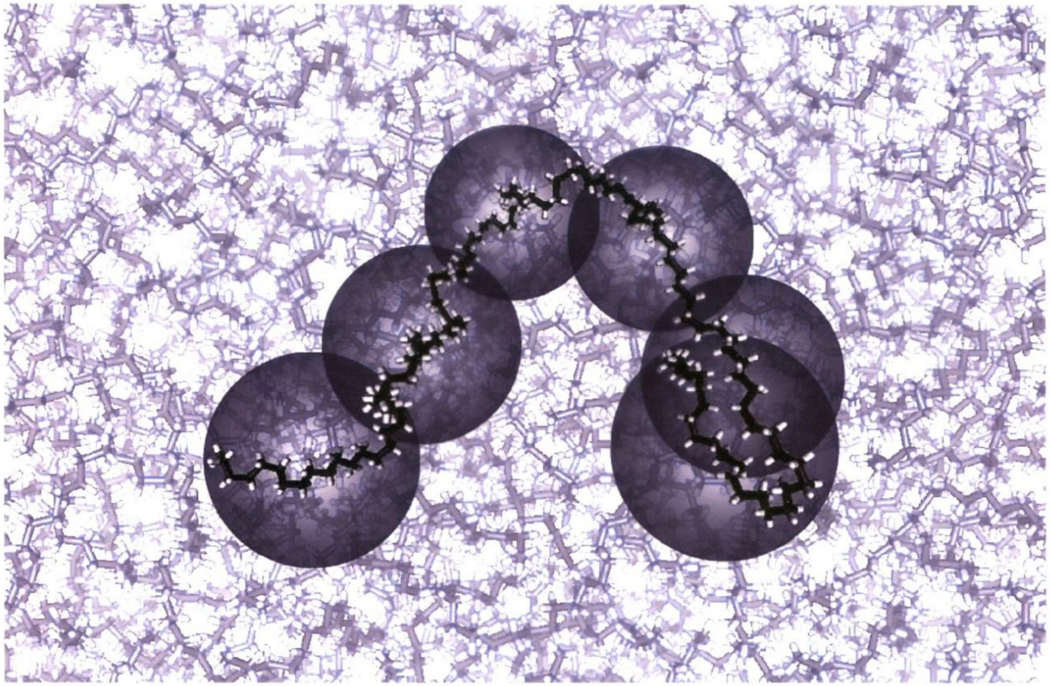
Memory Matters



W.J. Briels

A. Van den Noort, W.K. Den Otter, P. Kindt, J.T. Padding, J. Sprakel, I.S. Santos de Oliveira, D. Vlassopoulos, C. Bailly, J. Dhont, L. Liu.

Memory and transient forces in coarse grain simulations of complex polymers

Memory and transient forces in coarse grain simulations of complex polymers

But first

Netherlands and environments

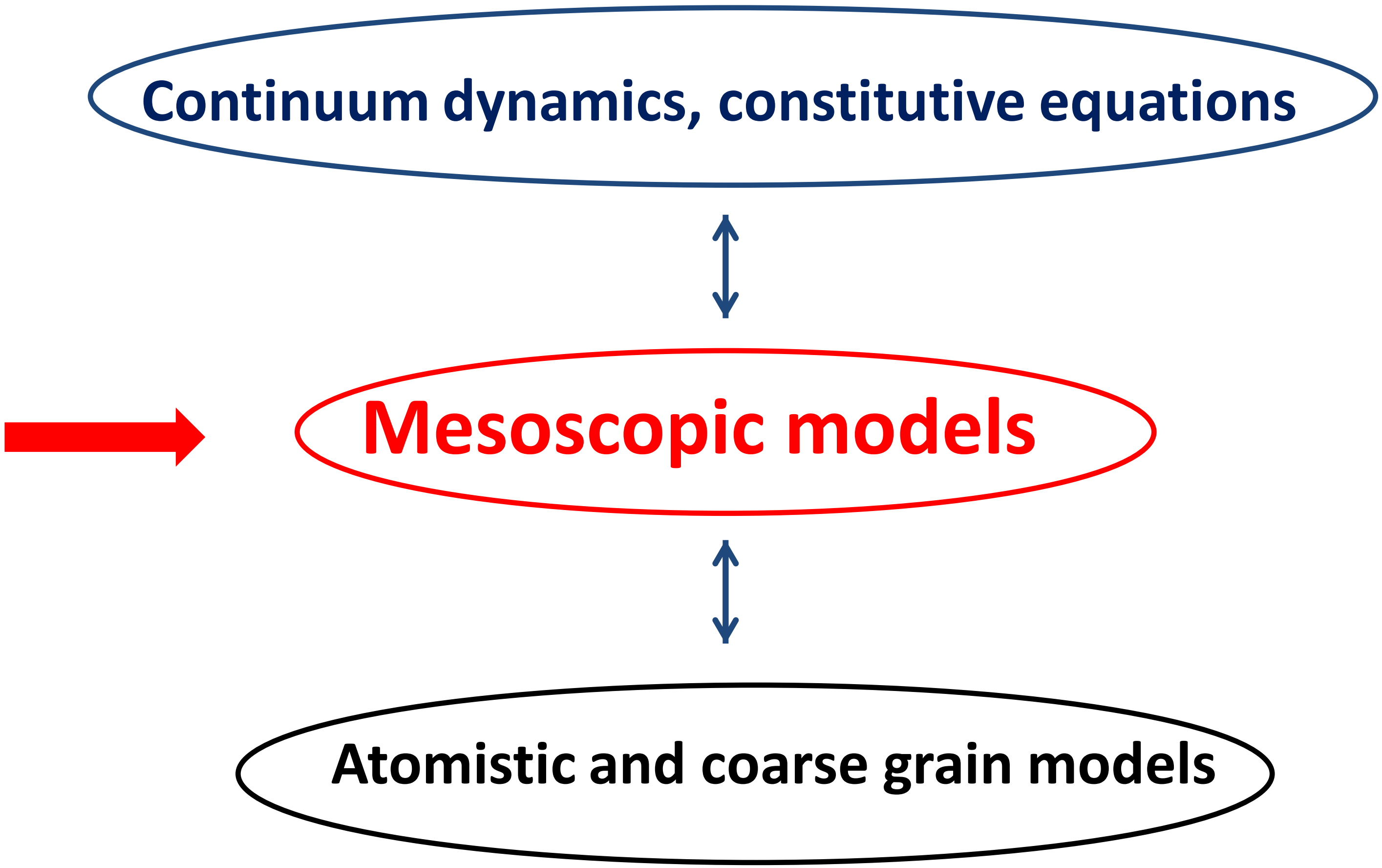
Netherlands and environments

Born

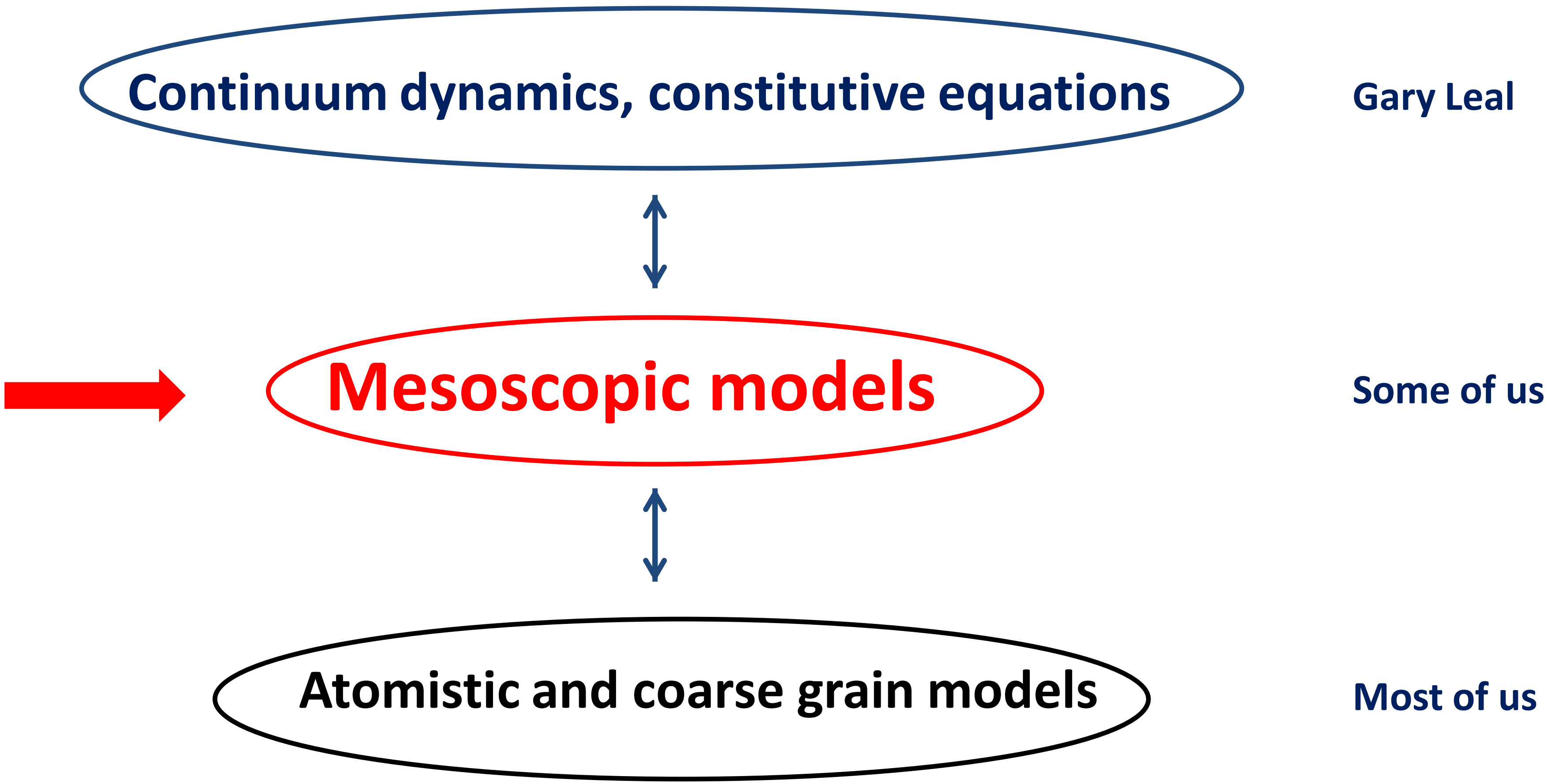
Enschede

Born

Goal


Continuum dynamics, constitutive equations
Mesoscopic models
Atomistic and coarse grain models

Goal



Continuum dynamics, constitutive equations
Gary Leal
Mesoscopic models
Some of us
Atomistic and coarse grain models
Most of us

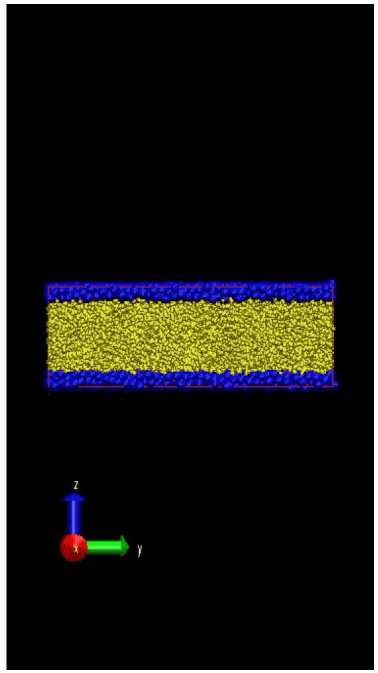
Examples

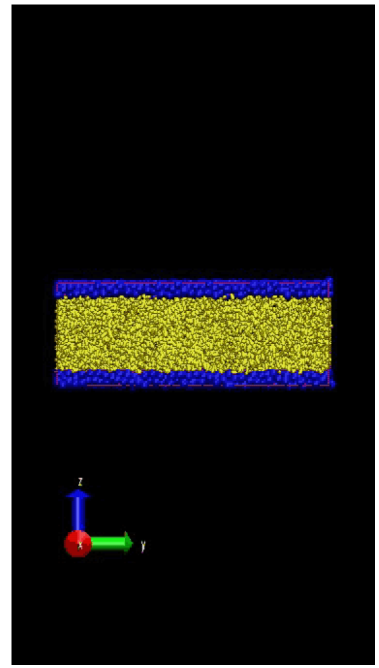
Rheology of

- Star polymers
- Telechelic polymer solutions
- Colloids in visco-elastic media
- Pressure sensitive adhesives

Interplay between internal and translational dynamics

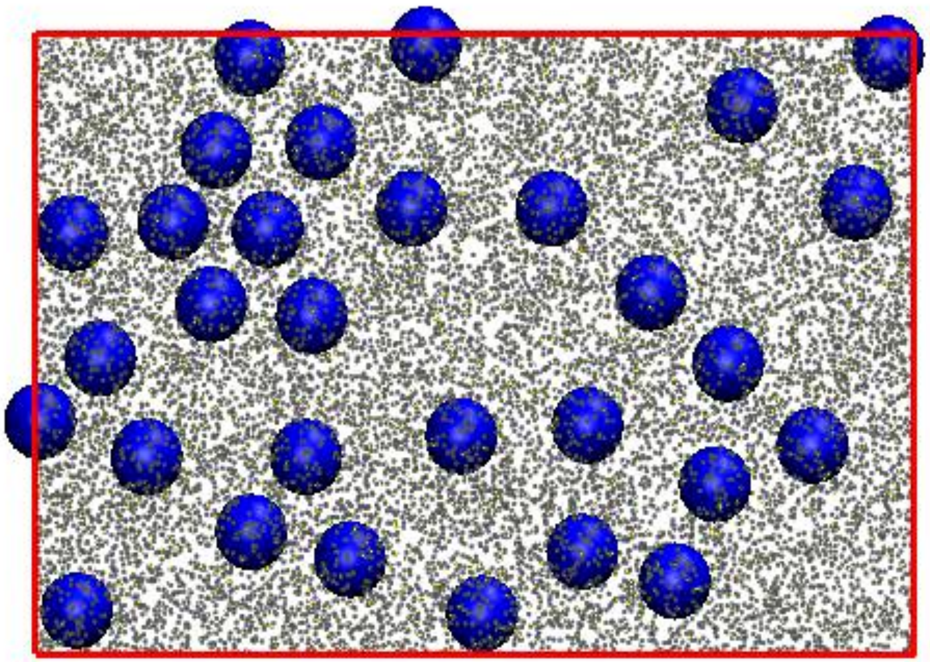
Pressure sensitive adhesives

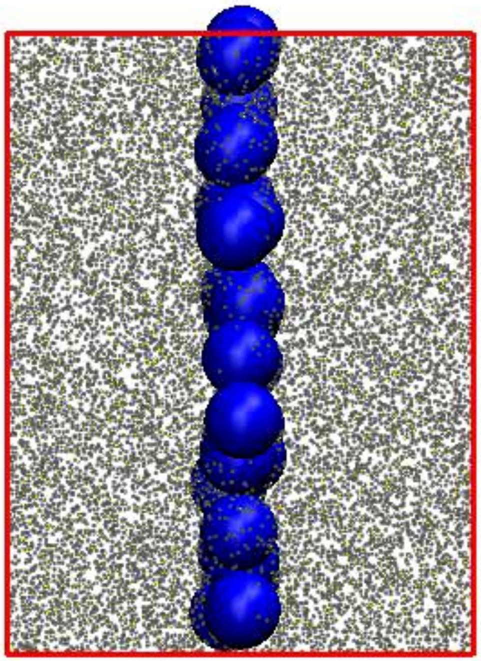




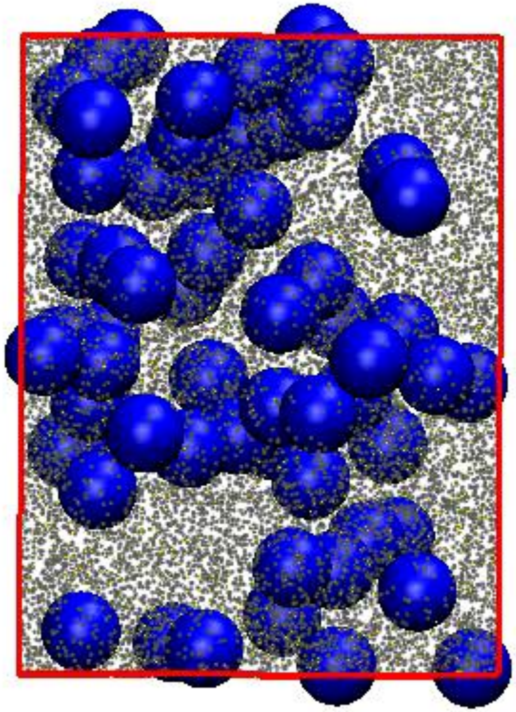
Weak adhesion **Strong adhesion**

Colloids in polymer solutions





You want it bigger?



Crash course on coarse graining

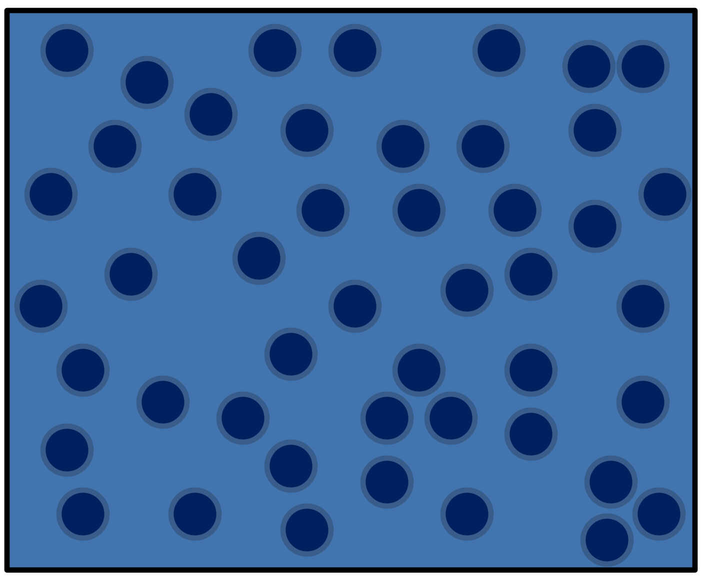
Crash course on coarse graining

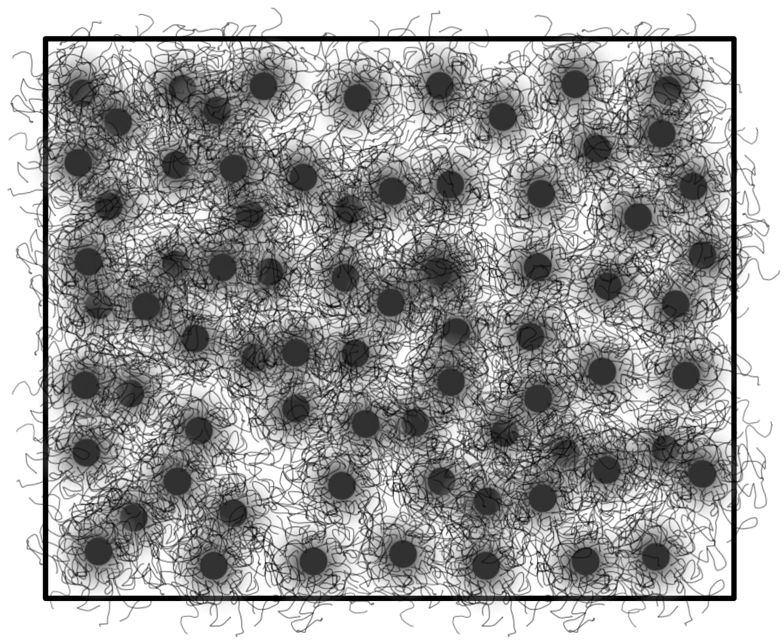
Terminology

Retained coordinates = Particles
Eliminated coordinates = Bath

Coarse Grain Picture

Experimentally: limited resolution
Simulationally: limited computing power
Conceptionally: enlarged understanding

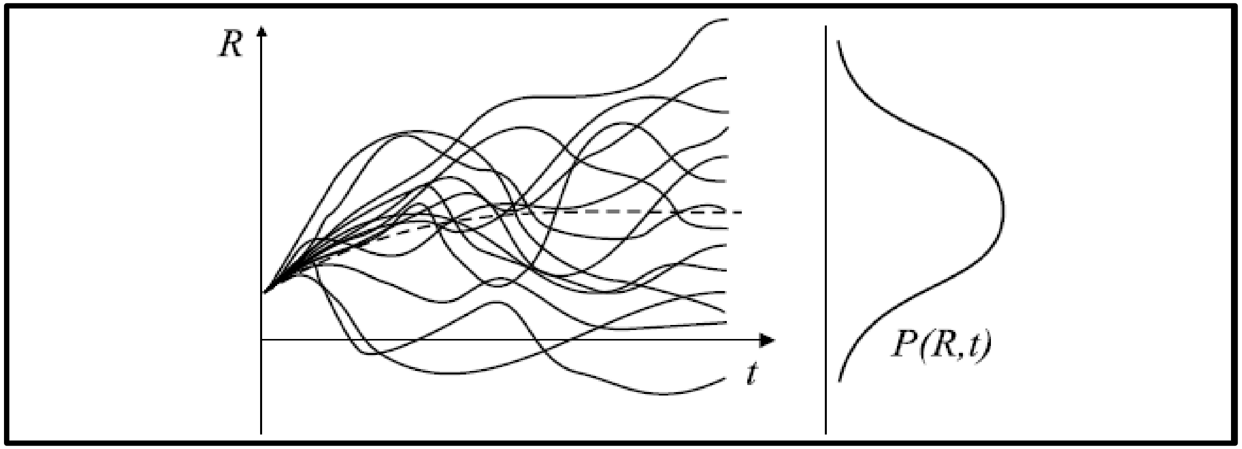




Strategy

Consider a particle with given initial position and initial velocity

Plot its path for different initial configurations and velocities of the bath



At time t you will get a distribution of positions and velocities

Equations of motion

Generalized Langevin equation

$$\frac{dP_n}{dt}(t) = -\frac{\partial A}{\partial R_n}(t) - \sum_m \int_0^t d\tau \, \frac{P_m(\tau)}{M} \beta \left\langle F_m^R F_{n,t-\tau}^R \right\rangle_B (\tau) + F_{n,t}^R \qquad \left\langle F_{n,t}^R \right\rangle_B = 0$$

Equations of motion

Generalized Langevin equation

$$\frac{dP_n}{dt}(t) = -\frac{\partial A}{\partial R_n}(t) - \sum_m \int_0^t d\tau \, \frac{P_m(\tau)}{M} \beta \left\langle F_m^R F_{n,t-\tau}^R \right\rangle_B (\tau) + F_{n,t}^R \qquad \left\langle F_{n,t}^R \right\rangle_B = 0$$

Markov approximation

$$\frac{dP_n}{dt}(t) = -\frac{\partial A}{\partial R_n}(t) - \sum_m \frac{P_m(t)}{M} \int_0^t d\tau \beta \left\langle F_m^R F_{n,t-\tau}^R \right\rangle_B (t) + F_{n,t}^R$$

Equations of motion

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$$\frac{dP_n}{dt}(t) = -\frac{\partial A}{\partial R_n}(t) - \sum_m \frac{P_m(t)}{M} \xi_{m,n}(t) + F_{n,t}^R \qquad \left\langle F_m^R F_{n,\tau}^R \right\rangle (t) = 2kT \xi_{m,n} \delta(t-\tau)$$

Equations of motion

Generalized Langevin equation

$$\frac{dP_n}{dt}(t) = -\frac{\partial A}{\partial R_n}(t) - \sum_m \int_0^t d\tau \frac{P_m(\tau)}{M} \beta \left\langle F_m^R F_{n,t-\tau}^R \right\rangle_B (\tau) + F_{n,t}^R \qquad \left\langle F_{n,t}^R \right\rangle_B = 0$$

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Overdamped; average over long periods

$$0 = -\frac{\partial A}{\partial R_n}(t) - \sum_m \frac{P_m(t)}{M} \xi_{m,n}(t) + \tilde{F}_{n,t}^R$$

See Masao Doi

Brownian dynamics

General

$$0 = -\frac{\partial A}{\partial R_n}(t) - \sum_m \frac{P_m(t)}{M}\xi_{m,n}(t) + \tilde{F}^R_{n,t}$$

$$\frac{P_n(t)}{M} = -\sum_m \frac{\partial A}{\partial R_m}(t)\xi^{-1}_{m,n}(t) + \sum_m \tilde{F}^R_{m,t}\xi^{-1}_{m,n}(t)$$

Brownian dynamics

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$$0 = -\frac{\partial A}{\partial R_n}(t) - \sum_m \frac{P_m(t)}{M}\xi_{m,n}(t) + \tilde{F}^R_{n,t}$$

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Simple example (diagonal friction matrix)

$$\frac{dR_n}{dt} = -\frac{1}{\xi_n}\frac{\partial A}{\partial R_n} + \frac{\tilde{F}^R_{n,t}}{\xi_n}$$

Brownian dynamics

General

$$0 = -\frac{\partial A}{\partial R_n}(t) - \sum_m \frac{P_m(t)}{M}\xi_{m,n}(t) + \tilde{F}^R_{n,t}$$

$$\frac{P_n(t)}{M} = -\sum_m \frac{\partial A}{\partial R_m}(t)\xi^{-1}_{m,n}(t) + \sum_m \tilde{F}^R_{m,t}\xi^{-1}_{m,n}(t)$$

Simple example (diagonal friction matrix)

$$\frac{dR_n}{dt} = -\frac{1}{\xi_n}\frac{\partial A}{\partial R_n} + \frac{\tilde{F}^R_{n,t}}{\xi_n}$$

A bit more precise

$$dR_n = -\frac{1}{\xi_n}\frac{\partial A}{\partial R_n}dt + \frac{\partial}{\partial R_n}\frac{kT}{\xi_n}dt + \sqrt{\frac{2kTdt}{\xi_n}}ran$$

How about memory?

Borneo

Netherlands
International boundary
Province boundary
National capital
Province capital
Railroad
Expressway
Road
North Sea
WEST FRISIAN ISLANDS
FRIESLAND
GRONINGEN
DRENTHE
NOORD HOLLAND
FLEVOLAND
OVERIJSSEL
UTRECHT
GELDERLAND
ZUID HOLLAND
ZEELAND
BRABANT
LIMBURG
Amsterdam
BELGIUM
FEDERAL REPUBLIC OF GERMANY
Heinsberg
N572
Havert
Born
Breberen
L227
Selfkant
Randerath
Sittard
Wehr
Gangelt
Kogenbroich
Geleen
Onderbanken
Geilenkirchen
B56
Schinnen
Brunssum
bing
Hoensbroek
© 2011 Microsoft

Mercator


Born
Op Bicht
Nustadt
Millen
Bafelen
Huengen
Breberé
Wauraid
Leemburg
Guttichauen
Sittert
Tudder
Gangelt
Birredo
Mesick
Weer
Berg
Vrmont
Munstergeleen
Lalbeec
Schinfelt
Hillesberg
Bruisen
Scarpezee
Stein
Beeck
Spaubeec
Nut
Gebroken
Schin
Oorbeec


ÆTATIS
SVÆ LXII.
GERARDI MERCATORIS RVPELMVNDANI EFFIGIEM ANNOR.
DVORVM ET SEX - AGINTA. SVI ERGA IPSVM STVDII
CAVSA DEPINGI CVRABAT FRANC. HOG. CIↃ. IↃ. LXXIV.

Mercator = Kremer

The cause of memory (star polymers)

Briels

In the small scale simulation the deformation of the eliminated degrees of freedom is correlated with the recent displacements of the particles

The cause of memory (star polymers)

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Briels

In the small scale simulation the deformation of the eliminated degrees of freedom is correlated with the recent displacements of the particles

Everaers

Particles move with their nose in the wind and their hair in the back

The cause of memory (star polymers)

Briels

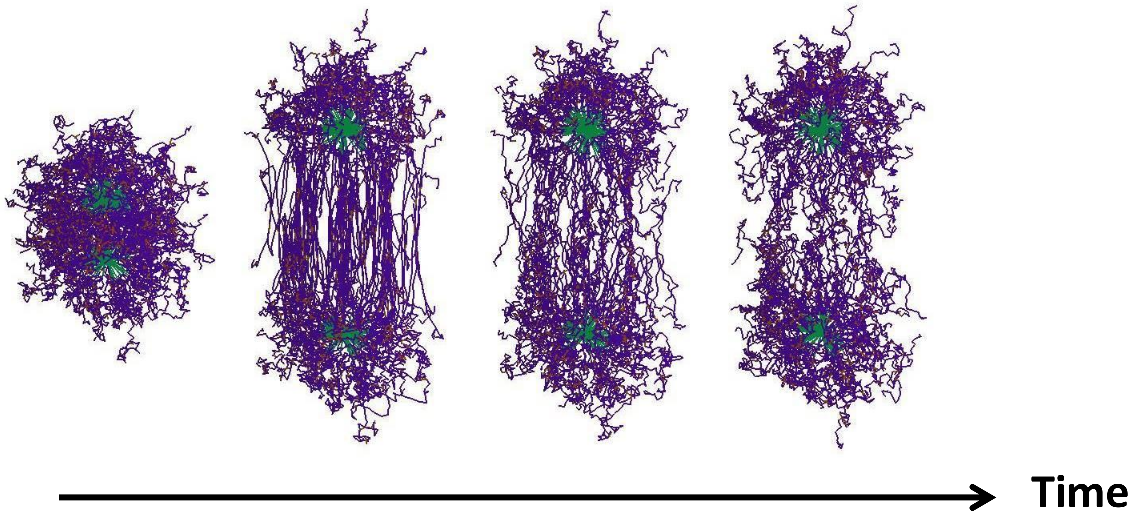
In the small scale simulation the deformation of the eliminated degrees of freedom is correlated with the recent displacements of the particles

Everaers

Particles move with their nose in the wind and their hair in the back*

*Not because of inertia, but because of entanglements with other stars

The cause of memory



Introduce variables to keep track of the state of the bath

RaPiD

Degrees of freedom

- **Particle positions** $\left\{\vec{R}_i ; i=1,\ldots,N\right\}$
- **State of the bath** $\left\{n_{ij} ; \forall pairs\right\}$

RaPiD

Degrees of freedom

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- **State of the bath** $\left\{n_{ij}; \forall pairs\right\}$

At equilibrium

$$\left\langle n_{ij}\right\rangle = n_0(R_{ij})$$

RaPiD

Degrees of freedom

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- **State of the bath** $\left\{n_{ij}; \forall pairs\right\}$

At equilibrium

$$\left\langle n_{ij}\right\rangle = n_0(R_{ij})$$

Free energy

$$\Phi(R^{3N},\{n_{ij}\}) = A(R^{3N}) + \frac{1}{2}\alpha\sum_{i,j}(n_{ij} - n_0(R_{ij}))^2$$

RaPiD, Eqs. of motion

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

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

Brown

Onsager

RaPiD, Eqs. of motion

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

Brown

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

Onsager

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

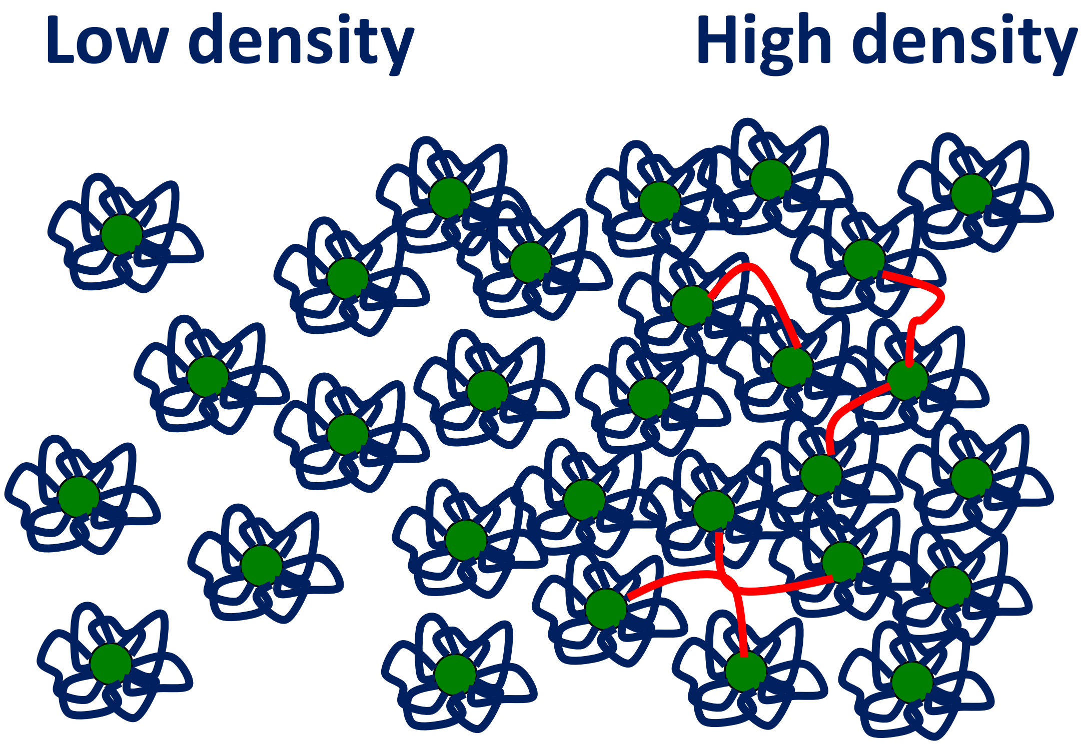
Transient force

Examples

-Telechelic Polymer Solutions

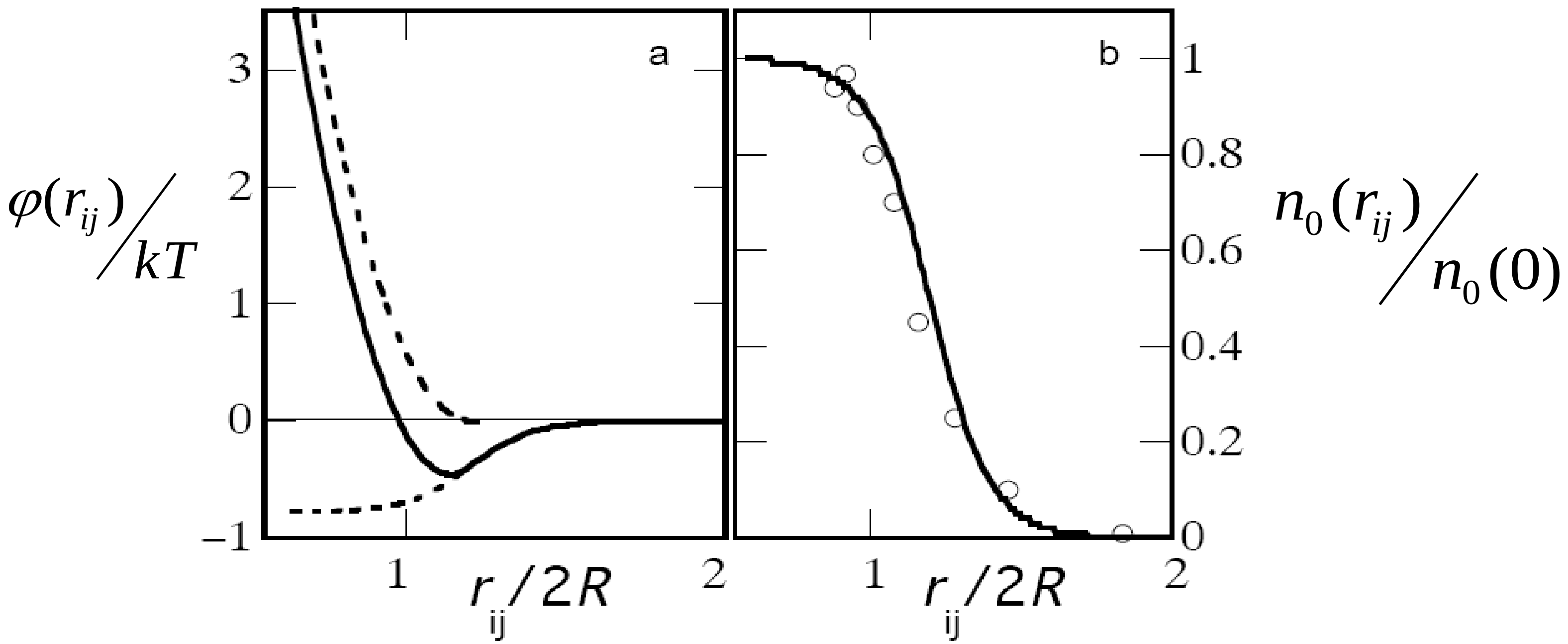
- Pressure sensitive adhesives

Telechelic polymers



n_{ij} = number of bridges

Phi and n



Pair-wise free energy from SCF calculations

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

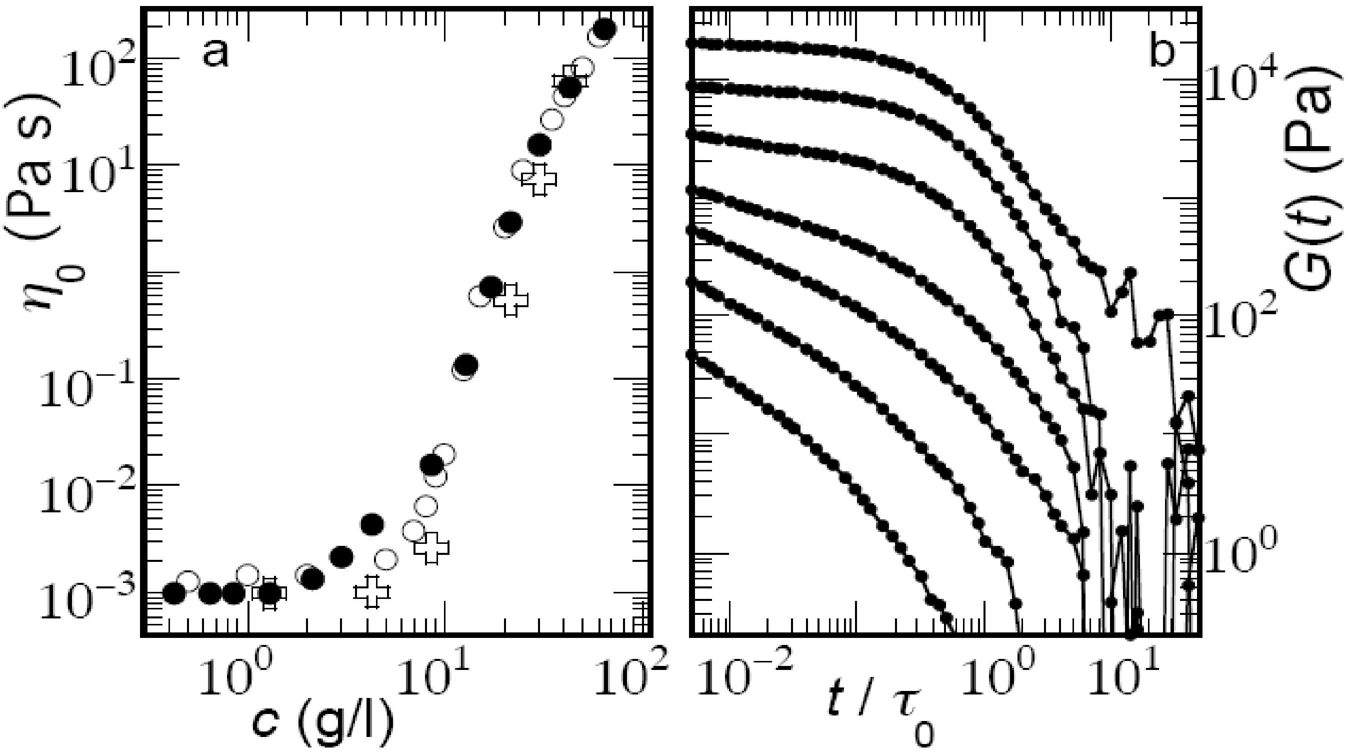
Parameters

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

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

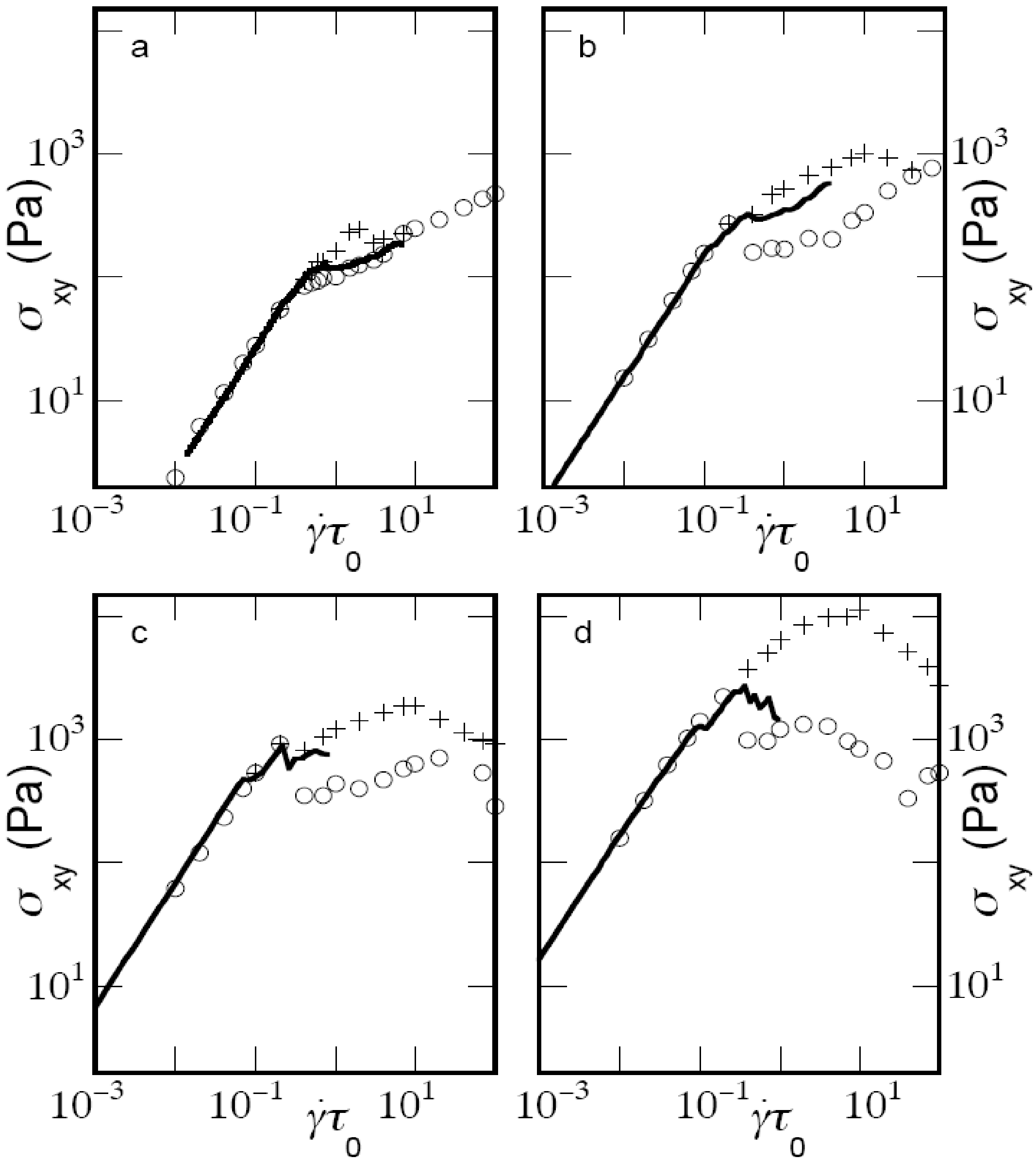
$$\lim_{R \to 0} n_0(R) = \frac{f}{12}$$

Linear rheology



Viscosities used to fix α

Predicted non linear rheology

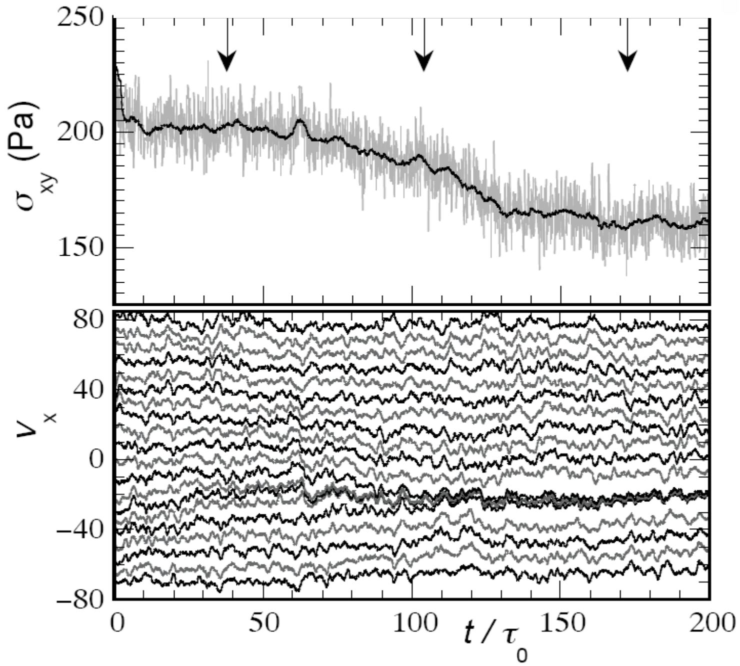


From upper left to lower right, increasing concentration

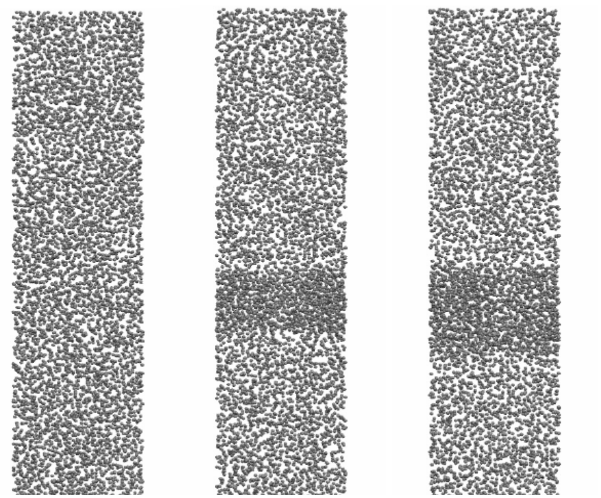
Shear banding

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

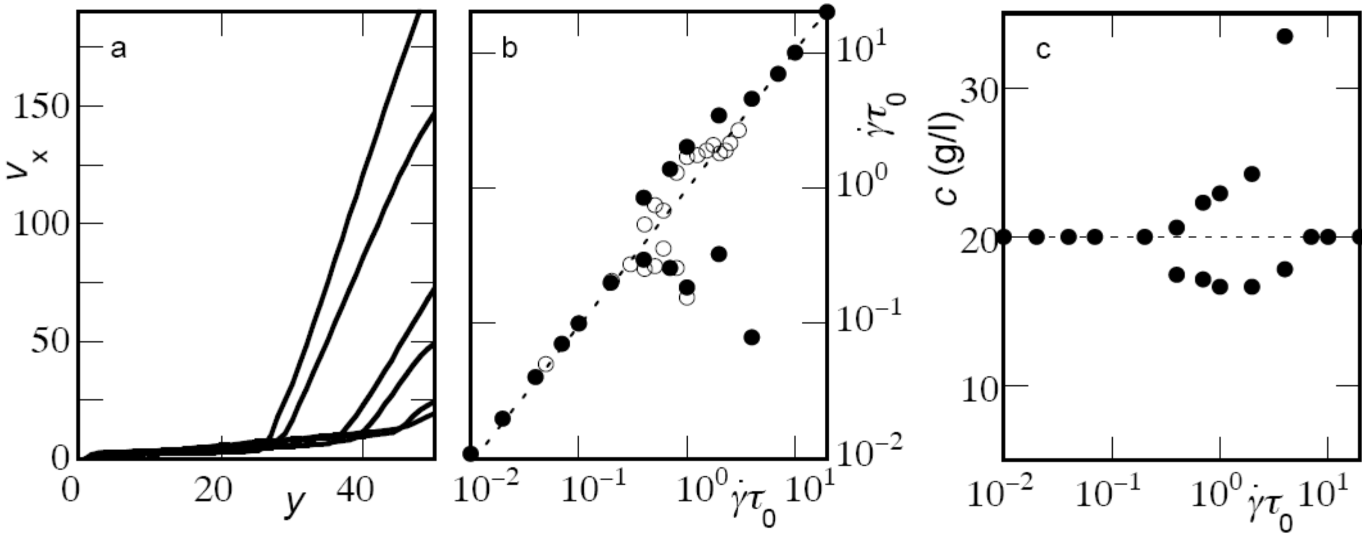
1 2 3



1 2 3

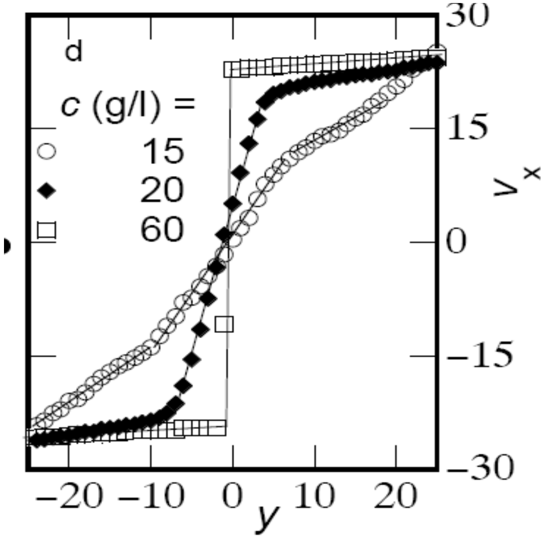


Shear banding 20 g/l

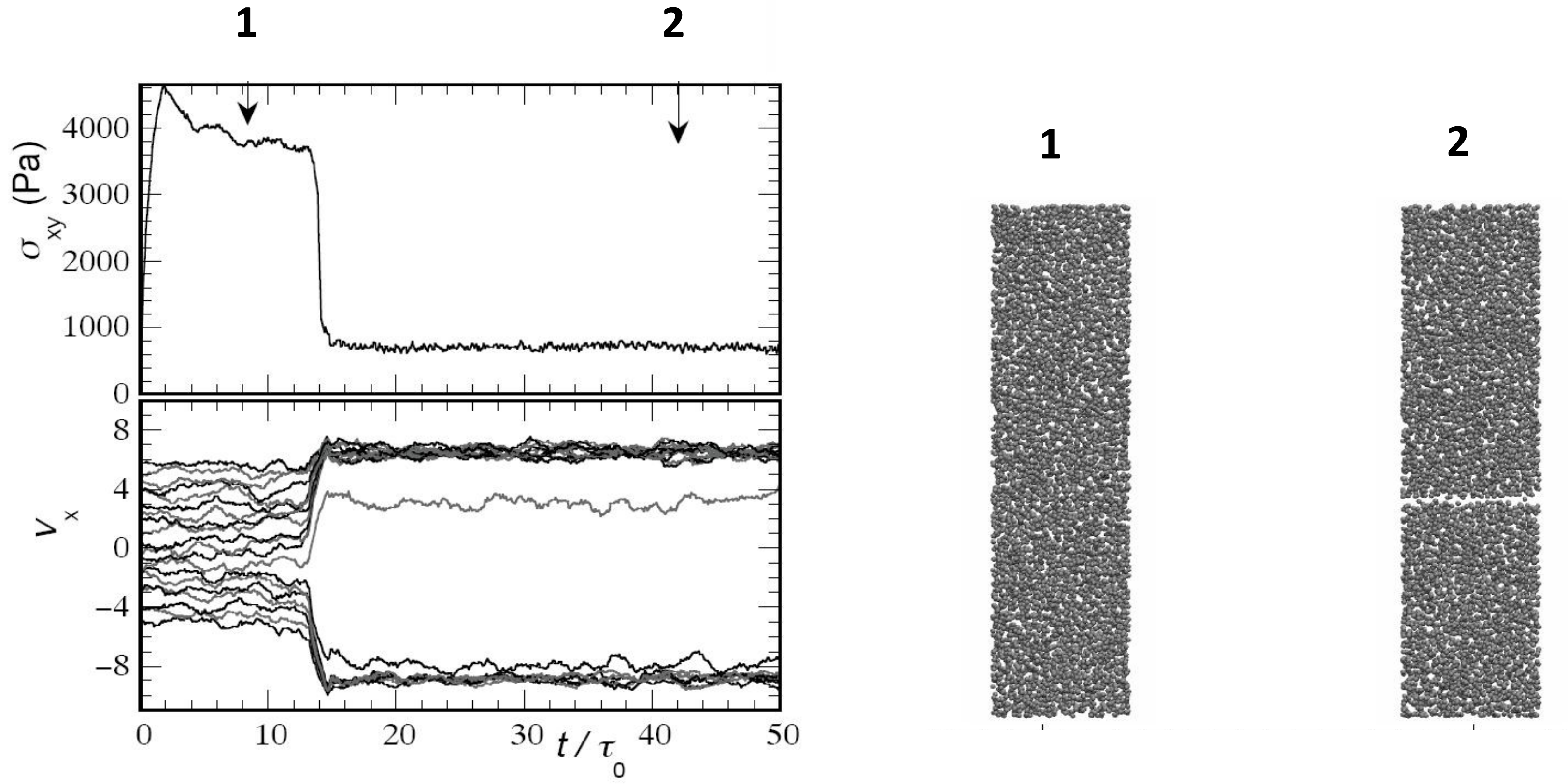


Open symbols from experiments, everything else from simulations

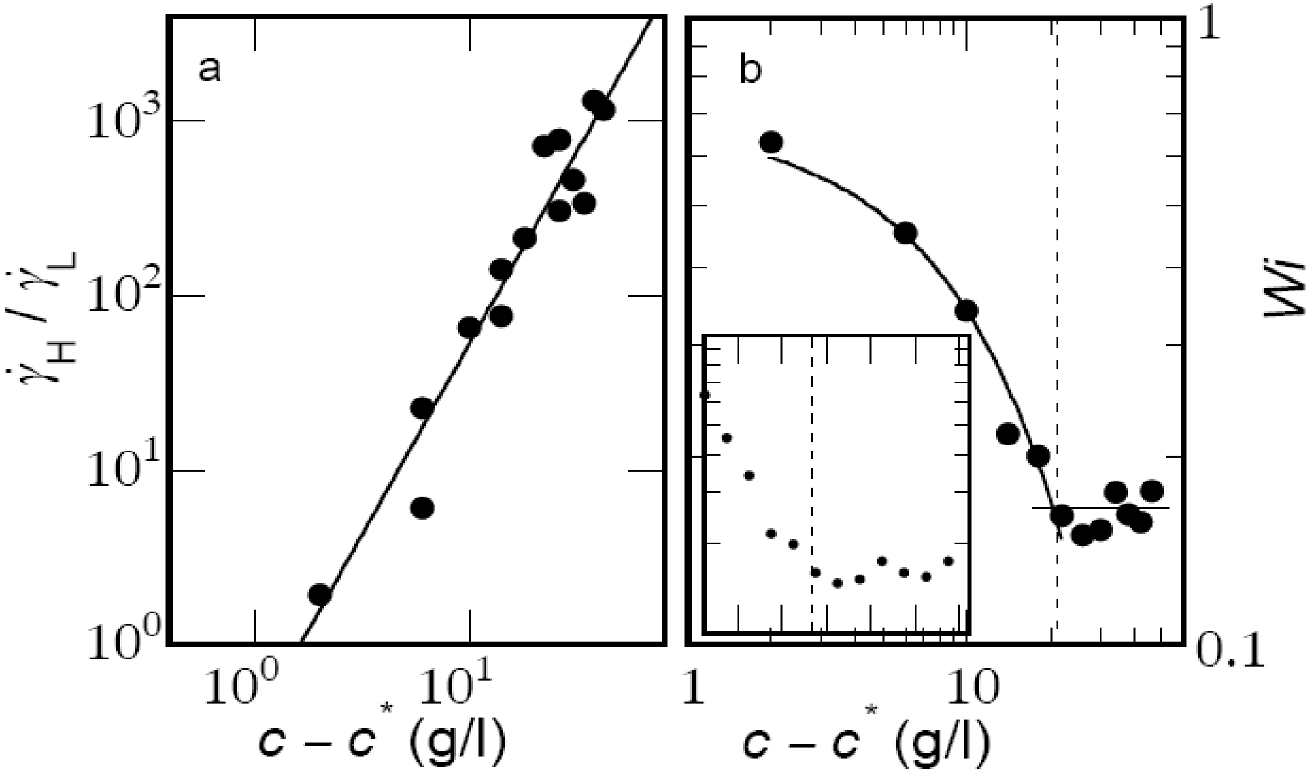
Banding to fracture



Melt fracture

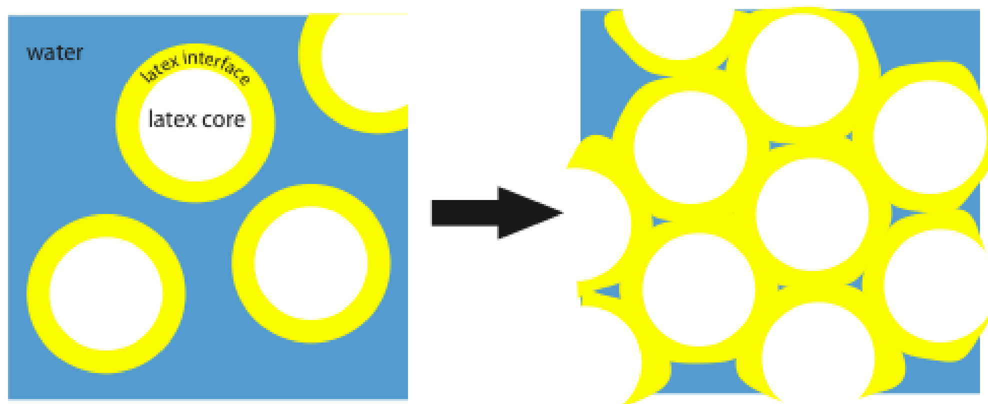


Melt fracture



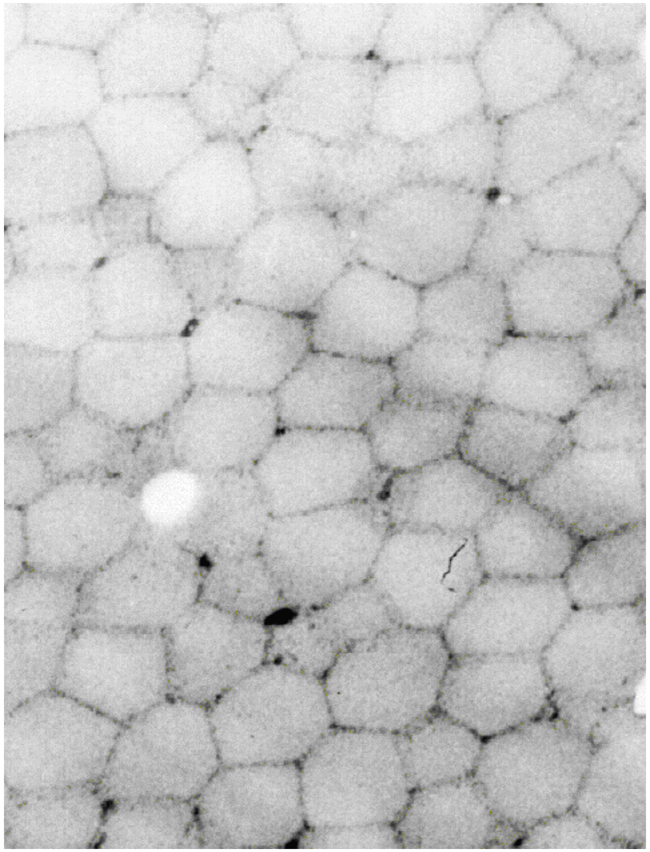
Pressure sensitive adhesives

Dry latex dispersion stabilized by surfactant



Can we simulate Scotch Tape ??

Pressure sensitive adhesives



Transmission Ellectron Micrograph

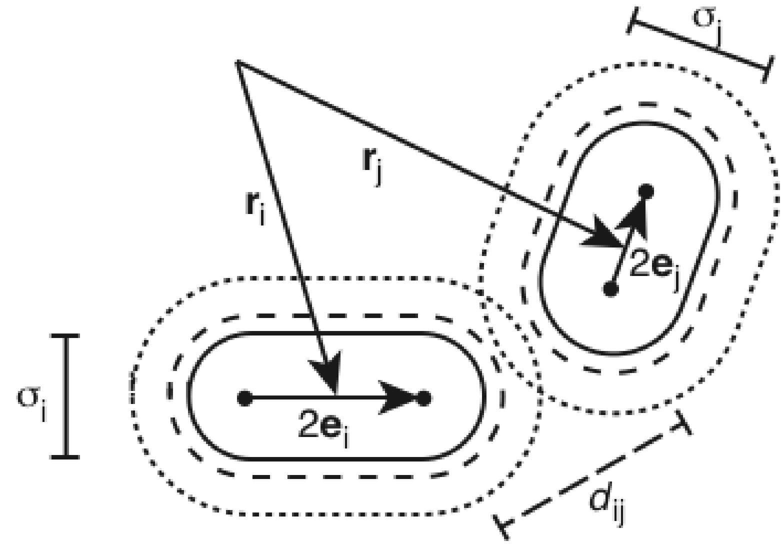
Sticky, deformable latex particles

Each latex particle is an extensible hemispherical cylinder

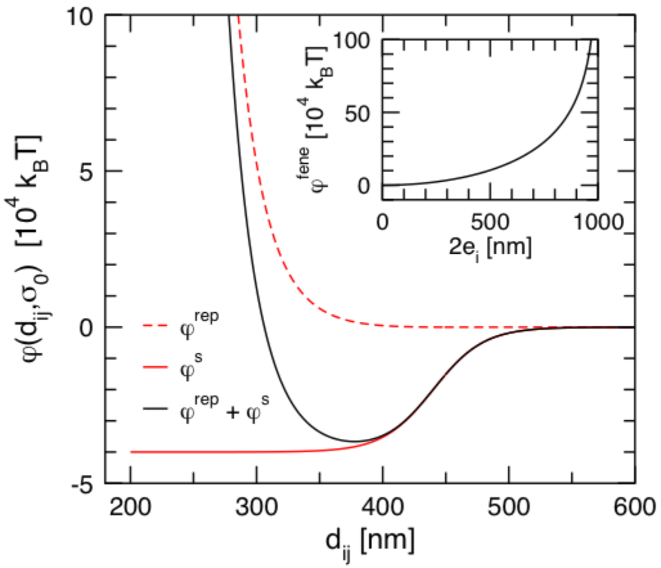
- **Extensible particle with constant volume**
- **Intraparticle fene spring**

$$\varphi^{fene}(e) = -\frac{1}{2}kR_0^2 \ln\left[1 - \left(\frac{2e}{R_0}\right)^2\right]$$

- **interparticle interactions are function of closest distance *d***



Conservative interactions



- **Soft repulsive interaction**
- **Attractive 'sticker' interaction, proportional to the number of hydrogen bonds**

Transient interactions

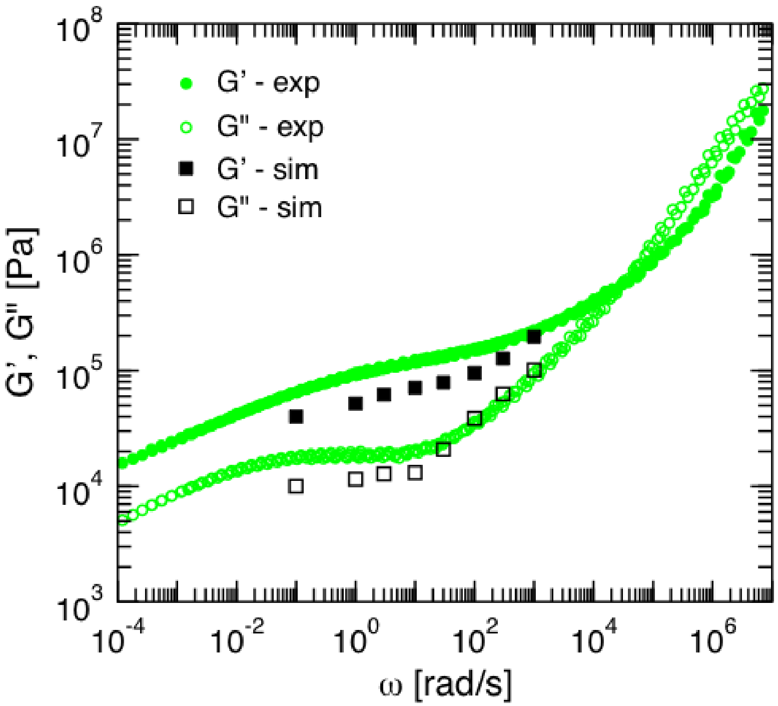
Total free energy

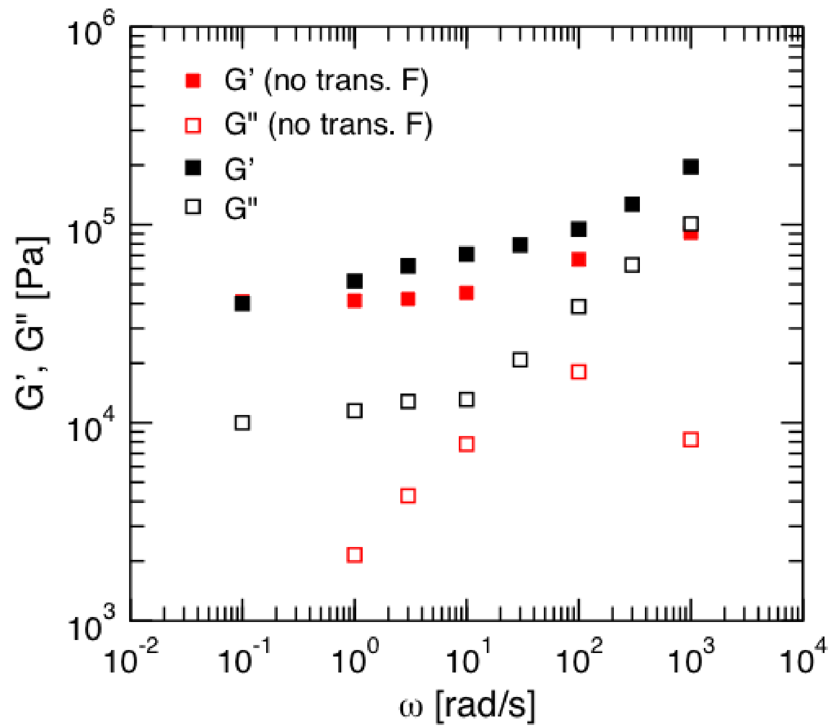
$$\Phi(R, n^s, n^e) = A(R) + B(R, n^s, n^e)$$

Two types of transient forces

$$B(R, n^s, n^e) = \frac{1}{2}\sum_{i \neq j}\left\{\frac{1}{2}\alpha^s\left[n_{ij}^s - n_0^s(d_{ij}, \sigma_{ij})\right]^2 + \frac{1}{2}\alpha^e\left[n_{ij}^e - n_0^e(d_{ij}, \sigma_{ij})\right]^2\right\}$$

Moduli using initial rough estimates for parameters

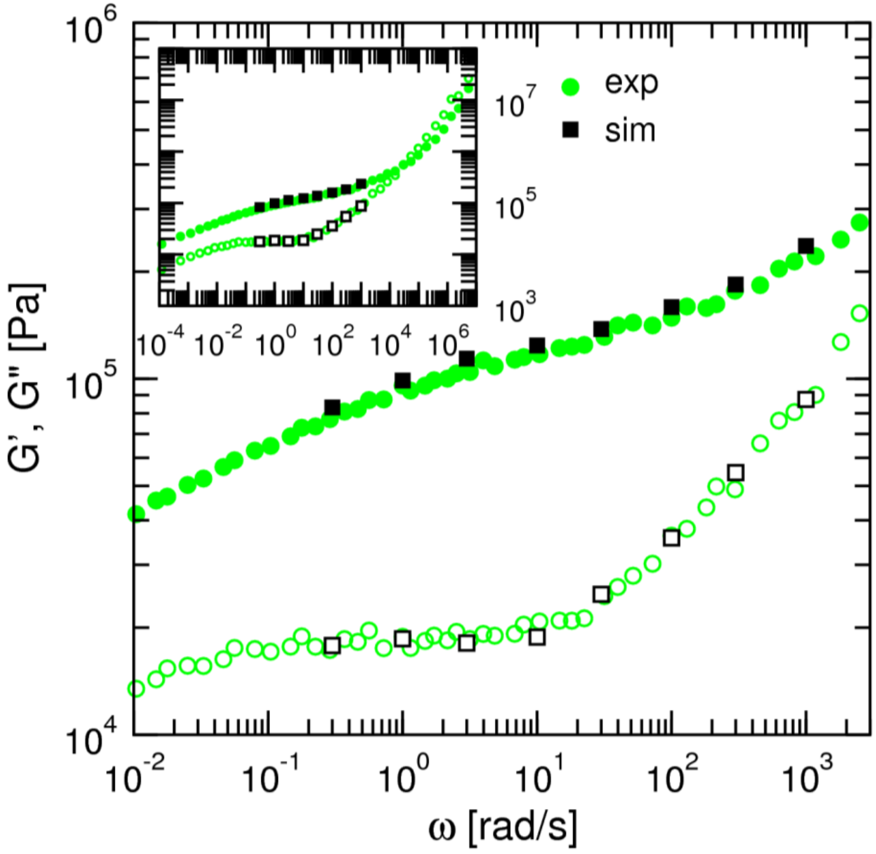




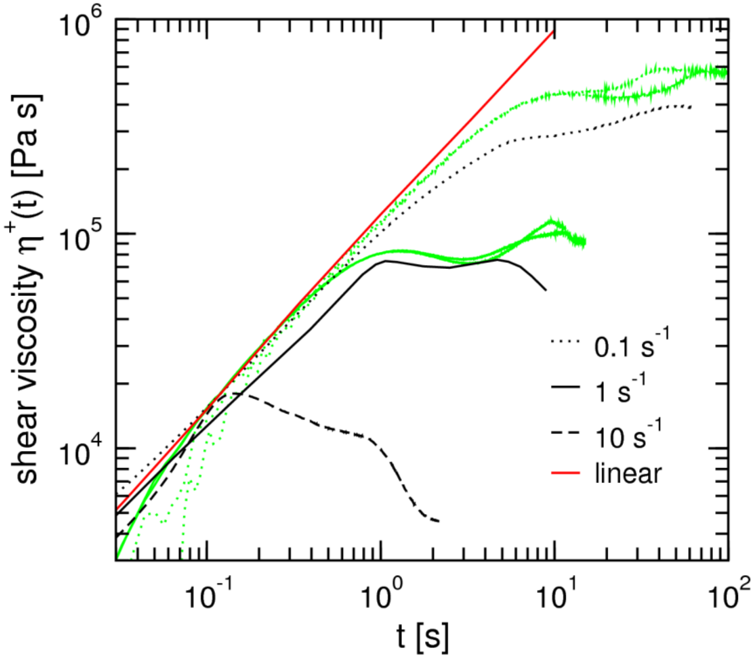
Black: simulation

Red: no transient forces

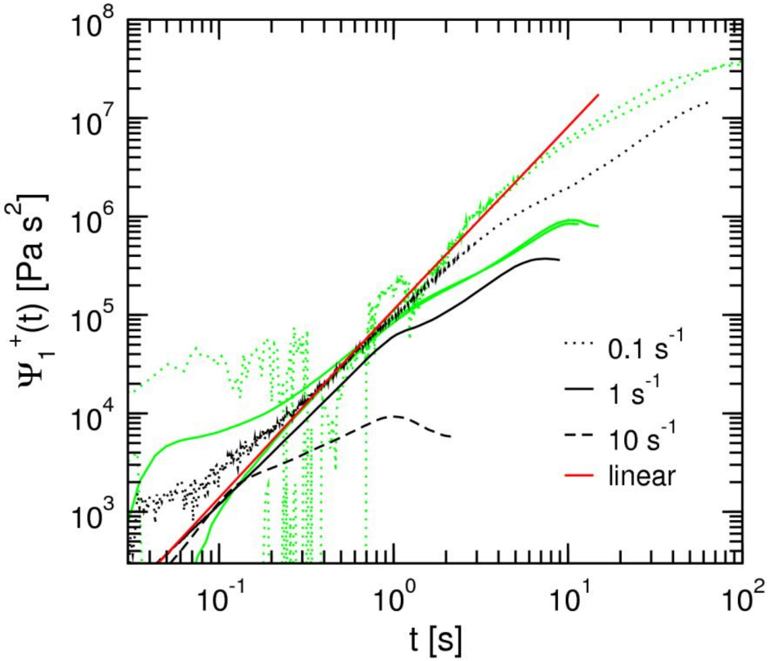
Moduli after some parameter tweaking



Onset of steady shear flow

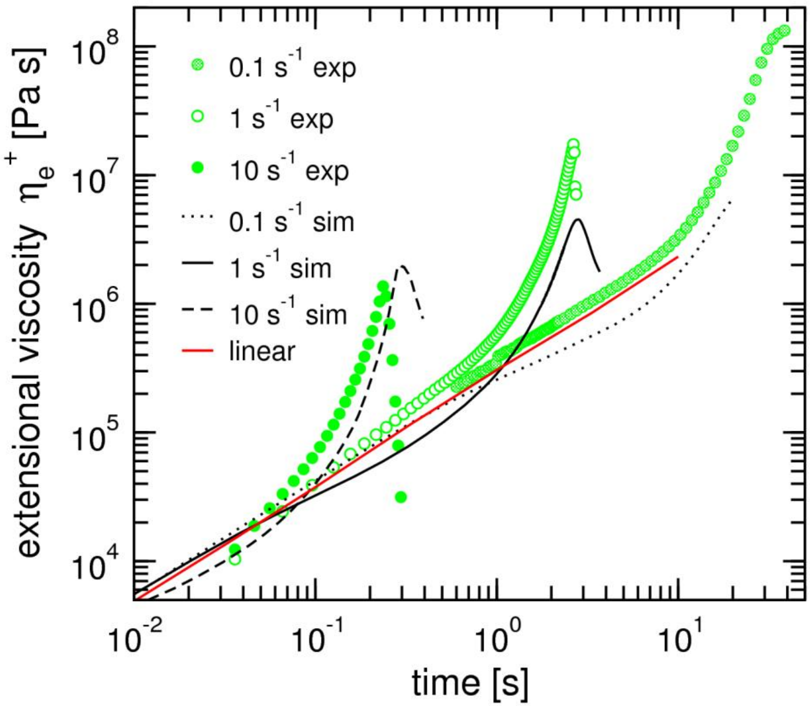


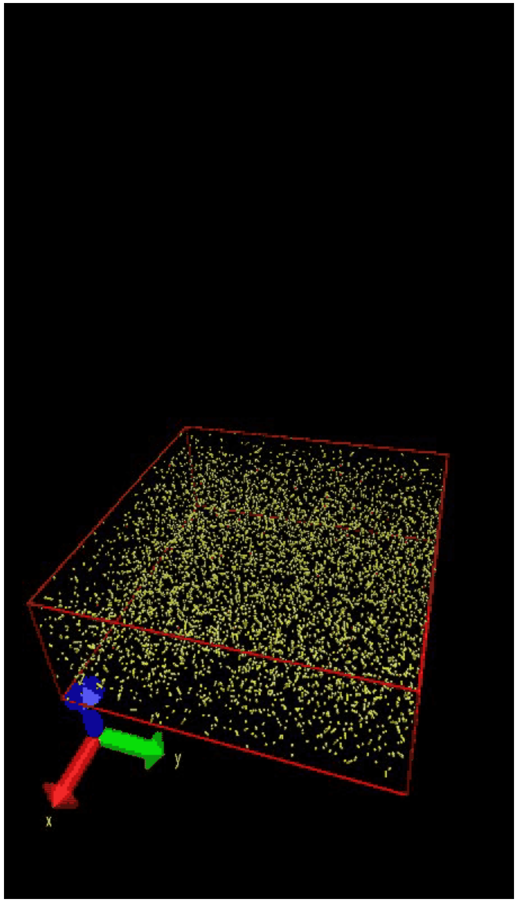
Shear viscosity



First normal stress

Onset of steady uniaxial extensional flow





- **Good agreement.**

Thank You

Brrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrriels

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

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

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