SDSU

Rheological study of a simulated polymeric gel: shear banding

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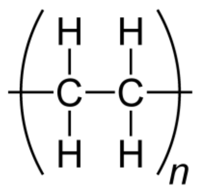
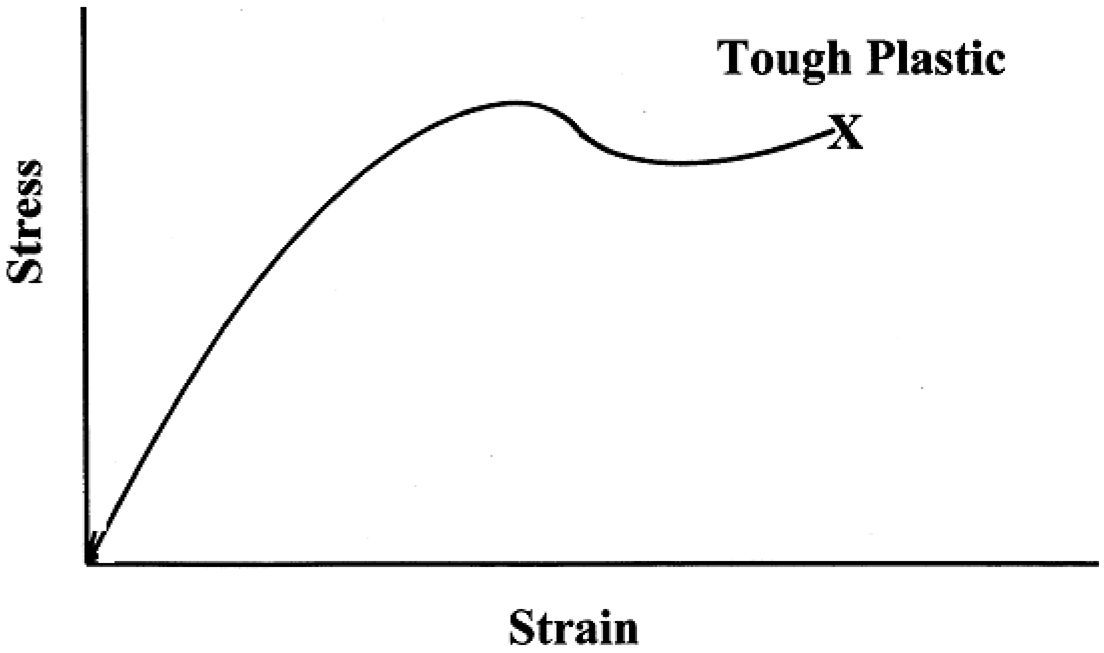
Polymers

- Long-chain molecules of high molecular weight

polyethylene





[Introduction to Physical Polymer Science, L. Sperling (2006)]

Motivation of research

Polymer science

Polymer chemistry (synthesis)

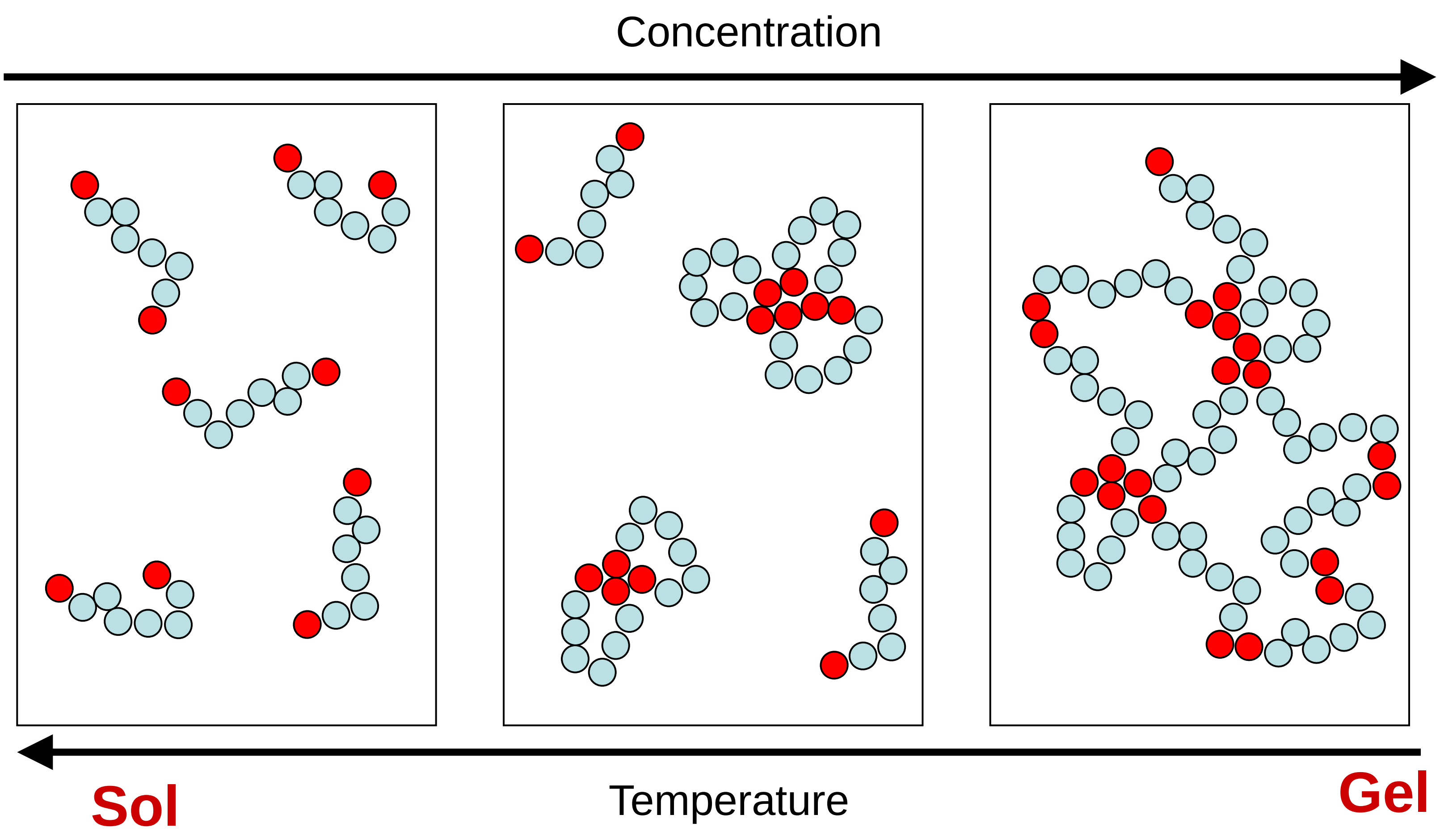
Polymer physics

Polymer rheology

Introduction: polymeric gels

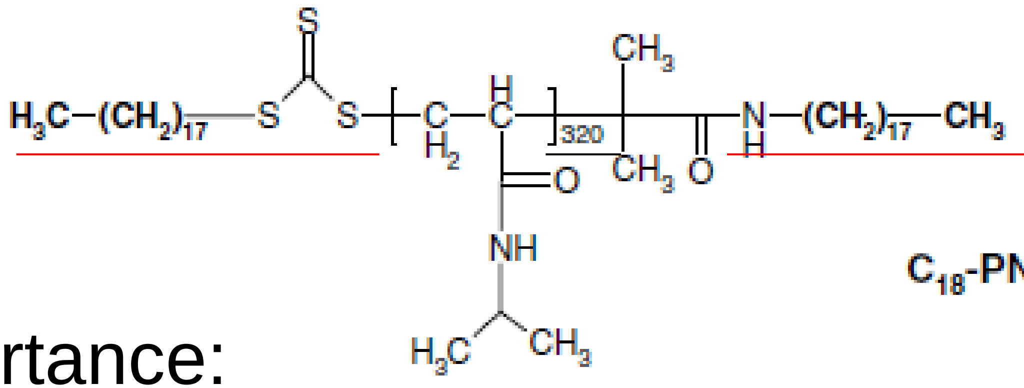
Polymeric gels

Reversible junctions between endgroups
(telechelic polymers)



Polymeric gels

- Examples
  – PEO (polyethylene glycol) chains terminated by hydrophobic moieties
  – Poly-(N-isopropylacrylamide) (PNIPAM)



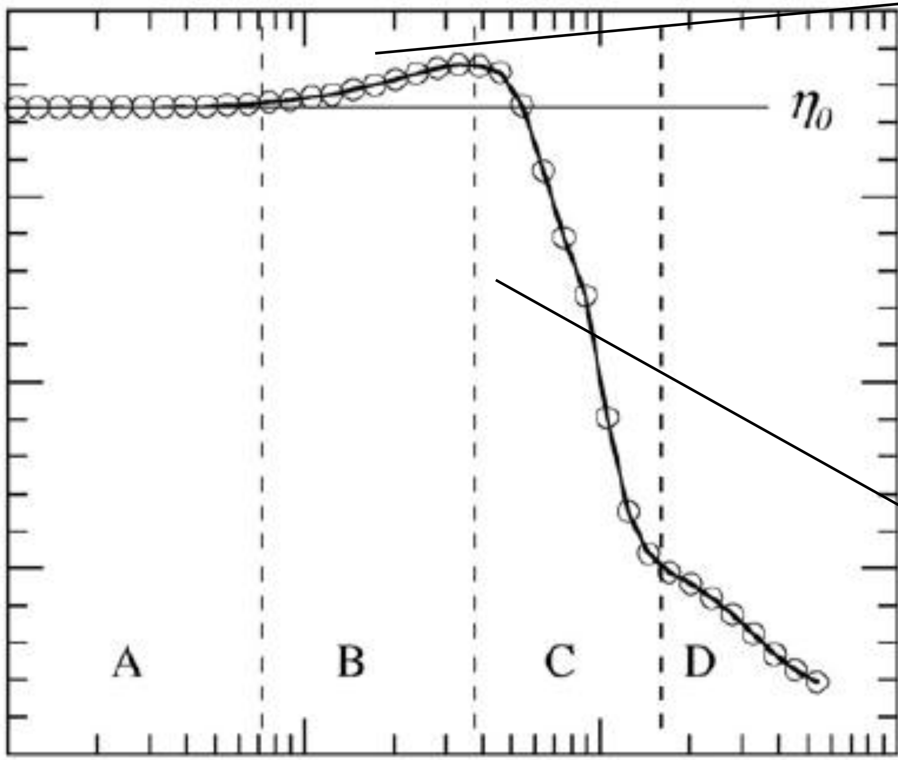
C_{18}-PNIPAM-C_{18}

- Importance:
  – laxatives, skin creams, tooth paste, paintball fill, preservative for objects salvaged from underwater, eye drops, print heads, spandex, foam cushions,…
  – cytoskeleton

Visco-elastic properties

$$\eta\,\dot{\gamma} = \text{stress}$$

Viscosity η



Shear rate $\dot{\gamma}$

[J.Sprakel et *al*., Soft Matter (2009)]

Hybrid MD/MC simulation of a polymeric gel

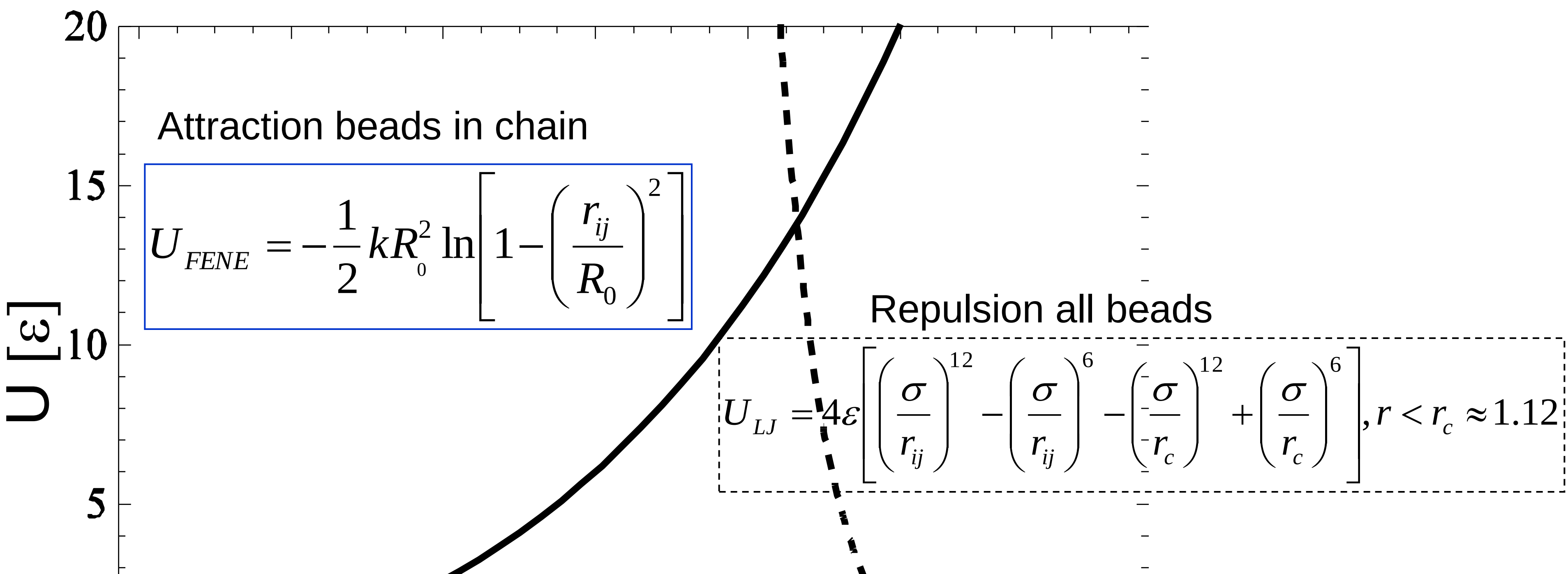
Molecular dynamics simulation

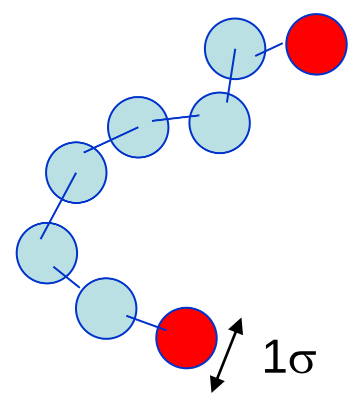
ITERATE

- Give initial positions, choose short time Δt
- Get forces $F = -\dfrac{dU}{d\vec{r}}$ and acceleration *a=F/m*
- Move atoms
- Move time t = t + Δt

Bead-spring model

[K. Kremer and G. S. Krest. J. Chem. Phys 1990]



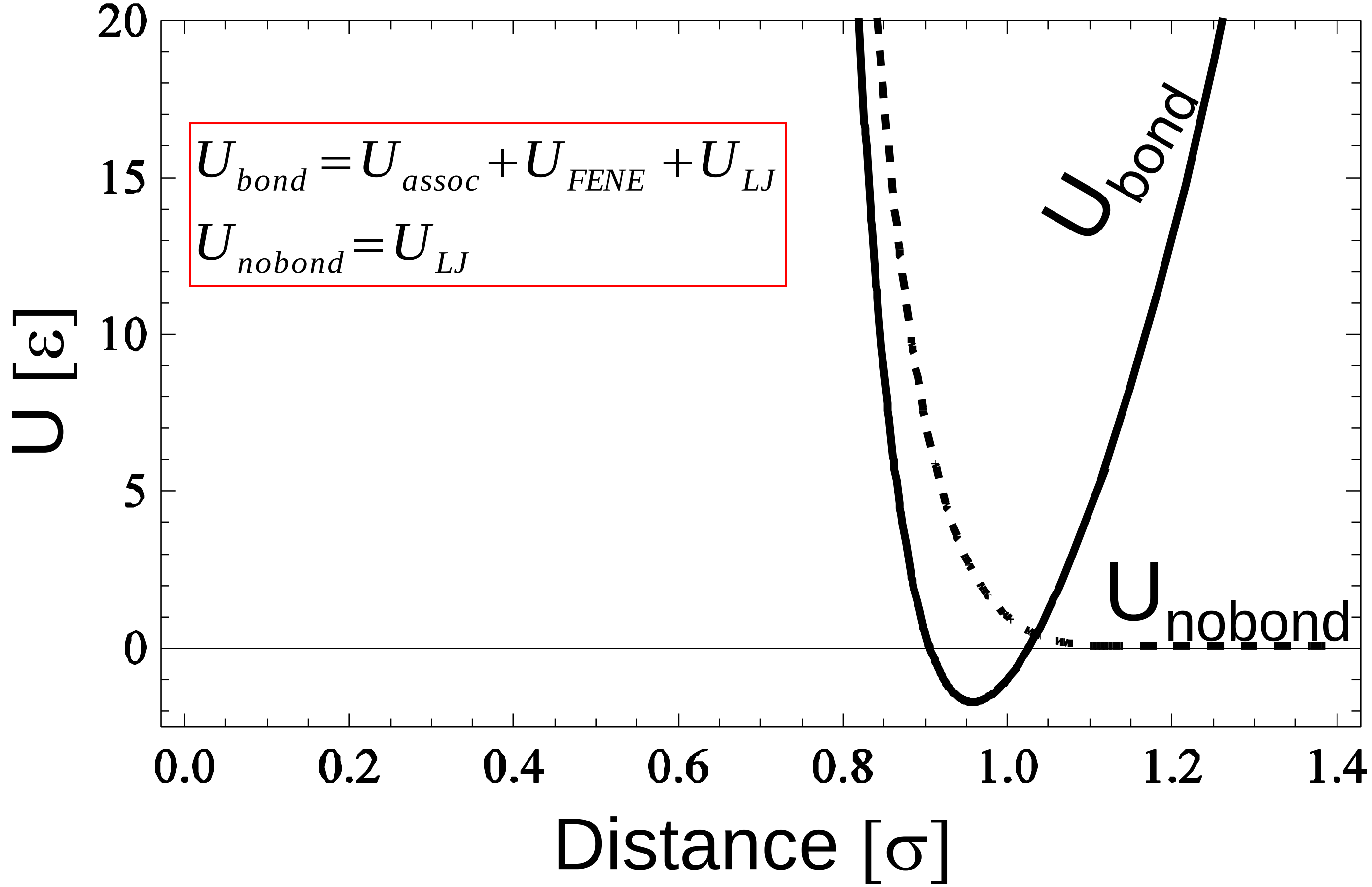


•Temperature control through coupling with heat bath

Associating polymer

[A. Baljon et al., J. Chem. Phys., 044907 2007]

- Junctions between end groups : FENE + Association energy
- Dynamics …

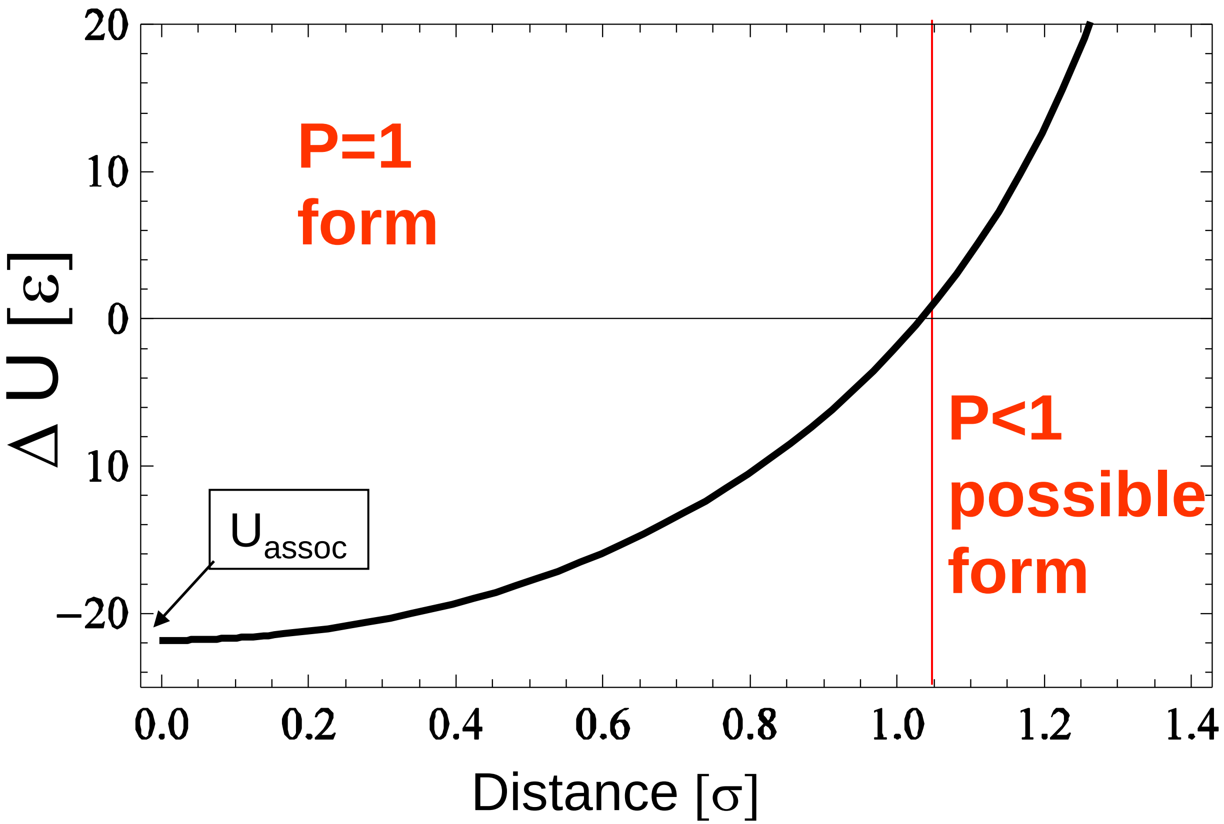


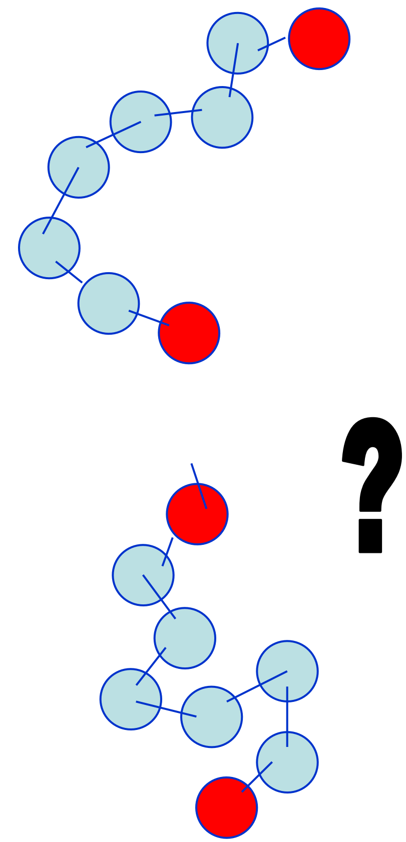
Dynamics of associating polymer (I)

- Monte Carlo: attempt to form junction

$$P \sim \exp\left(\frac{-\Delta U}{k_b T}\right)$$

$$\Delta U = U_{possiblenew} - U_{old} = U_{assoc} + U_{FENE}$$



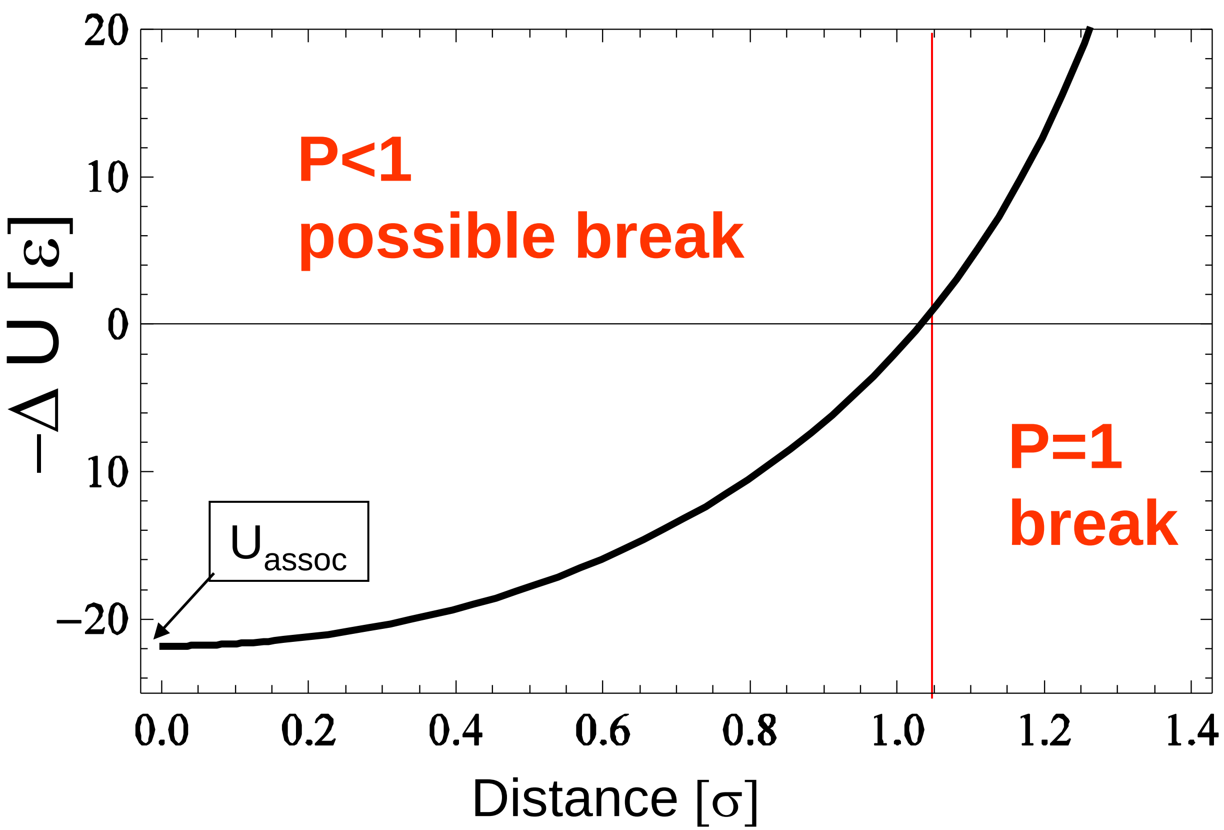


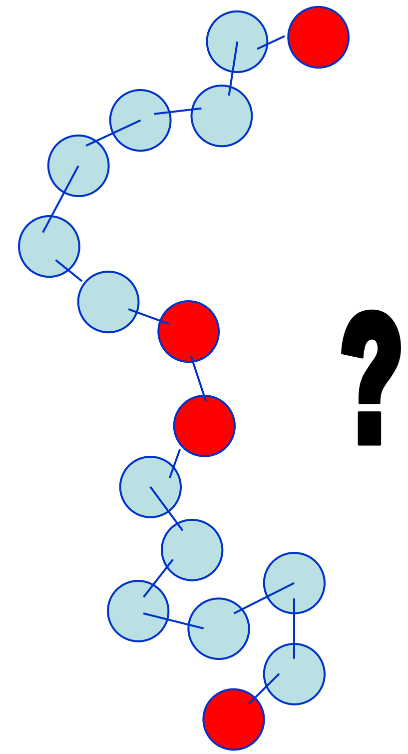
Dynamics of associating polymer (II)

- Monte Carlo: attempt to break junction

$$P \sim \exp\left(\frac{-\Delta U}{k_b T}\right)$$

$$\Delta U = U_{possible\,new} - U_{old} = -\left(U_{assoc} + U_{FENE}\right)$$

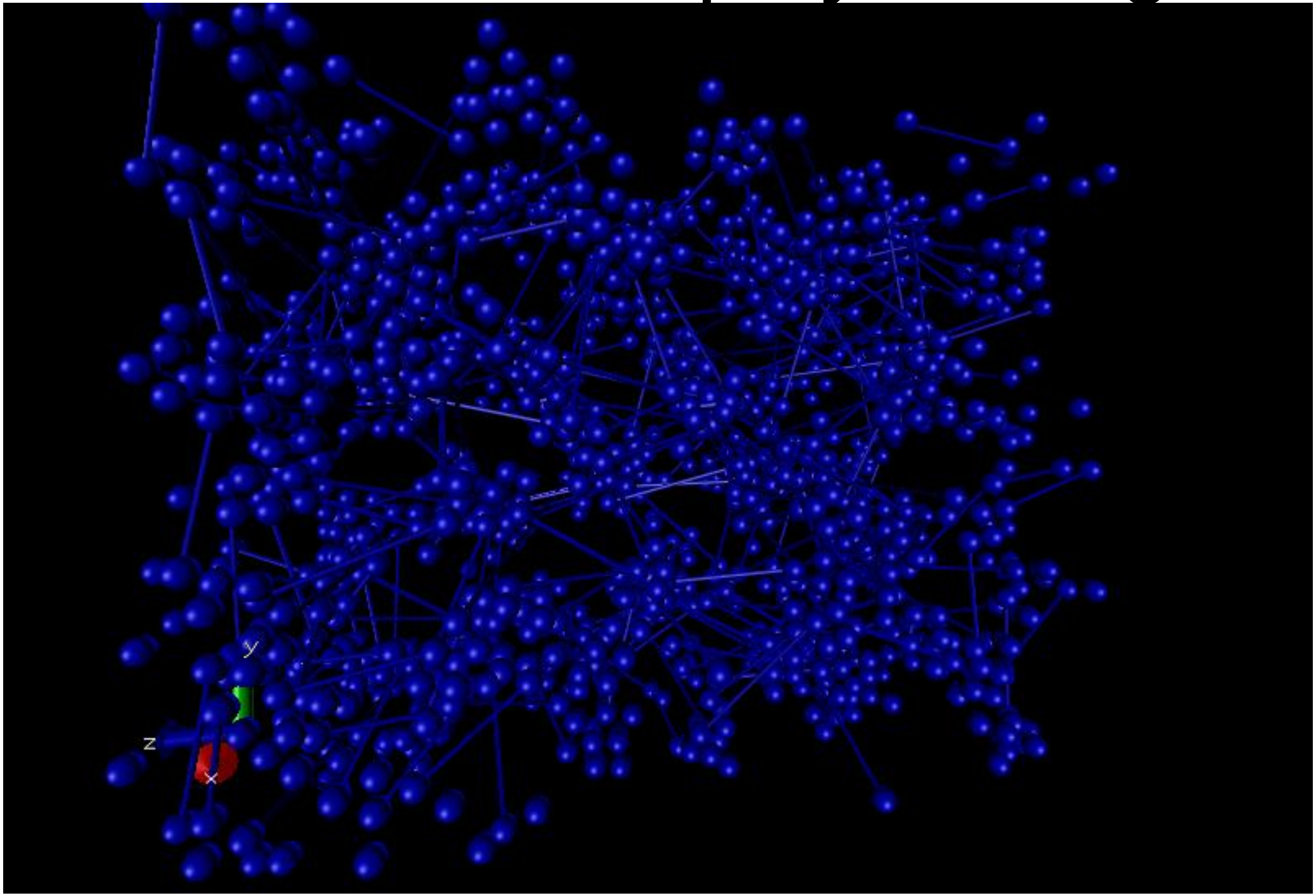




Simulation details

- 1000 polymeric chains, 8 beads/chain
- Units: σ (length), ε (energy&temperature), m (mass), $\tau=\sigma(m/\varepsilon)^{1/2}$ (time);
- Box size: (23.5 x 20.5 x 27.4) σ^3 with periodic boundary conditions

Simulated polymeric gel

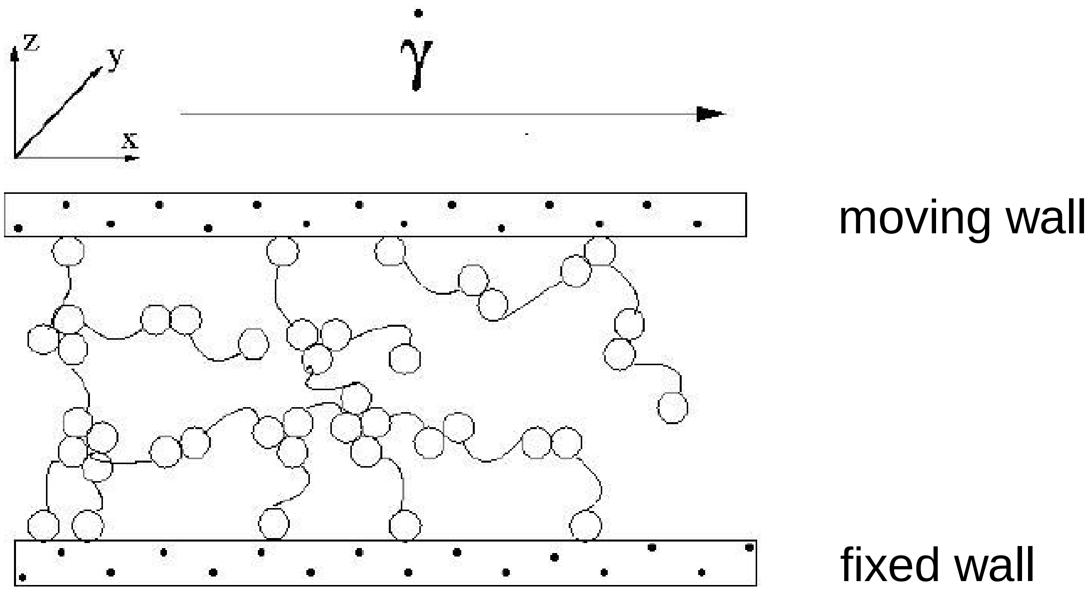


T=1.0
only
endgroups
shown

Shearing the system

Some chains grafted to wall;

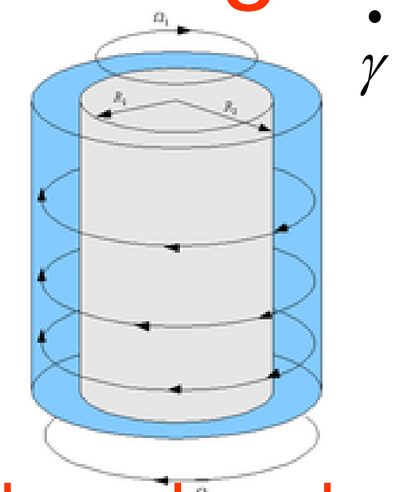
move wall with constant shear rate



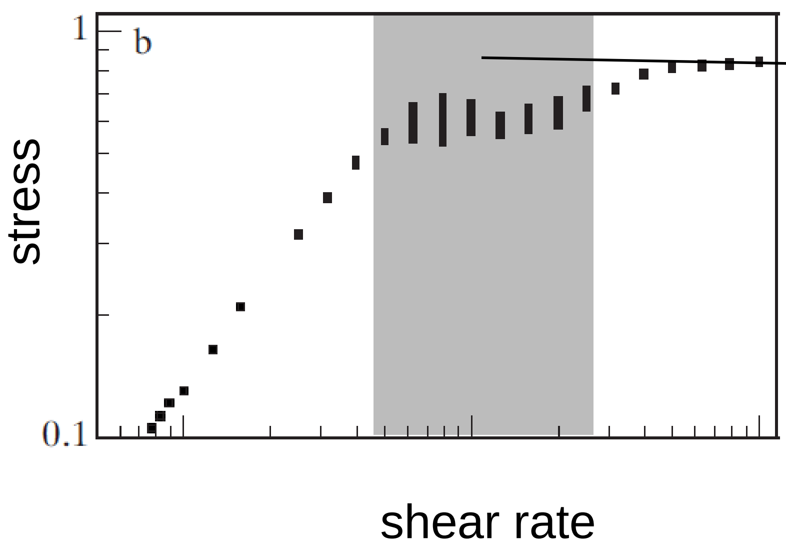
Shear banding in polymeric gel

Shear-Banding in Associating Polymers

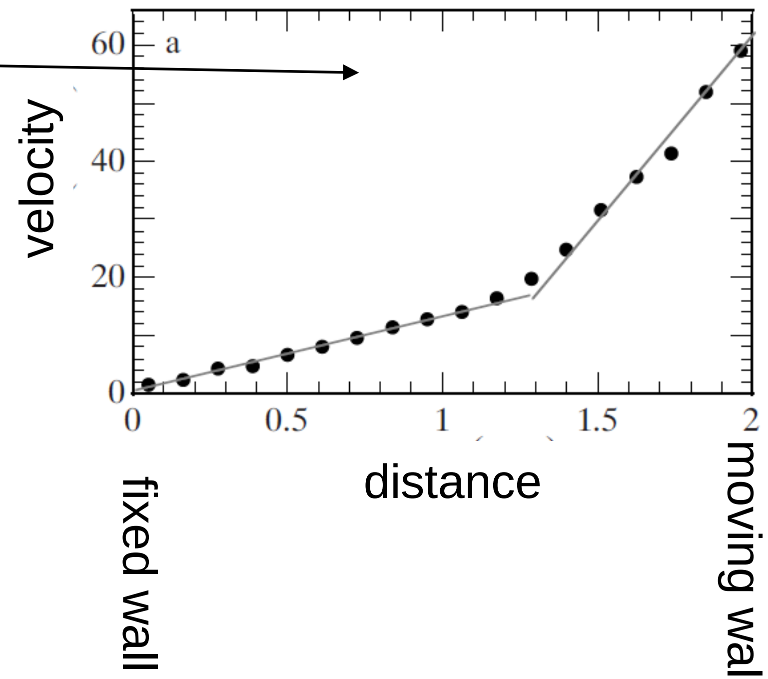
- PEO in Taylor-Couette system



Plateau in stress-shear curve



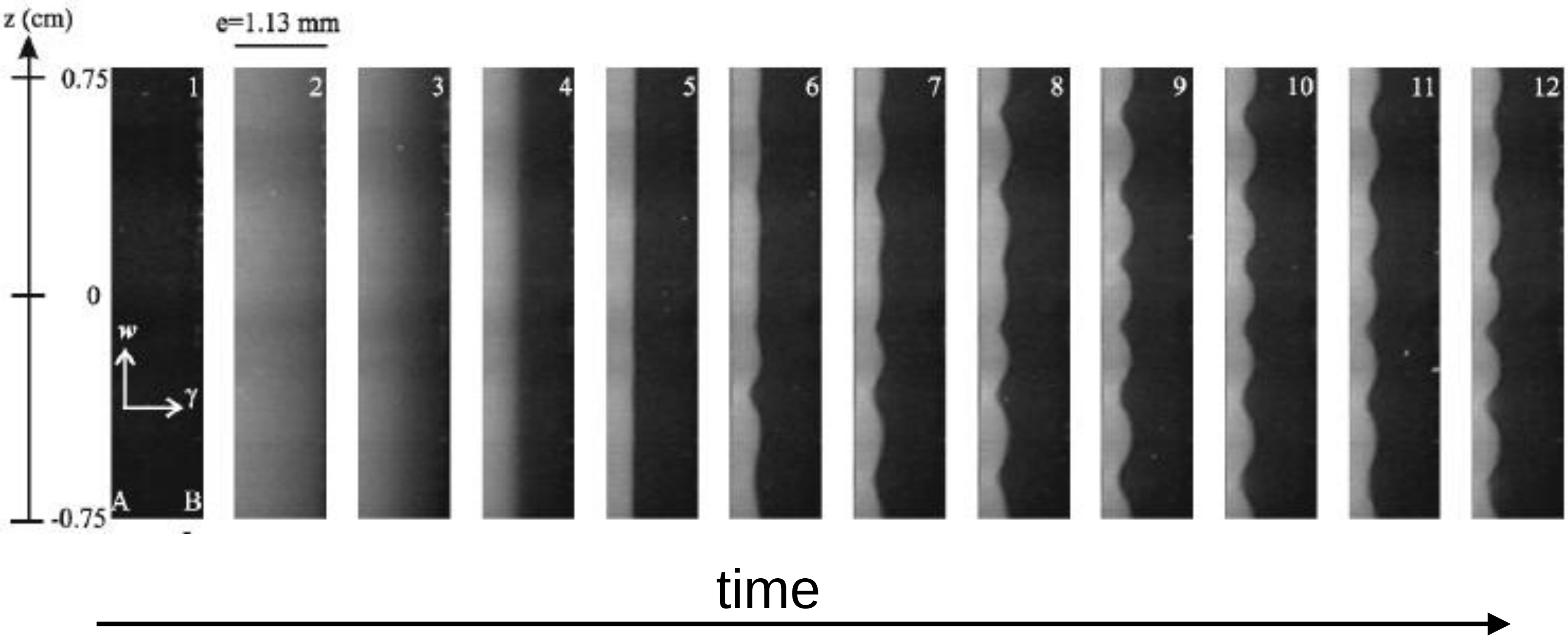
two shear bands



[J.Sprakel et *al*.,
Phys Rev. E 79, 056306 (2009)]

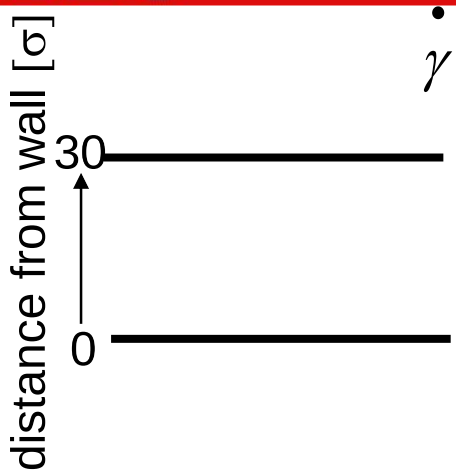
Shear-banding in viscoelastic fluids

- Interface instabilities in worm-like micelles

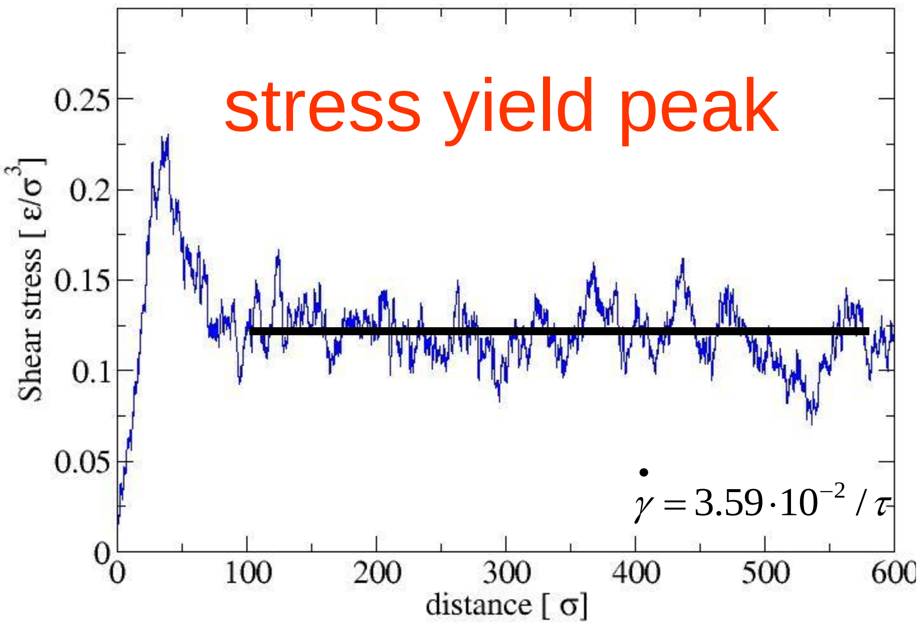


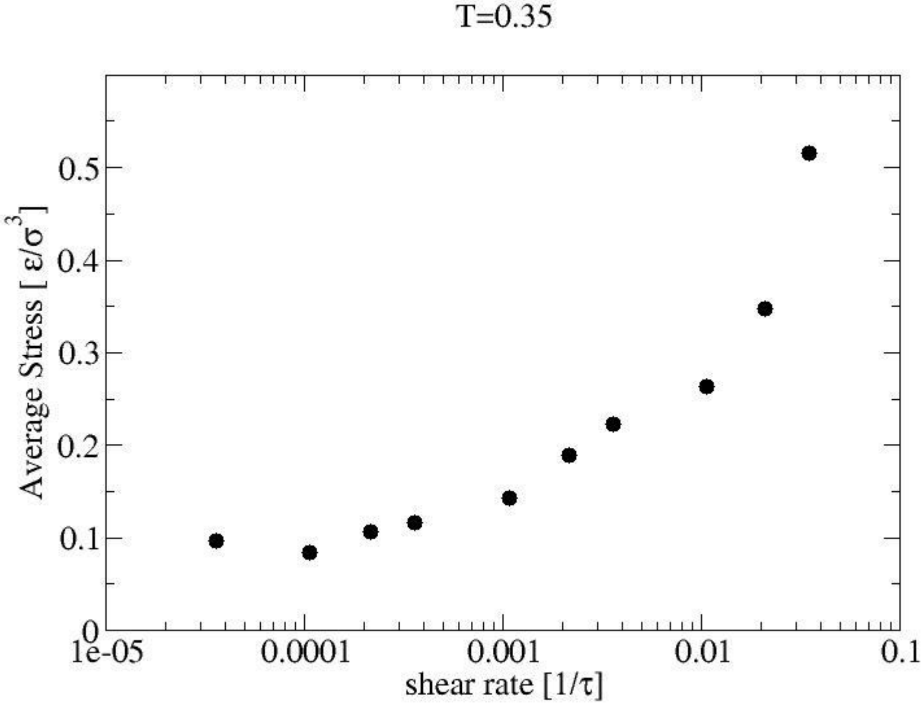
[Lerouge et *al*.,PRL 96,088301 (2006).]

Stress under constant shear

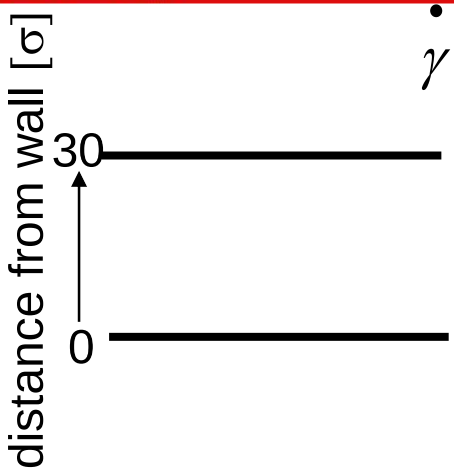


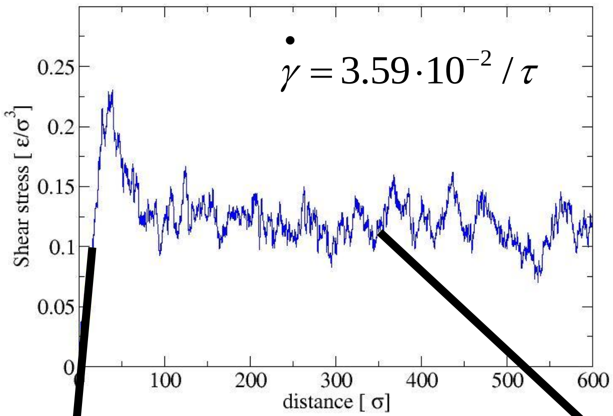
All results T=0.35 ε (< micelle transition T=0.5 ε)





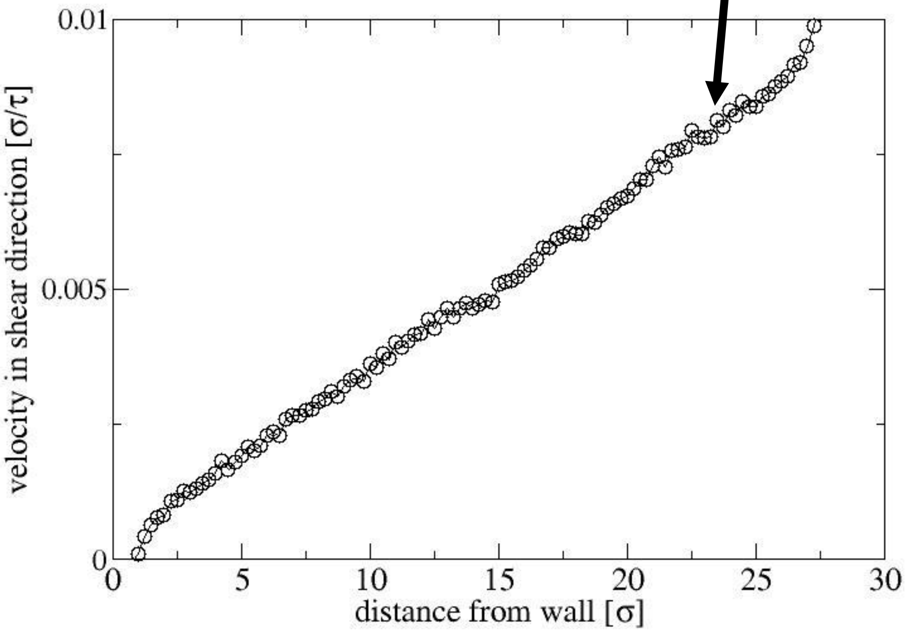
Velocity profiles

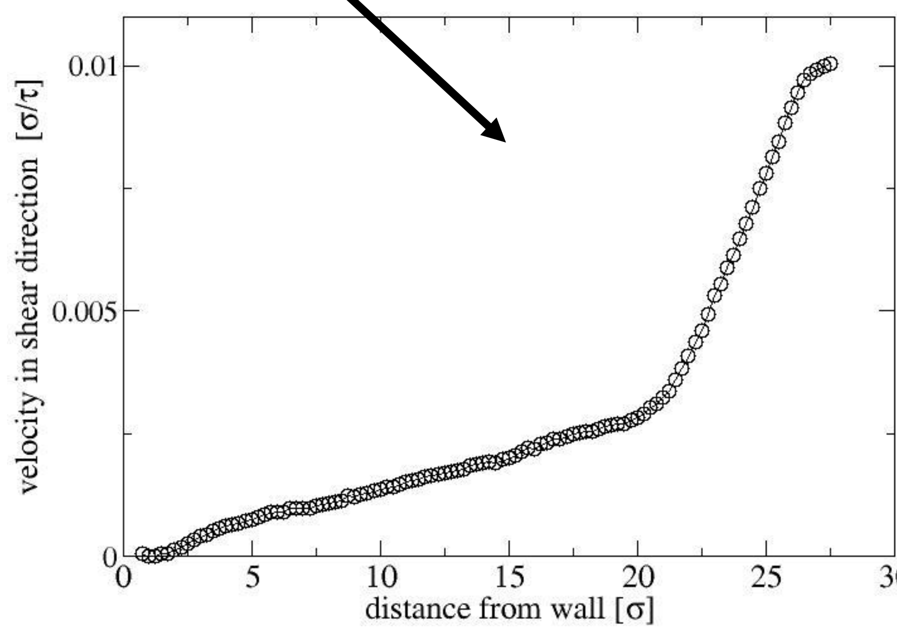




Before yield peak: homogeneous

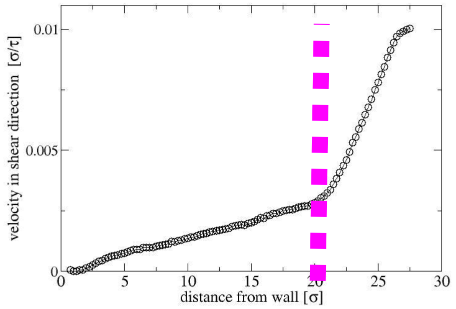
After yield peak: 2 shear bands

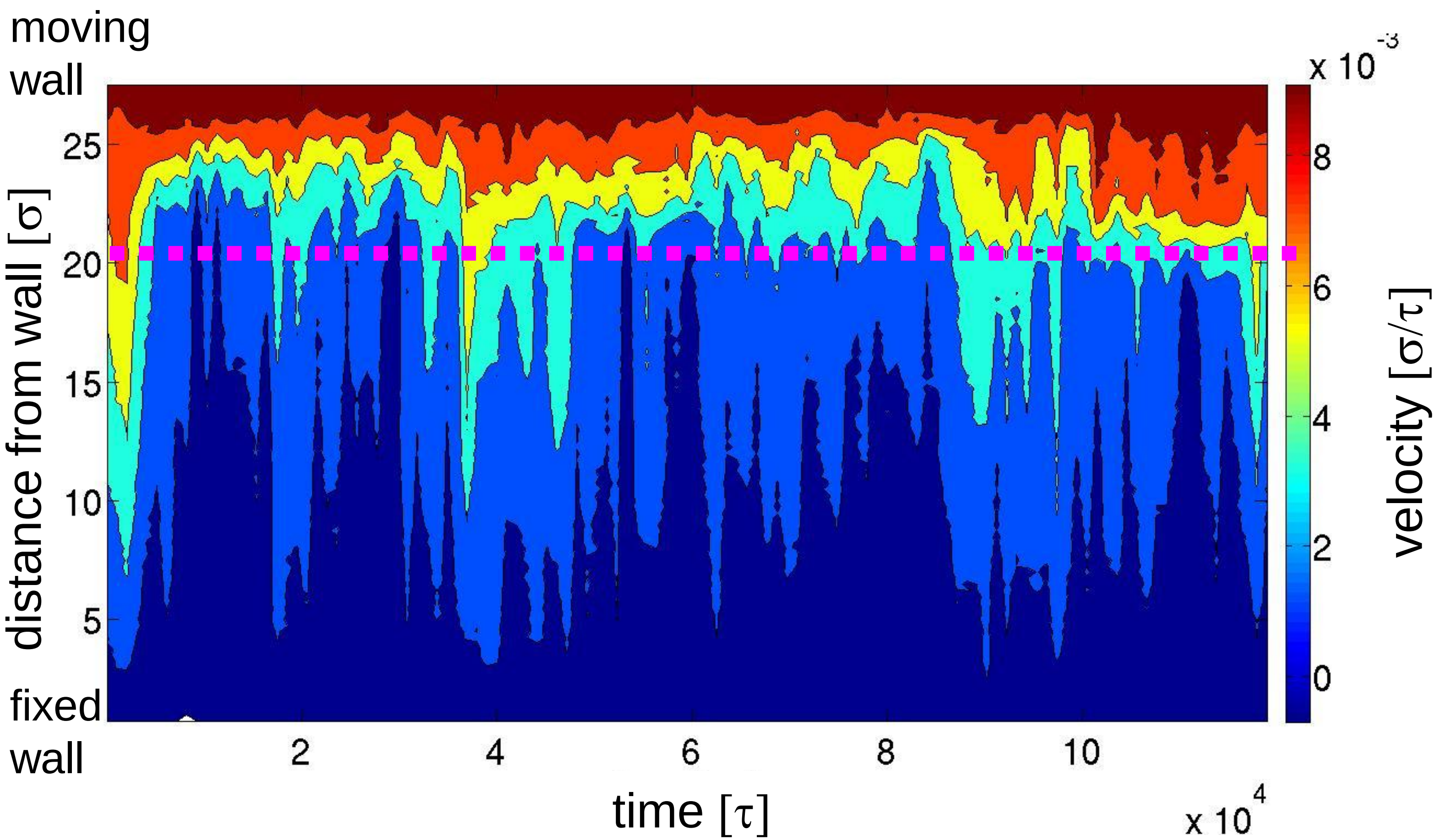




Velocity profile over time

- Fluctuations of interface

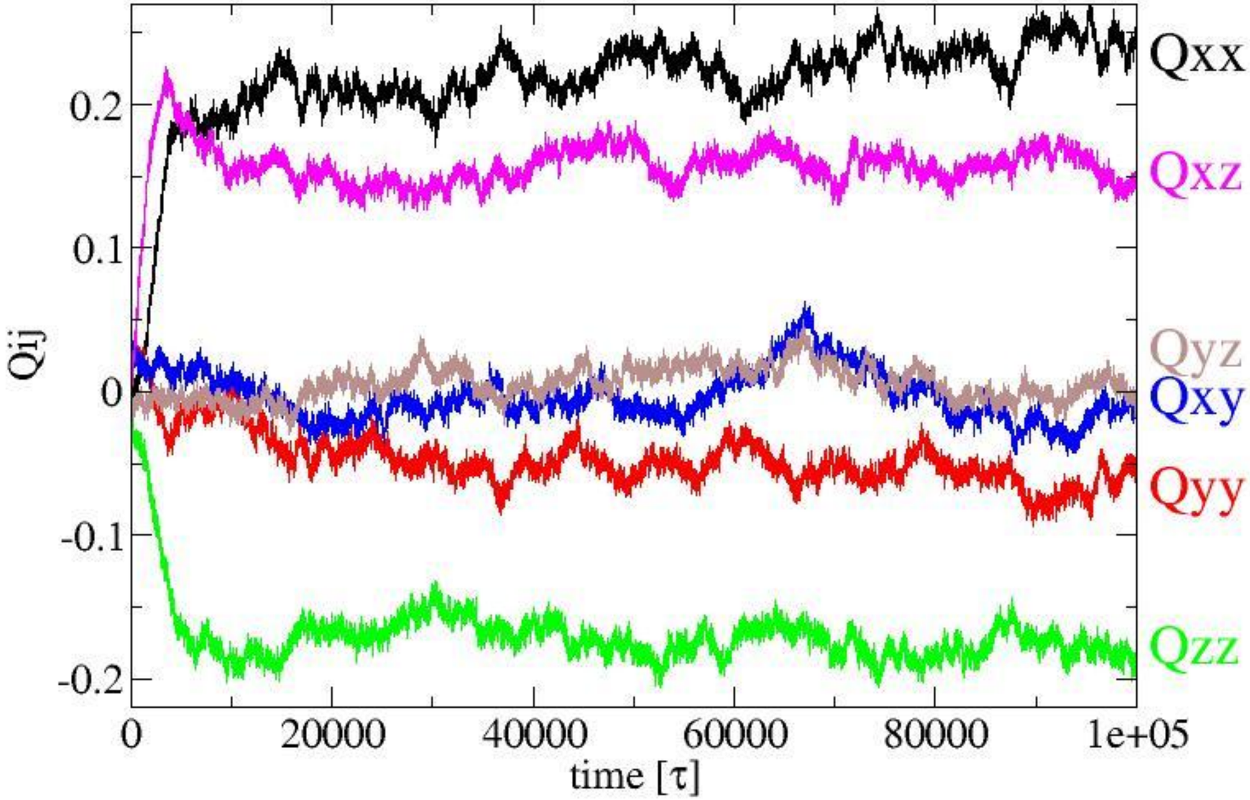


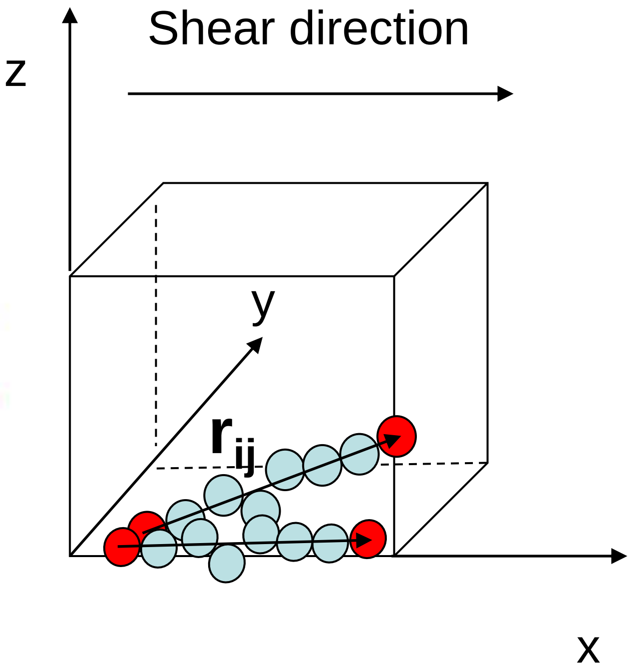


Chain Orientation

$$Qij = \left\langle \frac{3}{2}\left(\frac{r_i r_j}{r^2} - \frac{1}{3}\delta_{ij} \right) \right\rangle$$

$Q_{xx}=1$ $Q_{zz}=-0.5$

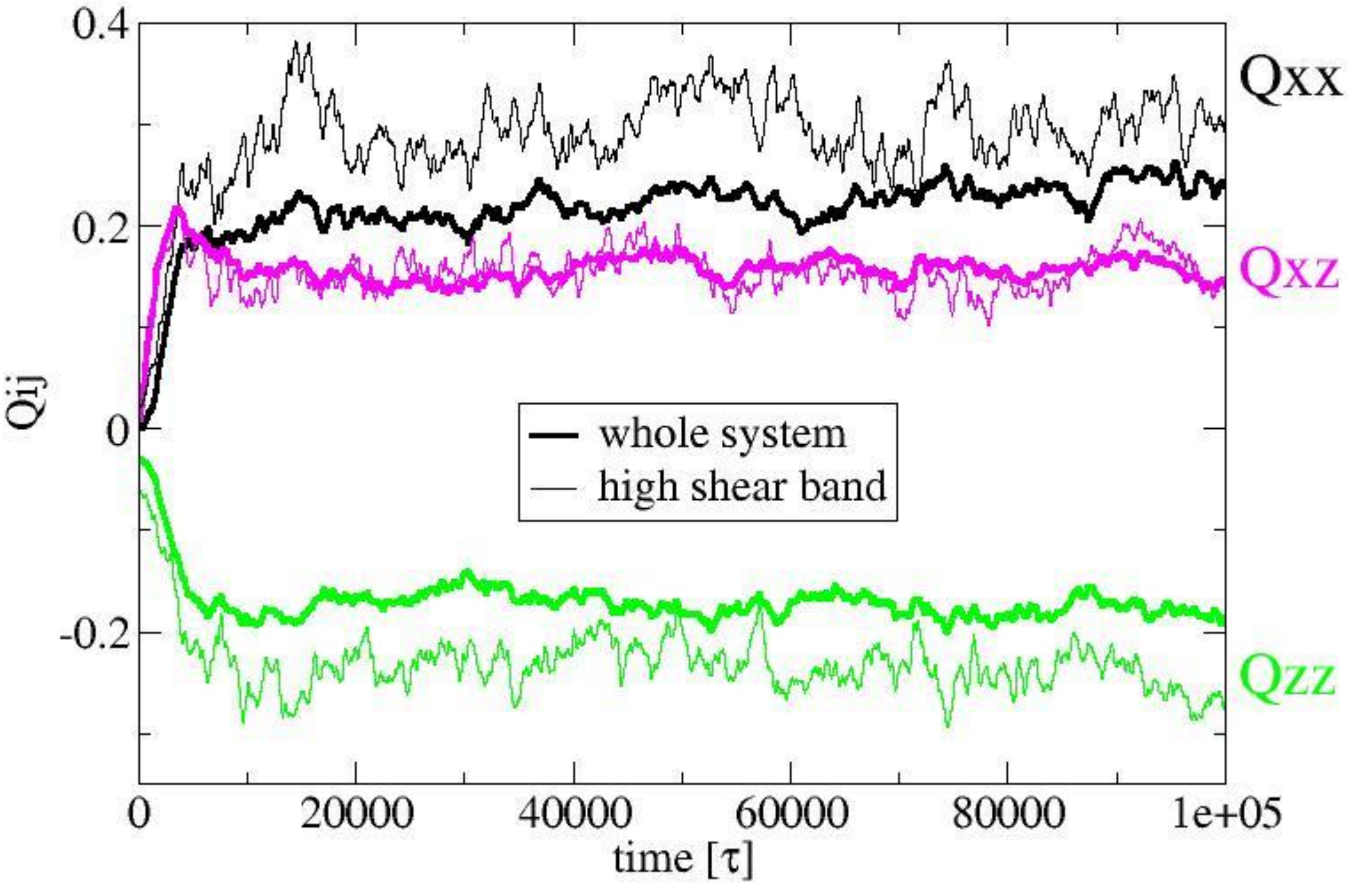




Chain orientation

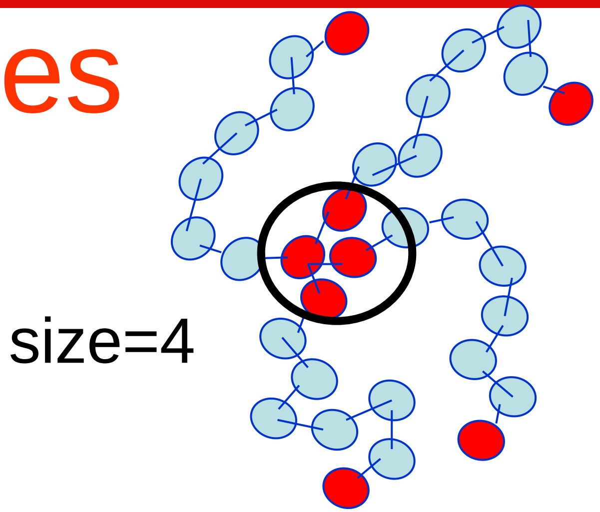
$$Qij = \left\langle \frac{3}{2}\left(\frac{r_i r_j}{r^2} - \frac{1}{3}\delta_{ij}\right)\right\rangle$$

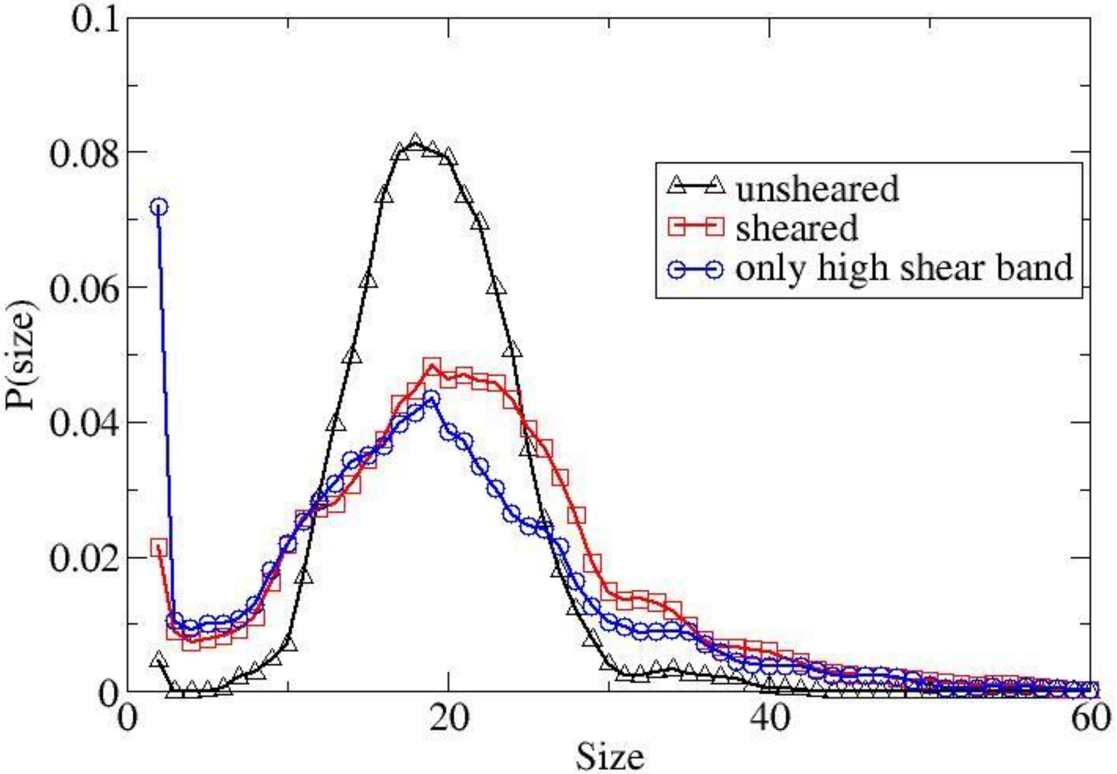
- Effects more outspoken in high shear band



Aggregate sizes

- Sheared: more smaller and larger aggregates
- High shear band: largest aggregates as likely





Conclusions

- MD/MC simulation reproduces experiments
  - Plateau in shear-stress curve
  - Shear banding observed
  - Temporal fluctuations in velocity profile
- Microscopic differences between sheared/ unsheared system
  - Chain orientation
  - Aggregate size distribution
- Small differences between shear bands
- Current work: local stresses, positional order, secondary flow, network structure

Equation of Motion

K. Kremer and G. S. Grest. Dynamics of entangled linear polymer melts: A molecular-dynamics simulation. *Journal of Chemical Physics*, 92:5057, 1990.

$$\ddot{r}_i = \nabla \sum_{j \neq i} U_{ij} - \Gamma r_i + W_i(t)$$

$U_{ij} = U_{ij}^{LJ} + U_{ij}^{FENE}$ •Interaction energy

Γ •Friction constant;

•Heat bath coupling – all complicated interactions

W •Gaussian white noise

•$\langle W_i^2 \rangle = 6\, k_B\, T\, \Gamma$ (fluctuation dissipation theorem)

Predictor-corrector algorithm

1)Predictor: Taylor: estimate at t+δt

$$\vec{r}^{\,p}(t+\delta t) = \vec{r}(t) + \delta t \vec{v}(t) + \frac{1}{2}\delta t^2 \vec{a}(t) + \frac{1}{6}\delta t^3 \vec{b}(t) + \ldots$$

$$\vec{v}^{\,p}(t+\delta t) = \vec{v}(t) + \delta t \vec{a}(t) + \frac{1}{2}\delta t^2 \vec{b}(t) + \ldots$$

$$\vec{a}^{\,p}(t+\delta t) = \vec{a}(t) + \delta t \vec{b}(t) + \ldots$$

$$\vec{b}^{\,p}(t+\delta t) = \vec{b}(t) + \ldots$$

2) From $\vec{r}^{\,p}$ calculate forces and acceleration $\vec{a}^{\,c}(t+\delta t)$ at t+δt

3) Estimate size of error in prediction step:

$$\Delta\vec{a}(t+\delta t) = \vec{a}^{\,c}(t+\delta t) - \vec{a}^{\,p}(t+\delta t)$$

4) Corrector step:

$$\vec{r}^{\,c}(t+\delta t) = \vec{r}^{\,p}(t+\delta t) + c_0 \Delta\vec{a}(t+\delta t)$$

$$\vec{v}^{\,c}(t+\delta t) = \vec{v}^{\,p}(t+\delta t) + c_1 \Delta\vec{a}(t+\delta t)$$

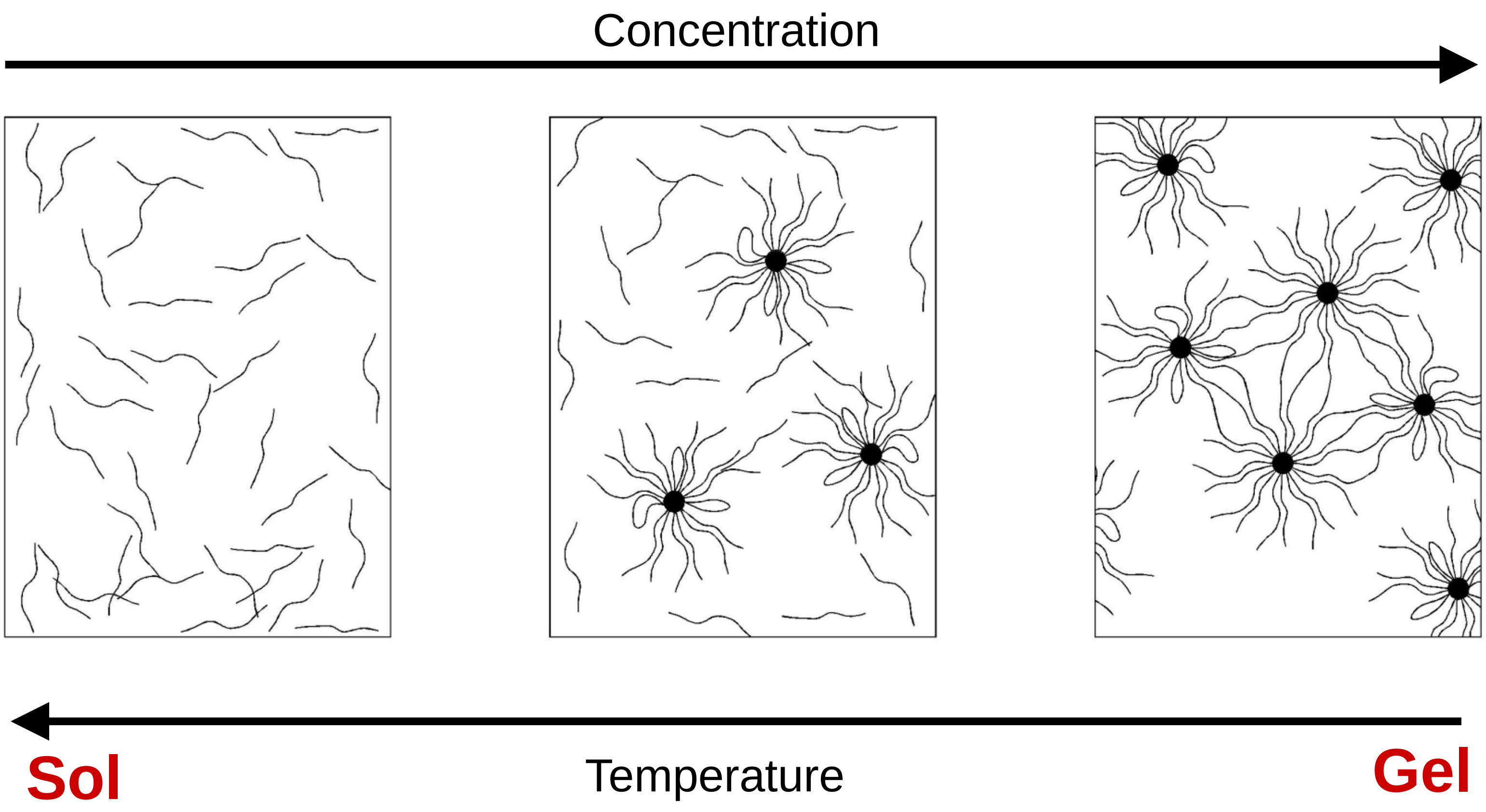
$$\vec{a}^{\,c}(t+\delta t) = \vec{a}^{\,p}(t+\delta t) + c_2 \Delta\vec{a}(t+\delta t)$$

$$\vec{b}^{\,c}(t+\delta t) = \vec{b}^{\,p}(t+\delta t) + c_3 \Delta\vec{a}(t+\delta t)$$

$\Delta t = 0.005\ \tau$

Polymeric gels

Associating: reversible junctions between endgroups



Simulation details

- 1000 polymeric chains, 8 beads/chain
- Units: σ (length), ε (energy&temperature), m (mass), $\tau=\sigma(m/\varepsilon)^{1/2}$ (time);
- Box size: (23.5 x 20.5 x 27.4) σ^3 with periodic boundary conditions
- Concentration = $0.6/\sigma^3$ (in overlap regime)
- Radius of gyration:

$$R_g^{\,2} = \frac{1}{N}\sum_{k=1}^{N}\left(r_k - r_{mean}\right)^2 = 2.69\sigma^2$$

- Bond life time > 1 / shear rate