

# Investigation of capillary (nano)suspensions

IFPRI Annual Meeting 2023

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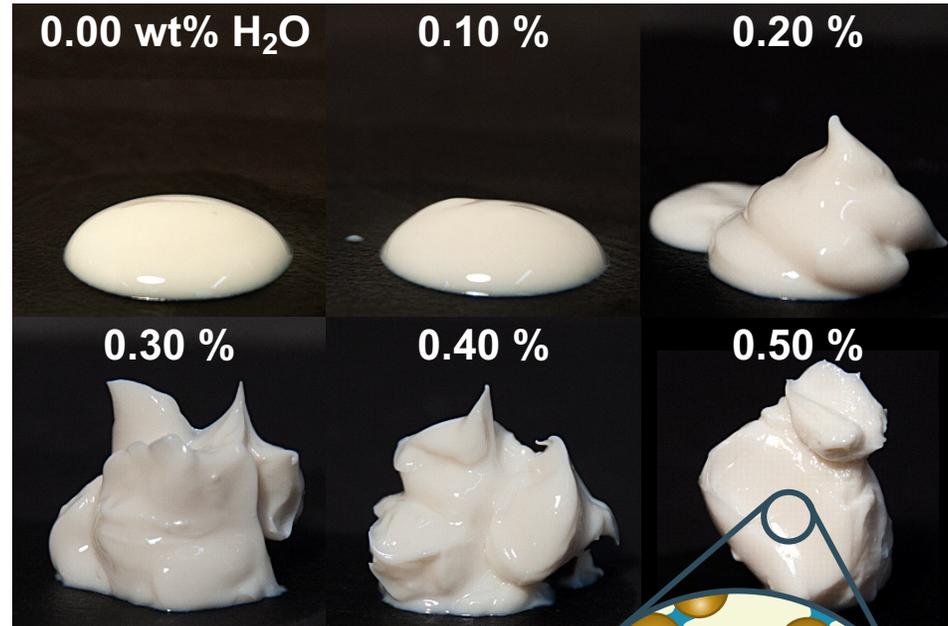
# The capillary suspension phenomenon



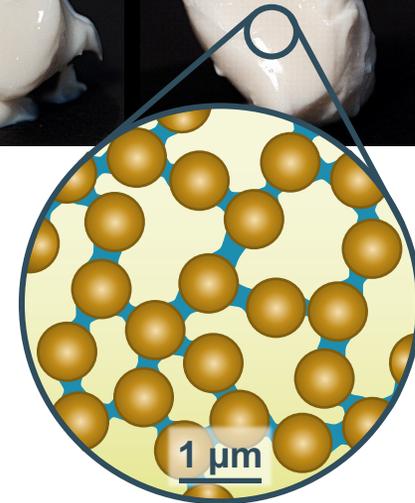
Micro- or nanoparticles



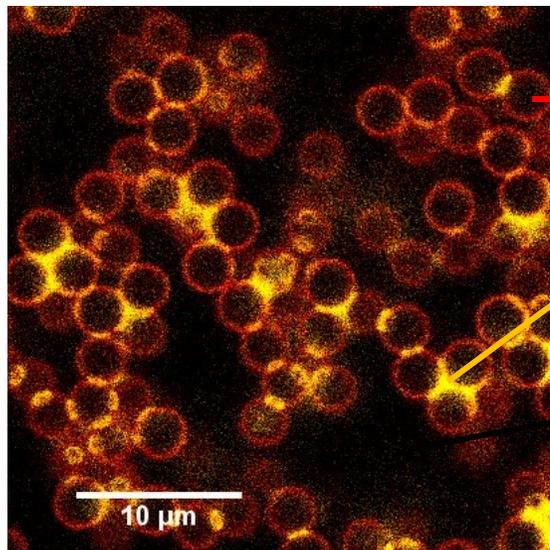
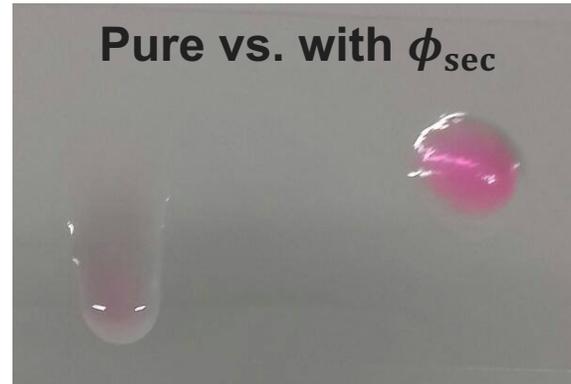
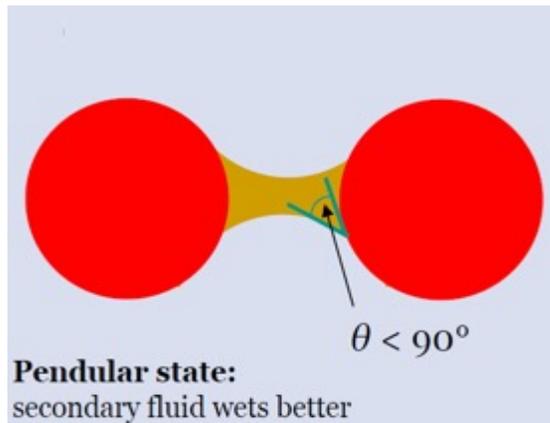
Two immiscible liquids



Capillary  
suspension



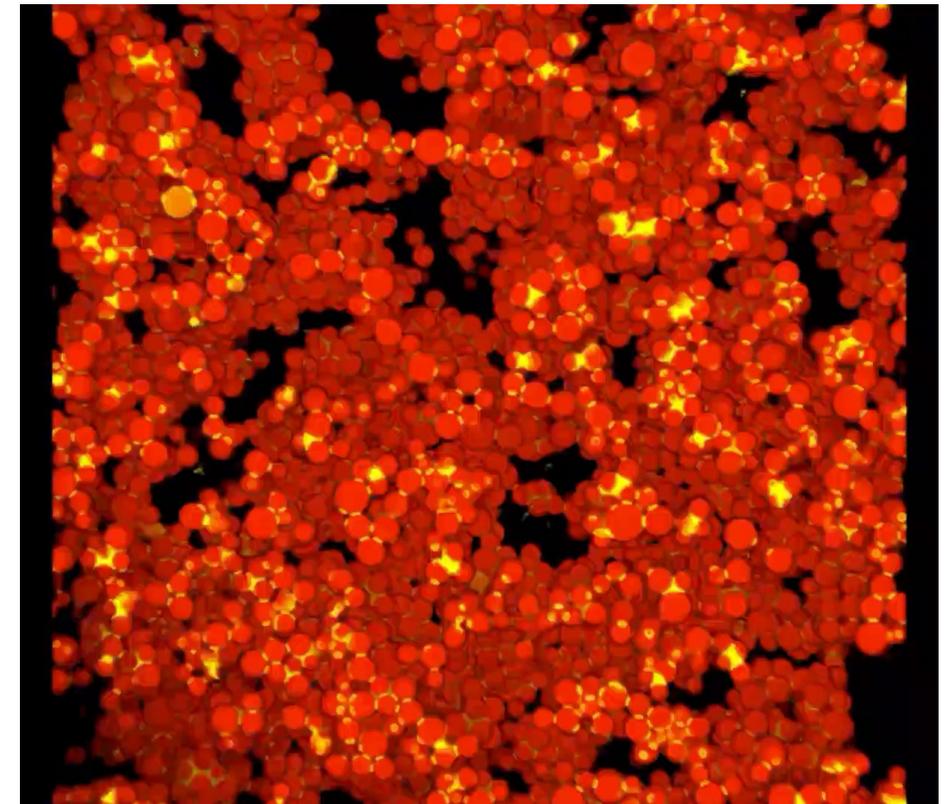
# Confocal model system



Silica dyed with rhodamine B

Aqueous glycerol dyed with promofluor 488

Oil phase (hexamoll dinch/dodecane)



$\theta = 61^\circ$ ,  $\phi_{\text{solid}} = 0.33$ ,  $\phi_{\text{sec}} = 0.04$

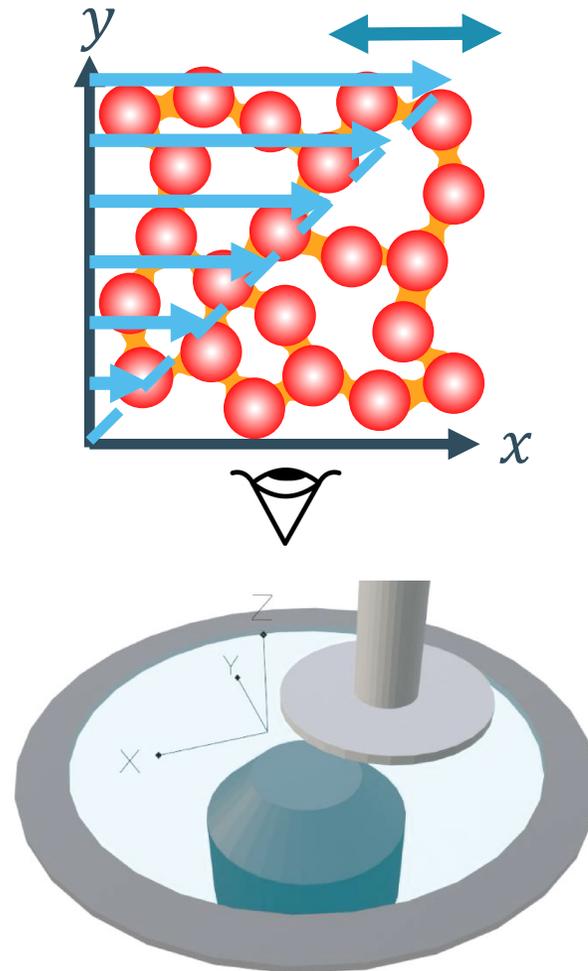
# Dynamic and structural investigation of capillary suspensions

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KU Leuven, Department of Chemical Engineering Section Soft Matter,  
Rheology and Technology<sup>1</sup>

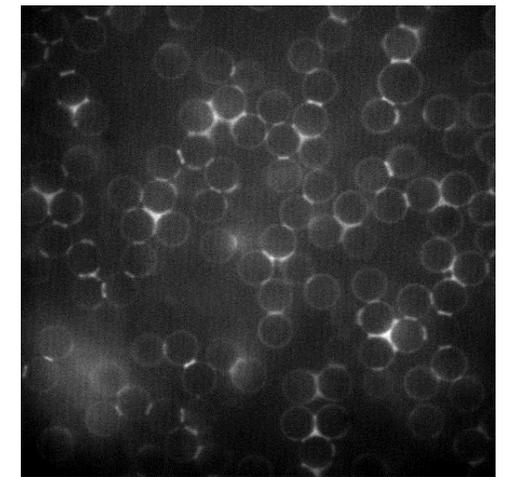
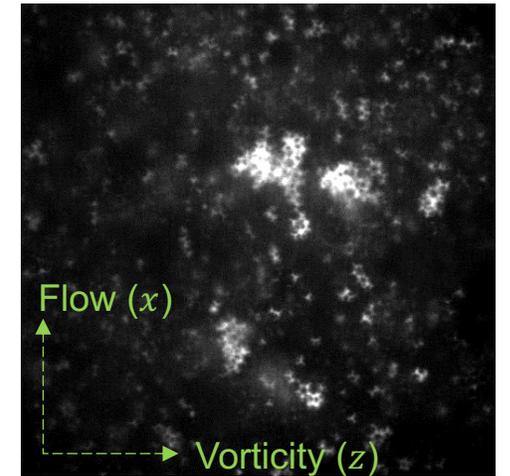
KU Leuven, Department of Physics and Astronomy Section Soft Matter  
and Biophysics <sup>2</sup>

# Simultaneous confocal imaging and rheology



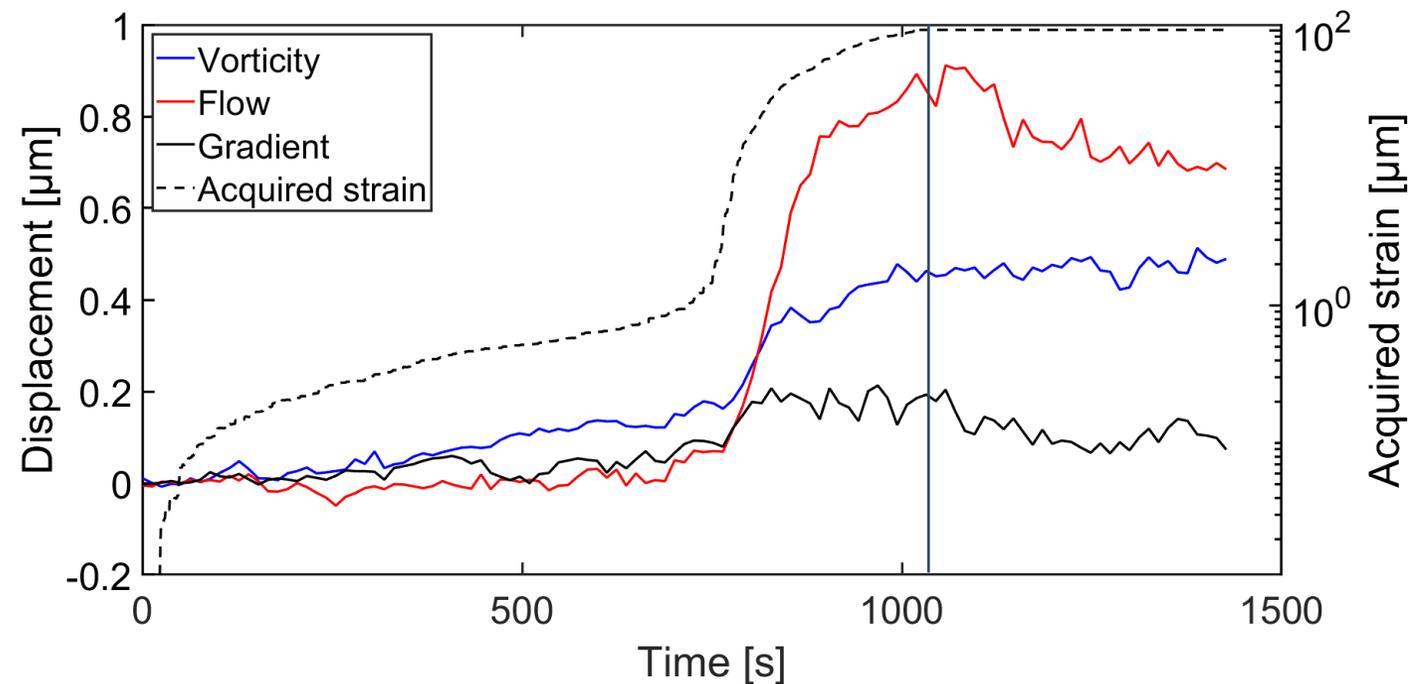
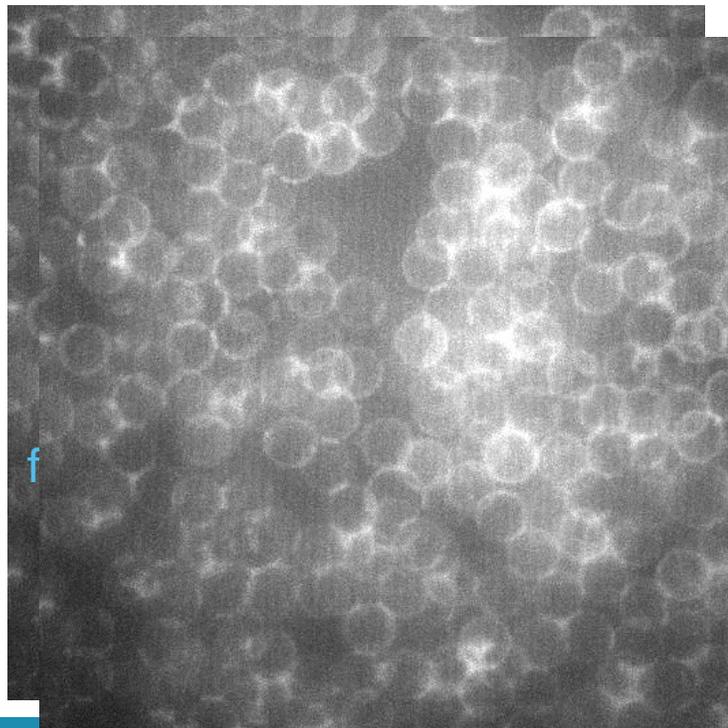
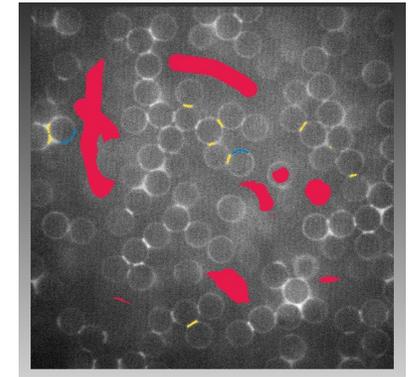
- Bridge (particle) tracking analysis

- Bridge breaking,
- Sequence of Physical Processes analysis

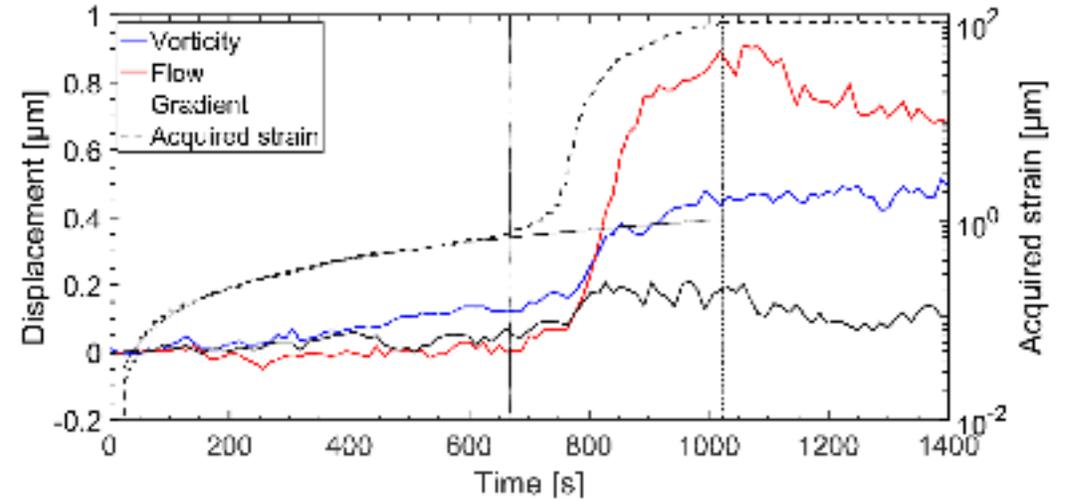
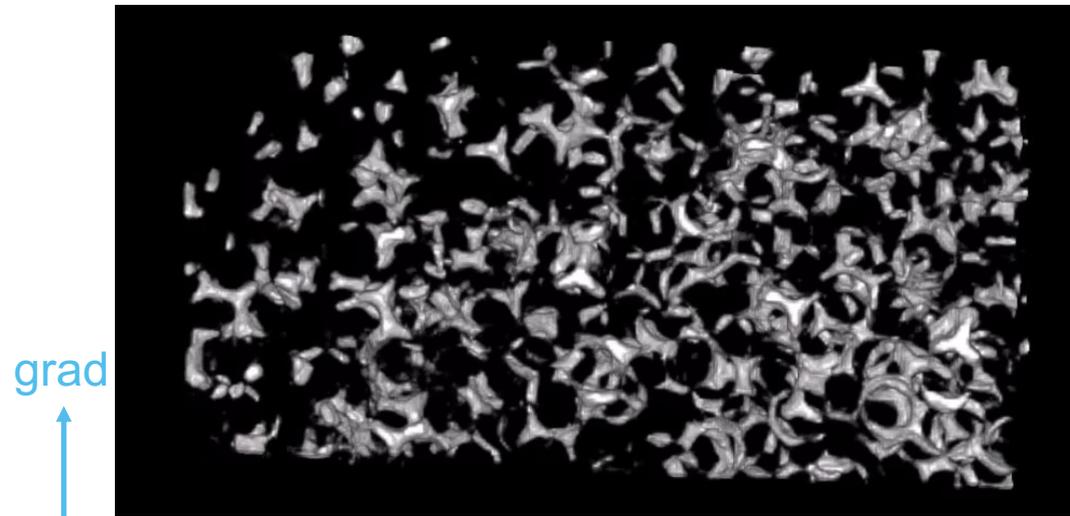


# Step stress near yield stress (50 Pa)

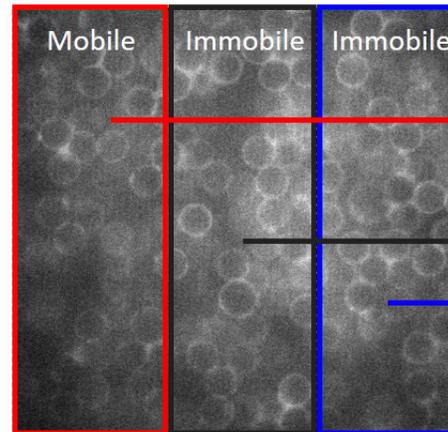
- Continuous 3D scanning (every  $\sim 13$  s for  $30 \mu\text{m}$  depth)
- AI software Ilastik to extract bridges, track bridge centroids



# Step stress near yield stress (50 Pa)

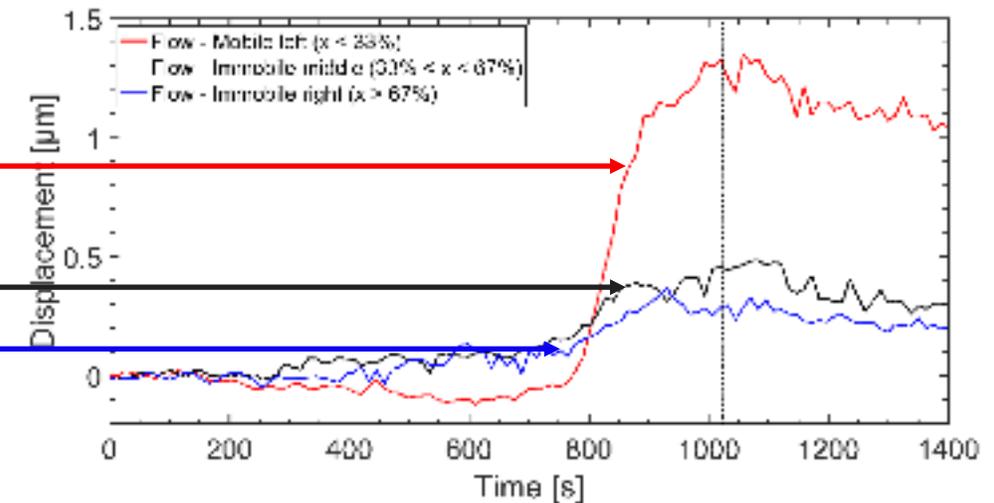


flow

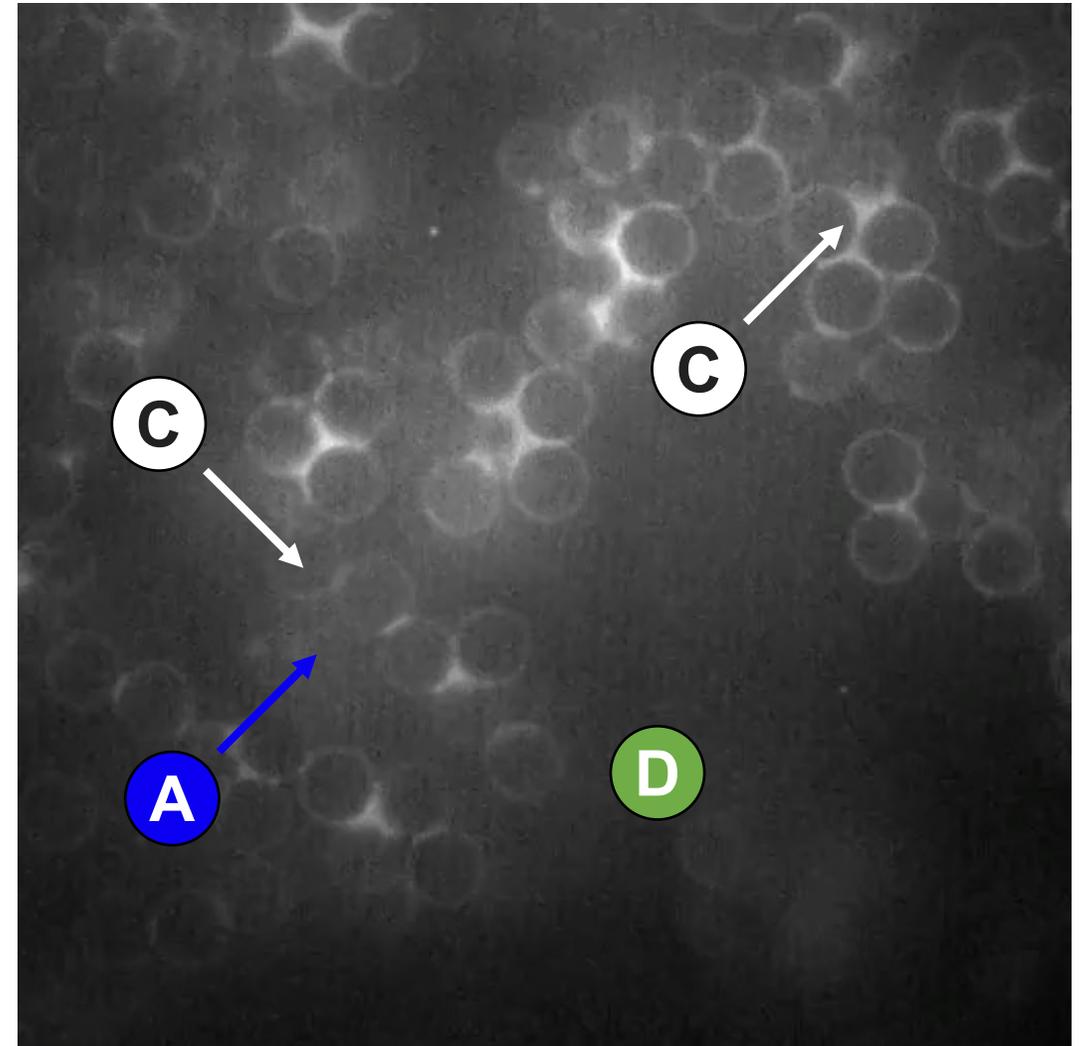
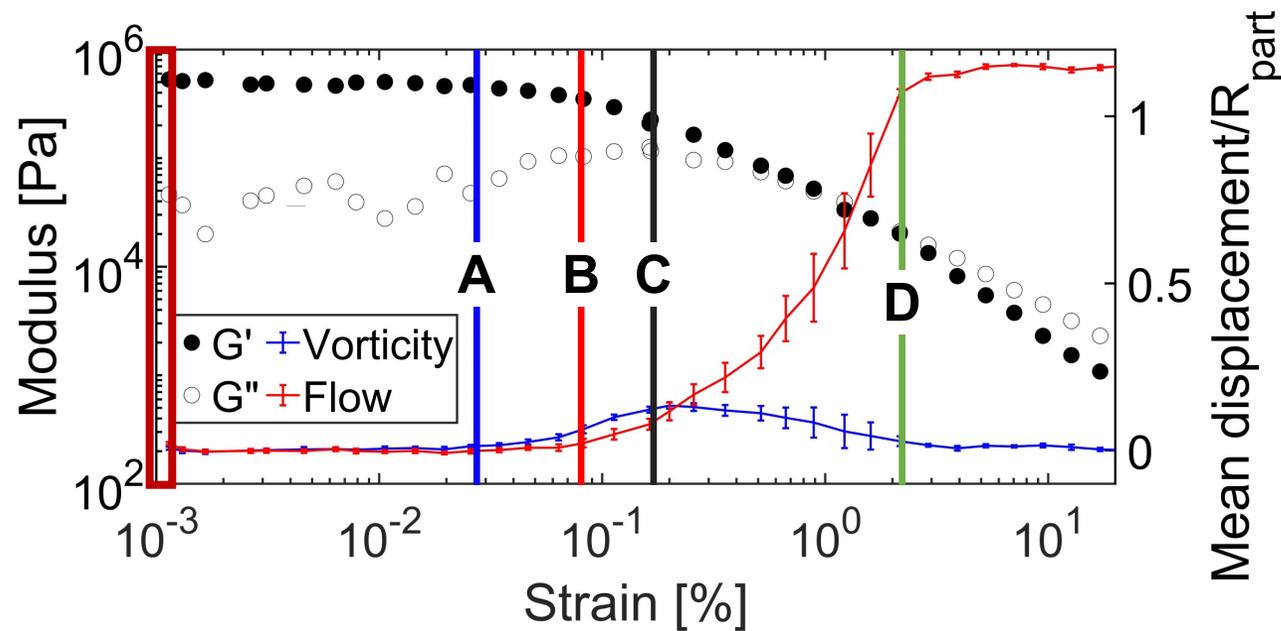


flow

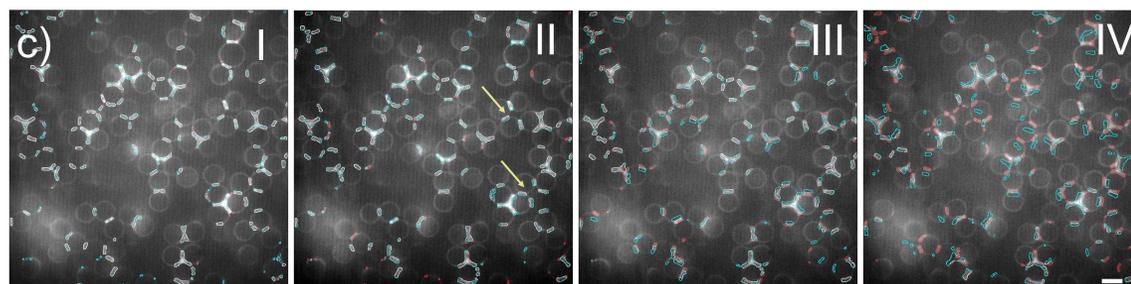
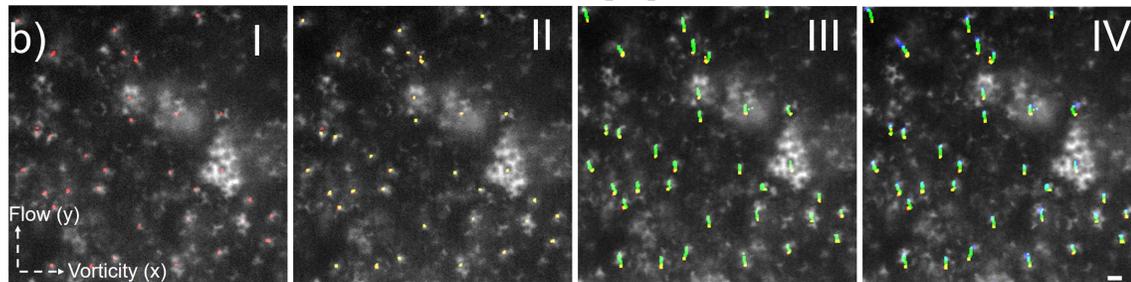
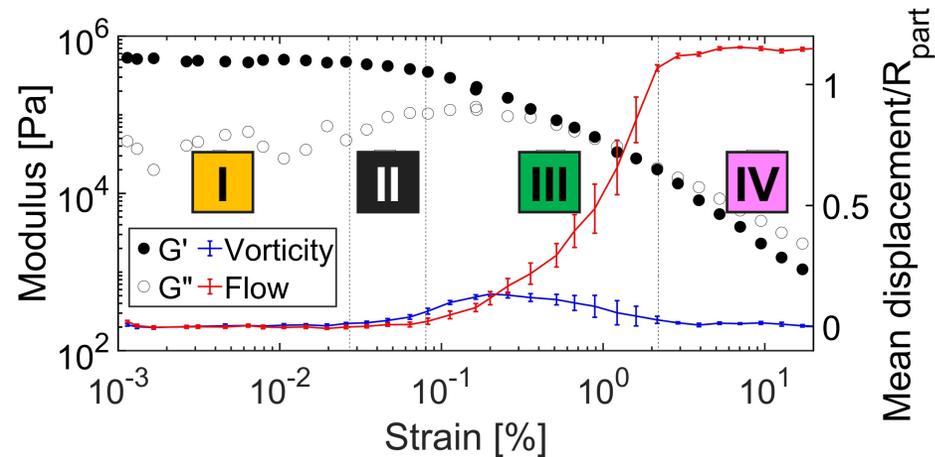
vorticity



# Full amplitude sweep with bridge tracking



# Full amplitude sweep with bridge tracking



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



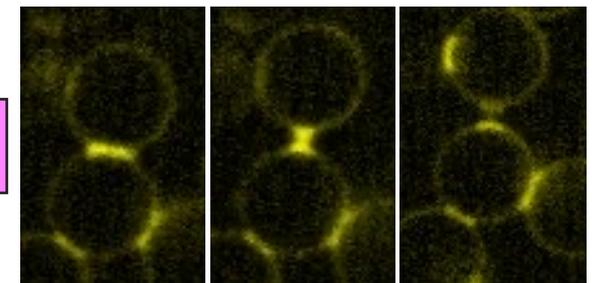
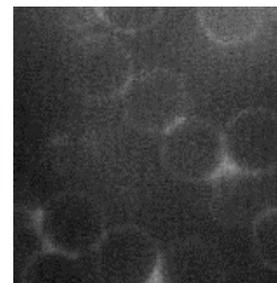
End of LVE but still reversible yielding, movement in vorticity direction, rotation of floppy connections



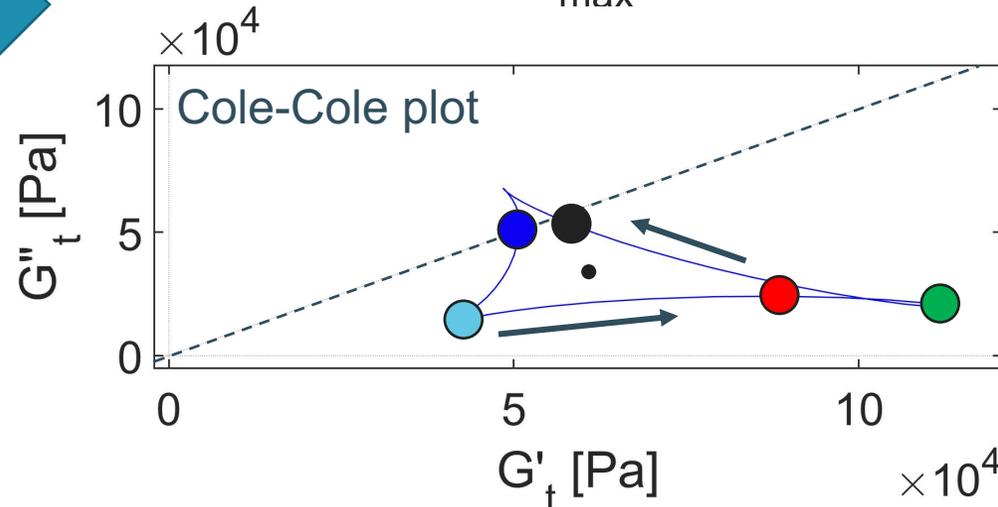
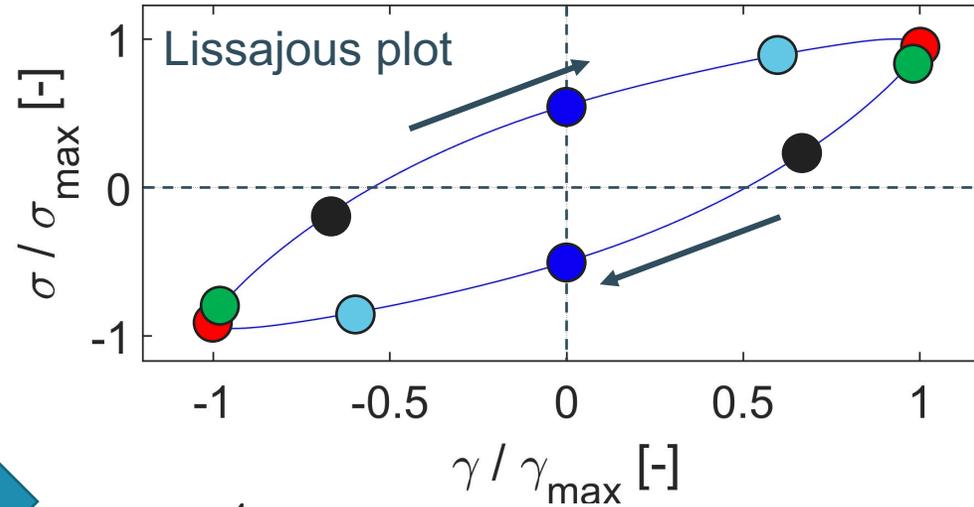
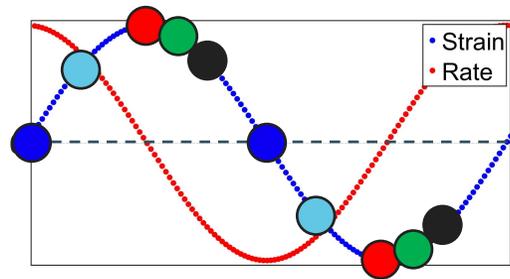
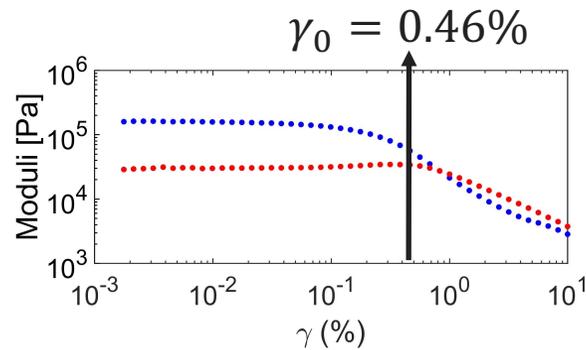
Large movement in flow direction starts, bridge stretching



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

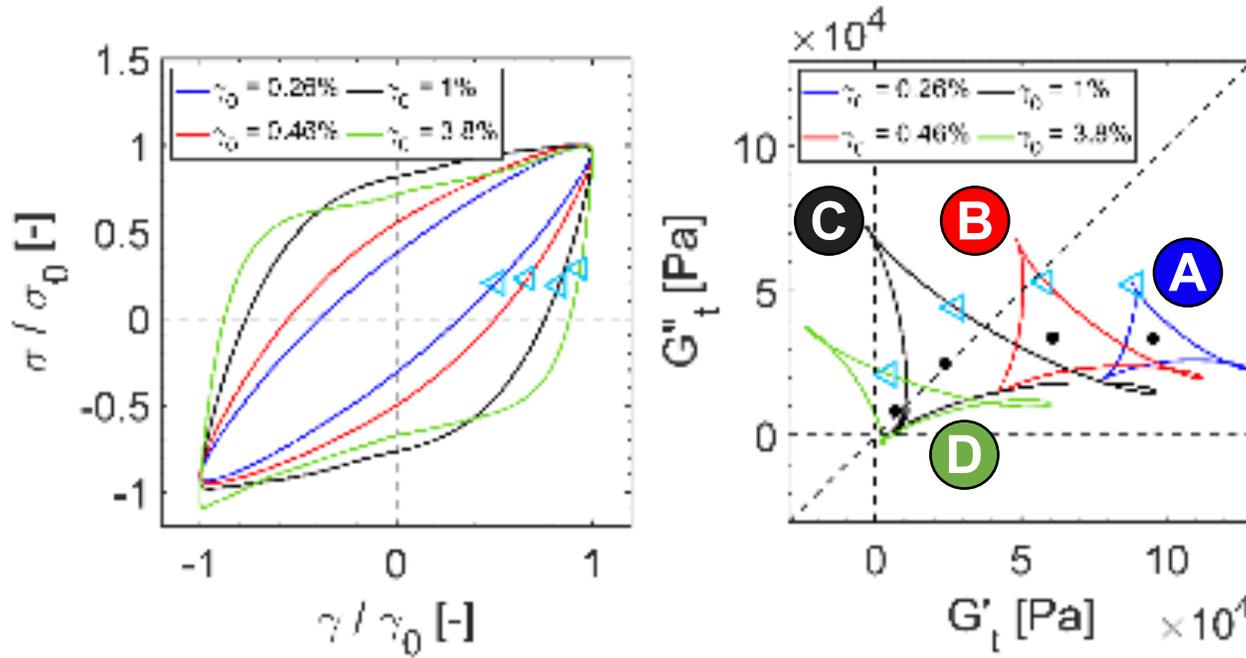


# A single oscillation: Lissajous diagrams and the Sequence of Physical Processes (SPP) [1,2]

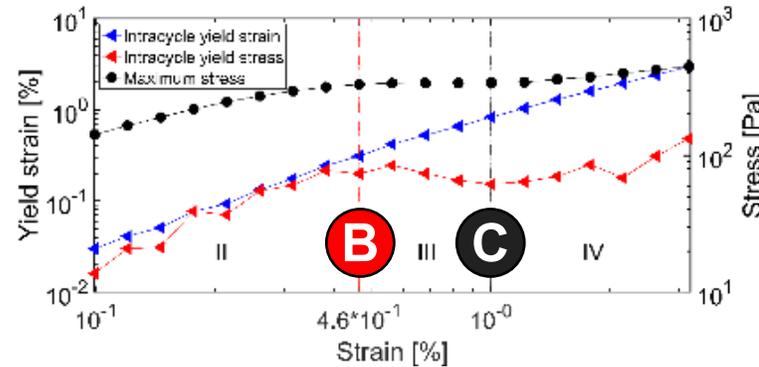
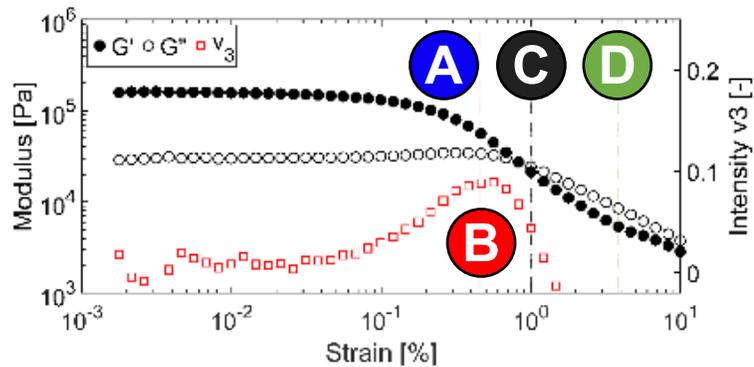


- A**  $\gamma = 0$
- B** Minimum  $G'_t$
- C** Maximum  $\gamma$
- D** Maximum  $G'_t$
- E** Maximum  $\dot{\delta}_t = \frac{\partial}{\partial t} \tan^{-1} \left( \frac{G''_t}{G'_t} \right)$  (Yield point)

# A single oscillation at different strains

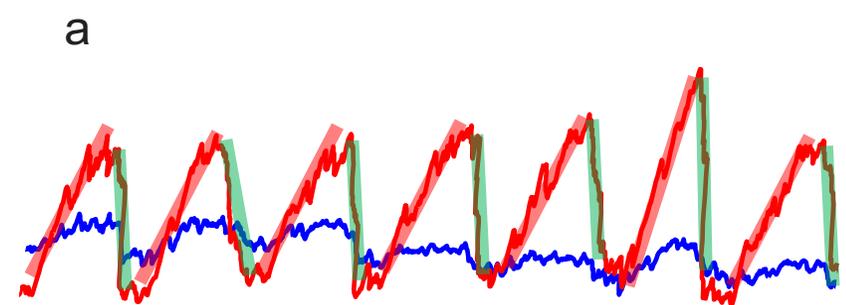
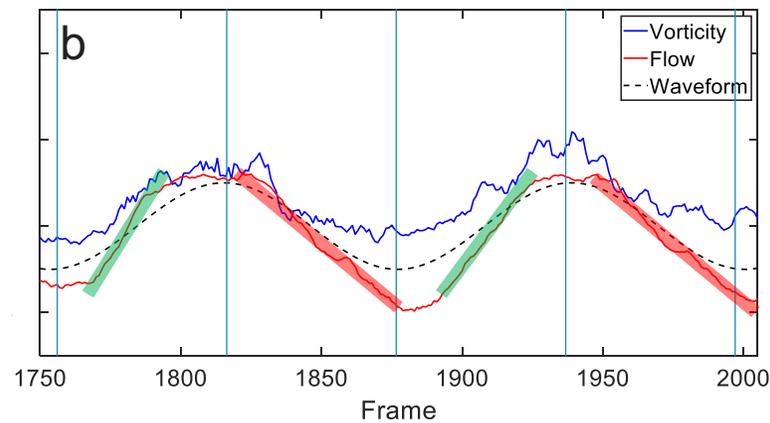
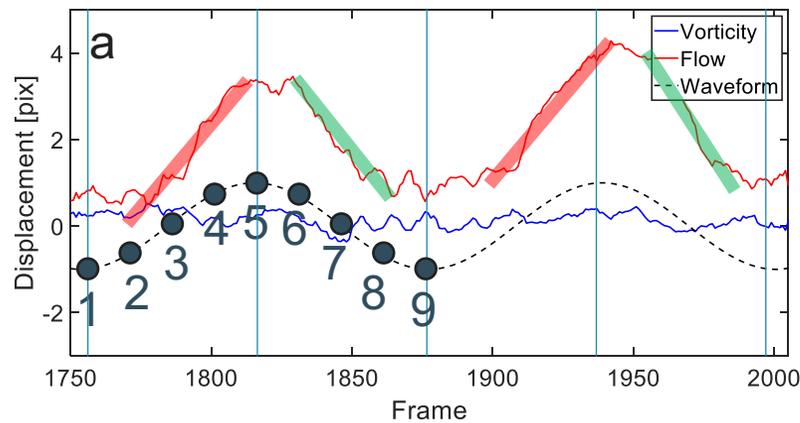
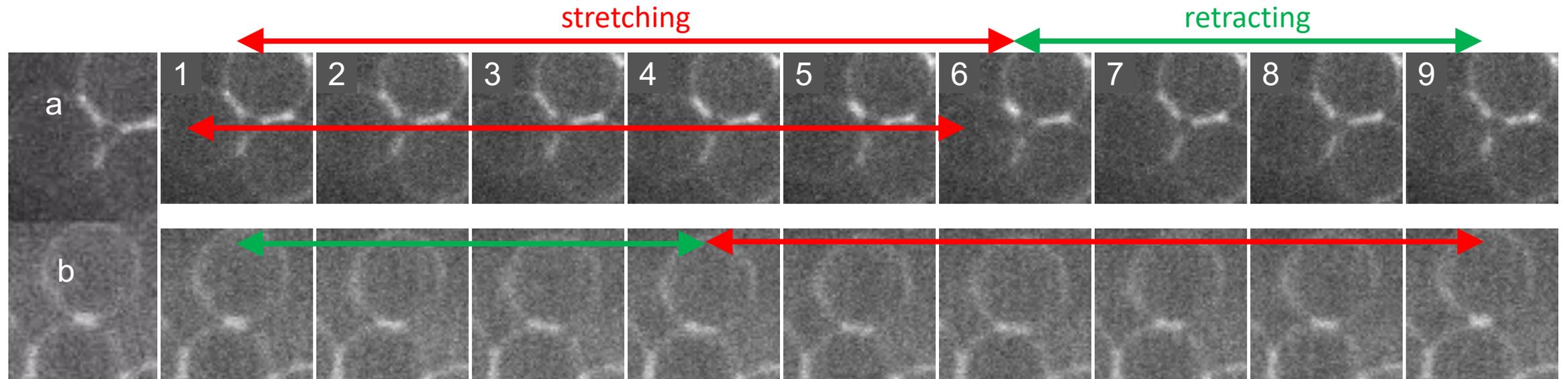


- A** Fully elastic cycle: removal of Hertzian repulsion, rotation
- B** First time shortly viscous dominated: flow direction movement starts
- C** Mostly viscous dominated: first bridge breaks
- D**  $G'_t$  goes negative: more reorganization than energy stored



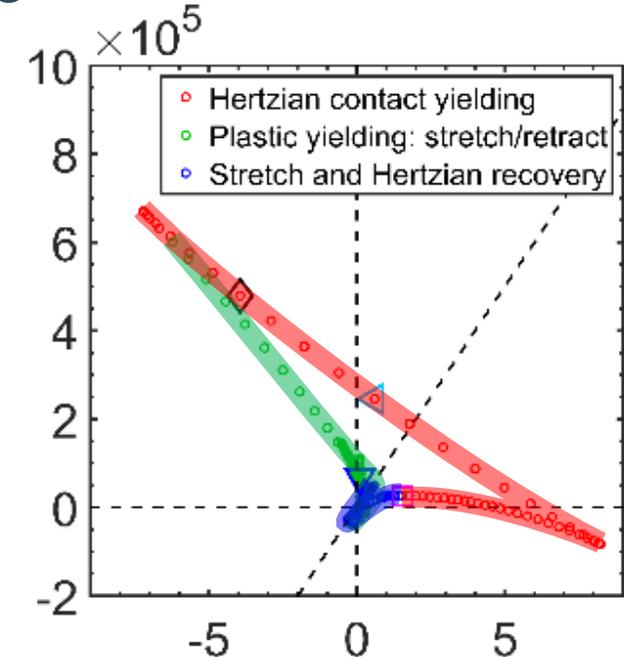
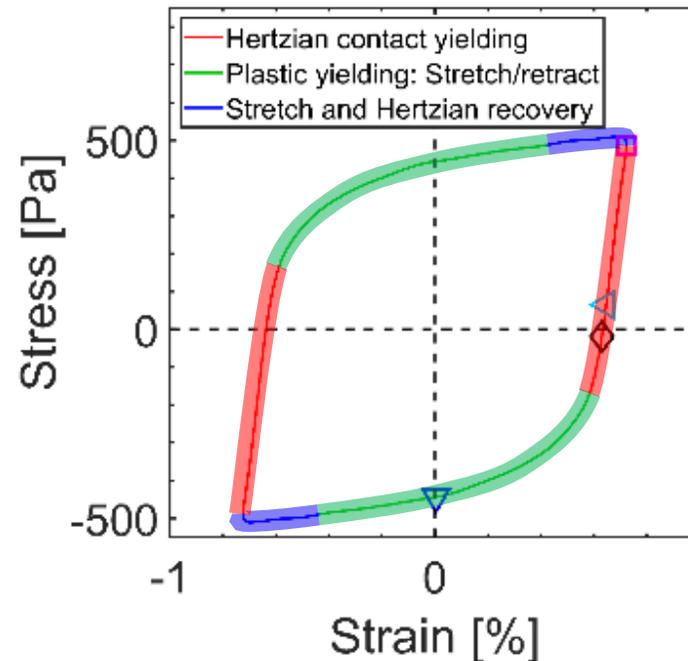
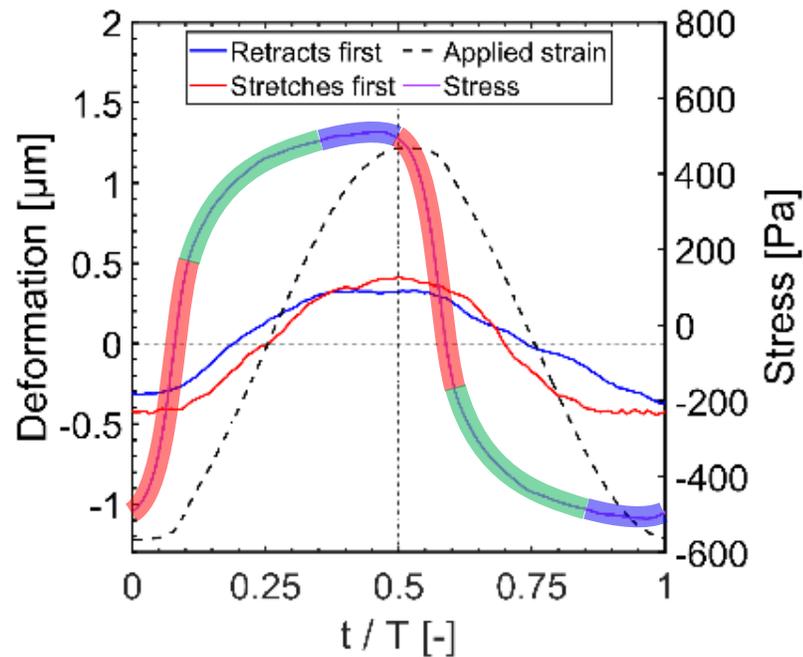
Intracycle yield stress reaches a plateau at transition from reversible to irreversible yielding

# Oscillatory deformation above flow point



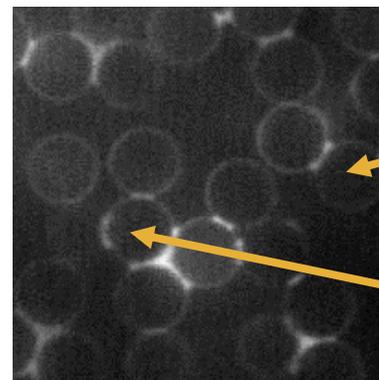
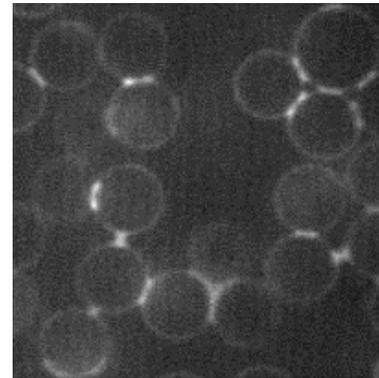
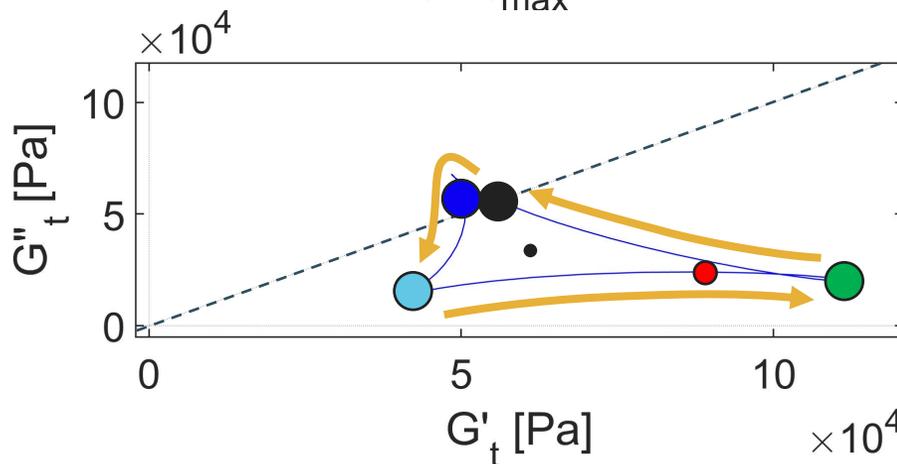
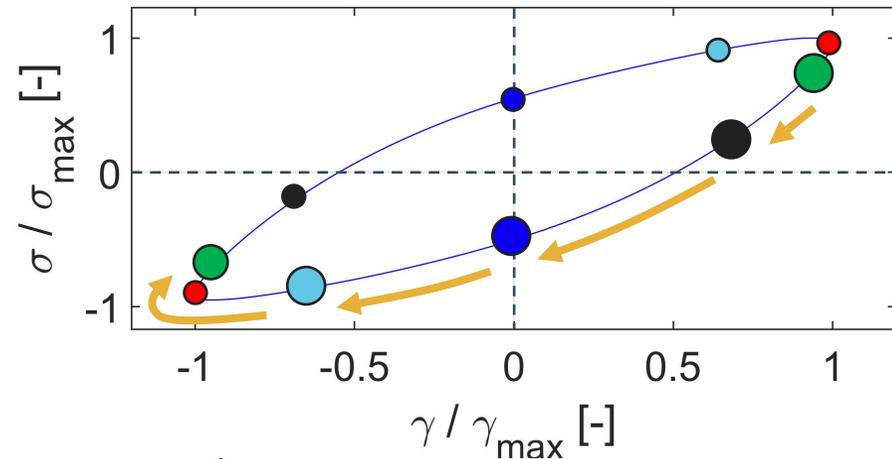
# Stretching vs retraction

- 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**

# 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

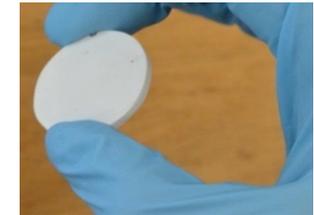
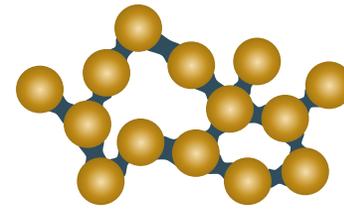
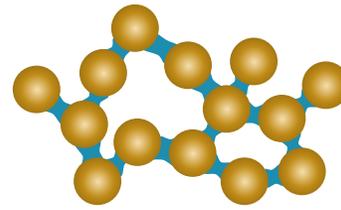
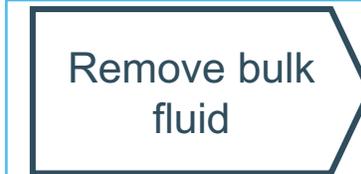
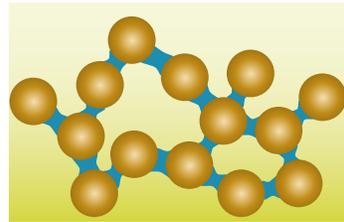
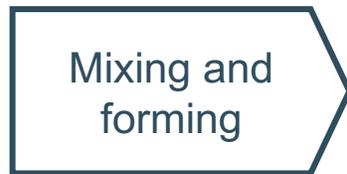
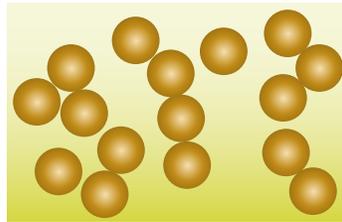
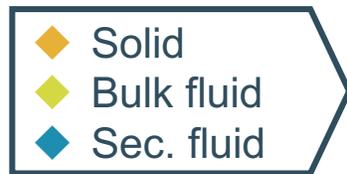
Liquid can move over particle surface (~ low CA, smooth surface)

# Lubrication effect of nanoparticles in capillary nanosuspensions

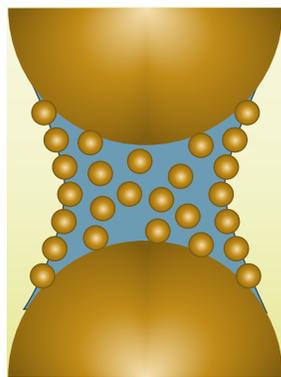
Lingyue Liu<sup>1</sup>, Jens Allard<sup>1</sup> and Erin Koos<sup>1</sup>

KU Leuven, Department of Chemical Engineering Section Soft Matter,  
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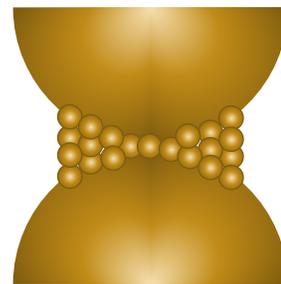
# Porous ceramics from capillary suspensions



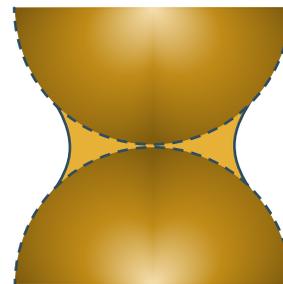
- Incorporate nanoparticles into bridging fluid



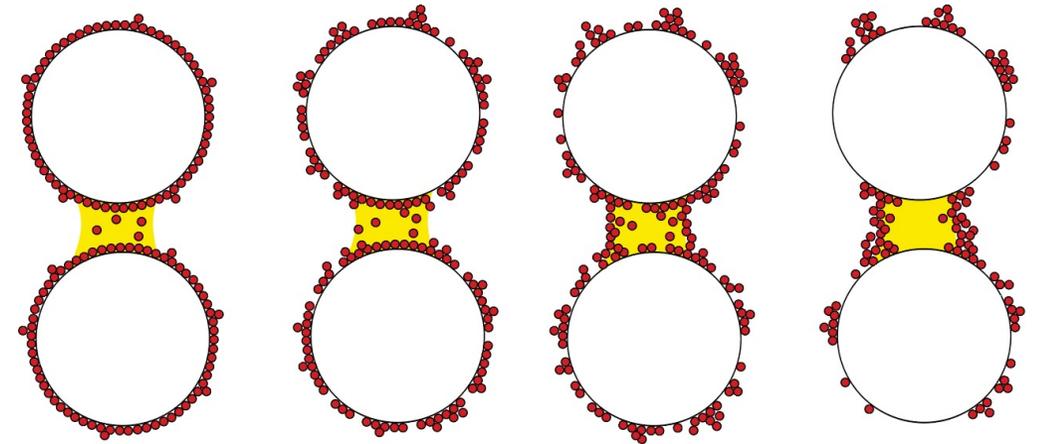
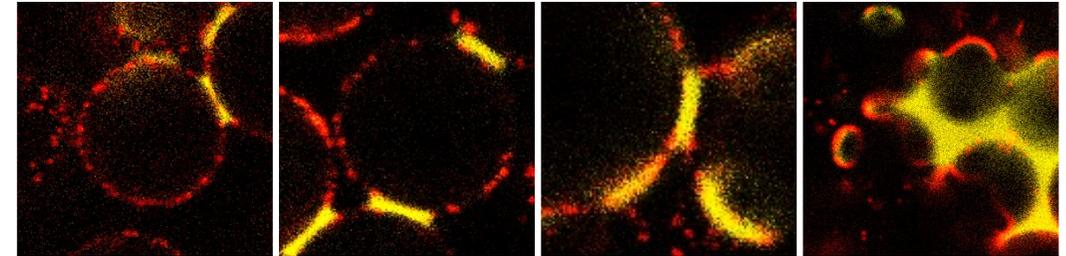
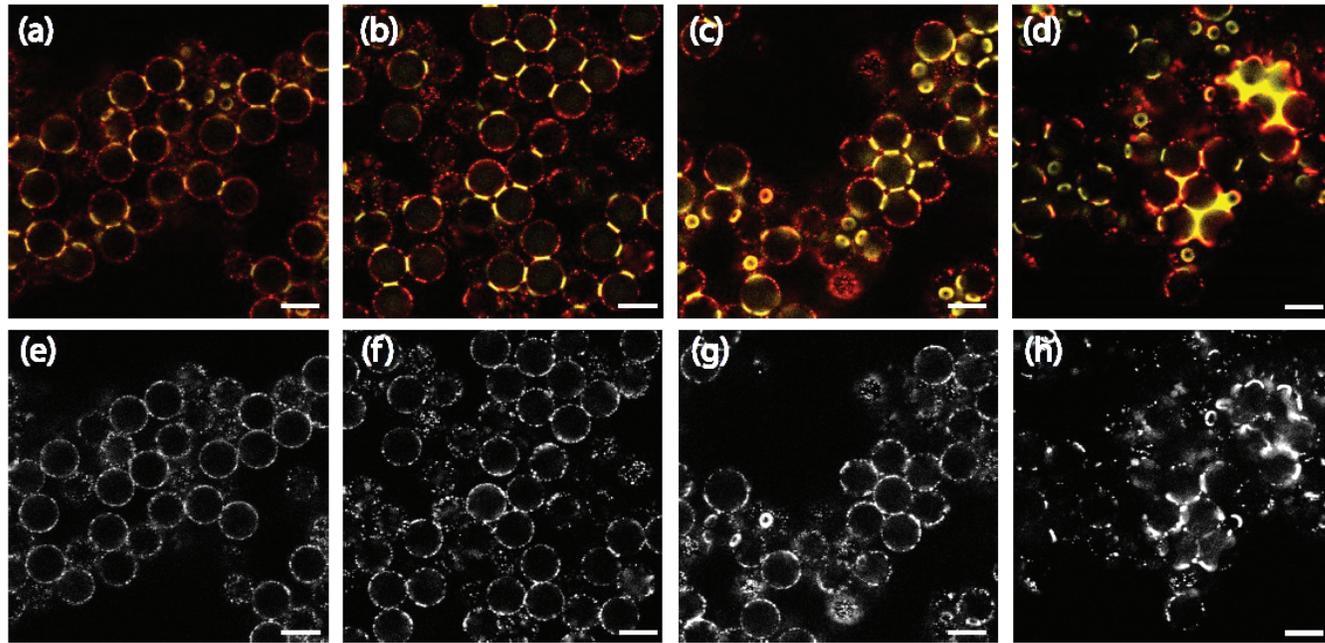
Dry



Sinter



# Influence of NP hydrophobicity



## HSR 0

- No location preference
- Well-spaced

## HSR 1

- Aggregates
- Slight preference for contact line

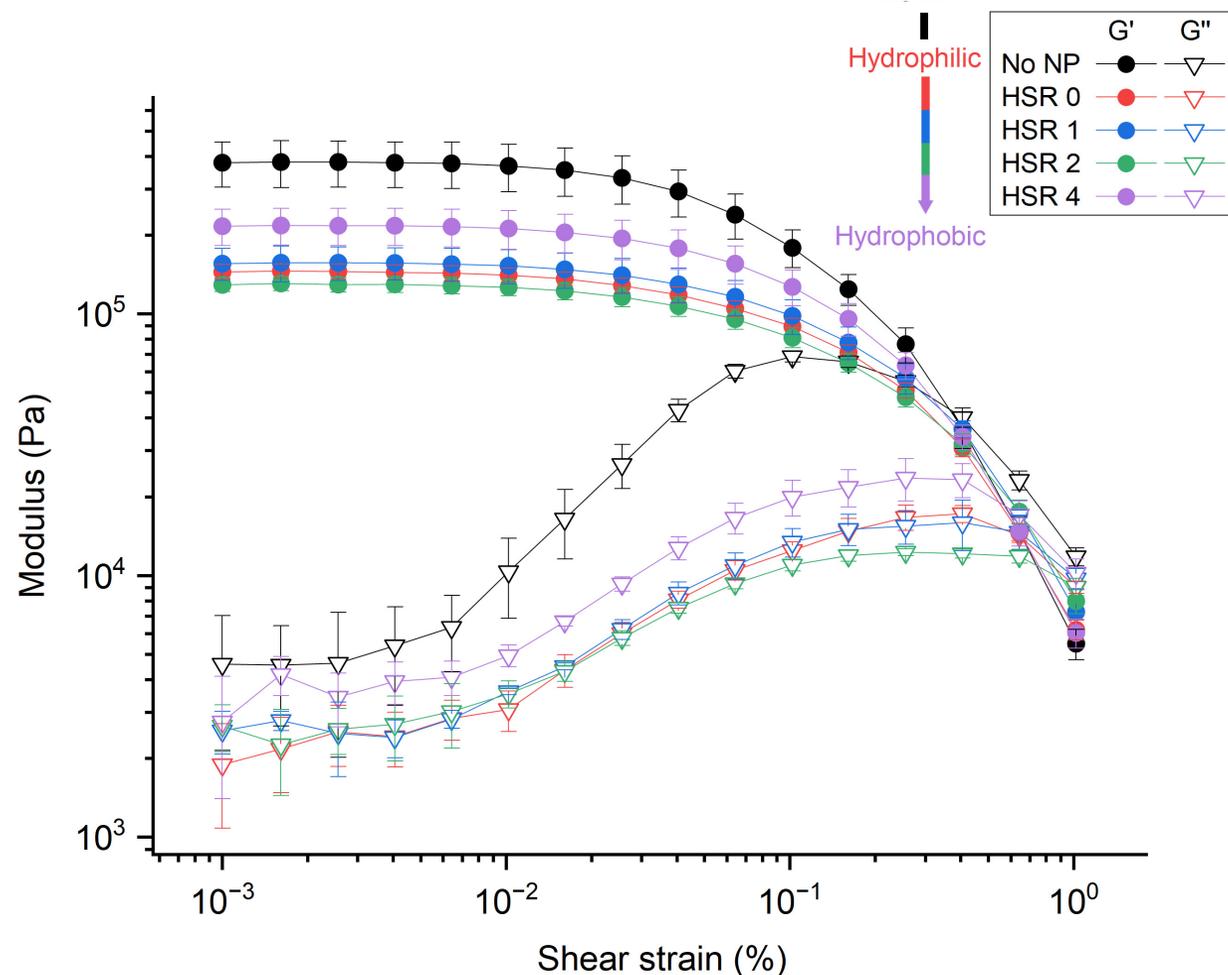
## HSR 2

- Migrate toward bridges
- Patchy on MP surface

## HSR 4

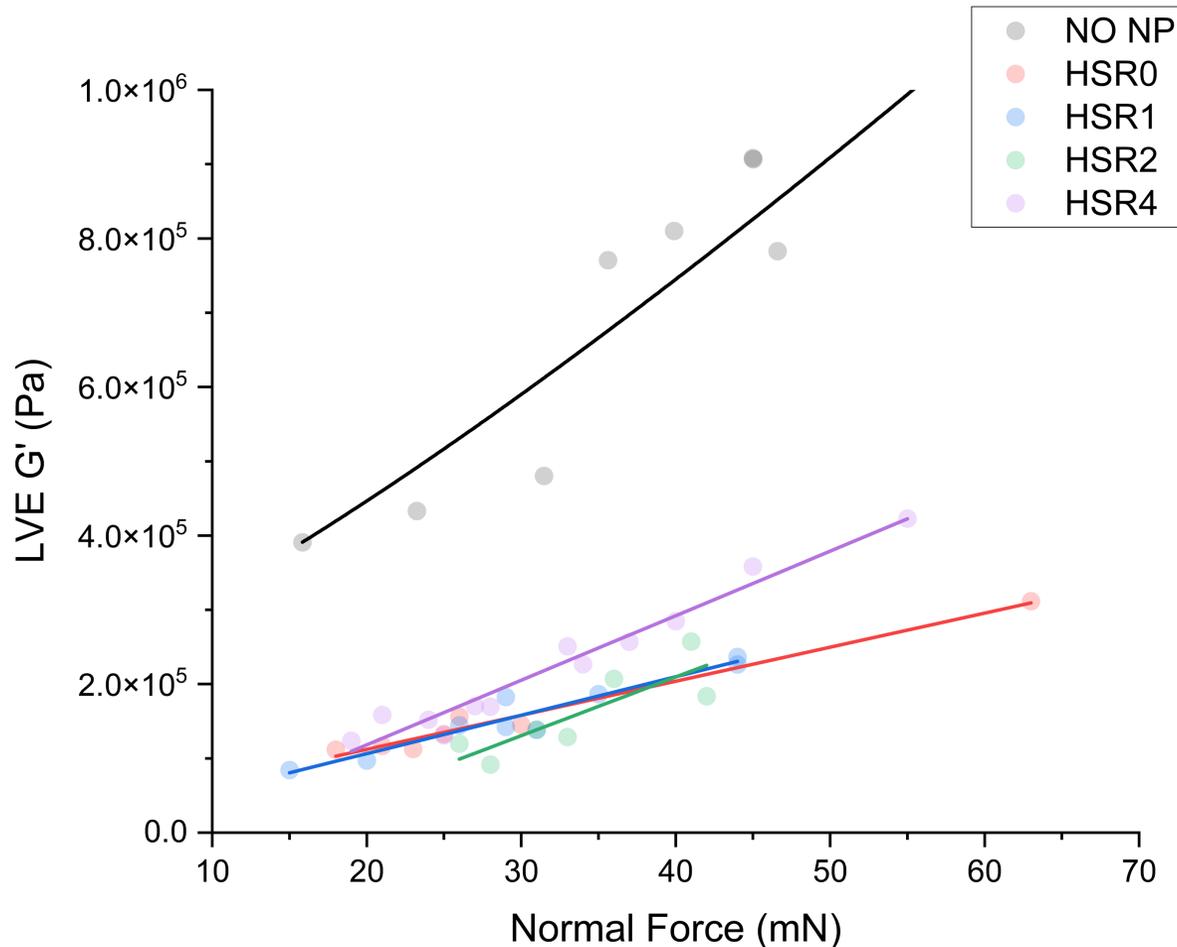
- Majority at LL interface
- Residual on MP surface

# 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?

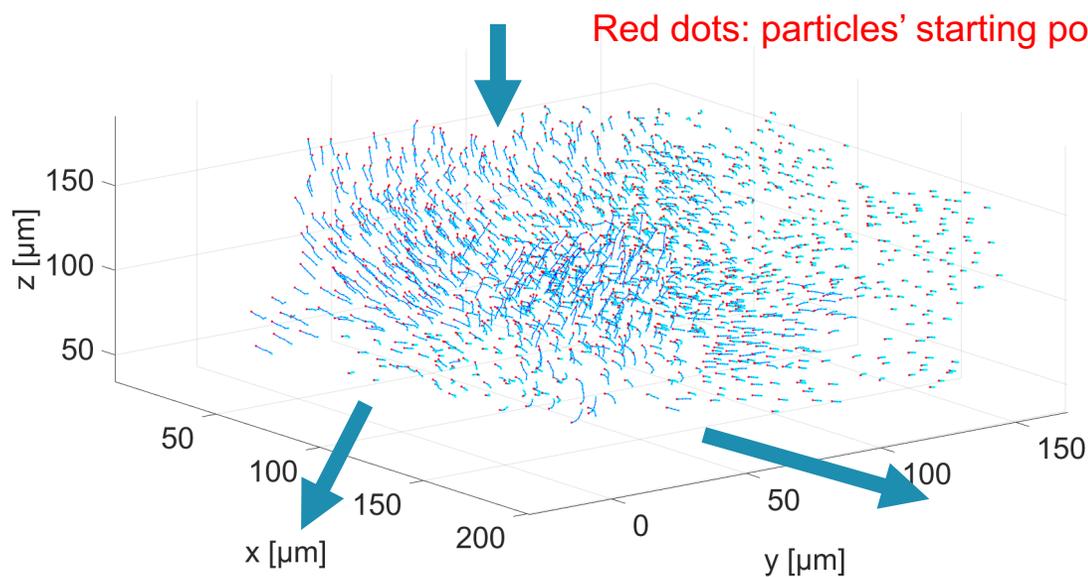
# Normal force & $G'$ at LVE



- $G'$  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

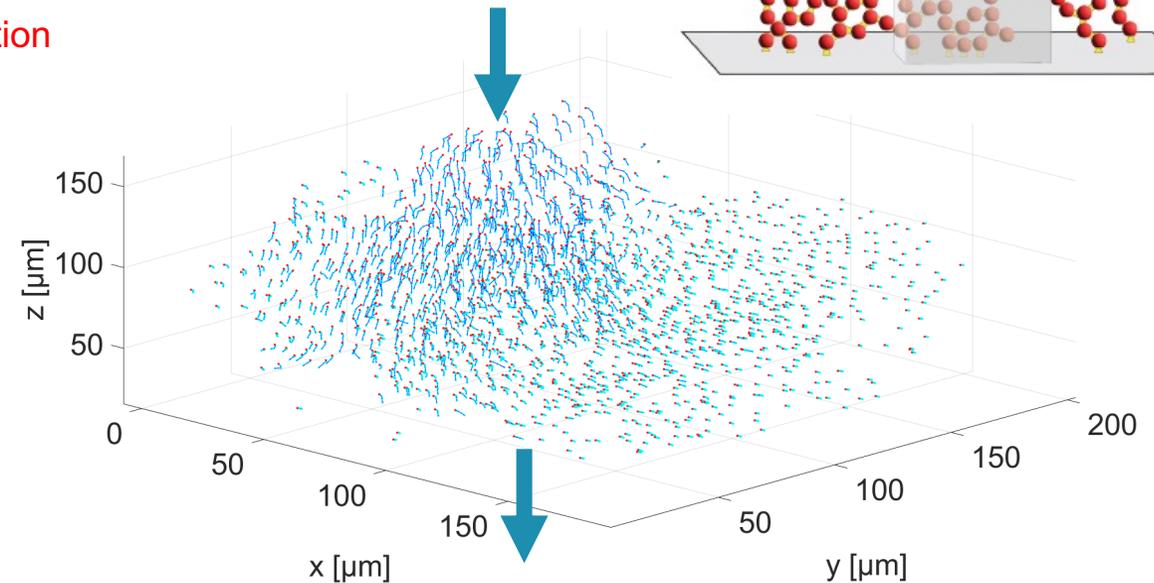
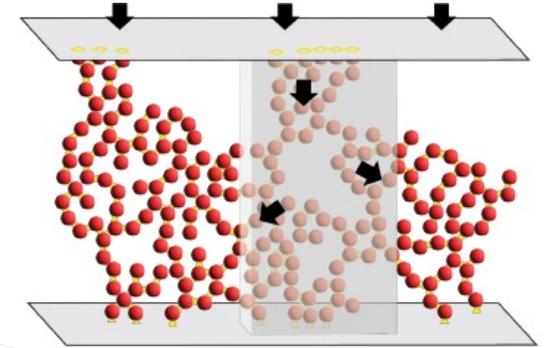
# Shell cell compression

- Compression downwards for 20 steps of 3  $\mu\text{m}$ , 3D scan



## 1. No NP

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

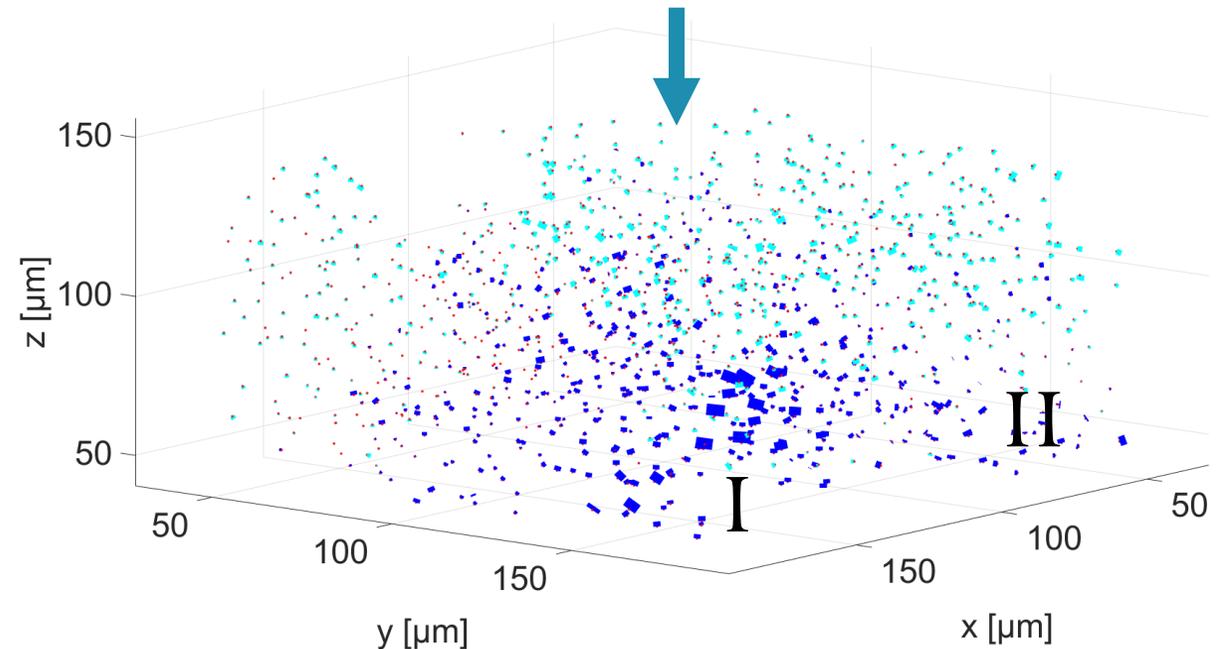
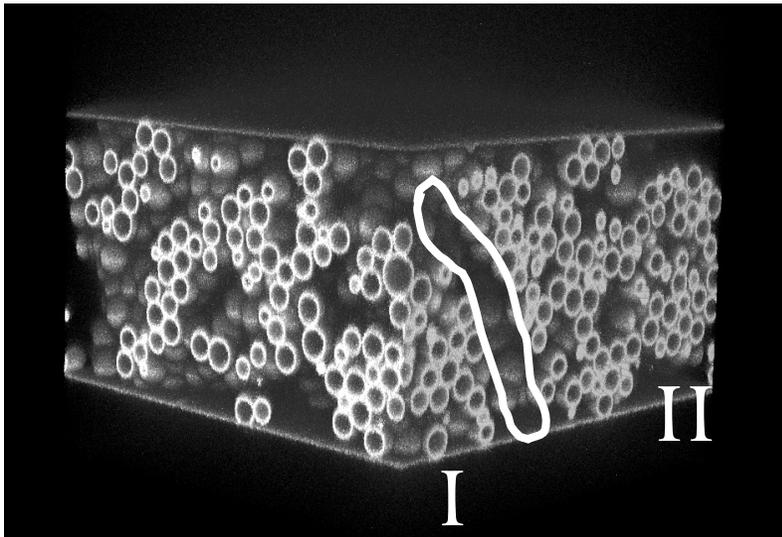


## 2. Hydrophilic NPs

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

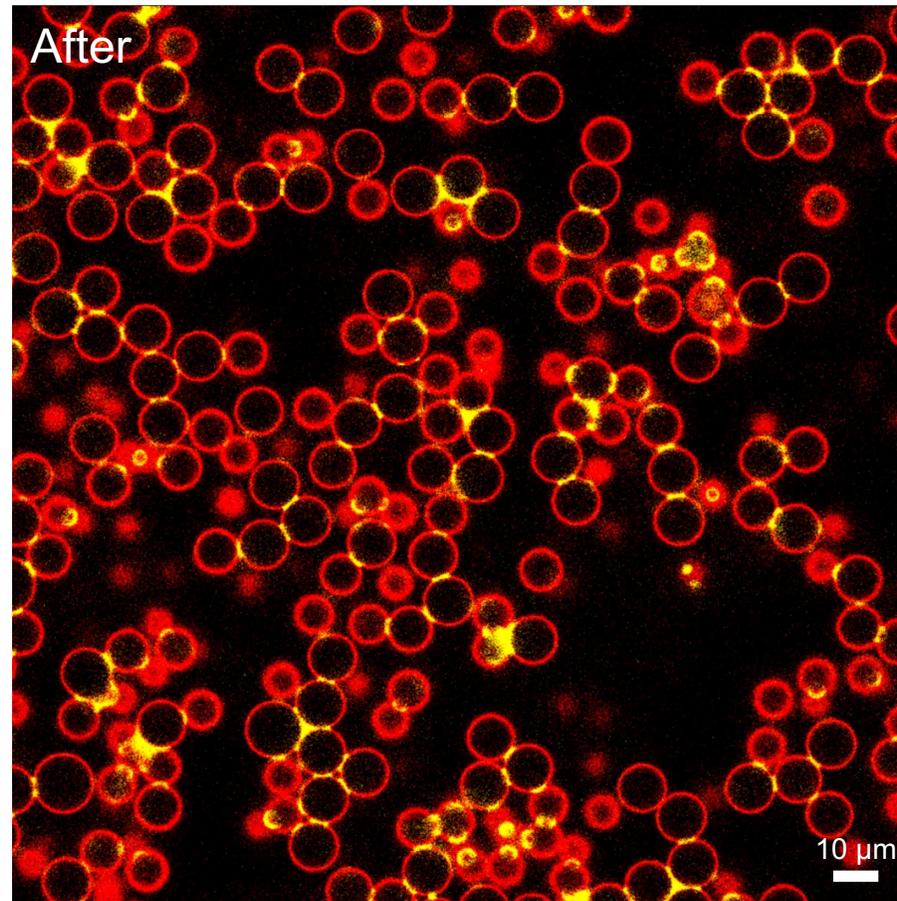
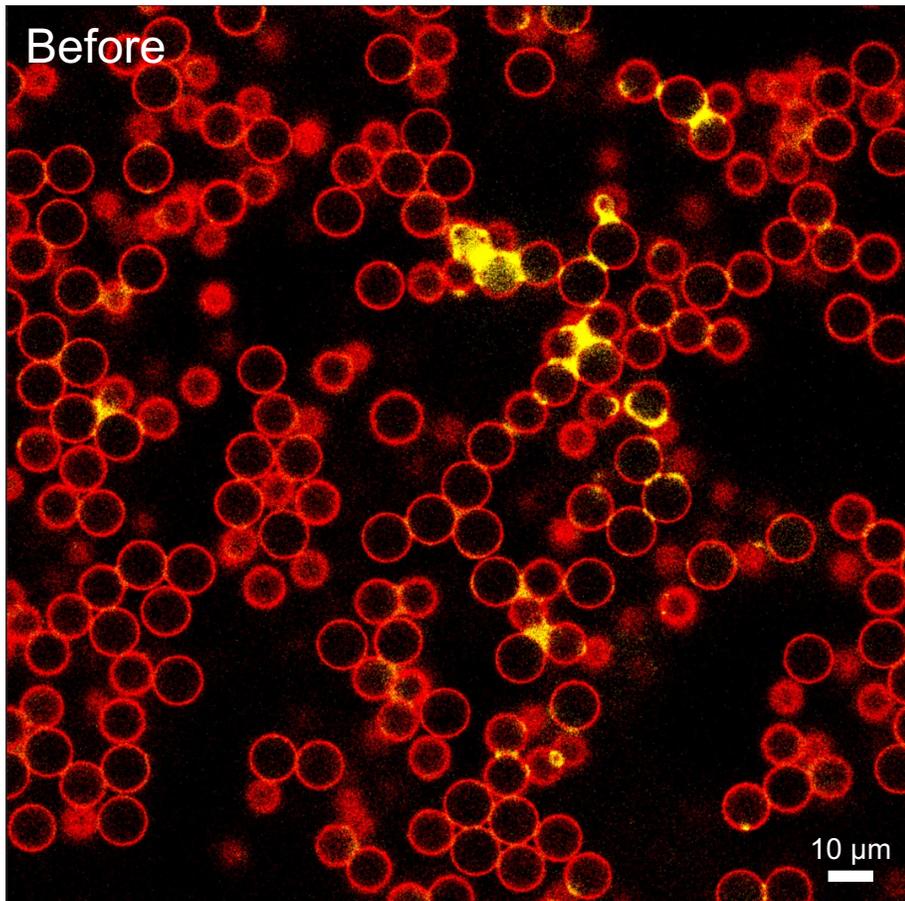
# Compression w/o NP – Relative Movement

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



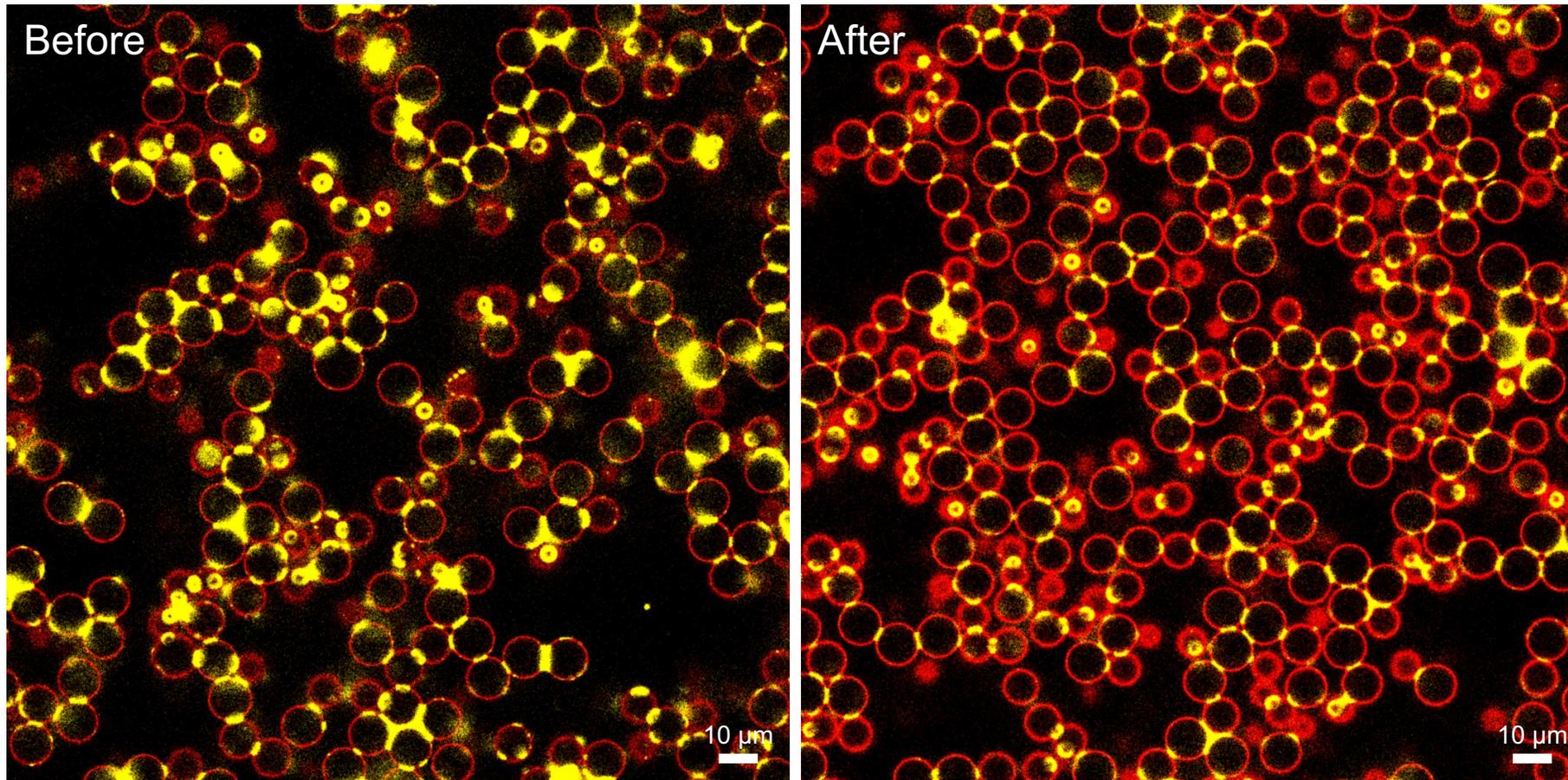
- Network I **resists** compression. Network II remains **rigid without** internal **relative movements**
- In capillary suspensions without nanoparticles, microparticles move in **bulk**

# Before & After compression without NP



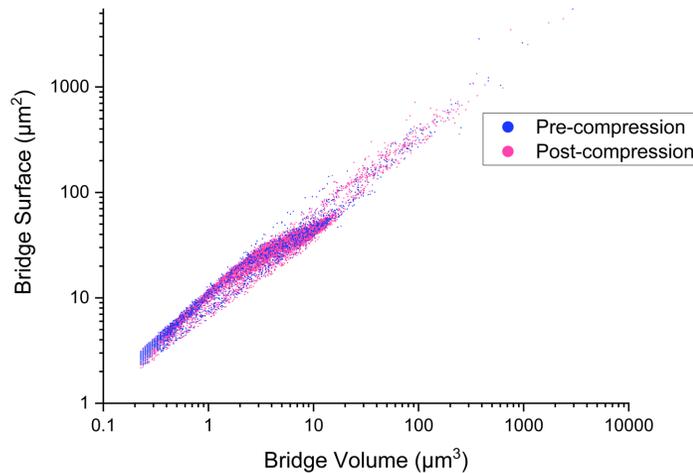
- 30 μm from bottom
- Sec. liquid redistribution
  - Bridge coalescence
  - Trimer breakage
  - Bulk liquid disappears
- No obvious increase  $\phi_{MP}$

# Before & After compression with NP



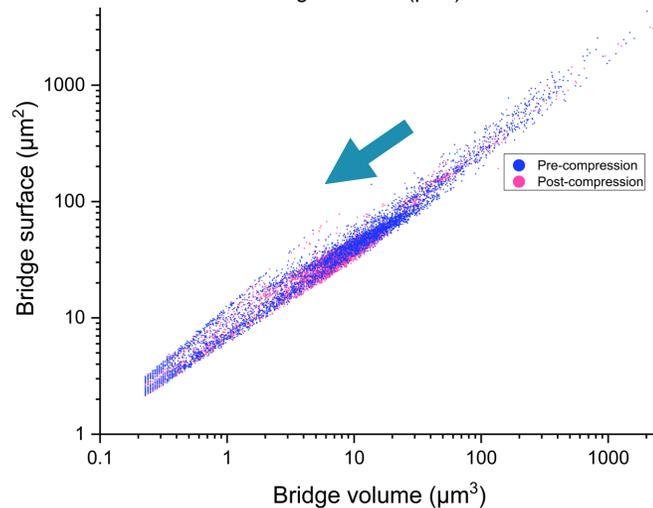
- 30  $\mu\text{m}$  from bottom
- Sec. liquid redistribution
  - Bridge size smaller
  - Bulk liquid disappear
- Strong increase in  $\phi_{MP}$

# Bridge distribution evolution



## No NP

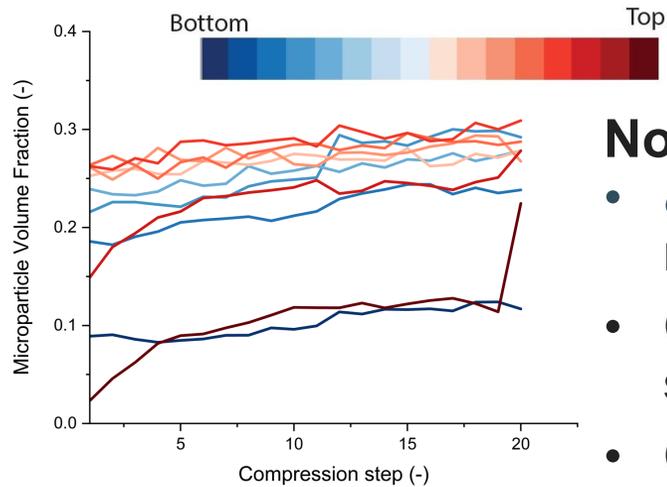
- Partial pre-compression bridges too small to analyze
- Bridge **coalescence**, trimer breakage
- Bridge volume generally **increasing**
- **Limited** liquid exchange



## Hydrophilic NP

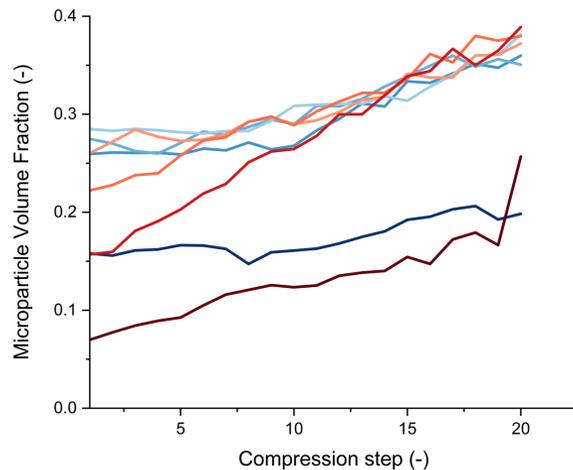
- Large agglomerates **disappear**
- **Small** bridges formed
- **Elevated** liquid exchange between bridges
- Due to NPs-induced **liquid films** at MP surfaces

# Microstructural changes



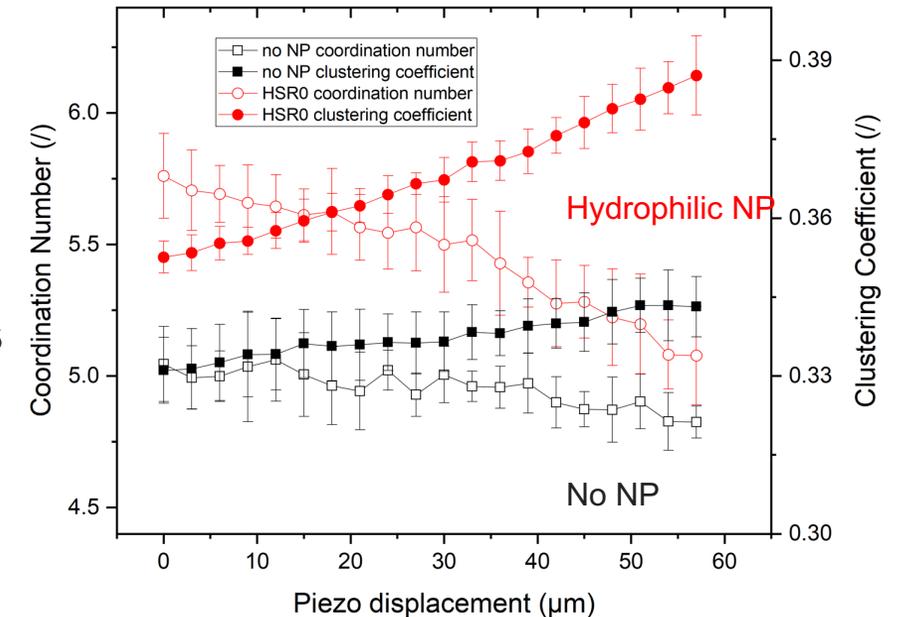
## No NP

- $\phi_{MP}$  increases **abruptly** and **mildly**
- Coordination number increases **slightly**
- Clustering coefficient **fluctuates**



## Hydrophilic NP

- $\phi_{MP}$  increases **homogeneously, converges**
- Coordination number increases **dramatically**
- Clustering coefficient **decreases greatly**



# 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

