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Welcome to ~~Leuven~~ Brussels

IFPRI Annual Meeting 2022

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Highlights

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Capillary suspensions and their applications

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Established by the European Commission

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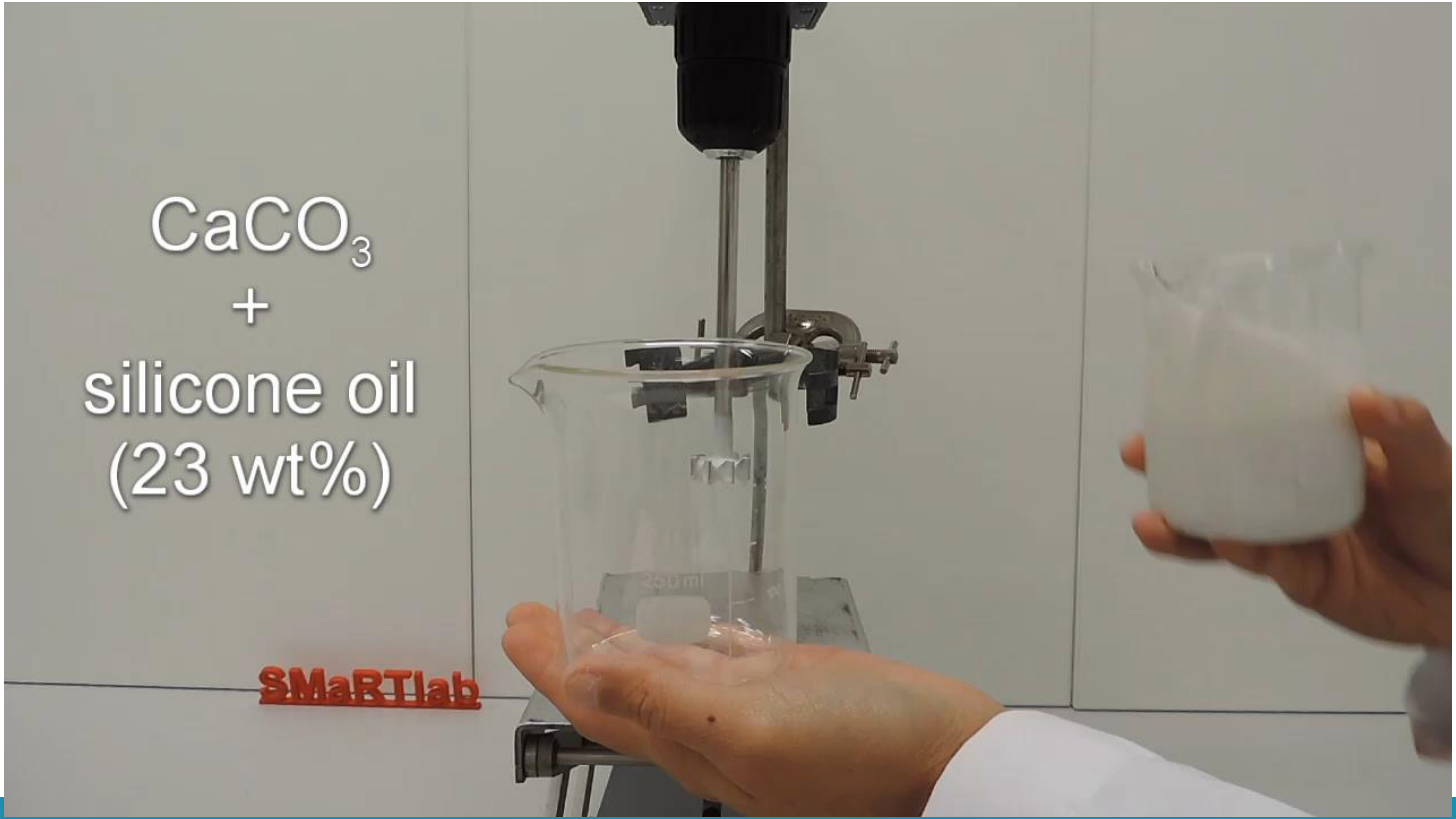
Capillary suspensions



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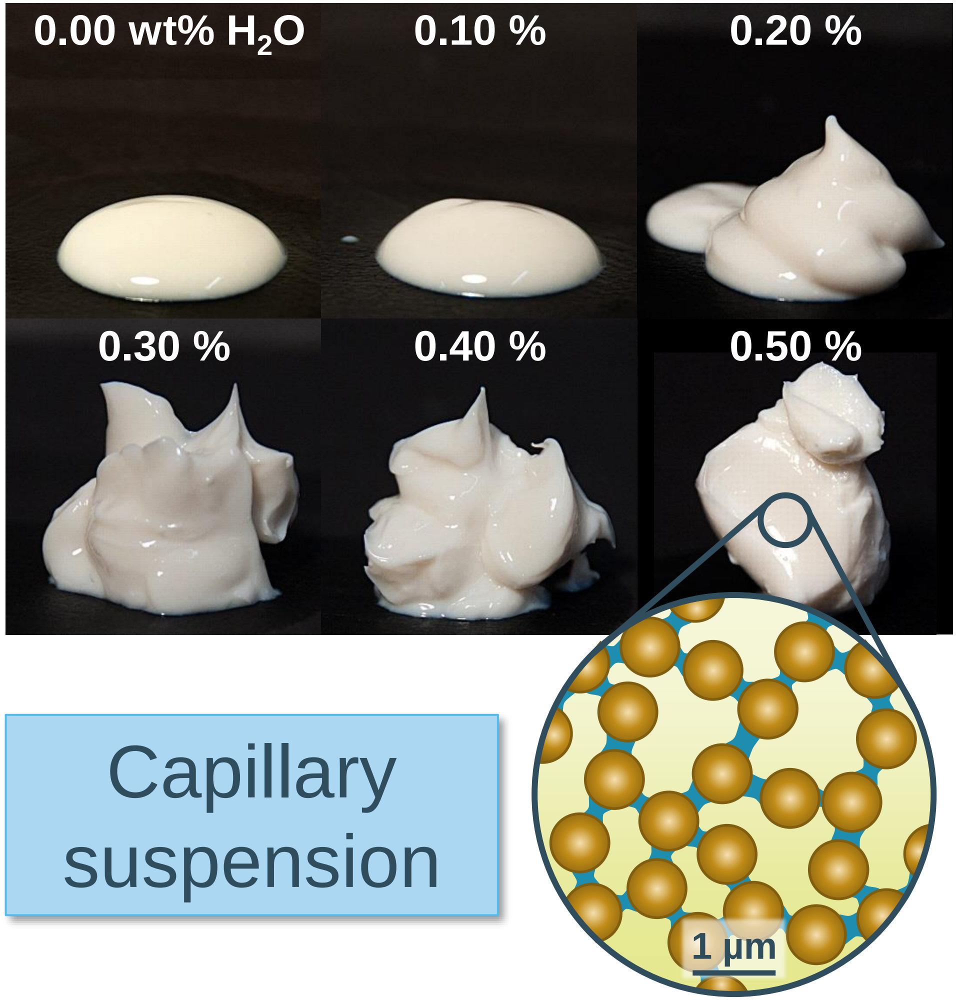
The capillary suspension phenomenon

Micro- or nanoparticles

Two immiscible liquids



Capillary suspension

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

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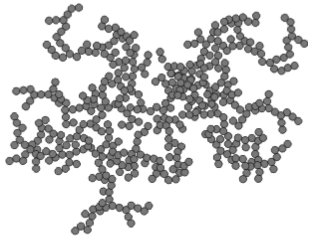
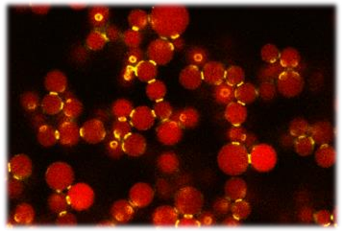
Interesting new material

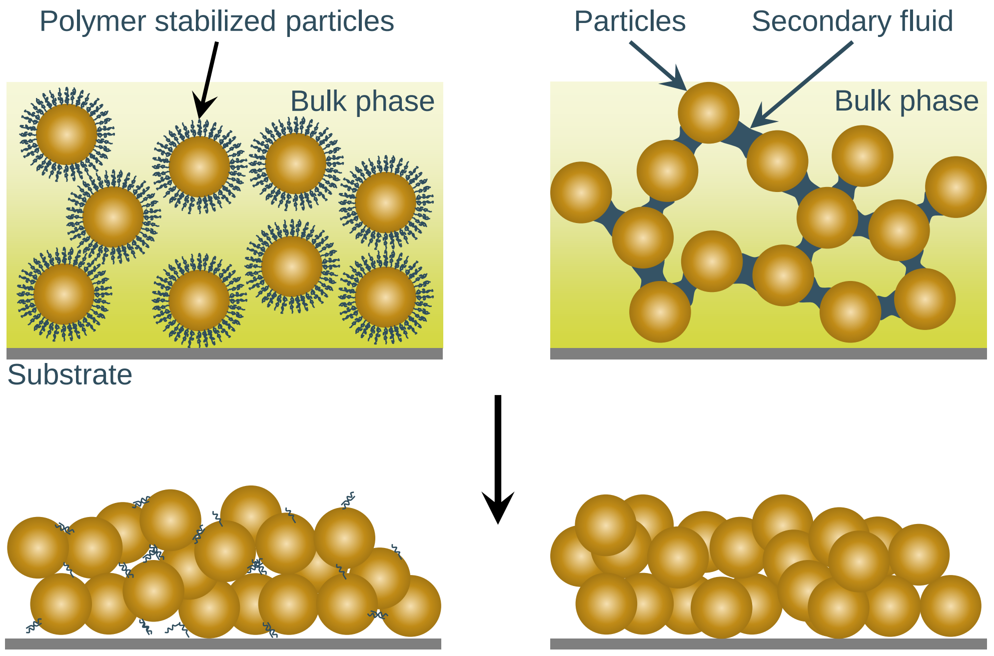
	Colloidal network	Capillary suspension	Wet granular matter
			
Composition	Solid-liquid	**Solid-liquid-liquid**	Solid-gas-liquid
Bulk transmits force	Yes	**Yes**	No
Particle size	Small	**Small**	Large
Attractive force	van der Waals	**Capillary**	Capillary
Interaction range	Short ($\ll R$)	**Longer ($\sim R$)**	Longer ($\sim R$)
Relative strength	Weak (~ diffusion)	**Strong**	Weak (~ gravity)
Solid loading	Low	**Intermediate**	High

E. Koos, *Cur. Opin. Colloid Interface Sci.* **19(6)**, 575 (2014)

Application 1: Printed electronics

- No surfactants or polymeric additives for stabilization or thickening
  - Liquid phases evaporates completely during drying process
  - No polymeric residues in the manufactured film
- Viscosity of ink adjustable to specific printing processes

Method	Viscosity
Inkjet Printing	0.001 – 0.04 Pas
Screen Printing	0.05 – 50 Pas



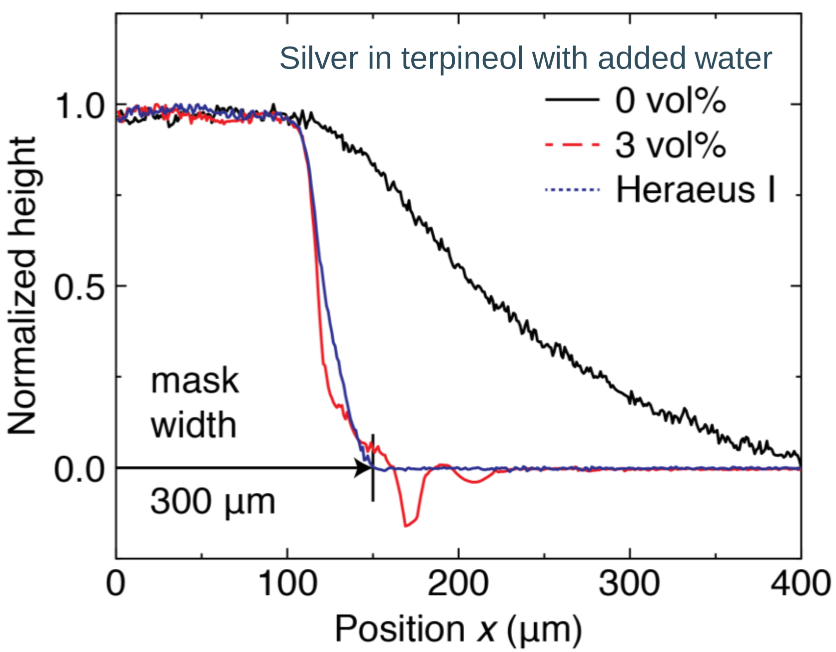
Polymer not removed: **reduced conductivity**

Both fluids removed: **increased conductivity**

M. Schneider, et al., *Sci. Rep.* **6**, 31367 (2016)

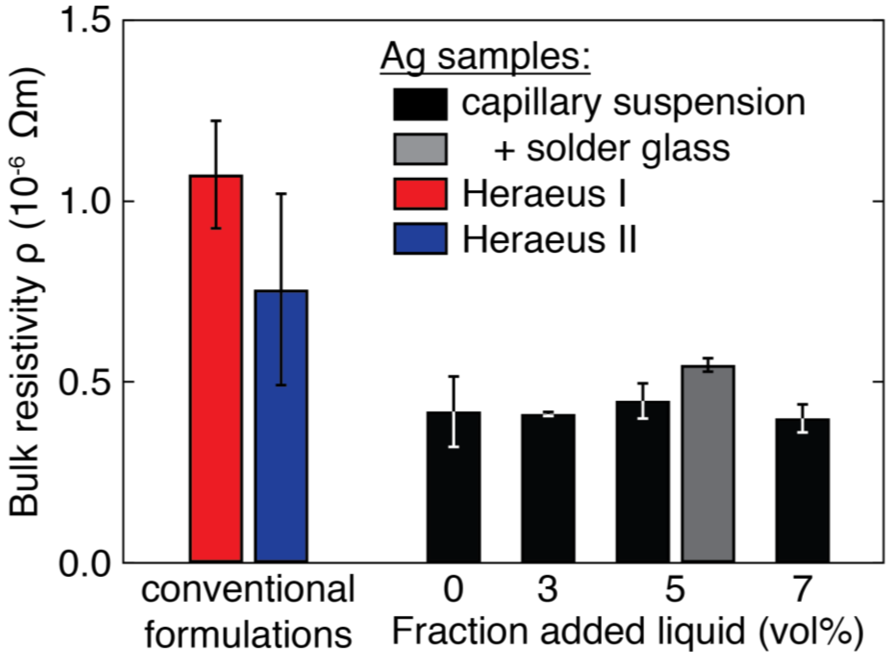
Particle network leads to better properties

Improved shape accuracy



→ **Increased feature density without short circuits**

High conductivity



→ **Lower resistivity than conventional formulations**

M. Schneider, et al., *Sci. Rep.* **6**, 31367 (2016)

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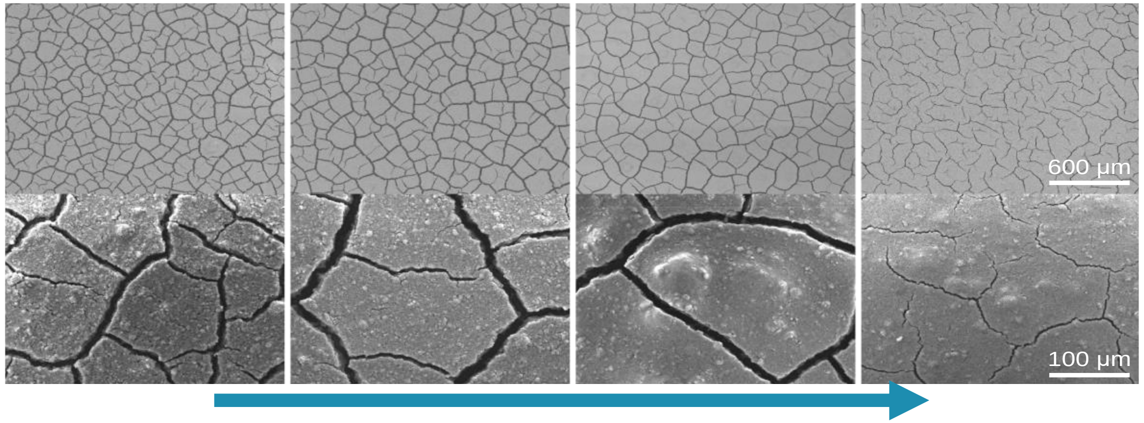
Further advantages: reduced cracking

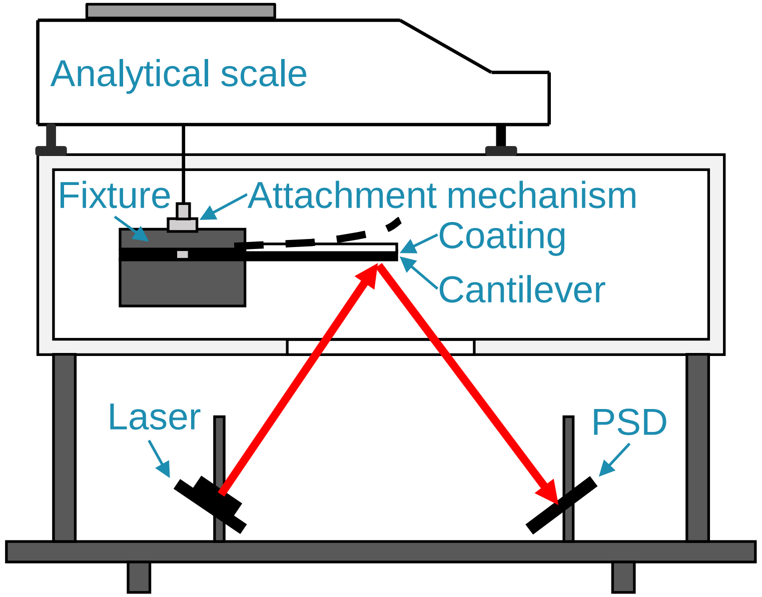
Capillary suspensions



Added secondary fluid

- Particle network opposes particle motion
- Lower drying stresses and reduced cracking

Simultaneous stress and weight loss measurement



- Control temperature and humidity
- Camera or laser observation of film

M. Schneider, et al., *ACS Appl Mater. Interfaces* **9(12),** 11095 (2017)
S.B. Fischer and E. Koos, *Rev. Sci. Instrum.* **91(12)**, 123904 (2020)

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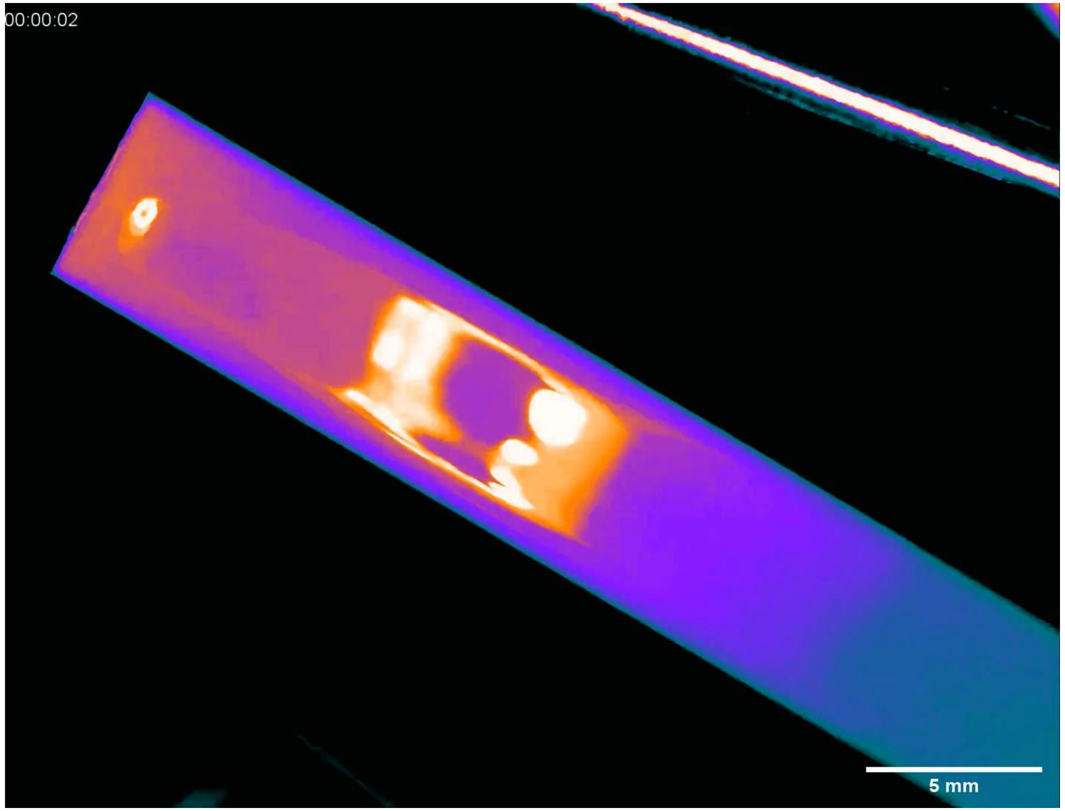
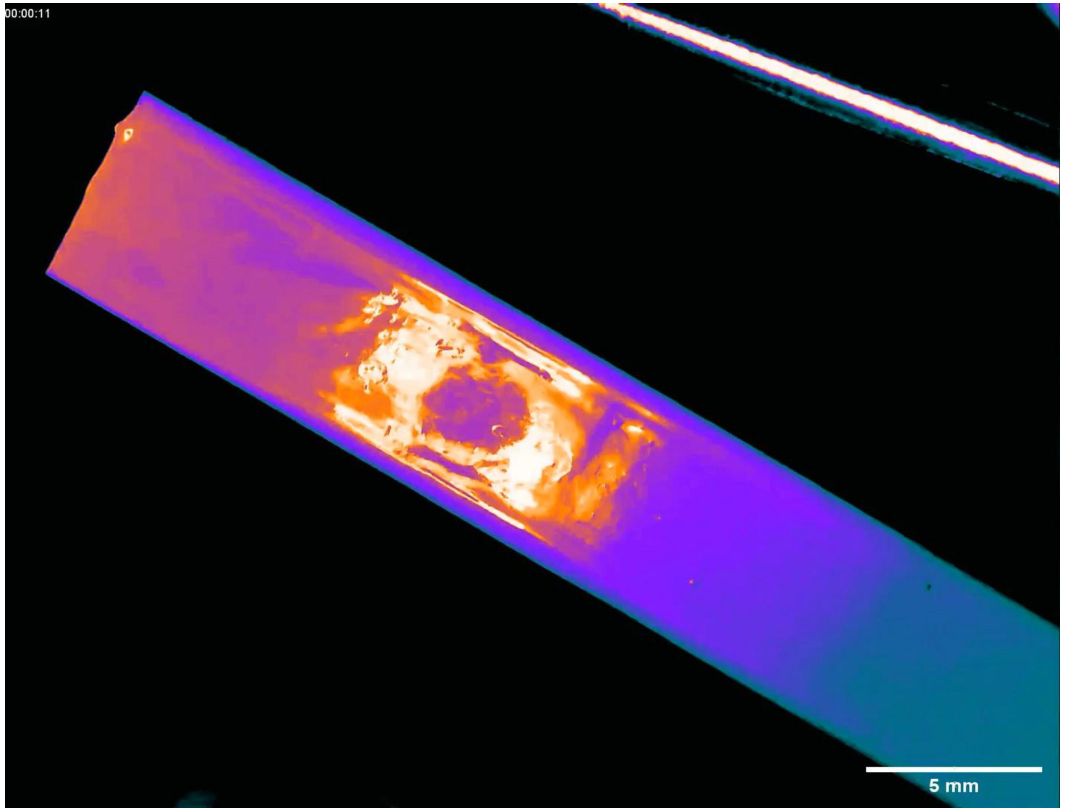
Drying of coated cantilevers

Pure suspension ($\phi_{H_2O} = 0$)

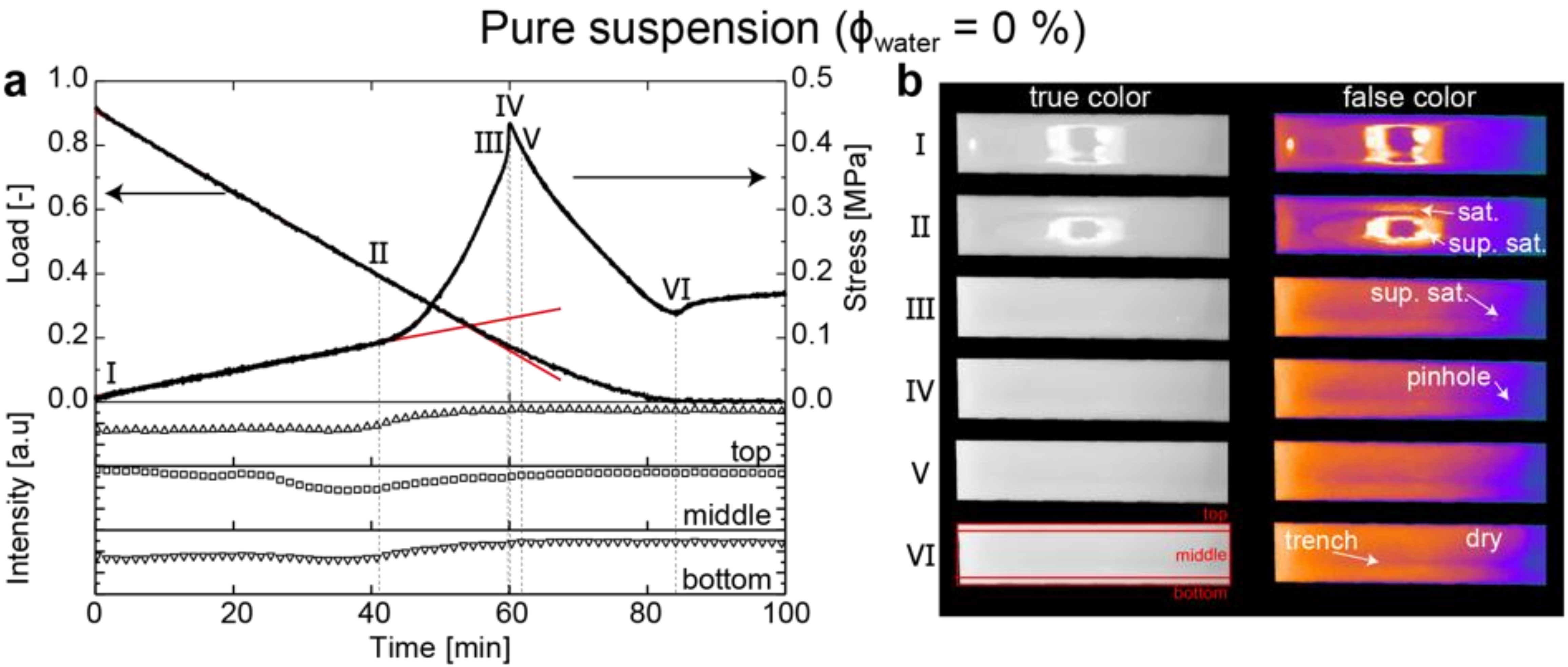


Capillary suspension ($\phi_{H_2O} = 0.025$)



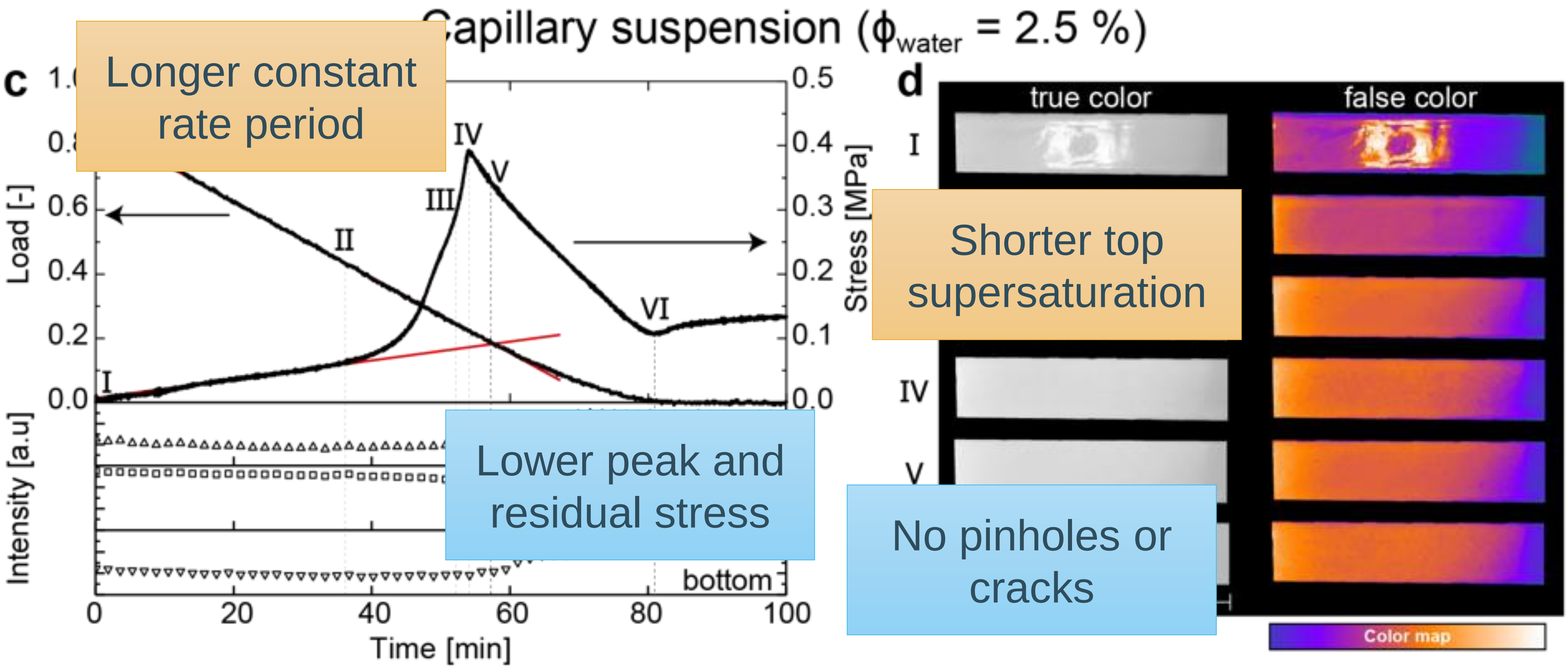
S.B. Fischer and E. Koos, *J. Colloid Interface Sci.* **582(Part B)**, 1231 (2021)

Example simultaneous measurements



S.B. Fischer and E. Koos, *J. Colloid Interface Sci.* **582(Part B)**, 1231 (2021)

Example simultaneous measurements



Longer constant rate period

Shorter top supersaturation

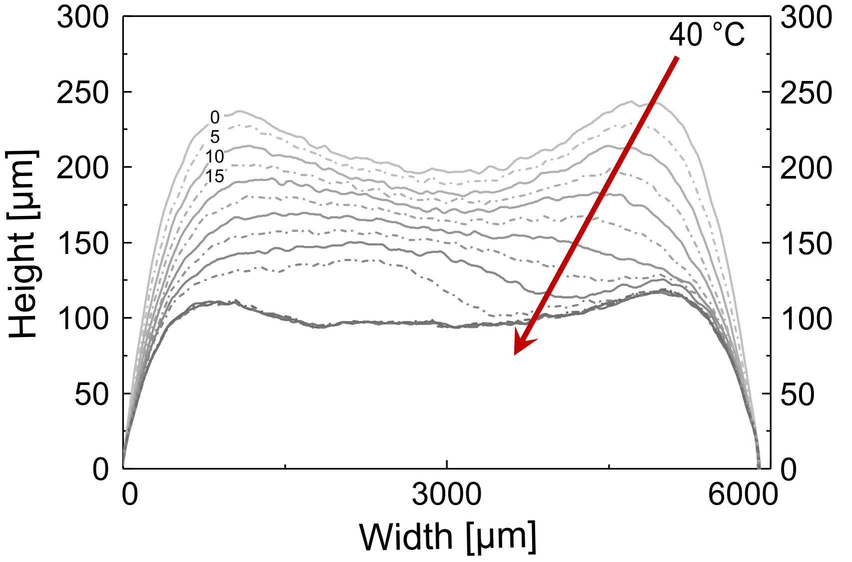
Lower peak and residual stress

No pinholes or cracks

S.B. Fischer and E. Koos, *J. Colloid Interface Sci.* **582(Part B)**, 1231 (2021)

Shrinkage and fluid/particle mobility

Pure suspension ($\phi_{H_2O} = 0$)

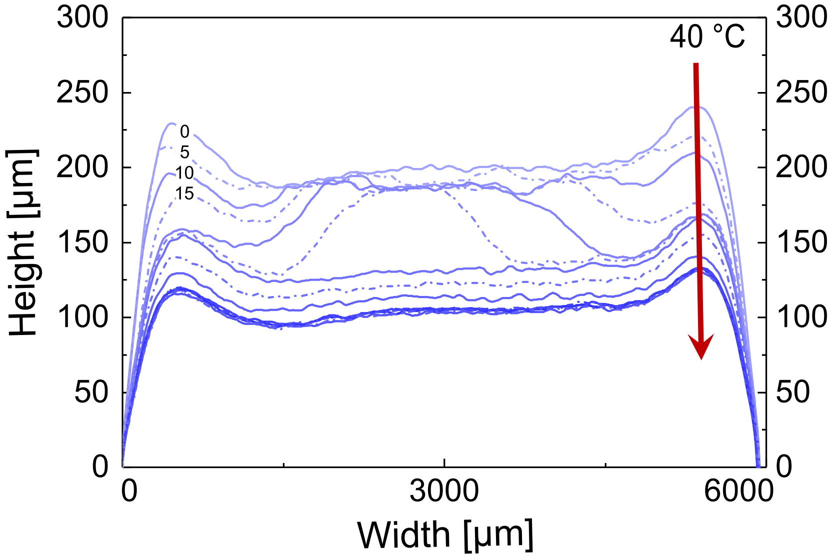


- Lateral drying

Dyed oil

- Continuous cross-sectional shrinkage

Capillary suspension ($\phi_{H_2O} = 0.025$)



- Initial lateral drying (reduced)

Dyed water

- Homogeneous shrinkage in height

S.B. Fischer and E. Koos, *J. Colloid Interface Sci.* **582(Part B)**, 1231 (2021)

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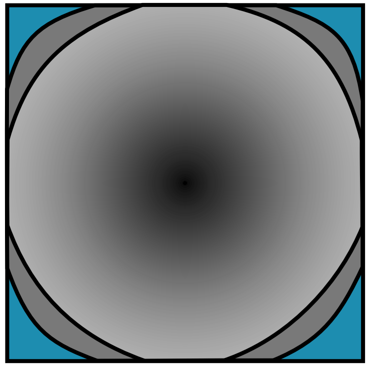
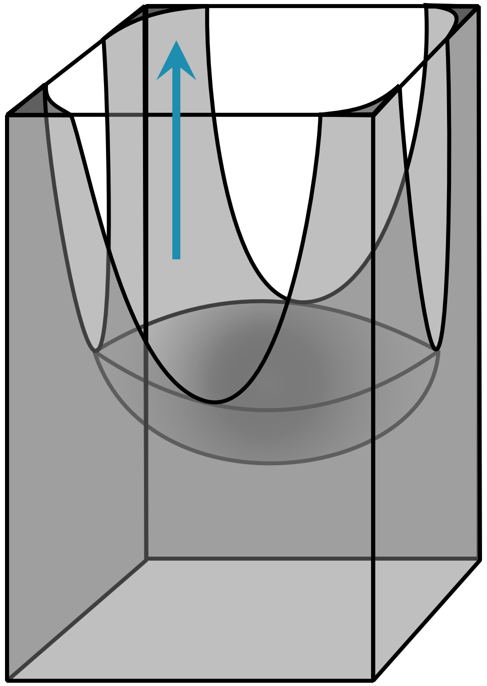
Longer constant rate period

- Bulk fluid moves away from substrate faster [1]
  → Transport of fluid from bottom up
- Shorter top supersaturation
  → Consolidated upper layer
- End of constant rate period corresponds to the peak stress (full compaction)
  → Particle network fully established

→ Capillary corner flow [2]

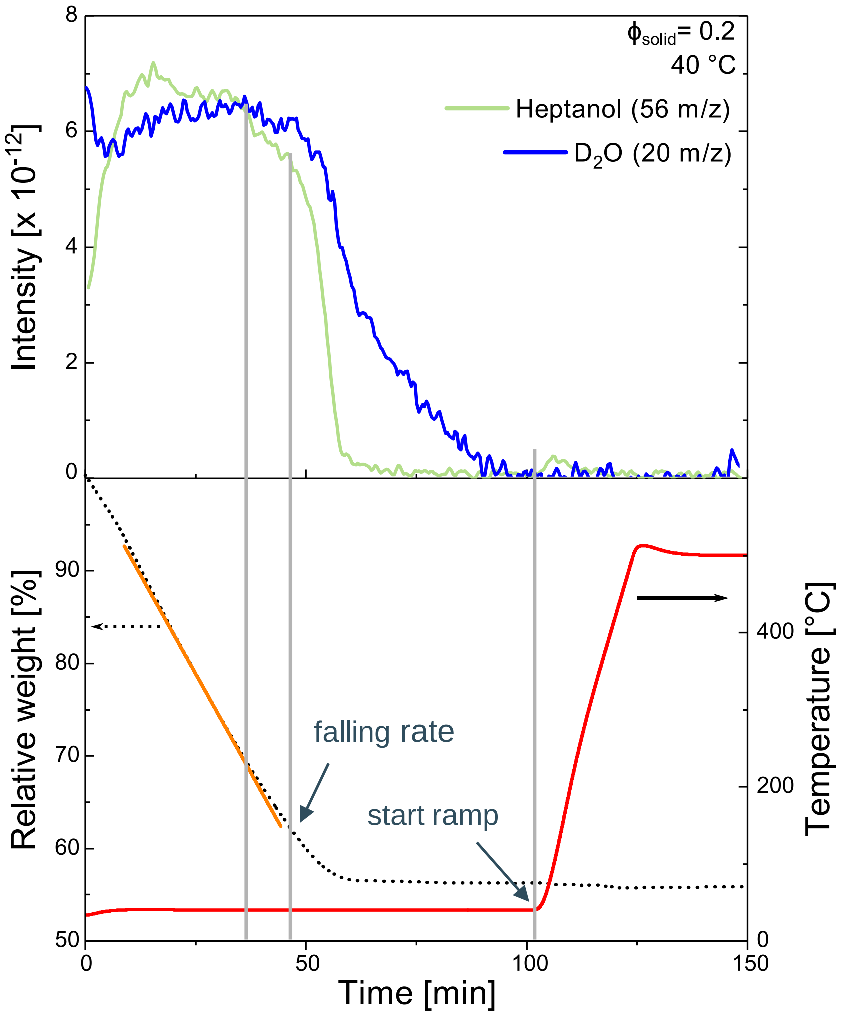
- Bulk oil covers the water bridges, that are sandwiched between the invading air
- Transport of liquid to surface





[1] M. Schneider, et al., *ACS Appl Mater. Interfaces* **9(12)**, 11095 (2017)
[2] M. Prat, *Int. J. Heat Mass Transf.* **50**, 1455 (2007)

Delayed evaporation of capillary bridges



- Drying occurs at a constant temperature of 40 °C, then ramp to 500 °C
  - TGA + headspace mass spectrometry
- Heptanol concentration drops when transitioning to the falling rate period
- Residual heptanol evaporates upon temperature increase

Extended evaporation of D_2O

S.B. Fischer and E. Koos, *J. Am. Ceram. Soc.* **104(3)**, 1255 (2021)

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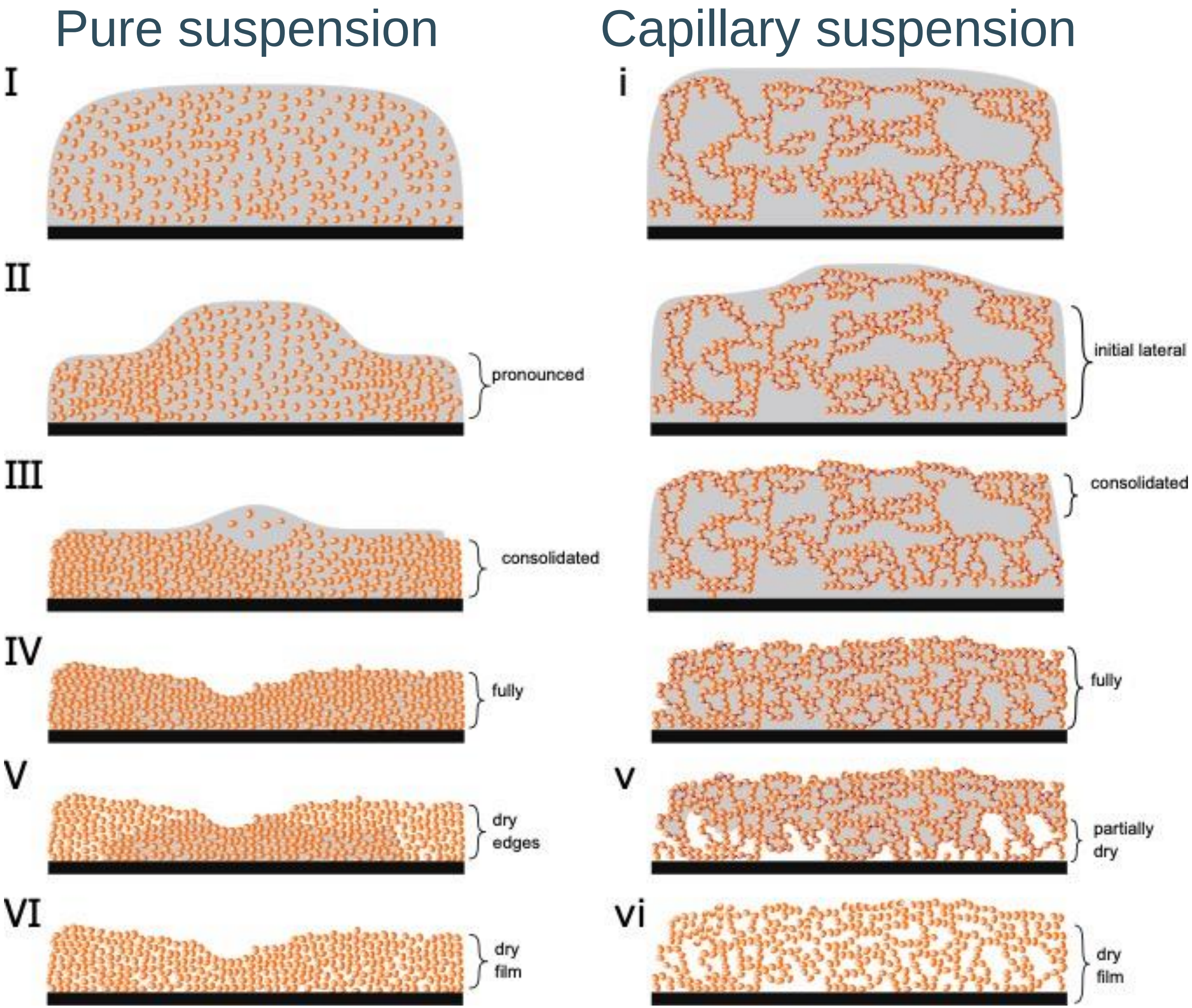
Hypothesis

- Reduced lateral drying
  - Less drying from edges
  - Less particle movement
- Yielding
  - Caused by particle network
  - Dissipates stress
- Bridges are long lasting
  - Still present when film is almost dry



S.B. Fischer and E. Koos, *J. Am. Ceram. Soc.* **104(3)**, 1255 (2021)

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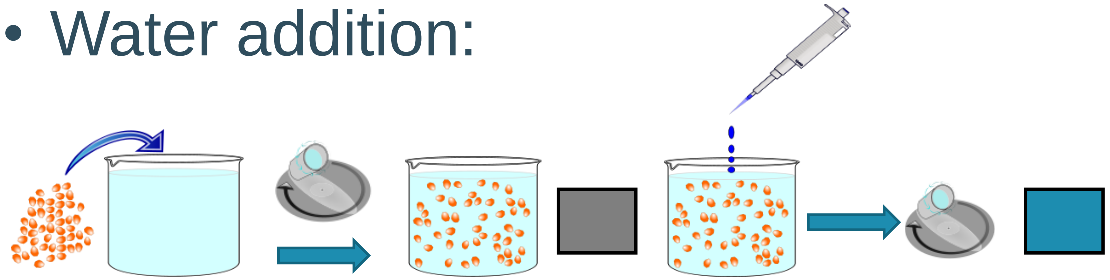
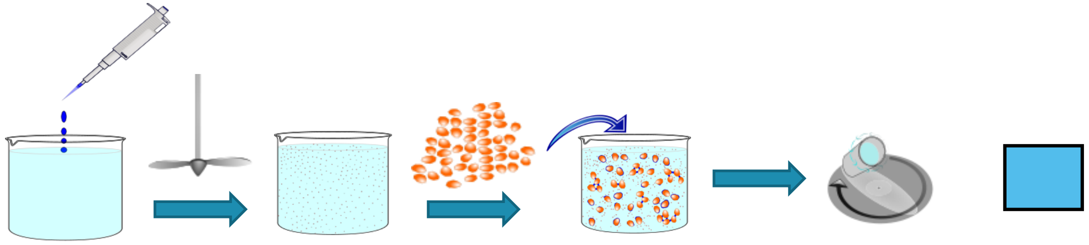
Formulation routes

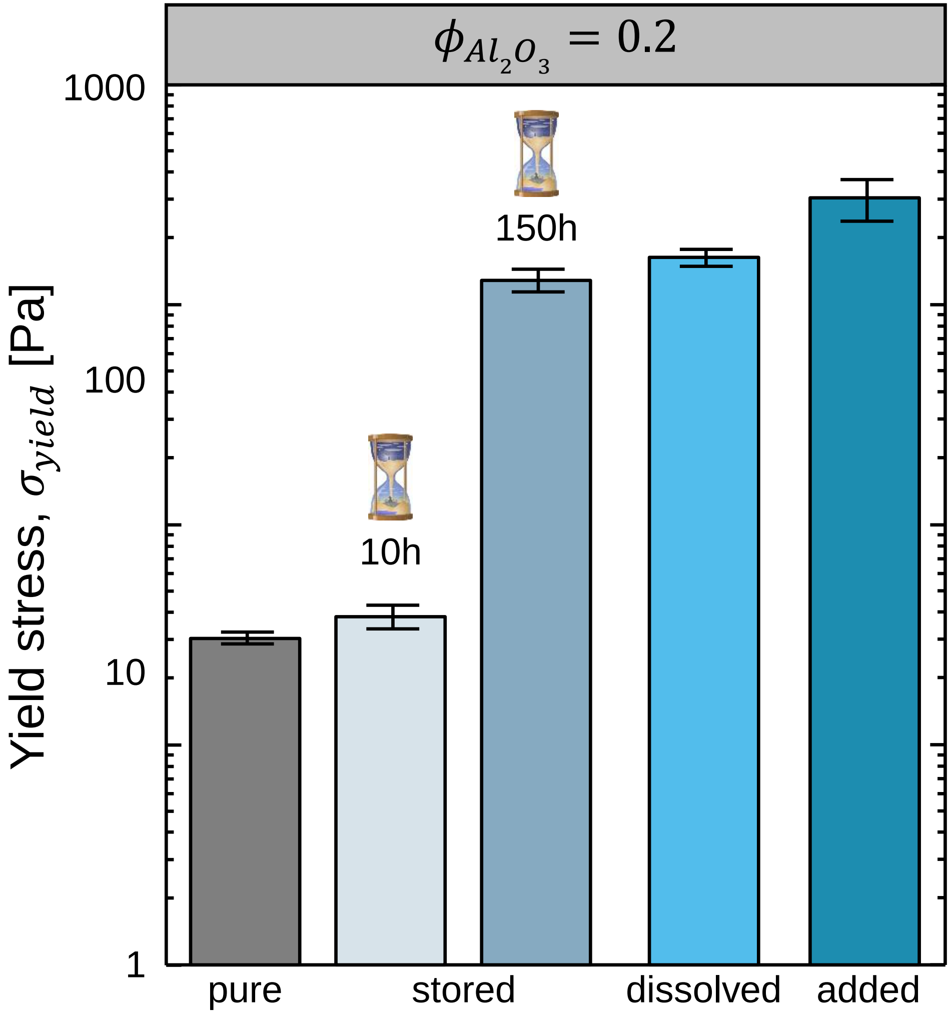
- Water addition:



- High humidity storage:

- Water dissolution:





S.B. Fischer and E. Koos, *Colloid Interface Sci. Commun.* **41**, 100373 (2021)
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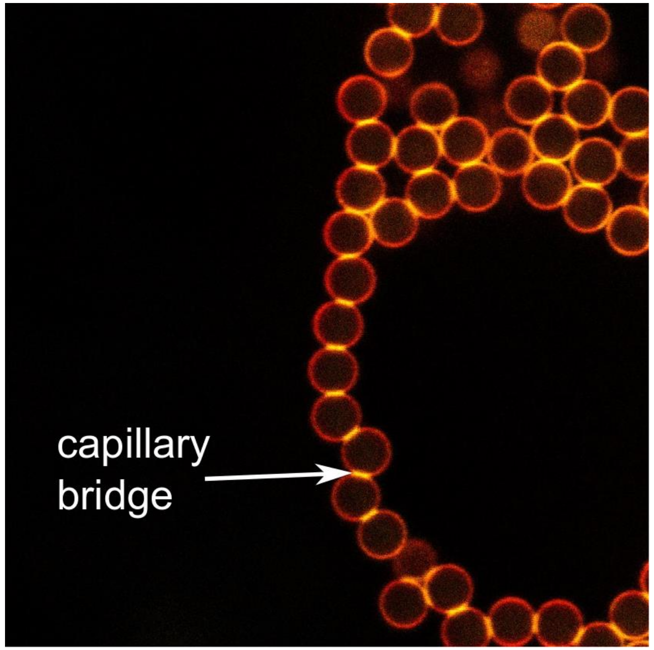
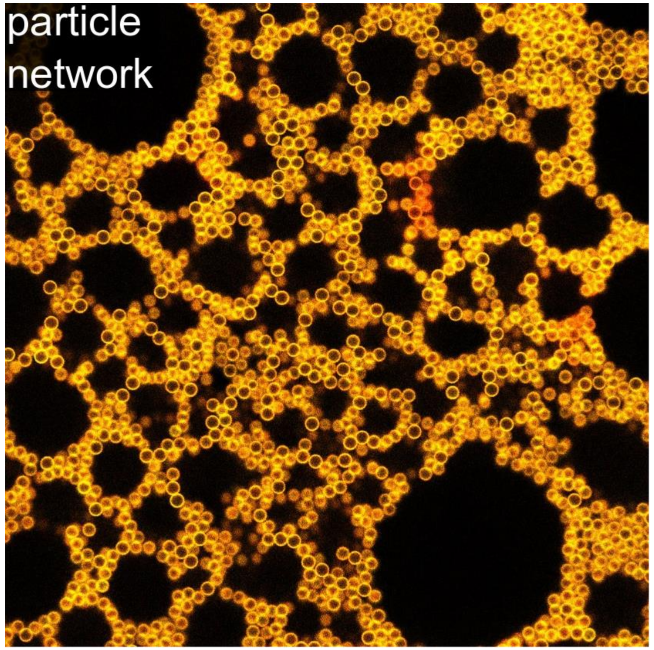
Confocal image of a capillary suspension from solution

- Glass particles ($\phi_{glass} = 0.05$) suspended in EtOH/dodecane
  - EtOH/dodecane are completely miscible at $T > 14$ ℃
  - Imaging carried out at 20 °C
- Separation occurs quickly after addition of particles
- Arrangement into bridged structures

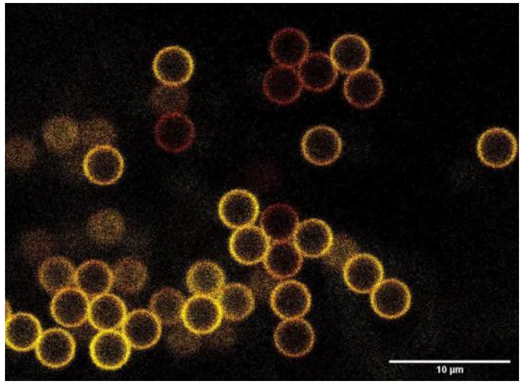


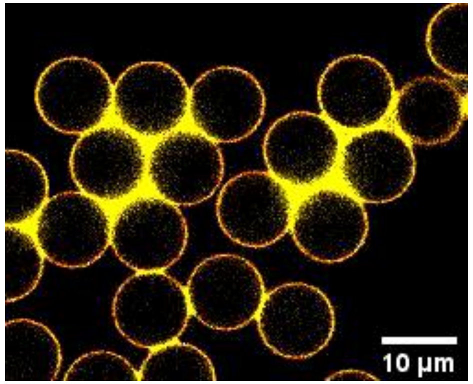


S.B. Fischer and E. Koos, *Colloid Interface Sci. Commun.* **41**, 100373 (2021)

Partially miscible system

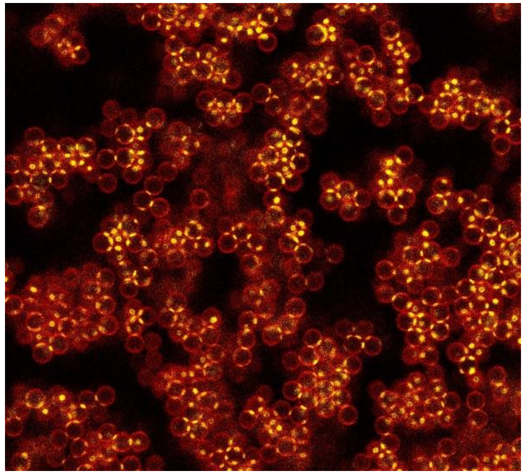
- Appearance/disappearance of the bridges

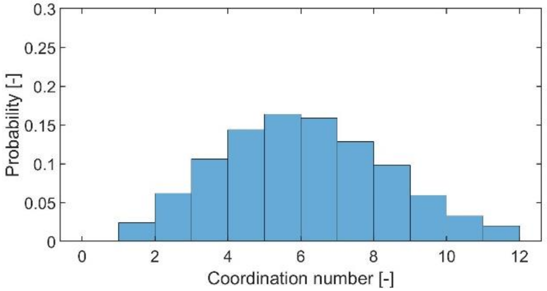


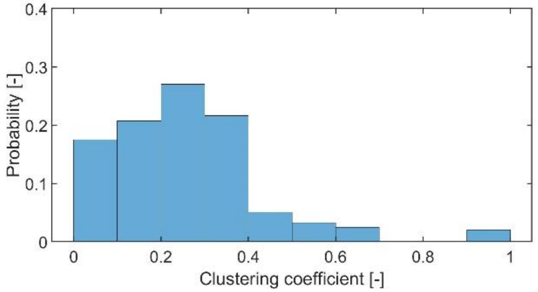


  - Depends on environment
  - Depends on local particle positions

- Structure can be more granular (sedimentation and then appearance of bridges)
  - Dodecane/ ethanol (85/15)
  - $z = 5.5 \pm 0.5$
  - $c = 0.25 \pm 0.01$







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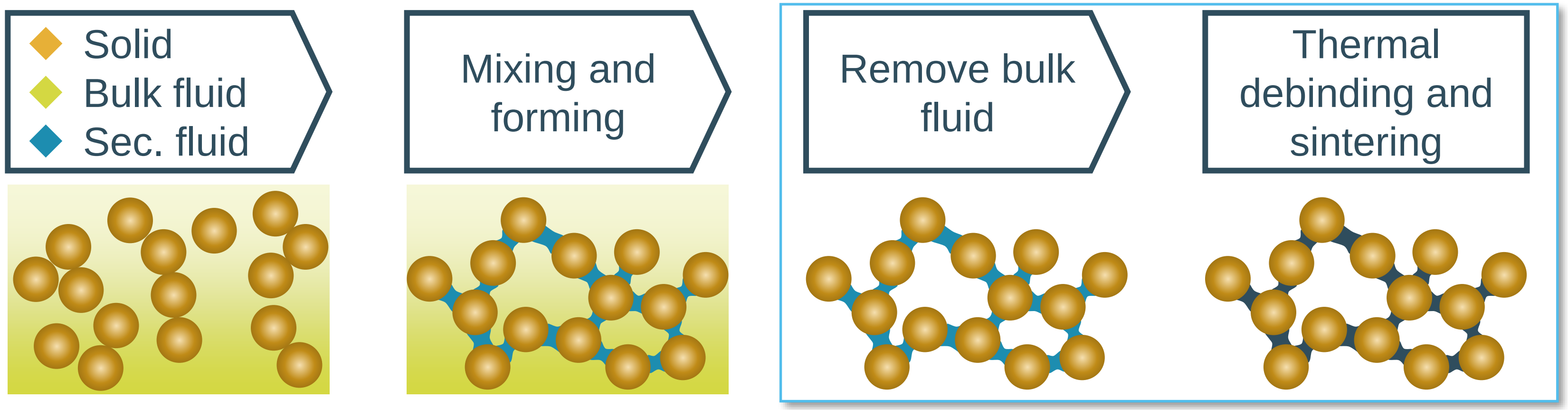
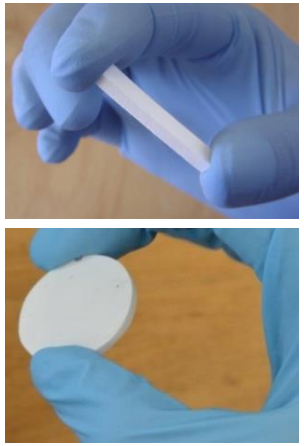
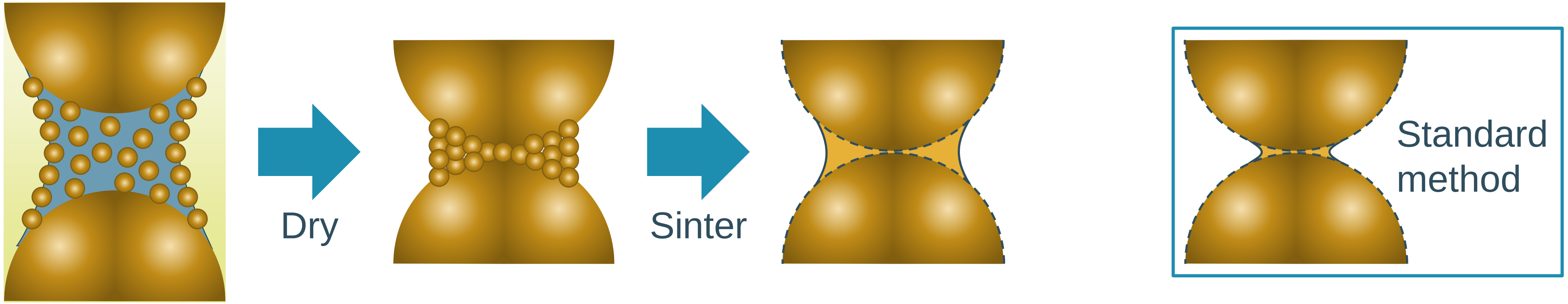
Application 2: Porous materials





- Incorporate nanoparticles into bridging fluid



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

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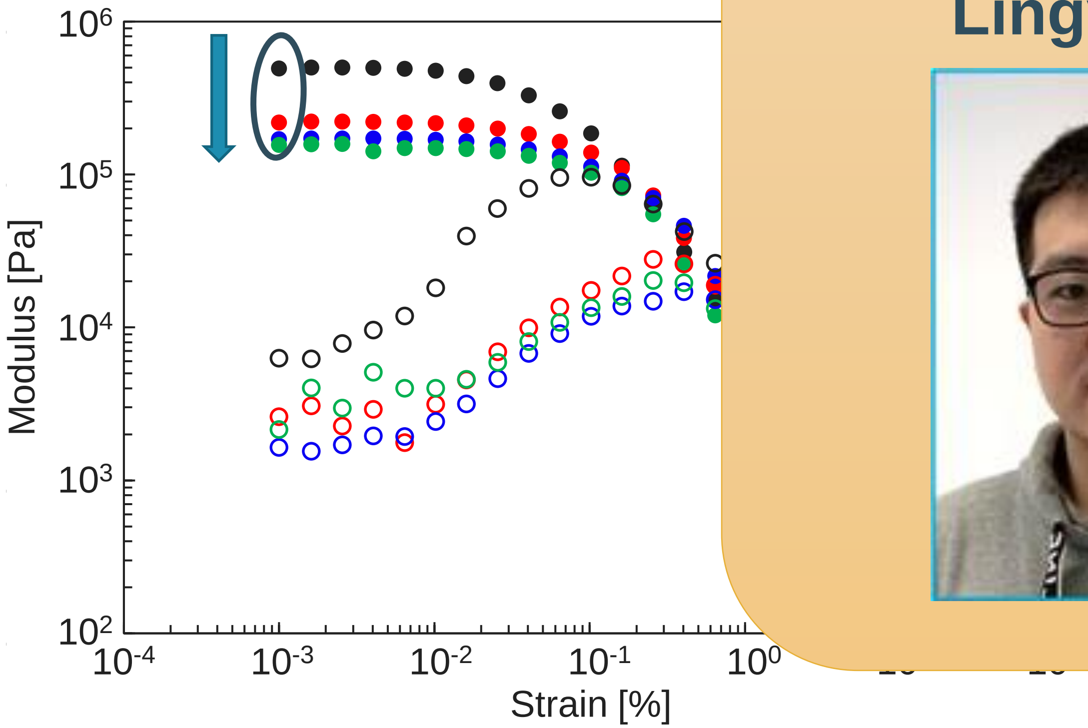
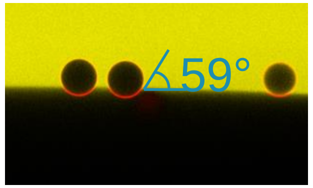
Nanoparticles incorporated into the bridges

- Lower G', longer LVE with … e in contact angle
  ϕ_{NP} in bridges ($\phi_{sec} = 1$ …

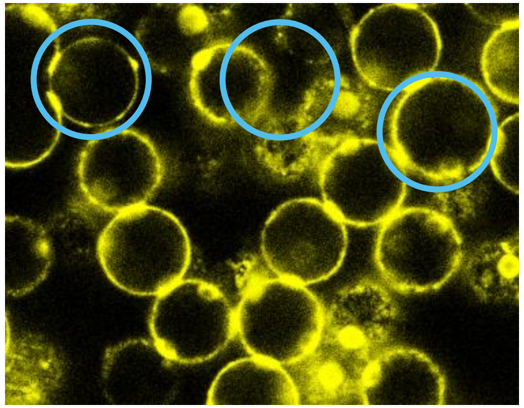


$\phi_{NP} = 15$ vol%



wetting

$\phi_{NP} = 10$ vol%



See poster of

Lingyue Liu

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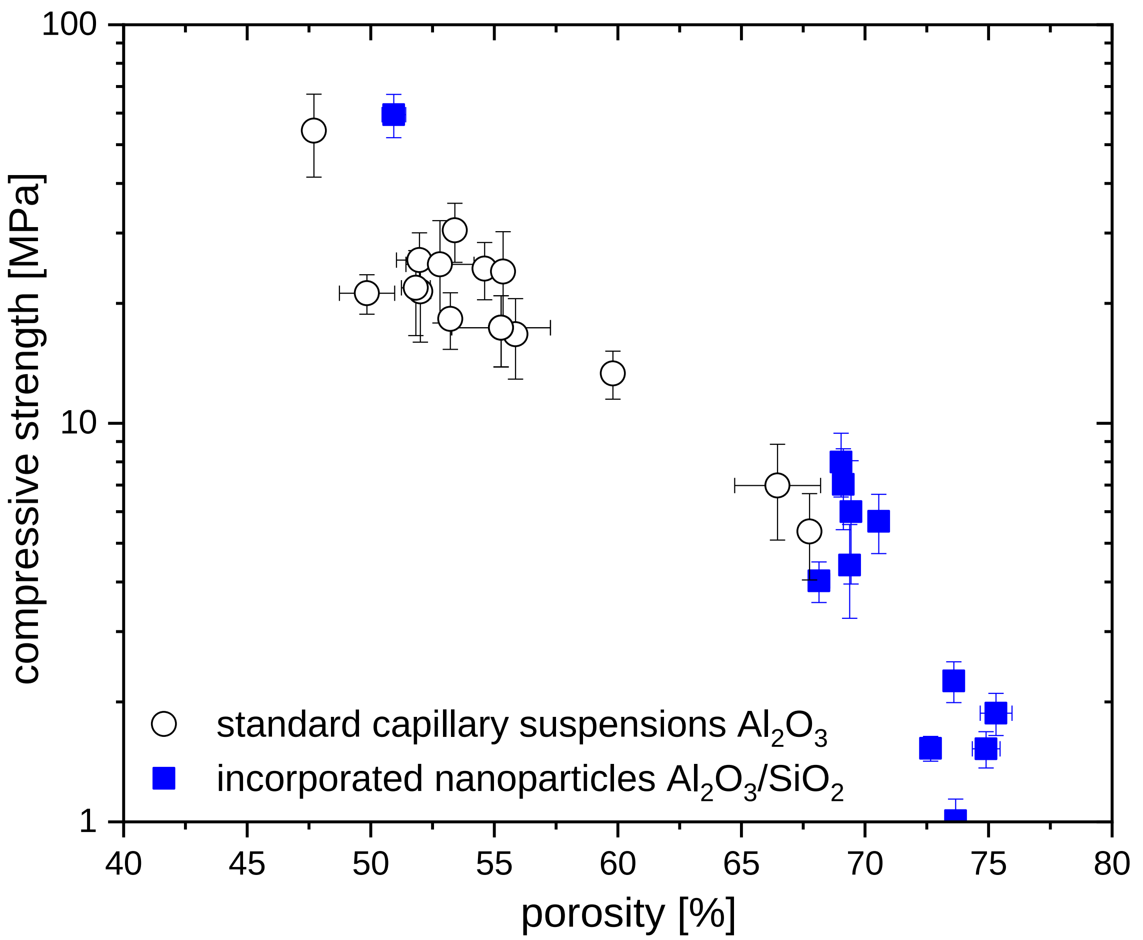
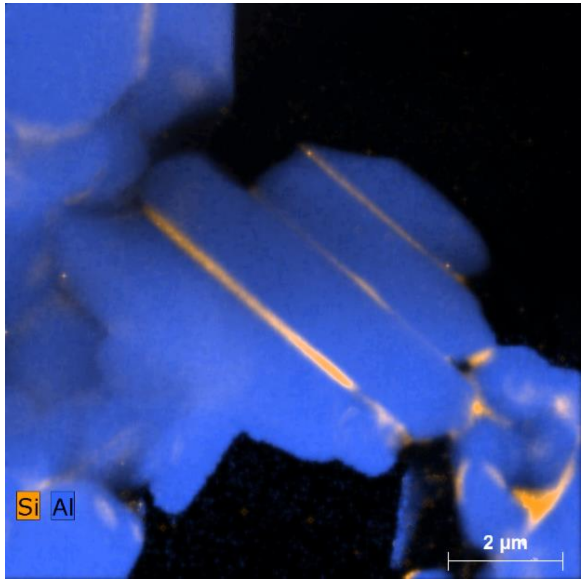
Mechanical properties





- Nanoparticles concentrated in bridges
- Higher compressive strength
- Higher porosity range

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

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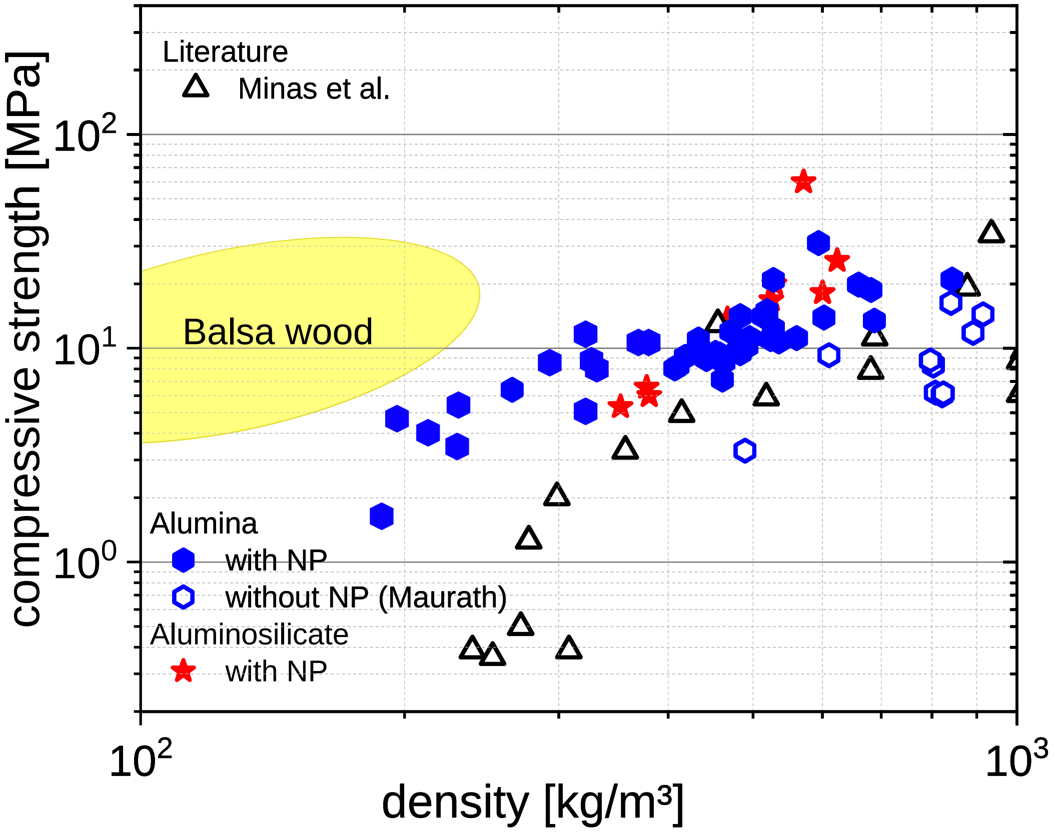
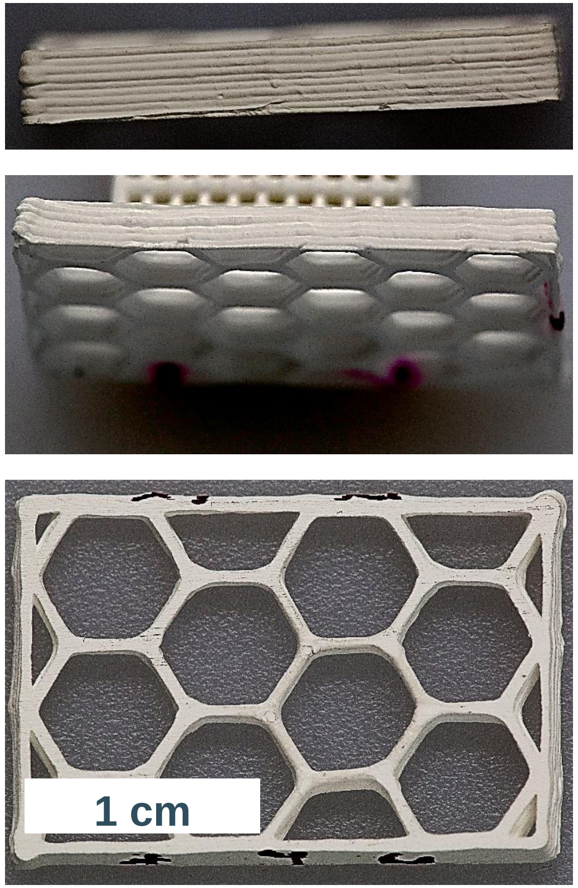
Pathway to lightweight materials





- Highest strength to weight ratio for macroporous ceramics
- Even works for aluminosilicate
  → Strength determined by bridging

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

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Bone fractures




Porous bone implants

- Bone healing more efficient
- Decrease morbidity and issues
- Reduced waiting time
- Scaffold will disappear with time

Solid loading

- Tricalcium phosphate
  Bioactive, $(Ca)^{2+}$, $(PO_4)^{3-}$

  OR

- Alumina
  Biocompatible

Secondary fluid

- Sucrose solution
  Strong network

  OR

- Silica nano-suspension
  Strong sintering necks

Bulk fluid

Camphene
Melting $T \approx 48\ ℃$

➔ **perfect for freeze-casting**

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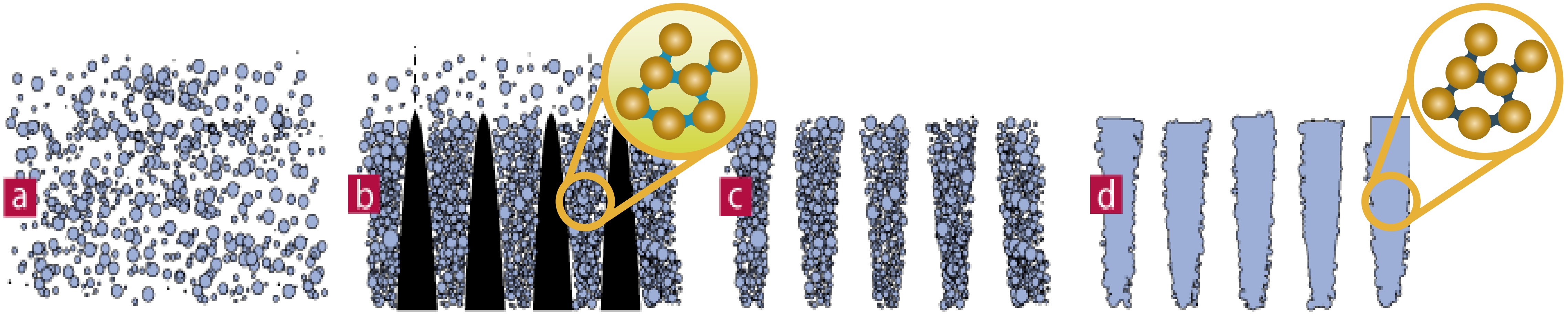
Hierarchical pore size



Capillary suspension	Freeze-casting	Freeze drying	Sintering
Al_2O_3 + Secondary fluid + Bulk fluid	Bulk fluid = camphene forms dendrites while solidifying	Removing of camphene	Dendrites ➔ macroporosity

Expectation: porous body with interconnected pores of two sizes

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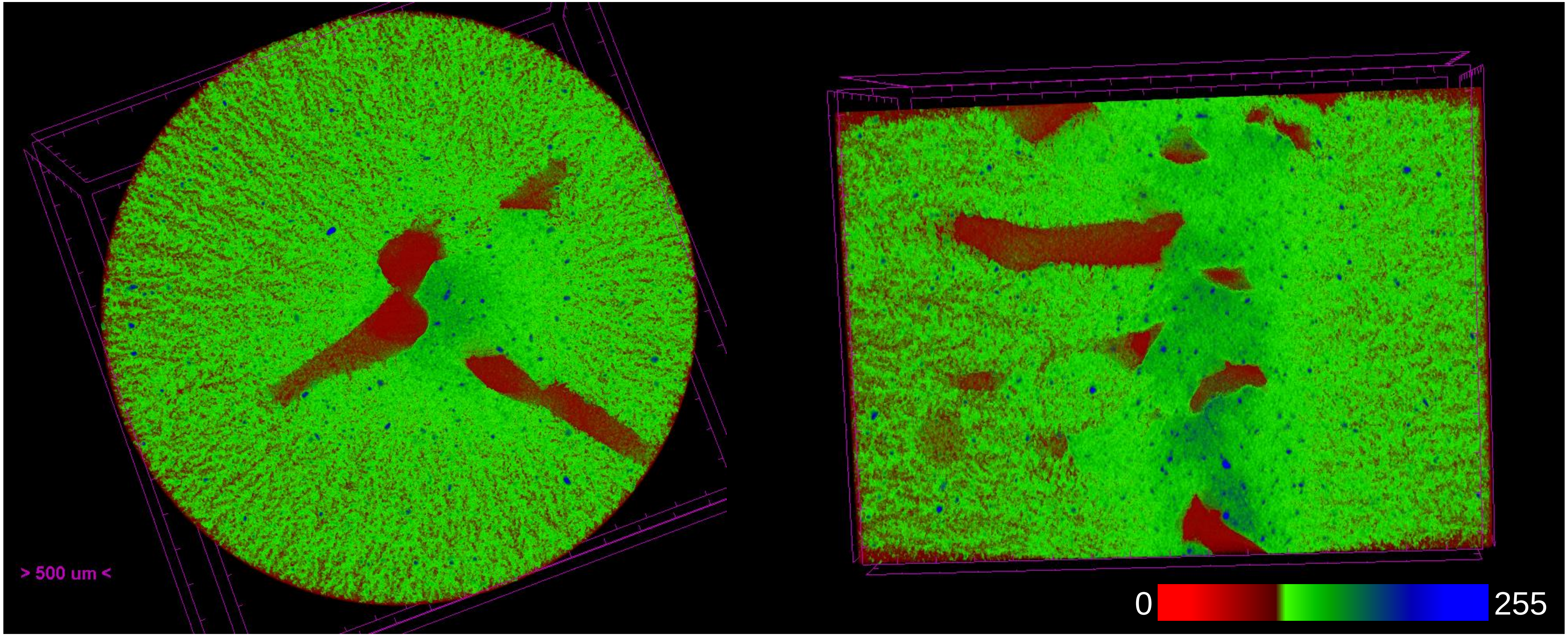
Resulting structures



Computational modeling

Connection between structure and rheology is hard to control in lab

- Influence of mixing conditions (distribution of bridge sizes)
- Feedback between external shear and network structure
  - Breaking of bridges and yielding of networks
  - Aging behavior
- Particle wetting and pinned contacts

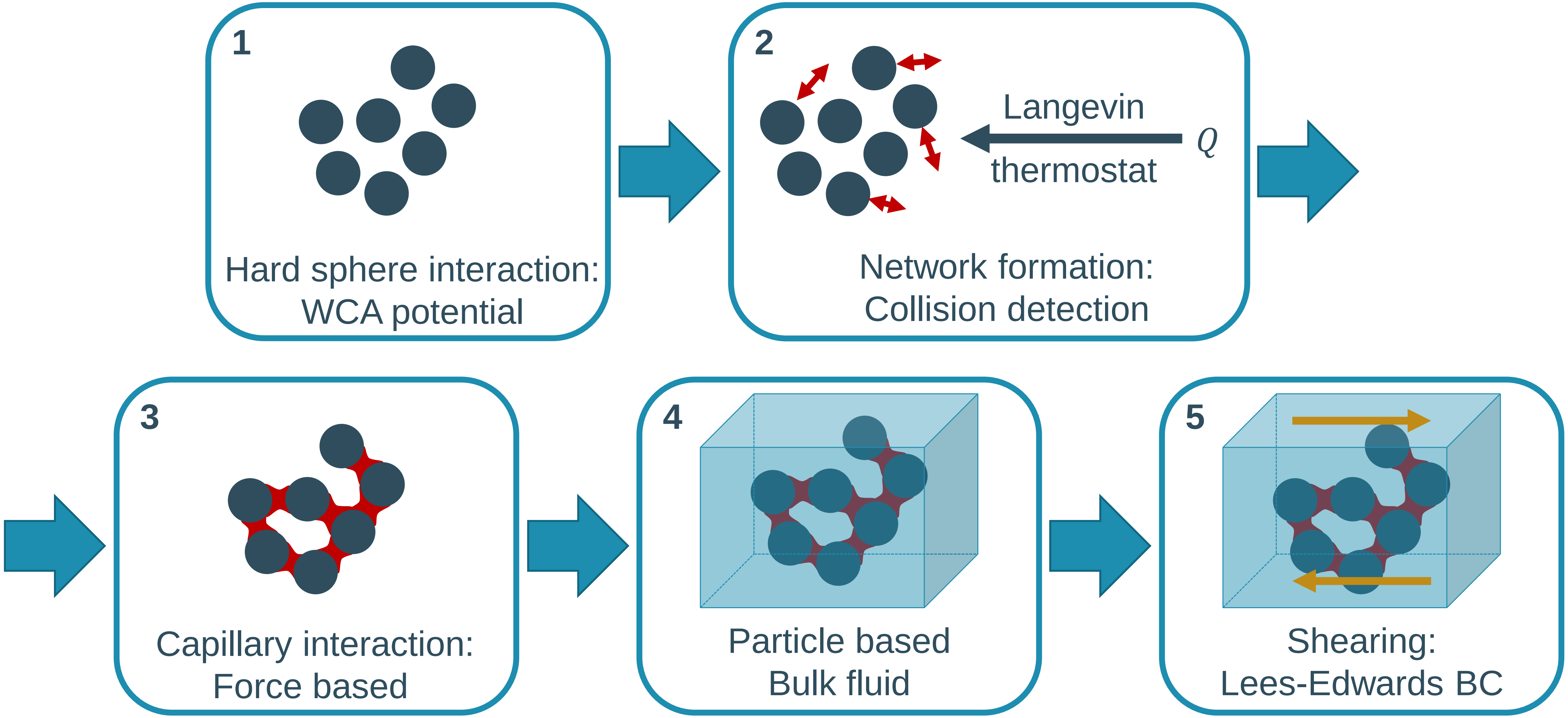
→ Computational model

ESPResSo

Extensible **S**imulation **P**ackage for **Res**earch of **So**ft matter

Arnold et al., *Lecture Notes in Computational Science and Engineering*, 89, 1 (2013); espressomd.org

Computational modeling strategy



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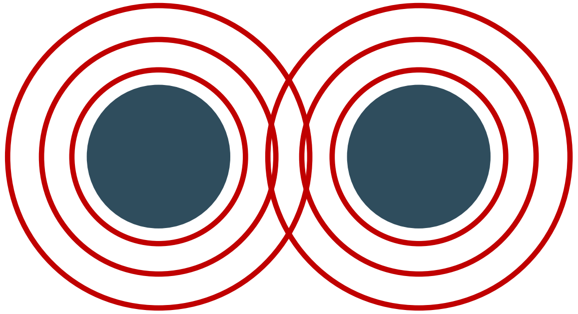
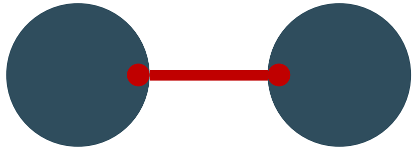
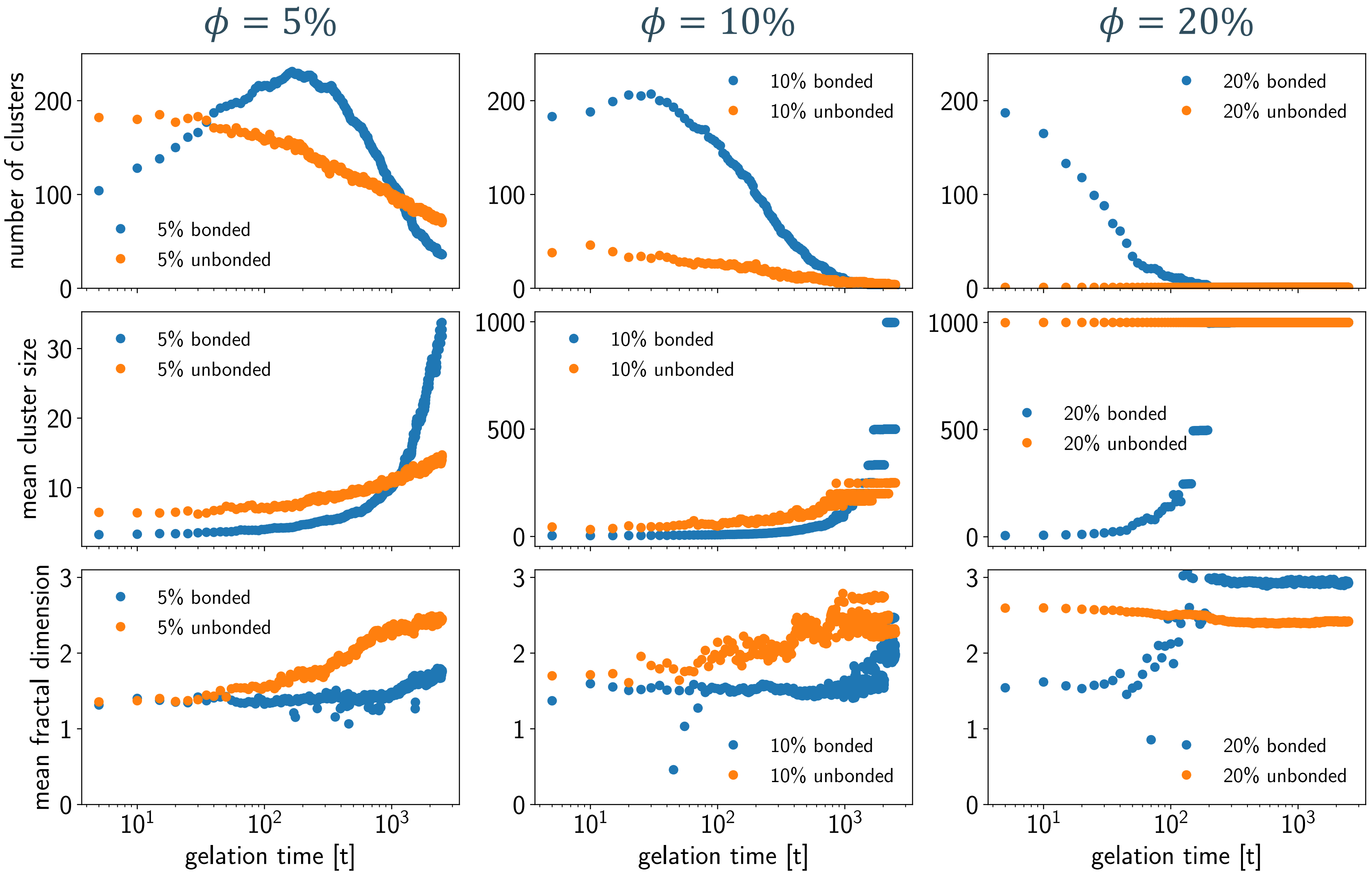
Network formation



Conservative force field
without explicit bonds
→ Unbonded



Explicitly bonded
→ Bonded



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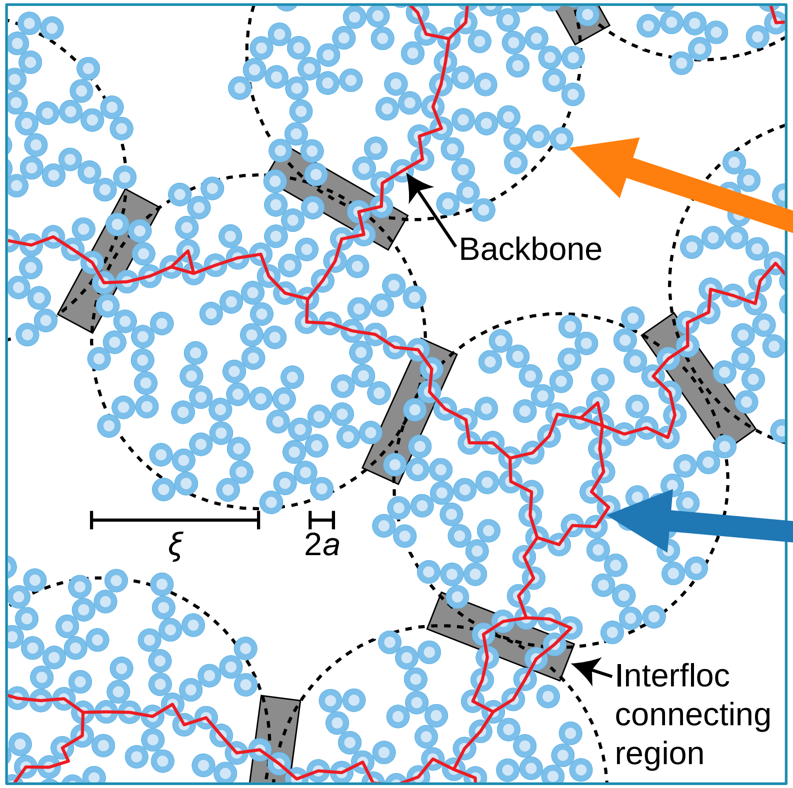
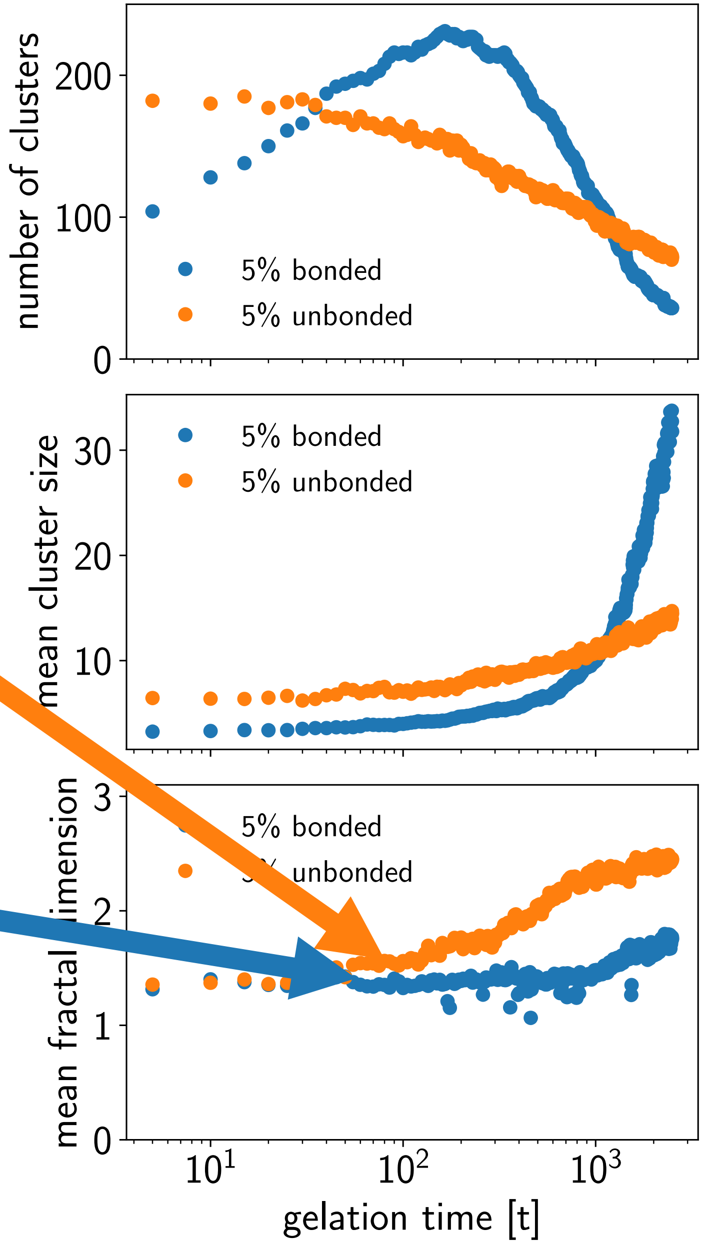
Comparison with in-silico networks



Fractal dimension of **flocs**

Fractal dimension of **backbone**



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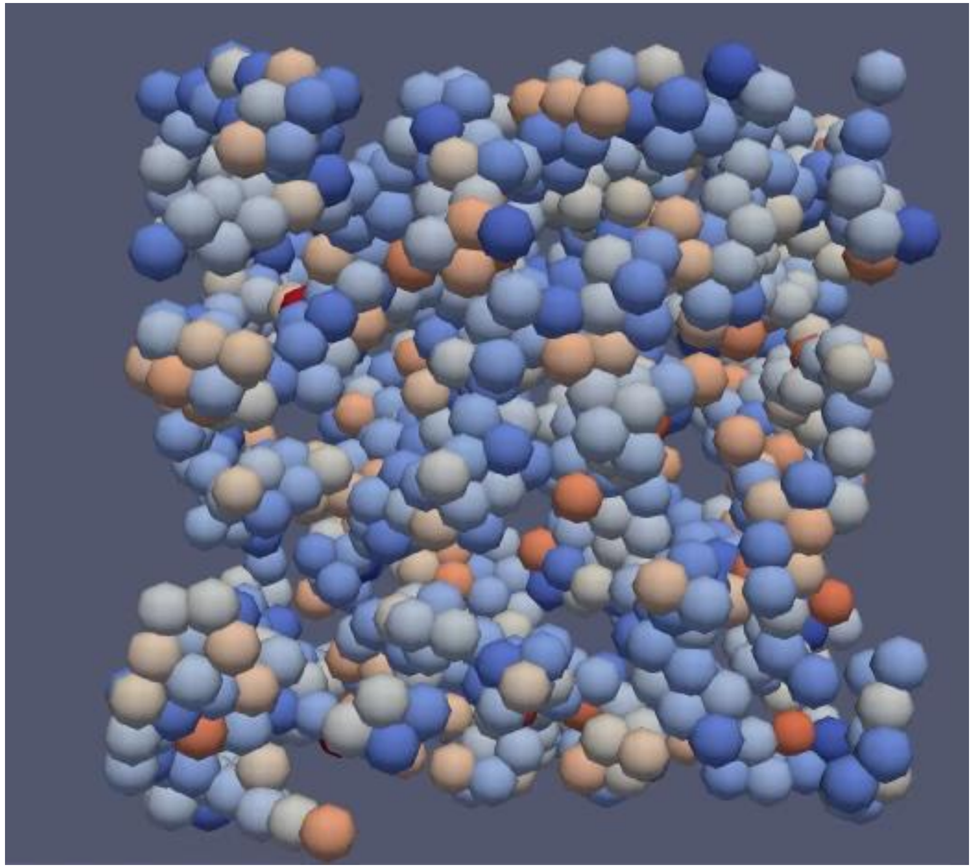
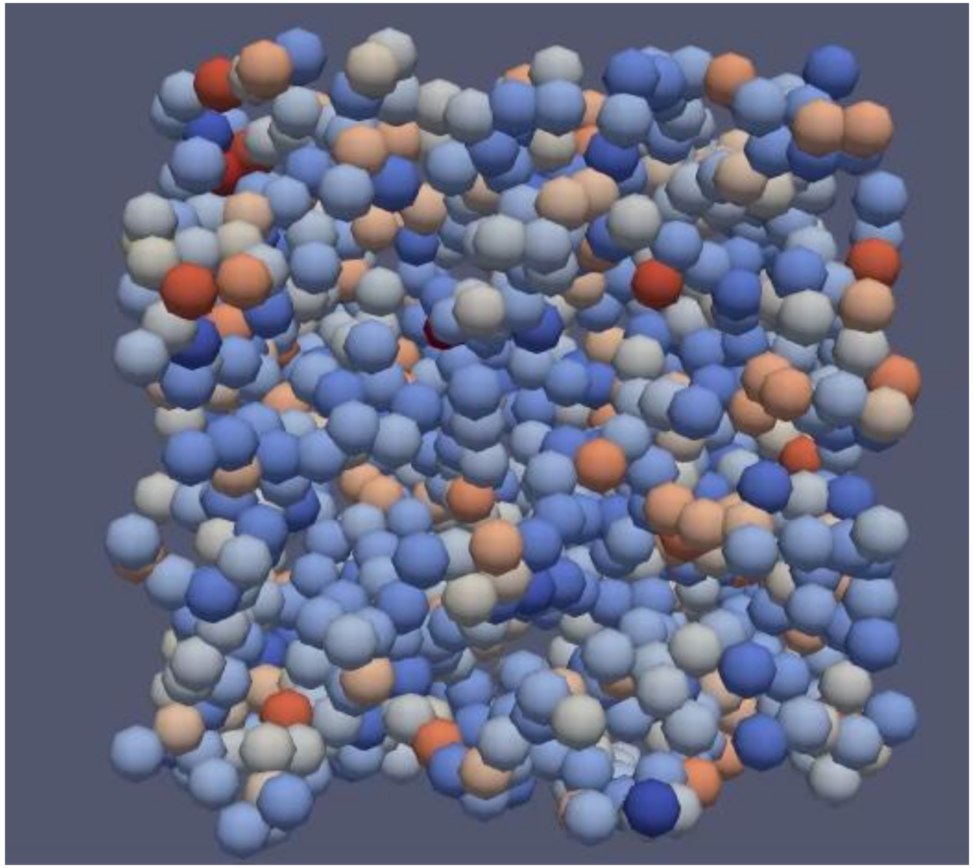
Network structures

Conservative force field, unbonded



Dense, clustered structure
Isolated clusters

Rigid body dynamics, explicit bonds



lighter, sparser network
Fully interconnected

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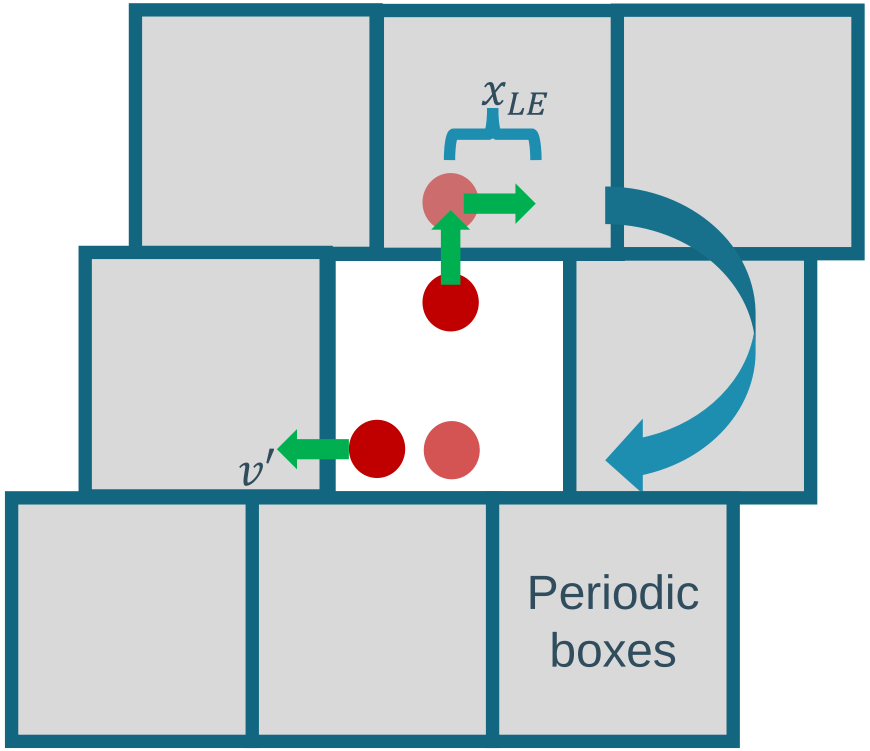
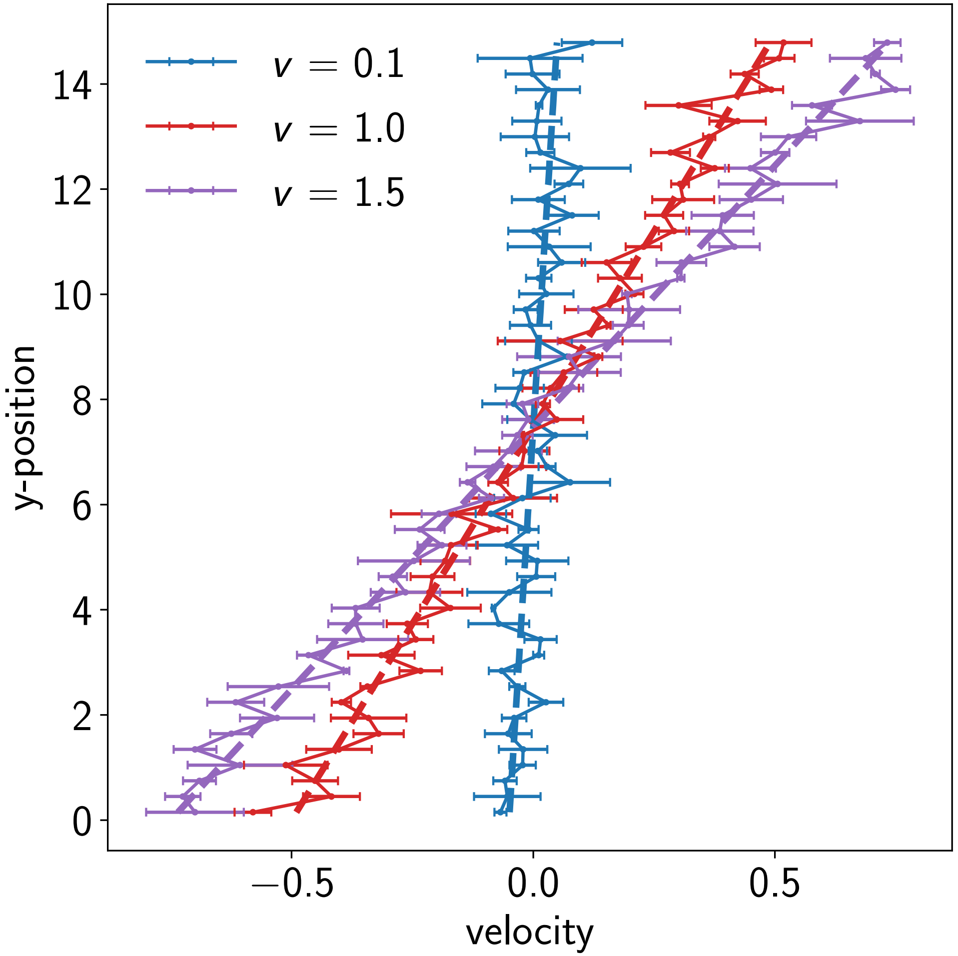
Introducing movement - Lees Edwards boundaries

$$x_{LE} = v * t$$
$$v' = v_x + v_{LE}$$





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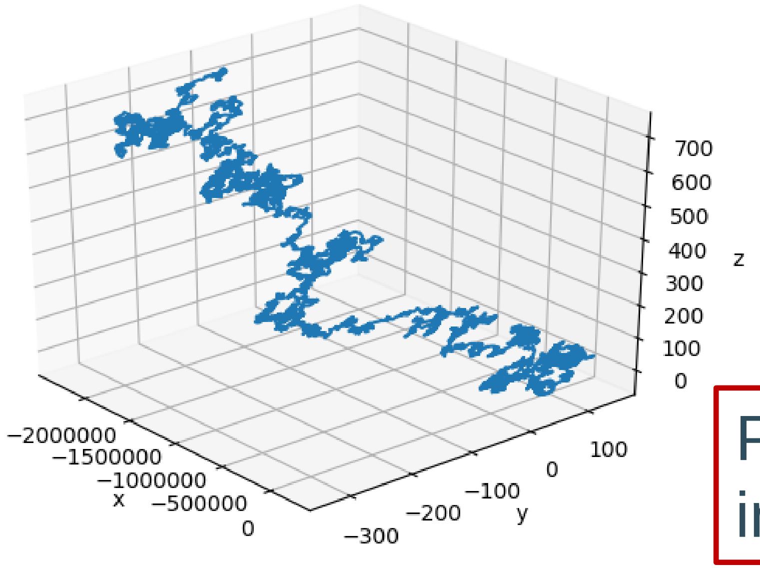
The anomalous diffusion contribution to steady shear experiments

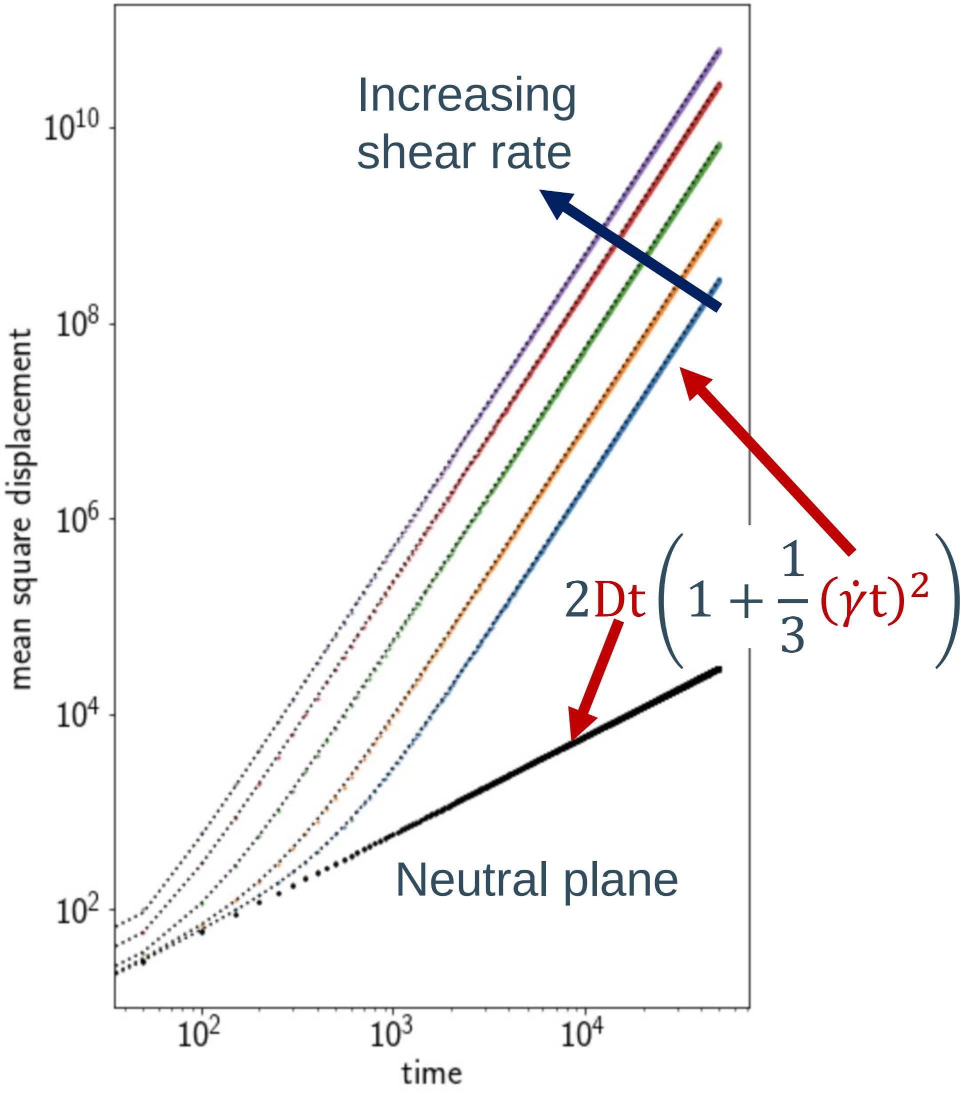
- Extra contribution due to shear gradient

$$\langle \Delta x(t)^2 \rangle = \langle (x(t) - x(0) - \dot{\gamma} y(0) t)^2 \rangle$$

$$= 2Dt\left(1 + \frac{1}{3}(\dot{\gamma}t)^2\right)$$



Particle trajectory in infinite system



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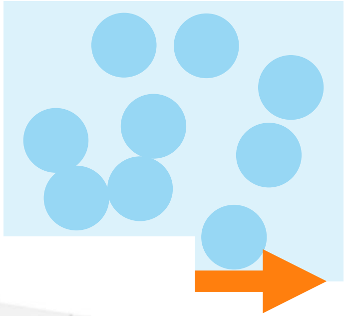
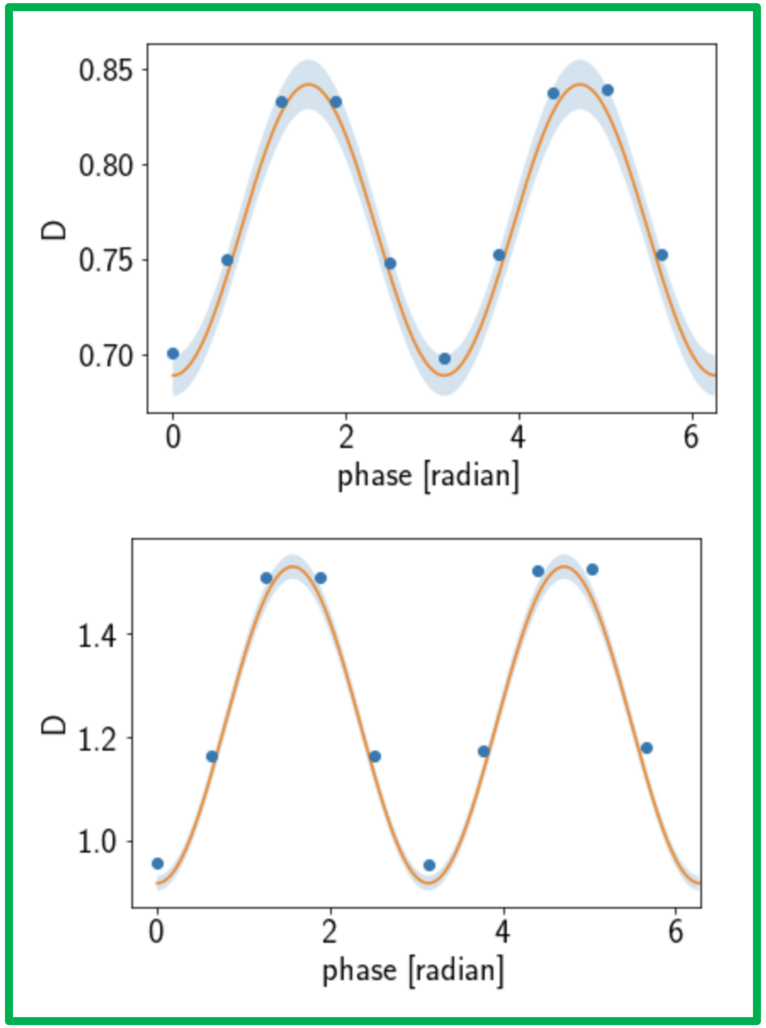
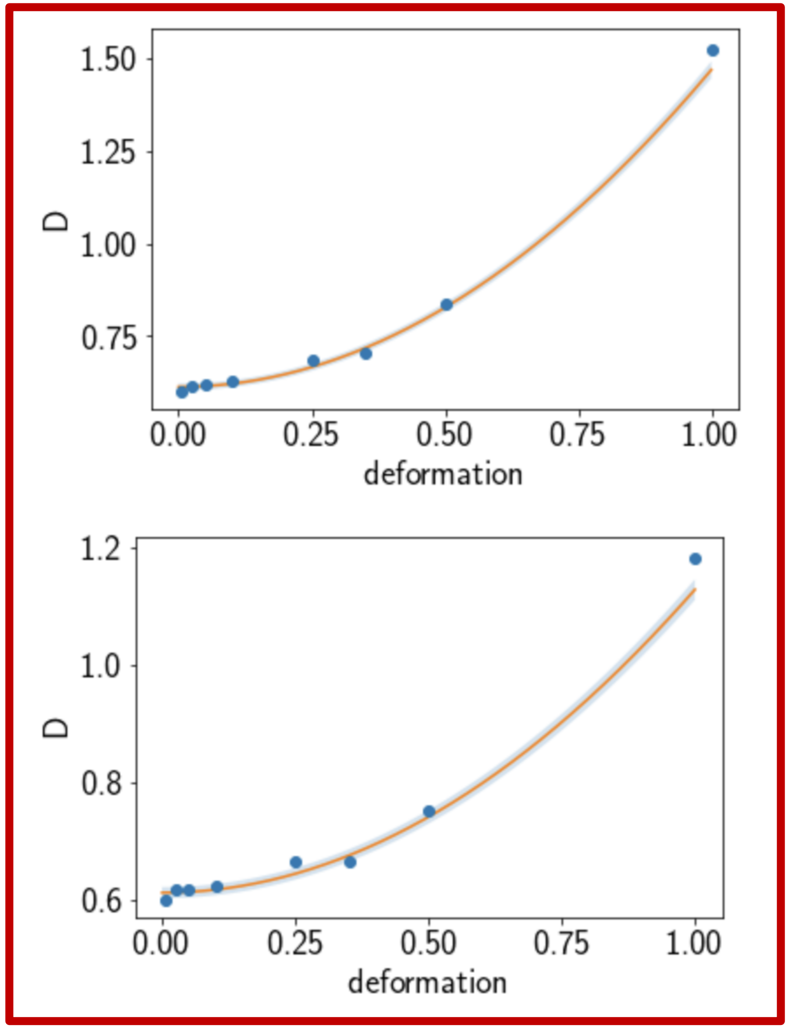
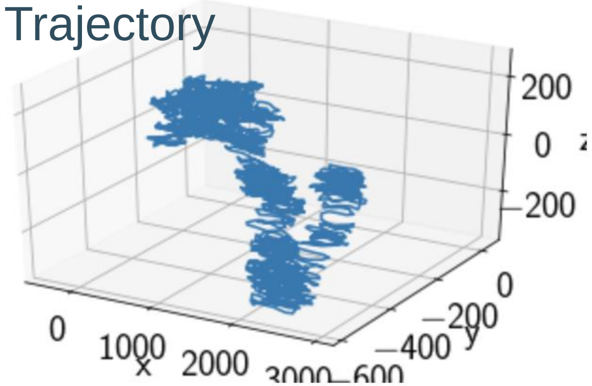
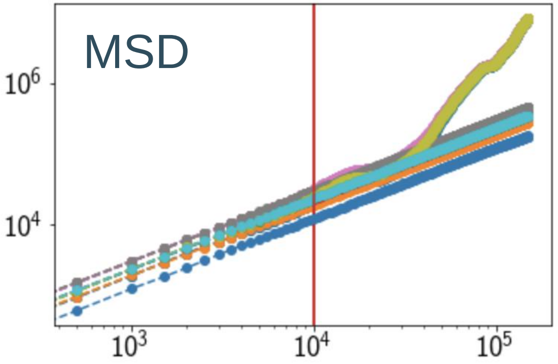
Oscillatory shear $\gamma_0 = 100\%, 200\%$











$$D\left[1+\frac{\gamma_0^2}{2}\left(2\sin\Phi^2+1\right)\right]$$

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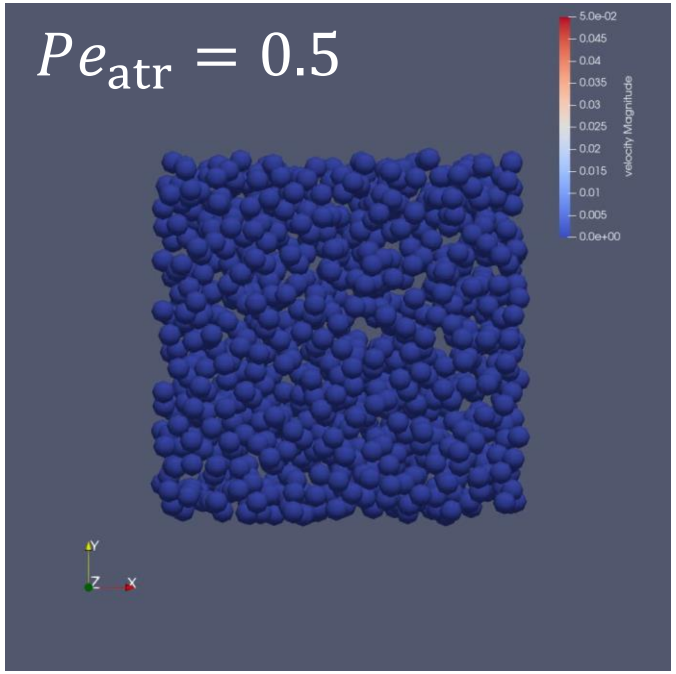
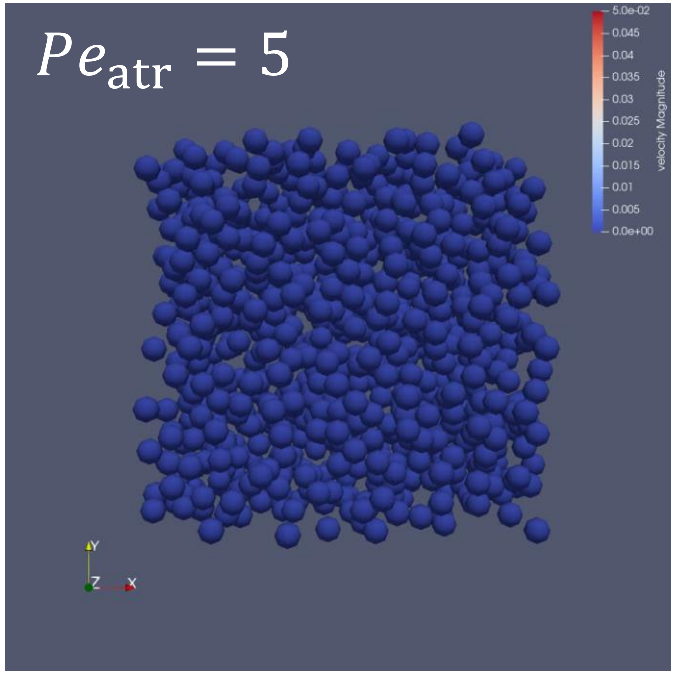
Sheared network

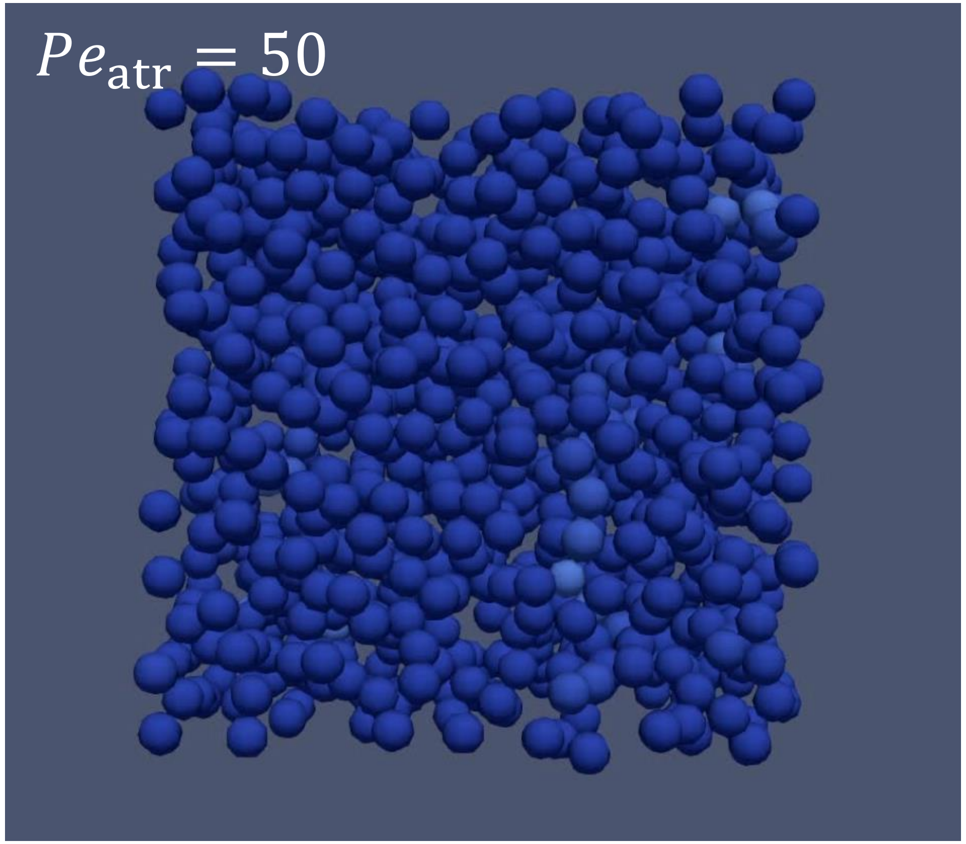
$$Pe_{\mathrm{atr}} = \frac{12\,\pi\zeta R^3\dot{\gamma}}{U_{\mathrm{atr}}(2R)}$$

Attraction range

Depth of potential at contact







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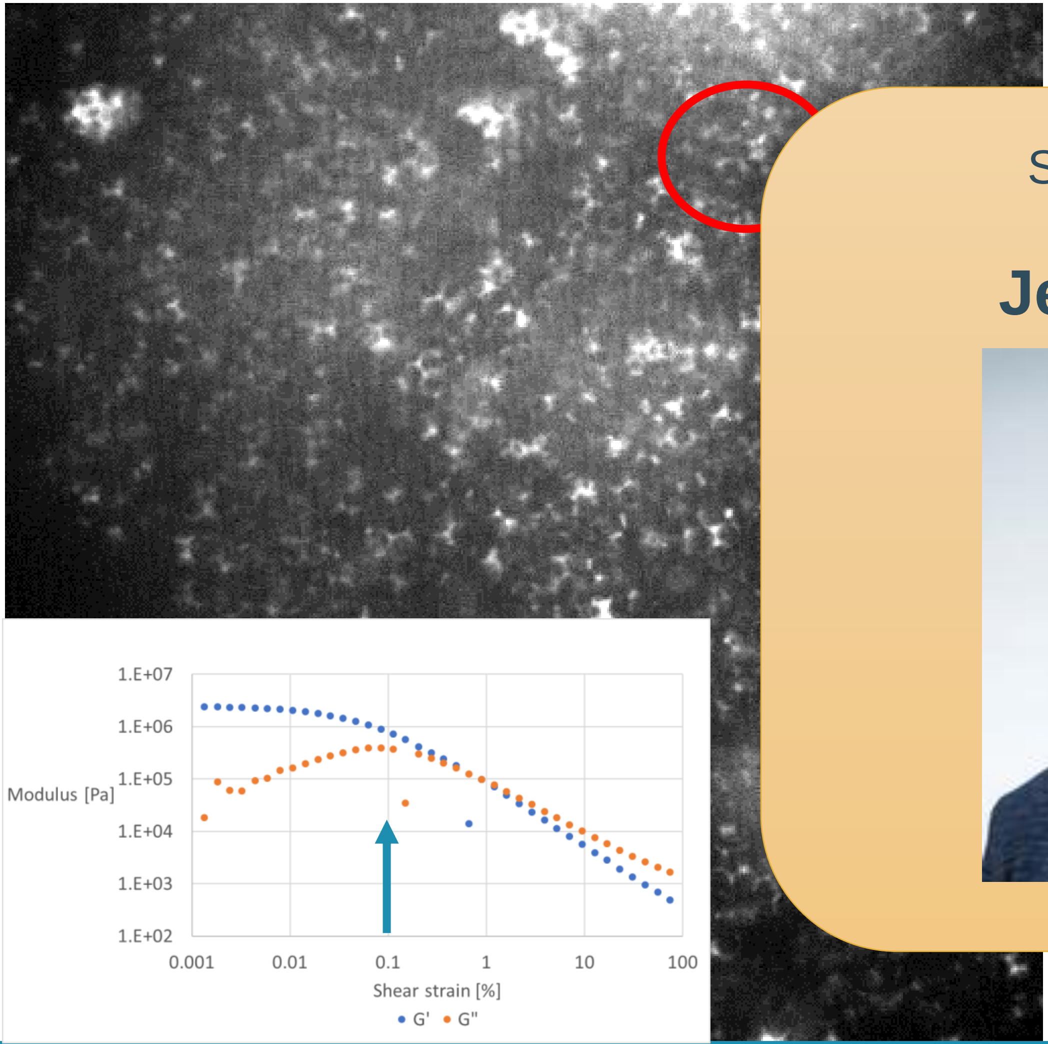
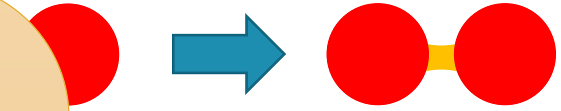
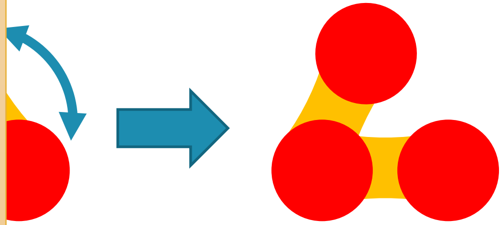
Yielding mechanism



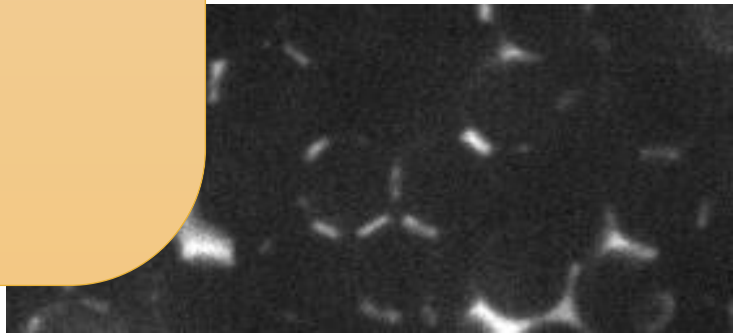
1. Bridge thinning and rupture



(or forming) of a trimer



acement is not uniform!



See poster of

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Conclusions

- Secondary liquid creates a capillary-driven attraction between particles
  - Dramatic change in material strength
  - Similarities and differences with colloidal networks and wet granular media
  - Promising area for computational modeling
- Strong sample-spanning network is useful for material design
  - Printed electronics with high conductivity and less cracking
  - Porous materials with high open porosity

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Thank you for your attention!

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