Signature of colloidal interactions on flow of $CaCO_3$

SLAMM 2019, Roscoff

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NANOHEAL

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How to control the properties of calcite?

Cement-like system:

Calcium Carbonate (calcite) paste

Tuning interactions forces with additives:

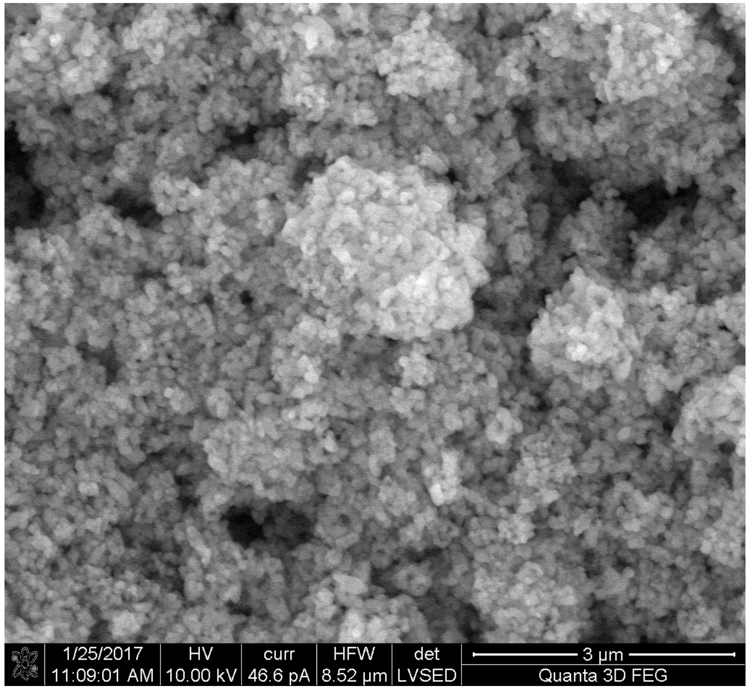
Ions (Ca(OH)2, Na(OH)) or carboxylic polymers

How to control the properties of calcite?

MACROSCOPIC rheological properties ⇄ MICROSCOPIC structure & interactions

Paste characterization

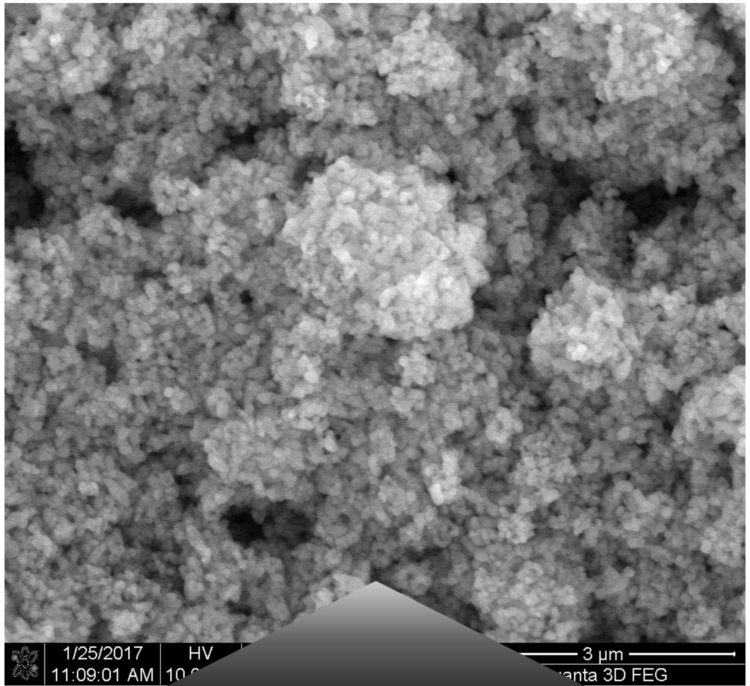
SEM image

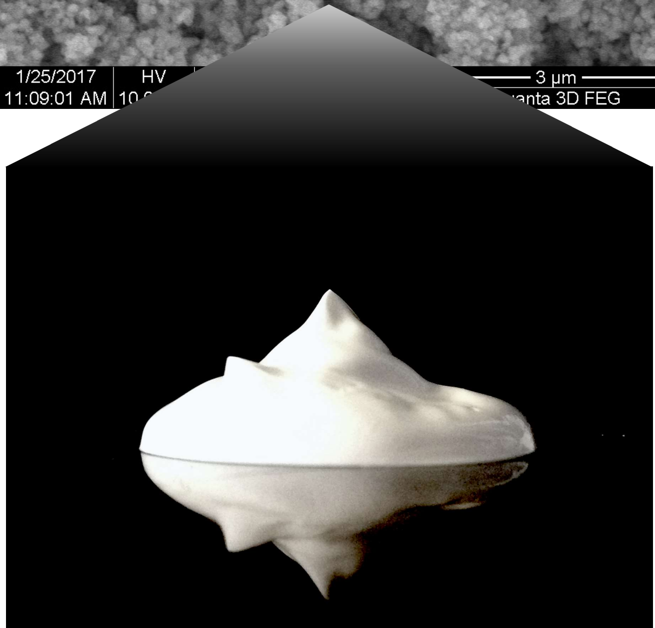


- Pure $CaCO_3$ powder
- $\langle d_P \rangle$ = 70 nm
- Rhombohedral shape
- Colloidal paste ϕ =[5-30] %

Paste characterization

SEM image





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Elastic modulus

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

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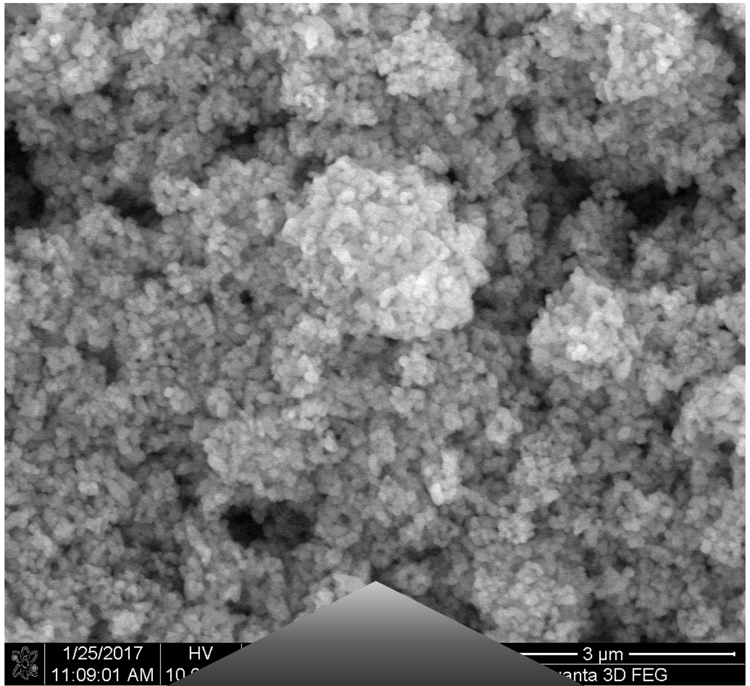

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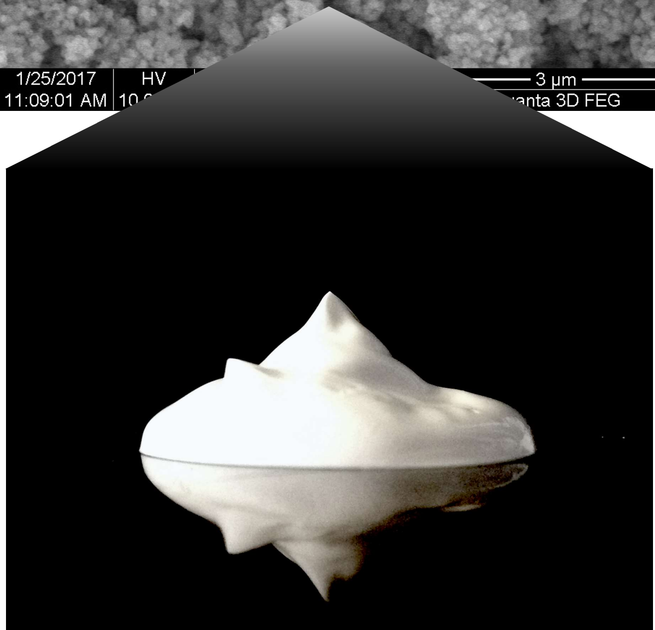

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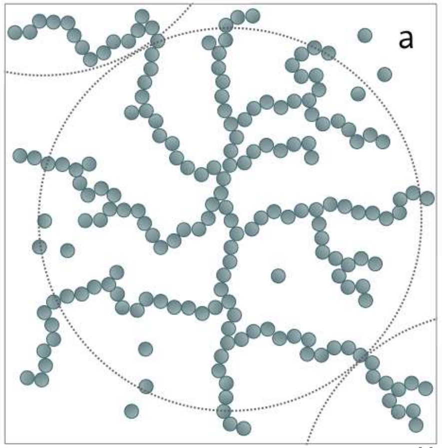
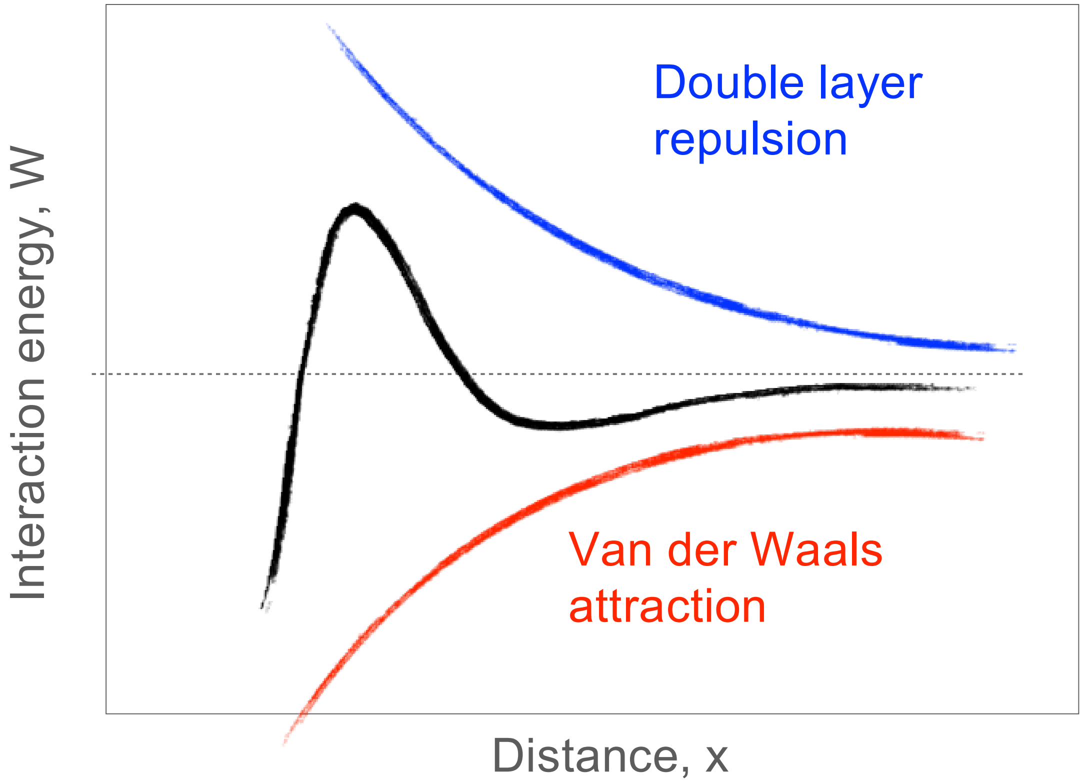


Microscopic Interactions: DLVO

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



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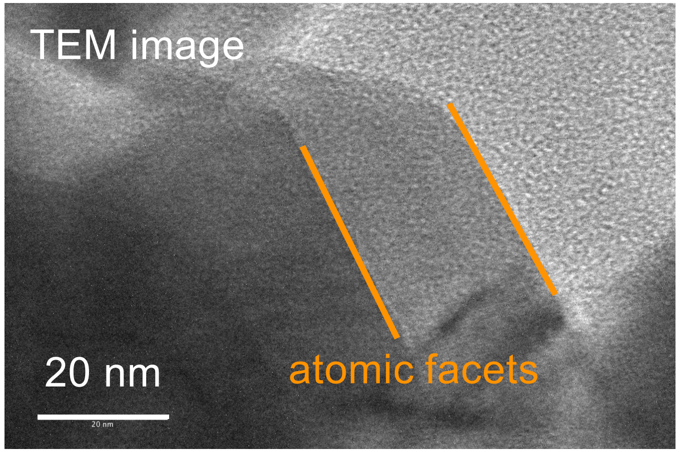

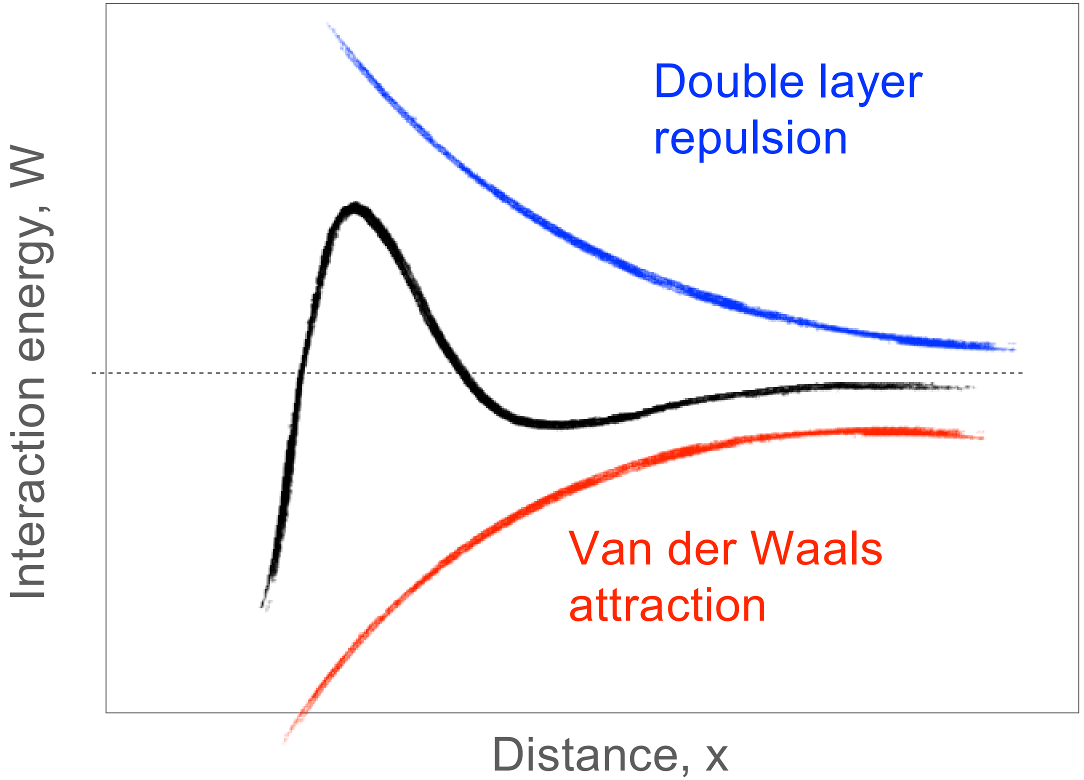

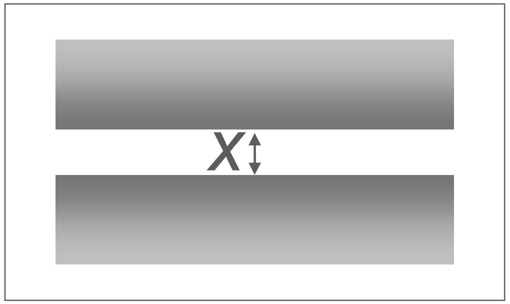

$A = 3.6\ k_B T,$

$\zeta\ \&\ \lambda_D$?

Microscopic Interactions: DLVO

Potentiel Zeta measurement for paste ϕ=10%

collaboration Anna Costa ISTEC Faenza, Italy

$$|\zeta| \sim 0 - 20 mV$$

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) ($K_{10} = 10^{2.45}$)

$$I \sim 1 - 100\ mM$$

$$\lambda_D \sim 10 - 1\ nm$$

Microscopic Interactions: DLVO

Focus on two systems:

- Pure $CaCO_3$: surface positively charged
- $CaCO_3$ + NaOH : superficial sites neutralised by OH^- ions

Microscopic Interactions: DLVO

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- Pure $CaCO_3$: surface positively charged
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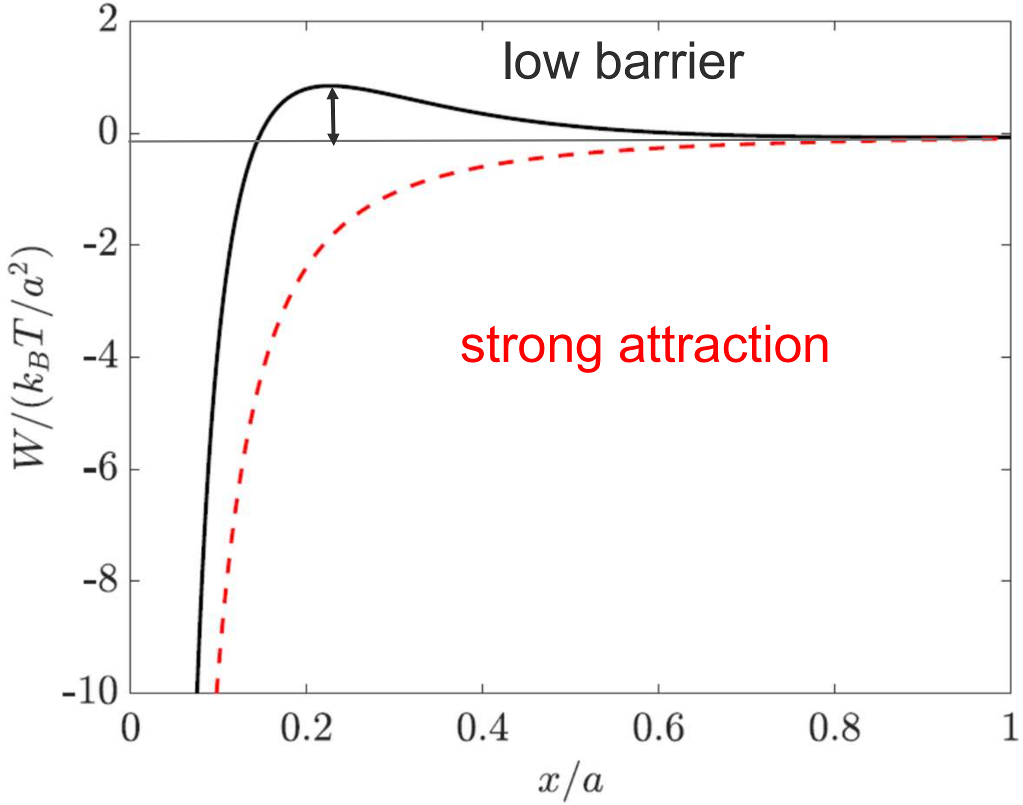
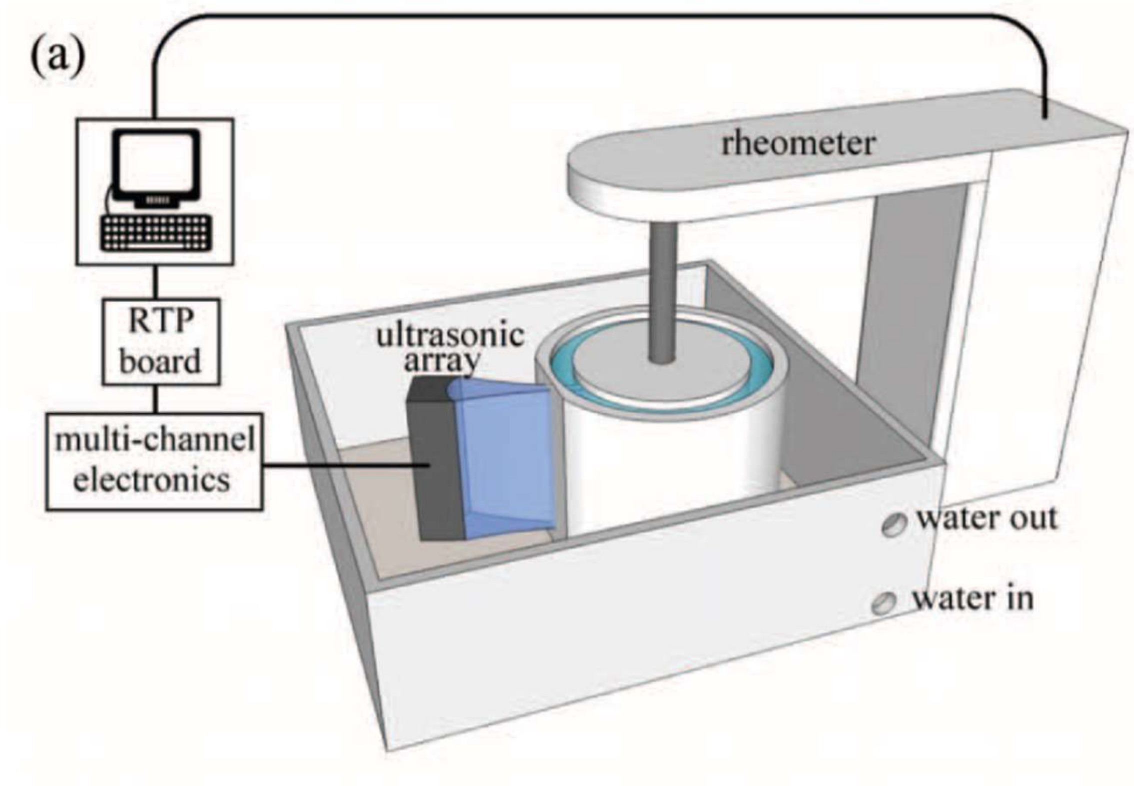
sample ϕ =10%	ζ (mV)
Pure $CaCO_3$	**8.6**
$CaCO_3$ +100 mM NaOH	**-2.4**



Rheology: flow

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



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

Ultrasonic velocimetry coupled to rheometry

- flow behavior: viscosity, flow curves
- velocity profiles

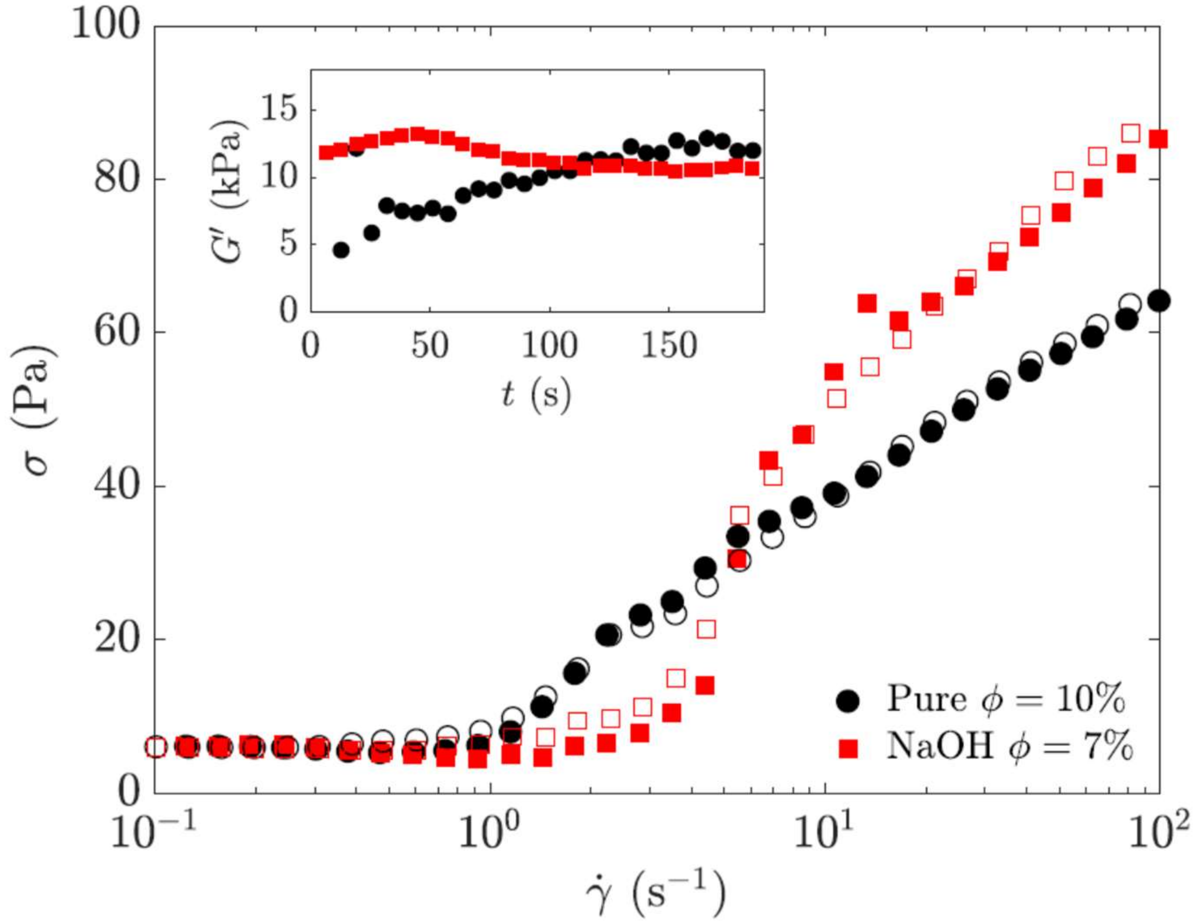
Rheology: macroscopic properties

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

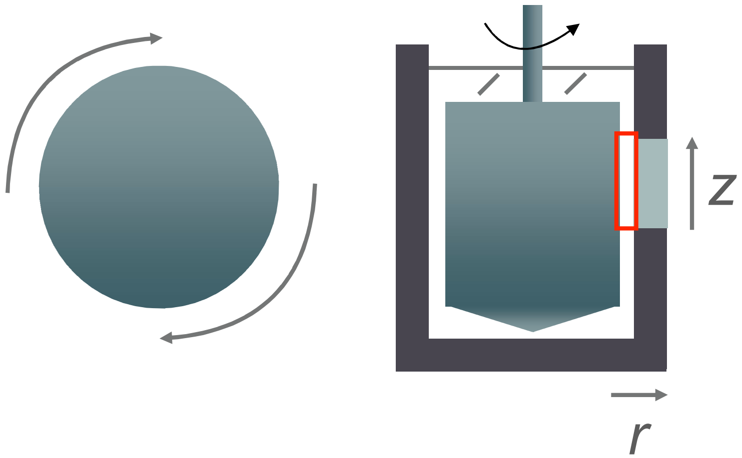
Rheology: macroscopic properties

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

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

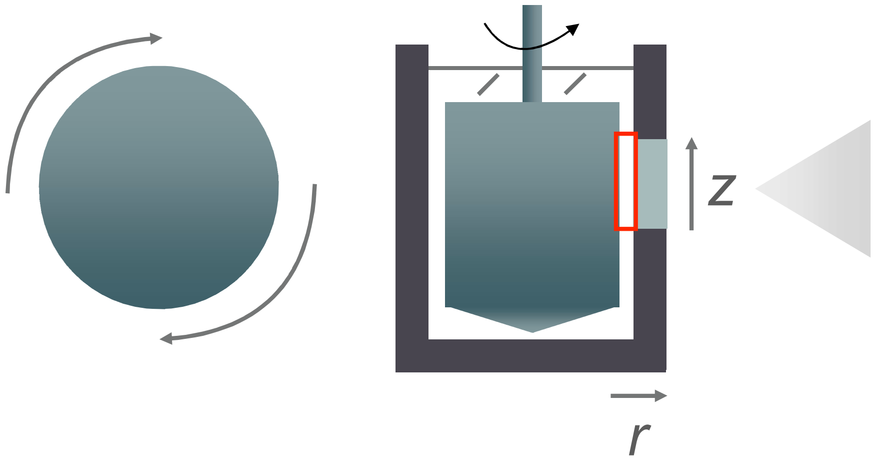


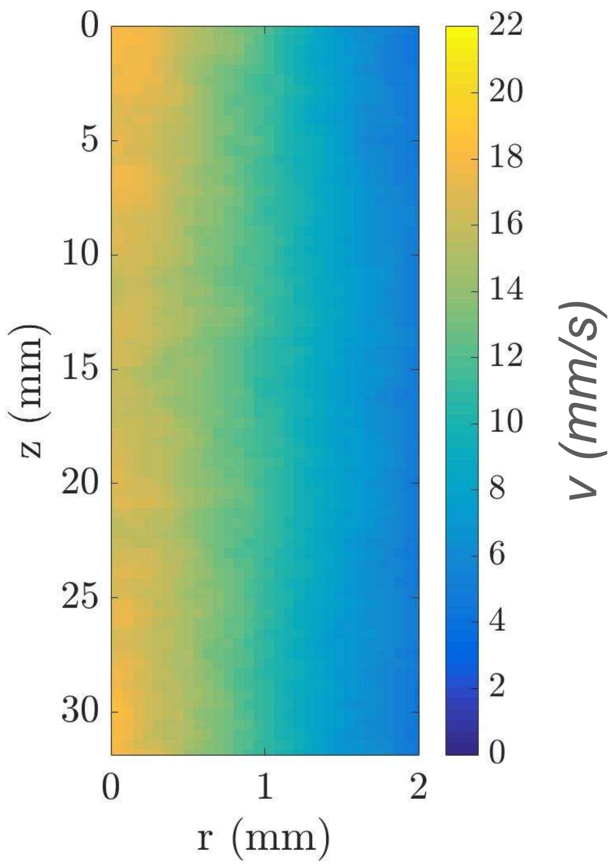
Rheology: velocity profiles



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

Rheology: velocity profiles





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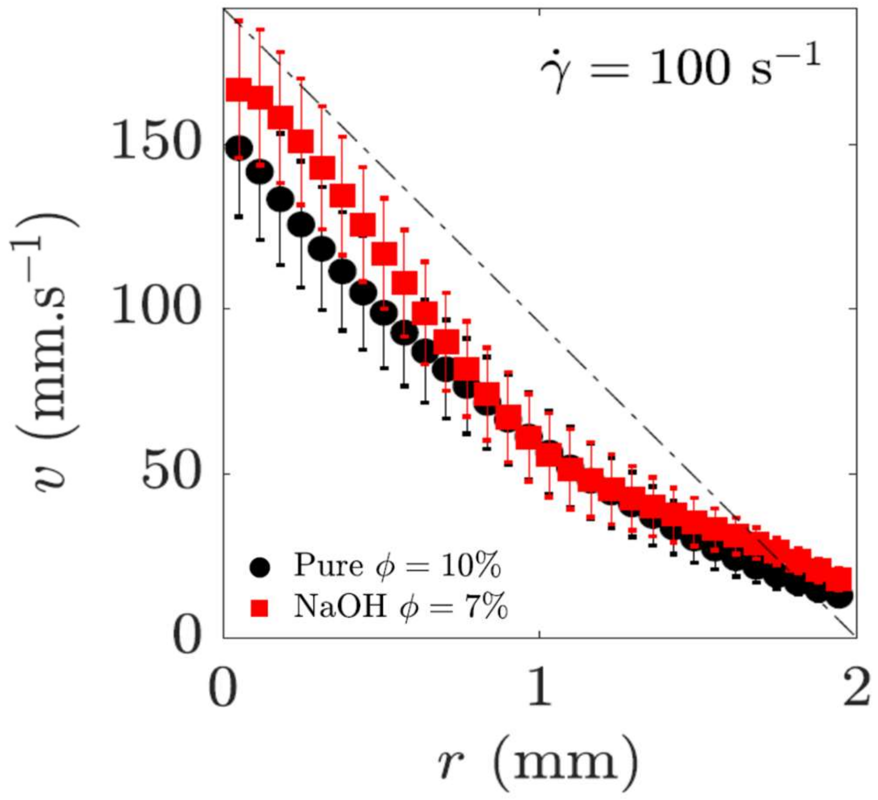
- time resolution 10 ms

spatial homogeneity

Velocity profiles comparison



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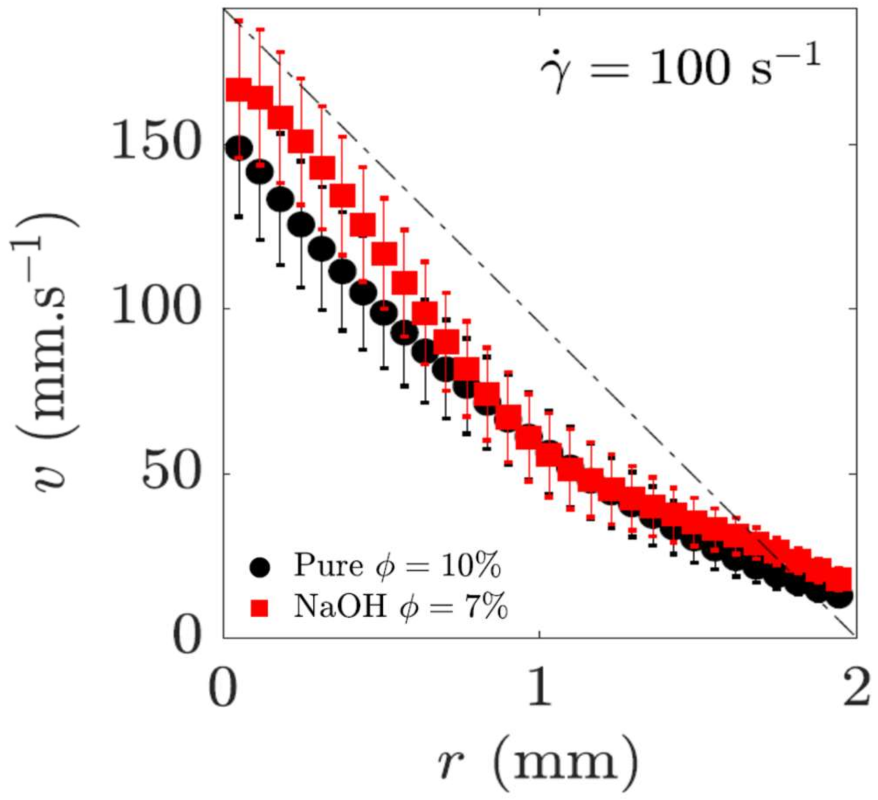
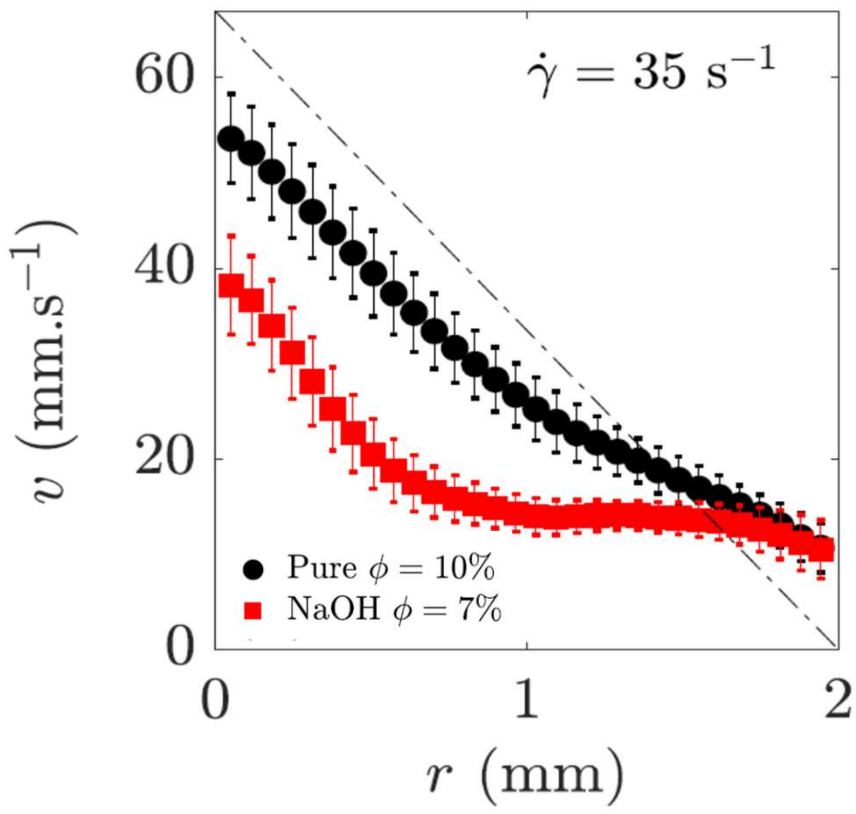
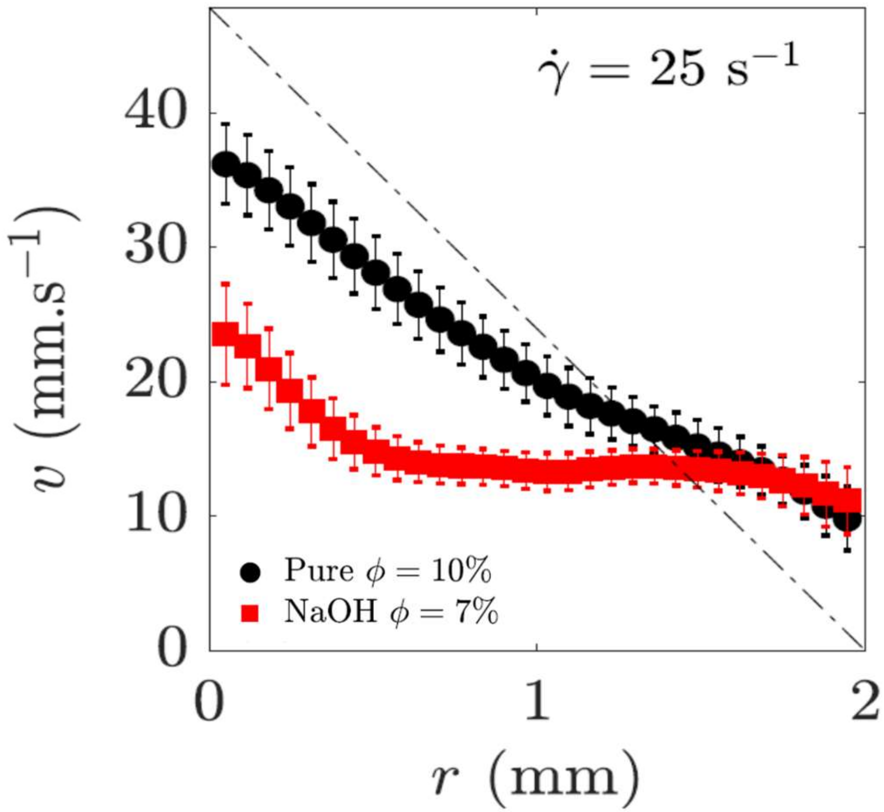
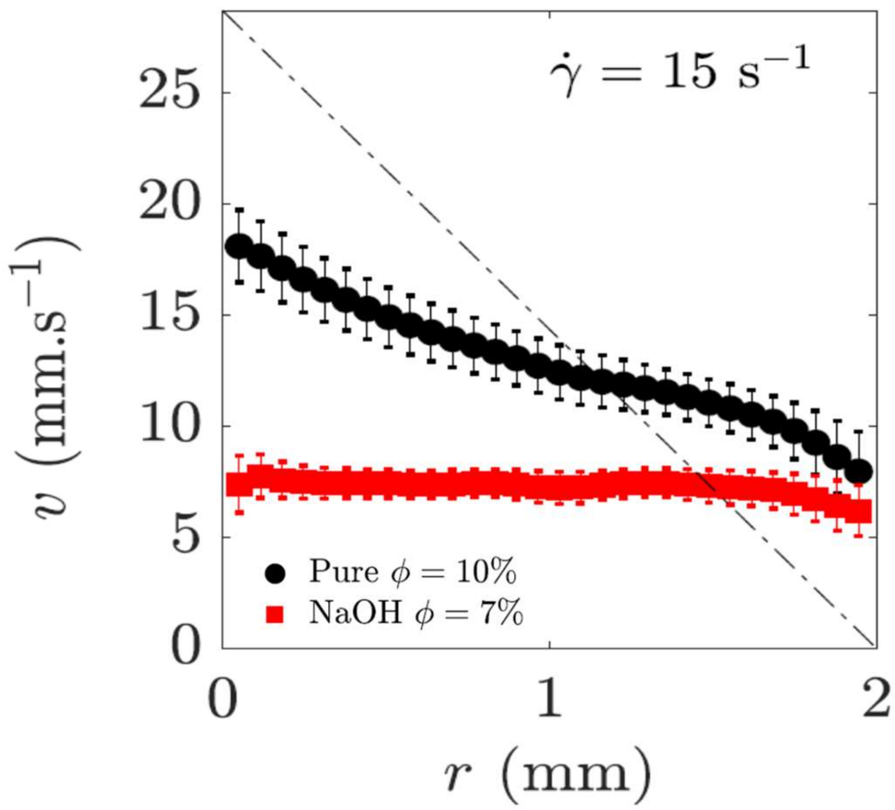




- Wall slip for both samples
- NaOH: shear banding (starting from 50 s^{-1})

Velocity profiles comparison





Second signature : Pure calcite paste never shows shear-bands

Attractive suspension exhibits shear-bands

Literature comparison

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

Yielding and Flow in Adhesive and Nonadhesive Concentrated Emulsions

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(Received 9 December 2005; published 3 April 2006)

attractive glass with shear banding

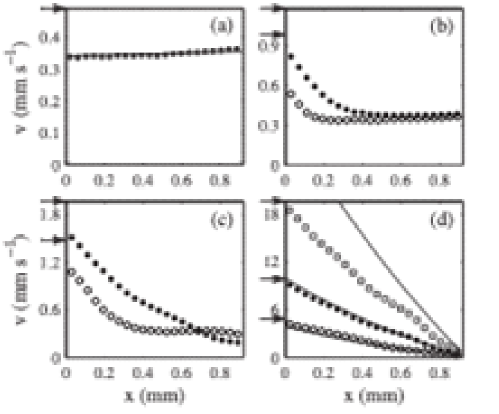


FIG. 4. Velocity profiles in the adhesive emulsion for (a) $v_0 = 0.49$, (b) $v_0 = 0.98$ (○), 1.17 (●), (c) $v_0 = 1.47$ (○), 1.96 (●), and (d) $v_0 = 4.78$ (○), 9.78 (●), and 19.5 mm s^{-1} (□). Arrows indicate the wall velocity v_0. The solid lines correspond to solid body rotation in (a) and to the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

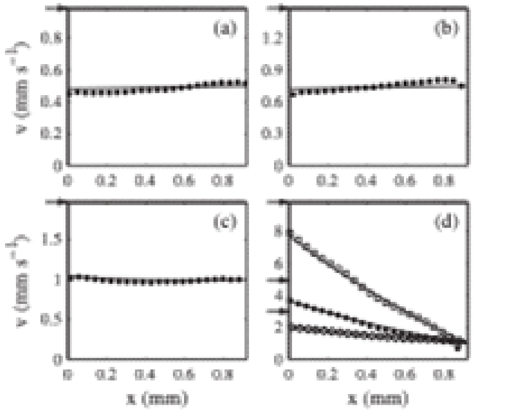
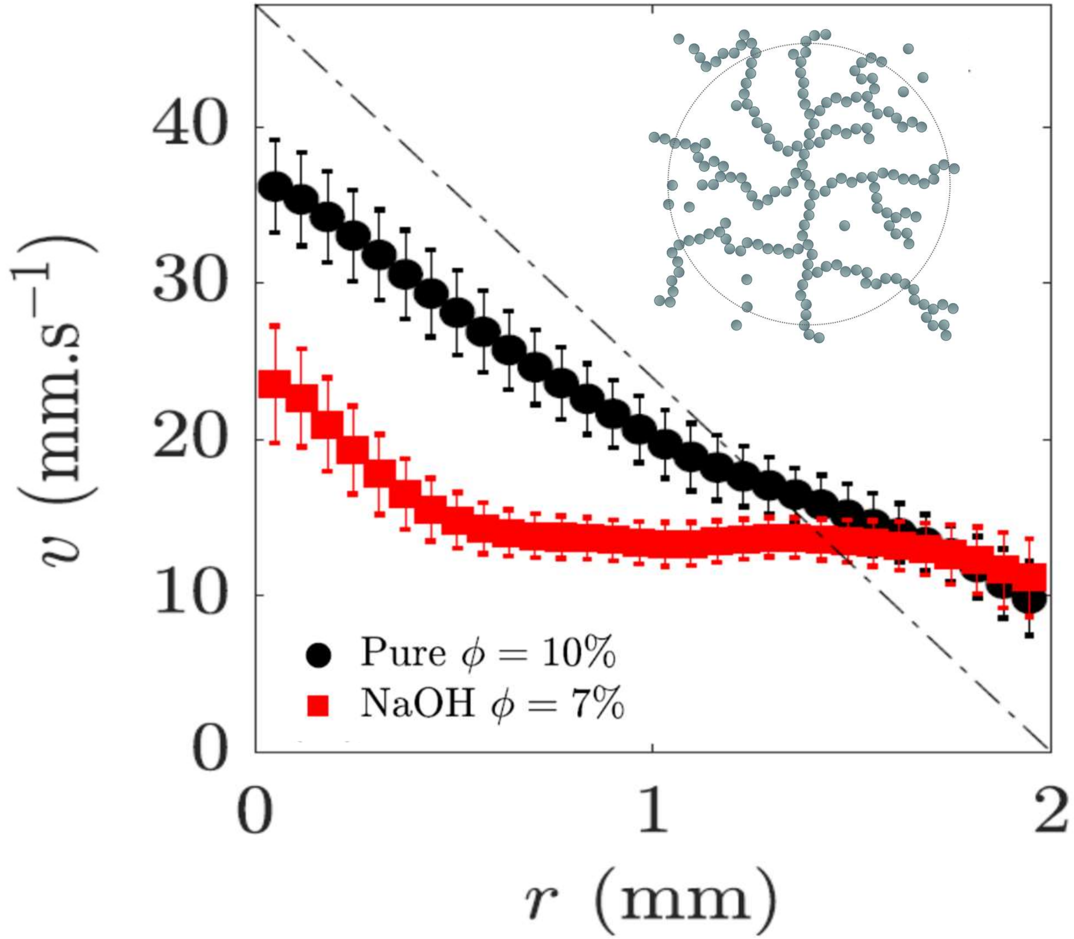


FIG. 3. Velocity profiles in the nonadhesive emulsion for (a) $v_0 = 0.98$, (b) $v_0 = 1.47$, (c) $v_0 = 1.96$, and (d) $v_0 = 2.94$ (○), 4.90 (●), and 9.79 mm s^{-1} (□). Arrows indicate the wall velocity v_0. The solid lines correspond to solid body rotation in (a) and (b) and to the Herschel-Bulkley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

glassy emulsion homogeneous throughout the yielding transition

- 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



- Colloidal fractal gel
- Simple ions tuning interactions

- Signature of interactions:
  - Homogeneous flow for low attractive system
  - Shear-bands for strong attractive

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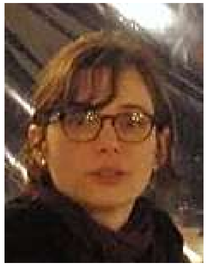
Questions?

Suggestions?

Comments?

LE-MERRER Marie



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