Simplified industrial dispersions

Lucio Isa and Jan Vermant
Department of Materials, ETH Zürich, CH

ETH zürich

SOFTMAT

IFPRI
International Fine Particle Research Institute

Dr. Florence Müller
(Postdoc Caltech)

Pierre Lehéricy
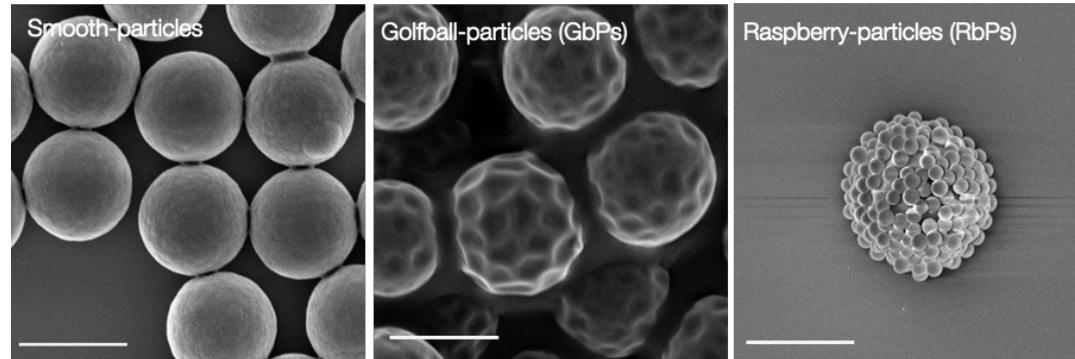(Defense Sept 2025)

Savannah McGowan
postdoc (since 04.2025)

Lukas Woolley

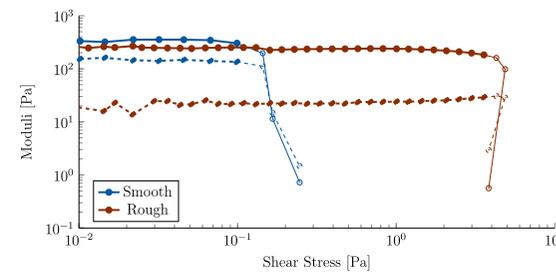Gabriele Pagani
(Defense Jan 2026)

Complexity in model systems

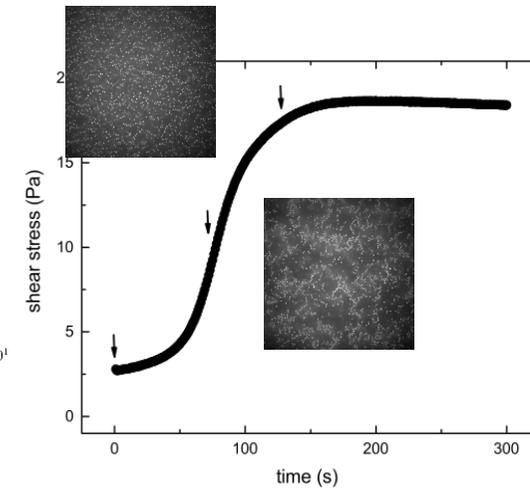Smooth-particles   Golfball-particles (GbPs)   Raspberry-particles (RbPs)

+ ability to systematically vary features and interactions
+   thermoreversible gels in particular

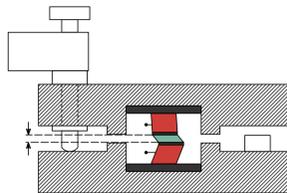## Simplified industrial dispersions
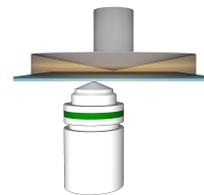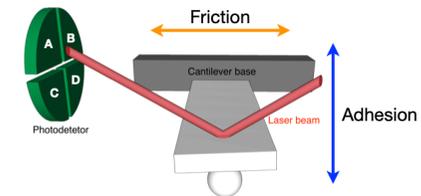

yielding

thixotropy

Analytical, structural and rheological methods tailored to interrogate structure

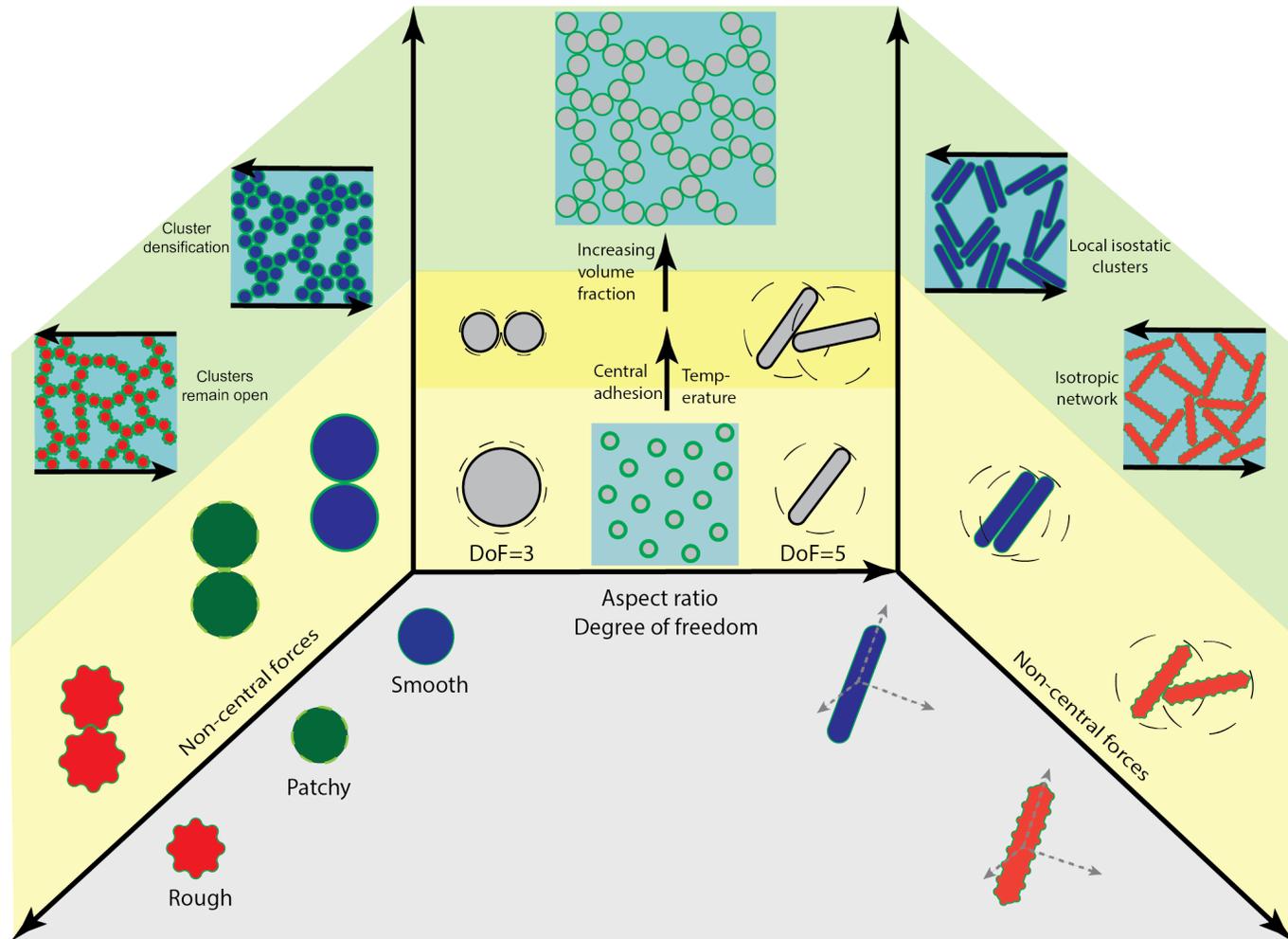stress deconvolution

4D-imaging

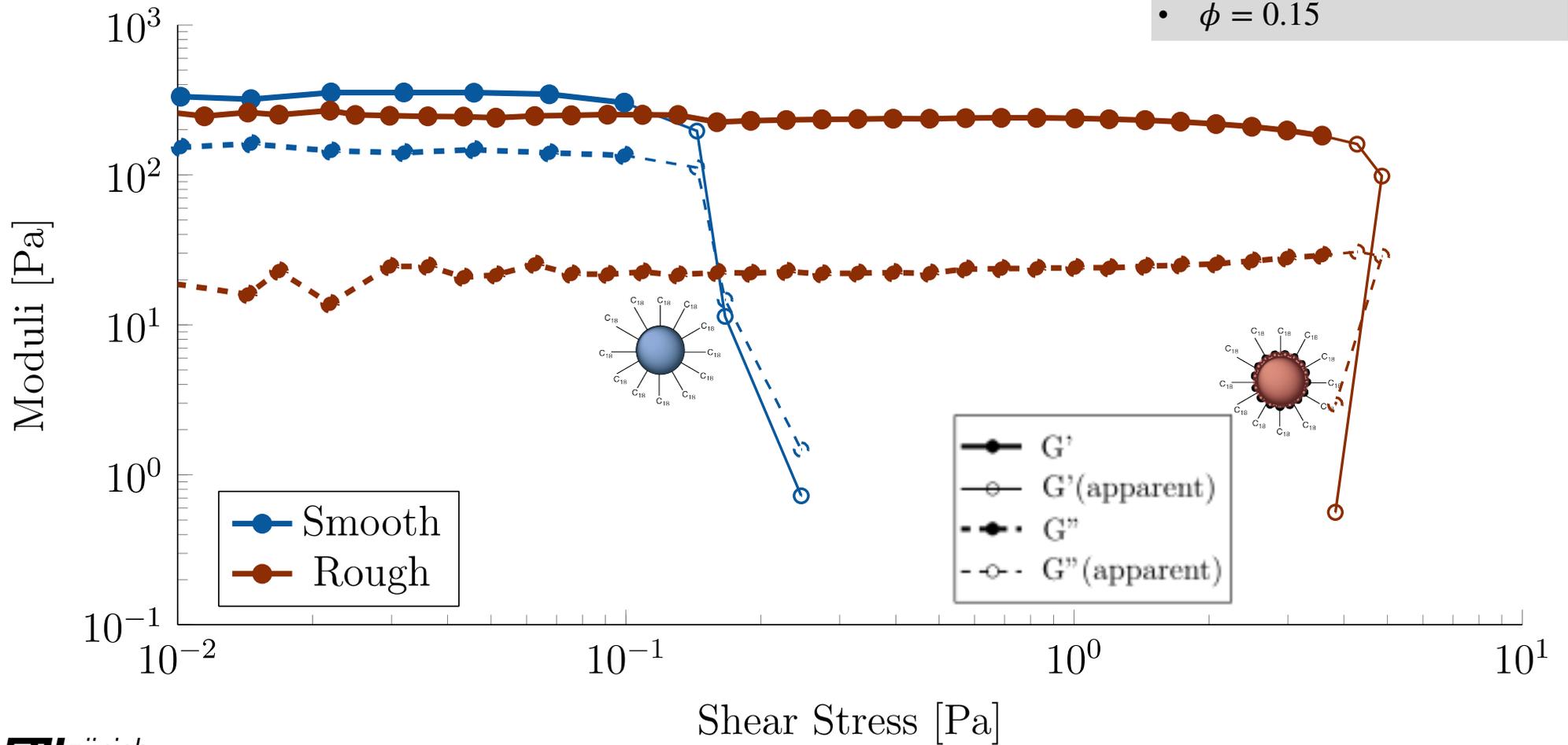local scale forces (OT/CP-AFM)

outline

- Increased complexity of the building block

- Elastoplastic behaviour
  - Modelling of elastoplasticity
  - Imaging of plastic events

- CP-AFM and Optical Tweezers

ETH *zürich*

parameter space

Cluster densification

Local isostatic clusters

Clusters remain open

Isotropic network

Increasing volume fraction

Central adhesion

Temperature

DoF=3

DoF=5

Aspect ratio
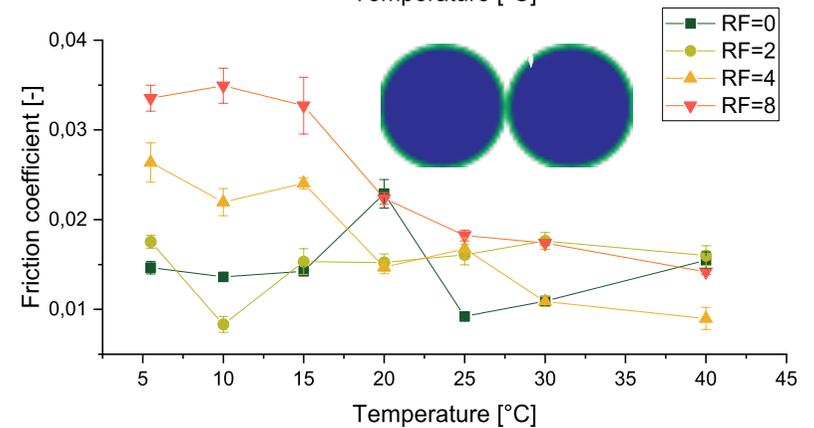Degree of freedom

Non-central forces

Non-central forces
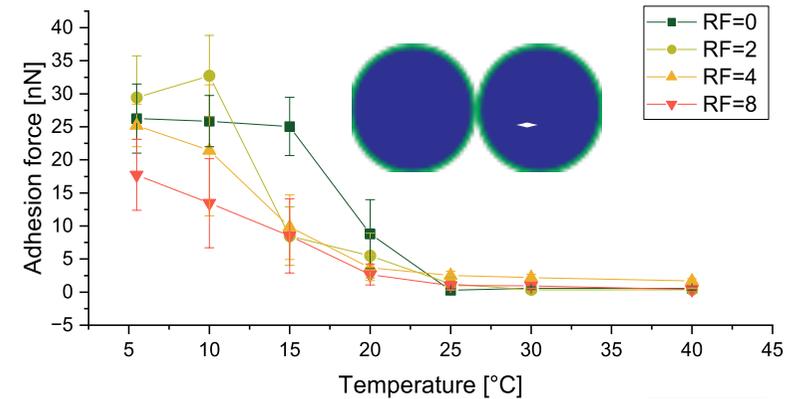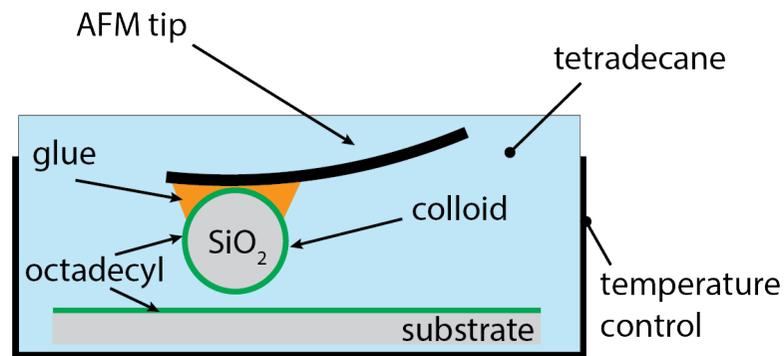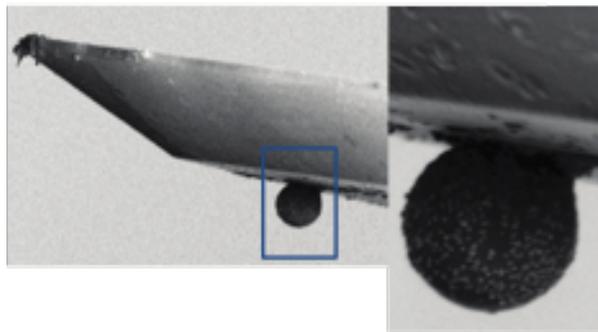
Smooth

Patchy

Rough

ETH zürich

Remember :
Rough particle gels delay yielding

- Thermoreversible gel
- Outer diameter: 300 nm
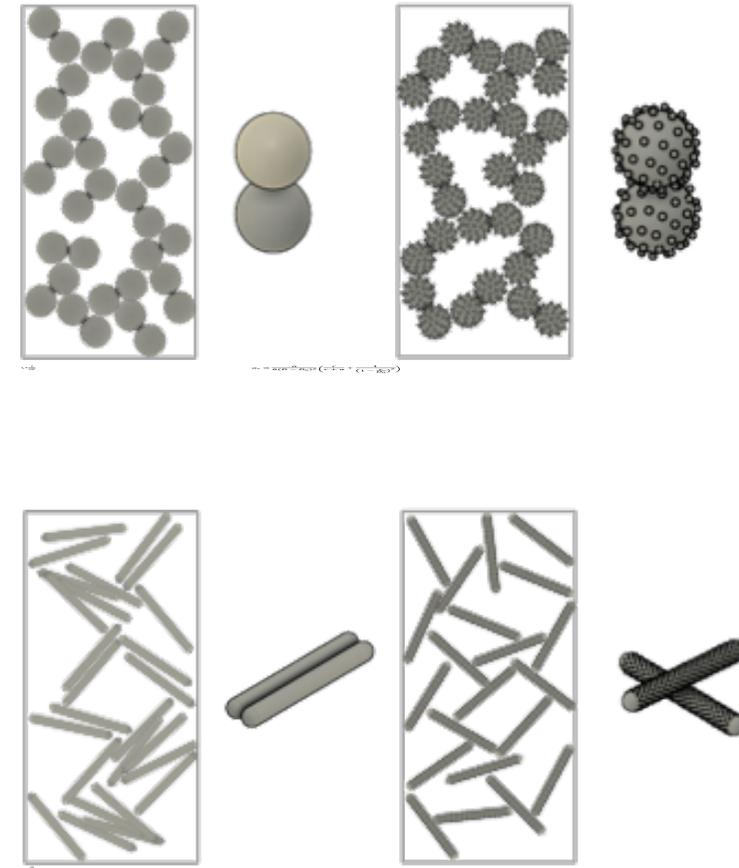- Octadecyl brush
- In tetradecane
- $\phi = 0.15$

Moduli [Pa]

Shear Stress [Pa]

Smooth
Rough

G'
G'(apparent)
G"
G"(apparent)

ETH zürich   Soft Materials Laboratory

Article 1 : Single particle / colloidal probe AFM / adhesion and sliding friction

article 2 : Synergistic effects of Roughness and Shape?
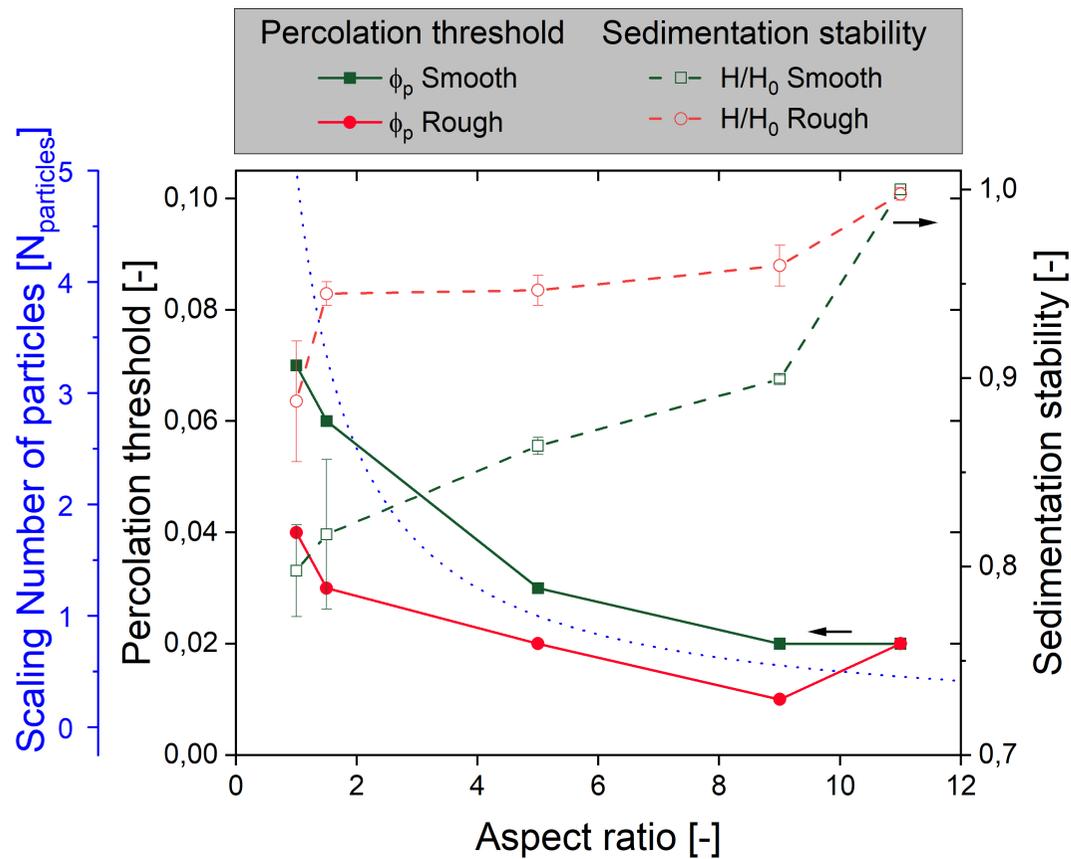
Muller et al., J Colloid Interface Sci, 2025 https://www.sciencedirect.com/science/article/pii/S0021979725006587

Tuning Colloidal Gel Properties: The Influence of Central and Noncentral Forces
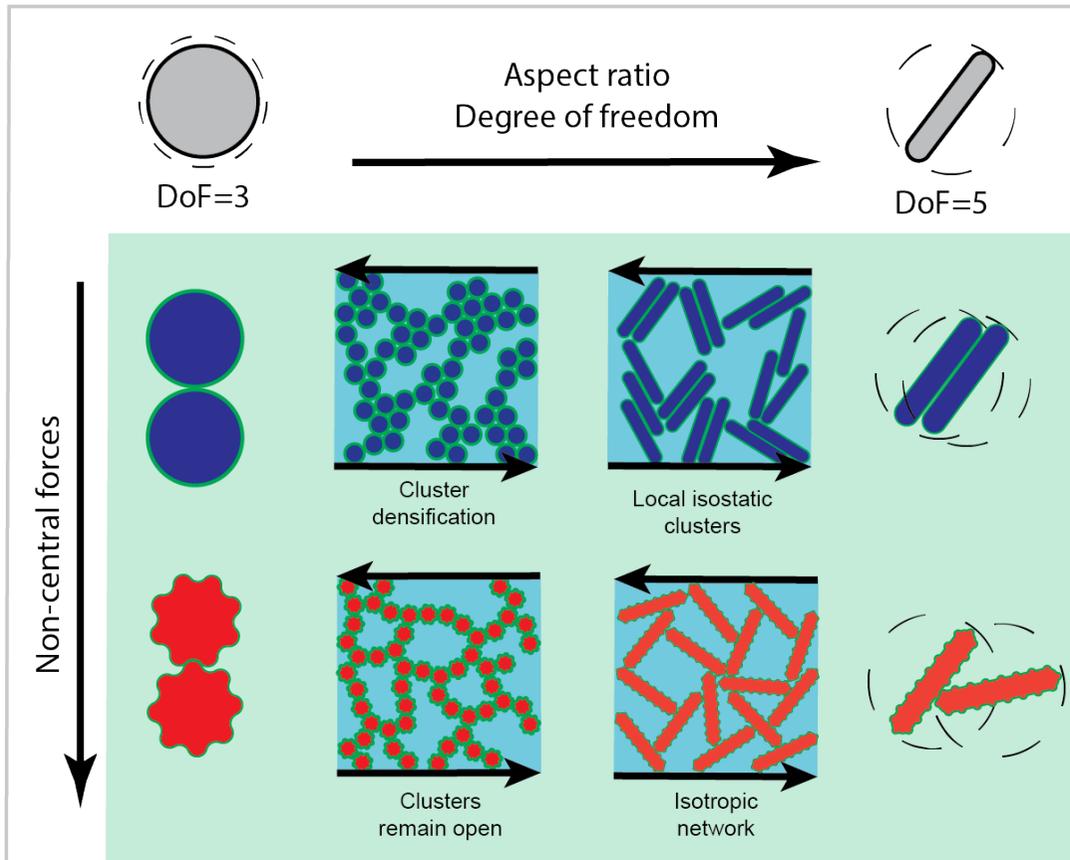
Particle aspect ratio :

- **Smooth particle systems**
    - Elasticity is proportional to aspect ratio
    - Increase bending rigidity in the local isostatic clusters
- **Rough particle systems**
    - Homogeneous isotropic network structure
    - Hindering of alignment
    - Gel properties are less dependent on the aspect ratio

- **Decouple elastic modulus** and **yield stress** through surface roughness
- Increase the **node stiffness** in colloidal gels through aspect ratio and surface roughness

Article 3 : Modelling of there adhesive interaction (with M. Bevan, JHU)
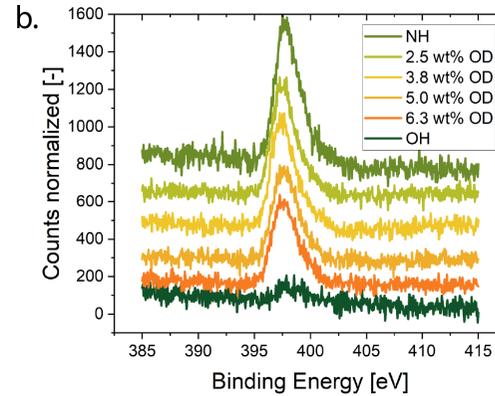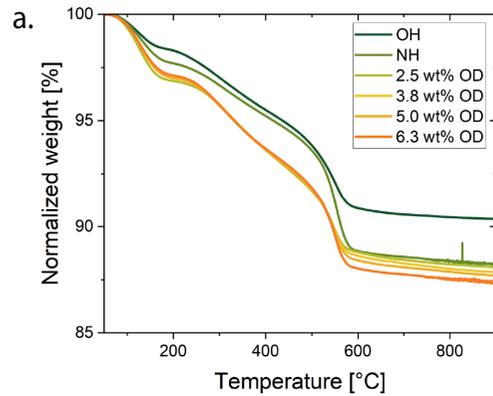
a. TGA measurement
b. XPS spectrum
c. Rheology
d. Grafting density
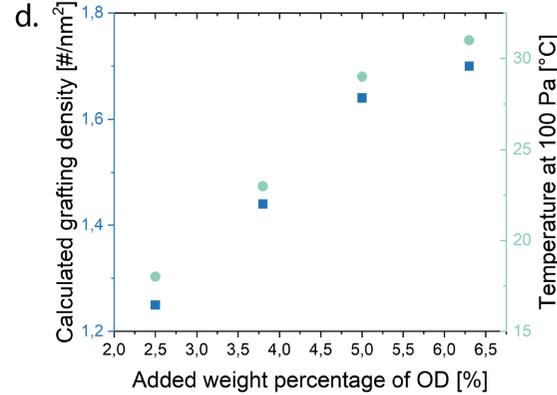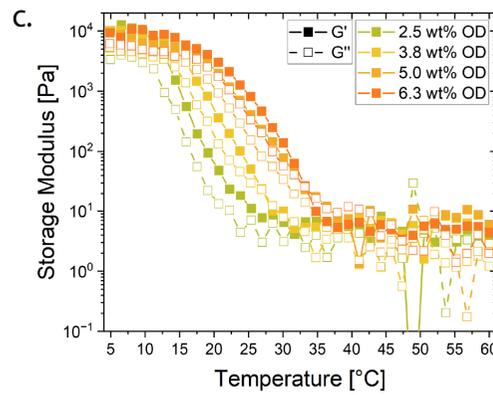
Muller et al. manuscript to be submitted.

ETH zürich

Article 3 : Modelling of there adhesive interaction (with M. Bevan, JHU)

VdW interaction of dense brushes insufficient to explain AFM results
Force needed to account for chain-chain interactions between octadecyl ligands
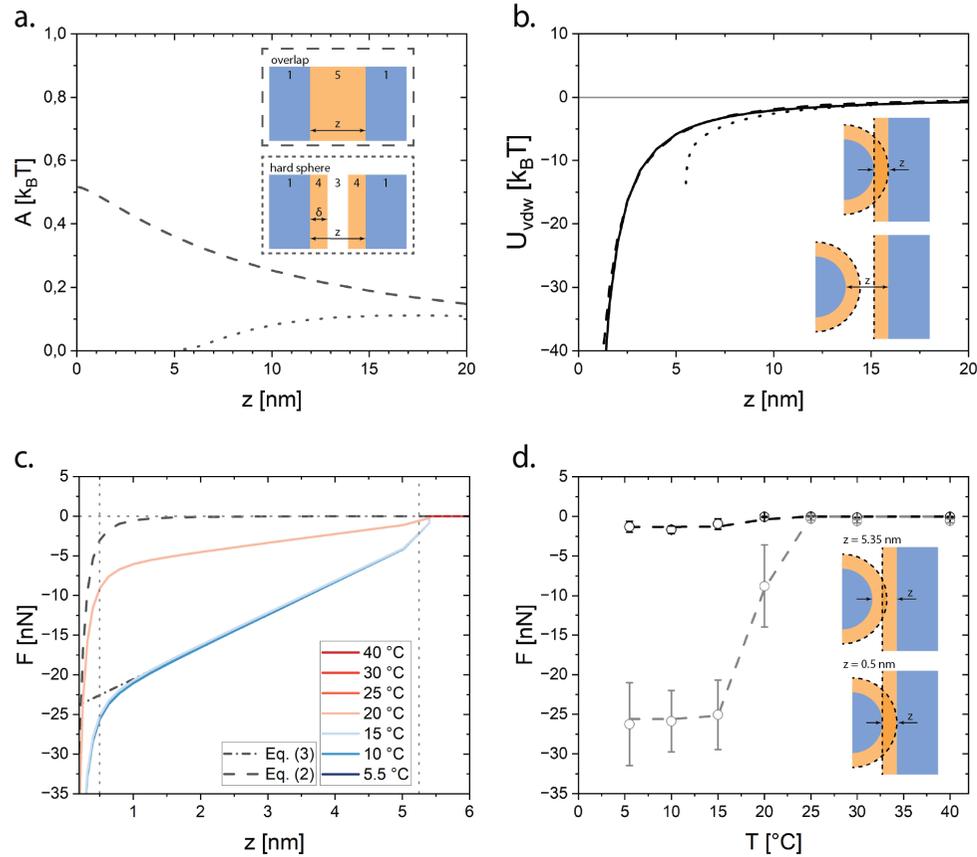
a. Hamaker functions
b. VDw forces between sphere and wall
c. Force curves
d. model versus calculations (approach/sep)

Muller et al. manuscript to be submitted.

ETH zürich

ART 4 : Universal Time-to-Failure Scaling in Colloidal Gels
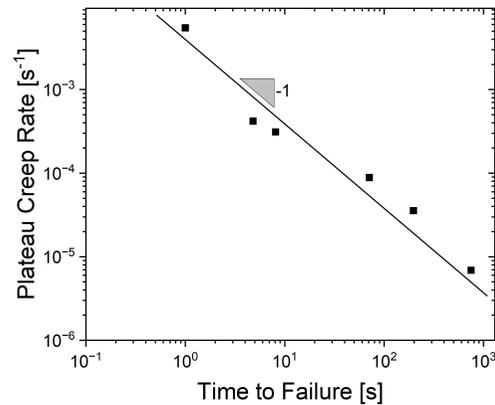
Muller et al. manuscript to be submitted.

ETH zürich

parameter space

Cluster densification

Clusters remain open

Increasing volume fraction

Central adhesion

Temperature

Local isostatic clusters

Isotropic network

DoF=3

DoF=5

Aspect ratio
Degree of freedom

Non-central forces

Non-central forces

Smooth

Patchy

Rough

ETH zürich

outline

ETH *zürich*

Projects and goals

Multimode model •

- Interplay between the activation function and the linear relaxation spectrum

- Use LAOS measurement as test for the model

Tensorial model •

- Validating the tensorial extension of the model

- Predicting complex flow protocols

Gel sedimentation •

- Real case application of the model

- Predicting slowing changing "solid" like movement

A typical yield stress fluid
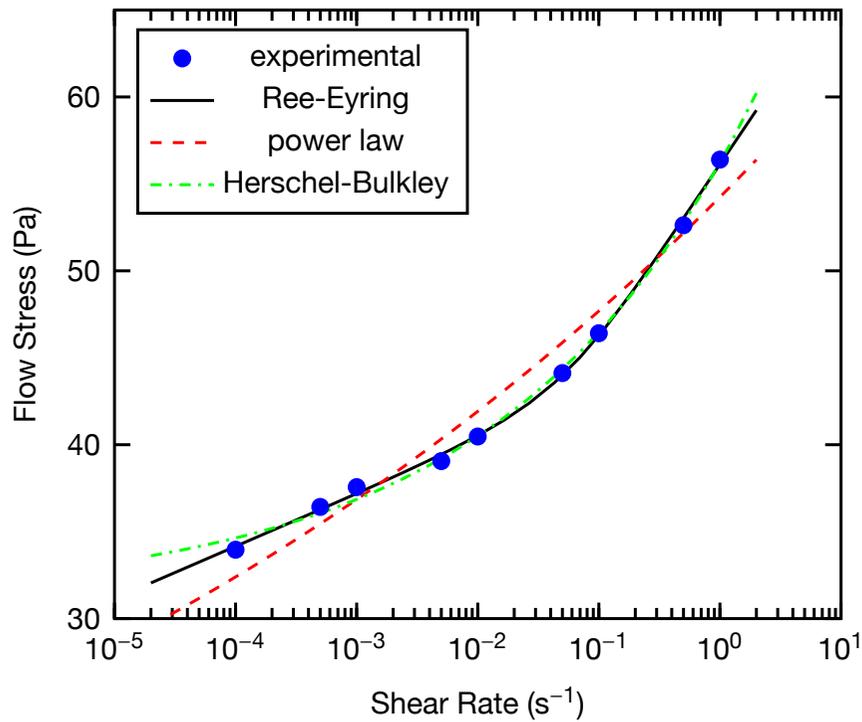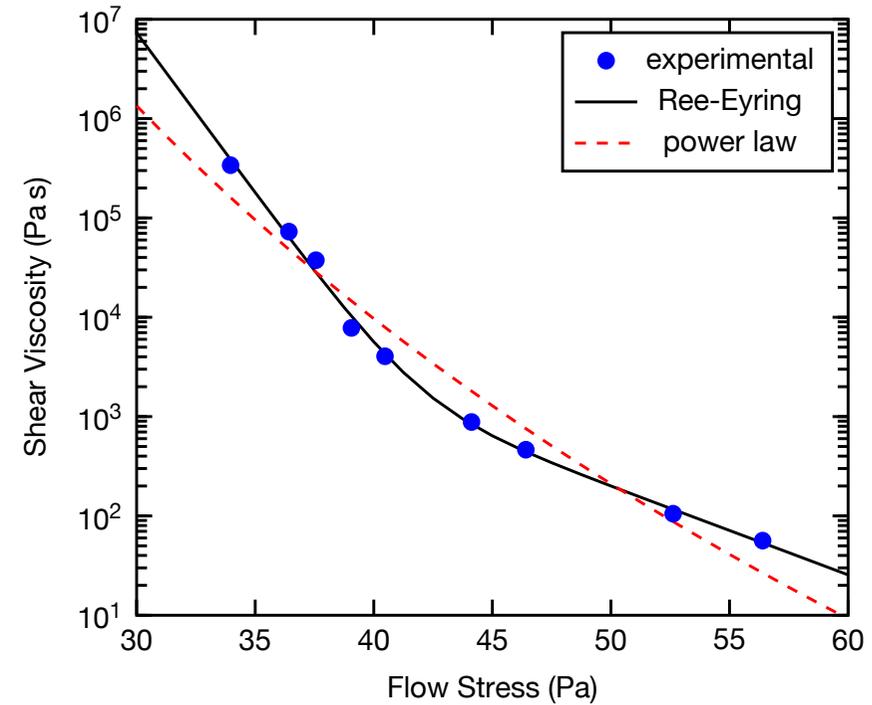
$$0.5\,\text{wt\%}\ \text{Carbopol}^{®}940$$

$$\sigma = \sigma_{\text{y}} + K\dot{\gamma}^{n}, \quad \sigma \geq \sigma_{\text{y}}$$

ETH *zürich*

1D EVP model

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

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

$$\dot{\gamma}_{\mathrm{p}} = \frac{\sigma}{\eta(\sigma_{\mathrm{eq}})}$$

$$\eta(\sigma_{\mathrm{eq}}) = \eta_0 a_\sigma(\sigma_{\mathrm{eq}})$$

$$\sigma_{\mathrm{eq}} = |\sigma|$$

$$\tau(\sigma_{\mathrm{eq}}) = \frac{\eta(\sigma_{\mathrm{eq}})}{G} = \frac{\eta_0 a(\sigma_{\mathrm{eq}})}{G} = \frac{\eta_0}{G} a_\sigma(\sigma_{\mathrm{eq}}) = \tau_0 a_\sigma(\sigma_{\mathrm{eq}}),$$

$$G \qquad \eta(\sigma)$$
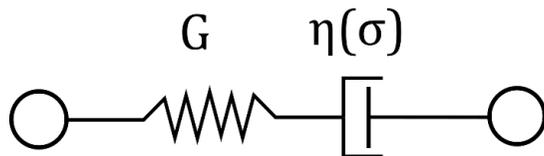
Pagani et al. J. Rheol, 2024
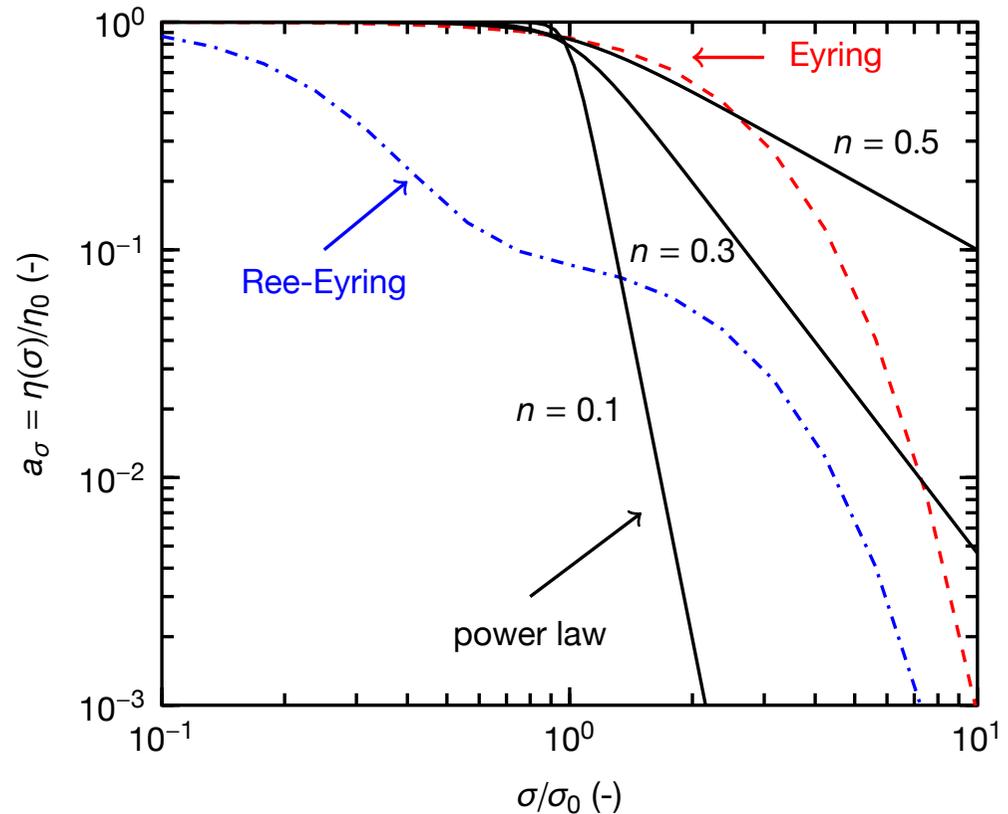
$$\eta_{\mathrm{RE}}(\sigma_{\mathrm{eq}}) = \eta_0^{\mathrm{RE}} \left(\left(\frac{\eta_{01}}{\eta_0^{\mathrm{RE}}}\right) \frac{\left(\frac{\sigma_{\mathrm{eq}}}{\sigma_{01}}\right)}{\sinh\left(\frac{\sigma_{\mathrm{eq}}}{\sigma_{01}}\right)} + \left(\frac{\eta_{02}}{\eta_0^{\mathrm{RE}}}\right) \frac{\left(\frac{\sigma_{\mathrm{eq}}}{\sigma_0}\right)}{\sinh\left(\frac{\sigma_{\mathrm{eq}}}{\sigma_0}\right)} \right) = \eta_0^{\mathrm{RE}} a_\sigma^{\mathrm{RE}}(\sigma_{\mathrm{eq}})$$

Eyring, H. (1936). Viscosity, plasticity, and diffusion as examples of absolute reaction rates. *The Journal of chemical physics*, 4(4), 283-291.

Bonnecaze, R. T., Khabaz, F., Mohan, L., & Cloitre, M. (2020). Excess entropy scaling for soft particle glasses. *Journal of Rheology*, 64(2), 423-431.

finding the shift function
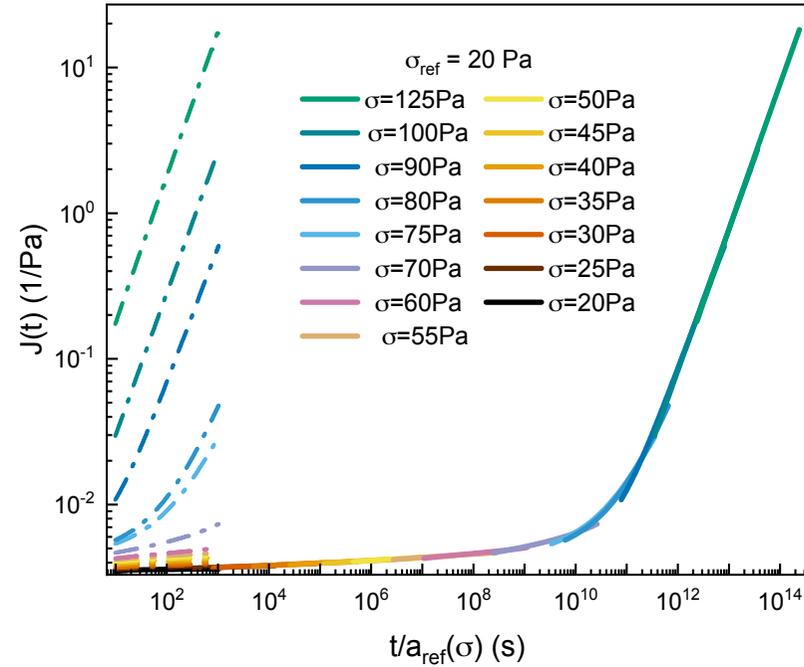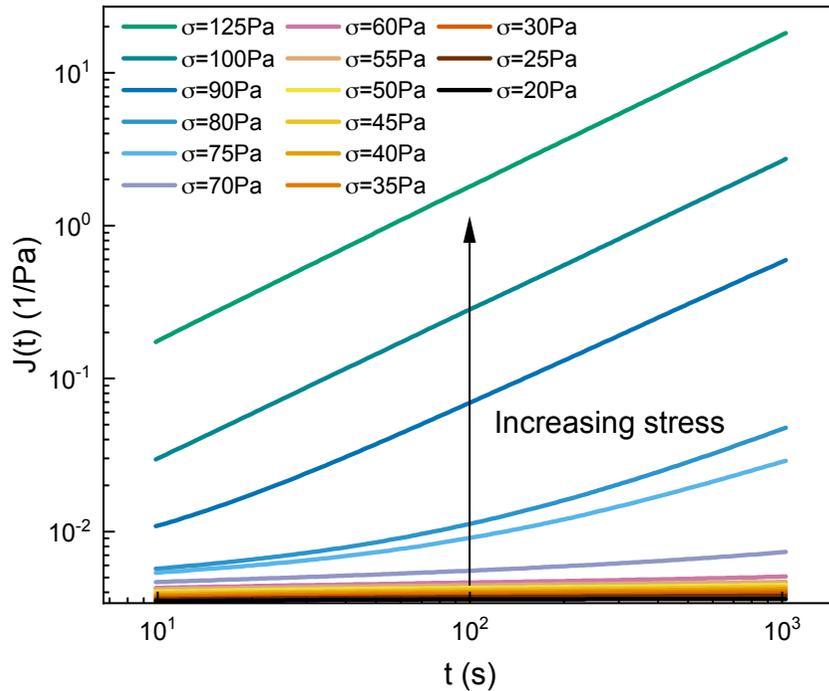
Pagani, G., Hofmann, M., Govaert, L. E., Tervoort, T. A., & Vermant, J. (2024). No yield stress required: Stress-activated flow in simple yield-stress fluids. *Journal of Rheology, 68*(2), 155-170.

ETH *zürich*

18

Constitutive model

3D model

$$\sigma^d = G B_e^d$$

$$D_t(B_e) = (L - L_p) \bullet B_e + B_e \bullet (L - L_p)^T$$

$$\sigma_{eq} = f(\sigma)$$

$$L_p = \frac{\sigma^d}{2\eta(\sigma_{eq})}$$

$$\eta(\sigma_{eq}) = \eta_0 a_\sigma(\sigma_{eq})$$

L_p: plastic velocity-gradient tensor

B_e: isochoric left-Cauchy-Green strain tensor

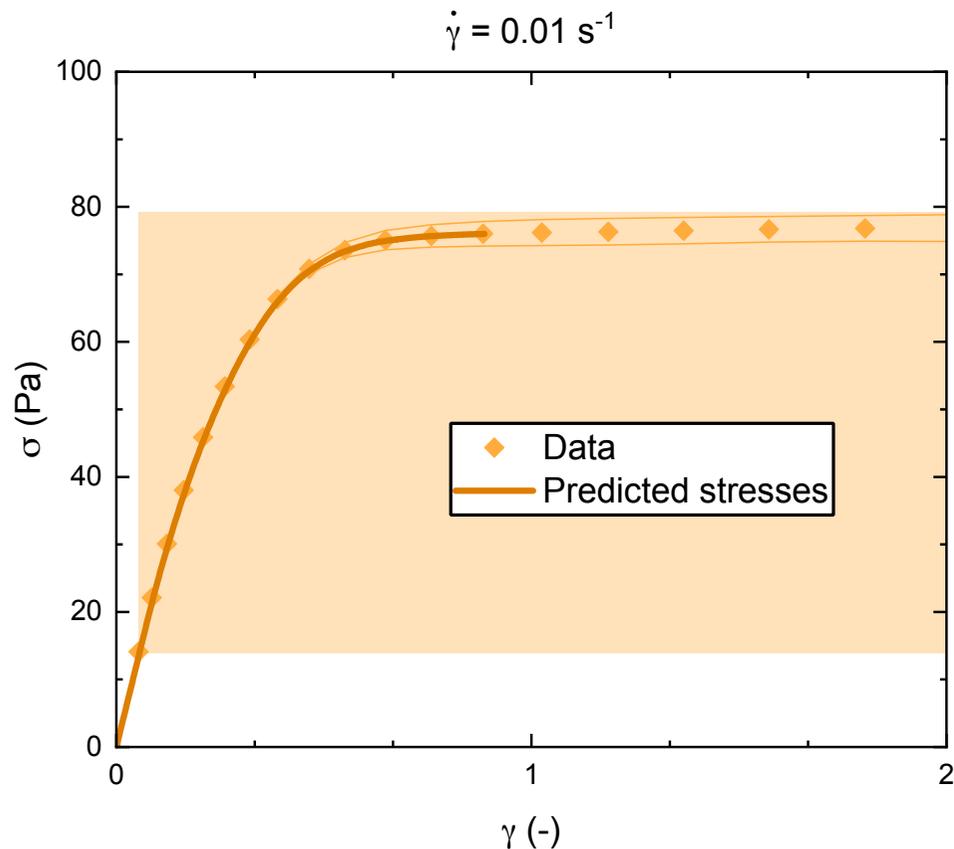A^d: deviatoric part of tensor A

Tervoort, J Rheol, 1996

Objective and **thermodynamically** admissible tensorial model

Multiple levers to adapt the model to the material studied:

1. **Equivalent stress definition**

2. **Activation functions**

3. **Linear relaxation spectrum**

ETHzürich

Parametrization relaxation spectrum

$\dot{\gamma} = 0.01 \text{ s}^{-1}$

Chart (σ (Pa) vs γ (-)):
- Legend: ◆ Data — Predicted stresses
- Y-axis: σ (Pa), 0 to 100
- X-axis: γ (-), 0 to 2

Using the **integral formulation** of the model it is possible to extract of the linear relaxation modulus from a **transient start-up**
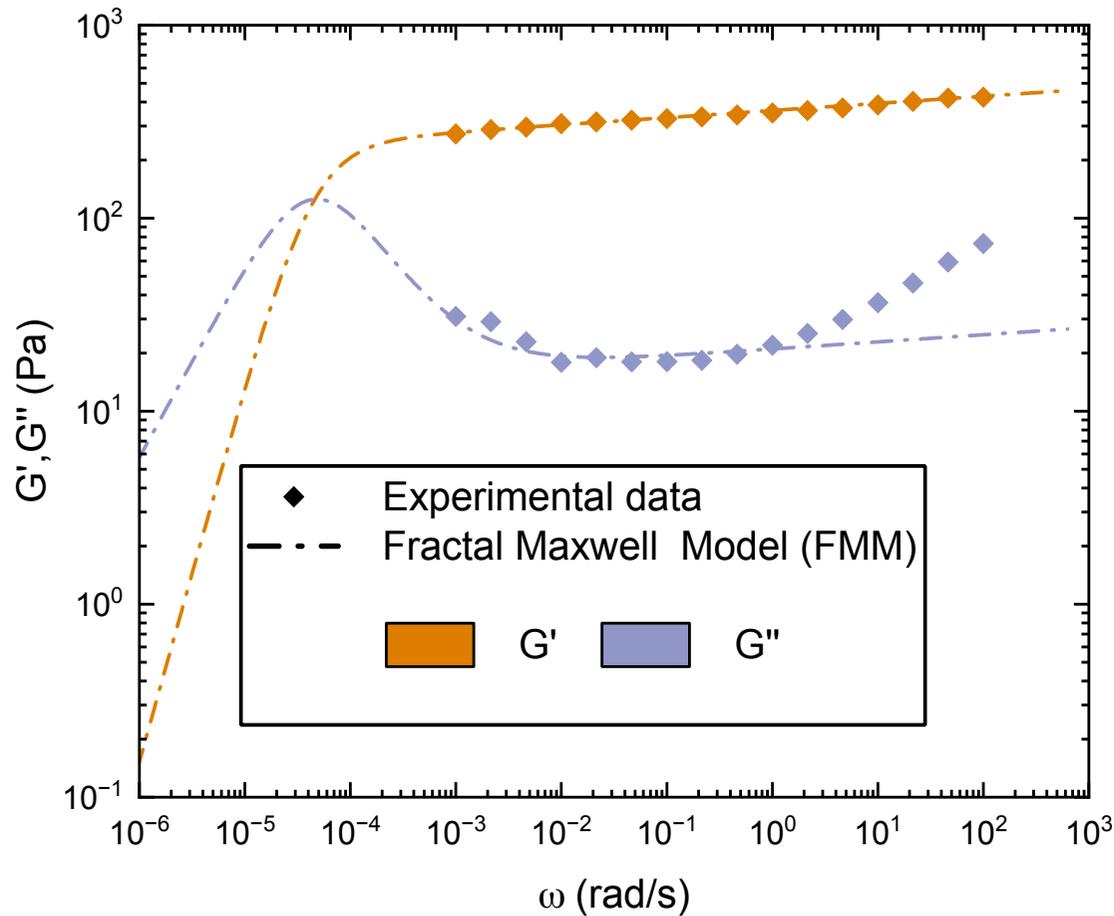
Integral shear model

$$\sigma(t) = \int_{-\infty}^{t} G(\psi - \psi')\dot{\gamma}(t')dt'$$

$$\psi = \int_{-\infty}^{t} \frac{dt''}{a_\sigma(\sigma(t''))} \qquad \psi' = \int_{-\infty}^{t'} \frac{dt''}{a_\sigma(\sigma(t''))}$$

Van Breemen, J Mechs Phys Solids, 2011
Schapery, Polymer Engineering & Science, 1969

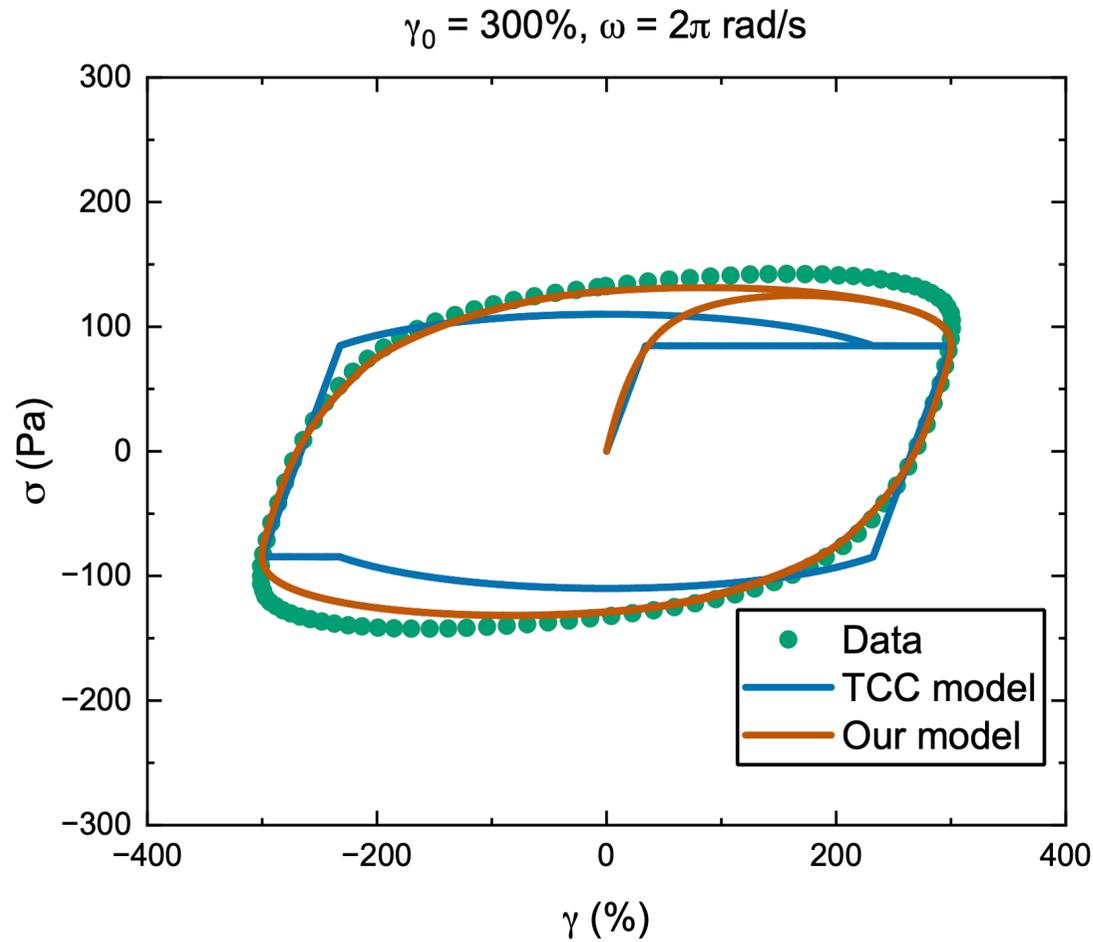# Parametrization relaxation spectrum

Linear relaxation modulus extracted by **transient** response during **Start-Up** experiments

Fractal maxwell liquid (FMM) model explain the behaviour of the material at low frequency

Loss moduli poorly predicted at high frequency indicate an **additional dissipation**
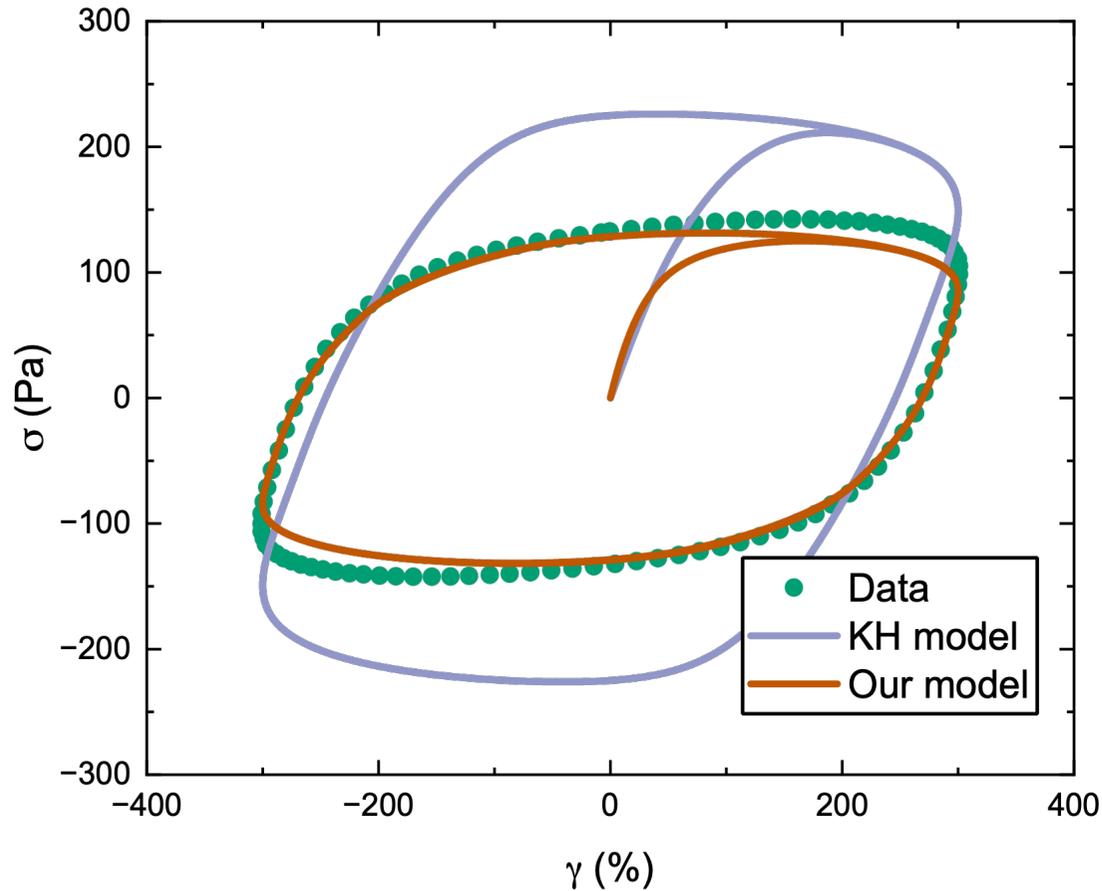
Comparison with different models (TCC)

$\gamma_0 = 300\%, \omega = 2\pi$ rad/s

Three component (TCC) model *Caggioni, J Rheol, 2020*

1.   TCC model   ⟶   Discontinuity

Comparison with different models (TCC, KH)

$\gamma_0 = 300\%$, $\omega = 2\pi$ rad/s

Kinematic Hardening (KH) model *Dimitriou, J Rheol, 2013*

1.   TCC model $\longrightarrow$ Discontinuity

2.   KH model $\longrightarrow$ Stress overestimation
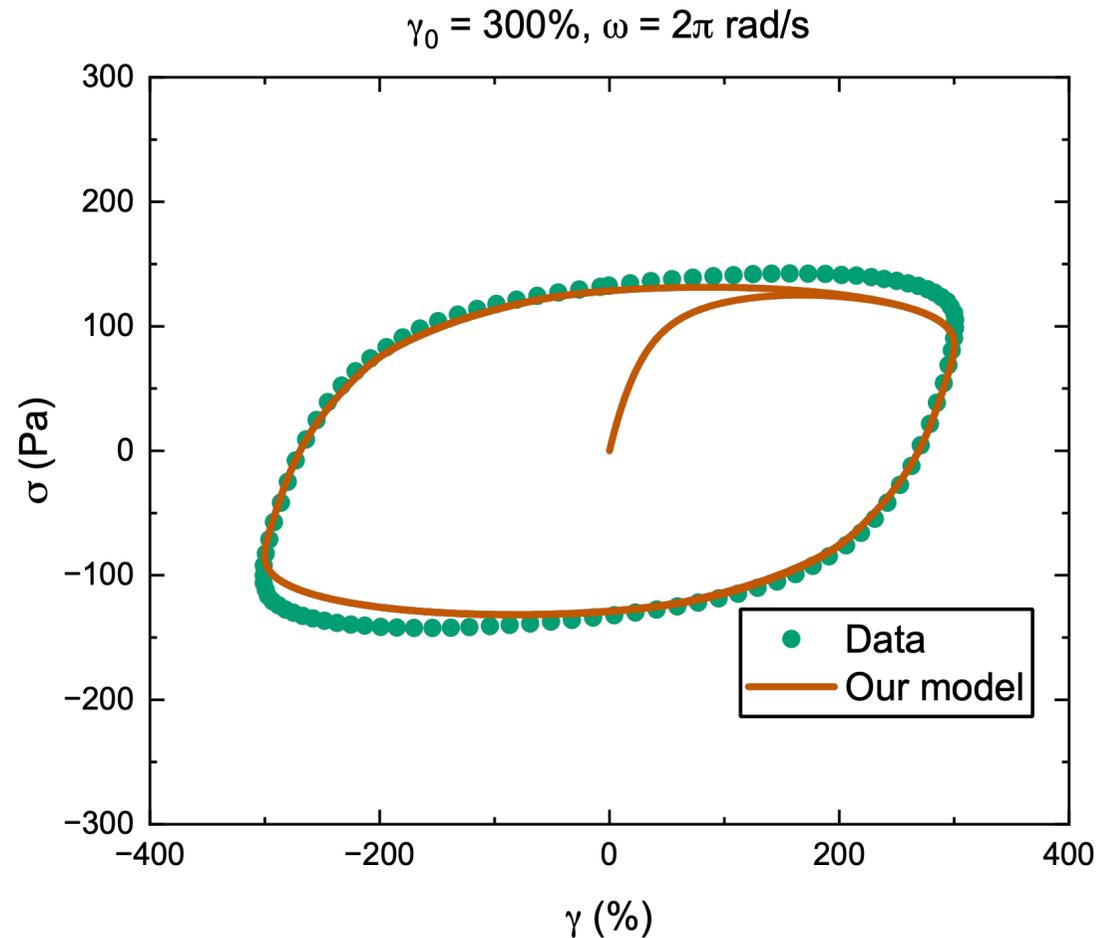
Conclusion – Multimode model

Simple model for EVP

Modified maxwell model with a stress-activated plastic viscosity

Physic informed model

Linear and non-linear regime can both be expressed as a function of physical knowledge

Intuitive fitting

Model fitting is performed on standard and quick experiments

$\gamma_0 = 300\%, \omega = 2\pi$ rad/s

- Data
- Our model

Projects and goals

Multimode model ⬤

- Interplay between the activation function and the linear relaxation spectrum

- Use LAOS measurement as test for the model

Tensorial model ⬤

- Validating the tensorial extension of the model

- Predicting complex flow protocols

Gel sedimentation ⬤

- Real case application of the model

- Predicting slowing changing "solid" like movement

Constitutive model

3D model

$$\boldsymbol{\sigma}^d = G\boldsymbol{B}_e^d$$

$$D_t(\boldsymbol{B}_e) = \left(\boldsymbol{L} - \boldsymbol{L}_p\right) \bullet \boldsymbol{B}_e + \boldsymbol{B}_e \bullet \left(\boldsymbol{L} - \boldsymbol{L}_p\right)^T$$

$$\sigma_{eq} = f(\boldsymbol{\sigma})$$

$$\boldsymbol{L}_p = \frac{\boldsymbol{\sigma}^d}{2\eta(\sigma_{eq})}$$

$$\eta\left(\sigma_{eq}\right) = \eta_0 a_\sigma\left(\sigma_{eq}\right)$$

$\boldsymbol{L}_p$: plastic velocity gradient tensor

$\boldsymbol{B}_e$: isochoric left-Cauchy-Green strain tensor

$\boldsymbol{A}^d$: deviatoric part of tensor $\boldsymbol{A}$

Tervoort, J Rheol, 1996

Objective and **thermodynamically** admissible tensorial model

Multiple levers to adapt the model to the material studied:

1. **Equivalent stress definition**

2. **Activation function** Pagani, J Rheol, 2024

3. **Linear relaxation spectrum**

ETH zürich

Testing modes

Simple shear

$$\sigma_m = \sigma_{12}$$

$$N_1 = \frac{\sigma_{12}{}^2}{G}$$

$F_N \sim N_1$

$M \sim \sigma_{12}$
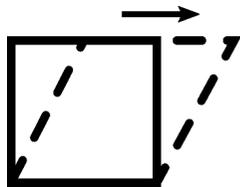
Uniaxial compression
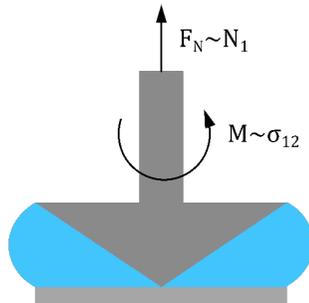
$$\sigma_m = \sigma_z = \sigma_{zz} - \sigma_{rr}$$

Von-Mises stress

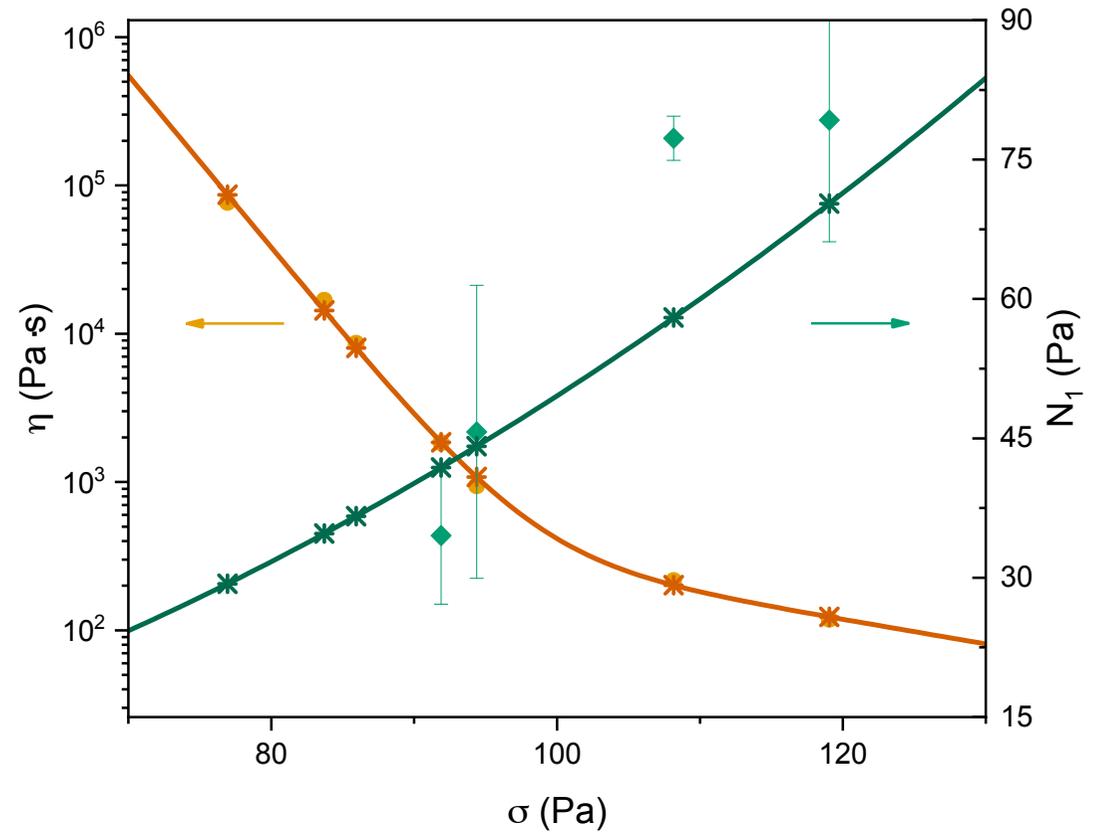$$\sigma_{VM} = \sqrt{3J_2} = \sigma_z = \sqrt{3}\,\sigma_{12}$$
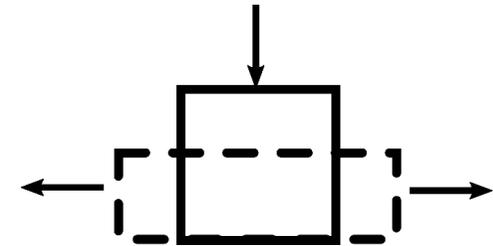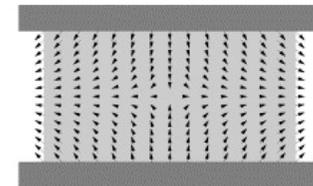
Engmann, J.NN. Fluid. Mech., 2005

Simple shear

Normal force

- Statistics needed due to the noise during normal force measurements
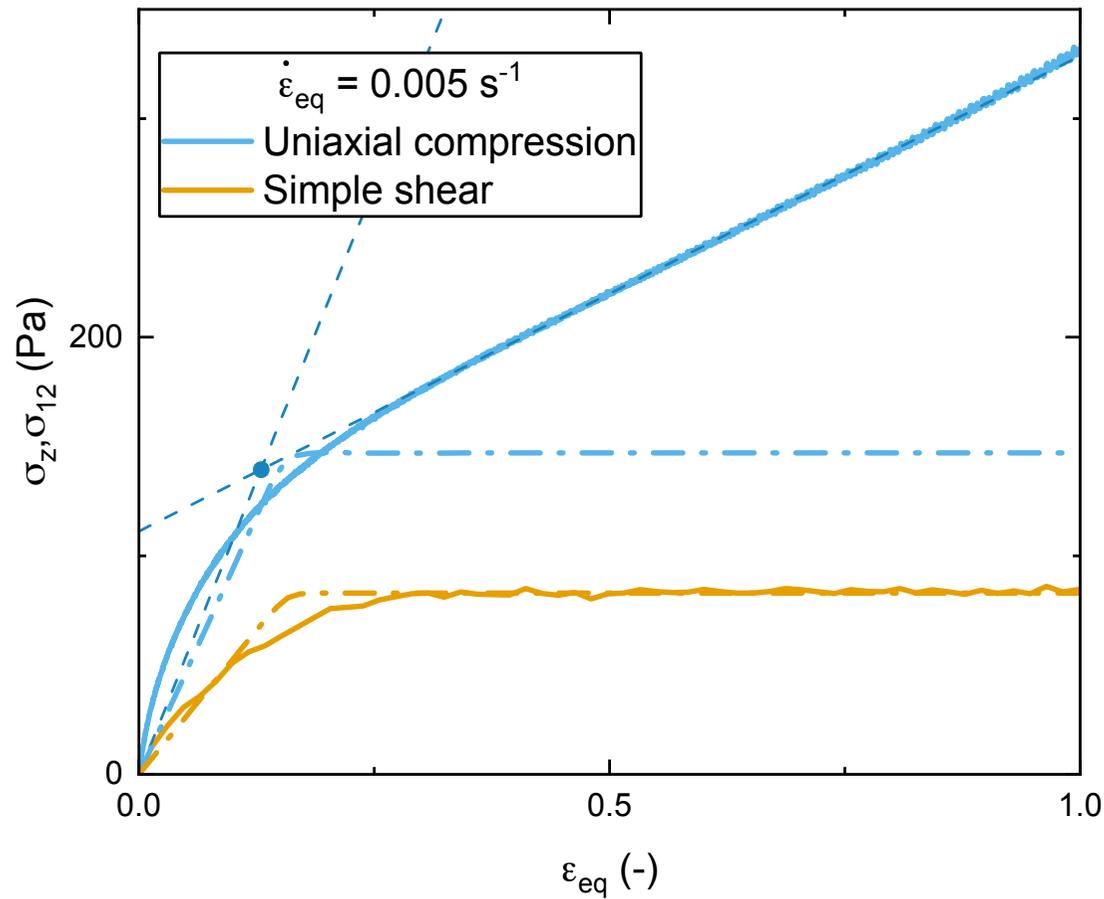
- Trend captured by the model prediction

Slip control

Slip promotion

- Perfect slip is needed to properly have uniaxial compression
- A polymer coating was developed to increase wall-slip
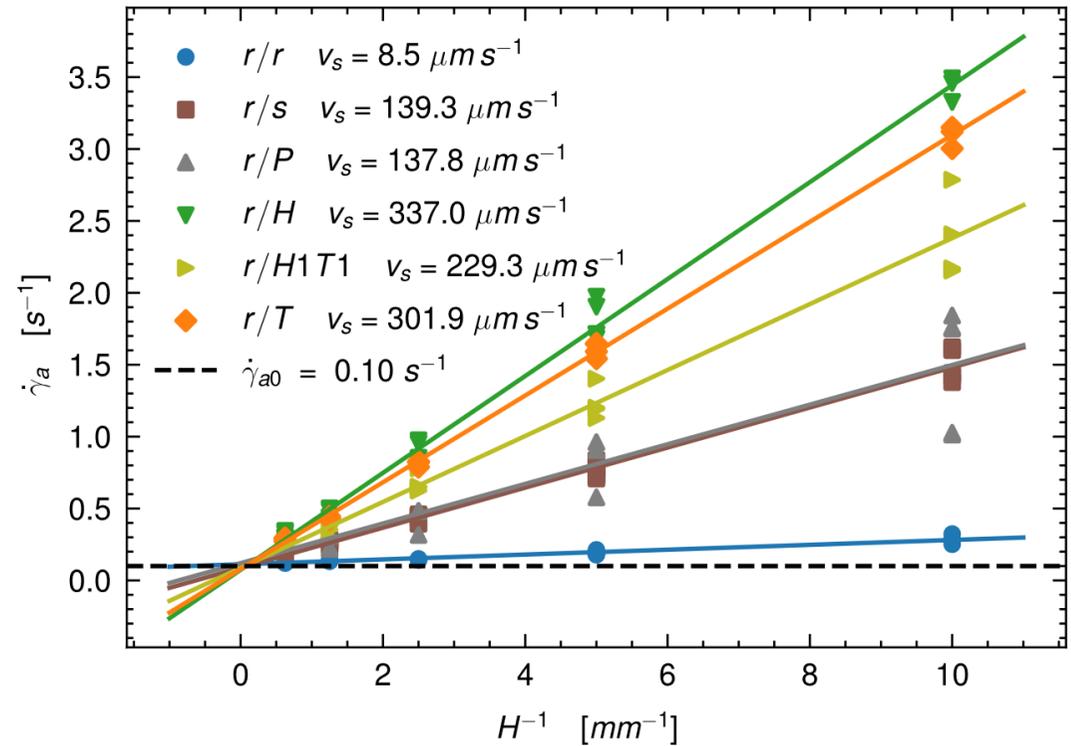
Uniaxial compression

Von-Mises stress

$$\sigma_{VM} = \sigma_z = \sqrt{3}\sigma_{12}$$

83 Pa	139 Pa	147 Pa

✓

Uniaxial compression

- Yielding stress captured by the model
- Carbopol show strain hardening

Conclusion – Multimode model

Slip control

A polymer coating was designed that actively promote slip during mechanical testing

Tensorial model

The testing the model on different deformation protocols show the generalizability to arbitrary flows
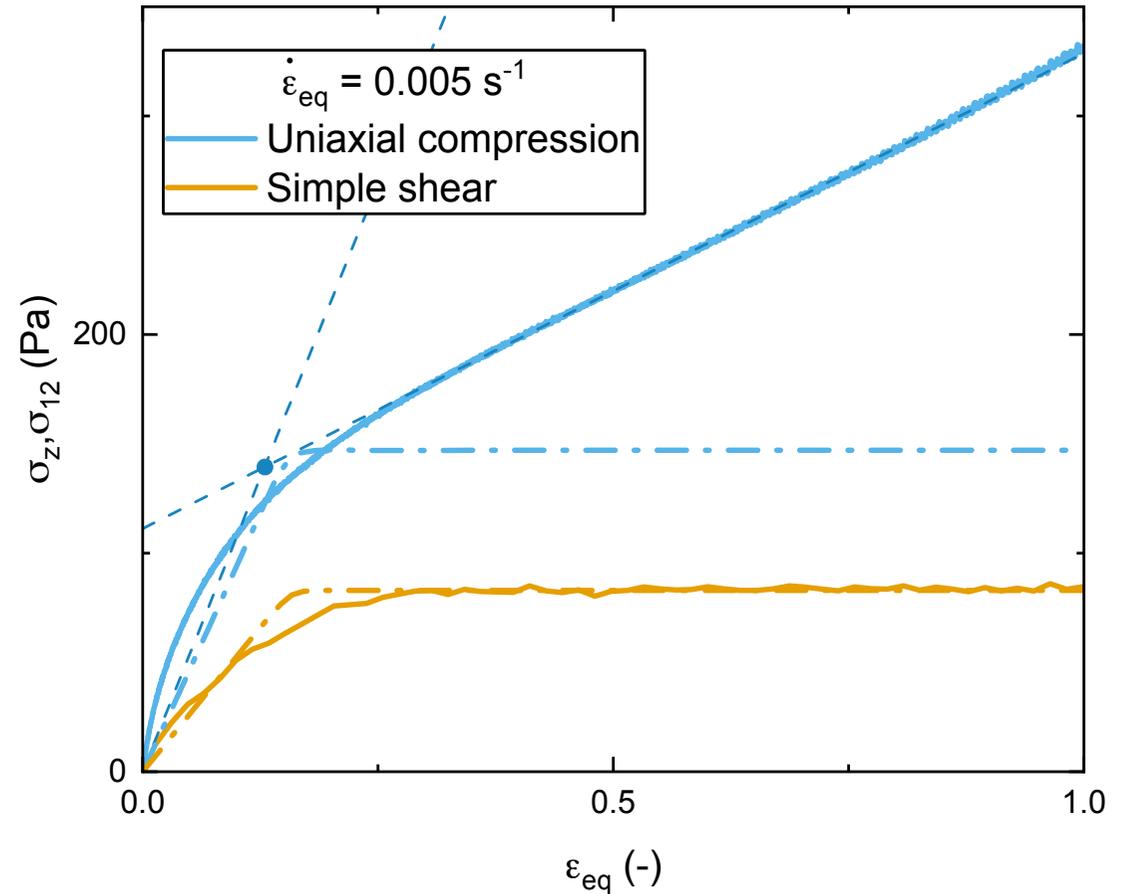
Projects and goals

Multimode model ●

- Interplay between the activation function and the linear relaxation spectrum

- Use LAOS measurement as test for the model

Tensorial model ●

- Validating the tensorial extension of the model

- Predicting complex flow protocols

Gel sedimentation ●

- Real case application of the model

- Predicting slowing changing "solid" like movement

Application

Sedimentation of gels

- Bentonite clays due to relevant industrial interest

- Stress field given by gravitational field

H_o

H

u_z

0
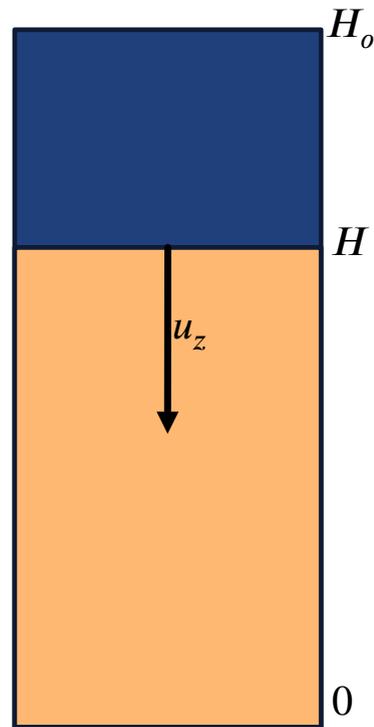
Assumption for simplification

Uniaxial compression

$$B_{zz}, \sigma_{zz}$$

$$\alpha(t, z) = \alpha(t)$$

Mass balance $\longrightarrow$ $\phi = \dfrac{\phi_0}{\alpha}$

Stress controlled deformation

Application

$$H_o$$

$$H$$

$$u_z$$

$$0$$
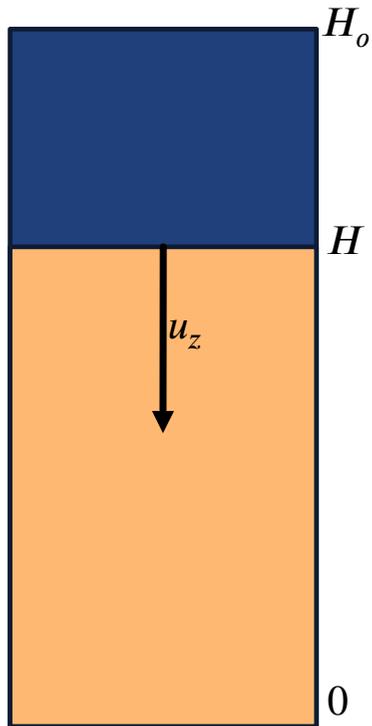
3D model

$$\boldsymbol{\sigma}^d = G\boldsymbol{B}_e^d$$

$$D_t(\boldsymbol{B}_e) = \left(\boldsymbol{L} - \boldsymbol{L}_p\right) \bullet \boldsymbol{B}_e + \boldsymbol{B}_e \bullet \left(\boldsymbol{L} - \boldsymbol{L}_p\right)^T$$

$$\sigma_{eq} = f(\boldsymbol{\sigma})$$

$$\boldsymbol{L}_p = \frac{\boldsymbol{\sigma}^d}{2\eta(\sigma_{eq})}$$

$$\eta\left(\sigma_{eq}\right) = \eta_0 a_\sigma\left(\sigma_{eq}\right)$$

Application
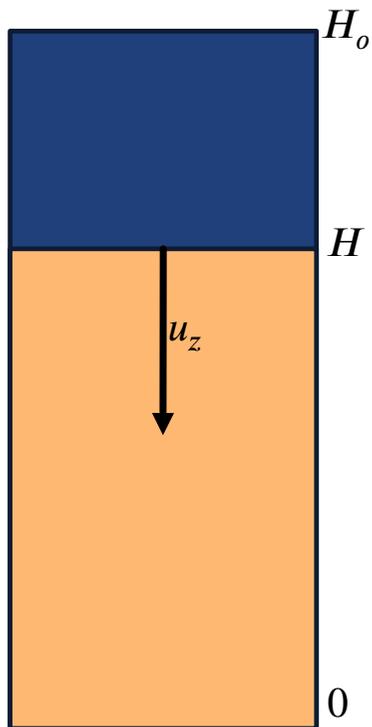
3D model

$$\boldsymbol{\sigma}^d = G\boldsymbol{B}_e^d$$

$$D_t(\boldsymbol{B}_e) = \left(\boldsymbol{L} - \boldsymbol{L}_p\right) \bullet \boldsymbol{B}_e + \boldsymbol{B}_e \bullet \left(\boldsymbol{L} - \boldsymbol{L}_p\right)^T$$

$$\sigma_{eq} = f(\boldsymbol{\sigma})$$

$$\boldsymbol{L}_p = \frac{\boldsymbol{\sigma}^d}{2\eta(\sigma_{eq})}$$

$$\eta\left(\sigma_{eq}\right) = \eta_0 a_\sigma\left(\sigma_{eq}\right)$$

Simplified model

$$\sigma_{zz} = f(z)$$

$$\sigma_{eq} = \frac{1}{2}\sigma_{zz}$$

$$\dot{\varepsilon}_p = \frac{\sigma_{zz}}{2\eta\left(\sigma_{eq}\right)}$$

$$\frac{\dot{\alpha}}{\alpha} = \dot{\varepsilon}_p$$

$$\frac{H(t)}{H_0} = \alpha(t)$$

Application
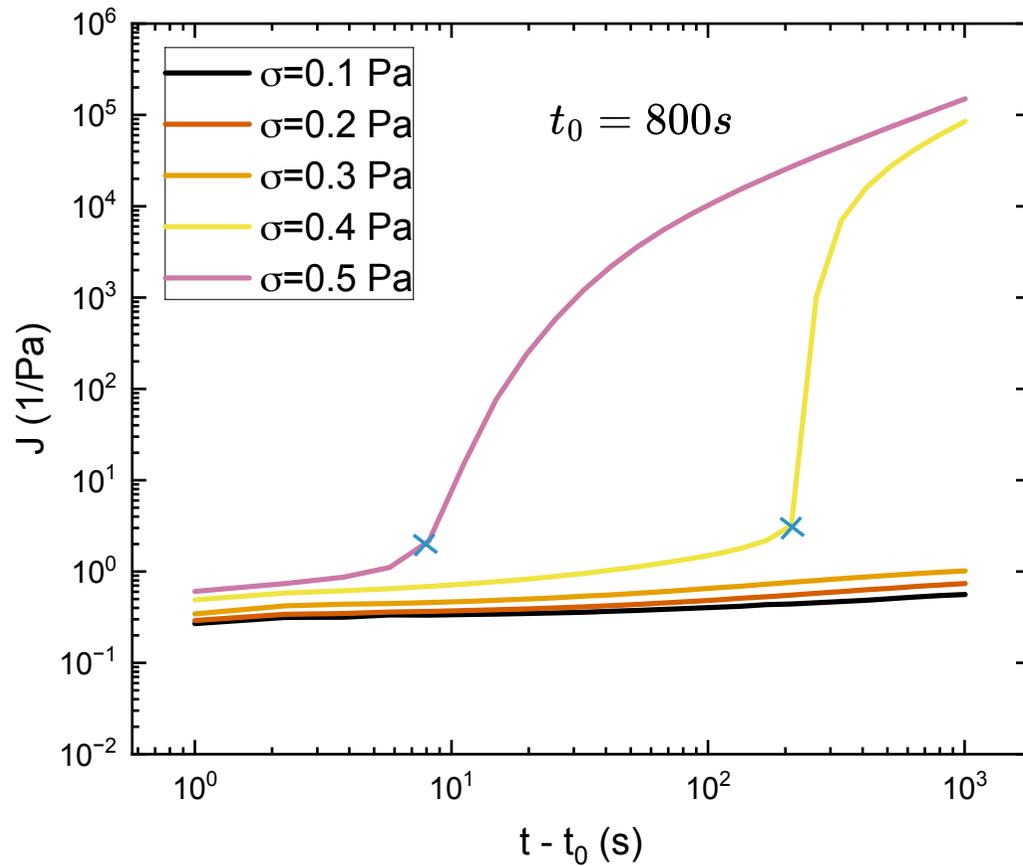
Characterization

- Model characterization from "solid" response

- Combination of creep and amplitude sweep

Application

First attempt

- Analytical solution obtained by assuming a constant effective stress

- Parametrization from flow curve
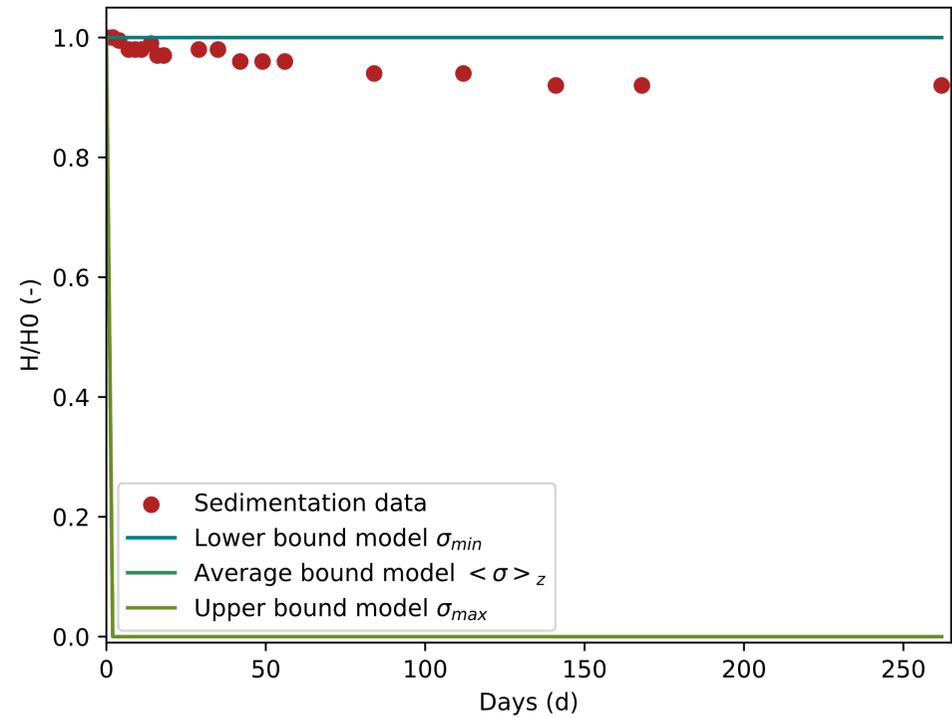
outline

☑ Increased complexity of the building block

☑ Elastoplastic behaviour
   ☑ Modelling of elastoplasticity
   ☐ Imaging of plastic events

☐ CP-AFM and Optical Tweezers

ART 5 : Kinetic Pathways to Gelation and Effects of Flow-Induced Structuring in Depletion Gels (in Spec Issue for W.R. Russel)

I. Diffusion of screening salt   II. Controlled preshear at Mn>10   III. Preshear through manual mixing
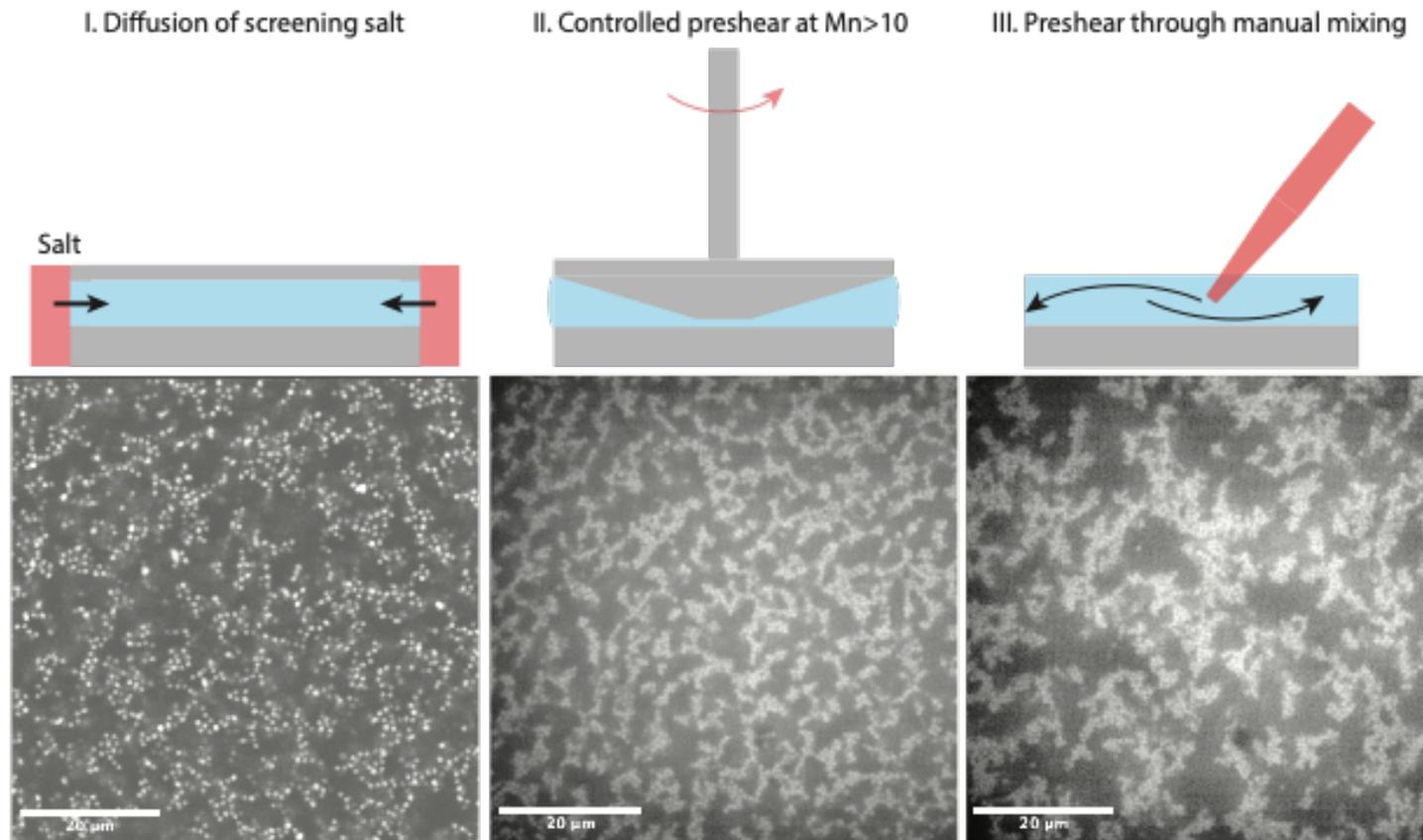
Rheoconfocal

Colombo et al. Industrial & Engineering Chemistry Research (2025) https://pubs.acs.org/doi/full/10.1021/acs.iecr.4c03873
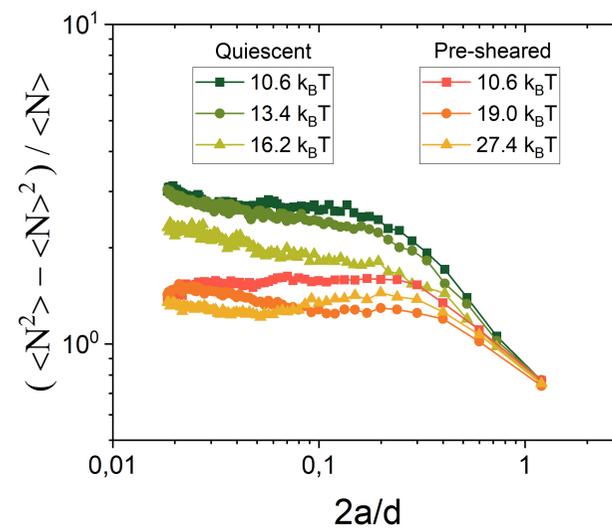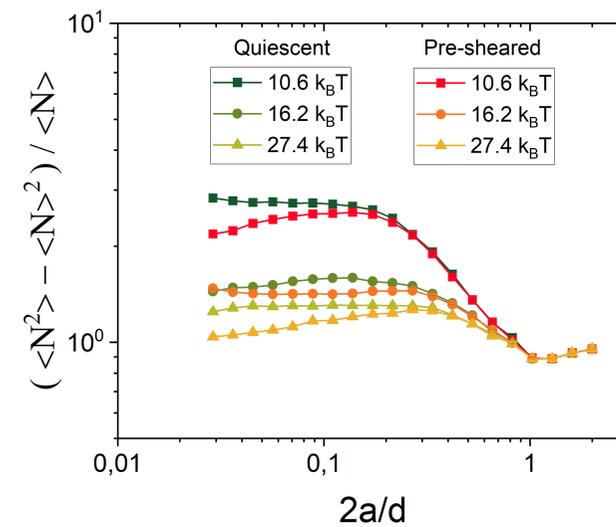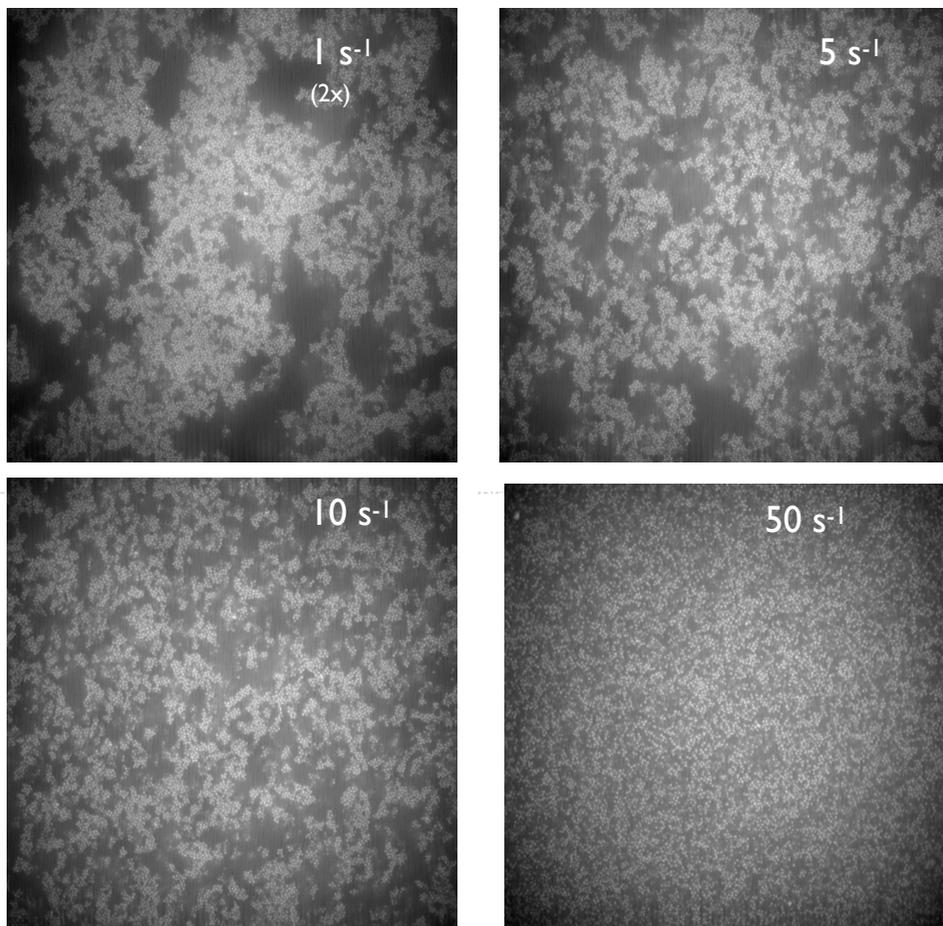
Experimental setup

Focus-tunable lens
Scan range : 10μm
2 VPS with 300 nm z-resolution

Stress-controlled rheometer

Flow reversal experiment
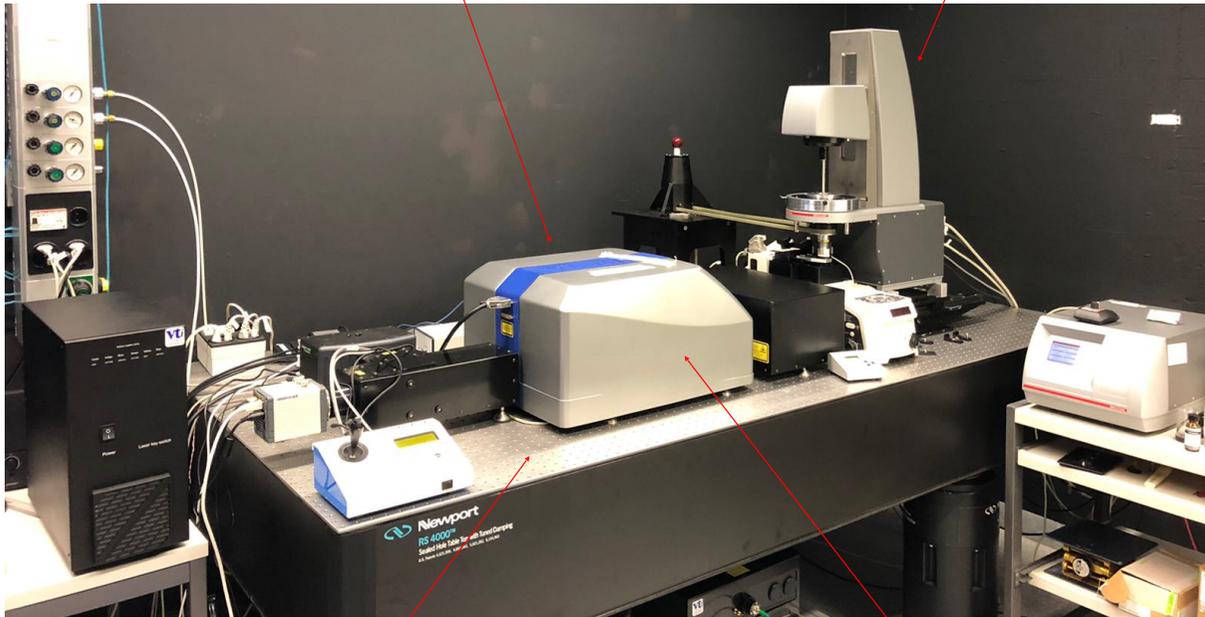
High speed fluorescence camera
100 FPS full frame resolution (4MP)

Confocal scanner
1000 FPS full frame

$\gamma(\%)$

1%

γ_c

$t(s)$

Elastic regime

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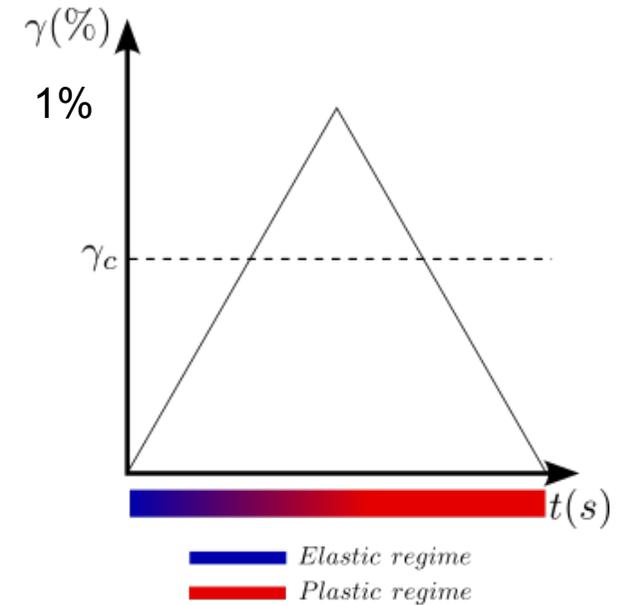
Colombo *et al.,* Korea-Aust. Rheol. J. **31,** *2019*

Microstructure evolution analysis methods

Particle tracking

10 µm
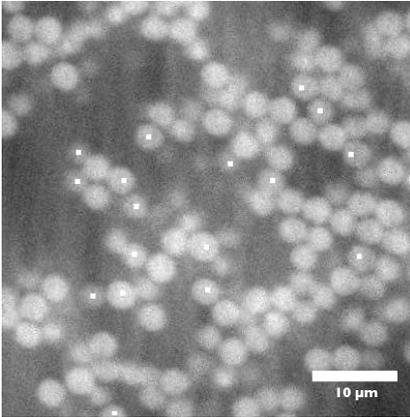
Adapted Crocker and Grier method for the detection of spherical objects in complex background

U. Gasser *et al.*, Optics Express 2021

15 µm
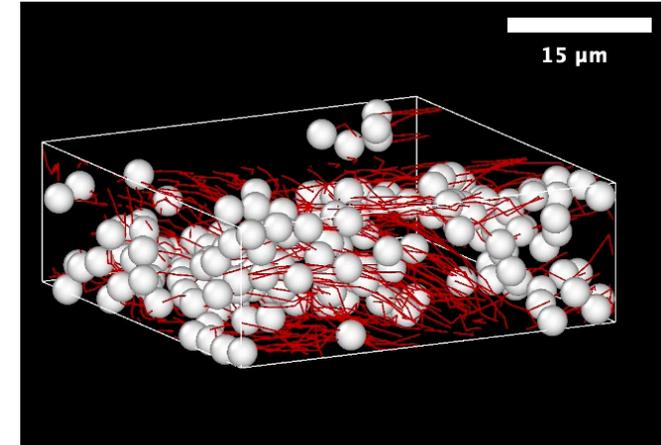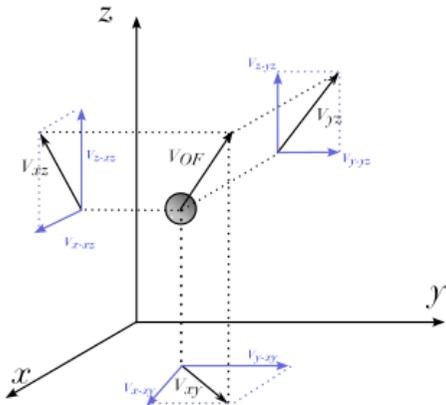
Optical flow

Application of 2D Farneback algorithm in each plane followed by reconstruction of the 3D optical flow vectors

G. Farneback, Proceedings of the 13th Scandinavian Conference on Image Analysis, 2003.

Generation and detection of the mecanisms of plasticity
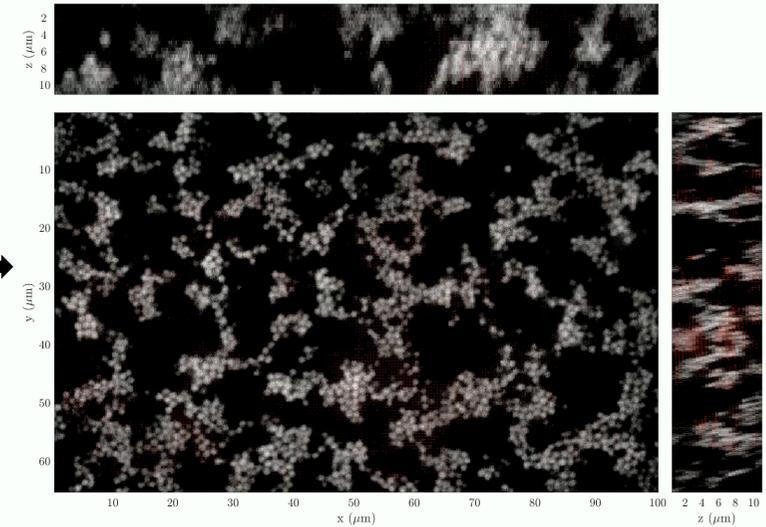
Forcing the gels to enter the plastic regime

Elastic regime
Plastic regime
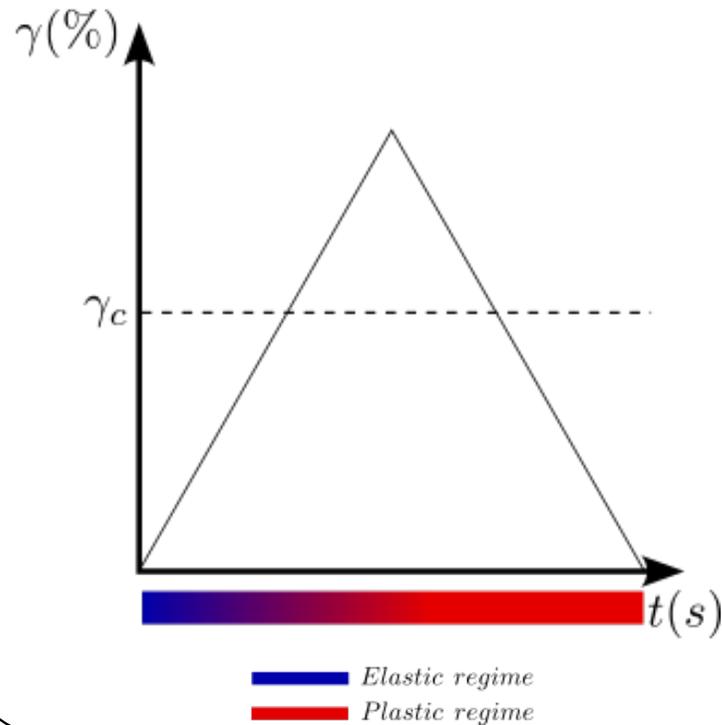
Using a metric of local plasticity at the particle level

$$D^2(t,\Delta t) = \sum_n \sum_i \left(r_n^i(t) - r_0^i(t) - \sum_j (\delta_{ij} + \varepsilon_{ij}) \right.$$

$$\left. \times [r_n^j(t-\Delta t) - r_0^j(t-\Delta t)] \right)^2,$$

$$i, j \in \{x, y, z\}^2 \qquad n \in E_N$$
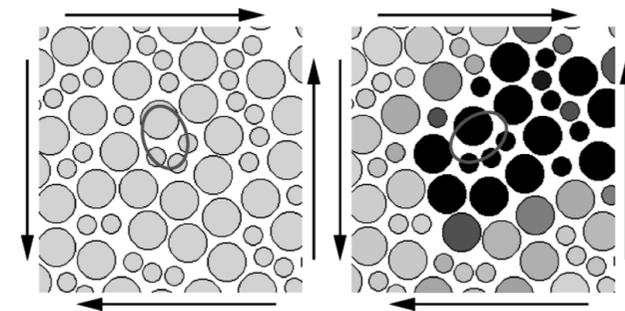
Falk and Langer, Phys. Rev. E. **57,** 1998

A closer look at the observable rearrangements

PMMA-g-PHSA depletion gel

$\phi = 45\%, \ U_{dep} = -15kT, \ \dot{\gamma}_{set} = 1.10^{-3}s^{-1}, \ \dot{\gamma}_{real} = 5.10^{-4}s^{-1}$
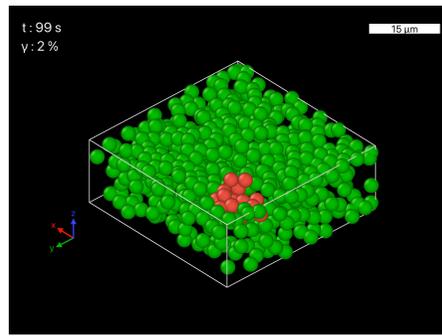
Isolation of particles involved in the rearrangement
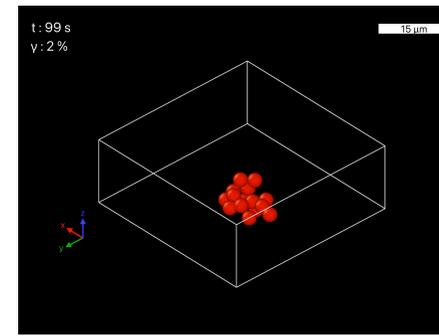
Coordination analysis shows this rearrangement happen at a weak spot…
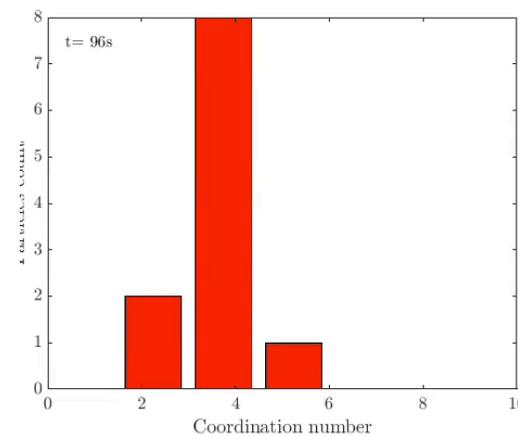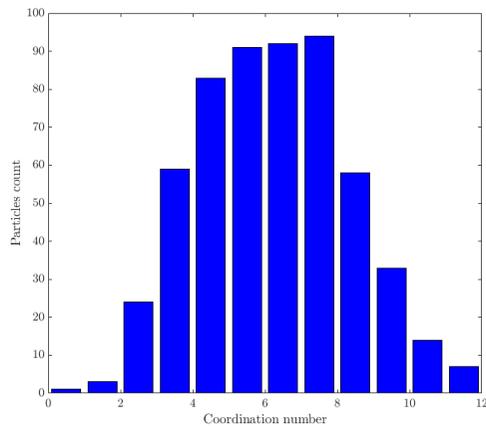
…and that the particle move in the vorticity direction

in preparation
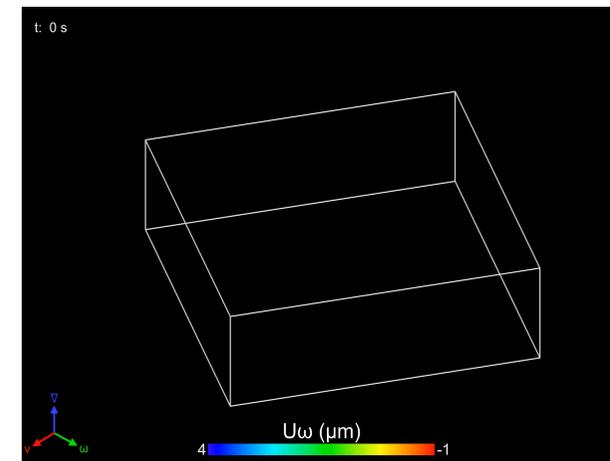
Measuring stress activation curves with optical flow

Applying creep at different stresses

a) creep
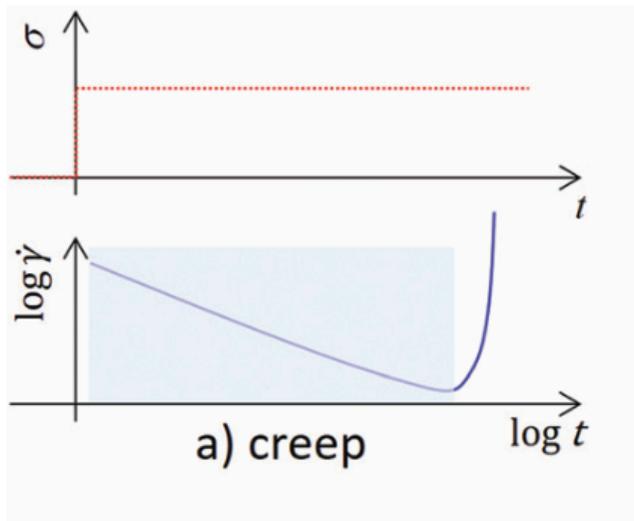
Measuring non-affine zones characteristics with high order motion analysis

$$\hat{V}(t \sim t + \Delta t)$$

$$F(t - \Delta t) \qquad F(t) \qquad F(t + \Delta t)$$
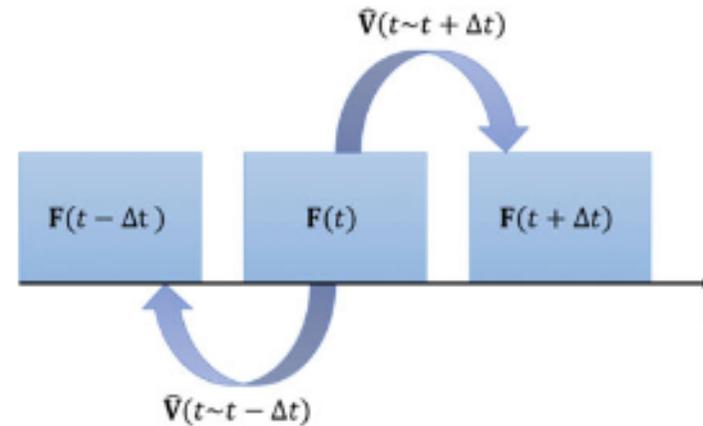
$$\hat{V}(t \sim t - \Delta t)$$

$$\hat{A}(t) = \hat{V}(t, t + \Delta t) - \hat{V}(t - \Delta t, t)$$

Non-affine activity at 50 mPa
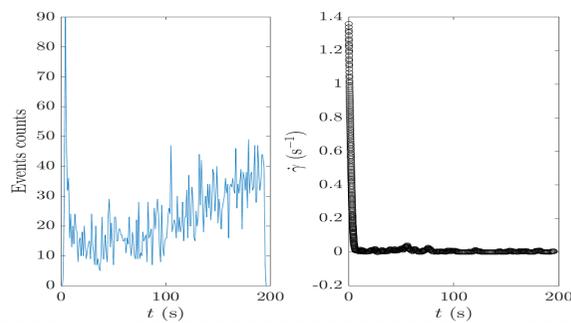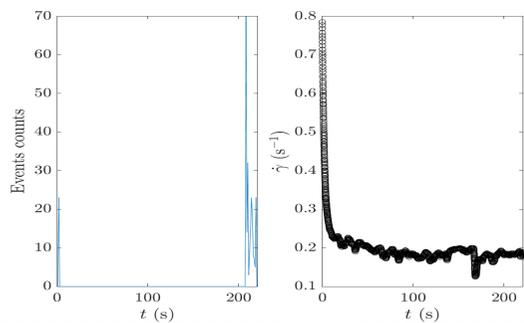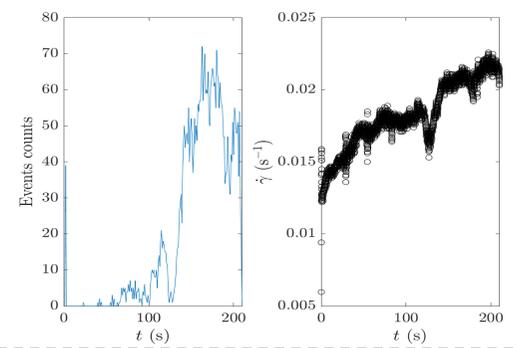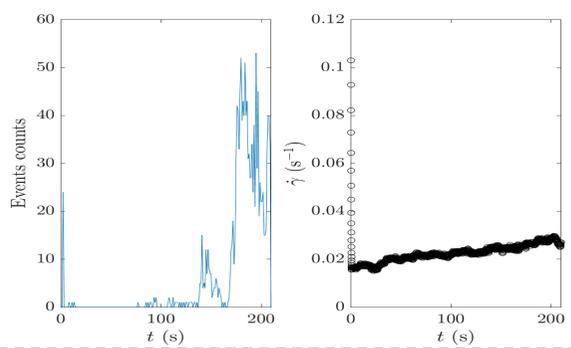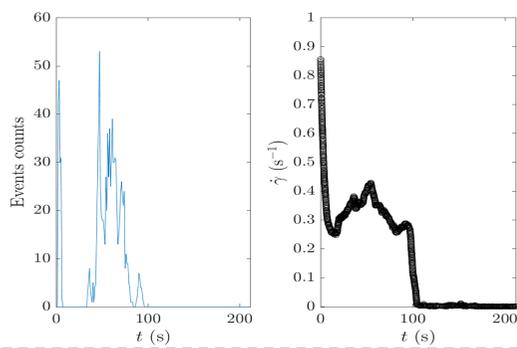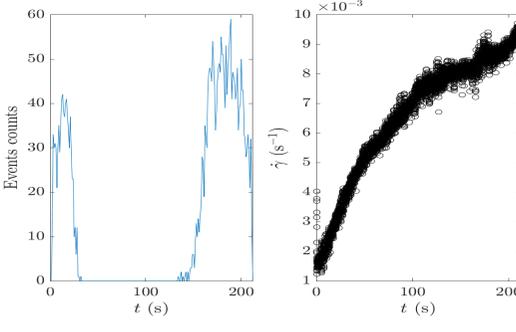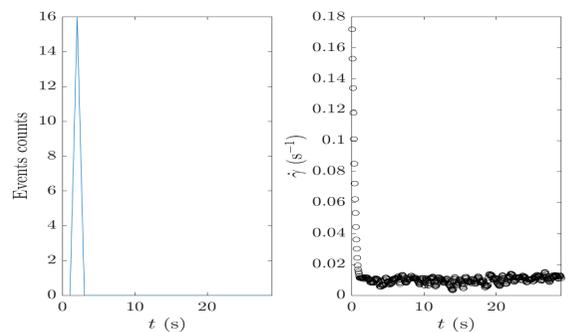
Non-affine activity zone size distribution at 50 mPa
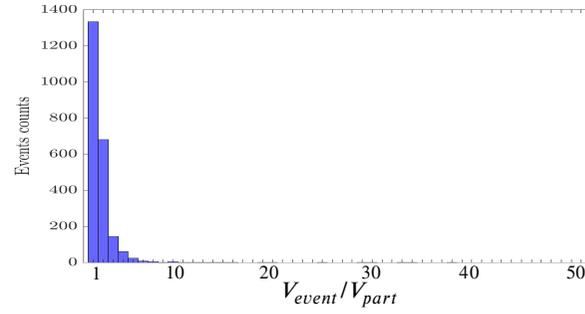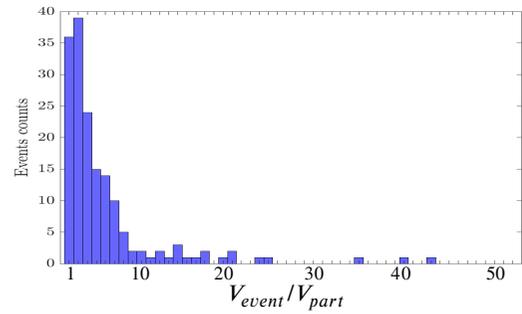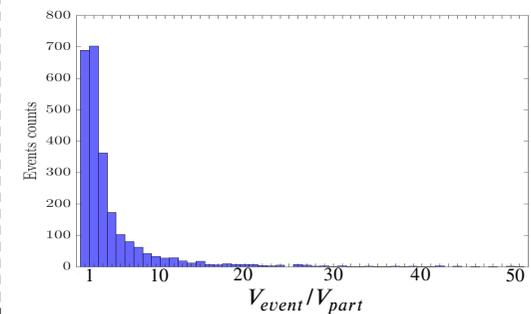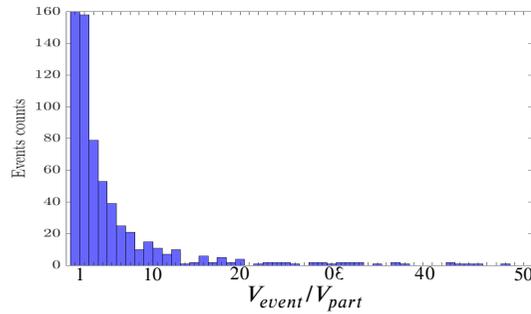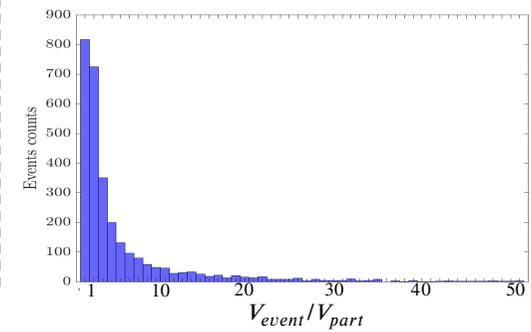
outline
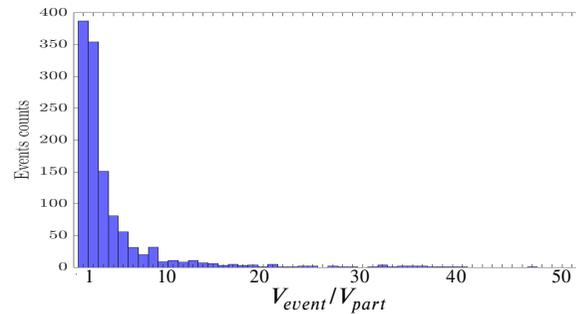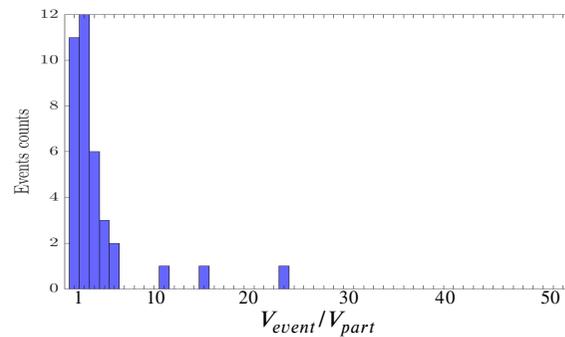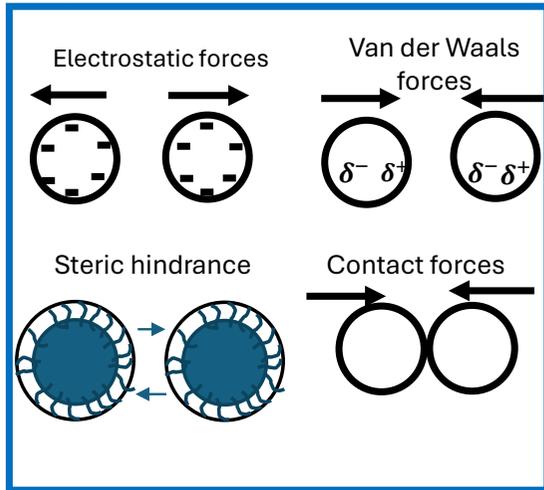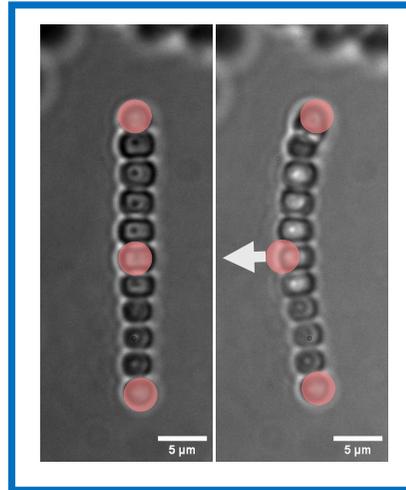
- ☑ Increased complexity of the building block

- ☑ Elastoplastic behaviour
  - ☑ Modelling of elastoplasticity
  - ☐ Imaging of plastic events

- ☐ CP-AFM and Optical Tweezers

ETH *zürich*

Rearrangements, configurations, metastability

Interparticle forces

Electrostatic forces

Van der Waals forces

Steric hindrance

Contact forces

$\delta^- \quad \delta^+$ $\quad \delta^- \quad \delta^+$

Cluster properties

5 µm   5 µm

Formation of spanning network

-G(r)
-Cooperative effects
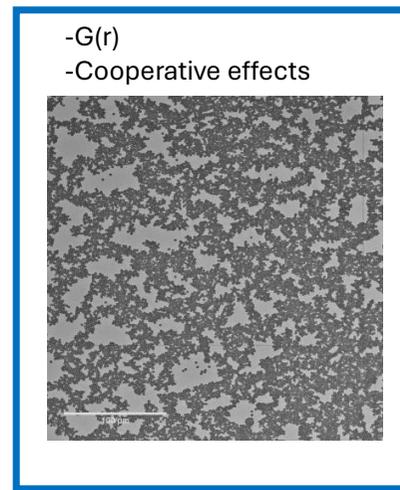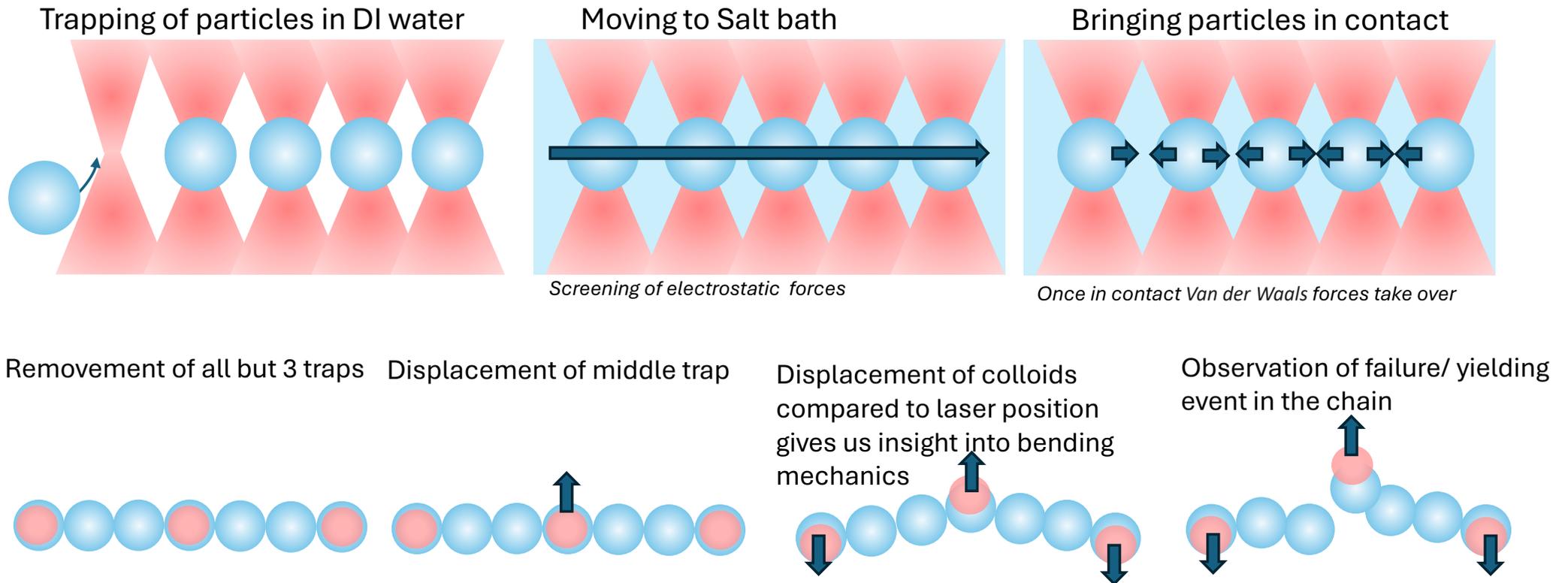
Rheological properties
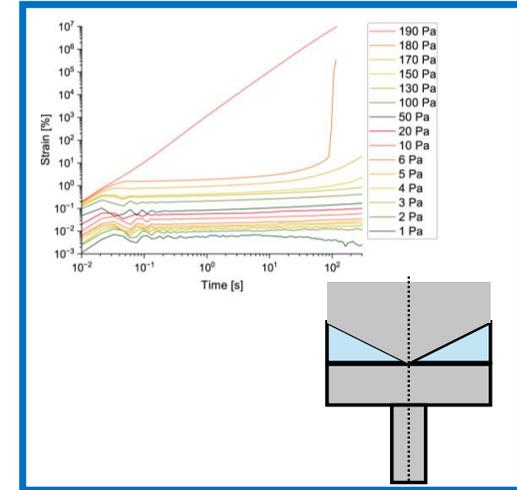
Assembly

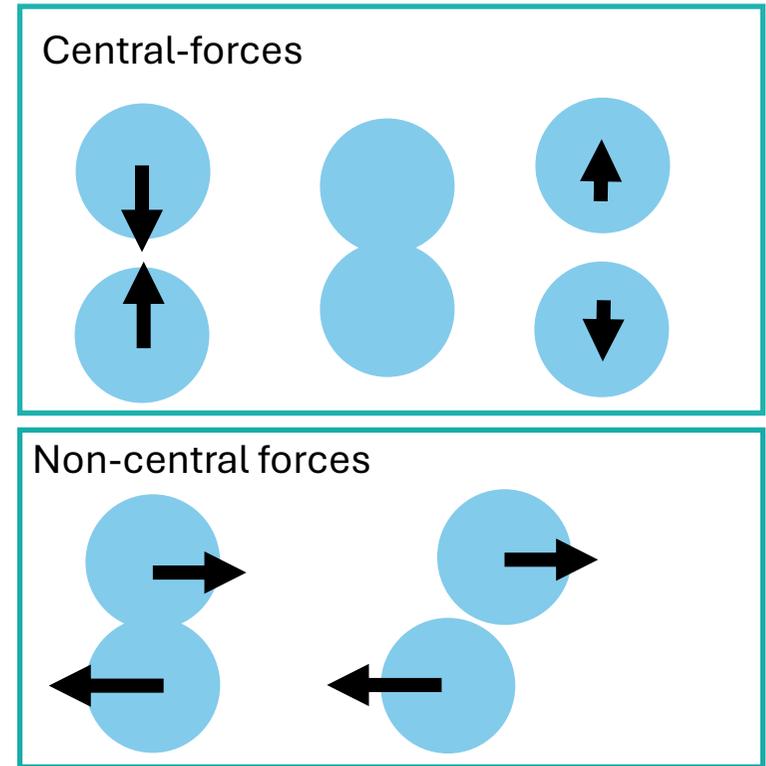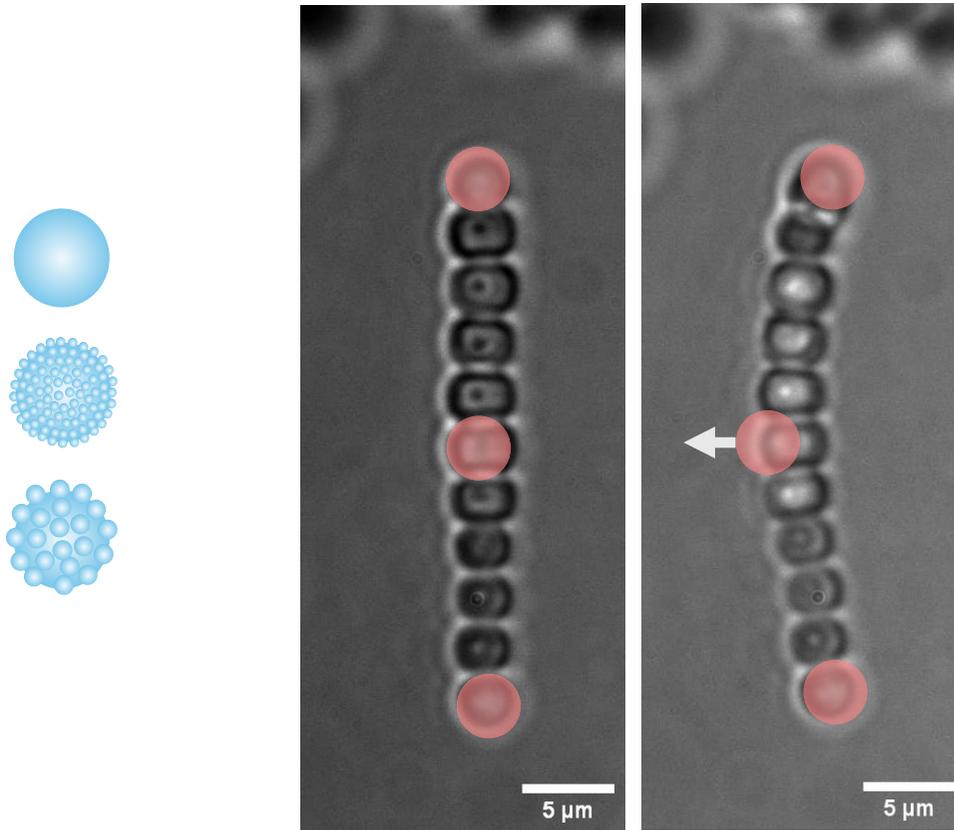Thixotropic and aging effects

- Increasing the interparticle **potential**, lowers the **coordination number.**
  - **Crowding** with particle needs more material.

The forces in contact can lead to a difference in aging and shear deformation

Introduce force anisotropy to dictate assembly process

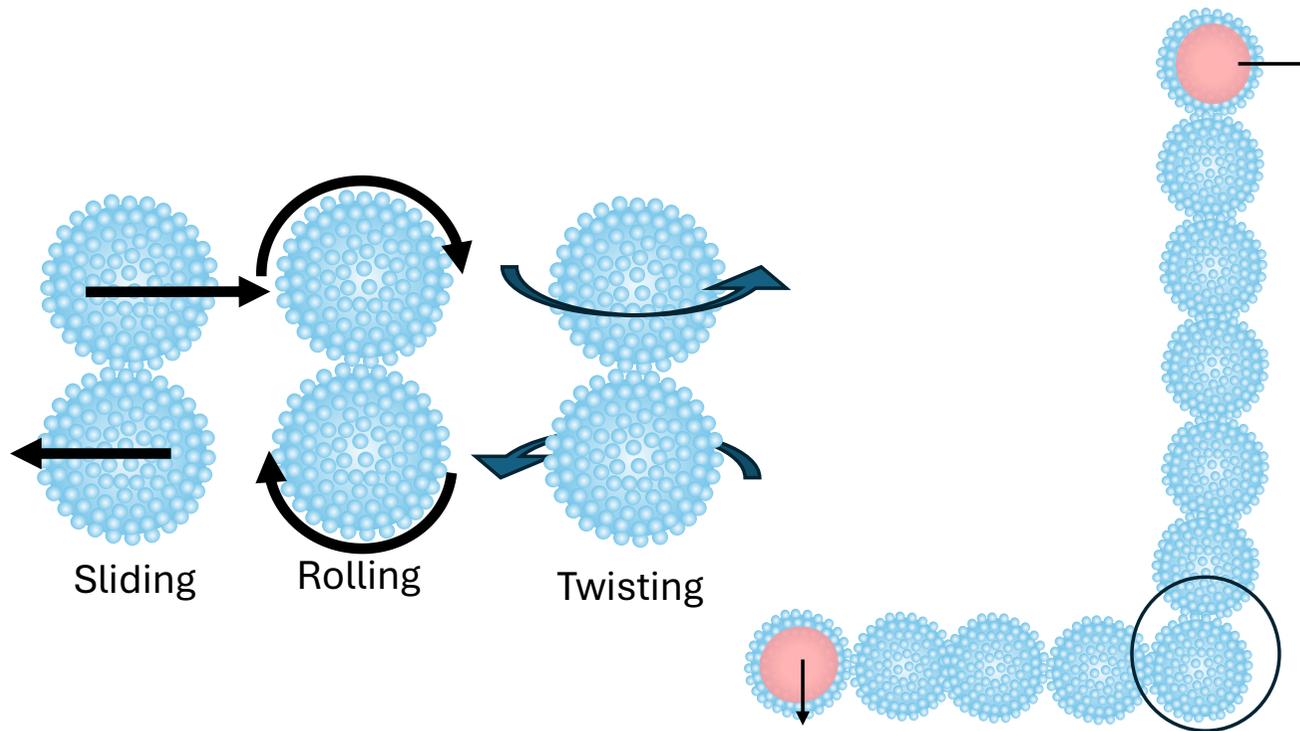Whitaker, Kathryn A., et al. Nature communications 10.1 (2019): 2237.

Bending experiments of linear aggregates using OT

SOFTMAT

Trapping of particles in DI water

Moving to Salt bath

Screening of electrostatic forces

Bringing particles in contact

Once in contact Van der Waals forces take over

Removal of all but 3 traps

Displacement of middle trap

Displacement of colloids compared to laser position gives us insight into bending mechanics

Observation of failure/ yielding event in the chain

Influence of roughness on bending stiffness

Deformation mode in more complex arrangements

Sliding   Rolling   Twisting

Observing failure of structure
under tension
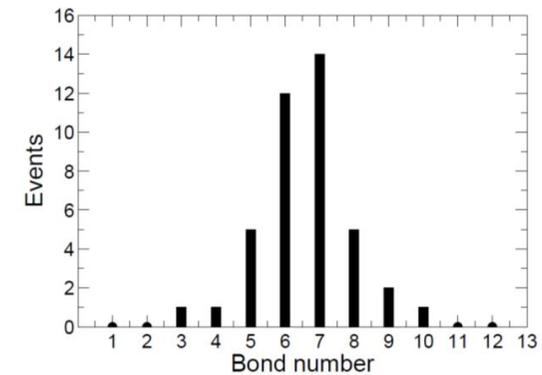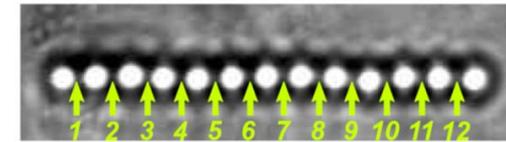
Histogram of the yielding events as
a function of the bond number
in the 13 particles rods.

outline

☑ Increased complexity of the building block

☑ Elastoplastic behaviour
    ☑ Modelling of elastoplasticity
    ☑ Imaging of plastic events

☑ CP-AFM and Optical Tweezers

ETH *zürich*