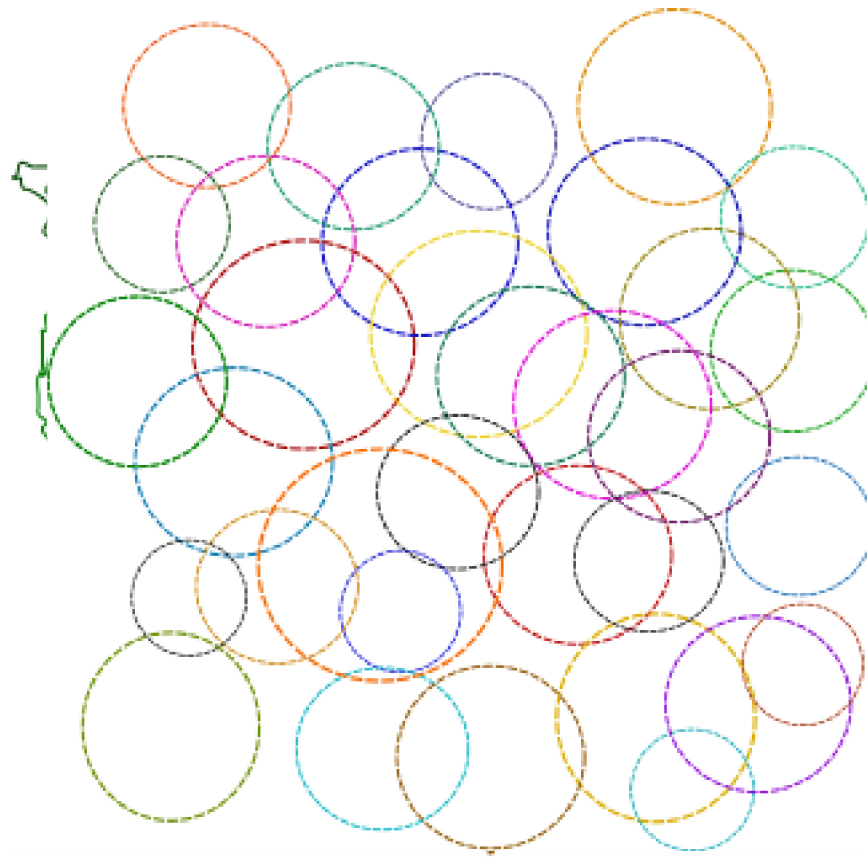


How rods give structure to fluids and how structure is distorted by flow

Pavlik Lettinga

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

Rods: extremely effective in structuring a fluid



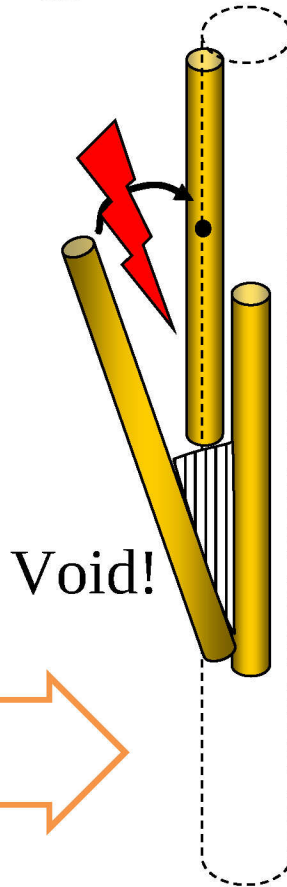
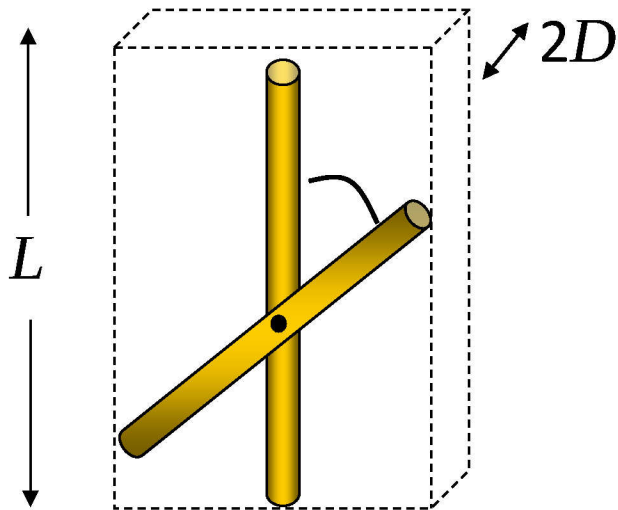
Rods: extremely effective in structuring a fluid



Phase transitions of colloidal rods

$$V_{ex} = 2DL^2 \sin\vartheta$$

$$V_{ex} = \pi LD^2$$

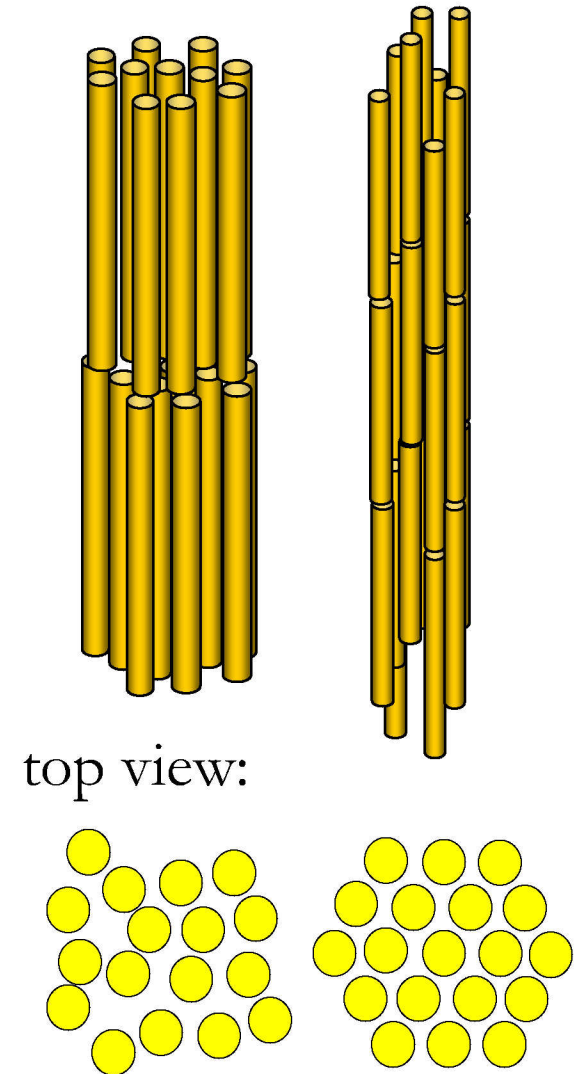


Onsager, 1949

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

Isotropic

Nematic

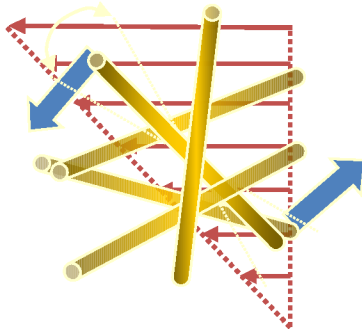


top view:

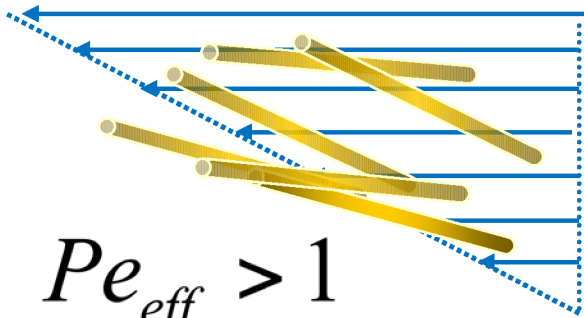
Smectic

Columnar

Colloidal rods in shear flow



$$Pe_{eff} < 1$$



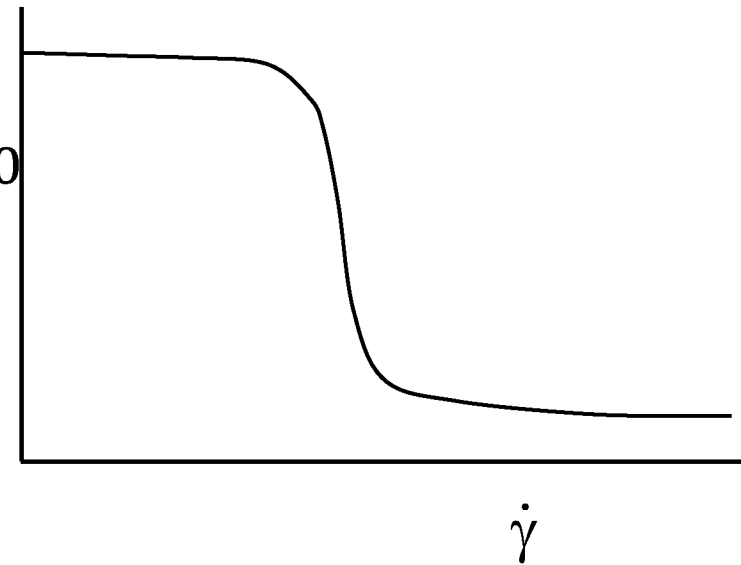
$$Pe_{eff} > 1$$

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

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

strong shear-thinning

$$\eta/\eta_0$$



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

Goal: understand shear thinning of systems like...

nano cellulose

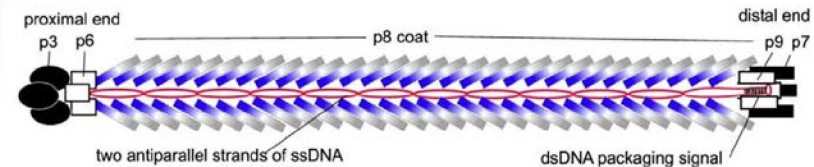
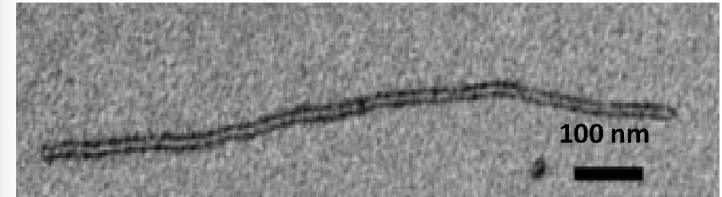
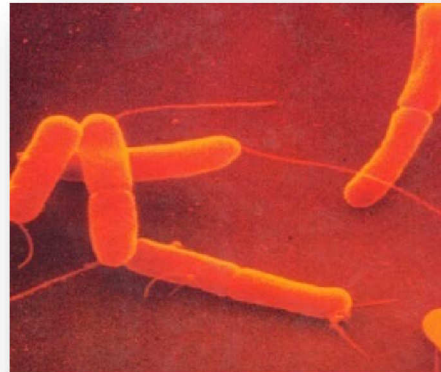
carbon nano tubes

amyloid

F-actin

Xanthan

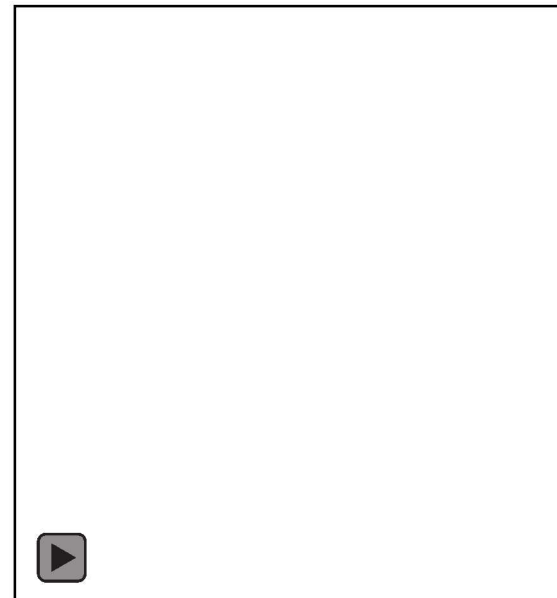
Bacteriophages as model system



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



Dynamics at increasing degree of ordering

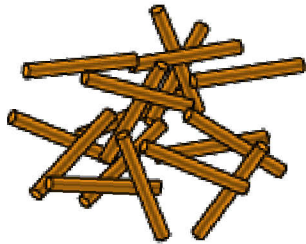
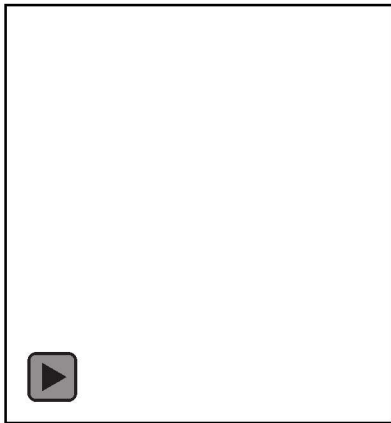
Connection between entropy and diffusion:

More free volume = More space per particle

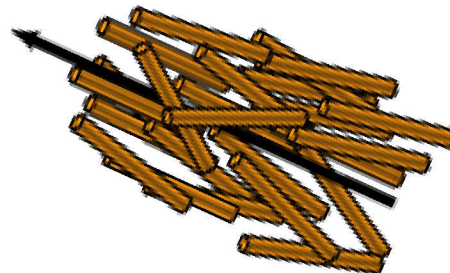
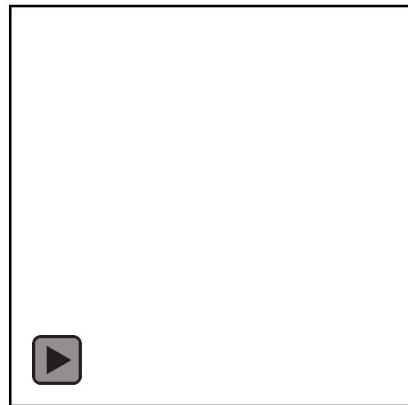
More space per particle = Higher positional entropy

More space per particle = Faster diffusion

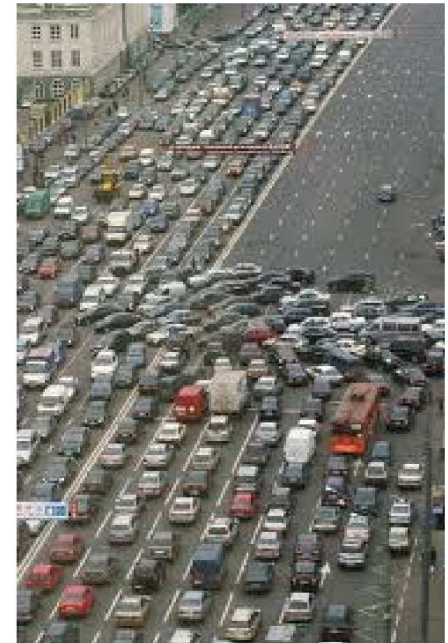
Faster diffusion = Signature for increase of translational entropy



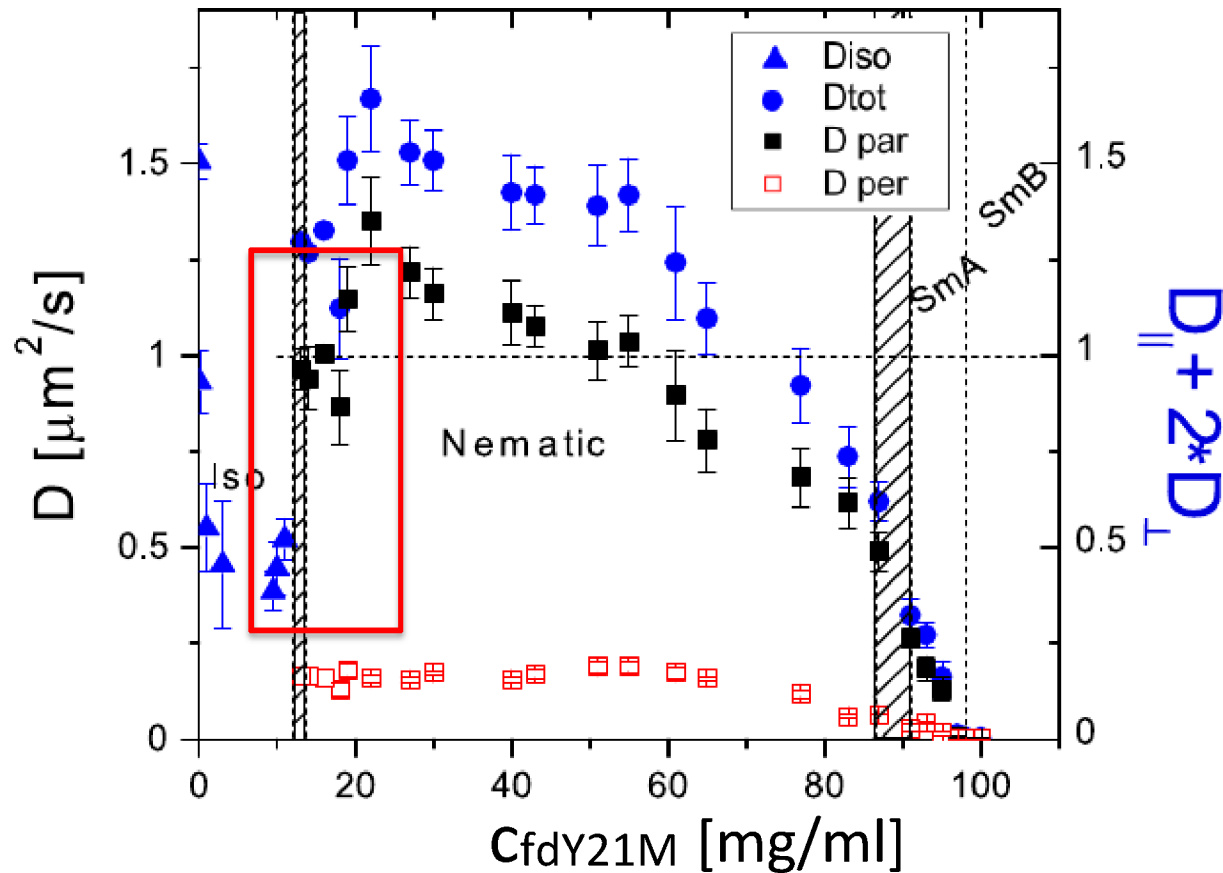
Isotropic



Nematic

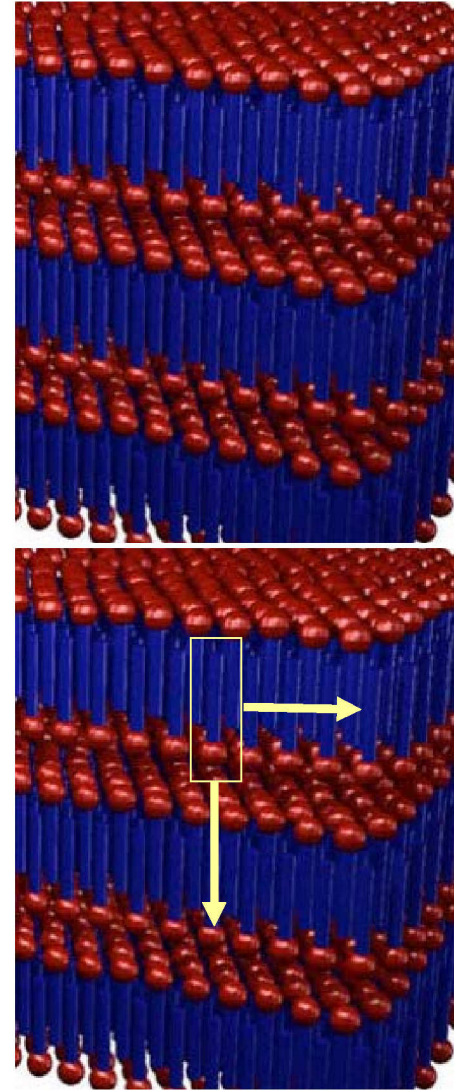
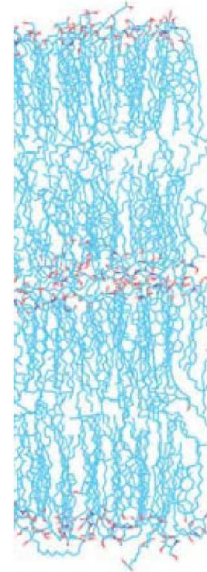
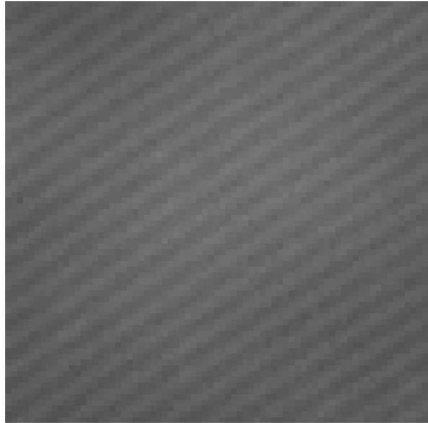
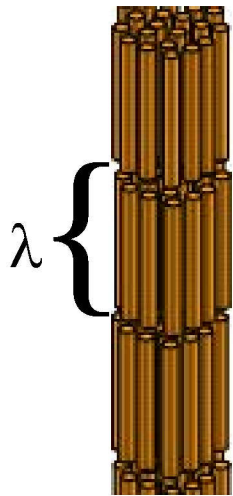


Dynamics at increasing degree of ordering



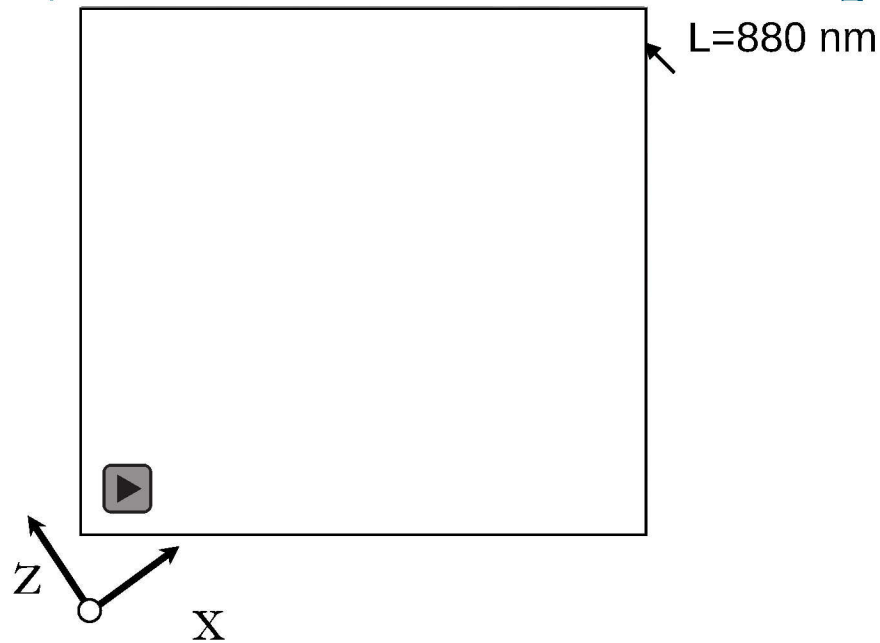
Signature increase entropy

Dynamics in the smectic phase

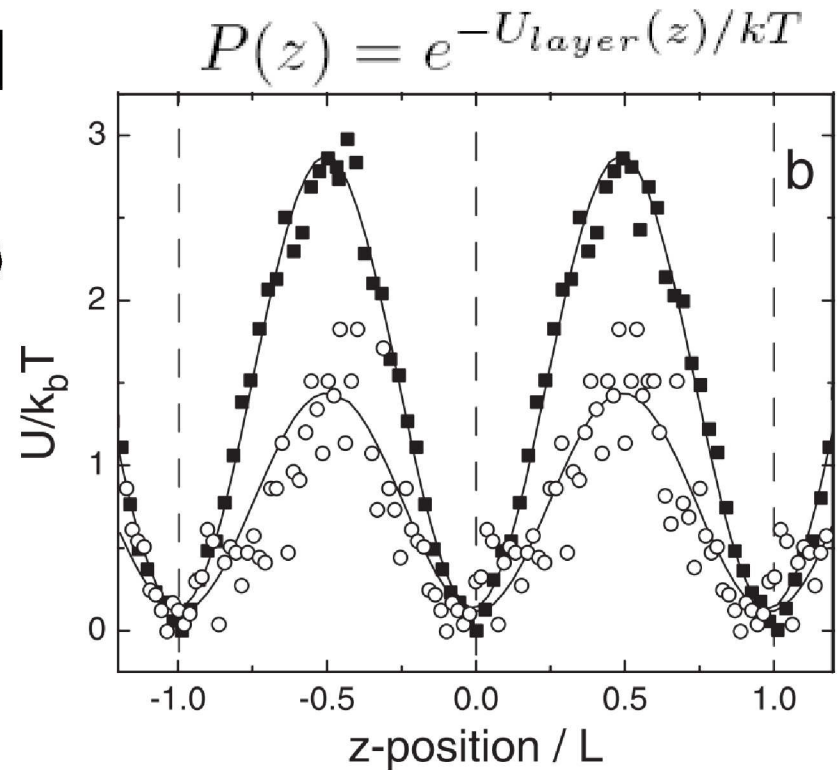
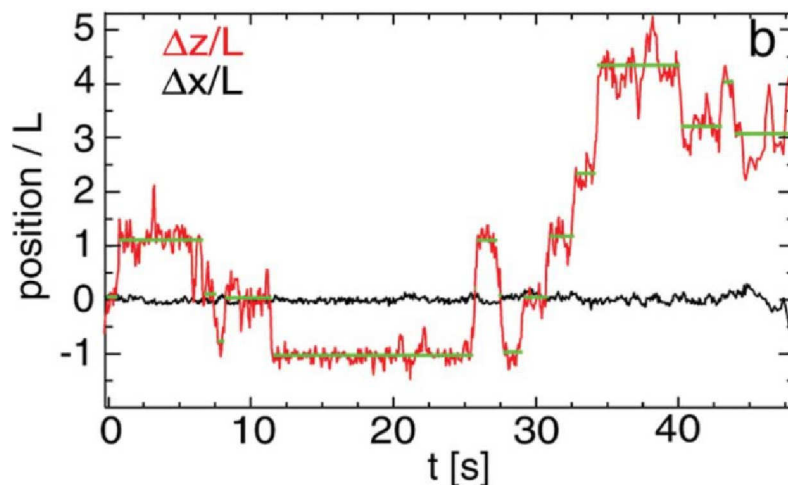


Permeation:
Transport through layers

Dynamics in the smectic phase



Find jumps in trajectories:



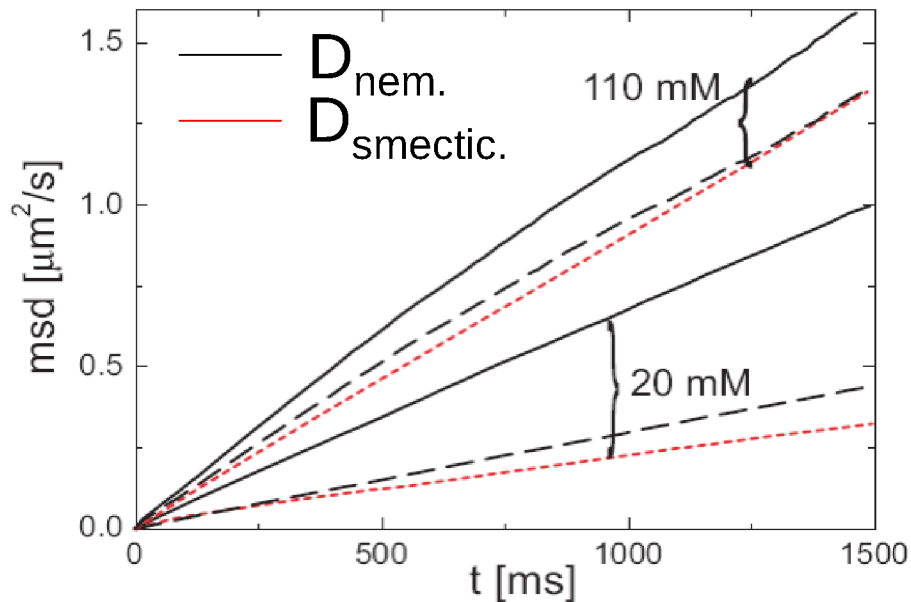
Open: 110 mM
Solid: 20mM

Dynamics in the smectic phase

Physica **90A** (1978) 229–244

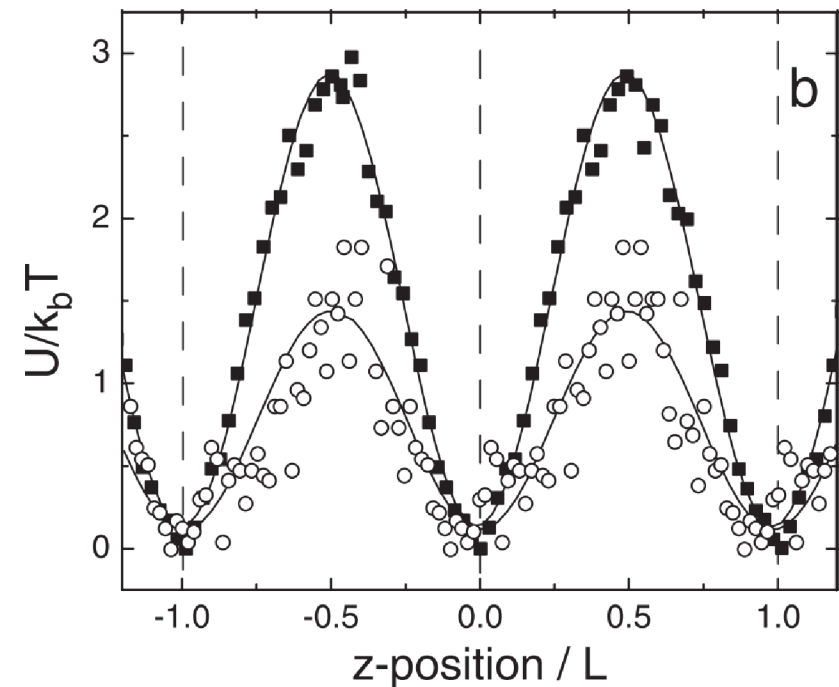
DIFFUSION COEFFICIENT FOR A BROWNIAN PARTICLE IN A PERIODIC FIELD OF FORCE

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



I. LARGE FRICTION LIMIT

R. FESTA and E. GALLEANI d'AGLIANO



Diffusion in Smectic = jumping in 1D periodic potential

So:



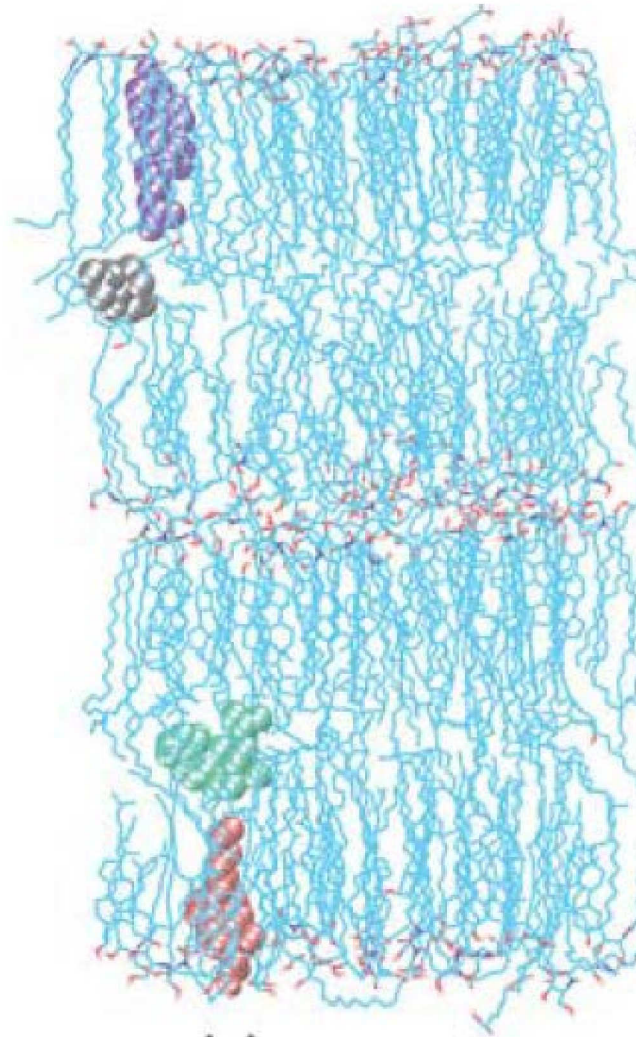
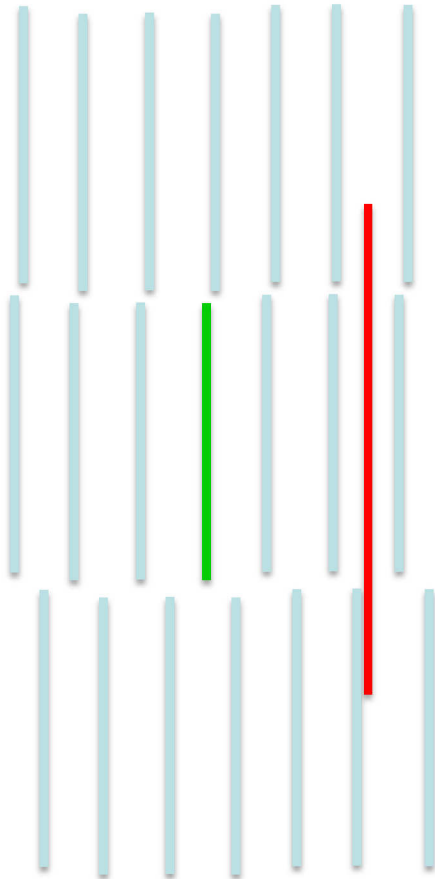
+



=

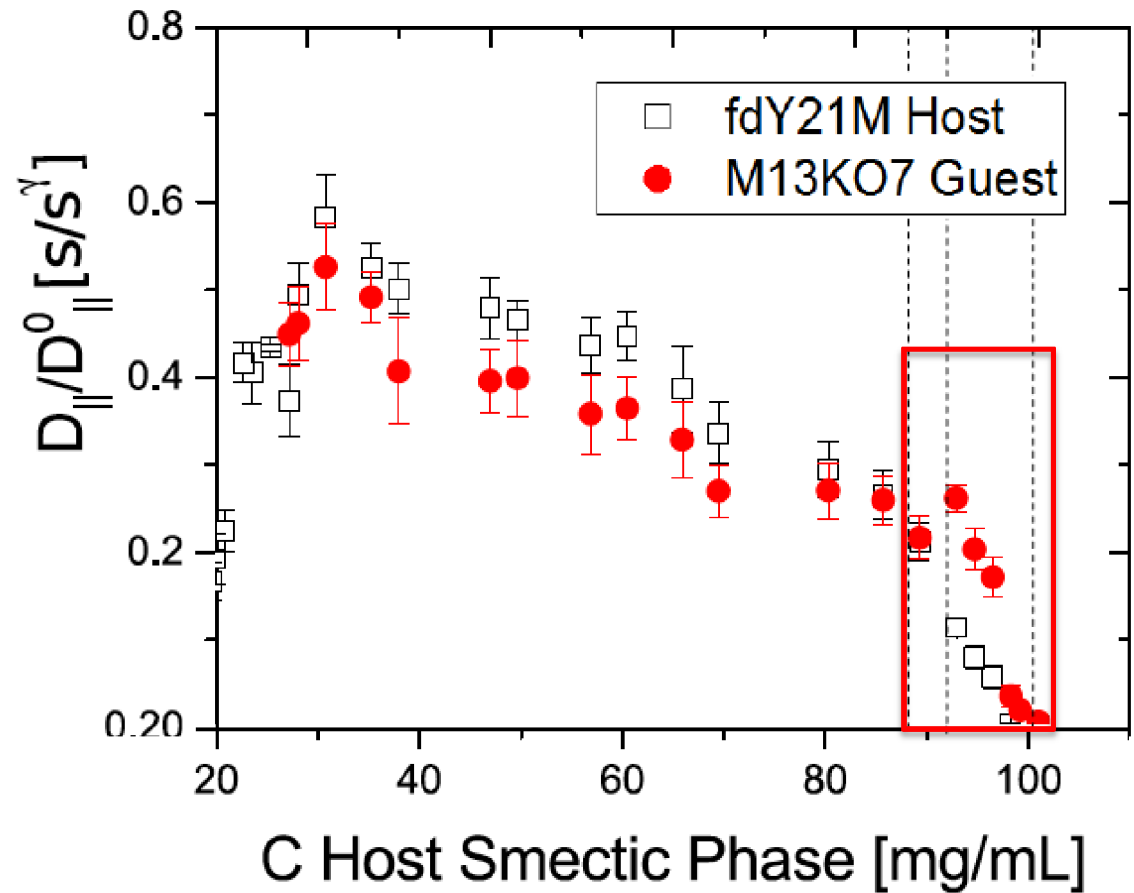
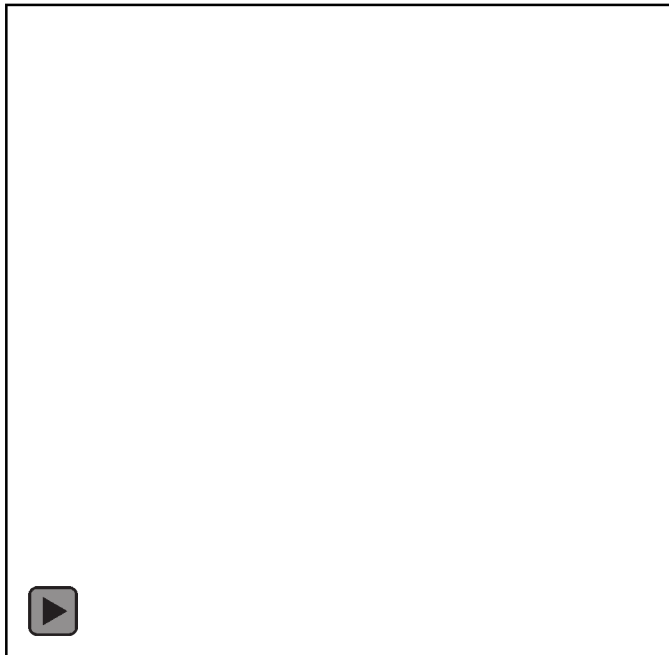


Put a guest in the layers



No fit

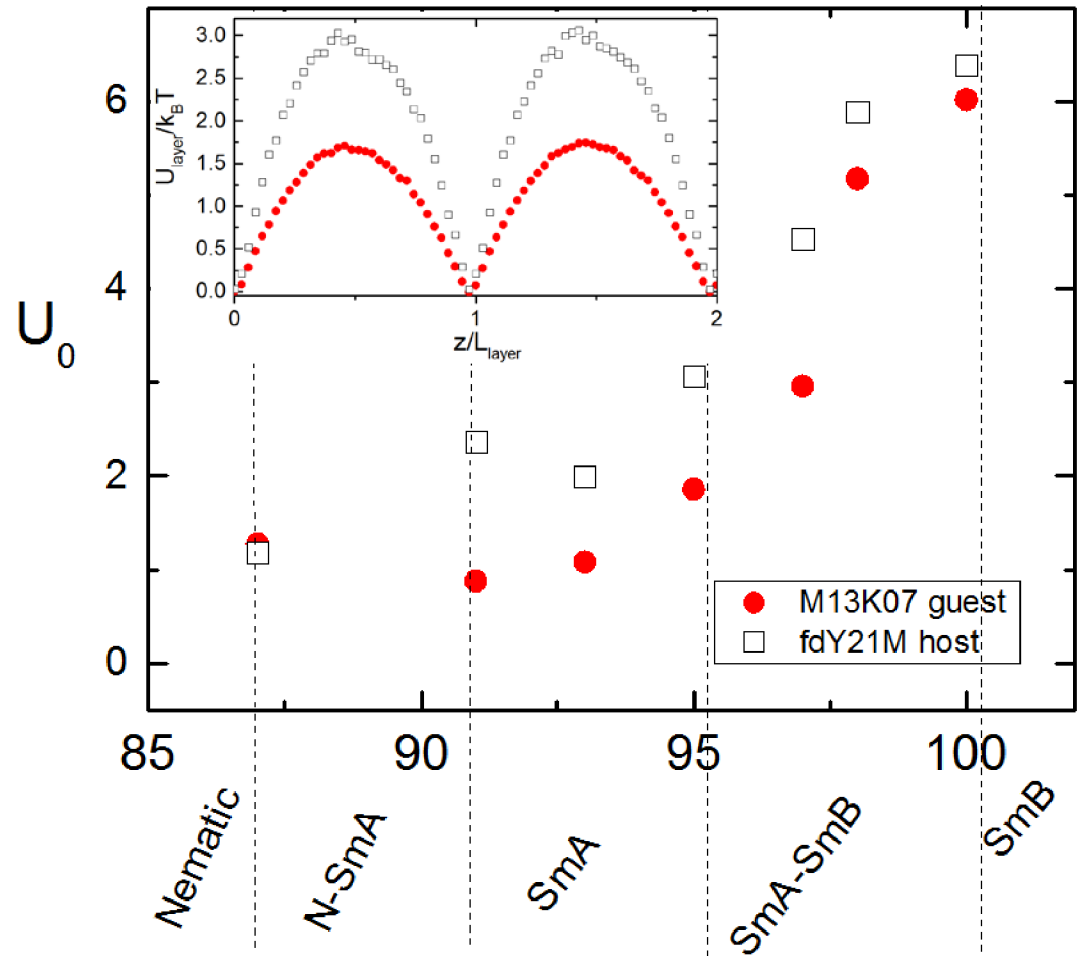
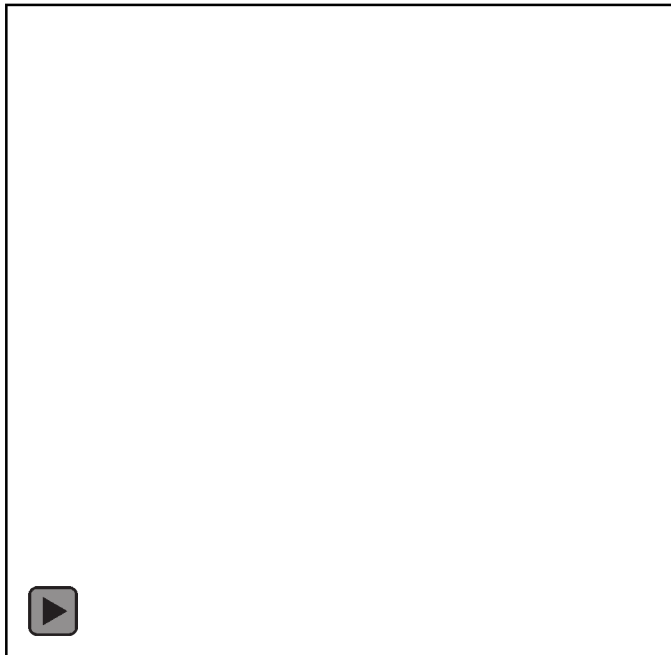
Longer is faster!



$$D = \frac{RT}{N} \frac{1}{6\pi\eta_0 a} = \frac{k_b T}{6\pi\eta_0 a}$$

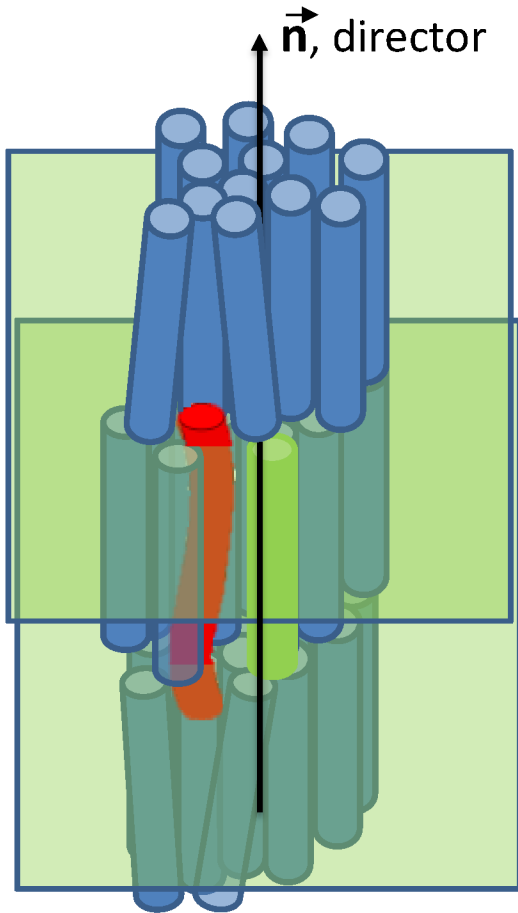
No fit

Longer is faster!

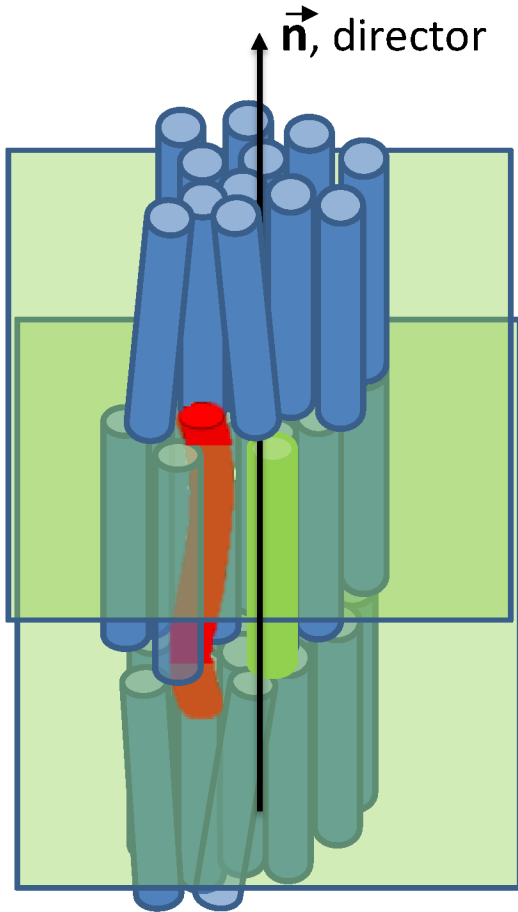


Alvarez et al PRL 2017

Some conclusions I



Some conclusions I

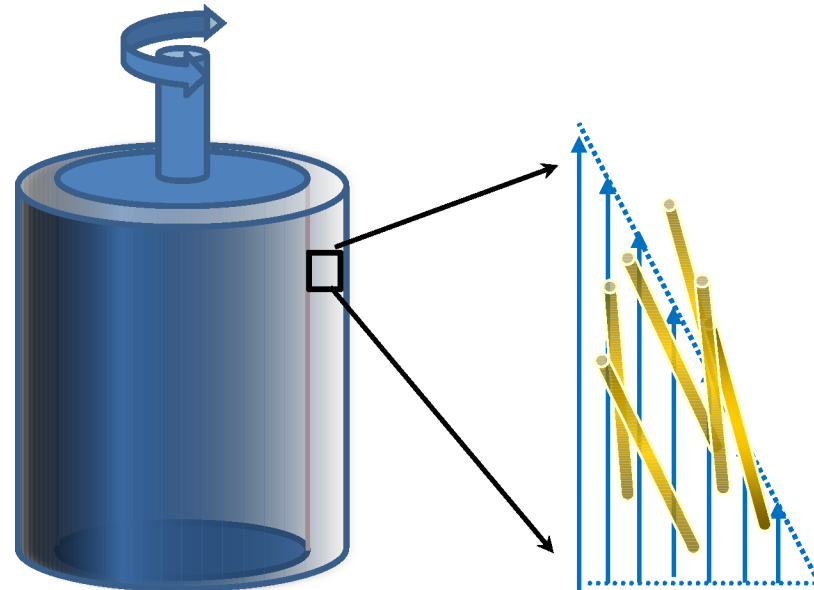


Vacancy needed to jump



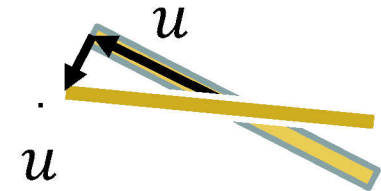
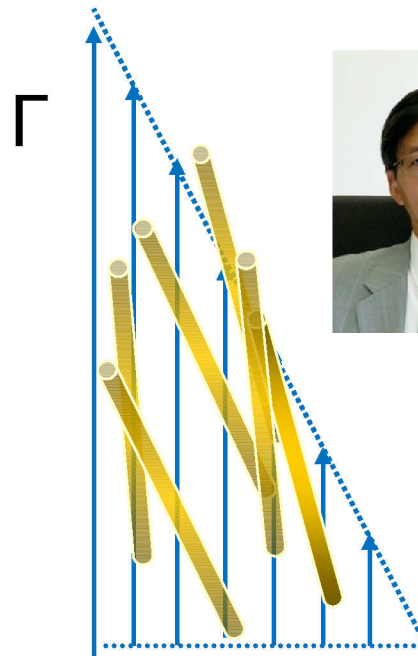
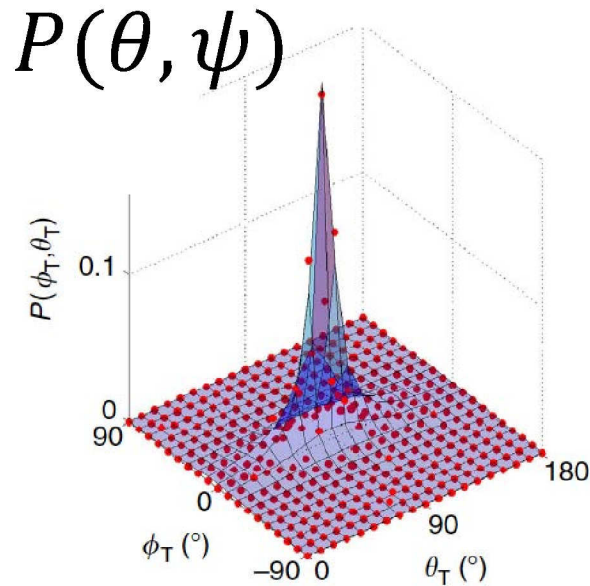
- Diffusion in Smectic = jumping in 1D periodic potential
- Long rods diffuse faster in a smectic layers of Short Host Particles...when size of particle does not fit length scale potential

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:

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

Brownian Motion

Particle Interaction

Flow Field

Theory for sheared rods: the Smoluchowski

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

Use $P(t, \mathbf{u})$ to calculate the orientational ordering tensor: $S(t) = \oint d\mathbf{u} \mathbf{u} \mathbf{u} P(\mathbf{u}; t) = \langle \mathbf{u} \mathbf{u} \rangle$

S characterised by largest eigenvalue:

$$\max(\text{eig}(S)) = \lambda_1 \sim \langle P_2 \rangle$$

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

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

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

Stress tensor characterised by viscosity

$$\eta(S, \dot{\gamma}) = \Sigma_{21}(S) / \dot{\gamma}$$

Typically plot zero shear viscosity

$$\eta_0 = \lim_{\dot{\gamma} \rightarrow 0} \eta$$

and reduced viscosity

$$\eta / \eta_0$$

Theory for sheared rods: rotational diffusion

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

What is the relevant diffusion coefficient?

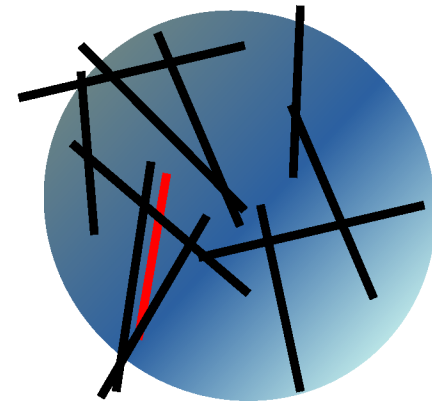
$$D_r^0 \sim L^{-3} \frac{3 \ln(L/d)}{\beta \pi \eta_s L^3}$$

Tube model for isotropic surrounding:

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

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

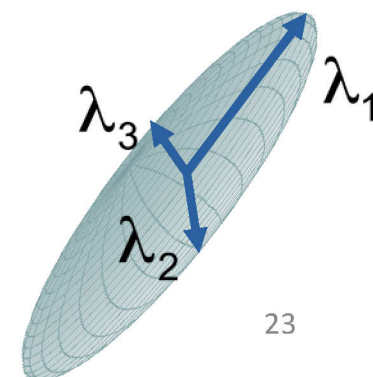
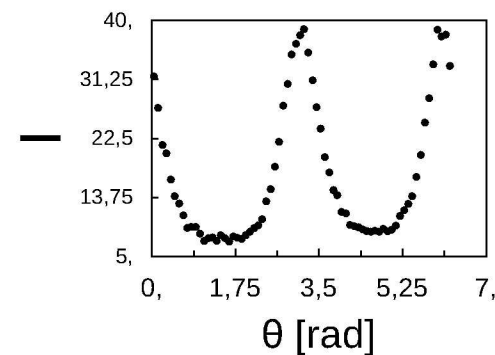
$c \approx 1.32 \times 10^3$
Teraoka et al. *J. Chem. Phys.* 91 1989]



Tube dilation for anisotropic surrounding:

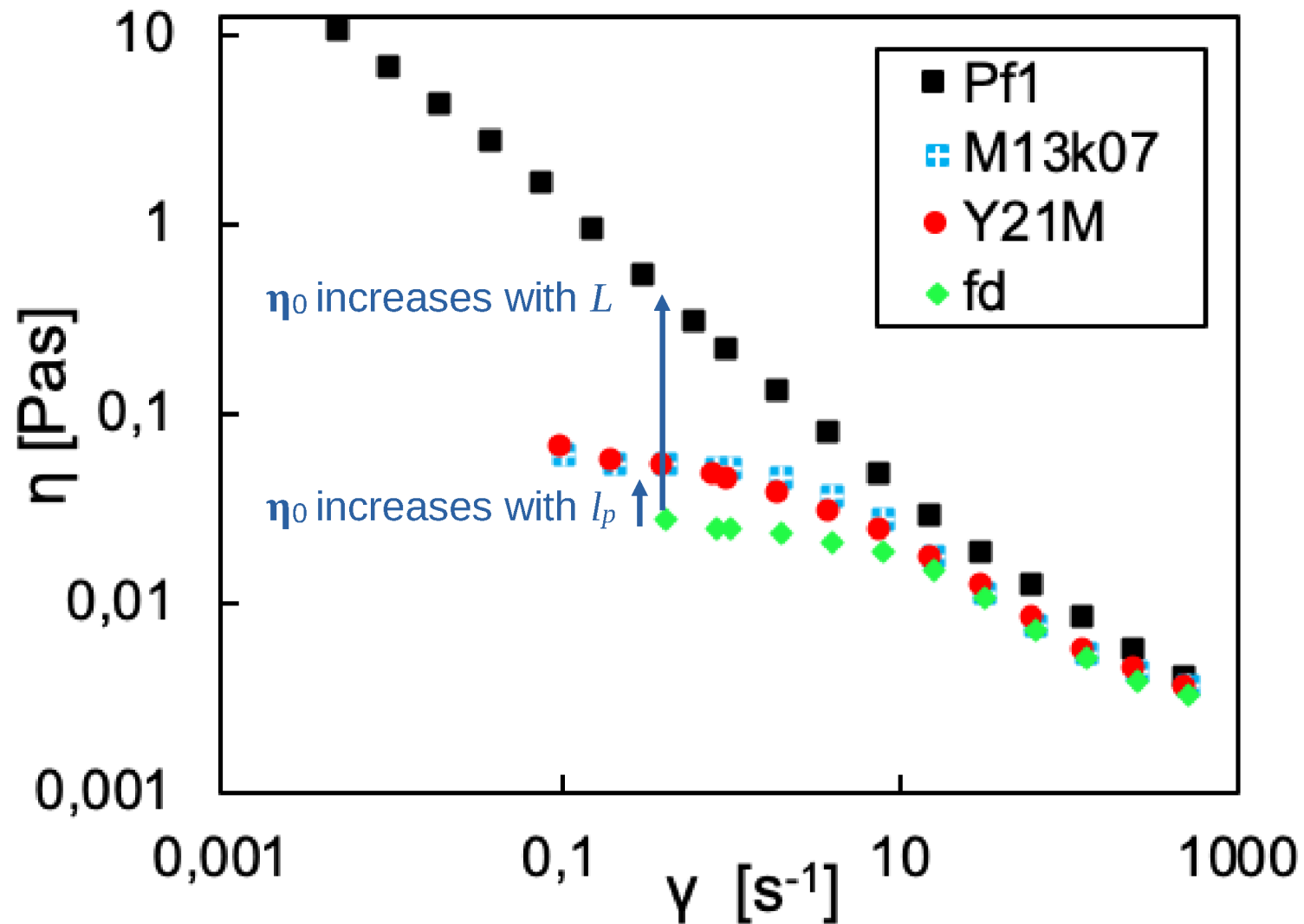
$$\langle D_r \rangle = c D_r^0 \left(\frac{5}{4} \rho L^3 \left(1 - \frac{3}{5} S:S \right) \right)^{-2}$$





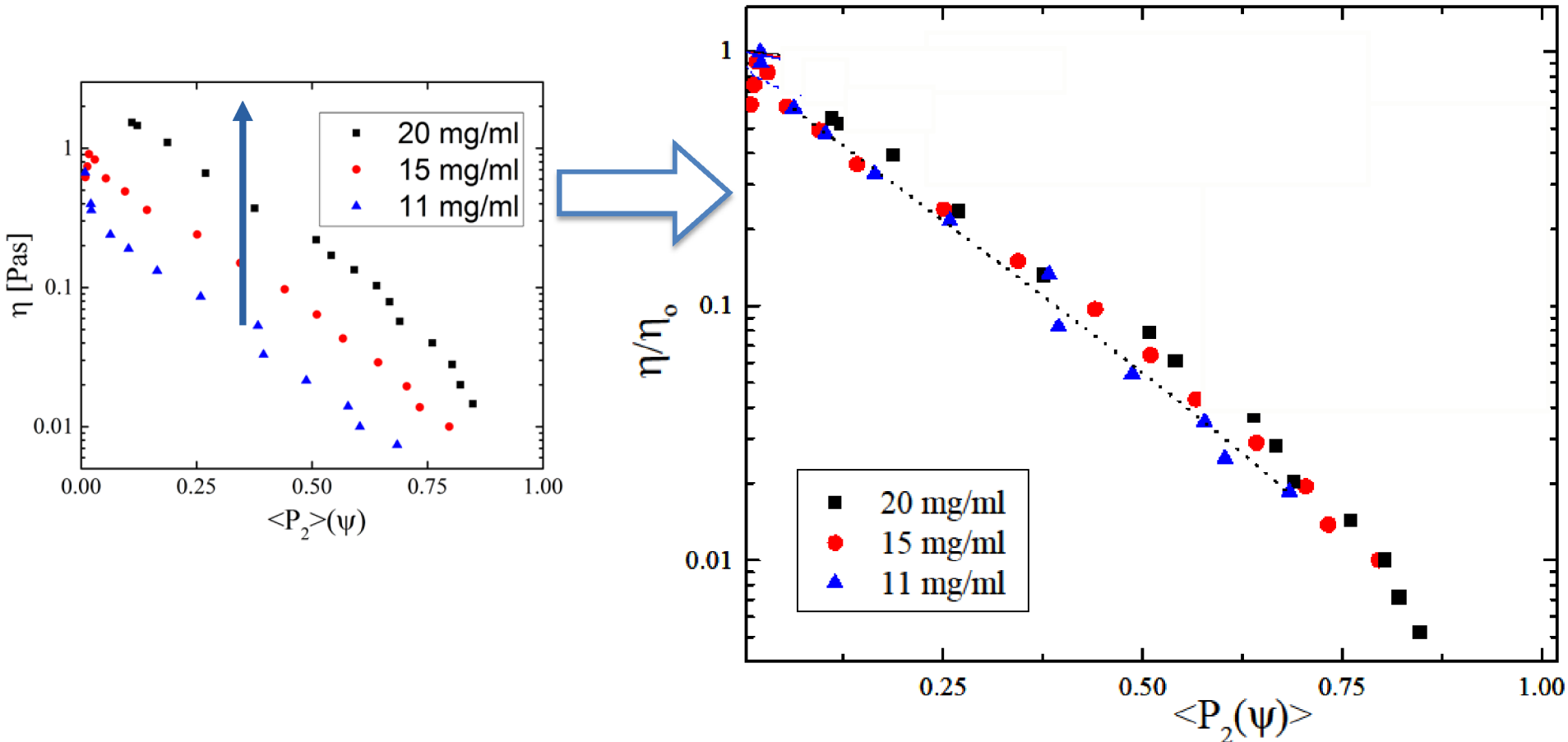
$$\lambda_1(\psi) \Rightarrow \psi_{\max} \equiv 0$$

Shear thinning rods: effect of length

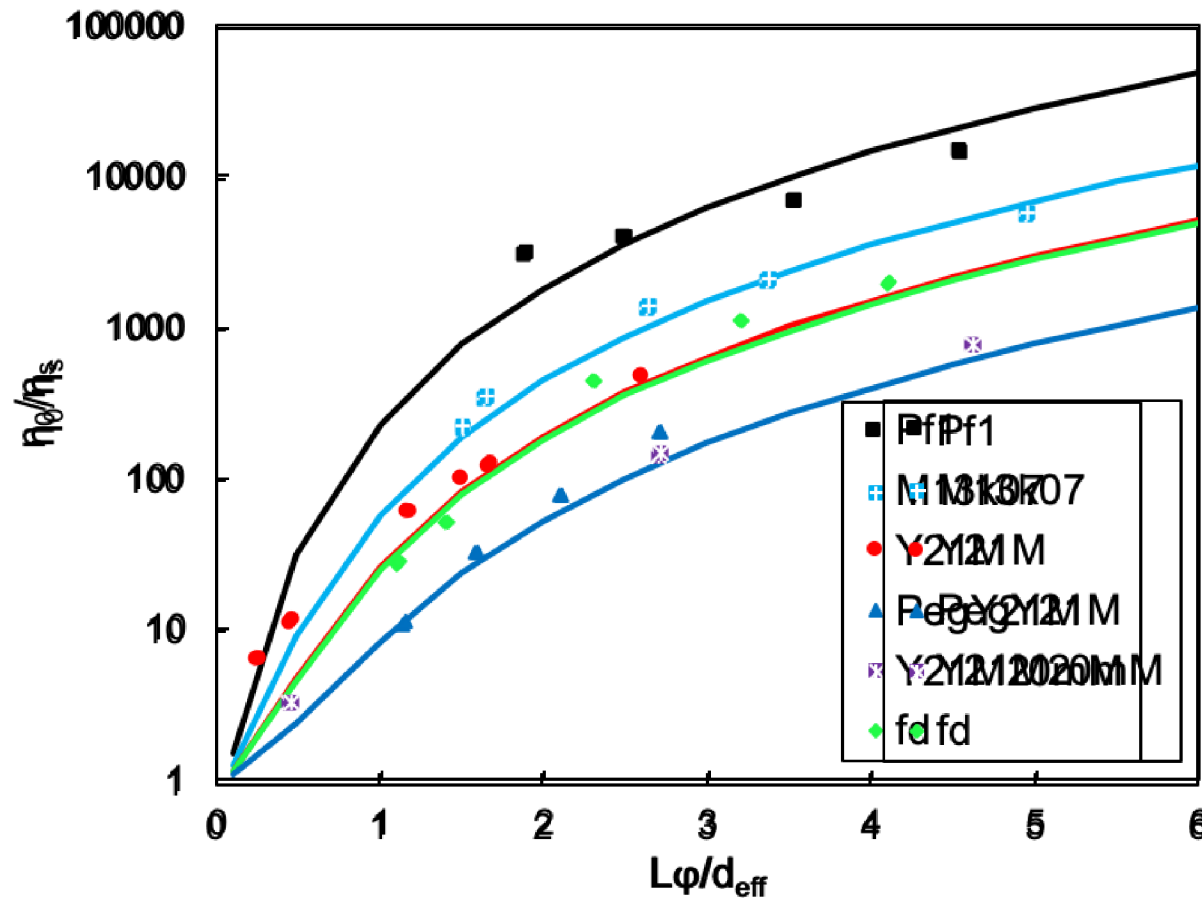


Use $\langle P_2(\psi) \rangle$ to scale viscosity

Assumption: shear thinning is caused by orientation

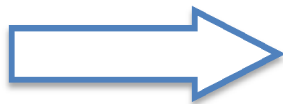
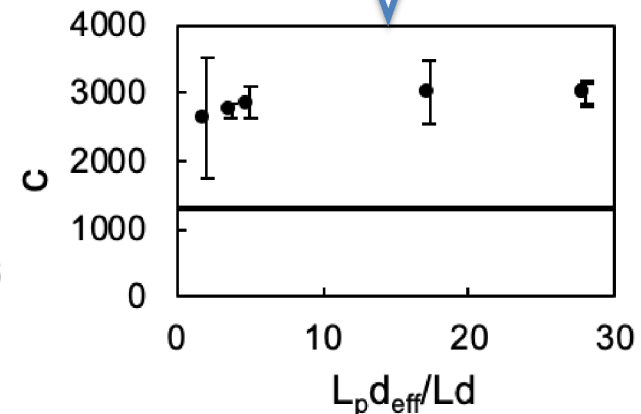


Zero shear viscosity of rods



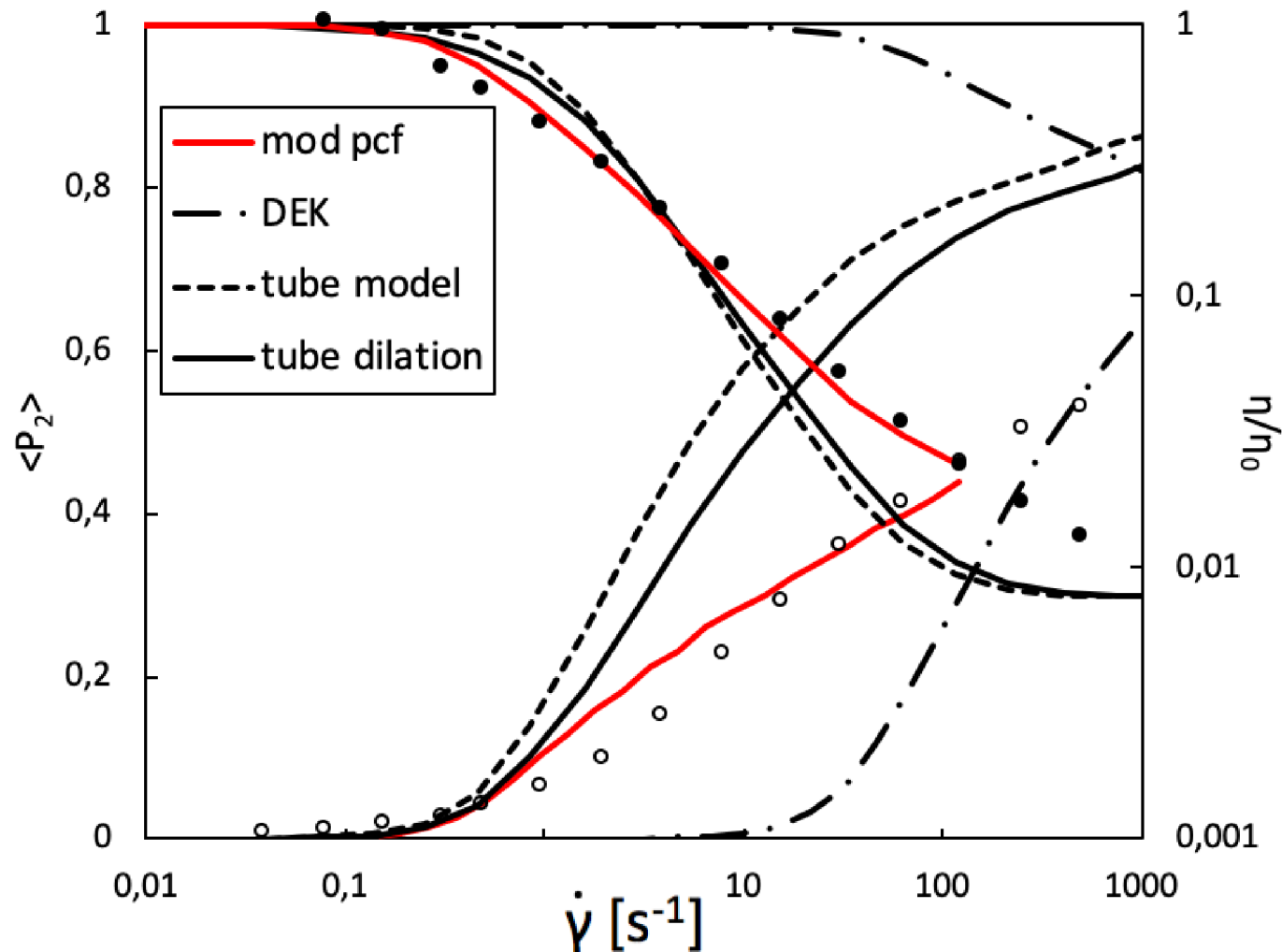
$$\eta_0 \simeq \eta_s + \rho/\beta D_r$$

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



We determined Teraokes constant!
We understand huge L dependence

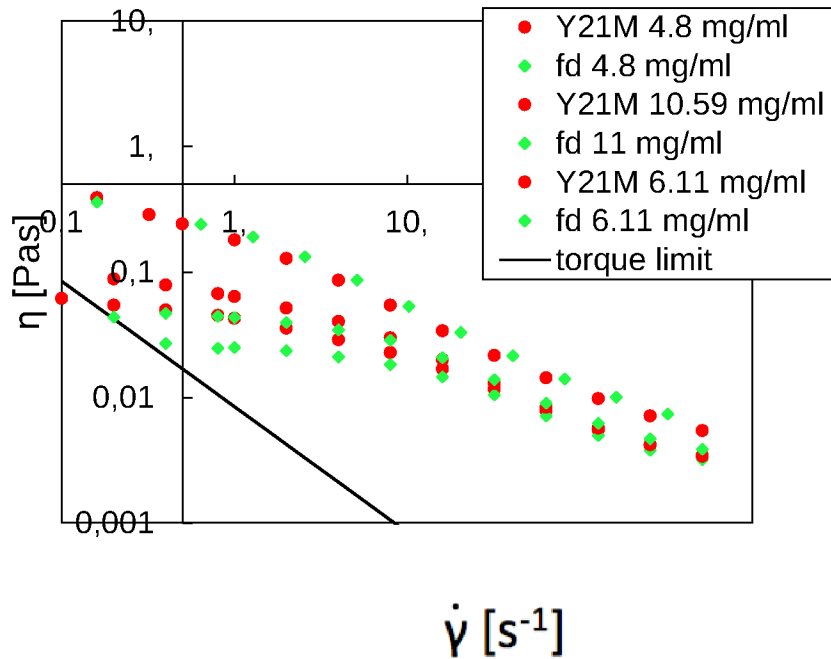
Understanding shear thinning



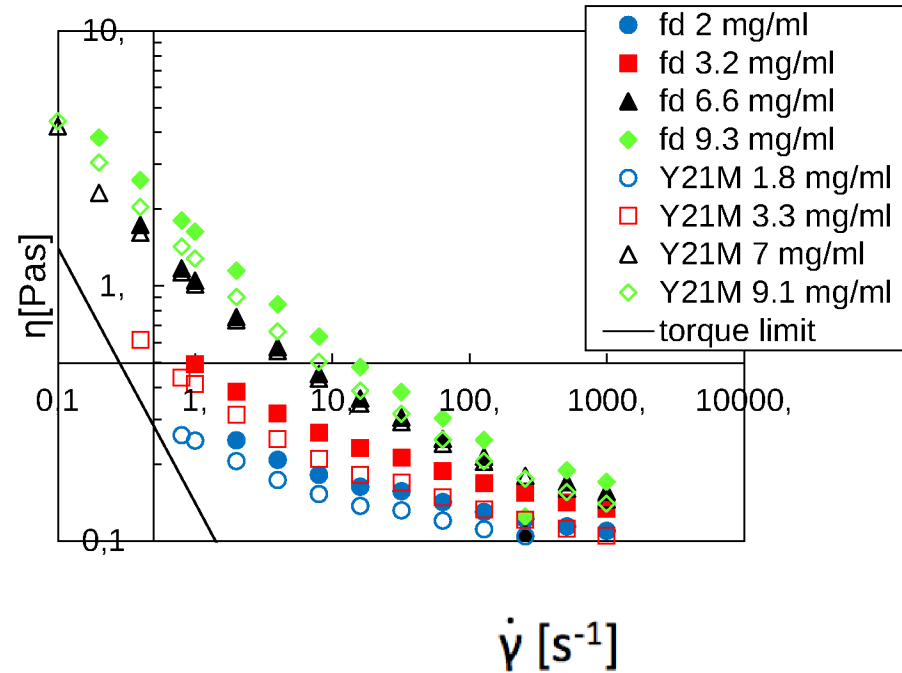
$$\partial_t g = D_r \mathcal{R} \cdot [\mathcal{R}g + \beta g \mathcal{R}U] - \mathcal{R} \cdot [gu \times \Gamma \cdot u]$$

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

Influence stiffness on flow response



Suspensions in water

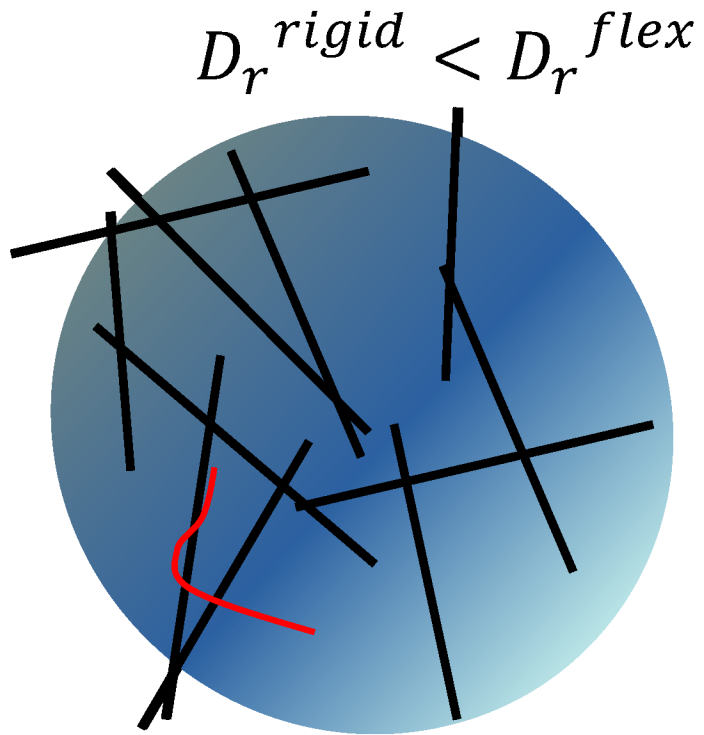


Suspensions in glycerol

Particle flexibility leads to a decrease in zero shear viscosity

The nonlinear viscosity shows the opposite!

Influence stiffness on flow response

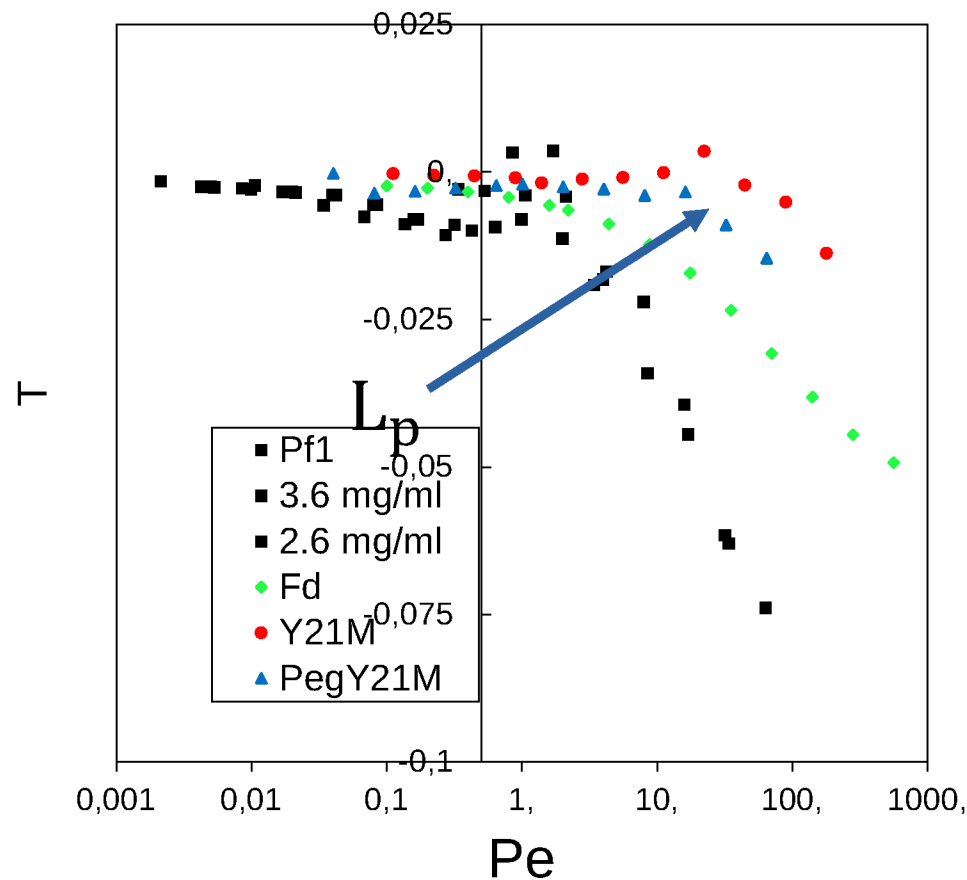


We understand zero shear result, but what about high shear result?

Effect of morphology on biaxiality

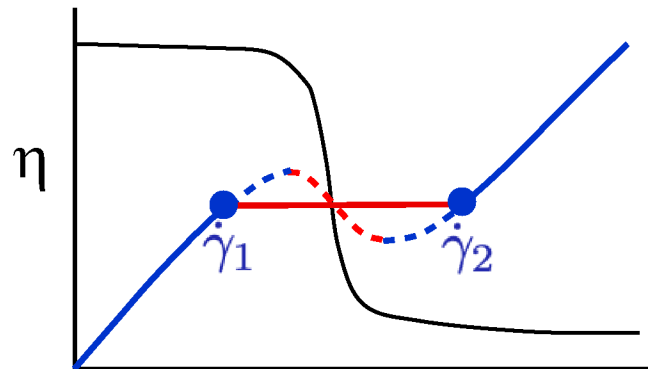
$$T = \frac{1}{2(2 - \lambda_1(\theta) - \lambda_1(\psi))} [\lambda_1(\theta)\lambda_1(\psi) - (\lambda_1(\theta))^2]$$

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

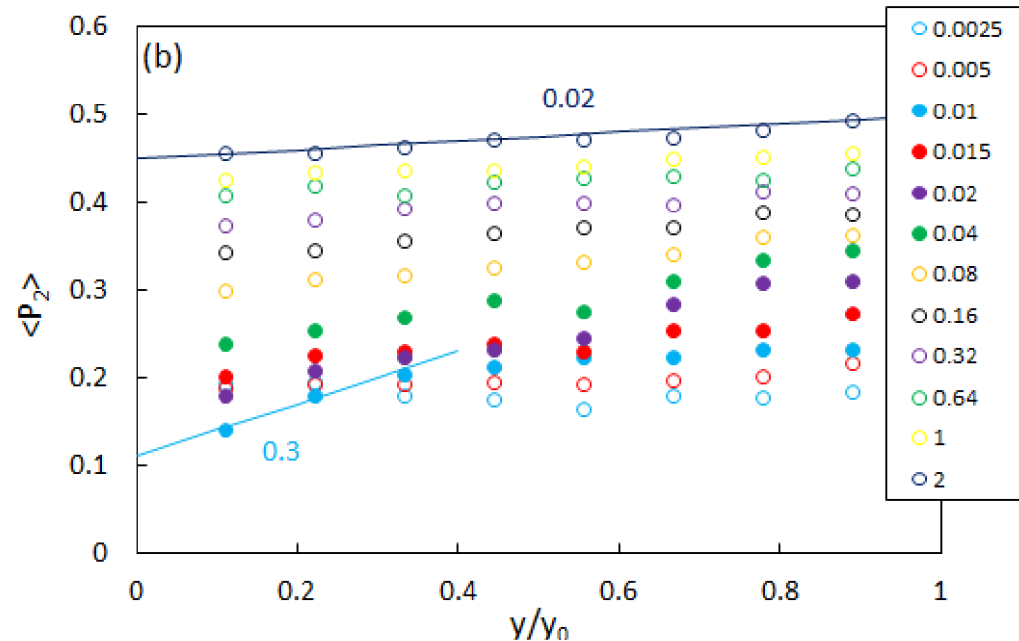
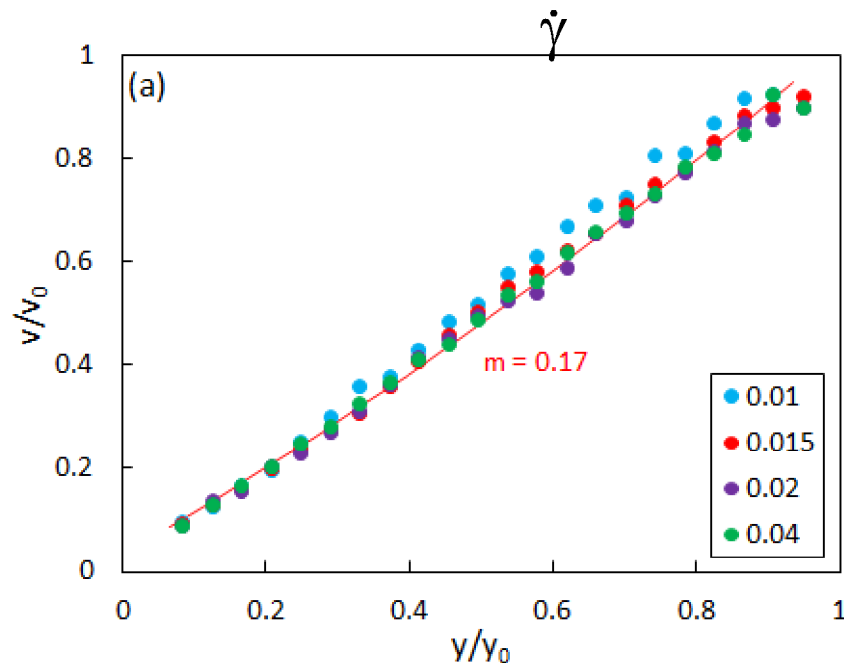
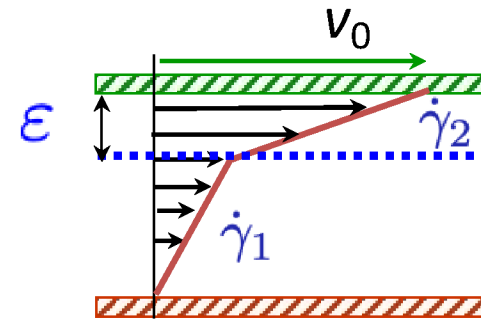


Velocity & ordering profiles of rods

Strong shear-thinning



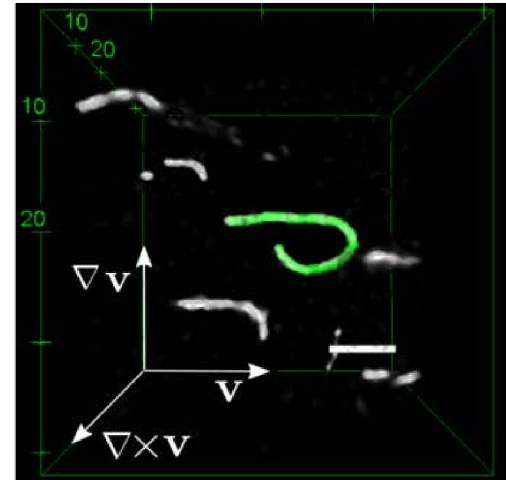
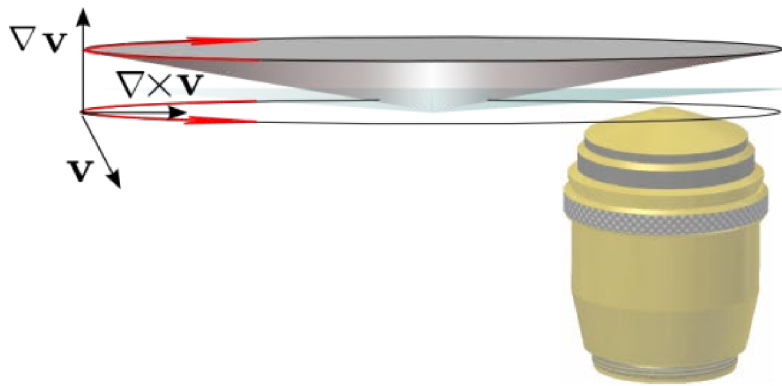
Flow instabilities: shear banding



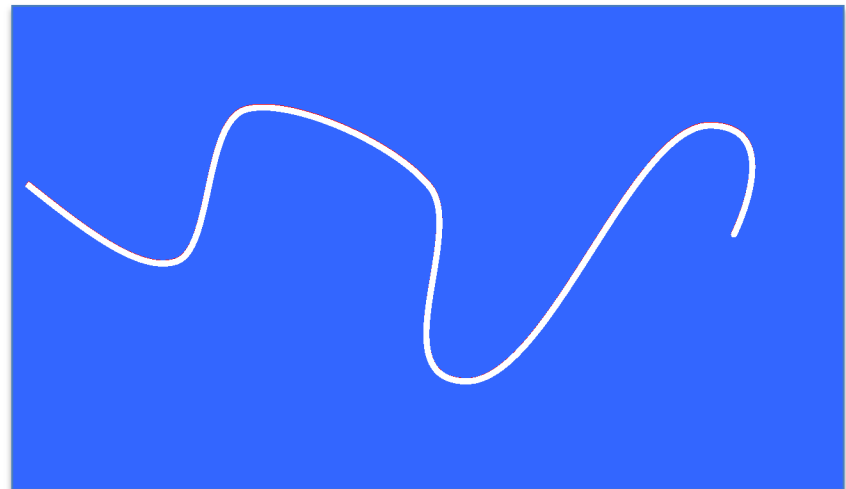
- Only very long and flexible rods show hints of shear banding

- 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

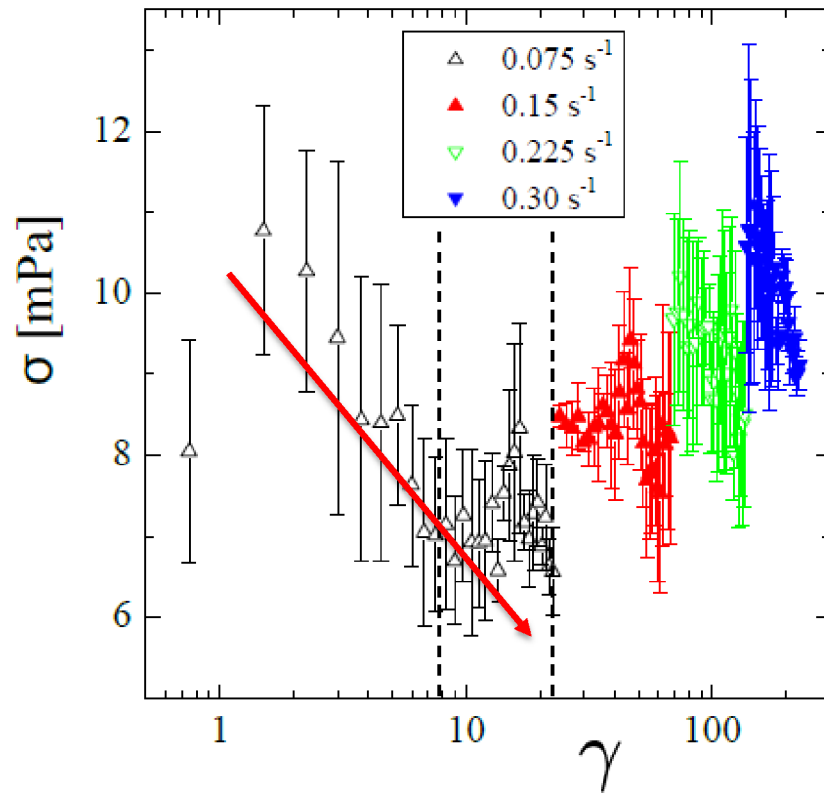
$$\langle L \rangle \approx 20 \mu\text{m}, d = 7 \text{ nm}, l_p = 17 \mu\text{m}$$



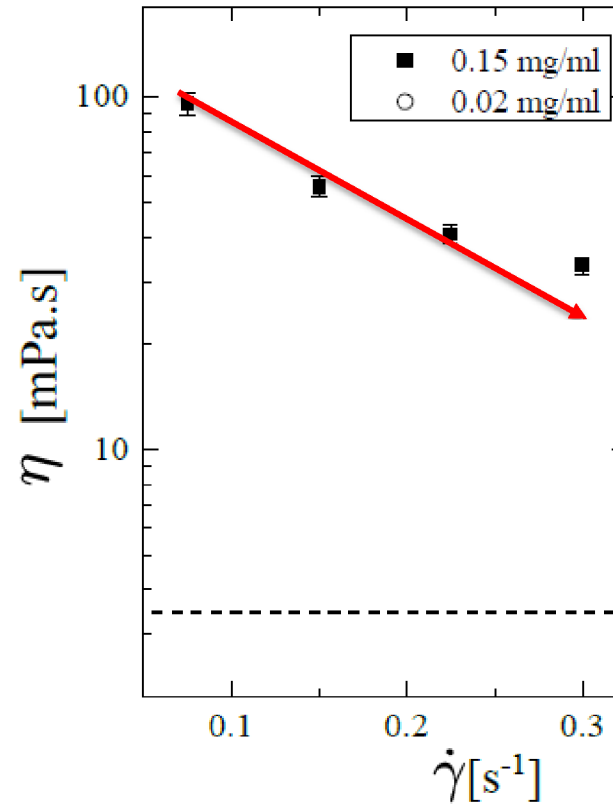
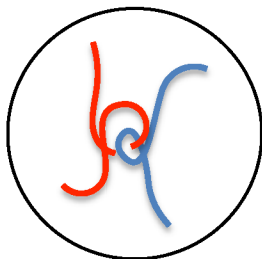
- Use three concentrations, label 1 per 100 filaments
- About 100 analyzed filaments per combination



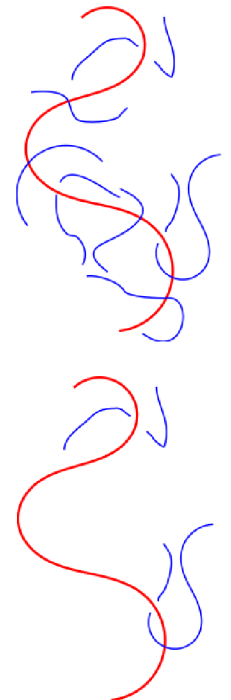
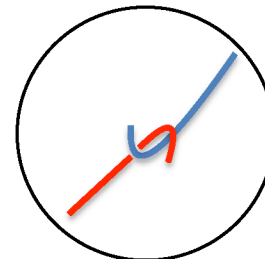
Rheological response of F-actin dispersions



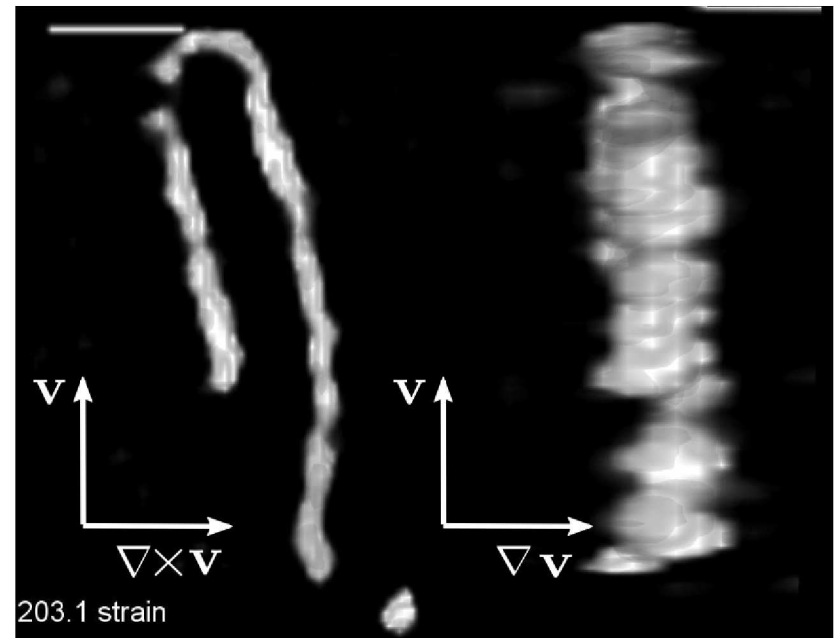
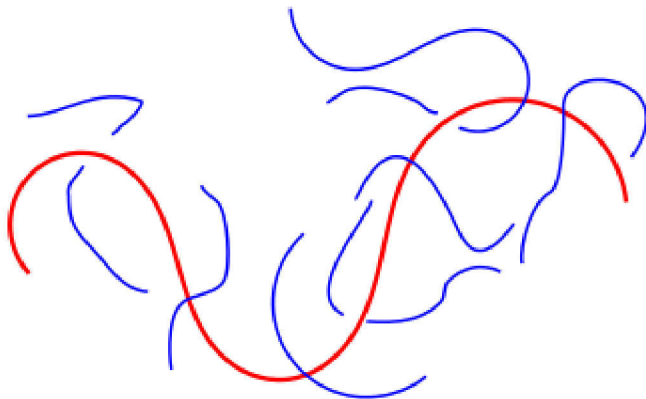
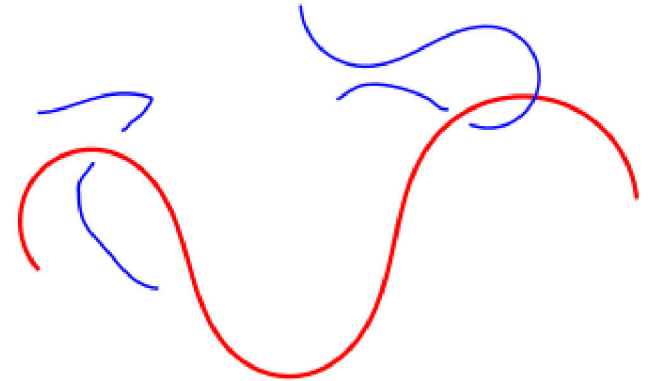
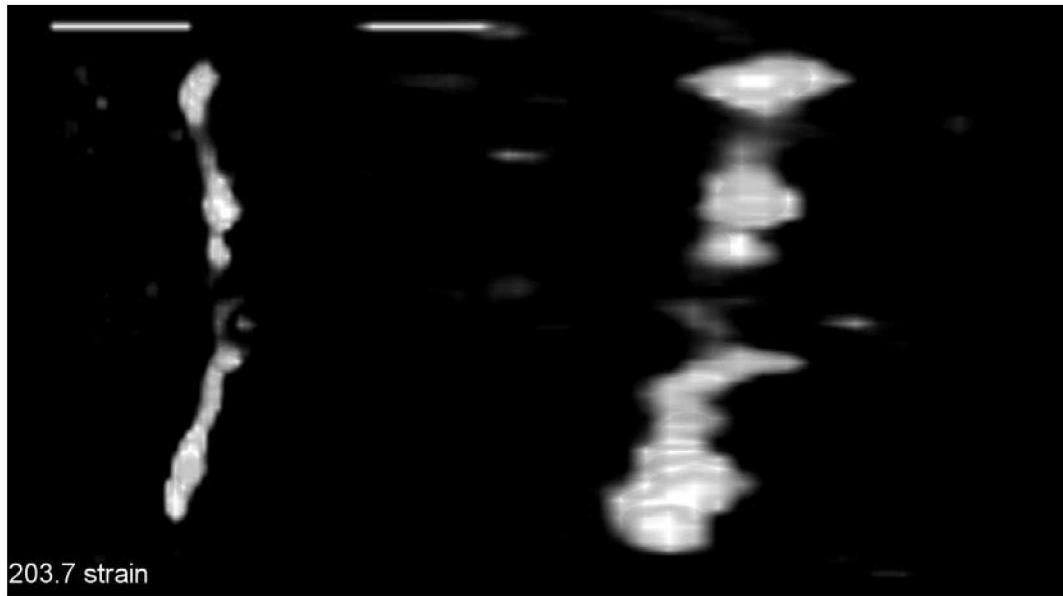
Strain softening



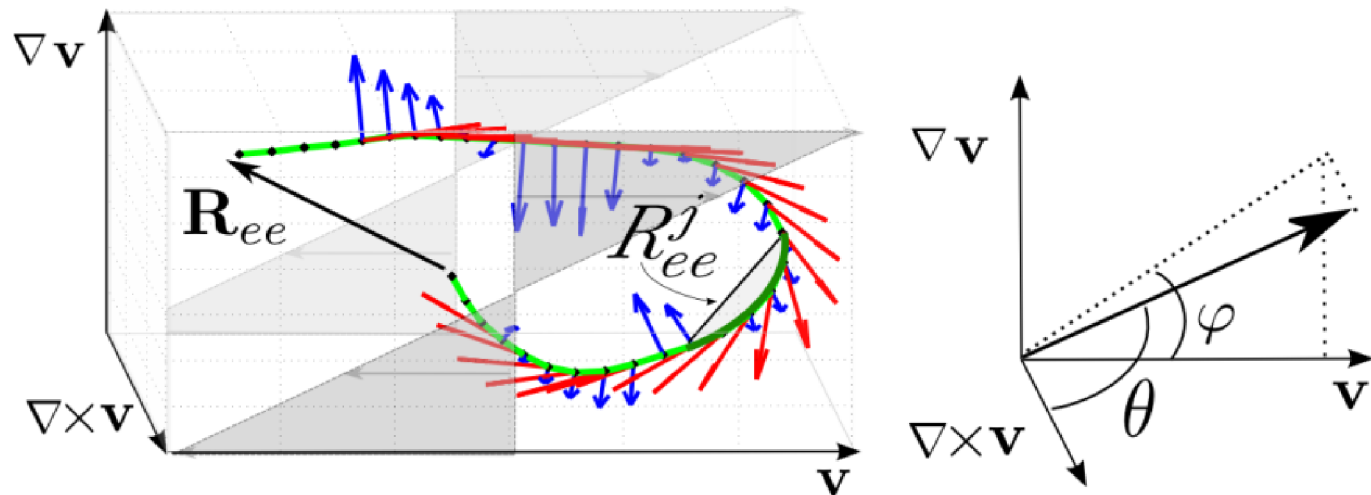
Shear thinning



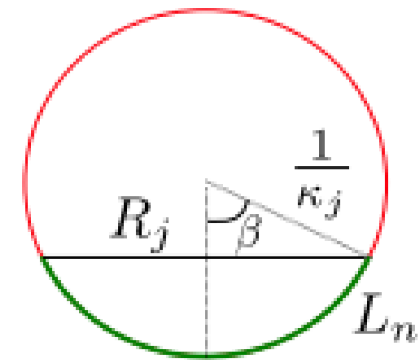
Sheared F-Actin in 3-D



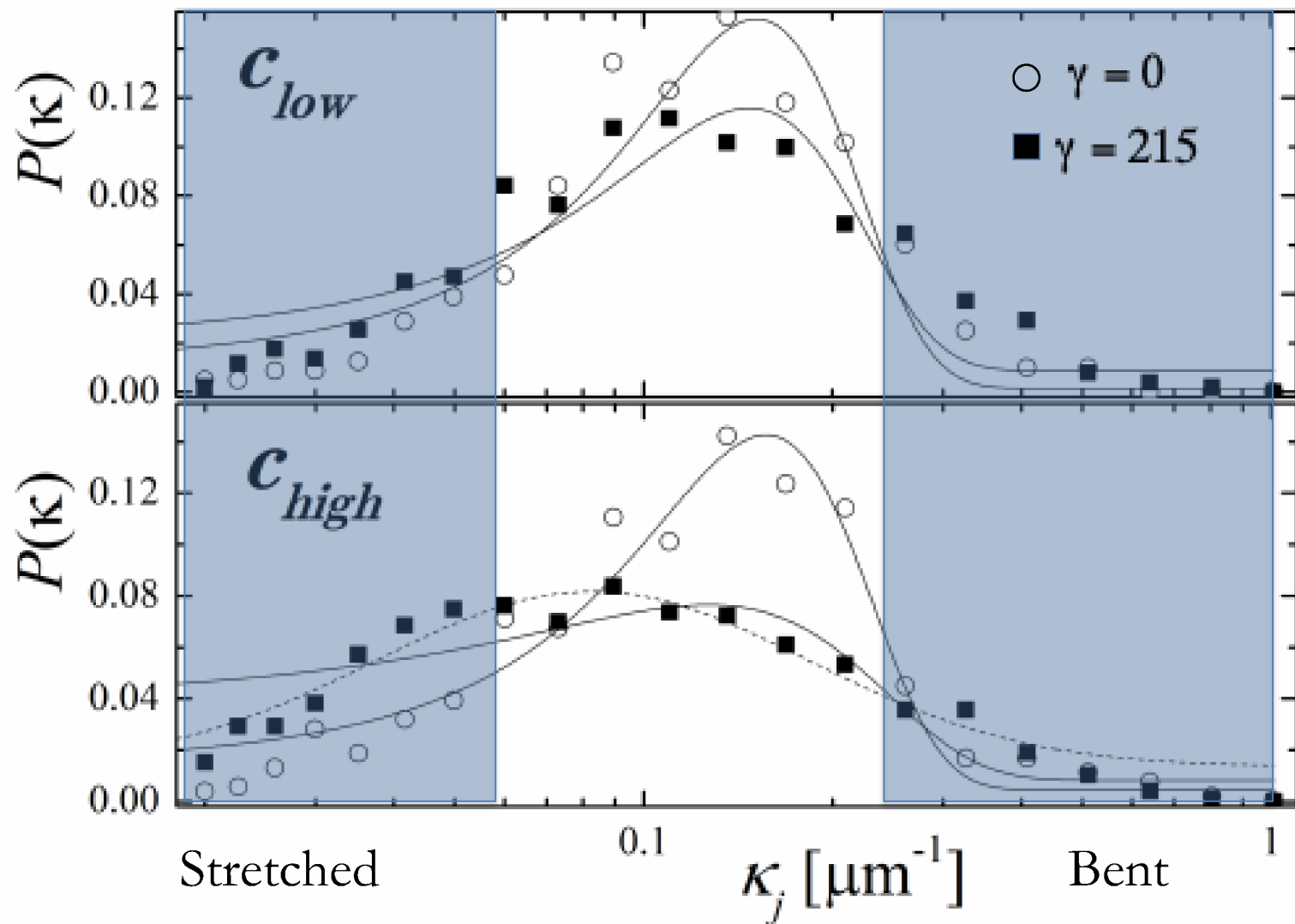
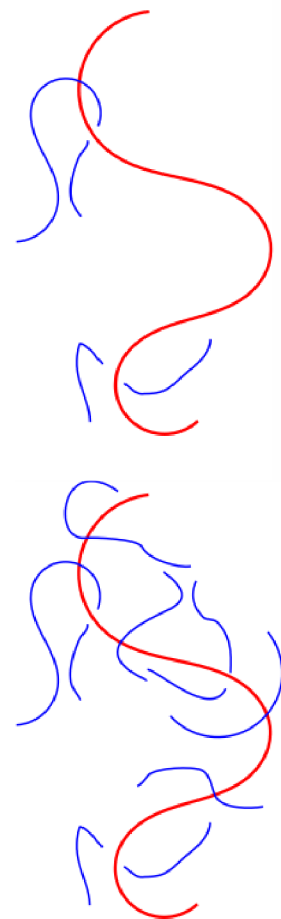
Analyze local bending and stretching:



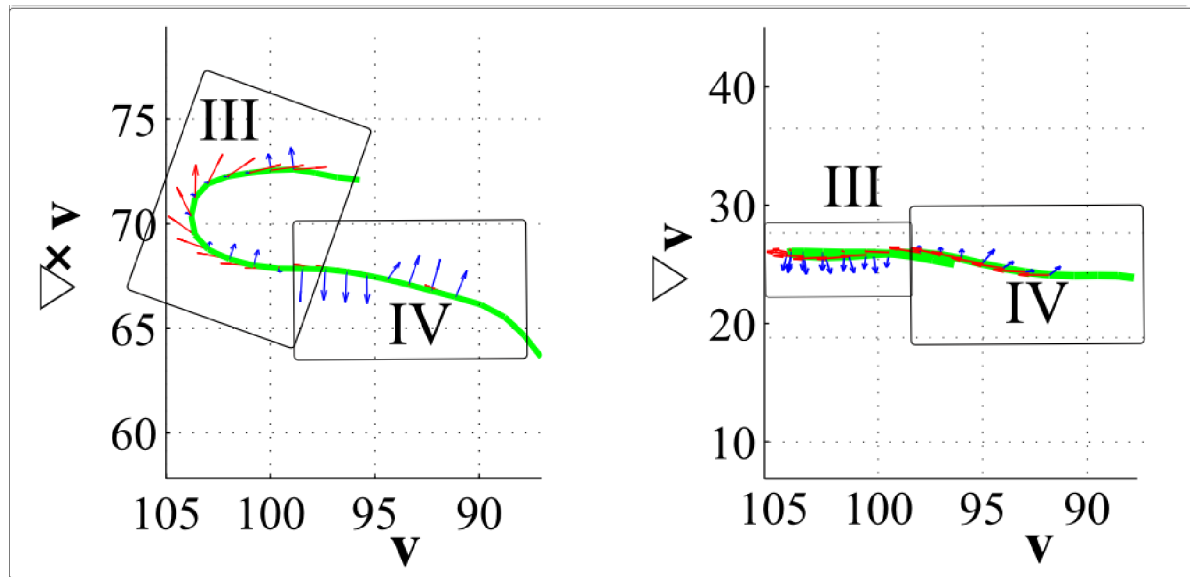
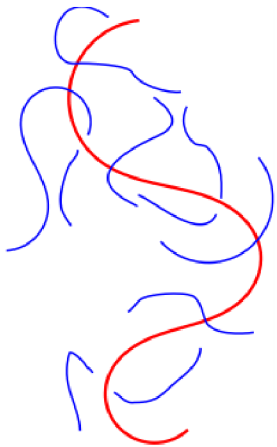
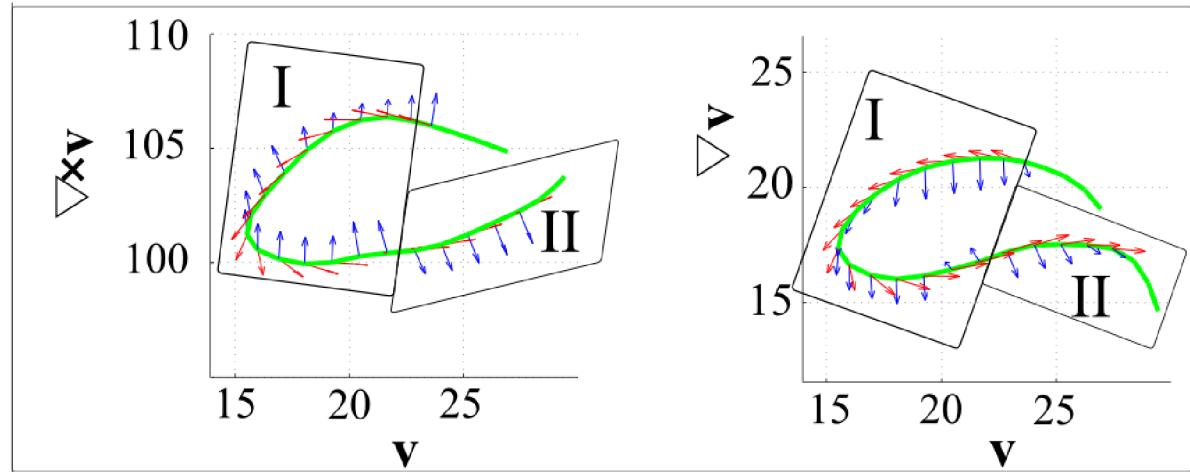
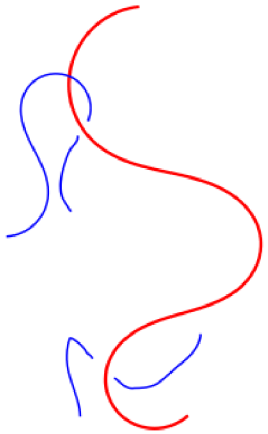
$$\hat{T}_j \equiv \frac{\dot{\mathbf{r}}_j}{|\dot{\mathbf{r}}_j|}; \hat{B}_j \equiv \frac{\dot{\mathbf{r}}_j \times \ddot{\mathbf{r}}_j}{|\dot{\mathbf{r}}_j \times \ddot{\mathbf{r}}_j|}; \kappa_j = \frac{|\dot{\mathbf{r}}_j \times \ddot{\mathbf{r}}_j|}{|\dot{\mathbf{r}}_j|^3}$$



Distribution of curvatures:

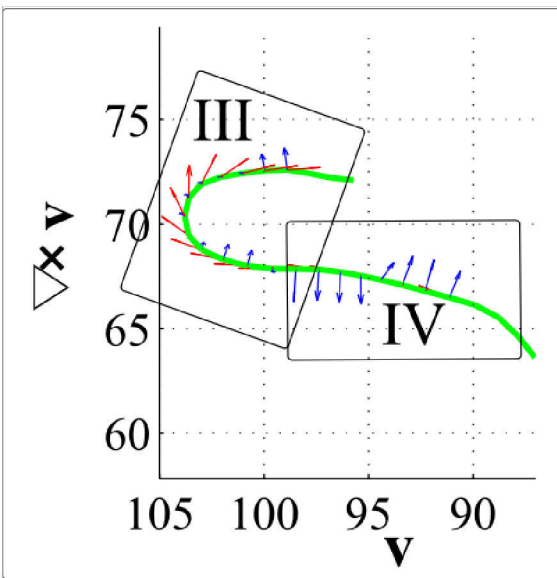


Typical examples:

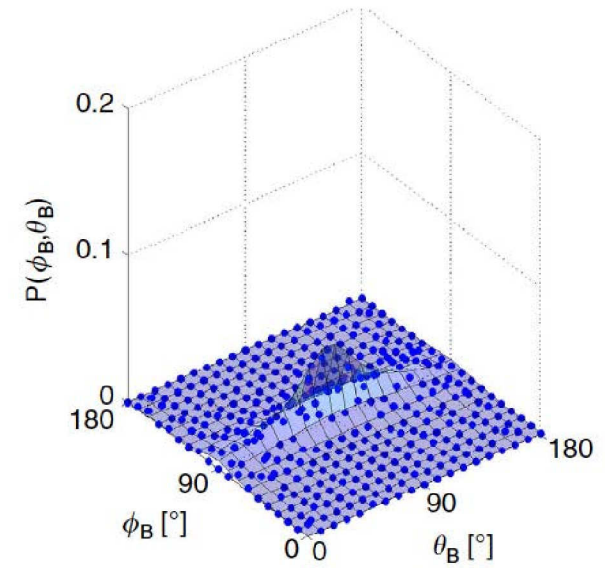
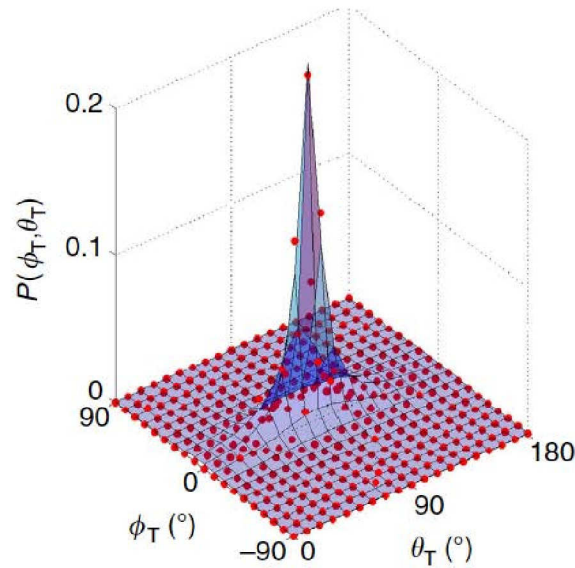


Distribution of angles

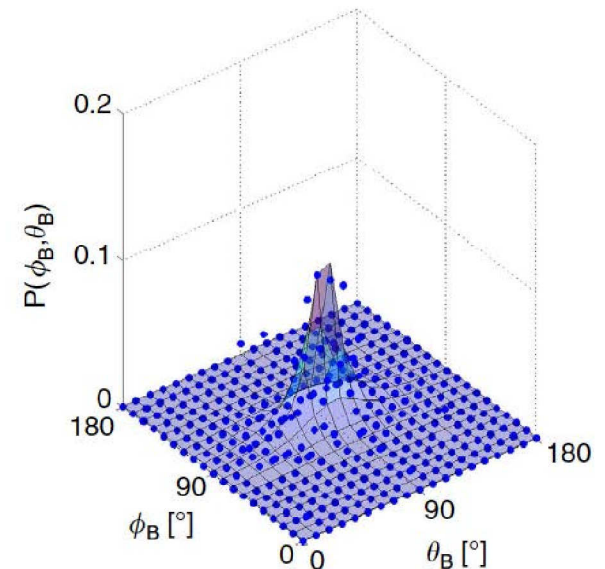
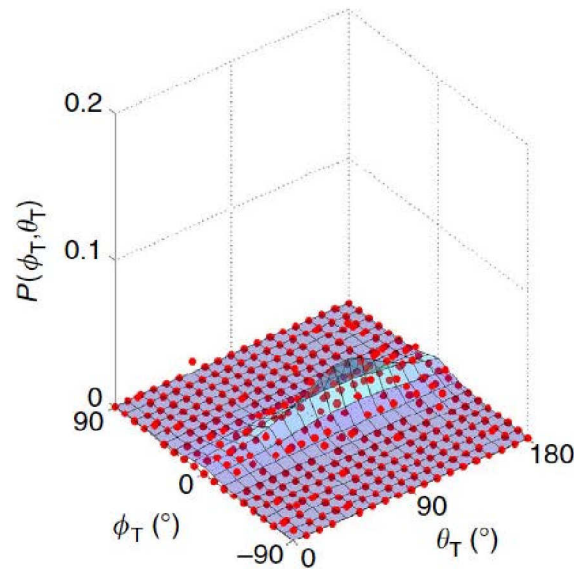
Stretched: IV



Bent: III



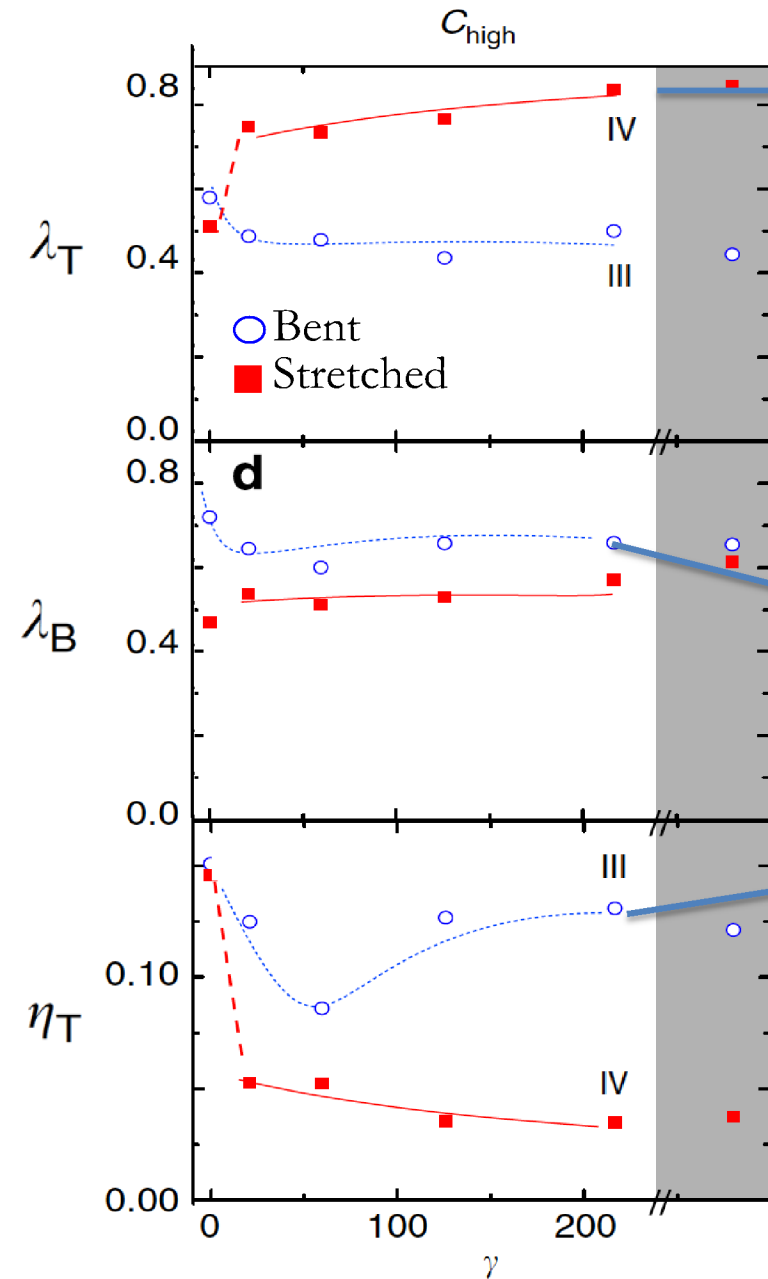
$$f(\theta, \phi) = a / \left(\left(\frac{\theta - \Delta\theta}{w_\theta} \right)^2 + \left(\frac{\phi - \Delta\phi}{w_\phi} \right)^2 + 1 \right)$$



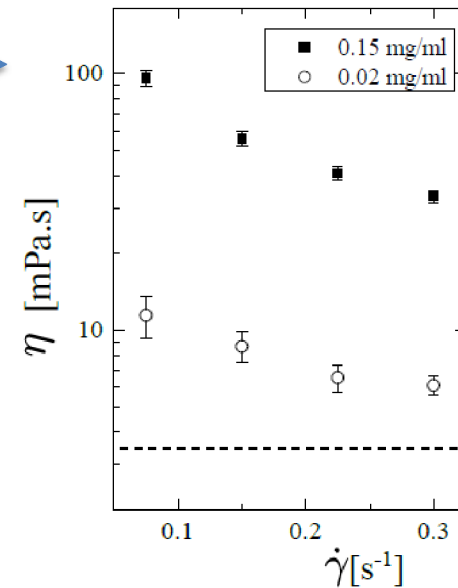
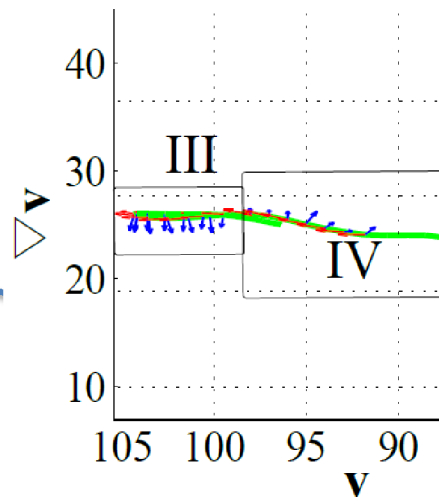
Connection between ordering and stress



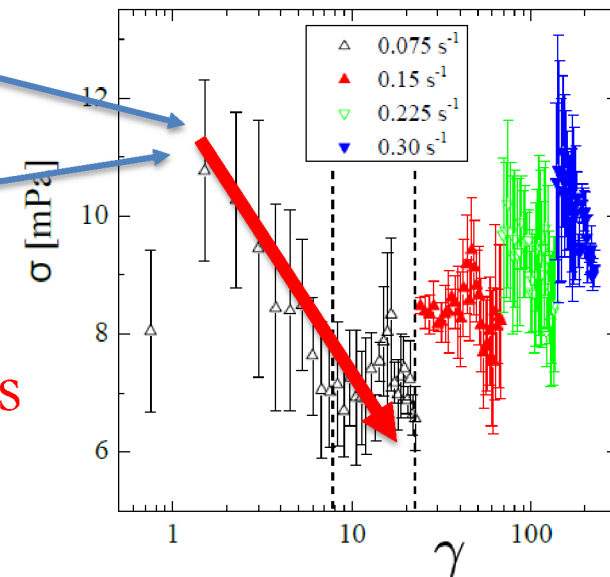
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Shear thinning:
Nematic=more space



Strain softening :
Oriented hairpins



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

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Laura Alvarez

MLZ, Garching:

Aurel Radulescu

PSI, Villigen:

Joachim Kohlbrecher

ILL, Grenoble:

Lionel Porcar

Amolf Amsterdam:

Gijsje Koenderink



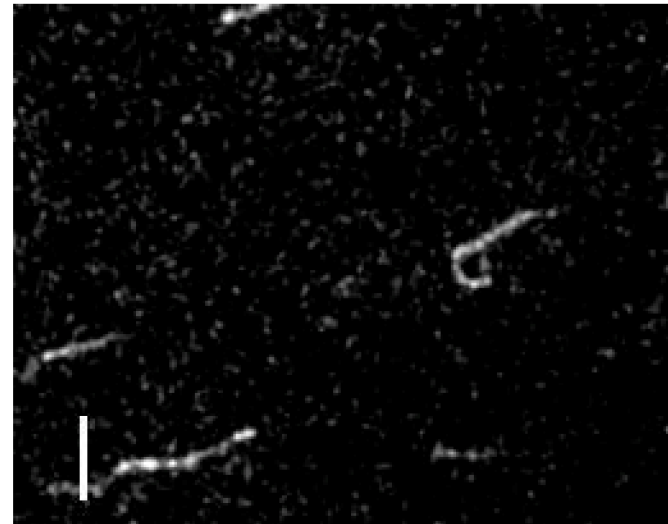
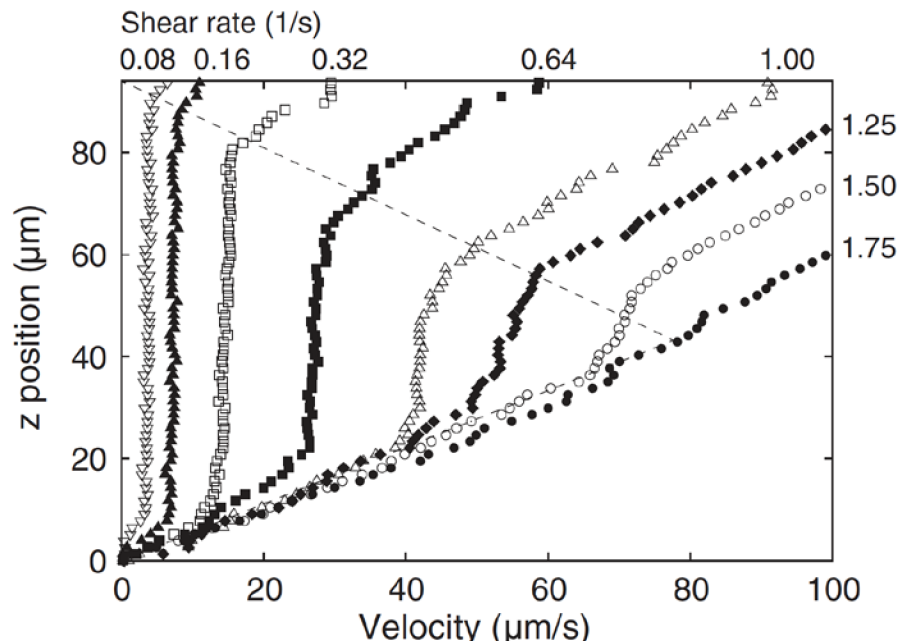
F-actin: stiffer and longer

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

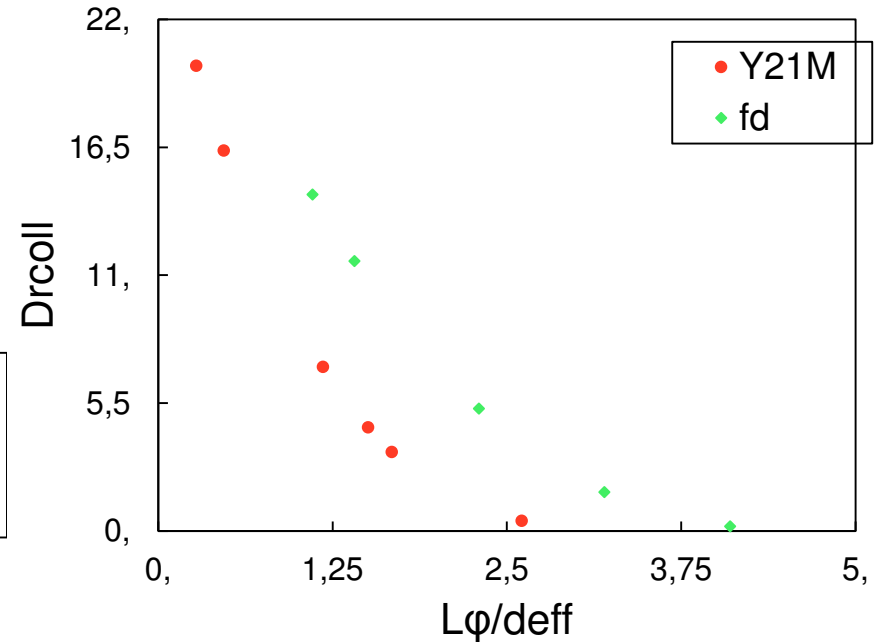
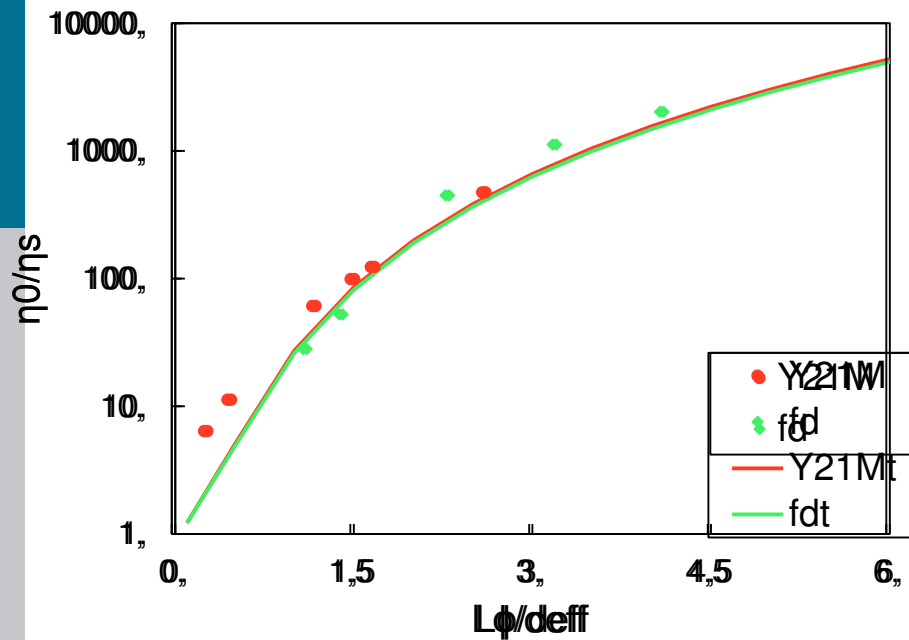
Shear banding has been identified by

Kunita et al, PRL 109, 248303 (2012)

Goal: obtain 3-D structural information

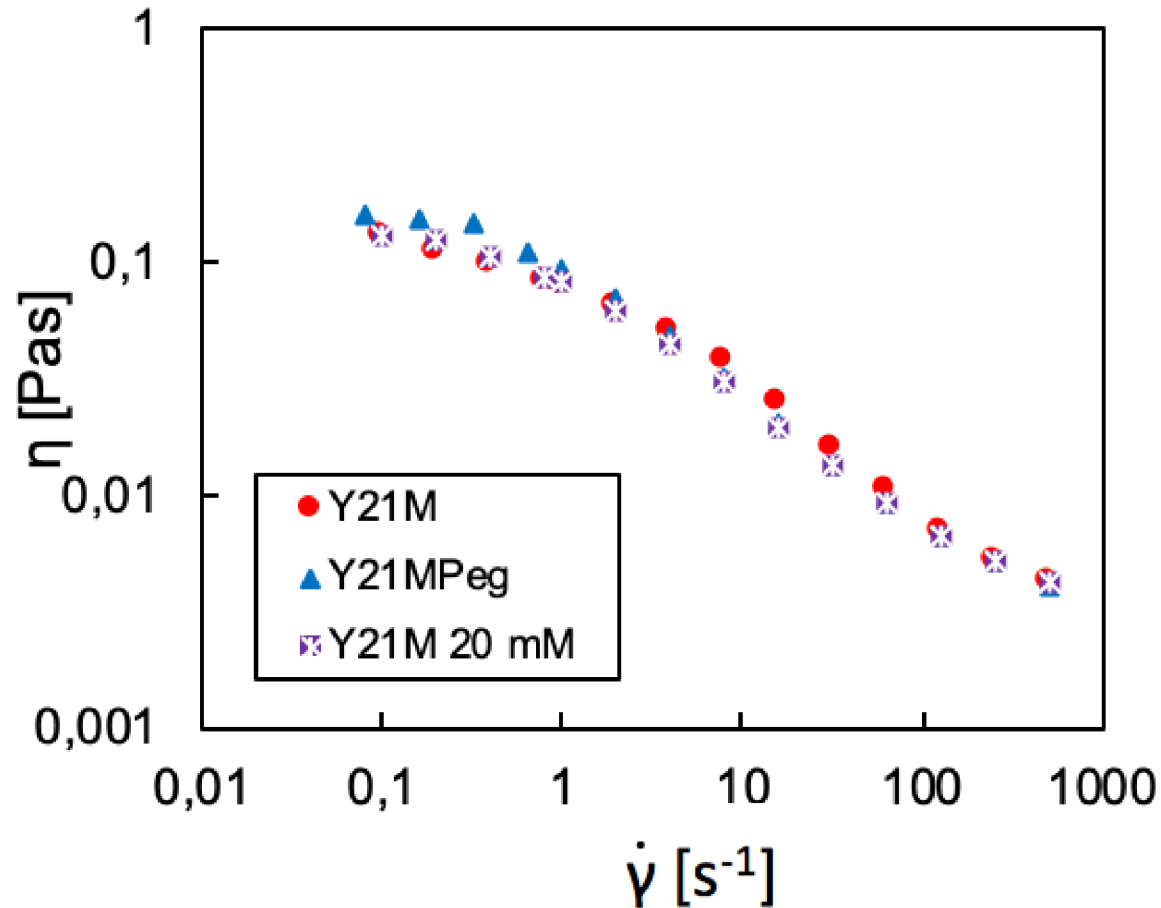


Morphological influences on shear flow



Indication of a flexibility dependence of the rotational diffusion coefficient

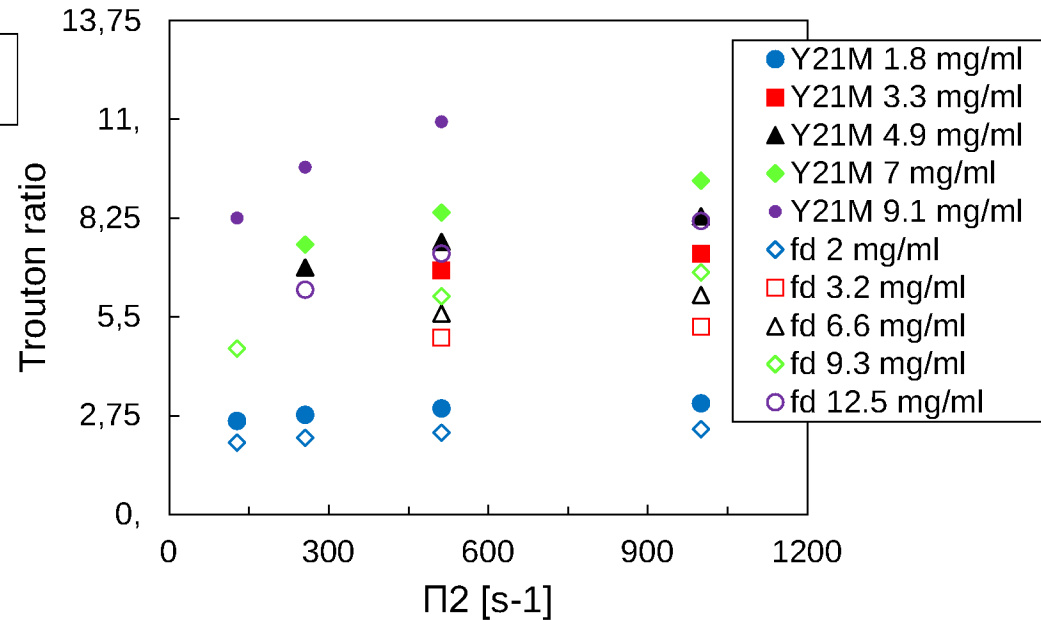
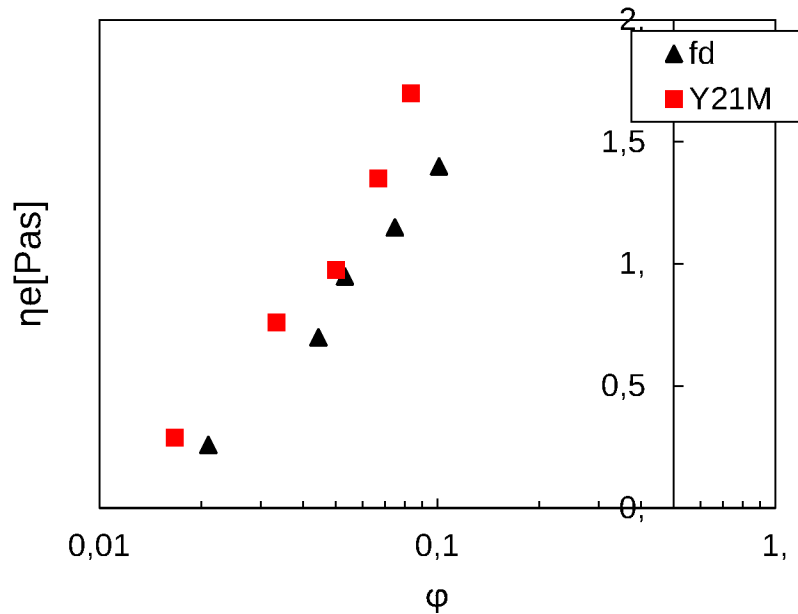
Influence thickness on flow response



Elongational flow of ideal and semiflexible rods

$$\text{Trouton ratio} = \eta_e / \eta$$

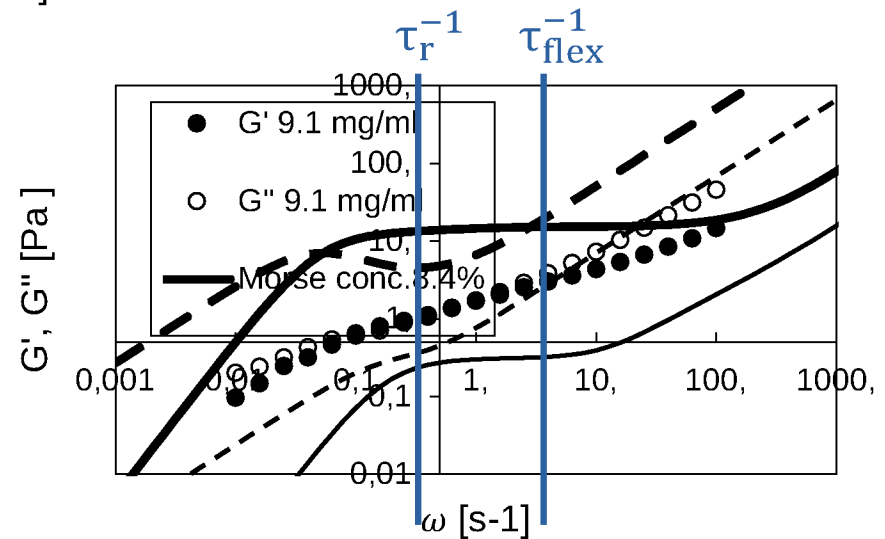
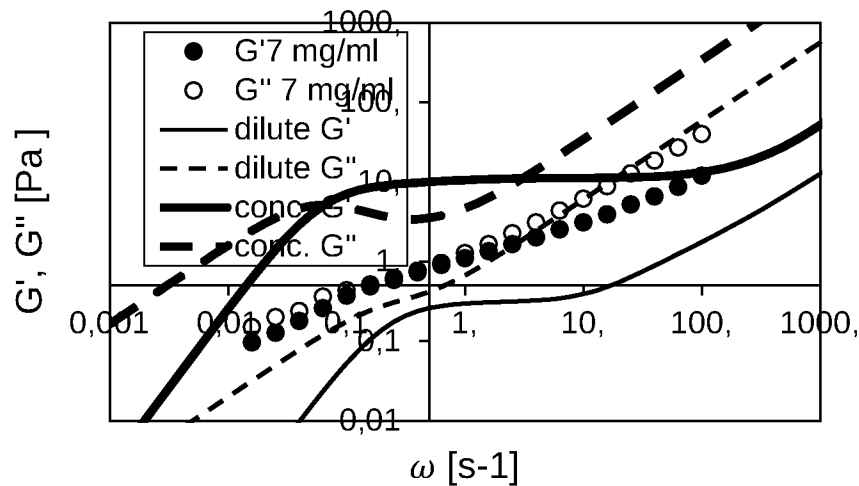
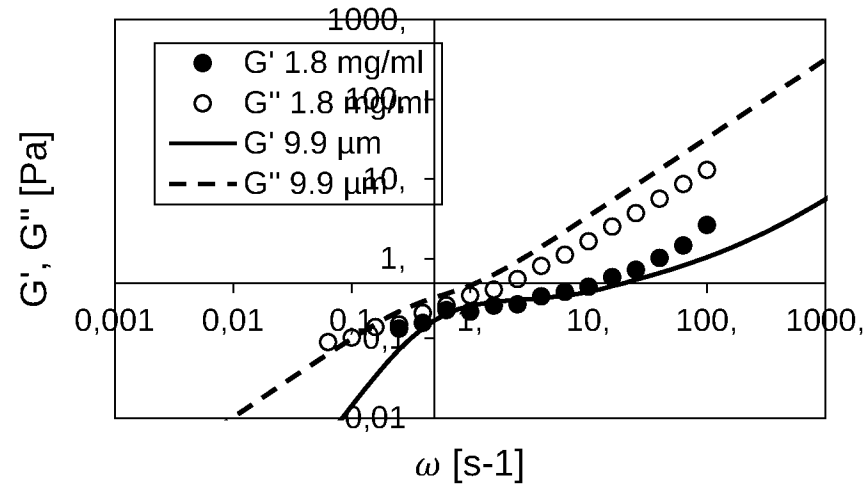
Newtonian fluids: $\eta_e / \eta = 3$



Pronounced effect of concentration on elongational viscosity

Rate dependent Trouton ratio reaching rather high values

SAOS and relaxation time spectrum of fdY21M



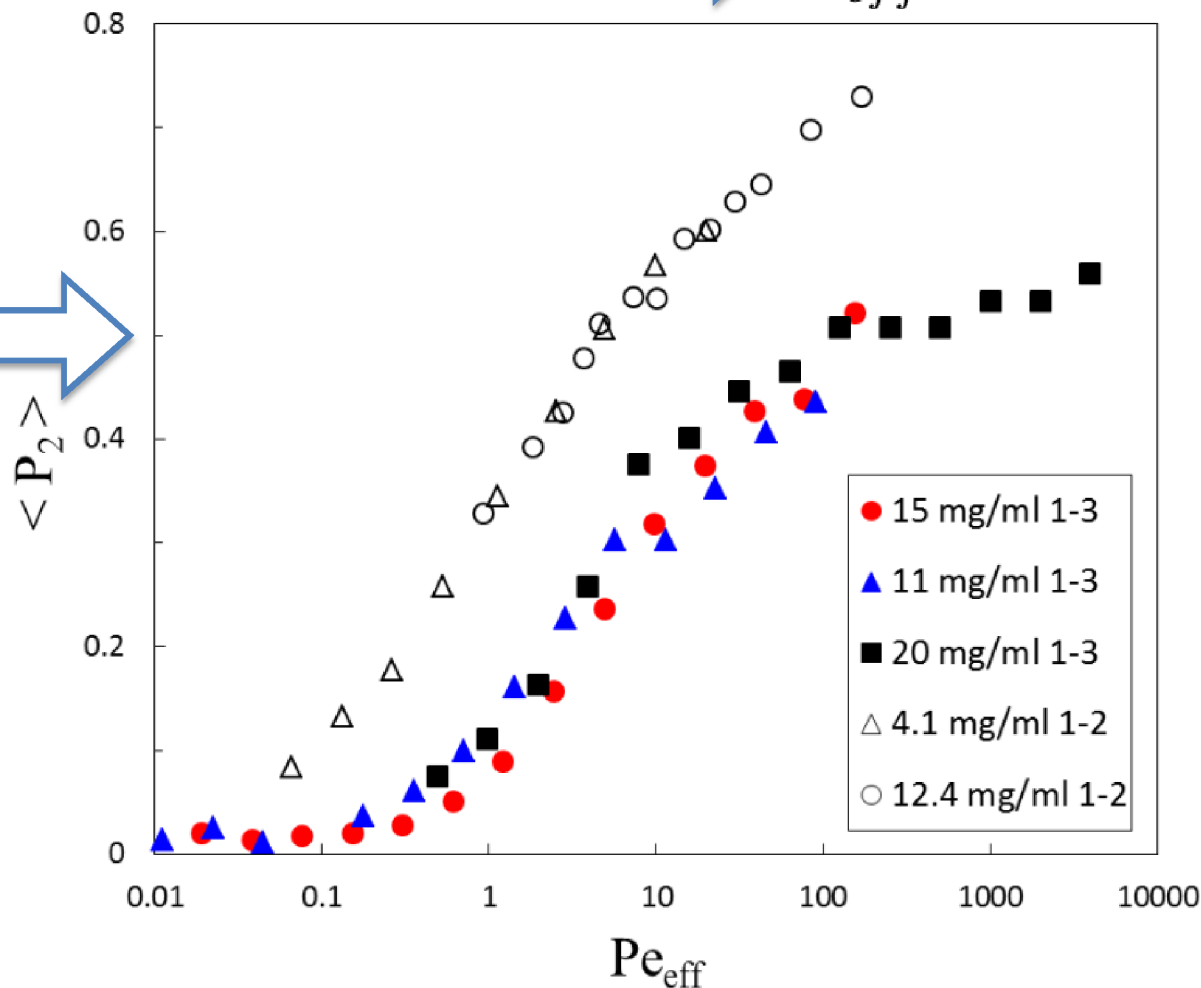
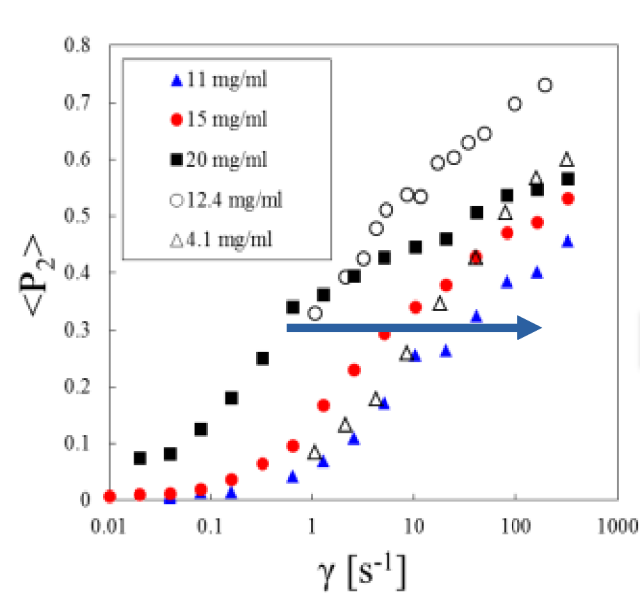


Obtain the I-N spinodal point



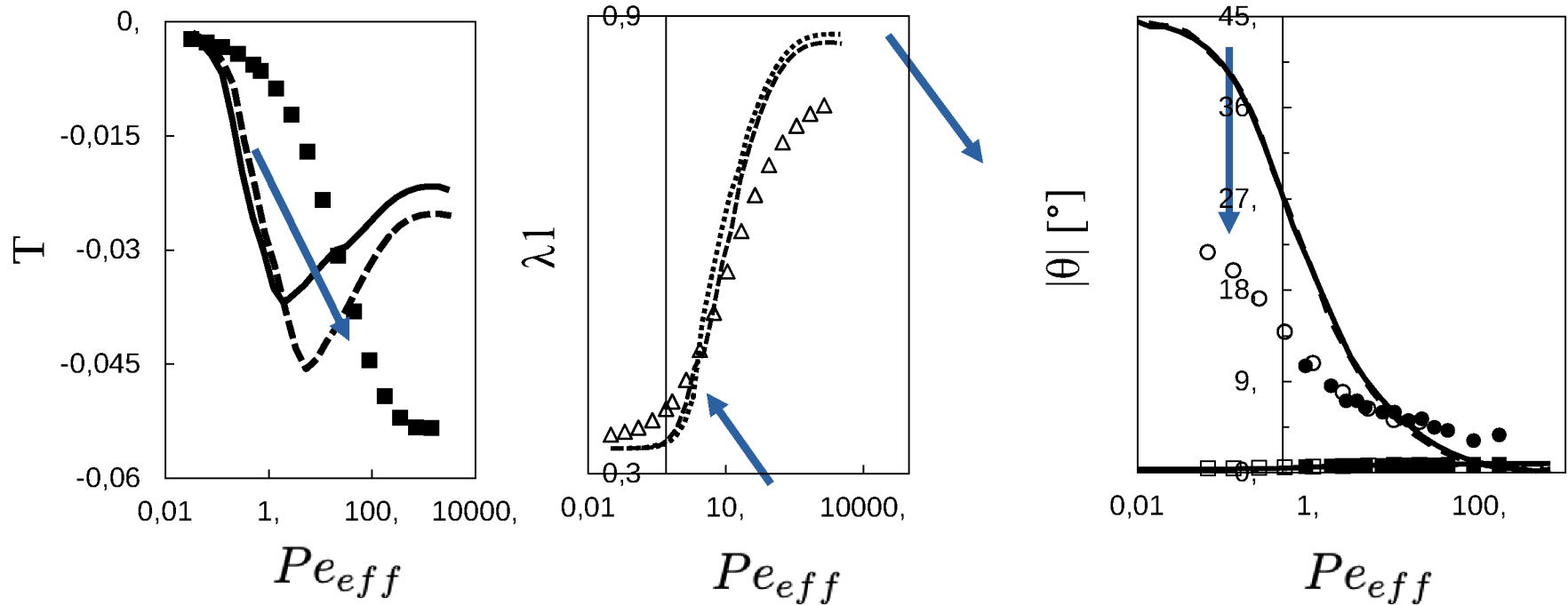
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Scale shear rate: $Pe_{eff} = \dot{\gamma}_0 / D_R^{eff} \Rightarrow \frac{L}{d_{eff}} \varphi_{IN} = 4.2$



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

Scaling other ordering parameters



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

Characterizing parameters

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

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

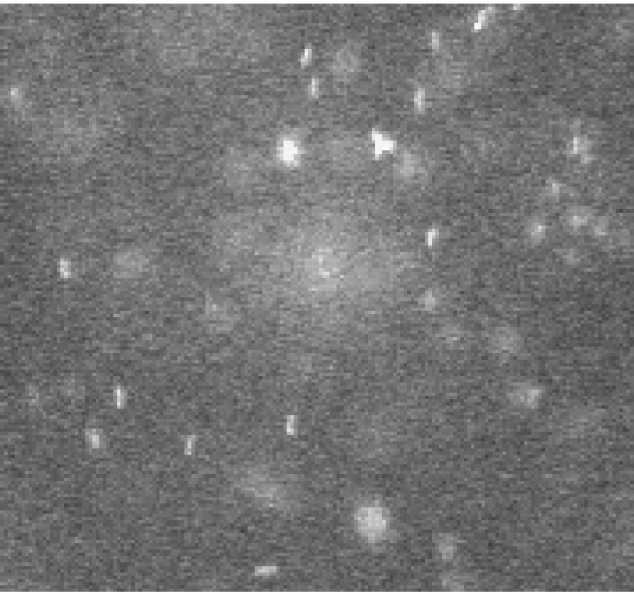
Biaxiality

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

Orientational order parameter

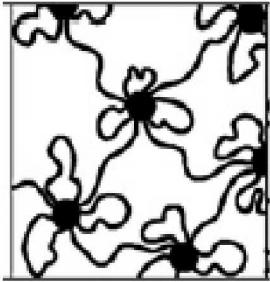
Note: this is the input for calculating stress tensor

Complex flow: Complex fluids



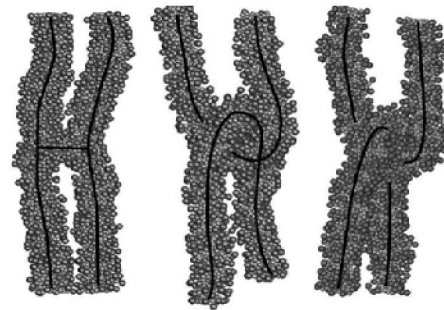
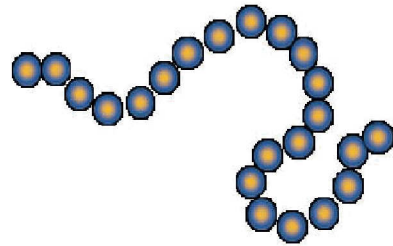
Possible shear thinners

Living gels:

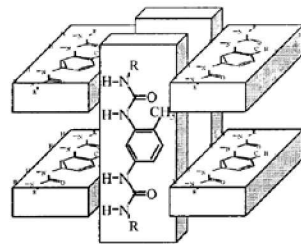


Sprakel et al, *Soft Matter*, **4**, (2008) 1696

Living polymers:

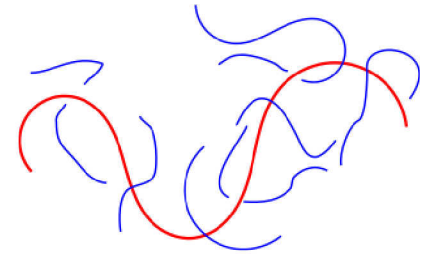


M. P. Lettinga and S. Manneville, *Phys. Rev. Lett.*, **103** 2009

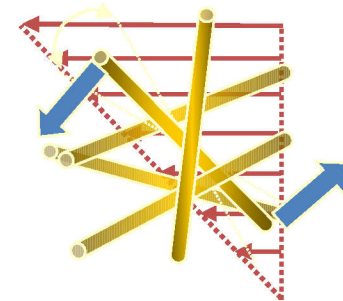


Van der Gucht et al *Phys. Rev. Lett.*, **97**, (2006) 108301

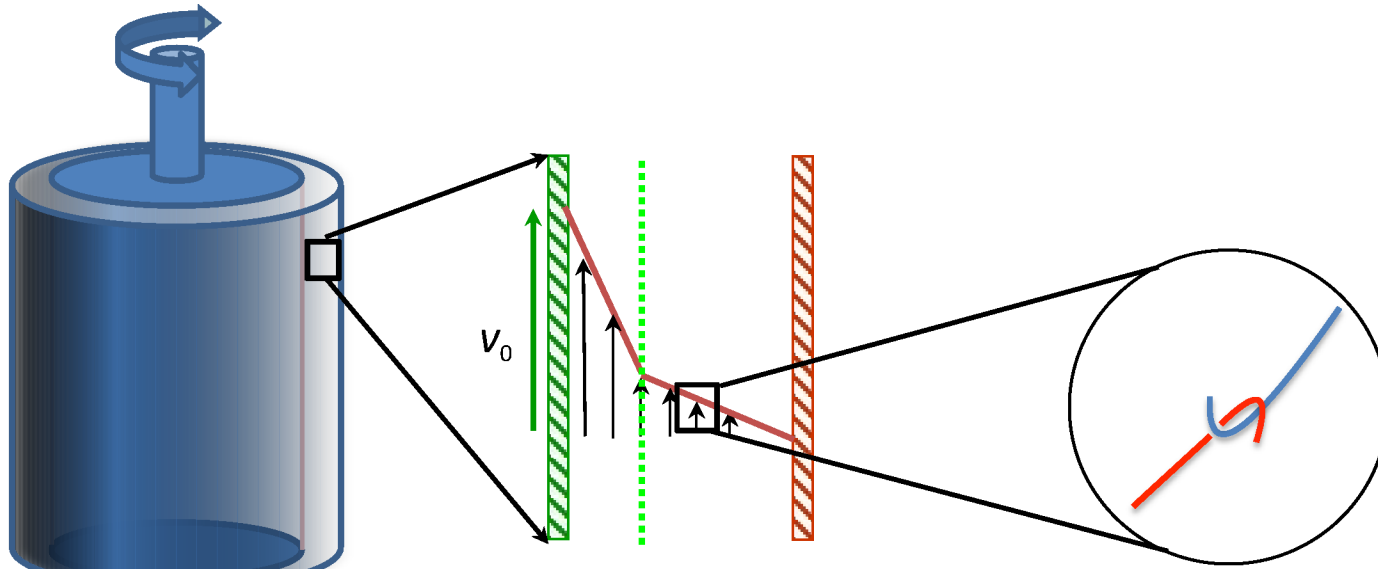
Stiff Polymers:



Rods:



Experimental input needed:

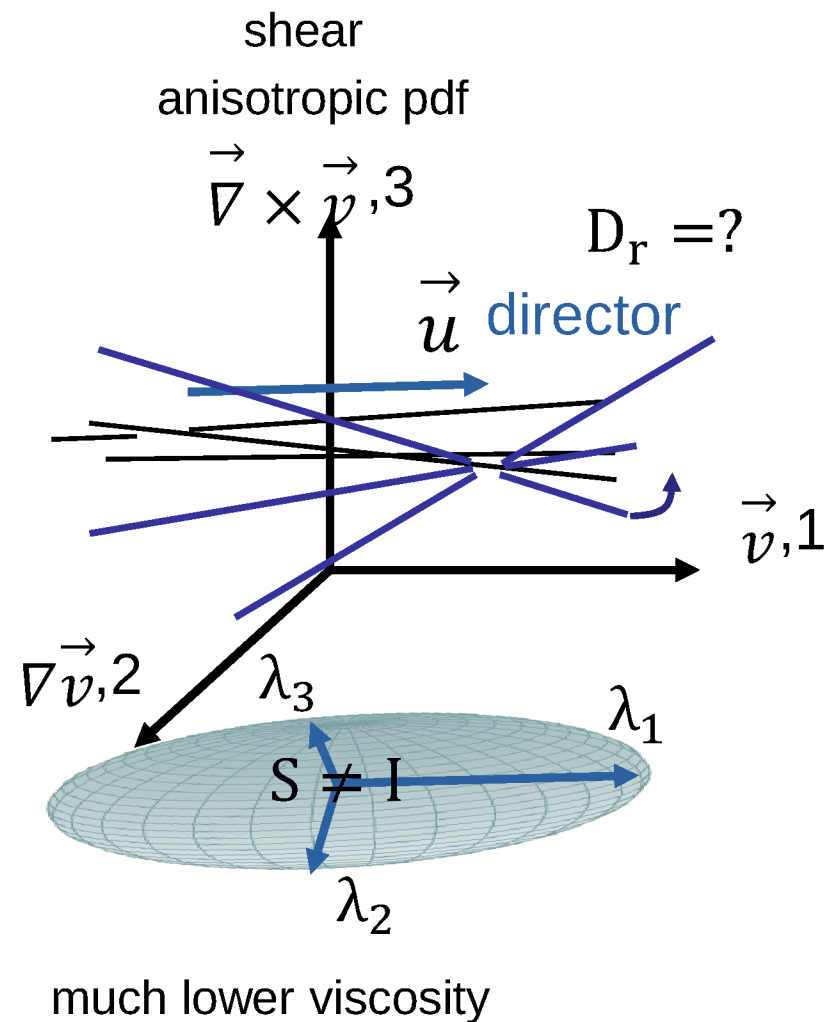
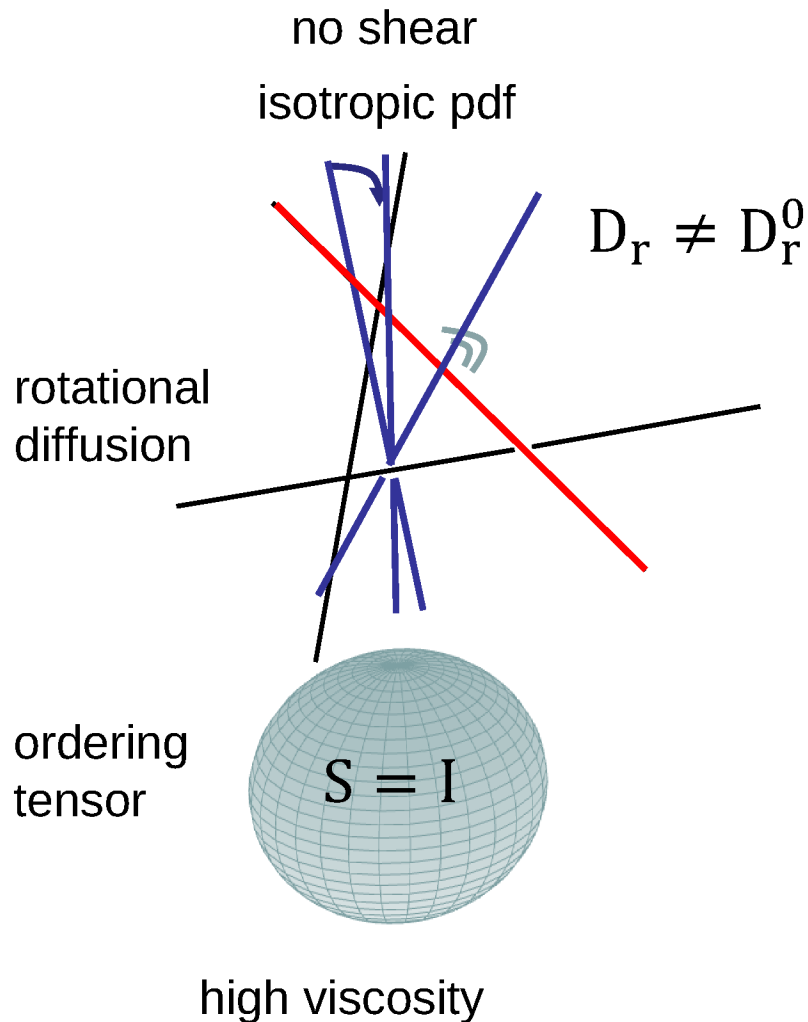


Information needed:

- 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.

$$\frac{d}{dt}\mathbf{S} = -6D_r \left\{ \mathbf{S} - \frac{1}{3}\hat{\mathbf{I}} + \frac{L}{D}\varphi \left(\mathbf{S}^{(4)} : \mathbf{S} - \mathbf{S} \cdot \mathbf{S} \right) \right\} + \dot{\gamma} \left\{ \hat{\mathbf{\Gamma}} \cdot \mathbf{S} + \mathbf{S} \cdot \hat{\mathbf{\Gamma}}^T - 2\mathbf{S}^{(4)} : \hat{\mathbf{E}} \right\}$$
$$\Sigma_D = 2\eta_0\dot{\gamma}\left[\hat{\mathbf{E}} + \frac{(L/D)^2}{3\ln\{L/D\}}\varphi \times \left\{\hat{\mathbf{r}} \cdot \mathbf{S} + \mathbf{S} \cdot \hat{\mathbf{r}}^T - \mathbf{S}^{(4)}:\hat{\mathbf{E}} - \frac{1}{3}\hat{\mathbf{I}}\mathbf{S}:\hat{\mathbf{E}} - \frac{1}{\dot{\gamma}}\frac{d\mathbf{S}}{dt}\right\}\right]$$
$$\Rightarrow \delta S(t) = \exp(-6D_R^{eff}t)\delta S(t=0)$$

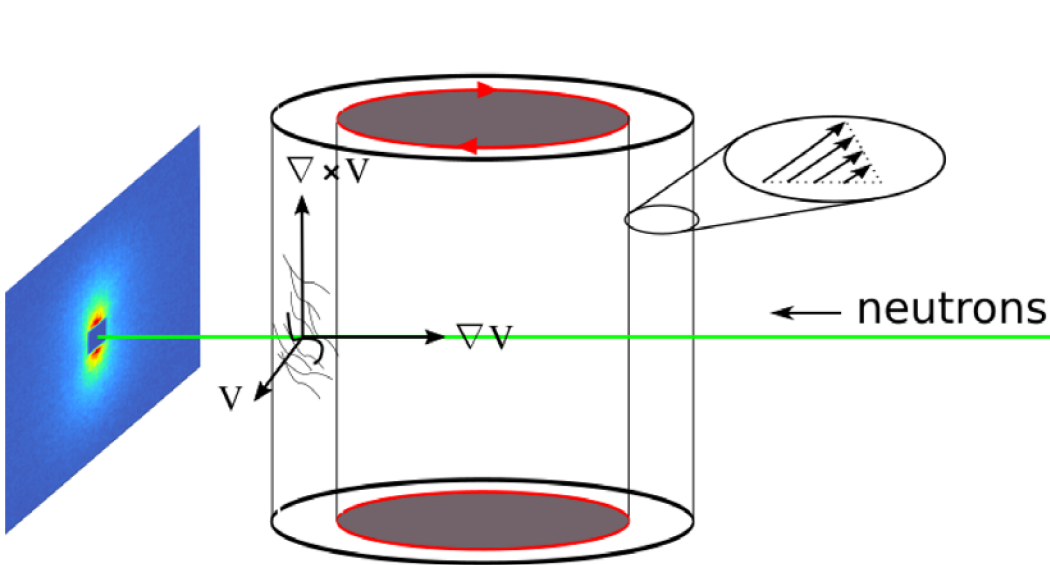
Brownian motion competes with shear flow:



t-SANS to probe segment ordering dynamics



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

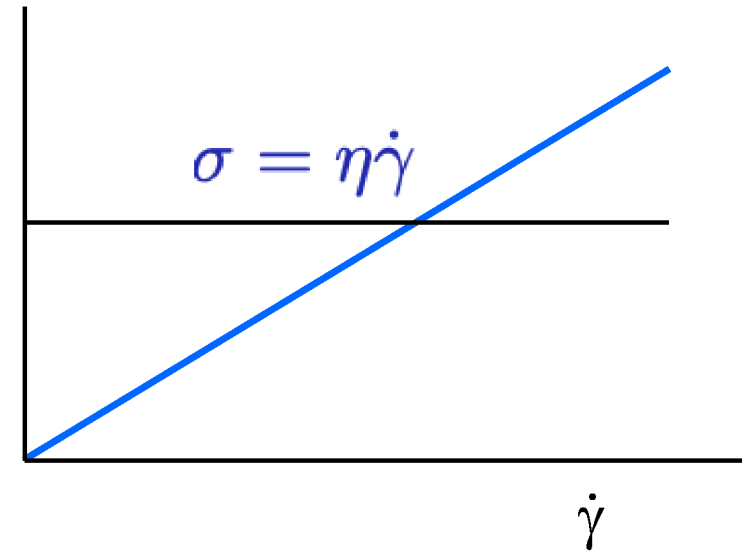
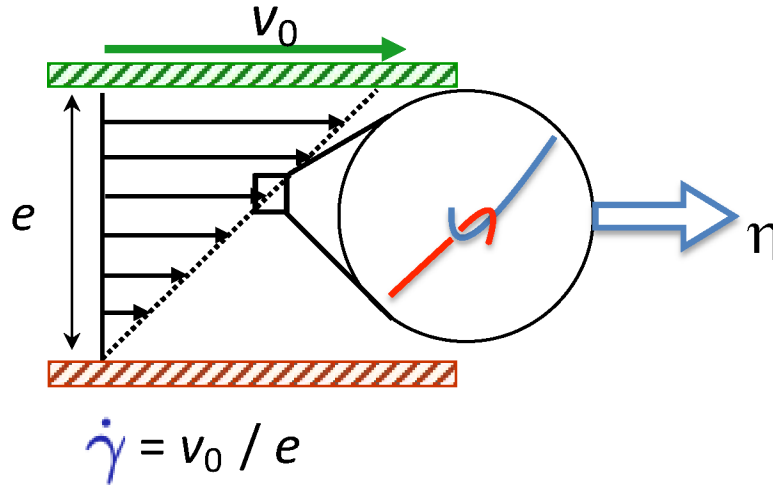
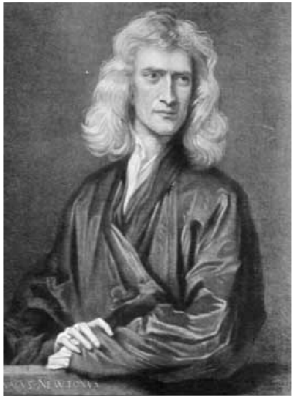
$$I(t_i, \vec{q}) = \sum_n^{N_{\text{cycle}}} I(t_i + n\Delta t, \vec{q})$$

← Orientational distribution function

$f(\theta)$

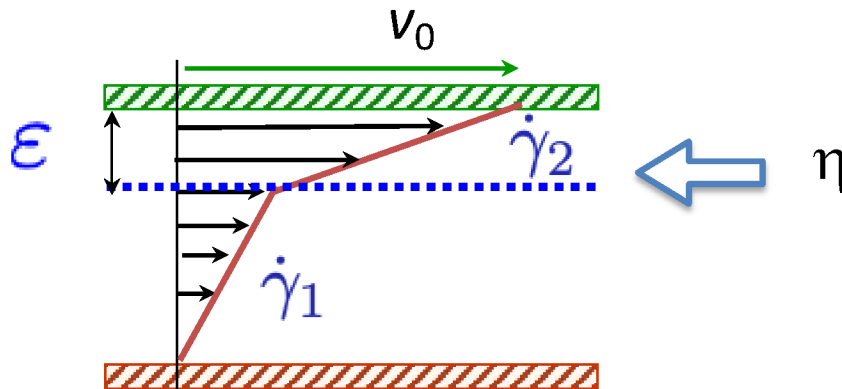
θ [rad.]

Ideal Newtonian fluids



Non-linear Newton: shear thinning fluids

Flow instabilities: shear banding



strong shear-thinning

