Role of surface roughness and friction in the rheology of dense colloidal suspensions

Lilian C. Hsiao

Department of Chemical and Biomolecular Engineering
North Carolina State University
e-mail: lilian_hsiao@ncsu.edu

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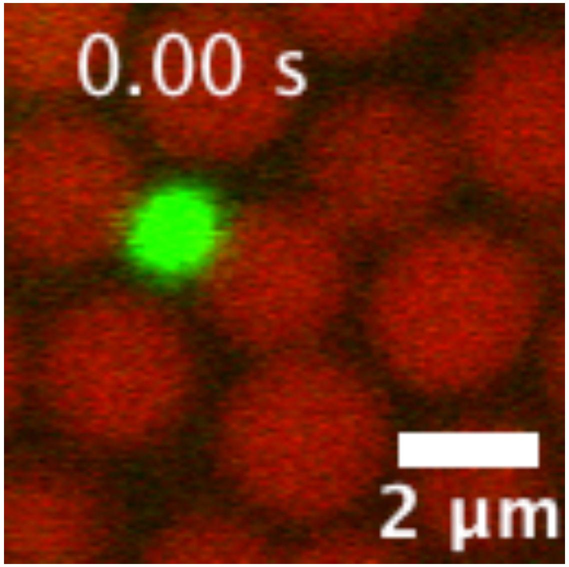
Colloids vs non-Brownian particles

Brownian motion

Pair potential interactions



$$\lim_{\Delta t \to \infty} \left\langle r^2(t) \right\rangle = 6 D_s^{\infty}(\phi) \Delta t$$

$$\lim_{\Delta t \to \infty} \left\langle \varphi^2(t) \right\rangle = 4 D_R^{\infty}(\phi) \Delta t$$

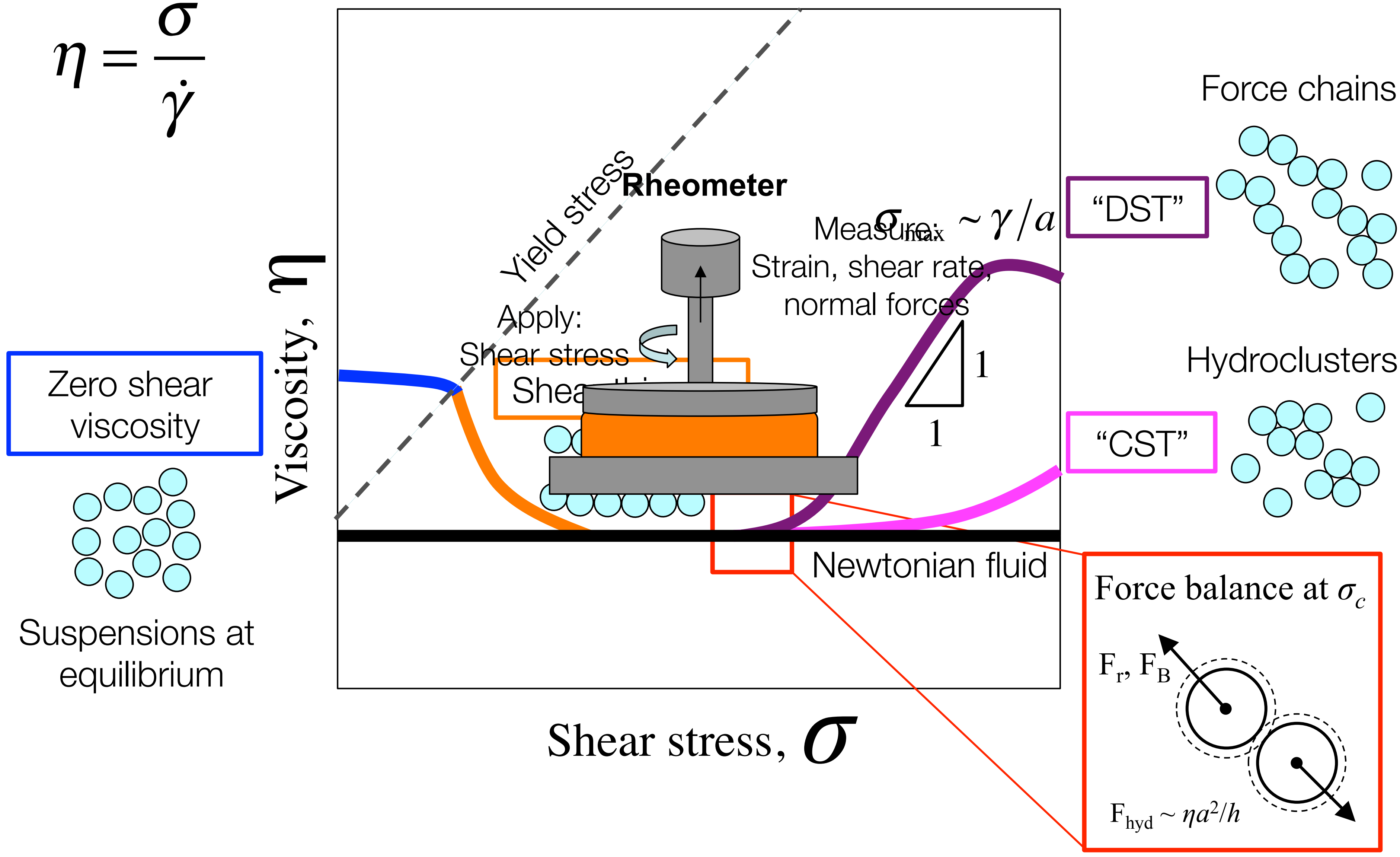
$$U(r) = 4\varepsilon \left(\left(\frac{\sigma}{r} \right)^{2\alpha} - \left(\frac{\sigma}{r} \right)^{\alpha} \right)$$

Nanoparticles	**Colloids**	Granular materials	
< 100 nm	**100 nm – 10 µm**	> 10 µm	Size →

Thermal motion ← **Negligible inertia**

Flow properties and connections to microstructure

$$\eta = \frac{\sigma}{\dot{\gamma}}$$



Confocal rheometer for visualization and rheology

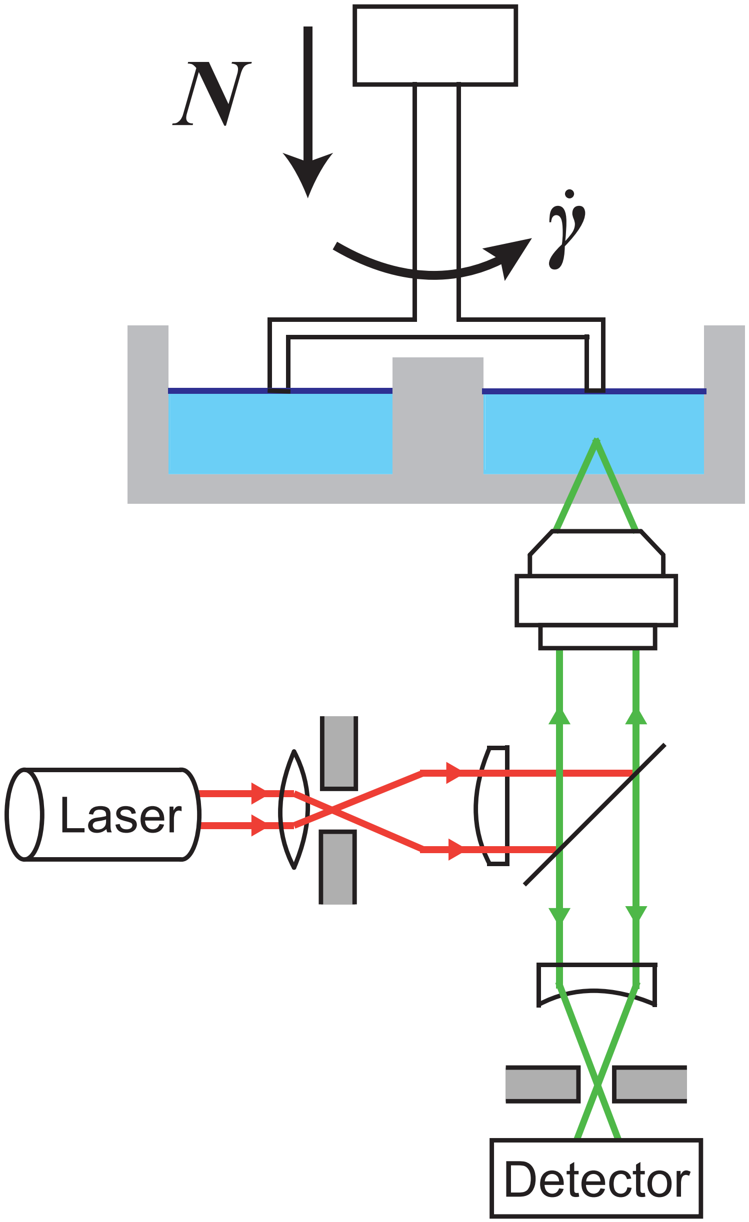
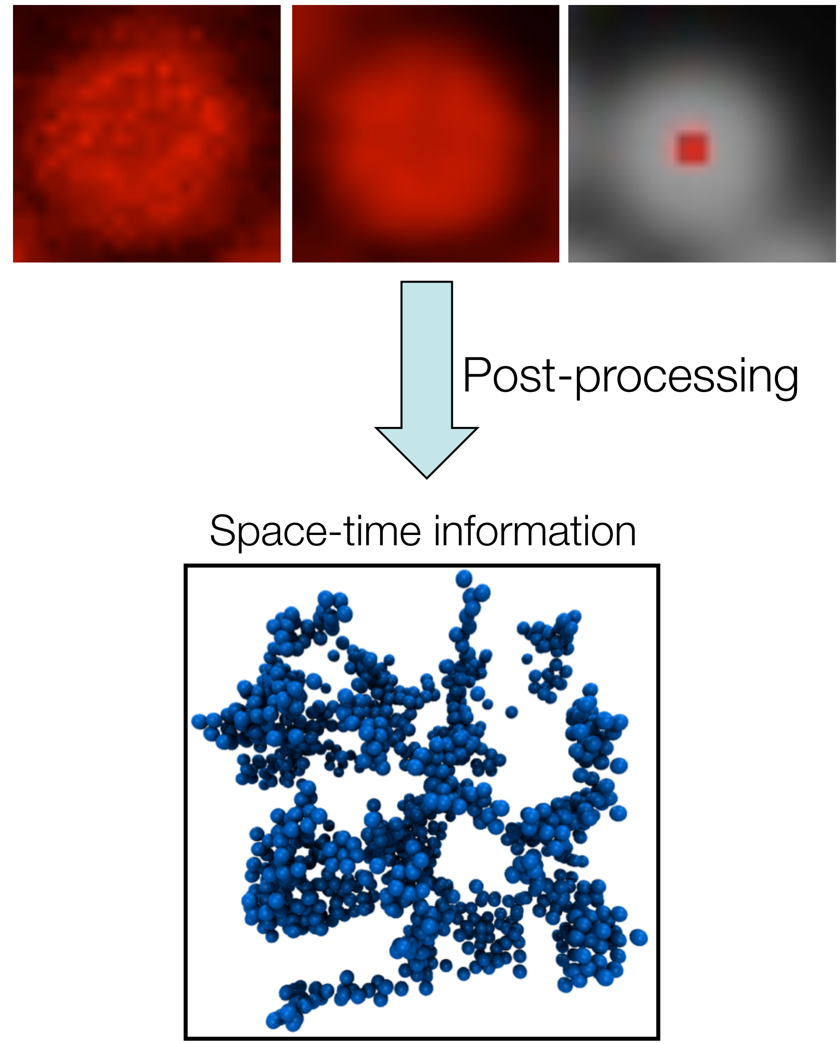
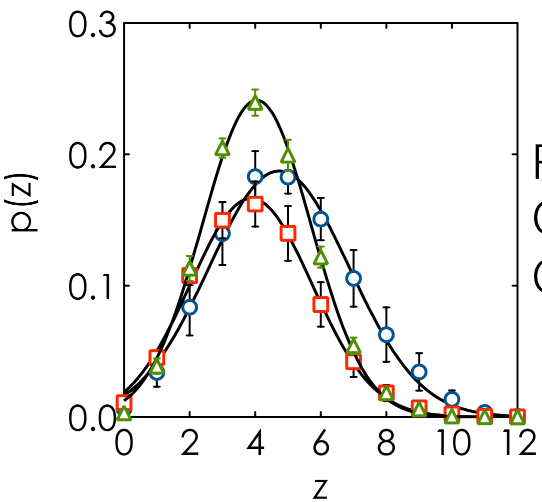


Image acquisition from confocal microscopy

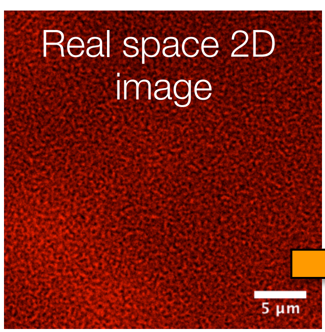


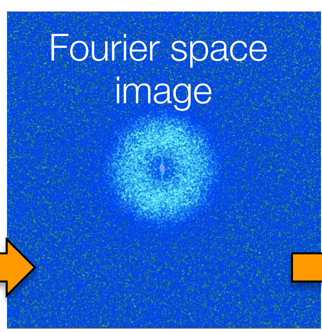
Characterizing structure and dynamics from images

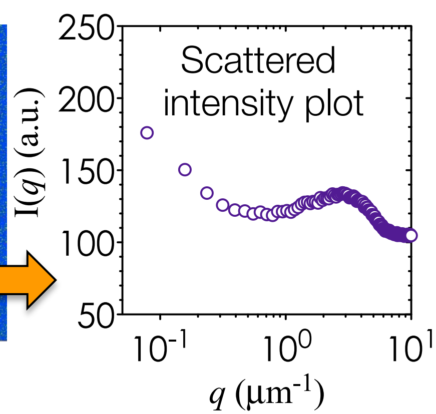
Microstructure



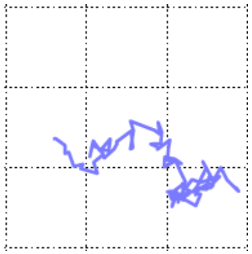
Radial distribution function
Contact number distribution
Cluster size distribution

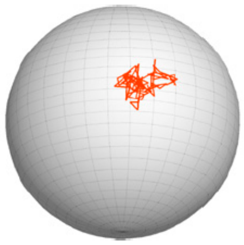


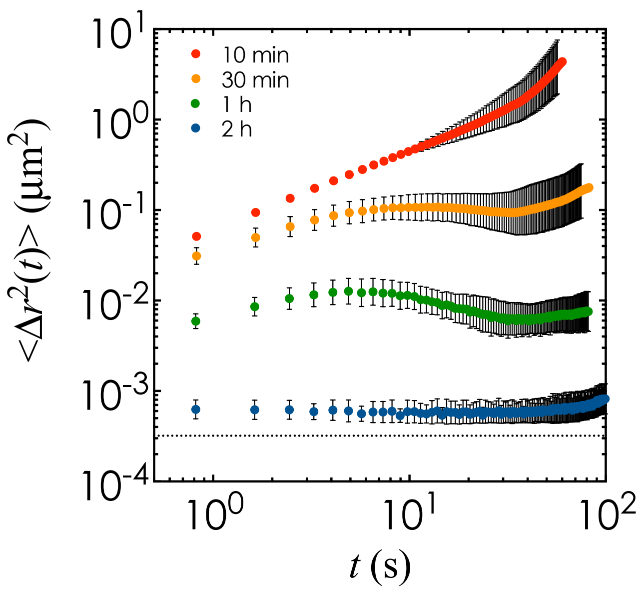




Translational and rotational dynamics

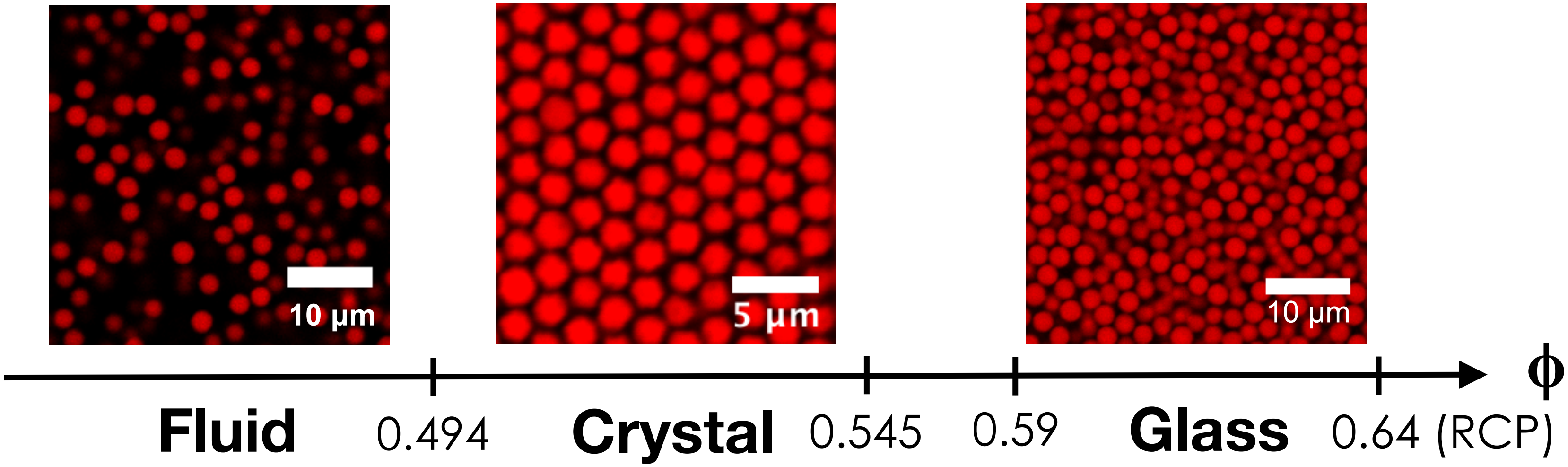


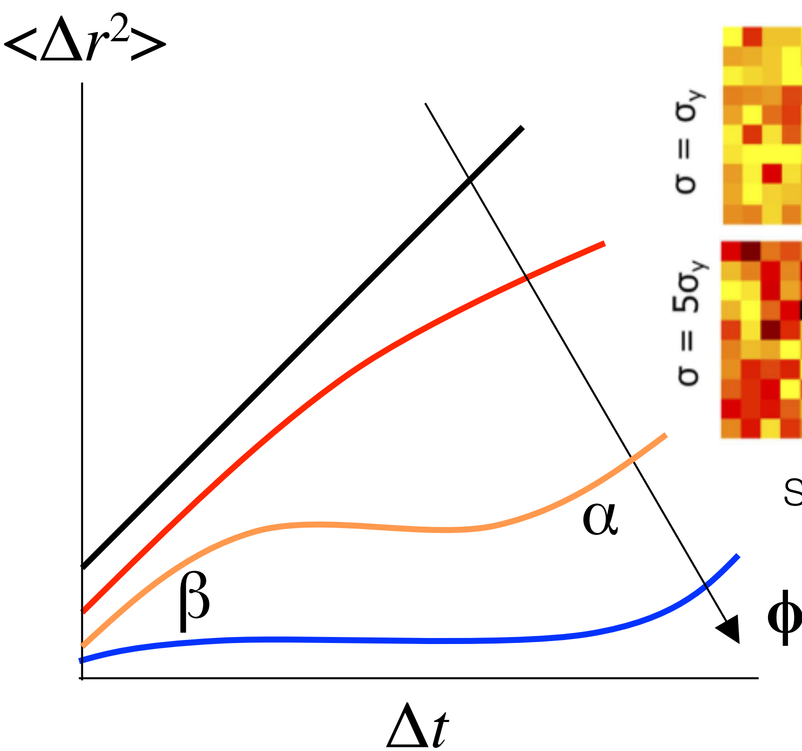


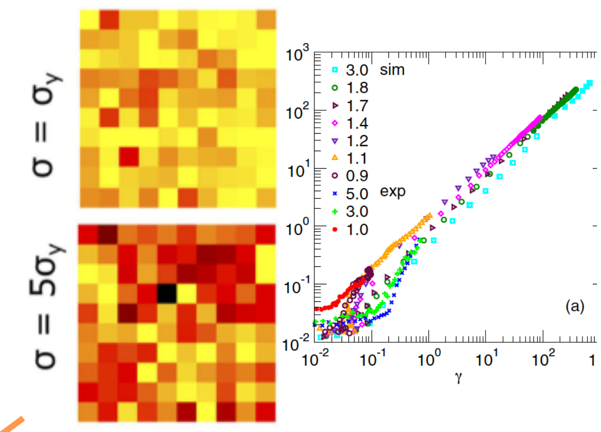


Mean squared displacement
Single particle correlations

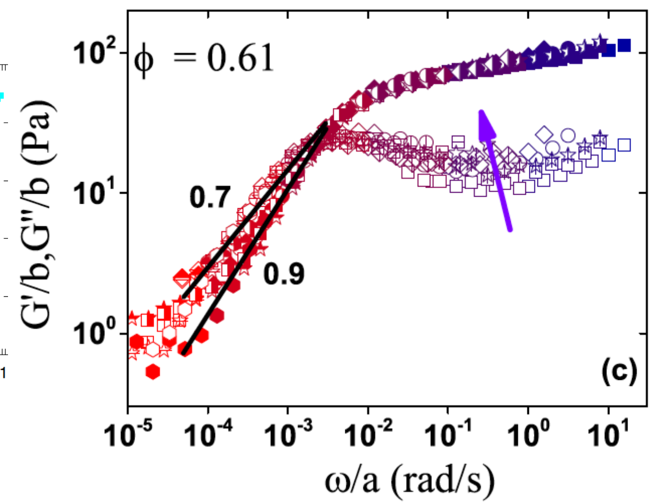
Rheology and dynamics of colloidal glasses







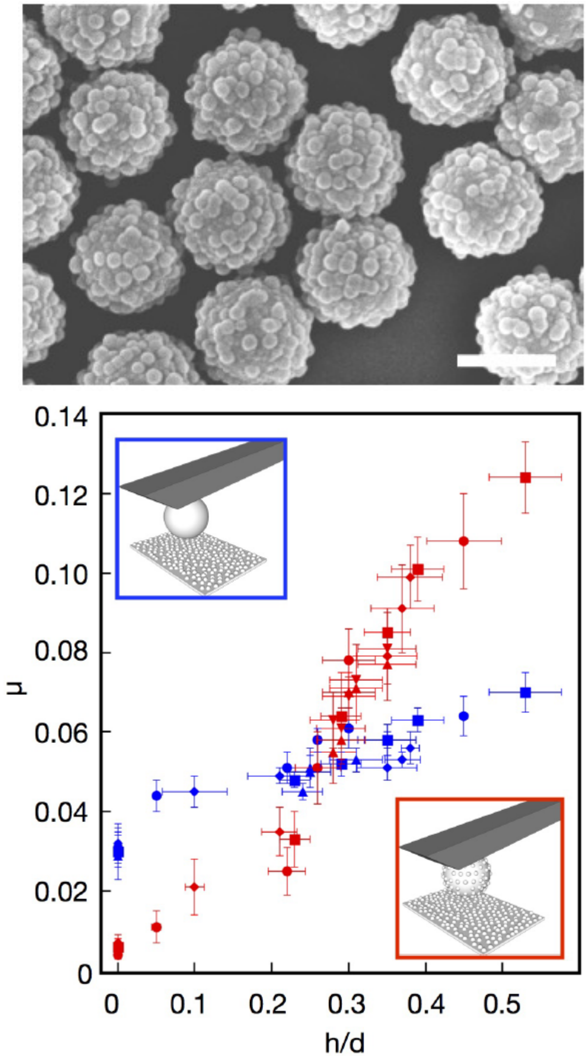
Sentjabrskaja et al. Sci Rep (2015).



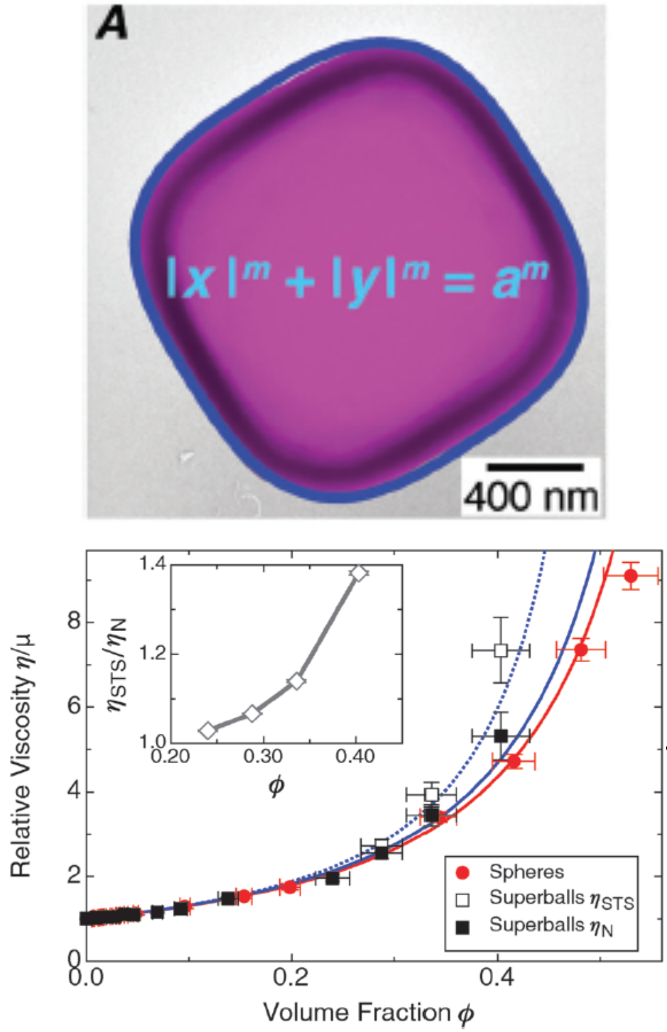
Jacob et al. PRL (2015)

Two dynamic relaxation modes responsible for cage + bond release under shear

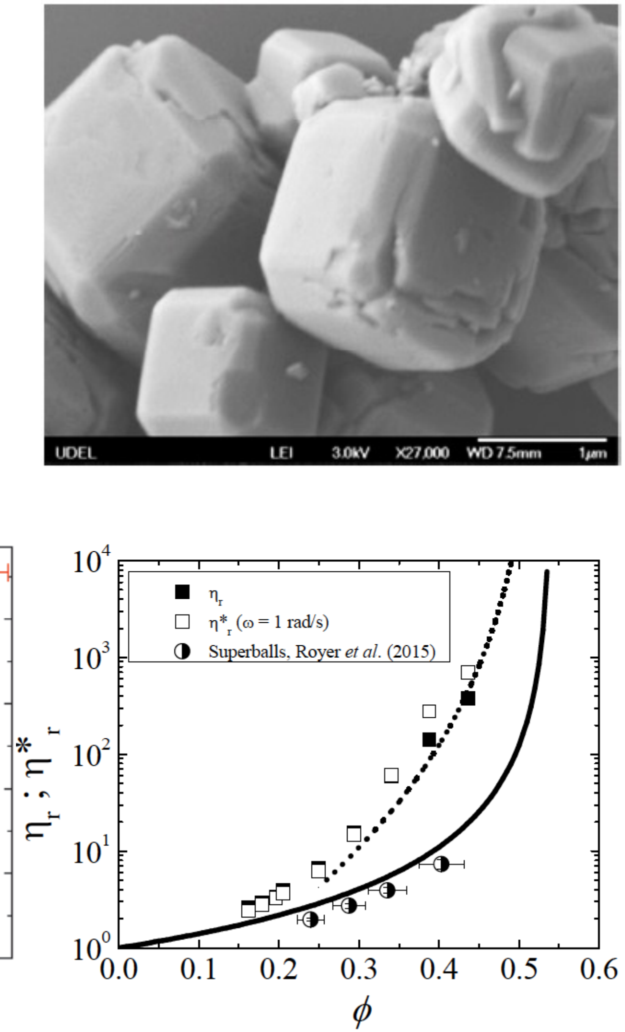
Effect of surface anisotropy on dense suspensions



Hsu & Isa et al. PNAS (2018).



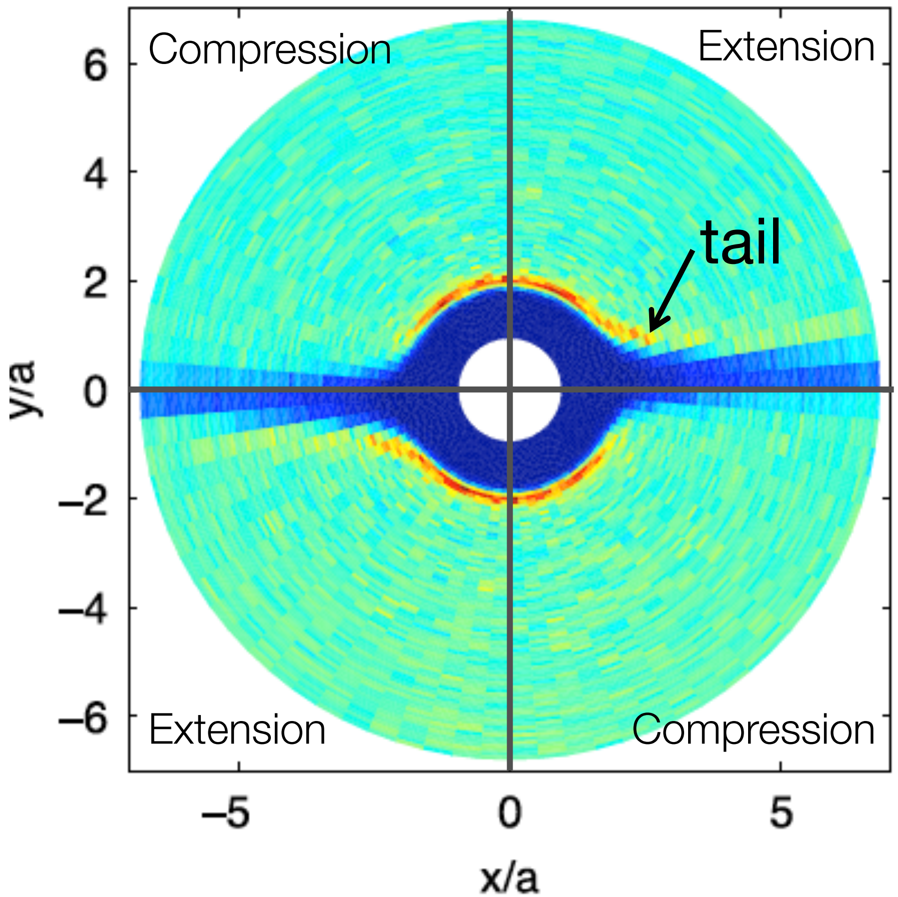
Royer, Blair, Hudson et al. Soft Matter (2015).



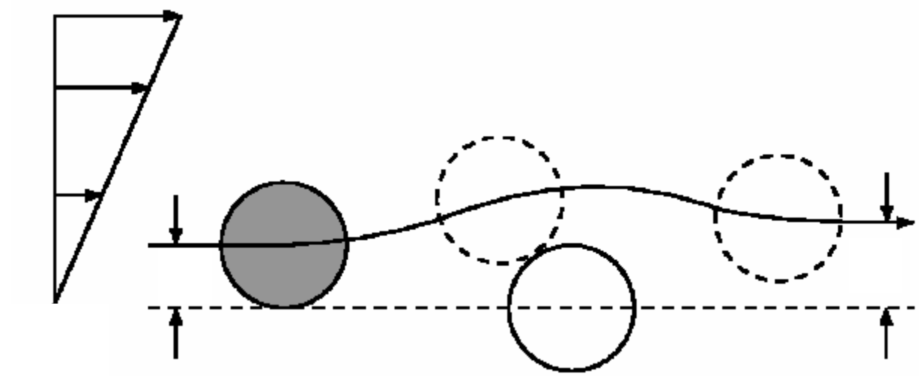
Cwalina & Wagner. Soft Matter (2016).

Roughness breaks fore-aft symmetry in simple shear

Experiments with non-Brownian PMMA ($\varphi = 0.05$) in Couette cell



Blanc et al. Phys Rev Lett (2011)



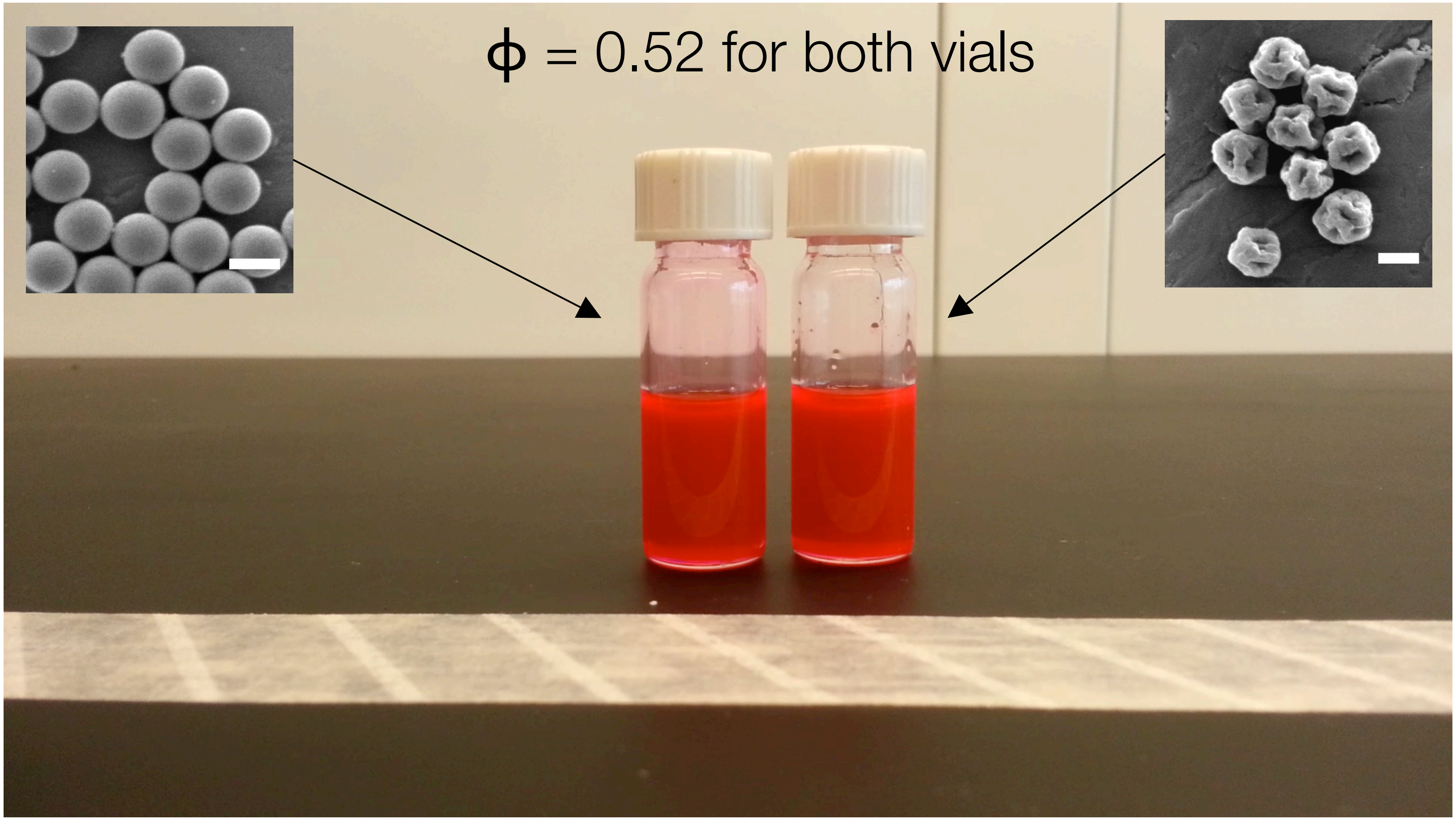
Davis et al. Phil Trans R Soc Lond A (2003)

Theoretical developments:

- Asperity prevents particle contact
- 2 limiting cases: slide (frictionless) and interlocking rigid bodies (frictional)
- Roughness brings Stokes flow irreversibility and symmetry breaking

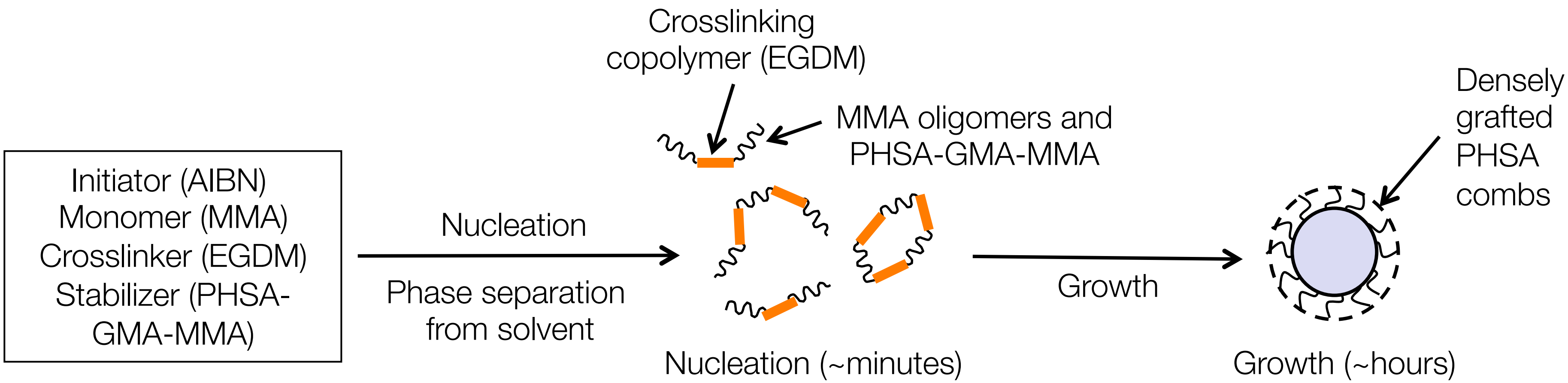
Smart & Leighton (1993), Gallier et al. (2014), Wilson & Davis (2002), Da Cunha & Hinch (1996), Sierou & Brady (2002)

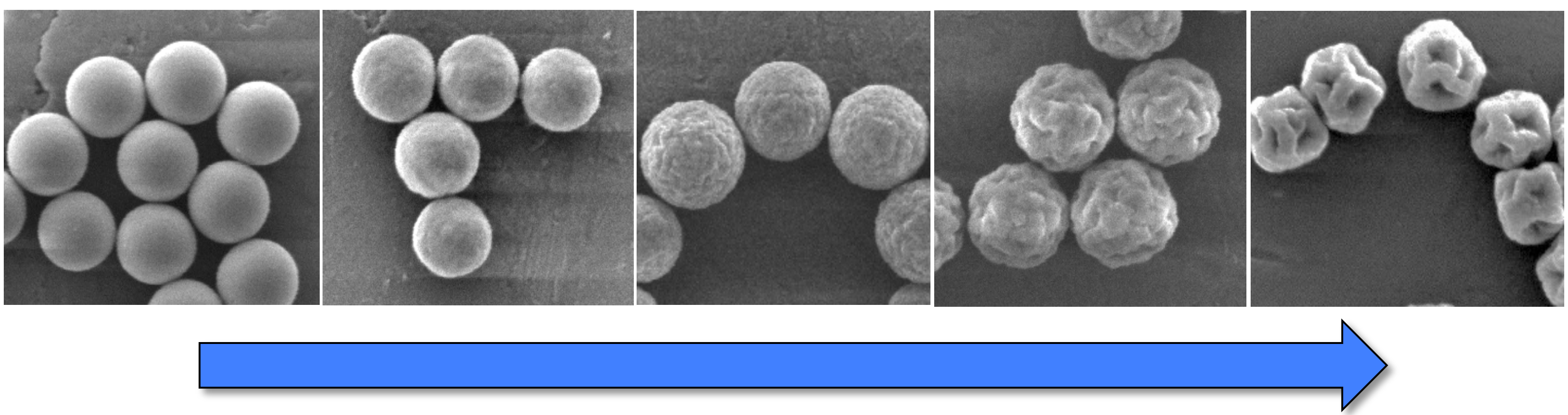
Particle roughness and shear thickening



Synthesis of PHSA-PMMA rough colloids

Free-radical dispersion polymerization

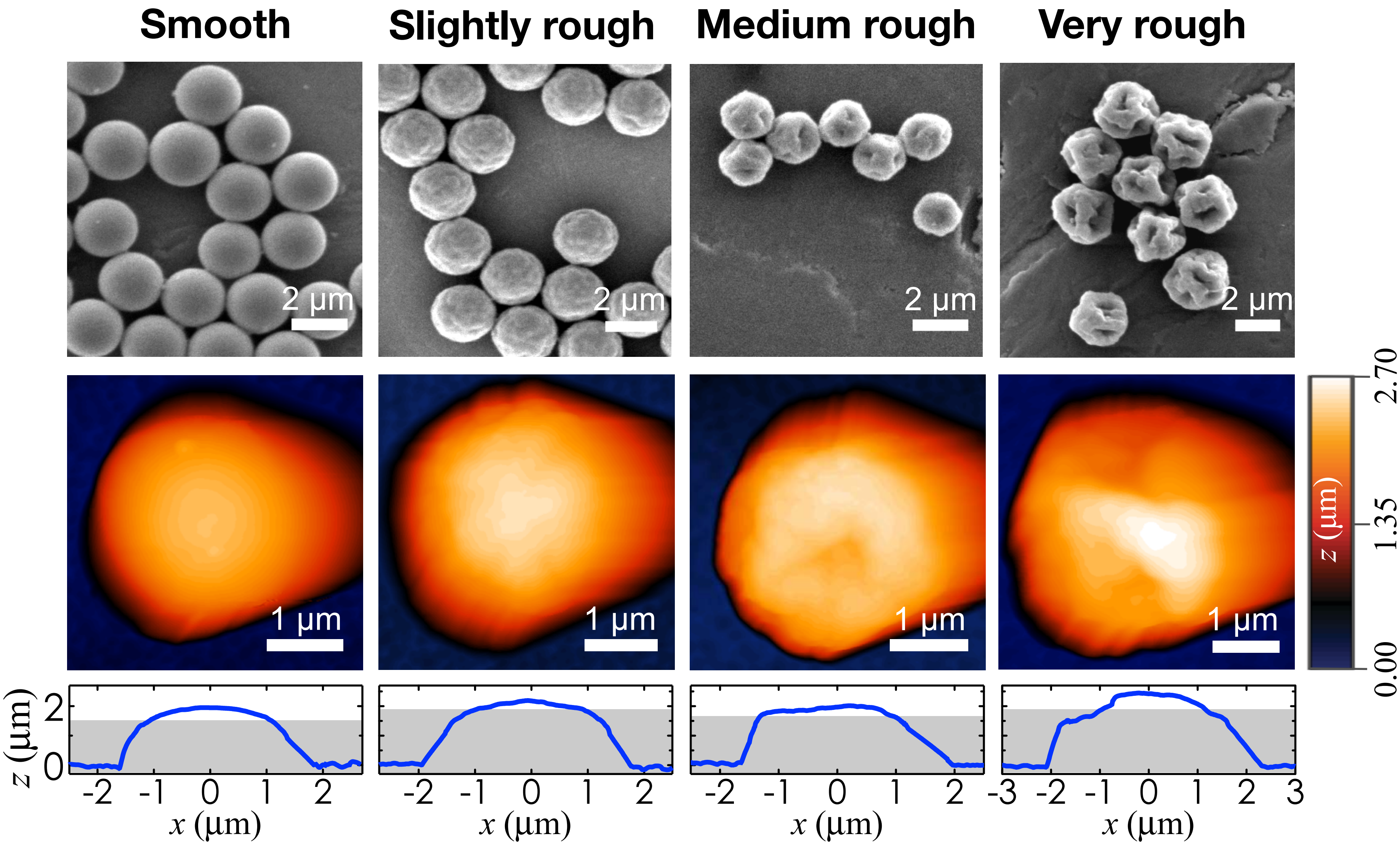




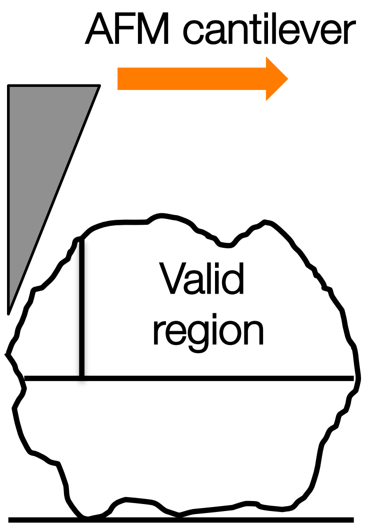
Increasing crosslinker concentration, Increasing roughness

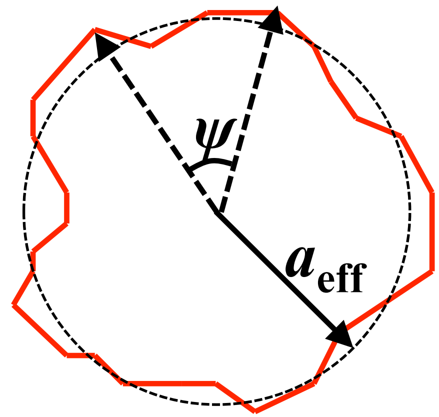
Colloidal particles of varying roughness

PHSA-stabilized PMMA colloids, $2a_{eff}$ = 1.9 to 2.5 μm, Size polydispersity = 3-4%

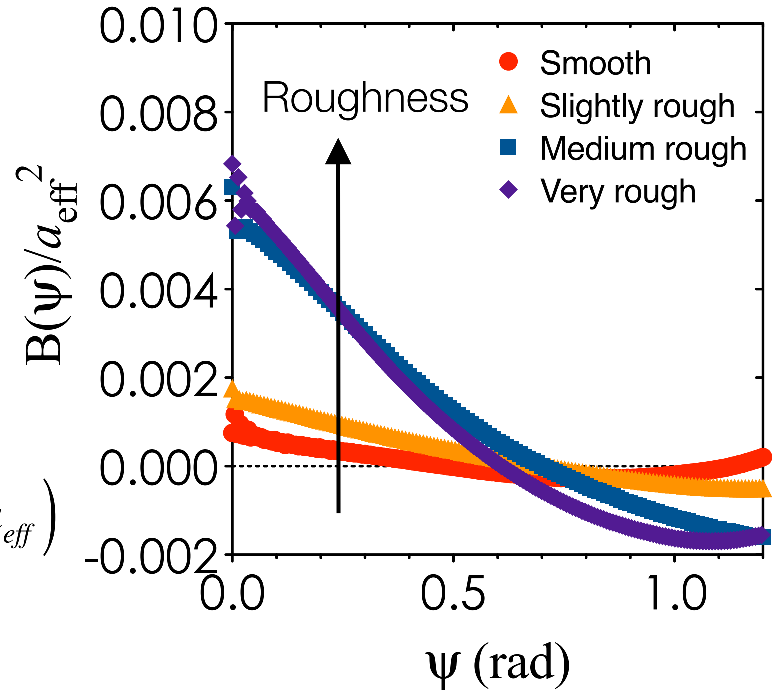


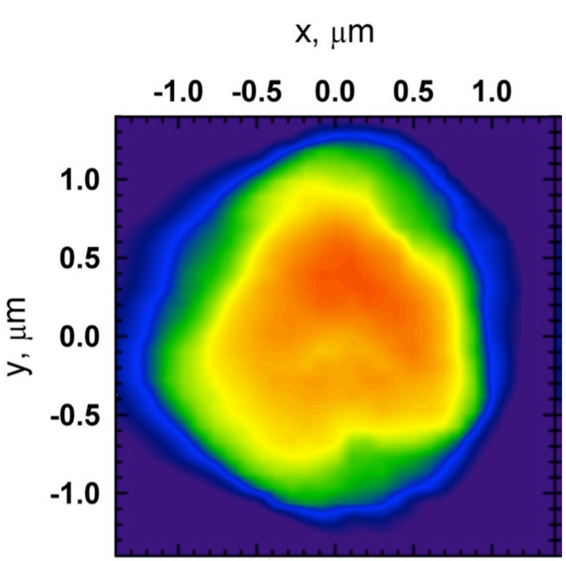
Extracting RMS roughness from AFM measurements





$$B(\psi) = \frac{1}{N} \sum_{\substack{i,j=1 \\ i \neq j}}^{\psi} \left(|\mathbf{r}_i| - a_{eff}\right)\left(|\mathbf{r}_j| - a_{eff}\right)$$

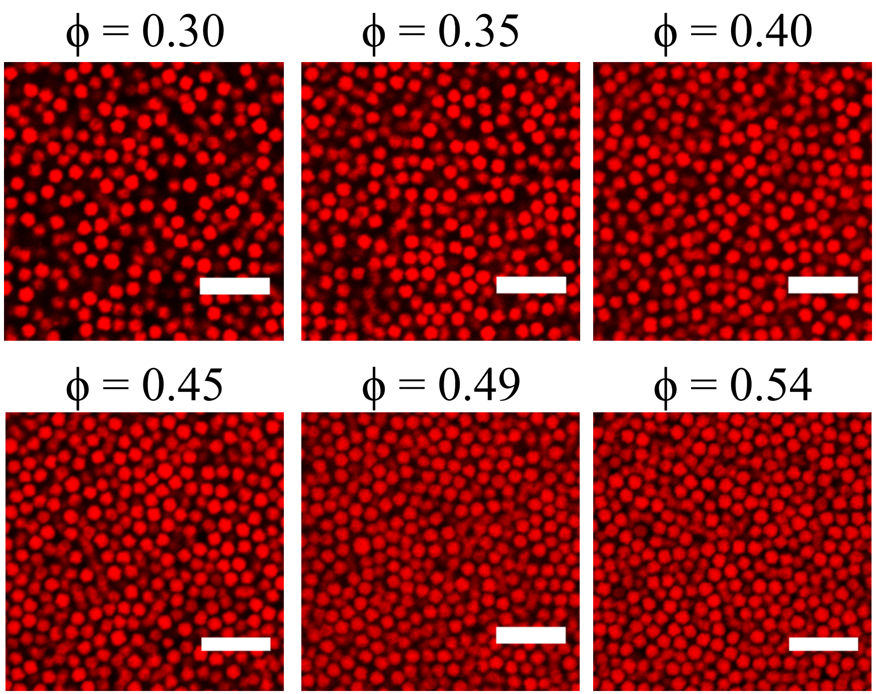




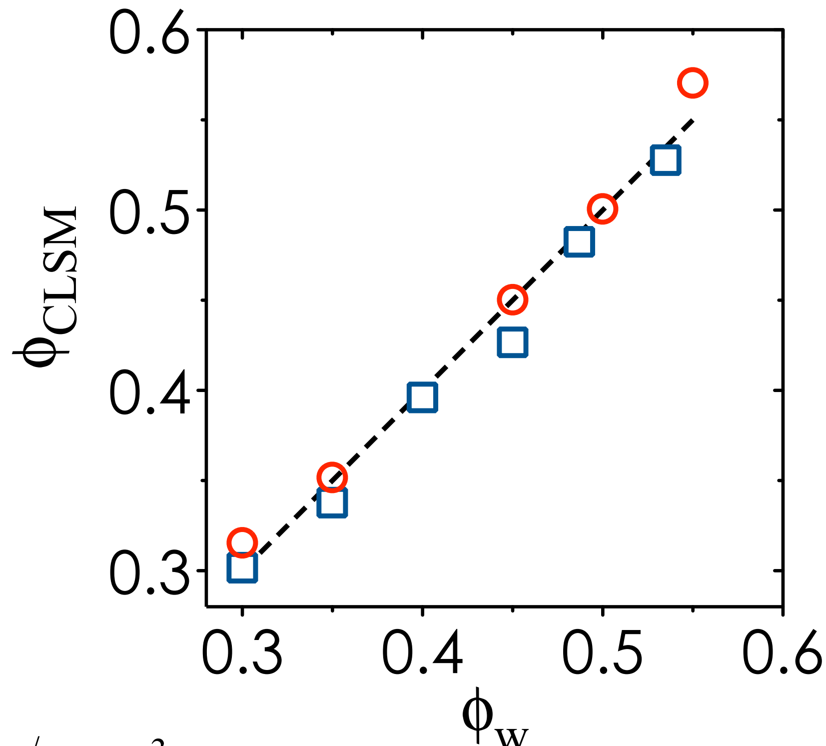
Geometry	$2a_{eff}$ (µm)	$(B(\psi = 0)/a_{eff}^2)^{1/2}$	Range of ϕ
Smooth	2.27 µm ± 5% 1.60 µm ± 4%	0.026 ± 0.003	0.30 to 0.55
Slightly rough	2.55 µm ± 2%	0.040 ± 0.002	0.45 to 0.55
Rough	1.95 µm ± 5% 2.06 µm ± 4% 2.47 µm ± 5% 1.91 µm ± 5%	0.075 ± 0.005	0.30 to 0.55
Very rough	2.78 µm ± 6%	0.082 ± 0.003	0.45 to 0.50

Calculation of the volume fraction

Effective size from AFM/SEM, particle counting from 3D confocal microscopy



Scale bar = 5 μm

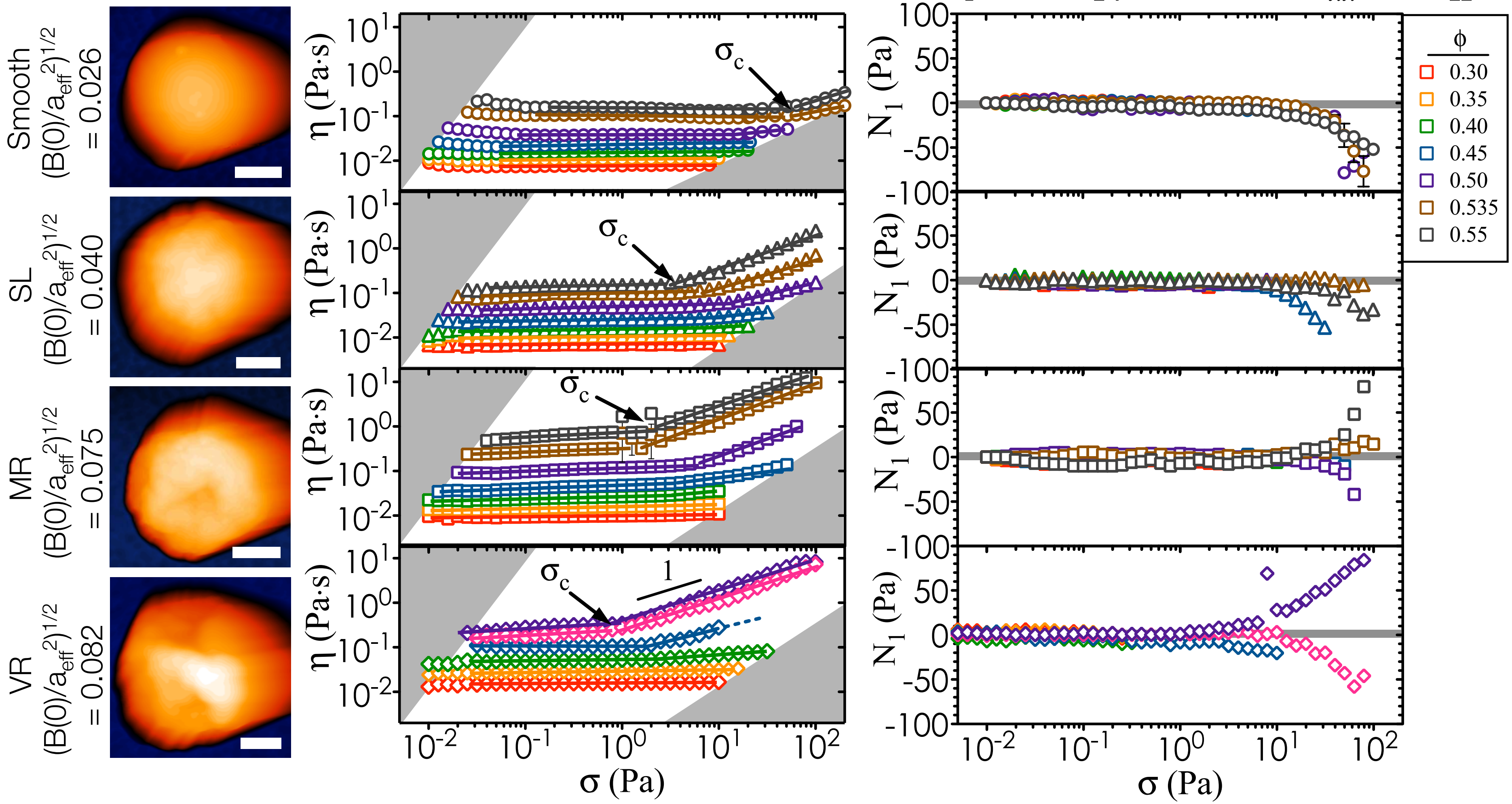


$$\phi_{\mathrm{CLSM}} = \frac{4/3\pi a_{eff}^{3} N_{p}}{V_{\mathrm{box}}}$$

Steady state viscosity and first normal stresses

$$\eta = \sigma/\dot{\gamma}$$

$$N_1 = 2F_z/\pi R^2 = \sigma_{xx} - \sigma_{zz}$$

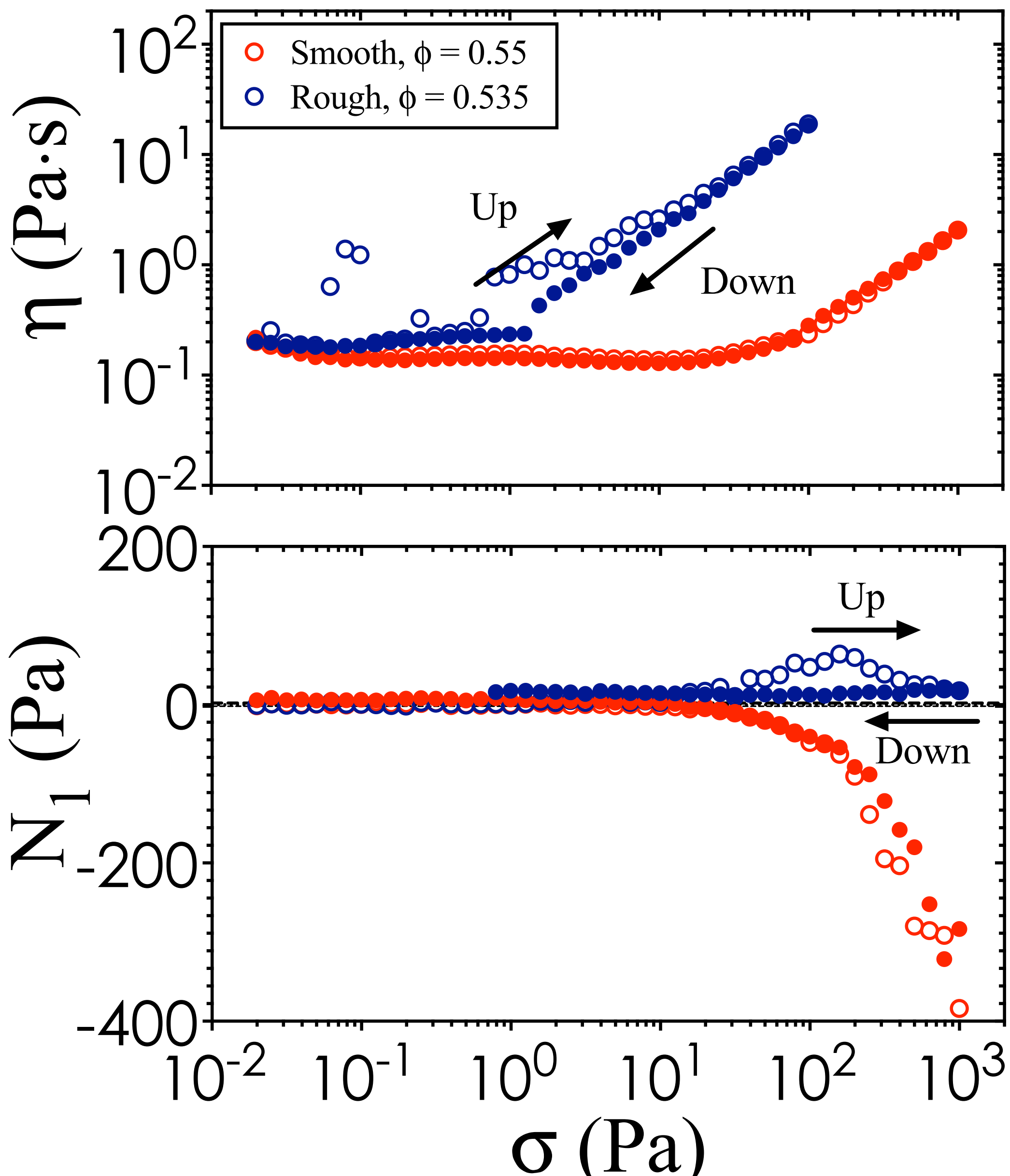


$$St = \frac{\rho_P a^2 \dot{\gamma}}{\eta_f}$$

$$10^{-7} \le St \le 10^{-3}$$

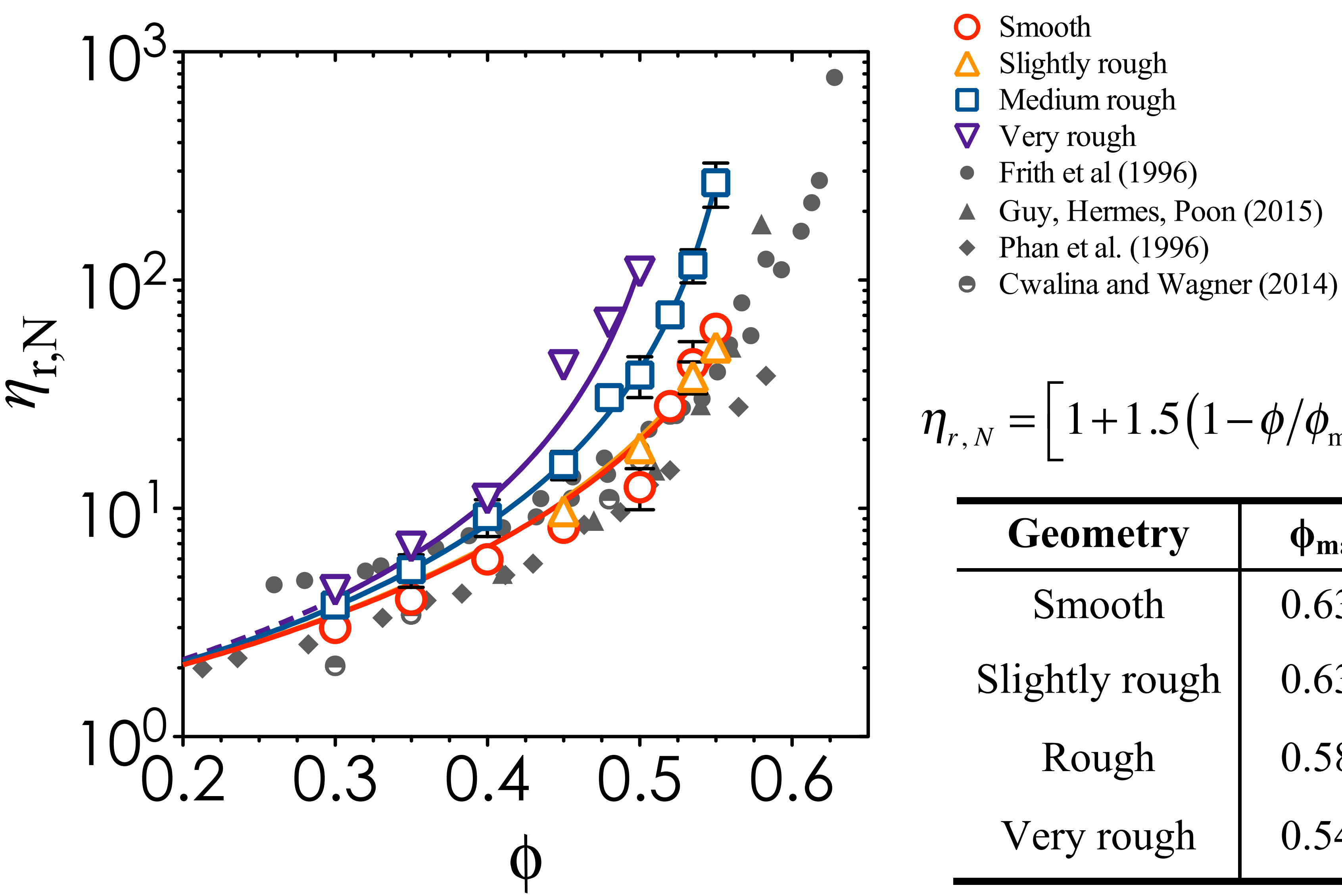
Hsiao et al. Phys Rev Lett (2017)

Hysteretic flow curves for frictional particles



Hsiao et al. Phys Rev Lett (2017)

Fitting the high-shear viscosity to the Eilers model

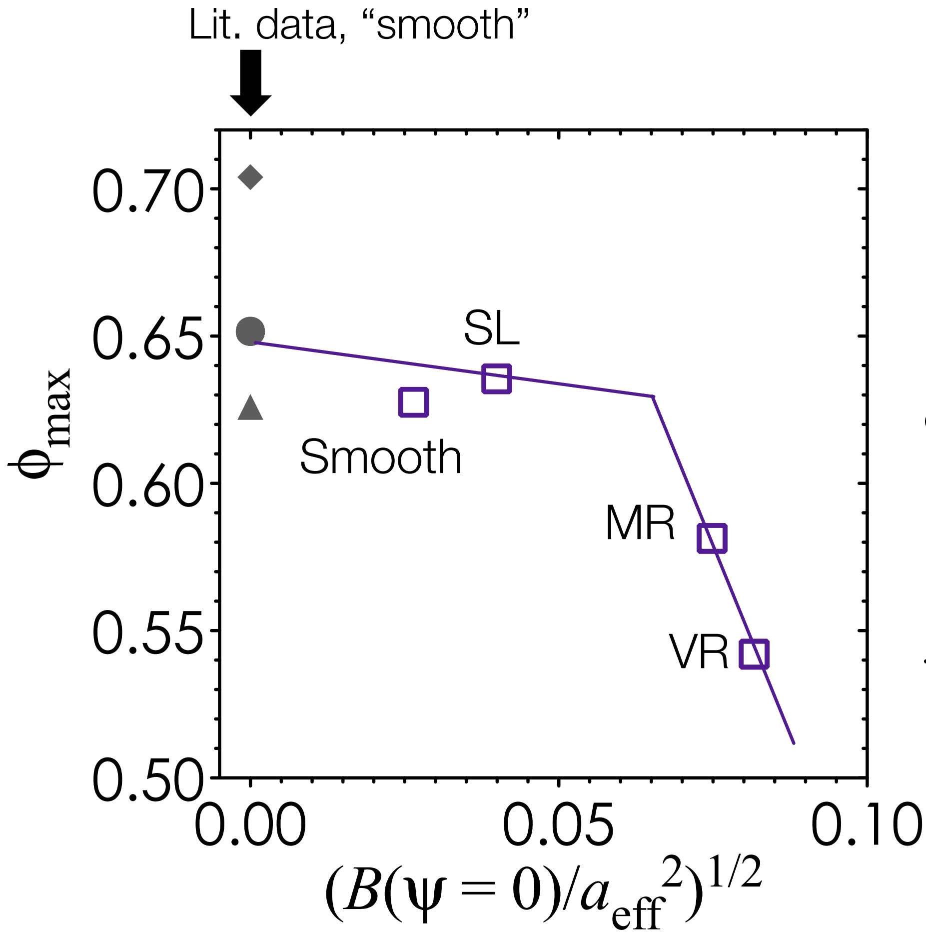


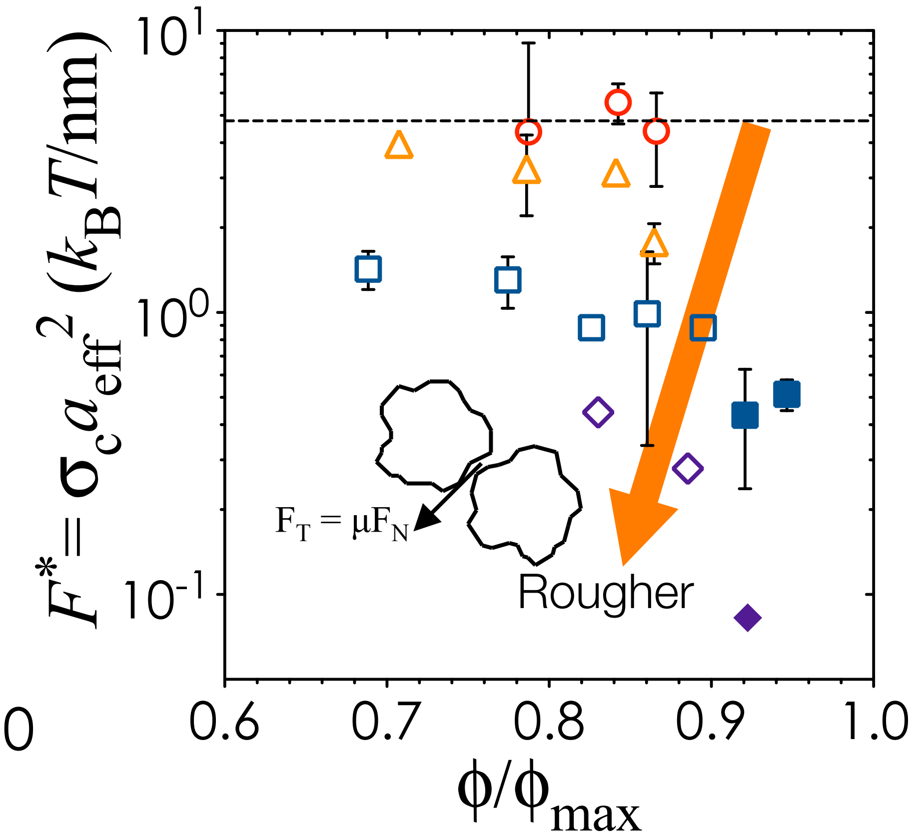
$$\eta_{r,N} = \left[1 + 1.5\left(1 - \phi/\phi_{max}\right)^{-1}\right]^2$$

Geometry	ϕ_{max}
Smooth	0.635
Slightly rough	0.636
Rough	0.581
Very rough	0.542

Hsiao et al. Phys Rev Lett (2017)

Effect of roughness on excluded volume



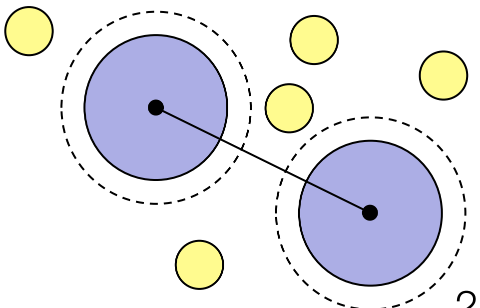


1. When RMS roughness increases, lubrication becomes less effective in keeping particles apart
2. It takes less force to push them into contact

Comparison with DPD simulations

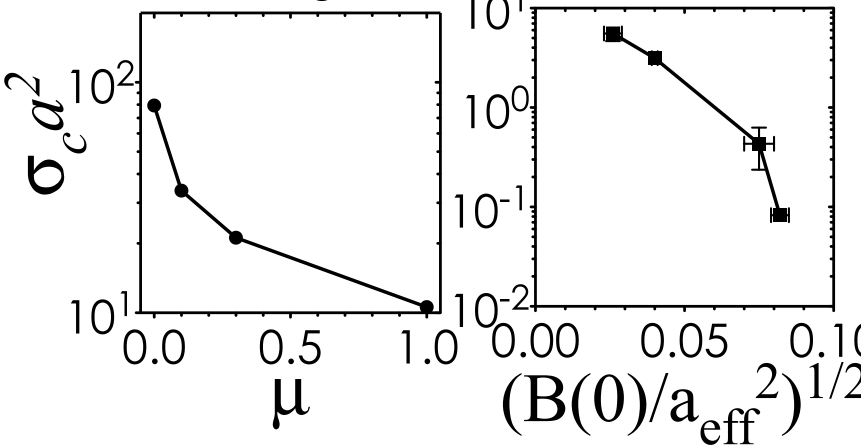
$$m\frac{dv}{dt} = f\left(F_T, F_N, F_h, F_{solvent}\right)$$

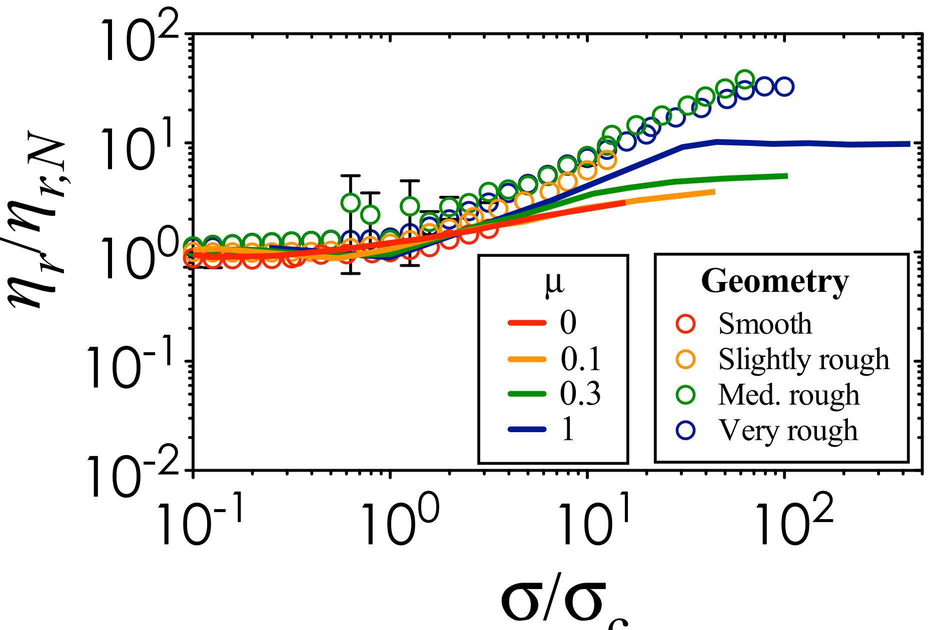
50,000 solvent molecules

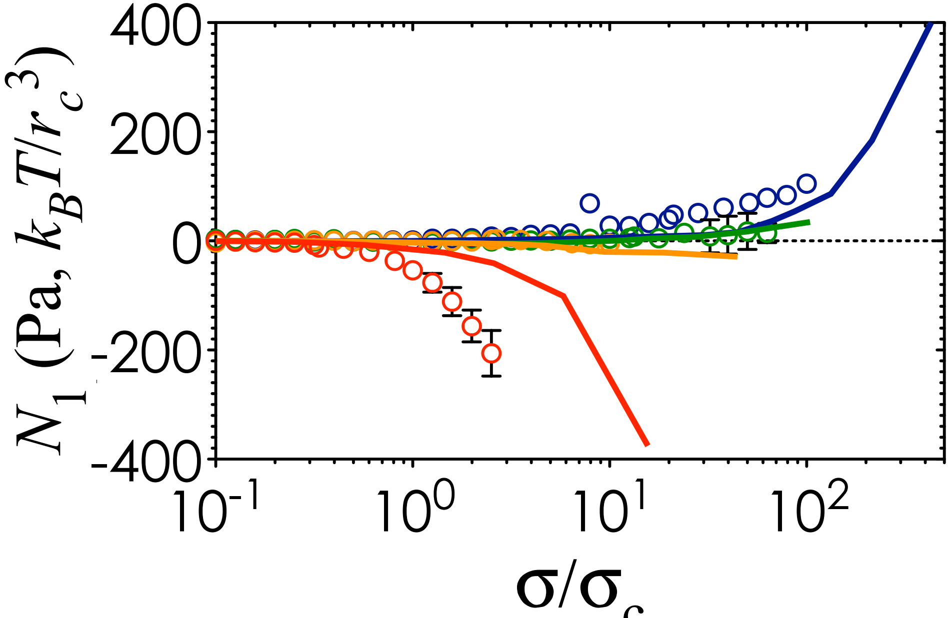


Prof. Safa Jamali
Northeastern U.

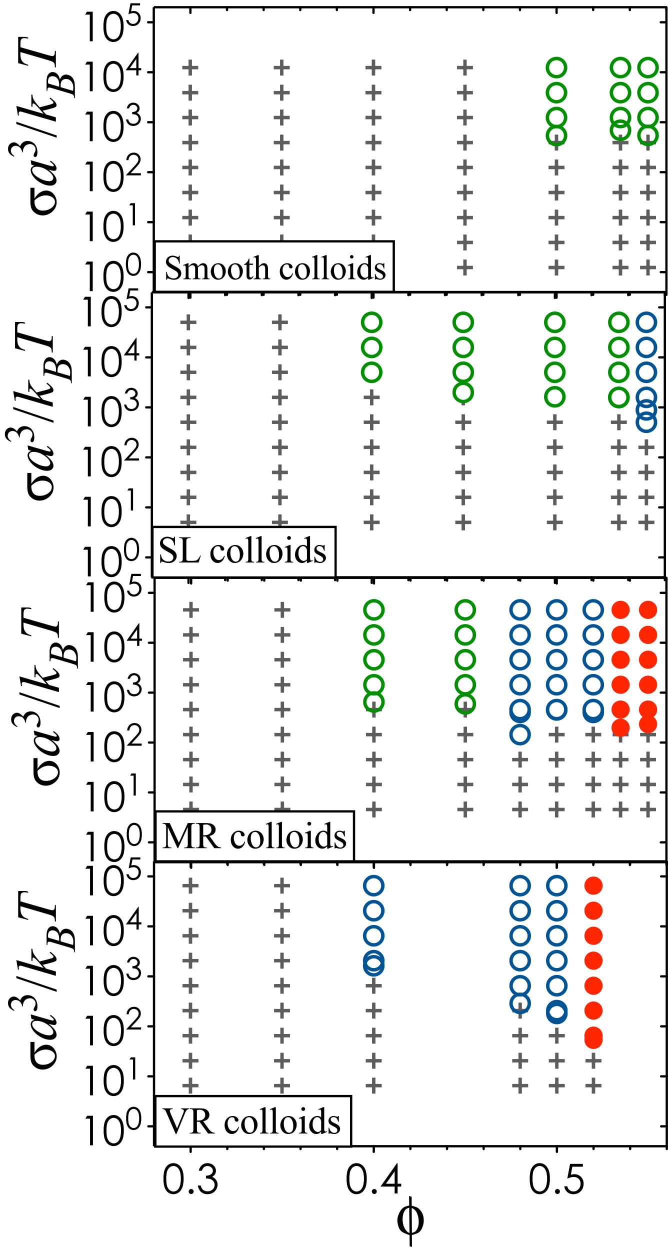
Onset stress depends on roughness and friction



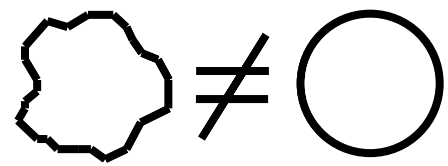




State diagrams for rough colloids in shear flow

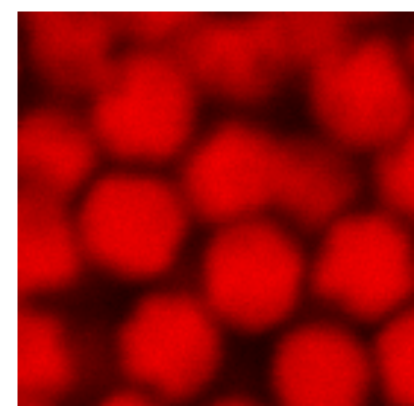


Engineering approach: Assume particle is a sphere.

But  **!**

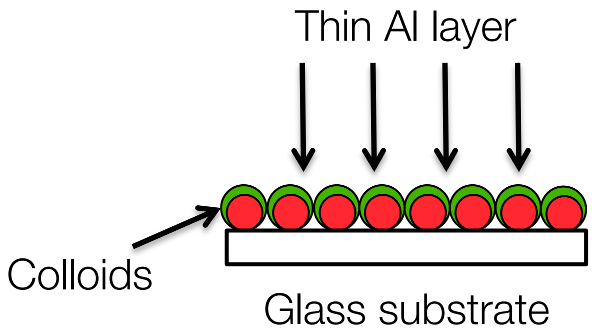
What is the microscopic reason?

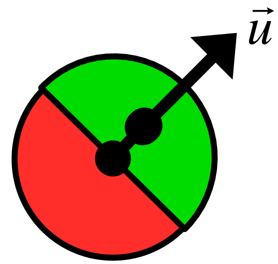
+ = Newtonian flow
○ = weak thickening
○ = strong thickening
● = dilatant ($N_1 > 0$)

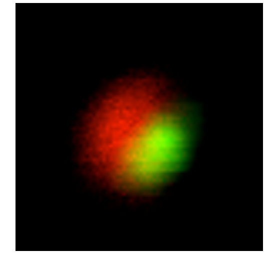


Measuring the 3D rotational dynamics of colloids

Inert Janus tracers to track rotational dynamics

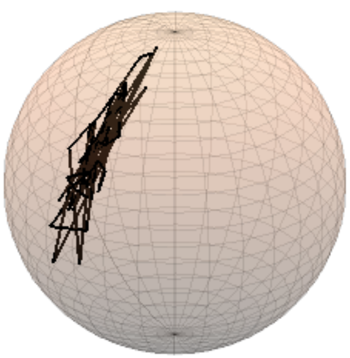




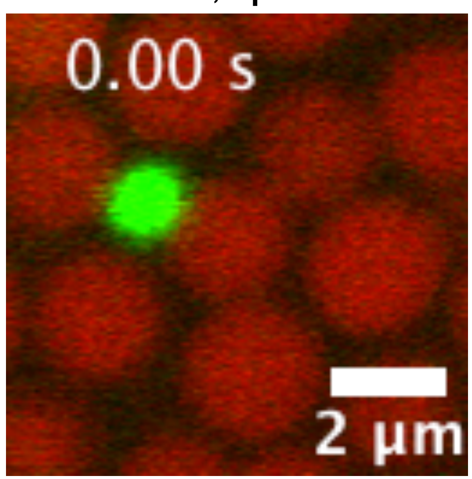


Mean-squared angular displacement

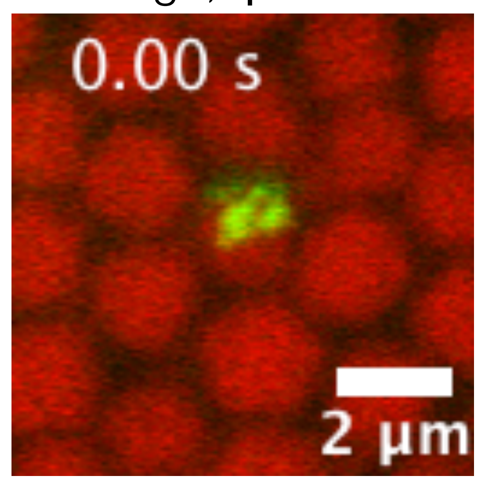
$$\left\langle \Delta\vec{\varphi}^2(\Delta t)\right\rangle = \left\langle \left[\vec{\varphi}(t+\Delta t)-\vec{\varphi}(t)\right]^2\right\rangle$$

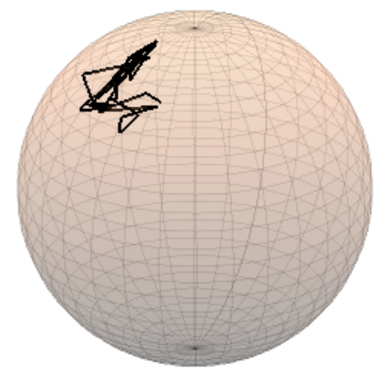


Smooth, ϕ = 0.50



Rough, ϕ = 0.50

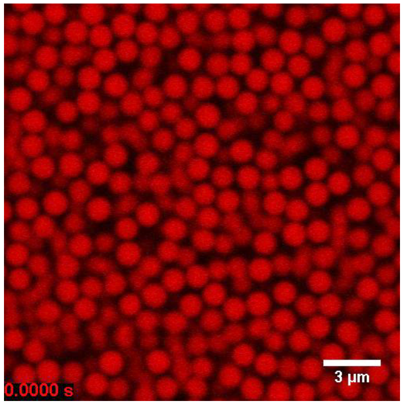


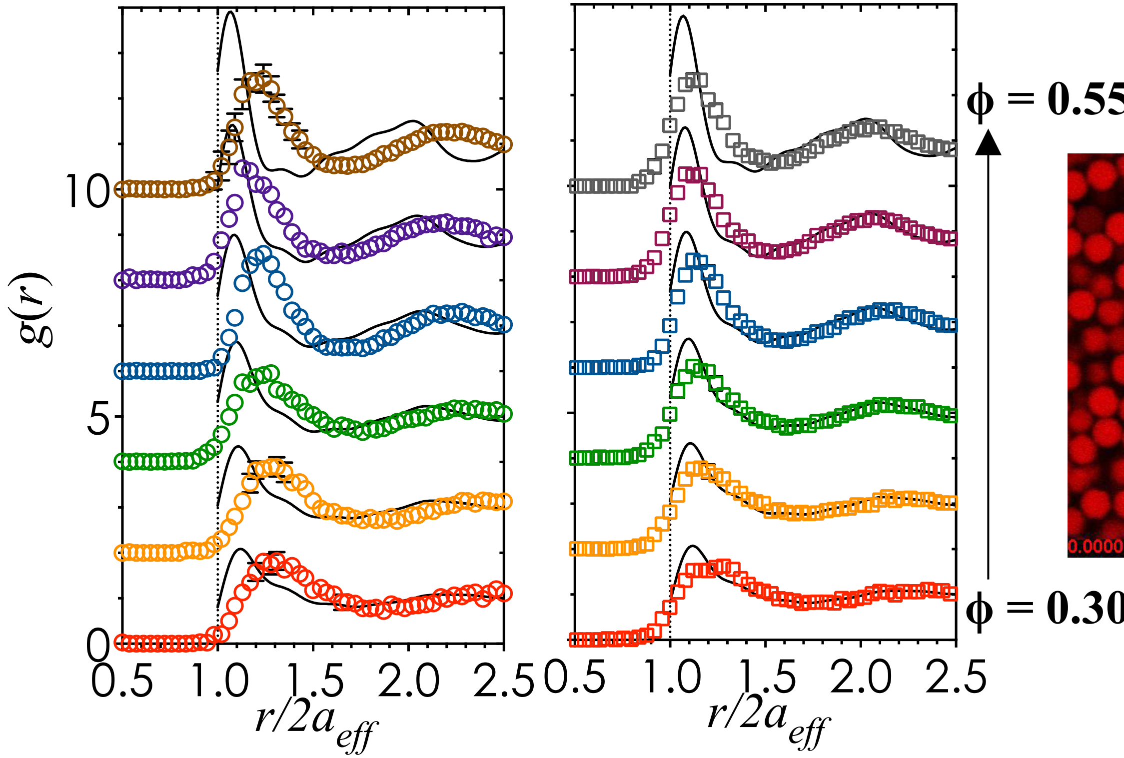


Hsiao et al. Soft Matter (2017)

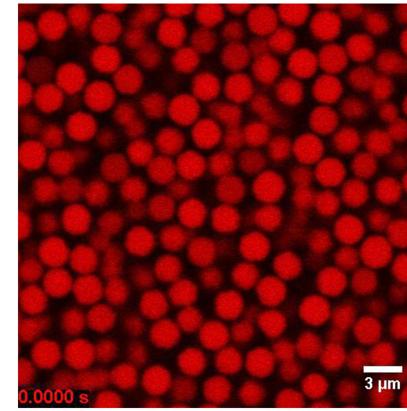
Accounting for repulsion in colloidal suspensions

Smooth





Rough



Yukawa electrostatics

$$U(r) = \pi\varepsilon_0\varepsilon\psi^2(2a)^2 \exp\left[-\kappa(r-2a)\right]/r$$

Mean spherical approximation closure to the Ornstein-Zernicke equation

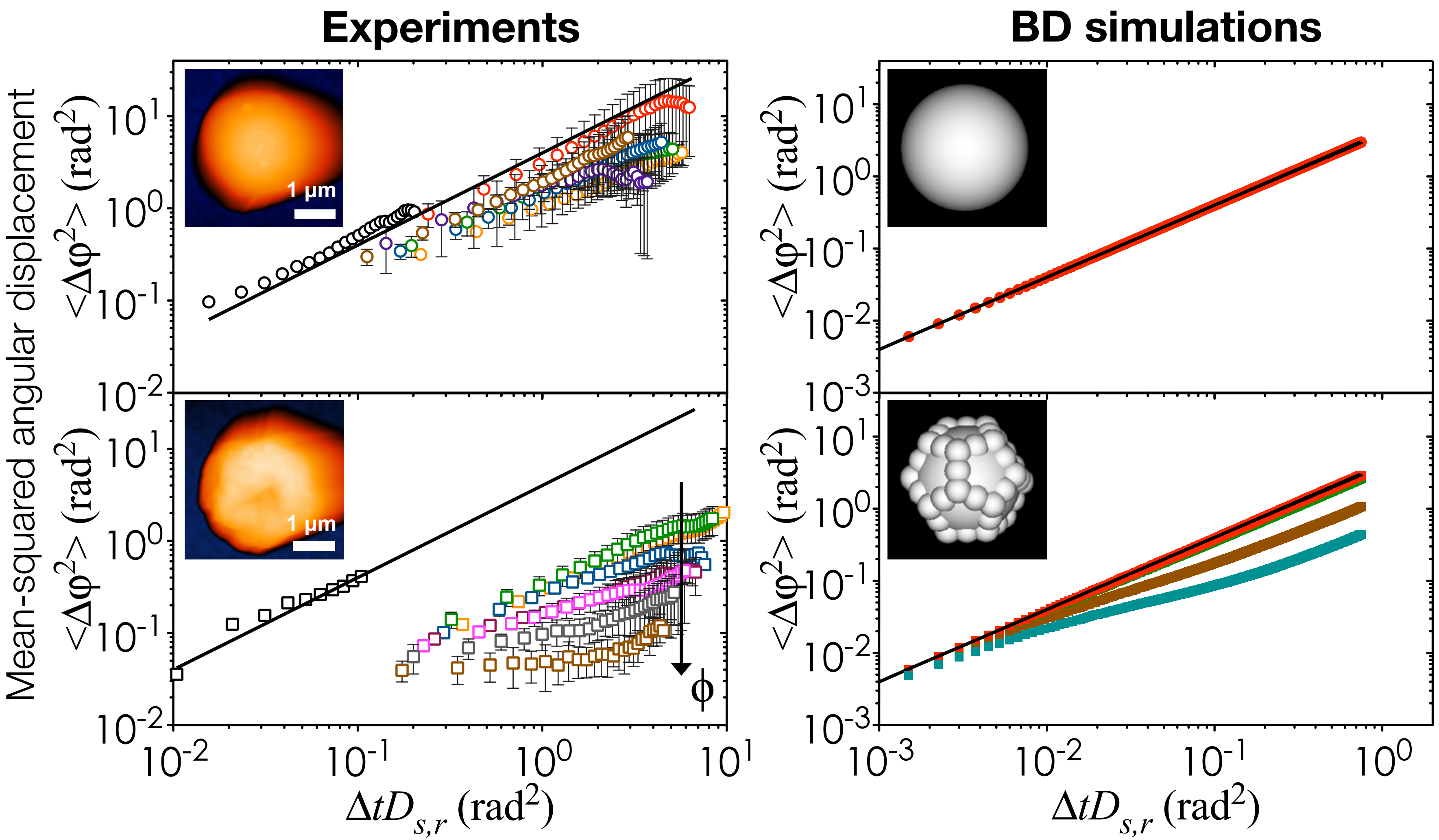
Hayter and Penfold, Mol Phys (1981)

$$c(x) = \begin{cases} A + Bx + \frac{1}{2}\eta A x^3 + \frac{C\sinh kx}{x} + \frac{F(\cosh kx - 1)}{x}, \; x = \frac{r}{2a} < 1 \\ -\gamma \exp(-kx)/x, \; x > 1 \end{cases}$$

$$g(x) = 1 + \frac{1}{12\pi\eta x}\int_0^\infty \left[S(K)-1\right] K \sin Kx \, dK$$

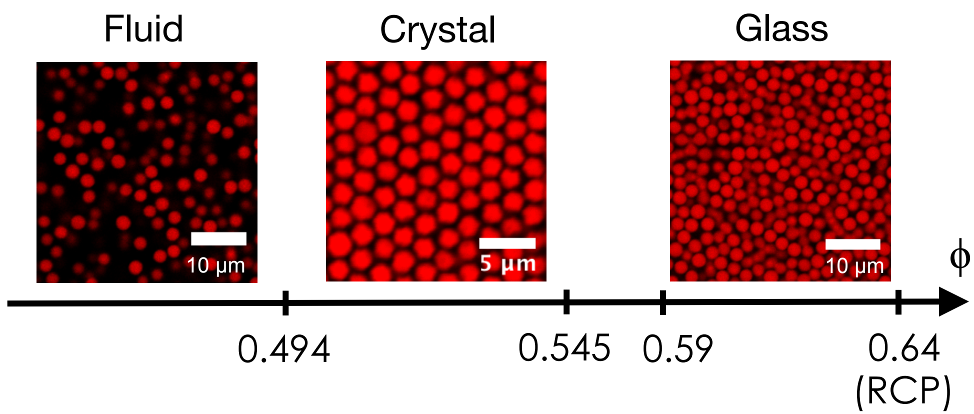
Hsiao et al. Soft Matter (2017)

Hindered rotational dynamics from surface geometry

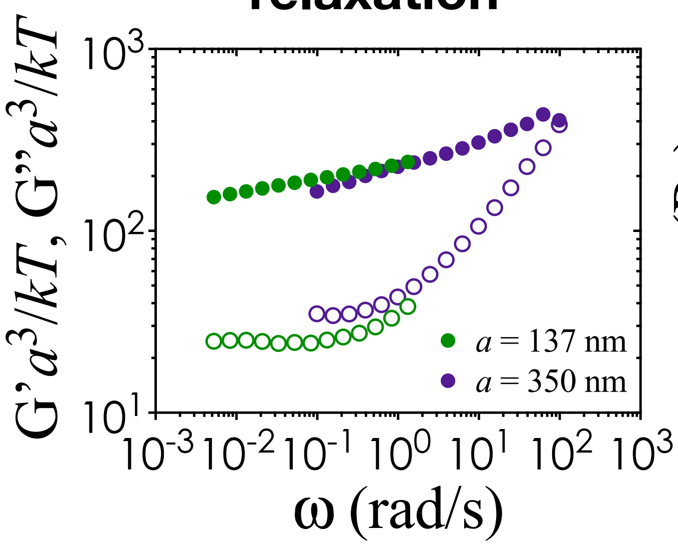


Hsiao et al. Soft Matter (2017)

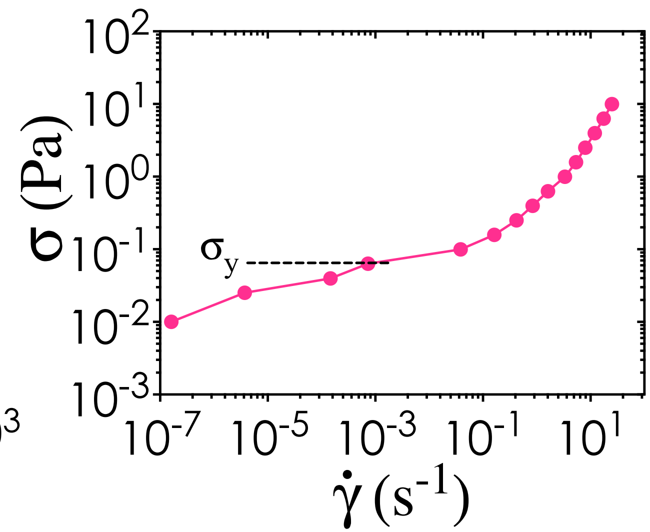
Rheological properties of colloidal glasses



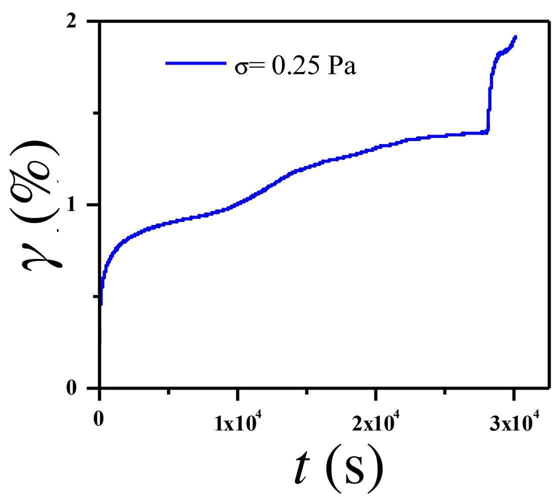
Viscoelastic 2-step relaxation



Yield stress behavior



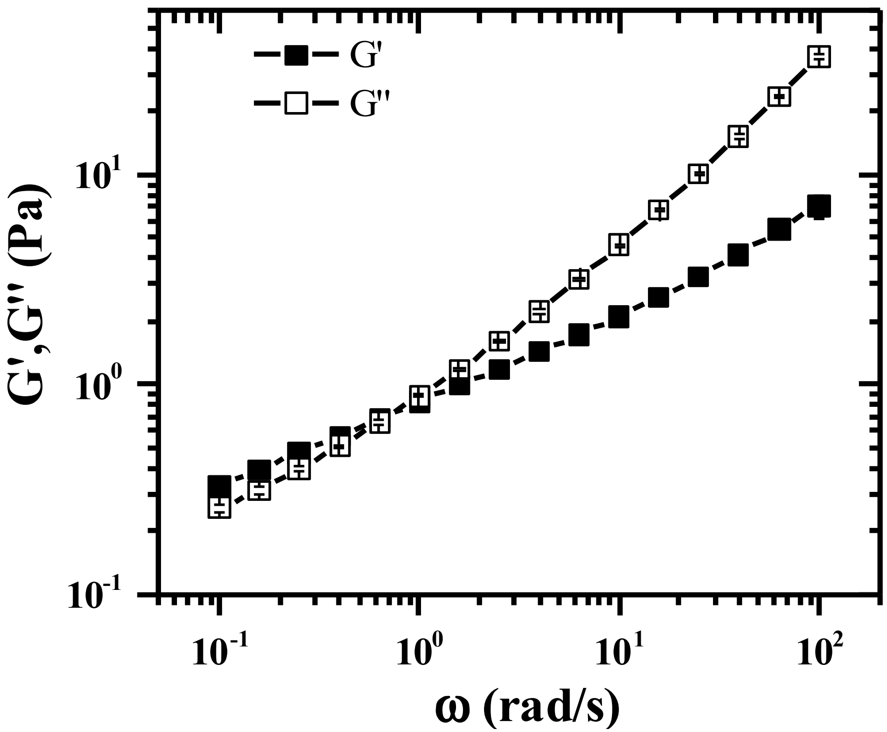
Creep near σ_s



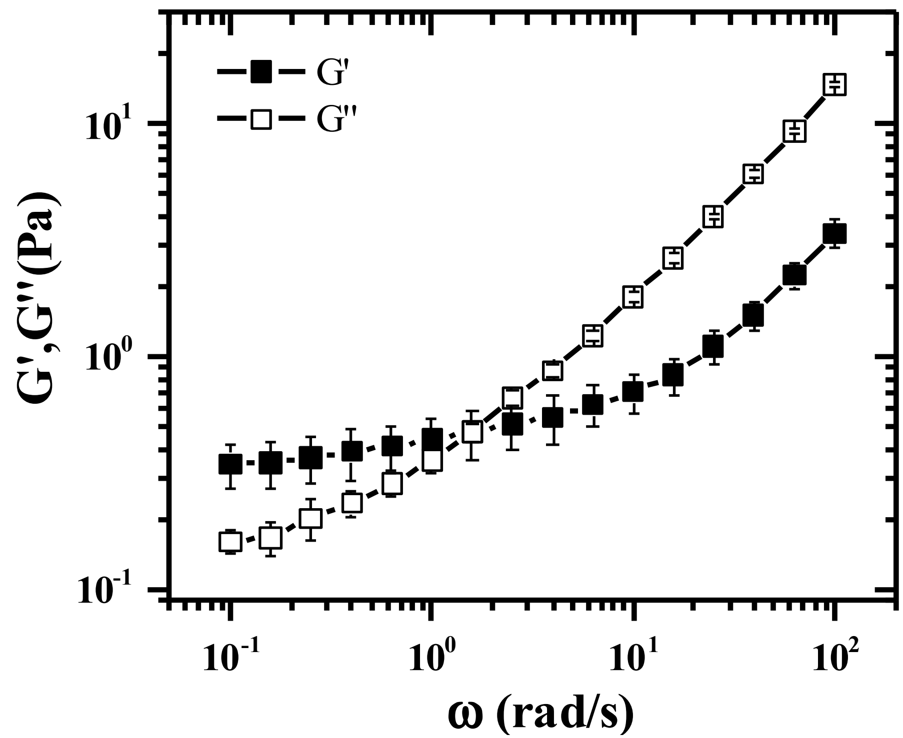
Courtesy: Alan Jacob

Viscoelastic comparison

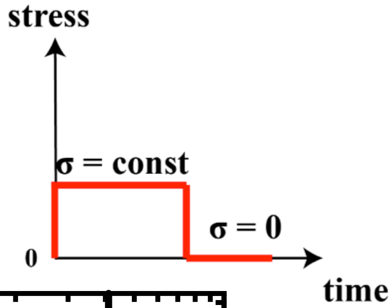
Smooth, ϕ = 0.64

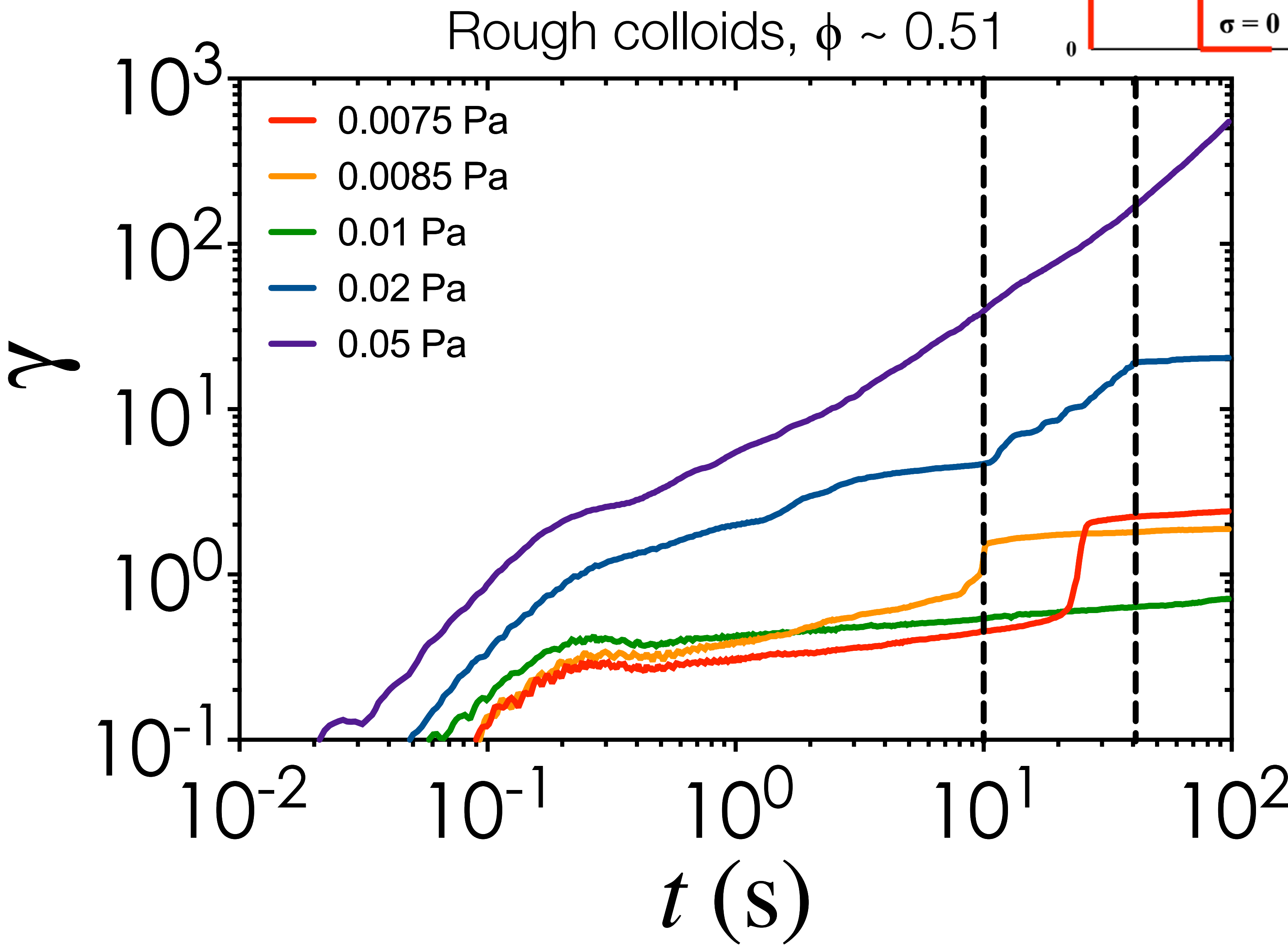


Rough, ϕ = 0.55

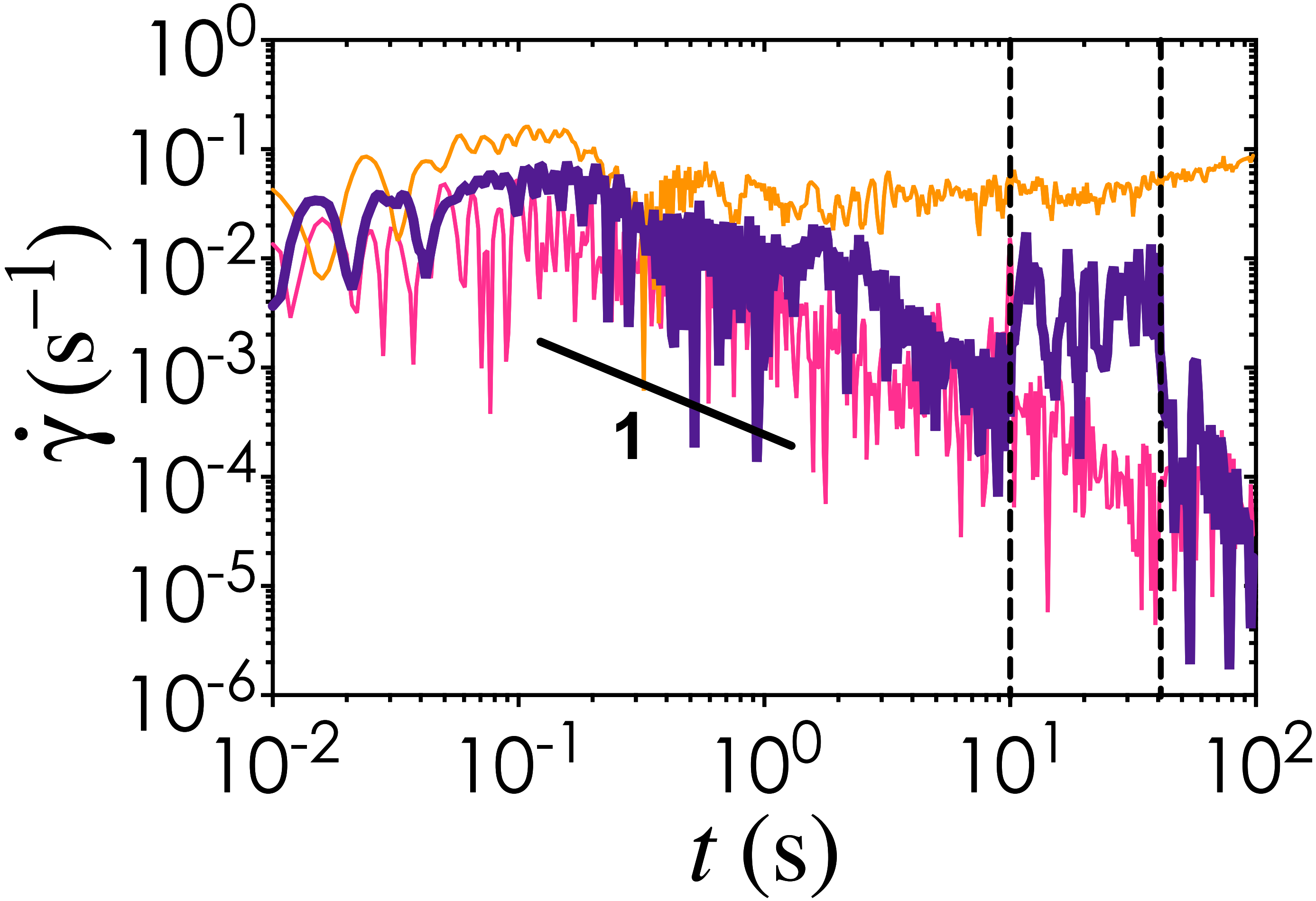


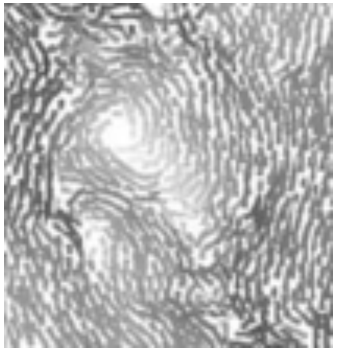
Creep under step stress



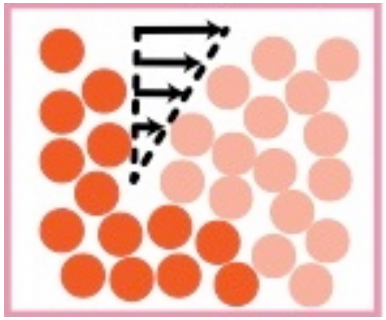


Creep shear rate showing transient fluidization

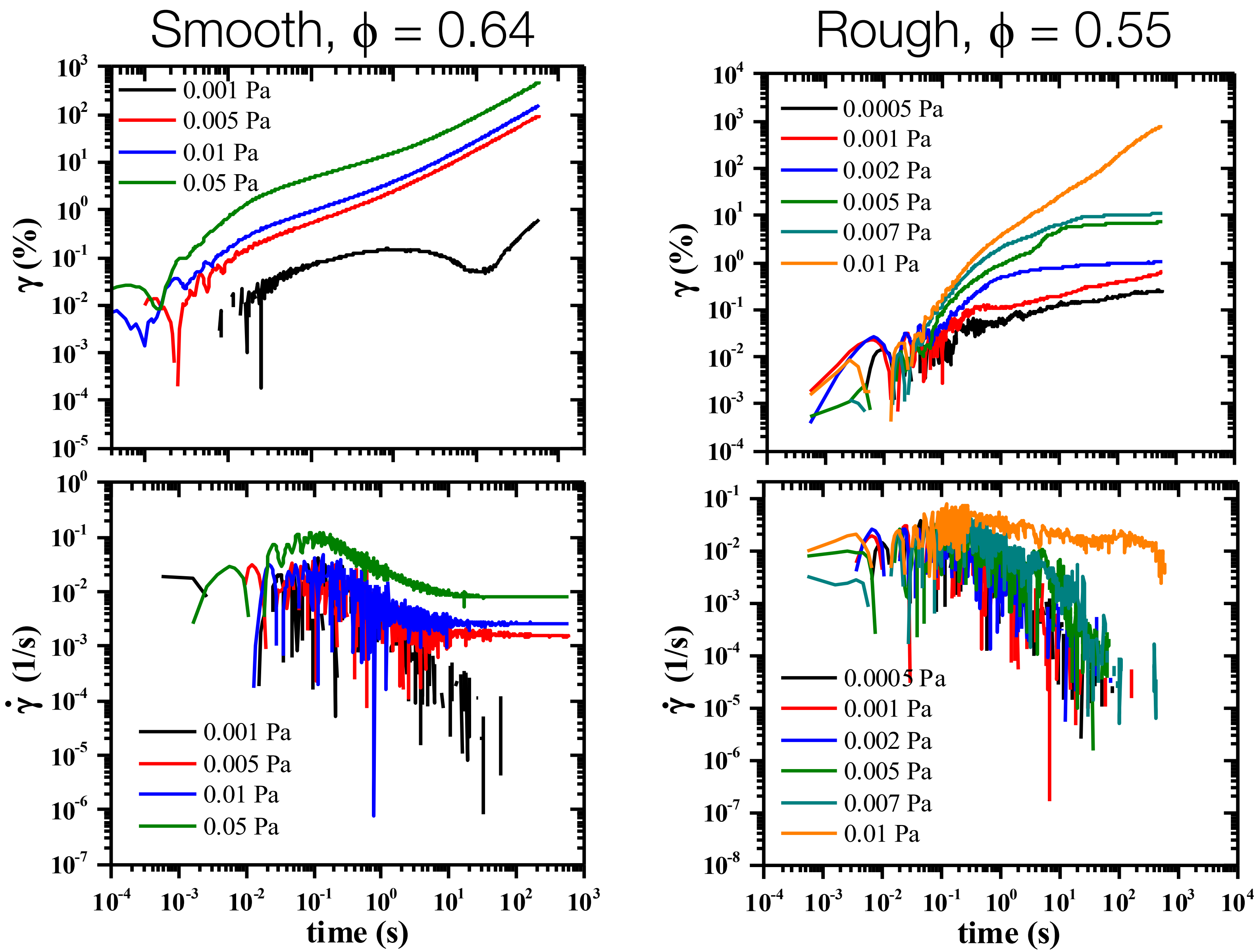




Maloney & Lemaitre.
PRE (2006).

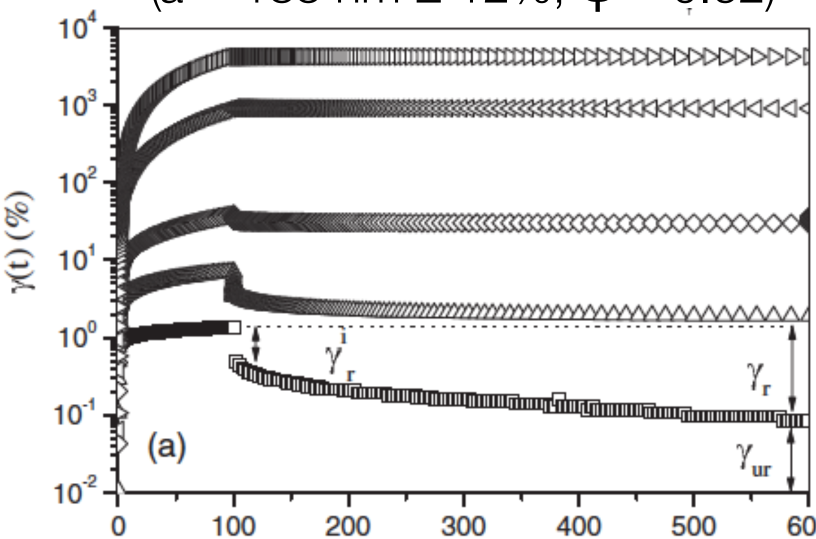


Comparisons between smooth and rough colloids



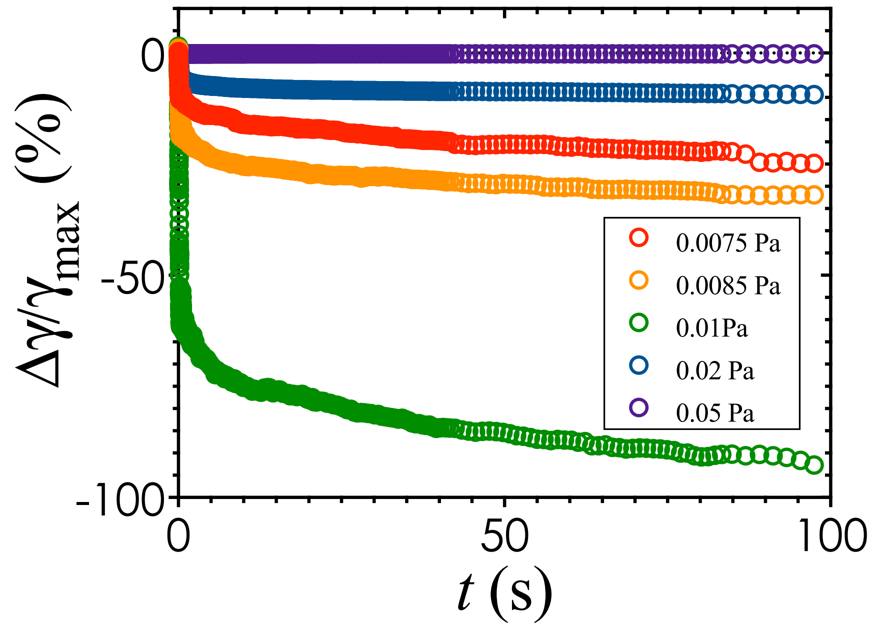
Strain recovery after creep cessation

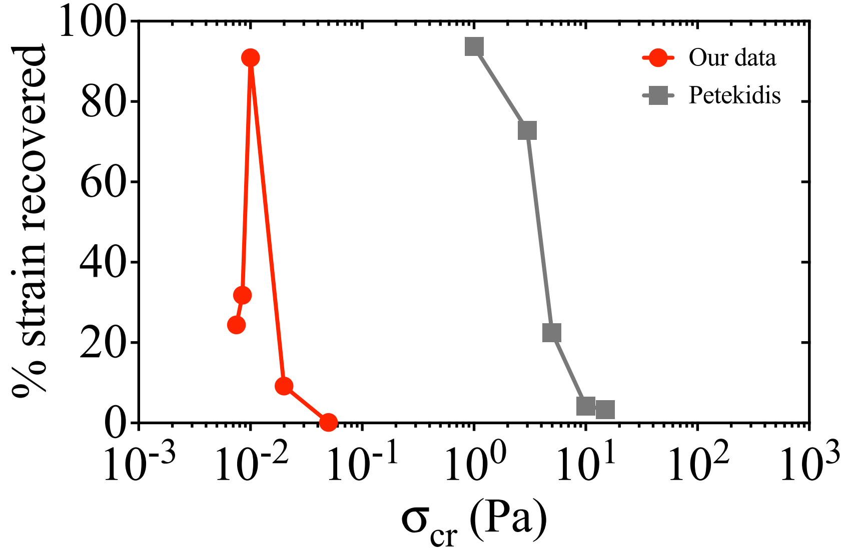
PHSA-PMMA smooth colloids
(a = 183 nm ± 12%, ϕ = 0.62)



Petekidis, Vlassopoulos & Pusey. JPCM (2004).

PHSA-PMMA rough colloids
(a = 1.7 μm ± 5%, ϕ = 0.49)





Testing nonlocal theories in dense suspensions

$$\mu(I,J,\phi)=\frac{\sigma_{xy}(J,\phi)}{P(J,\phi)}, I=\frac{2a\dot{\gamma}}{\sqrt{P/\rho_P}}, J=\frac{\eta_f\dot{\gamma}}{P}$$

Henann & Kamrin nonlocal theory

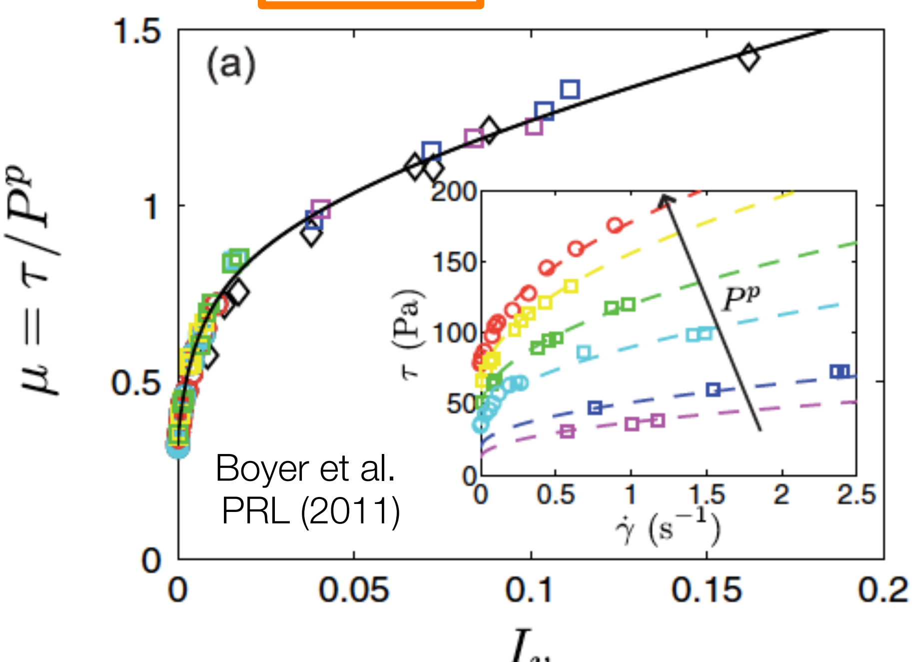
$$\sigma_{ij}=-P\delta_{ij}+\frac{2P}{g}\dot{\gamma}_{ij}$$

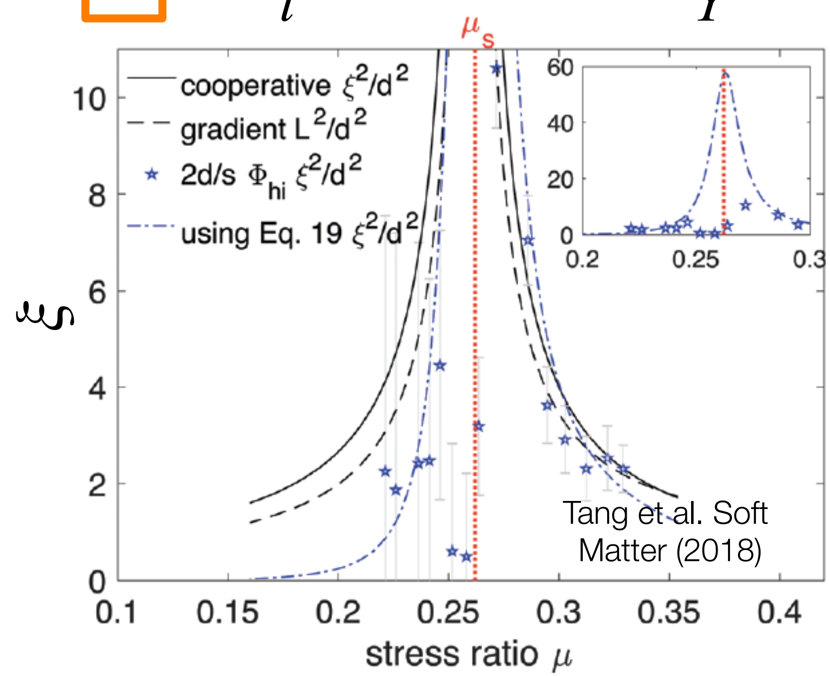
$$\nabla^2 g=\frac{1}{[\xi(\mu)]^2}(g-g_{loc}), g=\frac{\dot{\gamma}}{\mu}$$

Bouzid et al. nonlocal theory

$$Y=\frac{\sigma_{ij}}{\mu_s P}=\frac{\mu}{\mu_s}\left(1-A\frac{d^2(\nabla^2 I)}{I}\right)$$

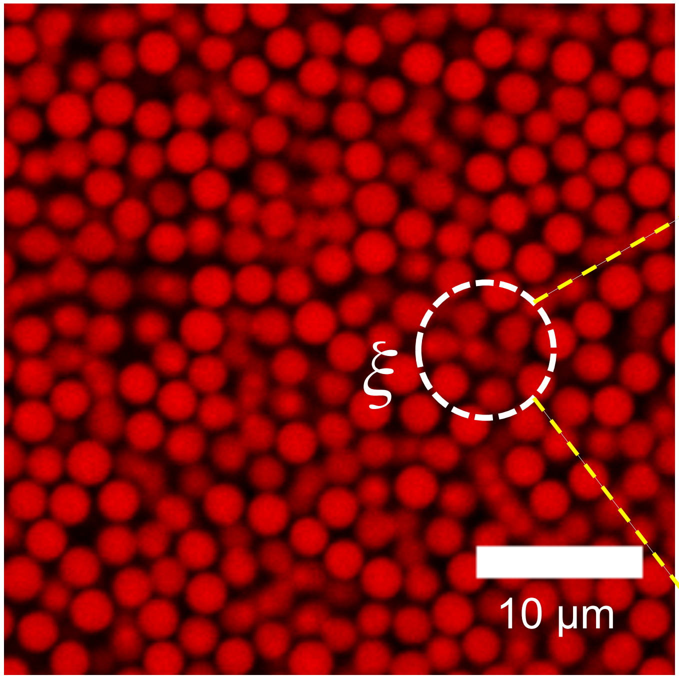
$$\dot{\gamma}=\frac{I_{loc}(f)}{t}-l^2\nabla^2 f, f=\frac{\dot{\gamma}}{Y}$$



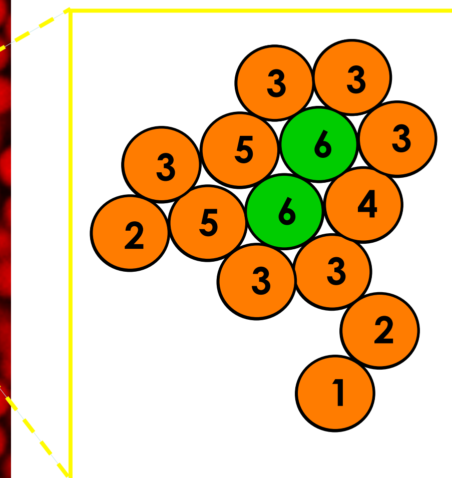


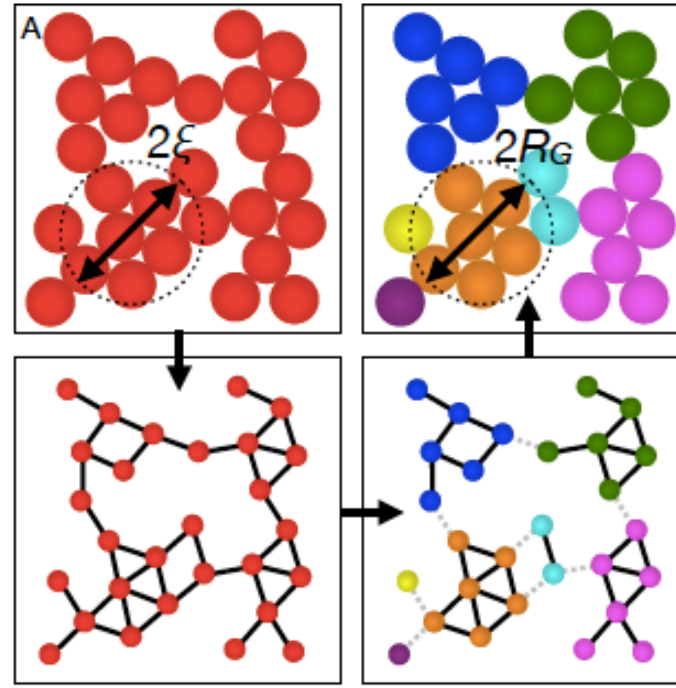
Measuring a correlation length scale

$$\xi\,(\phi, \mu, \dot{\gamma})$$



At ϕ = 0.60,
<z> ~ 8 for smooth
<z> ~ 6 for rough

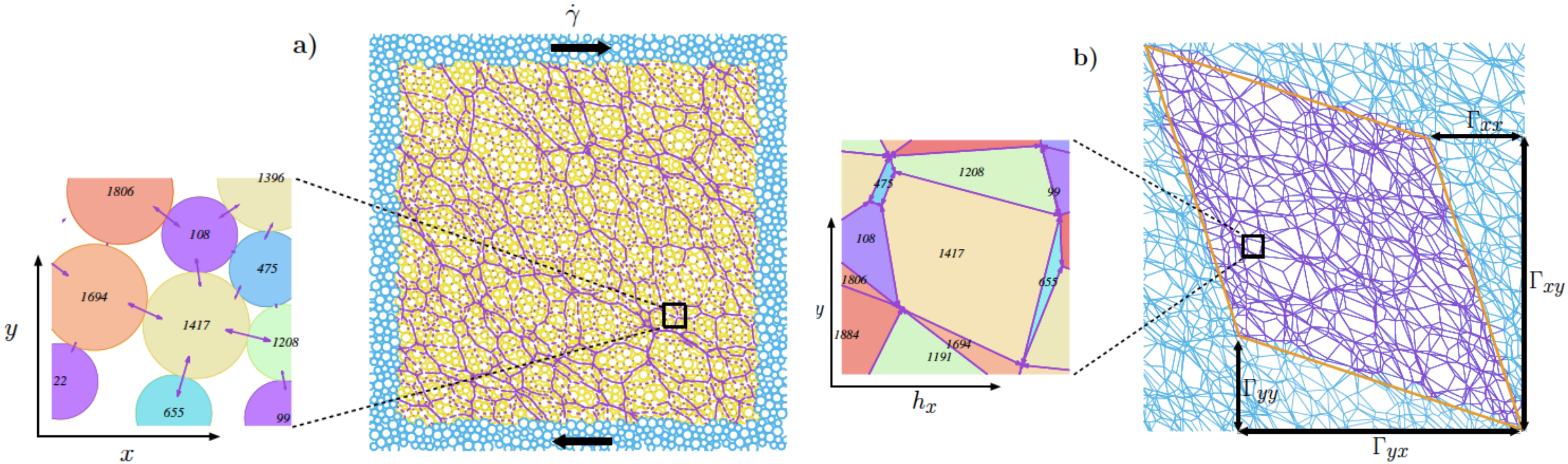




Whitaker & Hsiao et al. Submitted (2018).

Are local rigid clusters responsible for rheology?
Can we determine the length scale ξ as a function of φ?
Can we measure long-range velocity correlations?

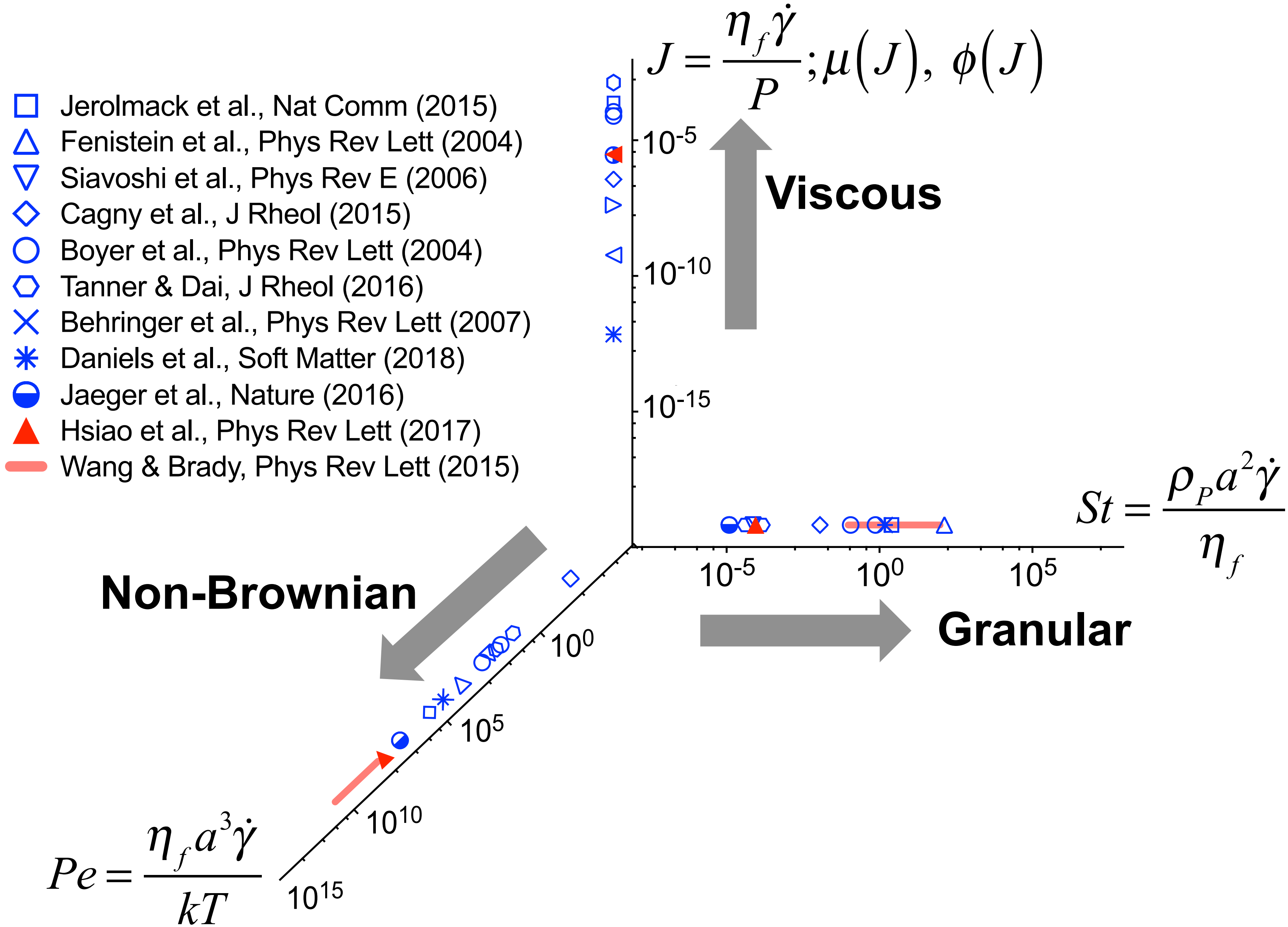
Testing force tiling concepts in suspensions



J. Morris & B. Chakraborty et al. arXiv.

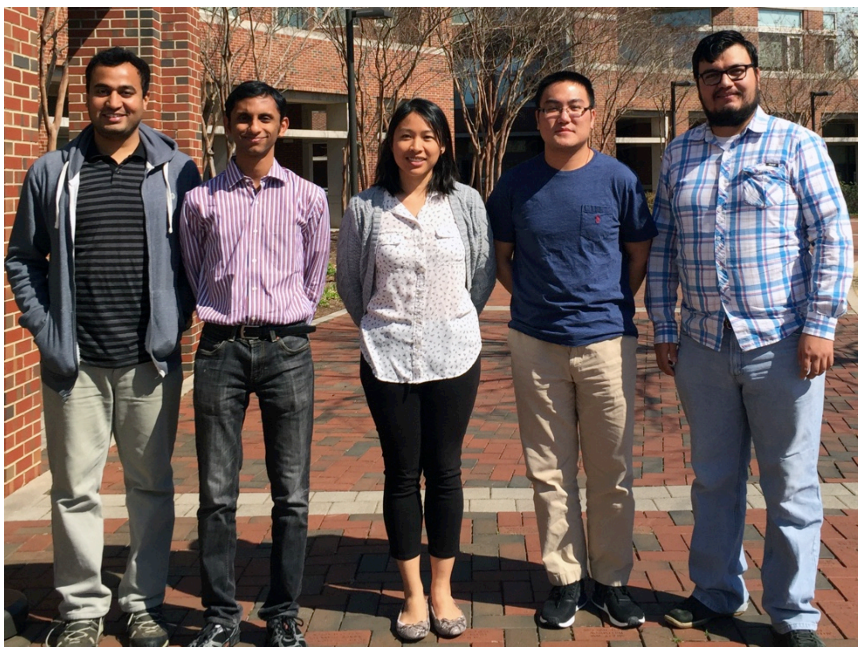
$$\mu = \frac{\sigma_{xy}}{P} \sim \frac{\sqrt{N_1^2 + \Sigma_{xy}^2}}{\Sigma_{xx} + \Sigma_{yy}}, \Sigma_{ij} = \sum_{i \neq j} L_{ij} F_{ij}$$

A state diagram for suspensions and granular flows



Summary

- Roughness introduces friction because it is difficult for particles to undergo full rotation
- Shifts maximum packing (based on viscosity divergence) to lower ϕ
- Causes glassy behavior at values of ϕ that is normally that of a fluid
- We may soon be able to test theories of $\mu(I, J)$ rheology in colloidal suspensions



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Local Arrangements Committee:
Saad Khan
Lilian Hsiao
Michael Rubinstein