



Flow of concentrated suspensions. shear thickening.

annie.colin@espci.fr

Guillaume Chatté, Brice Saint Michel, Sébastien Manneville, Guillaume Ovarlez, Hugues Bodiguel,, Jean Comtet, Alessandro Siria, Lydéric Bocquet, Antoine Nigues

Outlines

- Flow of non Brownian dispersions
- Macroscopic characterization: PVC in Pasticizer, Rheology, Velocity profiles, Liquid fraction profiles.
- How do suspensions flow in shear thickening regime?
 - Velocity profiles, Liquid fraction profiles.
 - Why do suspensions shear thin, shear thicken?
 - A few words dealing with cornflour.
- Outlooks and perspective

Non brownian suspensions

NON BROWNIAN SUSPENSIONS

- d the diameter of the particles [m]
- $\dot{\gamma}$ the shear rate involved in the flow [s^{-1}]
- η the viscosity of the suspended fluid [Pa.s]
- P the particular pressure [Pa]
- ρ the density of the particles [$kg \cdot m^{-3}$]

$$Re = \frac{\rho d^2 \dot{\gamma}}{\eta}$$

NON BROWNIAN SUSPENSIONS at low Reynolds

- d the diameter of the particles [m]
- $\dot{\gamma}$ the shear rate involved in the flow [s^{-1}]
- η the viscosity of the suspended fluid [Pa.s]
- P the particular pressure [Pa]

4 parameters, 3 fundamental units

Π theorem, dimension analysis
a single dimensionless number

Non brownian suspensions: a single dimensionless number

4 parameters, 3 fundamental units , Π theorem, dimension analysis a single dimensionless number:

$$Iv = \frac{\eta\dot{\gamma}}{P}$$

$$\tau = \mu(Iv)P$$

$$\phi = g(Iv)$$

$$\tau = \mu(g^{-1}(\phi)) \frac{\eta\dot{\gamma}d}{g^{-1}(\phi)}$$

*Da Cruz (2005),
Boyer, Pouliquen, Guazelli (2011)
PRL*

Consequences : in the situation where the solid fraction is imposed, the stress is proportional to the shear rate: Newtonian behavior expected.

An yield stress?

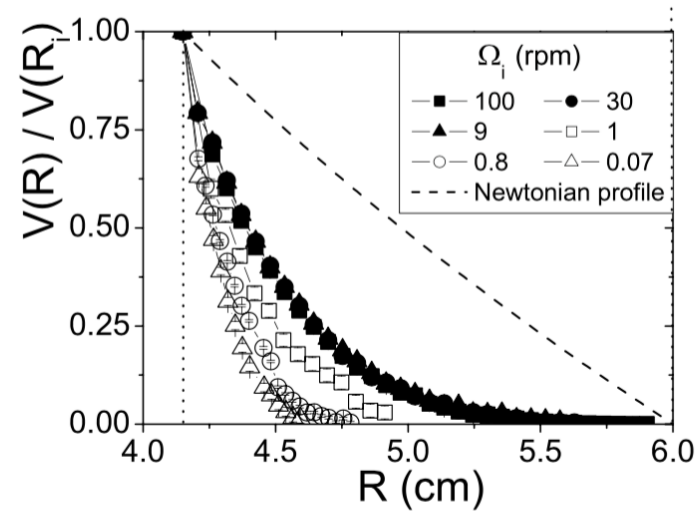


Figure 3: Dimensionless velocity profiles (from Huang *et al.* (2005)) in the steady state of a 58% suspension, at various rotational velocities ranging from 0.07 to 100rpm; the dashed line is the theoretical dimensionless velocity profile for a Newtonian fluid.

Variation of the concentration

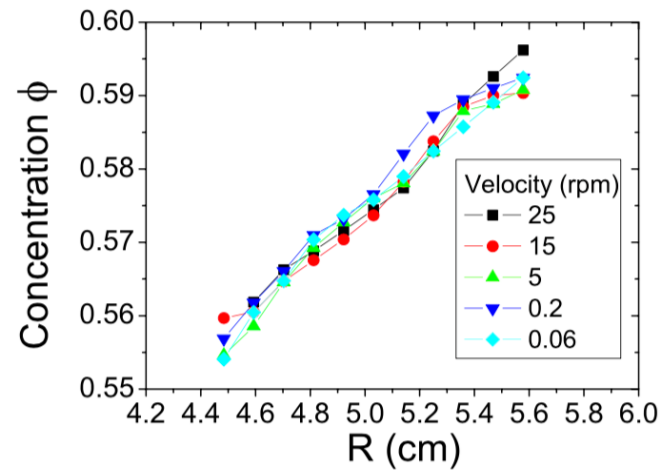


Figure 6: Concentration profiles measured in the gap of the Couette geometry for a suspension of mean volume fraction 58% sheared at various rotational velocities ranging from 0.06 to 25rpm.

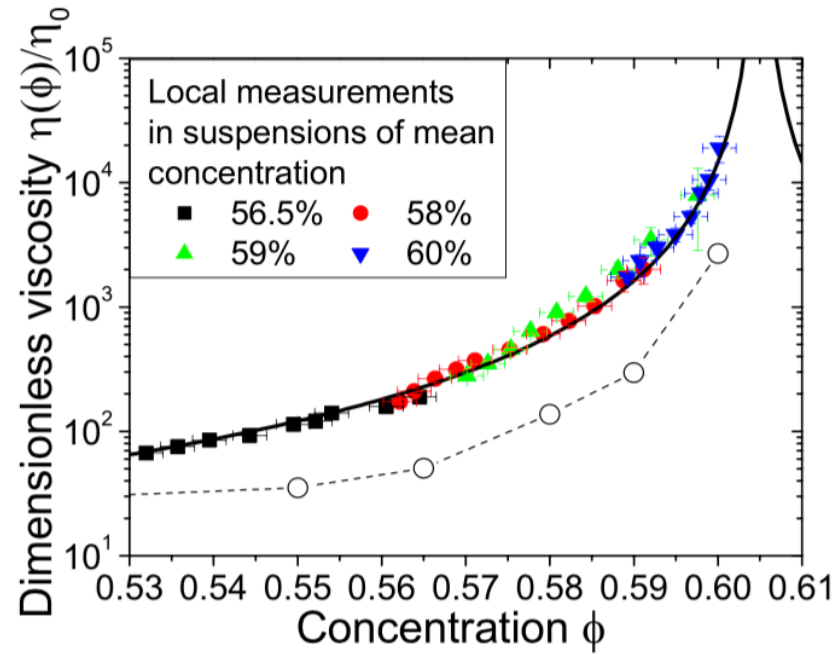


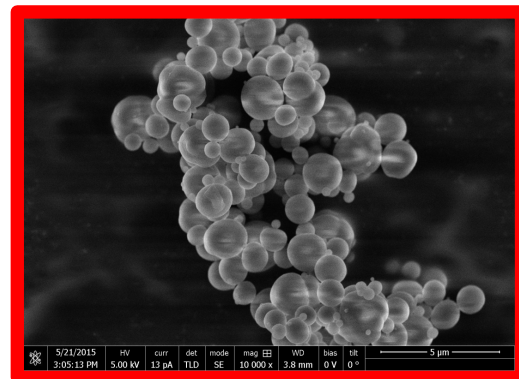
Figure 13: Local and macroscopic viscosity measurements on suspensions of various mean concentration ranging from 55% to 60%. The line is a fit to a Krieger-Dougherty law $\eta(\phi) = \eta_0(1 - \phi/0.605)^{-2}$.

How do these suspensions flow? Our study.

- System Under scrutiny
- Rheology.
- Flow profile, solid fraction profiles
- Flow in the shear thinning regime
- Flow in the shear thickening regime
- Shear thinning after the shear thickening regime

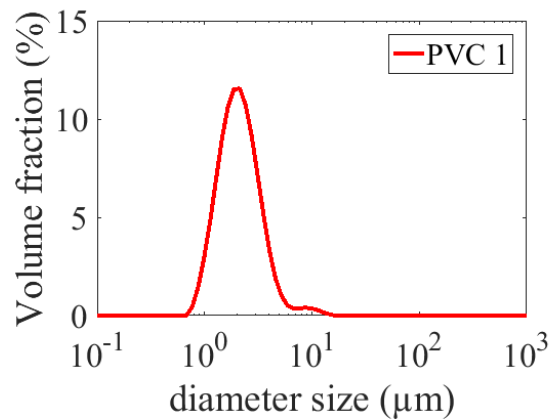
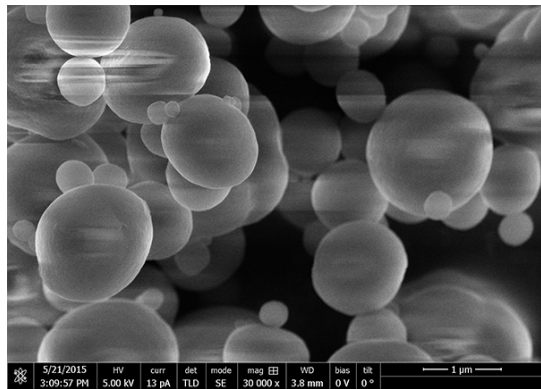
Outlooks

PVC suspensions non Brownian suspensions



2 μm

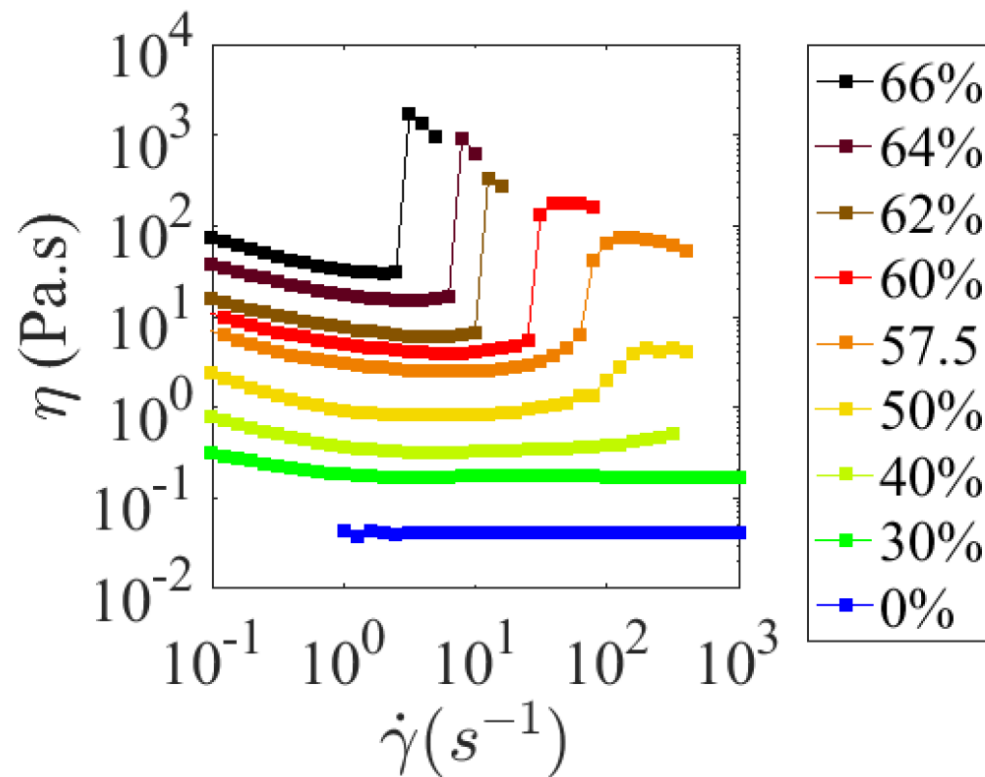
PVC suspensions in plasticizer



Polyvinyl chloride (PVC) particles in 1,2-cyclohexane dicarboxylic acid diisononyl ester (Dinch). The continuous phase is Newtonian and has a viscosity of 41 mPa.s at room temperature.

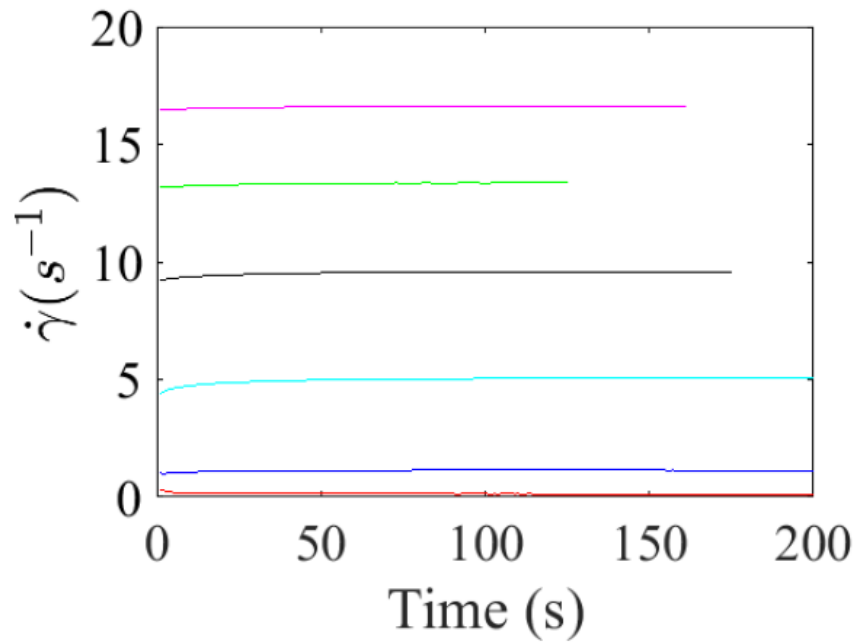
The density of PVC is 1.38 g/cm³ and the density of Dinch is 0.95 g/cm³. The mean particle radius, defined as $R_{32} = \langle R^3 \rangle / \langle R^2 \rangle$ is 1 μm. The size distribution is lognormal and the standard deviation estimated using the volume distribution is 45%.

Shear Thickening, Under applied shear rate

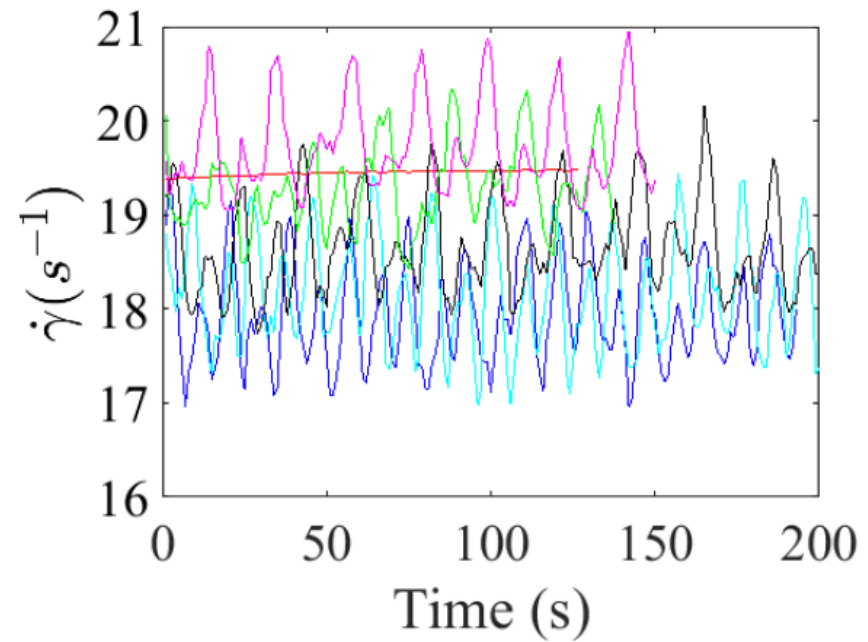


Under applied shear rate
Couette Cell 1mm gap

How do suspensions flow under applied shear stress?

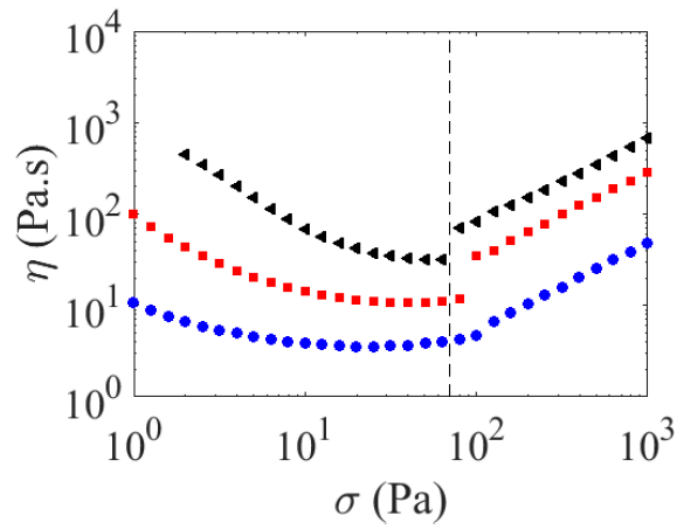


(a)

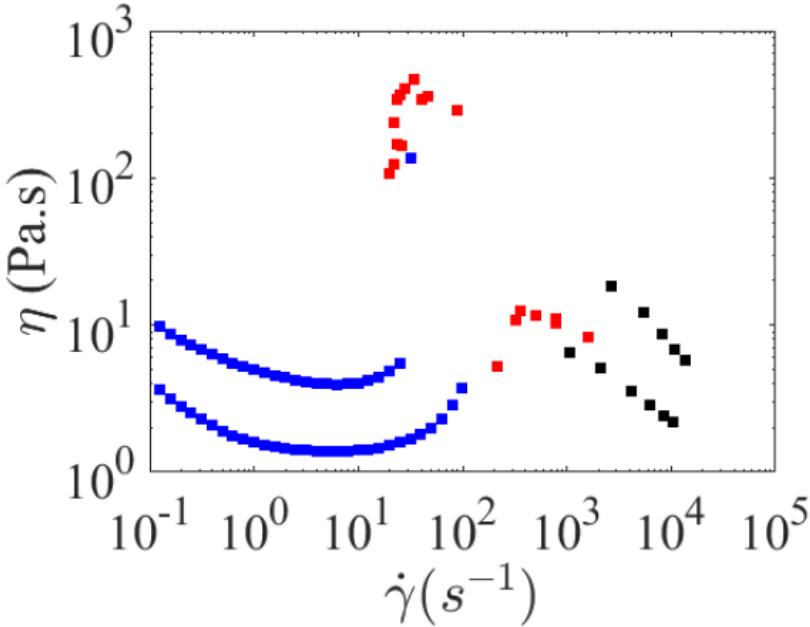


(b)

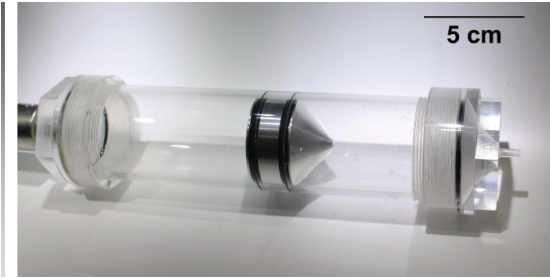
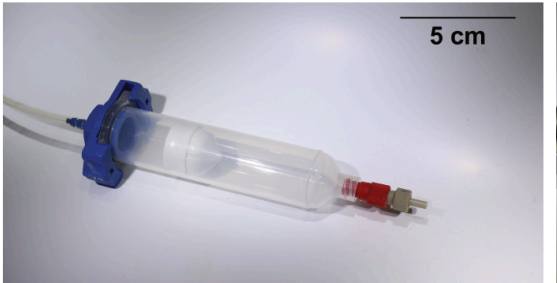
How do suspensions flow? Conventional rheometry in couette cell.



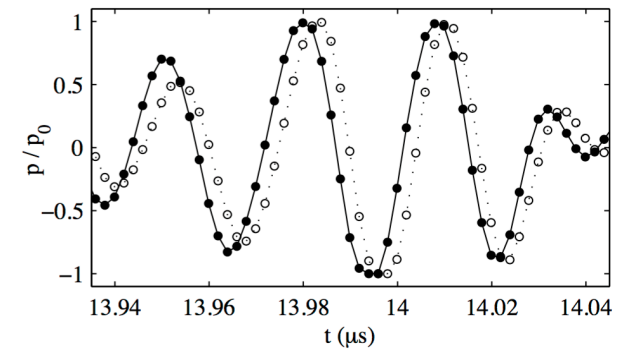
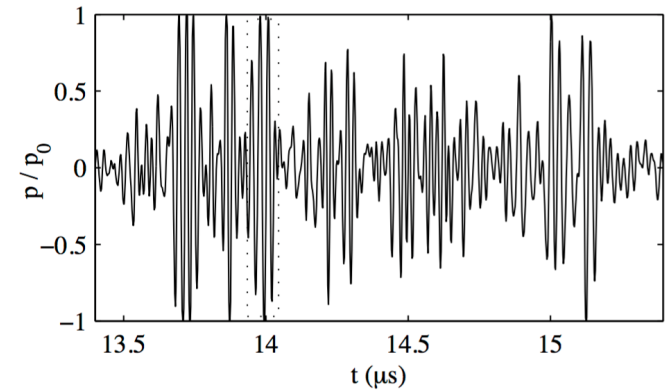
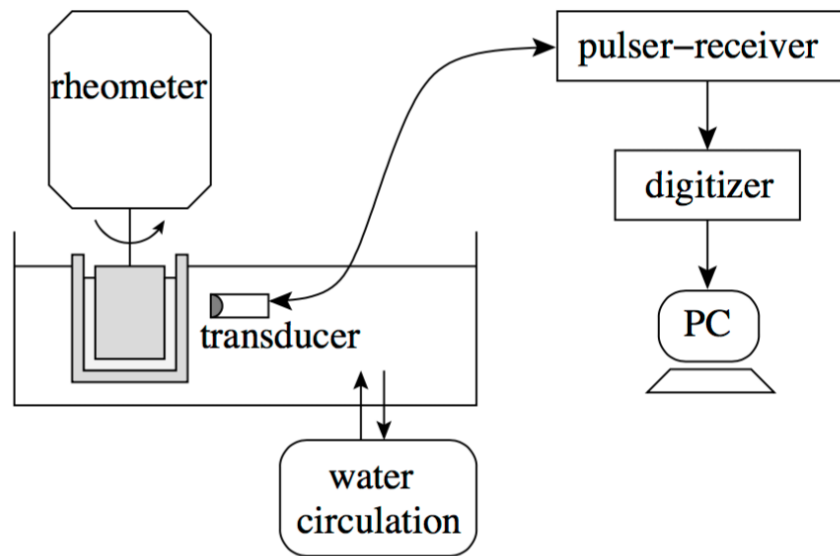
The entire flow curve with three different rheometers



Couette cell 1mm gap
Capillary rheometer
(home made)
Capillary rheometer



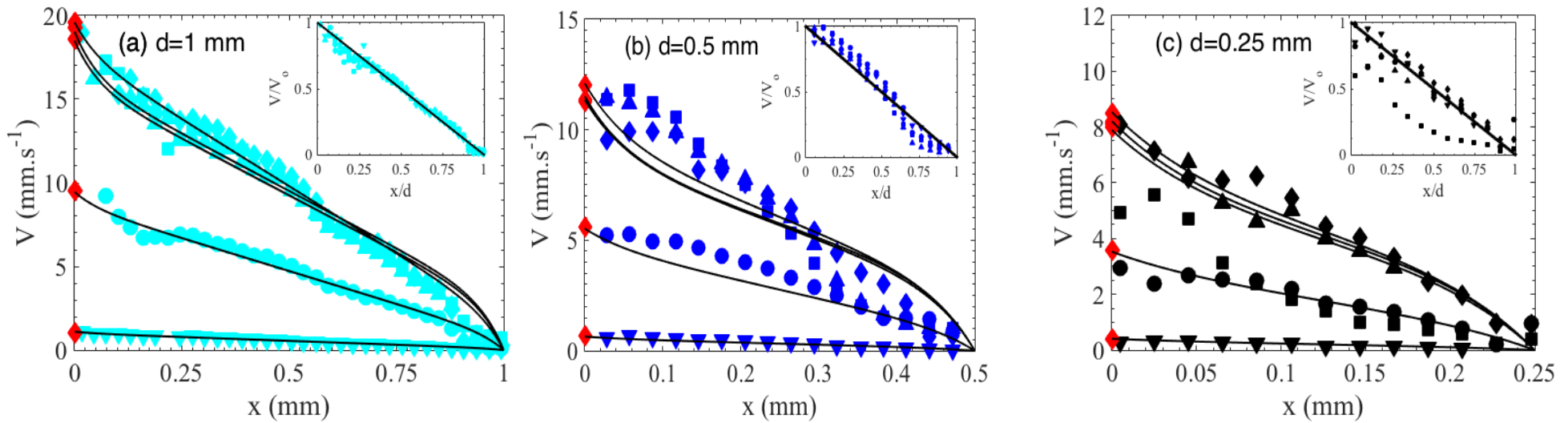
How do suspensions flow? Velocity profiles measurements



S. Manneville, L. Bécu, and A. Colin EPJE 2003

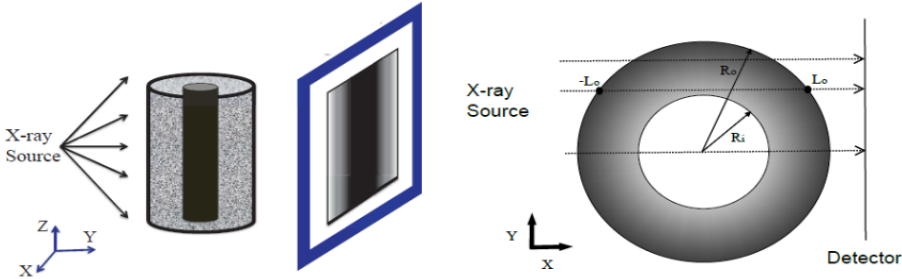
$$v = c_0 \frac{\delta t}{2T} \quad y = c_0(t_k - t_s)/2$$

Velocities profiles

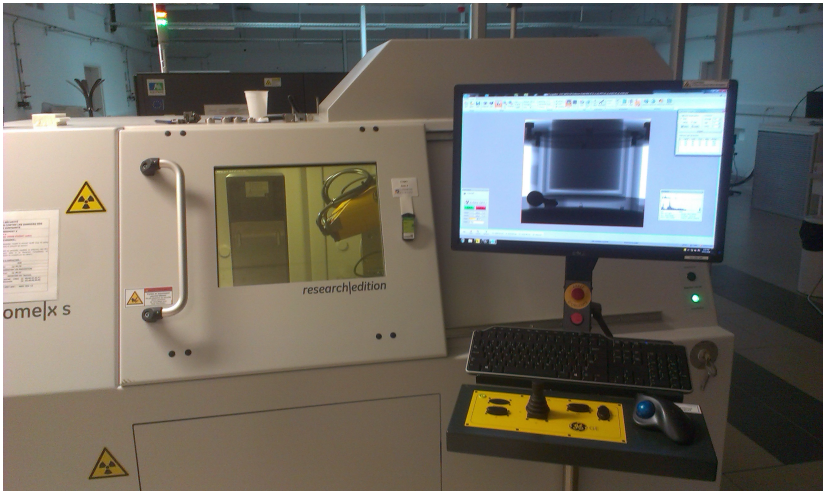


No slip at the wall → homogeneous flow

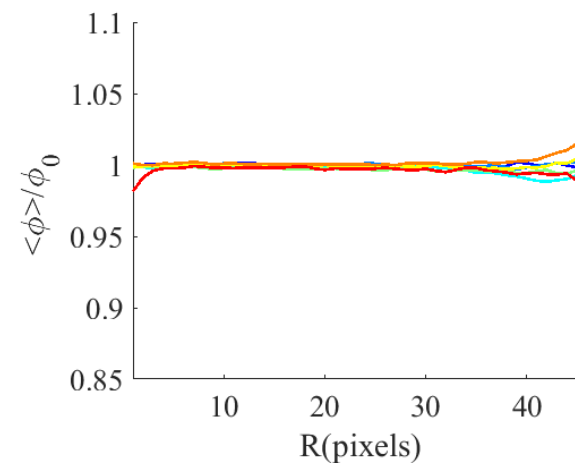
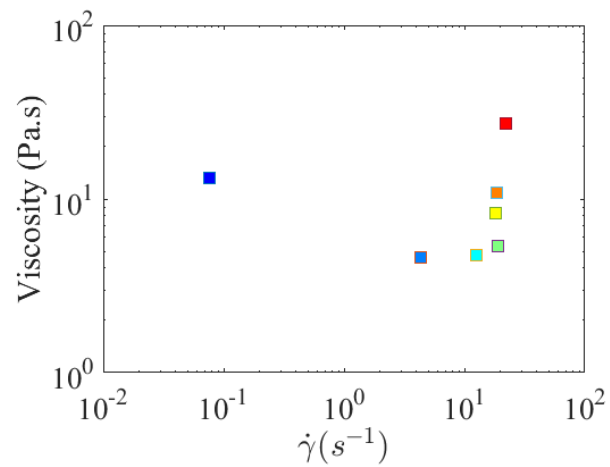
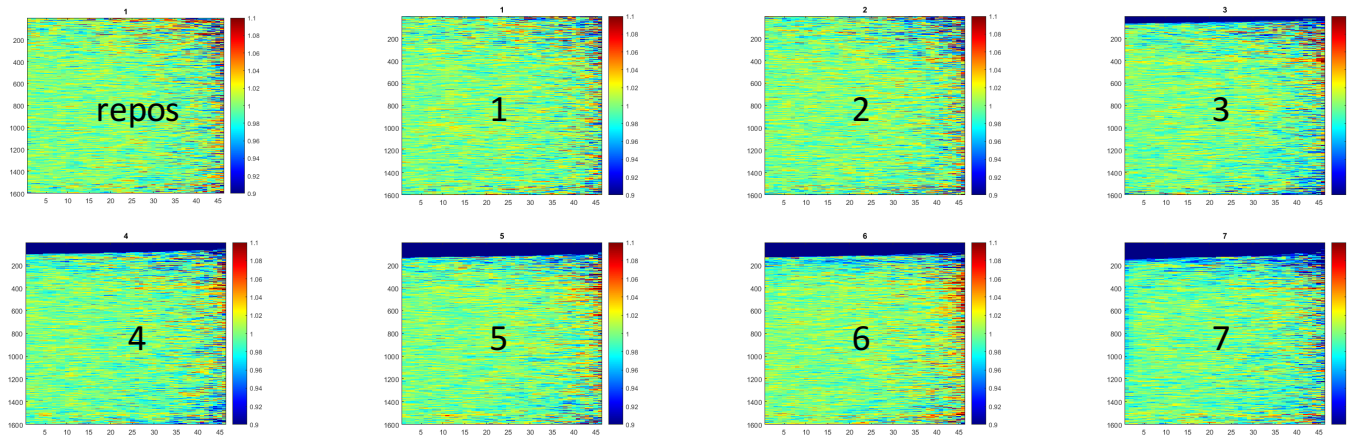
Solid fraction profile



Guillaume Ovarlez,
Nicolas Lenoir
Placamat.

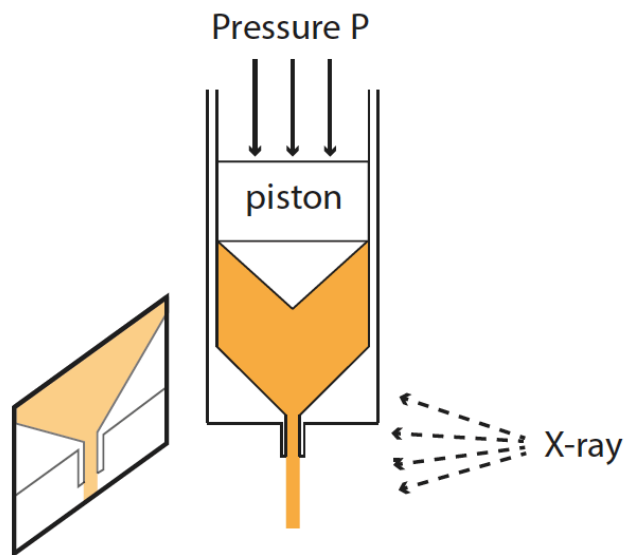


PVC 1 mm gap No migration, no bands

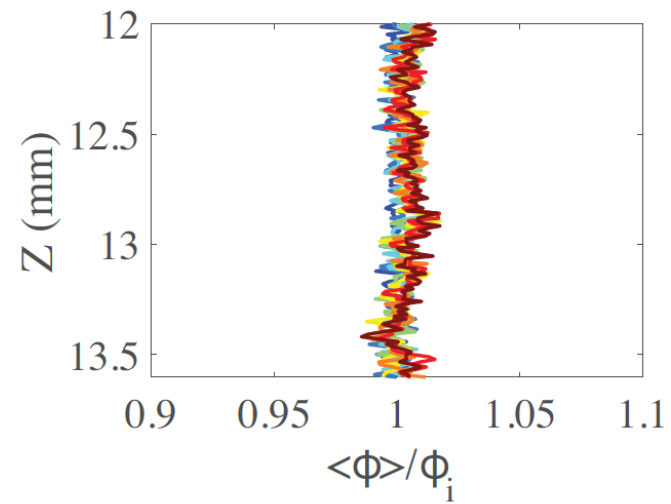


PVC no migration in a syringe

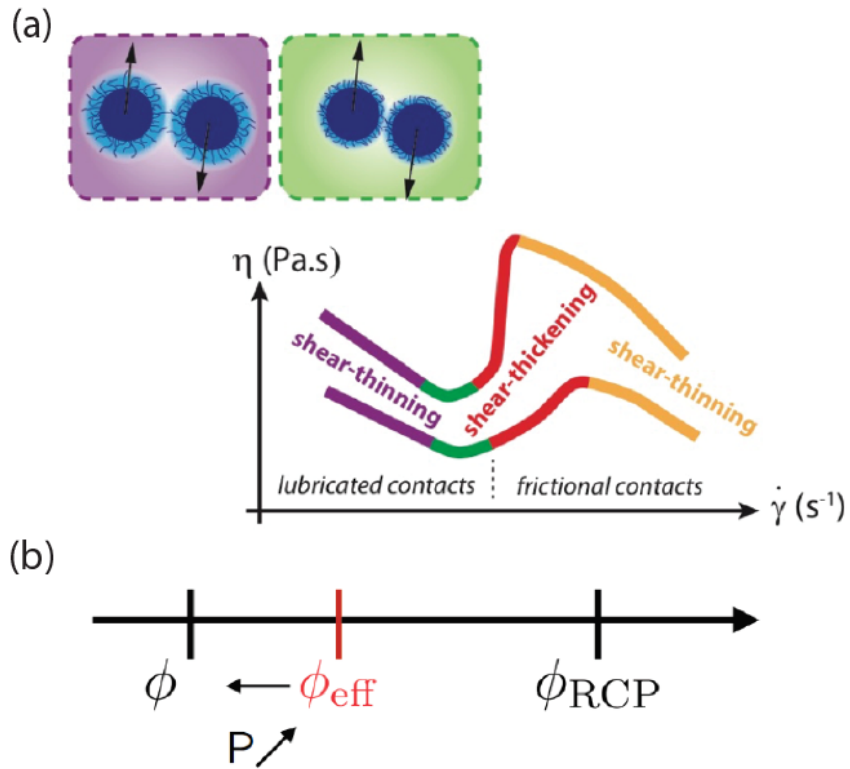
a.



a.



Shear thinning in non Brownian dispersion



Shear thinning in non Brownian dispersions

- The viscosity of a suspension of hard spheres follows the rheological law of Krieger-Dougherty.

$$\sigma/\dot{\gamma} = BP/\dot{\gamma} = \eta \quad (10)$$

$$\eta = \eta_s \left(\frac{\phi_{\text{RCP}}}{\phi_{\text{RCP}} - \phi} \right)^n \quad (11)$$



(a)

(b)

(c)

PVC

ϕ_{rcp}

$= 69\%$

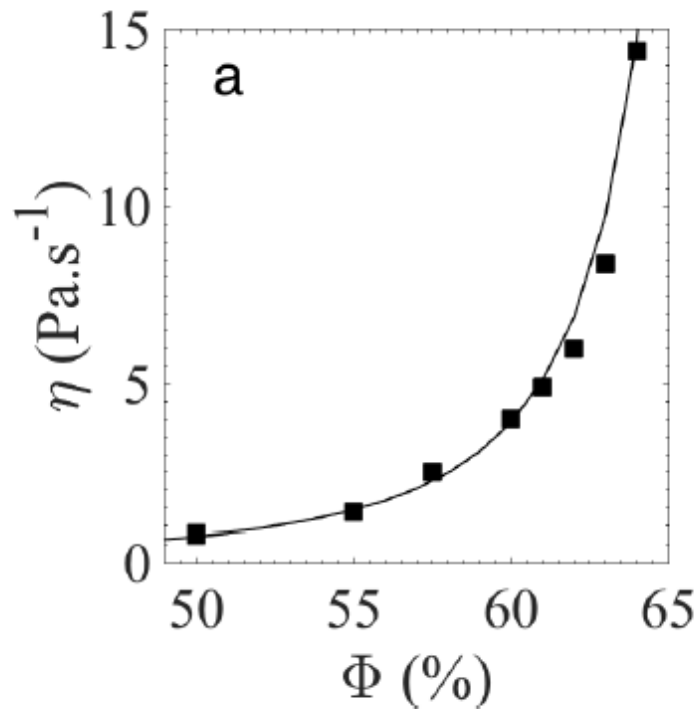


(d)

(e)

Figure 2.16: Plasticizer absorption test: (a) initial state with dry powder (b)(c)(d) with adding more and more plasticizer but not enough to obtain an homogeneous paste (e) with the right amount of plasticizer to wet all the powder.

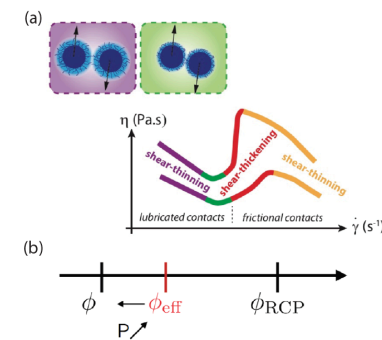
Determination of the critical liquid fractions Φ_{rcp}



PVC
 ϕ_{rcp}
 $= 69\%$

Shear thinning in the non Brownian dispersion

- The particles are covered by a polymer brush.
- The effective solid fraction varies because the effective size of the particle varies due to collision.
- Increasing the applied shear rate increases the applied shear stress, and thus the applied particular pressure.
- The mean distance between particles during the collision decreases
- The effective solid fraction decreases.



Shear thinning in non Brownian dispersions

- The viscosity of the suspension follows the rheological law of Krieger-Dougherty.

$$\sigma/\dot{\gamma} = BP/\dot{\gamma} = \eta \quad (10)$$

$$\eta = \eta_s \left(\frac{\phi_{\text{RCP}}}{\phi_{\text{RCP}} - \phi_{\text{eff}}} \right)^n \quad (11)$$

Shear thinning in the non Brownian dispersion : h during collision?

$$\sigma/\dot{\gamma} = BP/\dot{\gamma} = \eta \quad (10)$$

$$\eta = \eta_s \left(\frac{\phi_{\text{RCP}}}{\phi_{\text{RCP}} - \phi_{\text{eff}}} \right)^n \quad (11)$$

$$\phi_{\text{eff}} = \phi \left(1 + \frac{h(P)}{R} \right)^3$$

Shear thinning in the non Brownian dispersion : How to check this?

$$h = \left(\left(\frac{\phi_{eff}}{\phi} \right)^{1/3} - 1 \right) * R$$

$$\phi_{eff} = \phi_{RCP} - \left(\frac{\eta(\dot{\gamma})}{\eta(\dot{\gamma}^*)} \right)^{1/n} (\phi_{RCP} - \phi)$$

$$W(h) = PR = \sigma R / B = W_0(\sigma / \sigma^*)$$

Interactions between two particles

b

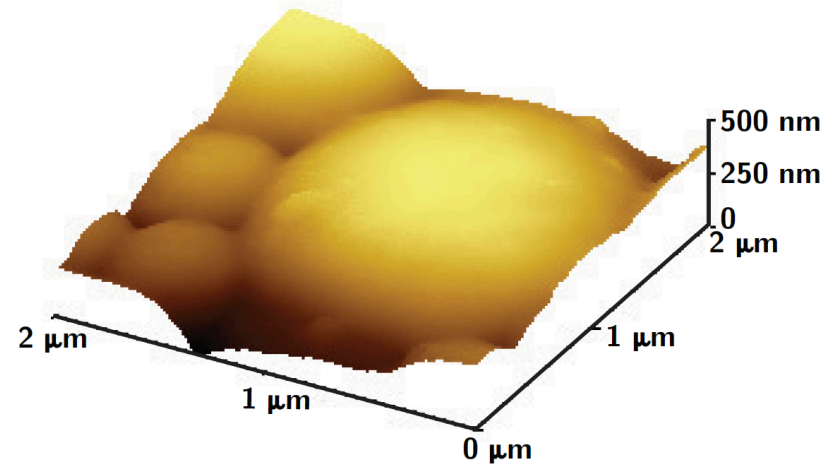
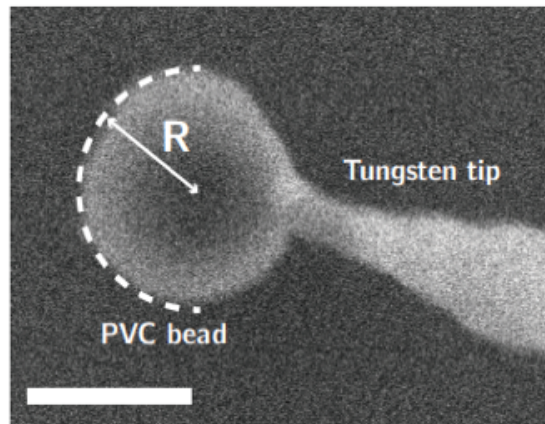
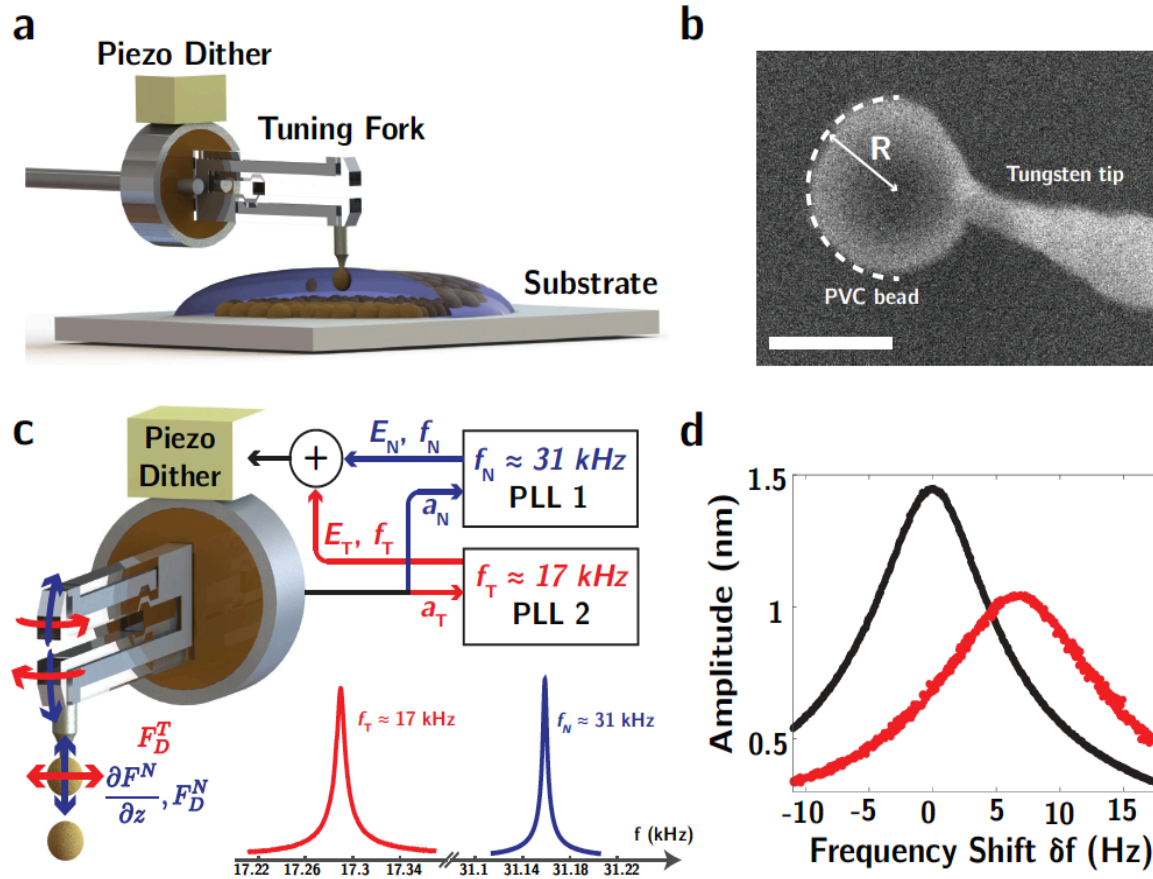


Figure S1: AFM image of one casted PVC particle at the surface of the substrate. RMS roughness is ≈ 2.2 nm on the upper part of the particle.

PVC and cornstarch particles are glued to the etched tungsten tip of the tuning fork using SEMGLU from kleindiek, and a nanomanipulation station in-situ a SEM

How to check the presence of solid friction? Characterization of the interaction: Tuning Fork



Analysis of the data

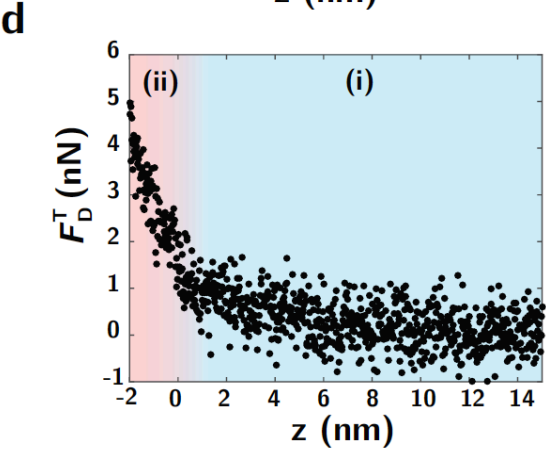
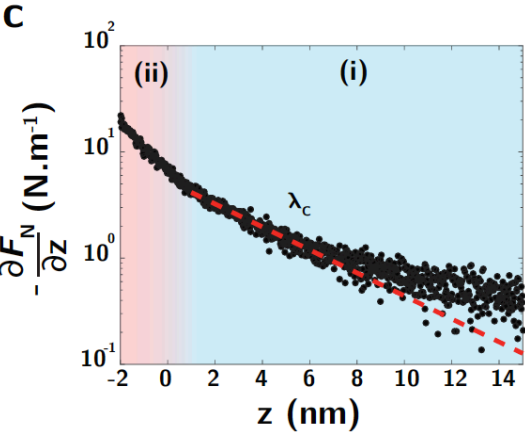
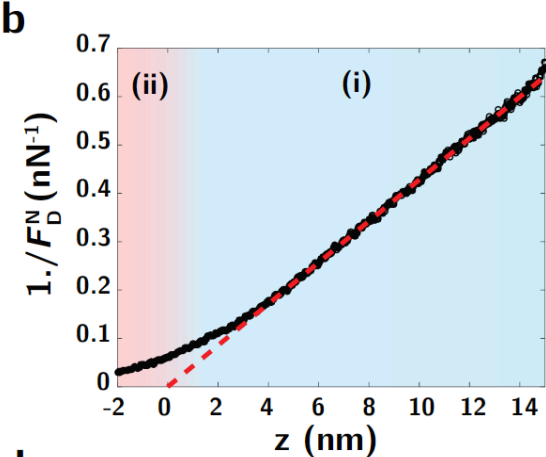
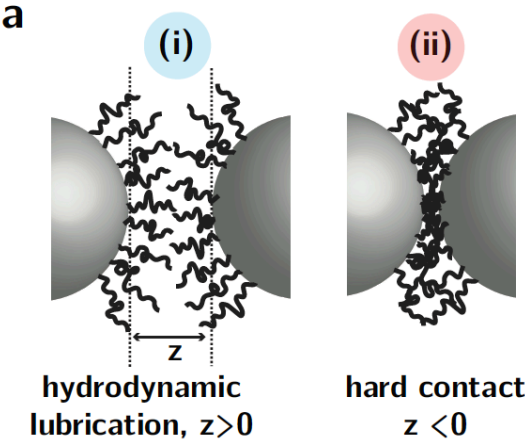
$$-\omega^2 \underline{X} + i\omega \frac{\gamma}{m} \underline{X} + \omega_0^2 \left(1 - \frac{1}{2k_i} \nabla F\right)^2 \underline{X} = \frac{1}{m} \left(F_{\text{ext}} - \frac{2F_s}{\pi}\right)$$

$$\frac{a_0}{Q} = \frac{(F_{\text{ext}} - 2F_s/\pi)}{k_i} \cdot \omega_0^2 \left(1 - \frac{1}{2k_i} \nabla F\right)^2$$

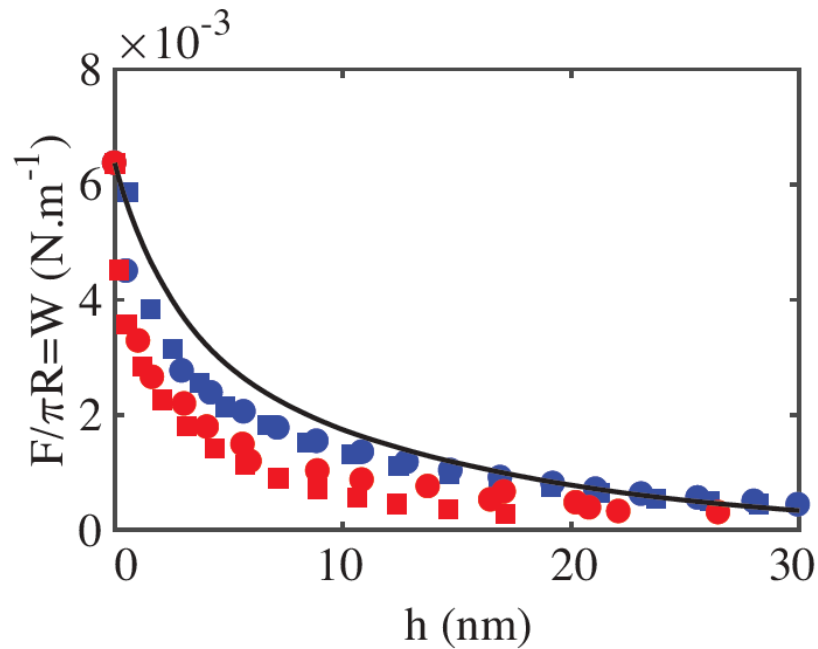
Shift of the resonance frequency gives the Force gradient

Monitoring the excitation voltage necessary to keep a constant oscillation amplitude a_0 gives us a direct measure of the sum of all forces acting on the tuning fork as $F_{\text{ext}} = FD = CV_{\text{ext}}$ to obtain an amplitude a_0 typically equal to 1-50 nm.

Tuning Fork experiments

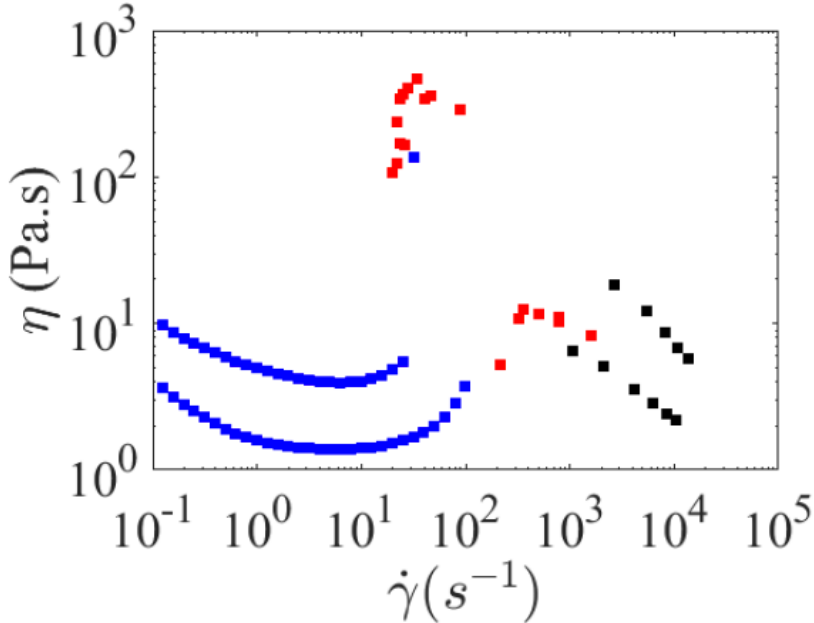


Comparison profile force from AFM , profile force from rheological measurements



Chatte et al Langmuir 2018

Shear Thickening



Shear Thickening Consequences: running on cornstarch



Shear Thickening Consequences : Liquid and comfortable Armor

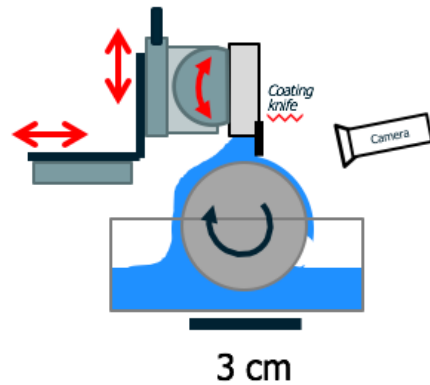
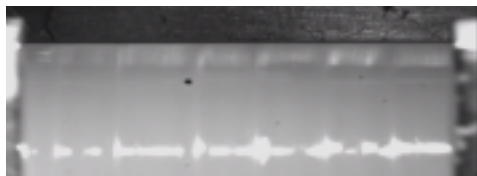
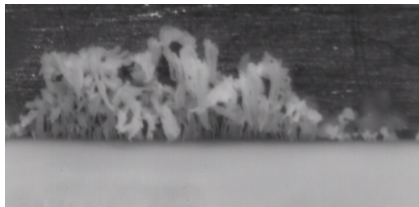


Kevlar soaked with STFluids
University of Delaware (Professor Wagner) in collaboration
With US Army.

Shear thickening in industrial processes.



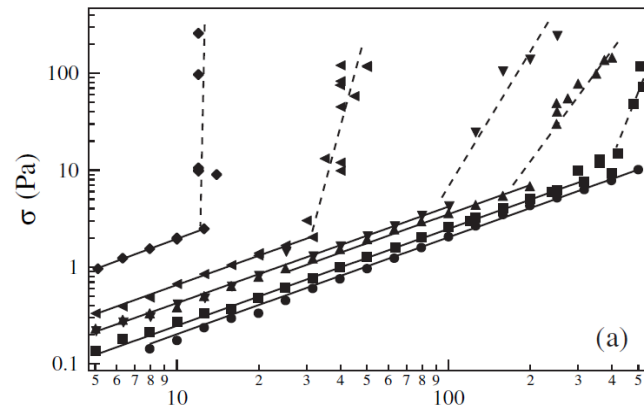
Shear thickening leads to high cost when pumping concrete over long distances in large building state.



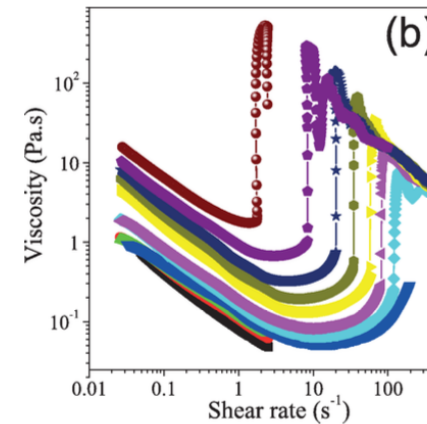
Shear thickening causes extrusion instabilities
In the manufacture of plastic floors.

Shear thickening

- Dense suspensions of solid particles immersed in newtonian solvent display complex flow properties.



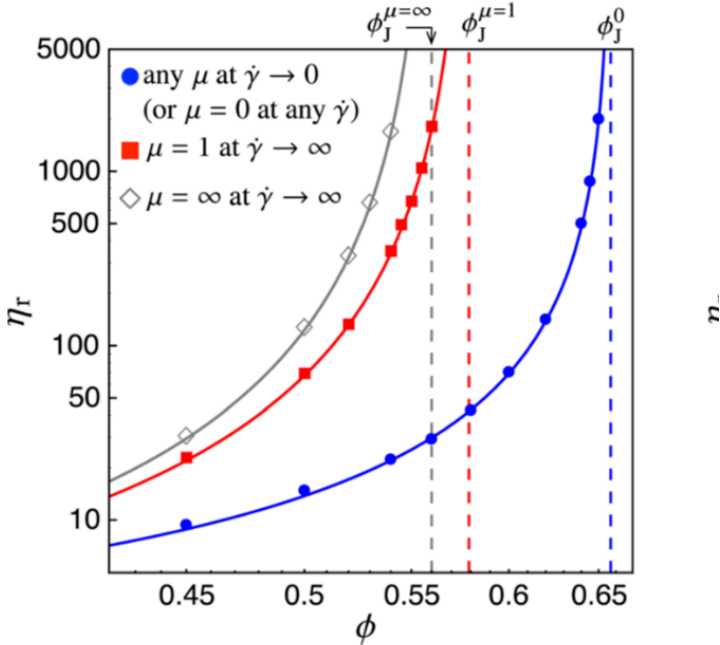
Lootens (2005)



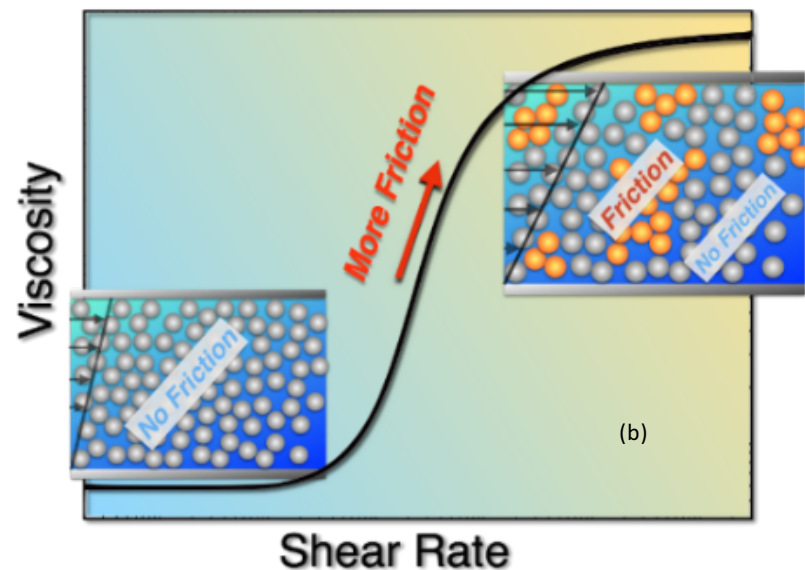
Ovarlez (PRL 2016)

- Concrete, silica suspensions, cornflour mixtures, latex suspensions, clays are examples of shear thickening systems

The viscosity varies as a function of the friction coefficient



Why does shear thickening occur?

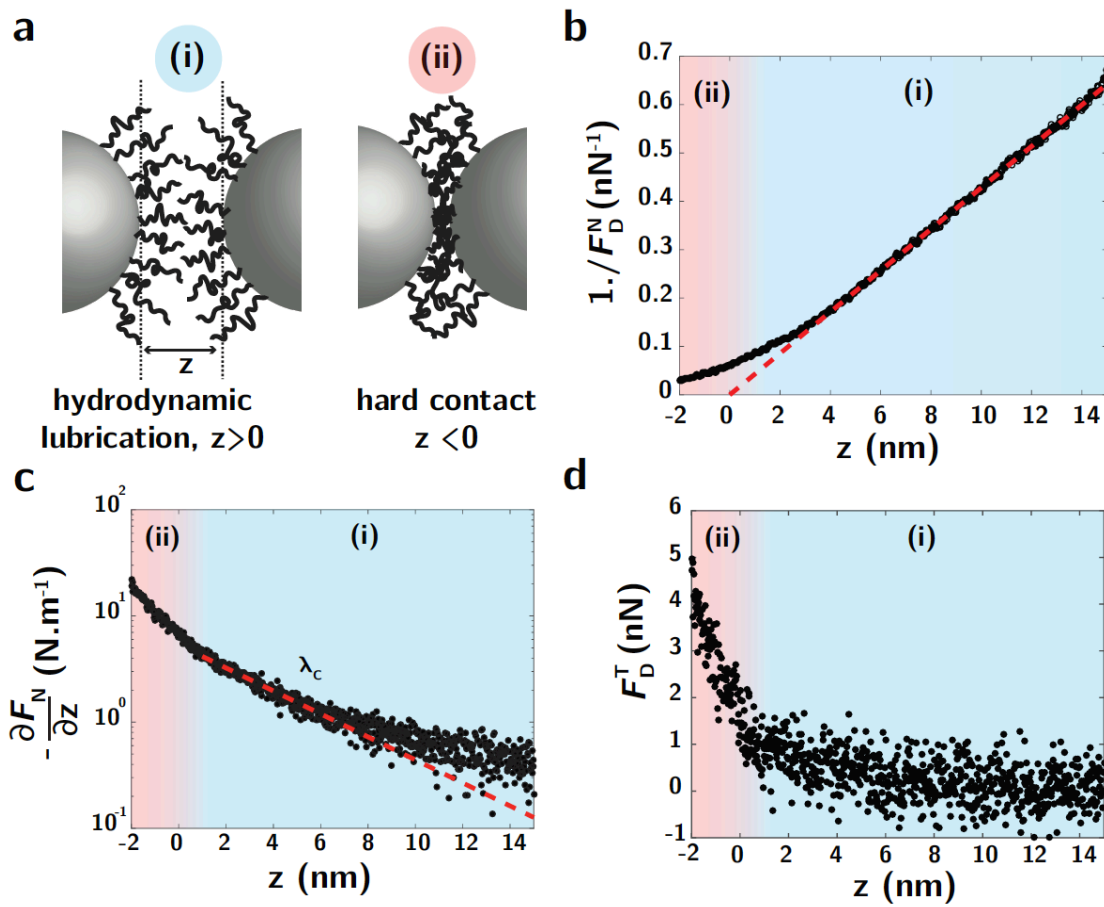


μ depends upon the applied stress

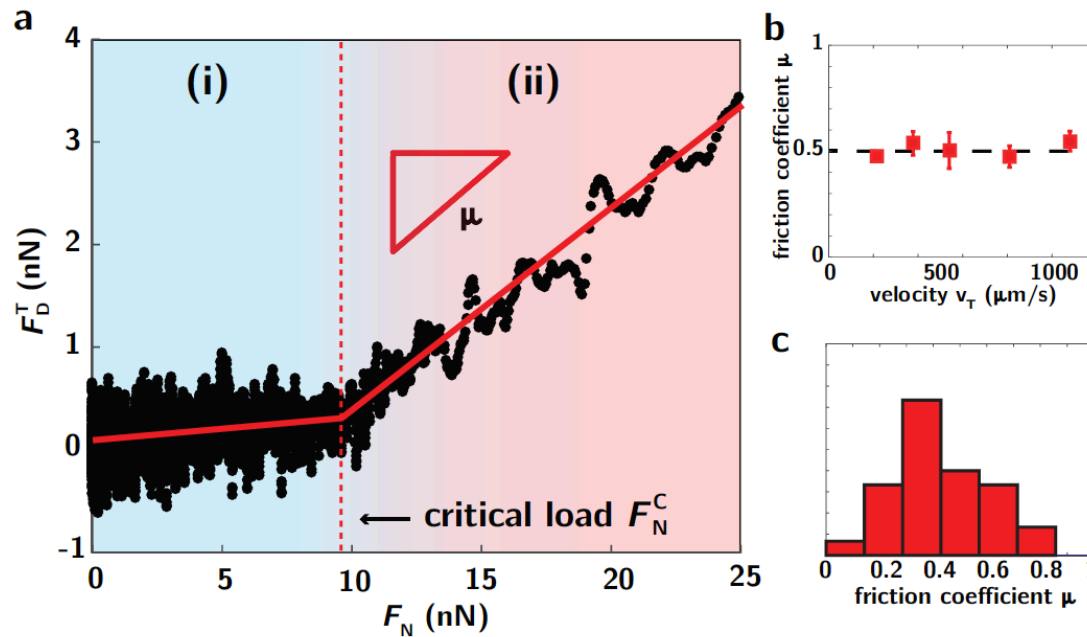
Shear thickening corresponds to a transition between a state with lubricated contacts between particles for low normal forces to a state with solid contacts between particles for high normal forces.

*J. Morris, R Seto, R Mari, JF Morris, MM Denn 2013 PRL Cates ,
Wyart 2015 PRL, figure from Blair.*

Tuning Fork experiments

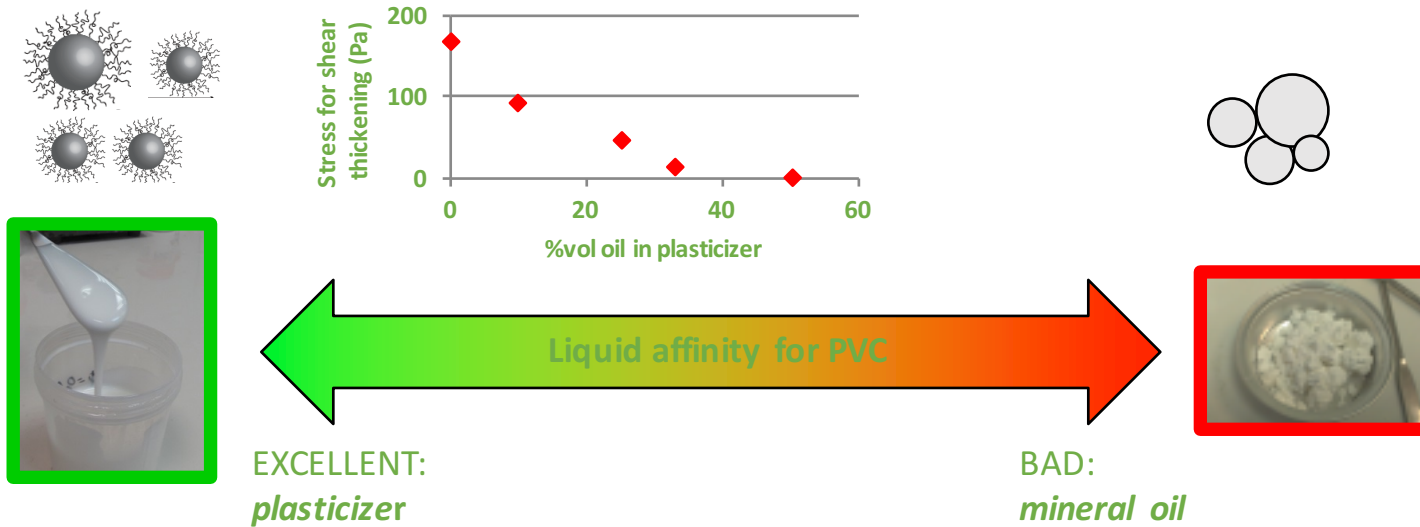


Tuning Fork experiments



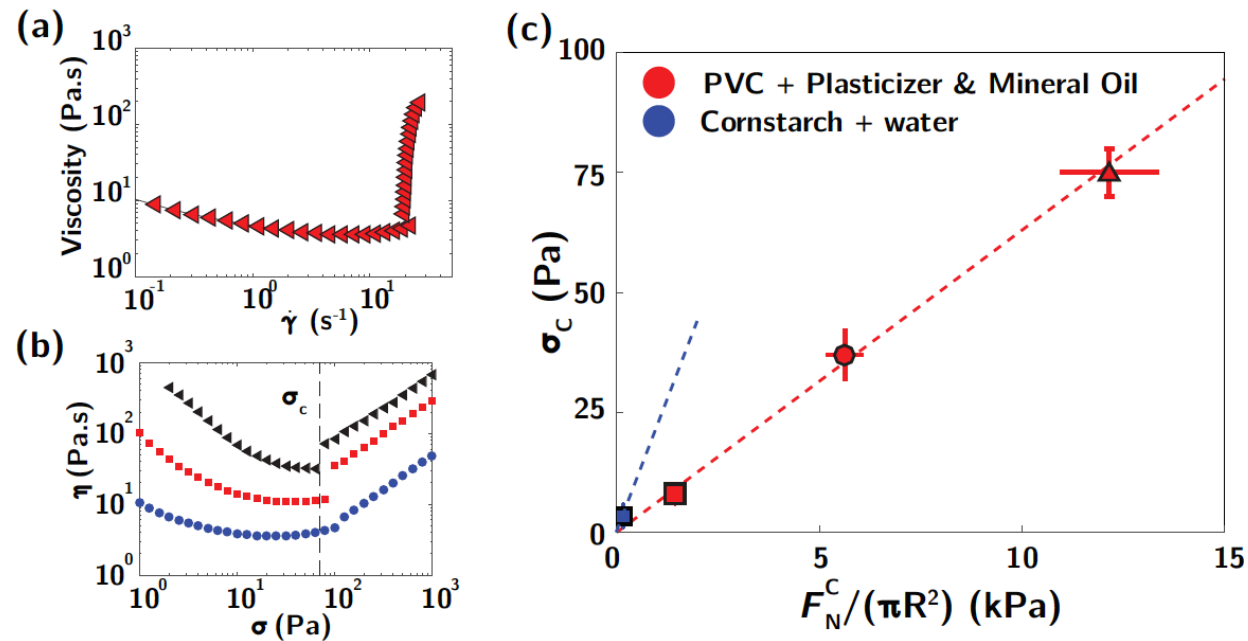
What is the critical load?

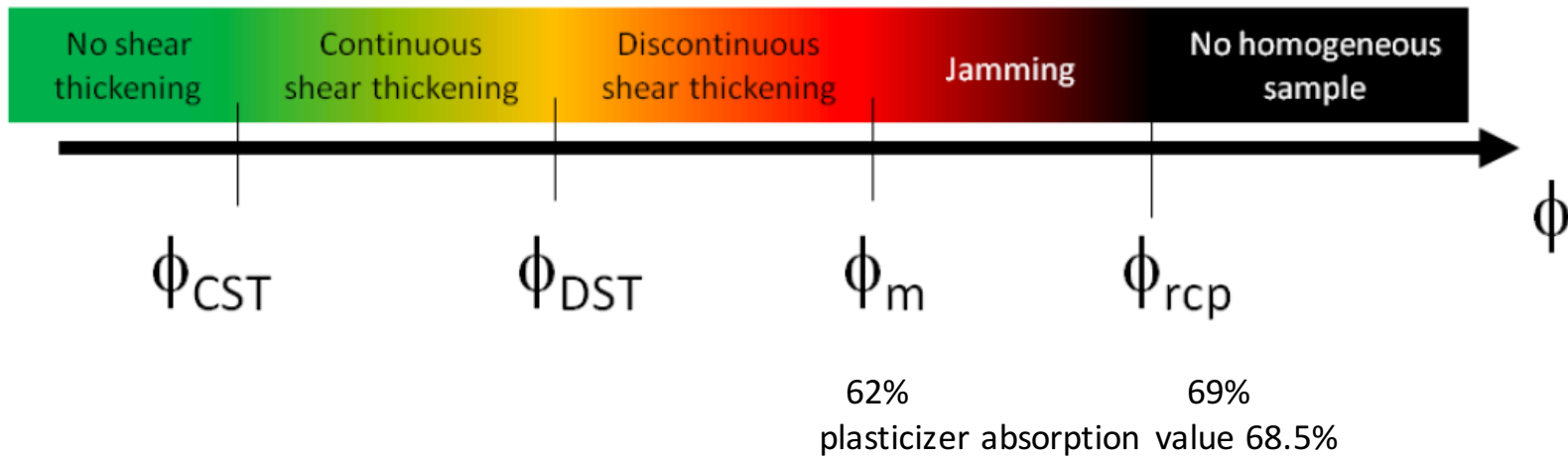
Our system: tuning repulsive forces



- Liquid = plasticizer \Rightarrow slowly swell particles \Rightarrow PVC « brush » (steric stabilisation)
- PVC in bad solvent (for e.g. mineral oil) = no swelling = no brush

Bridging the gap between the micro and the macroscale





How to estimate ϕ_m

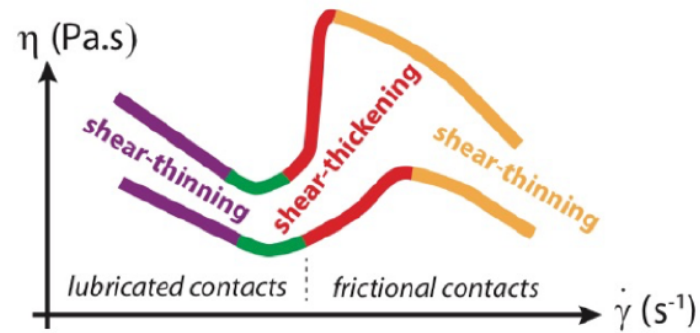
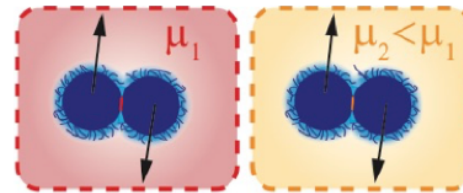
• $\eta = \eta_s \left(\frac{\phi_m}{\phi_m - \phi} \right)^n$ after the shear thickening

$\eta = \eta_s \left(\frac{\phi_{RCP}}{\phi_{RCP} - \phi} \right)^n$ Before the shear thickening

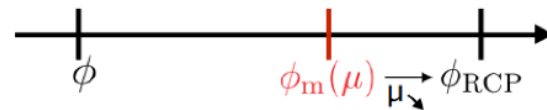
$\phi_m = 62\%$

Shear thinning after shear thickening

(a)



(b)



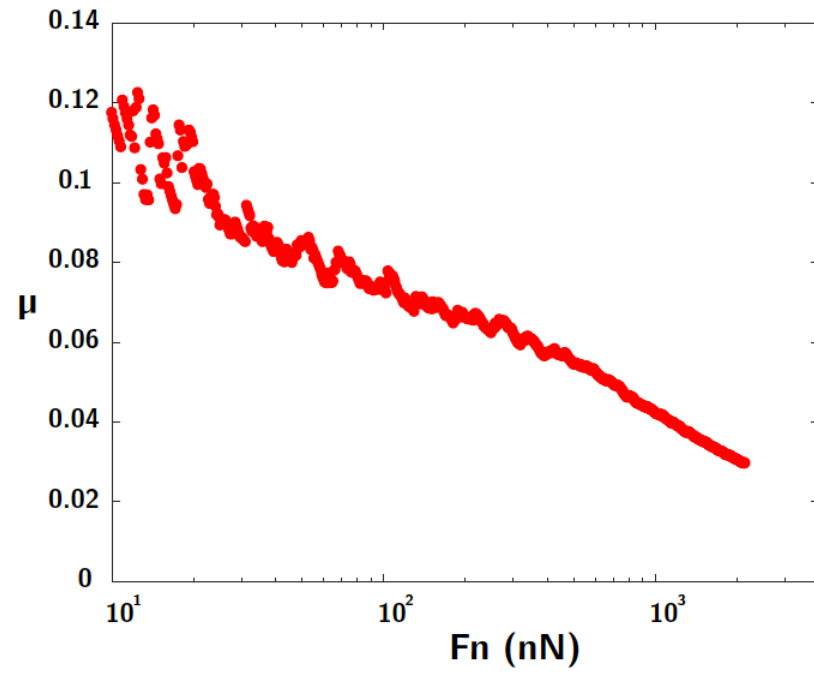
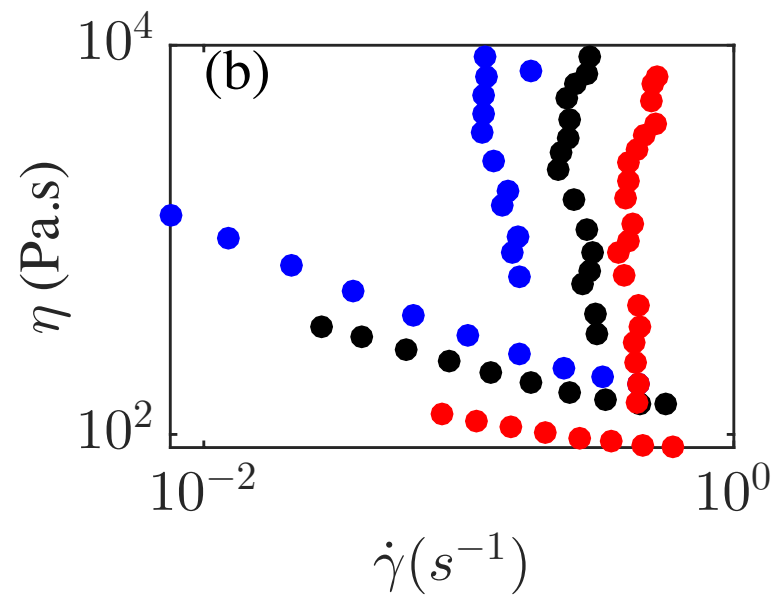
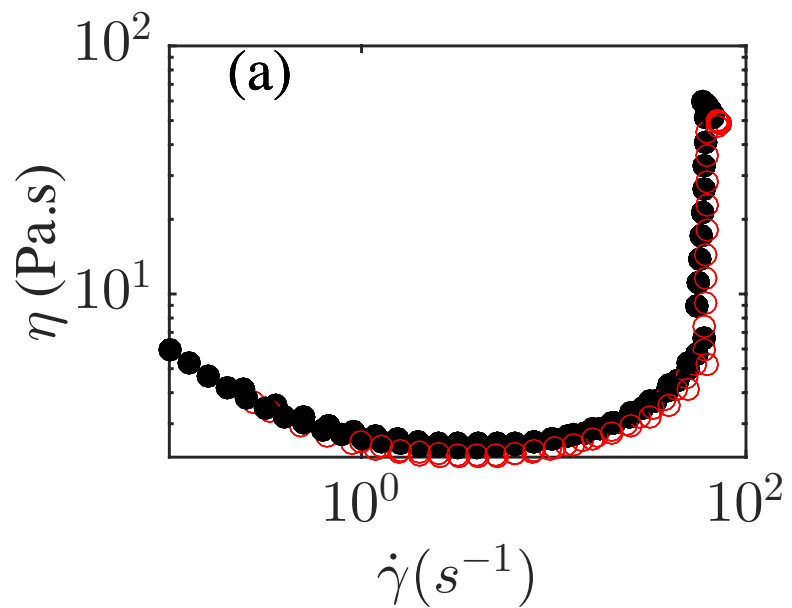


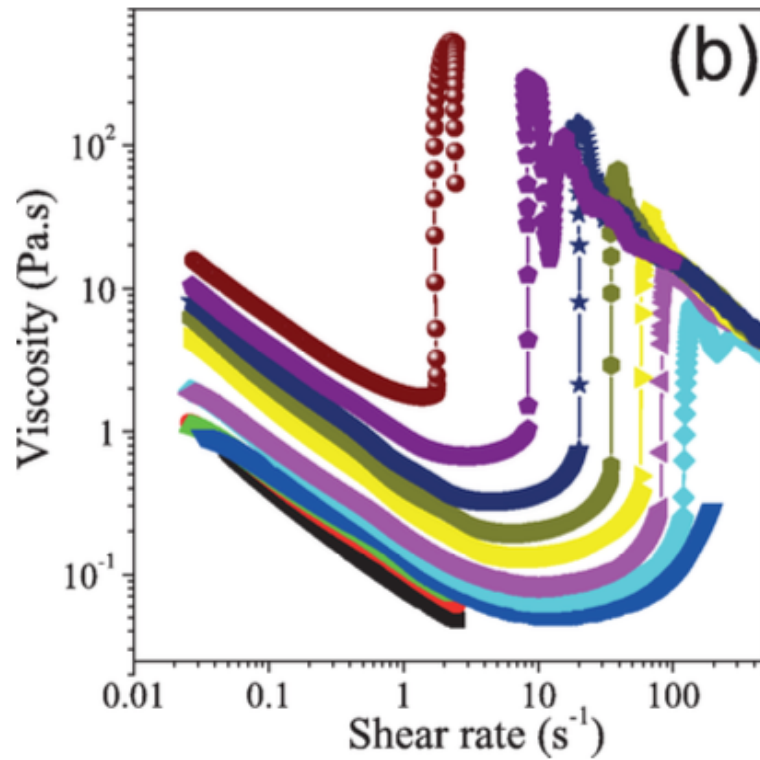
Fig. 11 Variation of the friction coefficient μ as a function of the normal load. μ decreases with increasing loads.

What happens for concentrated samples
→ transition from a liquid to a solid. Migration,
Fractures

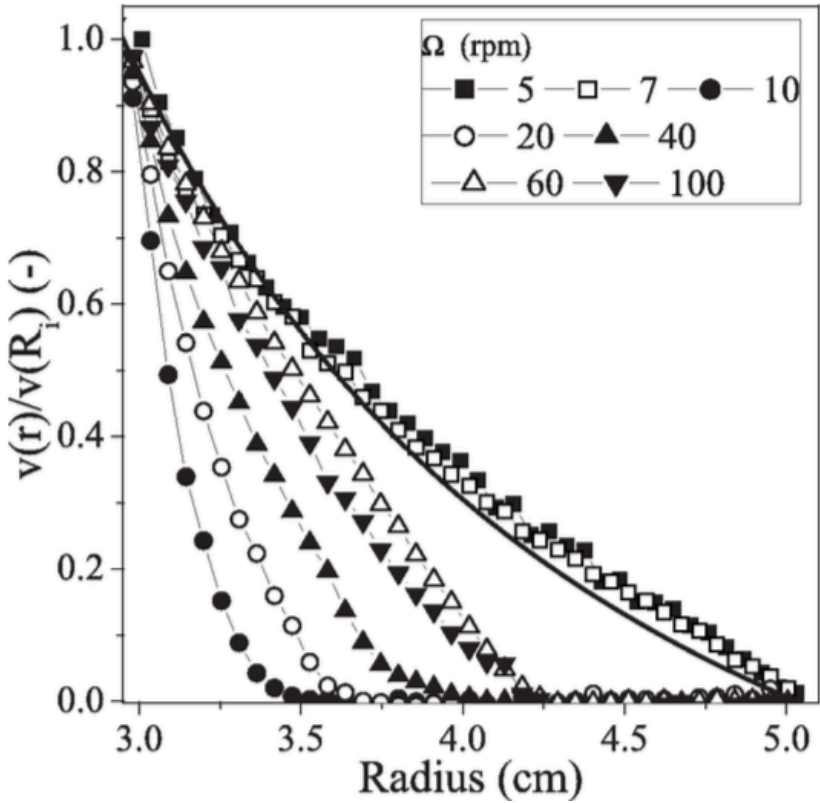
- A different picture



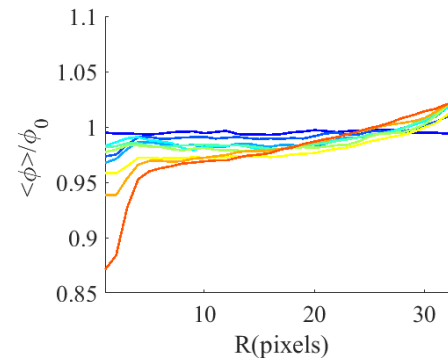
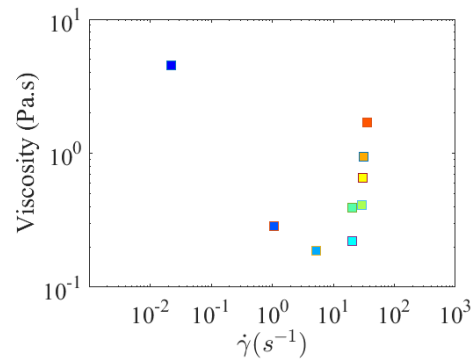
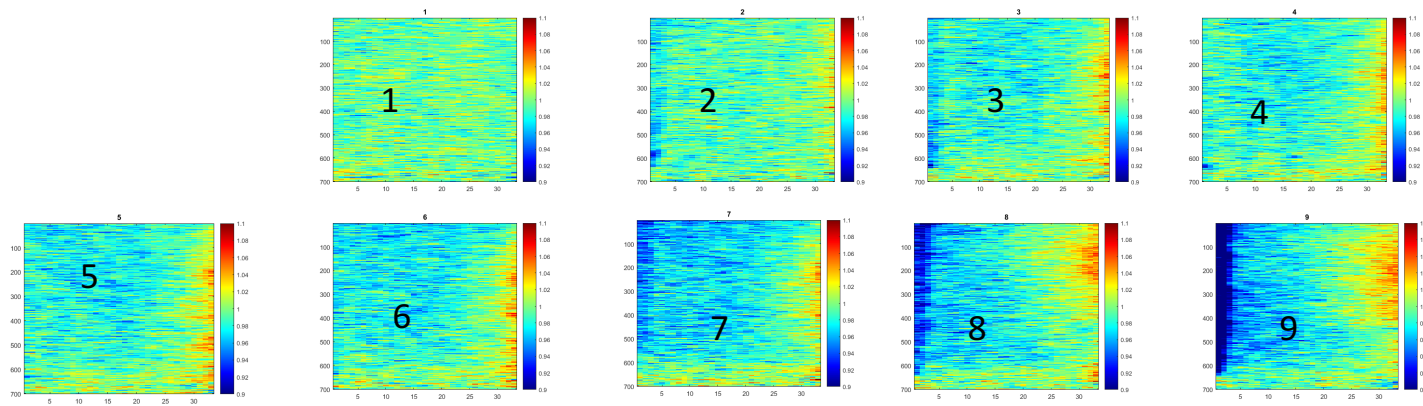
A few words dealing with cornflour



Velocities profiles cornstarch



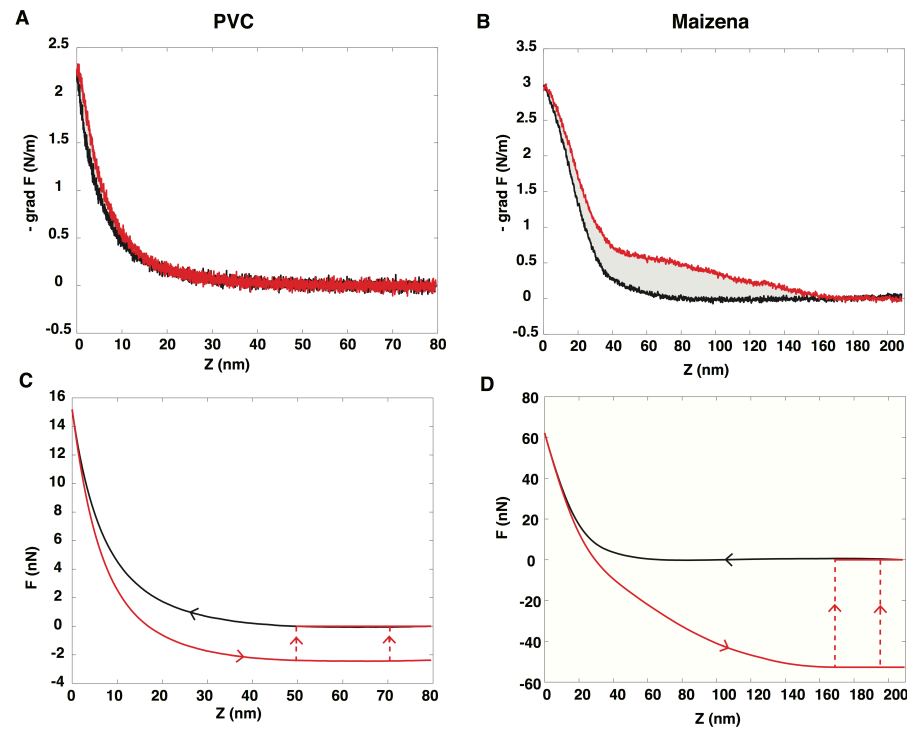
Cornflour 1 mm: migration



Why do we observe migration with cornflour and not with PvC?



Forces Profiles : huge adhesive forces for cornstarch.



Comtet et al . In preparation

Conclusion and Outlooks

- Shear thickening a transition between lubricated contacts and solid friction.
- Measurement of the solid fraction
- PVC suspension behaves as the theoretical model.
- Cornstarch suspensions?
- Flow in confined geometries
- Study of flow instabilities and role of confining