ETH zürich

Simplified industrial dispersions

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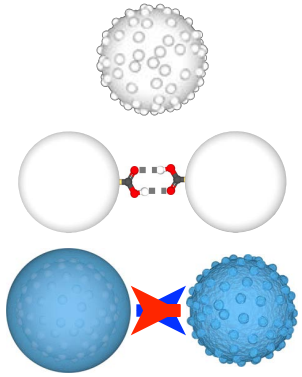
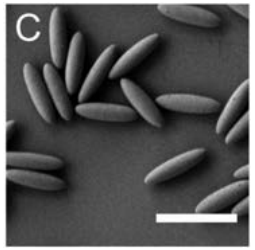
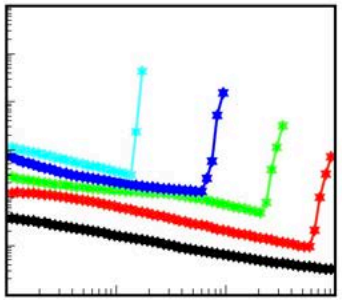
Complexity in model systems

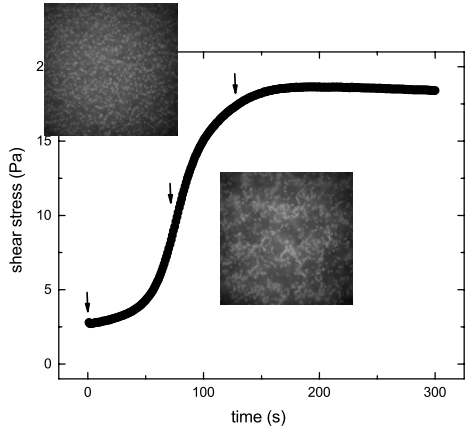




Simplified industrial dispersions

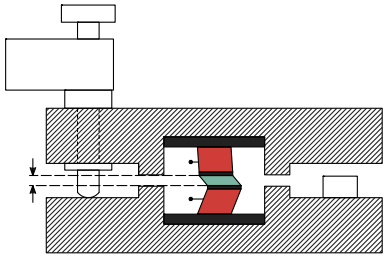


shear thickening

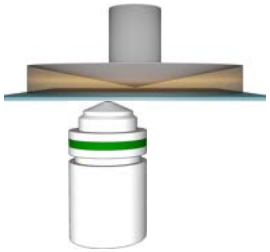


thixotropy

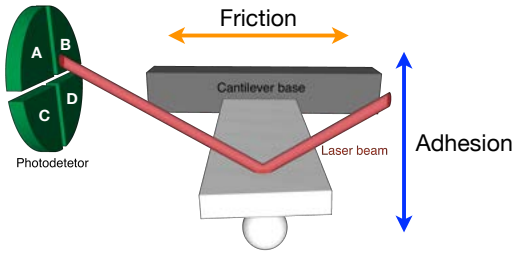
Analytical, structural and rheological methods tailored to interrogate structure



stress deconvolution



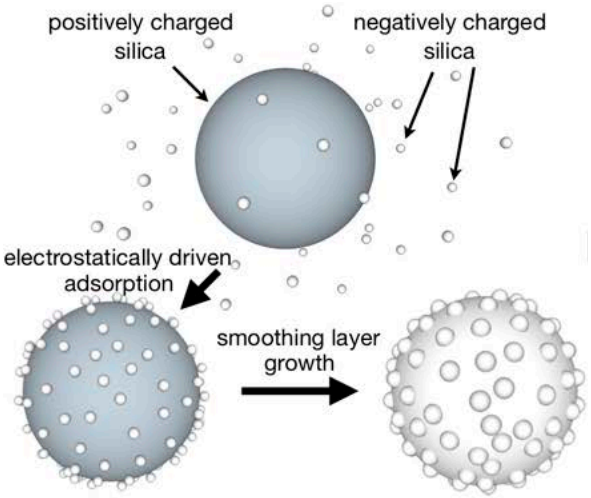
4D-imaging

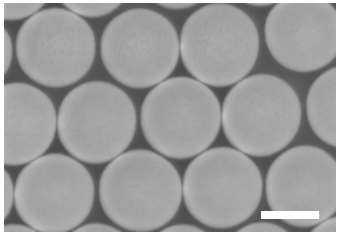


local scale tribology

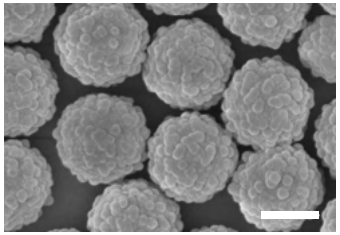
- Objectives
- Shear thickening : roughness and adhesion
- Thixotropy : strength and adhesion
- Conclusions / outlook

Model rough colloids

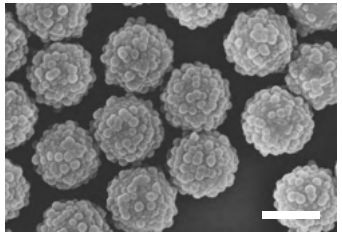




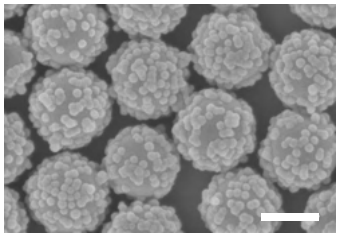
≈0



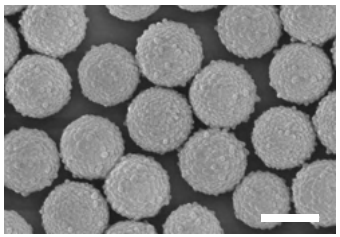
0.25±0.028



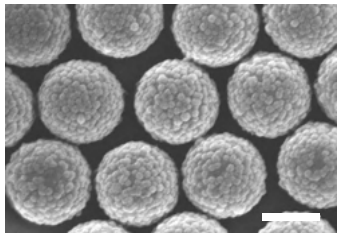
0.31±0.035



0.36±0.039

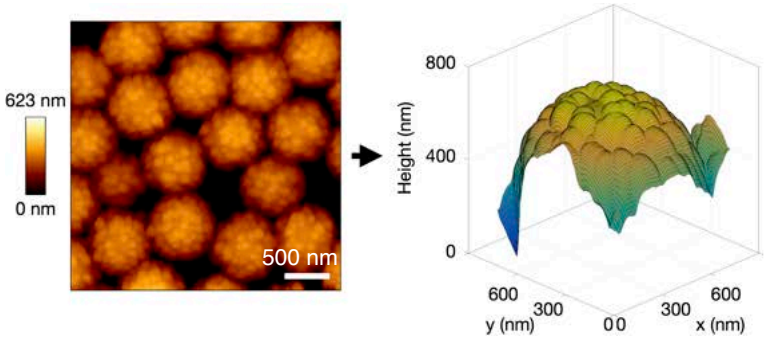


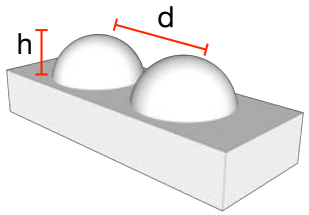
0.45±0.049



0.53±0.047

Scale bars = 500 nm





h: asperity height
d: inter-asperity distance

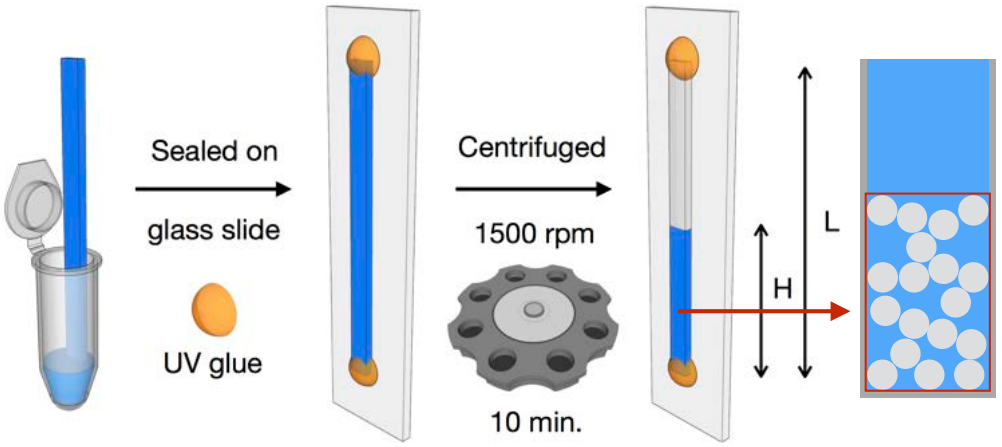
Dimensionless roughness parameter h/d

C. P. Hsu *et al.*, *PNAS* 115, (2018).

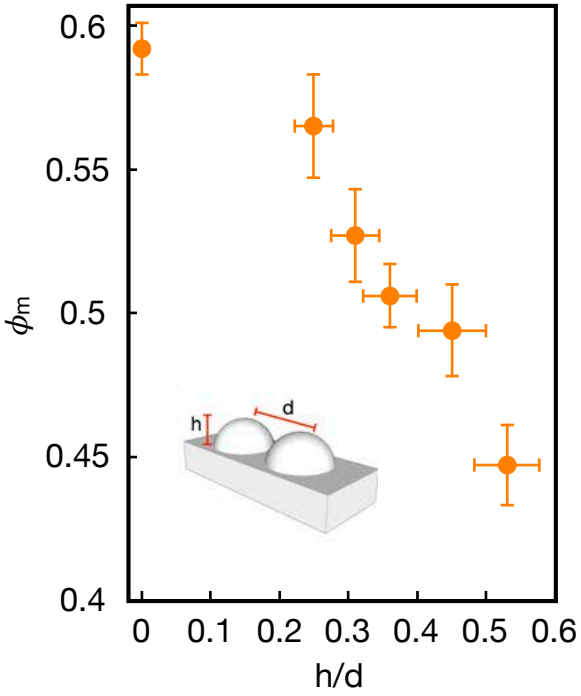
Sedimentation

characterization

ϕ_m, frictional packing fraction



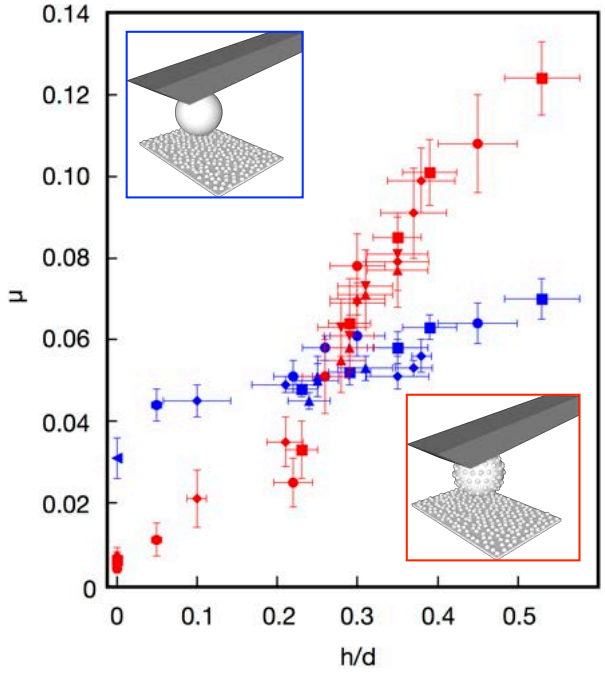
After centrifugation
H/L = ϕ_m

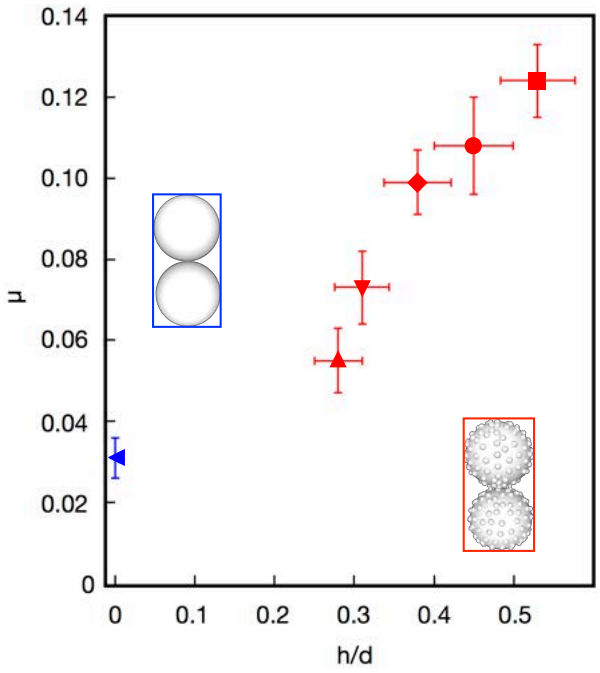


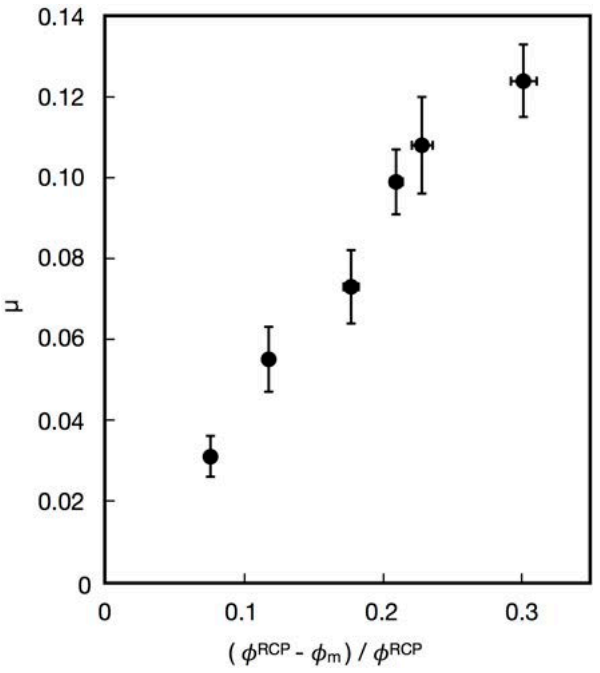
C. P. Hsu *et al.*, *PNAS* 115,

Higher h/d ➡
Lower ϕ_m

Rheology Meets Tribology





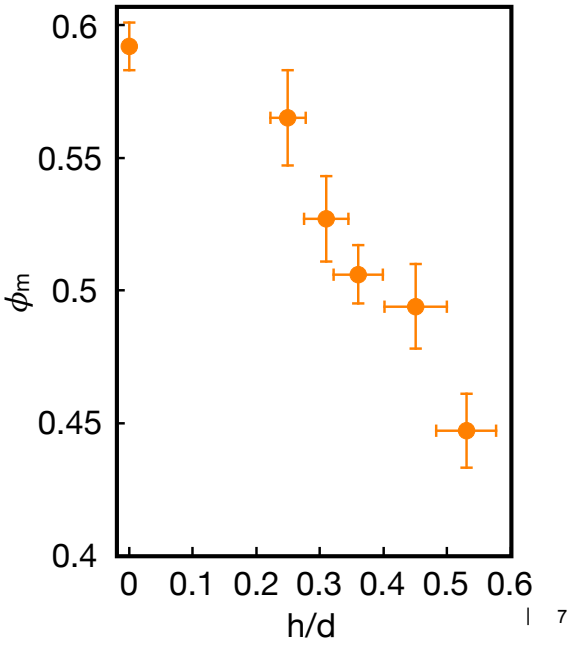


C. P. Hsu *et al.*, *PNAS* 115, (2018).

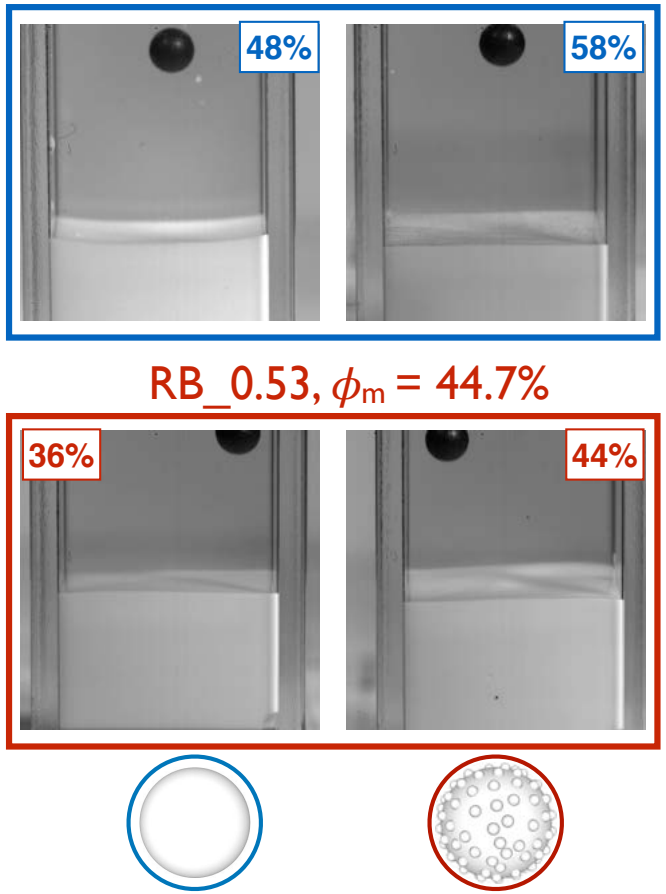
characterization : AFM

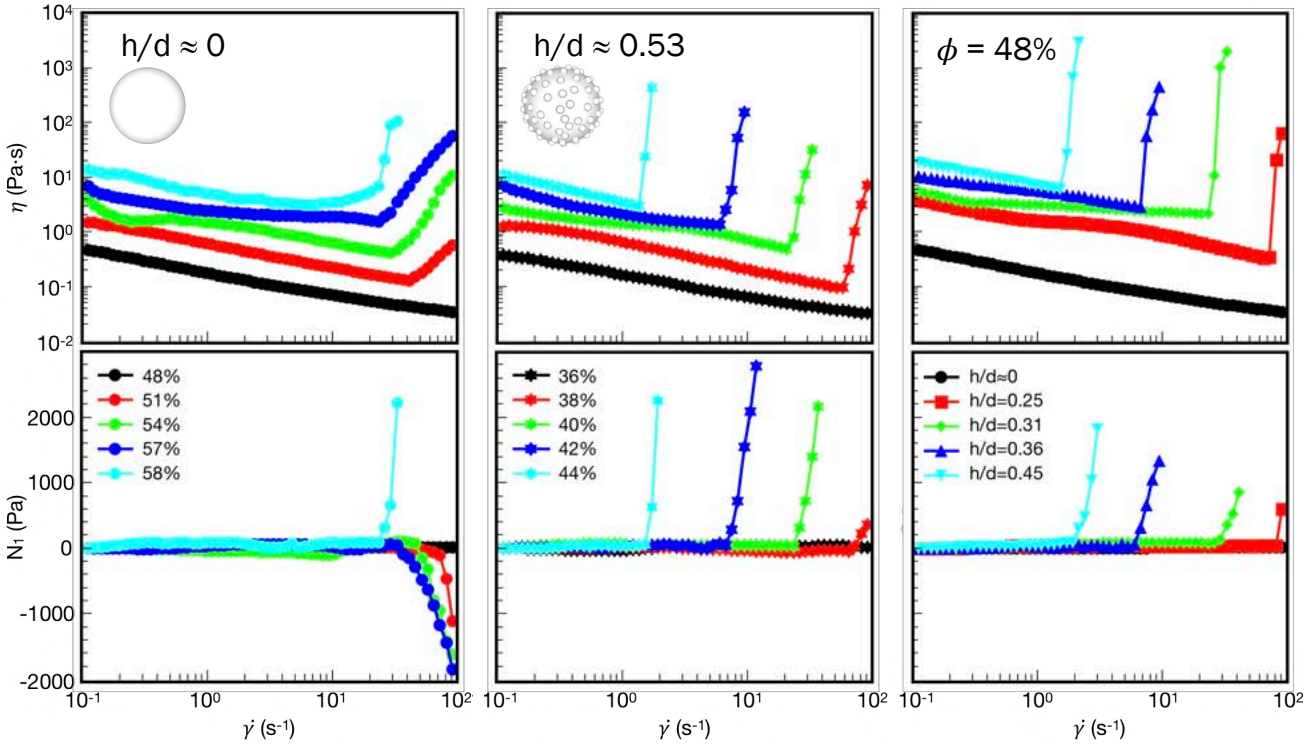
surprisingly simple relation

(topographic friction)



Smooth, ϕ_m = 59.2%





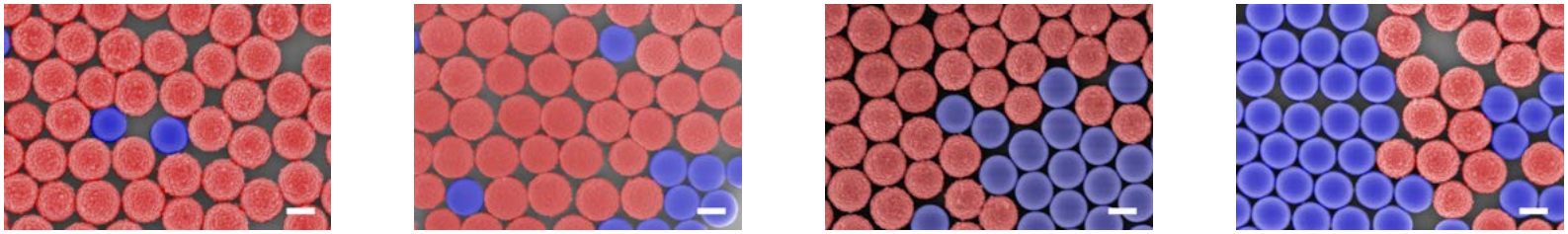
CST to DST

No CST

C. P. Hsu *et al.*, *PNAS* 115,

Rheology Meets Tribology

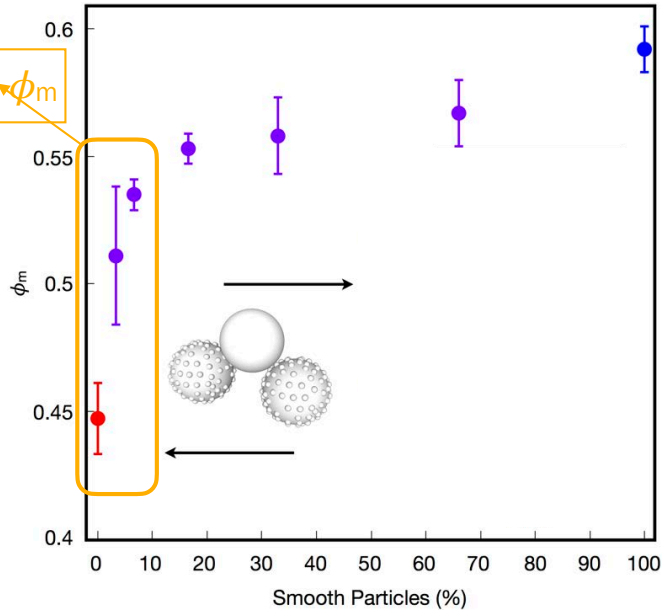
Friction between particles

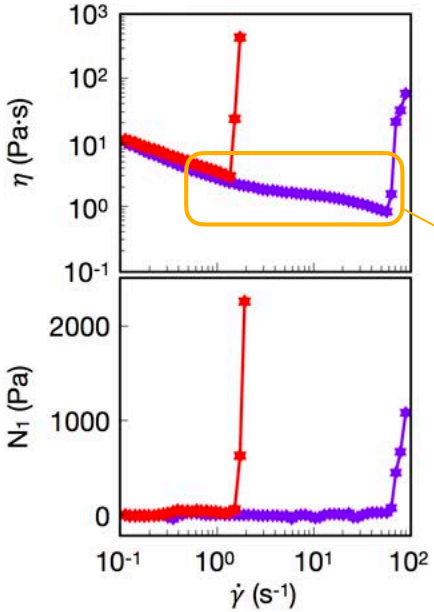


Scale bars = 500 nm

Vol% of smooth particles

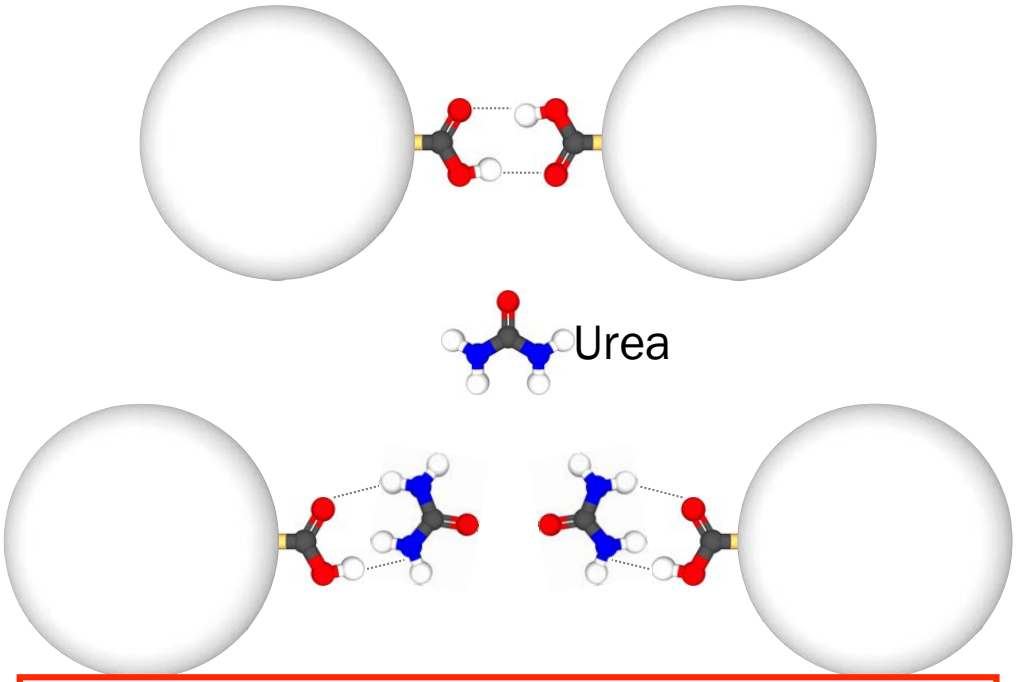
Large increase in ϕ_m



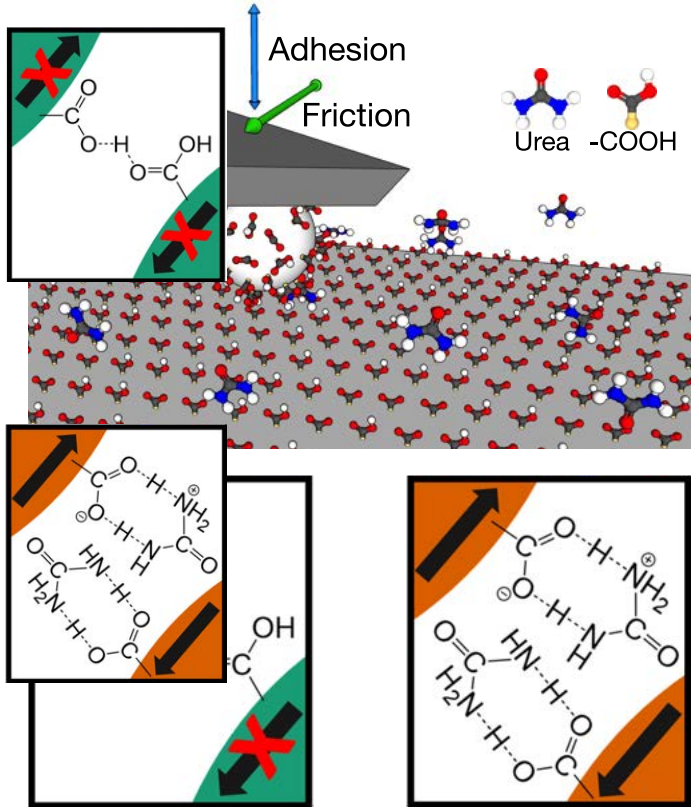


Large increase in $\dot{\gamma}_c$

Interparticle Hydrogen Bounding



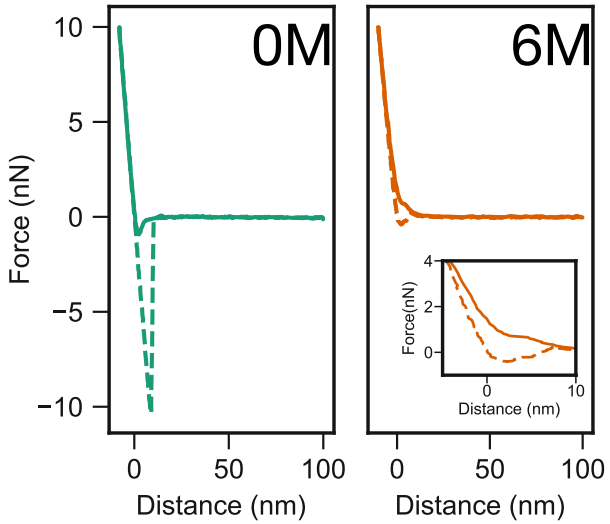
What is the role of adhesion introduced by interparticle hydrogen bonding?

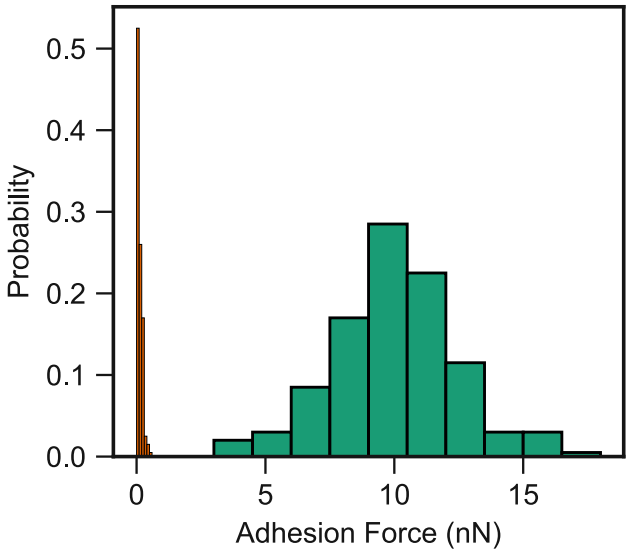


N. James & C. P. Hsu *et al.*, *JPCL* 10, (2019).

Adhesion ↔ Friction

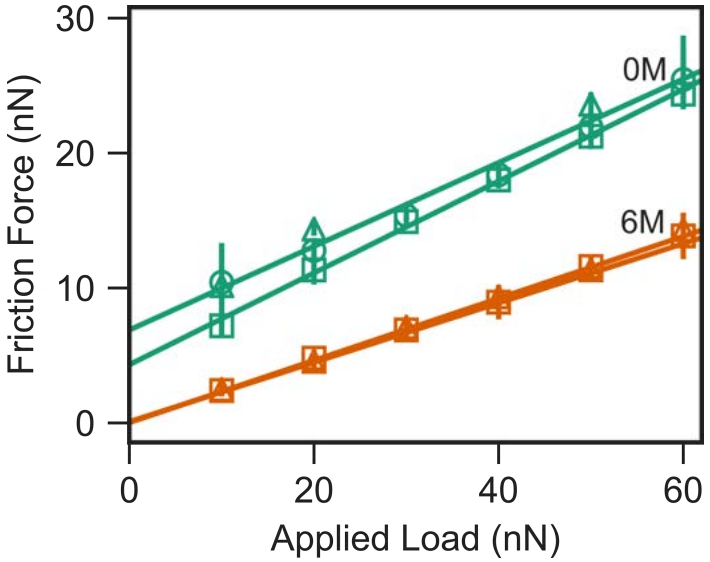
1 hr equilibration
in 69% (v/v) glycerol/water





F_{ad} = 10.0 ± 2.5 nN
F_{ad} ≈ 0.1 nN

$F_{friction} = F_0 + \mu \cdot L$

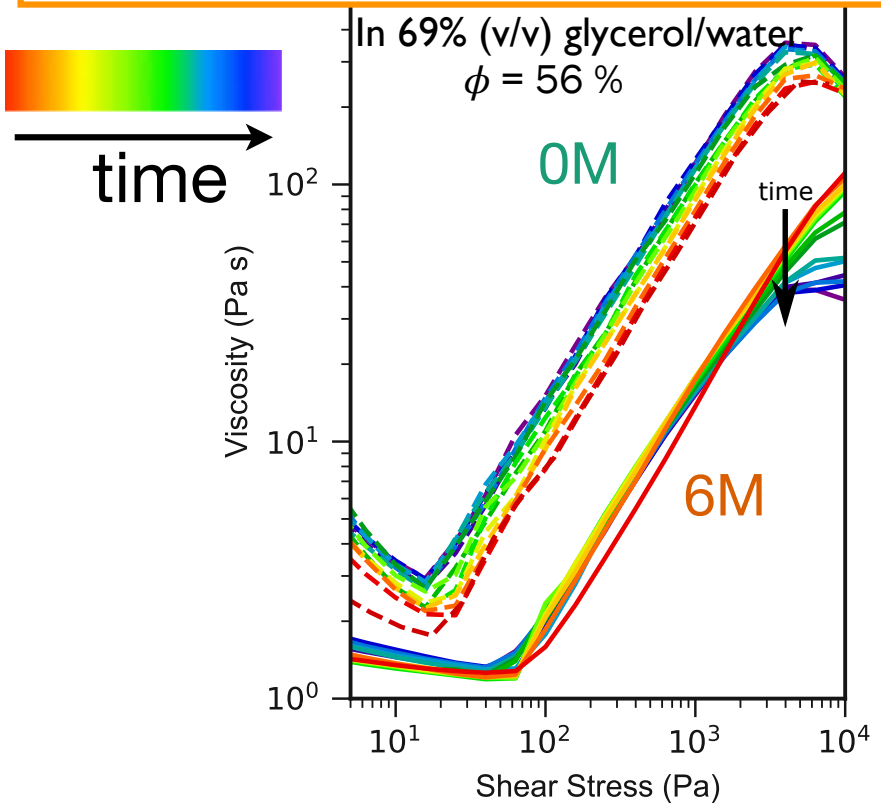


μ = 0.33 μ = 0.22

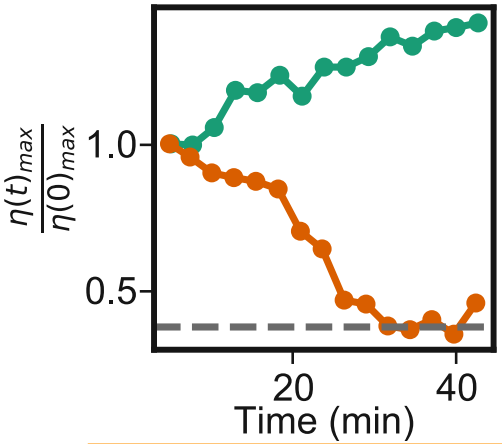
N. James & C. P. Hsu *et al.*, *JPCL* 10, (2019).

Connection to Bulk Rheology

High-shear rheology ↔ frictional interparticle interactions



N. James & C. P. Hsu *et al.*, *JPCL* 10,



Krieger-Dougherty relation

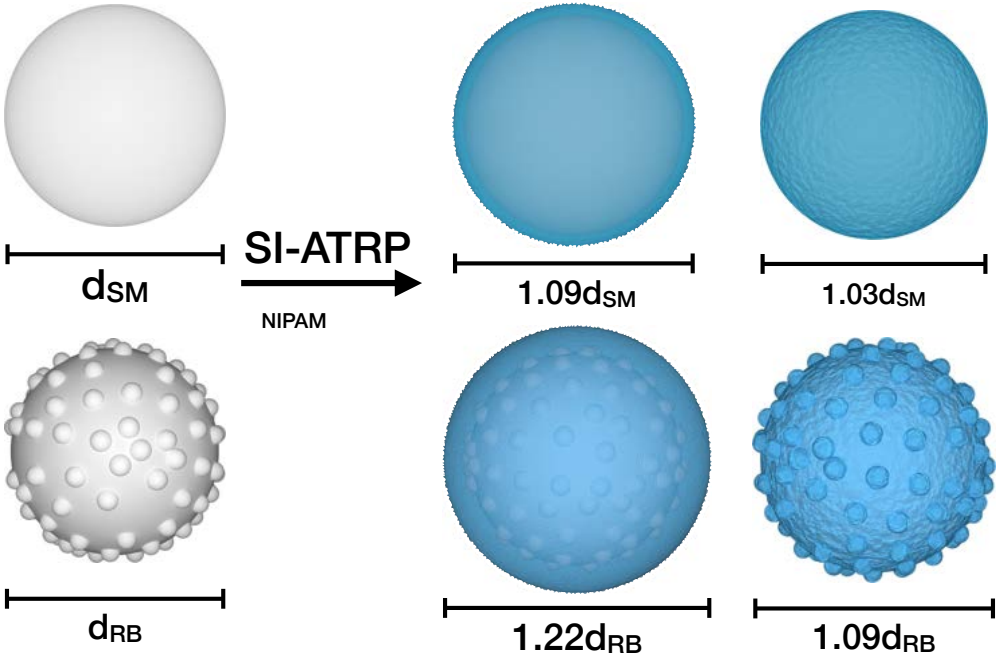
$$\eta = \eta_0 \cdot (1 - \frac{\phi}{\phi_m})^{-\alpha}$$

Urea sorption onto the particle surface

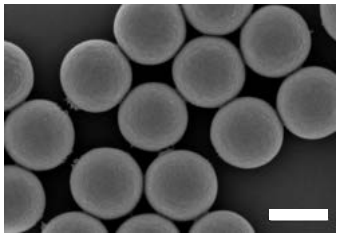
μ ⬇, F_0 ⬇

ϕ_m ⬆, η_{max} ⬇

PNIPAM-grafted Model Colloids

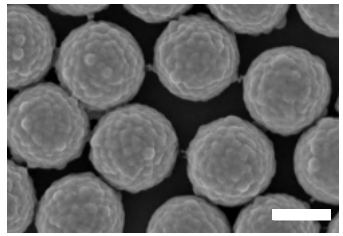


SM_PNIPAM
31 ± 3 nm



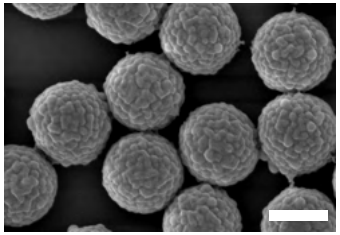
12 ± 2 nm

RB_0.36_PNIPAM
80 ± 5 nm



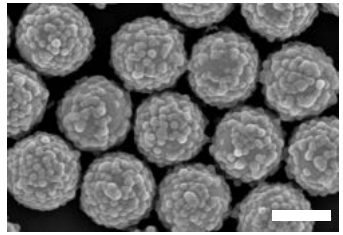
31 ± 5 nm

RB_0.46_PNIPAM
85 ± 6 nm



33 ± 3 nm

RB_0.52_PNIPAM
84 ± 6 nm

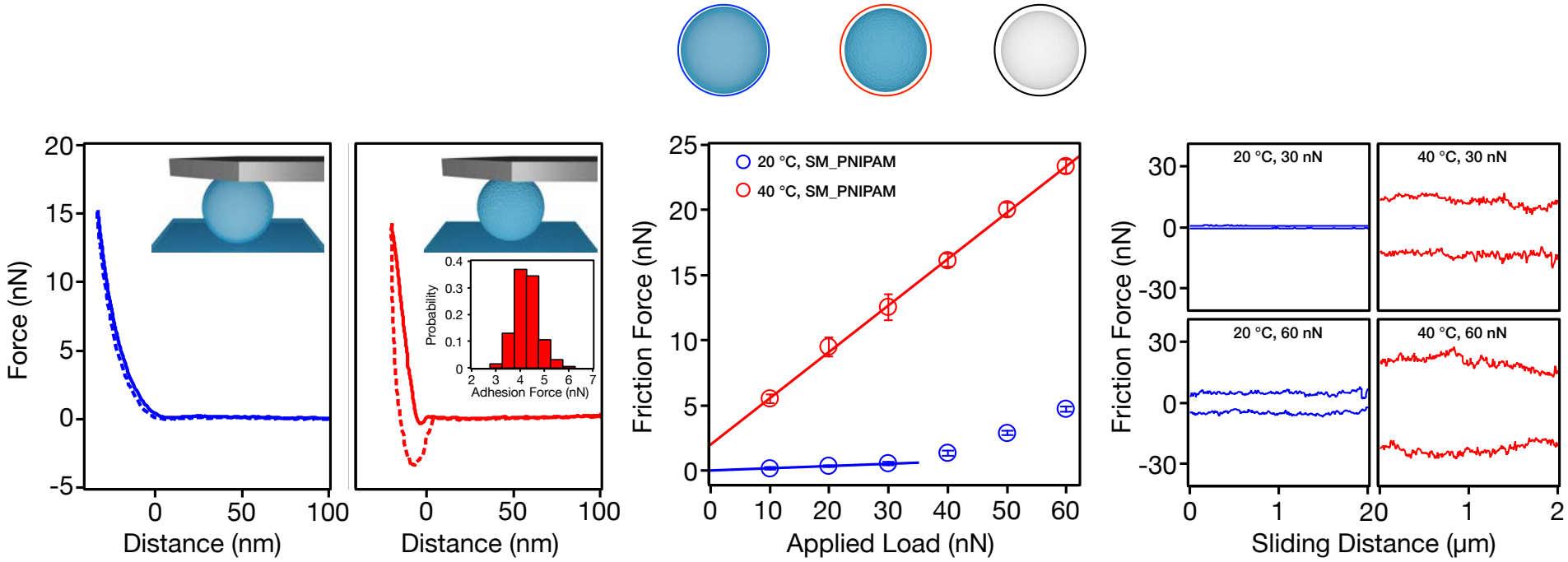


35 ± 4 nm

Scale bars = 500 nm

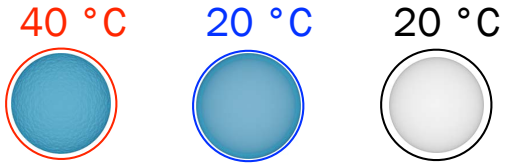
C. P. Hsu *et al.*, *arXiv:2004.05970*, (2020).

Friction ↔ Adhesion



F_{ad} = 4.2 ± 0.9 nN

C. P. Hsu *et al.*, *arXiv:2004.05970*, (2020).

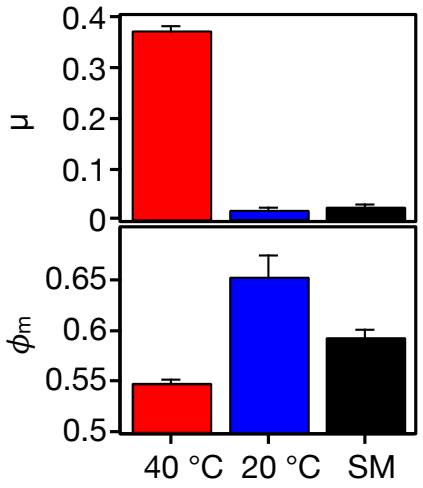


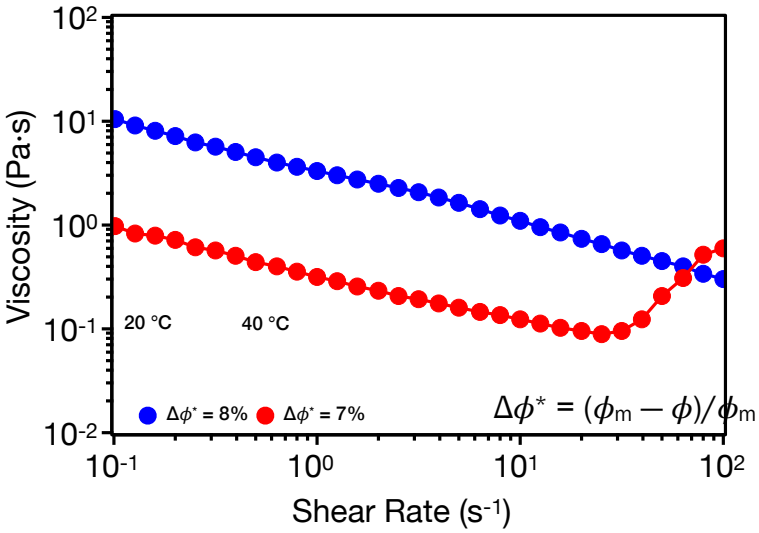
ϕ(T)

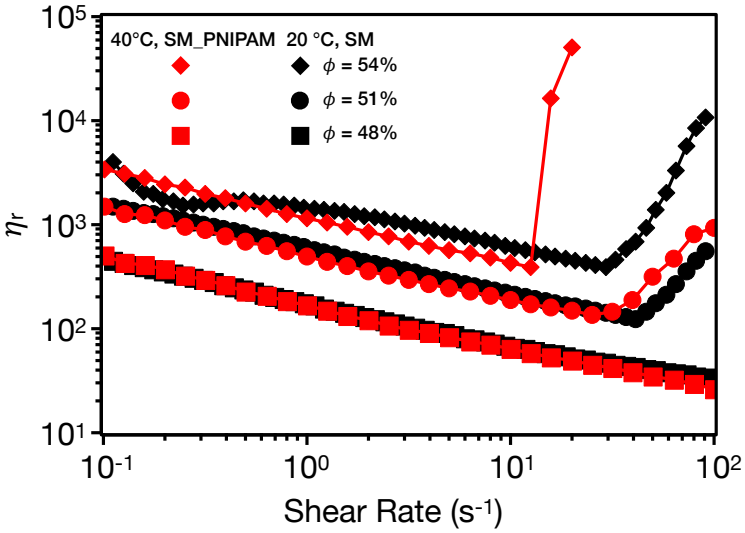
Friction ⬆ Adhesion ✔

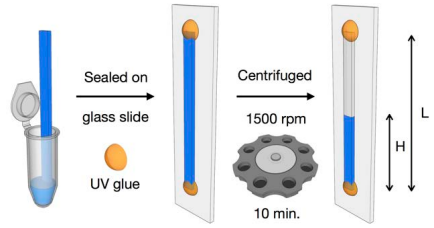
⇳

Friction ⬇ Adhesion ✖







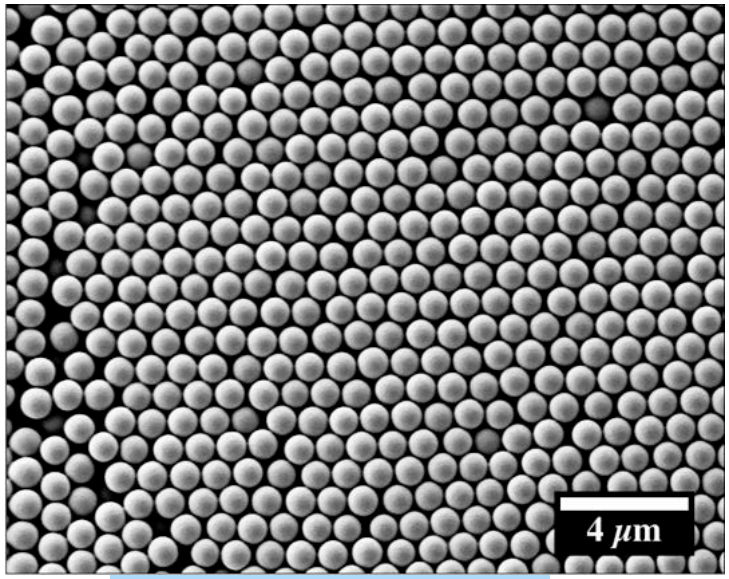


C. P. Hsu *et al.*,

- [x] Objectives
- [x] Shear thickening : roughness and adhesion
- [ ] Thixotropy : strength and adhesion
- [ ] Conclusions / outlook

Model system

Rhodamine B

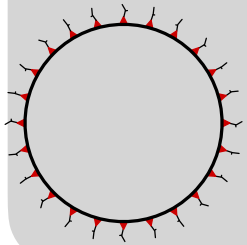


PMMA-g-PHSA (4)

$2a = 1.2\mu m$

Antl et al., *Colloids Surf.*, (1986) **17** , 67 -78
Palangetic, et al. (2016) *Faraday Discuss.* 191, 325

80% cyclobromohexane 20% cis-decalin



+ PS

$M_w = 925kDa$

$R_g = 41nm$

$\xi = 0.07$

Dissociation of Cyclobromohexane
creates HBR
Weak acid - induces charging

C. P. Royall, M. E. Leunissen, A. van Blaaderen *J. Phys.: Condens. Matter* **15** 3581 (2003)

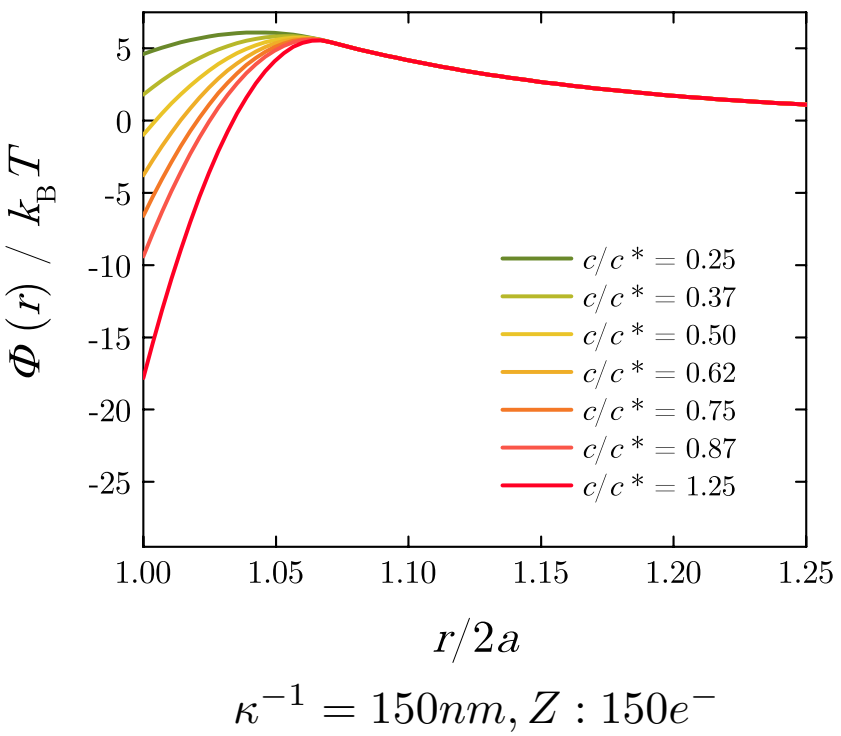
Supplier	Treatment	σ [nS/cm]	Appearance
Sigma Aldrich	as received	0.9	colorless
Sigma Aldrich	stored 2 years	2.1	colorless
Alfa Aesar	as received	6.4	colorless
Acros Organics	as received	3.1	yellowish
Acros Organics	alumina cleaned	0.05	colorless
Acros Organics	cleaned, saturated HBr	146.3	colorless
Acros Organics	cleaned, saturated HBr, 50x diluted	12.2	colorless

Control initial charge + Screen charges
tetrabutylammonium chloride or bromide
TBAC or TBAB

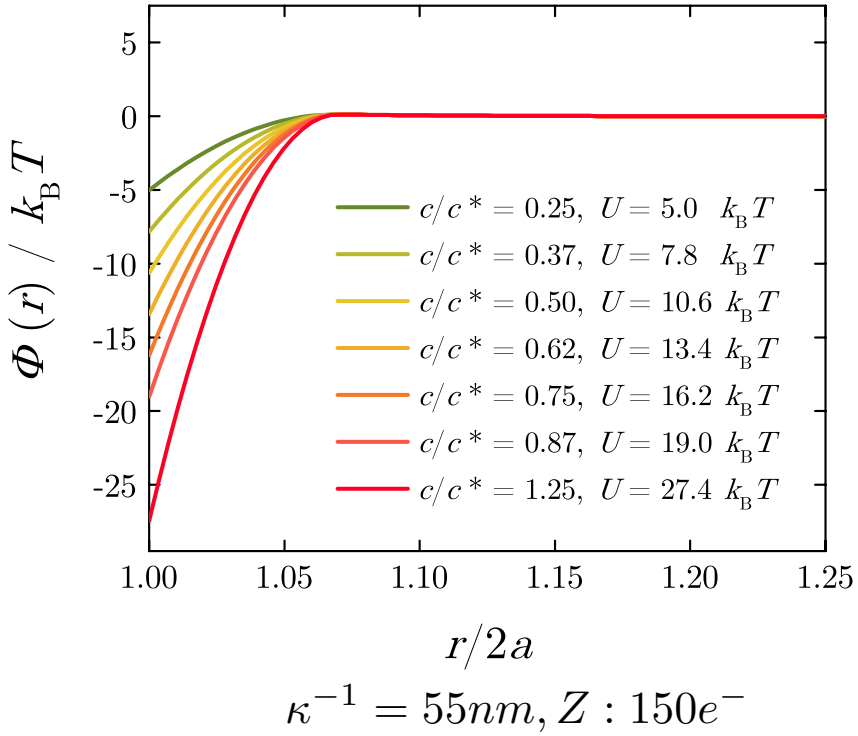
Interaction potential

Asakura-Oosawa + $$\Phi_{\mathrm{Y}}(r) = \frac{Z^2}{1+\kappa a}\frac{\lambda_{\mathrm{B}}}{2a}\frac{\exp(-\kappa 2a[r/2a-1])}{r/2a}$$

Debye length from conductivity, Z estimated from zeta potential



$\kappa^{-1} = 150nm, Z : 150e^-$



$\kappa^{-1} = 55nm, Z : 150e^-$

U

Lekkerkerker, H. N., & Tuinier, R. (2011). *Colloids and the depletion interaction* (Vol. 833). Springer.

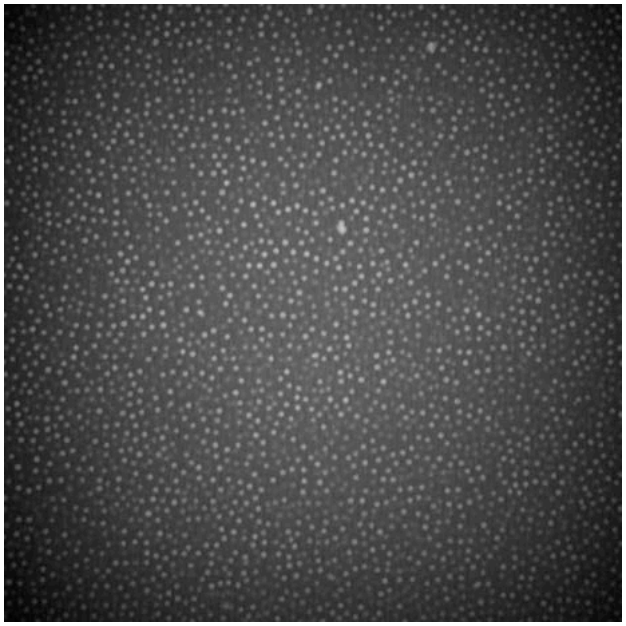
near field - steric repulsion / weak screening hydrodynamics

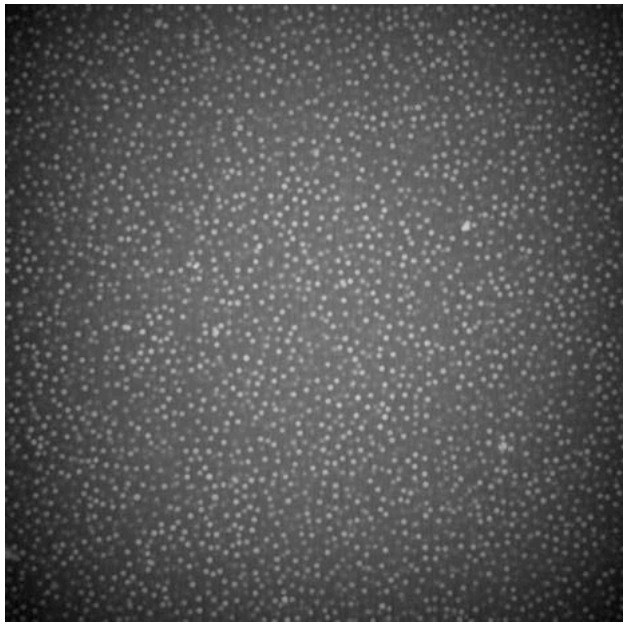
Schroyen, B., Hsu, C. P., Isa, L., Van Puyvelde, P., & Vermant, J. (2019). Stress Contributions in Colloidal Suspensions: The Smooth, the Rough, and the Hairy. *Physical Review Letters*, *122*(21), 218001.

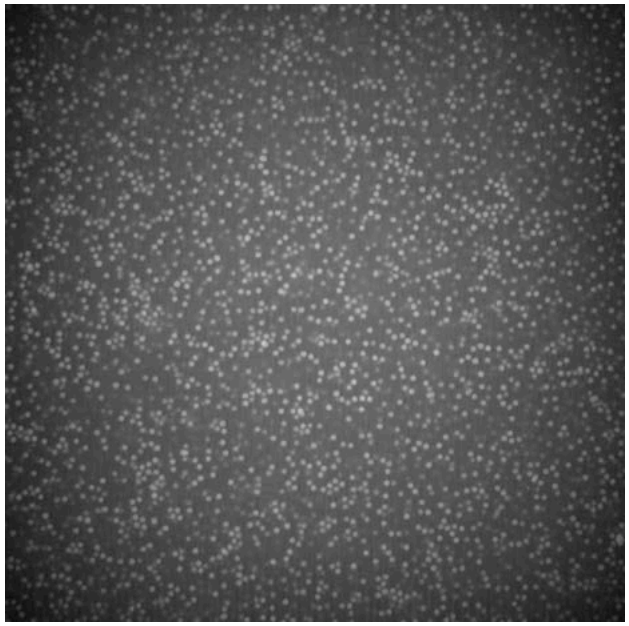
Slow, DC quenches

FOV:
100x100 µm

Φ = 0.2 (always)







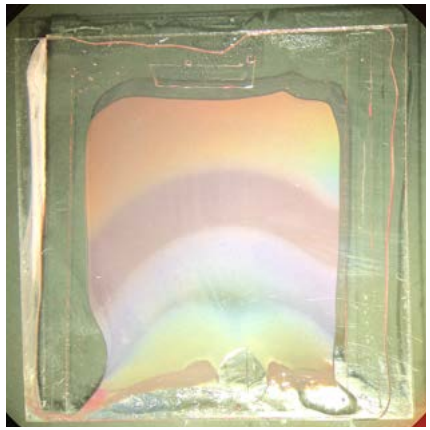
c/c* = 0.2
90 min timelapse

c/c* = 0.4
35 min timelapse

c/c* = 0.6
30 min timelapse

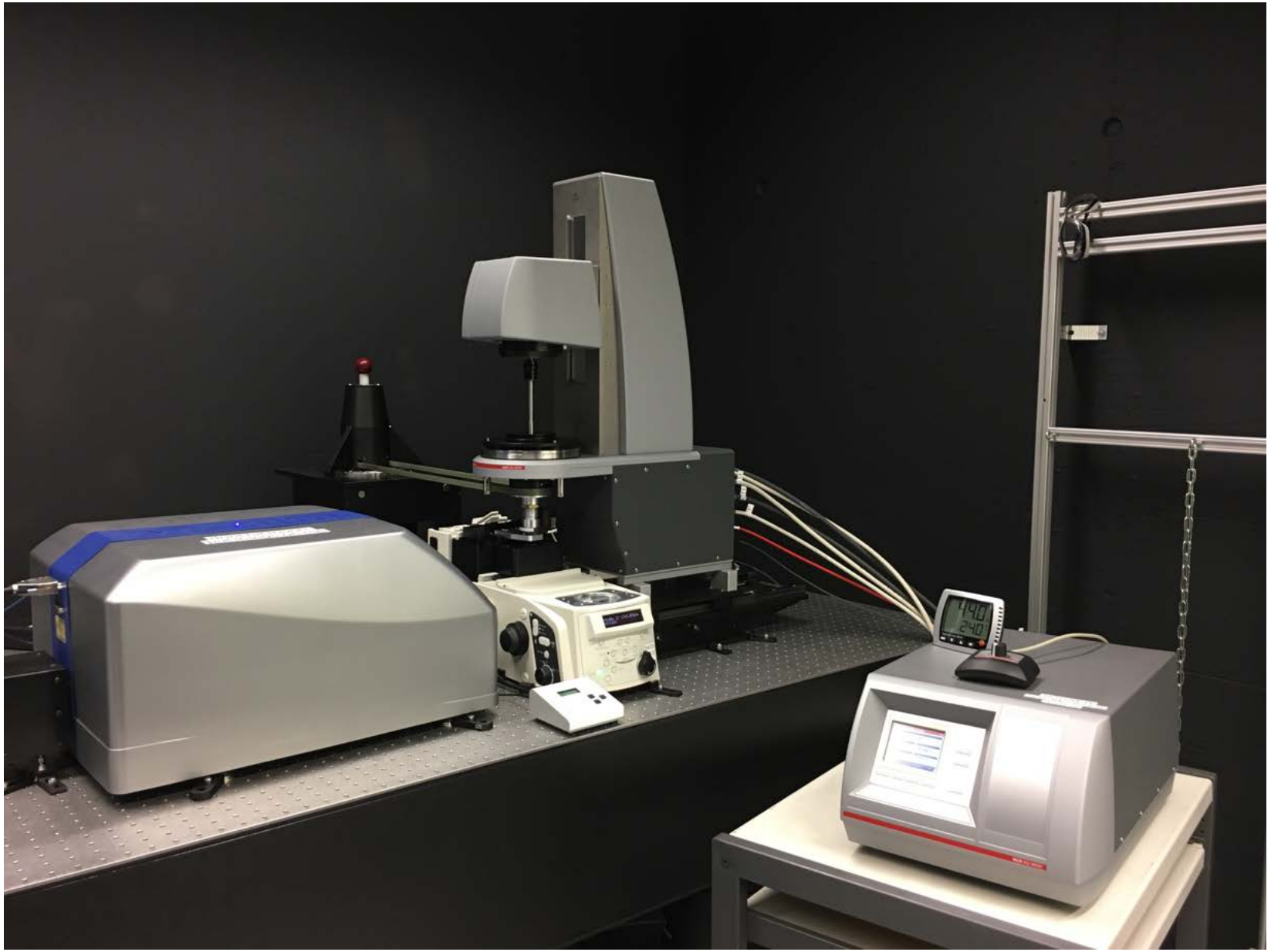
Charge-stabilized
colloid-polymer mixture

Diffusion of an organic salt
TBAC



FOV: 100x100 µm

ETH zürich Structural illumination multiarray rheo-confocal

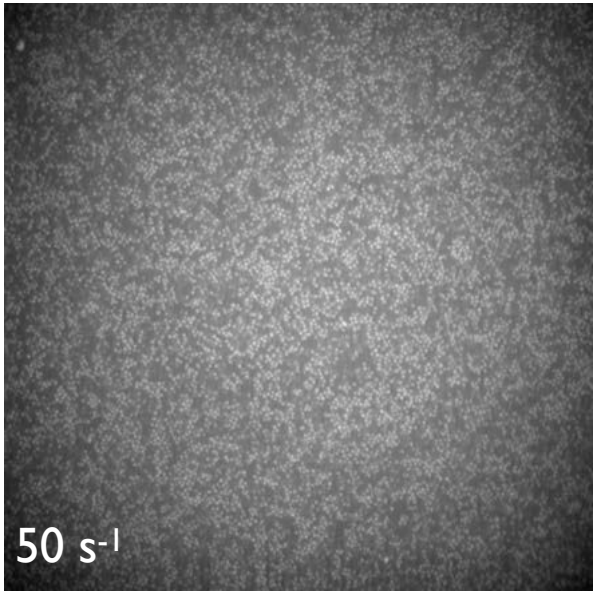


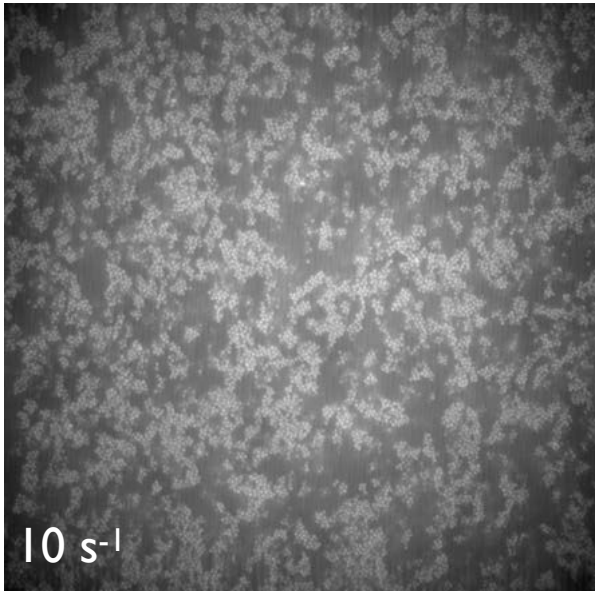
Steady state structures

$c/c^* = 0.7$

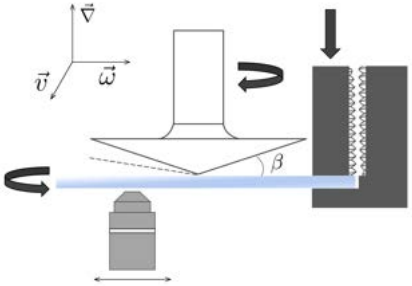
FOV: 150x150 µm

Pe = 40
real-time

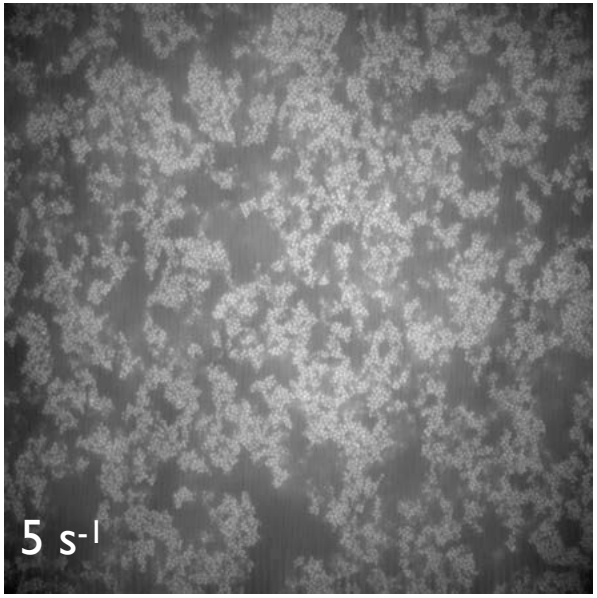


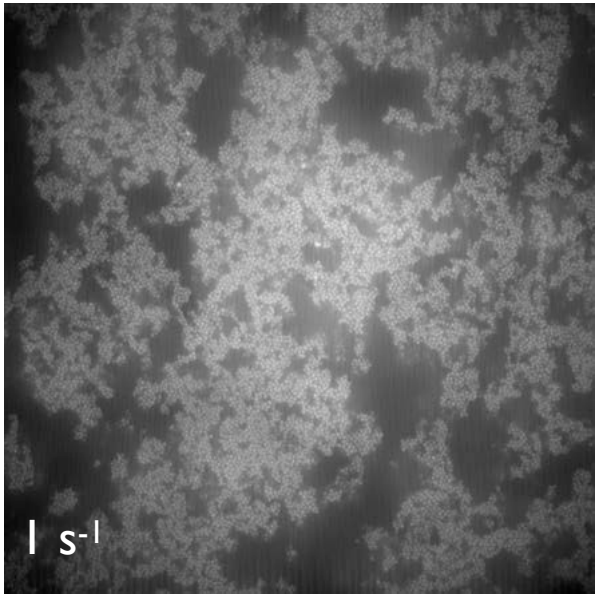


real-time



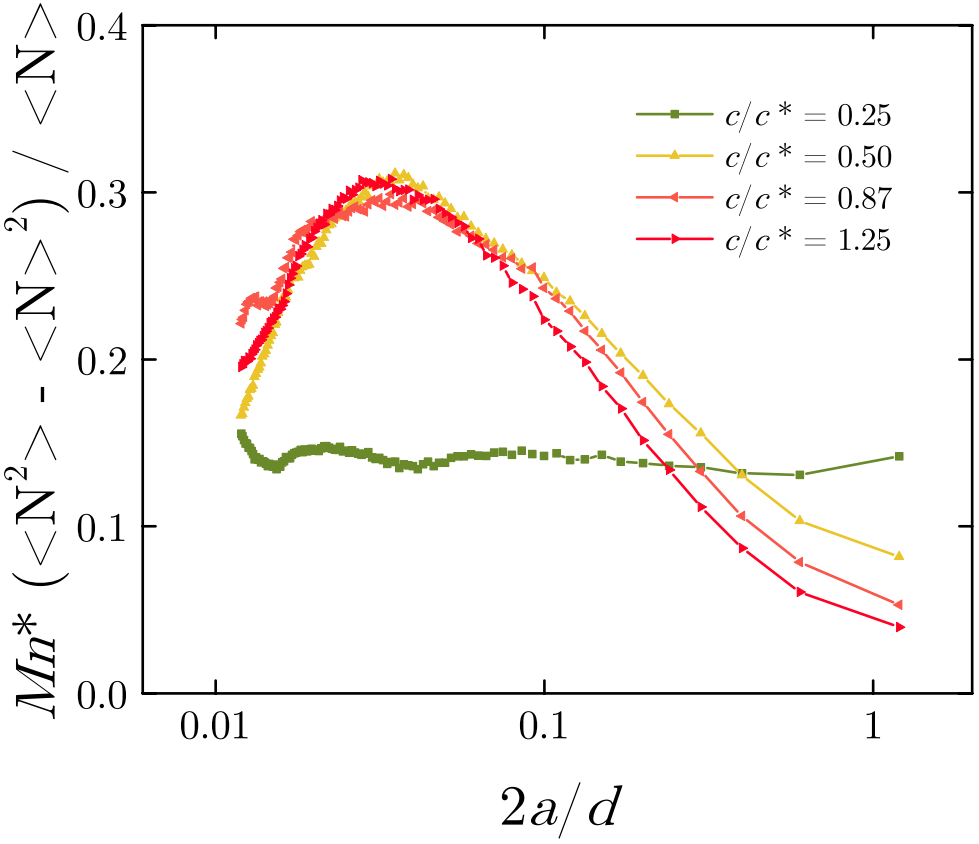
real-time





sped up 2x

Mason number scaling



$$Mn^* = MnU/(f^*\xi)$$

Z Varga, JW Swan Large scale anisotropies in sheared colloidal gels
Journal of Rheology 62 (2), 405-418

Scaling with Mn also for 2DSANS - Min Kim, J., et al.. Journal of Rheology, 58(5), 1301-1328. (2014)

Rheological stress deconvolution methods

Stress jump experiments

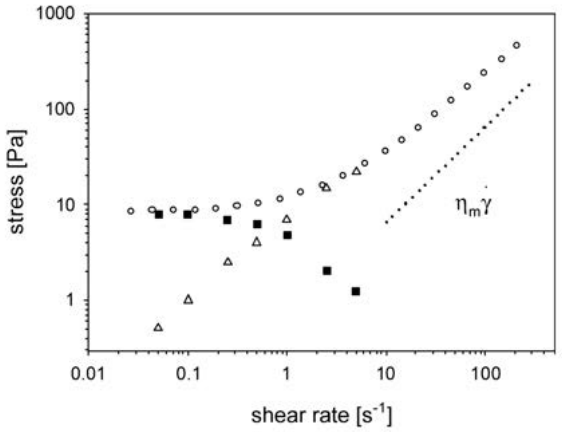
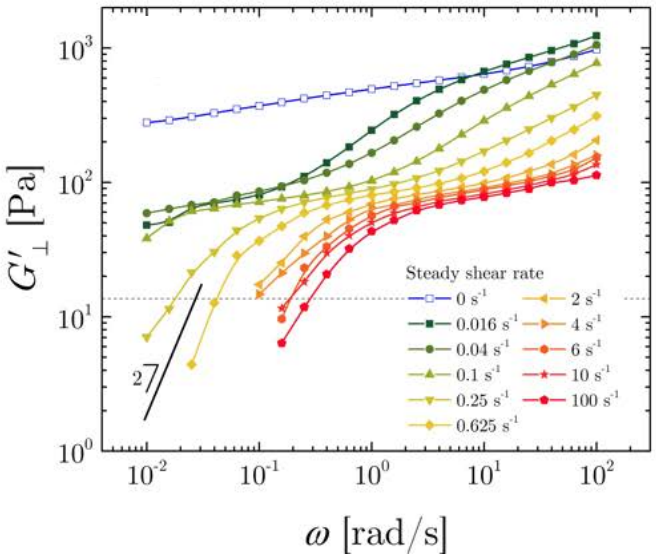


Fig. 3. Elastic (■) and viscous (△) contributions to the total steady stress (○) as a function of the shear rate (2.9 vol% fumed silica dispersion); the dotted line represents the medium contribution ($\eta_m\dot{\gamma}$).

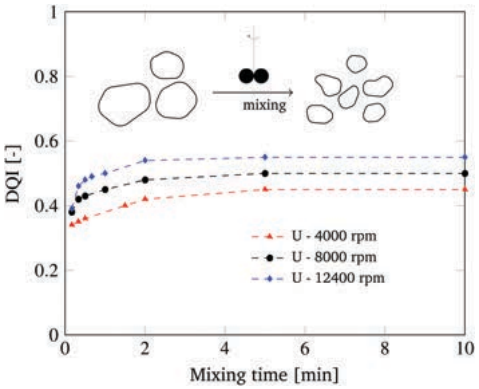
K. Dullaert, J. Mewis, *J. Colloid Interface Sci.* **287** 542 (2005)

Orthogonal superposition rheometry



G. Colombo et al. *J. Rheol.* **61** 1035 (2017)

HF rheology non-ideal systems

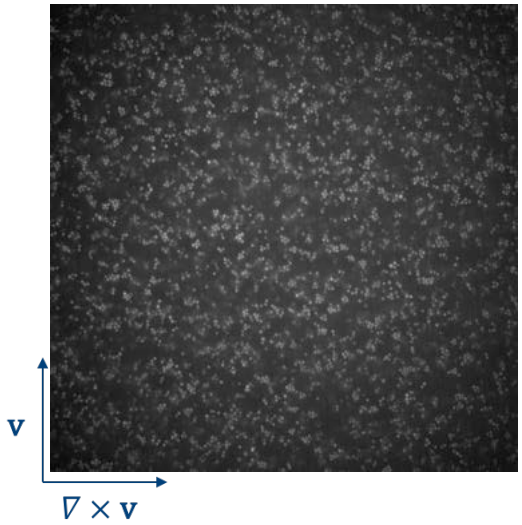


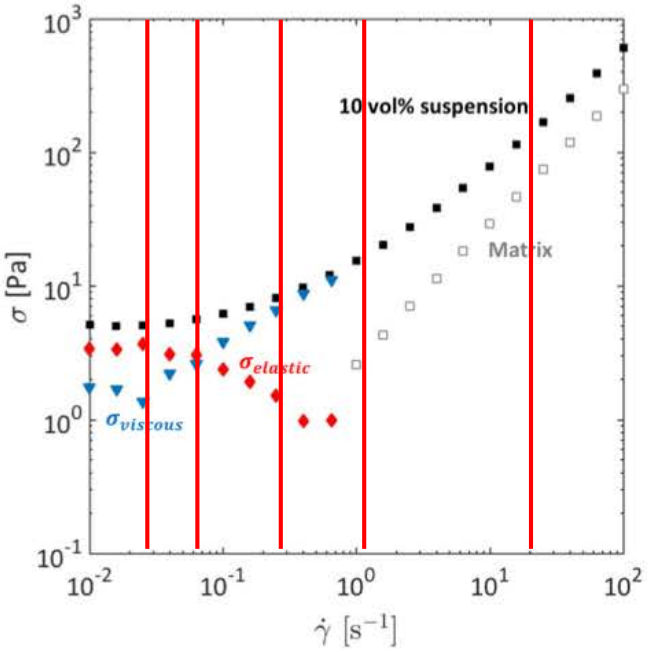
Schroyen, Swan, Van Puyvelde, Vermant (**2017**), *Soft Matter* 13, 7897

Flow reversals experiments

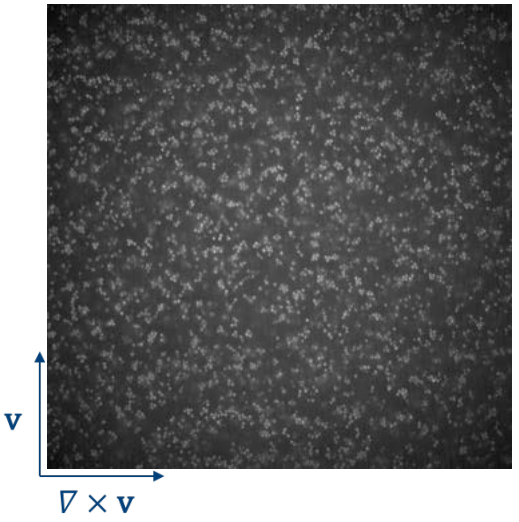
10 vol % PMMA in Newtonian (PDMS) matrix

$\dot{\gamma}$ = 0.025 s^{-1}

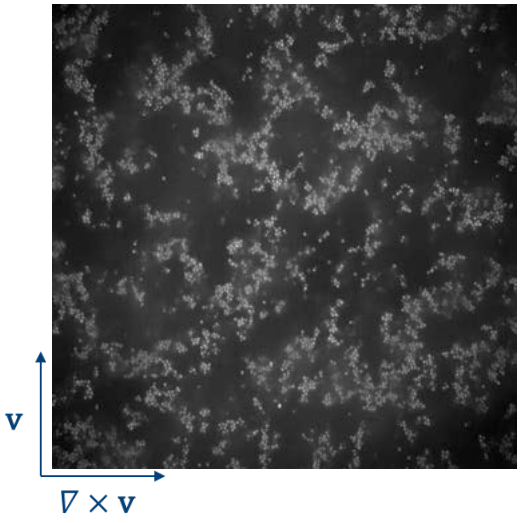




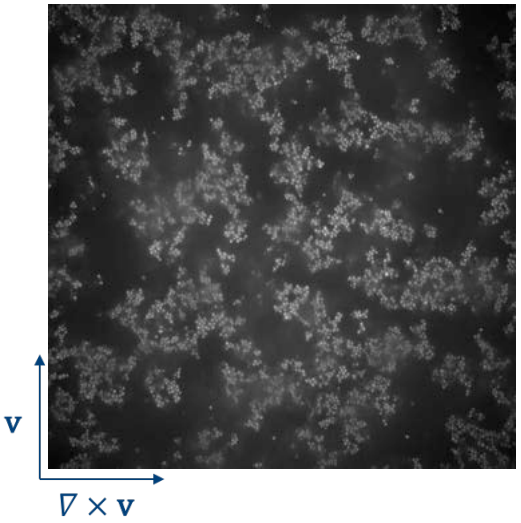
$\dot{\gamma}$ = 20s^{-1}



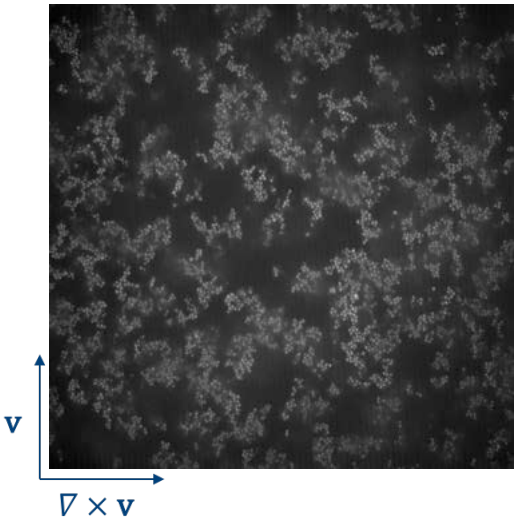
$\dot{\gamma}$ = 0.063 s^{-1}



$\dot{\gamma}$ = 0.25 s^{-1}

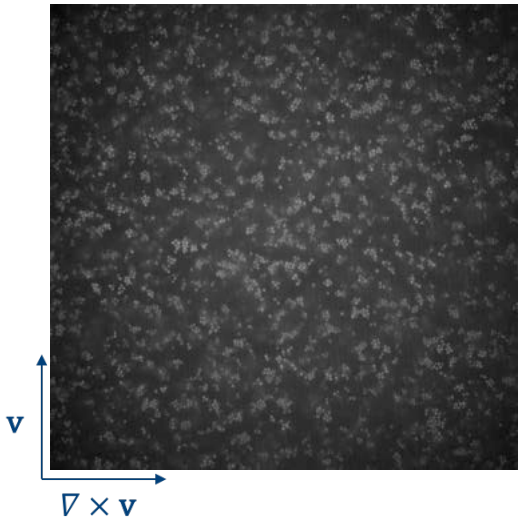


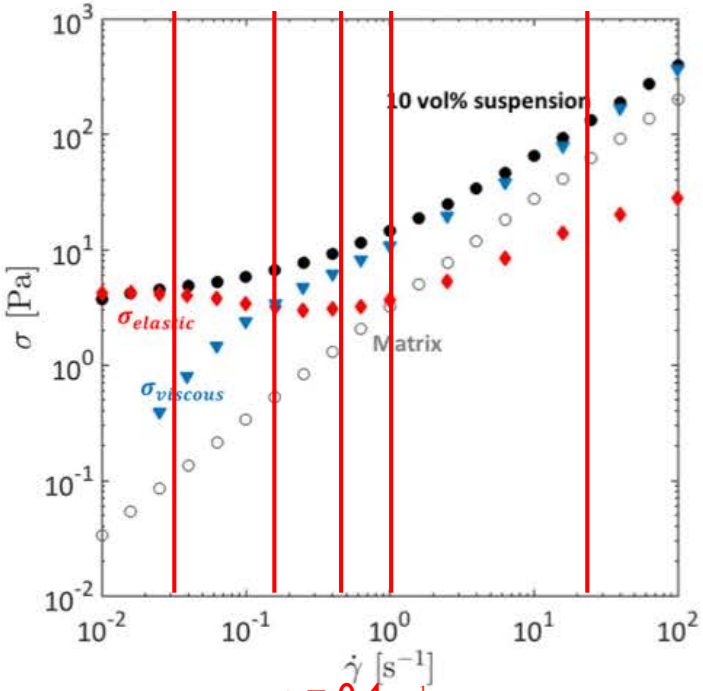
$\dot{\gamma}$ = 1s^{-1}



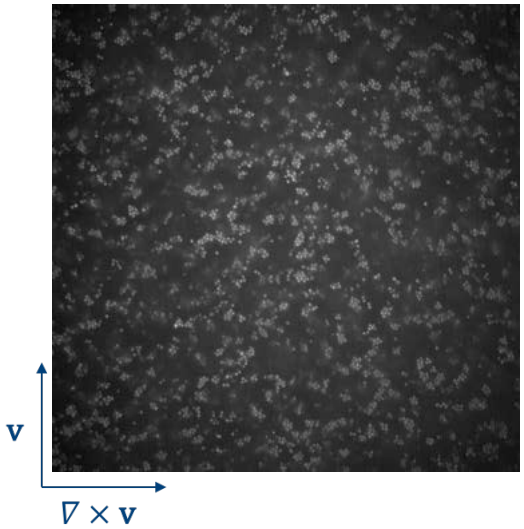
10 vol % PMMA in VE (PDMS) matrix

$\dot{\gamma}$ = 0.025 s^{-1}

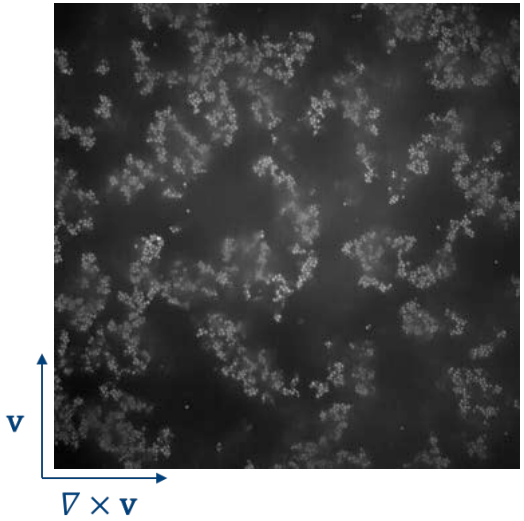




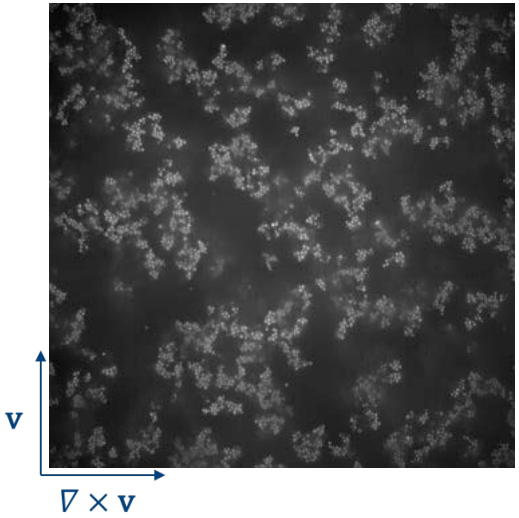
$\dot{\gamma}$ = 20 s^{-1}



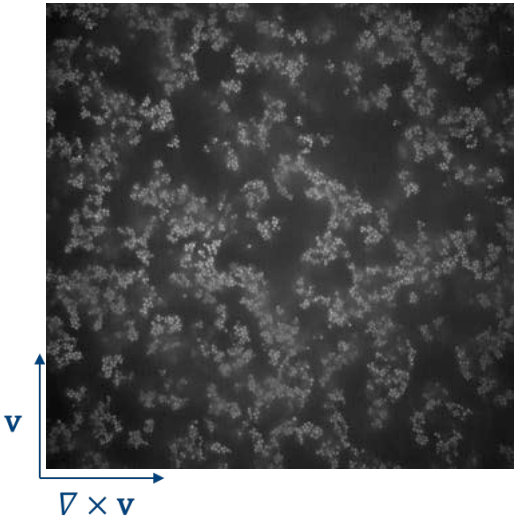
$\dot{\gamma}$ = 0.16 s^{-1}



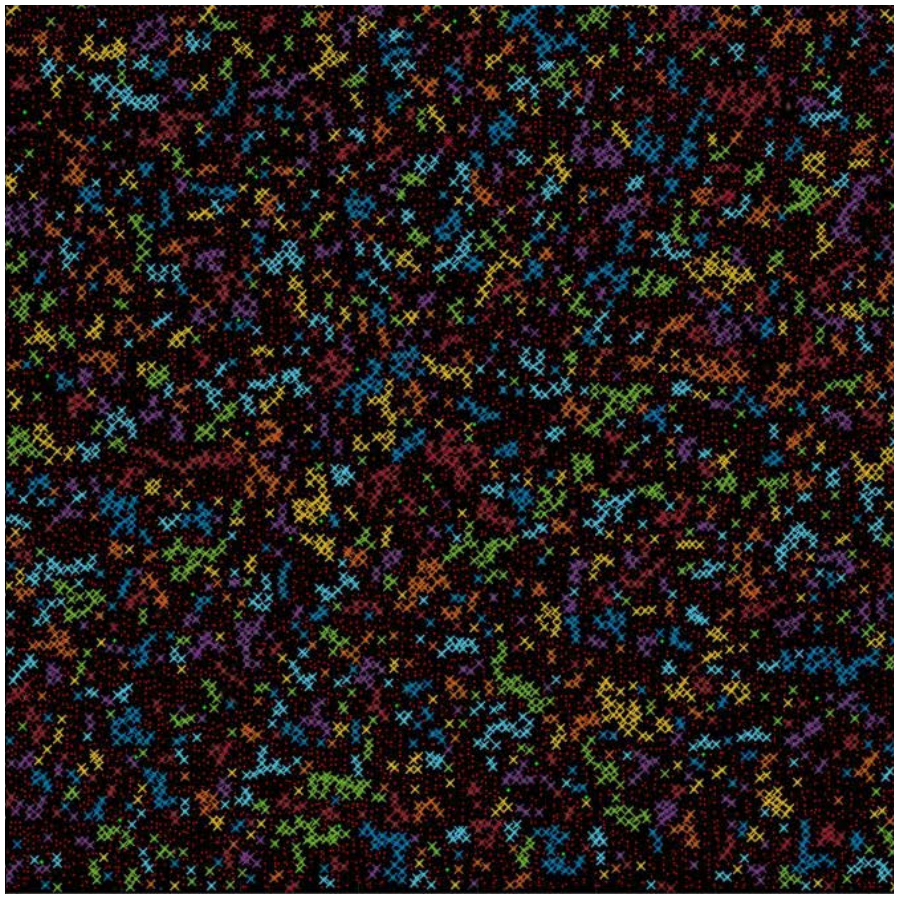
$\dot{\gamma}$ = 0.4 s^{-1}



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



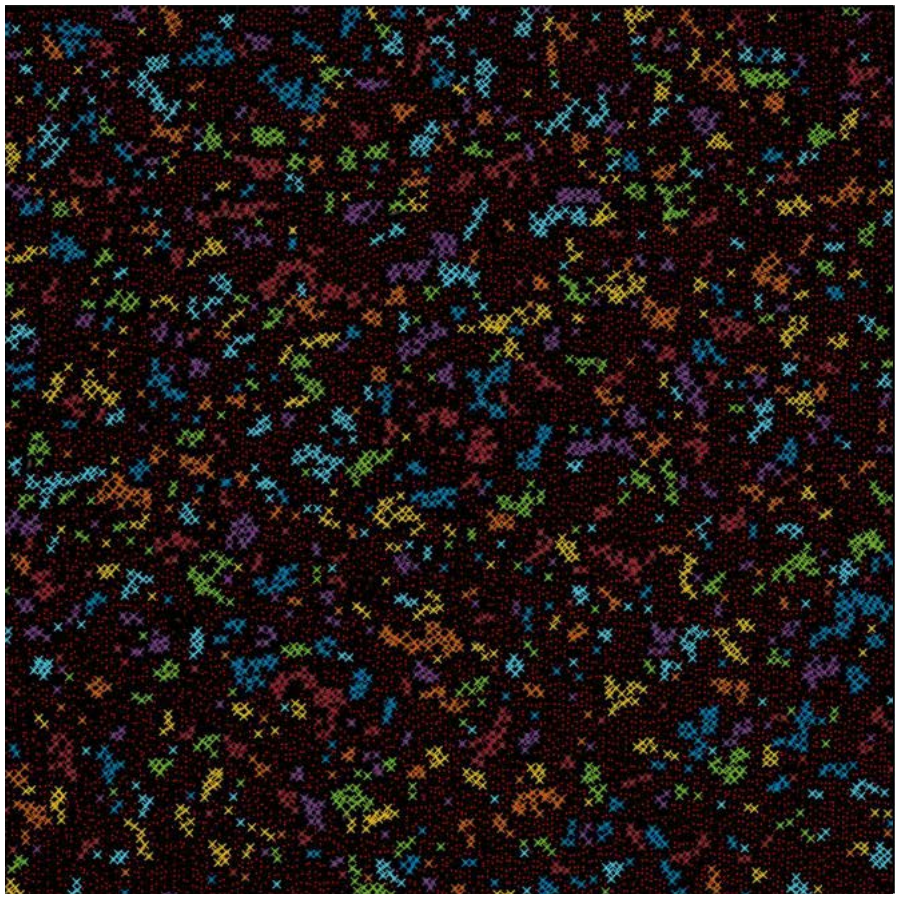
Suspension in linear matrix



ϕ_{eff}= 0.3

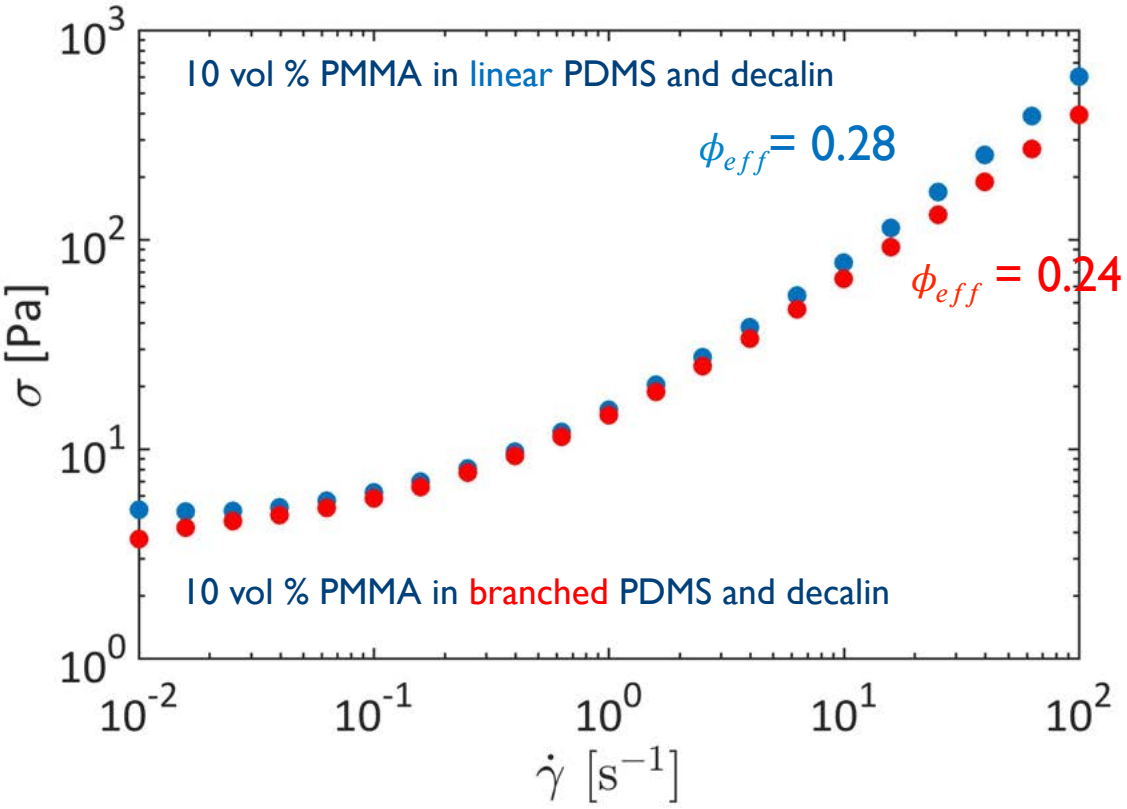
$\dot{\gamma}$ =20 s^{-1}
154x154µm

Suspension in branched matrix



ϕ_{eff}= 0.25

$\dot{\gamma}$ = 20 s^{-1}
154x154µm



$$\eta_r = \left(1 - \frac{\phi}{\phi_{max}}\right)^{-[\eta]\rho\phi_{max}}$$

I. M. Krieger and T. J. Dougherty, *Trans Soc Rheol.* 3 (1959), 137

- ☑ Objectives
- ☑ Shear thickening : roughness and adhesion
- ☑ Thixotropy : strength and adhesion
- ☐ Conclusions / outlook

Toolbox for colloidal gel 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:

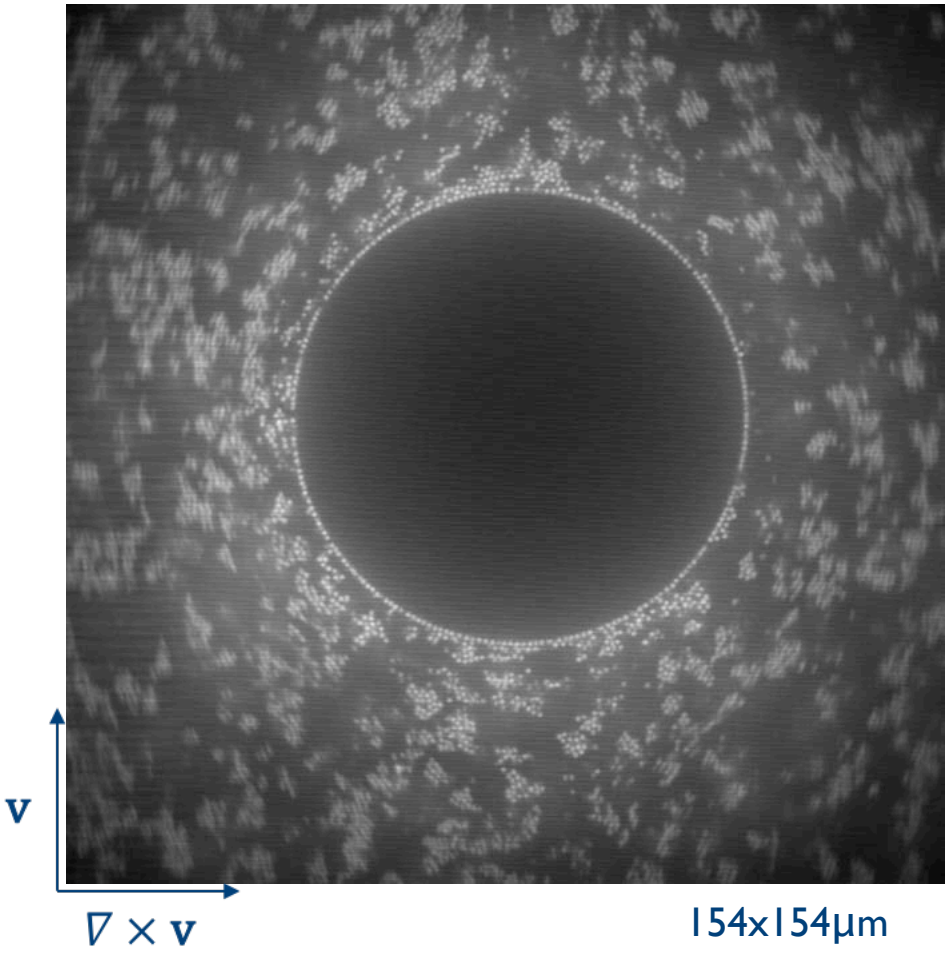
- ☐ non-model systems and yet interrogate mechanisms
- ☐ complex flows
- ☐ HF during flow/processing

Feedback requested :

- rheological profiles/problems (IFPRI members)
- selected industrial systems

Instrument : Rheo-confocal setup, Obj = 60 x
Particles on the coverslip: PMMA of 75-90 µn in diameter (Cospheric)
Sample: 10 vol% PMMA in CHB, cis- decalin and PS

100% upper motor, $\dot{\gamma} = 10\ s^{-1}$



- ✓ Compressional flow before single bead
- ✓ Rotational flow around the sphere
- ✓ Extensional flow after the bead