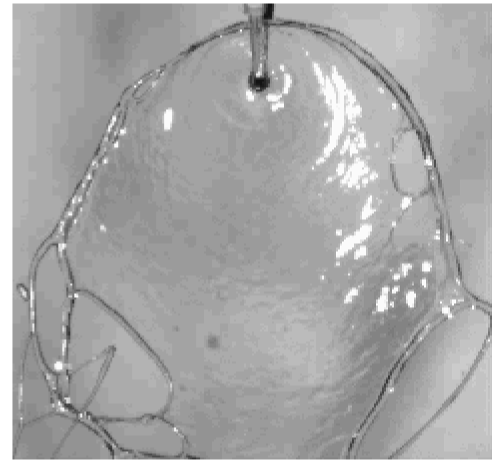
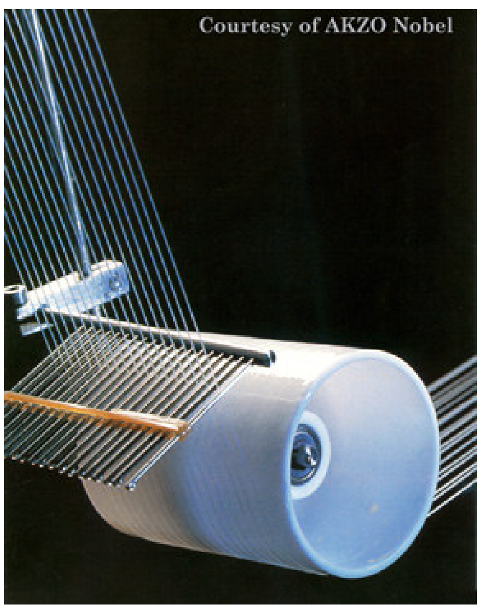
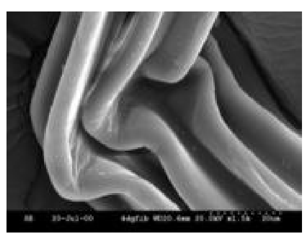
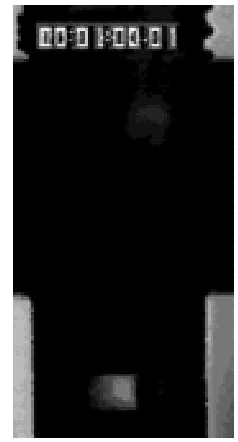
Rheology –
Materials subject to deformation

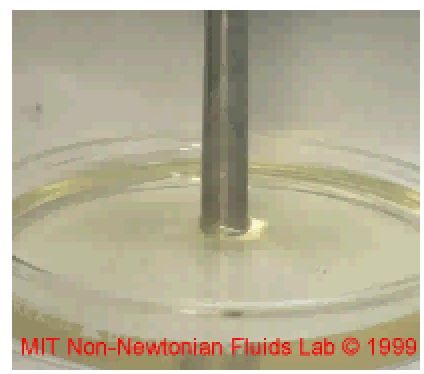


Miller et al 2005









Rheology of colloidal dispersions

Outline:

Introduction	colloids
	uses of colloids
	effect of interactions
Instrumentation	rheometers
	simple shear flow
Flow curves	Newtonian fluids
	non-Newtonian effects
Mechanisms	Brownian motion & Péclet number

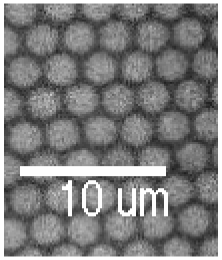
Concentration dependence of the low-shear viscosity

High-concentration rheology	glass transition
	yield stress

More complex systems

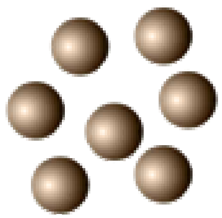
✓

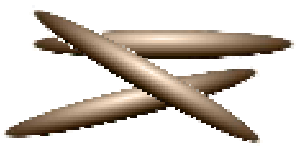
Colloidal dispersions

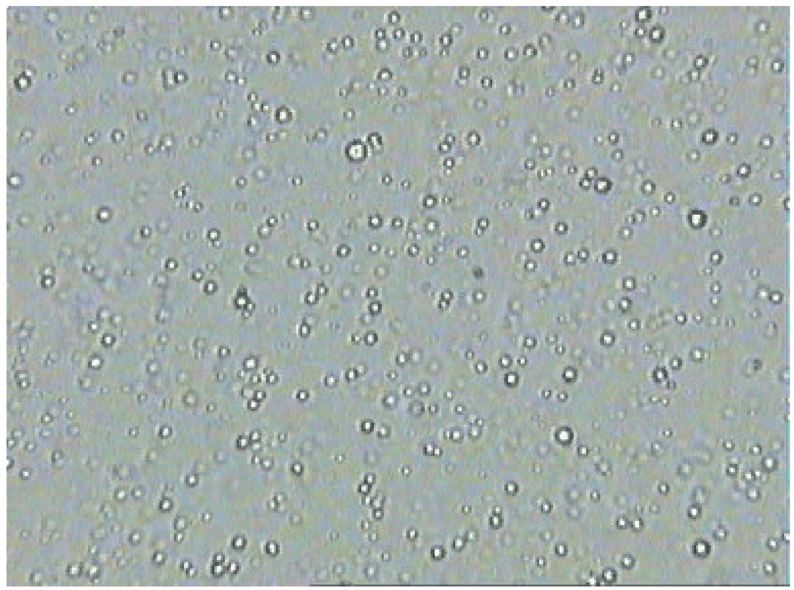


~ 1 nm – 10 μm ‘particles’ dispersed in a medium, typically a liquid

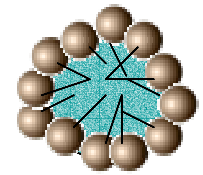
Brownian motion

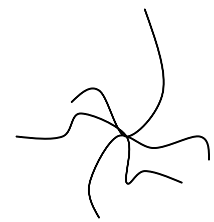






0.5-3 μm fat globules in milk



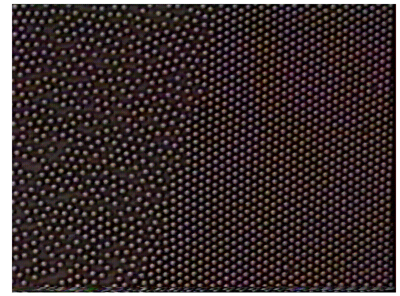


They flow – but not like simple liquids
They are weak – small number concentration
Rich behavior – interplay between Brownian motion, hydrodynamic interactions & direct, e.g., electrostatic and van der Waals, forces

Uses of colloids

Paints
Coatings
Polish
Cosmetics
Foods
Carpet backing
Inks
Adhesives
Films

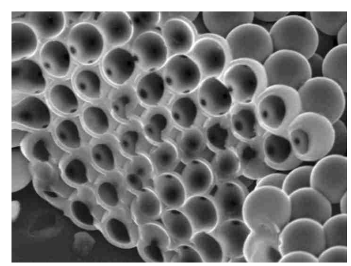
Phase behavior, dynamics and transport



Thermo-, pH-, electro-, magneto-responsive

A. P. Gast

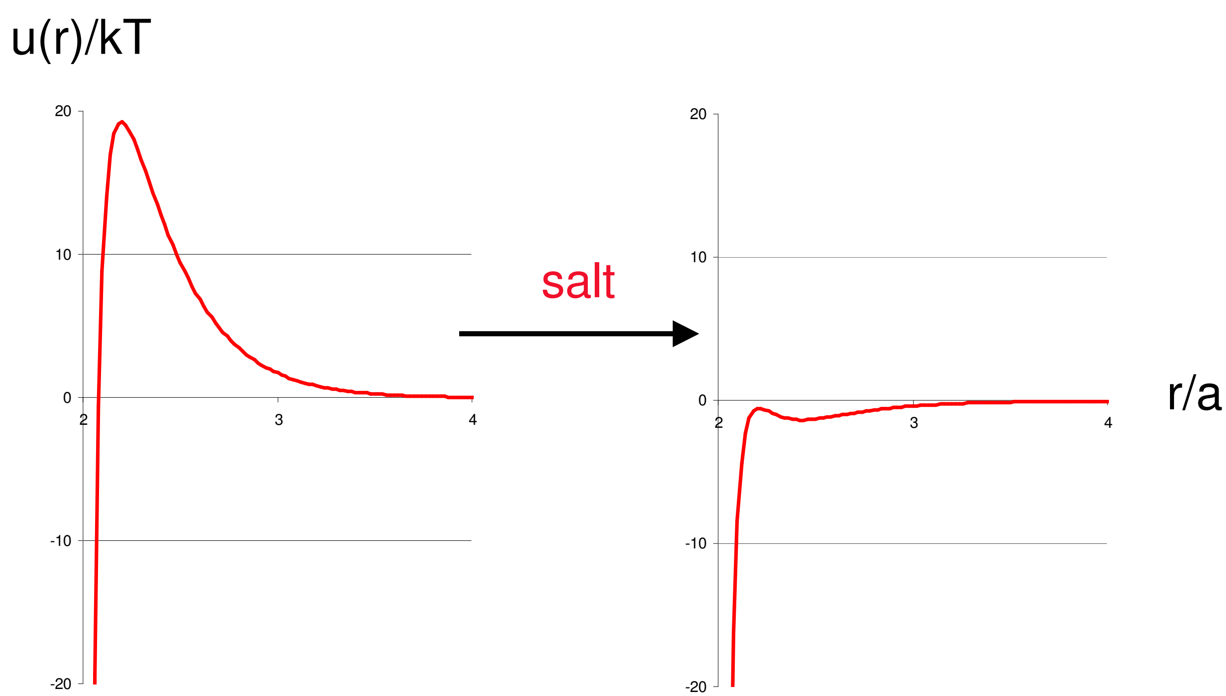
Building blocks of novel structures



A. van Blaaderen

Colloidal interactions

Courtesy of Leif Karlsson, Akzo-Nobel



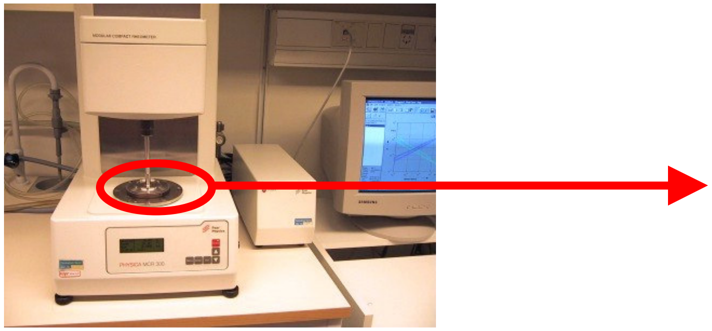
Interactions among particles strongly affect macroscopic properties, like the rheology

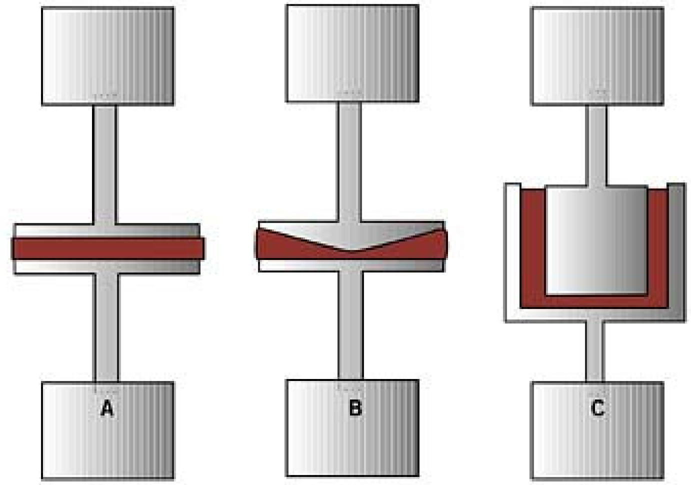
Can be used to tune the flow properties in a rational way!

AKZO NOBEL

Instrumentation

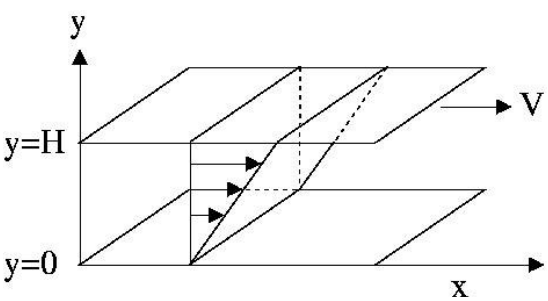
Rheometer

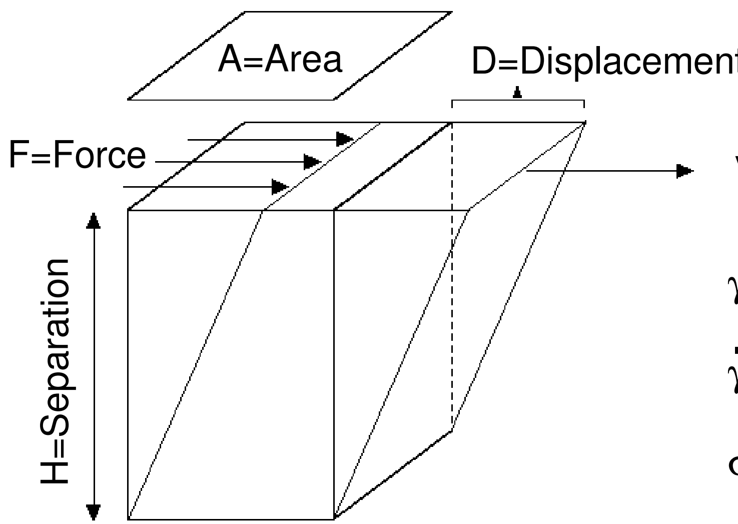




Geometries

Simple shear flow





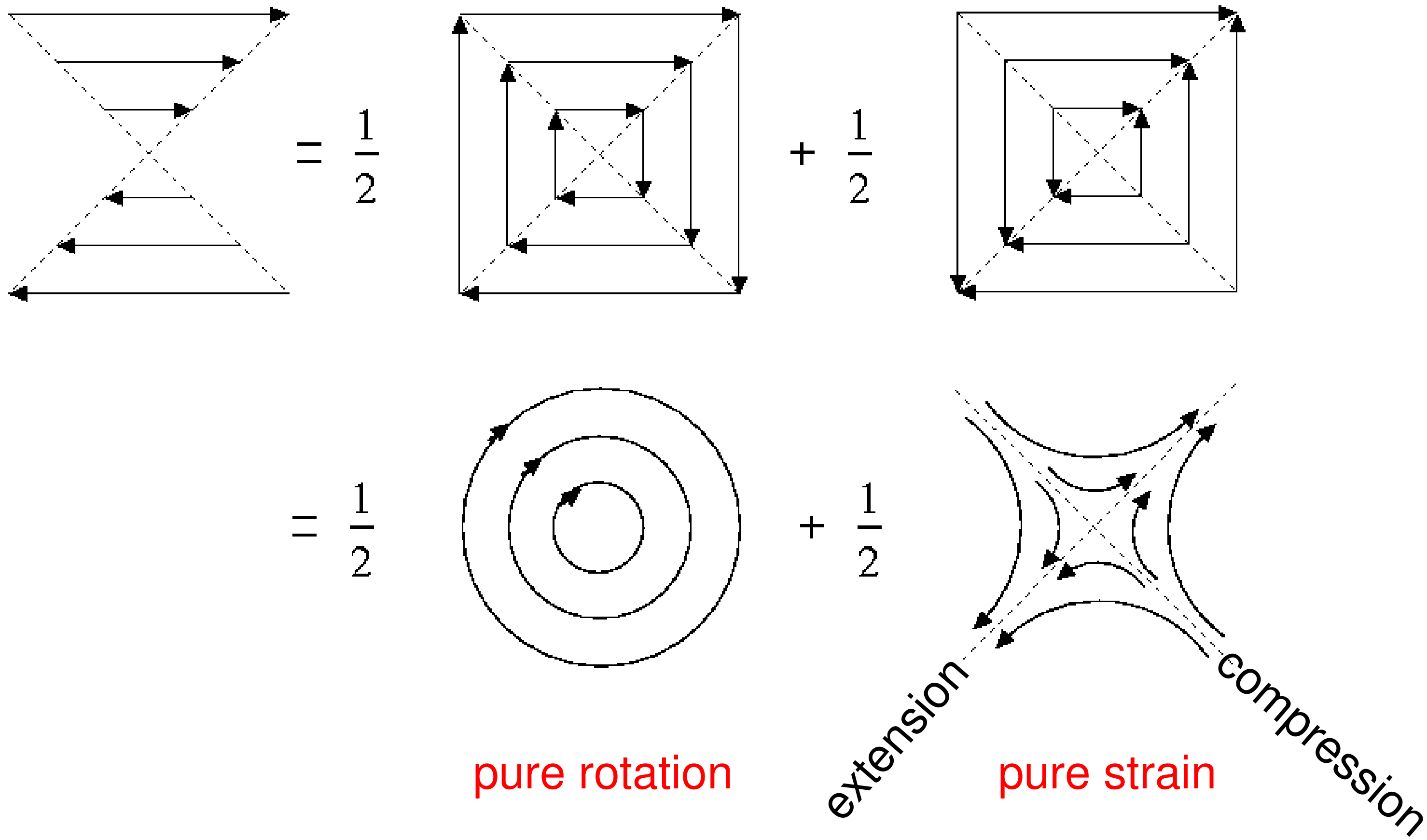
γ=Deformation=D/H

$\dot{\gamma}$=Shear rate=V/H

σ=Shear stress=F/A

More on ‘simple’ shear flow

not so simple after all



Flow curves

Newton's equation of viscosity

(linear) constitutive equation ← 'educated guess' in absence of detailed microscopic knowledge

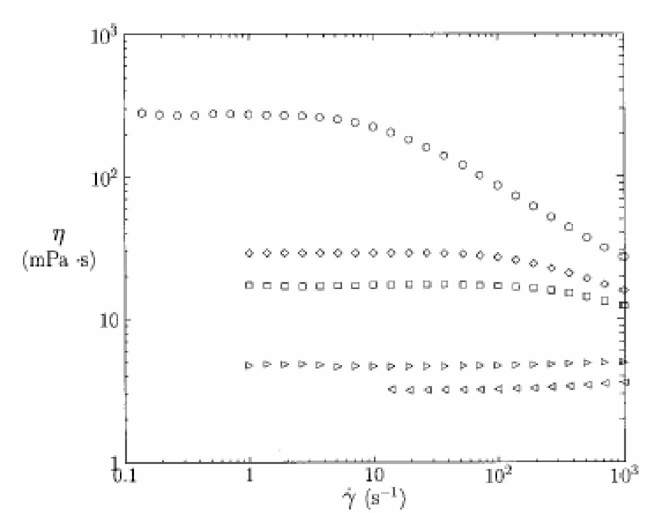
For a Newtonian fluid
(all gases and most simple liquids)

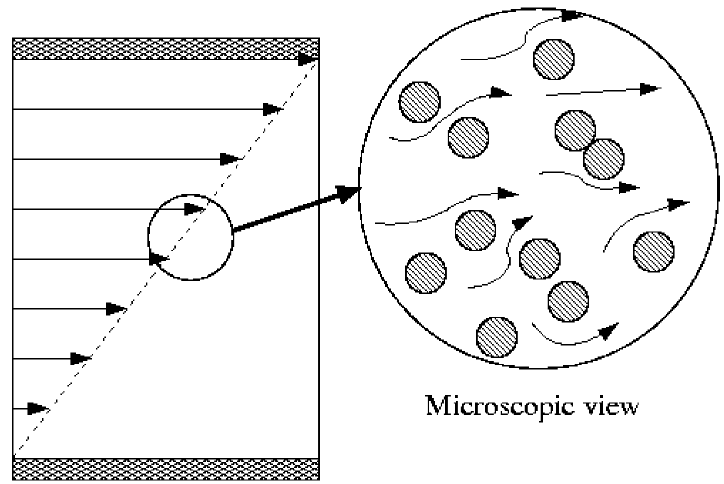
$$\sigma = \eta \dot{\gamma}$$

↑ constant (η)

$\eta_{water} \approx 1$ mPa s

Colloidal dispersions are non-Newtonian in general!





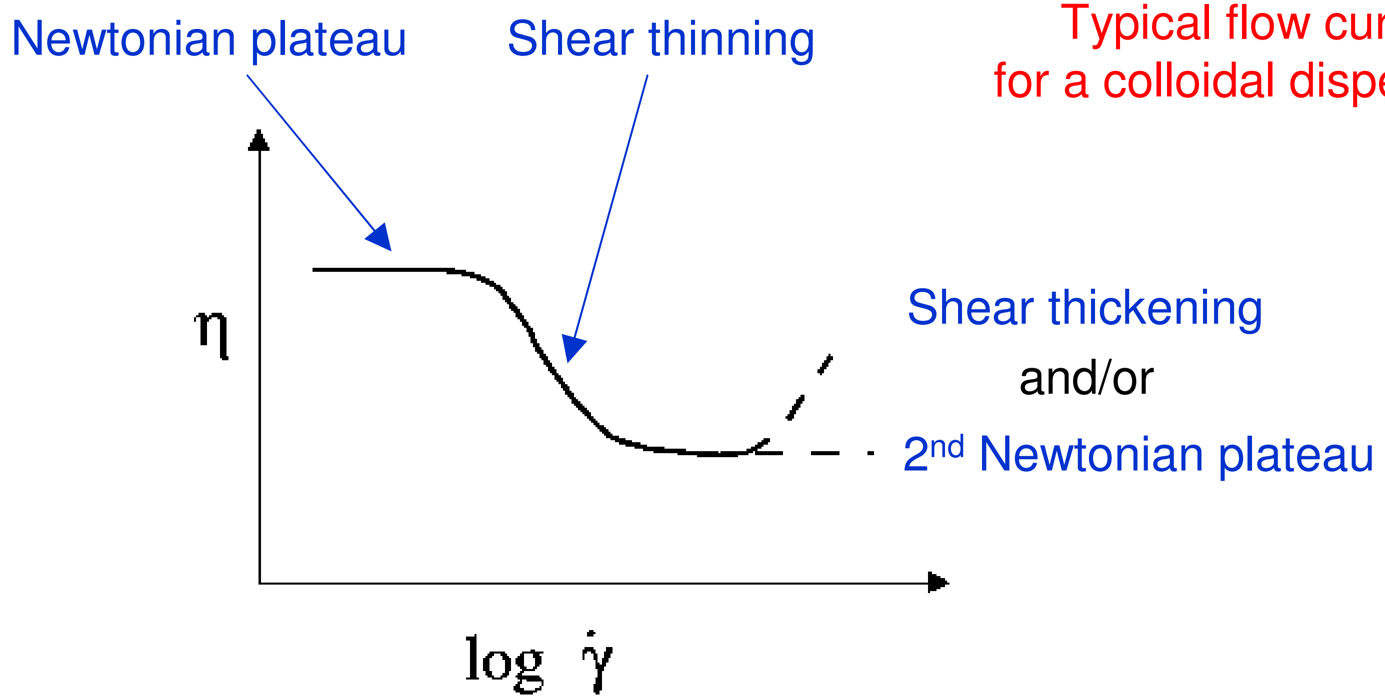
We use Newton's equation of viscosity but then the viscosity is a function of σ or $\dot{\gamma}$

Could try ~~$\sigma = \eta_1 \dot{\gamma} + \eta_2 \dot{\gamma}^2 + \eta_3 \dot{\gamma}^3 + \ldots$~~

$$\sigma = \eta(\dot{\gamma})\dot{\gamma}$$

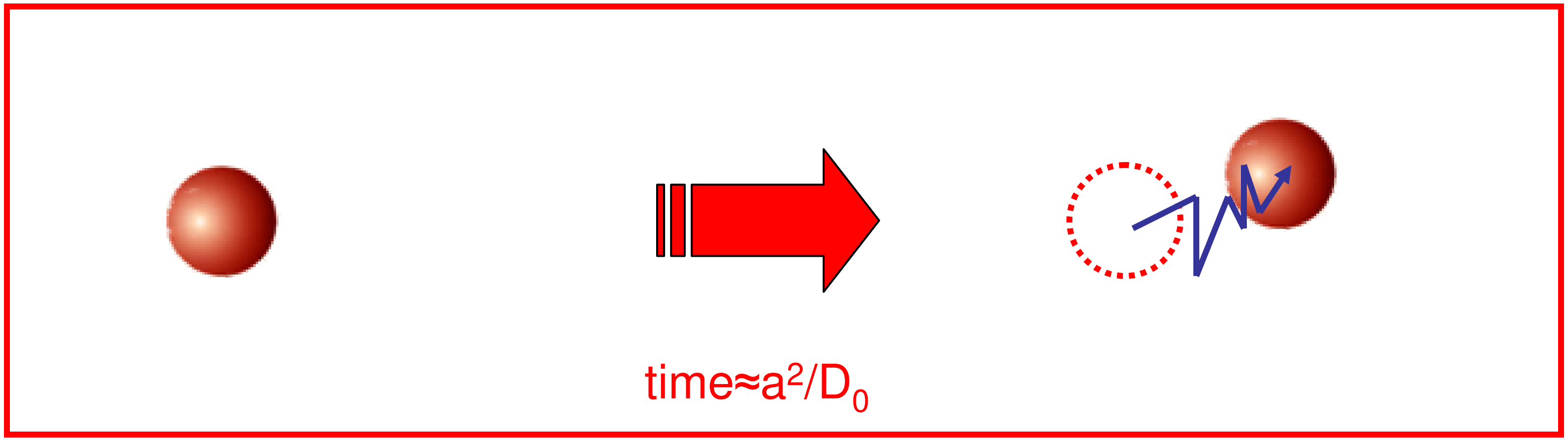
Flow curves

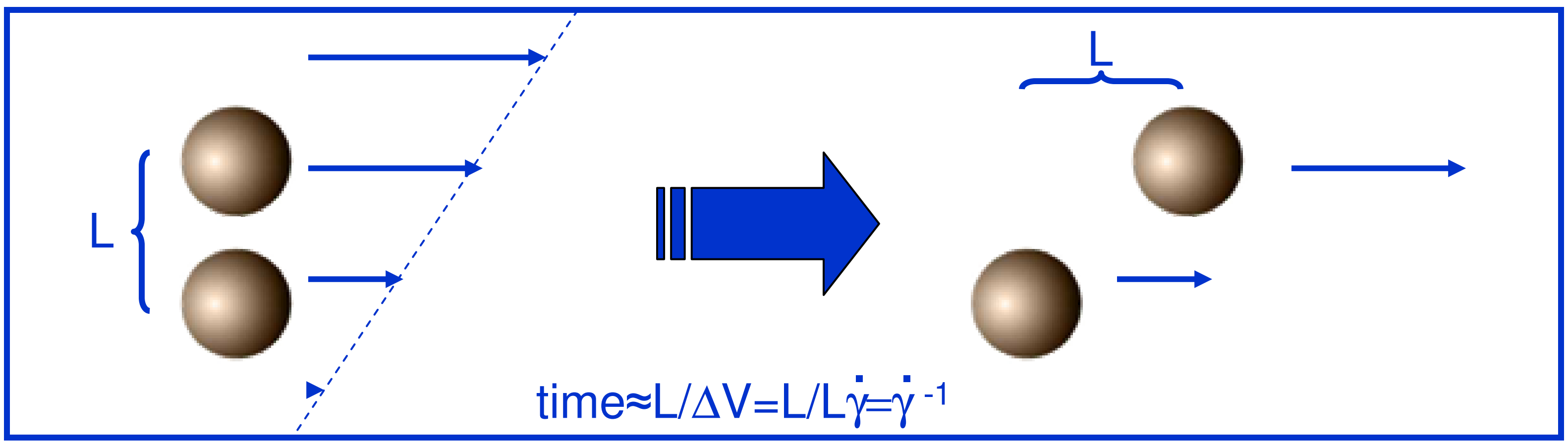
Typical flow curve
for a colloidal dispersion



Péclet number

Two important mechanisms: displacement owing to Brownian motion and shear flow

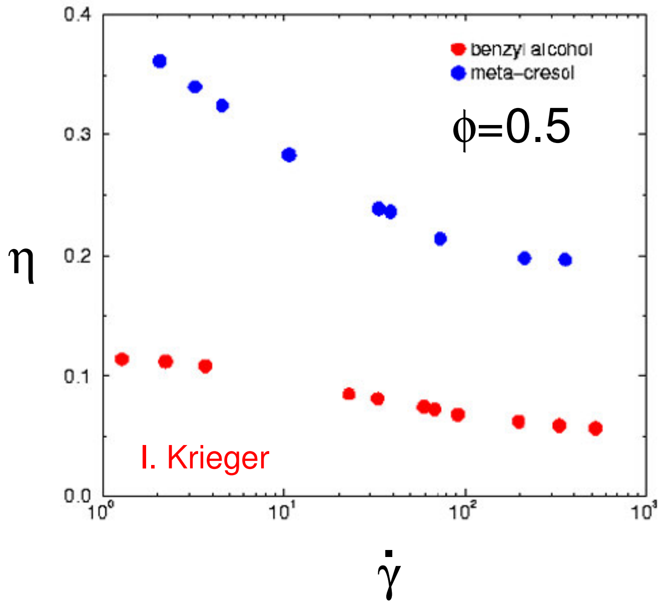




Péclet number = Pe =$(a^2/D_0)/(\dot{\gamma}^{-1}) = 6\pi\eta_0\dot{\gamma}a^3/kT$

Pe is a dimensionless shear rate that gauges the importance of Brownian motion relative to shear forces

Péclet number



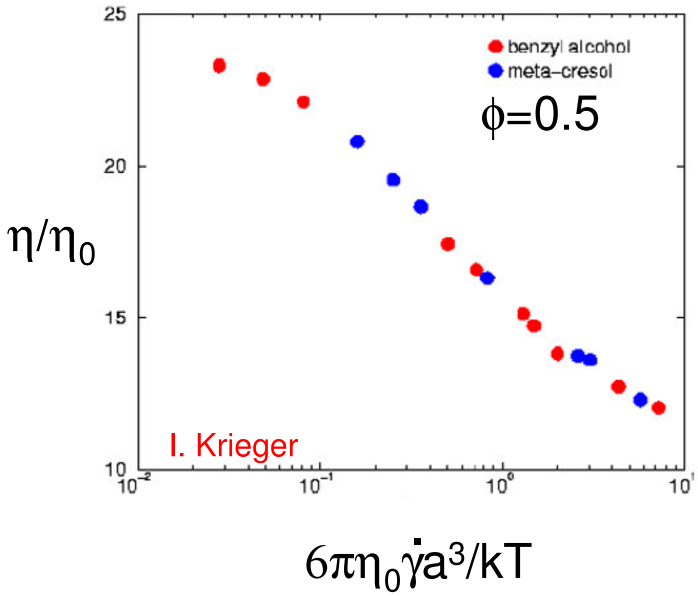
Example: effect of different solvents

Pe takes care of the main effects of particle size, solvent viscosity, and temperature
But, size, solvent, and temperature can produce additional effects through the interaction

In general ...

Pe«1 Brownian motion dominates, close to equilibrium
Pe»1 Flow forces dominate, far from equilibrium

Péclet number



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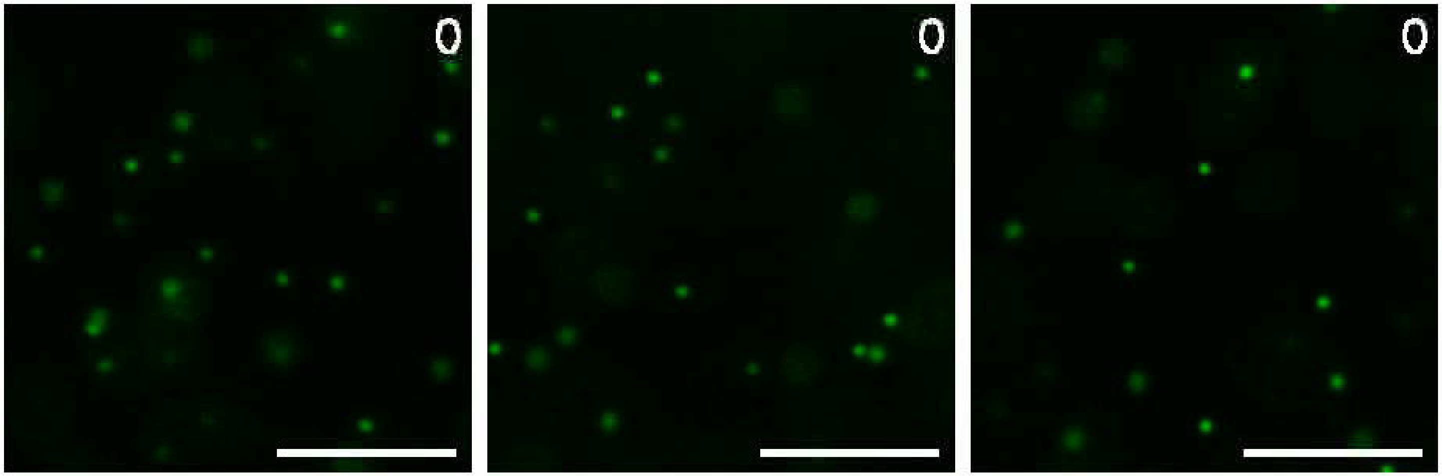

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Shear thinning

Hard spheres

Foss and Brady, J. Fluid Mech (2000)

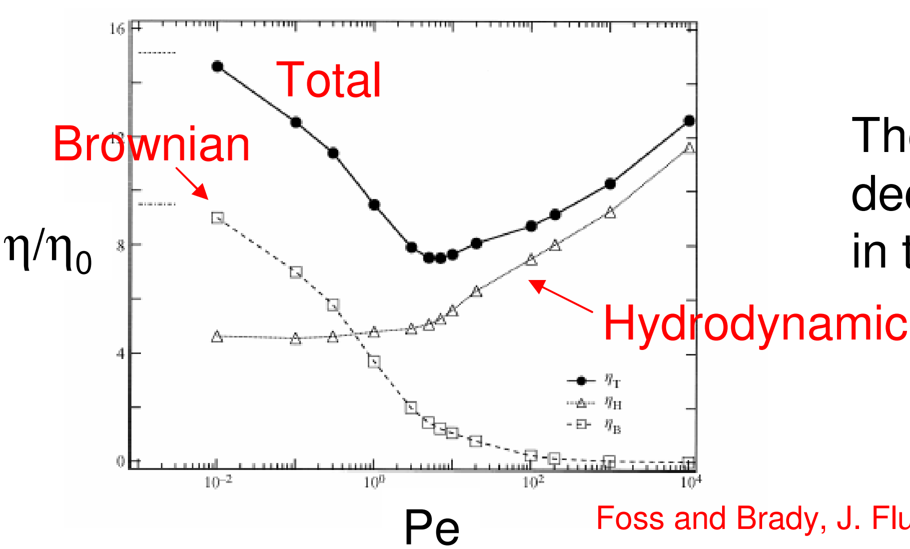
Pe=0.1, 10, 1000

No hydro

With hydro

The arrangement of particles depends on Pe! It is very different at large Pe!
Hydrodynamic interactions are important!

Shear thinning is caused by particles adopting a more flow-oriented arrangement, very different from the equilibrium arrangement

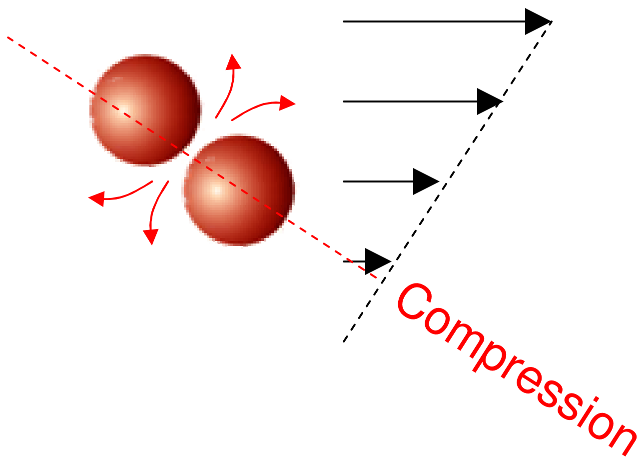


Foss and Brady, J. Fluid Mech (2000)

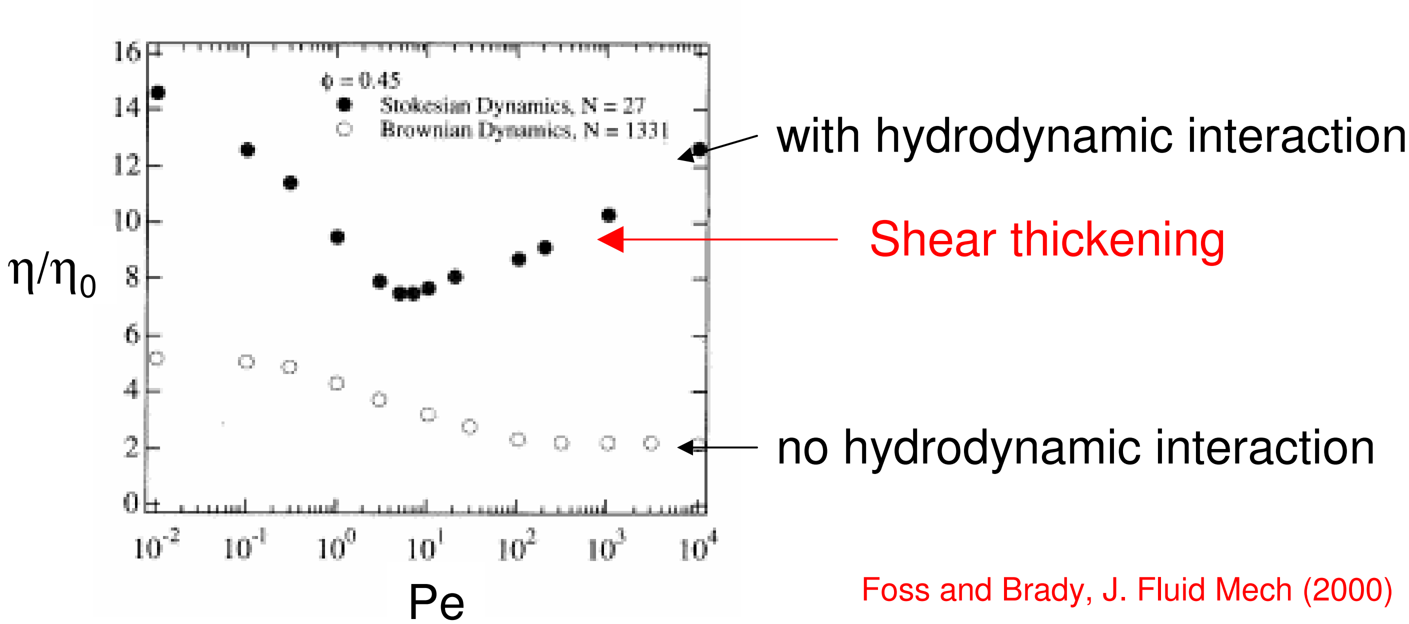
The (relative) importance of Brownian motion decreases with increasing Pe, and it shows up in the viscosity as shear thinning

Shear thickening

Squeezing of thin solvent film, Force~1/(r-2a)



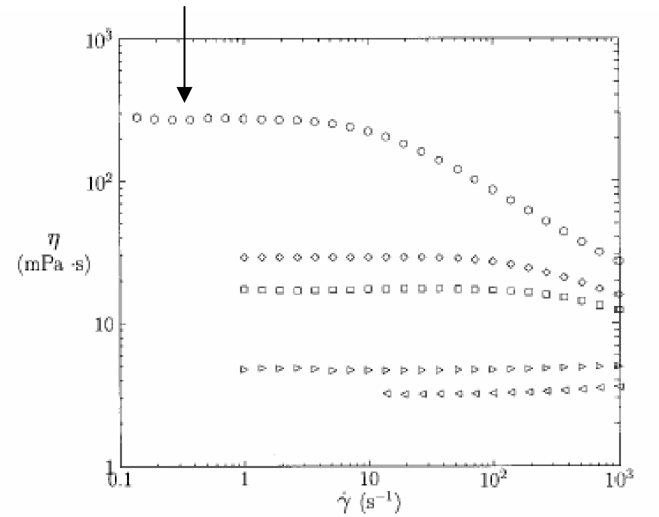
To delay onset of shear thickening try keeping particles separated, e.g., by polymer grafting



Foss and Brady, J. Fluid Mech (2000)

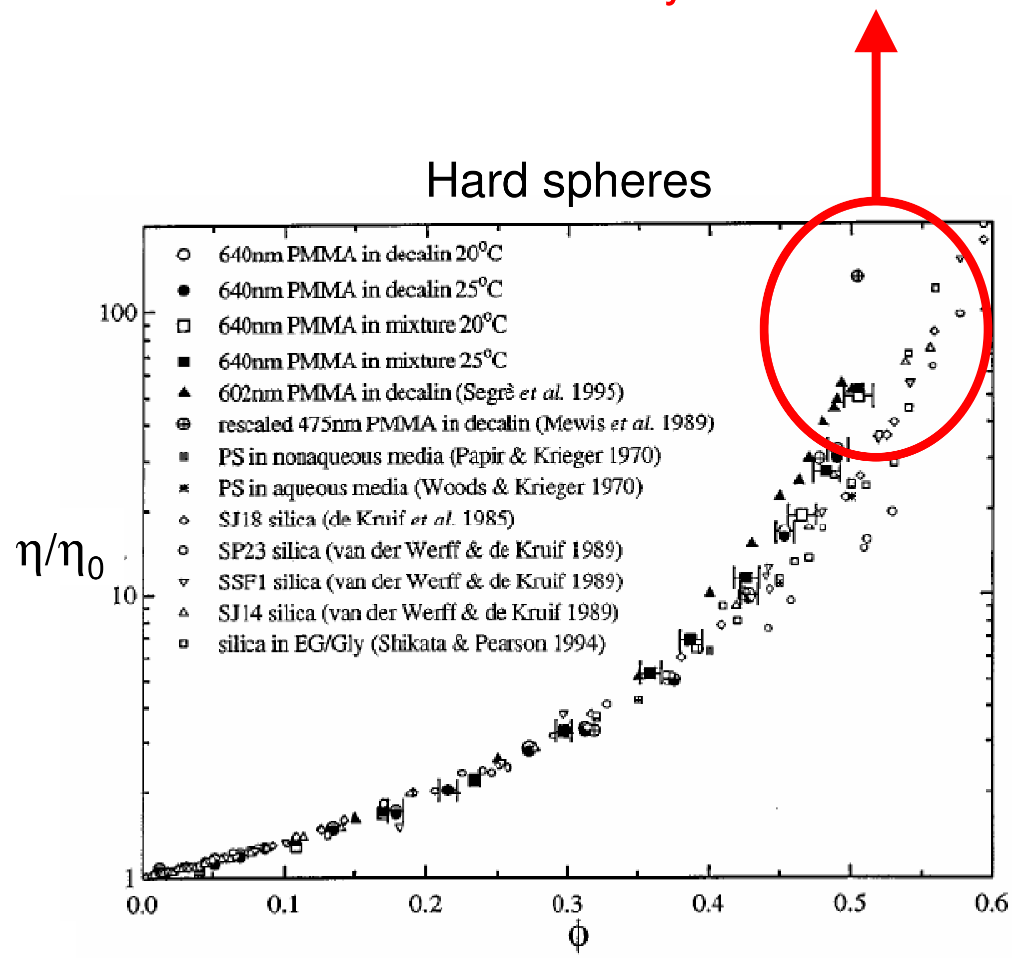
Zero-shear viscosity

η measured at first Newtonian plateau, where it is independent of $\dot{\gamma}$



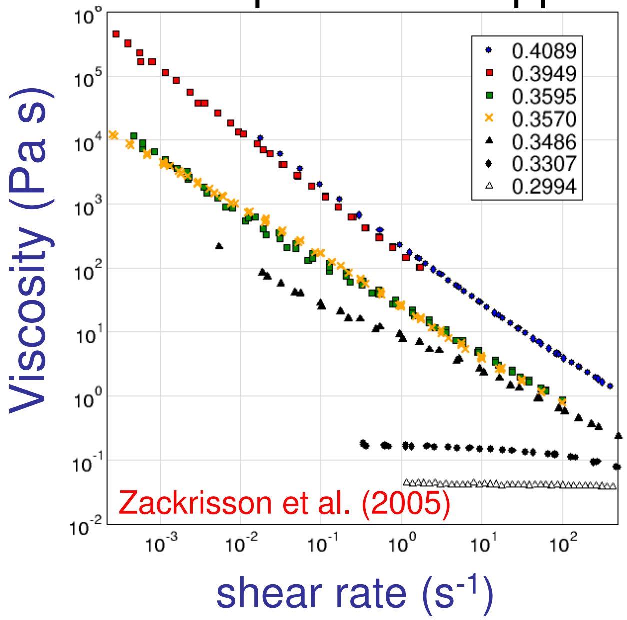
At what point does the system become solid?

Hard spheres



Low-shear viscosity

Newtonian plateau disappears!



Estimate for time scale of relaxation by Brownian motion, time≈a^2/D_0, is terribly poor at high concentration!

Should be, time≈a^2/D_{cage}, but $D_{cage} \rightarrow 0$ at the glass transition!

Weeks et al., Science (2000)

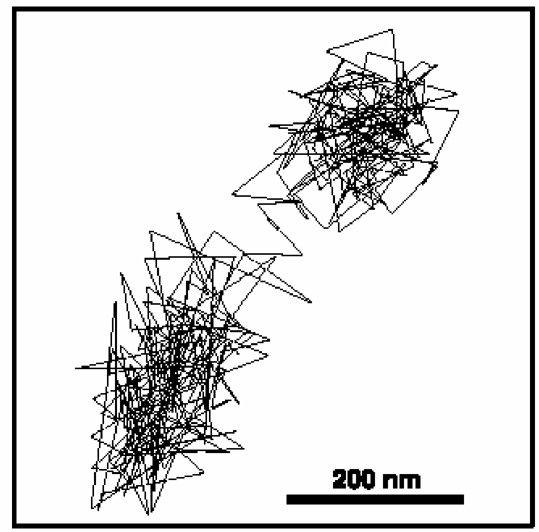
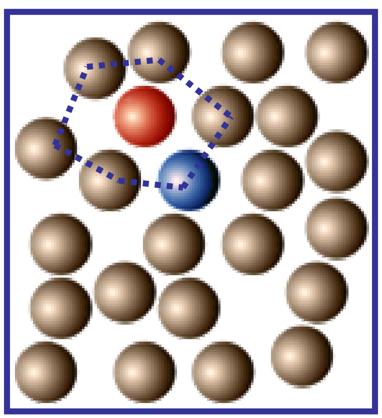


Fig. 2. A typical trajectory for 100 min for ϕ = 0.56. Particles spent most of their time confined in cages formed by their neighbors and moved significant distances only during quick, rare cage rearrangements. The particle shown took ~500 s to shift position. The particle was tracked in 3D; the 2D projection is shown.



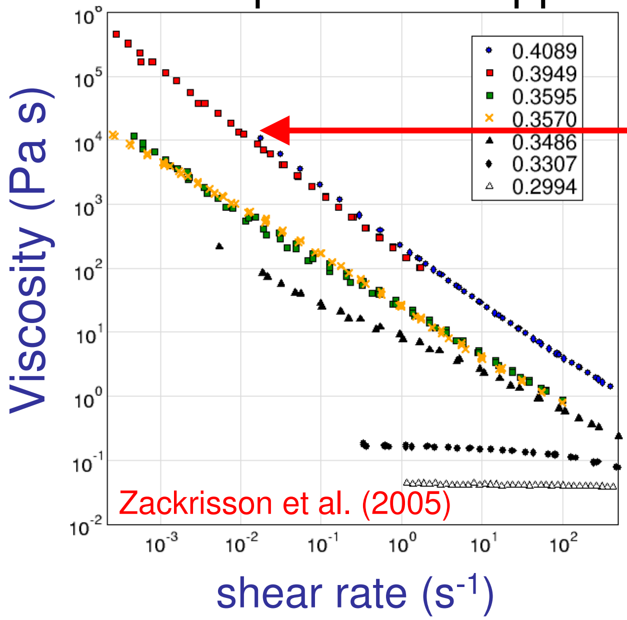
Cage effect

If we redefine Pe as, $(a^2/D_{cage})/\dot{\gamma}^{-1}$, then Pe remains very large even if $\dot{\gamma}$ is small

Yield stress

$$\sigma=\eta(\dot{\gamma})\dot{\gamma}$$

Newtonian plateau disappears!



$$\eta \sim \dot{\gamma}^{-1}$$

σ = constant
= yield stress

A yield stress can be defined at the glass transition, where the viscosity diverges and system becomes solid

<u>The dilemma:</u>
But what if we could measure at even lower shear rates?
Would we find a Newtonian plateau?

Thixotropy

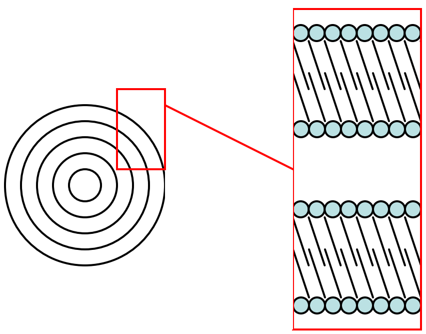
(η depends on time)

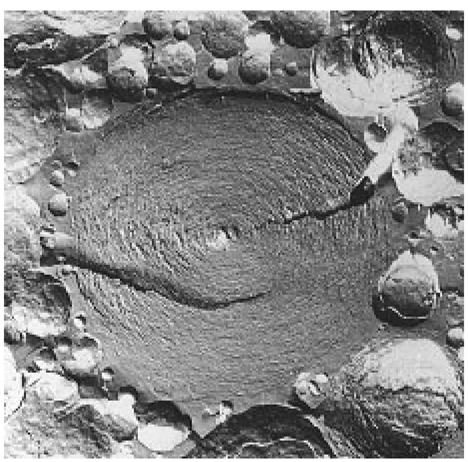
<u>Trivial causes:</u>
sedimentation
loss of sample
drying

<u>Non-trivial causes:</u>
structure evolution

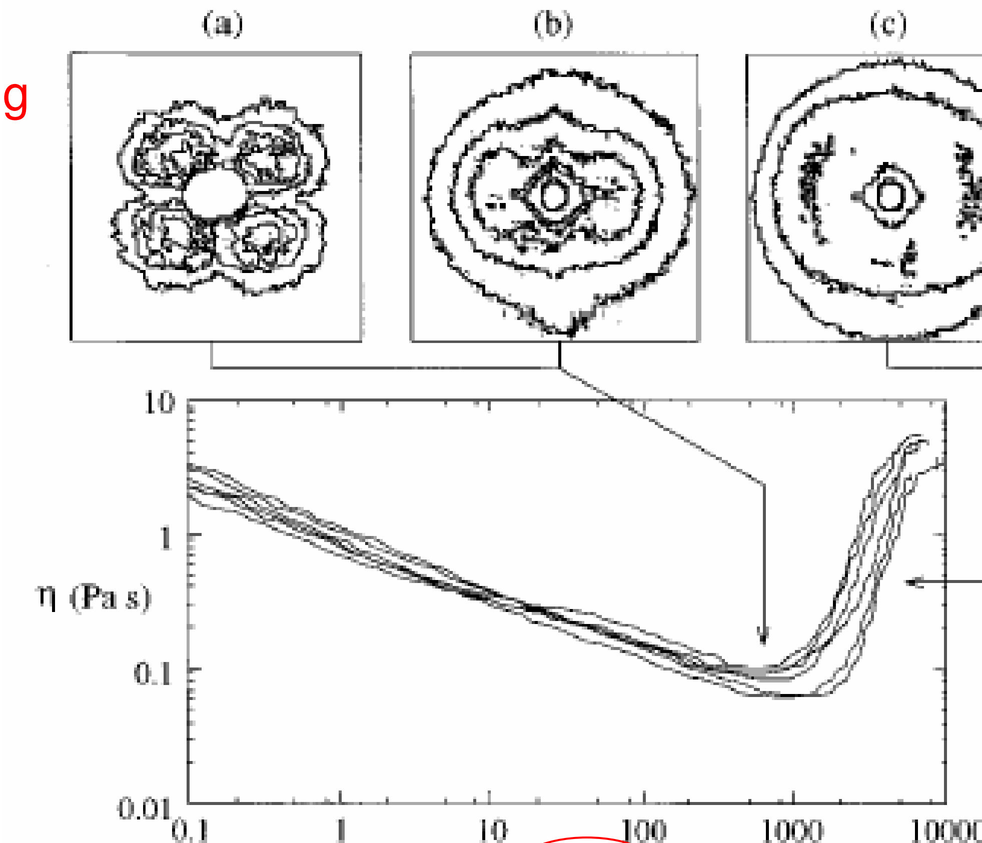
<u>Example:</u> Formation of multi-lamellar vesicles

in situ light scattering





Gulik-Krzywicki et al. (1996)



$\dot{\gamma}t$

amount of deformation

Bergenholtz & Wagner (1996)