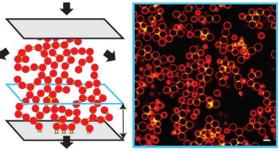# Investigation of capillary (nano)suspensions
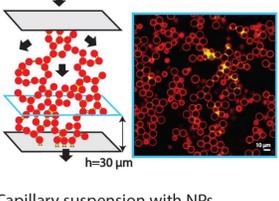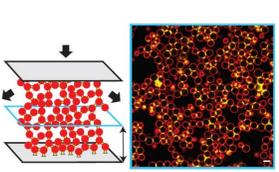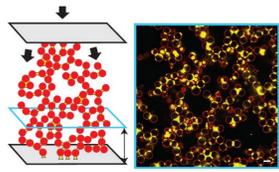
Lingyue Liu, **Erin Koos**

Enhanced contact flexibility from nanoparticles in capillary suspensions

Capillary suspension without NPs

Capillary suspension with NPs

Hydrophobicity influence on NP migration

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 %**
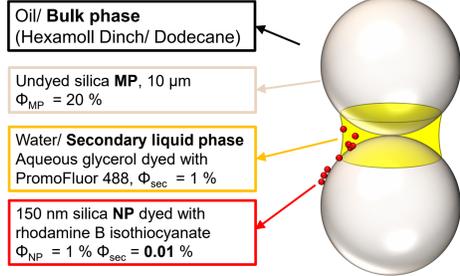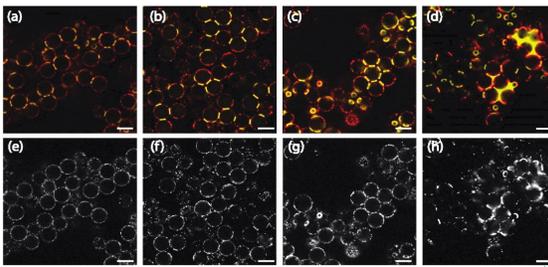
HSR 0
- No location preference
- Well-spaced

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

HMDS added to hydrophobize NPs
HSR = HMDS (µl) : Silica NP (mg)
Number ↑ = Hydrophobicity ↑

Uniaxial compression

Pre-compression
Post-compression

Pentamer
Trimer
Binary bridge

Bridge Surface (μm^2) vs Bridge Volume (μm^3)

Three-phase contact line pinning
Extra energy needed
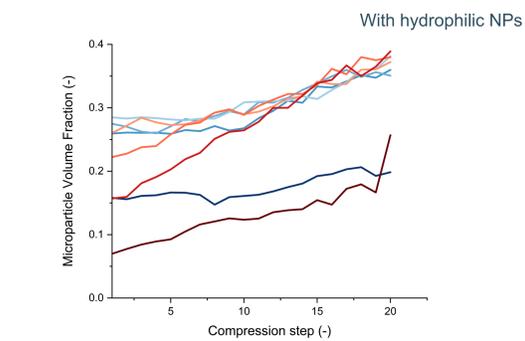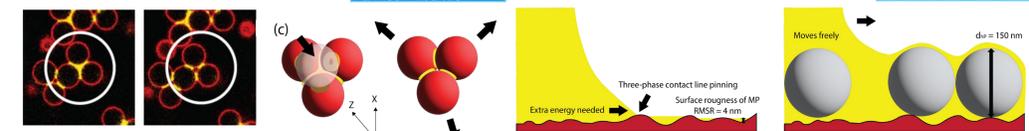Surface roughness of MP RMSR = 4 nm

Moves freely
d_{NP} = 150 nm

Bottom — Top

Without NPs

With hydrophilic NPs

Microparticle Volume Fraction (-) vs Compression step (-)

Coordination Number (/) vs Piezo displacement (µm)
- no NP coordination number
- no NP clustering coefficient
- HSR0 coordination number
- HSR0 clustering coefficient
Hydrophilic NP
No NP

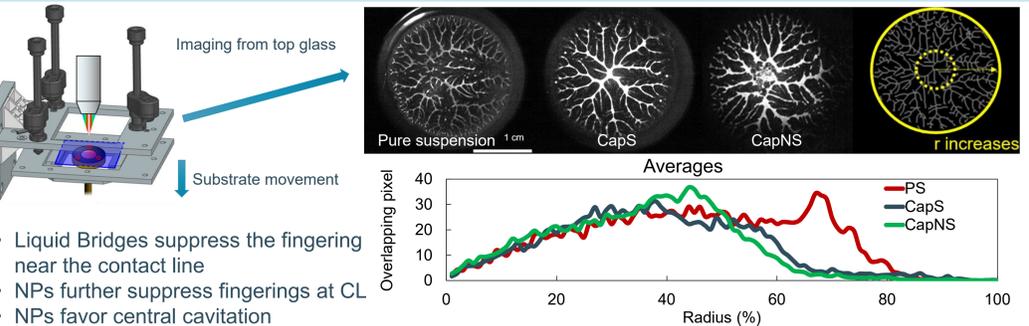Network without NPs is **rigid** and **does not compress**
- Hertzian compression, high rolling/sliding friction
- Bridges coalesce
- Force chains and rigid body motion sideways

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?

Fingering instability during the dewetting of nanocapillary suspensions

Imaging from top glass

Pure suspension   CapS   CapNS   r increases

Substrate movement

Averages
Overlapping pixel vs Radius (%)
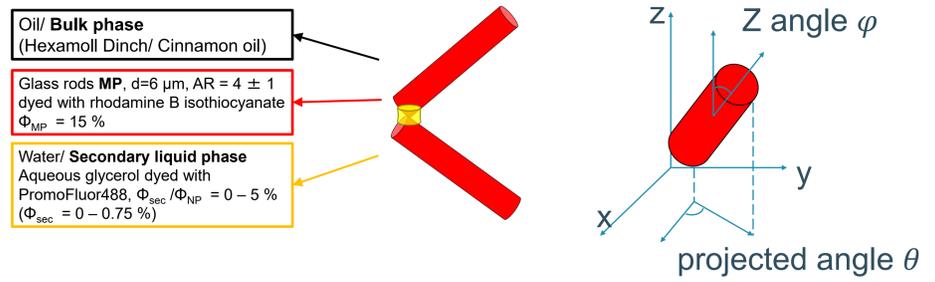- PS
- CapS
- CapNS

- Liquid Bridges suppress the fingering near the contact line
- NPs further suppress fingerings at CL
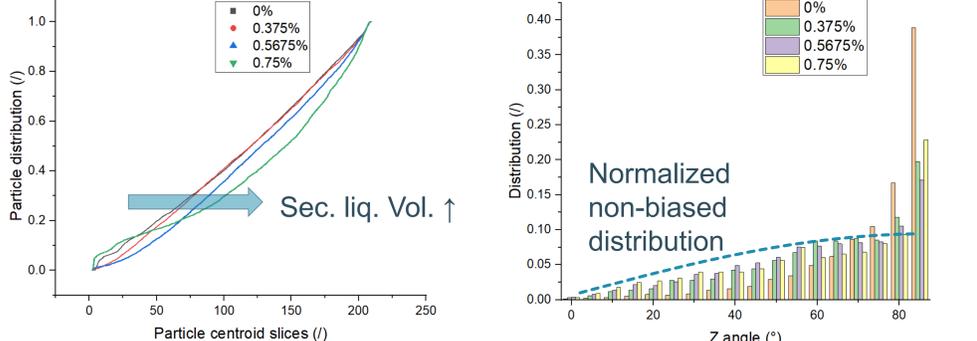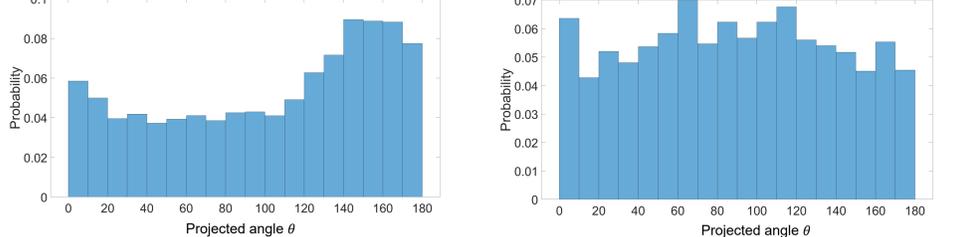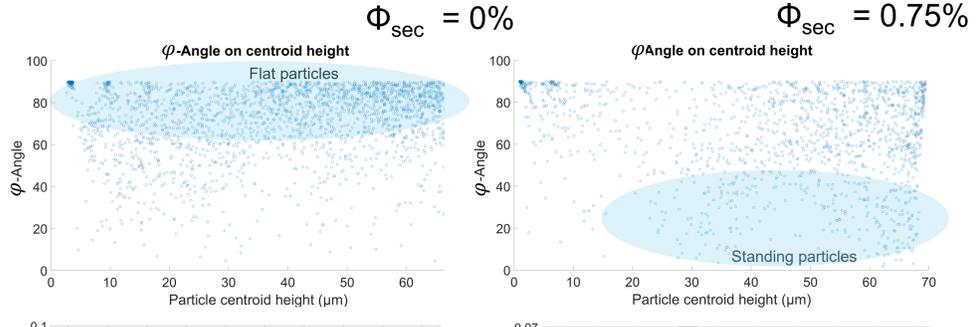- NPs favor central cavitation

Anisotropic capillary suspensions
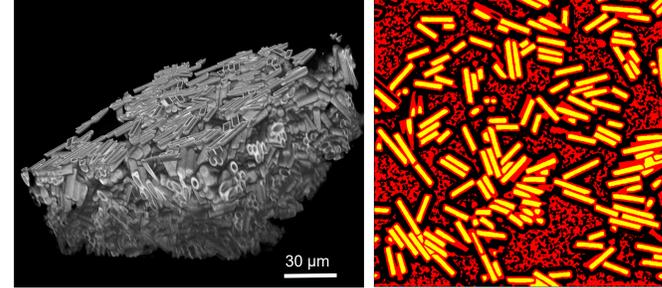
- Enclosed particles are filtered based on min/max size, circularity, smoothness, and solidity

- Each particle on an individual slice is detected, centroids are tracked using z (slice) with tolerance (memory)

30 µm

Oil/ **Bulk phase** (Hexamoll Dinch/ Cinnamon oil)

Glass rods MP, d=6 µm, AR = 4 ± 1 dyed with rhodamine B isothiocyanate Φ_{MP} = 15 %

Water/ **Secondary liquid phase** Aqueous glycerol dyed with PromoFluor488, Φ_{sec} /Φ_{NP} = 0 – 5 % (Φ_{sec} = 0 – 0.75 %)

Z angle φ
projected angle θ

- Eigenvectors of the detected 3d particles are calculated angles
- Z angle φ (tilts in gravitational direction) 0-90°
- X projected angle θ (oriented) 0-180°

Φ_{sec} = 0%

Φ_{sec} = 0.75%

φ-Angle on centroid height
Flat particles
φ-Angle vs Particle centroid height (µm)
Standing particles

Probability vs Projected angle θ

Particle distribution (/) vs Particle centroid slices (/)
- 0%
- 0.375%
- 0.5675%
- 0.75%
Sec. liq. Vol. ↑

Distribution (/) vs Z angle (°)
- 0%
- 0.375%
- 0.5675%
- 0.75%
Normalized non-biased distribution

- No secondary or too much sec. liquid → flat particles (Z angle > 70°) at bottom slides
- More liquid → More standing particles (Z angle < 40°) , closer to normalized non-biased distribution
- 0.75% sec. liquid → clusters and flat rods, but breaks directional assembly (X angle)
- Ongoing: rheoconfocal → network rearrangement/ breakup characterization

Miscible liquid in capillary nanosuspensions

No NPs

With NPs

1min   10 min   20 min   25 min   30min
t ↑

- Ethanol/Dodecane mixture + 10 µm silica microparticles mixed in a closed chamber
- Without NPs, ethanol condensates gradually at the MP contact region, then evaporates
- With NPs, aggregated, interconnected ethanol networks appear immediately after mixing
- NPs strongly shorten the interparticle distances → favors the phase separation