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Investigation of capillary (nano)suspensions

IFPRI Annual Meeting 2023

Jens Allard, Lingyue Liu, and Erin Koos

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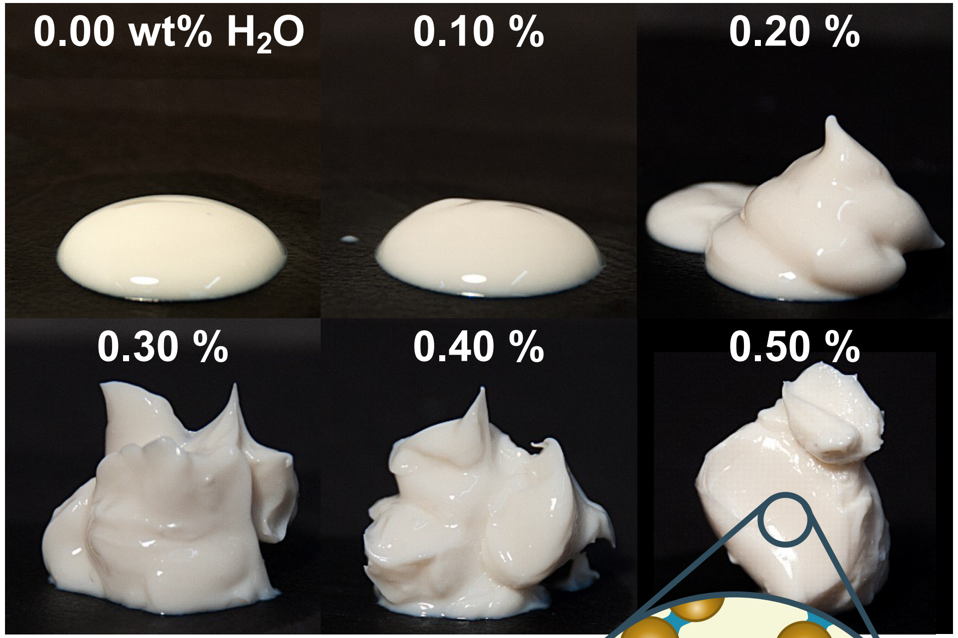
Department of Chemical Engineering
Section Soft Matter, Rheology and Technology

The capillary suspension phenomenon

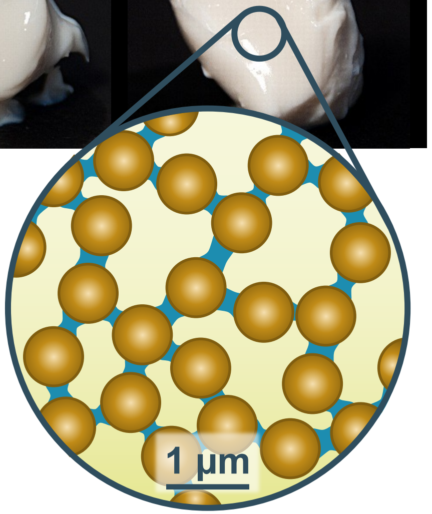
Micro- or nanoparticles

+

Two immiscible liquids



Capillary suspension



E. Koos and N. Willenbacher, *Science* **331(6019)**, 897 (2011)

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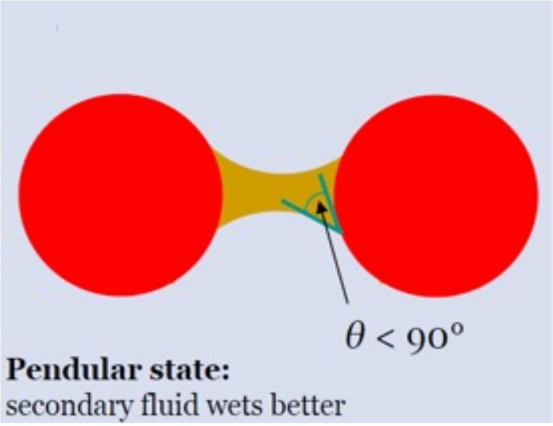
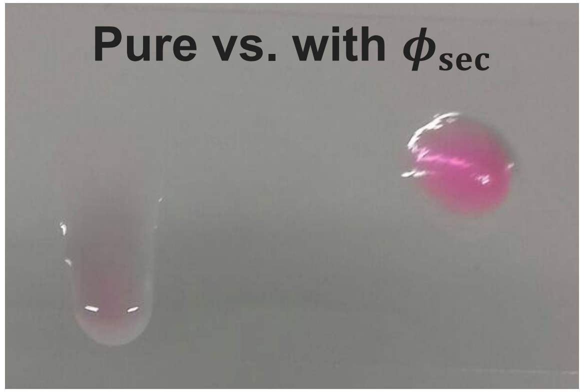
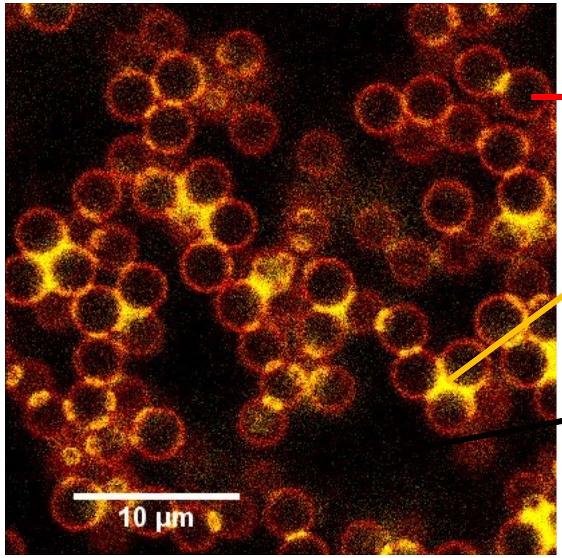
Confocal model system



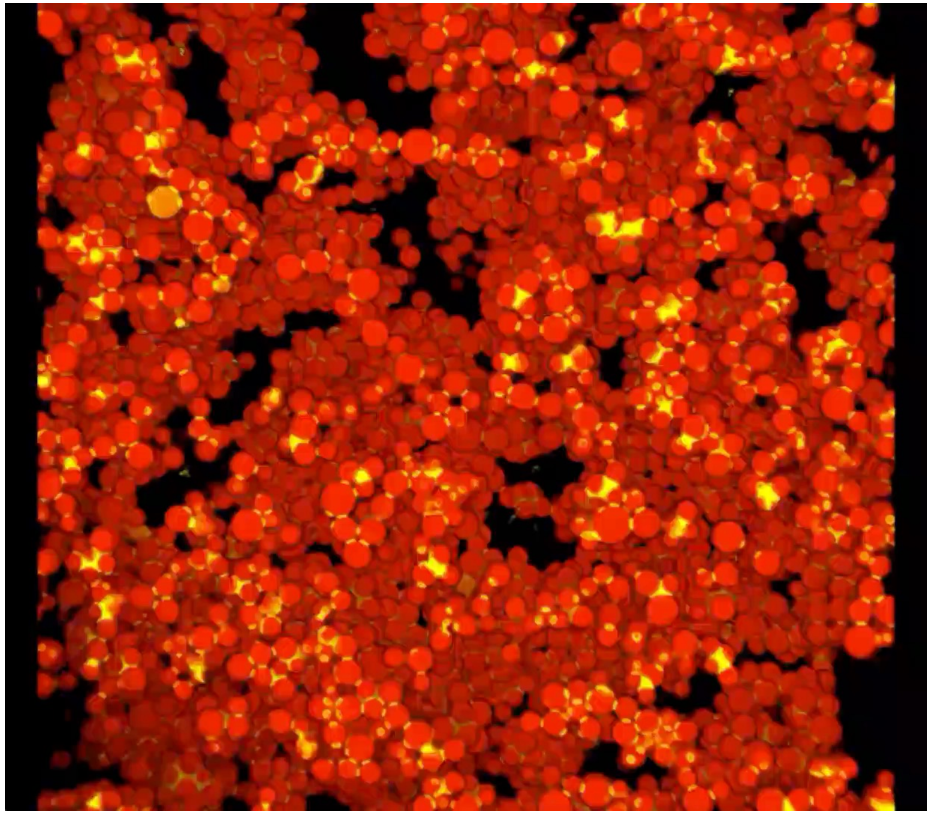




Silica dyed with rhodamine B

Aqueous glycerol dyed with promofluor 488

Oil phase (hexamoll dinch/dodecane)



$\theta = 61°$, $\phi_{solid} = 0.33$, $\phi_{sec} = 0.04$

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Dynamic and structural investigation of capillary suspensions

Jens Allard[1], Pavlik Lettinga[2] and Erin Koos[1]

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KU Leuven, Department of Physics and Astronomy Section Soft Matter and Biophysics [2]

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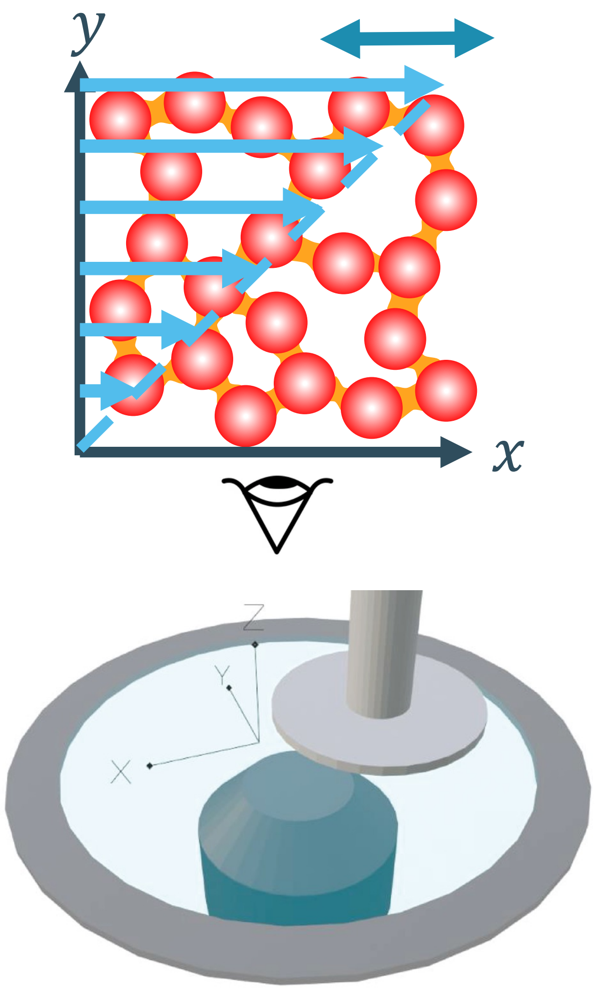
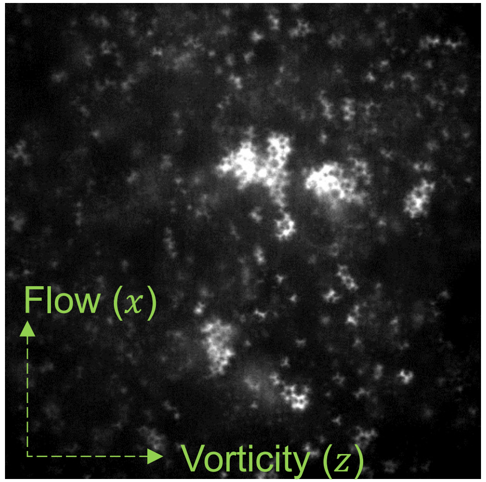
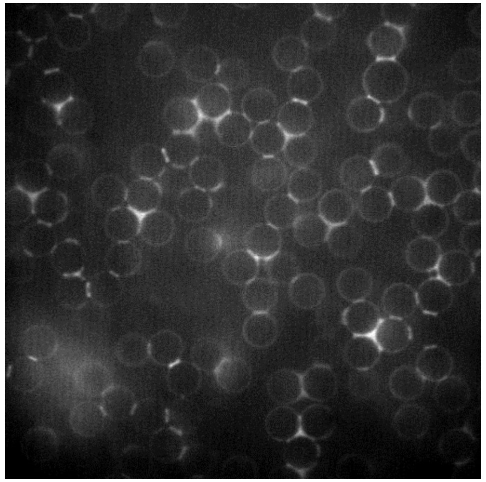
Simultaneous confocal imaging and rheology



- Bridge (particle) tracking analysis



- Bridge breaking,
- Sequence of Physical Processes analysis



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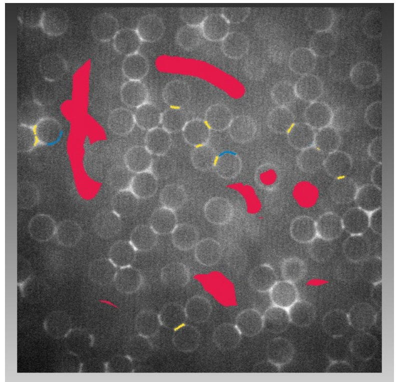
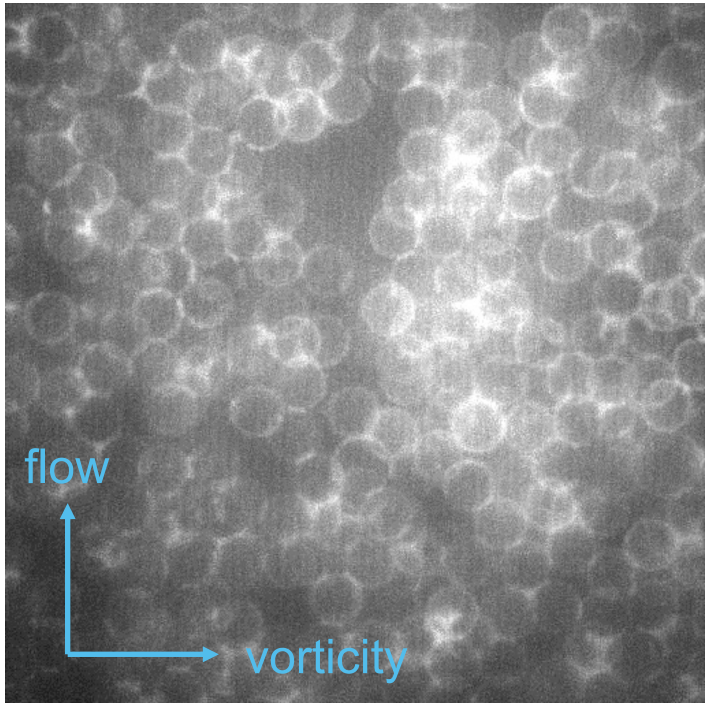
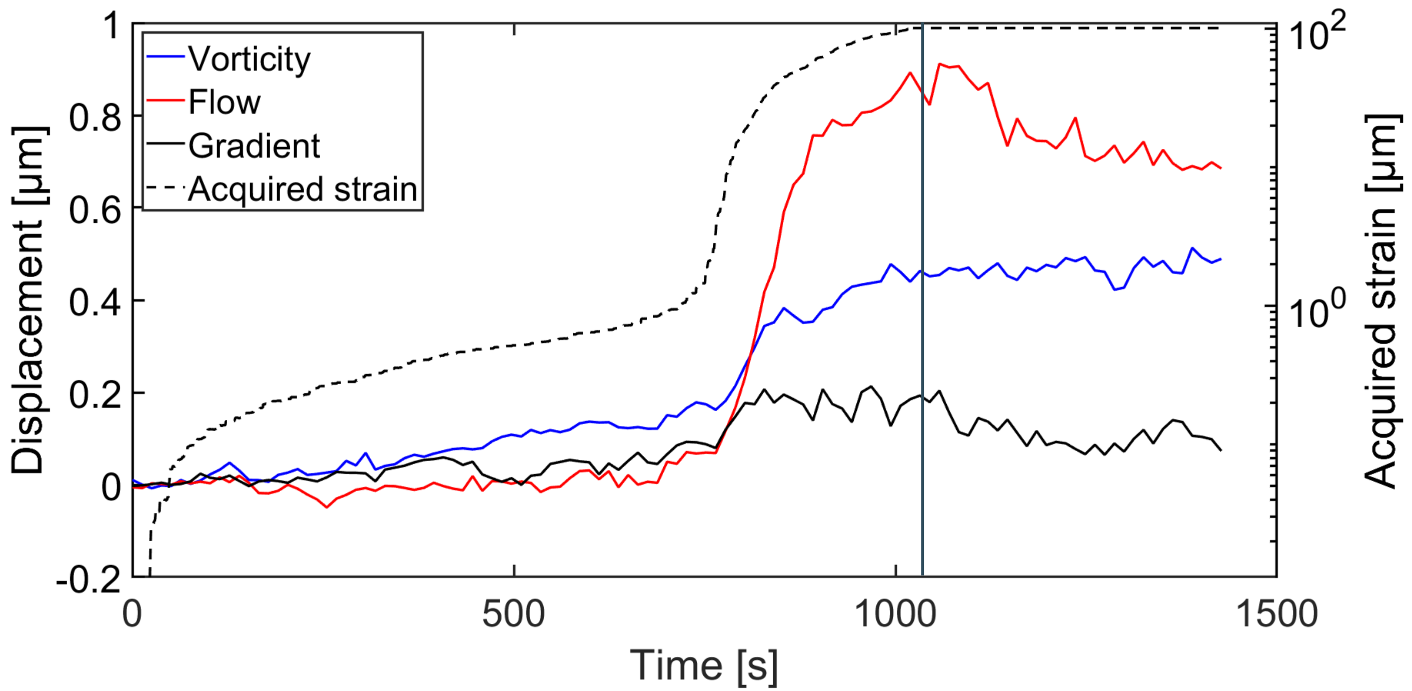
Step stress near yield stress (50 Pa)



- Continuous 3D scaning (every ~13 s for 30 μm depth)
- AI software Ilastik to extract bridges, track bridge centroids





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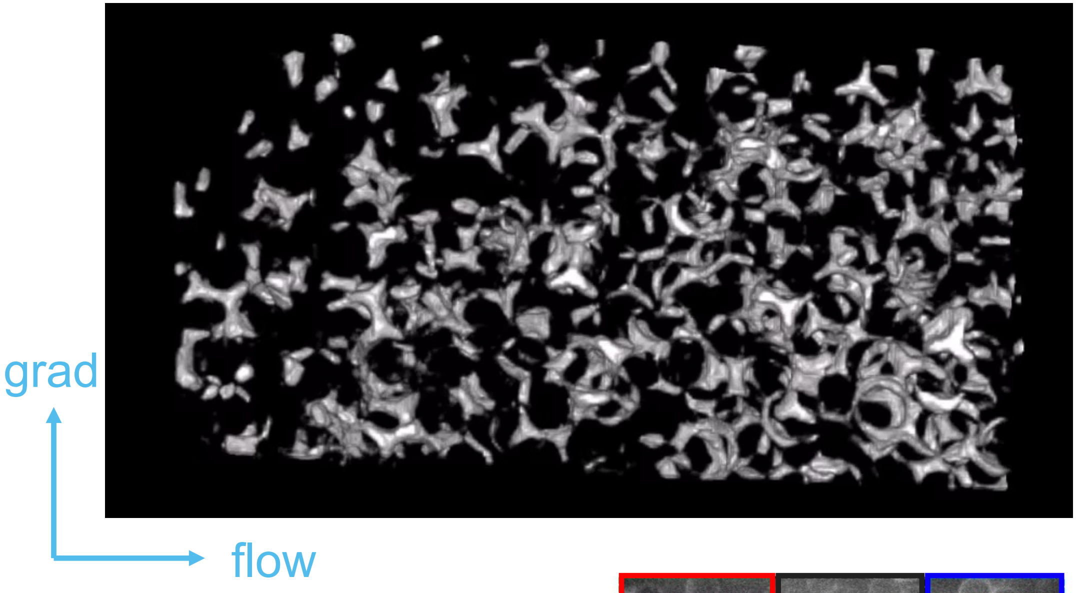

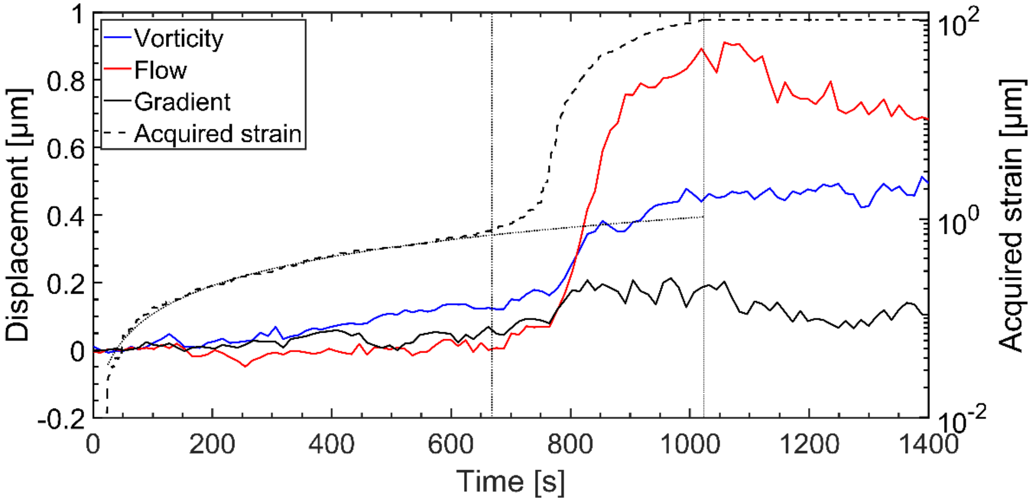

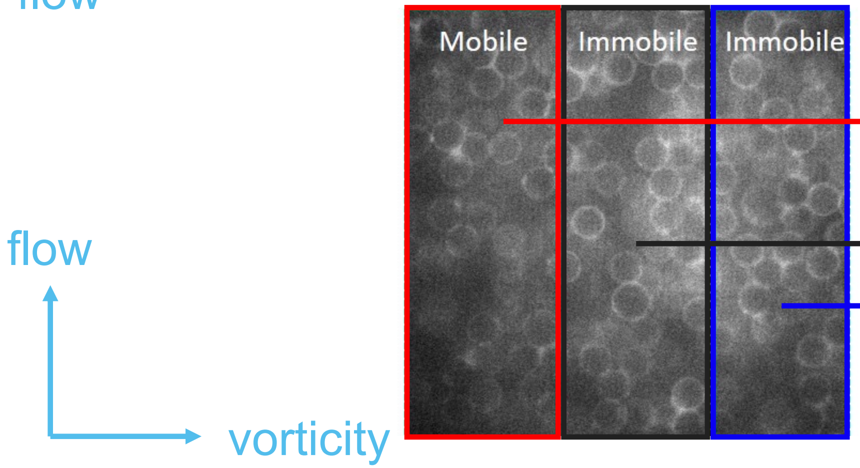

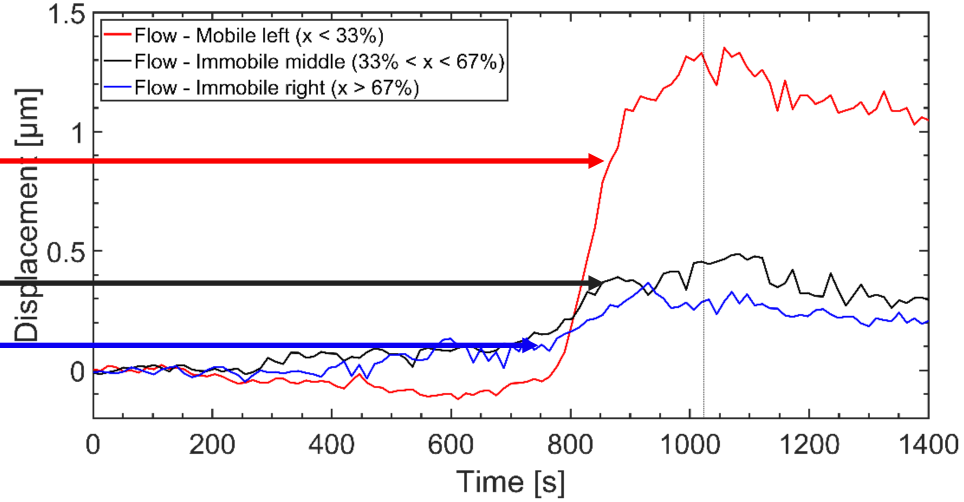

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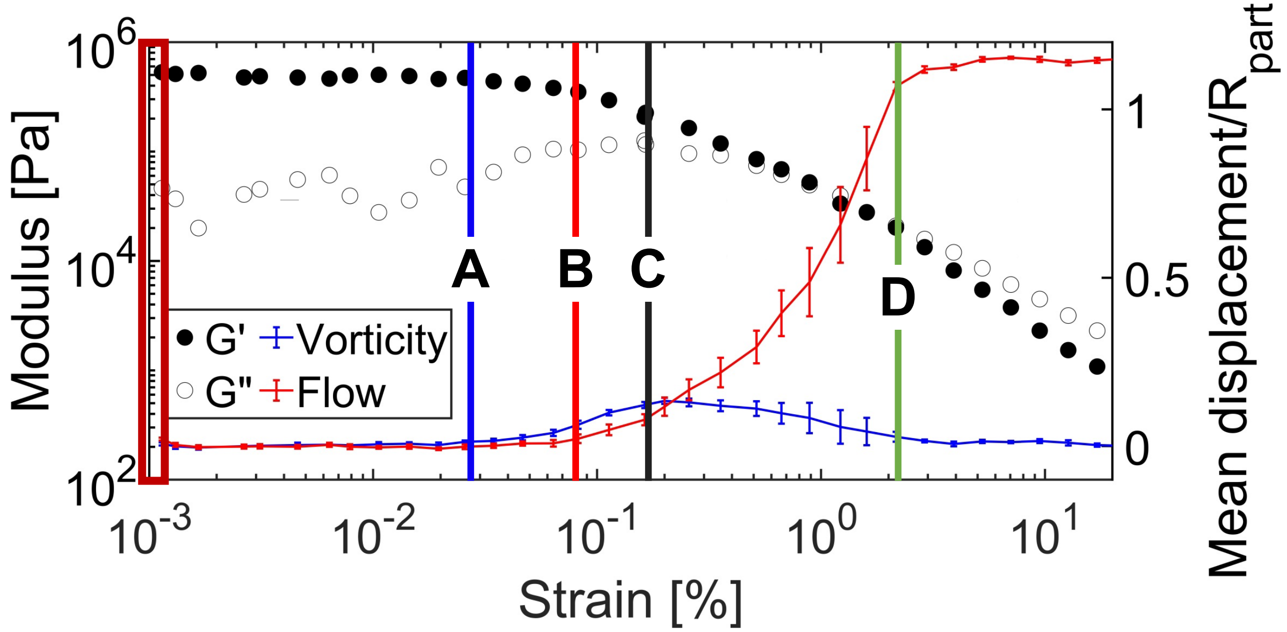
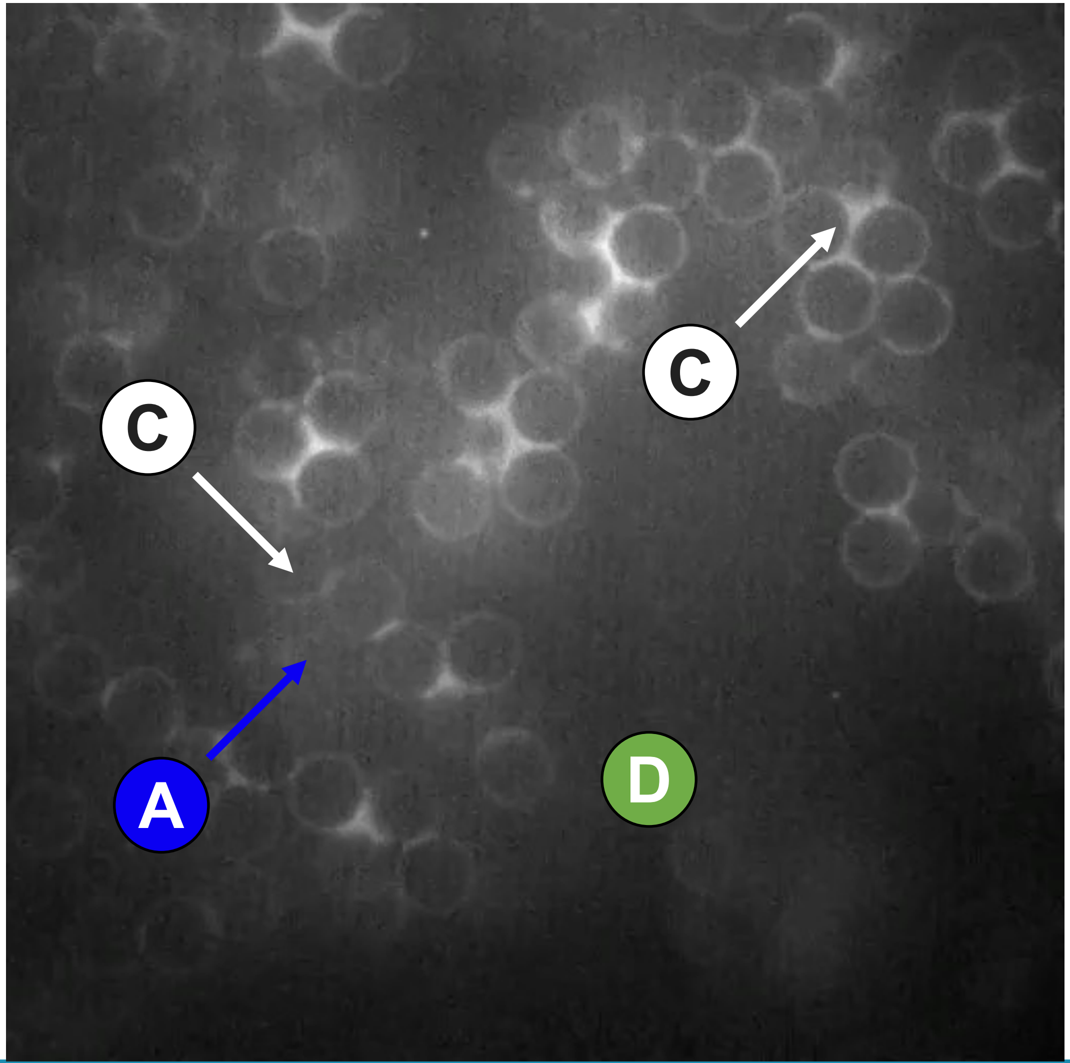
Full amplitude sweep with bridge tracking





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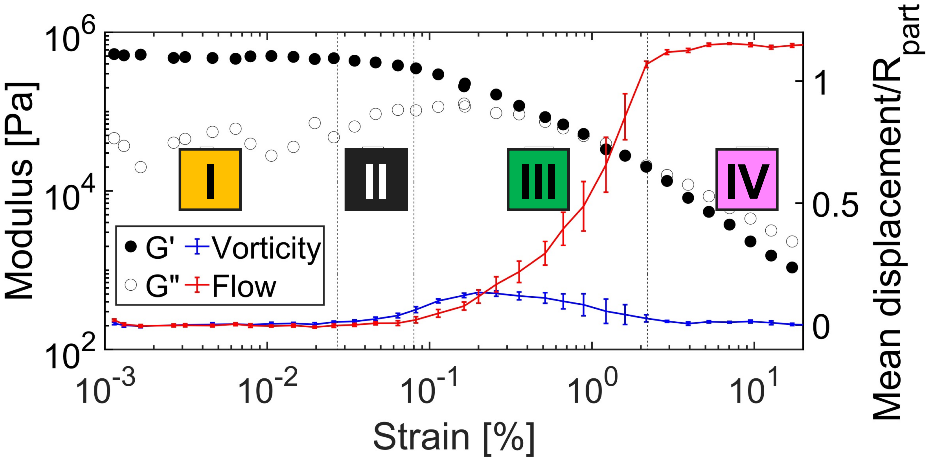
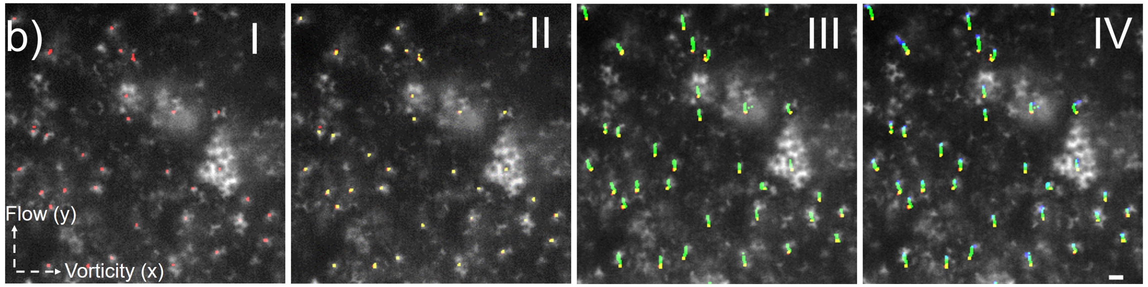
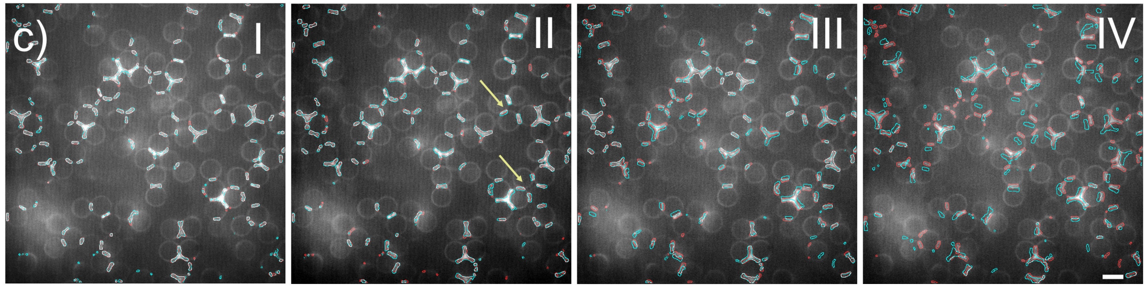






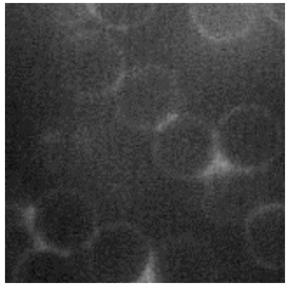
I LVE (constant G' and G''), very little displacement, some bridge merging

II End of LVE but still reversible yielding, movement in vorticity direction, rotation of floppy connections

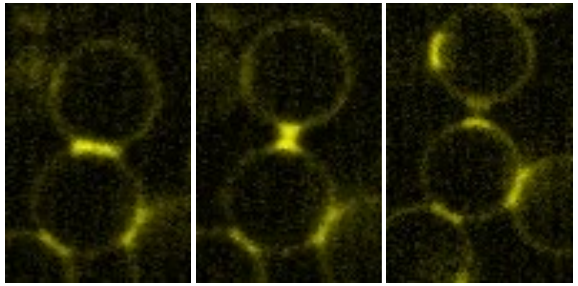
III Large movement in flow direction starts, bridge stretching

IV Clusters become disconnected, decrease in z, c and shear band

II



IV



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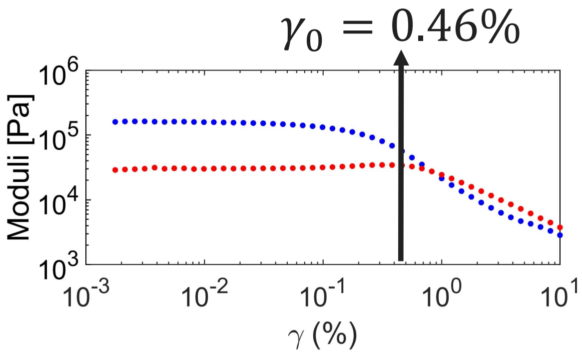
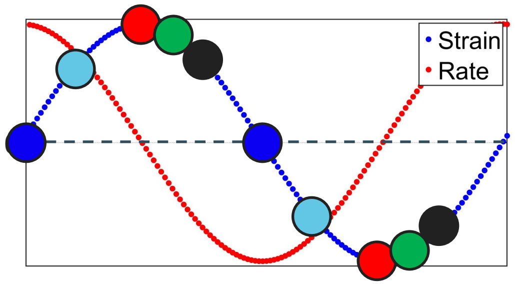
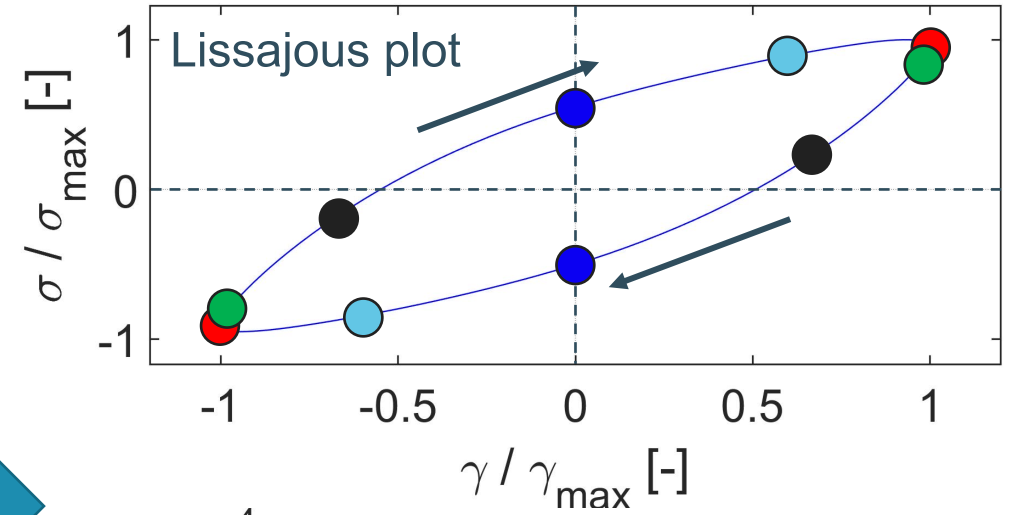
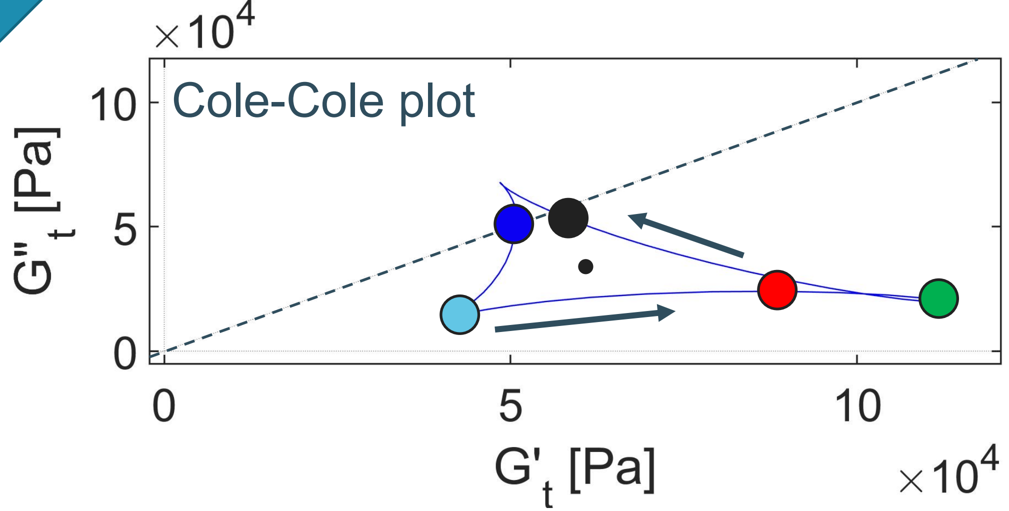
A single oscillation: Lissajous diagrams and the **Sequence of Physical Processes** (SPP) [1,2]









A $\gamma = 0$

B Minimum G_t'

C Maximum γ

D Maximum G_t'

E Maximum $\dot{\delta}_t = \frac{\partial}{\partial t}\tan^{-1}\left(\frac{G_t''}{G_t'}\right)$ (Yield point)

[1] S. Rogers et al., Journal of Rheology 55, 435 (2011)
[2] G.J. Donley et al., Journal of Non-Newtonian Fluid Mechanics 264 (2019)

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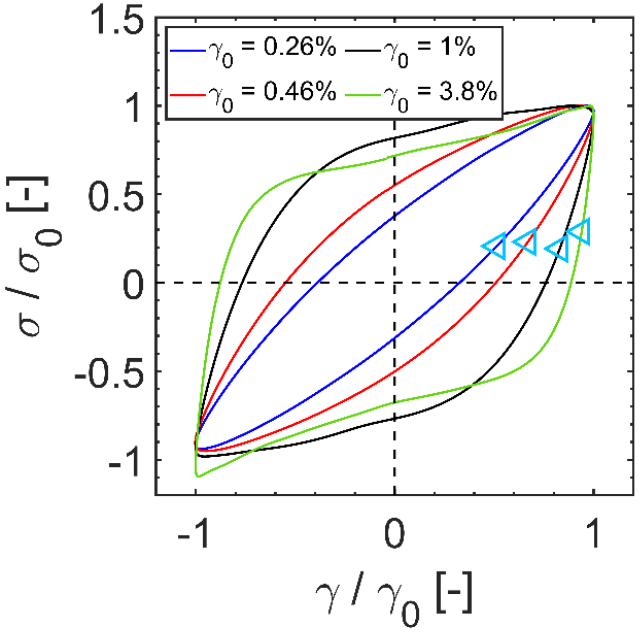
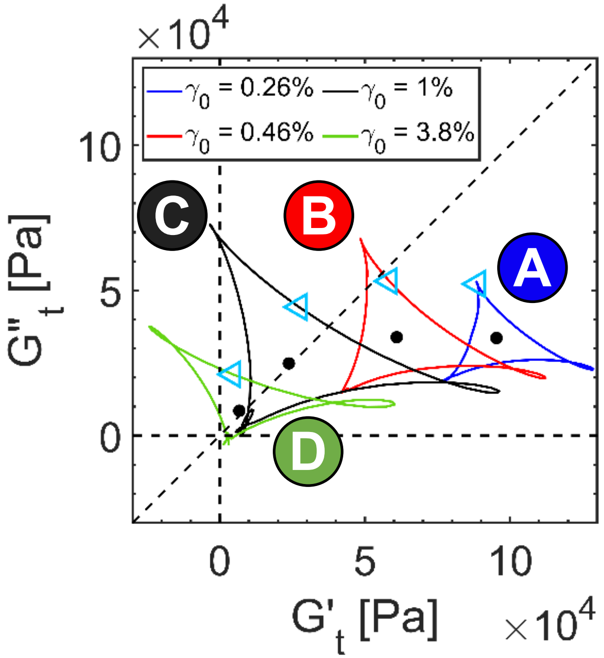
A single oscillation at different strains



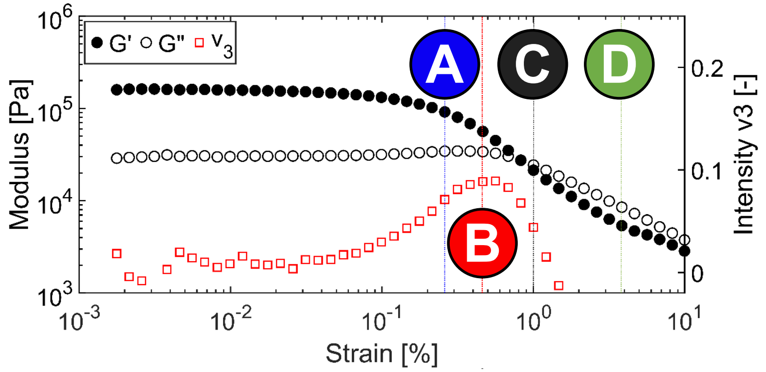


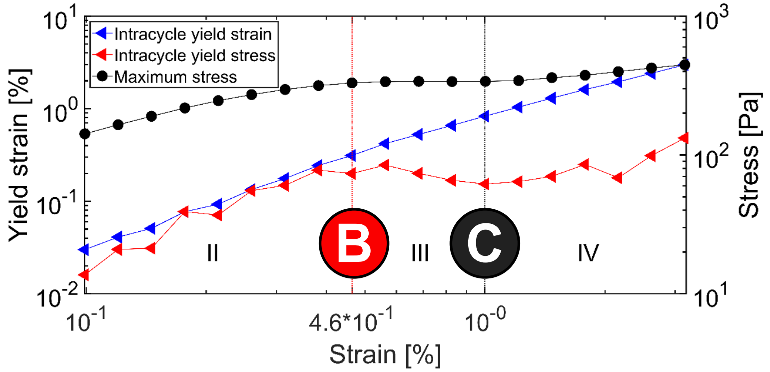
A Fully elastic cycle: removal of Hertzian repulsion, rotation

B First time shortly viscous dominated: flow direction movement starts

C Mostly viscous dominated: first bridge breaks

D G'_t goes negative: more reorganization than energy stored





Intracycle yield stress reaches a plateau at transition from reversible to irreversible yielding

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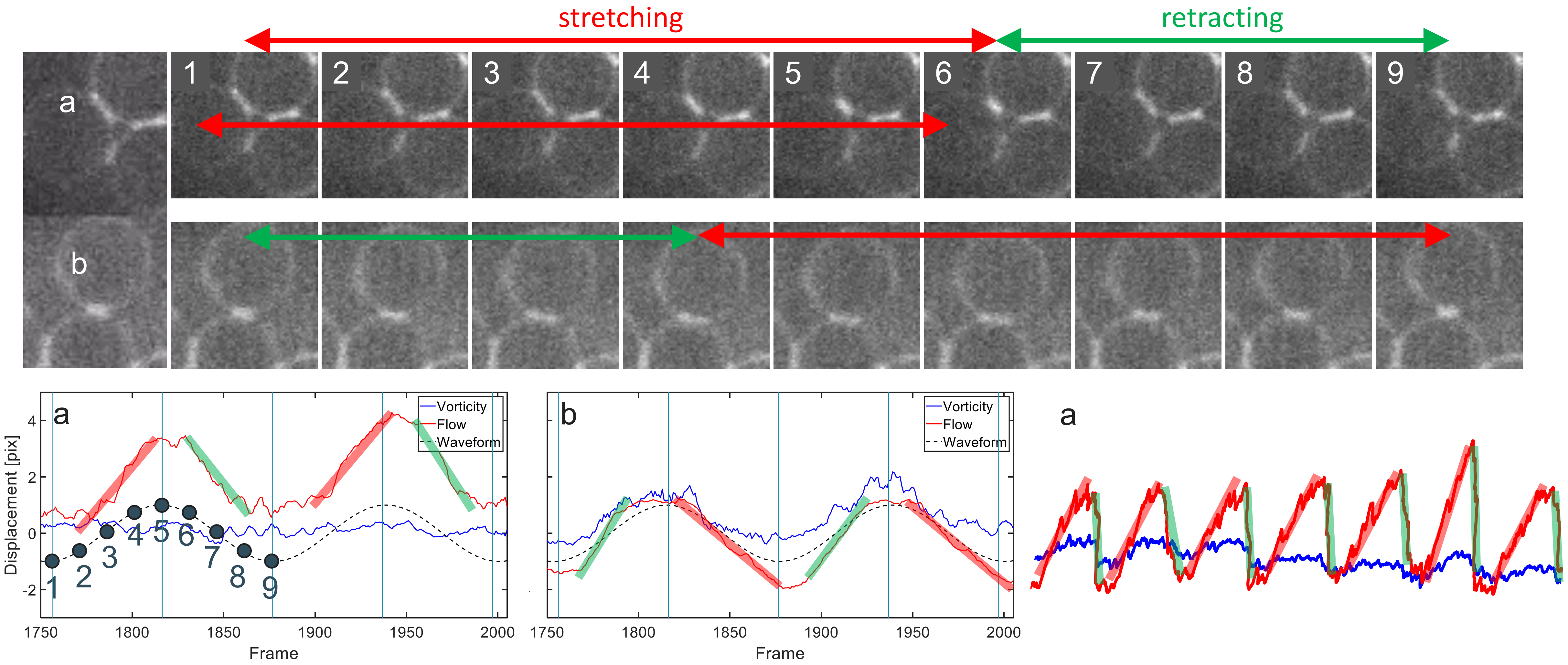
Oscillatory deformation above flow point



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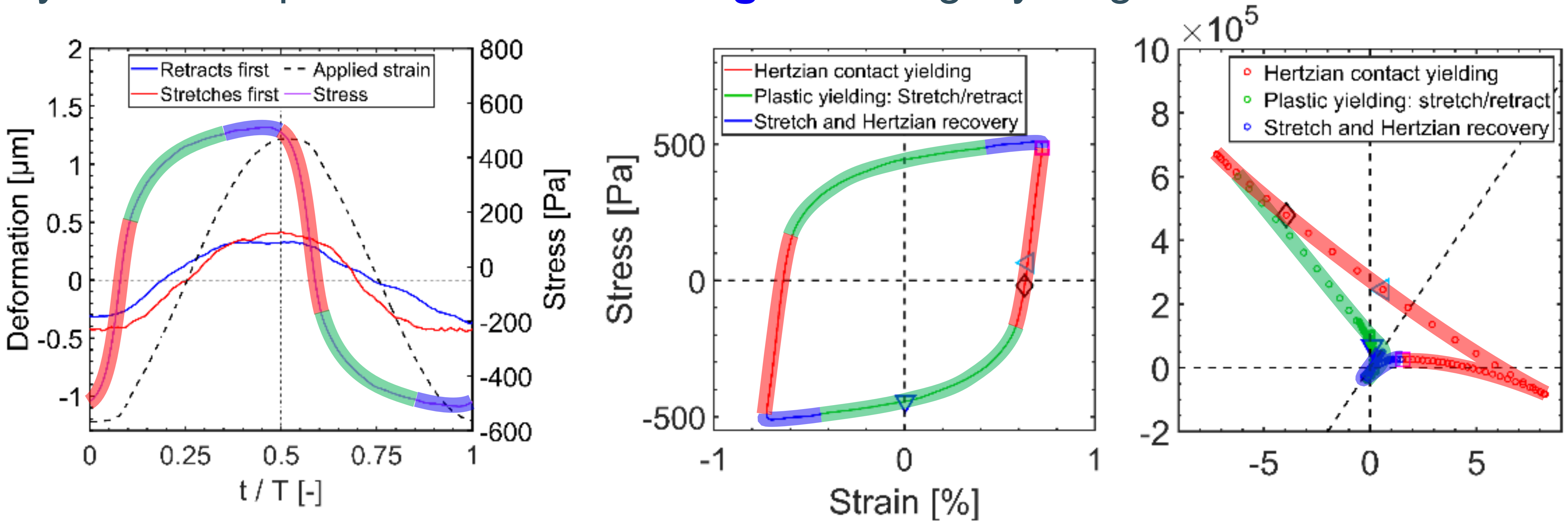
Stretching vs retraction

- Hysteretic displacements: **stretching** takes slightly longer than **retraction**!



1 Removal of **Hertzian** repulsion, no stretching

2 Intracycle yielding, bridges **stretch** and **compress**

3 Restoration of **Hertzian** contact, bridge **stretching**

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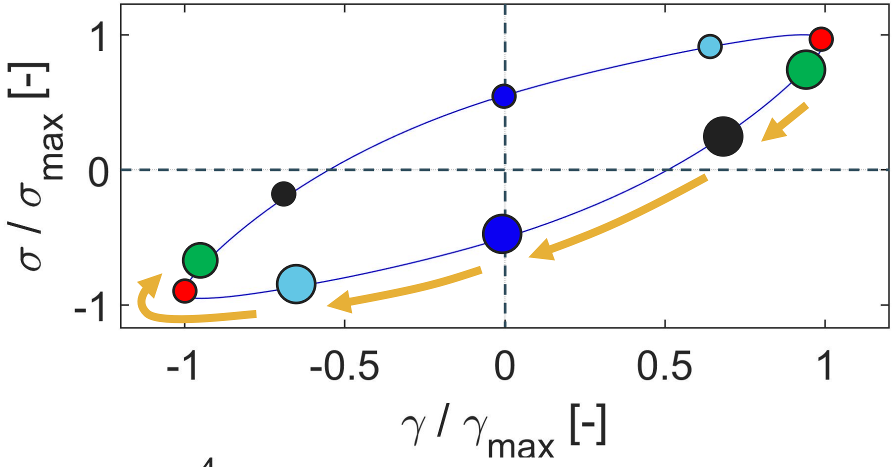
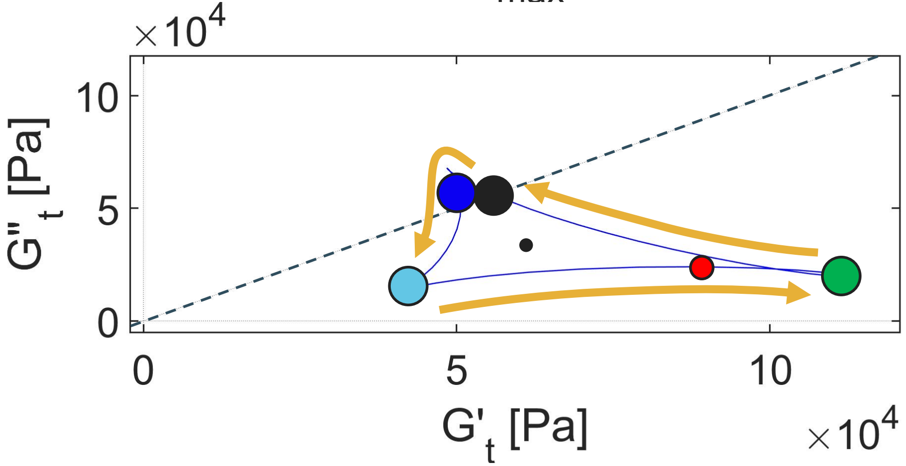
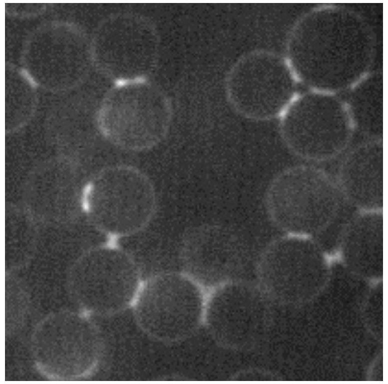
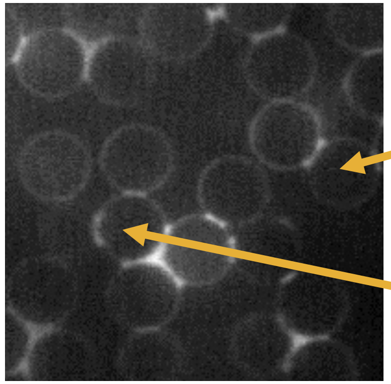
What do we see near yielding?









(videos above flow point for better visibility)

- to : Hertzian contact disappears, rotation without stretching
- to : Weak bridges stretch and break, **particle rearrangements**
- to : New bonds are reinforced
- to : Bridges retract when shear rate decreases

Liquid can move over particle surface (~ low CA, smooth surface)

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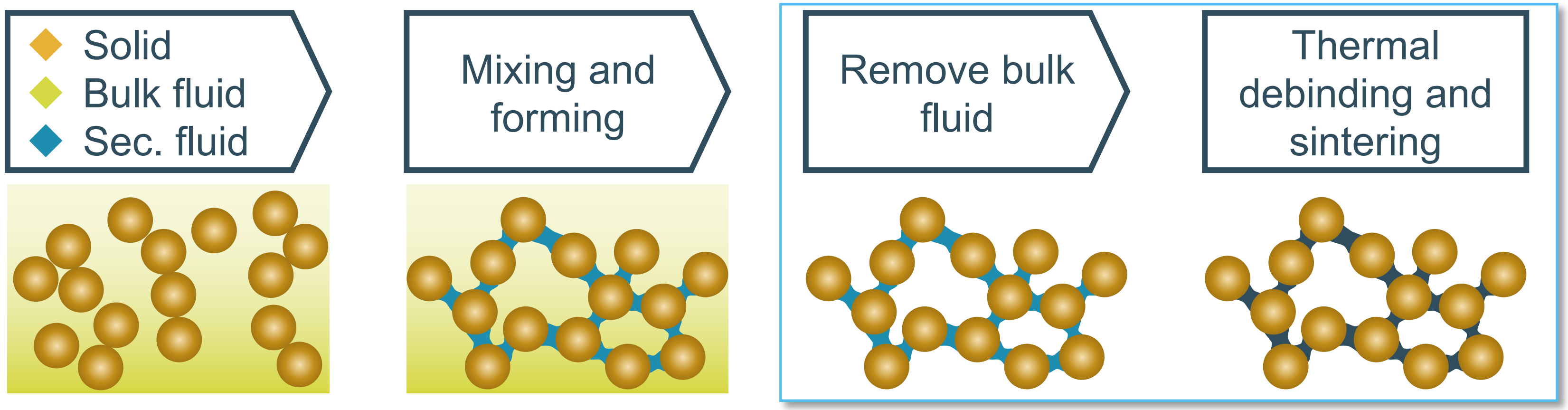
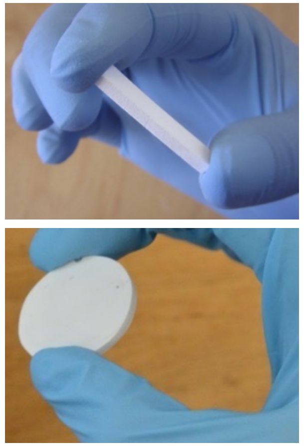
Lubrication effect of nanoparticles in capillary nanosuspensions

Lingyue Liu[1], Jens Allard[1] and Erin Koos[1]

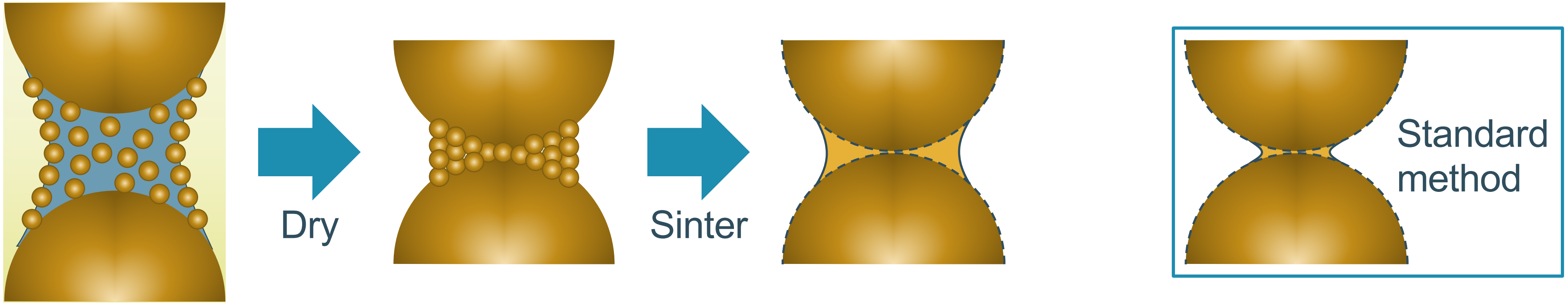
KU Leuven, Department of Chemical Engineering Section Soft Matter, Rheology and Technology[1]

Porous ceramics from capillary suspensions





- Incorporate nanoparticles into bridging fluid



M Weiß et al., *J. Eur. Ceram. Soc.* **40**(8), 3140 (2020)

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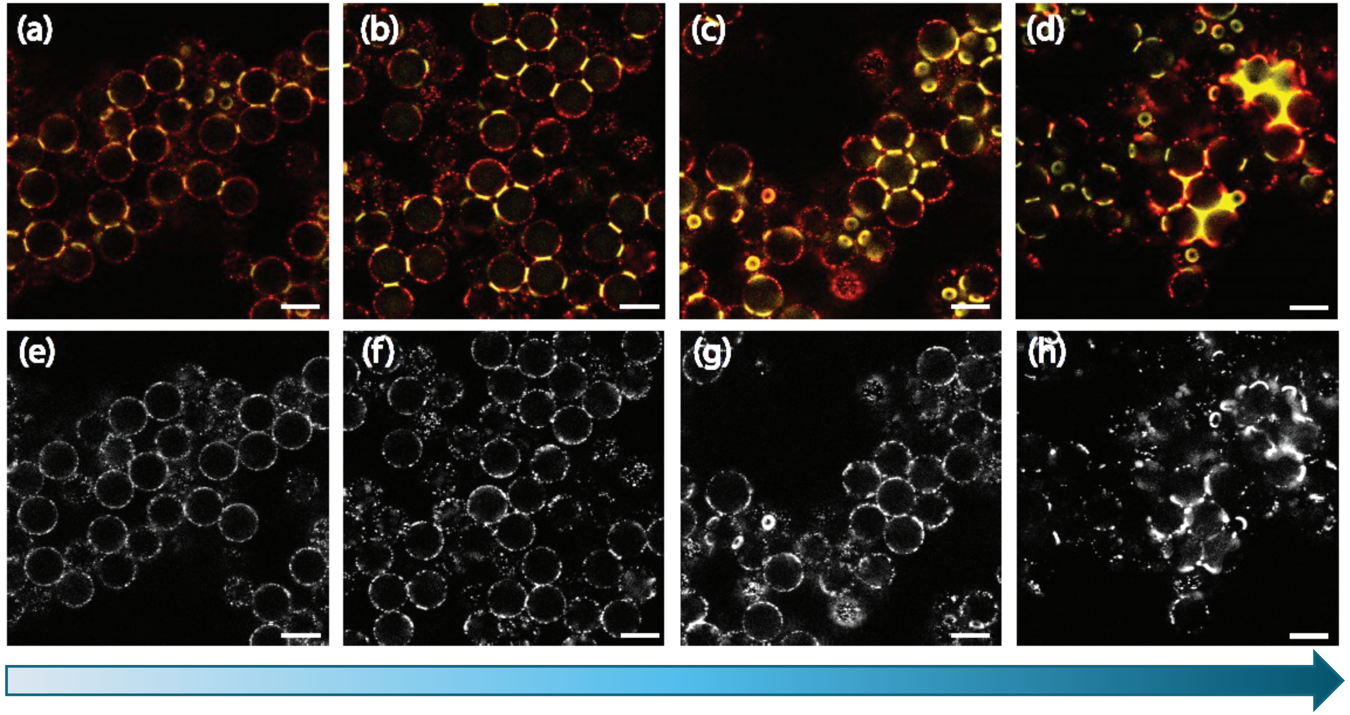
Influence of NP hydrophobicity

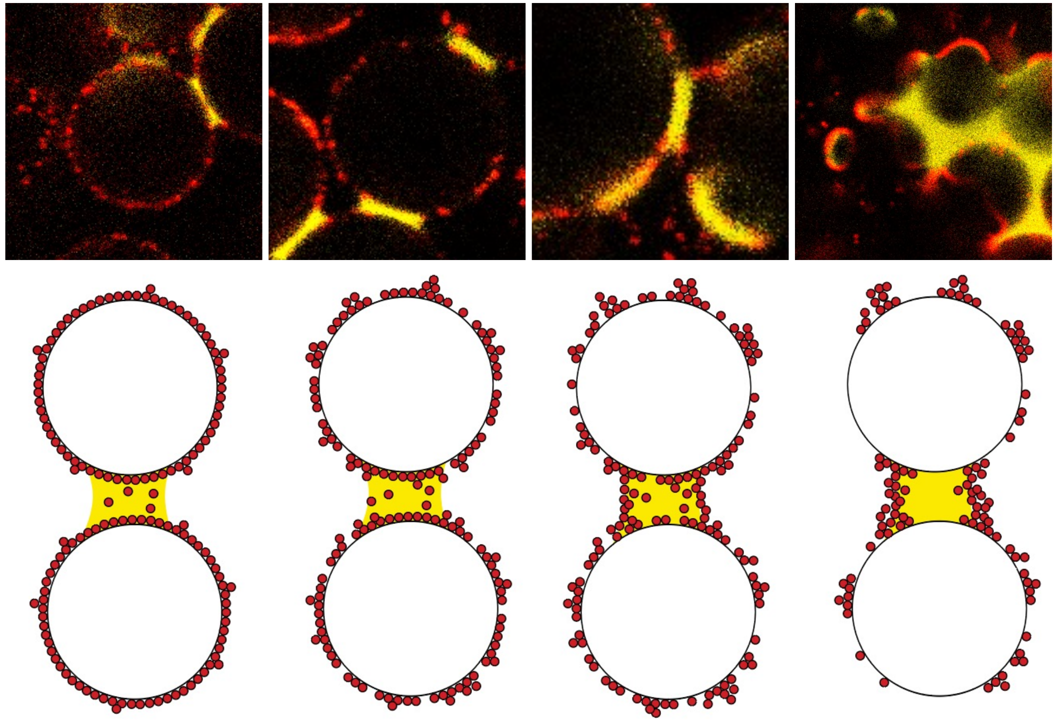


HSR 0
- No location preference
- Well-spaced

HSR 1
- Aggregates
- Slight preference for contact line

HSR 2
- Migrate toward bridges Patchy on MP surface

HSR 4
- Majority at LL interface
- Residual on MP surface



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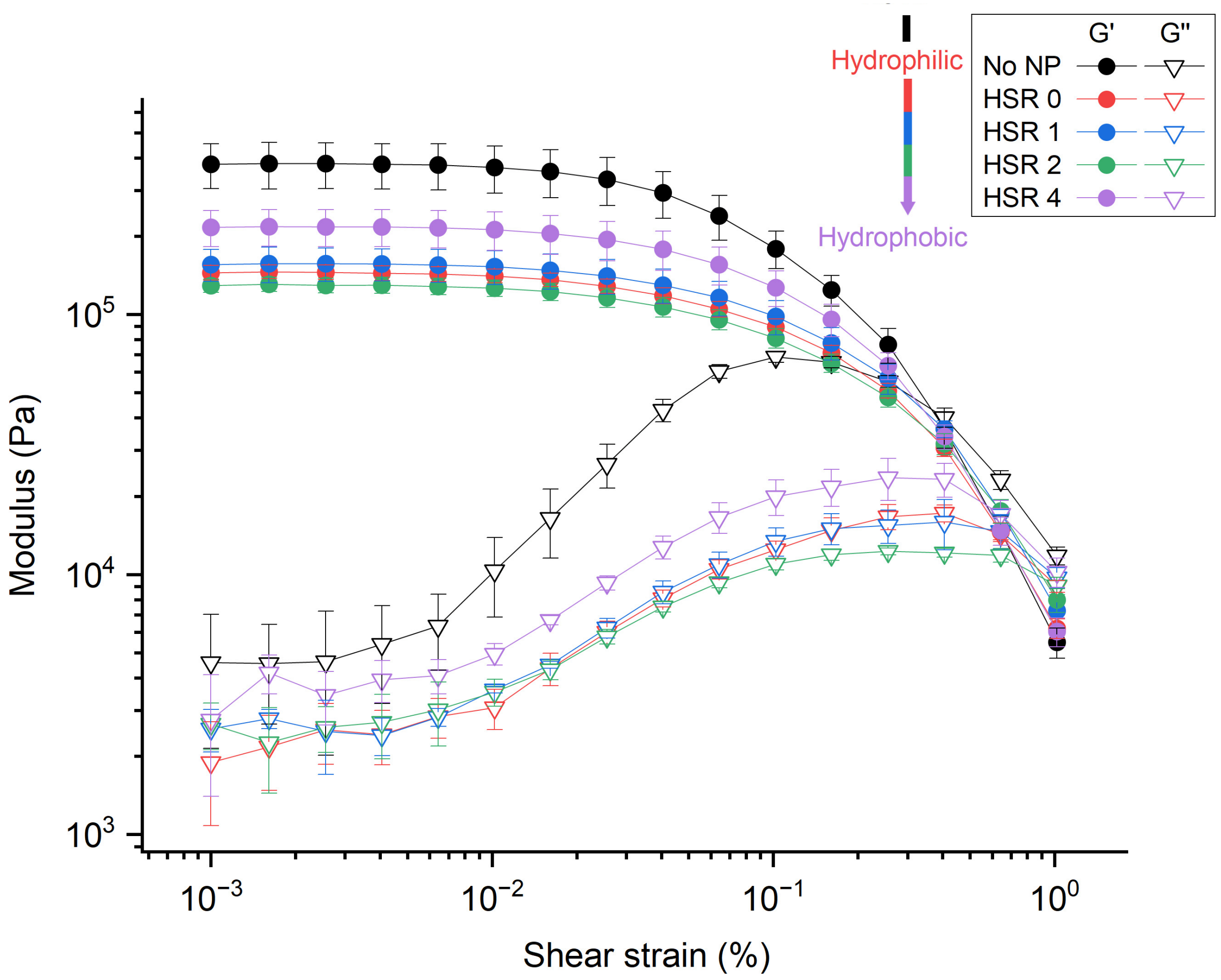
Rheological measurements



- Addition of nanoparticles reduces shear moduli
- HSR 4 has the highest moduli
  - Reinforcement of bridges and extra surface elasticity?
- HSR 2 has the lowest moduli
  - Merged bridges resulting in decreased bridge numbers?

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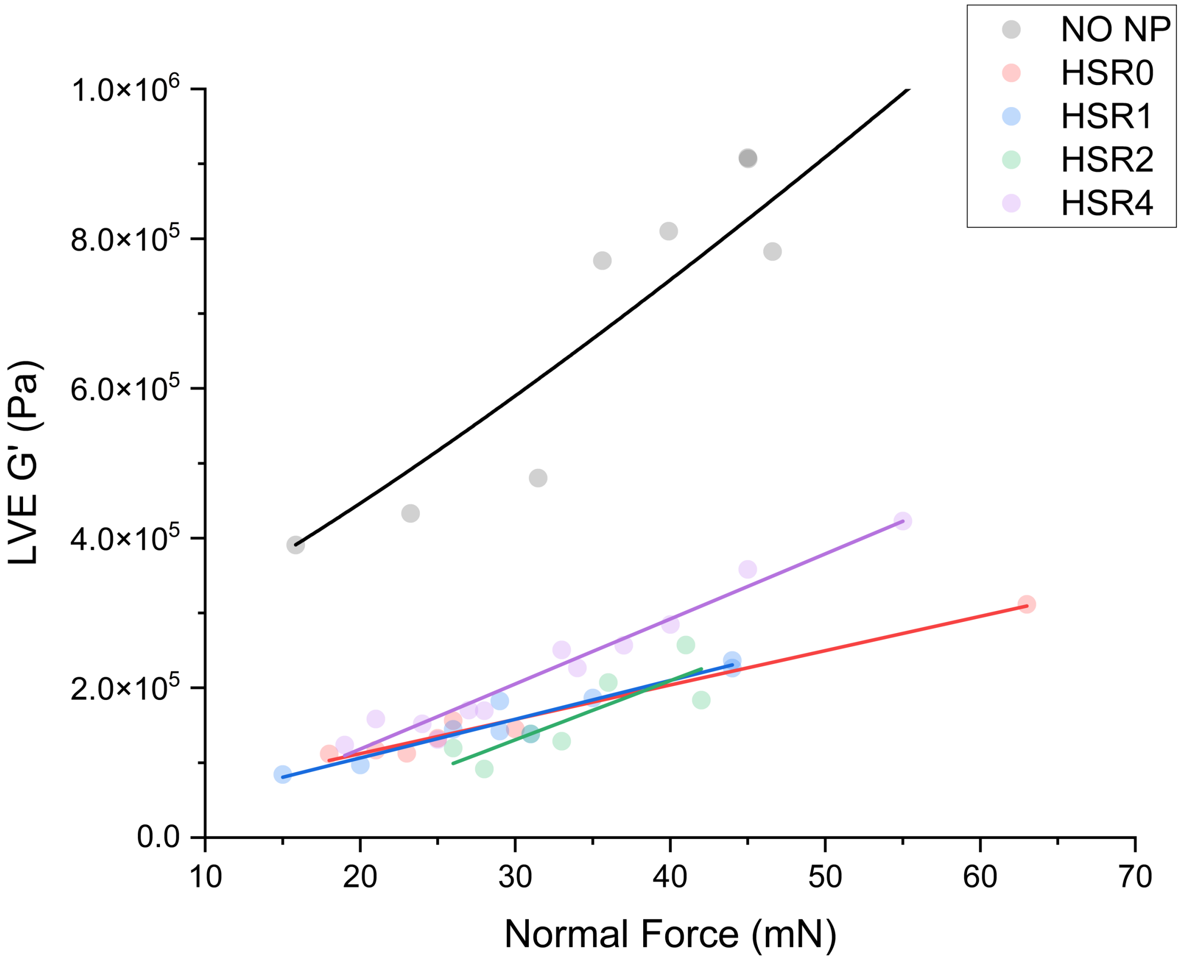
Normal force & G' at LVE



- G' at LVE versus normal force for 1.025 mm gap
- G'/F_N reflects the **rigidity** of network
- Sample without NPs has **highest** slope & G'
- Slope **increases** with **increasing** hydrophobicity
  - HSR0: 4589 ± 315
  - HSR1: 5173 ± 584
  - HSR2: 7906 ± 2254
  - HSR4: 8695 ± 550
- HSR4 distinguishable from the other 3 samples

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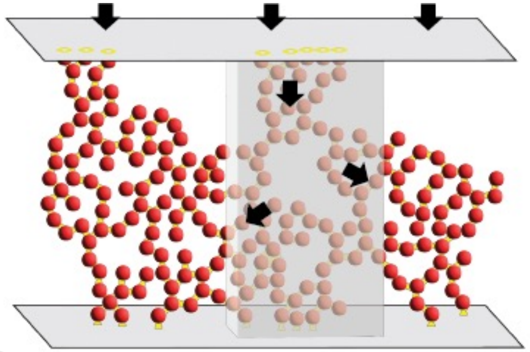
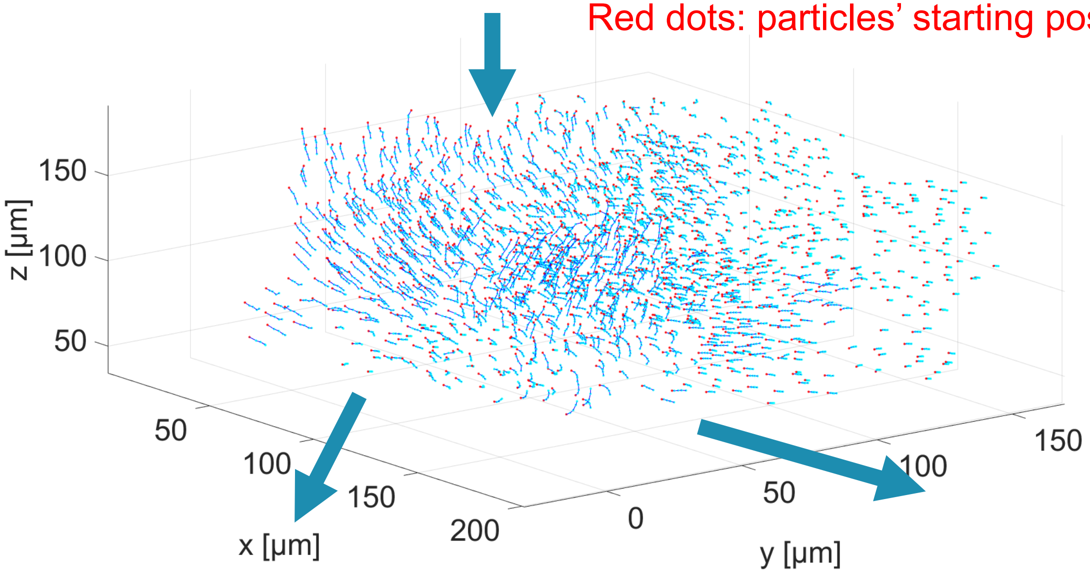
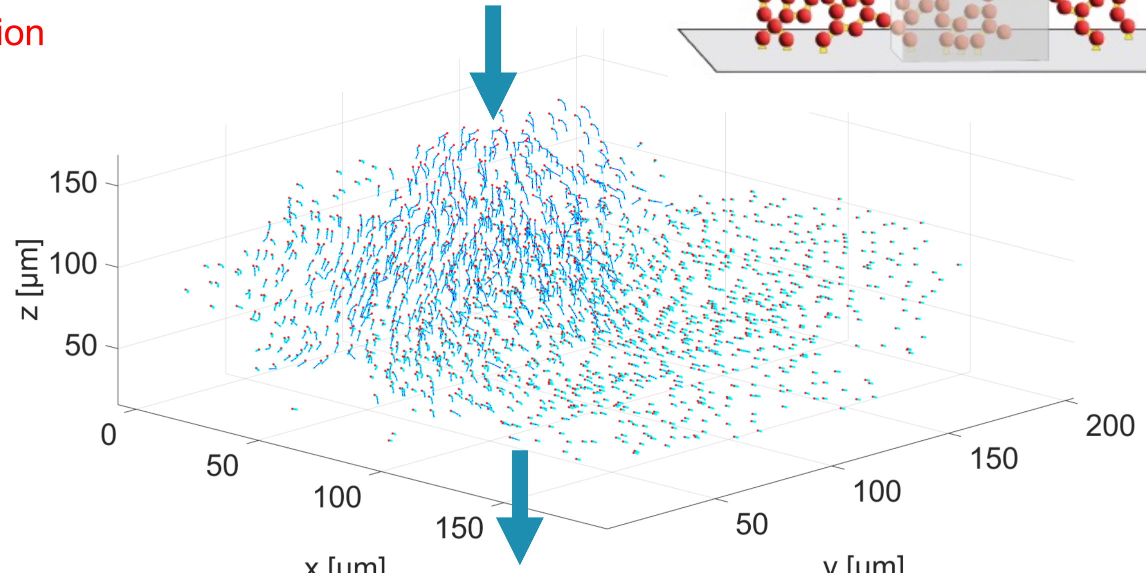
Shell cell compression



- Compression downwards for 20 steps of 3 µm, 3D scan

Red dots: particles' starting position





1. No NP

- **Rigid** network
- Force **propagates** through MP chains
- **X-Y** displacement

2. Hydrophilic NPs

- **Flexible** network, microparticle movements **lubricated**
- Force is **dampened** through the sample, **Z** displacement

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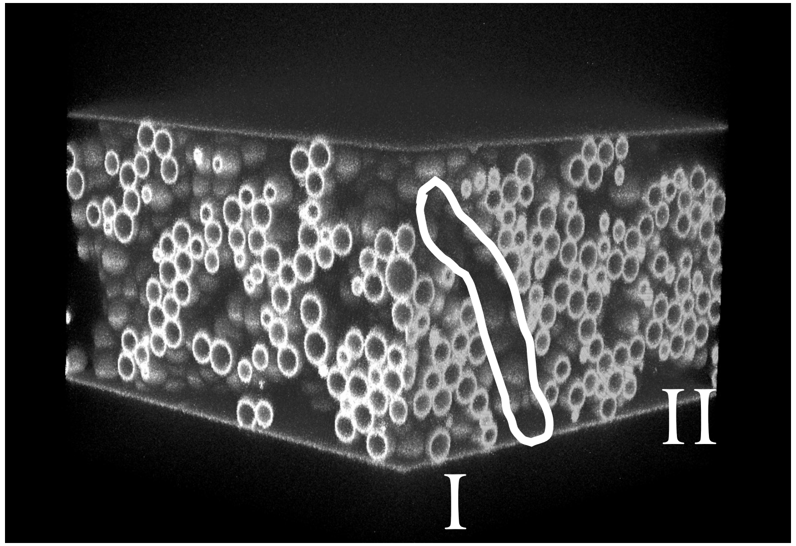
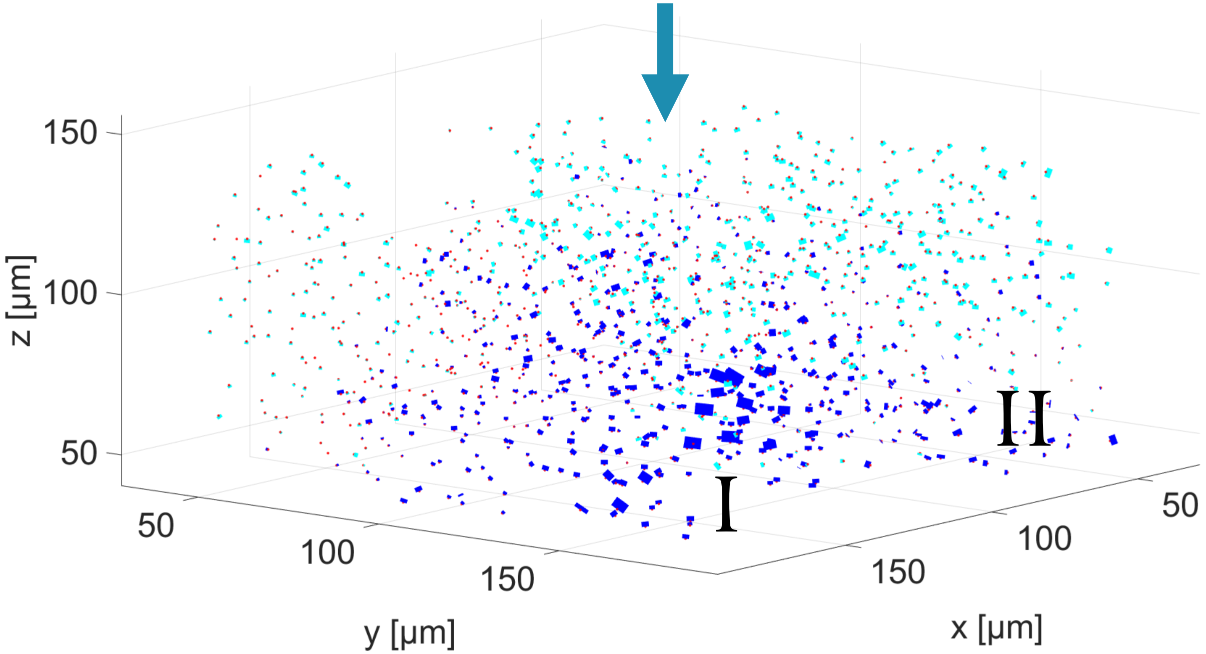
Compression w/o NP – Relative Movement

Cyan = Move downwards, Blue = Resist compression, Degree= Line width





- Network I **resists** compression. Network II remains **rigid without** internal **relative movements**
- In capillary suspensions without nanoparticles, microparticles move in **bulk**

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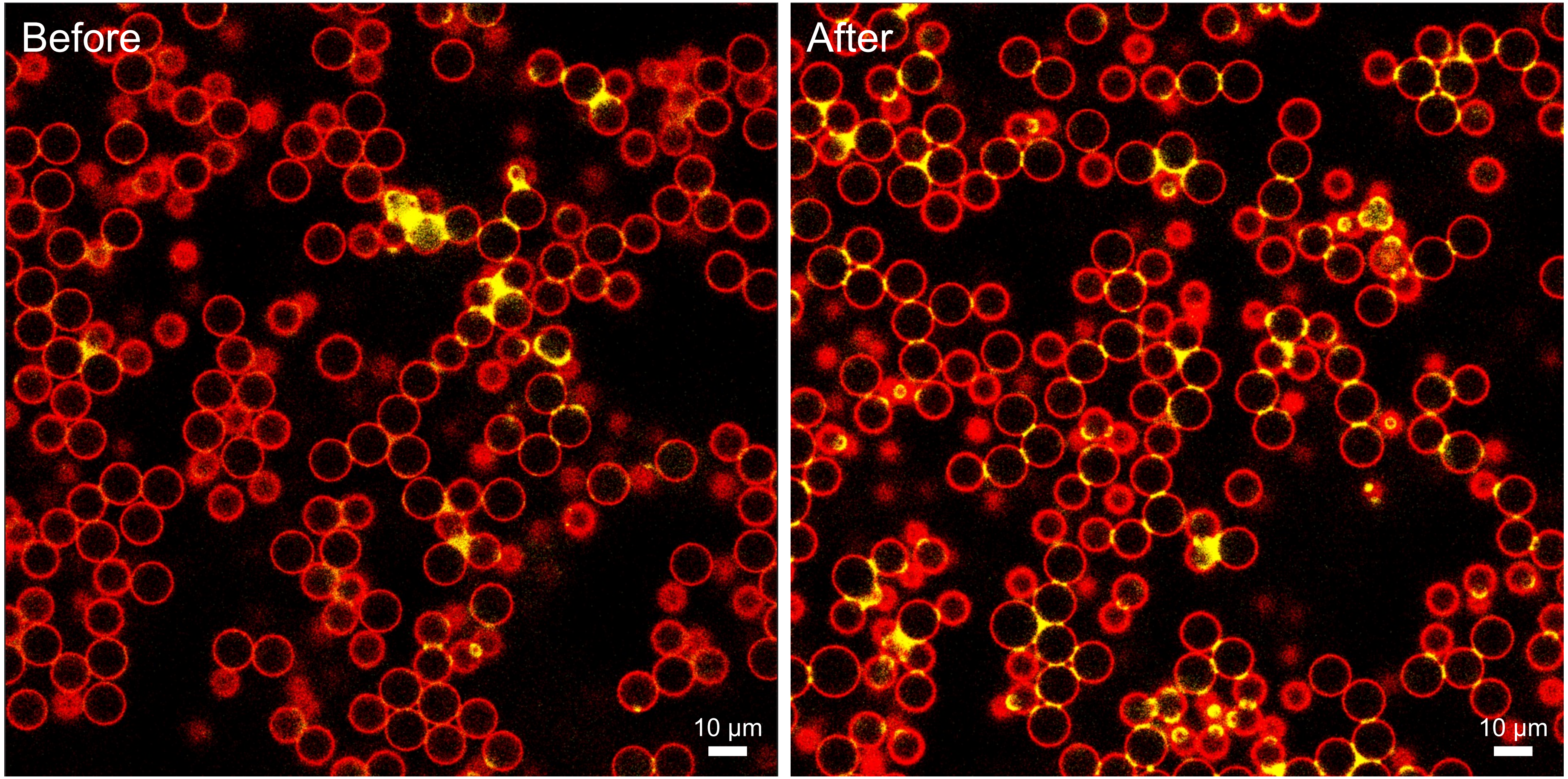
Before & After compression without NP



- 30 µm from bottom
- Sec. liquid redistribution
  - Bridge coalescence
  - Trimer breakage
  - Bulk liquid disappears
- No obvious increase ϕ_{MP}

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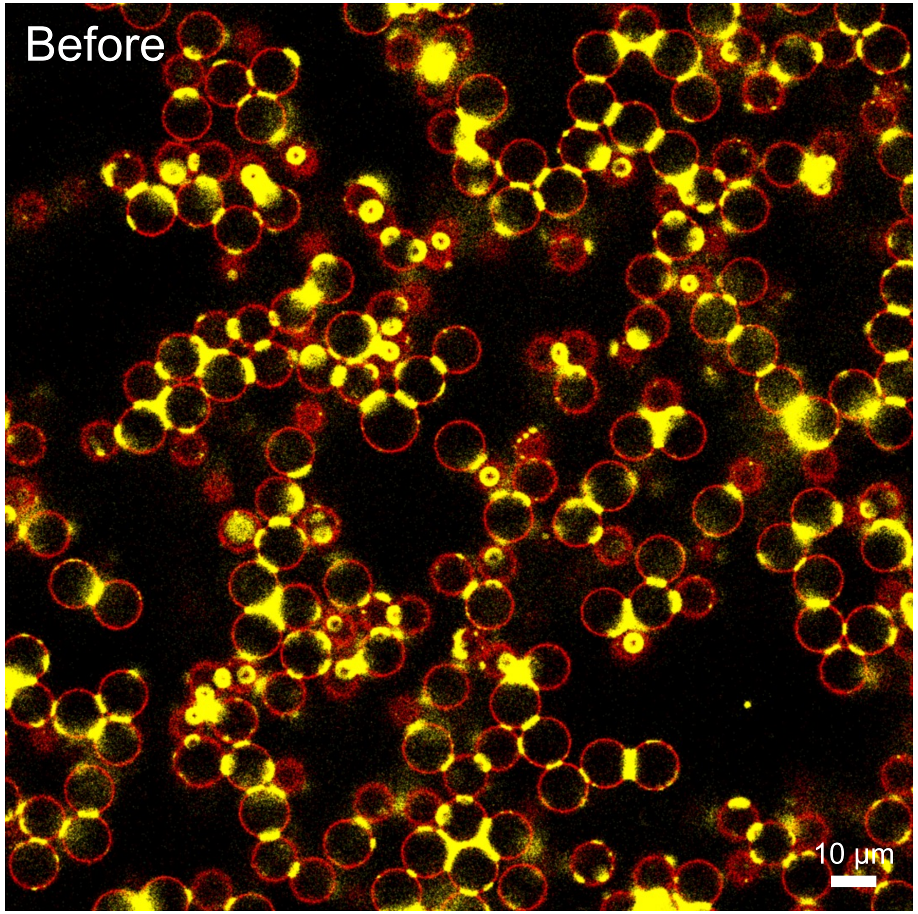
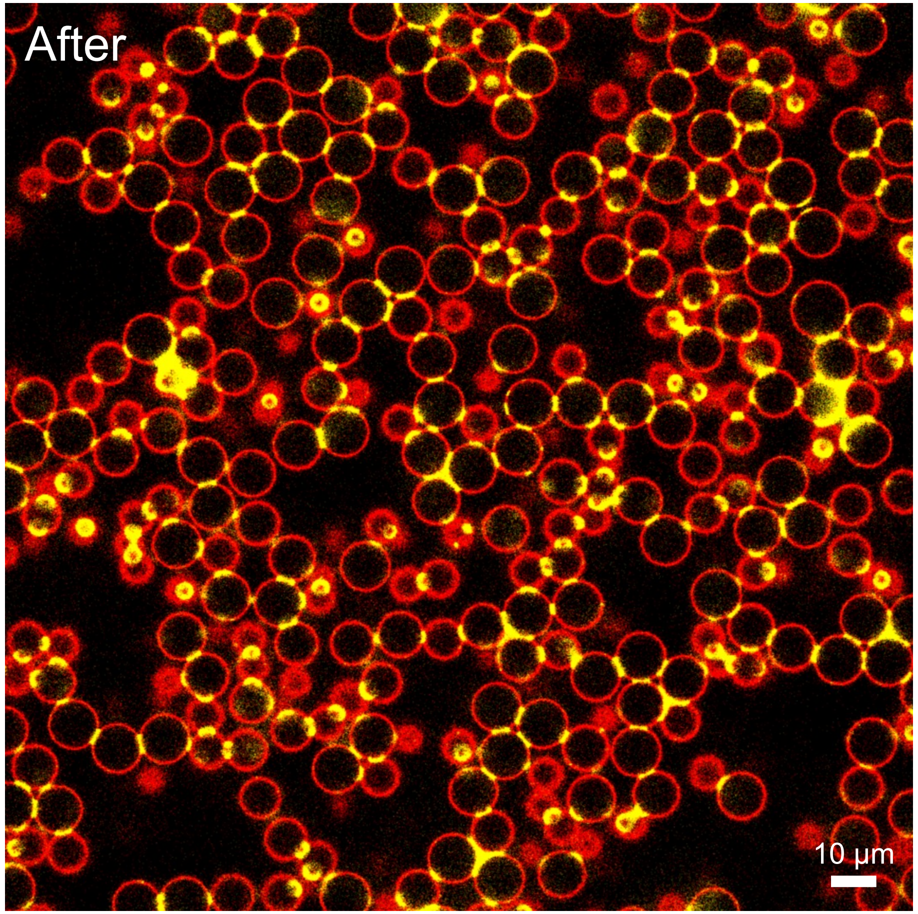
Before & After compression with NP





- 30 μm from bottom
- Sec. liquid redistribution
  - Bridge size smaller
  - Bulk liquid disappear
- Strong increase in ϕ_{MP}

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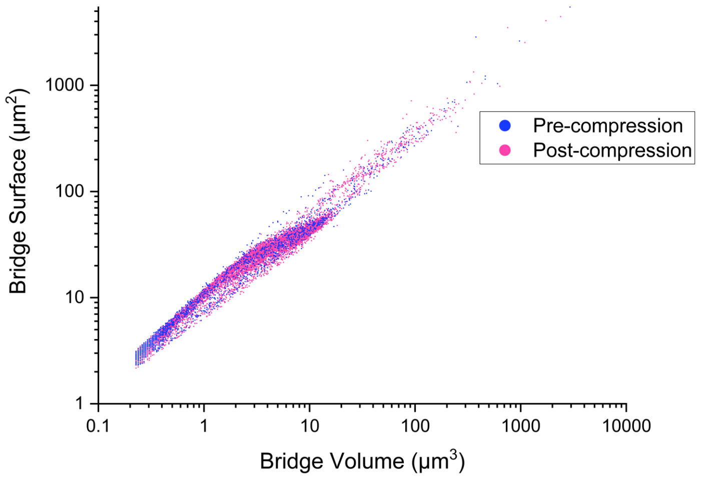
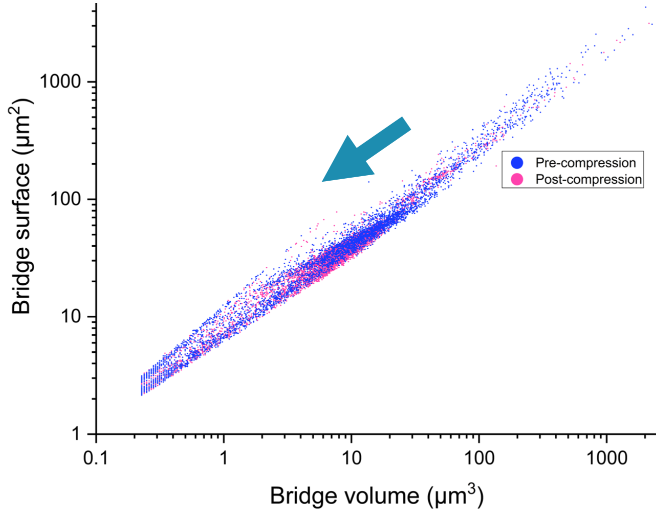
Bridge distribution evolution





No NP

- Partial pre-compression bridges too small to analyze
- Bridge **coalescence**, trimer breakage
- Bridge volume generally **increasing**
- **Limited** liquid exchange

Hydrophilic NP

- Large agglomerates **disappear**
- **Small** bridges formed
- **Elevated** liquid exchange between bridges
- Due to NPs-induced **liquid films** at MP surfaces

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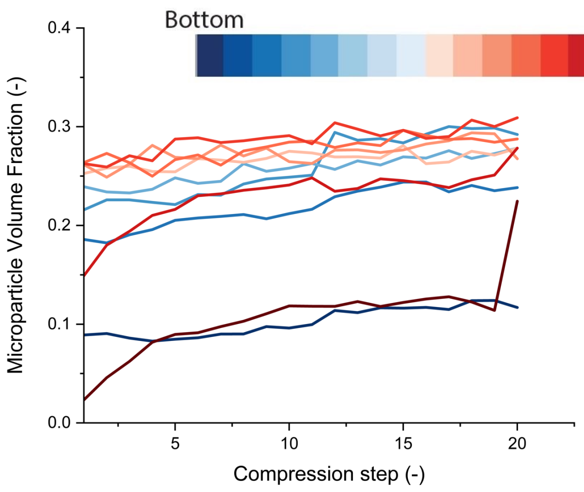
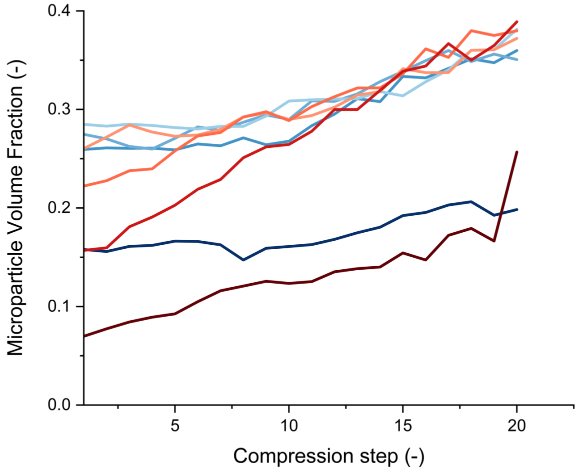
Microstructural changes



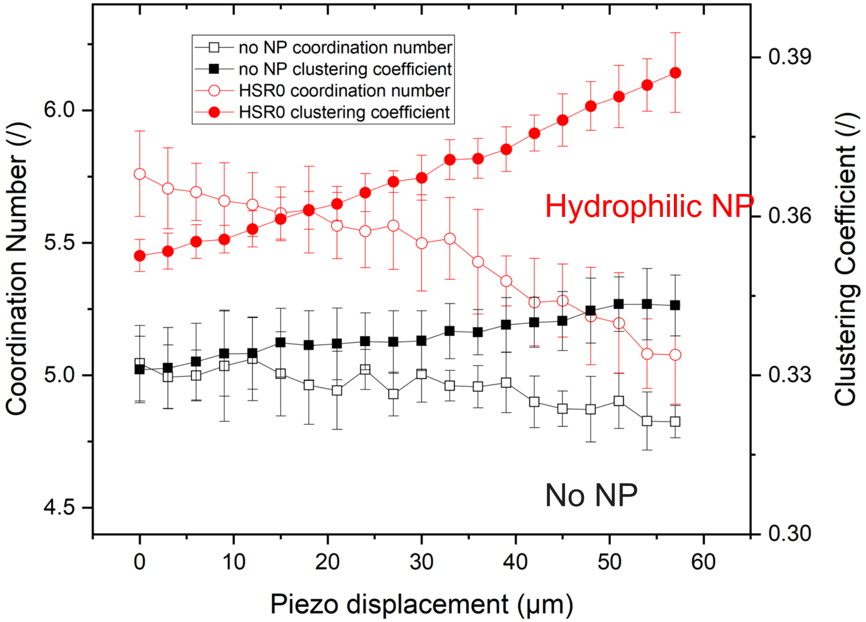


No NP

- ϕ_{MP} increases **abruptly** and **mildly**
- Coordination number increases **slightly**
- Clustering coefficient **fluctuates**

Hydrophilic NP

- ϕ_{MP} increases **homogeneously, converges**
- Coordination number increases **dramatically**
- Clustering decreases **greatly**



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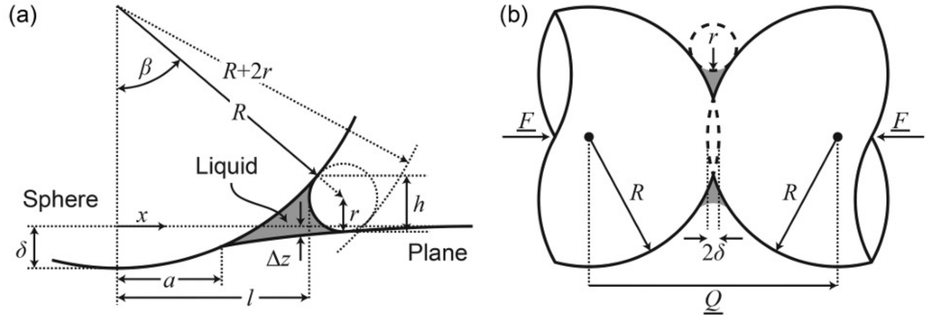
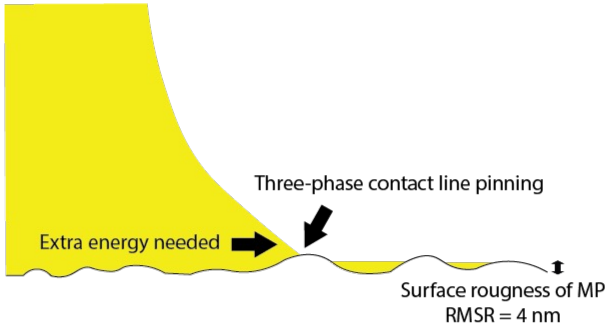
Department of Chemical Engineering
Section Soft Matter, Rheology and Technology
KU LEUVEN

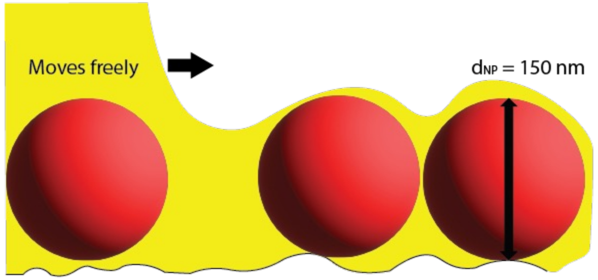
Conclusions

- NP **hinder** MP surface deformation, **Hertzian contact**
- Hydrophilic NP result in **lower** G'' at MAOS



- NP on MP **inhibit** the contact line **pinning effect**
- **Broken** force chains enable relative movement between MPs
- NP on MP surfaces **improve** the liquid exchange
- NP have a **lubrication** effect





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