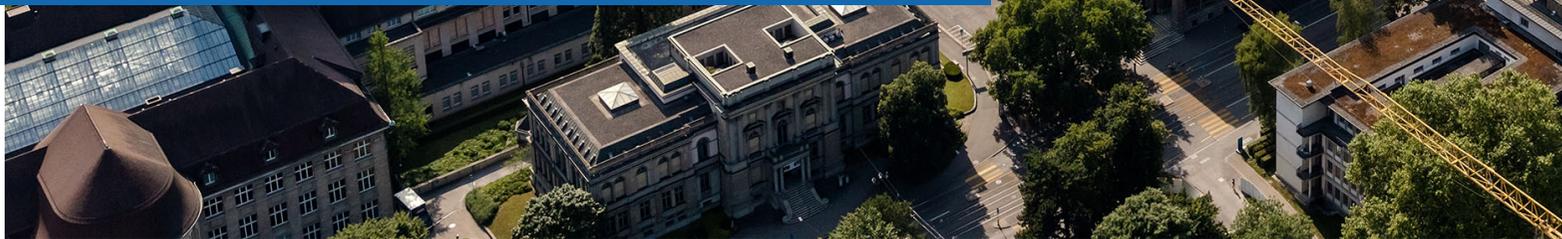




Simplified industrial dispersions

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





Florence Müller



Pierre Lehericy

SOFTMAT

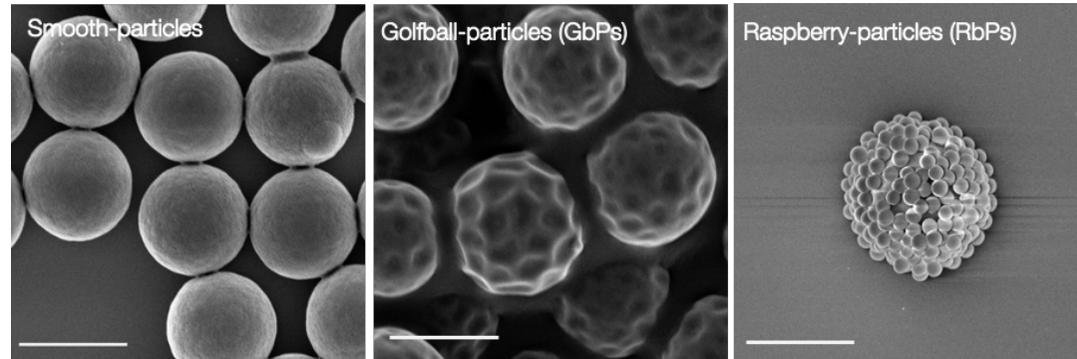


Lukas Woolley



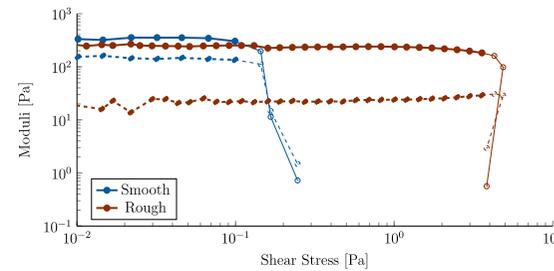
Gabriele Pagani

Complexity in model systems

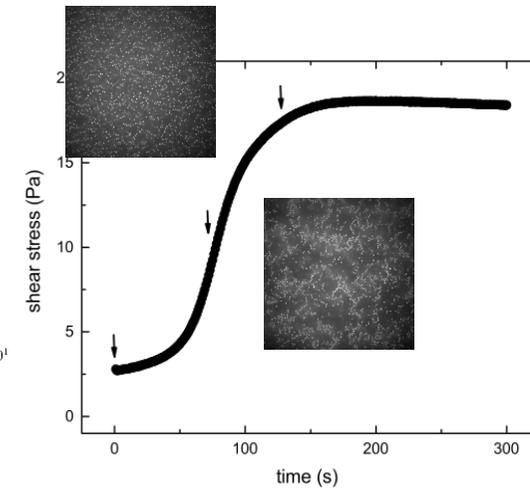


- + ability to systematically vary features and interactions
- + thermoreversible gels in particular

Simplified industrial dispersions

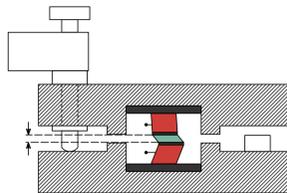


yielding

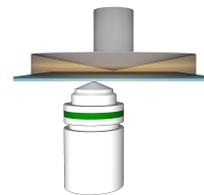


thixotropy

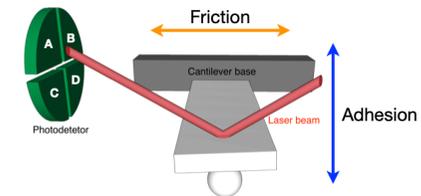
Analytical, structural and rheological methods tailored to interrogate structure



stress deconvolution



4D-imaging

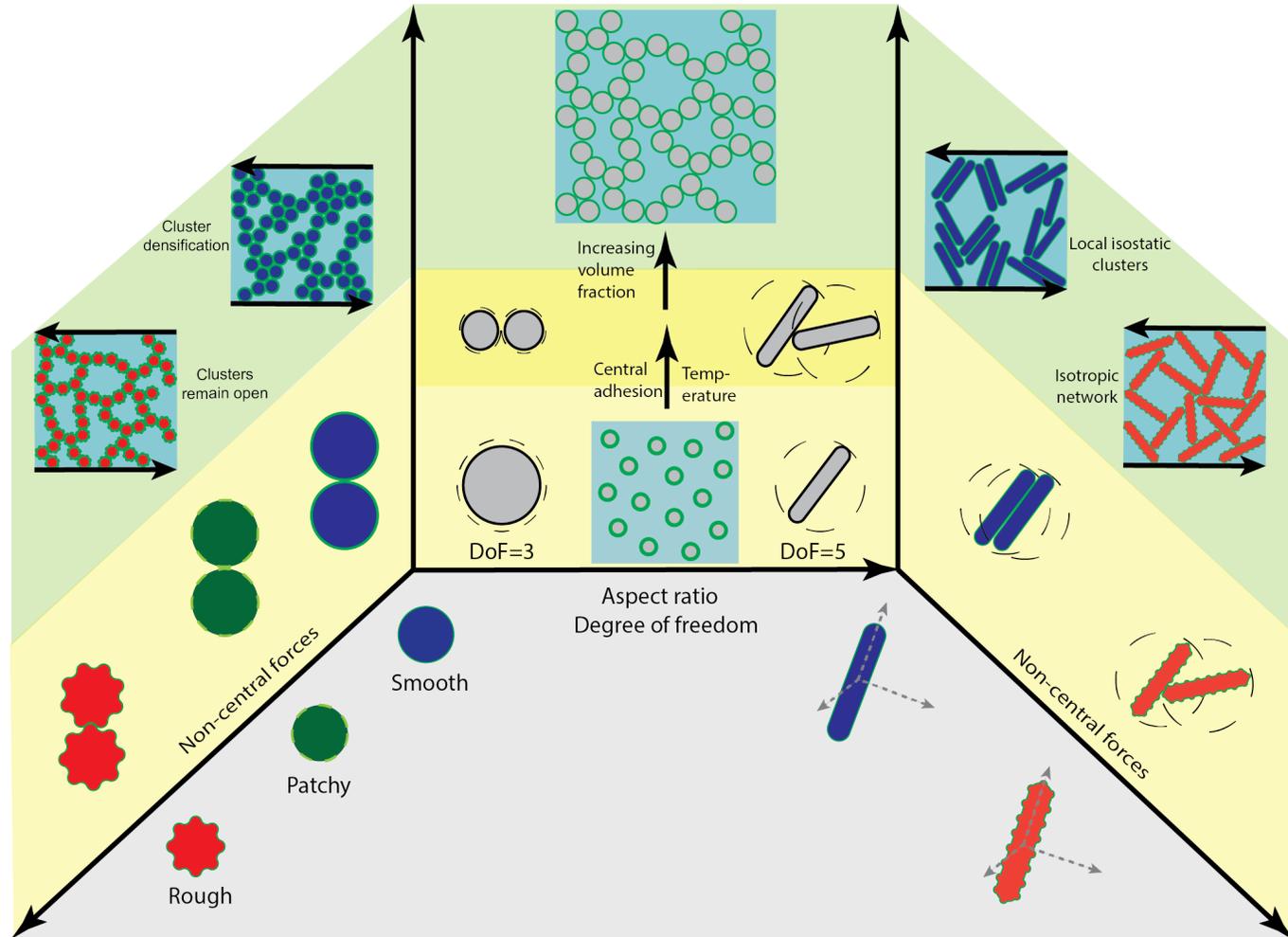


local scale forces (OT/CP-AFM)

outline

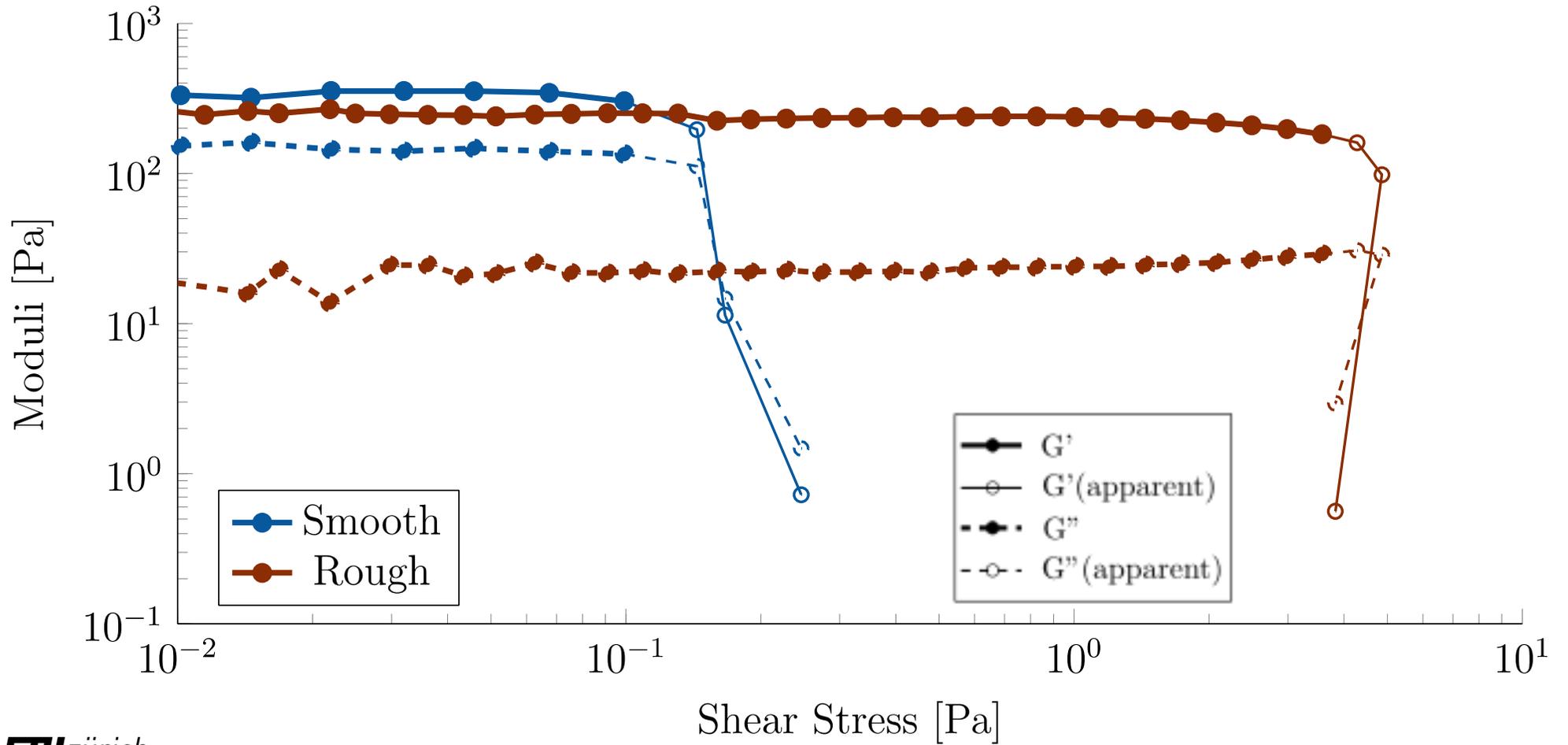
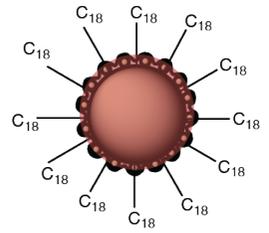
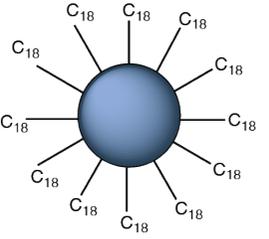
- ❑ Increased complexity of the building block
- ❑ Elastoplastic behaviour
 - ❑ Modelling of elastoplasticity
 - ❑ Imaging of plastic events
- ❑ CP-AFM and Optical Tweezers

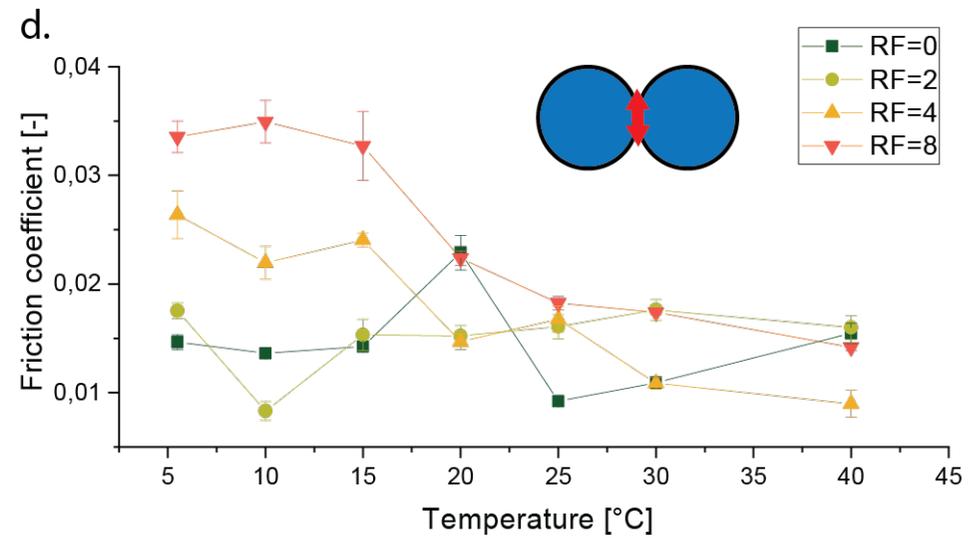
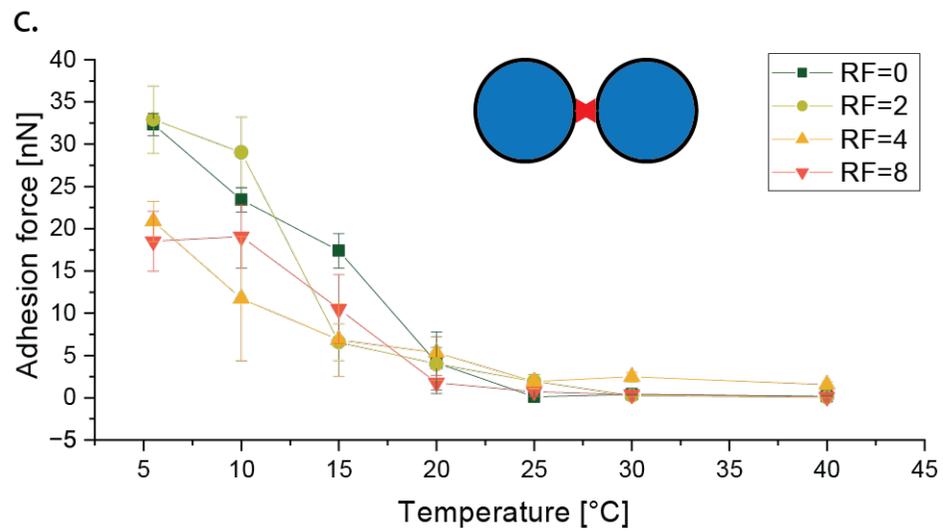
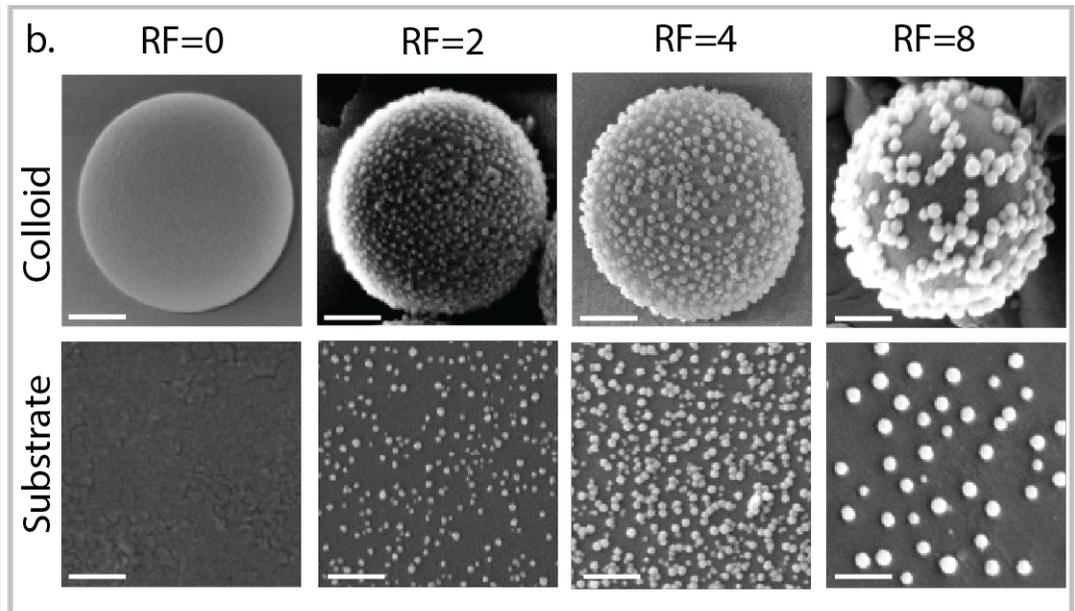
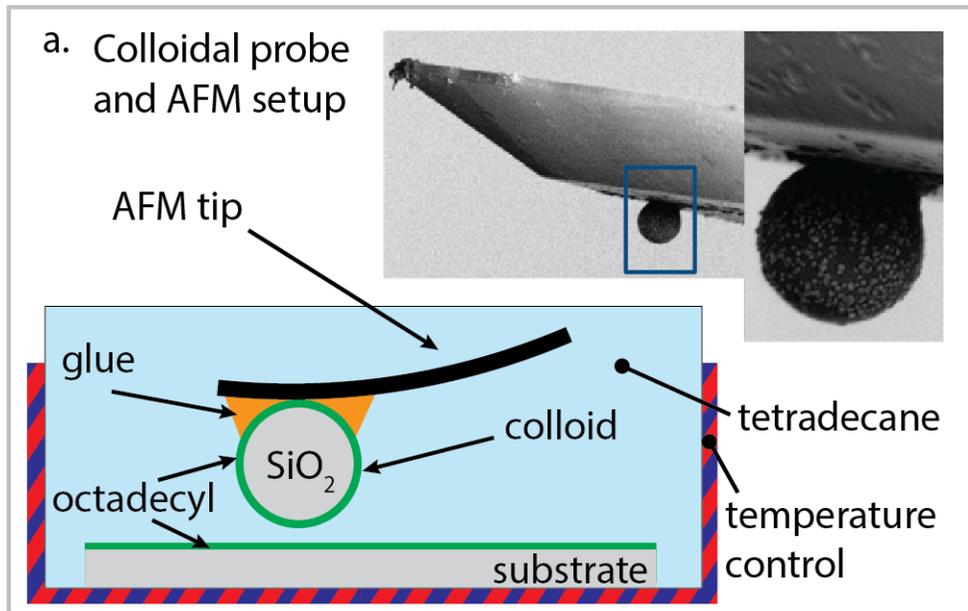
parameter space



Rough particle gels delay yielding

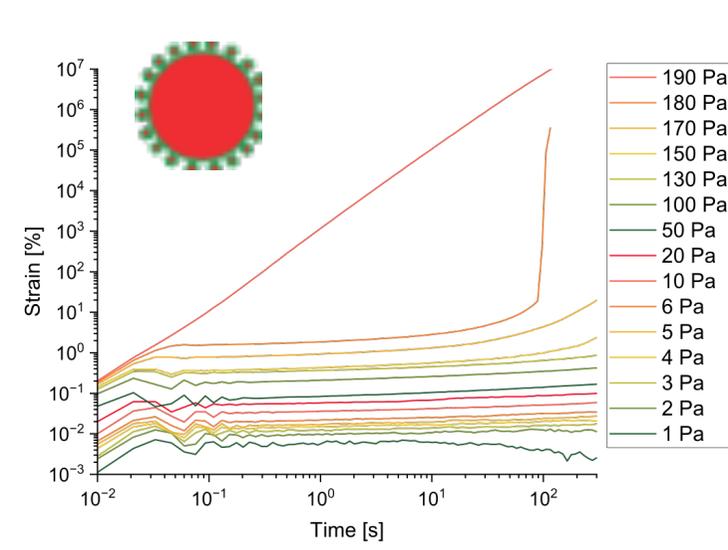
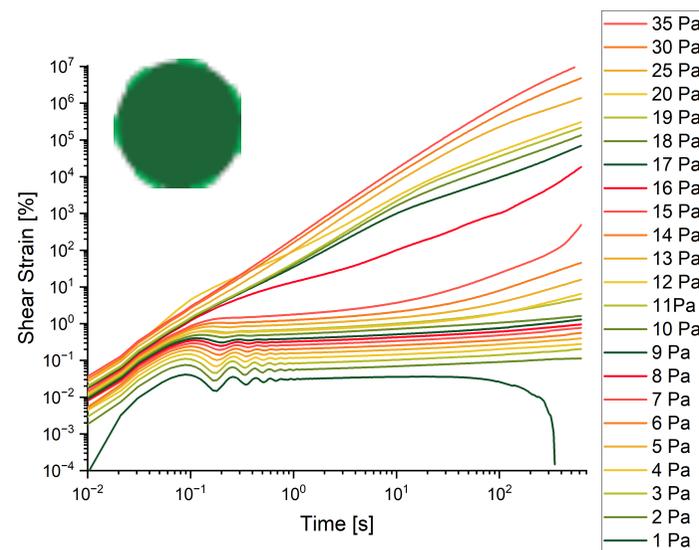
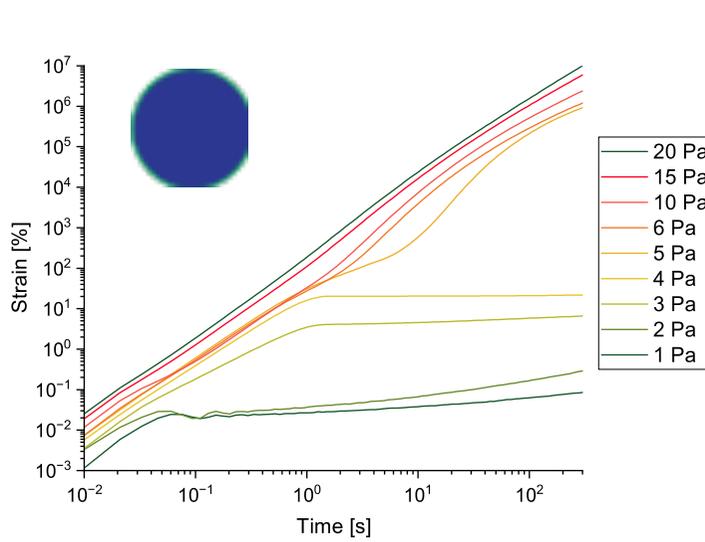
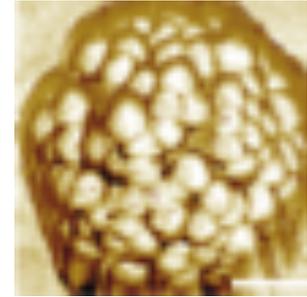
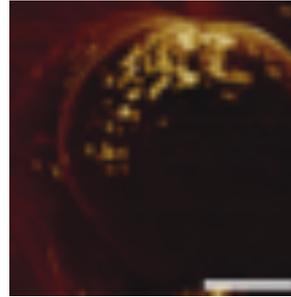
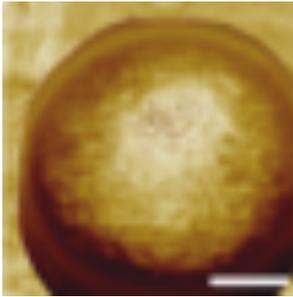
- Outer diameter: 300 nm
- Octadecyl brush
- In tetradecane
- $\phi = 0.15$



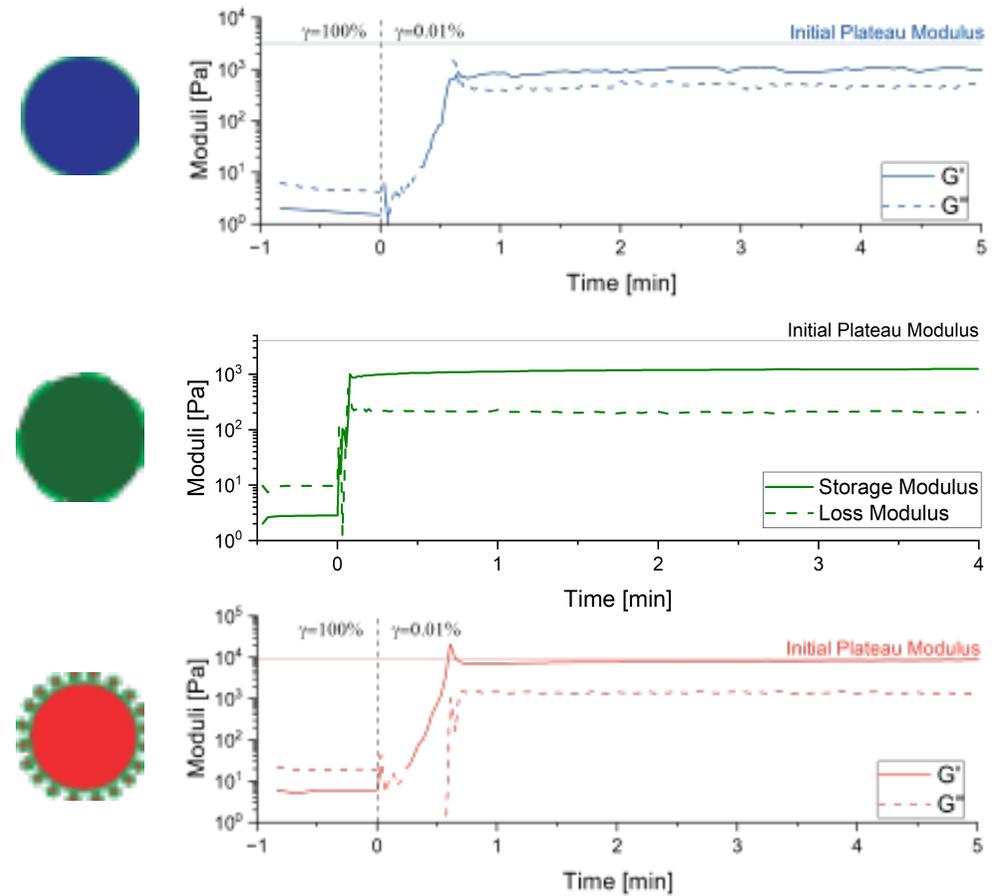
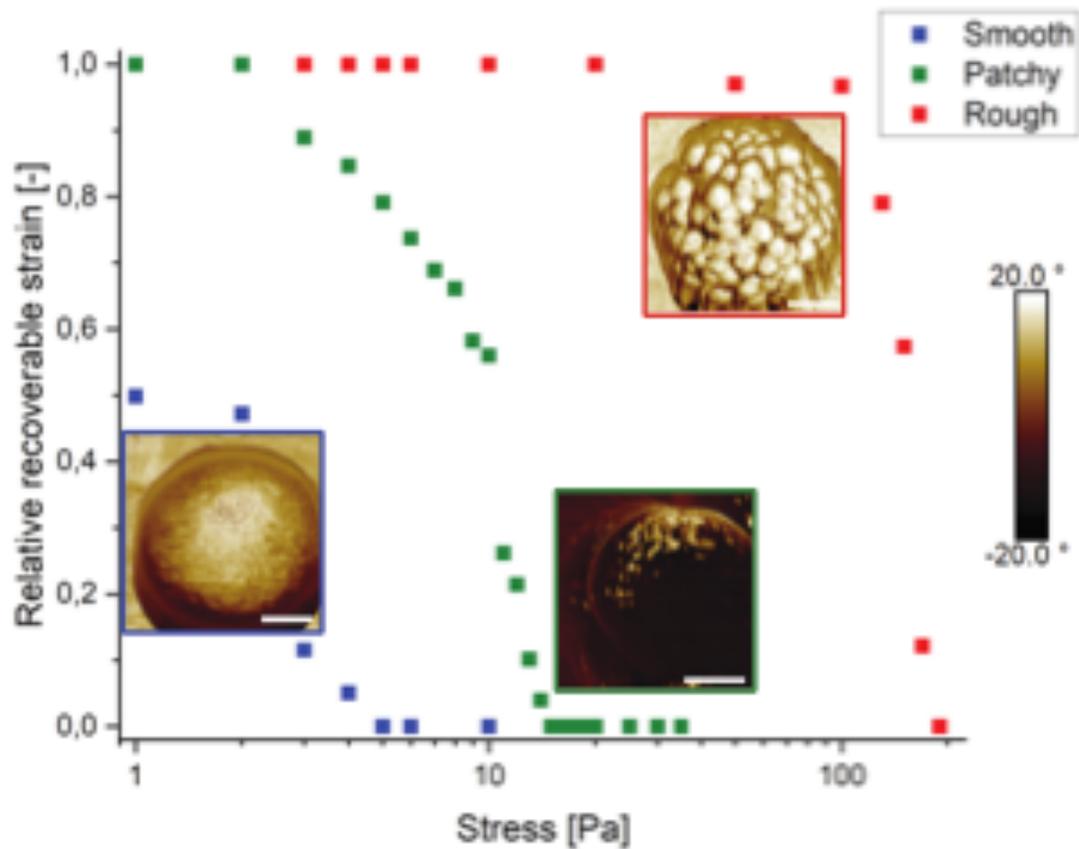


Surface roughness extends the linear response regime

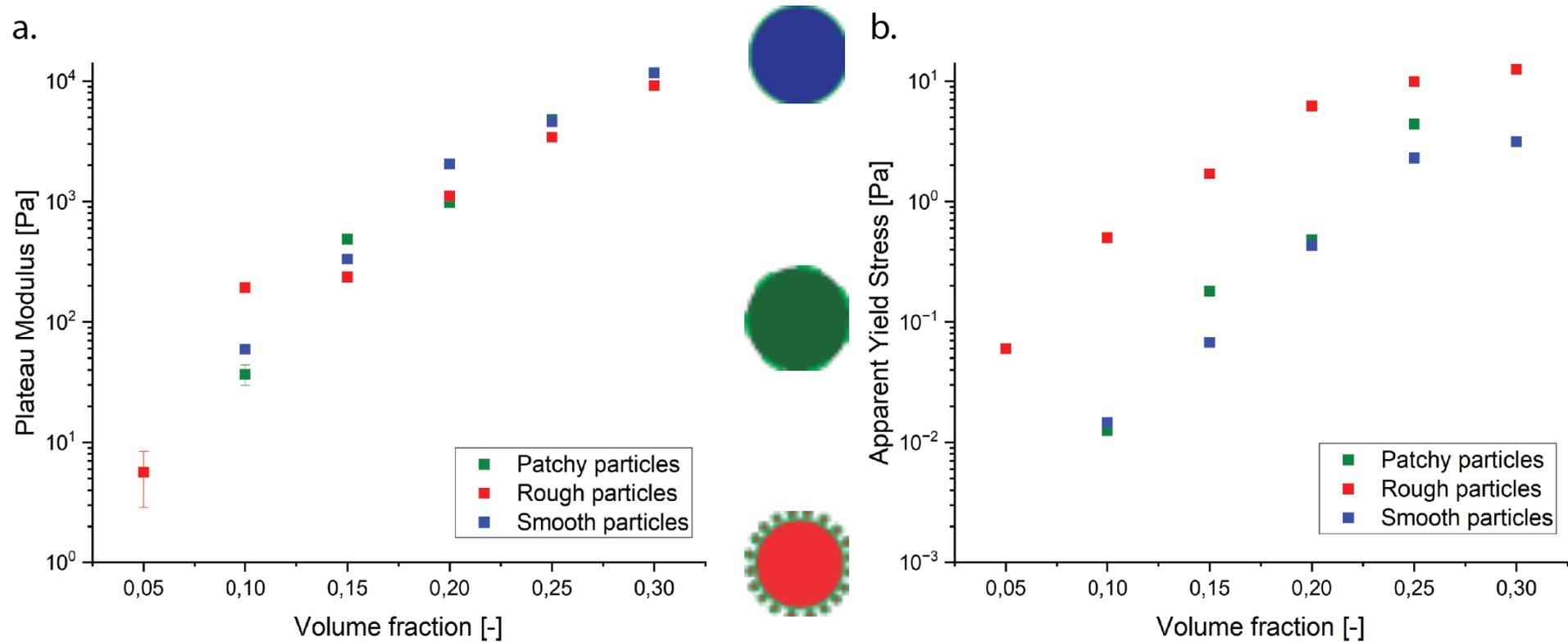
- Outer diameter: 300 nm
- Octadecyl brush
- In tetradecane
- $\phi = 0.25$



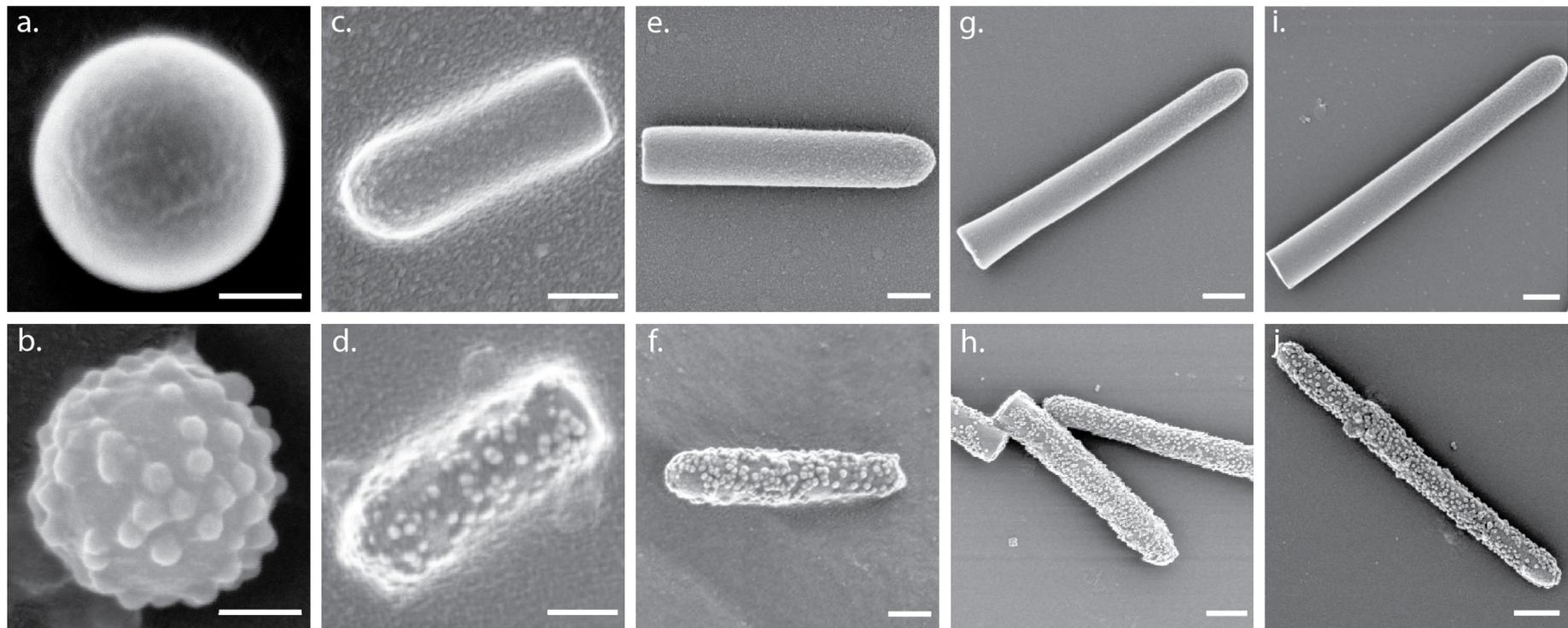
Non-central forces dominate the recovery behavior



Quiescent behaviors are independent of non-central forces

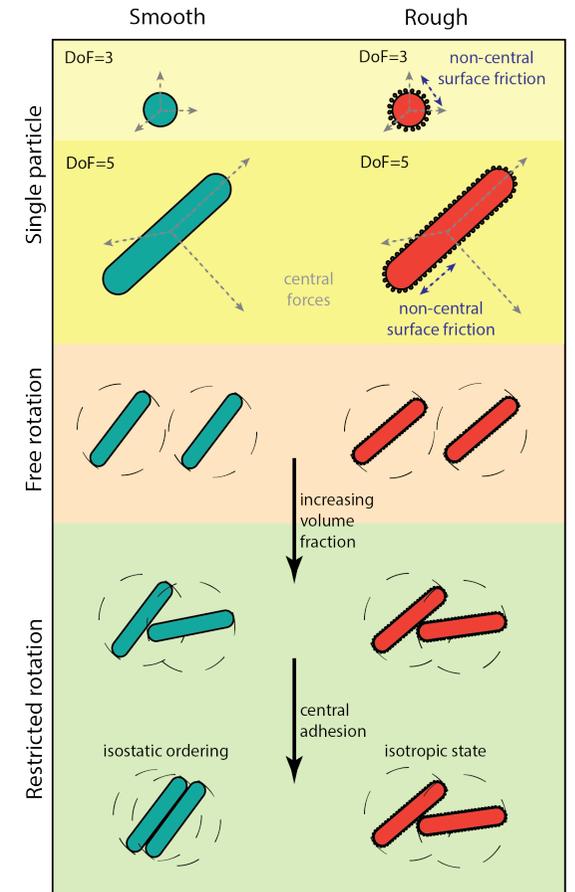
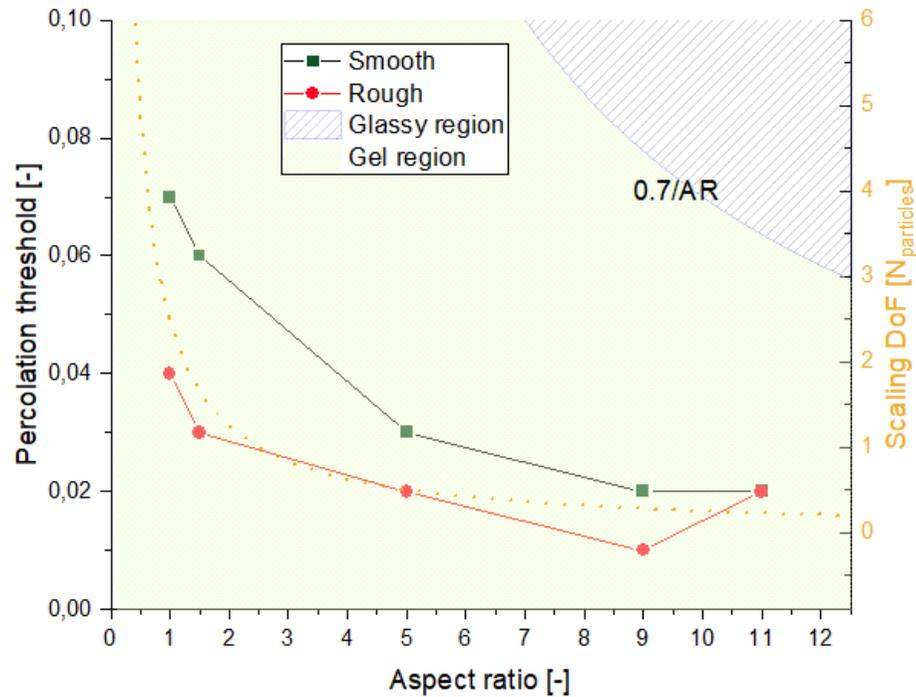
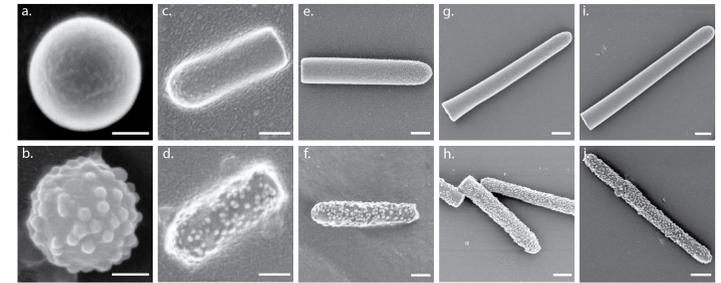


Rods with varying aspect ratio

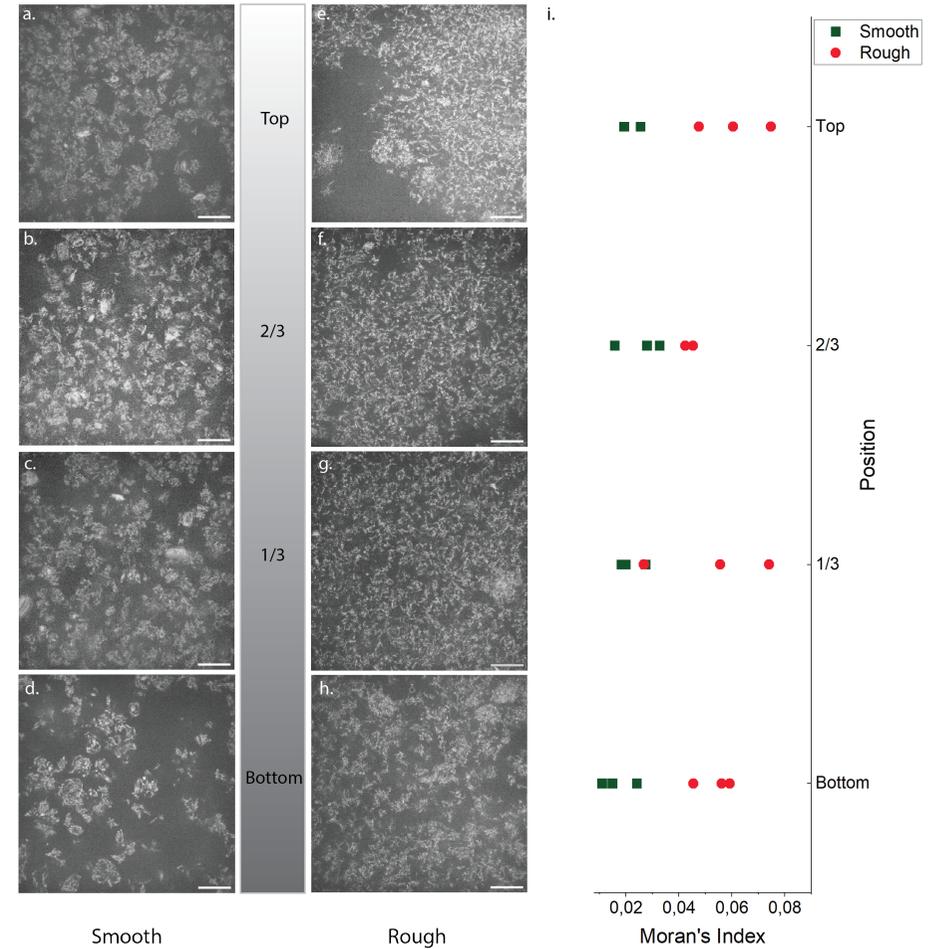
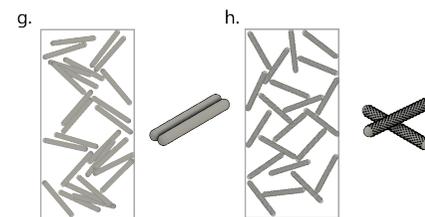
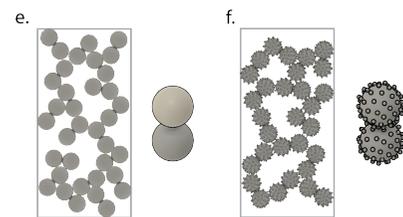
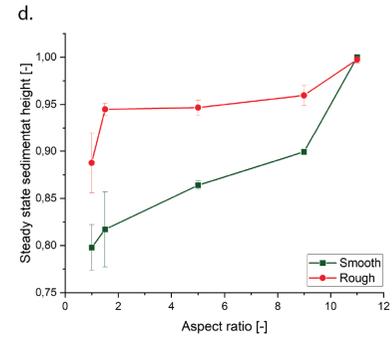
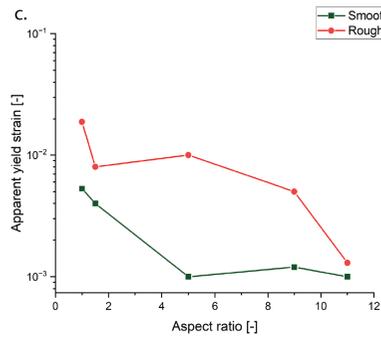
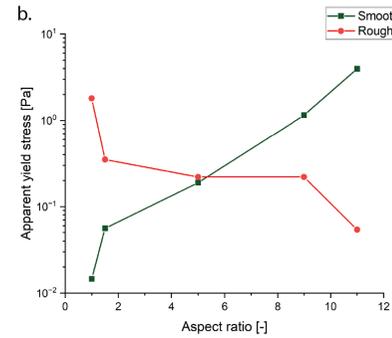
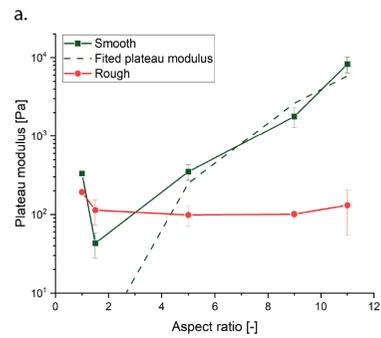


Aspect ratio induces reduces the degrees of freedom of the system in the far field

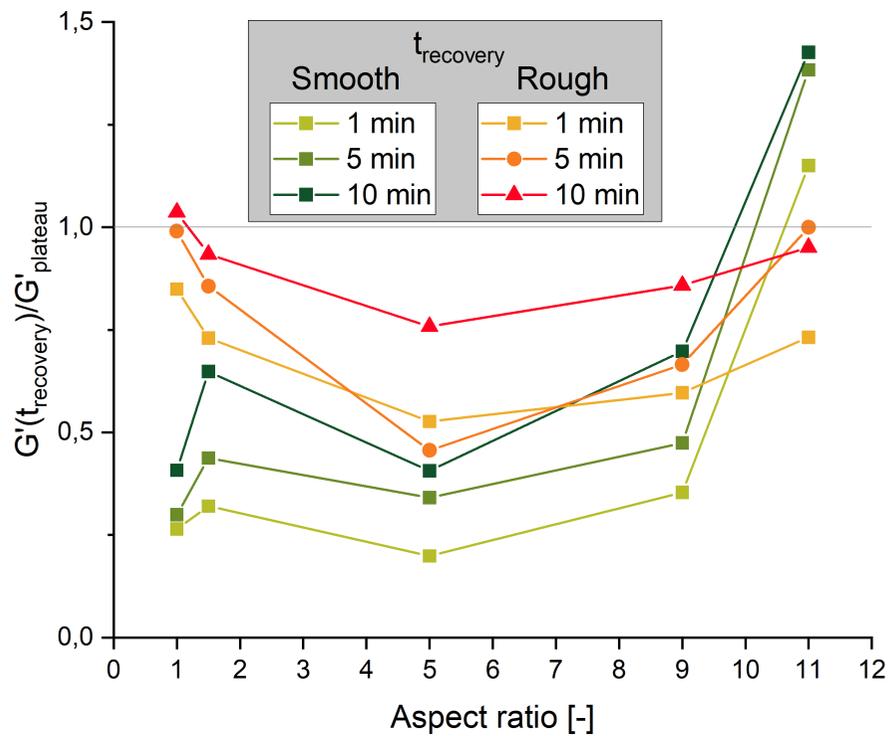
- **Surface roughness** decreases the DoF upon contact
- Increasing the **aspect ratio** decreases the DoF before contact



Smooth rods can align, while rough rods form a homogeneous microstructure

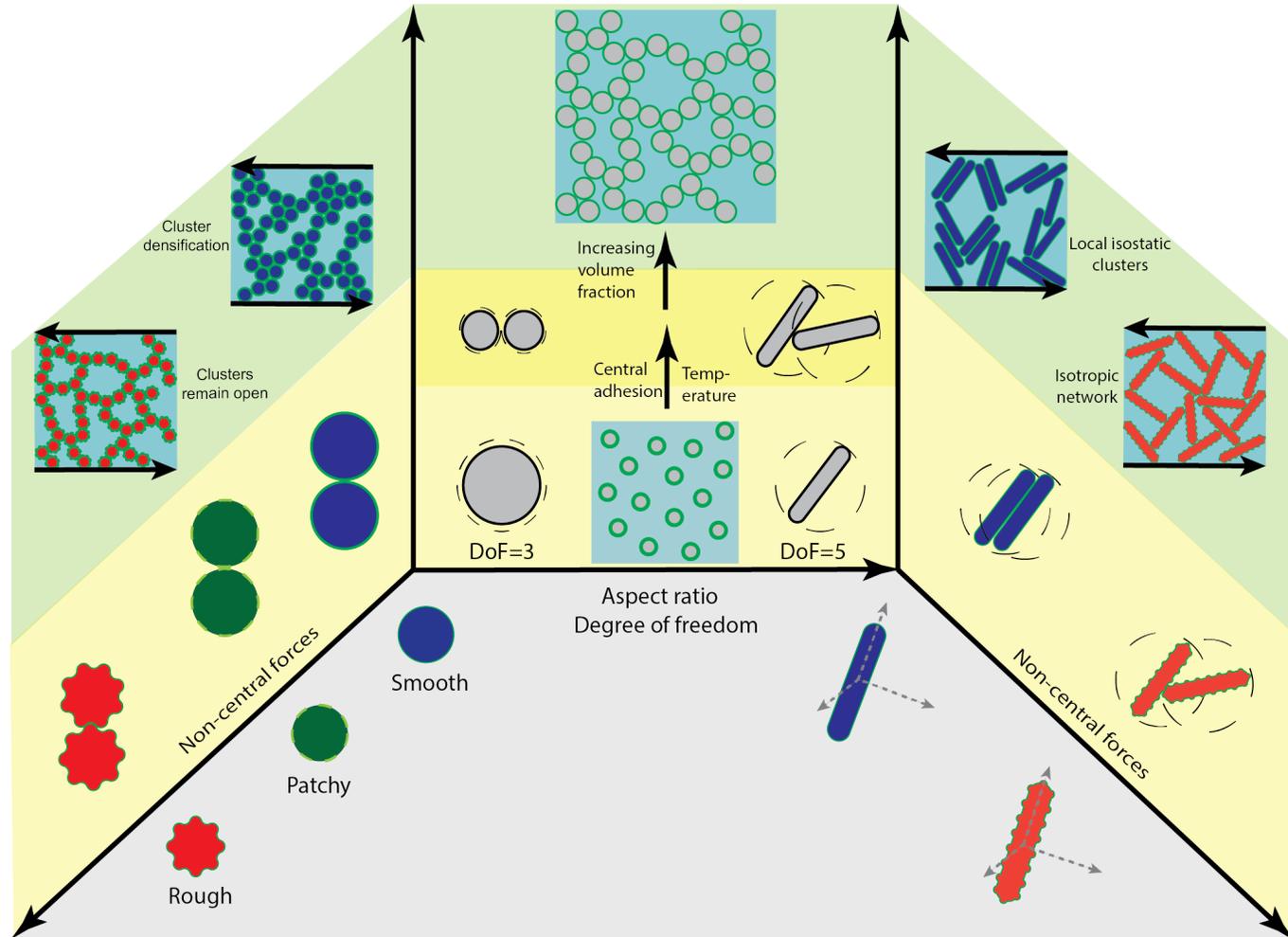


Shear forces increase the rods tendency to align



The homogeneous microstructure of the rough rod gel is more independent on aspect ratio than smooth rod gels. Driven by free volume interactions, shear forces will increase the rods tendency to align.

parameter space

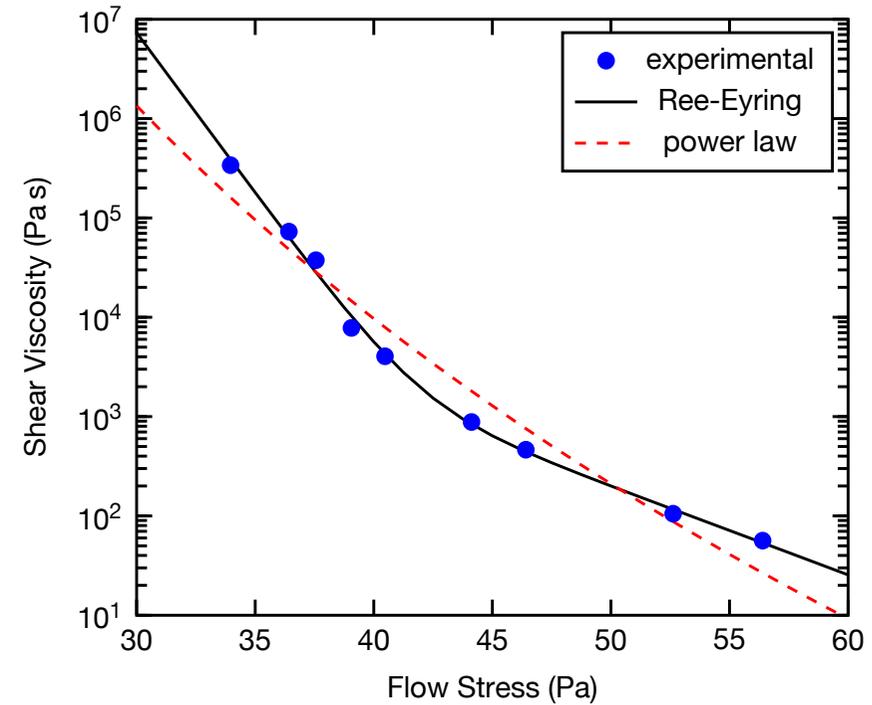
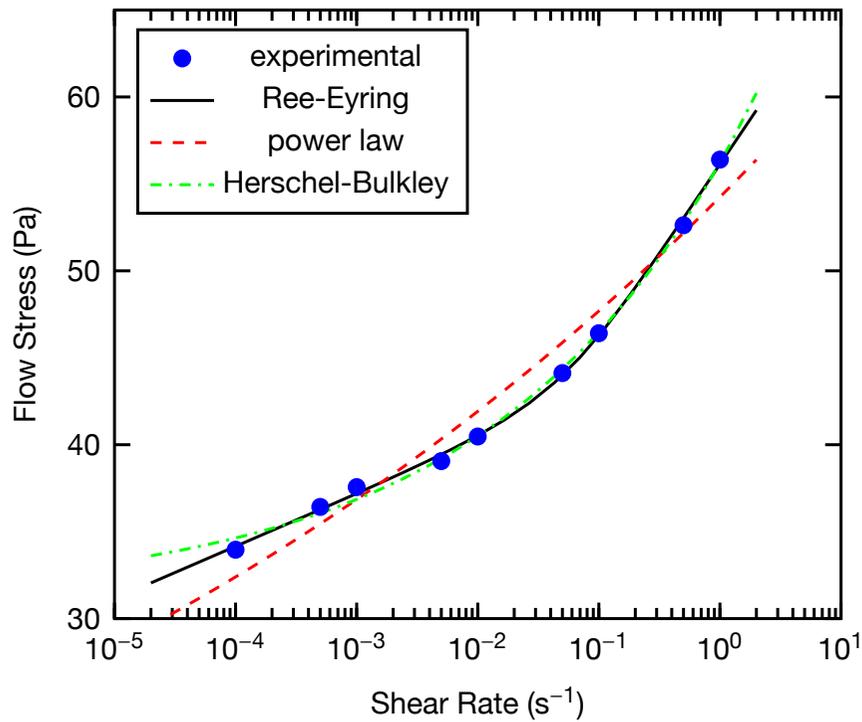


outline

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A typical yield stress fluid

0.5 wt% Carbopol[®]940



$$\sigma = \sigma_y + K\dot{\gamma}^n, \quad \sigma \geq \sigma_y$$

1D EVP model

$$\sigma = G\gamma_e$$

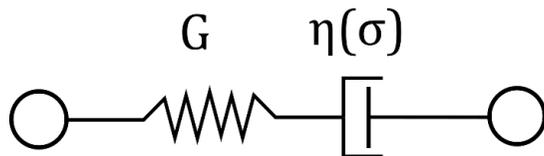
$$\dot{\gamma}_e = \dot{\gamma} - \dot{\gamma}_p$$

$$\dot{\gamma}_p = \frac{\sigma}{\eta(\sigma_{eq})}$$

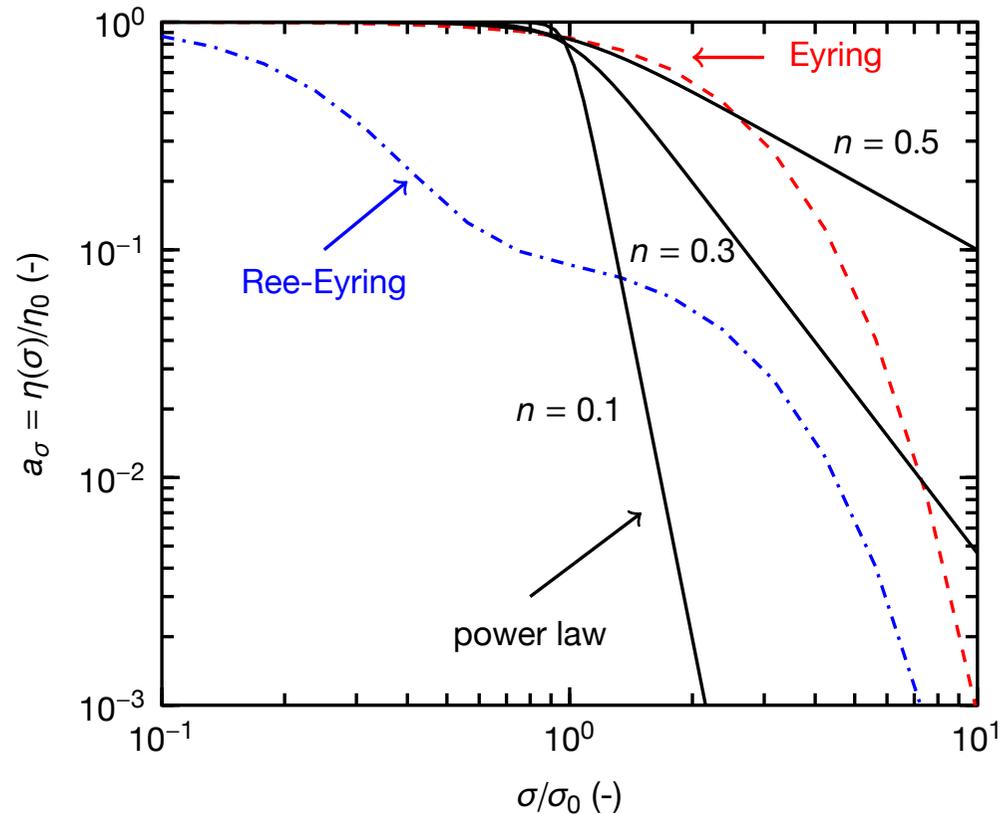
$$\eta(\sigma_{eq}) = \eta_0 a_\sigma(\sigma_{eq})$$

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

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



Pagani et al. J. Rheol, 2024

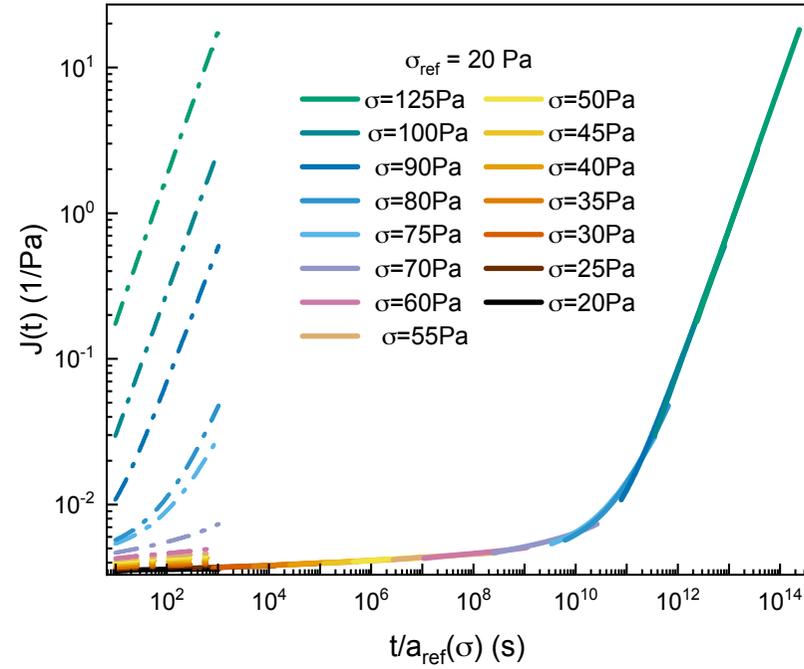
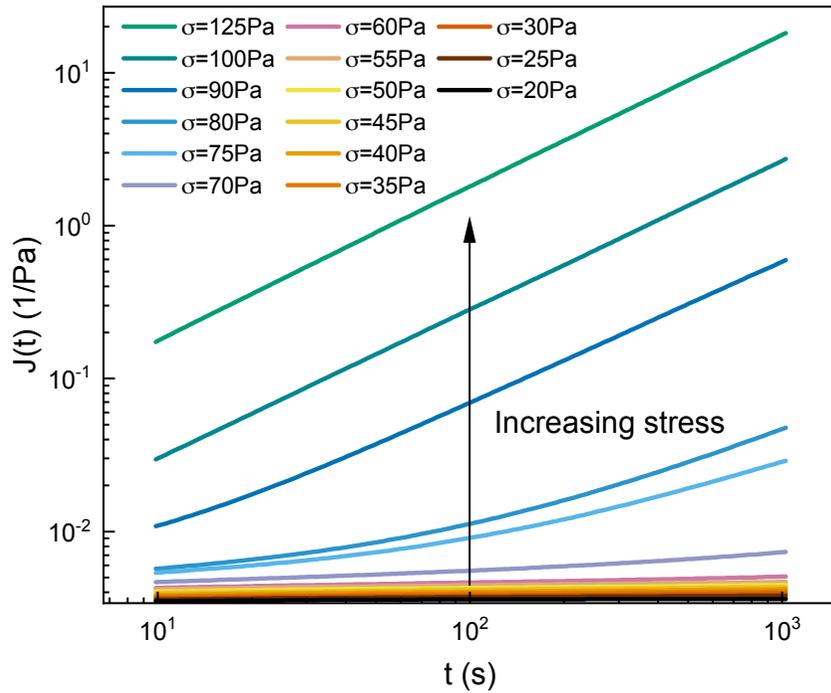


$$\eta_{RE}(\sigma_{eq}) = \eta_0^{RE} \left(\left(\frac{\eta_{01}}{\eta_0^{RE}} \right) \frac{\left(\frac{\sigma_{eq}}{\sigma_{01}} \right)}{\sinh \left(\frac{\sigma_{eq}}{\sigma_{01}} \right)} + \left(\frac{\eta_{02}}{\eta_0^{RE}} \right) \frac{\left(\frac{\sigma_{eq}}{\sigma_0} \right)}{\sinh \left(\frac{\sigma_{eq}}{\sigma_0} \right)} \right) = \eta_0^{RE} a_\sigma^{RE}(\sigma_{eq}),$$

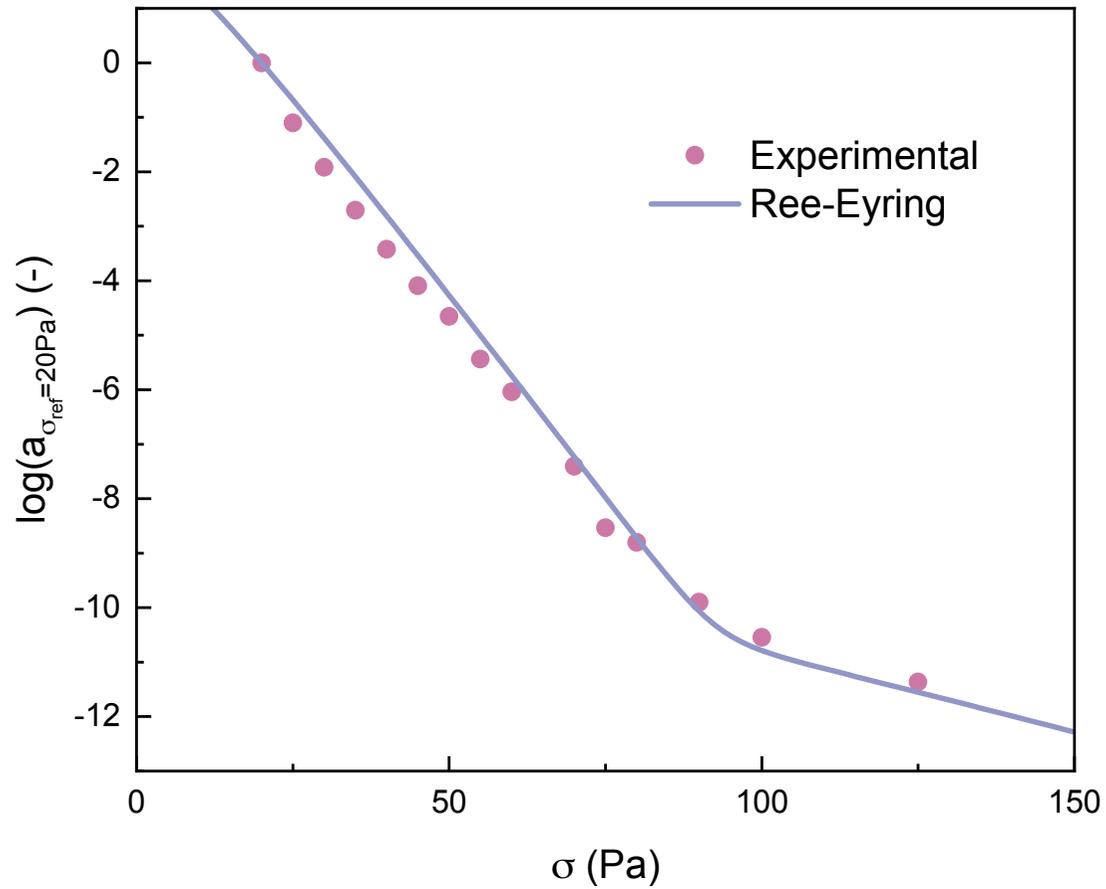
Eyring, H. (1936). Viscosity, plasticity, and diffusion as examples of absolute reaction rates. *The Journal of chemical physics*, 4(4), 283-291.

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



Experimental shift factor / Red Eyring



$$\log a^{\text{RE}}(\sigma)_{\sigma_{\text{ref}}} = \log \left(\frac{a_{\sigma}^{\text{RE}}}{a_{\sigma_{\text{ref}}}^{\text{RE}}} \right) = \log \left(\frac{\frac{\sigma/\sigma_{01}}{\sinh(\sigma/\sigma_{01})} + c_{12} \frac{\sigma/(\sigma_{01}+\sigma_{02})}{\sinh(\sigma/(\sigma_{01}+\sigma_{02}))}}{\frac{\sigma_{\text{ref}}/\sigma_{01}}{\sinh(\sigma_{\text{ref}}/\sigma_{01})} + c_{12} \frac{\sigma_{\text{ref}}/(\sigma_{01}+\sigma_{02})}{\sinh(\sigma_{\text{ref}}/(\sigma_{01}+\sigma_{02}))}} \right), \quad c_{12} = \frac{\eta_{02}}{\eta_{01}}$$

A minimal model for Elasto-Visco-plasticity

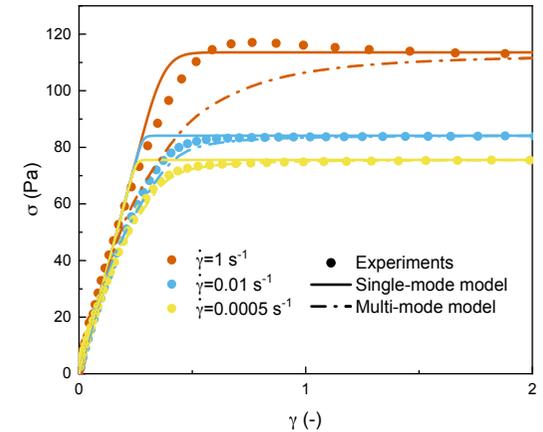
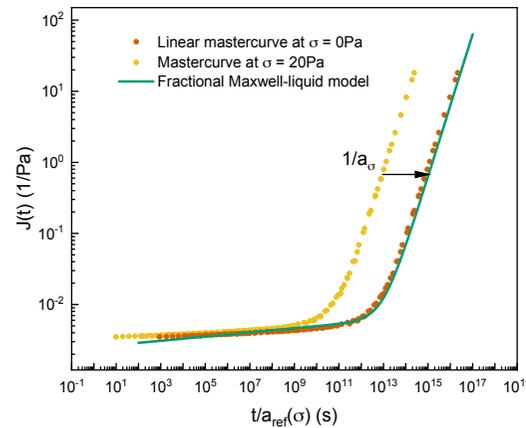
integral form

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

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

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

$$a_{\sigma}(\sigma) = \frac{\eta_{01}}{\eta_0} \frac{\left(\frac{\sigma}{\sigma_{01}}\right)}{\sinh\left(\frac{\sigma}{\sigma_{01}}\right)} + \frac{\eta_{02}}{\eta_0} \frac{\left(\frac{\sigma}{\sigma_{02}}\right)}{\sinh\left(\frac{\sigma}{\sigma_{02}}\right)}$$



A minimal model for Elasto-Visco-plasticity

tensorial form

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

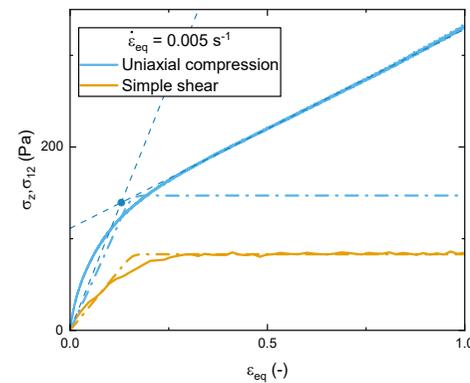
$$D_t(\mathbf{B}_e) = (\mathbf{L} - \mathbf{L}_p) \cdot \mathbf{B}_e + \mathbf{B}_e \cdot (\mathbf{L} - \mathbf{L}_p)$$

$$\sigma_{eq} = \sqrt{\frac{1}{2}\boldsymbol{\sigma}^d : \boldsymbol{\sigma}^d}$$

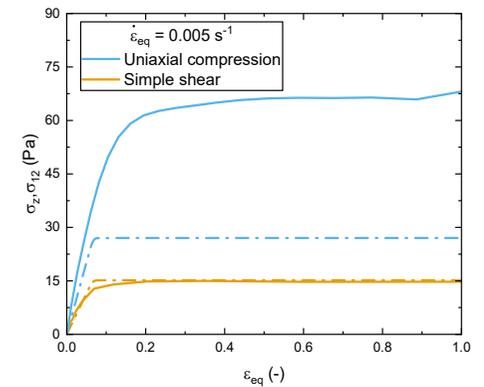
$$\mathbf{L}_p = \frac{\boldsymbol{\sigma}^d}{2\eta(\sigma_{eq})}$$

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

uniaxial compression



(a) 1% dispersion



(b) 0.15% dispersion

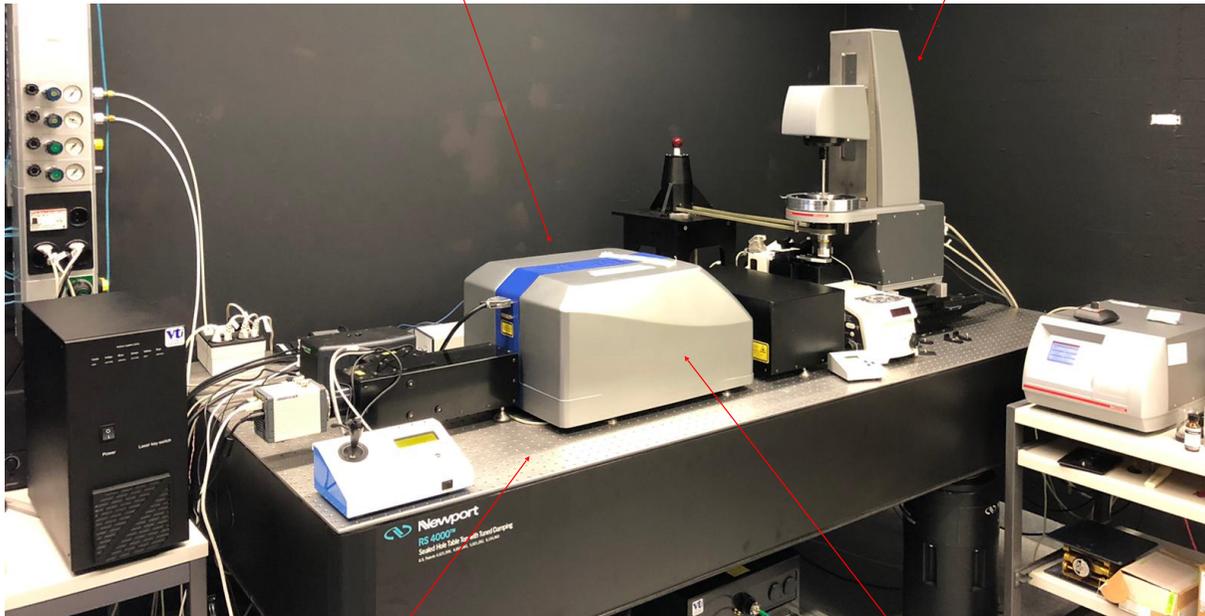
outline

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Experimental setup

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

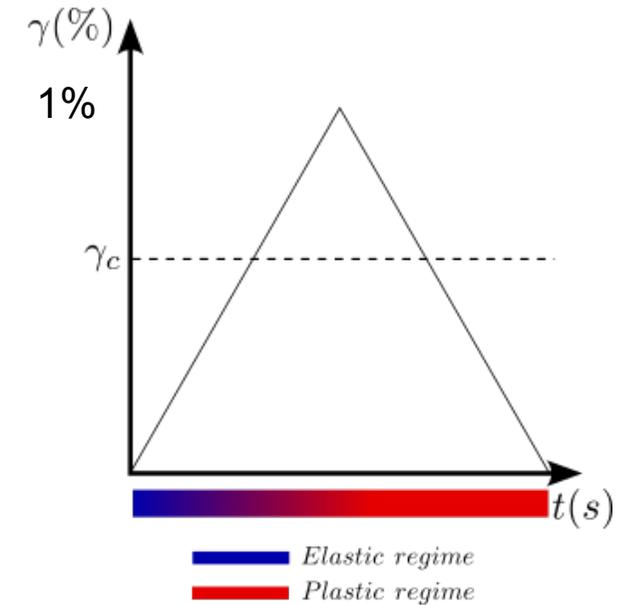
Stress-controlled rheometer



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

Confocal scanner
1000 FPS full frame

Flow reversal experiment

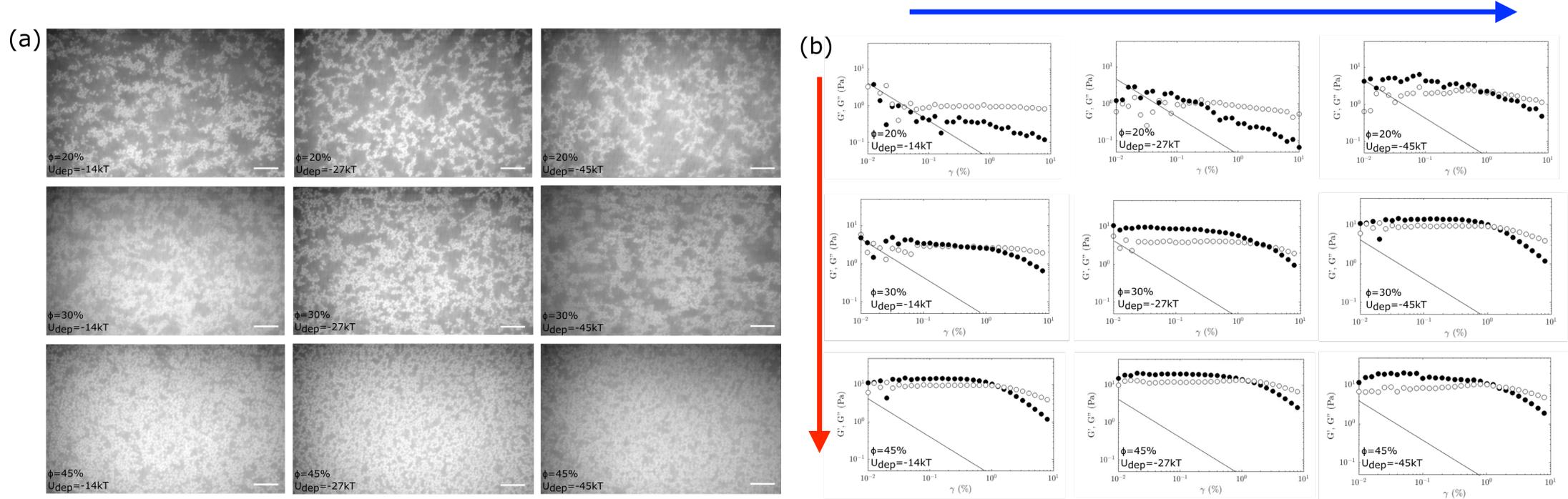


Colombo et al., Korea-Aust. Rheol. J. 31, 2019

System studied : PMMA-g-PHSA weak depletion system

$$\phi, U_{kT}$$

Gels observed and measured after a pre-shear at $Pe = 20$

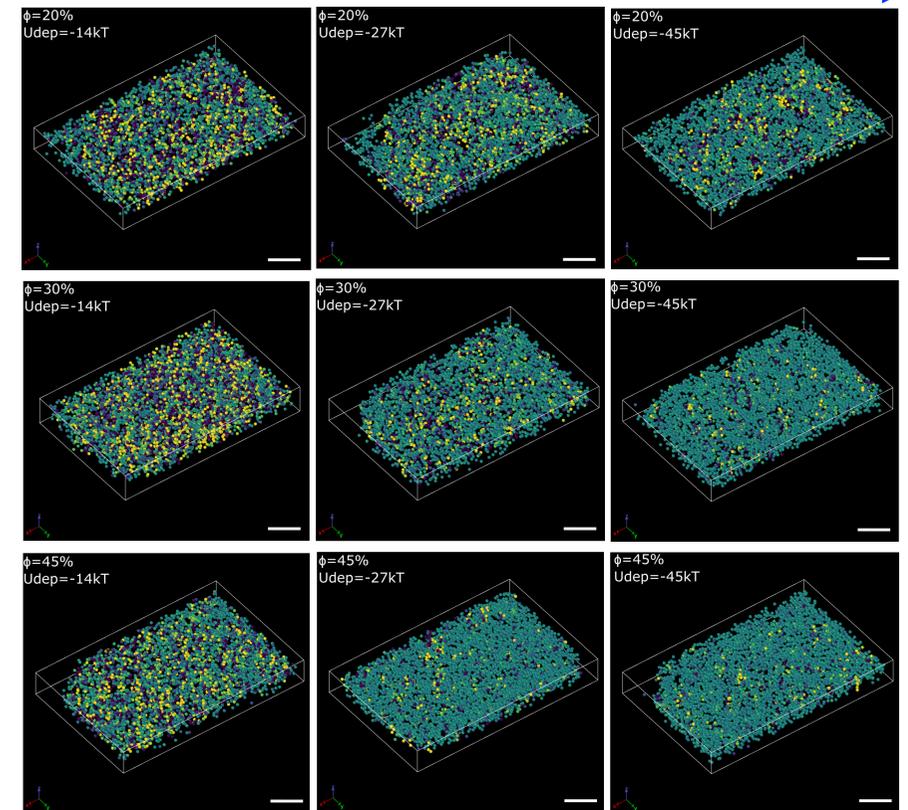
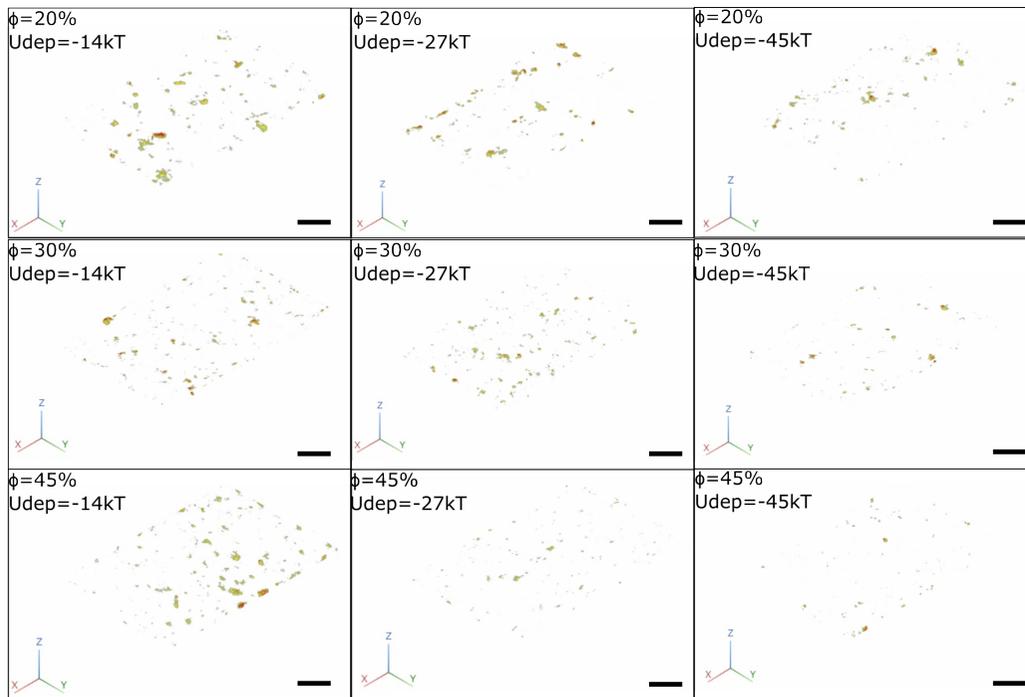


Detection of plastic events by optical flow and particle tracking

$$\phi, U_{kT}$$

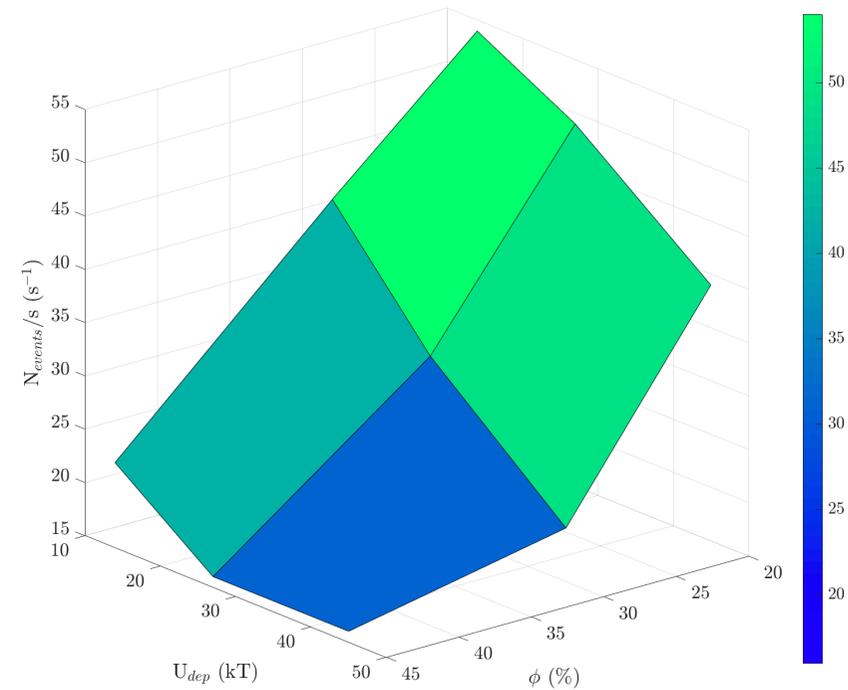
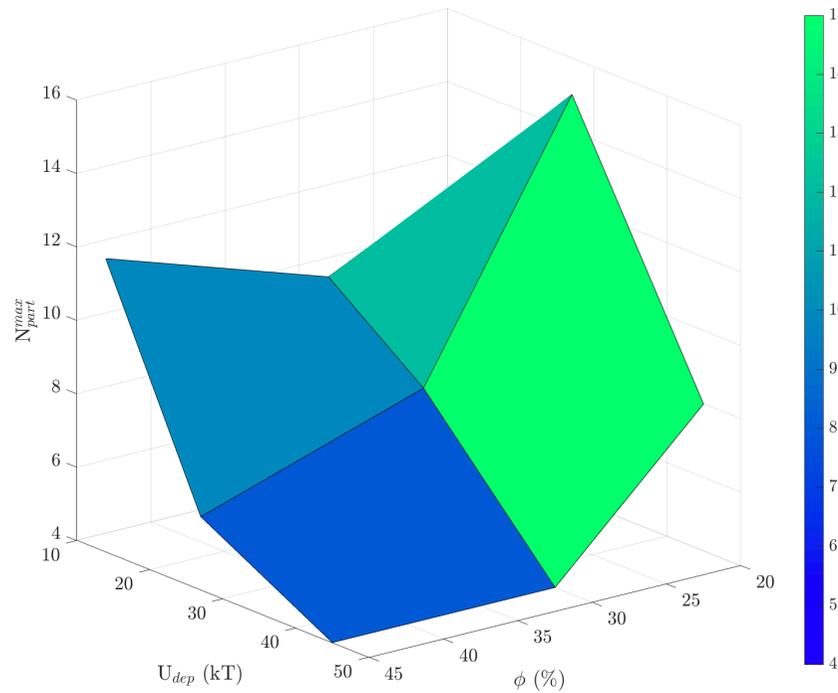
Detection of discontinuities with optical flow...

... linked to the local strain field



A first analysis of the plastic events from a small dataset

ϕ , U_{kT}



More particles involved in plasticity...

...and more particle movements

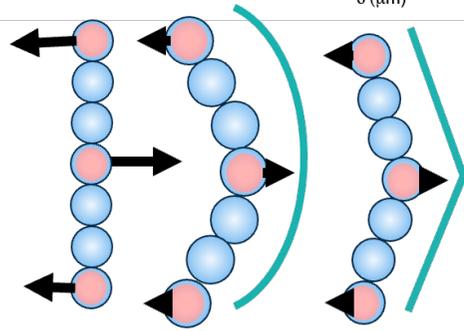
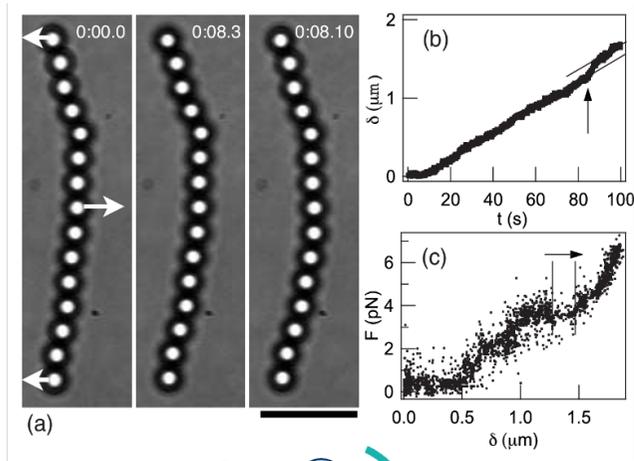
at low volume fraction and low interaction strength

Lower activation barrier to trigger plastic events

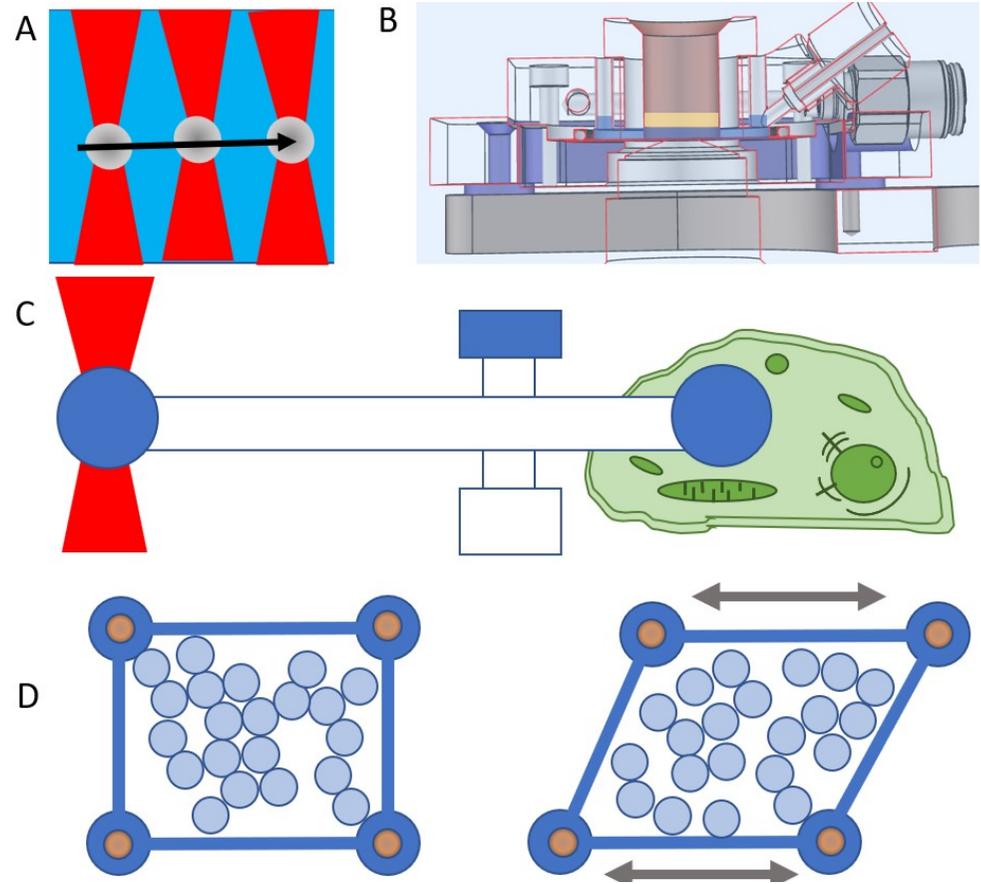
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Optical Tweezers



Furst, E., J. Pantina. *Physical Review E* 75.5 (2007): 050402.



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