of rods



$$\eta o \simeq \eta_s + \rho/\beta D_r$$

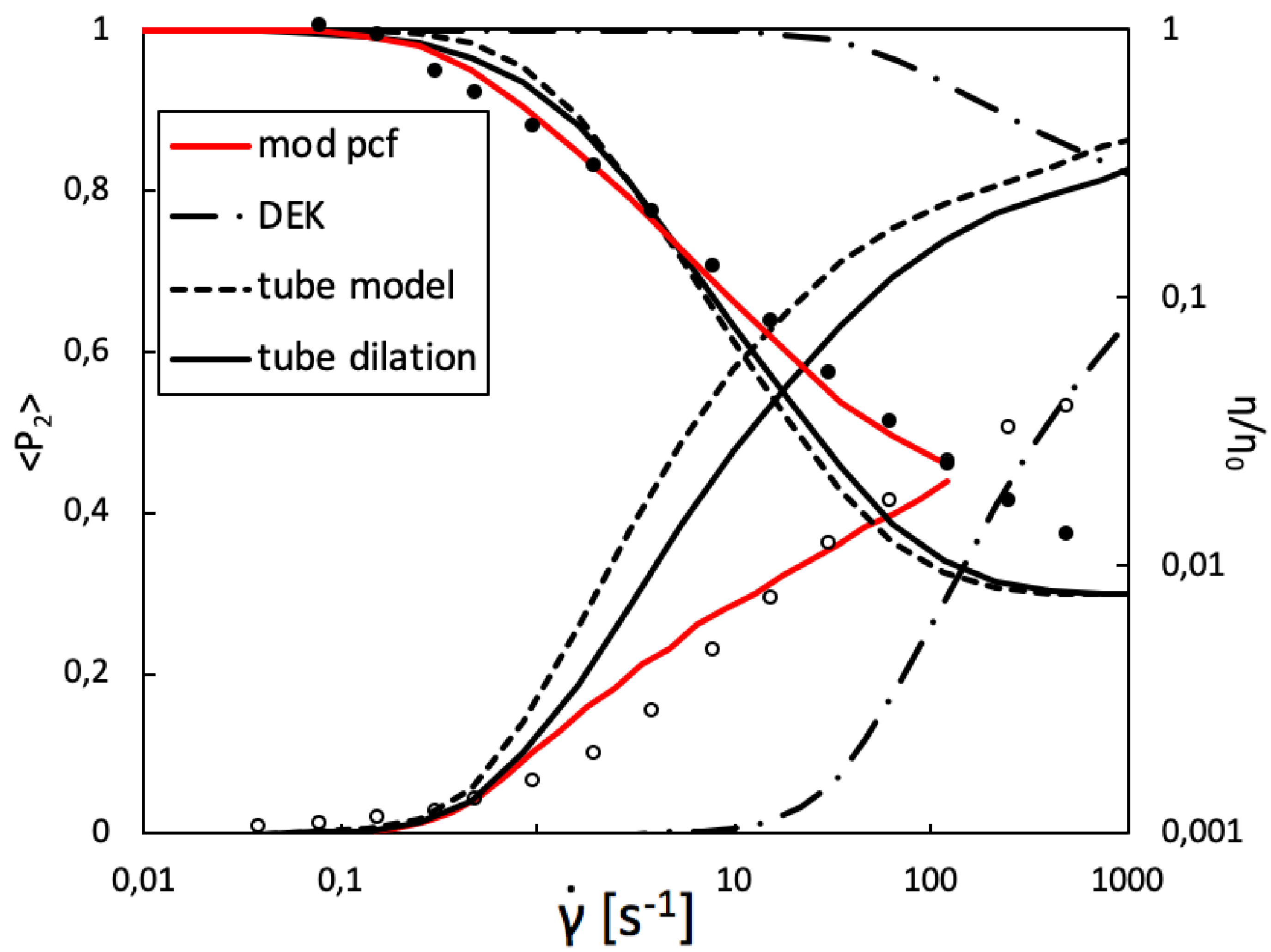
$$D_r = cD_r^0(\rho L^3)^{-2}$$



We determined Teraokes constant!

We understand huge *L* dependence

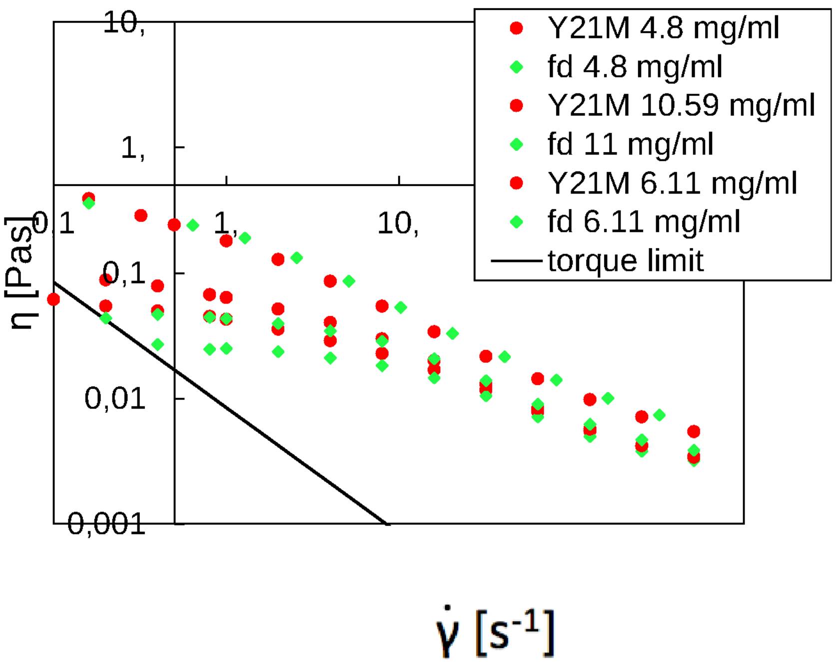
Understanding shear thinning



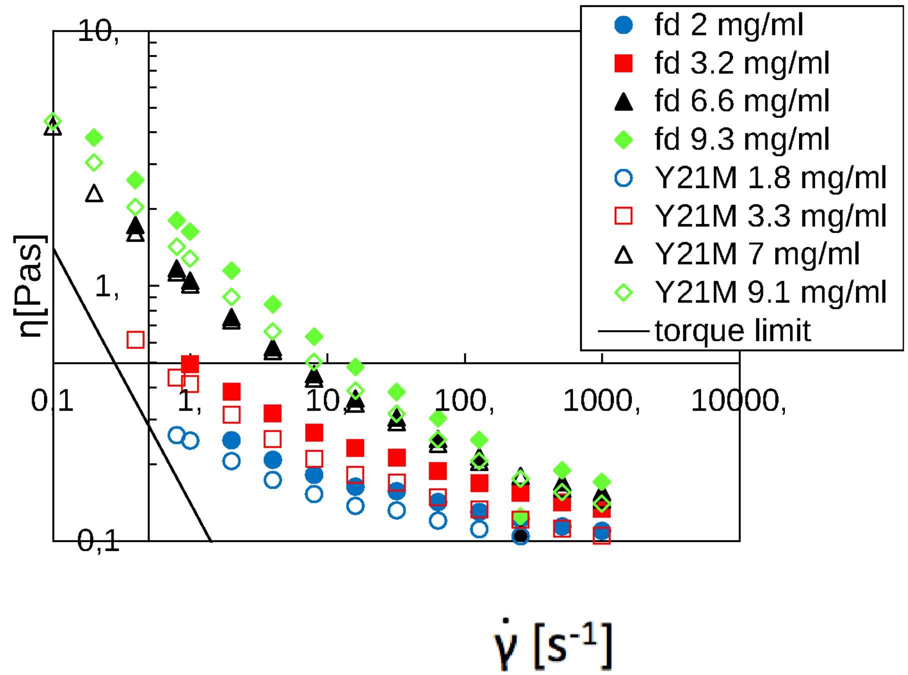
$$\partial_t g = D_r \mathcal{R} \cdot [\mathcal{R} g + \beta g \mathcal{R} U] - \mathcal{R} \cdot [g u \times \Gamma \cdot u]$$

$$g \approx \exp[-\beta V] + \dot{\gamma} \delta g^{(1)}$$

Influence stiffness on flow response



Suspensions in water



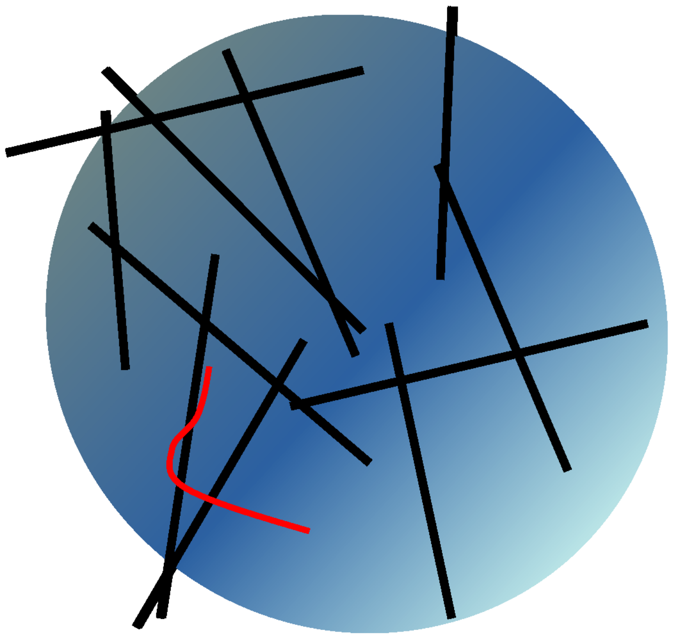
Suspensions in glycerol

Particle flexibility leads to a decrease in zero shear viscosity

The nonlinear viscosity shows the opposite!

Influence stiffness on flow response

$$D_r^{\,rigid} < D_r^{\,flex}$$

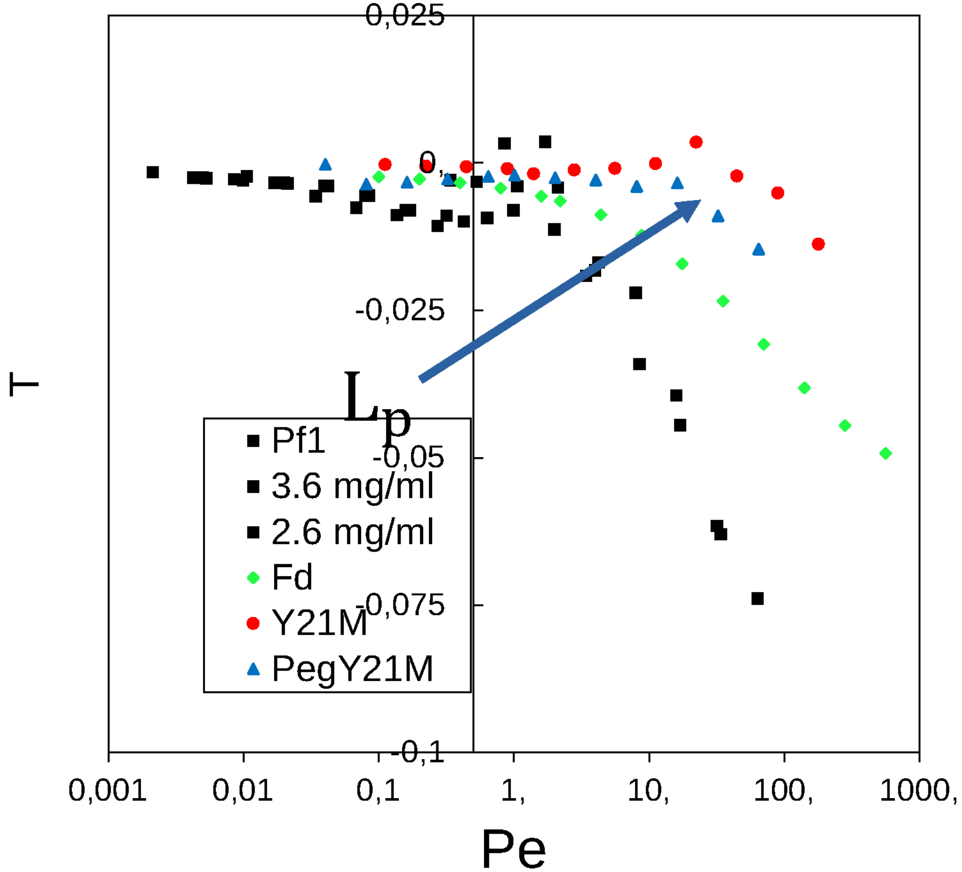


We understand zero shear result, but what about high shear result?

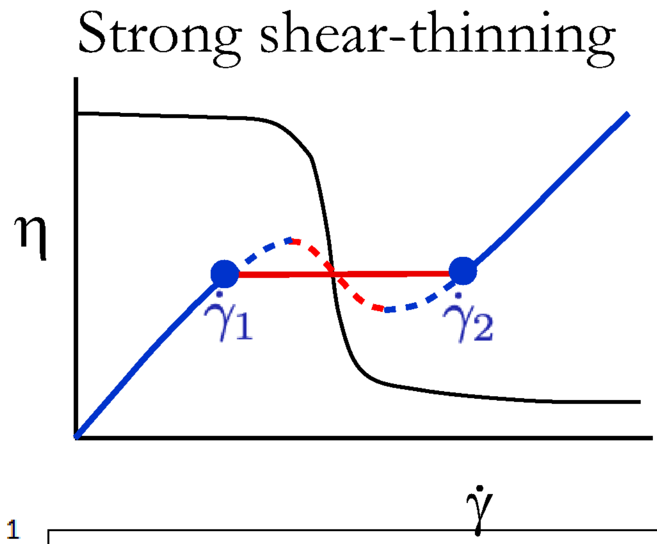
Effect of morphology on biaxiality

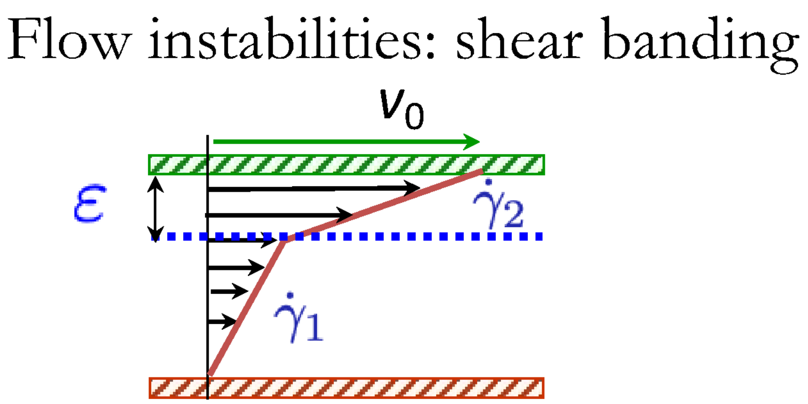
$$T = \frac{1}{2\left(2-\lambda_1(\theta)-\lambda_1(\psi)\right)}\left[\lambda_1(\theta)\lambda_1(\psi)-\left(\lambda_1(\theta)\right)^2\right]$$

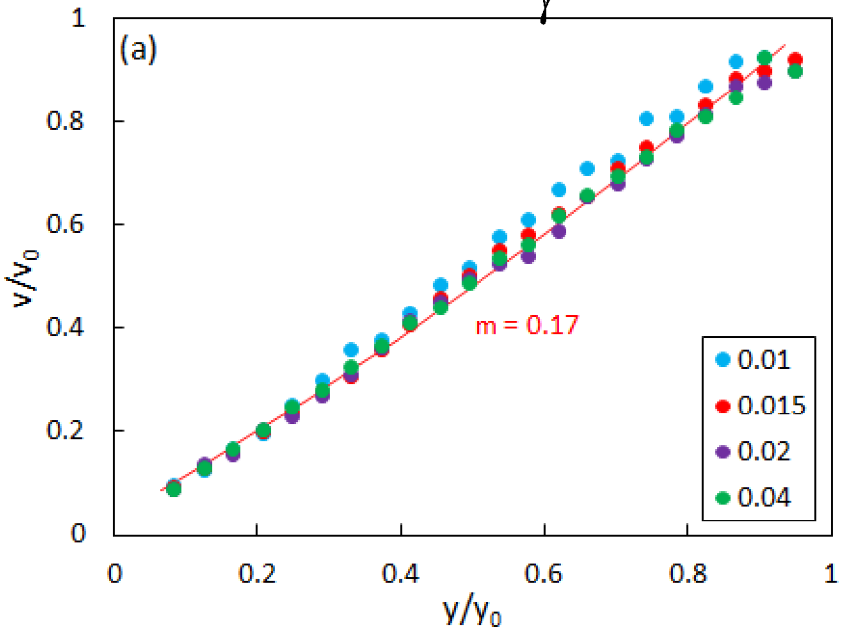
Lang et al, *Polymers* 2016, **8**, 291

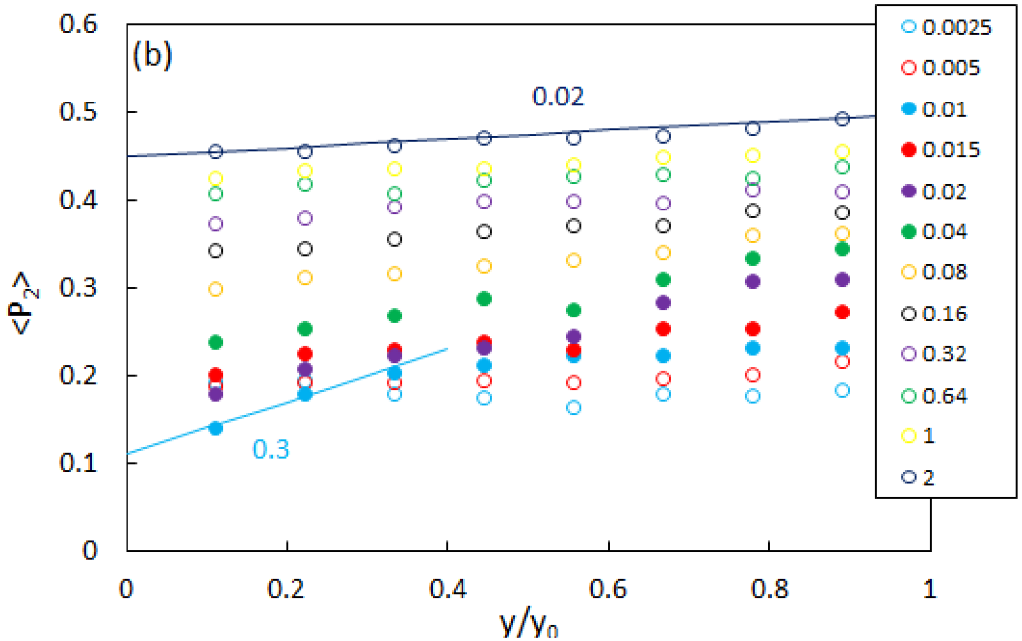


Velocity & ordering profiles of rods









- **Only very long and flexible rods show hints of shear banding**

Some conclusions II

- Understanding zero shear viscosity: now we can do predictions for all stiff systems

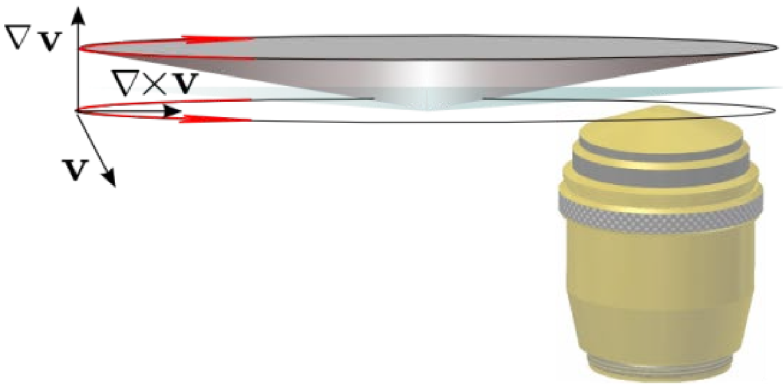
- Understanding shear thinning: now we can flow response

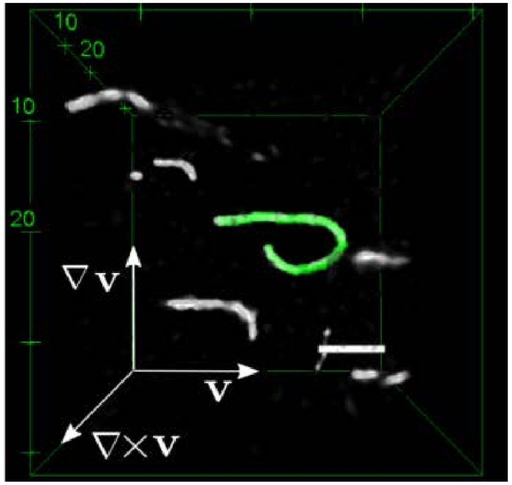
- No complete understanding of effect of stiffness

- Need microscopic input, as SANS takes ensemble averages

In situ confocal microscopy on entangled F-actin

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



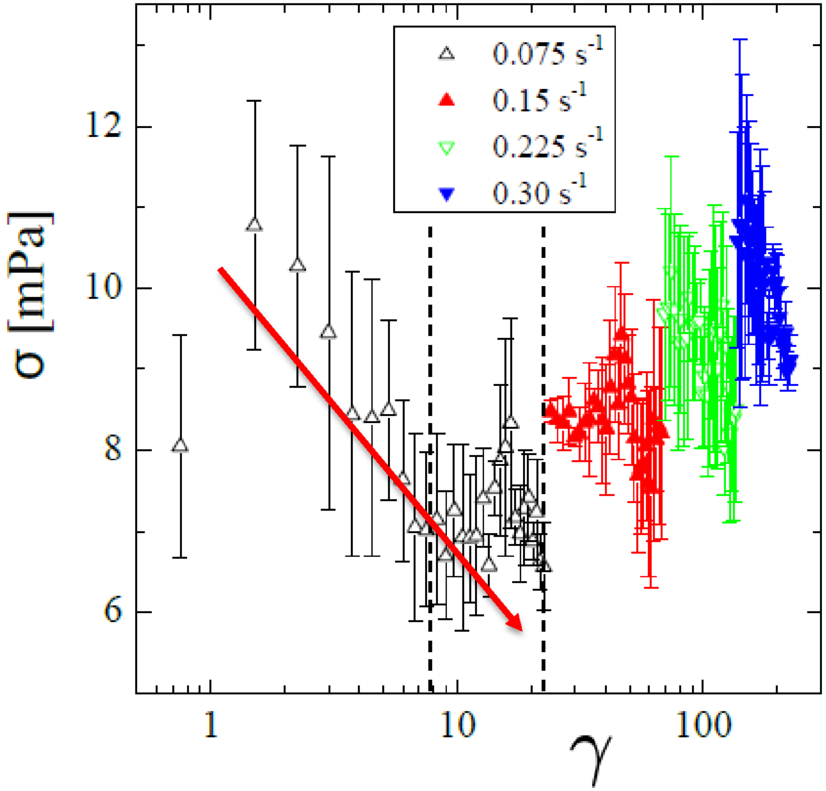


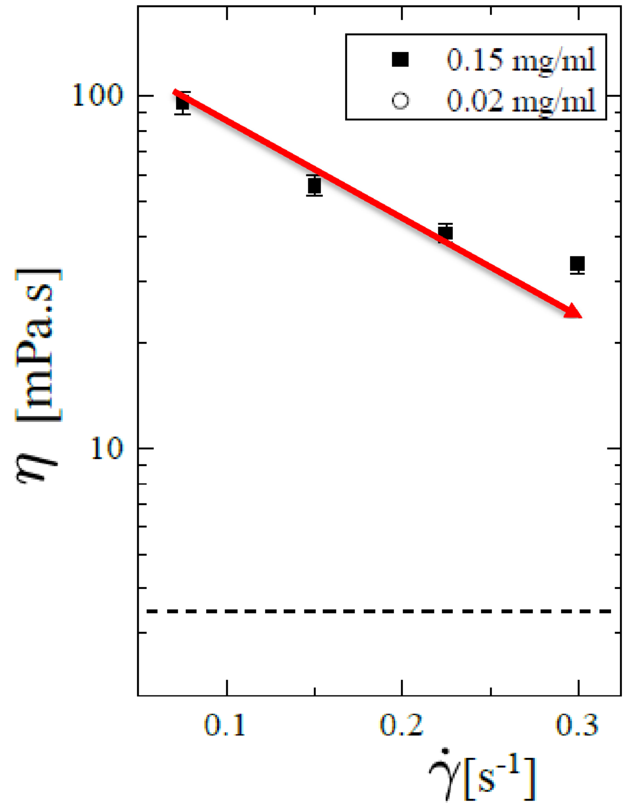
- Use three concentrations, label 1 per 100 filaments
- About 100 analyzed filaments per combination

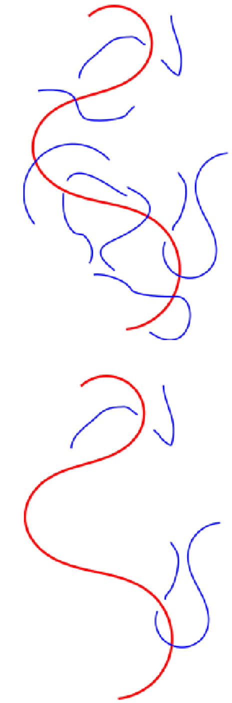
Kirchenbüchler et al *Nature Communications* 5:5060 (2014)

Rheological response of F-actin dispersions

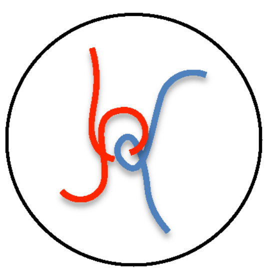
KU LEUVEN



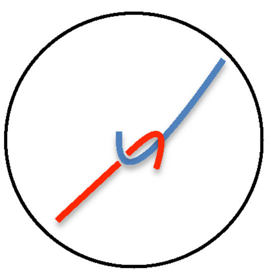




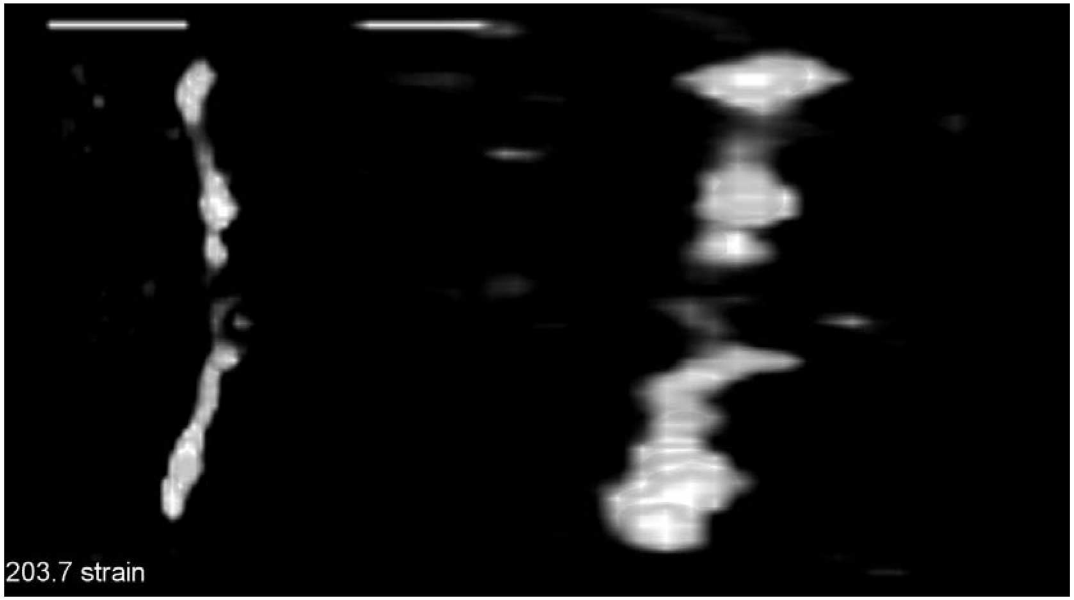
Strain softening

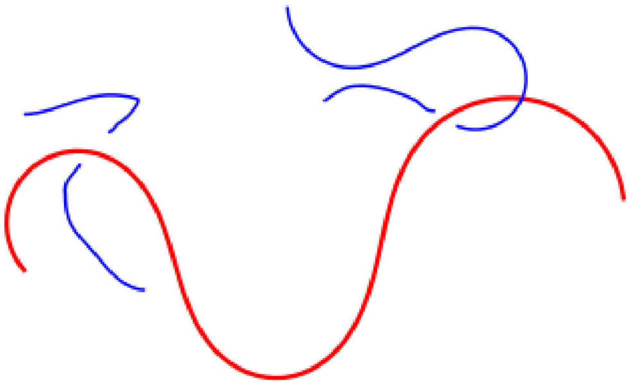


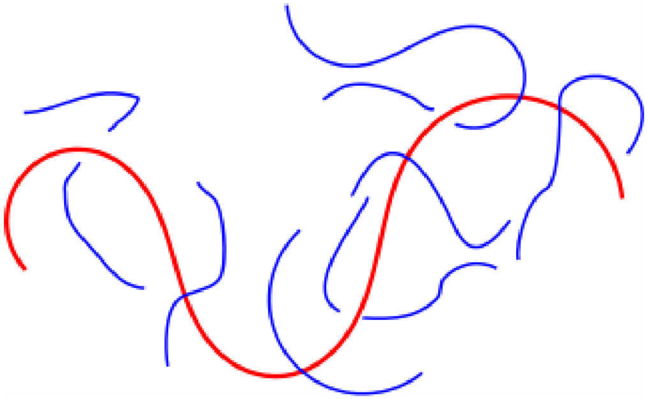
Shear thinning

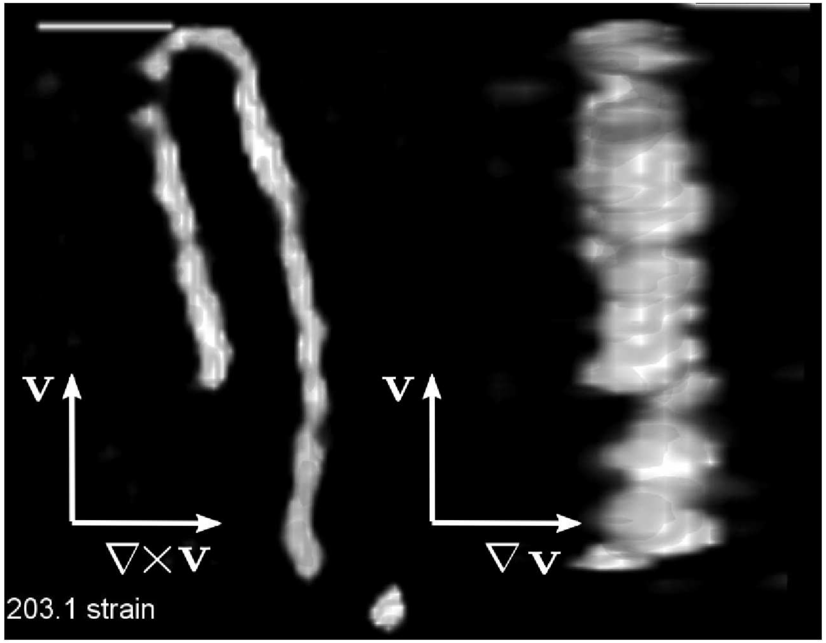


Sheared F-Actin in 3-D

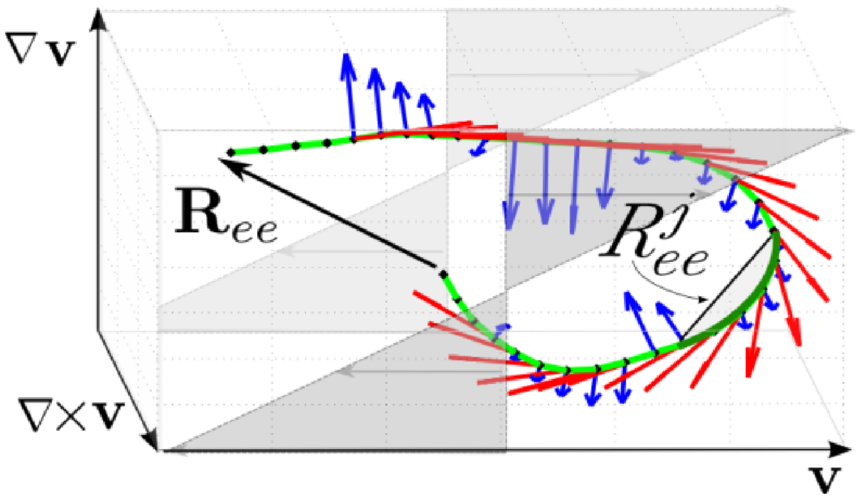


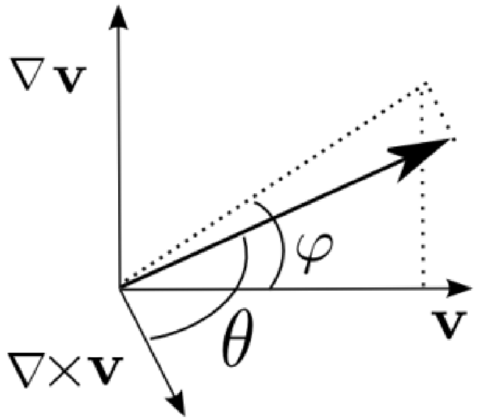




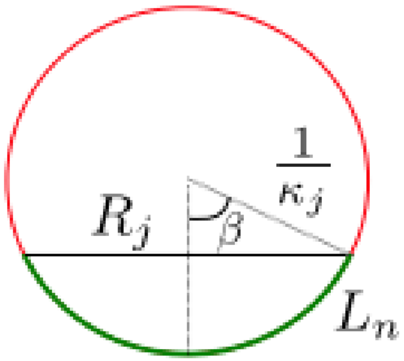


Analyze local bending and stretching:

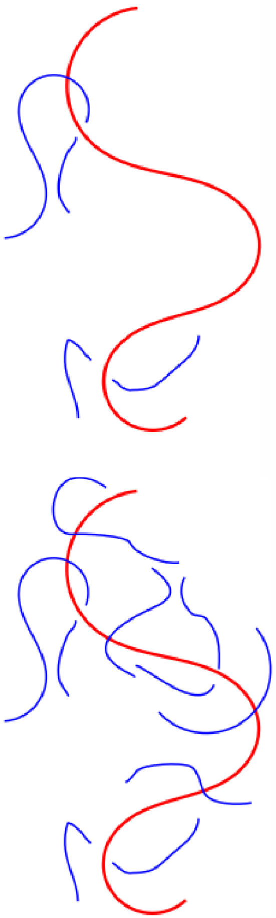


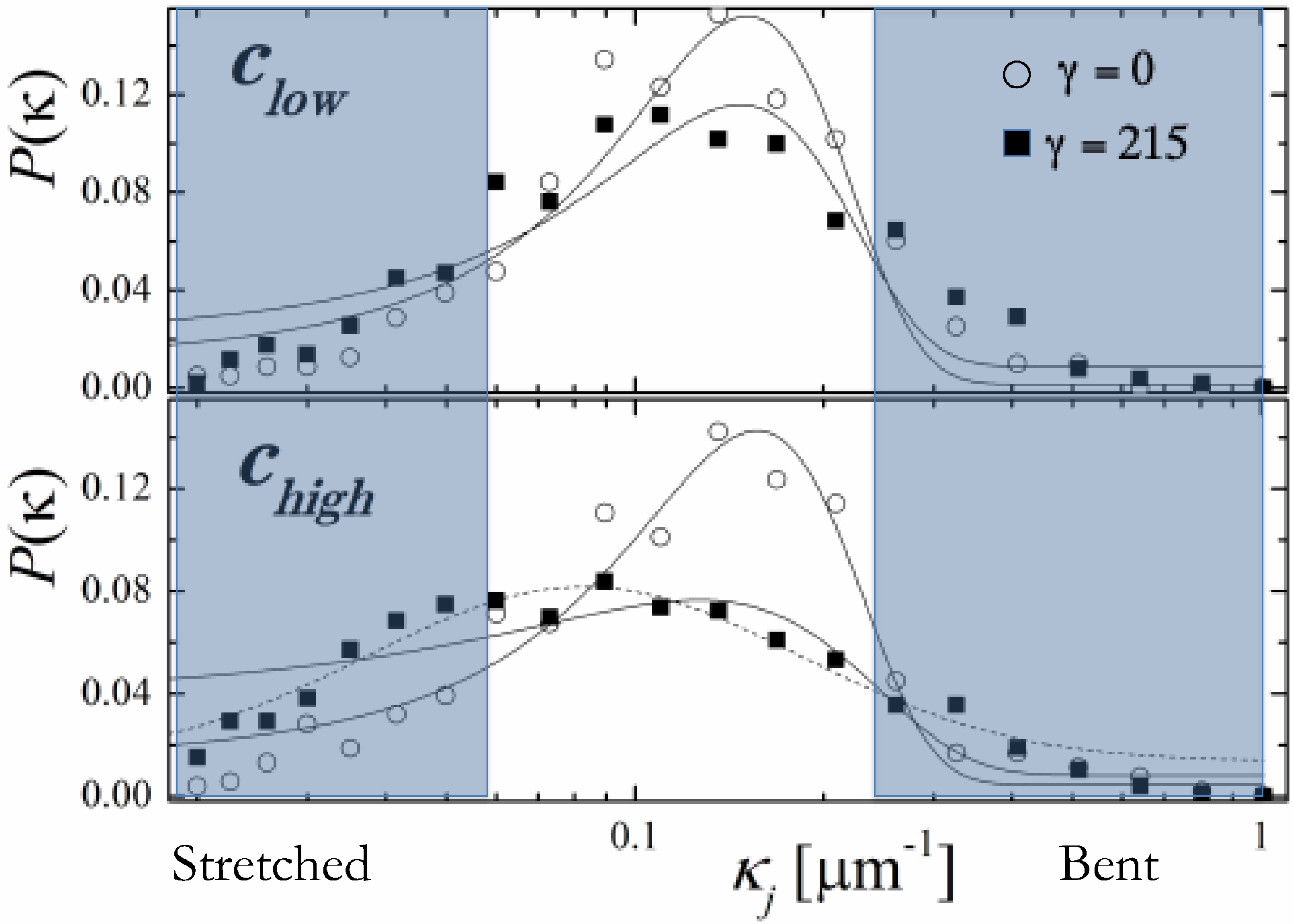


$$\hat{T}_j \equiv \frac{\dot{\mathbf{r}}_j}{|\dot{\mathbf{r}}_j|}; \hat{B}_j \equiv \frac{\dot{\mathbf{r}}_j \times \ddot{\mathbf{r}}_j}{|\dot{\mathbf{r}}_j \times \ddot{\mathbf{r}}_j|}; \kappa_j = \frac{|\dot{\mathbf{r}}_j \times \ddot{\mathbf{r}}_j|}{|\dot{\mathbf{r}}_j|^3}$$

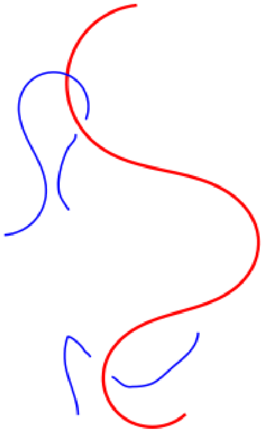


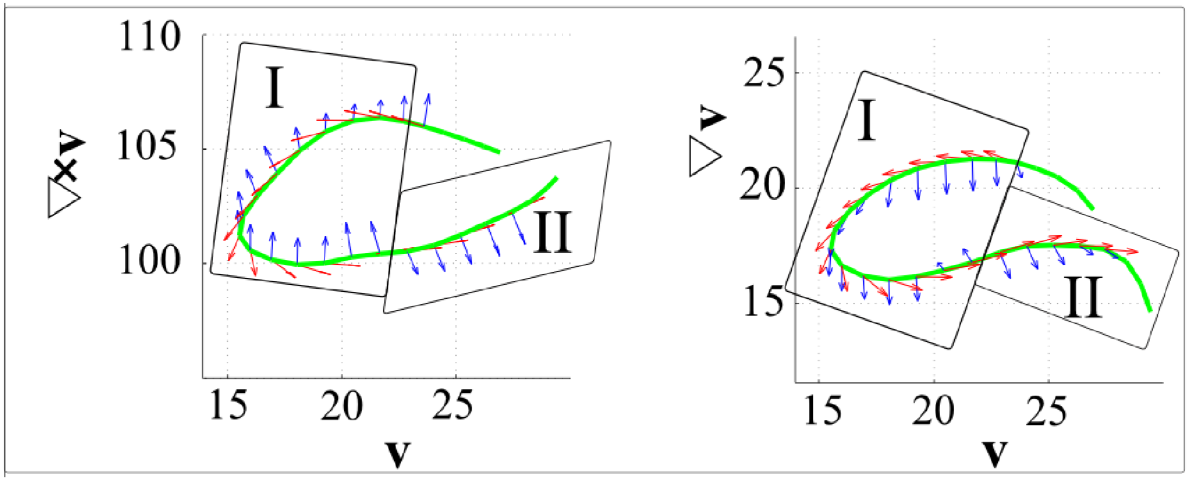
Distribution of curvatures:

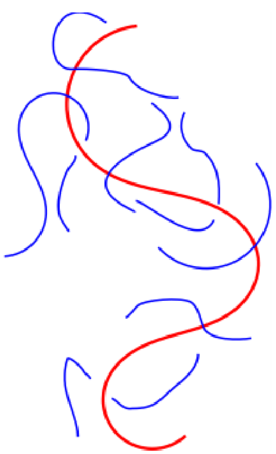


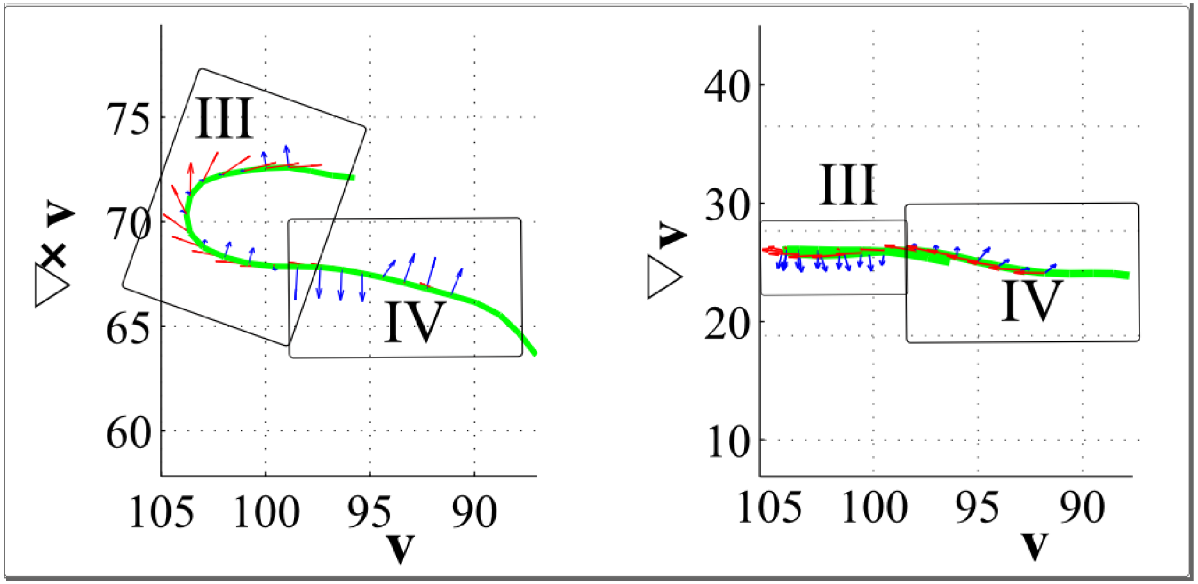


Typical examples:



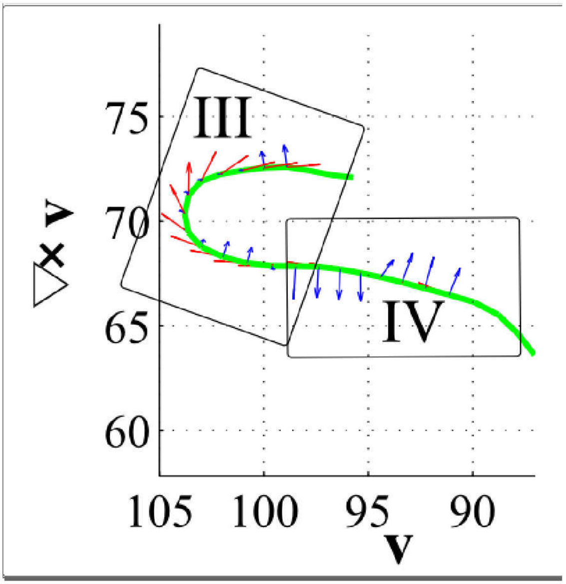


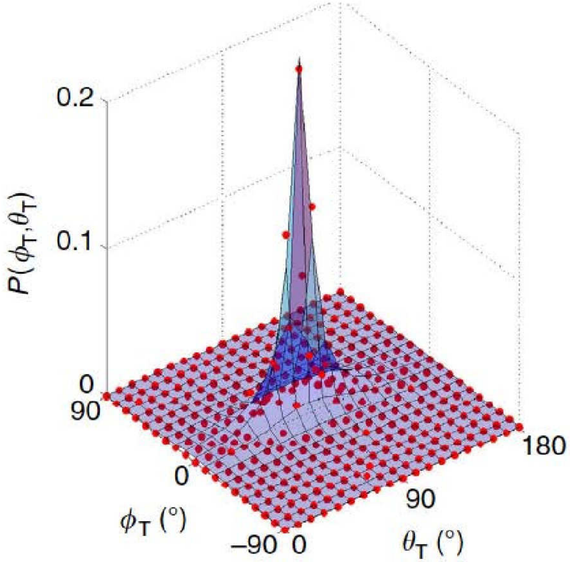


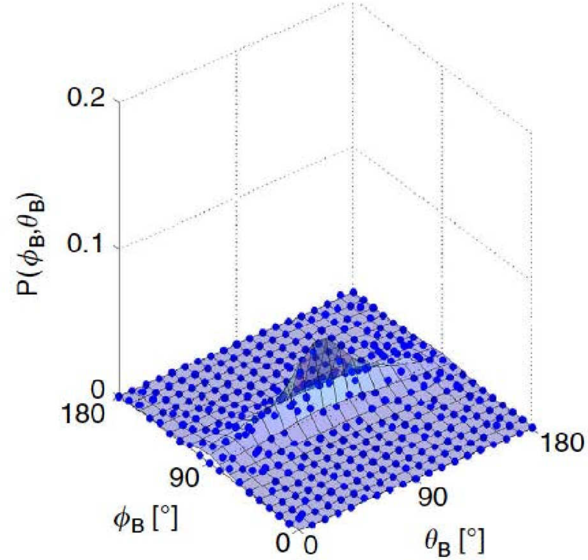


Distribution of angles

Stretched: IV

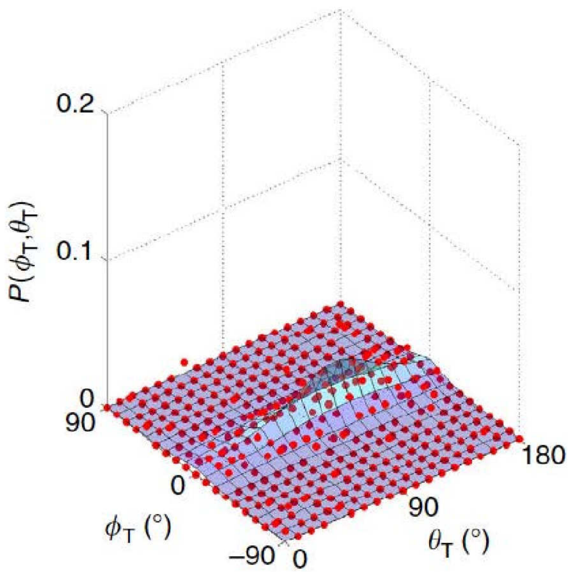


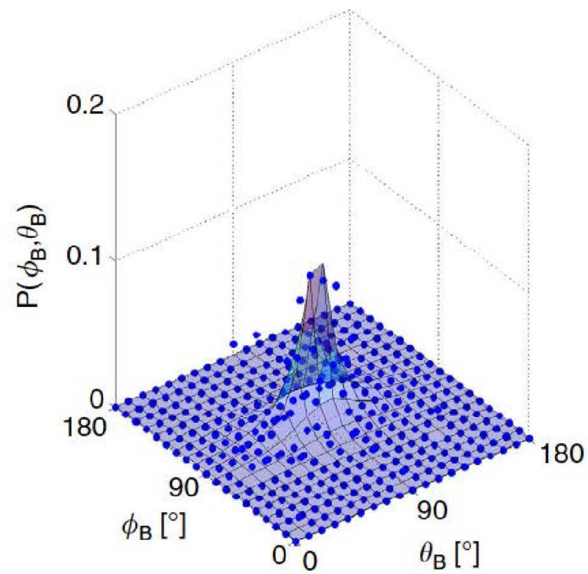




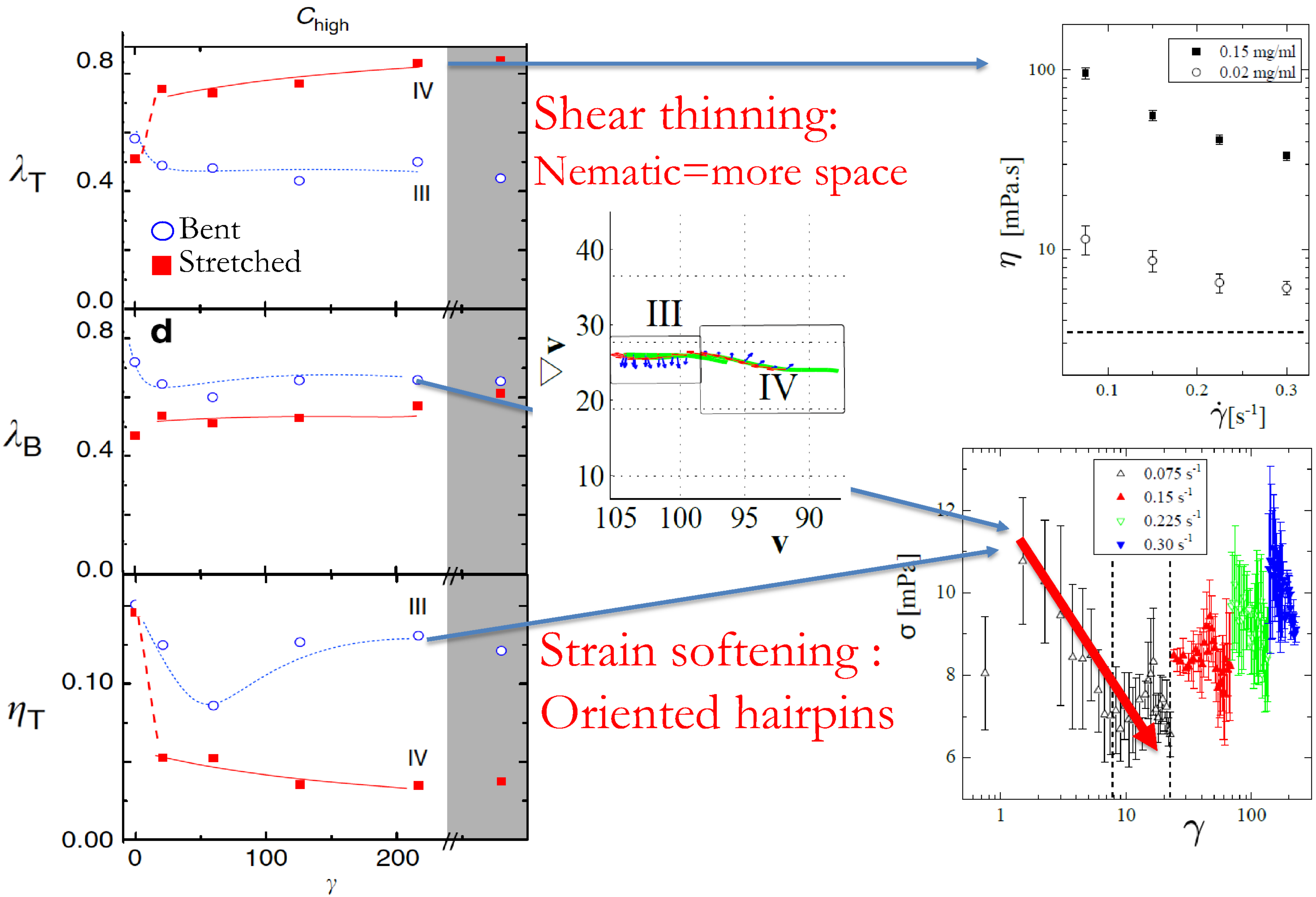
$$f(\theta,\phi) = a/\left((\frac{\theta-\Delta\theta}{w_\theta})^2 + (\frac{\phi-\Delta\phi}{w_\phi})^2 + 1 \right)$$

Bent: III





Connection between ordering and stress



Some conclusions III

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

Biggest need:

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

Acknowledgements

FZ Jülich:
Jan Dhont
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Eric Grelet
Laura Alvarez

MLZ, Garching:
Aurel Radulescu

PSI, Villigen:
Joachim Kohlbrecher

ILL, Grenoble:
Lionel Porcar

Amolf Amsterdam:
Gijsje Koenderink

KU LEUVEN

DiStruc
Directed Structure at the meso-scale

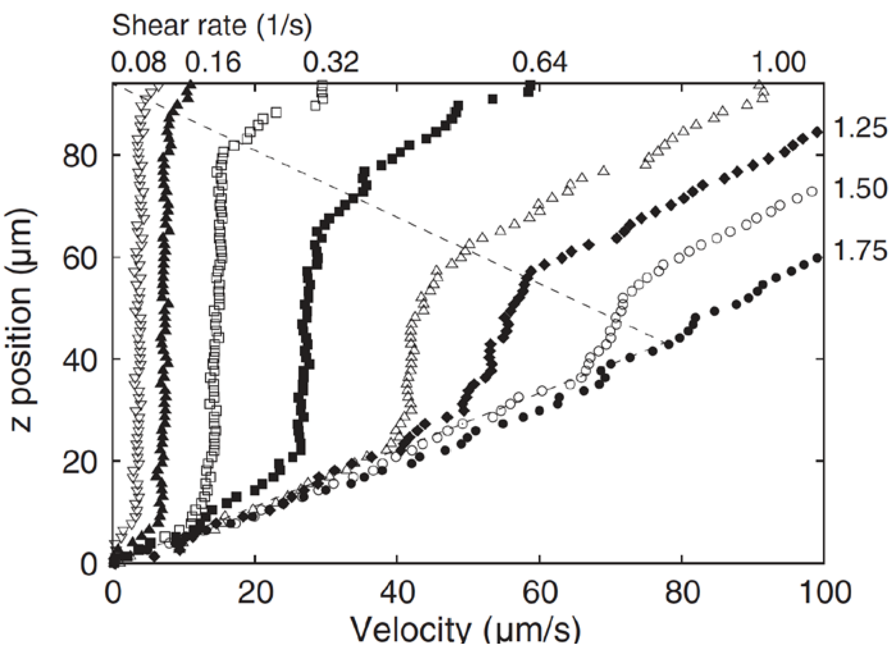
F-actin: stiffer and longer

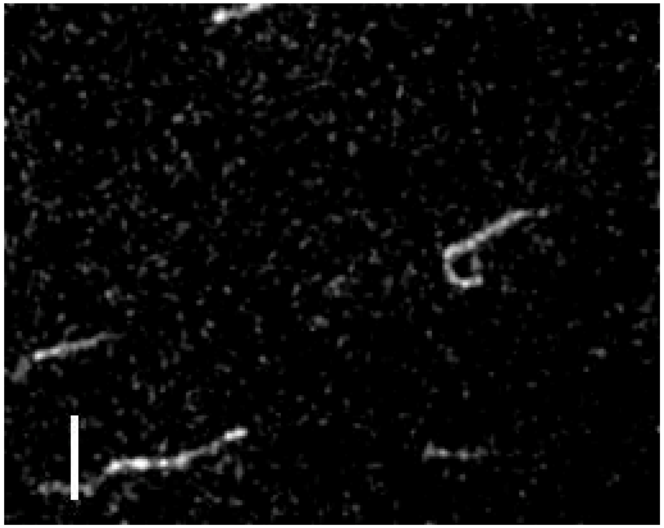
$<L>\approx 20\ \mu m$, $d=7$ nm, $l_p=17\ \mu m$

Shear banding has been identified by

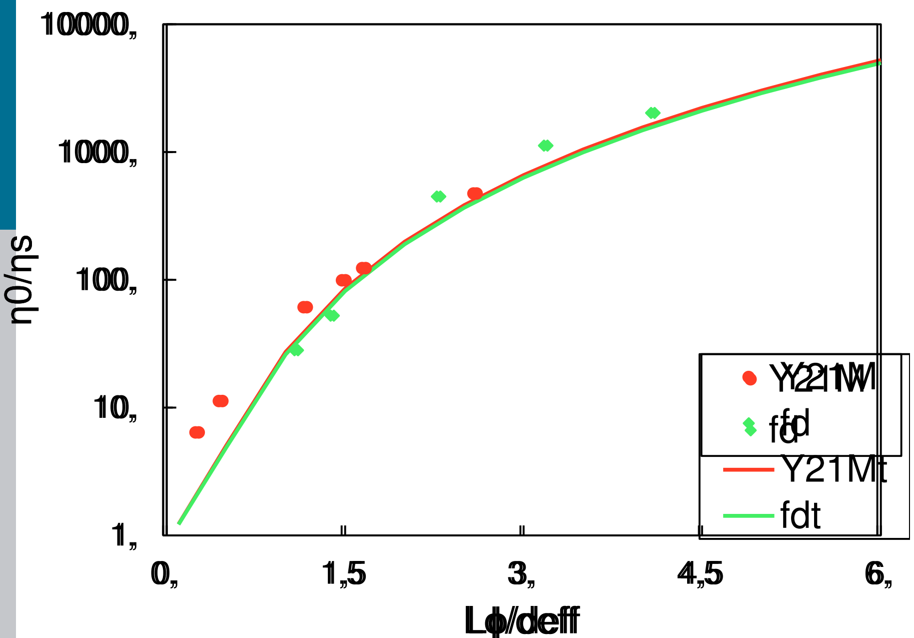
Kunita et al, PRL 109, 248303 (2012)

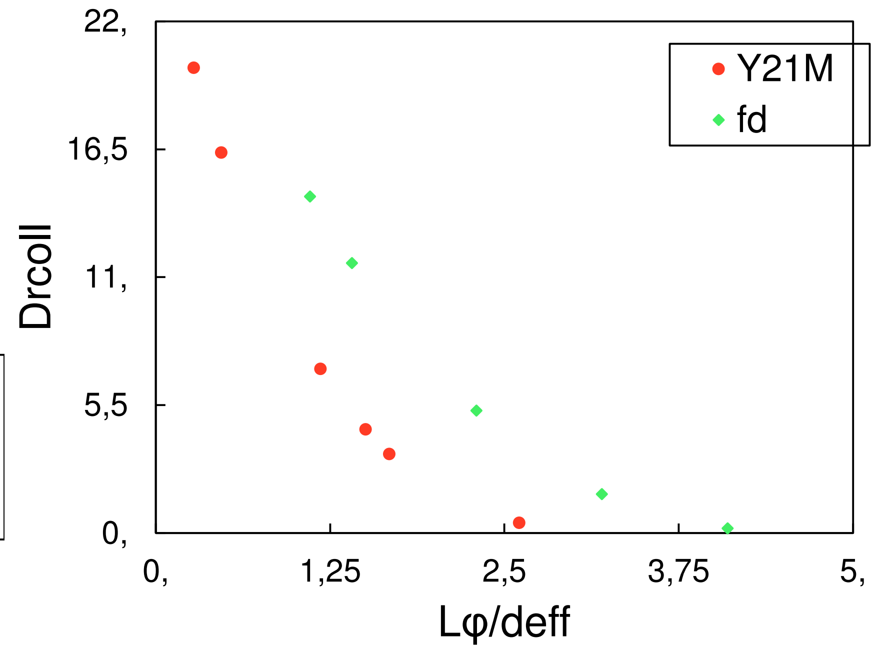
Goal: obtain 3-D structural information





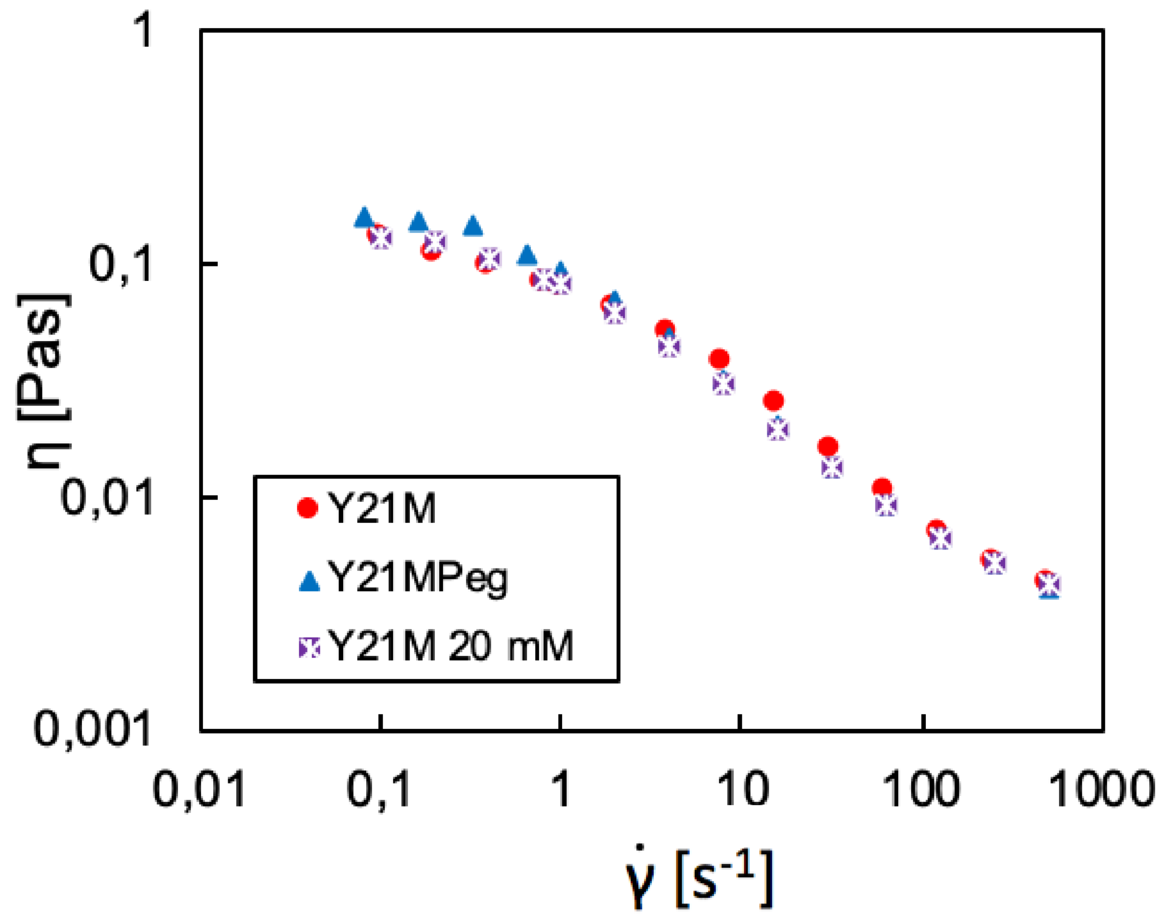
Morphological influences on shear flow





Indication of a flexibility dependence of the rotational diffusion coefficient

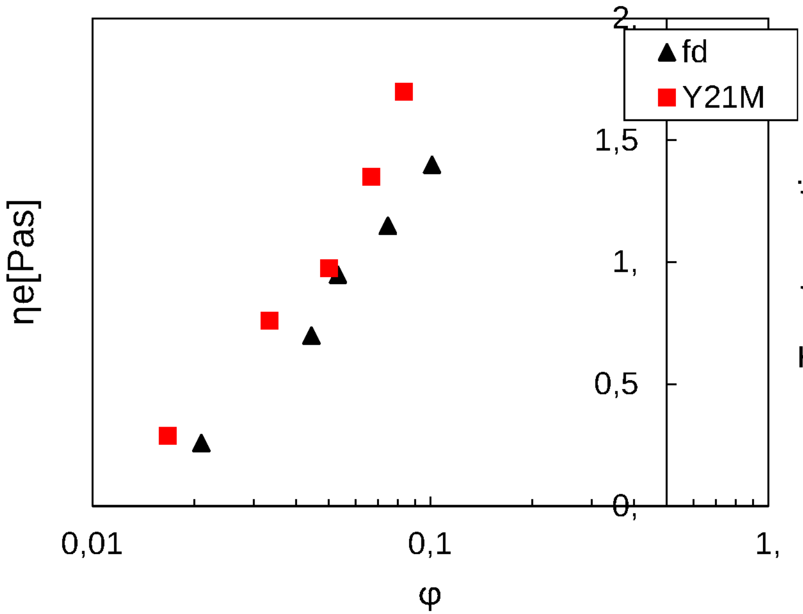
Influence thickness on flow response

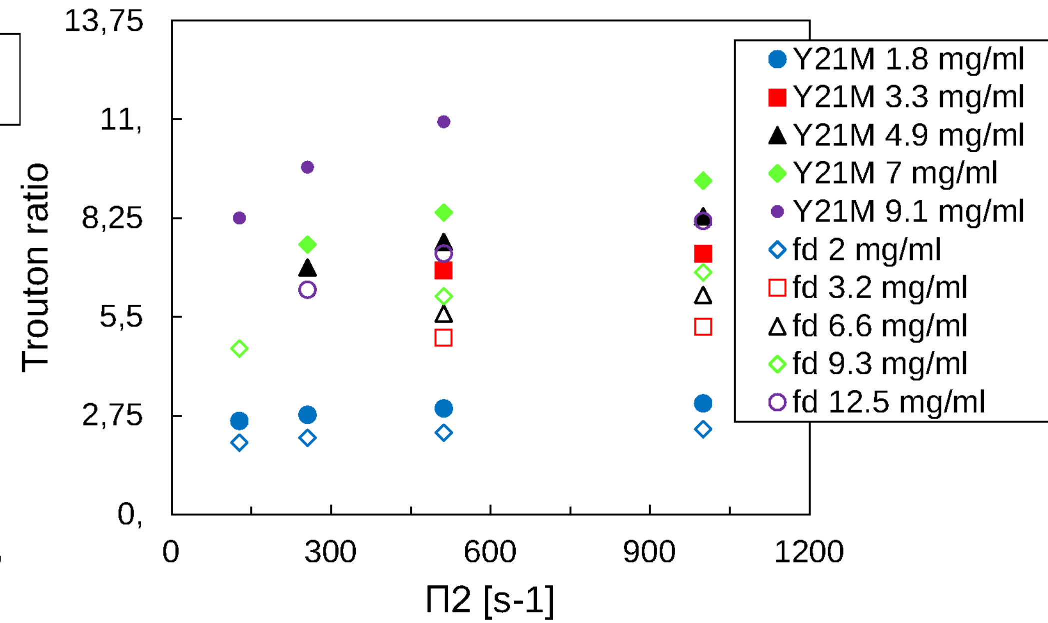


Elongational flow of ideal and semiflexible rods

Trouton ratio $= \eta_e/\eta$

Newtonian fluids: $\eta_e/\eta = 3$



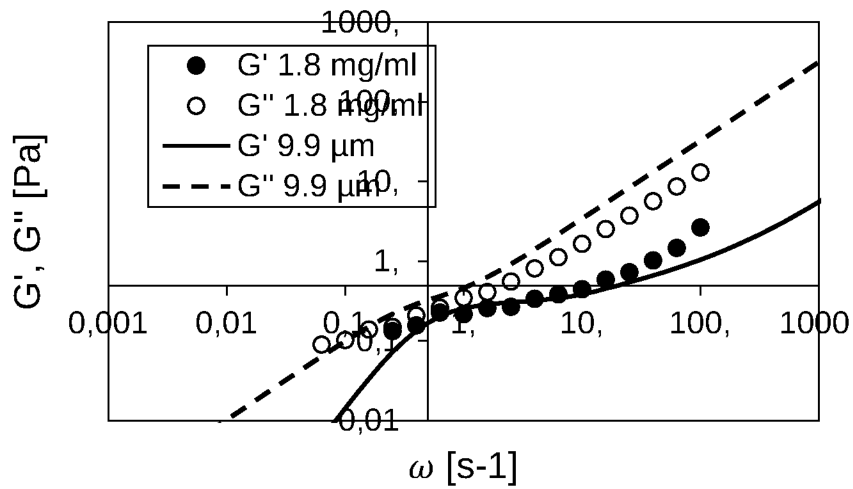


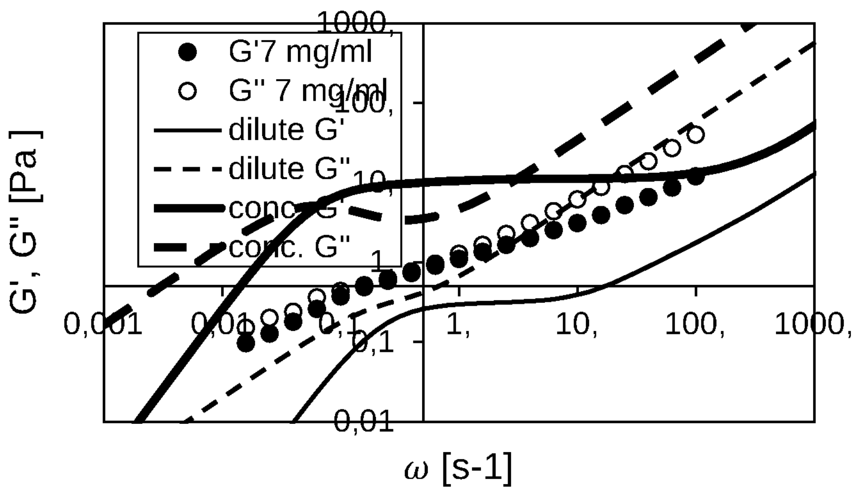
Pronounced effect of concentration on elongational viscosity

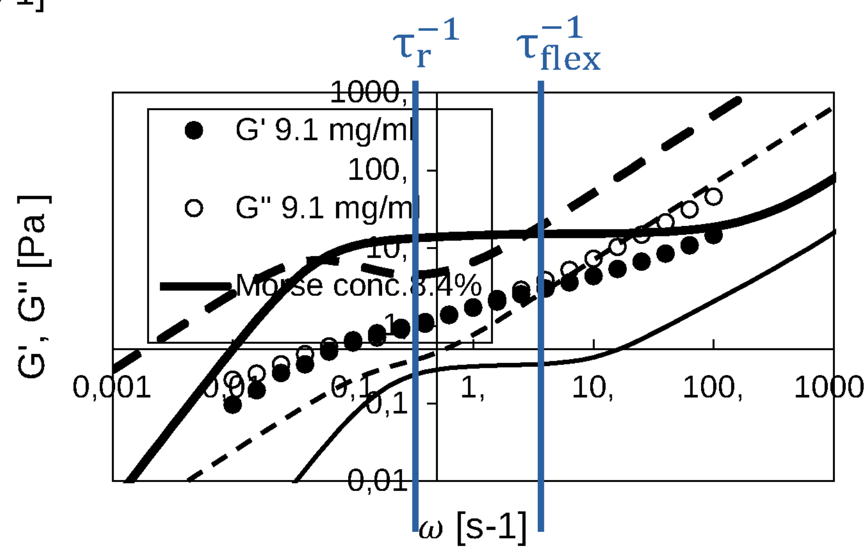
Rate dependent Trouton ratio reaching rather high values

Results

SAOS and relaxation time spectrum of fdY21M



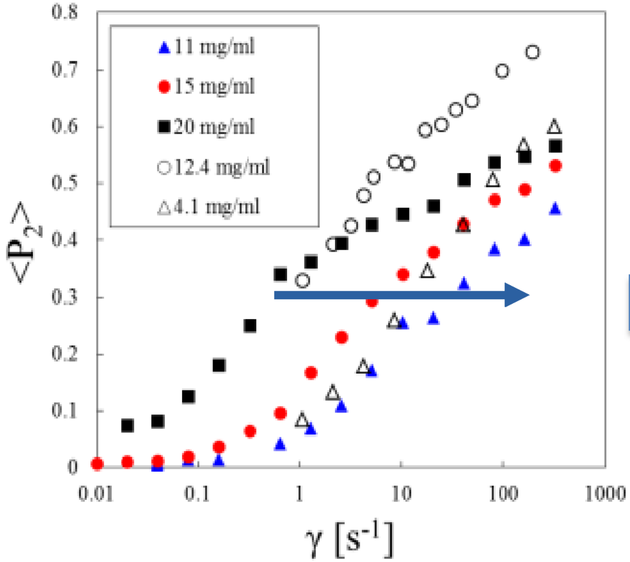


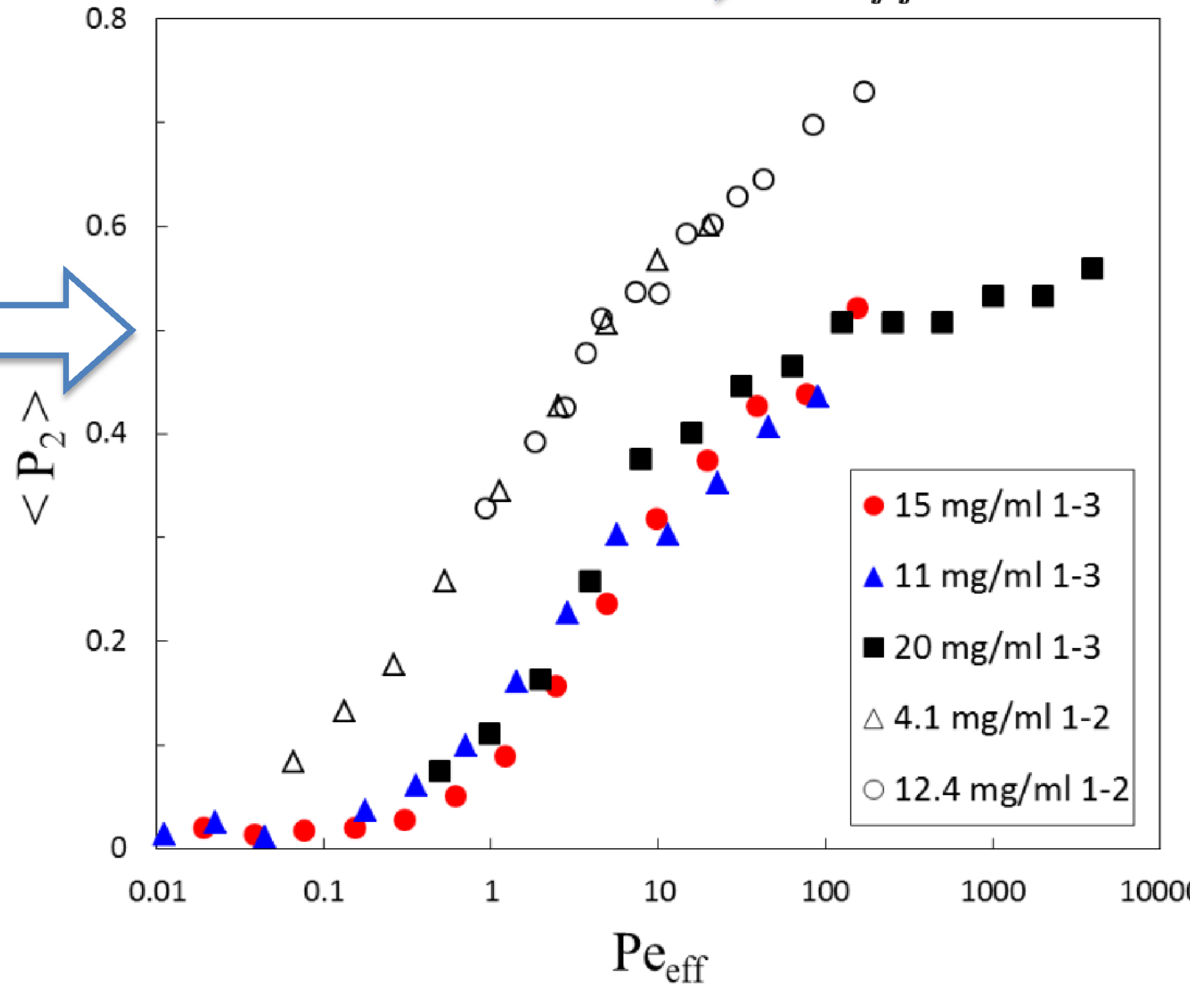


Obtain the I-N spinodal point

=?

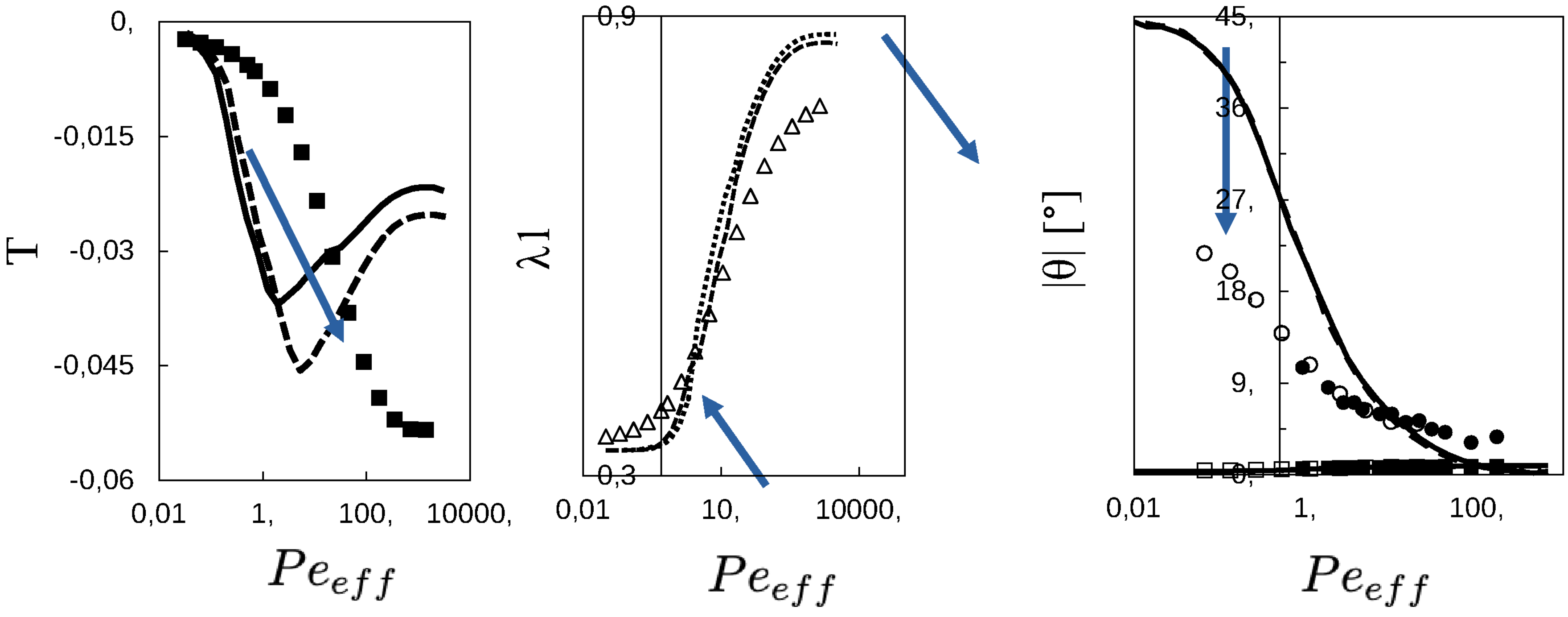
Scale shear rate: $Pe_{eff} = \dot{\gamma}_0 / D_R^{eff}$ $\Rightarrow$ $\frac{L}{d_{eff}} \varphi_{IN} = 4.2$





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

Scaling other ordering parameters



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

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

Characterizing parameters

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

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

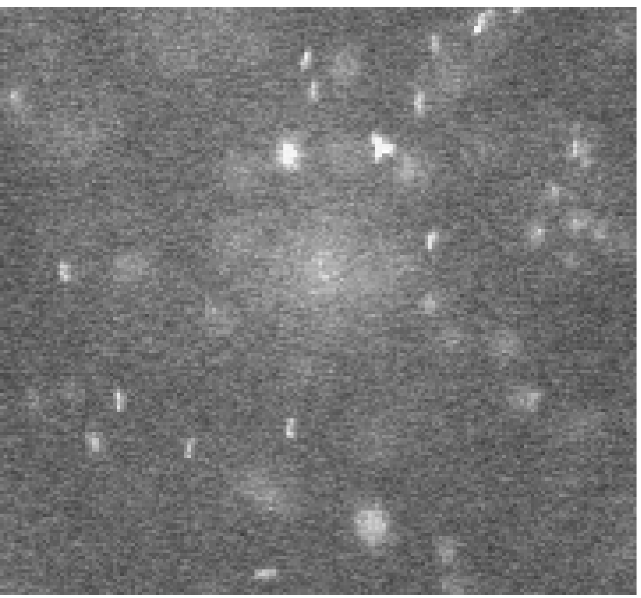
Biaxiality

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

Orientational order parameter

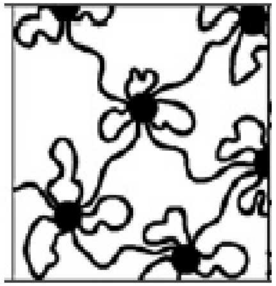
Note: this is the input for calculating stress tensor

Complex flow: Complex fluids



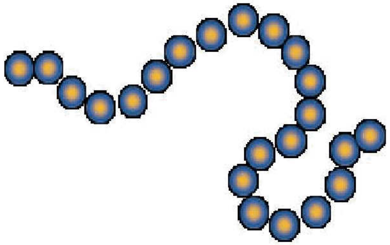
Possible shear thinners

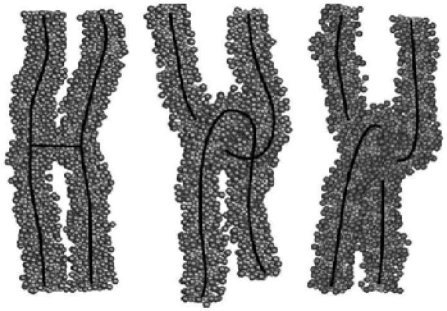
Living gels:



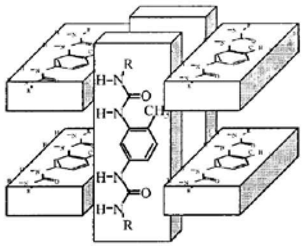
Sprakel et al, Soft Matter, **4**, (2008) 1696

Living polymers:



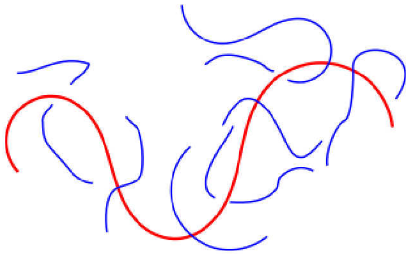


M. P. Lettinga and S. Manneville, *Phys. Rev. Lett.*, **103** 2009

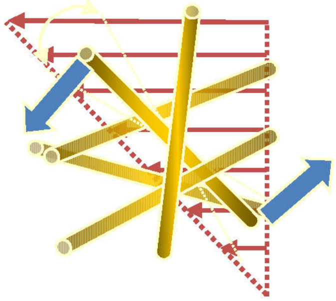


Van der Gucht et al Phys. Rev. Lett., **97**, (2006) 108301

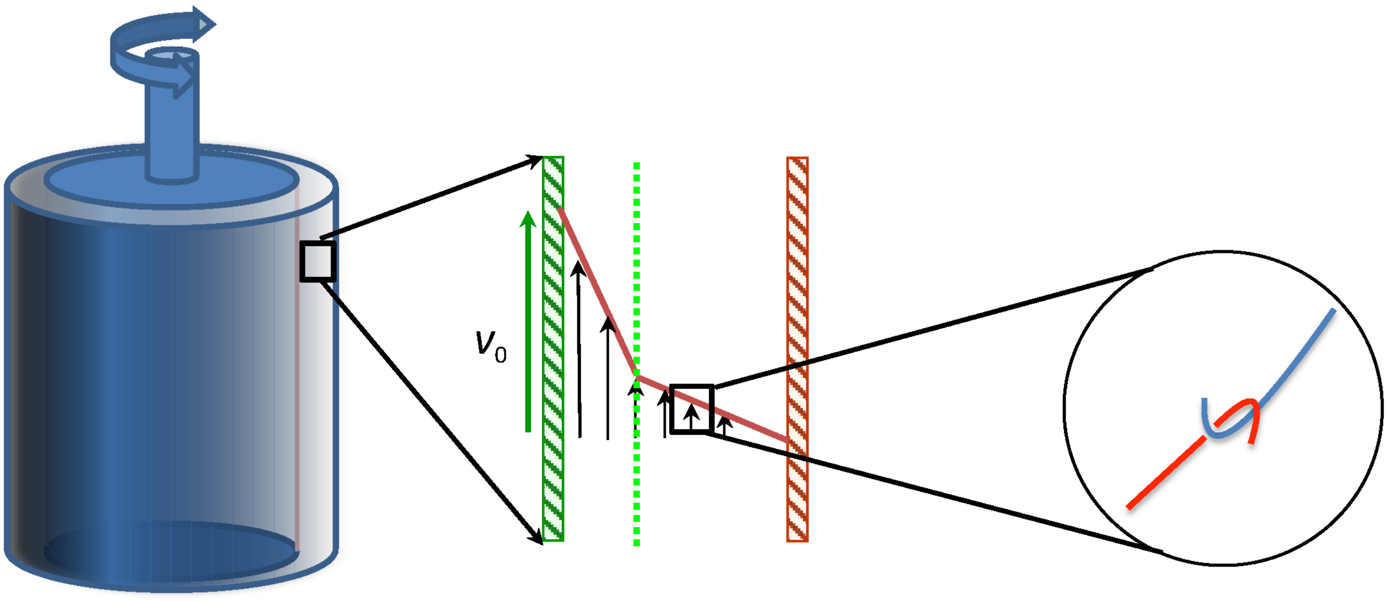
Stiff Polymers:



Rods:



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.

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

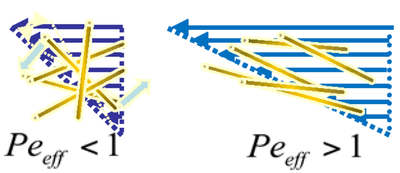
$$\delta S(t) = \exp(-6D_R^{eff}t)\delta S(t=0)$$

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

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

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

D_R^0 : rotational at *infinite* dilution



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

Introduction

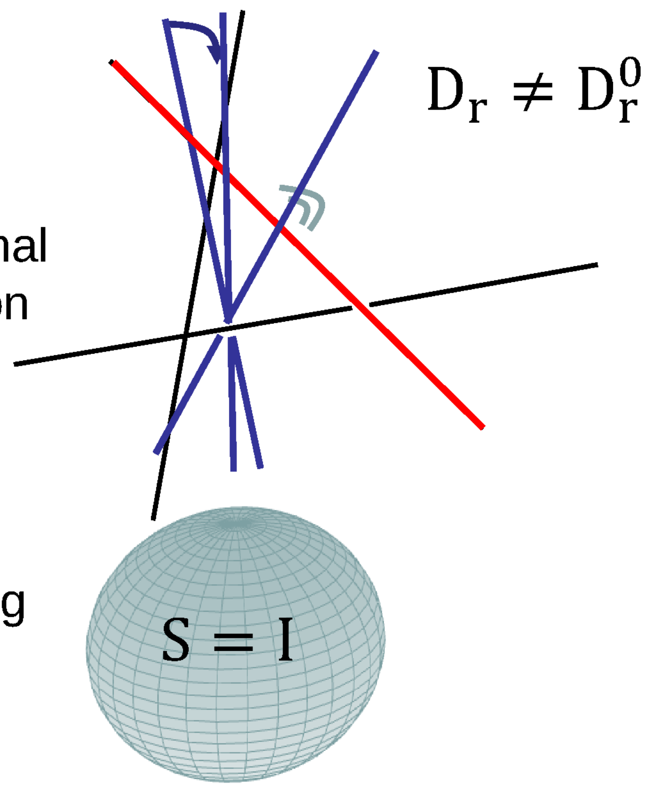
Brownian motion competes with shear flow:

no shear

isotropic pdf

rotational diffusion

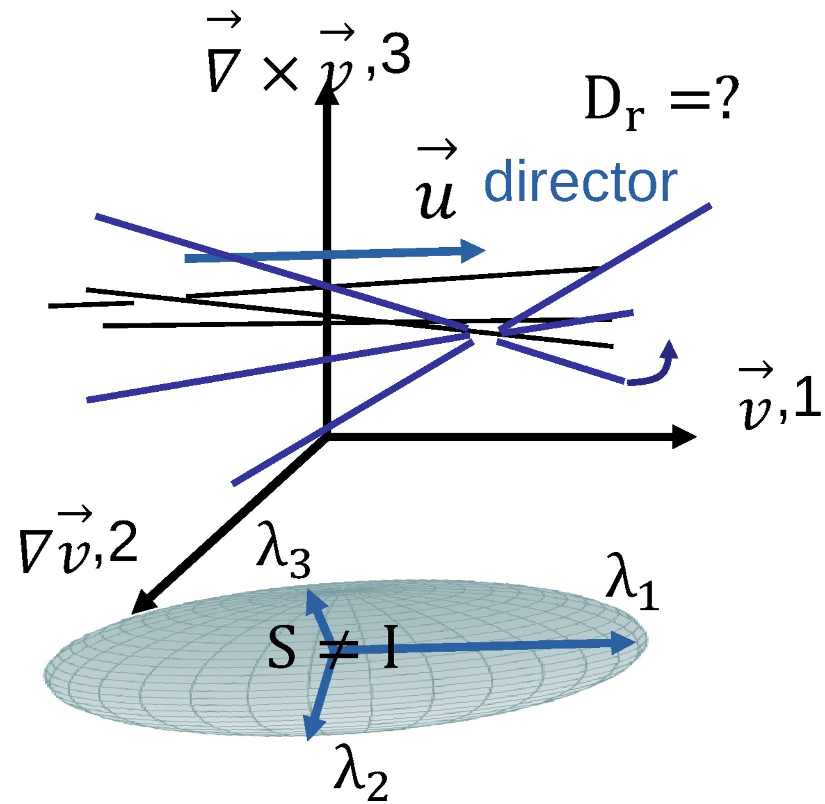
ordering tensor



high viscosity

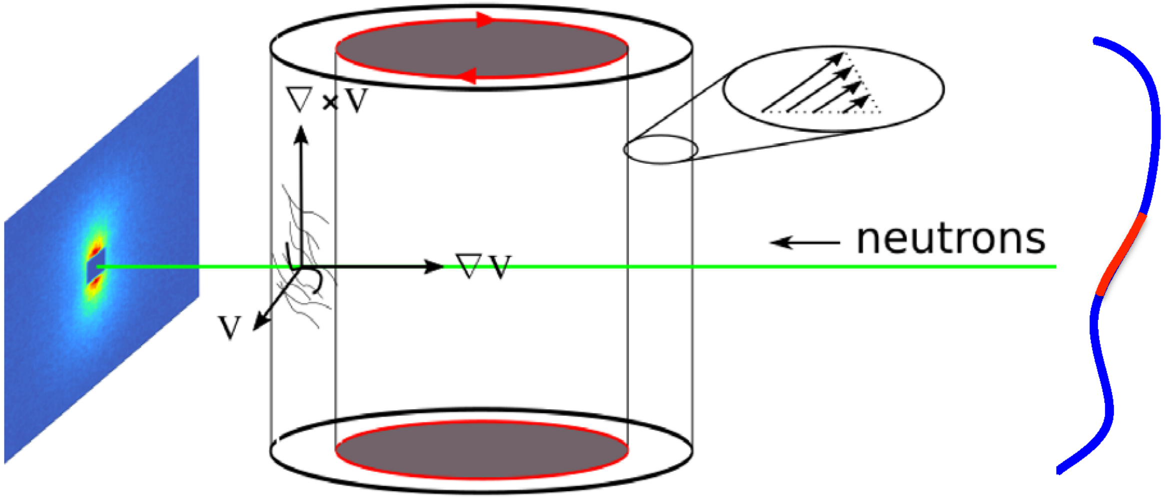
shear

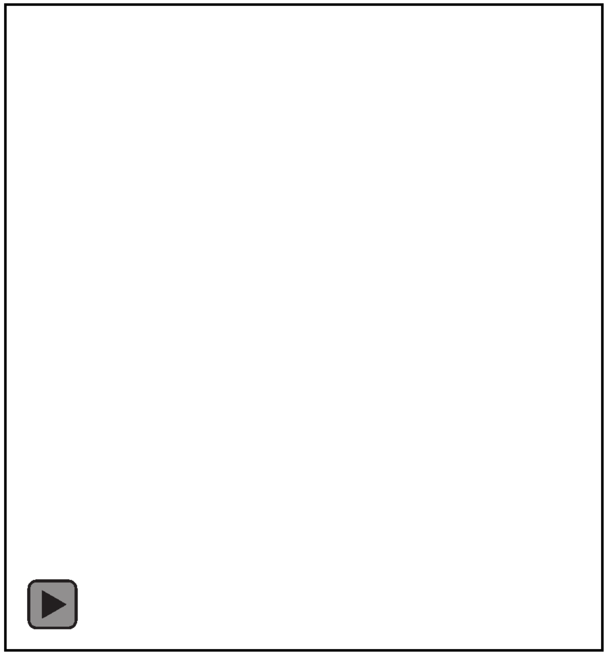
anisotropic pdf



much lower viscosity

t-SANS to probe segment ordering dynamics

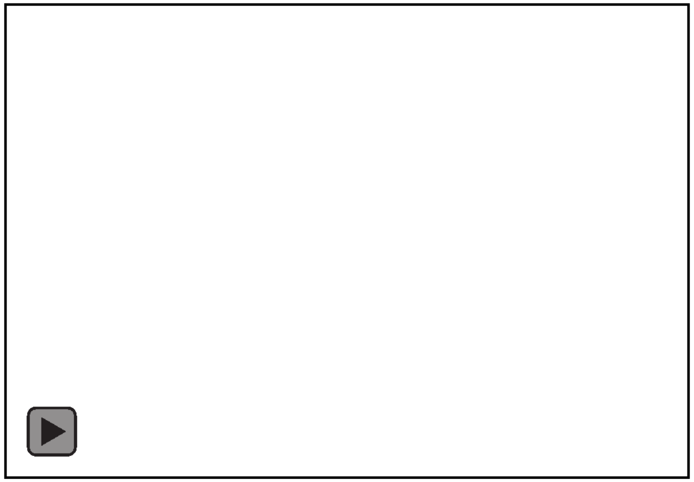




$$\langle P_2(t)\rangle = \frac{\int d\vartheta \sin(\vartheta)\, f(\vartheta) P_2(\vartheta))}{\int d\vartheta \sin(\vartheta)\, f(\vartheta)}$$

Orientational distribution function

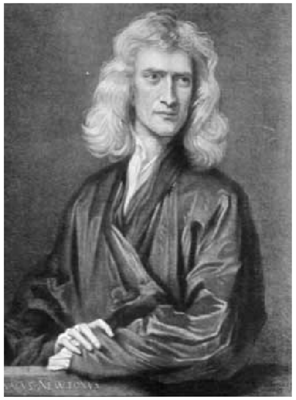
$f(\theta)$

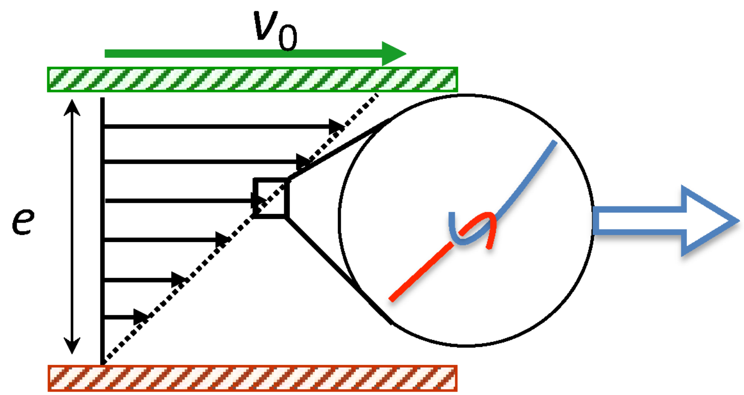


θ [rad.]

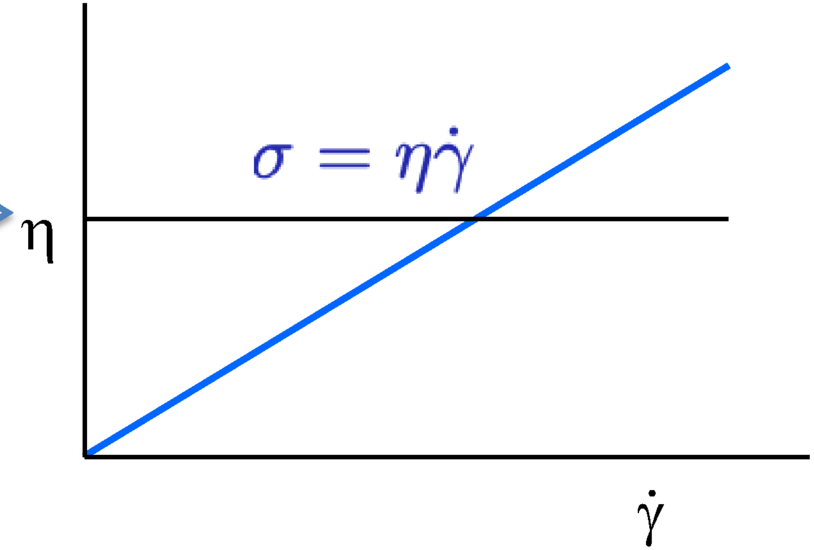
$$I(t_i,\vec{q}) = \sum_{n}^{Ncycle} I(t_i + n\Delta t, \vec{q}\ )$$

Ideal Newtonian fluids



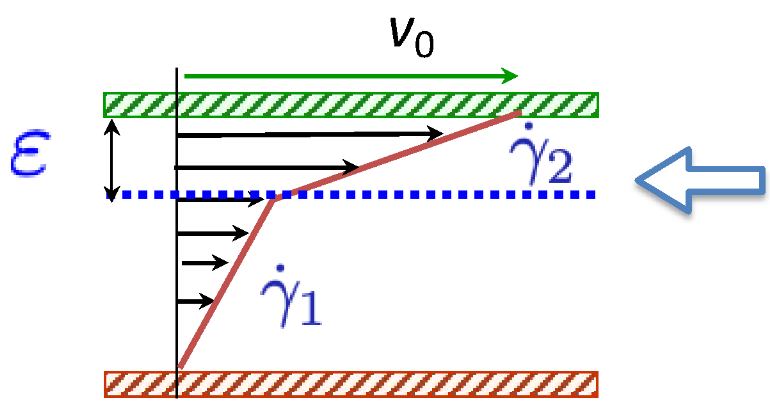


$\dot{\gamma} = v_0 / e$



Non-linear Newton: shear thinning fluids

Flow instabilities: shear banding



strong shear-thinning