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Simplified industrial dispersions

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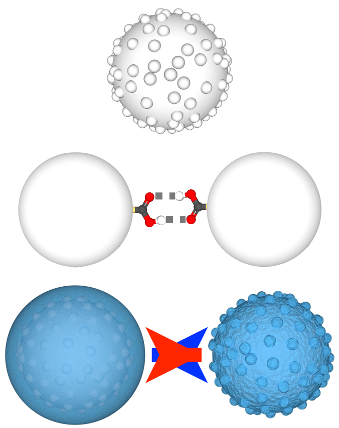
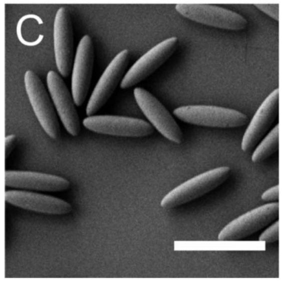
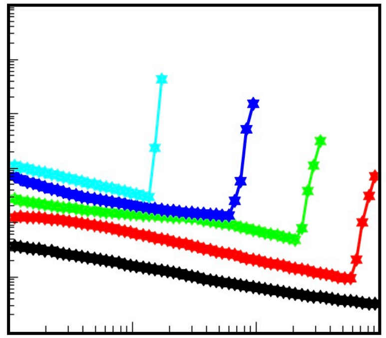
- [x] Objectives
- [ ] Bottom up SIDS
- [ ] Bottom down SIDS
- [ ] Outlook and plan for 22-23

Complexity in model systems

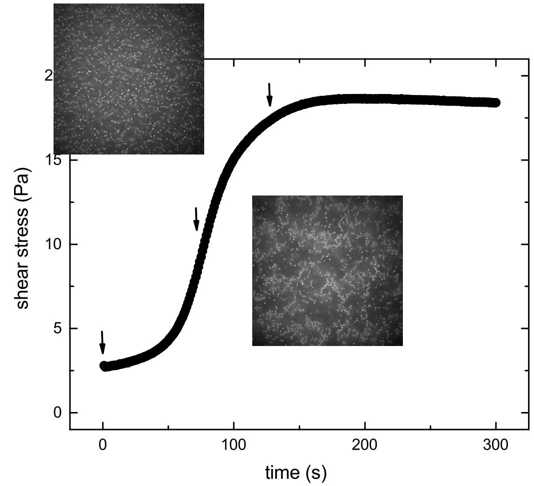




Simplified industrial dispersions

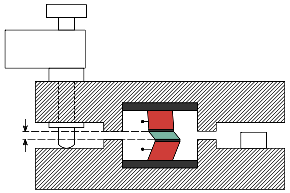


shear thickening

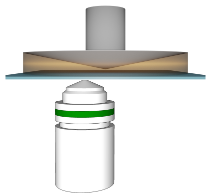


thixotropy

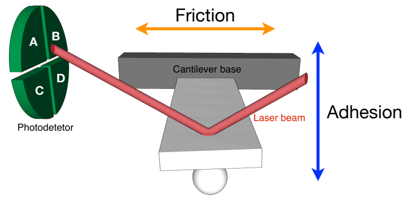
Analytical, structural and rheological methods tailored to interrogate structure



stress deconvolution



4D-imaging



local scale tribology

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- [x] Objectives
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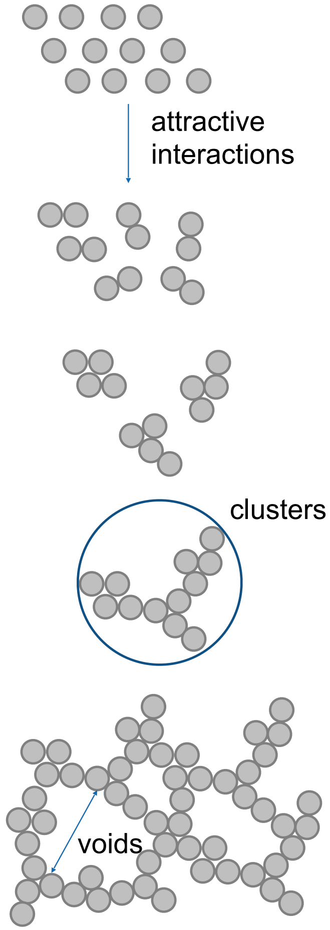
Targeted dispensing of colloidal gels

https://www.youtube.com/watch?v=NWbubR2pupg



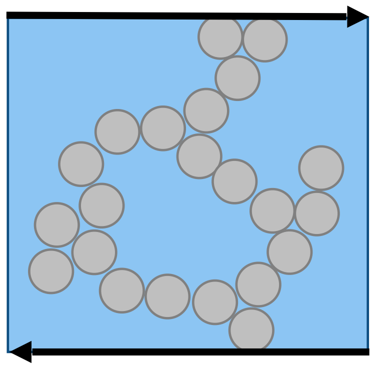
Engineer the gels microstructure through:

- **Primary particle properties**
  - Chemistry
  - Size and shape
  - Topography
- **Suspending media properties**
  - Composition
  - Density
  - Polarity
- **Interparticle forces**
  - Macromolecular composition
- **Processing**
  - Shear stresses

Koumakis, N., et al., *Tuning colloidal gels by shear.* Soft Matter, 2015. **11**(23): p. 4640-8.

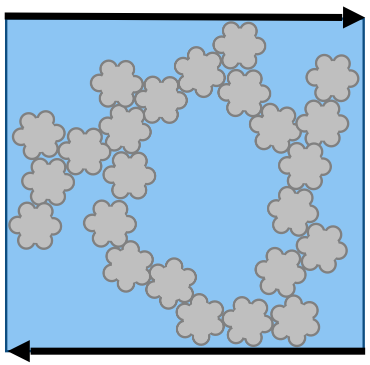
Investigating the influence of primary particle surface topography on bulk rheological properties under shear

Smooth primary particles



Rolling and sliding of particles under shear

Rough primary particles



Interlocking of particles under shear

Surface roughness:

Inhibits flow densification

➢ Open network structure

Goal:

- Investigate influence of surface roughness on the yielding behavior of particle gels
  - Comparable systems in terms of interparticle forces
  - Only tune the surface roughness

Problem:

- Thixotropic behavior of colloidal gels
- Pre-shear conditioning will modify the smooth and rough gels in a different way
  - Difficult to compare

Model system requirements

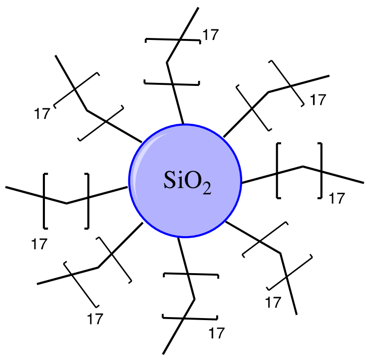
Solution:

- Thermoreversible system
- Induce gelation inside measurement cell

→

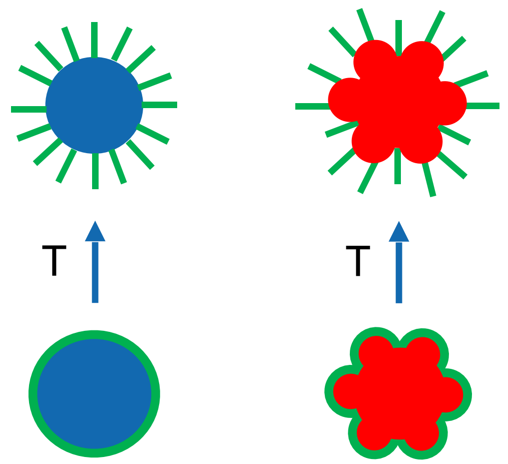
- Comparable attractive interactions
- "Rejuvinate" the structure between measurements

Model system



- SiO_2 particle
- Octadecyl brush (C_{18})
- Suspended in tetradecane (C_{14})

- Impart **different roughnesses** on the SiO_2 particles
- Maintain **comparable hydrodynamic radii**



Existing particle grafting approaches

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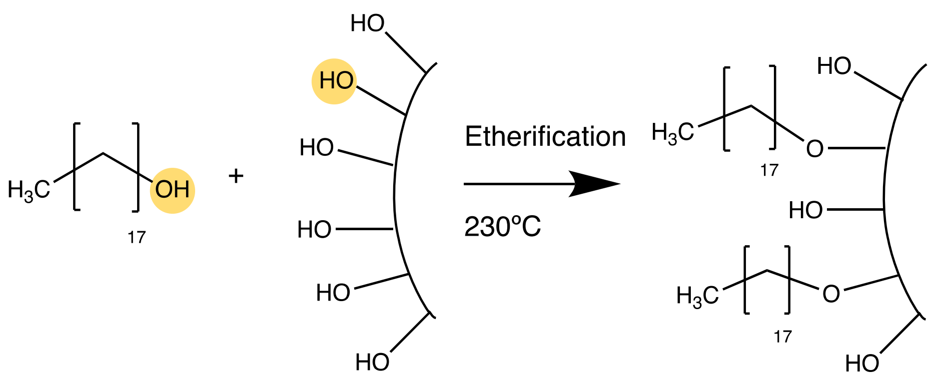
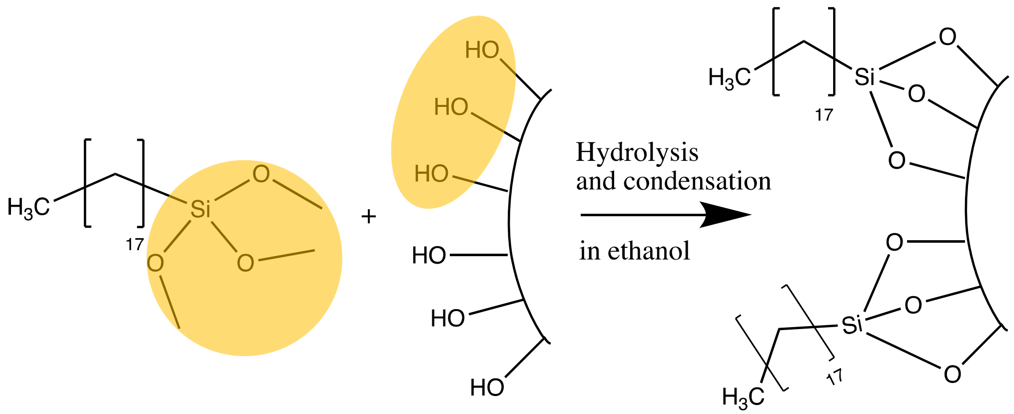
Etherification of Octadecyl



- 100 g scale
- Lengthy procedure
- Poor batch to batch reproducibility

Van Helden, A.K., J.W. Jansen, and A. Vrij, *Preparation and Characterization of Spherical Monodisperse Silica Dispersions in Nonaqueous Solvents.* Journal of Colloid and Interface Science, 1981.

Hydrolysis of Octadecyltrimethoxysilane



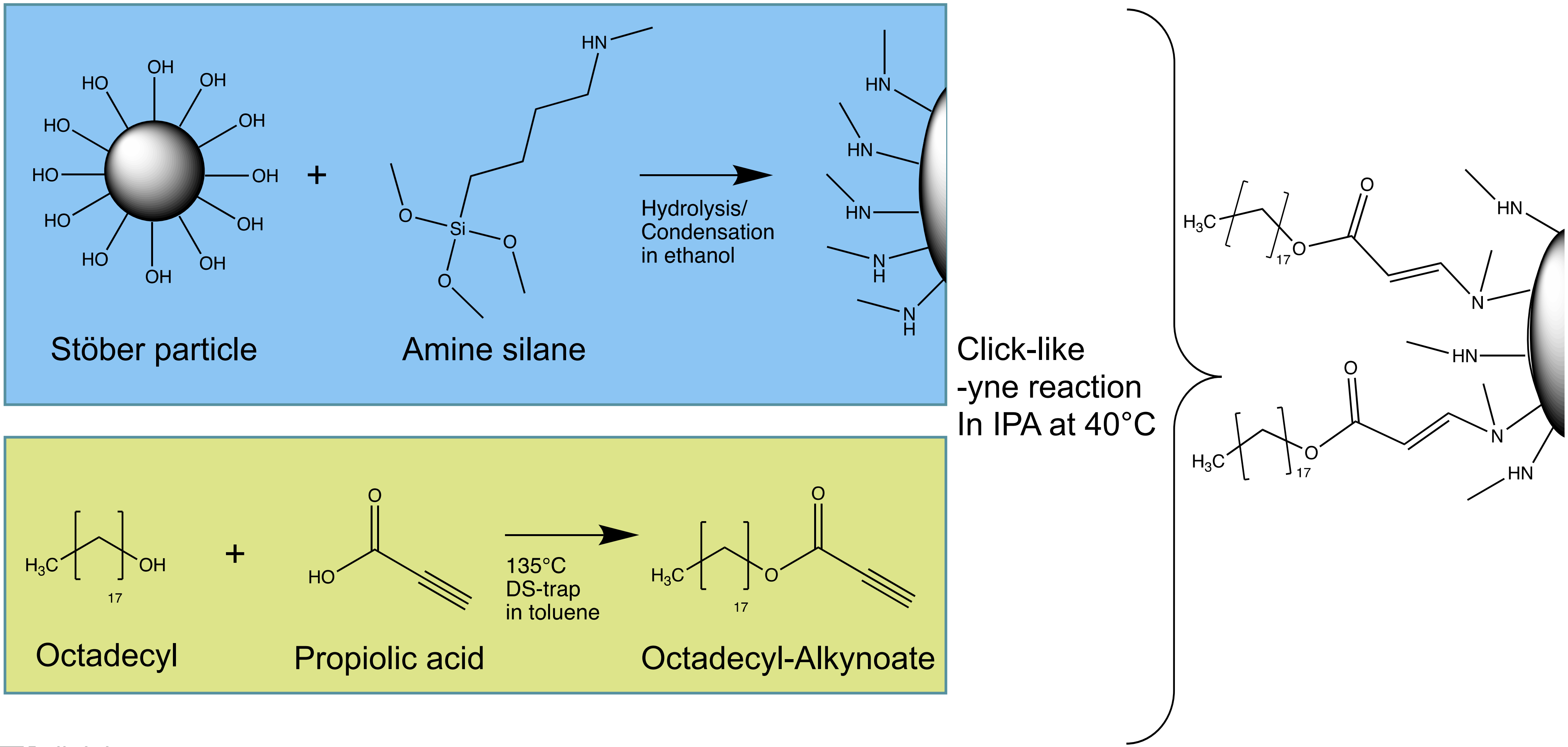
- ≤1 g scale
- One step grafting process
- Grafting density not tunable
- No thermoresponsive properties

Murray, Eoin, et al. "Synthesis of Monodisperse Silica Nanoparticles dispersable in Non-Polar Solvents." *Advanced Engineering Materials* 12.5 (2010): 374-378.

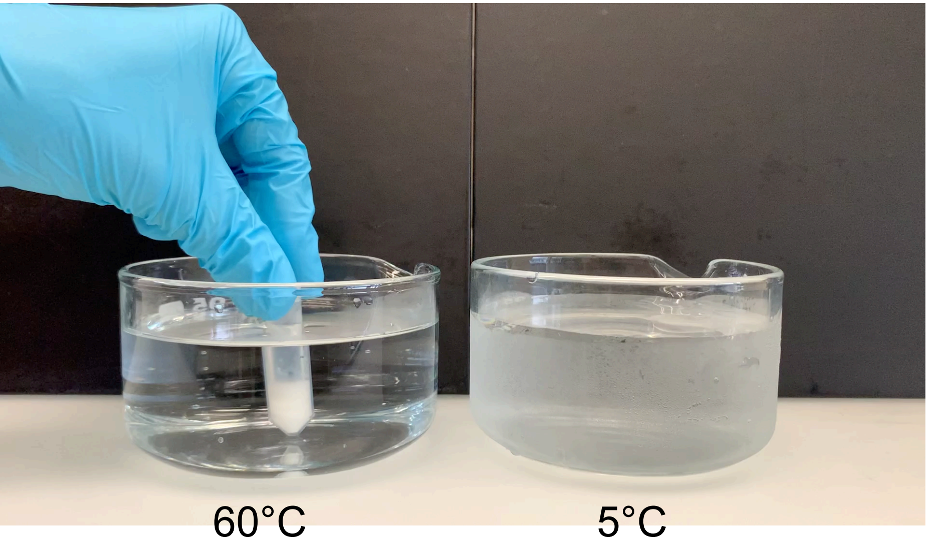
Synthesis approach for controlled octadecyl grafting to silica particles with –NH –yne click-like chemistry

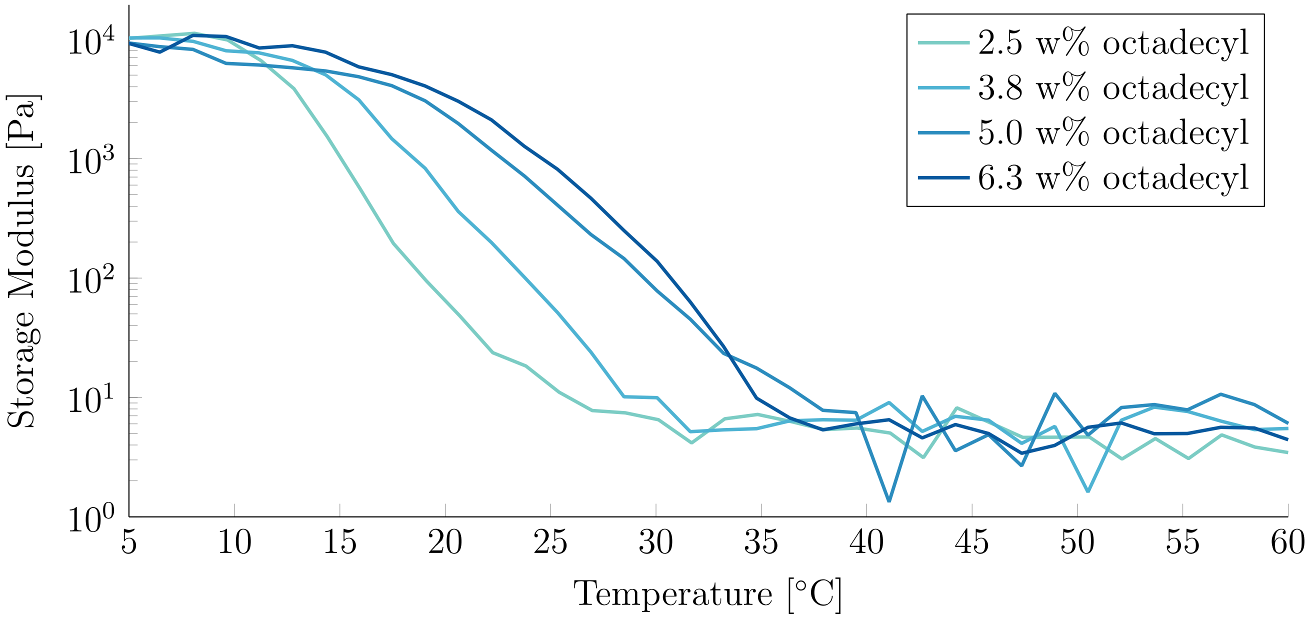
Functional particle grafting

Fischer Esterification



Thermoreversible colloidal gel system





- SiO_2 particles 300 nm
- Octadecyl brush
- 30 v%
- In tetradecane

Rough particle synthesis

Electrostatically driven heteroaggregation

200 nm

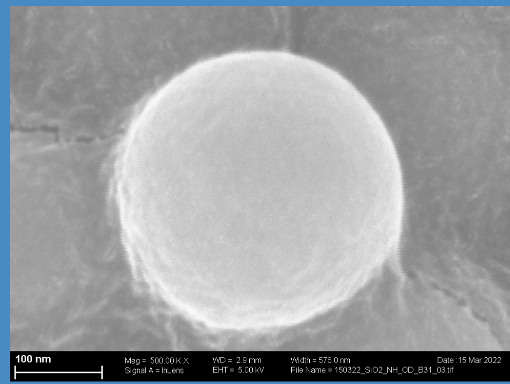
Positively charged core particle

Negatively charged berry particle

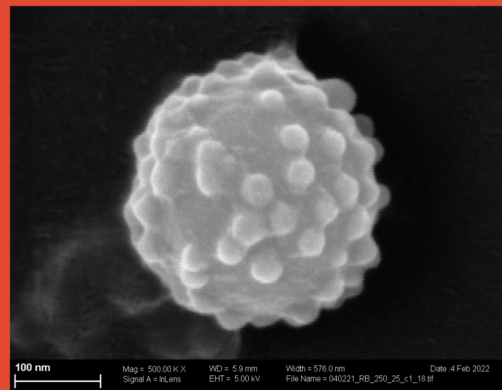
Coat with aminosilane as a stabilizing layer and functional grafting

Tune particle roughness:
- Size of berry particle
- Surface coverage of berry particles
- Thickness of stabilizing layer

Smooth SiO_2 particles

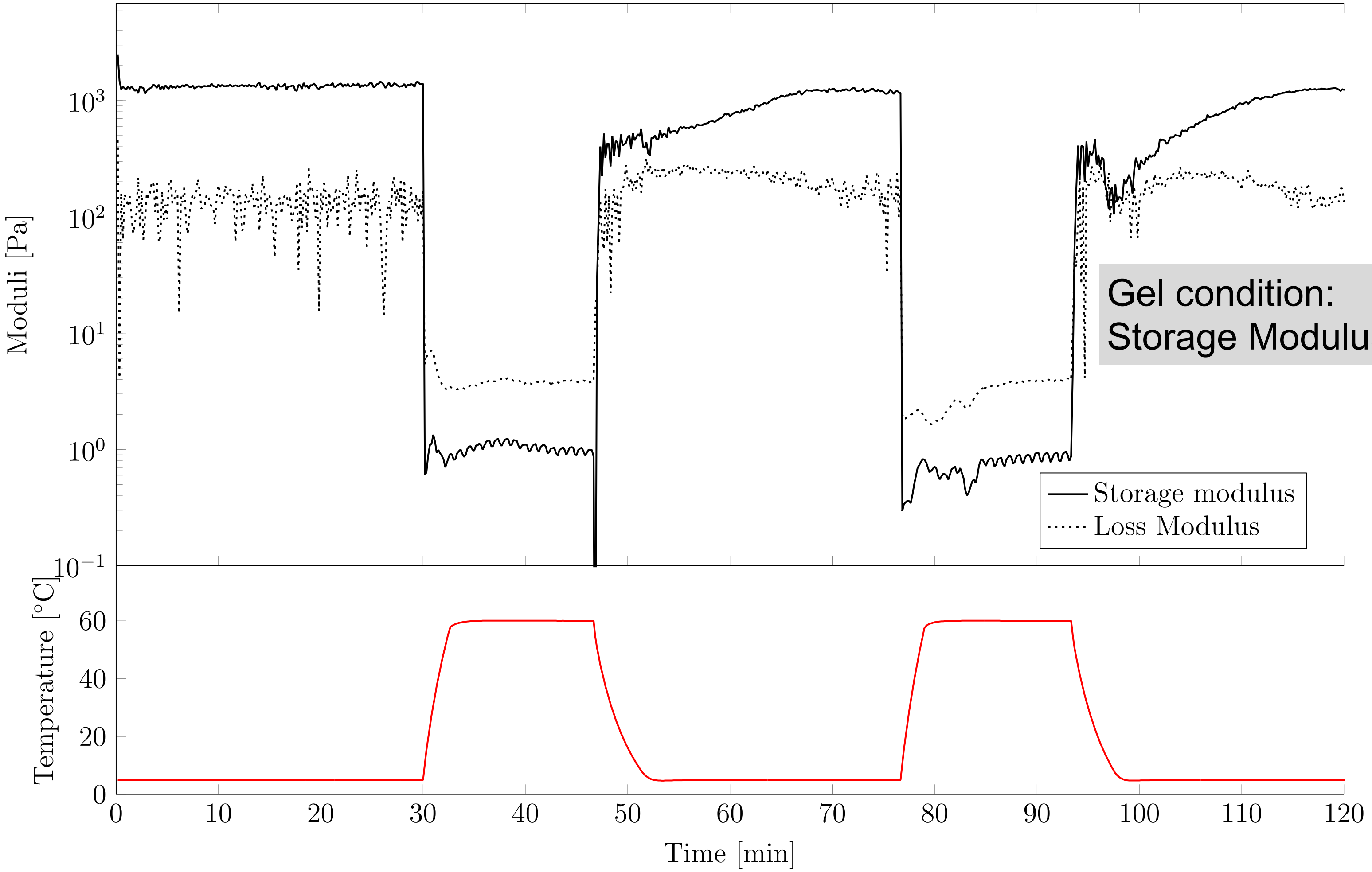


Raspberry particles



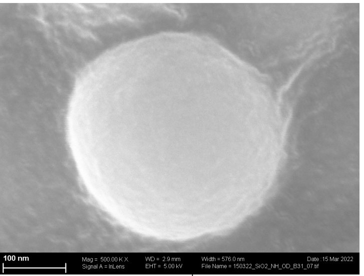
Zanini, M., et al., *Fabrication of rough colloids by heteroaggregation.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2017 **532**: p. 116-124.

Thermoreversible gels can be made with rough systems



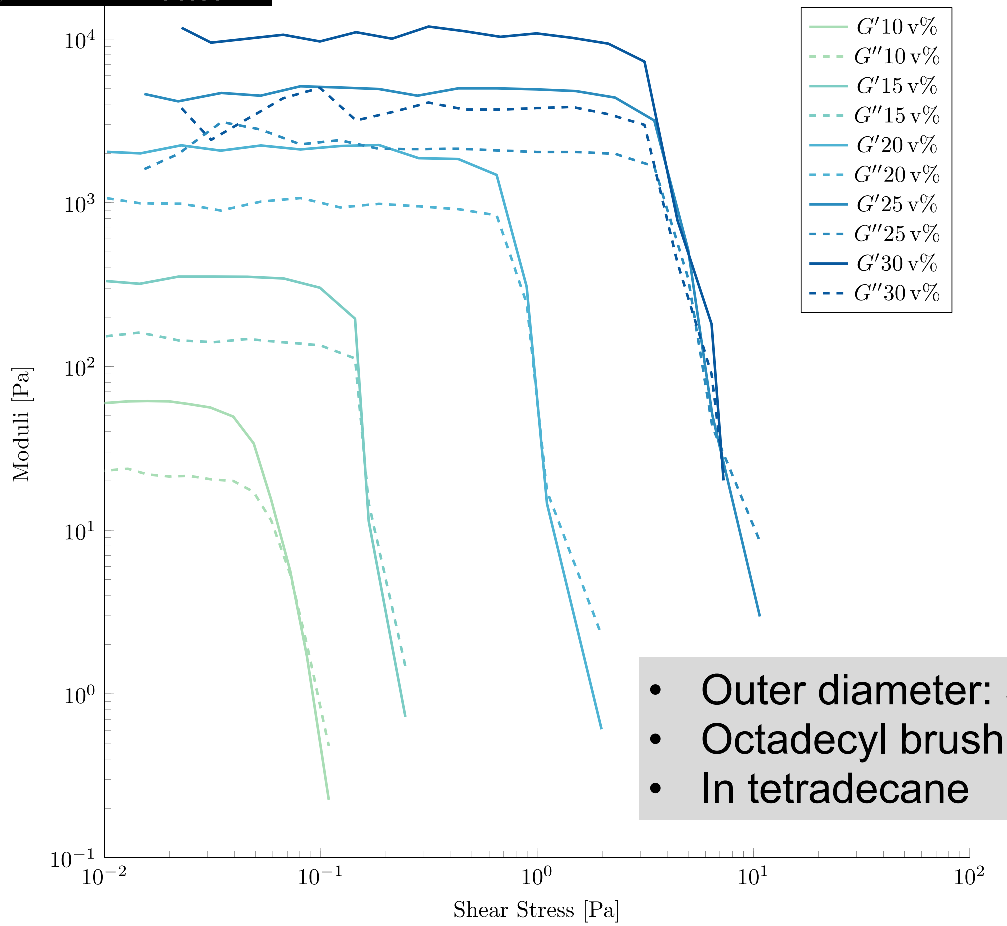
Gel condition:
Storage Modulus > Loss Modulus

Synthesis of a rough primary particle system with comparable properties to the smooth particle system



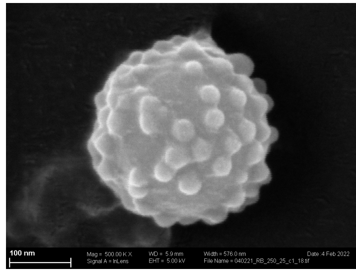
Rough particle gels delay yielding

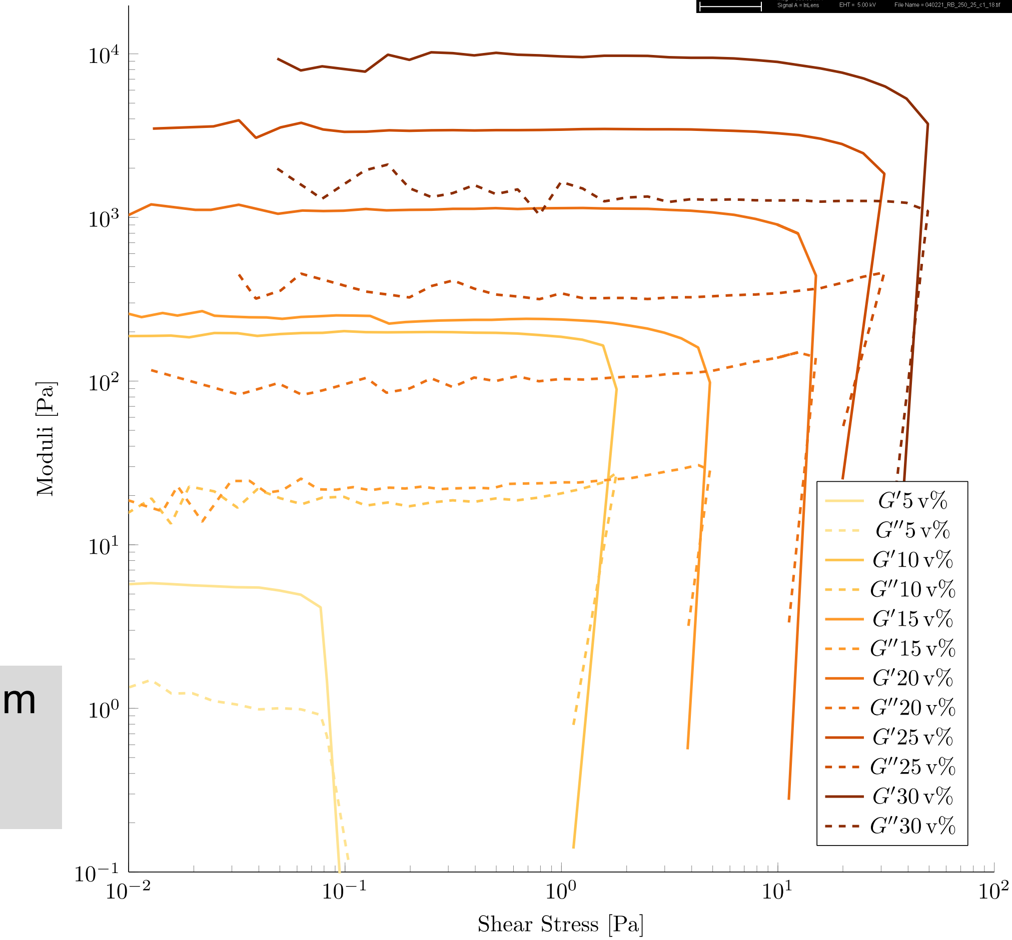
smooth



- Outer diameter: 300 nm
- Octadecyl brush
- In tetradecane

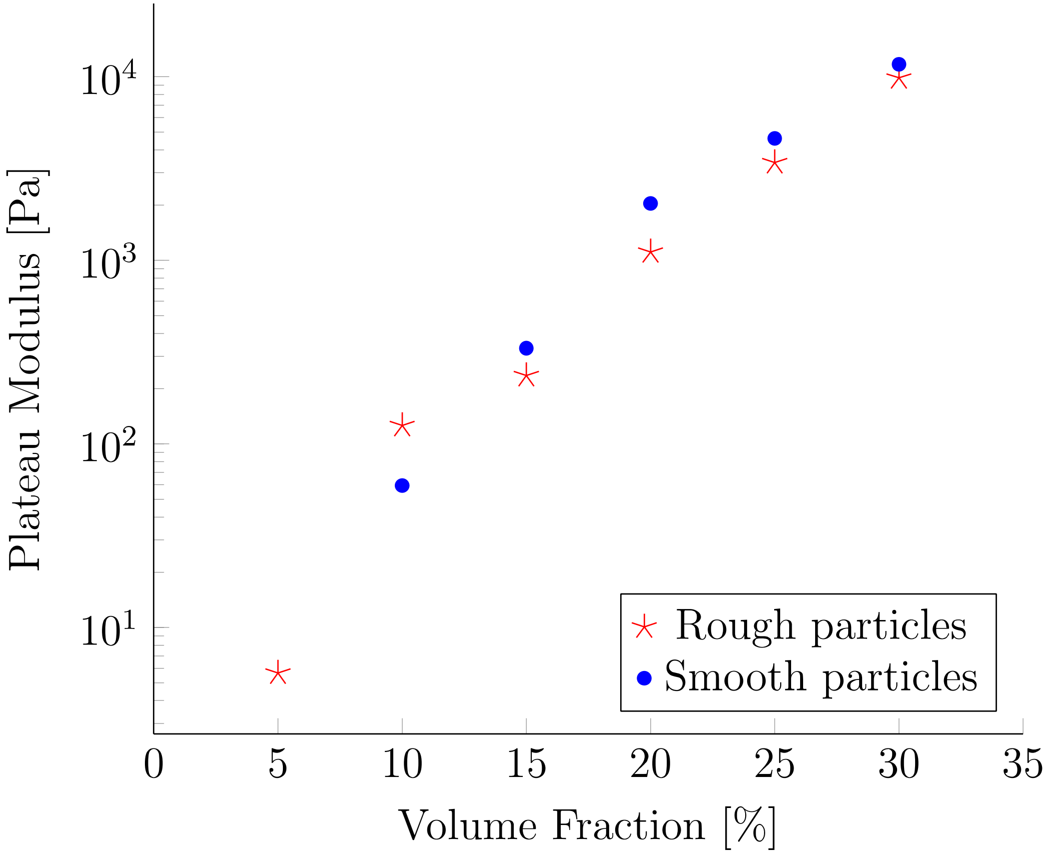
rough

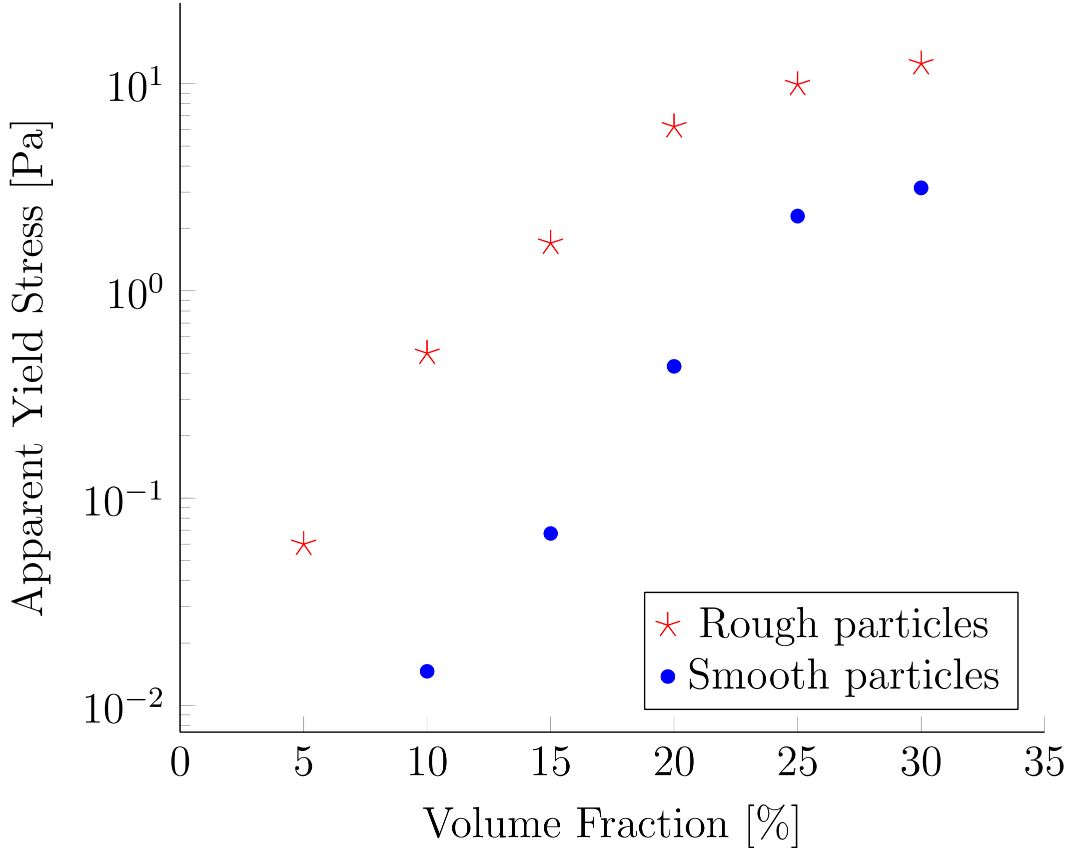




To be submitted

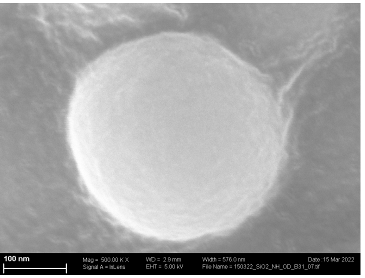
Surface roughness increases interparticle forces



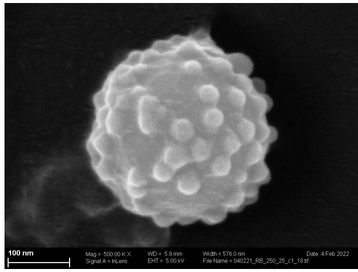


- Plateau moduli in gel state are comparable
- Roughness comes into play for low volume fractions

- Apparent yield stress is significantly higher for the rough particle systems

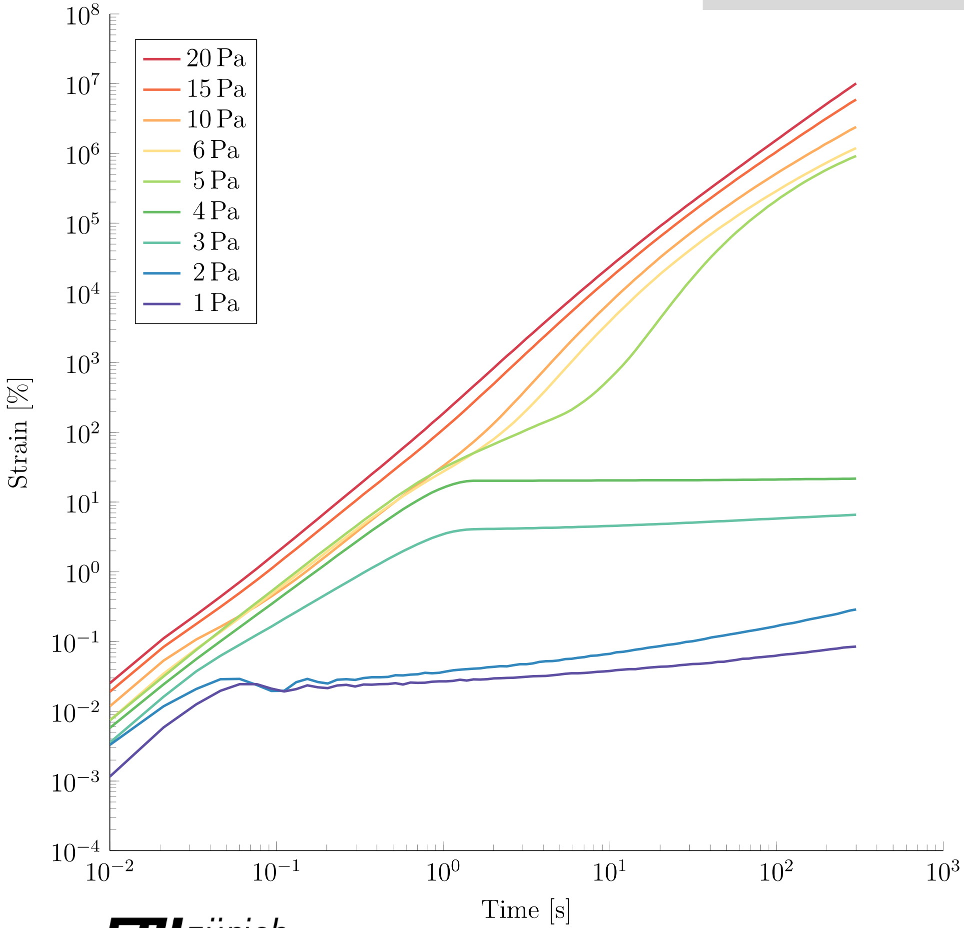


Surface roughness extends the linear response regime

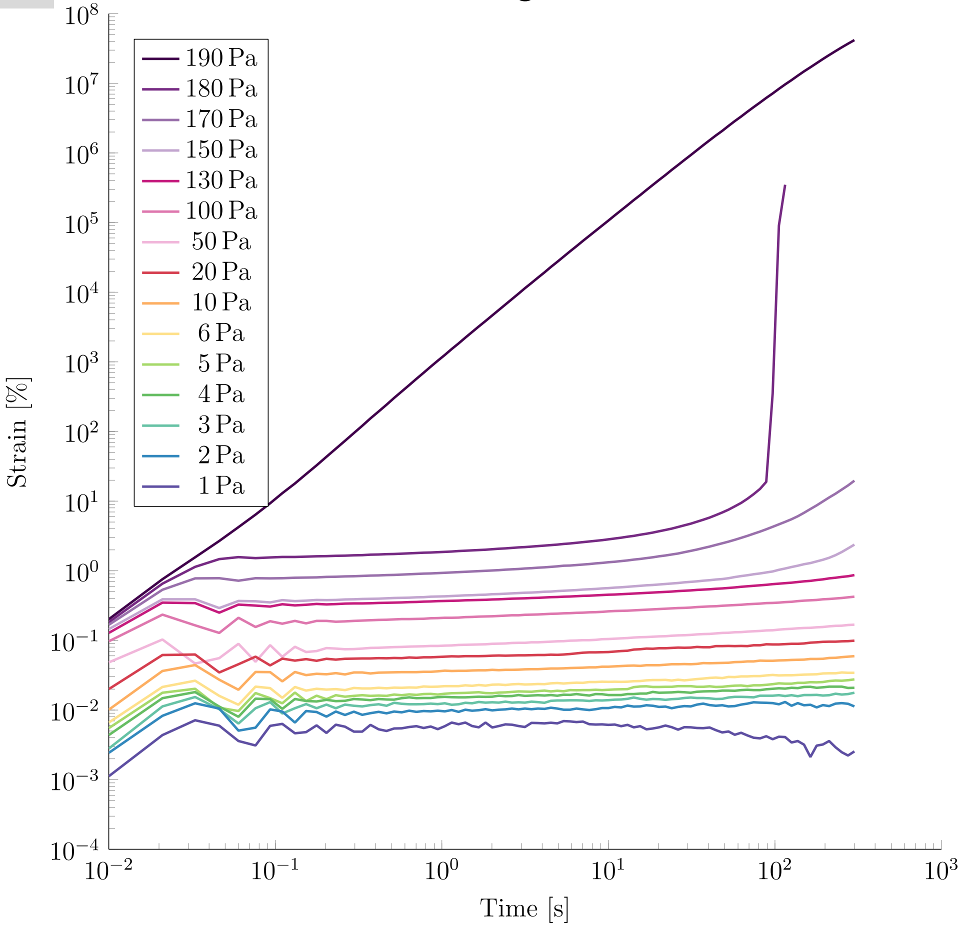


- Outer diameter: 300 nm
- Octadecyl brush
- 25v% in tetradecane

smooth

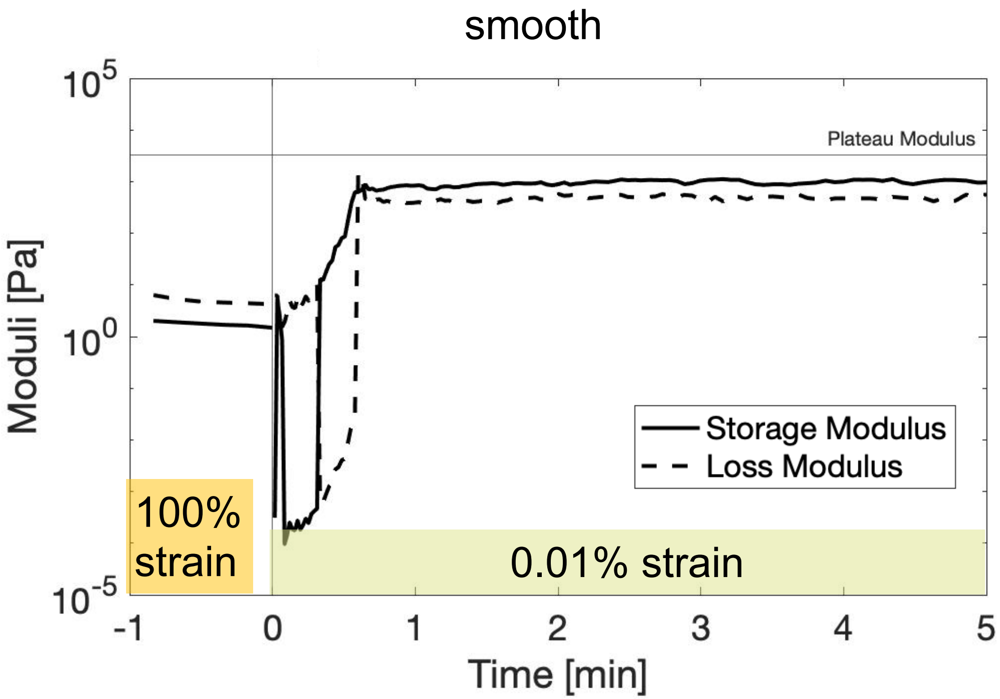


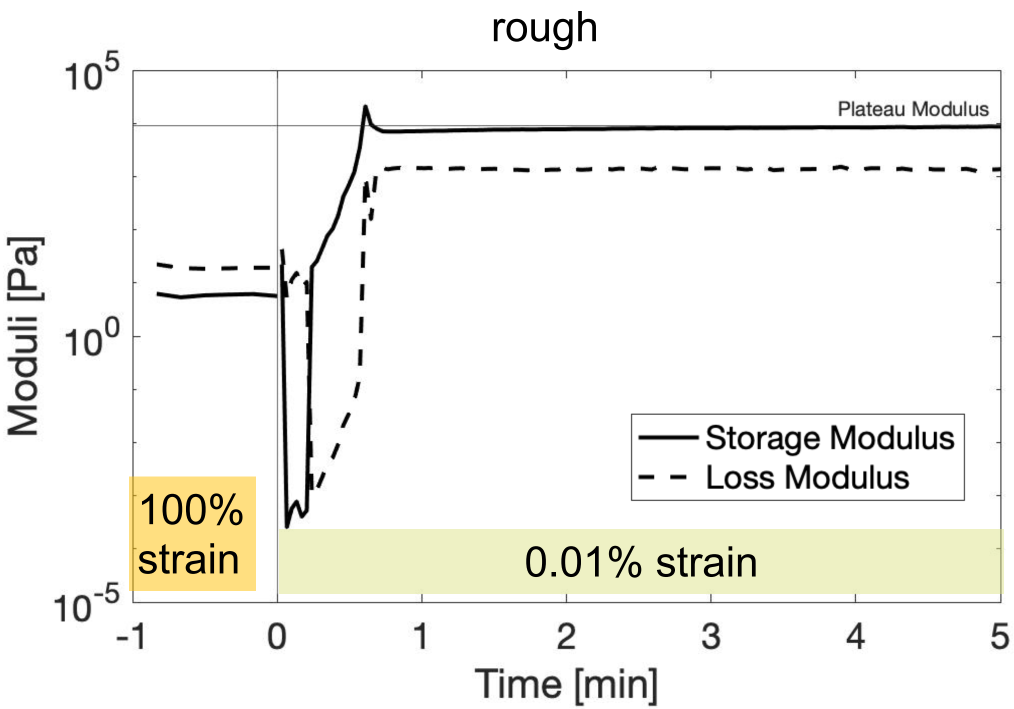
rough



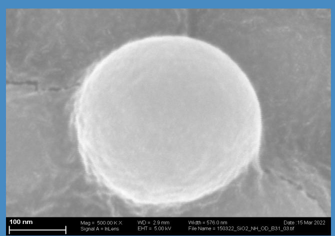
To be submitted

Rough particle gels recover fully and quickly





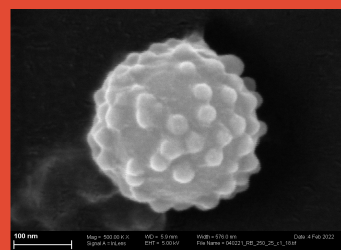
Smooth SiO_2 particles



Rough particle gels recover quicker

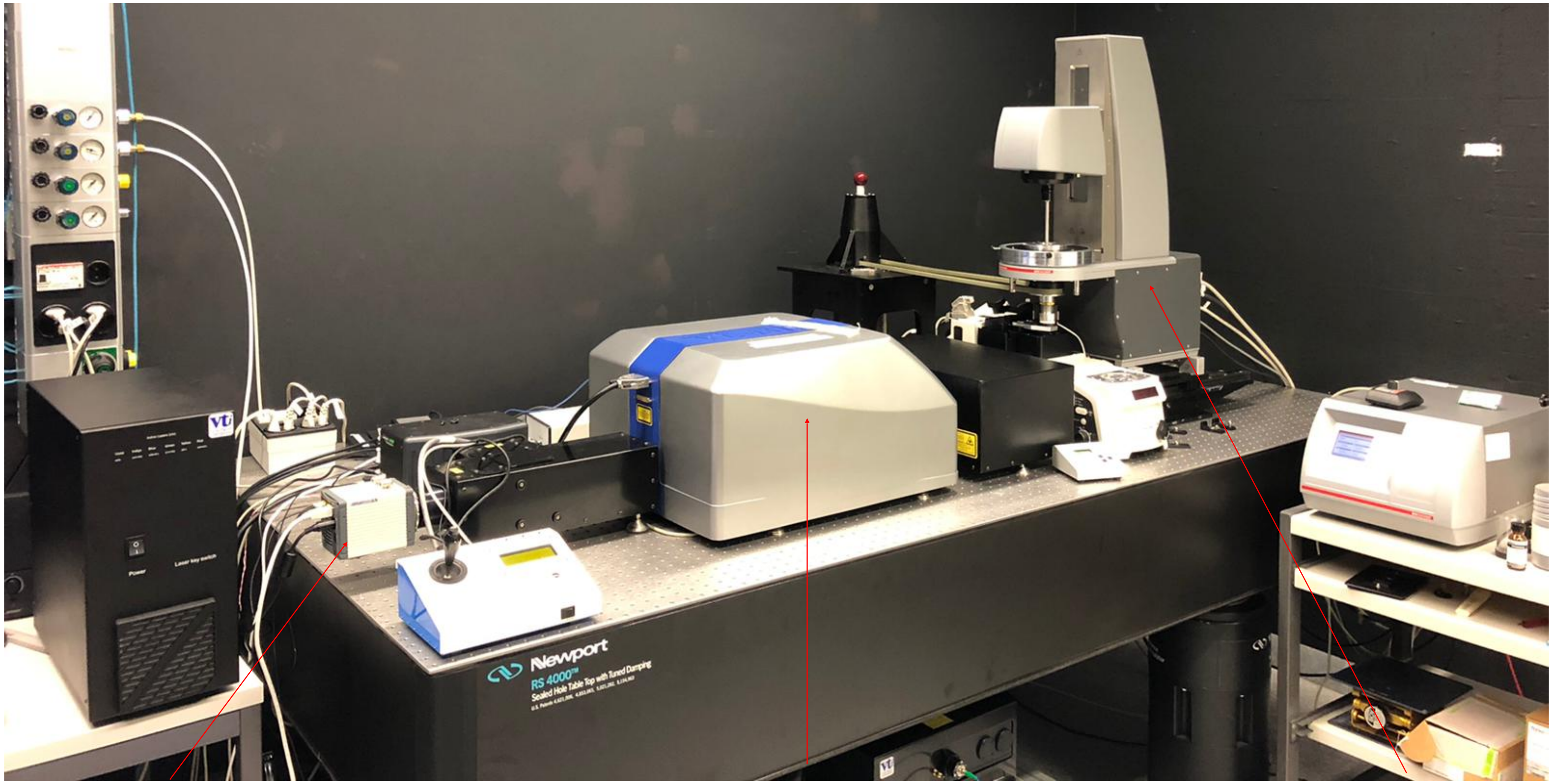
- Interlocking prohibits shear induced cluster densification

Raspberry particles



To be submitted

Ultrafast rheo-confocal setup



<u>Dual camera setup</u>
1200 FPS full frame (fast acquisition)
4 MP (high resolution acquisition)

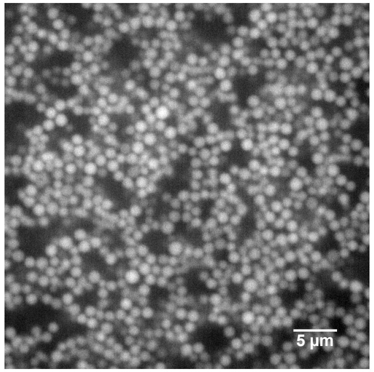
<u>Confocal scanner</u>
170nm xy resolution, 450nm z resolution
1000 FPS full frame

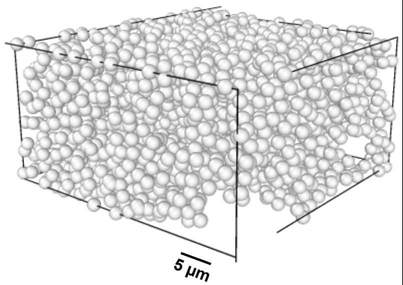
<u>Strain-controlled rheometer</u>
Counter-rotative shear cell with deported second motor

Colombo et al., Korea-Aust. Rheol. J. **31,** *2019*

Model depletion gel under shear

Model system





PMMA-g-PHSA depletion gel
- ϕ~44%
- 1.1µm diameter
- 8% polydispersity
- Suspended in squalene
- Polybutadiene, M=1.2.10^{6} g/mol, c/c*=0.42

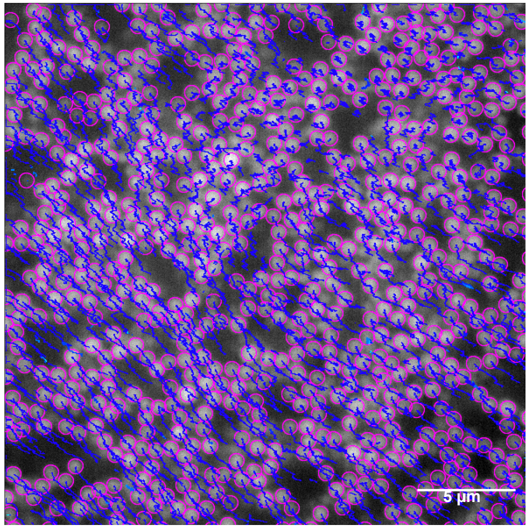
Confocal microscopy

- Laser line : 488 nm
- Exposure time : 200 ms
- Frame rate : 5 FPS
- Laser intensity : 10% I_{max}
- Imaging 20µm over the glass slide

Rheology

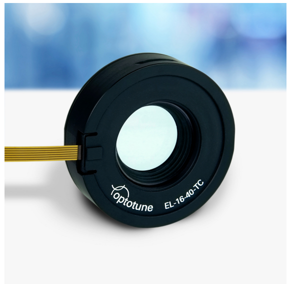
- CP15-6 geometry
- 200 s^{-1} pre-shear for 2 minutes
- 30 minutes, monitored by SAOS 1% at 1 Hz
- Shearing at constant shear rate in counter rotation mode

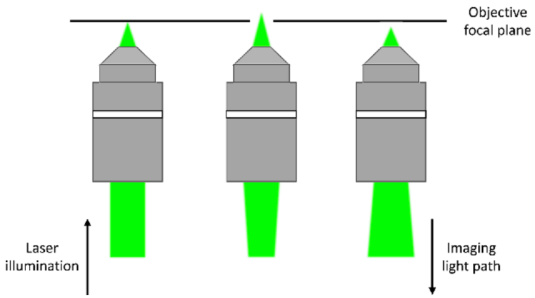
Particle tracking

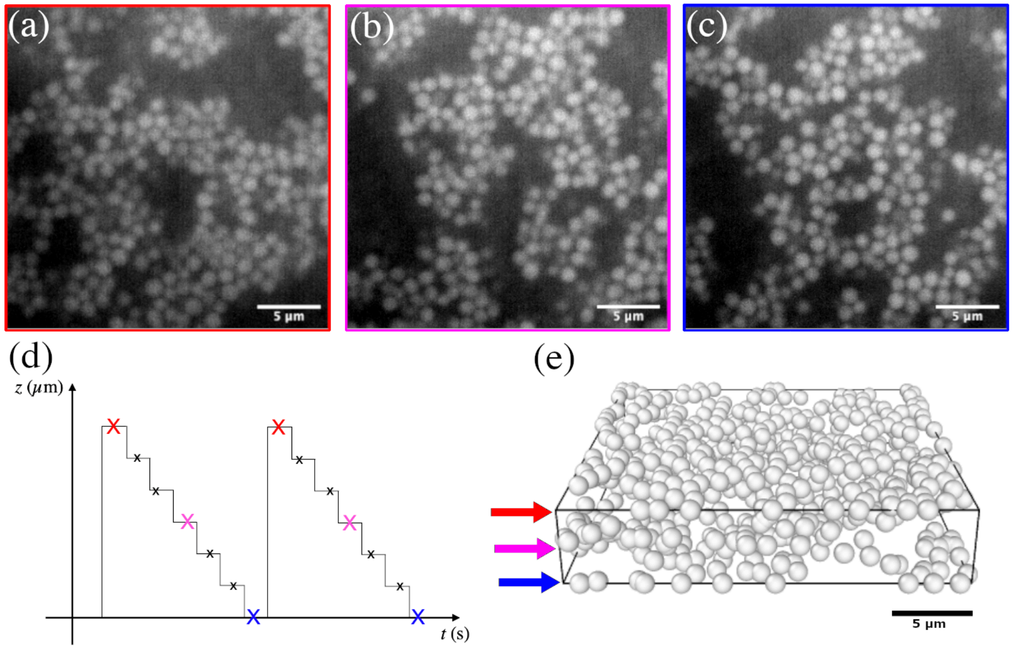


- ImageJ plugin TrackMate
- Extraction of particles
- Extraction of tracks

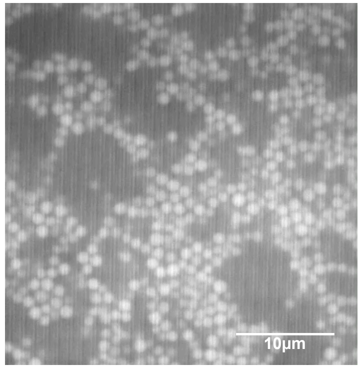
Setup upgrades – fast scanning liquid lens



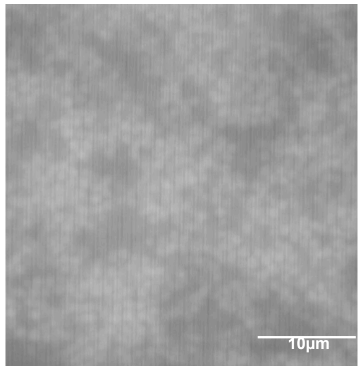




Breathing effect correction



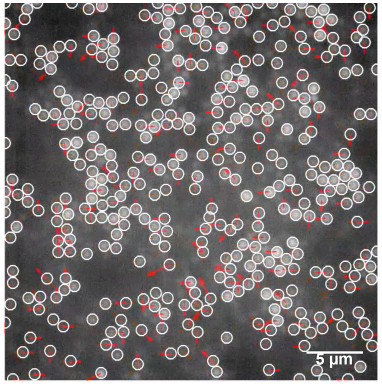
Radial drift



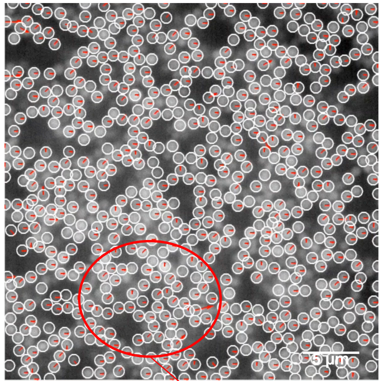
Reduced drift

Displacement fields (gels)

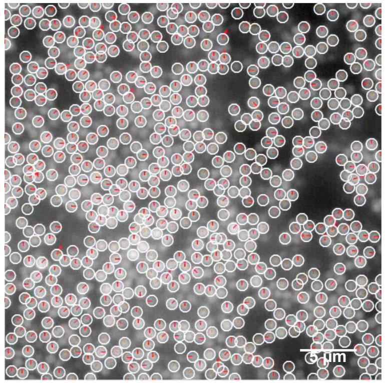
$\dot{\gamma} = 0.05\ s^{-1}$



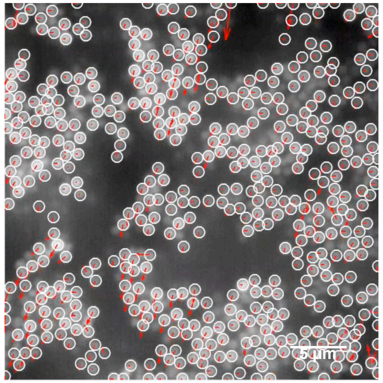
$\dot{\gamma} = 0.1\ s^{-1}$



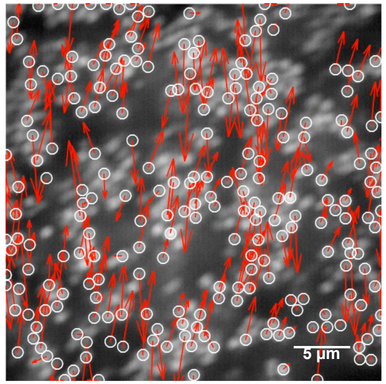
$\dot{\gamma} = 0.5\ s^{-1}$

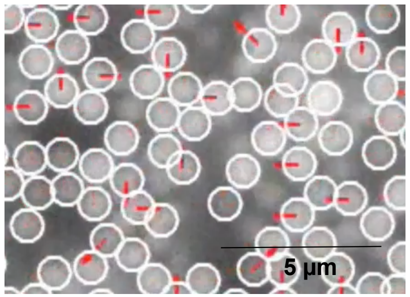


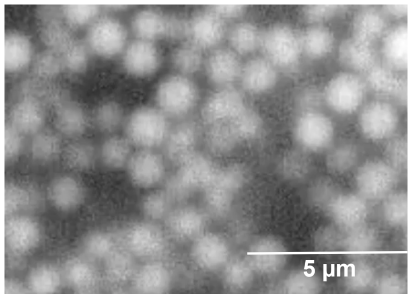
$\dot{\gamma} = 1\ s^{-1}$



$\dot{\gamma} = 5\ s^{-1}$

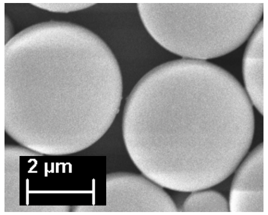


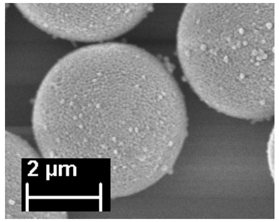


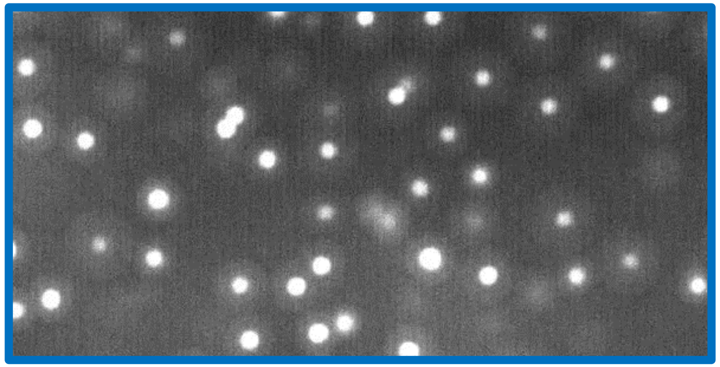


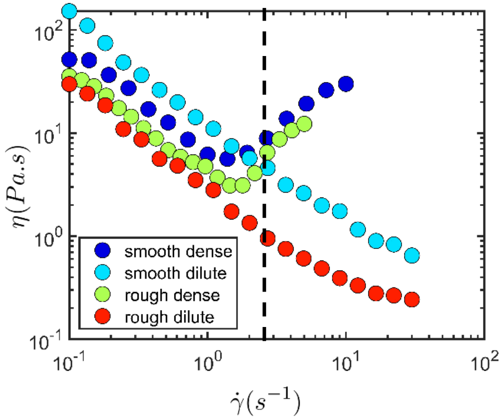
Localized zone of consistent displacement
Further propagation in the structure

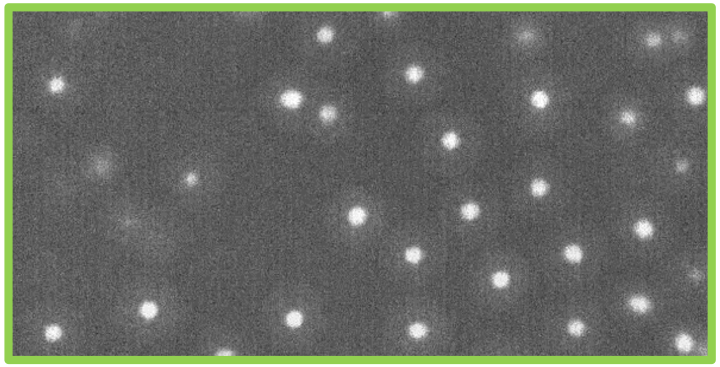
Thinning-thickening

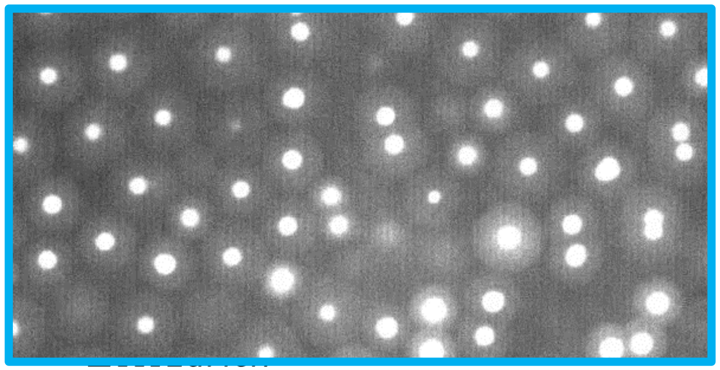


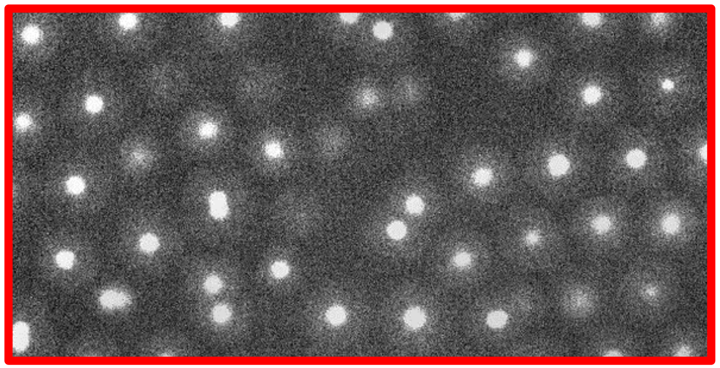




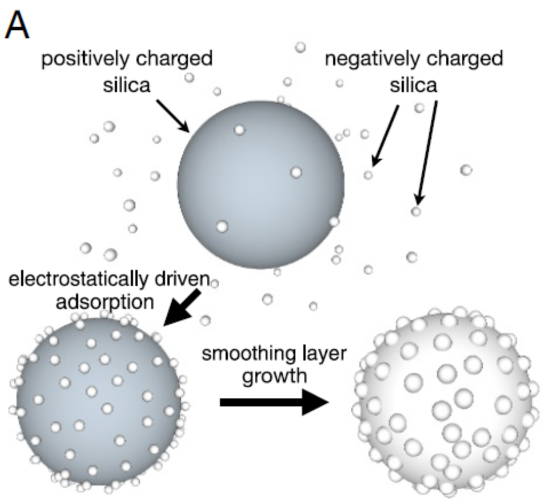




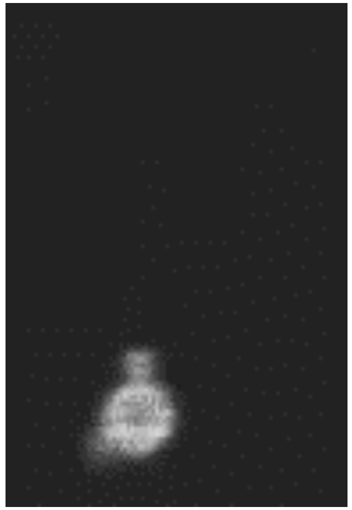


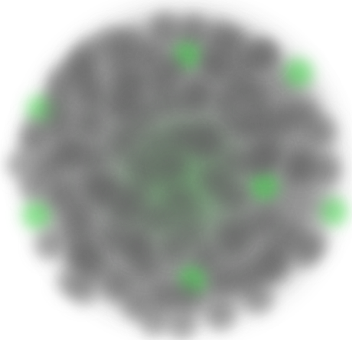


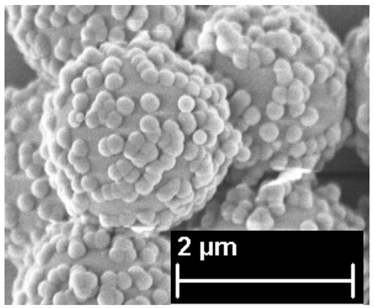
Particle suspensions : tracking rotation

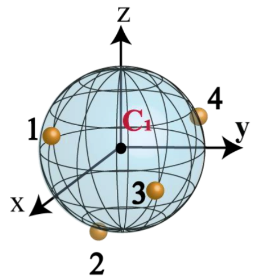


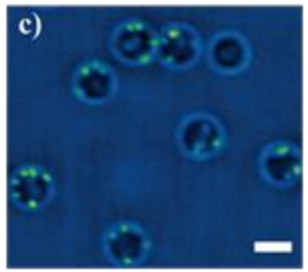
Few fluorescent asperities

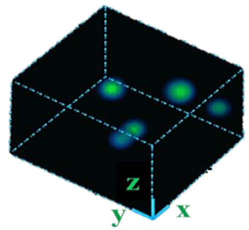






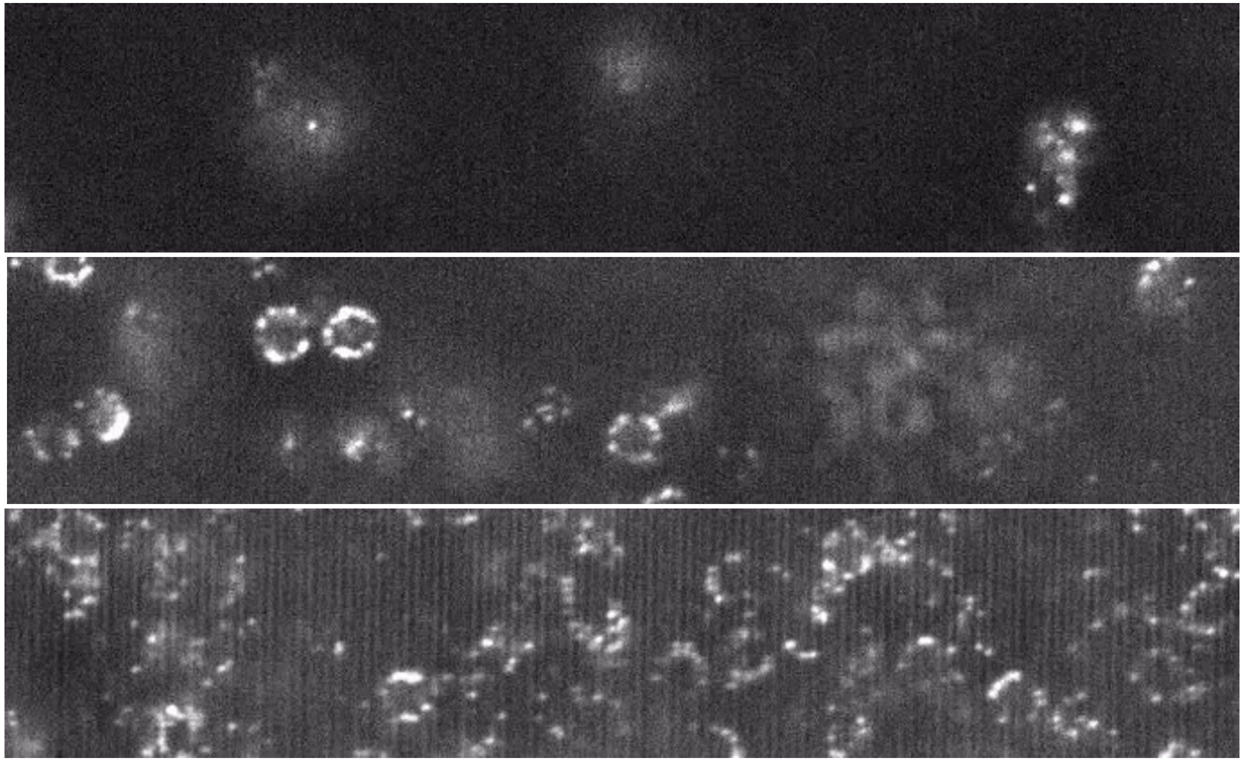




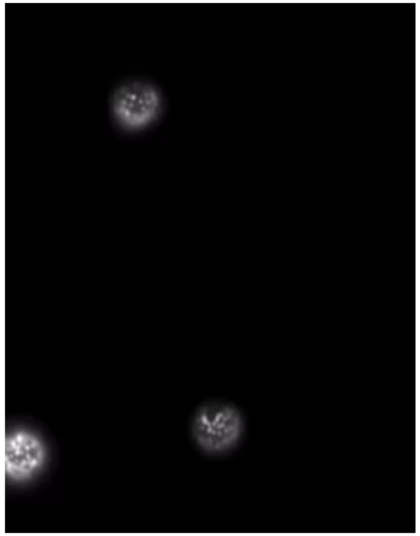


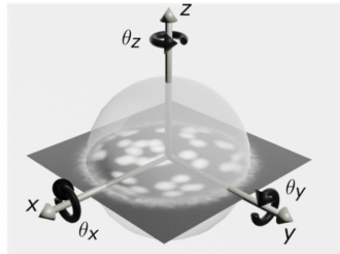
Ilhan *et al.*, *J. Colloid Interface Sci.* (2020)

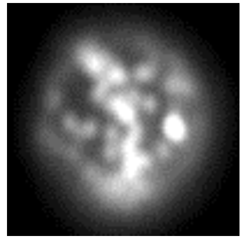
Particle suspensions : tracking rotation

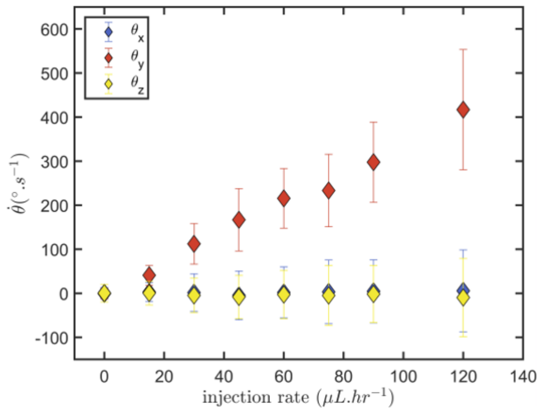


Fixed volume fraction ; increasing number of fluorescent particles







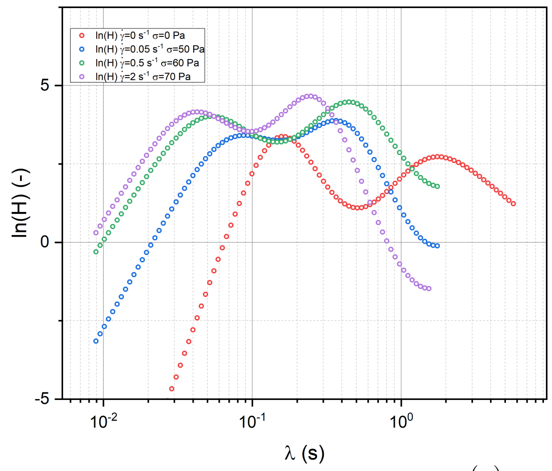


Niggel et al, *in preparation*

- [x] Objectives
- [x] Bottom up SIDS
- [x] Bottom down SIDS
- [ ] Outlook and plan for 22-23

SIDS

- Soft system : Carbopol
- Rougher system
- Latex - filler system
- Proteins as aggregated systems



$$\boxed{\tau = \tau_\mathrm{y} + K\dot{\gamma}^n, \quad \tau \geq \tau_\mathrm{y}}$$

$$\lambda(\tau) = \frac{\eta(\tau)}{G} = \frac{\eta_0 a(\tau)}{G} = \frac{\eta_0}{G} a_\tau(\tau) = \lambda_0 a_\tau(\tau)$$

$$\boldsymbol{\sigma}^d = 2\eta(\tau_\mathrm{eq})\boldsymbol{D}_p$$

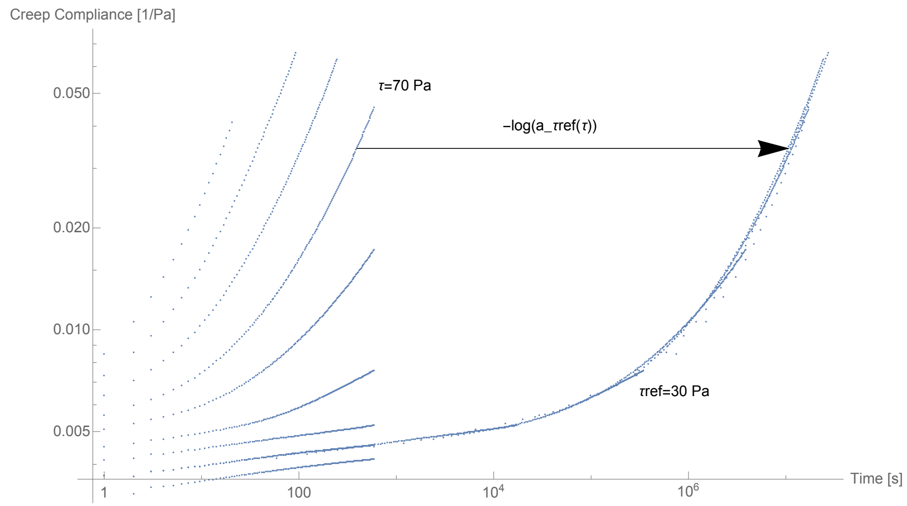
$$\eta(\tau_\mathrm{eq}) = \eta_0 \left(1 + \left(\frac{\tau_\mathrm{eq}}{\tau_0}\right)^2\right)^{\frac{n-1}{2n}} = \eta_0 a(\tau_\mathrm{eq})$$

$$\tau = G\gamma_\mathrm{e}$$

$$\dot{\gamma}_\mathrm{e} = \dot{\gamma} - \dot{\gamma}_\mathrm{p}$$

$$\dot{\gamma}_\mathrm{p} = \frac{\tau}{\eta(\tau_\mathrm{eq})}$$

$$\eta(\tau) = \eta_0 a_\tau(\tau)$$



- ☑ Objectives
- ☑ Bottom up SIDS
- ☑ Bottom down SIDS
- ☐ Outlook and plan for 22-23

Conclusions

Toolbox for colloidal rheology understanding and design:

- ☑ model systems which enable us to interrogate mechanisms
- ☑ rheological techniques which deconvolute the contributions to the stress
- ☑ structural techniques which probe pertinent time and length scales

Challenges:

- ☐ non-model systems and yet interrogate mechanisms
- ☐ complex flows
- ☐ HF during flow/processing