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Investigation of capillary (nano)suspensions

IFPRI Annual Meeting 2025, Marseille, France

Erin Koos

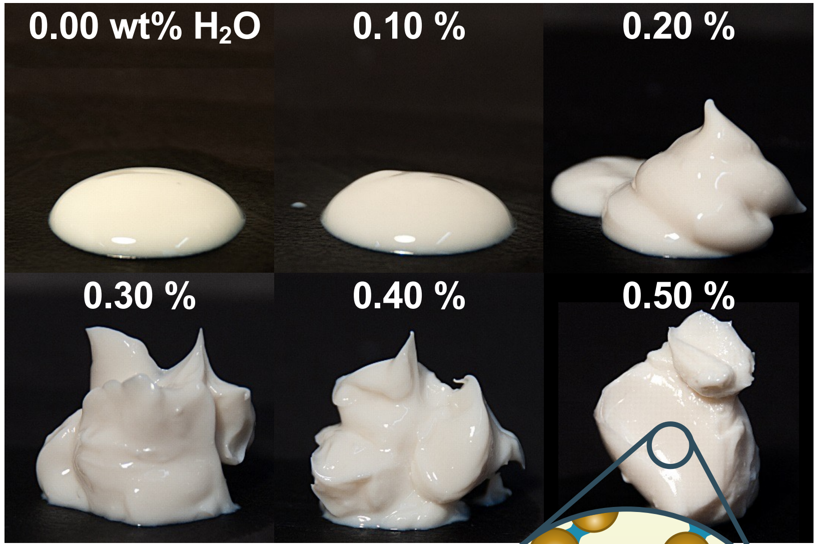
KU Leuven
Department of Chemical Engineering
Section Soft Matter, Rheology and Technology

The capillary suspension phenomenon

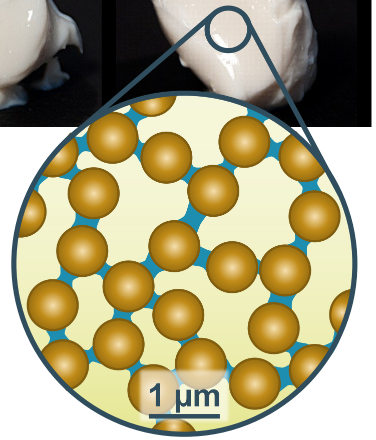
Micro- or nanoparticles

+

Two immiscible liquids



Capillary suspension



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

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Dewetting Fingering Instability in Capillary Suspensions: Role of Particles and Liquid Bridges

Lingyue Liu[1], Mete Abbot[2], Philipp Brockmann[2], Ilia V. Roisman[2], Jeanette Hussong[2], **Erin Koos**[1]

KU Leuven, Department of Chemical Engineering Section Soft Matter, Rheology and Technology[1]
Technical University of Darmstadt, Institute for Fluid Mechanics and Aerodynamics[2]

Liu, L., Abbot, M., Brockmann, P., Roisman, I.V., Hussong, J., Koos, E. Langmuir, 41(8), 5399-5409. (2025)

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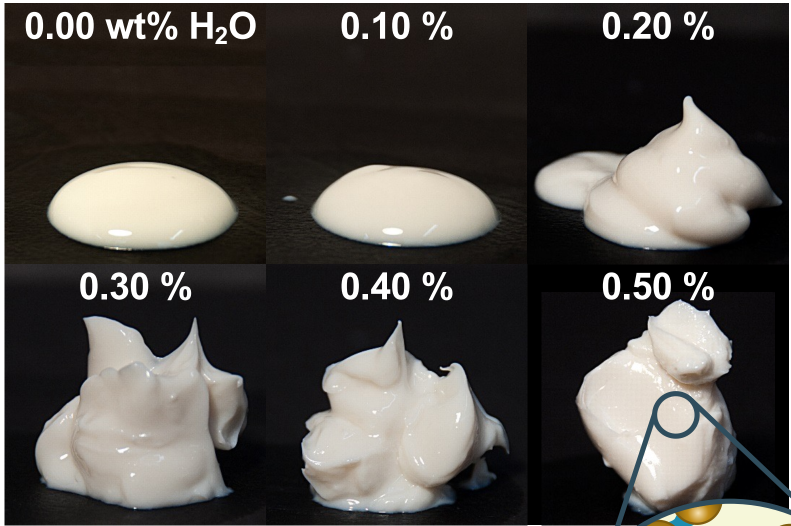
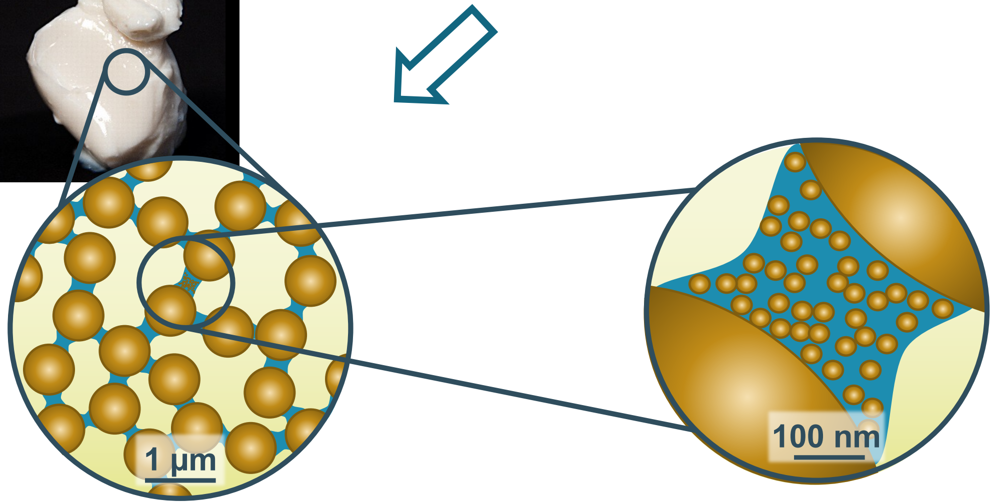
Capillary **nano**suspension (S-L-L-S)



Nanoparticles

Nanoparticles added with bridging liquid



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

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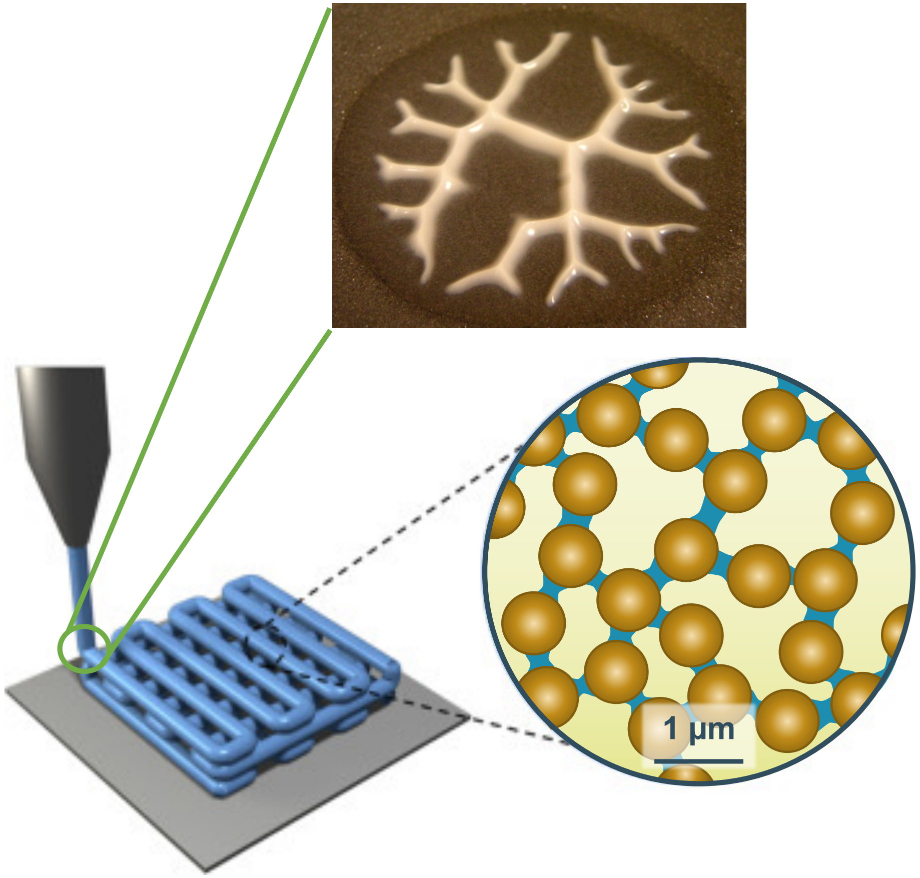
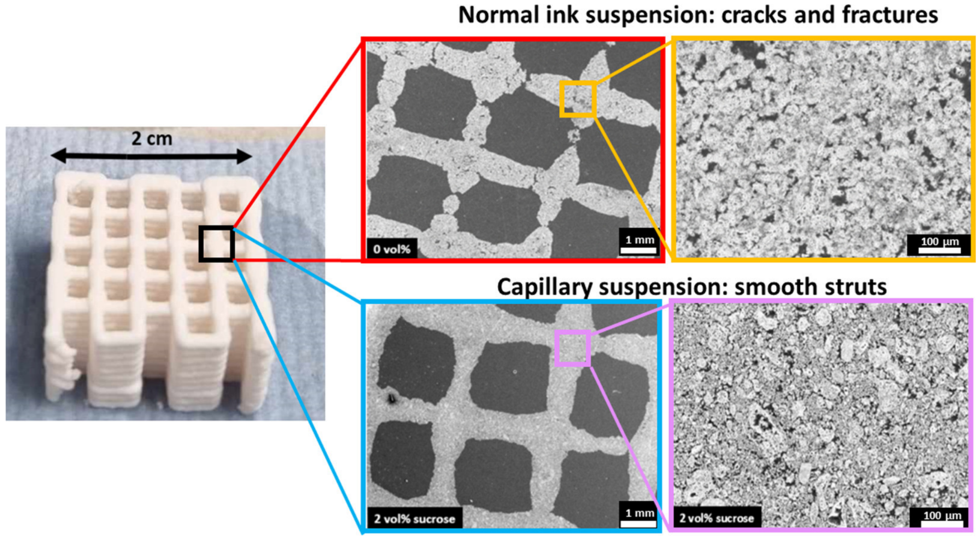
Direct ink writing of capillary suspension

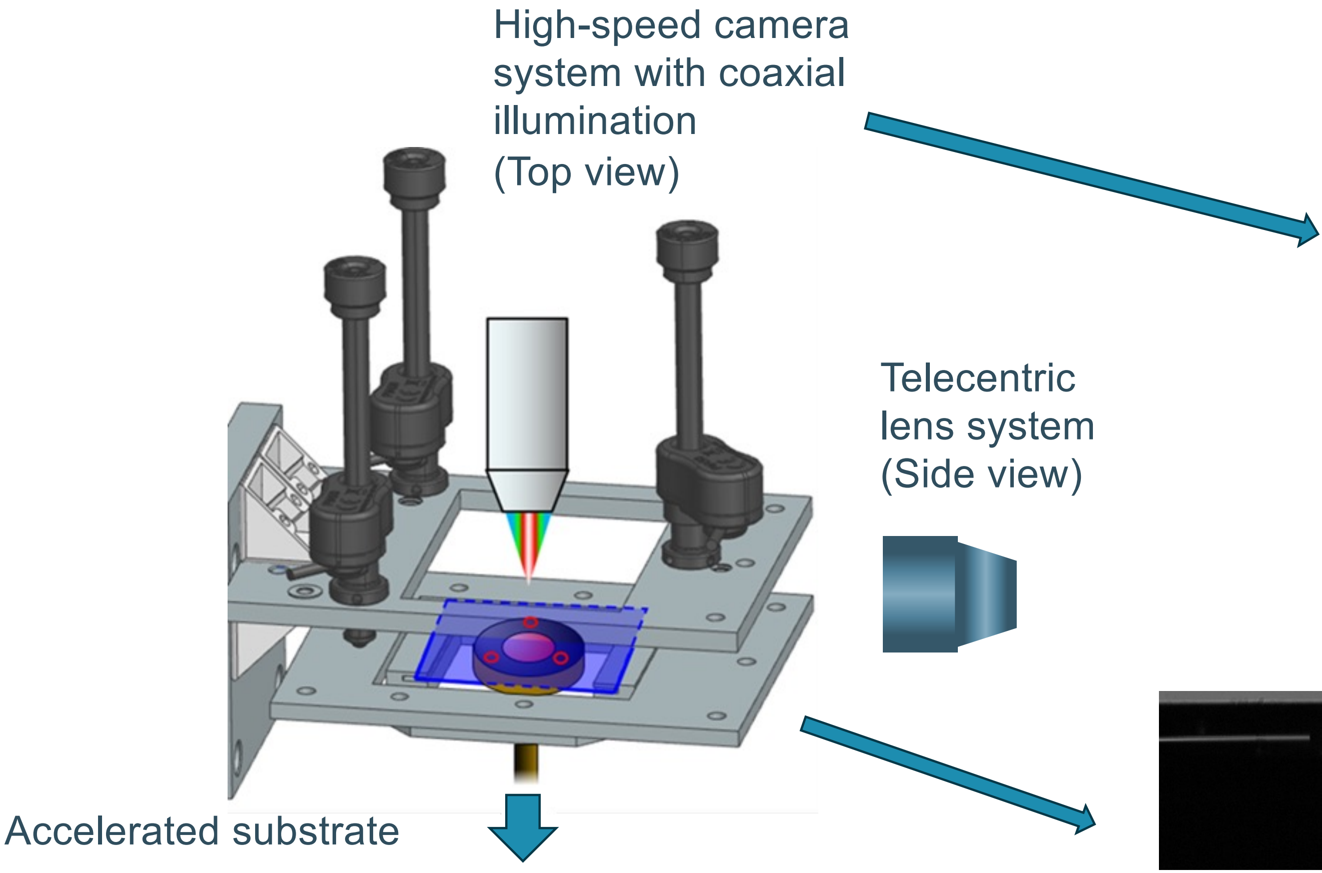


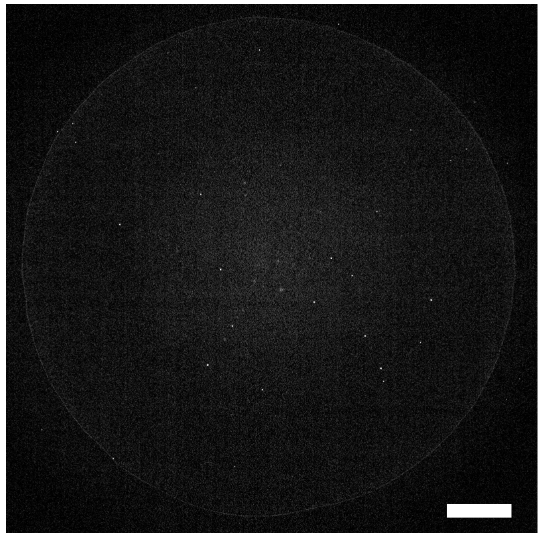


- Capillary suspension is useful for 3D printing
- Failure mechanism/residual not studied
- Stretching is important in fast printing

S. Smedt et al., *Curr. Opin. Colloid Interface Sci.* **75**, 101889 (2024)
Fadoul and Coussot, *Fluids*, 4(1), 53, 2019

Modified Hele-Shaw cell for fingering instability

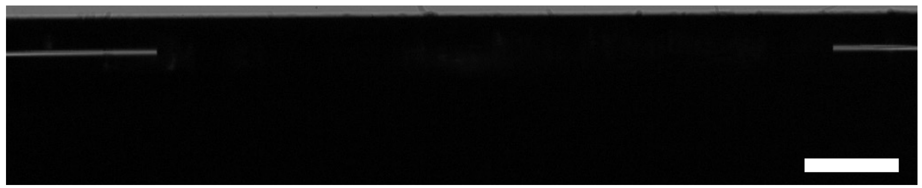




Particles fluorescently labelled

All scale bars = 5 mm

Initial gap height = 50 μm



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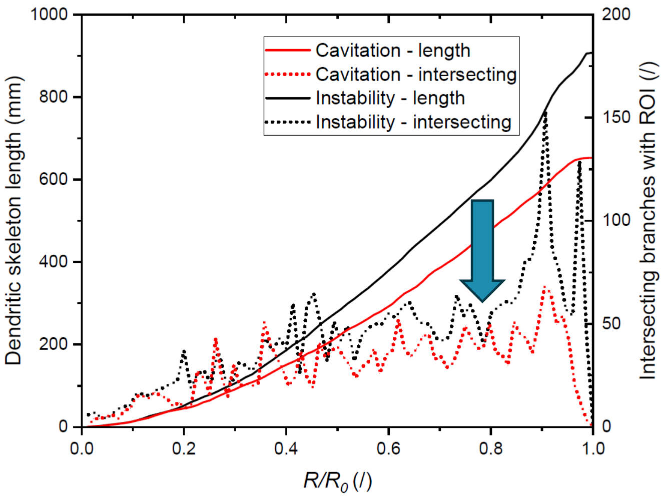
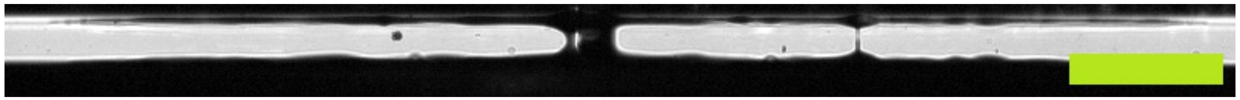
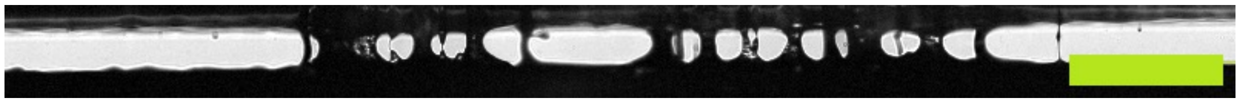
Suspension dewetting



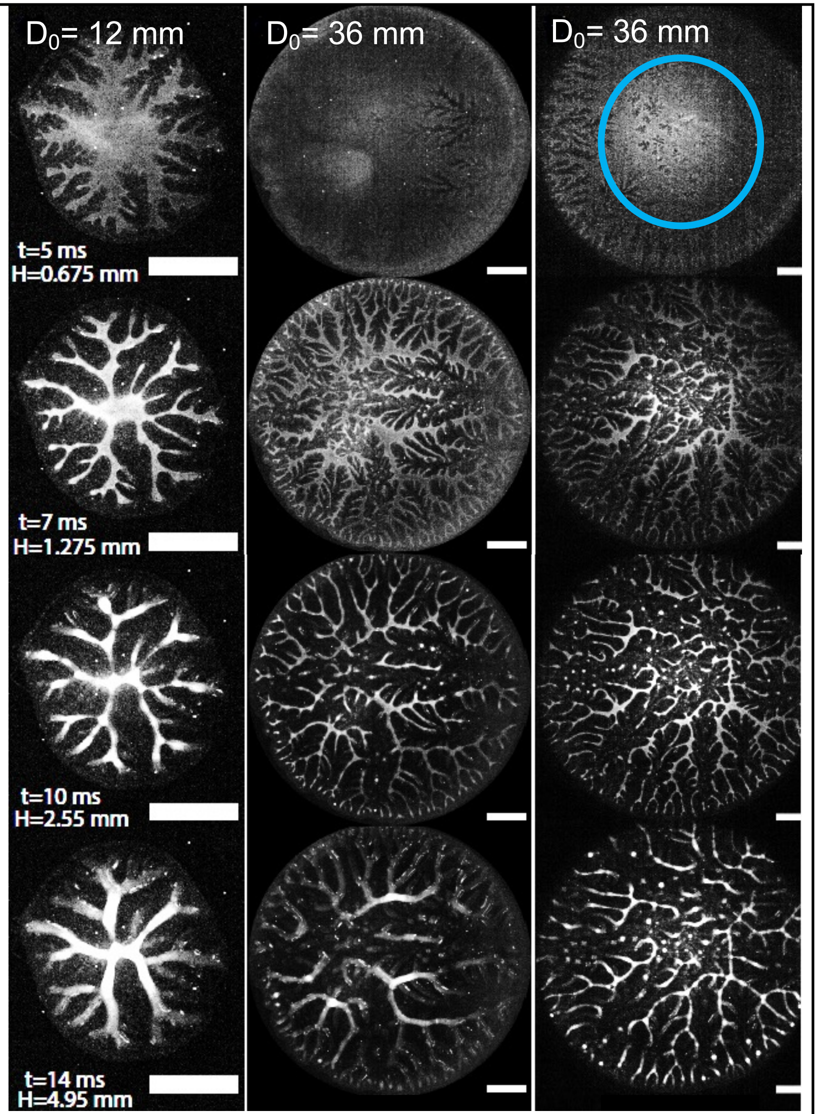
- Samples with smaller diameters → Patterns all internally connected
- Cavitation **cuts** liquid branches connections, causing more **smaller** dots, **decreasing length**



Middle: Instability dominant, one main liquid filament



Right: Cavitation dominant, multiple liquid filaments



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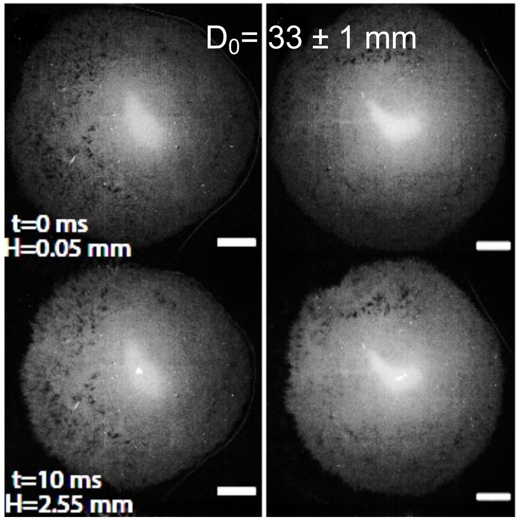
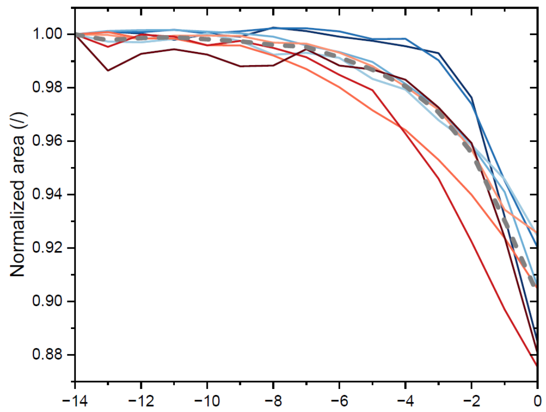
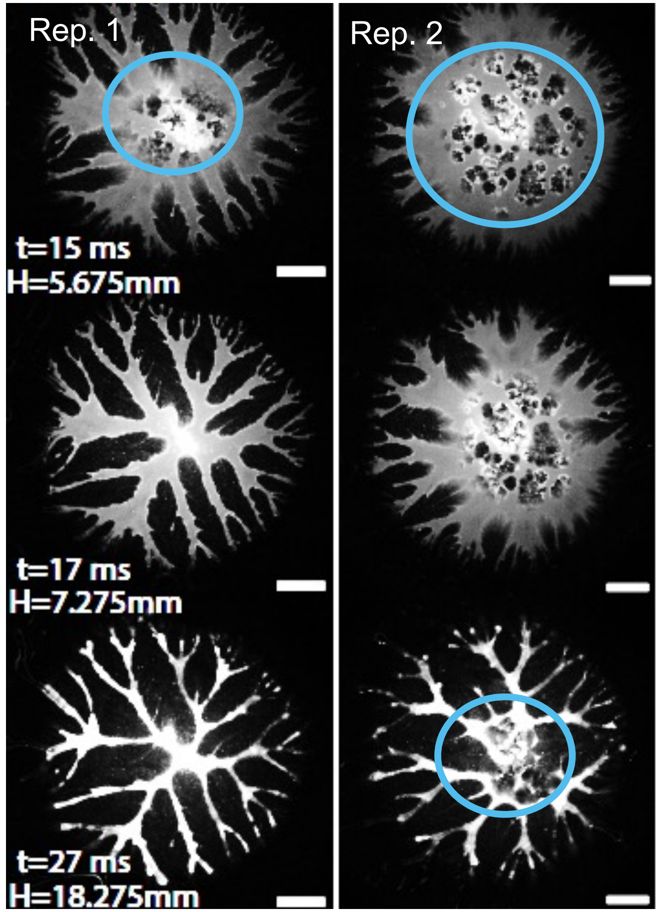
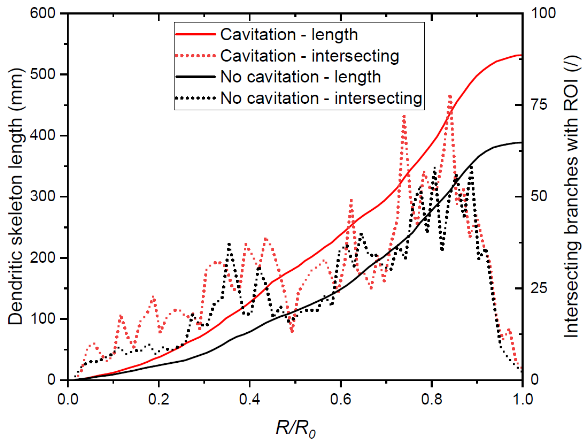
Capillary suspension dewetting







- Initial stage: homogenize (mostly) shrinkage up to 10% area
- Unstable stage: Instability high → pressure drop compensated by cavitation
- Cavitation **increases** pattern **length** that do not shrink like liquid suspensions



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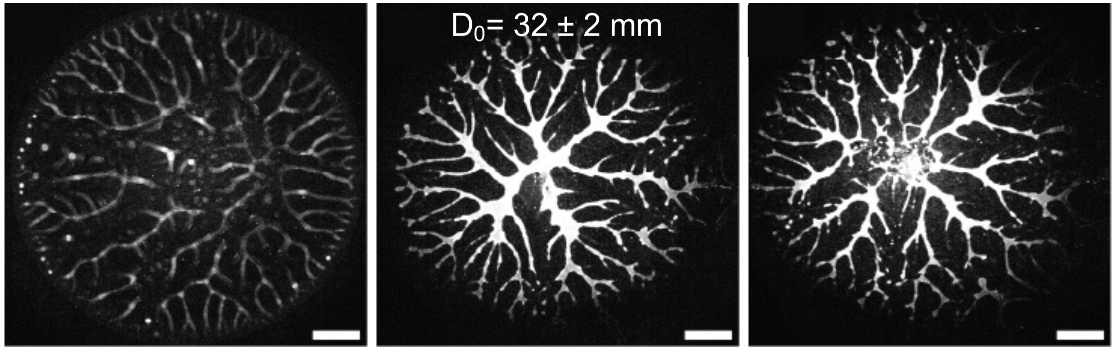
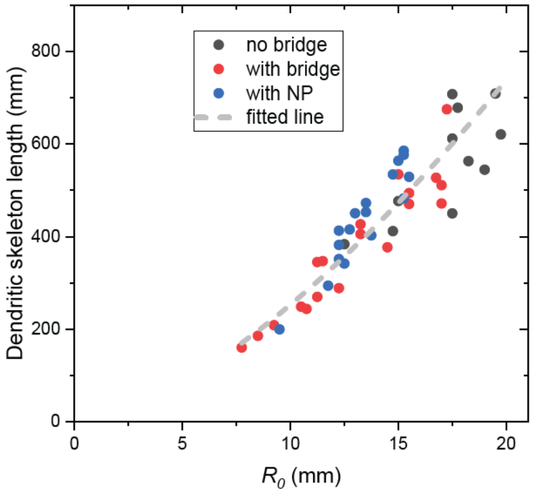
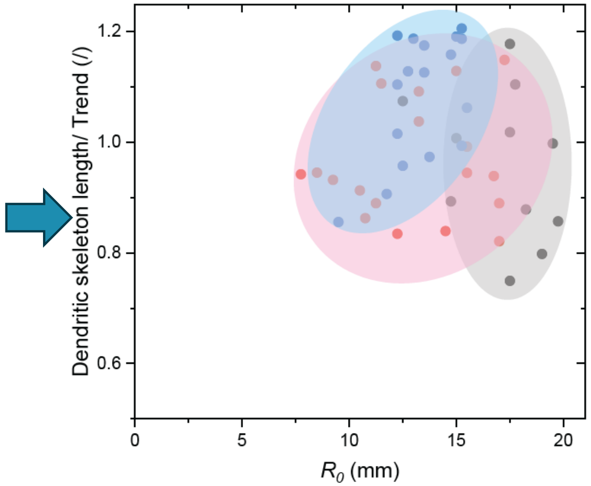
Capillary nanosuspension dewetting

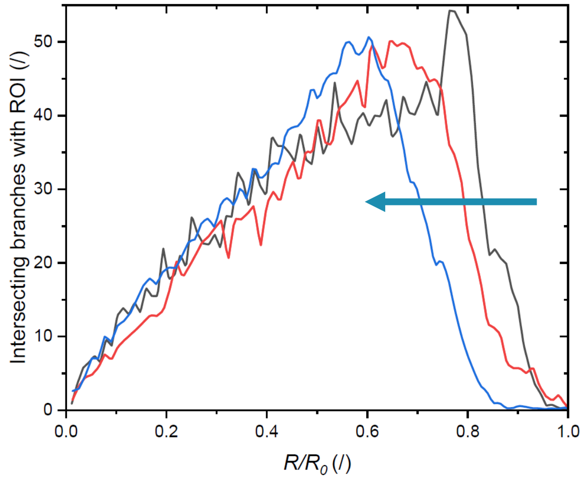


Suspension + Liquid bridges + NPs

- Pattern length fitted power law with R_0, coefficient = 1.55 < 2
- Capillary suspensions show **radius dependence**, NPs homogenize samples
- NPs **promote cavitation** → center complexity, pattern break at rims







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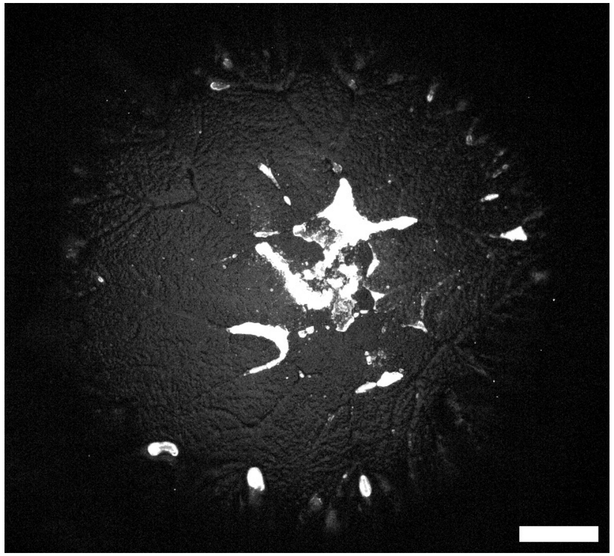
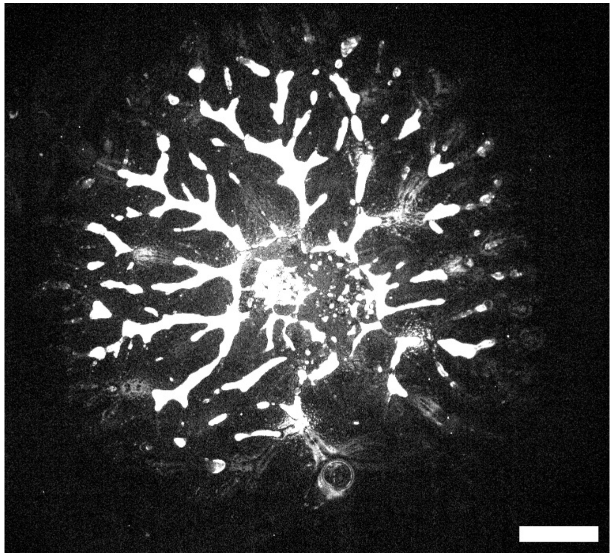
How does fingering instability influence sample deposition?

Without NPs

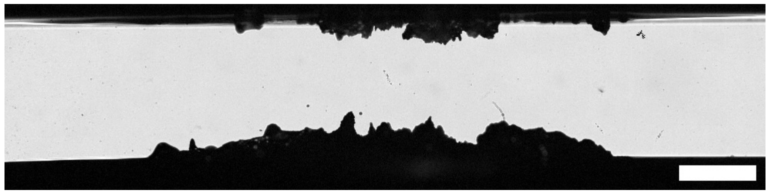
Top view

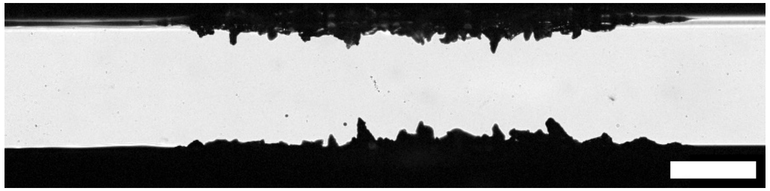


With NPs



Side view





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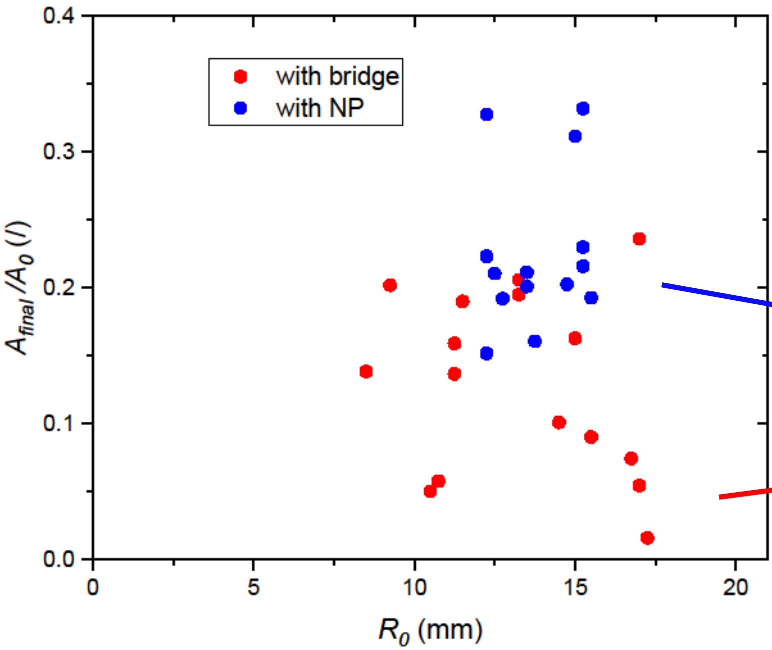
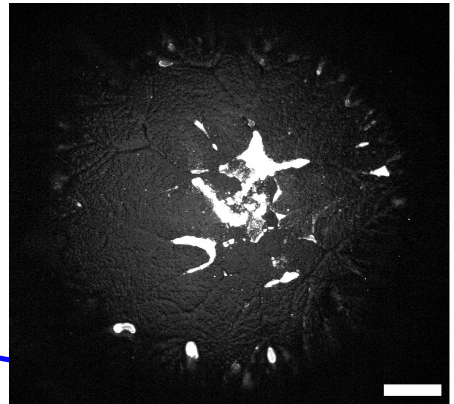
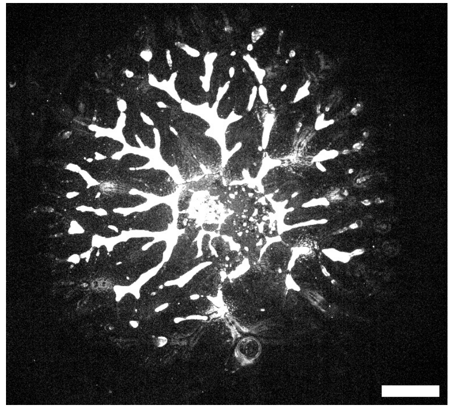
NP effect on residual area ratio A_{final}/A_0



Adhesive failure



Cohesive failure



Without NPs

With NPs

- Low residual ratio = sample stick to one side = **adhesive** failure
- High residual ratio = even distribution = **cohesive** failure
- **NPs** lubricate force chains → early breakage → more deposition

Owens C. E et al, *Physics of Fluidsm* 34, 043107 (2022)

Take home messages

- Microparticles in pure liquid **increase** the number of **fingers** and the total dendritic length, serving as nucleation sites.
- **Capillary forces** provide a strong sample-spanning network with high **elasticity**. The instability is significantly **suppressed** at the center and the outer regions.
- Just 0.01% **NPs** make patterns more **consistent** and **predictable**, reducing sample-to-sample variation
- **NPs** transfer sample splitting from **adhesive** failure (uneven distribution) to **cohesive** failure (even distribution)

Liu, L., Abbot, M., Brockmann, P., Roisman, I.V., Hussong, J., Koos, E. Langmuir, 41(8), 5399-5409. (2025)

Capillary force-driven particle orientation in rod networks

Lingyue Liu[1], Sebastian Gassenmeier[1] and Erin Koos[1]

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

L. Liu, S. Gassenmeier, E. Koos
Arxiv, JCIS (First revision) (2025)

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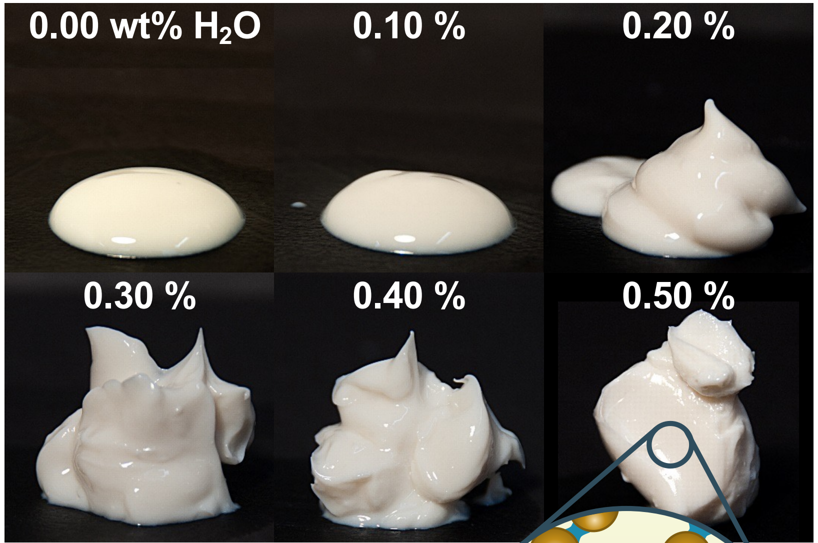
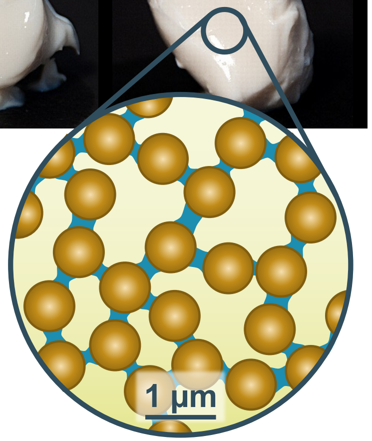
The capillary suspension phenomenon

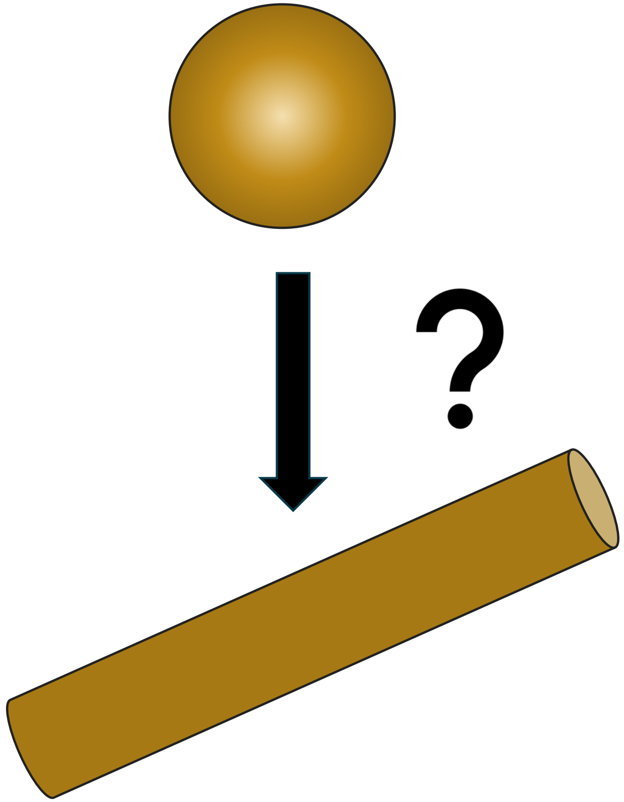
Microparticles

Two immiscible liquids





Capillary suspension



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

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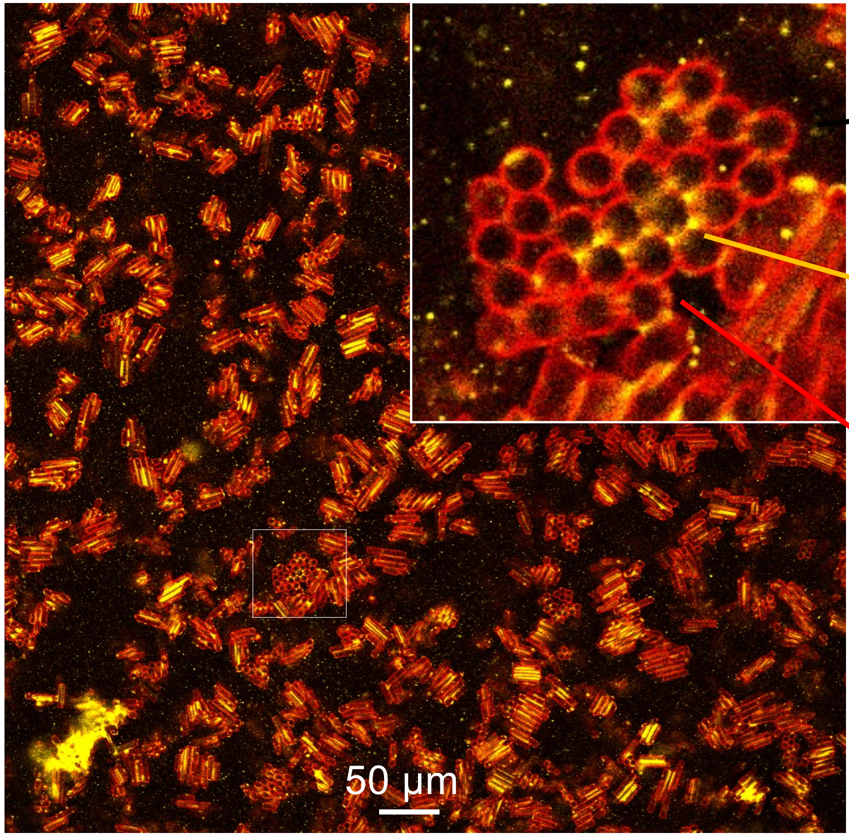
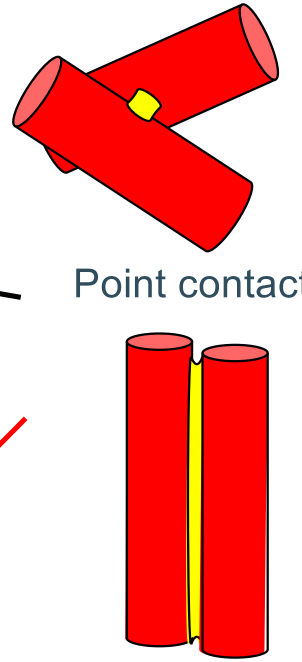
Confocal model system



Oil/ Bulk phase
(Cinnamon oil/ Hexamoll Dinch)
RI: 1.56

Water/ **Secondary liquid phase**
Aqueous glycerol dyed with PromoFluor 488, Φ_{sec} = 0-0.75 %
RI: 1.4 (aqueous phase mismatch)

⌀ = 6 µm glass **MP** (AR: 4 ± 1) dyed with rhodamine B isothiocyanate
Φ_{MP} = 15 vol%, RI: 1.56



- $\frac{F_{cap,side}}{F_{cap,point}} = \frac{2\gamma L}{\pi D \gamma \cos\theta} = 2\frac{AR}{\pi \cos\theta}$ = 2.5 (minimal)
- **Side contact** bridges are much harder to break → **cluster**

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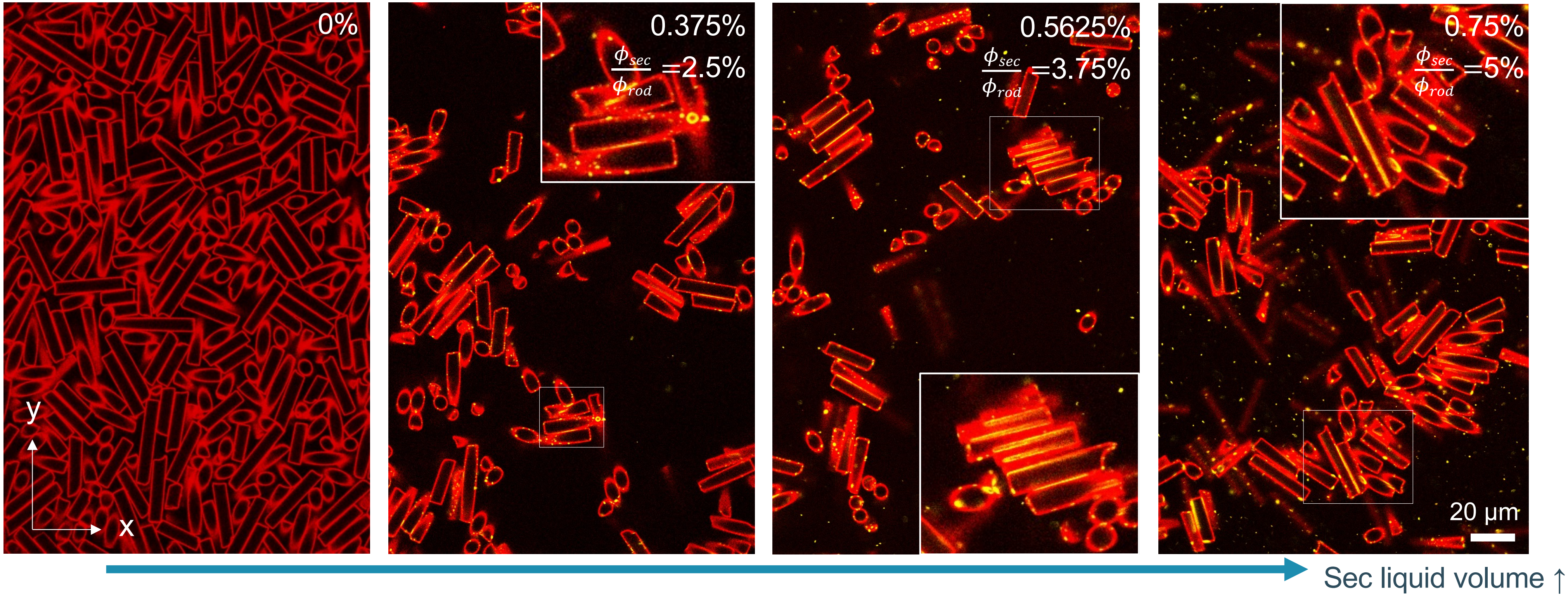
Influence of secondary liquid volume



- No sec liquid
  - Sedimentation
  - Longer axes oriented on x-y plane
- With increasing volume fraction
  - Sessile drops increase
  - More side contact
  - Particles orient randomly
  - Larger clusters oriented on x-y plane

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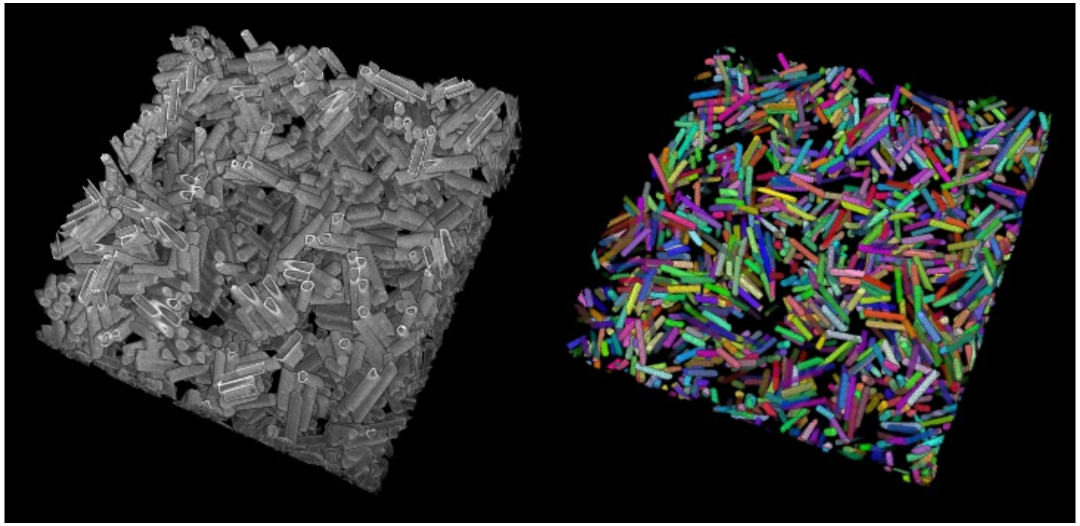
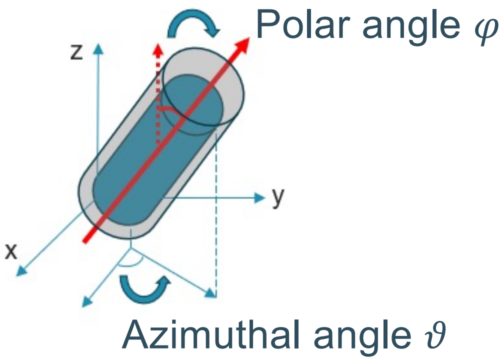
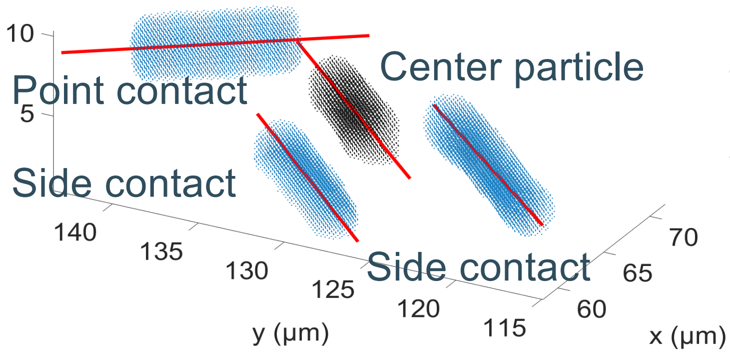
Image analysis – Detection & 3D tracking



- Particle eigenvector calculated using voxel list
  - Longer axis (red line) determined
  - φ (0 – 90°, vertical - flat)
  - ϑ(0 – 180°)
- Center particle in **black**, neighbors in **blue**
- Particle neighbor & contact type characterization
  - Surface distance criteria
  - Side: $\pm 10°$ in φ and ϑ
  - Point: all the non-side contact particles





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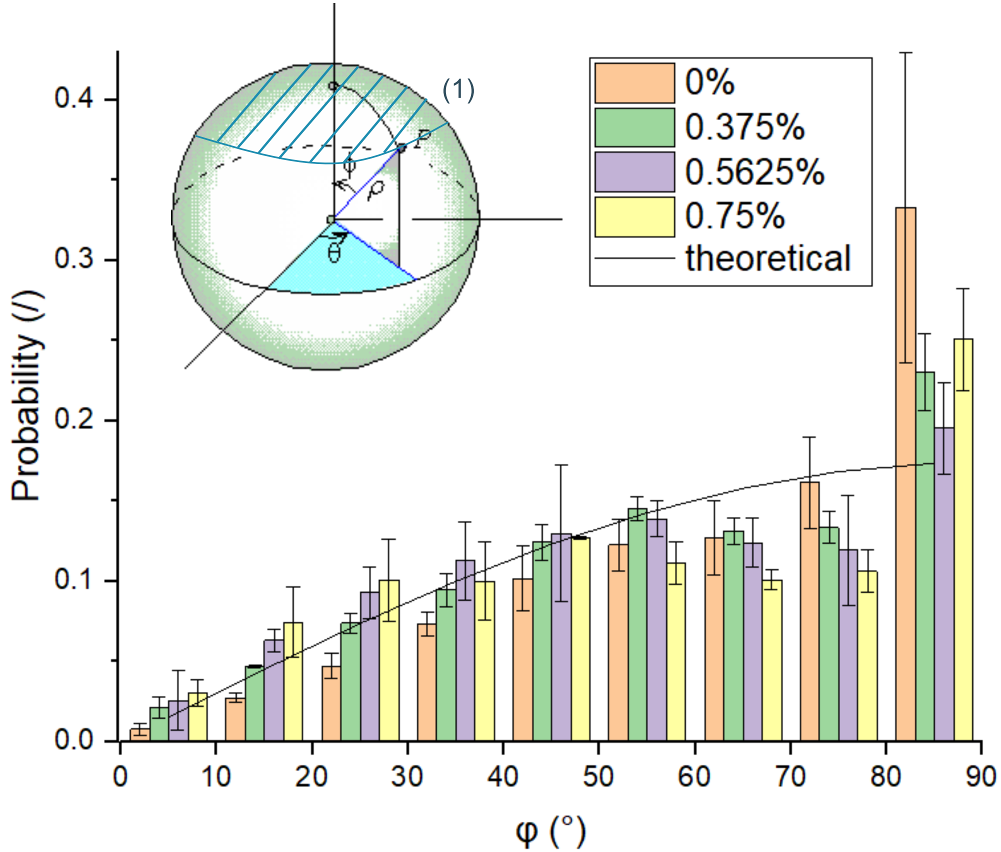
Secondary liquid vs averaged polar angle φ

- $\varphi = 0°$ → perfectly perpendicular to x-y plane
- Assistant line = theoretical distribution
  - Higher the φ, the larger the hemisphere area
- $\phi_{sec} = 0\%$
  - Granular bed
  - Mostly flat against slide $\varphi = 80° - 90°$
- $\phi_{sec} = 0.375\%$ and 0.5625%
  - Particle gel
  - Shift towards smaller angles and random distribution
- $\phi_{sec} = 0.75\%$
  - Saturation (large clusters)
  - Still fairly random, but some clusters oriented against (stick to) slide (≈ 90°)



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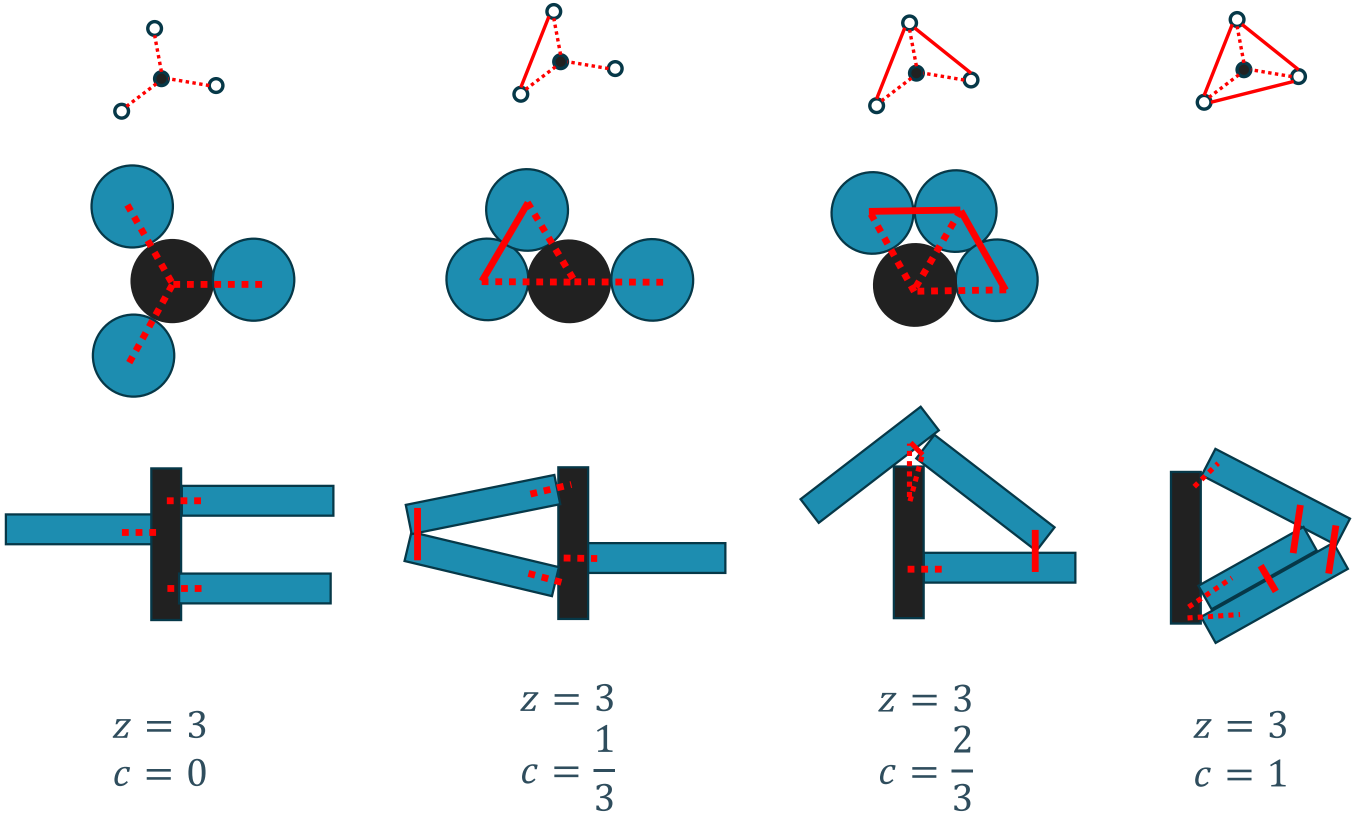
Coordination number z, clustering coefficient c

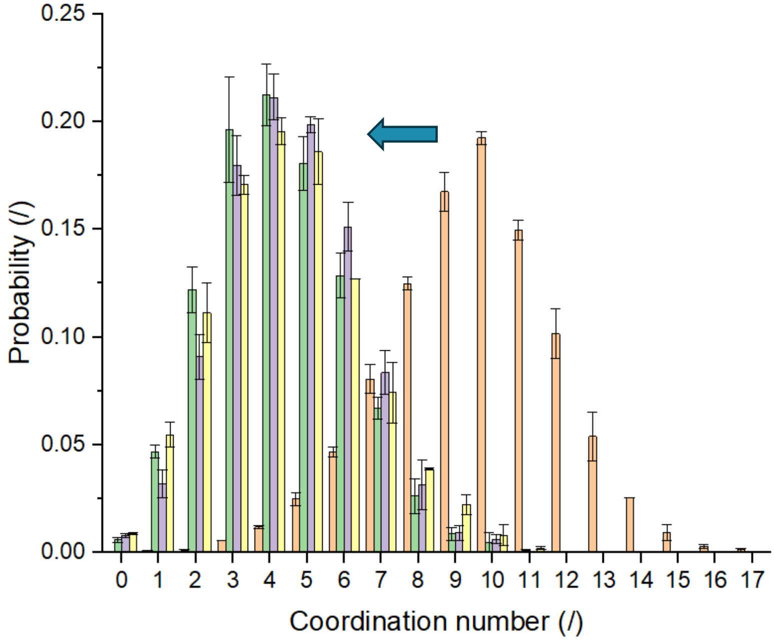


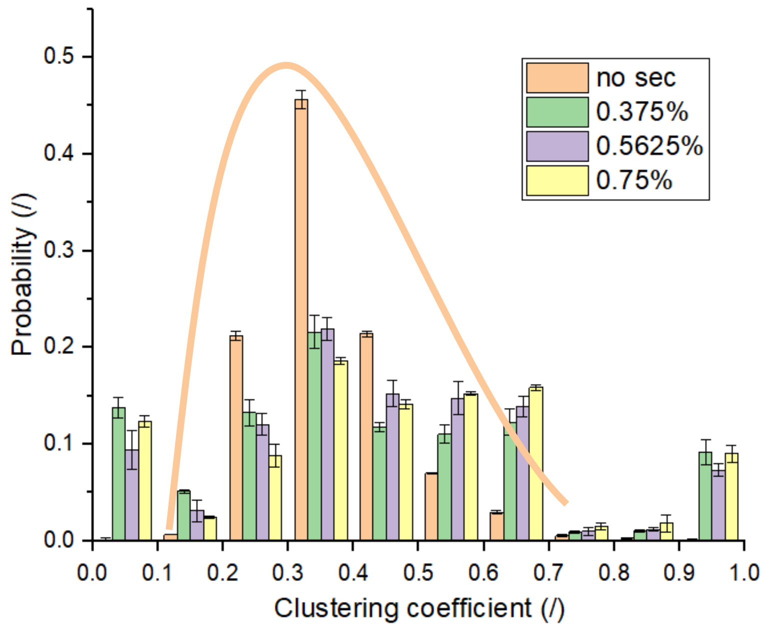
- Coordination number z
- Clustering coefficient c

$$c = \frac{2e}{z(z-1)}$$

  - e = solid bonds, neighboring conctact
  - z = dotted bonds, direct contact
- 2d sphere configuration:
  - For $z = 3, c \leq \frac{2}{3}$
- 2d rod configuration
  - For $z = 3, c = 1$ possible
- 3d configuration much more complicated

Secondary liquid on z & c





Secondary liquid shifts normal distribution towards **left**

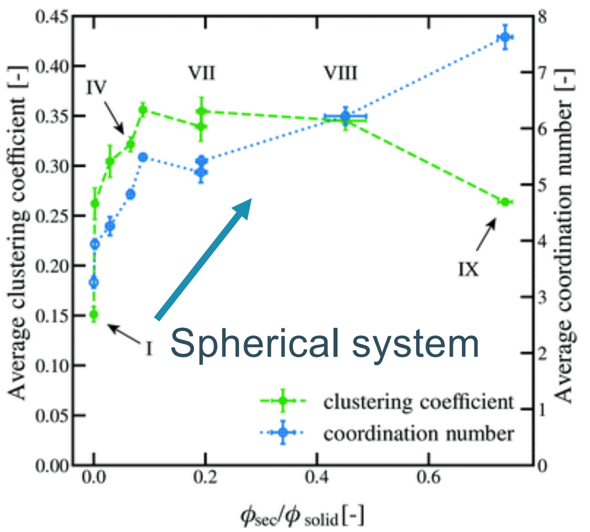
- Granular packing peaks at 10
- Capillary suspension peaks at 4

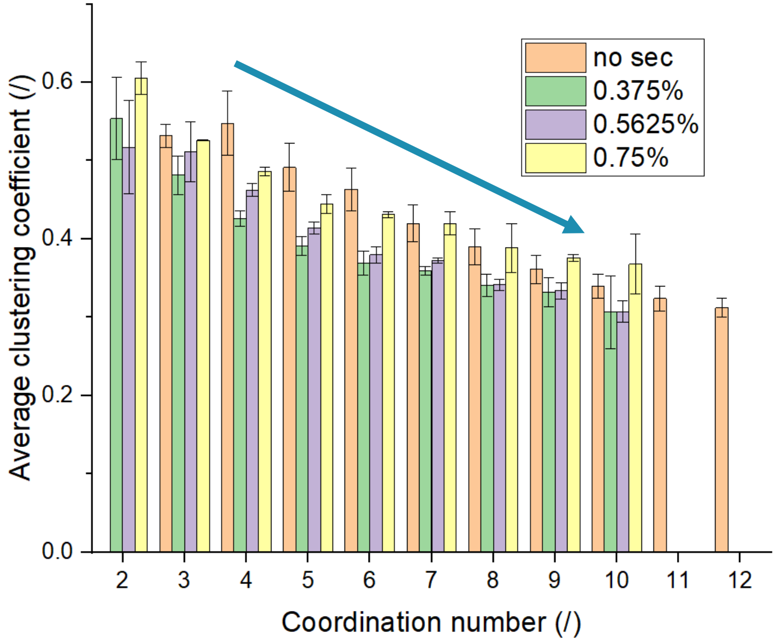
Liquid promotes c = 0 and c = 1

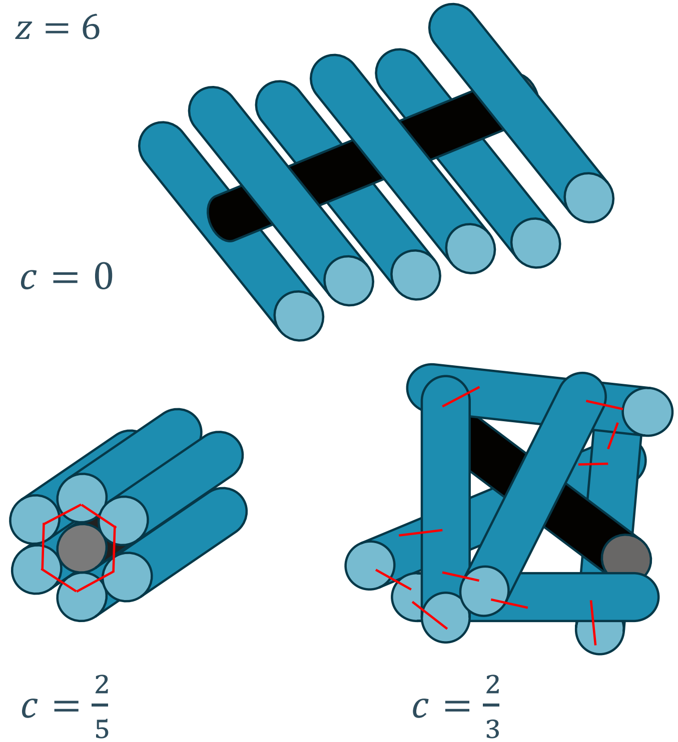
- c = 0, rods **random**, **homogenous**
- c = 1, rods **interconnected**, **point** contacts, **high local particle density**

Average c over z

(1)



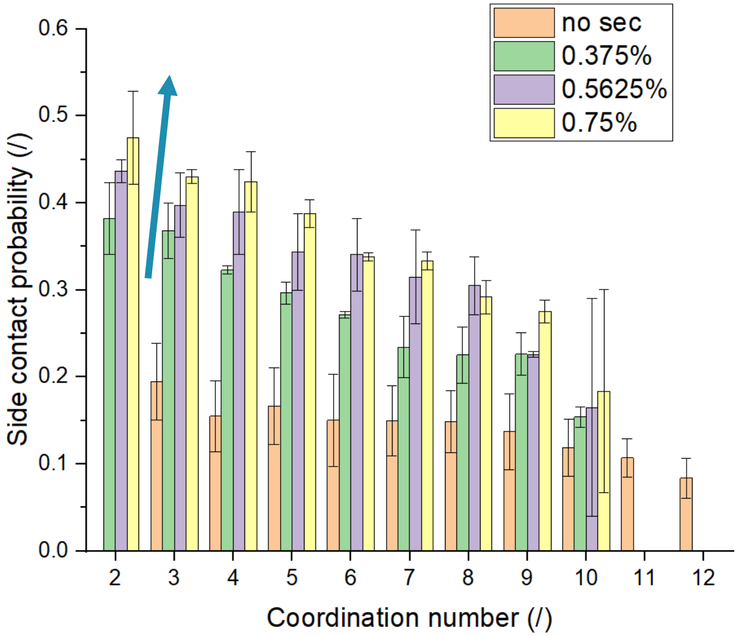


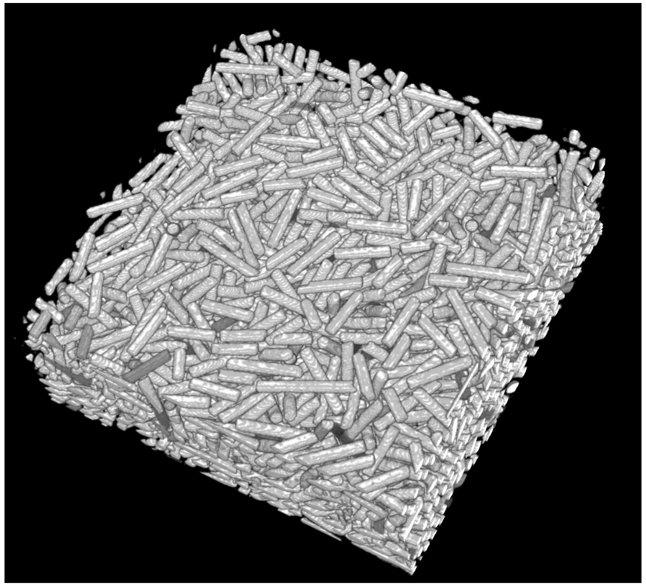


- In spherical systems: **high z** corresponds to **high c**, aggregation → more neighbors → more clustered structure
- In rod systems:
  - **higher z → lower c & lower side contact**
  - random distribution → more accommodation of point contact
- Note: particles with $z \leq$ **1** (with liquid) & **2** (granular) **eliminated** due to biased detected on the box edges

(1) Bindgen, S. et al. Soft Matter, *16*, 8380-8393 (2020)

Average side contact over z





Rod gels: **more** sec **liquid** → **more** chance of **side contact**

Rod suspensions: **fewer side contact** spotted**, lack** of capillary **bridges** for orientation alignment

Note: particles with $z \leq$ **1** (with liquid) & **2** (granular) **eliminated** due to biased detected on the box edges

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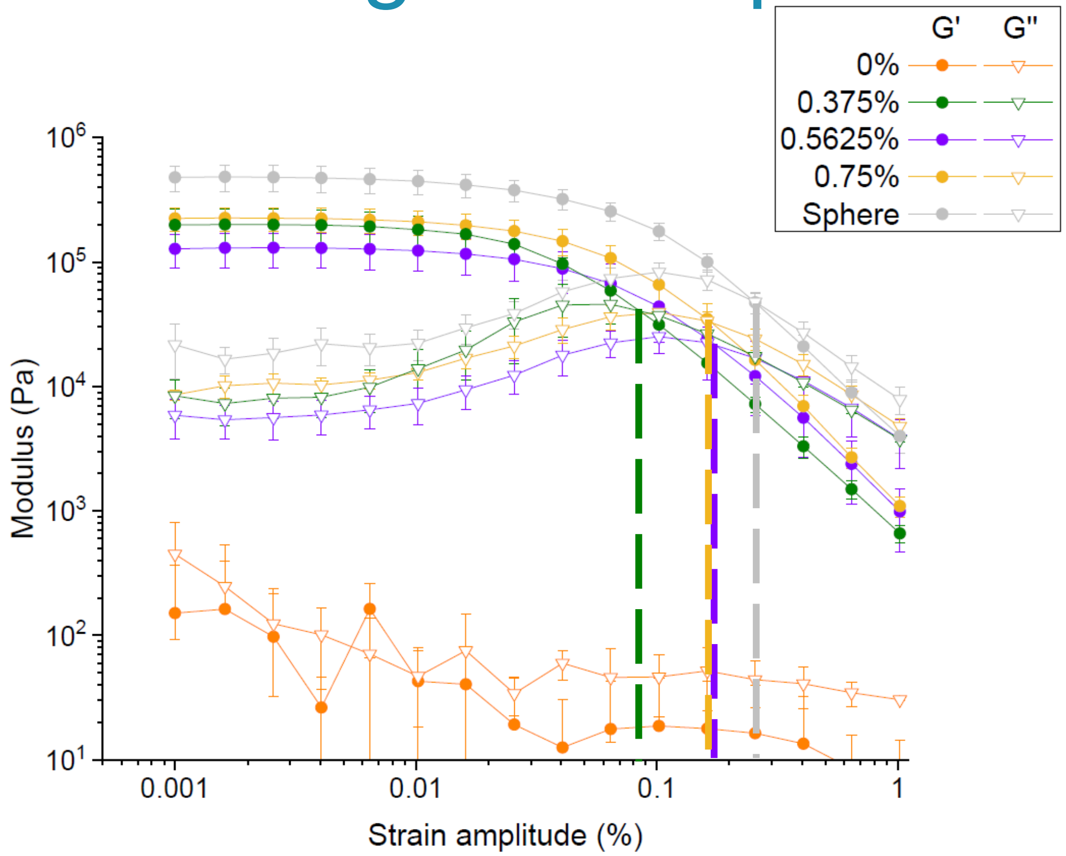
Rheological comparison



- 0% suspension → unmeasurable moduli
- 0.375% sec liquid
  - **Shorter** LVE
  - **Earlier** flow point
- 0.5625% & 0.75% liquid
  - **Prolonged** LVE
  - **Delayed** flow point
- Sphere system has a **longer** LVE and more **delayed** flow point (ϕ_{sphere} = 15 %, $\frac{\phi_{sec}}{\phi_{rod}}$ = 5%)
- Potential reasons:
  - From 0% → 0.375% liquid, weak gel formed
  - Random distribution with **less** clustered network
  - **Limited** liquid bridge volume & number resulting in brittle connection → **earlier** flow
  - Spherical particles are more **easily** to **reform** bridges once previous connections are broken

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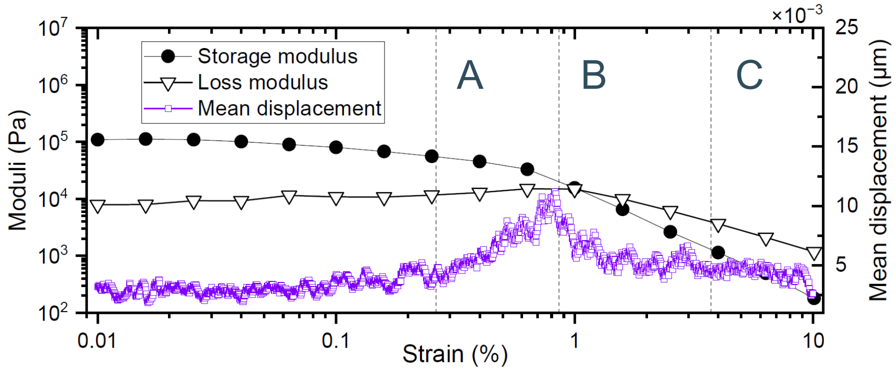
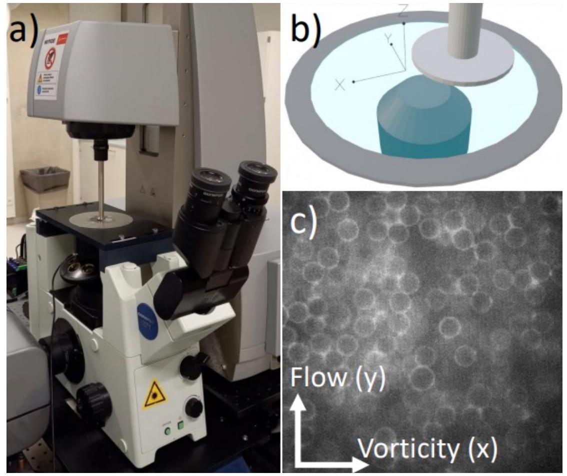
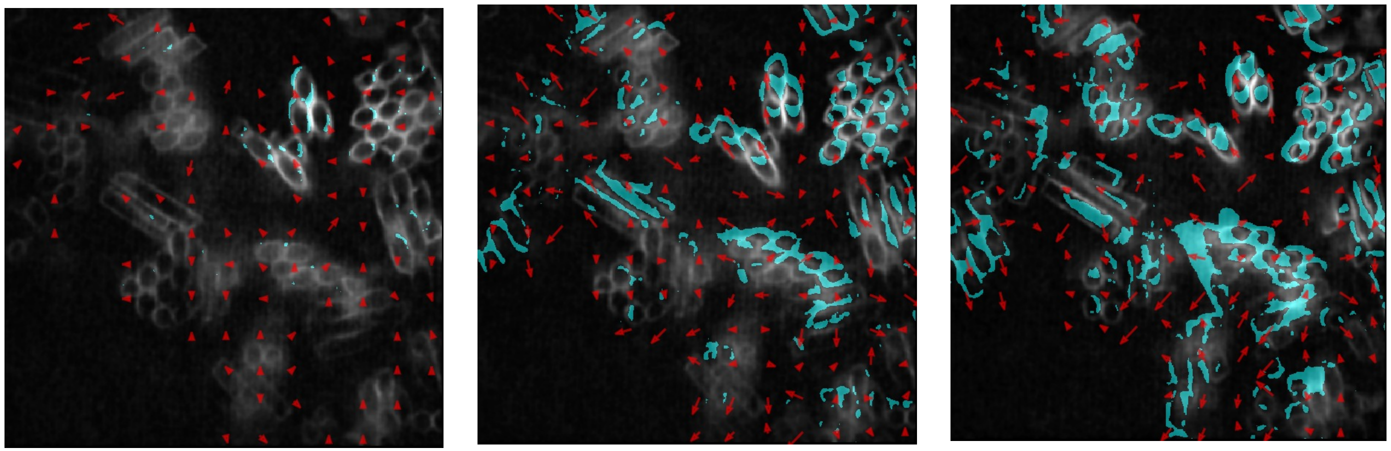
Rheoconfocal on rods

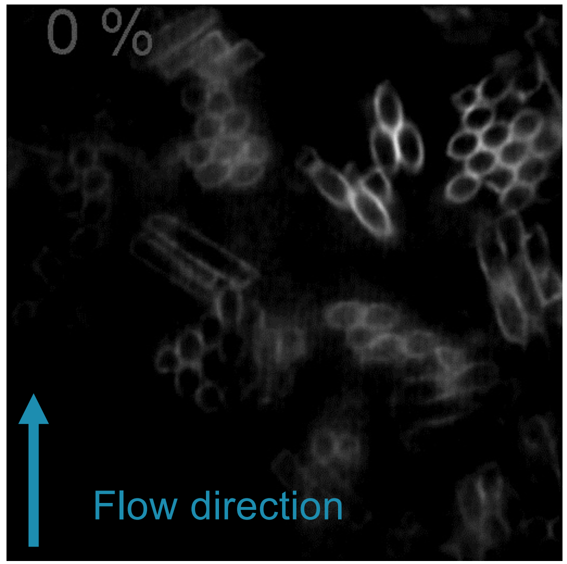


- A: Start to displace
- B: Maximum deformation
- C: Stabilize
- Rods rotate in clusters without clear direction





A B C



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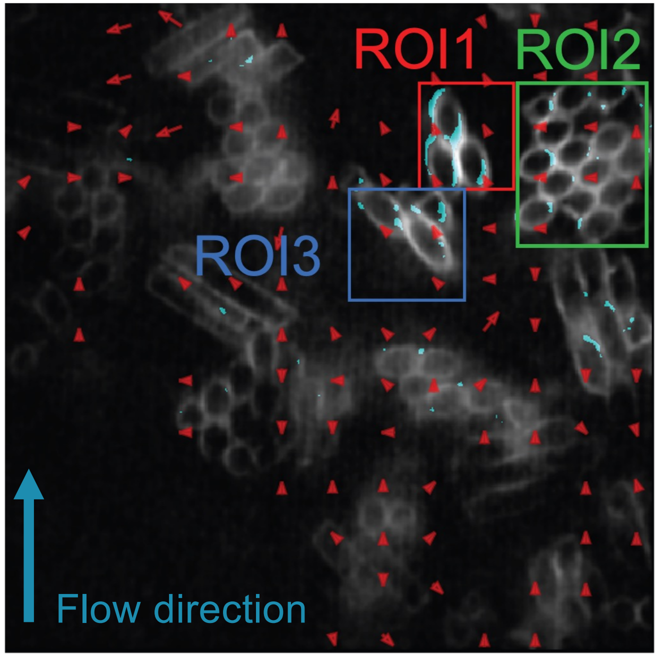
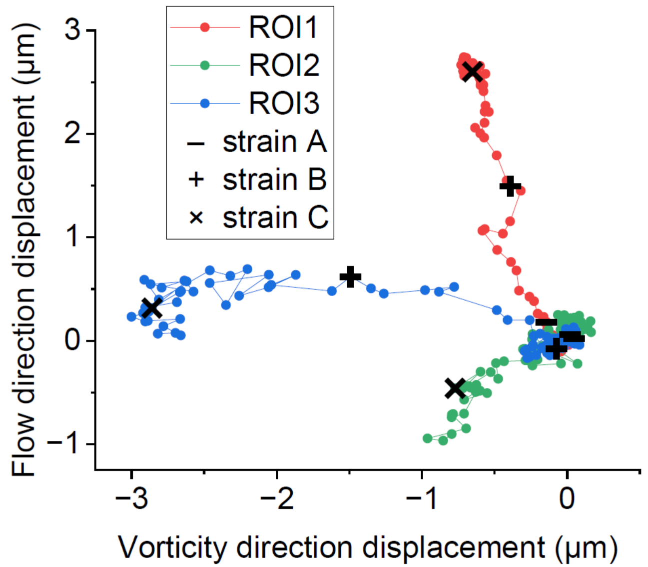
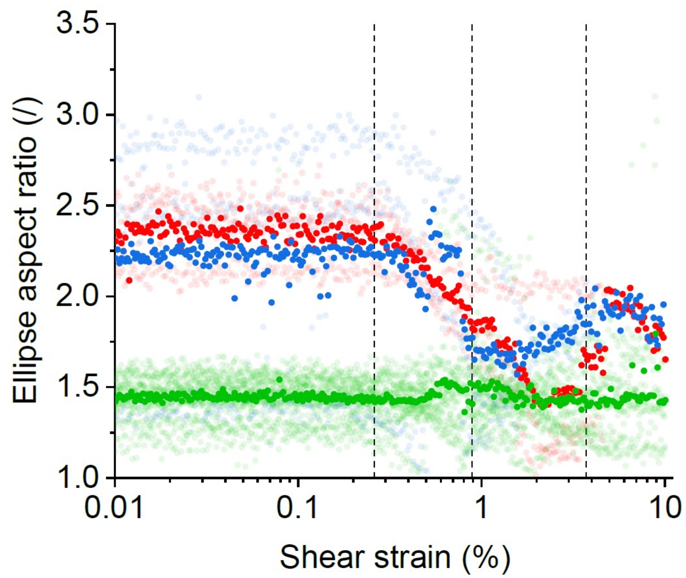
Cluster movement and rotation







- ROI 1, 2, 3 show movement in different directions
- Within clusters, the particle orientation show great alignment
- All three clusters rotate align in gradient direction under shear

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Take home messages

1. Rod-based capillary suspensions change contact type from point-to-point to side-to-side contact as secondary liquid increases.
2. Unlike spheres, the clustering coefficient of rods decreases with increasing coordination number.
3. Rod-based capillary suspensions exhibit **higher sensitivity to deformation**.
4. During yielding, particle clusters move in completely **different** directions with collective **rotation**, while **maintaining** their internal structure.

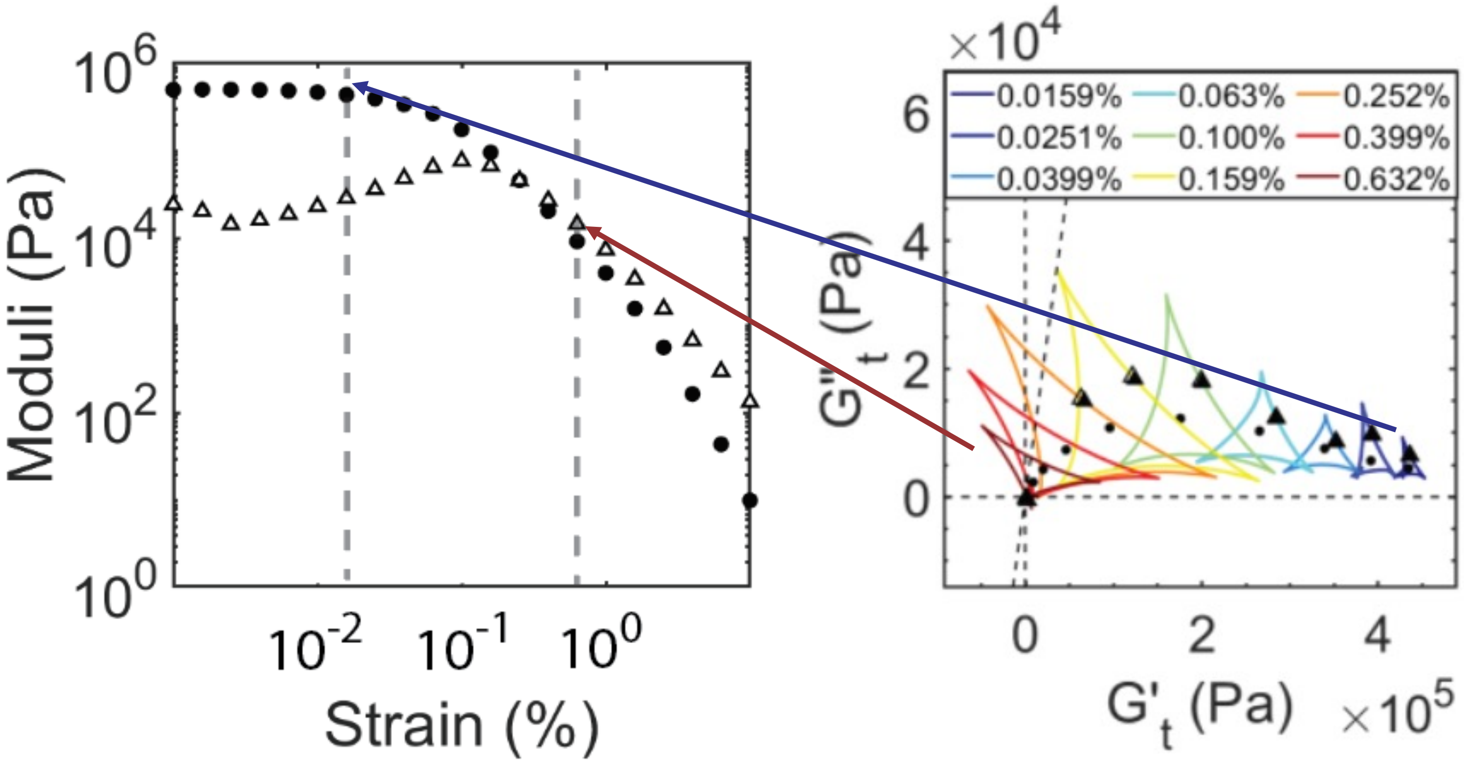
L. Liu, S. Gassenmeier, E. Koos
Arxiv, JCIS (First revision) (2025)

Identifying structural failure in attractive gels via recovery rheology

Lingyue Liu[1], Krutarth Kamani[2], Simon A. Rogers[2] and Erin Koos[1]

KU Leuven, Department of Chemical Engineering Section Soft Matter, Rheology and Technology[1]
University of Illinois Urbana-Champaign Urbana, Department of Chemical and Biomolecular Engineering[2]

Decomposed classic amplitude sweep



- As strain amplitude **increases**, structure breaks
- Normal amplitude sweep uses **averaged** moduli
- Using **SPP**, we decompose them into **instantaneous** moduli
- Interesting range = after **LVE**, before **slip**

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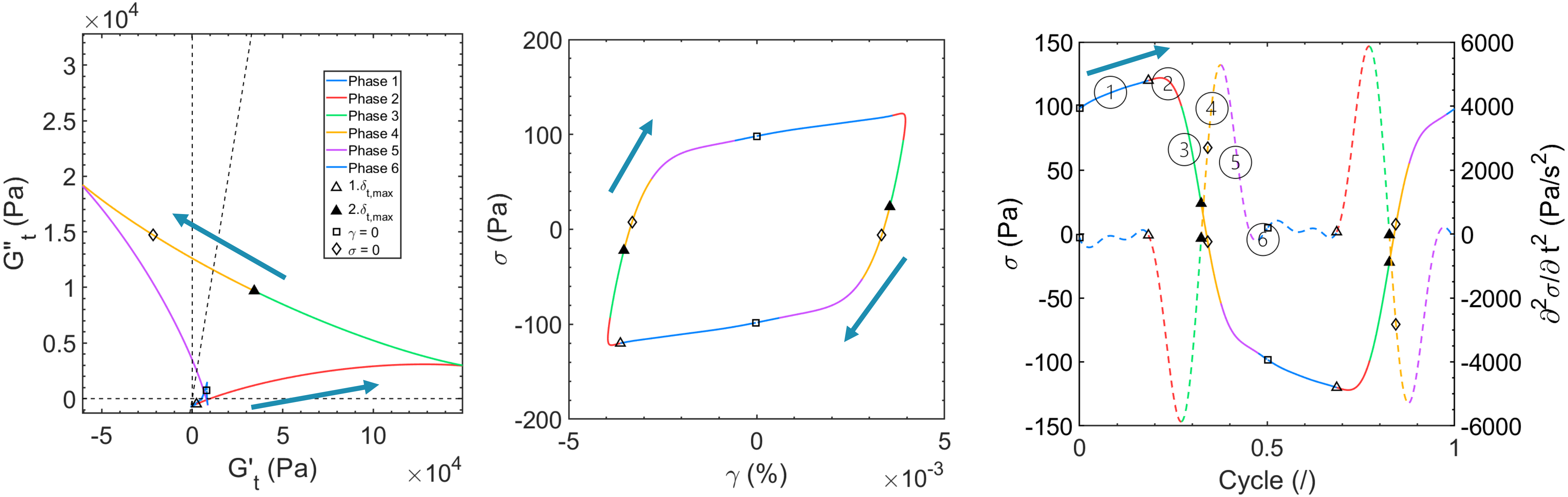
Physical meaning of each (half) cycle



1	Blue	from $\gamma = 0$
2	Red	from $\dot{\delta}_t$ peak (near t/T = 0.2)*
3	Green	from $\ddot{\sigma}$ minimum
4	Yellow	from δ_t peak (near t/T = 0.35)
5	Purple	from $\ddot{\sigma}$ maximum
6	Blue	from $\ddot{\sigma} = 0$ (near t/T = 0.4)*

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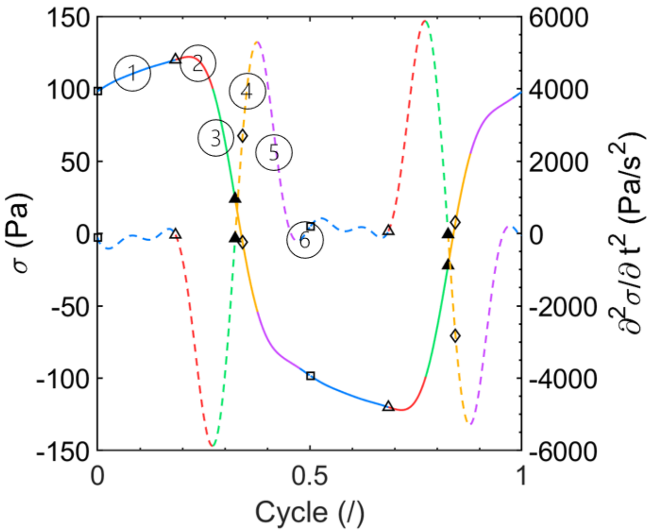
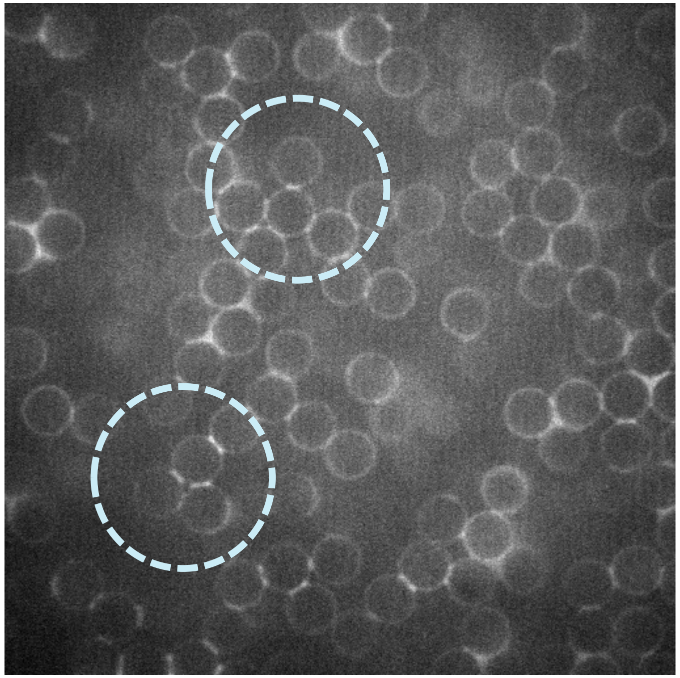
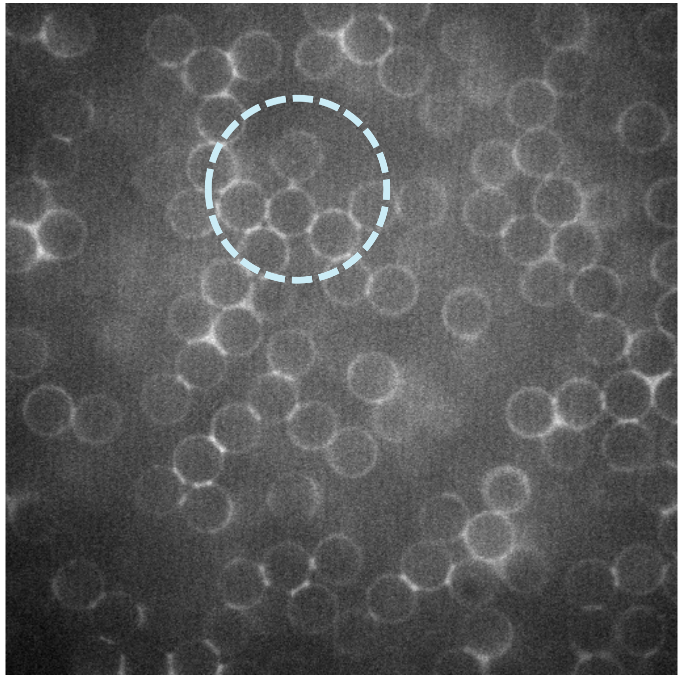
What we can see globally during each phase?



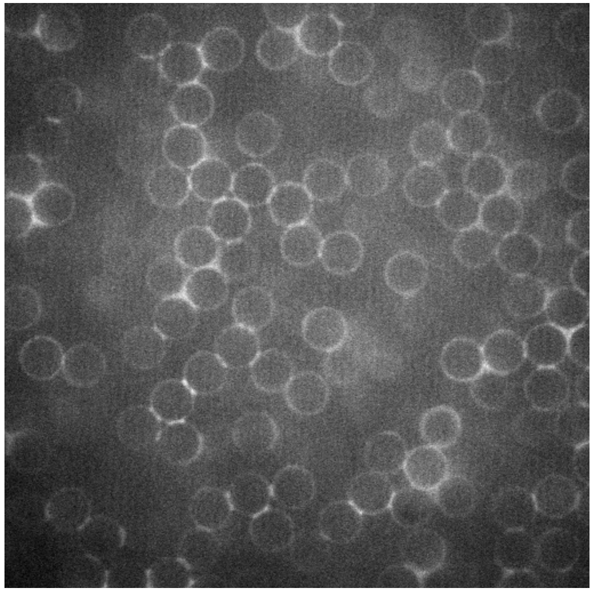


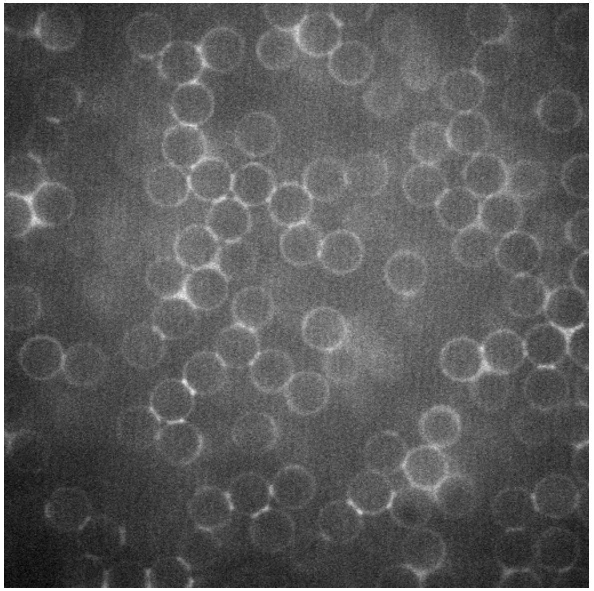
Phase1: Stretching/compression

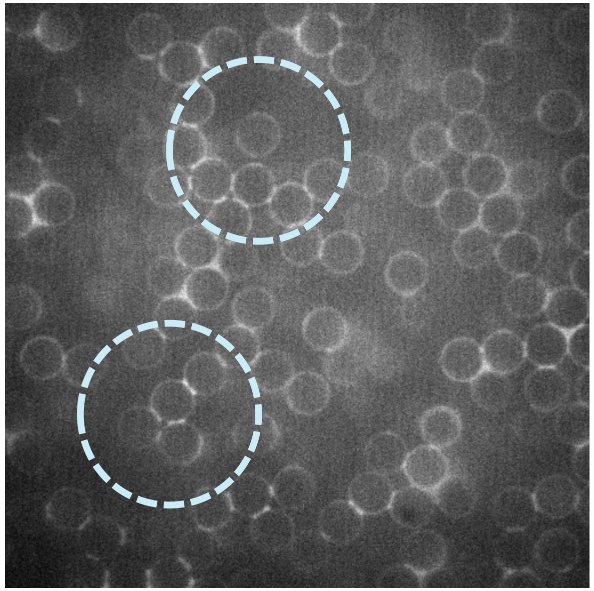


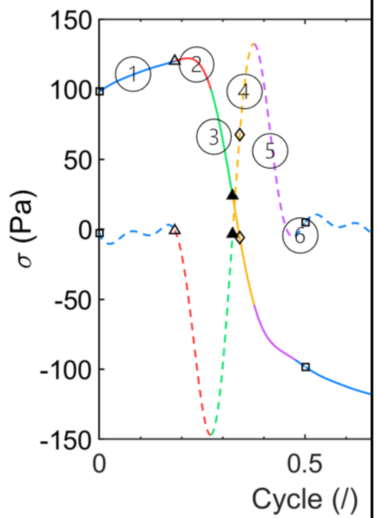
Phase2: Stretching/compression
+ Potential bridge snapping

What we can see globally during each phase?









Phase3: nothing optically

Phase4: nothing optically

Phase5: Relaxation

- Phase3 + 4 are responsible for the majority **stress** change, however, **no** optical displacement observed

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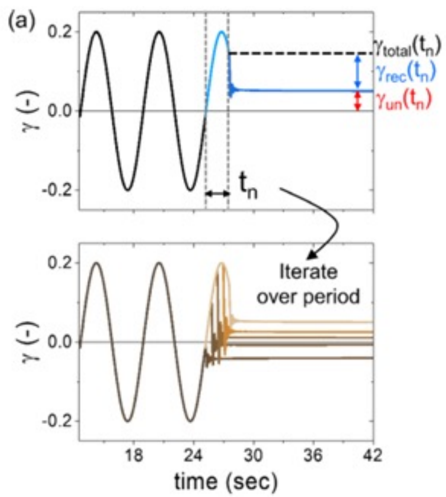
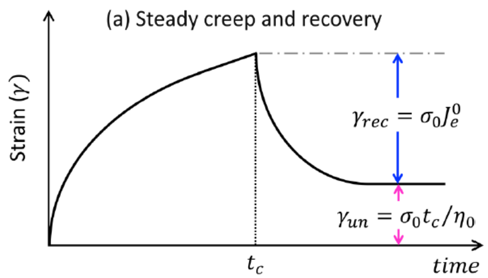
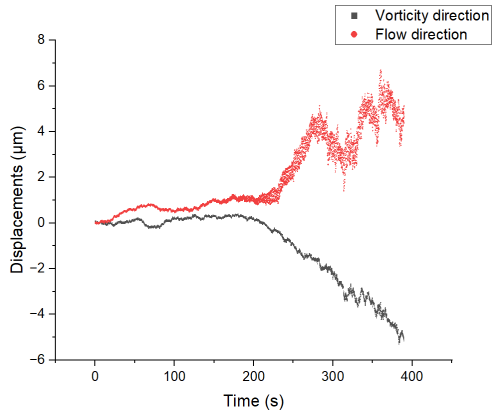
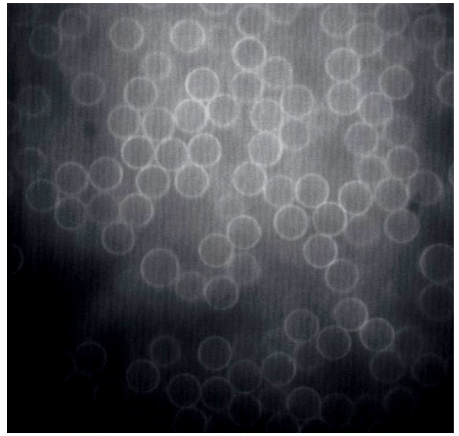
Rheo-optic recovery rheology of yield stress fluid

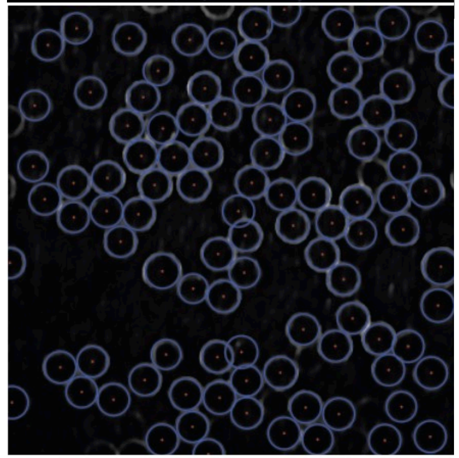
- Investigation: how the capillary suspensions relax differently at different parts of the oscillation cycle
- Decompose strain into (un)recoverable
- Combining with Rheoconfocal: track displacement of recovery





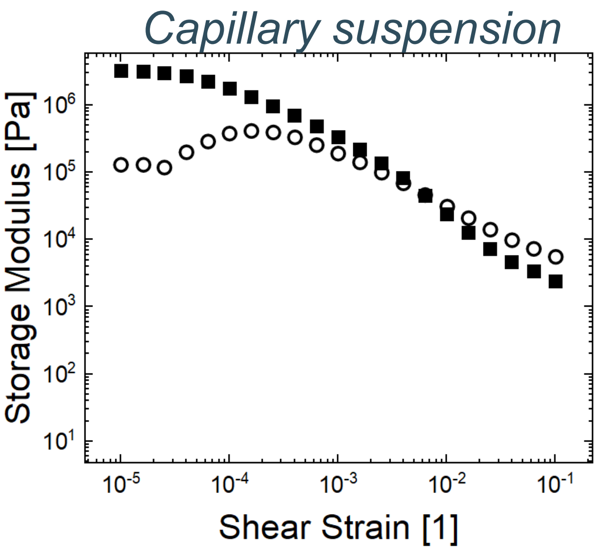


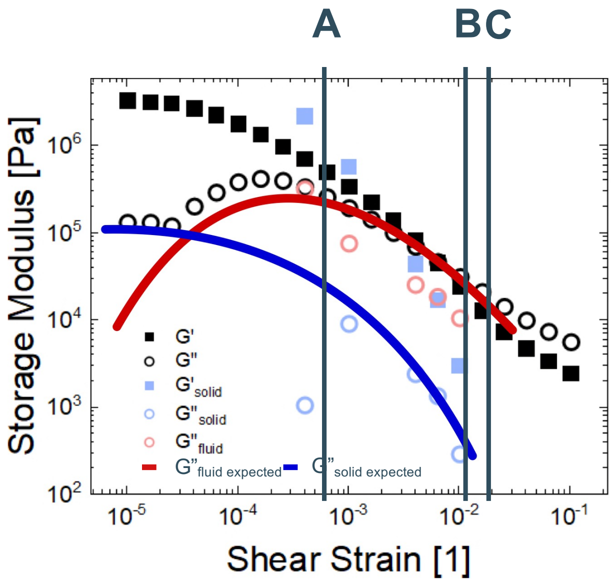


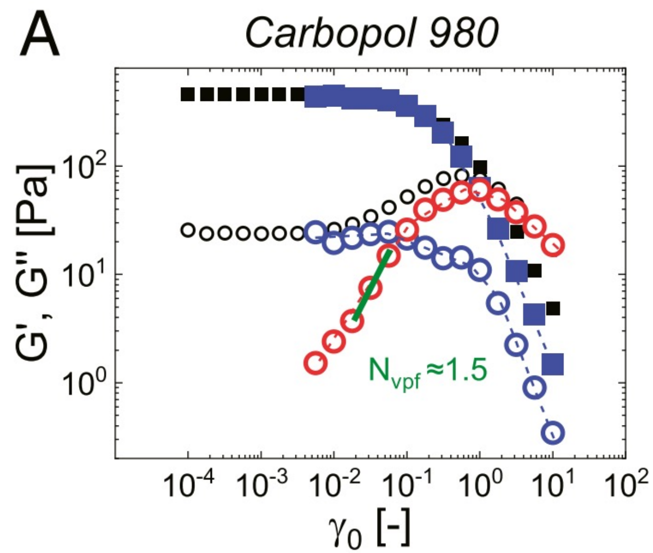


Y.H. Shim, S.A. Rogers;. *Physics of Fluids*, 2023; 35 (6): 063117
J. Lee, et al., *Journal of Rheology* , 2019; 63 (6): 863–881.
J. Allard, et al., in preparation

Understanding the average behavior through recovery

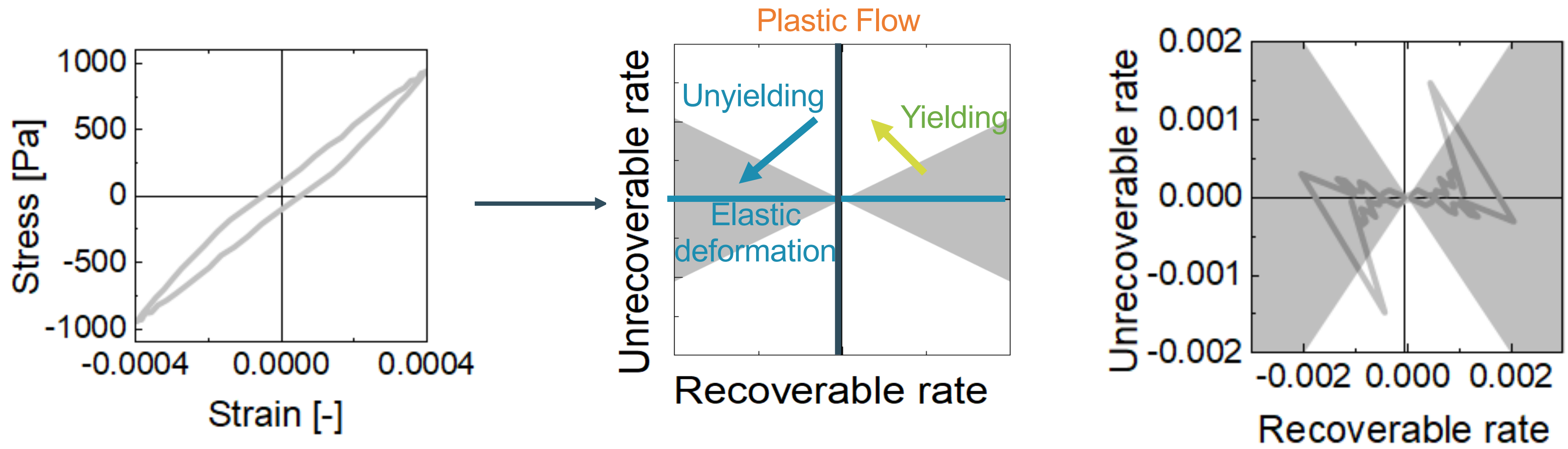






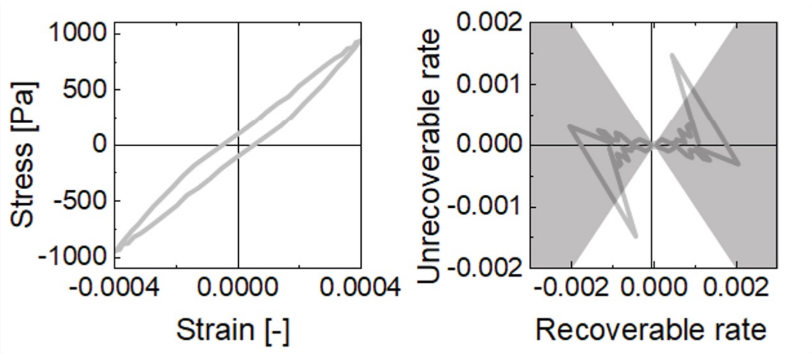
- Capillary suspension tested by UIUC
- Similar trends in G' and G'' as a Carbopol 980
- First: Amplitude sweep, pick interesting strain amplitudes A, B, C,

Tracking transient behavior through recovery

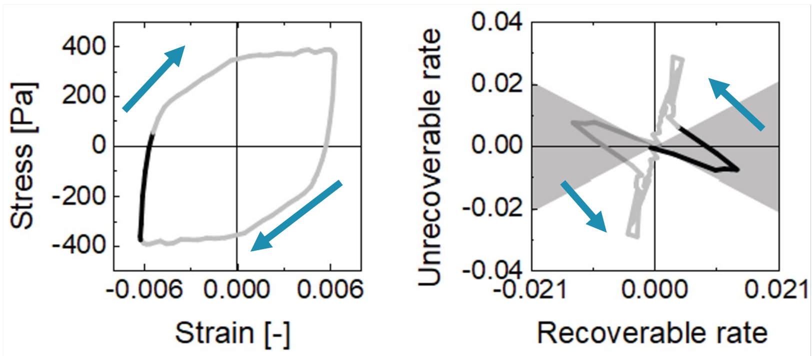


- Lissajous plot → Rate plot (Unrecoverable rate vs Recoverable rate)
- At this strain, experiments were repeated 64 times to plot (Un)recoverable rate plot
- Most points are dominantly recoverable strains with one outlier

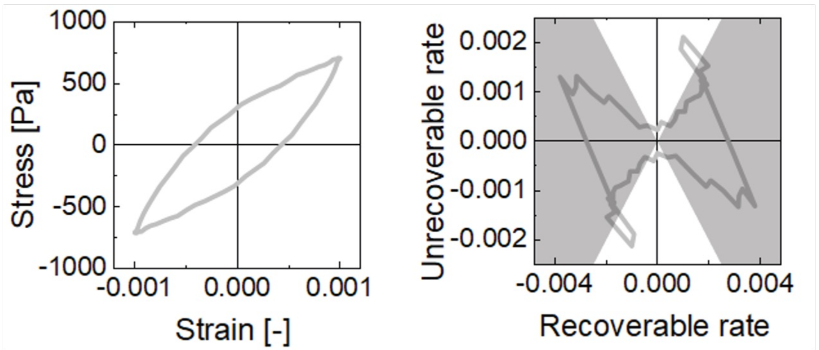
Rate plots at different strain amplitudes



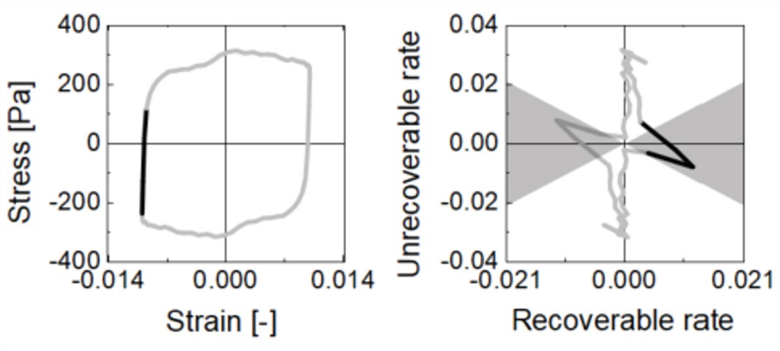
$\gamma_0 = 0.04$ %



0.4 %



0.1 %



1.4 %

- γ_0 increases, less points at the gray region (recoverable)
- Controdictory regrading physical meaning of phases

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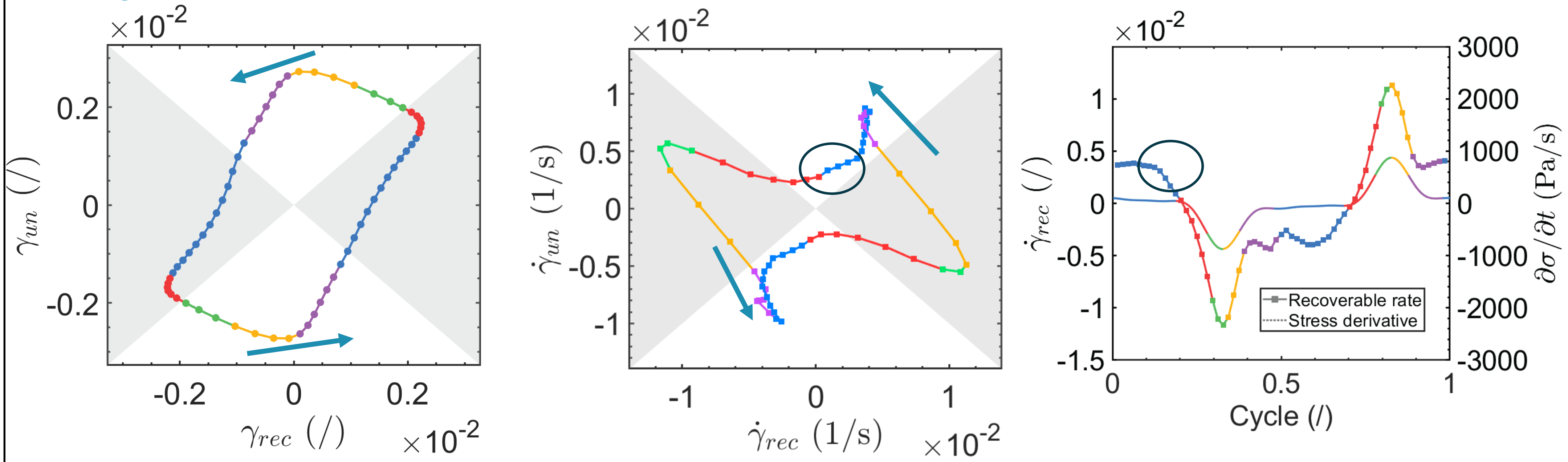
γ_0 = 0.4 %, strain, rate and stress derivative



- When recoverable rate & stress derivative plot over time (right), they align well
- Circled: sample acquire recoverable rate **slower**, $\delta\sigma/\delta t \approx 0$ → stretching contributes more to unrecoverable deformation. At $\dot{\gamma_{rec}}$ = 0, a γ_{rec} max is reached
- Traditional recovery rheology definition is not suitable for geometric constrained sample

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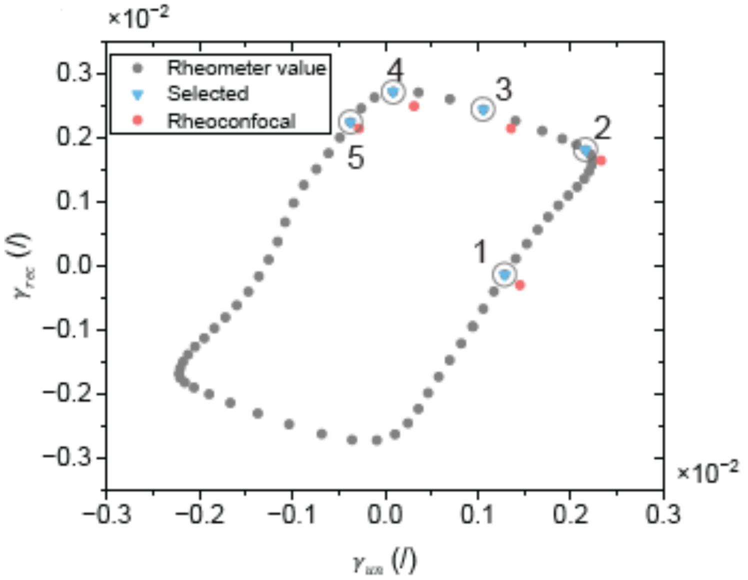
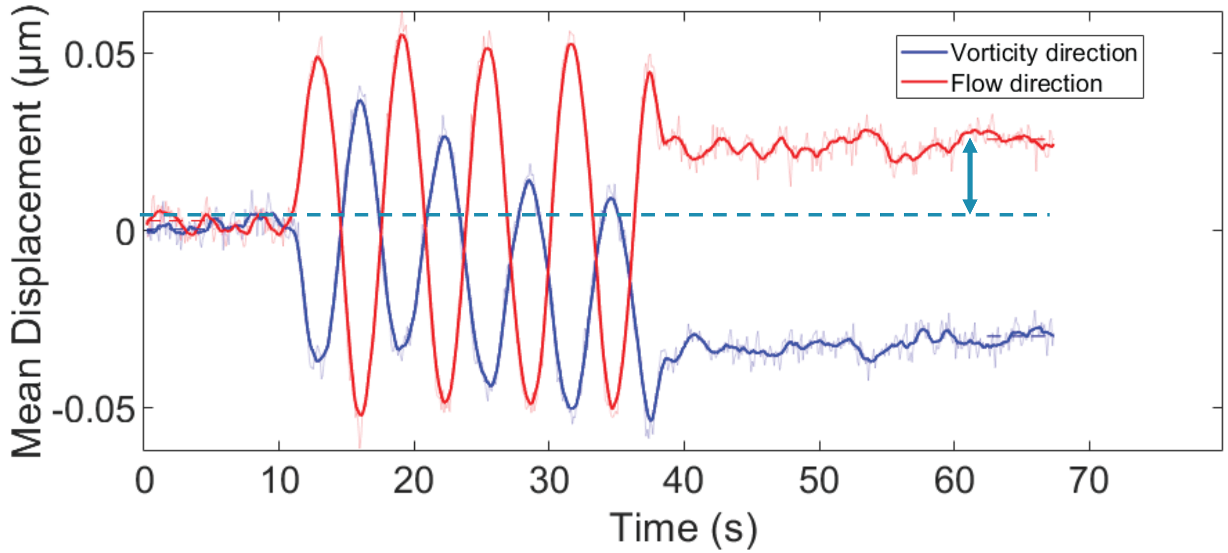
Outlook

- Detailed explanation of the physical meanings of phases → **Lingyue: Poster**
- Focus on the differences between the **optical** and **rheological** part
- Delve into the **strain** plot and **rate** plot, the **mechnisms** of yielding





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