Experimental Investigations of Shear-Thickening and Yield Stress: The Roles of Friction and Surface Chemistry

Philippe Bourrianne[1,2], **Rishabh More**[1,3] **and Gareth H. McKinley**[1]

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[2] ESPCI, Paris, France

[3] Monash University, Melbourne, Australia

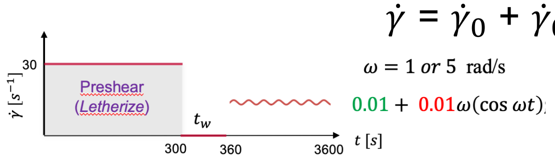
Experimental Investigations of Shear-Thickening and Yield Stress: The Roles of Friction and Surface Chemistry

- **Part 1**: *Tuning* of the Shear-Thickening Fluid Transition
  - Anisotropic (highly rough) particles (long range interactions)
  - Surface chemistry (short range chemical interactions)
  - How low a volume fraction can we get to and still achieve discontinuous shear thickening (DST)?
  - Appearance of a yield stress in some of these colloidal dispersions

- **[Part 2]:** (Computational and Experimental) Micromechanics of the Yield Stress
  - Thixotropy and material aging
  - The key role of rolling friction

- **Part 3**: **Parallel Superposition** (combining steady and oscillatory shear) with Gabor transform for time/frequency separation to probe the properties of thixotropic elastoviscoplastic (TEVP) fluids
  - In a **thixotropic elasto-visco-plastic** (TEVP) material the stress typically evolves on two (often) distinct time-scales; viscoelasticity characterized by τ_{ve} and thixotropy, characterized by τ_{thix}
  - Impose $\gamma(\mathrm{t}) = \dot{\gamma}_0 t + \gamma_0 \sin \omega t$

$$\dot{\gamma} = \dot{\gamma}_0 + \dot{\gamma}_0 \cos \omega t$$

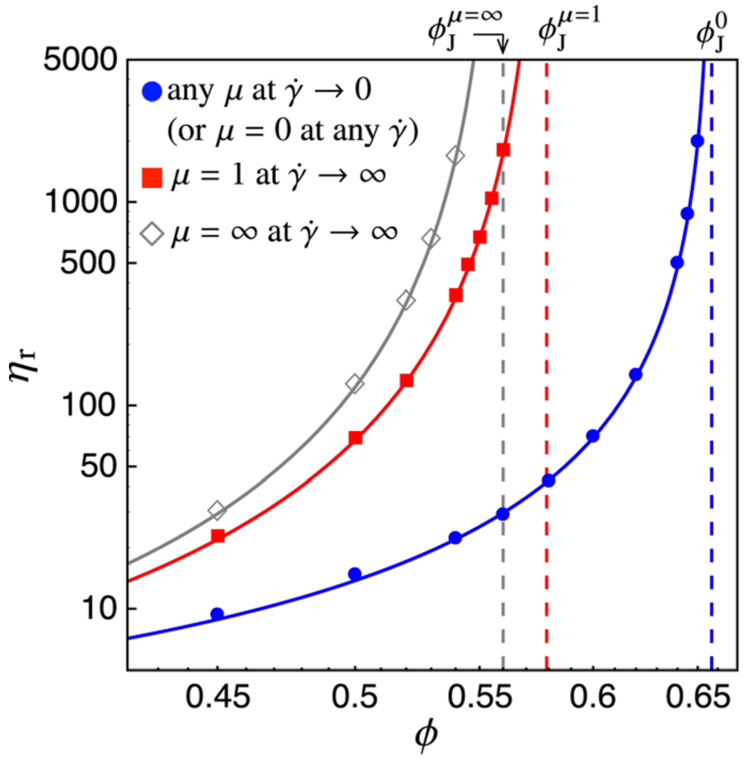


Monitor stress evolution in time:

$$\sigma(t, \omega, \dot{\gamma}_0) = \eta_{eff}(t, \dot{\gamma}_0)\, \dot{\gamma}_0 + \gamma_0 \{ G'_{||}(\omega, t) \sin\omega t \ + G''_{||}(\omega, t) \cos\omega t \}$$

The shear-thickening transition is set by **frictional interactions**

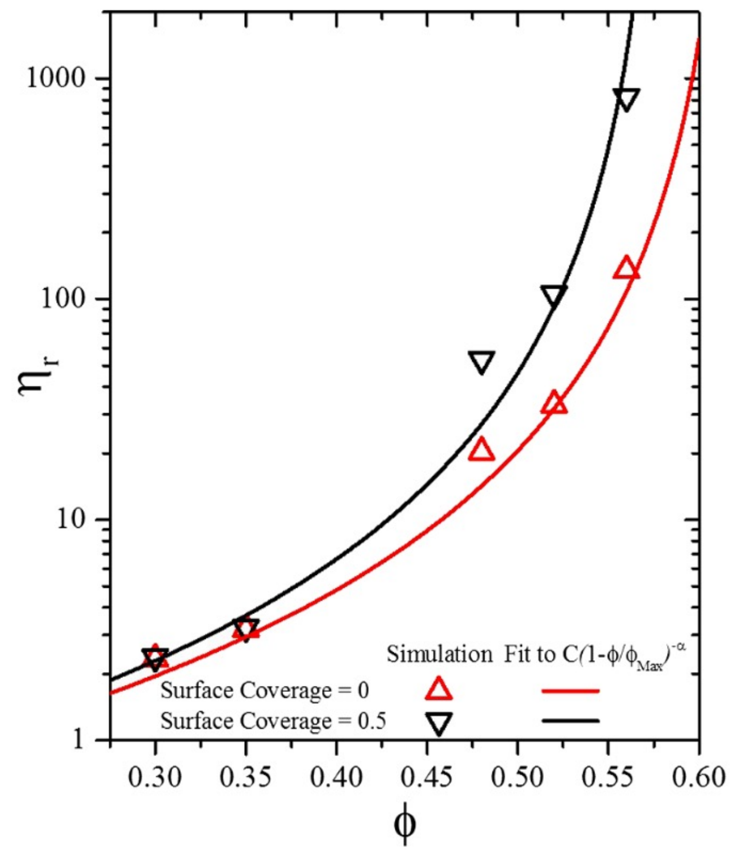
- Explore the competing roles of *roughness* (μ) **and** *surface chemistry* in controlling the shear thickening transition



Mari, Seto, Morris & Denn, 2014

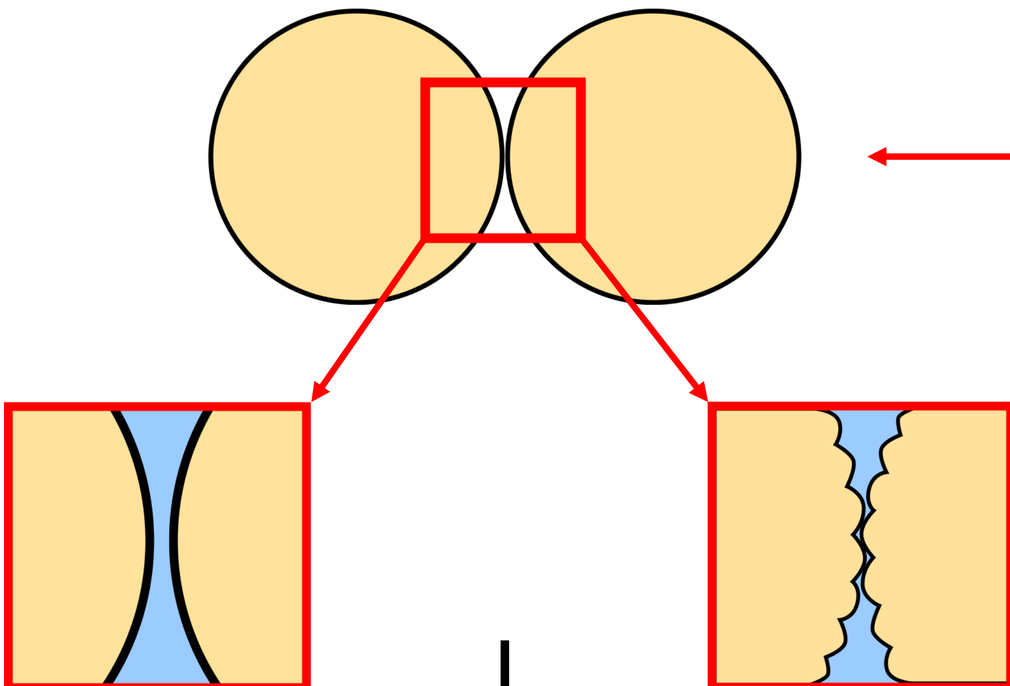
Boyer, Guazelli & Pouliquen, 2011

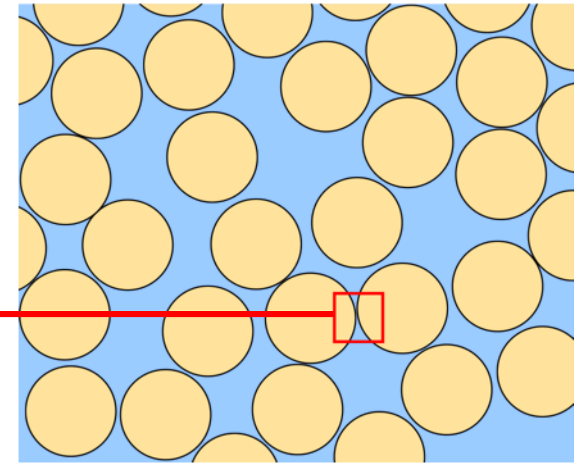
Wyart & Cates, 2014



Jamali & Brady, 2019

Frictional interactions





Hydrodynamic forces

Wagner *et al.*, 2009
Lin *et al.*, 2015
Jamali *et al.*, 2019

Solid friction

Wyart *et al.*, 2014
Mari *et al.*, 2014
Comtet *et al.*, 2015
Hsu *et al.*, 2018

PHYSICAL REVIEW RESEARCH **4**, 033062 (2022)

Tuning the shear thickening of suspensions through surface roughness and physico-chemical interactions

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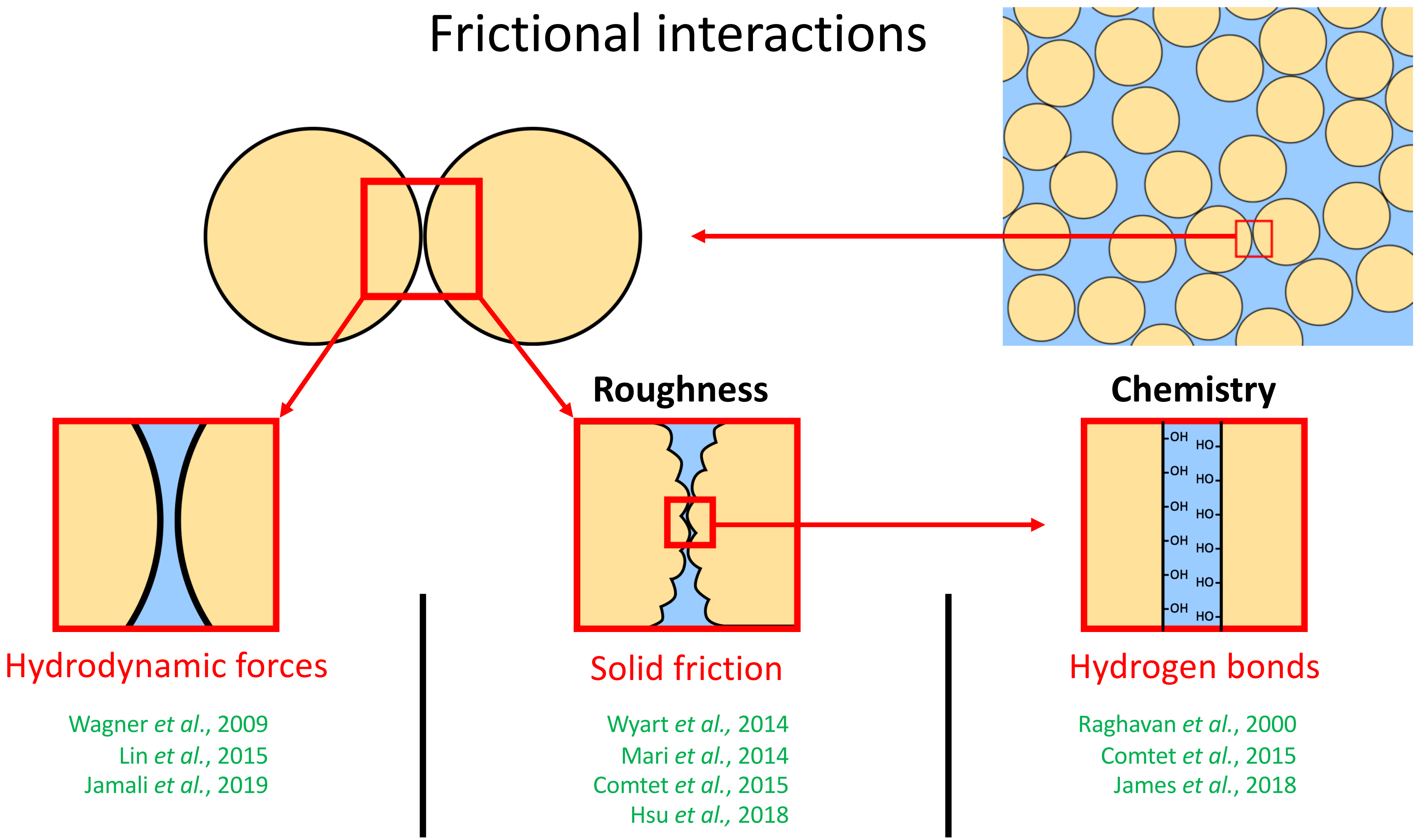
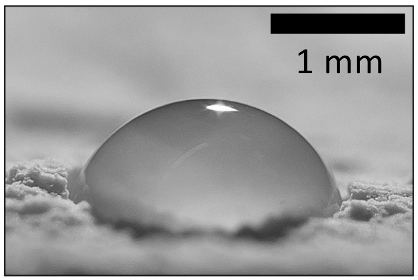
[2]*MultiScale Material Science for Energy and Environment, UMI 3466, CNRS-MIT, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA*
[3]*ENSL, CNRS, Laboratoire de Physique, F-69342 Lyon, France*

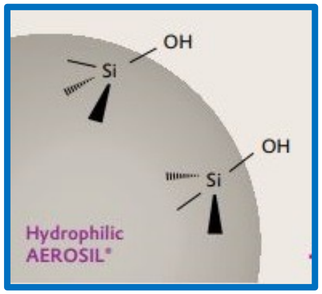
Bourrianne *et al.*, ***Phys Rev. Research 2022***


Frictional interactions
Roughness
Chemistry
-OH
HO-
Hydrodynamic forces
Wagner et al., 2009
Lin et al., 2015
Jamali et al., 2019
Solid friction
Wyart et al., 2014
Mari et al., 2014
Comtet et al., 2015
Hsu et al., 2018
Hydrogen bonds
Raghavan et al., 2000
Comtet et al., 2015
James et al., 2018

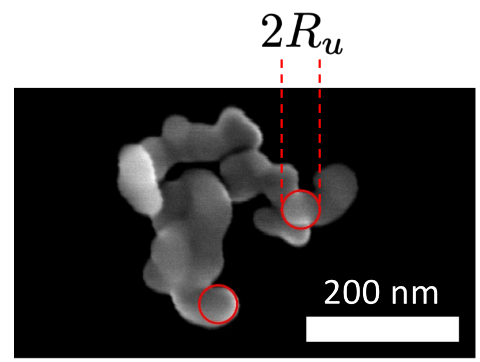
Suspensions of **fumed silica** in polypropylene glycol (polar solvent)

Raghavan *et al.*, 1995
Raghavan *et al.*, 1997



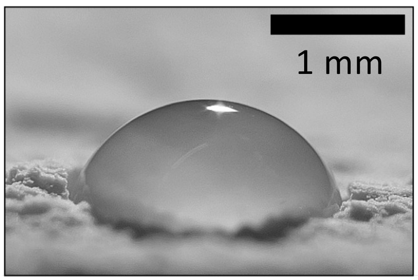


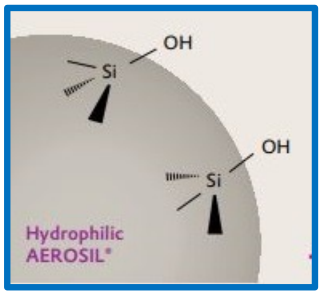
Hydrophilic (HP)



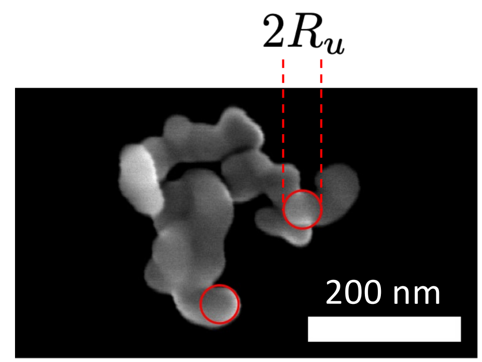
$$R_u = 25\ \mathrm{nm}$$
$$\Sigma_\mathrm{s} \sim 40\ \mathrm{m^2/g}$$

Suspensions of **fumed silica** in polypropylene glycol





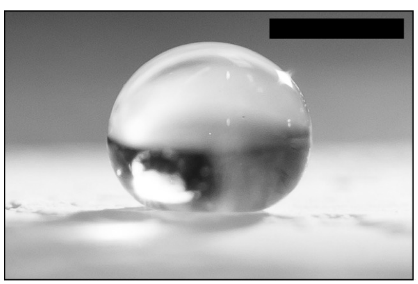
Hydrophilic (HP)

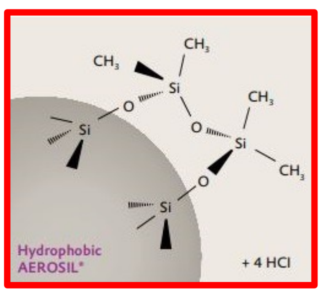


$$R_u = 25\ \mathrm{nm}$$

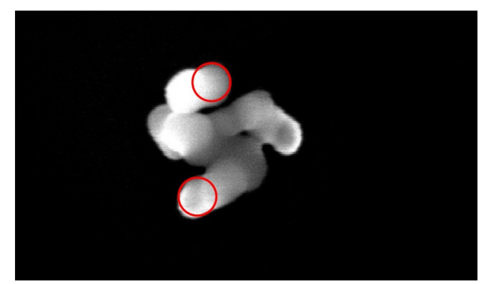
$$\Sigma_s \sim 40\ \mathrm{m^2/g}$$

CHEMISTRY

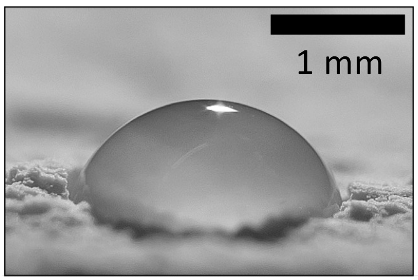


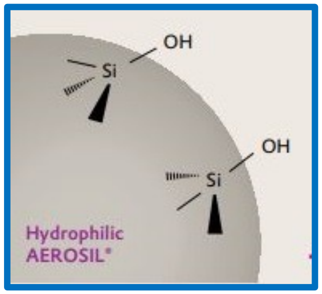


Hydrophobic (HB)



Suspensions of **fumed silica** in polypropylene glycol





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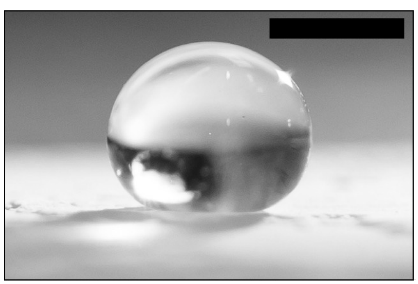
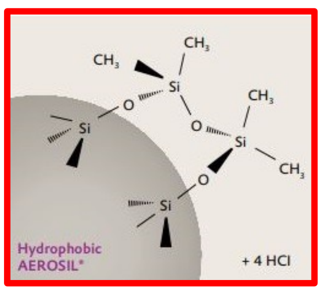
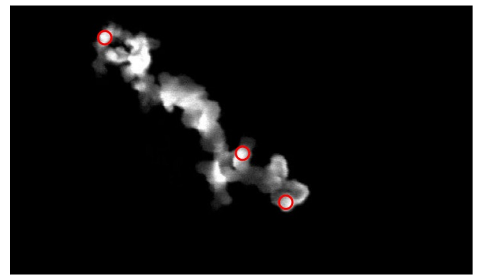
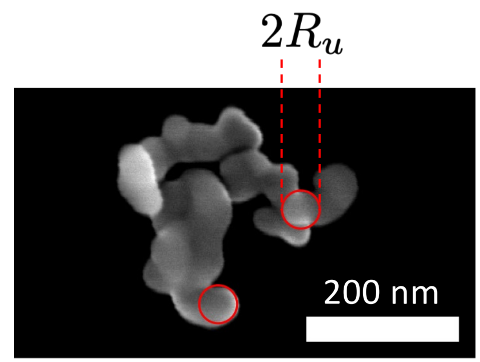




Hydrophobic (HB)

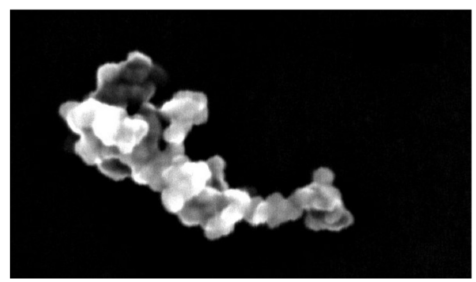
CHEMISTRY

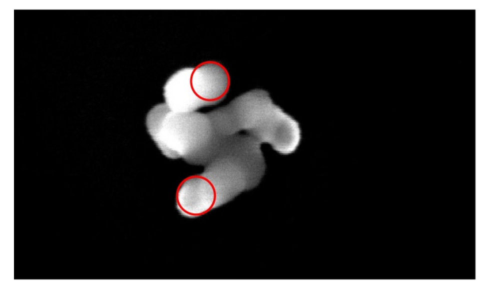




$R_u = 10$ nm
$\Sigma_s \sim 300\ \mathrm{m}^2/\mathrm{g}$

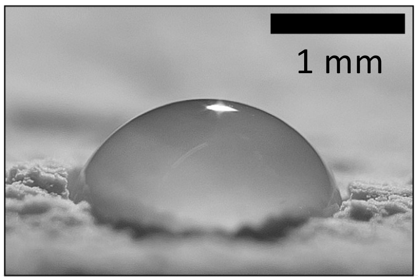
$R_u = 25$ nm
$\Sigma_s \sim 40\ \mathrm{m}^2/\mathrm{g}$





GEOMETRY – Nanometric roughness; high surface area/volume

Shear-thickening transition at low volume fraction



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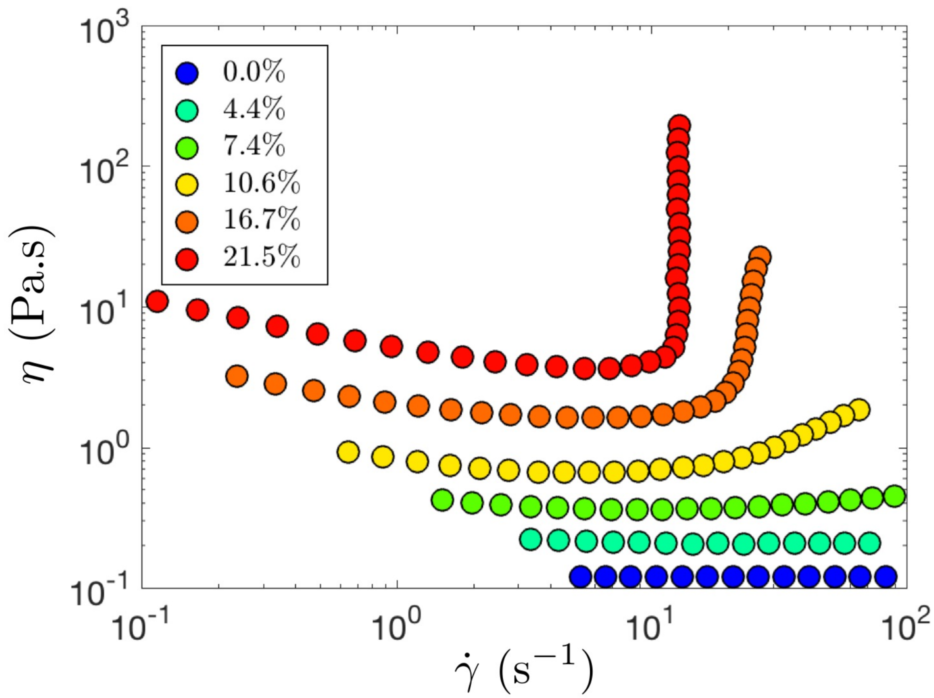
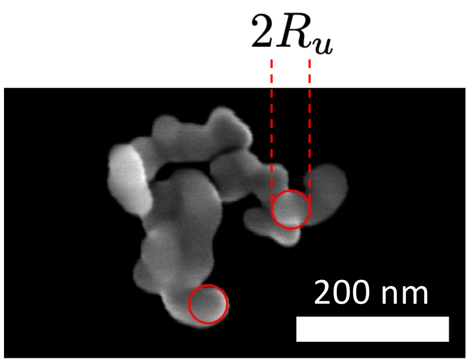
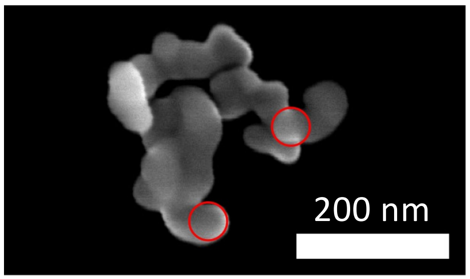




$$R_u = 25 \text{ nm}$$

- ❑ Continuous shear-thickening (CST)
  $\phi > 5\%$
- ❑ Discontinuous shear-thickening (DST)
  $\phi > 17\%$

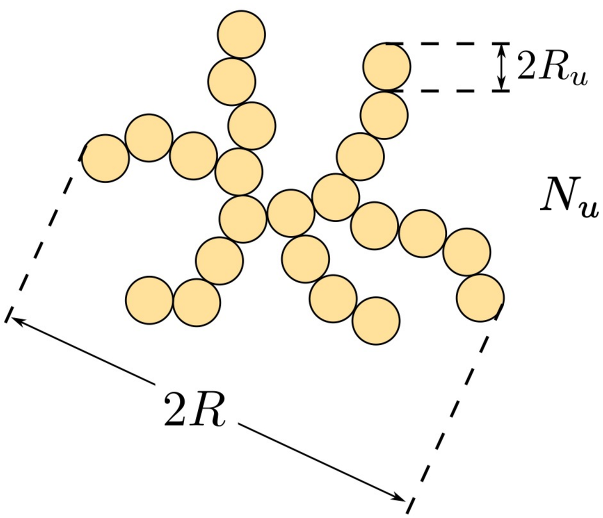
Onset of shear-thickening



Interparticle distance *L*

$$\phi = \frac{\Omega_p}{L^3}$$

$$\Omega_p = N_u \frac{4}{3} \pi {R_\mathrm{u}}^3$$



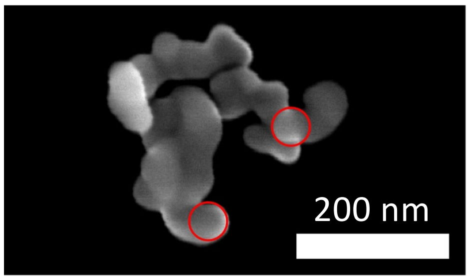
$$L = \left(\frac{4\pi {R_u}^3 N_u}{3\phi} \right)^{1/3}$$

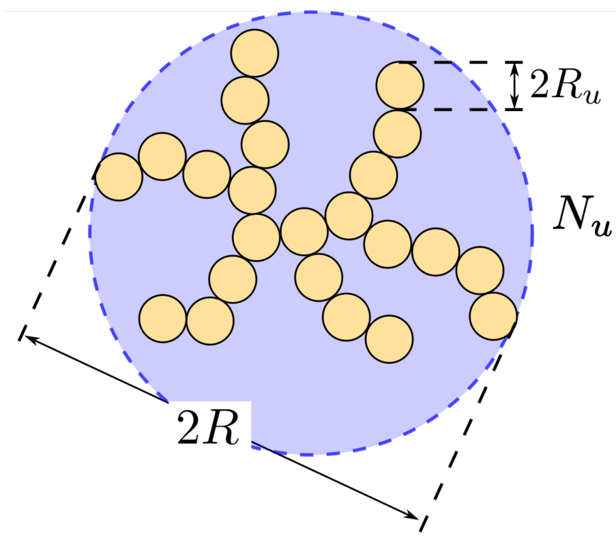
$R_\mathrm{u} = 25$ nm

$N_\mathrm{u} \sim 25$

$R = 150$ nm

Onset of shear-thickening





Interparticle distance *L*

$$\phi = \frac{\Omega_p}{L^3} \qquad \Omega_p = N_u \frac{4}{3} \pi {R_\mathrm{u}}^3$$

$$L = \left(\frac{4\pi {R_u}^3 N_u}{3\phi} \right)^{1/3}$$

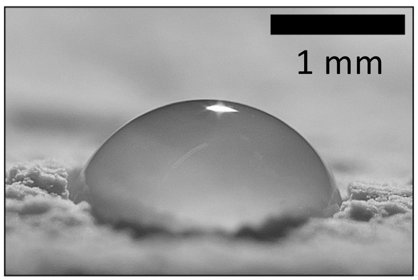
$R_\mathrm{u} = 25$ nm

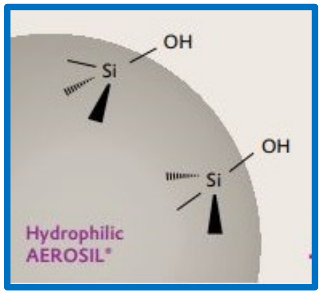
$N_\mathrm{u} \sim 25$

$R = 150$ nm

$$L(\phi^*) \sim 2R \qquad \phi^* \sim 6\%$$

Hydrophilic vs Hydrophobic





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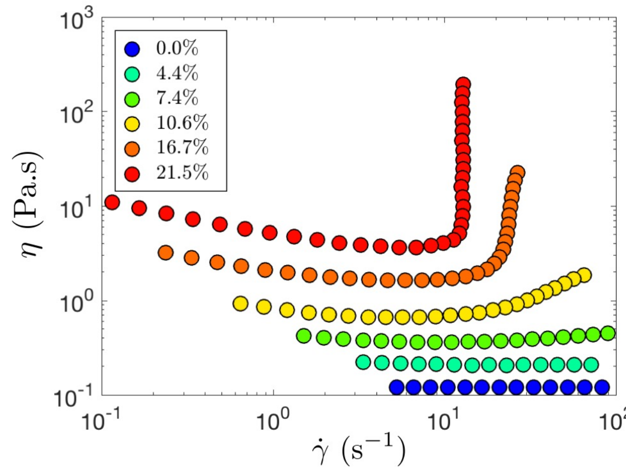
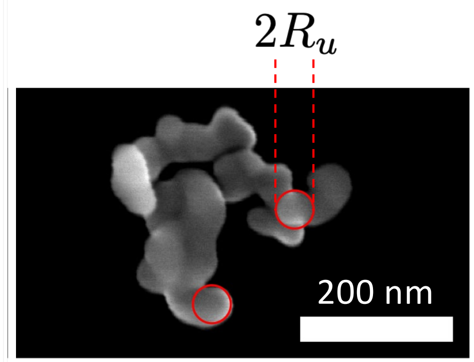
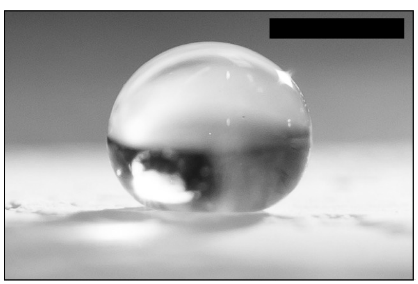


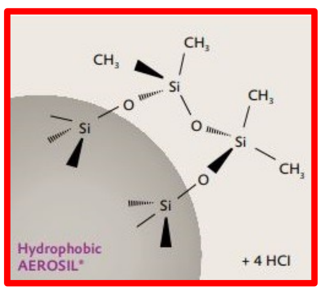


CHEMISTRY

$$R_u = 25 \text{ nm}$$

$\Sigma_s \sim 40\ m^2/g$





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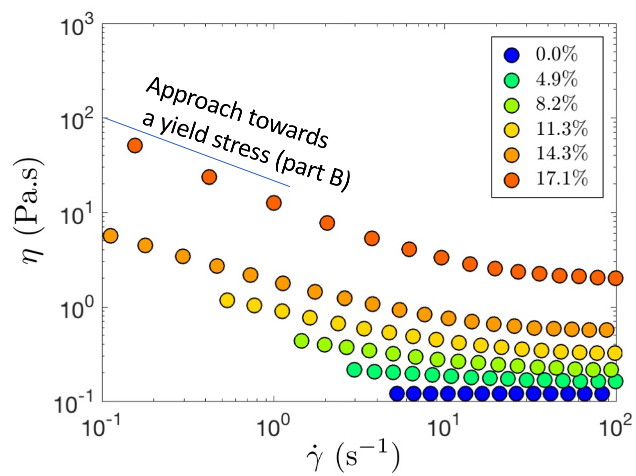
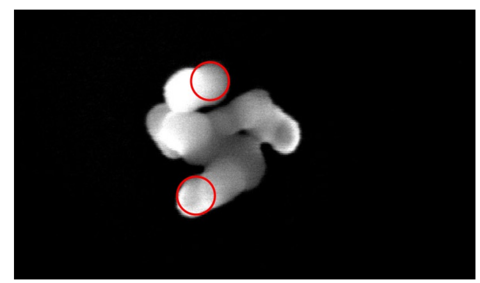
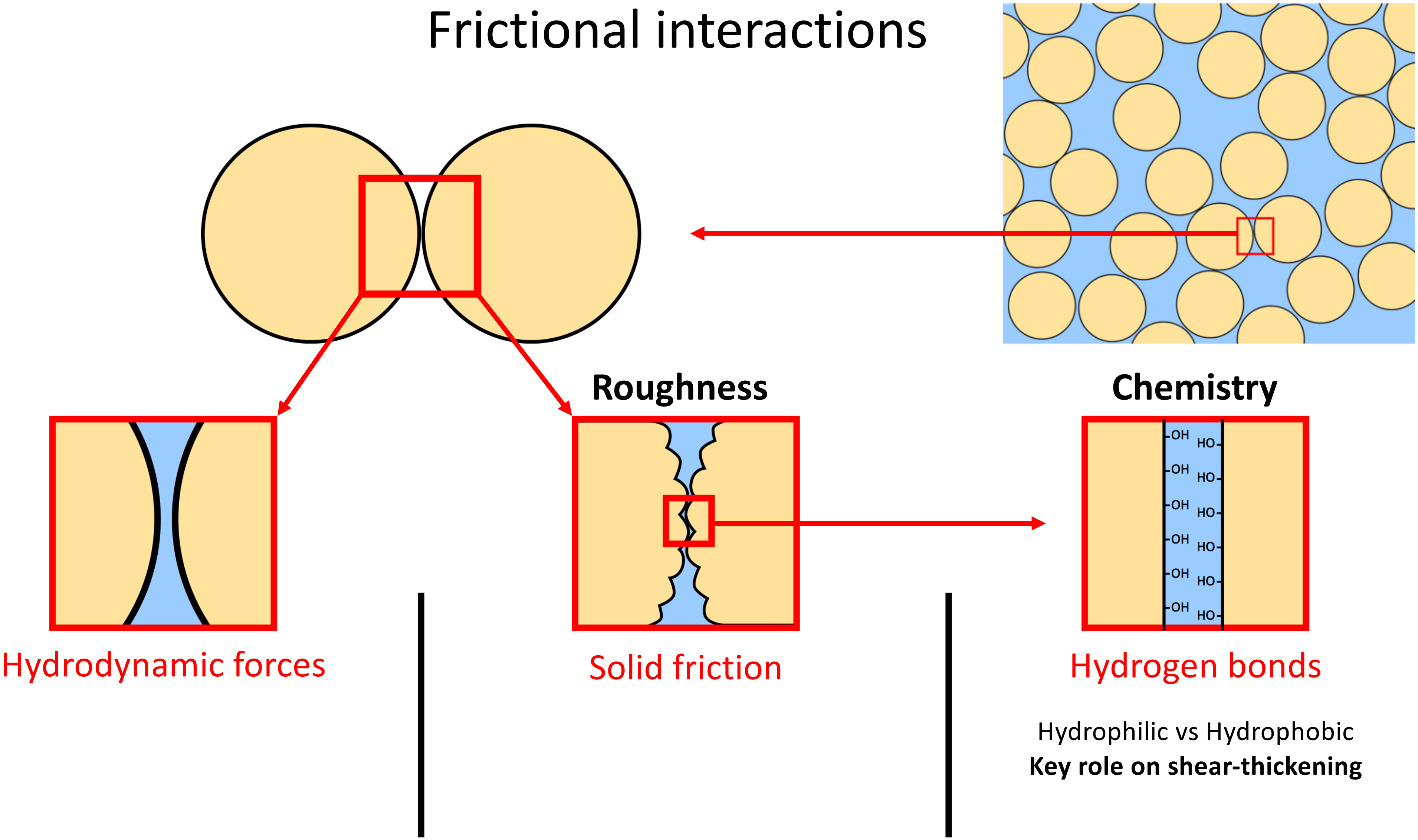




Frictional interactions



Shear-thickening quantification

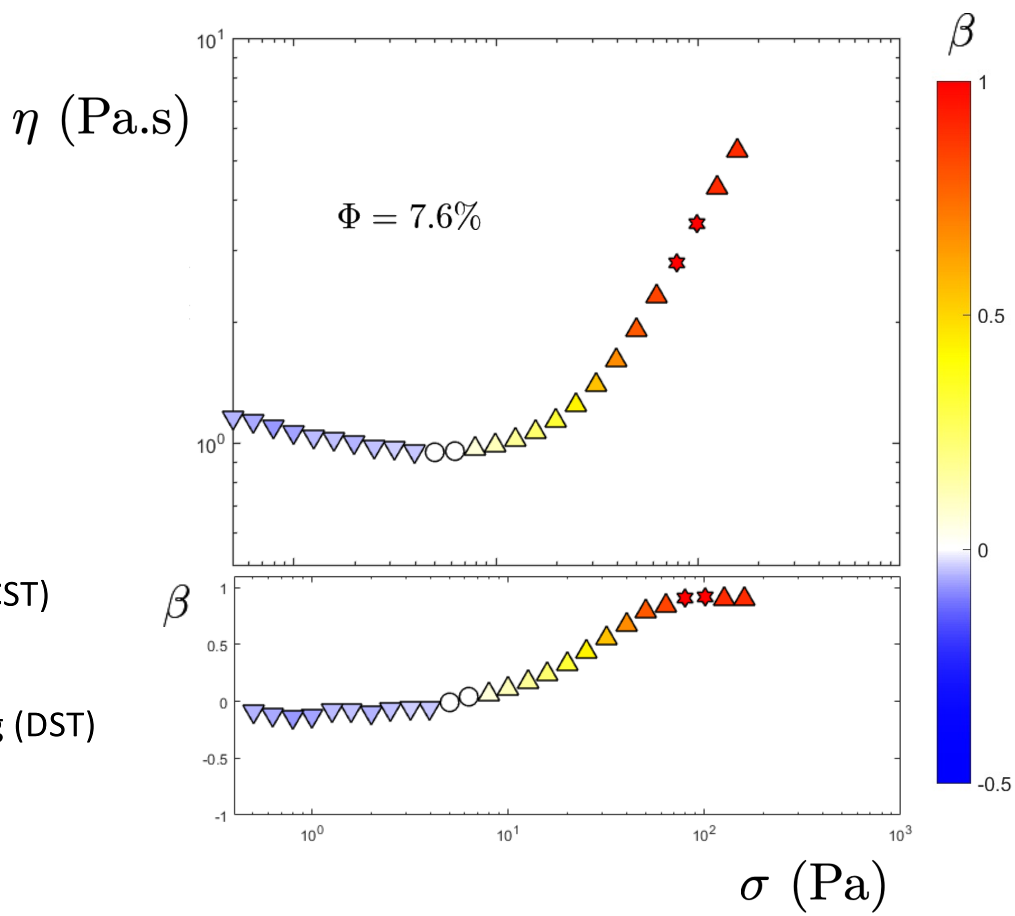
$$\beta = \dot{\gamma}\frac{d\eta}{d\sigma} = 1 - \eta\frac{d\dot{\gamma}}{d\sigma}$$

○ $\beta \approx 0$ $\Rightarrow$ Newtonian

▽ $\beta < 0$ $\Rightarrow$ Shear thinning

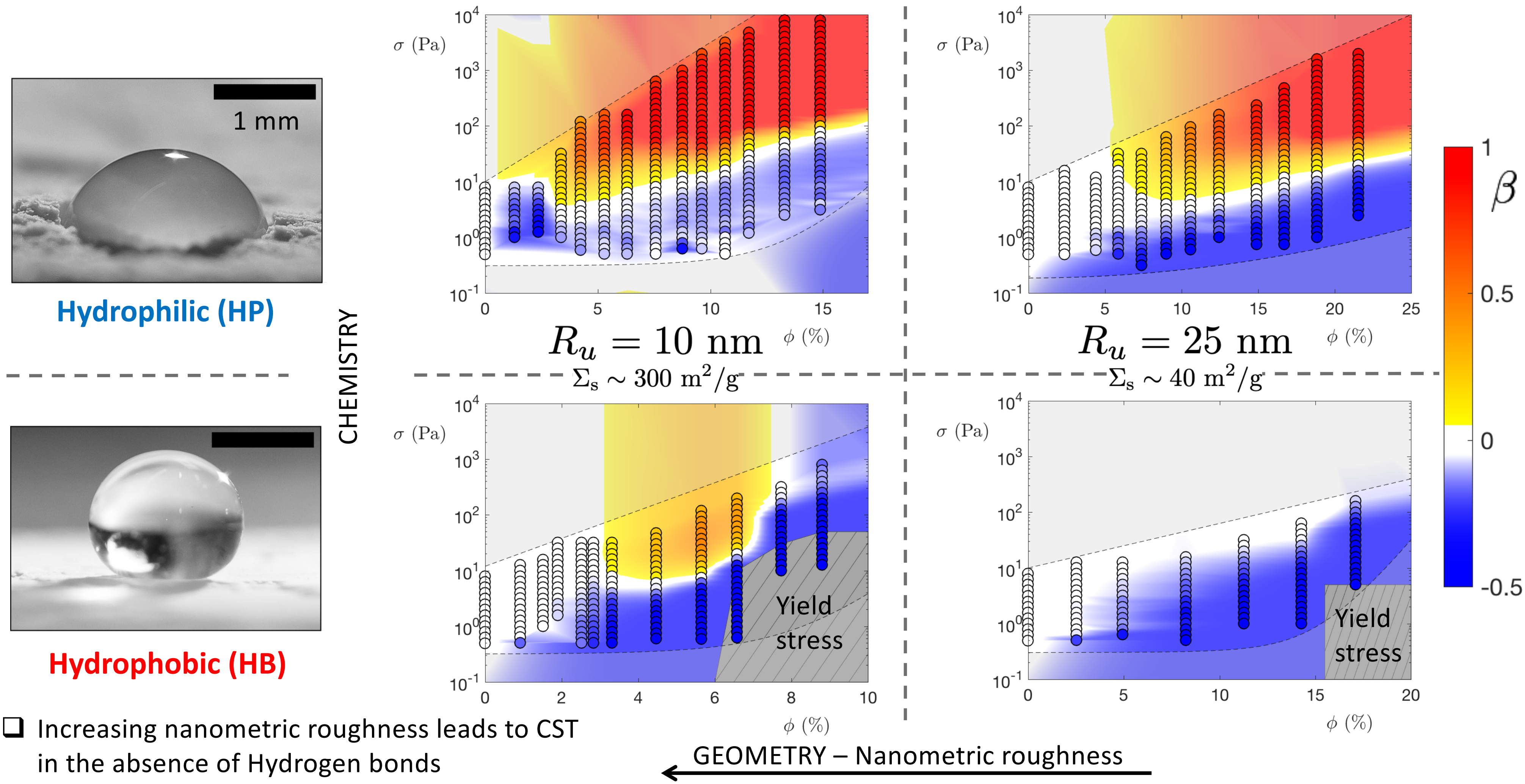
△ $0 < \beta < 1$ $\Rightarrow$ Continuous shear-thickening (CST)

✡ $\beta = 1$ $\Rightarrow$ Discontinuous shear-thickening (DST)



Brown *et al.*, 2009
Royer *et al.*, 2016

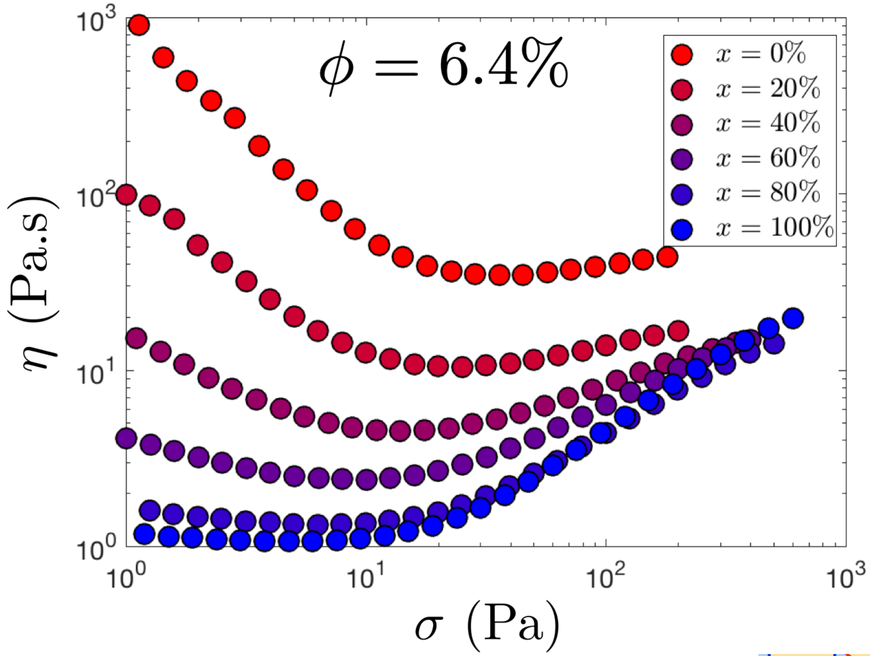
Influence of particle **nanometric roughness**

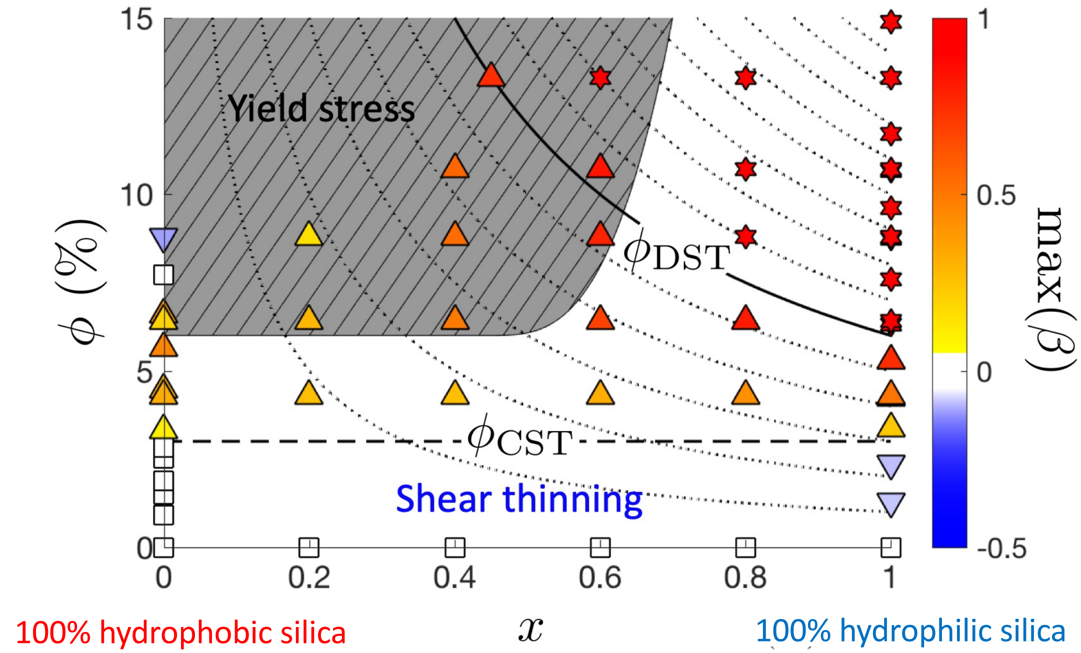


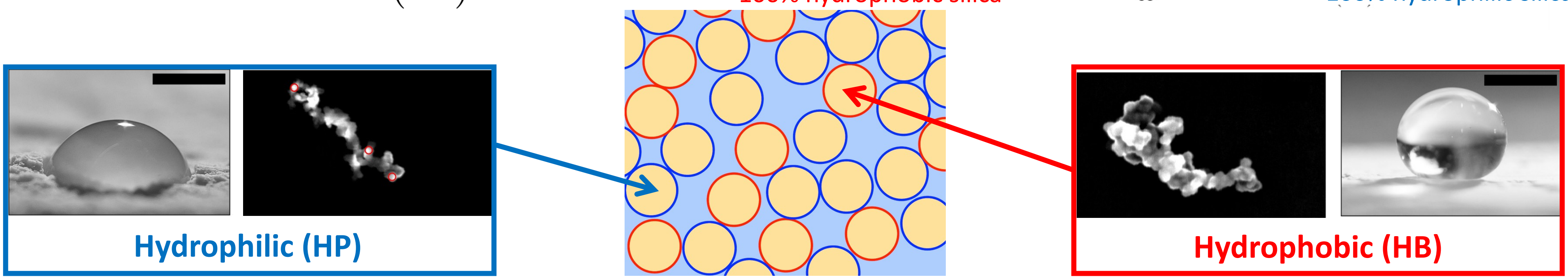
- ❑ Increasing nanometric roughness leads to CST in the absence of Hydrogen bonds

Mixtures – tuning the shear-thickening response

- Constant volume fraction (and vary *x* = *hydrophilic fraction)*





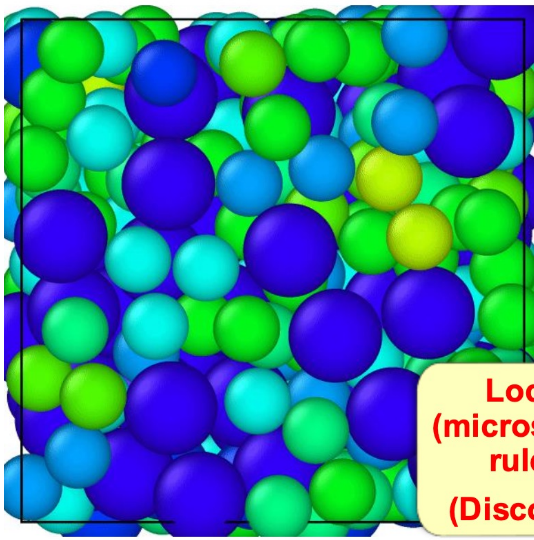


Simulations

Micromechanics of Particulate Soft Matter

The Governing Role of Inter-Particle Interactions

Experimental Methods (PSP)



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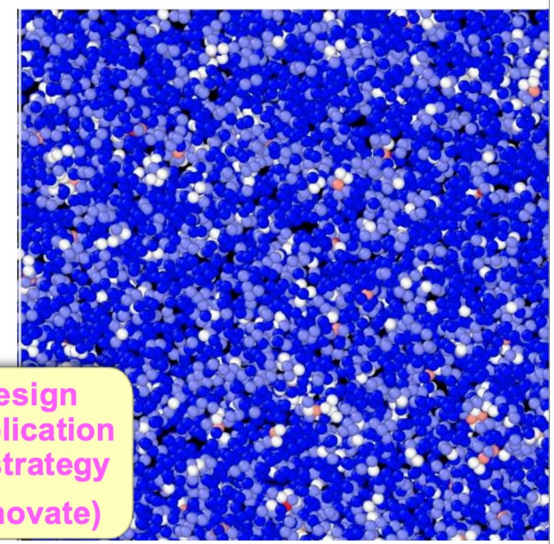
(morer@mit.edu)



Local (microscale) rules (Discover) → Latent (mesoscale) structure (Learn) → Global (macroscale) behavior (Predict) → Design (application) strategy (Innovate)

CompFlu-2023

18-20 Dec 2023

Indian Society of Rheology

Massachusetts Institute of Technology

PURDUE UNIVERSITY

MIT Portugal

NSF

Pharos Materials, Inc. Front Electrode Silver Paste Manufacturer

U.S. DEPARTMENT OF ENERGY

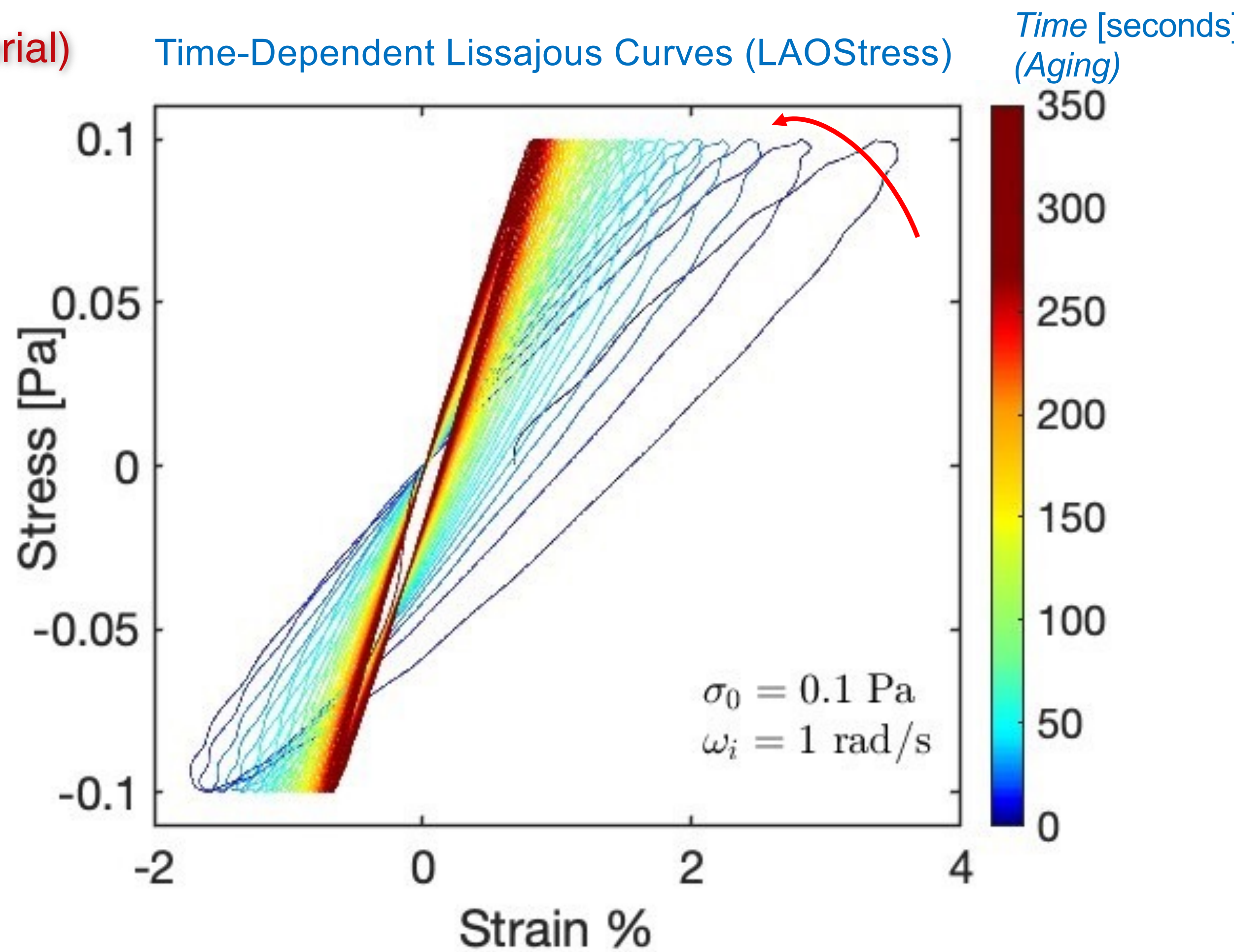
Evolving rheology of thixotropic wet suspension: clay-based drilling mud

(an *aging* TEVP material)

Material:	Bentonite;
Concentration:	5 wt.%;
Temperature:	25˚C
Geometry:	Cone 60 mm, 2°
Instrument:	DHR
Pre-shear Protocol:	500 s^{-1} for 30 s
Wait time after pre-shear (t_w) :	10 s.
SAOS Input:	$\sigma = \sigma_0 \sin(\omega_0 t)$
	σ_0= 0.1 Pa
	ω_0 = 1 rad/s

5wt% Bentonite dispersed in water

Time-Dependent Lissajous Curves (LAOStress)



Application of The Gabor Transform in Rheometric Measurements: *Gaborheometry*

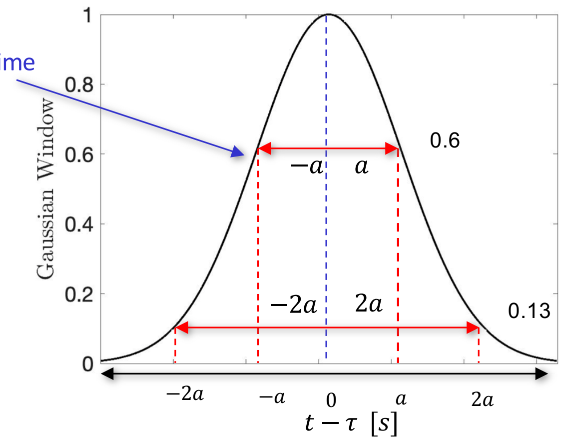
- The Gabor transform is a special case of the Short Time Fourier Transform (STFT) in which the window function is a **Gaussian**.

Dennis Gabor

Gabor Transform $X(\omega,\tau) = \int_{-\infty}^{\infty} x(t)\underline{g(t-\tau)}e^{-i\omega t}dt$

Gaussian Window $\underline{g(t-\tau)} = \frac{1}{\sqrt{2\pi}\,a}\exp\left(-(t-\tau)^2/2a^2\right)$

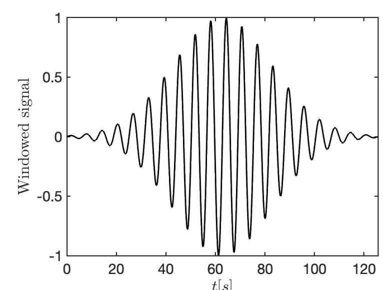
a has units of time



- ***In rheometry we care about getting amplitudes (moduli) right:***

For a sinusoidal signal $x(t) = A\sin(\omega_0 t)$, the power spectrum is given by:

$$|X(\omega,\tau=0)| = \left|\frac{A}{2}e^{-\frac{a^2}{2}(\omega-\omega_0)^2} - \frac{A}{2}e^{-\frac{a^2}{2}(\omega+\omega_0)^2}\right|$$



- For the Gabor transform to be accurate, the amplitude of the computed spectral coefficient needs to be $A/2$ at $\omega = \omega_0$ *and also* at $\omega = -\omega_0$.

At $\omega = \omega_0$ an amplitude error is incurred from the windowing: $|X(\omega,\tau=0)| = \frac{A}{2} - \frac{A}{2}e^{-\frac{a^2}{2}(2\omega_0)^2}$

- *Getting the amplitude wrong from the Fourier spectrum means getting the modulus wrong!*

…Evidently if the window length tends to infinity, we recover correct amplitude $\frac{A}{2}$.

Heisenberg's uncertainty principle in rheometry!

$$a \geq \frac{2.63}{\omega_0}$$

Rathinaraj & GHM, *J.Rheology* ***68*** Mar/Apr. 2023

Extracting $G'(\omega_0, t)$ & $G''(\omega_0, t)$ for an aging Bentonite clay (an *aging* TEVP material)

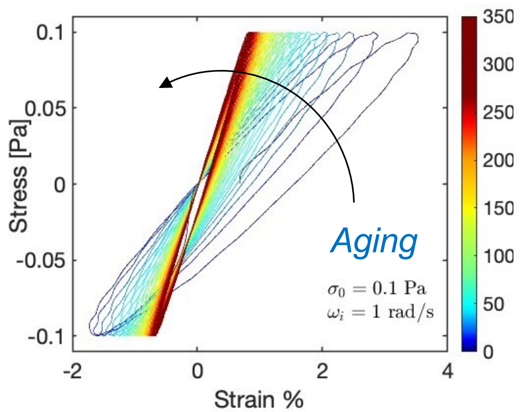
Material:	Bentonite;
Concentration:	5 wt.%;
Temperature:	25˚C
Geometry:	Cone 60 mm, 2º
Instrument:	DHR
Pre-shear Protocol:	500 s^{-1} for 30 s
Wait time after pre-shear (t_w) :	10 s.

Input: $\sigma = \sigma_0 \sin(\omega_0 t)$

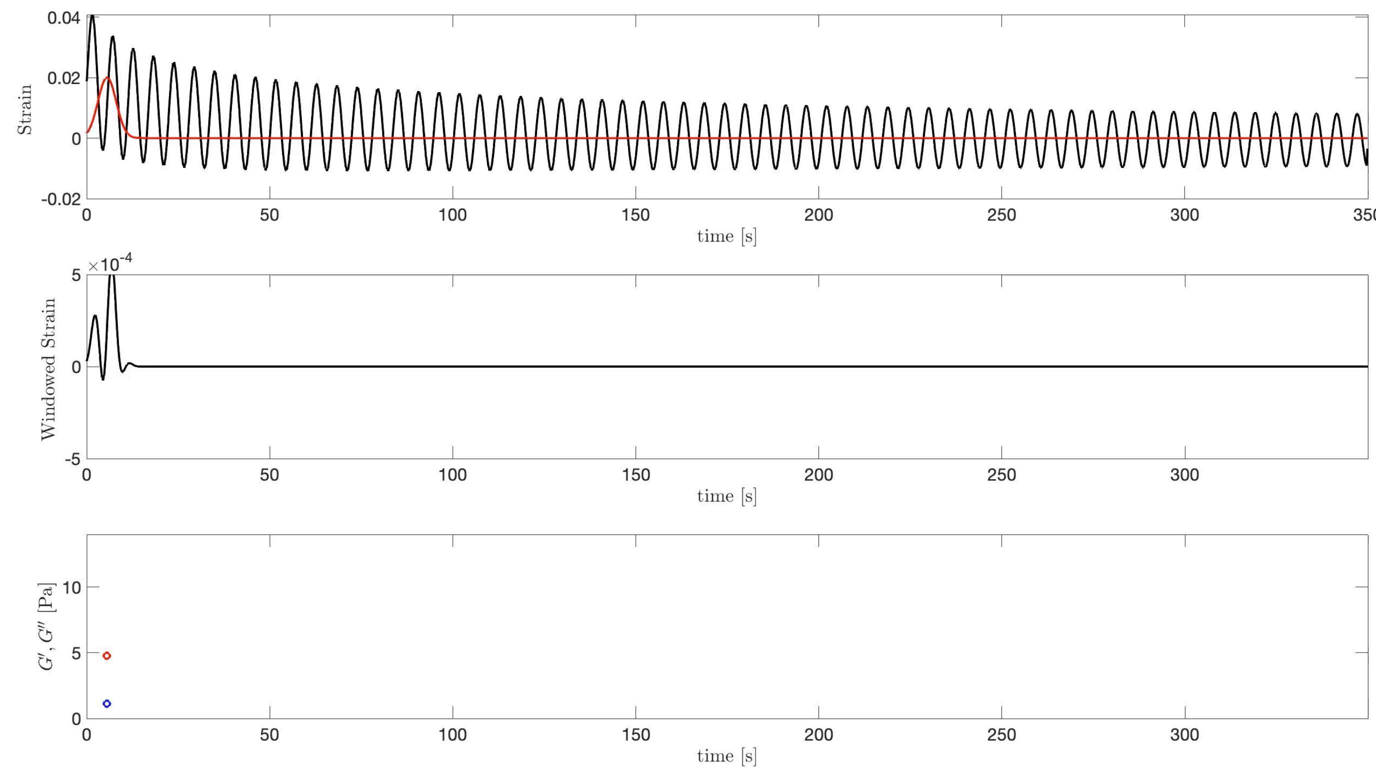
$\sigma_0 = 0.1$ Pa

$\omega_0 = 1$ rad/s

Thixotropic Lissajous Curve



Loss modulus   Storage modulus $a\omega_0 = 2.6$



Continuous logarithmic aging in time $G'(\omega, t_{age}) \approx G'(\omega) * \ln(\frac{t_{age}}{\tau_{thix}})$

Parallel Superposition & Gaborheometry During Start-Up of Shear

- In a **thixotropic elasto-visco-plastic** (TEVP) material the stress typically evolves on two (often) distinct time-scales; viscoelasticity characterized by τ_{ve} and thixotropy, characterized by τ_{thix}
- Impose $\gamma(t) = \dot{\gamma}_0 t + \gamma_0 \sin \omega t$

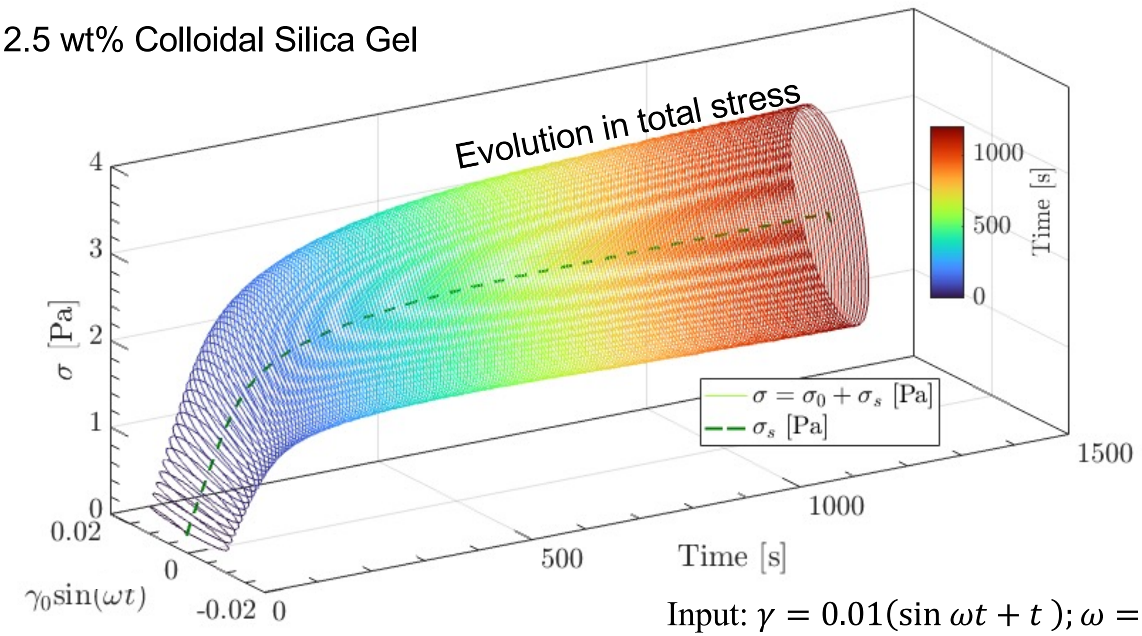
  $\dot{\gamma} = \dot{\gamma}_0 + \dot{\gamma}_0 \cos \omega t$

Monitor stress evolution in time:

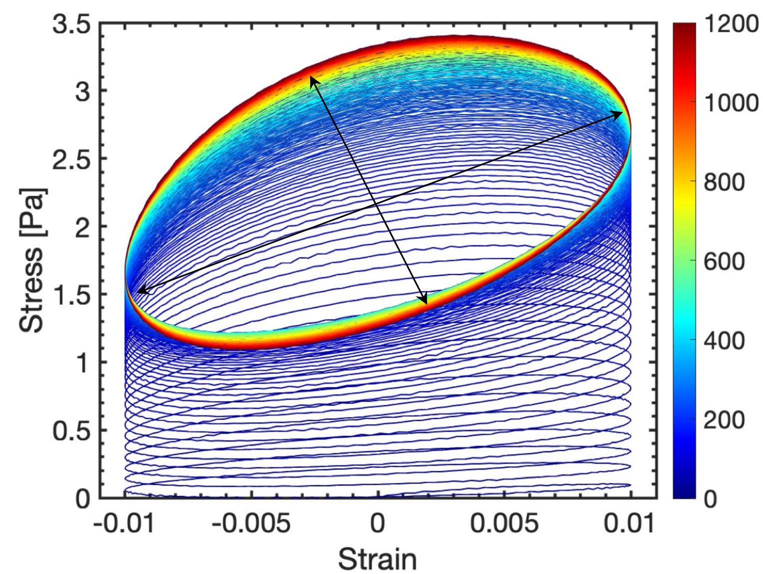
$$\sigma(t,\omega,\dot{\gamma}_0) = \eta_{eff}(t,\dot{\gamma}_0)\,\dot{\gamma}_0 + \gamma_0\{G'_{||}(\omega,t)\sin\omega t + G''_{||}(\omega,t)\cos\omega t\}$$

- Extract each component using *Gabor transform* with the optimal window $a\omega = 2.63$

2.5 wt% Colloidal Silica Gel

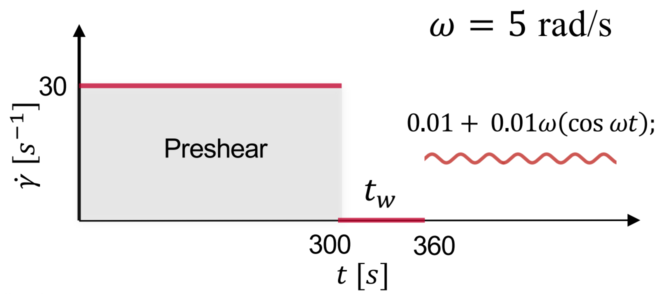


Lissajous projection illustrates VE response



Input: $\gamma = 0.01(\sin \omega t + t\ ); \omega = 1$ rad/s

Compare with a Viscoelastic Polymer Solution (3wt% high MW PIB in Paraffin)



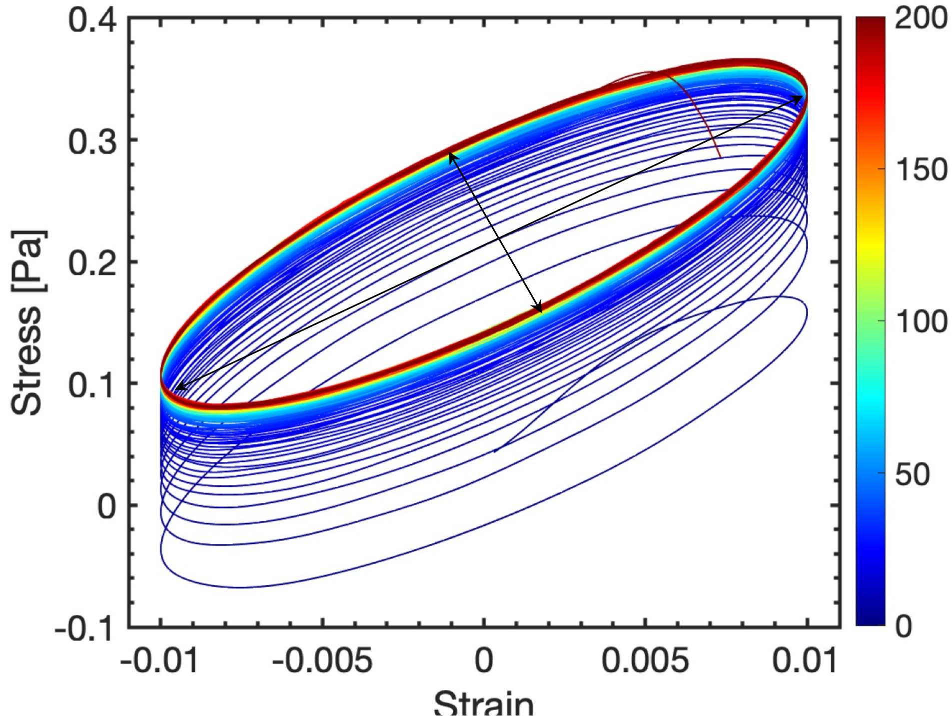
- Monitor the oscillating stress evolution in time:

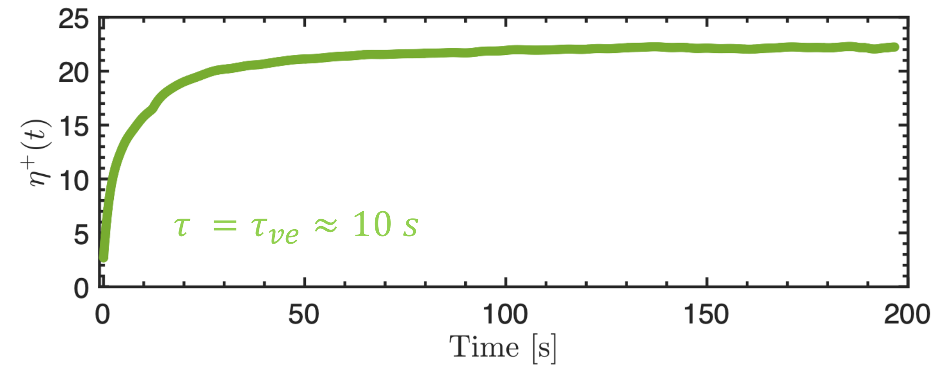
$$\sigma(t,\omega,\dot{\gamma}_0) = \eta^+(t,\dot{\gamma}_0)\,\dot{\gamma}_0 + \gamma_0\{G'_{||}(\omega,t)\sin\omega t + G''_{||}(\omega,t)\cos\omega t\}$$

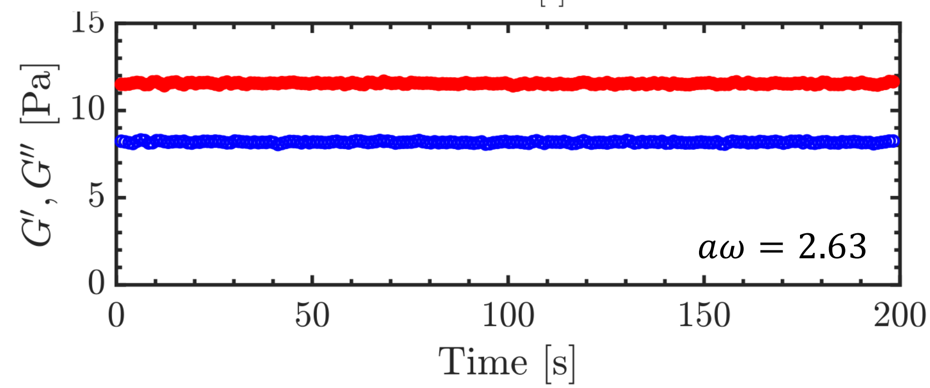
Evolution of DC term

Periodic evolution of viscoelastic response

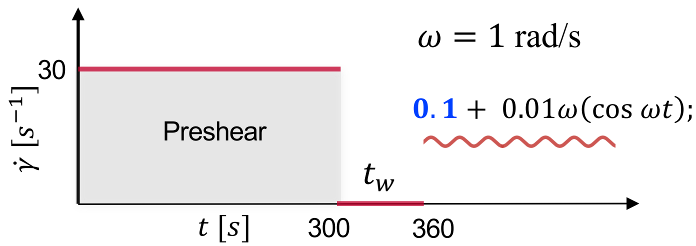
- Phase angle of the Lissajous ellipse *does not change in time*







Gabor-PSP rheometry for a silica dispersion at a high shear rate (*Wi* >> 1)

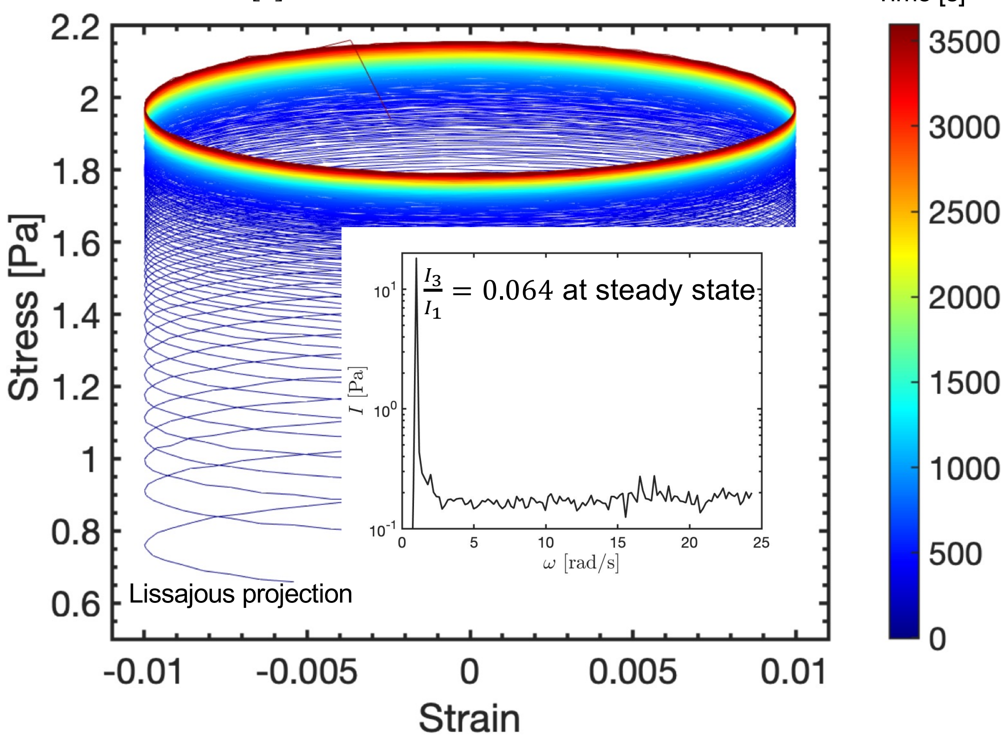


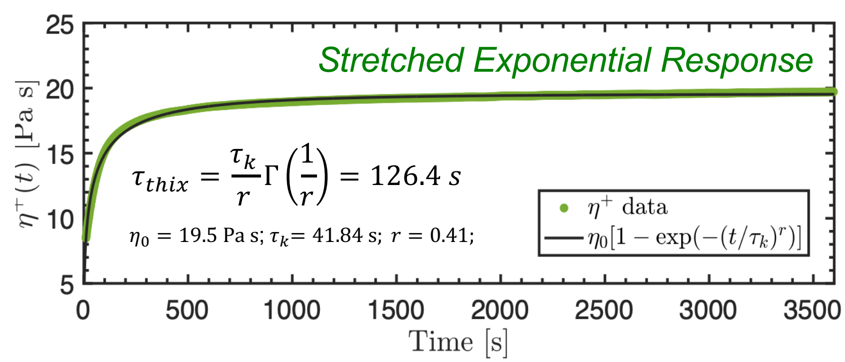
- *Shear-melt* the viscoelastic microstructure at high $\dot{\gamma}_0$

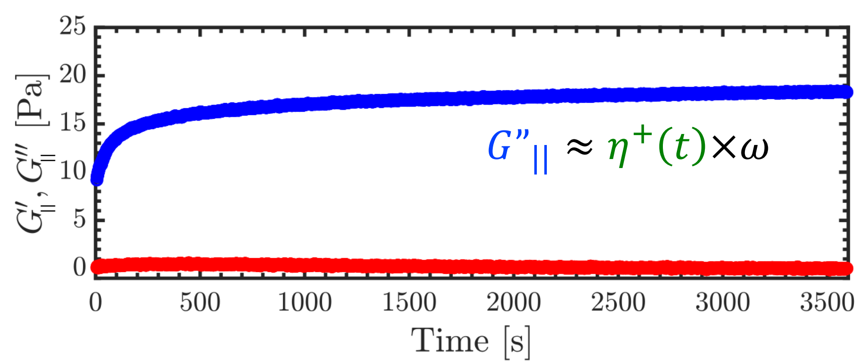
$$\sigma(t,\omega,\dot{\gamma}_0) = \eta^{+}(t,\dot{\gamma}_0)\,\dot{\gamma}_0 + \gamma_0\{G'_{||}(\omega,t)\sin\omega t + G''_{||}(\omega,t)\cos\omega t\}$$

"slow" (inelastic) thixotropic evolution of DC term

"fast" and periodic evolution of viscous response

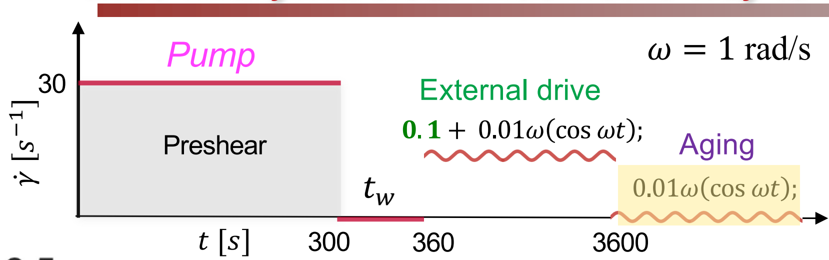






INELASTIC: Now the viscous response truly mirrors the thixotropic response; IDEAL THIXOTROPY

…so finally…a clear rheometric way to systematically distinguish *Thixotropy* from *Aging*

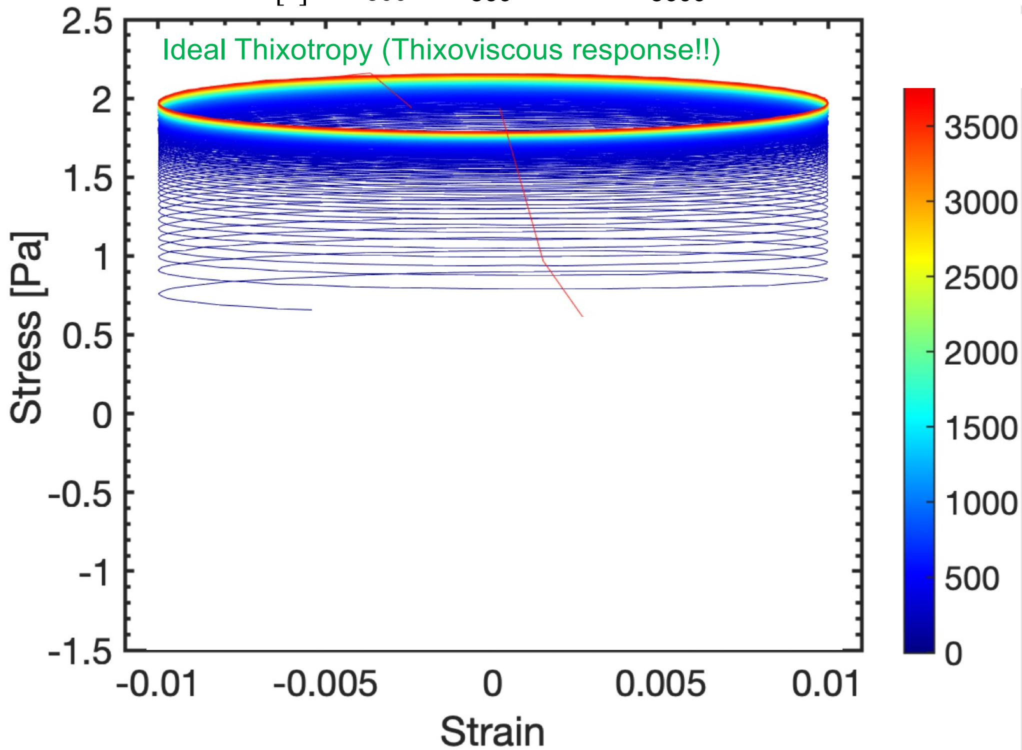


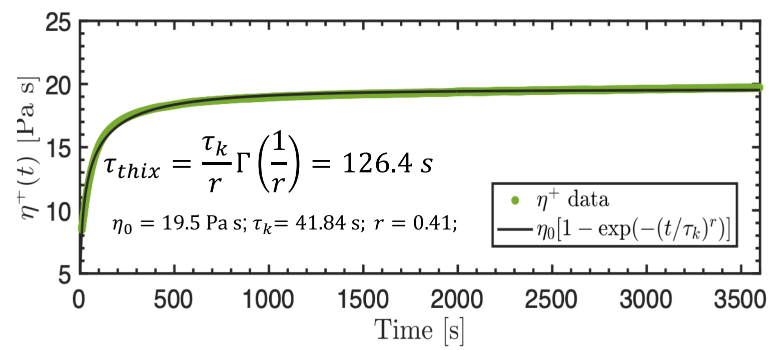
Monitor the oscillating stress evolution in time:

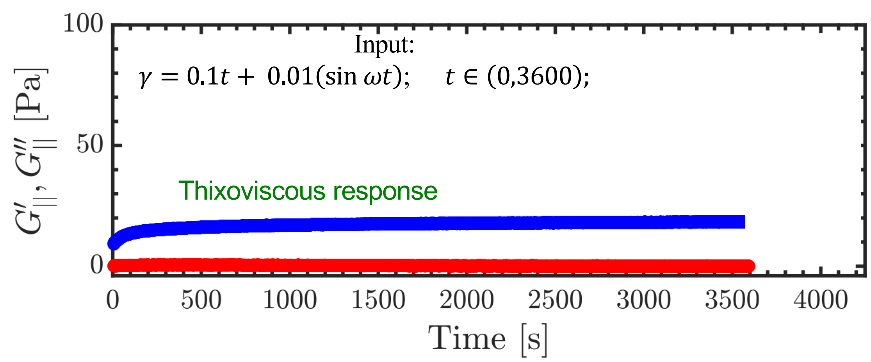
$$\sigma(t,\omega,\dot{\gamma}_0) = \eta^{+}(t,\dot{\gamma}_0)\,\dot{\gamma}_0 + \gamma_0\{ \quad + G''_{||}(\omega,t)\cos\omega t\}$$

"slow" (inelastic) thixotropic evolution of DC term

(Reversible) Aging Response



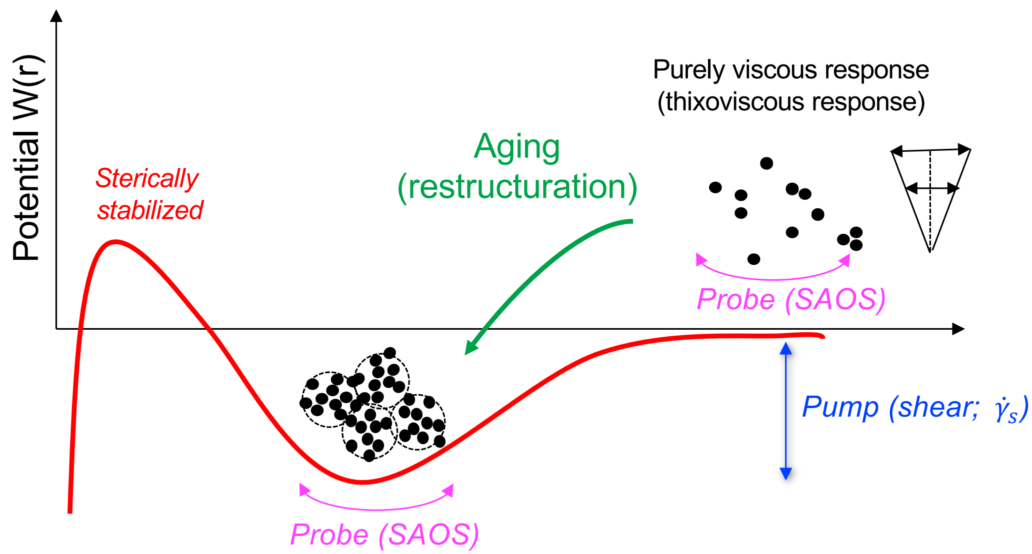




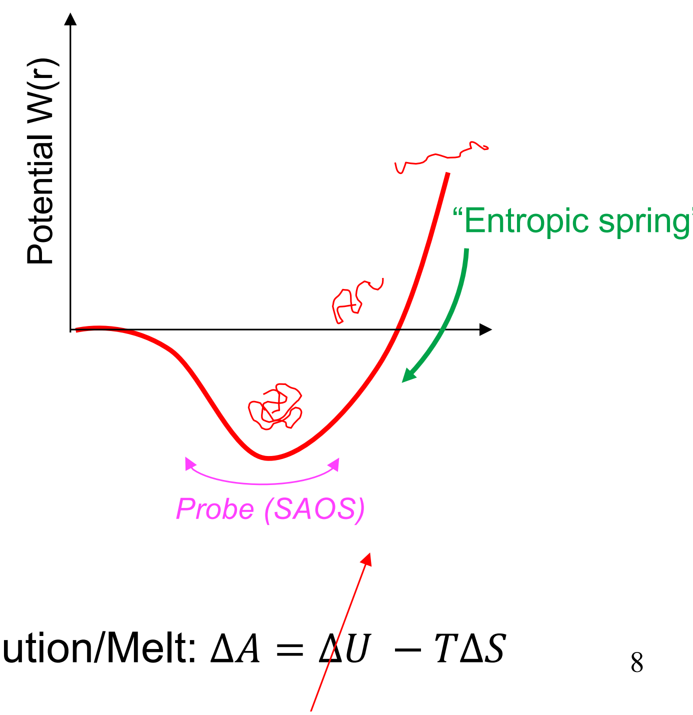
2.5 wt% Colloidal Silica Gel

PPR: Pump/Probe Rheometry (Schematic Thermodynamic Representation)

- **Drive** the system out of (local/instantaneous) equilibrium state using shear **(pump)** and **probe** resulting state *and its evolution in time* using small amplitude oscillatory shear (SAOS)
- In each case system seeks to minimize its Helmholtz Free Energy, *but different terms dominate*
- *Parallel Superposition Rheometry* (with Gabor transform for optimal separation of elastic, viscous and plastic contributions) in wet suspensions: Thixotropic Elastoviscoplastic (TEVP) fluids



Thixotropic Colloidal System: $\Delta A = \Delta U - T\Delta S$



Polymer Solution/Melt: $\Delta A = \Delta U - T\Delta S$