Université Claude Bernard Lyon 1

Mechanical properties of calcite gel controlled by simple ions

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Teresa Liberto

M. Le Merrer, J. Colombani and C. Barentin

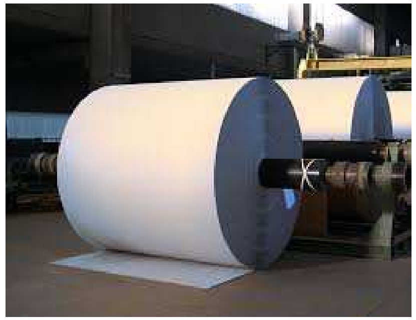
NANOHEAL

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 642976"

Calcite : stable polymorph of $CaCO_3$





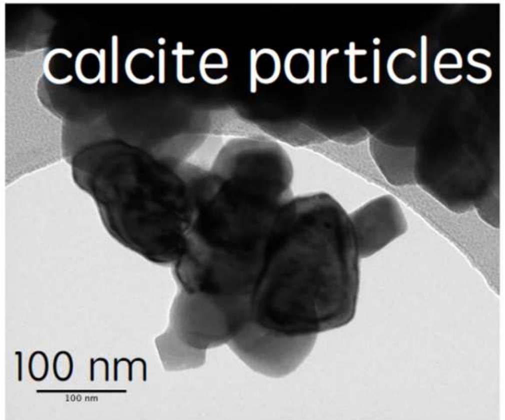
Construct-ion

Material filler

Mechanics of aqueous calcite suspension

Mineral and Rocks, ed. J. R. Wilson 2010

Micro-macro link ?



MACROSCOPIC
rheological
properties

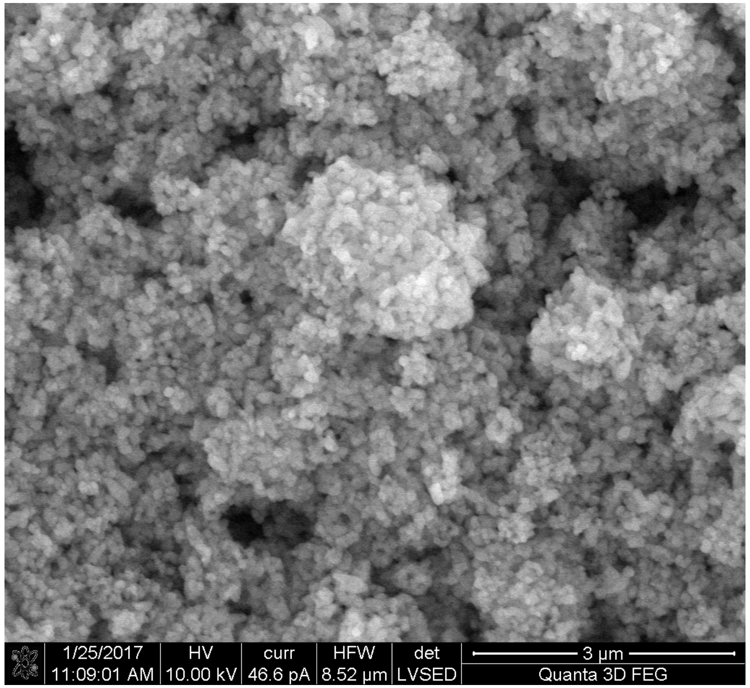
⇄

MICROSCOPIC
structure &
interactions

Influence of simple ions on mecanical properties

Paste characterization

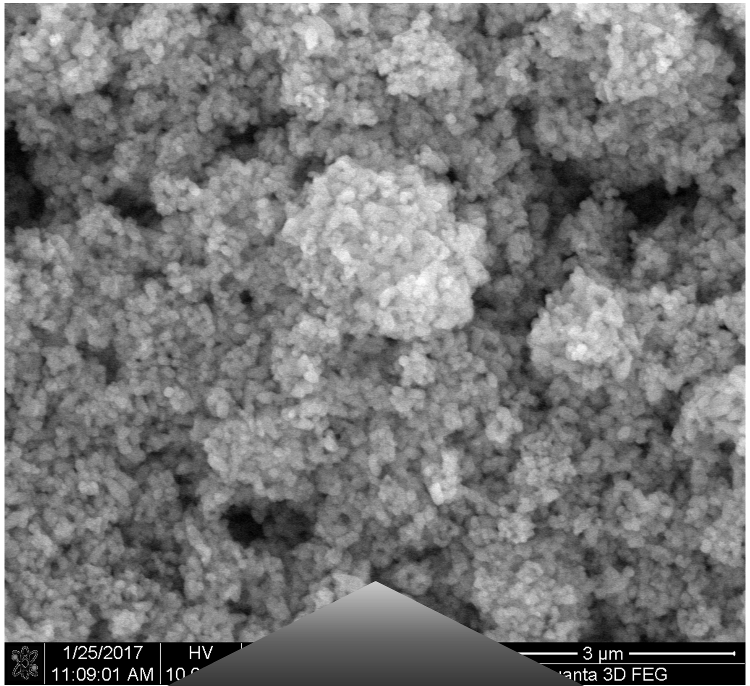
SEM image



- Pure $CaCO_3$ powder
- $<d_P>$ = 70 nm
- Rhombohedral shape
- Colloidal paste ϕ =[5-30] %

Paste characterization

SEM image



$CaCO_3$ paste ϕ=20%

- Pure $CaCO_3$ powder
- $<d_P>$ = 70 nm
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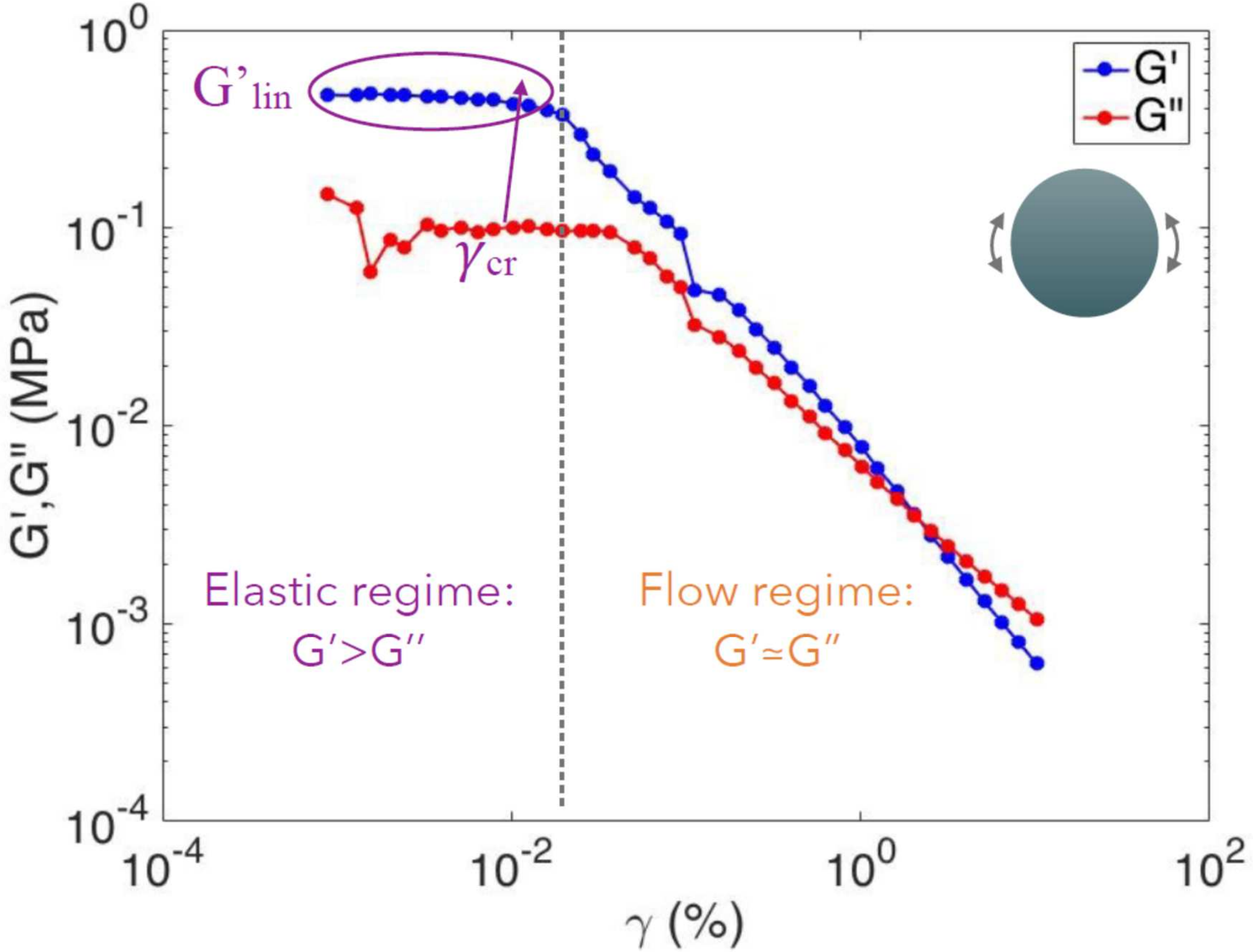
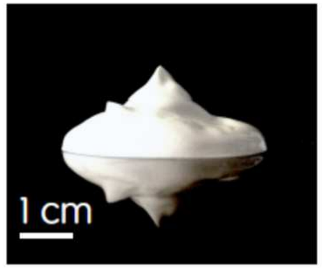
- Colloidal paste ϕ =[5-30] %

Elastic modulus

KPa < $G'(\phi)$ < MPa

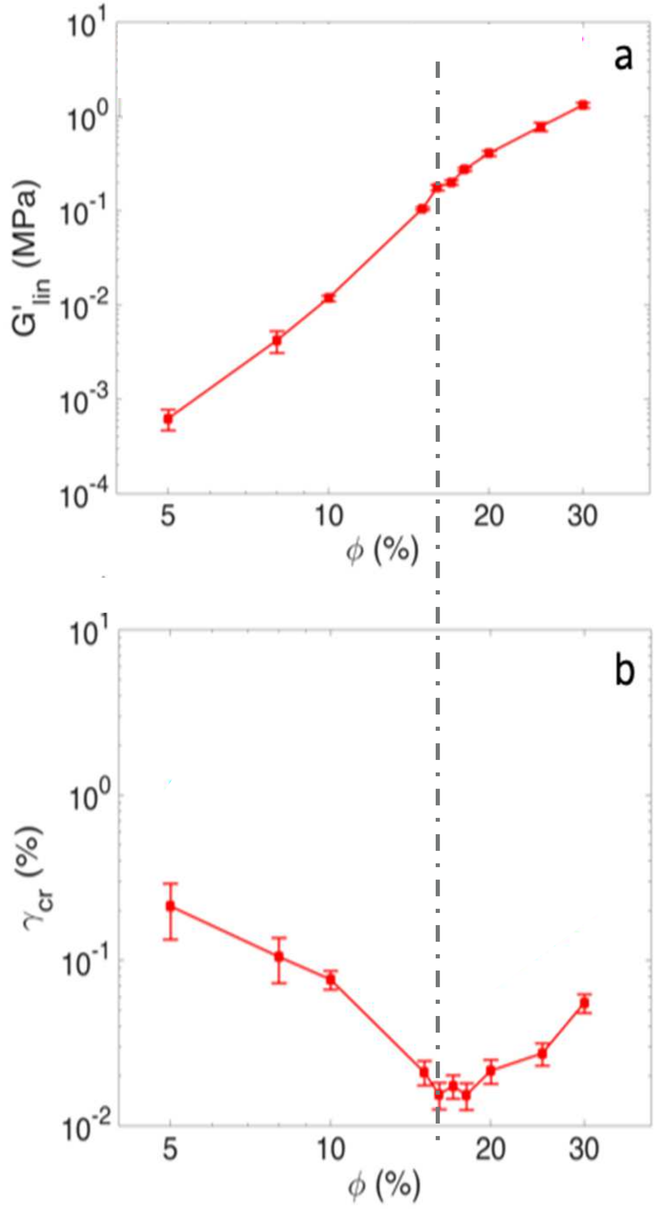
Elasticity and yielding of pure calcite paste





ϕ=20%

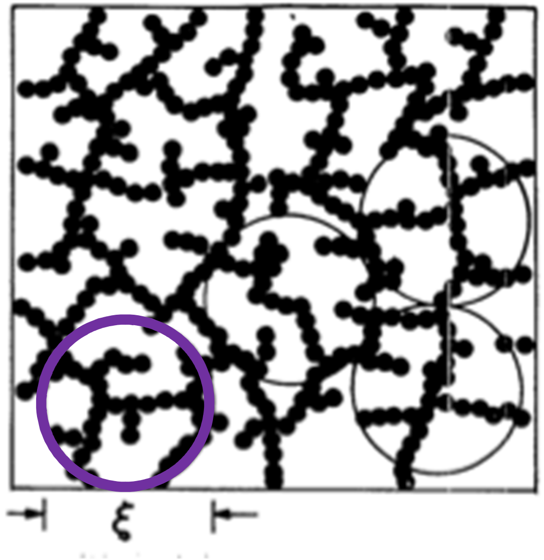
Elasticity and yielding : solid fraction



T. Liberto et al Soft Matter 2017

Minimum predicted by **Shih *et al.* PRA 1990**

Elasticity of **fractal colloidal gels**



$$G \sim \frac{k_0}{a}\phi^A$$

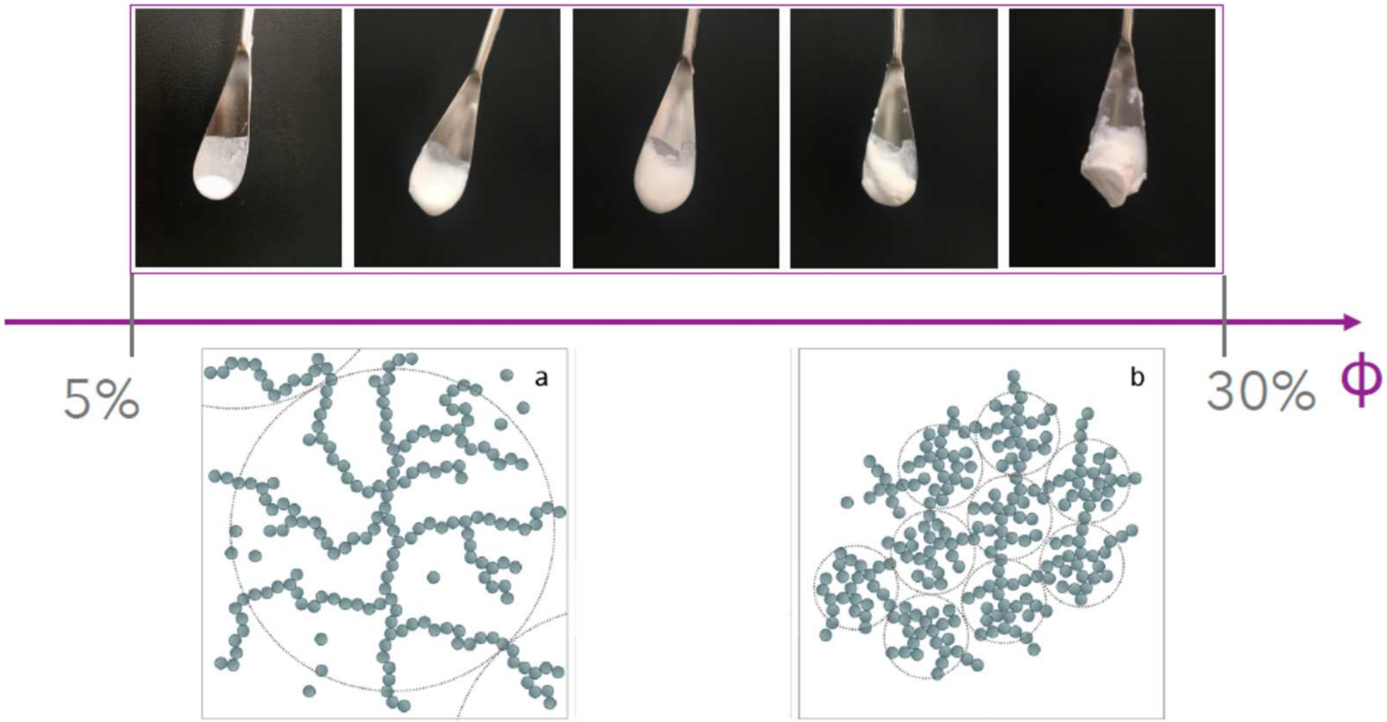
$$\gamma_c \sim \frac{F_c}{k_0 a}\phi^B$$

The exponents *A >0* and *B* depend on

- **the fractal dimension of the floc**
- the location of the weakest link

Calcite paste: a colloidal fractal gel

Following the model of colloidal gel proposed by **Shih *et al.* PRA 1990**



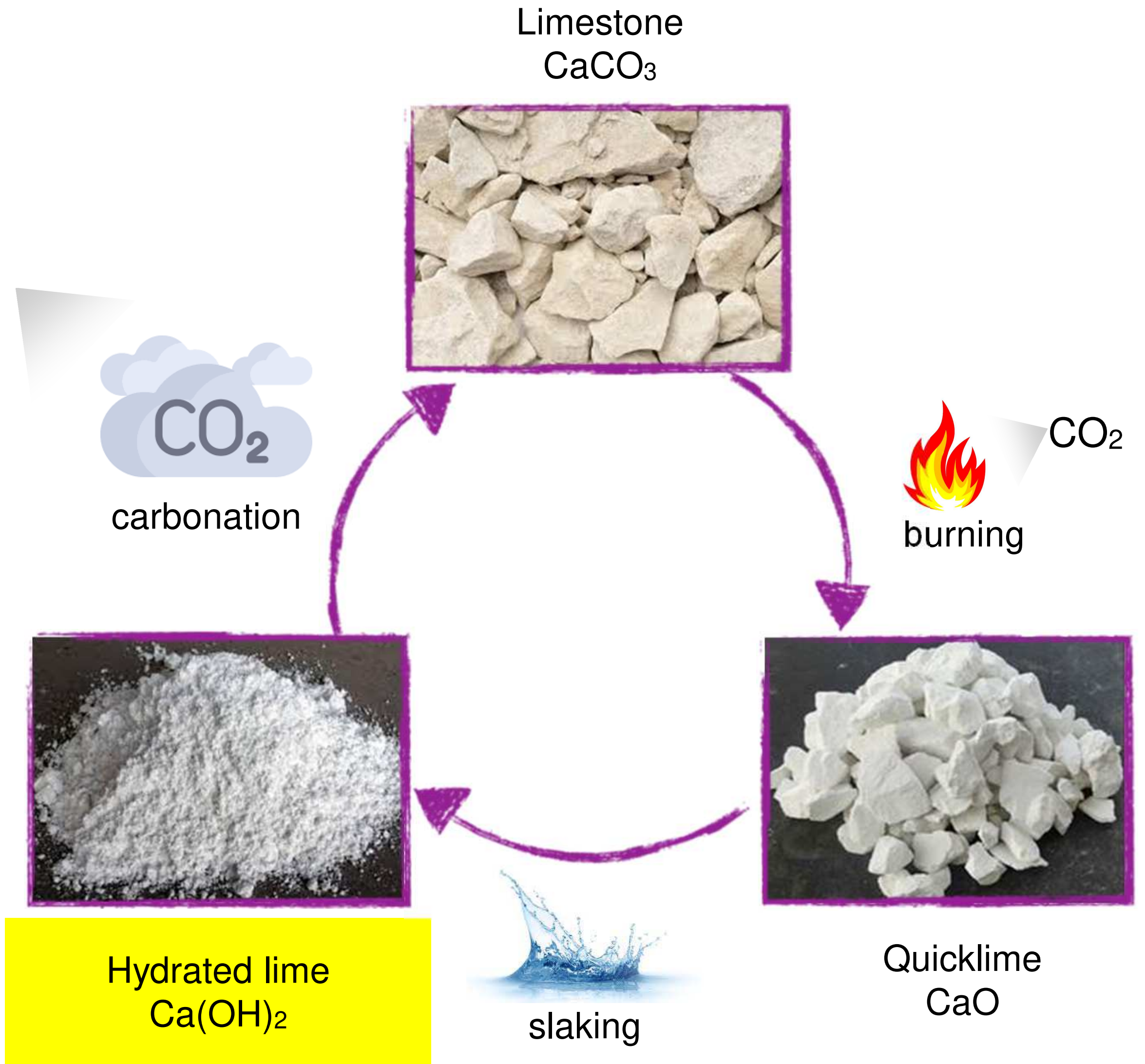
$d_f \simeq 2.2$
$\xi \sim 2$ µm
$G' \sim 10^{-3}$ MPa

$d_f \simeq 2.6$
$\xi \sim 0.5$ µm
$G' \sim$ MPa

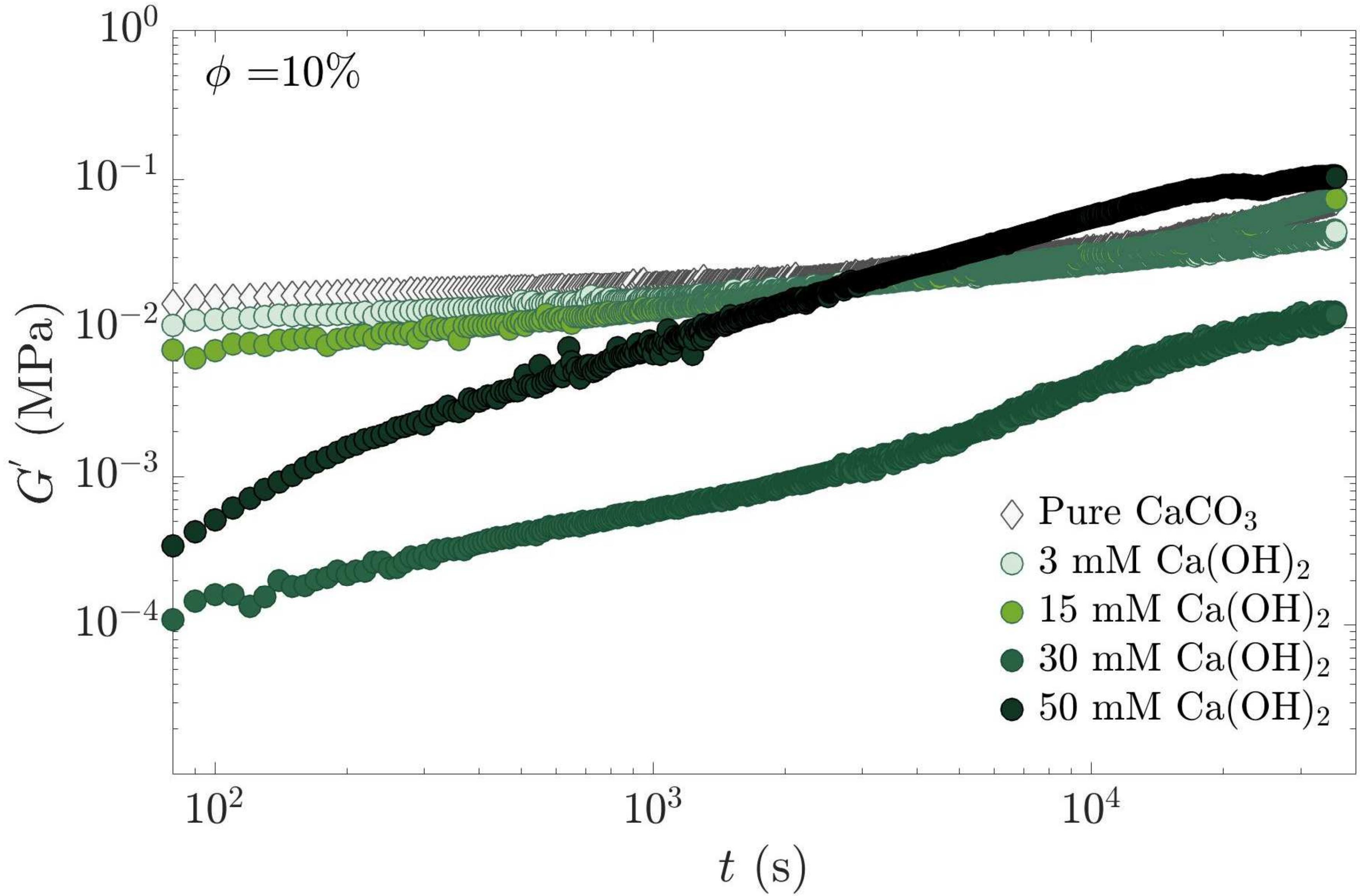
Changing interaction by physico-chemistry

Addition of calcium hydroxide $Ca(OH)_2$

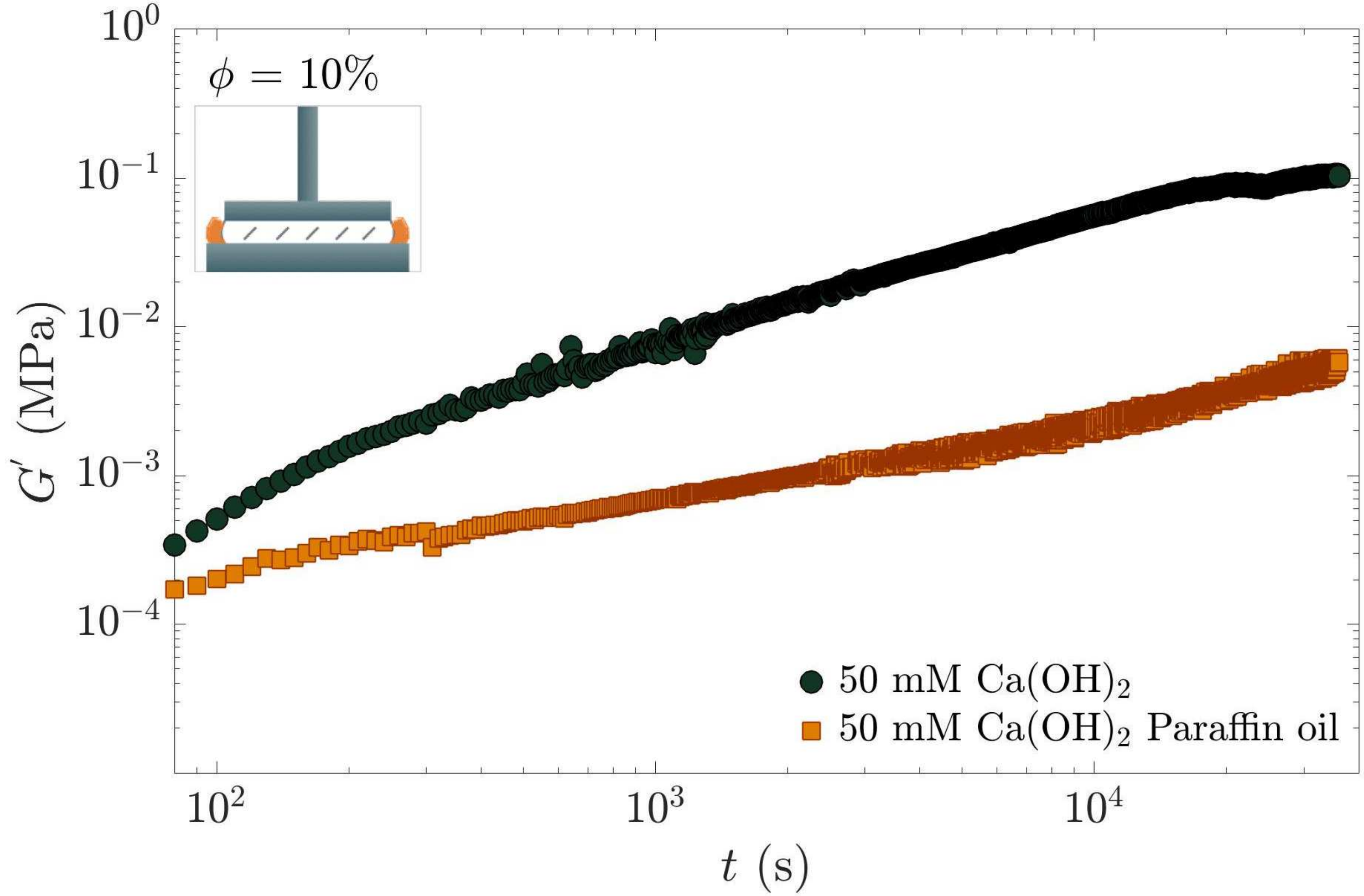
Lime cycle



Calcite with calcium hydroxide



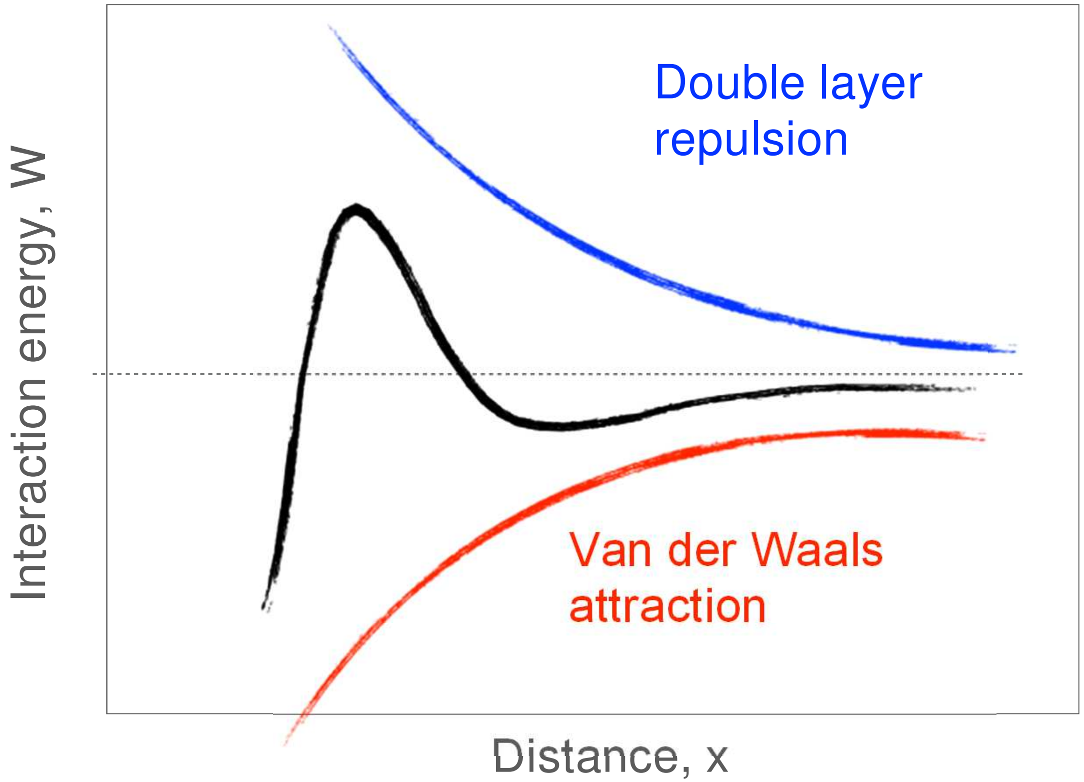
Carbonation changes elasticity



$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ *carbonation*

Microscopic Interactions: DLVO

$$W = -\frac{A}{12\pi x^2} + \frac{2\varepsilon}{\lambda_D}\zeta^2 \exp(-x/\lambda_D)$$



J. Israelachvili, Intermolecular and surface forces, 1992

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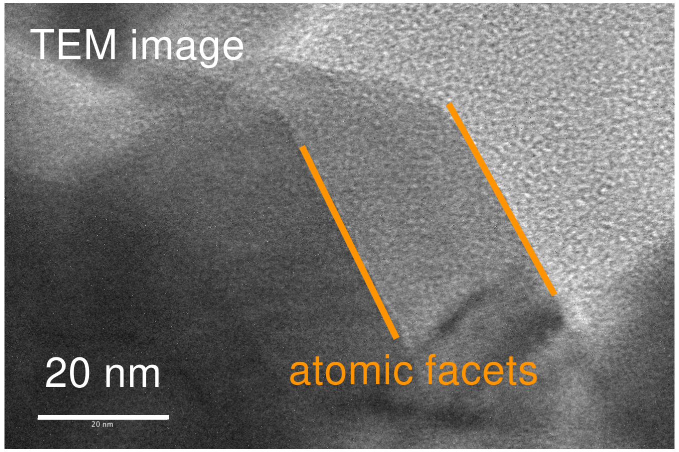
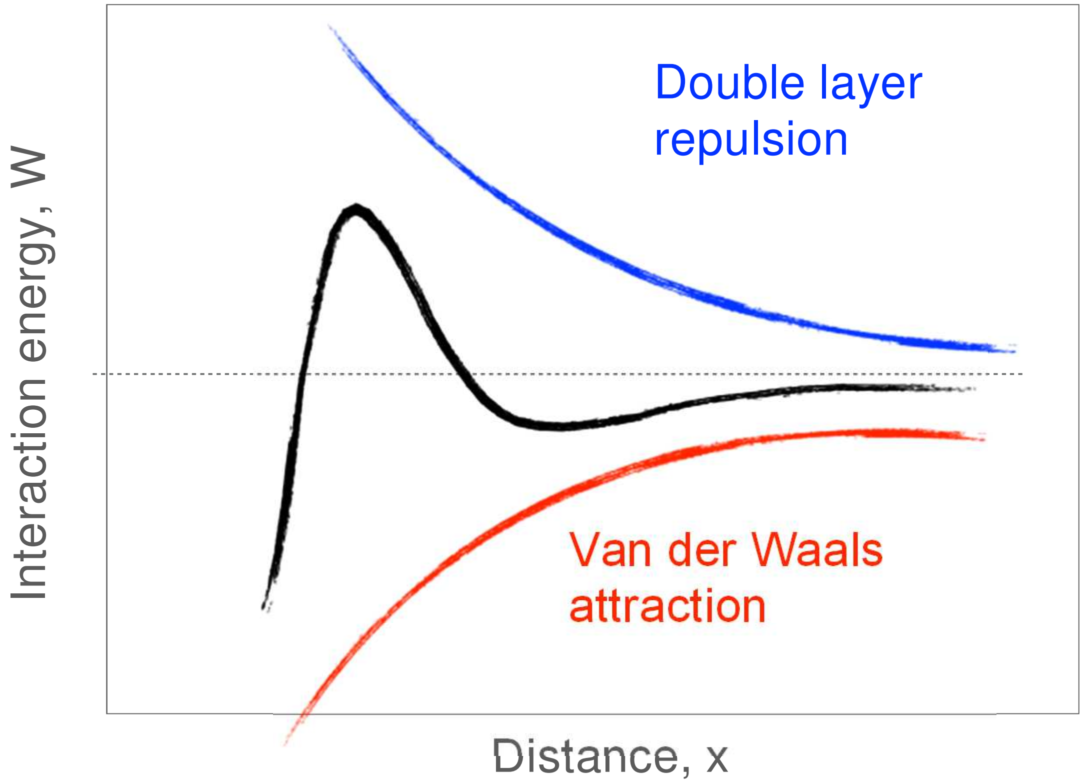
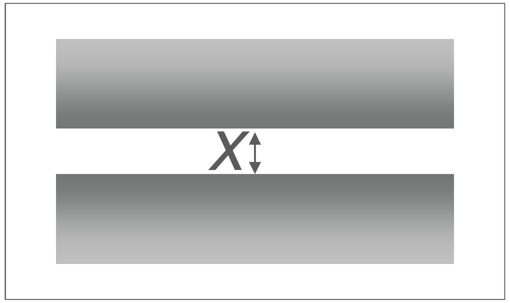






$A = 3.6\, k_B T,$
$\zeta \ \&\ \lambda_D$?

J. Israelachvili, Intermolecular and surface forces, 1992

Microscopic Interactions: DLVO

Debye length calculation: chemical speciation with Minteq

(1) $CaCO_3\ (s) \rightleftharpoons CaCO_3\ (aq)\ (K_1 = 10^{-5.09})$

(2) $CaCO_3\ (aq) \rightleftharpoons Ca^{2+} + CO_3^{2-}\ (K_2 = 10^{-3.25})$

(3) $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-\ (K_3 = 10^{-3.67})$

(4) $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-\ (K_4 = 10^{-7.65})$

(5) $H_2CO_3 \rightleftharpoons CO_2\ (g) + H_2O\ (K_5 = 10^{1.47})$

(6) $Ca^{2+} + HCO_3^- \rightleftharpoons CaHCO_3^+\ (K_6 = 10^{0.82})$

(7) $CaHCO_3^+ \rightleftharpoons H^+ + CaCO_3\ (aq)\ (K_7 = 10^{-7.90})$

(8) $Ca^{2+} + OH^- \rightleftharpoons CaOH^+\ (K_8 = 10^{1.40})$

(9) $CaOH^+ + OH^- \rightleftharpoons Ca(OH)_2\ (aq)\ (K_9 = 10^{1.37})$

(10) $Ca(OH)_2\ (aq) \rightleftharpoons Ca(OH)_2\ (s)\ (K_{10} = 10^{2.45})$

$I \sim 1 - 100\ mM$

$\lambda_D \sim 10 - 1\ nm$

P. Somasundaram et al. JCIS 1967

Adding calcium hydroxide

	initial experimental condition		
$Ca(OH)_2$ (mM)	pH_{meas}	*I* (mM)	$[Ca^{2+}]$ (mM)
0	8.9	0.73	0.24
30	11.8	10.20	3.30

Debye length decreases due

to the addition of $Ca(OH)_2$

Expect a decrease of electrostatic repulsion

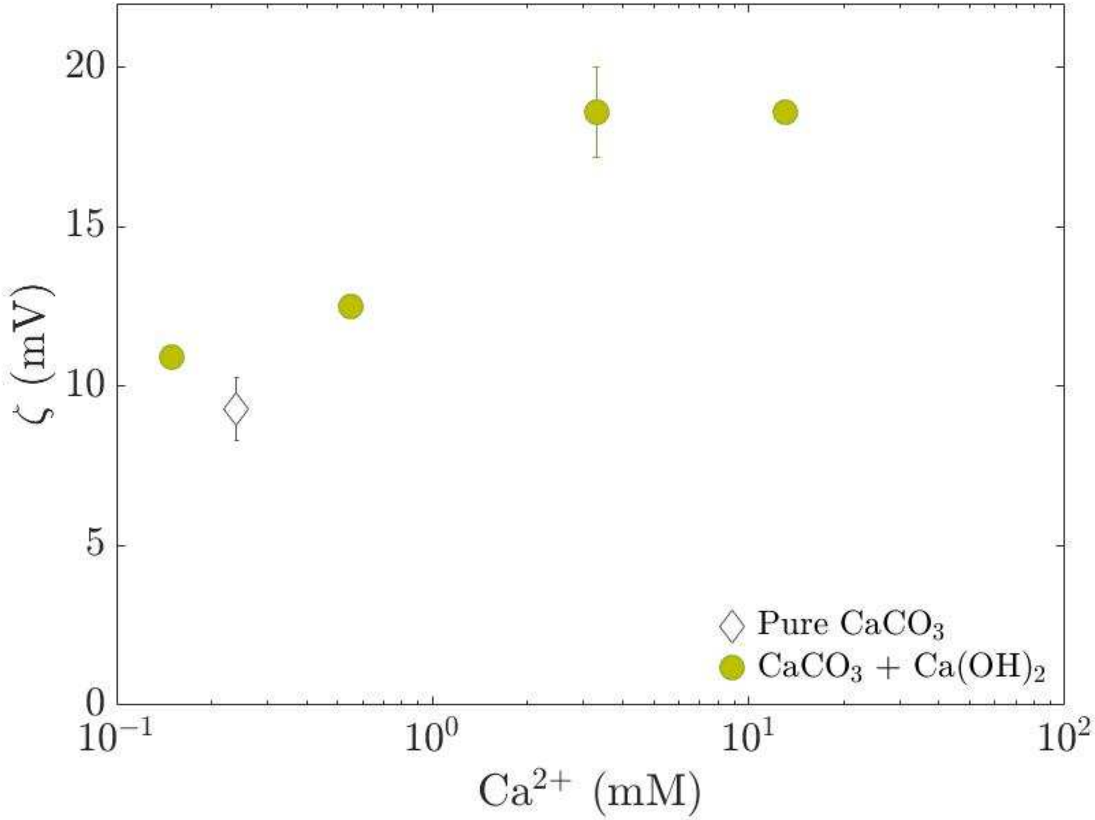
At long times, the ionic conditions are identical

pH monitors the degree of carbonation

Adding calcium hydroxide

Zeta Potential measurement for paste ϕ=10%

collaboration Anna Costa ISTEC Faenza, Italy



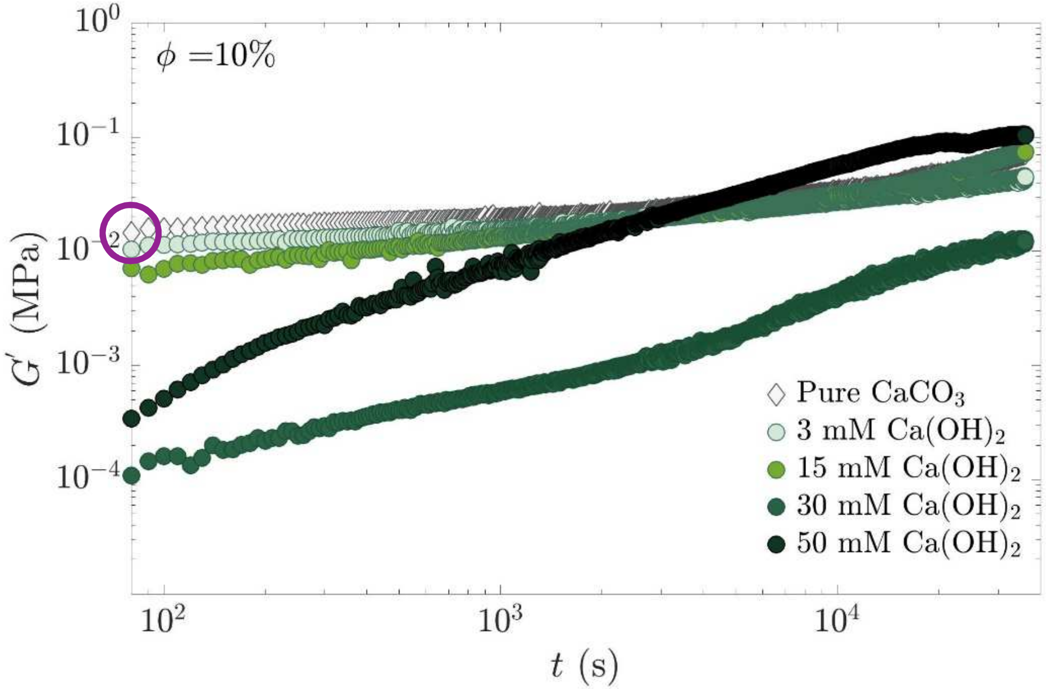
Adsorption of Ca^{2+} at calcite surface

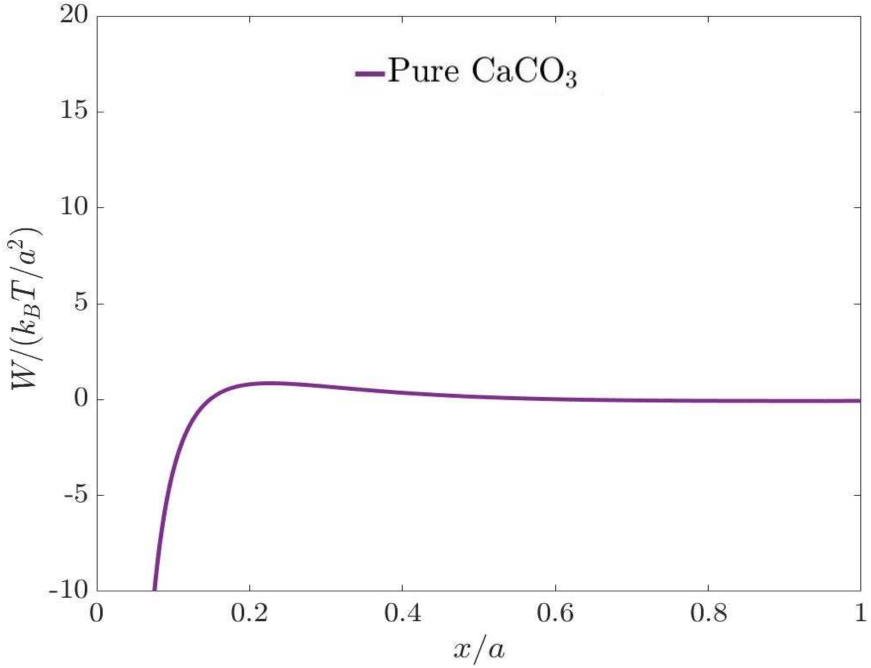
Increase of ζ

Increase of electrostatic repulsion

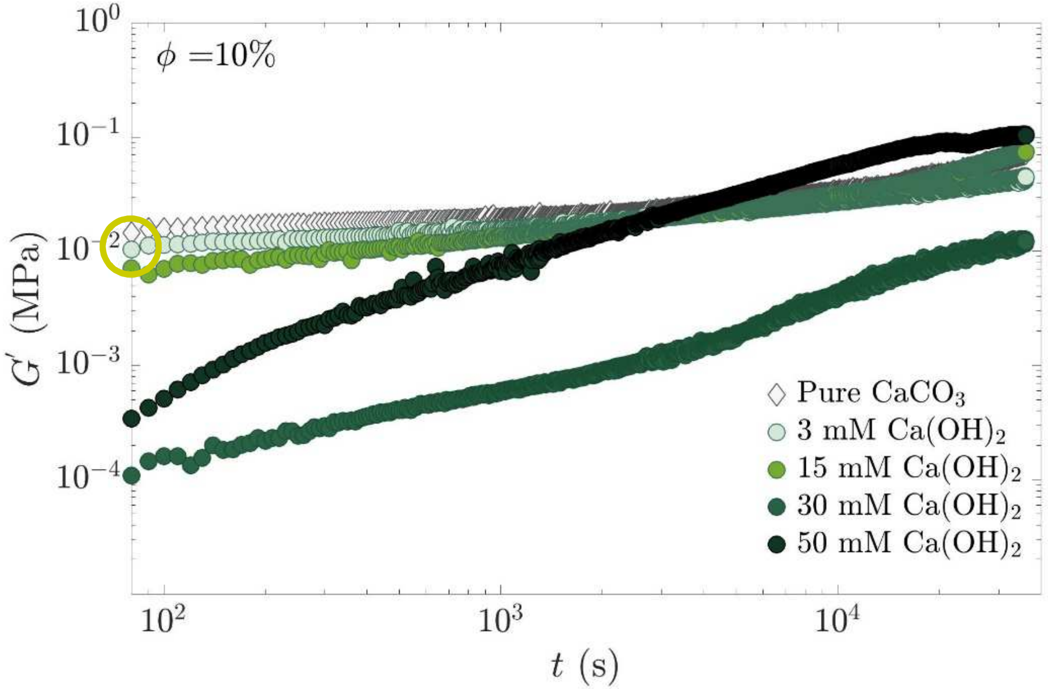
Antagonist effect of ζ and λ

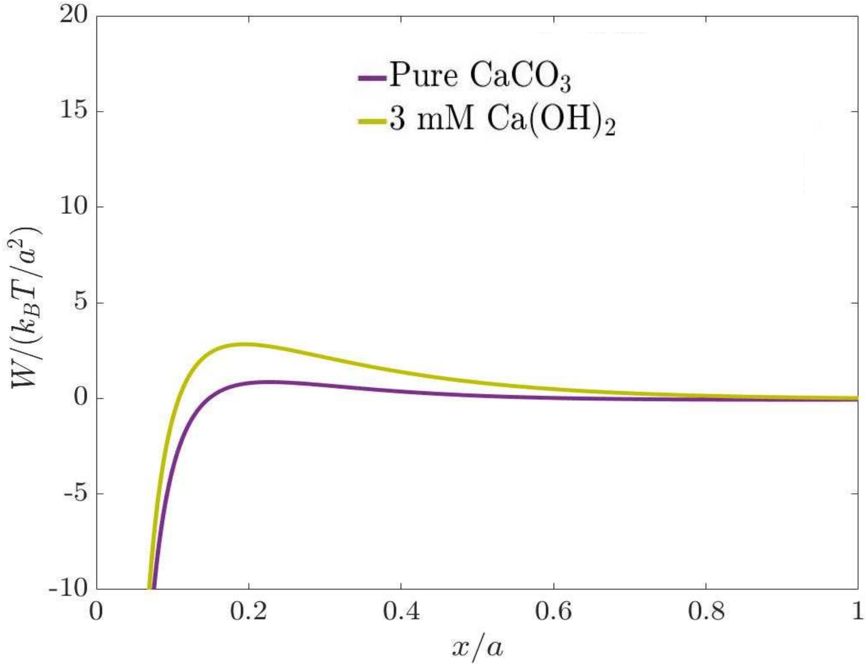
Elastic modulus vs DLVO interactions



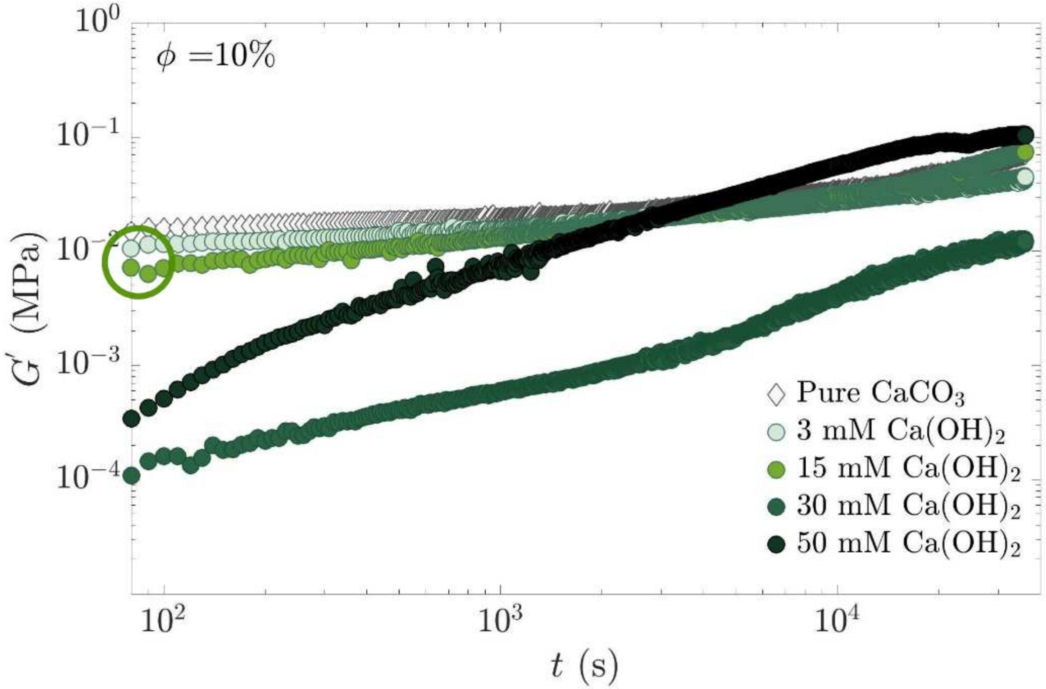


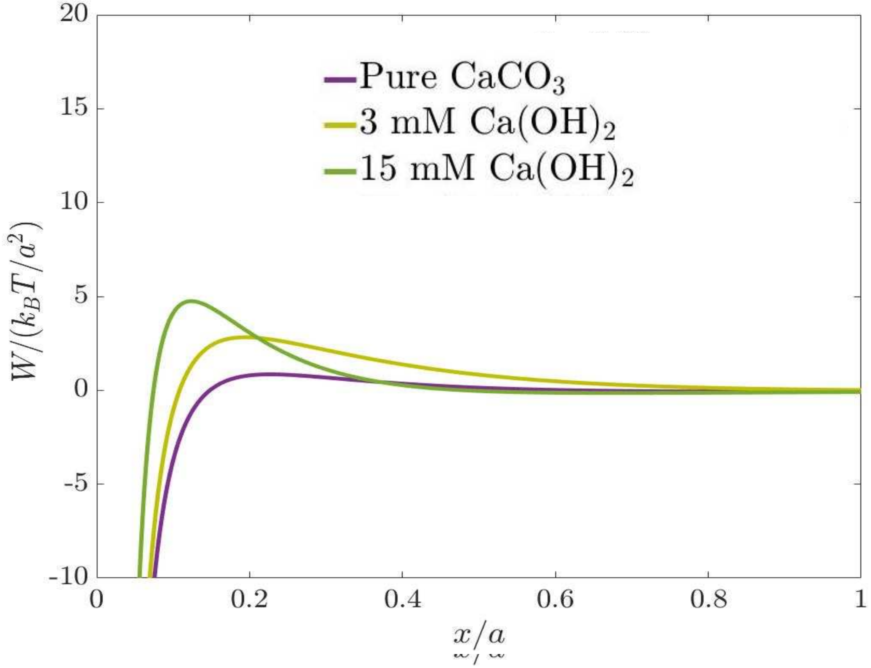
Elastic modulus vs DLVO interactions





Elastic modulus vs DLVO interactions





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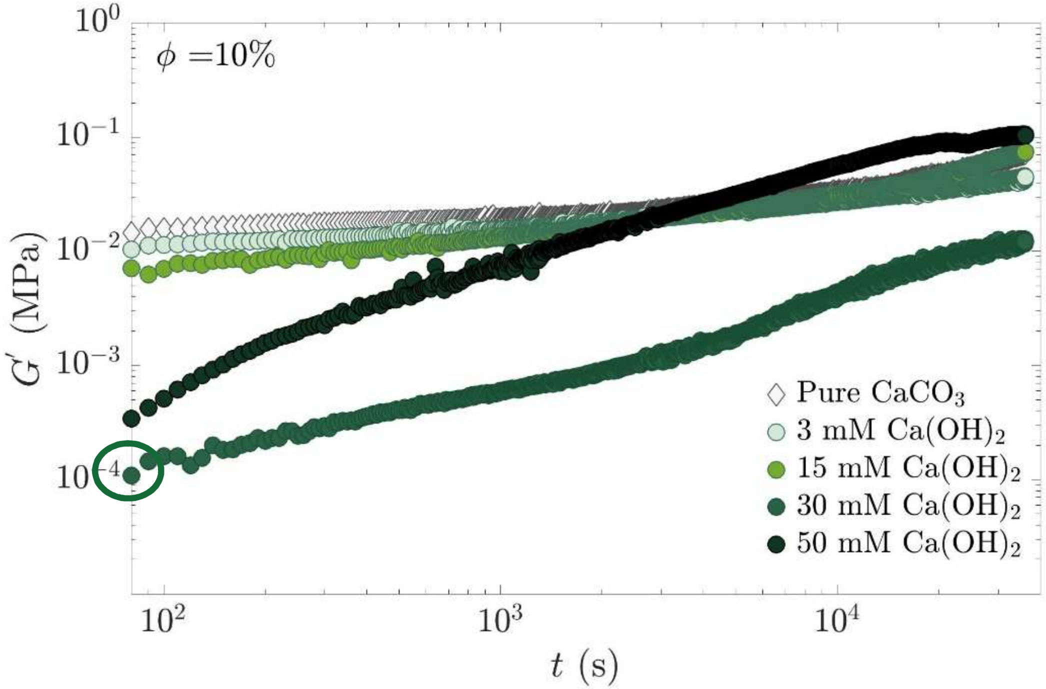

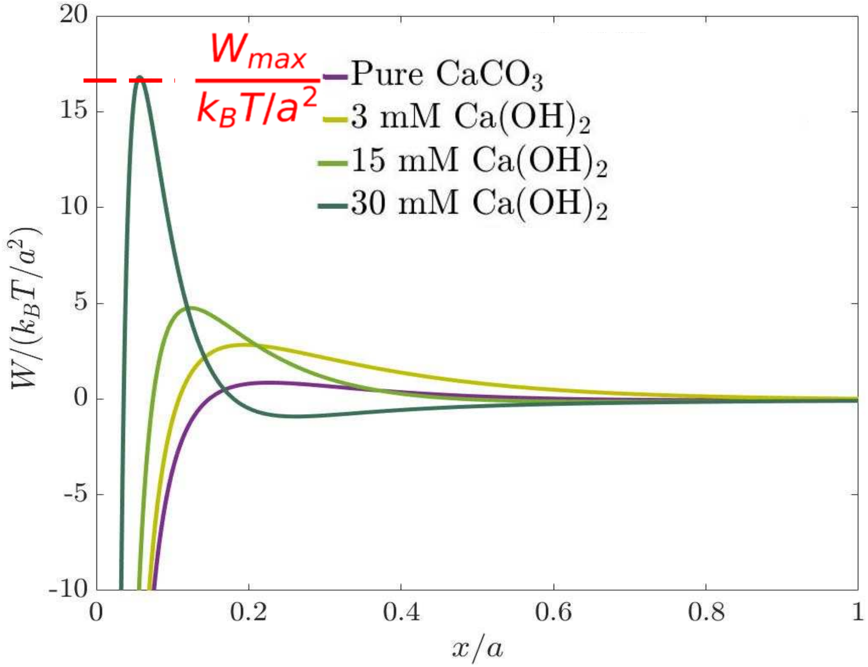

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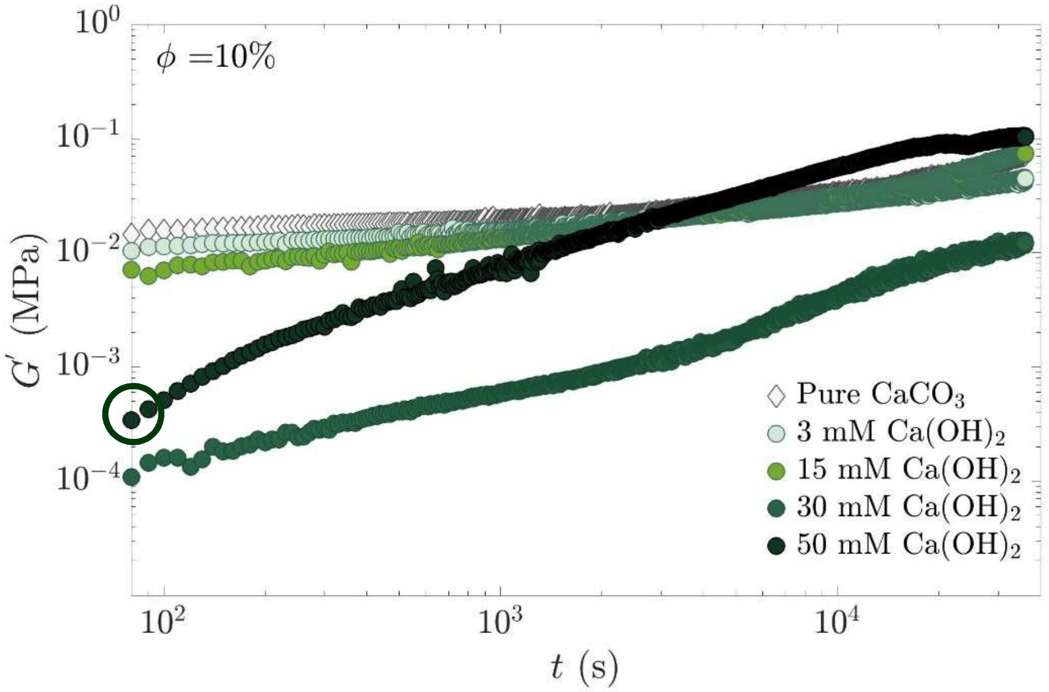
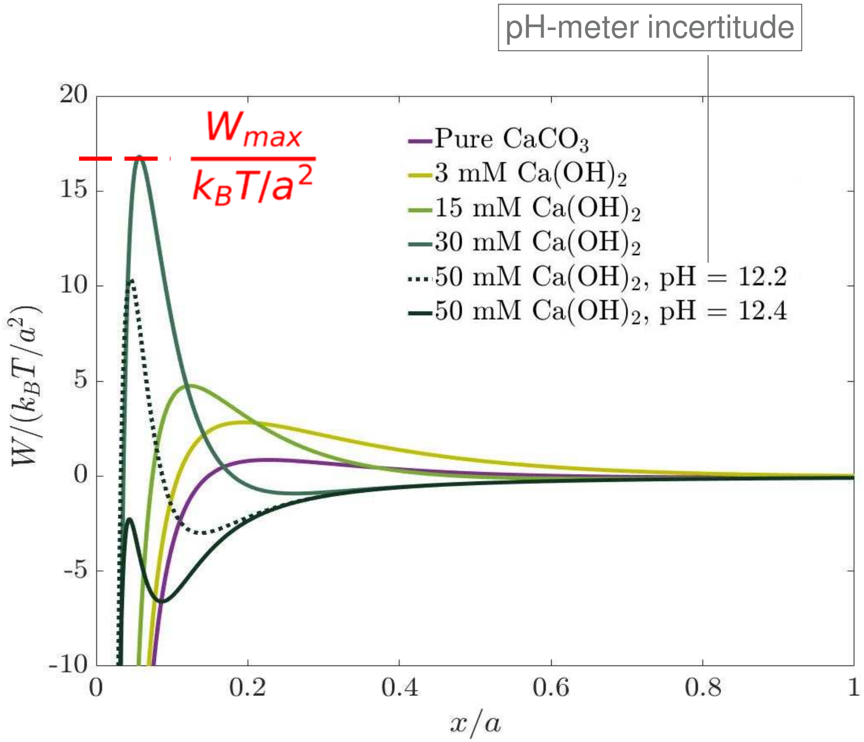


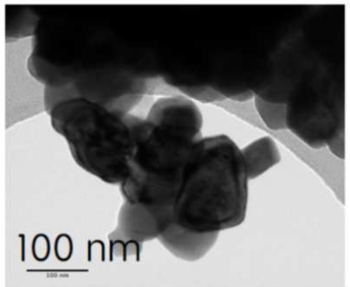


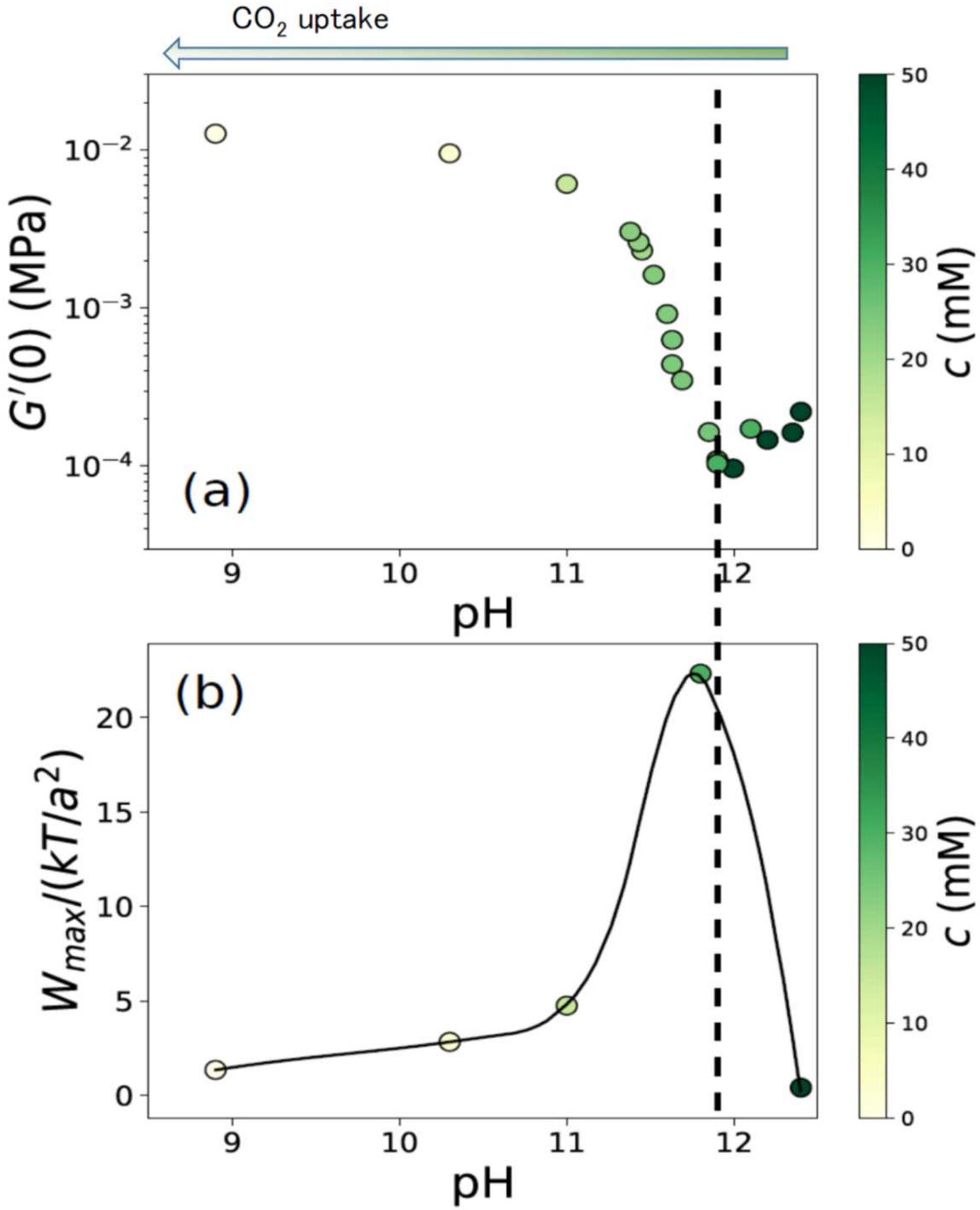
Correlation between G'(0) and 1/Wmax

Elastic modulus vs Wmax

macroscopic properties

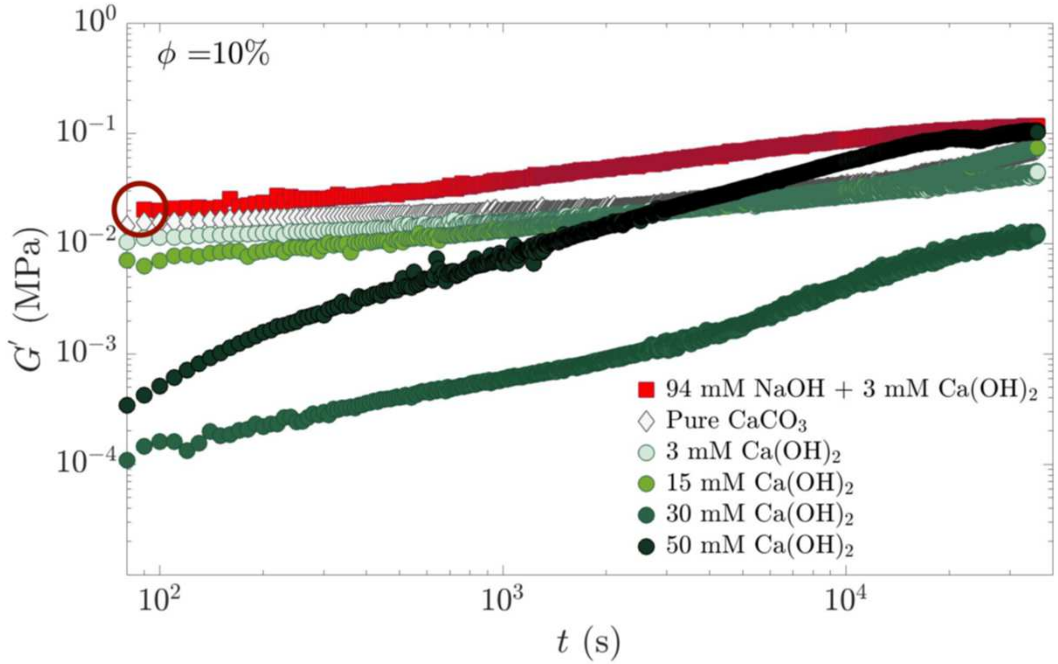
microscopic interactions

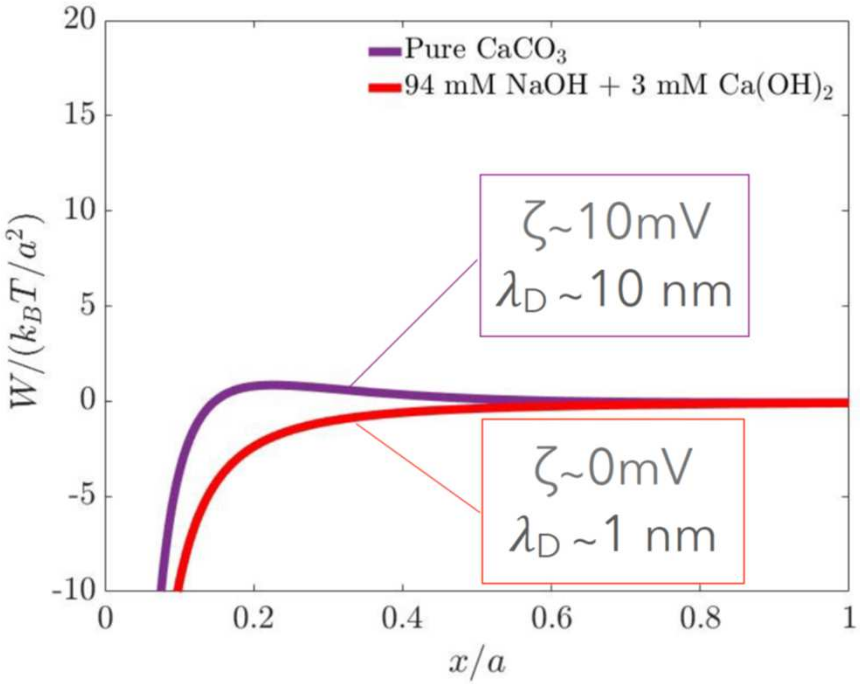




T. Liberto et al JCIS 2019

Addition of NaOH to calcite paste





Decrease of debye length and zeta potential

⬇

Attraction is optimal for calcite paste with NaOH

Influence of interaction on flow

PRL 96, 138302 (2006) PHYSICAL REVIEW LETTERS week ending 7 APRIL 2006

Yielding and Flow in Adhesive and Nonadhesive Concentrated Emulsions

Lydiane Bécu,[1] Sébastien Manneville,[1,*] and Annie Colin[2]

Shear banding in **attractive** emulsion

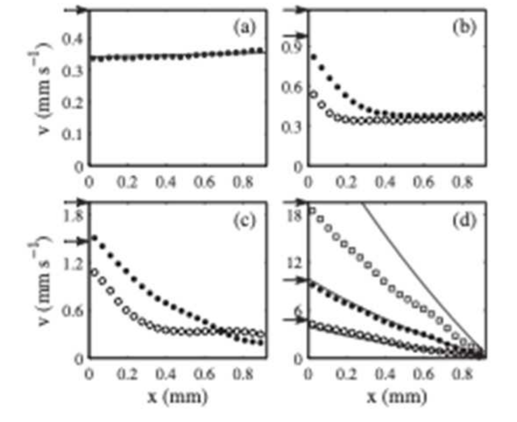


FIG. 4. Velocity profiles in the adhesive emulsion for (a) $v_0 = 0.49$, (b) $v_0 = 0.98$ (○), 1.17 (●), (c) $v_0 = 1.47$ (○), 1.96 (●), and (d) $v_0 = 4.78$ (○), 9.78 (●), and 19.5 mm s^{-1} (□). Arrows indicate the wall velocity v_0. The solid lines correspond to solid body rotation in (a) and to the Herschel-Bulkley model with $\sigma_0 = 88.9$ Pa, $A = 11.0$, and $n = 0.41$ in (d) [see Eq. (3)].

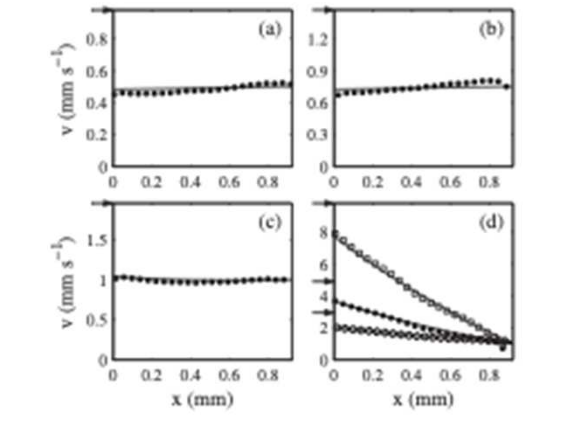


FIG. 3. Velocity profiles in the nonadhesive emulsion for (a) $v_0 = 0.98$, (b) $v_0 = 1.47$, (c) $v_0 = 1.96$, and (d) $v_0 = 2.94$ (○), 4.90 (●), and 9.79 mm s^{-1} (□). Arrows indicate the wall velocity v_0. The solid lines correspond to solid body rotation in (a) and (b) and to the Herschel-Bulkley model with $\sigma_0 = 58.0$ Pa, $A = 11.4$, and $n = 0.45$ in (c) and (d) [see Eq. (3)].

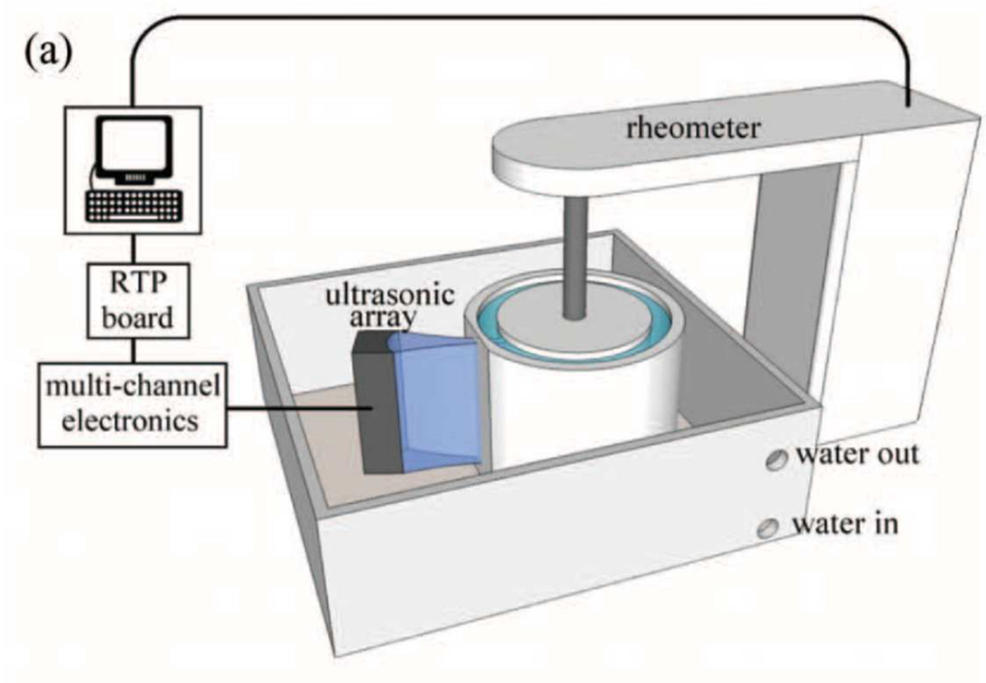
Homogeneous flow for **non-adhesive** emulsion

- Yielding transition in jammed system (300 nm)
- SDS surfactant tuning short range attractive forces (depletion forces)
- Flow: adhesive (8% wt SDS) and nonadhesive (1% wt SDS) systems

Influence of interaction on flows?

ÉCOLE **NORMALE**
SUPÉRIEURE
DE **LYON**

Collaboration with Sebastien Manneville



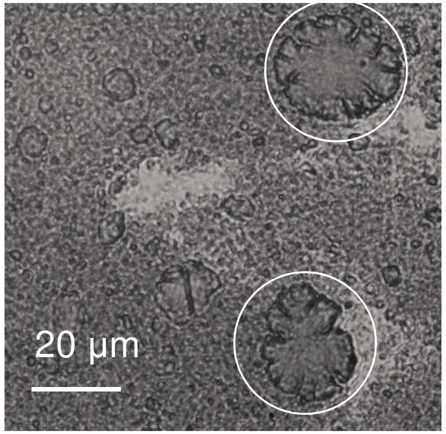
Ultrasonic velocimetry coupled to rheometry

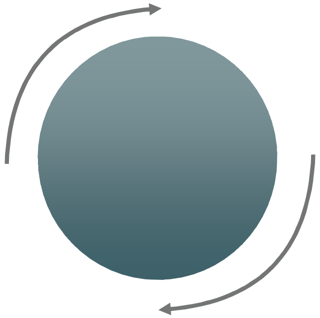
- flow behavior: flow curves
- velocity profiles

T. Gallot et al., *Review of Scientific Instruments* (2013)

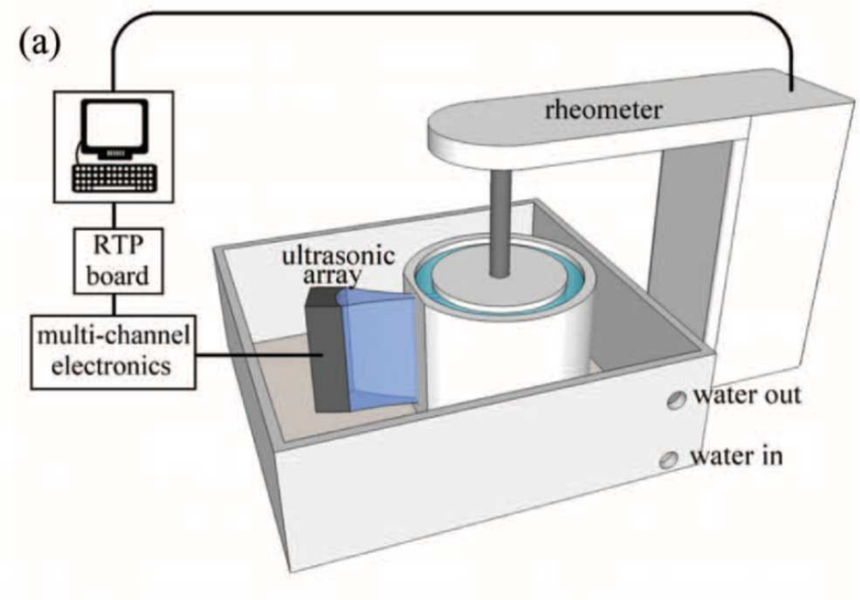
Rheology: rotational test

ÉCOLE **NORMALE**
SUPÉRIEURE
DE **LYON**





no-markers!



Gallot, T. et al., *Review of Scientific Instruments* (2013)

Ultrasonic velocimetry coupled to rheometry

- flow behavior
- velocity profiles

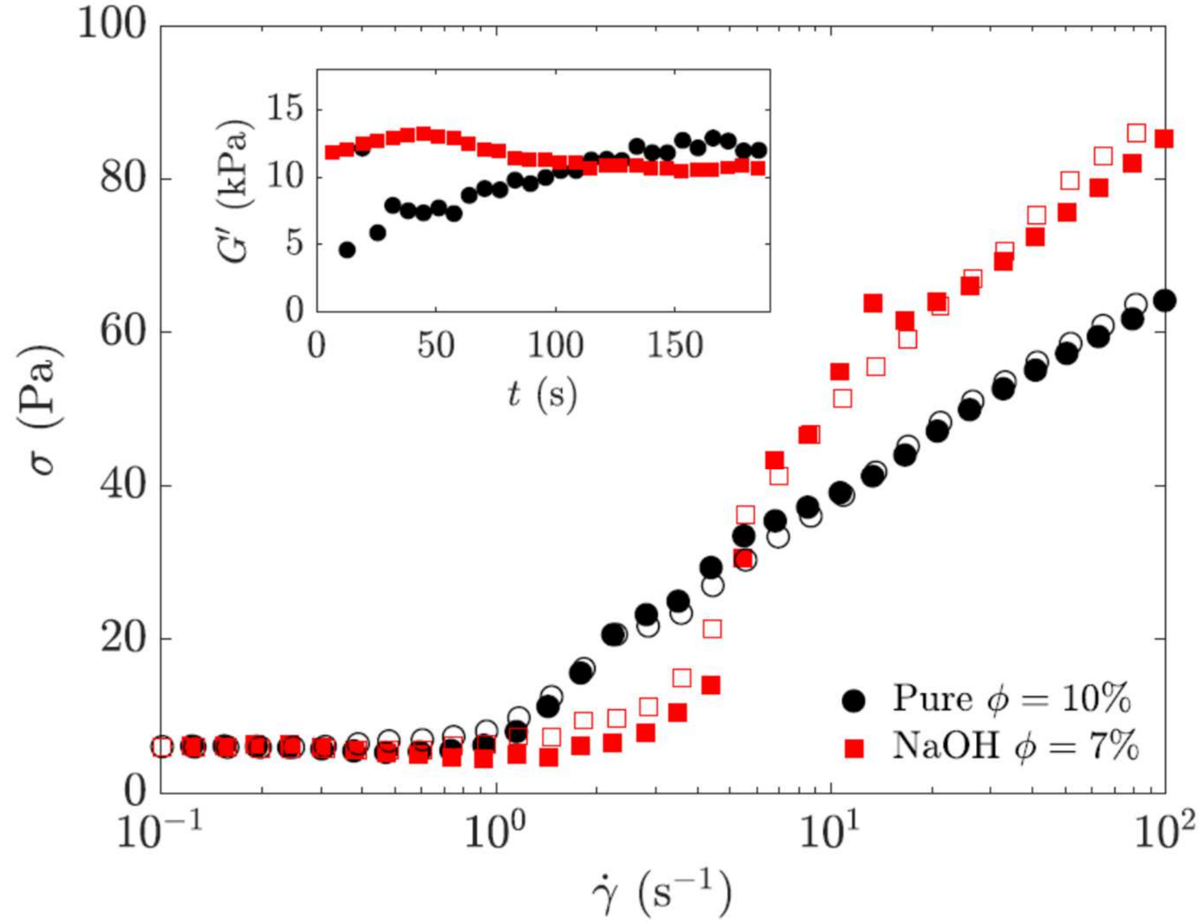
Rheology: macroscopic properties

First signature of interaction: G'(NaOH)>>G'(pure), ϕ=10%

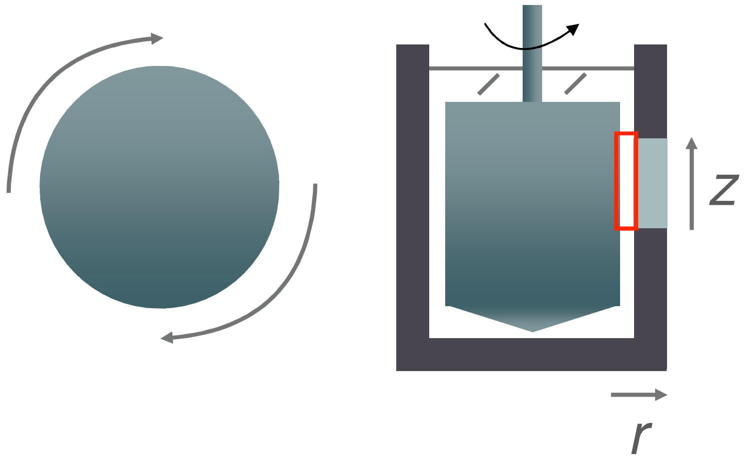
Rheology: macroscopic properties

First signature of interaction: G'(NaOH)>G'(pure)

Pure calcite ϕ=10%, Calcite + NaOH ϕ=7%

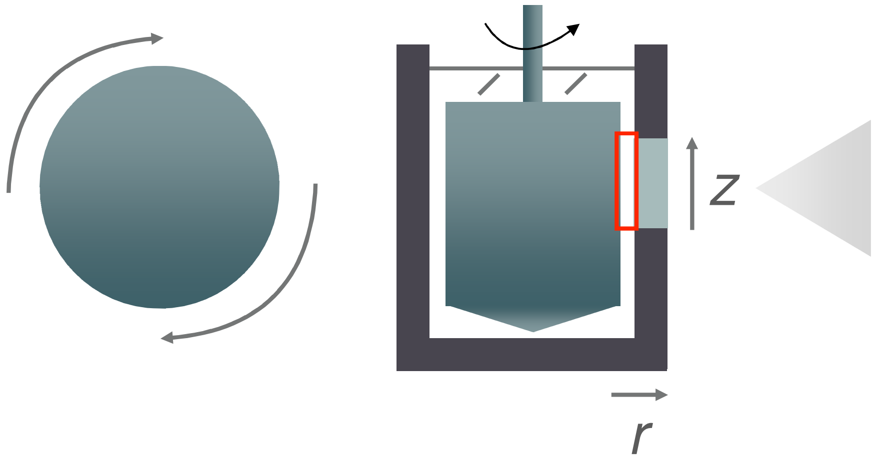


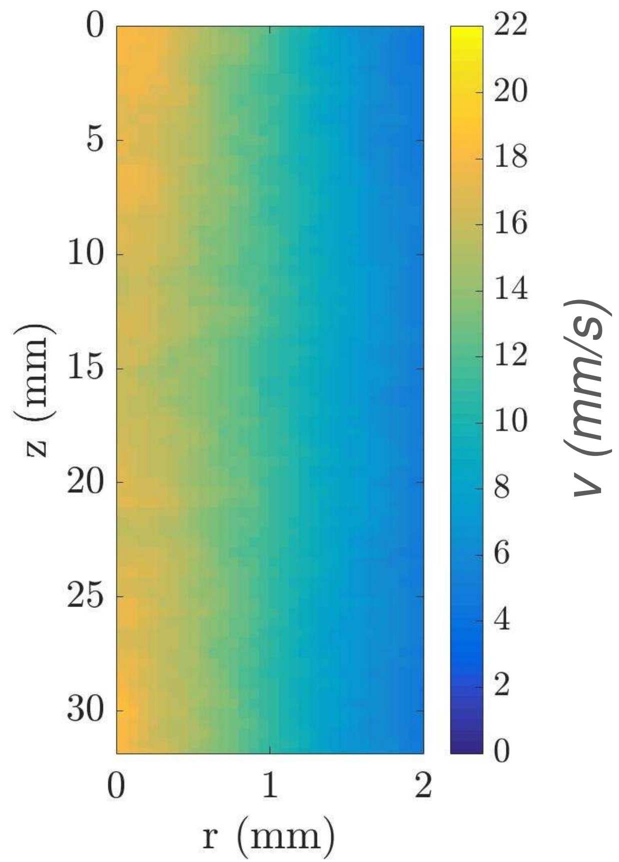
Rheology: velocity profiles



- gap 2 mm (R = 2 cm)
- z = 3 cm
- spatial resolution 100 μm
- time resolution 10 ms

Rheology: velocity profiles





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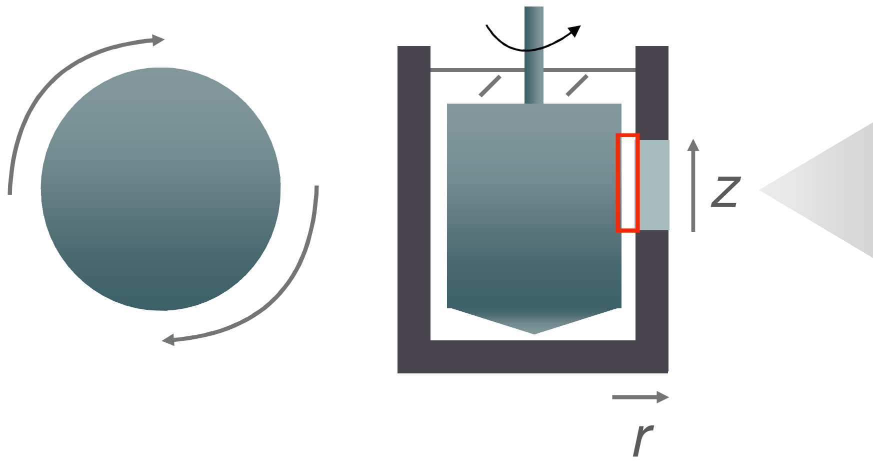
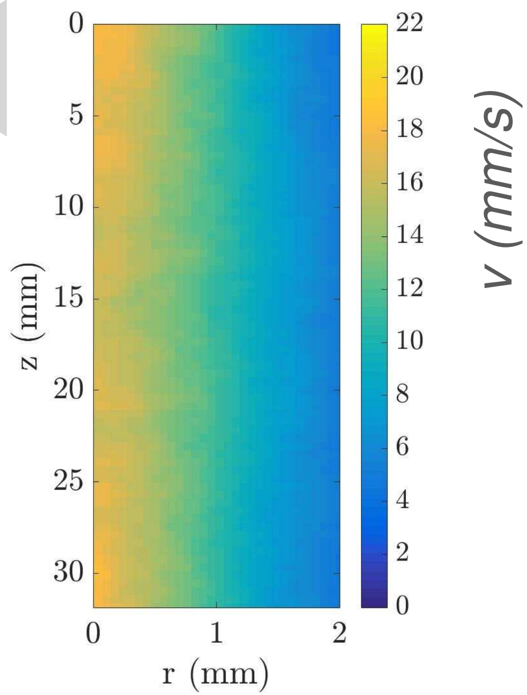
spatial homogeneity

Rheology: velocity profiles



spatial homogeneity



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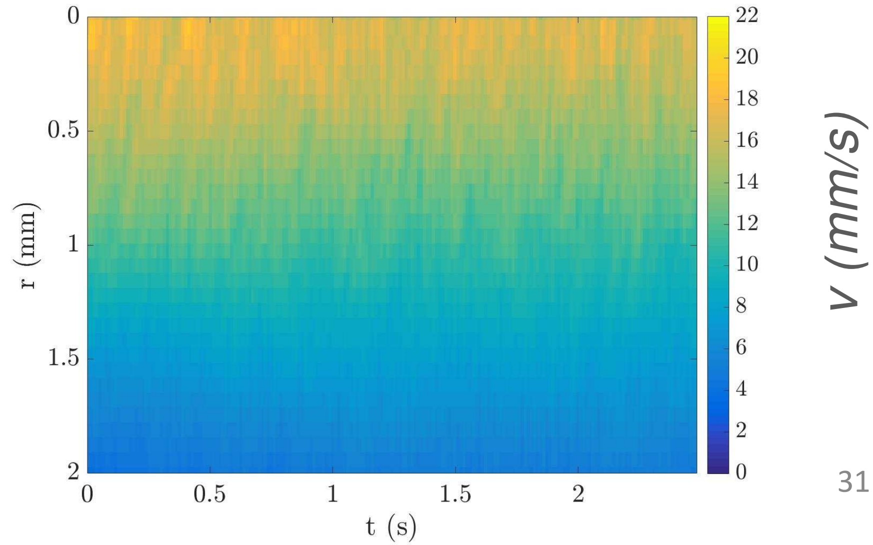
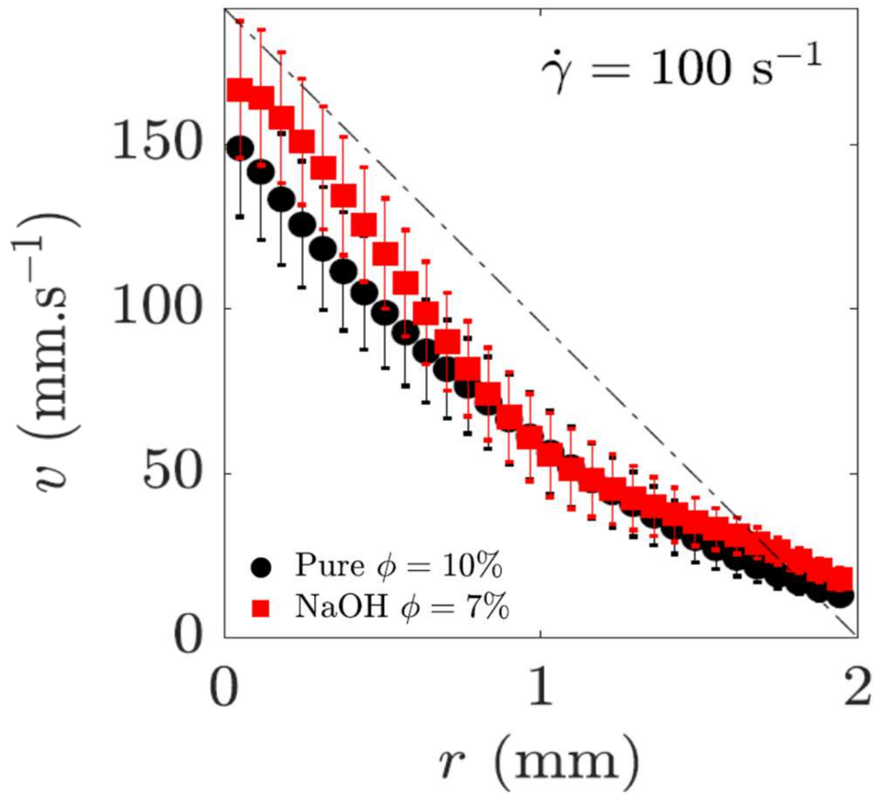
stationarity



Velocity profiles comparison



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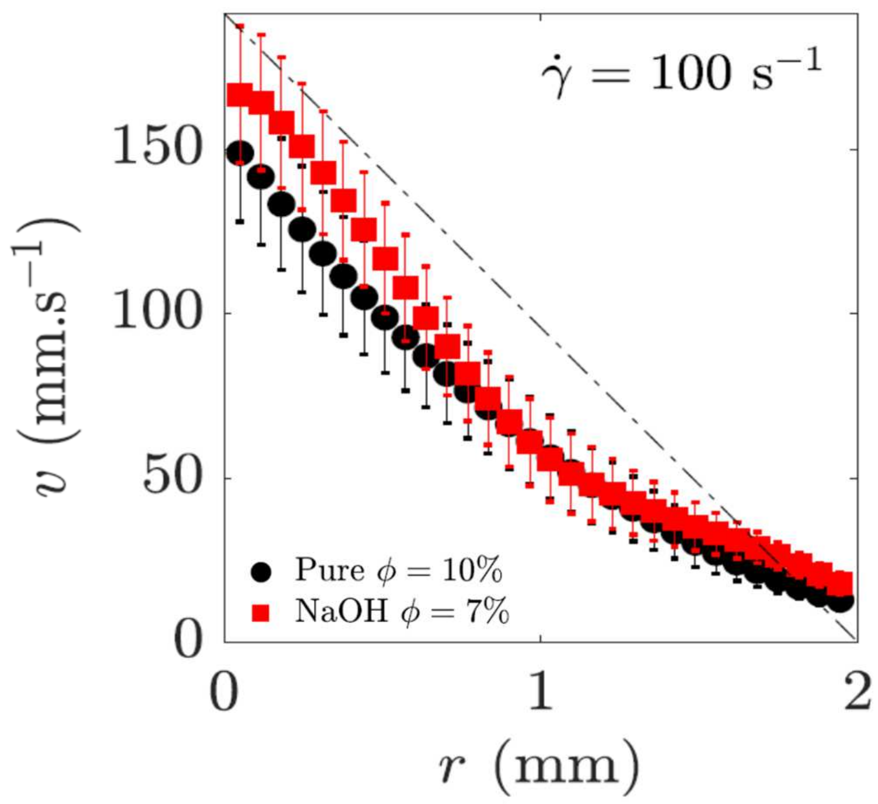
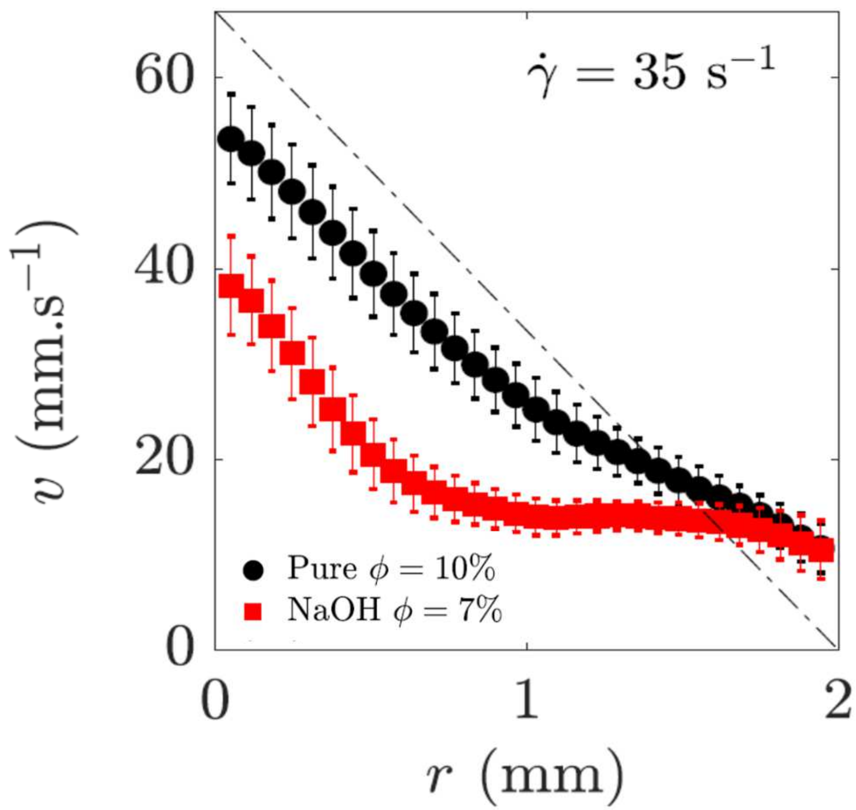
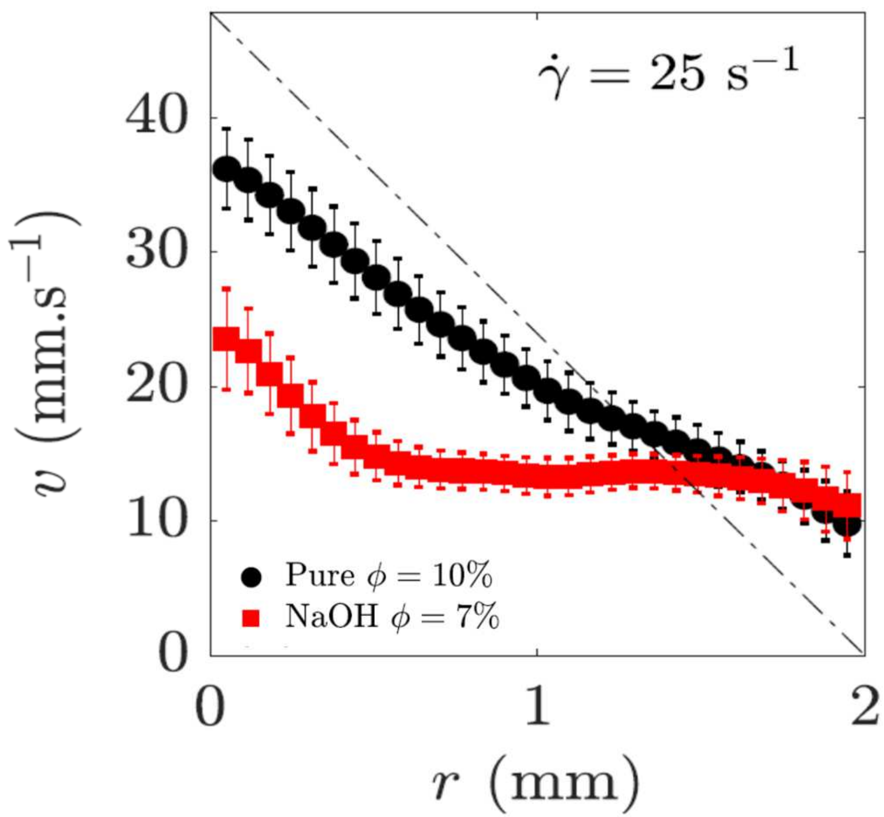


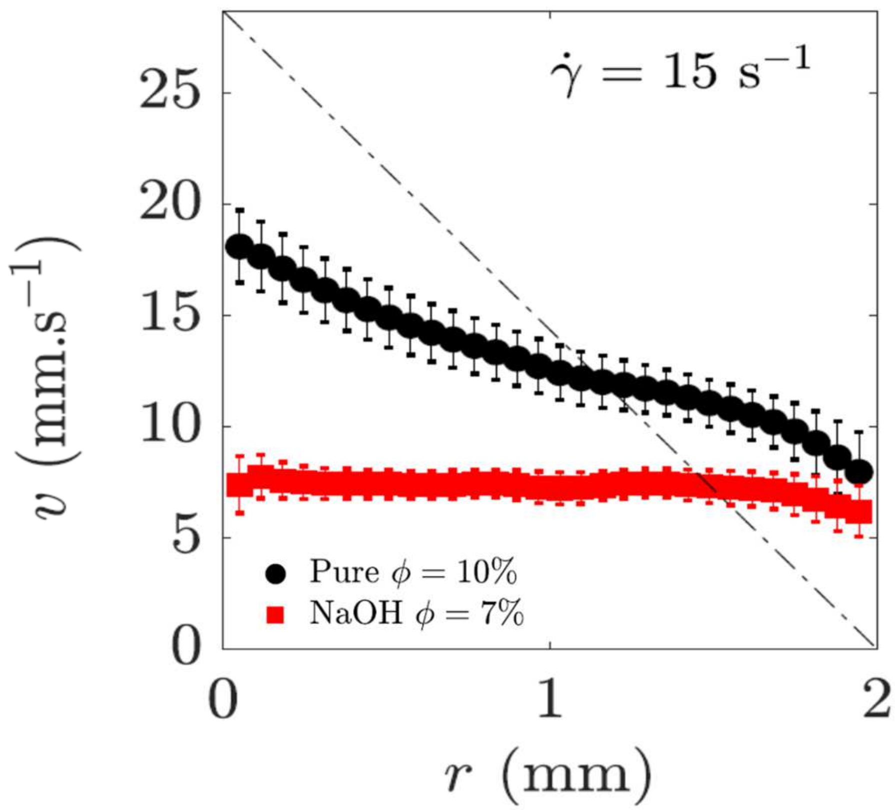


- Wall slip for both samples
- NaOH: shear banding (starting from 50 s^{-1})

Velocity profiles comparison

T. Liberto et al Soft Matter 2020





Pure calcite paste never shows shear-band

Attractive suspension exhibits shear-bands

First time with **colloidal gel**: influence of interaction on flows

Literature comparison

PRL **96,** 138302 (2006) PHYSICAL REVIEW LETTERS week ending 7 APRIL 2006

Yielding and Flow in Adhesive and Nonadhesive Concentrated Emulsions

Lydiane Bécu,[1] Sébastien Manneville,[1,*] and Annie Colin[2]
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[2]*Laboratoire Du Futur, UMR CNRS-Rhodia FRE 2771, 178 Avenue Schweitzer, 33607 Pessac, France*
(Received 9 December 2005; published 3 April 2006)

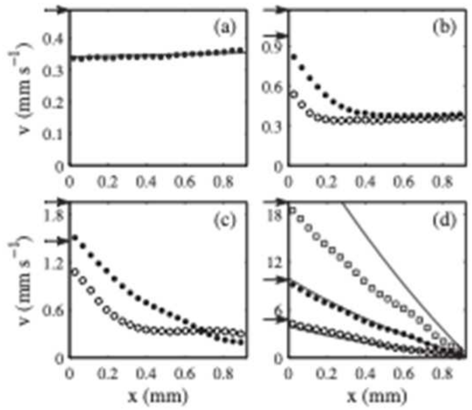

FIG. 4. Velocity profiles in the adhesive emulsion for (a) $v_0 = 0.49$, (b) $v_0 = 0.98$ (○), 1.17 (●), (c) $v_0 = 1.47$ (○), 1.96 (●), and (d) $v_0 = 4.78$ (○), 9.78 (●), and 19.5 mm s^{-1} (□). Arrows indicate the wall velocity v_0. The solid lines correspond to solid body rotation in (a) and to the Herschel-Bulkley model with $\sigma_0 = 88.9$ Pa, $A = 11.0$, and $n = 0.41$ in (d) [see Eq. (3)].

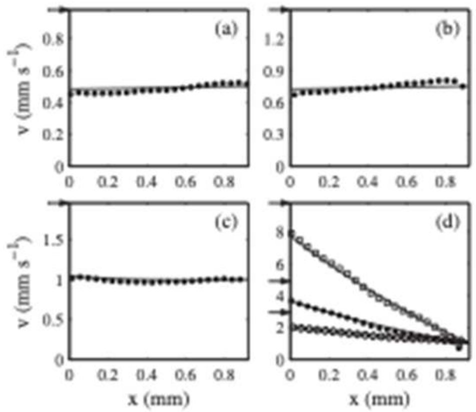

FIG. 3. Velocity profiles in the nonadhesive emulsion for (a) $v_0 = 0.98$, (b) $v_0 = 1.47$, (c) $v_0 = 1.96$, and (d) $v_0 = 2.94$ (○), 4.90 (●), and 9.79 mm s^{-1} (□). Arrows indicate the wall velocity v_0. The solid lines correspond to solid body rotation in (a) and (b) and to the Herschel-Bulkley model with $\sigma_0 = 58.0$ Pa, $A = 11.4$, and $n = 0.45$ in (c) and (d) [see Eq. (3)].

- Yielding transition in jammed system (300 nm)
- SDS surfactant tuning short range attractive forces (depletion forces)
- Flow: adhesive (8% wt SDS) and nonadhesive (1% wt SDS) systems

Literature comparison

PRL 96, 138302 (2006) PHYSICAL REVIEW LETTERS week ending 7 APRIL 2006

Yielding and Flow in Adhesive and Nonadhesive Concentrated Emulsions

Lydiane Bécu,[1] Sébastien Manneville,[1,*] and Annie Colin[2]
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(Received 9 December 2005; published 3 April 2006)

attractive glass with shear banding

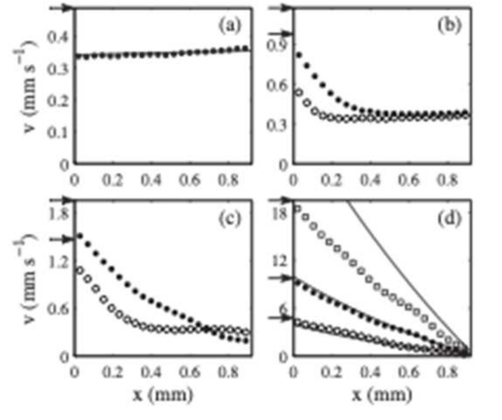


FIG. 4. Velocity profiles in the adhesive emulsion for (a) $v_0 = 0.49$, (b) $v_0 = 0.98$ (○), 1.17 (●), (c) $v_0 = 1.47$ (○), 1.96 (●), and (d) $v_0 = 4.78$ (○), 9.78 (●), and 19.5 mm s^{-1} (□). Arrows indicate the wall velocity v_0. The solid lines correspond to solid body rotation in (a) and to the Herschel-Bulkley model with $\sigma_0 = 88.9$ Pa, $A = 11.0$, and $n = 0.41$ in (d) [see Eq. (3)].

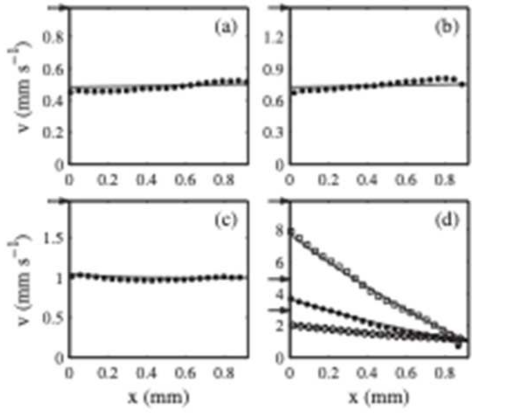
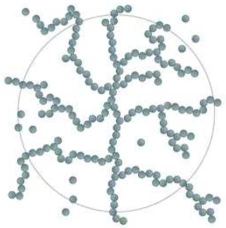


FIG. 3. Velocity profiles in the nonadhesive emulsion for (a) $v_0 = 0.98$, (b) $v_0 = 1.47$, (c) $v_0 = 1.96$, and (d) $v_0 = 2.94$ (○), 4.90 (●), and 9.79 mm s^{-1} (□). Arrows indicate the wall velocity v_0. The solid lines correspond to solid body rotation in (a) and (b) and to the Herschel-Bulkley model with $\sigma_0 = 58.0$ Pa, $A = 11.4$, and $n = 0.45$ in (c) and (d) [see Eq. (3)].

- Yielding transition in jammed system (300 nm)
- SDS surfactant tuning short range attractive forces (depletion forces)
- Flow: adhesive (8% wt SDS) and nonadhesive (1% wt SDS) systems

Conclusion on calcite paste

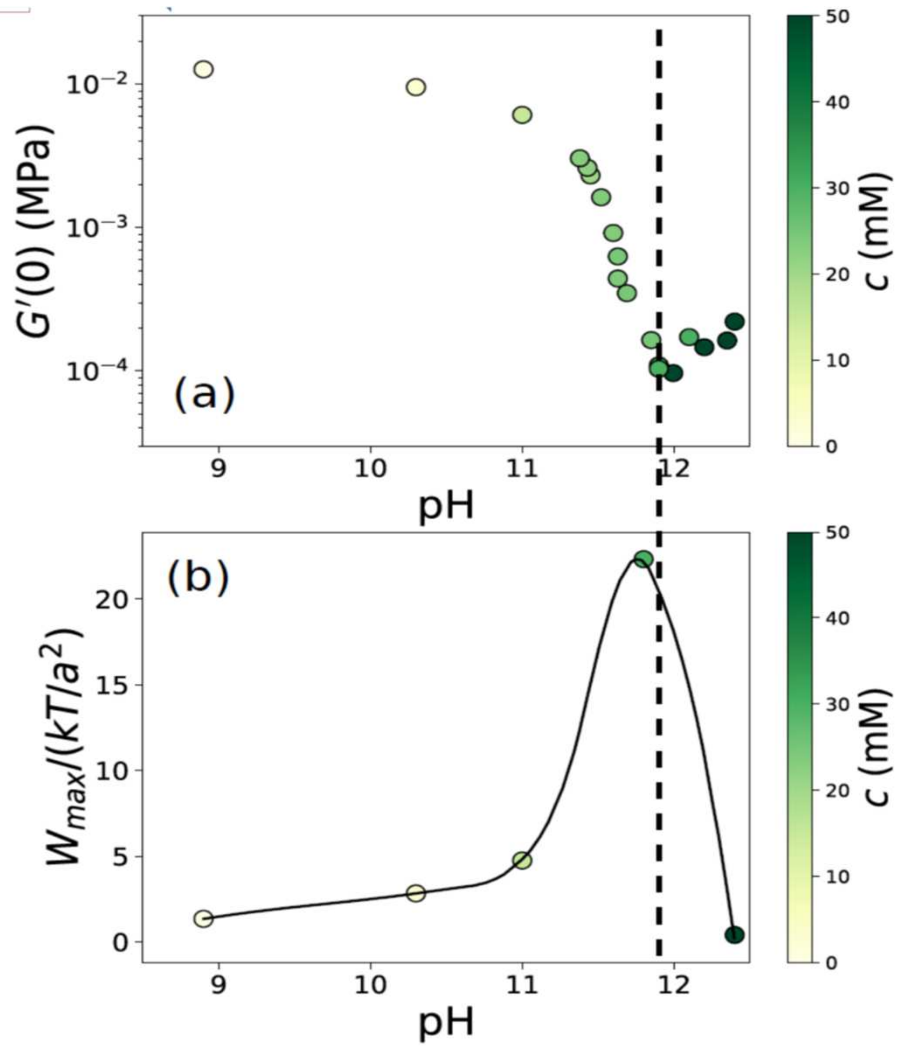


- Colloidal fractal gel
- Simple ions tuning interactions well described by DLVO theory

- Signature of interactions:

  - On elastic modulus correlated to the electrostatic barrier

  - On flows : Homogeneous for low attractive system & Shear-bands for strong attractive



NANOHEAL

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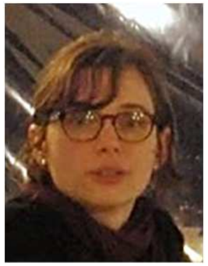
Questions?

Suggestions?

Comments?

LBERTO Teresa

LE-MERRER Marie



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ÉCOLE NORMALE SUPÉRIEURE DE LYON

PRL **112,** 188303 (2014) PHYSICAL REVIEW LETTERS week ending 9 MAY 2014

Impact of Attractive Interactions on the Rheology of Dense Athermal Particles

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Using numerical simulations, the rheological response of an athermal assembly of soft particles with tunable attractive interactions is studied in the vicinity of jamming. At small attractions, a fragile solid develops and a finite yield stress is measured. Moreover, the measured flow curves have unstable regimes, which lead to persistent shear banding. These features are rationalized by establishing a link between the rheology and the interparticle connectivity, which also provides a minimal model to describe the flow curves.

PHYSICAL REVIEW E **85**, 021503 (2012)

Inhomogeneous shear flows in soft jammed materials with tunable attractive forces

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(Received 25 November 2011; published 21 February 2012)

We perform molecular dynamics simulations to characterize the occurrence of inhomogeneous shear flows in soft jammed materials. We use rough walls to impose a simple shear flow and study the athermal motion of jammed assemblies of soft particles in two spatial dimensions, both for purely repulsive interactions and in the presence of an additional short-range attraction of varying strength. In steady state, pronounced flow inhomogeneities emerge for all systems when the shear rate becomes small. Deviations from linear flow are stronger in magnitude and become very long lived when the strength of the attraction increases, but differ from permanent shear bands. Flow inhomogeneities occur in a stress window bounded by the dynamic and static yield stress values. Attractive forces enhance the flow heterogeneities because they accelerate stress relaxation, thus effectively moving the system closer to the yield stress regime where inhomogeneities are most pronounced. The present scenario for understanding the effect of particle adhesion on shear localization, which is based on detailed molecular dynamics simulations with realistic particle interactions, differs qualitatively from previous qualitative explanations and *ad hoc* theoretical modeling.

DOI: 10.1103/PhysRevE.85.021503 PACS number(s): 83.10.Rs, 83.50.−v, 62.20.−x, 83.60.La

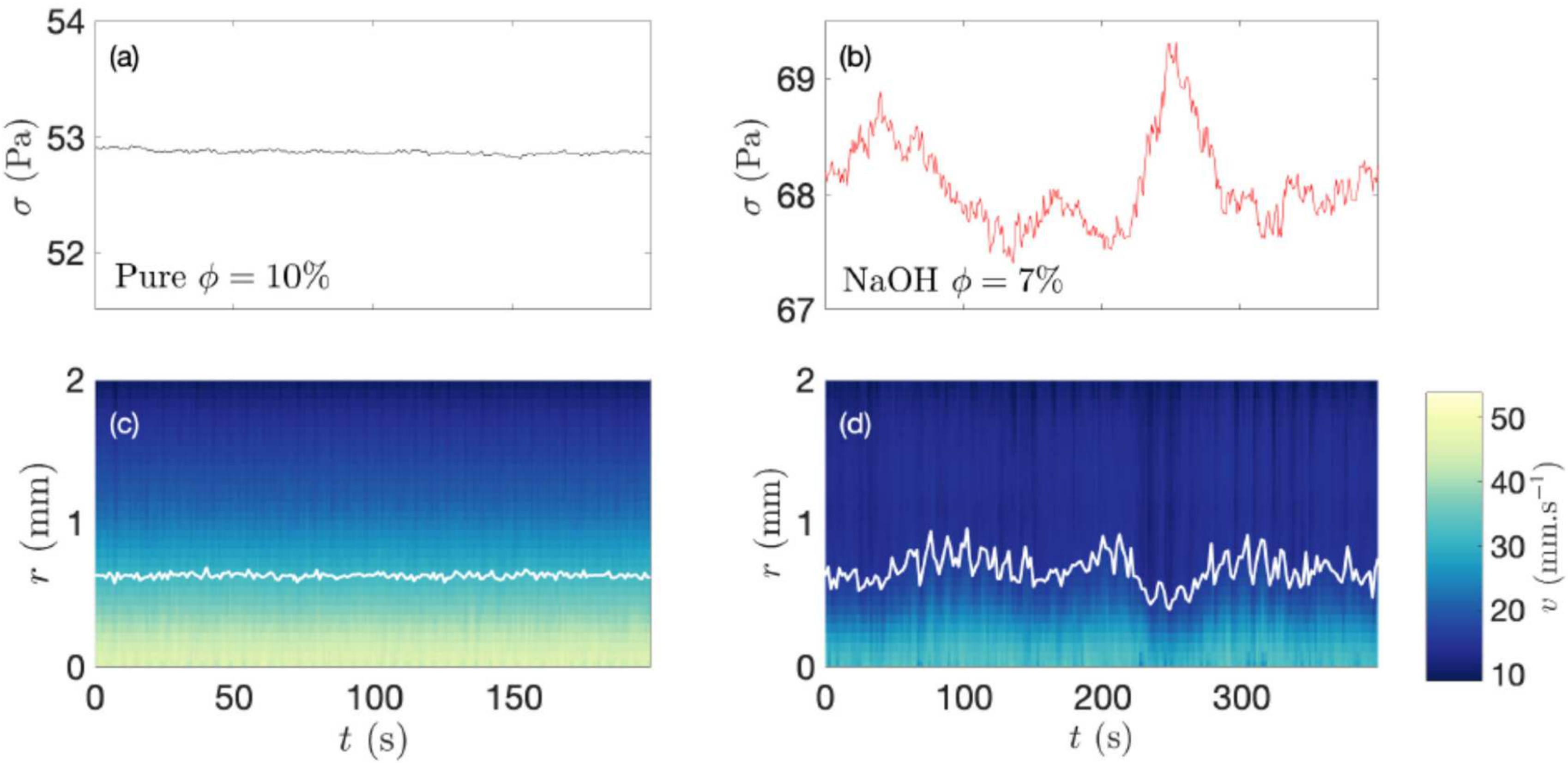

Fig. 4 Time-resolved analysis of the flow of a weakly attractive calcite gel [$\phi = 10\%$ in pure water (left panels)] and of a strongly attractive calcite gel [$\phi = 7\%$ in a sodium (94 mM) and calcium (3 mM) hydroxide solution (right panels)] for a fixed shear rate $\dot{\gamma} = 30\ s^{-1}$. (a)-(b) Shear stress σ as a function of time t. (c)-(d) Spatiotemporal maps of the z-averaged velocity $v(r,t) = \langle v(r,z,t) \rangle_z$. The white lines correspond to a a fixed velocity $v = 32$ mm/s in (c) and $v = 16$ mm.s^{-1} in (d). Experiments performed in a smooth Taylor-Couette geometry. See also Supplementary Movie 1.

increase of flow fluctuations with attraction has also been reported in simulations of jammed systems with tunable interaction

P. Chaudhuri, L. Berthier and L. Bocquet, Phys. Rev. E: Stat.