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Investigation of capillary (nano)suspensions

IFPRI Annual Meeting 2024

Erin Koos

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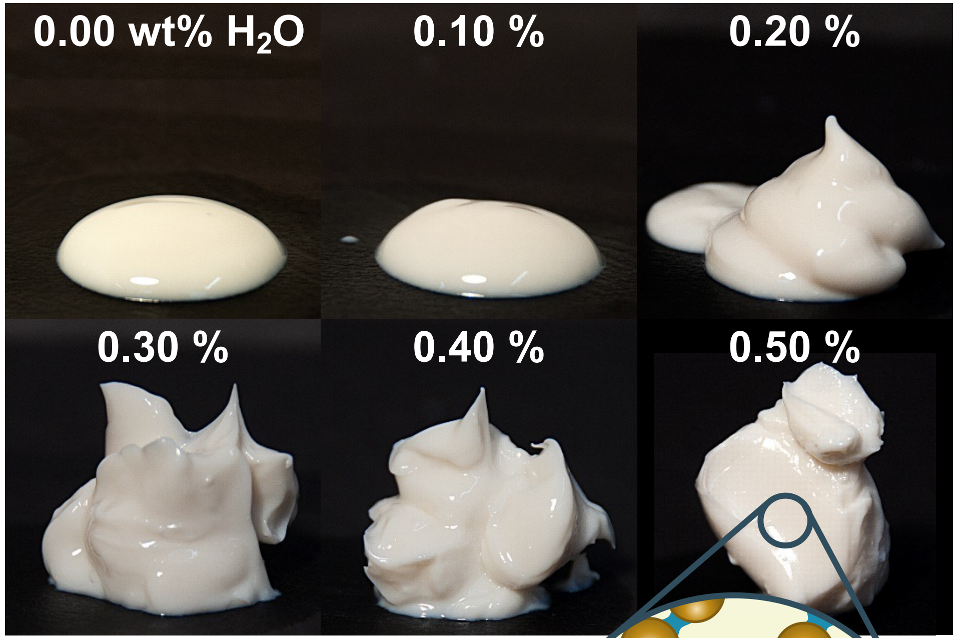
Department of Chemical Engineering
Section Soft Matter, Rheology and Technology

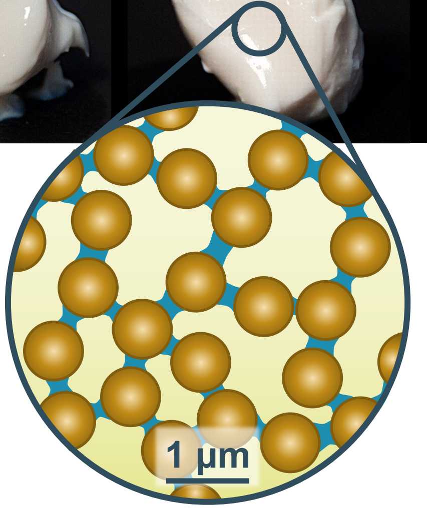
The capillary suspension phenomenon

Micro- or nanoparticles

Two immiscible liquids



Capillary suspension



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

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Enhanced contact flexibility from nanoparticles in capillary suspensions

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

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L. Liu, J. Allard, E. Koos, *J Colloid Interface Sci* **665**, 643-654 (2024)

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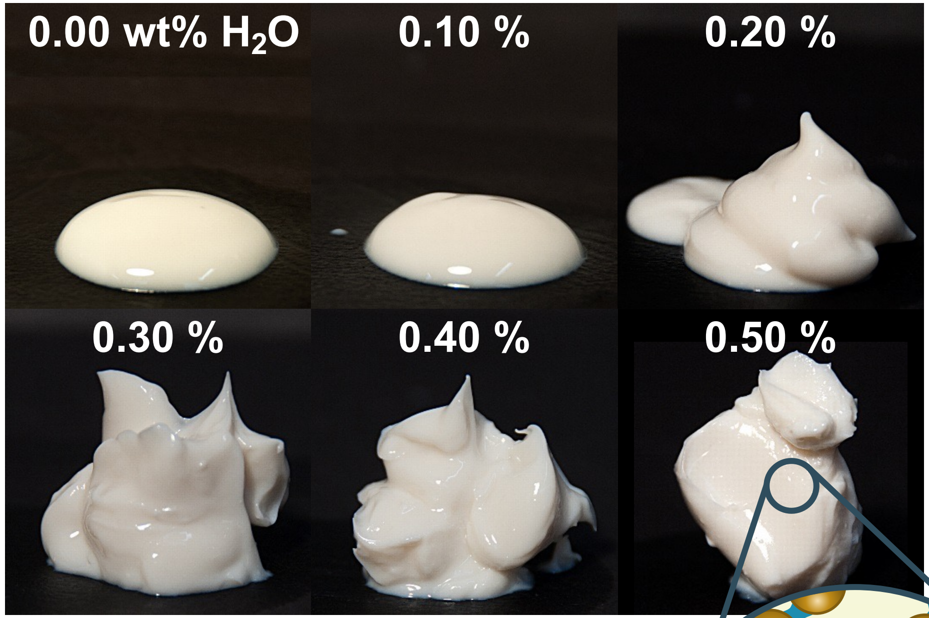
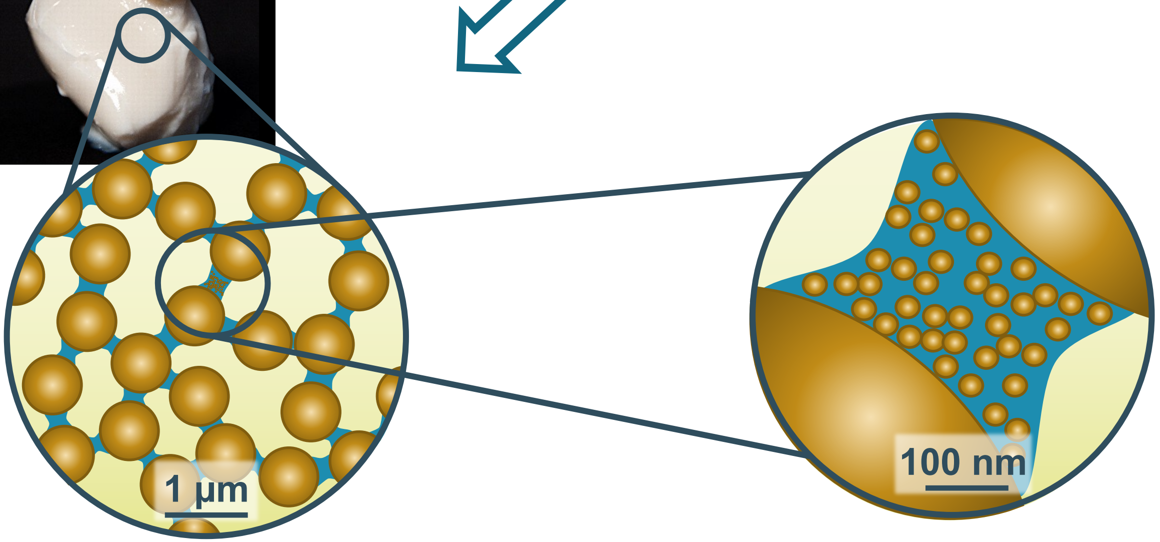
Capillary **nano**suspension (S-L-L-S)



Nanoparticles



Nanoparticles added with bridging liquid

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

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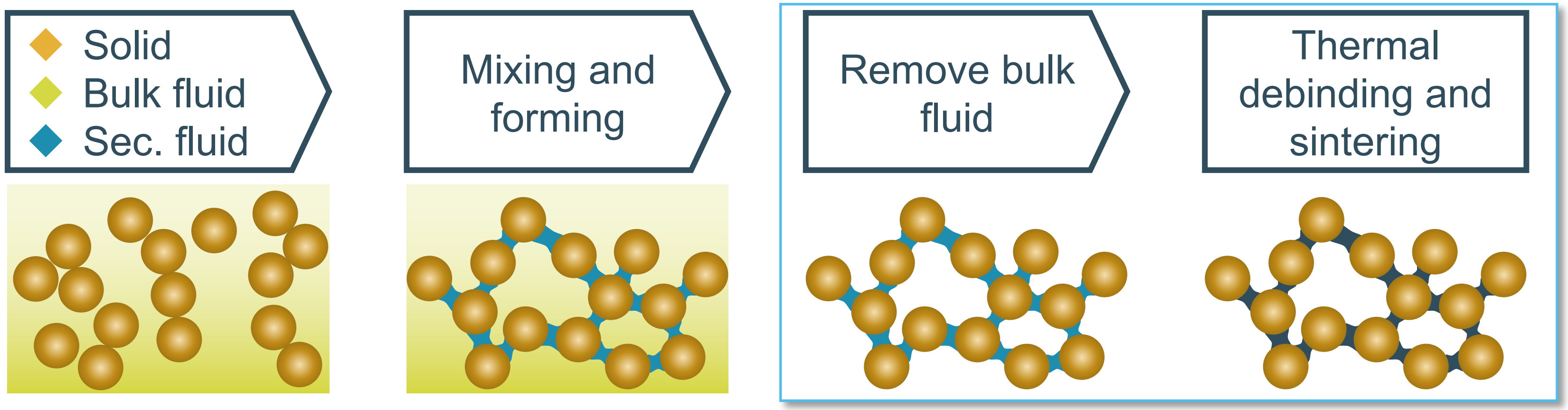
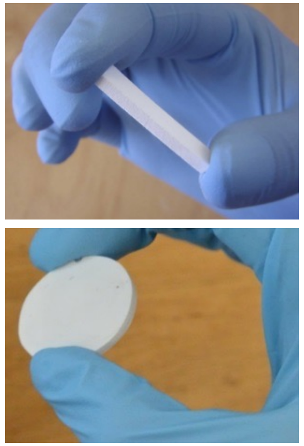
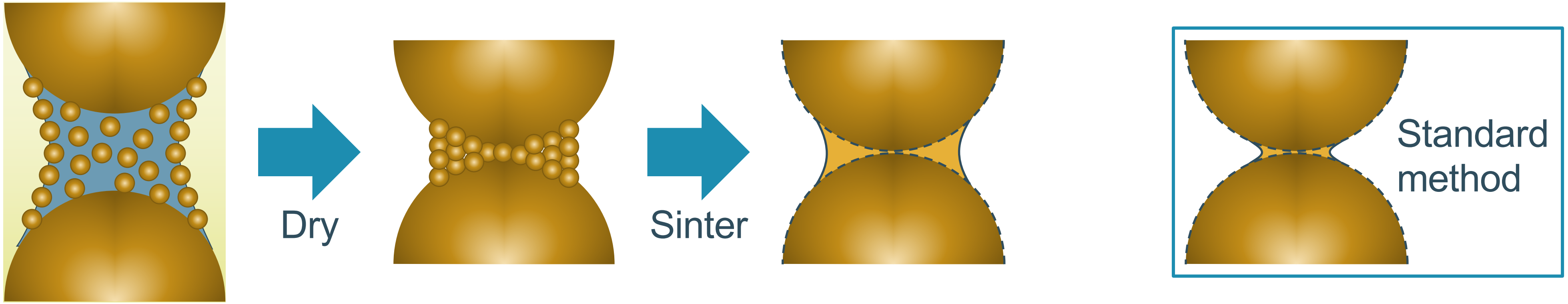
Porous ceramics from capillary nanosuspensions





- Incorporate nanoparticles into bridging fluid



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

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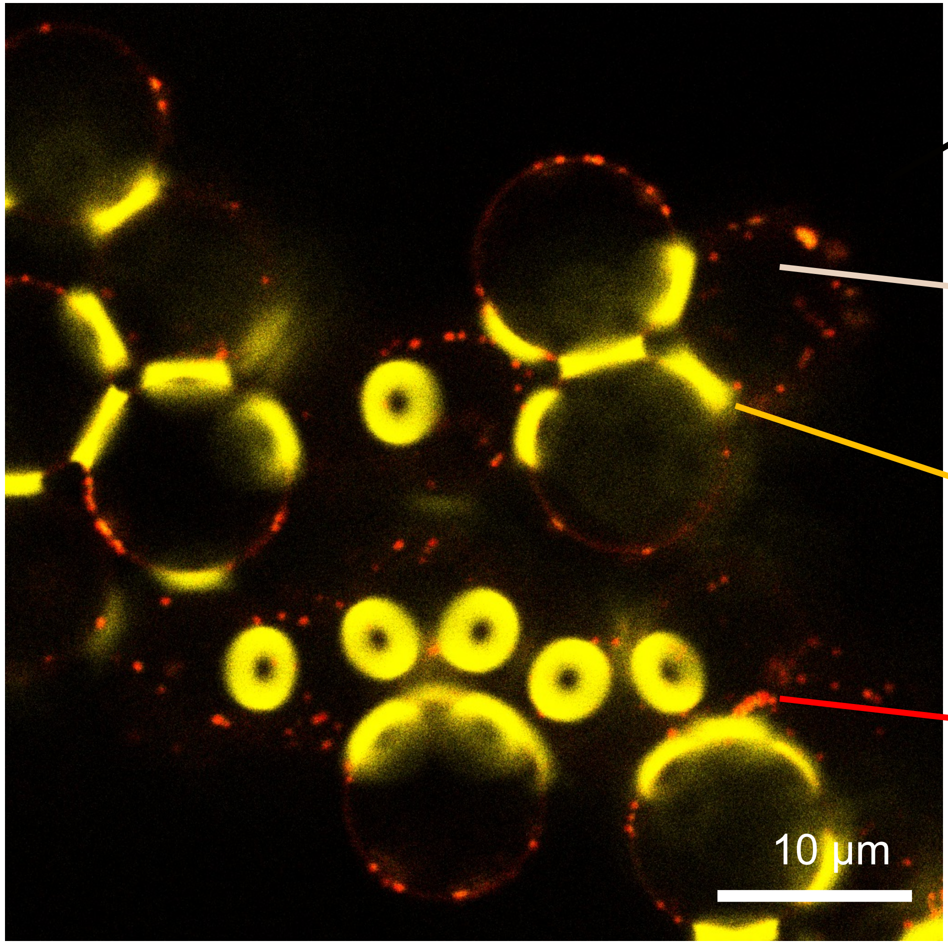
Confocal model system

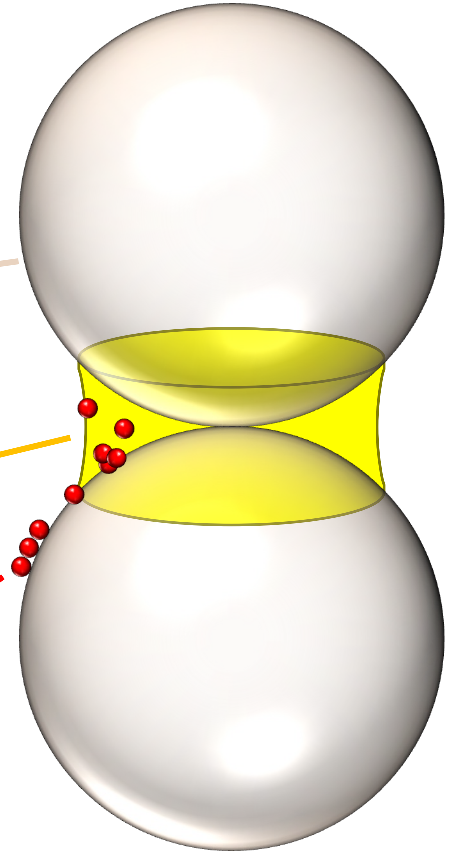


Oil/ **Bulk phase**
(Hexamoll Dinch/ Dodecane)

Undyed silica **MP**, 10 μm
Φ_{MP} = 20 %

Water/ **Secondary liquid phase**
Aqueous glycerol dyed with
PromoFluor 488, Φ_{sec} = 1 %

150 nm silica **NP** dyed with
rhodamine B isothiocyanate
Φ_{NP} = 1 % Φ_{sec} = **0.01** %



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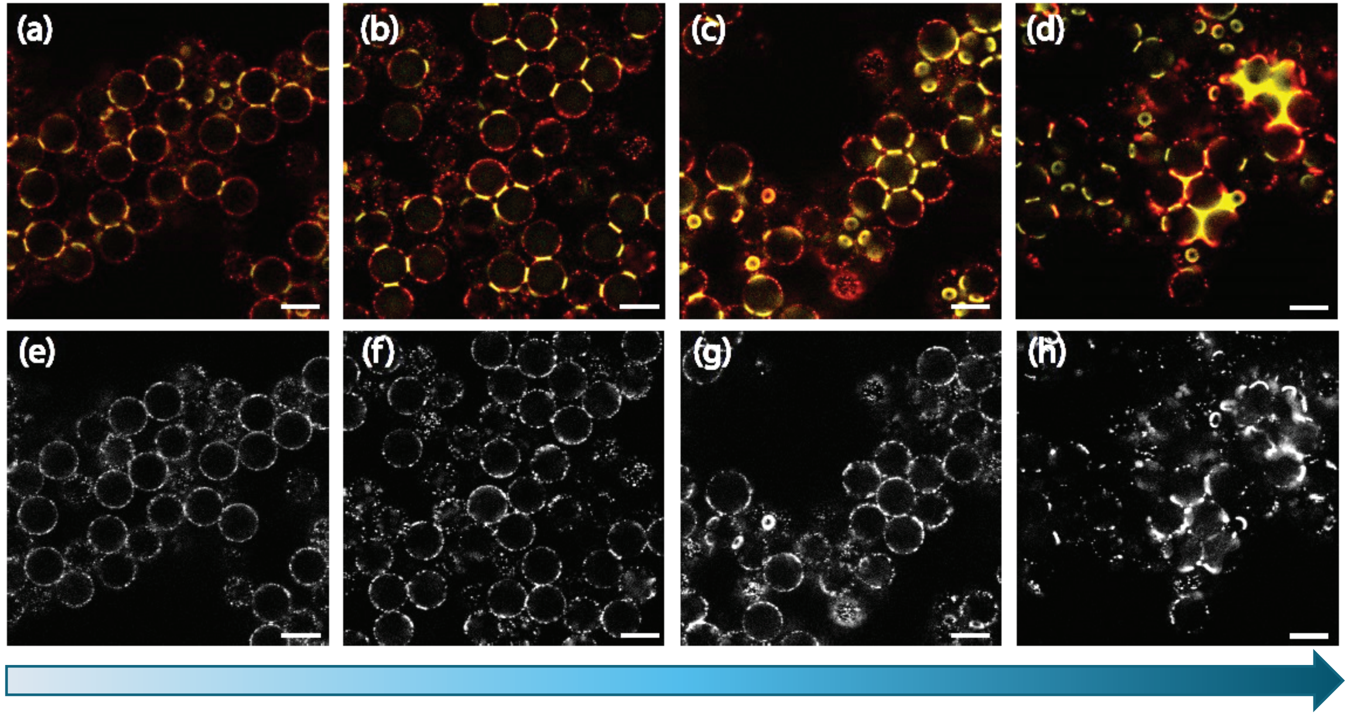
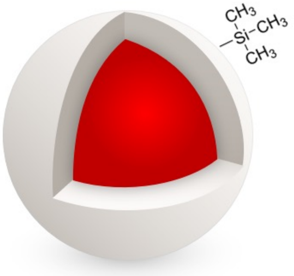
Influence of NP hydrophobicity

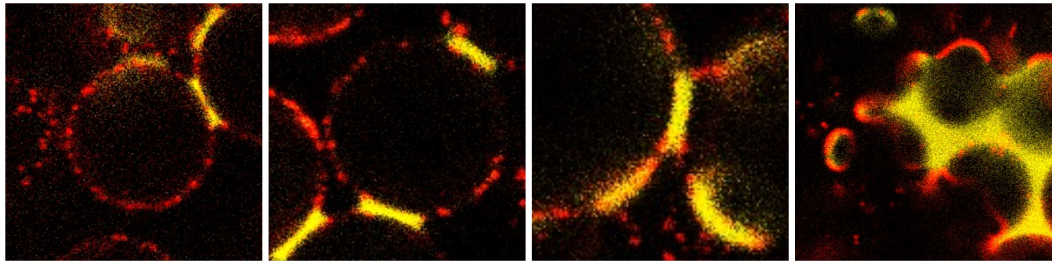


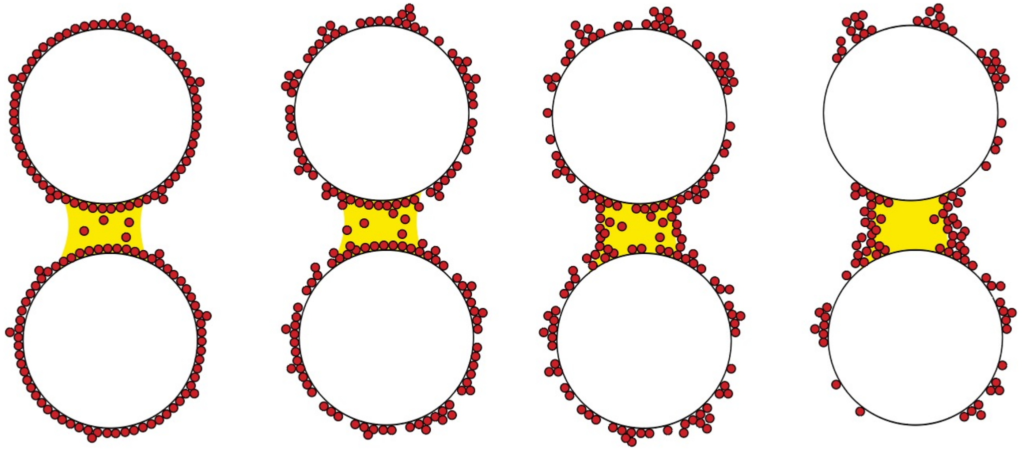


HMDS added to hydrophobize NPs

HSR = HMDS (μl) : Silica NP (mg)

Number ↑ = 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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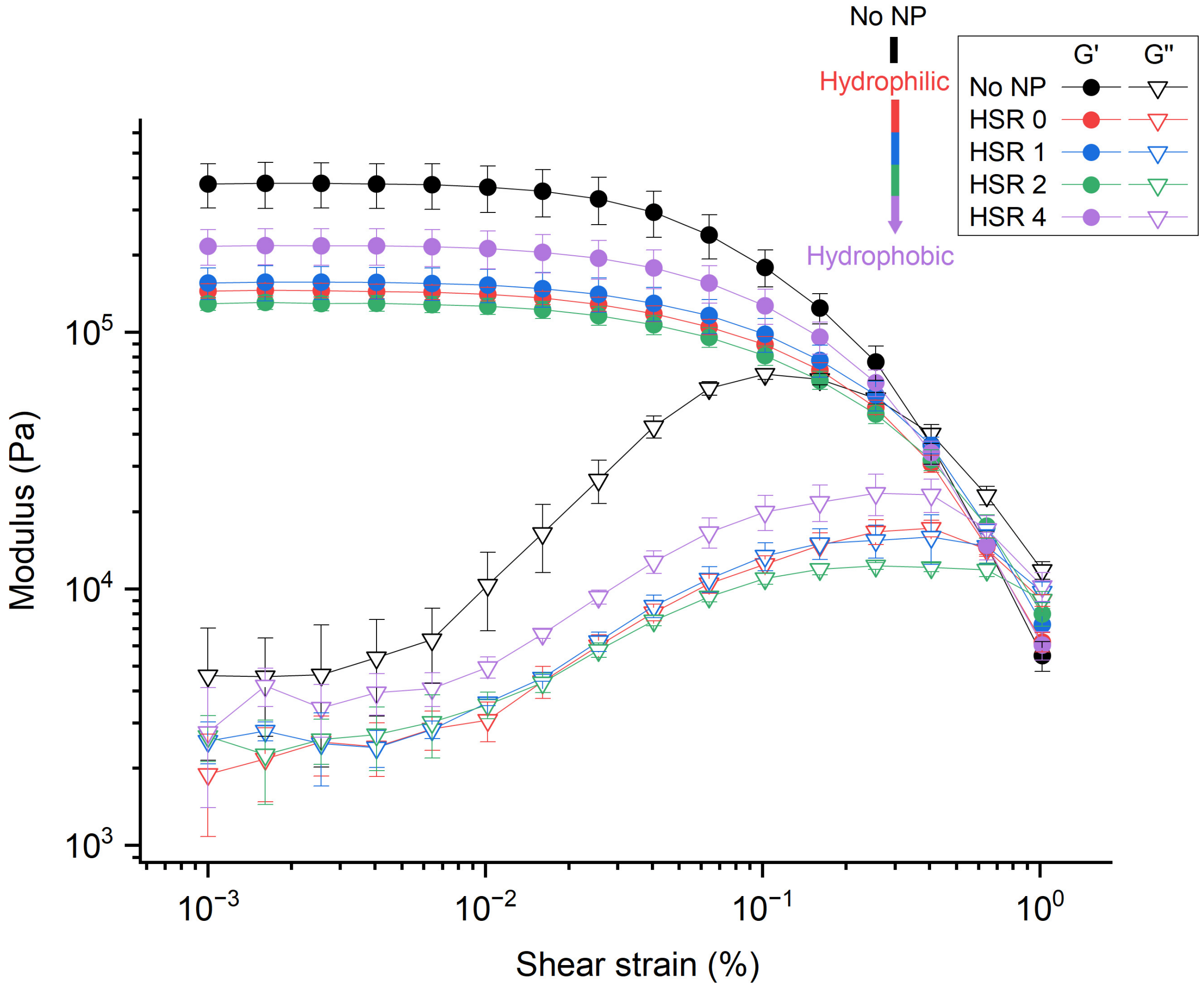
Rheological measurements



- Addition of nanoparticles reduces shear moduli
- Samples with NP have similar values & G'' peak
- HSR 4 has the highest moduli
  - Reinforcement of bridges and extra surface elasticity?

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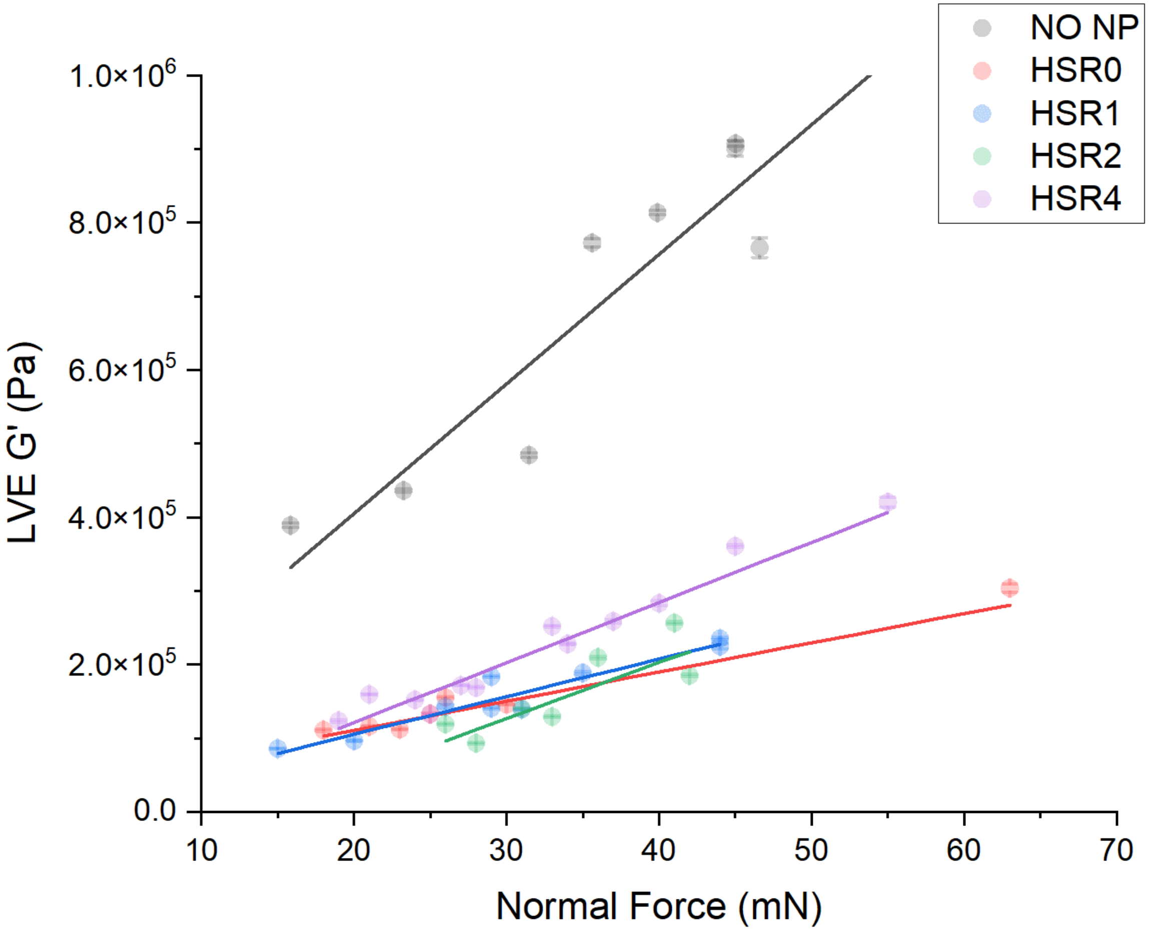
Normal force & G' at LVE



- G' at LVE versus normal force for 1.025 mm gap
- Sample without NPs has **highest** slope & G_0'
- G_0'/F_N reflects the **rigidity** of network
  - Slope **increases** with **increasing** hydrophobicity
    - No NPs: 18000 ± 1000
    - HSR0: 4000 ± 900
    - HSR1: 5100 ± 700
    - HSR2: 7600 ± 2000
    - HSR4: 8200 ± 900
  - HSR4 distinguishable from the other 3 samples

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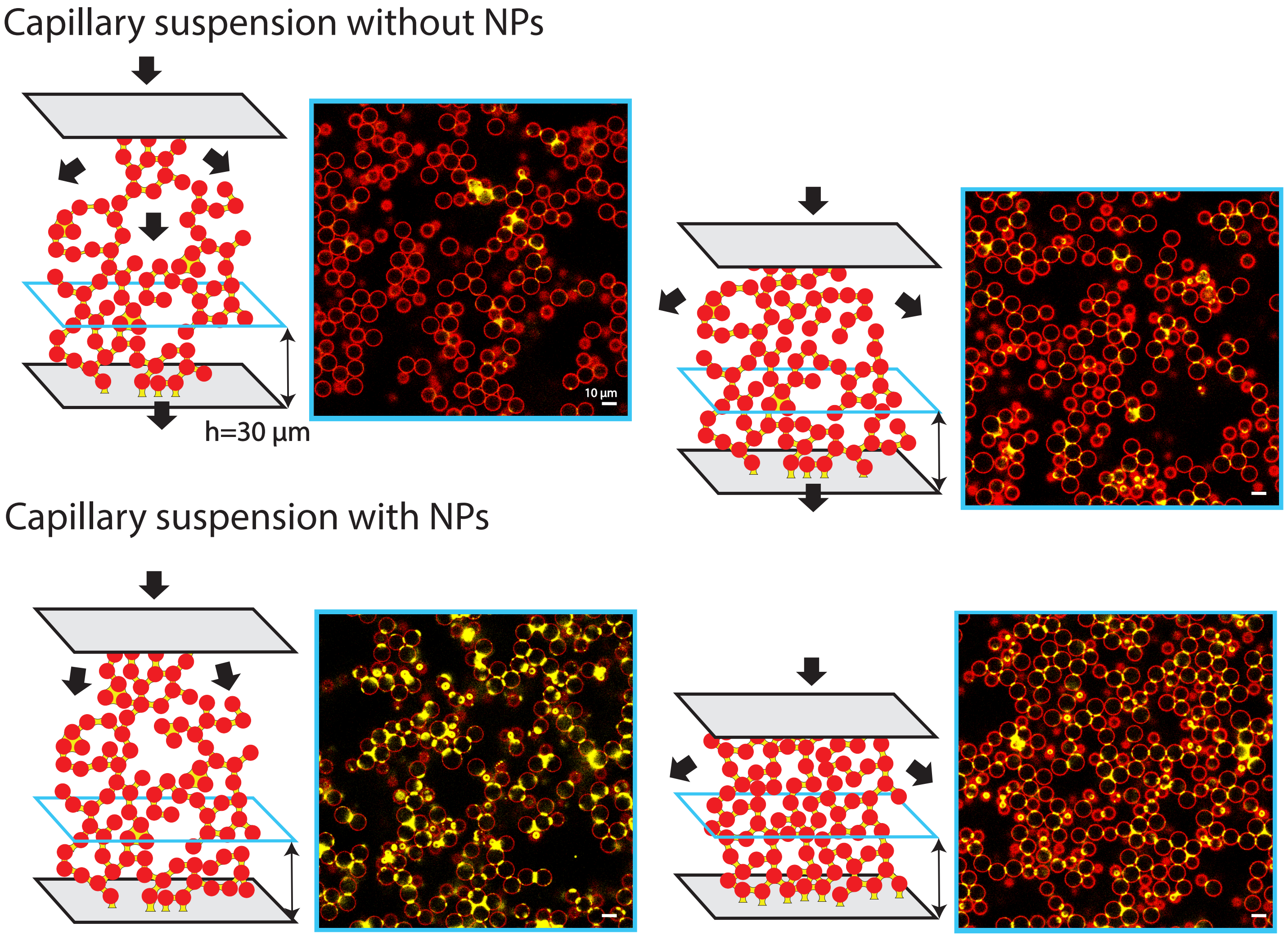
Compression experiments



No NP

- Bottom glass deflected
- Bridge coalescence
- Trimer breakage
- No obvious increase ϕ_{MP}

Hydrophilic NP

- Redistribution of liquid bridges
- Average bridge size decreases
- Strong increase in ϕ_{MP}

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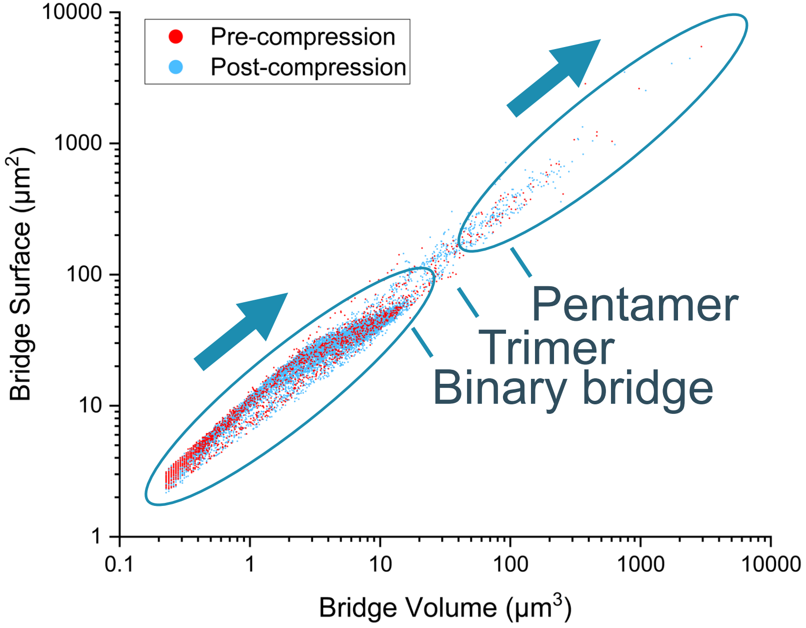
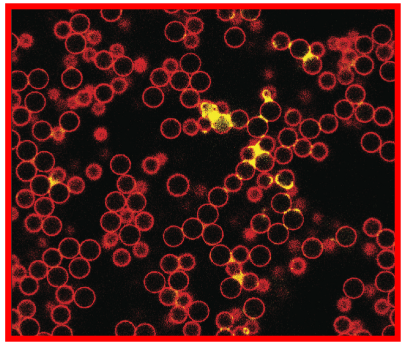
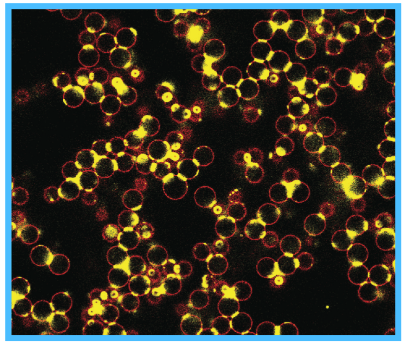
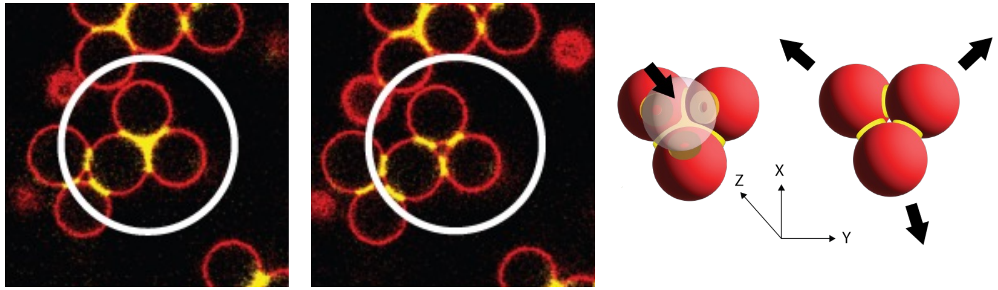
Bridge distribution evolution: No NP







- Start:
  - Small bridges between asperities
  - Few agglomerates
- End:
  - Larger pendular bridges
  - More agglomerates



- Mechanism
  - Asperity bridge coalescence
  - Trimers breaking
- Limited liquid exchange

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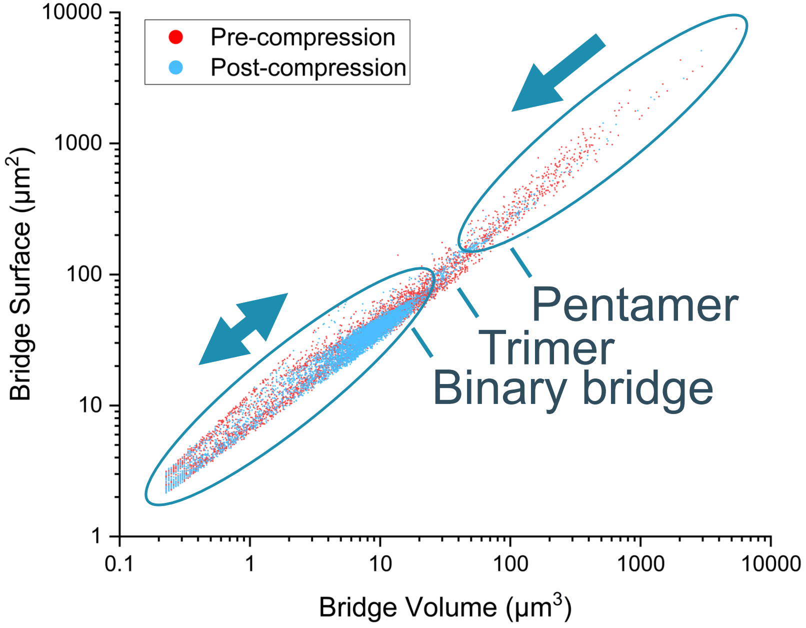
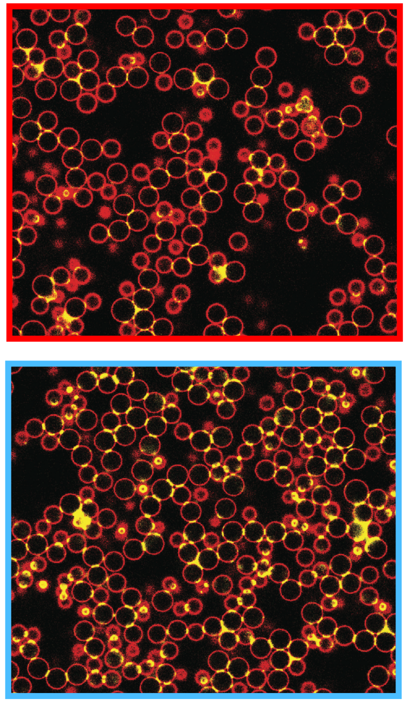
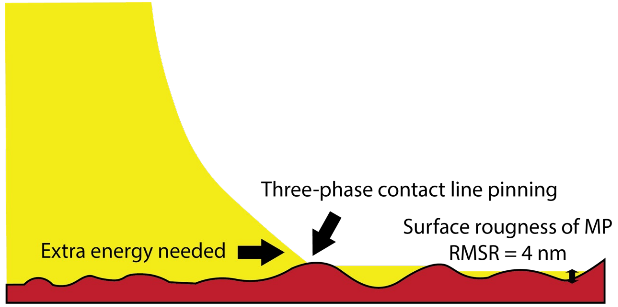
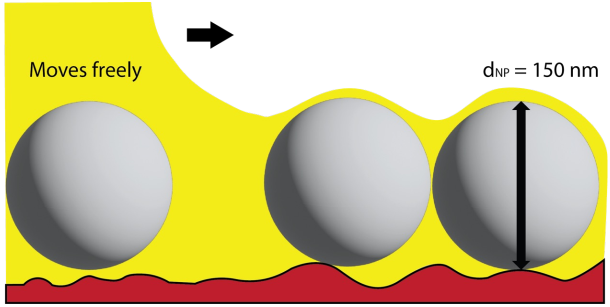
Bridge distribution evolution: Hydrophilic NPs





- Start:
  - Small bridges between asperities
  - Many agglomerates
- End:
  - More (including smaller) pendular bridges
  - Fewer agglomerates





- Mechanism
  - Compaction
  - Breaking of agglomerates
- NP-induced liquid exchange

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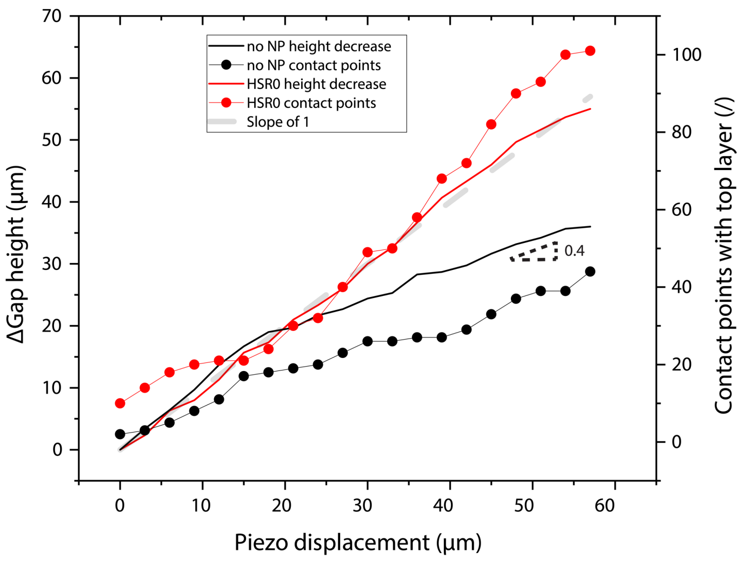
Particle volume fraction change

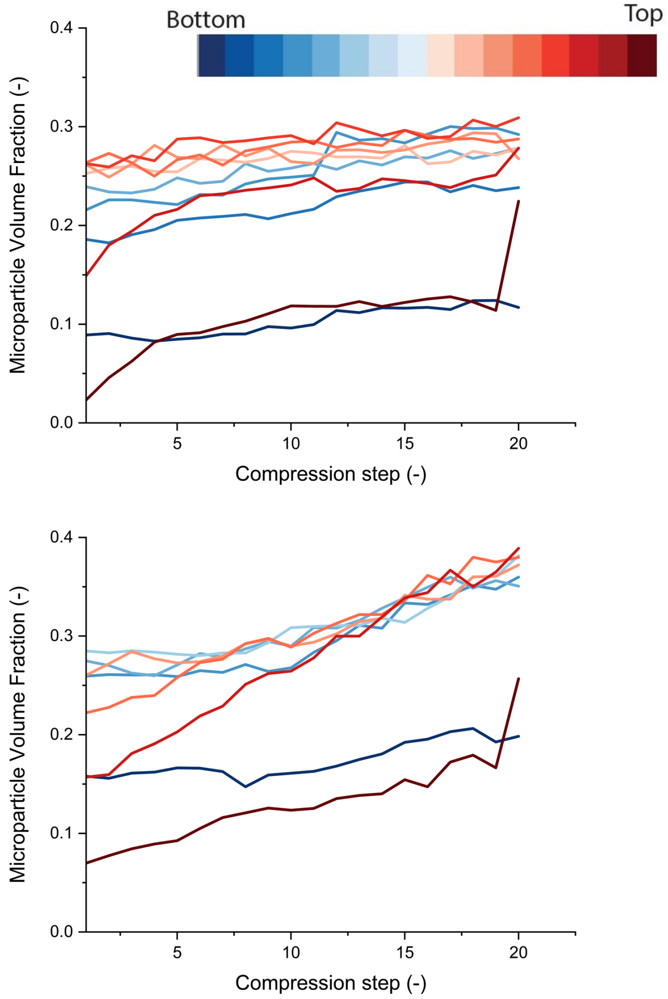
No NP
- Network resists compression
- ϕ_{MP} increases **abruptly** in first steps then **mildly**

→ **Rigid, Hertzian contact**

Hydrophilic NP
- Network readily compresses
- ϕ_{MP} increases uniformly, **converges**

→ **Flexible contact**





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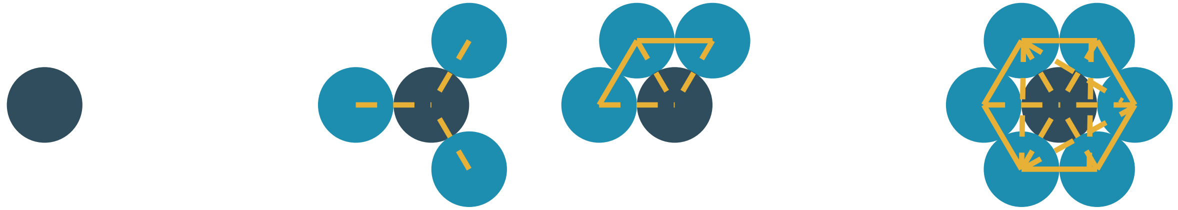
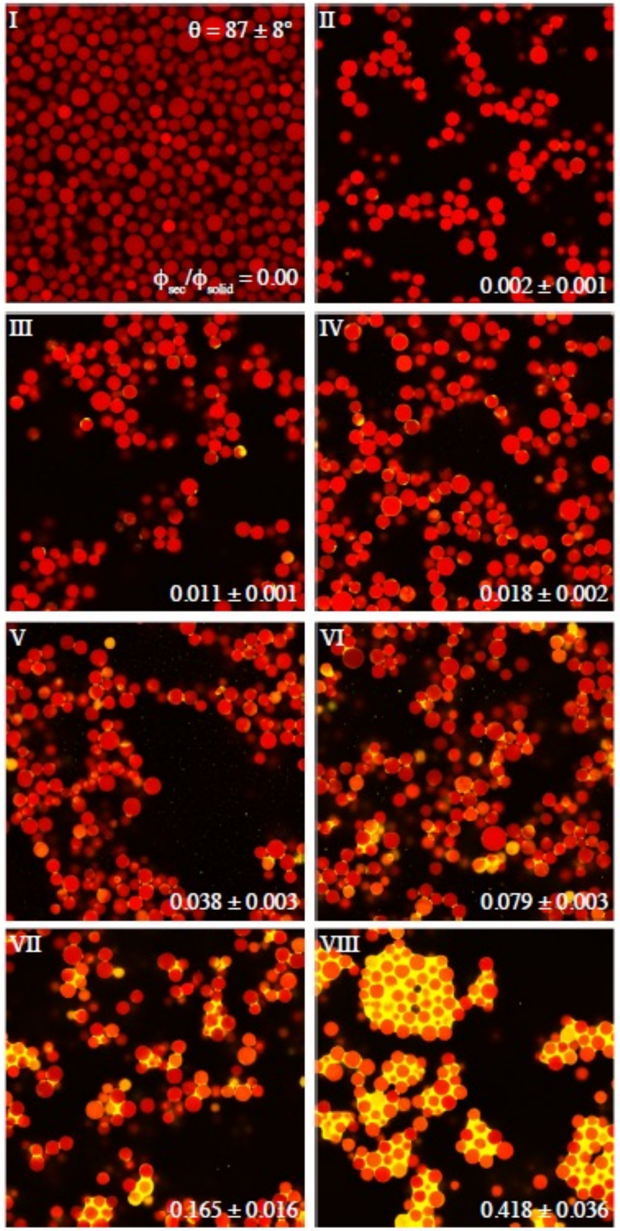
Local measures describe effects of ϕ_{sec} on shear moduli

Coordination number z and clustering coefficient c (semi-local measurements)



$z = 0$, $c = 0$ | $z = 3$, $c = 0$, $c = 2/3$ | $z = 6$, $c = 1$

- Transition between different structures
  - e.g. linear, clustered, bicontinuous, phase separation
- Bulk rheological response
  - storage and loss moduli



S Bindgen, et al., *Soft Matter* **16(36)**, 8380 (2020)

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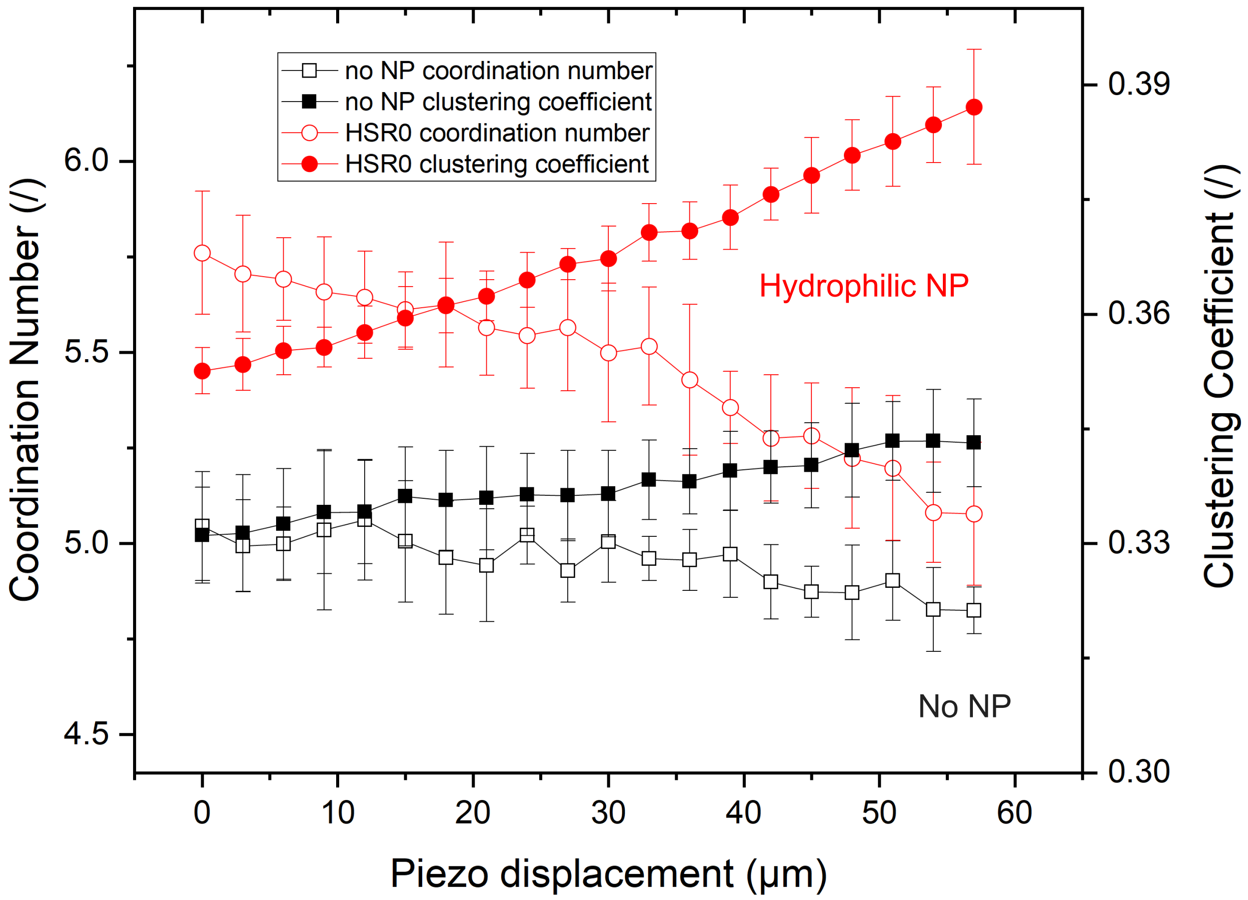
Microstructural changes

No NP

- Coordination number increases **slightly**
- Clustering coefficient **fluctuates**

Hydrophilic NP

- Coordination number increases **dramatically**
- Clustering decreases **greatly**



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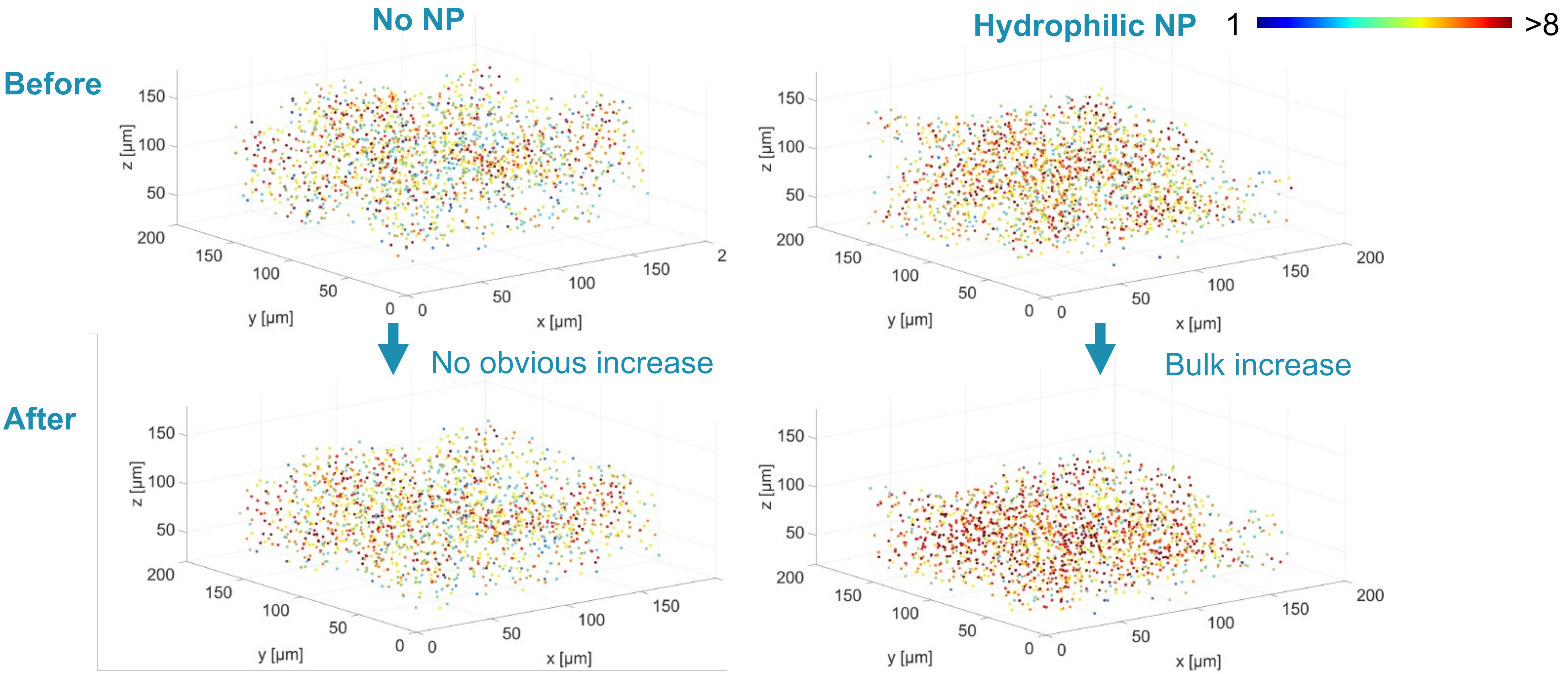
Coordination number pre-/post- compression



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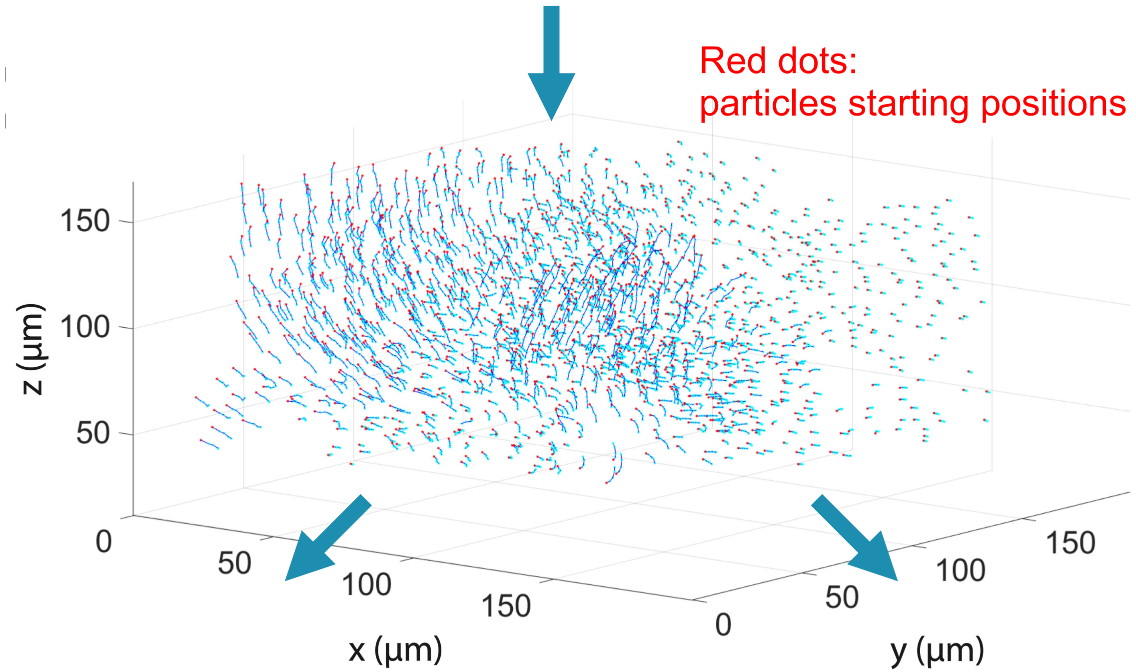
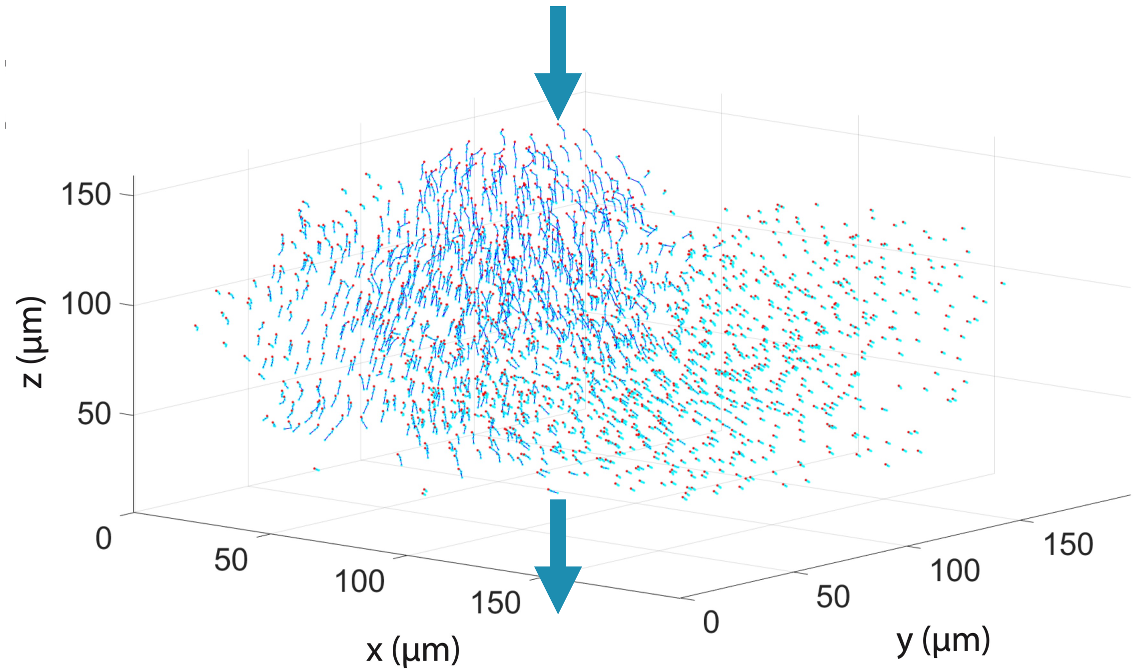
Tracking particle motion





No NP

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

Hydrophilic NP

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

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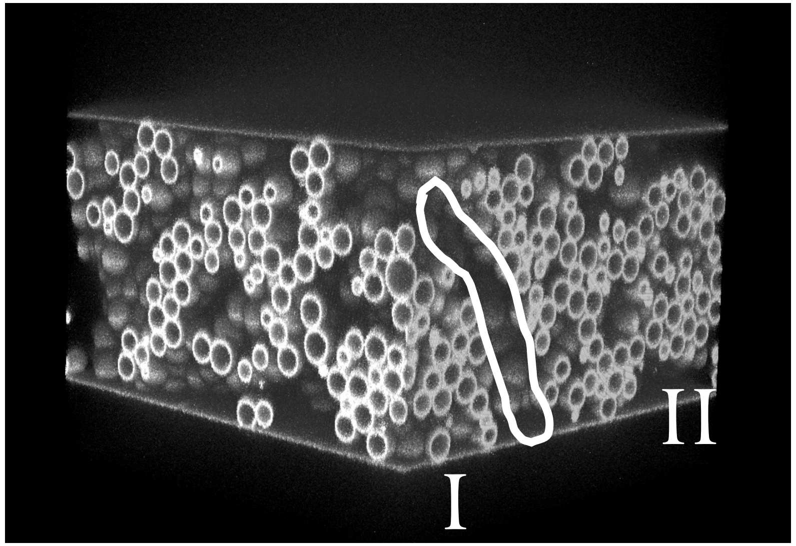
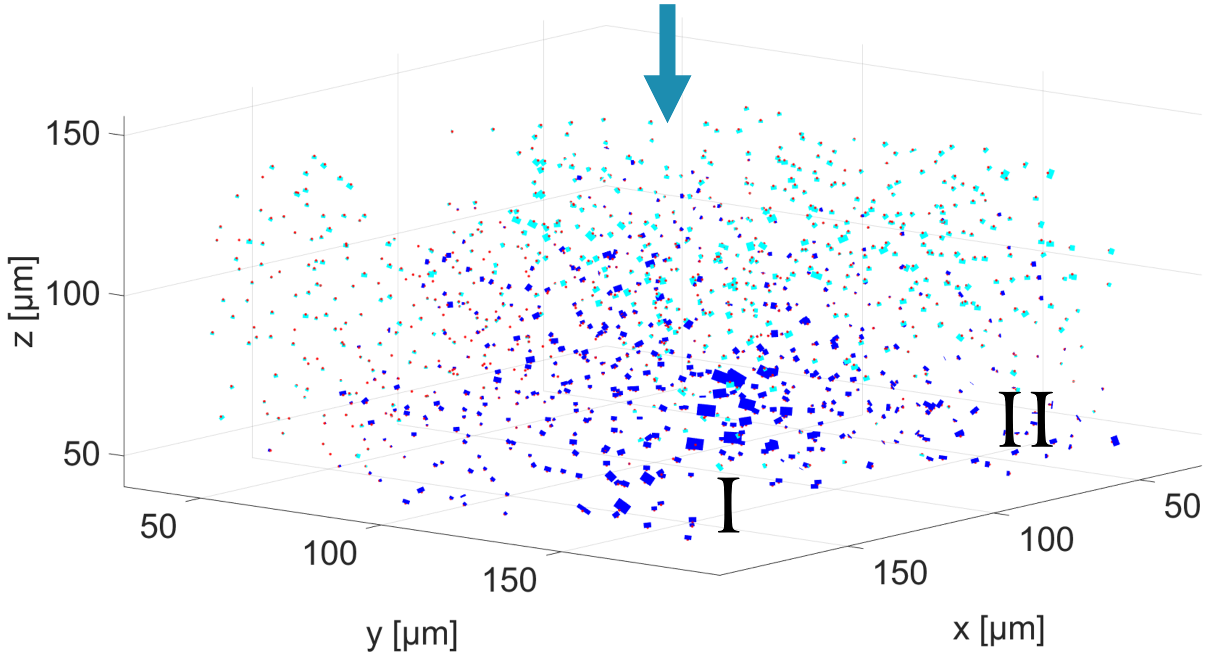
Compression w/o NP – Relative Movement

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





- Region I **resists** compression
- Region II remains **rigid without** internal **relative movements**

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Conclusions

- Hydrophilic NP result in **lower** G' in LVE and show reduced G'' peak
- Network without NPs is **rigid and does not compress**
  - Hertzian compression, high rolling/sliding friction
  - Bridges coalesce
  - Force chains and rigid body motion sideways
- Network with NPs is **flexible and easily compresses**
  - NP reduce Hertzian contact, decrease rolling/sliding friction
  - **Improved** liquid exchange due to hydrophilic particle wetting
  - No force chains and more uniform compression
- Ready rearrangement and flexibly good for 3D printing?

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Rod-shaped microparticles

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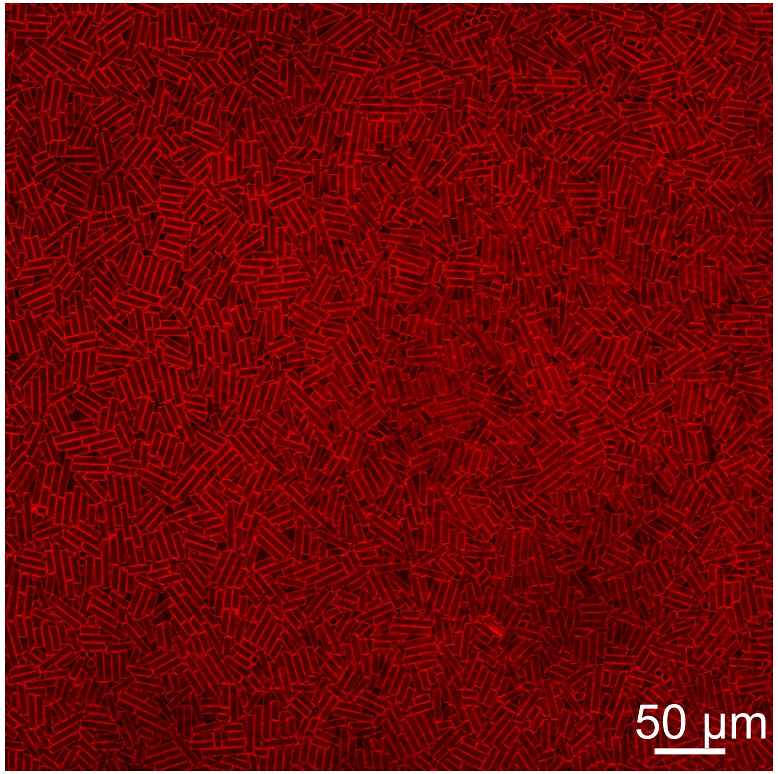
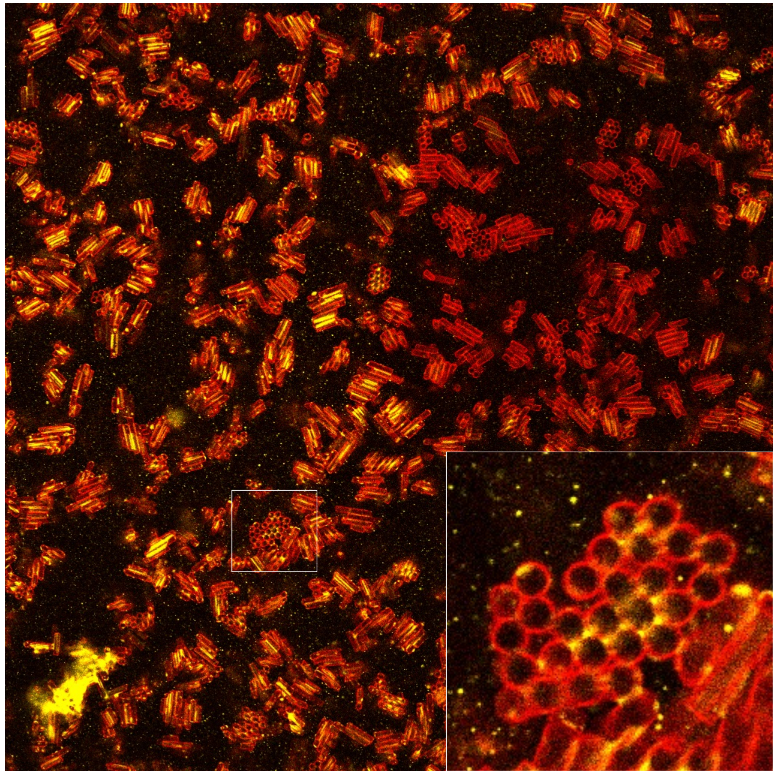
Pure rods suspension vs 15 vol%rods + 1.5 vol% sec.

$\phi_{sec} = 0$



$\phi_{sec} = 1.5\%$



- No sec liquid
  - Sedimentation
  - Longer axes oriented on x-y plane
- 1.5 vol% sec liquid
  - Gel structure
  - Bridges connecting longer axes
  - More random particle orientation
- Problem: sec liquid not perfectly index matched → more limited in depth

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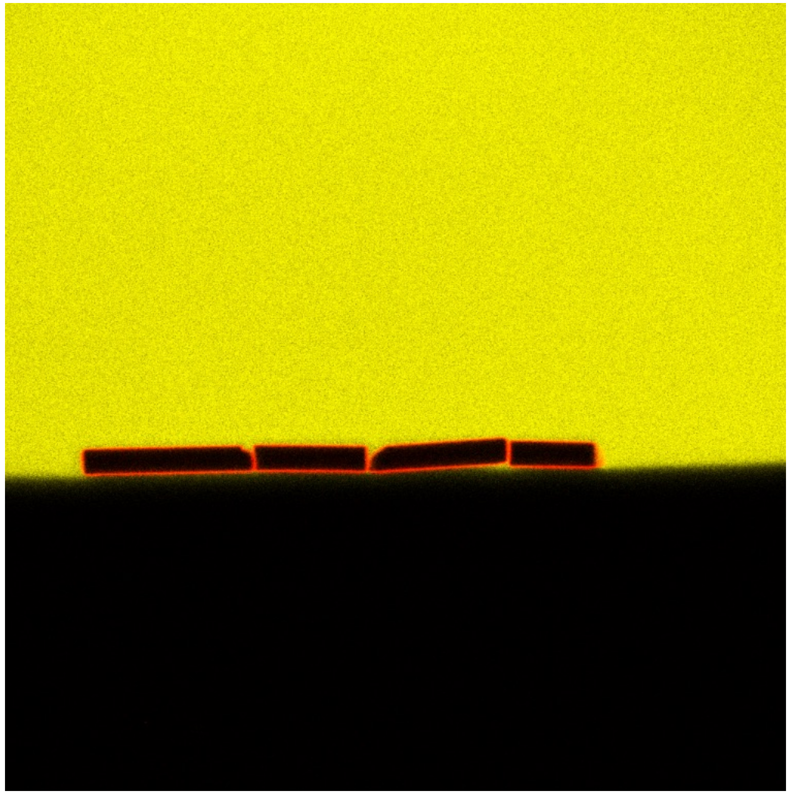
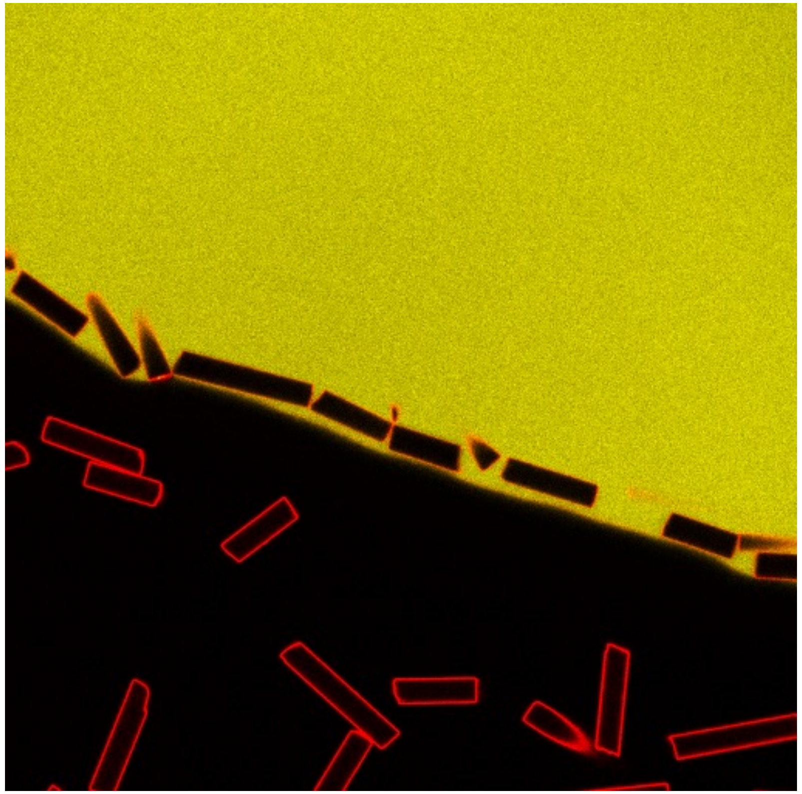
Three-phase contact angle





- Yellow: Aqueous glycerol 50%
- Red: Microrods (glass)
- Black: Cinnamon oil – Hexamoll Dinch mix

- Rods premixed in **oil**
- Inject oil onto water droplet
- Picture taken at equilibrium

- Very hydrophilic
- CA ≈ 0

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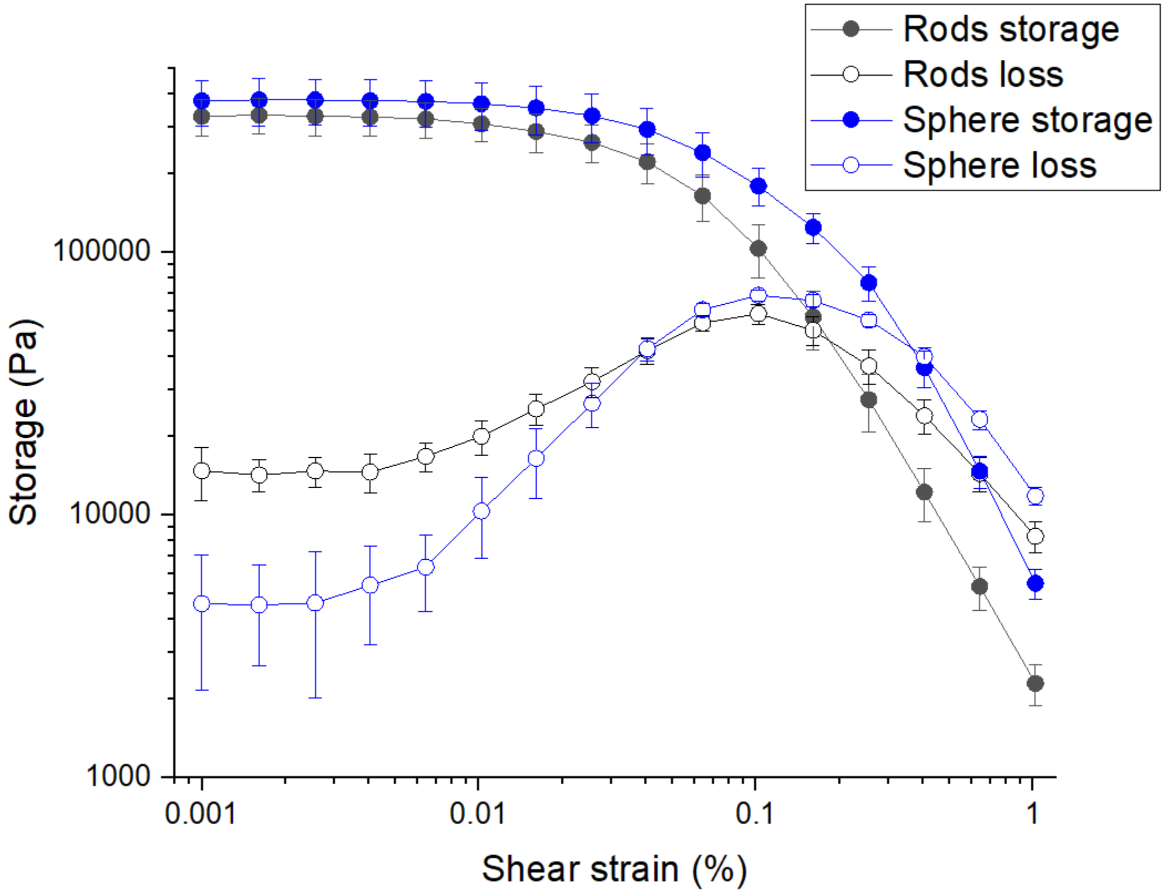
Rheological data



- 15 vol% 6 µm diameter rods, IFT = 11.7 mN/m
- 20 vol% 10 µm spheres, IFT = 25.5 mN/m

- Similar G' despite change in IFT and geometry
- Higher G'' in LVE, overshoot less pronounced

Values sufficient for good measurement on rheoconfocal

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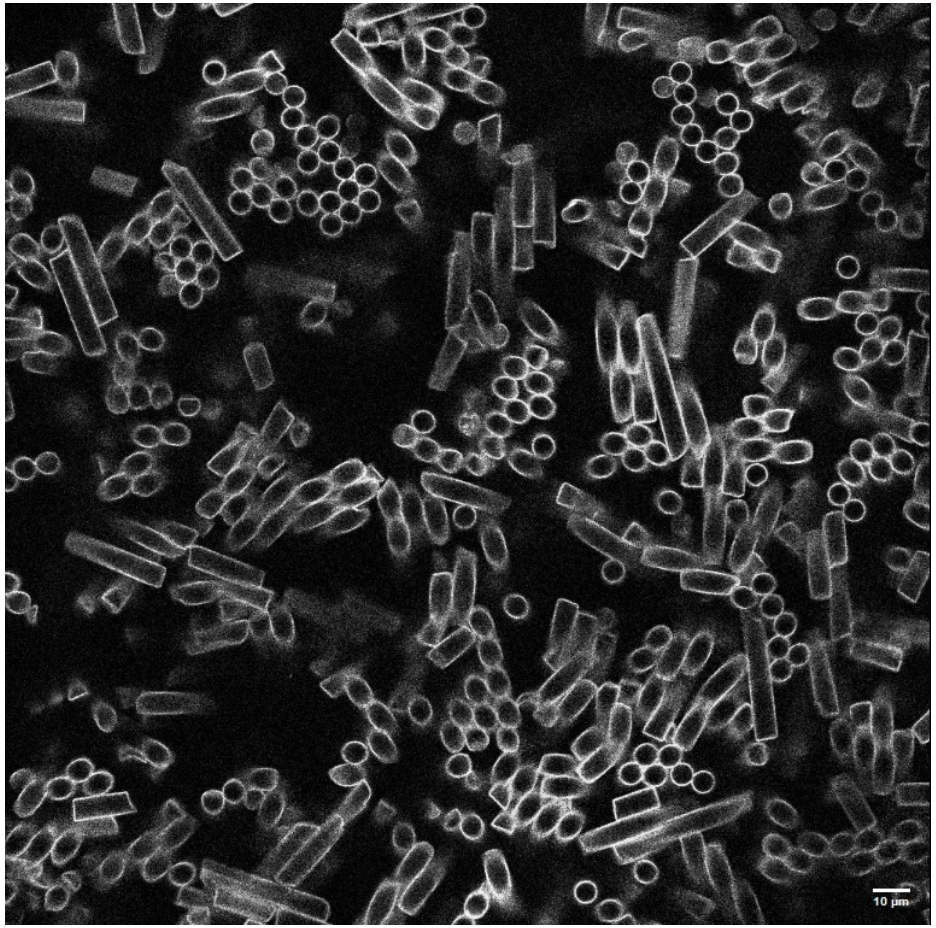
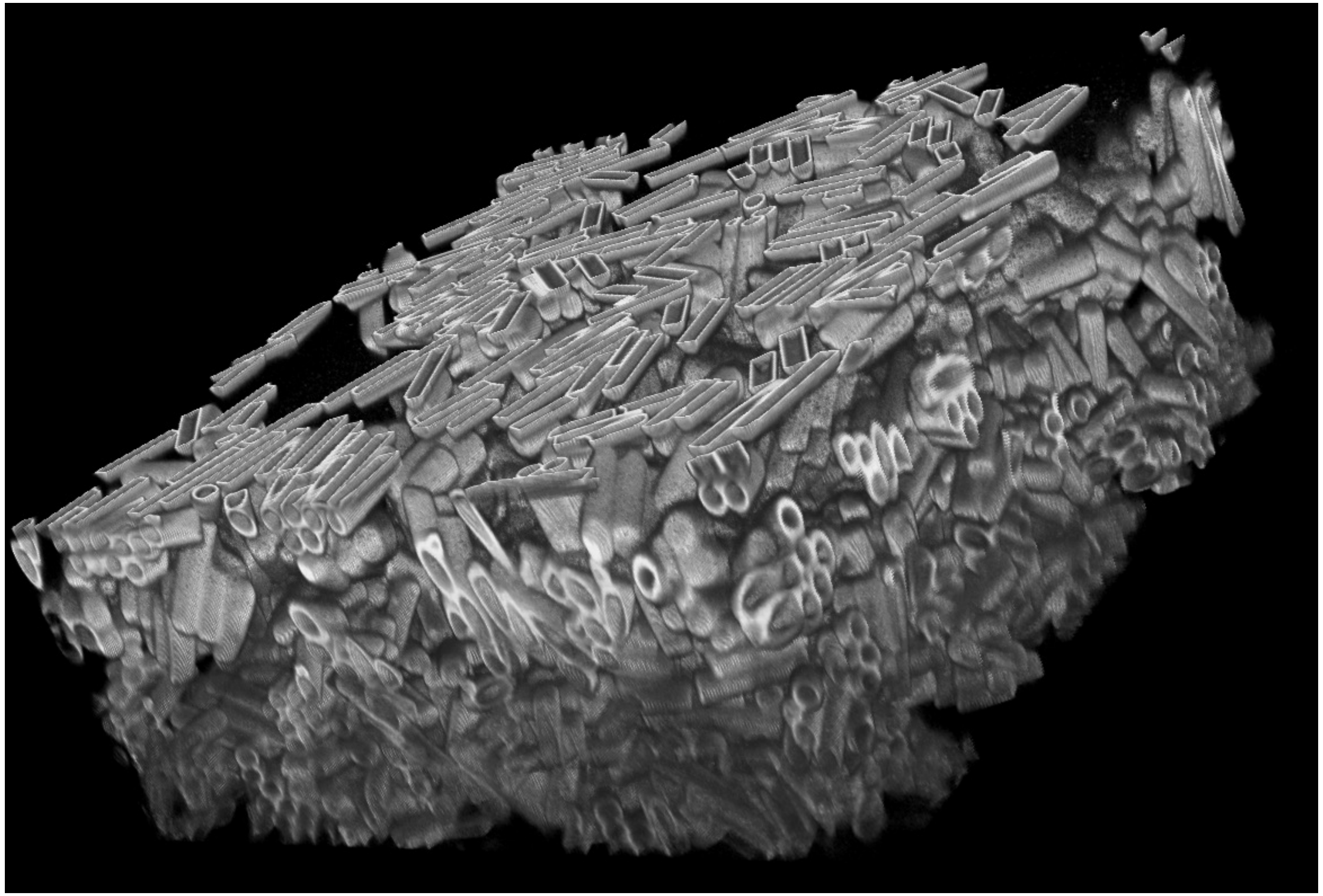
Anisotropic MP imaging





Problem in particle detection: edges of flat particles are not clear

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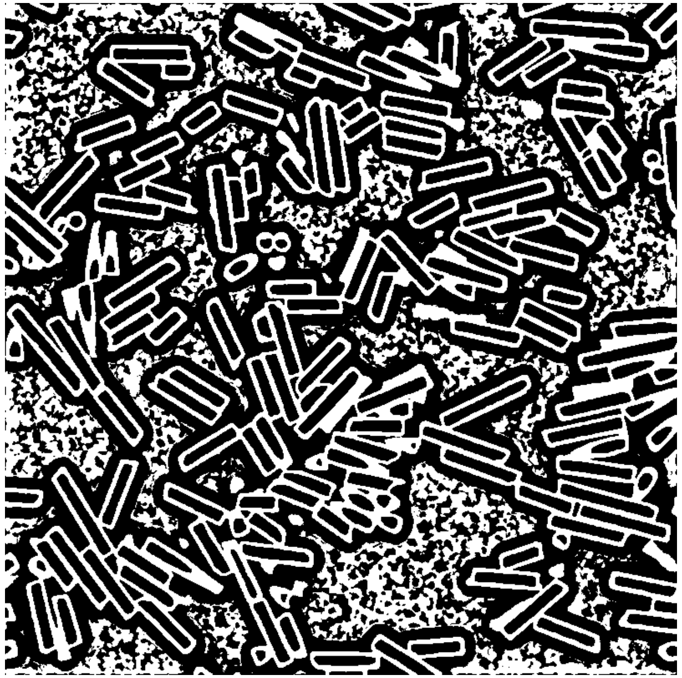
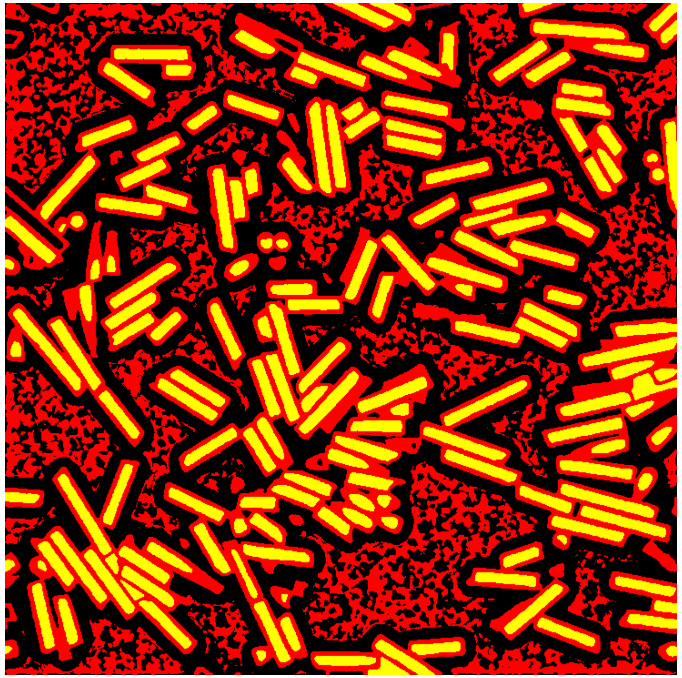
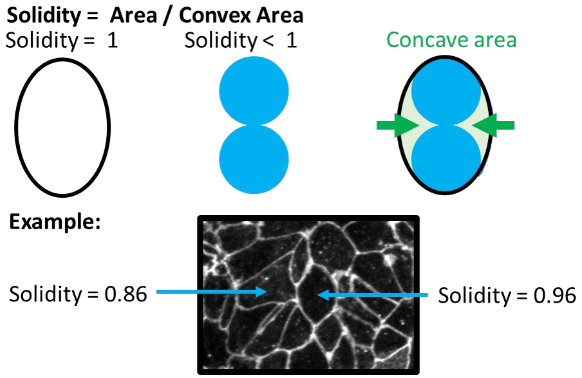
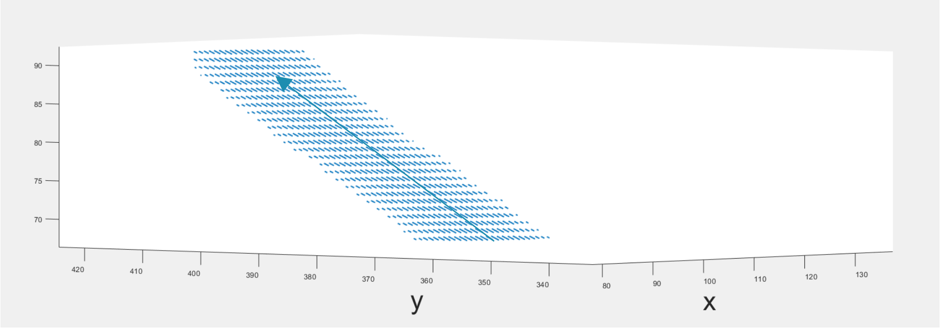
Image analysis – Detection & 3D tracking









- Local thresholding is used to remove background and variations in intensity with z depth
- Enclosed particles are filtered based on min/max size, circularity, smoothness, and solidity
- Each particle on an individual slice is separately detected, centroid are tracking using z (slice) as time, with to tolerance
- Each separately detected particle with voxel list is analyzed individually

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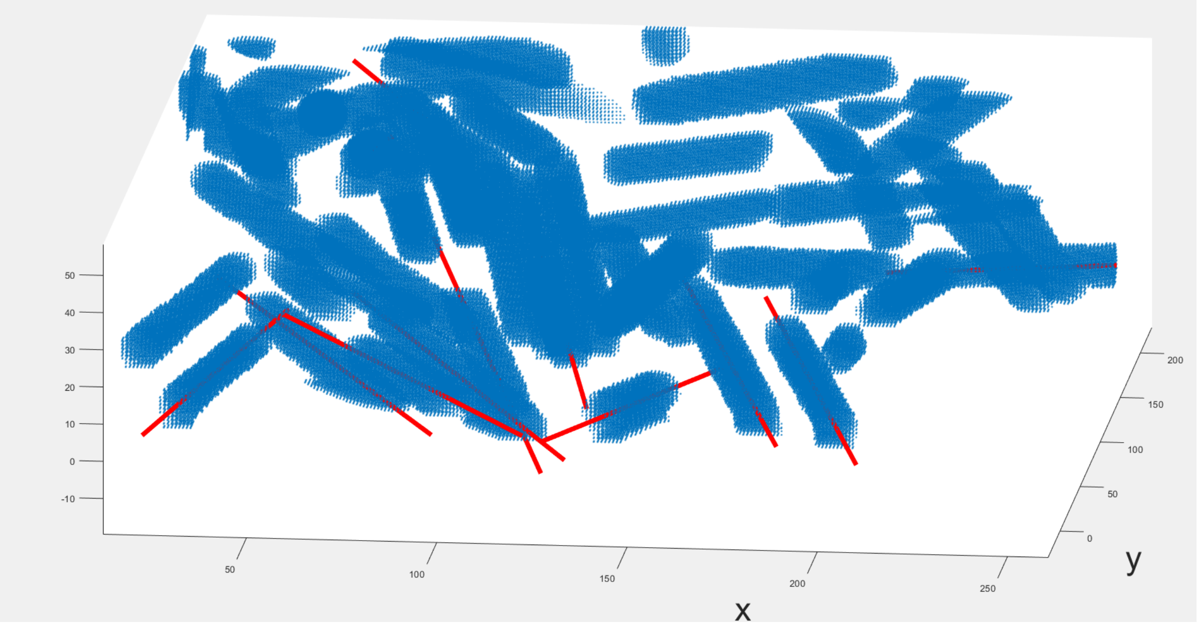
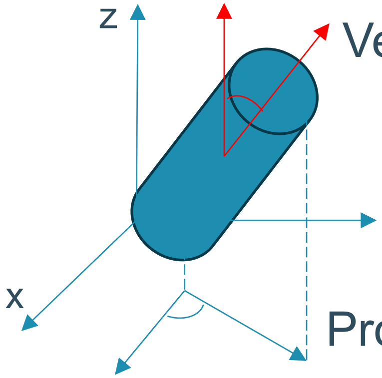
Particle characterization





- Particle eigenvectors calculated using vertical angle φ and projected angle θ
- Particle neighbors
  - Centroid proximity and surface contacts
  - Side: $\pm 15°$ in φ and θ
  - End: centroid distance > Σ (lengths)/2
  - Point: otherwise

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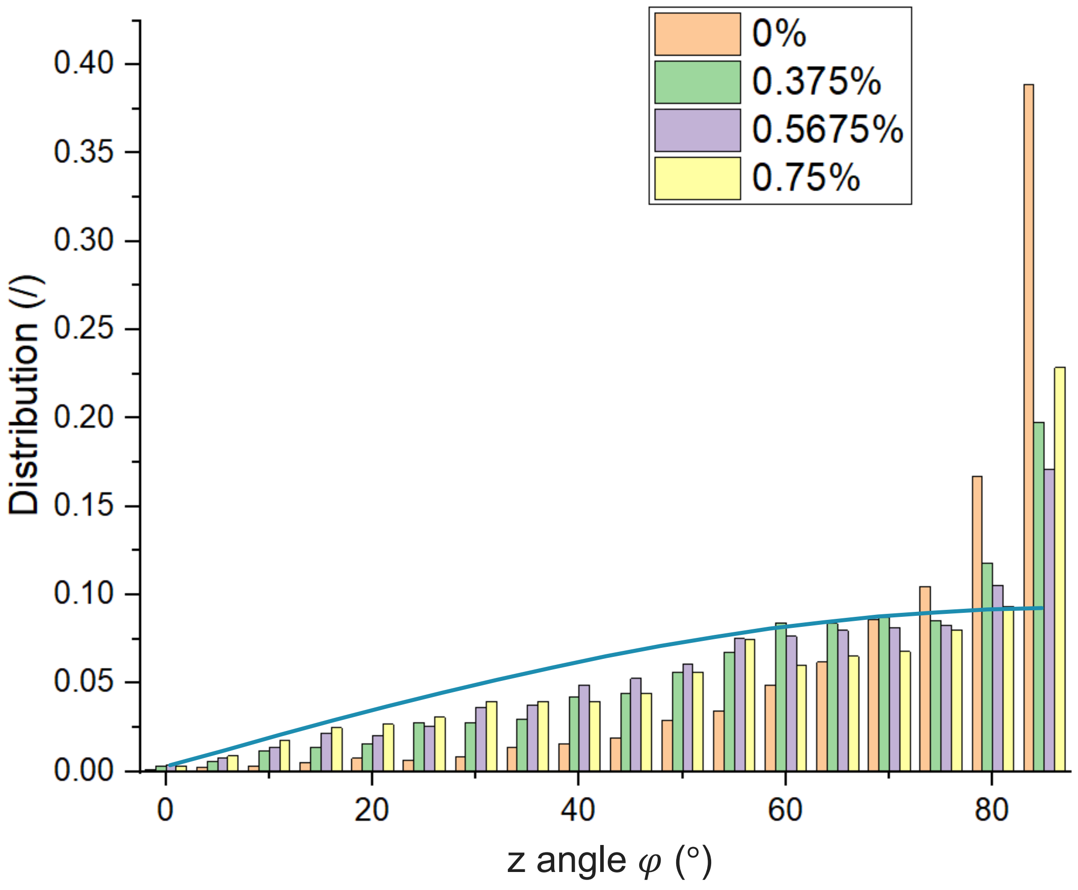
Secondary liquid vs averaged vertical angle φ

- $\phi_{sec} = 0\%$
  - Granular bed
  - Mostly $\varphi > 70$ (flat against slide)
- $\phi_{sec} = 0.375\%$ and 0.5675%
  - Particle gel
  - Shift towards smaller angles and random distribution
- $\phi_{sec} = 0.75\%$
  - Saturation (large clusters)
  - Still fairly random, but some clusters oriented against slide



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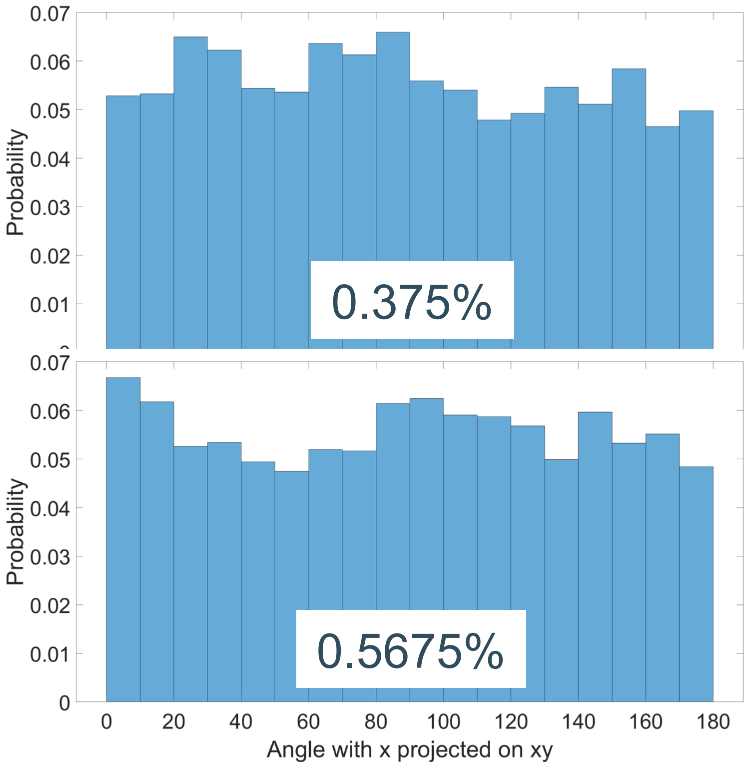
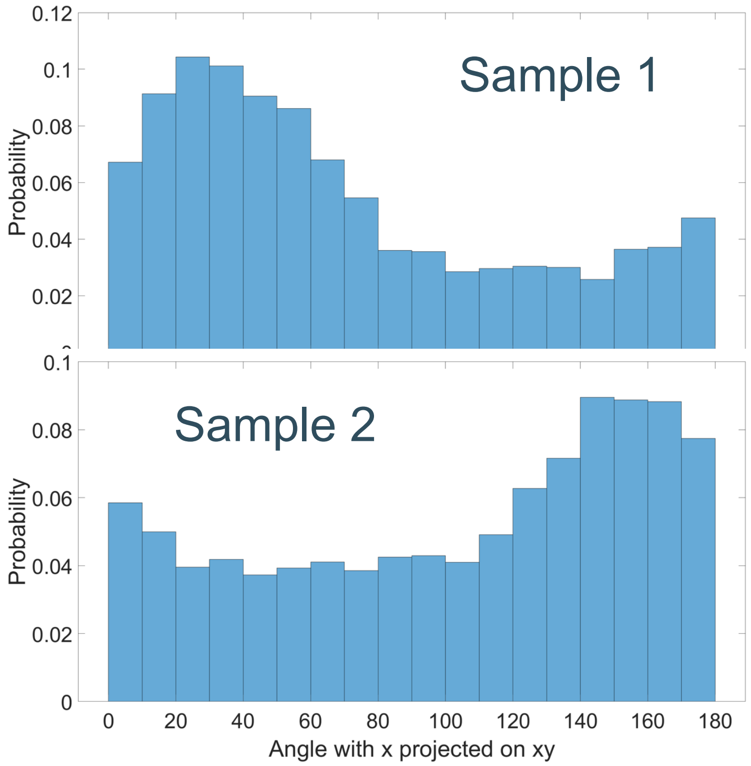
Secondary liquid vs averaged projected angle θ

- $\phi_{sec} > 0$: No preference
    - Fluctuation between samples



- $\phi_{sec} = 0$: Clear orientation
    - Dependent on loading, self-assembly, glass tilt etc.



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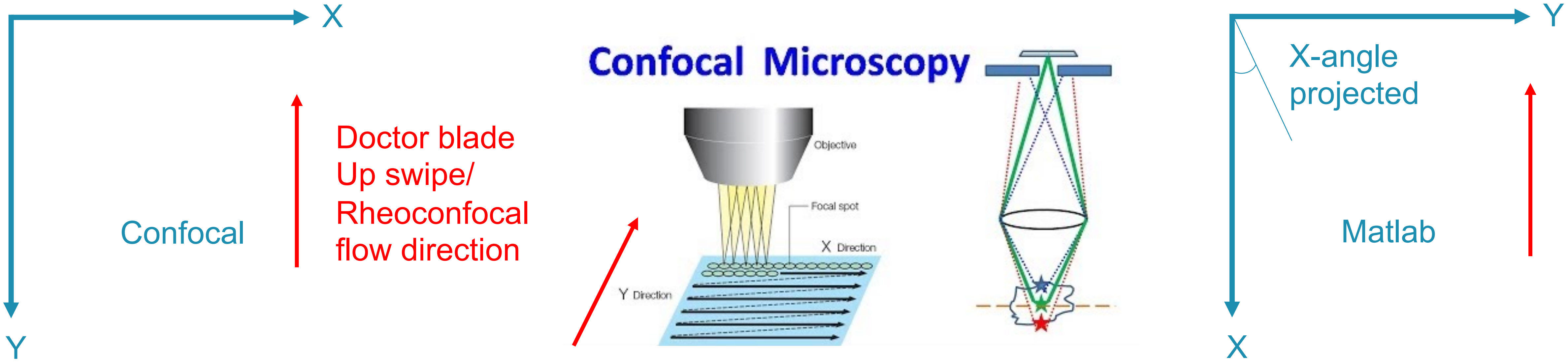
Doctor blade effect on particle orientation



- If the particle follows the flow, up blade would cause particles to align with x
  - More distribution to 0° or 180°
- Right blade → X-angle more towards 90°
- Images roughly taken at the same view, not preciously

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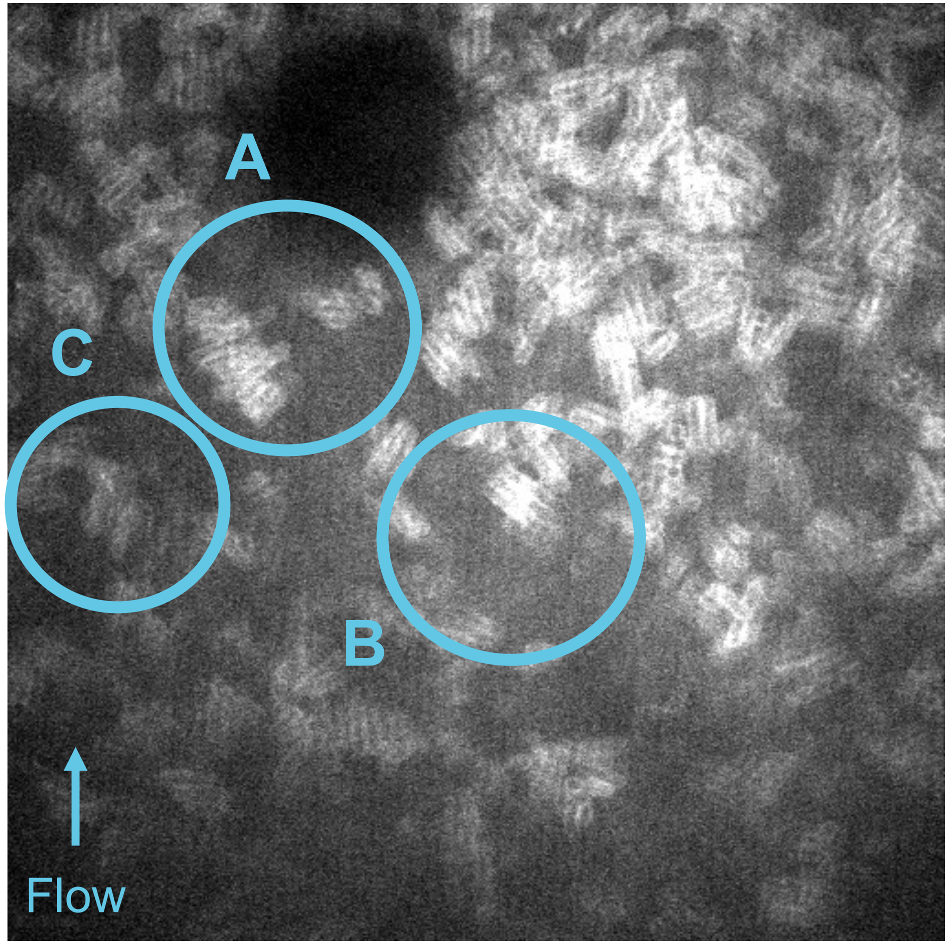
Rheoconfocal (flow-vorticity plane)



- Step strain (sum 1%)
  - Gap 300 µm, observed plane around 60 µm depth
  - Deformation a bit too large → redo test later
- A: Cluster flips perpendicular to flow direction
- B: Clusters rearrange in vorticity direction
- C: Clusters align in vorticity direction

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Outlook

- Focus on rheoconfocal measurements
  - Improvements
    - Particle dyeing and index matching to improve images
    - Particle detection and neighbor analysis
  - Preliminary tests
    - Initial configuration and sample loading
  - Step stress and oscillatory measurements
    - Sample yielding and recovery
  - Step strain and low shear rates
    - Sample re-orientation