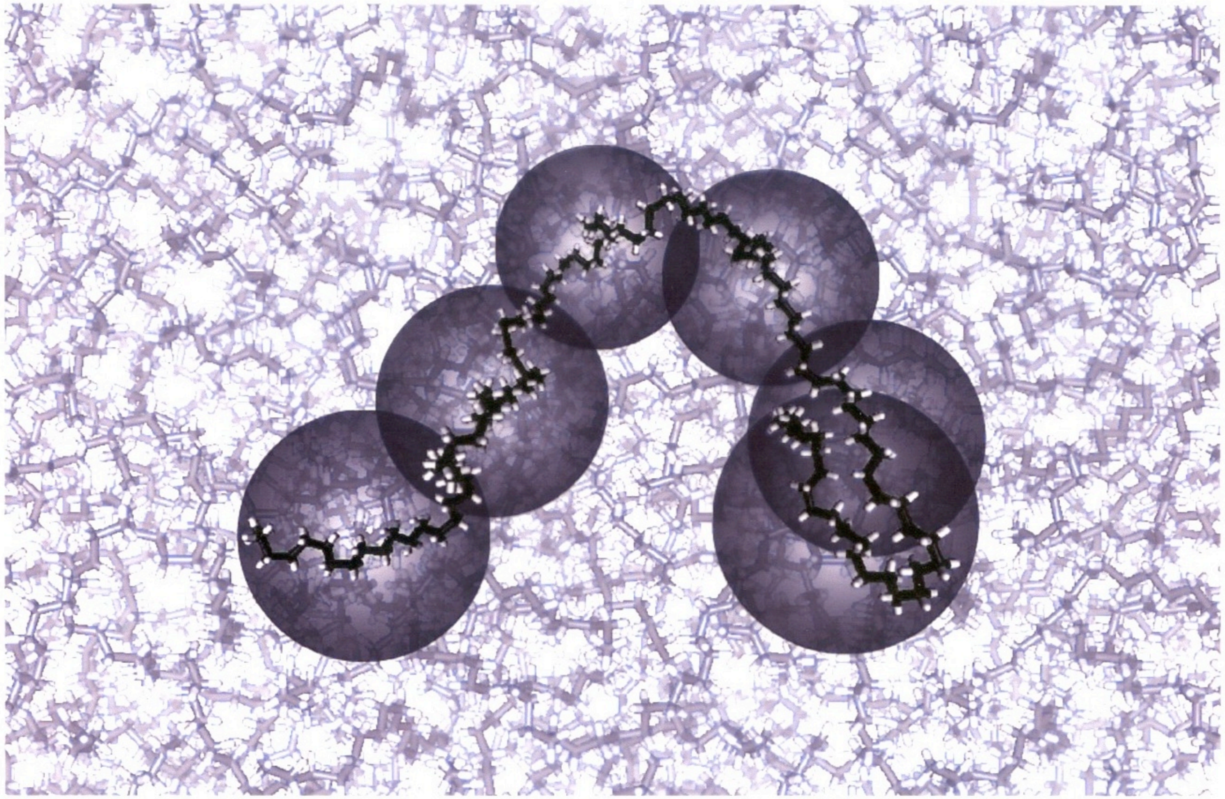
Can single particle models describe the rheology of complex polymer liquids?

W.J. Briels

J. Sprakel, J.T. Padding, E. van Ruymbeke and D, Vlassopoulos, J.K.G. Dhont

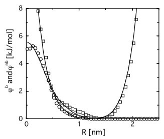
Contents

I. Coarse chains



Potential of mean force

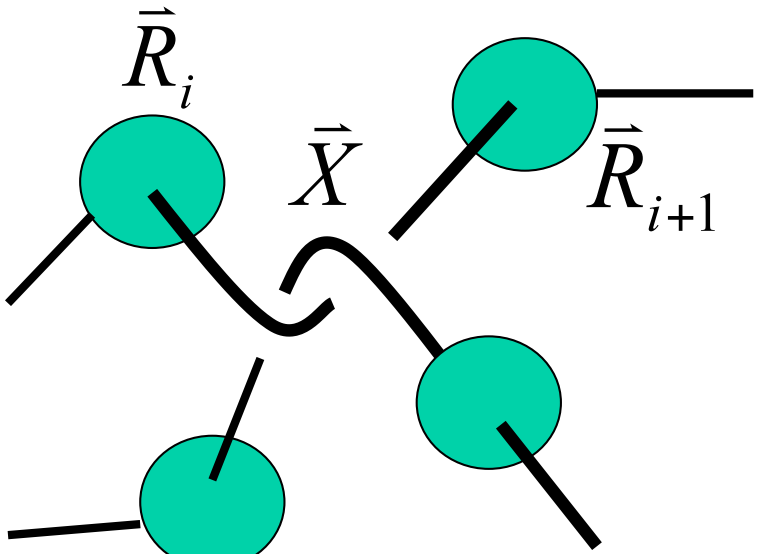
Simple Brownian dynamics with forces from



$\longleftarrow \phi^{fe}$

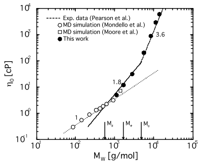
Calculated using Boltzmann inversion

Entanglements

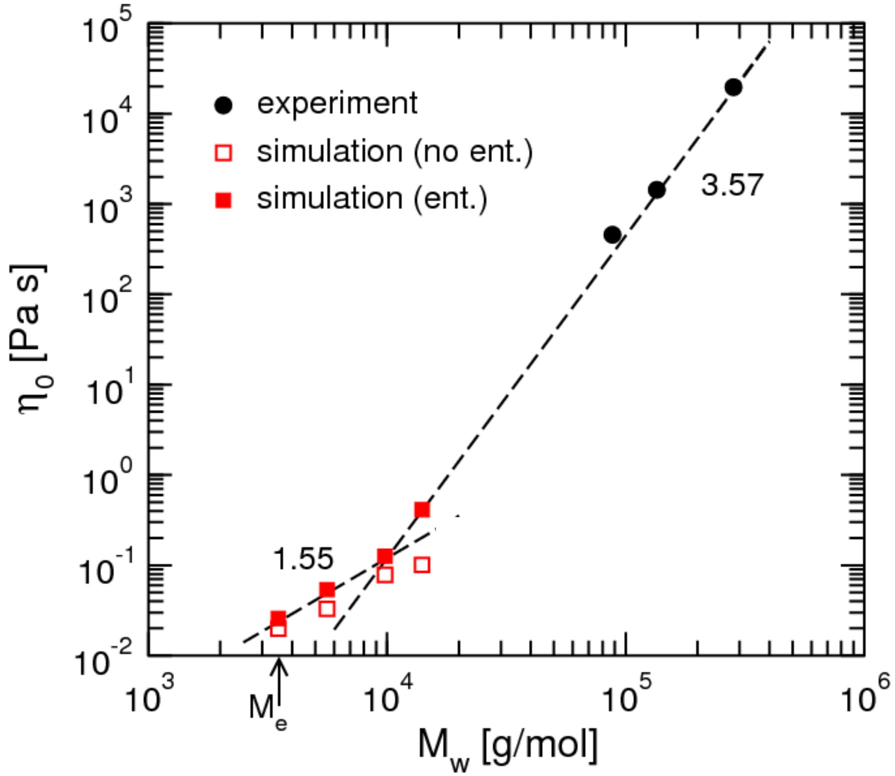


$$\Phi\left(R^{3N}\right) = \Phi^{NB}\left(R^{3N}\right) + \min_{X} \sum_{i} \phi^{fe}\left(L_{i,i+1}\left(R^{3N}, X\right)\right)$$

Viscosities PE



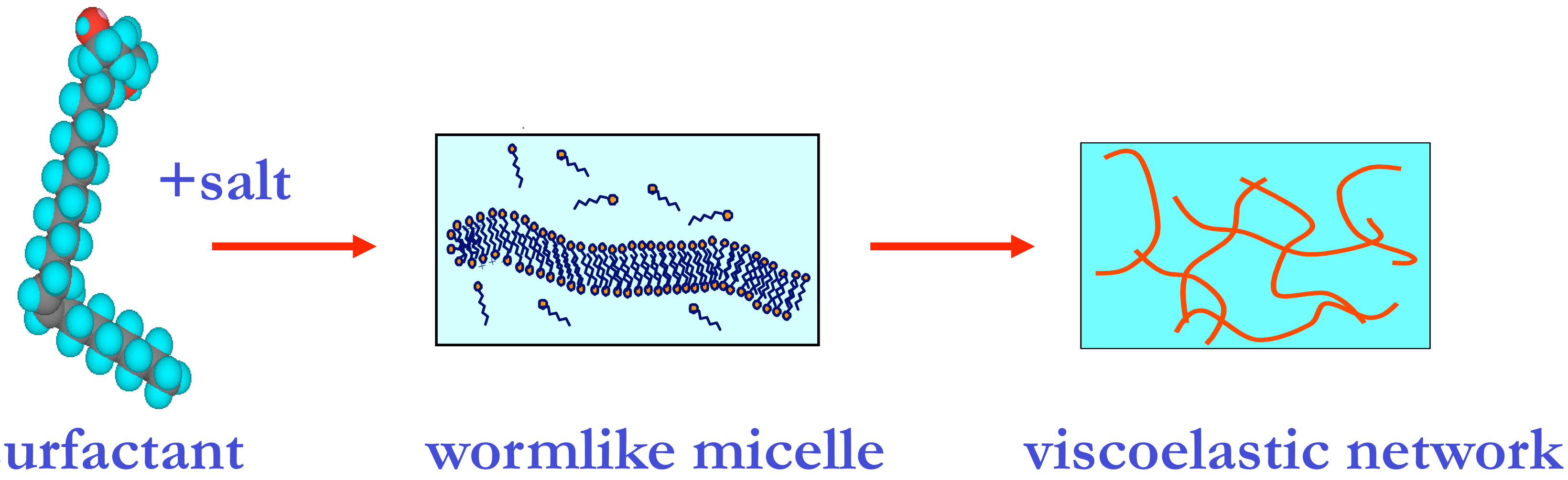
Viscosities PEP



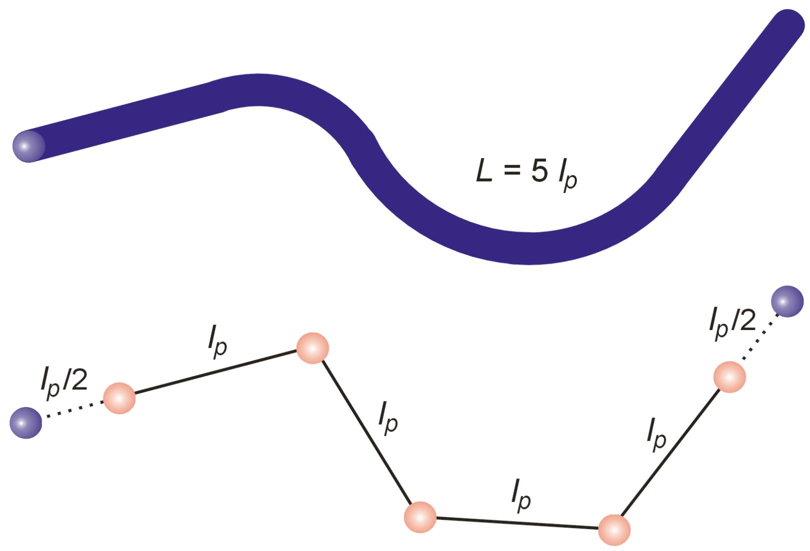
$$\eta = \int_0^\infty G(t)dt$$

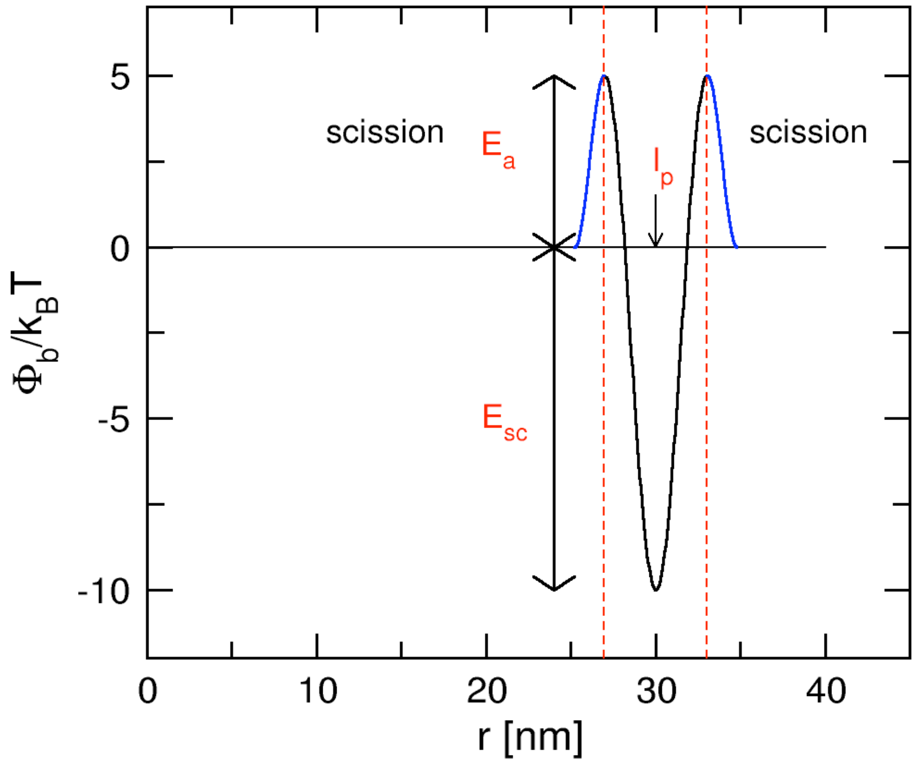
No fitting !!

I.a. Wormlike micelles



The coarse model





Join rods to form breakable chains

Parameters

l_P **Persistence length**

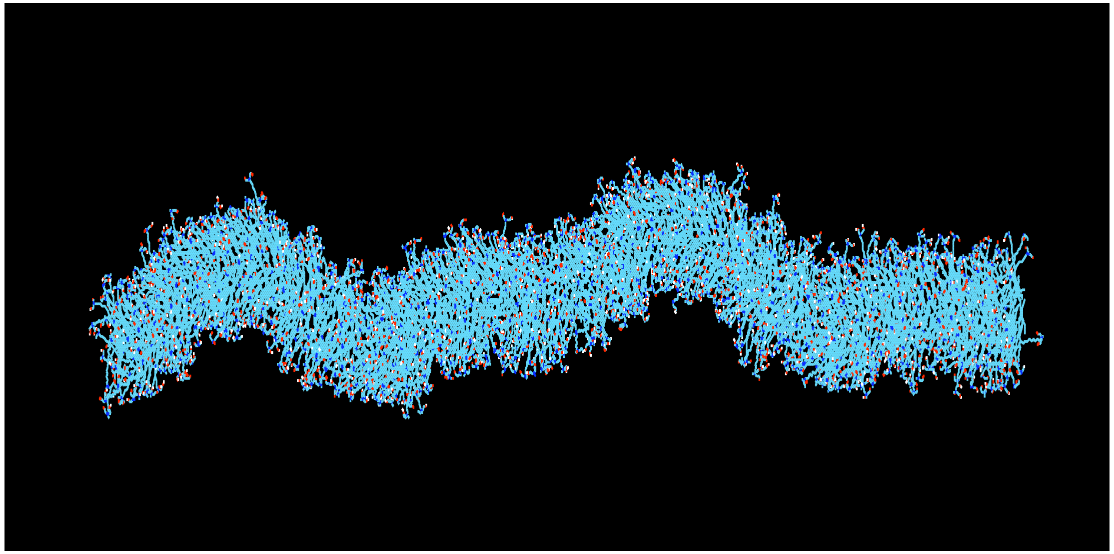
D **Diameter**

k_e **Elastic modulus**

E_{sc} **Scission energy**

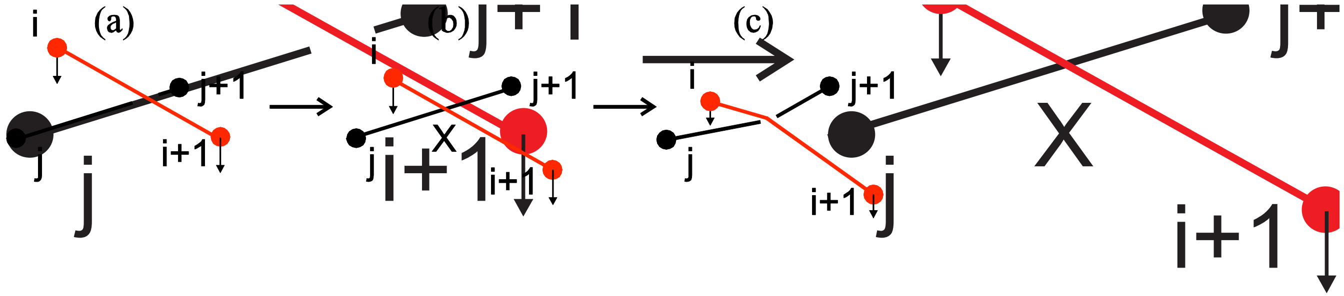
E_a **Activation energy**

Atomistic simulation



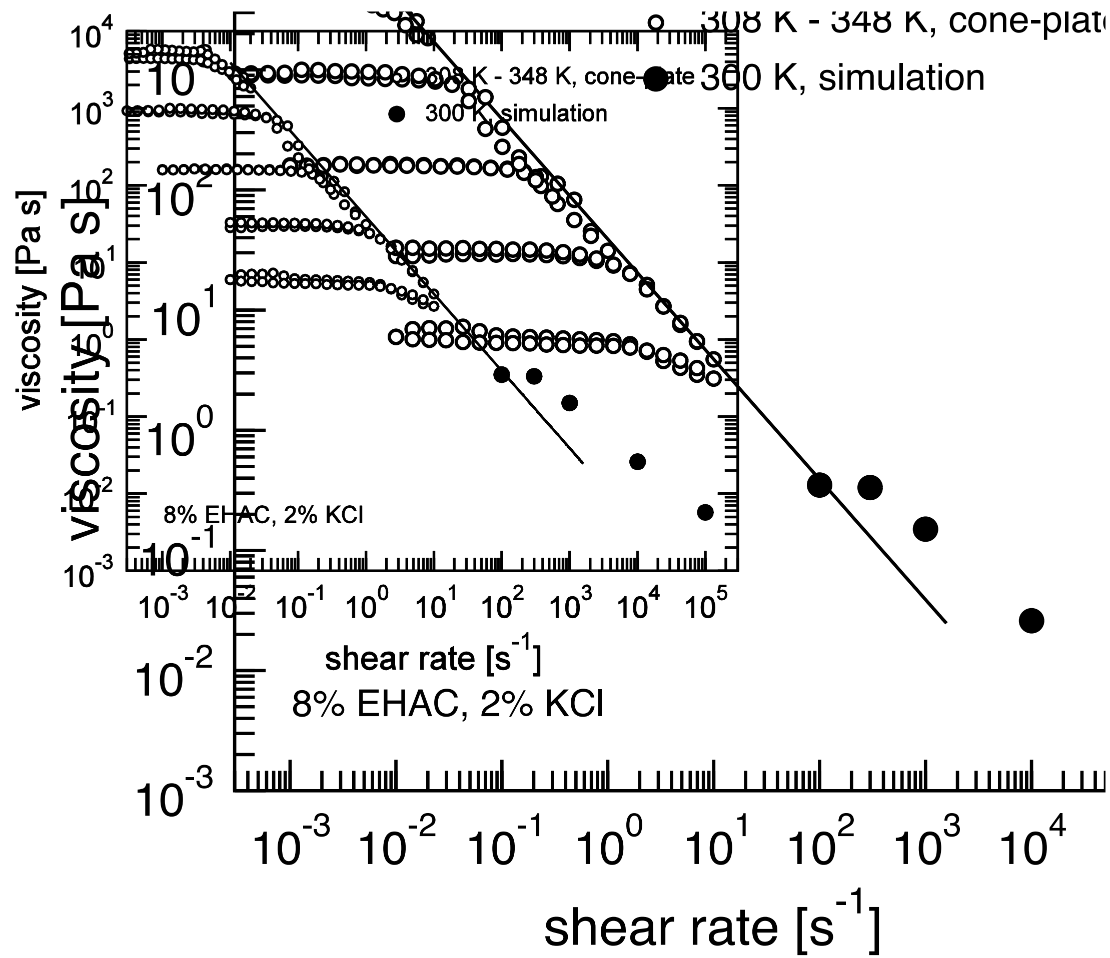
calculate persistence length, diameter and elastic modulus

Thou shall not cross



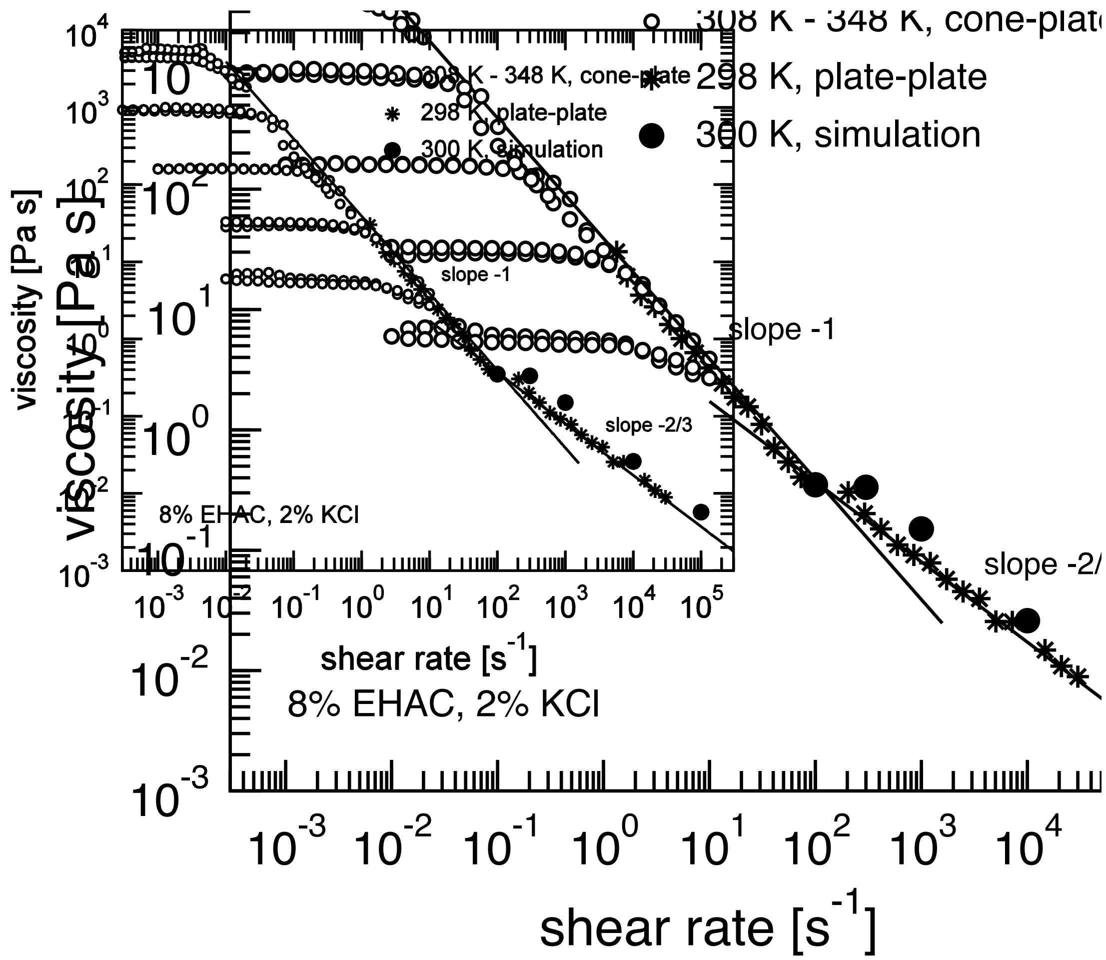
bead-bead interactions are short-ranged and soft, and cannot prevent bond crossing

Viscosities



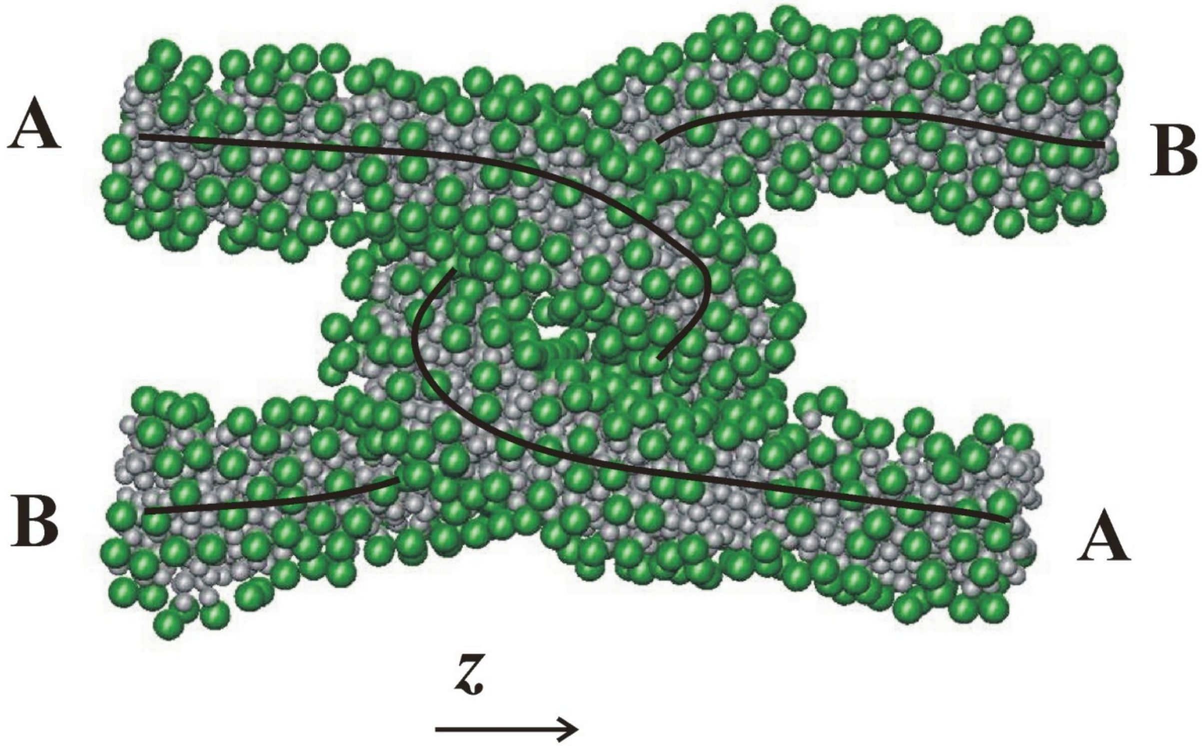
$$\eta = \int_0^\infty G(t)dt$$

Viscosities



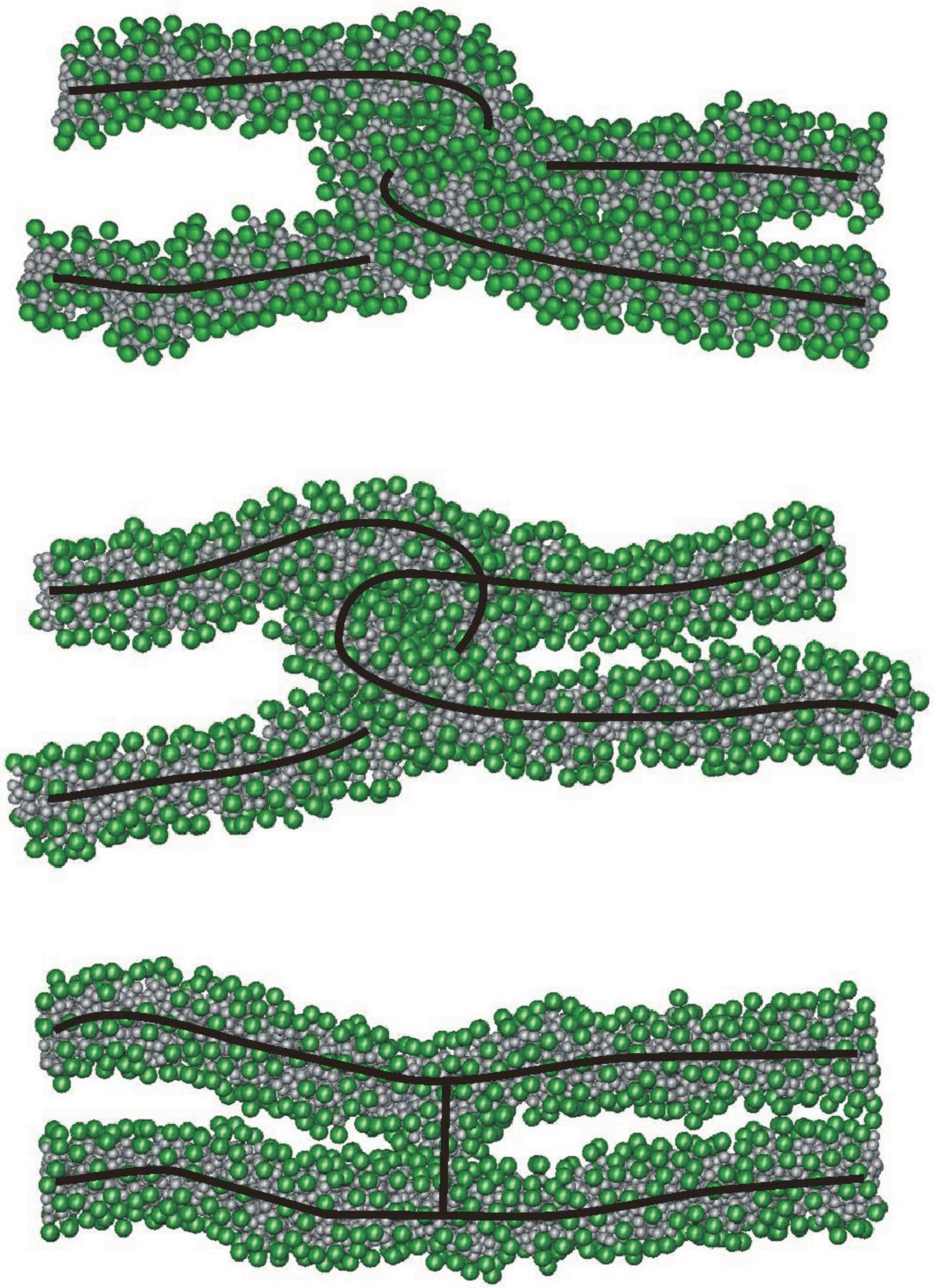
$$\eta = \int_0^\infty G(t)\,dt$$

No branching?

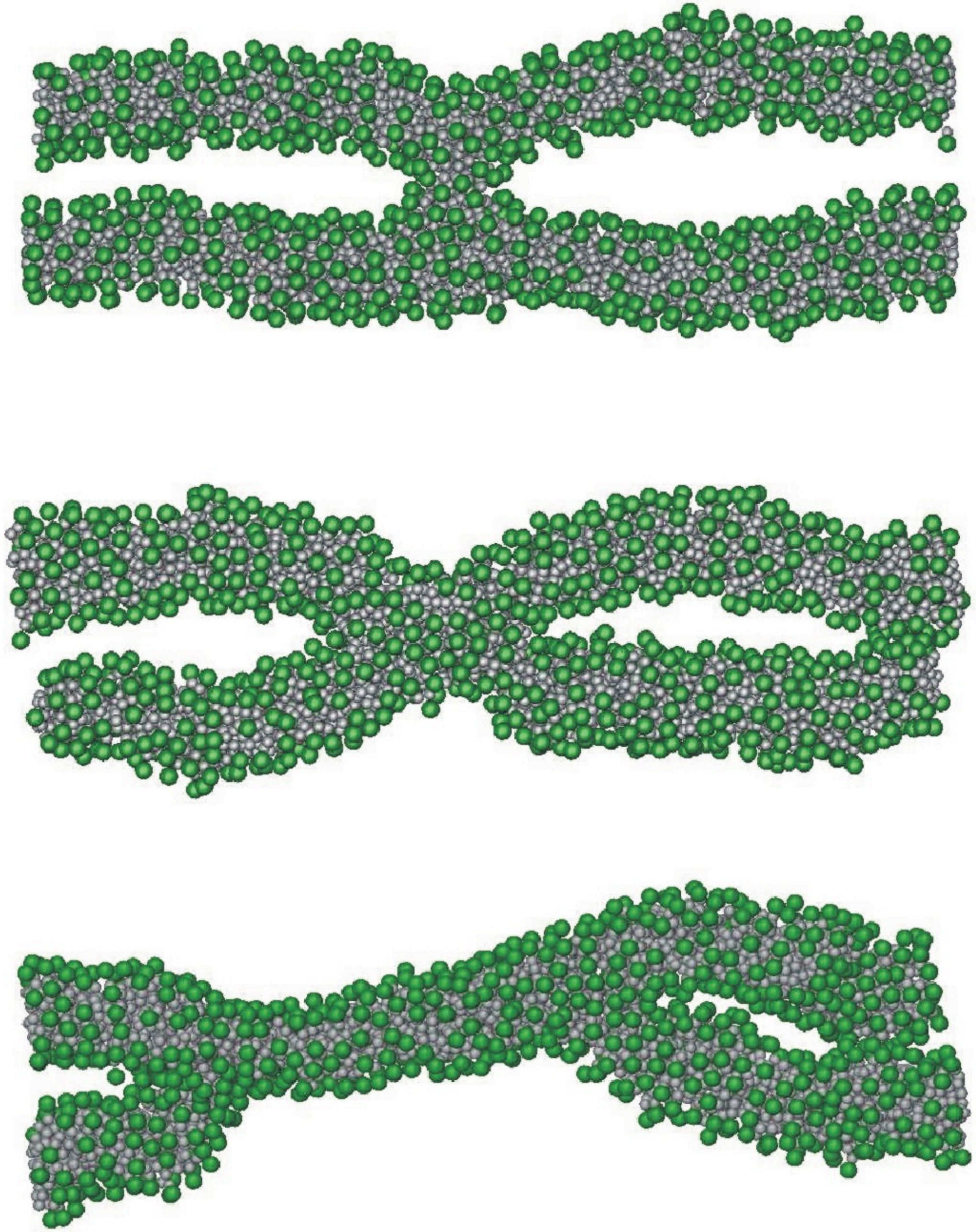


Twisted PBC:
M.P. Allen and A.J. Masters, *Mol. Phys.* **79**, 277 (1993)

Fusing



Relaxing

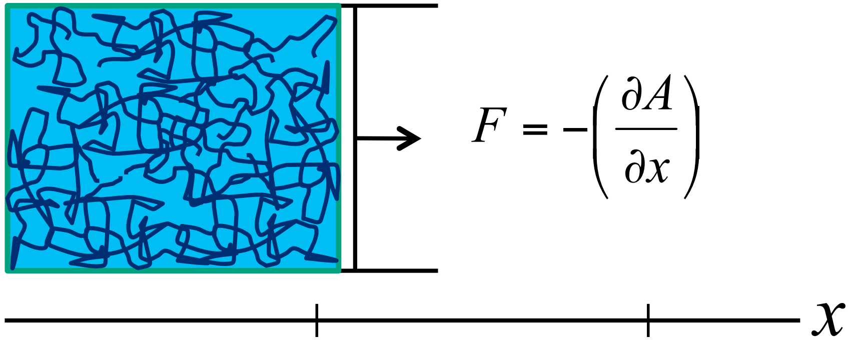


No branching !

- Branches cost a lot of free energy
- Branches easily slide off one end
- Sliding branches are difficult to simulate

II. Coarse graining

As coarse as coarse can be

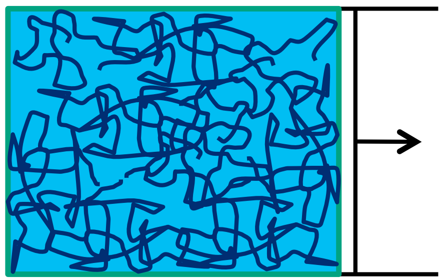


$$F = -\left(\frac{\partial A}{\partial x}\right)$$

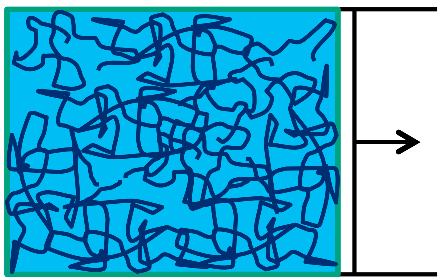
$$A(x) = -kT \ln \int dq^M \exp[-\beta V(x, q^M)]$$

Coarse graining

As coarse as coarse can be; a bit more resolution



$$F = -\left(\frac{\partial A}{\partial x}\right)$$

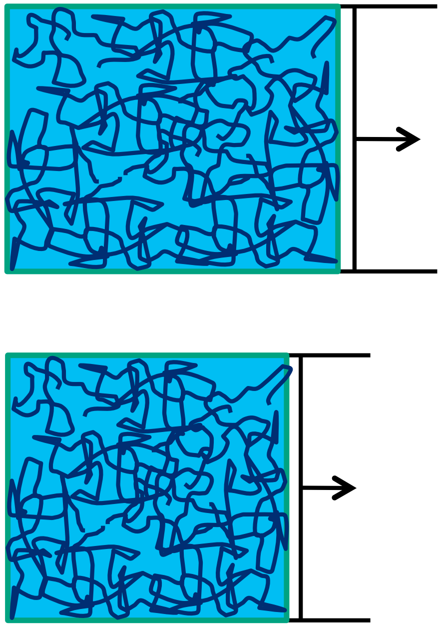


$$F(t) = -\left(\frac{\partial A}{\partial x}\right) - \int_{-\infty}^{t} \varsigma(t-\tau)\frac{dx}{d\tau}\,d\tau$$

Coarse graining

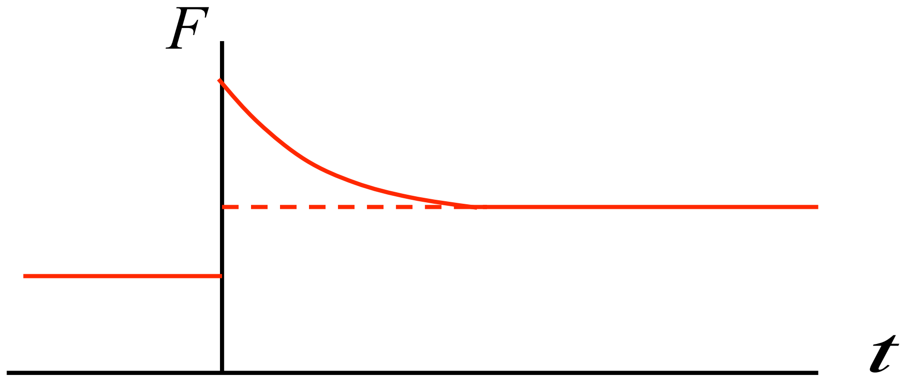
Transient forces after a compression

$$F(t) = -\left(\frac{\partial A}{\partial x}\right) - \int_{-\infty}^{t} \varsigma(t-\tau)\frac{dx}{d\tau}\,d\tau$$



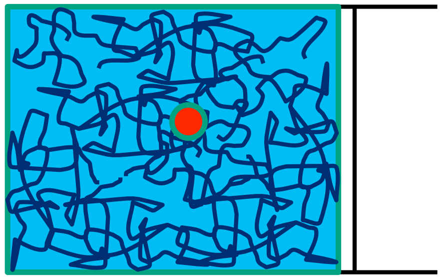
$$\frac{dx}{d\tau} = -|\Delta x|\,\delta(\tau)$$

$$F(t) = -\left(\frac{\partial A}{\partial x}\right) + |\Delta x|\,\varsigma(t)$$

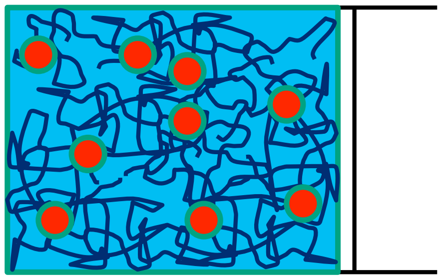


Coarse graining

A bit less coarse



$$\vec{F}(t) = -\left(\frac{\partial A}{\partial \vec{R}}\right) - \int_{-\infty}^{t} \varsigma(t-\tau;\vec{R})\frac{d\vec{R}}{d\tau}d\tau$$



$$\vec{F}_i(t) = -\left(\frac{\partial A}{\partial \vec{R}_i}\right) - \sum_{j=1}^{N}\int_{-\infty}^{t} \varsigma_{ij}(t-\tau;R^{3N})\frac{d\vec{R}_j}{d\tau}d\tau$$

Two ingredients

- **Potential of mean force**

$$A(R^{3N}) = -kT\ln\int dq^{M}\exp[-\beta V(R^{3N},q^{M}) + \ln J(R^{3N},q^{M})]$$

- **Friction/memory is due to non equilibrium of the bath**

$$\vec{F}_i^{\,fric}(t) = -\sum_{j=1}^{N}\int_{-\infty}^{t}\varsigma_{ij}(t-\tau;R^{3N})\frac{d\vec{R}_j}{d\tau}d\tau = -\sum_{j=1}^{N}\int_{-\infty}^{t}\varsigma_{ij}(t-\tau;R^{3N})d\vec{R}_j$$

W.J. Briels, Soft Matter 5 (2009), 4401

Memory

Introduce variables describing the state of the bath: $\{n_{ij};\forall pairs\}$
and write

$$A\left(R^{3N},n^{M}\right)=A(R^{3N})+\sum_{\langle i,j\rangle}\frac{\alpha}{2}(n_{ij}-n_0(R_{ij}))^2$$

i.e.

$$P\left(R^{3N},n^{M}\right)\propto \exp\left\{-\beta\left[A(R^{3N})+\sum_{\langle i,j\rangle}\frac{\alpha}{2}(n_{ij}-n_0(R_{ij}))^2\right]\right\}$$

W.J. Briels, Soft Matter 5 (2009), 4401

Dynamics

Brownian dynamics in a slow bath

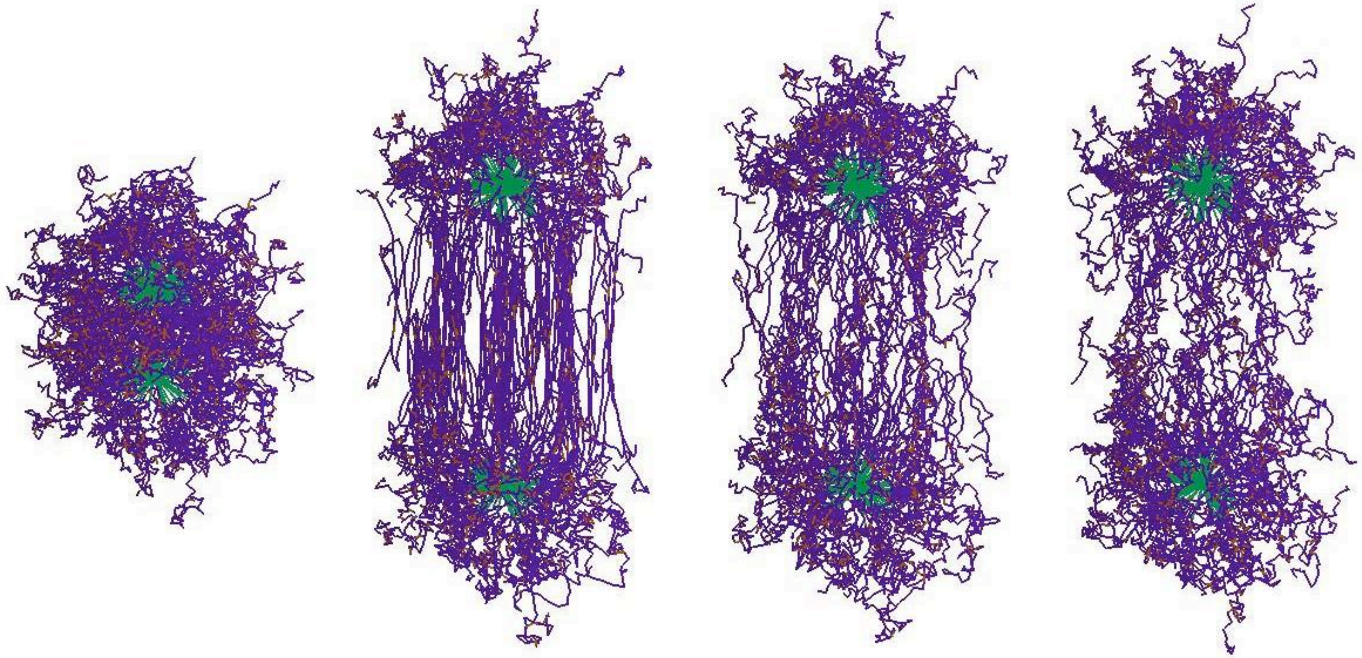
$$d\vec{R}_i = \frac{1}{\xi_i}\left[-\vec{\nabla}_i A + \vec{F}_i^T\right]dt + d\vec{R}_i^{ran}$$

$$\vec{F}_i^T = \alpha \sum_j \left[n_{ij} - n_0(R_{ij})\right]\vec{\nabla}_i n_0(R_{ij})$$

$$dn_{ij} = -\frac{1}{\tau(R_{ij})}\left[n_{ij} - n_0(R_{ij})\right]dt + dn_{ij}^{ran}$$

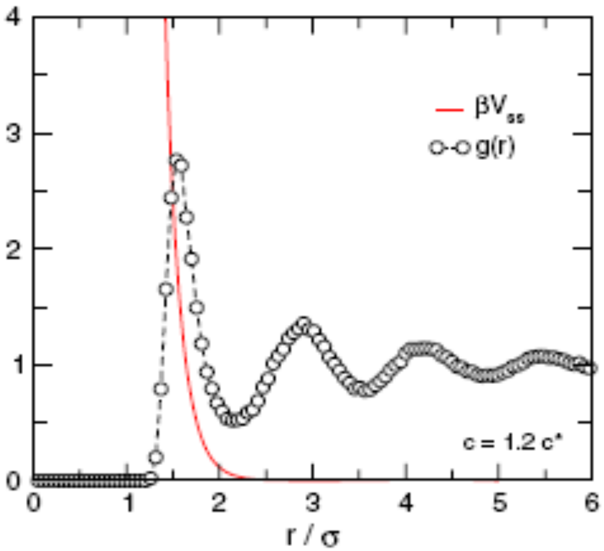
W.J. Briels, Soft Matter 5 (2009), 4401

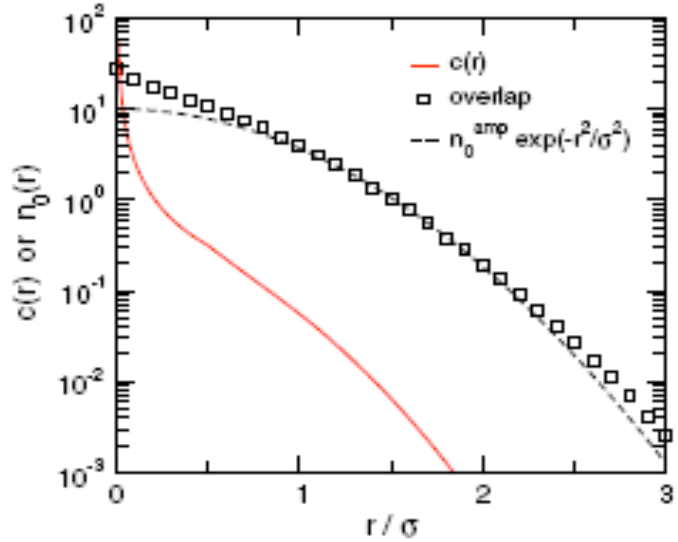
III.a. Star polymers



$n_{ij} = n_0(r_{ij})$ $n_{ij} \neq n_0(r_{ij}^{new})$ $n_{ij} = n_0(r_{ij}^{new})$

Potentials and overlap

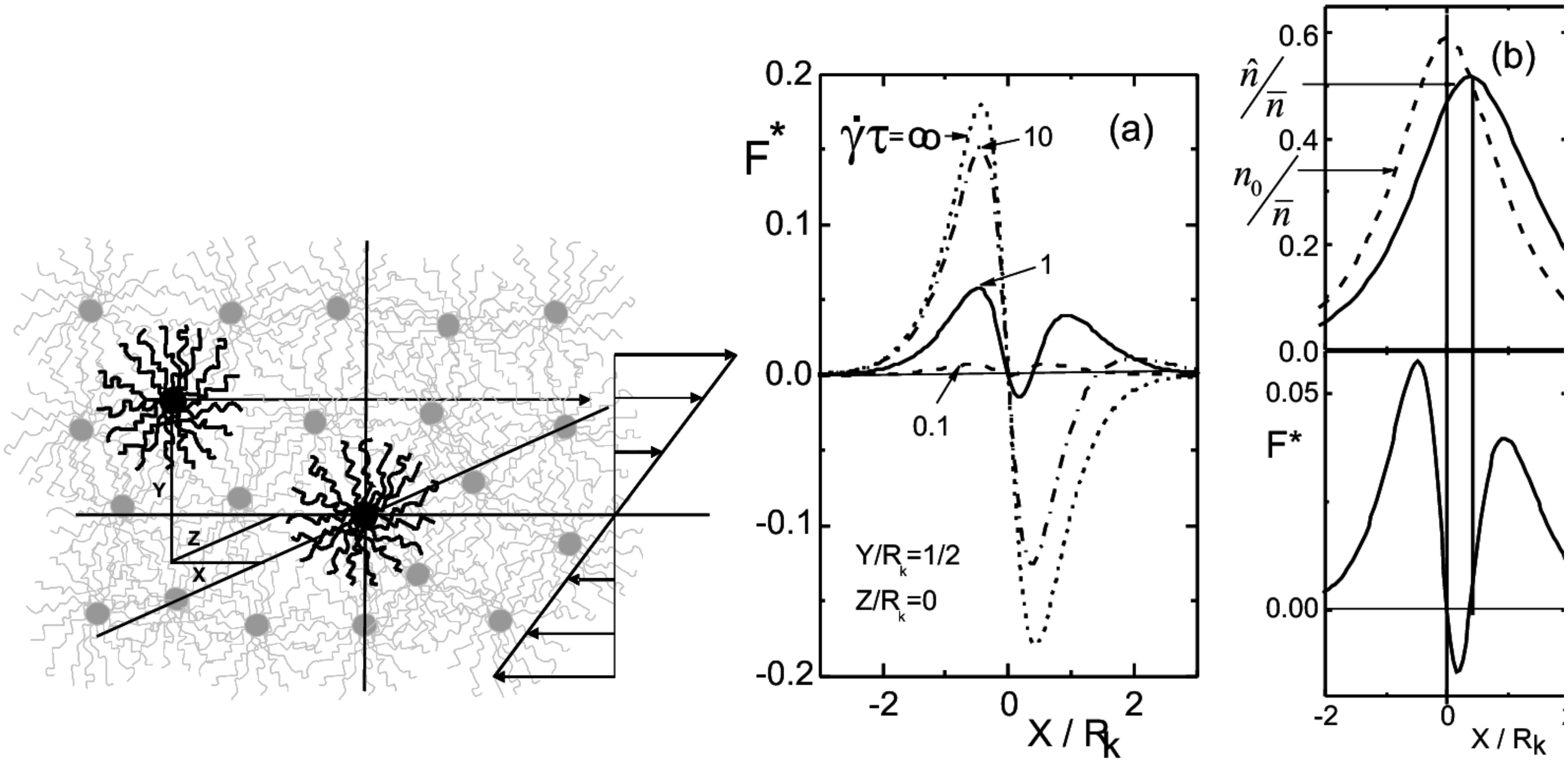




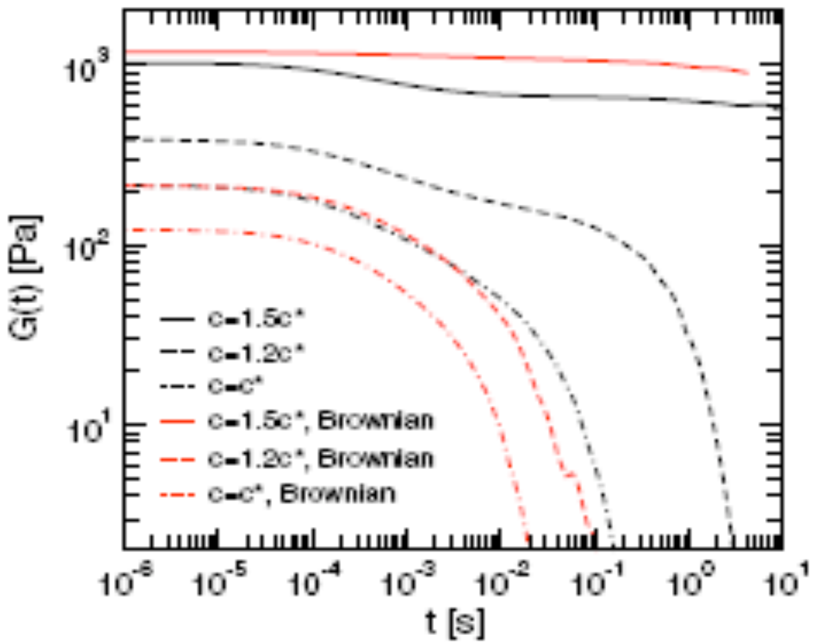
$$A(R^{3N}) = \sum_{<i,j>} \varphi(R_{ij})$$

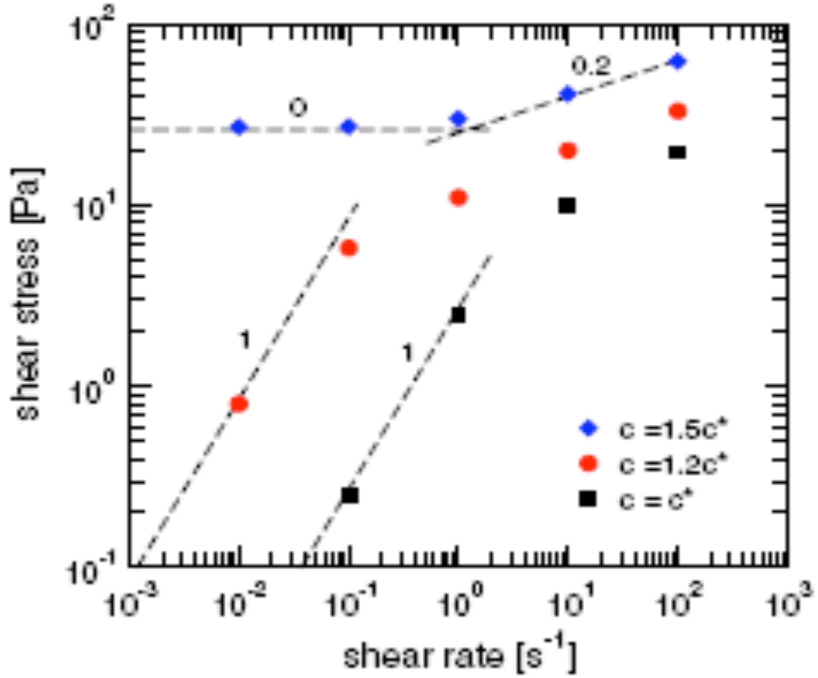
$$n_0(r) = \int d^3x c(\vec{x}) c(\vec{x} - \vec{r})$$

Transient forces



Linear rheology



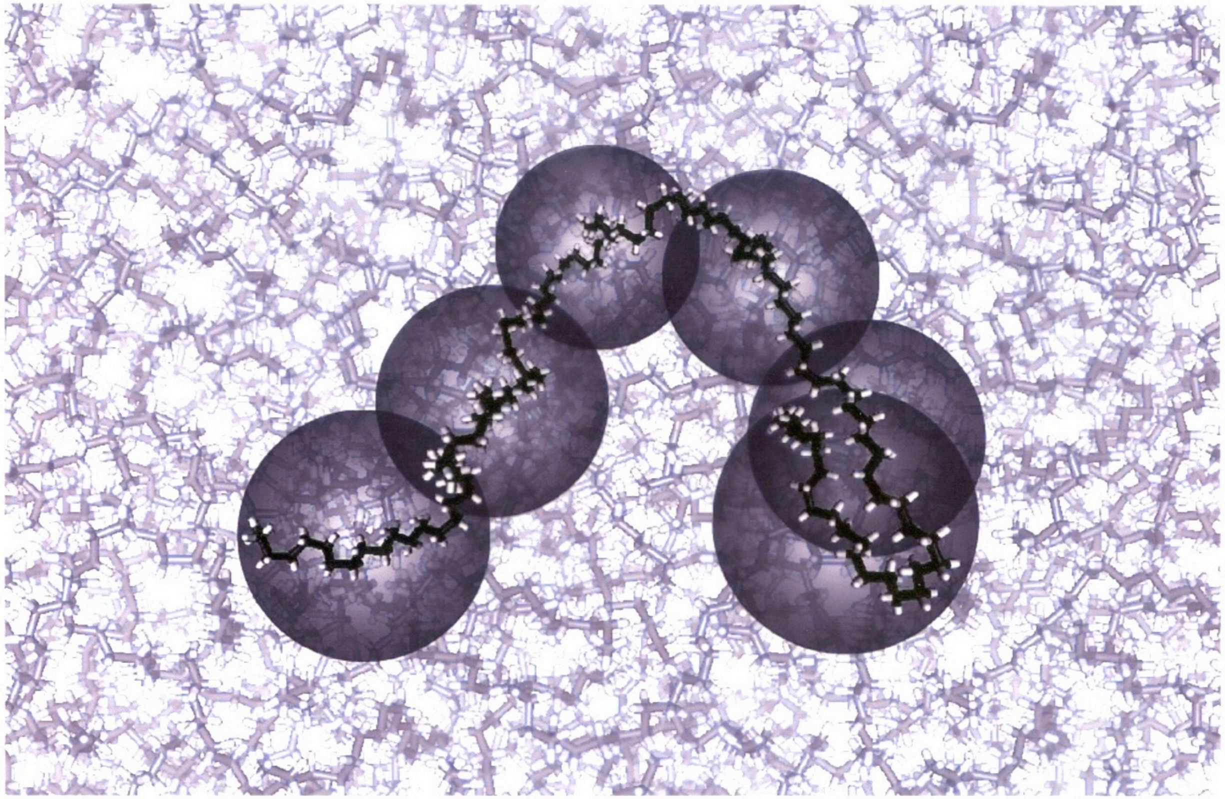


Theory for stars

(with Jan Dhont)

Assuming affine displacements, the stress tensor contains a shear thinning viscous term, a shear curvature term and coupling of diffusion and flow

III.b. Linear polymers



Potentials and overlap

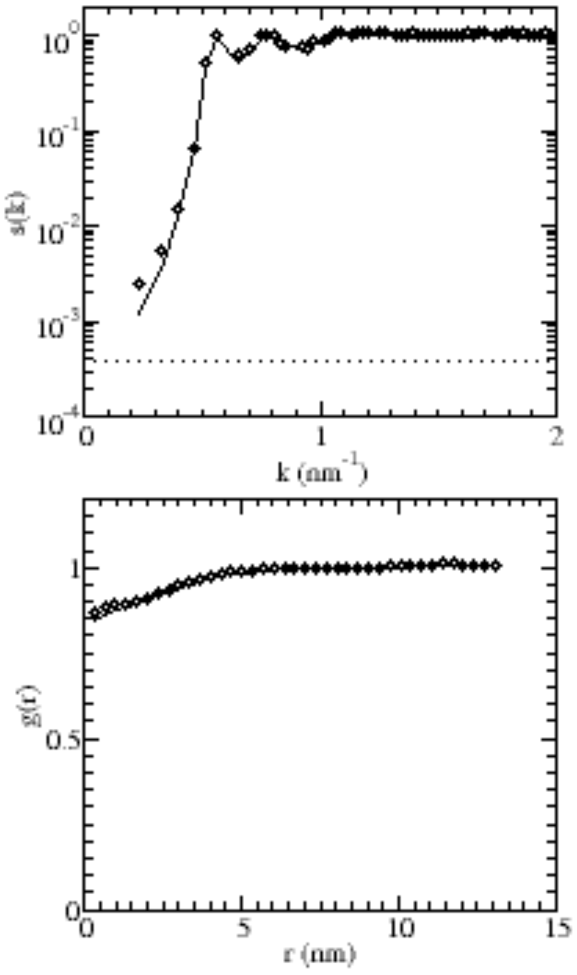
- Three body potential

$$A(R^{3N}) = \frac{1}{2\rho\kappa_T} \sum_j \left(\frac{\rho_j}{\rho} - 1 \right)^2$$

$$\rho_j(R^{3N}) = \sum_k w(R_{jk})$$

- Overlap functions: Gaussians

Polymer melts: $C_{800}H_{1602}$



Structure factor reproduces right compressibility.

'Ideal gas'

Potential of mean force

$$A(R^{3N}) = \sum_j a(\rho_j(R^{3N}))$$

$$\rho_j(R^{3N}) = \sum_k w(R_{jk})$$

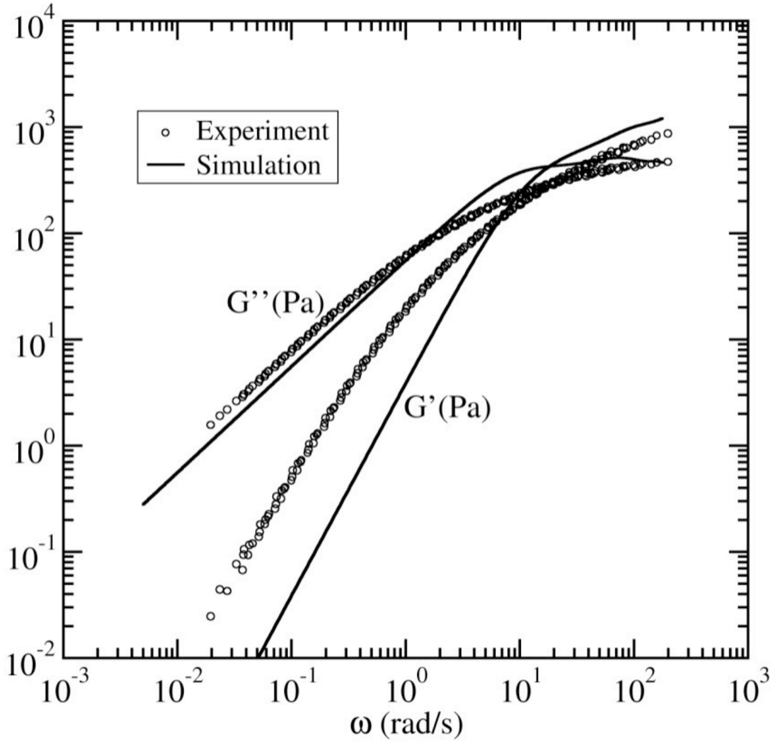
Taylor expansion

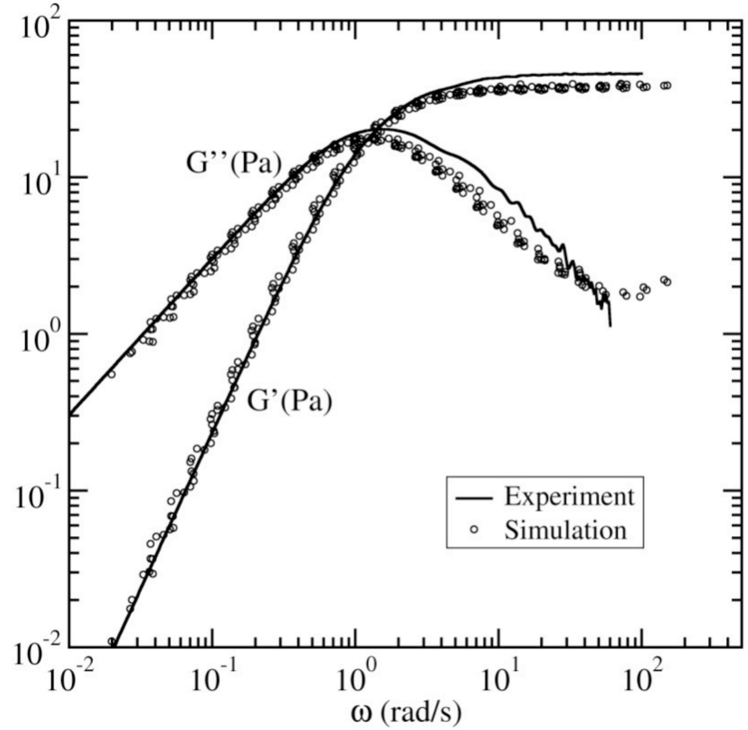
$$a(\rho_j) = a(\rho) + \frac{P}{\rho}\left(\frac{\rho_j}{\rho} - 1\right) + \frac{1}{\rho}\frac{1}{\kappa_T}(1 - 2\kappa_T P)\frac{1}{2}\left(\frac{\rho_j}{\rho} - 1\right)^2$$

$$- \frac{5}{\rho}\frac{1}{\kappa_T}\left(1 - \frac{6}{5}\kappa_T P - \frac{1}{5}\frac{\partial \ln \kappa_T}{\partial \ln \rho}\right)\frac{1}{6}\left(\frac{\rho_j}{\rho} - 1\right)^3 + \ldots$$

Three body interactions suffice !!

Polymer solutions



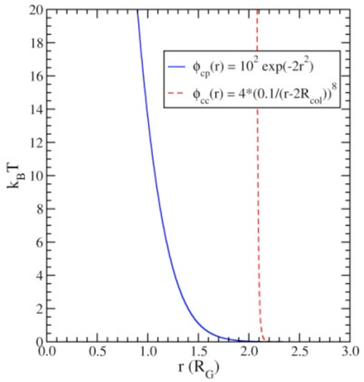


Polymer solution

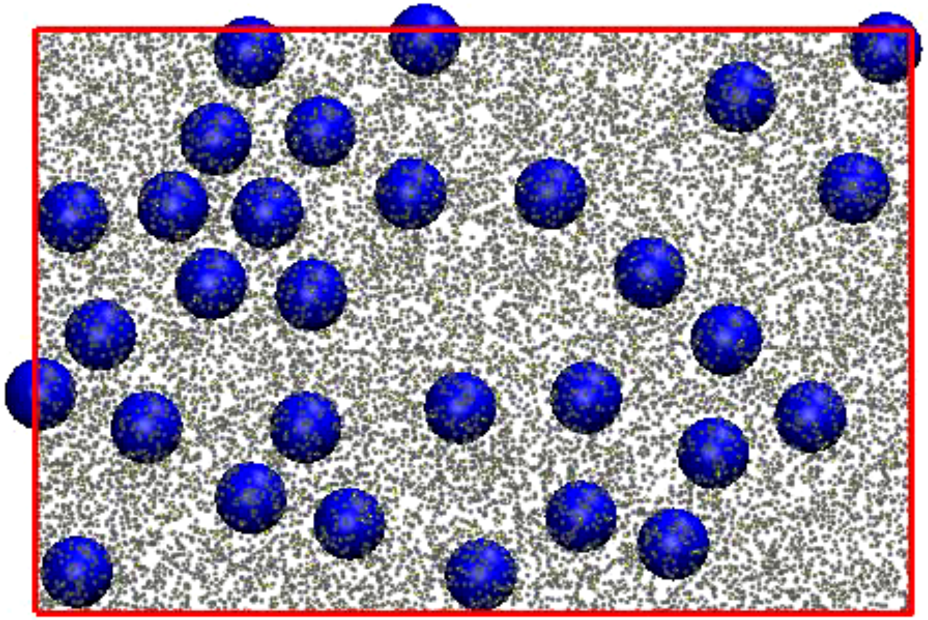
'Worm-like micelles'

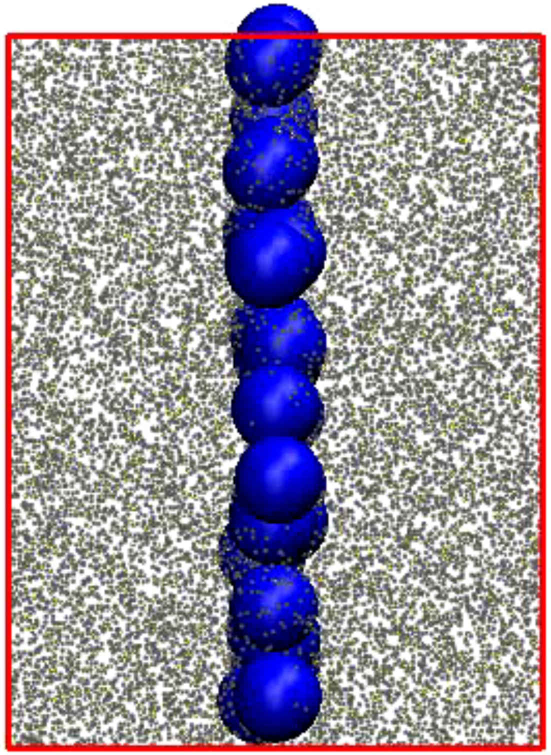
Free energy from Flory-Huggins

Chaining

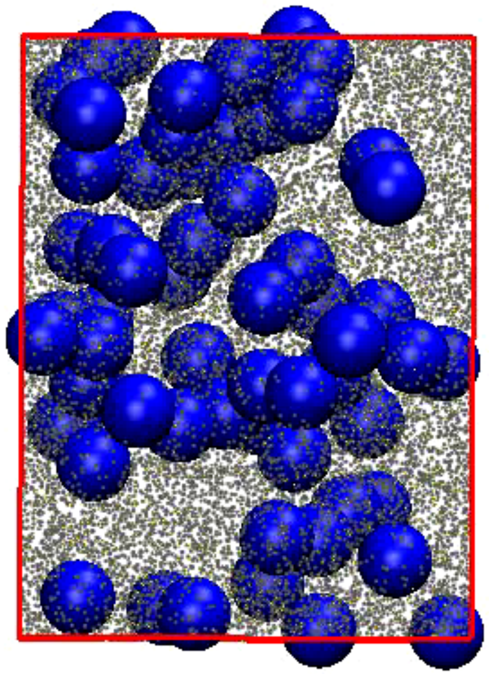


$\phi_{cp}(r) = 10^2 \exp(-2r^2)$
$\phi_{cc}(r) = 4*(0.1/(r-2R_{col}))^8$
k_BT
20
18
16
14
12
10
8
6
4
2
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
$r\ (R_G)$



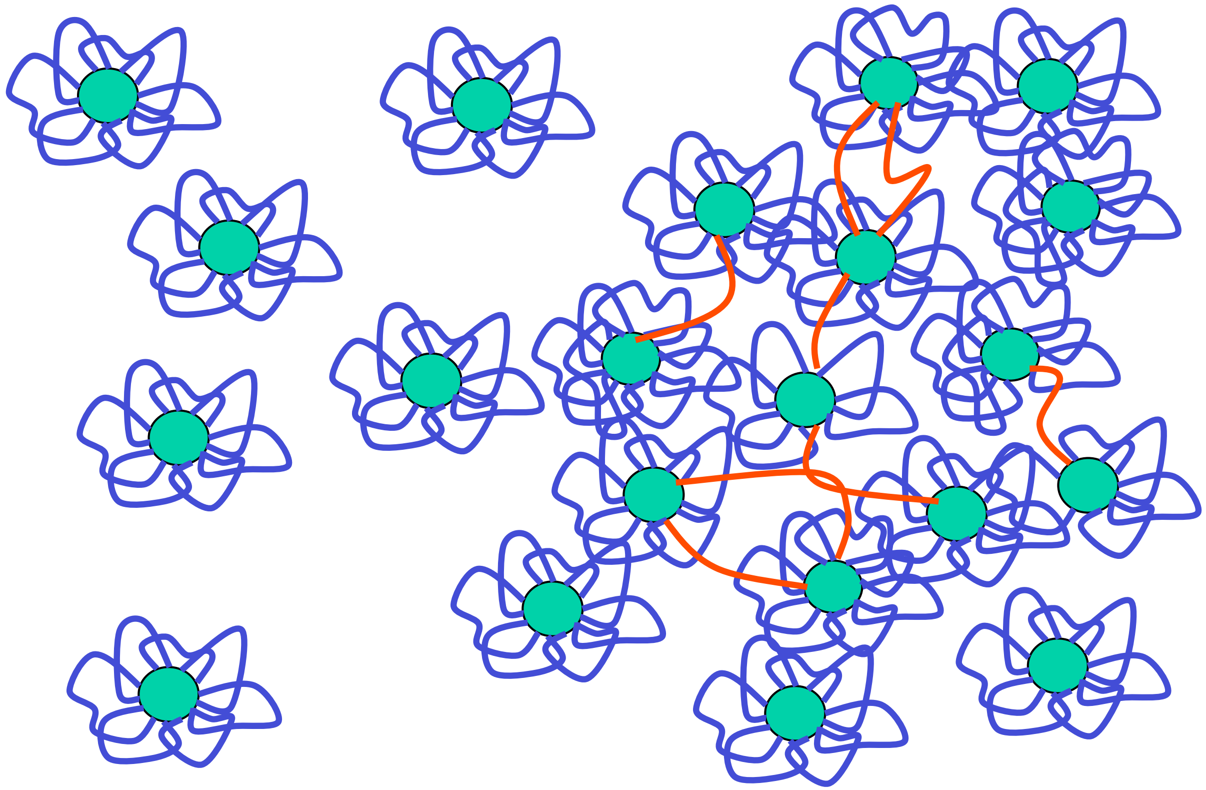


Chaining again



III.c. Telechelic polymers

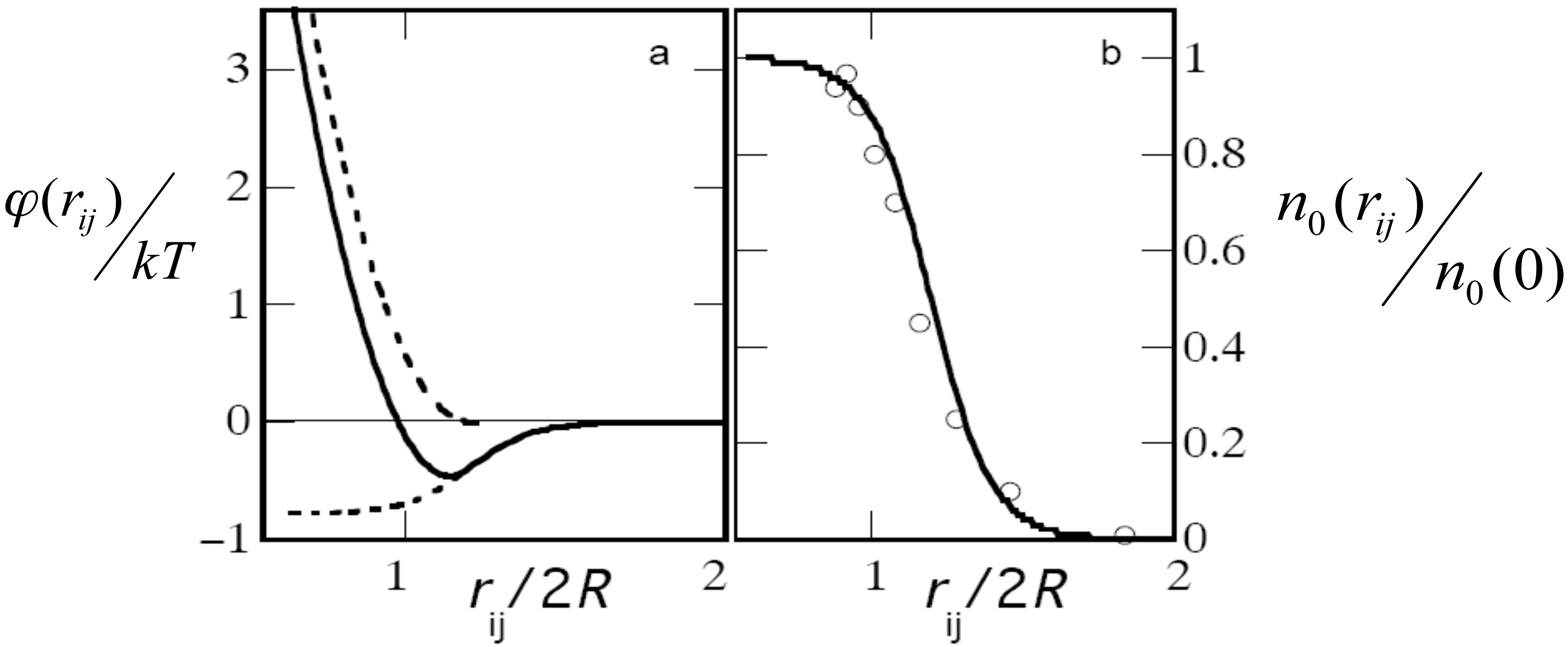
Low density **High density**



Flowers **Flowers and bridges**

Potential of mean force

$$A(R^{3N}) = \sum_{<i,j>} \varphi(R_{ij}) \qquad n_0(R_{ij}) \propto G_0(\rho = R_{ij}^{-3})$$



from SCF calculations **from plateau modulus**

Parameters

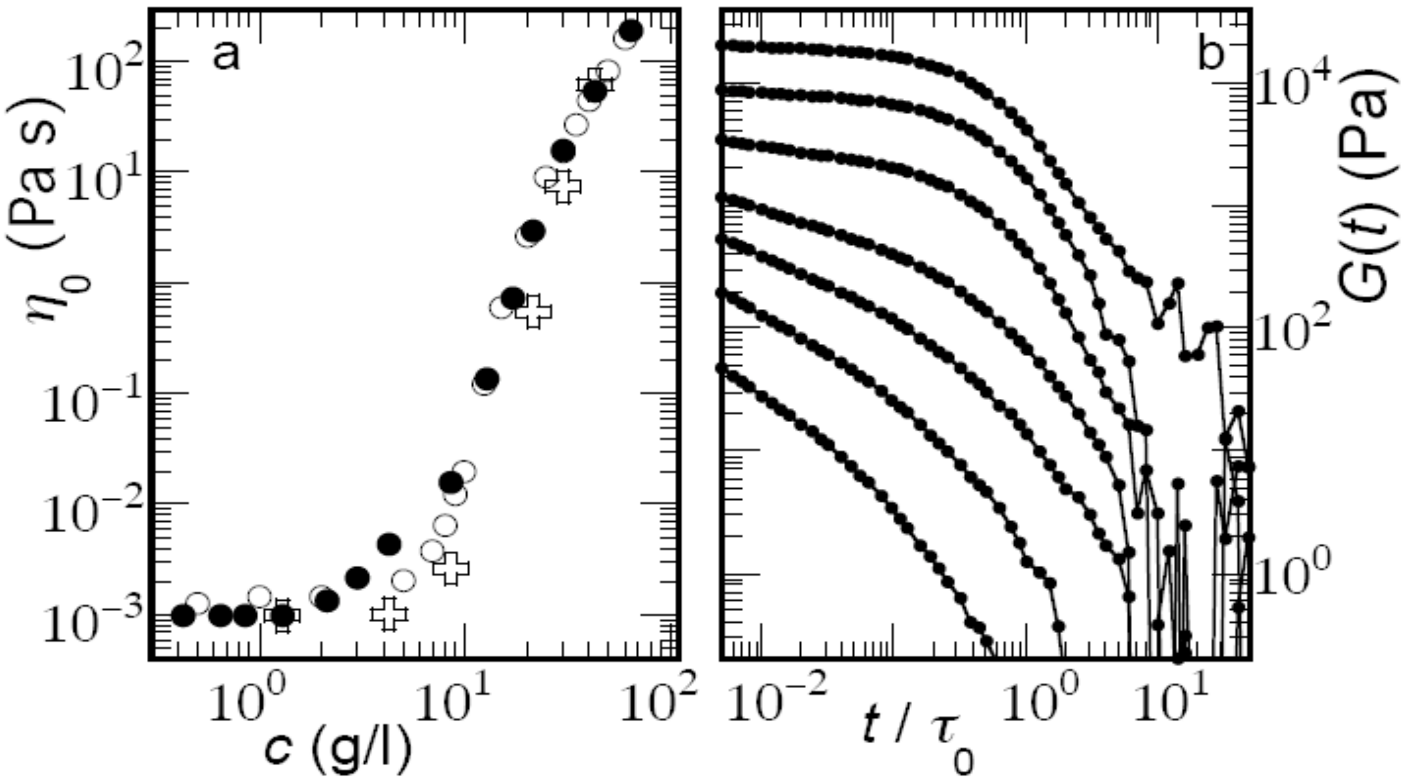
$$\tau(R_{ij}) = \tau_0 \exp(-R_{ij}/\lambda)$$

$$\xi_i = \xi_0 + \xi_b \sum_j \sqrt{n_{ij} n_0(R_{ij})}$$

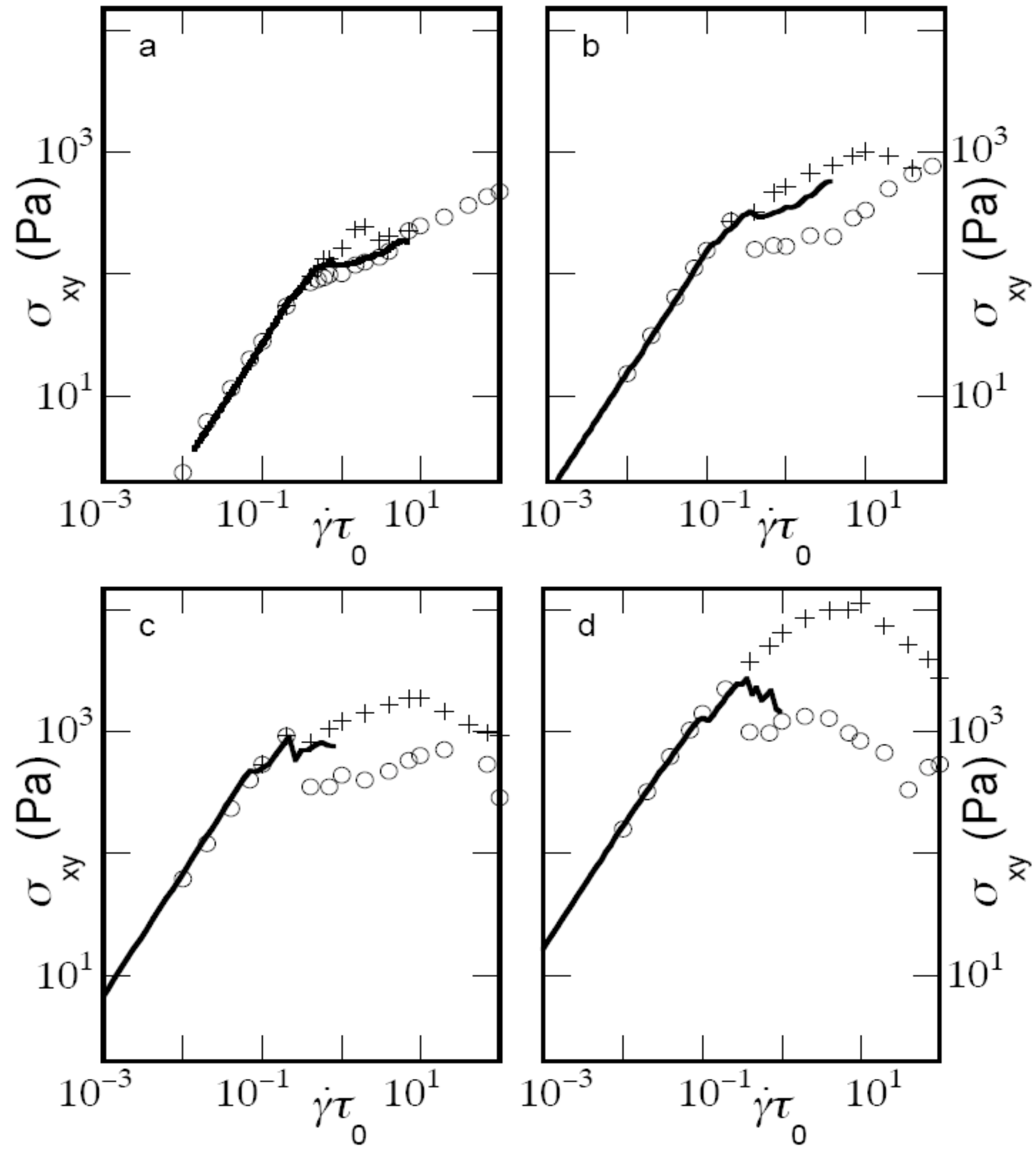
$$\lim_{R\to 0} n_0(R) = \frac{f}{12}$$

← **This will lead to intelligible values of α**

Linear rheology



Viscosities used to fix α

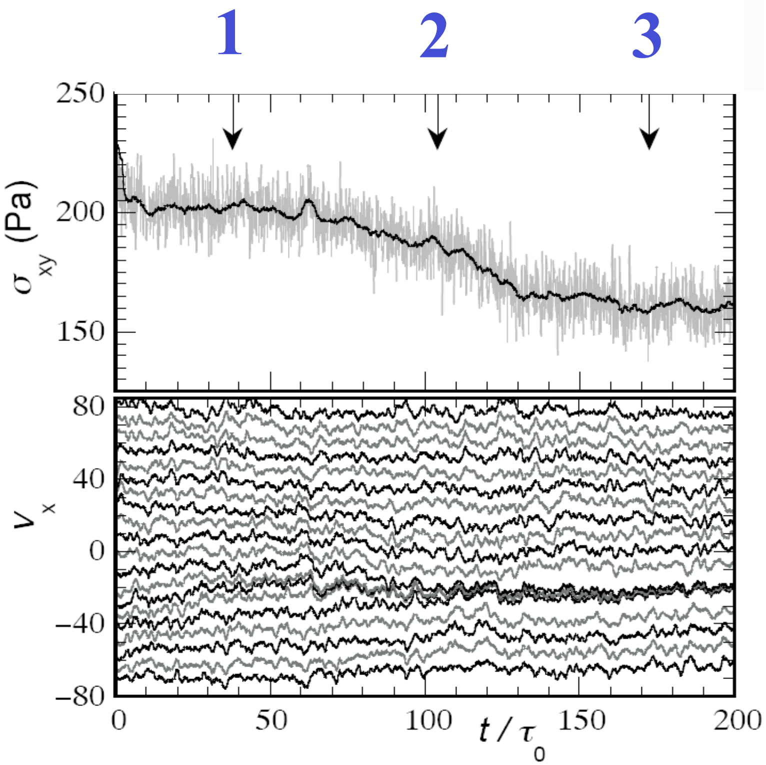


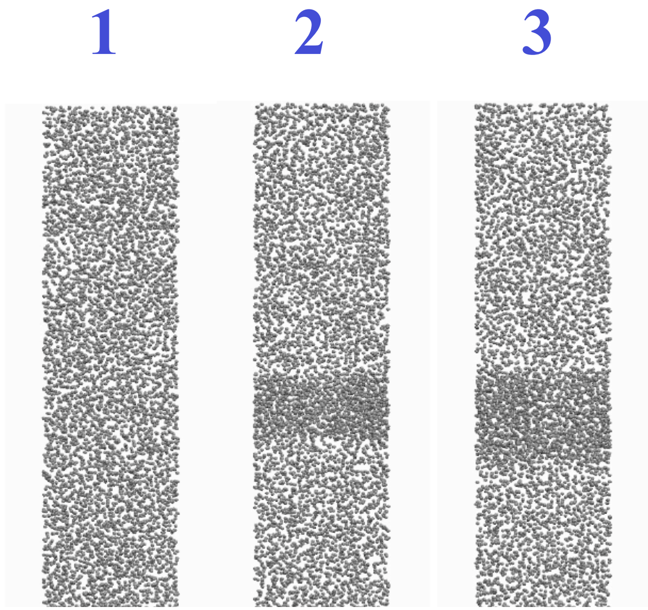
Predicted non linear rheology

From upper left to lower right, increasing concentration

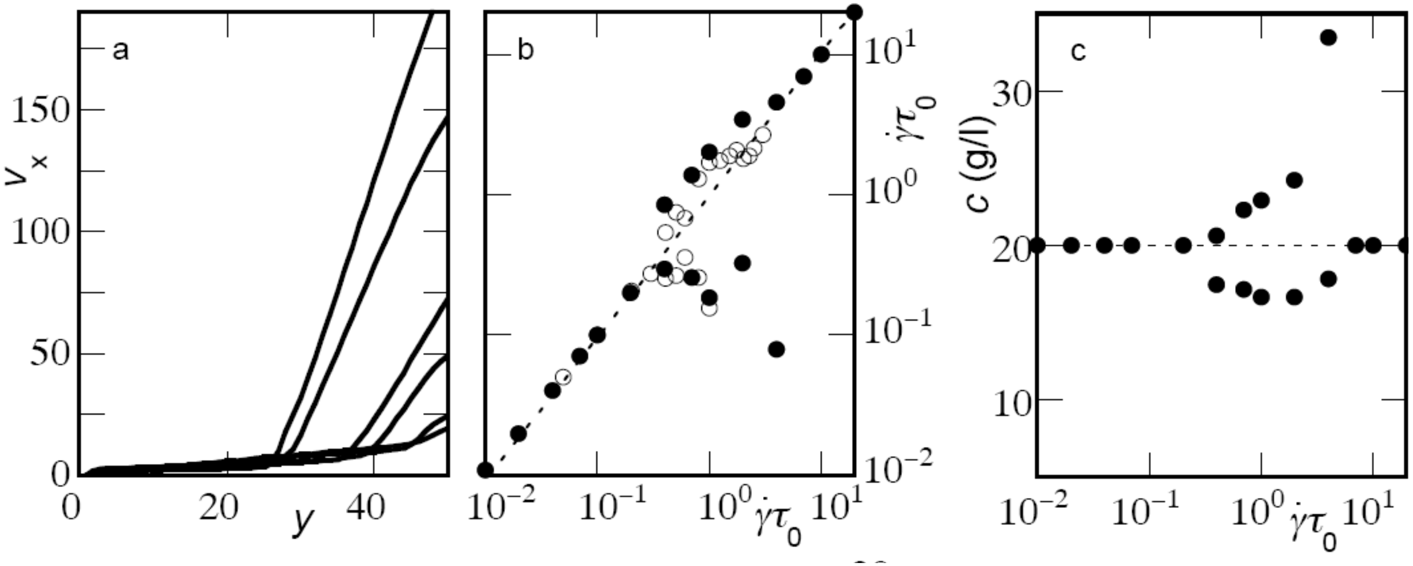
Shear banding

$$c = 20g/l, \dot{\gamma}\tau_0 = 4.0$$



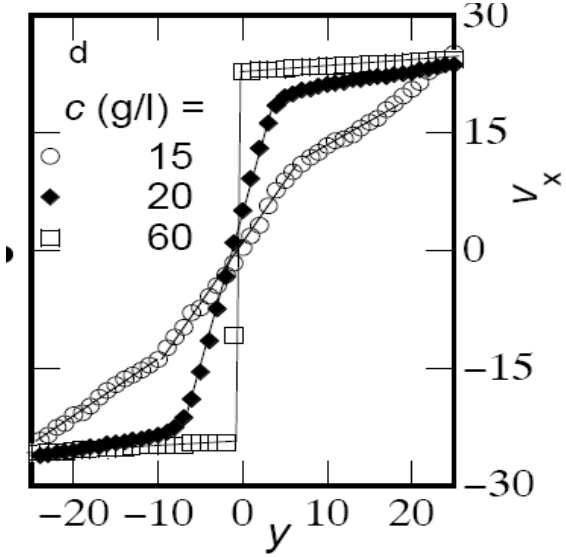


Shear banding 20 g/l

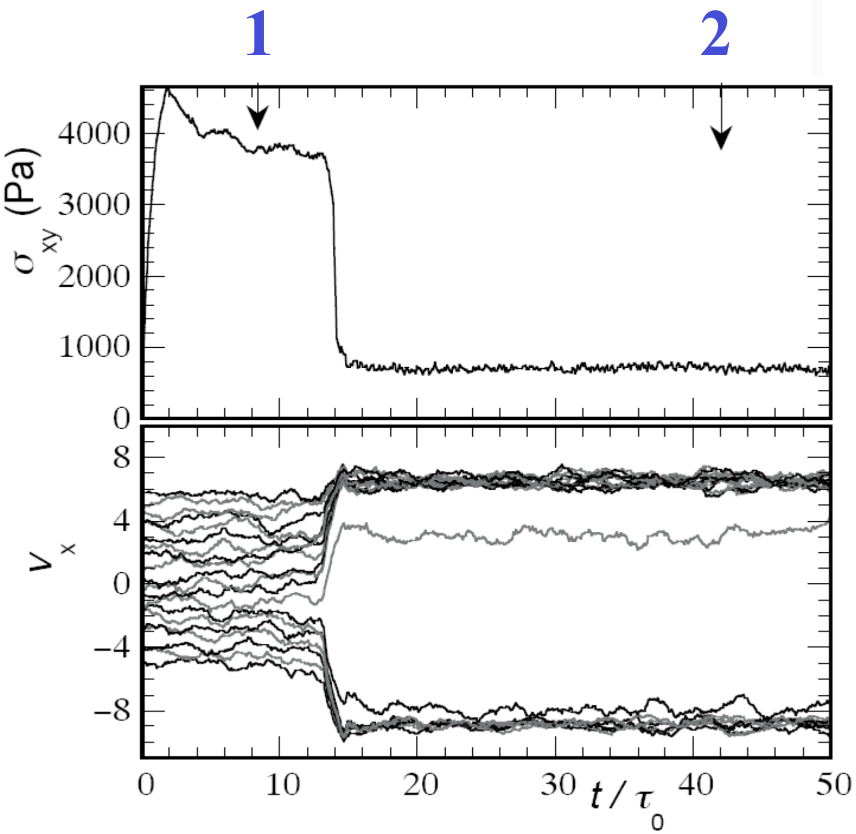


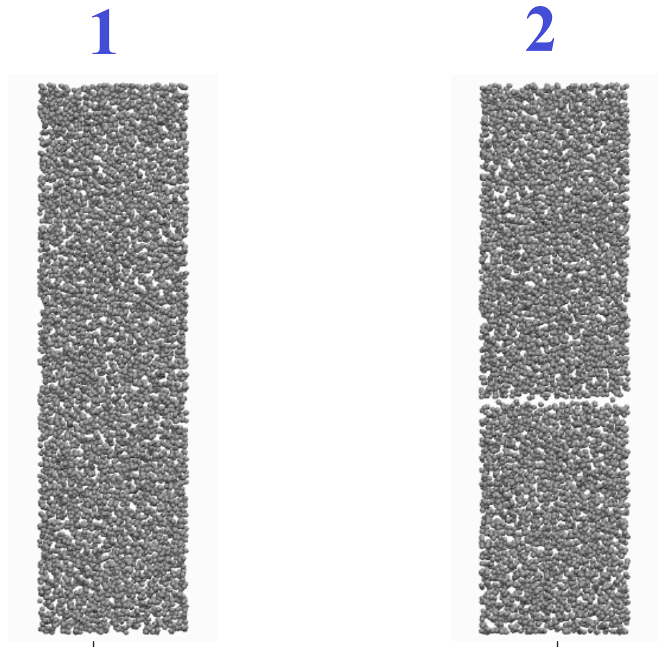
Open symbols from experiments, everything else from simulations

Banding to fracture

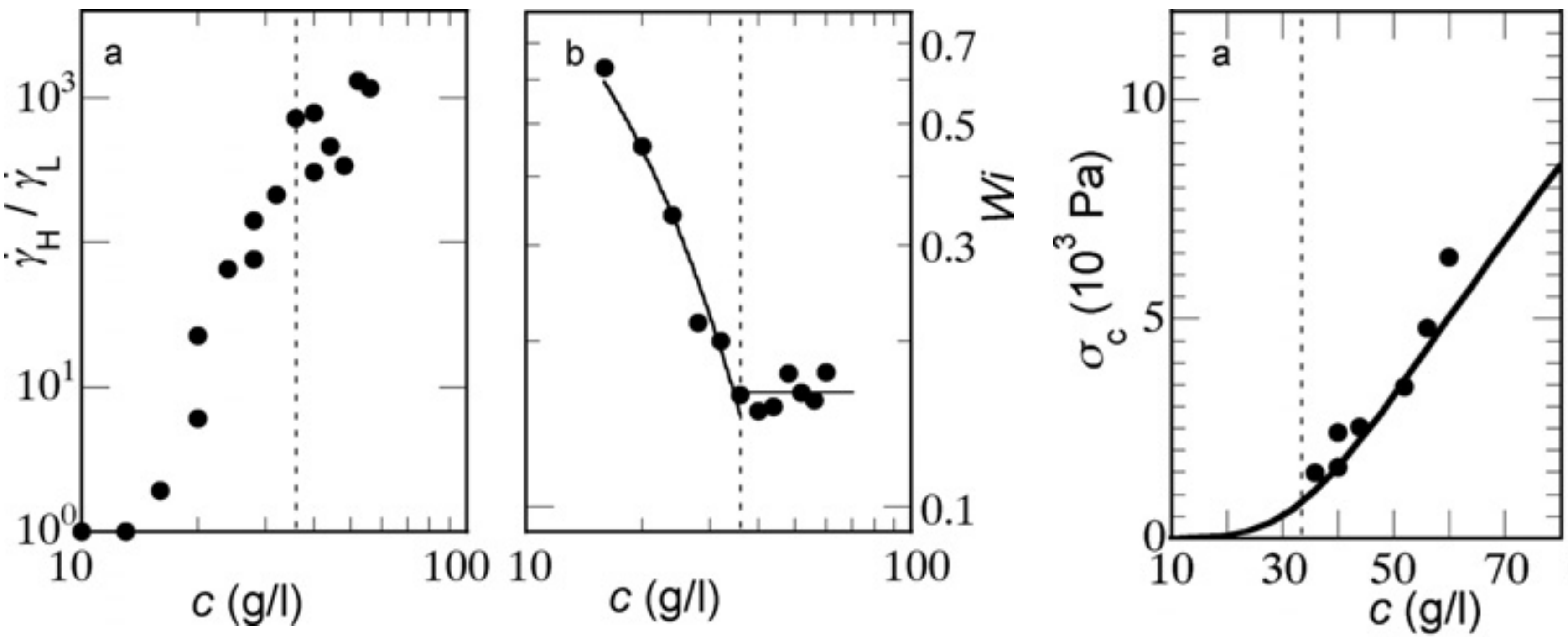


Melt fracture



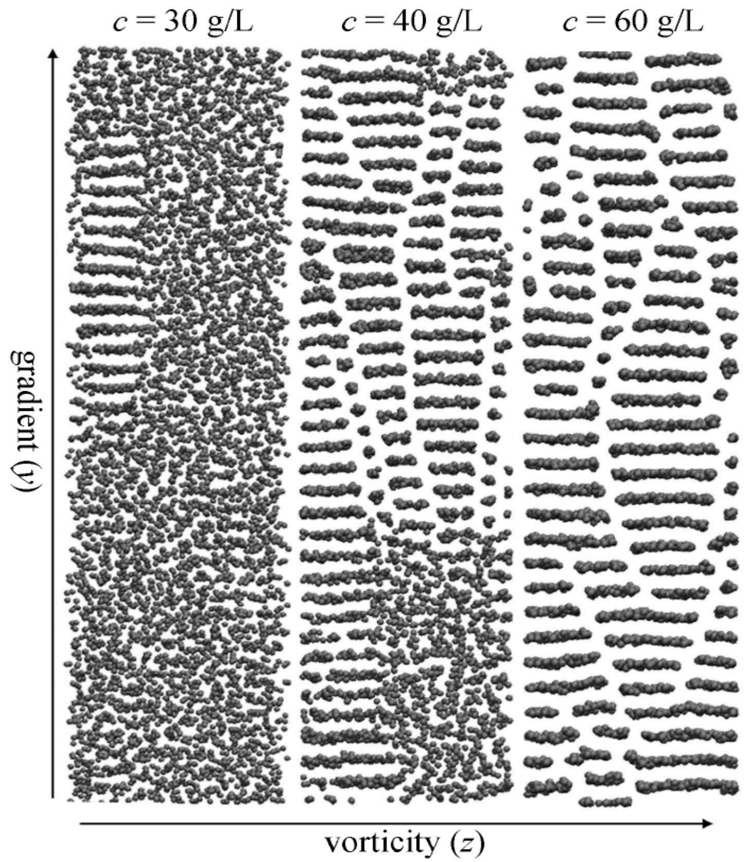


Melt fracture

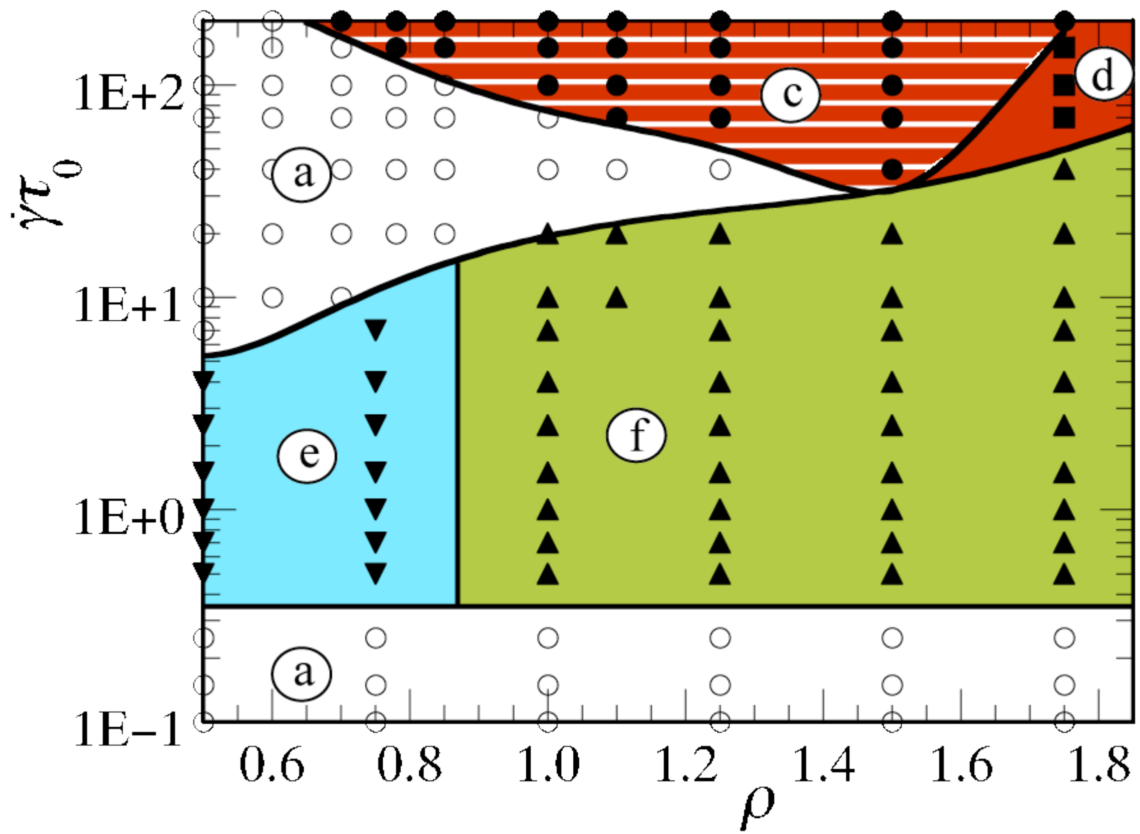


$$\dot{\gamma}\tau_0 = 1$$

Structure formation



Non-equilibrium phase diagram



Contents

1. Coarse chains
    - wormlike micelles
2. Coarse graining
3. Single particle models
    - star polymers
    - linear polymers
    - telechelic polymers

I am done

1. Coarse chains

   - wormlike micelles

2. Coarse graining

3. Single particle models

   - star polymers

   - linear polymers

   - telechelic polymers

Thank You

Brrrrrrrrrrrrrrrrrrrrrrrrrrriels

Simplified theory (1)

Langevin equation

$$M\frac{d^2\vec{R}_i}{dt^2} = -\nabla_i A - \xi\frac{d\vec{R}_i}{dt} + \vec{F}_i^{\,R}$$

$$\left\langle \vec{F}_i^{\,R}(t)\cdot\vec{F}_i^{\,R}(0)\right\rangle = 6k_B T\xi\delta(t)$$

Simplified theory (2)

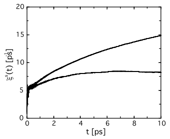
Potential of mean force

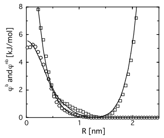
$$A(\vec{R}^N) = -k_B T \ln(P_N(\vec{R}^N))$$

$$P_N(\vec{R}^N) \approx \prod_{i=1}^{N-1} \prod_{j=i+1}^{N} P^{ev}(R_{ij}) \cdot \prod_i P^{fe}(R_{i,i+1}) \prod_i P^{ang}(\theta_{i,i+1})$$

$$A(\vec{R}^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi^{ev}(R_{ij}) + \sum_i \phi^{fe}(R_{i,i+1}) + \sum_i \phi^{ang}(\theta_{i,i+1})$$

Coarse model from atomistic simulation





Friction

Potential of mean force

Scaling with N

1) Characteristic time

$$\tau = \tau_R \propto N^2$$

2) Equilibrium $P_{eq} \propto \exp\left(-\frac{1}{kT} A(R^{3N}) - \frac{1}{kT} \sum_{\langle i,j \rangle} \frac{\alpha}{2} (n_{ij} - n_0(R_{ij}))^2 \right)$

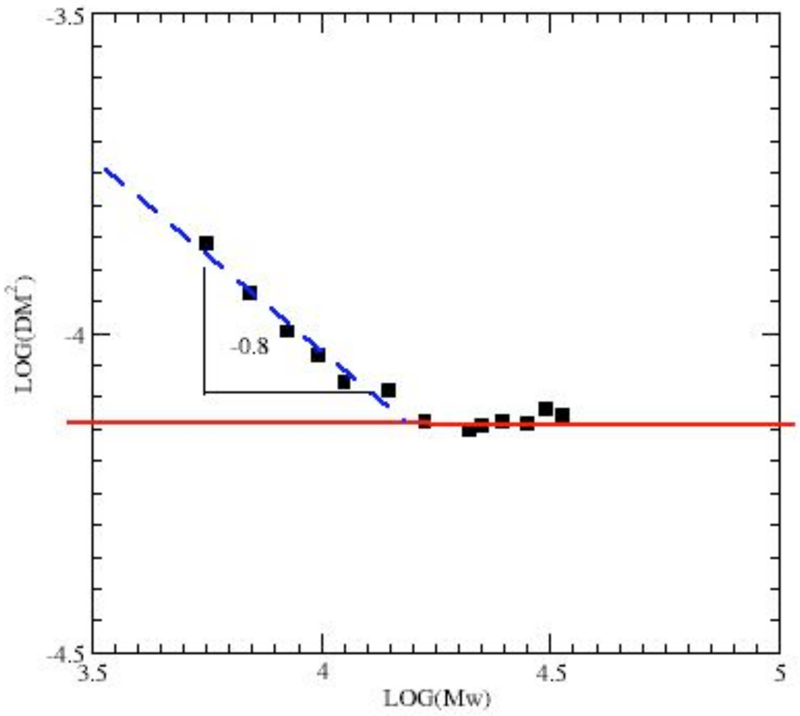
$$n_0(r) \propto \int d^3x \rho(\vec{x}) \rho(\vec{r} - \vec{x}) = n_0^{st}\left(\frac{r}{\sqrt{N}} \right)$$

$$\alpha = cst$$

3) Friction $\xi_i(\vec{r}_i) = \xi_e \sum_j \sqrt{n_{ij} n_0(r_{ij}) \Theta(n_{ij})} \propto N$

$$\xi_e \propto \sqrt{N}$$

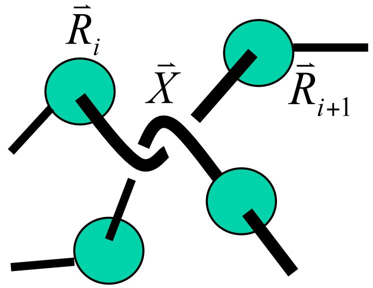
Diffusion coefficients of polymer melts



Discussion

• tubes conserve (to a large extent) prevalent configuration of centres of mass, as do the transient forces

• probabilities of entanglement survival-times decay exponentially; do we need tubes at long times?



• to describe elongational flow use dumbbells

• types of entanglements, and therefore their relaxation times depend on the distance between polymers.

Model and Dynamics

Brownian dynamics in a slow bath

$$d\vec{R}_i = \frac{1}{\xi_i}\left[-\vec{\nabla}_i\Phi + \vec{F}_i^T\right]dt + \sqrt{\frac{2kTdt}{\xi_i}}\vec{\Theta} + \vec{\nabla}_i\left[\frac{kT}{\xi_i}\right]dt$$

$$\vec{F}_i^T = \alpha\sum_j\left[n_{ij} - n_0(R_{ij})\right]\vec{\nabla}_i n_0(R_{ij})$$

$$dn_{ij} = -\frac{1}{\tau(R_{ij})}\left[n_{ij} - n_0(R_{ij})\right]dt + \sqrt{\frac{2kTdt}{\alpha\tau(R_{ij})}}$$

n_{ij} = **number of bridges between** i **and** j

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Coarse graining (dynamics)

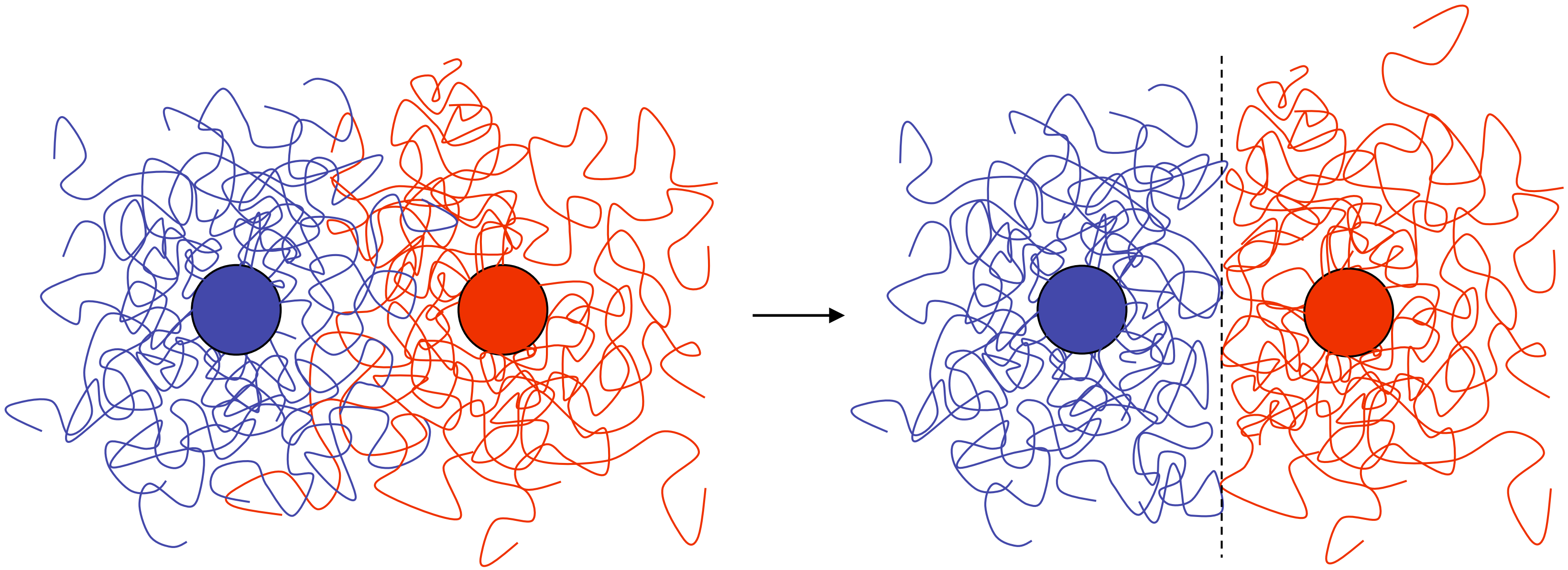
Eliminate variables: $\{R, \dot{R}, q, \dot{q}\} \Rightarrow \{R, \dot{R}\}$

$$m_n \frac{d^2 R_n}{dt^2} = -\frac{\partial \Phi}{\partial R_n} + \sum_m \int_0^t d\tau \varsigma_{n,m}(t-\tau) \frac{dR_m}{dt}(\tau) + F_n^R(t)$$

$$\left\langle F_n^R(t) F_m^R(0) \right\rangle = k_B T \varsigma_{n,m}(t)$$

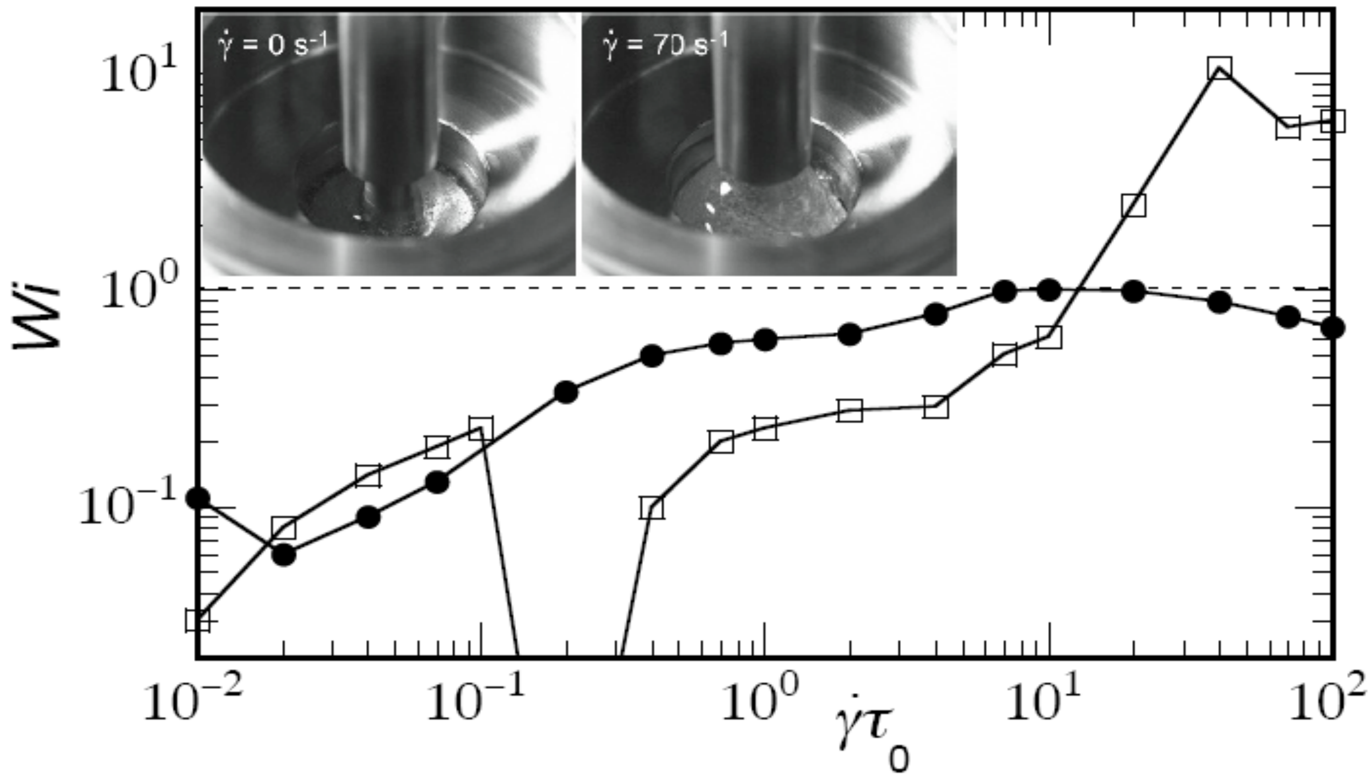
Only useful in case $q(t)$ is much faster than $R(t)$, i.e. when no memory occurs

Entanglement free energy



$$\Delta A = \frac{\alpha}{2}[n_0(R_{ij})]^2$$

Experiments



Open symbols 60 g/l, filled symbols 20 g/l