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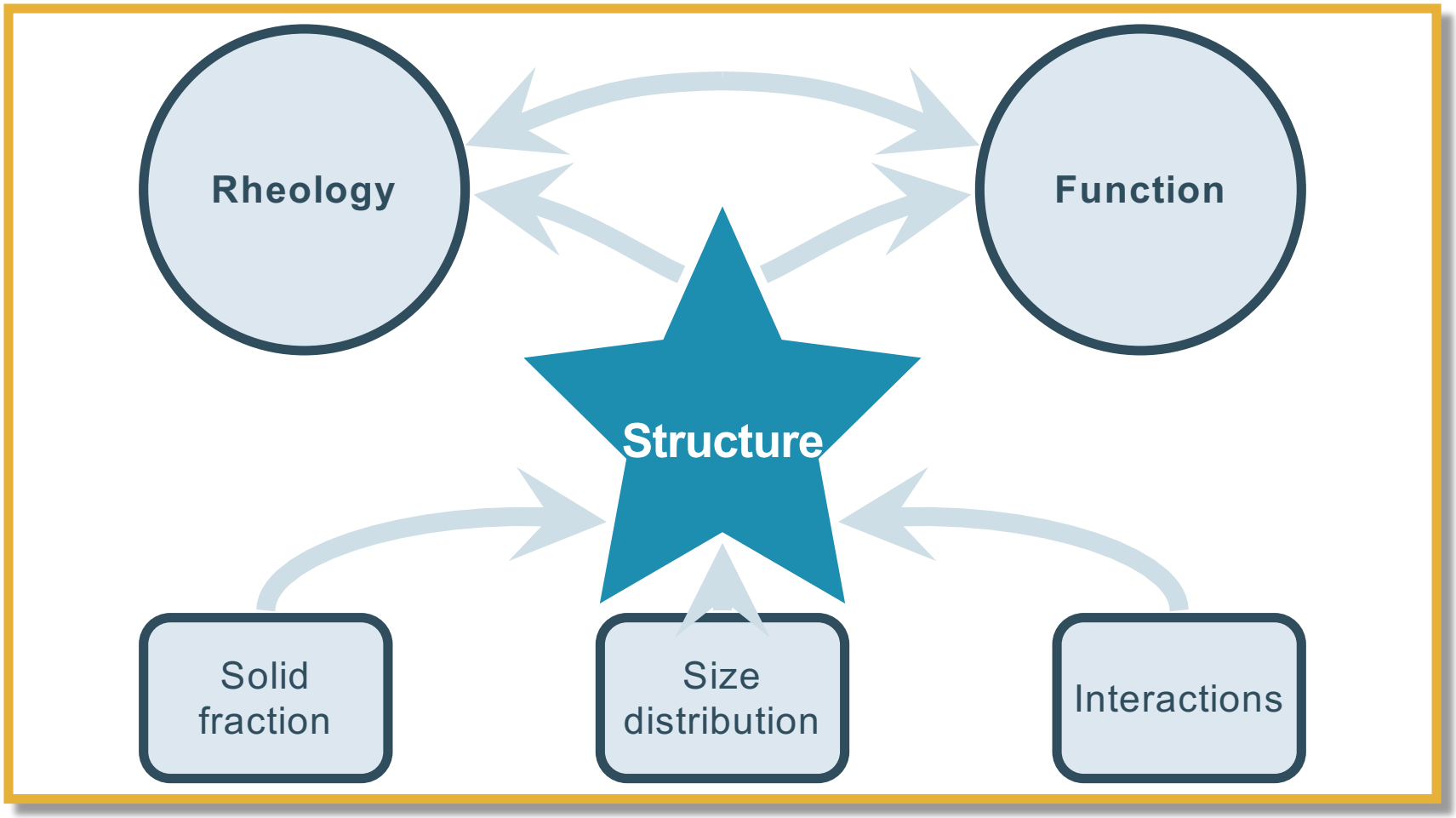
Methods to characterize microstructural transitions in suspensions

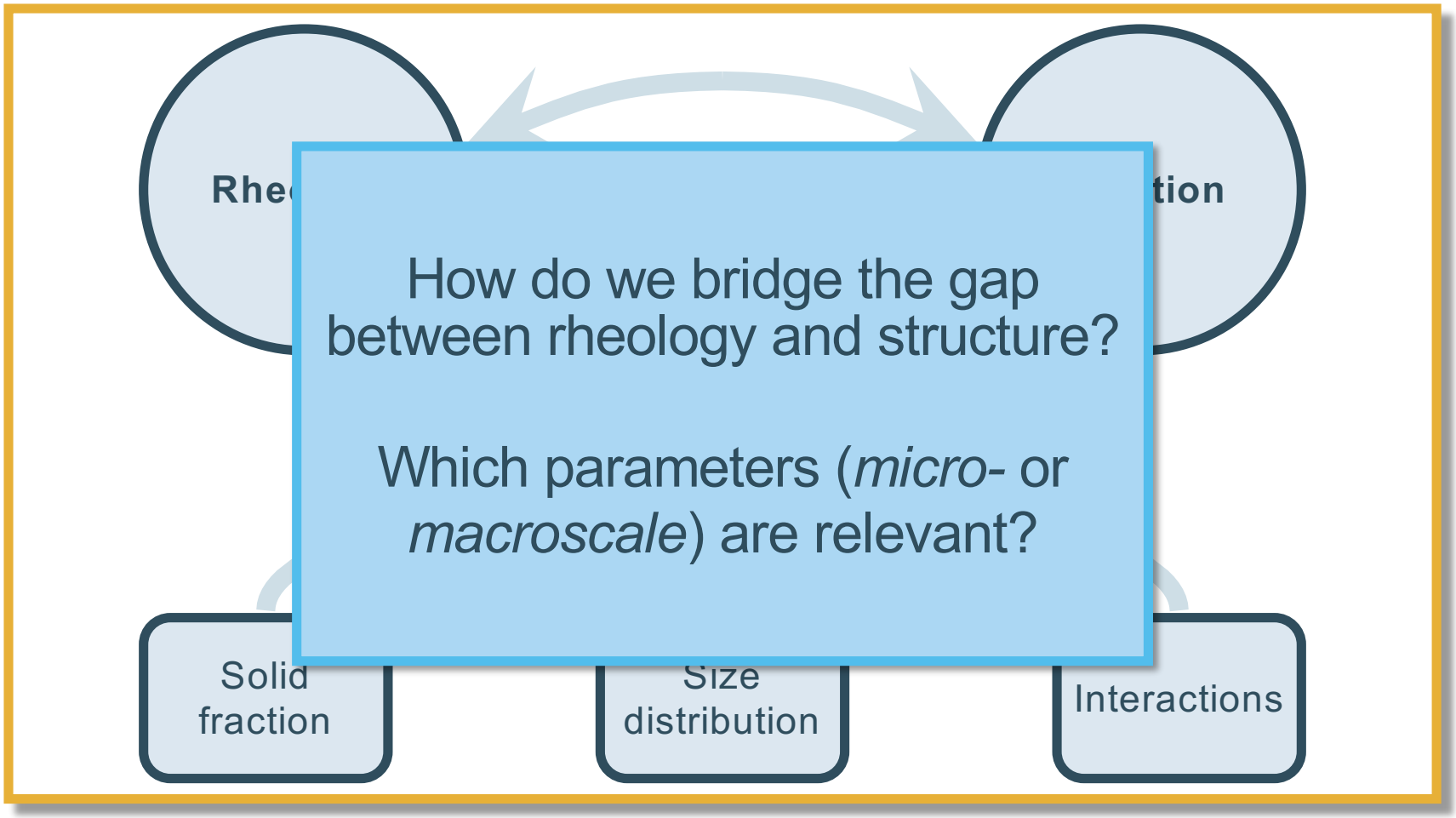
Erin Koos

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

Rheology and structure



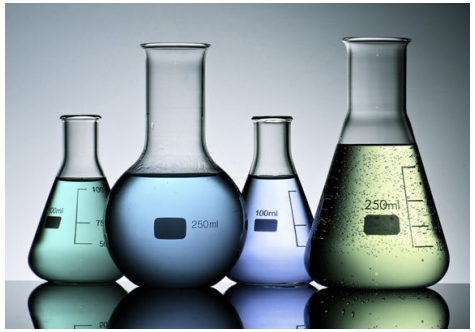
Rheology and structure



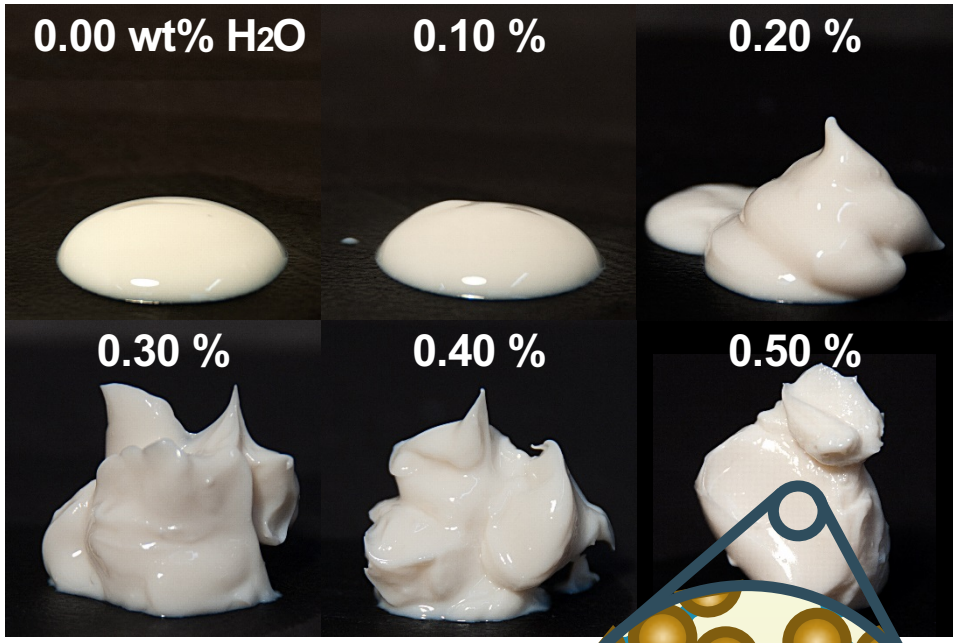
The capillary suspension phenomenon

Micro- or nanoparticles

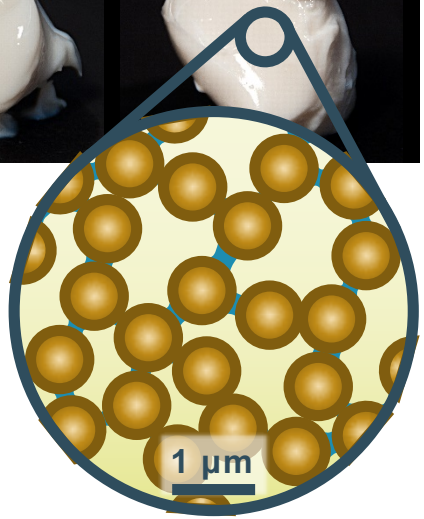
+



Two immiscible liquids



Capillary suspension



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

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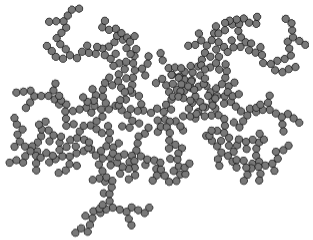
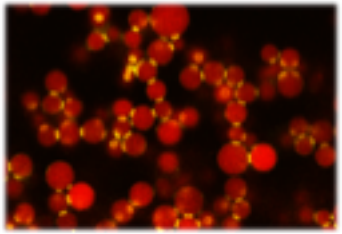
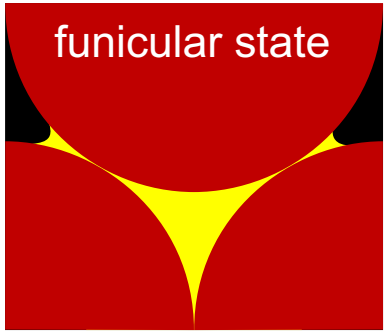
Interesting new material

	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

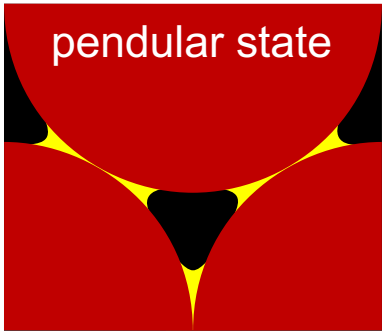
E. Koos, *Cur. Opin. Colloid Interface Sci.* **19(6)**, 575 (2014)

Contact angle and bridge structure

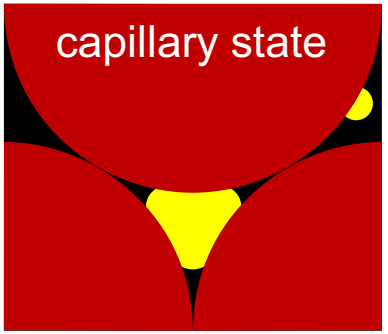
$\theta = 40°$

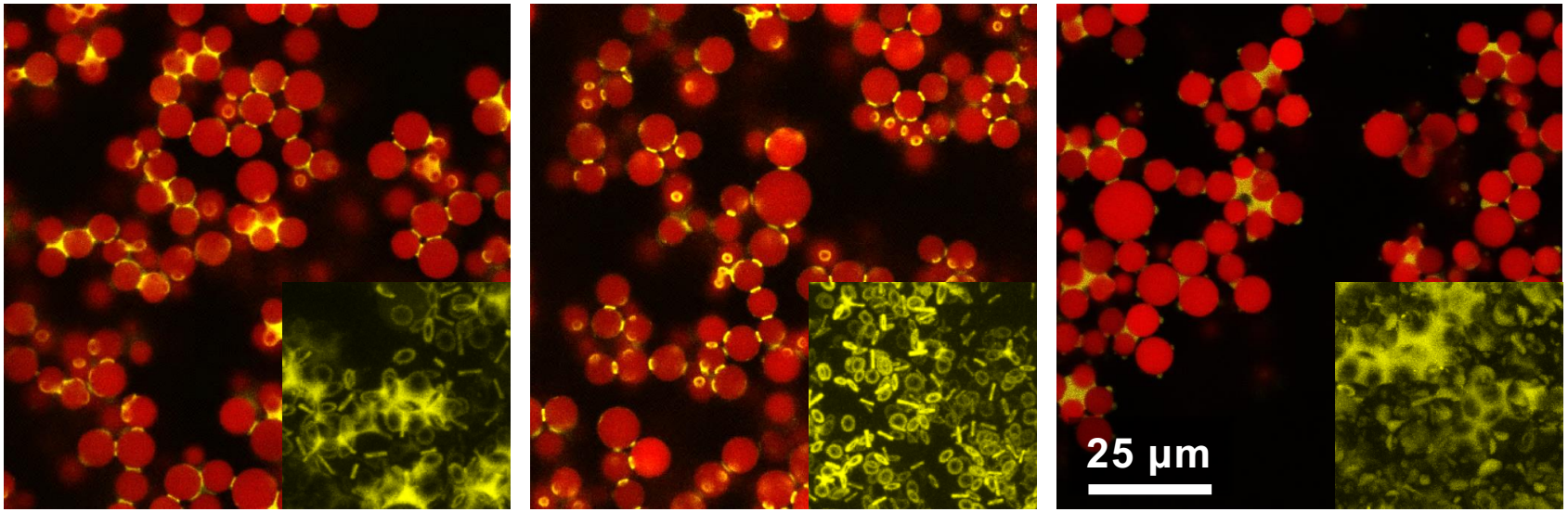


$\theta = 61°$



$\theta = 94°$





Silica particles in oil with added aqueous glycerol,
$\phi_{\text{solid}} = 0.25$, $\phi_{\text{sec}} = 0.0225$

F. Bossler and E. Koos, *Langmuir* **32(6)**, 1489 (2016)

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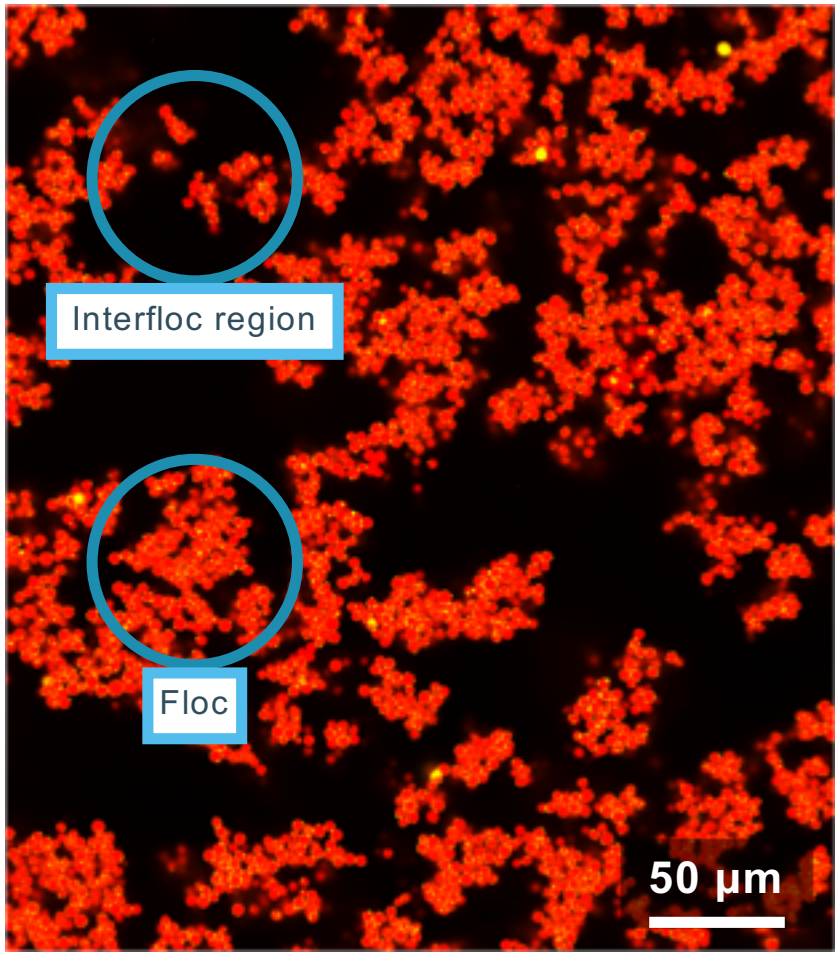
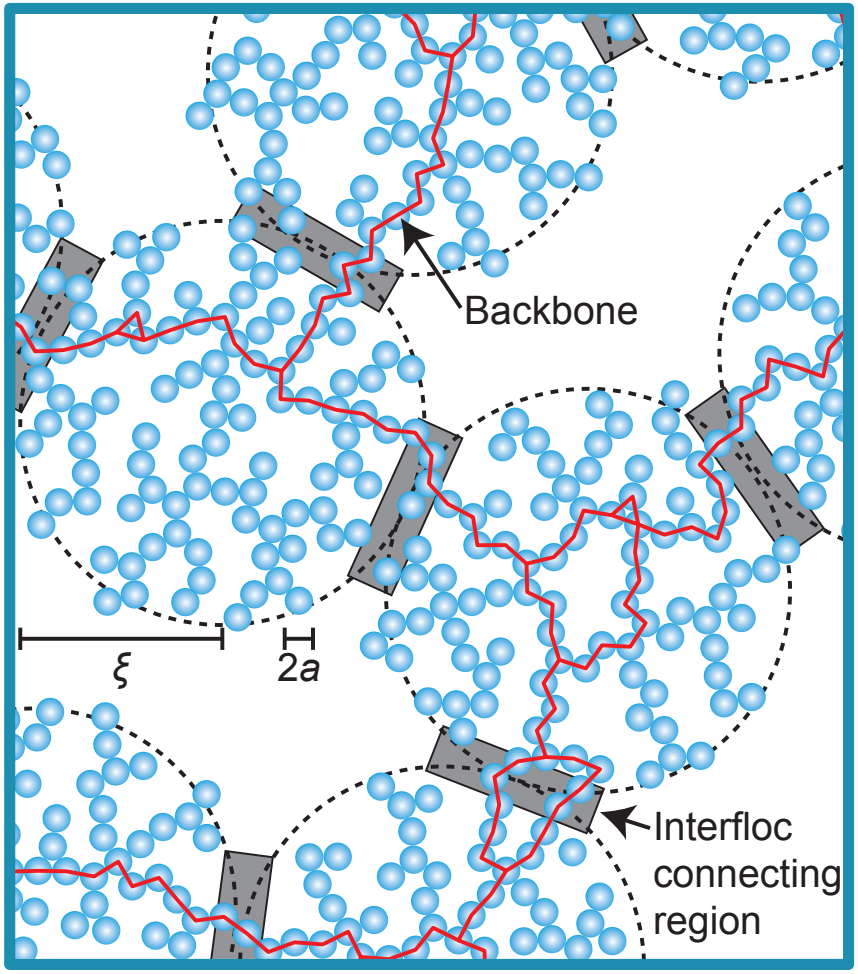
A network-level view



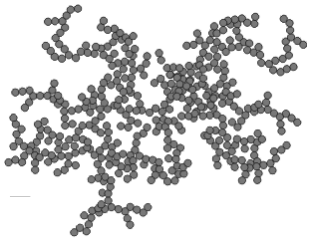


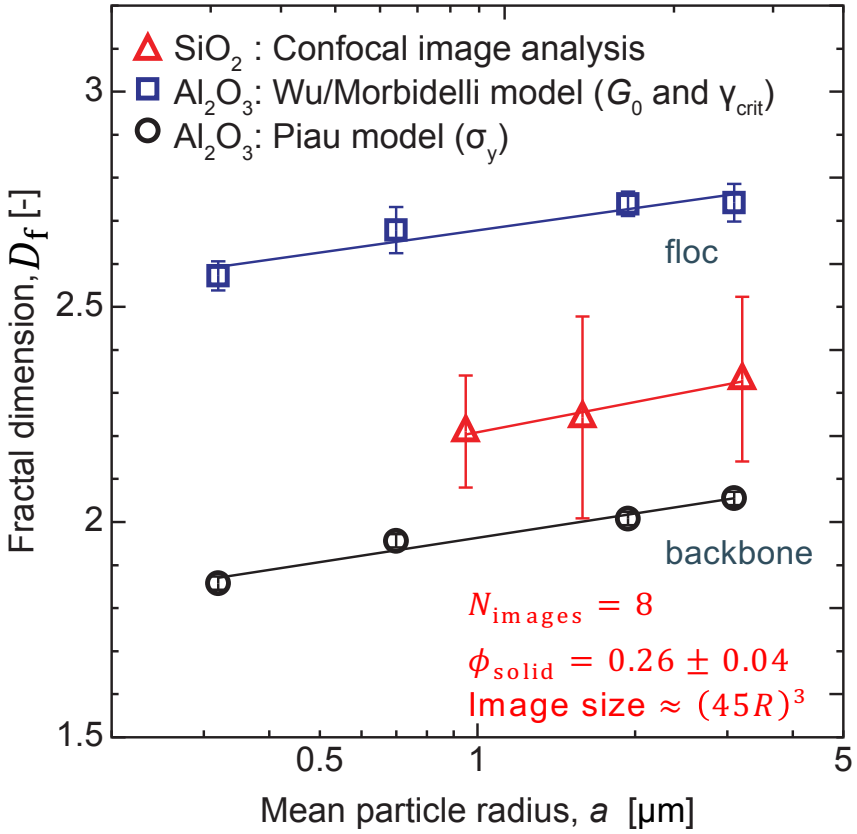
F. Bossler, J. Maurath, K. Dyhr, N. Willenbacher and E. Koos, *J. Rheol.* **62(1)**, 183 (2018)

Influence of size on fractal dimension

Small radius

Colloidal
$(D_f \approx 2)$





Granular
$(D_f = 3)$

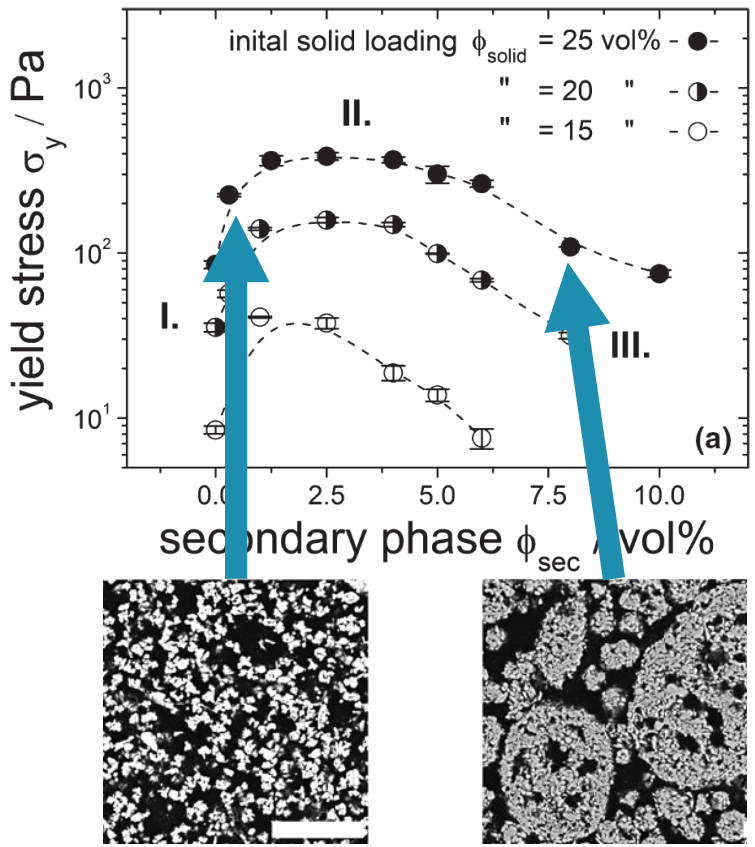
Large radius

→ Fractal dimension (partially) captures the rheological response

F. Bossler, J. Maurath, K. Dyhr, N. Willenbacher and E. Koos, *J. Rheol.* **62(1)**, 183 (2018)

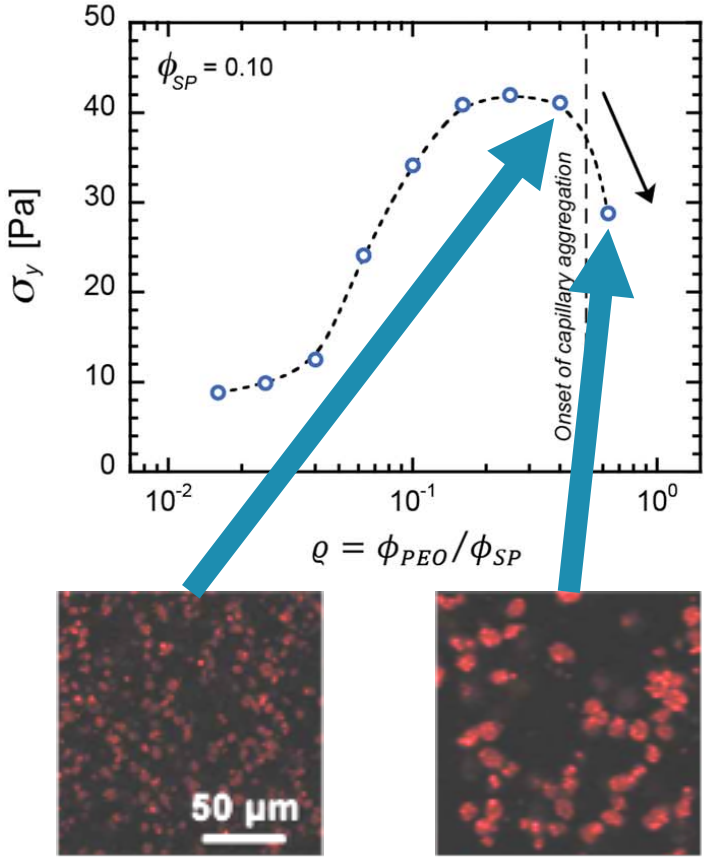
Variation of secondary fluid volume

- Alumina in paraffin oil + aqueous sucrose



J. Dittmann and N. Willenbacher, *J. Am. Ceram. Soc.* **97(12)**, 3787 (2014)

- Glass in polyisobutylene (PIB) + polyethylene oxide (PEO)



T. Domenech and S.S. Velankar, *Soft Matter.* **11(8)**, 1500 (2015)

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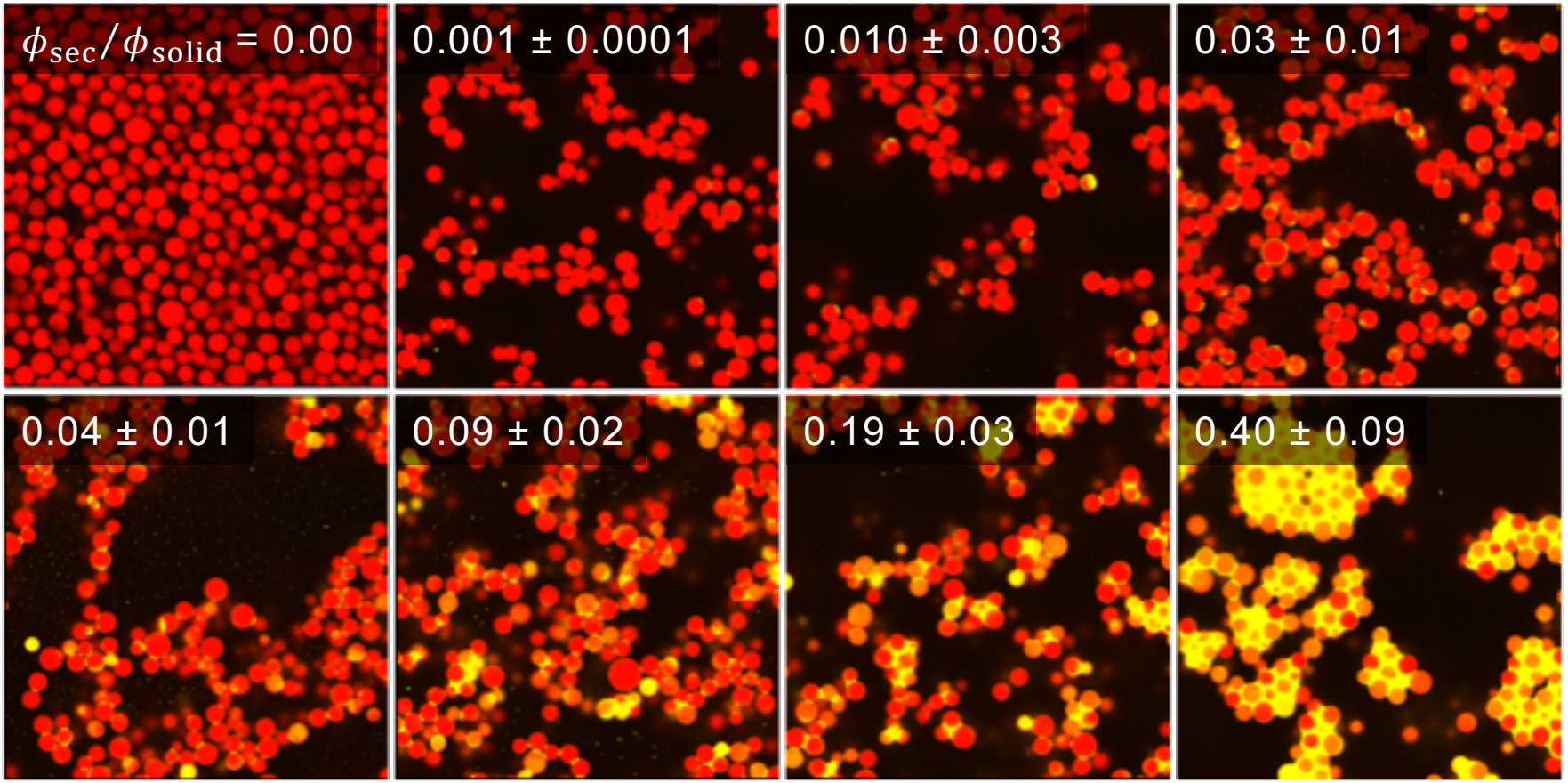
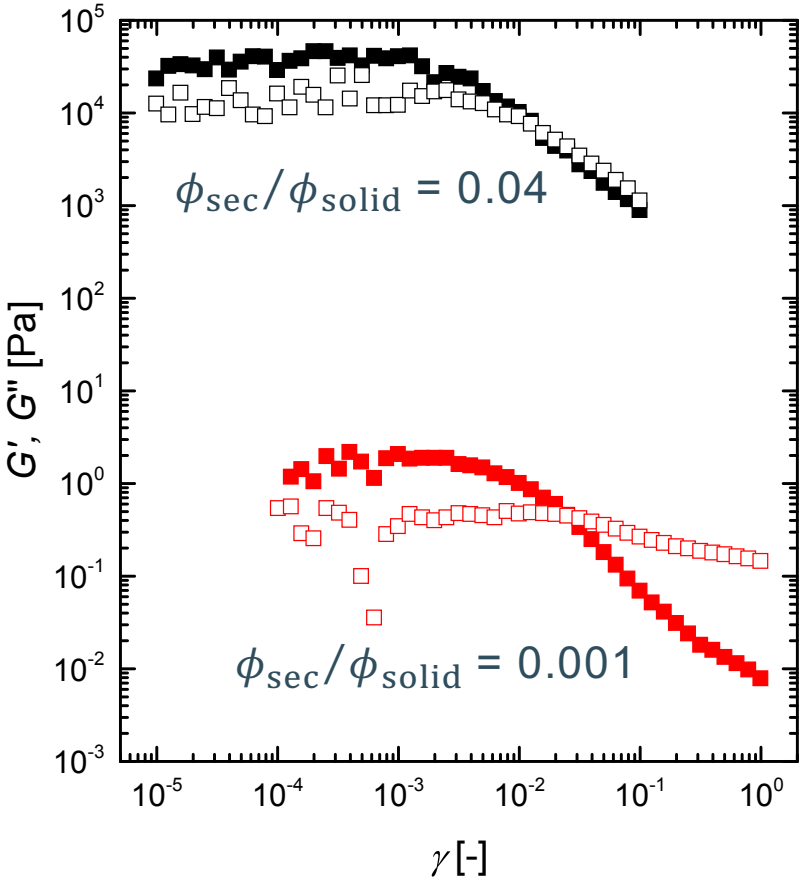
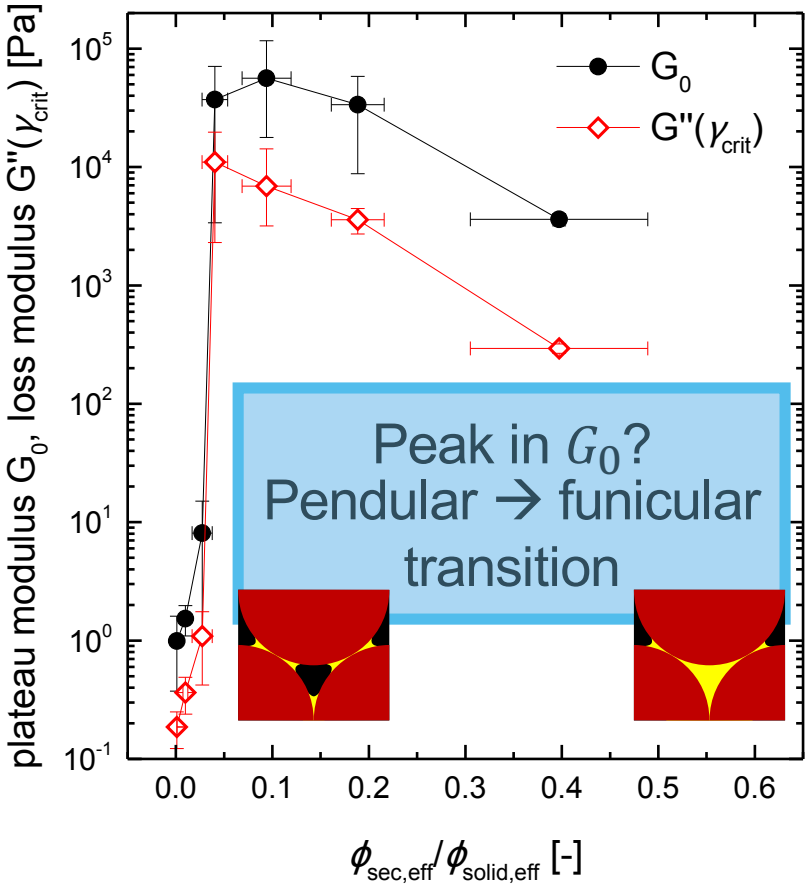
Variation of secondary fluid volume



Porous silica particles in oil with added aqueous glycerol,
$\phi_{solid} = 0.20, \theta = 87°$

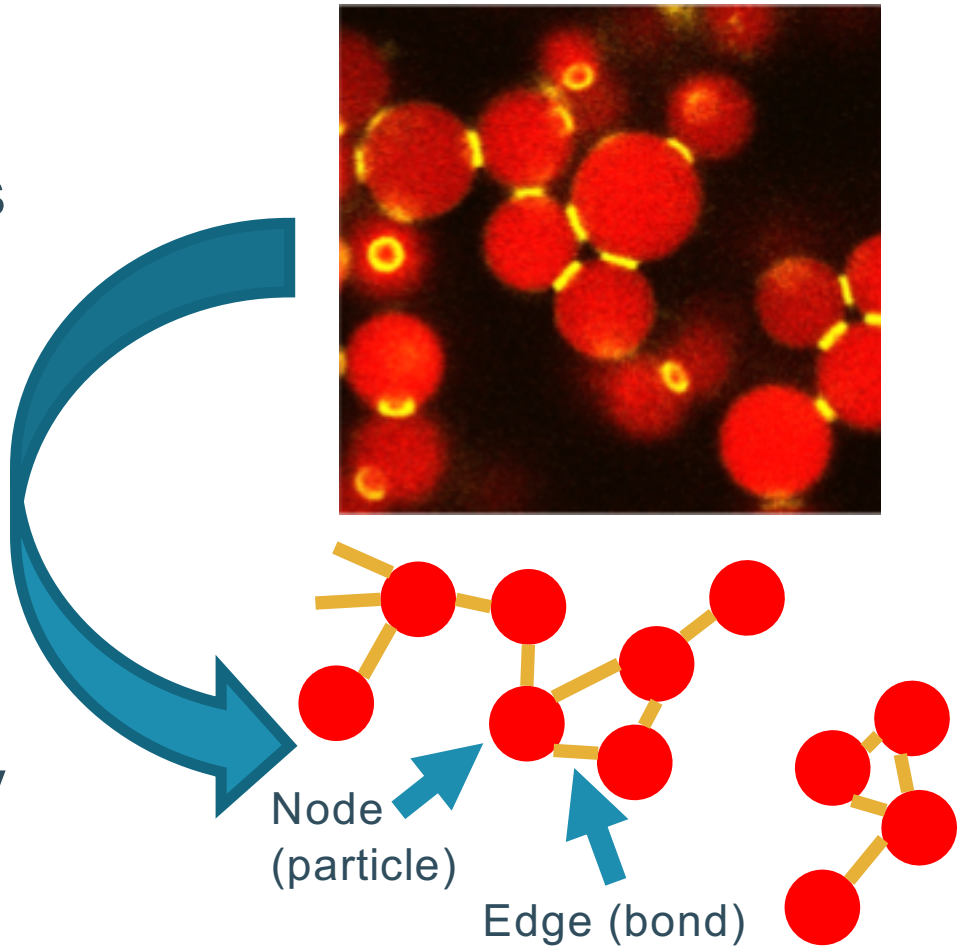
Rheological characterization





Graph theory

- Suspension rheology:
  - Assign particles and bonds to nodes and edges of a network
  - Result is an unweighted and undirected graph
  - A weighted graph can be produced by considering bond strength



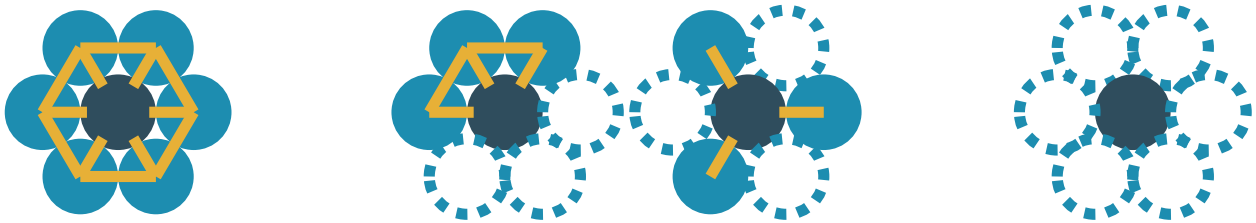
S. Bindgen, F. Bossler, J. de Graaf and E. Koos, *Manuscript in preparation*

Useful parameters

Micro

- Coordination number z_n:
  number of edges (neighbors) of node n
- Clustering coefficient C_n: Measure of group clique-ishness

$$C_n = \frac{2\,e_n}{z_n(z_n-1)},\ e_n = \text{edges between neighbors}$$



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

Macro

- Number of flocs: number of independent sets
- Other concepts from graph theory?
  - Connectivity, Centrality, …

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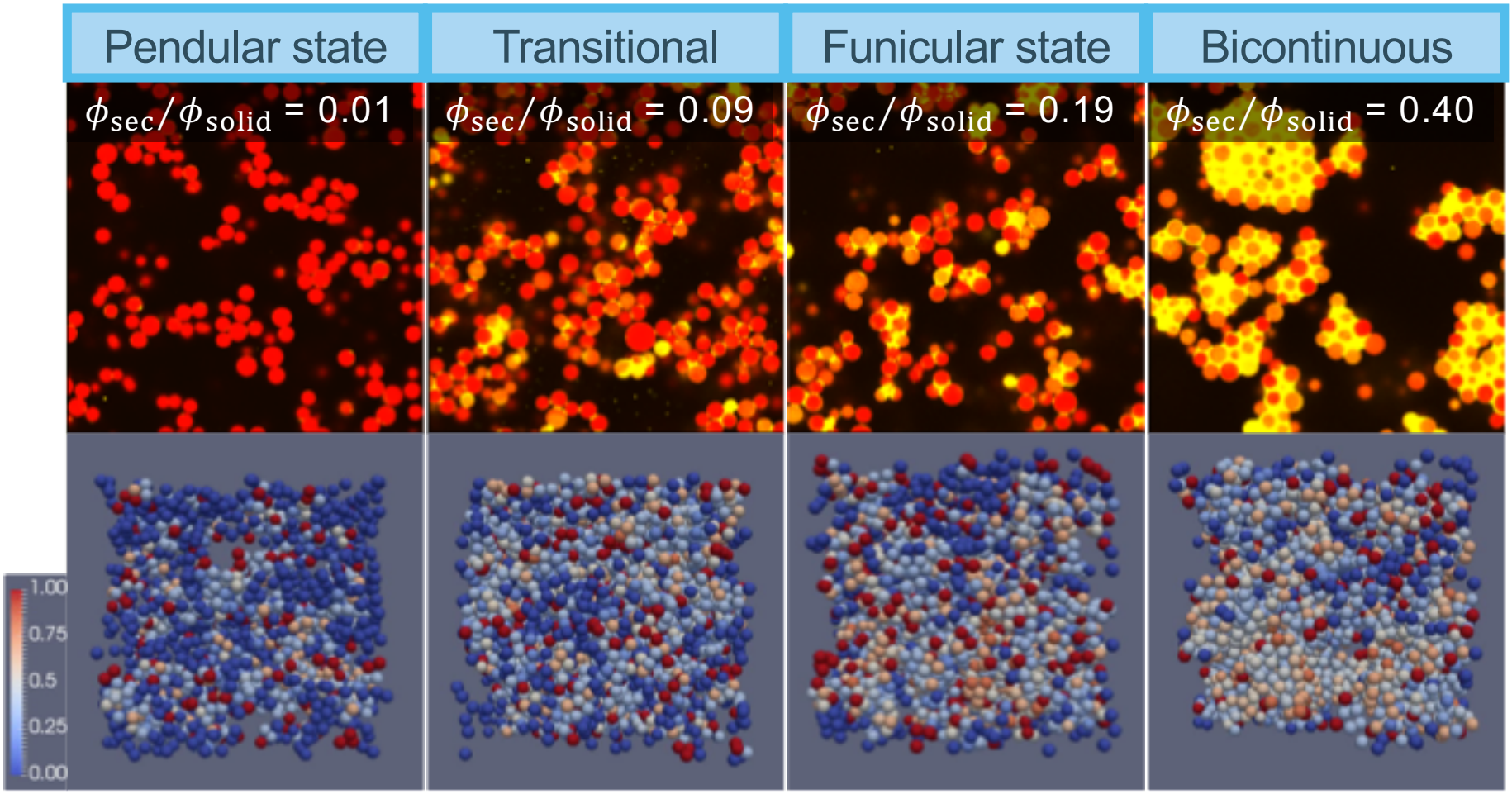
Variation of secondary fluid volume



Porous silica particles in oil with added aqueous glycerol,
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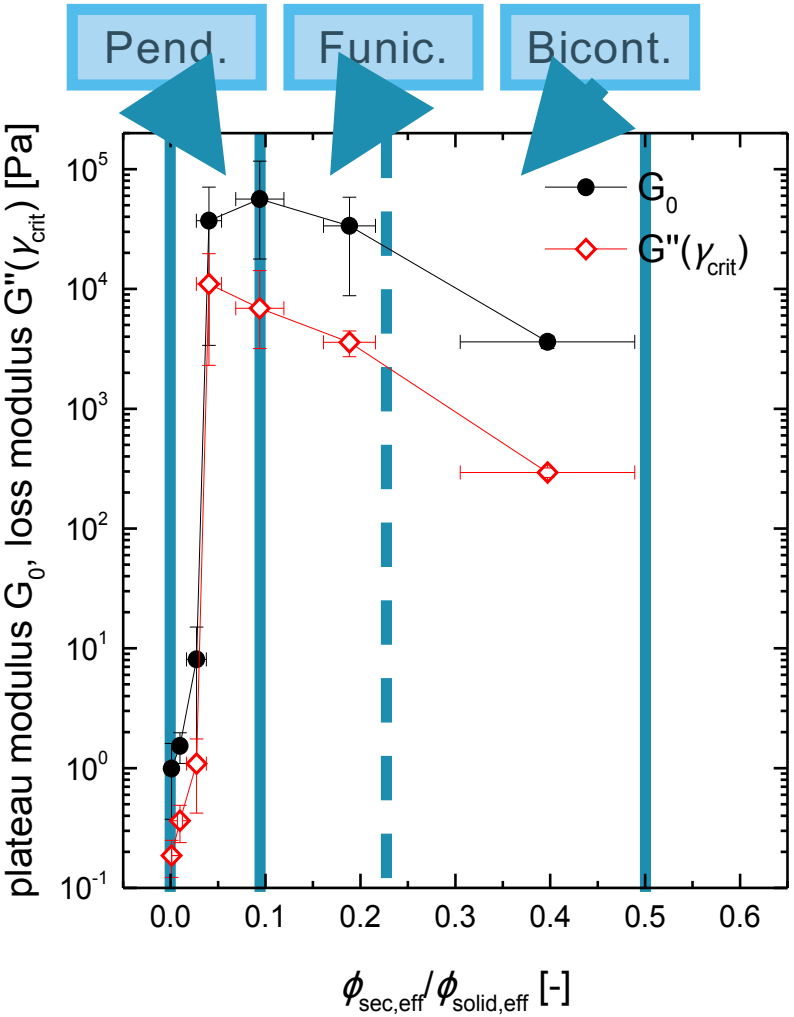
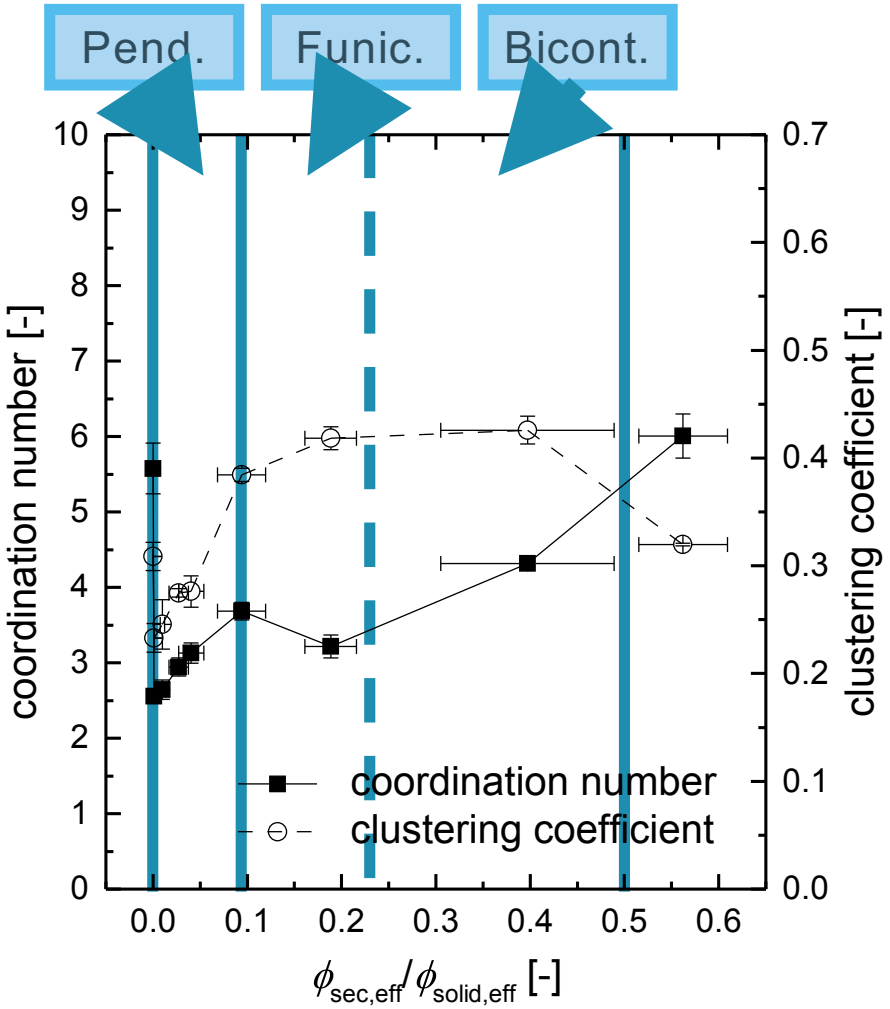
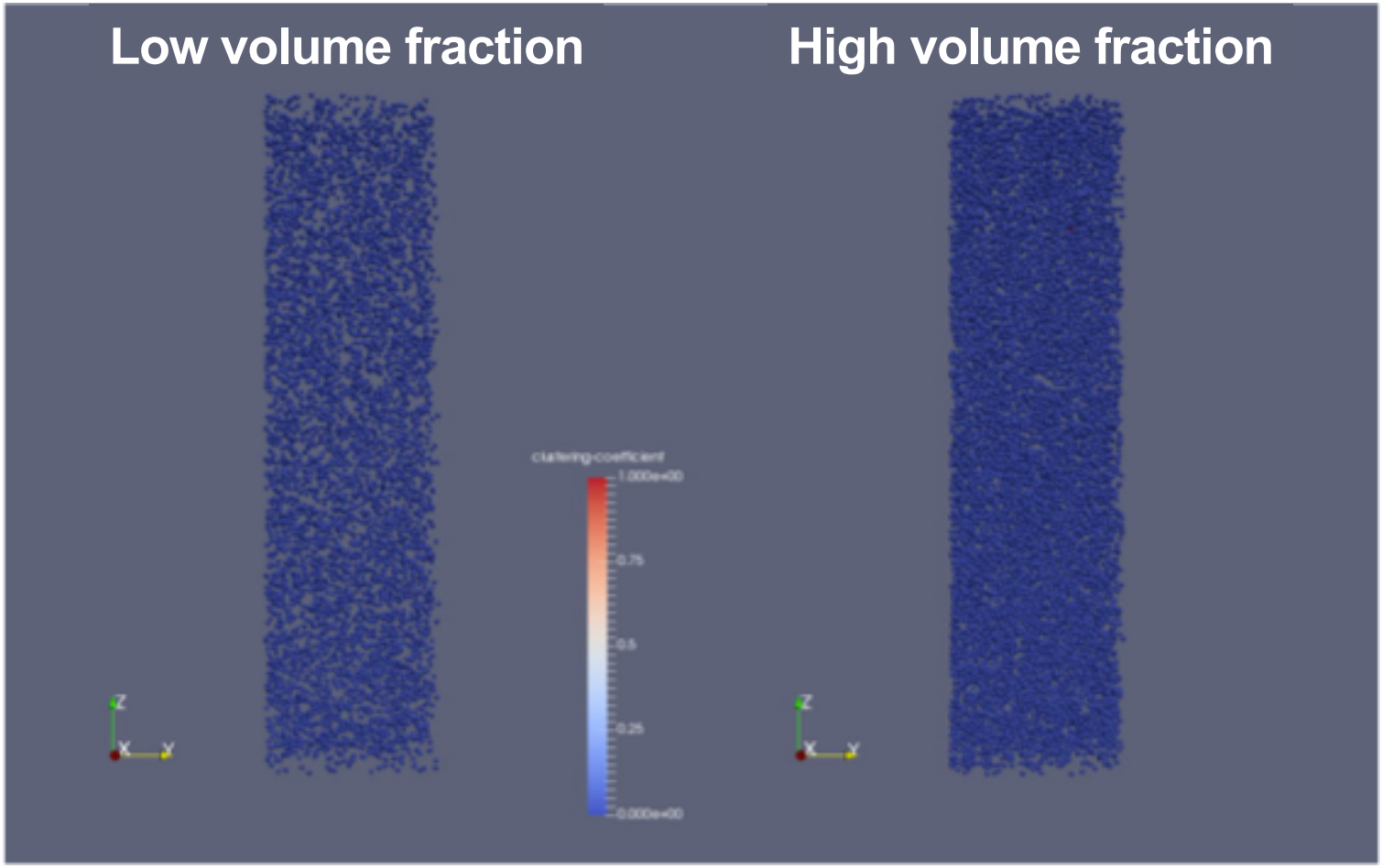
Agreement between microstructure and rheology





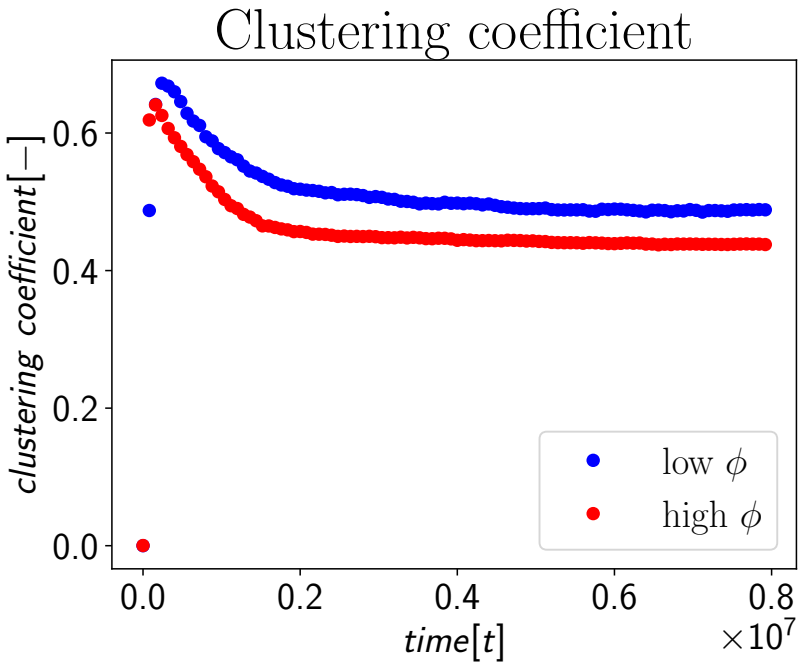
Gravitational sedimentation
(Joost de Graaf, Utrecht University)

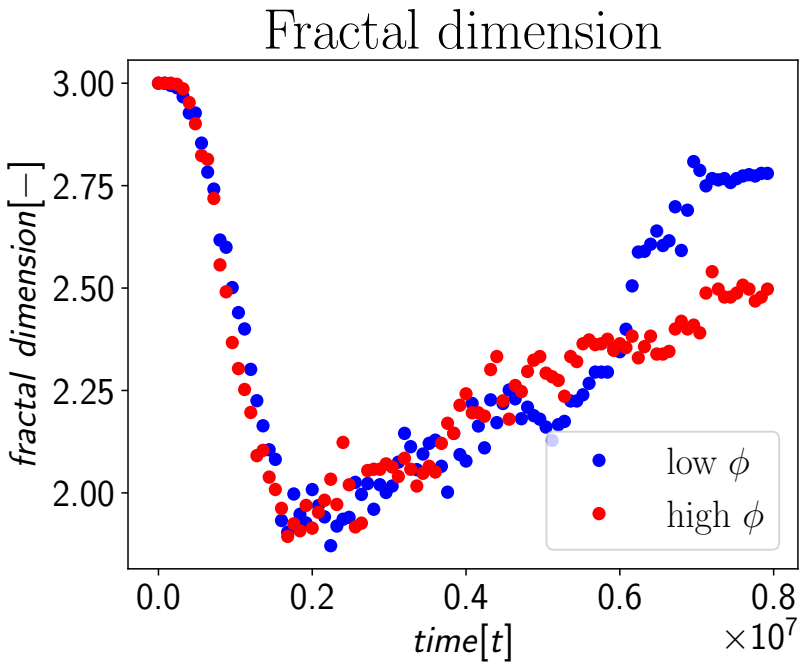


S. Bindgen, F. Bossler, J. de Graaf and E. Koos, *Manuscript in preparation*

Gravitational sedimentation

- Clear difference in final sediment structure with initial volume fraction





→ Difference in re-dispersibility?

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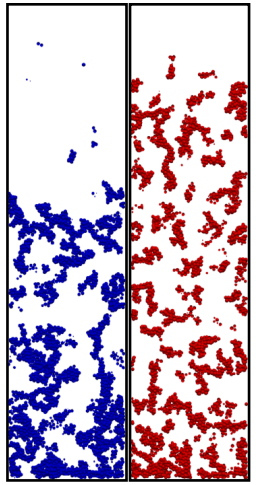
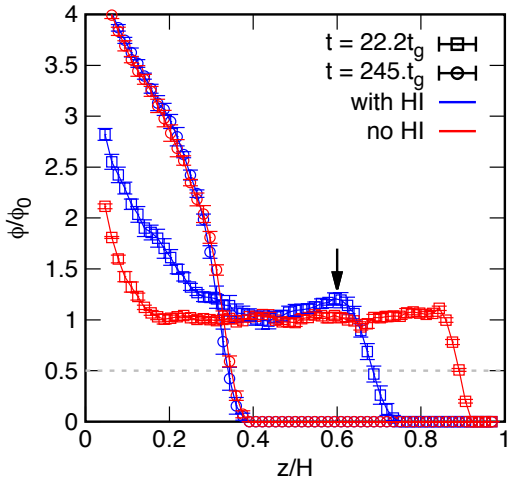
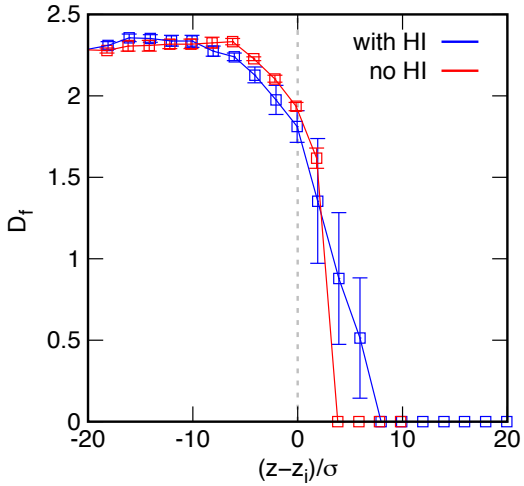
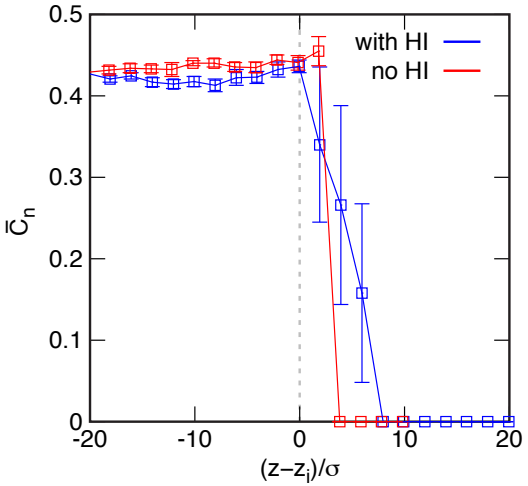
Gravitational sedimentation

- Sharper determination of the interface between the gel-rich and gel-devoid regions
  - Width of only 2σ without and 8σ with hydrodynamic interactions
  - Versus 15σ using $\phi(z)$ or 20σ using $D_f(z)$









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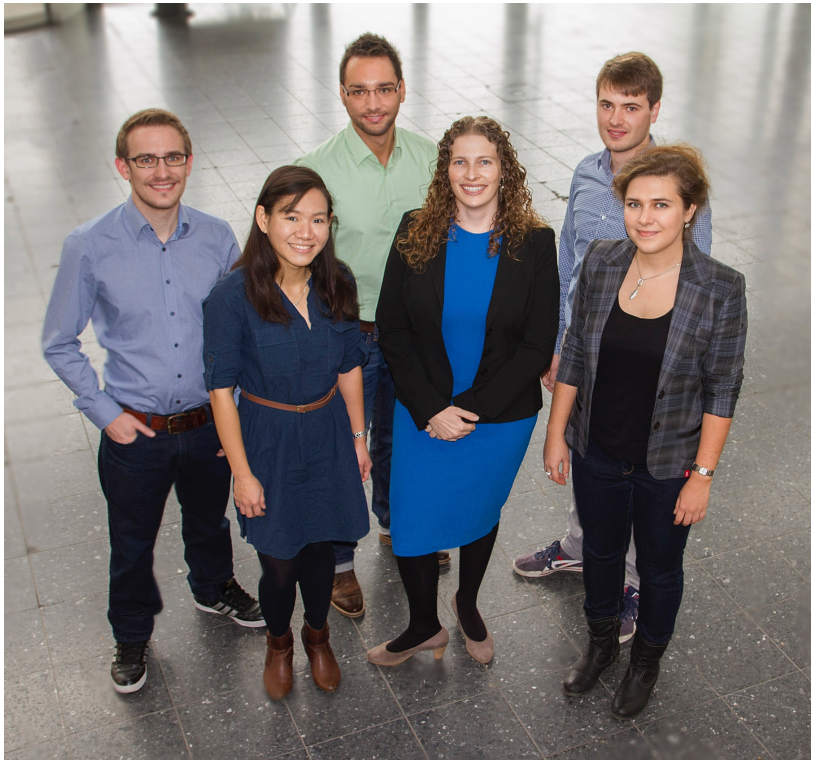
Conclusions

- Graph theory can be applied to particulate systems
  - New parameters to characterize **micro-** and **macroscales**
- Predictive of **rheological transitions**
  → Number and type of interactions
- Particularly useful for **inhomogeneous** systems
  - Capillary suspensions
  - Sedimenting gels

Acknowledgements

- F. Bossler
- S. Bindgen
- Joost de Graaf (Utrecht University)



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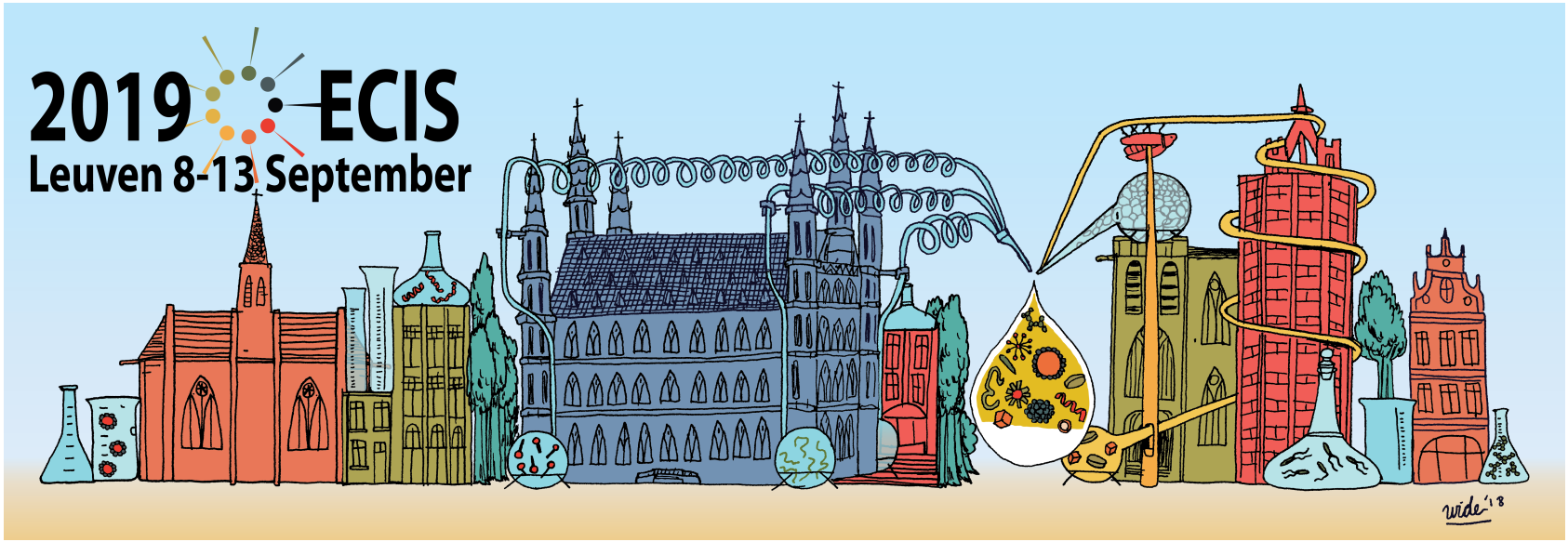

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