Fluides complexes

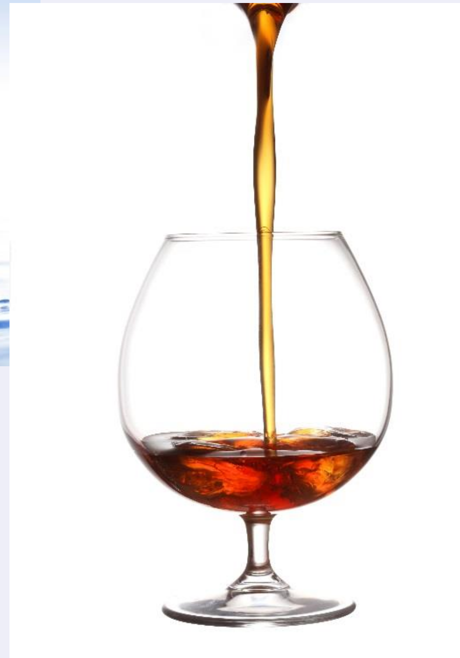
La matière dans tous ses états

P. Coussot

Univ. Paris-Est, Laboratoire Navier

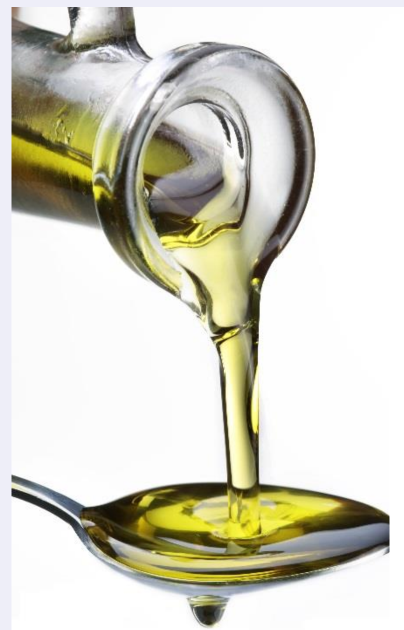



Various liquids poured under same conditions



Flow velocity ↘

Viscosity ↗



Complex fluids

Fresh concrete

Liquid chocolate

Mayonnaise

Foams

Magma

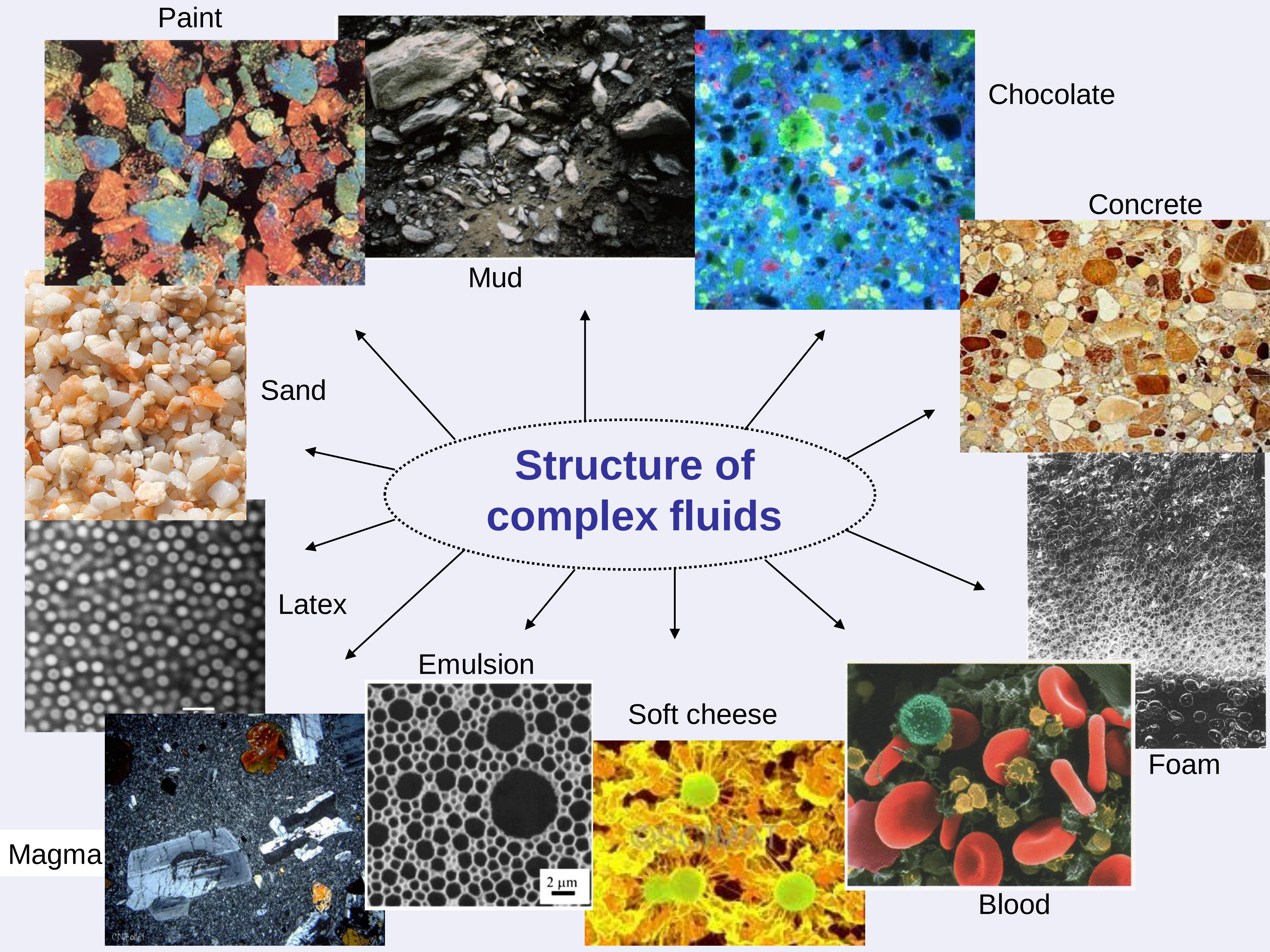
Blood

Polymer

« Fluids » : May be reversibly deformed at will

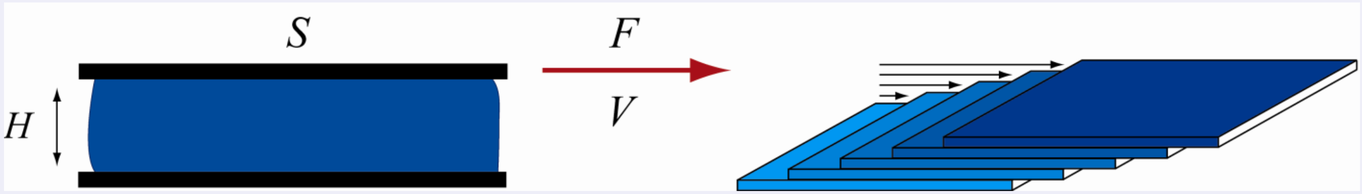
« Complex » : Viscous, elastic, and plastic

+ evolutions / velocity or time


Structure of complex fluids
Paint
Mud
Chocolate
Concrete
Sand
Latex
Emulsion
2 µm
Soft cheese
Foam
Blood
Magma

Characterization: Rheometry

Simple shear



Shear stress $\tau \approx \frac{F}{S}$

Shear rate $\dot{\gamma} \approx \frac{V}{H}$

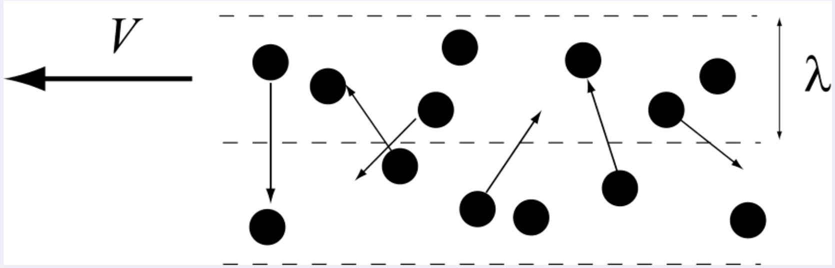
Apparent viscosity $\eta = \frac{\tau}{\dot{\gamma}}$

Newtonian fluid $\eta = \text{Cst.}$

Complex fluid $\eta(t) = \mathrm{F}_{\theta<t}(\dot{\gamma}(\theta))$

Shear-thinning, viscoelastic, thixotropic,
Viscoplastic, etc

Viscosity of a gas



(2)

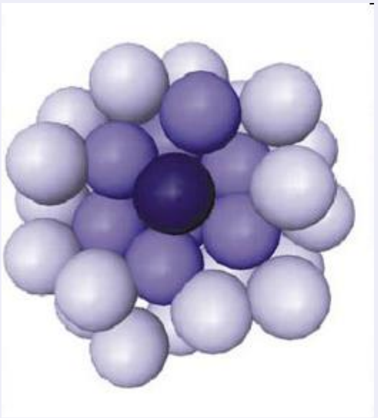
(1)

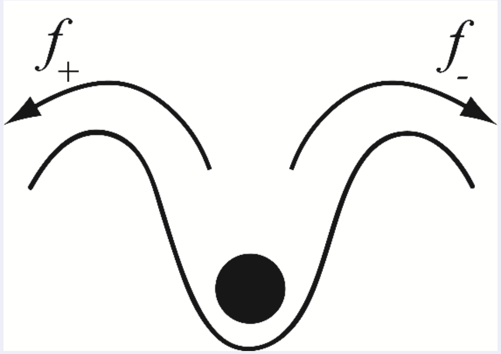
n Molecules per unit volume

λ Mean free path

$$\mu \propto n\lambda\sqrt{mk_B T}$$

Viscosity of a liquid



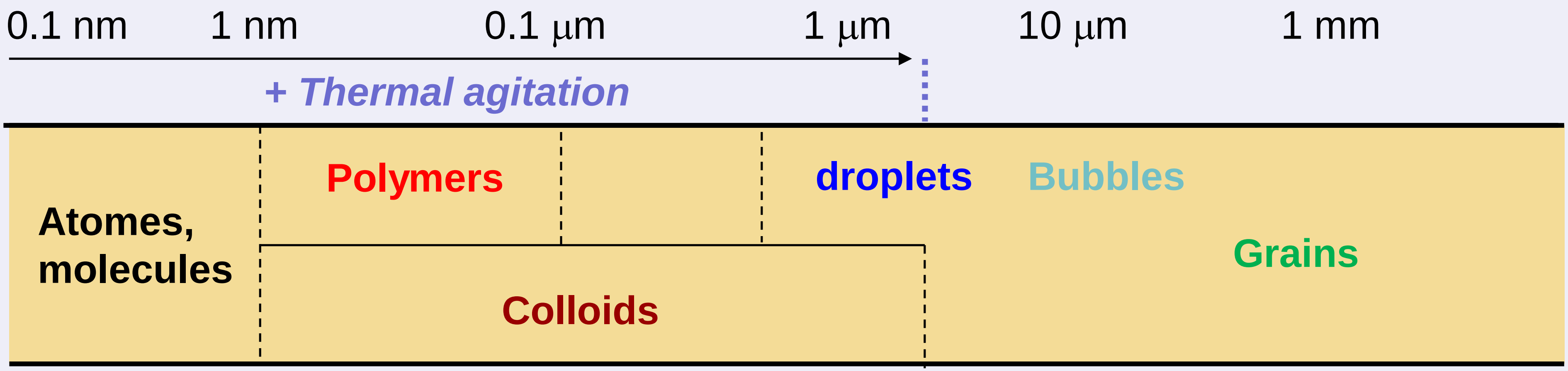


b Intermolecular distance

w Cohesion energy

$$\mu = \frac{\hbar}{b^3}\exp\frac{w}{k_B T}$$

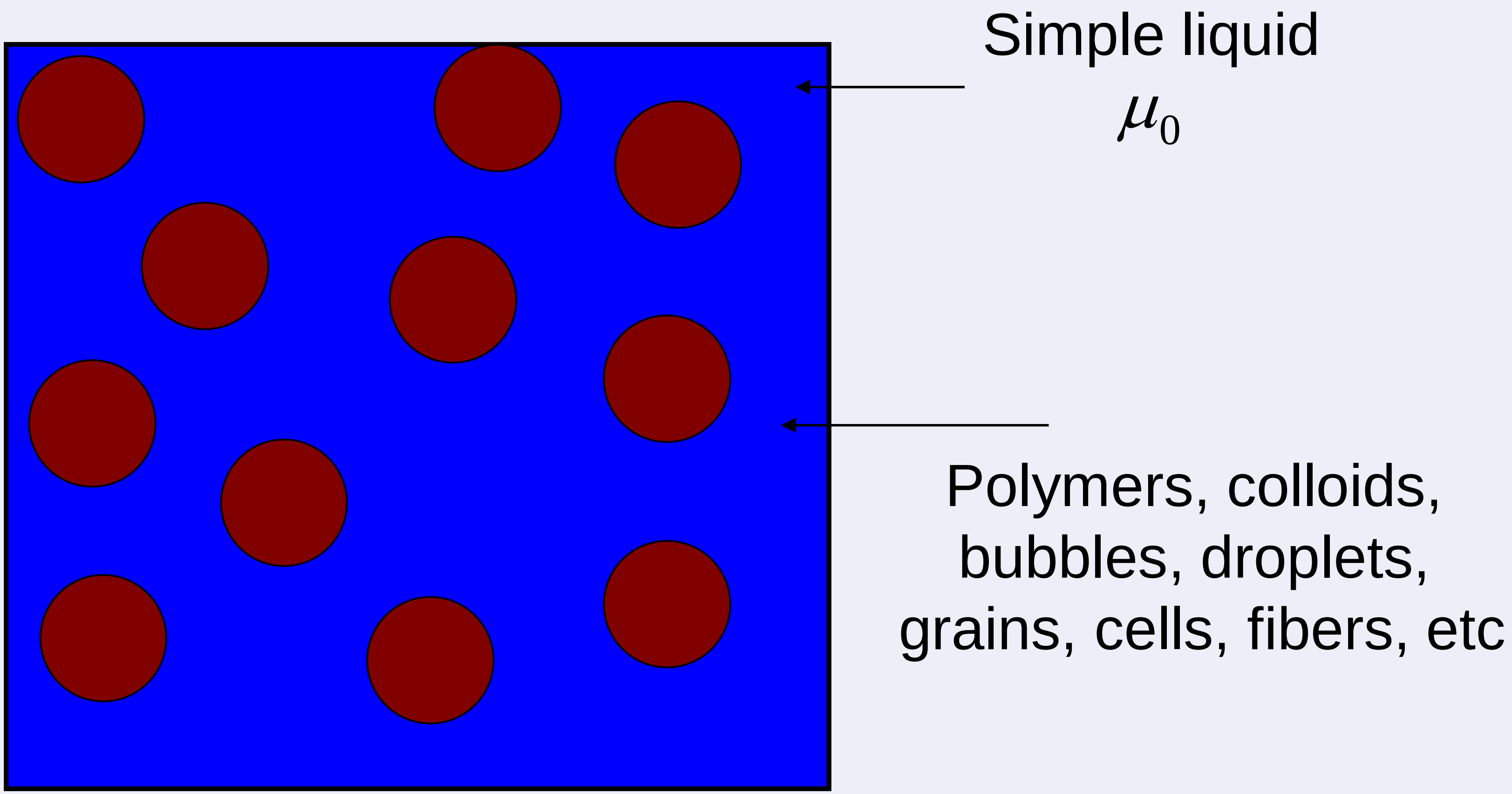
Components and scales



Mechanical behavior:

F(elementary components, dominant interactions, concentration, regime)

SUSPENSIONS

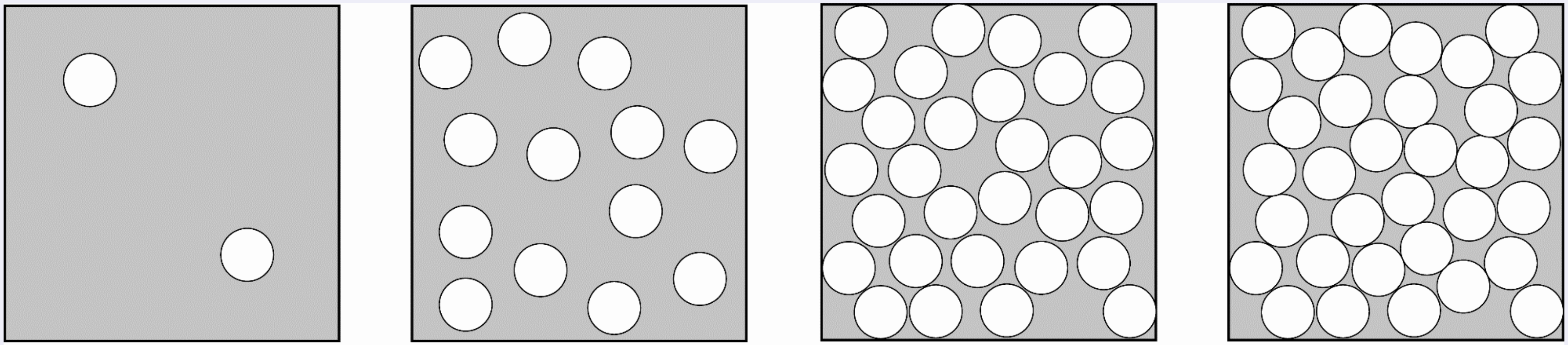


Volume fraction: $\phi = \dfrac{V_{Solid}}{V_{Total}}$

Maximum packing fraction:

$$\phi < \phi_m$$

Rheology of suspensions



Dilute	Semi-dilute	Concentrated	Compact
No hydrodynamic interparticle interaction	Hydrodynamic interactions	Hydrodynamic interactions + Steric interactions	Hydrodynamic interactions + Steric interactions + Contacts
$\phi << 0.1$	$0.01 << \phi < \phi_c$	$\phi_c < \phi < \phi_m$	$\phi \rightarrow \phi_m$

$$\mu = \mu_0 (1 + 2.5\phi)$$

Einstein

→

$$\mu = \mu_0 (1 - \phi / \phi_m)^{-2.5\phi_m}$$

Krieger-Dougherty

⋯⋯→

Granular pastes

POLYMERS

Flexibility - Resistance

Shaping

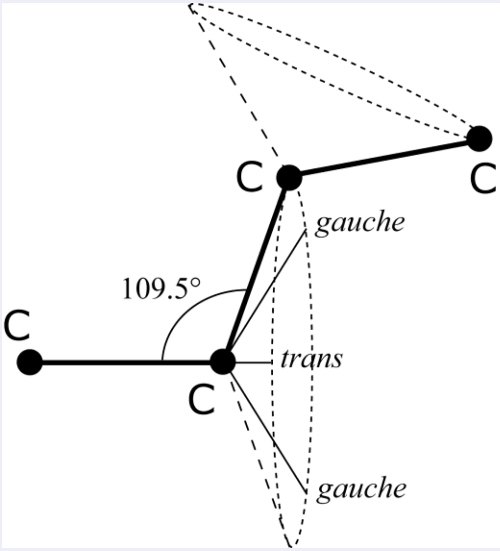
Deformability

« ***Plasticity*** » : Relative gliding of molecules
« **Elasticity** » : Molecule deformations
« **Rigidity** » : Glass transition, crystallisation, cross-linking

Extrusion - Moulding

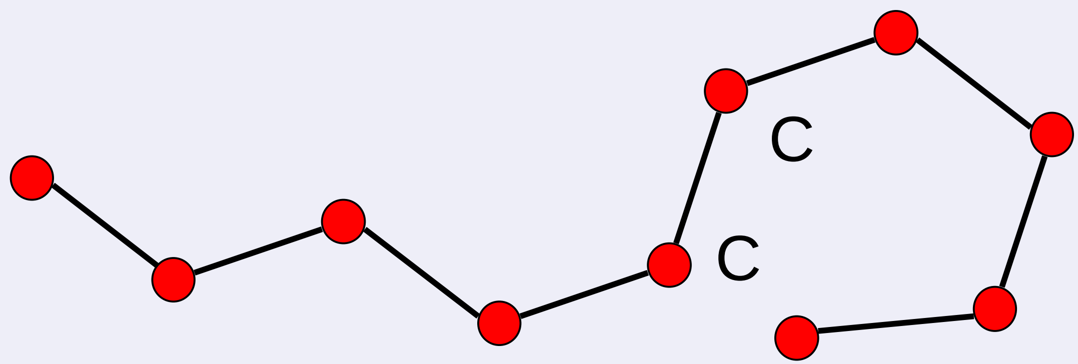
3D printing

POLYMERS



A few relative positions of successive Carbon atoms

Chain configuration



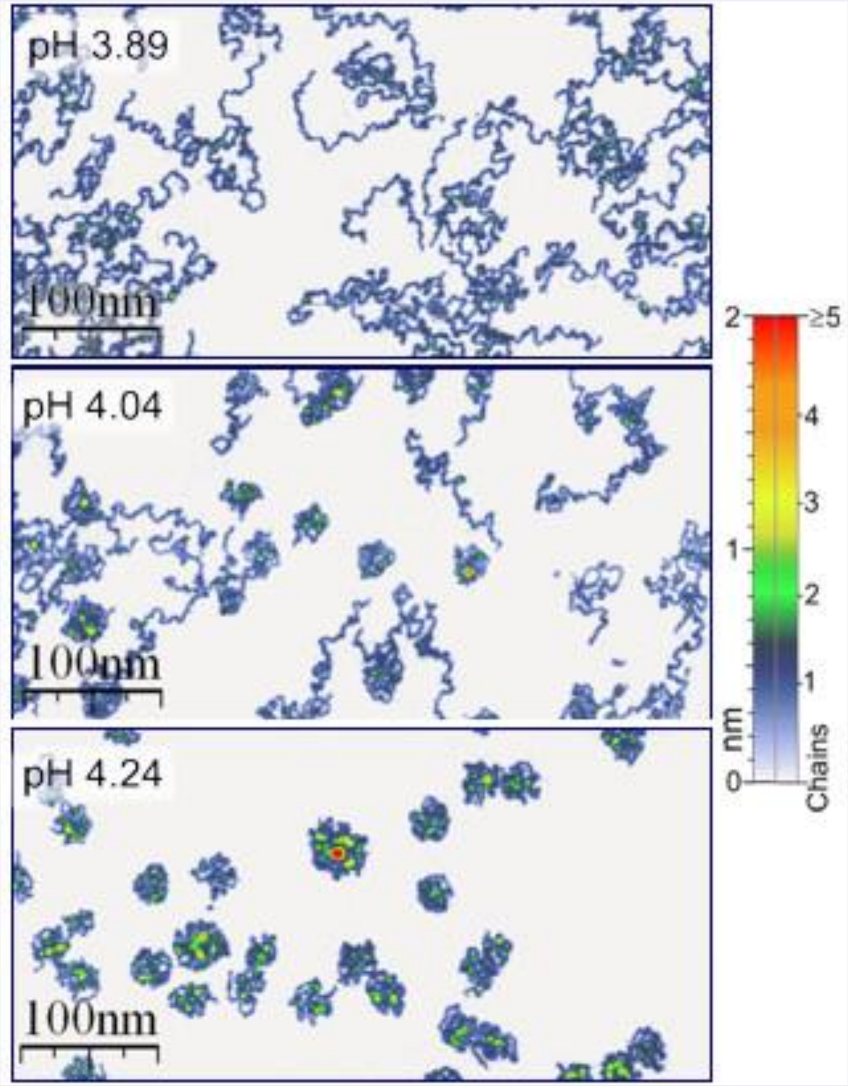
=> Variable shape and size possible around an equilibrium mean size

Polymers in solution

Affinity with solvent ↗

Apparent chain size ↗

Chain deposits on mica (from AFM)



Roiter and Minko, *J. Phys. Chem.* **2007**

Rheology of polymer suspensions

Simple liquid

Polymer chain

Effective volume υ

« Jammed water »

Ball radius R_G

ϕ Ball volume fraction

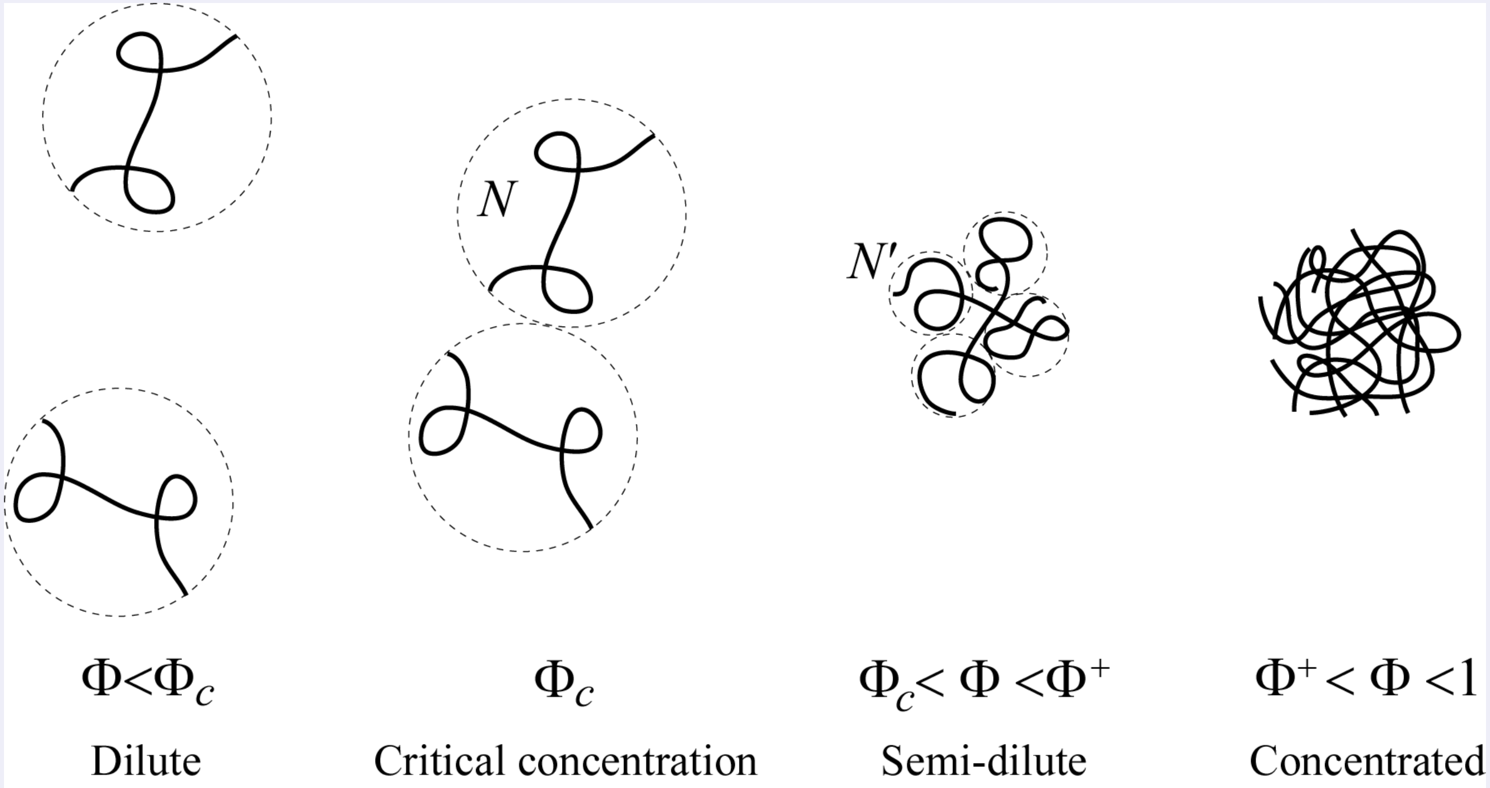
Φ Polymer volume fraction

$$\phi = \left(\frac{R_G{}^3}{\upsilon} \right) \Phi >> \Phi$$

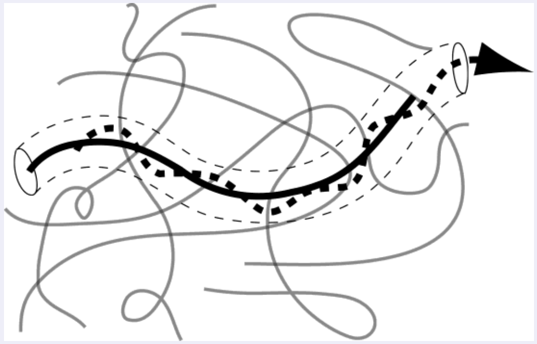
« Hydrodynamic effects »

$$\Rightarrow \mu = \mu_0 f(\phi) >> \mu_0 f(\Phi)$$

Rheology of polymer suspensions



« Reptation model »



Suspension viscosity as a function of ϕ
(Einstein -> Krieger-Dougherty)

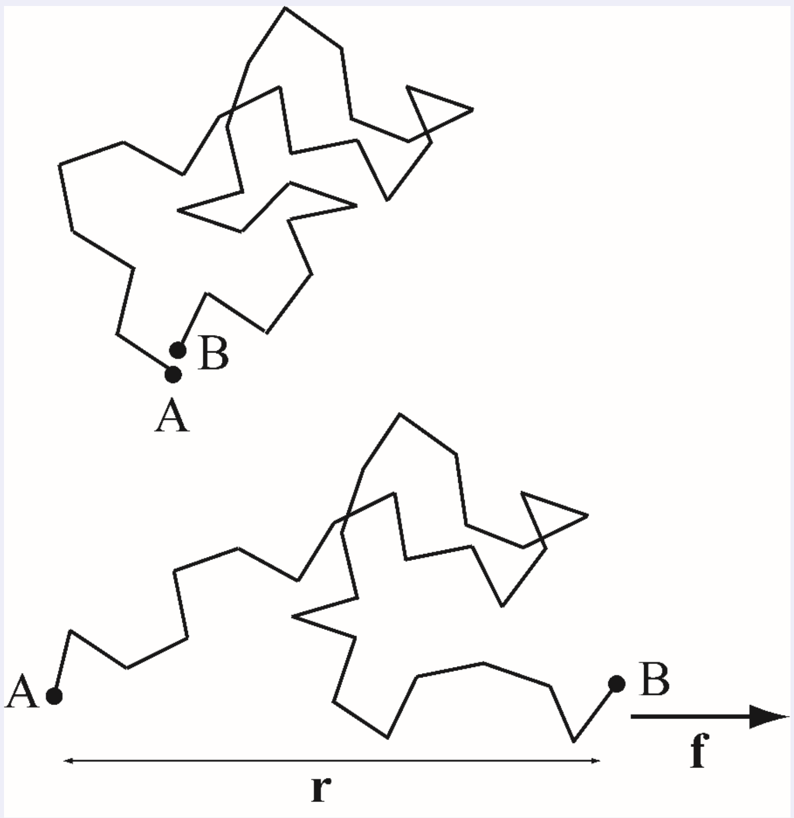
Mechanical properties of chains

Viscous friction :

Relative motion of chains

=> Viscosity = F(concentration, conformation, chain length)

Elastic deformation



Chain elongation: entropy loss

=> Supply energy to keep this length

$$\Delta G = f dr = -TdS$$

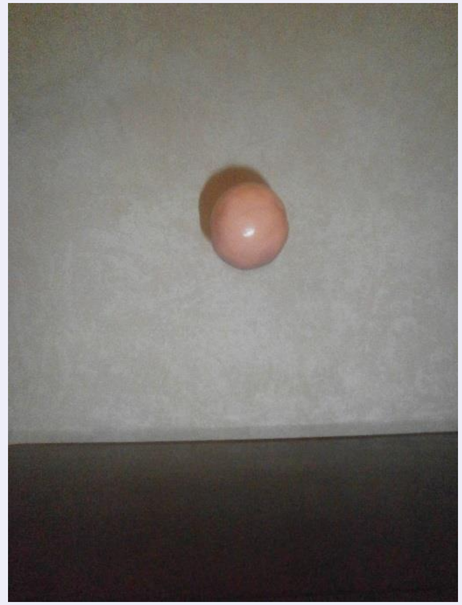
$$S = k_B \ln(\Omega_T \psi d\omega) = k_B \ln \psi + \mathrm{Cst.}$$

Ω_T Total number of configurations

$d\omega$ Characteristics volume

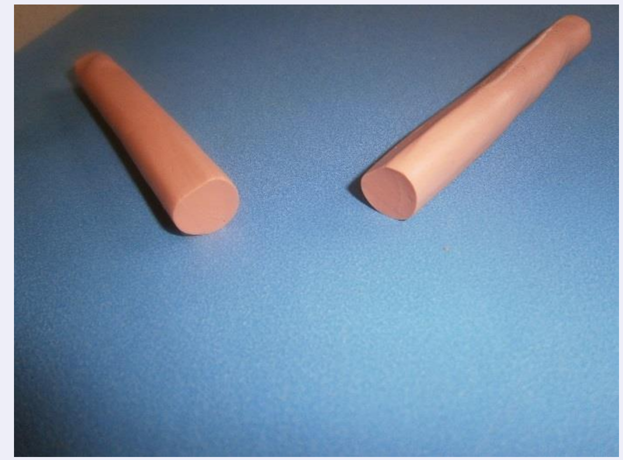
$\Rightarrow$ Force: $f = 2k_B T \beta^2 r$

Bouncing



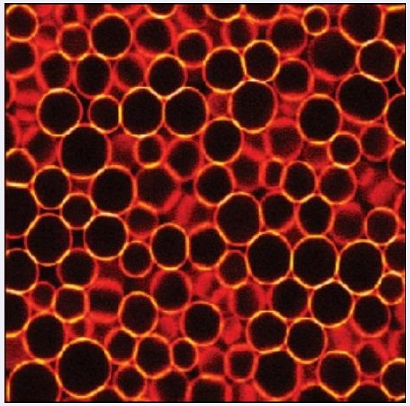
Flow

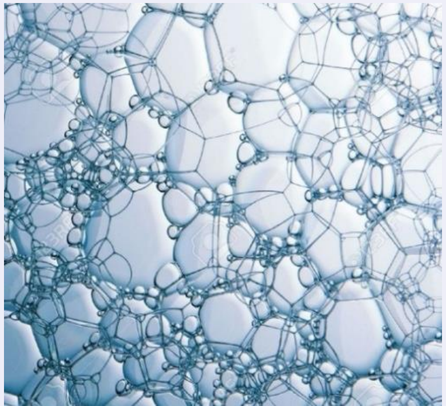
Ex: Silicone paste



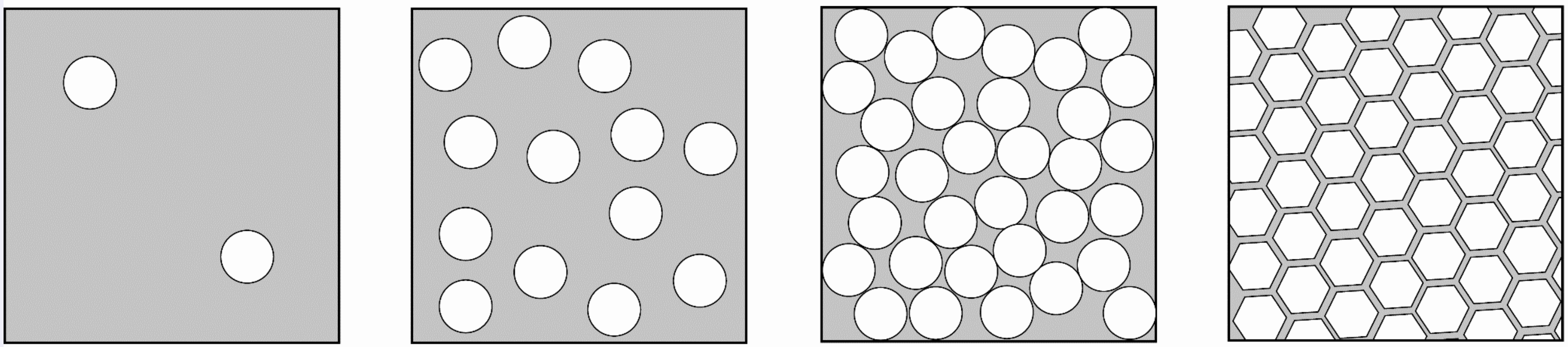
Breakage

EMULSIONS AND FOAMS





Rheological behavior: concentration regimes

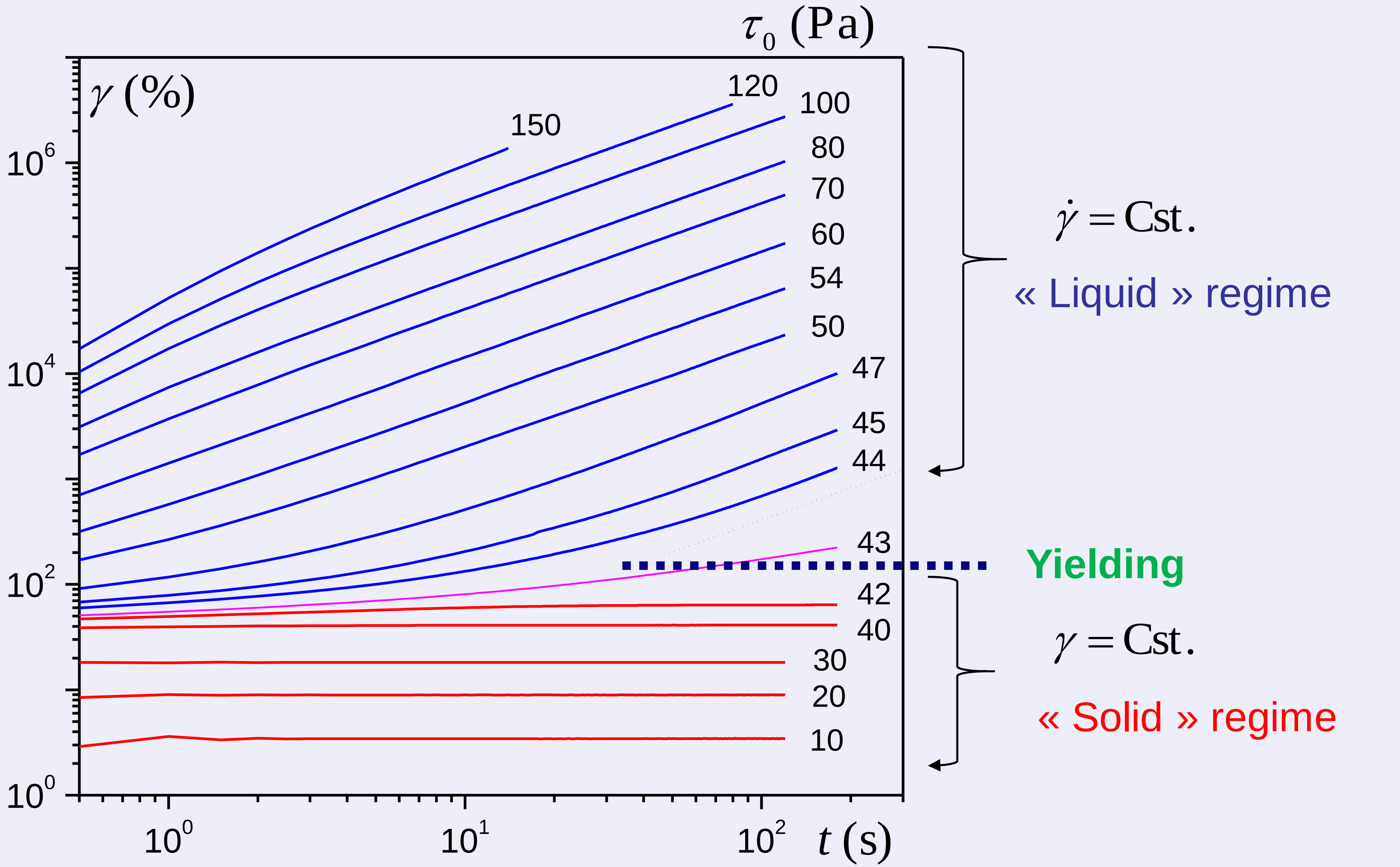


Dilute	Semi-dilute	Concentrated	Compact
$\phi << 1$	$0.01 << \phi < \phi_c$	$\phi_c < \phi < \phi_m$	$\phi \rightarrow 1$
No hydrodynamic interaction	Hydrodynamic interactions	Hydrodynamic interactions + Steric interactions	Hydrodynamic interactions + Steric interactions + Contacts => deformation

→ **essentially Newtonian**

→ **essentially yield stress fluids**

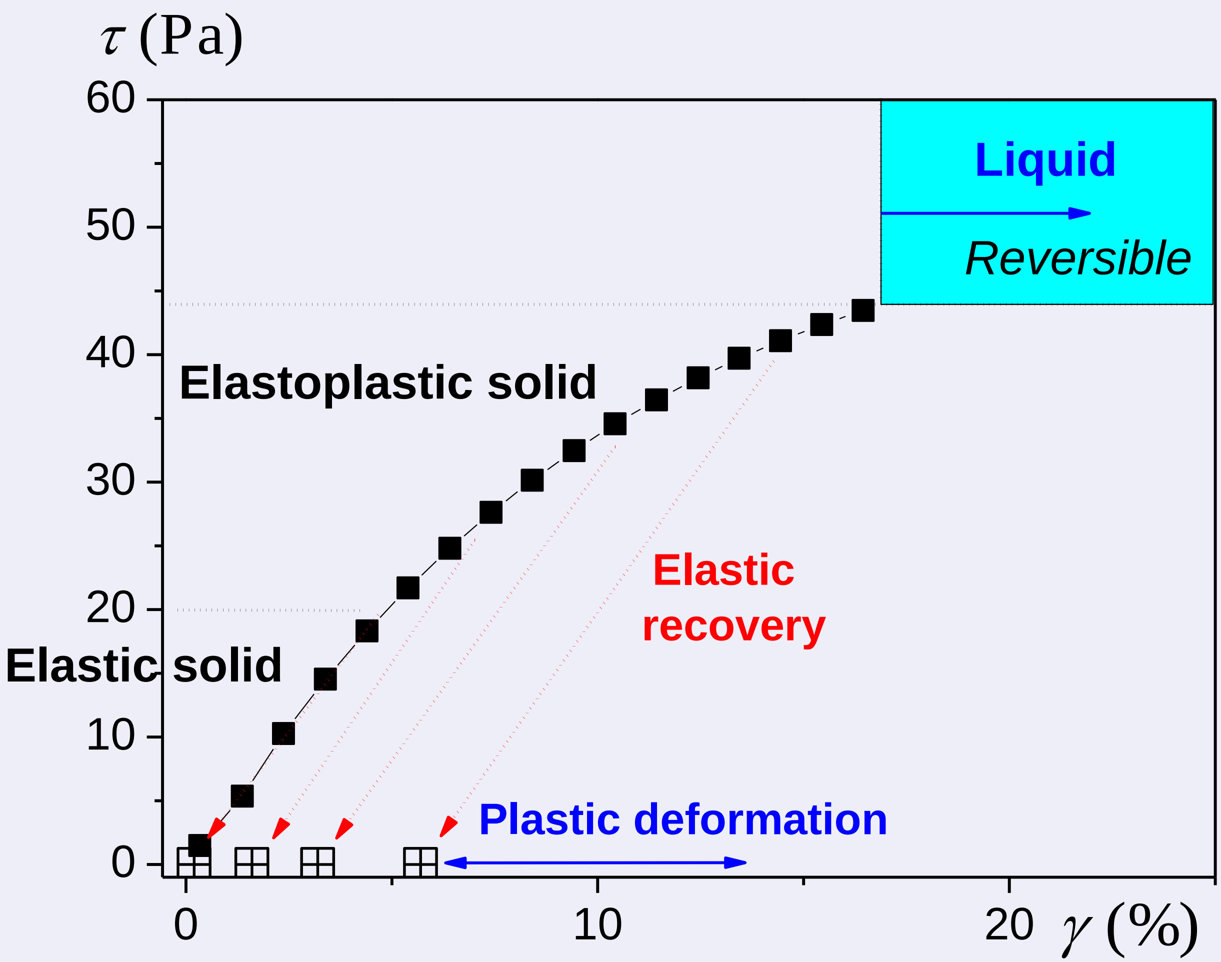
Simple shear creep tests, after same preparation, at different stresses: $\{\tau_0\}$

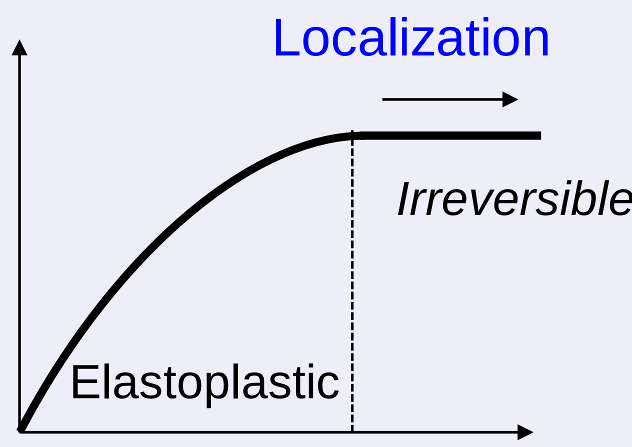


Oil in water emulsion (82%)
Rough parallel disks

$$\gamma \propto t^a \text{ and } a > 1 \Rightarrow \ddot{\gamma} < 0$$

Solid-liquid transition

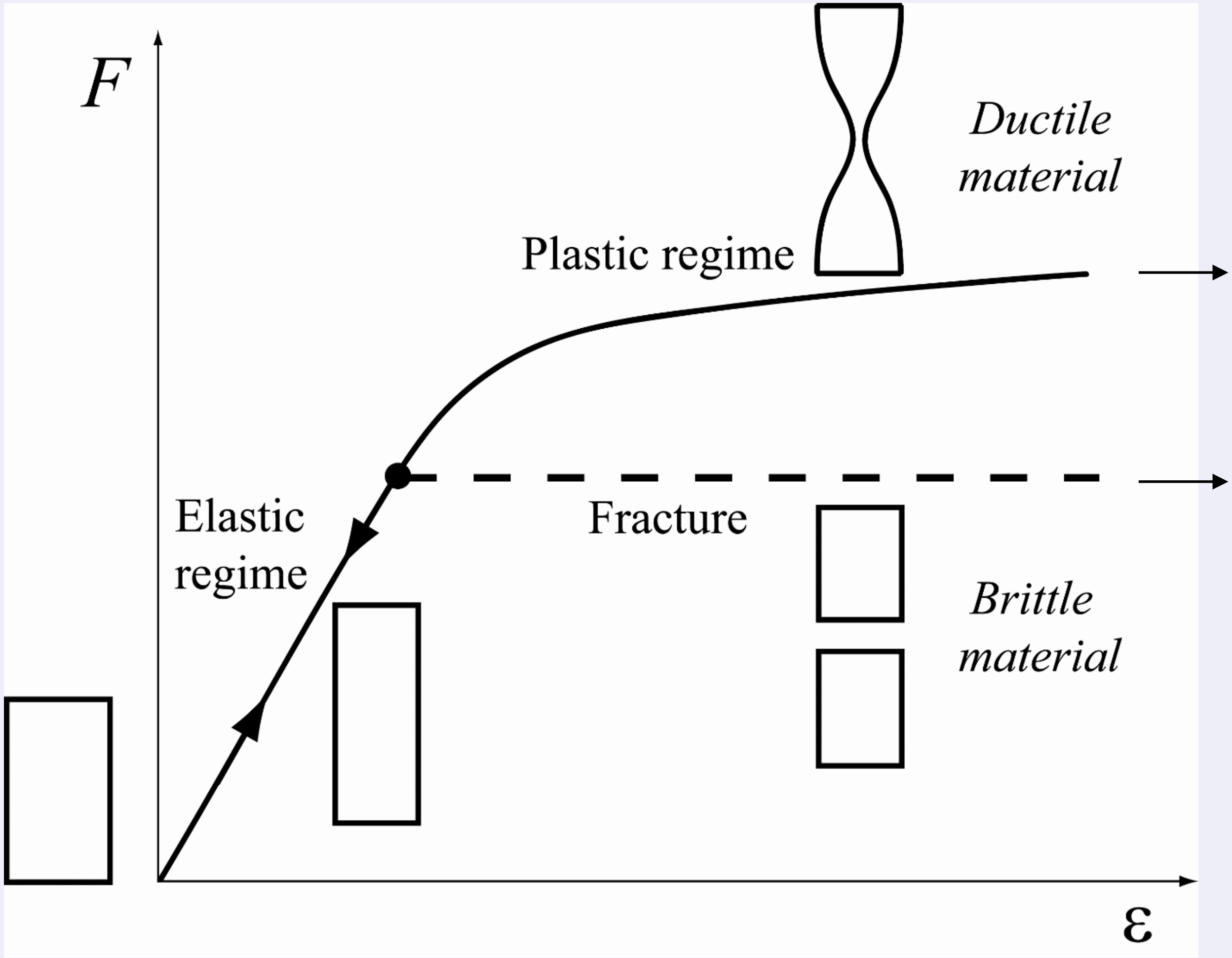




Yield stress fluid

« Standard solid »

Usual behavior of solids



Strong localization of the deformation

6 m

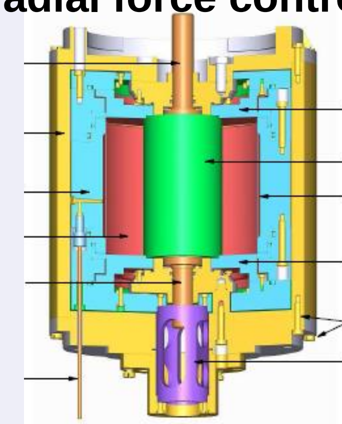
Rheometer

Injection-extrusion

Température control (-40 to +60°C)

+ Drying
+ Flow through porous medium

Shear cell with radial force control

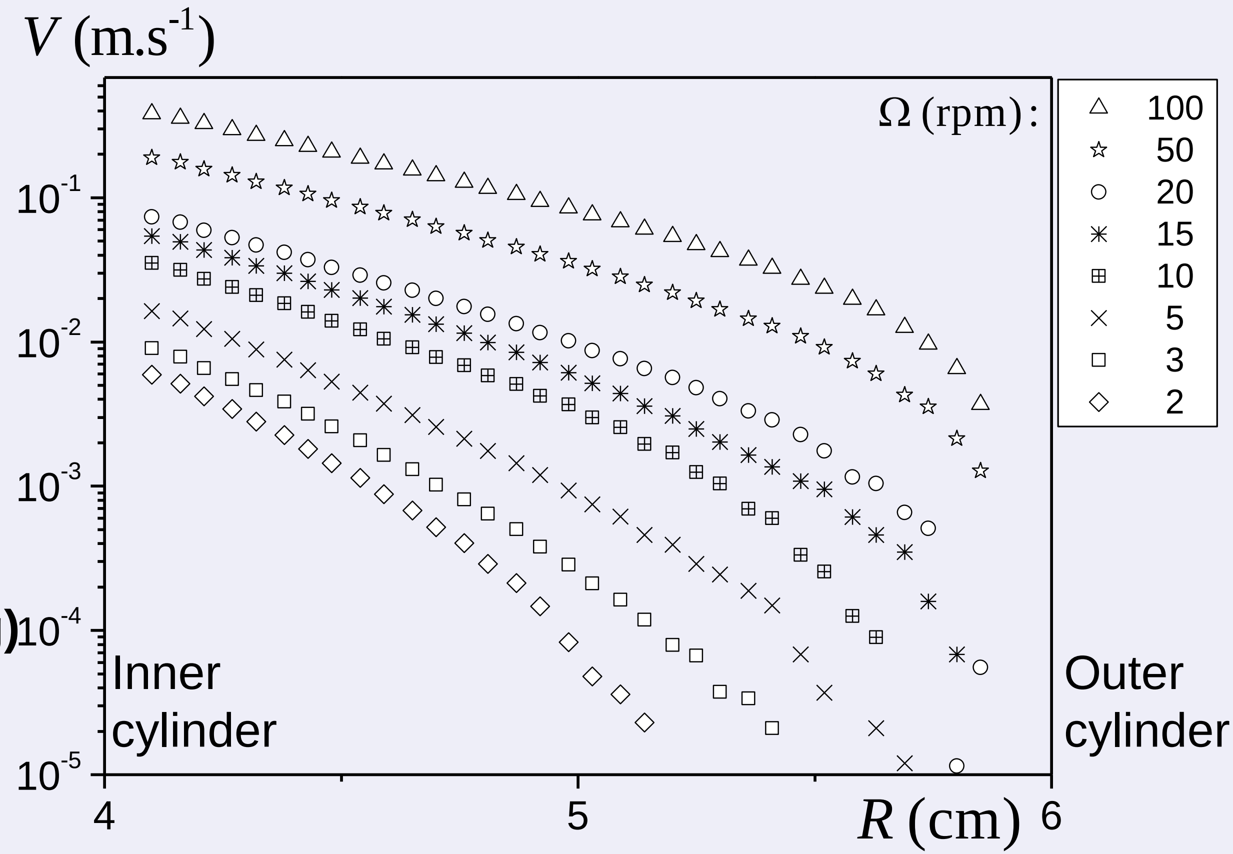


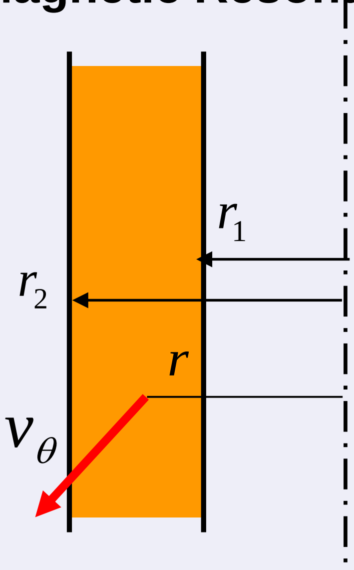
NMR experts:
P. Faure, S. Rodts, D. Courtier-Murias

Transversal Technical Team:
D. Hautemayou – P. Moucheront
C. Courrier - C. Mezière

« Local rheometry »

MRI
(Magnetic Resonance Imaging)

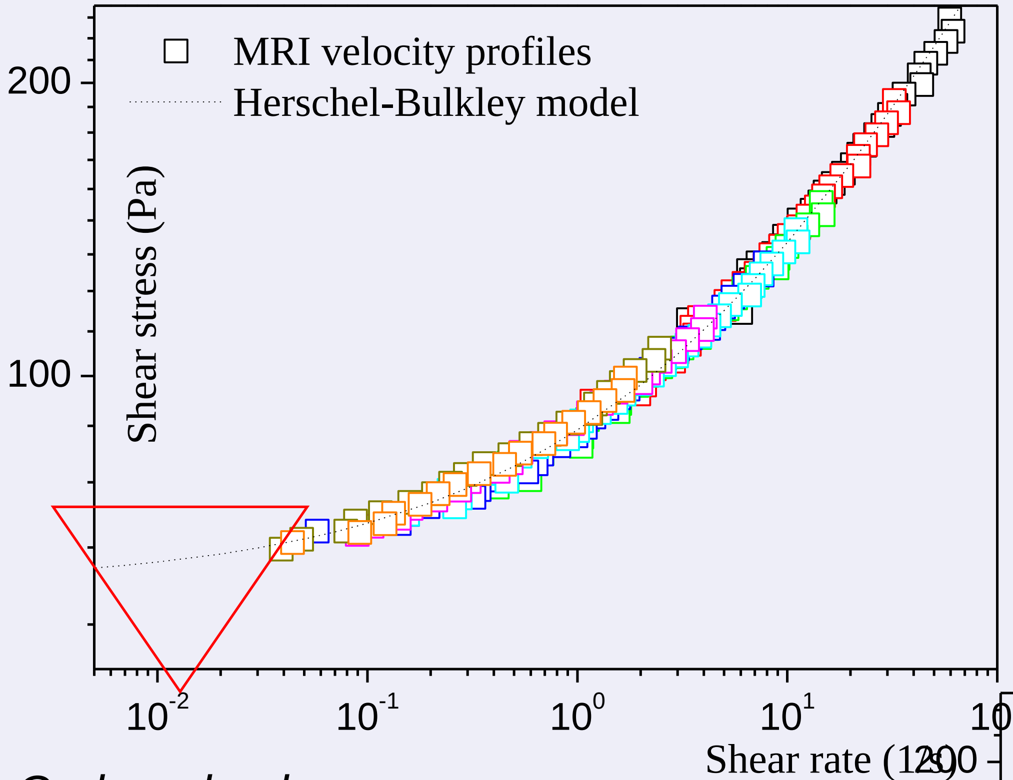




$$\dot{\gamma} = r\frac{\partial}{\partial r}\left(\frac{v_\theta}{r}\right)$$

$$\tau = \sigma_{r\theta} = \frac{C}{2\pi h r^2}$$

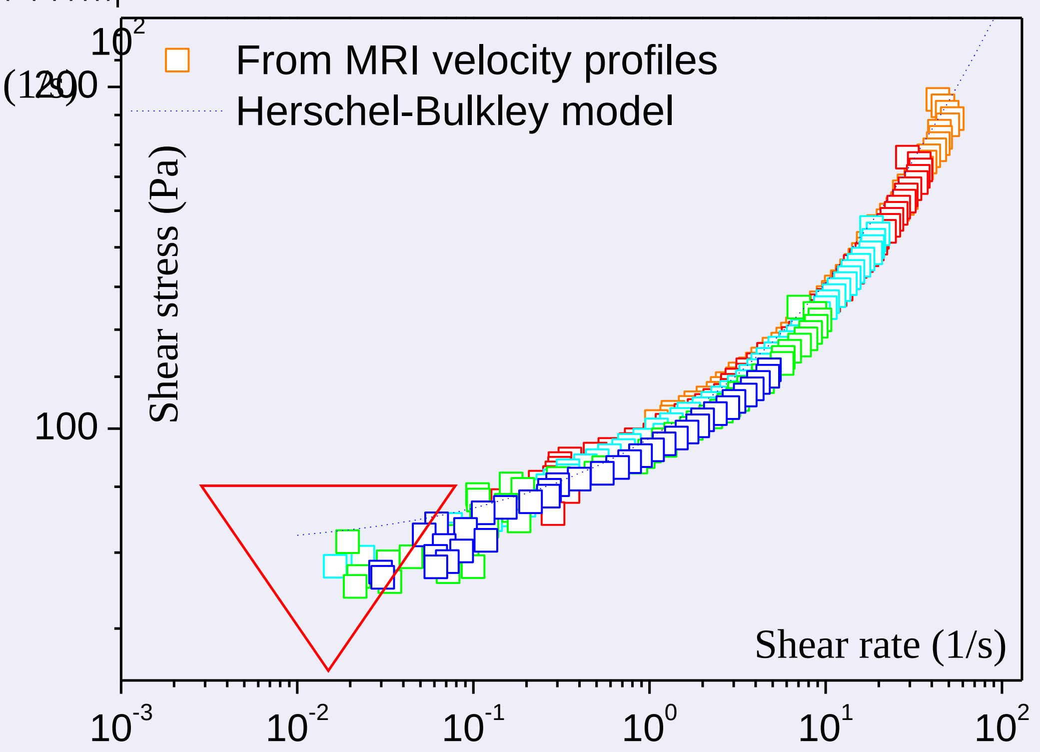
Steady-state velocity profiles under different imposed rotation velocities of the inner cylinder



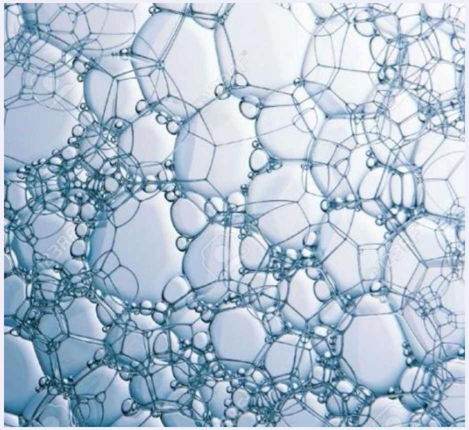
Carbopol gel

A unique, consistent, rheological behavior in the liquid regime

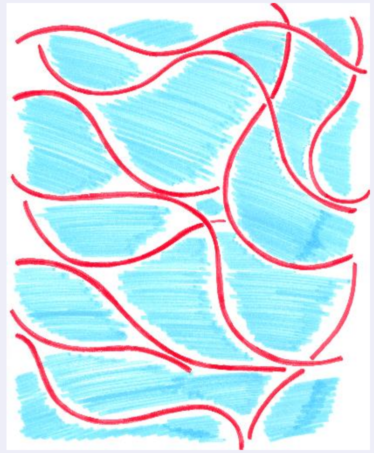
Emulsion



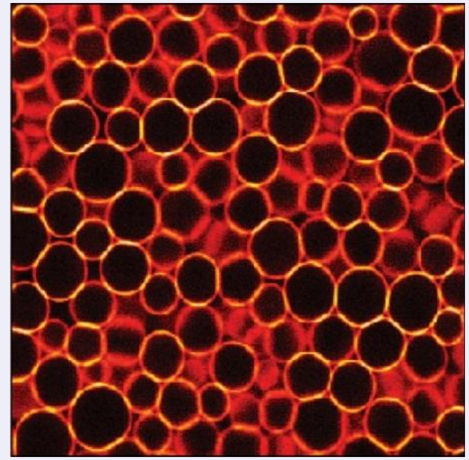
« Simple » yield stress fluids



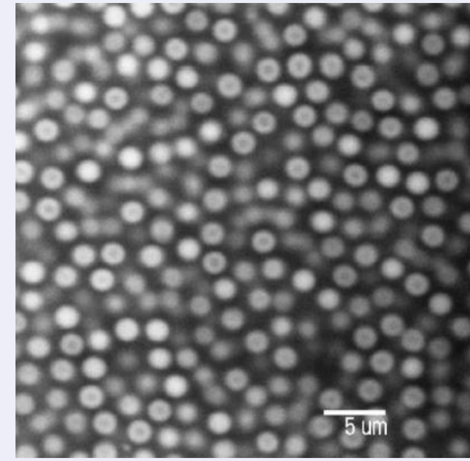
Foam



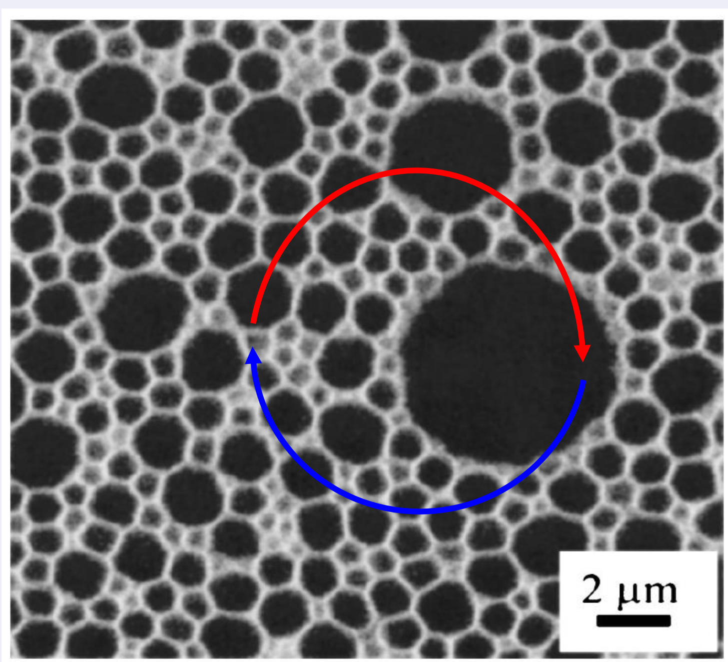
Physical gel



Emulsion



Colloids (repulsive)



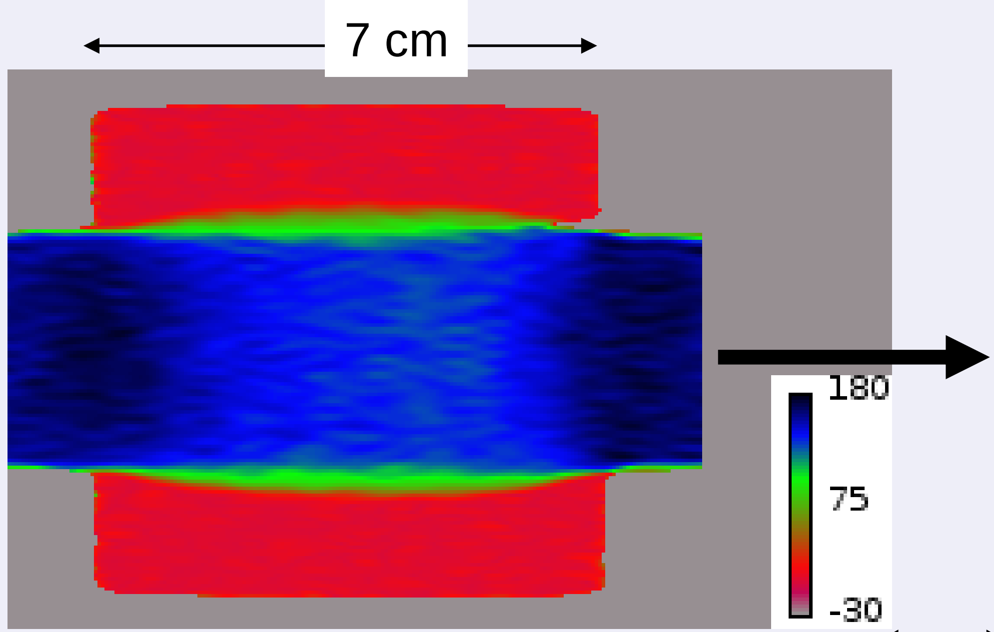
1) Jamming ←→ Solids

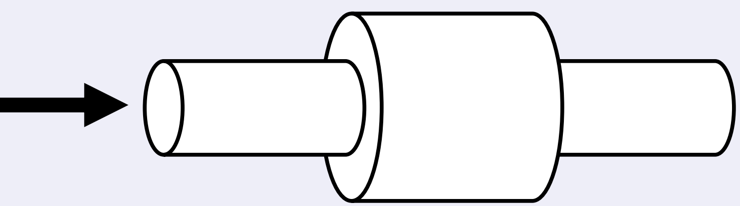
2) Fast relaxation :

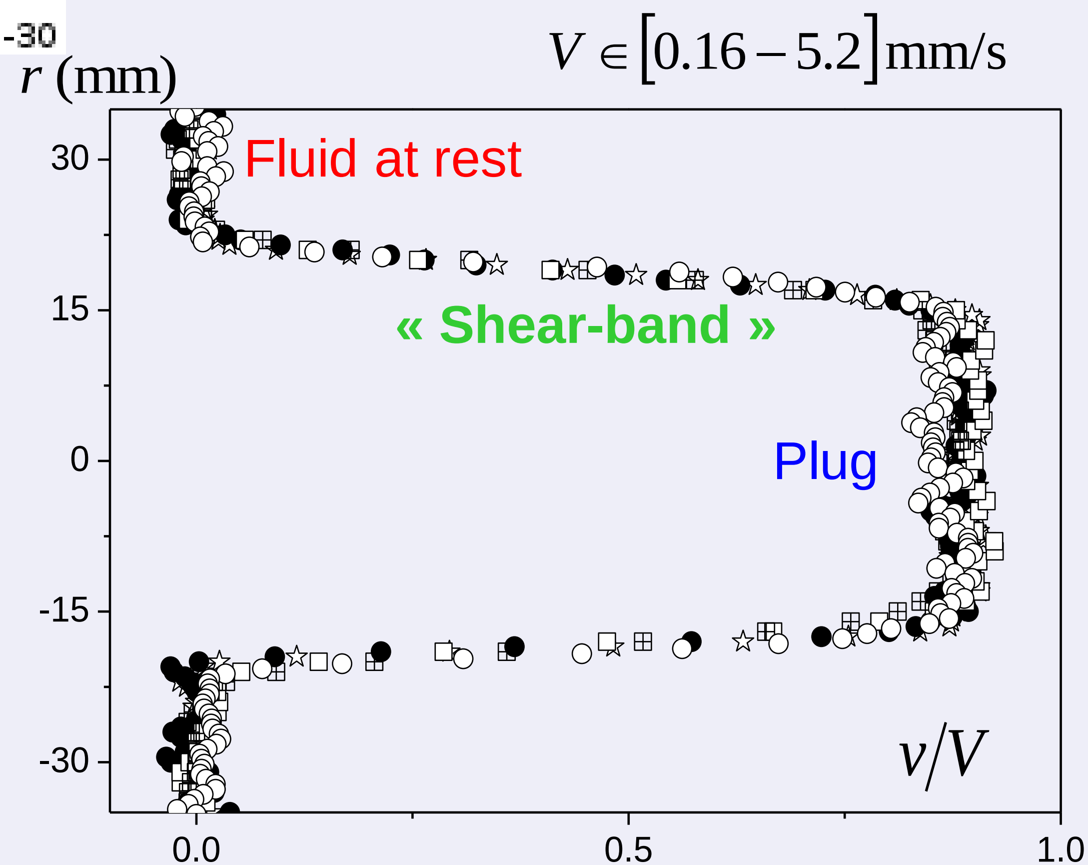
Soft interactions and Disorder

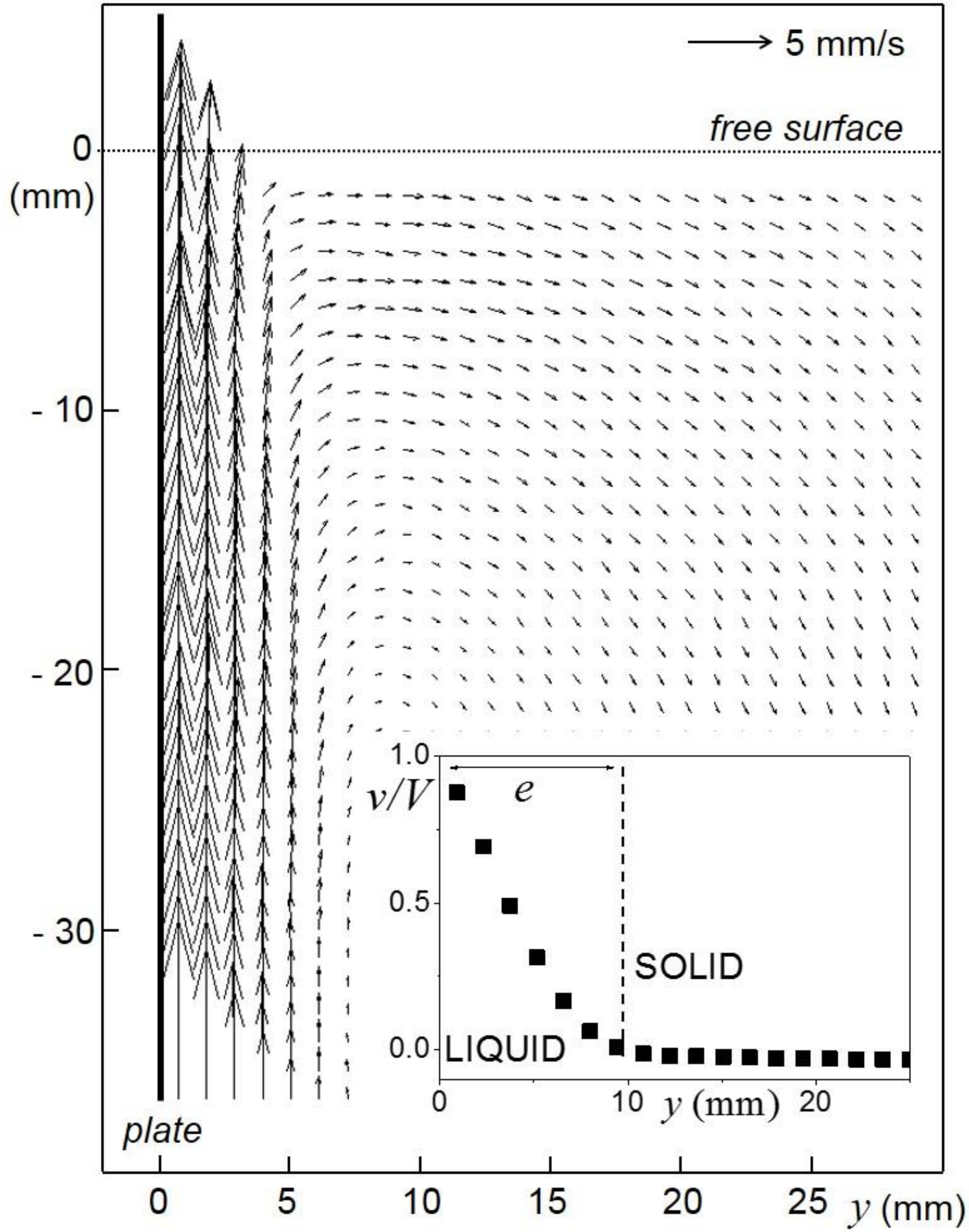
⇒ YSF: « Fast self-healing solids »

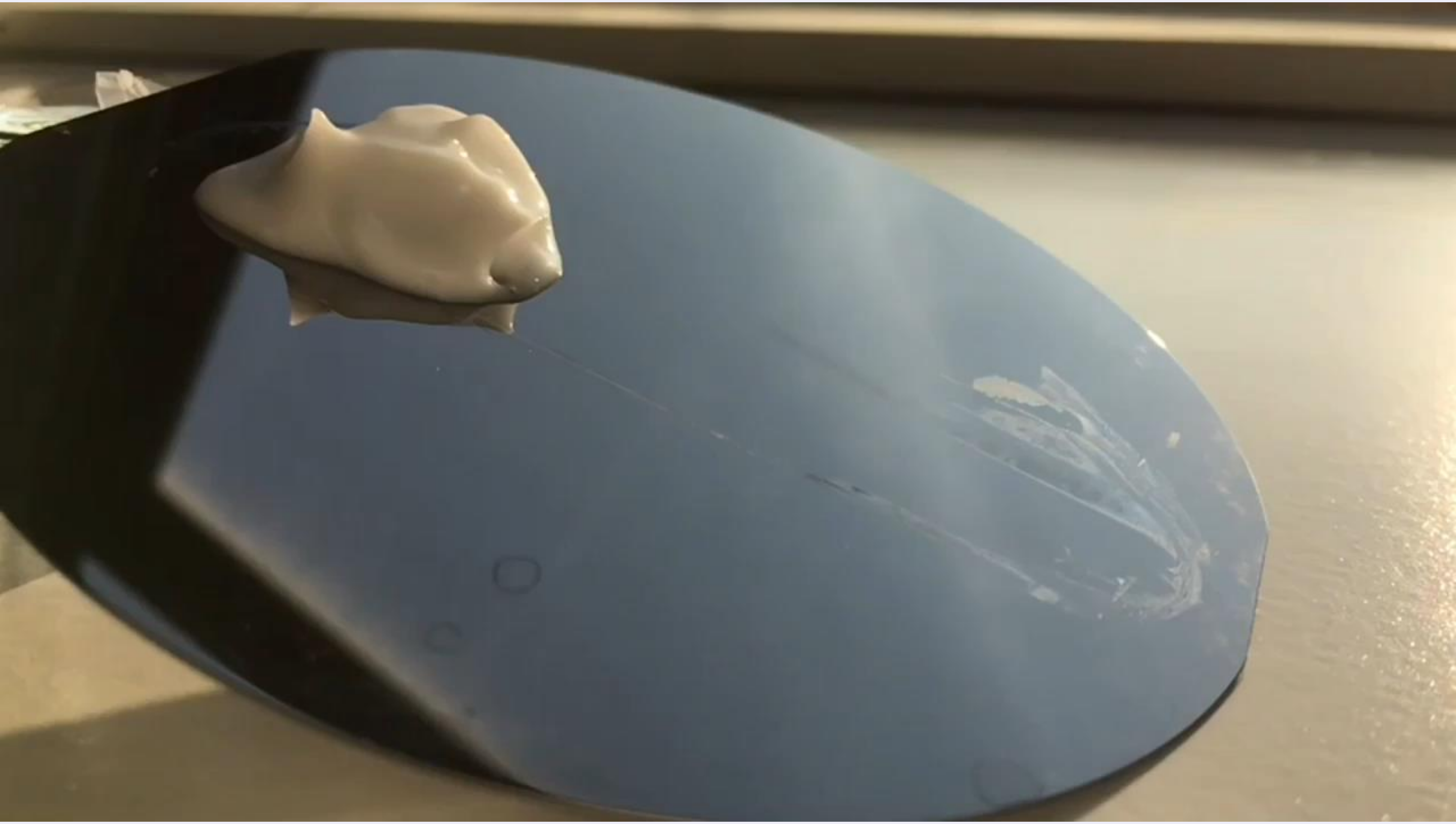
Flow of a yield stress fluid through a model pore



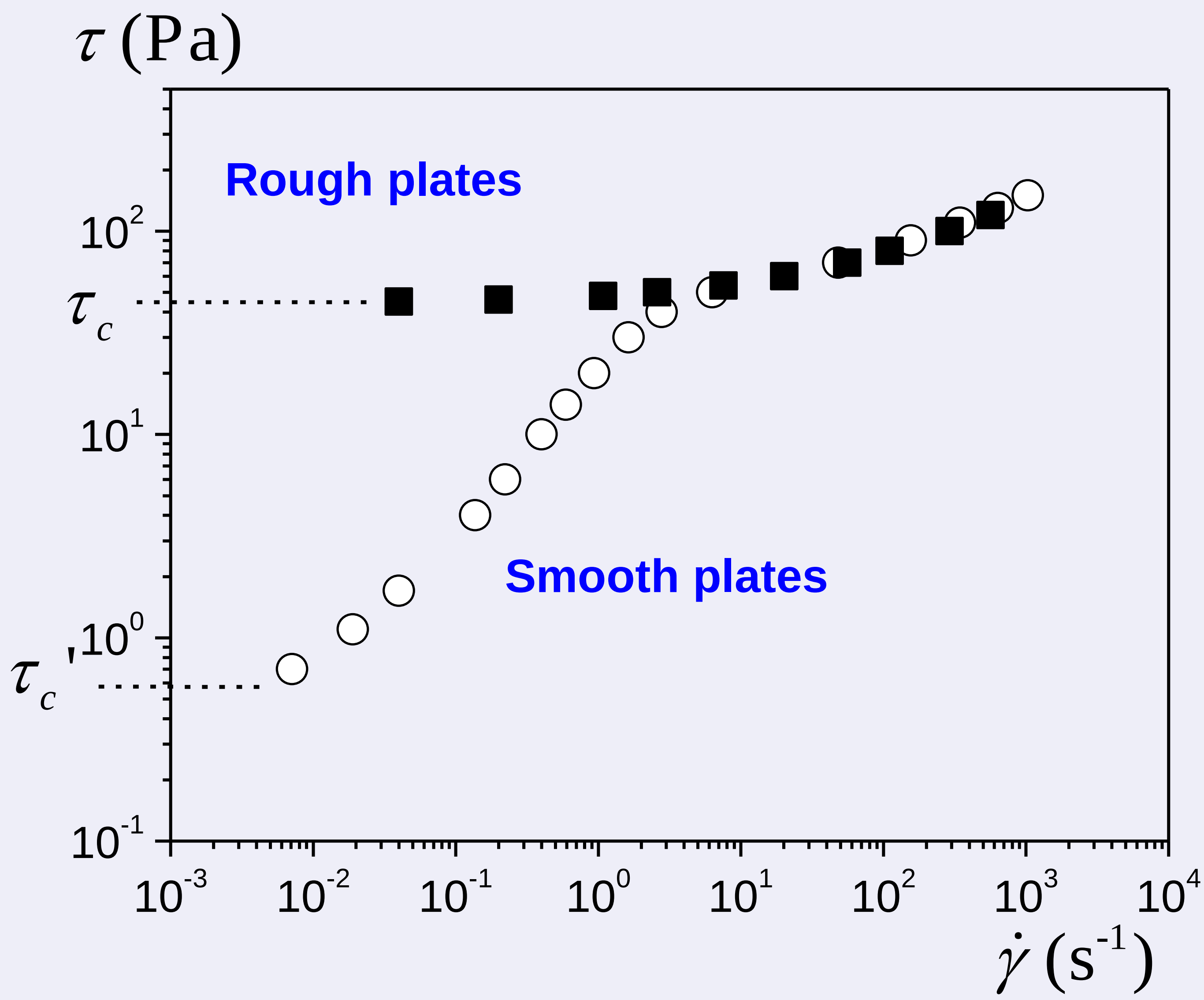





5 mm/s
free surface
0
(mm)
- 10
- 20
- 30
plate
0
5
10
15
20
25
y (mm)
1.0
v/V
e
0.5
0.0
SOLID
LIQUID
0
10
y (mm)
20

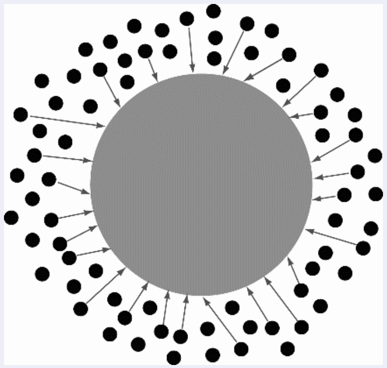


Apparent flow curve with smooth surface

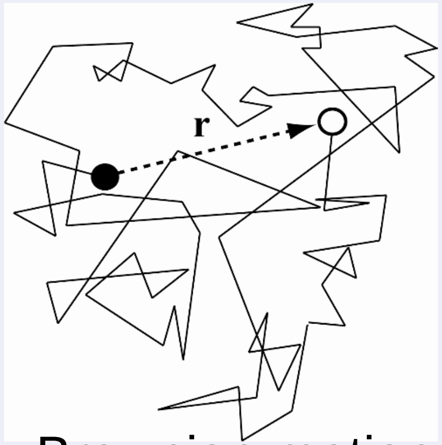


COLLOIDAL DISPERSIONS

Hydrodynamic interactions +



Thermal agitation:



Brownian motion

⇒ **Slow relaxation process**

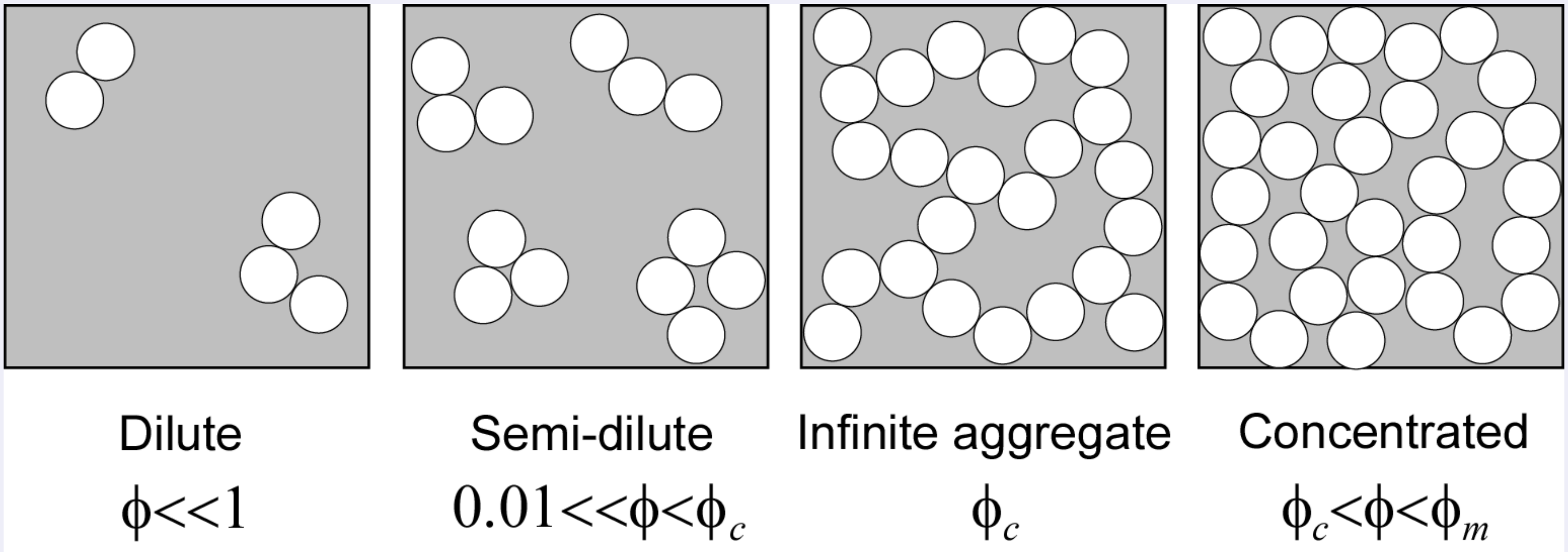
In a liquid: interactions between particles

- **Van der Waals attraction**
- **Electrostatic (repulsion)**
- **Depletion effect**
- **Steric repulsion**

⇒ **Weak attractive or repulsive forces**

Ex.: Silica, clay, latex, pollens (>10 μm), cement, micelles, microgels, micro-droplets

Attractive suspensions



Essentially Newtonian ⟶ **Yield stress fluids thixotropic (shear-banding)**

Attractive systems

Rest

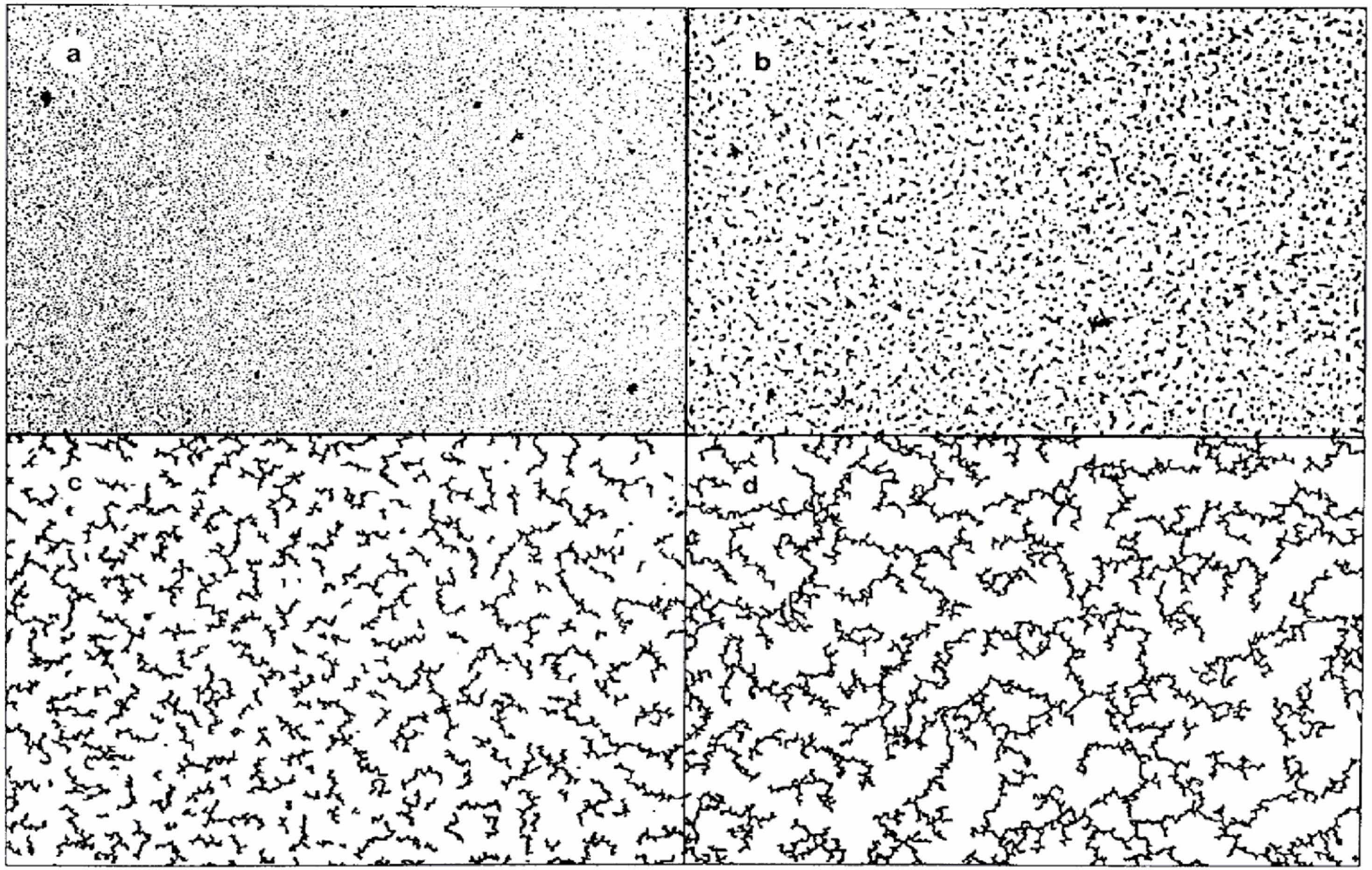
→

Shear

←

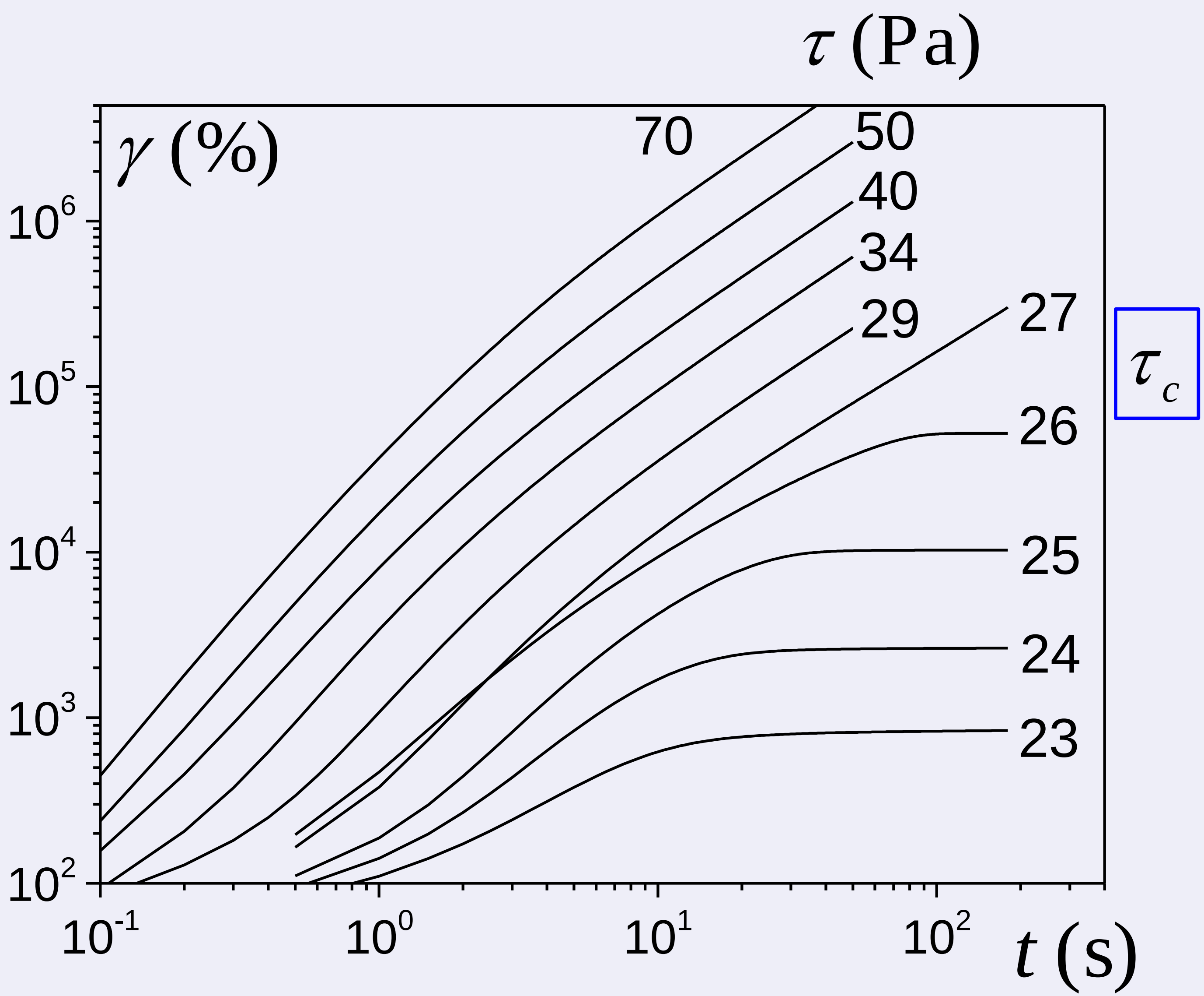
Monolayer of polystyrene beads (3.1mm) along an oil-water interface

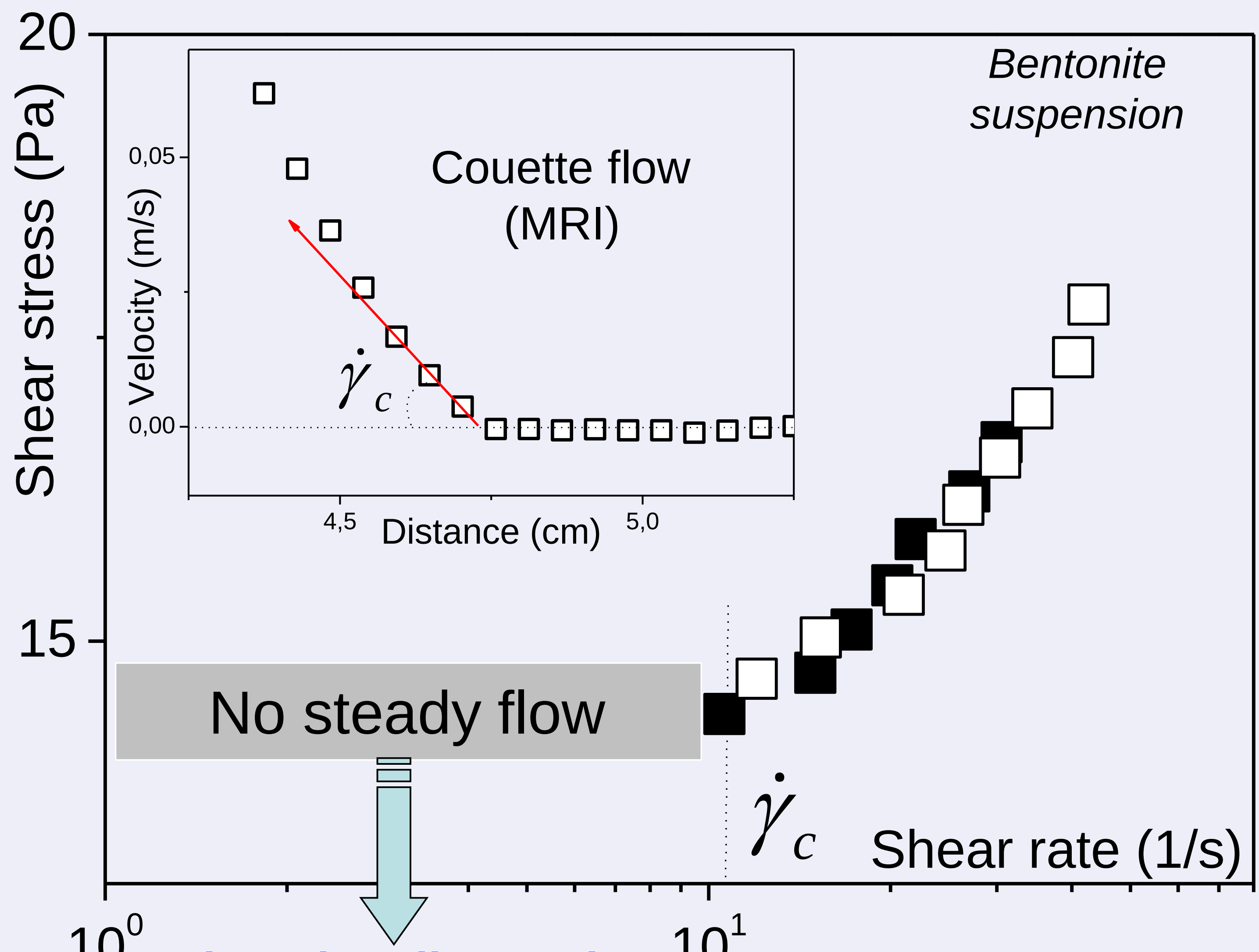
Park et al., *Langmuir*, 2008



Latex beads (15, 75, 105, 135 min after salt addition)

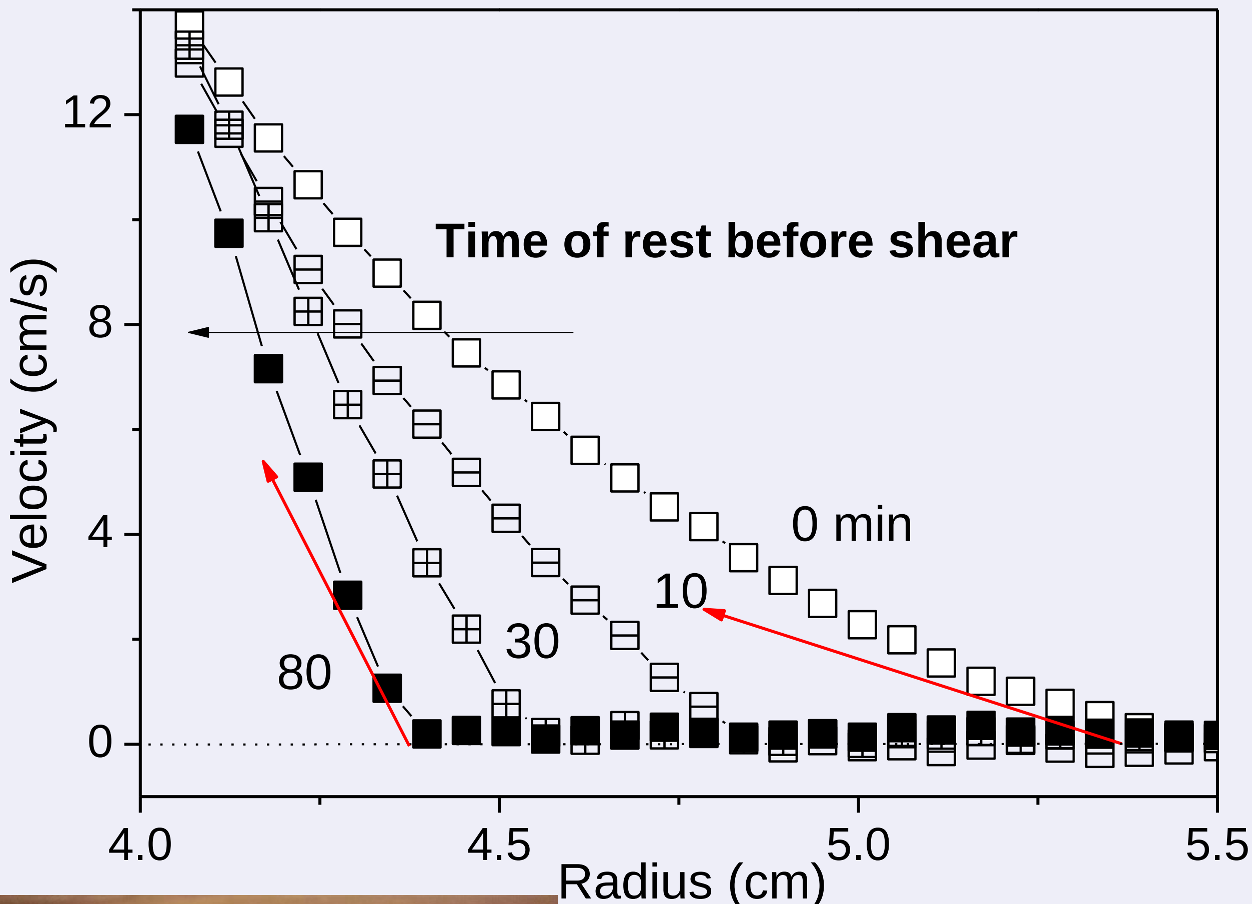
Creep tests with a thixotropic material





Shear-banding under controlled shear rate

Impact of time of rest

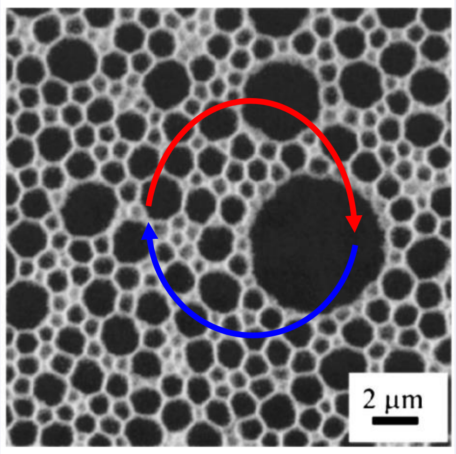


Steady state Couette flow after different times of rest

$\dot{\gamma}_c$ Increases with the time of rest

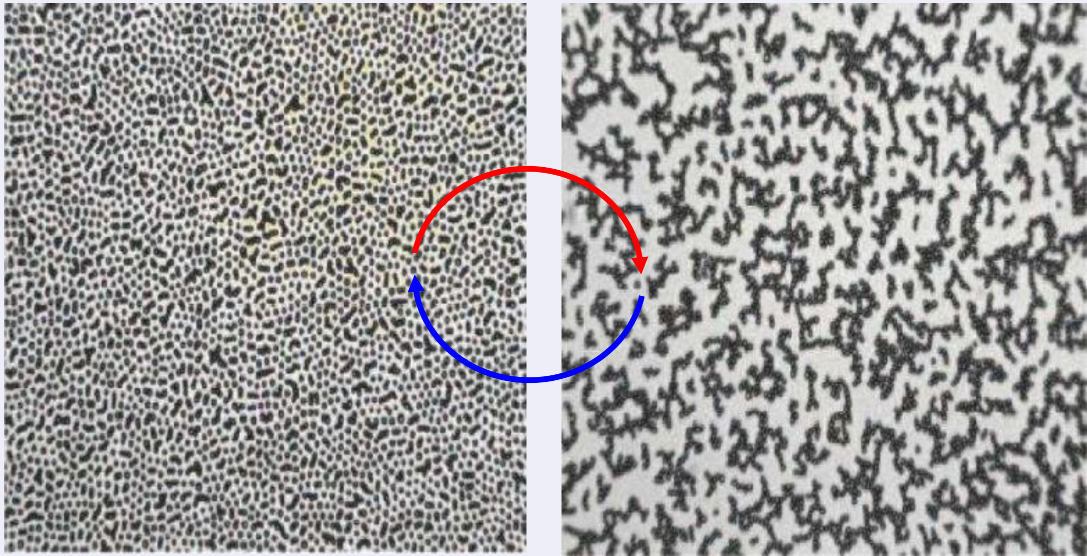
Bentonite suspension

Simple yield stress fluids



Thixotropic yield stress fluids

Slow restructuring



Park et al., *Langmuir*, 2008

Flow curve of concentrated attractive systems